



Encyclopedia of
**RENEWABLE
AND SUSTAINABLE
MATERIALS**

Saleem Hashmi and
Imtiaz Ahmed Choudhury

ENCYCLOPEDIA OF RENEWABLE AND SUSTAINABLE MATERIALS

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VOLUME 1



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Elsevier
Radarweg 29, PO Box 211, 1000 AE Amsterdam, Netherlands
The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, United Kingdom
50 Hampshire Street, 5th Floor, Cambridge MA 02139, United States

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Library of Congress Cataloging-in-Publication Data

A catalog record for this book is available from the Library of Congress

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library

ISBN 978-0-12-813195-4

For information on all publications visit our
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PREFACE

The *Encyclopedia of Renewable and Sustainable Materials* is a novel initiative, launched to cater for researchers, industrial practitioners and environmental conservationists to bring to the fore the issues of renewability, regeneration, recyclability and sustainability of natural material resources for the greater good of the environment, society and renewable resources. With these objectives the project was constituted of 11 sections, led by one Section Editor each. There are about 4,000 printed pages, accommodated in five volumes ranging from 600 to 1000 pages each.

This encyclopedia is the primary reference source for researchers at different levels and stages in their career in academia and industry and those with an interest in environmental protection and sustainability, including re-use and recycling of natural and synthetic materials and regeneration of natural materials. The work encompasses the knowledge and understanding of many experts into a single, comprehensive work of about 370 articles comprising a combination of review articles, case studies and research findings resulting from research and development activities in both industrial and academic domains. The encyclopedia, focuses on how some of these topics bring advantages for a broad range of technologies and environmental protectionists. These include harnessing existing materials both natural and synthetic, their re-usability and regeneration possibilities for the greater good of society and the environment. The aspects of feasibility, conservational objectives and practicability of implementation have been addressed through a number of relevant articles.

As Editors in Chief of this five-volume comprehensive publication, a truly collaborative work, we are greatly indebted to the 11 Section Editors who are internationally renowned experts in their fields, for guiding and selecting the topics for their respective sections which constitute the five volumes, commissioning authors and reviewing the contents so meticulously. Their true dedication to the scientific community and society is reflected in the time and energy they have given to this project. My sincerest thanks are due to all the authors – researchers, environmental protectionists and practitioners who have contributed extensive coverage of literature review as well as recent works of research to this substantial five volume encyclopedia. The excellent insight and specialist knowledge in their respective fields is reflected in the high quality content of this unique work.

Both of us and all the section editors are greatly appreciative of all the hard work undertaken by all concerned to turn this concept of the *Encyclopedia of Renewable and Sustainable Materials* into a publishable work. Our special thanks go to Ruth Rhodes and Michael Nicholls, the Project Manager, along with Kshitija Iyer and the rest of the team at Elsevier who served successively to keep the project on track through friendly nudges in order to ensure timely completion. We are also hugely grateful to other colleagues at Elsevier production unit for the coordination of the proofs.

The extensive research treatment of core ethos of renewability, recyclability and regeneration, supplemented by applied case studies has drawn together many areas of research and we sincerely hope that this work will prove to be of great help to both the young and experienced members of the international research community, academics and industrial practitioners associated with sensible utilization of natural and synthetic materials for many years to come.

Saleem Hashmi and Imtiaz Ahmed Choudhury
Editors in Chief – *Encyclopedia of Renewable and Sustainable Materials*

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Advent of an Agro Friendly Approach in Bangladesh

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Introduction

The 21st century has fueled a kinetic phase for Bangladesh unknown at any previous time in history. Here the predominant agrarian economy is giving way to boosting an industrialized economy; rural grounds are experiencing urbanization at an unprecedented scale and pace. The current process of unplanned and unregulated developmental activities is taking its toll on its environment and limited natural resources.

Land, a fundamental resource base for agriculture, fisheries, industry, and other economic activities, and which provides human and natural habitat as well, is under constant threat of decline ([National Land Zoning Project](#), Ministry of Land, Government of Bangladesh). However, agricultural land in the country is decreasing at an alarming rate. Indiscriminate settlement and industrialization is aggravating land conversion hence reducing farm production, leading to national food shortage for an increasing population. Under the current trend of urbanization, industrialization, and river erosion, studies claim that Bangladesh is losing 1% of agricultural land or 82,900 hectares (ha) every year; 17% is due to burnt clay brick production and construction of brick kilns, whereas approximately 80% is due to unplanned and unregulated rural housing and the remaining 3% is for unchecked urbanization and industrialization. The customary building construction trend is another major contributor to this phenomenon. In Bangladesh construction usually focuses on the use of burnt clay bricks and reinforced concrete, which are not environment or agro friendly. It has been estimated that every year Bangladesh produces 18 billion burnt clay bricks using around 45 million tons of agricultural topsoil ([Bharadwaj and Bhattacharjee, 2015](#)), which is also responsible for 25% of total national greenhouse gas (GHG) emission. As per COP21, in its INDC Bangladesh pledged an unconditional 5% GHG emission cut by 2030. It is estimated that only an alternative to fired bricks can cut the emission by 10% within the next 5 years.

A very pertinent question in this context is whether the existing construction system has the potential to be improved and adapted to meet the perpetual extremities of nature and ever depleting natural resources. Owing to the rise of such challenging conditions, Bangladesh immediately requires a paradigm shift in the construction sector and stringent measures regarding rural settlement planning across its borders.

Housing and Building Research Institute (HBRI; an autonomous organization dealing with housing and settlement problems and operating under the Ministry of Housing and Public Works, Government of Bangladesh) is working in this regard in bringing innovation including alternatives to traditional bricks with a target of achieving zero use of agricultural topsoil for brick production, and standardization of new construction materials through research. As per the Government's 7th five-year plan, special emphasis is given for extension services of the institute to disseminate newly developed technologies and building materials that will be agriculture and environment friendly, disaster resilient, and affordable. HBRI is also working under the projected Government policy of saving agricultural land stock and acting as a crucial player in developing design and planning schemes for multistory residence-based sustainable suburban/rural settlements. Development and application of ferrocement technology as an alternative to traditional RC construction as structural, infill, and roofing element; and multiple alternative blocks, for example, sand-cement block, thermal block, compressed stabilized earthen blocks from river-dredged soil, etc. are some of the emerging alternative materials that make up many of HBRI's research initiatives.

Therefore, the changed perception of sustainability in relevance of the new world context enables these activities of HBRI to attempt to step forward toward an agriculture friendly approach. This article showcases the outcomes of HBRI's applied research on alternative building material and its application in different sectors.

An Overview of Land Morphology in Bangladesh

Bangladesh is principally an agricultural country, characterized by rice paddy agriculture dominated landscapes. So, land resource is the major asset contributing wealth and livelihood in rural areas, although land-human ratio is very low, estimated to be 0.06 ha per person ([FAO, 2013](#)). The total area of Bangladesh has risen in the last few decades, i.e., an increase is noted from 144,873 km² in 1976 to 145,306 and 145,778 km² over the years of 2000 and 2010 respectively. The overall gain of land is 90,512 ha primarily due to accreted lands in the southern coastal zone ([Hasan et al., 2013](#)).

The land resource of the country is divided into two categories, i.e., agriculture lands and nonagriculture lands. However, a declining trend was observed for the total agricultural lands of the country, i.e., a decrease is noted from 91.83% in 1976 to 87.69% and 83.53% over the years of 2000 and 2010 respectively. A total of 561,380 ha agricultural lands was decreased during 1976–2000 and this number was increased to 565,370 ha during 2000–2010. Yearly average loss of agriculture lands was 23,391 ha and 56,537 ha during 1976–2000 and 2000–2010 respectively. The nonagriculture lands of the country were 8.17%, 12.31%, and 16.47% during 1976, 2000, and 2010, respectively. The extent of nonagriculture lands were increased by 2.13% and 3.43%

during 1976–2000 and 2000–2010, respectively. Annual land loss from crop agriculture is 68,700 ha, where land gained in rural settlement, urbanization and industry, and aquaculture is 30,809 ha, 4012 ha and 3216 ha, respectively, during 2000–2010 (Hasan *et al.*, 2013).

The shifting rate of agricultural land to nonagricultural use is said to be about 1% per year (Planning Commission, Ministry of Planning, Bangladesh, 2009), which is alarming in respect to the total crop production and food security in Bangladesh (Rahman and Hasan, 2003). The Soil Resource Development Institute (SRDI), Ministry of Agriculture, estimated approximately 0.13% land transfer from agriculture to nonagriculture sector per year during the period 1963 to 1983 (Rahman and Hasan, 2003). It is likely that the shifting rate may be much faster during the 2000s till date, because of faster economic growth and the infrastructure development implied (Hasan *et al.*, 2013).

Agricultural land has declined about 0.26% annually from 1976–77 to 2010–11 (34-year average), 0.42% annually from 1976–77 to 2000–01 (25-year average), 0.75% annually from 1983–84 to 1993–94 (10-year average) and 0.40% annually from 1993–94 to 2003–04 (10-year average). There is slight increase of agricultural land from 2000–01 to 2010–11 (average 0.14%) (Table 1). Rahman (2010) reported the overall land area of the country increased 4% during 1948 to 2006 due to reclamation of char lands and the cultivable land declined 0.10% annually, assuming transfer to housing, road, and industrial infrastructures. Total agricultural land reduced 1,126,750 ha during the past 34 years (1976–2010) with yearly average loss 33,140 ha. Data analysis reveals a rapid decreasing trend of agricultural land found during the period of 2000–2010 (Hasan *et al.*, 2013).

Average yearly agricultural land lost was 0.18%, 0.44%, and 0.25% during 1976–2000, 2000–10, and 1976–2010, respectively.

Agricultural land shifting rate is alarming because food security is the main economic and political concern of Bangladesh. Geospatial extent of cropland cover maps of Bangladesh are given in Fig. 1

Table 1 Availability of agricultural land from 1976–77 to 2010–11

Year	Land area of Bangladesh (million ha)	Cultivable land (million ha)	% Cultivable land
1976–77	14.28	9.39	65.75
1980–81	14.29	9.38	65.64
1985–86	14.48	9.44	65.19
1990–91	14.84	9.72	65.50
1995–96	14.84	8.72	58.76
2000–01	14.85	8.40	56.57
2005–06	14.84	8.42	56.74
2010–11	14.84	8.52	57.41

Source: Reproduced from Bangladesh Bureau of Statistics (BBS), 2011. Agricultural Census of Bangladesh. Dhaka: Ministry of Planning.

Note: Agricultural land is the summation of cropland, current fallow, and cultivable waste.

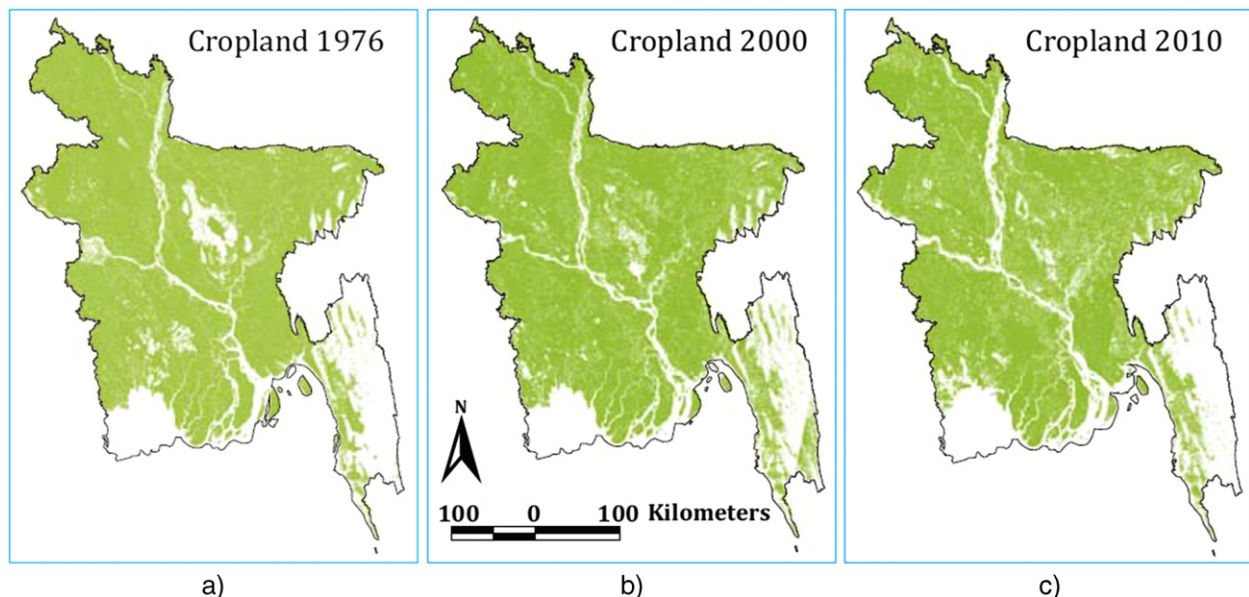


Fig. 1 Cropland maps of Bangladesh in the years of (a) 1976, (b) 2000, and (c) 2010, after satellite imagery interpretation. Reproduced from Hasan, M.N., Hossain, M.S., Bari, M.A., Islam, M.R., 2013. Agricultural Land Availability in Bangladesh, Soil Resource Development Institute (SRDI), Ministry of Agriculture.

Table 2 Total land area of Bangladesh, based on Landsat satellite data

Land cover type	1976		2000		2010	
	Area	% of total	Area	% of total	Area	% of total
Agricultural land	13,303,654	91.83	12,742,274	87.69	12,176,904	83.53
Nonagricultural land	1,183,605	8.17	1,788,307	12.31	2,400,867	16.47
Total	14,487,259	100	14,530,581	100	14,577,771	100

Source: Reproduced from Hasan, M.N., Hossain, M.S., Bari, M.A., Islam, M.R., 2013. Agricultural Land Availability in Bangladesh, Soil Resource Development Institute (SRDI), Ministry of Agriculture.

Nonagricultural land included rural settlement, brick kiln, urban and industrial estate, and accreted land. The nonagricultural land was estimated 1,183,605 ha; 1,788,307 ha and 2,400,867 ha, which correspond to 8.17%, 12.31%, and 16.47% during 1976, 2000, and 2010 respectively (**Table 2**). Maximum increasing of 612,560 ha was found during 2000–10, representing 0.42% yearly average increasing rate. Rural settlement area was estimated 885,637 ha in 1976 occupying 6.11% of the total area of the country. Rural settlement area consistently increased over time which grabbed 1,458,031 ha (10.03%) in 2000 and 1,766,123 ha (12.12%) in 2010. Yearly average increasing rate were 0.16% and 0.21% during 1976–2000 and 2000–10, respectively. The overall rate of increase in rural settlement was 0.18% during the 34-year period (1976–2010). Another driving force is urbanization and industrialization. The yearly increasing rate of urbanization and industrialization was higher (0.03%) during 2000–10, followed by 0.01% during 1976–2000. Yearly average 4012 ha land was transferred to urbanization and industrialization sector during 2000 to 2010.

Prevailing Construction Industry and Its Impact

The prevailing construction industry poses a major threat to our environment and agriculture.

Agricultural Impact

As per a report published in the national daily *The Daily Star*, heavy use of clay from agricultural land causes depletion of topsoil and acid deposits from brick kiln affect agricultural productivity (Roy and Roy, 2016). Various projects and initiatives have introduced technologies targeting to reduce GHG emission but traditional clay content, which requires burning, is still used in brick production. Up to 18 in. of topsoil is collected from a cropland whereas it loses its fertility even if only the top six inches of soil is removed. Farmers are often forced to sell topsoil to the owners of the brick kiln. The level of land adjacent to the kilns goes down when the owner sells the topsoil and then irrigation water cannot be held in other lands adjacent to those lands. This incident leaves no choice to the owners of these lands but to sell the topsoils eventually.

Brick kilns are destroying large areas of agricultural land every year, which increased into 5000 ha during the 1998 to 1999 period in different pockets of brick fields (Rahman and Khan, 2001). These affected areas are expanding rapidly due to the increase in brick production (IUSS, 2002). There are about 6000 brick manufacturers in Bangladesh, which produce about 18 billion pieces of brick a year consuming around 45 million tons of fertile soil – equivalent to around 2600 ha of agricultural land. At this rate, the country is quickly moving toward severe food shortages in the foreseeable future (Bharadwaj and Bhattacharjee, 2015). In addition, acid deposits from the sulfur dioxide (SO₂) and NO_x emitted from the brick kilns negatively affect agricultural productivity.

Environmental Impact

Construction impacts last for decades and affect the lives of current and future generations. Buildings consume major global resources. Almost 50% of global energy is consumed in buildings, while 50% water, 60% materials for buildings, 80% land loss to agriculture, 60% timber products, 90% hardwoods are all directly linked with building construction. Indirectly 50% of coral reef destruction and 25% of rain forest destruction are all attributed to buildings and construction (US Environmental Protection Agency). The brick industry emits 8.75 million tons of GHG annually and consumes 2.2 million tons of coal and 1.9 million tons of firewood annually. Around 30% of brick kilns use firewood illegally, aggravating deforestation (published in the national daily *The Independent* on 29 July, 2016).

The major impacts of construction are excessive energy use, global warming, and climate change. Energy is consumed when extracting raw materials, producing materials (manufacturing process), transporting materials, transporting workforce, building structures, using and powering structures, maintaining structures, and demolishing. In addition, energy is also required for the operation of any structure(s).

Approximately 120 million MT concrete, of which 10 million MT is water, 20 million MT is cement, and 90 million MT is aggregate, is used in Bangladesh. The total aggregate used in the world is 9 billion tonnes. So it is an important aspect in concrete

Table 3 CO₂ emission and energy consumption for building materials used in Bangladesh (construction phase only)

Sl.	Product description	Standard value per unit	
		CO ₂ emission (ton)	Energy consumption (GJ)
1	Cement (bags)	0.0194	0.0935
2	Brick (Nos)	0.00054	0.00575
3	Stone (cft)	0.00356	0.00483
4	Sand (cft)	0.00138	0.02346
5	Rebar (kg)	0.0000624	0.001365
6	Glass (kg)	0.0013	0.0184
7	Lime (ton)	0.47	5.69

Source: Reproduced from Alam, M.S., Ahmad, S.I., 2013. Analysis of life cycle environmental impact for residential building in Bangladesh. International Journal of Technology Enhancements and Emerging Engineering Research 2 (1), 1.

production and its production and transportation will emit carbon dioxide and consume fuel. So when using energy saving material, not sacrificing strength is important and locally available materials induce in concrete will help by the course (Alam and Ahmad, 2013). In case of clay burnt brick production, most of the CO₂ is produced during construction phase and huge amount of energy is consumed as well. In order to reduce CO₂ emission, we have to think of alternatives to conventional brick production methods. This table will encourage us to analyze more the environmental impact of building and will show the importance of reducing the emission of CO₂ (Table 3).

The concept of sustainable construction and green development incorporates and integrates a variety of strategies during the design, construction, and operation of building projects. The use of green building materials and products represents one important strategy in the design of a building. It needs to be understood that sustainable construction techniques are different than “good practices.” Green building materials are composed of renewable, rather than nonrenewable resources. Green materials are environmentally responsible because their environmental impacts are considered over the “life of the product” (Spiegel and Meadows, 1999).

Advent of a New Approach: Alternative Building Material and Construction Technology Developed by Housing and Building Research Institute

HBRI is an autonomous organization under the Ministry of Housing and Public Works, Government of Bangladesh, with a constitutional framework of a Governing Council headed by the Honorable Minister in charge of the Ministry. It runs by the allocation of Government grants from the revenue fund. Since the beginning, all the Divisions of the Institute rendered useful contributions in the field of housing. It renders extension services in the form of consultancy, laboratory testing, and planning pertaining to building activities in both public and private sectors. The Institute is the only national research institute that is entrusted to conduct research in housing problems, and innovation in construction materials, technology, and planning.

As per the Government’s 7th Five-Year Plan, HBRI will focus on bringing innovation including alternatives to traditional bricks with a target of achieving zero use of agricultural topsoil for brick production, and standardization of construction materials through research. Special emphasis will be given for extension services to disseminate newly developed technologies and building materials that will be agriculture and environment friendly, disaster resilient, and affordable. It will also continue updating the Bangladesh National Building Code (BNBC) and on a pilot basis steps will be taken for the construction of 75 low cost multistoried residential buildings in different villages during the 7th Plan period.

Regarding Bangladesh and COP21, in its Intended Nationally Determined Contributions (INDC) Bangladesh pledged an unconditional 5% GHG emissions cut by 2030, adding that with financing and technology support it will cut emissions by 15%.

As per Prime Minister’s Directives to HBRI, during her visit on 28 December 2014, to the Ministry of Housing and Public Works, the honorable Prime Minister provided some instructions:

- An intense initiative has to be undertaken to publicize the HBRI’s act of innovation regarding new building materials.
- Appropriate planning has to be drafted to properly utilize and apply the research outcomes.
- Ferrocement must be introduced in various housing and rural settlement development projects.
- Research initiative must be undertaken regarding construction of hollow blocks from river-dredged sand.
- Measures must be taken to produce environment-friendly bricks from river-dredged soil.

The United Nations’ Sustainable Development Goal 11: Sustainable Cities and Communities and Goal 13: Climate Action also falls in line with HBRI’s venture.

Addressing all the core issues, the main objective of HBRI can be summarized as:

- To conduct and promote action based technical research on alternative building material and construction technologies that are environment and agriculture friendly, disaster resilient, and cost effective.

With a target of achieving zero use of agricultural topsoil for brick production and standardization of new construction materials through research and dissemination, HBRI is continuously designing, developing, and upgrading different building materials and technologies. Several attempts have been taken as part of HBRI's noble venture in promoting an environment and agriculture friendly approach.

Given below is a list with detailed descriptions of alternative building materials and technologies and several examples of implemented and under-construction projects that have been developed with the alternative technologies by HBRI.

Wall Elements

Ferrocement

Specific feature (Fig. 2):

1. Raw Material
 - Cement
 - Sand
 - Wire mesh
 - MS bar



a)



b)

Fig. 2 Ferrocement wall. (a) cast-in-situ (source HBRI) and (b) precast. Data from Housing and Building Research Institute.

2. Engineering and physical properties

Cast-in-situ:

- Cement: sand = 1:2.
- Sylhet sand (FM 2.2–2.6)
- W/C = 0.45.
- Iron wire mesh = 2 layers of 18 BWG or 20 BWG with ½" opening.
- Skeleton MS Bar = 8 mm ϕ (both way) @ 2" c/c.

Precast

- Cement: sand = 1:2
- Sylhet sand (F.M 2.2–2.6)
- W/C = 0.38–0.45
- Iron wire mesh = 2 layers of 18 BWG or 20 BWG with ½" opening.
- Skeleton MS Bar = 8 mm ϕ (both way) @ 2" c/c.

Sandwich panel

Specific feature (Fig. 3):

1. Raw material

- Cement
- Sand
- Wire mesh
- MS bar
- Expanded polystyrene sheet (EPS)

2. Engineering and physical properties

- Total thickness of the concrete (cement:sand = 1:3) on interior and exterior faces = 25 mm
- Sylhet sand (FM 2.2–2.6)
- W/C = 0.45
- Iron wire mesh = 18 BWG with ½" opening
- Thickness of expanded polystyrene sheet (density = 15 kg/m³) = 56.25 mm
- Total finishing thickness = 87.5 mm

Sand-cement block (type I)

Specific feature (Fig. 4):

1. Raw material

- River-dredged soil/sand

Source: Brahmaputra River

Location: Jamalpur, Bangladesh

2. Physical properties

- Size: 400 × 200 × 100 mm³
- Weight: 9.5 kg

**Fig. 3** Sandwich Panel. Data from Housing and Building Research Institute.



Fig. 4 Sand-cement block (type I). Data from Housing and Building Research Institute.



Fig. 5 Sand-Cement Block (Type II: 3 Hole). Data from Housing and Building Research Institute.

3. Engineering properties
 - Compressive strength: 6 Mpa
 - Water absorption: <10%
4. Engineering economy
 - Economic w.r.t. burnt clay brick

Sand-cement block (type II: 3 hole)

Specific feature (Fig. 5):

1. Raw material
 - River-dredged soil/sand

Source: Feni River
Location: Chittagong, Bangladesh
2. Physical properties
 - Size: $400 \times 200 \times 100 \text{ mm}^3$
 - Weight: 9.5 kg
3. Engineering properties
 - Compressive strength: 30 Mpa
 - Water absorption: <5%
4. Engineering economy
 - Economic w.r.t. burnt clay brick



Fig. 6 Sand-cement block (type III: 11 Hole). Data from Housing and Building Research Institute.

Sand-cement block (type III: 11 hole)

Specific feature (Fig. 6):

1. Raw material
 - River-dredged soil/sand
- Source: Feni River
Location: Chittagong, Bangladesh
2. Physical properties
 - Size: $240 \times 175 \times 70 \text{ mm}^3$
 - Weight: 3.22 kg
 - Lightweight
3. Engineering properties
 - Compressive strength: 30 Mpa
 - Water absorption: <10%
4. Engineering economy
 - Economic w.r.t. burnt clay brick

Interlocking compressed stabilized sand block

Specific feature (Fig. 7):

1. Raw material
 - Cement: 10%, Coarse Sand: 90%
2. Physical properties
 - Size: $240 \times 175 \times 70 \text{ mm}^3$
 - Weight: 3.5 kg
 - Lightweight
3. Engineering properties
 - Water absorption: <10%.
4. Engineering economy
 - Economic w.r.t. burnt clay brick

Interlocking compressed stabilized earth block

Specific feature (Fig. 8):

1. Raw material
 - Cement 10%, River-dredged soil 90%



Fig. 7 Interlocking compressed stabilized sand block. Data from Housing and Building Research Institute.



Fig. 8 Interlocking compressed stabilized earth block. Data from Housing and Building Research Institute.

Source: Kopotakkho River

Location: Jessore, Bangladesh

2. Physical properties

- Size: $300 \times 150 \times 100 \text{ mm}^3$
- Weight: 7.5 kg

3. Engineering properties

- Compressive strength: 7.5 Mpa
- Water absorption: <10%

4. Engineering economy

- Economic w.r.t. burnt clay brick

Compressed stabilized earth block (type I)

Specific feature (Fig. 9):

1. Raw material

- Cement (10%), River-Dredged Soil (90%)

Source: Kopotakkho River

Location: Jessore, Bangladesh

2. Physical properties

- Size: $240 \times 115 \times 76 \text{ mm}^3$
- Weight: 3.95 kg

3. Engineering properties

- Compressive strength: 4.4 Mpa
- Water absorption: <10%



Fig. 9 Interlocking compressed stabilized earth block (type I). Data from Housing and Building Research Institute.



Fig. 10 Interlocking Compressed Stabilized Earth Block (Type II). Data from Housing and Building Research Institute.

4. Engineering economy
 - Economic w.r.t. burnt clay brick

Compressed stabilized earth block (type II)

Specific feature (Fig. 10):

1. Raw material
 - Cement (10%), River-Dredged Soil (90%), Jute Fiber

Source: Kopotakkho River

Location: Jessore, Bangladesh

2. Physical properties
 - Size: $240 \times 115 \times 76 \text{ mm}^3$
 - Weight: 4 kg
3. Engineering properties
 - Compressive strength: 4.7 Mpa
 - Water absorption: <10%
4. Engineering economy
 - Economic w.r.t. clay burnt brick

Compressed stabilized block with fly ash

Specific feature (Fig. 11):



Fig. 11 Interlocking compressed stabilized block with fly ash. Data from Housing and Building Research Institute.

1. Raw material
 - Cement 20%, fly ash 80%
2. Physical properties
 - Size: $240 \times 115 \times 76 \text{ mm}^3$
 - Weight: 2.5 kg
 - Lightweight
3. Engineering properties
 - Compressive strength: 3 Mpa
4. Engineering economy
 - Economic w.r.t. burnt clay brick

Aerated concrete block

Specific feature (Fig. 12):

1. Raw material
 - Cement, aluminum powder
2. Physical properties
 - Size: $254 \times 127 \times 127 \text{ mm}^3$
 - Weight: 3.2 kg
 - Lightweight
3. Engineering properties
 - Compressive strength: 2.5 Mpa
 - Water absorption: ~20%
4. Engineering economy
 - Economic w.r.t. burnt clay brick

Thermal block (two side mortar with key)

Specific feature (Fig. 13):

1. Raw material
 - Cement (25%), expanded polystyrene sheet, coarse sand (75%)
 - Source: local market
2. Physical properties
 - Size: $242 \times 114 \times 69 \text{ mm}$
 - Weight: 1.3 kg
 - Lightweight
3. Engineering properties
 - Compressive strength: 4.9 Mpa
 - Water absorption: <5%
 - Sand: FM: 2.5
4. Engineering economy
 - Economic w.r.t. burnt clay brick

Thermal block (four side mortar)

Specific feature (Fig. 14):



Fig. 12 Aerated concrete block. Data from Housing and Building Research Institute.



Fig. 13 Thermal Block (Two Side Mortar with Key). Data from Housing and Building Research Institute.



Fig. 14 Thermal Block (Four Side Mortar). Data from Housing and Building Research Institute.

1. Raw material
 - Cement (25%), coarse sand (75%),
 - expanded polystyrene sheet
 Source: local market
2. Physical properties
 - Size: $242 \times 114 \times 69 \text{ mm}^3$
 - Weight: 1.22 kg
 - Lightweight
3. Engineering properties
 - Compressive strength: 4.9 Mpa
 - Water absorption: <5%
4. Engineering economy
 - Economic w.r.t. burnt clay brick

Coconut coir board

Specific feature (Fig. 15):

1. Raw material
 - Cement (70%), coconut coir (30%)
2. Physical properties
 - Size: $600 \times 300 \times 25 \text{ mm}^3$
 - Lightweight
3. Engineering economy
 - Economic w.r.t. conventional interior

Roofing Elements

Precast ferrocement U-channel

Specific feature (Fig. 16):

1. Raw material
 - Cement, sand, wire mesh, MS bar
2. Physical properties
 - Width: 600 mm (including rib portions), length: 3800 mm (can be changed as per requirement)
 - Thickness:

Flange thickness: 25 mm

Rib thickness: 50 mm

3. Engineering economy
 - Economic w.r.t. conventional RC slab

Precast ferrocement folded plate

Specific feature (Fig. 17):

1. Raw material
 - Cement, sand, wire mesh, MS bar
2. Physical properties
 - Size:

Flange width: 125 mm

Thickness: 25 mm

Maximum depth: 150 mm

Length = Usually 3200 mm (can be changed as per requirement)

3. Engineering economy
 - Economic w.r.t. conventional RC slab

Precast ferrocement corrugated sheet

Specific feature (Fig. 18):

1. Raw material
 - Cement, sand, wire mesh, MS bar
2. Physical properties
 - Size:



Fig. 15 Coconut coir board. Data from Housing and Building Research Institute.



Fig. 16 Precast ferrocement U-channel. Data from Housing and Building Research Institute.

Flange width: 125 mm
 Thickness: 25 mm
 Maximum depth: 150 mm
 Length = Usually 3000 mm (can be changed as per requirement)

3. Engineering economy
 - Economic w.r.t. conventional RC slab

Precast ferrocement L-panel

Specific feature (Fig. 19):

1. Raw material:
 - Cement, sand, wire mesh, MS bar
2. Physical properties:
 - Size:

Rib depth: 125 mm
 Rib width: 50 mm
 Flange width: 530 mm

3. Flange thickness: 25 mm
 - Provision of 20–25 mm groove in the flange/top of the rib along the length is made for laps over the adjacent units.
4. Engineering economy:
 - Economic w.r.t. conventional RC slab

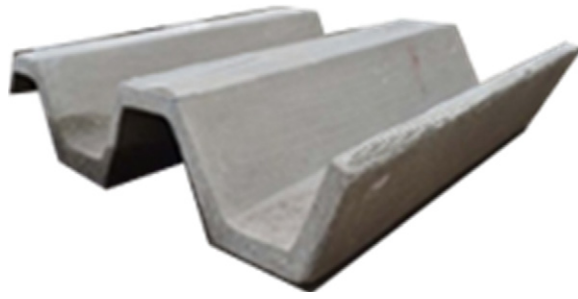


Fig. 17 Precast ferrocement folded plate. Data from Housing and Building Research Institute.



Fig. 18 Precast ferrocement corrugated sheet. Data from Housing and Building Research Institute.



Fig. 19 Precast ferrocement L-panel. Data from Housing and Building Research Institute.

Flooring Elements

Precast ferrocement floor tiles

Specific feature (Fig. 20):

1. Raw material
 - Cement, sand, wire mesh
2. Physical properties
 - Size: $600 \times 600 \times 25 \text{ mm}^3$
3. Engineering economy
 - Economic w.r.t. conventional floor tiles



Fig. 20 Precast ferrocement floor tiles. Data from Housing and Building Research Institute.



Fig. 21 Precast ferrocement column/beam. Data from Housing and Building Research Institute.

Structural Elements

Precast ferrocement column/beam

Specific feature (Fig. 21):

1. Raw material
 - Cement, sand, wire mesh, MS bar
2. Physical properties
 - Size: $125 \times 125 \text{ mm}^2$
 - Length: 3000–3600 mm
 - Hollow diameter: 75 mm
3. Engineering economy
 - Economic w.r.t. conventional RC column/beam

Precast ferrocement pile

Specific feature (Fig. 22):

1. Raw material
 - Cement, sand, wire mesh, MS bar



Fig. 22 Precast Ferrocement Pile. Data from Housing and Building Research Institute.

2. Physical properties
 - Size: $125 \times 125 \text{ mm}^2$
 - Length: 3000–3600 mm
 - Hollow diameter: 75 mm
3. Engineering economy
 - Economic w.r.t. conventional RC pile

Precast ferrocement footing

Specific feature (Fig. 23):

1. Raw material
 - Cement, sand, wire mesh, MS bar
2. Physical properties
 - Size: $1250 \times 1250 \text{ mm}^2$
 - Height: 900 mm
3. Engineering economy
 - Economic w.r.t. conventional RC footing

Miscellaneous Elements

Precast ferrocement louver

Specific feature (Fig. 24):

1. Raw material
 - Cement, sand, wire mesh, MS bar
2. Physical properties
 - Size: $37.5 \times 100 \times 2400 \text{ mm}^3$

Ferrocement irrigation drain

Specific feature (Fig. 25):

1. Raw material:
 - Cement, sand, wire mesh, MS bar
2. Physical properties:
 - Size: $1500 \times 600 \times 600 \text{ mm}^3$



Fig. 23 Precast ferrocement footing. Data from Housing and Building Research Institute.



Fig. 24 Precast ferrocement louver. Data from Housing and Building Research Institute.



Fig. 25 Precast ferrocement irrigation drain. Data from Housing and Building Research Institute.



Fig. 26 Multistoried house (rural type I). Data from Housing and Building Research Institute.

Application of Alternative Building Material and Construction Technologies

HBRI is implementing the use of alternative building materials and construction technology in building different residential, administrative, and public built forms. Alternative building technology is being applied in different demonstration projects as well. A few of the examples are discussed below:

Multistoried House (Rural Type I)

Special Features (Fig. 26):

- Building type: residential
- Foundation: RC
- Beam and column: RC
- Floor and roof: ferrocement channel
- Ground floor: soil-cement stabilized
- Wall: ferrocement, 3D panel and sand-cement block
- Staircase: ferrocement
- Plinth area: 130 m²
- Status: completed
- Location: HBRI premises

Multistoried House (Rural Type II)

Special features (Fig. 27):

- Building type: residential
- Foundation: RC
- Beam and Column: RC
- Floor and roof: ferrocement channel
- Ground floor: soil-cement stabilized
- Wall: ferrocement/thermal block/sandwich panel



Fig. 27 Multistoried house (rural type II). Data from Housing and Building Research Institute.

- Staircase: ferrocement
- Plinth Area: 156 m²
- Status: This design has been developed as part of HBRI's venture in formulating the Standard Guideline and Design for Rural Housing in Disaster Prone Areas of Bangladesh.

Precast Prefabricated Stilt House for Ethnic Community

Special features (Fig. 28):

- Building type: residential
- Foundation: ferrocement pocket footing
- Beam and column: ferrocement precast beam and column
- Floor: ferrocement channel
- Roof: ferrocement corrugated sheet
- Ground floor: soil-cement stabilized
- Wall: plastered bamboo matt
- Ladder: wooden
- Plinth area: 19 m²
- Status: completed
- Location: HBRI Premises and piloting in Borguna, Bangladesh as part of a Government project.

Display Center

Special features (Fig. 29):

- Building type: public facility
- Foundation: RC
- Beam and column: RC
- Floor: ferrocement channel
- Ground floor: soil-cement stabilized



Fig. 28 Precast prefabricated stilt house. Data from Housing and Building Research Institute.

- Roof: ferrocement folded plate
- Wall: sandwich panel and thermal block
- Plinth area: 650 m²
- status: under construction
- Location: HBRI Premises

Training Center

Special features (Fig. 30):

- Building type: institutional
- Foundation: RC
- Beam and column: RC
- Floor and roof: ferrocement channel
- Ground floor: soil-cement stabilized
- Floor tiles: ferrocement
- Wall: CLC block and sandwich panel
- Plinth Area: 375 m²
- Status: under construction
- Location: HBRI premises

Public Toilet and Waiting Facility

Special features (Fig. 31):

- Building type: public utility
- Foundation: ferrocement pocket footing
- Beam and column: ferrocement
- Floor: soil-cement stabilized
- Roof: ferrocement corrugated sheet and ferrocement channel
- Wall: ferrocement, thermal block
- Plinth area: 135 m²



Fig. 29 Display center. Data from Housing and Building Research Institute.



Fig. 30 Training Center. Data from Housing and Building Research Institute.

- Status: construction will initiate soon
- Location: HBRI premises

Innovative Projects by HBRI in Collaboration With National and International Bodies

HBRI has joined to different organizations to work in close collaboration regarding the research, implementation, and dissemination of alternative building material and construction technologies.

Standard Guideline and Design for Rural Housing in Disaster Prone Areas of Bangladesh

Bangladesh is predisposed to numerous natural extremities due to its geographic location and meteorological features. Every year the country faces multiple exposures to extreme natural phenomena that significantly affect the overall livelihood of the

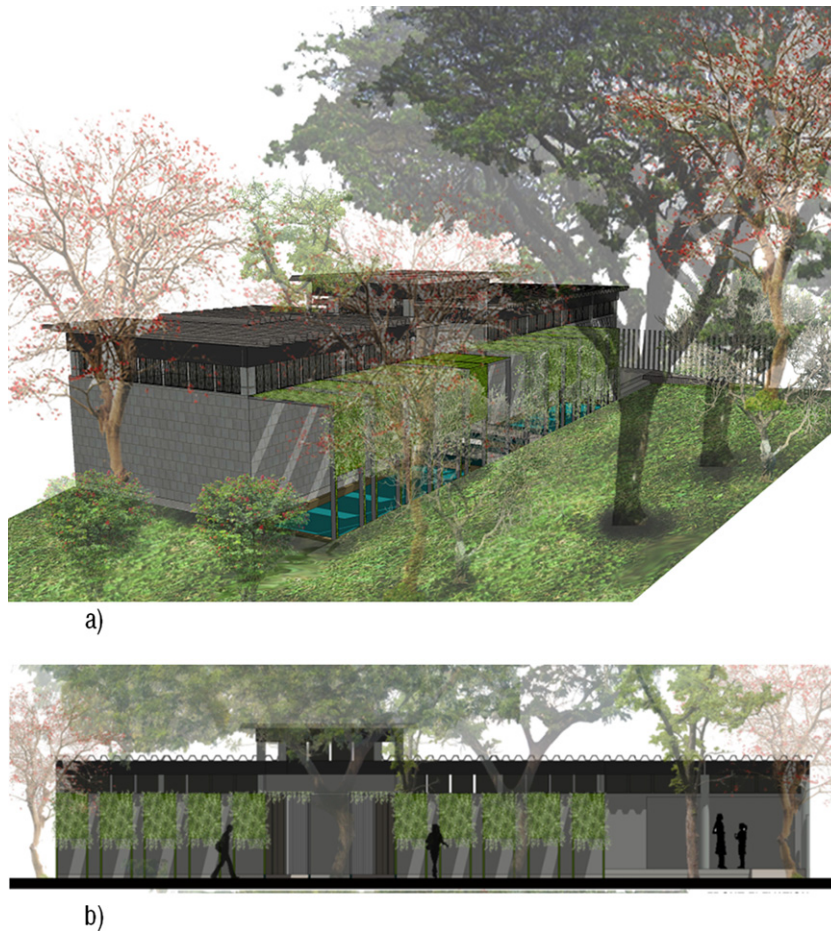


Fig. 31 Public toilet and waiting facility: (a) perspective view and (b) elevation. Data from Housing and Building Research Institute.

inhabitants. Predominantly housing is the most affected paradigm, facing the utmost adverse impacts of nature. Although Bangladesh has shown responsive approaches to disaster risk reduction and management, lack of an inclusive policy and guideline at a national level is obstructing the successful outcome of the overall process in most of the cases. In order to address the greater need of the nation, an inevitable demand has been felt to formulate a national guideline and design a manual for rural areas, especially areas prone to natural extremes. The aim of formulating this design guideline is to assist both the housing facilitators and end users living in extreme natural conditions (Fig. 32).

The project Standard Guideline and Design for Rural Housing in Disaster prone areas of Bangladesh was hosted by the Department of Disaster Management under the Ministry of Disaster Management and Relief, Bangladesh, in collaboration with HBRI under the Ministry of Housing and Public Works. A consultancy firm from Bangladesh, GHORAMIJON, which focuses mostly on development of sustainable, resilient and ecologically responsive habitat and settlements of marginalized communities who hardly gain any technical assistance from mainstream practitioners in dealing prevailing socioenvironmental crises, acted as the architectural, environmental, and climatic design consultant in designing and developing the design catalogue for the project. It was supported and comoderated by Friendship and IFRC Shelter Research Unit and sponsored by the Government of the Grand Duchy of Luxembourg and Friendship Luxembourg.

Promoting Sustainable Building in Bangladesh

Oxfam in partnership with Housing and Building Research Institute (HBRI), Bangladesh Environmental Lawyers Association (BELA), and Jagorani Chakra Foundation (JCF), have initiated actions to generate market transformation for alternative bricks (AB) and other green construction materials under the project titled “Promoting Sustainable Building in Bangladesh” funded by the European Union. The project will be implemented for promoting AB amongst consumer and producer groups for wider replication and commercialization across Bangladesh. The project aims to test a model that market incentives can lead toward sustainable consumption and production (SCP) practices through adoption of AB and other green construction materials within the construction sector.

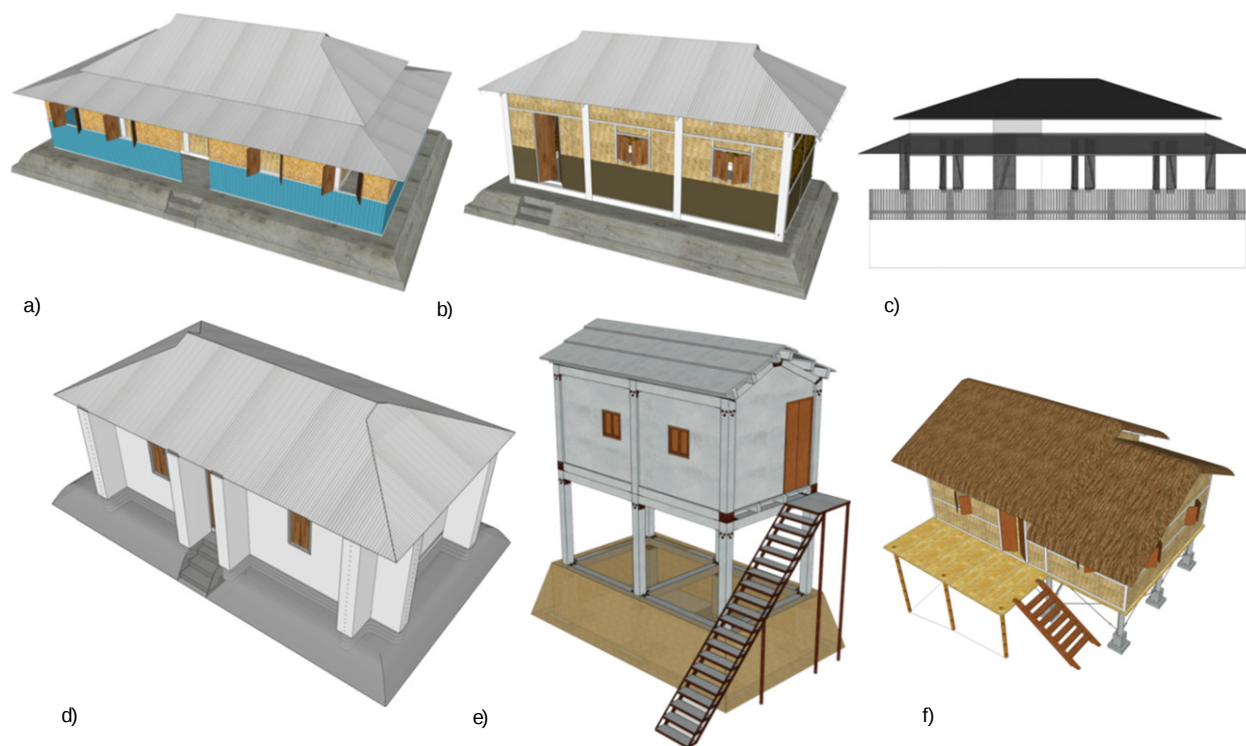


Fig. 32 Some of the designed house forms for different climatic zones of Bangladesh, from the Design Catalogue. (a) House form for coastal areas, (b) house form for flood plain areas, (c) floating house form, (d) load bearing Earth bag house form, (e) stilt house form, and (f) house form for hilly areas. Data from Housing and Building Research Institute.

Application of Ferrocement Technology in Rural Housing

This project is running in collaboration with the Prime Minister's office. The aim of this initiative is to disseminate the ferrocement technology in the rural areas of Bangladesh.

Technical Development to Upgrade Structural Integrity of Buildings in Densely Populated Urban Areas and Its Strategic Implementation Toward Resilience Cities in Bangladesh (Tsuib), The Verification Survey of NonFired Brick

This project has just been initiated in collaboration between HBRI and Japan International Cooperation Agency (JICA).

Conclusion

With a target of achieving zero use of agricultural topsoil and saving agricultural land stock HBRI is working relentlessly. It has already achieved success regarding research on the alternative building material; moreover special emphasis is required for extension services of the institute to implement and disseminate newly developed agriculture and environment-friendly technologies and building materials. Application of ferrocement technology as an alternative to traditional RC construction, and multiple alternative blocks to conventional bricks, are some of the emerging alternative materials that comprise many of HBRI's research initiatives. The government's attempt toward the agricultural land protection and land use bill may have some prospects, but special emphasis needs to be given regarding unregulated conversion of agricultural land to nonagricultural uses, restrictions regarding construction of brick fields, and production of bricks. Hence, there is an emerging need to build a new set of construction trends that is agriculture and environment friendly.

Acknowledgments

We would like to convey our warm gratitude to these personnel for their contribution in many ways: Ar. Mohammad Fuad Abdul Quaium (GHORAMIJON), Ar. Shafinaz Sameen, Md. Masbha Uddin, Ar. Tamanna Mannan, Ar. Sadia Sharmin, Ar. Hamidul Haque, Md. Riazul Halim, and other concerned staff from HBRI.

See also: E-Agriculture System by Object-Oriented Approach

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Analysis of the Indian Traditional *Loha Shodhana* Process for Biocompatibility

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Introduction

Indian metallurgical marvels have drawn the attention of scientists and technocrats across the globe. Some typical examples are: (1) The Delhi Iron Pillar which is a rustless pillar available in open air in Delhi, India and has excellent corrosion resistance since over 1700 years. (2) Damascus swords which are Wootz Steel swords with gold interlaced steel handles, are unable to be duplicated till date. (3) Bell metal canons and other metallic canons available and spread over several parts of India available till date. While there are these marvels on one side, on the other side there are several texts authored around the same time, which explain several material processing techniques including metals and non-metals like the rocks, gem stones etc. Gopalakrishnan (2009) lists out the names of 200 texts on *rasashastra*, the Indian materials science and material processing techniques and technologies, preparation of instruments and implements including surgical instruments used in traditional system of medicine.

A curiosity arose that in these texts, which are almost of the same time period as that of the metallurgical marvels, there could be directly or indirectly some information available related to material processing. Hence it was thought that investigating these literatures would be worth. One of these literatures is the '*Rasa Ratna Samucchaya*' (RRS) authored by Vagbhatacharya, is estimated to be written in dated in ninth century CE (Upadyaya, 2006; Dube, 1991). RRS has altogether 1230 *shlokas*/verses (Explanation/transfer of information/knowledge today is majorly in the prose form. Traditionally they were done in poetic form which was easy to learn by-heart and remember. One of such poetic forms of explanation are through what are traditionally called *shlokas*). (poetic explanations) (Satpute, 2006).

One of the *shlokas* on purification of metals aimed at detoxification looked to be quite interesting. Hence it was taken up for research. This *shloka* reads as follows:

taila takre gavāmūtre hyāranāle kulattaje

kramānnīśecayet taptam drāve drāve tu saptadā

svamādi loha patrāmām śuddhireṣā praśaśyate

The above *shloka* means: "Metals are made into thin leaves (sheets), heated intensively, and then quenched in *Taila* (Gingili oil (sesame oil)), *Takra* (Butter milk), *Gomutra* (Cow's urine), *Aaranala* (Rice gruel) and *Kulattha quatha* (Decoction of horse gram) in that order for seven times, in each of the liquids. This process suits the most to purify gold and other metals" (Satpute, 2006). This process is an initial phase of preparation of the nano-herbo-metallic complexes called the *bhasmas*. The other two phases are (1). Incineration, and (2). Special treatments based on the disease/disorder the *bhasma* is meant to cure. These *bhasmas* are used as ingredients in medicines to cure various diseases/disorders. These *bhasmas* are prepared of several metals like gold, silver, lead, tin, iron etc. If the *bhasmas* are prepared out of iron (*loha*), they are called *loha bhasma*. All these metals are detoxified by the same process as explained; although there are other alternate options in each case. However, after the above process called *samanya* (ordinary) *shodhana*, the metals undergo yet another stage of purification which is specific to the metal, called the *vishesha* (special) *shodhana*. In the current research iron is chosen. For *vishesha shodhana* of iron, the iron after the ordinary *shodhana* is subjected to seven more cycles of quenching with *triphalā* (Triphala=3 fruits: Indian gooseberry (Phyllanthus emblica), Chebulic myrobalans (Terminalia chebula), and Belleric myrobalans (Terminalia bellerica)) decoction as the quenchant. Thus in a complete *shodhana* process, the metal would undergo totally 42 steps of heat-quench cycles in six different quenchants as explained above. Fig. 1 shows a simplified flow chart of the process.

The modern work on the process only explain that the *shodhana* process is important in detoxifying the metal, and there are only limited studies from materials science point of view in the area. Further Nikalje (2015) who explain about the history of use of nano metallic medicine states that the first book on the same was authored by Freitas in 1999. However there are hundreds of traditional books available in India which explain about them which are centuries old. This indicates that modern researchers are not aware of the traditional literature, indicating poor availability of modern studies in the area; more so from materials science perspective. Hence this work was taken up. The aim of the current research was to determine the changes the metal undergoes during the *shodhana* process from materials science perspective.

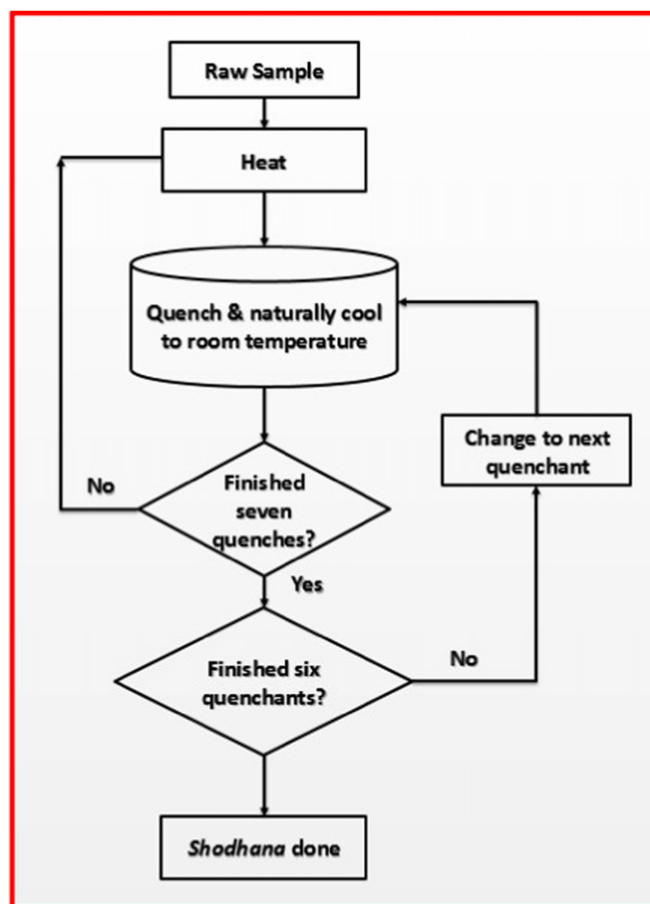


Fig. 1 Flow diagram of *shodhana* process.

Materials and Methods

The process of *shodhana* which is currently studied is a process which is common for metals like gold, silver, iron, copper, lead, tin etc., out of which *bhasmas* are prepared (Satpute, 2006). The current research is limited to *shodhana* of *loha* (iron/steel). Further pure iron, low carbon steel, high carbon steels are used in preparation of *bhasmas*. Considering the reported literature (Rajendraprasad *et al.*, 2010) and observations made in industries, in the current research *loha* (high carbon steel) was selected. Turnings were obtained from the *loha* rods, and were used as the raw material for *shodhana*.

Quenchant preparation: Branded Gingili oil (*Taila*) was purchased. Butter milk (*Takra*), Cow's urine (*Gomutra*), Rice Starch (*Hyaranala*), Horse gram decoction (*Kulatha*), three fruits' decoction were prepared as per traditional norms.

Performing *shodhana*: The turnings were heated to a temperature of 750 C in a muffle furnace. Arbitrarily 15 min of soaking time was provided. The red hot turnings were removed from the furnace and poured into oils that was kept ready. Once the turnings reached room temperature, they were removed from the quenchant, heated again and quenched. After each quench a sample was taken for characterization. The process is repeated for seven times. This completes one stage of 6 stages. The sample obtained at the end of first stage is taken for the second stage. As in the first stage, the sample was heated to 750 C, soaked for 15 min and quenched in the second fluid, the butter milk. The process is repeated for seven times to complete the second stage of *shodhana*. On similar lines, all the remaining four stages of *shodhana* was completed by quenching in cow's urine, starch, horsegam decoction and the three fruits (*triphala*) decoction, and samples was taken after each quench for characterization. The samples were labelled and stored in desiccators till they were taken for characterization.

Characterization: Although at the end of *shodhana* there are 42 samples, characterization was done only for samples obtained at the end of each stage. Raw sample and a commercial *loha* bhasma samples were also characterized. Thus characterization was done for six samples, and the raw sample; they being named as S0 (raw sample), S7 (sample obtained after seven quenches (at the end of stage 1)), S14, S21, S28, S35 and S42 and *loha bhasma* (LB). Powder X-Ray Diffraction (PXRD) technique was used to determine the change in composition and structure, Fourier Transform Infrared Spectroscopy (FTIR) and Raman Spectroscopy were used to determine the chemical composition of the samples. Several other chemical tests were used based on the results of the tests, and are explained in the Results and Discussion section.

Results and Discussion

PXRD Results

Fig. 2 shows the PXRD patterns of the *loha* before *shodhana*, at the end of each stage of *shodhana* and that of *loha bhasma*. The following observations can be made from the PXRD patterns pertaining to *loha* and *loha bhasma*. The raw *loha* sample (S0) shows two peaks at $2\theta = 44.77^\circ$ (A) and 65.19° (B) which correspond to cubic Fe (JCPDS No. 01-087-0722). The peak at A is actually a split peak with peaks at 44.77° and 45.07° . The peak at 44.77° is the one which corresponds to Fe (JCPDS No. 01-087-0722). Since Fe is expected in the raw sample, the same is considered here. The diffractogram also shows peak at $2\theta = 72.702$ which corresponds to Fe_2O_3 (JCPDS No. 01-084-0308).

At the end of first stage of *shodhana* the sample (S7), the peaks at $2\theta = 45.07^\circ$ (A) and 65.19° (B) of the untreated *loha* (S0), which correspond to Fe have disappeared. However the peak at $2\theta = 72.702^\circ$ (C) which corresponds to Fe_2O_3 (JCPDS No. 01-084-0308) is retained as it is in various stages of *shodhana*. The peak also appears in *loha bhasma*. New peaks have appeared at various angles. The same is explained hereon. A peak appears at $2\theta = 33.6^\circ$ (D). However this peak exists only in S7 and does not appear neither in any of the other stages of *shodhana* nor in *loha bhasma*. This peak could not be attributed to any element/compound due to their non-availability in the available databases. The peak at $2\theta = 36.14^\circ$ (E) corresponds to $\text{Fe}_{0.925}\text{O}$ (JCPDS No. 01-089-0686). This peak exists only in S7 and does not appear back in any of the other stages of *shodhana*. The peak does not appear in *loha bhasma* also. The peak at $2\theta = 44.61^\circ$ (G) refers to Fe. (JCPDS No. 00-006-0696). This peak appears in all the diffractograms from S7 to S42 except in S21. The peak also appears in *loha bhasma*. The peak at $2\theta = 63.08^\circ$ (I) refers to Fe_3O_4 , appears in S7. It does not appear in any other stages of *shodhana*; but appears in *loha bhasma*.

S14 has a number of other new peaks. The peak at $2\theta = 33.13^\circ$ (K) to Fe_2O_3 (JCPDS No. 01-079-1741). This peak continues to exist in all the stages of *shodhana*, and in *loha bhasma*. The peaks at $2\theta = 41.09^\circ$ (M) and 49.66° (N) corresponds to Fe_2O_3 (JCPDS No. 01-084-0308). These peaks continue to exist in all the stages of *shodhana*, and in *loha bhasma*.

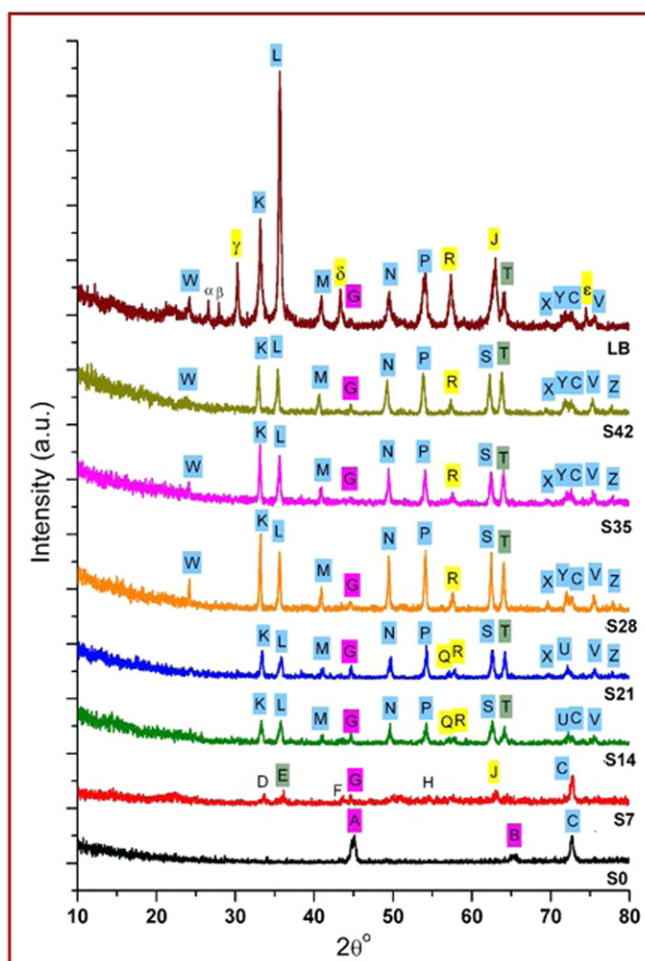


Fig. 2 PXRD patterns of *loha* before and after different stages of *shodhana*, and *loha bhasma*. (■ Fe, ■ Fe_2O_3 , ■ Fe_3O_4 , ■ $\text{Fe}_{0.925}\text{O}$).

The peaks at $2\theta = 35.66^\circ$ (L), 54.19° (P) and 75.60° (V) correspond to Fe_2O_3 (JCPDS No. 01-089-0599). These peaks continue to exist in all the stages of *shodhana*, and in *loha bhasma*. The peaks at $2\theta = 62.46^\circ$ (S) and 72.26° (U) correspond to Fe_2O_3 (JCPDS No. 00-033-0664). The peak at $2\theta = 64.19^\circ$ (T) corresponds to $\text{Fe}_{0.925}\text{O}$ (JCPDS No. 01-089-0689). The Fe_2O_3 peak at S continues to exist till all the stages of *shodhana*, but not in *loha bhasma*. The Fe_2O_3 peak at U exists only till S21. The two peaks that correspond to Fe_3O_4 are the ones at $2\theta = 56.93^\circ$ (Q) and 57.5° (R). The Fe_3O_4 peak at Q persists only till S21, but the one at R continues to appear in all the stages of *shodhana* as well as in the *loha bhasma*.

Two extra peaks start appearing at S21, they being the peaks at $2\theta = 69.65^\circ$ (X) and 77.95° (Z), both of which continues to exist till all the stages of *shodhana*, and in *loha bhasma* and correspond to Fe_2O_3 (JCPDS No. 01-079-1741).

Two new peaks start appearing from S28. The peak at $2\theta = 24.14^\circ$ (W) and 71.97° (Y). These peaks correspond to Fe_2O_3 (JCPDS nos. 00-033-0664 and 01-079-1741) respectively. There are no changes in the PXRD patterns of S35 and S42, and remain same as that of S28. However, in *loha bhasma*, there are new peaks at $2\theta = 30.30^\circ$ (γ), 43.36° (δ) and 74.51° (ϵ), all of which correspond to Fe_3O_4 (JCPDS No. 01-075-0449).

To summarize, PXRD results indicate that as the *shodhana* progresses, the Fe peaks deteriorate and disappear and a number of iron oxide peaks viz., Fe_2O_3 , Fe_3O_4 and $\text{Fe}_{0.925}\text{O}$ appear. Although Fe peak appeared, they are low intensity, non repetitive peaks. Of the iron oxide peaks, Fe_2O_3 peaks are prominent and have highest intensity. Formation of stable iron oxide (Fe_2O_3) is due to repeated heat-quench cycles as part of *shodhana*. *Loha bhasma* also showed highest intensity peaks for stable iron oxide (Fe_2O_3), with traces of unstable iron oxides (Fe_3O_4 and $\text{Fe}_{0.925}\text{O}$).

Results of FTIR of Shodhana

Fig. 3 shows the FTIR spectra of the *loha* before *shodhana*, at the end of each stage of *shodhana* and that of *loha bhasma*. The FTIR spectra shows peaks at wavenumbers of $470\text{--}475\text{ cm}^{-1}$ which indicates Fe_2O_3 peaks. The peak in this range has not appeared in S0

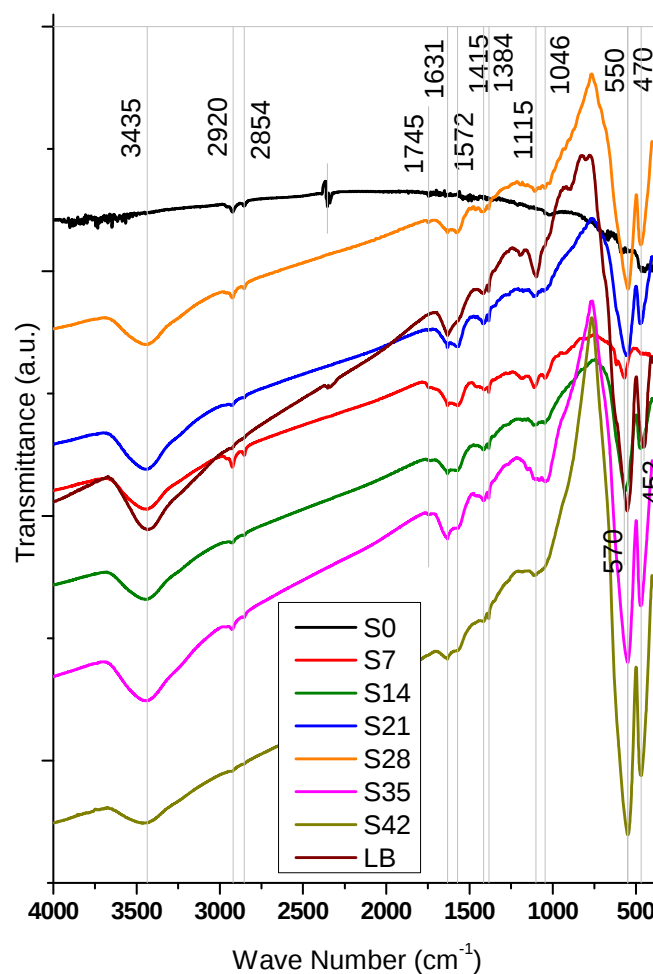


Fig. 3 FTIR spectra of *loha* before *shodhana*, at different stages of *shodhana*, and of *loha bhasma*. Note: The region covered by the legend had no peaks.

and S7; but has started with S14 onwards and persists in all the stages of *shodhana* (till S42). This suggests the formation of Fe_2O_3 due to oxidation of *loha* turnings.

The FTIR spectra of S0 shows low intensity peaks at 2920 and 2854 cm^{-1} which correspond to C–H alkane peaks (Xiong *et al.*, 2006) which remains as a weak peak as *shodhana* progresses. The peak could be because of the coolant used while turning. Rest, the spectra of S0 shows no other significant peaks. As the *shodhana* starts, S7 shows new peaks. The broad medium peak at 3435 cm^{-1} indicates water peaks which are due to adsorbed moisture. This peak exists in all the stages of *shodhana* and also in the *loha bhasma*. The peak at 1631 cm^{-1} corresponds to C–O bending peaks (Shokri *et al.*, 2009). This medium intensity peak exists in all the stages of *shodhana* and also in *loha bhasma*.

Another peak at 1572 cm^{-1} corresponds to carboxylate group (RCOO^-) (Sathyanarayana, 2015). This low intensity peak appears in all the stages of *shodhana* but does not appear in *loha bhasma*. The peak at 1745 cm^{-1} refers to carboxylic acid groups (Vander, 2002). The peak appears in S14, S28 and S35. The peaks at 1415 cm^{-1} refers to carboxylic acid moieties (Vander, 2002). This peak appears in all the stages of *shodhana* and in *loha bhasma*. The peak at 1384 cm^{-1} refers to carbonyl peak (Xiong *et al.*, 2006) which appears in all the stages of *shodhana* except S14. The peak does not appear in *loha bhasma*.

Another peak between 1104 and 1113 cm^{-1} appears in all the stages of *shodhana* as small peaks and in *loha bhasma* as a high peak. These peaks correspond to Si–O–Si stretching vibration mode (Senthil Kumar and Rajkumar, 2014). The peak at 1046 cm^{-1} appears in S7, S14 and S35. This peak corresponds to C–O–C symmetric stretching and is due to the presence of a ligand called sesamol, a component of gingili (sesame) oil (Mirghani *et al.*, 2003). The peak does not appear in *loha bhasma*.

Iron oxide (FeO) peaks at $\sim 570\text{ cm}^{-1}$ appears in S7 and S14 only. The peak does not appear later on, neither in *loha bhasma*. New peaks appear with S21 at 550 – 557 cm^{-1} . The peak continues to exist in all the stages of *shodhana* and in *loha bhasma*. The peak indicate vibrations corresponding to Fe_2O_3 (Zhang *et al.*, 2013). Fe_2O_3 peak start appearing with S14 and continues till the last stage of *shodhana*. This Fe_2O_3 peak is between 470 and 475 cm^{-1} (Woo *et al.*, 2003). There are several other new peaks that appear in *loha bhasma* alone which are all low intensity peaks, which could be attributed to later stages of *bhasma* preparation, viz., the *maarana* and *vishesha sanskarana*.

Overall, the presence of various organic bonds along with Fe–O bonds can be attributed to the interaction of the quenchant with the hot metal. These results are similar to the one obtained in *shodhana* of mild steel.

To summarize, through FTIR analysis of samples of *shodhana* it can be observed that Fe–O bonds of Fe_2O_3 are indicated. There are indications of presence of unstable FeO in the initial stages of *shodhana*. Apart from these metal oxide bonds, there are a number of organic bonds involving C–H bonds due to carboxylic acid groups, alkane peaks, aromatic groups whose presence is attributed to the organic quenchant since all organic compounds invariably have C–H bonds. In addition to these C–H bonds there are water peaks and C–O peaks due to adsorbed moisture and carbon-di-oxide. Si–O–Si bonds are indicated due to presence of Si in the *lohas*, which gets oxidized during quenching. *Loha bhasma* also indicated similar results. Overall, the results of FTIR with respect to formation of majorly Fe_2O_3 is in consistence with the results of PXRD.

Results of Raman Spectroscopy

Fig. 4 shows the Raman spectra of the *loha* before *shodhana*, at the end of each stage of *shodhana* and that of *loha bhasma*. The Raman spectrum of S0 shows no significant peaks. This is because of the fact that metals do not show peaks in a Raman spectrum. The Raman spectrum of S7 shows low intensity peaks at wavenumbers of 294 and 412 cm^{-1} . Both these peaks correspond to iron-oxygen bond vibrations of Fe_2O_3 (RRUFF No. R050300). The Raman spectrum of S14 shows only one low intensity peak at wavenumber of 294 cm^{-1} . This peak corresponds to iron-oxygen bond vibrations of Fe_2O_3 (RRUFF No. R050300). The Raman spectrum of S21 shows a high intensity peak at wavenumber of 226 cm^{-1} which corresponds to Fe_2O_3 (RRUFF No. R040025). The peaks at 244 , 246 , 292 , and 409 cm^{-1} corresponds to Fe_2O_3 (RRUFF No. R050300). The peaks at 494 and 609 cm^{-1} also correspond to Fe_2O_3 (Shim and Duffy, 2002). One low peak at 651 cm^{-1} corresponds to Fe_3O_4 (RRUFF No. R060222). The Raman spectrum of S28 shows a high intensity peak at wavenumber of 226 cm^{-1} which corresponds to Fe_2O_3 (RRUFF No. R040025). The peaks at 293 , 409 and 611 cm^{-1} also correspond to Fe_2O_3 (RRUFF No. R060191). Thus all the peaks in S28 correspond to Fe_2O_3 . The Raman spectrum of S35 shows a high intensity peak at wavenumber of 226 cm^{-1} which corresponds to Fe_2O_3 (RRUFF No. R040025). The peaks at 244 , 293 , 409 and 611 cm^{-1} correspond to Fe_2O_3 (RRUFF No. R050300). The peak at 494 cm^{-1} also corresponds to Fe_2O_3 (Shim and Duffy, 2002). A low intensity peak appears at 657 cm^{-1} which corresponds to Fe_3O_4 (RRUFF No. R060222). Peaks at 485 and 506 cm^{-1} could not be identified from the available database. Finally, in the Raman spectrum of last stage of *shodhana*, S42 shows a high intensity peak at wavenumber of 223 cm^{-1} which corresponds to Fe_2O_3 (RRUFF No. R040025). The peaks at 292 , 409 and 611 cm^{-1} corresponds to Fe_2O_3 (RRUFF No. R050300). The peak at 496 cm^{-1} also corresponds to Fe_2O_3 (Shim and Duffy, 2002). The peak at 488 cm^{-1} could not be identified from the available database. Raman database was checked for presence of Fe_3O_4 and it was found that there is no presence of Fe_3O_4 peaks other than those mentioned above.

Thus, the Raman spectra taken after different stages of *shodhana* of EN shows majorly peaks corresponding to the iron-oxygen bond vibrations of Fe_2O_3 . Low intensity peaks corresponding to the Fe_3O_4 bonds appear in S21 and S35. They are also indicated in the PXRD results. However PXRD results also show single peaks corresponding to Fe_3O_4 in all the stages of *shodhana* of EN except S7.

To summarize, Raman spectra indicate the presence of peaks corresponding to majorly the stable Fe_2O_3 in all stages of *shodhana* and in *loha bhasma*. Although there are peaks corresponding to other iron oxides, they are low intensity peaks. Further, though

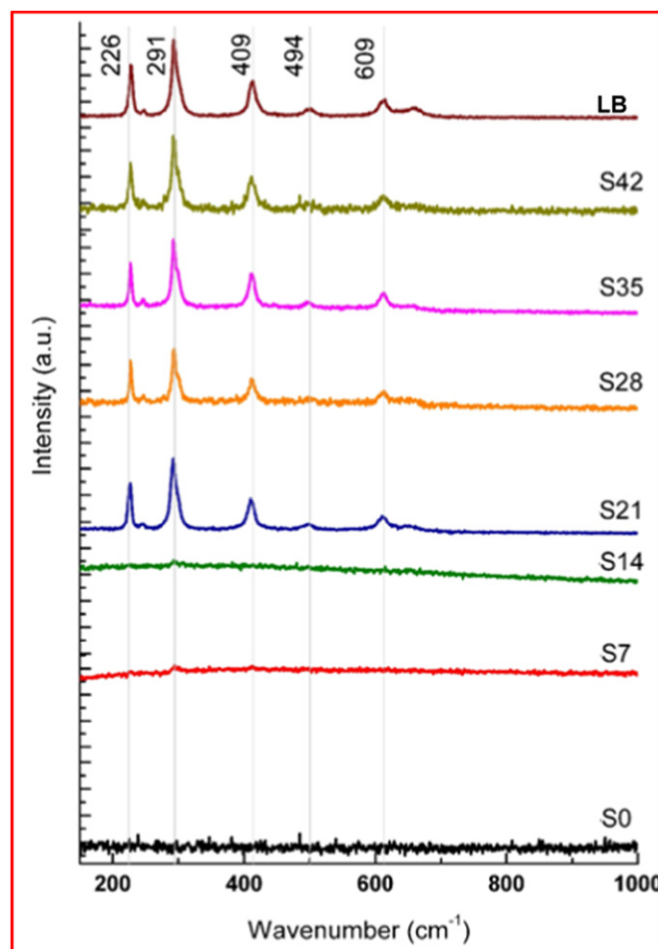


Fig. 4 Raman spectra of *shodhana* of loha, and *loha bhasma*.

there are other unidentified peaks, it was confirmed through the available RRUFF and other database that they are not corresponding to Fe_3O_4 . Several other peaks could not be identified which could be organic peaks. The results of Raman spectroscopy is in consistency with the results of PXRD and FTIR with respect to formation of majorly Fe_2O_3 .

Chemical Based Tests

From the PXRD, FTIR and Raman Spectroscopy tests it was noted that after *shodhana* the material has turned into a very stable Fe_2O_3 with a number of metallo-organic complexes. Minor peaks of Fe_3O_4 was also detected. Earlier reports, which was also a material science based work, indicate that *shodhana* renders the material into an easily digestible form (Krishnamachary *et al.*, 2012). Since the result was in contrary to the already published results, more tests were conducted to validate the current result. In order to validate the same several chemical based tests were conducted. The sample obtained at the end of *shodhana* was tested to be digested in strong acid and strong base. The sample was neither digestible in strong acid (pH ~ 1), nor strong base (pH = 10), even upon boiling in them.

Since the sample after *shodhana* could not be digested even after boiling in the strong acid/base it can inferred that it has turned into a form which cannot be digested by the human system,. Thus, this result is in contrary with an earlier published research. The difference in the result could be because earlier researchers had quenched the raw material for only 3 times in each quenchant, thus finishing the *shodhana* process in $3 \times 6 = 18$ steps, unlike in the current study it was $7 \times 6 = 42$ steps. Further, the heating temperature chosen by the earlier researcher was 530–560°C, and in the current research is 750°C. Even in the current research, during the pilot study a temperature of 530–560°C was chosen. However, by the time the material was removed from the muffle furnace and dropped into the quenchant, the temperature of the *loha* turned low indicated by the blackish color of the *loha* as it got into the quenchant. Further, the temperature chosen here was 750°C since earlier researchers, who have prepared *loha bhasma* for clinical research have reported a preparation temperature of 750–850°C (Rajendraprasad *et al.*, 2010; Rao and Naidu, 2011; Gupta and J, 2012). Also, in the current research it was noted that while conducting *shodhana* of low melting point metals like lead/tin the metal was liquefied and poured into the quenchants (Rajput *et al.*, 2013; Sarkar *et al.*, 2010). Considering this, a higher temperature was preferred, and thus chosen 750°C.

Thus from the current research it can be concluded that the *loha* after *shodhana* has turned the material to an indigestible form, and after completing the later stages of *bhasma* preparation, the resulting nano-herbo-metallic complex, the *loha bhasma* produced also is indigestible, which was also confirmed experimentally in the current research by testing commercially available *loha bhasma*. Another point that could be noted is that there were be traces of Fe_3O_4 which could provide easily assimilable Fe^{2+} ions upon reaction with digestive juices. Thus, with the current research, from materials science point of view, it can be hypothesized that human body cannot digest the major part of *loha bhasma*, and might only act as a messenger in the body, which needs to be confirmed by clinical studies by appropriate researchers. This property of the *loha bhasma* is attributed to the *loha shodhana* process.

Finally, what is biocompatibility? Whether the *loha bhasma* should be digestible or not digestible? Whether it is aimed at acting as a messenger by being inert or should it provide digestible form of iron ions upon its consumption? These are the question to be answered by the appropriate medical science community to decide on the process parameters for preparation of *loha bhasmas*; since the property of the end product significantly depends on the process parameters, and standard operating procedures for preparation of *loha bhasma* should be decided on by both material and medical scientists working together.

Conclusion

Loha shodhana renders *loha* (iron) into stable Fe_2O_3 , a form which is capped with organic bonds, which from materials science point of view is indigestible by the neither strong acid not base, and hence by the human digestive system also. The *loha bhasma* which is the end product after processing the *loha* after its *shodhana* is also indigestible the property of which is attributed to the *shodhana* process. The current research provides a hypothesis to the clinical researchers that *loha bhasmas* are indigestible form and might act as a messenger in the human body. Further, there needs standardization in the operating procedures for preparation of *loha bhasmas*, since there are significant differences in the property of the *loha* as the parameters vary.

See also: Multi-Stage Stamping of Lightweight Steel Wheel Disks by Controlling its Wall Thickness Distribution

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Analyzing Biodiesel Production From Cooking Oil

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Introduction

Biodiesel derived from waste cooking oil is considered highly environmentally sustainable since waste cooking oil is a waste product from domestic and commercial cooking processes and then recycled to a transportation fuel in Singapore. In addition, it avoids the conversion of land use for crop production.

The collectors and recyclers should convince the food establishments and suppliers of cooking oil of the benefits of recycling cooking oil, which in turn obtains a steady source of waste cooking oil as feedstock for biodiesel production. As the biodiesel life cycle defined is very much dependent on waste cooking oil as a feedstock, it is recommended to optimize the waste cooking oil collection route based on location of the suppliers.

In this article the collection of waste cooking oil is investigated based on the location of suppliers, such as a pilot-scaled collection and production scheme in large estates. For such purpose a waste cooking oil software is modelled which will help in the collection of waste cooking oil by optimizing the optimal route of the waste cooking oil based on the suppliers' locations.

Waste cooking oil management process could be very complex task because of many different suppliers and collectors. There is need to make optimal route for the most efficient transport of the waste cooking oil from users to the collectors. The main problem is suppliers motivation for such a process since they require simple and understandable process for the waste cooking oil management. Because of that it is suitable for the waste cooking oil transport to model an software which will make more motivation for suppliers and collectors to make stronger and more uniform connections. The software could determine the optimal routes for the waste cooking oil based on locations of suppliers. In this article object orientated approach is used for the software modeling (Lethbridge and Laganier, 2005; Jacobson, 1993).

Object-orientated modeling strategy is an attempt to encapsulate data and process into thing called objects. The data in the objects could be created, deleted or used only by some encapsulated processes or methods. Unified modeling language (UML) is a standard tool for object orientated modeling which could help to developers and engineers to make detailed specification and documentation of any system.

UML (Rumbaugh *et al.*, 2004) is a graphical language which is effective for visualization, specification, construction and documentation of a system's artifact which is software intensive. UML has standard practices for writing a blueprint of system. By using UML one can cover various conceptual things such as functionality by use cases and business processes.

Modeling and analyzing of various activities in any system by UML can help to visualize, specify, constructs and document the system artifact effectively which is helpful for better understanding of the problem and for various stakeholders of the application of the waste cooking oil.

Literature Overview

In paper (da Silva César *et al.*, 2017) authors examined the opportunity for biodiesel production from WCO as a potential source for future energy supply, particularly for biodiesel, and in this case, they analyzed the Brazilian scene. Several related aspects are covered, such as the physical and chemical properties of the WCO and the biodiesel made from it (da Silva César *et al.*, 2017). The waste cooking oil was used as a raw material for biodiesel production and their different fatty acids were determined by gas chromatography coupled with flame ionization detector (GC-FID) in article (Ullah *et al.*, 2017) where kinetic study of this transesterification reaction was evaluated and followed the first-order reaction mechanism. Paper (de Araújo *et al.*, 2013) aimed at the assessment of the methods of production of biodiesel from different types of used cooking oil. Researches into the productive chain of this type of biofuel were performed in Brazil while several scientific studies approaching processes of pretreatment and transesterification of waste cooking oil were analyzed with their possible variations: alkaline catalysis, acid catalysis, enzymatic catalysis and non-catalytic conversion techniques, highlighting the main advantages and disadvantages of each analyzed route. Transesterification reaction parameters to produce the lowest kinematic viscosity waste cooking oil biodiesel by using sodium hydroxide (NaOH) as catalyst and ethanol (C₂H₅OH) as alcohol was determined in article (Bilgin *et al.*, 2015) and according to results, reaction parameters giving the lowest kinematic viscosity of 4.387 cSt were determined as 1.25% catalyst concentration, 70°C reaction temperature, 120 min reaction time and 12:1 alcohol/oil molar ratio. Development of cleaner biodiesel production related to hydrodynamic cavitation of methyl ester synthesis from sustainable waste cooking oil via alkali-catalysed transesterification is gaining importance due to considerable lower energy requirement and time. The effects of the oil to methanol molar ratio (1:4–1:7), catalyst concentration (0.5–1.25 wt%) and reaction temperature (50–65°C) have been studied in a hydrodynamic cavitation and mechanical stirring system (Chuah *et al.*, 2017). In conclusion, waste cooking oil methyl ester produced via hydrodynamic cavitation proved to be time saving and energy efficient compared to mechanical stirring. This makes the process more environmental friendly

using hydrodynamic cavitation (Chuah *et al.*, 2017). The comprehensive spray and combustion characteristics of waste cooking oil (WCO) biodiesel (B100) and conventional diesel fuels were investigated in article (Hwang *et al.*, 2016) where the combustion imaging showed that the WCO biodiesel had lower flame luminosity and shorter visible flame duration than diesel. Study (Hong *et al.*, 2016) was carried out for manufacturing biodiesel from WCO using microwave assisted-transesterification reaction, and the efficiency of the original and new methods was compared. The biodiesel fuel properties such as fatty acid methyl ester (FAME) content, higher heating value (HHV), and kinematic viscosity (KV) of six acid value WCO based biodiesel were analyzed where it was found that as the acid value increased, more catalyst amount, microwave power, reaction time, and molar ratio of alcohol/WCO were needed. Therefore, biodiesel using commercial WCO can be produced without pretreatment process (Hong *et al.*, 2016). Used waste cooking oil (WCO) or frying oils are being considered as rich sources of economical feedstock for biodiesel production. To carry out the process of trans-esterification of WCO to methyl esters (biodiesel), zeolite/chitosan/KOH composite was used as solid heterogeneous catalysts. The conversion of biodiesel from WCO was obtained for 1 wt% catalyst concentration and alcohol/oil ratio of 1:7 at 40 V in the presence of water as 2 wt % of the whole solution in 3 h, produced 93% yield (Fereidooni and Mehrpooya, 2017). The catalytic esterification of waste cooking oil (WCO) with methanol could be easily achieved by using C-SO₃H and therefore the sulfonated carbon-based solid acid catalyst was thus designed to be an active, stable and reusable solid acid as an environmentally benign replacement for homogeneous catalyst (Wei *et al.*, 2017). The application of an environmentally benign sulfonated carbon microsphere catalyst for biodiesel production from waste cooking oil was investigated in article (Tran *et al.*, 2016) where the highest biodiesel yield (89.6%) was obtained at a reaction temperature of 110°C, duration time of 4 h, and catalyst loading of 10 wt % under elevated pressure 2.3 bar and 1.4 bar for first and second step, respectively. The reusability of the catalyst was investigated and showed that the biodiesel yield decreased by 9% with each cycle; however, this catalyst is still of interest because it is an example of green chemistry, is nontoxic, and makes use of xylose waste (Tran *et al.*, 2016). In study (Babaki *et al.*, 2017) was developed a multi-enzyme system to produce biodiesel with waste cooking oil and methanol where verification experiment confirmed the validity of the predicted model. Paper (Xiang *et al.*, 2017) studied the effects of using modified coal fly ash as a catalyst to convert waste cooking oil (WCO) into biodiesel under microwave-strengthened action where the experimental results showed that the modified coal fly ash catalyst improved biodiesel yields under the microwave-assisted system, and the maximum biodiesel yield from waste cooking oil reached 94.91% at a molar ratio of methanol to WCO of 9.67:1 with 3.99 wt% of modified coal fly ash catalyst (based on oil weight) at a 66.20°C reaction temperature. In work (Joshi *et al.*, 2017), high speed homogenizer has been used for the intensification of biodiesel synthesis from soybean oil and waste cooking oil (WCO) used as a sustainable feedstock. High acid value waste cooking oil (27 mg of KOH/g of oil) was first esterified with methanol using sulphuric acid as catalyst in two stages to bring the acid value to desired value of 1.5 mg of KOH/g of oil. Transesterification of soybean oil (directly due to lower acid value) and esterified waste cooking oil was performed in the presence of heterogeneous catalyst (CaO) for the production of biodiesel. Overall it can be concluded from this study that high speed homogenizer can be used as an alternate cavitating device to efficiently produce biodiesel in the presence of heterogeneous catalysts (Joshi *et al.*, 2017). The objective of the work (Qu *et al.*, 2016) was to investigate the influence of waste cooking oil biodiesel on oxidation reactivity and nanostructure of particulate matter (PM) where the test was carried out in a small agricultural diesel engine. Study (Jung *et al.*, 2017) laid an emphasis on the possible employment of biochar generated from pyrolysis of chicken manure to establish a green platform for producing biodiesel where to this end, the pseudo-catalytic transesterification reaction using chicken manure biochar and waste cooking oil was investigated. In study (Ali *et al.*, 2017), waste cooking oil (WCO) was evaluated as feedstock for biodiesel production using free lipase in liquid where the response surface methodology (RSM) was used to optimize the interaction between four factors: The reaction temperature, methanol-oil molar ratio, dosage of lipase as biocatalyst and rotational speed. Due to their excellent physicochemical properties, biodiesel and n-pentanol are regarded as two promising alternative biofuels for automobile. However, the fundamental data of spray and combustion characteristics of n-pentanol/biodiesel blends are still scarce. The objective of work (Ma *et al.*, 2017) was to investigate the effects of n-pentanol addition to waste cooking oil (WCO) biodiesel in different ratios (0%, 20%, and 40% in vol) on spray, ignition and combustion characteristics in a constant volume combustion bomb (CVCB) where result also suggested that, for multi-component fuels, flame lift-off length (FL) is the most reliable factor that influence the soot concentration level under spray combustion processes, rather than ignition delay or soot formation time. Study (Wei *et al.*, 2017) investigated the influence of waste cooking oil (WCO) biodiesel on the combustion, unregulated gaseous emissions and particulate emissions of a diesel engine. Experiments were carried out on a direct-injection diesel engine fueled with diesel, B20 (20% biodiesel on volume basis), B50, B75 and biodiesel, under the Japanese 13-mode test cycle where overall, the influence of biodiesel on the investigated emissions is proportional to the biodiesel content in the tested fuels (Wei *et al.*, 2017).

Methodologies for Software Development

Generally, the software development methodology consisted of procedures, techniques, tools and documentation which helps in the software development process. Software development methodology describes all steps and phases of the software development. The methodology suggests tools and techniques which should be used in the particular step of the software development. Also the methodology could suggest how to plan and track process of the software development and testing as well.

Many companies use the methodologies for software development in order to ensure the consistency of the problem solution, to decrease the possible errors, to acquire the full documentation for current and future projects and to get good final product which could be changeable and adaptable easily since the all steps and phases would be documented in detail and any new changes in the software models could be achieved before software coding.

Models could be describes as simplified presentation of reality. The models could be presented with some standard modeling language. The model presentation could be textual or graphical by diagrams. Each software could be described based on different aspects by structural models in order to show software structure with the main parts and their interconnections and relationships. Also there is behaviour models where one can track the software dynamics.

RUP Methodology

Rational Unified Process (RUP) is an interactive methodology for the software development based on architecture and use cases. RUP methodology is based on Unified Modeling Language (UML). UML is used for specification, visualization, construction and documentation of the software development.

RUP methodology has control of key or critical points through the development. In other words each phase of the RUP methodology should end with some control key or critical points where the achieved results are summed and future directions are planned based on the results. RUP methodology has artefacts (documents), models of model elements. Project requests are noted in the documents. Models are used to simplify the software architecture without unnecessary details. Model elements could help to visualize, construct and document the main structure and software behaviour. Fig. 1 shows the main elements of the RUP methodology. Each phase of the RUP methodology has iteration where disciplines are considered. The disciplines are described by process flow in details. The process shows activity and roles of everyone in the project. Finally, there are artefacts where one can see software documentation, software models and model elements.

RUP methodology has four main phases. The first phase is the initial phase or idea inception where one needs to understand what should be done and then the software vision and requirements are identified. This phase includes the identification of key software actors (users) and use cases. Also there is need to identify software domain. Use of case defines one sequence of an action which software performs that yields to an observable results. On the other hand one use case presents result of an action by actor (Fig. 2). Use case presents the main part of some complete software operation from beginning until to the end. It is used to capture the intended behaviour of the system in development. By use case models desired behaviour of the system could be specified but it is not strictly this desired behaviour to be carried out or implemented in the final product. Use case models can be developed for whole system or for the part of the system. Each part of the system or subsystem can be developed by use case models until the part produces some tangible amount of work and results. System complexity indicates the number of use cases. In the initial stage of system development main use cases are developed and additional use cases can be added or included when there is need for them.

The second phase is project elaboration where one needs to understand how to build the software and basic software architecture is showed in the phase. The third phase presents software construction where software testing is considered. The fourth phase presents software transition where software validation is performed. The RUP phases are shown in Fig. 3.

RUP models describe software in modeling. RUP models could be business models which describes business processes and business environment, use case models which describes what the software is doing and the software environment, projecting models which describe use case realization as code abstraction and implementation models which present collection of components and subsystems.

Software development process could have different problems which needs to be identified and solved before coding and testing. In order to solve problems there is need to find the problem causes. To remove the problem causes it is essential to use best

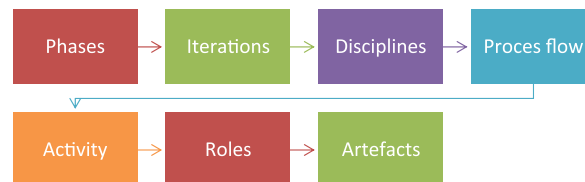


Fig. 1 Elements of RUP methodology.

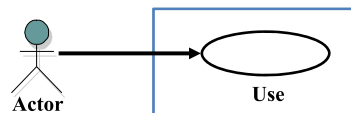


Fig. 2 Use case model.



Fig. 3 RUP methodology phases.

practices. For example in order to remove the confusion in communication between team members it is suitable to use standard language UML for the software visualization, specification and documentation. There are different types of UML diagrams which can be used in the software development process. There are two main classes of the UML diagrams. These are structural and behavioral diagrams. Structural diagram presents structure of the system in passive state and behavioral diagram present the active behaviour of the objects in a system or dynamical state.

Object-Orientated Modeling of Business Process

UML is used for object-oriented modeling of business process. As already mentioned there are different UML diagrams for describing of software architecture and software behaviour. UML as standard language is used for modeling, for analyzing, for projecting and for implementation of the software system. Based on the object-oriented modeling all processes could be presented by use case models as rough specification and by structural diagrams and behavioral diagrams as detail specification.

During modeling of the business process it is not recommended to use natural language because of its ambiguity. Also, formal programming languages are not understandable for many people in the project team. Therefore it is suitable to organize the natural language to avoid ambiguity. Modeling process is one of the solutions for understanding and clear communication between project team members.

Modeling of the Optimal Route for Waste Cooking Oil

Problem Description

The problem is intended for solving of collection of waste cooking oil which is carcinogenic material. The main target of the model are the suppliers which are implemented in the software of the estimation of optimal route of waste cooking oil. The suppliers in this study are market objects, tourist industry, catering industry and industry objects.

The main goals of the investigation is to decrease the emissions of the greenhouse gases and generally to decrease global warming. Also biofuels need to be introduced in the transport as much as it can. The main activity of the investigation should be to develop the GPS system for mapping of the waste cooking oil suppliers in order to optimize the waste cooking oil transport.

Object-oriented modeling concepts are used during analyzing and modeling of the process of the optimization of route of waste cooking oil. Two UML concepts are used for the software modeling like use case models, activity diagrams, state diagrams and scenarios of activities.

Software for Route Optimization for Waste Cooking Oil Transport

Software for route optimization for waste cooking oil transport should be used for organization of the waste cooking oil suppliers and collectors as well. The main advantage of the software for route optimization for waste cooking oil transport in the article is in its universality and in its online usage.

The main feature of the software for route optimization for waste cooking oil transport should be universal application for any subjects and any suppliers and collectors. The software for route optimization for waste cooking oil transport will be framework of the suppliers and collectors of the transport activity.

As users are considered suppliers in different parts of industry and collectors as well, all of the users should have username and password in order to access the waste cooking oil management database.

Collectors should make reports for different statistical analysis of the waste cooking oil. As the main problem of the current software for route optimization for waste cooking oil transport it was identified limitation of unified approach for all subjects. Therefore, it is required to develop information system which would allow to users to use the software anytime in order to enter desired data.

Software users

The software users could be divided based on natural basis according to working place, suppliers and collectors. All of the users have equal rights to access and use of the software. Therefore the main users of the software are:

- Suppliers (market objects, touristy industry, catering industry and industry objects).
- Collectors.
- Administrator.

Each of the users should have individual username and password in order to access to the software. Administrator of information system who needs to maintain the software and he is responsible for working of computer system and software as well. He gives permission to the staff's access to the waste cooking oil management database, maintains database, maintains web presentation of the waste cooking oil management and makes regular daily reports.

Software Analyzing

Each of the users should have individual username and password in order to access to the software. Administrator of information system who needs to maintain the software is responsible for working of computer system and software as well. He gives

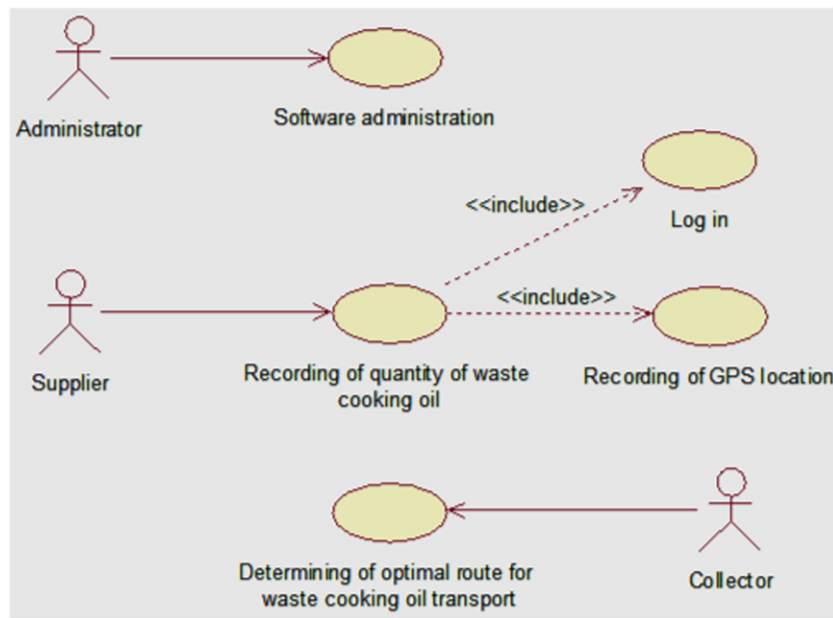


Fig. 4 Main use case diagram of the software for route optimization for waste cooking oil transport.

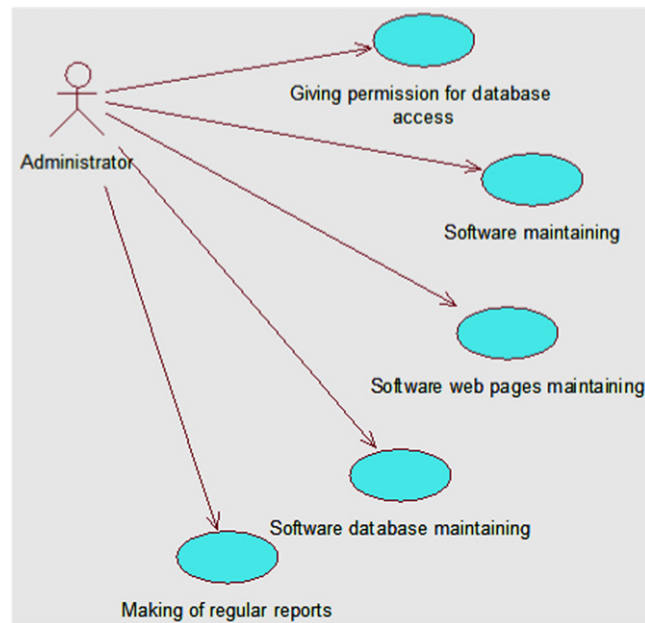


Fig. 5 Use case diagram – Software administration.

permission to the staff's access to the waste cooking oil management database, maintains database, maintains web presentation of the waste cooking oil management and makes regular daily reports.

During the analyzing process it is concluded that the suppliers and collectors of the waste cooking oil have the have universal software to improve the efficiency of the waste cooking oil acquiring. This software needs to have online and offline working regime since there is no need to be always online to track desired materials. The software should enable fast searching procedure for the material.

Main use cases diagram of the software

Transport process of the waste cooking oil are depicted by the main use case diagram as it shown in Fig. 4. The main use case diagram has several sub use cases which will be explained in detail. As can be seen, the administrator should perform the main administration process of the transport process in order to ensure smooth working processes by the software. Waste cooking oil transport clients or

Table 1 Specification of use case: Giving permission for database access

Title	<i>Giving permission for database access</i>
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the giving permission for database access
Pre-condition	PC is properly settled. Administrator has needed knowledge for the tasks
Post-condition	Client received authorization for database access of software
Main scenario	1. Administrator receives the request for the giving permission for database access of software 2. Administrator checks the request validity 3. Administrator fills the application form for the giving permission for database access of software 4. Administrator selects client category based on the quantity of the waste cooking oil 5. Administrator approves the request 6. Administrator prints the instruction for the application use 7. Administrator distributes the instruction to the client as the proof for the successful addition to the users of the waste cooking oil management software for the database access
Alternative	1. In the case if the request is incorrect filled based on the step 2. of the main scenario the administrator returns the request to the client with the instruction how to correct the errors in the request

Table 2 Specification of use case: Software maintaining

Title	<i>Software maintaining</i>
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the software maintaining
Pre-condition	PC is properly settled. Administrator has needed knowledge for the tasks
Post-condition	Backup of the waste cooking oil management software was made
Main scenario	1. Administrator checks if there is some large operation on the software 2. If there is some operation on the software, the administrator waits until the operation ends 3. If there is not operation on the software, the administrator prepares tools for the software maintaining 4. Administrator checks if the all functions of the software are proper 5. If some of the function of the software is not proper than the administrator starts the tool for correction of the function 6. Administrator starts the backup process of the software 7. Administrator records the time of the software backup
Alternative	None

Table 3 Specification of use case: Software web pages maintaining

Title	<i>Software web pages maintaining</i>
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the web pages maintaining of software
Pre-condition	PC is properly settled. Administrator has needed knowledge for the tasks
Post-condition	Backup of the web pages of software was made
Main scenario	1. Administrator checks if there is some large operation on the web pages of software 2. If there is some operation on the web pages of software, the administrator waits until the operation ends 3. If there is not operation on the web pages of software, the administrator prepares tools for the web pages of waste cooking oil management software maintaining 4. Administrator checks if the all functions of the web pages of software are proper 5. If some of the function of the web pages of education software is not proper than the administrator starts the tool for correction of the function 6. Administrator starts the backup process of the web pages of software 7. Administrator records the time of the web pages of software backup
Alternative	None

suppliers could record the quantity of the waste cooking oil if they are logged in the software database. Based on the GPS information of the suppliers the software should perform the calculation of the optimal route of the waste coking oil to the collectors.

Use cases of the software subsystems

Software administration

Based on the analyzing of waste cooking oil transport process it is noted that there is need for new computer system for the sector. Accordingly there is need for a person who will maintain administration of the software and the computer system. Therefore there is need for a software administrator.

Table 4 Specification of use case: Software database maintaining

Title	<i>Software database maintaining</i>
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the database maintaining of software
Pre-condition	PC is properly settled. Administrator has needed knowledge for the tasks
Post-condition	Backup of the database of software was made
Main scenario	1. Administrator checks if there is some large operation on the database of software 2. If there is some operation on the database of software, the administrator waits until the operation ends 3. If there is not operation on the database of software, the administrator prepares tools for the database of software maintaining 4. Administrator checks if the all functions of the database of software are proper 5. If some of the function of the database of software is not proper than the administrator starts the tool for correction of the function 6. Administrator starts the backup process of the database of software 7. Administrator records the time of the database of software backup
Alternative	None

Table 5 Specification of use case: Making of regular reports

Title	<i>Making of regular reports</i>
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the making of regular reports
Pre-condition	PC is properly settled. Administrator has needed knowledge for the tasks
Post-condition	The reposts were printed
Main scenario	1. Administrator checks if there is some large operation 2. If there is some operation, the administrator waits until the operation ends 3. If there is not operation, the administrator prepares tools for the making of regular reports 4. Administrator selects between standard procedure of the making of regular reports and nonstandard procedure where administrator can adjust the parameters of the reports. If nonstandard procedure was chosen than the administrator adjusts the parameters of the reports 5. Administrator starts the procedure of the making of regular reports 6. Administrator saves the backup of the reports 7. Administrator records the time of the database of making of regular reports
Alternative	None

Table 6 Specification of use case: Recording of quantity of waste cooking oil

Title	<i>Recording of quantity of waste cooking oil</i>
Actors	Suppliers
Trigger	It starts with the choosing of the option on user interface for the recording of quantity of waste cooking oil
Pre-condition	PC is properly settled. Waste cooking oil acquired
Post-condition	Recorded quantity of waste cooking oil
Main scenario	1. Client starts waste cooking oil management software 2. Client does login into waste cooking oil management education software 3. Client records the quantity of waste cooking oil 4. Client confirms the quantity
Alternative	1. The recording of quantity of waste cooking oil is canceled 2. Due to technical problems the service cannot be made

Administrator performs software administration in order to eliminate all unpredictable errors in the software and system. Administrator has full responsibility for the software maintenance. They will give permissions for other users access to the system, maintains the software, maintains the web pages of the software, maintains the software database, and makes regular daily reports. Fig. 5 shows the use case diagram of the software administration. As can be seen there are five functions of the administration which will be explained in details by scenarios.

Table 1 shows detailed specification of use case for giving permission for database access of the software by administrator.

Table 2 shows detailed specification of the use case of software maintaining by administrator.

Table 3 shows detailed specification of use case for web pages maintaining of software by administrator.

Table 4 shows detailed specification of use case for database maintaining of software by administrator.

Table 7 Specification of use case: Determining of optimal route of waste cooking oil

Title	<i>Determining of optimal route of waste cooking oil</i>
Actors	Collectors
Trigger	It starts with the choosing of the option on user interface for the determining of optimal route of waste cooking oil
Pre-condition	PC is properly settled. Waste cooking oil acquired
Post-condition	Determined optimal route of waste cooking oil
Main scenario	1. Collector starts software 2. Client does login into waste cooking oil management education software 3. Collector determined optimal route of the waste cooking oil from supplier to collector
Alternative	1. The determining of optimal route of waste cooking oil is canceled 2. Due to technical problems the service cannot be made

Table 5 shows detailed specification of use case for making of regular reports by administrator.

Recording of quantity waste cooking oil

Table 6 shows detailed specification for use case recording of quantity of waste cooking oil.

Determining of optimal route of waste cooking oil

Table 7 shows detailed specification for use case recording of quantity of waste cooking oil.

Conclusion

Fossil fuels' pollution and their non-renewability have motivated the search for alternative fuels. Some common examples of seed oils are sunflower oil, date seed oil, soy bean oil. For instance, soy methyl and soy-based biodiesel are the main biodiesel. Biodiesel is a clean diesel fuel that can be produced through transesterification reaction. Recycled cooking oil, on the other hand, is one of the inexpensive, easily available sources for producing biodiesel.

The main innovation of the investigation is analyzing and modeling of new software for acquiring of waste cooking oil. The main suppliers could enter quantity of cooking oil in the software. Based on the quantity the collectors could decide which reconditioning process is suitable for the waste cooking oil. The main output should be produced biodiesel for transport.

Also software could map the GPS locations of the suppliers of the waste cooking oil in order to optimize the route of the waste cooking oil transport in order to decrease the transport time.

See also: Optimization and Kinetic Modeling of Biodiesel Production. Sustainable Biodiesel Production. Sustainable Materials for Energy Conversion. Unified Modeling Language for Cooking Oil Management

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Application of Nano Porous Materials for Energy Conservation and Storage

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Introduction

Plastic recycling is an established process of recovering plastic scraps and waste into useful products. Based upon the waste management concept, plastic recycling can be broadly divided into four classifications namely: primary, secondary, tertiary and quaternary recycling (See Fig. 1). Primary and secondary recycling (recycling of clean, uncontaminated and single type waste: extrusion, moulding, heat treatment) are actually the mechanical recycling, tertiary recycling is performed by chemical means (dividing plastic waste into smaller molecules) and quaternary recycling is disposal by thermal utilization specially by energy recovery (Papargyropoulou *et al.*, 2014).

The primary recycling is an uncontaminated process in which only molecular arrangement/behavior are modified to apply the material in different processes (Kaminsky *et al.*, 1976; Singh *et al.*, 2017a). The secondary recycling is a mechanical mean of recycling process where polymers like, polyvinyl styrene (PVS), low density polyethylene (LDPE), high density polyethylene (HDPE), acrylonitrile butadiene styrene (ABS), polypropylene (PP), polyethylene terephthalate (PET), poly vinyl chloride (PVC), poly lactic acid (PLA) polystyrene (PS), polycarbonate (PC), polyamides (PA) and etc. are largely modified for preparation of feedstock or useful products (Seike *et al.*, 2018; Soo *et al.*, 2017; Wan *et al.*, 2017; Singh and Kumar, 2017b; Singh *et al.*, 2017c,d). The tertiary recycling process involves various methods of recycling including cracking, gasification, thermolysis and chemolysis (Hahladakis *et al.*, 2017; Horvat and Ng, 1999; López *et al.*, 2013). 'Incineration' is the quaternary recycling technique which is performed under the controlled combustion of the waste polymer. A small amount of the residue is the byproduct of this process which is further landfill or treated for environmental exposure (Gurgul *et al.*, 2018; Hwang *et al.*, 2017).

Differential scanning calorimetry (DSC) is an experimental thermo-analytical practice for investigating the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. The glass transition temperature, degree of crystallinity, degree of polymerization, melting points, and solidification points are some of important physiognomies of metals, alloys, thermoplastics and composites which are generally measured by the concept of DSC analysis Kumar *et al.*, 2017a,b,c, 2018a,b. Thermal analysis is liable to examine the thermal properties of any materials, including thermoplastic or thermosetting polymer matrix, as well as to determine the effect of micro or nano-composite added to polymers (Mei and Chung, 2001; Zhang *et al.*, 2006). DSC is an effective tool for examining the change in the specific heat after reinforcing nano-particle to the polymer matrix. Study reported for DSC analysis reveals that 0.01% graphene to polyester and 0.01% graphite improved the specific heat to 334% and 264% respectively (Bastiurea *et al.*, 2014). The thermal analysis can be helpful for those application areas where it is required to determine the thermal degradation of the polymer or resins (Santana *et al.*, 2011). One study highlighted that increase in the Barium Titanate as filler to the Poly (Methyl Methacrylate) matrix from 5% to 20% resulted in the increase in the thermal degradation (Elshereksi *et al.*, 2014). It can be understood from the thermal analysis that for some of the polymer, the specific type of filler contributed to the thermal degradation and change in the rheological properties (Liu and Lelievre, 1992). Modulated Temperature Differential Scanning Calorimetry (MTDSC) is the variant of DSC, the MTDSC is an

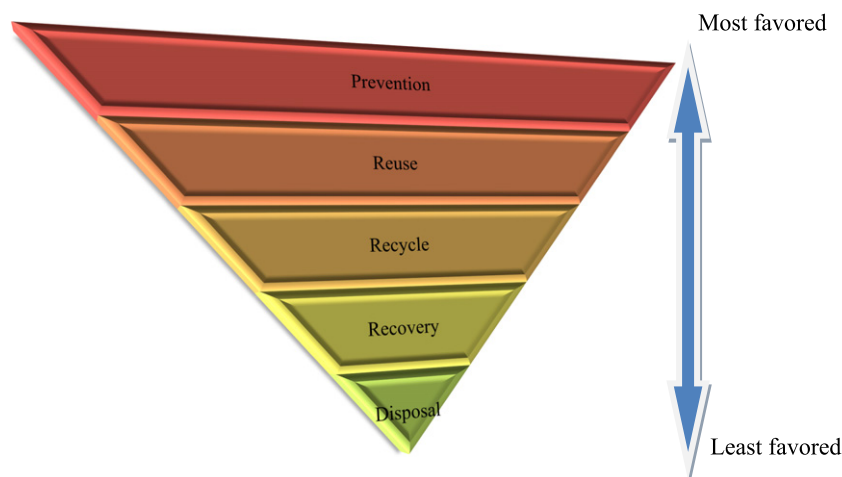


Fig. 1 Waste management hierarchy for plastic recycling. Reproduced from Papargyropoulou, E., Lozano, R., Steinberger, J.K., Wright, N., bin Ujang, Z., 2014. The food waste hierarchy as a framework for the management of food surplus and food waste. *Journal of Cleaner Production* 76, 106–115.

evaluation technique which can analyses the effect of temperature and other thermal properties on the specific heat of the sample. It was established that the heat capacity is more strongly dependent on the temperature than the thermal conductivity. Crystallinity is the one of the thermal analyses that can be helpful to check the affectivity of the fiber on the polypropylene composites (Panda and Das, 2007). lignocellulosic fiber obtained from orange wood reinforced to polypropylene resulted in the improved crystallinity as analyzed by DSC (Reixach *et al.*, 2015). It was reported for DSC that hydrophobic drug – phenacetin added to the polyethylene glycol (PEG) at defined proportion of 1–4:1 was liable to produce a solid dispersion phase (crystalline structure) (Gerasimov *et al.*, 2013). In relation to the constitute variation analyses of polymers, DSC is applicable to the examinations of the thermal variations occurring in polymer arrangements during chemical reactions (e.g. polymerization), oxidative degradation, vaporization, sublimation and desorption. The DSC results are justified by the way of X ray diffraction, scanning electron microscopy and transmission electron microscopy to explore the affectivity of the nanoparticle on the polymer nano-composite (Corcione and Frigione, 2012).

The reported literature highlights that tertiary recycled thermoplastic are processed further for quaternary recycling process (to lastly use the thermoplastic material for energy recovery by burning/decomposition). Since quaternary recycling produces harmful environmental pollution, it was considered as least favorable recycling technique. In the present study, DSC analysis of nano-composite reinforced tertiary recycled thermoplastic have been investigated in term of heat capacities to be applied as the nano-porous material in energy conversion or storage unit instead of quaternary recycling.

Materials and Method

In the present study, nano-porous material developed by reinforcement of nano-particle into thermoplastic matrix though extrusion process, undergone endothermic and exothermic reactions to evaluate their capacities of heat release or heat gain. Some of the thermoplastic namely; ABS, PA6, PVC, PLA, HDPE and LDPE were reinforced with different nano-particles were investigated though differential scanning calorimeter (DSC). DSC analysis were conducted on ABS reinforced with nano-sized Aluminum (Al) particle, PA6 reinforced with nano-sized iron (Fe) metal, PVC reinforced with nano-sized Hydroxyapatite (HAp), PLA reinforced with nano-sized HAp, HDPE with nano-sized Silicon carbide + Alumina ($\text{SiC} + \text{Al}_2\text{O}_3$) and LDPE reinforced with $\text{SiC} + \text{Al}_2\text{O}_3$.

The twin screw extrusion (TSE) is advancement in the extrusion technology which is used for providing excellent mixing/reinforcement of nano or micro-sized particles to thermoplastic matrix. The reinforcement of nano-sized material to the thermoplastic matrix ensures the preparation of nano-porous materials. In the present study, co-rotating type screw extrusion was used for reinforcement of nano-sized particles to thermoplastic matrix.

Experimentation

Initially virgin thermoplastic material was processed to pre-heating temperature (e.g., 250°C for ABS) to remove any thermal history associated with thermoplastic material. The TSE was used for mixing/reinforcing the nano-particle with thermoplastic material. Again the mixed composition was treated to pre-heating for removing thermal histories. Next the material was put in DSC chamber and processed in continuous cycles of endothermic (e.g., 30–250°C for ABS) and exothermic reactions (e.g., 250–30°C for ABS). Then results were interpreted by software integrated with DSC setup to investigate the outcomes of DSC. Fig. 2 shows detailed experimentation to investigate the effect of nano-particles on thermoplastic matrix.

Table 1 shows Operating condition of DSC for each of the material. The operating condition was selected by their nature of decomposition. The temperature ranges are selected in between the decomposition temperature of each of the thermoplastics under 50 ml/min N_2 gas supply and 2 alternating heating and cooling cycles.

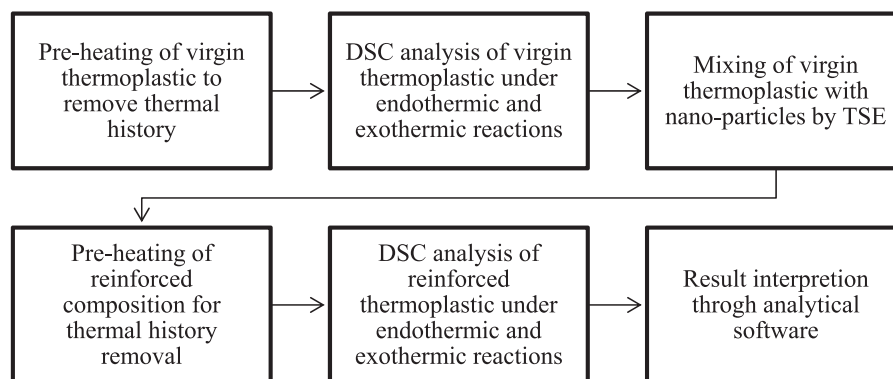
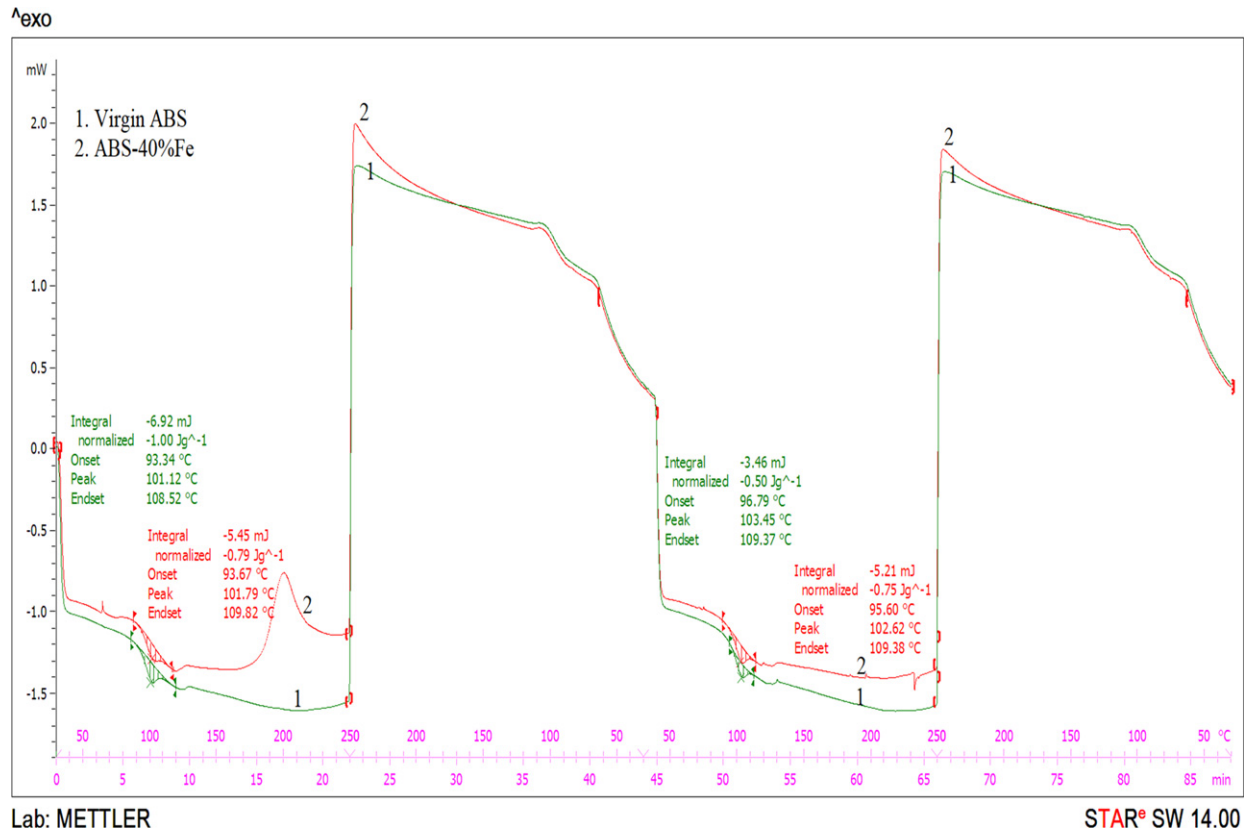


Fig. 2 Steps involved in DSC analysis of nano-particle reinforced thermoplastics.

Table 1 Processing condition for thermoplastic material through DSC

Materials	Reinforcement of nano-particle	Endothermic reaction	Exothermic reaction
ABS	40%Fe	30–250°C	250–30°C
PA6	40%Fe	30–250°C	250–30°C
PA6	30%TiO ₂	30–300°C	300–30°C
PLA	10%HAp	30–170°C	170–30°C
PVC	10%HAp	30–210°C	210–30°C
HDPE	10%SiC + Al ₂ O ₃	30–300°C	300–30°C
LDPE	10%SiC + Al ₂ O ₃	30–150°C	150–30°C

**Fig. 3** DSC Curves of Virgin ABS and ABS-40%Fe.

Results and Discussion

Different studies of ABS, PLA, HDPE, LDPE, PA6 and PVC thermoplastic under different reinforcement have been investigated to check the applicability of nano-porous material to use as energy conversion and storage applications.

ABS

ABS is common thermoplastic which is amorphous in nature and having high impact resistance, heat resistance and toughness, low thermal conductivity to potentially applicable in civil engineering field. The high moulding behavior of ABS makes it one of the best thermoplastic for possible preparations of nano-porous material in energy conversion and storage units. **Fig. 3** shows DSC curves of virgin ABS and ABS-40%Fe.

As ABS undergone DSC testing under controlled N₂ gas supply within endothermic and exothermic reactions, it was observed at glass transition peak that virgin ABS has taken 1.00 J/g energy for temperature transition of 93.34–109°C whereas ABS-40%Fe was taken 0.78 J/g energy for temperature transition of 93.67–109.82°C. The most interesting fact is appeared here that Fe reinforcement in the ABS matrix lead to the less energy requirement for transition between the specified temperature. In the second cycles it was recorded that thermoplastic material was unstable (thermally) after one heating and one cooling cycle as energy

integral of virgin ABS was reduced from 6.92 to 3.46mJ whereas energy integral of ABS-40%Fe was reduced only to small difference from 5.45 to 5.21mJ. It was also observed that energy requirement of virgin ABS was reduced from 1.00 J/g to 0.50 J/g but ABS-40%Fe was stable was reduced only from 0.79 J/g to 0.75 J/g. These prediction of DSC analysis reveals that reinforcement of Fe nano-particle has stabilized the ABS thermoplastic and can be applicable for preparation of nano-porous material for energy conversion and storage.

PA6

PA6 also known and poly-caprolactam or nylon 6 is a semi-crystalline polymer which has excellent mechanical, thermal properties but poor bio-degradability and generally not preferred for recycling processes. PA6 is a synthetic polymer which is extensively used in textiles, automobile and sportswear applications because of their durability and strength. As PA6 has the limitations for recycling purpose, so that it can be best use as the energy conversion and storage unit because it has excellent specific heat capacities.

PA6-30%TiO₂

Titanium oxide (TiO₂) is also known as titania is a natural oxide of titanium which is largely used for paint preparations. Since TiO₂ is having good bio-degradability and excellent electrical properties so that this is a potential material for recycling of polymeric waste for energy conversion and storage applications. As PA6 with 30%TiO₂ undergone DSC testing under controlled N₂ gas supply within endothermic and exothermic reactions. It was observed at melting transition peak that virgin PA6 was taken 625.52 J/g energy for temperature transition of 216-30-229.27°C whereas PA6-30%TiO₂ was taken 546.29 J/g energy for temperature transition of 217.79-229.16°C. The most interesting fact is appeared here that TiO₂ reinforcement in the PA6 matrix lead to the less energy requirement for transition between the specified temperature. In the second cycles it was recorded that virgin material was unestablished after one heating and one cooling cycle as energy integral energy of virgin PA6 was reduced from 625.52 to 490.24mJ whereas integral energy of PA6-30%TiO₂ was reduced only to small difference from 393.48 to 306.59mJ. It was also observed that energy requirement of virgin PA6 was reduced from 62.55 J/g to 49.05 J/g but PA6-30%TiO₂ was stable was reduced only from 46.29 J/g to 36.07 J/g (See Fig. 4). These prediction of DSC analysis reveals that reinforcement of TiO₂ nano-particle was stabilized the PA6 thermoplastic and can be applicable for preparation of nano-porous material for energy conversion and storage.

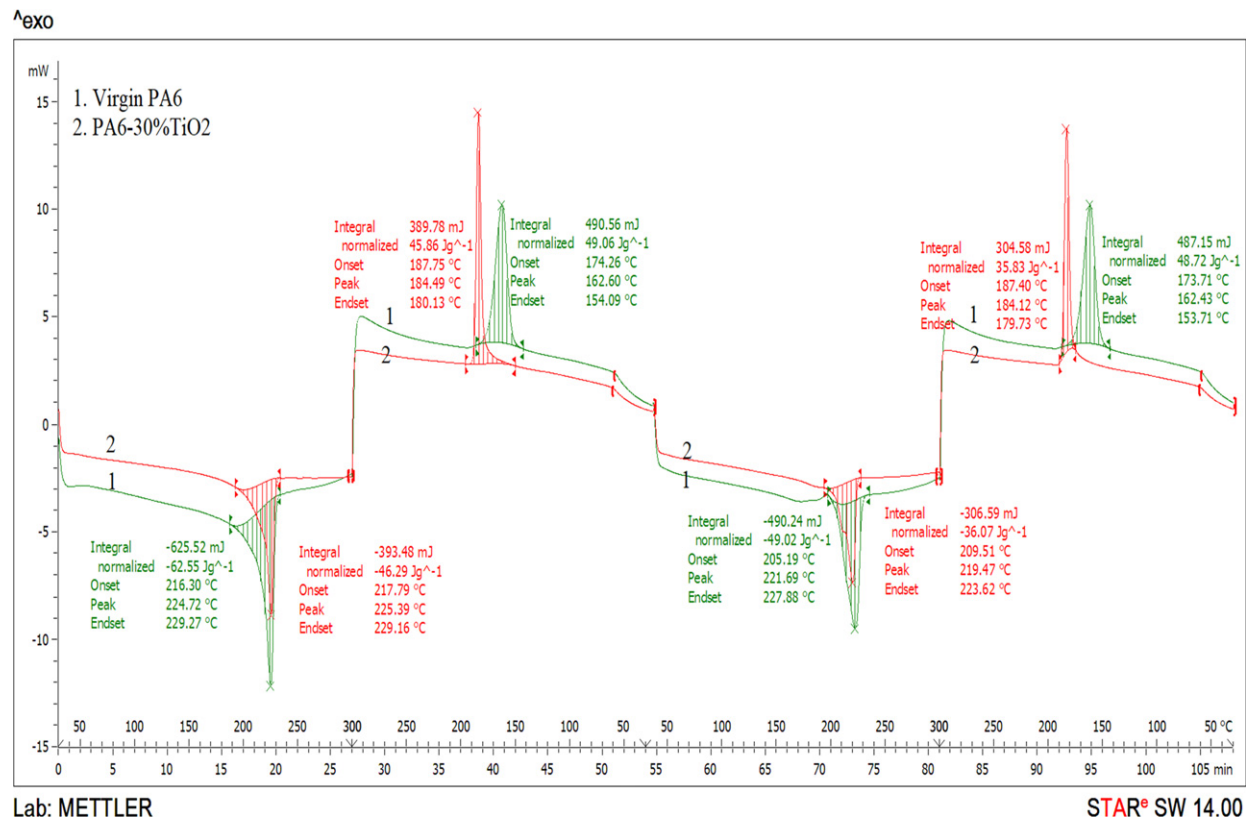


Fig. 4 DSC Curves of Virgin PA6 and PA6-30%TiO₂.

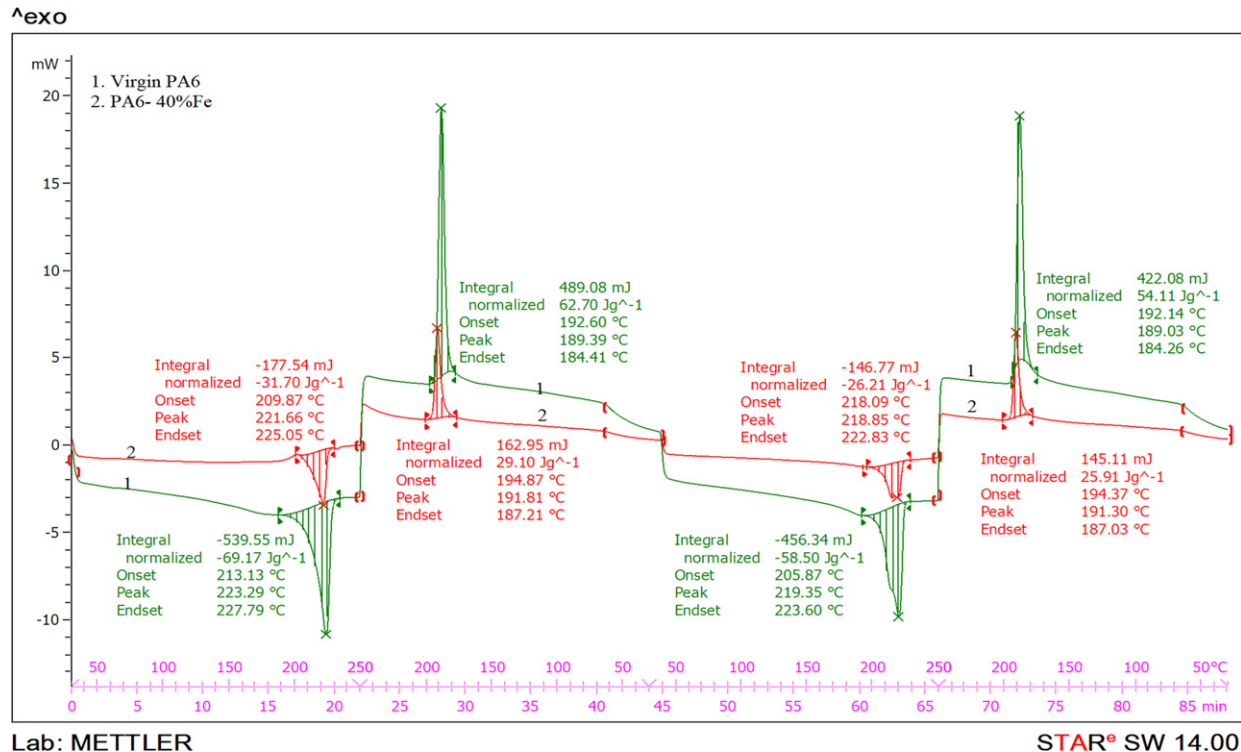


Fig. 5 DSC Curves of Virgin PA6 and PA6-40%Fe.

PA6-40%Fe

The next case study was the reinforcement of nano-sized Fe metal powder to the PA6 thermoplastic with 40% by weight. As PA6 with 40%Fe undergone DSC testing under controlled N₂ gas supply within endothermic and exothermic reactions. It was observed at melting transition peak that virgin PA6 was taken 69.17 J/g energy for temperature transition of 213.13–227.79°C whereas PA6-40%Fe was taken 31.70 J/g energy for temperature transition of 209.87–225.05°C. The most interesting fact is appeared here that Fe reinforcement in the PA6 matrix lead to the less energy requirement for transition between the specified temperature. In the second cycles it was recorded that virgin material was unestablished after one heating and one cooling cycle as energy integral energy of virgin PA6 was reduced from 539.55 to 456.34 mJ whereas integral energy of PA6-40%Fe was reduced only to small difference from 209.87 to 146.77 mJ (See Fig. 5).

PLA

PLA is also known as polylactide is a semi crystalline, bio-degradable and bio-active polymer which has wide application prospective in the 3D printing, injection moulding, film and sheet casting, spinning and biomedical implants fields. Although PLA has the wide bio-degradability but waste or contaminated PLA is still a dangerous aspects of environment and need to be minimized by apply it to in the energy conversion and storage. The next case study was the reinforcement of nano-sized Hap powder to the PLA thermoplastic with 10% by weight. As PLA with 10%HAp undergone DSC testing, it was observed at melting transition peak that virgin PLA was taken 19.27 J/g energy for temperature transition of 152.40–158.26°C whereas PLA-10%HAp was taken 10.88 J/g energy for temperature transition of 151.94–160.02°C. The most interesting fact is appeared here that HAp reinforcement in the PLA matrix lead to the less energy requirement for transition between the specified temperature. In the second cycles it was recorded that virgin PLA material was unestablished after one heating and one cooling cycle as energy integral energy of virgin PLA was reduced from 154.17 to 106.18mJ whereas integral energy of PLA-10%HAp was reduced only to small difference from 108.82 to 107.43mJ only. Similarly a large drop of normalized energy was observed (In one heating and cooling cycle) in the case of PLA where it was reduced from 19.27 J/g to 13.27 J/g whereas in case of PLA-10%HAp it was dropped only from 10.88 J/g to 10.74 J/g (See Fig. 6). This exhibited nature of PLA after 10%HAp reinforcement shows the affinity of its heat capacity for potential use in energy conversion and storage process.

PVC

PVC is most widely used synthetic polymer after polyethylene and polypropylene having the low degree of recyclability, because it possesses huge amount of pollution by heat treatment. PVC are heat stabilize by crucial additive of metal or ceramic. As PVC

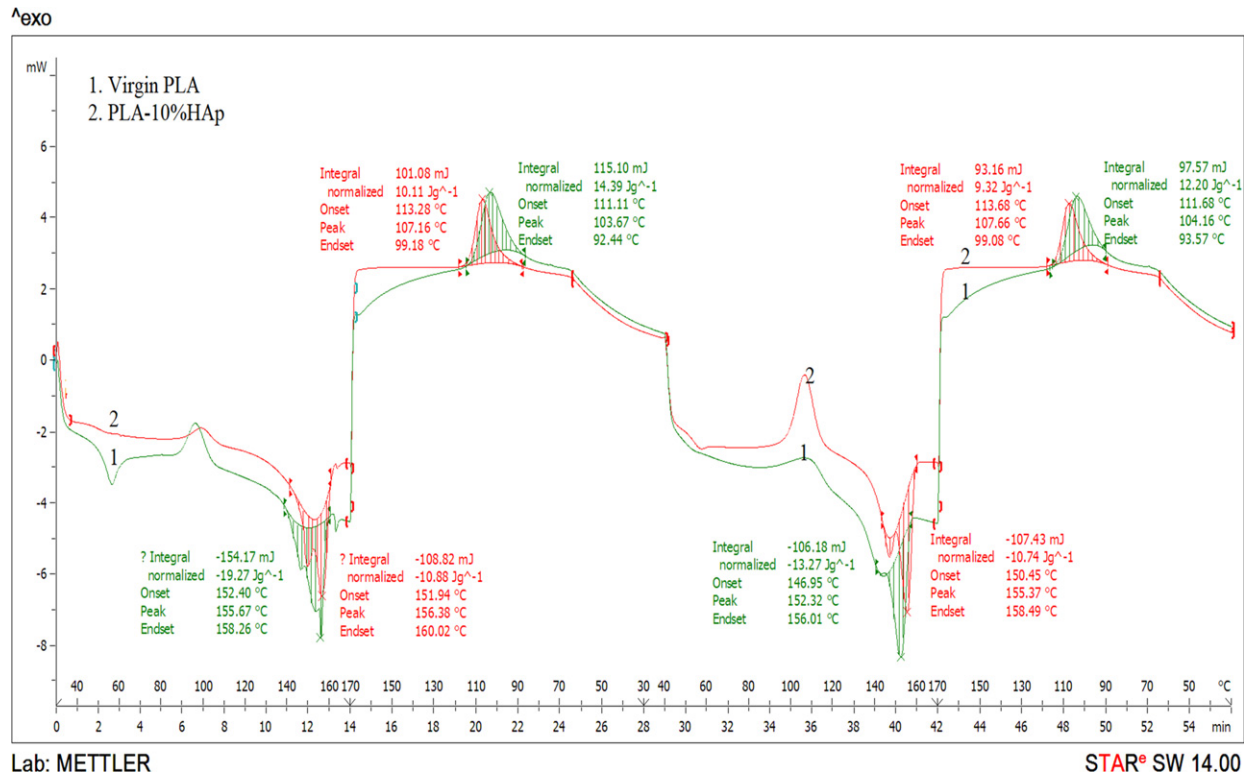


Fig. 6 DSC Curves of Virgin PLA and PLA-10%HAp.

having low degree of recyclability, so this can be potentially applicable for use as the energy conversion units. As PVC with 10% HAp undergone DSC testing, it was observed at melting transition peak that virgin PVC was taken 19.52 J/g energy for temperature transition of 145.29–164.27°C whereas PVC-10%HAp was taken 19.02 J/g energy for temperature transition of 147.49–164.64°C. The most interesting fact is appeared here that HAp reinforcement in the PVC matrix lead to the less energy requirement for transition between the specified temperature. In the second cycles it was recorded that virgin PVC material was unestablished after one heating and one cooling cycle as energy integral energy of virgin PVC was reduced from 171.76 to 107.13 mJ whereas integral energy of PVC-10%HAp was reduced only to small difference from 159.73 to 154.75 mJ only. Similarly a large drop of normalized energy was observed (In one heating and cooling cycle) in the case of PVC where it was reduced from 19.52 J/g to 12.17 J/g whereas in case of PVC-10%HAp it was dropped only from 19.02 J/g to 18.42 J/g (See Fig. 7).

HDPE

HDPE is made from petroleum products and is largely used in the production of plastic bottles, corrosion resisting pipes and plastic bags. HDPE is an excellent polymer due to its moulding capabilities. Thus HDPE is a best suited material for forming, extrusion, injection moulding and 3D printing. SiC and Al₂O₃ are ceramic material best known for reinforcement material in plastic matrix for recycling purposes. It was observed at melting transition peak that virgin HDPE was taken 110.97 J/g energy for temperature transition of 120.99–135.98°C whereas HDPE-10%SiC + Al₂O₃ was taken 90.07 J/g energy for temperature transition of 123.32–133.79°C. In the second cycles it was recorded that virgin HDPE material was unestablished after one heating and one cooling cycle as energy integral energy of virgin HDPE was reduced from 654.71 to 515.42 mJ whereas integral energy of HDPE-10%SiC + Al₂O₃ was reduced only to small difference from 405.34 to 395.83 mJ only. Similarly, in the case of HDPE, it was reduced from 110.97/g to 87.26 J/g whereas in case of HDPE-10%SiC + Al₂O₃, it was dropped only from 90.07 J/g to 87.96 J/g (See Fig. 8).

LDPE

LDPE is polymer made from monomer ethylene which is largely used for the corrosion resistance surfaces, flexible trays, juice and milk carton, plastic wrap etc. Since LDPE is highly chemical resistive so that tertiary recycling of it is practically uneconomical and hence applicable for preparation of porous materials for use in energy conversion and storage. It was observed at melting transition peak that virgin LDPE was taken 92.62 J/g energy for temperature transition of 122.89–134.60°C whereas

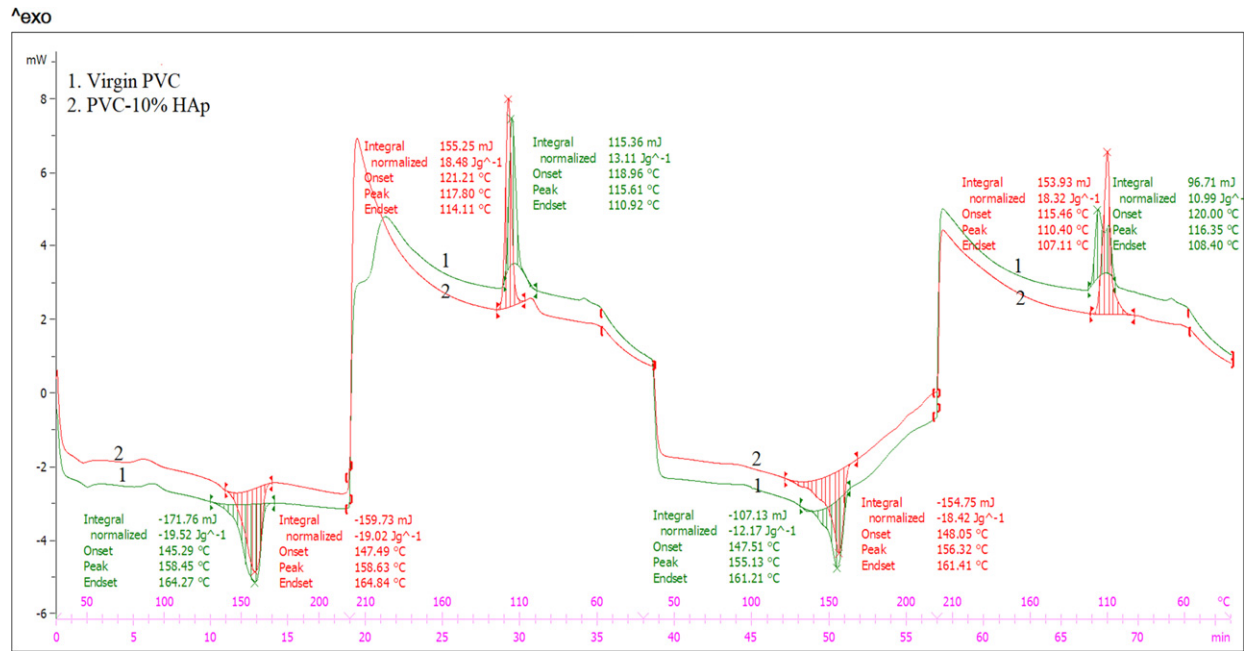
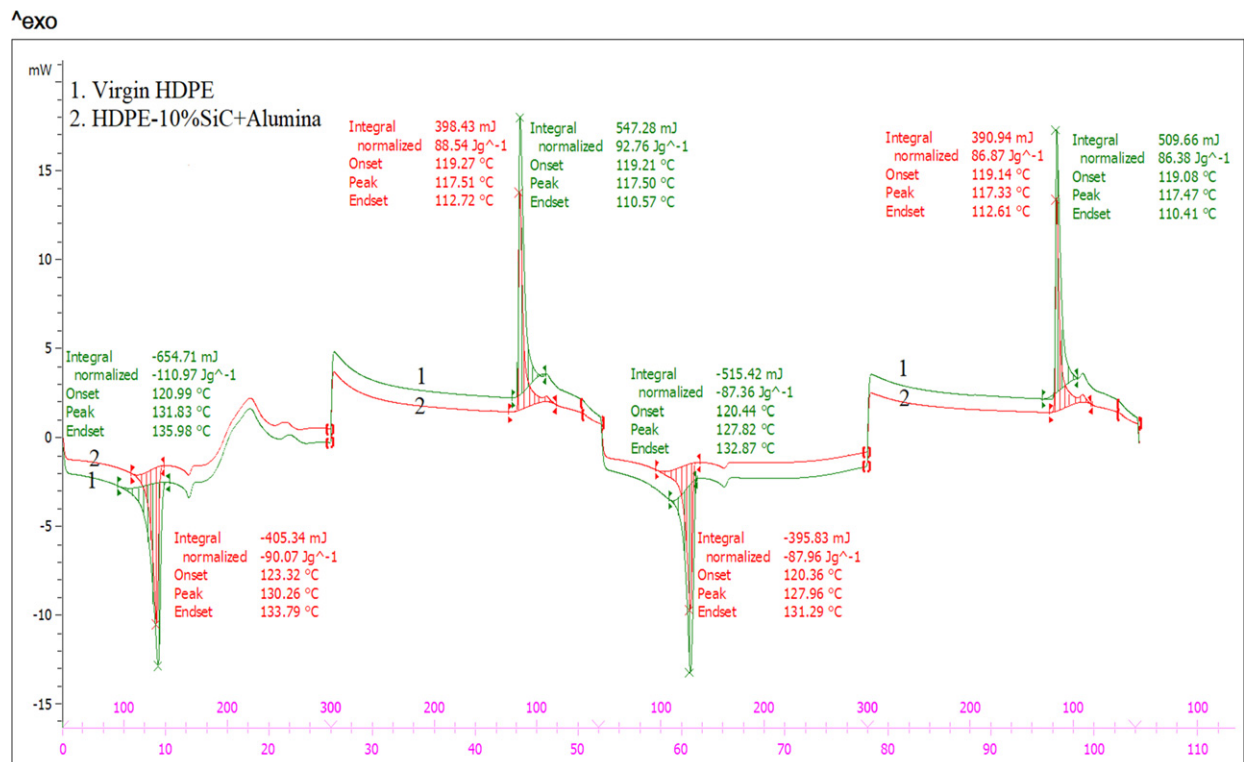


Fig. 7 DSC Curves of Virgin PLA and PVC-10%HAp.

Fig. 8 DSC Curves of Virgin HDPE and HDPE-10%SiC + Al₂O₃.

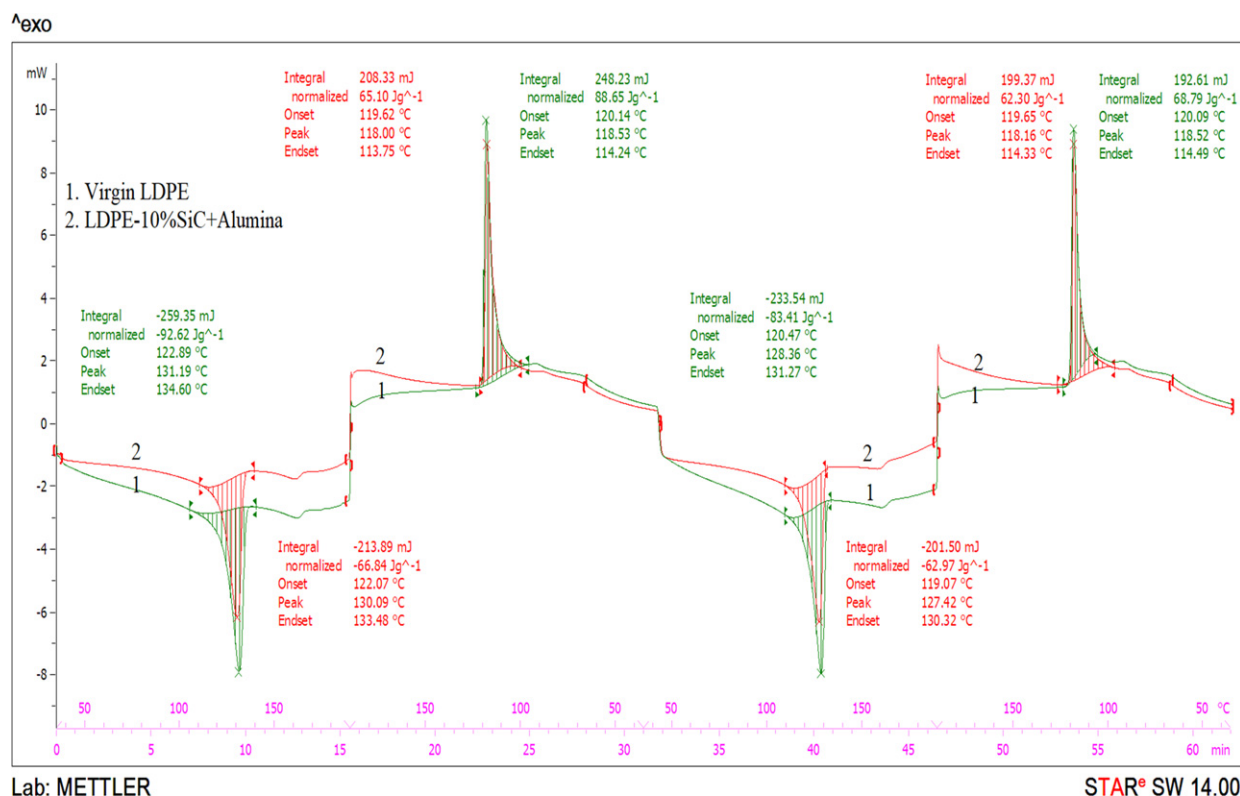


Fig. 9 DSC Curves of Virgin LDPE and LDPE-10%SiC + Al₂O₃.

LDPE-10%SiC + Al₂O₃ was taken 66.84 J/g energy for temperature transition of 122.07–133.48°C. In the second cycles it was recorded that virgin LDPE material was unestablished after one heating and one cooling cycle as energy integral energy of virgin LDPE was reduced from 259.35 to 233.54 mJ whereas integral energy of LDPE-10%SiC + Al₂O₃ was reduced only to small difference from 213.89 to 201.50 mJ only. Similarly a large drop of normalized energy was observed (In one heating and cooling cycle) in the case of virgin LDPE where it was reduced from 92.62/g to 83.81 J/g whereas in case of LDPE-10%SiC + Al₂O₃, it was dropped only from 66.84 J/g to 62.97 J/g (See [Fig. 9](#)).

Summary

Recycling of thermoplastic is a critical issue which can be a source of hazard if proper scientific methods are not applied. Among recycling techniques, quaternary recycling is most dangerous for environment as it produces large pollution in forms of fumes or gases. The quaternary recycling can be replaced with use of those thermoplastic in some useful application like; energy conversion and storage. As thermoplastic has the moulding capabilities, so addition of nano-sized reinforcements of metallic/ ceramic powder helps in heat stabilization to their matrix and can enhance the specific heat capacities (to be applied as energy conversation and storage by heating). In the present study, DSC analysis of nano-composite reinforced tertiary recycled thermoplastic have been investigated in term of heat capacities of material in energy conversion or storage unit instead of quaternary recycling. The study suggested that addition of nano-particle enhanced the tendency of heat retaining after a series of heating and cooling cycles, thus this is practically verified that those polymer can be best used as energy conversion and storage materials.

Acknowledgement

The authors are thankful to DST (GOI) for financial support for this project.

See also: Application of Nano Porous Materials for Energy Conversion Process. Electrochemical Energy Storage Using Batteries, Superconductors and Hybrid Technologies

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Application of Nano Porous Materials for Energy Conversion Process

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Introduction

3DP, Energy Conversion, GR, Twin, Feed Stock, FDM

3D printing, better known as “additive manufacturing”, forms the object by successive layers of materials for different application areas. 3D printing has the potential/impact to transform manufacturing supply chain, distribution channel and business model (Singh *et al.*, 2018a,b,c). Commercially fused deposition modeling (FDM), stereo lithography (SLA), inkjet printing, selective laser sintering (SLS), digital light manufacturing (DLP), selective laser melting (SLM), electronic beam melting (EBM) and laminated object manufacturing (LOM) are some of the commonly used 3D printing technologies for assembly, repair/maintenance, rapid tooling, waste management, energy storage etc. (Kumar *et al.*, 2017, 2018b,c; Singh *et al.*, 2016). Energy transformation, also termed as energy conversion, is a process for converting one form of energy into another form, for example a combustion process is used to convert chemical energy into thermal energy. In physics, energy is a quantity that provides the capacity to perform many actions – think of lifting or warming an object. Energy in many of its forms may be used in natural processes, or to provide some service to society such as heating, refrigeration, lightening or performing mechanical work to operate machines. For example, in order to heat your home, your furnace can burn fuel, whose chemical potential energy is thus converted into thermal energy, which is then transferred to your home’s air in order to raise its temperature. Thermoplastics are basically low cost material which is best suited for energy conversion where lightweight, design flexibility and intricate shapes are essential. But some of the hindrances are observed for polymeric material to use as energy conversion material as those having poor solid state morphologies, mismatch of energy gap and poor conductivities (Sun *et al.*, 2014). Organic semiconductor based photovoltaic devices offers the possibility of manufacturing low cost photovoltaic technology that can be 3D printed by roll to roll printing techniques. Existing organic photovoltaic devices are currently limited to solar power conversion efficiencies of 3%–5% (Shaheen *et al.*, 2005). Graphene is two dimensional materials which has extraordinary material characteristics like: High Young’s modulus, thermally and electrically superconductive (high mobility of charge and electron), surface insulating behavior and large aspect ratio for prototype fabrication. Graphite is a low cost raw source for extraction of graphene. Graphene generally extracted via different methods of processing like; chemical vapour deposition (CVD), micromechanical exfoliation, and ball milling etc. (Park and Ruoff, 2009; Su *et al.*, 2011; Calderon- Ayala *et al.*, 2017).

FDM processes as a 3D printing technique with feedstock prepared on twin screw extrusion process and is the best alternative for production of electrically conducting nano-porous polymeric composite materials for energy conversion and storage (Kumar *et al.*, 2018a). To introduce graphene reinforced polymeric composite as energy conversion material, it must fulfill the requirement of strong interfacial interactions of graphene and polymers so that maximum electrical and thermal conductivities should be achieved (Cui *et al.*, 2016). There are varieties of screw extrusion processes available for producing feedstock filament for FDM. Single screw extrusion is a conventional process for producing feedstock filament but defects like, tiny pores, blow holes, non-mixing are the major problems associated with this process. Twin screw extrusion has emerged as an advanced technique for producing feedstock filament free from defects. Twin-screw extruder are capable to ensure mixing, shearing, cooling, heating, compressing, transporting, shaping, pumping, etc. with very high level of flexibility. The main advantages of twin-screw extruders (intermeshing co-rotating) are their exceptional mixing capability that gives the remarkable characteristics to extruded products. In the twin-screw extrusion process, the raw materials may be solids (granules, powders & flours), slurries, liquids, and possibly gases (John *et al.*, 2014; Wang *et al.*, 2016a,b). FDM is the melt extrusion process in which robotic device is works on the CNC programming to control the heating and movement of the filaments. The extruded material through the nozzle head is directed on the print bed and immediately hardened to ensure the part fabrication. To ensure the better dimensional stability of the component formed it is required to process the printing below the melting point of the substrate. Properties of parts produced by the FDM is the function of the filament preparations, extrusion is the basic process which are uses for the preparation of feedstock filaments. Extrusion processes are largely used for the production of useful inputs for additive manufacturing techniques. The requirement of these processes is increasingly important from sustainability viewpoints when targeting waste management of thermoplastic materials. Mechanical properties of FDM fabricated parts are highly dominated by their filament processing. the mechanical sustainability of the fabricated parts are dependent upon the nature of processing of the initial component (grinding, extrusion etc.). Barrel temperature, rotational speed and torque are some of the input variable during the filament processing which largely affects the mechanical sustainability of the FDM fabricated parts (Singh *et al.*, 2017a, 2018d, 2017b; Singh and Kumar, 2017c; Singh *et al.*, 2017d). FDM as 3D printing technique is most economical way of producing 4D thermoplastic composite reinforced with nano-particle with use of extrusion process for development of energy conversion and storage devices. In the present study, the concept of 4D printing by use of FDM has been delivered for converting electrical energy into mechanical energy.

Application of Nano-Porous Materials for Printing of Transducer

As per Maxwell's right-hand thumb rule, assume current carrying wire in right hand, then thumb's direction denotes the direction of the current flow and the direction in which hand is being wrap represents the direction of magnetic lines of forces. If we take two different current carrying conductors, then two cases will emerge: In the first case flow of current in both conductors is in same direction and in second case flow of current in both conductors is in opposite directions. As reflected in Fig. 1(a and b), if the current of two current carrying conductor flow in a same direction then magnetic lines of forces will attract to each other and there will be contraction. Similarly, if the current of two current carrying conductors flow in opposite direction then magnetic lines of forces will repel each other and there will be an expansion.

As per Biot-Savart law, the magnetic field (B) generated by steady current (I) where charge is neither accumulate nor depleted at any point:

$$B = \frac{\mu_0 I}{4\pi} \int \frac{d\vec{l} \times \hat{r}}{r^2}$$

where vector $d\vec{l}$ is the vector line element with direction in the same sense as the current I , μ_0 is the magnetic constant, r is the distance between the location of $d\vec{l}$ and the location where the magnetic field is calculated, and $\hat{r}$ is a unit vector in the direction of r . and r is distance from the wire.

The Ampere's law can be helpful to measure value of magnetic fields for infinitely long current carrying conductors. Magnetic field can be measured as:

$$B = \frac{\mu_0 I}{2\pi r}$$

Proposed Application as Transducer

In actual field applications recycling of plastic waste is one of the serious problems. In the present study a novel method for recycling of plastic/ polymer waste has been proposed by use of this material for four dimensional printing applications. The idea is to use multi-jet (02) extrusion nozzles of fused deposition modeling setup for printing multi layers of conducting thermoplastic composite (like: Graphene reinforced thermoplastics) and non-conducting polymer waste (like ABS, Nylon6). The schematic (See Fig. 2) for same is given as under:

Now if current is passed in same direction between two parallel conductors than by basic principle two conducting wires will generate magnetic field and will attract each other. Similarly when the direction of current between two parallel conductors is reversed they will experience repulsive force.

This basic principle has been used to develop new/in-house, 4D printing materials. With this multi material sandwiched component, just by changing the direction of current flow the component will change its thickness, because of change in magnetic field. Finally this will help to develop in-house transducer at very low cost and also lead to waste management of polymer materials.

Proposed Methodology for 4D Printing of Nano-Porous Material for Energy Conversion

The proposed method of 4D printing illustrated in 4D printing is an innovative route for conversion of electrical energy into mechanical work. 4D printing of nano-porous material can be processed by integrating established FDM and extrusion technologies. The detailed method of such 4D printing technique can be processed as (See Fig. 3):

Graphene is an extraordinary material that is now days used largely to produced nano-porous materials. Graphene also has inherent material characteristics like: Excellent thermal and electrical conductivities, high mechanical strength and etc. In the proposed method of

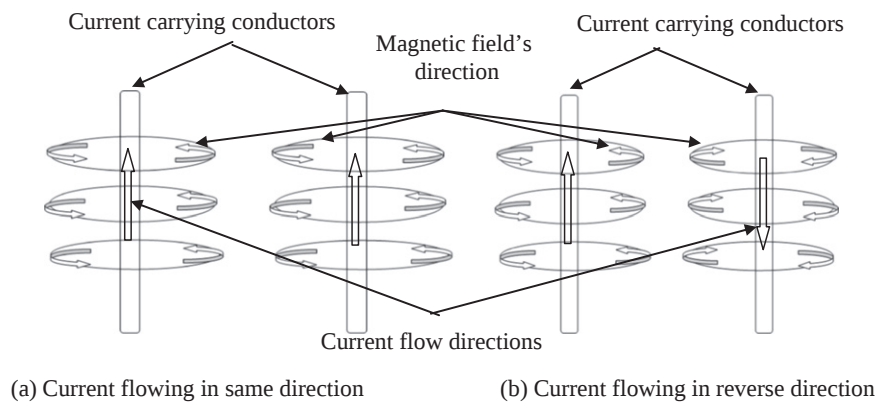


Fig. 1 Maxwell's right-hand thumb rule.

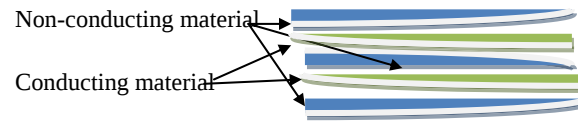


Fig. 2 Concept of 4D printing.

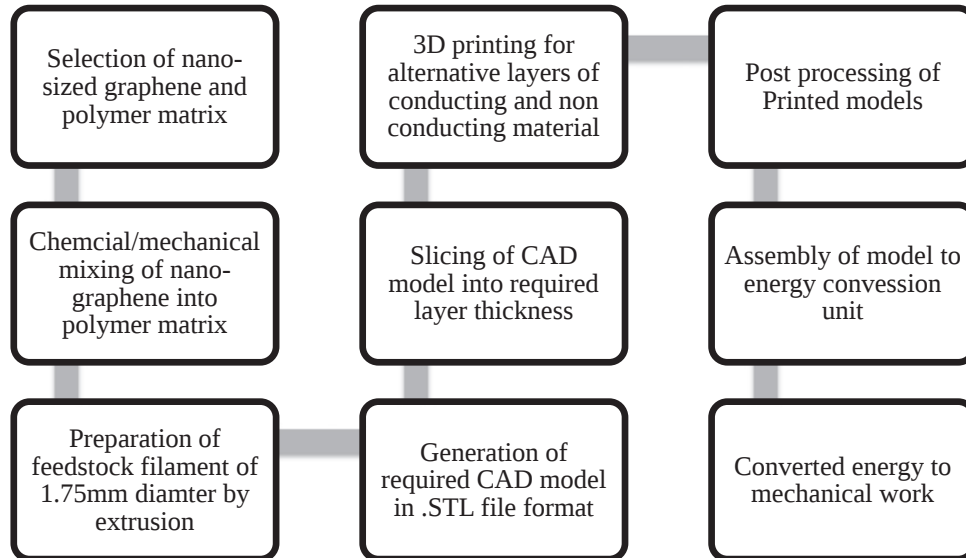


Fig. 3 Detailed methodology of 4D printing for energy conversion.

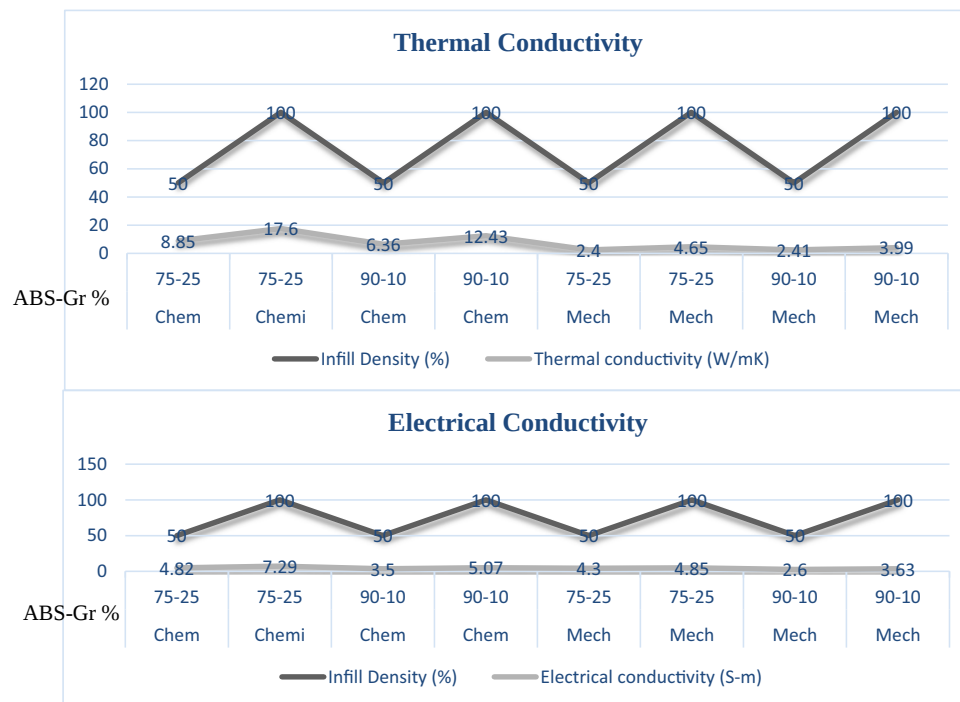


Fig. 4 Effect of graphene and infill density on thermal and electrical conductivities of ABS. Reproduced from: Kumar, R., Singh, R., Hui, D., Feo, L., Fraternali, F., 2018b. Graphene as biomedical sensing element: State of art review and potential engineering applications. Composites Part B: Engineering 134, 193–206.

4D printing for development of energy conversion unit a thermoplastic matrix will be used as main material. As acrylonitrile butadiene styrene (ABS) is having excellent molding stability so this can be selected as for fabrication of conducting as well as non-conducting layers. ABS is a non-conducting material, but when reinforced with nano-sized graphene into its matrix the excellent thermal as well as electrical conductivities can be achieved. As reported by Kumar *et al.* (2018b), thermal conductivities as well as electrical conductivities of ABS polymer matrix can be improved by reinforcement of graphene powder (See Fig. 4). There are two ways available for mixing of graphene into polymer matrix: Mechanical mixing and chemical mixing. The mechanical mixing is the process of mixing graphene into polymer matrix by using twin extrusion process in which granules of polymer matrix mixed with graphene through the compound screws of twin screw extrusion. In chemical mixing, granules of polymer and graphene are being treated under dissolution of chemical (As ABS is being dissolve in acetone solution). As study conducted, it was measured the electrical and thermal conductivities of graphene reinforced ABS mixed under chemical as well as mechanical mean. It is reported that chemical mixing of graphene reinforced ABS polymer matrix resulted in maximum electrical and thermal conductivities for ABS: Graphene ratio of 75:25 under 100% infill density. So it is clear from here that mixing of graphene into polymer matrix largely influences the electrical and thermal characteristics.

After mixing of graphene into polymer matrix it should be subjected to twin screw extrusion for preparations of feedstock filaments. It should be noted that twin screw extrusion is also used for mechanical mixing of graphene into polymeric matrix. After preparations of feedstock filaments, a CAD based model into STL file formatted must be prepared of required dimension on any design platform. The slicing will ensure the desired layers thickness and numbers of layers also. The energy conversion by this novel 4D printing will largely depend upon the number and thickness of additive layers. The FDM setup would be configured with at least two printing nozzles so that alternative layers of conducting and non-conducting material can be printed. The post processing in the ultrasonic chemical bath can be used as the post processing of the printed model to get best output. Finally, the printed part assembly to the main circuit of energy conversion unit lead to convert the electrical energy into some useful mechanical work. There are two types of mechanical motions can be achieved, one for contracting the structure when current in all 4D printed alternating layers flows in same direction, another for expanding the structures when alternating layers have current flow in reverse direction to each other (according to the Maxwell's right-hand thumb rule).

Summary

The proposed way of 4D printing for energy conversion has pointed out following consideration to be potentially applied in society.

- Printing of alternating layers of conducting and non-conducting materials by use of cost effective printing technology such as FDM is one of the innovative route for 4D printing.
- As established theories (Maxwell's right hands thumb rule, Lorentz force rule, Fleming's right hands rule etc.) suggested that current carrying material flowing in same direction will attract to each other and flowing in reverse direction will repel to each other, the proposed method of 4D printing has the great potential to use as the energy conversion tool in engineering applications.
- Graphene has the potential to be applied as the material for energy conversion and storage when reinforced into polymers matrix as it is having excellent electrical and thermal conductivity. On the other hand, nano-sized graphene is largely used for production of nano-porous material that has wider prospective in the energy conversion and storage fields.

Acknowledgement

The authors are highly thankful to Board of Research in Nuclear Science (BRNS) and manufacturing research lab (GNDEC, Ludhiana) for providing financial/technical assistance to carry out the research work.

See also: Application of Nano Porous Materials for Energy Conservation and Storage

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Further Reading

- Kumar, R., Singh, R., 2018. Prospect of graphene for use as sensors in miniaturized and biomedical sensing devices. In: Hashmi, S. (Ed.), *Reference Module in Materials Science and Materials Engineering*. Oxford: Elsevier, pp. 1–13.

Appraisal of E-Drought System Based on Object Oriented Approach

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Introduction

Drought is a disaster which could be very harmful especially for agriculture sector. Drought could be classified as meteorological, hydrological, agricultural and economic. Management of water and agriculture could be indicated by drought monitoring. Therefore there is need for accurate estimation and monitoring of drought. However there is need to present drought characteristics by some indicator in order to track it. There are many drought indices which could be used for drought estimation (Heim, 2002; Keyantash and Dracup, 2002). Water surplus variability index (WSVI) is a drought index which incorporate precipitation and reference evapotranspiration (Gocic and Trajkovic, 2014a).

The Palmer Drought Severity Index (PDSI) has been widely used to monitor drought but its characteristics are more suitable for measuring droughts of longer timescales, and this fact has not received much attention (Zhao *et al.*, 2017). Due to severe drought events and disastrous impacts in recent decades, substantial efforts have been devoted recently to drought monitoring, prediction and risk analysis for aiding drought preparedness plans and mitigation measures (Hao *et al.*, 2017a). Various drought information systems have been developed with different indicators to provide early drought warning (Hao *et al.*, 2017b). Drought indices are widely used for drought monitoring (Tian *et al.*, 2018). Results in article (Liu *et al.*, 2018) suggested that solar-induced chlorophyll fluorescence (SIF) is better fit in early drought monitoring, especially over closure canopy, while Normalized Difference Vegetation Index (NDVI) is more feasible when drought lasted over a long time scale. Our findings in the study might provide deep insight into the utility of SIF in drought monitoring. In article (Mishra *et al.*, 2017) was presented that the Soil Water Deficit Index (SWDI) is an effective agricultural drought indicator and it provides continuity and introduces new spatial mapping capability for drought monitoring. In paper (Nourani and Molajou, 2017), hybrid application of two data mining was offered to discover affiliation between droughts and de-trend Sea Surface Temperature (SST). Temperature vegetation dryness index (TVDI) and crop water stress index (CWSI) are two commonly used remote sensing-based agricultural drought indicators (Bai *et al.*, 2017). Timely and accurate monitoring of the onset and evolution of drought are important to reduce losses from drought (Wu *et al.*, 2015). The drought characterization becomes possible with the initiation of the meteorological, agricultural and hydrological drought indices (Haied *et al.*, 2017). Agricultural drought is a complex and insidious natural hazard further complicated by crop impacts (Zhang *et al.*, 2017). Remote sensing can provide real-time and dynamic information for terrestrial ecosystems, facilitating effective drought monitoring (Zhang *et al.*, 2016). Drought can consequently have substantial effects on agriculture and socioeconomic activities that cause social crises and political problems (Cunha *et al.*, 2015). As soil moisture is of key importance in understanding the interaction between the atmosphere and Earth's surface, it can be used to monitor droughts (Park *et al.*, 2017).

The main objective of the study is design a new e-drought information system for the drought monitoring and estimation. The drought monitoring is based on based on soft computing methodology, adaptive neuro-fuzzy inference system (ANFIS) (Jang, 1993), which is suitable for the nonlinear data pairs where there is lack of data for some regions. The e-drought system is developed and analyzed by unified modeling language (Lethbridge and Laganier, 2005; Jacobson, 1993).

Methodology

Climatic Data

The used climatic data are from World Bank Database for European Union. The following climatic input are used:

- T_{min} - input 1,
- T_{max} - input 2,
- e_a - input 3,
- RH_{min} - input 4,
- RH_{max} - input 5,
- U_2 - input 6,
- P - input 7,
- n - input 8

Drought severity can be obtained by the estimating of the Water Surplus Variability Index (WSVI) (Gocic and Trajkovic, 2013, 2014b).

ET Calculation

In this study FAO Penman-Monteith equation is used for ET calculation based on presented weather data. Based on the FAO Penman-Monteith equation ET index is calculated according to the weather data: minimal and maximal air temperatures, minimal

and maximal relative humidity, average wind speed and solar radiation. The weather data is acquired from World Bank Database for European Union. The input weather parameters are listed as follows:

- (1) Maximum air temperature [$^{\circ}\text{C}$]
- (2) Minimum air temperature [$^{\circ}\text{C}$]
- (3) Maximum relative humidity [%]
- (4) Minimum relative humidity [%]
- (5) Average wind speed [m s^{-1}]
- (6) Solar radiation [$\text{MJ m}^{-2} \text{day}^{-1}$]

E-Drought Information System

Modeling of an e-drought information system should include different climatic factors which have impact of drought. In this study the e-drought system has eight climatic factors. Unified modeling language (UML) is used for the modeling and analyzing of the system. This is standard methodology which are used for different aspects of the system modeling. UML could be used for specification, visualization, construction and documentation of information system. UML is based on object-oriented concepts and it is suitable for system modeling in initial stage before coding by some programming language.

The most important thing is the modeling process is to identify system actors or users and use cases. The use case presents one sequence of action which produce some visible. The use case is used to define system behavior. Therefore by used cases desired behavior of system could be presented. However the desired behavior might not be achieved in the final stage. The use case models could be used for modeling of the whole system or to model each part of the system.

Results

Use Case Diagrams of the E-Drought Information System

Fig. 1 shows the main use case diagram of the e-drought information system. As can be seen there are two actors in the system: users and WSVI-module. The users could import of climatic data. The WSVI-module is responsible for drought monitoring based on the climatic data. WSVI is estimated based on ANFIS model which is incorporated in the WSVI-module.

Fig. 2 shows the use case of importing of climatic data by user. The use case has eight activities. Each of the activity belongs to specific input parameter which is important for WSVI estimation and monitoring.

Fig. 3 shows the use case of calculating of drought index. As can be seen the use case has three activities. These activities is based on ANFIS training and testing procedure based on the given input/output climatic data pairs. The first activity is ANFIS training procedure. The second activity is ANFIS testing procedure. And the final activity should provide the drought output results based on the WSVI index.

Statistical Results

ANFIS models are trained and tested by the climatic data based on the calculated WSVI index. According to the results one can estimate the correlations between climatic data and drought index. If the ANFIS training results are small than the correlation between the parameters will be strong. **Table 1** shows that the parameter P has the strongest correlation since the training errors are the smallest for this input parameter. Combination of parameters $T_{\min}/e_a$ is the combination of two parameters which has the strongest correlation with drought index. Also $T_{\min}/e_a/P$ is the combination of three parameters which has the strongest correlation with drought index.

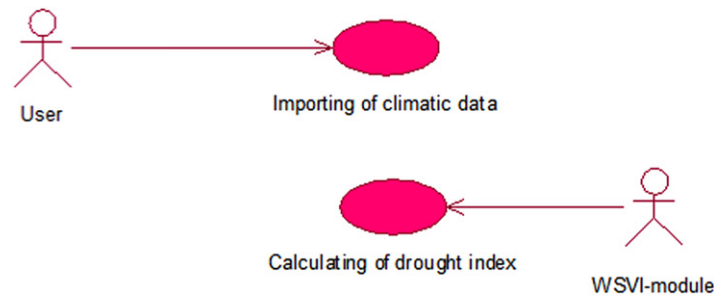


Fig. 1 Main use case diagram of the e-drought information system.

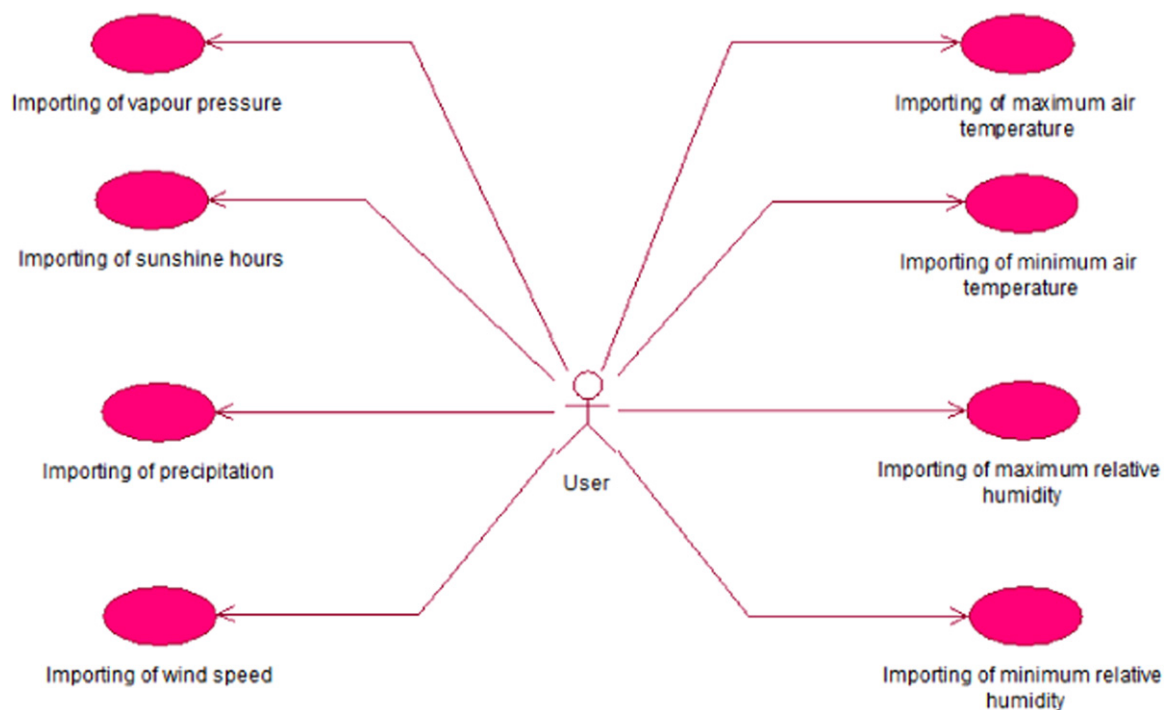


Fig. 2 Use case: Importing of climatic data.

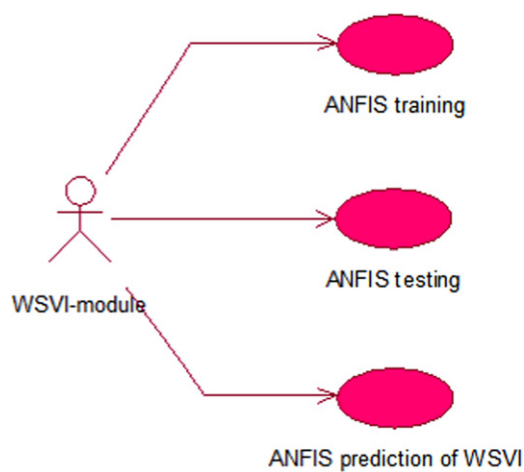


Fig. 3 Use case: Calculating of drought index.

Table 1 ANFIS correlation errors between climatic data and drought index

Climatic parameters	Training error	Checking error
P	0.9677	0.9622
T_{min}/e_a	0.9130	1.0028
$T_{min}/e_a/P$	0.8140	1.0960

Conclusion

Designing of new information systems for drought monitoring could be very important for agriculture and water management systems. In this study an object-oriented approach was applied for e-drought monitoring system. The system structure is incorporated with ANFIS methodology since drought index is calculated based on acquired input/output climatic data. The system is able to estimate the current values of drought based on imported climatic data by user.

See also: E-Agriculture System by Object-Oriented Approach

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Bamboo Fiber as Fillers for Polypropylene-Nanoclay via Injection Molding

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Introduction

Recently, in the polymer science field of research, composites made from the combination of polymer and natural fiber were becoming an uprising interest exploration. The fact that natural fibers are naturally economical solution due to its low density with certain useful possessions such as biodegradable and non-abrasive. Typical natural fibers are categorized into three groups, which are mineral, animal and plant, based on their origin. Some examples of plant natural fibers are cotton, flax, jute, coir, sisal and bamboo. Some of these fibers provide high stiffness, yet they are relatively sensitive to moisture with high variability of length and diameter. The high moisture sensitivity could overcome with certain treatment. This treatment could increase the cost due to additional process involved, nonetheless it is still affordable and cost effective (Wallenberger and Weston, 2003).

According to Food and Agricultural Organization (FAO) of the United Nations website, a thematic study had been prepared in the framework of the Global Forest Resources, which describe several information about bamboo, such as the extent of bamboo, the ownership, characteristics of bamboo growing stock, diversity of species, removals (poles and fuel wood) and value of bamboo removals and products (Lobovikov *et al.*, 2007). In this article, bamboo fiber was used as the reinforcement material in the polypropylene-nanoclay system. This fiber can be used as reinforcement in polymer, with the aid of compatibilizer, with consideration of type of product, mechanical properties, processing and environmental aspects. To support this statement, according to Bonse *et al.* (2010), adding bamboo fiber in a polymer system with the aid of compatibilizer will provide certain advantages on flexural strength and modulus, as well as tensile strength. However, there are drawbacks such as decrement of elongation at break and energy to break-typically define as area under the stress-strain curve. Optimum quality of mechanical bamboo pulps also could be obtained with a higher fiber yield, less broken with more slender fibers, with regard to proper treatment and characterization monitoring (Ashaari *et al.*, 2010).

Nanocomposites comes from a combination of several materials, whereby the matrix of this advanced mixture was reinforced with one or more nano size material. Usually by adding the nanomaterial, some properties could be improved. Recent nanocomposites applications have rapidly in demand and attracting manufacturing industries to revalue their material usage and consumption. One of the examples of nanocomposites is polypropylene-nanoclay. This blend was selected based on their good properties, clear processing and wide potential usage (Othman *et al.*, 2014b), even though the effects of processing conditions on nanofillers dispersion towards the outcomes should be taken into consideration (Rajesh *et al.*, 2012). Furthermore, this blend could be prepared through direct intercalation, whereby the preparation of nanocomposites by using this method was better than in situ or chemical compounding methods as per it is well-matched with present mass produce industrial and manufacturing process (extrusion/injection molding) as well as environmentally friendly because no solvents involvement (Ray and Okamoto, 2003).

Injection molding was chosen as the processing method since it was parallel with major plastic manufacturing industry. It can produce massive quantity of product in practical lead time, with cost effective gains. However, this process could produce numbers of defects and it is difficult to control the outcome consistently (Dumitrescu *et al.*, 2005). Noted that each of the processing conditions is reliant on each other, hence, facts about the processing optimization will assist the production to yield more productivity, cost savings and quality results (Mehat and Kamaruddin, 2011). One of the technique of process optimization is Taguchi method. A review had been summarized regarding research that used this approach with encouraging findings (Mehat, and Kamaruddin, 2012). For instance, an optimization process has been performed toward snap fit samples by using Taguchi method (Othman *et al.*, 2014a). However, beside optimization, analysis regarding the melt flow behavior also need to be carried out due to the existence of filler may produce interfacial adhesion issues with resistance to polymer flow (Liang *et al.*, 2015).

Material Preparation

There are four major components to prepare this feedstock for injection molding process. The components are polypropylene as the matrix, compatibilizer (polypropylene-grafted-maleic-anhydride), and nanoclay with bamboo fiber as filler. Typically the content of polypropylene and bamboo fiber will be manipulated. The type of polypropylene chosen for this system was homopolymer. To prepare this mixture of polypropylene-nanoclay-bamboo fiber, three different formulations were proposed. Table 1 shows the portion of each formulation, whereby 0 wt%, 3 wt% and 6 wt% of bamboo content were proposed. Polypropylene-grafted-maleic anhydride was selected as the compatibilizer, used in this mixture preparation. The weight percentage was set permanently at 15 wt%, the same setting of the nanoclay at 1 wt%. This fixed setting was decided based on previous research (Othman *et al.*, 2017a,b). The bamboo fibers first need a pre-heating process by using a convection oven. The suggested temperature was between 110 and 120°C temperature. The mixing process of polymer nanocomposite could be executed by using a twin screw laboratory type compounder. The mixtures need to be transformed into small pellets using used pelletizer with recommended diameters from 1.0 to 4.0mm for ease an injection molding process.

Optimizing Injection Molding Processing Condition

An injection molding machine was used to produce the injected molded samples for observation and evaluation. In this case, melt flow index (MFI), flexural strength, shrinkage and warpage were monitored as the outcomes. The processing conditions selected for control were melting temperature, packing pressure, screw speed and filling time. Three levels for each processing conditions were set to be optimized through the Taguchi method (signal to noise ratio assessment) based on level L_93^4 . The process condition settings based on orthogonal array L_93^4 were shown in Table 2.

The effect of the properties and defect with optimum processing condition of polypropylene-nanoclay with fiber bamboo as fillers had been analyzed, whereby through Taguchi optimization method, the maximum value of signal to noise ratio had been selected. These signal to noise ratio values were used to select which processing condition level that should be selected to produce higher value of the melt flow index and flexural strength, with the minimum value of warpage and shrinkage. Optimum results could be attained by using the optimum processing condition.

Table 3 shows the optimum processing condition for the melt flow index. The setting of formulation 3 wt% of bamboo content, the best combination processing condition for optimizing the value of MFI were 170°C for melt temperature, 35% of packing pressure, 30% of screw speed and 3 s for filling time. These settings could produce 21.07 g/10 min for the value of MFI. For the 6 wt% of bamboo content, the optimum combination processing condition for maximizing the value of MFI were 170°C for melt temperature, 40% of packing pressure, 30% for of screw speed and 1 s for filling time. Table 3 also shows that the additional of 3 wt% of bamboo will produce higher melt flow index.

Table 4 shows the optimum processing condition for flexural strength. As described in data analysis earlier, the highest value of signal to noise ratio indicate the best setting for the processing condition or factor. From the results in Table 4, the increment of bamboo filler shall make the specimen more flexible, since the flexural strength was increased. As for the best processing condition for 3 wt% formulation of bamboo content, the optimum setting were melt temperature at 165°C, packing pressure at 35%, screw speed at 30% and the filling time was at 1 s. The similar processing conditions were used for formulation 6 wt% of bamboo content accept the filling time increased to 2 s. By using this setting, the flexural strength could increase by 7.741 N (with the additional another 3 wt% content of bamboo filler).

Table 1 Polypropylene-Nanoclay-Bamboo fiber portion for each formulation

Formulation	Bamboo content	Polypropylene content	Compatibilizer content	Nanoclay content
1st formulation	0 wt%	85 wt%	15 wt%	1 wt%
2nd formulation	3 wt%	81 wt%	15 wt%	1 wt%
3rd formulation	6 wt%	79 wt%	15 wt%	1 wt%

Note: Othman, M.H., Rosli, M.S., Hasan, S., *et al.*, 2018. The optimization of processing condition for injected mould polypropylene-nanoclay-gigantochloa Scortechinii based on melt flow index. In: Proceedings of the IOP Conference Series: Materials Science and Engineering, vol. 324, no. 1, p. 012073. IOP Publishing.

Table 2 Taguchi orthogonal array selected based on level L_93^4

Trial no.	1	2	3	4	5	6	7	8	9
Melt temperature (°C)	165	165	165	170	170	170	175	175	175
Packing pressure (%)	30	35	40	30	35	40	30	35	40
Screw speed (%)	25	30	35	25	30	35	25	30	35
Filling time (s)	1	2	3	3	1	2	2	3	1

Note 1: Othman, M.H., Hasan, S., Ibrahim, M.H.I., Khamis, S.Z., 2017a. Optimum injection molding processing condition to reduce shrinkage and warpage for polypropylene-nanoclay-bamboo fiber with compatibilizer. In: Materials Science Forum, vol. 889, pp. 51–55. Trans Tech Publications.

Note 2: 1% of packing pressure is equal to 1.6 MPa.

Note 3: 1% of screw speed is equal to 2.4 rpm.

Table 3 Optimum processing condition for melt flow index

Bamboo content	Melt temperature (°C)	Packing pressure (%)	Screw speed (%)	Filling time (s)	Maximum MFI (g/10 min)
0 wt%	170	30	35	1	17.78
3 wt%	170	35	30	3	22.07
6 wt%	170	40	30	1	20.05

Note: Othman, M.H., Rosli, M.S., Hasan, S., *et al.*, 2018. The optimization of processing condition for injected mould polypropylene-nanoclay-gigantochloa Scortechinii based on melt flow index. In: Proceedings of the IOP Conference Series: Materials Science and Engineering, vol. 324, No. 1, p. 012073. IOP Publishing.

Table 4 Optimum processing condition for flexural strength

Bamboo content	Melt temperature (°C)	Packing pressure (%)	Screw speed (%)	Filling time (s)	Maximum strength (N)
0 wt%	165	40	35	2	30.01
3 wt%	165	35	30	1	32.25
6 wt%	165	35	30	2	39.91

Note: Khamis, S.Z., Othman, M.H., Hasan, S., Ibrahim, M.H.I., 2017. Characterization of flexural strength, warpage and shrinkage of polypropylene-nanoclay-nanocomposites blend with gigantochloa Scortechinii. In: Proceedings of the IOP Conference Series: Materials Science and Engineering, vol. 226, No. 1, p. 012163. IOP Publishing.

Table 5 Optimum processing condition for shrinkage

Bamboo content	Melt temperature (°C)	Packing pressure (%)	Screw speed (%)	Filling time (s)	Maximum shrinkage (%)
0 wt%	165	40	35	1	0.0030
3 wt%	165	35	30	1	0.0067
6 wt%	165	35	30	2	0.0067

Note: Othman, M.H., Hasan, S., Khamis, S.Z., Ibrahim, M.H.I., Amin, S.Y.M., 2017b. Optimization of injection molding parameter towards shrinkage and warpage for polypropylene-nanoclay-gigantochloa Scortechinii nanocomposites. Procedia Engineering 184, 673–680.

Table 6 Optimum processing condition for warpage

Bamboo content	Melt temperature (°C)	Packing pressure (%)	Screw speed (%)	Filling time (s)	Maximum warpage (mm)
0 wt%	165	40	35	2	0.004
3 wt%	165	35	30	1	0.004
6 wt%	165	35	30	2	0.004

Note: Othman, M.H., Hasan, S., Khamis, S.Z., Ibrahim, M.H.I., Amin, S.Y.M., 2017b. Optimization of injection molding parameter towards shrinkage and warpage for polypropylene-nanoclay-gigantochloa scortechinii nanocomposites. Procedia Engineering 184, 673–680.

Tables 5 and 6 shows the optimum processing conditions for controlling shrinkage and warpage, respectively. Based on the outcomes, there were not so much significant effect between the increment of bamboo content and the result of shrinkage and warpage. For instance, the setting for 3 wt% of bamboo content produced 0.0067% of shrinkage, the same results as the setting for 6 wt%. Moreover, the shrinkage value for the processing conditions also almost similar accepts filling time. Therefore, it is advisable to take the shortest time for productivity and high yield purposes.

Bamboo Fiber as Fillers for Polypropylene-Nanoclay

Based on the results after optimization, the addition of bamboo fiber as filler could increase the value of MFI and flexural strength, and at the same time could maintain the quality of the injected molded product by holding the value of shrinkage and warpage. As for the best processing condition, it is proposed to use 6 wt% formulation of bamboo content, the optimum setting were melt temperature at 165°C, packing pressure at 35%, screw speed at 30% and the filling time was at 1 s. By using this setting, a promising opportunity was provided to improve the quality of products made from this blend, via injection molding process. Not only that, adding bamboo fiber in a polymer system with the aid of a compatibilizer provides sufficient flexural modulus and tensile strength too (Bonse *et al.*, 2010). Via injection molding, many parts with massive quantity could be manufactured with minimum defects and higher productivity. The findings of this innovation could be useful for more detailed studies and put forward as a guideline for those who want participant or enhance the injection molding process in the future.

See also: Design and Performance Analysis of Small-Scale Parabolic Trough Solar Collectors Using Sustainable Materials. Recycled Clothes With Polypropylene-Nanoclay for Industrial Product via Injection Molding. Reuse of Waste Corrugated With Coir Fibers as a Packaging Material. Scaling Up and Intensifying Stakeholders Engagement for Evidence-Based Policymaking: Lessons Learned

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Challenges and Developments of Rubber Materials as Vibration Isolator

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Nomenclature

B Numerical factor
 c Damping constant
 E Young's modulus
 f Distributing frequency
 F Complex amplitude at the excitation force
 F_e Excitation force
 f_n Vertical natural frequency
 f_t Injected force
 F_t Transmitted force
 G Shear modulus
 K Static stiffness
 k Stiffness constant

K Stiffness matrix
 m Mass of the motor
 m_1, m_2 Mass of the rigid foundation
 T_F, T Transmissibility force
 x_y Static deflection of the spring
 Y Complex amplitude at the displacement
 y Displacement
 $\ddot{y}$ Acceleration
 $\dot{y}$ Velocity
 ξ Damping loss factor
 ω Frequency at harmonic motion
 ω/ω_n Normalized frequency
 ω_n Natural frequency at harmonic motion

Introduction

Generally, most of the mechanical, civil, naval, aerospace, air-conditioning, and construction systems are subjected to excitations that induce vibration energy. These vibration problems are usually undesirable and they have the potential to damage a system and finally make it fail. To avoid this problem, therefore, it is very important to develop vibration isolation systems to reduce or dissipate the vibration energy from transmitting to other places such as the base structure, structure body, etc.

A common annoying noise in a building is from the vibration of machines located on the floors or walls, respectively. Many engineers agree that the best place to locate a vibrating machine is on the ground floor; however, this does not solve the annoying noise problem, which emanates from the machine itself whilst it is in operation. This problem is found in rotating machines such as pumps, compressors, engines, blowers, and many more. To solve the problem, vibrating machines have been placed on the top floor or mounted on the roof. However, this does not solve the problem of vibration in a building because mechanical vibrations can be transmitted over long distances, and can also cause the building structure to vibrate, and can sometimes be transmitted hundreds of feet from the vibration source. This has been proven in a few cases involving building structures where the buildings have been damaged because of the vibration problem.

For example, in Korea, a five-story department store in Sampoong City collapsed due to the impact of vibration in 1995. Fig. 1 shows the five-story store before and after collapse. This disaster killed more than 500 people and injured over 900.



Fig. 1 Structural failure due to vibration at sampoong five-story department store: (a) before collapse and (b) after collapse. Koreanstandardtime, 2015. Available at: <http://koreanstandardtime.tumblr.com/tagged/sampoong-department-store> (accessed 15.03.15).

The problem occurred because the air-conditioning system was placed on the roof without any isolator between it and the roof structure. The uncontrolled vibrations caused cracking to the support column and the whole building's structure. This constant vibration generated by the air-conditioning system caused a big crack, which eventually widened, leading to a critical failure, and finally the building collapsed and many people died (Koreanstandardtime, 2015).

In another incident, in 2013, a factory building collapsed in Dhaka, Bangladesh, killing more than 1000 workers. The building was initially designed for office purposes, not to be a factory. According to the investigation, the investigator concluded that the illegally constructed upper floors were a source of the disaster. Large power generators had been installed on the upper floors and hence injected great vibration input power to the floor structure and finally caused structural failure. This is one of the worst disasters involving building structure collapse due to the vibration phenomenon. Fig. 2 shows the situation in that particular disaster (Theguardian, 2015).

Therefore, the vibration effect in buildings needs to be taken seriously to avoid disasters such as this happening again, which means vibration isolators need to be used to reduce or block unwanted vibration from influencing the building structure itself.

Vibration Control

Vibrations have undesirable effects on human quality of life and also on our material goods. In general, a very useful strategy to reduce vibrations is to reduce or block the propagation path between the source and receiver. Fig. 3 shows the general vibration control strategy between three components, which are the source, the transmission path, and the receiver. The source is a mechanical or fluid disturbance that is generated internally by the machine because of misalignment, unbalance, torque pulsations, poor gear meshing, fan blade passing, etc. Transmission path is the part or structural or airborne path by which the disturbance is transmitted or transferred from source to receiver. Receiver is the responding system, likely a mechanical system, which is structural, and which generally has natural frequencies that have a big potential to be excited by vibration frequencies generated by the source. In practice, there are three types of vibration control strategies: passive vibration control, semiactive vibration control, and active vibration control.

Passive vibration control is a one of a number of vibration control strategies involving the modification of the stiffness, mass, and damping values at source or receiver. The modification takes place via basic structural changes or including additional passive elements at the transmission path, as illustrated in Fig. 4.

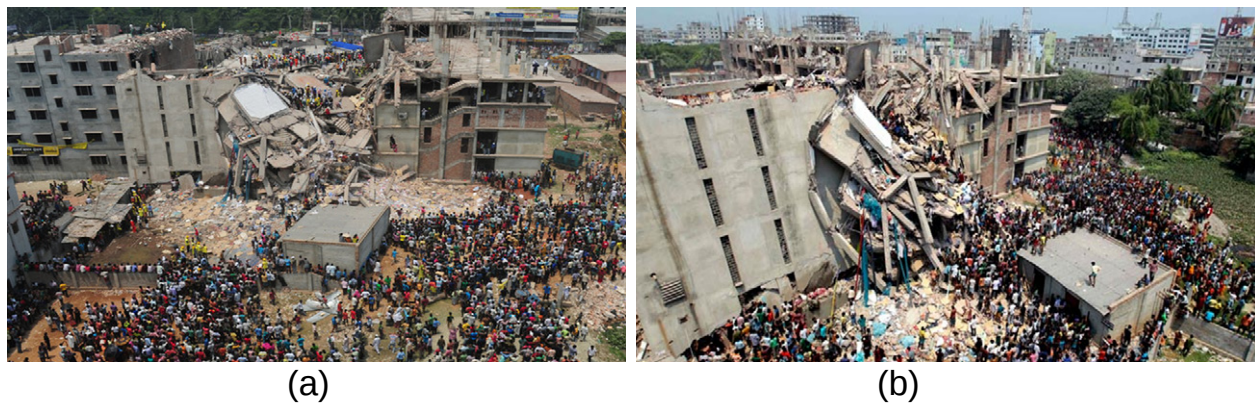


Fig. 2 Structural failure due to great vibration input power to the floor structure in Dhaka, Bangladesh: (a) front view and (b) side view. Theguardian, 2015. Available at: <http://www.theguardian.com/world/2013/apr/24/bangladesh-building-collapse-shops-west> (accessed 18.03.15).



Fig. 3 Schematic diagram of a general vibration control strategy.

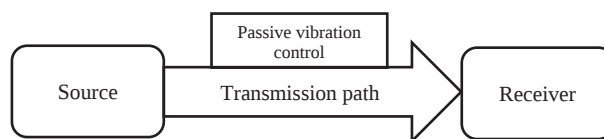


Fig. 4 Schematic diagram of a passive vibration control strategy.

For instance, passive vibration control can be modeled as a single-degree-of-freedom system, as shown in Fig. 5, in which this single-degree-of-freedom system is typically obtained from the mechanical vibrations system. On the other hand, this system consists of a rigid mass, which is representing the equipment, and a spring and damper representing the behavior of the isolator. Generally, rubber materials were used as a passive vibration control to reduce the effects of vibration naturally.

Semiactive vibration control is developed to adjust stiffness and damping in real time by applying a control scheme. The adjustment is based on the feedback from the response of the controller where the appropriate command signal is generated to the controller of the system. One of the current examples of an isolator that can change its stiffness or damping based on current or voltage is the magnetorheological (MR) isolator, and the materials used are fluid-based (Sun and Zhang, 2013). Fig. 6 illustrates the mechanism of a semiactive vibration control scheme.

Active vibration control, on the other hand, is the active application of force in an equal and opposite fashion to the force imposed by external vibration. It also works with actuators, sensors, electronic controllers, and signal-conditioning devices. Active control vibration has more advantages compared to passive and semiactive vibration control because it can provide better performance at high frequencies and at the same time reduce the volume and weight of the structure (Yan, 2007). However, this technique requires external energy to drive the active devices continuously. The schematic diagram for this scheme is shown in Fig. 7.

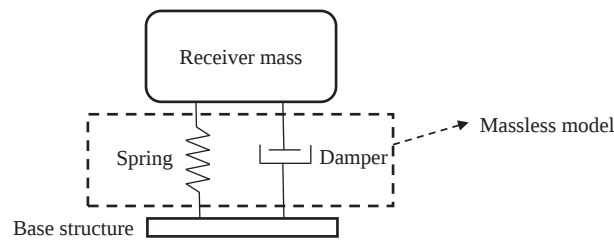


Fig. 5 Single-degree-of-freedom for passive vibration control.

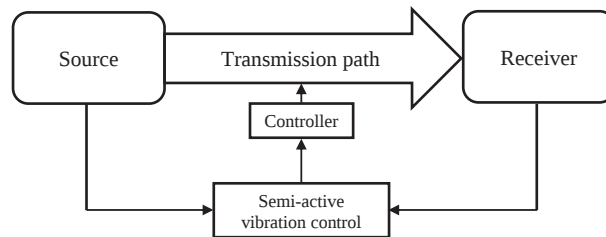


Fig. 6 Schematic diagram of a semiactive vibration control strategy.

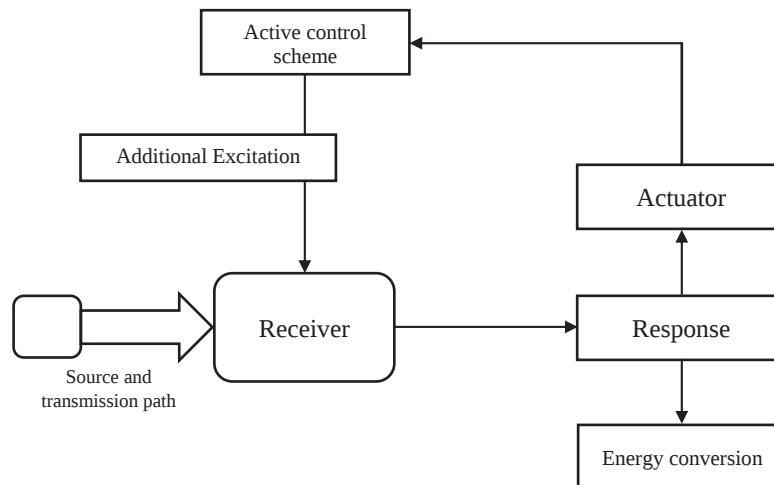


Fig. 7 Schematic diagram of an active vibration control strategy.

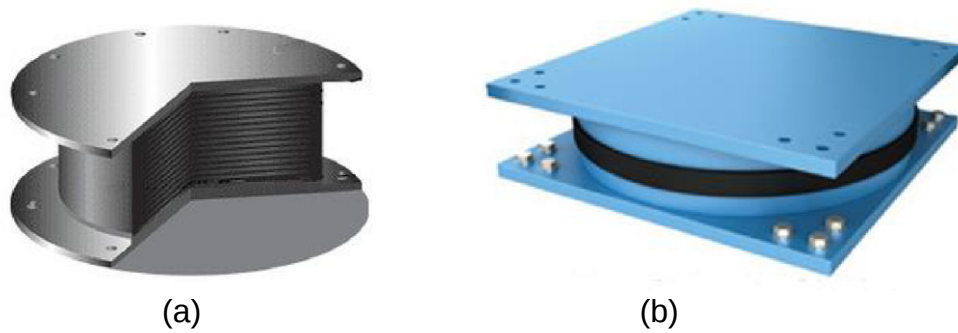


Fig. 8 Two categories of vibration isolator: (a) laminated-rubber bearing isolator and (b) frictional-type sliding isolator.

Recent Development of Vibration Isolators

Examples of vibration isolators can usually be found in buildings. They are used to reduce the risk of damage to structural integrity caused by earthquakes. The recent developments regarding vibration isolators, especially for buildings, including high-rise buildings, and bridges, can be divided into two main categories, which are laminated-rubber bearing and frictional-type sliding isolators, as shown in [Fig. 8](#). The first category is widely used and the second one is still in the early stage of development ([Ibrahim, 2008](#)). These vibration isolators are installed on the foundations of the structures to increase the damping value and to decrease stiffness during strong vibration. However, in this section only the laminated-rubber bearing is discussed in detail, as it relates to the objective of this study. The rubber bearing isolator is often used in base isolation for high-rise buildings because it can maintain the balance of the building ([Lin and Hone, 1993](#)).

A considerable amount of literature has been published on laminated-rubber isolators. The first discussion and analysis of this type of isolator that emerged were presented by [Gueraud *et al.* \(1985\)](#). The study investigated parameters affecting the performance of laminated-rubber isolators in a building located in New Zealand. Two years later, the results of the study were used as a reference for developing a new design of laminated-rubber isolator called resilient-friction-base isolator. This new design then worked in parallel with the previous isolator made from rubber materials, with a steel plate placed around the isolator using Teflon additive. The steel plate was used to maintain the stability of the rubber isolator structure to stop it from bending during strong vibrations. A paper described a comprehensive parametric study conducted on friction coefficient, natural period, damping value, and mass ratio on the resilient-friction-base isolator. Detailed examination of the parameters shows that the isolator can reduce the vibration accelerations and can perform well for lightweight equipment, but the isolator functions do not reach optimal levels if it is used in seismic systems. The isolator also had an ineffective reaction when fixed at the base structure and suffered slippage during strong vibrations. Other researchers have agreed with these findings.

An advanced study of the resilient-friction-base isolator was carried out in 1996 ([Jangid, 1996](#)). Some analysis has been to investigate the relationship between parameter variations on stochastic response in isolated buildings. Coefficient of friction on the resilient-friction-base isolator has been identified as a major contributing factor in the optimum damping of the building structure, and it is effective based on vibration occurrence. However, the above analysis is only valid when the top floor has a minimum root mean square (R.M.S) acceleration. In Japan, the effect of base-isolated structures during seismic activity has been studied ([Aiken, 1997](#)). The new formulation relating the development of base isolator was proposed to predict the seismic response of base-isolated structures. Following this analytical analysis, the mechanical properties of elastomer were identified accordingly into a large strain range. To ensure that the data from the model are trustworthy, a test-rig was developed that was used as a seismic source, and a model of a building was placed on it. A vibration isolator made from rubber was then placed between the building and the test-rig. An accelerometer was used to record all the data during the experiment, and then the obtained data were plotted in a graph where the analytical model data were previously plotted. Based on the study, it has been found that there is a similarity in experimental and analytical data, and, finally, the analytical model has been adopted for future analysis.

In 2004, an elastoplastic damper was proposed to replace the usage of laminated-rubber isolators and resilient-friction-base isolators ([Fujita *et al.*, 2004](#)). This type of vibration isolator has been developed using a spring-mass-damper model where a hysteresis damper was used. In this study, the seismic activity was examined using a hysteresis element and Ramberg–Osgood model. The Ramberg–Osgood model was used to describe the nonlinear relationship between stress and strain, which happen in the damper during seismic excitation. In a two-degree-of-freedom of elastoplastic dampers system, the upper side is used to examine the level of seismic motion, and all data are recorded in amplitude value.

In another major study into vibration isolators, in 1990, Kurihara investigated the effects on the horizontal and vertical stiffness of rubber bearings during large deformations by seismic activity. However, this study focused on nuclear plant buildings located in Japan. The study found that getting the optimum effects for both directions of a rubber bearing is impossible because it does not have a proportional relationship in order to dampen the seismic energy. This finding was validated by applying full-scale rubber bearings and then applying a seismic load of approximately 4900 kN at the bottom. Then, sensors were located at the horizontal and vertical directions of the rubber bearings. According to the experiment, the data showed that large deformations occurred at



Fig. 9 Location of a vibration isolator between building and foundations.

the horizontal direction compared to the other side. In 2007, other researchers also argued about why the above problem occurred (Suy *et al.*, 2007). Several tests have been conducted to validate the previous problem and, finally, it was proposed to combine the rubber bearings with viscous dampers and friction elements on buildings that vibrate due to seismic activities. Mathematical modeling for the combination of these materials was created and it was found that the result is better compared with the previous models developed.

Previously, vibration isolators were placed between the building and foundations because researchers agreed that vibration energy is transferred from the ground to the structure; the application is shown in Fig. 9. However, the first systematic study proposed locating the vibration isolator at the building's roof (Villaverde, 1998; Villaverde and Mosqueda, 1999). A vibration isolator was added between the building's roof and a column that would act as a support for the roof. One of the limitations with this study is that it does not satisfactorily explain by how much the seismic energy will be reduced. Therefore, there are only a few studies to date regarding this matter. The study of the horizontal direction for vibration isolators was continued in 2008. A two-dimensional hysteretic shear-beam type was used to support the vibration isolator during ground motion. This study used statistical analysis to determine several parameters with five different seismic levels. By using a shear-beam, it was found that the level of vibration amplitude transmitted from ground to building was slightly reduced.

Then, study of vibrations in buildings began to not only focus on building structure, but also on the installation of sensitive equipment inside the building, which contributes to the occurrence of vibration and damage. Therefore, in 2005, researchers addressed the damage level probability for sensitive instruments inside a building during vibration (Alhan and Gavin, 2005). It was suggested that these sensitive instruments must have their own mounting system to prevent them being damaged when large vibration energy happened.

Cheng *et al.* (2007) studied rubber bearing tension, focusing on laminated rubber bearing tension in high-rise buildings. The experimental data showed a significant amount of large vibration energy activity where the tension in the laminated rubber bearings did not perform well. Laminated rubber bearings under tension became the main problem if they are used to dampen the vibration occurrence for high-rise buildings during seismic activity. Therefore, a new method was proposed to avoid the possible tension phenomenon occurring. New arrangements for superstructures including column and beam were suggested and joined together with the vibration isolator. This modification was then examined and, finally, the tension behavior of laminated rubber bearings was successfully reduced. In 2009, the study of the low-rise base isolator was used in the previous modification made by Cheng in 2007 (Toopchi-Nezhad *et al.*, 2009). However, the research also employed the unbonded-fiber reinforced elastomeric isolator joint together with existing laminated rubber bearings. By using an analytical model, the result was predicted and the vibration energy from seismic activity was reduced 50 percent compared to previous research by Cheng. A new finding was identified, which is that shear activity took place at laminated rubber bearings when compression load was applied because the nonlinear lateral response behavior of the laminated rubber bearings occurred. Experimental investigations were also conducted in this study, so it can be verified correctly. Based on the experiment conducted, the peak lateral displacement was calculated by using time history analysis, but the result did not have any effect on the building. Finally, the researcher concluded that joining of existing rubber bearings and unbonded-fiber reinforced elastomeric can reduce discomfort inside a low-rise building.

A study of horizontal stiffness of laminated rubber bearings was conducted in 2011 (Du *et al.*, 2011). From the study, it was found that the horizontal stiffness occurred when compressive stress was applied to the structure. The model of a field matrix of a single laminated rubber bearing was derived and then it was connected to the column structure. The relationship

between internal force and isolator displacement was obtained and, finally, the transfer matrix equation was developed using the horizontal stiffness expression. Then, compression stress on horizontal stiffness was examined and the results showed that the inverse proportional relationship for both parties occurred, while the rubber bearing still remained in place, and did not move to another direction. Kobayashi introduced the study of lateral stiffness of laminated rubber bearings (Kobayashi *et al.*, 2012). First, the lateral stiffness was subjected to end rotation and, secondly, the design stress was concentrated at the end of the laminated rubber bearings. Mechanical properties of the laminated rubber bearings subjected to end rotation were evaluated by adopting the mechanical properties of laminated rubber bearings concentrated at the rotational spring. Finally, the degree of fluctuation for both lateral stiffness and bending moment were investigated by using the proposed analytical model, and this model produced some assumptions that need to be taken into consideration, which relate to the location of the isolator at the top of the pile.

An advanced study into the automotive engine isolation system was carried out in 1993 (Singh, 1993). According to the study, the growth of the automotive industry, such as advanced design of the power-train system, engine development, etc., can contribute to the unwanted level of vibration energy on the car body. Therefore, it was suggested that more studies about the automotive vibration isolator for vehicles should be conducted. A study about frequency response on hydraulic engine mounting was carried out by Colgate *et al.* (1995). In the study, nonlinearity behavior such as amplitude reaction on pistons was considered. The researchers believed this behavior could have an effect on vibration amplitude to the driver and passengers when driving. To reduce the effect, research into a new model of engine mount to prevent the large amplitude in automotive engines was carried out (Tiwari *et al.*, 2003) in 2003. Researchers developed a new model and simulated several engine mount designs with different frequency ranges to reduce large amplitude. However, jump phenomenon activity in the engine has also been identified as one of the main factors contributing to the large amplitude activities (Golnaraghi and Nakhaie Jazar, 2001). This problem was identified in 1965 (Timpner, 1965). According to the study, the investigations of nonlinear resonances in large amplitude at high frequencies cannot be predicted by using a simple model. In 1997, the modern engine mounting system was introduced to reduce or eliminate unwanted vibration level to give more comfortable conditions for the driver and passengers when traveling in a vehicle (Brach, 1997), and from this year much research regarding engine mounting began.

The lumped parameter systems model has been used to describe the nonlinearities and hysteretic behavior in hydraulic engine mounting. The lumped parameter systems model is a simplification of the description of the behavior of spatially distributed physical systems into a topology consisting of discrete entities that approximate the behavior of the distributed system under certain assumptions. Several limitations have been listed, especially the boundary condition of the engine mounting between the engine and the car body. A fixed-free boundary condition is chosen where “fixed” represents the condition between engine mounting and car body, while the “free” condition represents the top of the engine. Finite element analysis on hydraulic engine mountings was carried out to investigate the dynamic behavior of the mounting systems (Wenbin and Zhenhua, 2004). It showed that the mounting systems can reduce displacement of the engine from a chamber. A parametric study on hydraulic engine mountings was conducted. This study is very important because, by changing the value of certain parameters, the hydraulic engine mountings can be used to reduce vibration activity from different sources of excitation from an automotive engine. Recent evidence suggests that the value of Young’s modulus and thickness of the isolator can influence the isolator’s potential to reduce the effects of vibration. The first study using viscoelastic materials for engine mounting was conducted by Schmitt (Schmitt and Leingang, 1976). This study proposed using rubber material because its dynamic stiffness performed better at high frequencies due to its damping properties. Therefore, it has become a major factor to design an engine mounting that fulfills many design criteria. This engine mounting was proposed to be installed in the engine, engine cooling system, and car’s body frame because these locations have been identified as having large vibration amplitude, and this was verified by Yu *et al.* (2000). A comparative study between rubber material mounting systems and hydraulic engine mountings was conducted. According to the study, rubber material mounting systems give the ability to reduce large vibration amplitude at low frequency range, and provide better comfort for the driver and passengers in the vehicles. The development of engine mountings has continued to improve the amplitude-dependent properties. The existing rubber material mounting systems are focused on static deflection at low frequency levels, less than 100 Hz. The existing research has proposed the ideal engine mounting system that can be used for static and dynamic deflection at various frequencies. These various frequencies come from engine excitation in several ranges of speed (Peelamedu *et al.*, 2001). The dynamic stiffness for the engine mounting has been investigated to ensure that the system can be used to decrease the vibration levels of engine excitation.

Further study on engine mounting systems was carried out in 2014 (Sun *et al.*, 2014). According to the study, the finite element method was used to solve a problem on isolator stiffness. A two-stage vibration isolation system was used and developed using this method, and the vibration energy was applied at the bottom of the engine to give flexibility to the isolation system. A value of forced vibration was calculated using the finite element model and, based on this value, the quantum of stiffness was optimized. The vibration intensity at vibration isolation was examined and, by using dynamic analysis, it was found that the trend was consistent at the first and second stages of vibration isolation system. Then, the result was validated by using physical testing in the laboratory. From the testing, the trends of vibration intensity for both methods were found to be the same.

Based on the previous discussion of vibration isolators, one conclusion can be made, which is that many studies have been carried out up to now looking at the development of the ideal vibration isolator solutions to ensure that vibration energy can be reduced or eliminated. Hence, it provides stable structures of buildings, car engines, etc., and comfort, especially for environments that people frequent.

Challenges of Rubber Materials as a Vibration Isolator

From previous research (Imbimbo and De Luca, 1998; Manos *et al.*, 2007; Ibrahim, 2008; Bhuiyan *et al.*, 2010; Mishra and Igarashi, 2013; Spizzuoco *et al.*, 2014), researchers agree that rubber is a versatile and adaptable material. This material has been used successfully in many engineering applications such as in mechanical engineering problems, civil construction, automotive parts, aeronautical solutions, and many more, and the material is still sustainable and being used today. The rubber elastomer acts like a spring. Therefore, it can also be used as a component for a mounting system to reduce unwanted vibration amplitude in many fields. It also has a large strain capability and it can store more elastic energy per unit volume. Many studies have been conducted that demonstrate that this material is very safe and it is much better than steel material if produced properly (Ibrahim, 2008).

Static and Dynamic Behavior of Rubber Materials

This material has some inherent damping, which is very useful in springs, and so it can be used to counter resonance behavior when the frequency range of the material is the same as the environmental frequency (Yin *et al.*, 2010). Essentially, rubber can be bound together with other material such as metal, steel, aluminum, and others by using chemical additives. On the other hand, it implies that rubber can give more stiffness value to the other materials in shear and compression phenomena. The installation process of rubber is very simple and only takes a short time compared to other materials. Rubber requires less maintenance, and its elasticity and durability can be sustained for many years after the installation process.

Essentially, rubber has a high polymer content, and the chemical bonding acts as a smoothing agent that feels as smooth as silk, cellulose, and proteins (Mitra *et al.*, 2010). The bonding also has the same characteristic as in petroleum products, which are plastics, resins and synthetic rubbers. In chemical behavior, rubber has a very long molecule, which results in the creation of a durable repeating monomer. With this repeating monomer, rubber can be contoured and is flexible for working in an extreme ambient and very high temperature. At a high temperature, the rubber shape is deformed, but it will return to its original shape when the temperature goes down. The rubber is basically created by a hydrocarbon through an empirical rule (Dasgupta *et al.*, 2007). This hydrocarbon bonding is called a monomer, and is also known as isoprene. The rubber latex can easily be found in Malaysia. Rubber trees are tapped every day and the rubber milk is called latex. After the coagulation process, which takes some time, the crumbing process takes place and finally it is transformed to Standard Malaysian Rubber (SMR). The grade of SMR is dependent on the technical specifications, applications, mechanical properties, and resistance to environmental conditions.

To create the rubber that can be used in engineering applications, vulcanization or curing process is applied and some chemical materials are joined together to produce a chemical response, and this reaction is called vulcanization. The basic vulcanization process was established in 1839 and it was discovered by Charles Goodyear (Shelton, 1983; Raue *et al.*, 2014). Sulfur is used in this procedure to add durability and elasticity and reduce the sensitive behavior of the rubber due to temperature range (Yuan, 2010). Additionally, sulfur also gives a bonding effect inside the rubber molecule and at the same time the original length of the rubber molecule becomes shortened. When the rubber molecules become shortened by sulfur, it makes natural rubber more resistant to wear and tear when applied at high temperatures (Yuan, 2010).

In engineering applications, most rubber products are supplied with filler. This filler generally comes from carbon black, which must be 33 percent of the total weight before the vulcanization process starts. Basically, carbon black is divided into three categories: reinforcing, nonreinforcing, and semireinforcing behavior. In the reinforcing category, it is also called abrasion grade blacks (NR Technical Bulletin, 1992; Yuan, 2010). It can improve the tear and abrasion properties, and at the same time rubber in this category can increase the modulus, creep, and hysteresis behavior. On the other hand, rubber in the nonreinforcing category, also known as thermal blacks, has less effect on the behavior described in the previous discussion. Furthermore, the nonreinforcing type has moderate modulus, creep, and hysteresis effects. Lastly, the semireinforcing type gives additional effects to the other two categories, which are tensile strength, abrasion resistance, and chemical adsorption. Many researchers agree that rubber has unique behavior compared to other engineering materials. Firstly, the shear and Young's modulus value of rubber are very low and it is many times smaller than the bulk modulus value of the materials. Secondly, rubber is like other materials in that it can be deformed elastically, but the difference is that it can be stretched hundreds of times and never fail, and the shape will return to the original shape. The mechanical property of filled rubber is shown in Table 1 and, from this table, it was compared with three other materials. The table is very important in order to know the specification of rubber itself and also gives more information about its hardness, tensile strength, elongation, stress, and many more features. These data are adopted from the literature and have been verified by the Malaysian Rubber Board (NR Technical Bulletin, 1992).

Theoretically, the bulk modulus of rubber is around 2000 to 3000 MPa and this value is a thousand times larger than the value of the shear modulus. Agreeing with this value, one conclusion that can be drawn is that this material is hardly altered in volume when the deformation phenomenon occurs. When rubber changes shape, its stiffness value become much larger; in short, it becomes like a compressible spring. Moreover, Poisson's ratio for rubber is 0.5, which means that the material has little resistance for a small stream when a force is applied (NR Technical Bulletin, 1992; Boiko *et al.*, 2008). All of the discussion shows that this material has incompressibility behavior that makes it more durable and long lasting with less maintenance required, and not easily prone to wear and tear.

It is also important to have an in-depth knowledge of the stress-strain behavior of rubber. In an unfilled condition, rubber can be deformed in tension and compression. This deformation happens approximately in linear strains up to a certain percentage

Table 1 Comparison of a soft gum rubber, filled rubber, mild steel, and water

Property	Gum rubber ^a	Filled rubber ^b	Mild steel	Water
Hardness (IRHD) ^c	43	65	100	0
Tensile strength (MPa)	26	22	460	–
Elongation at break (%)	770	520	40	–
Young's modulus, E (MPa)	1.5	^d	210,000	–
Shear modulus, G (MPa)	0.49	1.3 ^e	82,000	–
Bulk modulus, E_{∞} (MPa)	2000	2200	170,000	2100
Poisson's ratio	0.4997	0.4997	0.29	–
Resilience (%)	90	70	100	–
Velocity of shear waves (m/s)	22	34	3200	–
Density (Mg/m ³)	0.97	1.15	7.9	1
Specific heat (kJ/kg/°C)	1.9	1.5	0.44	4.2
Thermal conductivity (W/m/°C)	0.15	0.35	52	0.59
Coefficient of volume expansion (per °C)	66×10^{-5}	5×10^{-5}	3.2×10^{-5}	21×10^{-5}
Electrical resistivity (Ω m)	10^{14f}	^g	1.8×10^{-9}	–
Dielectric constant ^h	3	15	–	80

^aMechanical properties dependent on type and degree of crosslinking.

^bMost properties dependent in type and amount of black and degree of crosslinking.

^cIRHD = International Rubber Hardness Degrees, scale range 0–100.

^dValue strongly strain-dependent.

^eValue for 0%–2% strain.

^fDependent on vulcanizing system.

^gStrongly dependent on amount and type of black. Compound conductives have values of $1\text{--}10^5 \Omega$ m.

^hStatic value.

Source: NR Technical Bulletin, 1992. Engineering Design with Natural Rubber. London: The Malaysia Rubber Producers' Research Association.

from the total length. Here, Young's modulus will play a role, which will take place on low strain regions (NR Technical Bulletin, 1992; Liao et al., 2011). On the other hand, a filled condition makes rubber gain more stiffness in value but in nonlinear strains. Thus, the rubber can be deformed in tension or shear even if the strain is less than one percent.

Hardness has been considered as one of the contributing factors for the mechanical behavior of rubber. The elastic deformations are measured under a specified load by using the Shore Durometer A. Rubber is totally different compared to metal materials, especially in hardness behavior, and, because of that, its irreversible behavior can be measured like that of other metals (Peters et al., 2009). International Rubber Hardness Degrees (IRHD) were verified in the 1980s. Hardness is relatively simple and easy to obtain but is subject to an uncertainty of about ± 2 degrees (Lee et al., 2014). The testing is carried out with 20 MPa force, where only a small region near the surface is used for the test because it is enough to represent the results for all of the material.

When applying forces to rubber, it is important to look at and discuss energy dissipation. Hysteresis occurrence is the correct term to be discussed because through this the energy dissipation occurring in the rubber will be better seen (Niemczura and Ravi-Chandar, 2011; Cao et al., 2014). According to the definition of hysteresis, it means the area between a loading and unloading curve in a load-deformation cycle (Ibrahim, 2008). Hysteresis occurs in all rubber types. It happens because rubber material is resilient and this means that, when any force or energy is applied to it, it reacts by returning to its original form. Nevertheless, this process depends on the distance of the polymer molecules, filling used, and also the compounding materials. For instance, when force is applied to rubber without filler, the hysteresis behavior is really trivial but when a force is applied to rubber with filler the behavior changes. When hysteresis increases, the rubber is suitable to be used instead of other materials in extensible applications; this is due to fear of crystallization occurring if other materials are used (NR Technical Bulletin, 1992). By applying higher heat, hysteresis also happens in this rubber material. The deformations will be repeated and, finally, the root point of the repeating area will be shifted. When low temperature is applied, hysteresis does not occur because the rubber becomes a thermal conductivity material. Also, with low hysteresis, rubber is suitable to be used as an isolator or a vibration absorber to block and break up the vibration energy. It can also produce more damping without any compromise and it also reduces the loss angle.

Rubber is not perfectly elastic and many researchers have showed this, and they also conclude that this material possesses a unique form, which is that the value is always less than the strain point of accumulation, but it is still better than other materials. Sinusoidal deformation takes place when the relationship between force and deformation is linear and also in the same frequency range. Modulus is one of the properties that contribute to the dynamic behavior of rubber. This is because, when the dynamic modulus of filled rubbers decreases in amplitude range, at the same time the strain applied is increased (Tsai and Hsueh, 2001). Essentially, the vulcanization process can be performed on this material with temperatures as low as 5°C and frequencies not exceeding 1000 Hz (NR Technical Bulletin, 1992; Yuan, 2010). For unfilled rubber, this process sees a minimum change over the shear modulus and it usually does not increase by more than 25% of the original value. The shear modulus of the material will experience dramatic changes if natural rubber is used in this process where the temperature and frequency are the same. When the frequency increases above 1000 Hz, the modulus will be directly proportional to the value of the earlier frequency. If the frequency increases, this implies that the modulus increases too. Rubber also will become as hard as glass when the vulcanization process is

performed at an ambient temperature. This often occurs when the temperature used is below 5°C and below the frequency of 1000 Hz. At this stage, the modulus will vary in its behavior due to it being a difficult process, and recording the actual modulus will become more complex.

Dynamic modulus for rubber will only happen on the filled type, and will occur if the amplitude of strains is increased. Some effects will occur that will cause a slow interaction between the filler and the rubber matrix. This will result in changes to the value of the static modulus where the value of strain will increase, and also change the quantum of magnitude. In theory, this will reduce the modulus and at the same time the strain value will increase.

Loss angle is employed to measure the damping value and the hysteresis value for rubber (Suzuki and Nishimura, 2010; Karabork, 2011). Both of these values are based on the cyclic deformation cycle. For unfilled types, during the vulcanization process at ambient temperatures and frequencies not exceeding 1000 Hz, the loss angle is too small. The loss angle is estimated to be around 4 degrees and only occurs at the lowest frequency of 60 Hz. Thus, the damping is more sensible to look at rather than the modulus, and, the damping is increased if the frequency increases, but at the same time bringing down the temperature value. At frequencies above 1000 Hz, regardless of whether the rubber is unfilled or filled, the vulcanization process will increase the damping value, even when the temperature is 20°C. A loss angle of 10 degrees only happens when the frequency reaches 2000 Hz. The value of the loss angle, which is recorded at high frequencies, is useful for designing isolator systems for engineering applications. The difference is significant if the comparison value for the loss angle between unfilled and filled types of rubber is conducted correctly. After the vulcanization process, the loss angle for the filled type has a high value compared to the loss angle of the unfilled type.

Effects of Spring Behavior in Rubber Materials

Most researchers agree that the nature of rubber is equal to the nature of a spring (NR Technical Bulletin, 1992; Ibrahim, 2008). Hence, it can be said that rubber can replace springs. In addition, rubber is the only material that can react like a spring. This is because rubber has a number of characteristics that are not available to other materials. One of the most important characteristics of rubber is the resistance to fatigue. This is because, if a tension force is imposed, rubber can overcome it and, finally, when the force is removed, the rubber will return to its original shape. Rubber also has high resilience because it can accommodate a large number of forces that are applied to it by small mechanical changes (NR Technical Bulletin, 1992; Ibrahim, 2008). Additionally, it also generates a very low heat when it flexes. Other than that, rubber also has a higher degree of strength, which makes it the most suitable material to be used under huge dynamic load. It also has low compression behavior, stress relaxation (which means it can be observed to decrease in stress in response to the same amount of strain generated in the structure), and a low damping ratio. All of the criteria mentioned above mean that rubber is suitable to be used as a spring. Nevertheless, it can also be used as bearings, isolators, mountings, tires, and for other industrial purposes.

From the description above, a number of differences between the use of rubber springs and metal ones have been identified, and some conclusions can be made. First, if using a rubber spring, unnecessary maintenance can be eliminated because of the nature of rubber itself. In addition, springs made from rubber can store a lot of energy and therefore these springs are able to withstand heavier loads than springs made of metal. Springs made from rubber are easier to optimize because the stiffness can be varied by simply changing the formula of the compound. Therefore, rubber springs are more widely used than other types. Rubber springs are also easy to install compared to other materials. A misalignment does not exist in this material too, therefore it can be used for a long time. This material also has high resilience; thus, it is more suitable to be used in places where there is high risk to exposure and to resonant vibrations.

Apart from the above discussion, it is also very important to discuss the natural frequency of rubber, because this will determine the dynamic stiffness of the material. Dynamic stiffness is used to control static deflection that happens on a body mounting system (Ibrahim, 2008). When a system is supported by a spring made from rubber, vertical natural frequency can be determined using the formulation given by

$$f_n = \frac{16}{x_y} \quad (1)$$

where x_y is the static deflection of the spring (Ibrahim, 2008).

Other than that, most of the engineering applications that use rubber as a mounting system emphasize the transmission of vibration energy to a structure (Burdzik, 2014; Brennan *et al.*, 2014). Thus, scientists and engineers have been using rubber as a vibration isolation system and it is believed to be used optimally and can prevent vibration energy from reaching the structure, as mentioned above, although it occurs at low frequency (Ibrahim, 2008).

Transmissibility, T_r , method is used to determine the ratio of vibrational energy generated before and after using the vibration isolation system. In addition, this method can also be used to divide the forces that have entered a structure with the force imposed on the structure, respectively. This transmissibility is expressed in terms of ratio between distributing frequency, f , to the natural frequency, f_n , resulting from the vibration isolation system.

Effects of Metal Plates Inside Rubber Materials

Currently, most rubber materials are used as springs because of the nature of the materials themselves (Chang, 2002; Banerjee, 2004). To maintain the natural properties of a spring, rubber should be used together with other materials, and currently the most

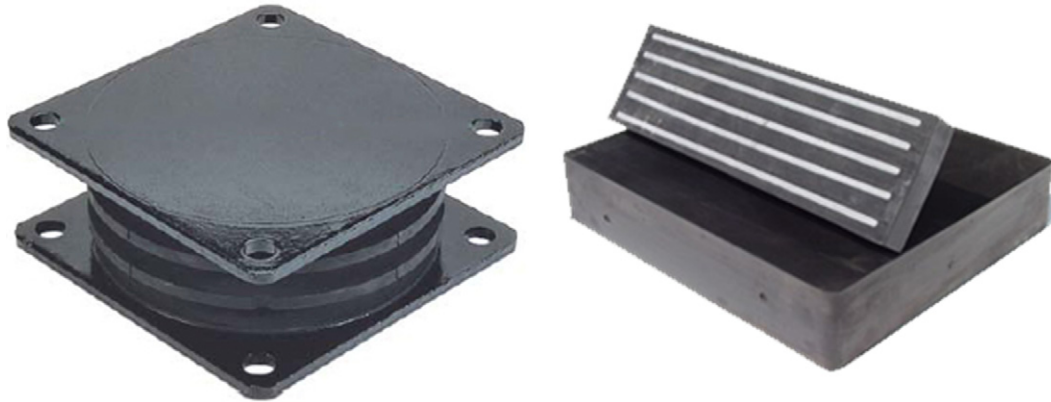


Fig. 10 Rubber materials bonded with a metal plate.

popular material in use with rubber is a metal plate. The main purpose is to tighten the grip and also the bonding property of natural rubber acts to connect it with the other material. In addition, the metal plate is applied to raise the vertical stiffness of a bearing or spring system, respectively. When a metal plate is utilized in conjunction with rubber, the bonding agent for both materials needs to ensure the rubber does not slip when force is applied. **Fig. 10** shows the arrangement of rubber materials with a metal plate.

Two criteria are important to consider in providing a strong bond between rubber and a metal plate: the strain concentration and friction (Nikiforova and Sheryshev, 2012). The strain concentration is used as a main factor to ensure the alliance between the two materials can be managed easily. If this factor is ignored, most likely the bonding will be damaged and the result will be an improper function or total failure. Errors that often occur are because many researchers only focus on the environment and condition in the middle between the rubber and the metal plate. But, the fact is those areas are not at high risk as there is a strong bonding condition. The main area for concentration of this strain should be focused on the corners or edges of the material itself. This is because most bonds that involve two or more different materials do not have a strong bonding in this area. The reason is that the surface area is too small and eventually the area becomes at risk of function failure. Friction is seen as the second-most important factor in this section. Very high-friction material will not slip when force is applied to the surface. Therefore, a sandblasting process should be performed on the metal plate so that the surface becomes rougher and provides greater grip. To ensure that the friction increases, the additives are used to make the bond stronger between rubber materials and metal plate (Tarhini and Hamade, 2012).

Transmissibility of Rubber Materials as Vibration Isolators

Vibration Isolators Performance

Currently, there are over 3500 articles – conference papers, journals, magazines, books, etc. – that discuss the role of vibration isolators in dissipating vibration energy (Nelson, 1994; Macinante, 1984). All of these articles have discussed the use of vibration isolators in many fields such as instrumentation, civil structure, mechanical systems, automotive, aeronautic application, aerospace vehicle, and earthquakes. There is a method to determine the performance of vibration isolators, which is called transmissibility.

It is very beneficial to assume that the base structure of a system is rigid, as it can give more simplicity in determining the transmissibility and, finally, it is easy to solve. But, if the base structure is not rigid, the transmissibility equation becomes more complex and difficult to solve. Available literature indicates that there are many different methods that can be used to solve the vibration isolator problem; however, all the methods are based on the approximation solutions, which use the differential equation formulation. The finite element method is also used to determine the solution for vibration isolators.

Previously, it has been shown that using a rigid base structure gives more advantages when solving a problem regarding vibration isolators. However, not all systems have a rigid base structure, as Blackwood and Nelson proved in 1993 and 1994, particularly. According to these two researchers, a flexible base structure will lower the vibration isolators' performance and make them less effective in reducing or blocking vibration energy transmitted by the isolator itself. Both researchers have suggested that base structure design is an important issue to consider in order to ensure that vibration isolators provide the maximum performance during vibration.

In 2007, Yan developed an approximation technique to determine the transmissibility of a flexible base structure. This technique uses a closed-form solution of distributed parameter system by associating it with a state-space technique, although it is very complex to solve the problem. The formulation is valid for self-joint and non-self-joint systems, and the boundary conditions must be nonhomogeneous with each other. After 2 years, Yan improved the formulation that determined the solution for complex problems generated by the distributed parameter systems. The new formulation can solve many complex problems that occur on the beam, plate, rod, point, and rigid bodies. The novelty is that the formulation does not involve any approximation

technique to solve the problem. An exact value is used to determine the eigenvalues and eigenfunctions for the flexible base structure. This new formulation is still used by researchers today.

Massless Isolators

Consider a machine with internal force, f_e supported with an elastic rubber, as shown in Fig. 11.

By assuming the machine vibrates only in the vertical direction with displacement at y , a simple model of the system can be assumed to consist of a mass, a spring, and a damper, as shown in Fig. 12, where the elastic mounting from the rubber has the property of stiffness and damping. The equation of motion for the single-degree-of-freedom system for this system can be expressed as

$$m\ddot{y} + c\dot{y} + ky = f_e(t) \quad (2)$$

where m is the mass of the motor, c and k are the damping and stiffness constant, respectively, and where $\dot{y} = dy/dt$ and $\ddot{y} = d^2y/dt^2$ (Salim *et al.*, 2014).

For harmonic motion at frequency ω where $f_e = F_e e^{i\omega t}$ and thus $y = Y e^{i\omega t}$, where F_e and Y are the complex amplitudes of the force and displacement, respectively, Eq. (2) becomes

$$(-\omega^2 m + i\omega c + k)Y = F_e \quad (3)$$

The injected force f_i to the base structure through the contact point of the mounting (spring and damper) can be represented by the free body diagram as shown in Fig. 13.

From Fig. 13, the equation of motion for the transmitted force f_t is given by

$$f_t = ky + c\dot{y} \quad (4)$$

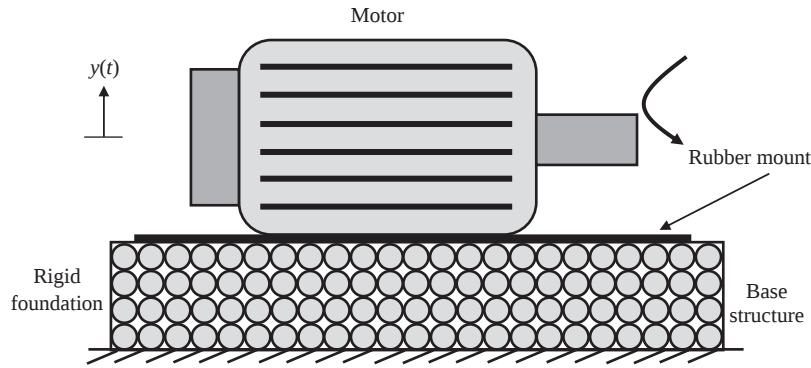


Fig. 11 Motor with supported elastic rubber mount.

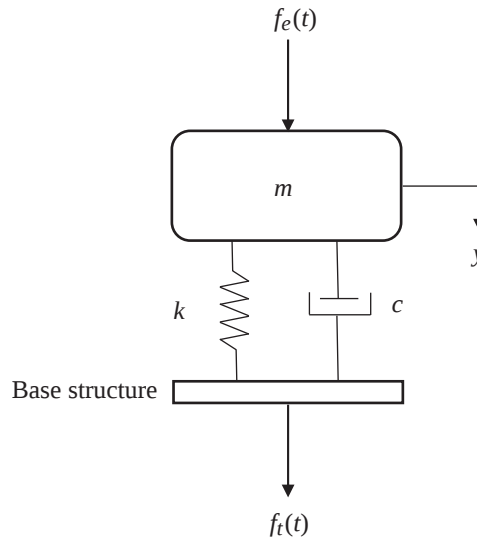


Fig. 12 Single-degree-of-freedom system for a massless isolator.

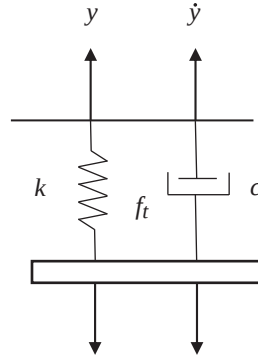


Fig. 13 Free body diagram for transmitted force for the single-degree-of-freedom system.

where, for harmonic motion, Eq. (4) thus becomes

$$F_t = (k + i\omega c)Y \quad (5)$$

From Eqs. (3) and (5), the transmissibility force, T_F between transmitted force, F_t and excitation force, F_e can be therefore expressed as

$$T_F = \left| \frac{F_t}{F_e} \right| = \left| \frac{k + i\omega c}{k - \omega^2 m + i\omega c} \right| \quad (6)$$

Eq. (6) can be written in terms of the natural frequency, ω_n and the damping loss factor ξ given by

$$T_F = \sqrt{\frac{1 + 4\xi^2(\omega/\omega_n)^2}{\left(1 - \frac{\omega^2}{\omega_n^2}\right)^2 + 4\xi^2\left(\frac{\omega}{\omega_n}\right)^2}} \quad (7)$$

where, $\xi = c/2\omega_n m$ and $\omega_n = \sqrt{k/m}$.

From Eq. (7) where the excitation frequency is much lower than the natural frequency of the system ($\omega \ll \omega_n$) yields

$$T_F \approx 1 \quad (8)$$

This is where the injected force is fully transmitted to the base. At resonance where $\omega = \omega_n$, Eq. (7) becomes

$$T_F = \frac{1}{2\xi} \quad (9)$$

where, the transmissibility is only controlled by the damping.

For the excitation frequency well above the natural frequency ($\omega \gg \omega_n$), Eq. (7) gives

$$T_F = \frac{2\xi\omega_n}{\omega} < 1 \quad (10)$$

where, the transmissibility can be further reduced as the frequency increases.

The transmissibility from Eq. (7) is plotted in Fig. 14 in terms of the normalized frequency, ω/ω_n . It shows that there is only one resonant peak and it represents the system resonance from the mass of the machine and the stiffness of the mounting. The frequency range below $1.4 \omega_n$ shows the transmitted force equal to or greater than the excitation force (amplification region) as indicated by Eqs. (8) and (9). Above $1.4 \omega_n$, the transmitted force becomes smaller than the excitation force. This is the frequency range where the mounting acts as the isolator. This transition frequency of $1.4 \omega_n$ can be shown as follows.

From Eq. (7) where $T_F < 1$ and assuming small damping ($\xi \ll 1$), this gives

$$\sqrt{\frac{1}{\left(1 - \frac{\omega^2}{\omega_n^2}\right)^2}} < 1 \quad (11)$$

As shown in Fig. 14, at the area of the isolator where $\omega > \omega_n$, thus Eq. (11) must be written as

$$\frac{1}{\frac{\omega^2}{\omega_n^2} - 1} < 1 \quad (12)$$

Finally, Eq. (12) yields

$$\omega > \sqrt{2}\omega_n \quad (13)$$

Fig. 15 shows the results of transmissibility for the increasing damping values. From Eq. (10), the damping is inversely proportional in the isolation region. By increasing the value of the damping, the transmissibility increases at the isolation region although the peak at resonance can be reduced. This is a “trade-off” situation for a machine system to have a low amplitude in the

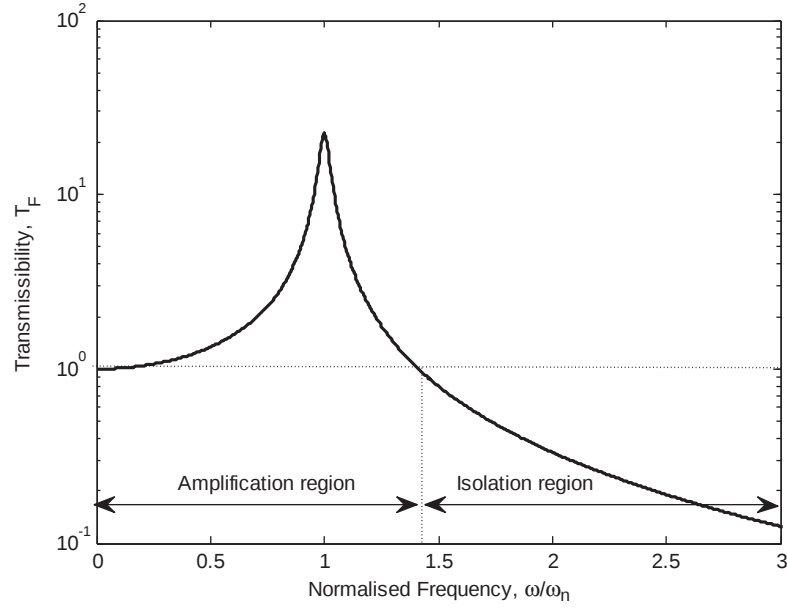


Fig. 14 Performance of the single-degree-of-freedom for a massless isolator.

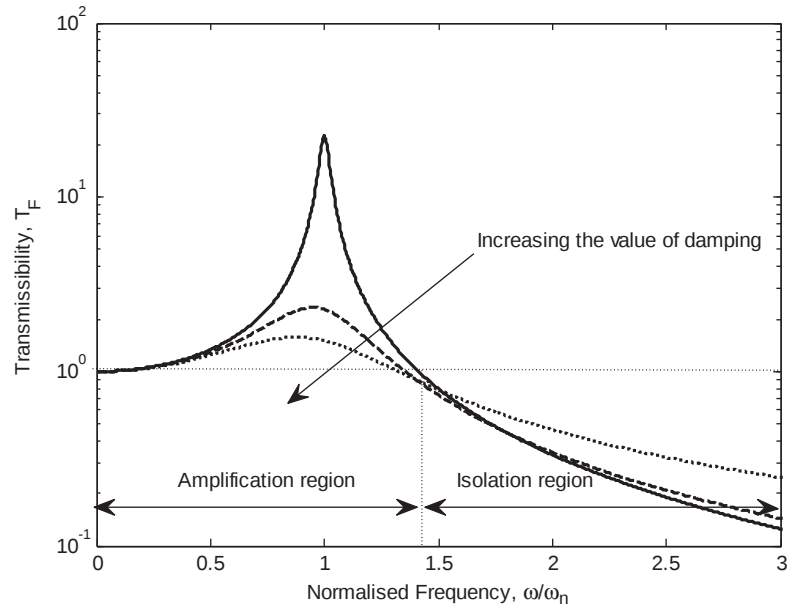


Fig. 15 Transmissibility of the single-degree-of-freedom for a mass isolator when increasing the damping value: - $\xi=0.02$; - - $\xi=0.04$; · · $\xi=0.06$.

case of resonance, but the isolation performance has to be sacrificed. Low amplitude at resonance is important, for example, during the machine start up where the machine will pass through the resonant frequency before finally reaching the steady-state speed.

Two-Degree-of-Freedom System of Massless Isolator

Considering the rigid foundation of the machine is located on another soft foundation having stiffness k_2 , and damping c_2 , as shown in Fig. 16.

The equation of motion can be derived as

$$f_e(t) = m_1 \ddot{y}_1 + c_1 (\dot{y}_1 - \dot{y}_2) + k_1 (y_1 - y_2) \quad (14)$$

$$0 = m_2 \ddot{y}_2 + c_1 (\dot{y}_2 - \dot{y}_1) + c_2 \dot{y}_2 + k_1 (y_2 - y_1) + k_2 y_2 \quad (15)$$

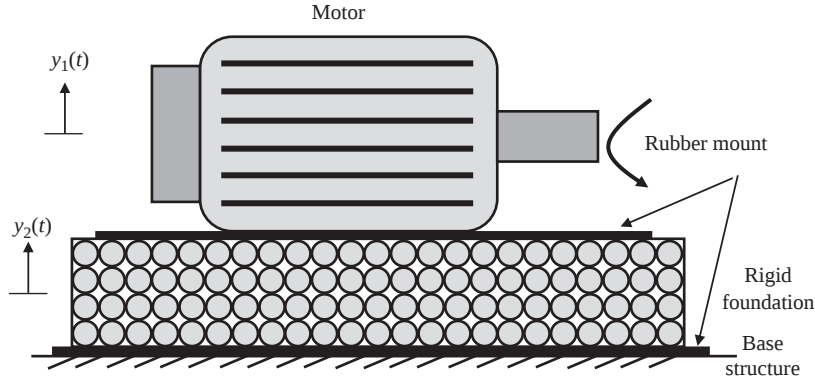


Fig. 16 Motor with two supported elastic rubber mounts.

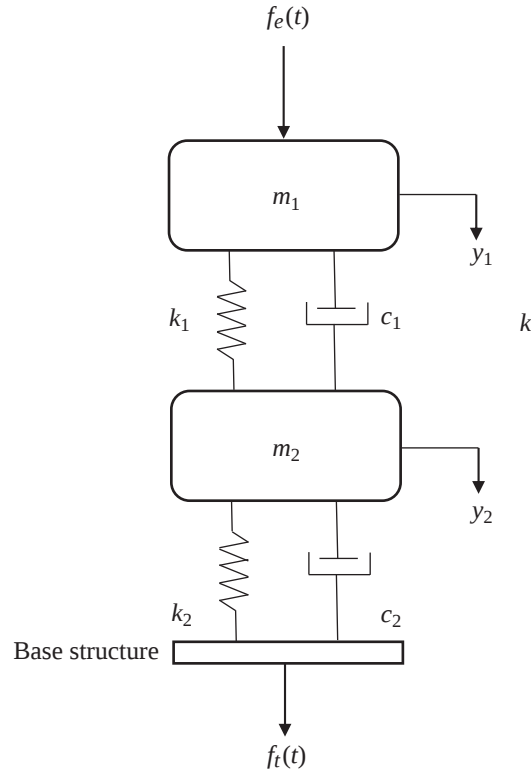


Fig. 17 Two-degree-of-freedom system.

and

$$f_t(t) = c_2 \dot{y}_2 + k_2 y_2 \quad (16)$$

where, m_1 is the mass of the motor, m_2 is the mass of the rigid foundation, c_1 and k_1 are the damping constant and stiffness constant of the rubber mount under the motor, and c_2 and k_2 are the damping constant and stiffness constant of the rubber mount under the rigid foundation.

The foundation can now move relative to the motion of the machine, say with displacement, $y_2(t)$, and the system which can now be modeled as the two-degree-of-freedom system, as shown in Fig. 17.

Following the derivation as in the single-degree-of-freedom system, Eqs. (14) until (16) can be written as

$$F_e = -\omega^2 m_1 Y_1 + j\omega c_1 (Y_1 - Y_2) + k_1 (Y_1 - Y_2) \quad (17)$$

$$0 = -\omega^2 m_2 Y_2 + j\omega c_1 (Y_2 - Y_1) + j\omega c_2 Y_2 + k_1 (Y_2 - Y_1) + k_2 Y_2 \quad (18)$$

and

$$F_t = j\omega c_2 Y_2 + k_2 Y_2 \quad (19)$$

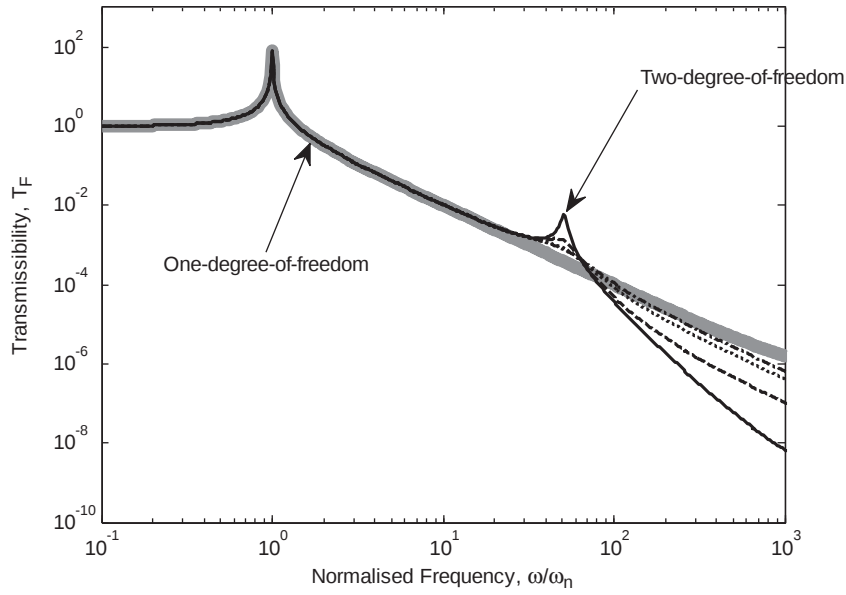


Fig. 18 Transmissibility of the two-degree-of-freedom system when increasing the damping value: - $\xi=0.02$; --- $\xi=0.04$; ... $\xi=0.06$.

Eq. (18) yields the relation between displacement of the motor and that of the foundation as

$$Y_1 = \left[\frac{-\omega^2 m_2 + j\omega(c_1 + c_2) + (k_1 + k_2)}{j\omega c_1 + k_1} \right] Y_2 \quad (20)$$

By substituting Eq. (20) for Eq. (17), the excitation force can be expressed by

$$\begin{aligned} F_e = & -\omega^2 m_1 \left[\frac{-\omega^2 m_2 + j\omega(c_1 + c_2) + (k_1 + k_2)}{j\omega c_1 + k_1} \right] Y_2 \\ & + \left[j\omega c_1 \left[\frac{-\omega^2 m_2 + j\omega(c_1 + c_2) + (k_1 + k_2)}{j\omega c_1 + k_1} \right] Y_2 - Y_2 \right] \\ & + \left[k_1 \left[\frac{-\omega^2 m_2 + j\omega(c_1 + c_2) + (k_1 + k_2)}{j\omega c_1 + k_1} \right] Y_2 - Y_2 \right] \end{aligned} \quad (21)$$

Using Eqs. (19) and (21), the transmissibility $T_F = |F_i/F_e|$ can be calculated.

The transmissibility results for the two-degree-of-freedom system are shown in Fig. 18 together with those for the single-degree-of-freedom normalized with respect to the fundamental natural frequency. The two peaks represent the first and the second natural frequencies of the system; each has a unique vibration behavior (mode shape). It can be seen that, apart from the existence of the second resonance, which degrades the oscillator performance of the original single-degree-of-freedom system around that frequency, the transmissibility is greatly improved above the resonant frequency. The second peak can be reduced by increasing the damping of the mount of the rigid foundation. However, as the damping is increased, the transmissibility above the second resonance frequency degrades approaching the transmissibility of the single-degree-of-freedom system.

Conclusion

The recent advances and challenges of rubber materials as a vibration isolator have been covered in this article. In conventional vibration isolation theory, vibration isolators consider several parameter elements, which are elastic springs and viscous damper, which is named as lumped parameter system in this article. Most of the previous study had developed the model of vibration isolators by presuming it to be a massless isolator. This simplification basically can be used at low frequencies, in which the wavelength of the vibration isolators is long enough compared to the exact dimension of the isolators. Thus, to model vibration isolators that can work in higher frequencies, the consideration of the distributed mass, stiffness, and damping are important; however, this is not covered in this article. In addition, this topic also represented the massless isolator with different number of degree-of-freedom. Overall, by increasing the number of degree-of-freedom, a new natural frequency is presented, and finally the transmissibility improved more than 30 percent above the previous frequency.

See also: Modeling Estimation and Performance Evaluation for Vibration Isolators. Rubber Scrap as Reinforced Material in the Production of Environmentally Friendly Brake Lining

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The Circular Economy: Additive Manufacturing and Impacts for Materials Processing

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Introduction

The move to a circular economy (CE) has been identified as an important and necessary shift in the way we do business and conduct our lives, locally and globally. Its potential impacts are manifold and wide ranging, leading to expected significant societal, environmental, and economic benefits. Primarily, the CE concept aims to decouple natural resource consumption from economic growth and activity. According to the Ellen MacArthur Foundation, this involves three key aspects: Designing out waste and pollution; keeping materials and products in use; and the regeneration of natural systems ([Ellen MacArthur Foundation](#)). The EU has implemented the ambitious 2018 action plan for the European transition towards a CE, again with several themes and target areas common to the Ellen MacArthur foundation: Maintaining and prolonging the value of products within the economy; ensuring a low carbon economy; and promoting efficiency and minimizing waste (EU). In the literature, however, the definition of the CE is not consistent and means different things to different stakeholders, with key principles of the CE approach often being selectively omitted, according to the interests of the definer. [Kirchherr et al. \(2017\)](#) analyzed 114 definitions of the CE concept in an effort to determine the current understanding of the CE concept among practitioners and scholars. Conceptual ambiguity, whether intentional or not, is a significant challenge for the implementation of the CE concept as the fundamental message can lose its potency, and in general become part of Engelman's language of "sustainable" ([Engelman, 2013](#)).

Notwithstanding the conceptual CE differences in the literature, there is an urgent need to reimagine how we utilize and manage our natural capital. Historically the capitalist economic model has often neglected the economic cost of natural resources ([Georgescu-Roegen, 1971](#)) and overlooked the vital contribution of the natural environment to economics ([Lovins, 2005](#); [Lovins et al., 1999](#)), and society in general. The capitalist economic model can be defined as linear: Primary resources are extracted from finite deposits in the natural environment and undergo preliminary processing; these resources are subsequently used as raw material inputs for manufacturing activities in conjunction with other inputs such as energy, water, and labor to transform the raw materials into consumer products. Note that these other inputs also require treatment/processing. The generated products are used by consumers and discarded after finite time periods, which vary according to the product type and life-cycle. It is important to recognize that each aforementioned stage involves various levels of waste generation and further associated resource utilization. The waste generated must be managed and mitigated to ensure that it too does not pose a further environmental threat, and the pattern continues. It is clear that this linear extract–use–dispose cycle is not sustainable with regard to either the extraction and subsequent depletion of natural resources or the generation and disposal of waste streams and pollution. Recent efforts have focused on developing a more sustainable economic model, with 4 "R" strategies such as Reduce, Reuse, Recycle, and Recover becoming more prevalent, and being recently superseded by the more nuanced nine "R" framework; see [Fig. 1](#) (10 strategies in fact).

The CE not only considers sustainability from an environmental perspective but seeks to embed it in our economic models and thinking. In principle, the concept of the CE and its implementation requires an integrated, interdisciplinary, and holistic approach spanning engineering and science, economics, policy and regulation, the broader humanities disciplines, and perhaps most importantly human behavioral changes.

Researchers have considered the CE approach and its impact on various manufacturing sectors. [Barrett et al. \(2018\)](#) reviewed the CE approach *inter alia* as a means to mitigate emissions and decarbonize the industrial sectors in the UK. They also considered methodologies such as exergy analysis and life cycle assessment (LCA). [Lieder and Rashid \(2016\)](#) reviewed CE implementation in the context of the manufacturing industry. [Winans et al. \(2017\)](#) considered the evolution of the CE concept and reviewed current applications of the CE concept across 20 countries, including the intersection between the CE and other thematic areas, for example, policy instruments, technological social and organizational innovation, and material flows and value chains.

The main objective of this article is to consider the CE approach in light of advanced, additive manufacturing and to assess any potential benefits with respect to traditional manufacturing processes. Furthermore, the CE approach will be compared with other engineering approaches to assess environmental impact, improve efficiency, and reduce waste.

Methodologies

Several methodologies are used to determine the environmental impact of production processes and production systems and to improve system efficiency, both economically and thermodynamically: Exergy analysis; thermoeconomics, which links thermodynamics and economics; LCA; and life cycle cost assessment (LCC).

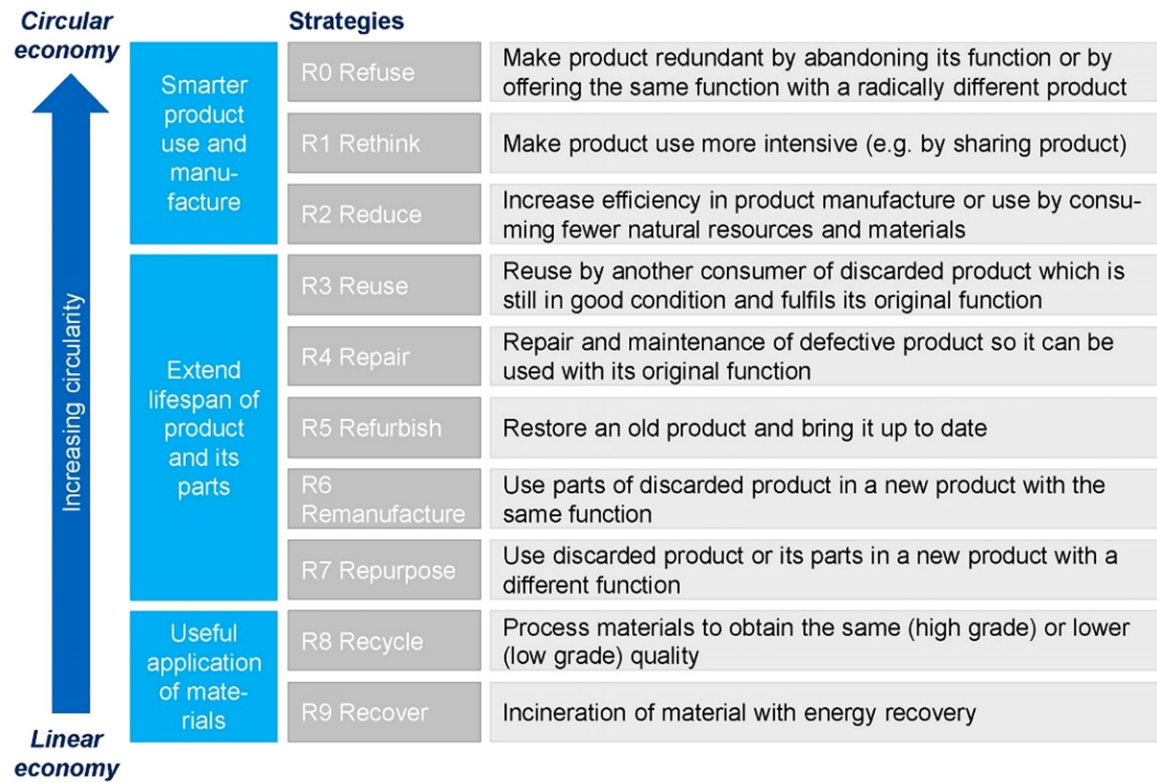


Fig. 1 The 9R framework. Adapted from Potting, J., Hekkert, H., Worrell, E., 2018. Circular Economy: Measuring Innovation in “The Product Chain”. The Netherlands: PBL Netherlands Environmental Assessment Agency. Kirchherr, J., Reike, D., Hekkert, M., 2017. Conceptualizing the circular economy: An analysis of 114 definitions. *Resources, Conservation and Recycling* 127, 221–232.

Exergy Analysis

Exergy analysis is widely used and accepted by many leading energy experts as providing a powerful basis for the characterization and optimization of thermal or energy systems. Incorporating both the first and second laws of thermodynamics, exergy analysis considers the quality and the quantity of energy in systems.

Exergy, a thermodynamic property, is a theoretical measure of the available (or potential) work a system can do as it comes into equilibrium with its environment. As a corollary, therefore, it is also a theoretical measure of the necessary work input to bring a system from its relevant reference environment to a desired thermodynamic state. The exergy at any point in a system is measured with reference to the “dead state,” that is, the state of the environment. Common forms of exergy include kinetic exergy, potential exergy, thermomechanical exergy, and chemical exergy. When equilibrium between the system and the environment is reached, the opportunity to do useful work no longer exists and the value of exergy is zero.

Thermodynamic irreversibilities are quantified by carrying out an exergy analysis, which consists of several stages:

- The exergy of process streams and systems is evaluated (mechanical, thermal, and chemical exergy with reference to the dead state);
- The rate of exergy destruction is determined using an exergy balance;
- The exergy balance and exergy destruction rates are used to calculate the exergetic efficiency of system components or overall system efficiency.

Although the rate of exergy destruction, initially, may not be significant as a stand-alone quantity, it does provide a critical benchmarking tool, both for the components within a multicomponent system and between similar systems. The rate of exergy destruction is also an ideal platform for assessing possible system improvements and optimization.

Life Cycle Cost Analysis, Life Cycle Assessment, and the Circular Economy

Manufacturing processes were reported to account for 19% of global greenhouse gas (GHG) emissions in 2010 (Díaz *et al.*, 2012). With global population growth predicted to exceed 8 billion by 2025 (Vörösmarty *et al.*, 2000), it is reasonable to assume that manufacturing-related GHG emissions and associated resource consumption will experience a relative increase in the coming years, particularly in developing regions such as Africa, Asia, and South America where the rate of industrial expansion is currently

twice that of the established industrial powerhouses (Maddison, 2007). It is important, therefore, that industry continues to develop sustainable manufacturing practices, improve energy efficiency, and reduce nonrenewable resource consumption, while at the same time maintaining economic viability. The challenges associated with achieving this *ideal* business model are varied and too numerous to explore in any great depth in this article. However, one area of particular importance is how to adequately measure or predict the efficacy of planned improvement actions, or novel technology implementation.

Life cycle cost analysis (LCCA) and LCA are terms often used interchangeably to describe analytical tools used for decision support. Both methods of analysis may be similar in objective, and to some degree scope, but can differ distinctly in their methodology, results, and sometimes in their final recommendations. Actions that might seem favorable on a company's balance sheet may not always align perfectly with a positive environmental profile. LCCA refers to a procedure in which the total *financial* cost of ownership of a product or system is evaluated over its entire economic life time. Historically, investment decisions would weigh heavily on initial capital expenditure (CAPEX). But in 1965 a report entitled *Life Cycle Costing in Equipment Procurement* (Logistics Management Institute LMI, 1965) prepared for the U.S. Department of Defence, it was determined that the cost of system acquisition may be small in relation to the cost of ownership (Eisenberger and Lorden, 1977). Dhillon (2009) reported that the cost of system ownership could range from 10 to 100 times the cost of acquisition. The LCCA concept introduced transparency to costing, and exposed hidden costs that were not immediately apparent with traditional costing methods. In his review of the LCC technique Harvey (1976) described the LCC of an item as "...the sum of all funds expended in support of the item from its conception and fabrication through its operation to the end of its useful life." The LCCA approach makes it possible to determine the most cost effective solution amongst a range of alternatives by considering all cash flows over the lifetime of the system, and allows practitioners to identify potential trade-offs between initial capital investment costs and long-term cost savings.

LCA is a holistic analysis tool used to assess or measure the environmental impact associated with a product or service. The main advantage of LCA is the scope or range within which it operates. Unlike other environmental assessment tools such as environmental impact assessment (EIA), ecological footprint, environmental risk assessment, or cumulative energy demand, which tend to focus on the immediate local environmental risk or impact, LCA considers all of the upstream and downstream processes associated with the production of goods or services throughout its entire life cycle. Indeed, in many cases the most significant source of environmental impact can occur far away from the point of production, use of goods, or provision of services, for example, the production of energy used in manufacturing processes is often the largest contributor to a product's environmental profile. The term "cradle to grave" is often used to describe the LCA process, which begins its resource use and emissions accounting from the acquisition of raw materials from the earth's natural resources, right through to the disposal or recycling of material at the end of the product or service life time (Fig. 2).

The LCA methodology, now an established framework set out in a series of ISO standards (ISO, 1997, 1998, 2000), allows practitioners to identify "hotspots" throughout a system and take appropriate actions for improvements in waste management, recycling, and energy use. This method of EIA has been practiced in one form or another since the late 1960s (Hunt and Franklin, 1996). However, in more recent times, the concept of a *cradle to cradle* (C2C), *closed loop*, or CE is considered by some to be the current gold standard in sustainability solutions.

At a European Union level the advocacy of the CE concept could be viewed as the latest in a series of measures taken by the European Commission (EC) to address the issues of economic and environmental waste management, resource-use efficiency, and consequently contribution to the reduction of European GHG emissions. In 2005 the EC published its report *Thematic Strategy on the Prevention and Recycling of Waste* (EU Commission, 2005). In 2009 The Waste Framework directive (2008/98/EC) outlined some basic waste management principles, and provided definitions for waste, recycling, and recovery (EU Commission, 2008). In February 2015, the EC released its action plan for the CE, in which "the value of products, materials and resources is maintained in the economy for as long as possible, and the generation of waste minimised." An approach believed essential to "develop a sustainable, low carbon, resource efficient and competitive economy" (EU Commission, 2015).

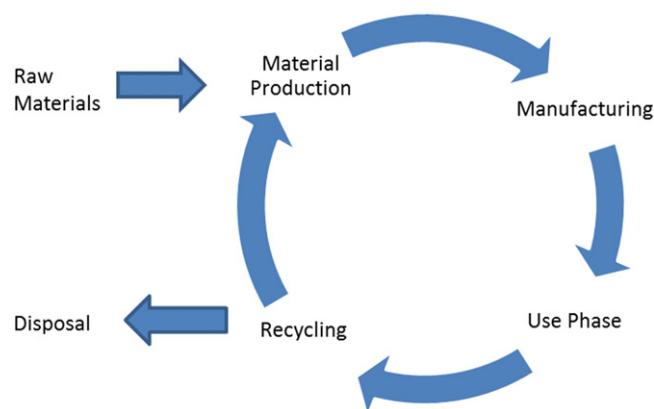


Fig. 2 Schematic of the product life cycle.

A macro level view of the CE concept coupled with a basic understanding of the objectives of LCCA and LCA methodologies would suggest an almost ideal synergy to achieve common goals, and this is true to some extent. LCA and LCCA allow management to test the assumptions of their CE business models, identify limitations, and formulate plans for continued improvement. However, a more detailed examination reveals areas where interpretations and subsequent recommendations may not align perfectly. Dieterle *et al.* (2018) suggest that CE [circular economy is referred to as C2C in the Dieterle report] and LCA objectives and recommendations may diverge in cases where trade-offs exist between energy and material use. In their example, substituting the primary materials used in the housing of an electric car engine with recycled material, contributes to closing the material loop, and complies with the CE concept; however, the recycled material may be lower in mechanical value requiring more of it to be used, thus, increasing the overall weight of the vehicle and contributing to the impact of increased energy consumption during the vehicle's use phase. This puts CE and LCA recommendations in direct conflict. However, it should be noted that the magnitude of impact from energy use is as dependent on the source of energy generation, as it is on the amount of energy consumed. Similar assertions could be made based on the results of the study conducted by Faludi *et al.* (2015). Additive manufacturing (AM) or "3D printing" is perceived as having *environmental benefits* when compared with other processes – in this case computer numerical control (CNC) machines. The research team chose LCA to test this thesis. The results of the study were to some degree inconclusive in determining the most "sustainable" solution due to the effect of variations in usage profiles and machine types. However, without any reference to CE in the study, it could be understood where LCA and CE recommendations would diverge. The CE approach on its own would not yield a fair or comprehensive environmental assessment in this type of study. AM is generally less material intensive than CNC milling, in the sense that less waste material is produced (Huang *et al.*, 2013). The cutting oils used in CNC machines are reported to pose significant health and environmental risks (Childers, 2006). The AM process does not use cutting oils but does have other chemicals that are used in their model materials, the impact of which has not yet been fully examined. From a CE perspective the reduction in material flow would appear to be the favorable option. However, this type of analytical approach provides only one part of the system's environmental profile. For example, it is claimed that some AM processes can require up to 50% of virgin material to be used along with recycled material, and that the AM materials can have a higher ecological impact per unit mass than CNC materials (Telenko and Seepersad, 2012). Additionally, AM processes are generally more energy intensive, which is not captured with CE, or at least not given the same weight of importance as closing the material flow cycle, whereas LCA operates with a much broader scope of energy, material, and waste flows.

The Faludi study highlights the importance of expanding the scope of comparative analysis to include the impacts from all of the flows associated with both manufacturing processes. Used in isolation, the CE approach as a decision support tool has its limitations. From an LCA perspective these limitations could be viewed simply as boundary definition issues. Conversely, Dieterle *et al.* (2018) view LCA as containing *gaps* when approaching problems with the CE mindset. The recommendation suggested by Bakker *et al.* (2010) is that LCA should be used as a complementary tool to CE as a means to assess whether the focus of a study should be on materials or energy. Although arguments between advocates and detractors of both CE and LCA will undoubtedly continue into the future, it should be encouraging to all environmental practitioners that these debates exist. In a broader sense, the CE concept and LCA have more in common than separates them.

Additive Manufacturing, Commonly Called 3D Printing of Metals

The American Society for Testing and Materials (ASTM) defines the AM process as "[t]he process of joining materials to make parts or objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies" (ASTM, 2009). The part is first designed as a CAD model before loading it to the 3D metal printer. In contrast, in the traditional subtractive process, a block of metal is machined by removing the material layer by layer by means of lathe or milling machines to produce the final part. AM describes a range of emerging production processes that have a high potential to enhance the capabilities of powder metallurgy production (Watson and Taminger, 2018; Dahmus and Gutowski, 2004; Morrow *et al.*, 2007; Chapman and Roberts, 1983; Walachowicz *et al.*, 2017; Wohlers, 2012). The process can be classified into seven technologies as shown in Fig. 3.

Among the seven AM techniques, a focus on metal powder printing is presented here due to its impact on industry and environment. In this process, the metal powder is deposited on the work platform mainly in two different ways blown powder and powder bed based techniques, Fig. 4. In the blown powder technique, the metal powder (or composite of powders) is fed onto the working stage and fused by the laser beam in the so called direct metal deposition process. In the case of the powder bed fusion (PBF), also called selective laser melting (SLM), the powder is spread and flattened on the work platform. The source of fusion in this process can be by a laser beam (SLM/PBF) or electron beam melting. The beam melts the powder in selective positions and coordination indicated by the CAD model. In both techniques, the working platform moves downward after the completion of each layer. The resolution of the movement is equal to the thickness of the built layer. Due to the mechanical stability of the metal powder, the unfused powder can largely be recycled and reused in a future production process.

The physical and mechanical properties of the produced part, such as surface roughness, dimensional accuracy, strength, coloring, surface hardness, and wear resistance are highly affected by the main processing parameters; see Fig. 5. These parameters include laser power, spot size, scanning velocity, hatch spacing/scan location, layer thickness, initial particle size, gas composition, flow rate, and powder bed temperature.

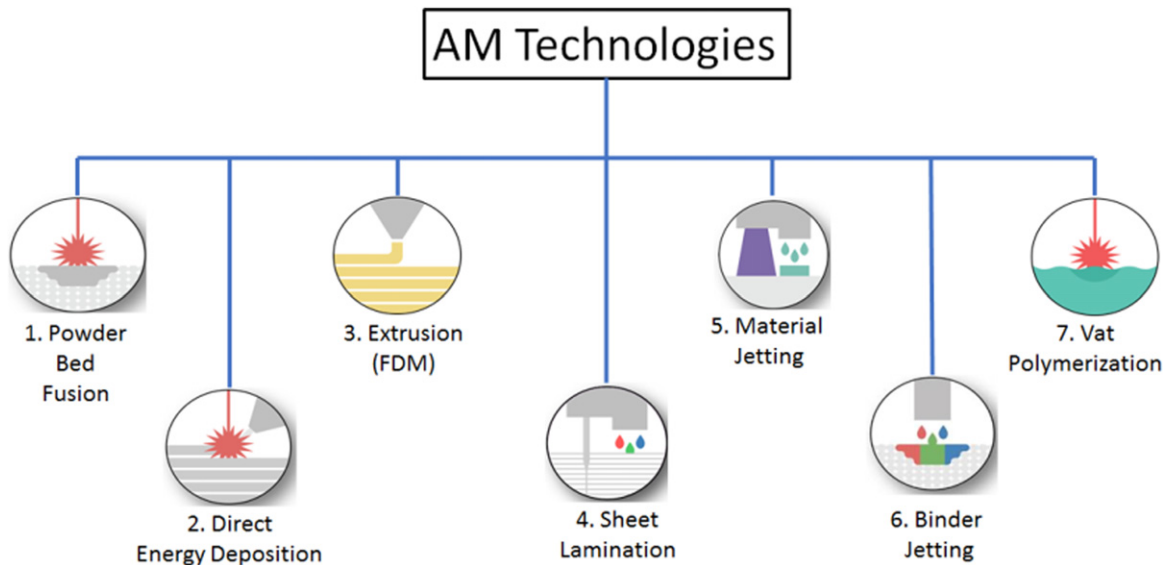


Fig. 3 The current technologies used in additive manufacturing.

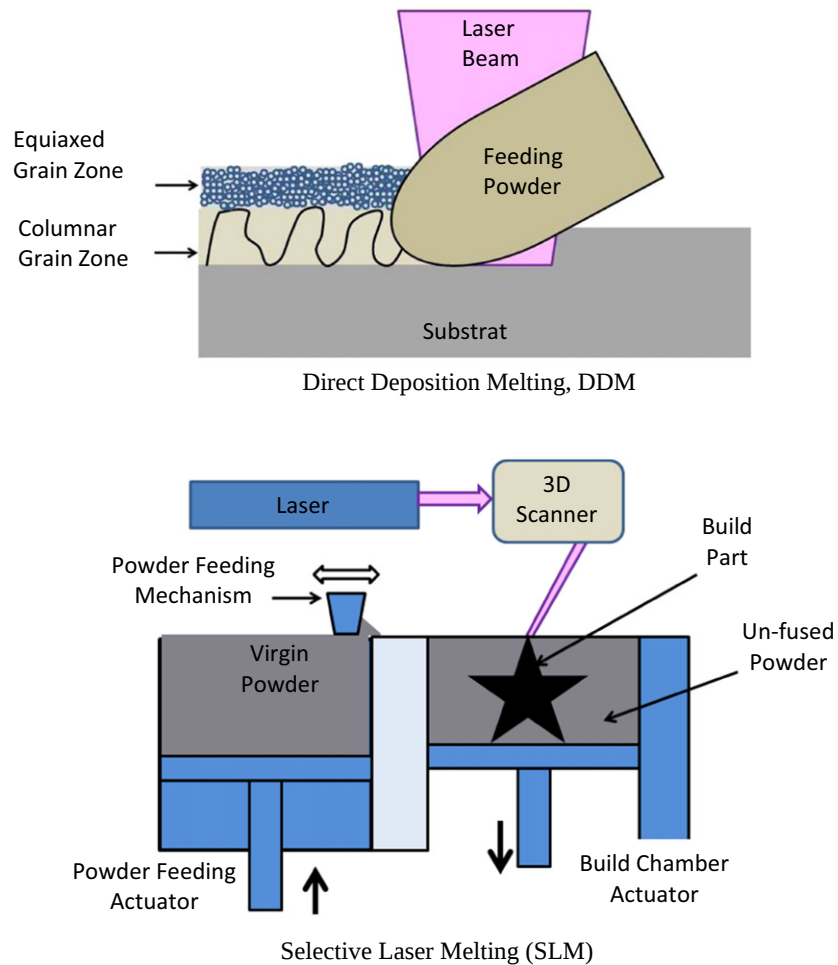


Fig. 4 Schematic of the direct energy deposition and powder bed fusion additive manufacturing processes.

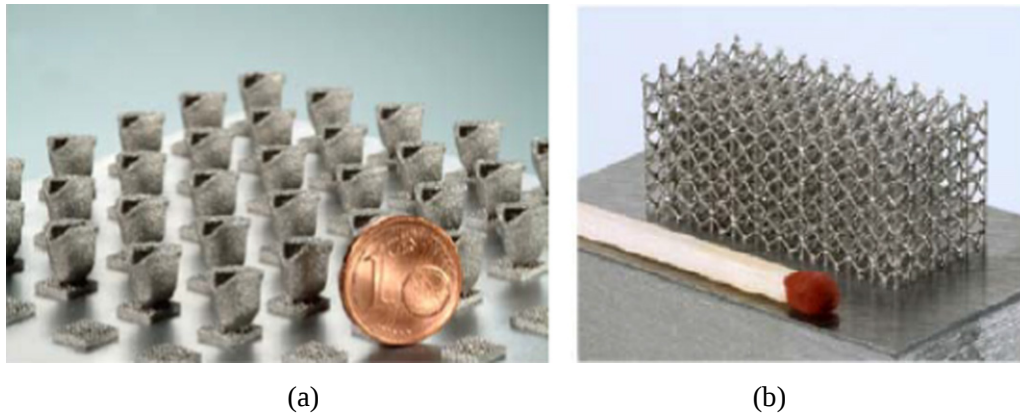


Fig. 5 Parts made by selective laser melting (a) Titanium dental caps and crowns and (b) SST air bone structure. Reproduced from Santos, E.C., Shiomi, M., Osakada, K., Laoui, T., 2006. Rapid manufacturing of metal components by laser forming. *International Journal of Machine Tools and Manufacture* 46 (12–13), 1459–1468.

Process Features

Advantages

The process enhances manufacturing by reducing lead times, manufacturing on-demand (reduce inventory and associated overheads), parts can be manufactured at internal/external customer's location to reduce shipping and logistics expenses, no material wasting, flexible design with no or less trials, products can be manufactured with fewer parts to reduce assembly, customized mass production, the ability to manufacture parts with complex geometry due to the no-tooling constraints, and new material compositions and multimaterial part production.

Disadvantages

Inconsistency and nonisotropic chemical and mechanical properties compared with traditional manufacturing can result due to the temperature and thermal gradient between the consecutive layers, high cost of machines and feedstock materials, lack of appropriate quality assurance, and development with lack of experience on some products and metal composites, in most cases limited build volume and constrained types of materials due to tool compatibility, parts with complex geometry might need supporting elements and postprocessing and subsequent heat treatment might be essential, that is, thermal stresses release, hardening, annealing, and surface polishing in addition to the high cost regarding the powders production.

Case Study

Problem and additive manufacturing solution

In Washington State, English Racing was struggling with their Mitsubishi 4G63 race engines (3D systems). The car reaches maximum speed of 185 mph in less than half a mile and an engine rotation of 10,000 rpm. This high level of rpm resulted in excessive oil pressure, which in turn would destroy the engine. Therefore, the design engineers decided to reduce the rotational speed of the oil pump to reduce the oil pressure inside the engine. To reach this solution, a bigger diameter driving pulley had to be manufactured and installed on the oil pump. The original pulley design was a part manufactured by melt injection molding requiring expensive tooling, time and money. After two years of trials, the part was made on a Prox DMP 300 3D printer. The working prototype took only five hours to print.

Tightening the Loop for the Circular Economy

In comparison with the most traditional (subtractive) manufacturing processes, additive manufacturing offers the ability to serve better in terms of the CE; see Fig. 6. In all types of AM processes, a high percentage of the unused material can be recycled and used in the next manufacturing process as a 100% virgin material. For many applications it is considered that only the metal powder attached to the produced part outer surface may suffer from excessive oxidation and change in its properties due to the high exposure temperature. For this reason, the later portion of the powder is preferably mixed with a fresh virgin powder to avoid the inconsistency in physical and mechanical properties, which might lead to part failure.

In the subtractive manufacturing, most of the waste metals are in cut metal chip form, cannot be remelted, and are difficult to handle and transport. Fig. 7 shows an example in which excessive waste chip material is generated by conventional manufacturing. In AM, only the exact amount of metal powder required to build the part is consumed, unlike the linear take–make–waste model. Obsolete and faulty parts from both processes can be recycled and used as raw material in most scenarios.

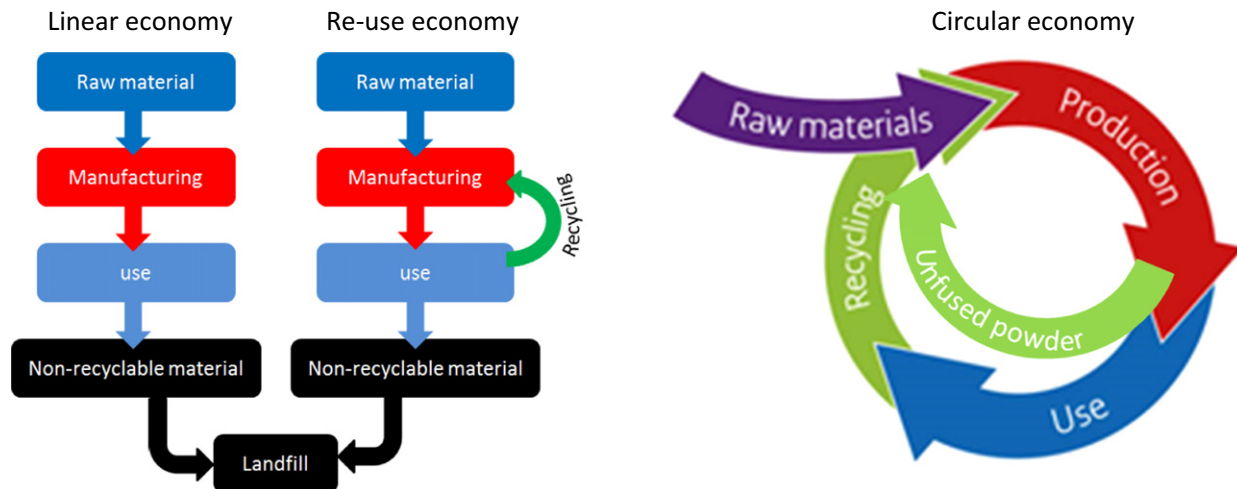


Fig. 6 Schematic of the linear, reuse, and circular economy modes.

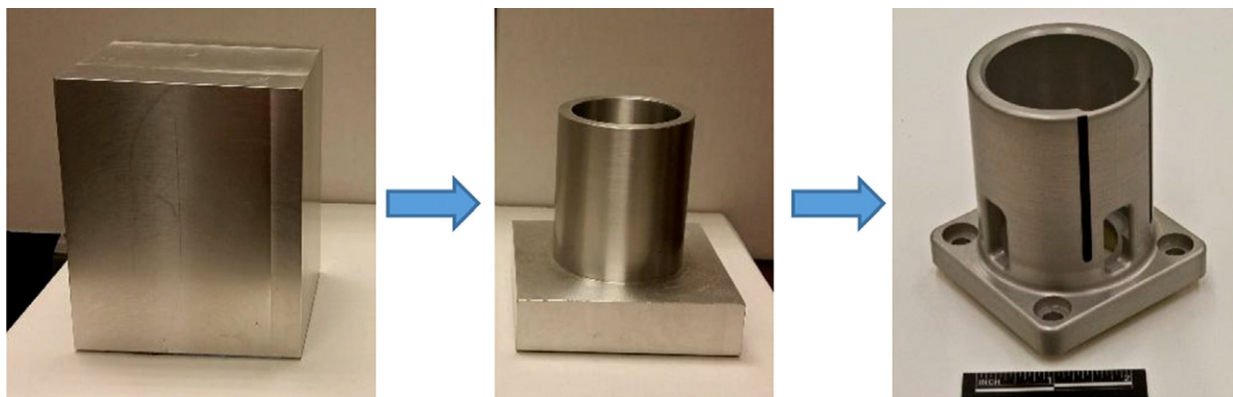


Fig. 7 Shows the amount of waste material that can result from traditional machining operations. Reproduced from Watson, J., Taminger, K., 2018. A decision-support model for selecting additive manufacturing versus subtractive manufacturing based on energy consumption. *Journal of Cleaner Production* 176, 1316–1322.

State of the Art in the Energy Consumption and Cost

One of the major drawbacks in additive manufacturing is the high cost of feedstock metal powders. The following [Tables 1–3](#) list the market pricing for some of the common metal powders used in AM, the energy consumption for different manufacturing processes and the hourly machining rates and labor cost. The specific energy consumed during the production of the raw material, powder atomization, and the related machining processes are listed in the following [Table 2](#). The production rates including the labor cost and tooling for various manufacturing methods are presented in [Table 3](#).

In the case of subtractive manufacturing, the production machine consumes a variable amount of electric energy depending on the material being machined, the feed rate, the spindle rate, and the tool configuration. In addition, there must be a substantial amount of energy, which is constantly consumed when the machine is on the standby mode during the tool and workpiece set-up even though the cutting operation is not initiated. This energy is required to run the axes motors and spindle drive, oil lubrication and hydraulic pumps to maintain their pressure levels, lighting, and CNC electronic boards. Sometimes the machine stays on the standby mode for several hours before processing the material. It is necessary to reduce this idle time to minimize the energy consumption.

In contrast, the energy consumption in the 3D printing machines includes the energy required for maintaining a continuous delivery of the metal powder, running the positioning stage motors, supplying the heat source (laser beam or EB) and running all the control sensors, extraction and vacuum systems, electronic boards and lighting, and any embedded heating elements. This energy consumption is different from one machine to another. It is difficult to compare between different 3D printing machines in terms of energy consumption. [Watson and Taminger \(2018\)](#) identify many reasons why this is difficult to do due to the different experimental set-up between researchers, such as the differences in the thermophysical properties of the printing metal from one research project to another and different part designs. The processing parameters were also not always optimized when these results were obtained.

Table 1 Market prices for selected metal powders used in AM

<i>Metal type</i>	<i>Powder (€/100 g)</i>
316L SST	402
316 SST	135
304 SST	157
Iron	10
Copper	80
Titanium	300

Abbreviation: AM, additive manufacturing.

Note: Sigma-Aldrich. Available at: <https://www.sigmaaldrich.com/catalog/search?interface=All&term=metal+powder&N=0&page=1&mode=match+partialmax&focus=product&lang=en®ion=IE> (accessed 03.04.19).

Table 2 The specific energy consumed during the production of raw material, metal powders

<i>Process</i>	<i>S. energy (MJ/kg)</i>	<i>Reference</i>
Tungsten carbide tooling	400	(Dahmus and Gutowski, 2004)
Bulk steel forming	20	(Morrow <i>et al.</i> , 2007)
Direct/indirect powder production	16/26	(Morrow <i>et al.</i> , 2007)
Bulk steel from virgin sources	31	(Chapman and Roberts, 1983)
Bulk steel from recycled sources	9	(Chapman and Roberts, 1983)
Atomization H13 tool steel	1	(Morrow <i>et al.</i> , 2007)
Atomization IN718	2.4	(Walachowicz <i>et al.</i> , 2017)
Atomization AlSi10Mg	8.1	(Faludi <i>et al.</i> , 2017)
Laser beam melting of 316 L	83–588	(Baumers <i>et al.</i> , 2011)
Laser beam melting of 17-4 PH	241–399	(Mativenga and Rajemi, 2011)
Turning	4.61	(Mativenga and Rajemi, 2011)
Milling	7.64	(Dahmus and Gutowski, 2004)
Hobbing	14	(Gutowski <i>et al.</i> , 2009)
Residual stress annealing	1.53	(Källen, 2012; Field <i>et al.</i> , 1994)
Preheating	3.5	(Källen, 2012)
Carburization	4	(Källen, 2012)
Hardening	8.2	(Källen, 2012)
Tempering	0.83	(Källen, 2012)

Note: Kamps, T., Lutter-Guenther, M., Seidel, C., Gutowski, T., Reinhart, G., 2018. Cost-and energy-efficient manufacture of gears by laser beam melting. CIRP Journal of Manufacturing Science and Technology 21, 47–60.

Table 3 Production rates including the labor cost and tooling

<i>Process</i>	<i>Hours/kg</i>
Sawing	9.5
Turning	15
Milling	35
Hobbing	80
Grinding	80
Labor	40
Case hardening	4
Laser beam melting	27

Note: Kamps, T., Lutter-Guenther, M., Seidel, C., Gutowski, T., Reinhart, G., 2018. Cost-and energy-efficient manufacture of gears by laser beam melting. CIRP Journal of Manufacturing Science and Technology 21, 47–60.

Kamps *et al.* (2018) developed two models to compare the cost and energy efficiency for the manufacture of a gear by SLM against two other industrial processes, hobbing and milling, depending on data collected from literature and for a production volume of up to 1000 pieces. The cost model included the cost for annealing and the removal of the residual stresses, removing the part from the platform by wire Electron Discharge Machine or sawing machine, machine rate and depreciation, argon gas

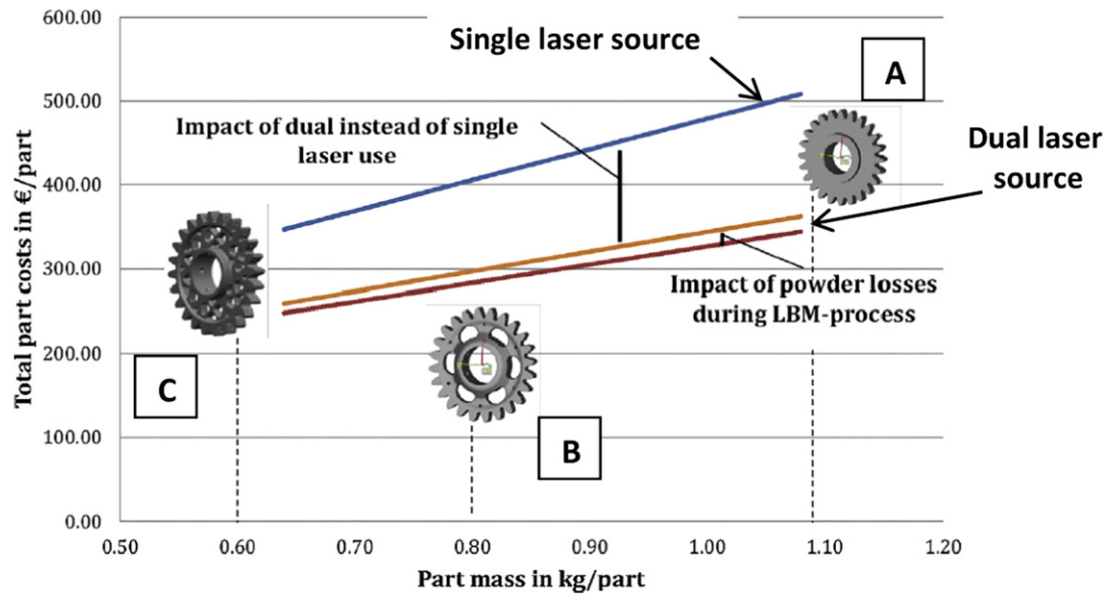


Fig. 8 Total cost calculation for the manufacture of four gear pieces using single and dual laser sources as a function of the mass. Reproduced from Kamps, T., Lutter-Guenther, M., Seidel, C., Gutowski, T., Reinhart, G., 2018. Cost-and energy-efficient manufacture of gears by laser beam melting. CIRP Journal of Manufacturing Science and Technology 21, 47–60.

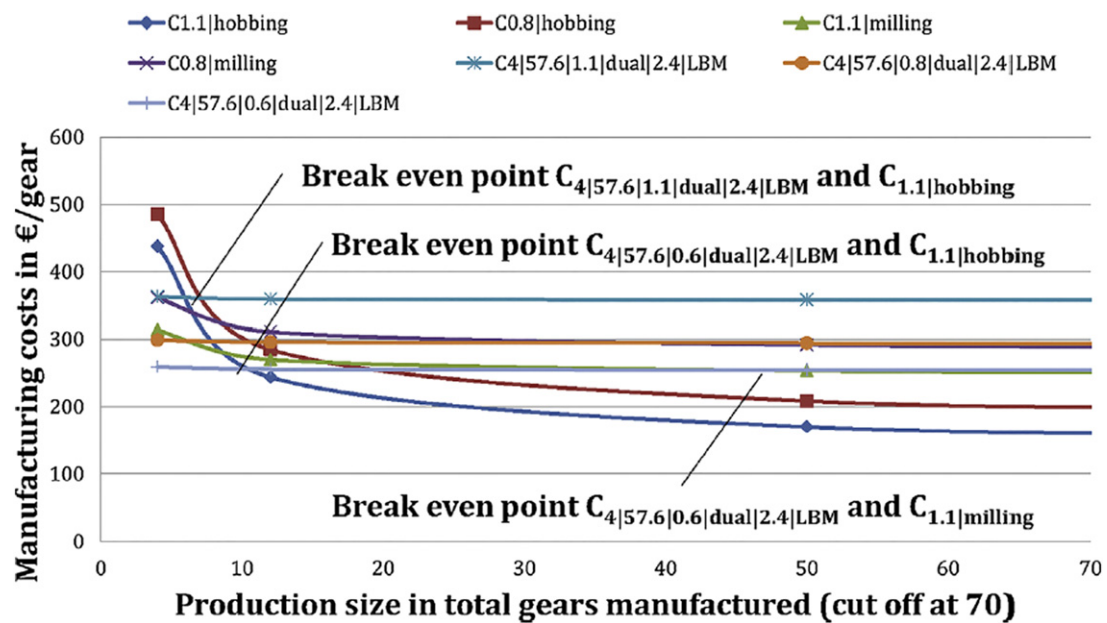


Fig. 9 The total cost of lightweight gear manufacture using two subtractive and LBM methods. Reproduced from Kamps, T., Lutter-Guenther, M., Seidel, C., Gutowski, T., Reinhart, G., 2018. Cost-and energy-efficient manufacture of gears by laser beam melting. CIRP Journal of Manufacturing Science and Technology 21, 47–60.

consumption, and the cost of the metal powder. Fig. 8 shows the total Laser Beam Melting (LBM) manufacturing cost per part as a function of the mass and the recycle rate for a production volume of four gears.

Fig. 9 shows several break-even points for one of the subtractive methods and the SLM depending on the size of production and the mass of the gear parts produced. Also, it can be concluded that SLM is an efficient alternative for small mass and small size of production (up to 43 pieces). For the larger mass of 1.1 kg, only small production capacity of four pieces is a good cost option, which can be compared with the milling of a 0.8 kg gear.

When investigating the life cycle analysis for this case of gear production, it was found that the production volume had no significant effect on the average specific energy consumption. Also, the employment of a dual laser source embedded in one SLM

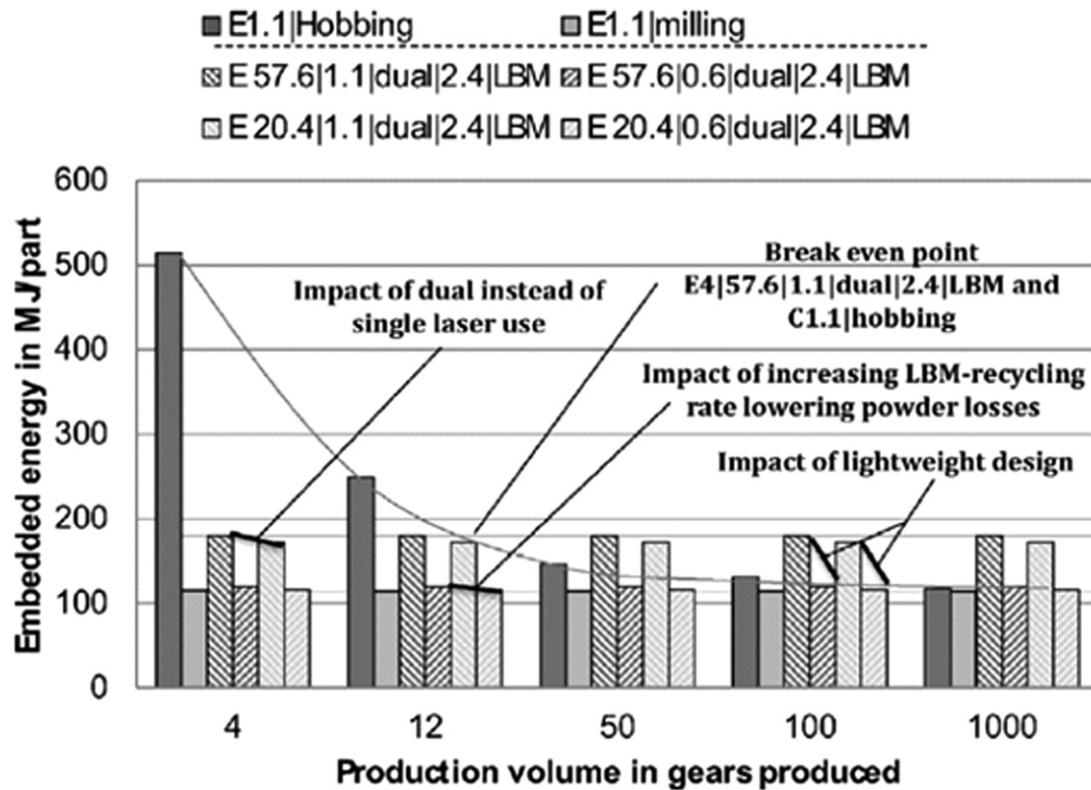


Fig. 10 The energy embedded of three manufacturing processes of a metal gear for the different production volume. Reproduced from Kamps, T., Lutter-Guenther, M., Seidel, C., Gutowski, T., Reinhart, G., 2018. Cost-and energy-efficient manufacture of gears by laser beam melting. CIRP Journal of Manufacturing Science and Technology 21, 47–60.

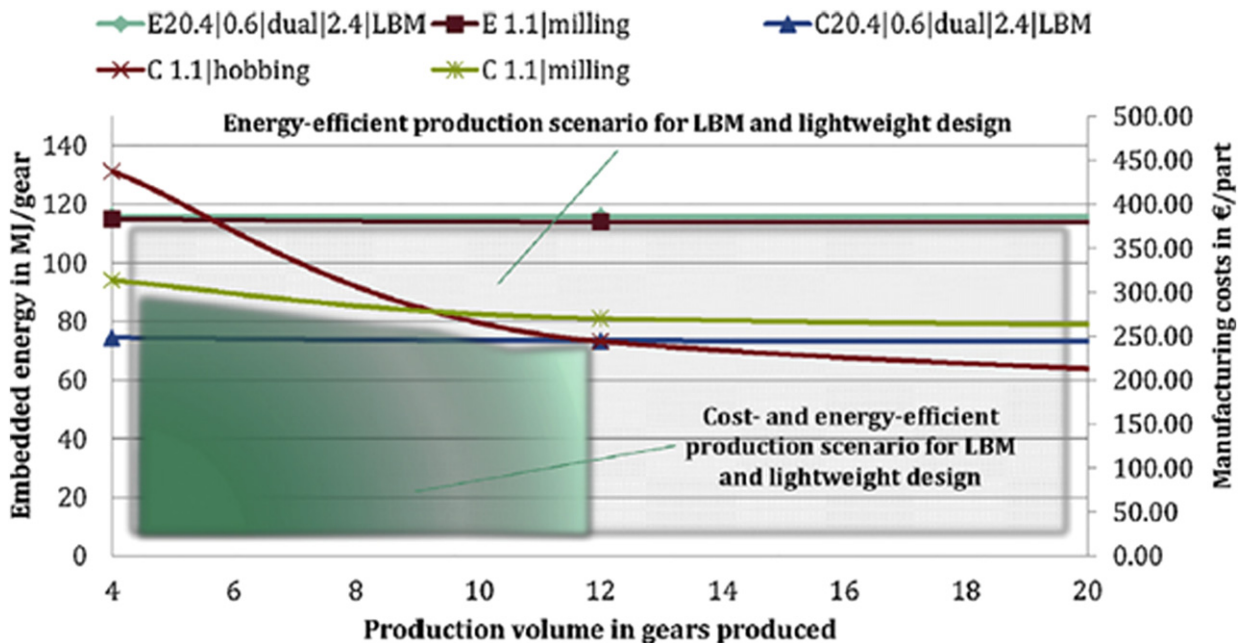


Fig. 11 The embedded energy and cost of the three processes for production volume of up to 20 parts. Reproduced from Kamps, T., Lutter-Guenther, M., Seidel, C., Gutowski, T., Reinhart, G., 2018. Cost-and energy-efficient manufacture of gears by laser beam melting. CIRP Journal of Manufacturing Science and Technology 21, 47–60.

machine is beneficial due to the doubling of the melting rates knowing that all the auxiliary equipment such as motion motors, control system, lubrication, powder feeding, and heating are shared between the lasers. The adoption of a lightweight part design in this case was found to be not a significant factor as it only increased the overall energy consumption by 3% compared with milling cavity holes to reduce the total weight from 1.1 to 0.8 kg as shown in A and B in Fig. 8. Fig. 10 shows a direct comparison of the embedded energy (E) for the three production processes.

As can be seen, at low production volumes, the hobbing process shows high embedded energy due to the extensive tooling necessary and decreases by increasing the production capacity. Both milling and LBM processes show constant energy levels for the different production sizes. It is clear that the lightweight parts (B and C in Fig. 8) require less energy.

At this stage, a direct comparison between the three processes in terms of the cost and energy consumption is beneficial as shown in Fig. 11.

The figure indicates that LBM is a good option for the low production capacity of <12 parts when taking into account the two models, cost and life cycle analysis based on the areas below the cost and energy plots. This means that LBM can be recommended for manufacturing of high variance models and designs such as aerospace.

Making a decision for which manufacturing process is more efficient for the production of a certain model designs and metal can be utilized by investigating the total cost and the life cycle analysis. These analyses in turn are highly related to several factors including design complexity, metal cost, processing parameters and their levels, machining cost rate, equipment, and tooling. The energy consumed must be measured experimentally and divided by the volume of material being added or removed for a direct comparison (Kamps *et al.*, 2018). The energy consumption in LBM technology comprised only 4% of the overall production cost. The material losses and tooling are significant factors in the conventional methods like milling, hobbing, and lathe. Additionally, postprocessing must be taken into account, which in most cases has high importance to adjust the final dimensions or surface finishing such as milling, grinding, and polishing or to release the surface thermal stresses and heat treatments such as annealing and hardening.

Finally, the SLM manufacturing method is now considered a mass manufacturing technique. Several companies are employing it for the production of many parts such as Boeing using this method for the manufacture of more than 200 parts on 10 production platforms (Huang *et al.*, 2013). This is a very important achievement attributed by the reduction of the AM parts weight, that is, it estimated that the reduction of the aircraft overall weight reduces the energy consumption by 2800×10^{15} J/year and the associated CO₂ by 215×10^6 MT/year (Huang *et al.*, 2016).

It is clear that in many cases, the metal AM process reduces the environmental impact and provides for increased manufacturing sustainability. It does not use water for cooling so no damage is caused to the terrestrial or aquatic system. It requires much less warehousing and transportation as material is requested according to the manufacturing specifications and on customers' demand and could be produced at the customer site, such that files are shipped rather than excessive shipment of materials or parts.

See also: A Comprehensive Study for 3D Printing of Rapid Tooling From Reinforced Waste Thermoplastics

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A Comparative Life Cycle Assessment for Utilising Laminated Veneer Bamboo as a Primary Structural Material in High-Rise Residential Buildings

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Glossary

Biomimetic The imitation of the models, systems, and elements of nature for the purpose of solving complex human problems.

Eco-Cost A measure to express the amount of environmental burden a product or system has. Represented in terms of Euros per kilogram i.e., €/Kg.

Global Warming Potential (GWP) (kg CO₂ eq) A measure of greenhouse gas emissions, such as CO₂ and methane. These emissions are causing an increase in the absorption of radiation emitted by the earth, increasing the natural greenhouse effect. This may in turn have adverse impacts on ecosystem health, human health, and material welfare.

Introduction

The aim of this research project is to establish, through a structural comparison review and comparative life cycle analysis (LCA), the overall contribution that laminated veneer bamboo (LVB) has to global warming potential against that of cross laminated timber (CLT). This study also aims to establish if engineered bamboo is a feasible alternative construction material for use in high density urban housing in a European context.

The project aims to achieve the following objectives:

- (1) Collate and critically analysis and data from the field of bamboo and laminated veneer bamboo.
- (2) Establish through structural data comparisons the potential for engineered bamboo products to be implemented into high rise construction.
- (3) Research the embodied carbon of LVB and CLT and apply this to the Life Cycle test results.
- (4) Conduct a comparative Life Cycle Analysis (LCA) on laminated veneer bamboo (LVB) and cross laminated timber (CLT) to assess the global warming potential of both.

Literature Review

Product (Laminated Veneer Bamboo)

Laminated veneer bamboo (LVB)

Laminated veneer bamboo (LVB) is a product that uses multiple thin strips of bamboo combined with an adhesive to form a board or sheet product. Manufactured by Glubam, Moso and Lamboo® Inc. to name but a few it typically consists of 3, 5, 7, and 9 layers laminated veneer bamboo is manufactured in a similar way to OSB or Plywood. A series of thin strips of bamboo are laminated together in alternating 90° angles for each layer.

The production of LVB can be divided into the following steps:

Slicing of bamboo poles longitudinally to create strips of bamboo. Strips are produced by feeding culms through a splitter machine that cuts the bamboo culm into slender strips.

Surfaces of the strips are scraped and planed to remove wax and silica as well as to create rectangular cross sections.

Strips are left to air-dry at room temperature for one week after they are cut.

Air-dried strips are then immersed in a boron solution and left to dry in the sun until their moisture content reach 12%.

Adhesive is applied to the strips that are then neatly arranged next to and on top of one another to create the final product.

Bamboo sheets are produced by placing bamboo strips side-by-side and edge-gluing them using tannin resorcinol formaldehyde (TRF) (Mahdavi *et al.*, 2012).

Fig. 1 below shows a graphical breakdown of the process.

Mechanical Properties

Bamboo as a material has been used in small local developments predominantly in Asia and South America for millennia. It is undeniable that bamboo has the capability to be considered as a structural material in its raw natural form. Many studies have been conducted on the application of bamboo in its natural form for construction purposes. A study by Albermania *et al.* (2007)

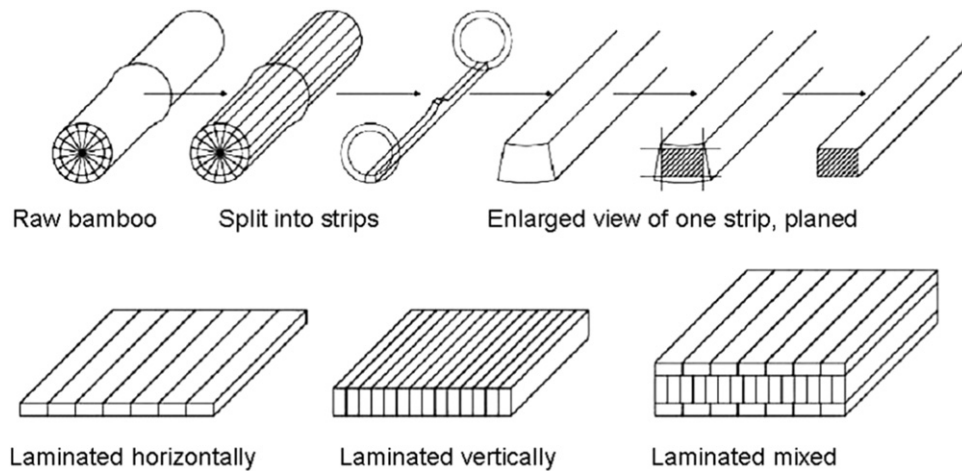


Fig. 1 Manufacture process of Laminated Veneer Bamboo. Reproduced from Rittironkand, S., Elnieiri, M., 2015. Modern bamboo structures. In: Investigating Laminated Bamboo Lumber as an Alternate to Wood Lumber in Residential Construction in the United States. Taylor & Francis, pp. 83–96.

on a lightweight bamboo double layer grid system indicate that, in practice using a special PVC jointing system devised by the team, these double layer grid systems could be applied for the construction of designs of small to medium span buildings (Albermania *et al.*, 2007). Furthermore, a study conducted by Yu *et al.* (2003) on the column buckling of structural bamboo demonstrates that “The proposed design method applied by the researchers is shown to be structurally adequate in accordance with modern structural design philosophy, and it may be used effectively, to correctly and appropriately design structural bamboo (*Phyllostachys Pubescens* & *Bambusa Pervariabilis*) in bamboo scaffolds and other bamboo structures”. This study along with the availability of design data on the dimensions and the mechanical properties of structural bamboo, in its natural form, allowed structural engineers to take the advantages offered by bamboo to build “light and strong bamboo structures to achieve enhanced economy and buildability” (Yu *et al.*, 2003).

These studies show the potential use of bamboo in its raw natural form.

The following is a comparison of board/sheet products under different mechanical properties; flexural and compressive strength, modulus of elasticity, shear strength and tensile strength. The mechanical properties for each of the materials in question were sourced from the market leading companies that produce these products. The values and figures presented were extracted from data sheets provided by SmartPly OSB/Plywood and by Lamboo® Inc. None of the mechanical properties presented were the result of any testing conducted by the author of this research or any persons associated with this research. The comparison of the materials and all comments associated to the comparison are the work of the author.

In order to ensure a comparison can be made between these products the means by which they are tested must first be evaluated. All materials were tested to ASTM international standards and sample sizes were manufactured according to ASTM 3501 for compressive strength testing, ASTM 3500 for tensile testing, ASTM D3043 for flexural testing, ASTM D3048 for shear testing and ASTM D 1037 for determining elastic modulus. ASTM international is an internationally recognised standards organisation. The ASTM testing of materials is similar to testing set out by The International standards organisation (ISO) and Eurocodes who follow the guidelines set out by ISO. The data was critically reviewed and test methods were evaluated against those of European Standards. This process was carried out as the majority of the research for bamboo specimens was conducted using an American standard for testing materials (ASTM) now ASTM international (ASTM, 2012; Lamboo, 2014). This review of standards showed identical testing procedures when compared to European standards. Relevant data was compiled and presented to show the capability of LVB against similar building products for instance Plywood and Orient Strand Board (OSB).

Test Specimen sizes for testing of board products are presented at the beginning of each sub-article. A thickness of 12 mm has been given to the laminated veneer bamboo. All other materials are presented with their thickness.

From the simple comparisons in Table 1 we can see that the laminated veneer bamboo product excelled in all but one of the test areas.

A full break-down of the data in the graphs previous is depicted in Table 1.

It is fundamental that if laminated bamboo is to be considered as a usable building material further research is needed on the mechanical properties of the sheet material including and taking into account a factor of safety. Furthermore, how the material is used i.e., as a sheet material, in a column or beam system or in a panelised system could change the structural characteristics of the material. This is particularly noticeable when using the material for high rise construction where the members used in the lower stories will be under considerably more load than that of the members used in the upper storeys of a buildings structure. The behaviour of the different ways LVB could be used needs further research and set of mechanical data need to be established for each system design as described in the panelised design later in this report. In terms of a general comparison of mechanical properties of LVB and other widely used timber sheet materials, please see table below:

Table 1 Comparison of mechanical data sheets for LVB, OSB and Plywood. Comparison of mechanical data for OSB, American Plywood, Swedish Plywood and Laminated Veneer Bamboo panels

Structural characteristics		Laminated Veneer Bamboo (LVB)	6–10 mm OSB	10–18 mm OSB	18–25 mm OSB	12.5 mm American plywood	21 mm American plywood	21 mm Swedish plywood	25 mm Swedish plywood
Flexural strength (Parallel to span)	N/mm ²	28.406	18	16.4	14.78	23.5	14.8	23	21.6
Perpendicular to span	N/mm ²		9	8.2	7.4	12.2	10.1	11.4	12.4
Shear strength (as racking)	N/mm ²	20.002	6.8	6.8	6.8	3.2	3.2	2.9	2.9
As floor decking	N/mm ²		1	1	1	0.9	0.9	0.9	0.9
Tensile strength (Parallel to Grain)	N/mm ²	147.996	9.9	9.4	7	13.6	10.5	15	15.4
Perpendicular to Grain	N/mm ²	3.744	7.2	9	6.8	7.2	6.9	12	11.4
Compressive strength parallel to grain	N/mm ²	92.966	15.9	15.4	12.7	15.9	10.6	15	15.4
Perpendicular to Grain	N/mm ²	20.98	12.9	14.8	12.4	8.1	7.7	12	11.4
Modulus of elasticity	N/mm ²	26,000							
Bending parallel to span	N/mm ²		4930	4930	4930	10,300	7800	9200	8700
Bending perpendicular to span	N/mm ²		1980	1980	1980	2050	2050	4600	5000
Tension and compression parallel to span	N/mm ²		3800	3800	3800	6800	5200	7200	7400
Tension and compression Perpendicular to span	N/mm ²		3000	3000	3000	4600	3900	4800	4600

Table 2 Description of life cycle stages

Profile Type	Life cycle stages included	Study units	Use for comparison	Responsible party
Cradle to gate	Production stage (raw material supply, transport and manufacturing of products and all upstream processes from cradle to gate)	Information module: Per tonne	Shall not be used for comparison	In-factory (gate to gate) data collected by manufacturer Per-factory data for raw materials provided by BRE Certification Ltd
Cradle to site	Production stage (raw material supply, transport, and manufacturing of products and all upstream processes from cradle to gate. Construction process stage (transport to the building site and wastage from building installation/construction only) including transport and disposal of waste.	Information module: Per meter ² installed element	Shall not be used for comparison	As above and Construction process data provided by BRE Certification Ltd
Cradle to grave	As above and Use stage: Repair, replacement, maintenance and refurbishment including transport of any materials and disposal of waste over the 60-year period. Demolition: is expected to occur at any time at or after the end of the study period and it includes transport and disposal of waste.	Functional Unit: Per square meter installed element over a sixty-year period in the building	Can be used for comparison if the functional unit is equivalent	As above and Life time data by BRE Certification Ltd

Note: ISO, 2013. 'ISO 14040:2006 – Environmental management – Life cycle assessment – Principles and framework'.

Life Cycle Analysis: A Review

Life cycle assessment (LCA) is an internationally recognised method for assessing the potential environmental impact of a certain material or process for its entire life cycle (Cradle to Grave/Cradle) or part of that life cycle (Cradle to Gate). A life cycle assessment is completed, by:

- Compiling an inventory of relevant energy and material inputs and environmental releases,
- Evaluating the potential environmental impacts associated with identified inputs and releases,
- Interpreting the results to help you make a more informed decision (US EPA, O., Sustainable Technology Division, 2012).

Life Cycle assessments are broken down into different profile types. These profile types are shown in Table 2 on the following page. These profile types define the parameters and extents of a life cycle study or system boundary.

There are four phases in an LCA study:

- The goal and scope definition phase,
- The inventory analysis phase,
- The impact assessment phase, and
- The interpretation phase.

Cradle to Cradle

Cradle to cradle design is a biomimetic approach to the design of products and systems. It models the human industry on nature's processes viewing materials as nutrients circulating in healthy, safe metabolisms (Braungart and McDonough, 2008).

In relation to the subject here a cradle to grave profile will be selected for the ability to compare different design/material options. The materials in question will be bamboo as it is manufactured into usable building products and timber as it is manufactured into usable building products. These building products will then be applied to an architectural design and building method and eventually be evaluated at the end of life phase. The stages of the life cycle that will be assessed are as follows:

- Raw material extraction,
- Product manufacture (Laminated Veneer bamboo) and associated emissions,
- Building Applications,
- End of life and associated emissions.

Transportation

Transportation of goods and its environmental impact is far beyond the scope of this research yet has a big impact on the life cycle of a material or product. In relation to sourcing bamboo from Vietnam or China a large quantity of the CO₂ emissions and overall environmental impact will be caused by the burning of fossil fuels in the transportation of the material to Europe from these areas of the world.

In the study by Van der Lugt et al this is the second highest contributor to eco-cost (28%–37%) and carbon footprint (15%–25%) depending on the material which is transported. Unavoidable for the European context, it is suggested that bamboo could be sourced closer to the location of use in areas such as Ethiopia or Central Africa reducing the effect of transportation by sea freight to Europe.

Local transportation contributes to approx. 10% of the eco-burden (Vogtlander and van der Lugt, 2014).

This figure, whatever it may be, will be constant and unavoidable and will likely contribute negatively towards the overall GWP of LVB and hence its integration into designs and buildings in Europe. In another study conducted at Delft University, Netherlands, by Vogtlander et al. (2010) transportation of bamboo poles from Shanghai harbour to Rotterdam harbour in the Netherlands contributed to 89% of total emissions (Vogtlander et al., 2010; van der Lugt et al., 2012).

In this study Vogtlander et al. (2012) measured emissions in terms of eco-cost. The eco-cost of a material is a measure to express the amount of environmental burden a product or system has. It is represented in terms of Euros per kilogram (€/Kg) and in simple terms is the amount of money that would need to be invested in renewable technologies or environmental strategies to mitigate the CO₂ emissions of the material tested.

The results from the report by Vogtlander et al. (2012) can be seen in Table 3 below.

The eco-cost of shipping equated to 25% of the total environmental burden of 3-layer plybamboo. Adding this to the other transportation steps in the process that equate to 20.4% the total contribution is 45.4%. This highlights that the carbon emissions due to transportation are still a major contributor to the overall global warming potential of bamboo products.

Table 3 Transportation Environmental impact (Eco-Cost)

Environmental impact assessment of carbonized 3-layer Plybamboo board

<i>Process step</i>	<i>Amount</i>	<i>Unit</i>	<i>Eco-cost (€/unit)</i>	<i>Eco-cost (€)/ Functional unit</i>	<i>Eco-cost (€)/kg</i>
Transport from plantation to strip manufacturing facility; Eco-costs of a 5-ton truck (transport of 92.4 FUs)	30	Km	0.243/km per 5 ton truck	0.316	0.0075
Transport from strip manufacturing facility to factory; Eco-costs of a 10-ton truck (transport of 310.4 FUs)	600	Km	0.32/km per 10 ton truck	2.474	0.059
Transport from factory to harbour; Eco-costs of a (28-ton truck)	3.13	ton.km/FU	0.033/ton.km	0.1032	0.0099
Transport from harbour to harbour; Eco-costs (20 ft container in a trans-oceanic freight ship)	200.24	ton.km/FU	0.0052/ton.km	1.0413	0.0999
Transport from harbour to warehouse; Eco-costs (28-ton truck)	1.2	ton.km/FU	0.033/ton.km	0.0396	0.0038

Note: Vogtlander, J.G., van der Lugt, P., 2014. The environmental impact of industrial bamboo products: Life cycle assessment and carbon sequestration, INBAR.



Fig. 2 Case study: Stadthaus, Murray Grove, London.

However, newer more efficient proposals for transporting goods, in particular one for a 'New Silk Road' Railway from 'east to west China, routed through Kazakhstan, Russia, Belarus, Poland, Germany, France and finally to Spain' (Dispatch, 2014) present an interesting argument that if transportation of goods becomes more efficient and produces less pollution then the overall contribution of the transportation stage to carbon footprint can be reduced. This efficient manner of acquiring goods will have a beneficial effect on the time frame of a project resulting in better, cheaper more efficient building projects and potentially lower carbon emissions. However, this area requires further specialised research.

Primary Research

Case Study (Stadthaus, Murray Grove)

Completed in 2009, the multi award winning, Stadthaus at Murray Grove is a nine story residential building located in Hackney, just north of the city of London. Consisting of both private and affordable apartments it is, according to the cross laminated timber company KLH, the "pioneer of timber residential tower buildings in the world" (KLH, 2015) (Figs. 2–4). The entire structure comprises of 29 apartments.

The entire tower is constructed using a series of Cross Laminated Timber panels produced by KLH which "form a cellular structure of timber load bearing walls" and "timber floor slabs" (KLH, 2015).

Stadthaus is currently one of the tallest habitable residential timber buildings in the world. Through the selection of timber as the primary construction material the design team were able to reduce the carbon footprint of the building in a number of ways.

"The designers calculated that had the building been of conventional reinforced concrete construction, it would have incurred an additional 124 tonnes of carbon generated during construction. Adding this to the 188 tonnes of carbon sequestered (locked away) (during the growth of the tree) in the 900 m³ of timber in the structure results in a total offset of some 310 tonnes of carbon" (TRADA, 2009). This offset allowed for the planning authority to grant a dispensation from the 'Merton' rule which usually requires that 10% of the energy for the building and its occupants be generated on-site using renewable energy equipment (Merton, 2015) (This rule has since been superseded by new amendments to the building regulations under Part L.).

Furthermore, the speed of construction using this method of cross laminated timber is also worthy to note with regards to the installation cost and emission caused during this phase as part of the life cycle assessment of the building. The entire super structure was erected within 27 working days. The entire building programme for the CLT build was 49 weeks, 7 weeks of which were for the erection of the CLT superstructure, 23 weeks shorter than if an equivalent concrete building had been constructed (KLH, 2015). This rapid building process again results in a positive outcome when it comes to the energy and carbon emissions associated with building construction.

Development of Panelised Building System

For the purposes of this research a standardised panel system has been developed to compete with cross laminated timber (CLT) panels. The initial panel system as seen in the images (Figs. 5 and 6) below utilised laminated veneer bamboo (LVB) ply sheets in an efficient manner to exploit the structural characteristics of LVB ply. This system was designed to be a series of interlocking pieces which could be efficiently cut using CNC and assembled either on site or in factory controlled setting and then transported to site fully assembled. Panels are glued and screwed to ensure a strong connection is made between each of the elements.

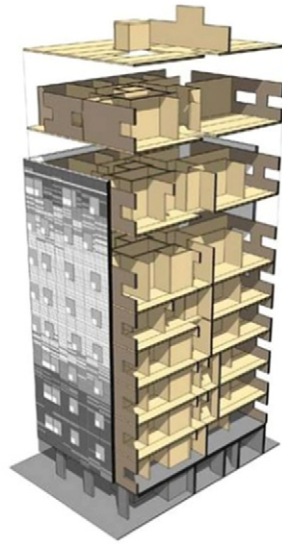


Fig. 3 3D Cross section of Stadthaus. Reproduced from KLH, 2015. KLH: Stadthaus, Murray Grove. Available at: <http://www.klhuk.com/portfolio/residential/stadthaus,-murray-grove.aspx> (accessed 31.07.2015).



Fig. 4 Internal view of CLT construction at Stadthaus. Reproduced from KLH, 2015. KLH: Stadthaus, Murray Grove. Available at: <http://www.klhuk.com/portfolio/residential/stadthaus,-murray-grove.aspx> (accessed 31.07.15).

Each panel comprises of two full 2440 mm × 1220 mm sheets (A) with studs or 'ribs' (B & C) placed at regular intervals in between the two sheets. Each panel was designed to efficiently use a 2440 mm × 1220 mm sheet. **Figs. 7** and **8** below show the cutting setup for each sheet that is required to assemble a single panel. **Table 4** shows a breakdown of the parts required.

Based on the comments by the specialist advisor and engineer, John Lauder, changes were made to the design of the panels. The changes are listed below:

- Panels are now designed without joints. Comments were made suggesting that the joints were not particularly necessary to ensure a connection between elements.
- The thickness of the studs or 'ribs' was increased from 12 mm to 24 mm. This was done to ensure there was no cracking or damage to the stud as the screw connection is made. Panels are now designed with pilot holes for screws and changes have been made to the thickness of the studs.
- Suggestions were also made to include a certain amount of bridging between the studs to minimise the potential buckling effect and provide the panel with extra rigidity.
- Completely enclose panel system with a footing piece and top capping piece. These like the studs will be 24 mm thick and 1220 mm long to fully enclose the panel. By placing a capping piece and a footing the overall height of the panel is increased to 2488 mm (2440 mm + 24 mm top and bottom).

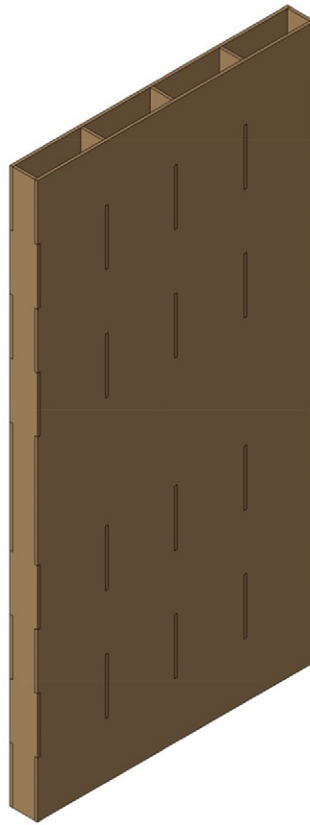


Fig. 5 First design – Laminated veneer bamboo Panel System. Reproduced from KLH, 2015. KLH: Stadthaus, Murray Grove. Available at: <http://www.klhuk.com/portfolio/residential/stadthaus,-murray-grove.aspx> (accessed 31.07.15).

- The main face sheets (A) remain at 12 mm thick.
- Comments were also made that panels should not be restricted to a height of 2440 mm.

The revised panel designs much like the first concepts are each made up of two full 2440×1220 sheets with studs or 'ribs' placed at regular intervals in between the two sheets. The panel has a $1220 \times 120 \times 24$ mm footing at the base and is capped with a similar head piece to completely enclose the panel. The images (Figs. 9 and 10) below show the parts required to assemble the panel system.

The requirements for each one of the panels can be seen in Table 5 below:

Construction Details

Some typical construction details utilising the panelised system have been designed and can be seen in Figs. 11 and 12 below.

Primary Life Cycle Analysis

Scope

The scope of this study is to determine the global warming potential, through life cycle analysis, of laminated veneer bamboo diaphragm construction panels against that of cross laminated timber panels for use in high density high-rise residential accommodation.

Definition of Goal/Product System

As stated previously the main goal of this study is to determine the global warming potential of laminated veneer bamboo diaphragm construction panels over the selection of cross laminated timber panels. The following report is set up to the standards set out in ISO 14040 and the LCID handbook.

Using the Stadthaus at Murray Grove case study for high density high-rise residential accommodation, laminated veneer bamboo diaphragm (LVBD) panels have been substituted as an alternative to Cross Laminated Timber (CLT) panels (see design details and concept design from previous section). The product system to be studied, as mentioned in the goal of the LCA, is an

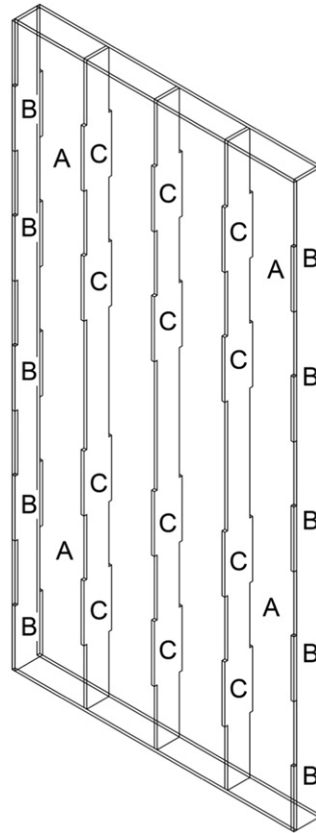


Fig. 6 First design – Laminated veneer bamboo Panel System (Wireframe).

application of LVBD Panels through a Cradle to Grave life cycle. The study will compare the application of LVB Panels to the current CLT option that has been utilised in Stadthaus, Murray Grove.

The life cycle testing is conducted on a full building model. As per the benchmark test conducted previously the testing is undertaken using an application, Tally[®], in conjunction with Autodesk Revit[®]. This application utilises reliable life cycle databases set up by PE international (now 'thinkstep'). Thinkstep is a provider of "the most comprehensive source of sustainability data in the world" with "72,000+ constantly evolving datasets compiled over 20 years" (Thinkstep, 2015). It provides the world's most up to date and reliable LCA data. The reason for selecting this platform to conduct the LCA was that it could be easily used in conjunction with a Revit[®]. By utilising skills in Revit the LCA application could easily take modelled materials and volumes from the Revit Families created for the projects and life cycle data could easily be applied to them in Tally[®]. Other applications like Gabi and Ecoinvent were explored and could have been used to conduct this study. However, the simplicity and ease of use of Tally[®] in Revit[®] was the reasoning behind its selection.

Functional Unit and Reference Flow

The functional unit is a measure of the function of the studied system and it provides a reference to which the inputs and outputs can be related. This enables the comparison of two essentially different systems (ISO, 2013).

The functional unit of the analysis is the usable floor space of the building under study.

The reference flow is the amount of material required to produce a building, designed according to the given goal and scope of the assessment, over the full life of the building. It is the responsibility of the modeller to assure that reference buildings or design options are functionally equivalent in terms of scope, size and relevant performance. The expected life of the building has a value of 50 years as manually specified by the modeller (Tally, 2015).

The System Boundary and Delimitations

The system boundary of LVB begins with the extraction of bamboo and ends with the disposal of the material at the end of its life cycle (*Cradle to Grave*). This system is depicted in graphical format in Fig. 13.

The manufacturing process includes all necessary life cycle data for the *cradle to gate* life cycle stages associated with the specific materials in the LVB and CLT design options.

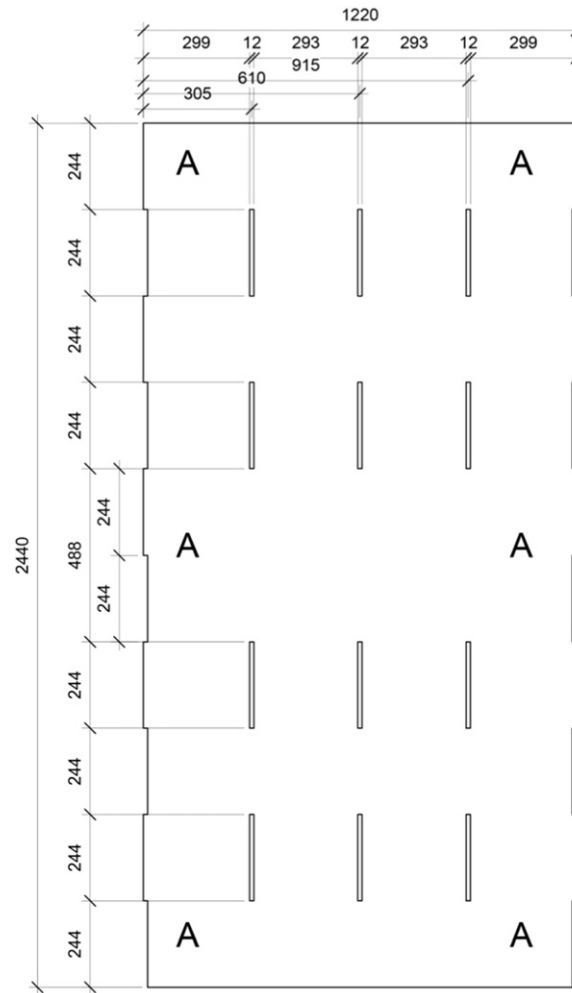


Fig. 7 Sheet A – First design panel concept.

The life cycle analysis (LCA) accounts for the full cradle-to-grave life cycle of the design options studied, including

- Material manufacturing,
- Maintenance and replacement, and eventual,
- End-of-life (disposal, incineration, and/or recycling), including the materials and energy used across all life cycle stages.

Architectural materials and assemblies include all materials required for the product's manufacturing and use (including hardware, sealants, adhesives, coatings, and finishing etc.) up to a 1% cut-off factor by mass with the exception of known materials that have high environmental impacts at low levels. In these cases, a 1% cut-off was implemented by impact.

Manufacturing includes cradle-to-gate manufacturing wherever possible. This includes

- Raw material extraction and processing,
- Intermediate transportation, and
- Final manufacturing and assembly.

Due to data limitations, however, some manufacturing steps have been excluded, such as the material and energy requirements for assembling doors and windows. The manufacturing scope is listed for each entry, detailing any specific inclusions or exclusions that fall outside of the cradle-to-gate scope.

Transportation of upstream raw materials or intermediate products to final manufacturing is generally included in the GaBi datasets utilised within this tool. *Transportation requirements between the manufacturer and installation of the product, and at the end-of-life of the product, are excluded from this study.* However, the eco-cost of transportation had been evaluated previously in a benchmark test conducted as part of the overall study. It is noted within the benchmark test, bamboo is specified to be sourced from China to an unknown final destination and this may result in further discrepancies between the results. CLT does not specify a source destination or a final destination. For this reason transportation is again highlighted as an unknown quantity.

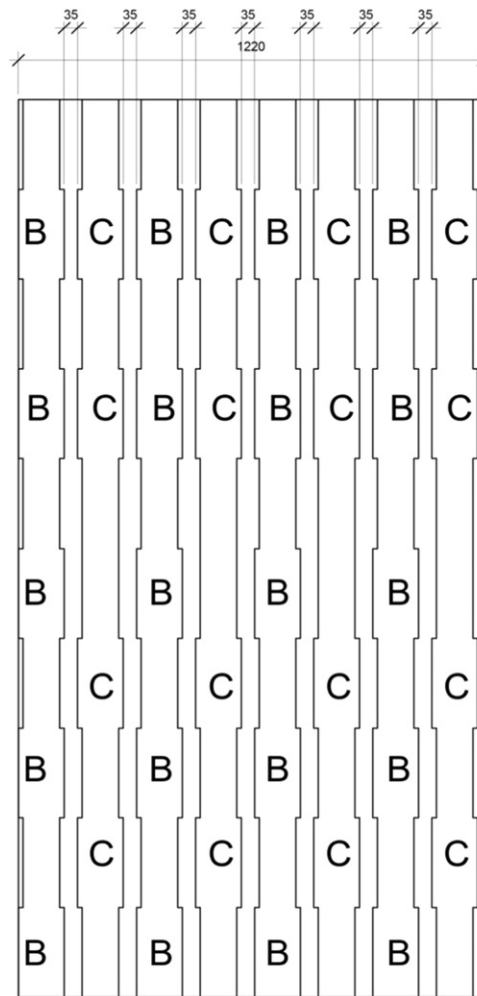


Fig. 8 Sheet B & C – First design panel concept.

Table 4 Initial panel design parts breakdown

<i>Criteria</i>	<i>Part A</i>	<i>Part B</i>	<i>Part C</i>
Number required per panel	2	2	3
Number of piece available per single 2440×1220 sheet	1	4	4

The data associated for transportation is an industry standard, an average. The data accounts for the average eco-cost and environmental burden for transportation of raw material to a product manufacturing site. The transportation from manufacturer to building site is not accounted for within the system boundary.

Infrastructure (buildings and machinery) required for the manufacturing and assembly of building materials, as well as packaging materials, are not included and are considered outside the scope of assessment.

Maintenance and replacement encompasses the replacement of materials in accordance with the expected service life. This includes;

- The end-of-life treatment of the existing products and,
- Cradle-to-gate manufacturing of the replacement products.

The service life is specified separately for each product.

End-of-life treatment is based on average US construction and demolition waste treatment methods and rates. This includes

- The relevant material collection rates for recycling,
- Processing requirements for recycled materials,
- Incineration rates, and
- Landfilling rates.

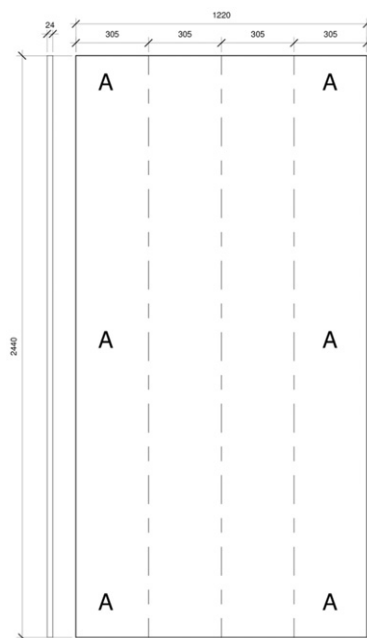


Fig. 9 Sheet A LVB panel system.

Along with processing requirements, the recycling of materials is modelled using an avoided burden approach, where the burden of primary material production is allocated to the subsequent life cycle based on the quantity of recovered secondary material. Incineration of materials includes credit for average US energy recovery rates. The impacts associated with landfilling are based on average material properties, such as plastic waste, biodegradable waste, or inert material. Specific end-of-life scenarios are detailed for each entry (Tally, 2015). Being a US company that develops the LCA tool European methods and rates were not available within the package. Thus, US rates were applied to the life cycle study.

Procedure

The following is an outline of the procedure undertaken to conduct the life cycle test. It includes the process of completing the Revit® Model and its subsequent use with Tally® life cycle software. The materials and definitions will also be outlined in this article and all assumptions and associated life cycle data will be clearly defined.

In order to conduct a life cycle with Tally® a 3D Revit® model must first be constructed and the modelled data and information extracted. Due to the convenience of using the two programmes together all data can be easily shared between the two. Data extracted from the Revit model to Tally includes:

- Materials
- Quantities
- Volumes
- Areas
- Weight

The entire model was built using simple components (Families) also designed and modelled within Revit®. For a full description of the procedure for the panel design can be found in the concept/design chapter (Section 5.0). A full list of these families can be viewed in the LCA report exported from Tally® in the appendix.

Using a similar process as the benchmark test two design options were modelled in parallel. Option A was constructed with laminated veneer bamboo (LVB) as the primary structural material while in Option B cross laminated timber (CLT) was designated as the primary structural material. These two models are depicted in Figs. 14 and 15 below.

It is of the utmost importance that the Revit® model is built with careful consideration as all values and quantities depend on the accuracy of the modelled elements.

The model of Stadthaus, Murray Grove, was constructed using a planning file submitted to Hackney council. (Planning application no. 2007/0988) Contact was made with Waugh Thistleton Architects to seek permission and information on the building. Though no additional information was received, an interest in the project was stated from the correspondence.

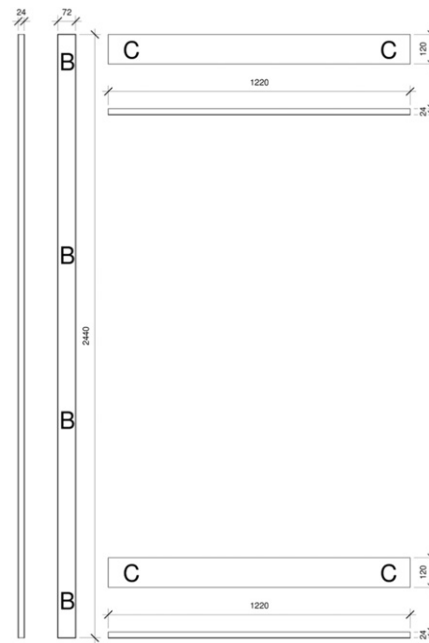


Fig. 10 Stud/Ribs (B) and top cap and footing (C).

The following outlines the elements included and those excluded from the Revit[®] model:

- For the purposes of this study *only the primary structural elements* were modelled. No secondary elements or finishes were applied to the model to ensure consistency. There is a large proportion of the as-built building not included in these models as this is a study on the structural building elements. And for that reason a portion of the overall impact of the overall building is not measured. *Only the structural elements were being tested in this LCA. Any other elements included are listed below.*
- No windows have been included in the model. However, openings have been included in the panels based on the elevations of the existing planning drawings.
- Curtain wall glazing has been included at the ground floor and at balconies.
- Internal doors have been included. Some doors have been placed in the model as independent elements and will show up in the LCA report as independent elements. LVB or CLT panels have been modelled to include doors and have been labelled appropriately in the report to show this. Doors have been modelled identically in both the LVBD and CLT design options. The doors were included in the model in order to ensure the volume of material in the door panel be it LVB or CLT was correct. This same principle applies to the openings cut in the window panel types.
- In both the LVB and CLT design options:
 - Wall panel thickness=128 mm,
 - Floor Thickness=146 mm,
 - Lift core wall thickness=300 mm (mass CLT or Mass bamboo in the bamboo options),
 - Stair core wall thickness=300 mm (mass CLT or Mass bamboo in the bamboo options),
 - Roof thickness=200 mm.

Impact Categories

The impact category under study in this LCA is Global Warming Potential (GWP). The global warming potential of a gas refers to the total contribution to global warming resulting from the emission of one unit of that gas relative to one unit of the reference gas, carbon dioxide, which is assigned a value of 1. This may also be commonly expressed as the 'Carbon footprint' of a material, product or unit output (US EPA, C. C. D, 2001).

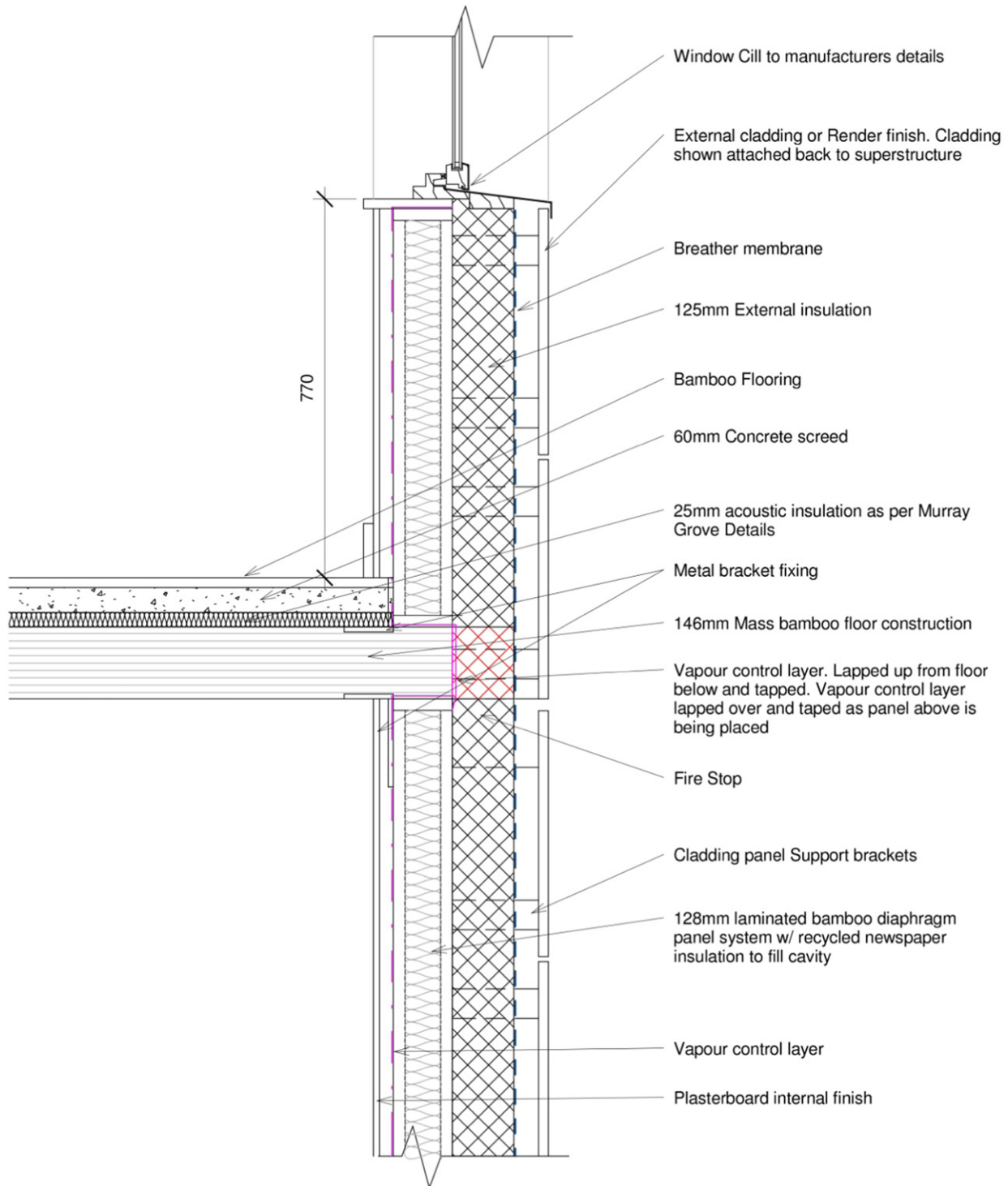
The GWP of a gas or substance depends on the timespan or what is more commonly known as the time horizon. Since GWP is measured over a prescribed period of time, in this instance 50 years, gases may be removed from the atmosphere at a fast rate thus initially having a large effect but, over prolonged time periods, as it diminishes, it becomes less important.

For instance, as can be seen in table 56 below taking carbon dioxide CO₂ as a reference value and assigning it a value of 1, methane is assigned a GWP of 56 over 20 years. However, this drops to 21 over 100 years. The same applies to nitrous oxide N₂O starting at a value of 280 over 20 years but increasing to 310 over 100 years before decreasing again to 170 over 500 years. See Table 6 below.

A full list of gases and substance and their specific contributions to GWP can be found in the appendix (U.N, 2015).

Table 5 Revised panel system parts breakdown

Criteria	Part A	Part B	Part C
Number required per panel	2	5	2
Number of piece available per single 2440 × 1220 sheet	1	9	18


Fig. 11 Construction detail A (not to scale) (Window Cill & Mid floor Junction) for LVB Panel system.

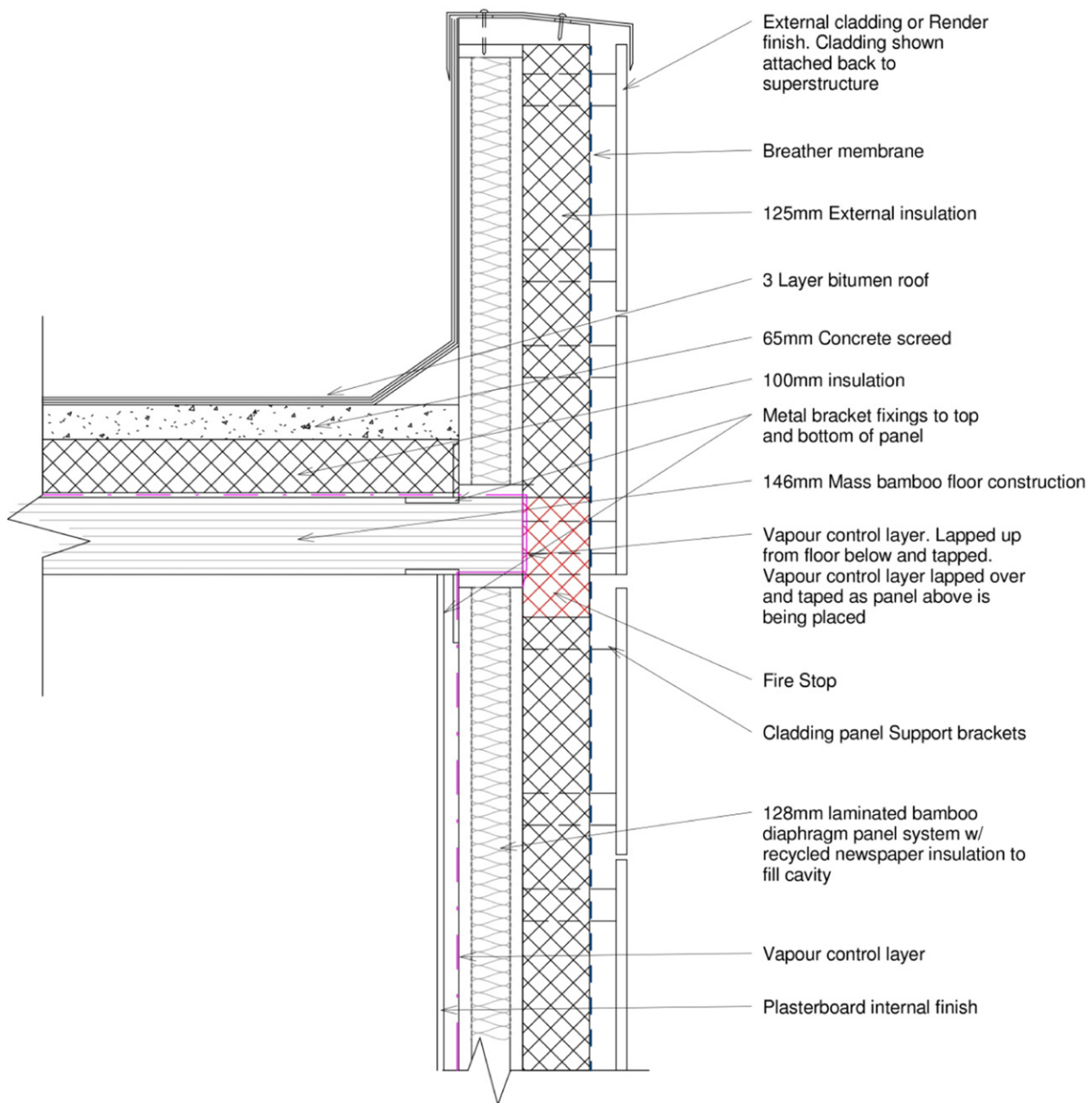


Fig. 12 Construction detail B (Not to Scale) (Parapet) for LVB panel system.

Life Cycle Impact Assessment

The life cycle impact assessment (LCIA) phase defines links between the life cycle inventory results and the potential environmental impacts (Puettmann, 2013). Fig. 16 below is a graphic representation of the LCIA impact categories of the project. Highlighted in red is the Global Warming Potential. This image also shows a comparison in the values associated to CLT and LVB in relation to an LCA not under consideration in this research. They include:

- Acidification potential,
- Eutrophication potential,
- Ozone depletion,
- Smog formation potential,
- Energy demand,
- Renewable and non-renewable energy.

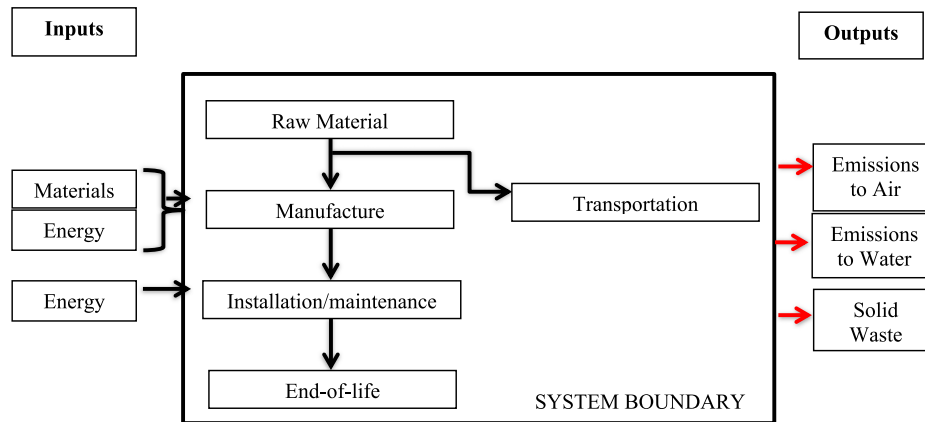


Fig. 13 System Boundary for life cycle assessment.



Fig. 14 Cross laminated timber Design Option.

Table 14 presents the environmental impact of the two design options based on the case study model of Stadthaus, Murray Grove. The values found in Table 7 are the total cumulative effect of all the process associated in implementing LVB or CLT. These associated impacts include:

- Forestry or bamboo plantation management,
- Bulk commodity transportation,
- Manufacture of products and all upstream process (energy required at manufacturing plant, glues, finishing, etc.),
- End of life impacts.

Interesting to note is the higher values for the *sum of smog formation potential total* and the *sum of non-renewable energy demand total* in the bamboo LVB diaphragm box build. As part of the total primary energy demand also presented in the LCA results shown a section of that energy demand is deemed nonreplicable or replaced at a very slow rate by natural means (Jolliet, 2016). This non-renewable energy usually comes in the form of fossil fuels where in most cases energy dissipates in the form of unusable heat. As previously discussed, action could be taken to assign an eco-cost to all materials to reinvest in renewable resources to combat this issue. However, in the current situation it is noted as a factor against the use of engineered bamboo, a factor which is 41% for the bamboo LVB option compared to 27% for the CLT option. However, to counter this issue the overall primary energy demand of 8,296,976 MJ is circa 16% lower than the 9,798,998 MJ used in the CLT option. Similarly the sum of renewable energy demand is 58% of the total energy demand compared to circa 72% in the CLT option.

Also worth noting is the sum of smog formation potential. The bamboo LVB option contributes 33% more to this compared to the CLT option in this instance. Considering the effects that this can have on human health it is an issue that must be considered and

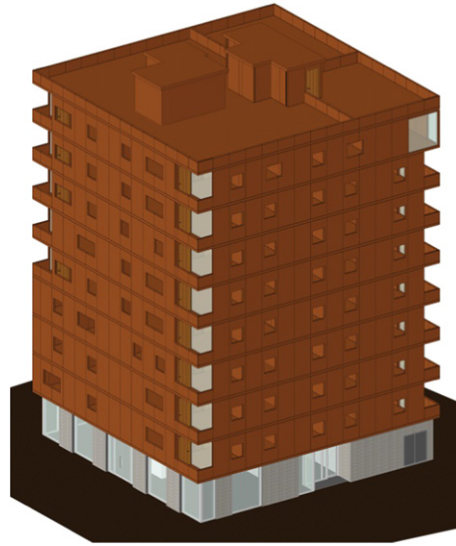


Fig. 15 Laminated veneer bamboo Design Option. Figures 14/15 above show 3D view of Revit® models created for Stadthaus, Murray Grove. These two models are identical in nature and size with the obvious difference in structural material and building method (i.e., Solid CLT or diaphragm panel where stated).

explored fully. Further research needs to be conducted on these areas to assess the differences between the two systems and their overall impact. As stated previously for this study, the global warming potential will be the main area of focus.

The entry source data or the data that was used to conduct the LCA can be seen below. The entry source data is provided by Thinkstep (formally PE International) within the Tally® application. For this LCA the data can be seen for each design option on the page over.

Bamboo diaphragm system

CN: Bamboo (estimation) PE (2012)

GLO: Bulk commodity carrier PE (2012)

US: Heavy fuel oil at refinery (0.3 wt% 0.3 wt% S) PE (2010)

CN: Electricity grid mix PE (2010)

DE: Phenol formaldehyde resin PE (2012)

Cross laminated timber

US: Laminated veneer lumber, at plant, US PNW USLCI/PE (2009)

US: Laminated veneer lumber, at plant, US SE USLCI/PE (2009)

Based on the identical designs and Tally® data input of Stadthaus at Murray Grove using cross laminated timber (CLT) and a laminated veneer bamboo (LVB) alternative, the results show that utilising a engineered bamboo diaphragm panel will result in a lower overall GWP. The LVB option out performs the CLT option by 33% or 207,975 kgCO₂eq. This lower GWP is based on the assumption that the LVB diaphragm panel system is structurally adequate to support the loading in a high rise construction. However, a range of values will be presented at the end of this should the diaphragm system not perform adequately.

Bamboo diaphragm system – 412,010 kgCO₂eq

Cross Laminated Timber – 619,985 kgCO₂eq

The Bamboo LVB diaphragm option out performs the cross laminated timber option in all three of the life cycle stages calculated as part of this study. See [Table 8](#) on the page over.

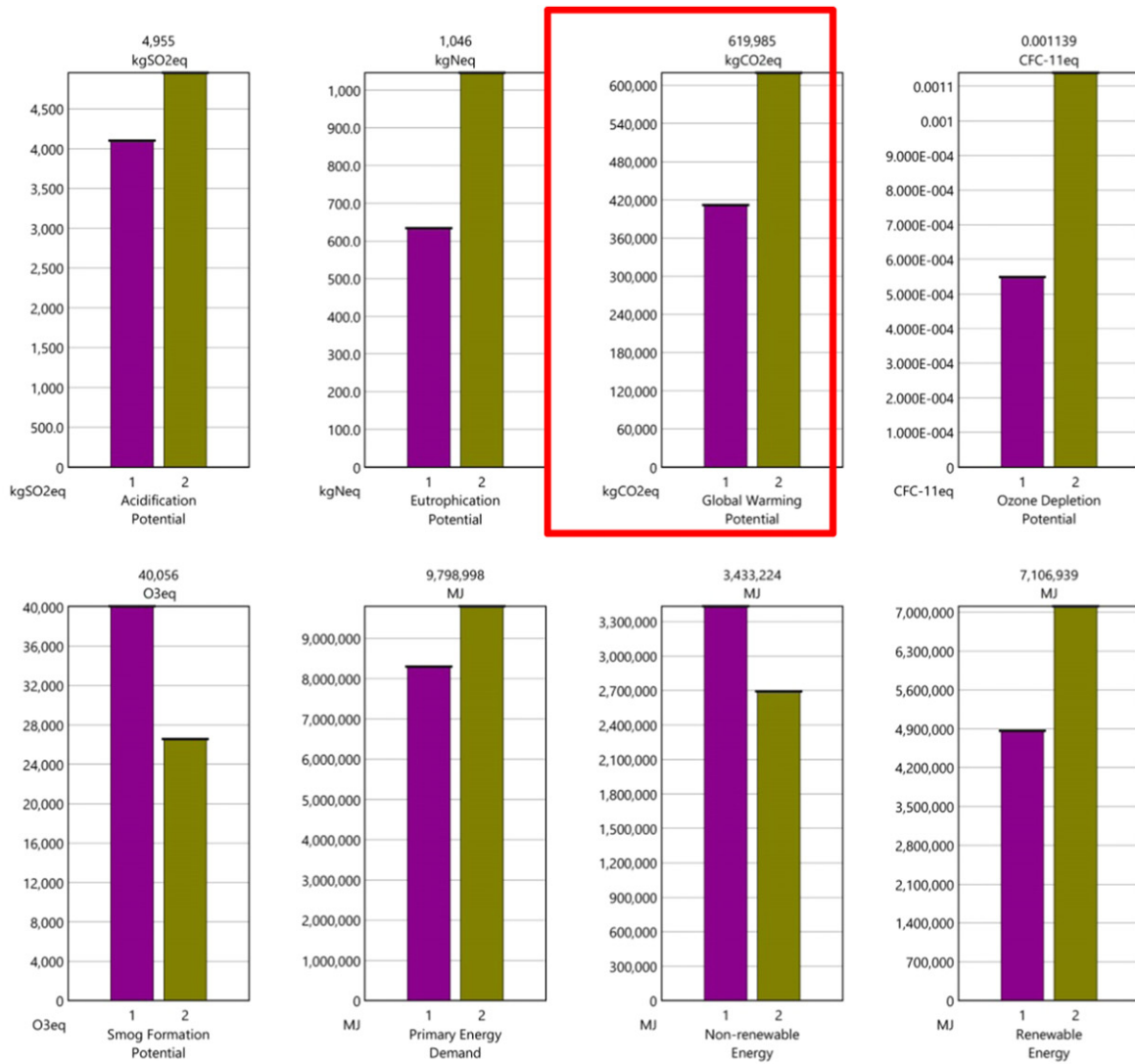
These three stages are:

- (1) The manufacturing stage; which includes the LCA data associated to all aspects of a *cradle to gate* LCA e.g., raw material acquisition, average transportation values of raw material to factory and all stages of the manufacture of the product/material.
- (2) The maintenance and replacement stage; which includes all environmental impact of constructing and maintaining the material over a 50-year period (the period of time defined within the Tally® application)
- (3) The end of life stage; which in both instances:
 - 14.5% recovered (credited as avoided burden),
 - 22% incinerated with energy recovery,
 - 63.5% landfilled (wood product waste) ([Tally, 2015](#)).

Table 6 Global warming potential of different gases

Species	Chemical formula	Lifetime (years)	Global warming Potential (Time horizon)		
			20 years	100 years	500 years
CO ₂	CO ₂	variable §	1	1	1
Methane *	CH ₄	12 ± 3	56	21	6.5
Nitrous oxide	N ₂ O	120	280	310	170

Note: U.N., 2015. 'The science of climate change: Summary for policy-makers and technical summary of the working group 1 report', p. 22.



Legend

Design Options

- Bamboo LVB Hybrid Box (primary)
- Cross Laminated Timber

Fig. 16 Comparison of impact categories for LVB and CLT Design options 12 mm sheetsx128 mm depth (Generated from Tally Application as a result of specification of materials).

Table 7 Environmental impact of laminated veneer bamboo and cross laminated timber design options 12 mm sheets × 128 mm depth

Impact category	Bamboo LVB diaphragm box (primary)	Cross laminated timber
Sum of mass total (kg)	328,341	575,986
Sum of acidification potential total (kgSO ₂ eq)	4,103	4,955
Sum of eutrophication potential total (kgNeq)	634	1,046
Sum of global warming potential total (kgCO ₂ eq)	412,010	619,985
Sum of ozone depletion potential total (CFC-11eq)	0.0005	0.0011
Sum of smog formation potential total (kgO ₃ eq)	40,056	26,588
Sum of primary energy demand total (MJ)	8,296,976	9,798,998
Sum of non-renewable energy demand total (MJ)	3,433,224	2,692,059
Sum of renewable energy demand total (MJ)	4,863,753	7,106,939

Advancing on these initial results and to further compare the selection of laminated veneer bamboo a series of further models and LCA tests were conducted on different configurations of panels. These models were created based on feedback regarding the structural capabilities of the LVB system from advisor John Lauder and ARUP engineers. These models were designed with the following materials and configurations:

- (1) 24 mm thick LVB sheets used to create a typical panel size of 1220 mm × 2440 mm × 128 mm with bridging supports at c.400 mm. (Variations were modelled for windows and doors but followed a similar design with the area for windows and doors removed). This was tested against the Murray Grove CLT option also with 128 mm depth panels.
- (2) 24 mm thick *plywood* sheets used to create a typical panel size of 1220 mm × 2440 mm × 128 mm with bridging supports at c.400 mm. (Variations were modelled for windows and doors but followed a similar design with the area for windows and doors removed). This was tested against a mass bamboo solid panel option of the Murray Grove also with 128 mm depth panels.
- (3) Finally a hybrid option of *Mass bamboo solid panels* with 128 mm depth were placed on floors 1–5 and the *LVB diaphragm* panels place on the remaining 3 levels floor 6–9. This was tested against the Murray Grove CLT option also with 128 mm depth panels. This model was constructed based on feedback from ARUP engineers on the most likely outcome based on the limited knowledge of the structural capacity of the panels.

The results of these tests showed that:

- The global warming potential of the 128 mm plywood diaphragm panel with 24 mm sheets was lower than a solid laminated veneer bamboo panel. This is due to the reduction of material used in this system. A margin of 23% or approximately 136,368 kgCO₂e is seen in the plywood diaphragm panel system against that of the solid laminated veneer bamboo panel system.
- The margin is marginally greater as seen in the LVB diaphragm option when compared to CLT. A margin of 25% or 153,374 kgCO₂eq for the 128 mm depth laminated veneer bamboo diaphragm panel system with 24 mm sheets or 33% or 207,975 kgCO₂eq difference for the 128 mm depth laminated veneer bamboo diaphragm panel system with 12 mm sheets v's cross laminated timber panel system. In this case LVB comes out more favourably when compared to CLT.
- The 128 mm depth laminated veneer bamboo diaphragm panel system with 24 mm sheets design option still marginally outperforms the Plywood diaphragm design option by 2% or 9681 kgCO₂eq whereas the 128 mm depth using the 12 mm sheet outperforms the Plywood diaphragm design option by 13% or 64,282 kgCO₂eq.
- A similar result can be seen in the cross laminated timber and solid laminated bamboo design options. The mass LVB design option outperforms the CLT design option marginally by 2% or 7325 kg CO₂eq.
- Finally the Mass bamboo and 128 mm LVB diaphragm panel Hybrid building option (Mass LVB panels floor 1–5 & LVB panel floor 6–9) outperforms a CLT option by 25% or 88,171 kg CO₂eq.

The results in [Table 9](#) below show that, when compared to CLT, under the environmental conditions outlined at the beginning of the article, a laminated veneer bamboo alternative superstructure has the potential to compete with and surpass an engineered wood-based superstructure.

Furthermore, by implementing a more efficient use of materials which has been done in the LVB diaphragm design option GWP can be reduced by potentially 33% when compared to CLT.

Given the comparison of the options above highlighting that an LVB superstructure is marginally superior we can explore the implications of selecting a LVB option over a number of building projects in a year.

With the requirement for circa 20,000–30,000 new housing units required per year in Ireland this small margin, for even the worst case; 2% for Mass bamboo v CLT, would grow exponentially. In theory the more projects LVB is selected for the great the saving on GWP or kgCO₂e produced and outputted into the environment. This coupled with a managed plantation system and crop rotation for bamboo as well as an increase in FSC certified bamboo plantations as discussed previously (section 1.4),

Table 8 Comparison of Life Cycle Stages 12 mm × 128 mm depth

<i>Life cycle categories</i>	<i>Bamboo LVB diaphragm box (KgCO₂e)</i>	<i>Cross laminated timber (KgCO₂e)</i>
Manufacturing	193,412	287,985
Maintenance and Replacement	1,014	5,462
End of Life	217,582	326,538
Totals	522,751	723,743

Table 9 Global warming potential of 4 different building panel typologies for Stadthaus, Murray Grove, London

<i>Building construction type</i>	<i>Life cycle categories</i>			
	<i>End of life</i>	<i>Maintenance and replacement</i>	<i>Manufacturing</i>	<i>Totals</i>
128 mm bamboo LVB diaphragm box 12 mm sheets	217,582	1,015	19,341	412,010
128 mm bamboo LVB diaphragm box 24 mm sheets	247,601	1,015	217,995	466,611
128 mm plywood diaphragm box 24 mm sheets	271,758	1,015	203,520	476,292
Mass Bamboo and 128 mm LVB diaphragm panel	283,445	1,015	247,354	531,814
Hybrid option with 24 mm sheets				
128 mm mass solid laminated bamboo	298,338	5,462	308,860	612,660
128 mm cross laminated timber	326,538	5,462	287,985	619,985

means that a positive and more environmentally friendly approach to designing and building high rise residential buildings can be achieved.

A full breakdown of the life cycle impact of both the cross laminated timber and laminated veneer bamboo diaphragm design options can be found in the appendix.

Conclusions and Discussion

The aim of this research project was to establish, through a structural comparison review and comparative life cycle analysis (LCA), the overall contribution that laminated veneer bamboo (LVB) has to global warming potential against that of cross laminated timber (CLT). This study also set out to establish if engineered bamboo was a feasible alternative construction material to be used in high density urban housing. The following are the conclusions that can be drawn from the two major aspects of this research.

Structural Potential

It can be concluded from the structural assessment that engineered bamboo shows the potential to be implemented into mainstream construction typologies. The comparison of mechanical data supplied by Lamboo and SmartPly showed that LVB was a better performing material in all but one of the criteria. However, these values did come under some scrutiny and this shows that there is still a requirement to conduct full scale tests (as was intended as part of this research). Further research is needed to establish the mechanical properties of a panelised system. The panel system was designed and a lack of testing meant that some assumptions had to be made on its design and potential capabilities. Further research in this area should include:

- Manufacture panels (both solid and diaphragm panels) and conduct mechanical tests; compression, shear, tension and flexural on these full scale samples.
- Further research on how engineered bamboo should be implemented. Determine if a panelised system is the best application of engineered bamboo or if utilising bamboo in a post and beam system would be a better approach.
- Develop a set of building codes for use with engineered bamboo similar to those set up in *Eurocode 5: Design of Timber Structures*. By completing this it would ensure all standards and mechanical data is compiled for LVB structures and set up so as all buildings using this material are built safely and efficiently.

Environmental Assessment

This research reveals, through the environmental impact assessment of the case study model of Stadthaus at Murray Grove, London, and based on the criteria and system boundary set up for this study, engineered bamboo has a lower global warming

potential in relation to cross laminated timber. The following are the conclusions on the environmental impact of a bamboo panelised system:

If bamboo is implemented efficiently into a diaphragm panel system (128 mm depth) it can be up to 33% more efficient, in terms of kgCO₂e, than CLT.

If implemented into a solid panel system (128 mm depth) it can be up to 2% more efficient, in terms of kgCO₂e, than CLT.

If implemented into a hybrid system of a solid panel system (128 mm depth) and a diaphragm panel it can be up to 25% more efficient, in terms of kgCO₂e, than CLT.

It can be concluded that by implementing an engineered bamboo solution over a CLT solution on a similar building typology a reduction of between 2% and 33% can be achieved. Further research on the structural properties and capabilities of a panelised engineered bamboo building system may well reduce the percentage range presented. By first testing panel capabilities and then implementing the findings into the Revit model a more accurate set of data can be compiled.

Furthermore, the ability of bamboo to grow at a rapid rate of 3–5 years has major benefits on the environmental impact of harvesting it for construction purposes. With its ability to sequester larger amounts of CO₂ compared to timber, the results show that bamboo is a more favourable, environmentally friendly and sustainable material. With an increase in market share the values presented here will only continue to decrease in favour of bamboo. Additionally as previously suggested with the requirement for circa 20,000–30,000 new housing units required per annum in Ireland alone by implementing an LVB solution over a typical construction method the results could yield a major carbon footprint saving. The marginal difference between the LVB and CLT designs would grow exponentially for each project LVB is selected for. A similar observation, although not in relation to environmental impact, is made by De Flander and Rovers (2009) in their report previously discussed in the literature review that:

"If we compare this potential (of bamboo mainstream construction materials) with the construction market of The Netherlands for example, with a current number of around 60,000 new-built houses per year and with an estimated market share of timber-frame dwellings of about 5% (and growing), we could say that laminated bamboo frame houses could easily replace these 3000 timber-frame houses and/or even better, take over part of the other non-bio-based mainstream construction materials such as concrete and bricks" (De Flander and Rovers, 2009).

With a projected rise in population of 1.3–3.5 billion people by 2050, according to the UN, and the requirement to house the growing population a shift to more environmentally friendly, low GWP building materials needs to be considered in order to avoid further damage to the environment and a rise in global warming.

See also: Development of Epoxy Based Composites Using Bamboo and Waste Metal Chips

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A Comprehensive Study for 3D Printing of Rapid Tooling From Reinforced Waste Thermoplastics

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Introduction

Plastic Recycling

Plastics are used in a number of applications on a daily basis (Santibáñez *et al.*, 2007). Yet some plastic items end up in the waste stream after a single use only (single-life or cycle) or a short time after purchase, e.g., food packaging (Anastas and Zimmerman, 2006). Re-using plastic is preferable to recycling as it uses less energy and fewer resources (Allwood *et al.*, 2011). A number of techniques have been developed in order to separate and sort PSW (Beigbeder *et al.*, 2013). In the recycling industry, sorting and identification must be attempted within a short time to positively affect a recycler's finances (Schultz *et al.*, 1995). Further, plastic recycling can be classified as following:

- Primary recycling
- Secondary/Mechanical recycling
- Tertiary/Chemical recycling

Rapid Prototyping Technology

Rapid prototyping (RP) is the technology of making three dimensional (3D) models utilizing CAD models with minimum human intervention without any tooling requirement within reasonable time and cost (Mahindru and Mahendru, 2013). RP applications include the development of prototypes quickly within the time constraints (Pham and Gault, 1998). RP technology development leads to reduction in lead times for prototype manufacturing (Eppinger *et al.*, 1994). The major advantage of additive manufacturing (AM) processes is the manufacturing of intricate geometries in an efficient way (Rajurkar *et al.*, 1999). Other advantages of using AM technology include reduction in: total number of parts, mating and fitting problems, handling time and storage requirement (Liou, 2011).

RP is an additive manufacturing process of creating a solid part combining plastic layers (Levy *et al.*, 2003). Whereas, other machining processes like: milling, drilling, grinding etc. are subtractive processes of material removal from the solid piece (Zhu *et al.*, 2013). The additive nature of RP enables the easy production of intrinsic shapes with complex features (Peltola *et al.*, 2008). Wastage of material is highly controllable in this process. RP technology is highly preferred when limited quantity of pieces are required promptly in prototype manufacturing (Horn and Harrysson, 2012). RP has advantage in case of sub-assemblies as problem of fit and tolerance is highly decreased (Srikanth and Turner, 1990). RP technologies have numerous applications in various fields of medical sciences as well, as identified by various researchers in recent times (Cormier *et al.*, 2003; Bernard *et al.*, 2009). In mechanical engineering, RP technology is widely used in product development (Bernard *et al.*, 2009), die casting inserts (Baldwin, 1999), patterns and moulds manufacturing (Pal *et al.*, 2002), functionally graded material manufacturing (Jackson *et al.*, 1999; Dimitrov *et al.*, 2006) and making of end products (Hopkinson and Dickens, 2001; Santos *et al.*, 2006).

Various RP techniques are being used commercially (Schwarzenbach *et al.*, 2006). The basic principles of all RP techniques are almost same with some variation as per build material (Benardos and Vosniakos, 2003). The main steps involved in production of a part with RP techniques are shown in Fig. 1.

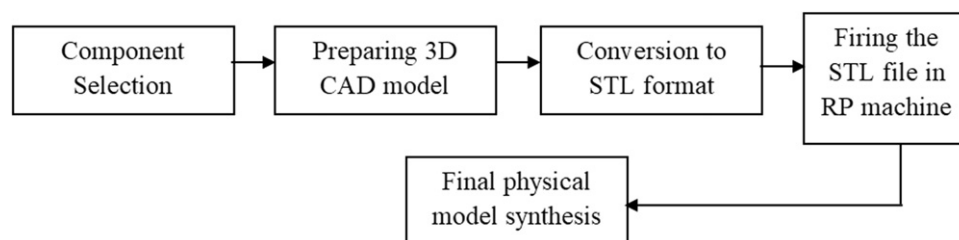


Fig. 1 Steps involved in production of a part with RP techniques.

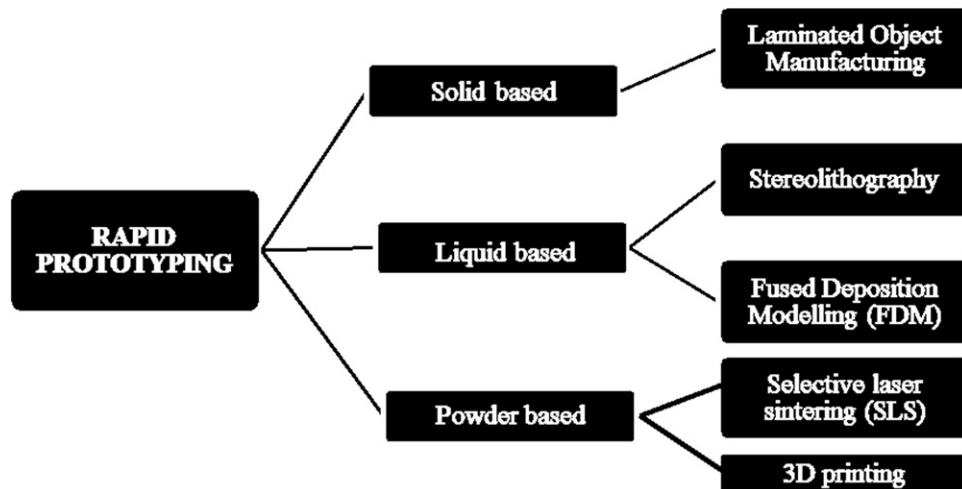


Fig. 2 Classification of RP techniques based on phase of material.

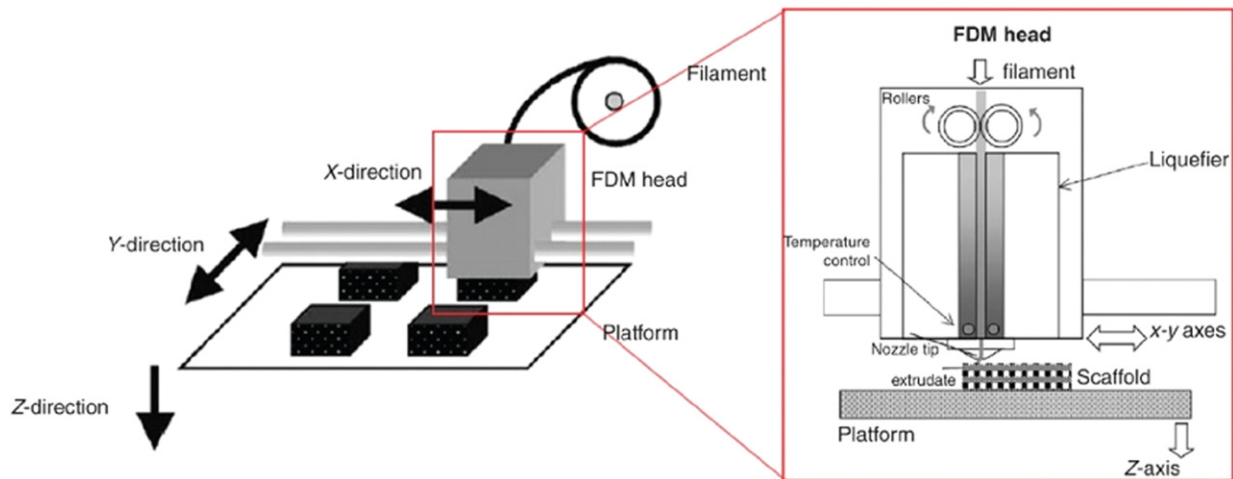


Fig. 3 Schematic of FDM process. Reproduced from Singh, S., Bedi, P., Fraternali, F., Ahuja, I.P.S., 2016. Effect of single particle size, double particle size and triple particle size Al_2O_3 in Nylon-6 matrix on mechanical properties of feed stock filament for FDM. Composites Part B 106, 20–27.

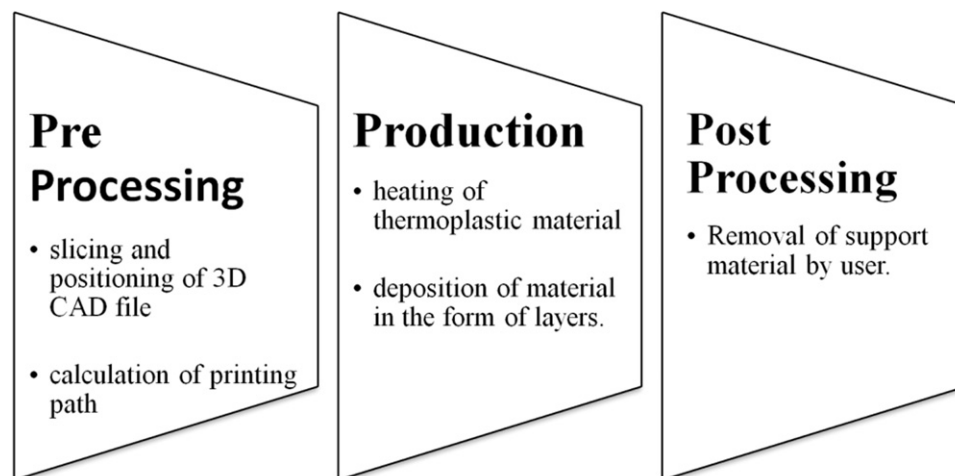


Fig. 4 Process of FDM.

Rapid Prototyping Techniques

RP techniques are mainly classified under different categories on the basis of the phase of material used for pattern (Flanagan, 1954). The material to fabricate patterns with RP techniques are used in three different phases solid, liquid and powder based (Leong *et al.*, 2003). The various RP processes are shown in Fig. 2.

Fused Deposition Modeling

Fused Deposition Modeling (FDM) is a layer additive manufacturing process that can use production-grade thermoplastic materials in order to produce prototypes as well as end-use parts (Macdonald *et al.*, 2014; Bedi *et al.*, 2018). Fig. 3 represents the schematic of FDM process.

In FDM machine an extruder head moves in two principle directions following a predetermined path taken from the file (Jafari *et al.*, 2000). The extruder head contains heated nozzle with a small orifice, through which a semi-solid thermoplastic or wax filament is extruded (Ahn *et al.*, 2002). After each layer the table is lowered and a new layer is formed (Singh and Singh, 2015a,b). The new layer makes the bond with the previous layer and cools down as platform is maintained at a lower temperature as compared to nozzle (Kumar *et al.*, 2012).

The process, merits, demerits and applications of fused deposition modeling is mainly consisting of following three steps (Figs. 4 and 5):

The step by step methodology of whole study has been described in Fig. 6.

- (1) *Finding Melt flow indices for different sets of combinations of base matrix and reinforcements thereby selecting best combinations based on pilot MFI values.*

The melt flow index basically measures the rate of flow of molten melt of a thermoplastic polymer. It is defined as the mass of polymer (in grams) that flows through a path (capillary) of particular diameter and length in ten minutes by applying pressure through specified weights provided at prescribed temperature conditions.

- (2) *Preparation of filament wires using twin screw extruder (TSE)*

The twin screw extruder was developed more than 20 years ago, for continuous production of highly uniform and finely structure products. It is widely used to produce bio-sourced plastics, cellulose pulps and food products. For this study commercial make: HAAKE Mini CTW, Germany has been used.

- (3) *Mechanical testing of filaments on universal tensile machine.*

Tensile test is the most accepted test regarding judgment for quality of filament wire prepared. This test is performed on universal tensile tester to check the tensile strength at peak as well at break. Plastic wires, plastic flats or strip of any size can also be measured using universal tensile tester. The filament wires produced were tested mechanically on Universal Tensile tester (UTT).

- (4) *Fabrication of pins and RT on FDM*

The filament wires so prepared were fired into FDM (make: Divide By Zero's Accucraft i250D) setup. Divide By Zero's Accucraft i250D is a hybrid dual extruder 3D printer with a build volume of 200 mm × 250 mm × 200 mm.

Merits	Demerits	Applications
• easier production of parts with complex design features. • easier production of limited quantities customized parts • parts prepared are highly durable, strong, chemical and heat resistant • highly environment friendly technology • low maintenance costs	• ribbing effect i.e., very fine lines are seen due to deposition of each layer • the head of extrusion must be continuously moving otherwise material may start depositing and form lumps.	• Aerospace • Commercial • Automotive • Industrial • Consumer • Medical

Fig. 5 Merits, demerits, and applications of FDM.

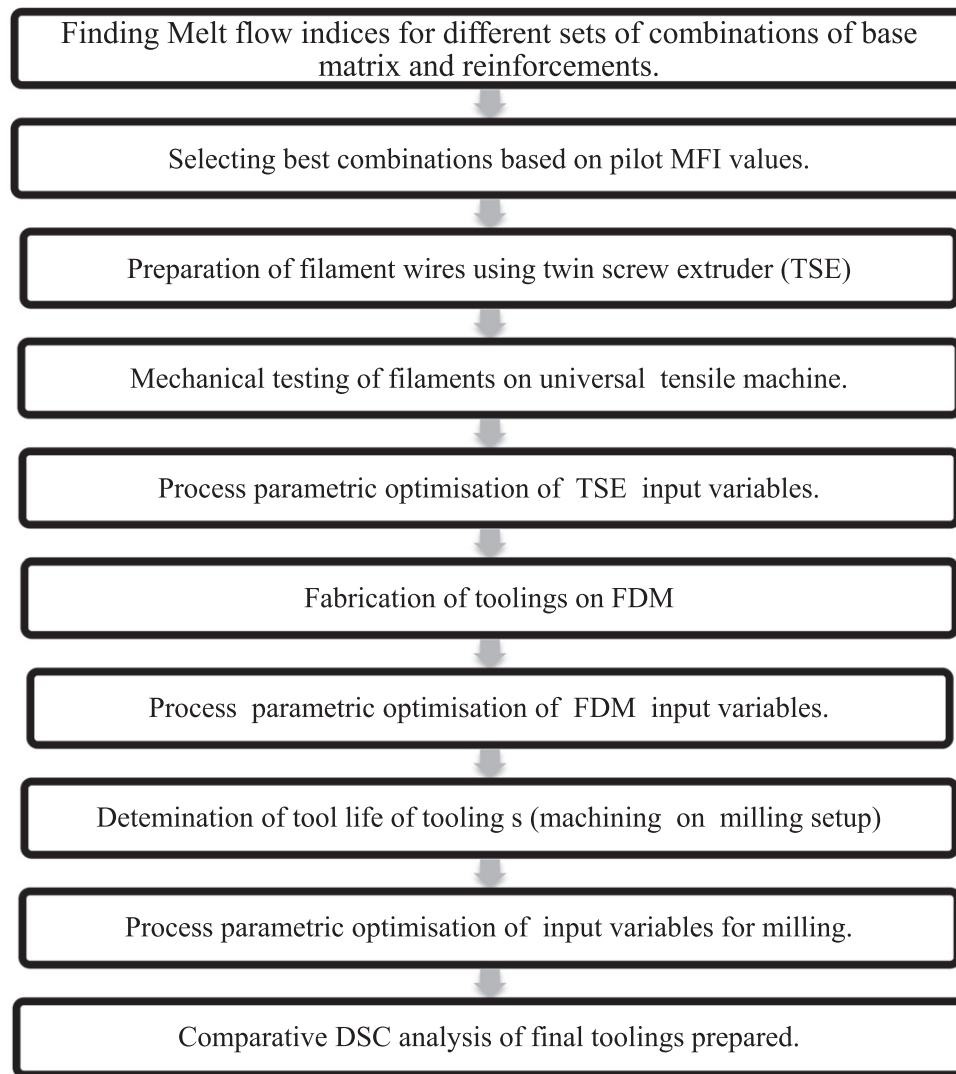


Fig. 6 Methodology of study.

(5) *Wear testing of pins prepared using FDM*

A pin on disk apparatus generally includes a stationary pin of material to be tested and a rotating disk (with emery paper in this case). As the disk rotates with specific rpm, the stationary pin being in contact with the disk starts wearing out and thereby this information is transmitted through the sensors to the meter attached further being transferred to the software installed on the system. Using the Win Ducom Data Acquisition System, a PC acquires test data online and displays it in several ways. Graphs of individual tests can be printed.

(6) *Fabrication of RT on FDM*

Further, RT and work pieces (WP) were printed using FDM. Total 18 WP of diameter as 40 mm and thickness as 10 mm were prepared (09 WP of LDPE (100% by weight) without reinforcement and 9 WP of HDPE (100% by weight) without reinforcement). Similarly, 18 RT of $10 \times 10 \times 35$ mm were printed from wires prepared (as 9 RT of HDPE-TPS Al_2O_3 and 09 RT of LDPE-DPS Al_2O_3) on commercial open source FDM setup (Make: Divide by Zero). The printing temperature used for 3D printing of TPS reinforced HDPE RT was $170 \pm 5^\circ\text{C}$ and DPS reinforced LDPE RT was $155 \pm 5^\circ\text{C}$.

(7) *Machining of WP and RT using vertical milling to compute tool life.*

The discs prepared were used as WP for machining on vertical milling machine and tooling prepared was mounted perpendicular to WP for machining of RT.

(8) *DSC analysis of final RT prepared.*

Mettler Toledo DSC setup has been used in the study. Thermal analysis of various benchmarks prepared was done by using DSC technique and thermal plots were plotted correspondingly

(9) *Process Capability Study*

Process capability study in the present research has been used to realise the capability of the process by comparing the actual process spread with the allowable process spread and measured by process σ levels. In this work, process capability analysis was

carried out with the help of computer software (Process Capability Wizard Software, version. 1.7.0.0). The process capability has been visualized through the statistical measurements of C_p , C_{pk} and parts per million (ppm) non-conforming parts. C_p is a measure of a process's ability to meet a specification. C_{pk} is an index that measures how close a process is running to its specification limits, relative to the natural variability of the process. The larger values of C_{pk} represent that there are less chances that any item will go outside the specifications.

Experimentation

As a part of pilot study, Melt flow index (MFI) has been checked for different sets/combinations of HDPE/LDPE granules as base matrix with different sizes of SiC/ Al_2O_3 as reinforcements. It should be noted that the SPS represents single particle size (of either 300, 400, 500

Table 1 Final shortlisted combinations considering minimum MFI values

S. No.	HDPE	Al_2O_3 300-G wt%	Al_2O_3 400-G wt%	Al_2O_3 500-G wt%	MFI (g/10 min)
1	50	0	0	50	9.24
2	50	0	25	25	10.60
3	90	3.33	3.33	3.34	10.02
S. No.	HDPE	SiC300-G wt%	SiC400-G wt%	SiC 500-G wt%	MFI (g/10 min)
4	50	0	0	50	6.16
5	60	25	25	0	3.71
6	60	13.33	13.33	13.34	7.14
S. No.	LDPE	Al_2O_3 300-G wt%	Al_2O_3 400-G wt%	Al_2O_3 500-G wt%	MFI (g/10 min)
1	50	0	0	50	6.85
2	50	0	25	25	10.53
3	50	16.67	16.67	16.67	13.58
S. No.	LDPE	SiC 300-G wt%	SiC 400-G wt%	SiC 500-G wt%	MFI (g/10 min)
4	50	0	0	50	4.32
5	60	0	20	20	6.48
6	60	13.33	13.33	13.33	9.83

Note: G represents grade of abrasives.

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Table 2 Detailed input parameters taken for Taguchi L18 array for HDPE and LDPE

Levels	Input parameters (for HDPE)				Input parameters (for LDPE)			
	A	B	C	D	A	B	C	D
L1	1	5	185	35	1	5	155	35
L2	1	10	190	40	1	10	160	40
L3	1	15	195	45	1	15	165	45
L4	2	10	185	35	2	10	155	35
L5	2	15	190	40	2	15	160	40
L6	2	5	195	45	2	5	165	45
L7	3	5	190	35	3	5	160	35
L8	3	10	195	40	3	10	165	40
L9	3	15	185	45	3	15	155	45
L10	4	15	195	35	4	15	165	35
L11	4	5	185	40	4	5	155	40
L12	4	10	190	45	4	10	160	45
L13	5	15	190	35	5	15	160	35
L14	5	5	195	40	5	5	165	40
L15	5	10	185	45	5	10	155	45
L16	6	10	195	35	6	10	165	35
L17	6	15	185	40	6	15	155	40
L18	6	5	190	45	6	5	160	45

Note: Where, A is composition, B is Load (in kgf), C is temperature (in degree Celcius), D is RPM.

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American foundry society (AFS) grade), DPS represents two particle sizes in equal proportion by weight (of combination of either of two from 300, 400, 500 AFS grade) and TPS represents three particle sizes in equal proportion by weight (of 300, 400 and 500 AFS grade). Minimum values of MFI have been selected for each set of SPS, DPS and TPS combinations (as per pilot study) and summarized in [Table 1](#).

As per [Table 1](#), filament wires have been made from HDPE and LDPE on twin screw extruder with stated amount of reinforcements with the minimum values of MFI values (closer to MFI for original equipment manufacturer wire) as shortlisted.

[Table 2](#) shows various combinations of input parameters taken for study for HDPE and LDPE as per Taguchi L18 orthogonal technique:

The filament wires so produced as per [Table 2](#) have been tested mechanically on Universal Tensile tester (UTT). The results of UTT (Peak load, peak elongation, break load, break elongation, Young's Modulus) for HDPE and LDPE are computed and summarized in [Table 3](#).

The cylindrical pins have been printed on FDM with bed temperature as 55°C and printing temperatures as 155°C & 170°C for LDPE and HDPE respectively. 9 pins (HDPE-TPS Al_2O_3) with composition as HDPE 90% by weight, Al_2O_3 300G 3.33% by weight, Al_2O_3 400G 3.33% by weight and Al_2O_3 500G 3.34% by weight and similarly, 9 pins (LDPE-DPS Al_2O_3) with composition LDPE 50% by weight, Al_2O_3 400G 25% by weight and Al_2O_3 500G 25% by weight have been printed and compared with corresponding pins printed with composition as HDPE (100% by weight) and LDPE (100% by weight) respectively. Three process parameters (with three levels); RPM, load and time have been taken for pin on disk standard experiment and summarized in [Table 4](#) for HDPE and LDPE as per Taguchi L9 orthogonal array.

Pin on disk experiments were carried out as per [Table 4](#) and wear values were observed separately for HDPE and LDPE cases and summarized in [Table 5](#) respectively. Further, initial and final weights of pins have been considered for calculation of weight loss.

Further RT (HDPE-TPS Al_2O_3 and LDPE- DPS Al_2O_3) and work pieces (HDPE and LDPE without any reinforcement) have been printed on FDM setup as per input parameters considered under Taguchi L9 technique. The printing temperature used for 3D printing of TPS reinforced HDPE RT was $170 \pm 5^\circ C$ and DPS reinforced LDPE RT was $155 \pm 5^\circ C$. The three process parameters (Infill Density, Infill angle, Infill speed) with three levels were selected for printing as per L9 orthogonal array technique for HDPE and LDPE RT as shown in [Table 6](#).

Further, Shore-D hardness and dimensional accuracy (in terms of Deviation in width i.e., Deviation X and Deviation in length i.e., Deviation Y) of HDPE and LDPE RT have been checked and summarized in [Table 7](#).

The RT prepared (both HDPE and LDPE) have been put to machining against work pieces (circular discs) on vertical milling machine as per L9 Taguchi orthogonal array with three input parameters (speed, Feed, depth of cut). Different cases have been considered to determine tool life and machinability of RT and work pieces.

Case 1: LDPE (100% composition) as work piece (WP) and HDPE - TPS Al_2O_3 (HDPE as 90% by weight, Al_2O_3 -300G as 3.33% by weight, Al_2O_3 -400G as 3.33% by weight, Al_2O_3 -500G as 3.33% by weight) as tooling.

In case 1, 09 work pieces of LDPE (100% by weight) and 09 RT of HDPE - TPS Al_2O_3 (HDPE as 90% by weight, Al_2O_3 -300G as 3.33% by weight, Al_2O_3 -400G as 3.33% by weight, Al_2O_3 -500G as 3.33% by weight) have been taken.

Table 3 Output parameters (mechanical properties) computed using UTT for HDPE

Levels	Output parameters (For HDPE)					Output parameters (For LDPE)				
	A	B	C	D	E	A	B	C	D	E
L1	11.8	2.14	10.22	2.04	1.37	9.8	3.04	9.08	2.23	6
L2	13.7	3.42	12.33	3.14	1.51	9.9	4.85	9.19	4.4	7
L3	11.7	3.8	10.53	3.25	1.22	10.2	6.08	10.14	6.06	7
L4	12.7	2.09	12.45	1.95	4.62	8.8	1.23	8.47	1.08	6
L5	16.1	2.47	14.49	2.25	4.88	8.9	2.9	8.88	2.28	6
L6	15.6	1.71	14.04	1.4	2.94	9.4	3.61	9.27	3.46	7
L7	38.1	4.7	25.99	4.25	3.22	7.9	1.71	7.45	1.28	3
L8	20.5	2.66	18.45	2.26	3.65	7.3	3.99	7.14	3.37	4
L9	32.7	5.41	25.13	5.14	2.4	7.8	4.9	7.47	4.09	4
L10	17.1	2.09	15.39	1.85	2.74	5.3	1.09	5.24	0.97	4
L11	21	2.28	18.9	2.08	2.89	6.8	2.09	6.78	2.08	4
L12	21.5	4.75	19.35	4.25	4.93	5.2	3.99	5.04	3.18	5
L13	21	5.7	18.9	5.17	3.66	9.3	2.65	9.22	2.44	7
L14	11.2	1.52	10.08	1.48	2.74	9.3	3.04	9.14	3.03	6
L15	19.6	3.04	17.64	2.48	2.74	9.8	3.8	9.45	3.89	7
L16	12.7	2.66	11.43	2.47	2.89	8.9	2.76	8.36	2.09	10
L17	10.7	2.28	9.63	1.92	4.26	8.3	4.94	8.23	4.46	9
L18	13.7	4.37	12.33	4.06	2.37	9.8	6.08	9.42	6.03	12

Note: Where A is Peak load (N), B is peak elongation (mm), C is Break load (N), D is break elongation (mm), and E is Young's Modulus (MPa).

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Case 2: HDPE (100% composition) as work piece (WP) and LDPE - DPS Al_2O_3 (LDPE 50% by weight, Al_2O_3 -400G 25% by weight, Al_2O_3 -500G 25% by weight) as tooling.

In case 2, 09 work pieces of HDPE (100% by weight) and 09 RT of LDPE - DPS Al_2O_3 (LDPE 50% by weight, Al_2O_3 -400G 25% by weight, Al_2O_3 -500G 25% by weight) have been taken.

Work pieces in both cases have been mounted on the base plate of milling machine (fixed) whereas tooling have been mounted on tool post perpendicular to the work piece and feed has been given horizontally parallel to base plate. Table 8 shows different levels of input parameters considered for machining on vertical milling set up as per Taguchi L9 technique.

Initial and final weights of discs (WP) and RT for both case 1 and case 2 have been noted to compute the weight loss during the machining and summarized in Table 9.

Results and Discussions

Results for Mechanical Properties of Filament Wires

SN ratio analysis has been done for each of the mechanical properties computed as per Taguchi L18 technique separately for HDPE and LDPE filament wires (as per Table 3) and summarized in Table 10.

Various SN plots, variance analysis and ranking tables for all mechanical properties for HDPE and LDPE have been obtained using Minitab 17 software. Fig. 7 shows the SN plots for different mechanical properties of HDPE filament wire. Tables 11 and 12

Table 4 Detailed process parameters taken for Taguchi L9 array for pin on disk experimentation as per Taguchi L9 array for HDPE and LDPE pins

Material	Levels	RPM	Load (in kgf)	Time (in min)
HDPE pure	L1	250	1	5
	L2	250	2	10
	L3	250	3	15
	L4	375	1	10
	L5	375	2	15
	L6	375	3	5
	L7	500	1	15
	L8	500	2	5
	L9	500	3	10
HDPE TPS	L1	250	1	5
	L2	250	2	10
	L3	250	3	15
	L4	375	1	10
	L5	375	2	15
	L6	375	3	5
	L7	500	1	15
	L8	500	2	5
	L9	500	3	10
LDPE pure	L1	250	1	5
	L2	250	2	10
	L3	250	3	15
	L4	375	1	10
	L5	375	2	15
	L6	375	3	5
	L7	500	1	15
	L8	500	2	5
	L9	500	3	10
LDPE DPS	L1	250	1	5
	L2	250	2	10
	L3	250	3	15
	L4	375	1	10
	L5	375	2	15
	L6	375	3	5
	L7	500	1	15
	L8	500	2	5
	L9	500	3	10

Note: Bedi, P., Singh, S., Ahuja, I.P.S., 2018. Investigations for Rapid Tooling Prepared With Waste Polymer-Based Hybrid Filament. Reference Module in Materials Science and Materials Engineering. Oxford: Elsevier, 1–18.

Table 5 Wear and weight loss values for HDPE pure, HDPE TPS Al_2O_3 , LDPE pure and LDPE DPS Al_2O_3 pins

Material	Levels	Wear (in μm)	Original weight (in gm)	Final weight (in gm)	Weight loss (in gm)
HDPE pure	L1	427	3.3685	3.3464	0.0221
	L2	341	3.3464	3.3288	0.0176
	L3	503	3.3288	3.3029	0.0259
	L4	225	3.3029	3.2913	0.0116
	L5	474	3.2913	3.2669	0.0244
	L6	1244	3.2669	3.2028	0.0641
	L7	262	3.2028	3.1895	0.0133
	L8	484	3.1895	3.1646	0.0249
	L9	1099	3.1646	3.1081	0.0565
HDPE TPS Al_2O_3	L1	425	1.6699	1.6478	0.0221
	L2	320	1.6478	1.6342	0.0136
	L3	455	1.6342	1.6008	0.0334
	L4	220	1.6008	1.5922	0.0086
	L5	380	1.5922	1.5796	0.0126
	L6	1120	1.5796	1.5555	0.0241
	L7	220	1.5555	1.5153	0.0402
	L8	410	1.5153	1.4319	0.0834
	L9	954	1.4319	1.3741	0.0578
LDPE pure	L1	721	2.8685	2.8423	0.0262
	L2	637	2.8464	2.8248	0.0216
	L3	821	2.8288	2.7964	0.0324
	L4	530	2.8029	2.7855	0.0174
	L5	785	2.7913	2.7619	0.0294
	L6	1559	2.7669	2.6886	0.0783
	L7	564	2.7028	2.6826	0.0202
	L8	782	2.6895	2.6617	0.0278
	L9	1358	2.6646	2.5972	0.0674
LDPE DPS	L1	612	1.6699	1.6455	0.0244
	L2	568	1.6478	1.6284	0.0194
	L3	725	1.6342	1.6044	0.0298
	L4	437	1.6008	1.5851	0.0157
	L5	649	1.5922	1.5636	0.0286
	L6	1453	1.5796	1.5034	0.0762
	L7	474	1.5555	1.5343	0.0212
	L8	645	1.5153	1.489	0.0263
	L9	1256	1.4319	1.3692	0.0627

Note: Bedi, P., Singh, S., Ahuja, I.P.S., 2018. Investigations for Rapid Tooling Prepared With Waste Polymer-Based Hybrid Filament. Reference Module in Materials Science and Materials Engineering. Oxford: Elsevier, 1–18.

Table 6 Input parameters for printing of HDPE-TPS Al_2O_3 RT and LDPE-DPS Al_2O_3 RT as per L9 orthogonal array

S. No.	Composition/Proportion by weight	Selected input parameters			Composition/Proportion by weight	Selected input parameters		
		Infill speed (in mm/s)	Infill density (in %age)	Infill angle (in $^\circ$)		Infill speed (in mm/s)	Infill density (in %age)	Infill angle (in $^\circ$)
Level 1	HDPE (90%), Al_2O_3 300G (3.33%), Al_2O_3 -400G (3.33%), Al_2O_3 -500G (3.33%)	40	60	45	LDPE (50%), Al_2O_3 -400G (25%), Al_2O_3 -500G (25%)	40	60	45
Level 2		50	60	60		50	60	60
Level 3		60	60	75		60	60	75
Level 4		50	80	45		50	80	45
Level 5		60	80	60		60	80	60
Level 6		40	80	75		40	80	75
Level 7		60	100	45		60	100	45
Level 8		40	100	60		40	100	60
Level 9		50	100	75		50	100	75

show analysis of Variance for SN ratios and Signal to noise ratios for different mechanical properties of HDPE filament wire respectively.

After combined optimization, It has been seen that level 3 of composition (HDPE 90% by weight, Al_2O_3 300G 3.33% by weight, Al_2O_3 400G 3.33% by weight and Al_2O_3 500G 3.34% by weight), level 1 of load (5 kgf), level 2 of temperature (190°C) and level 2 of RPM (40) are best settings for HDPE filament wire to have maximum mechanical strength. Further, composition came out to be the major factor contributing (with 51.15% contribution) for maximizing the mechanical strength of HDPE filament wire at 5% level of significance while effect of other parameters can be ignored as their p-value is coming more than 0.05.

Fig. 8 shows the SN plots for different mechanical properties of LDPE filament wire. Tables 13 and 14 show analysis of Variance for SN ratios and Signal to noise ratios for different mechanical properties of LDPE filament wire respectively.

Table 7 Output parameters for HDPE-TPS Al_2O_3 RT and LDPE-DPS Al_2O_3 RT printed

	S. No.	Width (proposed) (in mm) A	Width (printed) (in mm) B	Deviation (X) (B-A)	Length (proposed) (in mm) C	Length (printed) (in mm) D	Deviation (Y) (D-C)	Shore D hardness
HDPE-TPS Al_2O_3 RT	Level 1	10	10.42	0.42	35	35.27	0.27	57.5
	Level 2		10.44	0.44		35.28	0.28	58.0
	Level 3		10.45	0.45		35.30	0.30	59.0
	Level 4		10.17	0.17		35.29	0.29	58.0
	Level 5		10.15	0.15		35.31	0.31	60.0
	Level 6		10.16	0.16		35.33	0.33	60.0
	Level 7		10.24	0.24		35.30	0.30	56.0
	Level 8		10.25	0.25		35.31	0.31	57.0
	Level 9		10.29	0.29		35.32	0.32	57.5
LDPE-DPS Al_2O_3 RT	Level 1	10	10.28	0.28	35	35.35	0.35	43.5
	Level 2		10.27	0.27		35.29	0.29	45.0
	Level 3		10.15	0.15		35.24	0.24	46.0
	Level 4		10.29	0.29		35.41	0.41	42.5
	Level 5		10.22	0.22		35.28	0.28	44.0
	Level 6		10.12	0.12		35.22	0.22	46.0
	Level 7		10.32	0.32		35.38	0.38	43.0
	Level 8		10.19	0.19		35.29	0.29	44.5
	Level 9		10.15	0.15		35.26	0.26	45.0

Table 8 Different levels of input parameters for vertical milling of RT as per L9 OA

		Input parameters			
	S. No.	Feed (mm/min)	Composition	Depth of cut (mm)	Speed (RPM)
Case 1	Level 1	20	1	1	500
	Level 2	30	1	2	500
	Level 3	40	1	3	500
	Level 4	20	1	2	750
	Level 5	30	1	3	750
	Level 6	40	1	1	750
	Level 7	20	1	3	1000
	Level 8	30	1	1	1000
	Level 9	40	1	2	1000
Case 2	Level 1	20	2	2	500
	Level 2	30	2	3	500
	Level 3	40	2	2	500
	Level 4	20	2	3	750
	Level 5	30	2	1	750
	Level 6	40	2	3	750
	Level 7	20	2	1	1000
	Level 8	30	2	2	1000
	Level 9	40	2	1	1000

Where composition 1 represents HDPE as 90% by weight, Al_2O_3 -300G (150 μm) as 3.33% by weight, Al_2O_3 -400G (120 μm) as 3.33% by weight, Al_2O_3 -500G (100 μm) as 3.33% by weight (i.e., TPS) and composition 2 represents LDPE 50% by weight, Al_2O_3 -400G 25% by weight, Al_2O_3 -500G 25% by weight (i.e., DPS).

After combined optimization, it has been seen that level 3 of composition (LDPE 50% by weight, Al_2O_3 400G 25% by weight and Al_2O_3 500G 25% by weight), level 3 of load (15 kgf), level 2 of temperature (190°C) and level 1 of RPM (35) are best settings for LDPE filament wire to have maximum mechanical strength. Further, composition came out to be the major factor contributing (with 42.13% contribution) for maximizing the mechanical strength of LDPE filament wire at 5% level of significance while effect of other parameters can be ignored as their p-value is coming more than 0.05 (Table 14).

Table 9 Weight losses of WP and RT for case 1 and case 2

			Weight of WP before machining (g)	Weight of WP after machining (g)	Weight loss of WP (g)		Weight of RT before machining (g)	Weight of RT after machining (g)	Weight loss of RT (g)
Case 1	Level 1	LDPE	2.750	2.196	0.554	HDPE reinforced	2.877	2.856	0.021
	Level 2		2.780	2.058	0.722		2.742	2.714	0.028
	Level 3		2.458	1.425	1.033		2.846	2.800	0.046
	Level 4		2.482	1.930	0.552		2.764	2.740	0.024
	Level 5		2.894	2.148	0.746		2.487	2.453	0.034
	Level 6		2.587	1.546	1.041		2.549	2.510	0.039
	Level 7		2.984	2.420	0.564		2.657	2.629	0.028
	Level 8		2.567	1.806	0.741		2.841	2.803	0.038
	Level 9		2.354	1.300	1.054		2.981	2.934	0.047
Case 2	Level 1	HDPE	3.204	3.018	0.186	LDPE reinforced	2.235	1.773	0.462
	Level 2		3.214	2.990	0.224		2.249	1.757	0.492
	Level 3		3.025	2.779	0.246		2.357	1.796	0.561
	Level 4		3.425	3.243	0.182		2.192	1.733	0.459
	Level 5		3.475	3.229	0.246		2.259	1.770	0.489
	Level 6		3.224	2.945	0.279		2.367	1.793	0.574
	Level 7		3.146	2.954	0.192		2.320	1.893	0.427
	Level 8		3.164	2.956	0.208		2.204	1.722	0.482
	Level 9		3.012	2.698	0.314		2.014	1.442	0.572

Note: Case 3 and Case 4 with 100% LDPE (WP) and LDPE-DPS Al_2O_3 (tooling) & 100% HDPE (WP) and HDPE-TPS Al_2O_3 (tooling) respectively were not considered as it was observed that WP and RT got welded with each other leading to tool rupture during machining.

Table 10 S–N ratios for each computed mechanical properties for HDPE and LDPE

Levels	For HDPE					For LDPE				
	SN peak load	SN peak elongation	SN break load	SN break elongation	SN Young's Modulus	SN peak load	SN peak elongation	SN break load	SN break elongation	SN Young's Modulus
L1	21.43	6.60	20.18	6.19	2.73	19.82	9.66	19.16	6.97	15.56
L2	22.73	10.68	21.81	9.94	3.58	19.91	13.71	19.27	12.87	16.90
L3	21.36	11.59	20.44	10.24	1.73	20.17	15.68	20.12	15.65	16.90
L4	22.07	6.40	21.90	5.81	13.30	18.89	1.80	18.56	0.67	15.56
L5	24.13	7.85	23.22	7.04	13.77	18.99	9.25	18.97	7.16	15.56
L6	23.86	4.65	22.94	2.92	9.37	19.47	11.15	19.34	10.78	16.90
L7	31.61	13.44	28.29	12.57	10.16	17.95	4.66	17.44	2.14	9.54
L8	26.23	8.49	25.31	7.08	11.25	17.27	12.02	17.07	10.55	12.04
L9	30.29	14.66	28.00	14.22	7.60	17.84	13.80	17.47	12.23	12.04
L10	24.65	6.40	23.74	5.34	8.75	14.49	0.75	14.39	0.26	12.04
L11	26.44	7.15	25.52	6.36	9.22	16.65	6.40	16.62	6.36	12.04
L12	26.64	13.53	25.73	12.57	13.86	14.32	12.02	14.05	10.04	13.97
L13	26.44	15.11	25.52	14.27	11.27	19.37	8.46	19.29	7.75	16.90
L14	20.98	3.63	20.06	3.41	8.76	19.37	9.66	19.22	9.63	15.56
L15	25.84	9.65	24.93	7.89	8.76	19.82	11.60	19.51	11.80	16.90
L16	22.07	8.49	21.16	7.85	9.22	18.99	8.82	18.44	6.40	20.00
L17	20.58	7.15	19.67	5.67	12.59	18.38	13.87	18.31	12.99	19.08
L18	22.73	12.80	21.81	12.17	7.49	19.82	15.68	19.48	15.61	21.58

Note: (It should be noted that "larger the better" case is considered for SN values for peak load, break load and Young's modulus, "smaller the better" case is considered for SN values for peak elongation and break elongation and "larger the better" case is considered for combined optimization for both HDPE and LDPE cases).

Bedi, P., Singh, S., Ahuja, I.P.S., 2018. Investigations for Rapid Tooling Prepared With Waste Polymer-Based Hybrid Filament. Reference Module in Materials Science and Materials Engineering. Oxford: Elsevier, 1–18.

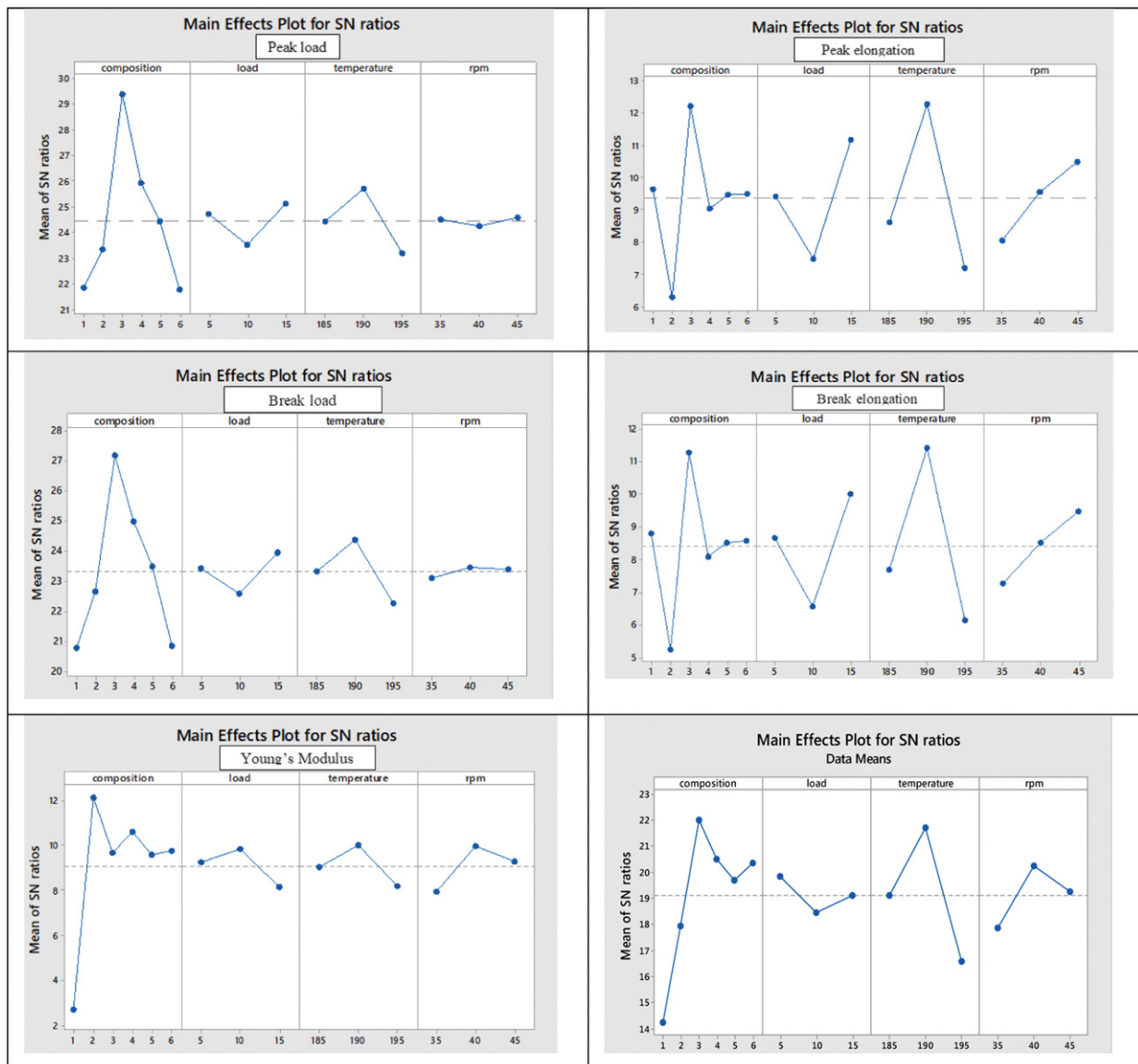


Fig. 7 SN plots for different mechanical properties of HDPE filament wire.

Results for Pin on Disk Experimentation of Pins Printed

SN ratio analysis has been done for wear of the pins printed on FDM as per Table 4. SN ratios (for smaller the better type case) for wear for pure HDPE, HDPE TPS Al_2O_3 , pure LDPE and LDPE DPS Al_2O_3 pins have been summarized in Table 15. Fig. 9 shows the SN plots for wear for pure HDPE, HDPE TPS Al_2O_3 , pure LDPE and LDPE DPS Al_2O_3 pins. Tables 16 and 17 shows variance analysis and response table for SN ratios for wear of pure HDPE, HDPE TPS Al_2O_3 , pure LDPE and LDPE DPS Al_2O_3 pins.

It has been seen that level 1 of rpm (250), level 1 of load (1 kgf), level 3 of time (15 min) are best settings for pure HDPE pin to have minimum wear. Further, load came out to be major factor contributing (with 70.63% contribution) for minimizing the wear of pure HDPE pin at 5% level of significance.

It has been seen that level 1 of rpm (250), level 1 of load (1 kgf), level 3 of time (15 min) are best settings for HDPE TPS Al_2O_3 pin to have minimum wear. Further, load came out to be major factor contributing (with 69.31% contribution) for minimizing the wear of HDPE TPS Al_2O_3 pin at 5% level of significance.

It has been seen that level 1 of rpm (250), level 1 of load (1 kgf), level 3 of time (15 min) are best settings for pure LDPE pin to have minimum wear. Further, load came out to be major factor contributing (with 71.36% contribution) for minimizing the wear of pure LDPE pin at 5% level of significance.

It has been seen that level 1 of rpm (250), level 1 of load (1 kgf), and level 3 of time (15 min) are best settings for LDPE DPS Al_2O_3 pin to have minimum wear. Further, load came out to be major factor contributing (with 74.18% contribution) for minimizing the wear of LDPE DPS Al_2O_3 pin at 5% level of significance.

Table 11 Analysis of variance for SN ratios for different mechanical properties of HDPE filament wire

	Source	DF	Seq SS	Adj SS	Adj MS	F	P	Percentage contribution (%)
Peak load	Composition	5	124.430	124.430	24.8859	10.36	0.006	74.69
	Load	2	8.346	8.346	4.1728	1.74	0.254	5.01
	Temperature	2	19.090	19.090	9.5452	3.97	0.080	11.46
	RPM	2	0.322	0.322	0.1611	0.07	0.936	0.19
	Residual error	6	14.411	14.411	2.4019			8.65
	Total	17	166.599					
Peak elongation	Composition	5	52.83	52.83	10.566	3.97	0.062	25.47
	Load	2	40.12	40.12	20.061	7.54	0.023	19.34
	Temperature	2	80.74	80.74	40.372	15.18	0.004	38.92
	RPM	2	17.79	17.79	8.897	3.35	0.106	8.58
	Residual error	6	15.96	15.96	2.660			7.69
	Total	17	207.45					
Break load	Composition	5	91.652	91.6524	18.3305	10.07	0.007	74.95
	Load	2	5.800	5.7997	2.8999	1.59	0.279	4.74
	Temperature	2	13.504	13.5038	6.7519	3.71	0.089	11.04
	RPM	2	0.403	0.4035	0.2017	0.11	0.897	0.33
	Residual error	6	10.923	10.9228	1.8205			8.94
	Total	17	122.282					
Break elongation	Composition	5	55.57	55.57	11.115	3.28	0.090	25.89
	Load	2	35.63	35.63	17.815	5.25	0.048	16.59
	Temperature	2	88.61	88.61	44.305	13.06	0.007	41.27
	RPM	2	14.53	14.53	7.264	2.14	0.199	6.77
	Residual error	6	20.36	20.36	3.393			9.48
	Total	17	214.70					
Young's Modulus	Composition	5	163.343	161.276	32.255	8.91	0.010	75.94
	Load	2	9.159	9.159	4.579	1.26	0.348	4.27
	Temperature	2	10.209	10.209	5.105	1.41	0.315	4.74
	RPM	2	12.838	12.838	6.419	1.77	0.248	5.96
	Residual Error	6	19.574	21.732	3.622			9.09
	Total	17	215.214					
Combined optimization	Composition	5	112.018	112.018	22.4035	22.98	0.001	51.15
	Load	2	5.660	5.660	2.8299	2.90	0.131	2.58
	Temperature	2	78.695	78.695	39.3475	40.35	0.000	35.94
	RPM	2	16.761	16.761	8.3803	8.59	0.017	7.65
	Residual error	6	5.851	5.851	0.9751			2.67
	Total	17	218.984					

Table 12 Response table for Signal to Noise Ratios for different mechanical properties of HDPE filament wire

	Composition	Load	Temperature	RPM
Peak load				
Rank	1	3	2	4
Peak elongation				
Rank	2	3	1	4
Break load				
Rank	1	3	2	4
Break elongation				
Rank	2	3	1	4
Young's Modulus				
Rank	1	4	3	2
Combined optimization				
Rank	1	4	2	3

The wear tracks for HDPE and LDPE pins (L1–L9 have been shown in Fig. 10, which clearly highlights the extent of wear on pins, when rubbed against the disk.

It has been observed that wear tracks for pure HDPE pin and pure LDPE pin were quite sharper than that of tracks for reinforced HDPE and LDPE pins which clearly indicates that wear decreases when HDPE gets reinforced with TPS Al₂O₃ reinforcement and LDPE gets reinforced with DPS Al₂O₃ reinforcement.

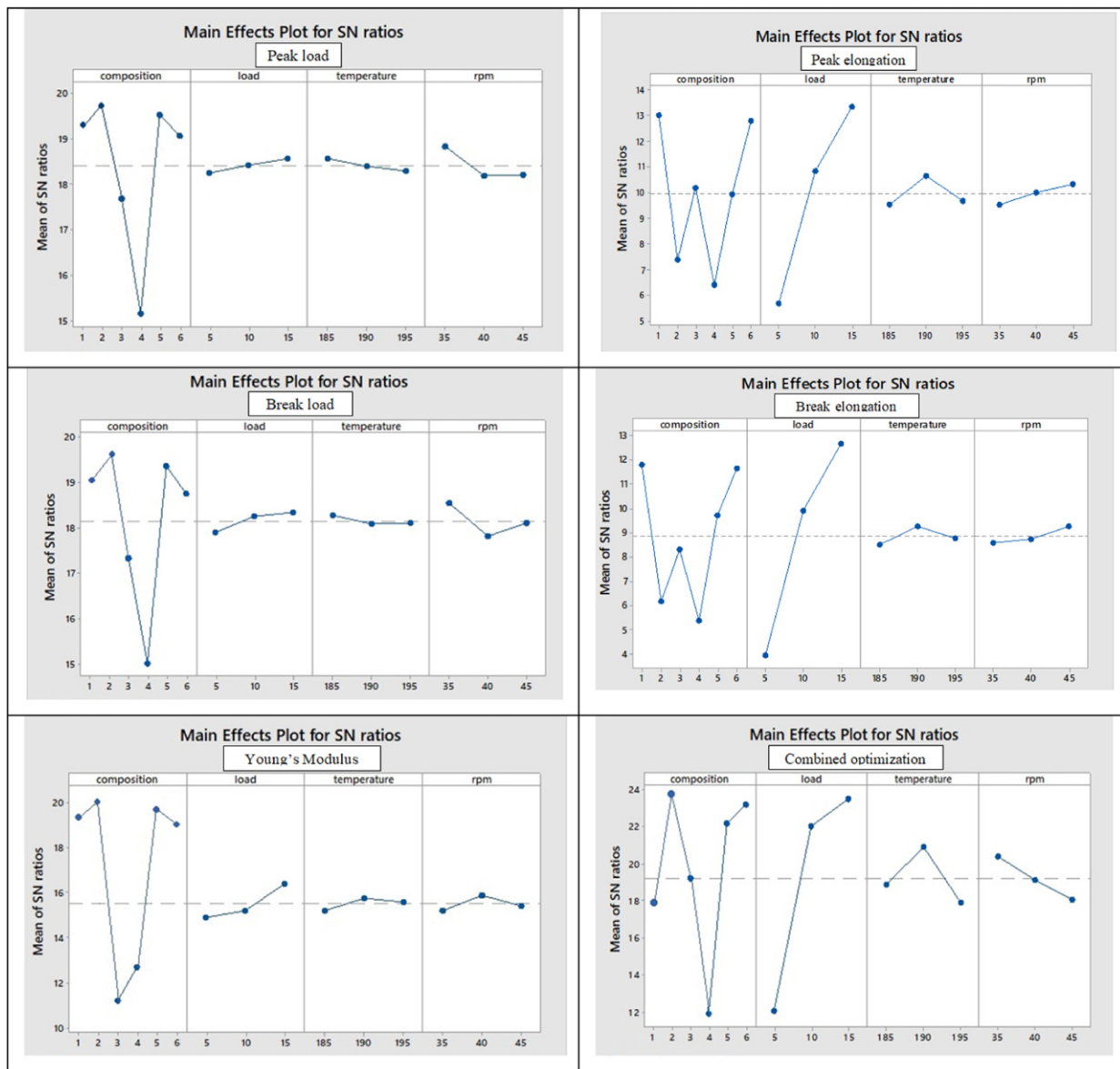


Fig. 8 SN plots for different mechanical properties of LDPE filament wire.

Results for RT Prepared

SN ratio analysis for dimensional accuracy (Deviation X and Deviation Y) and shore D hardness has been done for RT printed on FDM as per table 4.6. SN ratios for dimensional accuracy and hardness for HDPE TPS Al_2O_3 RT and LDPE DPS Al_2O_3 RT has been summarized in Table 18. Fig. 11 shows SN plots for dimensional accuracy in width and length (Deviation X and Deviation Y) and Shore-D hardness of HDPE and LDPE RT. Tables 19 and 20 shows variance analysis and response table for various HDPE and LDPE RT.

It has been seen that level 2 of infill density (80%), level 2 of infill angle (60°), level 3 of infill speed (60 mm/s) are best settings for pure HDPE TPS Al_2O_3 RT to have maximum dimensional accuracy in width (Deviation X) of HDPE TPS Al_2O_3 RT. Further, infill density came out to be major factor contributing (with 98.05% contribution) for maximizing the dimensional accuracy in width (Deviation X) of HDPE TPS Al_2O_3 RT at 5% level of significance.

It has been seen that level 1 of infill density (60%), level 1 of infill angle (45°), level 2 of infill speed (50 mm/s) are best settings for pure HDPE TPS Al_2O_3 RT to have maximum dimensional accuracy in length (Deviation Y) of HDPE TPS Al_2O_3 RT. Further, infill angle came out to be major factor contributing (with 50.08% contribution) for maximizing the dimensional accuracy in width (Deviation Y) of HDPE TPS Al_2O_3 RT at 5% level of significance.

It has been seen that level 2 of infill density (80%), level 3 of infill angle (75°), level 3 of infill speed (60 mm/s) are best settings for pure HDPE TPS Al_2O_3 RT to have maximum shore D hardness of HDPE TPS Al_2O_3 RT. Further, infill density came out to be

Table 13 Analysis of variance for SN ratios for different mechanical properties of LDPE filament wire

	Source	DF	Seq SS	Adj SS	Adj MS	F	P	Percentage contribution (%)
Peak load	Composition	5	47.1853	47.1853	9.4371	19.63	0.001	90.26
	Load	2	0.3132	0.3132	0.1566	0.33	0.734	0.60
	Temperature	2	0.2369	0.2369	0.1184	0.25	0.789	0.45
	RPM	2	1.6592	1.6592	0.8296	1.73	0.256	3.17
	Residual error	6	2.8838	2.8838	0.4806			5.52
	Total	17	52.2784					
Peak elongation	Composition	5	110.097	110.097	22.0194	6.34	0.022	34.56
	Load	2	181.538	181.538	90.7691	26.12	0.001	56.98
	Temperature	2	4.321	4.321	2.1606	0.62	0.568	1.36
	RPM	2	1.795	1.795	0.8977	0.26	0.781	0.56
	Residual error	6	20.850	20.850	3.4749			6.54
	Total	17	318.601					
Break load	Composition	5	44.2811	44.2811	8.85622	16.03	0.002	88.51
	Load	2	0.6752	0.6752	0.33759	0.61	0.573	1.35
	Temperature	2	0.1309	0.1309	0.06546	0.12	0.890	0.26
	RPM	2	1.6251	1.6251	0.81254	1.47	0.302	3.25
	Residual error	6	3.3147	3.3147	0.55245			6.63
	Total	17	50.0270					
Break elongation	Composition	5	110.666	110.666	22.133	8.76	0.080	30.01
	Load	2	239.668	239.668	119.834	47.43	0.000	64.99
	temperature	2	1.765	1.765	0.882	0.35	0.719	0.48
	RPM	2	1.499	1.499	0.750	0.30	0.754	0.41
	Residual error	6	15.159	15.159	2.526			4.11
	Total	17	368.756					
Young's Modulus	Composition	5	152.163	152.163	30.4327	47.70	0.000	91.88
	Load	2	7.155	7.155	3.5776	5.61	0.082	4.32
	Temperature	2	0.937	0.937	0.4685	0.73	0.518	0.57
	RPM	2	1.528	1.528	0.7642	1.20	0.365	0.92
	Residual error	6	3.828	3.828	0.6381			2.31
	Total	17	165.612					
Combined optimization	Composition	5	320.59	320.59	64.118	1.42	0.336	29.19
	Load	2	462.70	462.70	231.351	5.14	0.049	42.13
	Temperature	2	28.49	28.49	14.245	0.32	0.740	2.59
	RPM	2	16.33	16.33	8.166	0.18	0.839	1.49
	Residual error	6	270.11	270.11	45.018			24.60
	Total	17	1098.22					

Table 14 Response table for Signal to Noise Ratios for different mechanical properties of LDPE filament wire

	Composition	Load	Temperature	RPM
Peak load				
Rank	1	3	4	2
Peak elongation				
Rank	2	1	3	4
Break load				
Rank	1	3	4	2
Break elongation				
Rank	2	1	3	4
Young's Modulus				
Rank	1	2	4	3
Combined optimization				
Rank	2	1	3	4

Table 15 SN ratios for wear of pure HDPE, HDPE TPS Al_2O_3 , pure LDPE and LDPE DPS Al_2O_3 pins

Levels	SN for wear (Pure HDPE)	SN for wear (HDPE TPS Al_2O_3)	SN for wear (Pure LDPE)	SN for wear (LDPE DPS Al_2O_3)
L1	-52.6086	-52.6491	-57.1587	-55.7350
L2	-50.6551	-50.8814	-56.0828	-55.0870
L3	-54.0314	-56.2449	-58.2869	-57.2068
L4	-47.0437	-48.0280	-54.4855	-52.8096
L5	-53.5156	-54.3866	-57.8974	-56.2449
L6	-61.8964	-62.8227	-63.8569	-63.2453
L7	-48.3660	-57.8752	-55.0256	-53.5156
L8	-53.6969	-56.3645	-57.8641	-56.1912
L9	-60.8200	-61.0153	-62.6580	-61.9798

Note: (It should be noted that "smaller the better" case is considered for SN values for wear of, pure HDPE, HDPE TPS Al_2O_3 , pure LDPE and LDPE DPS Al_2O_3 pins).

Bedi, P., Singh, S., Ahuja, I.P.S., 2018. Investigations for Rapid Tooling Prepared With Waste Polymer-Based Hybrid Filament. Reference Module in Materials Science and Materials Engineering. Oxford: Elsevier, 1–18.

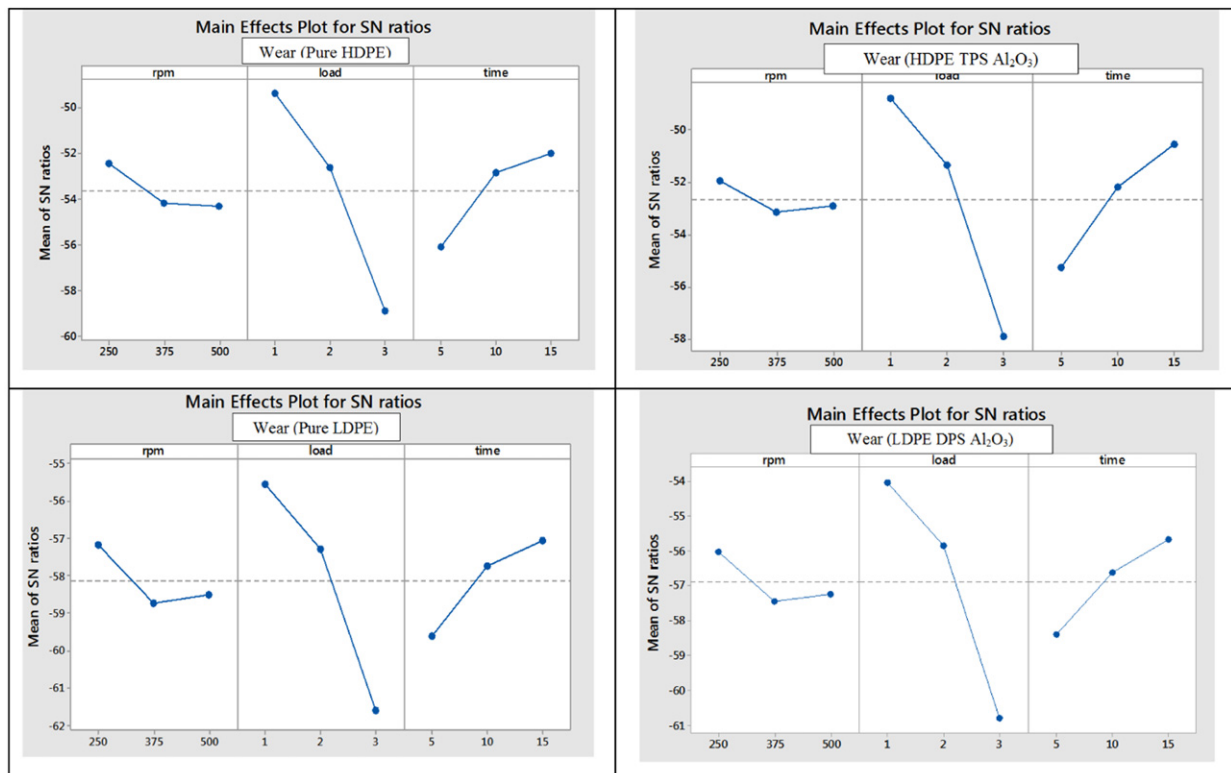
**Fig. 9** SN plots for wear for pure HDPE, HDPE TPS Al_2O_3 , pure LDPE & LDPE DPS Al_2O_3 pins.

Table 16 Variance analysis for wear of pure HDPE, HDPE TPS Al_2O_3 , pure LDPE and LDPE DPS Al_2O_3 pins

	Source	DF	Seq SS	Adj SS	Adj MS	F	P	Percentage contribution (%)
Wear (Pure HDPE)	RPM	2	11.449	10.449	5.224	0.26	0.793	5.69
	Load	2	142.095	142.095	71.047	5.75	0.048	70.63
	Time	2	27.952	27.952	13.976	1.13	0.469	13.89
	Residual error	2	19.694	24.694	12.347			9.79
	Total	8	201.190					
Wear (HDPE TPS Al_2O_3)	RPM	2	6.409	6.409	3.205	0.11	0.901	3.32
	Load	2	133.897	133.897	66.949	6.08	0.041	69.39
	Time	2	34.663	34.663	17.332	1.58	0.388	17.96
	Residual error	2	18.005	22.005	11.002			9.33
	Total	8	192.975					
Wear (Pure LDPE)	RPM	2	4.315	4.315	2.157	0.51	0.663	5.29
	Load	2	58.160	58.160	29.080	6.85	0.027	71.36
	Time	2	10.539	10.539	5.270	1.24	0.446	12.93
	Residual error	2	8.487	8.487	4.244			10.41
	Total	8	81.502					
Wear (LDPE DPS Al_2O_3)	RPM	2	4.555	4.555	2.2775	0.33	0.751	4.56
	Load	2	74.124	74.124	37.062	6.92	0.026	74.18
	Time	2	11.535	11.535	5.767	1.08	0.481	11.54
	Residual error	2	9.708	9.708	4.854			9.72
	Total	8	99.922					

Table 17 Response table for SN ratios for wear of pure HDPE, HDPE TPS Al_2O_3 , pure LDPE and LDPE DPS Al_2O_3 pins

	RPM	Load	Time
Wear (Pure HDPE)			
Rank	3	1	2
Wear (HDPE TPS Al_2O_3)			
Rank	3	1	2
Wear (Pure LDPE)			
Rank	3	1	2
Wear (LDPE DPS Al_2O_3)			
Rank	3	1	2

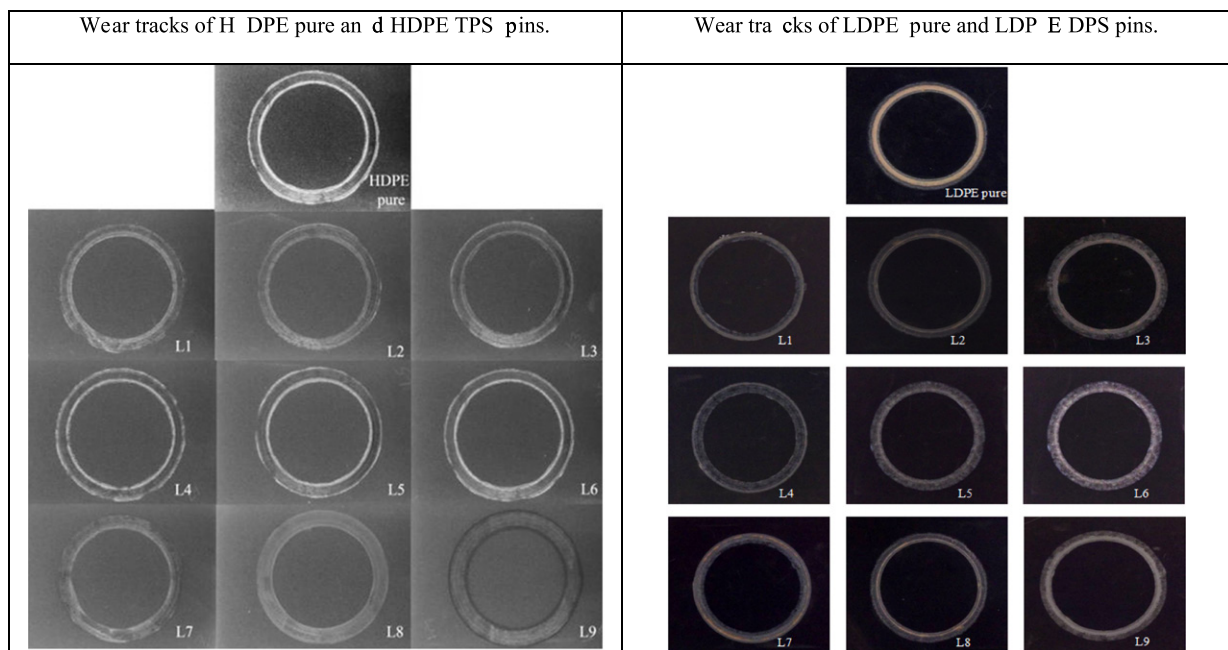
**Fig. 10** Wear tracks of HDPE pure; HDPE TPS pins and LDPE pure; LDPE DPS pins. Reproduced from Bedi, P., Singh, S., Ahuja, I.P.S., 2018. Investigations for Rapid Tooling Prepared With Waste Polymer-Based Hybrid Filament. Reference Module in Materials Science and Materials Engineering. Oxford: Elsevier, 1–18.

Table 18 SN ratios for dimensional accuracy and Hardness for HDPE TPS Al₂O₃RT

HDPE TPS Al ₂ O ₃ RT.			
S.No.	SN values for dimensional accuracy (deviation X)	SN values for dimensional accuracy (deviation Y)	SN values for Shore D Hardness
1	7.5350	11.3727	35.1934
2	7.1309	11.0568	35.2686
3	6.9357	10.4576	35.4170
4	15.3910	10.7520	35.2686
5	16.4782	10.1728	35.5630
6	15.9176	9.6297	35.5630
7	12.3958	10.4576	34.9638
8	12.0412	10.1728	35.1175
9	10.7520	9.8970	35.1934
LDPE DPS Al ₂ O ₃ RT.			
1	11.0568	9.1186	32.7698
2	11.3727	10.7520	33.0643
3	16.4782	12.3958	33.2552
4	10.7520	7.7443	32.5678
5	13.1515	11.0568	32.8691
6	18.4164	13.1515	33.2552
7	9.8970	8.4043	32.6694
8	14.4249	10.7520	32.9672
9	16.4782	11.7005	33.0643

Note: (It should be noted that "smaller the better" case is considered for SN values for deviation X and deviation Y and "larger the better" case is considered for SN values of Shore D hardness).

major factor contributing (with 65.35% contribution) for maximizing the shore D hardness of HDPE TPS Al₂O₃ RT at 5% level of significance.

It has been seen that level 2 of infill density (80%), level 3 of infill angle (75°), level 1 of infill speed (40 mm/s) are best settings for pure LDPE DPS Al₂O₃RT to have maximum dimensional accuracy in width (Deviation X). Further, infill angle came out to be major factor contributing (with 89.27% contribution) for maximizing the dimensional accuracy in width (Deviation X) of LDPE DPS Al₂O₃ RT at 5% level of significance.

It has been seen that level 1 of infill density (60%), level 3 of infill angle (75°), level 1 of infill speed (40 mm/s) are best settings for pure LDPE DPS Al₂O₃RT to have maximum dimensional accuracy in length (Deviation Y). Further, infill angle came out to be major factor contributing (with 92.18% contribution) for maximizing the dimensional accuracy in length (Deviation Y) of LDPE DPS Al₂O₃ RT at 5% level of significance.

It has been seen that level 1 of infill density (60%), level 3 of infill angle (75°), level 1 of infill speed (40 mm/s) are best settings for pure LDPE DPS Al₂O₃RT to have maximum shore D hardness of LDPE DPS Al₂O₃ RT. Further, infill angle came out to be major factor contributing (with 86.61% contribution) for maximizing the shore D hardness of LDPE DPS Al₂O₃ RT at 5% level of significance.

Further, from [Table 7](#), it has been seen that printed width and length for HDPE tooling printed as per level L5 is 10.15 and 35.31 respectively. Similarly, it has been seen that printed width and length for LDPE tooling printed as per level L5 is 10.32 and 35.38.

[Table 21](#) shows values for width and length of HDPE and LDPE RT printed repeatedly as per the best level specified before. Process capability analysis has been carried out for dimensional accuracy of HDPE TPS Al₂O₃ tooling and LDPE DPS Al₂O₃RT at best settings and summarized in [Table 22](#).

SN ratio analysis has been done for weight loss of WP (machinability) and weight loss for RT (tool life) while machining on vertical milling machine as per [Table 8](#). SN ratios for weight losses of WP and RT for case 1 and case 2 are summarized in [Table 23](#). [Fig. 12](#) shows SN plots for HDPE and LDPE RT. [Tables 24](#) and [25](#) shows variance analysis and response table for SN ratios respectively for HDPE and LDPE RT.

After combined optimization, it has been seen that level 1 of speed (500 rpm), level 3 of feed (40 mm/min), level 1 of depth of cut (1 mm) are best settings for maximizing the machinability of LDPE WP and tool life of HDPE TPS Al₂O₃ RT as per case 1. Further, feed came out to be major factor contributing (with 93.79% contribution) for maximizing the machinability of WP and tool life of RT under case 1 at 5% level of significance.

Similarly, after combined optimization, it has been seen that level 3 of speed (1000 rpm), level 3 of feed (40 mm/min), level 2 of depth of cut (2 mm) for maximizing the machinability of HDPE WP and tool life of LDPE DPS Al₂O₃ RT as per case 2. Further, feed came out to be major factor contributing (with 71.51% contribution) for maximizing the machinability of WP and tool life of RT under case 2 at 5% level of significance.

Further, Shore-D hardness and porosity of WP and RT has been checked for both cases. [Table 26](#) shows hardness and porosity of WP and RT for both case 1 and case 2.

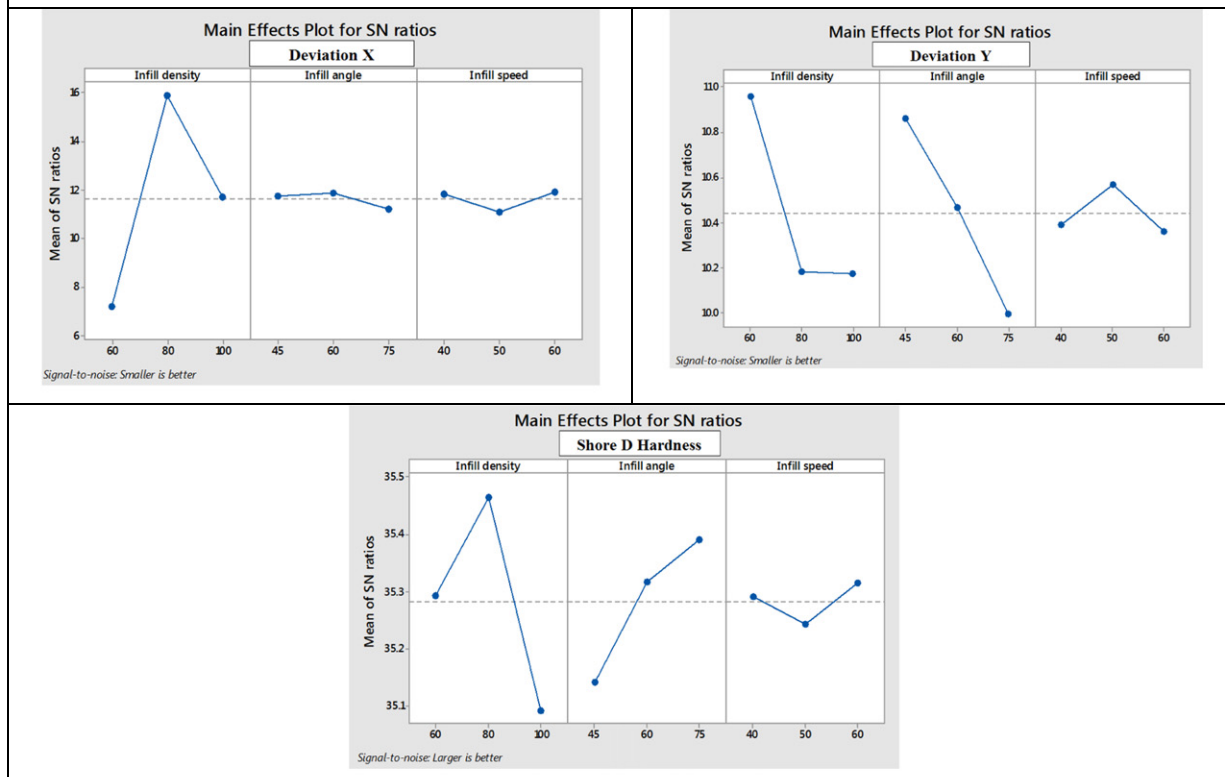
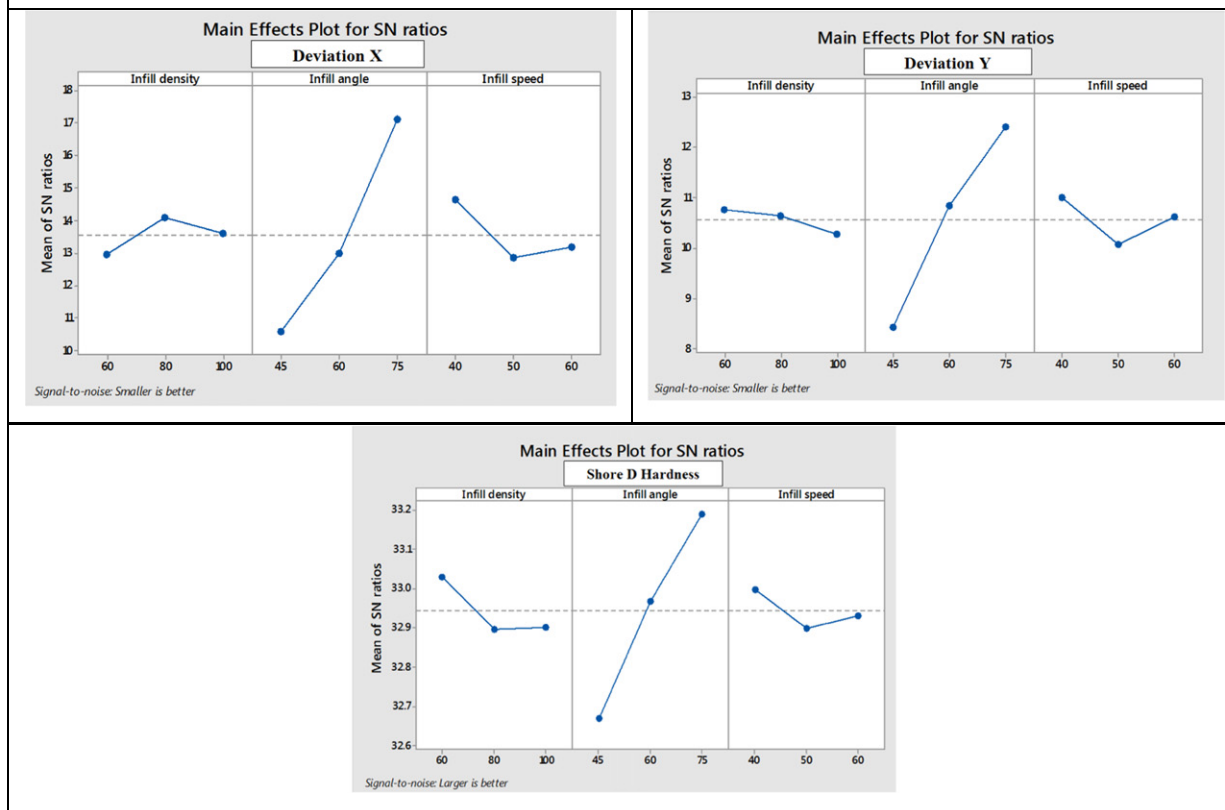
HDPE TPS Al₂O₃RT.LDPE DPS Al₂O₃RT.

Fig. 11 SN plots for dimensional accuracy in width and length (Deviation X and Deviation Y) and Shore-D hardness of HDPE and LDPE RT.

Zone B (machined portion) of WP and RT for case 1 and case 2 has been examined through optical microscope by support of software tool known as “Metallurgical Image Analysis Software (MIAS)”. Fig. 13 shows the optical micrographs at 100x along with the porosity values for all the WP and RT for case 1 and case 2.

Further, thermal analysis of WP and RT with the best tool life prepared under case 1 and case 2 has been performed for comparing both un-machined (zone A) and machined (zone B) portions by using DSC technique on Mettler Toledo- DSC setup. The thermal plots for WP and RT prepared under best settings as per combined optimization for case 1 and case 2 has been shown in Figs. 14 and 15 respectively. Repetitions had been necessary to eliminate any sort of effect arisen due to contamination and pre

Table 19 Variance analysis for dimensional accuracy in width and length (Deviation X and Deviation Y) and Shore-D hardness of HDPE and LDPE RT

		Source	DF	Seq SS	Adj SS	Adj MS	F	P	Percentage contribution (%)
HDPE TPS Al ₂ O ₃ RT.	Deviation X	Infill density	2	114.331	114.331	57.1654	578.89	0.002	98.05
		Infill angle	2	0.804	0.804	0.4020	4.07	0.197	0.69
		Infill speed	2	1.273	1.273	0.6365	6.45	0.134	1.09
		Residual Error	2	0.198	0.198	0.0988			0.17
		Total	8	116.605					
	Deviation Y	Infill density	2	1.12812	1.12812	0.564061	67.96	0.113	46.18
		Infill angle	2	1.22338	1.22338	0.611692	73.70	0.015	50.08
		Infill speed	2	0.07457	0.07457	0.037284	4.49	0.182	3.06
		Residual Error	2	0.01660	0.01660	0.008299			0.68
		Total	8	2.44267					
	Shore D hardness	Infill density	2	0.209502	0.209502	0.104751	41.53	0.024	65.35
		Infill angle	2	0.098156	0.098156	0.049078	19.46	0.059	30.62
		Infill speed	2	0.007886	0.007886	0.003943	1.56	0.390	2.46
		Residual Error	2	0.005045	0.005045	0.002522			1.57
		Total	8	0.320588					
LDPE DPS Al ₂ O ₃ RT.	Deviation X	Infill density	2	1.9483	1.9483	0.9741	3.01	0.249	2.64
		Infill angle	2	65.9549	65.9549	32.9775	102.06	0.010	89.27
		Infill speed	2	5.3335	5.3335	2.6668	8.25	0.108	7.22
		Residual Error	2	0.6462	0.6462	0.3231			0.86
		Total	8	73.8830					
	Deviation Y	Infill density	2	0.3651	0.3651	0.1826	1.04	0.490	1.39
		Infill angle	2	24.2998	24.2998	12.1499	69.23	0.014	92.18
		Infill speed	2	1.3440	1.3440	0.6720	3.83	0.207	5.10
		Residual Error	2	0.3510	0.3510	0.1755			1.33
		Total	8	26.3599					
	Shore D hardness	Infill density	2	0.03430	0.03430	0.017149	2.40	0.294	7.21
		Infill angle	2	0.41225	0.41225	0.206127	28.84	0.034	86.61
		Infill speed	2	0.01516	0.01516	0.007579	1.06	0.485	3.18
		Residual Error	2	0.01429	0.01429	0.007147			3.00
		Total	8	0.47601					

Table 20 Response values for SN ratios for dimensional accuracy in width and length (Deviation X and Deviation Y) and Shore-D hardness of HDPE and LDPE RT

Infill density	Infill angle	Infill speed
Deviation X (HDPE TPS Al ₂ O ₃ RT.)		
Rank 1	3	2
Deviation Y(HDPE TPS Al ₂ O ₃ RT.)		
Rank 2	1	3
Shore D hardness(HDPE TPS Al ₂ O ₃ RT.)		
Rank 1	2	3
Deviation X(LDPE DPS Al ₂ O ₃ RT.)		
Rank 3	1	2
Deviation Y(LDPE DPS Al ₂ O ₃ RT.)		
Rank 3	1	2
Shore D hardness(LDPE DPS Al ₂ O ₃ RT.)		
Rank 2	1	3

Table 21 Width for 10 HDPE and LDPE RT printed repeatedly as per level L5

<i>HDPE TPS Al₂O₃RT</i>				
<i>S.No.</i>	<i>Trial 1 (in mm)</i>	<i>Trial 2 (in mm)</i>	<i>Trial 3 (in mm)</i>	<i>Average printed width (in mm)</i>
1.	10.18	10.34	10.2	10.24
2.	10.12	10.18	10.15	10.15
3.	10.18	10.24	10	10.14
4.	10.15	10.32	10.19	10.22
5.	10.08	10.05	10.23	10.12
6.	10.12	10.02	10.1	10.08
7.	10.02	9.84	10.26	10.04
8.	10.14	10.04	10.18	10.12
9.	10.09	10.12	10.03	10.08
10.	10.54	10.11	10.07	10.24
<i>S.No.</i>	<i>Trial 1 (in mm)</i>	<i>Trial 2 (in mm)</i>	<i>Trial 3 (in mm)</i>	<i>Average printed length (in mm)</i>
1.	35.05	35.18	35.37	35.20
2.	35.1	35.12	35.23	35.15
3.	35.12	34.88	35	35.00
4.	35.11	35.21	35.28	35.20
5.	35.2	35.55	35.45	35.40
6.	35.28	35.4	35.4	35.36
7.	35.22	35.28	35.46	35.32
8.	35.15	35.26	35.34	35.25
9.	35.27	35.42	35.51	35.40
10.	35.16	35.28	35.16	35.20
<i>LDPE DPS Al₂O₃RT</i>				
<i>S.No.</i>	<i>Trial 1 (in mm)</i>	<i>Trial 2 (in mm)</i>	<i>Trial 3 (in mm)</i>	<i>Average printed width (in mm)</i>
1.	10.22	10.42	10.32	10.32
2.	10.14	10.24	10.22	10.20
3.	10.26	10.26	10.23	10.25
4.	10.18	10.24	10.24	10.22
5.	10.24	10.36	10.45	10.35
6.	10.44	10.28	10.06	10.26
7.	10.18	10.14	10.13	10.15
8.	10.34	10.39	10.53	10.42
9.	10.2	10.3	10.34	10.28
10.	10.14	10.11	10.05	10.10
<i>S.No.</i>	<i>Trial 1 (in mm)</i>	<i>Trial 2 (in mm)</i>	<i>Trial 3 (in mm)</i>	<i>Average printed length (in mm)</i>
1.	35.32	35.42	35.4	35.38
2.	35.12	35.28	35.2	35.20
3.	35.16	35.15	35.11	35.14
4.	35.34	35.4	35.37	35.37
5.	35.48	35.44	35.34	35.42
6.	35.12	35.19	35.11	35.14
7.	35.18	35.42	35.6	35.40
8.	35.34	35.25	35.49	35.36
9.	35.18	35.12	35	35.10
10.	35.4	35.37	35.61	35.46

Table 22 Process capability analysis table for dimensional accuracy (width and length) of HDPE TPS Al₂O₃RT and LDPE DPS Al₂O₃RT

<i>Term</i>	<i>HDPE TPS Al₂O₃ tooling</i>		<i>LDPE DPS Al₂O₃ tooling</i>	
	<i>Dimensional accuracy (width)</i>	<i>Dimensional accuracy (length)</i>	<i>Dimensional accuracy (width)</i>	<i>Dimensional accuracy (length)</i>
USL	10.40 mm	35.70 mm	10.80 mm	36.00 mm
LSL	9.80 mm	34.70 mm	10.00 mm	35.00 mm
Target value	10.00 mm	35.00 mm	9.80 mm	34.50 mm
Cp	1.586	1.538	1.511	1.476
Cpk	1.359	1.391	1.375	1.383
PPM < LSL	0.03	0.21	18.60	1.27
PPM > USL	22.84	15.13	0.39	16.67
PPM	22.87	15.34	18.99	17.95

Table 23 SN ratios for weight losses of WP and RT for case 1 and case 2

	CASE 1		CASE 2	
	SN ratios for weight loss of WP	SN ratios for weight loss of RT	SN ratios for weight loss of WP	SN ratios for weight loss of RT
Level 1	− 5.12980	33.5556	− 14.6097	6.70716
Level 2	− 2.82926	31.0568	− 12.9950	6.16070
Level 3	0.28201	26.7448	− 12.1813	5.02074
Level 4	− 5.16122	32.3958	− 14.7986	6.76375
Level 5	− 2.54522	29.3704	− 12.1813	6.21382
Level 6	0.34901	28.1787	− 11.0879	4.82176
Level 7	− 4.97442	31.0568	− 14.3340	7.39144
Level 8	− 2.60364	28.4043	− 13.6387	6.33906
Level 9	0.45681	26.5580	− 10.0614	4.85208

Note: (It should be noted that “larger the better” case is considered for SN values for weight loss for WP, “smaller the better” case is considered for SN values for weight loss for RT and “larger the better” case is considered for SN values for combined optimization for both case 1 and case 2).

stored history. It has been judged from thermal plots, enthalpy values for machined portions (zone B) for both the WP and RT (both cases) came out to be higher than that of un-machined portions (zone A) giving a clear idea that machined portion becomes more thermally stable than that of un-machined portion.

Conclusions

In this study, conclusions drawn at each stage/process are categorized as following:

Process Parametric Optimization for Twin Screw Extruder

- It has been seen that level 3 of composition (HDPE 90% by weight, Al₂O₃ 300G 3.33% by weight, Al₂O₃ 400G 3.33% by weight and Al₂O₃ 500G 3.34% by weight), level 3 of load (15 kgf), level 2 of temperature (190°C) and level 3 of RPM (45) came out to be best settings for HDPE filament wire to bear the maximum peak load. Further, composition came out to be the major factor contributing (with 74.69% contribution) for maximizing the peak load of HDPE filament wire at 5% level of significance.
- It has been seen that level 3 of composition (HDPE 90% by weight, Al₂O₃ 300G 3.33% by weight, Al₂O₃ 400G 3.33% by weight and Al₂O₃ 500G 3.34% by weight), level 3 of load (15 kgf), level 2 of temperature (190°C) and level 3 of RPM (45) are best settings for HDPE filament wire to have maximum peak elongation. Further, temperature came out to be the major factor contributing (with 38.92% contribution) for maximizing the peak elongation of HDPE filament wire at 5% level of significance.
- It has been seen that level 3 of composition (HDPE 90% by weight, Al₂O₃ 300G 3.33% by weight, Al₂O₃ 400G 3.33% by weight and Al₂O₃ 500G 3.34% by weight), level 3 of load (15 kgf), level 2 of temperature (190°C) and level 3 of RPM (45) are best settings for HDPE filament wire to bear the maximum break load. Further, composition came out to be the major factor contributing (with 74.95% contribution) for maximizing the break load of HDPE filament wire at 5% level of significance.
- It has been seen that level 3 of composition (HDPE 90% by weight, Al₂O₃ 300G 3.33% by weight, Al₂O₃ 400G 3.33% by weight and Al₂O₃ 500G 3.34% by weight), level 3 of load (15 kgf), level 2 of temperature (190°C) and level 3 of RPM (45) are best settings for HDPE filament wire to have maximum break elongation. Further, temperature came out to be the major factor contributing (with 41.27% contribution) for maximizing the break elongation of HDPE filament wire at 5% level of significance.
- It has been seen that level 2 of composition (HDPE 50% by weight, Al₂O₃ 400G 25% by weight and Al₂O₃ 500G 25% by weight), level 2 of load (10 kgf), level 2 of temperature (190°C) and level 2 of RPM (40) are best settings for HDPE filament wire to have maximum Young's Modulus. Further, composition came out to be the major factor contributing (with 75.94% contribution) for maximizing the Young's modulus of HDPE filament wire at 5% level of significance.

After combined optimization, It has been seen that level 3 of composition (HDPE 90% by weight, Al₂O₃ 300G 3.33% by weight, Al₂O₃ 400G 3.33% by weight and Al₂O₃ 500G 3.34% by weight), level 1 of load (5 kgf), level 2 of temperature (190°C) and level 2 of RPM (40) are best settings for HDPE filament wire to have maximum mechanical strength. Further, composition came out to be the major factor contributing (with 51.15% contribution) for maximizing the mechanical strength of HDPE filament wire at 5% level of significance while effect of other parameters can be ignored as their p-value is coming more than 0.05.

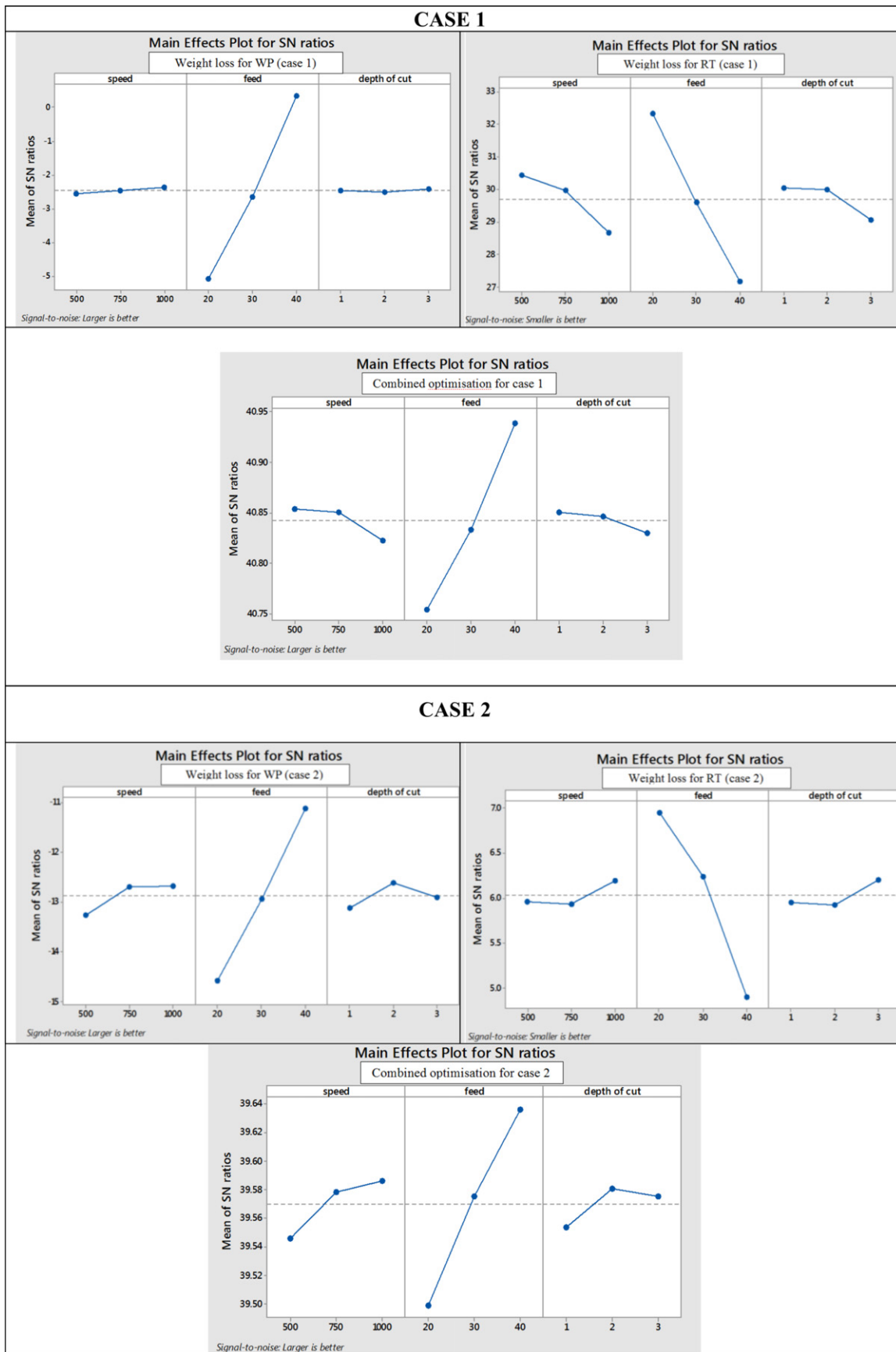


Fig. 12 SN plots for WP and RT as per case 1 and case 2.

Table 24 Variance analysis for WP and RT as per case 1 and case 2

		Source	DF	Seq SS	Adj SS	Adj MS	F	P	Percentage contribution (%)
CASE 1	Weight loss for WP	Speed	2	0.0519	0.0519	0.0259	3.68	0.213	0.12
		Feed	2	44.7473	44.7473	22.3737	3177.82	0.001	99.82
		Depth of cut	2	0.0146	0.0146	0.0073	1.04	0.491	0.03
		Residual Error	2	0.0141	0.0141	0.0070			0.03
		Total	8	44.8279					
	Weight loss for RT	Speed	2	5.100	5.100	2.5501	3.84	0.207	10.51
		Feed	2	40.217	40.217	20.1087	30.26	0.032	82.88
		Depth of cut	2	1.875	1.875	0.9375	1.41	0.415	3.86
		Residual Error	2	1.329	1.329	0.6646			2.74
		Total	8	48.522					
	Combined optimization	Speed	2	0.001732	0.001732	0.000866	1.73	0.366	3.16
		Feed	2	0.051398	0.051398	0.025699	51.41	0.019	93.79
		Depth of cut	2	0.000673	0.000673	0.000336	0.67	0.598	1.23
		Residual Error	2	0.001000	0.001000	0.000500			1.82
		Total	8	0.054802					100
CASE 2	Weight loss for WP	Speed	2	0.6692	0.6692	0.3346	0.28	0.781	3.11
		Feed	2	18.0844	18.0844	9.0422	7.58	0.017	84.08
		Depth of cut	2	0.3680	0.3680	0.1840	0.15	0.866	1.72
		Residual Error	2	2.3865	2.3865	1.1933			11.09
		Total	8	21.5082					
	Weight loss for RT	Speed	2	0.12256	0.12256	0.06128	2.02	0.331	1.79
		Feed	2	6.53454	6.53454	3.26727	107.61	0.009	95.22
		Depth of cut	2	0.14495	0.14495	0.07248	2.39	0.295	2.11
		Residual Error	2	0.06073	0.06073	0.03036			0.88
		Total	8	6.86278					
	Combined optimization	Speed	2	0.002709	0.002709	0.001355	0.36	0.733	6.77
		Feed	2	0.028607	0.028607	0.014304	3.85	0.026	71.51
		Depth of cut	2	0.001248	0.001248	0.000624	0.17	0.856	3.13
		Residual Error	2	0.007438	0.007438	0.003719			18.59
		Total	8	0.040002					

Table 25 Response table for WP and RT as per case 1 and case 2

<i>Speed</i>	<i>Feed</i>	<i>Depth of cut</i>
Weight loss for WP (case 1)		
Rank 2	1	3
Weight loss for RT (case 1)		
Rank 2	1	3
Combined optimization (case 1)		
Rank 2	1	3
Weight loss for WP (case 2)		
Rank 2	1	3
Weight loss for RT (case 2)		
Rank 3	1	2
Combined optimization (case 2)		
Rank 2	1	3

- It has been seen that level 2 of composition (LDPE 50% by weight, Al₂O₃ 400G 25% by weight and Al₂O₃ 500G 25% by weight), level 3 of load (15 kgf), level 1 of temperature (185°C) and level 1 of RPM (35) are best settings for LDPE filament wire to bear the maximum peak load. Further, composition came out to be major factor contributing (with 90.26% contribution) for maximizing the peak load of LDPE filament wire at 5% level of significance.
- It has been seen that level 1 of composition (LDPE 50% by weight, and Al₂O₃ 500G 50% by weight), level 3 of load (15 kgf), level 2 of temperature (190°C) and level 3 of RPM (45) are best settings for LDPE filament wire to have maximum peak elongation. Further, load came out to be major factor contributing (with 56.98% contribution) for maximizing the peak elongation of LDPE filament wire at 5% level of significance.
- It has been seen that level 2 of composition (LDPE 50% by weight, Al₂O₃ 400G 25% by weight and Al₂O₃ 500G 25% by weight), level 3 of load (15 kgf), level 1 of temperature (185°C) and level 1 of RPM (35) are best settings for LDPE filament wire to bear the maximum break load. Further, composition came out to be major factor contributing (with 88.51% contribution) for maximizing the break load of LDPE filament wire at 5% level of significance.
- It has been seen that level 1 of composition (LDPE 50% by weight, and Al₂O₃ 500G 50% by weight), level 3 of load (15 kgf), level 2 of temperature (190°C) and level 3 of RPM (45) are best settings for LDPE filament wire to have maximum break elongation. Further, load came out to be major factor contributing (with 64.99% contribution) for maximizing the break elongation of LDPE filament wire at 5% level of significance.
- It has been seen that level 2 of composition (LDPE 50% by weight, Al₂O₃ 400G 25% by weight and Al₂O₃ 500G 25% by weight), level 3 of load (15 kgf), level 2 of temperature (190°C) and level 2 of RPM (40) are best settings for LDPE filament wire to have maximum Young's Modulus. Further, composition came out to be major factor contributing (with 91.88% contribution) for maximizing the Young's modulus of LDPE filament wire at 5% level of significance.

After combined optimization, it has been seen that level 3 of composition (LDPE 50% by weight, Al₂O₃ 400G 25% by weight and Al₂O₃ 500G 25% by weight), level 3 of load (15 kgf), level 2 of temperature (190°C) and level 1 of RPM (35) are best settings for LDPE filament wire to have maximum mechanical strength. Further, composition came out to be the major factor contributing (with 42.13% contribution) for maximizing the mechanical strength of LDPE filament wire at 5% level of significance while effect of other parameters can be ignored as their p-value is coming more than 0.05

Process Parametric Optimization for Pin on Disk Experimentation

- It has been seen that level 1 of rpm (250), level 1 of load (1 kgf), level 3 of time (15 min) are best settings for pure HDPE pin to have minimum wear. Further, load came out to be major factor contributing (with 70.63% contribution) for minimizing the wear of pure HDPE pin at 5% level of significance.
- It has been seen that level 1 of rpm (250), level 1 of load (1 kgf), level 3 of time (15 min) are best settings for HDPE TPS Al₂O₃ pin to have minimum wear. Further, load came out to be major factor contributing (with 69.31% contribution) for minimizing the wear of HDPE TPS Al₂O₃ pin at 5% level of significance.
- It has been seen that level 1 of rpm (250), level 1 of load (1 kgf), level 3 of time (15 min) are best settings for pure LDPE pin to have minimum wear. Further, load came out to be major factor contributing (with 71.36% contribution) for minimizing the wear of pure LDPE pin at 5% level of significance.
- It has been seen that level 1 of rpm (250), level 1 of load (1 kgf), and level 3 of time (15 min) are best settings for LDPE DPS Al₂O₃ pin to have minimum wear. Further, load came out to be major factor contributing (with 74.18% contribution) for minimizing the wear of LDPE DPS Al₂O₃ pin at 5% level of significance.

Table 26 Hardness and porosity values for WP and RT for both case 1 and case 2

		WP				RT					
			Hardness for Zone A	Hardness for Zone B	Porosity before machining (%)	Porosity after machining (%)		Hardness for Zone A	Hardness for Zone B	Porosity before machining (%)	Porosity after machining (%)
Case 1	Level 1	LDPE	39.5	43	7.41	3.12	HDPE reinforced	71.5	80.5	30.21	15.48
	Level 2		40	46		3.94		74.5	81.5		14.21
	Level 3		42.5	41.5		7.48		74.5	81		24.23
	Level 4		41.5	40		3.22		73.5	78		14.58
	Level 5		40.5	46.5		4.29		77.5	80		17.66
	Level 6		42	47.5		7.81		74	81.5		16.98
	Level 7		40	44.5		3.47		76	80		14.34
	Level 8		39.5	41		4.78		72.5	83.5		17.97
	Level 9		40	46		8.42		77	87.5		22.42
Case 2	Level 1	HDPE	56.5	61.5	15.54	8.47	LDPE reinforced	44.5	50.5	22.79	13.47
	Level 2		58.5	64.5		12.49		48.5	58.5		14.54
	Level 3		57	62		10.22		48	52.5		15.49
	Level 4		56	67		9.64		45	57.5		14.41
	Level 5		56.5	68		11.49		43.5	55		16.74
	Level 6		57.5	64		12.09		45.5	56		18.49
	Level 7		56.5	65.5		9.43		48	55.5		15.42
	Level 8		58	61.5		10.69		50.5	58		16.57
	Level 9		59.5	63		14.57		48	52.5		19.54

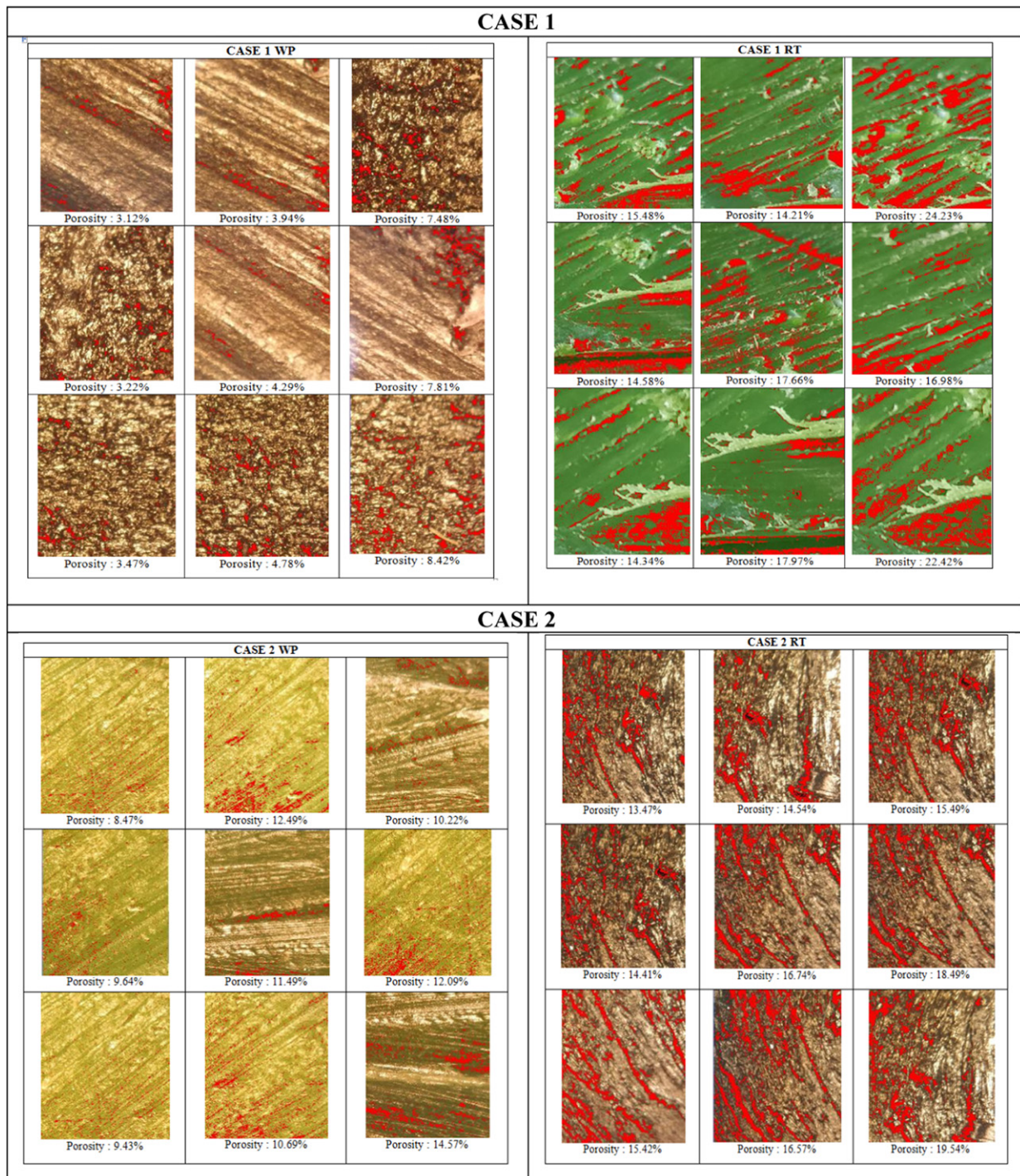


Fig. 13 Optical micrographs of WP and RT after machining (Zone B) (Case 1 and Case 2).

- It has been observed that wear tracks for pure HDPE pin and pure LDPE pin were quite sharper than that of tracks TPS based HDPE pins and DPS based LDPE pins which clearly indicates that wear decreases when HDPE gets reinforced with TPS Al_2O_3 reinforcement and LDPE gets reinforced with DPS Al_2O_3 reinforcement.

Process Parametric Optimization for Fused Deposition Modeling (FDM)

- It has been seen that level 2 of infill density (80%), level 2 of infill angle (60°), level 3 of infill speed (60 mm/s) are best settings for pure HDPE TPS Al_2O_3 RT to have maximum dimensional accuracy in width (Deviation X) of HDPE TPS Al_2O_3 RT. Further,

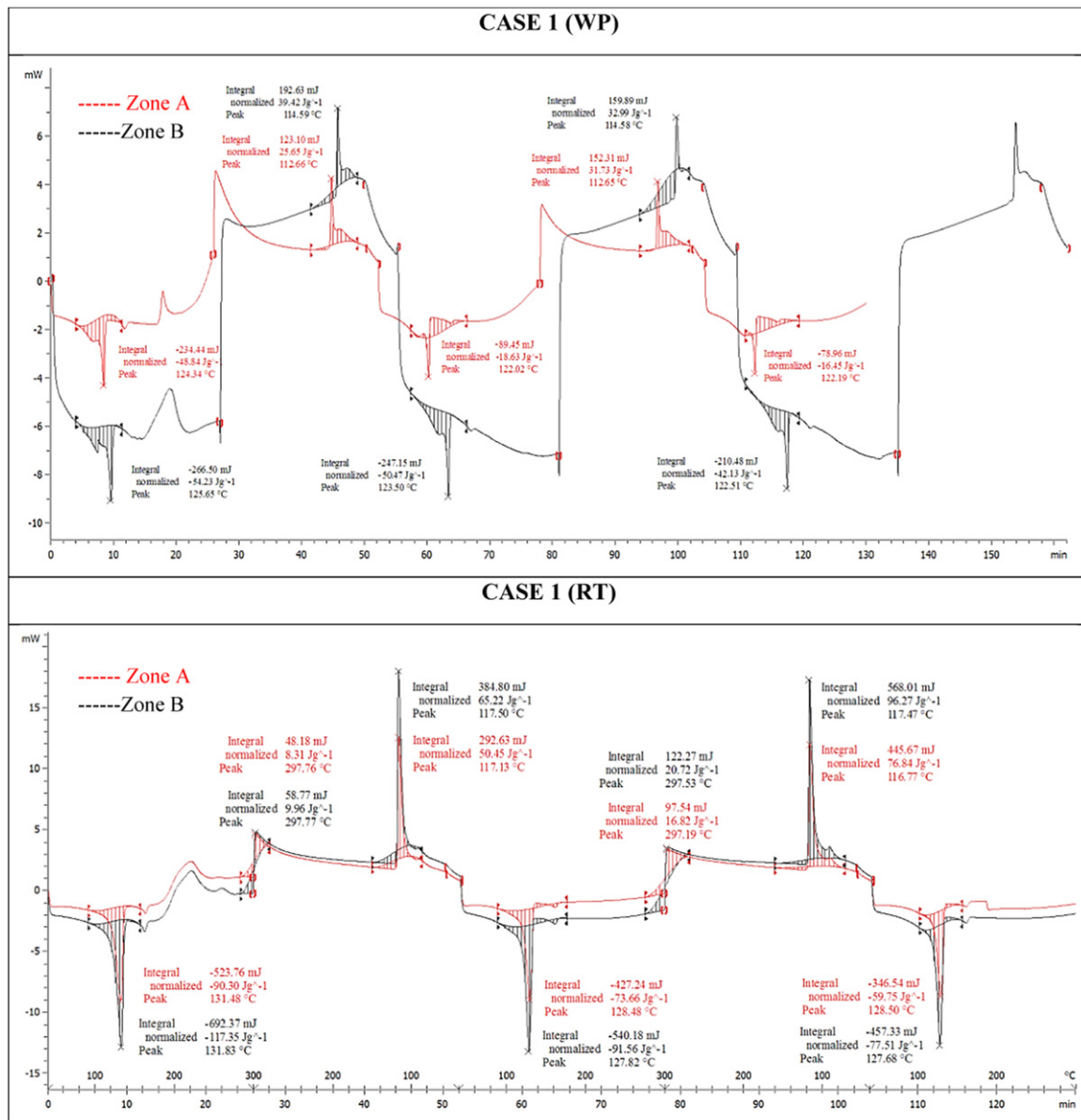


Fig. 14 Thermal plots for WP and RT prepared under best settings as per combined optimization for case 1.

infill density came out to be major factor contributing (with 98.05% contribution) for maximizing the dimensional accuracy in width (Deviation X) of HDPE TPS Al₂O₃ RT at 5% level of significance.

- It has been seen that level 1 of infill density (60%), level 1 of infill angle (45°), level 2 of infill speed (50 mm/s) are best settings for pure HDPE TPS Al₂O₃ RT to have maximum dimensional accuracy in length (Deviation Y) of HDPE TPS Al₂O₃ RT. Further, infill angle came out to be major factor contributing (with 50.08% contribution) for maximizing the dimensional accuracy in width (Deviation Y) of HDPE TPS Al₂O₃ RT at 5% level of significance.

After combined optimization, it has been seen that level 2 of infill density (80%), level 1 of infill angle (45°), level 1 of infill speed (40 mm/s) are best settings for HDPE TPS Al₂O₃ RT to have maximum dimensional accuracy (both in terms of width and length) of HDPE TPS Al₂O₃ RT. Further, infill density came out to be major factor contributing (with 94.94% contribution) for maximizing the dimensional accuracy in width and length (Deviation X and Deviation Y) of HDPE TPS Al₂O₃ RT at 5% level of significance.

- It has been seen that level 2 of infill density (80%), level 3 of infill angle (75°), level 3 of infill speed (60 mm/s) are best settings for pure HDPE TPS Al₂O₃ RT to have maximum shore D hardness of HDPE TPS Al₂O₃ toolings. Further, infill density came out to be major factor contributing (with 65.35% contribution) for maximizing the shore D hardness of HDPE TPS Al₂O₃ RT at 5% level of significance.

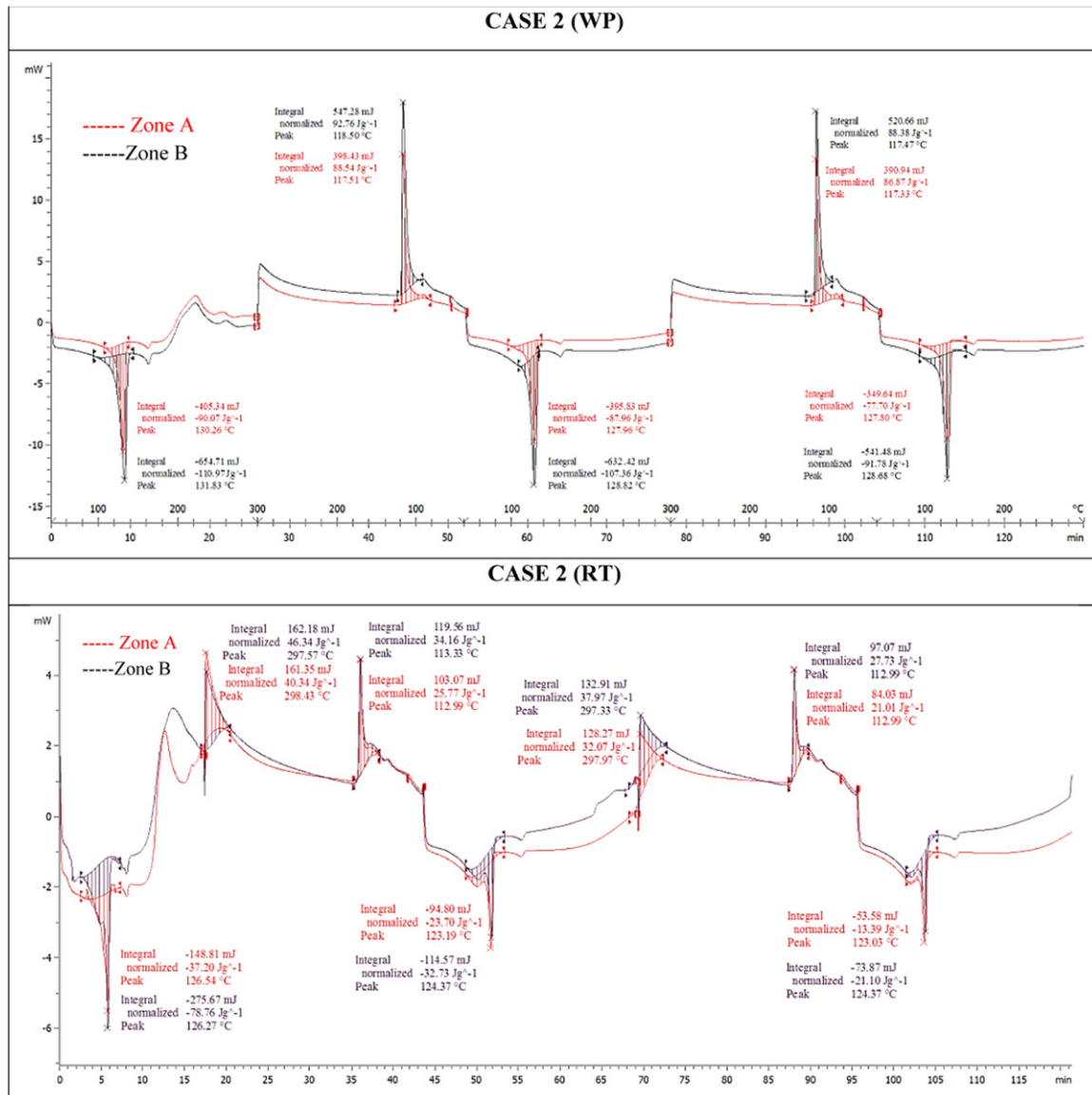


Fig. 15 Thermal plots for WP and RT prepared under best settings as per combined optimization for case 2.

- It has been seen that level 2 of infill density (80%), level 3 of infill angle (75°), level 1 of infill speed (40 mm/s) are best settings for pure LDPE DPS Al_2O_3 RT to have maximum dimensional accuracy in width (Deviation X). Further, infill angle came out to be major factor contributing (with 89.27% contribution) for maximizing the dimensional accuracy in width (Deviation X) of LDPE DPS Al_2O_3 RT at 5% level of significance.
- It has been seen that level 1 of infill density (60%), level 3 of infill angle (75°), level 1 of infill speed (40 mm/s) are best settings for pure LDPE DPS Al_2O_3 RT to have maximum dimensional accuracy in length (Deviation Y). Further, infill angle came out to be major factor contributing (with 92.18% contribution) for maximizing the dimensional accuracy in length (Deviation Y) of LDPE DPS Al_2O_3 RT at 5% level of significance.

After combined optimization, it has been seen that level 1 of infill density (60%), level 1 of infill angle (45°), level 2 of infill speed (50 mm/s) are best settings for LDPE DPS Al_2O_3 RT to have maximum dimensional accuracy (both in terms of width and length). Further, infill angle came out to be major factor contributing (with 92.00% contribution) for maximizing the dimensional accuracy in width and length (Deviation X and Deviation Y) of LDPE DPS Al_2O_3 RT at 5% level of significance.

- It has been seen that level 1 of infill density (60%), level 3 of infill angle (75°), level 1 of infill speed (40 mm/s) are best settings for pure LDPE DPS Al_2O_3 RT to have maximum shore D hardness of LDPE DPS Al_2O_3 RT. Further, infill angle came out to be major factor contributing (with 86.61% contribution) for maximizing the shore D hardness of LDPE DPS Al_2O_3 RT at 5% level of significance.

Process Capability Analysis

- The process capability analysis for dimensional accuracy (in terms of width) of HDPE TPS Al_2O_3 tooling has been done and values for C_p and C_{pk} came out to be 1.586 and 1.359 respectively (i.e., > 1.33) which clearly indicate that HDPE TPS Al_2O_3 tooling is dimensionally accurate (in terms of width).
- The process capability analysis for dimensional accuracy (in terms of length) of HDPE TPS Al_2O_3 tooling has been done and values for C_p and C_{pk} came out to be 1.538 and 1.391 respectively (i.e., > 1.33) which clearly indicate that HDPE TPS Al_2O_3 tooling is dimensionally accurate (in terms of length).
- The process capability analysis for dimensional accuracy (in terms of width) of LDPE DPS Al_2O_3 tooling has been done and values for C_p and C_{pk} came out to be 1.511 and 1.375 respectively (i.e., > 1.33) which clearly indicate that LDPE DPS Al_2O_3 tooling is dimensionally accurate (in terms of width).
- The process capability analysis for dimensional accuracy (in terms of length) of LDPE DPS Al_2O_3 tooling has been done and values for C_p and C_{pk} came out to be 1.476 and 1.383 respectively (i.e., > 1.33) which clearly indicate that LDPE DPS Al_2O_3 tooling is dimensionally accurate (in terms of length).

Process Parametric Optimization for Vertical Milling Machine

- It has been seen that level 3 of speed (1000 rpm), level 3 of feed (40 mm/min), level 3 of depth of cut (3 mm) are best settings for maximizing the weight loss (thus maximizing the machining) of pure LDPE WP. Further, feed came out to be major factor contributing (with 99.82% contribution) for maximizing the weight loss (thus maximizing the machining) of WP under case 1 at 5% level of significance.
- It has been seen that level 1 of speed (500 rpm), level 1 of feed (20 mm/min), level 1 of depth of cut (1 mm) are best settings for minimizing the weight loss (thus maximizing the tool life) of HDPE TPS Al_2O_3 tooling. Further, feed came out to be major factor contributing (with 82.88% contribution) for minimizing the weight loss (thus maximizing the tool life) of RT under case 1 at 5% level of significance.

After combined optimization, it has been seen that level 1 of speed (500 rpm), level 3 of feed (40 mm/min), level 1 of depth of cut (1 mm) are best settings for maximizing the machinability of LDPE WP and tool life of HDPE TPS Al_2O_3 RT as per case 1. Further, feed came out to be major factor contributing (with 93.79% contribution) for maximizing the machinability of WP and tool life of RT under case 1 at 5% level of significance.

- It has been seen that level 3 of speed (1000 rpm), level 3 of feed (40 mm/min), level 2 of depth of cut (2 mm) are best settings for maximizing the weight loss (thus maximizing the machining) of pure HDPE WP. Further, feed came out to be major factor contributing (with 84.08% contribution) for maximizing the weight loss (thus maximizing the machining) of WP under case 2 at 5% level of significance.
- It has been seen that level 3 of speed (1000 rpm), level 1 of feed (20 mm/min), level 3 of depth of cut (3 mm) are best settings for minimizing the weight loss (thus maximizing the tool life) of LDPE DPS Al_2O_3 tooling. Further, feed came out to be major factor contributing (with 95.22% contribution) for minimizing the weight loss (thus maximizing the tool life) of RT under case 2 at 5% level of significance.

After combined optimization, it was seen that level 3 of speed (1000 rpm), level 3 of feed (40 mm/min), level 2 of depth of cut (2 mm) for maximizing the machinability of HDPE WP and tool life of LDPE DPS Al_2O_3 RT as per case 2. Further, feed came out to be major factor contributing (with 71.51% contribution) for maximizing the machinability of WP and tool life of RT under case 2 at 5% level of significance.

Limitations and Future Scope of the Study

- In the present study, use of single reinforcement ($\text{SiC}/\text{Al}_2\text{O}_3$) has been studied. Further, study may be extended by using hybrid reinforcements like $\text{SiC} + \text{Al}_2\text{O}_3$ in different proportions.
- In the present study, HDPE and LDPE has been used as matrix material (as commercially, HDPE and LDPE constitute major portion of polymer waste) for printing of RT. Other waste polymer materials like acrylonitrile butadiene styrene (ABS), polylactic acid (PLA) etc. may be explored as matrix material for printing of RT.
- In the present study, thermoplastic materials have been used in printing applications. Till now, no work has been reported on use of thermosets as filler material in printing applications. Further, study may be conducted to use thermosets as reinforcement in thermoplastic matrix.
- In the present study, machining with RT on vertical milling has been explored. Further, studies may be performed for turning, drilling etc., along with their parametric optimization.
- In the present study, layers of same material (HDPE/LDPE) have been printed on FDM. In future studies, multi-material printing may be explored for tool life.
- In the present study, thermal analysis of RT has been done. Further, dynamic analysis may be done to calculate loss modulus/storage modulus.

Acknowledgement

The authors are highly thankful to DST (GoI) File No. file No.TSG/NTS/2014/104for providing financial assistance to carry out the research work.

See also: Prospect of Recycling of Plastic Product to Minimize Environmental Pollution

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CO₂ Laser Cutting of Glass Fiber-Reinforced Plastics

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Introduction

Laser cutting in general is an effective way to reduce production and manufacturing costs. This is due to the advantage of high production rates as well as the fact that lasers can be mechanized, computer controlled, and integrated into assembly lines. Many industries have been revolutionized by the application of laser equipment in their production lines. This is because of the high-quality and low distortion characteristics of the cutting action that can be achieved. Most materials can be cut by the process including metals, wood, plastics, rubber, composites, etc. On the other hand, some materials cannot be cut by this process due to safety reasons (Powell, 1998). GFRP, sometimes known as glass fiber-reinforced polymer (GFRP), is one of the materials that can be cut using a CO₂ laser beam. This composite material has been used for many decades for all engineering applications including the automotive, marine, and construction industries (Sathishkumar *et al.*, 2014; Masuelli, 2013). GFRP has several advantages including high strength to weight ratio, high fracture toughness, and excellent corrosion and thermal resistances. Currently, GFRP has become an economical alternative to other materials in highly corrosive industrial applications. Furthermore, ongoing research has ensured that GFRP now has a combination of properties such as high specific strength, high specific stiffness, and light weight, which makes it attractive for aircraft and aerospace applications. Actually, GFRP is a promising material for many other applications, including boats, automobiles, water tanks, roofing, and pipes (Eltawahni, 2011; Palanikumar, 2007).

Laser cutting of GFRP has attracted many authors (Di Illio *et al.*, 1990; Zhou and Mahdavian, 2004; Nuss, 1988; Tagliaferri *et al.*, 1985; Caprino and Tagliaferri, 1988; Caprino *et al.*, 1995a,b; Cenna and Mathew, 2002; Goeke and Emmelmann, 2010; Riveiro *et al.*, 2007; Dilio and Tagliaferri, 1989; Bamforth *et al.*, 2006). Di Illio *et al.* (1990) have studied the laser cutting of aramid fiber-reinforced plastics. They discussed the effect of process parameters on the quality of the laser cut. They succeeded in presenting a new method of digital image processing for evaluating the cut quality. Zhou and Mahdavian (2004) have discussed the capability of a low power CO₂ laser in cutting various nonmetallic materials including plastics. They developed a theoretical model to estimate the depth of cut that can be achieved if the material properties and cutting speed are known. It was found that the theoretical model agrees with the experimental cutting results. It was mentioned that this development will assist those in the manufacturing industries to choose a suitable laser system for cutting or marking nonmetallic materials. Also, it was demonstrated that a 60 W laser power can be used for cutting nonmetallic materials and is suitable for plastic board cutting. Finally, it was concluded that the deeper the cutting depth, the more energy is required. CO₂ laser cutting of reinforced plastic mold parts has been carried out and the cutting results have been compared with other cutting techniques, such as water jet cutting, milling punching, sawing, using a conventional knife, and using an ultrasonic excited knife. This work was carried out by Nuss (1988). It was shown that laser cutting is faster and cleaner and reduces the time spent on postoperation work. The laser cutting of composites of aramide, graphite, and glass cloth-reinforced polyester have been studied by Tagliaferri *et al.* (1985). They examined the morphology of the cut surfaces by scanning electron microscopy. It was found that the thermal properties of the fibers and matrix are the principal factors that affect cutting performance. It was concluded that the quality of the cut surfaces depends on the type of composite being cut.

Caprino and Tagliaferri (1988) have proposed a simple analytical model to predict the kerf depth and optimal working conditions. It was confirmed that in the laser cutting of carbon reinforced plastic composite materials, the poor quality of the cut surface is due to the difference in the thermal properties of the carbon fiber and the resin matrix. In fact, they observed the best results when laser cutting of aramid fabric reinforced polyester (AFRP) due to the polymeric nature of both of the fiber and matrix. It was reported that their experimental results are in excellent agreement with their theoretical predictions for GFRP, AFRP, and GFRP composites. It was proven that the depth of penetration is linearly correlated with the laser power. In addition, they formulated criteria for the classification of cut quality, based on kerf geometry and HAZ size, to help in selecting the optimum cutting conditions. Caprino *et al.* (1995a) investigated the CO₂ laser cutting of GFRP composites. They introduced an analytical model that allows the depth of kerf to be predicted as a function of the direction of the beam in relation to the direction of travel of the material being worked. They reported a substantial agreement between the experimental results and the theoretical predictions. They stressed the importance of the following when laser cutting of GFRP. This is to characterize the spatial distribution of power of the laser beam and to relate this to the distribution of the fiber in the matrix. The CO₂ laser cutting of glass fiber-reinforced plastic (GFRP) composites has been investigated separately by Caprino *et al.* (1995b). They again proposed an analytical model that allows the depth of the kerf to be predicted. It was found that the theoretical model is in substantial agreement with the experimental results. They developed an equation to determine the influence of the parameters of the material structure on the kerf depth. It was concluded that the optimal cutting conditions are strongly affected by any nonuniform distribution of the fibers across the thickness of the sample. Cenna and Mathew (2002) have presented a

theoretical model that considers the spatial distribution of the laser beam, the interaction time between the laser beam and the workpiece, the absorption coefficient, and thermal properties of the material. They reported a good agreement between their results and the theoretical predictions. It was found that the theoretical model successfully predicts the cut quality parameters such as kerf width, the angle of the cut surfaces, and the transmitted energy loss through the kerf. Moreover, it was suggested that a different material removal mechanism is involved in the laser cutting of GFRP. Finally, it was reported that as the cutting speed increases, the kerf width and the kerf angle decrease.

Goeke and Emmelmann (2010) have investigated the influence of laser cutting parameters on the quality of carbon fiber-reinforced plastic (CFRP) parts. Their challenge was to apply a CO₂ laser beam and a fiber laser to cut this material and achieve a small heat-affected zone (HAZ). A large HAZ is a result of the large difference between the decomposition temperatures of resin and fiber material (i.e., the decomposition temperature of carbon fiber is about 3000 K and that of epoxy resin is about 550 K). It was found that both the HAZ size and the kerf width decrease significantly with high cutting speeds and small energy inputs. Additionally, they demonstrated that both the CO₂ and the fiber laser beam sources are applicable for the laser beam cutting (LBC) of CFRP forming high-quality parts. However, it was found that when processing CFRP laminates with thickness between 1 and 7 mm the CO₂ laser has an advantage when compared with the fiber laser due to the higher absorption of the 10.6 μm wavelength, by the material. A study of the possibilities of using a high-quality CO₂ laser to cut 3-mm-thick samples of CFRP in plate form was presented by Riveiro *et al.* (2007). They investigated the influence of different processing parameters such as the pulse frequency, the pulse energy, the duty cycle, and type and pressure of the assist gas on the cut quality. They evaluated the quality of the cuts in terms of kerf width, perpendicularity of cut kerf, delaminating degree, and extension of the HAZ. It was reported that an adequate selection of values for the processing parameters allowed good quality cuts to be obtained. The thermal damage caused during laser cutting of aramid fiber/epoxy laminates was investigated by Dilio and Tagliaferri (1989). They examined samples cut with a 500 W CO₂ CW laser using different parameters by both optical and scanning electron microscopy. It was reported that cracks were detected in plies with the fiber direction at 90° to the cutting direction. They developed a model to relate the material damage to the cutting parameters. Bamforth *et al.* (2006) have investigated CO₂ laser cutting of nylon textiles with the aim of optimizing the edge quality. It was reported that nylon textiles can be cut using either a CW or a pulsed CO₂ laser. They optimized the process with the aid of a procedure referred to as 3D finite difference technique. It was mentioned that the edge quality can be significantly better when using the pulsed cutting mode.

If a manufacturer wishes to introduce laser cutting as a technique in any manufacturing process, it is necessary to study the effect of the process on a new material. A number of preferred characteristics such as accuracy of the cut and quality of the surface finish can be specified and also process characteristics such as high speed and low power usage can be also stipulated. It is then necessary to vary the laser input parameters and test whether or not the desired quality features are achieved. This procedure is usually performed by skilled workers. However, this procedure of selection of parameters is based on trial and error and is usually time-consuming. Moreover, the conventional one by one technique is not systematic and usually does not lead to an optimized combination of laser cutting parameters. This is due to the fact that the laser cutting process is affected by complex interactions of the different input and output parameters. A systematic study, based on design of experiment techniques followed by the analysis of the results using response surface methodology (RSM), will allow the detection and visualization of the interactive effects of the input parameters on the results. Once a study of this kind has been done, the optimum combinations of laser cutting parameters can be selected and then used to produce the desired specifications (Eltawahni, 2011). Therefore, it's the aim of this research work to apply RSM, using Box–Behnken design (BBD), to model and optimize the laser cutting process of GFRP and to explore the effect of each parameter on the quality features.

Experimental Procedure

Material

The properties of the GFRP sheet utilized in this research are listed in Table 1. A 3-mm-thick GFRP provided in sheet form with dimensions of 900 × 450 mm was used as a workpiece.

Laser Cutting

For GFRP, four process parameters were controlled laser power, cutting speed, air pressure and focal point position. Table 2 shows the process input parameters and experimental design levels used for 3-mm-thick GFRP. A conical shape nozzle was used with

Table 1 Mechanical properties of GFRP

Material	Tensile strength (MPa)	Flexural strength (MPa)	Elongation (%)	Density (kg/m ³)
Fiber, EMC450	133	175	2.1	–
Resin, polyester	47	90	2.2	1100

Abbreviation: GFRP, Glass fiber-reinforced polymer.

Table 2 Process variables and experimental design levels for GFRP

Parameter	Code	Unit	−1	0	+1
Laser power	A	kW	500	900	1300
Cutting speed	B	mm/min	2000	3500	5000
Argon pressure	C	bar	2	3	4
Focal point position	D	mm	−3	−1.5	0

Abbreviation: GFRP, Glass fiber-reinforced polymer.

Table 3 Design matrix for 3-mm-thick GFRP

Std	Run	Factors			
		A, W	B, mm/min	C, bar	D, mm
1	24	500	2000	3	−1.5
2	18	1300	2000	3	−1.5
3	27	500	5000	3	−1.5
4	17	1300	5000	3	−1.5
5	5	900	3500	2	−3
6	3	900	3500	4	−3
7	21	900	3500	2	0
8	13	900	3500	4	0
9	14	500	3500	3	−3
10	26	1300	3500	3	−3
11	1	500	3500	3	0
12	2	1300	3500	3	0
13	19	900	2000	2	−1.5
14	9	900	5000	2	−1.5
15	6	900	2000	4	−1.5
16	7	900	5000	4	−1.5
17	8	500	3500	2	−1.5
18	15	1300	3500	2	−1.5
19	12	500	3500	4	−1.5
20	23	1300	3500	4	−1.5
21	10	900	2000	3	−3
22	16	900	5000	3	−3
23	11	900	2000	3	0
24	22	900	5000	3	0
25	25	900	3500	3	−1.5
26	4	900	3500	3	−1.5
27	20	900	3500	3	−1.5
28	29	900	3500	3	−1.5
29	28	900	3500	3	−1.5

Abbreviation: GFRP, Glass fiber-reinforced polymer.

Table 4 Operating costs break down when compressed argon is used

Element of cost	Calculations	Cutting cost, €/h
Laser electrical power	$(20.88 \text{ kVA})(0.8 \text{ pf})(\text{€}0.12359/\text{kWh}) \times (P/1.5)$	$1.376 \times P$
Chiller electrical power	$(11.52 \text{ kVA})(0.8 \text{ pf})(\text{€}0.12359/\text{kWh})$	1.139
Motion controller power	$(4.8 \text{ kVA})(0.8 \text{ pf})(\text{€}0.12359/\text{kWh})$	0.475
Exhaust system power	$(0.9 \text{ kWh})(\text{€}0.12359/\text{kWh})$	0.111
Laser gas LASPUR208	$\{(\text{€}1043.93/\text{bottle})/(\text{1500 l/bottle})\} \times 7.5 \text{ l/72 h}$	0.072
Gas bottle rental	$(\text{€}181.37/720 \text{ h})$	0.252
Chiller additives	$(\text{€}284.80/\text{year})/(8760 \text{ h/year})$	0.033
Compressed argon	$\text{€}12.174 \times 10^{-3}/\text{liter} \times F[\text{l/h}]$	$12.174 \times 10^{-3} \times F$
Nozzle tip	$(\text{€}7.20/200 \text{ h})$	0.036
Exhaust system filters	$(\text{€}5/100 \text{ h})$	0.05
Focus lens	$(\text{€}186/\text{lens})/(1000 \text{ h})$	0.186
Maintenance labor (with overhead)	$(12 \text{ h}/2000 \text{ h operation})(\text{€}50/\text{h})$	0.30
Total operation cost per hour		$2.654 + 1.376 \times P + 12.174 \times 10^{-3} \times F$

nozzle diameter of 1.5 mm and the stand-off distance was maintained at a constant value of 0.5 mm. During the trial cut runs it was found that argon was the most suitable inert gas and leads to good quality cut with less edge burning and minimum HAZ, kerf, and roughness value. Therefore, argon gas was supplied coaxially as an assist gas. Specimens were cut from the panel for each condition in Table 3. Table 3 is a design matrix for four variables using BBD.

Estimation of Operating Cost

Laser cutting operating costs can be estimated as cutting per hour or per unit length. The laser system used in this work utilized CO₂ using a static volume of laser gases of approximately 7.5 l every 72 h. For this laser system with 1.5 kW maximum output power the operating costs generally falls into the categories listed in Table 4. The operating cost calculation does not account for any unscheduled breakdowns and maintenance, such as a breakdown in the table motion controller or PC hard disk replacement. The total approximated operating cost per hour as a function of process parameters can be estimated by $2.654 + 1.376 \times P + 12.174 \times 10^{-5} \times F$. While the total approximated operating cost per unit length of the cut is given by Eq. (1) assuming 85% utilization. Eq. (2) was used to calculate the cutting cost per meter for all samples. At pressure above 1.05 bar the compressed argon will flow in a supersonic manner. Note that these pressure values are independent of nozzle diameter. At pressure value above this threshold the flow rate in [l/h] of these fluids through a nozzle can be easily calculated from Eq. (3) (Eltawahni, 2011).

$$\text{Cutting cost [Euro/m]} = \frac{2.654 + 1.376 \times P [\text{kW}] + 12.174 \times 10^{-3} \times F [l/h]}{(0.85) \times S [\text{mm/min}] [60 \text{min/h}] [m/1000 \text{mm}]} \quad (1)$$

$$\text{cutting cost [Euro/m]} = \frac{2.654 + 1.376 \times P + 12.174 \times 10^{-3} \times F}{0.051 \times S} \quad (2)$$

$$\text{Flow rate [l/h]} = F = 492 \times d^2 (p_g + 1) \quad (3)$$

where:

d : Nozzle diameter [mm].

P_g : Nozzle supply pressure [bar].

Table 5 Experimentally recorded responses for 3-mm-thick GFRP

Std	Run	Responses				
		Upper kerf, mm	Lower kerf, mm	Ratio	HAZ, mm	Cost, €/m
1	24	0.413	0.336	1.231	0.078	0.0380
2	18	0.490	0.458	1.071	0.089	0.0488
3	27	0.324	0.298	1.090	0.044	0.0152
4	17	0.430	0.373	1.154	0.047	0.0195
5	5	0.690	0.348	1.982	0.084	0.0241
6	3	0.542	0.296	1.830	0.057	0.0256
7	21	0.356	0.409	0.871	0.082	0.0241
8	13	0.330	0.380	0.870	0.058	0.0256
9	14	0.661	0.247	2.682	0.065	0.0217
10	26	0.560	0.351	1.594	0.090	0.0279
11	1	0.332	0.207	1.602	0.054	0.0217
12	2	0.311	0.390	0.796	0.084	0.0279
13	19	0.388	0.415	0.935	0.078	0.0421
14	9	0.313	0.402	0.778	0.056	0.0168
15	6	0.336	0.439	0.765	0.075	0.0448
16	7	0.361	0.351	1.029	0.044	0.0179
17	8	0.390	0.219	1.783	0.078	0.0210
18	15	0.517	0.415	1.245	0.099	0.0272
19	12	0.418	0.306	1.368	0.060	0.0225
20	23	0.477	0.449	1.062	0.086	0.0287
21	10	0.743	0.324	2.292	0.078	0.0434
22	16	0.556	0.339	1.642	0.046	0.0174
23	11	0.388	0.432	0.899	0.082	0.0434
24	22	0.371	0.397	0.935	0.049	0.0174
25	25	0.347	0.351	0.989	0.064	0.0248
26	4	0.302	0.375	0.805	0.079	0.0248
27	20	0.382	0.365	1.047	0.065	0.0248
28	29	0.365	0.358	1.019	0.060	0.0248
29	28	0.325	0.354	0.920	0.061	0.0248

Abbreviations: GFRP, Glass fiber-reinforced polymer; HAZ: heat-affected zone.

Table 6 ANOVA table for upper kerf width reduced quadratic model for GFRP

Source	Sum of squares	DF	Mean square	F value	Prob > F	
Model	0.331	5	0.066	20.453	<0.0001	Significant
A	0.005	1	0.005	1.559	0.2243	
B	0.013	1	0.013	4.157	0.0531	
D	0.231	1	0.231	71.371	<0.0001	
A ²	0.011	1	0.011	3.525	0.0732	
D ²	0.077	1	0.077	23.685	<0.0001	
Residual	0.074	23	0.003			
Lack of fit	0.070	19	0.004	3.712	0.1060	Not Sig.
Pure error	0.004	4	0.001			
Cor total	0.405	28				
R ² = 0.816			Pred R ² = 0.681			
Adj R ² = 0.777			Adeq precision = 14.381			

Abbreviation: GFRP, Glass fiber-reinforced polymer.

Table 7 ANOVA table for lower kerf width reduced quadratic model for GFRP

Source	Sum of squares	DF	Mean square	F value	Prob > F	
Model	0.091	6	0.015	15.622	<0.0001	Significant
A	0.057	1	0.057	58.581	<0.0001	
B	0.005	1	0.005	5.126	0.0338	
D	0.008	1	0.008	8.223	0.0089	
A ²	0.008	1	0.008	8.470	0.0081	
B ²	0.006	1	0.006	6.046	0.0223	
D ²	0.004	1	0.004	4.636	0.0425	
Residual	0.021	22	0.001			
Lack of fit	0.021	18	0.001	12.287	0.0129	Not Sig.
Pure error	0.000378	4	0.000094			
Cor total	0.112	28.000				
R ² = 0.810			Pred R ² = 0.649			
Adj R ² = 0.758			Adeq precision = 15.629			

Abbreviation: GFRP, Glass fiber-reinforced polymer.

Table 8 ANOVA table for ratio reduced quadratic model for GFRP

Source	Sum of squares	DF	Mean square	F value	Prob > F	
Model	5.747	6	0.958	24.786	<0.0001	Significant
A	0.669	1	0.669	17.310	0.0004	
B	0.027	1	0.027	0.687	0.4163	
D	3.048	1	3.048	78.880	<0.0001	
BD	0.118	1	0.118	3.053	0.0945	
A ²	0.622	1	0.622	16.105	0.0006	
D ²	1.492	1	1.492	38.605	<0.0001	
Residual	0.850	22	0.039			
Lack of fit	0.813	18	0.045	4.836	0.0687	Not Sig.
Pure error	0.037	4	0.009			
Cor total	6.597	28				
R ² = 0.871			Pred R ² = 0.749			
Adj R ² = 0.836			Adeq precision = 17.282			

Abbreviation: GFRP, Glass fiber-reinforced polymer.

Table 9 ANOVA table for HAZ reduced quadratic model for GFRP

Source	Sum of squares	DF	Mean square	F value	Prob > F	
Model	0.005	3	0.002	22.971	<0.0001	Significant
A	0.001	1	0.001	15.496	0.0006	
B	0.003	1	0.003	42.749	<0.0001	
D	0.001	1	0.001	10.669	0.0032	
Residual	0.002	25	0.000			
Lack of fit	0.002	21	0.00008	1.259	0.4581	Not Sig.
Pure error	0.00024	4	0.00006			
Cor total	0.007	28				
$R^2 = 0.734$			Pred $R^2 = 0.621$			
Adj $R^2 = 0.702$			Adeq precision = 16.284			

Abbreviations: GFRP, Glass fiber-reinforced polymer; HAZ: heat-affected zone.

Table 10 ANOVA table for operating cost reduced quadratic model for GFRP

Source	Sum of squares	DF	Mean square	F value	Prob > F	
Model	0.002	6	0.0004015	6492.140	<0.0001	Significant
A-Laser power	0.0001318	1	0.0001318	2132.067	<0.0001	
B-Cutting speed	0.002	1	0.0020385	32964.025	<0.0001	
C-Argon pressure	0.0000079	1	0.0000079	127.822	<0.0001	
AB	0.0000105	1	0.0000105	169.505	<0.0001	
BC	0.0000006	1	0.0000006	10.162	0.0043	Not Sig.
B ²	0.00022	1	0.0002195	3549.25814	<0.0001	
Residual	0.0000014	22	0.0000001			
Cor total	0.00241	28				
$R^2 = 0.999$			Pred $R^2 = 0.998$			
Adj $R^2 = 0.999$			Adeq precision = 267.620			

Abbreviation: GFRP, Glass fiber-reinforced polymer.

$$\begin{aligned} \text{Upper kerf} = & 0.57218 - 4.05984\text{E} - 004 * \text{Laser power} - 2.23148\text{E} - 005 \\ & * \text{Cutting speed} + 0.048005 * \text{Focal position} + 2.54019\text{E} - 007 \\ & * \text{Laser power}^2 + 0.046823 * \text{Focal position}^2 \end{aligned} \quad (4)$$

$$\begin{aligned} \text{Lower kerf} = & 0.24754 + 5.64113\text{E} - 004 * \text{Laser power} - 1.05228\text{E} - 004 \\ & * \text{Cutting speed} - 0.017252 * \text{Focal position} - 2.18003\text{E} - 007 \\ & * \text{Laser power}^2 + 1.30976\text{E} - 008 * \text{Cutting speed}^2 \\ & - 0.011469 * \text{Focal position}^2 \end{aligned} \quad (5)$$

$$\begin{aligned} \text{Ratio} = & 2.65577 - 3.96840\text{E} - 003 * \text{Laser power} + 8.31539\text{E} - 005 * \text{Cutting speed} \\ & + 0.016723 * \text{Focal position} + 7.63331\text{E} - 005 * \text{Cutting speed} \\ & * \text{Focal position} + 1.87675\text{E} - 006 * \text{Laser power}^2 \\ & + 0.20663 * \text{Focal position}^2 \end{aligned} \quad (6)$$

$$\begin{aligned} \text{HAZ} = & 0.10854 + 2.42708\text{E} - 005 * \text{Laser power} - 1.07500\text{E} - 005 \\ & * \text{Cutting speed} - 8.05556\text{E} - 003 * \text{Argon pressure} \end{aligned} \quad (7)$$

$$\begin{aligned} \text{Operating Cost} = & 0.064484 + 1.77300\text{E} - 005 * \text{Laser power} - 2.28465\text{E} - 005 \\ & * \text{Cutting speed} + 1.73648\text{E} - 003 * \text{Argon pressure} - 2.69804\text{E} - 009 \\ & * \text{Laser power} * \text{Cutting speed} - 2.64247\text{E} - 007 * \text{Cutting speed} \\ & * \text{Argon pressure} + 2.48261\text{E} - 009 * \text{Cutting speed}^2 \end{aligned} \quad (8)$$

Results and Discussion

For this composite material, five responses were successfully measured, namely upper kerf, lower kerf, ratio between upper to lower kerfs, HAZ, and operating cost. The average values of at least three consistent measurements all measured responses are listed in Table 5. The operating cost was estimated using Eq. (2). The estimated operating cost for each experiment is presented in Table 5.

Development of the Mathematical Models

Design-expert software V7 was used to analyze the measured responses. The fit summary output indicates that, for all responses, the quadratic models are statistically recommended for further analysis as they have the maximum predicted and adjusted R^2 (Eltawahni, 2011). The test for significance of the regression models, the test for significance on individual model coefficients, and the lack of fit test were performed using the same statistical package for all responses. By selecting the step-wise regression method, the insignificant model terms can be automatically eliminated. The resulting ANOVA tables (Tables 6–10) for the reduced quadratic models outline the analysis of variance for each response and illustrate the significant model terms. The same tables show also the other adequacy measures R^2 , Adjusted R^2 and Predicted R^2 . All adequacy measures are close to 1, which are in reasonable agreement and indicate adequate models (Eltawahni et al., 2010, 2012). The adequate precision compares the range of the predicted value at the design points to the average prediction error. In all cases the values of adequate precision ratios are significantly greater than 4. An adequate precision ratio above 4 indicates an adequate model (Eltawahni et al., 2011). The developed mathematical models are shown in Eqs. (4)–(8) in terms of actual factors.

Table 11 Confirmation experiments for GFRP

Exp. no.	A	B	C	D		Upper kerf	Lower kerf	Ratio	HAZ	Cost
1	716.92	4844.97	3.75	−1.05	Actual	0.312	0.337	0.925	0.046	0.0173
					Predicted	0.305	0.343	1.000	0.044	0.0171
					Error %	2.257	−1.788	−8.128	4.348	1.0372
2	746.41	4796.57	3.99	−1.36	Actual	0.306	0.327	0.937	0.047	0.0178
					Predicted	0.325	0.346	1.000	0.043	0.0175
					Error %	−6.131	−5.800	−6.746	9.235	1.900
3	500	5000	2	−0.85	Actual	0.328	0.263	1.246	0.050	0.0147
					Predicted	0.314	0.283	1.367	0.051	0.0153
					Error %	4.173	−7.523	−9.753	−1.629	−3.858

Abbreviations: GFRP, Glass fiber-reinforced polymer; HAZ: heat-affected zone.

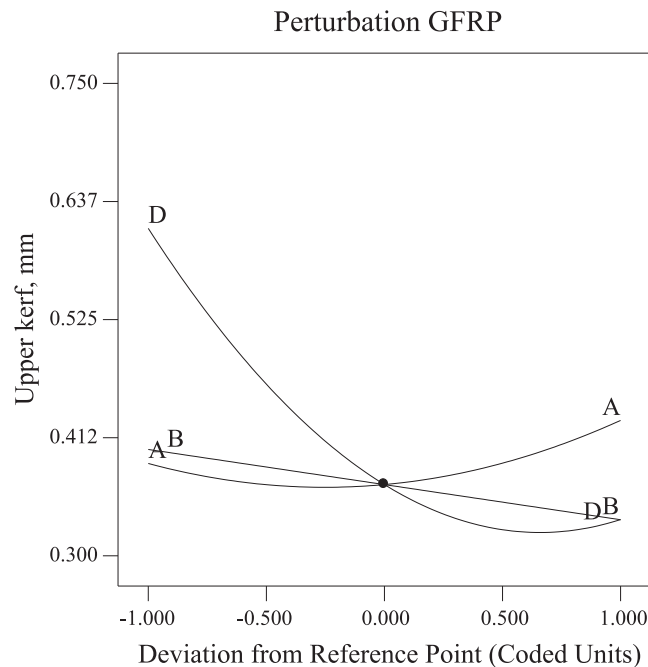


Fig. 1 Perturbation plots showing the effect of each factor on the upper kerf for 3-mm-thick glass fiber-reinforced polymer.

Validation of the Developed Models

With the aim of verifying the adequacy of the developed models furthermore, three confirmation experiments were carried out by using new test conditions. These experiments are taken from the optimization results, which are within the investigated range. By using the point prediction option in the software, all the response values can be predicted by substituting these conditions into the previously developed models. **Table 11** presents the experimental conditions, the actual experimental values, the predicted values and the percentage errors. It is clear that all the values of percentage error for all the five responses are in agreement with the values reported in *Benyounis et al. (2008)* and *Olabi et al. (2007)*. Therefore, it would strongly suggest that the models are valid.

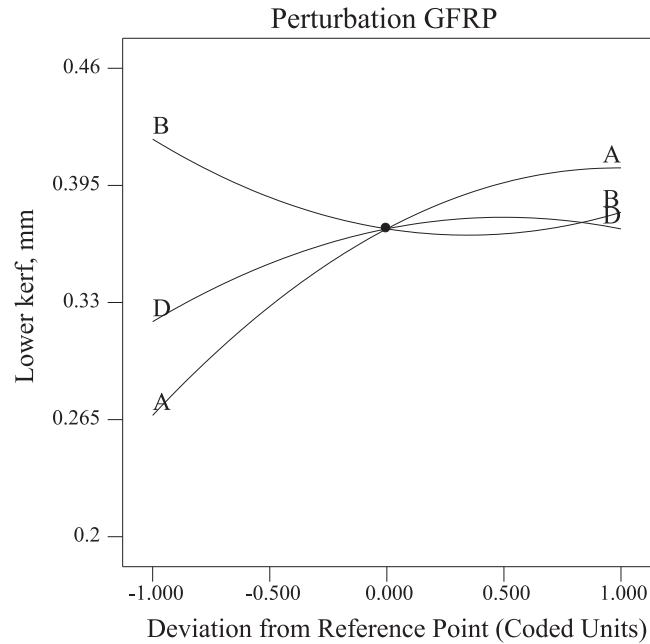


Fig. 2 Perturbation plots showing the effect of each factor on the lower kerf for 3-mm-thick glass fiber-reinforced polymer.

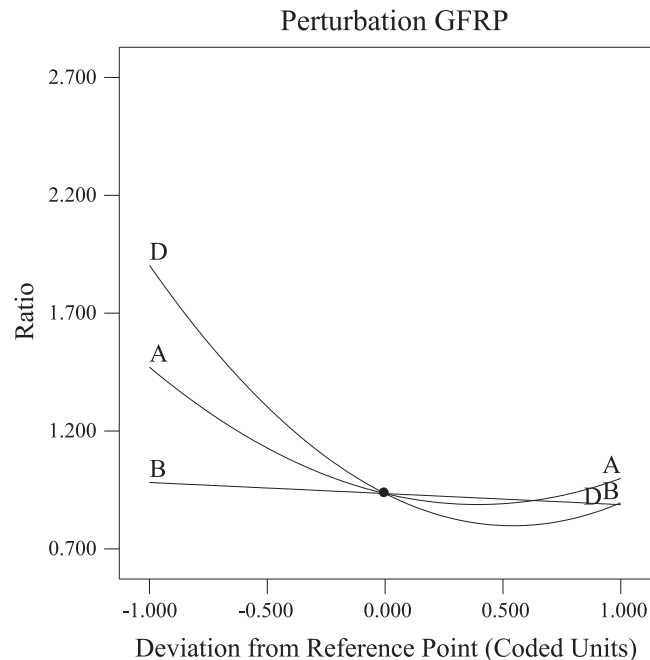


Fig. 3 Perturbation plots showing the effect of each factor on the ratio for 3-mm-thick glass fiber-reinforced polymer.

Effect of Process Factors on the Responses

Upper kerf

The results demonstrate that the laser cutting of GFRP is of acceptable quality and depends mainly on the distribution of the fiber along the thickness, which agrees with [Caprino et al. \(1995a\)](#). It is evident from [Fig. 1](#) that the focal point position has the most important significant effect on the upper kerf for GFRP, followed by the cutting speed and the laser power. However, the upper kerf increases as the focal position and cutting speed decrease, while it increases as the laser power increases. These results are in good agreement with the results reported in [Cenna and Mathew \(2002\)](#). The percentage changes in the upper kerf as a result of changing each factor from its lowest value to its highest value while keeping the other factors at their center values are as follows:

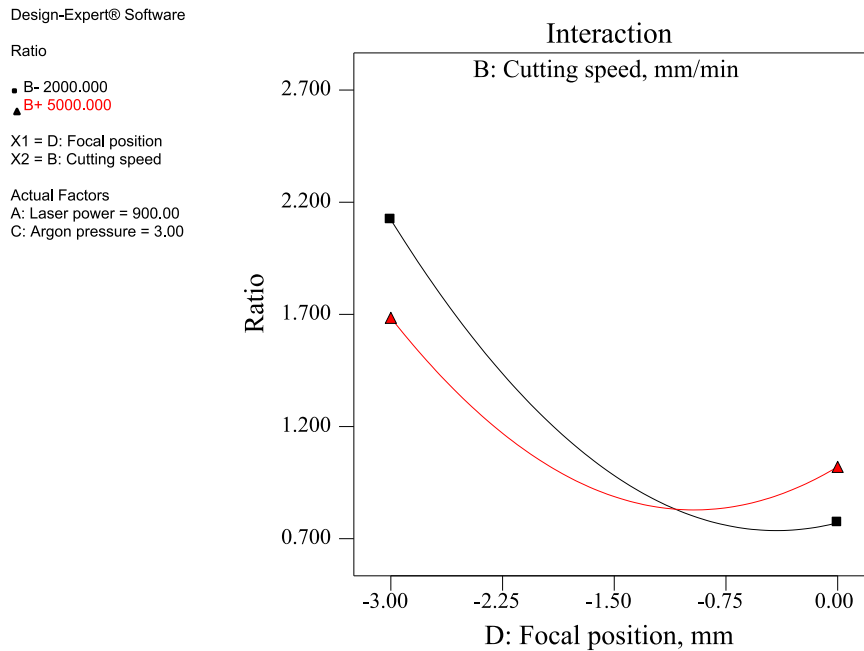


Fig. 4 Interaction graph between cutting speed and focal position for 3-mm glass fiber-reinforced polymer.

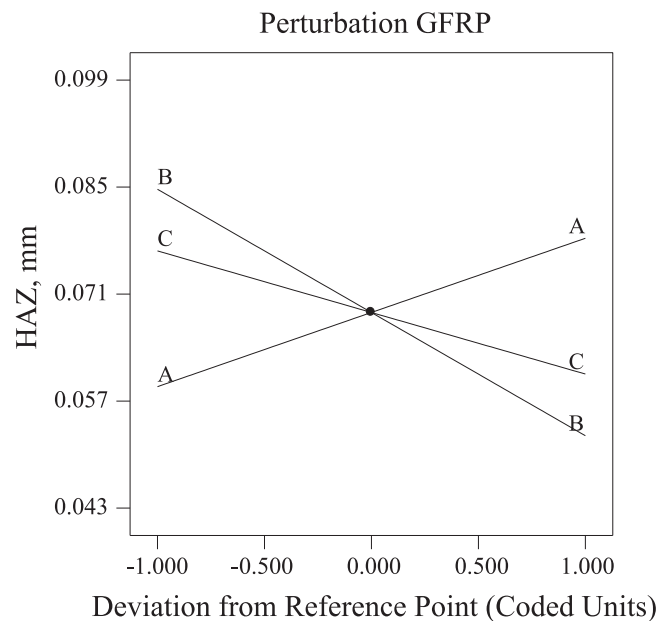


Fig. 5 Perturbation plots showing the effect of each factor on the ratio for 3-mm-thick glass fiber-reinforced polymer.

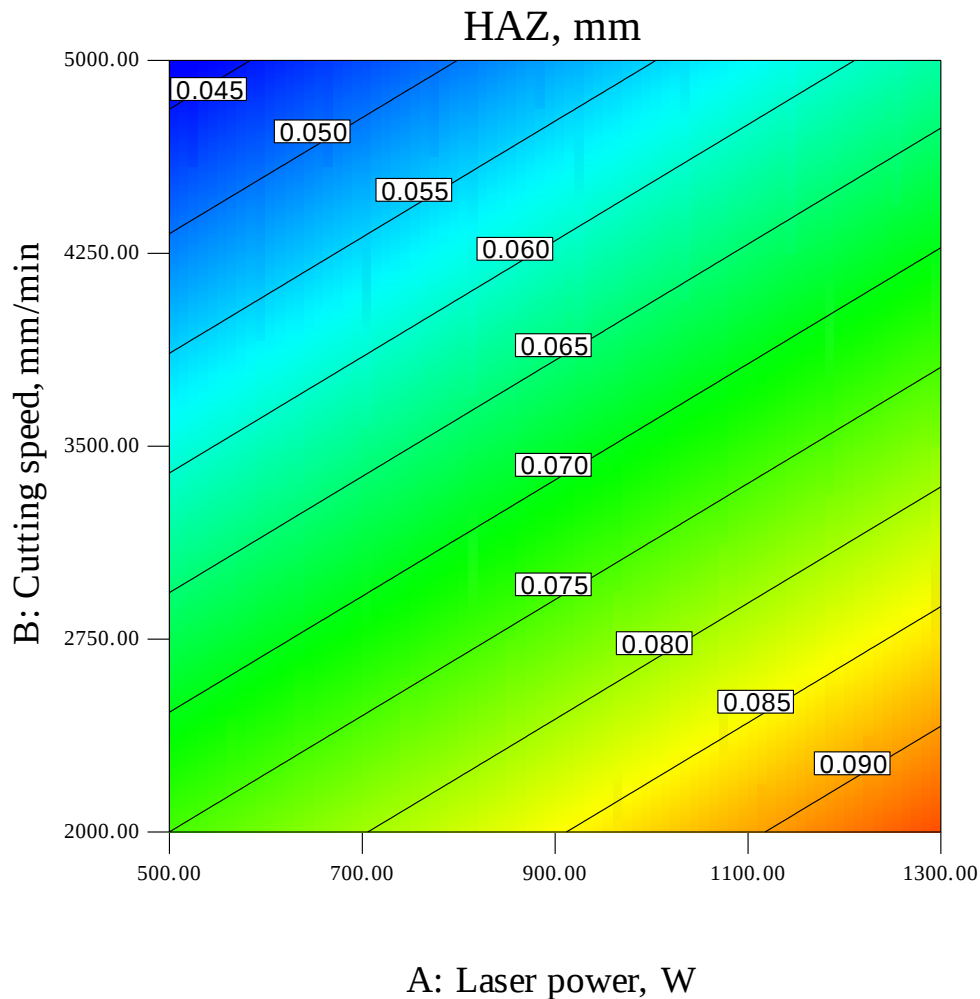


Fig. 6 Contours plot showing the effect of laser power and cutting speed on the heat-affected zone for 3-mm-thick glass fiber-reinforced polymer.

(1) changing focal position would result in a decrease of 45.34%; (2) changing the cutting speed would result in a decrease of 16.68%; and (3) changing the laser power would result in an increase of 10.57%. It is obvious that the argon pressure has no significant effect on the upper kerf.

Lower kerf

The perturbation plot for the average lower kerf width for GFRP is presented in Fig. 2. From Fig. 2 it is clear that the laser power is the key factor affecting the lower kerf. The results confirm that the lower kerf decreases as the laser power decreases and this agrees with result found in Cenna and Mathew (2002). When using the highest laser power, the lower kerf is on average 1.51 times wider than that obtained using the lowest laser power. It was found that the cutting speed and focal position have a significant effect on the lower kerf. By using the slowest cutting speed, the lower kerf is on average 1.11 times wider than that obtained using the fastest cutting speed. It is evident that the lower kerf width increases by 1.16 as the focal point position increases from its smallest level to its highest level. However, the air pressure has no significant effect on the average lower kerf for 3-mm-thick GFRP.

Ratio between upper kerf to lower kerf

Fig. 3 demonstrates that the focal position, the laser power, and cutting speed are the LBC parameters that affect the ratio. It was found that the focal position and laser power are the most important factors influencing the ratio. However, the cutting speed only has a minor effect on the ratio. It is clear that as the focal position and laser power increase the ratio would decrease. It is clear from Fig. 3 that a ratio of one is the desirable option to obtain a square cut edge. Fig. 4 is the interaction plot between the cutting speed and focal position. It is evident that at a focal position of -3 mm a ratio of 1.68 could be obtained if the maximum cutting speed of 5000 mm/min was applied. On the other hand, when the focal position is exactly on the surface of the substrate a ratio of 0.77 could be achieved if the slowest cutting speed of 200 mm/min was used. At a focal position of -1.08 mm a ratio of 0.82 might be obtained by using either maximum or minimum cutting speed.

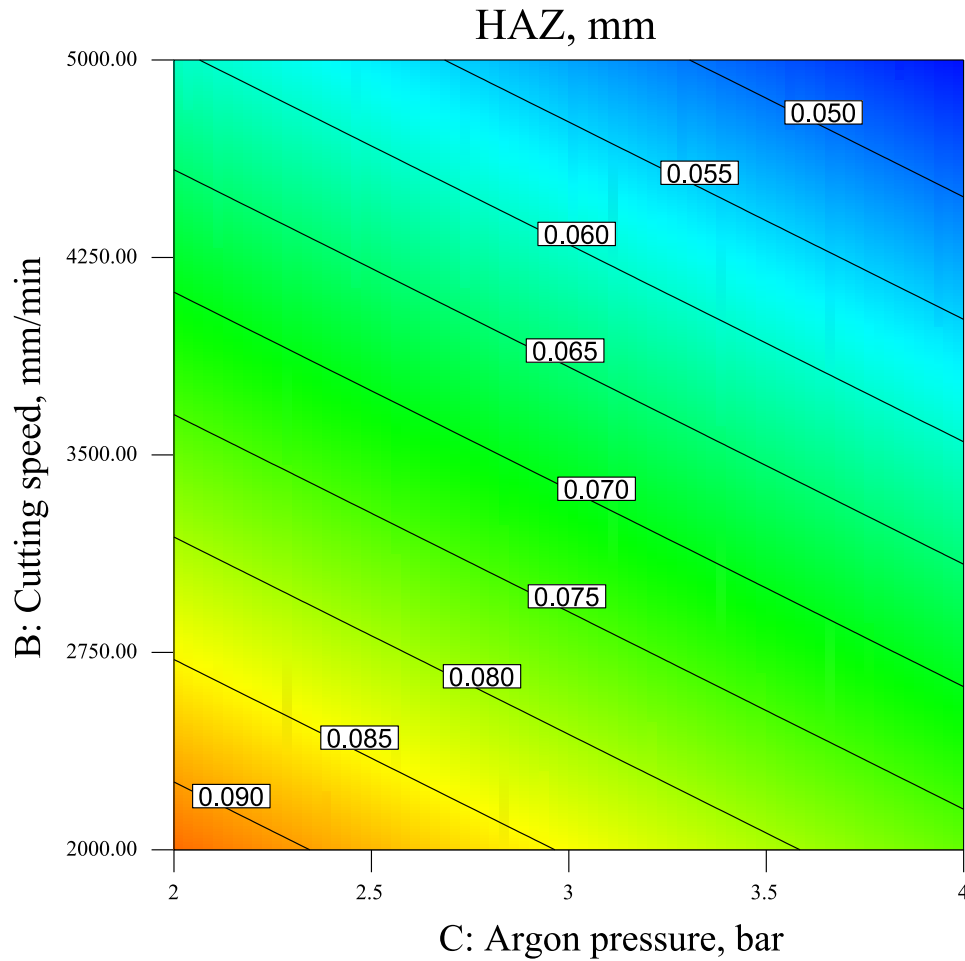


Fig. 7 Contours plot showing the effect of argon pressure and cutting speed on the heat-affected zone for 3-mm-thick glass fiber-reinforced polymer.

Heat-affected zone

For this material the HAZ was successfully modeled. The results indicate that the dimensions of HAZ are between 0.044 and 0.099 mm. [Fig. 5](#) is a perturbation graph showing the effect of the significant laser parameters on this response. It is evident that any increase in the cutting speed and argon pressure would result in smaller HAZ, whereas any increase in the laser power would lead to a larger HAZ. These findings are in agreement with the results reported in [Goeke and Emmelmann \(2010\)](#). The heat input plays an important role in the HAZ extent because as the heat input increases the HAZ becomes wider and vice versa. Therefore, any increase in the laser power results in a wider HAZ, especially at slow cutting speeds. In the case of the argon pressure effect, as mentioned above, the HAZ becomes smaller as the argon pressure increases. This could be related to the cooling effect as the argon pressure increases, which slows down the burning of the cut edge sides, and consequently, leads to a smaller HAZ. [Fig. 6](#) is a contour plot showing the effect of laser power and cutting speed on the HAZ of GFRP. Also, [Fig. 7](#) is a contours plot showing the effect of argon pressure and cutting speed on the HAZ extent of GFRP.

Operating cost

It is evident from the results that the cutting speed, laser power and argon pressure have a strong effect on the operating cost as shown in [Fig. 8](#). However, the laser power and argon pressure have a positive effect on the operating cost and the cutting speed has a negative effect. It is obvious from [Fig. 8](#) and the 3D plots shown in [Fig. 9](#) that the operating cost is more sensitive to the cutting speed than the other factors.

Optimization

Two optimization criteria are presented in [Table 12](#). Each factor and response have been given a specific goal and importance. For this composite material, the measurement of the surface roughness was not possible due to the inconsistency in the

surface roughness values for some specimens and surface roughness values already out of the tester range for some other specimens.

Table 13 shows the optimal laser cutting setting of the process parameters and the matching response values for both criteria for 3-mm GFRP. It is evident that the HAZ extent produced using the optimal setting of the first criterion is on average 13.7% smaller than the one produced by using the optimal setting of the second criterion setting. On the other hand, the cutting operating cost for the second criterion is on average cheaper than that of the first criterion by 10.5%. **Figs. 10** and **11** show green areas, which are the regions that meet the first and second criteria respectively.

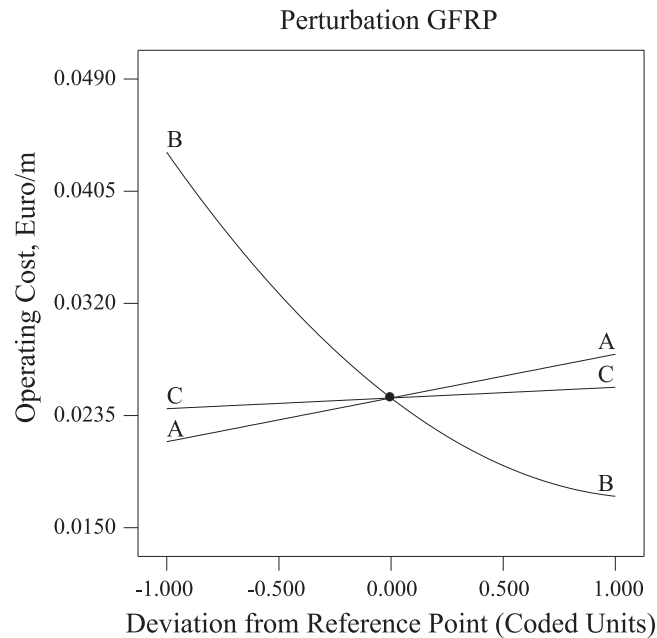


Fig. 8 Perturbation plots showing the effect of each factor on the operating cost for 3-mm-thick glass fiber-reinforced polymer.

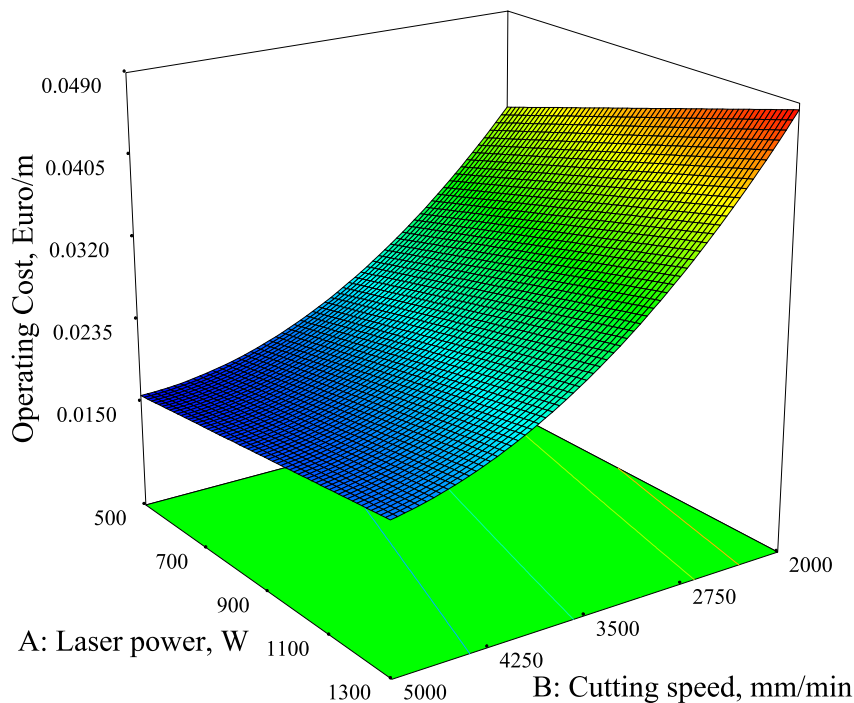


Fig. 9 3D plots showing the effect of cutting speed and laser power on the operating cost for 3-mm-thick glass fiber-reinforced polymer.

Table 12 Criteria for numerical optimization of GFRP

Factor or response	First criterion (Quality)		Second criterion (Cost)	
	Goal	Importance	Goal	Importance
Laser power	Is in range	3	Minimize	5
Cutting speed	Is in range	3	Maximize	5
Air pressure	Is in range	3	Minimize	5
Focal position	Is in range	3	Is in range	3
Upper kerf	Is in range	3	Is in range	3
Lower kerf	Is in range	3	Is in range	3
HAZ	Minimize	5	Is in range	3
Ratio	Target to 1	5	Is in range	3
Operating cost	Is in range	3	Minimize	5

Abbreviations: GFRP, Glass fiber-reinforced polymer; HAZ: heat-affected zone.

Table 13 Optimal cutting conditions as obtained by Design Expert for 3-mm GFRP

	No.	A, W	B, mm/min	C, bar	D, mm	Upper kerf, mm	Lower kerf, mm	HAZ, mm	Ratio	Operating cost, €/m	Desirability
1st criterion Quality	1	717	4845	3.8	-1.05	0.305	0.343	0.044	1	0.017	1
	2	727	4944	3.7	-1.21	0.312	0.346	0.043	1	0.017	1
	3	739	4972	3.7	-1.33	0.319	0.349	0.044	1	0.017	1
	4	733	4913	3.8	-1.27	0.316	0.346	0.043	1	0.017	1
	5	746	4797	4.0	-1.36	0.325	0.346	0.043	1	0.018	1
2nd criterion Cost	1	500	5000	2	-0.13	0.316	0.278	0.051	1.508	0.015	0.9995
	2	500	5000	2	-1.52	0.356	0.276	0.051	1.428	0.015	0.9995
	3	500	5000	2	-0.29	0.311	0.28	0.051	1.459	0.015	0.9995
	4	500	5000	2	-1.98	0.41	0.266	0.051	1.579	0.015	0.9995
	5	500	5000	2	-0.98	0.319	0.282	0.051	1.365	0.015	0.9995

Abbreviations: GFRP, Glass fiber-reinforced polymer; HAZ: heat-affected zone.

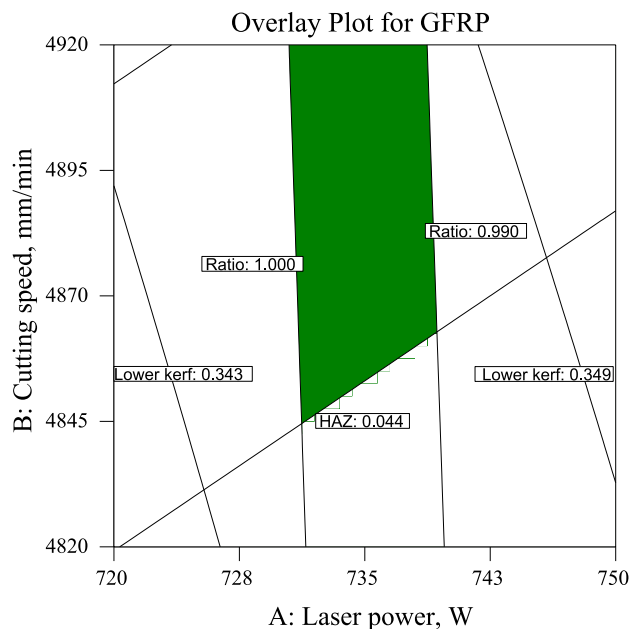
Design-Expert® Software

Overlay Plot

Upper kerf
Lower kerf
HAZ
Ratio
Operating Cost

X1 = A: Laser power
X2 = B: Cutting speed

Actual Factors
C: Argon pressure = 3.8
D: Focal position = -1.25

**Fig. 10** Overlay plot showing the region of optimal cutting condition based on the first criterion for 3-mm glass fiber-reinforced polymer.

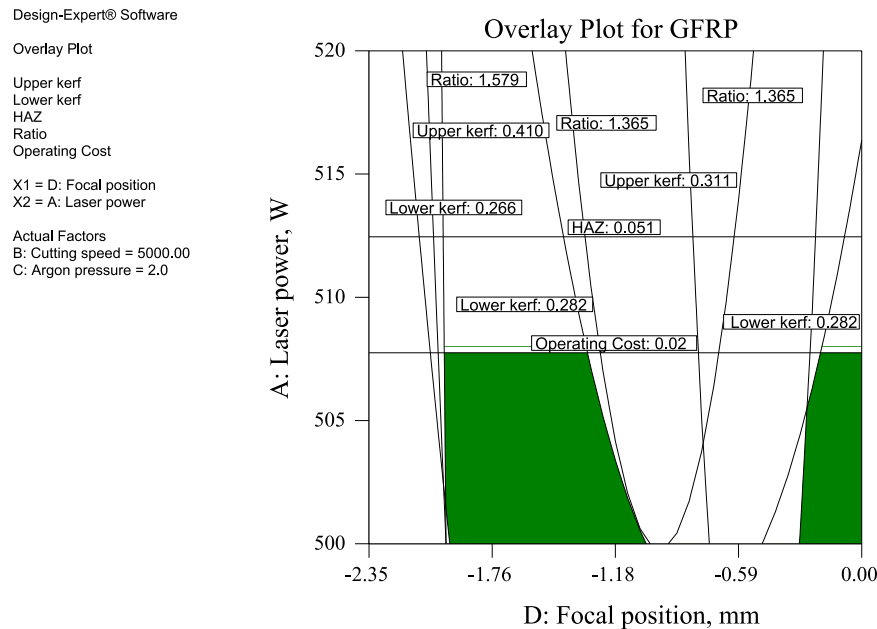


Fig. 11 Overlay plot showing the region of optimal cutting condition based on the second criterion for 3-mm glass fiber-reinforced polymer.

Conclusions

In this study the effect of LBC parameters was determined using mathematical models. The models were developed using Design-Expert software with the aim of assessing the main and interaction effects of the parameters on the quality of the cut section characteristics obtained under the experimental conditions. This contributed to an optimization of the LBC process to produce cuts that fully satisfy the end user requirements. The developed mathematical models and the optimal solutions are applicable within the cutting parameters ranges considered. The conclusions drawn from the study are summarized below:

- (1) The upper kerf increases as the focal position and cutting speed decrease, while it increases as the laser power increases.
- (2) Laser power is the key factor affecting the lower kerf. Also, the cutting speed and focal position have a significant effect on the lower kerf.
- (3) Focal point position and laser power are the most important factors influencing the ratio, with a negative effect. However, the cutting speed only has a minor effect on the ratio.
- (4) Any increase in the cutting speed and argon pressure would result in smaller HAZ, whereas any increase in the laser power would lead to a larger HAZ.
- (5) Cutting speed, laser power, and argon pressure have a strong effect on the operating cost. However, the laser power and argon pressure have a positive effect on the operating cost and the cutting speed has a negative effect.

See also: A Review on Utilization of Electronic Waste Plastics for Use Within Asphaltic Concrete Materials: Development, Opportunities and Challenges for Successful Implementation. Experimental Investigations for Friction Stir Welded 3D Printed Dissimilar Thermoplastics With Consumable Tool. Prospect of Recycling of Plastic Product to Minimize Environmental Pollution. Recycling of Plastics for Low Cost Construction. Renewable Agricultural Fibers as Reinforcing Fillers in Plastics: Mechanical Properties of Kenaf Fiber-Polypropylene Composites

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CO₂ Utilization Drivers, Opportunities and Conversion Challenges

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Introduction

Energy is life. It takes energy to get energy, as life thrives on life. Today, rising energy demand, growing population and climate change are the talk of the town. Mankind eats, consumes, and trades fossil fuels, which will continue to exist for many decades yet the energy transition to low carbon fuels is de rigueur to cope with perilous climate changes (Abas and Khan, 2014). Coal, oil, and gas brought unique economic prosperity, which seems difficult at present, independently with renewable energy sources. Solar and wind energy supply hardly 30% of electricity demand, which is 22% of global energy consumption (Herron *et al.*, 2015). The interesting truth is that the photovoltaic modules, hydrokinetics, and wind turbines themselves are manufactured by using fossil fuels emitting CO₂ in the atmosphere.

Population, economy, and energy are the major drivers of CO₂ emissions worldwide. A population of 7.2 billion is enjoying \$99 trillion gross domestic product (GDP) by using 13 to 14 GTOE fossil fuels and it is predicted that this will rise to 9 billion persons (IEA, 2014a), \$163 trillion GDP and 17 BTOE fossil fuels (BP 2030) by 2030. According to Shell it will increase to 14.9 BTOE by 2035 and 21 BTOE by 2050 (Saththawong *et al.*, 2014a). Annual electricity (23 PWh ~ 545 quadrillion BTU) and fossil fuel demands (14 GTOE) cause 40 GTCO₂/y CO₂ emissions. The current share of renewable sources include 1350 GW hydro, 365 GW wind, 150 GW solar, and 20 GW geothermal energies. Renewable energy sources supply 1856 GW energy. However, this huge contribution is only 20% of global energy demand whereas rest of 80% comes from fossil fuel. The seven sources of fossil fuels contributing to rampant CO₂ emissions include liquid fuels, for example, gasoline (36%), solid fuels like coal (35%), and gaseous fuels such as natural gas (20%), cement production (3%), bunkers (4%), flaring gases (~1%), and nonfuels (<1%) (Raupach *et al.*, 2007).

A rampant rise in fossil fuel consumption is causing rapid climate change, whose economic and ecological consequences will ensue within the lifetime of our teenagers. Worldwide CO₂ emissions were only 11.746 GTCO₂ in the 1970s, 23.485 GTCO₂ in the 1990s, and 29.89 GTCO₂ in the last decade, which later increased to 39 GTCO₂ in 2014. CO₂ emissions due to burning fossil fuels and biomasses are increasing, steadily, at the rate of 630 MtCO₂/y as discussed in our preceding work, shown in Fig. 1.

CO₂ concentration in the air was 280 ppm in 1750, which according to National Oceanic and Atmospheric Administration's (NOAA) keeling curve is 397.36 ppm as of September 2015 (NOAA, 2015). This is the highest level in the last 650,000 years. The natural water-based greenhouse effect had locked the earth's temperature at 14°C for the last 10,000 years; this has increased to 14.7°C in last 265 years, due to H₂O and CO₂ greenhouse effects. Combined H₂O and CO₂ gases' annual greenhouse gas index (AGGI) was 1.30 in 2011, which increased to 1.35 in 2015, thereby increasing the radiative forcing from 2.8 to 3.0 W/m².

The increase in the earth's temperature from 1997 to 2004 (warming period) caused drying of rosewood and acacia trees in Pakistan, which is described in our companion work, and Intergovernmental Panel on Climate Change (IPCC) measures caused a timely hiatus on further rise (Khan *et al.*, 2008). Rise in the earth's average temperature depends on our collective GHG emissions. Proven private and public sector fossil fuel reserves have a potential of 745 and 2795 GtCO₂, respectively, which must remain unused on earth to limit CO₂ below 450 ppm. The greenhouse effect is increasing the earth's temperature as a thermal runaway; a similar effect caused global warming on Venus. Atmospheric compositions of CO₂ and N₂ on Venus are 95.50% and 3.5%, which are opposite to 0.04% and 78% on earth. Climate Armageddon is believed to have happened in prehistoric times, and can happen on earth. Mars has no water yet the presence of 95% CO₂ causes a greenhouse effect, which has increased its temperature from –200 to –58°C.

The IPCC envisaged a policy of GHG emission reduction by increasing carbon capture and sequestration (CCS) rates, and converting CO₂ into fuels, chemicals, and value-added products. The climate change process is geared through growing population, rampant energy demands, and mushrooming economies as depicted in Fig. 2.

We have five decades to increase renewable energy from the current 20% to 50% by 2050 and from 50% to 80% by 2100 to revert global fossil fuels and renewable energy ratios. It is time to convert CO₂ into fuels and value-added products, when derived from the earth's increased concentration of CO₂ in the atmosphere. If we start capturing, storing, using, and converting CO₂ into fuels, chemicals, and building materials, then the energy transition process from conventional fossil fuels to renewable and alternative sources will become easier.

Fossil Fuels, GHGs Emission, and Impact of CO₂

Gases having the ability to trap heat in the atmosphere are called GHG, which include H₂O vapors, CO₂, CH₄, and O₃ with 36%–72%, 9%–26%, 4%–9%, and 3%–7% contributions, respectively. Solar spectrum reaching the earth's surface consists of 5% UV (300–400 nm),

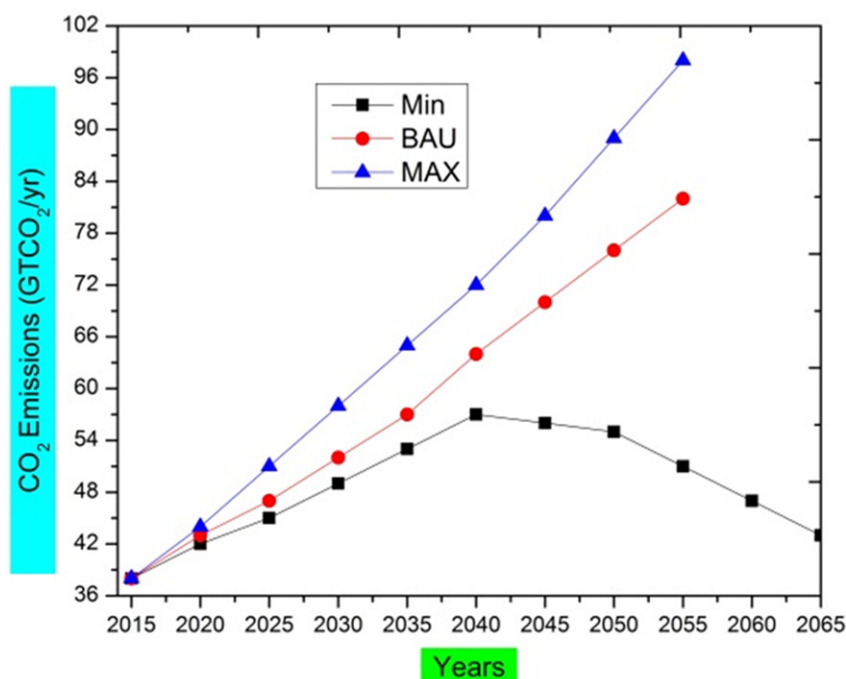


Fig. 1 Global CO₂ emissions and current rate of rise. Reproduced from Abas, N., Kalair, A., Khan, N., 2015. Review of fossil fuels and future energy technologies. *Futures* 69, 31–49. Available at: [doi:10.1016/j.futures.2015.03.003](https://doi.org/10.1016/j.futures.2015.03.003).

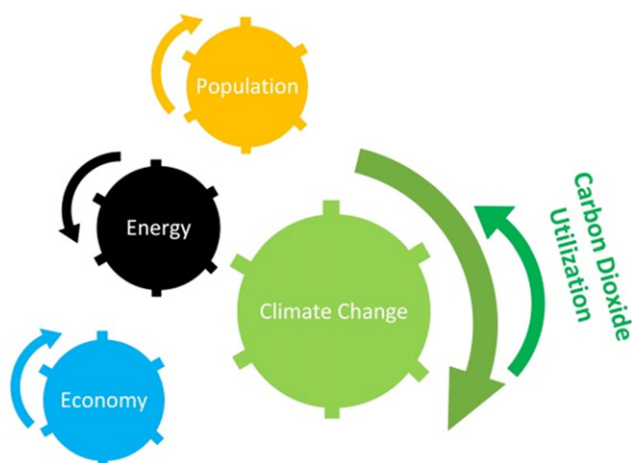


Fig. 2 Mitigation of climate change drives by CO₂ utilization.

43% visible (400–700 nm), and 52% NIR (700–2500 nm). The planet earth emits heat at 3.5–80 μm radiations to maintain its thermal equilibrium. Mostly, the earth radiations are absorbed by H₂O and CO₂ in the atmosphere. CO₂ traps 56%, methane 18%, chloro-fluorocarbons (CFCs) 13%, ozone 7%, and nitrous oxide 6% of the sunlight reflected from the earth's surface. Oceans absorb 90% sunshine and ice glaciers reflect 90% of incident light. The earth is steadily warming up at a rate of 0.6 W/m², which is akin to burning kindling under a 71% water filled cauldron (NASA, 2015). F gases are 1% of global GHG emissions but they have global warming potential (GWP), in addition to their ozone depleting effect, than other green gases. Radiative forcing of CO₂ (63%), CH₄ (18.2%), N₂O (6.1%), and F gases (12.6%) are 1.66, 0.48, 0.16, and 6.44 W/m². The lives of some hydrofluorocarbons (HFCs), SF₆, and per-fluorocarbons (PFCs) in the air are 270, 3200, and 50,000 years with a GWP of 11,700, 9200, and 23,900 as compared to 1 for CO₂. Human activities produce CO₂ (74%), CH₄ (14%), N₂O (8%), and fluorinated gases (1%). Annual GHG emissions from various sectors and their corresponding magnitudes of green gases are shown in Table 1 (Barker *et al.*, 2007).

A world community of 7.2 billion persons emits 2.63 GtCO₂/y from their body, which is easily absorbed by nearby trees and lakes. Oil and coal combustions emit CO₂ at the rate of 1.77 GtCO₂/1 Gt of oil and 485 Mt of CO₂/1 Gt of coal. US fossil fuel

Table 1 Global greenhouse gas (GHG) emission sources

Sources (sectors)	Shares (%)	GHGs (%)			
		CO ₂	CH ₄	N ₂ O	F gases
Power	21.3	29.5	0.00	1.10	0.23
Industry	16.8	20.6	0.00	5.90	0.66
Transport	14.0	19.2	0.00	1.50	0.00
Agriculture	12.5	0.00	40.0	62.0	0.00
Proc & Dist	11.3	8.40	29.6	0.00	0.00
Buildings	10.3	12.9	4.8	1.50	0.12
Land use	10.0	9.10	6.6	26.0	0.00
Waste H ₂ O	3.40	0.00	18.1	2.30	0.00
Global GHG% Ave	—	72	18	9	1.1 ^a

^aPercentages of F-gases in British and American GHG emissions were 2.6% and 3% which are being substituted.

consumptions from 1900 to 1999 have already emitted 283.30 Gt of CO₂ and the country's coal, oil, and gas reserves are 121.96 Gt, 694.69 Bb, and 42.3 Btoe with a potentials of 2.5 times more CO₂ emissions. Oil consumption rate was 87 Mb/day in 2008, 110 Mb/day in 2014, and is forecasted to be 120 Mb/day in 2020. Existing global GHG emissions are around 55 GtCO₂-eq/y, which may increase or decrease as is forecasted in [Fig. 3](#).

World oil reserves consist of 30% conventional, 30% oil sands or bitumen, and 25% extra heavy, 15% heavy, and shale oils. EIA expects a world energy mix in 2035 to consist of 29.3% petroleum, 27.2% coal, 22.7% natural gas, 6.7% nuclear, 14.2% renewable, and alternative energy sources ([Abas et al., 2015](#)). Annually, fossil fuel consumptions and land use patterns produce 54 Gt of GHGs out of which 40 Gt is CO₂. The bottom line is our infinite love for finite hydrocarbon honey down to the addiction level. Energy experts have no Holy Grail to provide any substitute for fossil fuels. IPCC energy and environment experts are running a nerve pulling a strenuous race against the clock to cope with climate change.

The Low Carbon Fuels: A Pathway to Grand Energy Transition

Grand energy transition (GET) from fossil fuels to the sustainable, renewable, and alternative energy sources is inevitable to decelerate climate change. GET desires mechanisms, opportunities, and challenges. The major challenges include climate change, population, economy dictating urgency, trade-off, and innovations. Oil, gas, and coal reserves will continue for the next several decades, yet the energy transition to low carbon intensity fuels is necessary to cope with rampant climate change. Globally, investment in the oil and gas sector increased from 2004 to 2011 and started decelerating after 2012.

More than 11,000 papers pointed out the urgency of energy transition to continue modern living standards. Drivers of energy transition are growing population, flooding urbanization, and globalization. More than three megacities are emerging every 4 years. Energy consumption in non-Organisation for Economic Co-operation and Development (OECD) countries surpassed OECD countries in 2005. Coal is fast replacing oil, natural gas liquids (NGL), and feedstock in primary energy ([Araújo, 2014](#)). The energy system is a capital intensive venture that takes \$1600 billion to supply world energy demands today. Worldwide gas fields (3.066 GTOE), oil wells (4.234 GTOE), and coal mines (3.942 GTOE), collectively, supply 13.80 GTOE (80.3%) energy, whereas the rest 2.758 GTOE (19.7%) emanates from a wide range of renewable and alternative energy resources ([Abas et al., 2015](#)). Total primary energy consumption is increasing at the rate of 243 MTOE/y. Global fossil fuels, renewable and alternative energy sources harvested out of esoteric natural energy resources, are shown in [Table 2](#).

We can make the task easier by changing our energy utilization patterns by incorporating renewable sources in our energy mix. We have 1575 EJ (438,000 TWh) solar, 640 EJ (180,000 TWh) wind, 5000 EJ (1,400,000 TWh) geothermal, 276 EJ (77,000 TWh) biomass, 50 EJ (14,000 TWh) hydropower, and 1 EJ (280 TWh) ocean energy sources to replace the fossil fuels, which are on their way toward peaking and depleting in the next few decades.

To make a successful transition from 2014 to 2035 we need more than \$8 trillion in end user efficiency in the residential, transport, and energy sectors and over \$40 trillion on fossil fuels ([IEA, 2014b](#)). Due to low energy-return-on-energy-invested (EROEI) and the oil depletion stories, investors suffer a leverage effect that affects the investment in energy sectors ([Kristoufek, 2014](#)). New global investments in the oil and gas sector have increased from 2004 to 2011 but started declining again after 2012 ([Ellabban et al., 2014](#)). Current status of oil, gas, and coal reserves is shown in [Fig. 4](#).

Annual energy demand of 14 BTOE results in the emission of 40 GtCO₂, which is likely to increase the business as usual to 75 GtCO₂ due to increase of energy demand to 24 to 25 BTOE. Hydro, wind, and solar power sources produce 4, 12, and 46 gCO₂/kWh as compared to 469, 750, and 1001 gCO₂/kWh by gas, oil, and coal, respectively. CCS technology for natural gas, oil, and coal consumption plants will have a positive impact on CO₂ reduction. Underground CO₂ storage seems to be a long-term solution as compared to converting into syngas ([Pau et al., 2010](#)). Coal beds, saline aquifers, salt caverns, and depleted oil and gas reservoirs may be used for CO₂ sequestration as shown in [Fig. 5](#).

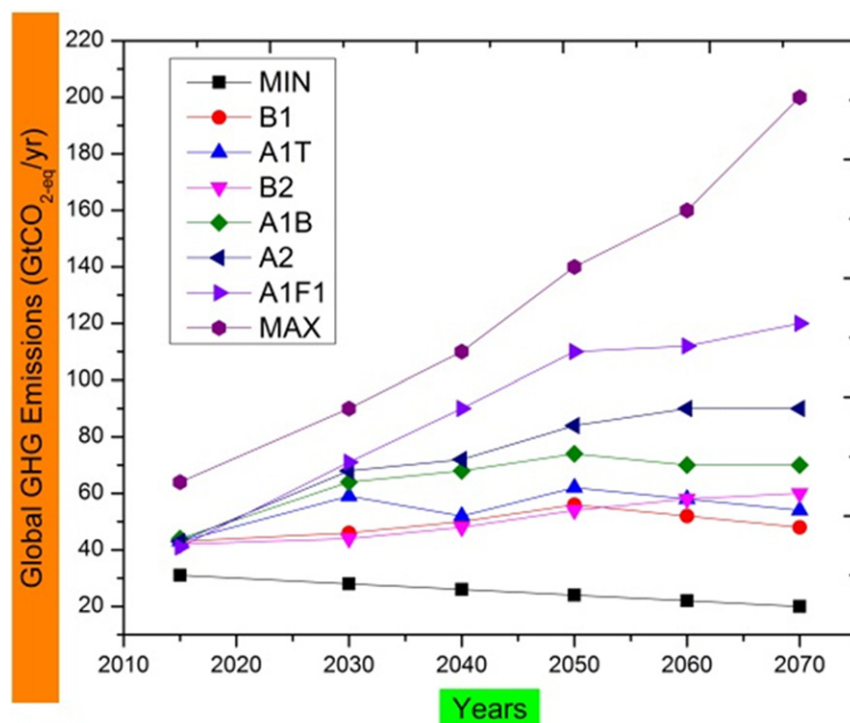


Fig. 3 Projected greenhouse gas (GHG) emissions during the 21st century. Reproduced from IPCC, 2007. Projections of future changes in climate. IPCC Climate Change 2007: Working Group I: The Physical Science Basis. Available at: http://www.ipcc.ch/publications_and_data/ar4/wg1/en/spmssp-projections-of.html#footnote14.

Table 2 Energy source variations in global spectrum

Resource (names)	Available reserves	Annual increase rate	Annual increase rates	
			Production	Consumption
Oil	1689 Bb	600 Mb	0.56 Mb	1.40 Mb
Gas	6558 TCF	400 BCF	3.4 BCF	4.50 BCF
Coal	891 Bt	0.15 Gt	19.3 MTOE	103 MTOE
Biofuels	506 MBOE	75 KBOE	75 KBOE	75 KBOE
Solar	177 GW	37.76 GW	37.76 GW	37.76 GW
Wind	320 GW	35.42 GW	35.42 GW	35.42 GW
Geothermal	11.71 GW	0.348 GW	0.348 GW	0.348 GW
Hydro	3880 TWh	97.9 TWh	97.9 TWh	97.9 TWh
Nuclear	2489 TWh	14.6 TWh	14.6 TWh	14.6 TWh
Oceans, etc.	1404 TWh	170 TWh	1404 TWh	1404 TWh
Electricity	23 PWh	492 TWh	492 TWh	492 TWh

Source: Reproduced from Abas, N., Kalair, A., Khan, N., 2015. Review of fossil fuels and future energy technologies. *Futures* 69, 31–49. Available at: [doi:10.1016/j.futures.2015.03.003](https://doi.org/10.1016/j.futures.2015.03.003).

CO₂ Utilization Opportunities

Carbon dioxide is perceived as a raw material of the future. Drivers of sustainable CO₂ capture, sequestration, separation and recovery, delivery, purification, and utilization business include conversion of it into energy carriers, fuels, polymers, feedstock; and construction materials, refrigerants, agriculture, artificial photosynthesis, and off-season agriculture. Carbon capture, utilization, and storage (CCUS) technologies mitigate climate change by providing niche business opportunities. Low-carbon green homes, cities, fuels, chemicals, and enhanced fuel recovery systems are recognized as the critical drivers of CO₂ utilization policy. CO₂ may be converted into methane, ethane, carbon monoxide, formic acid, and a wide range of value-added products. It can be converted into urea, fertilizers, methanol, water gas, methane, liquid fuels, syngas, and other useful chemicals. Commonly, it is mineralized into carbonates, polycarbonates, polymers, plastics, and bags. It is used for decaffeination in addition to its usage as an extraction for flavors, and fragrances. Biological conversion of CO₂ into algae, GHG, food and fuels happens all the time.

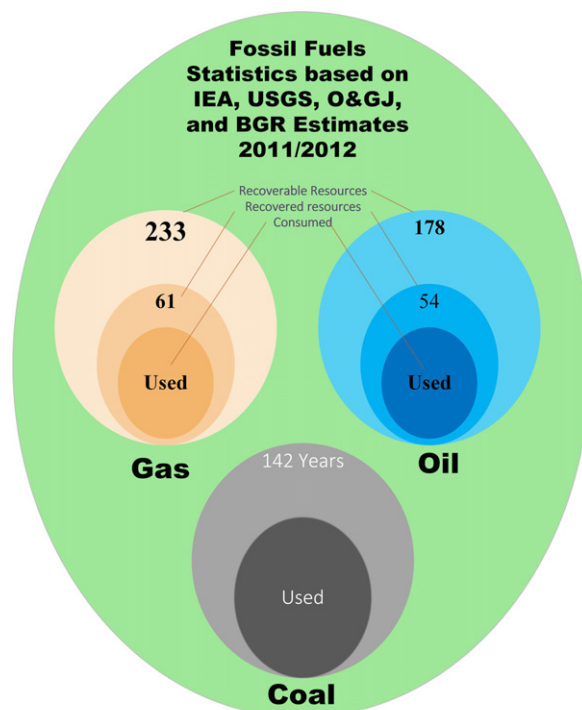


Fig. 4 Current status of fossil fuel reserves.

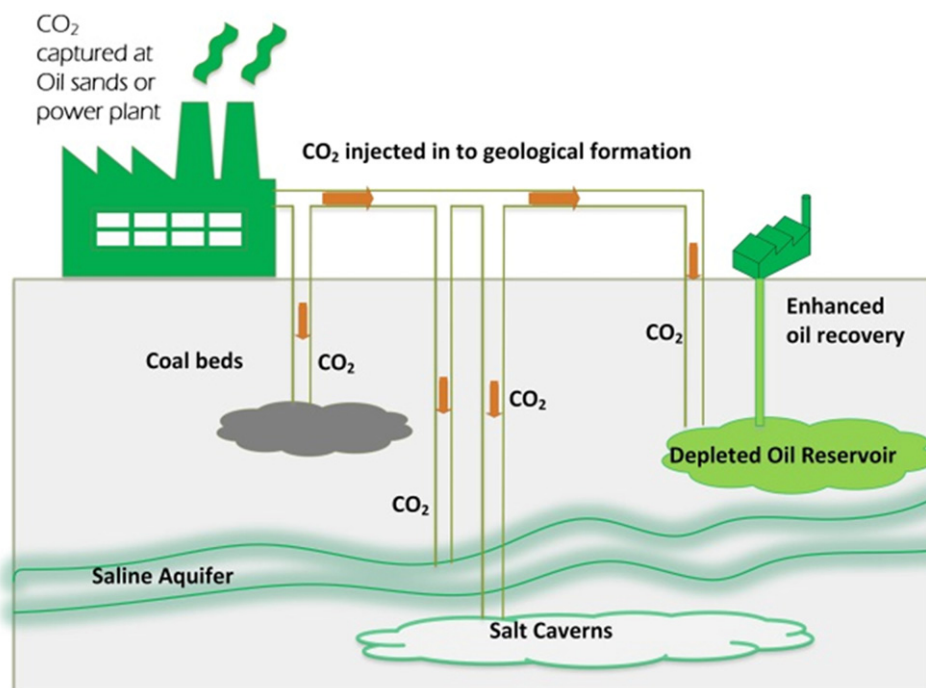


Fig. 5 On site CO₂ capture and sequestration options.

Nature uses sunlight and water to convert CO₂ into sugars and oxygen to support the life cycle. In short, the CO₂ is being used to produce a wide range of biomass products from foods to fuels as shown in [Fig. 6](#).

Captured CO₂ may be used as an inert agent for injecting into metal casting, as aerosol for propelling, and as dry ice pellets for blasting. It is being used for carbonization and fire extinguishing. K₂CO₃/Al₂O₃ adsorbents remove CO₂ from the flue gas ([Sengupta et al., 2015](#)) and amino acid salts for capturing CO₂ at high temperatures ([Yang and Wu, 2013](#)). Liquid absorption costs \$54 to \$64 per ton of CO₂ separation using 200 to 230 kWh energy. Solid absorption costs \$144 to \$186 per ton of CO₂

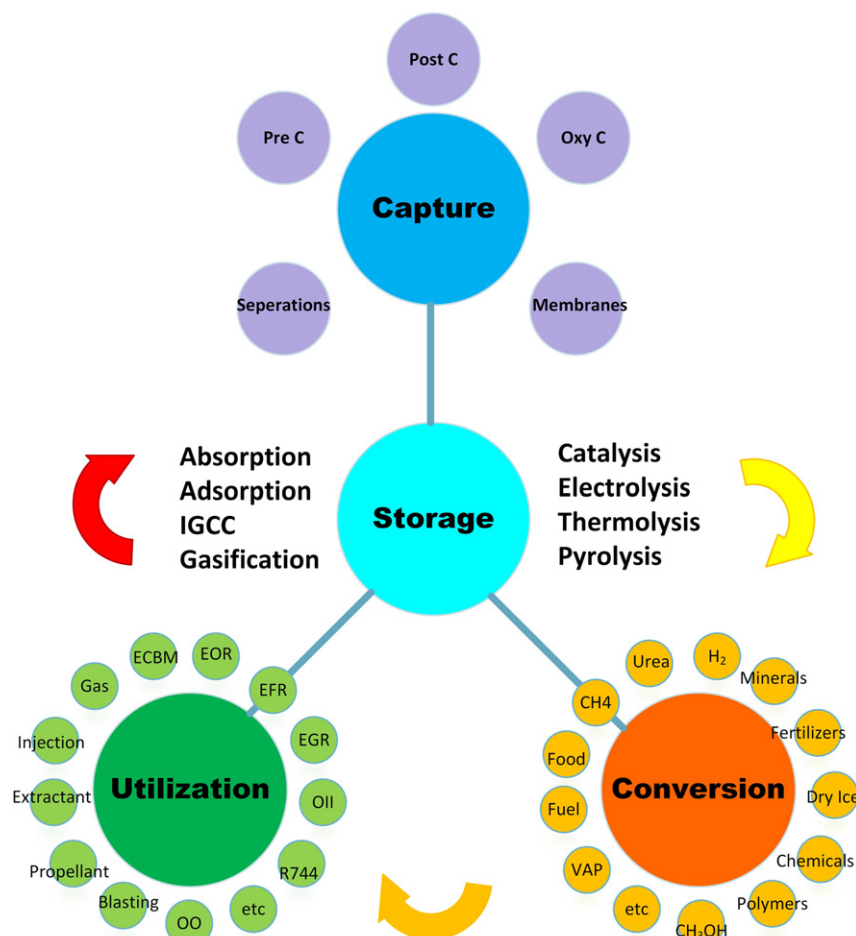


Fig. 6 An outlook to past, present, and future utilization of CO₂. IGCC, integrated gasification combined cycle.

separation using 640 to 680 kWh energy. Membrane technique may offer lower costs, when well developed (I2CNR, 2012). Microporous carbon such as African palm, Malaysian coconut, and spine nut shells by KOH activation leads to CO₂ capture (Deng *et al.*, 2014; Ello *et al.*, 2013). CO₂ sorption in coal depends on the pressure, which is viewed as a good carbon sequestration medium (Baran *et al.*, 2014). Calcium oxide powder under biomass gasification conditions captures CO₂ to form CaCO₃ under the carbonization process converting back into CO₂ in the calcination process. Akin to Lee and Shin's CO₂ capturing model in dry and wet steam the carbonization and calcination processes continuously capture and store CO₂ from plant and air (Kenarsari and Zheng, 2015). CO₂ capture and separation using porous materials and converting it into fuels, chemicals, minerals, and value-added products are global research priorities (Saleem *et al.*, 2015).

To convert CO₂ into chemicals on an industrial scale, it may be captured at the precombustion, postcombustion, or oxy-combustion stages in coal fired power plants in addition to absorption, adsorption, and separation techniques (Spigarelli and Kawatra, 2013). CO₂ may be used for enhanced oil and gas recovery (EOR, RGR), and enhanced coal bed methane (ECBM) to increase productivity of oil and gas. Injecting CO₂ into depleting oil wells, for EOR, is providing 5% of US oil production and is perceived to have further potential of 60 billion barrels in recoverable crude resources (Charles, 2012). Power plants, industries, and transport sectors are major sources of CO₂ emissions, which can be sequestered and transported to the oil fields at remote locations. CO₂ generated during methane combustion can be converted into water and gas (syngas) at 41% efficiency (Chen, 2014). Solvent absorption method has gained acceptance yet recovery of CO₂ again requires energy. Nanostructure silica with titanium metal was successfully used to convert CO₂ into fuels (Akhter *et al.*, 2014). Three phase (gas/liquid/solid) interface is another method to convert CO₂ into ethylene and fuels (Aeshala *et al.*, 2013; Ogura, 2013).

Photocatalytic reduction of CO₂ with H₂O on highly dispersed Ti-oxides anchored on porous silica glass produces CH₄, CH₃OH, and O₂ (Anpo, 2013).

Incorporation of metal nanoparticles in mercaptosilica enhances CO₂ adsorption capacities (Khdary and Ghanem, 2014; Khdary *et al.*, 2014). TiO₂ and platinum particle photoelectrodes in H-type cell may be integrated with sunlight carrying glass fibers to separate O₂ and H₂ from H₂O. Nitrogen-modified titanium oxide (TiO₂/N-100) photocatalyst expedites CO₂ adsorption in aqueous solution to produce methanol (Michalkiewicz *et al.*, 2014).

TiO₂ photocatalysts convert CO₂ into methane (Cybula *et al.*, 2015) and Cu or Co-TiO₂/ZSM-5 photocatalysts convert CO₂ into many energy products under low irradiation. Solar thermal energy was reported for use to convert CO₂, NaCl, and H₂O into Na₂CO₃ and HCl products (Forster, 2014). Nanoparticles-based TiO₂ photocatalysts (CdS/TiO₂) convert CO₂ into CH₄ and CO, which may be mixed with hydrogen to produce water gas (Ahmad, 2014). Thermal, electrochemical, and photochemical techniques of converting CO₂ into fuels and chemical products are under intensive investigation worldwide (Grace *et al.*, 2014; Hu *et al.*, 2013). CO₂, H₂O, and H₂ provide a route to infinite syngas energy. CO₂ is abundantly available and hydrogen may be produced by electrochemical (electrolysis), photobiological, photoelectrochemical (photolysis), thermochemical (thermolysis), and thermal decomposition techniques such as pyrolysis and gasification (Chen, 2014).

A fluorine modified Cu/Zn/Al catalyst has shown superior performance of CO₂ hydrogenation to methanol (Gao *et al.*, 2013, 2014). Bimetallic Fe-Co catalysts improve CO₂ hydrogenation to higher order hydrocarbon fuels (Sathawong *et al.*, 2013, 2014b). CO₂ is being investigated to form oxazolidinone for medicinal applications (NEAF, 2010). Selection of a catalyst for methanation is a highly selective skill (Dăce *et al.*, 2014).

Protic ionic liquids are efficient catalysts to form cyclic carbonate from CO₂ and epoxides (Xiao *et al.*, 2014). Steel industry waste slag based catalysts are used for fixation of CO₂ to produce cyclic carbonates (Kuwahara and Yamashita, 2013; Sun *et al.*, 2013). CO₂ dry reforming of methane is a highly endothermic process giving of water gas (Pakhare *et al.*, 2013). Ruthenium substituted La₂Zr₂O₇ pyrochlore improves dry CO₂ reforming of methane. Carboxylation of olefins and alkynes with CO₂ gives acrylic acids and carboxylic acid salts, which is a new scenario for green and sustainable chemical industry (Hwang and Radermacher, 1999; Yu *et al.*, 2013).

CO₂ is no more a waste product as it is a raw feedstock for fuels, chemicals, polymers, and value-added industrial products. CO₂ is perceived as precious raw material for a wide range of innovative products. Smart CO₂ transformation (SCOT) is a strategic European agenda focusing on technical and economic performance of emerging CO₂ transformation technologies. CO₂'s use, recycling, and reuse make a useful raw material supporting multiple industries, for example, food processing, pulp and paper, beverages, metal, and refrigeration and chemical industries (Koljonen *et al.*, 2004). Current utilization of 600 Mt/y CO₂ in the chemical industry is a minor fraction (1.5%) of global CO₂ emissions into the atmosphere. Changing paradigm of CO₂ utilization would lead to inventory applications (Aresta *et al.*, 2013; Aresta, 2010). Hydrogenation of CO₂ to methane and methanol (Miguel *et al.*, 2015), synthetic gas (Stechel and Miller, 2013) by electrolysis (Agrafiotis *et al.*, 2015) or thermolysis (Ermanoski *et al.*, 2014) and conversion of CO₂ into a wide range of value-added products is the precursor of a future CO₂ economy (Saeidi *et al.*, 2014).

Active Communications International (ACI) has played a great role in the promotion of CO₂ utilization by mediating international conferences. ACI conducted the latest CO₂ utilization conference (focusing on widespread industrial applications of CO₂) from 25 to 26 February 2015 in San Antonio, United States. Before this, ACI conducted a CO₂ utilization conference (focusing on CO₂ as a useful raw material) from 19 to 20 February 2014 in San Diego, United States and earlier than that ACI mediated a CO₂ utilization summit (focusing on conversion of CO₂ into fuel's 7 chemicals) from 30 to 31 October 2013 in Brussels, Belgium. In addition to ACI CO₂ utilization conferences, the ASME supercritical CO₂ power cycle symposium in 2012, APTA 2013, SES 2013, Chinese low carbon earth summit in 2014, Dutch CCS GHGT-12 symposium in 2014, Norwegian TCCS-9 in 2015, and ICC DU XIII conference focusing on photoelectrochemical and catalytic conversions into products scheduled for July 5–9, 2015 are promoting CO₂ utilization awareness in society. CO₂ utilization conferences, symposiums, and summits inform society by debating on technical applications. Industry experts in ACI 4th CO₂ utilization conference described the use of CO₂ in cultivation, conversion of CO₂ into polymers, plastics, bags, and bottles, utilization of CO₂ in geothermal systems, the use of CO₂ in the oil and gas industry for enhanced fuel extraction, CO₂ mineralization, and conversion into building construction materials.

CO₂ Industry Impediments

Carbon dioxide is thinly distributed in the air. It can be better captured at source as coal fired power plants produce 42% of all fossil fuels related emissions. Currently, 96% of organic chemicals are derived from the fossil fuels. Hydrogenation of CO₂ into hydrocarbon fuels and recycling into chemicals and industrial materials would mitigate the climate change process. Development of efficient electrolysis, catalysis, and thermolysis processes is the confronting challenge.

Nature converts CO₂ and water under sunshine into glucose (C₆H₁₂O₁₁), which subsequently transforms into sugars, cellulose, lignin, etc. It takes 8–10 photons to utilize one molecule of CO₂. Gibbs free energy for converting one mole of CO₂ to glucose is 381 kcal, whereas eight photons of 600 nm light have 381 kcal energy. About 45% of the light spectrum can cause photosynthesis, so the theoretical efficiency cannot be more than 30% the same as humans and engines. Due to reflection and respiration the actual plant efficiency is 1% to 10% (strictly to 3% to 6%). Our bodies and internal combustion engines convert 30% to 40% of food and fuel energies into useful power. In case of 100 J incident light flux the plants convert maximum 10 J into chemical energy which after combustion reduces to 3.5 J. Owing to low efficiency, plants waste more than 94% of solar energy (FAO, 1997). Photocatalytic oxidation and reduction reactions lead to the production of HCOOH, CH₃OH, and CH₄. Design of photoanodes, photocathodes, and nanostructured catalysts are frontiers of the modern research and might break the rocky barrier (Ohno, 2017). Photobioreactors convert CO₂ into fatty acids, lipids, proteins and other biodegradable products. Binary cultures of phototrophs and heterotrophs in photobioreactors can provide a sustainable closed loop environment. Modular bioreactors show promise of carbon neutral economies in protein production, pharmaceuticals, biofuels, amino acids, vitamins, and animal foods (photobioreactors).

Solar hydrogen produced by photoconversion using photocatalytic, photoelectrochemical, and photobiological processes is more environment benign than syngas produced by gasification (Abbasi and Abbasi, 2011). Photoelectrodes are made of doped semiconductor materials. A broader band gap enhances the absorption spectrum and narrow band gap promotes charge transportation. Photoelectrode surface is specially treated to reduce recombination and it is morphologically controlled to enhance absorption and to shorten the transport of charges. It needs a sensitizer to improve photoelectrochemical efficiency. In the photobiological process the hydrogenases have the capability to consume and create molecular hydrogen. Biophotolysis uses organisms to transform solar energy into chemical energy. Photoelectrolysis needs efficient electrode materials that do not yet exist (Huang, 2014).

According to Club CO₂, France and Geogreen (2011), today's major CO₂ applications are EOR (pressure), heat transfer (refrigerant), flame retardation, foods, beverages, and inert agents, which are likely to expand to dry cleaning (solvent) and hydrogenation and microalgae to produce hydrocarbons (HCs) and biofuels. CO₂ medium term applications include microalgae bioreactors, ex situ mineralization, and hydraulic fracturing in shale beds. Long-term applications would be catalytic conversion, in situ mineralization with IGCC plants, electrolytic conversion by artificial photosynthesis, and high flux solar driven thermochemical dissociation (thermolysis). At the moment catalysis, electrolysis, and thermolysis technologies are not cost effective, due to their lower efficiencies, which are the primary focus of researchers worldwide.

Researchers might develop cost effective CO₂ capturing membranes, catalysts, and electrolytic electrodes in the short term but in situ mineralization and efficient photoelectrolyzers would take time. Taniguchi's membrane operates under 30 and 1.0×10^{-10} m³(STP)/(m² s Pa) conditions, which need to improve to the 7.5×10^{-10} m³(STP)/(m² s Pa) level. As the CO₂ permeance depends on membrane thickness (10–500 μm), so it is a diffusion controlled device. Membrane thinning, akin to morphology controlled nanostructured photoelectrolytic electrodes, is a material science limitation. Composite organic and inorganic materials are being investigated to design CO₂ absorbing porous structures. Large MOF structures' membranes have poor adsorption and sorption properties. Atomic and molecular engineering tools, ideally, allow the fabrication of perforated thin membranes to separate any gas from random air mixture. A thin structure, smaller than 100 nm, may exhibit nonlinear behavior. I²CNER have identified three catalyst materials for selective conversion of CO₂ into CO. Nakashima, Fujigaya, and Gewirth focus on polymer wrapped, multiwall, nanotube supported nanoparticles. Gewirth concentrates on organometallic catalysts and Lyth on metal carbonitride catalysts yet nothing is on the market with faradic efficiency > 95%, energetic efficiency > 60% with 200 mA/cm² current densities (Shigenori, I²NCR). There are many biological, photochemical and photobiological pathways to convert CO₂ into fuels and chemicals, yet efficient catalysts and photocatalysts limitations do not let the process to go ahead. Anyhow, recycling CO₂ into value-added products might be a possible worthy answer to get rid of climate change over time (Huang, 2014). Catalysts are a tough science behind energy and climate change crises.

George Washington University's solar thermal electrochemical photovoltaic (STEP) process converts solar energy at 35% under 50 sunlight flux and at 37% under 500 sun's fluorescence. STEP used 2.7 V electricity to drive two molten electrolysis cells in series at 750°C to generate CO at 1.3–1.5 A on 0.9 V. About 700 km² area can effectively remove atmospheric CO₂ from air. Cost effective conversion of CO₂ into oils and H₂ is yet a remote reality, however climate considerations might dictate its urgency. The energy, population, food, and environmental problems are interrelated, so the cost factor will have to be adjusted elsewhere. Chemical and biological conversion of CO₂ is at least a viable routine if all alternatives fail (Hall and House, 1994). The good behind the CO₂ business is cost effective capture and utilization of CO₂ to reduce GHG emissions. Underground natural CO₂ reservoir costs 5–10 \$/t, which is 5–10 times cheaper than available CO₂ capturing alternatives. Scientists are developing innovative techniques to reduce capturing costs yet the desired technology has a long way to develop before it gets competitive with naturally occurring CO₂. The hurdle in CO₂-based products is that they are still more expensive than the earth based alternatives. Even the competitive CO₂ capturing and conversion costs will hardly make a small dent in annual 40 GtCO₂ emissions. CCS akin to solar technology will take a couple of decades to be cost effective. Current cement, timber, and plastics consumption is 6.25 billion tons, which may increase to 20 billion tons per year by 2100. Carbonization of beverages uses hardly 1 MtCO₂/y, which releases into the atmosphere on opening the bottles. We might need to decarbonize the future economy, which would depend on CO₂ fuels. We would need to pursue alternative ways to sequester CO₂ emissions, for example, by storing carbon in soils, trees, fertilizers, or underground reservoirs (Daily Western, 2014).

Unfortunately, utilization of CO₂ as feedstock does not contribute to the mitigation of greenhouse effects, even though CO₂ stands as a green reactant (Sakakura *et al.*, 2007). The chemical (or biochemical) fixation of CO₂ does not imply a reduction of CO₂ emissions as its transformation requires energy both to drive reaction (high temperatures and pressures) and separate products (separation occurs at low pressures and, hence, recycling unreacted CO₂ to the reactor requires recompression at the expense of high energy input). The energy demand of the world in order of magnitude is higher than the amount of CO₂ fixed by chemical utilization of CO₂ (Westenhaus, 2010). In the critical phase of its life cycle, organic chemicals will emit CO₂. Nevertheless, the relevance of CO₂ as raw material stands for being a renewable feedstock, replacing cost effective conventional fossil based routes. Industrial synthesis of fertilizers and carbonates involves CO₂. Global use of fertilizers (with 46% nitrogen) was 198.4 Mt in 2013, which is expected to increase to 236.3 Mt by 2017. Current utilization of CO₂ is lesser than the even anthropogenic emissions of 2.5 GtCO₂ every year (Abas *et al.*, 2014).

Revival of CO₂ (R-744) as Next Generation Refrigerant

CO₂ has been used as a refrigerant before 1950 in marine applications and later replaced by synthetic refrigerants. Though the Montreal Protocol (1987) banned the production and use of CFCs after 1995, some countries are still using them. The Kyoto

Protocol (1997) endorsed to limit the use of hydrochlorofluorocarbons (HCFCs) by virtue of their higher GWP by 2015 and time barred permission to use HFCs by 2020 for developed countries and 2030 for developing countries (Yang and Wu, 2013). The deadline is quite near yet many countries are unaware or reluctant to replace the existing refrigerants. F-gas law in Europe was implemented from January 2015, as a quest for low GWP in mobile air-conditioning devices saying goodbye to high GWP refrigerants. The F-gases include HFCs, PFCs, and sulfur hexafluoride (SF₆). Existing refrigerants do not fulfill the Montreal and Kyoto protocols and F-gas laws and will be replaced. The American Society of Heating Refrigeration and Air Conditioning (ASHREA) envisaged HCs, water, ammonia, and CO₂ as future natural refrigerants. HCs are flammable, water freezes below zero, and ammonia is toxic and reactive with copper. CO₂ (R-744) exhibits low critical temperature (31.1°C) and high critical pressure (73.3 bar), which requires transcritical operation in the propriety vapor compression cycle. This lowers the performance of CO₂-based cooling (Lorentzen, 1994) systems, whilst a lot of practical implications have been suggested by various authors for efficiency enhancement in CO₂-based refrigeration and air-conditioning systems (Robinson and Groll, 1998; Kim and Kim, 2002). However, in water and space heating the transcritical cycle operation appears to be more efficient as compared to other refrigerants (Neksa *et al.*, 1998). We have taken into account the lower critical temperature and high pressure of CO₂ as an opportunity and have designed a gravity driven solar water heater, which can work efficiently in mild sunshine (subzero temperature areas) with superior (80%–85%) collector efficiency (Abas *et al.*, 2017). The proposed system works in the supercritical phase employing evacuated glass tube collector with copper based U-tube heat removal system as shown in Fig. 7.

DENSO Japan introduced the eco-cute model of CO₂ fluid mediated heat transfer, which is getting very popular. When CO₂ is used as refrigerant in supermarkets the coefficient of performance for 90% of the year is higher than HFC based systems. Production and transportation of CO₂ have carbon equivalent of 1 kg CO₂-eq per kg, whereas NH₃ and HFC have equivalent carbon equivalent of 2 and 9 kg CO₂-eq per kg.

CO₂ Conversion Challenges

Carbon dioxide conversion bottlenecks include cost effective separation membranes, efficient photoelectrolytic electrodes, and smart chemical and enabling biological catalysts (Song, 2006; Li *et al.*, 2013). Extensive literature is available on CO₂ as raw feedstock (Aresta, 2010), yet CO₂ business does not compete in the interest driven market. We have to bend our necks upward to envision the high target of 40 GtCO₂ per year. Syngas based products, prepared by Fischer–Tropsch method, look promising for

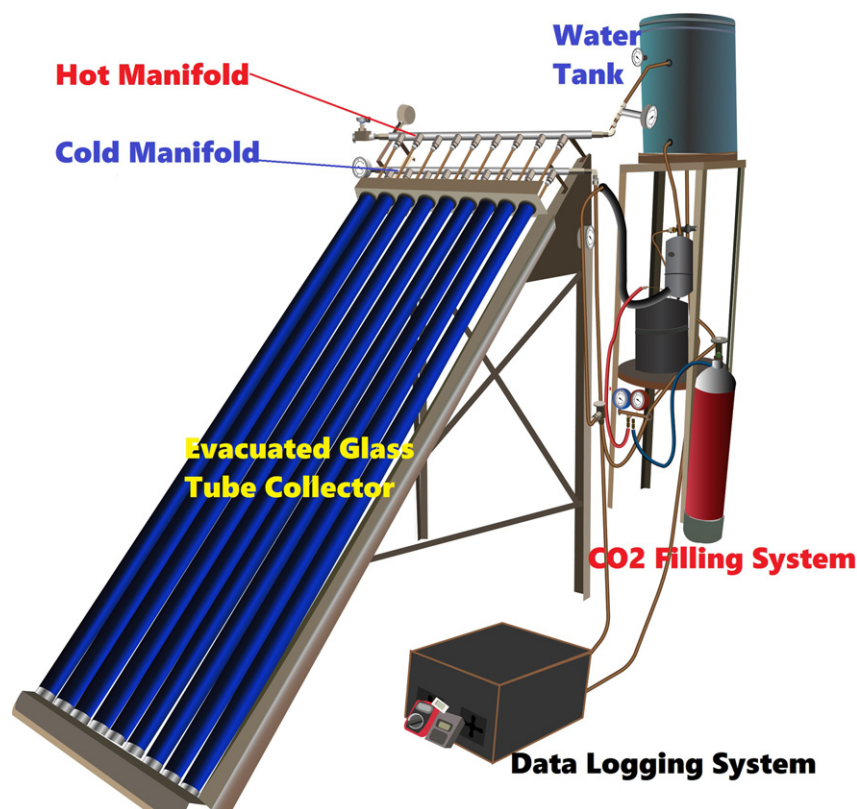


Fig. 7 CO₂ Mediated solar water heater. Reproduced from Abas, N., Khan, N., Haider, A., Saleem, M.S., 2017. A thermosyphon solar water heating system for sub zero temperature areas. Cold Regions Science and Technology 143, 81–92. Available at: [doi:10.1016/j.coldregions.2017.08.012](https://doi.org/10.1016/j.coldregions.2017.08.012).

the production of synthetic fuels like olefins, naphtha, and diesel. Methanol may be promoted as hydrogen carrier and feedstock or transesterification agent in biodiesel and dimethyl carbonate (DMC) production processes. The use of CO₂ as a carbon source in sustainable chemistry could be a profit oriented business. Conversion of CO₂ into chemicals is not considered a sustainable solution of GHG emissions as only 110 Mt of CO₂ is used in production of chemicals. Simply the conversion of CO₂ into energy products means the use of more hydrocarbon fuels. The synthetic fuels, for example, methanol (38), DMC (40), and dimethyl ether (DME) (52), have a lower percentage number of carbon atoms, so the heating values compared to propane (82), gasoline (85), and diesel (86). DMC acts as a carbonylation agent to replace hazardous phosgene in the synthesis of polycarbonate. DME is considered better than liquefied petroleum gas (LPG) and diesel for gas turbines. Pyrolysis and gasification techniques (Freitas and Guirardello, 2015) produce combustible syngas (Freitas and Guirardello, 2014) that again transforms back into CO₂, so it is not a very effective GHG mitigation process.

Climate change is recognized as a real extinction threat. Conversion of CO₂ in fuels and chemicals is perceived as it affects the environment (van der Giesen *et al.*, 2014; Cuéllar-Franca and Azapagic, 2015). There is a complete concurrence on cost effective utilization and efficient conversion of CO₂ into chemicals, minerals, fuels, and polymers to cope with climate change challenges.

CO₂ (R-744) has a vast potential in next generation refrigeration and heat pump applications. It has zero-effective GWP and ozone-depletion potential (ODP), and is nonflammable, cost effective, has a high working temperature range, and is easily available everywhere. The potential challenges, while using R-744 as a refrigerant in cooling applications includes heat rejection in transcritical cycle, high pressure compressors, throttling losses, low COP, and high system cost. Contrary to this when R-744 is employed for heating applications, which includes 47% of world's final energy utilization, it has superior performance compared to other refrigerants.

Conclusions

Population growth, rampant energy demands, and burgeoning economies are recognized to drive the climate change process. Natural greenhouse effect index due to natural water vapors and preindustrial level of CO₂ concentrations was 1.0, which has increased to more than 1.34 in recent decades. Climate change is affecting humans, animals, and trees. Stretching summers with intense heat waves and shrinking winters with extreme chills are the signs of peaking energy demands. We are entering into a vicious cycle in terra incognita. IPCC assumes, if the problem in this case, i.e., high CO₂ concentrations, is engineered to be a part of the solution by CO₂ storage, utilization, and conversion business, then the free market based corporate culture can reduce its concentrations to decelerate the climate change process. Interest driven carbon business can harness this global problem. Conversion of CO₂ into fuels and value-added products sounds good yet it needs efficient membranes, catalysts, and photoelectrodes, which are not available in the market. Short term research and energy transition processes require trillions of dollars to continue meeting energy demands by mitigating climate change.

Acknowledgments

This research was in part supported by a grant from the Pakistan–US Science and Technology Cooperation Program (Project ID No. 299), US Department of State (jointly administered by the National Academics and Higher Education Commission of Pakistan).

See also: CO₂ Laser Cutting of Glass Fiber-Reinforced Plastics

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Design and Performance Analysis of Small-Scale Parabolic Trough Solar Collectors Using Sustainable Materials

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Nomenclature

A Area [m^2]
 DNI Direct normal irradiance [W m^{-2}]
 D Diameter [m]
 h Heat transfer coefficient [$\text{W m}^{-2} \text{K}^{-1}$]

K Incidence angle modifier [–]
 $\dot{m}$ Mass flow rate [kg s^{-1}]
 $\dot{q}$ Heat flow rate [W]
 T Temperature [$^{\circ}\text{C}$ or K]
 U Overall heat loss coefficient [$\text{W m}^{-2} \text{K}^{-1}$]

Introduction

Parabolic trough collectors (PTC) are the most mature solar energy concentration technology that are now available on a commercial-scale. They have also intensively researched and today numerous prototype configurations and mathematical models are available in the scientific literature. Standard module sizes for single-axis tracking collectors are usually used in electrical power generation using concentrated solar energy. The use of parabolic trough solar collectors for process heating applications (up to 250°C operating temperatures) has numerous success stories all over the world. These types of installations normally involve utilization of small-sized parabolic trough solar collector systems. In most of cases, thermal oils are used in the collector loop as heat transfer fluids while in some cases, water is used as the working medium for direct hot water production or steam generation. The application range of such systems include industrial hot water or steam generation, solar cooling, desalination and the organic Rankine cycles for power generation.

An example of a commercialized small-scale parabolic trough collector system is shown in Fig. 1 (PolyTrough, 1800). The system is suitable for low-medium temperature applications with a single-axis tracking control system. Pressurized water or thermal oil can be used as heat transfer fluids.

In addition, systems with light structures and low cost technology for process heat applications up to 400°C could be obtained with parabolic trough collectors. They can effectively produce heat at temperatures between 50 and 400°C (Kalogirou, 2004).

PTC systems usually track the sun with one degree of freedom using one of three orientations: east-west, north-south or polar, Fig. 2 (Solar Photochemistry Technology). The absorber of a PTC is usually tubular, enclosed in a glass cover envelope to reduce radiative and convective losses. The convective losses can be minimized by creating a vacuum in the annular space between the absorber and the glass cover (Goswami *et al.*, 2000).

For linear concentrators, the thermodynamic limit for the concentration ratio is around 215, as demonstrated by Rabl (1975). Medium concentration parabolic trough collectors are very attractive for solar designers and thus highly researched for medium temperature applications. In most cases, a tubular receiver is implemented with a metal pipe coated with a selective absorbing material inside an evacuated glass envelope.

System Description and Components Design

Fig. 3 shows the flow diagram of the proposed parabolic trough collector system. The system consists of a small-scale parabolic trough reflector and its supporting structure, thermal receiver, thermal energy storage, circulating pump, heat transfer fluid conductors, tracking



Fig. 1 A small-scale parabolic trough collector system for commercial use. Reproduced from PolyTrough, 1800. Technical Specification v7. Available at: <http://www.nep-solar.com>.

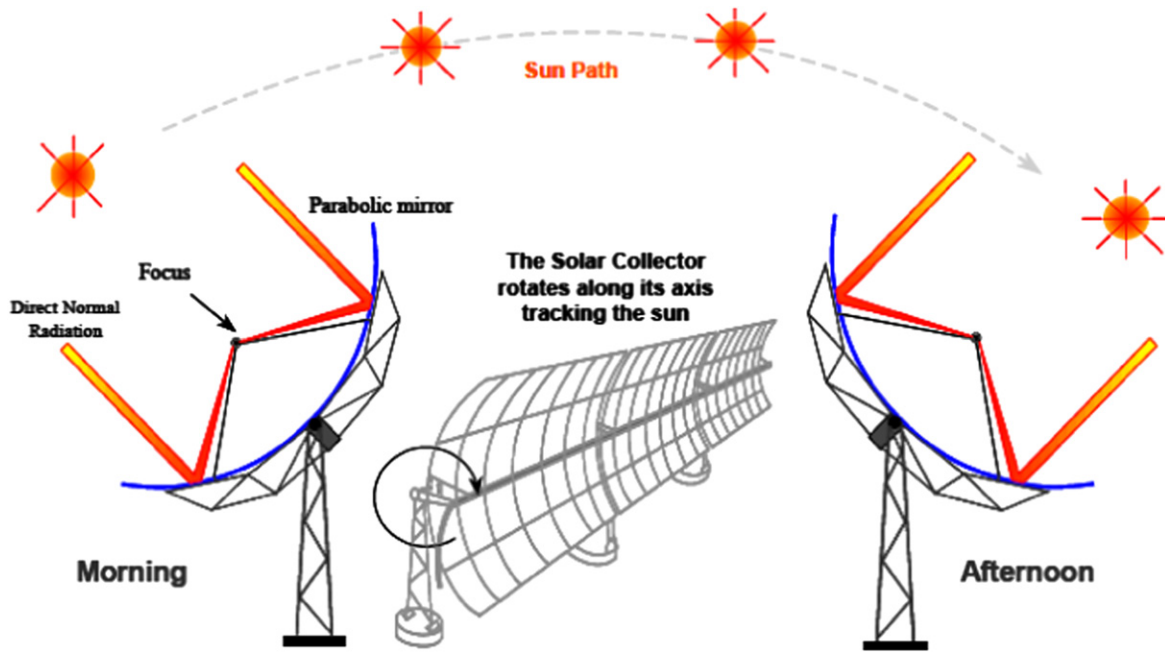


Fig. 2 Solar ray tracking for a single-axis parabolic trough collector. Reproduced from Solar Photochemistry Technology. Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas, Plataforma Solar De Almería, PSA-CIEMAT.

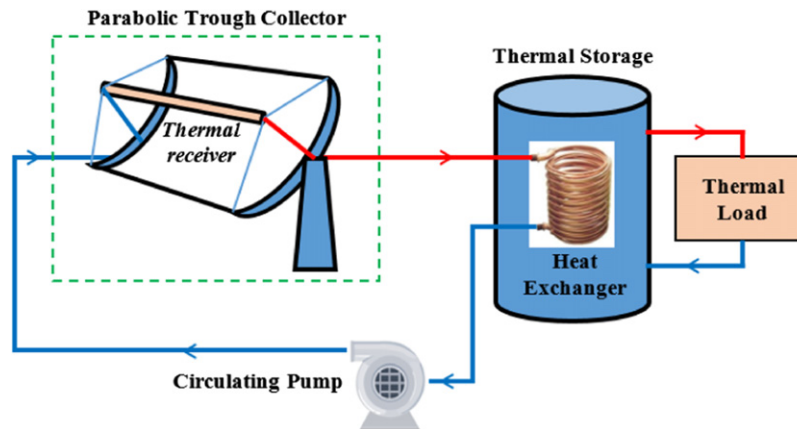


Fig. 3 Flow diagram of the parabolic trough collector system.

mechanism and a controller. The system design is simple and cost-effective in terms of material selected and thermal equipment structures. A small circulation pump conveys the heat transfer fluid (water) through the collector and thermal storage tank circuit. Concentrated solar rays on thermal receiver raise the heat transfer fluid temperature which in turn discharge thermal energy into the storage tank through the integrated helical heat exchanger. The thermal load profile during the day specifies the effective storage temperature. The main function of the controller is to ensure sun tracking of the PTC from sunrise to sunset. Other tasks include managing operation of circulation pumps or regulation of the heat transfer fluid flow rate, if applicable.

Parabolic Reflector and Thermal Receiver

Parabolic geometry

Fig. 4 shows the generic parabolic geometry, where the fixed line is called the directrix and the fixed point F is the focus. The parabola intersects its axis at a point V , called the vertex (Stine and Geyer, 2001).

If the origin is taken at the vertex V and the x -axis along the axis of the parabola, the equation of the parabola is

$$y = \frac{x^2}{4f} \quad (1)$$

where f is the focal length.

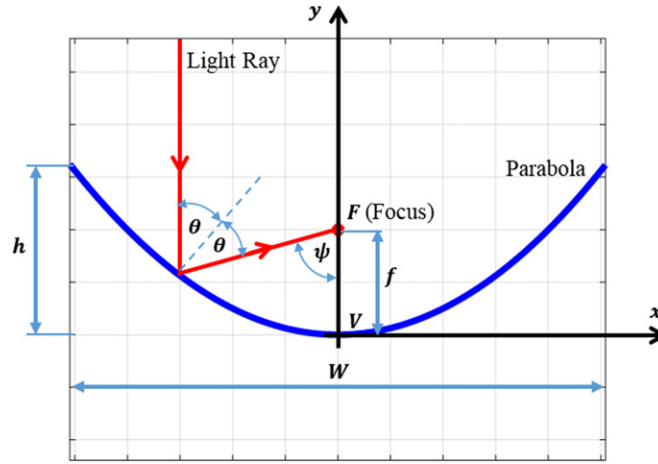


Fig. 4 Generic parabolic geometry.

If the origin is shifted to the focus F , as is often done in optical studies, the equation of a parabola becomes

$$y = \frac{x^2}{4f} - f \quad (2)$$

Once a specific portion of the parabolic curve has been selected (W), the height of the curve, h may be defined as the maximum distance from the vertex to a line drawn across the aperture of the parabola, i.e:

$$h = \frac{W^2}{16f} \quad (3)$$

Using the geometry of **Fig. 4**, the local rim angle ψ is double the reflection angle θ for a point on the parabolic curve. The rim angle ψ_{rim} may be found in terms of the parabola dimensions as

$$\tan(\psi_{rim}) = \left[\frac{W}{8h} - \frac{2h}{W} \right]^{-1} \quad (4)$$

Another property of the parabola that may be of use in understanding solar concentrator design is the arc length S ,

$$S = \left[\frac{W}{2} \sqrt{\left(\frac{4h}{W} \right)^2 + 1} \right] + 2f \ln \left[\frac{4h}{W} + \sqrt{\left(\frac{4h}{W} \right)^2 + 1} \right] \quad (5)$$

The following equivalencies are given for the convenience in evaluating parabolic geometry and related optical derivations:

$$\tan\left(\frac{\psi_{rim}}{2}\right) = \frac{W}{4f} \quad (6)$$

$$\frac{f}{W} = \frac{1 + \cos(\psi_{rim})}{4\sin(\psi_{rim})} \quad (7)$$

Fig. 5 shows the parabolic trough reflector profile and thermal receiver selected for the study.

Supporting structure

The proposed supporting structure is designed with a parabolic profile to carry the solar reflectors and to allow for solar tracking in an efficient way. The rotating reflector supports and thermal receiver assembly is shown in **Fig. 6**. The selected material for the reflector supports is wood for its less weight and sustainability. Woodchips can also be used with proper forming in a special die. The parabolic reflector material is selected to be polished metal sheets with back insulating coating.

Thermal Receiver

The thermal receiver is a steel pipe with the exposed half surface area coated with a selective coating (high temperature selective black paint) and the other half is thermally insulated. Metal tie rods connecting the reflector supporting structure are separated by 1 m for each reflector support along the trough length. Receiver supports connect the thermal receiver and reflector supports to hold the thermal receiver.

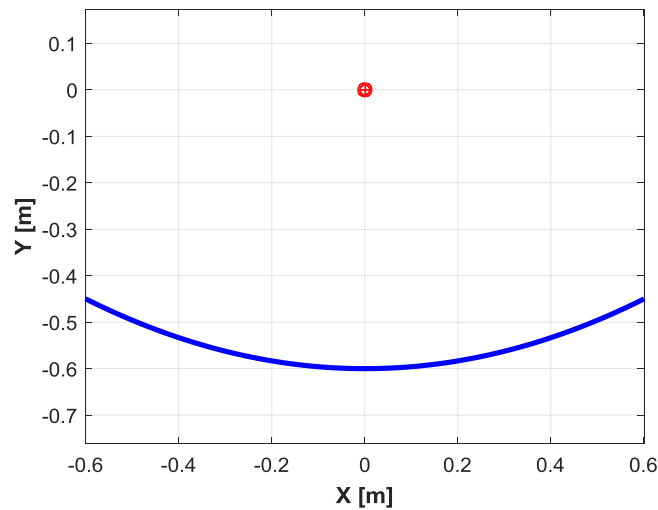


Fig. 5 Parabolic trough reflector profile and the thermal receiver.

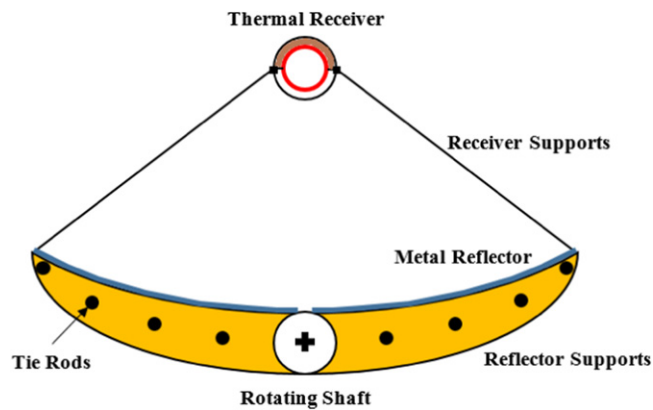


Fig. 6 Rotating reflector supports and thermal receiver assembly.

Thermal Energy Storage Unit

A cylindrical thermally insulated tank, made from recycled plastic, with 0.3 m^3 storage capacity is attached to the collector system for daily energy storage. A helical heat exchanger is integrated inside the storage tank and is made from copper. Hot water is drawn from the tank according to thermal load profile while makeup water is continuously supplied into the tank.

Heat Transfer Fluid Circulation System

The piping connecting the parabolic trough collector receiver with the thermal energy storage unit are made from insulated polypropylene (PPR) plastic, except for terminal flexible joints that are made from thermal plastic. In addition to circulating the heat transfer fluid through the collector circuit, the circulating pump slightly pressurize the fluid in order to maintain liquid-phase flow under the operating temperature range.

Controller and Tracking Mechanism

A DC stepper motor drive is used to supply the parabolic reflector structure with the power needed for solar tracking. The parabolic trough orientation is selected to be N-S aligned with single-axis tracking. The controller design is based on calculating solar angles according to local time, date, latitude and longitude of the collector location. A 1:1 gear ratio is selected, since the light weight of the supporting structure allows for low-torque requirements. [Fig. 7](#) shows an illustration of the tracking mechanism.

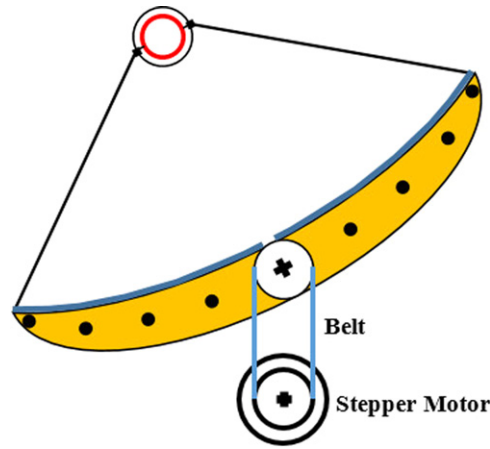


Fig. 7 Tracking mechanism for the small-scale PTC.

Table 1 Design parameters and materials of the parabolic trough solar collector.

Component	Parameter	Value	Material
Parabolic concentrator	Focal length [m]	0.60	Reflector supports: wood or woodchips Reflectors: polished steel sheets
	Parabolic arc length [m]	1.25	
	Aperture width [m]	1.20	
	Parabolic curve height [m]	0.15	
	Rim angle [°]	48.06	
	Parabolic trough length [m]	2.50	
	Metal sheet reflectivity [–]	0.90	
Absorbing coating	Absorptivity [–]	0.80	High-temperature paint
	Emissivity [–]	0.10	
Thermal receiver	Outer diameter of absorber tube [m]	0.0254	Carbon steel
	Inner diameter of absorber tube [m]	0.0194	
Thermal storage	Volume [m ³]	0.30	Plastic
Heat exchanger	Coil diameter [m]	0.20	Copper

The design dimensions, materials selected and computational parameters of the parabolic trough collector are summarized in [Table 1](#).

Mathematical Model

The mathematical model of the parabolic trough collector system is essentially dynamic, i.e., parameter simulation should be done in dynamic states. For this reason, a time-step simulation environment is employed for model building and performance evaluation of the parabolic trough solar thermal collector. High resolution (minutely) solar irradiance and meteorological data are obtained from the weather and solar monitoring station available at the Solar Energy Conversion Laboratory, Cairo University, Egypt (E 31° 00′ 30″, N 30° 02′ 10″). These data are used for assessing the performance of the system under real dynamic conditions.

Four demonstrative days during the year 2017 are selected to examine the system performance under dynamic conditions: vernal and autumnal equinoxes (March 20 and September 23), summer and winter solstices (June 21 and December 22). [Fig. 8](#) shows direct normal irradiance (DNI), ambient temperature (T_a) and wind speed (V_w) for equinoxes and solstices days, input to the mathematical model. For each day, fourteen hours of exposure, from 05:00 AM to 07:00 PM local time are assigned.

Optical Analysis

The optical efficiency model of the parabolic trough collector is given by

$$\eta_{opt} = \rho \alpha \gamma K_0 \quad (8)$$

where ρ is reflectivity of the metal reflectors, α is the absorptivity of the absorbing coating and γ is the intercept factor. A 2-D ray

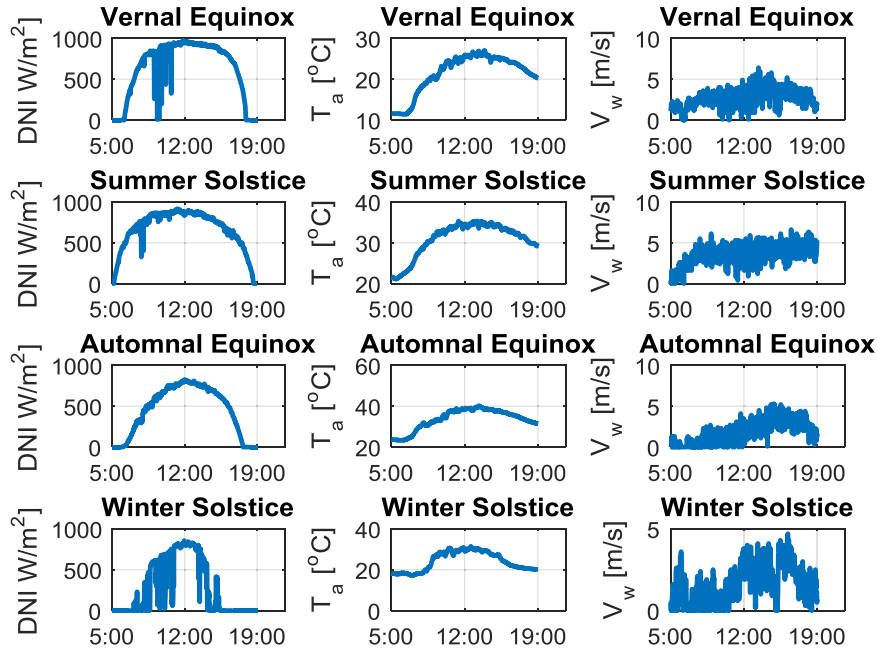


Fig. 8 Demonstrative days for the evaluation of performance of the PTC under dynamic conditions.

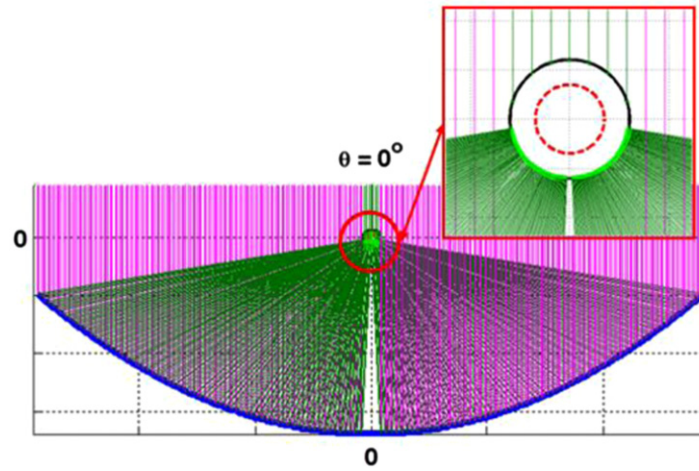


Fig. 9 A 2-D ray tracing diagram for optical performance of the PTC under dynamic conditions.

tracing analysis is performed for the ideal parabolic trough reflector profile and the results are shown in [Fig. 9](#). A practical value of $\gamma=0.95$ is used in the simulation to account for assembly and tracking errors.

The incidence angle modifier, IAM, factor (K_θ) is an extra loss due to the change of optical properties of the receiver materials with off-normal incidence angles. For single-axis parabolic trough collectors, the IAM model is given by [Eq. \(9\)](#). The constant b_o ranges from 0.27 to 0.4 for the EuroTrough prototype, as specified by the German Aerospace Center (DLR). An average value of $b_o=0.33$ is used for the present study.

$$K_\theta = 1 - b_o \left(\frac{1}{\cos(\theta)} - 1 \right) \quad (9)$$

where θ is the longitudinal component of the incidence angle of solar rays on the collector aperture.

Thermal Analysis

For the thermal receiver, it is assumed that all thermal losses are referred to the absorber area. The useful heat gain, $\dot{q}_u$ can be given, respectively, by [Eqs. \(10\)](#) and [\(11\)](#).

$$\dot{q}_u = h_{f,conv} A_{w,i} (T_{w,i} - T_f) \quad (10)$$

$$\dot{q}_u = \dot{m}_f c_{p,f} (T_{f,out} - T_{f,in}) \quad (11)$$

where $h_{f,conv}$ is the convection heat transfer coefficient of the working fluid inside the receiver, $A_{w,i}$ is the inner surface area of the absorber tube, $T_{w,i}$ is the wall inner temperature of the absorber tube and T_f is the mean fluid temperature of the heat collection element inside the absorber tube. The convection heat transfer coefficient $h_{f,conv} = Nu_f \lambda_f / D_{p,i}$, where Nusselt number (Nu_f) is given by Incropera *et al.* (2007).

$$Nu_f = \begin{cases} 1.86 \left(\frac{Re_f Pr_f}{L/D_{p,i}} \right)^{1/3} \left(\frac{\mu_f}{\mu_w} \right)^{0.14} & (Re_f \leq 2300) \\ \frac{(f/8)(Re_f - 1000)Pr_f}{1 + 12.7(f/8)^{1/2}(Pr_f^{2/3} - 1)} & (Re_f > 2300) \end{cases} \quad (12)$$

with $f = [0.790 \ln(Re_f) - 1.64]^{-2}$, $Re_f = 4\dot{m}_f / (\pi D_{p,i} \mu_f)$ is the Reynolds number of the fluid based on the inner tube diameter $D_{p,i}$ and Pr_f is the Prandtl number. $\dot{m}_f$ is the mass flow rate of the working fluid. Thermophysical properties of the heat transfer fluid are calculated based on the mean fluid temperature (T_f).

The useful heat gain is also calculated from the absorbed solar power reduced by thermal losses, Eq. (13). The absorbed solar power is given by Eq. (14) and the thermal losses is given by Eq. (15).

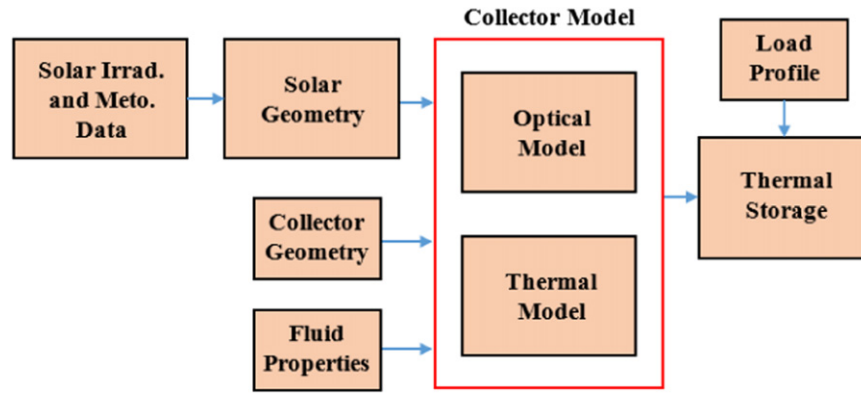


Fig. 10 Simplified block diagram of the simulation model.

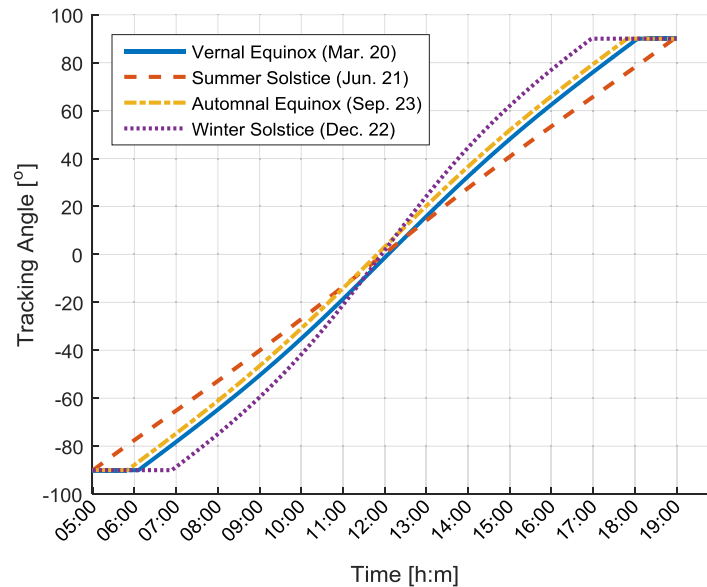


Fig. 11 Tracking angle of the parabolic trough collector for different simulation dates.

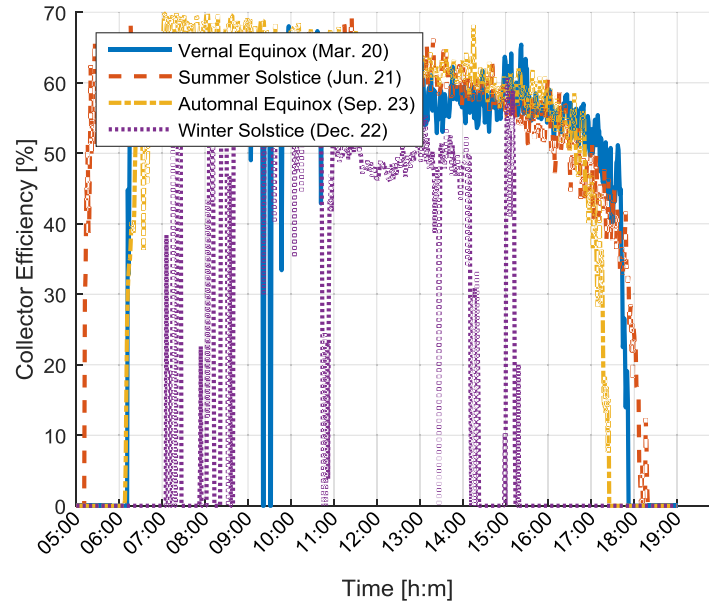


Fig. 12 Overall efficiency of the parabolic trough collector for different simulation dates.

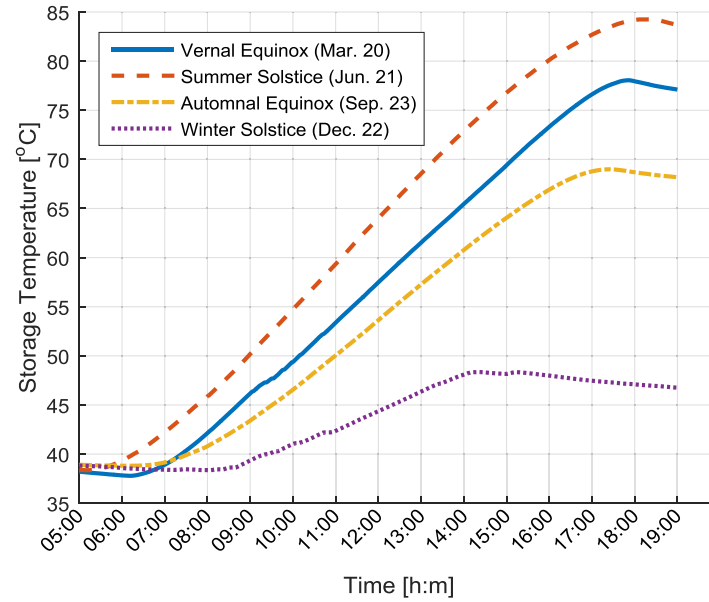


Fig. 13 Thermal storage temperature variations for different simulation dates.

$$\dot{q}_u = \dot{q}_p - \dot{q}_L \quad (13)$$

$$\dot{q}_p = \eta_{opt} \cdot DNI \cdot \cos(\theta) \cdot A_{ap} \quad (14)$$

$$\dot{q}_L = U_L A_p (T_p - T_a) \quad (15)$$

U_L is the overall heat loss coefficient.

Thermal Storage

The governing equation for the unstratified thermal energy storage tank, the heat exchanger and the thermal load is given by the relation (combined characteristics)

$$(mc)_s \frac{dT_s}{dt} = \dot{q}_u - \dot{q}_{Load} - \dot{q}_{L,s} \quad (16)$$

where $(mc)_s$ is the heat capacity of the thermal storage tank, $\dot{q}_{Load}$ is the thermal load profile and $\dot{q}_{L,s}$ is the thermal losses from the storage.

Results and Discussion

In order to produce simulation outputs for the single-axis parabolic trough solar collector, the developed mathematical model is implemented within a dynamic simulation environment under the pre-specified operating conditions. Numerical simulation algorithms are implemented in MATLAB-Simulink (MATLAB-Simulink Release, 2015b) environment to solve the developed sets of nonlinear algebraic and ordinary differential equations forming collector system models. Simulation outputs for different operating conditions are presented. A simplified block diagram of the simulation model is shown in Fig. 10.

Fig. 11 shows the tracking angle of the parabolic trough collector for different simulation dates. Fig. 12 shows the overall efficiency of the parabolic trough collector for different simulation dates. Transient cloud-cover effects of solar irradiance for the selected simulation dates are reflected on some efficiency values, especially for the winter solstice. Based on an initial storage temperature of 40°C and a zero thermal load profile (charging), the variation of the thermal storage temperature with time is given by Fig. 13 for different simulation dates.

Conclusions

The article introduced a simplified design of a small-scale parabolic trough solar thermal collector with most of components made from sustainable materials. A nonlinear dynamic model of the small-scale parabolic trough collector system was built and simulated for different representative dates (equinoxes and solstices) during the year. Optical and thermal mathematical models of the collector were introduced and the overall performance was investigated. It was shown that the design of this size of parabolic trough collectors is able to provide hot water at a suitable temperature range for domestic uses. The system simplicity and effectiveness are also comparable to similar system designs utilized for domestic hot water productions under the same operating conditions.

See also: Bamboo Fiber as Fillers for Polypropylene-Nanoclay via Injection Molding. Recycled Clothes With Polypropylene-Nanoclay for Industrial Product via Injection Molding. Reuse of Waste Corrugated With Coir Fibers as a Packaging Materials. Scaling Up and Intensifying Stakeholders Engagement for Evidence-Based Policymaking: Lessons Learned

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Development of Epoxy Based Composites Using Bamboo and Waste Metal Chips

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Introduction

Waste management is an integral part of a sustainable manufacturing system. Recently, there has been an increasing trend to use waste material as an ingredient of a composite material. For example, Thomas *et al.* (2016) replaced natural fine aggregate in a concrete by crumb waste tire rubber. Rubberized concrete can be used in an aggressive acidic environment. It can also be used in structures where there are chances of brittle failure. In a study, Thomas and Gupta (2016) observed that the crumb rubber might be used in a high strength concrete as a partial substitute for fine aggregate up to 12.5% by weight for attaining the compressive strength above 60 MPa. Similarly, granite dust has been used as a replacement of natural fine aggregate (Singh *et al.*, 2016). Other materials that have been used as the replacement of conventional aggregates are dimensional stone waste, fly ash, silica fume, slag, rice husk, ash and metakaolin (Rana *et al.*, 2016).

An important area of manufacturing requiring immediate attention for waste management is machining. Machining is one of the most widely used manufacturing processes. The chip disposal is a very important aspect of environmentally friendly machining (Dixit *et al.*, 2012). Recycling of chips, although a routine procedure in industry, needs a relook by the researchers. Some researchers have already paid attention to this activity. Gronostajski *et al.* (1996) used hot extrusion process to increase physical and mechanical properties of the chips and its alloy composites with addition of small amount of tungsten powder. Sherafat *et al.* (2009) used a small quantity of pure aluminum powder for preparing a composite material of aluminum alloy chips using hot extrusion. Mindivan *et al.* (2014) fabricated a composite using magnesium/aluminum chips and carbon nanotubes and evaluated the properties. Small addition of carbon nanotubes increased the hardness and corrosion resistance of composites compared to base alloy. Simon *et al.* (2016) reviewed the methods for recycling of contaminated metallic chips.

Karadag *et al.* (2016) prepared the composites using brass (CuZn30) and steel (S355JR) chips as constituents by cold pressing followed by liquid phase sinterization. The mechanical properties of the composite were obtained and were comparable with the mechanical properties of the bulk brass. Gronostajski and Matuszak (1999) developed the method of production of composite material by the conversion of chips directly (without melting processes) into the finished product using powder metallurgy technique followed by extrusion. The produced composites were characterised by good properties. The present work focuses on developing a composite by using metal chips. Lela *et al.* (2016) developed the mathematical model of products made from direct recycling of ENAW 2011 aluminum alloy chips by utilizing forward hot extrusion process. The influence of chip size, compaction force and extrusion temperature on mechanical properties were studied. The extrusion temperature was found to be the most significant factor influencing the mechanical properties.

Sakaray *et al.* (2012) conducted various test on Moso bamboo (a variety in China) to find their physical and mechanical properties. The tensile strength was found half as compared to mild steel. Agarwal *et al.* (2014) performed the axial and transverse loading test on bamboo reinforced columns and observed the load carrying capacity, lateral deflection, and failure mode pattern. Two-point load test was performed on beams to study their behaviour in bending. The tensile strength of bamboo-fiber reinforced plastic composite was comparatively equal to that of mild steel, whereas its density was only 12% of that of mild steel (Jindal, 1986). Zakikhani *et al.* (2014) described the processes for extracting fibers from raw bamboo culm followed by bamboo plastic composite preparation and its thermal analysis.

Chen *et al.* (1998) prepared the bamboo-fiber reinforced polypropylene composite by using maleic anhydride-grafted polypropylene (MAPP) as a compatibilizer for the composites and studied its effect on the mechanical properties of composites. Most of the properties of polyvinyl chloride (PVC)-based composites with Malaysian bamboo were compatible with wood-PVC composites, which is an evidence of potential utilization of bamboo as an alternative material for wood-plastic composites (WPCs) industry (Bahari and Krause, 2016). The utilization of Malaysian bamboo not only provides an alternative for WPCs, but also it encourages the development of thermoplastic composites towards green-oriented, cleaner production and to initiate bamboo for commercial industries in Malaysia. In this work, it was aimed to use waste metal chips for developing a sandwich-structured composite. It was attempted to develop a low cost composite using sized waste metal chips and locally available bamboo in the North Eastern part of the India. Epoxy was considered as base material for the first phase of proposed composite with waste metal chips.

Experimental Determination of Physical and Mechanical Properties of Bamboo

The properties of bamboo are affected by age, length, diameter and moisture content. Dry bamboo is used to manufacture bamboo-based product as in case of dry bamboo, properties do not change with time. Locally available matured Jati (a variety of

bamboo in India) bamboo pieces were collected for use in proposed experimental works. Procedures mentioned in relevant IS codes were adopted for determining the physical and required mechanical properties of bamboo.

Moisture Content of Bamboo

Moisture content is the quantity of water contained in a piece of bamboo and is considered to be one of the important physical parameters that reduces the strength of bamboo. In general practice, the moisture in raw bamboo is removed for further structural use of bamboo. Hence, the bamboos are seasoned naturally or mechanically. The specimens for determining moisture content were taken from the test specimens used for determining mechanical properties. In this case, three specimens with 25 mm length, 25 mm width and full wall thickness were taken for the determination of moisture content. Procedures mentioned in IS 6874: [2008] were followed to prepare specimens and to carry out test for determining moisture content. Specimen sizes were taken as per the Indian standard code. The samples were weighed correct to 0.01 g and then dried in an oven at a temperature of $103 \pm 2^\circ\text{C}$ for 24 h. The weights of specimen were observed at every 2 h interval up to total of 24 h. The final mass was taken as oven-dry mass. The loss in mass expressed as a percentage of oven-dry mass was taken as the moisture content of the test specimen. This was calculated correct to two place of decimal by the following formula:

$$\text{Percentage Moisture content} = \frac{m_i - m_o}{m_i} \times 100 \quad (1)$$

where m_i is the initial mass of the test specimen and m_o is the oven-dry mass. Normally green bamboo has an average of 50%–75% moisture content depending upon the age, season, geographical location, species and watering methods. The weights of specimen at 8, 16 and 24 h duration along with moisture content are presented in [Table 1](#).

From the observed experimental results, it is inferred that the moisture content in raw bamboo is very high. Generally, it is undesirable to use material that changes its moisture content rapidly because moisture affects the physical and mechanical properties. To overcome the problem, the bamboo pieces were kept in hot-dry oven for an average period of 8 h, because most of the moisture content is absorbed by hot-dry oven in first 8 h.

Density of Bamboo

The test specimens for determining density of bamboo were taken from the freshly felled culms with 25 mm width and 25 mm length with full wall thickness. Specimen sizes were taken as per the [Indian Standards IS 6874:\(2008\)](#). The volume of the specimens was measured by water displacement method. Two samples were taken from middle section (MS) and bottom section (BS). Specimen was weighted to an accuracy of 0.01 g. After determining green volume the specimen was immediately kept in hot dry oven. Specimen was weighted and dried thereafter. The weighing was carried out and recorded every 2 h for 24 h until the difference between successive weighing does not exceed 0.01 g, when the specimen was considered to be completely dry. The final mass was taken as oven-dry mass of specimen. The weights of specimen at 8, 16 and 24 h duration are presented in [Table 2](#).

The green volumes of bottom section and middle section were found to be 5.15 cm^3 and 5.12 cm^3 respectively. Similarly, densities of bottom section and middle section were found to be 644.95 kg m^{-3} and 625.97 kg m^{-3} respectively for oven-dry mass of 24 h. It is generally accepted that an increase in density of the culm is mainly due to thickening of the cell wall. The measurement of density at different culms gives different results.

Table 1 Moisture content in bamboo

	<i>Specimen-1</i>	<i>Specimen-2</i>	<i>Specimen-3</i>
Initial weight (g)	4.62	4.81	4.75
Weight at 8 h (g)	3.04	3.17	3.13
Weight at 16 h (g)	3.01	3.13	3.09
Weight at 24 h (g)	3.01	3.12	3.09
Total moisture content, %	34.85	34.96	35.00

Table 2 Weight of bamboo with time during oven-drying

<i>Time (hour)</i>	<i>Weight of specimen BS (g)</i>	<i>Weight of specimen MS (g)</i>
0	5.19	5.04
8	3.43	3.31
16	3.33	3.21
24	3.32	3.21

Tensile Strength of Bamboo

It is mandatory to know mechanical behaviour of raw materials prior to its use in new product. The major parameters that describe the stress-strain curve are the tensile strength, elastic modulus, percent elongation and the reduction in area, which were obtained through tensile test. In case of bamboo, specimens were prepared from the lower portion, middle portion and top portion of the dry log. Node was kept at the centre of specimen. The general direction of fibers in specimen was parallel to the longitudinal axis of specimen. In order to prepare specimen, first a bamboo was cut into two-piece length wise and the two halves were again divided longitudinally into three pieces without damaging the fibers. Fibers along the culm were distributed length wise. Universal Testing Machine (Make: Fine Testing Machine, India; Model: TUC 1000) was used to determine the tensile behaviour of reinforcing bars. Larger culms were split into approximately 19 mm wide as per the US naval laboratory recommendation or 20 mm wide as per IS 6874: [2008]. The total length of the specimens was approximately 450 mm long with a gauge length of 150 mm. Since grip length plays important role in holding the specimen without slip during test, extra length of approximately 150 mm on both ends of the specimens were kept.

The specimens were tested as per stipulations and guidelines provided in IS:6874: [2008] using Universal Testing Machine (UTM). Rate of loading was maintained at a strain rate of $6.67 \times 10^{-5} \text{ s}^{-1}$. Initially, the bamboo strip was elastically deformed giving a linear relationship of load and extension. The purpose of tensile test was to determine the tensile strength of bamboo and failure pattern with its locations, which indicates the quality of the specimen. Nine specimens were tested and the results are given in Table 3. Three samples were taken from each section of bamboo i.e., middle section (MS), bottom section (BS), and top section (TS).

It was very difficult to avoid crushing of specimen outside the gauge portion during tensile tests of specimen. This is because specimens were very sensitive to fail near the grip. In addition there was a problem of sliding of the sample in the grip before the failure in the gauge portion due to slippery nature of the material. Three types of failure patterns like typical splitting failure, typical failure at grip and typical failure at node were observed during the tests. Further, in some specimens, failure occurred firstly in the outer fibers and moved towards the core. The crack was initiated from node in the specimen and propagated towards grip because the fibers in the nodes were brittle and stiff. The fibers were much denser and disordered at nodes than those of internodes regions where fibers were straight.

From Fig. 1, it is observed that bamboo had very high tensile strength. The lower or bottom section (BS) of bamboo had less tensile strength than middle (MS) and top section (TS). This may be due to moisture retained in specimen because of thicker wall of bamboo. The middle and top section had almost same tensile strength. High tensile strength of bamboo gives high strength to composite materials.

Compressive Strength of Bamboo

The compressive strength is the property that helps a material to withstand loads acting along the axial direction. Specimen for compressive strength were taken from the lower portion, middle portion and top portion of the dry bamboo between two nodes and the length of specimens was taken equal to the outer diameter of the bamboo that was measured as described in IS 6874: [2008]. The end planes of the specimen need to be perfectly oriented at right angle to the length of the specimen. The end planes of the specimens were made flat with the help of a lathe machine, within a maximum flatness of 0.2 mm. The same UTM that was used for tensile test was also used for evaluating the compressive strength of bamboo. The specimen was placed at the centre of the platens fixed in the UTM cross head and a small load of 1 kN was applied to hold the specimen in the position. The load was applied continuously at a strain rate of $1.9 \times 10^{-3} \text{ s}^{-1}$.

The maximum compressive strength was calculated by the formula

$$\sigma_{ult} = \frac{F_{ult}}{A} \quad (2)$$

where F_{ult} is the maximum load and A is the area of cross-section of test specimen given by

$$A = \frac{\pi}{4} \{D^2 - (D - 2t)^2\} \quad (3)$$

where D is the outer diameter and t is the wall thickness. The maximum load at which specimen failed was recorded and rounded to the nearest 0.5 N mm^{-2} . Three samples were taken from each section of the bamboo i.e., middle section (MS), bottom section (BS) and top section (TS). The compressive strength of specimens is presented in Table 4. All sections of dry bamboo bear almost equal compressive strength. High compressive strength of bamboo will lead to good mechanical properties in the proposed composite material. Fig. 2 shows the stress-strain curves under compression for three sections of the bamboo. For each section, three replicates have been presented.

Table 3 Tensile strength of different section of bamboo (average of 3 replicates)

Specimen	Thickness (mm)	Width (mm)	Load (kN)		Tensile strength (MPa)	
			Average	Range	Average	Range
Bottom section (BS)	7.8	20	39.03	2.10	250.21	13.46
Middle section (MS)	5.63	20	30.10	4.00	270.26	26.61
Top section (TS)	4.6	20	22.80	2.80	248.54	30.43

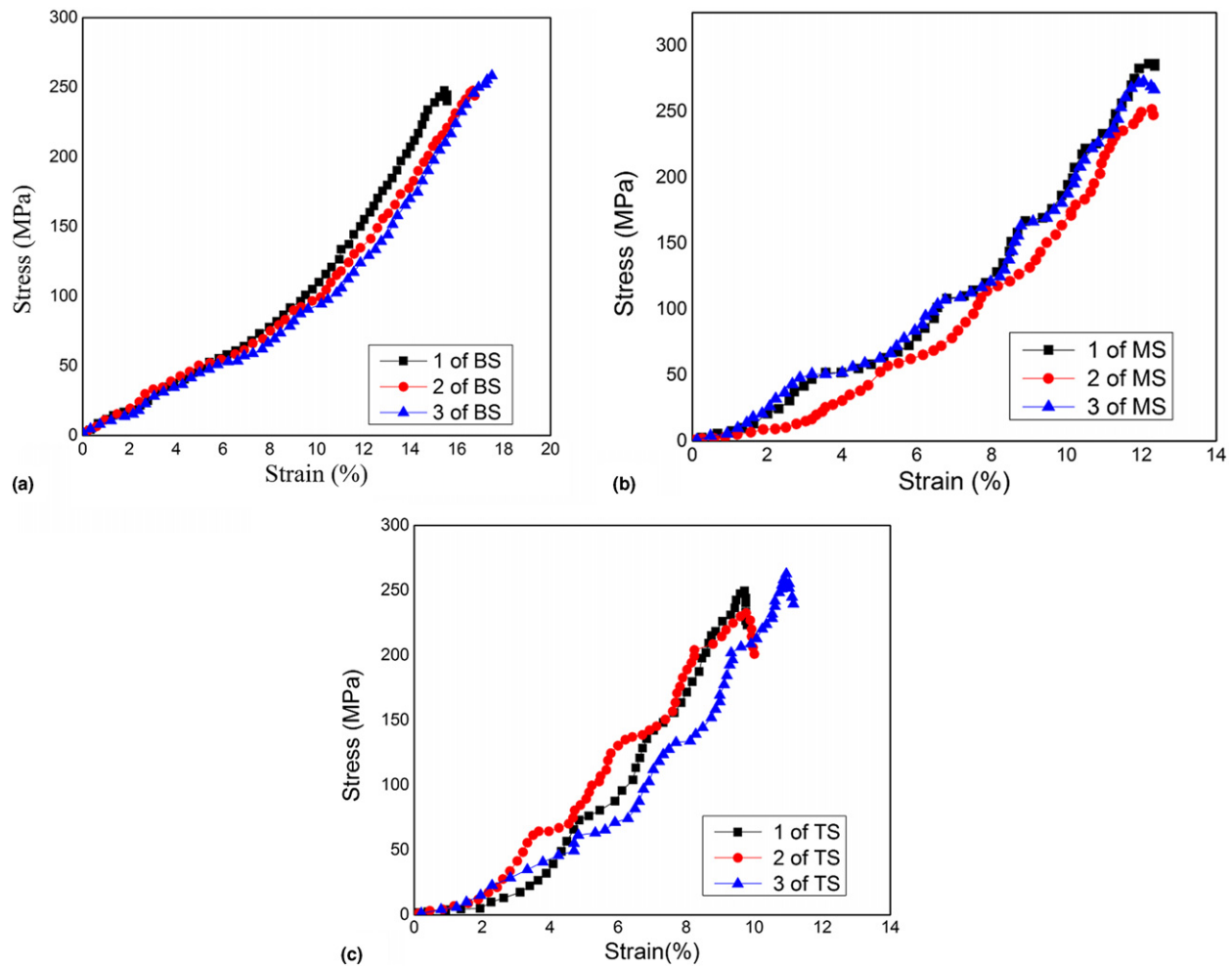


Fig. 1 Stress-strain diagram of bamboo strip under tension for (a) Bottom section, (b) middle section and (c) top section.

Table 4 Compressive strength of bamboo (average of 3 replicates)

Specimen	Thickness (mm)	Diameter (mm)	Load (kN)		Compressive strength (MPa)	
			Average	Range	Average	Range
Bottom section (BS)	8.2	56.2	78.00	3.60	63.07	2.91
Middle section (MS)	6.03	53.4	52.50	3.10	58.51	3.43
Top section (TS)	5.22	48.5	42.30	4.50	59.71	6.02

Fabrication and Properties of Matrix of Waste Metal Chip

Metal chips are waste material of different machining operation like turning, milling, drilling and shaping. Metals chips are categorized based on their shapes and sizes such as continuous, built-up edge, serrated and discontinuous chips. In this work, thin threads of partially continuous waste metal chips were collected from mechanical workshop. The chip-sizes vary from 1 mm to 5 mm in length and 0.5–2 mm in width. The mix of epoxy and metal chips were used as matrix and bamboo strip as reinforcement. Araldite and Fevicol were used as epoxy whereas metal chips were used as reinforcing constituents to form a matrix. Matrix of waste metal chips and two different epoxies were prepared in different proportions of waste metal chips and individual epoxy.

The proportions of waste metal chips and Araldite (by weight) were 10:1, 10:1.5, 10:2, 10:3, 10:4, 10:5, 10:6 corresponding to SA1, SA2, SA3, SA4, SA5, SA6, SA7, respectively. Similarly, the proportions of waste metal chips and Fevicol (by weight) were 10:2, 10:3, 10:4 corresponding to SF1, SF2, SF3, respectively. The matrix prepared with Araldite worked for all the proposed mix proportions of metal chips and Araldite. Hence, seven specimen of composite have been prepared with all the seven different proportion of metal chips-Araldite mix and bamboo strips. However, in case of matrix prepared with Fevicol, only three

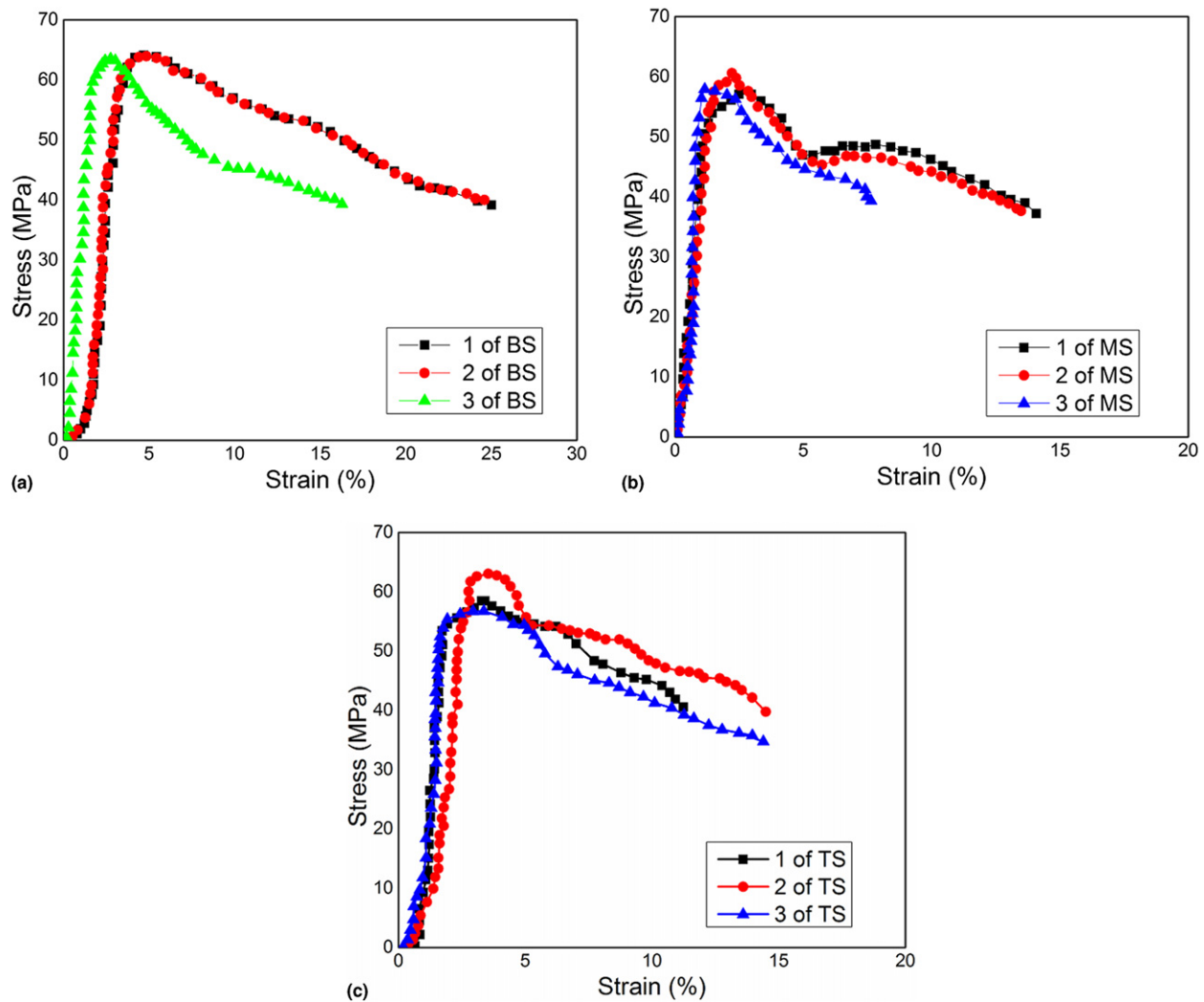


Fig. 2 Stress-strain diagram of bamboo under compression for (a) bottom section, (b) middle section and (c) top section.

proportions of metal chips and Fevicol worked good among more different proposed proportions. Hence, only three specimens of composites had been prepared with three different proportion of metal chips-Fevicol mix and bamboo strip. Only 10:3, 10:4 and 10:5 proportion of metal chips and Fevicol were found to be workable and result could be achieved.

Matrix of Metal Chips and Araldite

In these specimens, Araldite was used with chips for composing matrix. Different specimens were prepared with different chips to Araldite ratio. 21 specimens were prepared with seven different ratios. Specimens with less ratio of Araldite had rough surface finish than specimens with higher ratio of Araldite. The compressive strength of different specimens is presented in Table 5. The samples after testing under compression are shown in Fig. 3.

From Fig. 4, it is observed that the strength of matrix depends on proportion of chips as well as epoxy. The compressive strength of matrix first increases and then decreases with increase in the quantity of Araldite. The matrix with chip to Araldite ratio 10:4 showed higher compressive strength and thus, was used for making the new composites.

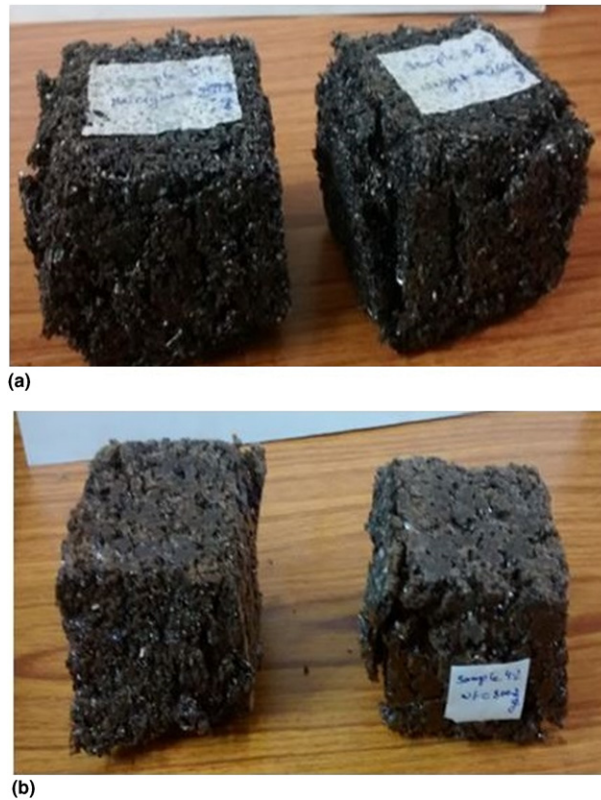
Matrix Made of Chips and Fevicol

In this case, matrix was formed by mixing Fevicol with metal chips. Six specimens were prepared from three different ratios. The compressive strength of different specimens is presented in Table 6.

From Fig. 5 and Table 6, it is observed that the load carrying capacity of the matrix was very low and the strength of the matrix depended on the ratio of chips and epoxy. The compressive strength of matrix increased first and then decreased with increase in

Table 5 Compressive strength of matrix made with metal chips and Araldite (average of 3 replicates)

Sample	Weight (g)		Compressive strength (MPa)	
	Average	Range	Average	Range
SA1	227.20	2.40	3.30	0.12
SA2	248.00	2.00	7.30	0.72
SA3	260.00	1.20	11.30	0.40
SA4	301.30	2.60	29.10	2.52
SA5	324.90	2.50	57.40	0.40
SA6	322.90	0.50	41.60	1.52
SA7	299.40	1.60	33.90	0.52

**Fig. 3** Tested specimens of matrix with metal chips and Araldite under compression (a) SA3 and (b) SA4.

the amount of epoxy. The maximum strength was observed at the ratio of 10:3 and thus, this proportion was used to form the new composites with Fevicol.

Fabrication and Determination of Properties of Bamboo-Chip-Matrix Composite

Bamboo logs of 250 mm long and strips of width 25 mm were prepared from matured bamboo. The thickness of single bamboo strips varied from 1.7 to 2.2 mm depending on position of log and type of bamboo. Three strips were joined with the help of epoxy (Araldite) side by side. The strips were joined side by side to form a flat panel of size 250 mm length and 75 mm width. In the first case, preparation of laminated composite of two layers and three layers of bamboo panels was attempted using Araldite in between to bond the bamboo panels. In the second case, specimens with bamboo-matrix composite was prepared. The matrix formed with epoxy and metal chips was again used with bamboo strip panels to give panel form of bamboo and metal chips composite. Matrix of 10:4 of metal chips to Araldite was selected to form new composite with Araldite. Similarly, matrix of chips to Fevicol ratio of 10:3 was utilized to form the composites. Specimen with thickness 14.5 mm had two layers of composite between three layers of bamboo strips and rest had one layer of composite between two layers of bamboo strips.

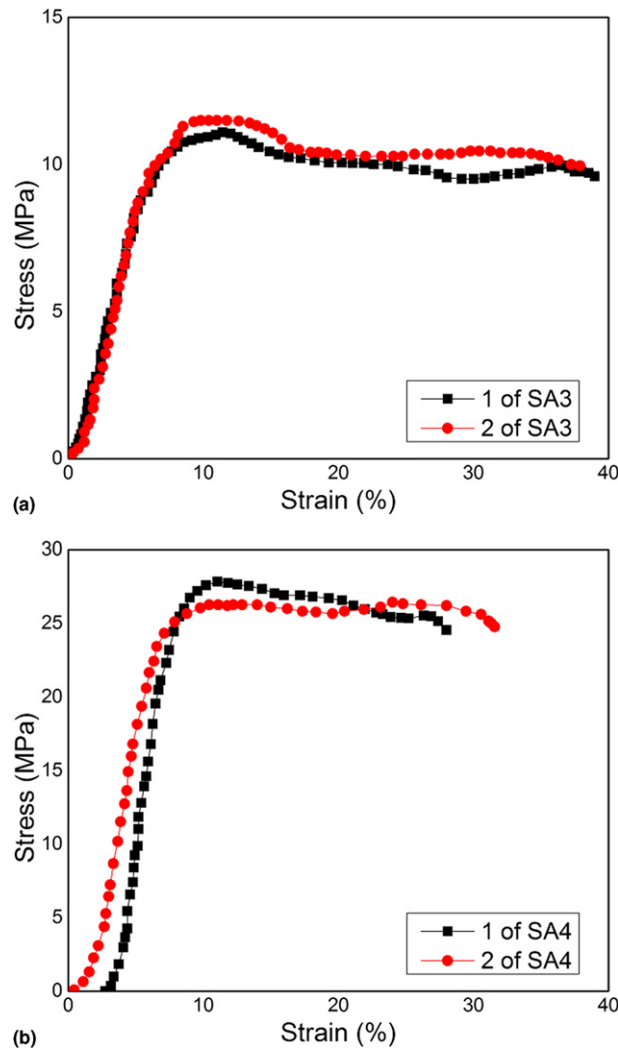


Fig. 4 Stress-strain diagram of matrix of metal chips and Araldite under compression for (a) SA3 and (b) SA4.

Table 6 Compressive strength for matrix made with chips and Fevicol (average of 2 replicates)

Sample	Weight (g)		Load (kN)		Compressive strength (MPa)	
	Average	Range	Average	Range	Average	Range
SF1	249.05	0.90	11.25	0.50	4.50	0.20
SF2	280.90	1.40	13.10	0.20	5.24	0.08
SF3	287.35	0.70	2.55	0.10	1.02	0.04

The prepared matrix was placed upon the prepared flat panel of bamboo strip with help of mason's trowel. The second panel of bamboo was kept upon the matrix on first bamboo panel. Both the composites were then kept on flat surface and a flat block of 10 kg weight was kept upon it to provide constant load to every part of the composite for attaining strong bonding between matrix and bamboo panel. Thereafter, the panel of both composites was cut into the specific size of 240 mm length and 20 mm width using manual hacksaw. Some of prepared composite specimens are shown in Fig. 6.

The use of epoxy (Araldite and Fevicol) between the layers of bamboo and matrix helps in protecting bamboo strips getting moisture because the epoxy is hydrophilic in nature. The preparation of matrix of metal chips and epoxy was carried out at room temperature.

Tensile Behaviour of Composite

Tensile test was performed on composites that were made up of bamboo strips, waste metal chips and epoxy. Tensile test was conducted on Universal Testing Machine model TUN 200. The middle section of 80 mm length of the specimen was considered as

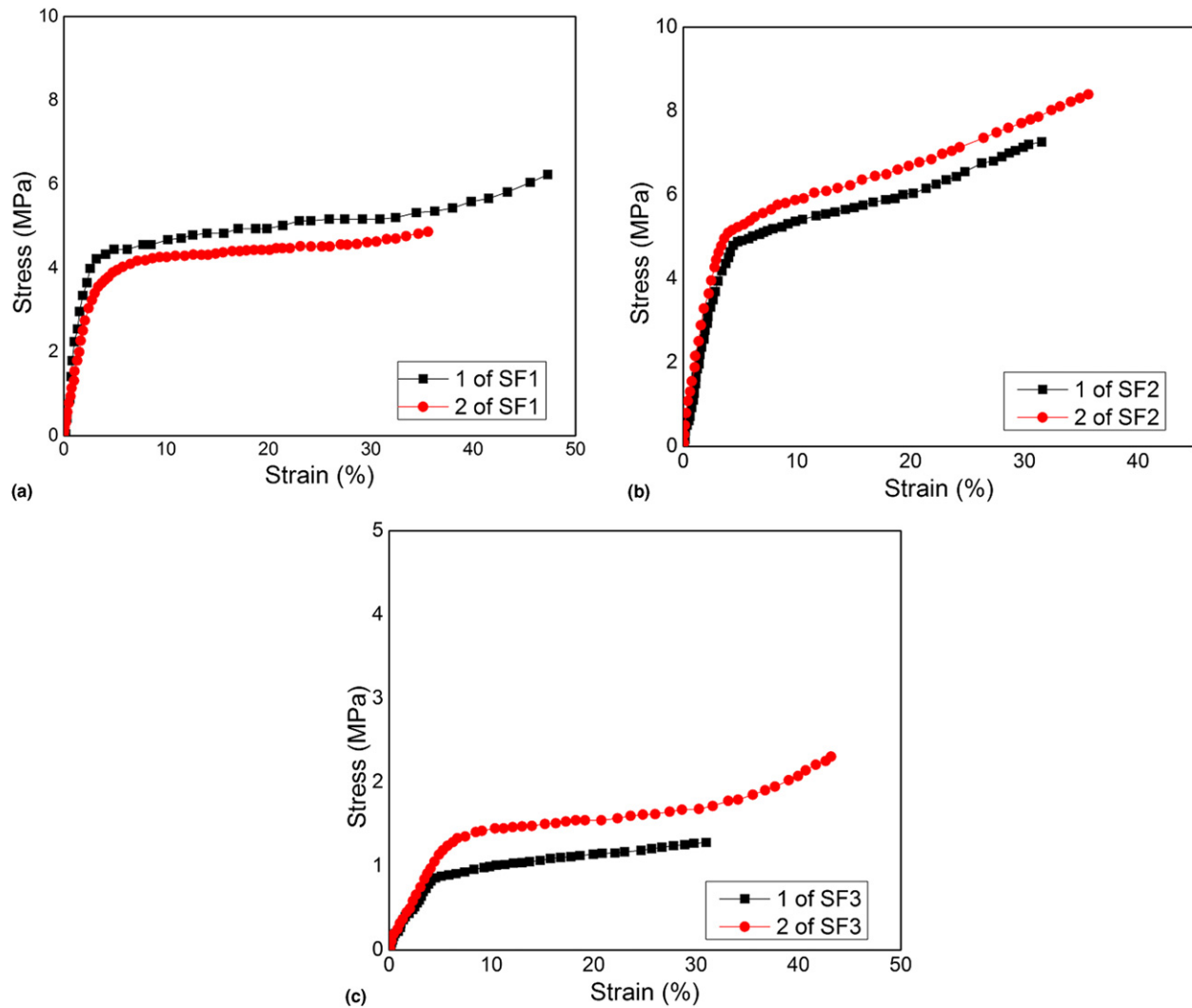


Fig. 5 Stress-strain diagram of matrix of metal chips and Fevicol under compression for (a) SF1, (b) SF2 and (c) SF3.



Fig. 6 Prepared composite specimens for tension test.

gauge length and rest are kept for clamping at both the ends. The load was applied continuously at a strain rate of $1.25 \times 10^{-3} \text{ s}^{-1}$. When the composite specimen was subjected to an external tensile loading, the composite strip had undergone elastic and plastic deformation.

Tensile behaviour of composite made with only bamboo strips and Araldite

Prepared specimens with length of 250 mm were tested using relevant clauses and stipulations mentioned in IS 6874: [2008]. Three specimens for two layers bamboo strips (BL2) and three layers bamboo strips (BL3) were tested. The tensile strengths of bamboo strips are presented in Table 7. From Table 7, it is observed that the tensile strength of two-layer bamboo strip was greater than tensile strength of three-layer of bamboo strip. Fig. 7 shows the corresponding stress-strain curves.

Tensile behaviour of composite made of bamboo and matrix of metal chips and epoxy (Araldite and Fevicol)

All the specimens were prepared with matrix of metal chips to Araldite ratio 10:4. The specimens had single and two layers of matrix between two and three bamboo strips, respectively. Specimen with thickness 14.5 mm had two layers of matrix between three bamboo strips and remaining specimens had one layer of matrix between two bamboo strips. The tensile strength for different thicknesses of composite is presented in Table 8.

Table 7 Tensile strength of composite with only bamboo strip (average of 3 replicates)

Specimen	Width (mm)	Weight (g)		Tensile strength (MPa)	
		Average	Range	Average	Range
BL2	20	13.47	0.70	92.57	5.50
BL3	20	21.70	1.90	74.95	4.85

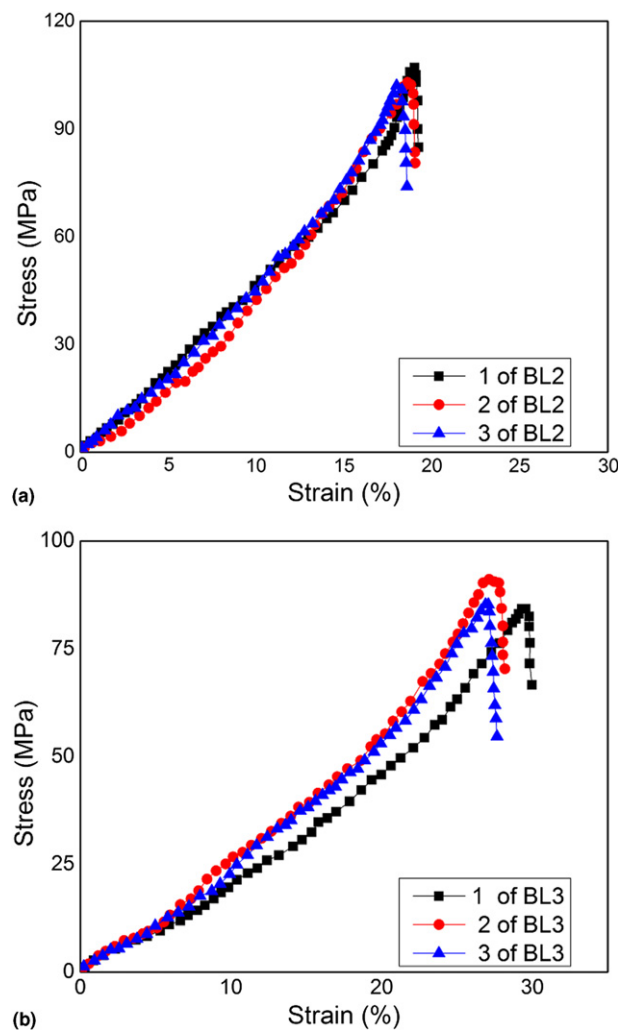
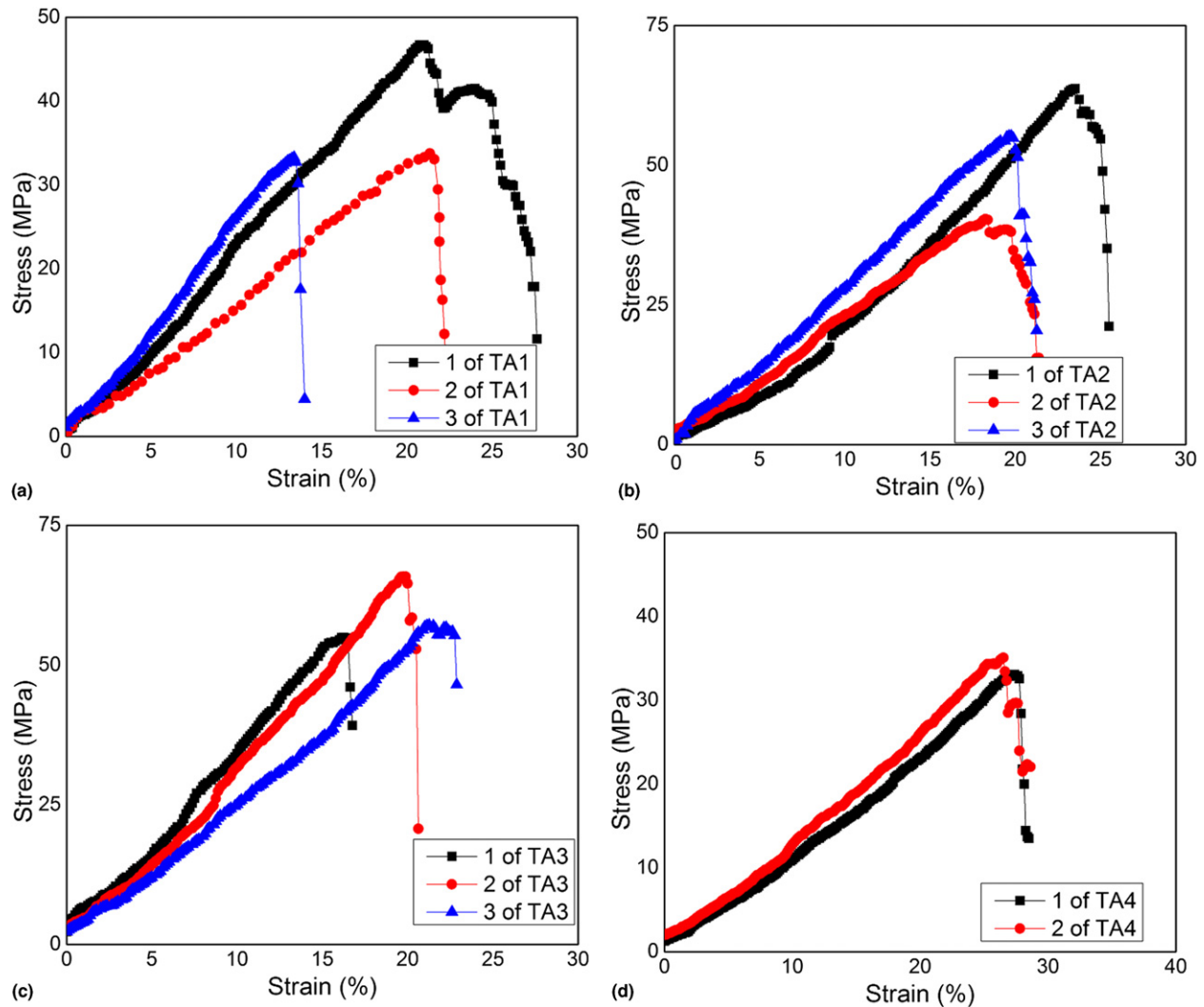


Fig. 7 Stress-strain diagram of composites of only bamboo strips under tension for (a) BL2 composites and (b) BL3 composites.

Table 8 Tensile strength for composite made with Araldite (average of 3 replicates)

Specimen	Thickness (mm)	Weight (g)		Load (kN)		Tensile strength (MPa)	
		Average	Range	Average	Range	Average	Range
TA1	15.20	156.20	3.80	11.97	4.08	39.43	13.50
TA2	12.10	111.83	10.46	12.88	5.76	54.86	20.80
TA3	8.50	66.03	3.00	10.31	1.85	59.86	10.80
TA4	14.50	123.50	7.00	9.88	0.58	34.30	2.60

**Fig. 8** Stress-strain diagram for tensile test of composites made with Araldite for (a) TA1 composites, (b) TA2 composites, (c) TA3 composites and (d) TA4 composites.

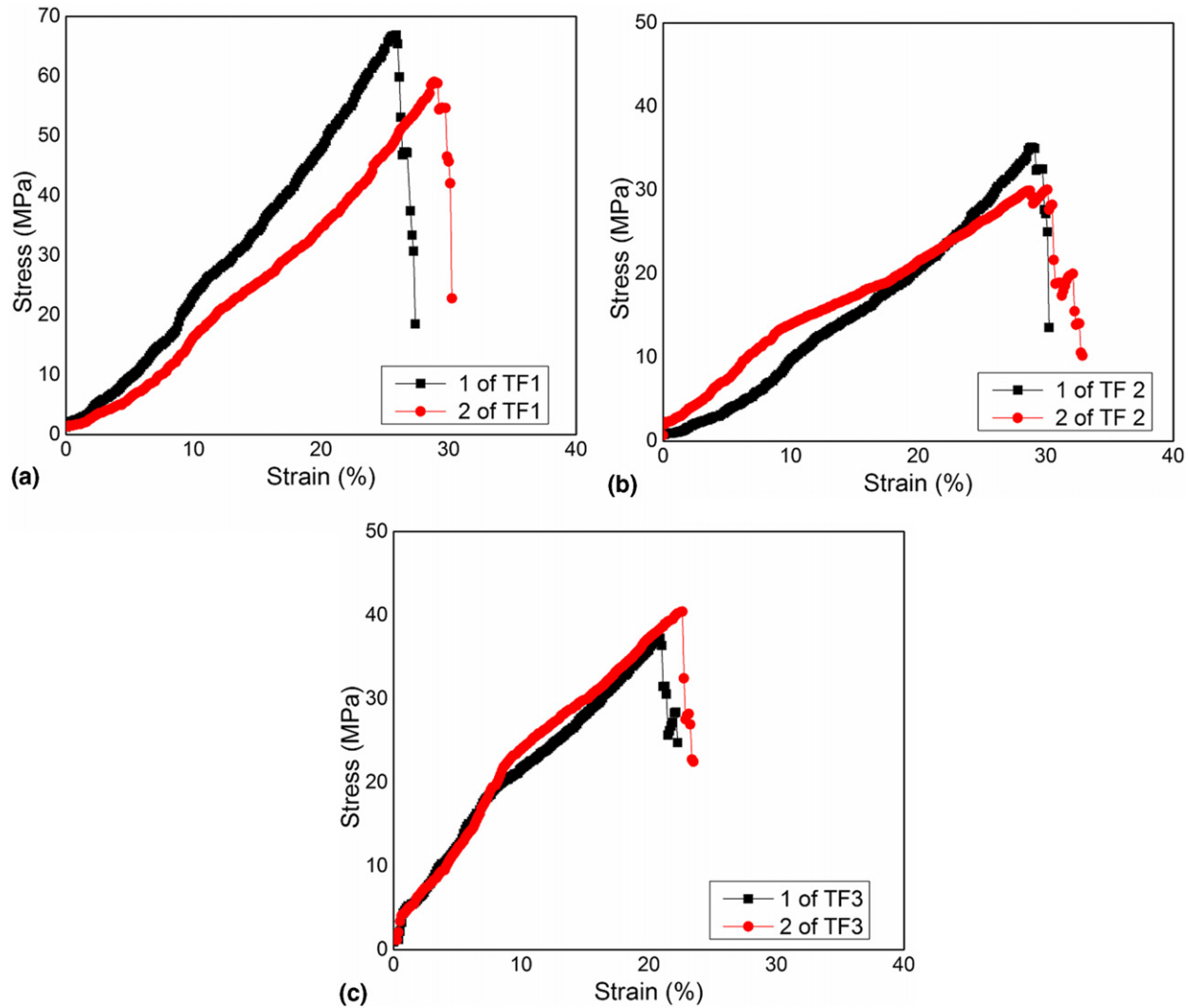
From **Table 8** and **Fig. 8**, it is inferred that different group of samples bear different level of tensile strength and strain. Further, two types of composites prepared using metal chips to Fevicol ratio of 10:3 were tested. One type had one layer of composite and two bamboo strips and other had two layers of composite and three bamboo strips forming a thickness of 14.40 mm. The tensile strength of composite is presented in **Table 9**. **Fig. 9** shows that the load carrying capacity of composites prepared with bamboo strips and matrix of metal chips and Fevicol was high and decreased with increase in thickness.

Flexural Behaviour of Composites

Flexural test is useful to determine strength of a particular element against bending due to application of load in the direction perpendicular to the axis of the element. The flexural behaviours of a beam element can be evaluated by testing the specimen with

Table 9 Tensile strength of composite made with Fevicol (average of 2 replicates)

Specimen	Thickness (mm)	Weight (g)		Load (kN)		Tensile strength (MPa)	
		Average	Range	Average	Range	Average	Range
TF1	8.60	54.15	3.70	10.85	1.35	63.15	7.70
TF2	14.40	98.20	1.60	10.18	1.47	32.56	5.07
TF3	10.60	80.45	3.10	6.73	2.33	38.60	3.20

**Fig. 9** Stress-strain diagram for tensile test of composites made with Fevicol for (a) TF1 composites, (b) TF2 composites and (c) TF3 composites.

the help of three point and centre-point loading methods. In this case second method was adopted for finding out flexural strength of composites and load was applied at the centre with the help of loading pin on the specimen supported with two pins on the opposite face of the specimen. Flexure test produces tensile stress in the convex side of the specimen and compression stress in the concave side. Centre-point bending test was conducted using Universal Testing Machine (Model: TUN 200). The load was applied continuously at constant speed of 0.1 mm s^{-1} . Following relationships were used for finding the flexural stress and flexural strain for rectangular specimen:

for flexural stress:

$$\sigma_f = \frac{3PL}{2bd^2} \quad (4)$$

for flexural strain:

$$\varepsilon_f = \frac{4Dd}{L^2} \quad (5)$$

where P is the maximum load at a given point on the load deflection curve, L is the support span, b is the width of specimen, d is the depth of specimen and D is the maximum deflection at the centre of specimen.

Flexural behaviour of composite made with only bamboo strips and Araldite

Two different types of specimens with thicknesses 4.5 mm and 7.0 mm were made ready for testing. Three samples were taken for each two layers bamboo strip (BL2) and three layers bamboo strip (BL3). The flexural strength of different layers of bamboo strip is presented in Table 10. From Fig. 10, it is observed that the load carrying capacity of three layers bamboo strip was more than that of two layers bamboo strip. The load carrying capacity for both specimens was very low.

Table 10 Flexural strength of composite made with only bamboo strip (average of 3 replicates)

Specimen	Thickness (mm)	Width (mm)	Weight (g)		Flexural strength (MPa)	
			Average	Range	Average	Range
BL2	4.50	25	18.50	1.90	46.44	2.95
BL3	7.00	25	27.50	1.40	38.78	6.12

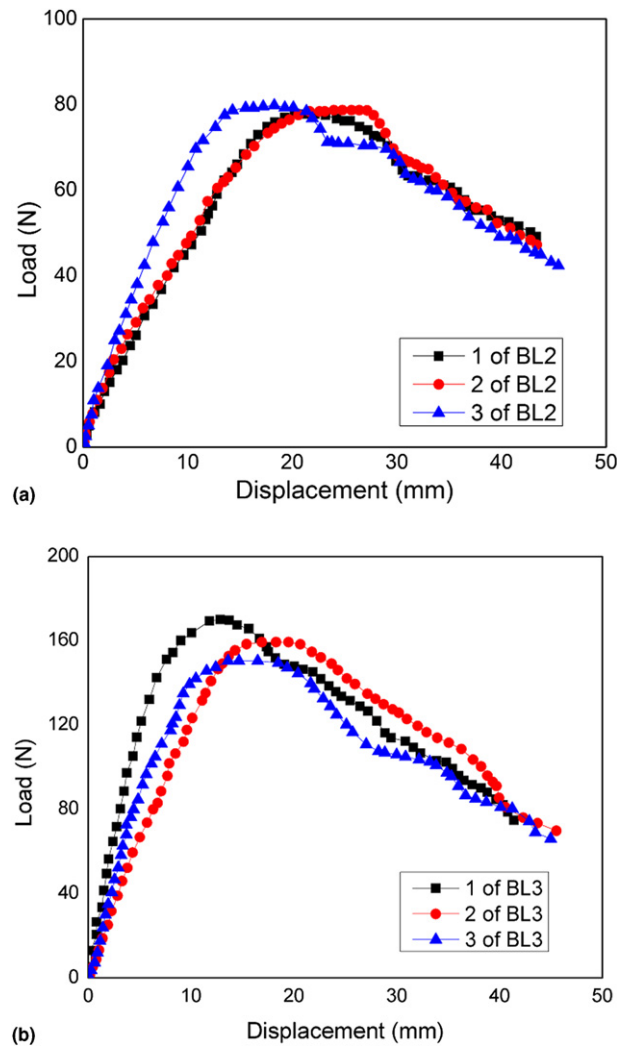


Fig. 10 Stress-strain diagram of composites made of only bamboo strips and Araldite under bending for (a) BL2 bamboo composites and (b) BL3 bamboo composites.

Flexural behaviour of composite made with bamboo and matrix of metal chips and epoxy (Araldite and Fevicol)

In these specimens Araldite was used with chips for making composite. Different specimens were made with different amount of chips but the ratio of chips to Araldite is equal for all specimens. These specimens were made from chips to Araldite ratio of 10:4. The flexural strength of composite is presented in Table 11.

The tensile stress acted on convex side of specimen that detached bamboo strip from composite. From Fig. 11, it is observed that the load carrying capacity of specimens decreased with decrease in thickness. Generally specimen cracked at the middle where the load was applied, but in a few cases it cracked at other places due to voids created during manufacturing. The flexural strengths of specimen prepared using matrix of metal chips and Fevicol ratio 10:3 are presented in Table 12. The specimens had thickness of 14.4 mm with two layers of composite and three bamboo strips; remaining specimens had single layer of composite and two layers of bamboo strips.

Table 11 Flexural strengths of composites made using Araldite (average of 3 replicates)

Specimen	Thickness (mm)	Weight (g)		Load (kN)		Flexural strength (MPa)	
		Average	Range	Average	Range	Average	Range
BA1	15.20	184.30	4.00	1.11	0.67	57.65	34.80
BA2	12.10	134.13	3.30	0.69	0.08	57.04	6.56
BA3	8.50	84.40	2.80	0.30	0.15	52.04	19.92
BA4	14.50	152.10	0.80	0.68	0.01	39.10	0.57

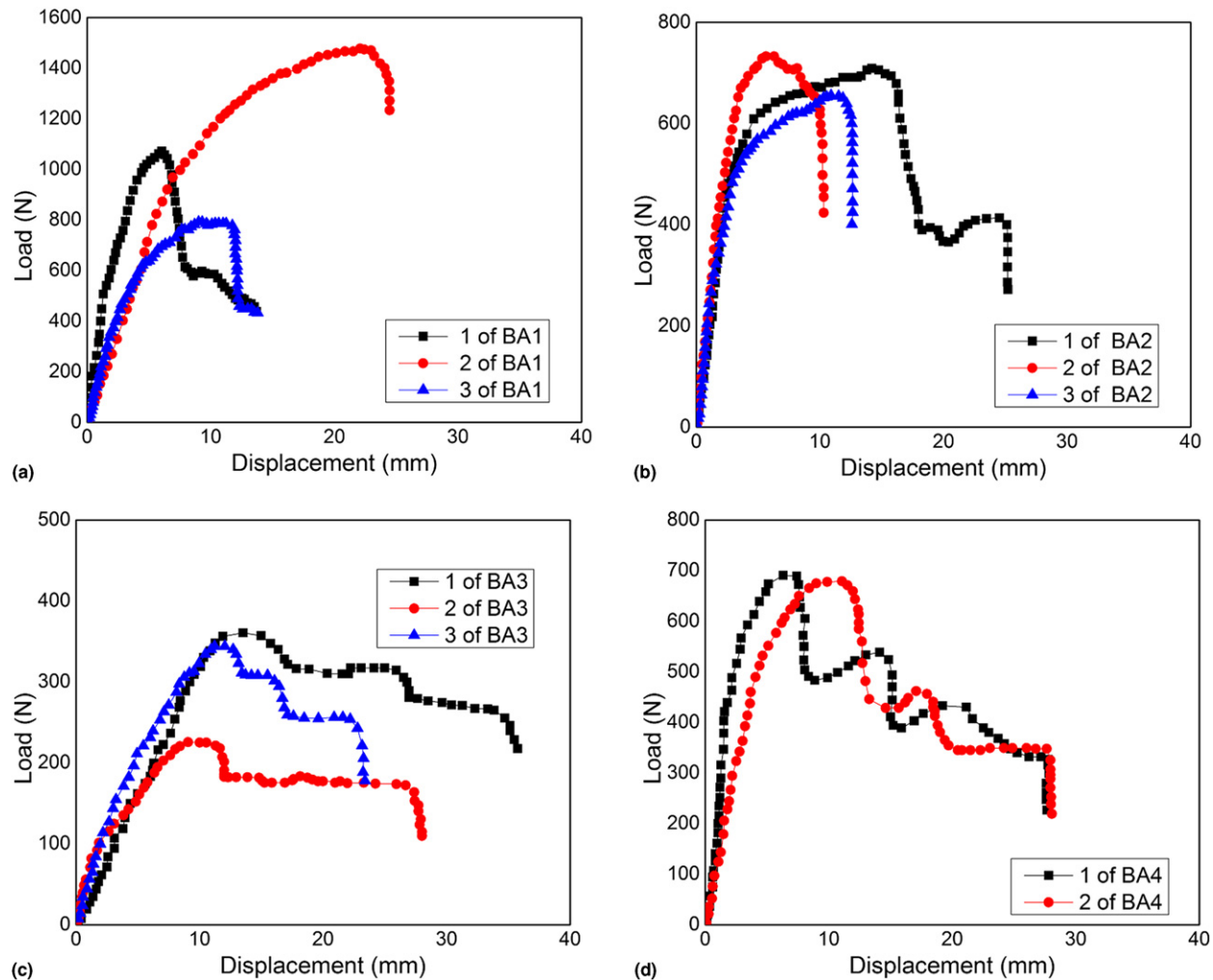
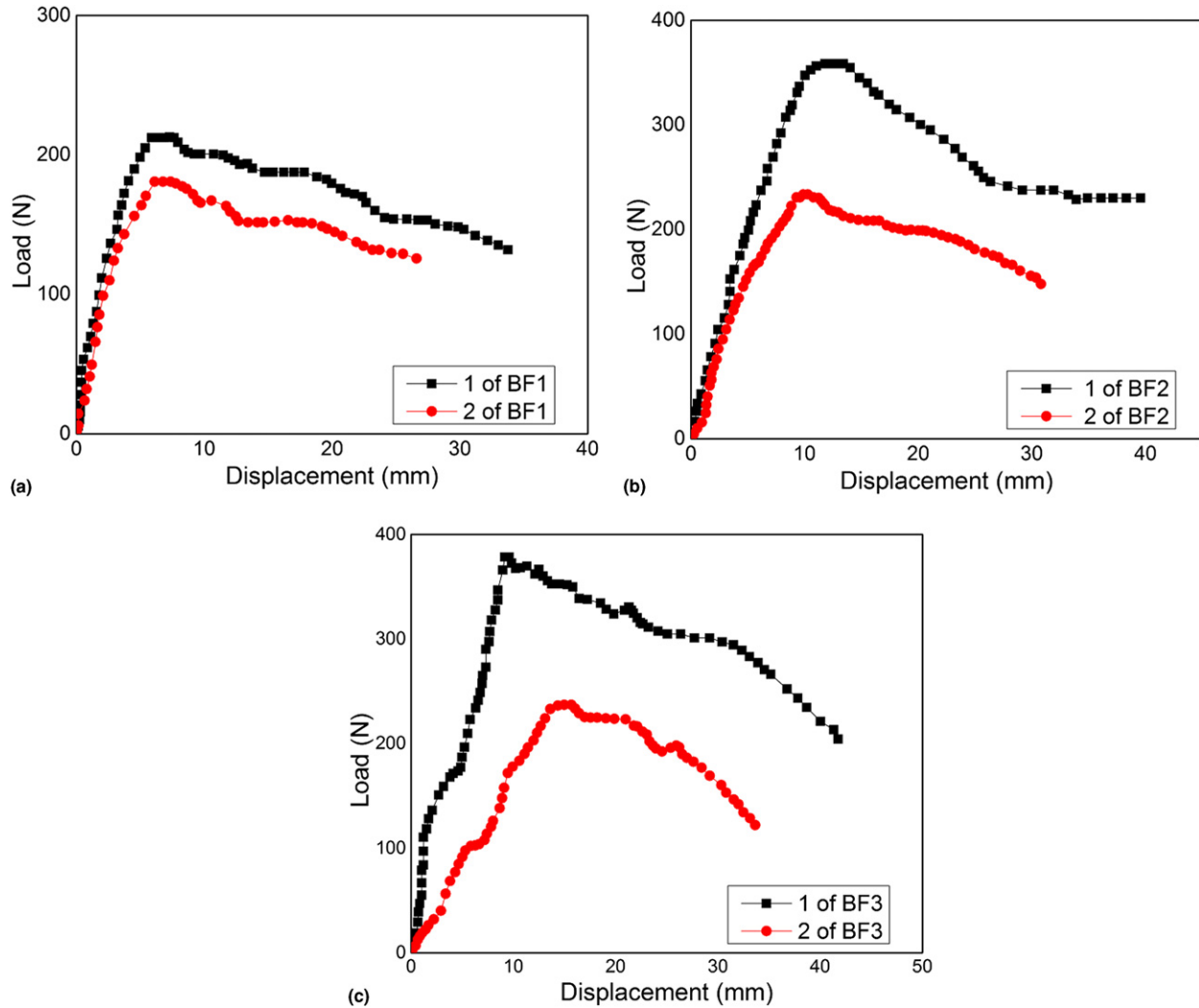


Fig. 11 Load-displacement diagram of specimens under transverse loading for (a) BA1 composites, (b) BA2 composites, (c) BA3 composites and (d) BA4 composites.

Table 12 Flexural strengths of composites made using Fevicol (average of 2 replicates)

Specimen	Thickness (mm)	Weight (g)		Load (kN)		Flexural strength (MPa)	
		Average	Range	Average	Range	Average	Range
BF1	8.60	68.75	0.50	0.19	0.03	31.24	5.33
BF2	14.40	126.65	4.90	0.29	0.14	16.79	8.08
BF3	10.60	104.75	3.50	0.30	0.15	32.57	16.02

**Fig. 12** Load-displacement diagram for specimens under bending load for (a) BF1 composites, (b) BF2 composites and (c) BF3 composites.

From Fig. 12, it is observed that the load carrying capacity of specimen was very less and its deformation was very high. This is due to low compressive strength of matrix with metal chips and Fevicol which is placed between layers of bamboo strips. Its load carrying capacity was slightly higher than the load carrying capacity of bamboo strips.

Conclusions

New composites using bamboo and epoxy based matrix of waste metal chips were developed. Experimental studies were carried out on individual constituents as well as on the composite for evaluating various properties. The optimum compositions were obtained based on the experiments. The physical and mechanical properties of bamboo were affected by variables such as moisture content and presence of nodes. The strength of the matrix depends on proportions of chips to epoxy. Two epoxies were

taken: Araldite and Fevicol. Between these two, Araldite provided more flexural strength; but its cost is higher. However, the addition of chips did not improve tensile strength.

The following are the additional conclusions:

- All parts of matured Jati bamboo exhibited comparable strength properties and can be used for making composites.
- The strength of the composite depended on proportions of chips to epoxy.
- The flexural strength of composite was higher than that of bamboo strip.

See also: Bamboo Fiber as Fillers for Polypropylene-Nanoclay via Injection Molding. Reuse of Waste Corrugated With Coir Fibers as a Packaging Material

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Development of HAp Reinforced Biodegradable Porous Structure Through Polymer Deposition Technology for Tissue Engineering Applications

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Introduction

Additive manufacturing (AM) is an imaginative innovation, which defeats the inadequacies of customary strategies for prototyping. It is also known as 3D printing, added substance manufacture, or free-form fabrication. AM empowers the acknowledgment of the primary starter model of something, particularly machines or some component of the item, from which different structures or forms are produced or replicated (Gibson *et al.*, 2015; Wohlers, 2014; Doe, 2015). The selection of AM technology in development and conquering new or improving existing products is predominantly influenced by three key factors: Quality, costs and time (Gress and Kalafsky, 2015; Talić, Čikmiš *et al.*, 2014; Singh and Ranjan, 2017). Recently, AM has become a focal point of consideration for its capacity to create distinctive items utilizing different materials. Maybe printing innovations are the most well-known kind of AM that is making progress in an extensive variety of modern and academic use. The 2D and 3D printing of various materials, for example, plastics, metals, ceramics and electronic practical materials is considered as the revolutionary innovation in science and innovation. Vitrally, these advancements are being utilized widely in restorative applications. Among every single developing innovation, AM may be has the most elevated potential to fundamentally disturb the worldwide purchaser showcase as well as more specific industry parts, for example, biomedical instruments, scaffolds and inserts (Lyons, 2014; Boisvert and Adelstein, 2015). The usage of AM in the medical services industry has just brought about the advancement of devices, prosthetics, therapeutic equipment's, and inserts. All the more as of late, AM advances are being converted into the TE and regenerative medicine (RM) industry to help in the recovery of tissues and organs (Melchels *et al.*, 2012).

These days, AM has penetrated into all segment of ventures e.g., aerospace, vehicle, combat hardware, dental, electronic, design, furniture, therapeutic gadgets, and inserts (Chhaya *et al.*, 2015). No big surprise, that the TE/RM segments are likewise investigating the appropriation of different AM innovations, altering and refining the current AM advancements to fit their applications and necessities (Tumbleston *et al.*, 2015). An examination of a few driving audits and in addition industry reports proposes that the TE/RM segments could be two of the best recipients of the use of AM innovation, with clear patient, biotechnology, and therapeutic equipment's industry benefits (Huang and Leu, 2014). TE, which means to create human tissues and organs, is profiting from the reproducible, computer controlled, and exact step that can be acquired by printers. 3D printings of platforms, cell-loaded bio-materials, and cell (scaffold-free) materials hold an awesome guarantee to propel the TE field toward the manufacture of useful tissues and organs.

TE is an inter-disciplinary field in which artificial organs are built utilizing materials, cells, and development factors. Bone is a vital organ that redesigns consistently amid a person's lifetime and structures the human skeletal scaffolds. Bone TE is an imperative part of regenerative drug and biotechnology. It gives elective remedial strategies to re-establish the capacity and repair dam-matured or deteriorating bone tissue (Singh *et al.*, 2017). Biomaterials with utilitarian sub-units give focal points that advance bone tissue recovery and encourage the repair of harmed bone tissue. They have critical applications in clinical orthopaedics amid reconstructive surgeries. Auto-logous trans-plantation is the best clinical procedure since it viably joins the host bone tissue without immunogenic complexities or the infection dangers related with allogeneic sources. Auto-logous trans-plantation is viable; however the supply is restricted in view of the therapeutic and financial limitations of the world's maturing populace. Moreover, orthopaedic recreation from injury, tumours, innate deformations, and wounds are at record numbers setting expanded request on bone recovery and embed advances (Wu *et al.*, 2014). Tissue engineers create useful materials for orthopaedic remaking that can convey bio-chemical signs to cells. Under-standing the natural impacts of these materials is an essential prerequisite of TE by confirming their appropriateness and explaining the part they play in tissue development (Bauer and Muschler, 2000; Stevens, 2008). In-bone TE, substitutes are designed as platforms that are non-dangerous, bio-compatible, bio-degradable in a controlled way, and osteo-conductive (Zhang *et al.*, 2015). Fig. 1 shows step by step procedure for developing of functional tissues from biomaterials (Polymers (PEEK, PLA), Ceramics (HAP, CS) and Composites).

Calcium HAp is a manufactured material indistinguishable to the substance in teeth and bones. Calcium HAp is a critical inorganic material in biological and chemistry science. Biological apatites, which are the inorganic constituents of bone, tooth finish, and dentin, are ordinarily extremely factor in their structure and morphology, and generally contain totally different impurities. By and large, these tainted natural apatites are assigned as calcium inadequate or non-stoichiometric apatites. A noteworthy segment and a basic element of typical bone and teeth. HAp makes up bone mineral and the grid of teeth. It is HAp that gives bones and teeth their unbending nature. The 'n-HAp' is a characteristic mineral type of calcium apatite that synthetically looks like the perplexing framework of bone. Its reconstruction needs substantial mechanical strength thanks to the character of natural bone. The n-HAp is a constituent of bone (around 70%) and is utilized to expand the auxiliary unbending nature of platforms, guaranteeing their appropriateness for bone tissue development methodology. There is broad research on the

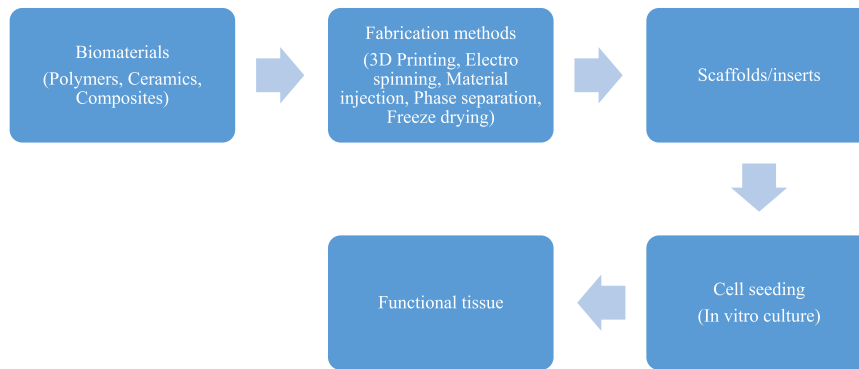


Fig. 1 Step wise process chart for creating functional tissues from biomaterials.

arrangement of bone substitutes utilizing n-HAp for biomedical applications due to the similitude of n-HAp to normal bone (Zhou and Lee, 2011). n-HAp is exceedingly osteo-conductive. It displays bone bonding limit, offers a suitable layout structure for bone arrangement, and advances cell working permitting the outflow of bone framing osteo-genic markers (LeGeros, 2002; Venkatesan *et al.*, 2015). In spite of these properties, n-HAp is weak and has constrained application in stacking bearing applications. n-HAp is frequently functionalized with different polymers, for example, CS, to give the mechanical properties required to an embed in the reconstruction and regeneration of bone, tissue (Wei and Ma, 2004; Mangano *et al.*, 2006; Piccirillo *et al.*, 2013)

Materials and Methods

Materials

Hydroxyapatite (HAp)

HAp is artificially like the mineral segment of bones and hard tissues in well evolved creatures. It is one of the suitable materials that are classed as bio-compatible and bio-active, implying that it will bolster bone ingrowth and Osseo-mix when utilized as a part of orthopaedic, dental and maxillofacial applications. HAp is a similar to structural and chemical resemblance to teeth and bone due to its key inorganic phosphate. HAp is a most prominent bio-material which discovers use as a teeth or bone substitution and regeneration and hard tissue repair (Orlovskii *et al.*, 2002; Huang *et al.*, 2011).

Key properties

- HAp decomposition temperature are very high; about 800–1200°C (depends upon its stoichiometry) that's why it is best suitable for creating/developing biomedical scaffolds/inserts.
- HAp is able to integrate in teeth/bone structure and helps in teeth/bone ingrowth, without dissolving and break down (i.e., HAp is bio-compatible, and bioactive material).
- Generally, HAp made scaffolds/inserts are biocompatible and bioactive as well as open porous structure which is best suitable for bone regeneration.

Applications

• Bio-ceramic Coating

HAp coating are frequently used to polymeric/metallic inserts to modify the surface properties. In this way the body sees HAp type material which it is easy to accept. Without coating the body would see as a external body and work as like surrounding tissue isolate them. To date, the main commercially acknowledged technique for applying HAp coatings to polymeric/metallic inserts is plasma showering.

• Bone Fillers

HAp might be utilized in different forms, for example powders, porous blocks or beads to fill bone deformities or voids. The bone filler will give scaffolds/inserts and empower the bone filling rate of the void by normally bone forming and gives another option to bone regrowth. It will treated turn out to be a piece of the bone structure and it will minimize the reassemble/regeneration/regrowth compared to the circumstance, if no bone filler was utilized.

Chitosan (CS)

CS is a sugar that is gotten from the hard external skeleton of shellfish, including crab, lobster, and shrimp. It is utilized for pharmaceutical/biomedical applications. Chitosan is utilized to treat corpulence, cholesterol, and Crohn's health problem. CS

used to treat issues that kidney failure patients on dialysis frequently confront, including cholesterol problem, anaemia, loss of strength and appetite, and sleeping problem (insomnia). A few people apply chitosan straightforwardly to their gums to treat aggravation that can prompt tooth misfortune (periodontitis), or bite gum that contains chitosan to counteract “cavities” (dental caries). With an end goal to enable “giver to tissue” modify itself, plastic specialists some of the time apply chitosan specifically to places from which they have taken tissue to be utilized somewhere else. In pharmaceutical assembling, CS is utilized as filler in tablets; as a transporter in controlled-discharge drugs; to enhance the way certain medications terminate.

Table 1 shows the principal characteristics and their potential applications in biomedical field of CS material. Today CS is one of the most usable materials and shows great current interest in biomedical applications. CS is one and only pseudo-natural cationic polymer. Its character (cationic) is unique. Its main applications in medical field are much diversified (as like; Dental implants, artificial skin, contact lenses, regeneration/regrowth of bone/teeth).

Methods

Today biocompatible and biodegradable scaffolds/inserts are most trending area/topic for biomedical or for research in the field of tissue/bone engineering application. HAp is one of the most useful materials (HAp is bioactive and biocompatible) in the field of tissue/bone engineering applications. Bone/tissue regeneration is the main properties of HAp. In this article, HAp is reinforced with biocompatible and biodegradable PLA (polymer) and CS (composite) in the accurate proportion (by weight) that non-toxic feed stock filament are to be prepared for the fabrication of non-toxic biocompatible, biodegradable and bioactive scaffolds/inserts using open source FDM (Singh *et al.*, 2018a,b). **Fig. 2** shows step wise procedure for fabrication/development of biodegradable, biocompatible and bioactive scaffolds/inserts using HAp, PLA and CS.

Experimentation

In the pilot experimentation, an effort has been made to prepare/find the best composition material (which is biocompatible, biodegradable, bioactive and non-toxic) for development of open porous biodegradable biomedical scaffold/implants/inserts in tissue/bone engineering applications. In pilot experimentation at first, we select the different composition of polymer (PLA) which is reinforced with biocompatible and bioactive composites (HAp and CS) in different compositions (shows in **Table 2**). After that some experimental study was conducted to understand MFI, flow continuity for wire drawing, dimensional accuracy, tensile properties, thermal properties and SEM analysis and finally best composition/proportion of reinforcement has been established for drawing the feed stock filament by using TSE. After parametric optimizations of TSE process and open source FDM functional prototypes have been printed. For TSE process input parameter selected are; temperature of TSE barrel, revolution of TSE screw and applied dead weight during experimentation and in open source FDM, input parameter selected are; layer thickness of single layer of sample (for tensile and flexural samples), deposition angle of polymer material and fill density of sample.

Rheological Properties

In the pilot experimentation at first different material compositions/proportions were selected (based upon literature review). Out of selected compositions/proportions (available in literature), eight different composition (by weight percentage) were shortlisted (based upon applications in TE) to determine the best composition/proportion of materials. The experiment was conducted to check the continuous flow ability and MFI value per 10 min. **Table 2** shows the different composition ratio of PLA-HAp-CS and its MFI value according to ASTM standard. The composite material is put into the pre-heated barrel of MFI tester. The weight and temperature as per the ASTM standard (D 1238-95) was put on the piston to expel the molten material from barrel and thereby made to exit out of die opening as extruded and weighed to find MFI in terms of gm/10min.

Table 1 Properties of CS according to use in biomedical applications

<i>Principal characteristics</i>		<i>Potential biomedical applications</i>
Biodegradable	→	Dental implants
Nontoxic, biological tolerance	→	Time release drugs for animals and humans
Hydrolyzed by lyzosome wound healing properties efficient against bacteria, fungi, viruses	→	Encapsulating material
Biocompatible	→	Surgical stitches
Film forming	→	Rebuilding/regrowth of bone
Renewable	→	Artificial skin
Hydrating agent	→	Corneal contact lenses

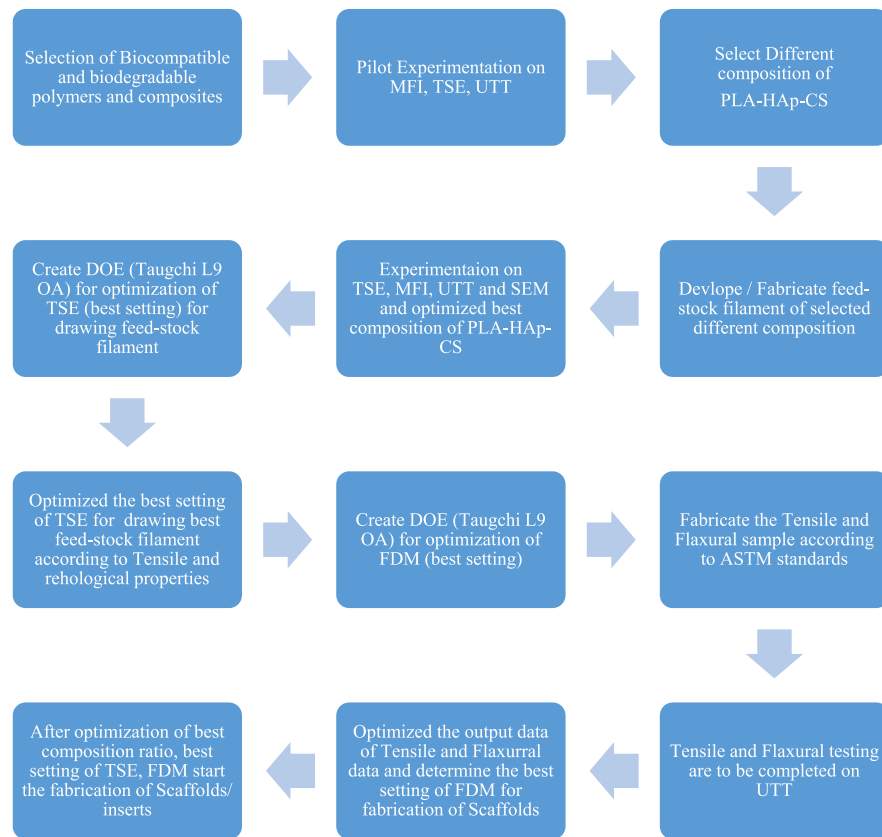


Fig. 2 Step wise procedure for fabrication of biodegradable scaffolds/inserts using HAp, CS, PLA.

Table 2 Rheological and flow-ability of different compositions of PLA-HAp-CS

S. no.	Material composition (PLA-HAp-CS) (by wt%)	MFI (gm/10 min)	Flow continuity	Remarks
1.	100-0-0	13.52	Yes	Adequate
2.	84-4-12	10.512	Yes	Adequate
3.	80-8-12	9.015	Yes	Adequate
4.	76-12-12	3.125	No	Not suitable
5.	91-8-1	12.352	Yes	Adequate
6.	90-8-2	11.575	Yes	Adequate
7.	89-8-3	7.474	No	Not suitable
8.	88-8-4	4.465	No	Not suitable

Dimensional and Tensile Properties

Based upon **Table 2**, 04 material compositions/proportions were selected to analyze dimensional and tensile properties (see **Fig. 3**).

After selection of four best compositions/proportions of feed stock filament, polymer matrix composite was processed on TSE (make: HAAKE Mini CTW, Germany). After the preparation of feed stock filament dimensional accuracy was checked by Mitutoyo's absolute digimatic micro-meter (as per ISO3611-1978) having accuracy up to 0.001 mm and tensile test on UTT.

Thermal Properties

In this experimentation part all four compositions/proportions of PLA-HAp-CS ready feed stock filament were analysed from thermal stability view point. Thermal analysis for all four compositions/proportions was carried out by METTLER TOLEDO, Model DSC3; Swiss make with STAR[®] (SW 14.00) software in N₂ gas environment. In this experimentation part glass transition temperature (°C), crystallization (%) and melting temperature (°C) were determined. **Fig. 4** shows the graphical as well as tabular data of thermal analysis of all four compositions of PLA-HAp-CS reinforced materials.

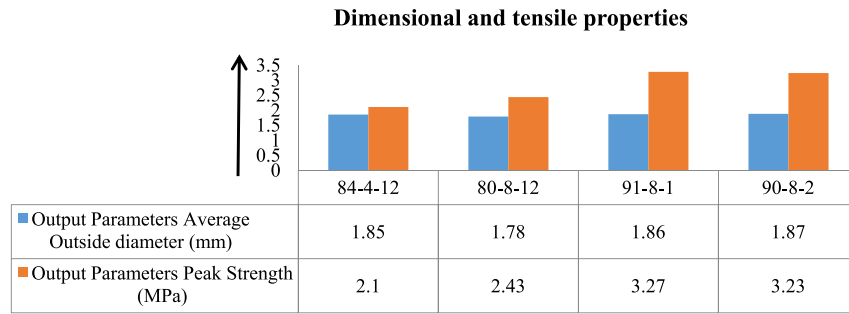


Fig. 3 Graphical representation of dimensional and tensile properties with different composition of PLA-HAp-CS.

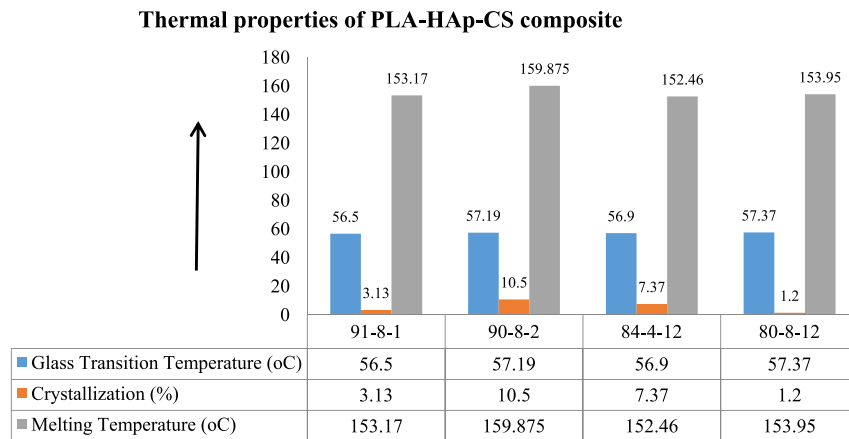


Fig. 4 Graphical representation of thermal properties of PLA-HAp-CS composites.

SEM Analysis

Based upon mechanical properties (see Fig. 3) and thermal analysis (see Fig. 4) PLA-HAp-CS with composition/proportion as 91%-8%-1% has been selected for further analysis as it has better mechanical properties and acceptable crystallization (%). Further for SEM analysis photographs were taken by SEM (Model no. JEOL JSM-6510LV SEM, Japan). Fig. 5 shows SEM image of composite material 91%-8%-1%, which shows open porous and fibrous structure suitable for TE applications.

DOE and Output of Tensile Test for Best Setting of TSE for Feed Stock Filament

After determining the best composition of PLA-HAp-CS materials; next step was to determine the best setting of TSE for preparation/drawing best feed stock filament according to tensile strength. The feed stock filament has been prepared as per Taguchi L9 ($\hat{3}3$) OA. Table 3 shows the DOE based upon Taguchi L9 ($\hat{3}3$) OA which was 9 runs of experimentation. A total of 9 sets of specimen (feedstock filament) has been prepared by using different factors (namely; Temperature of barrel, revolution speed of screw and dead weight applied during experimentation) and total of 27 (9×3) experiments were conducted to reduce the effect of human variations and environmental effect etc. Fig. 6 shows that 3D view of TSE.

Table 3 shows that DOE and its output results of tensile results (Strength at Peak (MPa) and Peak Load (N)) which was obtained on the UTT by testing all set of feed stock filament wire which was made by using TSE according to Taguchi L9 OA. In Table 3 SNRA for strength at peak and peak load are to be shown which was determine/obtained by Minitab 17.0 software.

DOE of FDM for Fabrication of Scaffolds/Inserts for Tissue/Bone Engineering Applications

According to Table 3 determine the best setting of TSE for drawing/preparation of best feed stock filament according to tensile strength. Before the preparation of scaffolds/inserts/implants for tissue/bone engineering application open source FDM must optimized; for optimization of FDM the DOE are chosen as Taguchi L9 ($\hat{3}3$) OA. There are total two types of sample tensile and flexural sample (according to ASTM standards) are to be prepared according to same DOE which was designed as Taguchi L9 ($\hat{3}3$) OA. A total of 9 sets of tensile and 9 sets of flexural specimen (ASTM standards) has been prepared by using different input factors (namely; Layer thickness of sample (mm)), deposition angle ($^{\circ}$ C) of extruded material through FDM nozzle and fill density (%) of both sample. Table 4 shows the DOE of open source FDM for fabrication/preparation of tensile and flexural sample according to ASTM standards.

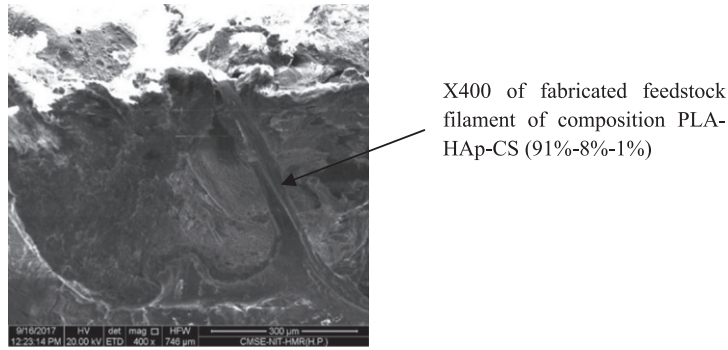


Fig. 5 Microphotographs of different composition (PLA-HAp-CS).

Table 3 DOE (Taguchi L9 OA) and output data with SNRA of feed stock filament (PLA-HAp-CS (91-8-1))

Experiment run no.	Input parameters			Output parameters			
	Temperature (°C)	Revolution (rpm)	Dead weight (Kg)	Strength at peak (MPa)	Peak load (N)	SNRA for strength at peak	SNRA for peak load
1	170	100	8	3.14	6.40	9.9386	16.1236
2	170	140	10	3.64	7.80	11.2220	17.8419
3	170	180	12	4.12	9.00	12.2979	19.0849
4	180	100	10	3.62	7.70	11.1742	17.7298
5	180	140	12	4.25	9.20	12.5678	19.2758
6	180	180	8	3.10	6.30	9.8272	15.9868
7	190	100	12	4.85	10.10	13.7148	20.0864
8	190	140	8	3.76	7.90	11.5038	17.9525
9	190	180	10	4.54	9.50	13.1411	19.5545



Fig. 6 3D view of TSE (Manufacturer; HAAKE MINICTW).

Fig. 7 shows that inner view/working area/operational view of open source FDM machine. Tensile and flexural sample are prepared according to ASTM standards (Tensile sample (ASTM D638 TYPE IV):- 125 mm (F.L.)*20 mm (F.W.)*6.5 mm (P.W.)*3.2 mm (H.) and Flexural sample (ASTM D790-17):- 125 mm (F.L.)*12.7 mm (F.W.)*3.2 mm (H.)). **Fig. 7** shows the flexural sample preparation on open source FDM using best feed stock filament which was prepared on TSE with best composition ratio of PLA-HAp-CS (91-8-1) (by weight percentage).

Where,

F.L.:- Full length of sample,

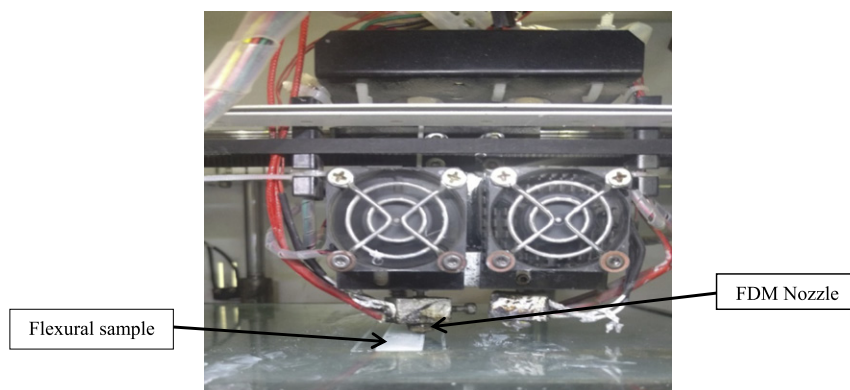
F.W.:- Full width of sample,

P.W.:- Parallel section width,

H.:- Thickness.

Table 4 DOE of FDM for fabrication of tensile and flexural sample according to ASTM standards

Experiment run No.	Input parameters		
	Layer thickness (mm)	Deposition angle ($^{\circ}$ C)	Fill density(%)
1	0.2	30	60
2	0.2	45	80
3	0.2	60	100
4	0.25	30	80
5	0.25	45	100
6	0.25	60	60
7	0.30	30	100
8	0.30	45	60
9	0.30	60	80

**Fig. 7** Inner/operational view of open source FDM during fabrication of Flexural sample (ASTM standards).

After preparation of tensile and flexural sample (ASTM standards) according to DOE Taguchi L9 OA total 18 sample (9 samples for tensile and 9 samples for flexural) are to be prepared on open source FDM. In **Fig. 8 (a)** shows that 9 fabricated sample of tensile sample according to DOE and **Fig. 8 (b)** shows that 9 fabricated sample of flexural sample according to DOE.

Fabricated parts of tensile and flexural sample are to be tested on UTT for tensile test and 3 point bending test. **Fig. 9** shows the 3D view of UTT (manufacturer; SHANTA ENGINEERING, Ludhiana) during tensile testing of tensile sample. Also close view/ exploded view clearly shows the setup of tensile testing. 3-point bending test is also performed on UTT only setup and some software setting were changed according to requirement.

Result and Discussions

Rheological Properties

After successful runs of pilot experimentation and literature review, it found that HAp is most suitable material for fabrication/development of scaffolds/inserts for TE/biomedical applications. HAp are reinforced with PLA and CS in some proportion (shows in **Table 2**). In MFI testing found that five out of eight composition are most suitable according to continuous flow ability test; In which one composition is pure PLA that is used for comparison are to be neglected because pure PLA are not used for development of scaffolds/inserts. So finally only four samples are to be selected for further testing for best composition selection. In **Table 2** MFI value of all the samples are to be shown.

Dimensional and Tensile Properties

After the selection of four compositions according to MFI and continuous flow ability are to be used for preparation of four feed stock filament on TSE. The main reason for fabrication of feed stock filament is fabrication/development of scaffolds/inserts on FDM machine. So, FDM input wire are required some special requirement (equal and in range diameter of feed stock filament). In **Fig. 3** shows that graphical representation of all four feed stock filament average diameter and it was found that all four sample according to dimensional analysis view are suitable for use. In **Fig. 3** tensile test (peak strength) result are to be obtained from UTT. In this result it conclude that after increasing of HAp and CS material in PLA polymers the strength of feed stock filament are to be decreased. So higher HAp and CS ratio for reinforcement in PLA polymers are not suitable.

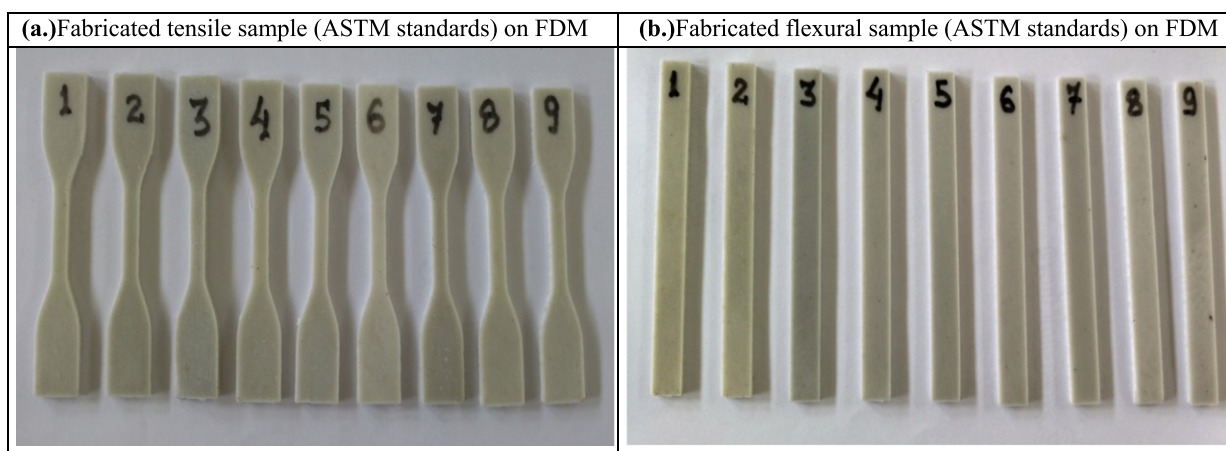


Fig. 8 Fabricated tensile and flexural sample on FDM with reinforcement of PLA-HAp-CS (91-8-1). (a) Fabricated tensile sample (ASTM standards) on FDM, (b) Fabricated flexural sample (ASTM standards) on FDM.

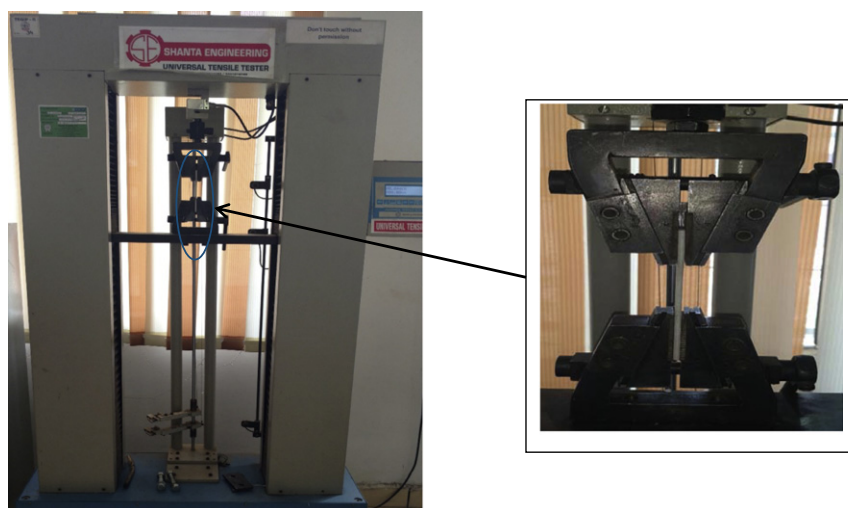


Fig. 9 3D view of UTT and operational view of tensile testing of tensile sample (ASTM standards).

Thermal Properties

In the thermal analysis experimentation are done on METTLER TOLEDO DSC. In this, all four feed stock filaments are cut in very small piece (3–10 mg) and two heating and cooling cycles are to be run in the presence of N_2 gas environment. In [Fig. 4](#) all thermal analysis data (glass transition temperature, percentage of crystallinity and melting temperature) are to be written and shows in graphical form. At first glass transition temperature data are to be checked and found no more significant difference so all the wire are suitable and same results are also shows in the case of melting temperature. At last crystallinity (percentage) are checked and found that 91-8-1 (PLA-HAp-CS) composition are less crystallinity which was best suited for TE/biomedical applications. 80-8-12 (PLA-HAp-CS) composition are also less crystallinity but due to less tensile strength.

SEM Analysis

Finally, for selection of best composition of PLA-HAp-CS SEM test performed on two composition (91-8-1 and 90-8-2). For SEM analysis at first gold plating are covered on sample and in vacuum chamber at different pixel, microphotographs are to be taken. [Fig. 5](#) shows the both microphotographs and it concluded that both the sample structure are open porous structure, which was good for growth of cells and are suitable in bio-medical application and fabrication of scaffolds/inserts for TE. The porous structure of an inserts provides channels for tissue ingrowth. Porous materials introduced to obtain biological fixation and improve longevity of orthopaedic inserts. Due to several clinically important disadvantages of dense biomaterials (polymeric), such as a high value of elasticity modulus, the fabrication of porous structures by powder metallurgy, foaming technologies, as well as AM methods have

been widely developed in the last decades to overcome the limitations. In addition, porosity enhances the biological interlock between implant and bone.

Tensile Testing for Best Setting of TSE for Feed Stock Filament

After the selection of best composition of PLA-HAp-CS DOE prepared this are shows in [Table 3](#). This test are to be perform for optimizing the TSE best setting for fabrication of feed stock filament of best composition (91-8-1 (PLA-HAp-CS)).

● For Strength at Peak

[Fig. 10](#) shows the main effects plot for signal-to-noise ratios (SNRA) for strength at peak output parameter (for larger the better type case).

As observed in [Fig. 10](#) it was suggested that best setting according to peak strength are 190°C of barrel temperature and screw speed are best suitable are 140 rpm and applied dead weight are best suited are 12 kg. [Table 5](#) shows response table for SNRA for larger is better type for strength at peak.

As shown in [Table 6](#), percentage error was 0.99%. It shows that the model has a higher degree of accuracy. Further, it was observed that temperature of barrel and dead weight are the only significant parameters, which contributes 36.25% and 62.44%, respectively and rotational speed of screw was not significant and have less percentage contribution of 0.32%. Finally, the calculated value for strength at peak is 5.00 MPa, which is close to the experimentally observed value ([Table 7](#)).

For optimization following formula based upon Taguchi L9 OA design has been used:

$$\eta_{\text{opt}} = m + (m_{A3} - m) + (m_{B2/3} - m) + (m_{C3} - m)$$

Where,

m is the overall mean of S/N data,

m_{A3} is the mean of S/N data for Temperature of barrel at level 3,

$m_{B2/3}$ is the mean of S/N data for RPM at level 2/3,

and, m_{C3} is the mean of S/N data for Dead weight at level 3.

$$y_{\text{opt}}^2 = (1/10)^{\eta_{\text{opt}}/10} \quad \text{for properties, lesser is better}$$

$$y_{\text{opt}}^2 = (10)^{\eta_{\text{opt}}/10} \quad \text{for properties, larger is better}$$

Calculation,

Overall mean of S/N ratio (m) was taken from Minitab software.

$$m = 11.71$$

Now from response table of signal to noise ratio, $m_{A3} = 12.79$, $m_{B2/3} = 11.76$ and $m_{C3} = 12.86$.

From here,

$$\eta_{\text{opt}} = 11.71 + (12.79 - 11.71) + (11.76 - 11.71) + (12.86 - 11.71)$$

$$\eta_{\text{opt}} = 13.99 \text{ db}$$

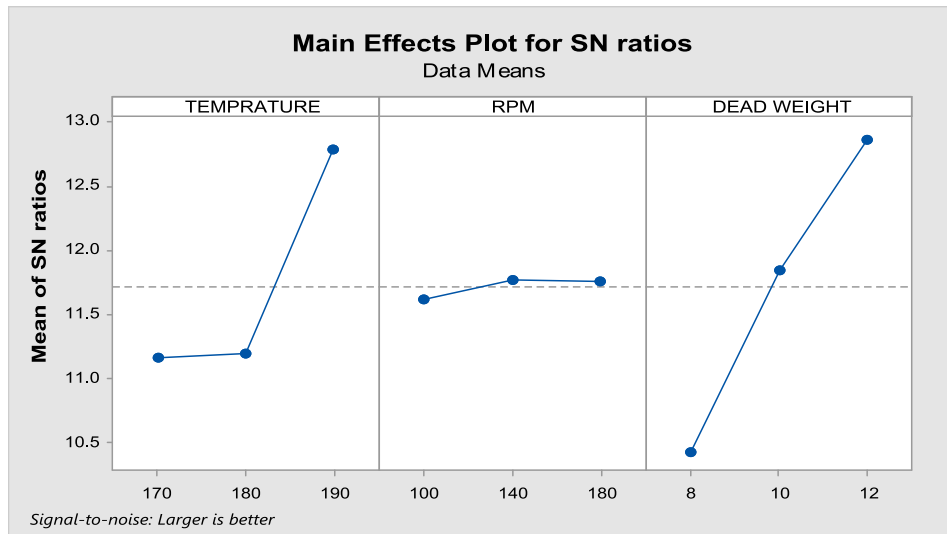


Fig. 10 Main effect plots for SNRA for strength at peak.

Table 5 Response table for SNRA larger is better for strength at peak (feed stock filament)

Level	Temperature	RPM	Dead weight
1	11.15	11.61	10.42
2	11.19	11.76	11.85
3	12.79	11.76	12.86
Delta	1.63	0.16	2.44
Rank	2	3	1

Table 6 Analysis of variance for strength at peak (feed stock filament)

Source	DF	Seq SS	Adj SS	Adj MS	F-value	P-value	%age contribution
Temperature	2	5.2203	5.2203	2.61014	36.81	0.026	36.25
RPM	2	0.0456	0.0456	0.02280	0.32	0.757	0.32
Dead weight	2	8.9917	8.9917	4.49584	63.41	0.016	62.44
Error	2	0.1418	0.1418	0.07091			0.99
Total	8	14.399					

Source: Abbreviations: Adj.MS, adjacent mean of squares; Adj.SS, adjacent sum of square; DF, degree of freedom; F, fishers value; P, probability; Seq.SS, sum of square.

Table 7 Response table for SNRA larger is better for peak load (feed stock filament)

Level	Temperature	RPM	Dead weight
1	17.68	17.98	16.69
2	17.66	18.36	18.38
3	19.20	18.21	19.48
Delta	1.53	0.38	2.79
Rank	2	3	1

Now,

$$y_{\text{opt}}^2 = (10)^{\eta_{\text{opt}}/10}$$

$$y_{\text{opt}}^2 = (10)^{13.99/10}$$

$$y_{\text{opt}} = 5.00 \text{ MPa}$$

Finally, the calculated optimum value for strength at peak is 5.00 MPa.

● For Peak Load

Fig. 11 shows the main effects plot for SNRA for strength at peak output parameter (for larger the better type case).

As shown in **Table 8**, percentage error was 1.20%. It shows that the model has a higher degree of accuracy. Further, it was observed that temperature of barrel and dead weight are the only significant parameters, which contribute 27.41%, and 70.09% respectively and rotational speed of screw was not significant and have less percentage contribution of 1.28%.

For optimization following formula based upon Taguchi L9 OA design has been used:

$$\eta_{\text{opt}} = m + (m_{A3} - m) + (m_{B2} - m) + (m_{C3} - m)$$

Where,

m is the overall mean of S/N data,

m_{A3} is the mean of S/N data for Temperature of barrel at level 3,

m_{B2} is the mean of S/N data for RPM at level 2,

and, m_{C3} is the mean of S/N data for Dead weight at level 3.

$y_{\text{opt}}^2 = (1/10)^{\eta_{\text{opt}}/10}$ for properties, lesser is better

$y_{\text{opt}}^2 = (10)^{\eta_{\text{opt}}/10}$ for properties, larger is better

Calculation,

Overall mean of S/N ratio (m) was taken from Minitab software.

$$m = 18.18$$

Now from response table of signal to noise ratio, $m_{A3} = 19.20$, $m_{B2} = 18.36$ and $m_{C3} = 19.48$.

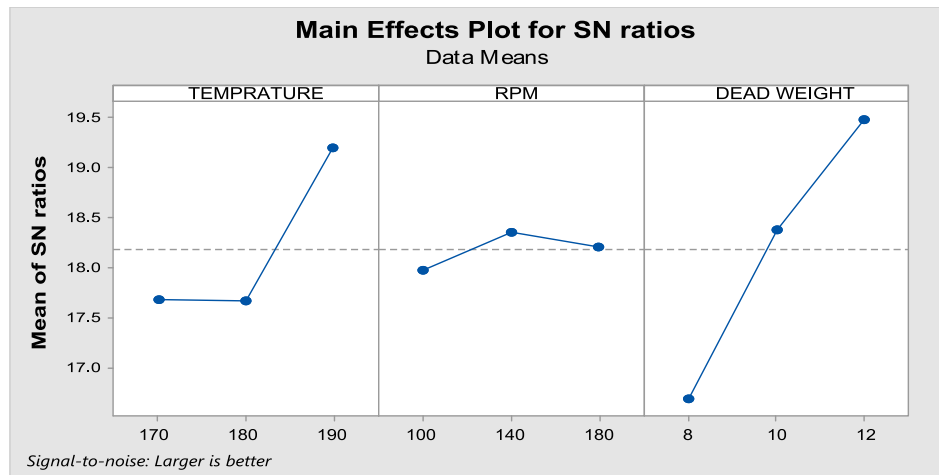


Fig. 11 Main effect plots for SNRA for peak load.

Table 8 Analysis of variance for peak load (feed stock filament)

Source	DF	Seq SS	Adj SS	Adj MS	F-value	P-value	% age contribution
Temperature	2	4.6459	4.6459	2.3229	22.73	0.042	27.41
RPM	2	0.2162	0.2162	0.1081	1.06	0.486	1.28
Dead weight	2	11.8841	11.8841	5.9421	58.14	0.017	70.09
Error	2	0.2044	0.2044	0.1022			1.20
Total	8	16.9506					

From here,

$$\eta_{\text{opt}} = 18.18 + (19.20 - 18.18) + (18.36 - 18.18) + (19.48 - 18.18)$$

$$\eta_{\text{opt}} = 20.68\text{db}$$

Now,

$$y_{\text{opt}}^2 = (10)^{\eta_{\text{opt}}/10}$$

$$y_{\text{opt}}^2 = (10)^{20.68/10}$$

$$y_{\text{opt}} = 10.81 \text{ N}$$

Finally, the calculated optimum value for peak load is 10.81 N.

Based upon peak values in Fig. 11, the confirmatory experiment for peak load was conducted and observed value was 10.89 N (which is very close to the calculated value).

Tensile and Flexural Testing of Fabrication of Scaffolds/Inserts for Tissue/Bone Engineering Applications

After the optimization of best setting of TSE feed stock filaments are prepared with composition of PLA-HAp-CS (91-8-1) are prepared and for fabrication of scaffolds/inserts/implants on open source FDM setting must be optimized. So DOE according to Taguchi L9 OA are to be designed which is shown in Table 4. Scaffolds must be good strength in view of tensile and flexural side; so both sample are to be formed according to this DOE.

Tensile properties according to ASTM standards with composition of PLA-HAp-CS

Table 9 shows that all the output data of tensile test and its SNRA data for tensile specimens (According to ASTM standards) (Table 10).

• For Break Load

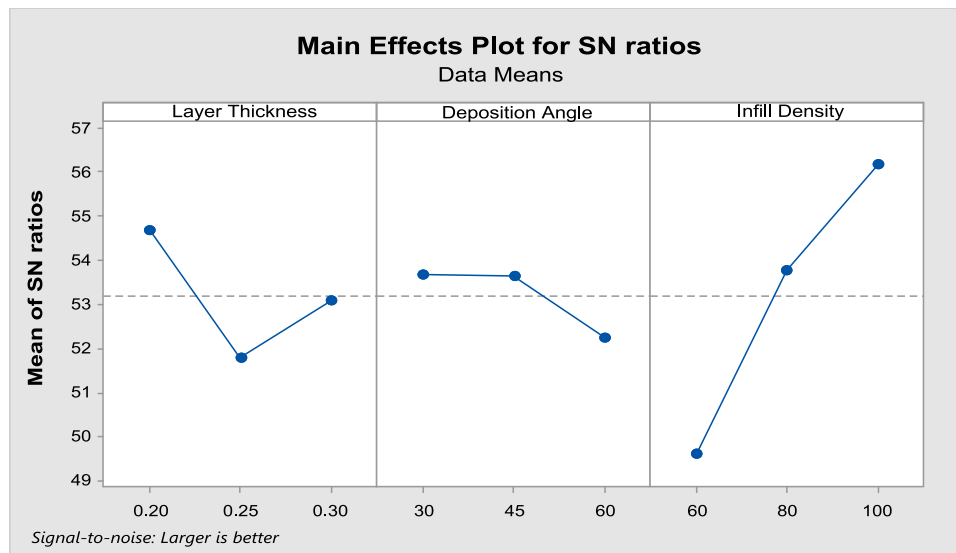
Fig. 12 shows the main effects plot for SNRA for break load for tensile specimen output parameter (for larger the better type case).

Table 9 Output of tensile sample and its SNRA data

Experiment run no.	Break load (N)	Break elongation (mm)	Young's modulus (MPa)	SNRA for break load	SNRA for break elongation	SNRA for Young's modulus
1	390.06	4.94	339.22	71.8226	13.8745	70.6098
2	554.22	5.7	206.55	74.8736	15.1175	66.3006
3	738.27	10.64	129.80	77.3643	20.5388	62.2656
4	473.04	3.61	280.42	73.4980	11.1501	68.9564
5	594.45	7.22	116.90	75.4823	17.1707	61.3564
6	210.06	3.23	235.19	66.4469	10.1841	67.4286
7	608.94	6.46	114.51	75.6915	16.2047	61.1769
8	339.75	3.8	89.31	70.6232	11.5957	59.0183
9	444.33	3.99	85.19	72.9541	12.0195	58.6082

Table 10 Response table for SNRA larger is better for break load (Tensile Specimen)

Level	Layer thickness	Deposition angle	Infill density
1	54.69	53.67	49.63
2	51.81	53.66	53.78
3	53.09	52.26	56.18
Delta	1.53	0.38	2.79
Rank	2	3	1

**Fig. 12** Main effect plots for SNRA for break load.

As shown in Table 11, percentage error was 1.20%. It shows that the model has a higher degree of accuracy. Further, it was observed that Infill density is the only significant parameter which contributes 76.69% and layer thickness and deposition angle was not significant and have less percentage contribution of 14.53%, 4.63%, respectively.

For optimization following formula based upon Taguchi L9 OA design has been used:

$$\eta_{\text{opt}} = m + (m_{A1} - m) + (m_{B1} - m) + (m_{C3} - m)$$

Where,

m is the overall mean of S/N data,

m_{A1} is the mean of S/N data for Layer thickness at level 1,

m_{B1} is the mean of S/N data for Deposition angle at level 1,

and, m_{C3} is the mean of S/N data for Infill density at level 3.

$$y_{\text{opt}}^2 = (1/10)^{\eta_{\text{opt}}/10} \text{ for properties, lesser is better}$$

Table 11 Analysis of variance for break load (Tensile Specimen)

Source	DF	Seq SS	Adj SS	Adj MS	F-value	P-value	%age contribution
Layer thickness	2	12.473	12.473	6.236	3.50	0.222	14.53
Deposition angle	2	3.977	3.977	1.988	1.12	0.472	4.63
Infill density	2	65.838	65.838	32.919	18.48	0.051	76.69
Error	2	3.562	3.562	1.781			1.20
Total	8	85.850					

$$y_{\text{opt}}^2 = (10)^{\eta_{\text{opt}}/10} \text{ for properties, larger is better}$$

Calculation,

Overall mean of S/N ratio (m) was taken from Minitab software.

$$m = 53.20$$

Now from response table of signal to noise ratio, $m_{A3} = 54.69$, $m_{B2} = 53.67$ and $m_{C3} = 56.18$.

From here,

$$\eta_{\text{opt}} = 53.20 + (54.69 - 53.20) + (53.67 - 53.20) + (56.18 - 53.20)$$

$$\eta_{\text{opt}} = 58.14 \text{ db}$$

Now,

$$y_{\text{opt}}^2 = (10)^{\eta_{\text{opt}}/10}$$

$$y_{\text{opt}}^2 = (10)^{58.14/10}$$

$$y_{\text{opt}} = 807.23 \text{ N}$$

Finally, the calculated optimum value for break load is 807.23 N., which is close to the experimentally observed value.

● For Break Elongation

Fig. 13 shows the main effects plot for SNRA for break elongation for tensile specimen output parameter (for larger the better type case) (**Table 12**).

As shown in **Table 13**, percentage error was 0.69%. It shows that the model has a higher degree of accuracy. Further it was observed that Infill density and layer thickness are the significant parameters which contribute 71.42%, 26.58% and deposition angle was not significant and have less percentage contribution of 1.31%.

For optimization following formula based upon Taguchi L9 OA design has been used:

$$\eta_{\text{opt}} = m + (m_{A1} - m) + (m_{B2} - m) + (m_{C3} - m)$$

Where,

m is the overall mean of S/N data,

m_{A1} is the mean of S/N data for Layer thickness at level 1,

m_{B2} is the mean of S/N data for Deposition angle at level 2,

and, m_{C3} is the mean of S/N data for Infill density at level 3.

$$y_{\text{opt}}^2 = (1/10)^{\eta_{\text{opt}}/10} \text{ for properties, lesser is better}$$

$$y_{\text{opt}}^2 = (10)^{\eta_{\text{opt}}/10} \text{ for properties, larger is better}$$

Calculation,

Overall mean of S/N ratio (m) was taken from Minitab software.

$$m = 14.20$$

Now from response table of signal to noise ratio, $m_{A1} = 16.51$, $m_{B2} = 14.63$ and $m_{C3} = 17.97$.

From here,

$$\eta_{\text{opt}} = 14.20 + (16.51 - 14.20) + (14.63 - 14.20) + (17.97 - 14.20)$$

$$\eta_{\text{opt}} = 20.71 \text{ db}$$

Now,

$$y_{\text{opt}}^2 = (10)^{\eta_{\text{opt}}/10}$$

$$y_{\text{opt}}^2 = (10)^{20.71/10}$$

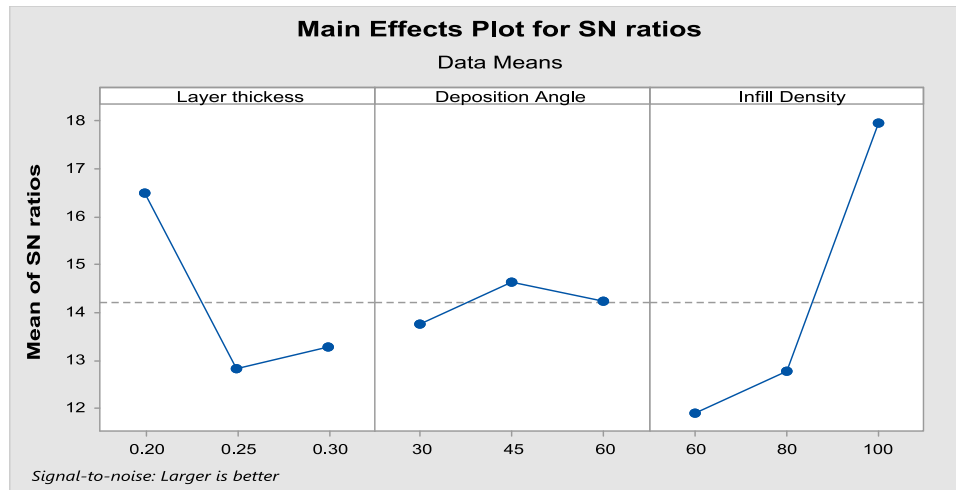


Fig. 13 Main effect plots for SNRA for break elongation.

Table 12 Response table for SNRA larger is better for break elongation (Tensile Specimen)

Level	Layer thickness	Deposition angle	Infill density
1	16.51	13.74	11.88
2	12.83	14.63	12.76
3	13.27	14.25	17.97
Delta	3.68	0.88	6.09
Rank	2	3	1

Table 13 Analysis of variance for break elongation (Tensile Specimen)

Source	DF	Seq SS	Adj SS	Adj MS	F-value	P-value	% age contribution
Layer thickness	2	24.1784	24.1784	12.0892	38.58	0.025	26.58
Deposition angle	2	1.1821	1.1821	0.5911	1.89	0.346	1.31
Infill density	2	64.9517	64.9517	32.4758	103.64	0.010	71.42
Error	2	0.6267	0.6267	0.3134			0.69
Total	8	90.9389					

$$y_{\text{opt}} = 10.852 \text{ mm}$$

Finally, the calculated optimum value for break elongation is 10.852 mm. That is close to the experimentally observed value.

- **For Young's Modulus**

Fig. 14 shows the main effects plot for SNRA for Young's modulus for tensile specimen output parameter (for larger the better type case) (**Table 14**).

As shown in **Table 15**, percentage error was 2.87%. It shows that the model has a higher degree of accuracy. Further it was observed that layer thickness is the only significant parameter, which contribute 54.85% and deposition angle and infill density was not significant and have less percentage contribution of 25.12% and 17.16%, respectively.

For optimization following formula based upon Taguchi L9 OA design has been used:

$$\eta_{\text{opt}} = m + (m_{A1} - m) + (m_{B1} - m) + (m_{C1} - m)$$

Where,

m is the overall mean of S/N data,

m_{A1} is the mean of S/N data for Layer thickness at level 1,

m_{B1} is the mean of S/N data for Deposition angle at level 1,

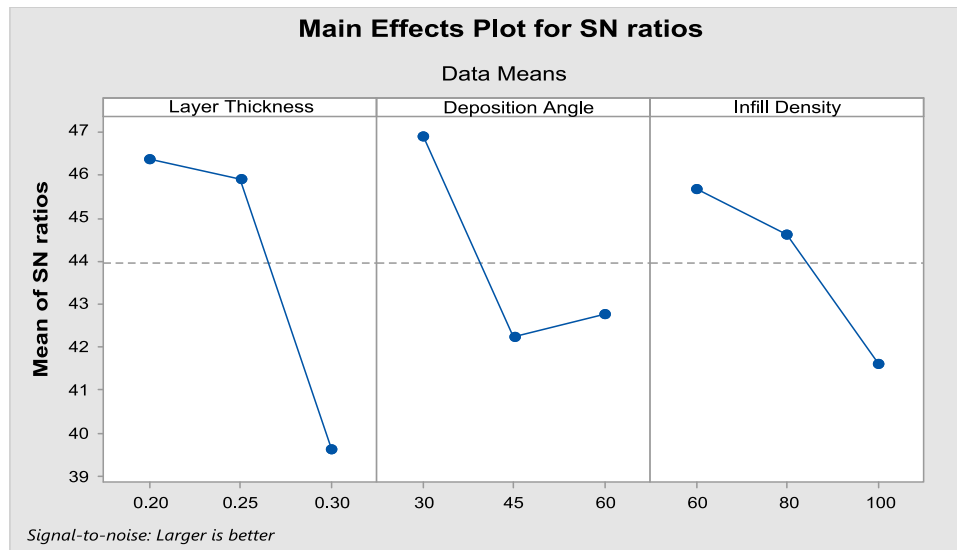


Fig. 14 Main effect plots for SNRA for Young's modulus.

Table 14 Response table for SNRA larger is better for Young's Modulus (Tensile Specimen)

Level	Layer thickness	Deposition angle	Infill density
1	46.39	46.91	45.69
2	45.91	42.23	44.62
3	39.60	42.77	41.60
Delta	6.79	4.69	4.09
Rank	1	2	3

Table 15 Analysis of variance for Young's Modulus (Tensile Specimen)

Source	DF	Seq SS	Adj SS	Adj MS	F-value	P-value	% age contribution
Layer thickness	2	86.194	86.194	43.097	19.09	0.050	54.85
Deposition angle	2	39.481	39.481	19.740	8.74	0.103	25.12
Infill density	2	26.960	26.960	13.480	5.97	0.143	17.16
Error	2	4.516	4.516	2.258			2.87
Total	8	157.151					

and, m_{C1} is the mean of S/N data for Infill density at level 1.

$$y_{\text{opt}}^2 = (1/10)^{\eta_{\text{opt}}/10} \text{ for properties, lesser is better}$$

$$y_{\text{opt}}^2 = (10)^{\eta_{\text{opt}}/10} \text{ for properties, larger is better}$$

Calculation,

Overall mean of S/N ratio (m) was taken from Minitab software.

$$m = 43.97$$

Now from response table of signal to noise ratio, $m_{A1} = 46.39$, $m_{B1} = 46.91$ and $m_{C1} = 45.69$.

From here,

$$\eta_{\text{opt}} = 43.97 + (46.39 - 43.97) + (46.91 - 43.97) + (45.69 - 43.97)$$

$$\eta_{\text{opt}} = 51.05\text{db}$$

Now,

$$y_{\text{opt}}^2 = (10)^{\eta_{\text{opt}}/10}$$

$$y_{\text{opt}}^2 = (10)^{51.05/10}$$

$$y_{\text{opt}} = 356.86 \text{ MPa}$$

Finally, the calculated optimum value for Young's modulus is 356.86 MPa. Which is close to the experimentally observed value.

Flexural properties according to ASTM standards with composition of PLA-HAp-CS

Table 16 shows that all the output data of 3-point bending test and its SNRA data for flexural specimens (According to ASTM standards).

• For Break Load

Fig. 15 shows the main effects plot for SNRA for break load of flexural specimen as output parameter (for larger the better type case).

Table 17 shows that in response table and ranking table for SNRA larger is better for break load (Flexural specimen).

As shown in **Table 18**, percentage error was 7.65%. It shows that the model has a higher degree of accuracy. Further, it was observed that Infill density is the only significant parameter which contributes 81.02% and layer thickness and deposition angle was not significant and have less percentage contribution of 3.99% and 7.34%, respectively.

For optimization following formula based upon Taguchi L9 OA design has been used:

$$\eta_{\text{opt}} = m + (m_{A3} - m) + (m_{B2} - m) + (m_{C3} - m)$$

Where,

m is the overall mean of S/N data,

m_{A3} is the mean of S/N data for Layer thickness at level 3,

m_{B2} is the mean of S/N data for Deposition angle at level 2,

and, m_{C3} is the mean of S/N data for Infill density at level 3.

$$y_{\text{opt}}^2 = (1/10)^{\eta_{\text{opt}}/10} \quad \text{for properties, lesser is better}$$

$$y_{\text{opt}}^2 = (10)^{\eta_{\text{opt}}/10} \quad \text{for properties, larger is better}$$

Calculation,

Overall mean of S/N ratio (m) was taken from Minitab software.

$$m = 53.76$$

Now from response table of signal to noise ratio, $m_{A3} = 54.34$, $m_{B2} = 54.35$ and $m_{C3} = 55.78$.

From here,

$$\eta_{\text{opt}} = 53.76 + (54.34 - 53.76) + (54.35 - 53.76) + (55.78 - 53.76)$$

$$\eta_{\text{opt}} = 56.95 \text{ db}$$

Now,

$$y_{\text{opt}}^2 = (10)^{\eta_{\text{opt}}/10}$$

$$y_{\text{opt}}^2 = (10)^{56.95/10}$$

$$y_{\text{opt}} = 703.88 \text{ N}$$

Finally, the calculated optimum value for break load is 703.88 N. Based upon peak values in **Fig. 15**, the confirmatory experiment for break load was conducted and observed value was 689.53 N (which is very close to the calculated value).

Table 16 Output of tensile sample and its SNRA data

Experiment run no.	Break load (N)	Strength at peak (MPa)	SNRA for break load	SNRA for strength at peak
1	396.9	305.2	51.9736	49.6917
2	506.7	389.63	54.0950	51.8130
3	547.2	420.77	54.7629	52.4809
4	502.2	386.17	54.0175	51.7356
5	684	525.96	56.7011	54.4191
6	290.7	223.53	49.2689	46.9867
7	621.9	478.21	55.8744	53.5924
8	410.4	315.58	52.2641	49.9822
9	555.3	427	54.8906	52.6086

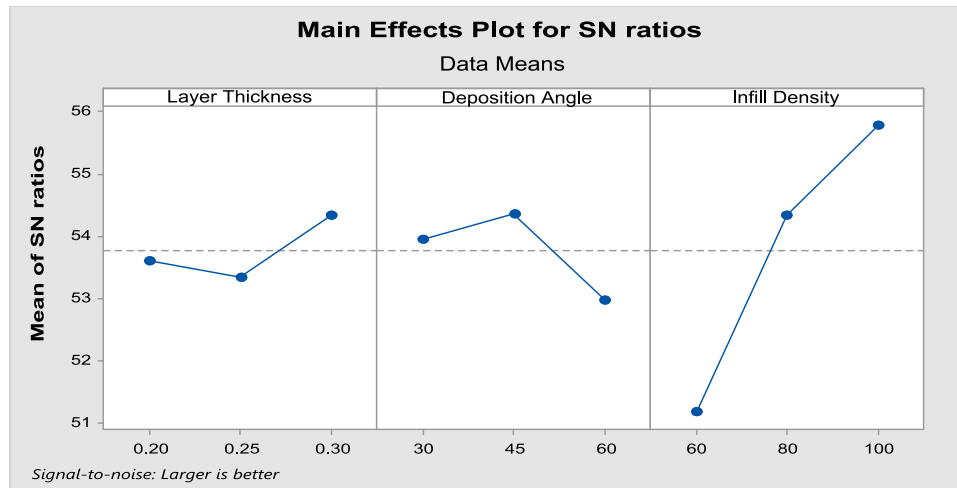


Fig. 15 Main effect plots for SNRA for break load (flexural specimen).

Table 17 Response table for SNRA larger is better for break load (Flexural Specimen)

Level	Layer thickness	Deposition angle	Infill density
1	53.61	53.96	51.17
2	53.33	54.35	54.33
3	54.34	52.97	55.78
Delta	1.01	1.38	4.61
Rank	3	2	1

Table 18 Analysis of variance for break load (Flexural Specimen)

Source	DF	Seq SS	Adj SS	Adj MS	F-value	P-value	% age contribution
Layer thickness	2	1.644	1.644	0.8218	0.52	0.657	3.99
Deposition angle	2	3.024	3.024	1.5118	0.96	0.510	7.34
Infill density	2	33.366	33.366	16.6831	10.60	0.086	81.02
Error	2	3.149	3.149	1.5744			7.65
Total	8	41.182					

● For Strength at peak

Fig. 16 shows the main effects plot for SNRA for strength at peak of flexural specimen as output parameter (for larger the better type case).

Table 19 shows that in response table and ranking table for SNRA larger is better for strength at peak (Flexural specimen).

As shown in **Table 20**, percentage error was 7.65%. It shows that the model has a higher degree of accuracy. Further it was observed that Infill density is the only significant parameter which contributes 81.02% and layer thickness and deposition angle were not significant and have less percentage contribution of 3.99% and 7.34%, respectively.

For optimization following formula based upon Taguchi L9 OA design has been used:

$$\eta_{\text{opt}} = m + (m_{A3} - m) + (m_{B2} - m) + (m_{C3} - m)$$

Where,

m is the overall mean of S/N data,

m_{A3} is the mean of S/N data for Layer thickness at level 3,

m_{B2} is the mean of S/N data for Deposition angle at level 2,

and, m_{C3} is the mean of S/N data for Infill density at level 3.

$$y_{\text{opt}}^2 = (1/10)^{\eta_{\text{opt}}/10} \quad \text{for properties, lesser is better}$$

$$y_{\text{opt}}^2 = (10)^{\eta_{\text{opt}}/10} \quad \text{for properties, larger is better}$$

Calculation,

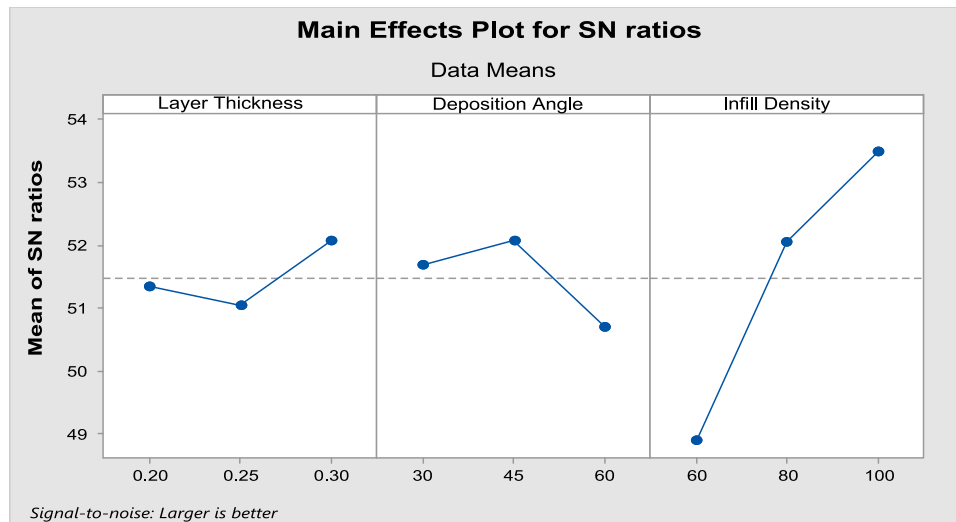


Fig. 16 Main effect plots for SNRA for strength at peak (flexural specimen).

Table 19 Response table for SNRA larger is better for strength at peak (Flexural Specimen)

Level	Layer thickness	Deposition angle	Infill density
1	51.33	51.67	48.89
2	51.05	52.07	52.05
3	52.06	50.69	53.50
Delta	1.01	1.38	4.61
Rank	3	2	1

Table 20 Analysis of variance for strength at peak (Flexural Specimen)

Source	DF	Seq SS	Adj SS	Adj MS	F-Value	P-Value	% age Contribution
Layer thickness	2	1.644	1.644	0.8219	0.52	0.657	3.99
Deposition angle	2	3.024	3.024	1.5120	0.96	0.510	7.34
Infill density	2	33.366	33.366	16.6831	10.60	0.086	81.02
Error	2	3.149	3.149	1.5745			7.65
Total	8	41.183					

Overall mean of S/N ratio (m) was taken from Minitab software.

$$m = 51.48$$

Now from response table of signal to noise ratio, $m_{A3} = 52.06$, $m_{B2} = 52.07$ and $m_{C3} = 53.50$.

From here,

$$\eta_{\text{opt}} = 51.48 + (52.06 - 51.48) + (52.07 - 51.48) + (53.50 - 51.48)$$

$$\eta_{\text{opt}} = 54.67 \text{ db}$$

Now,

$$y_{\text{opt}}^2 = (10)^{\eta_{\text{opt}}/10}$$

$$y_{\text{opt}}^2 = (10)^{54.67/10}$$

$$y_{\text{opt}} = 541.38 \text{ MPa}$$

Finally, the calculated optimum value for Strength at peak is 541.38 MPa. Based upon peak values in **Fig. 16**, the confirmatory experiment for break load conducted and observed value was 532.56 MPa (which is very close to the calculated value).

Conclusion

Following are the conclusions from present case study:

- HAp, PLA and CS are one of the best suitable materials for fabrication of biocompatible/biodegradable/bioactive scaffolds/inserts for TE/biomedical applications. HAp is best suited material because its characteristic is 99% similar to bone and teeth. CS is bioactive polymers which ignite the tissue in growth rate and PLA is biocompatible as well as biodegradable polymer.
- For fabrication of feed stock filament of different compositions/proportions of PLA-HAp-CS experimentation based study was conducted based upon thermal analysis, MFI, tensile testing, continuous flow ability and dimensional analysis. It was observed that best composition/proportion selected is 91%-8%-1%.
- In SEM analysis of feed stock filament it has been ascertained that the specimens/functional prototype prepared are structurally suitable for repair/regeneration of bone/fractured bone because the internal structure of the sample is fibrous, open and porous. The porous structure of an implant provides channels for bone ingrowth. In addition, porosity enhances the biological interlock between implant and bone.
- Based upon TSE optimization for determining the best setting of factors is barrel temperature 190°C, rotational speed of screw are 140 rpm and applied load 12 kg for fabrication of feed stock filament.
- Based upon FDM optimization for determining the best setting for tensile properties are layer thickness 0.2 mm, infill density of sample is 100 % and deposition angle is 45° and best setting of FDM for flexural test are obtained as layer thickness is 0.3 mm, infill density of sample is 100 % and deposition angle is 45°.

Acknowledgment

The authors are highly thankful to SERB under AISTDF Secretariat (File No. IMRC/AISTDF/R&D/P-10/2017, Dated 01-02-2018) for financial support.

See also: Recycled Clothes With Polypropylene-Nanoclay for Industrial Product via Injection Molding

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District Heating Systems From Environmental Waste

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Introduction

District heating systems (DHS) are based on production of heat and distribution of produced heat to consumers. Every DHS is comprised of three basic elements: heat source, distribution network and consumers. In order to be competitive with individual heating systems, DHS must use one of the five suitable strategic local energy resources: useful waste heat from thermal power stations (cogeneration); heat obtained from refuse incineration; useful waste heat from industrial processes; natural geothermal heat sources and fuels difficult to manage, such as wood waste, peat, straw, or olive stones (Werner, 2004) and have advanced control which will lower operation and distribution costs.

One of the first systematic analyses of heat load in whole district systems was provided (Werner, 1984) where comprehensive study of factors affecting the value and character of heat load was performed. Further analysis of heat load in district heating system was undertaken (Madsen *et al.*, n.d.) where different nonparametric and parametric methods and models were developed and tested with sampled data from Esbjerg district heating system. Review of parametric, non- and semi-parametric methods and models for heat load was presented in Nielsen and Madsen (2000).

Environmental waste could have high potential as resource for district heating system. In this study we analyzed potential of designing of district heating systems from environmental waste.

Literature Overview

Data centers seek solutions to increase energy efficiency and lower costs by novel methods. Waste heat utilization is considered to be one of the major trends in the near future, especially in the Nordic countries, where heat demand is high. In this paper, waste heat utilization was analyzed from the perspectives of both the data center and district heating network operators (Wahlroos *et al.*, 2017). District Heating System (DHS) using waste heat is highlighted as an attractive solution. Supported by technological assessment and emerging concepts of Industrial-Urban Symbiosis (I-US), in study (Dou *et al.*, 2016) was combined the system development of DHS and land use scenarios into a symbiotic design based on inventory survey and geographic database, and conducts a cost-benefit analysis to scientifically and quantitatively evaluate the effects brought from land-use policies. The refurbishment of existing buildings is often considered a way to reduce energy use and CO₂ emissions in the building stock. In study (Lidberg *et al.*, 2017) was analyzed the primary energy and CO₂ impact of refurbishing a multi-family house with different refurbishment packages, given various district heating systems. To meet the district heating demands and recover the industrial waste heat simultaneously, high-efficiency centrifugal heat pumps are applied for district heating and heat recovery (Hu *et al.*, 2017). Municipal solid waste has seen increasing annual volumes for many decades in contemporary Europe and constitutes, if not properly managed, an environmental problem due to local pollution and greenhouse gas emissions. From an energy perspective, waste is also an alternative fuel for power and heat generation; energy recovery from waste represents an effective measure to reduce landfilling and avoid disposal emissions while simultaneously reducing the equivalent demand for primary energy supply (Persson and Münster, 2016). Low-grade industrial waste heat could be a considerable potential energy source for district heating, on the condition that the heat from different industrial waste heat sources is integrated properly. In study (Xia *et al.*, 2016) was considered a method for integrating low-grade industrial waste heat into a district heating system and focuses on how to



Fig. 1 Heating plant for data acquisition.

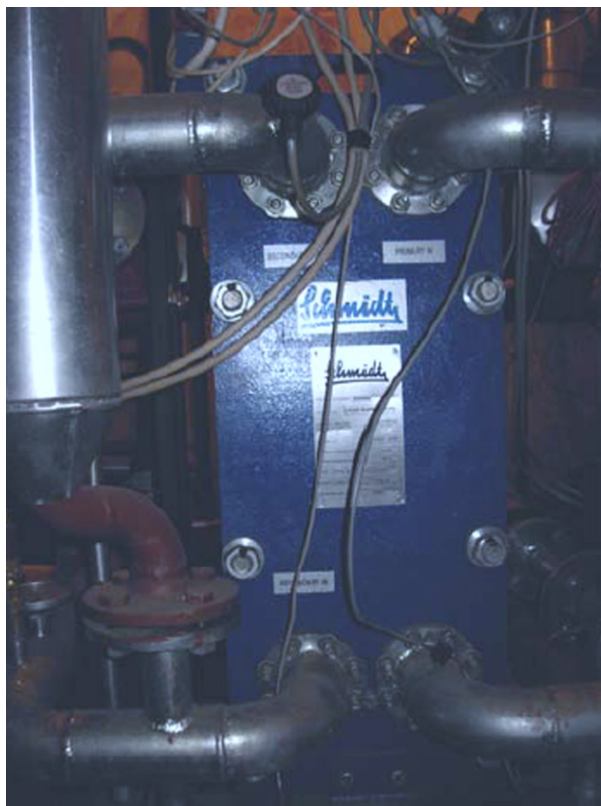


Fig. 2 Plate heat exchanger.



Fig. 3 Motorized flow control valve.

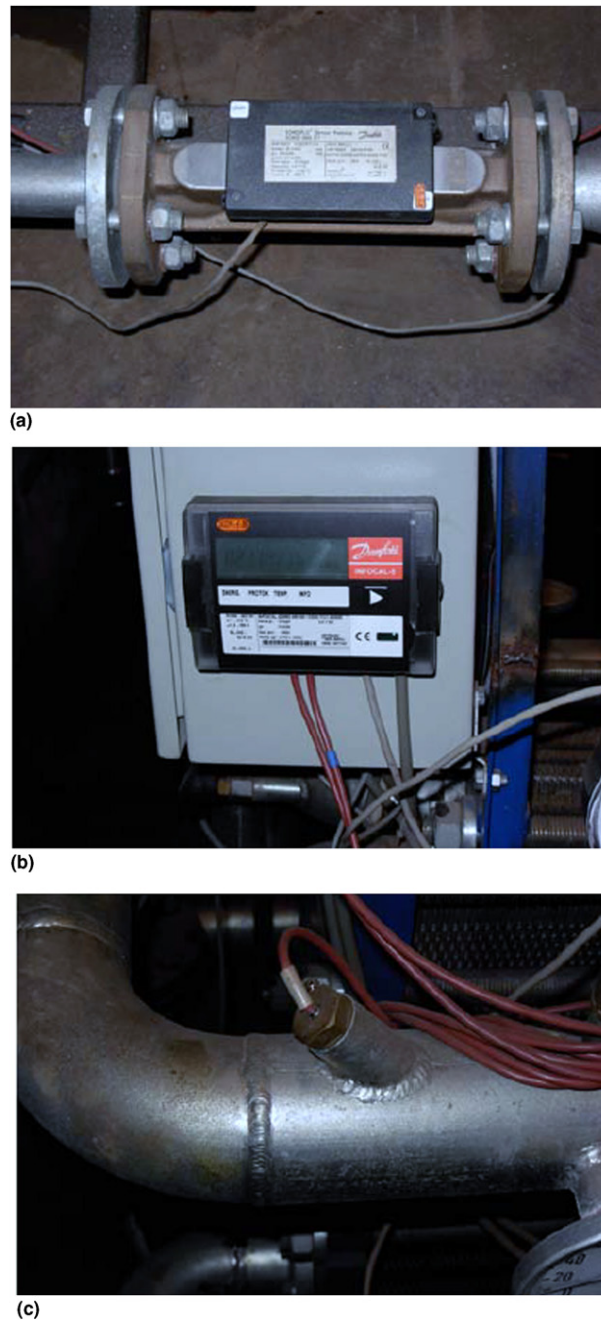


Fig. 4 Danfoss Ultrasonic heat meter: (a) INFOCAL 5 system, (b) SONO 2500 CT system, (c) PT 500 temperature sensors.

improve the outlet temperature of heat-collecting water by optimizing the heat exchange flow for process integration. District heating, the utilization of centrally produced heat for space heating and domestic hot water generation, has the potential to contribute to the eco-efficient use of energy resources in the parts of the world where space heating is needed. In literature, environmental studies on district heating mainly consider the emissions from heat generation; the environmental impact from the distribution system is seldom discussed. In paper (Fröling *et al.*, 2004) was presented a life cycle assessment of the production of district heating pipes, based on a cradle-to-gate life cycle inventory commissioned by the Swedish District Heating Association.

Methodology

Measurement and acquisition of data was performed in heating substation connected to heating plant with installed capacity of heat source (gas fired boilers) of 128 MW. The interior of heating substation is shown in Fig. 1.

Table 1 Statistical summary of gathered data

Heat load parameters	Minimum value	Maximum value	Mean	Median
Outdoor temperature [°C]	− 10.60	4.40	− 1.19	− 0.30
Primary supply temperature [°C]	30.70	88.70	65.71	72.30
Primary return temperature [°C]	25.70	54.30	43.75	46.50
Secondary supply temperature [°C]	27.20	59.10	47.39	50.80
Secondary return temperature [°C]	20.70	49.70	41.64	44.60
Flow on primary side [m ³ /h]	0.10	7.20	6.16	6.20
Heat load [kW]	− 8.74	273.40	157.83	182.48

The heating substation is indirectly connected to district heating system and hydraulic separation is accomplished through Schmidt-Bretten plate heat exchanger, model SIGMA X13-NCL (Fig. 2). Installed capacity of heat exchanger is 650 kW.

No domestic hot water preparation is envisaged. Heat from substation is delivered across the two-pipe system to cast iron radiators in sixty apartments. Delivered heat in apartments is manually regulated and no thermostatic radiator valves exist. Additionally, there is no measurement of indoor temperature. Flow control and consequently control of delivered heat to consumers is achieved through Danfoss AVQM (DN40) motorized flow control valve (Fig. 3).

In addition to motorized control, valve has control diaphragm for mechanical flow limitation in order to limit the excessive flow in substation. Circulation of water on secondary side is performed with constant speed Grundfoss twin pump UPSD 50-180/F. Regulation of delivered heat is achieved by Danfoss ECL comfort 300 controller which is placed in control box with other electrical equipment. Controller works on weather compensation principle and controls the temperature of delivered water to consumers/secondary side through temperature control curve, according to momentary measured outside temperature. There is no feedback from indoor temperature measurement. Two additional modules are integrated in controller: ECA 84 (for measuring of delivered heat) and ECA 87 for storage of measured values. Controller was connected with HCP HAWK high speed GPRS modem for remote data transfer. Archived data, from ECA 87 module were read off regularly during the heating season. Delivered heat is regularly measured and archived through Danfoss Ultrasonic heat meter (INFOCAL 5 (Fig. 4(a)) and SONO 2500 CT (Fig. 4(b)) system plus two PT 500 (Fig. 4(c)) temperature sensors).

Results

Gathered data were sampled on 15 minutes. Preprocessing of data was not taken into consideration. The aim was in developing recursive and robust model capable of producing the on-line predictions of consumers heat load for further use in control of DH systems. Following variables were simultaneously measured:

- Outdoor temperature [°C]
- Primary supply temperature [°C]
- Primary return temperature [°C]
- Secondary supply temperature [°C]
- Secondary return temperature [°C]
- Flow on primary side [m³/h]

Heat load was calculated based on measured values of primary supply and return temperatures and flow on primary side. Summary of statistical properties of the head load parameters is provided in Table 1.

Conclusion

District heating system from environmental waste could be very attractive domain for investigation sources. Environmental waste could has high potential as resource for district heating system. In this study we analyzed potential of designing of district heating systems from environmental waste.

See also: Sustainable Biofuels for Automotive Applications

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E-Agriculture System by Object-Oriented Approach

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Introduction

Application of information and communication technology (ICT) in business can enhance and improve the business because ICT has many advantages for consumers and users. One of the most important sectors for ICT application is agriculture. The system is known and e-agriculture can improve the agriculture business in many directions. E-agriculture could be described as a new field on enhancement of agricultural development through ICT processes. The system enables design, development, evaluation and application of innovative ways to use ICT in agricultural domain (Behera *et al.*, 2015).

Agriculture is facing continuously new and important problems and challenges and use of Information and Communication Technologies (ICTs) can be a major intervention for more efficient agriculture (Salampasis and Theodoridis, 2013). In order to generate meaningful improvements in food security and farm incomes, there must be commensurate efforts to promote ICT-based market information along with yield-augmenting agricultural seed technologies (Kiiza and Pederson, 2012). The infiltration of new technologies in the agricultural sector is fact and results in article (Botsiou and Dagdilelis, 2013) revealed four farm's ICT profiles. China's agriculture sector has been transformed from the traditional to modern practice through the effective deployment of ICTs (Zhang *et al.*, 2016). Agricultural extension in has often been criticized for its focus on linear knowledge transfer, and limited attention to systemic approaches to service delivery but there are high expectations of new-ICTs to enhance interaction and information exchange in extension service delivery (Munthali *et al.*, 2018). Farmers have strived for better access to information and communication and rapid technological process has now lead to a variety of new ICTs, which have the potential to address the information and communication needs of farmers much faster and with far more accuracy than ever before (Daum, 2018). ICT could be used for smart agriculture and climate-smart agriculture (CSA) is widely promoted as an approach for reorienting agricultural development under the realities of climate change (Thornton *et al.*, 2018; Dunnett *et al.*, 2018; Westermann *et al.*, 2018). Within business enterprises farmers lags behind in the uptake of new information technologies for the control and automation of farming systems (Ntaliani *et al.*, 2010; Somers and Stapleton, 2015).

The main goal in the article is to enhance the role of ICT in agricultural development by providing a framework to facilitate the processes of capturing and managing in agriculture. The system could provide the basis for monitoring of development and validation of conceptual models and methodologies in agriculture business. Object-oriented approach is used for e-agriculture system modeling (Lethbridge and Laganieri, 2005; Jacobson, 1993).

Methodology

E-Agriculture System

Introduction of ICT in agriculture sector could be empower farmer with relevant and timely information about different crop variety. Also the system could be helpful for reducing of farming risks about information on weather, production and cultivation techniques, seeds and fertilizers, plant nutrients and water usage. E-agriculture can reduce knowledge gaps and to increased knowledge sharing in order to increase productivity and boosting growth.

Object-Oriented Methodology

Rational Unified Process (RUP) is an interactive methodology for the software development based on architecture and use cases. RUP methodology is based on Unified Modeling Language (UML) (Rumbaugh *et al.*, 2004). UML is used for specification, visualization, construction and documentation of the software development.

RUP methodology has control, key or critical points through the development. In the other words each phase of the RUP methodology should end by some control, key or critical points where achieved results are summed and future directions are planned based on the results. RUP methodology has artefacts (documents), models i model elements. Project requests are noted in the documents. Models are used to simplify the software architecture without unnecessary details. Model elements could help to visualize, construct and document the main structure and software behavior. Fig. 1 shows the main elements of the RUP methodology. Each phase of the RUP methodology has iteration where disciplines are considered. The disciplines are described by process flow in details. The process shows activity and roles of everyone in the project. Finally there are artefacts where one can see software documentation, software models and model elements.

RUP methodology has four main phases. The first phase is initial phase or idea inception where one needs to understand what should to do and software vision and requirements are identified. This phase includes the identification of key software actors (users) and use cases. Also there is need to identify software domain. Use case defines one sequence of an action which software performs that yields to an observable results. In the other hands one use case presents result of an action by actor (Fig. 2). Use case

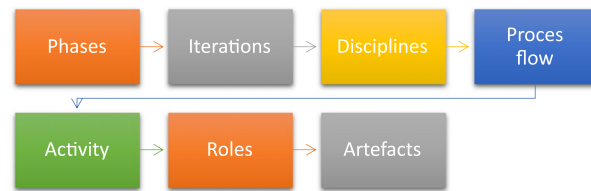


Fig. 1 Elements of RUP methodology.

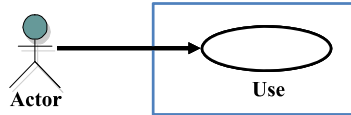


Fig. 2 Use case model.



Fig. 3 RUP methodology phases.

presents the main part of some complete software operation from beginning until to the end. It is used to capture the intended behavior of the system in development. By use cases models desired behavior of the system could be specified but it is not strictly this desired behavior to be carried out or implemented in the final product. Use cases models can be developed for whole system or for the part of system. Each part of system or subsystem can be developed by use cases models until the part produces some tangible amount of work and results. System complexity dictates the number of use cases. In the initial stage of system development main use cases are developed and additional use cases can be added or included when there is need for them.

The second phase is project elaboration where one needs to understand how to build the software and basic software architecture is showed in the phase. The third phase presents software construction where software testing is considered. The fourth phase presents software transition where software validation is performed. The RUP phases are shown in [Fig. 3](#).

RUP models describes software in modeling. RUP models could be business models which describes business processes and business environment, use case models which describes what software doing and software environment, projecting models which describes use cases realization as code abstraction and implementation models which presents collection of components and subsystems.

Software development process could has different problems which needs to be identifies and solved before coding and testing. In order to solve problems there is need to find the problem causes. To remove the problem causes it is suitable to use best practices. For example in order to remove the confusion in communication between team members it is suitable to use standard language UML for the software visualization, specification and documentation. There are different types of UML diagrams which can be used in the software development process. There are two main classes of the UML diagrams. These are structural and behavioral diagrams. Structural diagram presents structure of the system in passive state and behavioral diagram present the active behavior of the objects in a system or dynamical state.

Object-orientated modeling concepts are used during analyzing and modeling of the e-agriculture system. Two UML concepts are used for the modeling. The concepts are use case models with scenarios of activities and class diagram. Use case models show dynamic behavior of the software while class diagram depicts the main structure of the system in development.

Results

[Fig. 4](#) shows the main use case diagram of the e-agriculture system. As can see there are two users of the system. First of all there is forecasting platform and second there is remote sensing module. Forecasting platform is intended for collecting of ground data. The main tasks of the remote sensing module are to estimate the yield and crop area. The remote sensing module could not work without collecting the ground data.

[Fig. 5](#) shows the use case diagram for forecasting platform where can be see two additional use cases for the forecasting platform. These use cases are forecasting of wheat yield and forecasting of rice yield. There is possibility to add additional use case for another forecasting purpose.

[Tables 1](#) and [2](#) shows detail specification of use cases for forecasting of wheat yield and forecasting of rice yield.

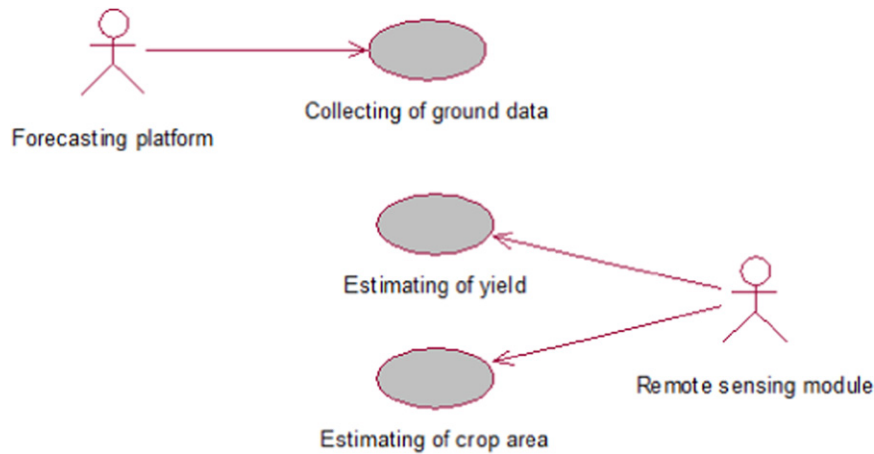


Fig. 4 Main use case diagram of the e-agriculture system.

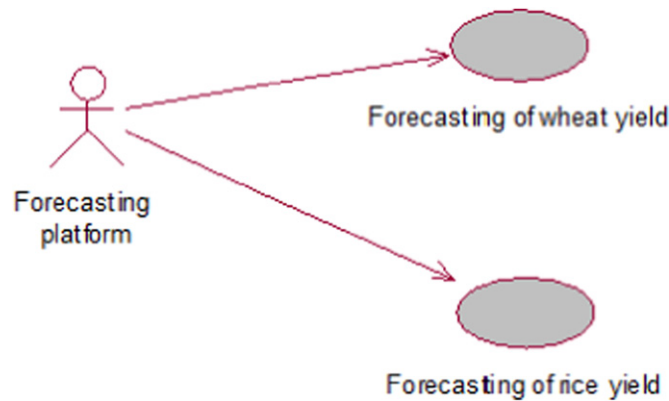


Fig. 5 Use case diagram – Forecasting platform.

Table 1 Specification of use case: Forecasting of wheat yield

<i>Title</i>	Forecasting of wheat yield
<i>Actors</i>	Forecasting platform
<i>Trigger</i>	It starts with acquiring raw wheat data.
<i>Pre-condition</i>	Platform is properly settled.
<i>Post-condition</i>	Forecasted wheat data.
<i>Main scenario</i>	1. Platform acquires raw wheat data from ground. 2. Platform starts software for forecasting purposes. 3. Platform performs forecasting of wheat yield. 4. Platform sends forecasted data to remote sensing module.
<i>Alternative</i>	None

Table 2 Specification of use case: Forecasting of rice yield

<i>Title</i>	Forecasting of rice yield
<i>Actors</i>	Forecasting platform
<i>Trigger</i>	It starts with acquiring raw rice data.
<i>Pre-condition</i>	Platform is properly settled.
<i>Post-condition</i>	Forecasted rice data.
<i>Main scenario</i>	1. Platform acquires raw rice data from ground. 2. Platform starts software for forecasting purposes. 3. Platform performs forecasting of rice yield. 4. Platform sends forecasted data to remote sensing module.
<i>Alternative</i>	None

Conclusion

In this study was established ICT in agriculture domain in order to develop e-agriculture system and to improve life quality. The system could help farmers and investors to get relevant information regarding agriculture, crop production and etc.

Visual modeling is a way of thinking about the problems from reality. The models are used for problems understanding, for communications between team members which are included in the project, for modeling of company, for documentation preparation and for program and database design. Modeling enable better understanding of requirements, clean design and better support and maiming of the systems.

See also: Appraisal of E-Drought System Based on Object Oriented Approach

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Eco Friendly Aspects in Hybridization of Friction Stir Welding Technology for Dissimilar Metallic Materials

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Introduction

The competitive manufacturing processes enforcing eco-friendliness focuses mainly to minimize the impact on the environment and optimum utilization of the resources. The sustainable manufacturing processes are aiming at efficient utilization of the materials and energy. In view of that, continuous modification of the manufacturing processes or substitute for existing process with alternate economic processes are going on. In this aspect, friction stir welding (FSW) is one of the green manufacturing technologies that ensures zero emissions to the environment and is known as a green technology (Mishra and Ma, 2005; Nandan *et al.*, 2008). Traditional fusion welding processes i.e., mainly arc welding and laser welding require significant amount of heat that may lead to cracking and porosity during solidification. FSW is capable of joining two materials with less amount of energy consumption and is more eco-friendly as compared to conventional fusion welding technologies. FSW is recently developed solid state welding process which is intended to overcome fusion welding limitations and both similar and dissimilar combination of materials are coalesced together through plasticization of the substrate materials (Arora *et al.*, 2009a; Buchibabu *et al.*, 2017). The schematic of FSW system along with standard terminology is depicted in Fig. 1.

In general, the liquid-phase manufacturing process i.e., fusion welding process utilizes more energy because of often reaches superheated temperature and possibility of high energy loss during transformation as compared to solid state welding process. However, the optimum utilization of resources depends on nature, type, and physical properties of the materials to be joined and a close relation exists between the quality of the joint with proper choice of the parameters. The eco-friendliness includes the green and sustainability concepts pertinent to the environment degradation, minimization of required energy, control on environmental pollution, minimum production of waste, maximum recyclability of the waste products, and, models for maintenance (Narayanan and Das, 2014). Fig. 2 depicts the support triangle and its basic elements for the development of eco-friendly welding process. A green technology aims to minimize the damage to the environment as well as maximize the use of resources that leads to savings in materials and energy while benefiting the environment (Ghodrati *et al.*, 2016). The process efficiency primarily depends on proper choice of parameters along with the material combination and secondarily the technology adapted for the processing of the material. The energy efficiency is decided by the type and nature of energy source with any environmental impact and the technology used to utilize this energy. However, economic use of material and energy according to the technology always brings in forefront the savings in resources by minimizing the waste product creation as well as by reducing the environmental pollution. In the present article, the eco-friendliness is described with reference to fusion welding and FSW processes. However, hybridization of FSW not always brings the green technology in forefront like conventional FSW process. The enhanced product quality is often compromised with eco-friendliness of the process. For high melting point and high hardness materials such as steel, the classic FSW cannot be utilized in the most economical way. It is limited by the expected tool life where the tool is often subjected to high temperature, static or dynamic load, and stress at variable temperature. Even for a costly polycrystalline cubic boron nitride (PCBN) tool having high relative hardness with respect to steel, tool wear remains high and tool life may not be economical when used in conventional FSW process (Rai *et al.*, 2011; Mehta *et al.*, 2011). These factors drive to explore various auxiliary energy sources to moderate the material to be joined and lead to develop various hybrid FSW (HFSW) processes not exceeding the melting point temperature. The hybrid technology effectively decreases the tool wear and increase the tool life i.e., creates the possibility of exploring the tool in the most economical way (Yaduwanshi *et al.*, 2015a,b; Padhy *et al.*, 2015).

There is a growing interest to the industries in hybridization of welding processes to overcome certain technological difficulties arises in conventional and fundamental processes. HFSW is quite innovative joining technique that has immense potential for extending its application to different fields of industrial problems. This technique, although classic FSW is the primary process, accomplishes mainly the hindrance of conventional FSW process. As an outlying benefit, it provides significant improvements in the weld quality and efficiency of the processes in manufacturing applications. Welding of relatively harder materials as compared to Al and Zn-based soft alloys is difficult to process by FSW due to high plasticization temperature. Secondary heat sources focusing to the harder alloys during welding process would reduce the amount of work required by FSW tool during operation. This additional heat also reduces the flow stress resistance of the workpiece by softening it without affecting the FSW tool. In effect, it improves the performance of the tool and tool life as well as the weld joint quality and efficiency (Bhadeshia and DebRoy, 2009; Nandan *et al.*, 2007). However, this additional heat may affect the environment to a lesser extent since the maximum temperature remains below the melting point of the substrate material. The nature of secondary heating is contributed from several sources and is known as so called hybrid FSW process when FSW act as primary process. HFSW processes are broadly categorised as thermal energy and mechanical energy assisted FSW. Direct use of thermal energy in HFSW are supplied from electricity

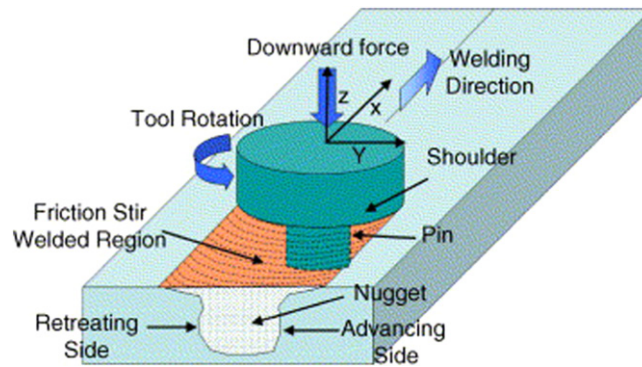


Fig. 1 Schematic diagram of FSW process. Reproduced from Mishra, R.S., Ma, Z.Y., 2005. Friction stir welding and processing. Materials Science and Engineering R 50, 1–78.

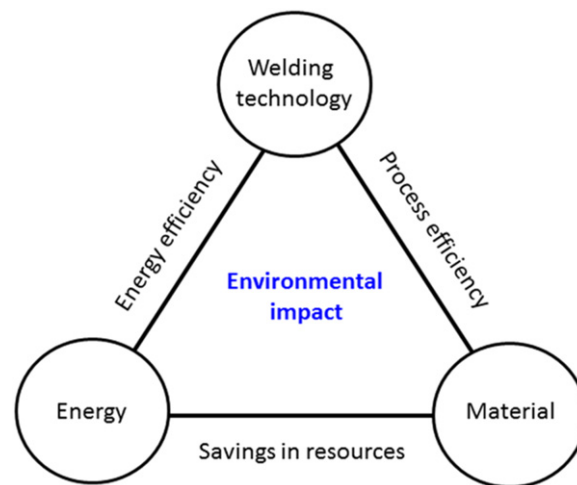


Fig. 2 Basic elements of green manufacturing technology.

(Nandan *et al.*, 2007; Long and Khanna, 2005; Santos *et al.*, 2014a,b; Potluri *et al.*, 2013; Liu *et al.*, 2015a), induction (DebRoy and Bhadeshia, 2010; Grant *et al.*, 2005; Sinclair *et al.*, 2010), laser (Palm, 2004; Bang *et al.*, 2010), plasma arc (Yaduwanshi *et al.*, 2018, 2016, 2014), hot gas stream (Lotfi and Nourouzi, 2014), gas torch (Choi *et al.*, 2011) etc. Resistance heating by direct electricity and heat generation by eddy current through induction coil do not have direct impact on the environment. However, electric arc, plasma arc, and laser as secondary heat source has less impact on environment when using with hybrid FSW process since low intensity heat energy i.e., just the heating mode is used rather than the welding mode. Mechanical energy as an auxiliary source is used in ultrasound assisted FSW process. The ultrasonic vibration directly or indirectly localize the softening behaviour of the harder material without much increment in temperature as well as least effect on whole workpiece (Lai *et al.*, 2014; Shi *et al.*, 2015; Strass *et al.*, 2014a,b; Liu *et al.*, 2015b,c; Liu and Wu, 2013).

Modern digital manufacturing process relies on data and information where the concept of green and sustainable technologies has been developed. Mathematical modeling and simulation of FSW process is an alternate way to design the process with minimum utilization of the resources. It reduces the expensive experiments, formation of prototyping, several trial-and-error repetitive experiments to identify the feasible range of parameters, and the cost by reducing significant amount of time (Ulysse, 2002; Chen and Kovacevic, 2003; Buffa *et al.*, 2006; Tseng, 2006; Heurtier *et al.*, 2006; Robson *et al.*, 2007; Okuyucu *et al.*, 2007; Schmidt and Hattel, 2008; Shojaeefard *et al.*, 2013; Wang *et al.*, 2013). In general, the index of eco-friendliness is measured by considering the elements like raw material consumed, the amount, nature, and type of emissions to the environment, and the energy efficiency for a particular manufacturing process. The sustainability of a manufacturing process is generally measured by the greenhouse emissions during the process which is almost zero in case of FSW process. However, there are several other approaches to analyse the eco-friendly aspect of the FSW process. These include broadly the optimum utilization of raw materials, reduction in specific energy consumption, reduction in waste generation, reduction in emissions, maximization of recycling, and enhanced use of renewable energy (Narayanan and Das, 2014). Fig. 3 depicts the essential elements of green manufacturing technology where the expected outcome is to develop the manufacturing process in the most economical way with minimum intervention of the environment as well as improved product quality. For the development of hybrid FSW technology, the parameters like the process

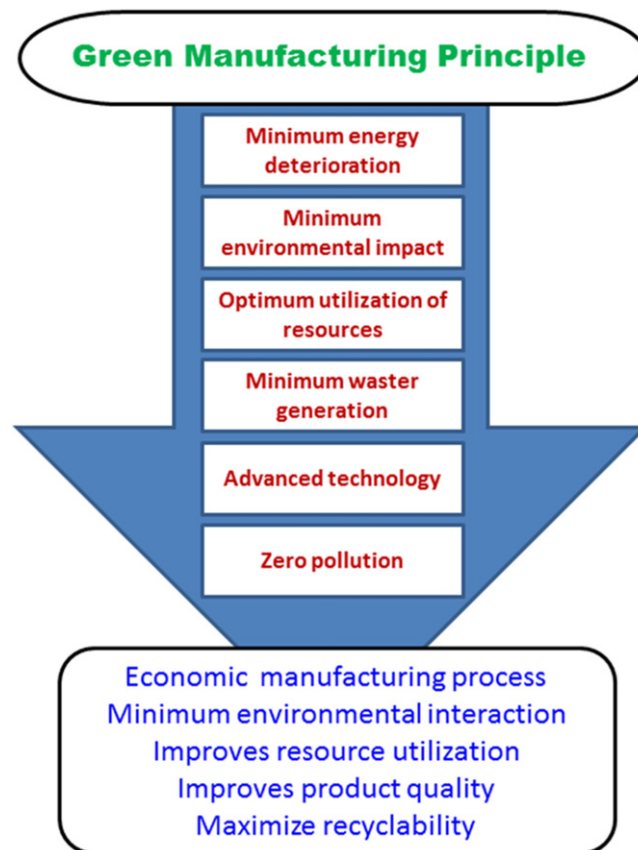


Fig. 3 The elements of green manufacturing technology and the expected outcome. Reproduced from Kopac, J., 2009. Achievements of sustainable manufacturing by machining. *Journal of Achievement in Material and Manufacturing Engineering* 34, 180–187.

efficiency, optimum utilization of energy, and enhanced product quality in terms of joint strength and status of the microstructure are the measurable quantities. The present article analysed all these significant elements based on qualitative assessment of arc welding, FSW and HFSW processes.

Eco-Friendly Aspect of Fusion Welding

The welding and joining environments is very complex in nature, specifically the fusion welding where the formation of numerous gases and particulate components from flux, shielding gas and electrode-coating impacts on the environment extremely (Palani and Murugan, 2006; Vidyarthi and Dwivedi, 2016; Liu *et al.*, 2016). Modern manufacturing process tends to shift towards green or clean technology where eco-friendly aspect of gas, arc, and laser welding is significant. At extremely high temperature of arc welding process, the hazardous environment is created by formation of fumes, vaporization of elements and condensation of vapours to solid particles. In plasma arc welding (PAW), gas metal arc welding (GMAW) and gas tungsten arc welding (GTAW), the shielding gas act as protective atmosphere rather than the use of flux from electrode coating. It may produce the metallic oxides and metallic particles during the process. The use of flux is essential for shielded metal arc welding (SMAW) and submerged arc welding (SAW) according to principle of the technology. All these processes bring three different aspects from economical point of view. The shielding gas (mostly inert type gas) is expensive than using coating on electrode or flux. Therefore, the economical aspect is significant here. GTAW is usually used for relatively thin material whereas GMAW is used for higher thickness material with a pre-defined groove. SMAW or SAW is normally used for large scale welding process. Secondly, the fumes or localized distribution of shielding gas creates the health hazards. Apart from all these difficulties, the consequence effect are impaired because of the melting of the materials to create permanent coalesces. Third, the degree of automation of this welding process is an important aspect since a semi-automatic system is partly manual. The controlling of so many parameters in arc welding process with a feed-back system is really a challenging task (Rout *et al.*, 2019). Most of the arc welding technology are manually operated or in the mode of semi-automatic. In that respect, the solid-state welding is automated with ease as compared to arc welding processes. Therefore, the melting of material as well as the arc welding technology both are negative factors to compromise with the eco-friendly aspect of the process.

Chang *et al.* (2015) analysed the environmental impacts of the fusion welding processes between manual and automatic GMAW, automatic laser-arc hybrid welding, and manual metal arc welding (MMAW). Out of these processes, the manual operation ensures the excess amount of energy consumption viz. the filler material as well the coating on it due to lack of control on metal transfer. Therefore, MMAW contributes the highest amount of emissions to the environment and consequently the global warming. The secondary impact of the manual process is to bring the risk of health hazard as compared to shop floor automatic process. In that respect, the laser welding is eco-friendlier and easy to automate than arc welding processes due to supply of well controlled and stable laser power, flexibility of power diffraction by pulsation and easily focus on a particular area (Kashaev *et al.*, 2018). Most often, laser welding is assisted with shielding gas and creates less hazardous environment as compared to arc welding processes. The electron beam welding (EBW) operates under vacuum and ensures the highest quality of fusion welded structure since the contamination of the weld pool is the minimum under protected atmosphere (Dinda *et al.*, 2019). Therefore, EBW is eco-friendlier than laser or arc welding processes, but, the cost of the technology is not comparable. The inverter power supplies for semiautomatic welding process create the economic benefit when welding is performed in a protective gas environment (Petrov *et al.*, 2017). It involves the machine installation and training cost along with cost of consumables like electrodes and shielding gas etc. Thus, the use of inverter power supply for the development of advanced welding equipment is technologically and practically justified from the economic point of view. Campbell *et al.* (2012) showed the economic and technological benefit of a sophisticated shielding gas flow controller based on self-regulating device than a conventional flow meter used in GMAW process. There was a cost savings of $\sim 50\%$ in shielding gas by reducing the gas flow rate to 6 L/min without compromising the weld joint quality. This technical upliftment has several lateral advantages. Clean weld is produced at this low gas flow rate which is free from localized current of gas. It enhances the potential savings by drastic reduction in gas flow rate. The electromagnetic gas saving device responds very rapidly which is beneficial to minimize the wastage of gas during short weld length or pulse welding condition. In this stitch welding case, the consumption of shielding gas is reduced by $\sim 20\%$. The impulse pressure generated by the valve further enhances the weld depth of penetration. Tseng (2006) utilized GA based optimization algorithm to achieve the highest quality of weld joint by minimizing the energy consumption in resistance spot welding process. An optimum combination of process parameters i.e., electrode force, weld on time, current and desirable sheet thickness has been established to accomplish the objective. It is thus obvious that by modifying the welding equipment, or by developing the automatic system or by using the optimum range of process parameters, the impact on environment is minimized or efficient utilization of energy is possible. It needs several interactive studies which currently lack in literature to make fusion welding a green technology or sustainable manufacturing process. In that respect, solid-state welding has the potential to be a green manufacturing process because of several technological advantages over conventional fusion welding processes.

The ultrasonic welding is one of the solid state welding processes which are eco-friendlier as compared to fusion welding processes (Ni and Ye, 2018). This process is limited in small scale joining where the thickness is limited to only 1 mm. Magnetic pulse welding is another cleaner technology which uses electromagnetic forces and join at a relatively high welding speed (Kapil and Sharma, 2015). The weld interface is free from melting and does not produce hazardous emissions like fume and spatter. However, the magnetic pulse welding is limited by the geometric shape and size of the workpiece which is mainly controlled by the design of the coil used to produce high density magnetic field. The FSW which is designed primarily for light weight structure can overcome the limited thickness of workpiece to be joined as compared to ultrasonic or magnetic pulse welding. However, hybridization of FSW is further development primarily meant for joining dissimilar materials and high strength or high hardness materials.

FSW as Green Technology

To enhance the fuel economy, the automotive industry focuses on to the manufacturing and processing of lightweight materials like aluminum alloys. However, the welding of aluminum using conventional fusion welding processes encounters serious problems like poor microstructure and porosity in the fusion zone (Praveen and Yarlagaadda, 2005). Therefore, processing of aluminum is often preferred by solid state welding processes. FSW is such process developed primarily for aluminum alloys where two materials are joined by plastic deformation through frictional heat generation by a non-consumable and hard tool. The localized frictional heating drives a non-symmetric mixing of the quasi-viscous material occurs due to difference in relative velocities between advancing and retreating sides (Yaduwanshi *et al.*, 2015a,b). Literature are enriched with numerical simulation and soft computing methods of FSW process to analyses the influence of process parameters on internal variables like strain, strain-rate, and temperature distribution. These parameters along with inherent material properties decides the mechanical properties and microstructural characteristics of the weld joint, and if there is any formation of defect (Okuyucu *et al.*, 2007; Xu *et al.*, 2001; Colegrove and Schercliff, 2004; Nandan *et al.*, 2006; Arora *et al.*, 2009b; Neto and Neta, 2013; Chiumenti *et al.*, 2013; Mehta *et al.*, 2015; Fratini *et al.*, 2009; Boldsai Khan *et al.*, 2011; Alkayem *et al.*, 2017). With the advancement of high performance computational facility, the process model of industrial need are of growing interest either for processing of a new material or to analyse the differential influence of process parameters. Therefore, a reliable modeling and simulation of FSW process demands the validation with experimental result. However, the requirement of the number of experiments is less which minimizes the adverse effect on environment. Also, the economical aspect in conducting the experiments in terms of usage of materials, involvement of cost and time, power or fuel usage and emission to environment are reduced substantially. The green manufacturing pertinent to computational facility and sustainability of electronic items are significant for analysing the

eco-friendliness of computer model for FSW process. The main challenge is the disposal of computer waste like lead and recovery of gold from circuit boards during recycling of computer wastes (Williams, 2004; Kahhat and Williams, 2009; Babbitt *et al.*, 2009; Chu *et al.*, 2009; White *et al.*, 2003; Fukuda *et al.*, 2003). Development of green and biodegradable electronic products is one of the solutions to reduce the environmental impact where organic materials are good candidate to be used in electronics manufacturing (Bar-Cohen and Iyengar, 2003; Irimia-Vladu *et al.*, 2012). Organic paper can be used to produce low voltage circuit and an electronic sensor can be made from biodegradable silk. The flexible conductive polymer (polyaniline and polypyrrole) can be used in biological system that holds other mechanical properties while being nontoxic (Irimia-Vladu *et al.*, 2012).

FSW is environment friendly due to absence of any smoke and fumes which is usually common in conventional fusion welding processes. The frictional heat is responsible for the plastic deformation and mixing of softened material where heat generation is restricted to below melting point temperature. FSW ensures effective utilization of the energy as compared to fusion welding processes and the eco-friendliness is explained from several aspects. There is no use of shielding gas and fumes from coated electrode in FSW. No production of infra-red, ultra-violet ray or x-ray like laser or electron beam welding processes. In general, FSW technology is free from air, water, and soil pollution and therefore, is considered as a green technology. FSW is easily automated as compared to arc welding process where the uncertain factors related to arc stability, arc gap and responsive feedback system play significant role. To alleviate this probabilistic effect, the control system becomes complicated and expensive in arc welding process. Therefore, the possibility of automation provokes FSW as economically sound process as compared to conventional and advanced fusion welding processes.

FSW is significantly less energy intensive than competing technologies, while offers cost savings, and increases in productivity by sophisticated and automated system. The limitation of FSW is the inability to be used on-site and lack of development of this technology for relatively thick-section welding. With different grades of aluminum alloy, FSW is widely used in mainly aerospace, shipbuilding, automotive sector, and power generation sectors. Dawood *et al.* (2014) investigated the environmental impact in a comparative analysis mode between FSW and GMAW in joining of Al alloys. For similar range of weld joint strength, the power consumption has been reduced to one-fourth using FSW technology. Also GMAW creates higher heat affected zone (HAZ) than FSW process. GMAW releases large amount of greenhouse gases (CO - 2.7 ppm and CO₂ - 346 ppm) as opposed to 0.6 ppm and 211.6 ppm, respectively, in case of FSW. The microstructure of weld nugget consists of small grains as compared to solidified fusion zone which helps to predict higher tensile strength for FSW process (Anjaneya and Prasanna, 2013). Kumarana *et al.* (2011) analysed the eco-friendly aspect of friction welding during joining between tube and flat workpiece by comparing with GTAW process. A detail analysis of the material wastage, mass utilization, labor cost, consumable and power utilization were performed. It was concluded that the eco-friendly aspect for GTAW is hindered due to loss of alloying elements, high distortion, requirement of flux, use of filler wire and shielding gas, formation of defects like porosity and crack.

It is thus obvious that FSW has several accredited advantages over fusion welding processes. It has also limitation in several aspects, specifically for joining of high strength material and joining of dissimilar combination. The practical solution of these limitations drives towards the development of hybrid FSW process with optimum utilization of resources as well as to deliver the highest quality product. For example, the welding between steel and aluminum dissimilar combination by conventional FSW process insufficiently plasticized the steel at nearly melting temperature of aluminum. Mixing of these metallic materials may create porosities and other kind of welding defects. Moreover, high welding force and variable stress on the tool due to difference in hardness impairs tool wear and demands proper design of fixture, tool, and backing plate. The common solution of the problem is encountered in two different ways. The first one is to develop FSW tool made from very hard materials like tungsten carbide, silicon nitride, or PCBN with complex geometric shape. The second option is to explore different hybrid process where secondary energy sources are integrated with primary process. However, the objective parameters of hybrid process is to reduce the load on tool, reduction in tool wear i.e., enhanced tool life, alleviating faster weld speed, and minimizing the energy consumption.

Hybridization of FSW

The global warming enforces the development of eco-friendly manufacturing processes that have minimum impact on the environment and energy demand. FSW is one of the finest green manufacturing processes where environment impact is the minimum as compared to fusion welding processes. However, conventional FSW may not be feasible always or may not utilize optimum resources for high strength and high melting point material, and specifically for welding of dissimilar material where a wide difference in physical properties exists. In principle, hybridization of the FSW process holds the advantages of conventional FSW process but enhance the application towards the difficult-to-weld material within a frame of solid-state process. FSW is hybridized by introducing different kinds of secondary heat sources like arc, oxy-fuel, induction coil, and ultrasonic vibration etc. Use of induction coil and ultrasonic assisted FSW does not involve any greenhouse gas and maintain almost similar eco-friendliness like FSW. However, arc-assisted or laser-assisted or oxy-fuel assisted hybrid FSW creates environmental hazard to a lesser extent since the maximum temperature of the system is restricted to below the melting point temperature of the substrate material. The objective of hybridization is to enhance the product quality which is otherwise difficult to achieve using conventional FSW process alone. Hybrid FSW is an intermediate status quo between the limitation of FSW for relatively harder material, less tool wear and enhanced tool life, and conventional fusion welding processes. It is obvious that the product quality is enhanced in hybridization of FSW process by compromising the eco-friendliness with the application of external heat. Frictional heat and tool wear may not appropriate in case of classic FSW process to weld relatively harder material. Hence the efficient utilization of energy is compromised by adding other secondary heat sources. The loss of heat energy by

convection and radiation is high due to arc or oxy-fuel heat source otherwise FSW tool utilize frictional and deformation heat energy with minimum loss. However, HFSW may be more energy efficient than conventional FSW process because of the reduction of tool force with the application of auxiliary heat source.

Literature are rich in the development of HFSW processes mainly categorized as induction, ultrasonic, laser, plasma arc, gas tungsten arc, and oxy-acetylene assisted FSW processes (Sinclair *et al.*, 2010; Álvarez *et al.*, 2014; Palm, 2004; Bang *et al.*, 2010; Yaduwanshi *et al.*, 2018, 2016, 2014; Lotfi and Nourouzi, 2014; Choi *et al.*, 2011; Lai *et al.*, 2014; Shi *et al.*, 2015; Strass *et al.*, 2014a,b; Liu *et al.*, 2015a,b; Liu and Wu, 2013). Friction surfacing assisted HFSW is another variant of hybridization of the process. The secondary heat source plays dual role in hybridization of FSW process. One is the reduction of the flow stress difference and other is the partial heat treatment of the welded joint. HFSW applied for light weight dissimilar combination of materials mainly reduce the self-weight in aerospace and automobile structure. In effect, the light weight reduces the fuel efficiency and hybrid process moderate the environmental pollution. In this aspect, the light weight joint between Al and Mg alloys is mostly used in industry. However, the main obstacle of successful weld joint is the formation of brittle intermetallic layer at the interfaces. The harmful intermetallic phase is more easily controlled in hybridization of the FSW process as compared to conventional arc or laser welding processes. The offset of the secondary heat source towards harder material enhance material flow and the offset of FSW tool towards softer material control the brittle intermetallic components during joining of dissimilar combination of materials. A number of successful HFSW technologies have been developed during last decade having their own limitations in terms of application area, environmental friendliness, efficiency and economical aspect (Padhy *et al.*, 2016; Seif *et al.*, 2018; Bang *et al.*, 2013, 2012; Joo, 2013; Campanelli *et al.*, 2013; Merklein and Giera, 2008; Chang *et al.*, 2011; Ruilin *et al.*, 2014; Conrad, 2000; Pitschman *et al.*, 2010; Luo *et al.*, 2014; Long and Khanna, 2005; Álvarez *et al.*, 2014; Nguyen-Tran *et al.*, 2015; Siddiq and Sayed, 2012; Tarasov *et al.*, 2017; Benfer *et al.*, 2017; Park *et al.*, 2008; Strass *et al.*, 2014a,b).

Seif *et al.* (2018) developed oxy acetylene flame assisted HFSW process for TRIP steel. Although oxy-fuel creates CO and CO₂, the welded joint achieves several technological benefits. The presence of martensite and bainite phases in the welded joint enhances the hardness. Welding of high carbon steel by assisted with gas torch effectively influences on the cooling rate during welding (Choi *et al.*, 2011). Reduced cooling rate decreases the volume fraction of martensitic phase and hence the weld joint strength and elongation are enhanced as compared to conventional FSW process. Lotfi and Nourouzi (2014) investigated the influence of preheating by using a gas heating system on aluminum alloy. It was observed that the formation of defects is reduced noticeably with extra heat supplied by auxiliary gas heating system. The weld joint efficiency enhanced remarkably not exceeding than 83%. However, burning of the fuel to the on-site process development is not a feasible solution for the development of green technology. Moreover, localization of the heat concentration is not up to the mark by a gas heating system since heat energy distributes over a large area to produce relatively wide HAZ. The arc based secondary heat source is better option to create more concentrated heat energy.

HFSW of aluminum alloy and titanium alloy was successfully achieved using GTAW process that preheats the sample towards Ti alloy (Bang *et al.*, 2013). Offsetting heat source towards Ti-side reduces the flow stress difference, and equilibrates the temperature distribution. The significant improvement of ultimate tensile strength and elongation were achieved by HFSW as compared to conventional FSW process. During joining between aluminum alloy and stainless steel, the elongation of the joint increases significantly due to ease of material flow and partial annealing effect when the external heat offsets towards stainless steel (Bang *et al.*, 2012). Joo (2013) applied gas tungsten arc as preheating source on steel plate during joining with magnesium alloy. The tensile strength achieved by the hybrid process was more than that of conventional FSW process which was ~ 91% of the base material. Similarly, the gas tungsten arc was placed an offset distance towards mild steel. It was reported that the tensile strength was enhanced significantly because there was no adverse effect of brittle intermetallic compounds FeAl and FeAl₃.

Plasma arc-based HFSW has been developed to weld between copper and aluminum (Yaduwanshi *et al.*, 2018, 2016, 2014). High intensity plasma arc supply the required heat energy to recover the lost heat due to high thermal conductivity of copper and cylindrical tool offsetting towards aluminum side suppresses the formation of intermetallic components in the weld joint. Fig. 4 depicts the schematic diagram of plasma assisted HFSW process. PAW produces more constricted arc than GTA welding, hence,

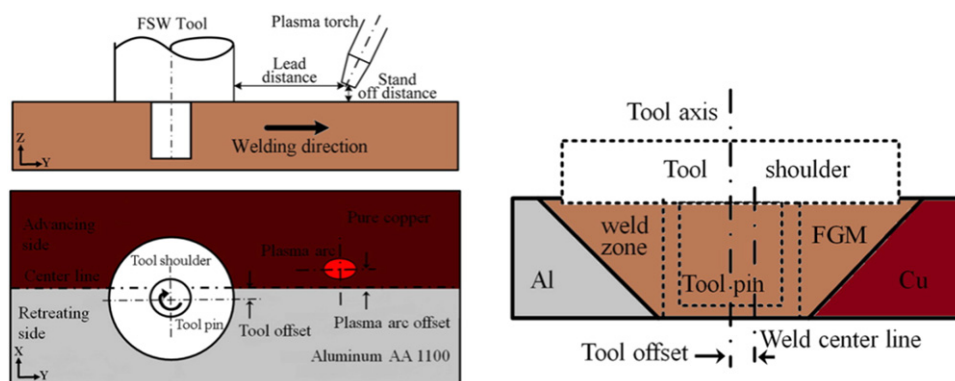


Fig. 4 Schematic of plasma assisted friction stir welding process. Yaduwanshi, D., Bag, S., Pal, S., 2016. Numerical modeling and experimental investigation on plasma-assisted hybrid friction stir welding of dissimilar materials. *Materials and Design* 92, 166–183.

suitable for joining high conductive material. The efficiency of plasma arc-based HFSW when joining high conductive material is comparatively low because of high heat energy loss to the backing plate. The laser source creates high power density as compared to arc or oxy-fuel based heat source and confined into a small focused area. However, there may be the chances of melting with laser until it is not controlled in the heating mode only.

The laser is more sophisticated heat source in hybridization of FSW process. The emission of hazardous gases to the environment is limited as compared to arc or oxy-fuel based system. In laser assisted HFSW of aluminum alloy, apart from enhanced micro hardness and elongations, the longitudinal residual stress in the weld zone was reduced. Moreover, pre-treatment by laser significantly reduces the transverse residual stress (Campanelli *et al.*, 2013). Merklein and Giera (2008) investigated the preheating effect on steel by a diode laser spot when joining with aluminum. The placement of laser on steel enhanced the energy absorption (> 55%) and the consequence effect was the reduction of intermetallic compounds. Chang *et al.* (2011) developed laser based HFSW process by introducing the third metal as Ni during welding between Al and Mg. This technique helps to remove brittle intermetallic phases and promotes more amounts of ductile phases at the weld interface. The joint strength improves considerably with hybrid process because of Ni-based intermetallic phases which is less brittle than intermetallic formed by Al-Mg.

One of the anticipated objectives of hybridization of the FSW process is to eliminate the oxide alignments, formation of root defect and lack of proper penetration due to deficiency of proper viscoplastic material flow (Santos *et al.*, 2014a; Ruilin *et al.*, 2014). Heat generation by Joule effect improves the material flow. However, the use of external electrical energy is dissipated into the conventional FSW systems by two different ways. The first one is to create the resistive heating where the tool becomes intricate part of the system and delivers high intensity current to a localized area (Santos *et al.*, 2014b). The secondary is to pass the electric current to an external system or to utilize induction coil aided to the conventional FSW system. Fig. 5 depicts the development of electrical energy assisted hybrid FSW processes. It mainly accounts how the electrical circuit is embedded with the conventional FSW system (Padhy *et al.*, 2015). There are several advantages of using electric current in traditional FSW process. The electric current influences the solid-state transformation by the formation of intermetallic compound, precipitation, and recovery, recrystallization and grain growth (Pitschman *et al.*, 2010). Electricity could affect the material structure other than resistive heating. The deformation behaviour due to application of electric current eliminates the springback effect and reduces tool wear (Pitschman *et al.*, 2010).

Santos *et al.* (2014b) indicated that the resistance heating by a conducting medium through small part of the FSW tool provides good stirring of the material during welding of aluminum alloy. The tool may also equip with several other features like gas shielding, cooling channel, and insulation (Luo *et al.*, 2014). This tool is used in more beneficial way for joining similar and dissimilar materials aided by resistance heating. Even the whole tool of FSW acts as an electrode through which the current flow and this hybrid system has been used to join steel and titanium (Long and Khanna, 2005). This hybrid system helps to reduce the flow stress resistance in through thickness direction because of large area involvement by the FSW tool. However, Joule heating may create electro-plastic effect i.e., soften the material during plastic deformation without substantial increment of temperature. This effect is significant for metals subjected to either high density pulse of extremely short duration or smaller continuous current. However, FSW tool equipped with so many features create the design of the tool more complex and often compromised with tool strength due to resistance heating and electro-plastic effect that leads to considerable tool wear. Liu *et al.* (2015a) developed an electrically assisted FSW system which creates the Joule effect externally where the conductive electrode is attached with the tool. It is advantageous since the tool is not involved in the electrical circuit as well there is no restriction on geometric size to be welded. This hybrid FSW is used to join dissimilar combination of aluminum alloy and TRIP steel. Along with Joule heating, the electro-plastic effect reduces the axial force and confines the crack initiation within the intermetallic layer at the weld interface. The electro-plastic effect becomes more prominent at low rotating speed of tool and at very low tool offset.

Sinclair *et al.* (2010) developed the hybrid FSW system by placing the induction coil under the aluminum sample insulated from the welding machine. The induction heating results in a noteworthy reduction (43%) of the axial force and the flow of the material has been improved over a relatively large area to produce stronger weld joint. Álvarez *et al.* (2014) applied induction heating for welding of commercial cast super duplex stainless steel. With the preheating technique, the welding speed is enhanced to twice when compared with conventional FSW process. The enhanced strength and hardness of the joint is attributed to the refinement of grain size by dynamic recrystallization. The fine-grained banded structure in the stir zone consists of ferrite and austenite. In general, electrically assisted manufacturing processes are aided by the theory of electro-plasticity (Nguyen-Tran *et al.*, 2015). This technique is energy efficient, cleaner with reduced processing time as compared to other auxiliary energy sources. However, the fundamental study on the application of electro-plasticity pertinent to the development of hybrid FSW processes is lacking in esteemed literature. Moreover, the controlling of localized heating by induction coil is more challenging due to placement of coil in appropriate position. It is limited by the geometric shape and size of the workpiece. In mechanically assisted FSW, the ultrasonic energy is more appropriate to affect directly the micro scale behaviour by localization of energy as compared to induction heating.

Ultrasonic impact is normally used in welded structure to relieve the residual stress where a compressive stress is produced on the subsurface layer. With similar principle, high frequency ultrasonic energy decreases the yield strength of the material over a much localized area having similar effect of thermal softening. A rough estimation shows that the ratio of required ultrasonic energy to thermal energy to produce same amount of softening is $\sim 10^7$ (Siddiq and Sayed, 2012). The ultrasonic energy is mainly absorbed in localized dislocation and surface defects of crystal structure whereas the thermal energy spreads almost homogeneously over a large area. Acoustic softening effects are responsible for the reduction of yield strength which depends on the intensity, but independent of frequency. However, the effective transmission of ultrasonic energy in a hybrid FSW system depends

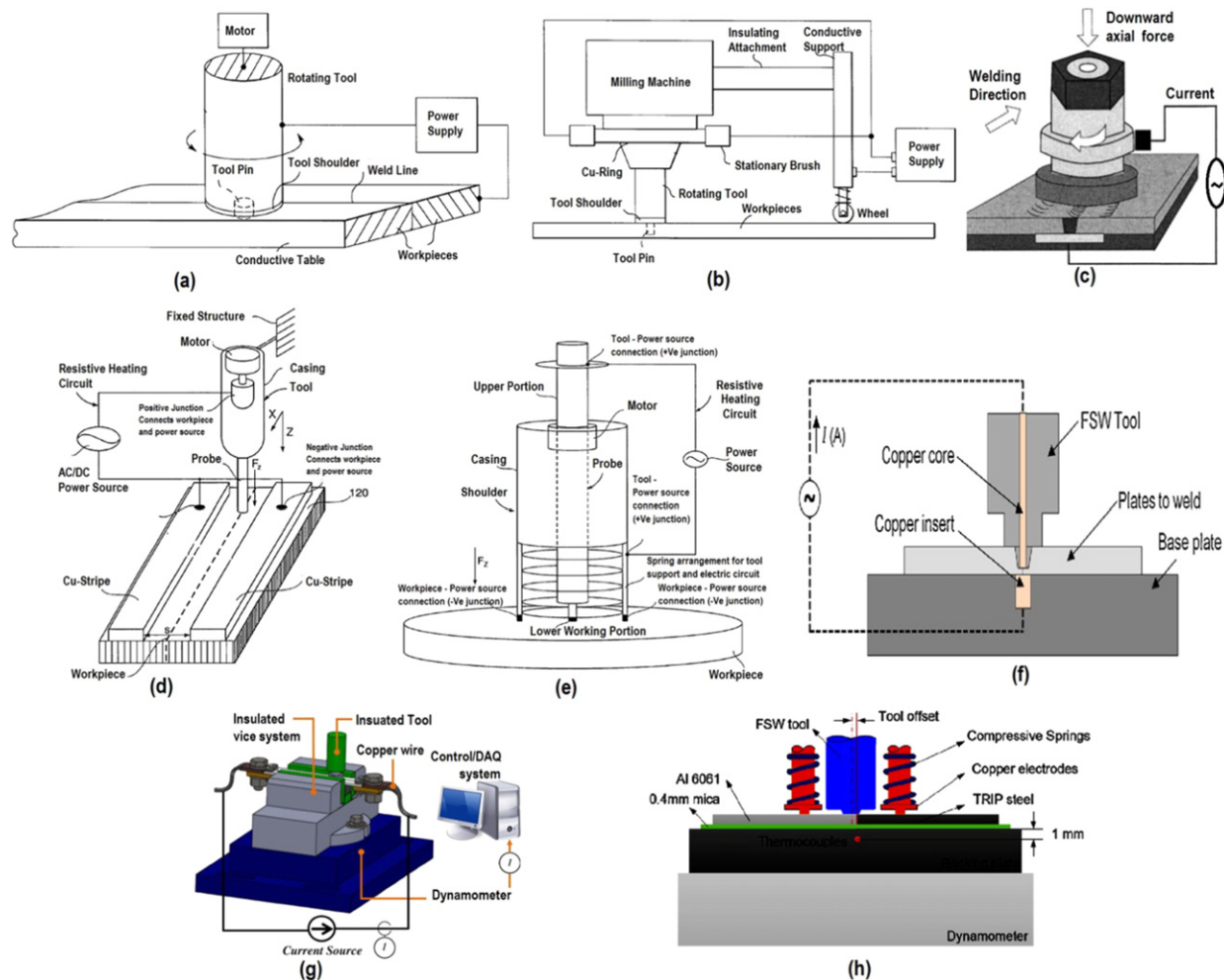


Fig. 5 Schematic of electric energy assisted hybrid FSW processes. Reproduced from Padhy, G.K., Wu, C.S., Gao, S., 2015. Auxiliary energy assisted friction stir welding – Status review. *Science and Technology of Welding and Joining* 20, 631–649. Spinella, D.J., Streicher E.T., Kastelic R., 1998. Resistance heated stir welding. US patent no. 5829 664, published 3 November 1998. Long, X., Khanna, S.K., 2005. Modeling of electrically enhanced friction stir welding process using finite element method. *Science and Technology of Welding and Joining* 10, 482–487. Ferrando, W.A. *et al.*, 2008. The concept of electrically assisted friction stir welding (EAFSW) and application to the processing of various metals. Report no. NSWCCD-61-TR-2008/13. West Bethesda, Maryland, USA: Naval Surface Warfare Center Carderock Division. Ferrando, W.A., 2012. Electrically assisted friction stir welding. The United States of America as represented by the Secretary of the Navy, Washington, DC, USA, US patent no. 8 164 021 B1, published 21 April. Luo, J., Li, F., Chen, W., 2013. Experimental researches on resistance heat aided friction stir welding of Mg alloy. *Quarterly Journal of the Japan Welding Society* 31, 65s–68s. Luo, J., Chen, W., Fu, G., 2014. Hybrid-heat effects on electrical-current aided friction stir welding of steel, and Al and Mg alloys. *Journal of Materials Processing Technology* 214, 3002–3012. Santos, T.G., Miranda, R. M., Vilaca, P., 2014a. Friction stir welding assisted by electrical joule effect to overcome lack of penetration in aluminium alloys. *Key Engineering Materials* 611, 763–772. Santos, T.G., Miranda, R.M., Vilaca, P., 2014b. Friction stir welding assisted by electrical Joule effect. *Journal of Materials Processing Technology* 214, 2127–2133. Pitschman, M., Dolecki, J.W., Johns, G.W., Zhou, J., Roth, J.T., 2010. Application of electric current in friction stir welding. In: *Proceedings of the International Manufacturing Science and Engineering Conference*, pp.185–189. Pennsylvania, USA: ASME. Potluri, H., Jones, J.J., Mears, L., 2013. Comparison of electrically assisted and conventional friction stir welding processes by feed force and torque. In: *Proceedings of the ASME 2013 International Manufacturing Science and Engineering Conference MSEC2013*, pp. V001T01A055–V001T01A055. Madison, WI, USA: ASME. Liu, X., Lan, S., Ni, J., 2015a. Electrically assisted friction stir welding for joining Al 6061 to TRIP780 steel. *Journal of Materials Processing Technology* 219, 112–123.

on whether the unit is attached to the tool or to the workpiece (Padhy *et al.*, 2015). Fig. 6 depicts different configuration of ultrasonic assisted hybrid FSW processes (Padhy *et al.*, 2015). Directly transfer of ultrasonic energy to the tool may affect the material properties due to acoustic effects. The positioning of the sonotrode on the workpiece is also an important factor for effective utilization of ultrasonic energy. The inclined sonotrode's axis does not ensure full utilization of energy and only normal component of oscillation transmits to the workpiece. Moreover, there may be loss of energy due to friction and deformation when there is a lack of stiff contact between sonotrode and the workpiece (Padhy *et al.*, 2016). The intense localized deformation and heating is favoured by high-frequency and low amplitude ultrasonic vibrations. Here the heating works in two folds i.e., softening of localized material and reduction in work hardening effect of sonotrode tip. Tarasov *et al.* (2017) followed different approach

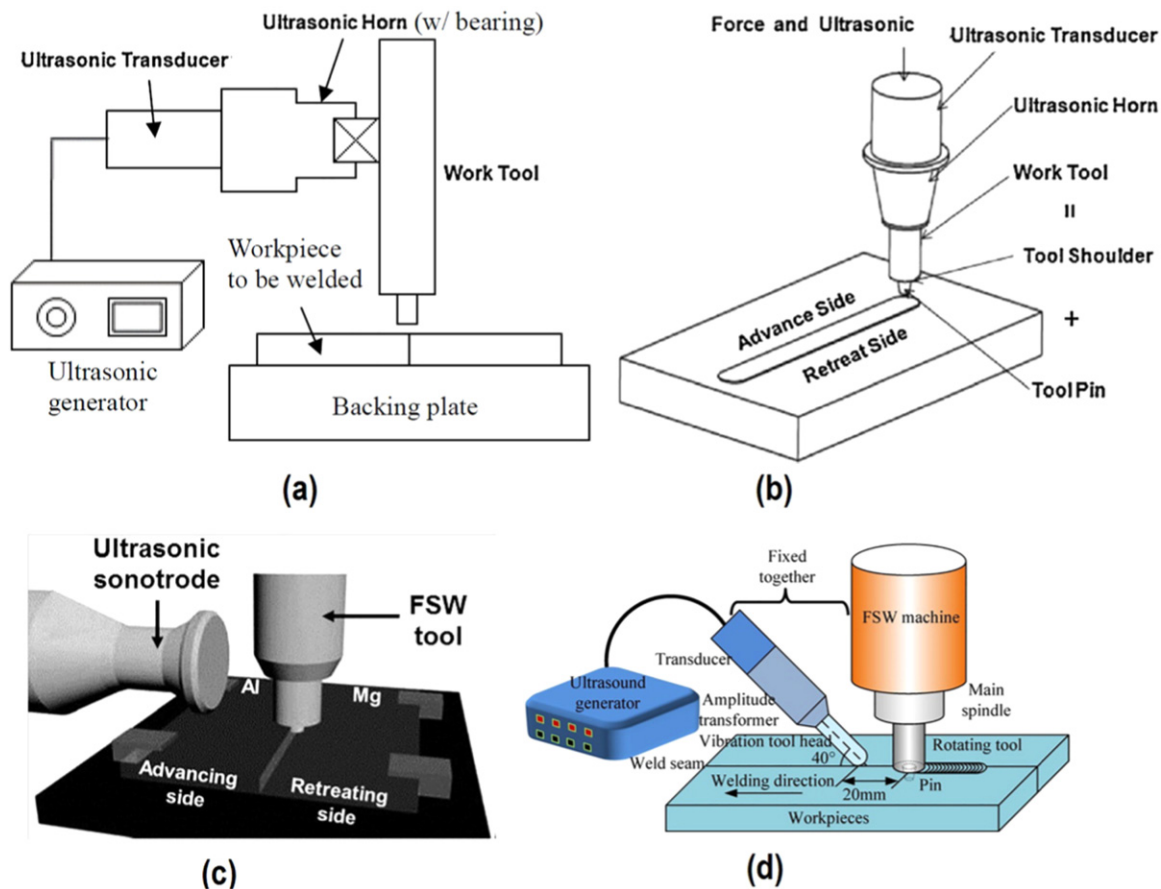


Fig. 6 Schematic of ultrasonic assisted FSW processes. Reproduced from Padhy, G.K., Wu, C.S., Gao, S., 2015. Auxiliary energy assisted friction stir welding – Status review. *Science and Technology of Welding and Joining* 20, 631–649. Park, K., Kim B., Ni, J., 2007. Design and analysis of ultrasonic assisted friction stir welding. In: *Proceedings of the ASME International Mechanical Engineering Congress and Exposition*. Seattle, WA, USA, November, Paper IMECE2007-44007. Strass, B., Wagner G., Eifler, D., 2014. Realization of Al/Mg-hybrid joints by ultrasound supported friction stir welding. *Material Science Forum* 783–786, 1814–1819. Strass, B., Wagner, G., Conrad, C., *et al.*, 2014. Realization of Al/Mg-hybrid-joints by ultrasound supported friction stir welding-mechanical properties, microstructure and corrosion behavior. *Advanced Materials Research* 966, 521–535. Lai, R.L., He, D.Q., Liu, L., Ye, S.Y., Yang, K., 2014. A study of the temperature field during ultrasonic-assisted friction-stir welding. *International Journal of Advanced Manufacturing Technology* 73, 321–327. Shi, L., Wu, C.S., Liu, X.C., 2015. Modeling the effects of ultrasonic vibration on friction stir welding. *Journal of Materials Processing Technology* 222, 91–102.

where the ultrasonic energy is directly transmitted to the workpiece through backing plate. This technology ensures homogeneous effect of ultrasonic energy throughout the workpiece.

In general, ultrasonic assisted FSW impacts more on microstructural phenomena. It facilitates the intermetallic precipitates, reduces the grain size by recrystallization, and enhances precipitation of coherent metastable phases. This process eliminates the brittle intermetallic Al_3Mg_2 and increases the weld joint strength between Al and Mg (Tarasov *et al.*, 2017; Benfer *et al.*, 2017; Park *et al.*, 2008). Localization of ultrasonic energy also facilitates the strain induced dissolution of coarse Al-Cu-Fe-Mn particles (Siddiq and Sayed, 2012). Liu *et al.* (2015c) showed that ultrasonic energy influences on strain or strain rate induced deformation and material flow behaviour that impact on the metallurgical characterization of the welded joint. Benfer *et al.* (2017) showed that the corrosion properties of welded joint have been improved with the introduction of ultrasonic assisted hybrid FSW process between aluminum and steel. Liu *et al.* (2015b) investigated the ultrasonic assisted FSW on aluminum alloy in butt joint configuration. The mechanical properties like joint strength and micro hardness, and welding speed has been improved. The fracture location has been shifted from nugget zone to HAZ or THAZ. Ruilin *et al.* (2014) indicates that the ultrasonic energy does not increase the temperature much at low welding speed whereas it is significant at higher welding speed. Strass *et al.* (2014a,b) showed that ultrasound smashes the brittle interlayer during welding between aluminum and magnesium and improves the joint strength up to 30% as compared to conventional FSW process. Fusion welding of heat-treatable Al-Cu-Li-Mg-V alloy has the difficulty of producing both voids and hot cracks. Using FSW for this material, the risk of hot cracking aided by high tensile stress in the HAZ is reduced. However, the presence of in-homogeneously distributed residual stress is generally removed by laser and shot peening. Using ultrasonic assisted FSW improves the weld joint strength for such a complex alloy (Tarasov *et al.*, 2017). The process of friction surfacing assisted hybrid FSW technology has been developed mainly to avoid the pin abrasion for joining of

dissimilar Ti/Al joints (Huang *et al.*, 2017). The FSW tool is designed with enlarged head and concave end-face to facilitate the widening of lap width. It promotes the material flow mixing over a large area. The hybridization of FSW by integrating another solid state based processing technology open some new window for improving the joint strength as well as promotes greener or cleaner technology.

Conclusions and Future Scope

Literature indicates that the hybridization of FSW process has been developed at aiming some practical problems faced by either FSW or fusion welding processes. However, the development of hybrid FSW processes has the potential to explore as a futuristic eco-friendly process. The current status indicates that the economical and sustainability aspect is less focused for hybrid FSW process since very few literatures has come up to this particular subject. However, there is potentiality to improve this process in the forefront of clean technology or green technology. The present article describes the technological advancement of hybrid FSW processes first and then the economic benefit arises due to hybridization of FSW process. Although many hybridization of FSW process have been developed, all processes are not in the forefront of green technology. The developments occur as a cause of current industrial needs rather to the consequence effect on the environment. The developments of hot gas stream, gas/arc, laser assisted FSW is to-some-extent crude process where the effects on environment is not negligible and may not economic always since there may be considerable loss of energy from the secondary heat sources. Electrically assisted and ultrasound assisted FSW fulfilled certain industrial need and free from any kind of direct impact on environment. However, all these developments are not commercially successful for welding on a large scale due to capital and maintenance costs as well as difficulty in up scaling of the process (Potluri *et al.*, 2013). In that sense, the electrically assisted FSW has less geometric constraint to use in a large scale welding process. It is more economic process when the direct current passes through the workpiece. There is considerably decrease in feed force (average $\sim 59\%$) and the initial torque required by the tool as compared to conventional FSW process.

The auxiliary energy assisted FSW mainly modify the deformation behaviour of materials measured by internal parameters like strain, strain rate, and temperature. The flow stress behaviour, macro, and micro structural characteristics mainly affect the weld joint hardness, strength properties, and elongation. The fundamental work on the interaction of electric current with the engineering materials for the development of hybrid FSW process is lacking in the esteemed literature. These studies are expected to optimize the process time and manufacturing cost in hybridization of FSW process. The development of hybrid FSW considering electro-plasticity effect has still not been fully developed and there is a possibility for further development using fundamental theory. A sustainable model seems lacking in HFSW processes. Although very limited literature is found corresponding to the eco-friendly aspect of HFSW processes, there is a huge scope to establish HFSW as a promising technology that balance between technological challenges and environmental impact.

See also: Sustainable Cutting Fluids: Thermal, Rheological, Biodegradation, Anti-Corrosion, Storage Stability Studies and its Machining Performance

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Eco Friendly Flocculants: Synthesis, Characterization and Applications

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Introduction

The treatment of waste water and industrial effluent may be carried out using either with inorganic or organic coagulants and flocculants. For coagulation and flocculation, although the basic function remains the same, subtle distinction is made between these two terms. The coagulation means the destabilization of a stabilized system (e.g., colloidal system) but flocculation means the floc formation of the destabilized colloidal system, where the addition of flocculant to the destabilized colloidal system results in flocculation. The flocculants may be either inorganic or organic type. Among the inorganic flocculants, the multivalent metallic compounds like aluminium and iron salts are generally used. The organic polymeric flocculants are preferred due their ease in handling, low dosage requirements, less sensitivity to system pH, existence of large cohesive forces between the flocs and the ease in synthesizing the flocculants. Polysaccharides such as starch, amylose, amylopectin, guar gum, xanthan gum and carboxymethyl cellulose have been used for as long as natural flocculants. However, they are less effective flocculating agents when compared with synthetic flocculants. Polyacrylamides have also been used for long some time as synthetic flocculants. Although their flocculation efficiencies are higher than the natural flocculants, these synthetic polyacrylamide flocculants are easily amenable to shear degradation even at low ppm concentrations. Whereas, polysaccharides are fairly shear stable but are not very efficient flocculants. Their aqueous solutions are also subjected to rapid biodegradation. It has been observed that by grafting polyacrylamide branches on the backbone of polysaccharide molecule, efficient flocculants with biodegradable resistant as well as shear resistant properties could be developed.

Synthesis of Graft Copolymers

Materials and Methods

The following materials have been used for the synthesis of the graft copolymerization experiments: (i) Soluble potato starch (GR grade) Loba Chemie, India; (ii) amylose from corn (Practical Grade), Sigma Chemicals Co., USA; (iii) acrylamide (GR grade), Merck-Schuchardt, Germany; (iv) ceric ammonium nitrate (Reagent grade), Loba Chemie, India; (v) nitric acid (Analar grade), BDH, India; (vi) acetone (Analar grade), BDH, India; (vii) Magnafloc-1011, Allied Colloids, UK.

Synthesis of Graft Copolymers

The starch solution was prepared in deionised double distilled water at 80°C and then cooled to room temperature. Subsequently, the grafting reactions were performed using ceric ammonium ion initiated redox polymerization technique and scaled up as mentioned elsewhere (Ungeheuer *et al.*, 1989). For amylose grafted copolymers, only the laboratory scale experiments were carried out for 3, 5 and 7 h using the same procedure as above.

The details of the graft copolymers are given in Table 1.

For each set of reactions 1 g of starch/amylose was taken. The acrylamide and catalyst concentrations in the reaction mixture were 0.14 and 0.03×10^3 moles respectively.

SAM-L-I: Starch grafted polyacrylamide (Laboratory-I)

SAM-L-II: Starch grafted polyacrylamide (Scale up-II)

AML-AM-L-3: Amylose grafted polyacrylamide (Laboratory, 3 h.)

AML-AM-L-5: Amylose grafted polyacrylamide (Laboratory, 5 h.)

AML-AM-L-7: Amylose grafted polyacrylamide (Laboratory, 7 h.)

Table 1 Details of the graft copolymers

Graft Copolymers	Yield %	$[\eta]$ at $30 \pm 0.1^\circ\text{C}$	Number average mol.wt. $M_n \times 10^6$	Weight average mol.wt. $M_w \times 10^6$
SAM-L-I	85.70	660	1.10	1.88
SAM-L-II	89.71	820	1.52	2.46
AML-AM-L-3	58.93	700	1.20	2.02
AML-AM-L-5	75.20	720	1.25	2.09
AML-AM-L-7	74.45	710	1.22	2.06

Characterization of the Synthesised Flocculants

The intrinsic viscosities $[\eta]$ at $30 \pm 0.1^\circ\text{C}$ of the graft copolymers have been evaluated as per standard procedures and are given in **Table 1**. From the intrinsic viscosity values, the approximate molecular weights of the grafted products have been calculated using the following equations (Mendelson, 1969):

$$[\eta] = 6.8 \times 10^{-4} (\text{Mn}^-)^{0.66} \quad (1)$$

$$[\eta] = 6.31 \times 10^{-5} (\text{Mn}^-)^{0.80} \quad (2)$$

The above relationships have been used for evaluating the molecular weight of the graft copolymers of polyacrylamide (Erciyes *et al.*, 1992). The results obtained are given in **Table 1**.

Elemental Analysis

The results obtained from the elemental analysis have been given in **Table 2**.

It has been found that out of the five synthesised copolymers, SAM-S-II and AML-AM-I-5 are having the higher percentage of elemental nitrogen in their molecules. The increased percentage in nitrogen content indicates higher grafting efficiency and higher yield of the synthesised graft copolymer. McCormick and Lin (1981) also found the similar results while synthesizing dextran-grafted acrylonitriles by Ce(IV)/HNO₃ induced initiation method. They observed that when the nitrogen percentages were high in the grafted products, the intrinsic viscosities as well as the molecular weights were also high.

Scanning Electron Microscopy

Scanning electron micrographs for the monomers and the graft copolymers are shown in **Figs. 1–8**.

It is clearly found that in the graft copolymers of starch, granular structure of starch and the polycrystalline structure of acrylamide are absent in both laboratory scale and scale up products. For both starch and amylase grafted products, substantial amount of grafting is noticed for all the grafted products. The above phenomenon supports the grafting of acrylamide onto starch/ amylase. Similar results were also obtained by Yao and Tang (1992) during characterization of starch-g-poly (acrylamide-co-sodium allylsulfonate) synthesised by Ce (IV) method.

Thermal Analysis

To find the effect of grafting on thermal stability and various transition in polymers, thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out for starch, amylose and their grafted products.

During TGA, the change in weight of a sample is measured as a function of temperature while the sample is subjected to a controlled heating programme. On the other hand, DSC is the process whereby the energy change is measured as a function of temperature during the controlled heating programme of the sample. Thus, TGA measures the loss in weight and DSC gives the information about absorption or evolution of heat during the reaction.

Thermal analyses were carried out using STA 625 STANTON REDCROFT thermal analyzer. The sample was varied from 4.5 to 5.5 mg. The sample was heated at the rate of 10°C per minute under nitrogen using Al₂O₃ as reference from 0° to 600°C . Initial and final decomposition temperatures (IDT and FDT) were recorded along with various stages of decomposition. The results are presented in **Table 3**. The loss of weight in the region up to 100°C depicts minor endothermic reactions due to the loss of moisture contents (5%–11%).

For starch, the gelation temperature is found to be 65°C followed by strong endotherms at around 280°C . For SAM-I-1, the gelation temperature is noticed at 68°C and the initial decomposition starts at 230°C and final decomposition takes place at around 421°C . In case of SAM-S-II initial melting or fusion takes place 228°C and final decomposition takes place at 442°C .

For amylose, after a gelation temperature of 66°C , the initial decomposition takes place at 264°C and the final decomposition temperature at 360°C . For amylose grafted products, the initial decomposition temperatures are found to be 265°C for AML-AM-I-3, 320°C for AML-I-5 and AML-I-7 products. The final decomposition temperatures for AML-AM-I-3, and AML-I-5 and AML-I-7 were found to be 410°C , 422°C and 425°C respectively.

Table 2 Results of Elemental Analysis

Materials	N(wt%)	C(wt%)	H(wt%)
SAM-I-I	14.5961	42.5644	6.9940
SAM-I-II	15.0278	42.0223	7.2146
AML-AM-I-3	14.5087	42.3729	7.4273
AML-AM-I-5	15.0863	42.5099	7.1554
AML-AM-I-7	14.7809	42.4432	6.8857
Acrylamide	19.6303	50.2129	7.2206
Starch	—	44.0000	6.1700

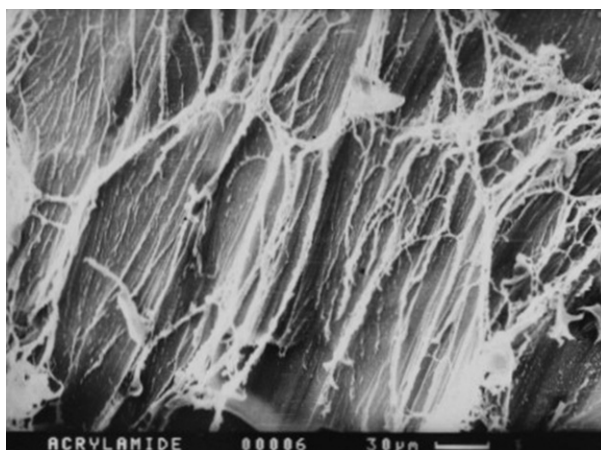


Fig. 1 SEM of acrylamide.

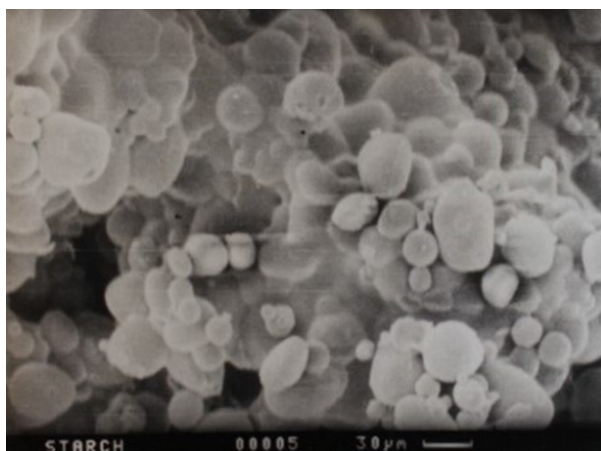


Fig. 2 SEM of starch.

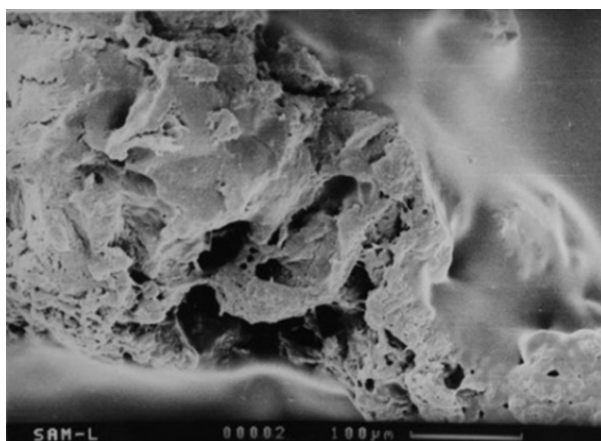


Fig. 3 SEM of SAM-L-I.

It has been observed that the initial decomposition temperature for amylose and their graft copolymers are higher than that of starch and starch graft copolymers. Severe restrictions of amylose chain motion are believed to involve thermally stable (at temperatures $< 100^{\circ}\text{C}$) junction zones with chain segments of degree of polymerization ~ 50 , which support the thermal stabilities of amylose and its graft copolymers at higher temperatures.

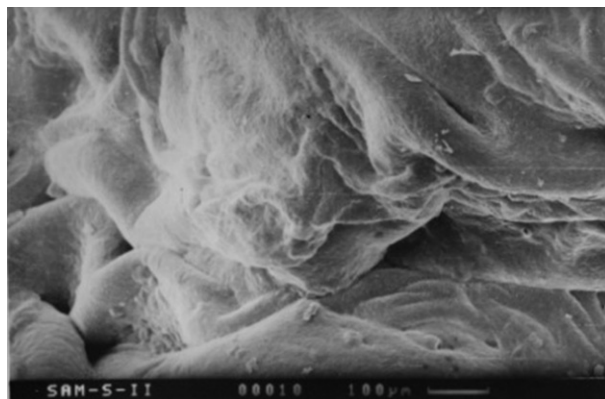


Fig. 4 SEM of SAM-S-II.

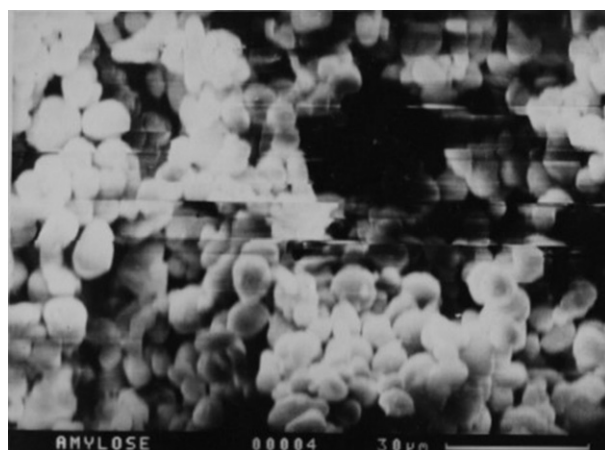


Fig. 5 SEM of Amylose.

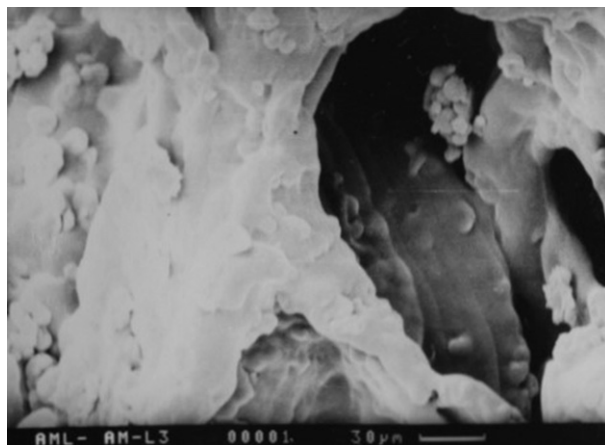


Fig. 6 SEM of AML-AM-L3.

Investigation of the Flocculation Efficiency of the Graft Copolymers

To investigate the flocculation efficiency, screening tests were carried out with bentonite clay-water system. Detailed investigations were carried out to determine the efficiency of starch-g-polyacrylamide and amylase-g-polyacrylamide in comparison with commercial flocculating agents for industrial effluents and hematite slimes.

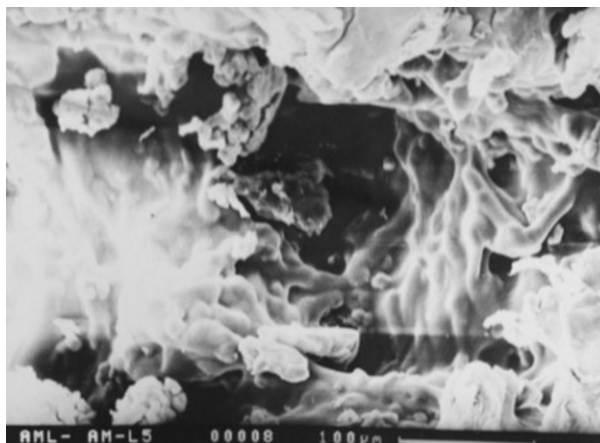


Fig. 7 SEM of AML-AM-L-5.

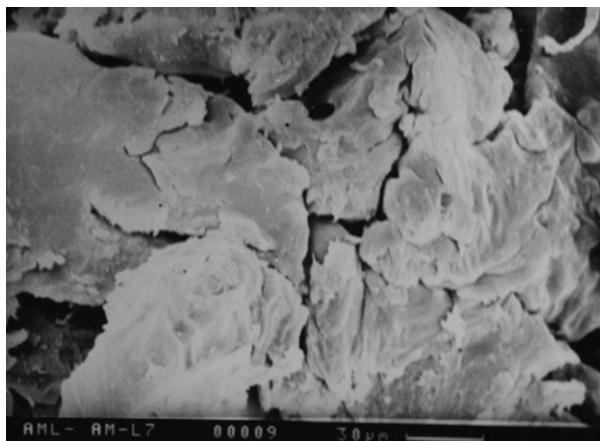


Fig. 8 SEM of AML-AM-L-7.

A laboratory jar test apparatus known as flocculator (MB-Flocculator; M. B. Instruments, Mumbai, India) was used for flocculation measurements. It consists of six stirrer blades connected to a motor, the speed of which can be controlled automatically with the help of a selector switch fitted on the panel board. The following sequence of operations was followed:

- (1) Four to six numbers of effluent samples were taken in beakers according to the respective plan of studies. Care was taken so that the stirrer blades were submerged in the effluents up to sufficient depth for proper stirring/mixing.
- (2) Rapid mixing at 60/75 rpm for 2 min was done immediately after the addition of the flocculant for complete mixing of the flocculant with the particles in the effluent.
- (3) Slow mixing at 20/25 rpm for 10–15 min was given for the floc formation at a low stirrer speed of the flocculator.
- (4) Settling time of 25–30 min was provided for the flocs to consolidate at the bottom of the beaker. This was done after removing the stirring shaft and taking out the beakers from the flocculator base plate. As the flocculation and the consolidation of the flocs were over, the supernatant liquid was used for turbidity measurements using a turbidity meter. For all systems, the flocculation efficiency and turbidity values were determined as per standard methods used by American Public Health Association (APHA, 1998).

Turbidity Measurements

A Systronics Digital Nephelo-Turbidity Meter 132 (Systronics, Ahmadabad, India) was used for the measurements of the turbidity of the supernatant liquids in standard Nephelometric Turbidity Units (NTU). The principle operation of this instrument is based on the Tyndall effect. Standard turbidity suspension was prepared prior to the standardization of the turbidity meter. The turbidity measurements were performed as follows.

The instrument was switched on and allowed for 10–15 min to warm up. The selector switch was placed in the appropriate range of NTU values (0–1, 10, 100 and 500 NTU). The ‘standardize’ control was set at maximum. The test tube (provided with the

Table 3 TGA of starch, amylose and their graft copolymers, Temperature range: RT-600°C

Sample	T_{H_2O} °C	IDT °C	T_{Final} °C	T_{Res} °C	H ₂ O content, wt%	Wt. of the sample, mg	Wt. of the residue, mg	Wt. Loss %
Starch	RT-100	280	366	563	6.0	5.1	0.85	83.40
SAM-L-I	RT-100	230	421	560	11.0	5.2	1.13	78.30
SAM-S-II	RT-100	228	442	550	5.0	5.4	0.67	87.56
Amylose	RT-100	264	360	555	10.3	5.8	1.00	82.76
AML-AM-L-3	RT-100	265	410	550	0.6	3.1	0.85	72.46
AML-AM-L-5	RT-100	320	422	568	5.0	2.8	0.48	82.70
AML-AM-L-7	RT-100	320	425	560	4.0	5.9	1.46	75.23

Source: RT: Room temperature; T_{H_2O} , °C: Temperature of elimination H₂O; IDT, °C: Initial decomposition temperature; T_{Final} , °C: Final decomposition temperature; T_{Res} , °C: Residue (%) at that temperature; SAM-L-I: Starch-g-Acrylamide-Lab I; SAM-S-II: Starch-g-Acrylamide-Scale up-I I; AML-AM-L-3: Amylose-g-Acrylamide Lab 3 h; AML-AM-L-5: Amylose-g-Acrylamide Lab 5 h; AML-AM-L-7: Amylose-g-Acrylamide Lab 7 h.

instrument) was filled with deionised double distilled water and was inserted into the cell holder. It was then covered with the light shield. The 'Set Zero' control was adjusted for the zero setting of the Digital Panel Meter (DPM) to read zero. The test tube was then removed and was replaced with another test tube containing standard solution. The test tube was aligned as per markings on cell holder. 'Standardize Control' was then adjusted such that the DPM indicates '100' in accordance with the standard solution of the appropriate range. The instrument was then ready for test samples. The test tube containing unknown sample was inserted in the cell holder and the reading on DPM was noted in NTU. For 0–500 NTU range, a cell riser was inserted prior to standardization and standardization was done in such a way that 500NTU solution reads '50' on the meter.

Flocculation of Clay Materials

Starch, amylase and their graft copolymers, and bentonite clay were used. To find out the flocculation efficiency of the graft copolymers, screening tests with bentonite clay-water solutions were carried out. For starch and amylase, 100 ppm concentration and for the starch/amylase graft copolymers, 10 ppm concentrations were used for the screening tests. During screening tests, only flocculant was used for floc formation and was observed visually. In each of the six beakers of 1 litre capacity, 8 gms of clay samples were dispersed in 800 ml of distilled water. Starch, amylase and their graft copolymers are used as flocculants. With care, the stirring shafts of the flocculator were lifted and beakers were placed beneath the respective stirrers. Then the stirring shafts were lowered and required amount of flocculant solution of specified concentration was added to respective beakers. With speed control switch, the stirrer speed was selected at 50 rpm for 2 min. The stirring was continued for another 15 min at 20 rpm and then flocs were allowed to settle for 25 min. It was observed that starch and amylose grafted polyacrylamides were more efficient than either starch or amylose. Later on, the flocculating efficiency of the starch-grafted and amylose-grafted was tested with hematite slimes and industrial effluents.

Flocculation Studies With Hematite and Industrial Effluents

In this study the flocculation experiments were carried out for hematite slimes of size 80%, – 9.66 micron. Starch, amylose and their graft copolymers along with a commercial flocculant Magnafloc-1011 were used as flocculants. The effect of varying pH, solid concentration of pulp and flocculant dose was studied.

The flocculation studies on the hematite slime sample were carried out using settling tests and filtration tests. The settling tests following the flocculation of the particles were carried out in a 100 ml graduated cylinder by recording the movement of the suspension-liquid interface as a function of time. The contents of the cylinder were inverted 20 times before being allowed to settle for observation of flocculation and sedimentation. The filtration subsequent to flocculation was studied by observing the amount of filtrate passing through the membrane as a function of time (Karmakar, 1994).

The above standard tests were performed while carrying out the flocculation studies using the above synthesised flocculants. The results of the above tests are given in Figs. 9 and 10.

Standard jar test methods (Karmakar, 1994; Gregory and Guibai, 1991) were followed to study the flocculation efficiency of AML-AM-L-5 (initial rate of mixing was 75 rpm) using a flocculator as mentioned above. Magnafloc-1011 was used as a flocculant for comparison. The supernatant turbidity values in Nephelometric turbidity units (NTU) were recorded as a function of time after a period of mixing and settling. The results are given in Fig. 11.

Fig. 9 shows the height of interface against time at normal pH(6.4) and at pH 5.0 for 10% pulp density of hematite fines, as described earlier, using AML-AM-L-5 along with amylose and Magnafloc-1011. A flocculant dose of 30 ppm was selected for comparison because settling rate is largely effective in this range (Karmakar and Singh, 1998). When the flocculation was carried out at pH10, no flocculation was observed using AML-AM-L-5 (Karmakar, 1994). Since Magnafloc-1101 is a linear chain high molecular weight polyacrylamide, a greater number of acrylamide groups are available in Magnafloc-1011 for flocculation.

Fig. 10 shows the variation of total volume of filtrate with time for various flocculants at normal pH (6.4), pH 5.0 and pH 10.0. The effectiveness of AML-AM-L-5 is compared with amylose and Magnafloc-1011. It is clearly indicated that the performance of

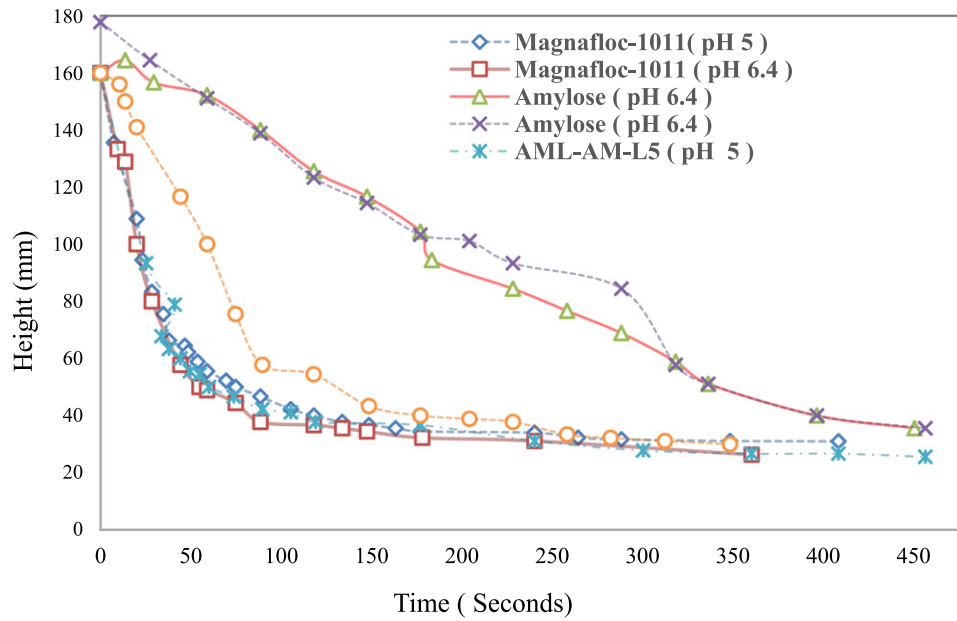


Fig. 9 Variation of the height of interface with time for various flocculants at 10% pulp density.

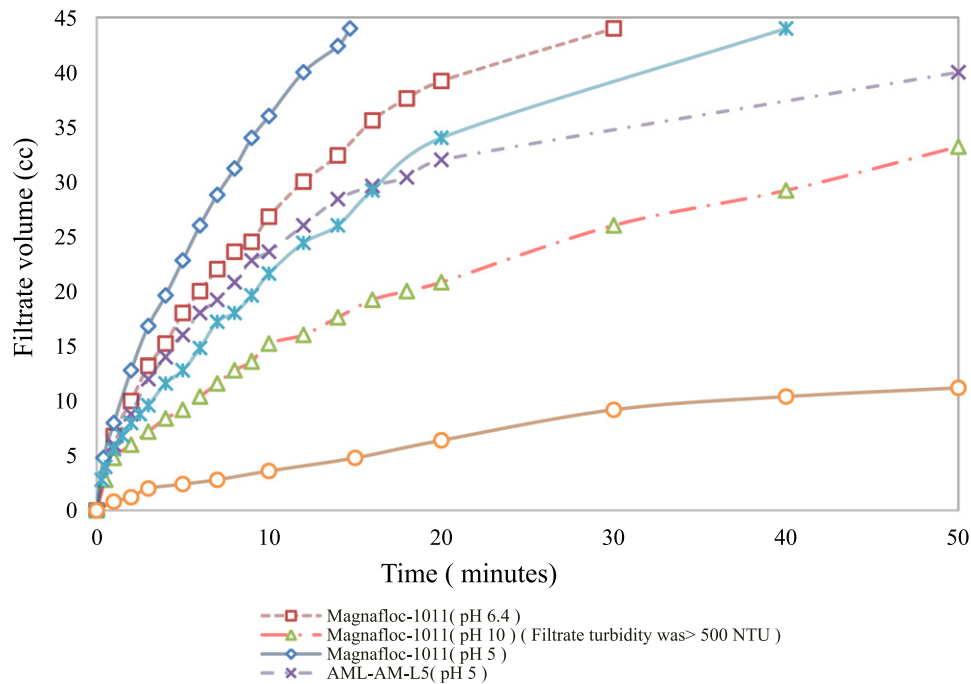


Fig. 10 Variation of total volume of filtrate for various flocculants at 10% pulp density.

AML-AM-L-5 is better than that of amylose. However, the performance is not at par with that of Magnafloc-1011 at normal pH (6.4) and at pH 5.0. It is also observed that at pH 10.0, AML-AM-L-5 is not a very effective flocculant for the above system (Karmakar, 1994).

Effect of Shear Rate

The initial turbidity values of the slimes without addition of any flocculant at pH 6.4, pH 5.0 and pH 10.0 were found to be 64 NTU, 52 NTU and 512 NTU respectively (Fig. 11). However, after the initial mixing with a specified amount of AML-AM-L-5 at 75

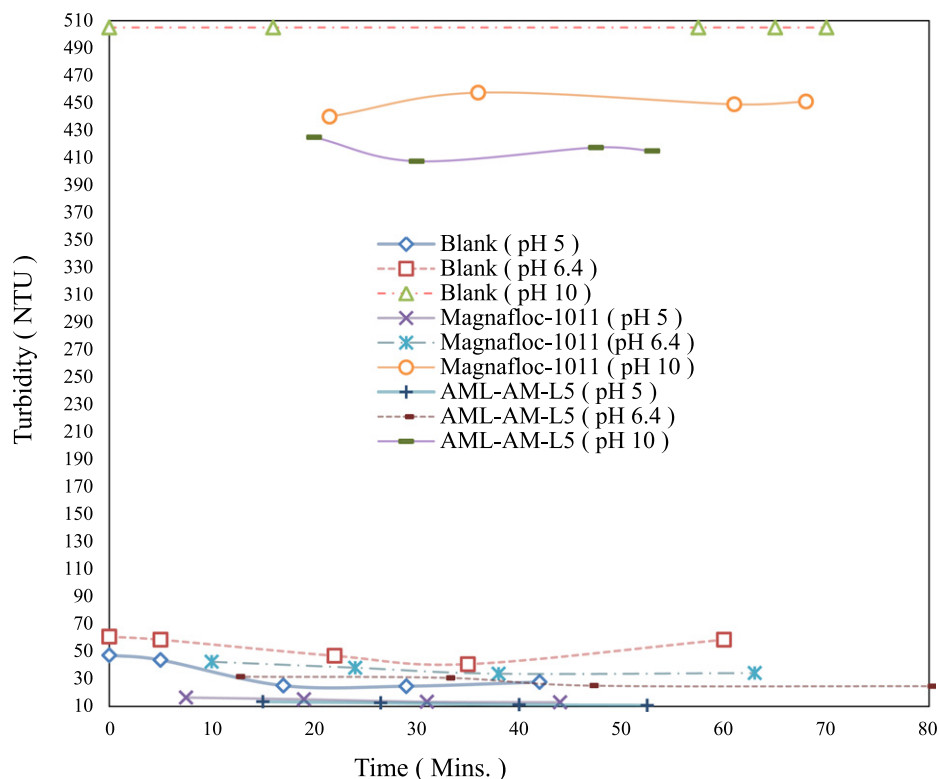


Fig. 11 Variation of the supernatant turbidity with time for various flocculants at 10% pulp density.

rev min⁻¹ during the flocculation by standard jar test method and then settling, the turbidity values reached the lowest points for all pH values while using AML-AM-L-5 as flocculant. This is due to the effect of the shear degradation resistance of the amylose-grafted copolymer. Magnafloc-1011, being a linear chain polyacrylamide, is not so effective at high shear rates. In the acidic pH range the turbidity becomes the lowest.

In grafted amylose, the approachability of polyacrylamide branches to contaminants increases, making it an effective flocculant (Singh, 1995). It appears that grafted amylose is more shear stable than Magnafloc-1011 due to the multiplicity of polyacrylamide branches on it. The pH has a significant effect on the flocculation efficiency. The settling rates fall substantially in the alkaline range due to a shift from the point of zero charge (6.2) of the hematite fines, and possibly due to adverse coiling of macromolecular chains.

Flocculation Studies With Paper Mill Effluents

Effluent samples were collected from Emami Paper Mills, Balasore, India. The initial pH of the effluent was 5.8 and the turbidity value was above 500 NTU. While treating the effluent, it was observed that it was very difficult to treat this effluent with either alum or polymer alone. Only a combination of coagulation and flocculation can effectively flocculate the diluted effluent. The concentrated effluent solutions (dilution less than 10 times) could not be treated effectively. This is due to the fact that the paper mill effluents mainly contain lignosulfonates, lignin, oligo- and polysaccharides and other high molecular weight colour forming compounds. Even after dilution of 10 times with water, it was very difficult to flocculate the particles with polymeric flocculants alone. The coagulation of the colloidal system was necessary with the metallic coagulants like alum or ferric chloride prior to flocculation. The solubles are generally anionic in character and can be expected to react with added coagulants to generate new colloidal components in the system, as well as to reduce the dose of coagulant/flocculant (Donnan *et al.*, 1981). Again, at high dilution, the initial turbidity is increased due to the presence of the solubles. For the clarification of such system of fines along with the solubles both coagulation and flocculation are needed.

The effluent after collection was diluted up to 20, 40 and 50 times. Afterwards, it was coagulated with three different coagulants, viz., $\text{Al}_2(\text{SO}_4)_3 \cdot 0.14 \text{ H}_2\text{O}$, $\text{Al K}(\text{SO}_4) \cdot 12\text{H}_2\text{O}$ and FeCl_3 . SAM-S-II and Magnafloc-1011 were used as flocculants. Standard jar test method was followed for flocculation and the supernatant turbidity values in NTU were measured after specified period after flocculation.

Fig. 12 shows the coagulation-flocculation after 10 times dilution of the effluent. The diluted effluent was first coagulated with $\text{Al}_2(\text{SO}_4)_3 \cdot 0.14 \text{ H}_2\text{O}$ by fast mixing at 50 rpm for 2 min. Subsequently it was subjected to slow mixing for 10 minutes and settling for 30 minutes. The 10 ppm concentration of polymer SAM-S-II was fixed while varying the alum concentrations from 50 to 2250

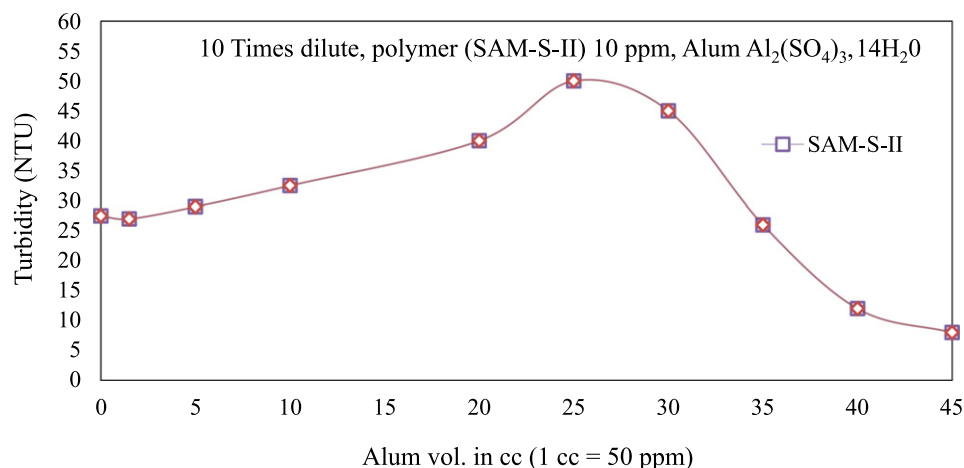


Fig. 12 Variation of supernatant turbidity with changing alum doses for paper mill effluents.

ppm. It is observed that as the alum concentration increases, the turbidity of the supernatant liquid increases from 27.5 NTU at 50 ppm to nearly 50 NTU at 1250 ppm of alum concentration. When the alum concentration is increased further, bigger size of floc formation is observed at 1500 ppm onwards and the turbidity of the supernatant liquid is gradually lowered to 7.8 NTU at 2250 ppm of alum concentration.

Next, the effluent sample was further diluted to 20 times with water and then was coagulated and flocculated by addition of the same alum and polymer respectively, by standard jar test method. The variation of the supernatant turbidity for various coagulants and flocculants is plotted in Fig. 13. It is observed that after an initial destabilization with 50 ppm concentration of alum, the increase in alum concentration causes restabilization of the fines and the maximum supernatant turbidity of 70 NTU is obtained with 350 ppm concentration of alum. Thereafter, suddenly the supernatant turbidity falls with the addition of more alum and reaches 5.7 NTU at 1000 ppm concentration of alum. It clearly indicates that the dilution of the effluent helps the coagulation of the colloidal system by generating new colloidal systems. Although the polymer concentration of 10 ppm remains constant for both 10 times and 20 times dilution, it can be seen that total quantity of required coagulant for diluted systems is less than the concentrated system alone (at 10 times dilution, 2250 ppm can lower the turbidity to 7.8 NTU and at 20 times dilution, $1000 \times 2 = 2000$ ppm reduces the turbidity to 5.7 NTU).

Similar trend is also observed for more diluted effluents (40 times and 50 times) and the results are depicted in the same Fig. 13.

The effect of various coagulants was also studied in 20 times diluted effluent. The flocculation efficiency of the SAM-S-II after coagulation is shown in Figs. 13 and 14. It can be seen that for this particular effluent, $\text{AlK}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ is better coagulant than $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ and FeCl_3 is the best among these three coagulants.

When FeCl_3 was used keeping fixed dose of 5 ppm SAM-S-II, the turbidity value of the 20 times diluted effluent was lowered to 9.7 NTU with addition of 50 ppm of FeCl_3 . This was further lowered to 0.5 NTU at 600 ppm of FeCl_3 . When compared with Magnafloc-1011, it is observed that, at the lower coagulant dose range (50–70 ppm), the ability to flocculate the coagulated particles by Magnafloc-1011 is better than SAM-S-II. However, beyond 350 ppm dose, increase in coagulant concentration results in sudden fall in the supernatant turbidity to 0.5 NTU by SAM-S-II at 600 ppm (5.8 NTU by Magnafloc-1011) indicating almost total flocculation of the coagulated particles (Fig. 15). Thus when the complex paper industry effluent is diluted and coagulated with ferric chloride and flocculated with the starch-g-copolymer, the supernatant turbidity can be lowered to an acceptable value of 0.5 NTU.

The major control being the electrostatic or charge neutralization, the coagulation must be carried out prior to flocculation by bridging the flocculated particles in the paper industry effluents. Ferric chloride is better coagulant than the alums. This is due to the complicated hydrolysis reactions of aluminium salt solutions which is responsible for the narrower pH range often evident for optimum destabilization when compared with iron salt solution. With iron salts, adsorption follows a Langmuir adsorption isotherm, whereas, with aluminium, adsorption often follows a Freundlich isotherm. This is a further indication of complicated hydrolysis products formed by aluminium salts (Bratby, 1990).

The initial pH of the effluent was 6.9 and after dilution also, the pH remained almost constant. When alum was added, the pH was becoming slowly acidic; but treating with only polymer, no change in pH of the system was observed. This is due to the increase in Al^{+++} ions in the system during the addition of the alum. The same trend of decrease in pH in the system was observed with FeCl_3 treatment due to the increase in Fe^{+++} ions in the system.

While treating the paper mill effluents it is observed that neither a coagulant nor a flocculant can completely flocculate such complex systems. After destabilizing such effluent system with a suitable coagulant, starch-g-copolymer can be used as a flocculant aid for the complete flocculation of the contaminants present in the system. After diluting the effluent, it is possible to clarify the supernatant liquid turbidity below 5 NTU by the combined use of coagulant and SAM-S-II (Karmakar and Singh, 1996).

Besides the above, an account of more detailed studies on polysaccharide based grafted copolymers and their flocculation characteristics have been reported elsewhere by the author and his co-workers (Singh *et al.*, 2000; Karmakar, 2017).

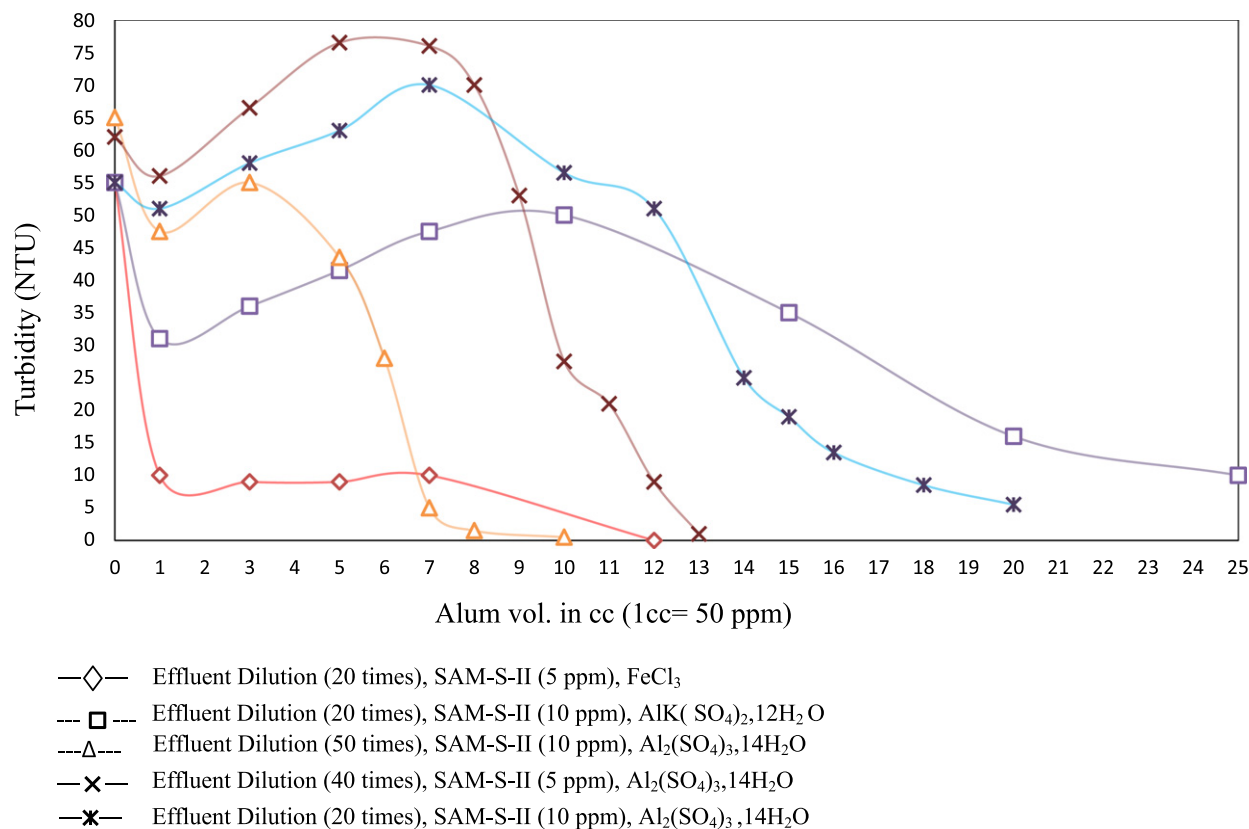


Fig. 13 Variation of supernatant turbidity with changing alum doses and polymer for paper mill effluents.

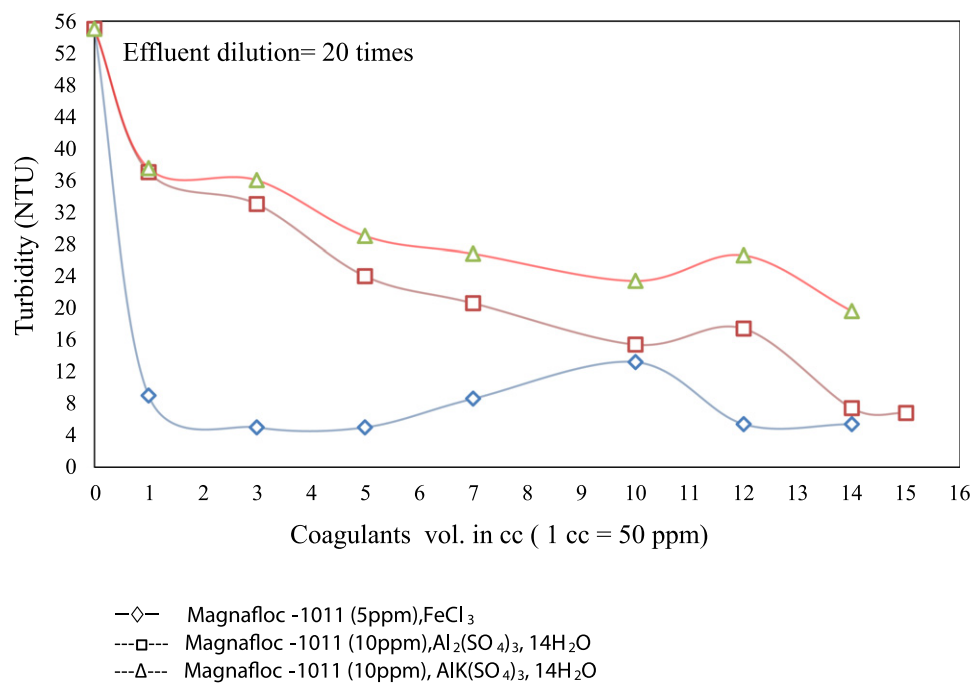


Fig. 14 Variation of supernatant turbidity with various coagulants and their varying doses for paper mill effluents.

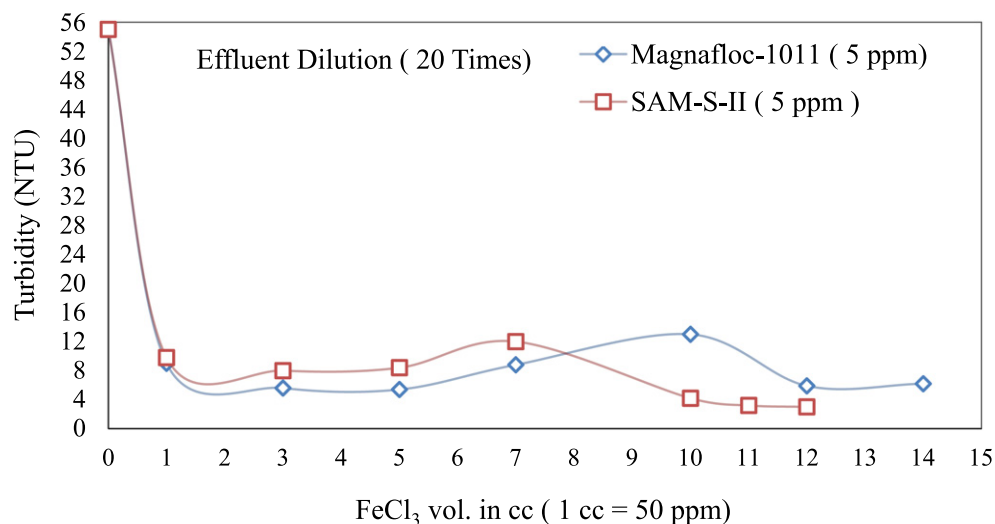


Fig. 15 Variation of supernatant turbidity with various FeCl_3 doses using various polymers for paper mill effluents.

Conclusions

Starch-g-Polyacrylamides are found to be very efficient flocculants for industrial use. The synthesis of these graft copolymers are simple and can be easily manufactured in a large scale. However, real comparison with other commercially available flocculants can be made only when the molecular weights, length of the molecules and number of polyacrylamide chains could be determined by chemical and advanced analytical techniques. The use of the above flocculants also depends on the nature of the effluent to be flocculated. So, the chemical analysis of the effluents is also essential before taking up any industrial project for flocculation.

Amylose, another polysaccharide can be modified by grafting acrylamide monomer onto its backbone to produce a better flocculant using a simple polymerization technique. The amylose-grafted polyacrylamides in small doses have better effectiveness than the commercial flocculant Magnafloc-1011 at high shear rates for a wide range of pH range.

It has also been observed that neither a coagulant nor a flocculant can completely flocculate complex systems. A suitable coagulant may be used to coagulate first and then grafted copolymers can be used for the complete flocculation of such systems.

See also: Use of Novel Nanostructured Photocatalysts for the Environmental Sustainability of Wastewater Treatments

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Electrochemical Energy Storage Using Batteries, Superconductors and Hybrid Technologies

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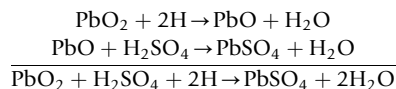
Introduction

The indispensable requirement of high potential electrochemical energy storage devices (ECESDs) such as batteries, superconductors and hybrid technologies have remarkably increased day by day. It is also critical for highlighting energy crises and environmental issues (Chen *et al.*, 2017). Moreover the performance of these devices also improved dramatically with the advent of advanced materials (Lv *et al.*, 2016). Presently, ECESDs have great demand in electric vehicles and renewable power houses in homes and industries. Despite significant improvement in terms of power density and life span, still it needs improvement for better efficiency. In order to cater for the demand of high performance ECESDs, the efforts were made by many researchers for the development of high performance electrode materials. The three-dimensional (3D) carbon nano-materials due to their distinguished structural patterns of interlinked architecture have various applications for supercapacitors and next generation batteries (Chen *et al.*, 2017). Further they have excellent flexibility, more specific surface areas, tunable interfacial chemical properties and good electrical conductivities, which support executable platforms for the expedition of lithium-sulfur batteries, lithium-ion batteries, lithium-air batteries and super capacitors (Kong *et al.*, 2018).

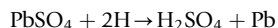
The above mentioned ECESDs consist of basically four components (electrodes, electrolyte, current collectors, and separators) and 3D printing emerges as a well-timed, flexible tool, presently available with various printing technologies (Tian *et al.*, 2017). Many researchers (Zhang *et al.*, 2017; Ambrosi and Pumera, 2016) reviewed the use of 3D printing technologies for the prosperous of ECESDs. These techniques gains popularity due to its great flexibility in geometrical designs (interfaced with computed aided design and manufacturing) compared to subtractive manufacturing methods (Wu *et al.*, 2015). Moreover, the use of thermal-responsive/ conductive polymers as filament materials in fused deposition modeling (one of the low cost 3D printing techniques) is a step in next-generation smart ECESDs. Foster *et al.* (2017) also demonstrated the use of 3D graphene-based conductive PLA filament for making 3D prints of useful electrochemical parts with bespoke and conceptual designs. Carbon materials have good chemical certainty and versatile nano-structure, can be used in feedstock filament for 3D printing. Moreover, the shape and dimensions of an electrodes (anode/cathode) printed with 3D-printing technology can be precisely controlled besides tailoring the composition (Fu *et al.*, 2017).

Lead Acid Battery

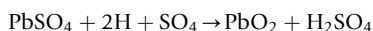
Lead acid batteries are notably used as a storage batteries or secondary batteries, commonly for general application. The materials used for these storage cells are lead peroxide (PbO_2), sponge lead (Pb) and dilute sulphuric acid (H_2SO_4). The positive plate of lead acid battery is made of PbO_2 (dark brown brittle hard substance). The negative plate of lead acid battery is made up of pure lead which is in soft sponge condition. The dilute H_2SO_4 and water have a ratio of 1:3. The PbO_2 plate and sponge lead plate are dipped in a dilute sulphuric acid. A load is externally connected between these two plates. In dilute H_2SO_4 acid, the molecules of acid, split into positive hydrogen ions (H^+) and negative sulphate ions (SO_4^-). The H^+ ions on reaching at PbO_2 plate, receive electron from it and become hydrogen atom (H) which further attack PbO_2 and form lead oxide (PbO) and water (H_2O). Newly formed PbO reacts again with H_2SO_4 and forms lead sulphate (PbSO_4) and H_2O . The SO_4^- ions are moving freely in the solution and some of them reached to pure Pb plate where they give there extra electrons and become radical sulphate (SO_4). Apparently, radical sulphate cannot exit alone, so it attacks pure Pb and become PbSO_4 .



During this process, positive hydrogen ion take electron from lead peroxide plate and negative sulphate ions loose electrons to lead plate, it causes an inequality of electrons between the plates. Hence, the current starts flowing through the external load between these two plates in order to balancing this inequality of electrons. This process is called discharging of battery. As the load is replaced by DC source by connecting lead sulphate covered lead peroxide plate with positive terminal and lead peroxide covered lead plate with negative terminal. During discharging, the density of sulphuric acid falls but there still there is some sulphuric acid exists in the solution. The part sulphuric acid also remains as positive hydrogen ions and negative sulphate ions in the solution. Hydrogen ions being positively charged, moved to the electrode connected with the negative terminal of the DC source. Here each hydrogen ion takes one electron and become hydrogen atom. These newly formed hydrogen atoms, further attack lead sulphate and form lead and sulphuric acid.

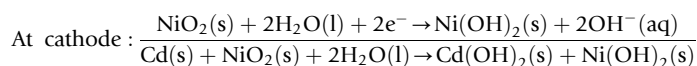


The negative sulphate ions proceeds toward the electrode connected with the positive terminal of DC source and loses their extra electrons and become radical sulphate. This radical sulphate reacts with the lead sulphate of anode and form lead peroxide and sulphuric acid. Hence by charging, the lead acid storage battery cells becomes ready for delivering energy to load (discharging).



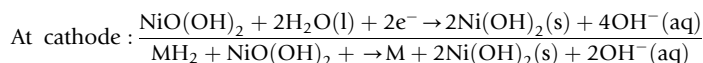
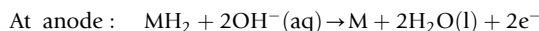
Nickel Cadmium Battery

In this cell, the anode and cathode are made up of cadmium and metal grid (containing nickel oxide) respectively. In this case, the electrolyte is potassium hydroxide (KOH) solution. The cell has a capacity to generate a voltage of about 1.4 V. No gaseous product produced during the discharge of battery and the solid product formed during the process, adhere to the electrodes which therefore are reconverted by the charging process. These cells are extensively used in electronic watches and calculators.



Nickel Metal Hydrate Battery

The anode in this battery is metal hydride and cathode is nickel oxy hydroxide NiO (OH)_2 . The electrolyte is potassium hydroxide (KOH) solution. Both anode and cathode is made up of nickel alloys and separated by an insulator. Metal hydride is made up of alloys of either zinc, vanadium, titanium, chromium etc. the entire battery is kept in a glass or steel container. Before lithium ion battery is commonly used in laptops and electric vehicles.



Lithium Ion Battery

Lithium ion battery is the indispensable power source of modern electric vehicles. It is rechargeable and have high energy density than other commercially available batteries. Due to its light weight it also used in smart phones, laptops etc. Each battery consists of number of batteries generally called cells. The electric current reaches the cells via conductive surfaces. For these batteries, aluminium and copper are the mostly used conductive surfaces. Like other batteries it also have positive and negative electrodes namely cathode (+) and anode (-). The cathode which is a positive electrode consists of very pure lithium oxide (LiMO_2 ; $\text{M} = \text{Co, Ni}$). More the uniformity in its chemical composition, better is its performance and battery life. The negative electrode (anode) is placed on the other side, is made up of graphite (a form of carbon layer structure). Graphite has been commonly used as the anode material for commercial Lithium ion battery due to its low cost, natural abundance, high coulombic efficiency and flat potential profile during charging and discharging process. A part of above, Lithium alloys are also promising anode materials due to their higher Li storage capacity, which provides higher energy density than commercial Li-intercalated carbons (Guo *et al.*, 2008).

Both anode and cathode have high capability rate but the cycle life of such cells are often limited by the cathode. The unexpected low cathode power competency may be due to either its high electrical resistance or slow transport of Li^+ ion within the solid phase (Gu *et al.*, 2013). A part of above, the metal dissolution from the cathode is also strongly accelerated at elevated temperatures. The battery is built up with a transport medium (the electrolyte) so that the lithium ion carrying charge can move freely. This electrolyte must be extremely pure. To prevent short circuit, there is a layer placed in between two electrodes called separator. The separator is actually permeable to the tiny lithium ions. The experts called this property as a micro-porosity. During charging process, the positive charge lithium ions passed from the cathode through the separator into the layered graphite anode structure where they are stored. On the other hand when battery discharges, the energy is removed from the cell. The lithium ions travels back to cathode via electrolyte through the separator. The motor converts the electric energy into mechanical energy makes the vehicle to run. It is not a one way energy conversion process, the reverse is also possible, electrical energy is also converted into chemical potential and same can be stored in a system. Fig. 1 illustrates the schematic of lithium ions battery.



The availability of energy and its battery life is closely related to the quality of material used. In other words higher the quality of pure materials along with the customized formulation leads to the better performance and longer battery life.

As already mentioned this battery have high energy density which means that it can store larger energy per unit volume or per unit mass as compare to the other batteries (it is almost two times the nickel cadmium batteries. It can be rechargeable until its

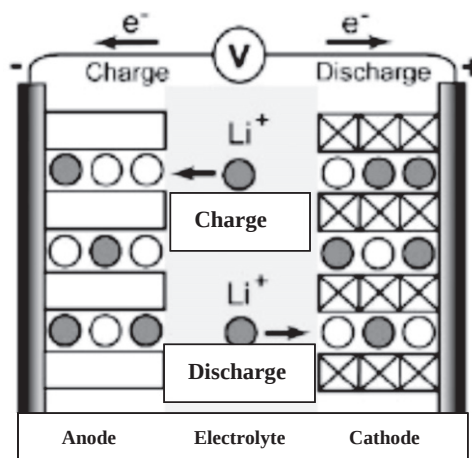


Fig. 1 Schematic of lithium ion battery. Reproduced from Guo, Y.G., Hu, J.S., Wan, L.J., 2008. Nanostructured materials for electrochemical energy conversion and storage devices. *Advanced Materials* 20 (15), 2878–87.

battery life is over. It also have no memory effect which means that there is no need to discharge them completely before recharging. It can hold its charge for a certain time (5% energy loss per month)). Even a high energy density battery, it has certain disadvantages. It has a limited life (2–3 years from the date of manufacturing) and very much sensitive to high temperature. If the separator get damaged, it can be burst in to flames.

Future Energy Storage Devices

Super Capacitors

A super capacitor, also known as an ultra-capacitor, is an energy storage device, having much larger capacity than conventional physical capacitors (Liu *et al.*, 2010). Super capacitors are capable of delivering the power at much higher rates than batteries and have been recently used by number of automobile companies (Toyota, Tesla) in energy recovery systems. Super capacitors looks similar to the batteries with low energy density (10–100 times less than Lithium ion battery), high power density (10–200 time more power than Lithium ion battery) and exceptional cycle life (typically 1 million charge and discharge cycles). The longer life of super capacitors is due to the physical movement of ions instead of chemical reactions as the ordinary battery goes. Generally, according to the materials and electro-chemical charging/discharging mechanism, it can be classified as electric double layer capacitors (EDLC) using ion adsorption and pseudo-capacitors having fast surface redox reactions (Cakici *et al.*, 2017) (Fig. 2).

Super capacitors overcomes the limitations of batteries or provides better solution than batteries. Super capacitors are bigger capacitors were invented in the same time of batteries, about 150 years ago. Super capacitors are inherently better storage devices than chemical batteries. They are more efficient, last longer, have resilience to temperature, do not degrade and memory effect. Although with the number of advantages but still they have certain challenges and restricted them to use for specific applications. The challenges includes fast charging and discharging. In order to use super capacitors as a storage media in the battery world, one need to be able to charge them as required by the load but also discharge them slowly. The capacitors are inherently low voltage device so in order to use them operationally, they have to put them in series and make them operationally at commercial voltage. During this process they have a tendency to become unstable and it is very difficult to scale in megawatts. Balancing algorithm or balancing technology is used to stable the super capacitors during charging and discharging process. Further, mathematical modeling and simulation will be the key to success in designing of future high-energy and high-power devices (Simon and Gogotsi, 2010). Moreover, the specific energy or energy stored in kilograms of weight, which is also has been traditionally a problem and it affected form factor. Wang *et al.* (2018) reviewed the recent progress of Micro-super capacitors as a new class of high-power miniaturized electro-chemical energy-storage devices.

From the safety aspects, super capacitors can be discharge to zero volt so in case of emergency the super capacitors can discharged full energy to zero energy within seconds without any kind of damage. Secondly it does not have noxious flammable chemicals in it with no risk of thermal run away. Thermal runaway becomes the most serious safety issue in lithium-ion batteries and super capacitors (Yang *et al.*, 2018). So in case of fire one can discharge the energy completely and it acts as fire retardant. It is one of the most suitable candidates for green energy storage. Among the applications the super capacitors

- (1) Can be deployed at any scale and in any location, independent of or connected to available infrastructure.
- (2) When deployed in remote locations with no or poor grid access, can supply electricity from 100% renewable generation, eliminating dependency on fossil fuel-based generators.
- (3) Can be deployed with any combination of generation sources from exclusively renewables to a combination of renewables and fossil fuel.

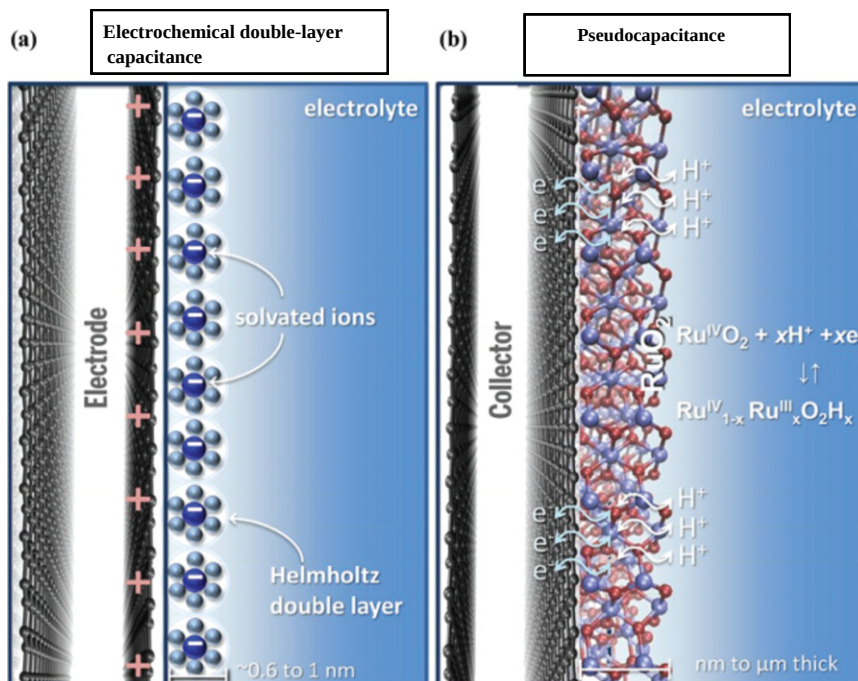


Fig. 2 Schematic of super capacitors. (a) Electric double layer capacitors (EDLC) using ion adsorption and pseudo-capacitors having fast surface redox reactions. Reproduced from Jian, X., Liu, S., Gao, Y., *et al.*, 2016. Carbon-based electrode materials for supercapacitor: Progress, challenges and prospective solutions. *Journal of Electrical Engineering* 4, 75–87.

- (4) Categorized as a long-term asset due to long cycle life of the storage and long design life of the server.
- (5) Delivers reliable and stable utility grade electricity. In locations with grid access, can be deployed at mission critical facilities that depend on uninterrupted supply: Military bases, hospitals, fire and police stations, data centers, etc.

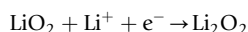
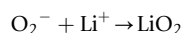
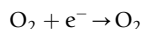
Lithium Sulfur (Li-S) Batteries

The common Li – S batteries, sulfur composite cathode, metallic lithium anode, and organic electrolyte are its main constituents (Mai *et al.*, 2014). Sulfur is the tenth most abundant element and this is actually considered as a waste by industries. Fundamentally it is cheap and can be used as a material for energy storage.

Lithium Oxygen (Li-O₂) Batteries

Two main challenges in batteries are to cut cost and improvement in performance of battery technology. As an estimation 17% of battery cost is as materials and everything else is subject to technological improvement. The other option of improvement is a new better technology. The anode lithium is possibly be a light element and comparing with air cathode make it really light and hence the advantage of its high energy density also electrochemical equivalent of metallic lithium is very high. Fig. 3 illustrates four different architectures of Li-air batteries which all assume the use of lithium metal as an anode. Namely these architectures are aprotic, aqueous, mixed aprotic-aqueous system and fully solid state architecture. Primary components are as labelled in the Fig. 3. The Spontaneously occurring solid electrolyte interface on the lithium anode are shown as dashed lines, while in case of artificial it is illustrated as a solid lines.

In lithium air battery, metallic lithium is anode, porous carbon is cathode and an electrolyte which is ion liquid. During the discharge of battery lithium ions coming out into solution and in the presence of oxygen from the air form lithium peroxide or oxide depending upon the extent to which the battery is discharged. In other words it uses oxidation of lithium at anode and reduction of oxygen at the cathode to induce the current flow. Originally proposed in 1970, it is a possible source of power for electric vehicles, hybrid vehicles and eco-friendly technologies.



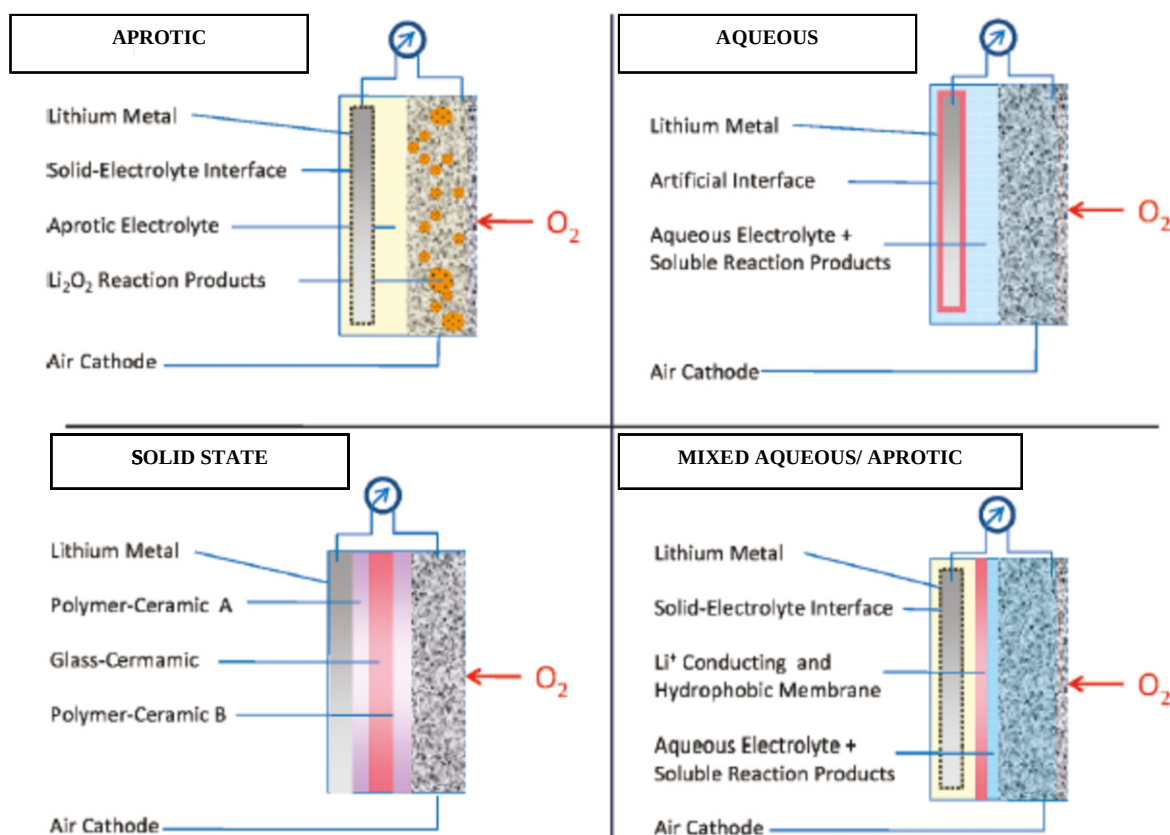


Fig. 3 Various architectures of Li-air batteries. Reproduced from Girishkumar, G., McCloskey, B., Luntz, A.C., Swanson, S., Wilcke, W., 2010. Lithium – air battery: promise and challenges. *The Journal of Physical Chemistry Letters* 1 (14), 2193–2203.

The energy density (that is the amount of energy that can be extracted out of kilogram of material) of lead acid batteries is very less (40 Wh/kg), lithium ion have substantially high (around 120 Wh/kg) but lithium air batteries have exceptionally high value (1700 Wh/kg) as shown in [Fig. 4](#). So this battery is 10 times more operational than lithium ion battery having same weight.

The abundant availability of sodium makes sodium ion batteries cost-effective, which are potentially competitive with LIBs in large-scale energy storage system such as electricity grid.

Materials

[Yu et al. \(2017\)](#) suggested Polyhedral-like NiMn-layered double hydroxide/porous carbon (NiMn-LDH/ PC-x) composites as anode and activated carbon as cathode for super capacitors. [Cakici et al. \(2017\)](#) developed carbon fiber fabric/MnO₂ based hybrid materials for large-scale energy storage systems (super capacitor) applications in which MnO₂ was uniformly coated on the surface of carbon fiber fabric (CFF). The Energy storage capacity of the double layer capacitors can be enhanced by using large specific surface-area electrodes with the use of nanostructured carbon materials (graphene, nanotubes, etc.) On the other hand, the pseudo capacitors mainly use nanostructured metal oxides with the combination of carbon materials, which leads to the increase of energy storage and specific capacitance ([Cakici et al., 2017](#)). [Liu et al. \(2018\)](#) presented carbon textiles that are uniformly covered with NiCo₂-xFe_xO₄ nanotubes as electrode materials in energy storage devices. Although carbon-based materials have abundant supply and also have high surface area but the capacitance and energy density are still relatively poor than batteries and further it can be enhanced by using electrochemically active materials with high pseudo capacitance such as RuO₂, MnO₂, Co₃O₄, Co(OH)₂, Ni(OH)₂ and so forth ([Mai et al., 2014](#)). The combination of these materials has also been proposed for further improvement (enhancement of electrochemical performance is called “synergistic effect”).

Being available in different allotropes such as graphite, diamond and fullerenes/nanotubes, carbon has a rich electrochemical properties due to its mesoporous character ([Frackowiak and Beguin, 2002](#)). Moreover it has various micro-textures and a variety of dimensionality (from 0 to 3D). Further its application as an electrode material (due to its easy processability and low cost) makes carbon as a material for the storage of energy in electrochemical capacitors ([Frackowiak and Beguin, 2001](#)). Many researchers also reported the use of conductive papers as a storage device. [Pushparaj et al. \(2007\)](#) demonstrated the use of nano porous cellulose paper embedded with aligned carbon nanotube electrode and electrolyte for building various flexible storage devices such as super capacitor, battery, hybrid, and dual-storage battery-in-super capacitor devices. [Hu et al. \(2009\)](#) also suggested the use of conductive

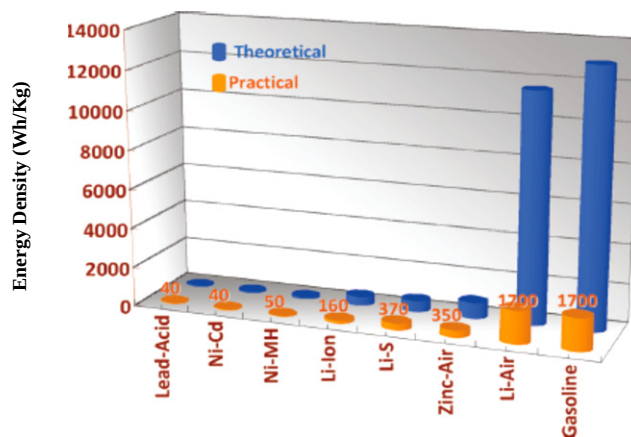


Fig. 4 Energy densities of various types of rechargeable batteries. Reproduced from Girishkumar, G., McCloskey, B., Luntz, A.C., Swanson, S., Wilcke, W., 2010. Lithium – air battery: promise and challenges. *The Journal of Physical Chemistry Letters* 1 (14), 2193–2203.

paper (Prepared with 1D nano-materials and commercially available paper) for high-performance energy storage devices. Moreover this can be a highly scalable and low-cost solution. Nano-materials constituted by nanoparticles or Nano-architected materials although have certain challenges like difficulties in controlling the size and size distribution of the particles or clusters but have led to the development of new super capacitor technologies by significantly changing the electrode and electrolyte properties, and consequently their performance for energy storage and conversion (Arico *et al.*, 2011). Among Two-dimensional (2D) nanomaterials, especially graphene, have been in the focus of researchers due to its wide range of applications. Summarized the recent advancements of solution processed two-dimensional (2D) metal dichalcogenide (MDC) and their hybrid nano-materials for energy storage and conversion applications, which includes rechargeable batteries, super-capacitors, electro catalytic hydrogen generation and solar cells. Chaudhary *et al.* (2017) reported the development of ternary Au/ZnO/rGO nano-composites prepared with microwave-assisted hydrothermal method for high performance supercapacitor applications. Results demonstrate that Au/ZnO/rGO nanocomposites acts as an active electrode materials for electrochemical pseudo-capacitors performance and can be used for electrochemical storage devices with both high energy and power densities. The nano sized electrode materials have distinction in terms of kinetics and capacity, but it also suffer from low thermodynamic stability and high activity towards surface reactions (Guo *et al.*, 2008).

Summary and Outlook

This review has been focused on the recent advancements for new and improved electrode materials and electrochemical energy storage devices. However, the high performance electrochemical energy storage mediums has been extensively developed in past decades, with the typical characteristics such as the high energy density, high power density, thermal stability and long cycling life. The high performance electrochemical energy storage mediums with these superior parameters are required for further development. Another interesting direction would be to develop new materials for 3D printing for much improved electrochemistry, which can not only help in better fundamental understanding of hybrid technologies, but also achieve optimized device performance as a storage medium. Additionally, it is also believed that nanostructured materials will play an important role in enhancing the performance of electrochemical energy conversion and storage mediums. Besides solving various challenges in energy storage applications, the researchers from a range of disciplines will be required, and their success will contribute the development of next generation eco-friendly and sustainable energy devices.

See also: Application of Nano Porous Materials for Energy Conservation and Storage. Application of Nano Porous Materials for Energy Conversion Process

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Energy Efficiency Analysis in Building Walls in Tropical Climate Using Thermal Insulation System

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Nomenclature

A	Area of wall (m^2)	k_{ins}	Insulation material's thermal conductivity ($\text{W/m } ^\circ\text{C}$)
C_A	Insulation material cost per unit volume (RM/m^3)	LCC	Life-cycle cost (RM)
ADH	Annual degree hours (hr)	N	Service lifetime (year)
C_e	Electricity cost (RM/kWh)	O_h	Annual operating hour of the air conditioner (hr)
$C_{t_{ins}}$	Insulation material cost (RM/ m^2)	PE_i^1	Fuel mix percentage in year i (%)
$C_{t_{uns}}$	Total energy cost without insulation (RM/ m^2)	R_{ins}	Insulation material resistance ($\text{m}^2\text{ } ^\circ\text{C/W}$)
$C_{t_{ins}}$	Total energy cost with insulation (RM/ m^2)	R_{wall}	Un-insulated wall resistance ($\text{m}^2\text{ } ^\circ\text{C/W}$)
d	Electricity price increase rate (%)	R_{wt}	Total wall resistance without insulation ($\text{m}^2\text{ } ^\circ\text{C/W}$)
E_A	Annual energy consumption of the air conditioner (kWh)	$T_{o,av}$	Annual average temperature of outside air ($^\circ\text{C}$)
EM_i	Consumed electricity in year i (GWh)	T_o	Design outside temperature ($^\circ\text{C}$)
EM_p^1	Emission for fuel type n (kg)	T_i	Design inside temperature ($^\circ\text{C}$)
h_i	Inner surface convection heat transfer coefficient ($\text{W/m}^2\text{ } ^\circ\text{C}$)	TS	Total saving (RM/ m^2)
h_o	Outer surface convection heat transfer coefficient ($\text{W/m}^2\text{ } ^\circ\text{C}$)	U	Heat transfer coefficient ($\text{W/m}^2\text{ } ^\circ\text{C}$) ($\text{W/m } ^\circ\text{C}$)
i	Discount rate (%)	x_{ins}	Insulation thickness (m)
k_n	n^{th} wall layer's thermal conductivity ($\text{W/m } ^\circ\text{C}$)	x_n	n^{th} layer of wall's thickness (m)
		x_{opt}	Optimal insulation thickness (m)
		ΔT	Difference between inside and outside design temperature ($^\circ\text{C}$)

Introduction

The global energy map is changing and the demand is increasing every day due to the industrialisation, urbanisation, technological development and population growth (Mofijur *et al.*, 2012; Ong *et al.*, 2011). Global energy demand grows by more than one-third over the period to 2035 with China, India and the Middle East accounting for 60% of the increase (Mofijur *et al.*, 2013). Worldwide the energy consumption is distributed among four main sectors namely industrial, building (residential/commercial), transportation and agricultural areas. It has been reported that currently 36% of global final energy is consumed by both buildings and buildings construction sectors which causes nearly 40% of total direct and indirect CO_2 emissions. In the United States (US) alone 65% total energy is consumed by the building sector and 42% of energy is consumed by the European Union (EU) (Wang *et al.*, 2018) themselves. However, the numbers of commercial and institutional buildings in 2050 will be three times higher than that of 2010. It is evident that the energy demand from building sector continues to rise, driven by improved access to energy in developing countries, greater ownership and use of energy-consuming devices, and rapid growth in global buildings floor area, at nearly 3% per year.

The building sector is one of the largest energy consumers in Malaysia. As a developing country, Malaysia has experienced a significant increase in energy demand (Mahlia *et al.*, 2012) and nearly 40% of consumed energy is required for building cooling and heating. The concern related to energy consumption and related CO_2 emission will be more acute as the number of houses in Malaysia is increasing every year. It has been suggested that the growth of energy consumption in Malaysia can be reduced by introducing energy efficiency systems (Mahlia, 2004; Mahlia and Chan, 2011; Mahlia *et al.*, 2002a, 2004a, 2003, 2005a,b; Mahlia *et al.*, 2010; Mahlia and Yanti, 2010; Taufiq *et al.*, 2007).

However, to ensure sustainable development by lowering the global energy demand and its negative impacts, an efficient energy usage system needs to be developed. The energy consumption of a building is mainly reliant on the properties of its envelope and the thermal performance of building walls is an important factor to improve the energy efficiency as well as to reduce the emissions (D'Alessandro *et al.*, 2016). Furthermore, correct insulation materials, its thickness and its position can play an important role to offer thermal comfort and huge energy savings. It has been reported that better thermal insulation with low thermal conductivity contributes significantly to new construction and retrofitting existing buildings.

There are many studies in the literature (Bonakdar *et al.*, 2014; Daouas *et al.*, 2010; Nematchoua *et al.*, 2017) on the determination of the impact of insulation materials on energy savings in building and environmental in some tropical countries

are discussed by [Mahlia \(2002, 2003\)](#), [Mahlia et al. \(2002b, 2004b\)](#) and [Ong et al. \(2011\)](#). But the information regarding the practical use of insulation materials in a tropical climate is very limited. Thus, this study investigated the effect of Ten type's thermal insulation materials on the energy savings and cost benefits of building walls in tropical countries. In addition, the effect of leaving air gaps in Malaysian building walls on the energy savings and cost benefits is also investigated.

Materials and Method

This study focuses on the aspect of energy savings and economy of insulation material and air gap in the building wall. Life-cycle cost analysis is utilised to evaluate the economic impact and determine the optimal insulation thickness. In the first part of the study, an insulated wall structure with no air gap is investigated and the comparison is done for the selected ten insulate in materials. The most economic insulation is determined and evaluated based on introducing an air gap. The final results of this study provided support for the decision process to select suitable insulation materials.

Material Selection

It is very important to select a good insulation material for efficient building energy conservation. There are many factors such as cost, durability, climate, availability, mode of heat transfer, installation, building orientation that need to be taken into consideration in the material selection process ([Mahlia and Iqbal, 2010](#)). In this study, ten insulation materials namely fiberglass (rigid), fiberglass (batts), urethane (rigid), urethane (roof deck), fiberglass-urethane, cellulose, extruded polystyrene, perlite, rock wool and styropor were selected and investigated. The thermal conductivity and cost of insulation data of selected insulation materials are tabulated in [Table 1](#) ([Mahlia et al., 2012](#)).

Wall Structure

The common materials for the building construction include concrete, stones and bricks and iron bars for reinforcement. Insulation in the building wall is introduced to increase the thermal resistance of the building as well as reduce the cooling loads. In the present study, the building wall construction was a sandwich type wall in which a two-piece horizontal hollow brick-layers with plaster. The insulation materials were installed on the internal side of the wall surface. The insulated wall structure is illustrated in [Fig. 1](#).

Data Collection

In this study, Malaysian commercial building has been considered because Malaysia has a tropical climate includes hot and humid. Climate data were collected from the Meteorological Department, Malaysia for a period of two years with an outdoor constant temperature between 23.7 and 31.3°C ([Malaysian Meteorological Department, Ministry of Energy, Science, Technology, Environment and Technology, 1972–1997](#)). Generally, commercial buildings are occupied from 8 am to 5 pm; thus, the average temperature and relative humidity were estimated at 29°C and 75% respectively ([Mahlia et al., 2007](#)). The effective temperature of 21°C is selected as the optimal comfort temperature for building occupants according to the data presented in [Table 2](#). Thermal comfort can be defined as the condition for satisfying the thermal environment for the inhabitants ([Olesen, 2000](#)).

Methods

The methodology of this study is divided into two sections. The first section includes the energy consumption calculation through heat transfer and the second section includes the life-cycle costs to evaluate the economic impact.

Table 1 Data for insulation materials

Insulation materials	Thermal conductivity, K_{ins} (W/m °C)	Cost of insulation, C_{ins} (RM/m ²)
Fiberglass -urethane	0.021	214
Fiberglass (rigid)	0.033	304
Urethane (rigid)	0.024	262
Perlite	0.054	98
Extruded polystyrene	0.029	182
Urethane (roof deck)	0.021	221
Cellulose	0.043	175
Fiberglass (batt)	0.045	145
Rock wool	0.043	228
Styropor	0.030	100

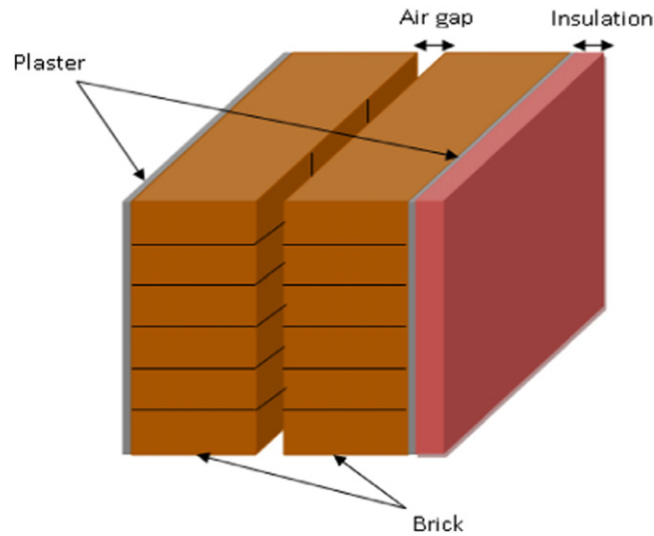


Fig. 1 The relative humidity and average temperature from 8:00 a.m. to 5:00 p.m. Reproduced from Mahlia, T.M.I., Taufiq, B.N., Ismail, Masjuki, H.H., 2007. Correlation between thermal conductivity and the thickness of selected insulation materials for building a wall. *Energy and Buildings* 39, 182–187.

Table 2 The effective temperature for each comfort range in hot climate

Comfort range	Effective temperature F ($^{\circ}\text{C}$)
Above acceptable	Above 76 (above 24.5)
Upper acceptable	73–76 (22.8–24.5)
Optimal	69–73 (20.6–22.8)
Lower acceptable	66–69 (18.9–20.6)
Below acceptable	Below 66 (below 18.9)

Calculation of energy consumption and heat transfer

Heat loss or gain in the building is occurred due to the heat transfer through windows, walls, floor, ceilings and infiltration of air (Diamant, 1965). In this study, heat gain was considered only through the building wall. In hot weather, the heat flows from outside to inside and the indoor air temperatures are regulated by the cooling load. The total heat transfer through the wall is calculated using the following equations:

$$Q = UA(T_o - T_i) = UA\Delta T \quad (1)$$

Where, T_o and T_i are the outside and inside ambient temperature respectively, U is the overall wall heat transfer coefficient and A is the area of the wall. Thus, heat gain per unit area becomes (Mahlia and Iqbal, 2010):

$$q = U\Delta T \quad (2)$$

The U -value of a wall is depending on the thermal conductivity of the wall and the convective coefficient of any solid/air interface. The equation for U -value is (Mahlia and Iqbal, 2010):

$$U = \frac{1}{\left(\frac{1}{h_o} + \frac{x_1}{k_1} + \frac{x_2}{k_2} + \dots + \frac{x_n}{k_n} + \frac{1}{h_i}\right)} \quad (3)$$

Where h_i and h_o are the inside and outside surface convective heat transfer coefficients, k_x is the thermal conductivity for each wall layers, x_x is their thickness. Air gap in a composite wall is a confined area and air flow is restricted, therefore the convection factor in air gap can be neglected (Mahlia and Iqbal, 2010).

The insulation thermal resistance, R_{ins} can be calculated by:

$$R_{ins} = \frac{x_{ins}}{k_{ins}} \quad (4)$$

$$U = \frac{1}{\left(R_{tw} + \frac{x_{ins}}{k_{ins}}\right)} \quad (5)$$

As a result, the annual energy consumption, E_A per unit area for cooling is:

$$E_A = \frac{ADH \times q}{COP} \quad (6)$$

Where COP of air-conditioner and the annual degree hours, ADH can be calculated by:

$$ADH = \frac{O_h(T_{o,av} - T_i)}{(T_o - T_i)} \quad (7)$$

Where O_h is air-conditioner operating hours and T_i , T_o indicate temperature for inside and outside air, respectively, while $T_{o,av}$ is the average of annual outside temperature.

Finally, the annual consumed energy per unit can be rewritten as:

$$E_A = \frac{ADH \times U \times \Delta T}{COP} \quad (8)$$

Economic analysis

The present worth factor is determined in order to convert the total cooling cost over the service lifetime of N years to its present value (Hasan, 1999). The PWF can be defined as (Ghrab-Morcos, 1991):

$$PWF = \sum_{u=1}^n \left(\frac{1+i}{1+d} \right)^u = \begin{cases} \frac{1+i}{d-i} \left[1 - \left(\frac{1+i}{1+d} \right)^n \right] & i \neq d \\ \frac{n}{1+i} & i = d \end{cases} \quad (9)$$

Where i is the discount rate and d is electricity increase rate adjusted for inflation.

Therefore, the consumed energy cost per unit wall surface area is:

$$C_t = PWF(E_A \times C_e) \quad (10)$$

Where, C_e is the electricity tariff rate.

The cost of insulation material, C_{ins} is obtained as below:

$$C_{ins} = C_A \times x_{ins} \quad (11)$$

Where, C_A is insulation cost per unit volume and x_{ins} is the thickness of insulation.

Finally, the total life-cycle cost saving (TS), is the net savings from total consumed energy cost without insulation, $C_{t_{uns}}$ deducts the sum of the total consumed energy cost with the insulation, $C_{t_{ins}}$ and insulation cost, C_{ins} . TS can be expressed in the following equation (Mahlia and Iqbal, 2010):

$$TS = C_{t_{uns}} - (C_{t_{ins}} + C_{ins}) \quad (12)$$

Results and Discussion

The comparison of ten selected insulation materials based on tropical condition over a life-cycle period of twenty years has been discussed. Firstly, life cycle cost and energy saving for each selected materials have been determined and compared. In the second part, the effect of introducing an air gap in the insulation material has been evaluated.

Comparison of Selected Insulation Materials

Using more insulation, energy uses will decrease. That will lower the energy cost, but is also be beneficial to the environment. However, there is a limit when exceeding certain insulation thickness, the potential energy saving will not exhibit extra life-cycle cost saving.

Life cycle cost analysis

The calculated life-cycle cost is presented in Fig. 2. Life cycle cost savings vary from 73% to 85%/m² wall, depending on the insulation material. Styropor is the most economical option. It can save up to 84.74%/m² wall in 20 years by an optimal thickness of 0.139 m. This is because of more insulation thickness for energy saving can be installed due to the low insulation cost of styropor. Although Perlite has low insulation cost, it is not possible to achieve as high-cost saving as styropor because of high thermal conductivity properties. It Perlite has too poor in thermal resistance to retard heat flow into buildings and reduce the cooling loads. On the other hand, urethane (rigid) shows the lowest cost saving (73.05%/m²) as a result of the highest thermal conductivity cost.

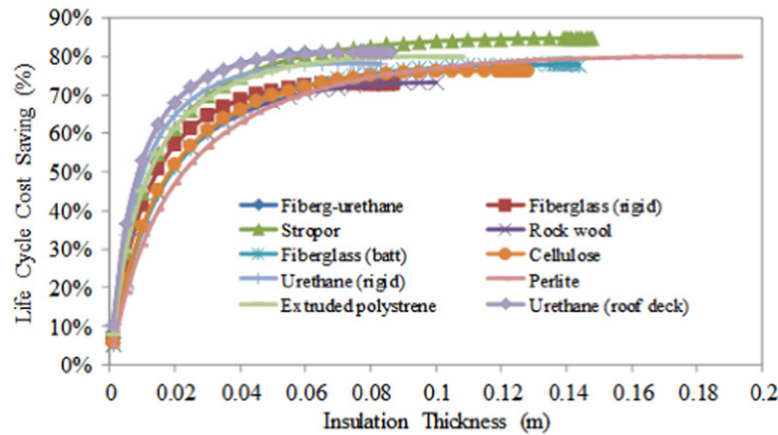


Fig. 2 LCC saving by insulation thickness for each insulation materials.

Table 3 Energy saving at optimal insulation thickness

Insulation type	Energy saving at an optimal thickness (%/m ²)
Rock wool	85.69
Fiberglass (batt)	88.31
Fiberglass (rigid)	85.53
Cellulose	87.37
Fiberglass-urethane	90.28
Styropor	92.05
Urethane (rigid)	88.52
Perlite	89.44
Extruded polystyrene	89.42
Urethane (roof deck)	90.16

Energy savings

The energy saving using optimal thickness for selected material is tabulated in Table 3. Styropor shows the highest energy saving (92.05%/m²) while fiberglass (rigid) has the lowest energy saving (85.53%/m²) compared to all insulation materials.

The Effect of Introducing an Air Gap

According to the brick industry association, an air gap is introduced to improve the insulation effect by retarding the heat flow into the building. The larger air gap is desired to protect the building from heat gain, hence reduced cooling load. However, a larger air gap size will affect the construction of the building wall and reduce the occupied space of buildings. The cavity or air space between walls should be between 50 mm and 114 mm. Air spaces less than 50 mm cannot practically be kept free from mortar bridging. Air spaces greater than 114 mm do not allow the normally prescribed ties to properly transfer lateral loads. Air spaces different from these can be used, but more care in design and construction would then be required. If larger air spaces were used then additional ties and/or thicker ties may be necessary (Brick Industry Association US, 1998). Styropor is the most economic insulation materials based on the results. Therefore, it is selected for the investigation of the air gap implementation. The effect of introducing air gap on the optimal thickness, life cycle cost saving potential of styropor is discussed in the following section.

Life cycle cost analysis

When there is no insulation, by solely introducing air gap, life cycle cost saving of 38.37%/m² walls, 44.98%/m² wall, and 50.31%/m² wall can be achieved by using an air gap of 2 cm, 4 cm, and 6 cm, respectively. Increased air gap tends to have higher cost saving. Table 4 shows the life cycle cost saving after introducing an air gap for styropor. Additional life cycle cost saving of 0.64%/m² wall, is obtained by applying a 6 cm air gap on styropor insulation at optimal thickness.

Energy saving

Potential energy saving of 38.37%/m² wall, 44.98%/m² wall, and 50.31%/m² wall can be achieved by applying air gap of 2 cm, 4 cm, and 6 cm, without insulation. The effect of introducing an air gap on energy saving for styropor is tabulated in Table 5. There is no significant effect on emission reduction when applying air gap on styropor insulation at its optimal thickness. This is because cost saving is achieved by reducing insulation cost, instead of energy savings.

Table 4 Life cycle cost saving of each air gap sizes for styropor

Insulation thickness	Life cycle cost saving (%/m ²)			
	No air gap	2 cm air gap	4 cm air gap	6 cm air gap
No insulation	0.00%	38.37%	44.98%	50.31%
Optimal thickness	84.74%	85.13%	85.26%	85.38%

Table 5 Energy saving for each air gap sizes for styropor

Insulation thickness	Energy saving (%/m ²)			
	No air gap	2 cm air gap	4 cm air gap	6 cm air gap
No insulation	0.00%	38.37%	44.98%	50.31%
Optimal thickness	92.05%	92.08%	92.04%	92.06%

Conclusion

In this paper, annual energy saving and life-cycle cost are calculated for ten types of insulation material in Malaysian building walls. The results indicated that insulation material improve the life-cycle cost savings which vary from 73% to 85%/m² wall, and energy saving vary from 85–92%/m² wall. Styropor insulation material is found to be the most economic insulation material, while fiberglass shows the lowest cost-saving material. In addition, introducing an air gap in the wall is important and only 6 cm air gap without insulation improve the life cycle cost saving up to 50.31%/m² wall. There is an additional 0.64%/m² cost saving is found by introducing 6 cm air gap to a styropor insulated wall. Finally, it can be said that thermal insulation in building a wall is important as it improves energy efficiency significantly.

See also: Optimization of Electrical Energy Usage in Two Secondary Schools Using Different Types of Glass Materials. Use of Bio-Fibers in Various Practical Applications

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Energy Efficient Composite Materials

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Background

Here history of materials is not related to their existence rather it relates to their functionality for human welfare. Material use started with stones well before 10,000 BC and the period was known as Stone Age. In that period human created different tools, weapons, and other commodities in crude form from stones. In the Palaeolithic era, it was realised that heavy and round objects could be easily displaced by rolling, hence, fallen trees were placed underneath large and heavy objects to act as rolling bearing for shifting goods from one place to another. It is well documented that potter's wheel was used in Mesopotamia (Iraq) in 3500 BC, at that period only wheel came into existence. The oldest wooden wheel was discovered in Ljubljana, Slovenia in about 3200 BC. It is the period when wheel was first used in chariots for transportation purpose. Later, it was replaced by spoked wheel, and for greater strength by iron rims and finally by a rubber wheel using compressed air which paved the way for automobile. Stone continues to be part of our life as a material for building and construction application. The seven wonders of the World are all of stone construction, and exhibit excellence in engineering and art. In about 3000 B.C. bronze was created by mixing tin and copper and it is called Bronze Age. Later zinc was also mixed in a small amount to make it more versatile for various applications. Though it was named gun metal but actually it was beginning of "age of alloys" and it laid the foundation of "material design". Later, it gave way to atomic energy, space flight, air travel, communications systems and microelectronic devices, buildings, vessels & commodity items, by different metal combinations. 2000 B.C. to 1100 B.C. is referred as Iron Age in which steel came into existence. Alloying of iron, heat treatment and secondary processing was used to enhance hardness, strength or toughness (Anonymous, 1906; Tylecote, 1992).

As time went by from different ages such as stone, wood, copper, iron to alloys, super alloys etc., the scientific community kept on exploring to develop new improved materials. Objective has always been to create something new or to improve existing one to have better efficiency of machines. It is well understood that metals and alloys do have limitations of properties but composites can be tailored to achieve wide range of properties to suit a particular application with better efficiency.

The range of application is very wide if we look for energy efficient materials and in one article it will not be possible to do justice while considering large number of applications. Hence, article will be restricted to energy efficient materials for limited tribological applications.

Tribological Components

Tribology is science and engineering of industrial components. The components are designed on reliability and durability criteria. In broader sense, components transmit power to achieve desired motion. Hence, the scope of wear and friction studies become wider, and depending on application aspect it can be classified as tribology of plain bearings, rolling element bearings, gears, rotary dynamic seals, space, automotive, diesel engine, rail transport, earthmoving, mining & mineral processing, marine equipment, manufacturing, magnetic storage devices, micro-electro-mechanical systems (MEMS), etc.

Applications With Conventional Materials

Sliding-Contact Bearings

Sliding-Contact Bearings are machine parts used to support moving shaft. These are designed in a way to transmit force between surfaces having relative motion. In sliding bearing, load is transferred among moving parts through sliding contact. Such bearings are also termed as plain bearings or bushings. Thrust and journal bearings are most widely used among all bearings (Bisson and Anderson, 1964; Neale, 1973; Booser, 1984; Fuller, 1984). In such bearings lubrication can be provided in any form such as gaseous, fluid or solid. Selection of material is crucial due to optimisation of properties like thermal conductivity, compressive & fatigue strength, ability to embed & conform and resistance to wear & corrosion. Moreover, the cost part cannot be ignored. Alone proper selection of material cannot stop wearing of parts for certain operating conditions but certainly delay the failure. Failure generally takes place by abrasive, adhesive or corrosive wear mechanism and or it may have combination of these mechanisms.

It's common to use unlubricated sliding bearings which result in high friction and wear loss. Though use of proper lubrication drastically reduces these losses. Lubrication regimes have a important role to play. There are three levels of lubrication:

- Boundary lubrication
- Full film lubrication
- Mixed film lubrication

In all the cases material selection which is based on metals, non-metals and their alloys is of prime importance (Ku, 1970; Neale, 1973; Booser, 1984; Fuller, 1984; Glaeser, 1992; Bhushan and Gupta, 1997). Precious metals, tin- and lead base babbitts, brasses & bronzes, cast irons, and aluminium alloys have been in wide use, whereas, among non-metals ceramics, cermets, graphites are important. Bi- & tri-metallic bearings with steel backings are also used as sliding bearing. In certain applications coated materials using different deposition techniques are also used (Ron Pike and Conway-Jones, 1992).

Rolling-Contact Bearings

Rolling-Contact Bearings have balls or rollers between two surfaces known as races or rings. The outer race is stationary and is mounted on bearing housing, while inner one is either carried by shaft or journal. The balls or rollers are held in angularity in a separator. These bearings have very less area of contact, hence, observe much less friction than sliding bearings. Due to low friction these are also termed as antifriction bearings. These bearing have very high load bearing capacity and stiffness. As the actual area of contact is very low (nearly zero), therefore, they face high contact stresses of the order of 500 MPa. (Bisson and Anderson, 1964; Neale, 1973; Booser, 1984; Harris, 1991; Zaretsky, 1992). Generally, grease or liquid lubricants are used with these bearings and in case of high temperatures or vacuum self-lubrication is essential. Rolling contact bearings generally fail by fatigue cracking/spalling leading to dislodging of large pieces from contact regions (Tallian *et al.*, 1974; Zaretsky, 1992; Summers-Smith, 1994). In cases of substantial sliding, surface damage takes place as scuffing or smearing abruptly changing adhesive mode of wear from mild to severe (Tallian, 1967; Scott, 1977).

SAE 52100 grade high-carbon chromium steel has been a standard bearing material with 58 HRC hardness. It also contains Mn, Si, Ni, Cu, and Mo in small amounts. It can work up to 200°C while high speed steels can be used up to 320°C. These steels are not suitable in corrosive media but AISI 440 C stainless steel can be used. Case hardened 4320 & 4360 AISI steels are also used in roller bearings (Neale, 1973; Bamburgh, 1980; Zaretsky, 1992; Bhushan and Gupta, 1997). In high-performance applications of high speeds and/or high temperatures silicon nitride is most suitable due to its almost three times hardness and less than half coefficient of friction of bearing steels. Further, its good fracture toughness and nature to maintain strength & oxidation resistance up to 1200°C, makes it a promising material (Bhushan and Sibley, 1982). Silicon nitride bearings are widely used in automotive, aerospace and defense industries. Silicon nitride ball bearings with steel rings called hybrid ball bearings are also used due to lower density, high rigidity, low friction and improved stiffness even though these are more expensive (Bhushan and Gupta, 1997; Harris, 1992). Though the material choice is of prime importance but lubrication aspect cannot be ignored because it:

- Forms a film between the rolling elements and raceways, rolling elements and cage etc. which minimises metal-to-metal contact, thereby, reducing friction and wear
- Contains a chemical additive that minimises wear and corrosion
- Also dissipates heat generated due to friction

Bearing failure could be caused by either of mechanisms namely adhesive wear, corrosive wear, abrasive wear, surface indentation, pitting or fatigue spalling or combination of these. Such situations arise due to inadequate supply of lubricant; hence, it is important to separate contacting surfaces effectively by hydrodynamic and elasto-hydrodynamic action (Harris, 1992).

Gears

Gears are very common machine parts, though, it looks simple but their effective design requires knowledge from several engineering disciplines. Gear designing depends on the requirements for a particular application. Depending on that geometry of gear, material, manufacturing route, heat treatment cycle, and lubricants are decided. From designing aspect resistance to scuffing & wear and reasonable strength is important. Gears are toothed wheels. These are designed to change rotation speed & transmit rotary motion from one shaft to another (Dudley, 1964; Merritt, 1971; Shigley and Mischke, 1989; Errichello, 1992). Hence, it becomes important to work on following factors:

- Geometry of gear tooth
- Kinematics of tooth motion
- Static and dynamic forces acting on gear tooth
- Physical and chemical aspect of tooth material
- Lubricant properties
- Environmental effects

Various types of gears may encounter different kind of stresses. Spur gears teeth are straight and parallel to the axis which transmit rotary motion between parallel shafts, while in helical gears teeth are not parallel to the axis of rotation and these are used for parallel and nonparallel shafts. The smooth transfer of load in helical gears from one tooth to another provides ability to transmit heavy loads successfully even at high speeds. In bevel gears rotational axes are not parallel. These are made for a shaft angle of 90° or any odd angle. These gears face Hertzian stresses just like rolling-contact bearings. Like different kind of stresses lubrication regimes are also different for gears. Overall situation provides likelihood of typical failure modes such as abrasion, corrosion, pitting, scuffing, surface fatigue, scoring, etc. Hard materials are preferred to take care of high Hertzian stresses at contact

points (Coleman, 1970; Lee and Cheng, 1991; Dudley, 1964; Merritt, 1971; Neale, 1973; Bhushan and Gupta, 1997). Gear wear is reduced by suitable heat treatments or thermochemical treatments and appropriate use of coatings can minimise wear losses in gears. Most widely steels are used as gear material in power transmission applications, however, cast iron, bronze, non-metallics, aluminium, brass, zinc, and plastics materials are also used in different applications.

When contact stresses are very high failure takes place by micro-pitting or pitting due to Hertzian fatigue. To prevent pitting in gearsets the following points are recommended (Ueno, 1980; Winter and Weiss, 1980; Shipley, 1982):

- Reduce contact stresses by load reduction or optimal gear geometry
- Use high hardness carburised and clean steel
- Use of smooth tooth surfaces
- Use of clean, dry and cool lubricant with adequate viscosity and amount

Failure also takes place by mild adhesive wear. When new gears are used first time, manufacturing inaccuracies may restrict optimum contact between the gear teeth. Adhesive wear occurs during running-in and it subsides with time. This wear is beneficial if it smoothens the tooth surfaces and increases the area of contact by removing minor imperfections. But once bending fatigue becomes possible, extent of wear is treated as excessive. It has been observed that high lubricant viscosity has maximum effect in reducing slow-speed adhesive wear (Winter and Weiss, 1980), but presence of sulphur and phosphorus increases the wear significantly. The adhesive wear in gearsets can be minimised by (Errichello, 1992):

- Smooth tooth surfaces
- Operating new gearsets first 10 h with half the load
- Avoiding sulphur & phosphorous and any other contamination in lubricants

Contamination of the lubricant by hard and/or sharp particles causes abrasive wear failure. It is common to have sand, grinding dust, machining chips, etc. in new gearboxes. It is important to drain these out. All maintenance procedures must be performed with care to prevent any kind of contamination in gearbox. Hence, to prevent abrasive wear in gearsets (Errichello, 1992):

- Contamination from new gearboxes must be drained
- Surface-hardened smooth gear teeth should be used with high-viscosity lubricants to minimise internally generated wear
- Tight oil seals should be used
- Lubricant must be changed after every 2500 h

Polishing wear may also lead to failure of gear if additives in the lubricant are chemically too reactive. It may create a good looking bright gear with inaccurate result. Anti-scuff additives form iron-sulfide and iron-phosphate films in gear teeth area having high temperatures. If the rate of reaction is too high continuous removal of the surface films leads to high polishing wear. It can be prevented by less chemically active additives such as potassium borate (Errichello, 1992).

Scuffing is localized damage by metal transfer due to solid-phase welding and fracture of sliding surfaces. It occurs in any sliding or rolling contact due to insufficient lubricating film failing to separate the surfaces. It ends up with rough, and torn surfaces. Nitralloy 135 M has very high resistance to scuffing, while stainless steels and anodized aluminium have very poor scuffing resistance. To restrict failure due to scuffing (Errichello, 1992):

- Smooth tooth surfaces should be used
- Gear teeth should be protected during the critical running-in period by coating
- Lubricants with high-viscosity and anti-scuff additives should be used
- Coolant should be used
- Gear tooth geometry should be optimised

Seals

The primary function of seals is to limit the loss of lubricants and to restrict system contamination due to environment. Seals can be static and dynamic. Static seals such as gaskets, O-ring etc. are used in static openings while dynamic seals like labyrinth, floating ring, ferrofluidic, mechanical face, lip and abradable seals are used in system with moving fluids (Lebeck, 1991). Lubrication of the sealing interface varies from hydrodynamic lubrication to zero lubrication.

In order to prevent asperity contact and to minimise wear, seal must be provided with hydrodynamic film lubrication with a thickness sufficient enough to prevent asperity contact. The seal contact pressure should be enough to balance pressure difference between the process fluid and the atmosphere. This way leakage, friction and wear all can be minimised (Iny, 1971; Snapp and Sasdelli, 1973; Mayer, 1970). When a lip seal is used on a steel shaft to seal mineral oil, as long as proper lubrication and proper pressure conditions are maintained wear is minimum and takes place only at start-stop conditions with almost infinite life of seal. However, with time abrasive particles get introduced in the oil, and act as third body wear. In this case to reduce wear the frequent change of oil is required to delay or prevent losses.

Abrasion occurs due to suspended particulates in the lubricating oil, wear debris due to inadequate lubrication, corrosion products, dust, or poor surface finish. Glass or asbestos fibers used in seals may create grooves. Adhesive wear occurs when the asperities of different surfaces observe welding and fracture phenomena. Asperities of softer material are sheared off forming

debris. Cavitation may occur when pressure difference causes bubble formation. These bubbles may expand and explode detaching the particles from the surface leading to leakage and failure (Haardt, 1974; Beatty and Hughes, 1990; Shapiro and Colsher, 1971). In different operating conditions failure may also take place by corrosion or fatigue. Hence, the main failure modes of seals are adhesion, abrasion, erosion, corrosion and fatigue (Neale, 1973; Johnson and Schoenherr, 1980; Stair, 1984). Material choice depends on design and operating conditions. In different working conditions materials such as alumina, tungsten carbide, silicon carbide, boron carbide, cemented carbides, babbitts, bronzes, graphites, thermoplastics, elastomers, Ni-resist iron, tool steel, hard-faced steel, Monel, Hastelloys, Stellite), PTFE, polyimide, or phenolic composites, silicone, fluoro-silicone have been widely used. The main prerequisites for seals are hardness and/or high abrasion resistance (Paxton, 1979; Stair, 1984; Bhushan and Gupta, 1997; Dray, 1992).

Role of seals is very crucial in systems (i) when it acts as pressure boundary between components like piston and cylinder having contrast of pressure, (ii) while preventing mixing of two incompatible fluids and (iii) when one component in contact has different nature such as static and dynamic (Dray, 1992).

Cams and Tappets

Cams and Tappets are widely used in engineering systems like automotive valve trains or textile machines to transform reciprocating sliding motion to rotary motion or vice versa. Contacts are generally points or line but they become rectangular and elliptical contact areas with load conditions. There is mix-up of rolling with sliding motion in rolling direction. These also wear in very similar modes those of gears. These may encounter mild adhesive wear, abrasive wear or scuffing due to fatigue wear (Neale, 1973; Lee and Cheng, 1991). The wear of cams and tappets could be minimised by hard material or surface hardening of steels by coating etc. Grey hardenable cast iron with Cr, Mo, and Ni is a commonly used tappet material in automotive applications. Hard coatings of titanium nitride/carbide by PVD and CVD technique can be used to minimise coefficients of friction and wear.

Piston Rings

Piston Rings act as sealing agents to lubricants in reciprocating rods, pistons, piston plungers, etc., inside cylinders. These are placed in the grooves of the piston to act as moving seal between the piston and the cylinder bore to retain lubricants intact. There are two types of piston rings i.e., compression and oil-control. Compression rings are used close to top portion of the piston to restrict downward movement of gases from the combustion chamber while oil rings are placed below compression rings to prevent the spilling of excess lubricant into the combustion chamber (Neale, 1973). Piston ring material should have low friction coefficient with mating surface having good resistance to wear and scuffing, good running-in wear behaviour, tolerance to marginal lubrication and fast changes in environmental conditions. Its performance should be consistent with reliability and low cost.

Grey cast iron is widely used for compression and oil rings. In the heavy-duty engine applications, chromium molybdenum iron, spheroidal graphitic iron, malleable iron and even some ball-bearing steel are also used. Chromium coated rings are used to improve resistance to corrosion, oxidation and wear. With this friction is also reduced. Plasma-sprayed Mo, Mo-Cr- Ni alloy, and chromium oxide have also been used to improve scuffing resistance (Neale, 1973; Scott *et al.*, 1975; Taylor and Eyre, 1979; Ting, 1980; Bhushan and Gupta, 1997). To increase cylinder liner strength Ni, Cr, Cu, Mo, Ti, and V are added in grey cast iron. Use of steel cylinder liners have added advantage that the walls can be made much thinner. In order to have high hardness to counter scuffing they also need hard Cr plating. But to keep friction coefficient low Cr plated liners should not be used against Cr plated piston rings. In recent years, Al-Si cylinder liners have replaced other liners due to lightweight and superior properties (Taylor and Eyre, 1979; Ting, 1980). Non-metals are used for unlubricated piston rings to avoid metals tendency to weld under dry sliding conditions (Scott *et al.*, 1975; Fuchsluger and Vandusen, 1980). Plastics, carbons, and ceramics are extensively used non-metals.

Brake

Brake lining material used for brake systems are termed as friction materials. These are needed for different grades of vehicles such as passenger cars, drum and disk brakes for light or heavy trucks etc. Wear aspect of brakes is more sensitive to road conditions rather than friction of brake. These systems have to face high pressure as well as temperature. Flash temperature may go as high as 1000–1100°C. Internally expanding shoes with brake linings are used in drum while disk brakes use shoes that load a much smaller portion of disk rubbing surface. Disk brakes cool faster due to larger exposed surface but are more vulnerable to contamination. Three types of friction materials such as organic, metallic, and carbon have been in use. Asbestos, non-asbestos with fibers, semi-met organics, copper or iron based, sintered bronze and mullite, sintered iron with graphite, have been used in lining of automobiles. Brakes need to operate under different conditions. Heavily loaded automobiles on steep slope need hard brake while on highways there is minimal brake usage. In all cases brakes should be reliable and these should not get affected by environment and working conditions (Anderson, 1992).

Other Applications

Tribology of magnetic storage devices, automotive, railroads and aircrafts parts with relative motion are of prime importance (O'Connor *et al.*, 1968; Neale, 1973; Peterson and Winer, 1980; Booser, 1983; Bhushan, 1996, 2001; Bhushan and Gupta, 1997). Internal combustion engines which are backbone of automotive industries are almost perfect choice for use in automobiles (Rogowski, 1953; Taylor, 1966, 1968; Crouse, 1970; Judge, 1972; Heywood, 1988). In IC engines, fuel is burned and energy produced provides linear reciprocation motion to piston in its cylinder and by connecting rod to crankshaft by rotating motion. The crankshaft attached to the drive shaft provides power to wheels for movement. Nowadays, four stroke engines are common, however, some two stroke engines are also used (Rogowski, 1953).

An automobile engine is composed of number of parts and these parts face different environment and working conditions, accordingly the material choice is made. Cylinder blocks, piston, piston rings have already been discussed. Among other parts, crankshaft is made from forged steel/nodular cast iron. Forged steel or hardenable irons are used for cams, tappets, rocker arms, and also for camshafts. Forged alloy steel works well for valves. While connecting rod bearing are made from copper alloys, tin or lead babbitts and aluminium alloys. Above all the proper lubrication is key to long life of the engine (Chamberlin and Saunders, 1983; Heywood, 1988).

In last thirty to forty years serious efforts have been made to reduce emissions and improve fuel economy to meet stringent legislated emissions norms and Corporate Average Fuel Economy (CAFE) standards. These include (Kovach *et al.*, 1982; Davis, 1992):

- Reduction in vehicle weight and to reduce aerodynamic resistance improvement in exterior
- Downsizing of engine to reduce the power-to-weight ratio
- Design improvements with a view to improve efficiency with weight saving
- Drive-train improvements such as friction losses
- Advanced exhaust system to meet emission norms
- Maximizing fuel economy with minimum emissions
- Reduction in chassis friction and tire rolling resistance
- Use of lightweight, durable ceramics and ceramic coatings

Further, fuel economy goals have led to improvement in designing to achieve improved tribological performance. Studies indicate 1%–2% fuel economy improvement in four-cylinder engine with 6.9 kPa mean effective pressure reduction in engine friction. In order of importance major engine friction components are piston ring assembly, valve train, crankshaft bearings, oil pump etc. (Kovach *et al.*, 1982).

In all reciprocating engines some kind of lubricating oil is used. Viscosity of the oil is important issue. If oil with proper viscosity is not chosen or oil gets deteriorated during service, it causes wear to pistons cylinders/ cylinder liners, piston rings, camshafts, valve trains, etc. Water vapour generated due to combustion carries corrosive gases. If these gases are settled on engine parts, they readily form acids and cause severe corrosive wear. Other modes of wear such as adhesive wear and scuffing in cylinder liners and piston rings, abrasive wear in cams, tappets and rocker arms, and pitting due to fatigue wear in cams and tappets may also take place (Lyman, 1961).

In IC engines, piston and piston ring assembly contribute largest share in terms of wear and friction losses and it is almost 25%–75% of total engine losses (Lichty, 1951; Pinkus and Wilcock, 1971; McGeehan, 1978). Hence, there has been a shift from steels to aluminium silicon alloys (Kearney, and Rooy, 1990).

Energy Efficient Materials

Advanced composite materials have proven capability over conventional materials to an extent that these have been accepted in a number of engineering applications. Advanced polymer-matrix composites were judged as potential industrial material in 1940–41 when fiber-reinforced plastics were examined for aircraft applications at Wright-Patterson Air Force Base and aft fuselage of the Vultee BT-15 trainer aircraft was designed and fabricated in composites. It proved to be about 50% stronger than existing construction. Since then, advanced composite materials have found large number of applications in aerospace, space, marine, automobiles, sports, recreation equipment specially to enhance the performance. In last 60–65 years, scope of composites has increased tremendously and it is getting widespread & diverse usage in all walks of life (Hunt, 2001).

Production of metal-matrix started in 1970s and since then these have also gained importance even in specialised applications like space shuttle, Hubble telescope, aerospace, automobile parts brakes, drive shafts, and cylinder liners. Their tailoring capability has also increased their scope in electronic packaging and thermal-management applications. Market trends suggest growth in MMC market and cost cutting is indicative of bright future (Hunt, 2001).

CMCs are proving their worth in applications like cutting tool inserts and wear-resistant parts of aerospace and military equipment including engines and energy-related applications. Though these are high performance but presently are very expensive. However, their stability at high temperature and high corrosion resistance has made them attractive in aerospace and industrial sectors (Hunt, 2001).

For last twenty years MMCs have established themselves in commercial production of automotive parts due to combination of properties like high specific stiffness, good wear resistance and light weight along with improved high-cycle fatigue resistance (Allison and Cole, 1993; Hunt, 2001). Though the cost part is still higher for discontinuously reinforced aluminium (DRA) but with time wider applications of this technology with performance improvements and new processing ideas will cut down the cost. Tables 1 and 2 provide comparison of mechanical and wear properties of some AMC and corresponding alloys. Improvement in properties is evident on incorporation of reinforcement but ductility part is not very satisfactory.

Applications of Energy Efficient Materials in Engines

Pistons

During service pistons have to go through extreme dynamic thermal and mechanical conditions. These must be capable to resist cyclic mechanical loading even at high frequencies of about 100 Hz, which means they must have excellent fatigue resistance. Maintaining highest degree of combustion pressure requires tight tolerance of piston with the cylinder and piston material should also be able to withstand ring groove pounding. Further, dynamic strength with excellent wear resistance is important for long life. Piston material should be able to resist temperature of about 300°C without deformation of the dome. To minimise thermal stresses caused by thermal gradients and thermal cycling high thermal conductivity is desirable. Also the coefficient of thermal expansion of piston top plate and ring groove region must be comparable to cylinder (Kevorkijan, 1999; Hunt, 2001).

Production of diesel engine pistons made up of aluminium matrix composite (AMC) by Toyota Motors, Japan was a major breakthrough which was brought into commercial production by Japan in 1983 (Donomoto *et al.*, 1983). These pistons consisted of chopped fiber preform only in the ring groove region which was very prone to wear and thermal fatigue. The selective reinforcement of Al-alloy provided remarkable improvement in wear resistance. Permanent die mould was used to place chopped fiber preform and infiltration technique was used under pressure with molten metal to prepare aluminium matrix composite pistons. The squeeze casting technique provides high quality parts at low cost. With this technique high production rate of 100,000 parts per month could be maintained (Kevorkijan, 1999). The important feature is that the low coefficient of thermal expansion of AMC which also permits redesigning of piston with tight tolerance. This overall change has led to high combustible pressure with improvement in heat transfer properties (Rittner, 2000). The decreased density of piston with AMC also provides improved performance. The single step squeeze casting process, with reinforced top plate and ring groove material has also reduced overall cost as compared to earlier one. Though, on unit basis the cost of AMC seems to be higher but overall cost reduction is achieved due to selective reinforcement and simple technique of production to which performance improvement is an added advantage.

The use of metal-matrix composite piston with selective reinforcement has not been considered widely in U.S. market because in North America size of diesel engines is larger and operational speeds are lower. As a result, fatigue and wear requirements are not very stringent, and so the advantages are not as compelling. Nonetheless, metal-matrix composites pistons provide a strong advantage in Asian and Western European designs, and continued growth is expected in this area. For example, Mazda Ford Motor Company introduced a selectively reinforced piston produced by a low pressure die casting process in 1998 (Rittner, 2000). SiC whisker/particulate reinforced aluminium forgings in racing engine applications are few other piston applications. Lower coefficient of thermal expansion of the MMC reduces clearances between the piston and cylinder wall. In certain cases, an order of magnitude reduction in the specified clearance may be possible (Rittner, 2000). MMC pistons have exhibited better performance as compared to conventional hypereutectic aluminium-silicon alloys in drag racing bikes (Harrigan, 1994; Hunt, 2001).

Cylinder Liners

Increased applications of aluminium/aluminium alloys engine blocks has made it imperative to have protective cylinder liners. Many of the reasons fall in line with aluminium/aluminium alloys pistons use as have already been discussed in previous section. Since very beginning cast iron has been most widely used material for inserts as well as for engine blocks due to good wear resistance with high performance. Even today, it holds the largest share. Now primary considerations are changing in order to improve efficiency which requires materials with high thermal conductivity and low density. That has caused switching over of liner materials from cast iron to aluminium alloys/composites. Honda Prelude 2.3 liter engine brought industrial revolution for AMCs cylinder liners in 1990 (Hamajima *et al.*, 1990). The AMCs cylinder liners were produced by infiltrating molten aluminium in hybrid preform of carbon and alumina while pressure squeeze casting engine block. With this process one also gets rid of need of separate liners and number of assembling steps as well as parts to be assembled are also reduced (Hunt, 2001).

Introducing AMCs in this application brought about a dramatic weight reduction of about twenty percent with improved wear resistance as compared to cast iron that definitely improves engine efficiency (Kevorkijan, 1999). Further, better thermal conductivity of AMCs also allows lower operating temperatures and extended engine life. It is also important to note that AMCs liners are much thinner as compared to cast iron liners that increases engine displacement. Large number of such engines have been produced so far. Honda has introduced AMCs liners even in their sports edition S2000, in Porsche Boxter and premium version of Acura NSX (Rittner, 2000). Engine of Toyota Celica also introduced AMCs liners and large number of units are on the road. High performance bikes of Honda are also using MMC liners (Kevorkijan, 1999; Hunt, 2001).

Table 1 Mechanical properties of alloys and composites

Sr. no.	Materials		Mechanical Properties						References
			YS (MPa)	UTS (MPa)	%Elongation	Hardness	Strain hardening exponent, <i>n</i>	Strength coefficient, <i>K</i> (MPa)	
1	AA5052-Al ₃ Zr composites	AA5052 alloy	59	89	6.08	28.47 (BHN)			Gautam and Mohan (2016)
		10 vol% Al ₃ Zr	64.4	106.2	12.88	35 (BHN)	–	–	
		12.5 vol% Al ₃ Zr	78.1	110	11.5	37.32 (BHN)	–	–	
		15 vol% Al ₃ Zr	84.6	118.5	11	39.43 (BHN)	–	–	
		20 vol% Al ₃ Zr	69.2	110.5	7.5	43.20 (BHN)	–	–	
2	AA5052-ZrB ₂ composites	30 vol% Al ₃ Zr	66.5	103.6	2.4	52 (BHN)	–	–	Gautam <i>et al.</i> (2016a)
		1.5 vol% ZrB ₂	–	103	25	36 (BHN)	–	–	
		4.5 vol% ZrB ₂	–	139	14.4	39 (BHN)	–	–	
		7.5 vol% ZrB ₂	–	155	13.6	44 (BHN)	–	–	
		3 vol% ZrB ₂	70	128	16.23	38 (BHN)	0.18111	220	
		6 vol% ZrB ₂	89	153	14.3	41 (BHN)	0.16258	254	
		9 vol% ZrB ₂	112	161	12	48 (BHN)	0.14603	280	
		10 vol% ZrB ₂	111	142	7.7	52(BHN)	0.12477	248	
3	AA5052/(Al ₃ Zr + ZrB ₂) composites	10 vol% Al ₃ Zr + 1 vol% ZrB ₂	92.5	134.5	18.74	38 (BHN)	0.128	200	Gautam and Mohan (2015)
		10 vol% Al ₃ Zr + 3 vol% ZrB ₂	116.5	150.3	13.01	47.47 (BHN)	0.088	208	
		10 vol% Al ₃ Zr + 5 vol% ZrB ₂	106.7	124.2	5.62	50.32 (BHN)	0.1	198	
4	Al-Fe composites	Al-1.67% Fe	59	142	32	95 (VHN)	–	–	Srivastava and Mohan (2011)
		Al-3.36% Fe	70	153	30	131 (VHN)	–	–	
		Al-6.23% Fe	74	159	27	163 (VHN)	–	–	
		Al-11.2% Fe	83	184	17	179 (VHN)	–	–	
5	Al-fly ash composites	10 vol% fly ash		129	4	67 (BHN)	–	–	Sarkar <i>et al.</i> (2014)
		2%Si + 10 vol% fly ash		145	3	70 (BHN)	–	–	
		2%Mg + 10 vol% fly ash		159	2	86 (BHN)	–	–	
6	Al-graphite composites	0.5 wt% Gr	64.3	133.2	21	39 (BHN)	–	–	Mohan <i>et al.</i> (2002)
		1 wt% Gr	66.1	135.4	19.2	41.2 (BHN)	–	–	
		1.5 wt% Gr	61.4	128.1	18	44.3 (BHN)	–	–	
7	Al-SiC composites	0.6% SiC	179.1	234.5	1.9	77 (BHN)	–	–	Pathak <i>et al.</i> (2006)
		1.5% SiC	155.6	254.7	1.7	89 (BHN)	–	–	
		2.2% SiC	192.3	261.2	1.2	96.3 (BHN)	–	–	
		12 wt% B ₄ C	–	215	–	58.6 (BHN)	–	–	

Table 2 Tribological properties of alloys and composites

Sr. no.	Materials		Wear rate, $\text{m}^3/\text{m} \times 10^{-12}$ (at 20 N Lad, 1 m/s sliding velocity)	Coefficient of friction (COF) (at 20 N Lad, 1 m/s sliding velocity)	References
1	Al-Al ₃ Zr composites	AA5052 alloy	2.93	0.33	Gautam and Mohan (2016)
		10 vol% Al ₃ Zr	2.51	0.43	
		12.5 vol% Al ₃ Zr	2.36	0.44	
		15 vol% Al ₃ Zr	2.22	0.46	
		20 vol% Al ₃ Zr	2.03	0.49	
		30 vol% Al ₃ Zr	1.71	0.52	
2	Al-ZrB ₂ composites	1.5 vol% ZrB ₂	1.23	0.39	Kumar <i>et al.</i> (2016)
		4.5 vol% ZrB ₂	1.19	0.41	
		7.5 vol% ZrB ₂	0.98	0.43	
3	Al ₃ Zr + ZrB ₂ composite		1.57	0.48	Mohan <i>et al.</i> (2016)
4	Al-Fe composites	5 wt% Al ₃ Fe	5.23	0.19	Agrawal <i>et al.</i> (2014)
		10 wt% Al ₃ Fe	3.58	0.24	
		15 wt% Al ₃ Fe	2.89	0.30	
		20 wt% Al ₃ Fe	2.45	0.36	
5	Al-SiO ₂ composites	5 wt% SiO ₂	12.75	–	Mohan <i>et al.</i> (2016)
		10 wt% SiO ₂	1.77	–	
		15 wt% SiO ₂	9.11	–	
		20 wt% SiO ₂	10.92	–	

Valves

Working of intake and exhaust valves is very crucial in automotive engines. They coordinate the transportation of the air-fuel mixture for combustion as well as exhaust gases. In this course of action, they have to face high frequency mechanical loading, hence, good fatigue properties are very important. The valves have to go through very adverse environment, hence, requires good sliding wear resistance in valve guide. The neck faces the maximum stress due to high gas temperatures of about 900°C in exhaust valve region so requires high creep resistance. Further, exhaust valve also requires good oxidation resistance due to oxidizing compositions of the gases. Finally, the valve also undergoes hammering forces at high frequency which could result in galling/adhesion on the valve seat so it is important to have resistance against galling. Typically, low cost austenitic steels are used for automotive valves applications so these have relatively high mass. Functioning requires high spring forces so as to maintain continuous contact between the valve follower with camshaft lobe. The high rpm requires good amount of spring mass. The high force due to spring causes high degree of friction force on the cam, tensile stress at neck, and the contact forces at cylinder head. It results in loss of energy required to compress the springs and overall fuel efficiency is decreased.

Toyota Altezza 2.0 liter I-4 engine was the first one to replace austenitic steel valves by discontinuously reinforced titanium (DRTi) composite in 1998 (Froes and Jones, 1999). This DRTi was prepared by a powder metallurgy route using powders of titanium hydride, matrix alloys, and titanium di-boride (Saito, 1995). All powders were blended thoroughly, pressed in die and finally sintered. During sintering TiB₂ reacted to form stable titanium mono-boride. Homogenization and densification also took place during sintering step. Sintered billets were extruded followed by upset forging to be processed into valves. Ti-6Al-4V and Ti-6.5Al-4.6Sn-4.6Zr-1Nb-1Mo-0.3Si alloys were used for intake and exhaust valves respectively (Froes and Jones, 1999; Saito, 1995). Endurance testing at high rpm of 10,500 is also part of rigorous certification. Since the introduction of the Altezza, large number of DRTi valves have been produced and no defective units were reported. A set of DRTi valves reduces weight by about 40 percent i.e., about 270 g (Froes and Jones, 1999). In addition, including valve spring mass total engine weight reduction is around 380 g. With these composites, cam contact frictional forces and the energy required to compress the springs are also reduced. Initially, the cost of the DRTi valves was about twice as compared to steel and likely to decrease with volume of production i.e., with full-scale production. Yamaha Motor Corporation also took up DRTi valves in their large volume motorcycles production (Hunt, 2001).

Pushrods

Cylindrical pushrods are used to transfer motion from cam to the valve train in OHV engines. An eight-cylinder OHV engine has sixteen pushrods of ultra-high-strength steel. Pushrod essentially transfers desirable motion from cam to valves. High engine rpm limits behaviour of engine which includes pushrod flexure, valve toss or lofting as a result of contact problem. Flexure, lofting, and valve bounce affect engine performance, whereas, severe vibrations limit the life of valvetrain components, especially springs. These problems can be overcome by using low density and high damping capacity materials (Hunt, 2001).

In recent years, conventional 4340 steel pushrods materials has been replaced by fiber-reinforced aluminium matrix composites are now used in high-performance OHV racing engines for pushrods. The 60% of Nextel 610 Al₂O₃ fibers is infiltrated with an

aluminium matrix. 3M Corporation has produced this material for producing hollow pushrods of different diameters. In these pushrods fibers are axially aligned along the pushrod length. Ends of the AMC tubes are bonded with hardened steel end caps. These aluminium composite pushrods have double the damping capability along with 25% superior bending stiffness while comparing with conventional 4340 steel pushrods (Mendelson, 1996). Further, less than half density of AMC as compared to steel increases the engine speed by nearly 250–400 rpm before valve bounce starts. Superior damping capacity of AMC pushrods improves the spring life by six times (Mendelson, 1996). Higher life of valvetrain springs also provides cost benefit. Further benefits can be achieved by optimisation of cam design (Hunt, 2001).

Connecting Rods

There has been a focus on improvement in drivetrain components, especially connecting rod (Harrigan, 1994). The secondary shaking forces which are mostly observed in small engines are minimised to a larger extent by mass reduction of connecting rod/piston assembly. In addition, lower reciprocating loads also have lesser load effects on crankshaft and less friction losses. This improves performance with increased fuel efficiency (Allison and Cole, 1993). It is important to note that every unit of weight reduction from the connecting rod helps to reduce almost seven times from supporting load (Rittner, 2000). MMC connecting rods applications in high volume vehicles have not yet been introduced because getting an MMC with combination of low cost and high-cycle fatigue performance has been difficult so far. Though hot forged AMC connecting rods have successfully been produced and tested but with reasonably high cost of production, hence, further cost reduction is required (Hunt, 2001).

Brake System Applications

High thermal conductivity and excellent wear resistance of AMCs offer them as a very useful replacement to cast iron in brake system applications. AMCs can provide 50%–60% weight savings in disk brake rotors and brake drums. The weight reduction is unsprung, hence, inertial forces are also reduced, and that further, reduces fuel consumption providing an additional benefit. AMC rotors also increase acceleration and reduce braking distance. It is also reported that AMC rotors have less brake noise and wear, and as compared to cast iron rotors they provide a uniform friction over the entire testing sequence (Allison and Cole, 1993). Aluminium matrix composites brake rotors and drums can be successfully produced by gravity casting method. Aluminium-magnesium and aluminium-silicon alloy matrices have been used with 20 vol% of SiC and/or Al_2O_3 particle reinforcements. Several automobiles companies are using AMC brake parts. The Lotus Elise used four discontinuously reinforce aluminium brake rotors in vehicle and Plymouth Prowler has also used it for rear wheels. Discontinuously reinforced aluminium rotors have attracted lightweight automobiles makers and are used in few editions of Volkswagen and Audi. In addition, now number of electric and hybrid vehicles are also using AMC brake components (Hunt, 2001).

Discontinuously reinforced aluminium brake rotors are now being used in trains such as Inter City Express (ICE), high-speed trains, etc. MMCs brake discs are also used in ICE-1 and ICE-2 train. Application of higher-priced AMCs in automotive racing applications is also in practice, where improved performance is important. Brake calipers for Formula 1 race cars produced from a 2124/SiC/ 25p AMC provide much less displacement, high leverage, and much faster stops, due to high stiffness of the material (Hurley, 1995). AMCs brake pads are also used in conjunction with the Porsche ceramic-matrix composite brake rotors (Hunt, 2001).

Driveshaft Applications

AMCs provide higher specific stiffness in the driveshaft as compared to conventional materials. Currently driveshafts have restriction of speed at which shaft may become dynamically unstable irrespective of material used. This critical speed of the driveshaft depends on the specific stiffness, length and also on outer and inner radius. There are vehicles which have packaging constraints and increased driveshaft diameter is not possible. AMCs may provide desirable solution in the form of longer driveshaft lengths at a given diameter, or vice-versa. This situation is generally faced in large passenger or luggage carriers, where due to length restrictions, two-piece driveshaft has to be used. So, replacement of two piece driveshaft by single DRA driveshaft provides a direct reduction in weight as well as cost. Further, it also reduces weight and cost associated with the support structure used for two piece driveshaft, and reduces the mass needed for corrective counterweights as well as for balancing. Around 9 kg of weight is decreased (Rittner, 2000). Hence, driveshafts of 6061/ Al_2O_3 produced by stir casting and with subsequent extrusion into tube have been used. DRA driveshafts were introduced in some versions of Chevrolet and GMC pickup trucks. Later, DRA driveshafts became standard for Chevrolet Corvette. AMC driveshaft are also used in police interceptor version of Ford (Hunt, 2001).

Other Applications

AMCs are widely used in number of application such as brackets, pulleys, brake calipers, pump housings, turbocharger & supercharger compressors, and suspension systems (Allison and Cole, 1993). In addition, these are also used in suspension pushrods, clutch parts,

rockers, gearbox and other engine parts (Hurley, 1995). Discontinuously reinforced titanium may also be considered for some of the applications. 6061/Al₂O₃ drawn wire has been used in manufacturing snow tire studs. In Finland, MMC tire stud jackets have been successfully applied since 1990s, and represent an annual market of about 150 metric tonnes (Rittner, 2000; Hunt, 2001).

Conclusions

Growth of MMC/AMC market has been appreciable in last few decades particularly in automotive sector. Number of important applications specially performance oriented have emerged due to weight saving because benefits have over powered component cost. Performance has improved drastically due to better thermal properties & wear resistance and low coefficient of thermal expansion. But still there is need of new materials which could exactly fit into the application so that larger volumes could be generated for cost cutting. Further, for market growth stern environmental emission norms and fuel efficiency part needs to be given proper attention so that growth rate in existing applications could be improved and new avenues could be opened-up.

From last few decades, possibility of MMCs is also being explored in applications related to commercial and military aircrafts such as aero-propulsion systems and in aeronautical subsystems. Newly developed MMCs are also paving way for numerous structural and thermal management system applications. The excellent combination of specific strength with stiffness relative to existing structural materials is putting MMCs in driving seat for several aeronautical applications. DRAs and DRTi have gained importance due to high specific stiffness, fatigue resistance, damage tolerance, and durability. In terms of life cycle, MMCs also provide significant cost reductions that could provide them a wider platform from application point of view.

See also: Eco Friendly Aspects in Hybridization of Friction Stir Welding Technology for Dissimilar Metallic Materials

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Environmental Analysis Waste Management Model

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Introduction

Flood risk and waste management has come under serious consideration by many different groups in recent times. The creators' group originates from a software engineering foundation, and especially from the range of information administration and investigation. It is elusive data and current examination chips away at information administration and investigation for flood risk and waste assessment. One of the principles is that such works have been distributed in an extensive variety of discussions (Saito, 2014; Kenley *et al.*, 2014). Consequently, we chose to tackle the errand of finding and sorting out this information so as to uncover the best in class research. We concentrated on different sources, extending from diary distributions to government reports, and met with neighborhood flood and waste management authorities, to think of an arrangement of future examination headings for researchers – particularly from the ranges of information administration and investigation – that will significantly advantage flood risk and waste management groups. That is, we endeavor to extend fundamental research and practice in this area (Abosuliman Shougi *et al.*, 2014). The Federal Emergency Management Agency (FEMA) classifies disasters as Natural (e.g., earthquakes, hurricanes, floods, wildlife fires etc.) or Technological (e.g., terrorism, nuclear power plant emergencies, hazardous materials etc.) (Rieu-Clarke, 2018). Other order plans exist, yet whatever the reason, certain components are attractive for administration of all disasters:

- Prevention,
- Advance warning,
- Early detection,
- Analysis of the problem, and assessment of scope,
- Notification of the public and appropriate authorities,
- Mobilization of a response,
- Containment of damage,
- Relief and medical care for those affected.

Further, flood risk and waste management can be separated into the accompanying four stages: (a) Preparedness; (b) Mitigation; (c) Response; and (d) Recovery. Mitigation efforts are long-term measures that attempt to prevent hazards from developing into flood risk and waste altogether, or to reduce the effects of flood risk and waste when they occur (Schanze *et al.*, 2006; Wang *et al.*, 2015).

Flood Risk and Waste Data Management and Analysis Challenges

The significance of opportune, exact and successful utilization of accessible data in flood risk and waste management situations has been broadly talked about in writing. Data administration and handling in flood risk and waste management are especially testing because of the one of a kind mix of qualities (individual attributes show up in different spaces also) of the information of this area (Kar *et al.*, 2015; Chandanala *et al.*, 2013). The information that are accessible for flood risk and waste management comprise of the accompanying:

- News articles/declarations: these are mostly message information with extra characteristics on time and area, and so forth.
- Business reports,
- Remote detecting information,
- Satellite symbolism information and other interactive media information like video.

The Information Science in Flood Risk and Waste Management

The administration of flood risk and waste management information includes the incorporation of different heterogeneous sources, information ingestion and combination. Information may have static or spilling nature. The data investigation of flood risk and waste management information includes the use of all around concentrated on data advancements to this one of a kind space (Jacobsson *et al.*, 2011; Neal *et al.*, 2012). The information examination advancements that we will audit for surge hazard and waste – related circumstances are:

- Information extraction,
- Information retrieval,

- Information filtering,
- Data mining,
- Decision support.

Flood Risk and Waste Management Workflow

There are distinctive sorts of groups that require flood risk and waste data management devices and frameworks to cover the present circumstance, offer foundation and asset information, and trade other crisis interchanges (Chang *et al.*, 2012). From the point of view of the crisis administration group, authoritative performing artists incorporate the province crisis administration workplaces, cooperating offices like police and fire offices, transportation offices, utility divisions, and other basic private base like statewide vitality organizations. Crisis administration divisions take after occurrence charge frameworks benchmarks that gives conventions and procedures to control, coordination and correspondence among the aforementioned offices with purview that normally react to a flood risk and waste occasion. In a substantial scale flood risk and waste, an administration framework records close continuous circumstance reports from several sources. As recommended by occurrence summon frameworks, common reports incorporate an episode activity arrangement and circumstance report (Dagdeviren *et al.*, 2015). These reports are produced by the partaking organization and area division and give data concerning the objectives of the reacting office amid the reporting period, the moves made to accomplish these objectives and what was really accomplished. For instance, when the province crisis operations focus is actuated ahead of time of a danger, the provincial water administration office may report in an occurrence activity arrange for that it is checking precipitation and channel levels to moderate flood hazard while reporting in the circumstance report what the recorded precipitation and waterway water levels are and how that may influence the group (Sarigiannidis *et al.*, 2015). The branch chief audits and compresses these reports from every organization and produces a synopsis report that is sent to the operations executive. The operations executive joins every branch reports to create a general circumstance report for the occurrence authority. Apparatuses are utilized to record such reaction and recuperation activities to apply and get government flood risk and waste recuperation stores. Different correspondences components are utilized to transmit and report situation status, for example, messages, mailing records, faxes and even paper. For the private division, keeping up a business progression plan safeguards the association is considering the dangers that may hinder the coherence of operations and characterizes particular activities to moderate these dangers (Horita *et al.*, 2015). Taking into account the sort of flood risk and waste occasion and the measure of exertion contributed, the business coherence arrangement gives direction on what steps the business progression group will take in view of the calamity's period occasion. Business congruity groups are dependable to set up the proper interchanges and reports on situation status and readiness/reaction measures endorsed by the business coherence plan to administration and workers. Workers may be required to overhaul contact data and give operational status, sellers contracted for extraordinary debacle recuperation administrations are put on stand-by, and unnecessary hardware is moved out of hurt's way (Wadey *et al.*, 2015).

Data Integration in Flood Risk and Waste Management

Information joining is the procedure of consolidating information dwelling at diverse sources and furnishing the client with a bound together perspective of these information. This procedure rises in an assortment of circumstances both business and investigative. The issue of information combination turns out to be more basic as the measure of information that should be shared increments. By information ingestion, we mean the procedure of embedding to a framework information, which is originating from various heterogeneous sources. Adaptability is a vital issue in information ingestion, since the stream of data may be high amid the season of a basic occasion (Mason *et al.*, 2014).

Flood risk and waste data are to a great degree heterogeneous, both fundamentally and semantically, which makes a requirement for information joining and ingestion with a specific end goal to help the crisis administration authorities in quick surge hazard and waste recuperation at whatever point disasters happen. Flood risk and waste information to be gathered and incorporated for examination and administration can be:

1. Information, for example, episode activity arrangements and circumstance reports;
2. Damage examination reports;
3. Geographic information and open/conclusion status about roadways/parkways/spans and other framework;
4. Logistics information about vehicles, conveyance times, and so on.
5. Communication and message information;
6. Financial information expected to deal with the gathering and dissemination of gifts;
7. Data in sites.

All these information are in a wide range of configurations, have changed attributes, and are accessible from distinctive sources. Further, such information is regularly questionable. The accessibility of such information represents a test for the outline and improvement of compelling techniques for information obtaining, ingestion, and association. The way to get understanding and information from the heterogeneous surge hazard and waste-related information sources is to distinguish the relationship of

information from different sources. Henceforth, advancements are required for information joining and ingestion so it is conceivable to question disseminated data for flood risk and waste administration (Schlafer *et al.*, 2015).

Solutions for Data Integration

To have the capacity to handle the heterogeneous flood risk and waste information from various sources and proficient arrangements are expected to address the information incorporation and ingestion issues (Penning-Rowsell and Johnson, 2015; Vinke-de Kruijf *et al.*, 2015). The arrangements can be classified into three primary segments that cooperate with each other, and association coordination and correspondence. As appeared in Fig. 1, the surge hazard and waste administration information spaces are built up to get, ingest, sort out, and speak to the heterogeneous information. Once the information spaces are set up, the cosmology and semantic Web segment and the association coordination and correspondence part interface with one another to conquer the issue of semantic heterogeneity and to guarantee the ideal procurement of flood risk and waste-related data for quick choice making in a profoundly planned way (Neuhold, 2013).

Information Extraction in Flood Risk and Waste Management

Information extraction (IE) is the order whose objective is to consequently concentrate organized data, i.e., sorted and logically and semantically all around characterized information from a sure area, from unstructured machine-comprehensible archives. More often than not, the objective is to populate tables, given an arrangement of content reports (Tran *et al.*, 2008).

Information Retrieval in Flood Risk and Waste Management

Information retrieval is the art of hunting down archives important to a client question. The inquiry is generally communicated as an arrangement of watchwords, and the reports are returned as a positioned rundown, requested by diminishing significance. In conventional data recovery, reports are positioned in view of a positioning capacity, that is, a capacity that relies on upon the term recurrence and the backwards archive recurrence of the inquiry terms in the records. Term recurrence indicates the quantity of events of a term in a report – higher term recurrence prompts higher score – and the backwards record recurrence is corresponding to the number's opposite of archives that contain the term – higher the reverse record recurrence is better in light of the fact that it implies that the term is more occasional in the information.

Information Filtering in Flood Risk and Waste Management

Information filtering framework is a framework that expels excess or undesirable data from a data stream utilizing (semi) automated or automated systems preceding presentation to a human client. Its primary objective is the data's administration overburden and addition of the semantic sign to-clamor proportion. Data separating is a capacity to choose helpful or intriguing data for the client among a lot of data. When all is said in done, data separating frameworks channel information in view of (a) the similitude between a client profile and the printed substance of an occasion and (b) the client pertinence criticism, that is, if a client likes an occasion then comparable occasions ought to additionally be sent to that client. Data separating has numerous likenesses to data recovery. The key contrasts are that (an) in data sifting the information is spilling and (b) in data separating the inquiry is the client profile.

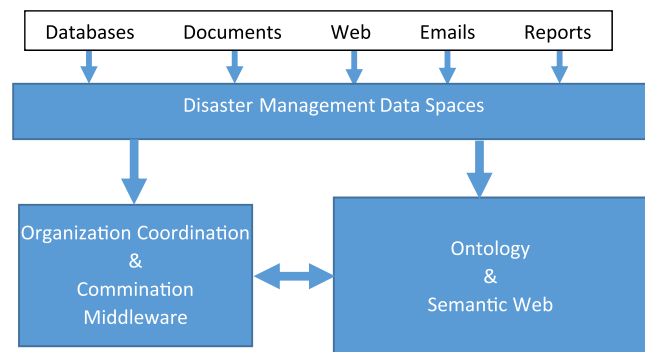


Fig. 1 Components of data integration for disaster data management.

Data Mining in Flood Risk and Waste Management

Data mining or learning disclosure is the nontrivial extraction of certain, beforehand obscure, and conceivably valuable data from extensive accumulation of information. Practically speaking, information mining alludes to the general procedure of removing abnormal state learning from low level information in the connection of extensive databases. To efficiently survey information mining exploration in flood risk and waste administration, we utilize the structure which comprises of an iterative arrangement of the accompanying steps: information administration, information preprocessing, information mining undertakings and calculations, and post-handling. The information administration is extraordinarily identified with the execution of information mining frameworks. Next, information preprocessing, is a critical stride to guarantee the information quality and to enhance the proficiency and simplicity of the mining procedure. True information in surge hazard and waste administration tend to be inadequate, uproarious, conflicting, high dimensional and multi-tangible and so on and consequently are not straightforwardly suitable for mining. Information preprocessing more often than excludes information cleaning to uproot boisterous information and anomalies, information joining to incorporate information from different data sources, information decrease to diminish the dimensionality and many-sided quality of the information and information change to change over the information into suitable structures for mining, and so on. Third, information mining assignments and calculations, which are the center of this area, are fundamental strides of learning disclosure. There are a wide range of information mining assignments, for example, affiliation mining, exploratory information examination, characterization, grouping, relapse, and substance recovery and so forth. Different calculations have been utilized to do these assignments and numerous calculations could be connected to a few various types of undertakings. At last, we need post-preparing stage to refine and assess the learning got from our mining strategy. For instance, one may need to streamline the separated learning. Additionally, we might need to assess the extricated information, imagine it, or just record it for the end-client. We may translate the information and join it into a current framework, and check for potential clashes with already actuated learning.

Decision Support in Flood Risk and Waste Management

Decision support frameworks are a particular class of data frameworks that backings business and authoritative choice making exercises. Specifically, an appropriately composed choice emotionally supportive networks is an intuitive programming based framework expected to help leaders arrange valuable data from assorted information sources and/or plans of action to distinguish and take care of issues and decide. The essential parts of a choice emotionally supportive networks incorporate (1) the information administration segment, (2) the model administration segment, (3) the learning motor, (4) the client interface, and (5) the user (s). Fundamentally, the information administration part stores data from different sources including association's information storehouses and outer information accumulations. The model administration part handles representations of semantic occasions and circumstances and gives different enhancement models, scientific and information mining apparatuses. The learning motor deals with the area information and in addition the information created by different models and apparatuses in the model administration part. The information motor can likewise give deduction abilities and web search tools for learning designing. The client interface permits clients to collaborate with the framework and handles the dialog.

Components of Flood and Waste Management

Based on the definition of flood risk and waste management, three tasks with specific components can be used for structuring the management activities ([Fig. 2](#)). The main tasks are:

- Flood risk and waste analysis,
- Flood risk and waste assessment and,
- Flood risk and waste reduction.

Flood risk and waste analysis provides information on previous, current and future flood risk and waste, flood risk and waste assessment deals with their perception and evaluation and flood risk and waste reduction is dedicated to interventions with a potential to decrease the flood risk and waste. To achieve the aims of each task certain components are required. They range from hazard determination to the specification of post-flood interventions ([Neuhold and Nachtnebel, 2011](#); [Oh and Kang, 2013](#)).

Flood and Waste Management Process

Management of the flood risk and waste system requires further consideration of the linkages between the tasks and components as well as their application by representatives of the society. Links between flood risk and waste analysis, flood risk and waste assessment and flood risk and waste reduction are the prerequisite for a consistent approach to steering a flood risk and waste system. Due to widely varying methods and tools incorporating these into an operation system is challenging. It should be realized

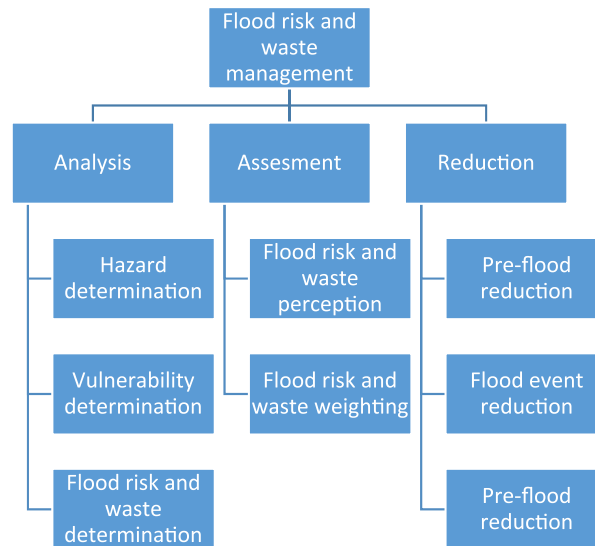


Fig. 2 Components of flood risk and waste management.

that the application of tasks and components by the representatives of the society within flood risk and waste management will normally not follow only a formal textual logic. Instead, various aspects of societal behavior influence decisions and their implementation. The usability and real usage of scientific contributions to flood risk and waste analysis, flood risk and waste assessment and flood risk and waste reduction in societal discussions and decisions are, therefore, of special importance for understanding flood risk and waste risk management.

Future Research Directions

While there are existing methodologies endeavoring to address the difficulties in incorporation and ingestion of flood risk and waste-related information, a versatile, adaptable, and adjustable arrangement that can be immediately conveyed and developed with the surge's periods hazard and waste is being looked for. Upgrades upon the functionalities and/or philosophies of the current fiasco administration frameworks, ought to be explored to guarantee a flood risk and waste planning and recuperation system that can be used under distinctive catastrophe conditions.

The information in misfortune administration application areas are gathered and put away in different media sorts, configurations, and structures from various data sources. A considerable lot of these information are gushing information and gathered progressively, which may have fleeting and spatial qualities. These information may have distinctive levels of culmination and certainty, and may be conflicting. To exacerbate things, there is likewise data shift issue in these applications. That is, the data/learning may be continually changed, obsolete, and inadequate. To our best learning, there are no current techniques and/or calculations that can legitimately address the previously stated issues acceptably. Creating novel methods for overseeing and investigating information that are from heterogeneous sources, having a blend of unstructured and organized sorts, of diverse fleeting and spatial attributes, with different wellsprings of vulnerability, is a testing errand and is critical.

Conclusions

In this paper we display surprisingly a thorough review of the endeavors on using and propelling the administration and examination of information to serve flood risk and waste administration circumstances. We sorted out our discoveries over the accompanying software engineering controls: information mix and ingestion, data extraction, data recovery, data sifting, information mining and choice backing. At long last, we displayed solid future exploration bearings for researchers to propel the information of connected information administration and investigation in surge hazard and waste administration.

See also: Modeling of Information System for Solid Waste Management

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The Environmental Challenges Associated With the Anaerobic Digestion Process when Applied Extensively

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Introduction

The amount of surplus food around the world is estimated at 1.3 billion tons annually. While more than 800 million hungry people exist in the world (Food and Agriculture Organization of the United Nations, 2013 (FAO)), the large amount of waste, which accounts for a large proportion of food production, contributes to many environmental, health, and social issues (Parfitt *et al.*, 2010). To reduce the issue of disposal of surplus food to landfill, its reuse must be exploited. Exploiting waste can be achieved by educating consumers about the harmful effects of food disposal; managing the waste generated by residential complexes, public places such as restaurants and hospitals would also assist in the reduction of waste accumulation in landfill. Additionally, energy plants play an important role in waste management when the waste is used in renewable energy production processes (Kibler *et al.*, 2018). The aim of this study is to demonstrate the importance of using and applying the digestate resulting from the anaerobic digestion (AD) process in a correct way and to show its negative effects on the environment when incorrectly applied.

Waste Management

The incentive for waste minimization and management has become essential, as waste accumulations lead to growing environmental hazards. This involves the recycling, reuse, or application of waste via waste generation techniques. Dealing with waste properly helps reduce greenhouse gases and thus works to reduce global warming. The UK Climate Change Act of 2008 recommended a reduction of the amount of harmful emissions by 80% by 2050 (Levidowa and Ramanb, 2019). Fig. 1 shows the EU hierarchy of waste disposal priorities by reducing, reusing, recycling, or utilizing them in energy production and finally disposal (which is the least favored option) (European Commission, 2008).

A waste management system is an integrated waste management process that begins with waste handling and ends with recycling or destruction. The waste management process goes through several steps as represented in Table 1 (Demirbas, 2011). Failure to exploit and properly utilize waste leads to loss of a source of energy in addition to the other damages caused by its accumulation (Milke, 2008).

Anaerobic Digestion

AD is an efficient and reliable method process to produce energy from natural sources. The AD process is the process of converting organic matter into biogas in the absence of oxygen through different types of bacteria. Biogas contains

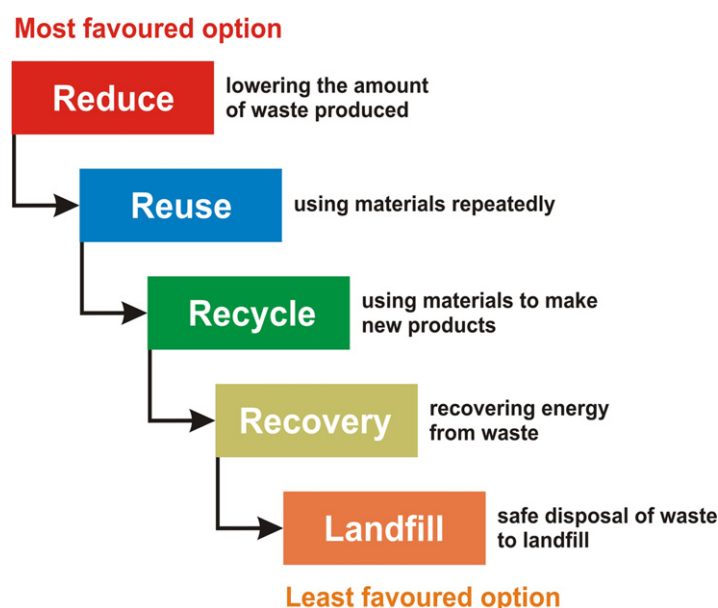


Fig. 1 Waste hierarchy. Reproduced from European Commission, 2008. Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives.

Table 1 Steps involved in a waste management system

<i>Initial step</i>	<i>Substep</i>
Production of materials	Waste sources Source separation Internal collection Production rates Waste types
Collection and transport	Collection Transport Transfer
Treatment	Physical: Shredding, sorting, compacting Thermal: Incineration, gasification Biological: Anaerobic digestion, aerobic composting
Final disposition	Recycling Landfilling

different gases in different rates. Methane is the main component of biogas generally reaching up to 60%–70%. The remaining gases contain up to 45% carbon dioxide (CO₂) and the balance includes hydrogen sulfide (Milledge and Patricia, 2018; Vanegas and Bartlett, 2013). Several types of inoculum, such as sludge from wastewater treatment plants and sludge of manures, are used in the AD process. The process of producing biogas through AD goes through four stages as described in Fig. 2 (Monlau *et al.*, 2014). There are many factors that influence the AD process, for example, the temperature effect in the thermophilic (50–60°C) condition is different than its effect in mesophilic condition (30–40°C) (Samaras *et al.*, 2012). The result of a fast reaction rate in thermophilic conditions results in a biogas that is higher than in mesophilic conditions with the potential for acidification, which affects the AD production. The rise in temperature leads to an increase in the energy used, thus raising the production cost. Mesophilic conditions are less sensitive to environmental changes and have better stability; however, the methane yield is lower than that in thermophilic conditions (Mao *et al.*, 2015; Bowen *et al.*, 2014).

Moreover, the pH, C/N ratio, retention time, and the organic load rate also have an effect on the AD process and thus affect the quantity and quality of the process output (Mao *et al.*, 2015). The bacteria growth process is affected by the pH, so the optimal value of the pH is 6.8–7.4 (Fang and Liu, 2002). Adjusting the C/N ratio to 20–25 contributes to the improvement of the AD production (Yen and Brune, 2007). The time required to keep the organic material in the reactor to complete the biogas production process is known as the retention time. The retention time depends on the temperature used and is associated with the organic load rate. The time required for completing the degradation process and producing the biogas within a mesophilic condition is 15–30 days while it is a little shorter within a thermophilic condition (Kwietniewska and Tys, 2014).

In addition to biogas, a rich nutrient digestate can be produced from an AD process. Fig. 3 shows an overview of the resulting products and their use (Møller *et al.*, 2009). Exploitation of this digestate leads to an enhanced benefit in using the AD process, by increasing the process products. The resulting digestate can be used in many fields such as a biofertilizer in agriculture. In addition to that the resulting digestate can be recirculated to reuse it in a two-stage AD process (Lia *et al.*, 2019; Wua *et al.*, 2018).

Digestate

The digestate consists of the residues of the AD process. The digestate can be used for several applications rather than just disposal (Akilaa *et al.*, 2019). The digestate is generally composed of dead microorganisms and indigestible feedstock. The rise in the price of compost makes the use of digestate as a biofertilizer more desirable (Mouat *et al.*, 2010). Nitrogen (N), phosphorus (P), and potassium (K) that exist in the feedstock reside in digestate; this presence is essential when used in agriculture (Digestate, 2019). Digestate contains carbon, which ends up being stored in the soil, thus preserving the environment from global warming (Møller *et al.*, 2009). The use of inorganic fertilizers with pesticides may lead to soil and agricultural crop damage in the future (Uthirapandi *et al.*, 2018). Biofertilizers are more favored than chemical fertilizers as they help in improving the soil and thus increase soil retention. This leads to reduced water consumption used during an irrigation process. Moreover, the need to use pesticides with biofertilizer is less than that with chemicals, leading to improved soil. The digestate represents a significant percentage of the AD residues (Møller *et al.*, 2009).

Since the soil quality is determined based on its organic material content, according to the European Commission for Standardization (AFNOR: FD CR 13456, 2001), therefore any material that modifies the soil properties can be considered as soil amendment (Nkoa, 2014; Thornton and McManus, 1994). Some digestates have shown high nitrogen levels of more than 60%, which is preferred when applied as a biofertilizer (Tambone *et al.*, 2010). Whereas for digestates where the proportion of nitrogen is around 36%, use as a soil amendment is recommended (Teglia *et al.*, 2011).

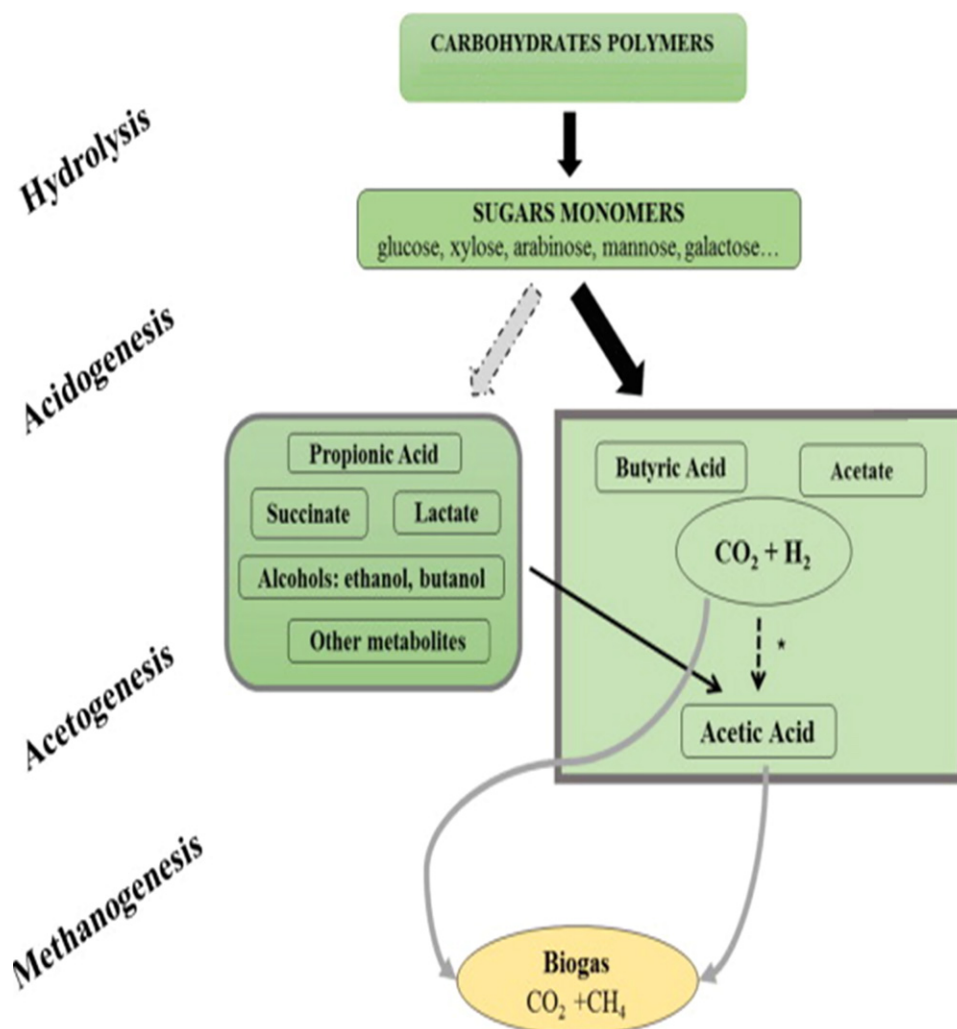


Fig. 2 Anaerobic digestion stages. Reproduced from Monlau, F., Sambusiti, C. Barakat, A., *et al.*, 2014. Do furanic and phenolic compounds of lignocellulosic and algae biomass hydrolyzate inhibit anaerobic mixed cultures? A comprehensive review. *Biotechnology Advances* 32, 934–951.

Digestate Uses

Organic fertilizer is widely used in agriculture as soil fertilizer and soil amendment. It is also used in some nonagricultural areas such as animal litter (straw). The use of digestate is mostly based on its component properties as well as the method of treatment.

In agriculture

The exploitation of huge quantities of digestate resulting from an AD process in agriculture faces challenges as an acceptable process by farmers and consumers. This is due to a lack of awareness of this type of digestate as a fertilizer and its benefits to the environment (Dahlina *et al.*, 2015). Prior to employment, the digestate produced in the agricultural field requires further treatment. In European countries, approximately 95% of the digestate produced by AD is used as an organic fertilizer substitute for chemical fertilizer in the agricultural field (Saveyn and Eder, 2013). In terms of organic products, farmers prefer organic fertilizer that complies with controlled specifications, rather than the chemical fertilizers. It also relies on biofertilizer as animal litter (straw). Some horticulture workers and home gardeners are selective in the type of fertilizer they use and rely on organic fertilizer to decorate/maintain their gardens (Dahlina *et al.*, 2015). The majority of the digestate produced by AD plants in the UK are used as a biofertilizer, while the excess quantity is disposed (Mouat *et al.*, 2010).

Recirculated in two phase anaerobic digestion

Some studies have been interested in recirculating the digestate in the AD process to produce biogases. This process has contributed by improving the biogas production yield, reducing operational costs, and reducing digestion treatment process. The recirculation process does not affect the pH of the digestate; rather it reduces its alkalinity (Wua *et al.*, 2018; Cavinato *et al.*, 2011).

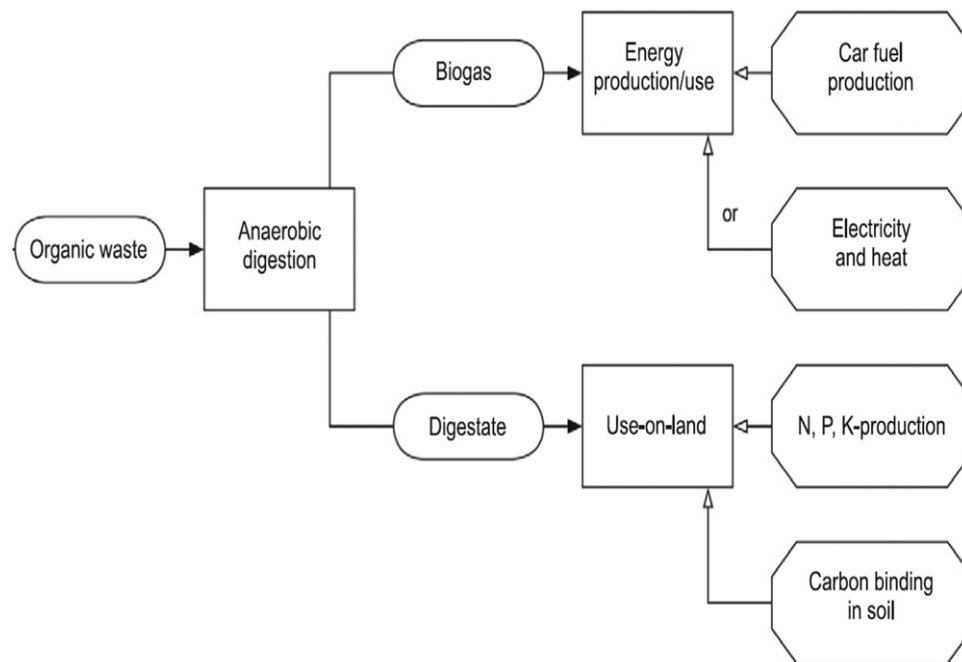


Fig. 3 Anaerobic digestion products and uses. Reproduced from Møller, J., Boldrin, A., Christensen, T.H., 2009. Anaerobic digestion and digestate use: Accounting of greenhouse gases and global warming contribution. *Waste Management and Research* 27, 813–824.

Future uses

There are some areas where digestate can be applied, which may increase its reliability for consumers. It can be used in football or sports grounds. In addition, it has the potential to be expanded as a soil conditioner in private and public gardens. Biofertilizer may also be targeted towards forestry and sold at agricultural retail stores (Mouat *et al.*, 2010).

Digestate Forms

The digestate produced from the AD process can be used in the agricultural field either as whole digestate, liquid form, or solid form as shown in Figs. 4 and 5 (Nkoa, 2014; WRAP, 2012). The whole digestate is the residue of the AD process, in which the dry content ratio is less than 5%. Liquid digestate is the isolation of solids from the whole digestate. Solid digestate is known as “fiber,” and it is similar to compost, which is a solid substance isolated from liquid digestion (WRAP, 2012). Depending on the dry matter (DM) content, the digestate can be divided into three forms. The first form is dewatered where the amount of DM may reach to 35%. The second form is alkaline; where the DM ratio is up to 60%. The third form, which is fairly solid, has a DM content of up to 92% (Department of Environment and Local Government, 2013).

The presence of nitrogen and carbon in the digestate plays a major role in the possibility of using it in agriculture (Nkoa, 2014; Thornton and McManus, 1994). The digestate that is produced from food waste contains organic matter; therefore it can be used directly in the agriculture field as a soil amendment or organic fertilizer. In addition, it is also possible to separate the fibers from the liquid and use them separately. Liquid digestate can be used as an organic fertilizer, while solid digestate may be used as a soil amendment or in landscaping (Mouat *et al.*, 2010). A digestate containing a high percentage of carbon and nitrogen is preferred to be used as a biofertilizer (Tambone *et al.*, 2010). In contrast, digestate with low carbon and nitrogen content can be used as a soil amendment (Teglia *et al.*, 2011), whereas the use of liquid digestate in soil treatment increases the probability of microbes existing in the digestate and oxidation of ammonia (Nkoa, 2014).

Digestate as a Biofertilizer

The use of digestate, which contains the necessary nutrients as organic fertilizer, has a clear value. N is available in biofertilizer at high rates, especially if it is not lost during the AD process, but less than that found in compost. The availability of P and K is similar to that found in compost. Compared with compost, the use of digestate, which contains a high percentage of N as a biofertilizer, leads to increase their value in the short term (Bonten *et al.*, 2014). Fertilization of soil by composting with the participation of biofertilizer contributes to the organic balance of the soil. The presence of organic matter in the soil works to provide nutrients in the soil, which keeps its fertility (Palm *et al.*, 2001). The addition of biofertilizer to compost in soil helps in keeping the organic matter balance within the soil (Miller and Wali, 1995). In addition to that, using the digestate as organic fertilizer instead of disposal helps to reduce waste accumulation (Tambone *et al.*, 2007).

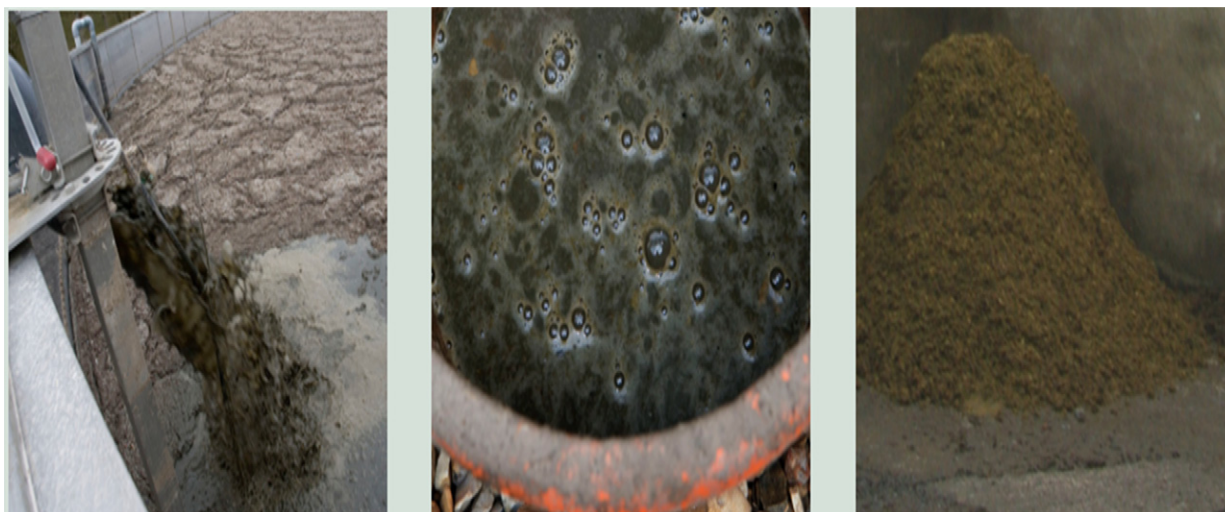


Fig. 4 Images showing three states. Reproduced from WRAP, 2012. Quality digestate: Using quality anaerobic digestate to benefit crops. 3/4/2019. Available from: <http://www.wrap.org.uk/sites/files/wrap/Usingqualitydigestatetobenefitcrops.pdf>.

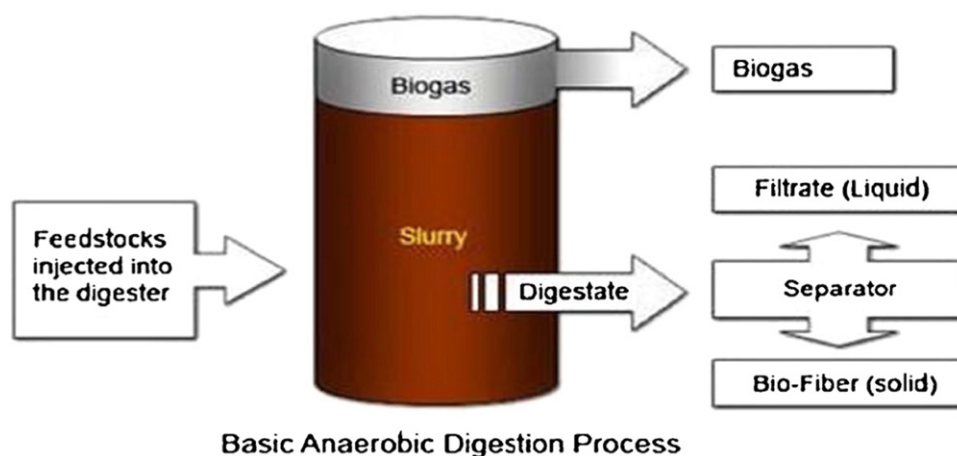


Fig. 5 Anaerobic digestion solid and liquid digestate. Reproduced from Nkoa, R., 2014. Agricultural benefits and environmental risks of soil fertilization with anaerobic digestates: A review. *Agronomy for Sustainable Development* 34, 473–492.

The contribution of the AD process in the reduction of emissions is not only associated to the production of biogases. Maintaining the carbon in the soil for use as natural fertilizer is another factor in reducing harmful emissions (Møller *et al.*, 2009). **Table 2** shows the difference in digestate values from organic and inorganic feedstocks produced from the AD process.

Digestate Quality

The quality of digestate depends on three main factors. The first of these factors is the quality of the chemical product, where it is intended to contain the digestate on the three essential elements: N, P, and K. The quantity of minerals should be balanced and should not contain heavy metals and salts at high rates. Obtaining a certificate of specifications conformity contributes to greater consumer confidence. The second factor is the absence of pathogens through hygiene and heat treatment. The third quality factor is the purification of digestate from inorganic and nonbiodegradable materials such as glass, plastic, and stone, as the presence of these substances reduces the efficiency of biofertilizer and the consumer confidence. Adding some substances and structural materials to the digestate works on improving the digestate's unpleasant smell and removing dust. Digestate with high DM content makes it more likely to last longer, whereas in contrast, a fully dry digestate is not recommended as it can be exposed to wind erosion (Dahlina *et al.*, 2015).

Table 2 Digestate values based on feedstock type

Organic material	N content	Dry matter (DM) %	C/N	Fertilizer value %
Legume coarse meal	40–60 kg t ⁻¹	95	10–13	35–45
Horn/feather/leather meal	130 kg t ⁻¹	95	3–4	50–70
Brewery/distillery residues	3 kg m ⁻³	6	8–10	30–35
Meat/blood/bone meal	75–120 kg t ⁻¹	95	3–5	60–80
Green manure	10–35 kg t ⁻¹	100	10–30	10–40
Biocompost	6 kg m ⁻³	60	13–20	0–20
Solid manure	6 kg m ⁻³	25	12–15	10–20
Sewage sludge (high DM)	4–5 kg t ⁻¹	25	6–8	15–30
Dried poultry excrement	30 kg t ⁻¹	55	5	60–70
Sewage sludge (low DM)	1–2 kg m ⁻³	5	3–5	45–55
Cattle slurry	4 kg m ⁻³	7.5	8	35–45
Digestate from plant biomass	2–3 kg m ⁻³	8	5–8	40–60
Digestate with cofermentation	3–15 kg m ⁻³	5	2–5	50–70
Poultry slurry	10 kg m ⁻³	15	4	70–85
Urine	4 kg m ⁻³	2	1–2	90–100

Note: Nkoa, R., 2014. Agricultural benefits and environmental risks of soil fertilization with anaerobic digestates: A review. *Agronomy for Sustainable Development* 34, 473–492.

Constraints of Digestate Uses

There are a number of barriers that limit the use of digestate in agriculture. Digestate has no market value, so it is distributed free of charge to farmers. The small percentage of DM makes the digestate transportation process costly. Further treatment of the digestate is necessary to reduce the DM (Mouat *et al.*, 2010). Concentrating on the biogas yield produced by the AD process, without taking into account the digestate produced efficiency, can result in the producing unsuitable digestate. For example, the reduction of the retention time or temperature in the AD process to reduce the production cost may lead to the emission of unpleasant odors from the digestate or containing toxic organic compounds (Nkoa, 2014).

There is a possibility that greenhouse gases can be released from the digestate when stored or used in agriculture as fertilizer or soil amendment. Improper storage and use of the digestate causes an emission of nitrogen or nitrous oxide from it (Nkoa, 2014). Combining methane and CO₂ in biogas resulting from the AD process leads to an increase the amount of nitrogen present in the digestate and thus decreases the C/N ratio (Möller and Stinner, 2009). Temperature and pH play a significant role in the determination of the C/N ratio and subsequently the gaseous emissions. Furthermore, factors such as humidity, ammonia concentration, and wind speed have an effect on gaseous emissions (Holm-Nielsen *et al.*, 2009). 80% of the ammonia emitted from the soils fed by the digestate remains in the air and the rest returns to the ground in an area of about one kilometer (Nkoa, 2014). These high levels of ammonia in the air have led to the formation of fog in the air, which limits the level of visibility. Small and volatile ammonia atoms may penetrate the human body causing respiratory health problems (EPA, 2004).

Nitrous oxide has a strong and harmful effect on global warming, often hundreds of times more than the effect of CO₂ (Ravishankara *et al.*, 2009). Emissions from soil account for about 50% of total emissions and the same proportion represents agricultural emissions from the soil emissions (Denman *et al.*, 2007). More than 70% of nitrous oxide emissions are from agricultural applications (Lemke *et al.*, 1998). Emissions of ammonia increase with digested fertilizer compared with undigested, while nitrous oxide is reduced with the digestion process. This may be due to the low carbon ratio that has been converted into biogas (Vallejo *et al.*, 2006). The decrease in nitrous oxide emissions may reach more than 60% with digested fertilizer (Chantigny *et al.*, 2007). Proper use of biofertilizer produced from the AD process, which helps in aeration and good drainage of soil, helps to reduce nitrous oxide emissions (Nkoa, 2014).

On the other hand, pollution is also a concern generated due to the presence of nutrient contents in high ratios on the surface water and ground water. The amount of mineral in biofertilizer is higher to what is found in compost (Haraldsen *et al.*, 2011). The association of compost with environmental issues is likely to increase with applying biofertilizer, especially if precautions are not taken to prevent this when using and producing the AD digestate (Mulla *et al.*, 2001). Caution also extends to the possibility of contaminants, such as physical (plastic or glass), chemical (toxic compounds, heavy metals), and biological (bacteria) (Nkoa, 2014).

Digestate Treatment

Difficulties facing the use of digestate, such as the difficulty of transportation, storage, and its direct use in some cases, lead to the reason to investigate the benefits of the treatment process. There are some other methods of treatment, but to choose the favorite one is complex, as the consumer desires various characteristics of the biofertilizer produced. The determination of the method of treatment depends on the digestate formed (liquid or solid). Moreover, the costs of the treatment methods have a role in determining the ideal method (Mouat *et al.*, 2010). If the liquid digestate contains less than 5% DM (WRAP, 2012), it is easy to spread onto the soil and use directly as a biofertilizer. The dry digestate can be used directly as a soil amendment or be treated and used as a biofertilizer (Rapport *et al.*, 2008).

Dewatering of the digestate is a process of removing water from the digestate to obtain the liquid and solid digestate separately. Distilled water can be used for irrigation, due to its acceptable quality, which contributes in the reduction of water use. This process reduces the transportation costs and the ease of storage. The dewatering process can be carried out in several ways. *Gravity tables*: The costs of this process are low as they depend on the costs of establishment. Based on the feedstock, this process may reduce water content by 15%. *Press*: This technique does not require a lot of energy. Press is currently applied in small and medium-sized factories. *Drying*: This is drying the digestate by heat evaporation. Drying controls the desired dryness degree of digestate. The drying equipment is the main cost of the process, but the process produces less water combined with the digestate. It cleans the digestate from impurities and health hazards. *Rolling*: The solids are separated from water instead of removing water from digestate. Small particles accumulate around the tank wall during a rolling process and then are converted into pellets, which can be easily removed from the liquid (Mouat *et al.*, 2010).

Liquid and solid digestate can be mixed with enhancing materials to attain better results. Liquid digestate can be mixed with sawdust to add longer consumption periods. It is possible to mix solid digestate with nutrients to enhance it; these may be used in gardens and horticulture. It also facilitates the transportation process and allows for longer storage (Mouat *et al.*, 2010).

Further Studies

Further studies are required with respect to the digestion resulting from waste treatment, especially from AD. Some of the topics that need to be investigated have already been specified in this article. The relationship between the feedstocks and the digestate require more clarity, especially with respect to the proportions and properties of organic substances in the digestate. Furthermore, the long-term effects of using the digestate in agricultural soils on soil properties need to be further studied. Some types of digestate may contain bacteria and fungal pathogens and thus need to be identified and controlled. There is also a need to study the harmful emissions from the digestate such as the emissions of ammonia and nitrous oxide, which adversely affect the environment and the efficiency of digestate (Nkoa, 2014).

Conclusion

Waste management in general and food waste in particular contribute to reducing the environmental and health effects of the accumulation of waste. This is done by raising the awareness of the community and society about the importance of waste recycling or its use in different fields. AD is one of the technologies used broadly, which is proven to be effective in converting waste into biogas and digestate.

The low proportion of DM in the digestate makes storage difficult and transportation to far destinations impossible. The shortage of sources for the emissions of the digestate and its impacts on the environment are an impediment to its application. Despite that the application of digestate as a biofertilizer in agriculture can cause damage to the plants and others, it could help in mitigating the obstacles threatening the sustainability of the AD, if it is properly handled. However, more investigations are required for increasing the awareness of farmers and others on the digestate, thus, increasing the reliance on and use of it.

However, the digestate is a promising alternative to chemical fertilizers if treated appropriately, especially with the rise in the price of compost compared with biofertilizer. Moreover, its exploitation by AD plants may enhance the feasibility of the process and reduce its operational costs.

Acknowledgments

The author gratefully acknowledges the financial support provided by the Ministry of Education of the Kingdom of Saudi Arabia represented by the Saudi Cultural Bureau in Ireland.

See also: Analyzing Biodiesel Production From Cooking Oil. Optimization and Kinetic Modeling of Biodiesel Production. Sustainable Biodiesel Production

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Experimental Investigation of Microtest Specimens of Renewable Material-Based Composite Materials by Injection Molding

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Introduction

Plastic Injection Molding

Plastic products can be found everywhere. These plastic products have many advantages, including their lightweight, high stiffness, ease of production, ability to be produced in high quantities, and high quality (Kitayama and Natsume, 2014). Injection molding is the most common processing technique used in the plastic industry. It can be used to process several types of materials and to produce products with complex geometries. However, some defects exist in plastic injection molding, such as warpage, volume shrinkage, weld lines, and short shots. The plastic injection molding process can be divided into four phases: filling, packing, cooling, and ejecting (Kitayama and Natsume, 2014; Gerber *et al.*, 2006).

The processing parameters of plastic injection molding are nonlinear and interacting. Control of the melt temperature for injection molding is very important. It can be considered to be the most critical factor in injection molding because it directly influences the viscosity of the melt. Having good control of the melt temperature is also important for reducing the setup time, assuring consistent product quality, and preventing the melt from being thermally degraded. The melt temperature and melt viscosity can influence the velocity of the translational injection, the speed of the rotational reciprocating screw, and the cavity pressure–time profile (Dubay, 2002). In this study, a rotating twin screw extruder was used to investigate the processing parameters of kenaf fiber composites at two different temperatures, low processing temperature (LPT) and high processing temperature (HPT). The tensile modulus increased with the increase in the compounding temperature and fiber loading when processed at LPT and HPT. Conversely, by increasing the content of the fiber, the tensile strength of the composites decreased at both LPT and HPT. However, the composites processed at HPT presented better tensile strength than those at LPT. The tensile strains of the composites decreased with increasing fiber loading, whereas composites processed at LPT showed higher tensile strain than those at HPT. In summary, the composites processed at HPT showed the best performance of tensile properties (Salleh *et al.*, 2014).

Huang (2007) stated that the process control parameters for injection molding are a complex problem. The melt temperature is a very important process parameter for all phases of the cycle of injection molding, such as filling, packing, holding, and cooling. Control of the melt parameter is difficult due to nonlinear polymeric melting processes. Because the melting of plastic is an endothermic process, and because the situation is further complicated by the poor conductivity of plastics, it is difficult to control the melt temperature. Due to the viscosity dependence on temperature, the melt temperature will influence some other parameters, including the rate of melt flow, the nozzle pressure, and the cavity pressure–time profile. As a result, the melt temperature will affect the final quality of the molded part. Holding happens once the cavity is filled. Then, holding pressure will be maintained, while the additional plastic melt is packed into the cavity to compensate for the plastic shrinkage caused by cooling. Packing–holding pressure will affect the injection molding quality. Different types of packing profiles will affect the part weight, shrinkage, flash, thickness distribution, and evenness (Bobzin *et al.*, 2011). Processing parameters, such as holding pressure and mold temperature, were investigated in this study for their effects on residual stresses in the molded parts (Murakami *et al.*, 2007).

Micro Plastic Injection Molding

Microinjection molding is a process that transfers a granule form of thermoplastic from the hopper into a heated barrel to heat the thermoplastic into a molten state. Then, using pressure, the thermoplastic is pushed inside a mold cavity where it is subjected to holding pressure for a certain amount of time to prevent the thermoplastic from shrinking. As the temperature of the mold decreases, the thermoplastic inside the mold cavity solidifies. Then, the part is ejected and the cycle is repeated (Attia *et al.*, 2009). The main elements that influence the quality of the part produced by microinjection molding are the temperatures of melt and mold and injection speed. If the temperature of the mold increases, then the cycle time also increases. As a result, this will cause a reduction in the process output and in the costs of the parts. However, high melt and mold temperatures and high injection speeds will provide a good influence on the melt flow in tiny cavities (Sha *et al.*, 2007). Microinjection molding requires special conditions that will affect the chemical, physical, and thermal properties of the injected polymeric material. The material behavior is different from that during the classical process of injection molding. Hence, the parameters of the injection process need to be optimized (Gheorghe *et al.*, 2014). Zhao *et al.* (2003) stated that a microsystem has been given considerable interest in recent years. It is expected to extend toward miniaturization of components and to be increasingly applied for micro-sized devices. The microinjection molding process of polymers is the key to enabling the microsystem to be capable of mass production of microcomponents at a low cost. Polymers play an important role in the growth of microsystem applications because they are available in various compositions, properties, and forms and can be fabricated into complex structures. The demand for increasingly smaller molded plastic components has increased because of the trend toward miniaturization. Yao and Kim (2002)

stated that there are many advantages to further development of microinjection molding. The advantages comprise the vast variety of plastics available and the possibility of fully automated operation with short cycle times, cost-effectiveness for mass production, high accuracy of shape replication, good dimension control, and low maintenance costs of the capital equipment. Microinjection molding is crucial for micro-manufacturing because it is capable of producing large amounts of standardized products with low component costs. With the development of micro-engineering technologies, product miniaturization has increased (Sha *et al.*, 2007). It is not surprising that miniaturized parts exist in many places in our daily lives (Piotter *et al.*, 2002). Kukla *et al.* (1998) defined the meaning of microinjection molding. First, the weight of the microinjection-molded part is just a few milligrams. The part does not need to have dimensions with a scale of micrometer. Second, an injection-molded part with micro-structured regions is usually a part on a conventional scale that is characterized by dimensions in the micrometer range. Third, a micro-precision part can have any dimensions but has tolerances in the micrometer range.

Microinjection Molding Machine

Injection machines have been challenged to produce micro-features. This is because of the processing requirements to fill the cavities of the mold completely in the micro-range before solidification of the material starts. This challenge existed before the spread of microinjection molding, when the same problem was encountered by thin-wall injection molding. This problem can be solved by changing some processing parameters in conventional injection machines, such as the injection speed and pressure. To solve the problems of producing parts with micro-features, injection machines need to be modified to produce the parts. Some modifications include smaller plasticization units, clamping units with lower tonnage, advanced control systems with accurate parameter control, temperature variation programs, air evacuation systems, and handling and inspection. Many manufacturers are beginning to show an interest in producing microinjection molding machines (Attia *et al.*, 2009).

Natural Fiber Composite

A fiber-reinforced polymer is a composite material comprising a polymer matrix embedded with fibers with higher strength. Polymers can be divided into two types, thermoplastics and thermosetting. Normally, thermoplastics are used as matrices for natural fibers. Malkapuram *et al.* (2008) and Groover *et al.* (2004) presented that polypropylene (PP), poly vinyl chloride (PVC), and polyethylene (PE) are the most common thermoplastics used for fiber-reinforced polymers. Natural fiber composites are becoming more and more popular. This is because natural fibers are lightweight, nontoxic, low cost, and biodegradable. Moreover, the use of natural fibers is positive for the environment because of their disposability and raw material utilization (Narayan, 1992). Natural fibers are made from animal, plant, and mineral sources. A plant fiber is a very important part of natural fibers, which include fibers from bast, leaf, seed, fruit, wood, cereal straw, and grass. Over the past few years, natural fibers have become an attractive alternative to synthetic fibers. This is because of the advantages of natural fibers, such as low density, less damage to the machine, recyclability, renewability, and good mechanical properties. Natural fibers can be used to replace the existing glass fiber-reinforced polymer composites because their strength is comparable to that of glass fibers (Hojo *et al.*, 2014).

Scientists and technologists have been attracted to natural fibers because of their various applications. Natural fibers have good thermal and insulating properties, better electrical resistance, higher resistance to fracture, and are renewable. Natural fibers do not cause skin irritations and possess relatively high strength and stiffness. However, natural fibers do have disadvantages, such as low thermal stability, moisture uptake, and quality variations. Many studies have investigated the properties of natural fiber composites. The results have shown similar outcomes indicating that natural fiber composites possess good stiffness but have lower strength levels than glass fiber composites (Oksman, 2001). There are several elements that can affect the properties of natural fiber composites. The properties of the natural fiber composites can be affected by the content of fiber or amount of filler and the hydrophilic nature of the fiber. To achieve high performance of the composites, the fiber content needs to be high. The fiber content has a significant influence on the performance of natural fiber composites. The increase in fiber loading can cause an increase in the tensile properties (Arib *et al.*, 2006). Furthermore, the processing parameters are very important because they significantly affect the performance of the natural fiber composites (Ku *et al.*, 2011). Sathishkumar *et al.* (2012) stated that several authors have researched natural fibers due to the demand to create natural fiber composites. Athijayamani *et al.* (2009) used the fibers of roselle and sisal to compare their experimental tensile and flexural strength using the Hirsch theoretical model. Bakare *et al.* (2010) investigated the mechanical properties of the sisal fiber composite under two conditions, with and without the water treatment process. Cao and Wu (2008) found out that the optimum strength of the bamboo fiber is higher than that of other fiber-reinforced green composites. Gonzalez-Murillo and Ansell (2009) proposed that the results of chemically treated fiber composites and untreated fiber composites are similar. Silva *et al.* (2008) studied the tensile properties of the sisal fiber. Joseph *et al.* (1999) studied and compared the tensile strength and modulus of natural fiber composites.

PP-Based Composites

Composites of bast fibers, which are an annual fiber crop, with PP provide materials with interesting price or performance ratios. These composites are suitable for making interior parts for cars. Their fiber and matrix properties can be improved with modified PP, which increases compatibility (Bos *et al.*, 2002). Many materials have been used as reinforcing agents to improve the

mechanical properties of PP. Asbestos tailings were recycled and chemically modified to increase the compatibility with the PP matrix (Zhai *et al.*, 2014). Olive stone flour extracted from the solid residue of olive oil has been used to reinforce the PP. These materials are definitely creating new perspectives regarding the functions of industry by-products (Naghmouchi *et al.*, 2015).

Kenaf fibers

Kenaf fiber is a natural and environmentally friendly fiber used to produce natural fiber composites. There are several methods of producing natural fiber composites, such as extrusion, compression, and injection molding (Salleh *et al.*, 2014). Nishino *et al.* (2003) performed an investigation regarding the fiber content and mechanical properties of kenaf fiber composites. In their investigation, Young's modulus and tensile strength increased with an increase in fiber content. Kenaf fiber is a high performance biodegradable polymer composite. It does not cause environmental problems when disposed of like conventional and traditional fiber-reinforced composites do.

Rice husk fibers

Rice husk is the outer layer of rice grains. It is an agricultural by-product. Rice husk ash results from burning the rice husk and contains a high amount of silica. Rice husk ash can be a supplementary material used to replace Portland cement. Rice husk ash can act as a reinforcing agent in the making of cement; it can reinforce the strength of cement. A high level of fineness of rice husk ash can enhance the compressive strength of cement (Hamzeh *et al.*, 2013). As an agricultural by-product, rice husk is useful and has been applied for bio-fertilizers, animal husbandry materials, absorbent materials, and pest control agents. Due to its abundance, composition, and low cost, several studies have investigated the possible functions of rice husk. However, rice husk has not yet been included in bio-based composites used in melt blending (Battezzore *et al.*, 2014).

Flax fibers

Mechanical properties of flax fibers, such as tension and compression have been studied. The clamping length can greatly affect the tensile strength of technical fiber bundles. The compressive strength of elementary flax fibers can be reduced by the decortication process. The failure behavior of elementary flax fibers under compression is similar to that of a stranded wire. It was presented that flax is one fiber that possesses the best mechanical properties (Bos *et al.*, 2002).

Coconut shell fibers

Coconut shell, which is an agricultural by-product, is the waste product of food processing that possesses sufficient value regarding fibers. It is a cheap engineering material that can help to reduce waste (Bledzki *et al.*, 2010). The potential of grain by-products, such as soft wood and coconut shell, as the reinforcements for thermoplastic was investigated in this study. The thermal degradation characteristics of coconut shell fibers were studied for their potential to be processed as reinforcements for PP.

Numerical Studies

ABAQUS, a finite element software, was used in implementation of the extended finite element method (X-FEM), a powerful numerical procedure for the analysis of crack problems. The crack growth modeling capabilities of X-FEM can be beneficial for those familiar with ABAQUS (Giner *et al.*, 2009). The capabilities of ABAQUS to extend the finite element code were presented to simulate the history of heat treatment phase transformations and distributions of residual stress. Simulation is a tool that is inexpensive, secure, and time-saving (Yaakoubi *et al.*, 2013). Shallow, thin-walled parts of wood polymer composites were produced by injection molding. The parts were investigated by conducting a simulation with Autodesk MoldFlow Insight software. The simulation was performed by using a set analysis of "Fill + Cool + Fill + Pack + Warp" (Azaman *et al.*, 2014).

Summary

Injection molding is widely used in the plastic industry to produce parts. Because the market now prefers products that are small, light, and slim, the parts produced need to be as small as possible. The industry also started noticing the importance of microinjection molding and how profitable it could be. The processing parameters and materials used for injection molding were studied to improve the process. Due to the increasing awareness of the public regarding environmental conservation, environmentally friendly materials are more likely to become the materials of choice. Natural fiber composites are environmentally friendly because they are made from natural fibers. Therefore, many experiments have been performed to study the mechanical properties of the natural fiber composites. It has been discovered that studies regarding the effects of processing parameters of injection molding on the mechanical properties of specimens made from different types of PP-based natural fiber composites are limited. Hence, this study was conducted to investigate the effects and to provide more information regarding the future utilization of PP-based natural fiber composites. Microtensile specimens will be prepared by injection molding with different types of natural fiber composites and combinations of processing parameters. Specimens will be tested and the experimental results will be compared with the finite element analysis (FEA) obtained from ABAQUS.



Fig. 1 Vertical injection molding machine.

Methodology

In this study, three phases were performed to investigate the mechanical properties of the natural fiber composites.

1. Injection molding: microtensile test specimens with different types of natural fiber composites and processing parameters need to be prepared by injection molding. The microtensile test specimens are prepared by using the D1708-02a standard.
2. Microtensile test: the microtensile test specimens are tested by following the standard D638. The mechanical properties of different specimens will be studied. Then, data collection and analysis are performed.
3. ABAQUS tensile test simulation: simulation of the tensile test for the specimens will be performed by using the data collected during microtensile testing via FEA software (ABAQUS). The experimental results will be compared with the results obtained by ABAQUS.

Injection Molding Apparatus

The test specimens used in this study were produced by a vertical injection molding machine (**Fig. 1**; *Azuddin et al., 2015*). The original unit used a pneumatic system to generate the plunger injection motion. However, injection molding of natural fiber composites requires higher pressure than thermoplastics because of their higher viscosity. Hence, the injection molding machine was modified and the pneumatic unit was replaced by a hydraulic unit due to insufficient pressure. The hydraulic pump can provide higher pressure to the injection plunger to deliver melted natural fiber composites into the mold cavity. The machine also includes a temperature controller to control various melt temperature.

Mold for Microtensile Specimen

The mold cavity was fixed and the dimensions of the test specimen were used following the standard of the microtensile specimen, D1708-02a (standard test method for tensile properties of plastics by use of microtensile specimens) (**Fig. 2(a)**). **Fig. 2(b)** shows the mold used to produce the microtensile specimen.

Materials

For composites preparation, fibers were mixed with PP in a mixer using standard compounding operations. Fibers were responsible for 30 wt% of the composition. The fiber was compounded on a twin screw extruder. At the end of the extruder, the melt goes through a die plate and into a water bath. Finally, a cutter is used. Three types of natural fiber composites (from RheTech, Inc., United States) were used in this study:

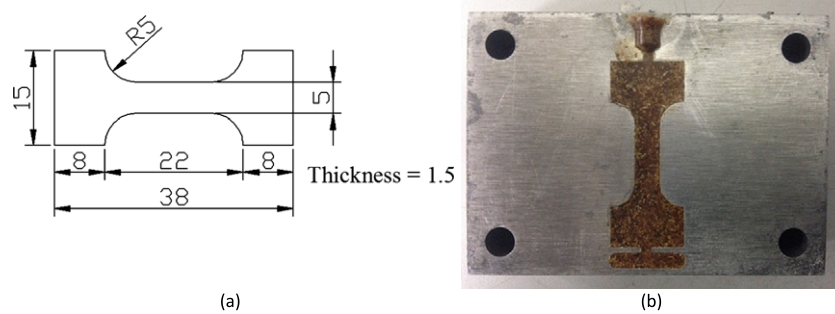


Fig. 2 (a) Dimensions of the microtensile specimen in millimeter and (b) the mold.

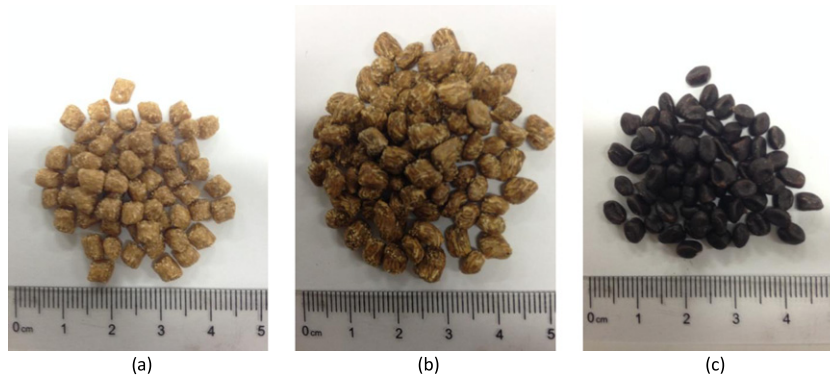


Fig. 3 Fiber material used in the experiment: (a) rice husk, (b) flax, and (c) coconut shell.

1. 30% Rice husk fiber-reinforced PP copolymer.
2. 30% Flax fiber-reinforced pp copolymer.
3. 30% Coconut shell fiber-reinforced PP copolymer.

A unique characteristic of the rice husk is that it is naturally flame-resistant. Rice husk is stiff, dimensionally stable, has low moisture absorption, has lower specific gravity than minerals, has excellent chemical resistance, and is naturally flame-resistant. **Fig. 3(a)** shows raw rice husk material. Flax is grown for flax seed, oil, and fiber. Flax fiber-reinforced material (**Fig. 3(b)**) are dimensionally stable, have low moisture absorption, and have excellent chemical and mold resistance. It is suitable for glass fiber replacement. Coconuts are a staple product grown around the world and have multiple uses. Both fine and coarse ground coconut shells are utilized to produce PP compounds (**Fig. 3(c)**). Coconut shell-reinforced materials have good surface hardness, stiffness, low moisture absorption, and are suitable for mineral replacement. All natural fiber PP composites used for this study were from RheTech. **Fig. 4** shows the raw fiber material and microtensile specimen after being molded.

Processing parameters

Only two processing parameters were varied in this study:

1. Melt temperature, which can be controlled by adjusting the temperature of the heater. The melt temperatures used were 230, 240, and 250°C.
2. Holding time, which can be controlled by holding the pressure of the hydraulic pump. The holding times used were 3 and 5 s.

Tensile Test

The ISO standard D1708-02a microtensile specimen was used to perform the test for tensile properties of the natural fiber composites. This test method was superseded for general use by Test Method ASTM D638, which is the test method for tensile properties of plastics. The Instron 5569 mechanical testing system was used to conduct the tensile test. Five test specimens were tested for each natural fiber composite and processing parameter. Results obtained for test specimens that broke because of some obvious fortuitous flaw or at the edge of the grips were discarded and retests were performed. Testing was the velocity of the separation of the two grips of the testing machine when it was not under any load. The speed of testing used for this project was



Fig. 4 Fiber material used in the experiment, raw pallet, and microtensile specimen after injection molding: (a) rice husk, (b) flax, and (c) coconut shell.

1.0 mm/min. **Fig. 5** shows the microtensile specimen before and after testing. It clearly shows the location of failure after the tensile test was conducted.

Tensile Test Simulation

In this study, ABAQUS CAE was used for the modeling and analysis of mechanical components and assemblies and for visualizing the result of FEA. The tensile properties of the test specimens made from different types of natural fiber composites and different combinations of processing parameters were simulated using ABAQUS. The analysis types used for ABAQUS simulations were 3D, deformable solid, and dynamic explicit. The dynamic explicit FEM analysis uses an incremental procedure. At the end of each increment, the stiffness of matrix based on geometry changes is updated. Then, a new stiffness matrix is constructed and the next increment of displacement is applied to the system. Therefore, more accurate results can be achieved. The steps begin with microtensile geometry construction according to the standard. After meshing the part geometry with the element type in this study, the types of elements used were the 4-node bilinear axisymmetric quadrilateral (CAX4R) and the 3-node linear axisymmetric triangle (CAX3). The total number of nodes was 493 and number of elements for the microtensile geometry was 428. Next, we applied the boundary conditions and minimal constraint of the bottom surface of the microtensile, and we prevented rigid body motion. A second boundary condition was created to impose vertical displacement along the top surface of the microtensile. The microtensile was loaded by imposing displacements because that results in a more gradual failure process than a similar loading using applied forces. Then, the ABAQUS simulation was performed. Finally, we viewed and interpreted the results. From these simulation results, load displacement and stress-strain results were obtained. After the simulation, results from the FEA need to be validated with the experimental result to investigate whether the results obtained from ABAQUS were theoretically accurate. **Fig. 6(a)** and **(b)** shows the composite after tensile testing and ABAQUS simulation; the microtensile specimen break locations were similar to those predicted by the ABAQUS simulation and the crack location after testing and the highest stress value (red) during the ABAQUS simulation.

Result and Discussion

Experimental Result

During injection molding, five specimens are made for each type of natural fiber composite material and combination of processing parameters. There are three types of natural fiber composite materials and six combinations of processing parameters for each material. Hence, 90 specimens are made and 18 experiments are conducted. **Table 1** shows the average of tensile strength values obtained during the tensile test for the specimens created by three types of natural fiber composite materials with different processing parameters. The flax fiber-reinforced PP copolymer had the highest tensile strength value among the three materials regardless of the combination of processing parameters, whereas the rice husk fiber-reinforced PP copolymer has the second highest value, followed by the coconut shell fiber-reinforced PP copolymer.

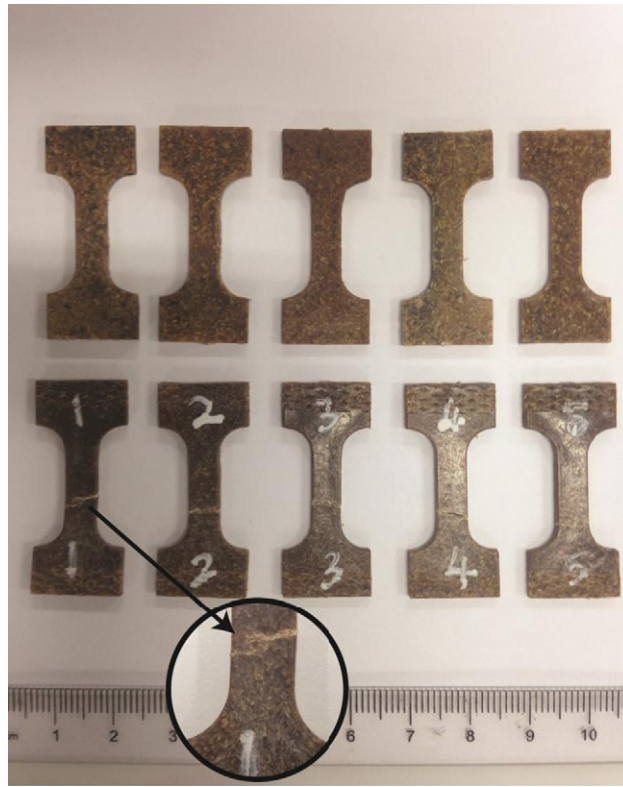
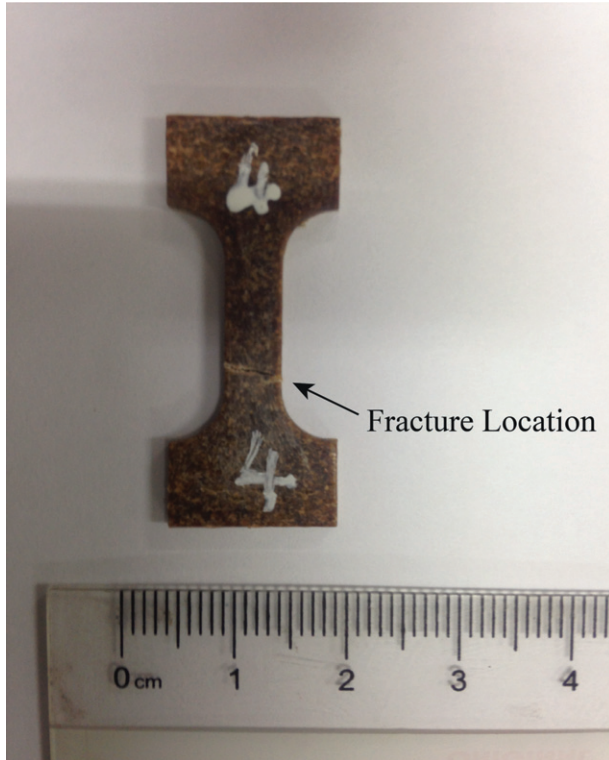
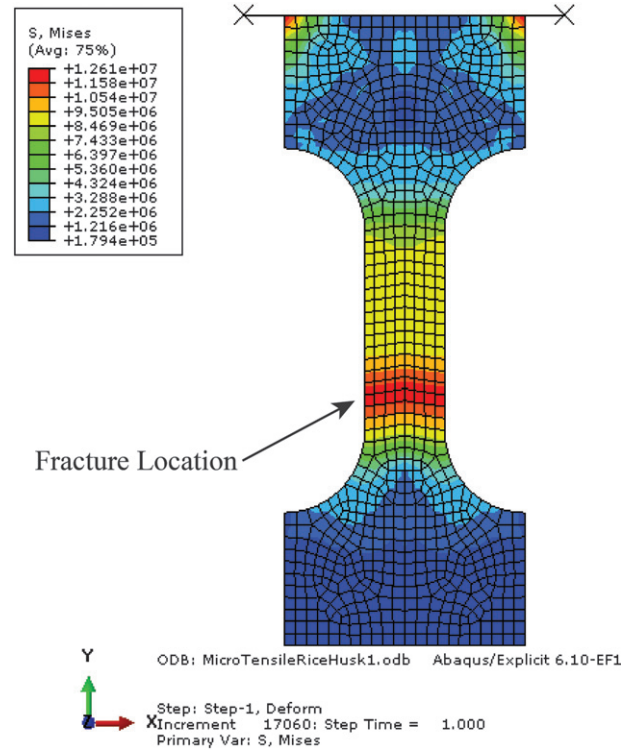


Fig. 5 Microtensile specimens before testing (top) and after testing (bottom).



(a)



(b)

Fig. 6 (a) The composite after tensile testing and (b) ABAQUS simulation.

Table 1 Tensile strength for three different types of fiber-reinforced polypropylene (PP)

Experiment	Material	Melt temperature (°C)	Holding time (s)	Young's modulus, E (MPa) average	Tensile strength (MPa) average
1	Rice husk-reinforced PP copolymer	230	3	1512.4112	12.21
2			5	1694.676	13.208
3		240	3	1601.8112	12.008
4			5	1527.3378	11.632
5		250	3	1443.7216	10.874
6			5	1558.7406	10.804
7	Flax fiber-reinforced PP copolymer	230	3	1838.7948	14.638
8			5	2635.9876	14.958
9		240	3	2477.0482	16.032
10			5	2401.6192	15.936
11		250	3	2232.9858	16.278
12			5	2354.7464	16.514
13	Coconut shell fiber-reinforced PP copolymer	230	3	984.7912	9.54
14			5	600.4156	7.36
15		240	3	472.6668	5.458
16			5	575.1648	6.776
17		250	3	501.2308	7.374
18			5	579.8768	8.07

Young's Modulus

For the rice husk fiber-reinforced PP copolymer, **Table 1** shows that the Young's modulus increased 5.9% to 1601.8112 MPa when the holding time was 3 s, and the melt temperature increased from 230 to 240°C. However, when the melt temperature increased from 240 to 250°C, Young's modulus decreased 9.9% to 1443.7216 MPa. In addition, when the holding time was 5 s, Young's modulus for the rice husk fiber-reinforced PP copolymer decreased 9.9% to 1527.3378 MPa. The melt temperature increased from 230 to 240°C, but Young's modulus increased slightly (2.1%) to 1558.7406 MPa when the melt temperature increased 10°C more to 250°C.

Table 1 also shows Young's modulus for the flax fiber-reinforced PP copolymer of different processing parameters. When the holding time was 3 s, the value of its Young's modulus processed at the melt temperature of 230°C was 1838.7948 MPa. First, Young's modulus increased quarterly (25.8%) to 2477.0482 MPa, whereas the melt temperature increased to 240°C. Then, Young's modulus of the copolymer experienced a decrease of 9.9% to 2232.9858 MPa when the melt temperature increased from 240 to 250°C. Moreover, when the holding time was 5 s, the increase in melt temperature from 230 to 250°C resulted in decrease in Young's modulus of the flax fiber-reinforced PP copolymer (overall 10.7%). At a melt temperature of 230°C, Young's modulus was 2635.9876 MPa. It then decreased to 2401.6192 MPa at 240°C. Young's modulus continued to decrease to 2354.7464 MPa at 250°C.

Comparisons of Young's modulus for the coconut shell fiber-reinforced PP copolymer of different processing parameters are shown in **Table 1**. When the holding time was 3 s, Young's modulus for the coconut shell fiber-reinforced PP copolymer processed at the melt temperature of 230°C was 984.7912 MPa. It was then approximately halved by 52% to 472.6668 MPa for the copolymer processed at the melt temperature of 240°C. However, Young's modulus for the coconut shell fiber-reinforced PP copolymer increased marginally (5.7%) to 501.2308 MPa when the melt temperature of the copolymer increased 10°C from 240 to 250°C. Furthermore, when the holding time was 5 s, Young's modulus for the coconut shell fiber-reinforced PP copolymer remained steadily ($\pm 4.4\%$) at three different melt temperatures: 230, 240, and 250°C.

By comparing these three types of natural fiber-reinforced PP copolymers, the flax fiber-reinforced PP copolymer exhibited the highest Young's modulus value among the three copolymers; the rice husk fiber-reinforced PP copolymer had the second highest value; and the coconut shell fiber-reinforced PP copolymer had the lowest value. This indicated that the flax fiber-reinforced PP copolymer possessed the greatest stiffness among the three copolymers; the rice husk fiber-reinforced PP copolymer had the second greatest stiffness and the coconut shell fiber-reinforced PP copolymer had the lowest stiffness.

Stress–Strain Curve

The stress–strain curve is an extremely important graphical measure of a material's mechanical properties. It is unique for each material. The stress–strain curve is found by recording the amount of deformation at distinct intervals of tensile loading. The curve can be used to determine many properties of material, such as the modulus of elasticity, yield strength, and many more.

Raw data were obtained from the tensile test and curves were plotted. In **Figs. 7–9**, comparisons of stress–strain curves for each type of natural fiber composite material with different processing parameters are exhibited. The shapes of the curves for these three natural fiber composites were not exactly same, but an identical trend was shown. First, every curve started with an increasing gradient. After it increased to a certain extent, the curve remained constant and became flat. The curve rose again until the specimen

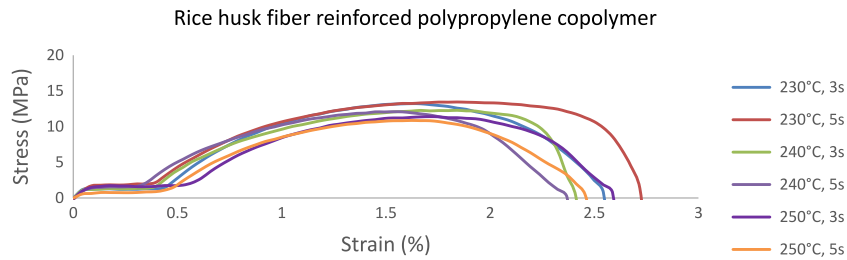


Fig. 7 Comparison of stress–strain curves for the rice husk fiber-reinforced polypropylene (PP) copolymer with different processing parameters.

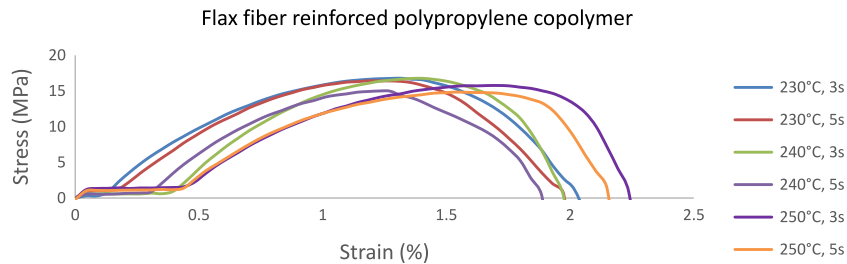


Fig. 8 Comparison of stress–strain curves for the flax fiber-reinforced polypropylene (PP) copolymer with different processing parameters.

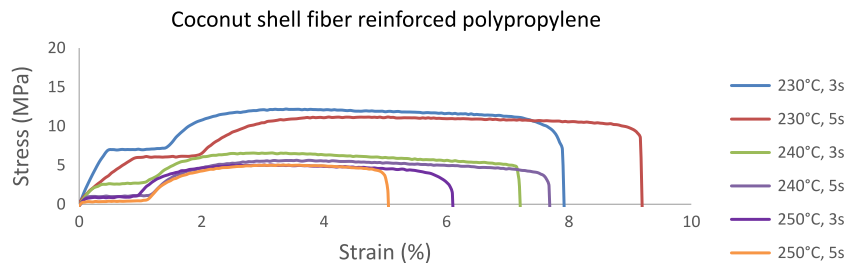


Fig. 9 Comparison of stress–strain curves for the coconut shell fiber-reinforced polypropylene (PP) copolymer with different processing parameters.

broke, and then it gradually fell. This trend of the curves for natural fiber-reinforced PP copolymers showed differences from those of neat PP, which does not undergo the constant stage in the stress–strain curve like the fiber-reinforced PP copolymer does. This constant stage in the stress–strain curve of the fiber-reinforced PP copolymer may be caused by a phenomenon called fiber pull-out. Fiber pull-out is a failure mechanism for fiber-reinforced composite materials. The cause of fiber pull-out is weak adhesive bonding between the fibers and the polymer matrix.

Effect of Melt Temperature and Holding Time

Rice husk fiber-reinforced PP copolymer

Fig. 10 shows the tensile strength for the rice husk fiber-reinforced PP copolymer with different processing parameters. The tensile strength exhibited the same trend for both holding times. The increase in melt temperature from 230 to 250°C results in an overall decrease of 10.9% in tensile strength with 3 s of holding time and 18.2% in tensile strength with 5 s of holding time. Tensile strength values reached the highest point at a melt temperature of 230°C. When the holding time was 3 s, the tensile strength value was 12.21 MPa at a melt temperature of 230°C. The value then decreased 1.7% to 12.008 MPa at 240°C. As the melt temperature continued to increase to 250°C, the tensile strength decreased 9.4% again to 10.874 MPa. Furthermore, when the holding time was 5 s, the tensile strength value was 13.208 MPa at the melt temperature of 230°C. The value then decreased 11.9% to 11.632 MPa at 240°C. As the melt temperature continued to increase to 250°C, the tensile strength decreased 7.1% again to 10.804 MPa.

Flax fiber-reinforced PP copolymer

Fig. 11 shows the tensile strength for the flax fiber-reinforced PP copolymer with different processing parameters. Both of the lines exhibited the same trend for both holding times. Overall, it increased 11.2% with 3 s of holding time and 10.4% with 5 s of holding time when the melt temperature increased from 230 to 250°C. Tensile strength values reached the highest point at the melt temperature of 250°C. When the holding time was 3 s, the tensile strength was 14.638 MPa at a melt temperature of 230°C. It

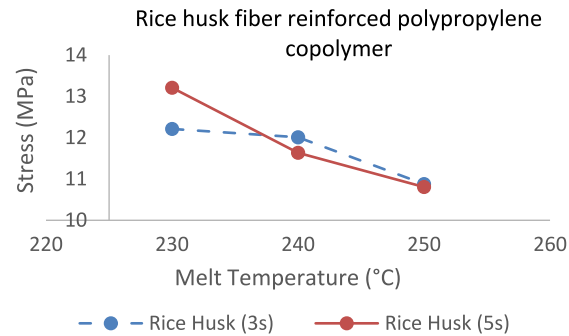


Fig. 10 Comparison of tensile strength for the rice husk fiber-reinforced polypropylene (PP) copolymer with different processing parameters.

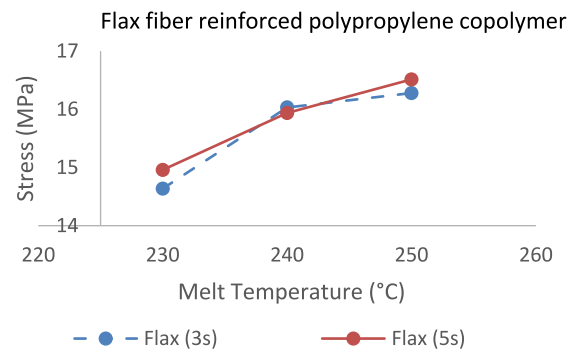


Fig. 11 Comparisons of tensile strength for the flax fiber-reinforced polypropylene (PP) copolymer with different processing parameters.

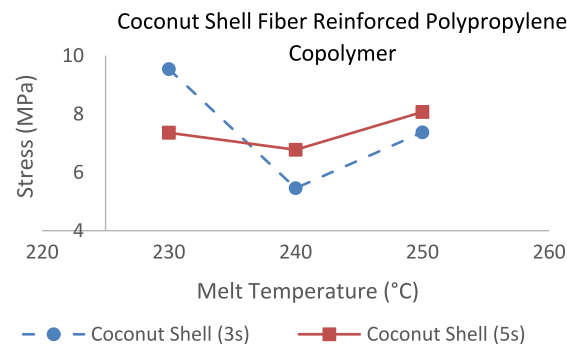


Fig. 12 Comparisons of tensile strength for the coconut shell fiber-reinforced polypropylene (PP) copolymer with different processing parameters.

increased 9.5% to 16.032 MPa at 240°C. Then, it continued to increase 1.5% to 16.278 MPa as the melt temperature increased to 250°C. When the holding time was 5 s, the tensile strength was 14.958 MPa at a melt temperature of 230°C. It increased 6.5% to 15.936 MPa at 240°C. Then, it continued to increase 3.6% to 16.514 MPa as the melt temperature increased to 250°C.

Coconut shell fiber-reinforced PP copolymer

For both holding times, Fig. 12 shows that the tensile strength for the coconut fiber-reinforced PP copolymer displayed the same trend, with the curves decreasing when the melt temperature increased from 230 to 240°C but increasing when the melt temperature increased from 240 to 250°C. When the holding time was 3 s, the copolymer reached the highest tensile strength value at a melt temperature of 230°C (9.54 MPa). It then decreased (42.8%) to 5.45 MPa at 240°C. Nonetheless, as the melt temperature increased to 250°C, the tensile strength of the copolymer increased 35.1% to 7.374 MPa. When the holding time was 5 s, the tensile strength of the copolymer was 7.36 MPa at a melt temperature of 230°C. A slight decrease (7.9%) occurred at 240°C, resulting in a value 6.776 MPa. At a melt temperature of 250°C, the tensile strength value increased 19.1% and reached the highest point (8.07 MPa).

Figs. 10–12 show comparisons of tensile strength values for each of the three types of natural fiber-reinforced PP copolymers with different processing parameters. The trend of the tensile strength for the coconut shell fiber-reinforced PP copolymer was

inconsistent. Therefore, it can be concluded that there was no significant relationship between tensile strength and processing parameters for the coconut shell fiber-reinforced PP copolymer. Regarding the flax fiber-reinforced PP copolymer, a different observation was made. A trend can be noticed from the values of tensile strength. The tensile strength of the flax fiber-reinforced PP copolymer increased with the increase in the melt temperature. Additionally, a trend was observed for the rice husk fiber-reinforced PP copolymer. The trend indicated that the tensile strength of the rice husk fiber-reinforced PP copolymer decreased with the increase in melt temperature. By comparing these three types of natural fiber-reinforced PP copolymers, it was shown that the flax fiber-reinforced PP copolymer exhibited the highest tensile strength value among the three copolymers. This indicated that the flax fiber-reinforced PP copolymer can withstand more stress while being stretched or pulled than the other two copolymers. It could be observed that the tensile strength for all three types of natural fiber-reinforced PP copolymers used in this study was lower than that of neat PP (25–40 MPa). Although this shows that the strength of fiber-reinforced PP copolymers is weaker than that of neat PP, using fiber-reinforced PP copolymers has advantages. For example, natural fiber-reinforced PP copolymers are more environmentally friendly.

Experimental and Simulation Results

Simulations of the microtensile test for the specimens made from three natural fiber composite materials with different combinations of processing parameters were conducted by using ABAQUS software. Some data obtained from the microtensile test were inputted in ABAQUS to perform simulations. These data were Young's modulus, Poisson's ratio, yield stress, and plastic strain. Furthermore, the density of the material is also needed for the simulation. A total of 18 simulations were performed.

Fig. 13 shows an example of a comparison of the simulated stress–strain curve with the experimental curve for the coconut shell fiber-reinforced PP copolymer processed at a melt temperature of 230°C and holding time of 3 s. Two curves are displayed in the figure. The solid curve represents the ABAQUS simulation results; the dotted curve represents the results of the experiment. These two curves were plotted using the raw data obtained from the experimental tensile test and the ABAQUS simulation of the tensile test. From the graph, it can be observed that two curves have an identical shape and show an identical trend.

Rice husk fiber-reinforced PP copolymer

Comparison of the simulated stress–strain curve with the stress–strain curve obtained after the experiment for the rice husk fiber-reinforced PP copolymer at melt temperatures of 230, 240, and 250°C with a holding time of 3 s is shown in Fig. 14. There was not

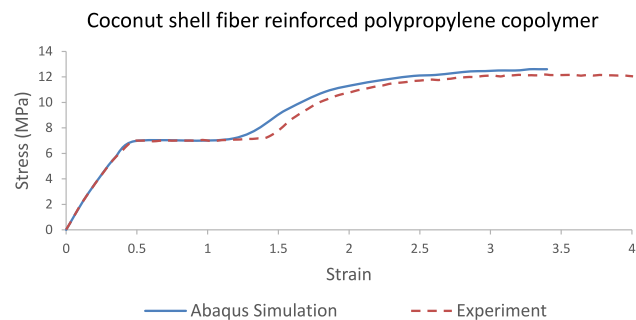


Fig. 13 Example of comparison of the simulated stress–strain curve with the experimental curve (coconut shell fiber-reinforced polypropylene (PP) copolymer: melt temperature, 230°C; holding time, 3 s).

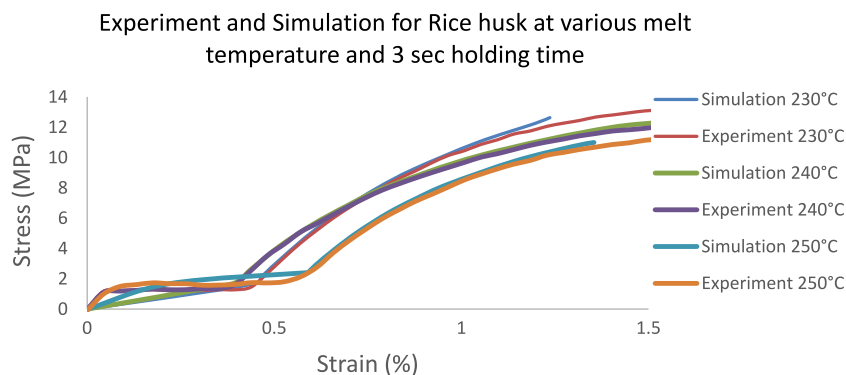


Fig. 14 Simulated and experimental stress–strain curves. Rice husk fiber-reinforced polypropylene (PP) copolymer. Melt temperatures of 230, 240, and 250°C. Holding time of 3 s.

much difference observed for the stress–strain curve for the melt temperatures of 230 and 240°C for both the experiment and simulation results. However, there was a 50% increase in strain in plastic deformation with the 250°C melt temperature. The same observations recorded for the sample with a 5-second holding time are shown in Fig. 15.

Flax fiber-reinforced PP copolymer

Figs. 16 and 17 show the simulated and experimental stress–strain curves for the flax fiber-reinforced PP copolymer with melt temperatures of 230, 240, and 250°C and holding times of 3 and 5 s. The strain increment was more than 100% for plastic deformation with melt temperatures of 240 and 250°C. With the 5-second holding time, as the melt temperature increased, the strain percentage for plastic deformation increased (Fig. 17). This indicates that the higher the melt temperature, the greater the strain.

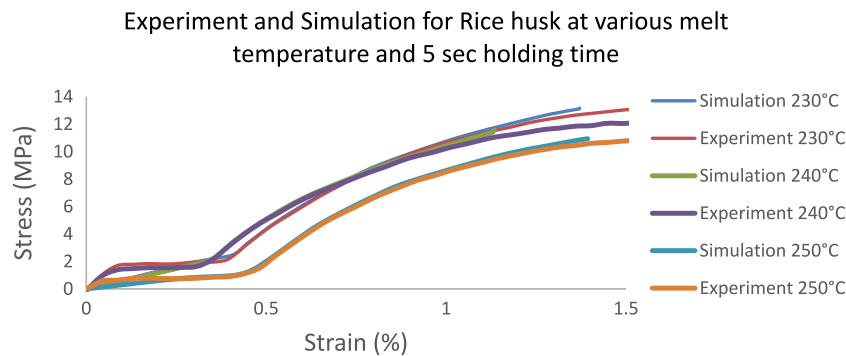


Fig. 15 Simulated and experimental stress–strain curves. Rice husk fiber-reinforced polypropylene (PP) copolymer. Melt temperatures of 230, 240, and 250°C. Holding time of 5 s.

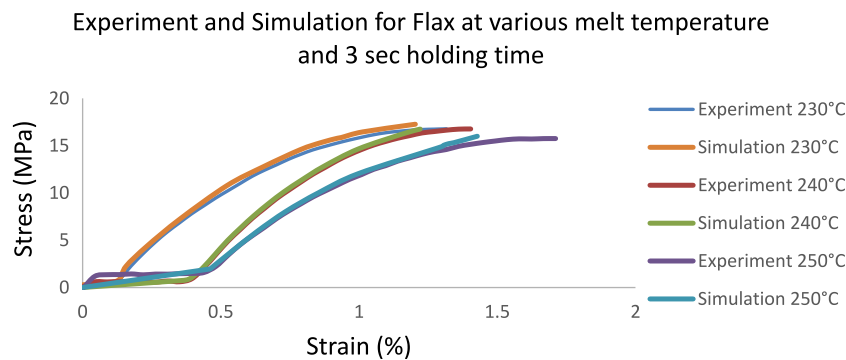


Fig. 16 Simulated and experimental stress–strain curves. Flax fiber-reinforced polypropylene (PP) copolymer. Melt temperatures of 230, 240, and 250°C. Holding time of 3 s.

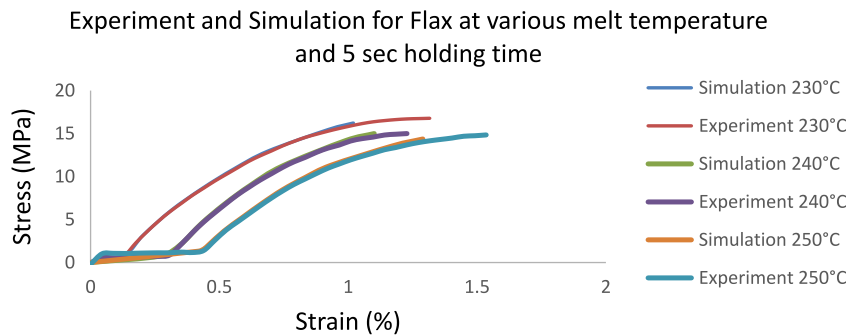


Fig. 17 Simulated and experimental stress–strain curves. Flax fiber-reinforced polypropylene (PP) copolymer. Melt temperatures of 230, 240, and 250°C. Holding time of 5 s.

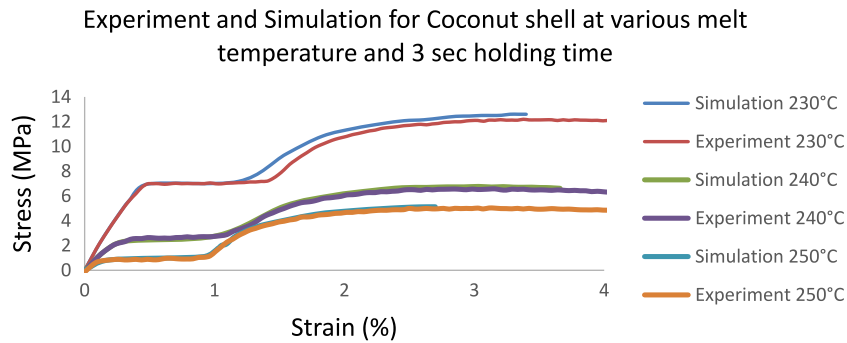


Fig. 18 Simulated and experimental stress–strain curves. Coconut shell fiber-reinforced polypropylene (PP) copolymer. Melt temperatures of 230, 240, and 250°C. Holding time of 3 s.

Coconut shell fiber-reinforced PP copolymer

The simulated and experimental stress–strain curves for the coconut shell fiber-reinforced PP copolymer at melt temperatures of 230, 240, and 250°C with 3 s of holding time are shown in Fig. 18. As the melt temperature increased, the stress decreased drastically to more than 70%, indicating that the coconut shell fiber-reinforced PP copolymer had decreased strength due to the increased processing temperature. Therefore, it is better to mold parts made from coconut shell fiber at lower melt processing temperatures to maintain their strength.

Based on Figs. 14–18, the experimental and simulated FEA results displayed identical trends for the three natural fiber-reinforced PP copolymers with different combinations of processing parameters. The curves obtained from both results were in similar trend. All simulated models provided good agreement with the experimentally tested method. Hence, the simulated models used for ABAQUS simulation can be used to simulate the tensile test with other conditions, such as different testing speeds. In other words, it was proven that the results obtained using ABAQUS were theoretically accurate.

Conclusions

Tensile testing for three types of natural fiber-reinforced PP copolymers was conducted experimentally and also simulated by using FEA software (ABAQUS). The mechanical properties for these three types of natural fiber-reinforced PP copolymers were also investigated. The results of this study provide the following conclusions:

1. The flax fiber-reinforced PP copolymer possesses better stiffness and can withstand more stress while being stretched or pulled than the other two natural fiber-reinforced PP copolymers.
2. Processing parameters affect the mechanical properties of the microtensile specimen. In this study, the effect of melt temperature on the tensile strength of the microtensile specimen was significant for flax fiber-reinforced and rice husk fiber-reinforced PP copolymers.
3. The simulated results of tensile testing were compatible with the experimental results. The results of both produced similar curve trends. Therefore, for the same material, the simulated model can be used to simulate tensile testing with different conditions.

Acknowledgments

The authors acknowledge financial support from the Ministry of Education, Malaysia, under University Malaya Research Grant (UMRG) project number RP033A-15AET.

See also: Bamboo Fiber as Fillers for Polypropylene-Nanoclay via Injection Molding

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Experimental Investigations for Development of Aluminum MMC With Hybrid Reinforcement and Vacuum Molding

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Introduction

Today, there is an expanding demand worldwide for the advanced materials with a specific end goal to get the coveted properties. This is because that a solitary material by and large can't meet the necessities of cruel engineering conditions. That is the reason the requirement for metal matrix composites (MMC's) with extraordinary properties (high strength, high stiffness and low weight) compared to monolithic material is developing every day (Kok, 2005). MMC's are made from two or more diverse metals, inter-metallic compounds (reinforcement) in which scattered stages are implanted inside the metallic matrix. The ceramic reinforced MMC's exhibit better tribological properties due to the shielding of matrix (soft metal) with reinforcement (hard ceramic) particles (Suresha and Sridhara, 2010). The insoluble reinforcement size, kind, their relative amount controls the properties of the composites.

Among all MMC's, Aluminium metal matrix composites (Al-MMC's) have found wide applications in today's fast growing automobile and aviation industry (Singh *et al.*, 2015b). There are a few preferences in utilizing particles reinforced Al-MMC's materials than un-reinforced/monolithic materials (cast iron, steel) such as- more prominent strength (tensile strength) with less weight, progressed stiffness, low thermal extension coefficient, high thermal conductivity, increased wear resistance, improved mechanical properties (hardness) and made strides damping capabilities (Surappa, 2003). Al-MMC's are very promising materials for foresaid industry not only due to their excellent combination of properties, but also can be processed by conventional manufacturing processes such as forging, rolling, extrusion and subsequent machining (Iqbal and Nuruzzaman, 2016). Al-MMC's based components are mostly used in tribological system which needs excellent wear performance. It has been observed that the hard non-metallic and ceramic particles like SiC, Al₂O₃, B₄C, Gr etc. have been successfully used as reinforcements in Al-MMCs to impart excellent mechanical and tribological properties (Sahin, 2003; Kok and Ozdin, 2007; Das *et al.*, 2007; Yigezu *et al.*, 2013). The lower weight of Al-MMC's material based engine components reduces the fuel consumption in automobile and aircraft which further reduces the air pollution (Surappa, 2003). In 1992, UK Advisory Council on Science & Technology expressed that the Al-MMC's could be able to swap for existing materials with superior properties (Surappa, 2003).

The new generation hybrid Al-MMC's development with the incorporation of more than one type, shape and size of reinforcement into a single matrix (Al) are gaining more importance (Matsunaga *et al.*, 1996). Hybrid Al-MMC's have the potential to fulfil industry requirement due to their superior properties (tribological and mechanical) as compared to single reinforced composites (Ahlatci *et al.*, 2006), since it is troublesome to consolidate a wide range of properties within the composite materials with single reinforcement. Bindumadhavan *et al.* (2001) reported that the dual particle size (DPS) reinforced A356/SiC composite exhibit better wear resistance as compared to the single particle size (SPS) reinforced composite due to shielding of smaller SiC particles by larger one in DPS. Whereas, Maleque and Karim (2008) had observed that the triple particle size (TPS) Al/20% SiC exhibited better wear resistance properties compared to DPS reinforcement. The effect of multiple particle size (80 µm, 40 µm and 15 µm) of SiC reinforced Al-MMC on the wear characteristics was also investigated and observed that coarse particle has significantly influence the wear resistance as compared to the intermediate and fine particle sizes (Abdulmumin *et al.*, 2015).

The hybrid material gives more freedom to design a material for any specific application with less cost. Hybrid Al-MMC's have better wear resistance and high specific strength with less weight due to which it is widely used in automotive engineering applications such as: piston rods, piston pins, pistons, brake discs and pads, shaft, etc. (Uvaraja and Natarajan, 2012). The improved tribological properties of hybrid composites have made it more suitable choice for structural application in the aerospace industry.

The fabrication process and the reinforcement (type, shape, size & quantity) governed the properties of the composites (Hashim *et al.*, 1999; Surappa, 2003). The target properties can be successfully achieved by getting requisite wetting, bonding and stability among the matrix and reinforcement (Hashim *et al.*, 1999) with a homogeneous distribution of the reinforcement in the matrix. The diverse processing route has been adopted to fabricate Al-MMC's such as:

- (1) Solid state processing route (Powder metallurgy, Diffusion bonding and Physical vapour deposition),
- (2) Liquid state processing route (Stir casting, Infiltration process and Spray deposition).

The stir casting (SC) is one of the most preferred economical liquid state processing route among the all processing routes due to its simplicity, flexibility and suitability for large scale production (Surappa, 1997). In SC, the reinforcement particles are uniformly mixed in a molten metal (matrix) with a mechanical stirrer (see Fig. 1), then further the molten mix (matrix and reinforcement) is poured into die in the case of die casting or mould in case of sand casting. The cost of production associated with

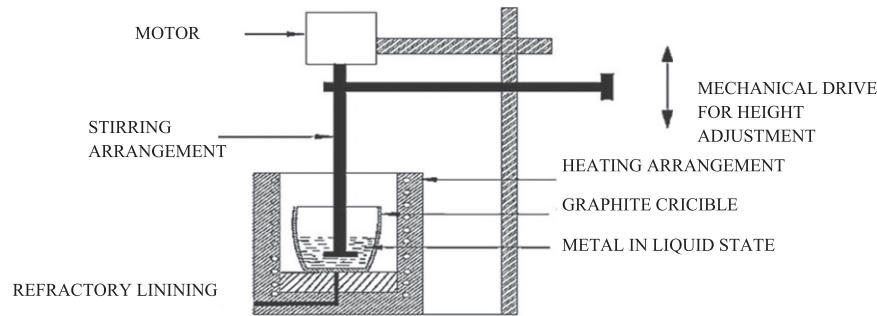


Fig. 1 Metal Matrix Composites through SC.

SC is one third as compared to other process (Surappa, 1997; Shankar *et al.*, 2013) and make this is the first choice for large scale production.

The cast component needs an additional machining process to get the exact size and shape which may become difficult due to the presence of abrasive reinforcement in the Al-MMC's casting. It has been found that the subsequent high cost and time is required for the development and modification of the pattern in sand casting. So, to overcome the limitations of conventionally used fabrication process the synergistic combination of rapid prototyping processes with the modern casting technique V-process which can greatly contribute towards decreasing the lead time while maintaining the quality standards is introduced in this study.

Rapid Manufacturing of Patterns

It is well established that large range of metal parts are manufactured with sand casting for many years. The pattern is the key element of the casting process used to create the cavity with desired feature. A lot of conventional manufacturing processes (turning, milling, drilling etc.) are involved to develop the pattern. During prototyping which involved development of the product and its performance testing, excessive time is involved in the manufacturing of product pattern. Whereas in case of customized based product manufacturing in which the required quantity is very limited excessive lead time is consumed in the development process. Along with excessive development time high level skill is also required for the development of pattern with conventional process. The major concern for today's industry is to remain competitive in the market and which is not possible without reducing the product development cycle time. Hence, there is strong motivation to incorporate rapid prototyping (RP) technology for the development/manufacturing of pattern. However the major limitations related to RP for this purpose are size of component and the high cost of infrastructure. The use of RP introduced few decades ago gives new look to this sector and emerged as rapid tooling for the manufacturing of application oriented product in less time. RP is entirely CAD and modeling software based process to develop a 3D model of the product. With the application of computer the CAD based data are split into slice/layer which further develops the object layer wise. RP process is effectively able to reduce the product development cycle with efficiently controlling the development time and human interaction in comfortable work conditions. Due to these excellent features RP is not limited to manufacturing industry now it becomes a prominent field of research. The practice of RP technique to develop rapid tooling provides a platform for the development of functional based product particularly for medical research.

RP can be able to manufacture multiple and complex geometry part in single build without changing tool and with a minimum skill requirement. Among all the RP techniques, Fused Deposition Modeling (FDM) developed by Stratasys Inc. is widely accepted for rapid manufacturing of the pattern, wherein a plastic filament of Acrylonitrile-Butadiene-Styrene (ABS) material is used. It is also reported that the FDM has significantly reduced the product development time and cost and become the first choice of the researchers (Bakar *et al.*, 2010; Chohan *et al.*, 2017).

FDM is a rapid prototyping technology suited for producing parts with complex geometries. The FDM machine is basically a computer numerically controlled gantry machine, carrying two miniature extruder head nozzles, one for the modeling material and the other for the support material (Sun and Rizvi, 2008). In the FDM process, parts are fabricated by extruding a molten filament through a heated nozzle in a prescribed pattern onto a platform (Fig. 2). As the material is deposited, it cools, solidifies and bonds with the adjoining material. When one whole layer is deposited, the base plate moves down by an increment equal to the height of the filament and the next layer is deposited. FDM prototypes can be viewed as composites structures composed of partially bonded filaments. A key feature of the FDM process is its potential to fabricate parts with locally controlled properties such as porosity, density and mechanical properties (Li *et al.*, 2002). FDM requires minimal manpower and is increasingly used to fabricate customized products for engineering as well as medical applications (Singh *et al.*, 2018a). The several applications of FDM generated parts are illustrated in Fig. 3.

Singh *et al.* (2017b) established that the manufacturing of customized biomedical implant (hip joint) is feasible through the combined route of FDM (to develop pattern), chemical vapour smoothing (to improve surface finish), vacuum casting and

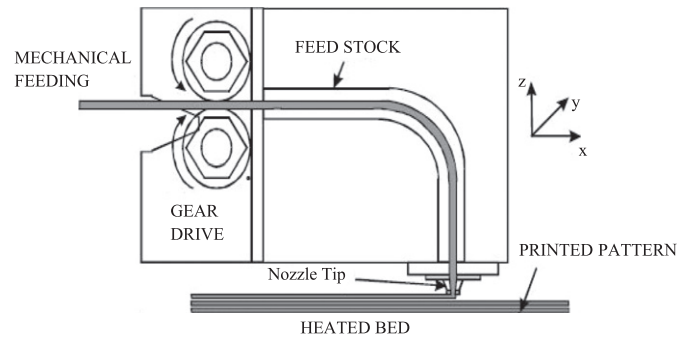


Fig. 2 Schematic of FDM setup.

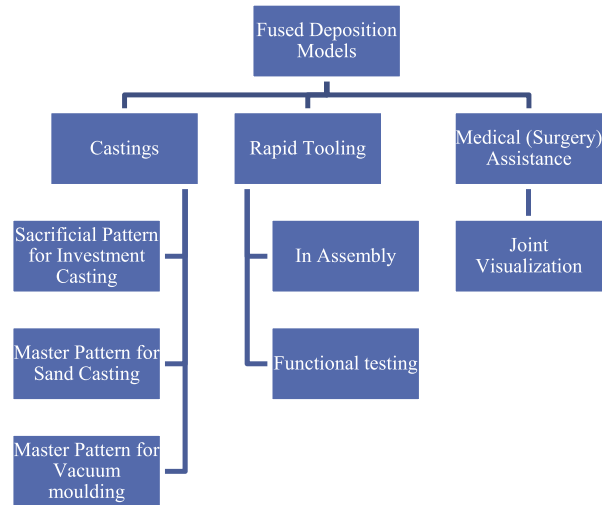


Fig. 3 Application of FDM parts. Reproduced from Singh, J., Singh, R., Singh, H., 2017a. Dimensional accuracy and surface finish of biomedical implant fabricated as rapid investment casting for small to medium quantity production. *Journal of Manufacturing Processes* 25, 201–211.

investment casting. The combined processing route was successfully delivered adequate dimensional accuracy and surface finish to the implant. Further, the tolerance grade of the selected dimension of the casting (implant) was found in accordance with ISO standard UNI EN 20286-1 (1995).

V-process/Vacuum Moulding (VM)

The quality of the product and its control is the prime requirement of the manufacturing industry. The metal casting industry is also growing continuously with the aim of consistent quality production to survive in this fast developing competitive industry. To overcome the limitation of the conventional moulding process such as heavy machinery, casting defects (blow hole, poor surface finish) and pollution, V-process/vacuum moulding (VM) has emerged as one of the modern technique to deliver adequate quality with minimal defects (Kumar *et al.*, 1999).

The vacuum sealed moulding/V-process was invented and patented by the Japanese in 1971 and introduced to the foundry men in 1972 (Bishop and Bose, 1983; Clegg, 1985). First V-process plant was successfully commissioned for commercial production under the able leadership of Dr. R. Kono at Toyokawa works of Sinto (Japan) in 1972 (Clegg, 1985). VM has received significant importance due to its potential to create dimensionally precise, smooth casting and high return rate of sand at 95% (Kumar *et al.*, 1999). The fundamental distinction among VM and conventional sand moulding processes is the manner wherein sand is bounded to form the mould cavity. VM entails the formation of mould cavity via thermal and vacuum forming of plastic film over the pattern, backed by dry un-bonded sand compacted by mean of vibration and further gets encapsulated between plastic films under the influence of imposed vacuum (250–450 mm Hg) (Clegg, 1985). On pouring, the molten metal fills the cavity under vacuum, precisely duplicating all of the features. The vacuum was maintained until the metal solidifies and the sand was dropped away very easy to leave the casting with the

fine surface finish. The casting produced by this green process is free from draft allowance with a high degree of dimensional accuracy which further helps to reduce the machining time and cost (Regnet, 2000). VM has also retrenched the high investment on the dies and equipment as compared to the die casting process. In VM, cracking defect encountered in die casting is also eliminated due to the good withdrawal ability of the unbounded sand. VM is emerging as environment friendly process as compared to conventional sand casting due to the absence of pollution caused by the burning of the binder and reuse of moulding sand without further treatment (Jain and Gaindhara, 1986; Barua *et al.*, 1996; Grefhorst and Muller, 2000; Singh *et al.*, 2017c). The lower solidification rate of metal in a vacuum mould also promotes the development of fine grain microstructure and further causes improvement in the mechanical properties of the cast components (Kubo *et al.*, 1973; Kumar and Gaindhara, 1997). Singh and Singh (2015) prepared Al-MMC's consisting of Al-6063(matrix) reinforced with SiC (SPS-100 μm ; DPS-100 and 120 μm ; TPS-100, 120 and 150 μm) in the proportion of 5 wt%, 7.5 wt% and 10 wt% through FDM based pattern and vacuum assisted SC. The tribological performance of the developed Al-MMC's was examined on the basis of dry sliding wear test by using a pin-on-disc (ϕ 8 mm $\times$ 25 mm) at sliding speed of 239 rpm, sliding diameter of 80 mm and a load of 19.61N for 10 min. The effect of V-process assisted SC parameters (particle size of SiC, the proportion of SiC, vacuum pressure and sand grain size) on wear performance of Al-MMC's were also studied. The study highlighted the percentage contribution of sand grain size, vacuum pressure, particle size of SiC and composition for wear are 5%, 10.14%, 10.71% and 73.2%, respectively. Singh *et al.* (2015a) have examined the effect of particle size of hybrid reinforcement (fixed proportion, 10% by weight.) Al_2O_3 and SiC on wear performance of Al-MMC prepared by SC and VM. The result shows that the particle size of hybrid reinforcements have greatly influenced (70%) the wear performance of casted composites and the single particle size (SPS) hybrid reinforced composite exhibits better wear resistance. Singh and Singh (2017) have successfully developed Al- Al_2O_3 based biomedical implant (dynamic condylar screw) by using the combined process comprising of FDM, VM and stir casting. The contribution and optimum level of various process parameters (percentage composition of Al and Al_2O_3 , vacuum pressure and grain size of silica) towards micro hardness of the implant was investigated. The study highlighted the moulding sand (74%) is most contributing factor followed by vacuum pressure(14.73%) and Al_2O_3 composition(6.2%) and prosed the best parametric setting (Al_2O_3 5%, AFS no. 60 and vacuum pressure 300 mm of Hg) for maximum micro hardness.

Singh *et al.* (2018b) developed Al-MMC's with hybrid reinforcement (5%, 7.5% and 10% by weight) of double particle size (DPS) and triple particle size (TPS) Al_2O_3 and SiC, by using VM (V-process) assisted SC process and examined the process capability of the hybrid process in term of dimensional accuracy. The study highlights the percentage contribution of significant process parameters (particle size 9.19%, type of reinforcement 12.99%, vacuum pressure 35.18% and moulding sand grit size 28.10%) on the dimensional accuracy of hybrid Al-MMC. Finally the calculated value of process capability indices (Cpk) more than 1.3 highlighted that the developed hybrid process is statistically controlled for batch and mass production.

Considering the novel features of FDM and V-process/VM (VM) a synergistic combination of FDM and VM can be explored as new route for the development of hybrid Al-MMC's. The resulting green process will lead to rapid casting solutions for metal matrix composites (MMC's). It is quite evident in the literature that the Al-MMC's are widely used in the tribological application. So, in the present study attempt has been made to examine the process capability of this novel route in term of the performance characteristics such as wear, micro hardness and dimensional accuracy of the hybrid Al-MMC's.

Procedure to Develop Hybrid Al-MMC's

The brief description about the procedure to develop hybrid Al-MMC's with the novel fabrication route including FDM, VM and SC process is as mentioned below:

Development of pattern with FDM: After selecting the component/benchmark, the CAD file of the selected component was exported into STL (Standard Triangulation Language) format and sliced down on Catalyst-EX[®] FDM system inbuilt software. The perforated ABS pattern of the selected component was printed on FDM machine with tiny holes (ϕ 1 mm) to induce vacuum suction for the proper sticking of plastic film during the V-process.

Mould formation with VM: FDM based pattern is used to create mould with V-process/VM, the schematic view of VM setup is shown in Fig. 4.

For the mould formation, the perforated pattern (of selected component) is placed at the centre of the base plate and a preheated thin plastic sheet was drawn onto the pattern contour by imposing vacuum (300–400 mm of Hg), as shown in Fig. 5(a). Then a mould box (drag) was placed on the base plate and the formed plastic sheet was fixed with the mould box (Fig. 5(b)). The dry un-bonded silica sand (AFS No. 50–70) fills in the mould box and gets compacted by vibration (3–5 s), as shown in Fig. 5(c). The other open side of the mould box was sealed with second plastic sheet and then further vacuum was applied to compact the sand (Fig. 5(d)). The vacuum of the base plate was released and the mould box flipped off. The pattern easily slipped out and the required cavity/mould was formed (Fig. 5(e)). After developing mould/cavity, place second mould box (cope) on the first mould box (Fig. 5(f)). Fig. 5(g) shows, the proper gating arrangement given to the formed cavity. The mould box (cope) was filled with dry unbounded sand and sealed with a plastic sheet (Fig. 5(h)). The sand gets compacted with the application of vibration and vacuum. The two halves were properly sealed and the mould cavity under vacuum was ready for metal pouring.



Fig. 4 Schematic of VM setup. Reproduced from Singh, R., Singh, S., Hashmi, M.S.J., 2017c. Vacuum molding. In: Hashmi, S., (Ed.), Reference Module in Materials Science and Materials Engineering. vol. 13. Oxford: Elsevier, pp. 1–18.

Preparation for hybrid Al-MMC's with SC: For the development of Al-MMC, the required quantity of aluminium alloy was melted in a graphite crucible at 800°C and the reinforcement particles (SiC and Al₂O₃) were preheated at 450°C to drive off the moisture before charging. A mild steel stirrer is immersed up to two thirds depth of the molten metal and stirred at the speed of 450 RPM (Fig. 6(a)). Finally, the molten Al-MMC was poured into the mould under negative pressure and get solidify (Fig. 6(b) and (c)). Fig. 6(d) shows, after cooling the vacuum is released and free-flowing sand drop away, leaving a clean required casting without sand lumps.

Case Study

In order to develop hybrid Al-MMC's through synergistic combination of FDM, VM and SC investigate and validity of this novel route has been established by examine the process capability in term of the performance characteristics such as wear, micro hardness and dimensional accuracy of casting, a case study has been discussed.

In the present case study, a disc of 50 mm diameter and 10 mm thickness was selected as a component/benchmark (see Fig. 7) and the perforated ABS pattern of the selected component was printed on FDM machine. The FDM based pattern was used to create mould with VM, the performance characteristics of the casting obtained through VM are governed by the various input control factors of the process such as vacuum pressure (mm of Hg); moulding sand grit size (AFS No.); and vibration time (s). Based upon the various trails the best parametric setting of VM considered for this study is given in the Table 1.

For the development of Al-MMC, aluminium alloy Al-6063 alloy (≥ 99.6 wt% Al) was used as a matrix material and Al₂O₃ and SiC of particle size 122 μ m and 102 μ m are used as reinforcement. The detailed chemical composition of matrix (Al-6063) and the properties of reinforcement (Al₂O₃ and SiC) are given in Tables 2 and 3, respectively. The particle size and composition of reinforcement strongly affect the tribological performance (wear) and mechanical properties (micro hardness) of the Al-MMC's. In the present study, reinforcement composition of 10 wt% with double particle size (DPS) was used, the DPS reinforcement was obtained by mixing of 122 μ m and 102 μ m particle size in equal proportion by weight. The parametric setting of stir casting employed for the present case study is given in Table 4.

Six repetitive trials were conducted at the selected parametric setting of VM (Table 1) and SC (Table 4) by following the procedure explained in Section "Procedure to Develop Hybrid Al-MMC's". The performance characteristics (wear, micro hardness and dimensional accuracy) of the casted discs were examined.

Wear Test: As per ASTM G 99 standard, testing pin of size $\phi 8$ mm $\times$ 25 mm was prepared from all the casting. The contact surface of the pins was polished on 800 grit emery paper. Wear test pins were slides against EN-31 steel disc hardened to 60 HRC and ground to 1.6 Ra. Tests were conducted at constant conditions of normal load, sliding track diameter and sliding speed of 30 N, 100 mm and 1 m/s, respectively, for 10 min. Three repetitions of experiments were conducted to minimize the error and the corresponding results of tests for wear (μ m) were obtained, as given in Table 5.



Fig. 5 Mould formations with VM.

Table 1 The parametric setting of VM

S. No.	Input factor	Value
1	Vacuum pressure (mm of Hg)	350
2	Moulding sand grit size (AFS No.)	50
3	Vibration Time (sec.)	4

Table 2 Chemical composition of Al-6063

Element	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
Wt %	0.2–0.6	0.35	0.10	0.10	0.45–0.9	0.10	0.10	0.1	Balance

Table 3 Properties of reinforcement

Material	Density (g/cm^3)	Melting point ($^{\circ}\text{C}$)	Hardness (kg/mm^2)	Modulus of elasticity 'E' (GPa)
Al_2O_3	3.69	2072	1175	300
SiC	3.2	2730	2800	410

Table 4 Parametric setting of SC

S. No.	Input factor	Value
1	Particle size	DPS
2	Type of reinforcement	SiC + Al_2O_3
3	Composition (%)	10

Table 5 Results of the performance characteristics of hybrid Al-MMC's

Trail No.	Wear (μm)	Micro hardness (HV)	Dimensional deviation (mm)
1	70.0	40.5	0.72
2	71.0	41.4	0.69
3	70.9	41.1	0.75
4	70.2	40.6	0.73
5	70.7	41	0.71
6	70.4	40.8	0.71


Fig. 6 Preparation for hybrid Al-MMC using SC.

Hardness Test: Micro hardness of the Al-MMC's based castings was examined by using computerized Vickers hardness tester as per ASTM E384.A load of 0.1 N was applied for 10 seconds on polished specimens of composites developed under ambient laboratory conditions. Each hardness value reported is an average of three readings, as given in [Table 5](#).

Dimensional Accuracy: Dimensional accuracy in term of dimensional deviation examined the capability of the process to regenerate the dimensions/features as per design. Thickness of the disc was selected for this study and dimensional

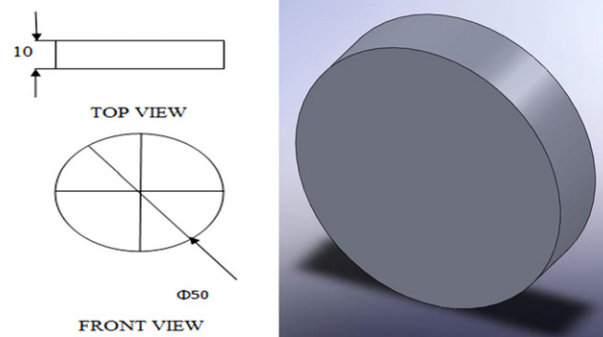


Fig. 7 Dimensions of benchmark disc.

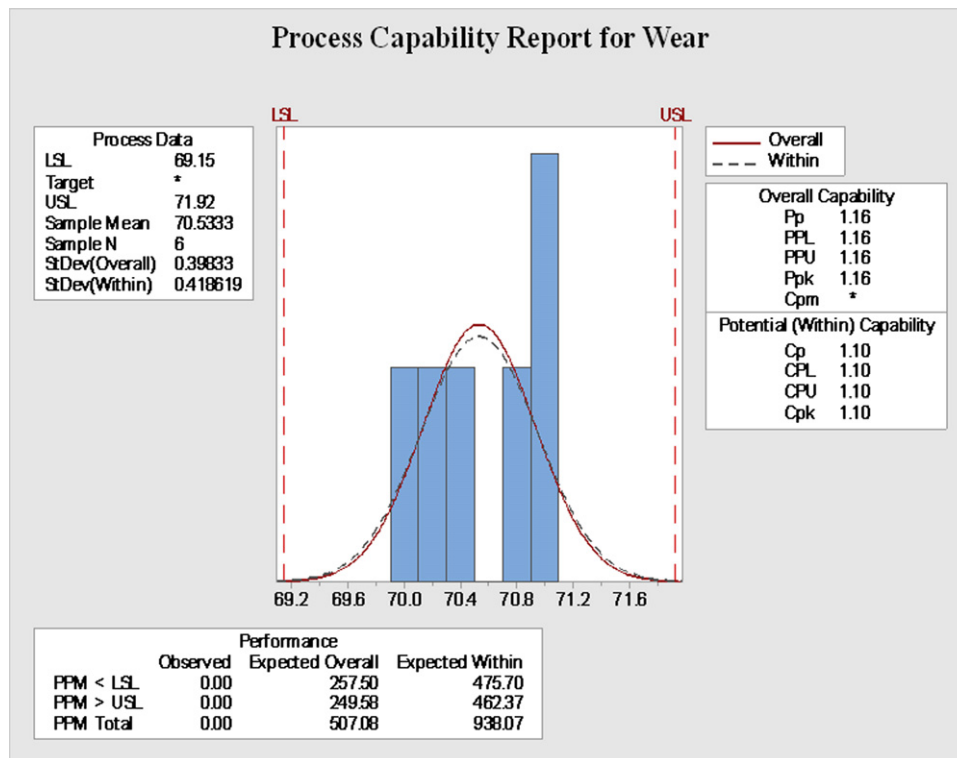


Fig. 8 Process capability histogram for wear.

deviation (Δt) of each casted Al-MMC's disc of designed dimension ($t=10$) was calculated. Thickness of the disc was measured from different points and an average value of dimensional deviation (Δt) of each casting is presented in Table 5.

Process Capability: After the satisfactory results, the development process of hybrid Al-MMC's and its performance characteristics (wear, micro hardness and dimensional deviation) were further examined to understand whether the developed process is statistically controlled or not? The process capability analysis of the process under study has been visualized through the process capability indices (C_p and C_{pk}). Minitab-17 software was used to plot process capability histograms and to determine process capability indices.

The histogram plot illustrating process capability indices for wear, micro hardness and dimensional deviation are shown in Figs. 8–10, respectively. The calculated value of process capability indices for each performance characteristics are tabulated in Table 6 and found the value of each process capability indices is greater than 1. The process with C_p and C_{pk} values of 1 or greater 3 indicated that the proposed process is statistically controlled and generally recommended for industry benchmarks which can be further improved under closed monitoring.

Thus, the process capability study based upon process capability indices deduced that the synergistic combination of FDM, VM and SC is quite capable in producing dimensionally accurate castings of hybrid Al-MMC's with adequate wear resistance and micro hardness. There is high probability for this process to be statistically stable and controlled for batch and medium production.

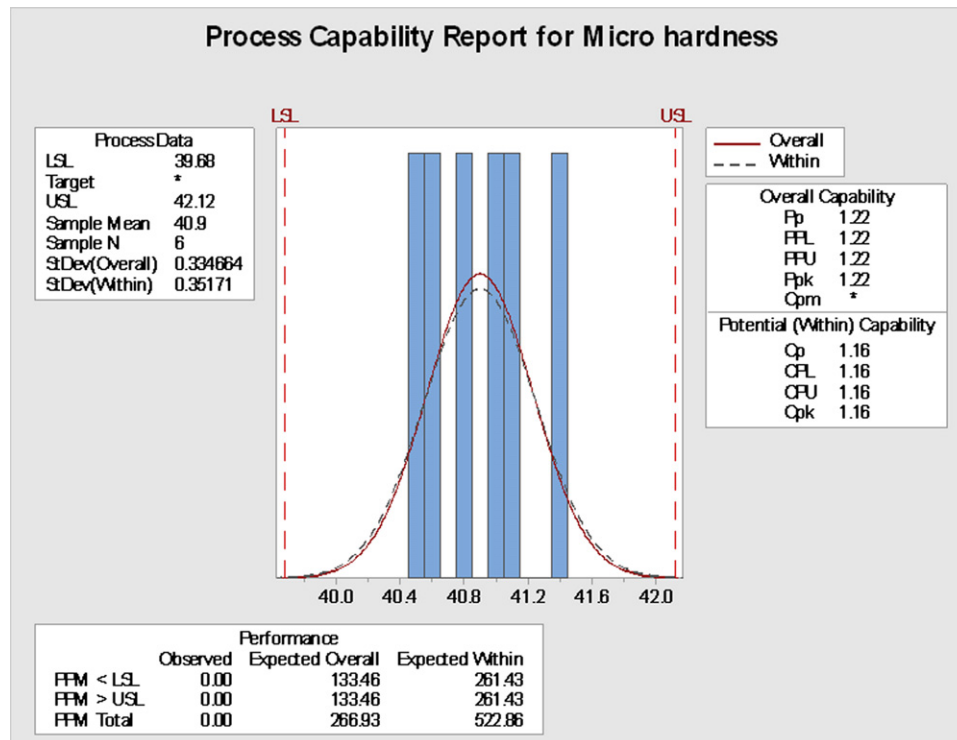


Fig. 9 Process capability histogram for micro hardness.

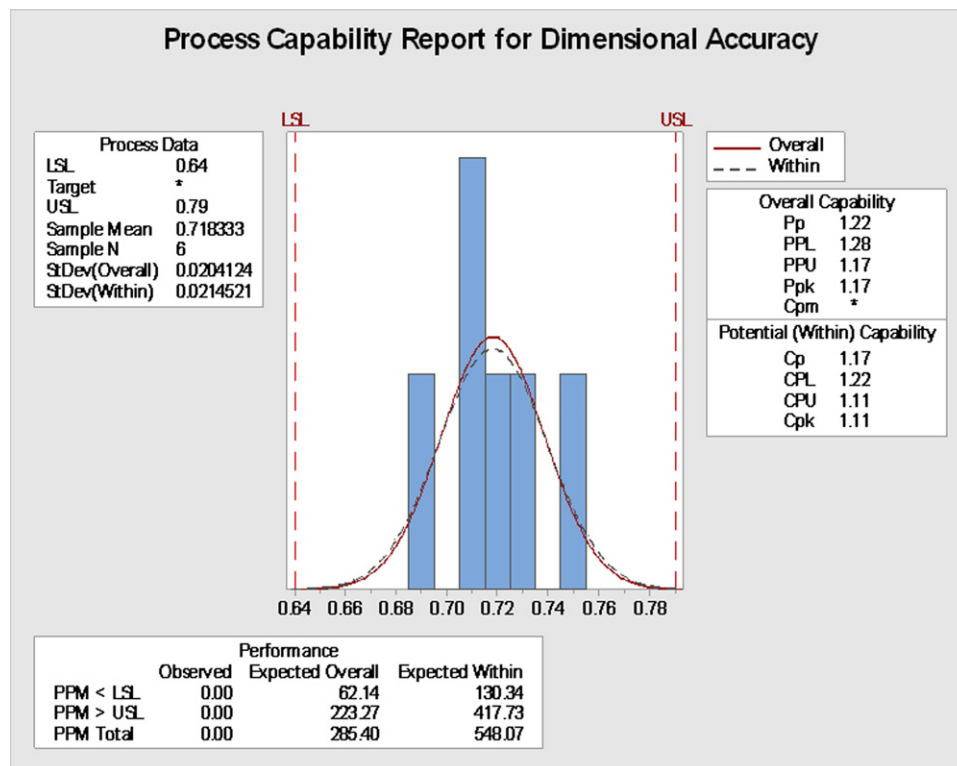


Fig. 10 Process capability histogram for dimensional deviation.

Table 6 Process capability indices for wear, micro hardness and dimensional deviation

Process capability indices	Performance characteristics		
	Wear	Micro hardness	Dimensional deviation
C_p	1.10	1.16	1.17
C_{pl}	1.10	1.16	1.22
C_{pu}	1.10	1.16	1.11
C_{pk}	1.10	1.16	1.11

Conclusions

The significance of the present study is to explore the feasibilities of the development of Al-MMC's with hybrid reinforcement by using the synergistic combination of FDM, VM and SC. The results of the study also established the competences of the new processing route for developing Al-MMC's with hybrid reinforcement (10 wt%) of DPS Al_2O_3 and SiC. The process capability histogram plot for wear, micro hardness and dimensional deviation illustrating that the process capability indices (C_p and C_{pk}) of each performance characteristic is greater than 1 confirmed that the process under study is statistically controlled. Thus, the proposed process is recommendable for industry benchmarks.

Acknowledgment

The authors are thankful to I.K.G. Punjab Technical University, Kapurthala (Pb.), India and Guru Nanak Dev Engineering College, Ludhiana (Pb.), India for providing this opportunity and support.

See also: Experimental Investigations for Development of Conductive Ceramic Composites with Microwave Sintering and Their Electric Discharge Machining. Investigations for Barium Titanate and Graphene Reinforced PVDF Matrix for 4D Applications. Sustainable Machining With Self-Lubricating Coated Mechanical Micro-Textured Cutting Tools

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Experimental Investigations for Development of Conductive Ceramic Composites with Microwave Sintering and Their Electric Discharge Machining

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Introduction

Ceramics are the first man made materials (Bhargava, 2011) having excellent mechanical, chemical, thermal and structural properties (Bhosale *et al.*, 2014). However, owing to its brittleness and bad electrical properties it is not possible to use ceramics in their natural form for various engineering applications. Therefore, the primary objective to make ceramic matrix composites is to overcome those deficiencies which can be a barrier in its applicability to different applications. Composite is basically a compound which contains a matrix phase and reinforcement phase (Vasiliev and Morozov, 2001).

CMCs obtained by different processing methods are generally having better wear properties, excellent creep behavior, fracture toughness and more resistant to thermal shocks. The basic purpose of reinforcement is to distribute stresses to nearby areas of crack tip which helps to alleviate the intensity of crack propagation (Callister, 2001). Due to this, CMCs are mostly preferred to use in the severe and hard environmental conditions where high thermal shocks and temperature is involved. The use of CMCs are generally in the field of aerospace, cutting tools, brakes, heat exchangers, gas turbines and many more. (Kaya, 1999; Chawla, 1995). The commonly used reinforcements for the CMC's are boron nitride (BN), titanium nitride (TiN), titanium carbide (TiC), carbon nanofibres (CNF), carbon nanotubes (CNT's), graphene and carbon black. Fabrication of ceramic composites can be done in different ways (see Fig. 1).

Fabrication by Using Gas Phase Processes

This process involves the controlled chemical reaction between the matrix and reinforcement material to form a composite. Few examples of gas phase reaction processes are chemical vapor deposition (CVD), reaction bonding and chemical vapor Infiltration (CVI) processes. This process has certain benefits over the other processes such as less processing time, temperature as well as lower energy requirement for nucleation and growth, and increased densification rate and capability to produce near net shape (Chiang *et al.*, 1991; Rahaman, 2003; Weimer *et al.*, 1997; Maitra, 2014). But, the major problem that arises during the formation of composite using gas phase processes is the increased porosity which deteriorates the mechanical properties of composites (Chiang *et al.*, 1991; Rahaman, 2003; Weimer *et al.*, 1997; Maitra, 2014; Yarbrough and Messier, 1990; Han *et al.*, 2014). Fig. 2 shows the set-up of commercial CVD system.

Fabrication by Using Liquid Phase Processes

Liquid phase processes primary include Sol-gel (see Fig. 3) and Polymer infiltration pyrolysis method. In this method, first step is to infiltrate the required polymer with the fiber reform in order to manufacture CMC's. Second step is the consecutive curing and pyrolysis to form a highly porous matrix, which is undesirable for most applications. Third stage involved polymer infiltration and pyrolysis up to number of cycles until the final product with better quality is achieved. It usually takes five to eight cycles to achieve best results (Ziegler *et al.*, 1999; Kotani *et al.*, 2003; Rocha *et al.*, 2006). Low yield and increased shrinkage volume and time to form a highly dense composite are the major drawbacks of this process (Rosso, 2006). In addition to this, crack formation during drying process in the matrix is another demerit of this process (Zou *et al.*, 2012; Almeida *et al.*, 2015).

Fabrication by Using Solid Phase Processes

Powder metallurgy is one of the solid processing methods which include the mixing and blending of different powders with required binders and lubricants, followed by the compaction of mixed powder and in the last sintering of the compact under controlled condition (Angelo and Subramanian, 2012). Powder metallurgy is used for the production of different parts from ferrous and non ferrous materials. This method is best suitable for the materials having low ductility and high melting point and for the materials which otherwise are not suitable for casting processes (Callister, 2001). Whereas in slip casting method, reinforcement is put into the matrix melt and time is allowed to solidify. The materials having different specific gravities can be easily mixed together by using slip casting process (Shiono and Noda, 1997).

Limitation to form simple shapes with specific dimensions, poor grain growth and mechanical properties are some of the disadvantages of the solid processing methods (Wang *et al.*, 2006; Zhang *et al.*, 2010). Table 1 shows the detailed comparison of different fabrication processes.

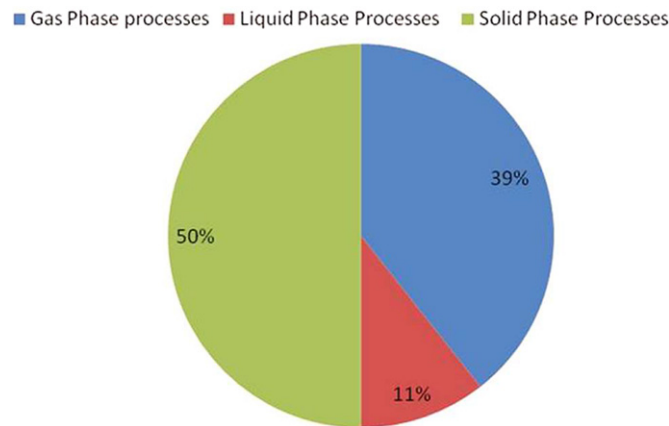


Fig. 1 Methods employed for fabrication of ceramic composites. Reproduced from Rayat, M.S., Gill, S.S., Singh, R., Sharma, L., 2017. Fabrication and machining of ceramic composites – A review on current scenario. *Materials and Manufacturing Processes* 32(13), 1451–1474.

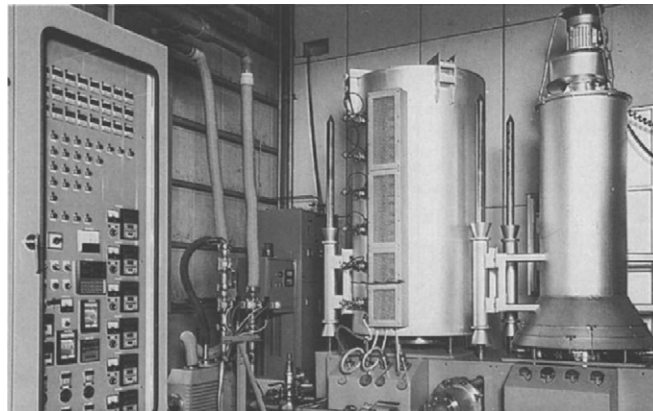


Fig. 2 Commercial CVD system. Reproduced from Weimer, A., Besmann, T., Stinton, D., Lowden, R., Lee, W., 1996. Chemical vapor deposition (CVD) and infiltration (CVI). *Carbide, Nitride Boride Material Synthesis Process*, 547–577.

Machining of Ceramic Matrix Composites

The primary disadvantage of the different fabrication methods is that they are not able to produce accurate geometrical shapes due to shrinkage and other fabrication limitation (Jianxin and Taichiu, 2000; Li *et al.*, 2005). So, further need for machining is required either by traditional or by modern machining methods. Drilling and grinding are the most commonly used traditional methods for the machining of ceramic and its composites (Rayat *et al.*, 2017). But there are number of different non traditional machining processes which are used for machining (Pawar *et al.*, 2015) and listed below.

- (1) Ultrasonic machining: This machining process is based on the ultrasonic frequency and the material removal takes place with the help of mechanical abrasion.
- (2) Laser beam machining: This process uses thermal energy for the removal of material and suitable for both conductive and non-conductive materials.
- (3) Abrasive jet and abrasive water jet machining: In this process abrasive particles with the help of carrier medium either water or gas are made to strike on to the workpiece to remove material.
- (4) Electrochemical discharge machining: In this machining process instead of dielectric, electrolyte is used to machine the non conducting materials.
- (5) Electron discharge machining: This machining process involves the machining of material in the presence of dielectric and only suitable for electrical conductive materials.

Literature Review

Zhu *et al.* (2008) fabricated a $\text{ZrB}_2\text{-B}_4\text{C}$ particulate ceramic composite by using microwave sintering technique and found that as the temperature of sintering increased from 1630°C to 1720°C there was a rise in the relative density. Above temperature 1700°C

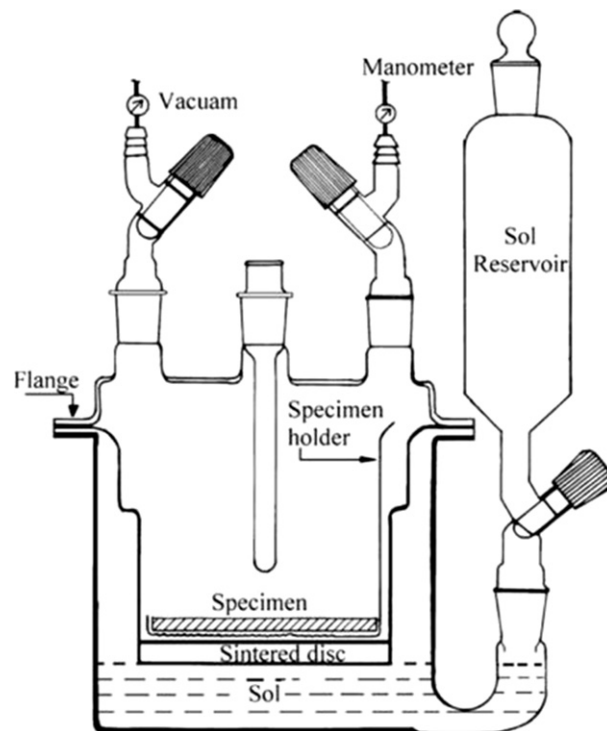


Fig. 3 Schematic of sol- infiltration set-up. Reproduced from Naskar M.K., Basu, K., Chatterjee, M., 2009. Sol-gel approach to near-net-shape oxide-oxide composites reinforced with short alumina fibres – The effect of crystallization. *Ceramic International* 35(8), 3073–3079.

Table 1 Comparison of different fabrication methods

S.No.	Route	Advantages	Disadvantages	Cost	Temperature
1	Reaction bonding	● Near net shape ● Low processing time ● High densification properties	● Limited to simple shapes ● High porosity	High	Up to 1700°C
2	Chemical vapor deposition	● Enhanced mechanical properties ● High deposition rate ● Applicability to number of materials	● Hazardous by- product produced during chemical reaction ● Leads to stresses in films due to difference in thermal expansion co-efficient	High	Up to 1600°C
3	Chemical vapor infiltration	● Flexibility in selecting fibers and matrices ● Complex shapes can be produced ● Uniformity and purity of matrix	● Low processing time ● High residual porosity ● Low production rate	High	Up to 1800°C
4	Sol-gel and polymer Infiltration pyrolysis	● Better control over matrix composition ● Densification temperature is less	● Long processing time ● Multiple iterative processes to obtain dense structure ● Low production rate ● Crack formation in matrix during cooling phase	Low	Up to 1400°C
5	Powder processing	● Simple and complex shapes can be formed depending upon the sintering process ● High densification properties ● Good mechanical properties ● Rapid process	● Uniform distribution of reinforcement into matrix phase is difficult task ● High processing temperature ● Chances of damage to reinforcement during compaction process	Medium	Up to 1800°C

Note: Rayat, M.S., Gill, S.S., Singh, R., Sharma, L., 2017. Fabrication and machining of ceramic composites – A review on current scenario. *Materials and Manufacturing Processes* 32(13), 1451–1474.

for conventional and microwave sintering nearly fully dense composite was formed. Minimum grain growth was observed in case of microwave sintering.

Wang *et al.* (2010) prepared and characterised a ceramic composite at ultra high temperature by microwave sintering. During his experimentation he found that when the percentage of SiC (whiskers and nano particle) reached at 30% the relative density

almost reached at 100% and the addition of SiC improved the densification. From microstructure it was revealed that the increasing volume fraction of SiC inhibited the grain growth of ZrB_2 and it also affects the fracture surfaces. The mechanical properties such as flexural strength and fracture toughness increased up to a percentage of 30% of SiC but after that decreases due to the formation of agglomeration.

Cheng *et al.* (2014) studied the feasibility of producing alumina and titanium carbide micro composite having better micro structural and mechanical properties by using microwave sintering at different operating temperature. The relative density of the composite increase with respect to the increase in sintering temperature and it reaches to maximum of 99% at temperature of 1600°C due to the presence of liquid phase produced by MgO and microwave electromagnetic energy. XRD confirms that there is no chemical reaction take place between alumina and titanium carbide which leads to formation of pores and ultimately affects the mechanical properties. Improvement in fracture toughness and Vickers hardness number were also reported.

Cha *et al.* (2005) studied the fabrication of Alumina and CNT nanocomposites through molecular level mixing in conjunction with spark plasma sintering (SPS) and found that the strength and fracture toughness enhanced due to bridging effect. Strength of nanocomposites increased up to 1% of CNT but start decreasing as the percentage increased more above 2% due to agglomeration.

Inam *et al.* (2010) has done the characterization of electrically conductive alumina-carbon nanocomposites prepared by spark plasma sintering. The electrical conductivity of Alumina- CNT (2 wt%) is more as compare to alumina- Carbon black nanocomposites of same wt% due to the large aspect ratio of CNT and also due to undamaged CNT during SPS method. Electrical conductivity also depends upon grain size as the grain size increases grain boundary area decreases. Some agglomeration was observed in alumina- carbon black nanocomposites material which was the reason for isolation of carbon black nanocomposites particulate. Good dispersion was found in case of CNT – Alumina material due to its fibrous nature which also effect electrical conductivity.

Hvizdos *et al.* (2012) had studied the tribological and electrical properties of ceramic matrix composite doped with CNT and carbon nanofibres. The relative density was more effective when the ceramic matrix composite fabricated through spark plasma sintering as compared to hot pressing. As compared to CNT coefficient of friction was effectively decreased with the addition of carbon nanofibres which act as a solid lubricant. Electrical conductivity also proved to be increased effectively with the addition of small amount of CNF as compared to CNT.

Hirota *et al.* (2007) fabricated carbon nanofibre (CNF) and alumina by using pulsed electric current pressure sintering (PECPS) and investigated mechanical properties and electrical properties. At 5.95% vol of CNF there was a consistent increase in bending strength and fracture toughness but decrease in hardness value due to weak cohesion bonding forces between CNF and Alumina. Agglomeration and dispersion was observed as a factor of particle size and zeta potential and concluded that good dispersion could be achieved by using small particle size. Bulk density and relative density decreased as the percentage of CNF in Alumina increased.

Zhang *et al.* (2010) fabricated alumina and carbon nanotube by pressure less sintering and found that the highest relative density was achieved at a temperature of 1500°C for time duration of 2 h. Flexure strength was increased which results due to pinning affect of CNT which inhibits the grain growth in the alumina composite. Fracture toughness was also increased due to CNT pullout phenomenon.

Shi *et al.* (2011) investigated the effect of CNF reinforced aluminium nitride composites prepared by plasma activated sintering on the mechanical and electrical properties and found that with higher percentage of CNF the relative density of the composite decreased due to restriction on the rearrangement of AlN particles. Similarly high percentage of CNF leads to decrease in the mechanical properties such as fracture toughness, hardness, flexure strength etc. which may be due to weak interfacial bonding between CNF and AlN that weakened the crack bridging effect. DC conductivity of the specimen considerably increased for small percentage of CNF.

Hanzel *et al.* (2014) studied the new approach for the distribution of carbon nanotubes in Al_2O_3 . During his experimentation he found that granulated homogenous mixture was formed which was necessary for the improvement in electrical conductivity and other mechanical properties. The highest electrical conductivity was achieved when 10 vol% MWCT added. Fracture toughness increased as the percentage of CNT content increased due to bridging of cracks and pull out mechanism. Vickers hardness value decreased due to the lower hardness value for carbon nanotubes.

Michalek *et al.* (2014) fabricated and characterised the alumina/MWCNT and alumina/zirconia/MWCNT composites. The relative density was slightly more in case of alumina/zirconia/MWCNT as compared to alumina/ MWCNT composite due to the refined microstructure and pinning effect. The hardness value decreased due to formation of agglomerates, coarse grained microstructure and weak interfacial bonding. The fracture toughness increased in both composites. The electrical conductivity was achieved where high percentage of MWCNT was added.

Jianxin and Taichiu (2000) compared the surface integrity obtained in electro- discharge machining, ultrasonic machining and diamond saw cutting of ceramic composites. Ceramic composites surface indicates that the thermal spalling, brittle fracture and brittle fracture during chipping occurred in case of EDM, Ultrasonic machining and diamond saw cutting machine respectively. Surface roughness value was high in case of EDM due to surface cracks, craters and droplets. Better quality surface was obtained in USM and diamond saw cutting.

Muttamara *et al.* (2003) has performed experiment to find out the probability of precision micromachining of insulating Si_3N_4 ceramics by electric discharge machining. Two different layers have been used as assisting electrode out of these carbon baked layer was most effective. Material removal rate was greatly affected by the tool diameter. Machining properties depends on the area effects of tool electrode size and generation of concentration discharge waveform.

Lauwers *et al.* (2004) investigated the material removal mechanism in EDM of composite ceramic materials. Three different material removal mechanisms were identified such as melting, spalling and oxidation which were confirmed through the analysis of debris and surface quality. Cracks were generally formed by spalling and also it depends on the material properties such as thermal conductivity, fracture toughness, melting point and strength. Spalling effect was not in case of ZrO_2 – TiN specimen having high fracture toughness.

Zhang (2004) studied the effect of wire electric discharge machining parameters on the surface integrity of the nanocomposites ceramic. Material removal rate was evaluated as a function of power transistor number as the power transistors increases the MRR was also increased. MRR decreases as the pulse off time value increases. From the surface analysis it was found that surface roughness also depends upon power transistor number, large craters were formed when using more number of power transistors. From EDS spectrum analysis and XRD analysis it was found that some amount of tool material was transferred to the machined surface due to melting and solidification during spark formation.

Fukuzawa *et al.* (2009) performed the three dimensional machining of insulating ceramics material with electrical discharge machining and found that as the open circuit voltage increased the material removal rate also increased but the bending strength of material decreased. The thickness of the conductive layer also increased while increasing open circuit voltage and the layer consists of wire tool electrode and workpiece material.

Tak *et al.* (2011) has done the characteristics evaluation of alumina and carbon nanotube (CNT) for micro electric discharge machining and found that electric conductivity of material depends upon the percentage of CNT, as the content increases the electrical conductivity of the material also increases. But the high percentage of CNT has adverse effect on the surface finish due to the formation of tangles which cause violent spark and lead to poor dimensional accuracy although the material removal rate was increased. Critical point was addition of 5% CNT after which the electrical conductivity abruptly increases.

Malek *et al.* (2011) studied the effect of conductive phases for machining insulating ceramics and found that the multiwall carbon nanotubes (MWCNT) doped ceramic has approximate three times less tool wear rate as compared to other conductive phase that is TiC. Also the CNT doped ceramic can be machined easily on electric discharge machine with very less vol% addition compare to other material. Discharge energy directly affects the crater dimension of machined surface and also it leads to the degradation of MWCNT due to graphitisation. Material removal rate is almost doubled in case of MWCNT doped ceramic compared to reference material.

Hanaoka *et al.* (2013) has done experimental investigation on electric discharge machining behavior for ceramic composite fabricated by using different carbon nanostructure (MWCNT, graphene). It was found that the density of the ceramic composite is approximately 99% theoretical value and homogenous dispersion was there. Material removal rate was decreasing as the percentage of conductive phase increases in case of electric discharge machining and was also less than assisted electrode machining. Carbonisation of ceramic composite and large chipping area was also observed that depends upon the conductive phase.

Wei *et al.* (2013) optimised the process parameters for electric discharge machining of ceramic matrix composites reinforced with ceramic fiber. The MRR and surface finish increased due to improved flushing and electrode vibration without sacrificing tool wear rate and surface integrity. Peak current and pulse duration are the dominating factors that affect MRR. The mechanism for MRR includes cracking, crack propagation and stripping off.

Li *et al.* (2005) studied and optimised the process parameters for rotary ultrasonic machining of ceramic matrix composites. The reduced cutting force and improved material removal rate can be achieved significantly as compared to diamond drilling process with which high quality holes were made. Material removal rate was greatly affected by feed rate as compared to the other process variables such as ultrasonic power and spindle speed.

Kim *et al.* (2009) performed laser micromachining of CNT/Fe/ Al_2O_3 nanocomposites and found that nanocomposites having high content of CNT produced good machining result and ablation depth of alumina and CNT nanocomposites increase logarithmically with laser influence. No microstructural damaged occurs by laser energy.

Gaps in the Study

Different fabrications methods have been employed for the successful dispersion of the reinforcement and they got positive results and also they find out percolation threshold for machining with electric discharge machining. As the research continues the MWCNT replaces the other electrical conductive phases due to its excellent electrical conductive properties which can be dispersed with conventional methods and by modern methods in ceramic matrix. But on the other hand CNT's are the soft material which can affect the mechanical properties adversely.

Valuable efforts were made in the past to investigate the addition of MWCNT as reinforcement in the ceramic matrix composite in terms of its electrical conductivity, mechanical properties and structural properties. Most of the researchers have fabricated the MWCNT and ceramic with the help of hot pressing, spark plasma sintering and pressure less sintering.

Machining of ceramic is one of the difficult tasks to be performed due to its various mechanical properties which make the ceramic hardest, excellent wear resistant and having high strength material among the various engineering and structural material. Electric discharge machining is the modern machining method which is primarily used for the material having good electrical conductivity. But in case of ceramic as it good insulator so it cannot be machined directly.

Few areas for research have been identified from the above literature review:

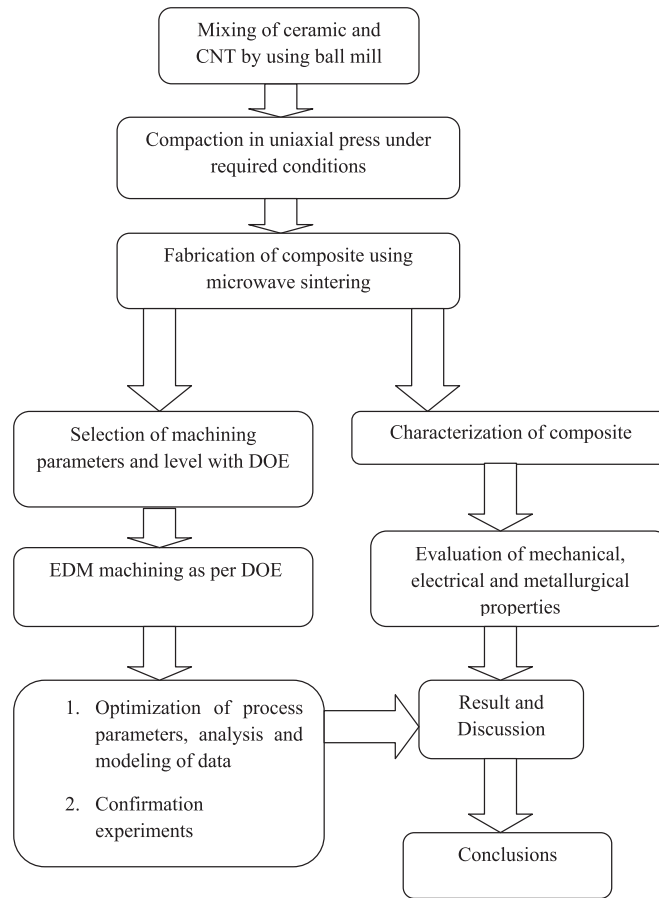


Fig. 4 Flow chart for preparation of CMC's and its EDM.

- (1) Fabrication of ceramic matrix composite by using microwave furnace still required to be investigated systematically.
- (2) Although numbers of machining methods are available, each process has its own limitations cannot be directly applied to ceramics or its composites.
- (3) The influence of microwave on the properties of MWCNT's and the ceramic matrix composites.

The scope of this study is limited to the fabrication of ceramic matrix composite by using different percentage of MWCNT with the help of microwave sintering furnace at different temperature followed by evaluation of its electric discharge machining.

Methodology and Planning of Work

Fig. 4 shows the step by step procedure for preparation of CMC's and its EDM.

Case of Relative Density and Porosity

To evaluate the effect of the percentage of MWCNT's on the relative density and porosity of the ceramic composite, one case study is discussed here.

Case Study 1

In this case study, the starting material were used – Al_2O_3 powder (CTC 20, Almatix ACC India Ltd., 99.8% pure, density- 3.92 gm/cm^3), multiwall carbon nanotube (MWCNT) ($>98\%$ purity, outer diameter- 20 nm , density- 2.1 gm/cm^3 , length- $\text{Av } 20 \mu\text{m}$ as described by the supplier). Samples have been prepared by mixing MWCNT's in different weight proportions such as (1, 3, 5 wt%) with the help of ball milling.

Once the milling is over, compaction of the powder is done with the help of compaction press (as shown in **Fig. 4**) at a pressure of 300 MPa . The samples were of circular cross section having diameter 10 mm and thickness of 2 mm (**Fig. 5**).

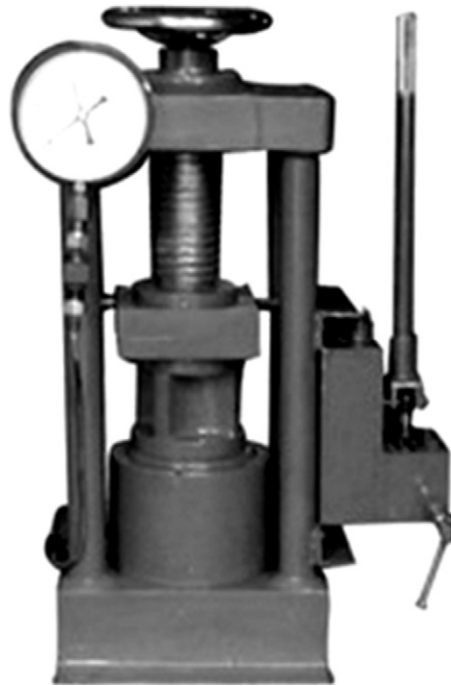


Fig. 5 Compaction press.



Fig. 6 Microwave sintering furnace.

All the samples were sintered in the microwave furnace (see Fig. 6) at VB ceramics Chennai having magnetron of 2.54 GHz at a temperature of 1500°C for about 15–20 min in inert atmosphere.

Evaluation of porosity and relative density

After the sintering, the samples (see Fig. 7) were tested to evaluate the theoretical density, relative density and porosity of the composites. The porosity was calculated with the help of Archimedes principle. In this first samples were weighted in the air and then in the water. Theoretical densities of the composites were calculated with the help of “rule of mixture” and tabulated in Table 2 and relative density was calculated by the formula given below and the values are as shown in Table 3.

Formulas:

Actual Density = $(m_A / (m_A + m_W)) \times \text{density of distilled water}$.

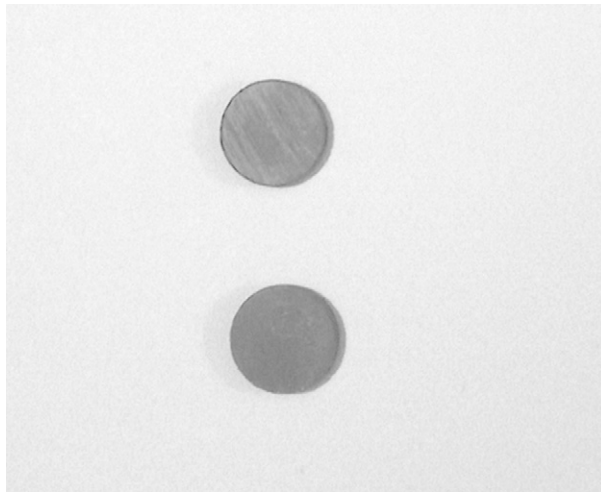


Fig. 7 Sintered samples of Alumina- MWCNT.

Table 2 Theoretical density of different samples

S.No	Sample number	Alumina (wt%)	MWCNT (wt%)	Theoretical density (g/cm ³)
1	A	100	0	3.92
2	B	99	1	3.9018
3	C	97	3	3.8654
4	D	95	5	3.829

Table 3 Relative density % of different samples

S.No	Sample number	Alumina (wt%)	MWCNT (wt%)	Relative density (%)
1	A	100	0	97.45
2	B	99	1	95.63
3	C	97	3	94.31
4	D	95	5	92.88

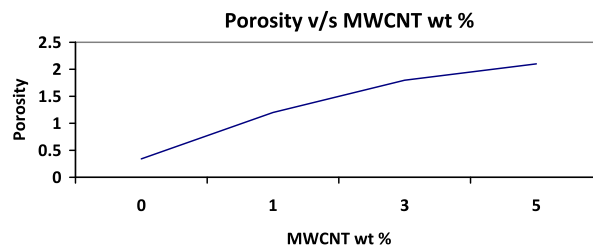


Fig. 8 Relation between porosity and MWCNT wt%.

m_A = Mass of sintered sample in air

m_W = Mass of sintered sample in distilled water

Relative density = (Actual density/Theoretical density) $\times$ 100%

Porosity = $\rho_{th} - \rho_c / \rho_{th}$

ρ_{th} = Theoretical density of composite

ρ_c = Actual density of composite

Density of distilled water (liquid) in this case is taken as 1 gm/cm³.

Sintering of samples at 1500°C by using microwave sintering furnace resulted in the improved relative density % of composite containing MWCNT from 0 to 5 wt%. The highest value for relative density was achieved in the composite having MWCNT wt% of

1 and least in the wt% of 5. The decrease in the relative density of the composite with increase in the weight percentage of MWCNT's was due to the poor dispersion of MWCNT's into the matrix phase. On the other hand there was a significant increase in the porosity of the nanocomposites with increased weight percentage as shown on Fig. 7 (Fig. 8).

Conclusion

In this chapter a frame work for EDM of ceramic composite has been proposed. The result of the present work shows the feasibility and development of CNT- ceramic matrix composites by microwave sintering. Moreover, characterization of the developed CNT- ceramic composites (based upon mechanical, electrical and metallurgical properties) needs to be performed before EDM. In order to make the machining of ceramic composites economical the process parametric optimization of EDM for developed CNT- ceramic composites can be explored.

Acknowledgement

The authors are thankful to IKGPTU Jalandhar and Manufacturing Research Lab (GNDEC Ludhiana, India) for financial support.

See also: Experimental Investigations for Development of Aluminum MMC With Hybrid Reinforcement and Vacuum Molding. Investigations for Barium Titanate and Graphene Reinforced PVDF Matrix for 4D Applications. Sustainable Machining With Self-Lubricating Coated Mechanical Micro-Textured Cutting Tools

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Food Waste for Sustainable Packaging Materials

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Introduction

Plastics are considered the materials of the 21st century. During the last 150 years, they have been the key of innovation and have contributed to the development and to the progress of our society. The largest application is in the packaging sector, but thanks to their versatility and high efficiency, plastics have become key materials in many other sectors. Plastics are efficient during the service life, help to avoid food waste and save energy. At the end of their life, they can be re-used, recycled or allowed for energy recovery. In order to guarantee a sustainable development, taking into consideration the fast-growing population, the food security requirements and the climate change problems, the most efficient solution needs to be chosen. Special attention has been recently devoted to chemicals isolated from food waste, coming from food processing industries and considered renewable resources. In this contest, plastics obtained from those resources have been considered as sustainable alternatives to petroleum-derived plastics. Approximately 99% of the plastics produced in the world are obtained from petroleum resources. According to Plastic Europe ([Plastics- The Facts, 2017](#)), from 2015 to 2016 the European plastic production increased from 58 to 60 million tonnes while the world plastic production increased from 322 to 335 million tonnes. Asia (with China and Japan) is the largest producer of plastics (about 50% of the total production), followed by Europe (19%), USA (18%), Middle East Africa (7%) and Latin America (4%). For 2017 and 2018 further increments of +2.5% and +1.5% are estimated. In Europe, the total converter demand is of 49.9 million tonnes, with a demand more than 3000 million tonnes from the six larger European countries such as Germany (24.5%), Italy (14.2%), France (9.6%), Spain (7.7%), United Kingdom (7.7%) and Poland (6.3%). Production, demand and waste management of plastic materials give a great contribution to the world circular economy. Plastics are source of jobs, growth, innovation and sustainability. Plastic is present in several sectors such as healthcare, aerospace, automotive, maritime, construction, electronics, textile, energy generation and packaging. This last one sector is the most important, with a plastic employment of 39.9% of the total demand. Plastic materials and solution were and still are fundamental for the innovative success and growth of such sectors. Plastic materials as well as plastic products are important and efficient resources, along their whole life. At the end of their life they can be reused, recycled or allowed for energy recovery. Unfortunately, due to the large production of plastics materials, there is ever more waste. But wastes could be considered actually as new resources, becoming part of the plastics life cycle. In order to choose the most sustainable solution, several factors such as the plastic waste management, the recycling, the energy recovering considered as complementary option and reducing landfill deposit to the minimum, must be considered. Understanding the life cycle of plastics is fundamental for environmental concerns but not all plastics products are the same. Some plastics present a shelf life of less than one year, some others for more than 15 years and some have a shelf life of 50 years if not even more ([Plastics- The Facts, 2017](#)). For this reason, the volume of wastes does not match with the volume of plastic production and consumption. Between the collected plastic waste, about 27.3% are landfilled, about 31.1% are recycled and about 41.6% are used for energy recovery. Beside in the last ten years the plastic waste recycling has increased by almost 80% and the energy recovery has increased by 61%, plastic litter is omnipresent. Landfill in many countries is still the first option of treatment for waste coming from post-consumer plastic. In Europe only some countries such as Switzerland, Austria, Germany, Netherlands, Sweden, Denmark, Luxembourg, Belgium, Norway and Finland have a landfill rate of plastic wastes less than 10%. For the rest of countries the landfill rate is at 30%–50% and over. The plastic packaging waste is of about 16.7 million tonnes, 20.3% are landfill wastes. For several years, the attention of legislators as well as of public opinion has been focalized on the negative environmental impact of packaging. Its potentiality for food waste reduction and its fundamental role in the product safeguard has been put in a second level. Packaging reduction is consequently seen as the only believable alternative for the environmental impact reduction. But reducing the food waste as well as increasing the food shelf life is in contrast with the final packaging characteristics. Plastics are the most used materials for packaging purpose. They are low cost materials, highly versatile, flexible, transparent, heat sealable, with good thermal, mechanical and barrier performance. But, they are not biodegradable, causing environmental problems not only related to their waste treatment but also because they contribute to the depletion of fossil resources.

So, due to the strong public concern about plastics wastes, a great motivation is driving the development of new materials with strong environmental attributes. Biobased plastics new materials, which could be biodegradable and that could be obtained from renewable resources, are driving this progress. Of course, these polymers could replace synthetic polymers for at least some applications. As reported from [Licciardello \(2017\)](#) and according to [Chen and Patel \(2012\)](#), to [Molina-Besch and Pålsson \(2016\)](#) and according to the definition of European Plastics organization, biopolymers could be obtained from renewable resources (biobased plastics) or could be biodegradable and/or compostable. Consequently, biopolymers obtained from renewable resources could not be biodegradables. As for example, bio-polyethylene (bio-PE) and bio-polyethylene terephthalate (bio-PET) obtained from bio-resources are chemically identical to the conventional ones and consequently are not biodegradable. On the contrary, polymers such as polylactic acid (PLA), polyhydroxyalkanoates (PHAs), polybutylene succinates (PBS) are biodegradable

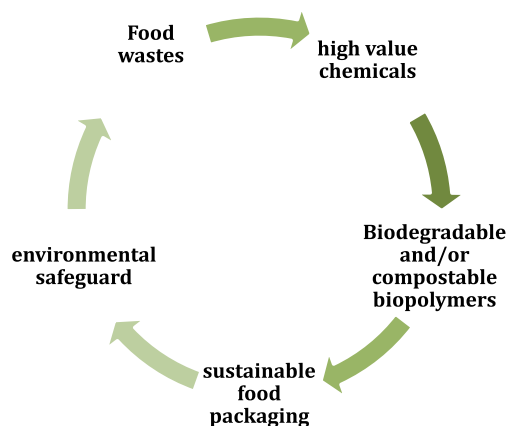


Fig. 1 Circular economy for sustainable packaging materials coming from food wastes.

polymers, that could be obtained from petroleum resources or from renewable resources. Their biodegradable behavior is related to their chemical structure rather than to their origin (Siracusa and Dalla Rosa, 2018; Siracusa *et al.*, 2008; Peelman *et al.*, 2013).

Very recently, great interest is devoted to the production of polymers starting from monomers obtained from renewable resources coming from agro-industrial and marine wastes and their byproducts. They have been considered as important sustainable alternatives to petroleum-based polymers. A further training force is the consumer's concerns related to food safety, nutritional value and health, that increased the interest to natural substances rather than to the synthetic ones.

In any case, biodegradable or simply bio-based polymers, offers environmental advantages in terms of waste disposal reduction, safeguard of petroleum resources, use of renewable resources coming from the food processing industry that otherwise could become wastes. This process is part of a circular economy, summarized in Fig. 1, followed by retailer and industries to safeguard the environment.

Perpetual disposal in the environment of several food waste, sources of high nutritional compounds and by-product that could be used for several purposes, is a practice that must be stopped. The modern food industry must follow a new strategy for a sustainable bio-economy. Further, the fast growing population, the depletion of food sources, the even more increasing need of high nutritional food and so on is, will be duly this process.

Food Wastes From Industry and Consumers

Every year about 45 billion kg of fresh food such as vegetables, fruits, milk, grain products as well as meat and fish are lost as wastes. Further, fruit and vegetable, olive oil, fermentation, dairy, meat and seafood industries produce a largely quantity of wastes, always related to the food. In order to develop a sustainable food system, food waste treatment technologies as well as food chain management and recovery of high value products from food waste are actually the object of great consideration. A great amount of food wastes comes from retailers, restaurants and consumers and, as reported from Kosseva (2009), every tonne of food waste means 4.5 tonnes of CO₂ emissions in the atmosphere. In the industrialized world, after producing, processing, transporting, sold and take at home, about 33% of food became garbage, and consequently landfilled. In landfill, methane gas is produced, more problematic than CO₂ gas emission. Fresh vegetables, fruits and salad are the major contributors to this process. Further, as reported from Arora *et al.* (2002), vast volumes of aqueous wastes are generated from food-processing industry. Apart from the environmental concerns, such streams represent a great opportunity for the recovery of potentially components that could be used to generate high potential products. These streams include fruit and vegetable residues, molasses and bagasse from sugar refining, bones, flesh and blood from meat and fish processing industries, stillage from wineries, distilleries and breweries, dairy waste such as cheese whey and so on. Wastewaters coming from food industries operation such as washing, blanching and cooling containing also suspended solids and dissolved materials. Actually these products obtained from food industry wastes include animal feed, protein, fermented edible products, yeast coming from bakery products, organic acids, amino acids, enzymes, flavors, pigments, microbial gums, polysaccharides (Joshi, 2002). Despite the great interest confirmed by the numerous scientific patents, articles, book, conferences and so on, the developed technologies remain rather limited. This is because the industrial recovery process is a complex approach that requires careful consideration. A new product can be manufactured and commercialized only if the operating process can be adapted to the existing methodology. This approach requires a certain degree of flexibility, both for the materials than for the technologies just in-use actually. Advantages and disadvantages of the new processing technology must be evaluated, adapting the different approach for the recovery strategy, nature of food waste and the characteristic of the final product.

In order to develop a universal recovery strategy, as reported Galanakis (2015), five-stage recovery approach were described and accepted by the scientific community, that are: a macroscopic pretreatment, macro and micro-molecules separation, extraction, purification and isolation and finally product formation. The conventional technologies must be implemented by following these stages.

Plant Origin	Animal Origin	Fermentation Industry
• Fruits and vegetables (apples, carrots, cherries, corn, grapefruit, pear, peas, tomatoes, mandarine, orange, apple, peach, apricot, banana, kiwi, pineapple and so on) • Cereals (wheat, rye, barely, oat, rice, millet, corn sorghum) • Root and tubers (potatoes, sweet potatoes, cassava, yams, edible aroids, taro) • Oil crops (rapeseed, sunflower, flax, peanuts, sesame) • Pulses (lentil, pea, chickpea, bean, lupin)	• Meat and poultry • Fish and seafood by-products (crab, shrimp, prawn, Antarctic krill, cray fish) • Dairy (whole and skim milk, cream, whey, cheese)	• brewing • distilling • wine manufacture • beer

Fig. 2 Food Waste origination.

Sources of Food Wastes: Challenges for Added-Value Products Recovery

As mentioned before, several food wastes can be taken into consideration for the production of high value added components. The recovery of food by-product for commercial and environmental purpose has inspired the scientific community, to obtain new natural compounds that can be used for the production of bio-based packaging materials as well as for edible films and coatings (Persin *et al.*, 2011; de Moraes Crizel *et al.*, 2016).

First of all, according to the European Union (EU) Commission Council Directive 2008/98/EC, “waste is any substance or object that is discarded”. “Food Waste” instead, according to the Foresight Project reports of the Government Office for Science (Foresight, 2001; Foresight Project, 2011), is defined as “edible material intended for human consumption that is discarded, lost, degraded, or consumed by pets as food travels from harvest to consumers”. Lastly, the European Commission defined the “food waste” as food lost from the food supply chain, without including in this definition the food used as starting materials (monomers) for bio-based products and food for animal feed or used for redistribution (donation). According to the FAO (2014), one-third of worldwide food produced for human consumption are lost or wasted. Thanking into consideration that the objective is to reduce food waste by at least 30% between January 1, 2017 and December 31, 2015 (Otlés *et al.*, 2015), several efforts will be made by all the scientific communities and by industries to reach this goal, for the development of new commercial applications in several sectors such as food, pharmaceutical, biomedical, cosmetics and so on.

It must be considered that food by-products and wastes contain different and complex component with high value. In order to preserve their quality and structure, emerging technology of extraction, purification and characterization are involved.

As reported in Fig. 2, three main groups can be considered for food recovery waste. Each group contains different categories of products that could be considered as sources of different compounds and by-product for new materials production.

For each of these categories, during the industrial and agricultural production and food processing stages, several by-products and waste stream are produced, also containing high value compound. In respect to the food waste recovered at the end of the supply chain, these compounds could be susceptible of deterioration. The waste produced in individual households is instead difficult to recover, and are consequently lost as possible sources of valuable components.

Production of biodegradable packaging material as well as edible films and coatings for food packaging application is grown quickly due to the public attention for environmental problems. These new materials could be a great alternative to synthetic packaging materials in several application, thank to their capacity to prevent loss of aroma, moisture, gas penetration, water absorption and so on (Cazón *et al.*, 2017). Mainly proteins (including collagen, casein, fish gelatin, quinoa protein, whey protein, corn zein, wheat gluten, egg white protein, soy protein, keratin protein), lipids (including waxes, acylglycerols, fatty acids) and polysaccharides have been used to produce biodegradable and edible films. Chitosan starch, pectin, alginate, carrageenan, pullulan and kefiran are interesting candidates for film production (Elsabee and Abdou, 2013; Galus and Kadzińska, 2015). In the majority of cases, their properties have to be improved and the use of different plasticizers is required. The use of natural plasticizer, like triglycerides from vegetable oils and fatty acid esters (Veira *et al.*, 2011) are of course of great interest in order to respect the environmental attributes of the synthesized materials. Alginate and carrageenan films are highly hygroscopic and can be used as thin films on the surface of food to absorb water and protecting the food moisture loss.

Food Waste From Plant

Fruit and vegetable wastes

As reported from Mullen *et al.* (2015), depending on the fruit and vegetables processing technologies, several type of wastes and by-product are produced:

1. Solid wastes such as pomace, pulp, peels, cores, seeds, stems,
2. Liquid wastes such as juices, wash water, chilling water, cleaning chemical water.

Since these wastes are rich in biologically substances, the use of fruit and vegetables by-product as a source of active and functional compounds is a very interesting technological and environmental tool. These types of wastes are produced in large

amount and also constitute a source of municipal solid compost wastes because of their high biodegradability (Misi and Foster, 2002). The waste coming from fruits and vegetables processing industries contains large amount of suspended solid (SS). The organic fraction is formed by about 75% of sugar and hemicellulose, 9% of cellulose and 5% of lignin. In practice, these wastes are made in major measure of hydrocarbons and small amount of proteins and fat, with moisture content of about 80%–90%. In general is difficult to use the wastewater stream because it contains a high amount of dissolved compound such as pesticides, herbicides and cleaning chemicals.

Of course the best solution for a green and environmental production is to reduce drastically the waste production but this is not possible at all, so the actual interest is to valorize by-products and residues of the fruit and vegetables processing technology. Several approaches are followed such as the extraction of flavors, dietary fibers for bread and beverages, pectin and gelling agents to be used firstly in the food sector as well as in others such as for animals food, cosmetic and so on. The advantage of course will be economical (resources preservation, niche market with high profits, reduced cost for waste disposal) and of course for the environment.

One of the most interesting and studied, low cost and abundant fruit byproduct is the apple pomace, formed by peel, core, calyx, stem and soft tissue, with high water content and insoluble carbohydrate such as cellulose, hemicellulose and lignin. Also sugars (glucose, fructose, sucrose), minerals, proteins and vitamins are present (Kosseva, 2009). The most important biotechnological application of apple pomace is the production of enzymes, aroma compound, ethanol, organic acid, polysaccharides, baker's yeast and pigments. Vendruscolo *et al.* (2008) reviewed all the bibliography regarding this product, its transformation in high value added compounds and their use for emerging technologies. The utilization of this product is important not only because it is a low-cost resource but also because it is a resolution of the pollution problem due to the high amount of wastes disposal. The most important application is the production of enzymes that could be used for food application as well other sectors such as textile. As reported from Hofvendahl and Hahn-Hagerdal (2000), apple pomace could be used to produce lactic acid by enzymatic hydrolysis. Taking into consideration that the world market is growing and that its current production is at about 150 million lb for year, the possibility to use food waste renewable resources is of great interest. Biodegradable polymer polylactic acid (PLA), obtained from the polymerization of lactic acid, is actually one of the most used as food packaging. Its behavior was just fully investigated (Siracusa *et al.*, 2012, 2017; Siracusa and Ingrao, 2016). As reported from Kosseva (2009), from apple pomace is possible to obtain high level of glucose and fructose, excellent carbon sources for lactic acid production, high level of cellulose, starch, hemicellulose that can be hydrolysed to produce monosaccharides and that could be used to produce starch derived polymers.

Cazón *et al.* (2017) in their review reported the possibility of producing biodegradable film and coating coming from polysaccharide. Not only apple pomace was investigated but also orange and lemon pomace as well as peels of several fruits such as orange, lemon, pear, banana and melon. From apple and citrus peel is possible to obtain pectin, one of the main components of plant cells. Its structure is strictly related to the microstructure. The carboxylic groups can be esterified with methanol, obtaining several rate of esterified carboxyl groups (>50%, high methoxyl pectin; <50%, low methoxyl pectin), related also to the molecular weight. These parameters are important for other properties such as gelling, texture and stability, important for the future film production. Pectin-based films show good gas permeability properties, poor water barrier behavior, retard in moisture loss and lipids migration (Gutiérrez-Pacheco *et al.*, 2016).

Taking into consideration the high cost of aromas, fragrances and flavors compound production from raw materials such as plants and considering the high cost of the used technology on an industrial scale, there is a great interest on low cost processes using food wastes resources.

Iahnke *et al.* (2015) reported the preparation technique of a gelatin film obtained from linseed oil and carrots, both coming from processing industries wastes. This film was tested as sunflower oil package and was found that the presence of carotenoids protected the oil from the natural oxidation process.

Cereals wastes

In this category are comprised nine species of Gramineae family, that are wheat, rye, barely, oat, rice, millet, corn, sorghum and triticale (Mullen *et al.*, 2015), that represent the most important source of food for human and meat preparation. They are an important source of several compounds such as carbohydrate, proteins, lipid and vitamins. The process followed to obtain refined products (dry milling, pearling, malting) such as white bread, pasta, white rice and so on give a great portion of wastes with high concentration of bioactive compounds. In general, those compounds are used as reinforcement for biodegradable materials, especially in order to improve their mechanical and barrier properties, fundamental characteristics for the packaging sector. Straw coming from the processing of wheat, rice and corn, consists principally in cellulose, hemicellulose, lignin, ash and protein, and is the most abundant lignocellulosic biomass. Wheat mill, rice mill, oat mill, barely mill are all reach of antioxidant, hypocholesterolemic, anticancer and antitumor compounds. They are also used as ingredients for animal feed. As reported from several authors (Aider, 2010; Elsabee and Abdou, 2013; Jiménez *et al.*, 2012; Psomiadou *et al.*, 1996) polysaccharide based films have low cost, is available and specific properties. They present good barrier properties against gas such as O₂ and CO₂ that is an important property to avoid oxidation and ripening of packed food. Further, it is important to retard the loss of organic vapours (aroma compounds) during storage and to prevent external contamination and food quality loss. But, being hydrophilic, they show poor water vapor barrier properties that could be improved with other functional substances.

Cellulose is the most abundant component coming from renewable resources. It is low cost, non-toxic, biocompatible, biodegradable and chemically stable. It can be isolated from plants and it is the most common choice as filler for plastic materials (Kolybaba *et al.*, 2006). It is insoluble in polar solvent such as water, due to the high length of the cellulose molecular chain and due to its high crystallinity. As it is a very important raw material for biodegradable film production, their solubility in no-chemical

solvent is under study in order to guarantee the environmental attribute. The films obtained are transparent, water soluble, odourless, tasteless, flexible, with moderate strength and resistance to lipid environment (Dhall, 2013; Baldwin *et al.*, 1996).

Starch is a natural polymer and a good alternative to be used for produce packaging material. It is abundant, low cost, biodegradable and edible. It is present in different plants such as wheat, corn, rice, bean and potatoes. The shape, size, structure and chemical composition varies depending on the source. The two main polysaccharides present in starch are amylose and amylopectin. Lipid and protein are also present. Amylose is a linear polymer responsible for the film forming properties while amylopectin is a highly branched polymer. The amylose/amylopectin ratio is responsible for the crystalline structure. The crystalline region is associated with the short-branched chains of amylopectin meanwhile the amylose is associated with the amorphous region. The film could be obtained by two techniques: dry process and wet process. In the dry process, the starch is plasticized and heated above its glass transition temperature and then extruded. In the wet process the polymer is solubilized and the film is formed after solvent evaporation. This last process, is preferred for edible film forming or coating obtained by dipping, brushing and spraying onto the food surface. The first method is preferred at industrial level (Peressini *et al.*, 2003; Jiménez *et al.*, 2012). The films are brittle due to the amorphous regions formed by amylose. To overcome this problem, plasticizer could be used, improving flexibility and extensibility. Another possibility could be to blend the starch with other biodegradable polymers in order to maintain its biodegradability while improving the mechanical properties (Cazón *et al.*, 2017).

Roots and tubers wastes

Roots and tuber crops are potatoes, sweet potatoes, cassava (manioc, mandioca, yucca), yams, edible aroids (malanga, new cocoyam, acumo, tannia), taro (dasheen, eddoe, old cocoyam). Cassava, potato and sweet potato are the most produced for human consumption. About 55% of the total production is used for human food, while the rest is used for animal feed or for producing starch, distilled spirits, alcohol. They represent the second rate wastes after fruit and vegetables.

The waste and by-products coming from potato processing industry comprise peels, cutting waste, wastewaters, pulp and liquor after potato starch processing, scraps (broken fried chips and so on). From peels is obtained the great amount of carbohydrates, followed by protein, moisture, ash and sugar. Phenolic compounds (chlorogenic acid, gallic acid, caffeic, p-coumarin, ferulic, vanillic) are present in potato peel and can be used as antioxidant agents for active packaging materials. From potato peel can be extracted dietary fiber and it is an excellent substrate for the production of bioethanol.

Cassava, the major root crop used in developing countries such as Nigeria, Thailand, India, Indonesia, Bolivia, and so on, is used as primary food but also to manufacture starch and bioethanol (Padmaja and Jyothi, 2012). The wastes obtained during processing are made of starch residues (pomace) used for the production of bioethanol and lactic acid (Ray *et al.*, 2008), peels, stumps, whey and wastewaters.

Oil crops and pulses

The most oilseed groups cultivated for oil production are olive, rapeseed, sunflower, flax, peanuts, sesame. In general the oilseed processing includes several stages such as cleaning, dehulling, cooking and oil extraction. Each stage generates several types of wastes that could be recovered. Stems, pods, leaves, broken grain, dirt, small stones are obtained. Waste of oil production, coming from industrial processing, is a dark-colored juice, with organic substances such as sugar, organic acids, polyalcohol, pectin, colloids, tannin and lipids (Kosseva, 2009). As reported from Galanakis (2015), the first success on the food waste treatment was the recovery of oil from the olive kernel, inspiring the scientific community to intensify their research toward the valorization of such and similar by-product.

Pulses are the second most important kind of food in the World. It is rich in protein and others nutrients such as carbohydrates, dietary fiber, vitamins and minerals. Their by-products are used for bioethanol production and for biodegradable and edible films (Mullen *et al.*, 2015; Del Campo *et al.*, 2006).

Recently the production of edible films and biodegradable polymers has been the object of several studies from researcher, by utilization of proteins, polysaccharides and lipids coming from such type of wastes. Protein films show great mechanical performances, better than the films obtained from lipid or polysaccharides starting materials (Mariniello *et al.*, 2003). As reported from Mullen *et al.* (2015), pulse and oilseed by-product are suitable materials for the synthesis of films. Soy protein, among the other plant protein sources, gives flexible, smoother and clear biodegradable polymer films. By combining different type of polymers with different origin (composite films) is possible to mix several characteristics, giving rise to films with improved properties in respect to a single polymer. Salmoral *et al.* (2000a,b) described polymer films obtained from bean protein, using starch glycerol as plasticizer. Garrido *et al.* (2013) reported their study focalized on the preparation of soy protein thin films, obtained by casting and compression methods. Optical, barrier and mechanical properties were found to be influenced by the processing procedure, due to the changes observed in their structure during film forming. By casting method were obtained films with better flexibility and transparency, lower yellowish color and gloss and higher resistance against water. By extrusion instead the properties were influenced by the temperature used to press the films. Garrido *et al.* (2014) reported their study on biodegradable films obtained from soy coming from waste of soy oil industry. Was analyzed the effect of plasticizer content on the best formulation, processing condition and functional properties of the final films as well as their structural change.

de Moraes Crizel *et al.* (2018) reported their study on the production of chitosan based films with the addition of several percentage of flour and microparticles of olive pomace flour. The obtained film, studied from mechanical, barrier, optical and antioxidant properties point of view, showed good performance. The films were tested on the oxidation rate of nuts, during 31 days of storage.

Food Waste From Animal

Meat and poultry

Meat industry produces a great amount of wastes coming especially from the slaughterhouses and processing units. In particular blood, fats, intestine, paunch grass, manure are the principal residues (Cournoyer, 1996). The wastewater streams are rich of moisture, phosphorus, nitrogen and pathogens that must be eliminated, and is always more difficult to treat in respect to the solid food wastes. From meat residues is possible to isolate collagen, that could be used to produce edible films with excellent mechanical properties (Osburn, 2002). In the packaging sectors, films and foils obtained from meat protein hydrogels present high barrier behavior for oxygen (to avoid food oxidation), carbon dioxide (important for modified atmosphere packaging technology for preserve fruits and vegetables), and aromas (for finished food products). The disadvantage is their lower moisture barrier capacity due to the hydrophilic character and high water solubility, coming from their natural origin. Further, the mechanical behavior is lower (mechanical strength and elongation at break) with high fragility compared to the synthetic polymers used in the same field. This negative effect could be controlled by adding suitable plasticizer that could however increase the hydrophilic character and consequently reduce further their moisture barrier capacity. The hydrophilic character can be modulated by crosslinking reaction with specific enzymes or aldehydes.

Collagen protein, obtained from enzymatic hydrolysis of meat wastes, can produce hydrogels applicable for the synthesis of biodegradable packaging materials to be used in food, cosmetic and pharmaceutical sectors (Kosseva, 2009). Thank to this procedure, as reported from Langmaier *et al.* (2008), the ammonia pollution of wastewaters coming from collagen processing technology, as well as the collagen solid wastes in landfills could be avoided, with a great advantage for the environment.

Fish and seafood by-products

In general, about 25%–30% of the total fish and seafood weight became waste. Waste generated from fishing, aquaculture, and fish processing industries are the most important environmental problems in the coastline areas. Generally fish and seafood wastes are dumped into the sea, without any kind of treatment. They are of course lost without any possibility of valorization. The shellfish industry produces a great amount of crustacean waste materials. The most harvested species are crab, shrimp, prawn, Antarctic krill, cray fish. The use of such crustacean wastes is of great interest by researchers because they are very rich in protein, chitin, chitosan and carotenoids. Chitin is the most abundant natural polymer in the World (Santhosh and Mathew, 2008) and is obtained from shrimp shell waste. Thank to their low toxicity and higher biocompatibility, it is used in medicine, cosmetics, textiles, food and so on. Glucosamine and carboxymethylchitin are two of the main derivatives of chitin.

From alkaline N-deacetylation of chitin is obtained chitosan. It is commercially available from renewable resources such as waste coming from shell-fish industry (Kim *et al.*, 2006). It is a linear polysaccharide, non toxic, biodegradable and biocompatible, with high antimicrobial activity. The films could be obtained by several procedures. One of them is by casting method, where chitosan is dissolved in a suitable solvent, with the possibility to add plasticizers. The solution is poured on a flat surface and the solvent allowed to evaporation. Of course, this could not be used as commercial procedure. Extrusion instead could be the most economical procedure when foils have to be obtained. But chitosan degrade before its melting point and therefore cannot be extruded or molded and the film cannot be heat-sealed. To overcome this problem, chitosan is blended with other natural polymers such as poly(butylene succinate), poly(butylene succinate adipate) in order to improve the thermal properties (van der Broek *et al.*, 2015). The films obtained show good mechanical properties and permeability to CO₂ and O₂. Due to its high water permeability its use is limited, especially in high relative humidity environment, in the case where an effective moisture control is required for avoid quality and safety food loss. For this reason several strategies have been studied such as the plasticization or mixing with other component such as protein or polysaccharides.

Tuna is the most favorite fish species and its processing to produce different tonnes of skin, bone and fin as food wastes, used for fish-feed or fertilizers. In order to reduce the fish processing waste cost and the management and disposal waste cost, the interest for those wastes is increased. They can be used for enzyme, protein, collagen and gelatin recovery (Klomklao *et al.*, 2005; Slizyte *et al.*, 2005; Fernandez-Díaz *et al.*, 2001; Muyonga *et al.*, 2004a,b; Choi and Regenstein, 2000).

From wastewaters coming from the industrial processing of octopus, several groups of peptones could be obtained through enzymatic hydrolysis, promoting the growth of lactic acid bacteria. From industrial point of view, such bacteria are the most important for the production of lactic and acetic acid, ethanol, diacetyl and 2,3-butanediol molecules, that could be used as monomer for future polymerization processes (Kosseva, 2009).

Ettxabide *et al.* (2016) reported their study on fish gelatin films obtained from food wastes, obtained by solution casting with solution of different pH value. Mechanical, barrier and optical properties were evaluated as well as their environmental impact by Life Cycle Analysis technology.

Dairy

The dairy industry covers a great part of the food industry and consequently the production of waste is really consistent. The demand for milk and dairy products is still increasing, especially in Europe and North America. They contain principally fatty acids, lactose and suspended solids. The wastewater may contain proteins, salt, fatty substances, lactose and cleaning chemicals (Kosseva *et al.*, 2003). The wastewater streams are difficult to treat due to the high concentration of detergents, surfactants, like polyphosphates, EDTA, that remain after treatment and that is problematic for the ecosystems of rivers because their toxicity for aquatic animals (Thassitou and Arvanitoyannis, 2001).

Etxabide et al. (2017) in their review, fully described gelatin film obtained from bovine food waste (but also from porcine and fish), to be used for producing active packaging. The incorporation of natural antioxidant and antimicrobials into films can be seen as a tool to extend the food shelf-life, reducing food losses.

Wastes From Fermentation Industry

Liquid wastes produced from the fermentation industry are similar and contain many common compounds such as tannins, phenols and organic acid. These streams are difficult to treat.

Grape pomace, consisting of skins, seeds and stalks, coming from wine production, could be used to produce aroma compounds. But, the chemical composition is very complex because alcohol, acids, aldehydes, esters, pectin, polyphenols, mineral substances, sugar and other chemicals are present (*Torres et al., 2002*). Grape pomace is used also for ethanol distillation, which could be used as bio-resource of monomers for the production of bio-polyesters.

From brewing industry, a great amount of brewers' spent grain is obtained, used principally in animal feed thanks to the high protein and fiber content. It is also rich in bioactive compound such as phenolic acid and other chemical components (*Peterson and Qureshi, 1993; Sz wajgier et al., 2010*).

Future trends

Environmental concerns about the even more large quantities of food wastes produced in the World have generated a great interest versus new and alternative technologies, environmental friendly. These wastes could be used as substrates for producing chemicals with great economic value. First of all, microorganisms coming from these wastes may be important because capable of converting such materials into valuable products. Industrially, at the moment, in this area much more has to be done, for reaching a technological and economic feasibility.

The use of vegetable wastes can contribute to a reduction in the use of raw materials as well as in the waste minimization production.

Fruit and vegetable processing is used to obtain by products with high functional attributes is important to reach. For this, much research is still need in order to found the best food processing technology, in order to develop the best method for a complete utilization of by-products coming from food wastes, to reduce the presence of toxins and to assess the bioactivity and toxicology of such new chemicals. Functional food is an important area of the food market. However, if obtained from food waste by-products, the potential risks must be carefully controlled. Their stability and interaction with other food during processing as well as during storage must be fully investigated.

Starch based industrial wastes are important substrates for the production of polyhydroxybutyrate polymers (PHBs), contribution not only in the reduction of the sludge landfilled but also in the reduction of the cost for their synthetic production.

The mechanical as well as the barrier properties of biodegradable polymers and edible films coming from food wastes products are away from properties of the most common synthetic plastics used in packaging. They have been improved by combining each other several polymers but further research has to be enhanced. Of course, the goal is to obtain biodegradable polymers with properties much more similar to commercial ones. Probably in a near future these polymers will be a good alternative to replace the synthetic ones, more economic and commercialized.

The production of biogas is also viewed as a great new opportunity for energy natural recovery. As an example, the anaerobic digestion of the fruit and vegetables waste is a commercially process to obtain methane gas. Production of hydrogen from dairy waste effluent is currently worth investigating.

While the anaerobic technologies are simple and low cost for producing biogas, aerobic technologies are still highly energy intensive and still require more research to adapt them to the economic World concept.

In order to well understand the environmental impact of the new funding the most important tool is the Life Cycle Assessment (LCA) analysis technology (*Leceta et al., 2014*). Thank to this approach, it is possible to understand and identify the steps that in the food chain have the largest impact, in order to target the improvement efforts. It is important to choose the correct raw material, packing system, as well as all the input use for choosing the best waste management strategy. Adapting the LCA technique to the social value, as well as to the ethical and moral value recognized from the World, is the future step in the development of the correct food waste management.

Conclusions

The increasing interest versus high-quality food products and the increasing interest versus the environmental preservation encouraged the researchers to develop new edible films as well as biodegradable films and coating, to be used in the food packaging sector. For their production, renewable resources could be used and among them, food waste resources are gaining even much more interest in the scientific and industrial world. Edible films are used to preserve food from its surrounding, and could be obtained from biopolymers hydrocolloids (such as gelatin, keratin, collagen casein, soy protein, whey protein, wheat gluten, corn zein, starch, cellulose, plant gums), lipids (such as waxes, acylglycerol, fatty acids), resins (such as shellac and wood resin) and composites (lipid and hydrocolloids). In general they are obtained by thermoplastic processing technology (extrusion and

compression molding), commercial processing with high potentiality for the large-scale production. In order to avoid facilitating the processability avoiding deformation and thermal degradation and to undergo the glass transition temperature, natural additives such as glycerol, sorbitol, sucrose, water and other plasticizers could be used.

Films packaging obtained from food waste and used as wraps, pouches, bags, casings and sachets for food protection, requires a full base characterization in terms of mechanical, thermal, barriers and microstructure, as well as the possibility of their recyclability.

The development of such new environmentally products must come from an interdisciplinary activity. Integration between market, research, manufacturers, consumers and society is fundamental for pollution control and waste management, for the reduction of the environmental contamination. The innovation must be obviously focused on consumer needs but without losing the respect for the environment. Unfortunately, some recent developments consider the public demand more important than the respect to sustainable resource utilization. So, the current trend in the development of a new product and technology is to consider the quality perceived from the consumer as the starting point and, around this, build the future. Market orientation is fundamental for the success of an innovation, especially for the food sector. In the food market three strategies are fundamental for development that considers the increase of bioenergy demand, the decrease of water consumption and natural resources. Without innovation, consumers' needs cannot be affordable. Innovative packaging and processing technology are two answers to be addressed in order to reach such innovation and to provide better opportunities for consumers.

See also: Prospect of Recycling of Plastic Product to Minimize Environmental Pollution

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Global Economy Increasing by Enterprise Resource Planning

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Introduction

Based on the thorough fundamental analysis of relevant literature and actual cases, the main characteristics that need to be taken into consideration when planning the implementation of integrated software solutions in a project are presented in this paper. Market ERP on supply and demand is segmented to systems for small, medium, and large enterprises (**Fig. 1**) (**Denić, 2010**). The division is not only dictated by annual revenues, the number of employees, and other parameters, but also the speed and extent of changes in the process of the business itself. **Fig. 1** outlines the largest and most successful vendors of software applications throughout the world (**Denic et al., 2013a**). As each vendor achieved success with their first application, they developed other applications for other business processes or united existing applications. Successful vendors have software applications for almost all major business processes, in which all applications are assembled into one product and which is called enterprise resource planning ERP or integrated information systems.

ERP Facts

The actual state of ERP systems has been to initiate more and more specialists to deal with current issues and points of great importance, characteristics and the performance of the ERP system. **Roger Rigelhof (2003)** describe the reasons why ERP systems are a special type of information system:

- In their design, ERP systems have the widest use of all organizational information systems and software packages – they are used in all functional areas and at all levels of organization.
- ERP systems present an advantage as they are constructed in the manner that most organizations use information systems. ERP systems are complex systems; they are not used separately in extremely large organizations or are only used in certain industries.
- Due to their complexity and the fact that an organization's success is dependent on the rapid response of these systems, they have sophisticated skills and experts in the implementation process; therefore, the introduction of ERP systems are one of the most sought-after professions today.

All ERP systems are based on (**Dahlen and Elfsson, 1999**):

- Data (the information required for business),
- The integration of data (processing and transport),
- Functionality (collection, storage, and display-transfer).

Table 1 presents the successful implementation where 5 of 9 listed companies carried out the implementation of SAP.

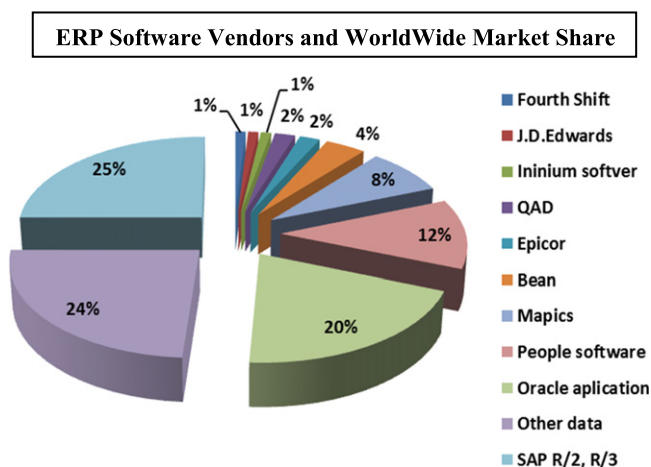


Fig. 1 Market share of ERP applications. Reproduced from Chorafas, D.N., 2001. Integrating ERP, CRM, Supply Chain Management, and Smart Materials, str.77. Exhibit 6.3.

Table 1 ERP successes derived from literature review

Organization	Industry	Implementation scope	Why success?
Earth Grains	Bakery products (USA)	SAP's R/3	The project started with the clear strategy and each department had analyst reporting issues to management. Change compensation system to employees after implementation. Involved interpersonal skills for training and strong knowledge on technical and the company business process.
Monsanto	Chemical and life sciences	SAP	Success factors in Monsanto project dealt with the management structure, the redesign of business process, and investment in re-skilling by proving training, and acquisition of external expertise.
U.S. Mint	Coin production	PeopleSoft \$40 million	The project started with a business requirement. Employers were able to see how everything needed to be coordinated. People received training in the use of the system and used of external consultant on the project. The Project also involved Senior management and organizations understand that the undertaken project will be painful and expensive but expected to provide savings of \$80 million over the next seven years.
Ralston Purina	Manufacturing	Oracle	The CSF for Oracle project at Ralston included Strong management support, experienced technical consultants and project manager and effective user training.
Sigma Chemical	Chemical industry	SAP	Support from top management, BPR, Invest in training and re-skilling and used of consultants.
Scripps Metabolic Clinic	Multi specialty medical group and clinical research institution.	Lawson ERP integrated solution on HP 9000	Reliable vendor partnership and successful system integration.
Houston Independent School District	Public sector and education	SAP ERP modules	Project started with well plan BPR and focused on the integrating legacy system and an existing PeopleSoft Inc. Selected a right team also become part of success factor. The system already has shown a 42% return on investment and has lowered inventory by \$1M.
Experience Point	Manufacturers of aircraft	Not provided	The project started with the used of external consultant. Manage to get top management support and user participation. The company also provided training to the user in order to improve their understanding towards the system.
Anheuser Busch	Manufacturer of Beer and related food product	SAP	Provided a cost savings based upon integration of data and processes, a common database, and increase leverage of purchasing and buying. The critical success of the implementation included used of external consultants, project champion, BPR, top management support, technical and business knowledge.

Note: Wong, B., Tein, D., 2003. Critical success factors for ERP projects. In: Unknown (Ed.), Proceedings of the Project Management Conference, Alice Springs, Australia, October 2003 in Australian Institute of Project Management Conference Program 2003, Sydney, Australia: AIPM, pp. 1–8.

ERP Implementation

Some of the factors the ERP system and the implementation of integrated information systems are here presented below. Other well-known experts and authorities on the ERP system highlight the peculiarities and specificities of these systems, such as the authors [Skok and Legge \(2001\)](#) who point out that ERP systems are often seen as the new paradigm for the development of information systems, due to the following factors that differentiate them and make them recognizable:

- The number and diversity of investors in any implementation project,
- High cost implementation and consultation,
- Integration of business functions,
- Resultant software configurations that represent basic processes,
- Change management and policy issues related to BPR (Business Process Reengineering) projects,
- Commitment to education and training needed for familiarization.

ERP can be described by five basic facts ([Wallace and Kremzar, 2001](#)):

- A wide range of tools that align supply and demand,
- Connecting buyers and suppliers in a unique value chain (a value chain represents the activities of individual steps through which all services or products the company achieves added value),
- The efficiency of a company is reflected by its adopted business decisions,
- Inter-linking sales, marketing, manufacturing, logistics, finance, and human resources development,
- A common goal is a high level of productivity and low cost.

Some of the most important guidelines in the process of introducing modern sophisticated information systems are here presented below. It is very important that when implementing ERP systems or the introduction of a new information system to pay special attention to cooperation bidder and suppliers who aim to achieve a partnership (Denic *et al.*, 2014). This allows both parties to achieve their goals. On the one hand, an important role is played by the personnel structure of suppliers, which reduces associated human factor risks; however, the supplier is also a bidder of solutions tested in practice due to their knowledge introduced in the company (Roger Rigelhof, 2003). One of the largest manufacturers of sophisticated ERP in the world is SAP, who recommend that their customers compose design teams be led by a project manager, which corresponds to the executive and steering committee, formed by experts of SAP (functional analysts and leaders of functional teams) and a SAP associate partner – the leader of the technical team, technical analysts, and system administrators (Larocca, 1999). A very important role in the introduction and implementation of ERP systems is to have users who know the needs of introducing a software solution. This, however, does not constitute the user's request, since the requirements are not clearly defined. At the beginning it is necessary to predict the (Roger Rigelhof, 2003):

- The details of the work,
- Changes in circumstances in which the program is running,
- Usage,
- The availability and accessibility of the system,
- The criteria for accepting or rejecting changes,
- Response time and time frames the possibility of changing requirements,
- A method to document changes that are usually associated with additional costs.

The last phase in introducing the ERP system is the actual implementation of information systems, setting up the network, the installation of personal computers, user training, and data migration to the new system. The technical team shall perform the following tasks (Bancroft, 1996):

- Construct the network infrastructure,
- Install shortcuts,
- Train and support users,
- Communicate,
- Enter the correct data in production system,
- Start the system.

The reasons for the implementation of ERP systems in Serbia, the United States, and Sweden can be seen in Table 2.

It is evident from Table 2 that the reasons for the implementation and introduction of sophisticated ERP systems generally coincide, regardless of the geographical area of the companies. However, some discrepancies in the values show that there are some specifics in business and business systems in developed economies of the world and companies in the Western Balkans (Denic *et al.*, 2013b). The following Fig. 2 shows the use of ERP solutions in Serbia.

To study the global market, in addition to the relevant literature used, sources from Gartner, a leader in providing information on the state of the market in the field of ERP services have been examined. To study the local market, one of the sources is self-attained experience in this area, where many years of active work have been reflected in numerous surveys that have been conducted in several hundred major IT companies in Serbia, which is the basis for thoroughness of the research. Business systems and enterprises in Serbia usually implement modules related to finance and accounting, human resources, sales, and distribution (Denic *et al.*, 2013a). Less commonly implemented modules are those that are related to product lifecycle management and advanced planning, as well as supply chain management. The implemented ERP solutions of Serbian manufacturers are presented in Fig. 3.

Table 2 Comparative reasons for implementing ERP solutions

Reasons for implementing ERP systems	Serbia		United States		Sweden	
	Important	Rank	Important	Rank	Important	Rank
Replacing old (legacy systems)	4,39	1	4,06	1	4,11	1
Simplification and standardization of systems	4,07	2	3,85	2	3,67	2
Improving interaction with suppliers and customers	3,97	3	3,55	3	3,16	4
Gaining strategic advantages	3,90	4	3,46	4	3,18	3
Pressure to keep up with the competition	3,85	5	2,99	7	2,48	8–9
Integration into global activities	3,78	6	3,17	5	2,85	6
Restructuring the organization	3,54	7	2,58	9	2,70	7
Ease of upgrade (improvement) to the system	3,24	8	2,91	8	2,96	8

Note: The Company Research, found April 01, 2014. Available at: <https://www.idc.com/analysts/analysthome.jsp>.

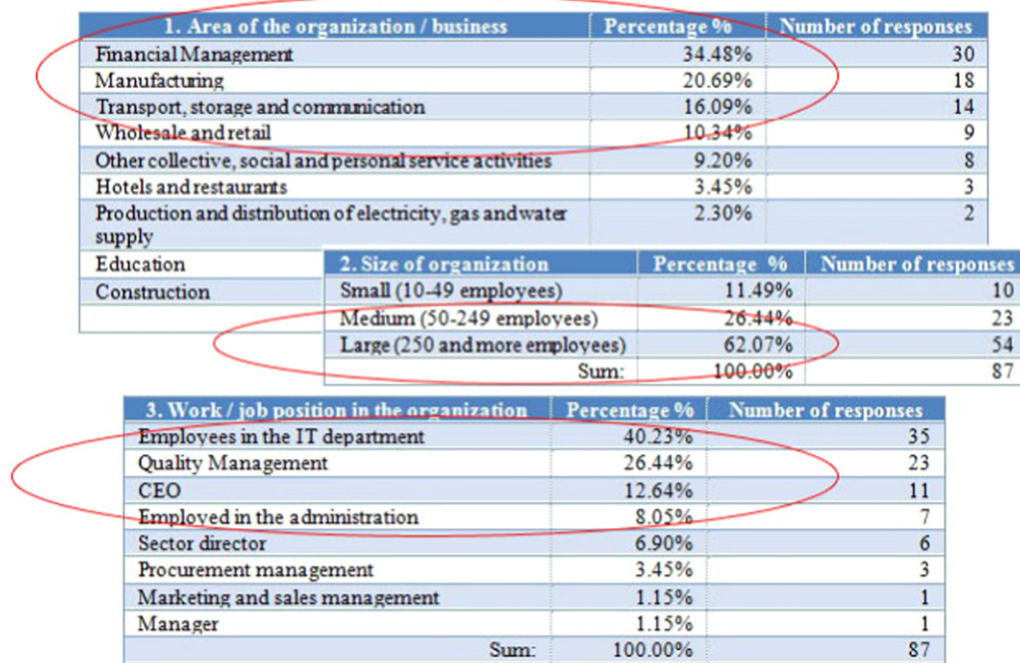


Fig. 2 Use of ERP solutions in Serbia. Reproduced from The Company Research, found April 01, 2014. Available at: <https://www.idc.com/analysts/analysthome.jsp>.

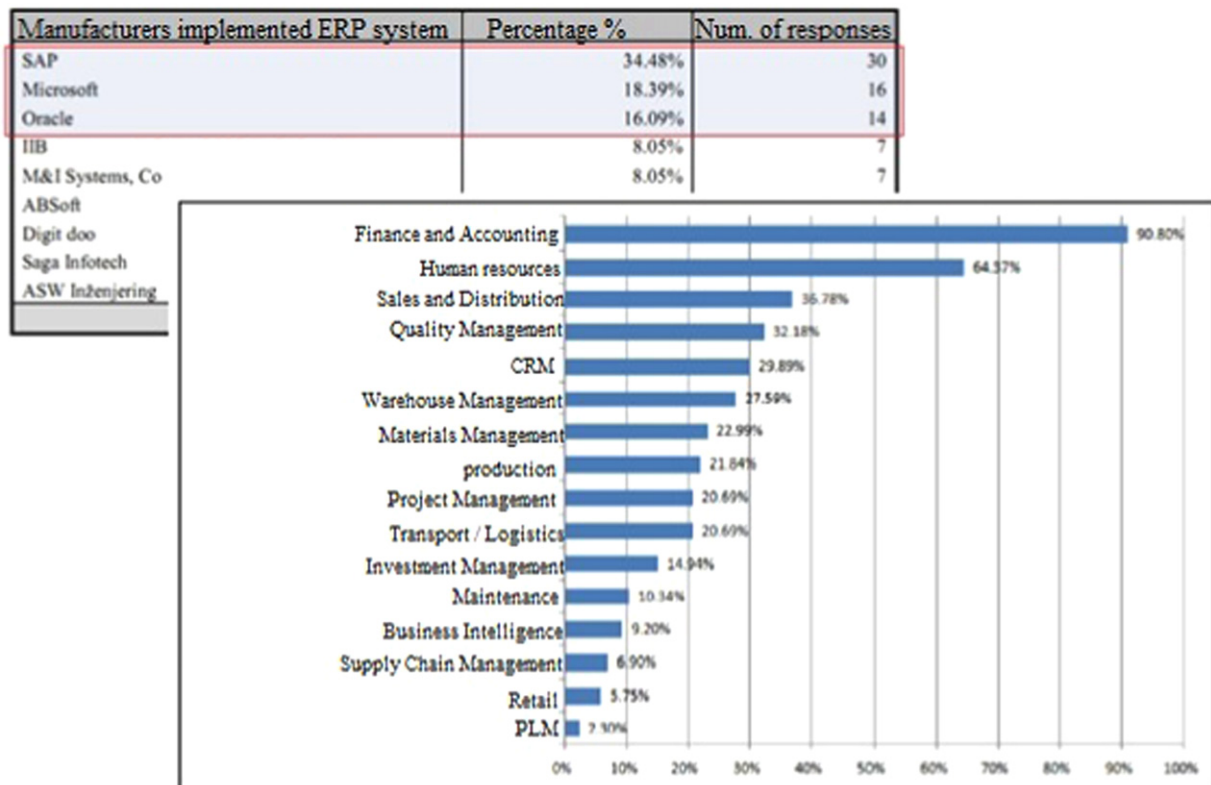


Fig. 3 Manufacturers of implemented ERP solutions in Serbia. Reproduced from The Company Research, found April 01, 2014. Available at: <https://www.idc.com/analysts/analysthome.jsp>.

The IT market in Serbia and in the Balkans (Fig. 4) has made progress in the previous decade, but not yet enough. In order for the economy and society to emerge out of its crises of the last two decades, it is essential that IT investments in Serbia double every 5 years (15% yoy). Investment is off to a good start. From 2005–2008, the market doubled, but from 2009 to 2011, IT investments deteriorated, so much so that the average annual growth rate for the years 2005–2011 fell below 10% (Enterprise Research, 2014).

Really high growth rates are needed for a modest state in the year 2020 (Fig. 5).

The potential IT market in Serbia is much higher than what has been achieved in recent years. The potential is great, but is currently unable to go even higher. If Serbian ERP investment cannot be duplicated in the next five years, Serbia's economy and society will fall even deeper into a crisis (Fig. 6) (Enterprise Research, 2014). The ERP market has plenty of room for growth. Typically, 10% of the ERP market in Serbia is about 7% (Fig. 7). However, it is necessary to be careful with personnel who are increasingly being outsourced (Enterprise Research, 2014).

According to percentages, 15% of small enterprises (10–49 employees) 1522/10,000, 30% of medium-sized companies (50–249 employees) 308/500, 60% of large companies (250–999 employees) 308/500, 100% of very large companies and systems (greater than 1000) 75/75 (Fig. 8) (Enterprise Research, 2014).

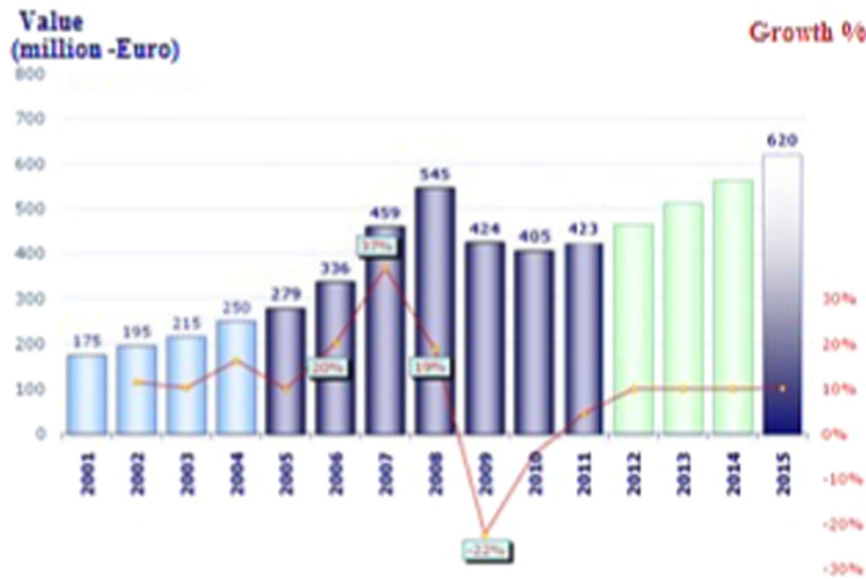


Fig. 4 The PC market and its trends to 2015, Serbia. Reproduced from Enterprise Research, found 02 April 2014. Available at: <http://www.gartner.com/technology/analysts.jsp>.

	IT services per capita [€]		The average annual growth [%]
	2011	2020	2011-20
EU10-West	800	1.000	2.2%
EU10-East	250	500	7.0%
Serbia	60	250	15.3%
Serbia as a [%] of the EU10	24%	50%	

Fig. 5 IT ERP investment per capita. Reproduced from Enterprise Research, found 02 April 2014. Available at: <http://www.gartner.com/technology/analysts.jsp>.

ERP market	Worth millions [€]	Participation [%]
ERP licenses	16,30	55,2%
ERP implementation	8,70	29,4%
ERP application development according to customer requirements	4,53	15,4%
Total	29,53	100,0%

Fig. 6 ERP market in Serbia. Reproduced from Enterprise Research, found 02 April 2014. Available at: <http://www.gartner.com/technology/analysts.jsp>.

ERP licenses	Worth millions [€]	Participation [%]
International ERP vendors	8,78	53,9%
local ERP vendors	6,93	42,5%
Regional ERP vendors	0,58	3,6%
Total	16,30	100,0%

Fig. 7 Market ERP licenses in Serbia according to the origin of the vendor. Reproduced from Enterprise Research, found 02 April 2014. Available at: <http://www.gartner.com/technology/analysts.jsp>.

Size of the buyer	Number of installations	Participation [%]
Micro-enterprises (less than 10 employees)	2,306	45,9%
Small Business (10-49 employees)	1.522/10.000	30,3%
Medium-sized companies (50-249 employees)	816/2.000	16,2%
Large companies (250-999 employees)	308/500	6,1%
Very large companies and systems (over 1000 employees)	75/75	1,5%
Total	5.027	100,0%

Fig. 8 Shows the number of ERP installed base by the number of customers in Serbia.

Conclusion

In a research paper is presented to the importance of the success of the introduction of an information system in Serbia. ERP solutions on the market today, more or less successfully cover core business processes and enable the efficient governance of enterprise resources. However, the specificity is mastering the business processes that the company provides a competitive advantage. The world's leading ERP packages are technologically modern, integrated and represent reliable software support. The

quality of built-in software support, however, is surprisingly good. Customization and implementation of the ERP solutions can take from six months to two years or more, resulting in a wide range of product prices and the cost of customization specific to the customer's needs. The main reason for the high cost of an information system that is being built in this manner, is the need for simultaneous adaptation of software solution to the organization and adapting of the organization and its business processes to the software solution. The very use of the software in the enterprise does not have any problems, such as meeting the needs for normal operation. So far we have not had the need to the required analysis, justified by its small size and management by financial owners. Also modern sophisticated ERP solutions offer many possibilities, but these possibilities and benefits are not used in a good deal of business entities and companies in Serbia and the region, some because of their small size, but in most cases also due to lack of knowledge of positive impact of business intelligence or technology for business decision making.

During the global economic crisis in 2008, when it covered the global market, many companies in the region experienced a smaller decline in business only during the period of three months, just because of new clients situation has improved as it was. Source of given data is useful, the only question is whether management had an interest for such changes.

See also: Opportunities for Digital Marketing in the Viticulture of Kosovo and Metohija

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High Dynamic Range Imaging and its Use in Daylight and Lighting Design

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Introduction

There are many metrics in use today that will measure a variety of aspects of daylight and artificial lighting. The aim is to determine adequacy and consistency of light levels including the absence of glare for visual tasks in the built environment. The focus historically has been “ensuring a consistent level of light was achieved over large areas” (Cuttle, 2010). There has been, until recent years, a focus on “illuminance regardless of the direction of the incidence of light on a horizontal, 2-dimensional plane” (Cuttle, 2010).

Following on from this, the focus has turned to one of human need for lighting and the idea of visual performance. However, the predominant measuring of illuminance, which has no visual effect, is disconnected from what the viewer sees (Cuttle, 2010).

Few, if any, metric measures exactly what is actually seen by the human eye. It is not possible to relate these metrics to, or to capture the light levels from, the visual scene entering the eye. In recent years the development of affordable digital single-lens reflex (DSLR) digital cameras has given rise to the use of high definition range imaging (HDRI) as a means of making this important connection.

In photography, the term *dynamic range* usually represents the ratio between luminance values spread across the spectrum of darkness to brightness. The human visual system can easily adapt to visual scenes within the range of 10 orders of magnitude for a single scene, and its range overall is 1,000,000–0.0000001.

Widespread technological instruments currently used for imaging such as LDCs and regular cameras are not capable of capturing the full dynamic range of scenes in a single exposure that can be seen from the human eye in real life. This is due to the properties of the photo sensor within the camera that converts photons to electrons (Jacobs, 2007).

A small number of professional instruments capable of capturing, in a single shot, the dynamic range that humans perceive are being developed, but effective and affordable solutions are still rare (Jacobs, 2007).

One solution to this problem is represented by the HDRI technique. The HDRI is an image processing technique that allows the capture of a greater dynamic range of exposure than normal low dynamic range (LDR) technology. It is based on combining multiple images with different exposures (ranged between low exposure value images to high exposure value images) to create a single image that captures the full dynamic range. From this HDR image containing light data a measurable luminance map can be produced.

Over spot luminance meters, this technique has the ability to capture luminance in the human field of view more rapidly and with a higher resolution.

The accuracy of luminance measurement with HDR photography is widely influenced by the care taken during acquisition and treatment. A measurement error of less than 10% can be expected (Cauwerts and Pederit, 2018).

A Brief History of HDR

The first time cameras were used as measuring tools to capture photometric measurements was in the early 1960s. In the mid-1970s, photographic instruments were used to measure the luminance distribution in the sky vault. This was the start of a number of research groups setting up systems to analyze sky luminance. The most significant collaboration of research groups in this area, SERI-LM23 was set up in 1984 and included the Solar Energy Research Institute. Their system developed to be a basis for sky models and covered a luminance range between 200 and 16,000 cd/m² with a field view of pi steradians (Bellia and Spada, 2014).

These systems had difficulties as a result of the limited range of luminance. Another luminance analysis system called “Cap-Calcul” in the early 1990s improved on previous developments by introducing a variable focal length lens. It had an improved luminance range also of between 70 and 27,000 cd/m² (Rea and Jeffrey, 1990).

Bellia and Spada note, “Berrutto and Fontoynt (1995) set up a portable system for wide-angle luminance mapping. This system was connected to a computer for automatic setting and for the storage and processing of data. In particular the setting of the sensitivity range (i.e., the adjustment of the quantity of light), was carried out by means of an electronic shutter driven by software acting on exposure times, abandoning the technique of acting on lens aperture. All the problems connected to film were swept away by the advent of digital video and photographic devices based on CCD and CMOS sensors.”

In the last 25 years, video and camera technology has developed significantly and it is now possible to obtain good quality equipment at affordable prices.

Jacobs (2007) notes: “several companies such as Radiant Imaging, Lumetrix, Optronik, Opsira and TechnoTeam produce and sell tools for photometric measurements, while others such as Art-innovation are specialists in the field of instrumentation for spectral analysis.”



Fig. 1 Low dynamic range images with different exposure times. *Source:* Author.

Process

The process for getting luminance charts starts by taking a series of differently exposed images. A calibrated DSLR camera can be used. A number of images from 3 to 8 of the same scene with different exposure are needed. The exposition of a digital camera can be manipulated in different ways: Firstly, the aperture (f-number), secondly the shutter speed (exposure time), and the thirdly by varying the sensitivity of the camera imaging sensor or ISO. Only one should vary; the other two should be fixed. A tripod and a remote camera controller are needed to ensure stability of the camera. The camera and lens should be calibrated by spot luminance measurement using a luminance meter and a known color reference point. The sequence of images obtained will be put together by computer simulation software such as Radiance or photo based applications such as Photosphere. The HDR corrected image will be generated.

$$E = L \frac{\pi d^2}{4 h} \cos^4 \Phi$$

With a typical imaging system irradiance E on a pixel is related to the scene luminance L as described in the above equation (Jacobs, 2007).

Each single pixel on the screen will correspond to a specific luminance value, although this information needs to be extracted from each pixel, as the relationship of luminance to pixel is nonlinear. A false color image can then be generated (Figs. 1–4).

Luminance is measured by using a HDR image technique: Taking photographs (low dynamic range images) using Canon EOS 5D Mark II DSLR camera with Sigma 8-mm fisheye lens, at the same point in time. To obtain stable images, the camera was placed on a tripod at a steady, standing position. The camera was connected to a computer laptop installed with EOS Utility 2 software, which acted as the camera remote controller. By doing so, one would not need to touch the camera directly, thus minimizing the movement of the camera. Changing the shutter speed values, while maintaining the ISO value and aperture as constant, varied the camera exposure setting. The selected shutter speed values were 1/4000, 1/2000, 1/1000, 1/500, 1/400, 1/250, 1/125, 1/100, and 1/25 s, while the ISO value was 100 and the aperture value was 4.0. To calibrate the data, several daylight physical variables, i.e., vertical illuminance and scene luminance, were physically measured; vertical illuminance was measured with a lux meter at various points representing the occupant's point of view. Meanwhile, scene luminance was measured with a luminance meter. Calibration was carried out by marking the area to be calibrated on the HDR image (the same area measured using the luminance meter). The results of the luminance values were then inserted in the calibration column "postprocessing." The photography images that have been taken with a different exposure were then combined to get a HDR image using WebHDR Jaloxa. The HDR images were processed using Hdrscope based on Evalglare software to obtain the daylight variables in terms of average of the total luminance of the scene, as well as the indicators of visual comfort such as Daylight Glare Probability (DGP) and Daylight Glare Index (DGI) glare index.

Applications

The main use of HDR images is for luminance distribution evaluation within the field of view.

High dynamic range imaging techniques are increasingly used in daylight and lighting design as a data acquisition tool for the purpose of acquiring information related to lighting quantity and lighting distribution. Luminance value measurements within the

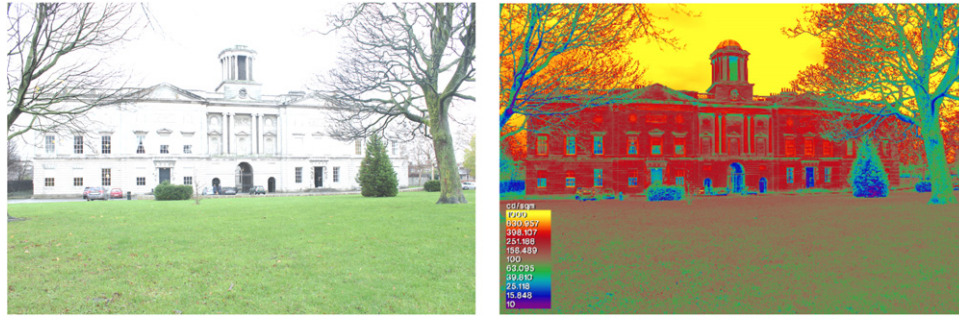


Fig. 2 Corrected combined HDR image and false color image. *Source:* Author

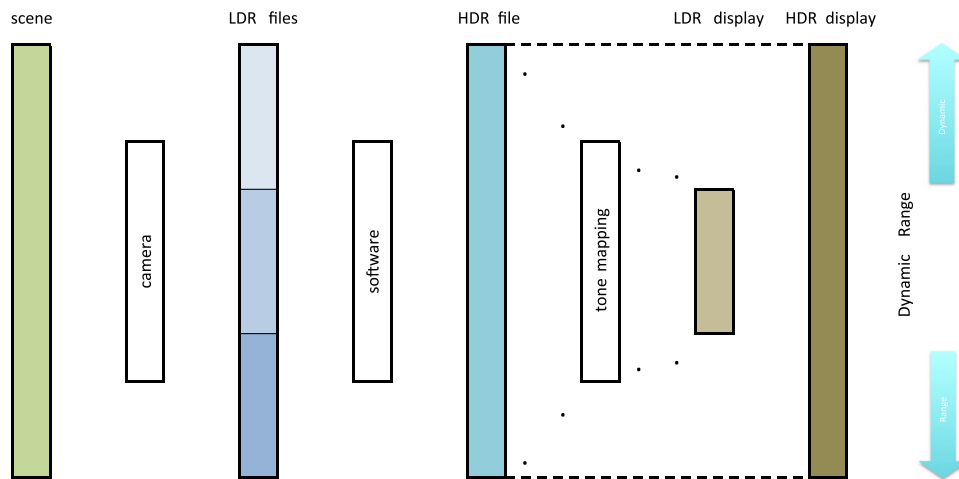


Fig. 3 LDR to HDR/luminance capture process. Adapted From Jacobs, A., 2007. High dynamic range imaging and its application in building research. *Advances in Building Energy Research* 1 (1), 177–202.

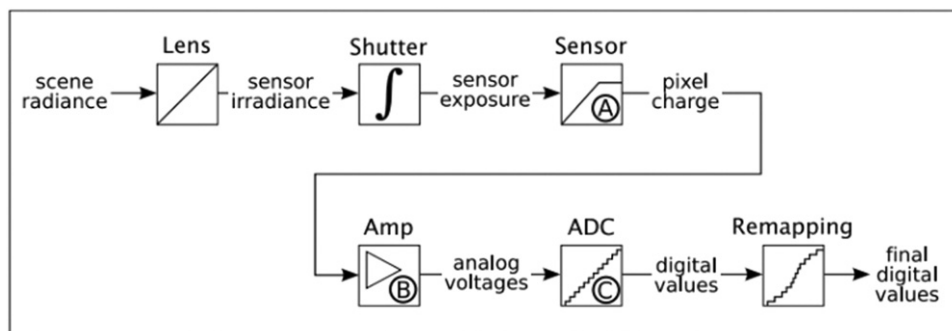


Fig. 4 Image acquisition sequence. Adapted From Jacobs, A., 2007. High dynamic range imaging and its application in building research. *Advances in Building Energy Research* 1 (1), 177–202.

occupant field of view and investigation of visual discomfort are other direct applications. This photographic technique also makes it possible to map sky luminance.

HDR images offer an accurate measure of luminance values within a space; illuminance values can be also detected and false color can be applied to quantitatively analyze the scene.

HRD images can be used for Unified Glare Rating (UGR) measurement and also for glare detection. For the UGR measurement, using photometrically and spatially calibrated images, the exact luminance, direction, and solid angle of each pixel is defined and the UGR glare rating or different glare indices such as DGI and DGP can be derived.

HDR images can replace, in some cases, sophisticated metrological station monitors when these instruments are used for mapping sky luminance. To optimize building performance, data such as percentage of cloud cover and daylight hours are really important considerations for designers. Existing meteorological stations provide this data using costly scanners with limited spatial resolution. HDR

images of the sky can be taken with a 180-degree fisheye lens that provides a better spatial resolution. This data can be then analyzed using different software. Only the number of pixel on the camera limits the quality of the data from this method of measurement.

The affordability and effectiveness of luminance chart data, along with the small amount of error using this technique, have supported the development of different technique applications within the artificial light and daylight research and practice sectors. An example of such work is the measure of complex luminous fluxes across large areas, the enhancement of complex luminance based evaluations for design purposes and some alternative lighting metrics such as mean room surface exitance measurement, climate-based daylight modeling (CBDM), etc., (Cuttle, 2010).

CBDM is the prediction of various radiant or luminous quantities (e.g., irradiance, illuminance, radiance, and luminance) using sun and sky conditions that are derived from standard meteorological datasets. Climate-based modeling delivers predictions of absolute quantities that are dependent both on the locale and the building orientation, in addition to the building's composition and configuration. HDR images are used to create a database of daylight related information usually gathered within a year, that have been found to be as reliable as the ones from standard meteorological stations.

Other fields of application relating to daylight and lighting using video luminance meter include:

- Lighting control for museums
- The control of light pollution
- Energy saving
- Evaluation of visual comfort in indoor and outdoor environments
- Availability of daylight
- Measurements in scale and full scale models
- Photometric measurements for data collection
- Glare

Cuttle (Bellia and Spada, 2014) and others are currently exploring the use of HDR imaging as a new lighting metric because of its direct relationship with what we see that can be measured in lighting terms. This research is currently being carried out in a new area of artificial lighting science known as mean room surface existence (MRSE). This technique also allows for the possibility of light pattern modeling.

Despite a significant number of research papers on the subject of HDRi, it is widely acknowledged that a standardized method for capturing and processing of LDR to HDR and luminance mapping is required (Cai and Chung, 2011).

HDRi images can be evaluated for glare with the software Evalglare. It has three different algorithms, one of which is "task luminance," which can be used to compare and calculate which areas in the task area are a multiple of the average luminance of that area (Rodriguez et al., 2015).

HDR imaging has been used in conjunction with LMK software, to compare the accuracy of glare prediction with Dialux, an industry wide lighting software package. A subjective assessment shows HDRi to be more accurate for the prediction of glare when compared with the subjective evaluation (Jacobs, 2007).

Conclusion

As technology develops, the desire and need for a greater number of professionals applying the various applications of HDRi metric becomes more attainable and desirable. Not least because of the legibility of the technique as an image based application for the lighting professional and wider built environment community, but also because the accuracy of the process will improve and expand as technology develops as is evidenced by its history. As it becomes more commonplace, in time it will inevitably fulfill its potential for a myriad of lighting and daylight applications.

Looking to the future for HDRi the following quote sums up what we can hope for:

"High dynamic range (HDR) images and video contain pixels, which can represent

much greater range of colors and brightness levels than that offered by existing,

standard dynamic range images. Such "better pixels" greatly improve the

overall quality of visual content, making it appear much more realistic and appealing

to the audience. HDR is one of the key technologies of the future imaging

pipeline, which will change the way the digital visual content is represented and

manipulated." (Mantiuk et al., 2016)

Multiple HDR video imaging techniques are already in use in the assessment of light distribution in different scenarios. So it is not unreasonable to expect this type of application where light entering the eye of the viewer in motion can be measured accurately in the near future.

See also: Natural Lignite Resources in Kosovo and Metohija and Their Influence on the Environment

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Induction Heating in Sustainable Manufacturing and Material Processing Technologies – A State of the Art Literature Review

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Introduction

The rate at which the modern materials are being developed, the processing techniques also gets updated to deal with the advanced materials or biomaterials. High productivity, ease of processing, optimum utilization of resources, minimum negative impact on environment is the desirable criteria for modern material processing techniques. Heating is the primary requirement of every material processing technology and it is also the cause of emissions, environmental pollution, and contamination. Conventional heating method used in manufacturing processes use fossil fuels, petroleum products etc., which generate a considerable amount of gasses like fluorides, carbon monoxide, carbon dioxide, and other hydrocarbons leads to pollution, greenhouse effect and acts as a barrier in the process of sustainable manufacturing (Popović *et al.*, 2014; Szewczyńska *et al.*, 2015; Jin *et al.*, 2017; Ma *et al.*, 2019). Thus, there is a need for choosing a heat source that is sustainable in nature and able to produce clean technology. Induction heating is a non-contaminated, emission-free sustainable process making it popular among the available sources in recent times. It offers uniform heating, faster rate, consistency, flexibility, and ease of use for intricate shapes and sizes. Latest induction heating system offers the options for accommodating different part geometries, usability on vast material dimensions from very thick steel pipe to small scale material processing like nanotubes and powders at confined space (Lupu *et al.*, 2004; Li *et al.*, 2008; Grande *et al.*, 2012; Rashad *et al.*, 2012). It also offers ease of use no matter the weather conditions but gas (mostly inert gas) shielding should be used if the material has oxidation prone. Various configuration of induction coil is available that sit on the top of a substrate and may not necessary to be wrapped around the workpiece. Induction heating is applied directly on conductive materials, however, non-conductive and nonmagnetic materials can be heated through the use of susceptors which transfers heat to nonconductive parts and assist indirect heating of these materials. In effect, susceptors act as a passive medium to make non-conductive material absorbing heat indirectly and perform like a conductive and magnetic metal (Bayerl *et al.*, 2014). In principle, the process of induction heating is similar for all applications, but there is always a difference in intensity and distribution across all manufacturing processes. In some application, heating rate as well as heat flux intensity requirement is low and in some cases, it is very high. Therefore, based on low or high frequency, the application of induction heating is categorized (Ahmed *et al.*, 2005; Bayerl *et al.*, 2014; Lucía *et al.*, 2014). Also, the coils are always custom built according to the shape and size of the substrate material. Coil geometry is a major challenge in producing the required eddy current at specified area. In most of the applications, the methodology is similar, but, the coil geometry, use of shielding gasses to protect heating zone, use of magnetic shielding to protect nearby area and magnetic flux concentrator to increase the heat flux, specific design of fixture, frequency in use, time duration, exposure area etc., are the factors that differentiate each application of induction heating from another.

Sustainable manufacturing modestly refers to satisfying the need of future generation as well as satisfying the need of present generation by minimum utilization of resources along with least impact on the environment. It indicates the development of manufacturing processes that are energy efficient i.e., consuming lesser energy (may be hydro-power, wind, electrical), use of bio-degradable raw materials, production process with lower maintenance, and minimization of waste products and emissions. According to Badurdeen and Jawahir (2017), there are four steps in sustainable manufacturing that are pre-manufacturing, manufacturing, use, and post-use and it incorporates a 6R policy i.e., Reduce, Redesign, Reuse, Recover, Recycle and Remanufacture. Furthermore, sustainability in the manufacturing process is primarily assessed on the basis of the consumption of natural resources and environmental emissions. Fig. 1 depicts the relation between resource consumption and environmental hazards for different manufacturing systems. It is obvious that both the use of natural resources and the creation of environmental hazards and emissions are substantially reduced from traditional manufacturing to sustainable manufacturing in comparison to the green manufacturing system. In contrast to green manufacturing where only the process is emission and hazard free, sustainable manufacturing encounters the green manufacturing process, satisfying the need of future generation by consuming lesser natural resources and contributing almost zero emissions to nature. Hence, sustainable manufacturing accounts the benefit of green manufacturing apart from minimum resource utilization. Although electromagnetic induction heating is a cleaner technology, the manufacturing processes developed by utilizing this heating method may not always be sustainable in nature. The factors like the minimum waste products by optimum utilization of resources, minimum energy, and water consumption, maximum utilization of renewable energy may not be feasible always to develop a sustainable process. Eastwood and Haapala (2015) indicate that the sustainability performance should contemplate economic, environmental, and social features concurrently and include the elements like manufacturing-associated expenditures, energy and material use, and manpower related medical issues. In general, the conservation of energy, energy efficiency, and energy waste of a process is the key measurement of sustainability. The induction heating is the most energy efficient and fast heating process as compared to other conventional systems. However, the sustainability of industrial process developed by induction system depends on how the heating process has been adopted according to the complexity of the manufacturing systems. Generally, the induction heating system fit to the existing production line with relatively ease and efficient way as compared to other heat source utilization.

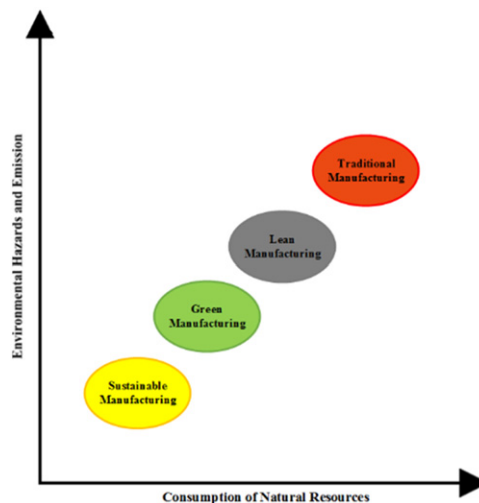


Fig. 1 Natural resource consumption and emission from different manufacturing ideologies.

Electromagnetic induction heating, a green technology is used for several material processing technologies like casting, forming, welding, heat treatment, curing and annealing of metallic materials and processing of non-metallic materials (Hong-ming, 2010; Yan *et al.*, 2010; Pappadà *et al.*, 2015; Smusz *et al.*, 2018). Induction heat treatment of shape memory alloy is one of such applications to provide the desired memory effects in alloys like nitinol. Nitinol is the most used alloy in the biomedical application and is used as stents during heart blockage (Haldar and Lagoudas, 2018). Also, in the aid of sustainability of conventional heating processes, the induction heating process is being used to improve the calorific value of lower rank coke and enhance their metallurgical properties too (Valia and Harrison, 1994). Biofuels are now being produced with the help of induction heating methods which is another step towards sustainable manufacturing. Napier grass is regarded as an exceptional non-forage green stock to produce energy as it grows fast and is a low nutritional demand bioresource with high yields of moisture-free matter. Bio-oil production from Napier grass through induction heating has been effective due to its non-emissive nature and fast process time (Lee *et al.*, 2010). Similarly, induction heating is used to convert food processing and industrial sewage into bio-oil separating them from polycyclic aromatic hydrocarbons which are a matter of environmental concern to contribute greenhouse pollutants. However, induction heating pyrolysis is an effective method to treat food and industrial sewage, and to obtain bio oil for future generations (Tsai, *et al.*, 2009a,b). Another sustainable application of induction heating is bio-gas reformation aided by wind energy. This is a process of reforming renewable energy using sustainable heating approach, which might be the best multi-technology approach to date. Fig. 2 describes a setup that transforms a mixture of biogas with some amount of carbon dioxide and inert gas to synthesize gas with the help of wind power and induction heating system via an energy storage medium. This system is fed with a mixture of methane and carbon dioxide which are major components of natural biogas with the addition of inert gas. The mixture is then induction heated through the reactor to provide fast heating that converts the natural biogas to synthesized gas having a higher heat value. With the use of the induction heating process, high and stable conversion rate was achieved as well as the qualitative value of the biogas which is an also renewable gas was enhanced. In effect, very quick response time, low carbon deposition and low inertia make the induction heating process a preferable choice over other methods (Pérez-Camacho *et al.*, 2015). Since thermalization is essential for all manufacturing and material processing techniques, induction heating process finds its use in a broad spectrum of application.

Sustainable manufacturing is also introduced at the forefront of an environmental issue such as cleaning up of existing pollutants and accordingly the material processing techniques has been developed. A novel thermal drying of sewage sludge (heat treatment) with the application of induction heating has been designed (Fig. 3). The sewage sludge is collected after mechanical dewatering with chemical treatment from the plant. Three iron media (as susceptors) i.e., electromagnetic induction net (EMI-N), electromagnetic induction fiber (EMI-F), and electromagnetic induction plate (EMI-P), respectively, are used in this process. EMI-F and EMI-N are mixed with the earlier treated sludge and EMI-P is used as a container to collect the fine layer of sludge in it. The electromagnetic induction heater is used to dry the sewage sludge for treatment. There is the rapid formation of cracks and sewage sludge shrinkage after moisture evaporation. This reflects the process capability of induction heating to clean up the sewage sludge for commercial application (Xue *et al.*, 2018).

In general, the conventional heating process is used in the casting process which is associated with environmental issues. In continuation of the application of induction heating for the development of casting technology of steel is more sustainable to its conventional counterparts. It provides fast heating rates which prevent oxidation with negligible emissions. Also, there is no product contamination as induction heating is a non-contact process (Hong-ming, 2010). Apart from the casting process, the use of induction heating for warm forming of stainless steel has been developed. The setup generates a heat flux of asymmetric pattern in the formable zone which leads to the variable temperature gradient. However, this asymmetric pattern may not always desirable for a sustainable warm forming process. The lack of use of magnetic flux concentrator is the sole reason for the cause. Further

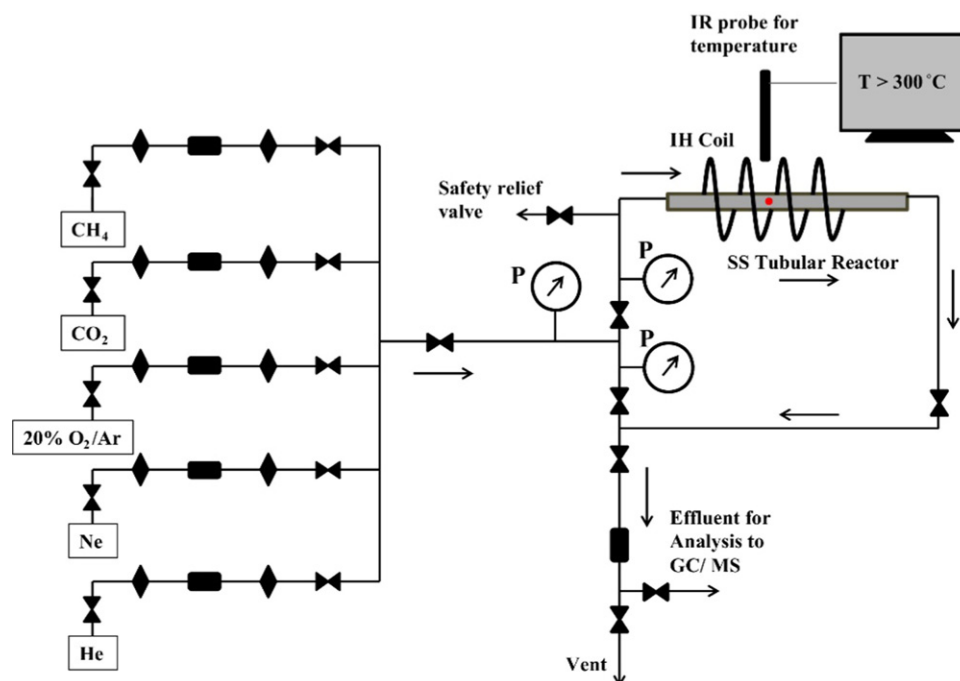


Fig. 2 Schematic setup of biogas enhancement by using wind energy and induction heating. Reproduced from Pérez-Camacho, M.N., Abu-Dahrieh, J., Rooney, D., Sun, K., 2015. Biogas reforming using renewable wind energy and induction heating, *Catalysis Today* 242 (Part A), 129–138.

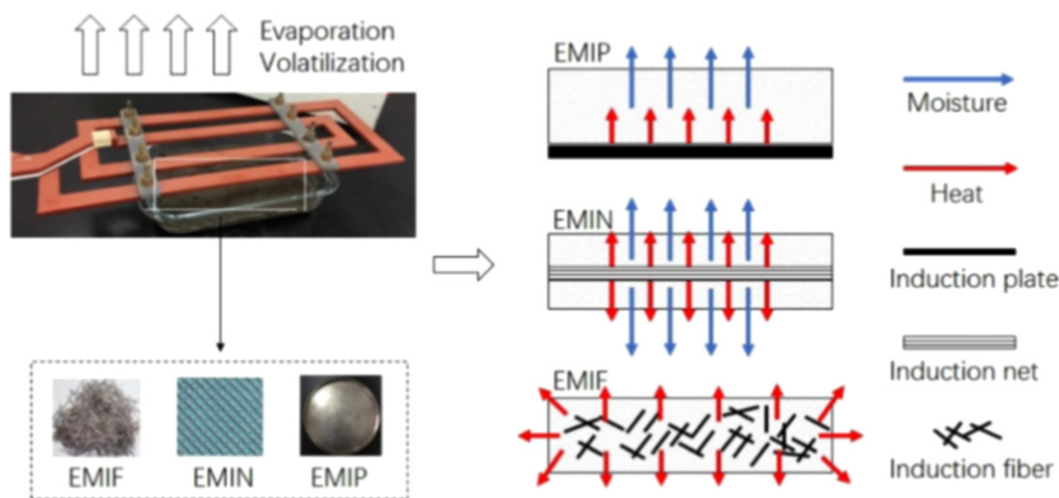


Fig. 3 Schematic of sewage sludge treatment by application of induction heating method. Reproduced from Xue, Y., *et al.*, 2018. Thermal treatment on sewage sludge by electromagnetic induction heating: Methodology and drying characterization. *Waste Management* 78, 917–928.

modification of setup with the use of latest magnetic flux concentrator would optimize the heating process and would lead to better quality of products (Smusz *et al.*, 2018). Further, induction heating has been used for hardness compensation, stress relieving or addition, and defect rectification (Babakri, 2010a,b; Paquet *et al.*, 2014; Eastwood and Haapala, 2015; Sorrija and Nascimento, 2017; Udhayakumar and Mani, 2017). While induction heating is a commonly used method for heat treatment in manufactured pipes and welded components, this method also gives great flexibility and advantage in welding applications involving other intricate shapes including the flat plate. Welding using induction heating is a great step towards sustainable manufacturing as it produces no smoke and emissions to the environment. Mostly, the induction coils used are circular in nature that is utilized to develop the joining of pipes extensively. The welding method is well set for various materials like high strength low alloy steel, structural reinforcement steel, corrosion resistant stainless steel, dissimilar combination of cemented carbide and alloy steel, but, there is no limitation on the quality and dimension of welding specimen as it all depends on the design of coil that can be manufactured according to the requirement (Wang *et al.*, 1999; Yan *et al.*, 2011; Huang *et al.*, 2013; Ju *et al.*, 2014;

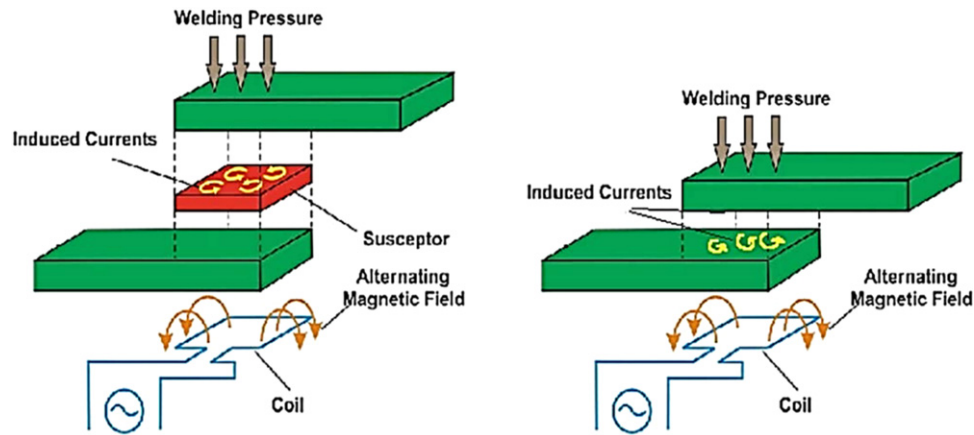


Fig. 4 Schematic for the application of induction heating in welding of non-conductive and conductive materials. Reproduced from Ahmed, T.J., Stavrov, D., Bersee, H.E.N., 2005. Induction welding of thermoplastic composites-an overview. *Composites Part A: Applied Science and Manufacturing* 36 (1), 39–54.

Udhayakumar and Mani, 2017). In principle, the induction heating requires the work part to be conductive. However, non-conductive or non-magnetic materials, non-metals, and composites are processed with the help of metallic susceptors that indirectly transfer the heat. Fabrication of composite panel, welding of the thermoplastic composite, aluminum-nitride-graphene composites, carbon-fiber reinforced thermoplastics are some of the focus areas in which induction heating has found its application towards the development of sustainable manufacturing of composites (Rudolf *et al.*, 2000; Pappadà *et al.*, 2015; Shon, 2017; Shon and Kim, 2017). Zeolites were also synthesized using the induction heating process without any environmental emissions. The mobile heating of accelerating ions takes the working temperature to crystalline temperature early and hence faster zeolite formation takes place in this case. Further extensive research is suggested to find out an optimal window for zeolite synthesis (Slangen *et al.*, 1997).

It is obvious that induction heating is applied in most of the material processing technologies starting from the production of bio-oils, sewage treatment to manufacturing and heat treatment processes. It is preferred where the application of thermal energy in a controlled rate is the primary requirement. This is an indirect boon as induction heating technology is relatively clean and do not contaminate the environment by emissions. However, the material processing technology using the induction heating may not utilize the resources in an optimum way or may not minimize the waste product. Hence, the present article investigates the application of induction heating in different manufacturing processes and how the sustainability of these processing technologies is evaluated. The principal, details methodology, and applications to different manufacturing processes are analyzed in subsequent sections.

Principle of Induction Heating

The basic elements of the induction heating system consist of frequency inverter, transformer, capacitor, induction coil, and the workpiece. The transformer is optional and utilized to adopt the required current and voltage that finally leads to generate the magnetic field. The capacitors may be a part of the inverter that helps to create the desired resonance frequency. When an alternating current pass through the induction coil, it creates a magnetic field around it. As the magnetic field passes through the workpiece, it generates eddy current in the workpiece material. The resistance of the metal fights against the flow of the eddy current which leads to the heating of the workpiece by the principle of Joule heating. If the work part is magnetic, then hysteresis loss provides additional heating until the Curie temperature of the working material after which only the Joule's heating is left with. Conductive and magnetic materials are directly heated through induction coil but heating of non-conductive and non-magnetic materials require special arrangements such as susceptors. Fig. 4 shows that secondary heat carrying material is designed to transfer the heat flux generated by the eddy current. The important process parameters are found to be coil geometry, magnetic flux concentrators (impeders), coupling distance, frequency, and inductor current. Also, some of the major effects associated with electromagnetic induction are skin effect, proximity effect, ring effect and edge effect (Ahmed *et al.*, 2005; Bayerl *et al.*, 2014).

Eddy Current Heating and Hysteresis Losses

From Faraday's Law, due to the varying alternating magnetic field of the coil induced currents called eddy current (also Foucault current) that flow against the electrical resistivity of the metal, contributes to heating of the elements. Eddy current flows through conducting material in closed circular loops, and in a plane that is perpendicular to the magnetic field. The measure of the eddy current in a particular loop is directly proportional to the strength of the magnetic field, the loop area, the rate of change of

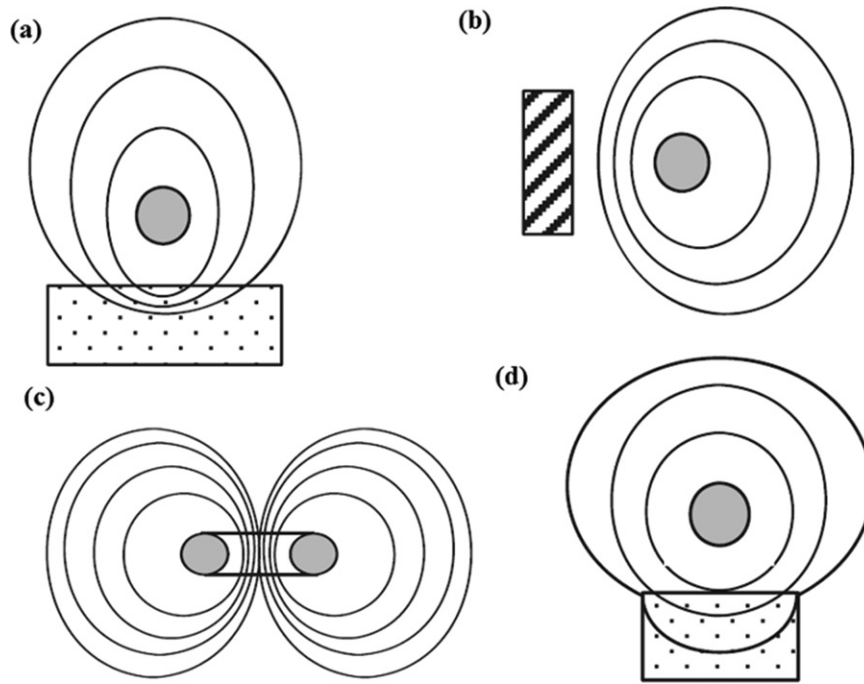


Fig. 5 Summary of EMI effect: (a) Skin effect (b) proximity effect (c) ring effect (d) edge effect. Reproduced from Bayerl, T., *et al.*, 2014. The heating of polymer composites by electromagnetic induction – A review. *Composites Part A: Applied Science and Manufacturing* 57 (2014) 27–40. Rapoport, E., Pleshivtseva, Y., 2007. *Optimal Control of Induction Heating Processes*. Boca Raton: CRC Press.

magnetic flux, and inversely proportional to the resistivity of the material. Lenz's law states that the magnetic field created by the eddy currents repels the source magnetic field that created it. Under the quasi-static condition, power lost (P) due to eddy current is calculated as

$$P = \frac{\pi^2 B_p^2 d^2 f^2}{6k\rho D} \quad (1)$$

where ρ is the resistivity of the material (ohm m), D is the density of the material (kg/m^3), f is the frequency (Hz or kHz), B_p is the peak magnetic field (T), k is the constant equal to 1 for a thin sheet and 2 for a thin wire, and d is the thickness of the sheet or diameter of the wire (m).

Hysteresis loss can be defined by the energy loss due to the reversal of magnetic dipoles when magnetic material come in the influence of alternating magnetic field. This energy loss in the form of heat is used in induction heating till Curie temperature is reached after which the material loses its magnetic property. It is proportional to the frequency of the alternating current that is used to generate the alternating magnetic field (Zinn and Semiatin, 1988; Cheremisinoff, 1996; Bayerl *et al.*, 2014). Under the quasi-static condition, the power loss due to electromagnetic hysteresis is estimated as

$$W_h = K_h f B_m^n \quad (2)$$

where K_h is the material hysteresis constant, B_m is the maximum flux density (Wb/m^2), n is the Steinmetz exponent (varies from 1.5 to 2.5 and it is 1.6 for iron). The total power loss due to eddy current heating and hysteresis loss is equivalent to net heat generated during the induction heating process. Further, due to an alternating magnetic and electric field, different types of consequence effects are observed which are explained in subsequent sections.

Effects Due to Electromagnetic Induction

Skin effect

When the frequency of the alternating current creating magnetic field is very high, the eddy current produced does not penetrate deep into the material and tend to flow on the surface. The amount of current flow reduces from the surface to the interior of the material irrespective of the dimension and nature of magnetic material. It is known as the skin effect and is depicted schematically in Fig. 5(a). This skin effect renders the quasi-static condition of eddy current loss and approximately 86% of power is concentrated on the surface or skin depth. The skin depth (δ) for a good conductor can be calculated as

$$\delta = \frac{1}{\sqrt{\pi f \mu \sigma}} \quad (3)$$

where σ is the electrical conductivity of the material (S/m), and μ is the magnetic permeability of the material (H/m). The depth at which the eddy current is 37% or $1/e$ in comparison with the surface value is called the skin depth and at this depth, the power density is $1/e^2$ or 14% of the surface power density. The current diminishes exponentially as

$$I_x = I_0 e^{-\frac{x}{\delta}} \quad (4)$$

where x is the depth from the surface (m), I_x is the current at depth x with respect to the surface (A), and I_0 is the current at the surface (A). The frequency is an important process parameter for controlling of skin depth and thus temperature rise in the edges. In high-frequency induction welding (HFIW), the skin effect results in the current flowing only on the material surface and edges to heat it to the melting temperature (Bayerl *et al.*, 2014).

Proximity effect

Eddy currents cause secondary magnetic fields around the path they are flowing. When two nearby work parts have induced eddy current and subsequent magnetic field, they tend to get attracted towards it, which is mainly beneficial in case of induction welding. This effect is known as the proximity effect. This further helps to increase the current density at the edges. Fig. 5(b) schematically describes the proximity effect.

Ring effect

This effect is mainly observed when circular coils are used. The magnetic field lines get concentrated in a circular path and leads to the heating of the coils. However, it is not a desirable phenomenon with any kind of applications and can be reduced by the use of magnetic flux concentrator or impeder at the target zone (Fig. 5(c)).

Edge effect

When there is a difference in magnetic permeability of the work parts that results in a change of electrical path and field lines, it is known as the edge effect. This results in an undesired heating pattern in the work part. Fig. 5(d) depicts the edge effect in induction heating.

Importance of Impeder

The objective of using an impeder is to focus the magnetic flux to the desired location. It is achieved by increasing impedance of the current path at the heating location, hence, concentrating more current at the heating zone. The efficiency of the use of impeder depends on impeder material, design, and placement. The impeder is desired to have maximum saturation flux density and amplitude permeability with negligible electromagnetic losses. The position of impeder around the heating zone is also extremely important. An impeder is most advantageous if used close to the desired heating zone (Ahmed *et al.*, 2005; Bayerl *et al.*, 2014). The analysis of the effect of impeder was also studied and few results like microstructure and the effect of process parameters have been reported.

Continuous efforts are going on to improve the fatigue life of induction welded micro-alloyed steel tubes. However, the process is interacted with several parameters like strip width, V-length, impeder diameter, heat input, and V-angle that affect the fatigue life. Optimal parameters lead to better quality of weld characteristics. When the welded tubes are heat treated at sub-critical temperature of 650°C or 700°C, there is significant improvement of fatigue life (Udhayakumar and Mani, 2017). During the welding of metallic tubes, the magnetic flux around the weld zone is concentrated by the use of impeder. It was observed that upon changing the impeder position with respect to the welding zone affects the temperature distribution. It is due to change in current concentration and focusing of the magnetic field around the weld zone and subsequent generation of heat. When the impeder is exactly positioned over the weld zone, better quality of the weld is obtained (Spahiu, 2007). A new magneto-dielectric (MD) material is proposed i.e., Fluxtrol for the impeder and a two-step heating process for the improvement in high-frequency welding is suggested. The positioning of impeder decides the passage of magnetic lines of force through the work part under or above which the impeder presents. The heat generation is concentrated over that region as shown in Fig. 6. Further, by use of Fluxtrol, there is no increase in carbon implying the good quality of weld with better microstructures as shown in Fig. 7 (Milicevic and Radakovic, 2006).

Coil Design

Induction heating coil design is an integral and basic need while thinking of the application of induction heating in any material processing and manufacturing process. The coils used in induction heating are generally made up of pure, oxygen-free copper those are brazed with cooling tubes to lower their electrical resistance. Eddy current generation by the varying magnetic field produced by work coils and subsequent heat generation is the base of induction heating mechanism. So, it has to be designed in such a way that the desired work area gets the required amount of heat. Depending upon that single turn, multi-turn, and pancake type, the design of the coils exists. Fig. 8 illustrates some commonly used induction heating coils. A single turn circular coil produces a magnetic field that is focused around its coil diameter and is mostly used for circular workpieces like pipe and rods to perform welding and heat treatment processes. In comparison with single turn coil, multi-turn coils provide more symmetrical heating zone. Pancake coils are used where flat surface heating is required and it provides good localization of heating. Further, hairpin coils are used where miniature work parts with localized heating are needed. On the other hand, split coils are used for

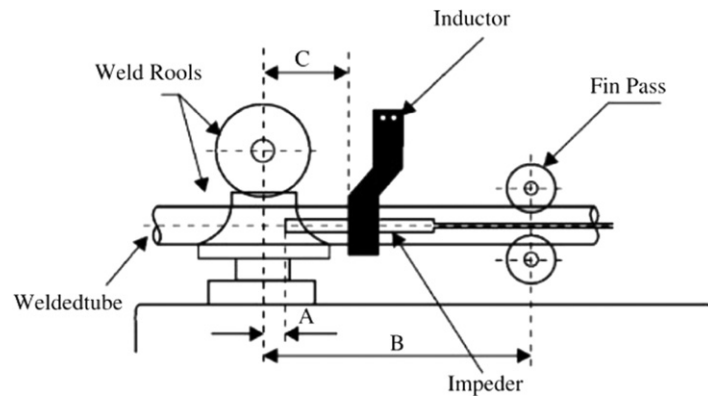


Fig. 6 Schematic of high-frequency induction welding with Fluxtrol impeder. Reproduced from Milicevic, M., Radakovic, Z., 2006. Quality improvement of steel pipes produced by seam welding with new magneto-dielectric impeder. *Materials Transactions* 47 (6), 1464–1468.

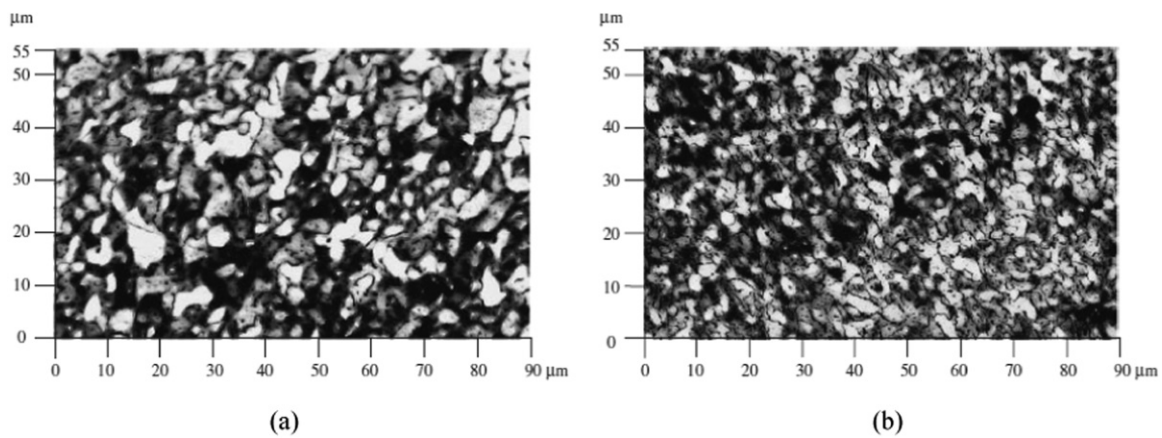


Fig. 7 Microstructure of the welded steel pipe produced using the (a) TDK and (b) Fluxtrol impeder. Reproduced from Milicevic, M., Radakovic, Z., 2006. Quality improvement of steel pipes produced by seam welding with new magneto-dielectric impeder. *Materials Transactions* 47 (6), 1464–1468.

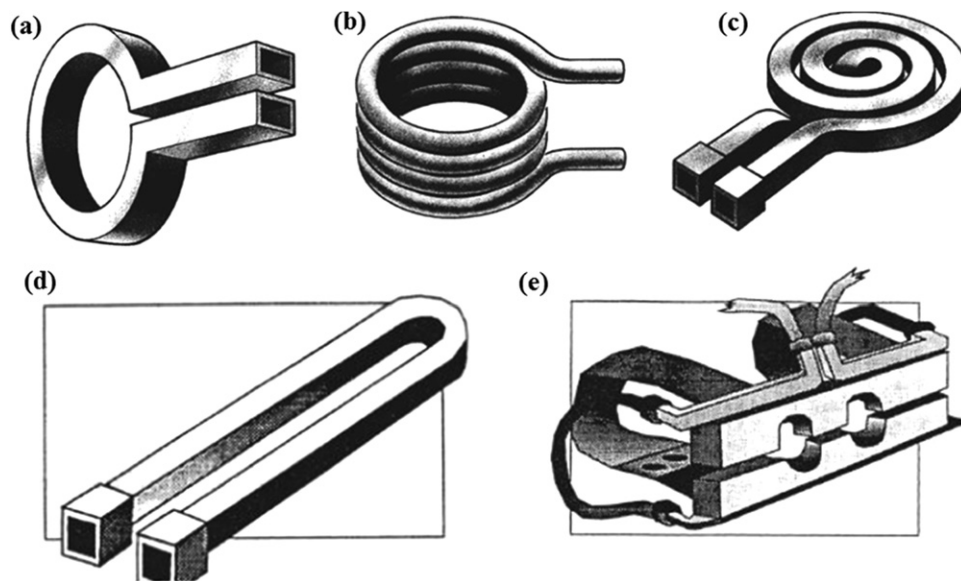


Fig. 8 Different induction work coils: (a) single turn; (b) multi-turn; (c) pancake; (d) hairpin; (e) split. Reproduced from Ahmed, T.J., Stavrov, D., Bersee, H.E.N., 2005. Induction welding of thermoplastic composites-an overview. *Composites Part A: Applied Science and Manufacturing* 36 (1), 39–54.

customized heating of work parts. It is thus obvious that depending upon the application and substrate geometry, the coils can be designed accordingly. The coil diameter, no of turns, the air gap between the coils also affect the generation of required magnetic flux and hence heat generation (Ahmed *et al.*, 2005). The magnetic flux (ϕ_β) generated by an induction coil is estimated by approximation of Ampere's law as

$$\phi_\beta = (\mu_0 I_C n) (\pi r_0^2) \quad (5)$$

where, r_0 is the mean radius of the coil turns, I_C is the coil current (A), μ_0 is the permeability constant $= 4\pi \times 10^{-7}$ (Wb/A m), and n is no of turns in the coil. Eq. (5) indicates the flux generated from an induction coil without the use of any impeder. The variation of the magnetic flux generated or the heat flux generated with respect to coil current, no of turns of coil, and the coil radius can be derived from this equation.

Current Research and Applications of Induction Heating

Heat source at different intensity has been the essential component of material processing technologies since the beginning of the manufacturing industry i.e., from casting to heat treatment. In recent times, sustainable manufacturing and processing is a prime concern to the industry and hence the utilization of induction heating is an opportunity to develop a sustainable process. Induction heating is a non-contact process with least impact on the environment and hence, is preferred over the rest of the available sources. The heating through induction heating is mainly through eddy current by Joule's heating and magnetic hysteresis loss till the Curie temperature. Since polymers are non-conductive, it is heated through a susceptor and the heating is affected by its properties like Curie temperature, density, heat capacity, magnetic and electrical property. Broadly, induction heating applications are categorized in two groups depending upon the frequency in used i.e., high and low frequency. Lower frequency applications include casting, forming, waster treatments etc., where entire substrate heating is required and higher frequency is used where a localized heating is needed like welding, localized stress relieving etc. This difference is due to the effect of skin depth achieved during the process (depicted by Eq. (3)). Lower frequency leads to higher skin depth and consequently promotes in-depth penetration. The induction welding operation can be carried out in two modes of i.e., thermal mode and electric power mode. When the skin depth is larger than thermal depth, the welding is performed under electric power mode and the opposite is termed as a thermal mode. Lowest welding power requirement, narrowest HAZ and least sensitivity to process parameters are observed in a thermal mode in comparison with electric power mode (Scott, 1999).

Thus, the induction heating process has taken a shift to industries in recent times due to increasing demand of sustainable manufacturing process and government regulations. A wide variety of applications of induction heating for various material processing operations like casting, welding, production of bio-oils, heat treatment operations, manufacturing of polymers and composites has been explored in this section. The induction heating application has intruded into so many areas that it now becomes an emerging sustainable heat source and the researchers are exploring the benefits out of it.

Welding

Induction welding is advantageous over arc welding processes as it is a non-contact and environment-friendly process. The heat is produced within the part itself and the efficiency of the heat transfer rate is relatively high (~60%). High quality and stress-free welds are produced without the use of filler material. There is no need for surface treatment before the start of welding process. Since there is internal heat generation inside the work part that distributes over the volume, there is not much thermal stress developed within the processed zone. Still, there is some issue with welding using induction heating. There may be decarburizing in the weld zone of the part produced and cost involved in developing and optimizing the work coil, and the design of fixture (Wright, 1999; Rudnev *et al.*, 2003; Frogner *et al.*, 2011; Lucía *et al.*, 2014; He *et al.*, 2017; Troughton, 2017). Till date the focus has been preoccupied mostly with welding of seamless steel line pipes but, the welding of high strength low alloy steel, structural reinforcement steel, stainless steel, dissimilar welding of cemented carbide, alloy steel has also been performed. There is a no restriction on size and shape of welding as it all depends on the custom coil geometry according to the dimension of work material (Wang *et al.*, 1999; Huang *et al.*, 2013; Ju *et al.*, 2014; Udhayakumar and Mani, 2017).

In comparison with the arc welding process, the induction welded specimens were found to have better metallurgical properties. In welding of reinforcement steel, there is an increase in hardness in welded areas is approximately 30% by induction heating as compared to arc welding. Even, the hardness values increases from 80 to 115 HBN if welding duration is increased from 2 to 5 min (Sari, 2016). Further, induction welding of dual phase steel shows that heating rates to be significantly different before and after the Curie temperature. However, a complete coalescence of the welding surface was achieved with minor hardening. This concludes that high-frequency welding has potential for joining of coils in steel processing lines (Baumer and Adonyi, 2009). Stainless steel wires were also welded using a frequency of 2 MHz with argon shielding gas. Fig. 9 illustrates the schematic setup for induction welding of steel wire. Inside a quartz tube, the welding operation has been carried out with the inert gas atmosphere. Infrared pyrometer was used to record the temperature. Steel wire was welded after aligning inside the induction coil. Tensile strengths of the joints were found to be superior at higher welding temperature (1050°C) in comparison with lower temperature (1030°C). Small holding time or lower heating temperature resulted in lower ferrite formation and vice versa. Higher temperature or longer holding time resulted in a reduction in the cooling rate and hence higher ferrite count was observed (Huang *et al.*, 2013). Apart from welding of steels, the welding of dissimilar

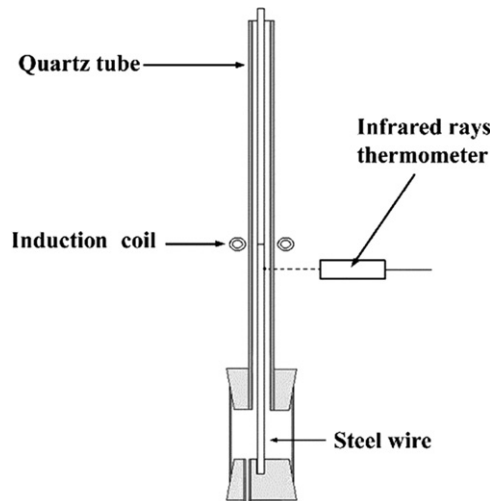


Fig. 9 Schematic of induction welding setup for steel wire. Reproduced from Huang, C.-Y., *et al.*, 2013. Rapid welding of stainless steel wires using ultra-high frequency induction heating. *Journal of the Chinese Institute of Engineers* 36 (6), 806–809.

cemented carbide and alloy steel using brazing filler metal (Cu-Zn-Ni-Mn alloy) has also been reported. It was found that the heating and cooling rates affect the residual stress largely. The residual stress influenced by cooling rate in cemented carbide was more sensitive than steel (Ju *et al.*, 2014). With decrease in heating rate, the residual stress reduces in material and a big drop is observed at higher range of heating rate than lower range. In induction welding of iron-based powder-metal bearing, the joining surface area increases with processing time whereas the hardness decreases with processing time. The grain growth occurs at the welded zone and a coarse grain structure imparts low hardness value. With decrease in processing time, the hardness values of the bearings increase from 50 BHN to 62 BHN. The bending strength and tensile strength values are also higher than the base material (Çavdar and Gülşahin, 2014; Çavdar and Kusoglu, 2014; Sari, 2016). During induction welding of pipes, hydrogen induced cracking (HIC) is sometimes developed due to the influence of residual stress. Cold forming of the steel rolls before the welding process is the main reason for the developed residual stress which has a negative influence on the resistance of pipes. It was inferred that both longitudinal and circumferential stresses have no negative influence on the welding of pipes through induction heating. Apparently, with the help of the residual stress HIC damage can be minimized (Gungor *et al.*, 2010).

The analysis of the process parameters in finding out an optimal window for defect-free welding is also significant in reference to the process repeatability and precision welding. The application of induction heating is a boon in the field of welding as most of the conventional heat sources contribute to environmental hazard as well as pollution. Secondly, this is a non-contact process hence chances of weld contamination by secondary elements is less. Thirdly, the process produces defect-free, stress and distortion free welds with narrow heat affected zone. Still, there is a need to design appropriate coil according to requirement and its positioning. Proper design of fixture, selection of inert gas shielding, use of magnetic flux concentrator for optimizing the heating zone may result in improved product quality, lesser use of natural resources and reduction in environmental contamination.

Heat Treatment

The application of induction heating in heat treatment processes is an important tool as it can reach out in mobile locations by custom coil. Heat treatment by induction heating is being carried out by industries for seeking out sustainable manufacturing processes (Eastwood and Haapala, 2015). The heat treatment processes are generally used for stress and hardness compensation those are either generated due to conventional heating process or by use of induction heating process. The heat treatment of micro-alloyed steel pipe has been conducted to relieve the residual stresses developed during the welding. Fig. 10 illustrates the schematic of the induction heat treatment setup. The setup constitutes of induction coil, water cooling system to keep the coil at room temperature, argon gas shielding to prevent oxidation and the required control unit (Çöl and Yilmaz, 2006). Often, in a welded structure, a predetermined amount of tensile surface residual stress is introduced for enhancement of fatigue life. In high strength low alloy steel, after 50,000 cycles which correspond to its half-life, compressive residual stress was found on the specimen surface (Paquet *et al.*, 2014). In post weld heat treatment of micro-alloyed steel tubes, optimal selection of process parameters like V-angle, V-length, strip width, impeder diameter, and heat input leads to better mechanical properties and also enhance the fatigue life (Udhayakumar and Mani, 2017). However, the analysis shows that the weld line acts as a stress enhancer and hence reduces the fatigue resistance (Sorrija and Nascimento, 2017).

Studies on the failure of the induction welded pipes in the flattening test reflect that there are two major defects i.e., the cold defect and the penetrator defect, where the former is due to lack of power and the latter is due to excessive power. Oxidation of the weld zone is one of the factors for flattening failure of the welded pipes. Post weld heat treatment to normalize the welded pipe at austenitic temperature is suggested for the improvement (Babakri, 2010a,b). It reduces the residual stress and brings uniformity in hardness

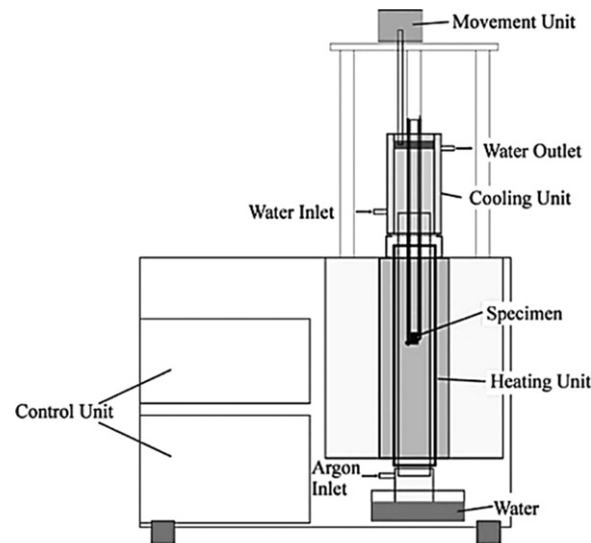


Fig. 10 Schematic of induction heating treatment setup. Reproduced from Göl, M., Yilmaz, M., 2006. The determination of heat treatment parameters of X52 micro alloyed steel after high-frequency induction welding. *Materials and Design* 27 (6), 507–512.

distribution at the welded structure. Weld joints of steel are found to be associated with inclusions of manganese and silicon oxides as well as aluminum and calcium-rich oxides. The heat treatment was unable to affect any inclusion. However, grain structure was found to be coarser than base material after heat treatment (Yan *et al.*, 2010a,b, 2011). Extensive research has been carried out for process improvement and defect rectification during heat treatment by induction heating system. There are issues associated with an uneven distribution of hardness and residual stresses in a welded structure. Generally, heat treatment is carried out to neutralize these effects. In the case of micro-alloyed HSLA steel, it has been found that due to their homogeneous microstructure the mechanical properties of the base, HAZ and weld zones are similar. It is concluded that Nb-micro-alloying restricts ferritic grain growth and provides strength to the ferrite by precipitate hardening during the heat treatment process (Tazedakis *et al.*, 2010).

It is obvious that most of the welded structure is associated with uneven distribution of residual stress that essentially reduces the fatigue life of the specimen. The effectiveness of heat treatment process releases the residual stress at a certain extent and may bring uniformity in hardness distribution in the weld zone. However, the speed of heat treatment process affects the weld quality. If the heat treatment speed is too low, then coarse grains are formed. At high heat treatment speeds, there are chances of incomplete process and decarburization of the weld zone may lead to the presence of residual stresses at high pace. In general, the induction heating process finds its application in the heat treatment process due to its localized application with low intensity, and fast heating process. The use of induction heating on the heat treatment process for different types of materials is ever increasing owing to minimum impact on the environment and to produce a cleaner and sustainable technology. However, the optimal selection of parameters like heat treatment speed, frequency, and coil design has a desirable impact on the effective and sustainable process.

Processing of Non-Conductive Materials

Induction heating also plays an important role in the development of a sustainable manufacturing process for non-conductive materials like thermoplastics, fiber-reinforced composites etc. Heating of non-conductive and non-magnetic materials require special attention as susceptors or secondary heat carrying material that has to be designed to transfer the heat flux generated by eddy current (Bayerl *et al.*, 2014). In the recent scenario, composites are being used due to their light weight and good metallurgical and mechanical properties and cost-effectiveness in comparison to their metallic counterparts. Electromagnetic heating of thermoplastics readily produces reliable seals on the substrate material. The process adapts for deformation and distortion in the parts as voids are filled by the material flow. Since the surfaces are resin-starved they are filled without any effort. Hence, induction welding is precise and distortion free and its rejection rate is very low (Sanders, 1987). Carbon-fiber reinforced thermoplastics were fabricated using the induction heating process. The important process parameters that affect the quality of the product are the distance between induction coil and laminate, electromagnetic frequency, coil geometry, laminate lay-up, and generator power. Heat is only generated when closed fiber loops exist through which current can flow. Eddy current flowing through the carbon fiber laminate results in Joule's heating (Rudolf *et al.*, 2000). Thermoplastic matrix composite and polyphenylene sulfide (PPS) reinforced with carbon fibers were used to fabricate a composite stiffened panel by the application of induction heating. The setup consists (Fig. 11) of a single turn induction coil, compacting cylinder and cooling nozzle. The induction coil is used to heat and melt the composite and then compacting cylinder is rolled along with the cooling nozzle to solidify the sintered matrix composite. Infrared pyrometer was used to record the working temperature of the process (Pappadà *et al.*, 2015).

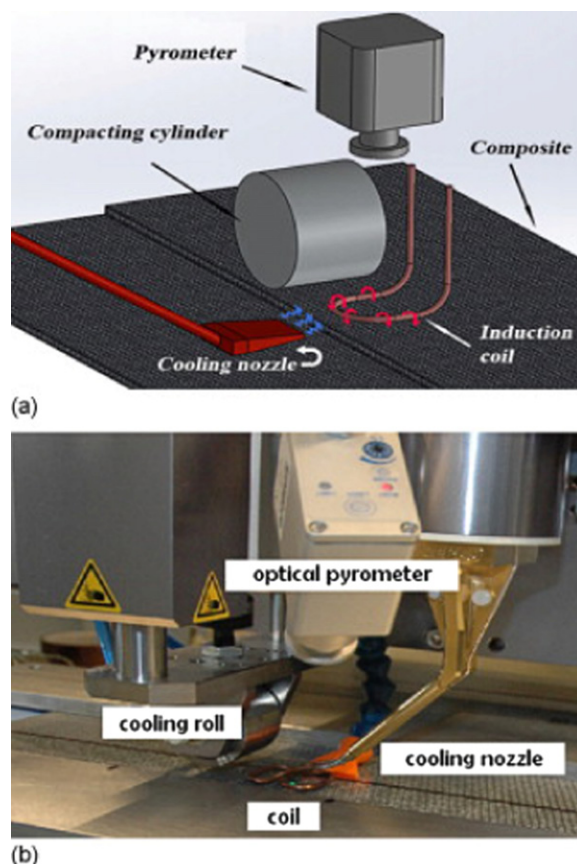


Fig. 11 (a) Schematic of the induction welding setup; (b) Induction welding setup. Reproduced from Pappadà, S., *et al.*, 2015. Fabrication of a thermoplastic matrix composite stiffened panel by induction welding. *Aerospace Science and Technology* 43, 314–320.

Not only in the fabrication of composites, the curing and density modification of composites through induction heating have also been achieved. From mechanically activated powders (i.e., a mixture of Ti and Al_4C_3), nano-powders of Al-TiC were produced by induction assisted high energy ball-milling. The relative density of the composites was found to be 99.5%. It was observed that the fracture toughness of TiC gets enhanced by the addition of Al (Shon, 2017; Shon and Kim, 2017). The induction welding of thermoplastic composite (TPC) and hybrid material (metal to composite) has been reported. The process parameters that were found to affect the welding characteristics are coil current, frequency, and electrical conductivity of the material (Wan *et al.*, 2014). The high-frequency induction heating was used for sintering of nanostructured CoTi-3ZrO_2 composites. The sintering was done under 80 MPa pressure for the 60 s. Up to 98% density achieved by the use of this process and the process was very fast and effective in comparison to conventional processes. Its hardness value was improved due to grain refinement. Fracture toughness can be improved with the addition of Co-Ti in the composite (Shon, 2016). Nanostructured aluminum nitride-graphene composites were manufactured by high-speed ball milling process and then induction sintered to enhance its mechanical properties. Nearly full density composites were achieved within 120 s of induction sintering of the composites. It was found that the addition of graphene improves the hardness and fracture toughness due to grain refinement (Shon, 2017; Shon and Kim, 2017). In an induction welding process, carbon fiber reinforced polyphenylene sulfide laminates were fabricated. It was observed that due to skin effect, the heat energy distribution mostly concentrated at the surface and later travelled through the plate in the thickness direction. This could lead to deconsolidation and thermal damages. When the carbon-fiber reinforced laminates were induction heated, the laminate thickness was found to be smaller than the penetration depth, (Hümbert, 2014).

The induction heating method has been used for various kind of material processing of non-conductive and non-magnetic materials by the virtue of susceptors. Thus, susceptor design and fabrication is a challenge in this case. Different kind of products starting from composite panels, thermoplastics etc., are manufactured using this process. Still, further exploration of the optimal use of this process will lead us to a sustainable technology for non-conductive material.

Other Applications of Induction Heating

Induction heating finds its application for the development of many trivial material processing technologies like pyrolysis of rice straw, coconut shell, and sugarcane bagasse, synthesis of thermo-responsive fluids, extraction of pectic etc., due to its high heating

rate and non-contamination features. Also, higher yielding and controlled heating help in optimizing the manufacturing process (Schmidt, 2005; Tsai *et al.*, 2006; Idakiev *et al.*, 2015; Zouambia *et al.*, 2017).

Manufacturing of Silicon-Carbide nanowires of range 8–20 nm was carried out by high-frequency induction heating of SiO and activated carbon fibers without the use of any catalyst. Validated morphologies display the quality of nanowires at par with conventionally manufactured nanowires (Zhou *et al.*, 2006). Similarly, single-walled carbon nanotubes ranging from 0.8 to 1 nm and lengths up to 10 μm were synthesized by application of high-frequency induction heating. The fast heating rate through induction helps in preventing the formation of the additional graphitic layer (Li *et al.*, 2008). Further, Fe-Cr nanocrystalline alloy wires are induction heated. The mean temperature of a capillary bath increases on the application of induction heating due to losses incurred by eddy current and hysteresis effect. It is evident that Joule's heating due to eddy current is dominant since at Curie temperature material losses its magnetic property and hysteresis loss ceases out (Gómez-Polo *et al.*, 2012).

Hascoët *et al.* (2018) presented the consumable wire deposition using induction heating to develop additive manufacturing system. This approach by inductive heating controls the temperature gradient between the tip of the wire and the deposited layer. It increases the effective utilization of heat energy as well as the control of metal transfer in a wire-based additive manufacturing technology. Similarly, induction heating has been used for depositing metallic materials with high melting point onto their substrate by a drop-on-demand deposition system at low thermal input. The Inconel 625 metallic wire was melted at 1623 K and deposited on the substrate of same metal successfully. It has been found that the disposition temperature is directly proportional to the current frequency and density (Sun *et al.*, 2019). Catalytic chemical vapor deposition method was assisted by induction heating process in lieu of heating furnace to produce carbon nanostructures. The comparison on the basis of the rate of production of nanofibers with use of conventional furnace and induction assisted furnace was reported. The energy consumption with the help of induction heating was found to be 2–3 times lower than generally used the furnace and with better morphology (Lupu *et al.*, 2004).

The comprehensive literature survey indicates that induction heating has reached almost all kind of manufacturing and material processing techniques starting from high melting point casting to low-temperature sewage waste treatment. It is evident that induction heating has substantial advantages being sustainable in nature to produce a clean technology and act as a flexible heating technique to suit a variety of material processing technologies. Over the days, its application is increasing tremendously. However, there are challenges to use this clean heating technique for the development of manufacturing processes.

Challenges With Induction Heating

With flexibility in the system, ease of handling, wide range of applications of induction heating, and its sustainability, there are some minor points of concern in actual industrial practice. The requirement for custom-built coil for an individual application, the high cost of equipment, the design of susceptor for nonconductive specimen, necessity of skilled labors and material compatibility are some of the issues that need immediate attention. Still the process being sustainable in nature, its demand is ever increasing and widening its application range over day by day. Since it is a non-contact process and the heating pattern is based on the generation of magnetic field and eddy current distribution on the work part, the design of induction coil is a challenge to enhance the thermal efficiency. In certain applications, the localized heating is important whereas throughout heating over a large volume are significant in some cases (Bayerl *et al.*, 2014). Although induction is a cost-effective method, a number of limitations are associated with conventional induction heating technology. Provision for water cooling system of the coils brings additional cost and complexity of the system. The magnetic field may create health hazards for open coil system without any shielding option. Uniform heating over a large area is difficult to obtain with the conventional system (Frogner *et al.*, 2011). The analysis was carried out using induction heating of an injection mold using the single-layered, double layered and triple layered coil. The single layer coil produces asymmetric magnetic field and hence the heating pattern is non-uniform, whereas multi-layered is found to be in better correlation for practical use with symmetric field and symmetric temperature profile in comparison to the single and triple layered induction coil (Huang and Huang, 2010). The coil design is an important aspect for a crystal growth system like high melting oxide Czochralski system. The alignment of the crucible and the coil is utmost important and dependent on their dimension, placement, and orientation to each other. The proper choices of coil type and design are significant for large and moderate growth rate system to develop advanced technology (Tavakoli *et al.*, 2009). Further, in induction heating, non-uniformity in temperature distribution is found due to coil movement which has electrical, magnetic as well as thermal linkage to the work part. The identification of hard (high-temperature gradient) and soft spot (low-temperature gradient) is important in this case. There is a large temperature gradient in the gear ring when the coil traverse speed is slow. At optimum condition, the temperature non-uniformity should be reduced to get precise results (Wen and Han, 2017).

At the initial phase, there were material limitations as only conductive and magnetic material was able to meet induction heated. Now, susceptors help in induction heating of work parts which are non-conductive and non-magnetic. It requires to customize the coil design and susceptors to be manufactured for the development of the process (Bayerl *et al.*, 2014). When there is a requirement of lower heating rate, low Curie-point magnetic materials are alloyed in the work part as the magnetization decreases with an increasing percentage of rare earth metals (Samarium, Gadolinium, Dysprosium, Yttrium) and Al with Curie point in the range of 100–300°C (Todaka *et al.*, 2008). In comparison to traditional oven curing of adhesive, induction heating of adhesives with iron particles as susceptor creates a faster process. But, there was a maximum drop of 15% shear strength using internal susceptor curing whereas it was 6% in external susceptor curing (Severijns *et al.*, 2017). Therefore, the computational model of the induction process is the most convenient way to define the thermal field and magnetic field. However, the cost of

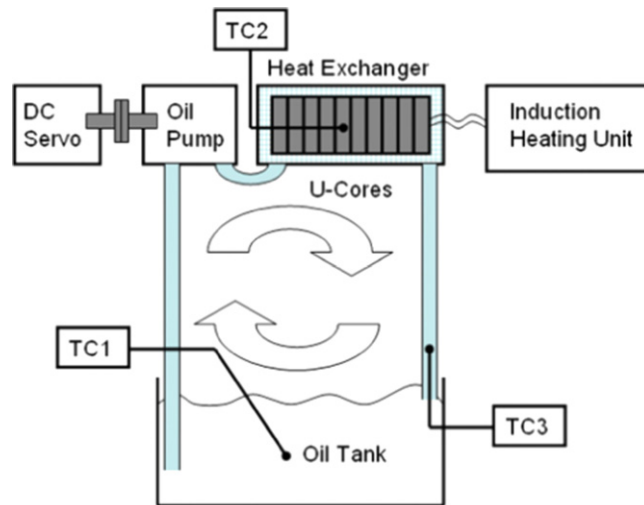


Fig. 12 Schematic of the cooling system by lubricant oil in induction heating process. Reproduced from Kucukkomurler, A., Selver, R., 2012. A preliminary experimental assessment of the utility of magnetic oil for incrementally improving the energy efficiency of an induction heating system. *Journal of Thermal Science and Engineering Applications* 4 (3), p. 035001.

computational time and integration of the subsystems is the major challenge. In most of the cases, the computational design of an induction coil for the required application helps to fabricate the coil (Sun *et al.*, 2013; Nian *et al.*, 2014; Khodamoradi *et al.*, 2015; Lee *et al.*, 2016; Drobenko *et al.*, 2017).

The optimization of heating time, temperature profile, and localized heating of sprockets have been performed using both circular coil and profile coil in induction heating process. Profile coil accomplished higher heating rate and accurate localized heating with lower heating time due to the localization of magnetic flux and corresponding heat generation at that location. Hence, custom made coil is evident to have better efficiency than commercially available general purpose coil (Han *et al.*, 2016). In induction heating process, reduction of thermal losses due to radiation and convection is an important concern as the effective heat transfer is till now 60% and there is a scope of achieving higher heat transfer efficiency. This can be achieved by using proper shielding and design of enclosures so that the heat loss is trapped and utilized (Park and Dang, 2013). The cost of insulation is not high but the design and implementation of it take a major toll to the engineers. It infers that the energy production may be costly, but proper utilization and conservation of produced energy is an important aspect of sustainable manufacturing process.

With several other limitations and challenges for the induction heating system, the sustainability of the process is aided by improving the process efficiency. In most of the cases, the thermal efficiency of induction heating is around 60%. In general, water is used for the cooling of the induction coil. An attempt has been made to use magnetic oil for the cooling purpose in the electro-magnetic heating application as shown in schematically by Fig. 12. The oil pump is used to pump the magnetic oil into the coil and being circulated throughout the process. The objective was to develop a low-cost method to enhance the energy efficiency. The attempt, however, reflects no substantial improvement in the efficiency of the system (Kucukkomurler and Selver, 2012). One of the limitations of induction heating is to produce a uniform temperature of the thin workpiece which is even difficult to achieve using other methods. Use of multiple induction coils has the potential for spatial control of heat generation and permits uniform temperature distribution (Frognier *et al.*, 2011). The zone control induction heating (ZCIH) maintains the same current phase angle at a selective combination of frequencies to prevent interaction. In traveling wave induction heating (TWIH), the combination of frequency and phase shift may produce very high efficiency and uniform heating. The efficiency of utmost 93% can be achieved by using anti-parallel or series connection of inductors with uniform temperature distribution. It is thus obvious that research is going on for improving the effectiveness of the induction heating process by improved coil design, use of multiple coils, proper design of magnetic flux concentrator, improving the efficiency of the heating system, and integrated system design. All these factors are related to the sustainability issue of the process which is in the preliminary stage and needs to investigate from various aspects.

Conclusion and Future Scope

The literature review projects that heat source are essential for a manufacturing unit, but is usually associated with environmental pollution and health hazard due to emissions as a byproduct. Finding a sustainable heat source is a feasible solution to suppress harmful byproducts. The application of industrial heating for different manufacturing processes like welding, heat treatment, brazing, hardening, bonding, sintering, sealing, soldering, drying, curing, degassing, etc., are obvious from literature. Many of these processes are developed using fossil fuel and some of the operations are performed using induction heating. A comprehensive study on the application of induction heating in sustainable material processing and manufacturing technologies has been carried out and the significant features are highlighted. Apart from energy savings, the elite advantages of induction heating are the

reduction of total heating time, positioning to the desired location, and substantial reduction in decarburization, scaling, and unwanted structural changes. Induction heating is also an environmentally friendly process with almost zero emission to the environment. The non-contact process of heating works with the help of eddy current and magnetic hysteresis losses in the work part. Hence, induction heating is being adapted widely ranging from synthesis of chemicals, sewage treatment, production of bio-oils and manufacturing of nanotubes to conventional manufacturing processes like welding, heat treatment etc. The shortcomings of conventional heating methods like slow heating rate, production of emissions, and contamination to parent material are successfully addressed by the induction heating method. The flexibility in coil design and accordingly the controlling of the heating rate makes it possible to apply locally to perform hardening, grain refinement, complete melting like casting and even in wire additive manufacturing process. Frequency selection is an important aspect to alleviate the skin effect. Lower frequency tends to penetrate deep into the material and higher frequency eddy current tend to stay on the surface. In general, the application of induction heating is ever increasing due to the least environmental impact and sustainability aspect as well as a faster process with well-controlled heat affected zone. With proper design of coil and fixture, induction can be applied in a variety of fields where the conventional heating process has limitations. The geometric configuration of multiple coil arrangements and the amplitude and phase shift of applied current may bring a uniform heating pattern which can satisfy a particular need of manufacturing process. Furthermore, magnetic field shaping and obtaining of a temperature profile of desired pattern using shielding and flux concentrator has been given special attention. However, reducing the size of the setup as well as a reduction in radiation and convective losses is a challenging issue. A continuous effort to improve the system performance is going on. Still, there is a huge scope of applying the induction heating in trivial manufacturing and material processing sectors.

See also: New Educational Models to Train Engineers and Executives On Eco Friendly Technologies, Products and Sustainability Policies

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Investigation of the Fuel Value of Selected Wood Samples Using Artificial Neural Networks

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Introduction

The world's primary source of energy is fossil fuel, which is nonrenewable in nature and rapidly diminishing. Therefore, researchers are exploring renewable energy sources. Wood and its by-products, which have been used as fuel sources by humans for thousands of years, are receiving more attention in the research domain because they are good, renewable energy sources. In addition, caloric values of biomass such as agriculture and forest residues are being investigated throughout the world.

MacFarlane [1] investigated the urban wood and wood waste of 13 counties in Michigan for energy production. The results suggested that urban trees and wood waste offer a modest amount of biomass that could contribute significantly more to regional and national bio-economies than previously. Caloric values of pine residues that originated from cuts and forestry tasks were studied and measured using a static bomb calorimeter in an oxygen atmosphere [2]. In addition, the effects of the grinder configuration, wood-cutting bit type, and the wood-particle filtering screen size on bulk density and fuel consumption when processing forest harvest residues for energy purposes have been analyzed [3]. The results showed that the fuel consumption was only affected by filter screen size when processing the size class comprising branches and tops.

Sheng and Azevedo [4] proposed a new correlation between the higher heating value and dry ash content of biomass in weight percent using data available from the literature. Wood and Rowley [5] studied the feasibility of a number of biomass-fueled community housing project systems when operated in the context of community housing/mixed use. Six systems comprising differing technologies have been analyzed with the assumption that the systems operate within an energy services company (ESCO) supply scenario. The results have indicated that within specific realistic ESCO operating scenarios, the combined heat and power (CHP) of biomass can demonstrate positive net present values without the need for capital subsidies.

Fifty-two facilities in British Columbia, Canada, were surveyed to gather statistics regarding the rates of fiber use for energy, thermal and electrical energy capacity, and net production [6]. In that research, it was estimated that from 2000 to 2011, an average of 9.4 metric tons (Mt) of wood fiber (oven-dried), or approximately one-third of the total harvested biomass, were used annually to produce energy. Based on the results, it was concluded that wood-based bio-energy supplied approximately 10% of British Columbia's energy demands in 2011. Everard *et al.* [7] studied the accuracy of visible and near-infrared spectroscopy in conjunction with chemometrics to predict gross caloric values of some bio-energy crops. Kumar *et al.* [8] analyzed the fuel wood characteristics of 26 trees, including shrub species, from the dry deciduous forest in the Aravally region of Rajasthan, India. In this work, the fuel wood value index was determined based on the properties of caloric value, wood density, and ash.

Munalula and Meincken [9] investigated six types of fuel woods commonly used in the western cape of South Africa with regard to their caloric values and environmental impacts when burned. Properties such as density, ash content, and elemental composition were determined and related to the caloric value. It was demonstrated that the wood with the highest caloric value was not necessarily the best option as fuel wood if environmental factors were taken into account. Telmo and Lousada [10] determined the caloric values of wood pellets from different wood species using a Parr 6300 bomb calorimeter. They proposed a correlation between the lower heating value and the moisture content of the wood pellets.

In this work, the functional correlation between caloric value and wood properties was derived based on the experimental values. An ANN model was also used to estimate the caloric values for different wood samples.

Experimental Measurement

An Autobomb calorimeter and the Standard Test Method for Heat of Combustion outlined in ASTM D240 were used to determine the caloric value of the wood samples. The reference data regarding the wood density were collected from the literature available from the Forestry Department of the Government of Brunei Darussalam [11]. The ash content was determined according to the Technical Association of the Pulp and Paper Industry (TAPPI) standard T 211 om-85 [12]. During the experiment, a total of 16 wood samples were used. First, nine samples were collected from the Brunei tropical forest [13,14], and the other seven samples were collected from Indian firewood [15]. These wood samples were weighed before they were placed in a furnace at 575°C for 4 h.

The samples were weighed in a tin capsule and combusted in a furnace at 11,500°C. Then, a conductivity detector was used to measure the evolved gas and to determine the composition. In this study, the wood density, caloric value, carbon content, nitrogen content, sulfur content, and ash content were determined. The botanical names and the measured properties of different wood samples are shown in Table 1.

Results and Discussion

Functional Relationship

To derive a functional relationship between the caloric values of different wood samples and the corresponding wood density values, two steps were used. During the first step (Table 1), the measured caloric values were plotted as a series of data points for each of the corresponding wood density values, as shown in Fig. 1.

During the second step, the curve fitting process was performed to construct the curve (solid line in Fig. 1) that provided the best fit for the series of data points plotted previously. Based on the curve fitting results, the relationship between the wood density (ρ) and the caloric value (cv) with a maximum determination of coefficient of 61.92% was found to be:

$$cv = -7e^{-7}\rho^3 + 0.0016\rho^2 - 1.1486\rho + 282.72 \quad (1)$$

Fig. 1 shows that the caloric values decrease sharply with the increase in density from 400 to approximately 600 kg/m³. Between 600 and 900 kg/m³, an increasing trend in the caloric values is observed, and again the caloric value decreases beyond this density point. Therefore, it is necessary to further investigate the other components of combusted wood. Using the same two-step method, the caloric values with respect to the percentage of carbon released by the combusted wood samples are shown in Fig. 2.

Fig. 2 shows that the caloric value increases with an increase in the carbon percentage, and it reaches a maximum value of the 22.51 MJ/kg at a carbon count of 44.4%. Further increases in the carbon percentage result in decreases in the caloric value. The increasing trend of the caloric value with the increase in the carbon percentage can be explained logically because carbon is one of the main contributors to the caloric value. However, the decreasing trend needs to be further investigated by considering the other components of the combusted wood samples.

The relationship between the caloric value (cv) and the carbon percentage (C) with a correlation coefficient of 69.21% is:

$$cv = -0.0703C^2 + 6.1835C - 113.84 \quad (2)$$

It has been found that the relationship between the cv and the amount of carbon has been found [16] by assuming a linear relationship as follows:

$$cv = 0.4065C \quad (3)$$

Using the same assumption, the present investigation has the following relationship:

$$cv = 0.3755C \quad (4)$$

The results of the present investigation are very similar to the previous results.

In Fig. 3, the caloric value for each wood sample is plotted with respect to the corresponding sulfur content of the combusted wood sample.

Table 1 Wood sample properties

Scientific name	Density (kg/m ³)	Caloric value (MJ/kg)	Ash (%)	C (%)	N (%)	S (%)	Reference
<i>Agathis borneensis</i> (Ab)	480	18.42	0.45	46.58	0.10	0.10	[13]
<i>Gonystylus</i> species (Gs)	655	14.70	0.48	44.26	0.39	0.04	
<i>Shorea negrosensis</i> (Sn)	720	12.60	1.13	47.03	0.46	0.10	
<i>Dryobalanops rappa</i> (Dr)	755	21.65	0.49	45.43	0.50	0.16	[14]
<i>Dipterocarpus</i> species (Ds)	815	20.79	0.47	47.15	0.42	0.11	
<i>Upuna borneensis</i> (Ub)	995	20.42	0.47	50.2	0.37	0.05	
<i>Shorea</i> species (Ss)	1010	11.55	0.63	46.38	0.41	0.04	[15]
<i>Rhizophora apiculata</i> (Ra)	820	15.00	1.09	34.42	0.12	0.04	
<i>Shorea parvifolia</i> (Sp.)	405	32.26	0.35	46.89	0.13	0.008	
<i>Acacia nilotica</i>	978	23.40	2.8	46.6	0.39	0.143	[15]
<i>Acacia leucophloea</i>	967	22.51	2.7	44.4	0.43	0.092	
<i>Prosopis cineraria</i>	942	21.93	2.5	43.3	0.38	0.140	
<i>Tectona grandis</i>	889	21.68	2.2	41.2	0.41	0.099	
<i>Cassia fistula</i>	847	21.64	1.6	39.8	0.37	0.087	
<i>Butea monosperma</i>	789	20.49	1.8	38.6	0.40	0.159	
<i>Sterculia urens</i>	686	19.70	1.4	37.8	0.47	0.163	

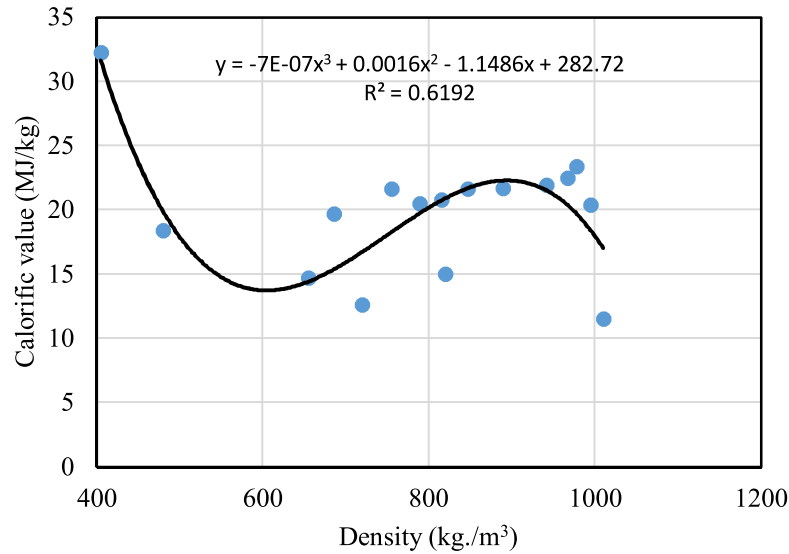


Fig. 1 Caloric value versus density.

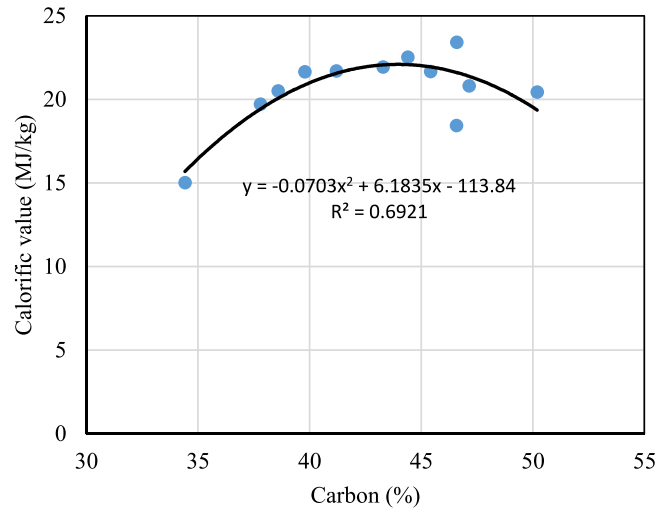


Fig. 2 Caloric value versus percentage of carbon.

Fig. 3 shows that the caloric value is 32.26 MJ/kg for a sulfur content of 0.005%. This value decreases sharply with the increase in sulfur content and reaches a minimum value of 14.6 MJ/kg at a sulfur content of 0.06%. After that, it increases and reaches a maximum value of 23.4 MJ/kg. Further increases in the sulfur content decreases the caloric value. It is interesting to note that the trends of **Figs. 1** and **3** are similar. Therefore, a curve between the wood density and the sulfur content was attempted, and it was found that there was less of a correlation between these two properties. With a maximum correlation coefficient of 57.12% between the caloric value (cv) and the sulfur percentage (S), the relationship between these two quantities has been found to be:

$$cv = -37443S^3 + 10903S^2 - 889.75S + 37.056 \quad (5)$$

The caloric values versus the percentage of ash produced by the combusted wood samples are plotted in **Fig. 4**.

Fig. 4 shows that the caloric value decreases as the ash content increases. It reaches a minimum value of 11.55 MJ/kg at an ash content of 0.63%. Then, it increases slowly with an increase in the ash content. The correlation between the caloric value (cv) and the percentage of ash (A) content with a maximum determination of coefficient of 49.72% is:

$$cv = -9.2927A^3 + 49.956A^2 - 66.296A + 42.225 \quad (6)$$

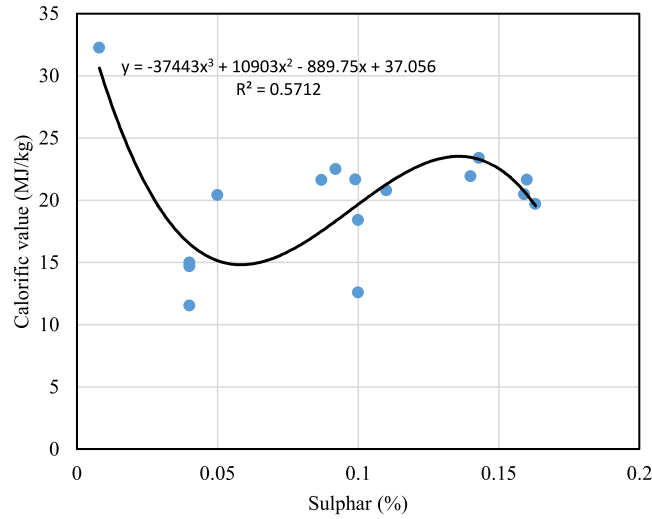


Fig. 3 Caloric value versus percentage of sulfur.

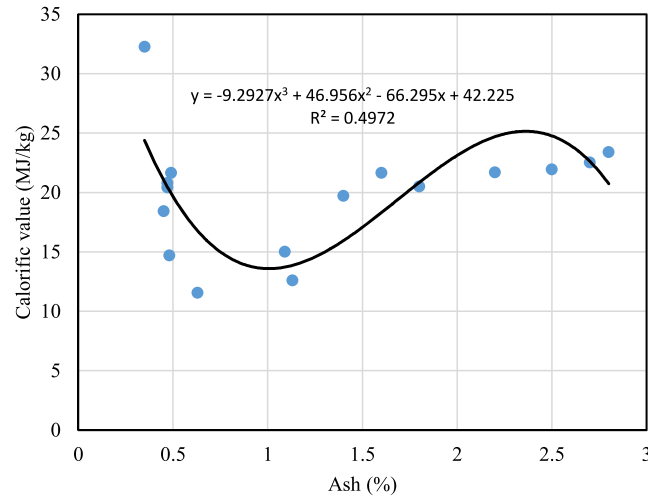


Fig. 4 Caloric value versus percentage of ash.

ANN Modeling

Estimation of the caloric value has been performed using a multi-layer, feed-forward, back-propagation paradigm of the artificial neural network (ANN) based on five input parameters (wood density, ash content, carbon, nitrogen, and sulfur content of evaluated sawdust species). The ANN model used here is a supervised learning method based on the generalization of the least mean square error (LMS) algorithm. It uses the gradient descent method to minimize the cost function, which is the mean square difference between the target and actual net output. To estimate the caloric value, the input parameters were first normalized between 0 and 1 so that appropriate activation functions could be used. There were seven cases available with five input parameters and one output. The network was designed using five input neurons and one output neuron, as shown in [Fig. 5](#).

Different numbers of hidden layers and hidden layer neurons were tested. A general ANN with N input layer neurons, one hidden layer with M neurons, and an output layer with O neurons can be represented as N - M - O architecture. In this study, with five input layer neurons and one output layer neuron, one-layer ANN and two-layer ANN with different numbers of hidden layer neurons (2, 5, 10, 15, 20) were tested. The *tansig* and *logsig* activation functions were used in hidden and output layers, respectively, and the output of each layer was calculated by using [Eqs. \(7\) and \(8\)](#).

$$\text{Output}_{\text{hidden}} = \text{TanSig} \left(\sum_{i=1}^P \text{input}_{h,i} \times w_{h,i} + b_h \right) \quad (7)$$

where

$\text{Output}_{\text{hidden}}$: output of the current hidden layer unit h .

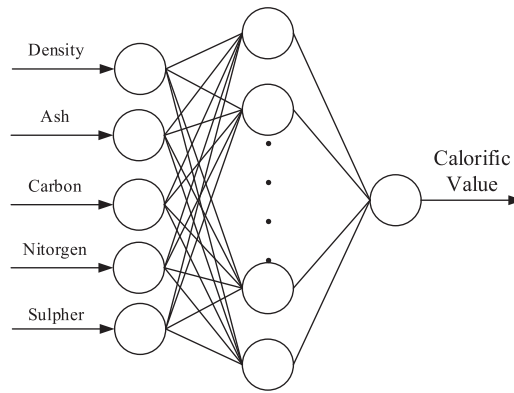


Fig. 5 ANN structure.

Table 2 ANN architecture with coefficient of determination for single hidden layers

ANN architecture	Mean coefficient of determination (R^2) (%)
5-2-1	87.74
5-5-1	86.95
5-10-1	58.63
5-15-1	36.90
5-20-1	5.21

P : either the number of units in the previous hidden layer or the number of network inputs.

$\text{input}_{h,i}$: an input to unit h from either the previous hidden layer unit i or the network input i .

$w_{h,i}$: the weight modifying the connection either from unit i to unit h or from input i to unit h .

b_h : bias for unit h .

Similarly, the output of the output layer can be calculated as

$$\text{Output}_{\text{hidden}} = \text{LogSig} \left(\sum_{i=1}^P \text{input}_{h,i} \times w_{h,i} + b_h \right) \quad (8)$$

where

$\text{Output}_{\text{out}}$: output of the current hidden layer unit h .

P : number of units in the previous hidden layer.

$\text{input}_{h,i}$: an input to unit h from the previous hidden layer unit i .

$w_{h,i}$: weight modifying the connection from unit i to unit h

b_h : bias for unit h .

The TanSig and LogSig activation functions are defined as follows:

$$\text{TanSig}(x) = \frac{e^x - e^{-x}}{e^x + e^{-x}} \quad (9)$$

$$\text{LogSig}(x) = \frac{1}{1 + e^{-x}} \quad (10)$$

The weights for the connections were initially randomly assigned and the learning rate (η) was set to 0.1. The ANN were trained and validated using the leave one out cross-validation (LOOCV) method, whereby one observation from the sample is used as validation data and rest of the observations are used for training the network. This process was repeated 10 times for each case and a mean coefficient of determination (R^2) was computed for each architecture. The coefficient of determination (R^2) for the architecture of each single layer of hidden network is shown in [Table 2](#).

The training/testing results of single hidden layers with different numbers of neurons are shown in [Figs. 6–10](#).

Similarly, the coefficients of determination (R^2) for each two-layer hidden network architecture are shown in [Table 3](#).

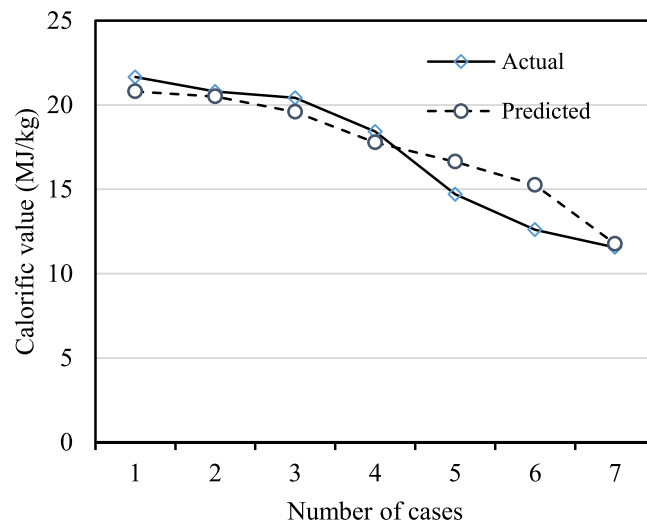


Fig. 6 Training and testing of 5-2-1 ANN architecture.

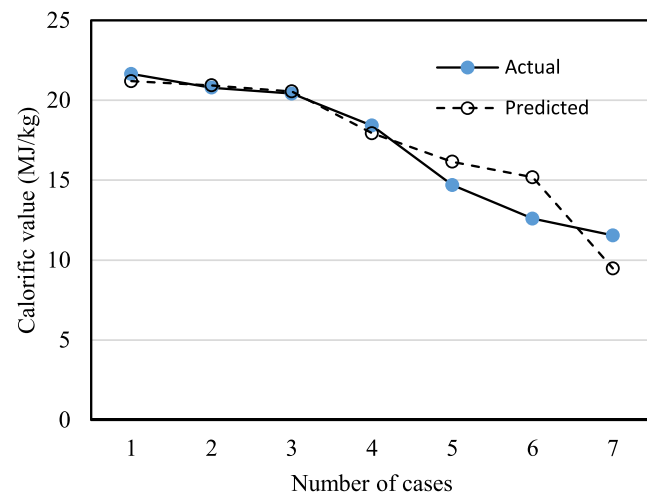


Fig. 7 Training and testing of 5-5-1 ANN architecture.

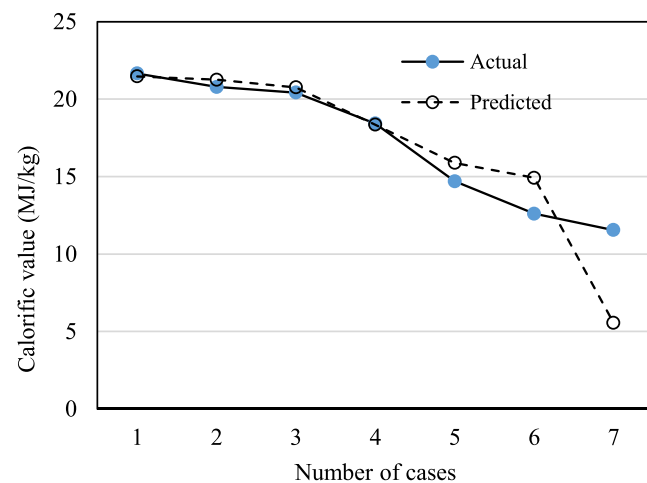


Fig. 8 Training and testing of 5-10-1 ANN architecture.

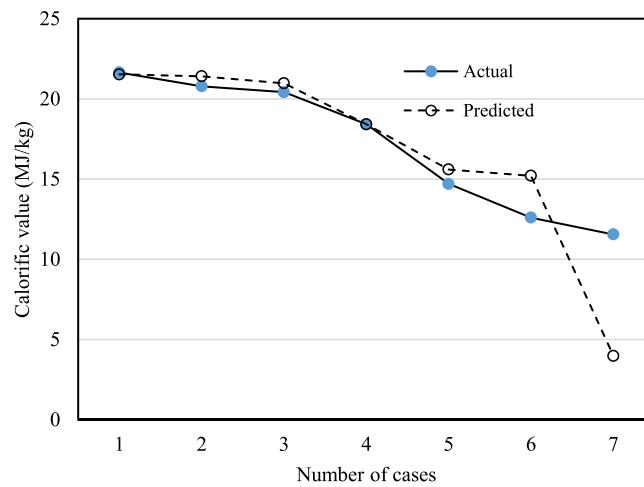


Fig. 9 Training and testing of 5-15-1 ANN architecture.

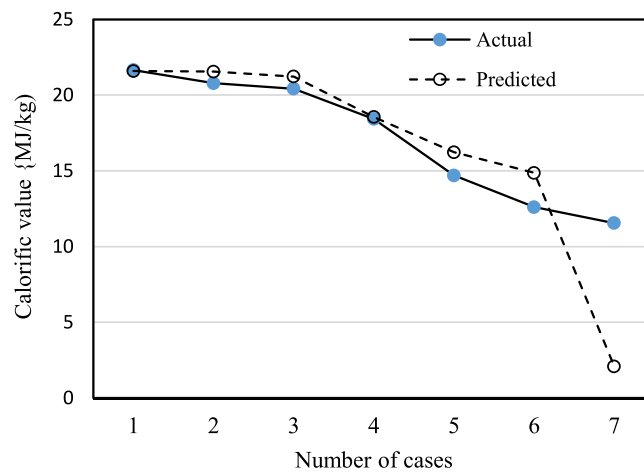


Fig. 10 Training and testing of 5-20-1 ANN architecture.

Table 3 ANN architecture with coefficient of determination for two hidden layers

ANN architecture	Mean coefficient of determination R^2	ANN architecture	Mean coefficient of determination R^2
5-2-2-1	30.69	5-10-15-1	46.78
5-2-5-1	32.12	5-10-20-1	42.28
5-2-10-1	69.11	5-15-2-1	44.98
5-2-15-1	73.24	5-15-5-1	31.26
5-2-20-1	48.47	5-15-10-1	61.98
5-5-2-1	33.18	5-15-15-1	73.69
5-5-5-1	58.33	5-15-20-1	85.85
5-5-10-1	55.65	5-15-25-1	84.86
5-5-15-1	82.45	5-20-2-1	35.79
5-5-20-1	71.56	5-20-5-1	46.16
5-5-25-1	74.32	5-20-10-1	44.38
5-10-2-1	47.66	5-20-15-1	52.29
5-10-5-1	48.89	5-20-20-1	63.36
5-10-10-1	68.51	5-20-25-1	73.01

For single hidden layers of the ANN, the maximum value of R^2 of 87.74% was found for 5-2-1 architecture. Table 2 shows that the value of R^2 decreased as the number of neurons in the hidden layer increased. However, for ANN architecture with two hidden layers, the maximum value of R^2 was found to be 85.85% for 5-15-20-1. In general, no advantage could be achieved using the ANN with two hidden layers.

Conclusion

Functional relationships between the caloric value and wood density, carbon content, sulfur content, and ash content have been derived from the experimental data collected from 16 different wood samples from Brunei Darussalam. To validate the experimental findings, an ANN model considering five input parameters with a single hidden layer and two hidden layers was used. In the ANN model, a multi-layer, feed-forward, back-propagation paradigm is used. For a single hidden layer, the coefficient of determination (R^2) was found to be 87.74% for 5-2-1 architecture. However, with two hidden layers in the 5-15-20-1 ANN architecture, R^2 was found to be 85.85%. There was no advantage to using ANN architectures with two hidden layers, but the results and high R^2 values validate the experimental findings. Using these results it can be concluded that the wood and wood by-products from Brunei Darussalam can be used efficiently as good, renewable energy resources.

See also: Development of Epoxy Based Composites Using Bamboo and Waste Metal Chips. Manufacturing, Applications and Mechanical Properties of Lightweight Wood-Based Sandwich Panels. Waste Resources Recycling in Achieving Economic and Environmental Sustainability: Review on Wood Waste Industry

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Investigations for Barium Titanate and Graphene Reinforced PVDF Matrix for 4D Applications

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Introduction

Additive manufacturing (AM), commonly known as three-dimensional (3D) printing or rapid prototyping has been commercially introduced in late 1980s. Although a considerable amount of progress has been made in this field, still lot of research work needs to be done in order to overcome the various challenges remained (Khoo *et al.*, 2015). Among the major advances that this process presented to product development are the time and cost reduction, human interaction, and consequently the product development cycle (Wong and Hernandez, 2012), also the possibility to create almost any shape that could be very difficult to machine. However, at the present time it is not yet adopted in the manufacturing sector, but scientists, medical doctors, market researchers and artists use it extensively (Flowers and Moniz, 2002; Noorani, 2006). With AM, scientists can rapidly build and analyse models for theoretical comprehension and studies. Doctors can build a model of a damaged body to analyse it and plan better the procedure, market researchers can see what people think of a particular new product, and rapid prototyping makes it easier for artists to explore their creativity (Cooper, 2001).

Today, various AM machines/setups are found not just in industry but in households, as the price of 3D printers has fallen below US\$1000. One can print almost anything, which opens up unlimited opportunities for us to manufacture toys, household appliances and tools in our living rooms (Raviv, 2014a,b). Thermoplastics, metal powders, photopolymers and ceramic powders are some important and useable materials for AM process (Tofail *et al.*, 2017).

AM processes take the information from a computer-aided design (CAD) file that is later converted to a stereo lithography (STL) file. In this process, the drawing made in the CAD software is approximated by triangles and sliced containing the information of each layer that is going to be printed (Wong and Hernandez, 2012).

Fig. 1 shows classification of AM processes broadly as liquid base, solid based, and powder based. The processes included in this are considered the most relevant in the past, and promising for the future of the industry (Kruth, 1991).

The polymeric component by AM can be better alternatives in the following manners (Ligon *et al.*, 2017):

- Cost effective;
- Produced lightweight component;
- Ease of fabricate the parts;
- Better dimensional manipulations;
- Requirement of low temperature for production etc.

But there's more that can be done with 3D printed materials to make them more flexible and more useful for example the structures that can transform in a pre-programmed way in response to a stimulus. Recently given the popular name of "4D printing", perhaps a better way to think about it is that the object that transforms over time (Mouzakis, 2018).

Basics of 4D Printing

4-dimensional printing uses the same techniques of 3D printing through computer programmed deposition of material in successive layers to create a three-dimensional object. However, 4D printing adds the dimension of transformation over time (Tibbitts, 2014). It is therefore a type of programmable matter, wherein after the fabrication process, the printed product reacts with parameters within the environment (humidity, temperature, etc.) and changes its form accordingly. The ability to do so arises from the near infinite configurations at a micrometer resolution, creating solids with highly engineered molecular spatial distributions (Li *et al.*, 2016) and thus allowing unprecedented multifunctional performance. 4D printing is a relatively latest in bio fabrication technology and rapidly emerging as a new paradigm in disciplines such as bioengineering, materials science, chemistry, and computer sciences (Le Feuvre and Scrutton, 2018).

Types of 4-D printing

4-D printing can be defined as the ability of a material to change its shape or physical properties with the passage of time, automatically and autonomously, that is, without any external intervention. Many common terms such as autonomic-4D printing and autonomic self-changing are used to define such a property in materials. Incorporation of changing in physical properties in manmade materials very often cannot perform without an external trigger. Thus, 4-Dimensional printing can be of the following two types:

- Autonomic (without any intervention);
- Non-autonomic (needs human intervention/external triggering).

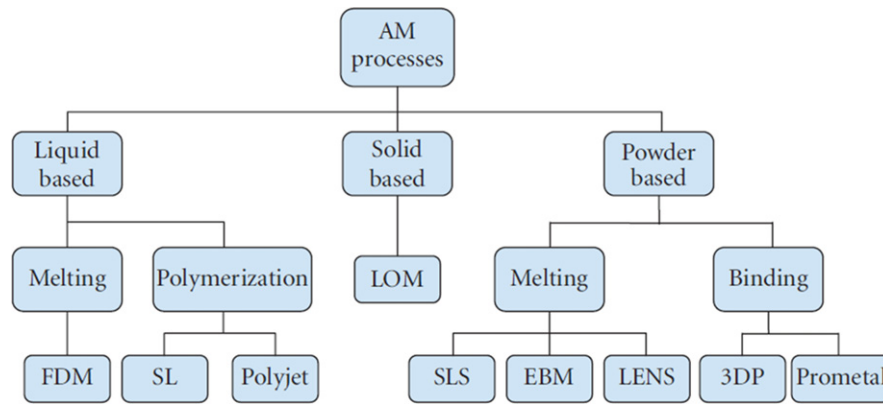


Fig. 1 Three-dimensional printing processes.

Recently, one of the actively researched areas lies in the additive manufacturing of smart materials and structures. 4D printing may be defined as an additive manufacturing process that integrates smart materials into the starting form of the printing material for 3D printed structures/components. After fabrication, the 3D object would respond in an intended manner to external stimuli from the environment or through human interference, resulting in a change in shape or physical properties over time (Khoo *et al.*, 2015).

Smart Materials

Smart materials are those materials that have the ability to change their shape or properties under the influence of external stimuli. With the introduction of smart materials, the AM-fabricated components are able to alter their shape or properties over time (the 4th dimension) as a response to the applied external stimuli. Hence, this gives rise to a new term called '4D printing of smart materials' to include the structural reconfiguration over time (Khoo *et al.*, 2015).

Piezoelectricity

A piezoelectric material accumulates electrical charges when mechanical stress is applied. This is called piezoelectric effect, while conversion of the electric field to mechanical strain is called reverse piezoelectric effect. Before understanding various coefficients of piezoelectricity for solid piezoelectric material, the direction of material due to the anisotropic nature of piezoelectric material must first be defined. Typical piezoelectric coefficients are denoted as A_{ij} where i denoted as the direction of the electrical measurement, and j denotes the direction of the mechanical movement (Ueberschlag, 2001). Fig. 2 shows the typical dimensions of piezoelectric material for defining the piezoelectric constants.

Some of the important piezoelectric constants regarding this study are:

Piezo strain constant: d_{3j} ($C/m^2/N/m^2$) represents the piezoelectric effect in the film. This constant indicates how much charges can be accumulated in $1 m^2$ when $1 Pa$ of pressure is applied along the " j " axis. Typical values of d_{33} for PVDF and its copolymer are between 20 and 30 $C/m^2/N/m^2$.

Piezo stress constant: g_{3j} ($V/m)/(N/m^2)$ represents the electric field induced in " 3 " direction by a stress of $1 Pa$ is applied along the " j " axis. It is often called piezo voltage constant and the typical g_{33} values for PVDF polymer are around 200–300 $V/m/N/m^2$ (Bauer and Bauer, 2008; Xu *et al.*, 2009).

Electroactive Polymers (EAP)

Electroactive polymers, or EAPs, are polymers that exhibit a change in size or shape when stimulated by an electric field. A typical characteristic property of an EAP is that they will undergo a large amount of deformation while sustaining large forces (Biggs *et al.*, 2013). EAP materials can be easily manufactured into various shapes due to the ease in processing many polymeric materials, making them very versatile materials.

EAP are of two types

- (1) Dielectric EAPs are materials in which actuation is caused by electrostatic forces between two electrodes which squeeze the polymer. Dielectric elastomers are capable of very high strains and are fundamentally a capacitor that changes its capacitance when a voltage is applied by allowing the polymer to compress in thickness and expand in area due to the electric field (Anderson *et al.*, 2012).
- (2) Ionic EAPs, in which actuation is caused by the displacement of ions inside the polymer. Only a few volts are needed for actuation, but the ionic flow implies a higher electrical power needed for actuation, and energy is needed to keep the actuator

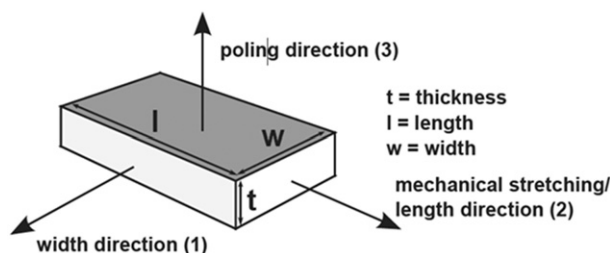


Fig. 2 Schematic representation of dimensions in piezoelectric material. Reproduced from Ueberschlag, P., 2001. PVDF piezoelectric polymer. Sensor review 21 (2), 118–126.

at a given position. Examples of ionic EAPS are conductive polymers, ionic polymer-metal composites (IPMCs), and responsive gels (Biddiss and Chau, 2006).

Ferroelectric polymers (dielectric polymers) are a group of crystalline polar polymers that are also ferroelectric, meaning that they maintain a permanent electric polarization that can be reversed, or switched, in an external electric field (Wang, 2001). Ferroelectric polymers, such as polyvinyl diene fluoride (PVDF), are used in acoustic transducers and electromechanical actuators because of their inherent piezoelectric response, and as heat sensors because of their inherent pyroelectric response (Kochervinskii, 2003).

PVDF

PVDF is lightweight, flexible, has low acoustic impedance and high piezoelectric constant, making it a good candidate for acoustic or biomedical sensors. The crystallinity of the PVDF polymer will be a major factor on the piezoelectric constant of polymers (Xu *et al.*, 2009). Typical piezoelectric polymers have a crystalline region that has an internal dipole moment. These dipole moments are randomly oriented without any mechanical or electrical poling process (Sencadas *et al.*, 2009), and the net dipole moment is zero in this condition. This type of structure is called α -phase PVDF film that has no piezoelectric response. The α -phase PVDF film is commonly used as insulating material because of its low thermal conductivity, low density, and high chemical and heat resistance. With post processes such as mechanical stretching and electrical poling under a high electric field, crystalline regions inside the bulk PVDF film will align in electric field direction (Kim and Arias, 2015). The PVDF structure with this morphology is called β -phase film. It has been shown that the higher β -phase portion of PVDF film shows a higher piezoelectric constant as sensor material. Typically, around 90%~95% of β -phase portion shows a strong piezoelectric response for PVDF polymer (Satapathy *et al.*, 2008). Copolymers of PVDF such as PVDF tetra fluoro ethylene (PVDF-TrFE) show higher crystallinity due to its chemical structure, resulting in better piezoelectric response. Upon application of post processes to the PVDF film, the β -phase PVDF film retains its morphology unless there are severe changes in temperature to the film. The maximum operating temperature for the β -phase PVDF film is 80°C and 110°C for the β -phase PVDF-TrFE film (Kim and Arias, 2015).

Table 1 shows the material property of common piezoelectric materials.

Piezoelectricity in Semi Crystalline Polymers

A PVDF film without any post processes such as mechanical stretching or electrical poling results in the alpha phase PVDF structure that has a zero net dipole moment in the crystalline region, as shown in Fig. 3. This type of crystalline structure has no piezoelectric characteristic, because the α -phase PVDF crystalline regions will align such that all dipole moments cancel each other. On the other hand, the β -phase PVDF structure of PVDF has Fluorine on the one side and Hydrogen on the other side, as shown in Fig. 4. This will form a net dipole moment in a stacked direction inside the β -phase PVDF crystalline regions. When stress is applied to this stacked polymer chain region, it will change the local dipole distributions and induce an electric field in the stack. The induced electric field accumulates the charges at both the top and bottom of the film, demonstrating the principle of piezoelectric effect. Various studies show ways to increase the β -phase portion in the film by mechanical or electrical poling (Lau *et al.*, 2013). A copolymer of PVDF, PVDF-TrFE, shows a higher temperature range of use, a slightly higher piezo strain constant, and a higher portion of β -phase morphology with just thermal annealing process (Wang *et al.*, 2015). PVDF-TrFE is a good candidate material for piezoelectric polymer sensor because it can achieve high portion of β -phase morphology without poling process.

Barium titanate

Barium titanate is the inorganic compound with the chemical formula BaTiO_3 . Barium titanate is a white powder and transparent as larger crystals (Veith *et al.*, 2000). This titanate is a ferroelectric ceramic material, with photorefractive effect and piezoelectric properties. It is used in capacitors, electromechanical transducers and nonlinear optics (Xu, 2013).

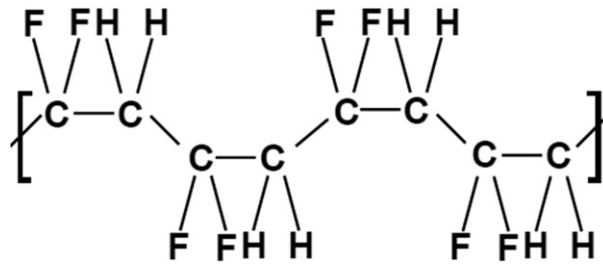
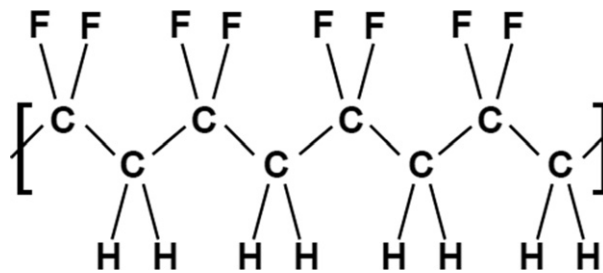
Graphene

Graphene is an allotrope of carbon having single layer sp^2 hybridization arranged in a two-dimensional hexagonal lattice. It is the basic structural element of many other allotropes of carbon, such as graphite, diamond, charcoal, carbon nanotubes and fullerenes

Table 1 Material property of common piezoelectric materials

Material property	Units	PVDF	Nylon 11	PVC	PZT	Barium titanate
Density	g/cm ³	1.78	1.15	1.45	7.5	5.7
d ₃₁ piezoelectric constant	pC/N	23	0.26	0.7	1200	1700
g ₃₁ voltage constant	Vm/N	216	2.5	6.6	10	5
Acoustic impedance	106 kg/m ² s	2.7	2.9	3.27	30	30

Note: Kim, T.H., Arias, A.C., 2015. Characterization and applications of piezoelectric polymers (A Tehnical Report).

**Fig. 3** Chemical structure of α phase PVDF structure. Reproduced from Kim, T.H., Arias, A.C., 2015. Characterization and applications of piezoelectric polymers (A Tehnical Report).**Fig. 4** Chemical structure of β phase PVDF structure. Reproduced from Kim, T.H., Arias, A.C., 2015. Characterization and applications of piezoelectric polymers (A Tehnical Report).

(Neto *et al.*, 2009). Graphene has many unusual properties. It is the strongest material ever tested. The material has been of intense interest because of its mechanical, thermal, and electrical properties (Zhang *et al.*, 2010).

Twin-Screw Extrusion (TSE)

The TSE process was started by 'Clextral', over 20 years back, for continuous production of exceedingly uniform and finely structure components. It is generally used to deliver bio-sourced plastics, fabrication of feed stock filament, and reinforcement of polymers with fillers or ceramics. Fig. 5 demonstrates the schematic of TSE process.

The primary purpose of TSE processing is blending of the at least two materials equally and producing a good quality components/parts with precise control of process conditions. There are extensive variety of barrel and screw plan, different process capacity and screw profile to be set up as indicated by requirements of process. Twin-screw extruders are competent to guarantee blending, shearing, cooling, warming, compacting, molding, and so forth with abnormal state of adaptability. The fundamental points of interest of twin-screw extruders (intermeshing co-turning) are their uncommon blending capacity that gives the amazing qualities to expelled items. In TSE process, the crude materials could be solids (granules and powders form) or fluids (Dombe *et al.*, 2015).

Literature Review

3D Printing

Li *et al.* (2002) worked for fabrication of ABS based FDM Prototypes with Locally Controlled Properties deposition density and deposition orientation and make a comparison between the theoretical and experimental analysis. They observed that the parts fabricated at raster angle 45/-45 having minimum young's modulus as compare to parts fabricated at 0/90 raster angle having maximum young's modulus and also there is a difference between the theoretical and experimental outcome values.

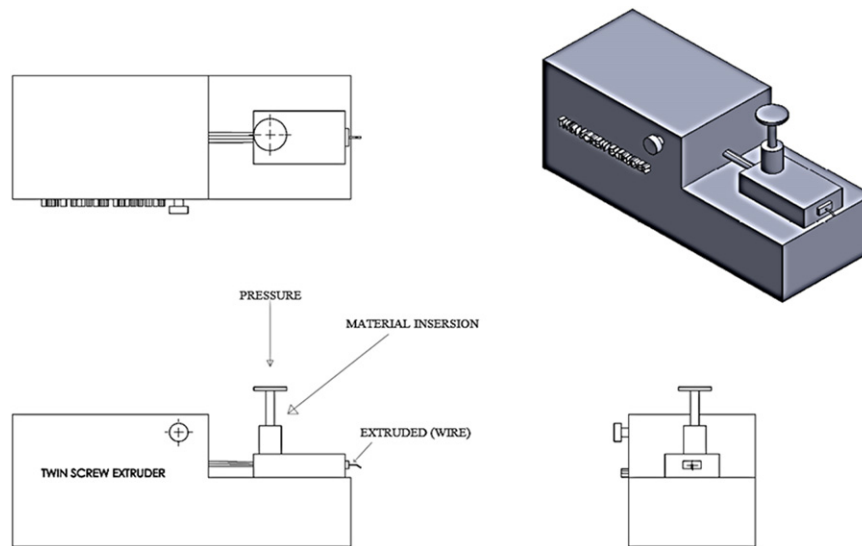


Fig. 5 Schematic of TSE techniques. Singh, R., Sandhu, G.S., Penna, R., Farina, I., 2017. Investigations for thermal and electrical conductivity of ABS-graphene blended prototypes. *Materials* 10 (8), 881.

Upcraft and Fletcher (2003) compared various rapid prototyping technologies including stereo lithography, selective laser sintering, fused deposition modeling, laminated object manufacturing, three-dimensional printing and multi-jet modeling. It also covers surface roughness considerations and mechanical properties including dimensional accuracy and compares costs of various systems. They concluded that in the case of FDM when the raster angle was increased from 10° , 20° up to 90° , the surface roughness of the fabricated model was decreased. The dimensional accuracy FDM parts were 97% when compared to CAD data. The FDM is cost effective way to produce 3D structures as compared to other RP techniques.

Modeen (2005) highlighted that the file generated in CAD model could be easily converted into layer fabricating files. The strong point of layer depositing technique is its capability to create the mirror image of CAD design.

Novakova-Marcincinova *et al.* (2012) shared the data about progress and normal accessible materials that are utilized for item fabricating by FDM. i.e., a RP innovation. While utilizing diverse innovation of fast model the primary condition of item material might be accessible in many shape. There can be fluid, powder shape or solid form. It can be also accessible in different types of solids like wire, laminates or beds. The material utilized as a part of this exploration paper incorporates nylon, paper, resin wax, ceramics. In FDM be materials that is utilized are ABS, polypropylene, polyamide and polyethylene. some extraordinary materials are utilized in the FDM system are nitrile, hydroxyapatite, silicon, stainless steel, PZT and Al_2O_3 .

Romero *et al.* (2015) compared the 3D printed product with the conventional master cast and also studied the material consumption and cost occurred in both processes. It was concluded that Rapid manufacturing produced the best fit parts with negligible material wastage when compared to conventional manufacturing class. The results also show the saving of cost in RP process.

Torres *et al.* (2015) optimized the process parameters' of FDM (infill percentage, layer thickness and post heat treatment on the mechanical strength of the prototypes ANOVA was used for optimization process. They concluded that the layer thickness and infill percentage has more effects on the mechanical strength. Whereas the post heat treatment (at three different time intervals 0–20 mins)) affects the mechanical strength of less dense part only.

Singh *et al.* (2017) studied that the reinforcement of graphene in ABS polymer matrix can be directly printed with an open source 3-d printer and graphene is responsible for enhance the electrical and thermal conductivity of the ABS polymer.

Lin *et al.* (2015) demonstrated the first three-dimensional (3D) printed graphene complex structures by stereolithography with good combination of strength and ductility. With only 0.2% GOs and found that, the tensile strength is increased by 62.2% and elongation increased by 12.8%.

Dul *et al.* (2016) fabricated 3d parts with graphene nanoplatelets (xGNP) reinforcement into ABS. It has been found that, there is a decrease in both stress and strain at break was observed when xGNP is added to ABS. Moreover, a higher thermal stability was induced on 3D printed parts by xGNP, as indicated by a reduction in both coefficient of linear thermal expansion and creep compliance.

4D Printing

Polyjet printing and syringe printing are the most popular forms of 4D printing, but other 3D printing technologies such as FDM, SLS, and stereo lithography are processes that could be incorporated in 4D printing technology; however, some 4D printing technologies may require multi-materials and multiple nozzles, which limits what 3D printing methods can be used. Exploring different printing methods may allow for different smart materials to be 3D printed that are stronger, lighter, induce different property changes, and react to different stimuli.

According to Pei (2014), 4D printing is the process of building a physical object using appropriate additive manufacturing technology, laying down successive layers of stimuli-responsive composite or multi-material with varying properties. After being built, the object reacts to stimuli from the natural environment or through human intervention, resulting in a physical or chemical change of state through time.

Tibbitts *et al.* (2013) stated 4D printing as a new process that 'entails multi-material prints with the capability to transform over time, or a customised material system that can change from one shape to another, directly off the print bed' with the fourth dimension described here as the transformation over time, emphasising that printed structures are no longer static, dead objects; rather, they are programmably active and can transform independently.

Zhou *et al.* (2015) outlined that rigid materials can be 3D printed along with smart materials to create specific areas of a part that act as joints and hinges for bending. This process of 3D printing parts that change shape over time when exposed to an external energy has been termed 4D printing by Skylar Tibbitts from Massachusetts Institute of Technology (MIT).

Leist and Zhou (2016) highlighted the onset of multi-material 3D printing and the combination of smart materials into the printable material has led to the development of an exciting new technology called 4D printing. This paper will introduce the background and development into 4D printing, discuss water reactive 4D printing methods and temperature reactive 4D printing, modeling and simulation software, and future applications of this new technology. Smart materials that react to different external stimuli are described, along with the benefits of these smart materials and their potential use in 4D printing applications; specifically, existing light-reactive smart materials. 4D printing has the prospective to simplify the design and manufacturing of different products and the potential of automating actuation devices that naturally react to their environment without the need for human interaction, batteries, processors, sensors, and motors.

Tibbitts (2012) highlighted that construction must be made smarter and solve the problems of wasting large amounts of energy, materials, money, and time for building. These issues can be solved using design programs and software to embed information into the materials that makes the material and construction more accurate. At the beginning, Tibbitts proposed a process called self-assembly, which uses small units that form larger structures when exposed to external energy.

Tibbitts *et al.* (2011) outlined that self-assembly may be applied to 1D strands forming organized 2D and 3D shapes, along with 2D planar shapes forming 3D objects. Self-assembly may not be efficient for every purpose, which means different sectors and applications must be identified that benefits most from self-assembly.

A market research report predicts that the 4D printing industry could be worth \$63.00 million in 2019 and \$555.60 million in 2025 (Markets and Markets, 2015). The market report predicts that 4D printing may find applications in the automotive, textiles, construction, healthcare, utility, aerospace, and military industries. It is predicted the defense and military sector would have the largest share, followed by the aerospace industry. These are just a minor number of application ideas for 4D printing that reflect a number of 3D printing methodologies and activation energies. This paper presents the current research focused on 4D printing methods, smart materials that allow for its activation, and the future applications for this exciting innovative technology.

Smart Materials

Developments in 4D printing

In this section, some developments of 4D printing that exhibit physical changes of the printed components/ structures are illustrated. They are classified according to whether they are printed with a combination of multiple materials or with a single material.

4D printing with single material

In this section, 4D printing of either a single smart material or a mixture of smart material and conventional material as the starting form for printing has been detailed.

Kim *et al.* (2017) proposed an integrated 3D printing process with corona poling to fabricate piezoelectric PVDF sensors without post poling process. This proposed process, named 'Integrated 3D Printing and Corona poling process' (IPC), uses the 3D printer's nozzle and heating bed as anode and cathode, respectively, to create poling electric fields in a controlled heating environment. The nozzle travels along the programmed path with fixed distance between nozzle tip and sample's top surface. Simultaneously, the electric field between the nozzle and bottom heating pad promotes the alignment of dipole moment of PVDF molecular chains. The crystalline phase transformation and output current generated by printed samples under different electric fields in this process were characterized by a Fourier transform infrared spectroscopy (FTIR) and through fatigue load frame. It is demonstrated that piezoelectric PVDF films with enhanced β -phase percentage can be fabricated using the IPC process.

Kamila (2013) outlined that the printed components consisting of a single smart material or a mixture of smart and conventional materials, the smartness of the materials plays a more important role in achieving the intended response than in the case of a multi-material component. The smartness of the smart materials or mixtures describes the self-adaptability, self-sensing, shape memory, decision making and multiple functionalities of the materials or mixtures.

Kim *et al.* (2014) stated those characteristics that determined how the printed components change their properties in response to the external stimulus and they provide various promising applications of these materials. In the following, recent developments of 4D printing that consist of either a single smart material or a mixture of materials as the starting form will be highlighted, including enhanced smart nanocomposites and 3D printing of SMPs.

Dadbakhsh *et al.* (2014) studied the effect of SLM process parameters on the transformation temperature of fabricated parts Nickel titanium and found that SLM restores the 0.5% SME in the fabricated structure. SLM process eliminates the inhomogeneity of starting powder

Rossiter *et al.* (2009) fabricated thin membrane with a thick circular collar (thickness of the central membrane was approximately 90 μm) of acrylic-based photopolymer by PolyJet and found that thin membrane produces large strains upon activation by electricity. Thus it demonstrated that 3D printing have potential to produce electroactive actuators.

Bodkhe *et al.* (2017) demonstrated the production of 4 V from a 3d printed sensor of PVDF reinforced with BaTiO_3 . The 3d scaffolds were fabricated with Solvent evaporation-assisted 3D printing process and were able to stabilize the β -phase at room temperature.

Enhanced smart nano-composites

Uchino (2017) highlighted one important type of smart material that has been used widely is the piezoelectric material that is able to produce electrical charge or voltage when experiencing an externally applied stress and vice versa. Different categories of piezoelectric materials offer different capabilities.

Kim *et al.* (2014) stated that piezoelectric polymeric materials have some unique characteristics as compared to other piezoelectric materials. These materials are suitable for systems that require mechanical flexibility, small active elements, biocompatibility and solution-based processability. However, it is still a difficult task to fabricate piezoelectric polymeric materials into complex 3D structures or small active elements. Thus, further improvement in the manufacturability of piezoelectric polymers will definitely have a huge contribution to the development of various applications which require micro-scale and nano-scale piezoelectric polymers, such as biodiagnostic devices, micro-scale and nano-scale electromechanical systems, imaging systems, compact sensor designs and electronics.

4-D printing of multiple materials

Raviv *et al.* (2014a,b) found an important factor to consider when designing a component with multiple materials is the availability of the 3D printing technology. Moreover, in the developments of 4D printing of multiple materials, the design of the components plays a critical role as the conventional materials do not react to the external stimulus. Hence, the degree of the change in the printed components upon activation is usually determined by the design of the components. In order to illustrate this point, some examples of the developments in 4D printing of multiple materials are discussed. These examples include printed actuators for soft robotics, self-evolving structures, anti-counterfeiting system.

Srivastava *et al.* (2010) stated another class of smart materials that are gaining popularity are shape memory polymers (SMPs). SMPs possess the ability to remember a permanent shape and transform to a temporary shape when exposed to a number of external stimuli such as temperature,

Hager *et al.* (2015) studied that SMP could create products that react to their environment automatically without the need for complex, heavy, and expensive electronic actuation systems. Some other smart materials, called self-healing materials, that possess the ability to react to external stimulus and repair themselves, which may prove useful for devices exposed to extreme environments.

Gladman *et al.* (2016) at Harvard's School of Engineering and Applied Sciences (SEAS) were capable of 3D printing a single smart material using a syringe nozzle and photo polymerization of their smart material for their 4D printing research.

Lendlein, (2010) stated that smart materials are essential to the development of 4D printing research. There are many smart materials in development; however, not every smart material can be 3D printed. Also, smart materials do not need to possess shape change in order to be important to 3D printing research. Materials that possess the ability to change color, hardness, or transparency may become important in camouflage technology, signaling for users, detecting foreign substances, and biomedical applications.

Ge *et al.* (2013) created a 4D printing technique that uses a combination of heat and stress to activate a shape memory composite to bend at different rates and directions depending on the design of the hinges. Glassy polymers in the form of fibres exhibit shape memory effects (SMEs) when heated above their glass transition temperature (T_g) and are 3D printed within an elastomeric matrix combination of elastomer and glassy polymer fibres creates a soft composite, which the team has named printed active composites (PACs).

Mao *et al.* (2015) were successful in implementing their 4D printing techniques for the creation of self-assembling origami structures: A box, pyramid, a three hinged airplane, and a five hinge airplane. A box with the six rigid sides connected by PAC hinges is 3D printed in a flat shape. The PAC hinges are pre-programmed with definitive bending angles using the relation of PAC hinge length and applied strain to determine the bending angle. The walls of the box should bend at a 90° , so the hinges required a strain of 20% to be applied while the material is heated above its glass transition temperature (T_g), cooled, then releasing the prestrain. The component managed to form the box shape with minor irregularities due to inconsistencies when straining the material (see Fig. 6(a and b)).

Ge *et al.* (2014) found that the inclusion of smart materials in their 3D printing components could save time and material. 3D printing a 20 mm $\times$ 20 mm $\times$ 20 mm hollow cube with a wall thickness of 1 mm could take 10 minutes when printed in a flat 2D shape then activated to become a 3D cube. However, direct 3D printing a cube with the same dimensions takes 3 h to print and post processing of removing support material can take numerous hours.

Kravchenko *et al.* (2011) found that light is an effective activation technique because it is an abundant source of energy, wireless, and controllable. However, it can be difficult to transform light energy into mechanical energy for use in SMPs. Light-activated SMPs have been used in areas of self-assembly structures, complex folding methods, transformative surface deformations.

Based on literature review, following gaps have been identified:

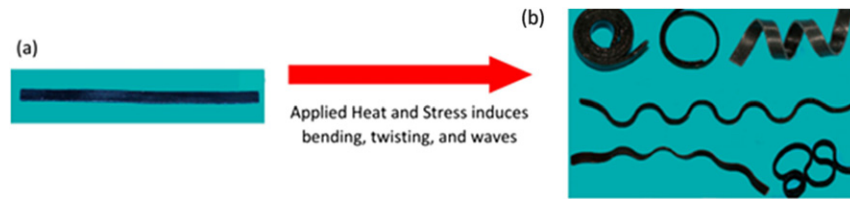


Fig. 6 (a) Initial flat shape of PAC without heat activation. 6(b) Flat PAC material displays bending, twisting and wave shape changes when heat and stress is applied depending on the orientation of the PAC fibre.

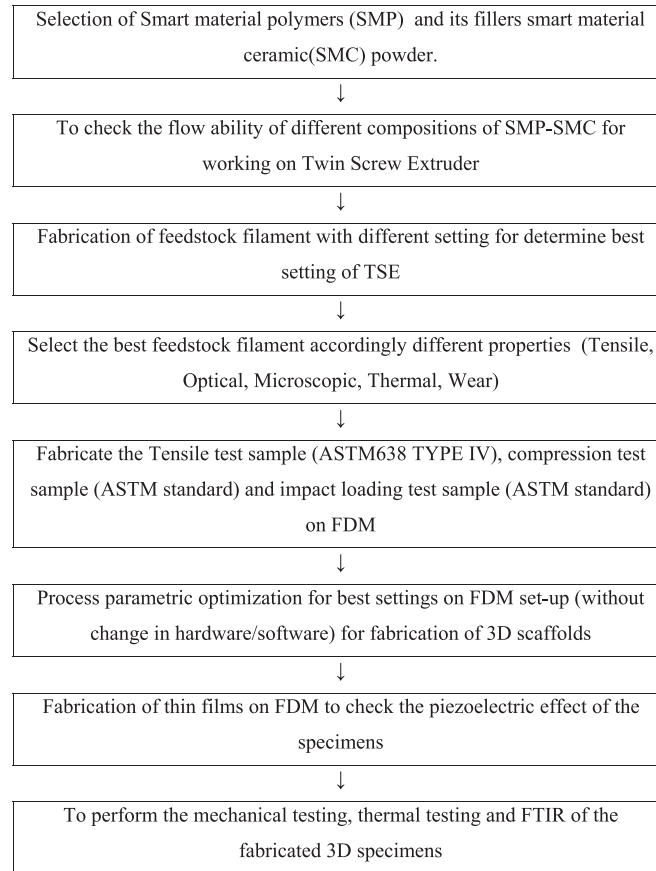


Fig. 7 Flow chart for detailed methodology.

- It has been observed that many researchers have been worked in the field of 3D printing of commercially available materials only, but very few have reported the 3D printing of EAP matrix for 4D applications. Since 4D printing is upcoming field in AM, not much data has been reported regarding the 4-D printing with fused deposition modeling (FDM) which is one of the low cost AM technique.
- Smart materials are used in actuators, sensors applications and can be fabricated by conventional manufacturing processes as well as by 3D printing. Some of the commonly reported smart materials are PVDF and BaTiO₃. Still no work has been reported for preparing 4D printed parts by using PVDF, Gr and BaTiO₃ with FDM process.

Proposed Methodology/Frame Work for 4D Applications

The detailed methodology for 4D printing applications is shown in form of block diagram (see Fig. 7).

Summary

In this article detailed procedure has been outlined for preparing different proportions of BaTiO₃, Gr reinforced PVDF matrix for 4D printing applications. Commercially for preparing FDM feed stock filament (for open source 3D printer) of BaTiO₃ and Gr

reinforced PVDF mechanical mixing with twin screw extruder/chemical mixing may be used. The future studies may be focused on detailed rheological (melt flow index), thermal analysis of feed stock filaments prepared by using (mechanical/chemical mixing) and there is strong need to perform parametric optimization of feedstock filament wire (prepared by mechanical/chemical mixing), based upon mechanical and metallurgical testing (tensile test, scanning electron microscope) for final selection of feed stock filament for 3d printing. Finally parametric optimization from mechanical/piezoelectric properties view point needs to be performed for printed functional prototypes on FDM.

See also: Experimental Investigations for Development of Aluminum MMC With Hybrid Reinforcement and Vacuum Molding. Experimental Investigations for Development of Conductive Ceramic Composites with Microwave Sintering and Their Electric Discharge Machining. Sustainable Machining With Self-Lubricating Coated Mechanical Micro-Textured Cutting Tools

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Investigations for Metal Matrix Composites Prepared by Using Waste Polymer-Based Sacrificial Rapid Pattern in Investment Casting

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Introduction

Fiber reinforced resins, thermosets as well as thermoplastics, are increasingly used to replace metals in a number of industrial, sporting, and transport applications. One of the biggest challenges posed by fiber reinforced composites is their recycling. Environmental legislation is becoming more and more restrictive, and just the environmental impact of these materials disposed in landfills is accelerating the urgency to reach more industrial scale solutions to the recycling of composites. Landfill is a relatively cheap disposal route but is the least preferred waste management option (Jacob, 2011; Oliveux *et al.*, 2015; Bos, 2002; European Union, 2008). Polymeric waste materials should be considered resources for the manufacture of new products through recycling processes, with a similar status to virgin fossil-based plastics and biopolymers from renewable resources (Vilaplana and Karlsson, 2008). In the case of high impact polystyrene (HIPS), thermooxidative degradation affects more severely than multiple processing the long-term stability and properties; degradation during service life seems therefore to determine the further possibilities of employing HIPS recyclates in second-market applications (Vilaplana and Karlsson, 2008). Other synthetic plastics such as polyolefins (high-density polyethylene (HDPE) and PP) and PET are more affected by thermomechanical degradation by multiple processing than they are by thermooxidative aging, indicating that special attention should be focused on controlling the processing conditions during mechanical recycling (Vilaplana and Karlsson, 2008; Badia *et al.*, 2017). Polymers suffer chemical and physical changes during their processing and service life. They undergo oxidative reactions at every stage of their life cycle, and the new functional groups formed during the oxidation process may enhance the sensitivity of the recyclates to further thermal and photodegradation (Vilaplana and Karlsson, 2008). Various researchers have used different methods for recycling of the polymers by using the various kind of fillers or reinforcement to increase their life cycle and application domain (Singh *et al.*, 2016).

Materials

Nowadays, investment casting is basically used to prepare complex parts with high accuracy by using wax as pattern. The polymeric parts produced by additive manufacturing (AM) technology can be used for prototypes, sacrificial patterns for investment casting, and even they can be used as functional prototypes. In addition to industrial polymers, biocompatible polymers, such as poly-ε-capro-lactone (PCL) and polyetheretherketone (PEEK) and starch-based polymers, also have been investigated by many researchers with selective laser sintering (SLS), fused deposition modeling (FDM) and other commercial 3-dimensional printing (3DP) processes for biomedical applications such as implants and tissue scaffolds (Schmidt *et al.*, 2007; Leong *et al.*, 2007; Ramanath *et al.*, 2008; Ramanath *et al.*, 2007; Lam *et al.*, 2002). Metal parts can also be produced by using rapid casting (RC) by combining AM produced patterns, or casing shells and cores, and subsequently casting with molten metal, such as investment casting and sand casting (Cheah *et al.*, 2005). Casting patterns built using AM processes were also applied to investment casting, such as polymer patterns via stereo lithography (SLA), wax patterns via FDM, paper patterns via laminated object manufacturing (LOM), polymer patterns via 3DP and SLS. Other AM processes, such as SLA, FDM and 3DP, can fabricate metal parts (like turbine blades) for aerospace applications by building casting patterns for investment casting. Integrally cored ceramic molds for investment casting of turbine blades have been fabricated using ceramic stereo lithography (Bae, 2008), and as well as by gel casting ceramic slurry into plastic molds made from SLA patterns (Wu *et al.*, 2009a,b). The shortcomings of the traditional investment casting are a complex process, a long manufacturing time, high cost, and that they pose the bottleneck of pattern making (Feng and Zhang, 1999). In today's competitive environment, the manufacturing industries are striving for development of next generation products due to increasing competition among the products and continuously changing customer needs. Among the challenging tasks the manufacturers are facing include increasing product complexity. This has emerged the concept of rapid physical realization of products well before its manufacturing (Ingole *et al.*, 2009). The cost of WAX pattern making with the help of conventional investment casting method is costlier than the ABS pattern making in FDM. The use of benefits in terms costs have proved that the adoption of AM technology is technoeconomically justifiable for the Indian manufacturing industries. AM has proved to be a cost-effective and time-efficient approach for the development of pattern making, thereby ensuring the possibility for technology transfer in Indian manufacturing industries (Jauhar *et al.*, 2012). Many methods for rapid tooling (RT) have been developed so far, for the application on many production processes including injection molding (Barlow *et al.*, 1996; Masood and Song, 2004; Vasconcelos *et al.*, 2004, 2006; Ma *et al.*, 2007; Ingole *et al.*, 2009, 2002; Hsu *et al.*, 2008), investment casting (Ingole *et al.*, 2009), sheet metal forming (Colton and Park, 2003), and resin transfer molding (RTM) (Gibbons *et al.*, 2010).

The first use of AM-fabricated patterns as sacrificial patterns in traditional investment casting (IC) started in 1989 (Greenbaum and Khan, 1993). Since then all major AM techniques have been used in different casting methods to provide RC solution for producing metal parts. HDPE, being an abundantly available material, has been chosen for this purpose. HDPE is primarily used for the production of bottles especially for food products, detergents and cosmetics, containers, toys, house wares, fuel tanks and industrial wrapping and film, sheets, gas, and waste pipes. However recycled HDPE is used for producing industrial bags, detergent bottles, pipes, containers, and wood substitute, for example, animal flooring and fencing (APME, 1993). HDPE is a linear polymer with the chemical composition of polyethylene, $(CH_2)_n$, and is defined by ASTM D1248-84 as a product of ethylene polymerization with a density of 0.94 g/cm^3 or higher. Postconsumer recycled HDPE exhibits adequate process ability and a balance of physical properties adequate for a number of noncritical applications in blow molding (Ashraf, 2000). These processes usually use commodity polymers such as PVC, PS, PP, LDPE, and HDPE. The extrusion part of the process is continuous and the rest is cyclic (McCrum *et al.*, 1997). The principal types of polymers in municipal solid waste (MSW) are polyolefins (PO), consisting of polyethylene (low density or LDPE and high density or HDPE) and polypropylene (PP), polystyrene (PS), polyvinylchloride (PVC), and polyethylene terephthalate (PET) (Alter, 1993). In this article an effort has been made to prepare a metal matrix composite by using the investment casting route. Further, waste polymer, mainly HDPE and LDPE, has been selected as matrix material and some of the reinforcements, namely, SiC and Al_2O_3 , have been used as filler material.

Process

Fig. 1 shows the process flow diagram for preparation of aluminum matrix composite (AMC).

This study highlights the processing of HDPE with ceramic reinforcements, keeping the aim of preparing the final product via investment casting route. Initially, waste polymer was collected from industry and recycled for its further use. Recycling of HDPE includes extrusion through single screw. There are various methods available for recycling of polymer including primary, secondary, tertiary, and quaternary (Al-Salem *et al.*, 2009). Primary and secondary recycling includes extrusion, injection molding, and drawing. In tertiary recycling chemicals are used for processing of the polymer and in the quaternary scheme energy recovery is the main motive behind recycling (Hopewell *et al.*, 2009). This article purely concentrates on the recycling by extrusion route and further use of the delivered product in the form of wire in 3D printing applications for preparation of the patterns for investment casting. An effort has been made to develop FDM filament wire by using the waste (HDPE) as matrix material and SiC/ Al_2O_3 as reinforcements. Waste material and reinforcement were blended together in various proportions by using mini compounder and then processed by using the single screw extruder and rheological and thermal behavior was tested. After experimentation SEM analysis was carried out to ensure dispersion and structure of obtained filament wire. After getting all the results from the SEM analysis those wires were made to run in a 3D printing machine to prepare the patterns for the investment casting. Patterns made by using fused deposition modeling were then carried for the final stage of casting and layers were laid on the pattern for further step. Finally aluminum metal was poured into the sprue and castings were obtained after disposing of the outer structure of investment casting. Finally, the obtained parts were studied for their enhanced properties. The main motive of this work was to prepare a functionally graded material having presence of the reinforcements that were added to the HDPE.

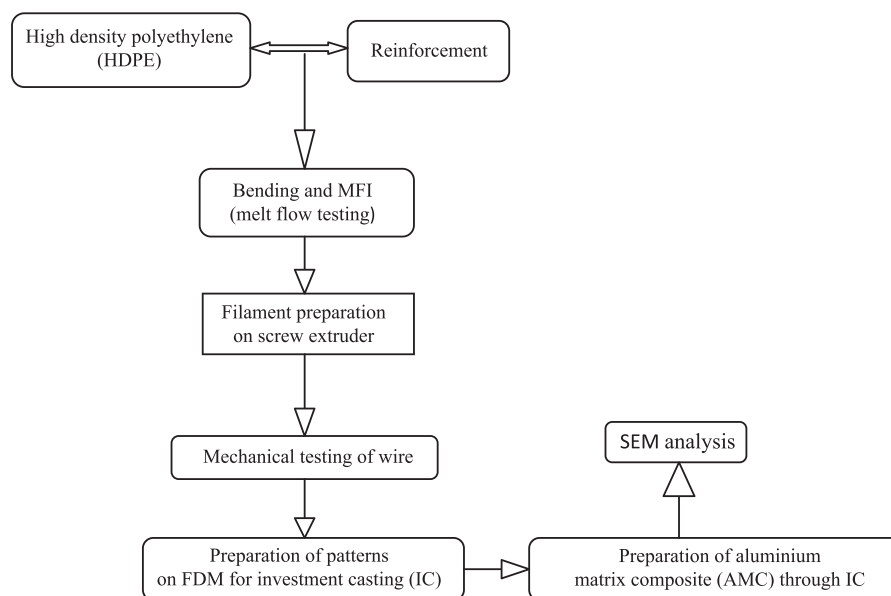


Fig. 1 Process flow diagram.

Material Processing

HDPE and ceramic material (Al_2O_3 and SiC) have been selected as matrix material and reinforcement respectively. The aim of this study was to investigate the new possibilities of reusing the plastic solid waste (PSW) while reinforcing some of the foreign particles. HDPE is available in various grades as we are working in area of extrusion so extrusion grade HDPE has been selected. Both the materials were blended together, in various proportions by using twin screw extruder (Fig. 2), in weight percentage and tested for their rheological properties (MFI) (as per ASTM-D-1238 standard), which came out to be in range of 12 g/10 min.

Setup of twin screw extruder has been shown in Fig. 2, used for uniform mixing of the matrix material and reinforcements. Rheological properties of HDPE may vary as it is very difficult to know about the number of processes done on available material. Further, thermal behavior of various proportions was tested by using DSC testing equipment. The major reason behind thermal testing is to get information about the melting and decomposition range of the proposed material. After getting results from DSC, proportions were prepared in higher quantities and fed into the twin screw extruder for uniform dispersion of reinforcement and matrix material and obtained in form of pellets. After getting material from the twin screw extruder, pellets were fed into the single screw extruder (L/D ratio-20) and filament wires were obtained according to Taguchi L9 array. Those wires were tested for their mechanical and thermal properties on universal tensile testing machine and DSC, respectively.

Experimentation

Experimentation of HDPE and reinforcement starts with the blending of the materials with the help of the proper bonding agent, i.e., paraffin wax. Three different proportions were prepared in weight percentage. For this study $\text{SiC}/\text{Al}_2\text{O}_3$ of size 20 μm were used in equal weight percentage, i.e., 10%, 20%, and 30%. After preparing three different proportions of base matrix and reinforcements as said above MFI (melt flow index (grams/10 min)) was calculated by using the melt flow indexer machine to understand flow behavior of materials as this material has to be run through the FDM setup. The reason behind testing of rheological and thermal properties is that FDM setup optimizations have to be done on the basis flow behavior and thermal behavior of reinforced material. Table 1 shows the MFI data for the various proportions of HDPE and $\text{SiC}/\text{Al}_2\text{O}_3$ reinforcements.

The MFI is one of the standard tests for ascertaining the rheological properties of polymeric materials. It defines the ease with which a thermoplastic polymer can flow. In the present study MFI investigations have been conducted as per ASTM-D-1238 standard. As observed from Table 1, MFI values for different proportions of reinforcement are coming in range of 10–12 g/10 min, where as MFI value for 100% HDPE is coming around 9–10 g/10 min. Hence it can be said that after adding the reinforcements, MFI of the composite material increases up to some extent. After establishing the MFI of the composite material, further thermal behavior was tested by using differential scanning calorimeter (DSC).

Thermal Testing

The thermal testing of the material comprises of the DSC test, where material can be tested along the line of the melting range, which ensures the proper and accurate measurement of thermal characteristics of the material. Fig. 3 depicts the basic setup of the DSC machine.

Melting range of the material comprises melting temperature, enthalpy, and the decomposition of the material. Various samples of the waste polymer comprising of the HDPE, Al_2O_3 , and SiC were prepared by using the twin screw extruder to ensure

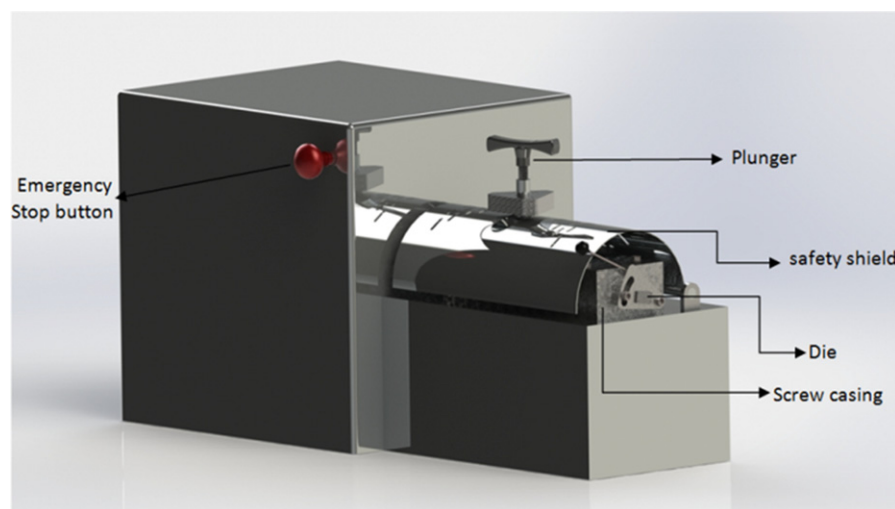
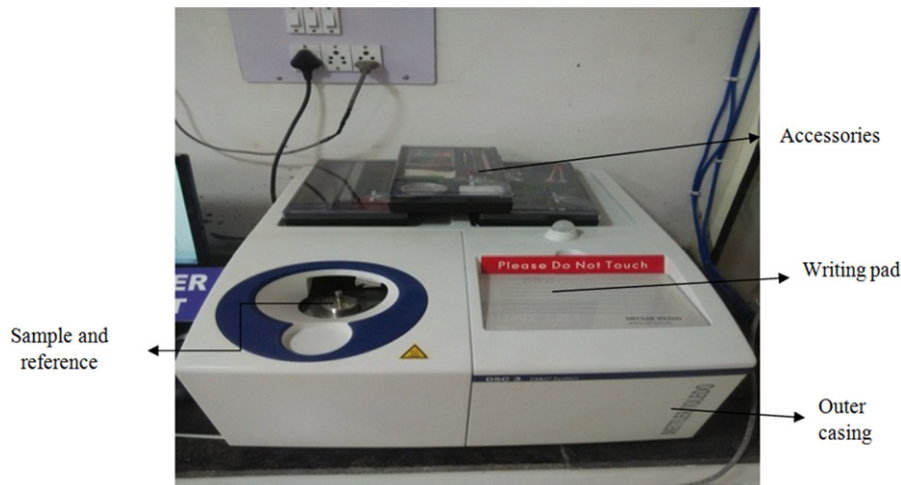


Fig. 2 Twin screw extruder setup.

Table 1 Melt flow index (MFI) values for different proportions by weight percentage

Serial number	High-density polyethylene (HDPE) 100%	HDPE + SiC + Al ₂ O ₃ (by weight)		
		Proportion 1 90% + 5% + 5%	Proportion 2 80% + 10% + 10%	Proportion 3 70% + 15% + 15%
1	8.935	11.19	10.03	9.98
2	10	11.8	10.825	11.185
3	9.94	10.8	11.01	12
Avg	9.625	11.26333	10.62167	11.055

**Fig. 3** Differential scanning calorimeter (DSC) setup.

the high dispersion rate and tested to study the effect of the reinforcement on the thermal properties of the waste polymer. **Fig. 4** shows the DSC graph of 90% HDPE and 10% (Al₂O₃ and SiC).

Fig. 4 shows the DSC graph of the waste polymer consisting of a defined quantity of the reinforcement. Under this, three cycles of testing were performed to eliminate any kind of stress and materials history as this material is a waste polymer that may consist of some prestored history because of the number of recycling cycles done previously. In the first cycle of heating all the stress was assumed to be relieved. Further it can be clearly seen that melting temperature of the proportion varies from 120°C to 122°C, shown in hatched area in graph. Melting of the material starts from 122°C and ends at 132°C. While under melting state, the material's enthalpy was calculated to be -500.51 mJ while enthalpy of the material also follows a particular trend. In the first cycle after melting of the material at 122°C–132°C, a small drop in the graph line occurs, which shows the melting of the material. As primary material, HDPE has been melted previously at 122°C. This sudden drop might be due to the melting of the some pigment (color) present in waste polymer. Al₂O₃ and SiC cannot melt at this temperature as these contain melting range above 1000°C. After the first cycle of heating up to 300°C, the material was given a cooling cycle. It can be seen from **Fig. 4** that when the temperature came close to 119°C a sudden peak appears, which shows the convergence of material from melt stage to solid stage releasing some energy, i.e., 471.85 mJ and continuing to release energy. In the second cycle of heating after melting of material, the curve remains stable unlike in the first heating cycle and continues to follow same trend in the third heating cycles also. Pigment or any impurity is assumed to be eliminated in the first cycle of heating. Another sample of different proportion, i.e., 80% HDPE and 20% reinforcement (Al₂O₃ and SiC), was tested to ensure the trend followed by the previous sample. After DSC, test material was set for further experimentation.

Filament Preparation

After successful testing of the composite material all three proportions (as per **Table 1**) were prepared in higher quantities and subjected to single screw extruder for preparation of filament wire that could possibly run on the FDM machine. **Table 2** shows various parameters selected and their corresponding signal to noise (SN) ratios for selected output parameters according to the Taguchi L9 orthogonal array.

Form SN ratio analysis it has been observed that the second level of composition (80% HDPE + 10% SiC + 10%Al₂O₃), first level of die temperature 110°C, and third level of barrel temperature 130°C give the best result but this combination does not exist

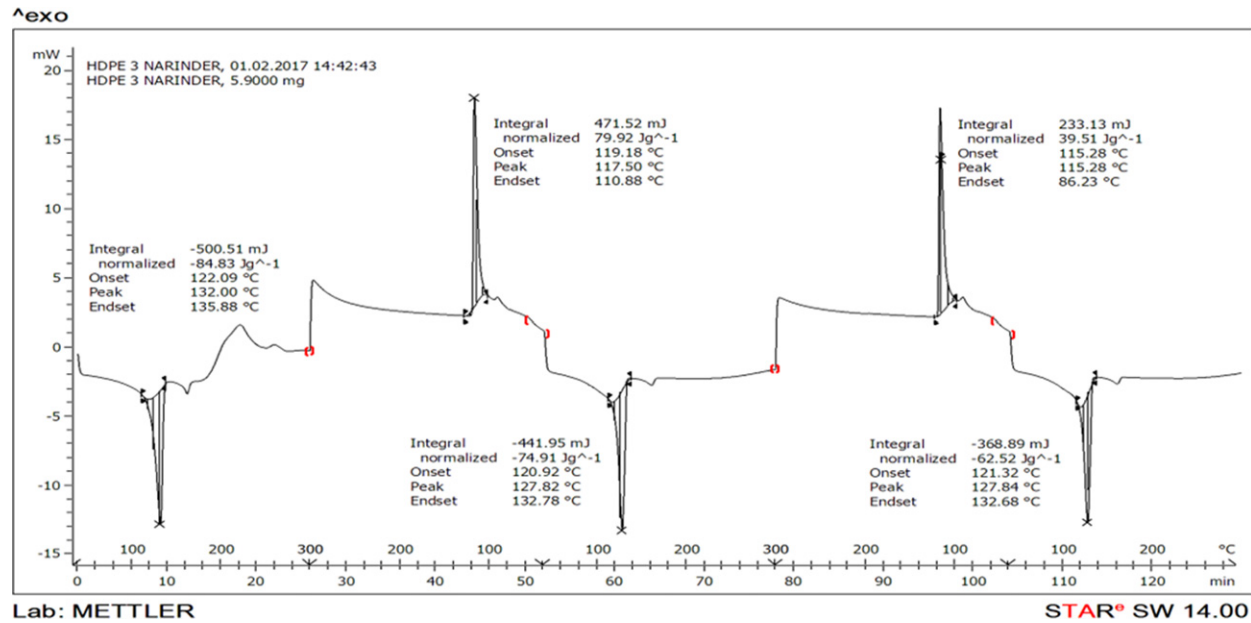


Fig. 4 Differential scanning calorimeter (DSC) graph for the proportion 90% high-density polyethylene (HDPE) and 10% (Al_2O_3 and SiC).

Table 2 Control log for experimental study

S.No	Proportions	DT	BT	PS	SN for PS	PL	SN for PL	B S	SN for BS	%age elongation	SN for % elongation
1	1	110	110	21.03	26.45	51.04	34.15	20.11	26.07	11.265	21.034
2	1	120	120	22.2	26.92	52.3	34.37	20.99	26.44	12.556	21.977
3	1	130	130	23.24	27.32	53.33	34.53	21.53	26.66	13.256	22.448
4	2	110	120	21.3	26.56	51.4	34.21	20.25	26.13	10.2569	20.220
5	2	120	130	22.36	26.98	52.45	34.39	20.95	26.42	11.256	21.027
6	2	130	110	23.52	27.42	53.61	34.58	21.03	26.45	11.968	21.560
7	3	110	130	21.62	26.69	51.59	34.25	21.25	26.54	11.021	20.844
8	3	120	110	22.48	27.05	52.51	34.40	21.86	26.96	12.211	21.735
9	3	130	120	23.87	27.55	53.92	34.63	22.59	27.08	13.456	22.578

Note: DT, BT, PS in (MPa), PL in Newton, BS (MPa) signifies Die temperature in °C, barrel temperature in °C, peak strength, peak load and break strength respectively.

in the present analysis. So, a confirmatory experiment was performed and values were counterverified. Finally, peak strength 24.53 MPa, peak load 55.16 MPa, break strength 24.56 MPa, and % elongation 10.01% has been attained.

Proportions, which were prepared according to the [Table 1](#), were processed on single screw extruder for filament preparation (see [Fig. 5](#)). After preparation of filament wires, samples from each wire have been taken to test thermal properties on DSC testing equipment.

After obtaining all the results for the mechanical testing, the wire was made to run on the fused deposition modeling machine (3D printer). Further, parts with definite dimension (20 mm × 20 mm × 20 mm) were made by the same route and prepared for the investment casting. [Fig. 6](#) shows the actual photographs of HDPE parts prepared by the 3D printer. The motive of the investment casting of the parts is to enhance the surface properties of the metal or material that is being used for casting. In this process, after dewaxing, reinforcement would remain inside and would adhere to the metal surface being casted. This process would make final casted product a functionally graded material, carrying reinforcements on its surface enhancing surface properties.

After making all the 3D parts with the help of FDM machine, parts were taken for the investment casting as per steps recommended ([Singh, 2013](#)). For investment casting, aluminum has been chosen being a soft metal as compared to the other metal so that effects could be seen clearly. For investment casting purpose an IC tree was designed first as given in [Fig. 7](#). Different parts of the IC tree have been labeled.

After preparing the IC tree all the parts prepared on 3D printing machine have been attached to the arms of the tree, and the process for the IC has been followed.

At first stage of experimentation, pilot experiments were conducted wherein cubical patterns were prepared. It has been found that size of FDM reinforced pattern expands while layered on the platform and expansion of patterns lies between 0.13 and 0.67 mm.



Fig. 5 Filament wire prepared by single screw extruder.



Fig. 6 Parts prepared by fused deposition modeling (FDM) machine by using filament wire.

Barrel finishing, one of the widely used processes for surface finishing of FDM parts, was introduced at the intermediate stage for the improvement of surface finishing of FDM reinforced patterns prior to ceramic molding. Ceramic molding was done using zircon sand and ceramic molds were prepared. Finally, the prepared IC molds and the pouring of molten Al metal into cavity are shown in **Fig. 8(a)** and **(b)**, respectively.

Fig. 8(a) and **(b)** shows the various stages completed during the investment casting. After completion, the IC parts were then segregated and collected. Further collected parts were then finished by disk polishing machine in order to clean the surface and then optical micrographs were taken to ensure the presence of the SiC and Al_2O_3 on the surface of the casted product. **Fig. 9** shows the optical micrographs of the final parts showing reinforcements of the surface.

In **Fig. 9**, the presence of the reinforced particles (SiC, Al_2O_3) can be clearly seen. Further to ensure the presence of the reinforcements, part was subjected to the scanning electron microscope and the image was taken as shown in **Fig. 10**.

In **Fig. 10**, the presence of the reinforced particle can be clearly seen on the surface of the casted product. Further it would lead to the enhancement of the surface properties of the final product. In this article focus was to develop the functionally graded material in the form of metal matrix composite leading to the increase in the application domain of the material prepared.

Conclusions

In the present case study, aluminum matrix composite (AMC) has been successfully developed using new methodology. Initially, in-house prepared filament wire was tested for the mechanical properties and very promising results (peak strength 24.53 MPa, peak load 55.16 MPa, break strength 24.56 MPa, and % elongation 10.01%) have been attained. After filament wire testing, wire was used to prepare patterns on then FDM machine. Patterns were then used for sacrificial investment casting and AMC was

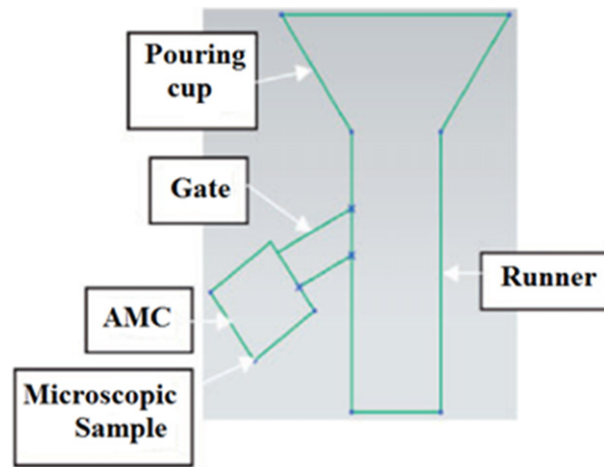


Fig. 7 Design tree for investment casting.



(a)



(b)

Fig. 8 (a) Final prepared patterns and (b) pouring of aluminum metal.

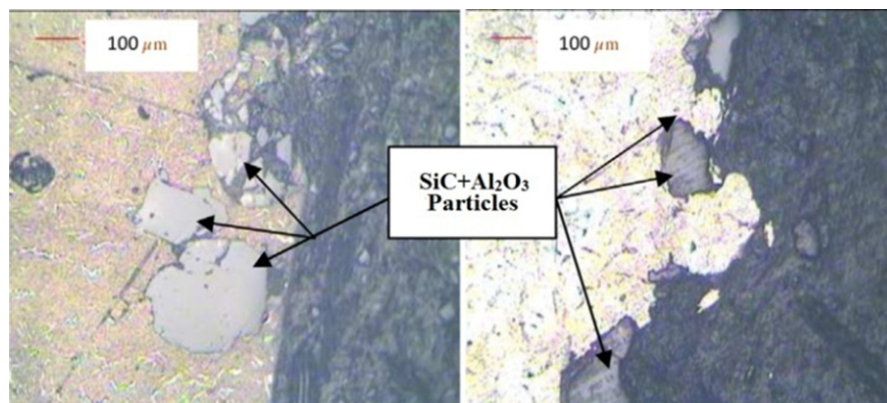


Fig. 9 Photomicrographs of finally prepared casting.

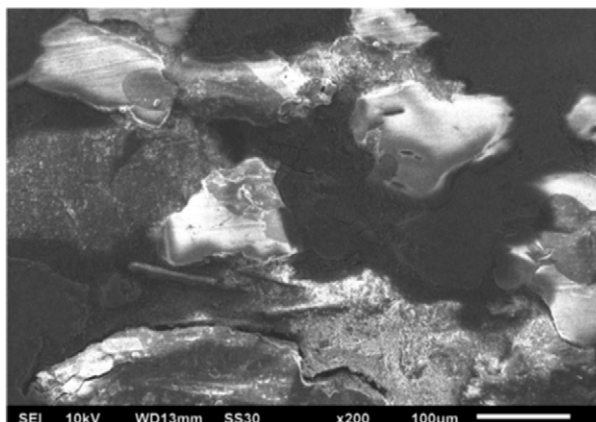


Fig. 10 SEM analysis of MMC.

obtained. AMC was subjected to microstructure evaluation, which highlighted the presence of SiC and Al_2O_3 particles. Further in this article various other processing techniques have been discussed that are necessary for taking out the vital results in terms of the surface properties. After casting of the product, SEM analysis was carried out, which shows the uniform presence of SiC and Al_2O_3 particles on the surface to ensure the formation of the functionally graded material.

Acknowledgment

The authors are thankful to DST (GoI) for financial support.

See also: Development of HAp Reinforced Biodegradable Porous Structure Through Polymer Deposition Technology for Tissue Engineering Applications. Investigations for Rapid Tooling Prepared With Waste Polymer-Based Hybrid Filament

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Further Reading

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Investigations for Rapid Tooling Prepared With Waste Polymer-Based Hybrid Filament

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Introduction

The rapid development of plastic/polymer consumption in different applications led to the research of innovative recycling procedures and improvement in previous strategies (Al-Salem *et al.*, 2009). Plastic/polymer solid waste (PSW) is showing new challenges and opportunity to the universe regardless of its technological advances and sustainability awareness (Al-Salem *et al.*, 2009). Most common waste plastic accumulation is in municipal solid waste (MSW). Plastics in MSW consist of different kind of polymer wastes like high density polyethylene (HDPE), polyethylene terephthalate (PET), plastic films made of low density polyethylene (LDPE), and of hard plastic made of HDPE (Rigamonti *et al.*, 2014). After a single use, most of the plastic/polymer is disposed resulting in huge amount of waste collection (Jayaraman and Halliwell, 2009). The level of plastic waste in landfills is increasing, taking up a larger and larger space, and taking hundreds of years for disposal (AnuarSharuddin *et al.*, 2016). That is why recycling of PSW becomes a present-day need. Polymer recycling is a method for reduction of environmental problems caused by polymeric waste generation from day-to-day applications of polymer materials such as packaging and construction (Hamad *et al.*, 2013). Reusing plastics has a number of advantages, characterized by (1) conservation of fossil fuels since plastic production uses 4%–8% of global oil production, i.e., 4% as feedstock and 4% during conversion (Perdon, 2004; JCR, 2006); (2) reduction of energy and MSW; and (3) reduction of carbon dioxide (CO₂), nitrogen oxides (NO_x), and sulfur dioxide (SO₂) emissions. The continued development of recycling and recovery technologies, investment in infrastructure, the establishment of viable markets, and participation by industry, government, and consumers are all considered priorities of the highest order (Scheirs, 1998). Various recycling methods are available in the present-day scenario; some of them are primary, secondary, tertiary, and quaternary. Further they can be subdivided in to various techniques like mechanical, chemical, incineration, etc. (Kumar *et al.*, 2011). Amongst these techniques and methods, mechanical methods are more popular and simple including extrusion, pelletizing, drawing, etc. (Campbell and Spalding, 2013). In life cycle assessment (LCA) studies, a “system” is defined (with boundaries indicated by broken lines). Energy and raw materials from the “environment” are used in the system. Emissions, including solid waste, leave the system and enter the environment. Waste prevention includes the role of cleaner production, innovative services, sustainable consumption, and prevention by design (Kirkby *et al.*, 2004). Fig. 1 shows roles of waste prevention and integrated waste management. The low cost and remarkable properties like strength, temperature/chemically resistance, nonconductivity, and reprocessability or reusability (Rosato *et al.*, 2001) of polymers attract the interest of researchers for their use in various applications in the field of engineering, aerospace, biomedical science, etc. Thermoplastics materials have low melting point and could be easily molded into a variety of shapes by heating (Bodener and Micklos, 2004). The biocompatibility of some polymers makes them possible for use in biomedical applications. The polymers like PVC, PP, polyether ether ketone (PEEK), poly lactic acid (PLA), etc. are the most widely used polymers in the biomedical field, particularly in the fields of tissue engineering and drug delivery.

Biocompatibility is defined as adaptability of some foreign component by the body environment without producing any adverse effect to the functionality of the system. In medical science, biocompatibility is known as the interaction of any medical part or component material with the tissue or living system. So in general a biocompatible object does not provide any harm to the patient (Lendlein and Sisson, 2011; Tian *et al.*, 2012). Most plastics intended for medical devices including medical grades of PVC, polyethylene, polycarbonate, PEEK, Ultem PEI, polypropylene, polysulfone and polyurethane, and all these have to undergo the stringent tests before their actual use in medical applications (Majumdar, 1998). As compared to other materials the mechanical processing of the polymers requires much less energy (Rosato *et al.*, 2001; Abeykoon *et al.*, 2014). The extrusion process is mainly used for conversion of raw polymer grains into usable rod or wire form. For reinforcement of ceramic or metal particles in the polymer matrix, a twin-screw extruder has been generally used (Erdmenger, 1964). Twin-screw extruders have numerous advantages over single-screw extruders like better feeding and more positive conveying characteristics, i.e., allow the machine to process hard-to-feed materials (Wendaal, 2014). Some studies highlighted that the synthetic HAp particles were reinforced into a polymer matrix to produce composites for medical applications and corotating twin-screw compounding produces an effective and homogeneous distribution of HAp particles in a polymers matrix, which is maintained after compression molding (Wright, 2016; Wang *et al.*, 1994).

These polymer filaments can be easily used in the biomedical applications with the help of additive manufacturing (AM). The traditional way of implant fabrication has been now replaced with AM, in which the implants have been directly fabricated from the 3D CAD data (Kurtzman, 2010). Nowadays the AM and CAD have been directly integrated with the 3D imaging techniques, i.e., MRI, CT scan, etc. (Tukuru *et al.*, 2008). In AM, functional and nonfunctional prototypes of the polymers have been fabricated by continuously adding layer by layer of material until the digital CAD model has been completely converted into a real-time 3D object (Huang *et al.*, 2015). During the past decade a number of patents have been claimed by inventing vivid types of AM

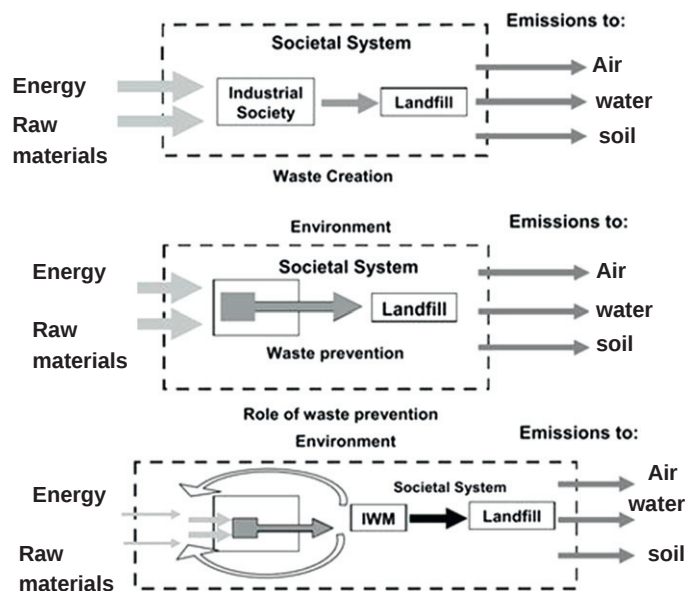


Fig. 1 Respective roles of waste prevention and integrated waste management. Powers, R.W., 1995. The role of recycling in municipal solid waste management to the year 2000. *Japan Tappi Journal* 49(3), 513–519.

technologies, thus resulting in more and more users being able to install 3D printers to produce functional products (Wohlers and Caffrey, 2013; Korpela *et al.*, 2013; Zein *et al.*, 2002). The scope of AM is continuously increasing for biomedical applications with the combination of natural and synthetic polymers by reinforcement of ceramics, metals, and other foreign particles in these polymers (Seitz *et al.*, 2005).

FDM is one of the most widely used AM techniques for fabrication of 3D scaffolds having adequate mechanical, thermal, as well as surface properties for proper implant placement (Galantucci *et al.*, 2009; Sood *et al.*, 2009). FDM produces the best fit bio-functional parts in very short duration without waste material. FDM uses the 3D CAD model to fabricate the actual product. Initially the CAD created file has been converted into STL format, i.e., machine language, by using a preprocessing software (Boschetto *et al.*, 2013; Singh *et al.*, 2016, 2017). The .stl file has been further sliced into two dimensional layers by using an open source software K-Slicer (Chua *et al.*, 2010). The filament has been extruded through the extrusion head having temperature near about the melting point of the material. The temperature of the chamber remains constant to prevent the solidifying material from experiencing thermal stress and distortion. The main advantages of FDM over other AM techniques are its trouble-free handling, and it provides controllable factors that have been adjusted according to the required properties of the fabricated part (Sahebrao *et al.*, 2009; Ivanova *et al.*, 2013). The controllable parameters of FDM affect the various properties of the extruded products (Singh *et al.*, 2016).

In this work the detailed procedure has been highlighted for development of RT by preparing feed stock filament wire from recycled/waste HDPE and LDPE polymers as base matrix with different particle sizes of SiC/Al₂O₃ as reinforcement. The HDPE and LDPE were collected from household waste and after manual segregation, different particle size (i.e., single particle size (SPS), double particle size (DPS), and triple particle size (TPS) in different proportions) of SiC/Al₂O₃ were added independently to HDPE and LDPE. The melt flow index (MFI) of these combinations/proportions was computed as per ASTM D1238-73 standard. After evaluation of MFIs, the best combinations were selected and used for filament wire preparation on the twin-screw extruder. The output properties, i.e., peak strength, break strength, peak elongation, break elongation, etc., were modeled for multifactor optimization. The filament wires were made to run on commercial fused deposition modeling (FDM) three dimensional printer (open source) for preparation of cylindrical pins (selected as RT) for wear testing. These pins were made to run on pin on disk apparatus for ascertaining the wear properties. Finally differential scanning calorimetry (DSC) was also performed to predict thermal behavior for field engineers.

Methodology

Melt Flow Index Tester

As stated, HDPE and LDPE have been selected as parent material for this study. The reason behind the selection of HDPE and LDPE was that some of the researchers have gotten good results after making reinforcements of different materials like talc powder, waste printed circuit boards, recycled wood, sand, natural fiber in HDPE and LDPE (Sanchez-Soto *et al.*, 2008; Yang *et al.*, 2015). In this work metallic powder like SiC, Al₂O₃ have been selected as reinforcement to improve the mechanical properties. After selection of reinforcements a pilot experiment was performed for establishment of MFI for various combinations of proportions of SiC, Al₂O₃ with HDPE and LDPE matrix on melt flow indexer machine (see Appendix A). MFI is the standard test for obtaining

flow behavior of polymer (Navratil *et al.*, 2015). MFI of ABS is 2.411 g/10 min as per ASTM-D-1238 standard (at 230°C temperature and 3.8 kg force) (Singh and Singh, 2015). MFI of HDPE and LDPE was established by varying various combinations/proportion of HDPE and SiC, Al_2O_3 .

Procedure to determine MFI:

- To determine MFI of certain composition, mixture is poured into the cylinder and a temperature condition is set.
- Then the machine is left for some time to achieve the predefined temperature.
- After establishing a predefined temperature, pressure is applied with the piston bar into the cylinder by certain weight above the piston bar.
- With application of pressure with certain weight, flow of material occurs through the die face in the form of wire.

The material collected in 10 min is further subjected to weighing balance to determine its mass. So, deposition of material through the melt flow tester in 10 min is considered as the MFI. Fig. 2 shows the basic schematic and pictorial view of MFI tester.

From Appendix A, various composition sets for SPS, DPS, TPS particles of SiC/ Al_2O_3 were considered and least values for each set are shortlisted in Appendix B.

Twin-Screw Extruder

The twin-screw extruder was developed more than 20 years ago, for continuous production of highly uniform and finely structure products. It is widely used to produce biosourced plastics, cellulose pulps, and food products. Figs. 3 and 4 show the schematic and pictorial view of a twin-screw extruder. For this study commercial make HAAKE Mini CTW, Germany has been used.

As per Appendix B, various combinations of HDPE/LDPE and SiC/ Al_2O_3 were selected and used for filament wire preparation on twin-screw extruder. Fig. 5 shows the wires of HDPE and LDPE prepared on twin-screw extruder. Four process parameters were taken for twin-screw extruder (namely, composition, load, rpm, and temperature of barrel). Six levels of one parameter (composition/proportion) and three levels of the other three parameters (load, rpm, and temperature of barrel) were taken and explored by using Taguchi L18 orthogonal array technique separately for HDPE and LDPE. Appendix C shows various combinations of input parameters taken for this study.

Universal Tensile Tester

Tensile test is the most accepted test regarding judgment for quality of weld. This test is performed on a universal tensile tester to check the tensile strength at peak as well at break of joint. Fig. 6 shows the universal tensile tester having capacity of 5000 N, used only for the plastic or rubber material. Plastic wires, plastic flats, or strips of any size can be measured by this universal tensile tester.

The filament wires so produced as per Appendix C were tested mechanically on a universal tensile tester (UTT). The results of UTT are summarized in Appendix D. Fig. 7 shows peak load versus elongation curve of HDPE reinforced filament.

Fused Deposition Modeling

In 1988, FDM was invented in the United States and was patented in 1992 as a rapid prototyping/AM technology. Commercially the FDM is marketed by the Stratasys Inc. Nowadays, FDM is a well-known additive technology used for the fabrication of actual or nonactual prototypes. Similar to other AM technology, it is also a manufacturing tool that produces the part by stacking the material in a layer-by-layer technique. It is commonly used for pattern making, modeling, and various production applications. Fig. 8 shows the complete view of the FDM process.

Various advantages and disadvantages of FDM process are listed as in Table 1.

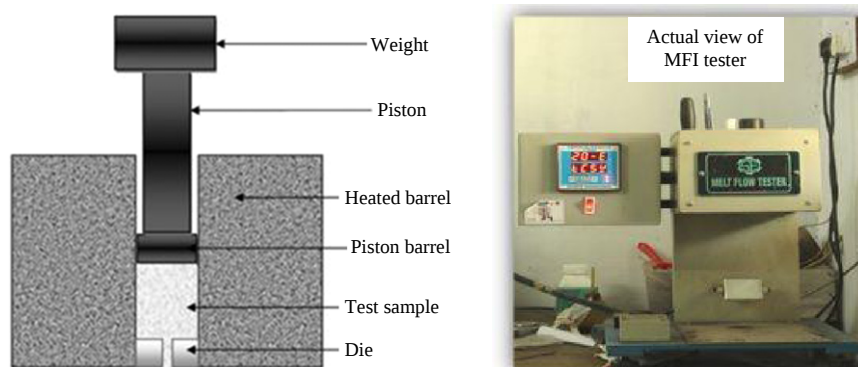


Fig. 2 MFI Testing.

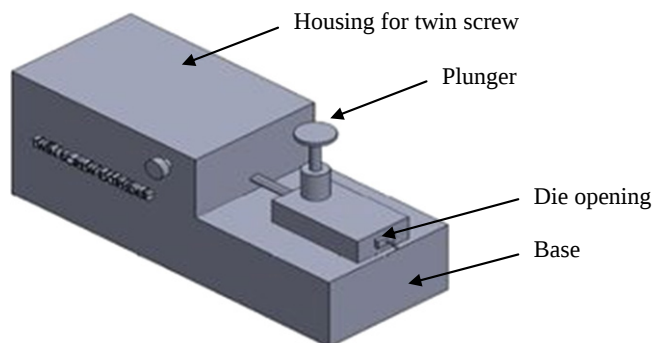


Fig. 3 Schematic of twin-screw extruder.

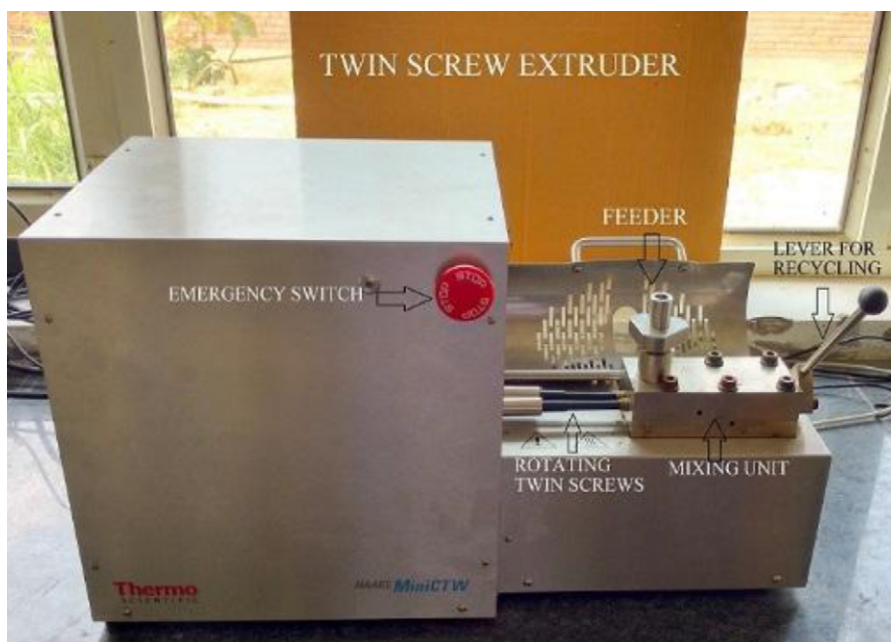


Fig. 4 Pictorial view of twin extruder (make: HAAKE Mini CTW, Germany). Wire of HDPE, Wire of LDPE.

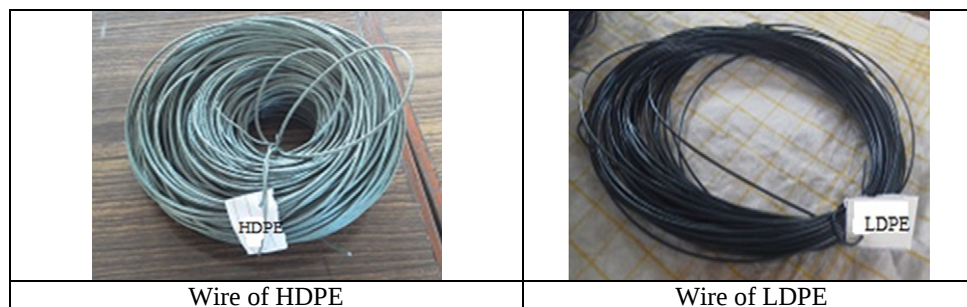


Fig. 5 Wires of HDPE and LDPE made using twin-screw extruder.

Cylindrical pins of Pure HDPE (100% by weight), pure LDPE (100% by weight), TPS reinforced HDPE (i.e., HDPE as 60% by weight), Al_2O_3 -300G as 13.33% by weight, Al_2O_3 -400G as 13.33% by weight, Al_2O_3 -500G as 13.33% by weight, and TPS reinforced LDPE (i.e., 60% by weight), SiC-300G as 13.33% by weight, SiC-400G as 13.33% by weight, SiC-500G as 13.33% by weight as shown in Fig. 9 were prepared on commercial FDM setup without change in any hardware or software of the system.

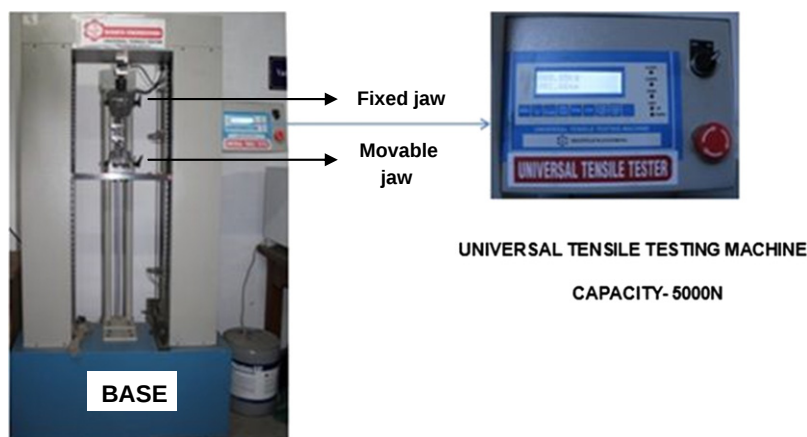


Fig. 6 Universal tensile tester in manufacturing Research Lab (GNDEC, Ludhiana).

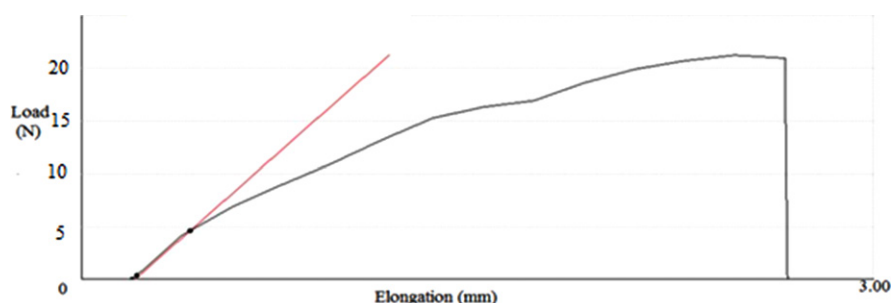


Fig. 7 Peak load versus elongation curve for HDPE.

Pin on disk experimentation

The pin on disk wear test was performed as per the ASTM G99 standard under dry sliding conditions at room temperature with a sliding velocity of 0.63 m/s and 80 mm track diameter. The machine was equipped with a data acquisition system.

The counter sliding surface for the pin was prepared by pasting silicon carbide (SiC) paper (600 grit size) on a steel disk (EN-32; hardness 65 HRC). **Fig. 10** shows a schematic of the pin-on-disk process.

The three process parameters i.e., RPM, load, and time, were taken for pin on disk standard experiment. Appendix E and F show wear values (in μm) for pure HDPE, TPS SiC HDPE, TPS Al_2O_3 HDPE and pure LDPE, TPS SiC LDPE, TPS Al_2O_3 LDPE pins under different conditions as per L9 orthogonal array technique.

Based upon Appendix E, it can be summarized that the Al_2O_3 based TPS reinforcement pin exhibits lesser wear values than that of pure HDPE and HDPE TPS SiC pins for the same trial runs ensuring better wear properties of the HDPE TPS Al_2O_3 pin.

Similarly, based upon Appendix F, it can be summarized that the SiC based TPS reinforcement pin exhibits lesser wear values than that of the pure LDPE and LDPE TPS Al_2O_3 pins for the same levels ensuring better wear properties of the LDPE TPS SiC pin.

Scanning electron microscopy

Scanning electron microscopy (SEM) has been performed on all HDPE based pins, i.e., pure HDPE, HDPE SiC pin, and HDPE TPS Al_2O_3 pin. **Fig. 11** shows SEM images of the pins at X400 magnification.

Since HDPE has high crystalline and low amorphous regions (more than 90% crystalline), it contains several side chains per 200 carbon atoms in the main carbon skeleton leading to long linear chains. As a result, it is closely packed and highly crystalline in nature. Further, density of HDPE is high and can range from 0.95 to 0.97 g/cm^3 . Although, HDPE with SiC as reinforcement should yield better wear properties than that of Al_2O_3 , as SiC is a harder material than Al_2O_3 , in this case, Al_2O_3 is proving to give better wear results when reinforced with HDPE. This may be due to the fact that the density of Al_2O_3 is more than that of SiC (3.98 g/cm^3 as compared to 3.21 g/cm^3), which means that there will be more particles of Al_2O_3 per unit volume in the HDPE matrix causing more ploughing of reinforcement particles from HDPE matrix when rubbed against the disk (during the pin on disk experiment), thus ensuring better wear properties. Similarly, SEM has been done for pure LDPE, LDPE SiC pin, and LDPE TPS Al_2O_3 pin. **Fig. 12** shows SEM images of the pins at X400 magnification.

As observed from **Fig. 12**, voids were created due to dislocation of reinforcement particles from LDPE matrix when rubbed against the disk during the pin on disk experiment. It can be clearly seen that small dislocations have been created in the case of the SiC reinforced pin as opposed to that of Al_2O_3 . Since LDPE has low crystalline and high amorphous regions and it contains fewer side chains per 100 carbon atoms in the main carbon skeleton, as a result, it is not very closely packed and less crystalline in nature.

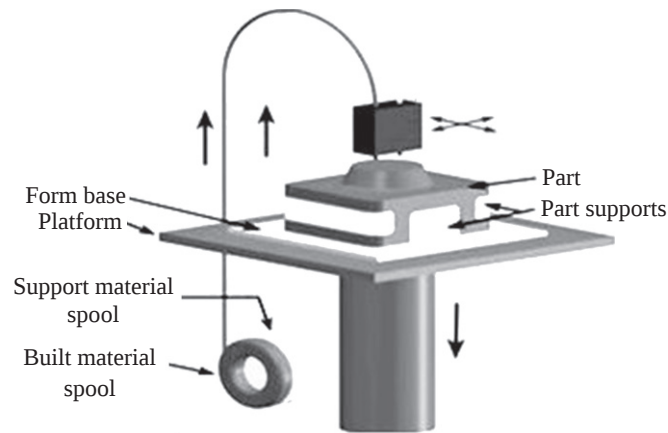


Fig. 8 Fused deposition modeling (FDM) process. Source: www.custompart.net.

Table 1 Advantages and disadvantages of FDM process

Advantages of FDM process	Disadvantages of FDM process
● Fabrication of functional prototypes/parts ● Availability of raw material ● Wastage of material is minimum ● No need of any toxic solvent ● Very low tolerance ● Ease in material change ● Support removal is easy	● Swelling of material in case of high temperature ● Surface finishing is not up to the mark ● Formation of gap in between the layers reduces the part strength ● Choking of nozzle head ● Slow manufacturing process ● Unpredictable distortion and shrinkage



Fig. 9 From left to right: Pins of pure HDPE, TPS SiC HDPE, TPS Al₂O₃ HDPE, pure LDPE, TPS SiC LDPE, TPS Al₂O₃ LDPE.

Further, density of LDPE is in range from 0.91 to 0.94 g/cm³. SiC, being a harder material than Al₂O₃, gave better wear results, when reinforced with LDPE as lesser ploughing of reinforcement particles from LDPE matrix will be there when rubbed against the disk, thus ensuring better wear properties.

Differential scanning calorimetry

Thermal behavior of the material is one of the major constraints for the use of developed filament in clinical dentistry. For thermal testing of the material in the present study DSC has been used. The term DSC simply implies that during a linear temperature ramp, quantitative calorimetric information can be obtained on the sample. This constantly rising temperature ensures the proper and accurate measurement of thermal characteristics of the material. The material exhibits heat flow as a function of temperature and time. DSC comprises of glass transition, melting point, enthalpy change, and decomposition of the material with respect to the rising of temperature. Common usage includes investigation, selection, comparison, and end-use performance evaluation of materials in research, quality control and production applications. For thermal analysis METTLER TOLEDO, Model DSC3, Swiss make with STAR[®] (SW 14.00) software was used in N₂ gas environment. The typical DSC setup determines the behavior of applied samples by taking references from a standard sample, both enclosed in a metallic crucible (Al or platinum). Further, thermal analysis of above stated TPS sample at level 3 for composition (major contributing factor, i.e., HDPE as 60% by weight, Al₂O₃-300G as 13.33% by weight, Al₂O₃-400G as 13.33% by weight, Al₂O₃-500G as 13.33% by weight), level 2 for temperature

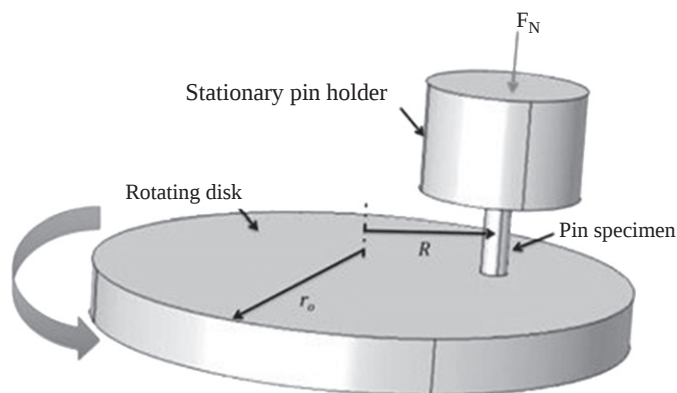


Fig. 10 Schematic of the pin-on-disk process. Reproduced from Kennedy, F.E., Lu, Y., Baker, I., 2015. Contact temperatures and their influence on wear during pin-on-disk tribotesting. *Tribology International* 82, 534–542.

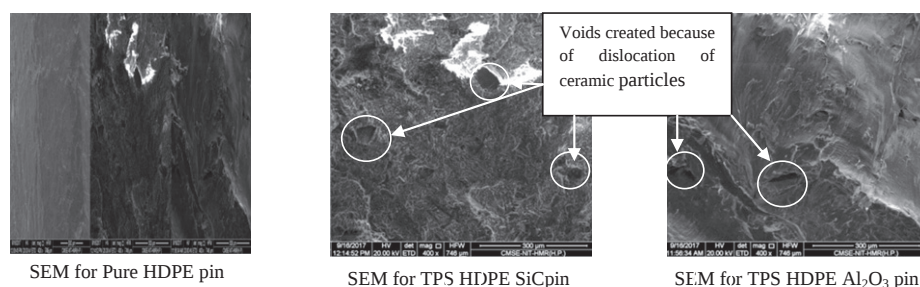


Fig. 11 SEM images of different HDPE pins. SEM for pure HDPE pin, SEM for TPS HDPE SiC pin, SEM for TPS HDPE Al₂O₃ pin.

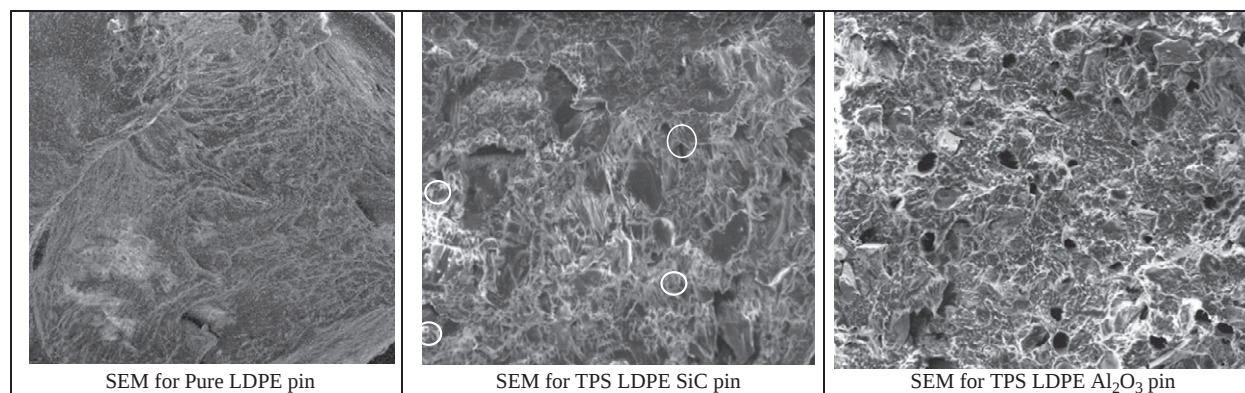


Fig. 12 shows SEM images of different LDPE pins. SEM for pure LDPE pin, SEM for TPS LDPE SiC pin, SEM for TPS LDPE Al₂O₃ pin.

(190°C), level 2 for RPM (40 rpm), and level 1 for load (5 kgf) was performed by using commercial DSC setup (Make: Mettler Toledo-DSC). The thermal plot for this sample is shown in **Fig. 13**.

Fig. 13 clearly depicts the 03 number of cycles for testing on DSC setup. These repetitions were necessary to eliminate any sort of effect arisen due to contamination and prestored history. The first cycle has probably removed the above said effect. Further melting range of the material can be clearly seen in the graph in the hatched area i.e., 175°C to 180°C. Melting of material starts at 175°C and goes to 180°C. Enthalpy in that melting range was counted to be – 229.65 mJ with a trend. In the first cycle of the DSC testing a heaped hatched curve was seen after the melting of HDPE. This shows the decomposition of some substance but surely this is not HDPE, as HDPE decomposes above 300°C. So, this might be decomposition of some of the contamination present in the form of the pigment (color). After that, the cooling cycle starts and sudden cooling can be seen as a straight vertical line. It can be easily observed that there is no evidence of decomposition of HDPE. Some uniformity has been observed in the 2nd and 3rd cycle also without any evidence of HDPE decomposition. After 3 cycles of heating, no significant effect was observed in terms of

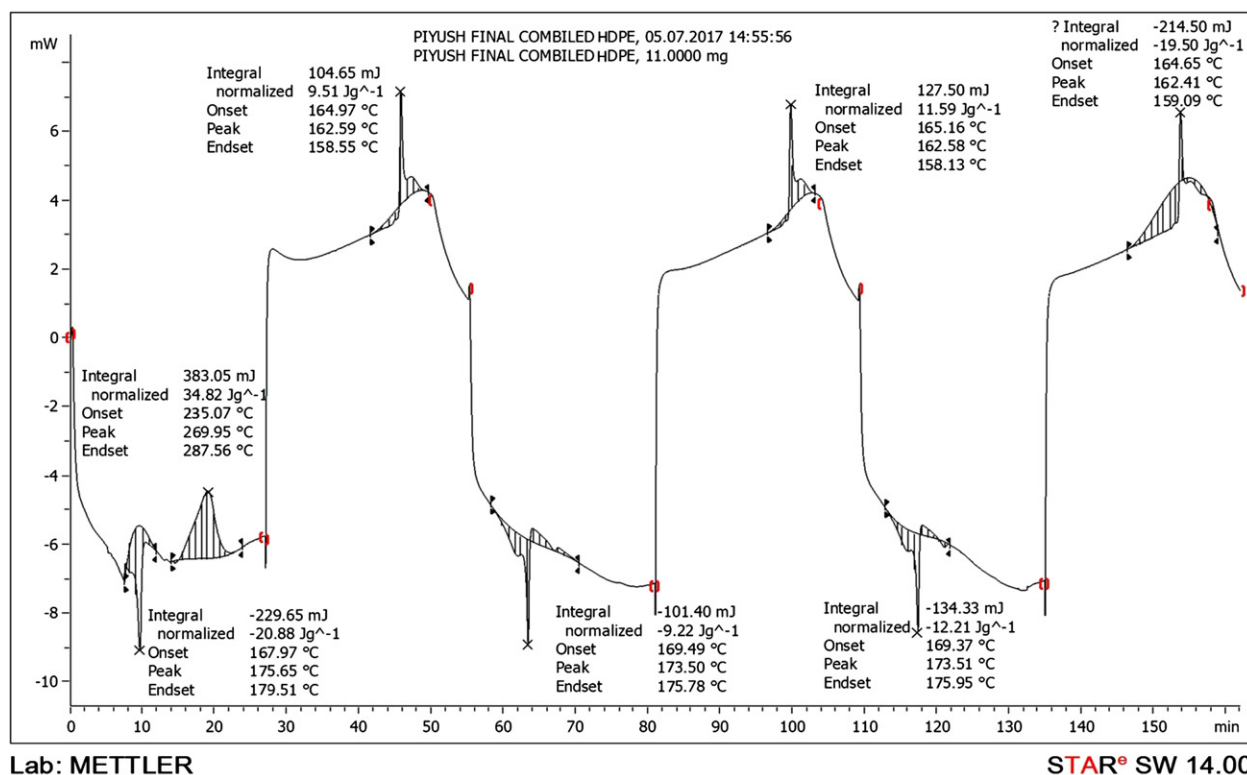


Fig. 13 DSC results of TPS Al₂O₃ reinforced HDPE sample.

melting and decomposition of material thus it can be ascertained that the part prepared from such filament wire will have high thermal stability. The results are in line with the observations made by other investigators.

Similarly, thermal analysis of above stated TPS SiC based LDPE sample (LDPE as 60% by weight, SiC-300G as 13.33% by weight, SiC-400G as 13.33% by weight, SiC-500G as 13.33% by weight) at level 1 for RPM (250 rpm) (major contributing factor), level 2 for time (10 min) and level 2 for load (2 kgf) was performed by using commercial DSC setup (Make: Mettler Toledo- DSC). The thermal plot for this sample is shown in Fig. 14.

Fig. 14 clearly depicts the 03 number of cycles for testing on DSC setup. These repetitions were necessary to eliminate any sort of effect arisen due to contamination and prestored history. First cycled has probably removed the above said effect. Further melting range of the material can be clearly seen in graph in the hatched area i.e., 125°C to 129°C. Melting of material starts at 125°C and goes to 129°C. Enthalpy in that melting range was counted to be - 94.34 mJ with a trend. In the first cycle of the DSC testing a heaped hatched curve was seen after the melting of LDPE. This shows the decomposition of some substance but surely this is not LDPE, as LDPE decomposes above 300°C. So, this might be decomposition of some of the contamination present in the form of the pigment (color). After that, cooling cycle starts and sudden cooling can be seen as a straight vertical line. It can be easily observed that there is no evidence of decomposition of LDPE. Some uniformity has been observed in the 2nd and 3rd cycle also without any evidence of LDPE decomposition. After 3 cycles of heating, no significant effect was observed in terms of melting and decomposition of material thus it can be ascertained that the part prepared from such filament wire will have high thermal stability. The results are in line with the observations made by other investigators.

Results and Discussion

Various signal to noise (SN) ratios of mechanical properties (by considering larger the better type case, independently for each property) as obtained by analysis of variance (ANOVA) by using Minitab software are summarized in Appendix G. Based upon Appendix G, Appendix H shows the percentage contribution of different input parameters on mechanical properties independently (by considering maximum the better type case). The results are at 95% confidence level. As observed from Appendix H, for HDPE, composition is the major factor contributing to peak load, break load, and Young's modulus and temperature is the major factor contributing to peak elongation and break elongation. Similarly, for LDPE, it can be seen that composition is the major factor contributing to peak load, break load, and Young's modulus and load is the major the factor contributing to peak elongation and break elongation. Based upon SN ratios analysis (for combined factor optimization), the overall effect of all the process parameters on mechanical properties is shown as in Table 2.

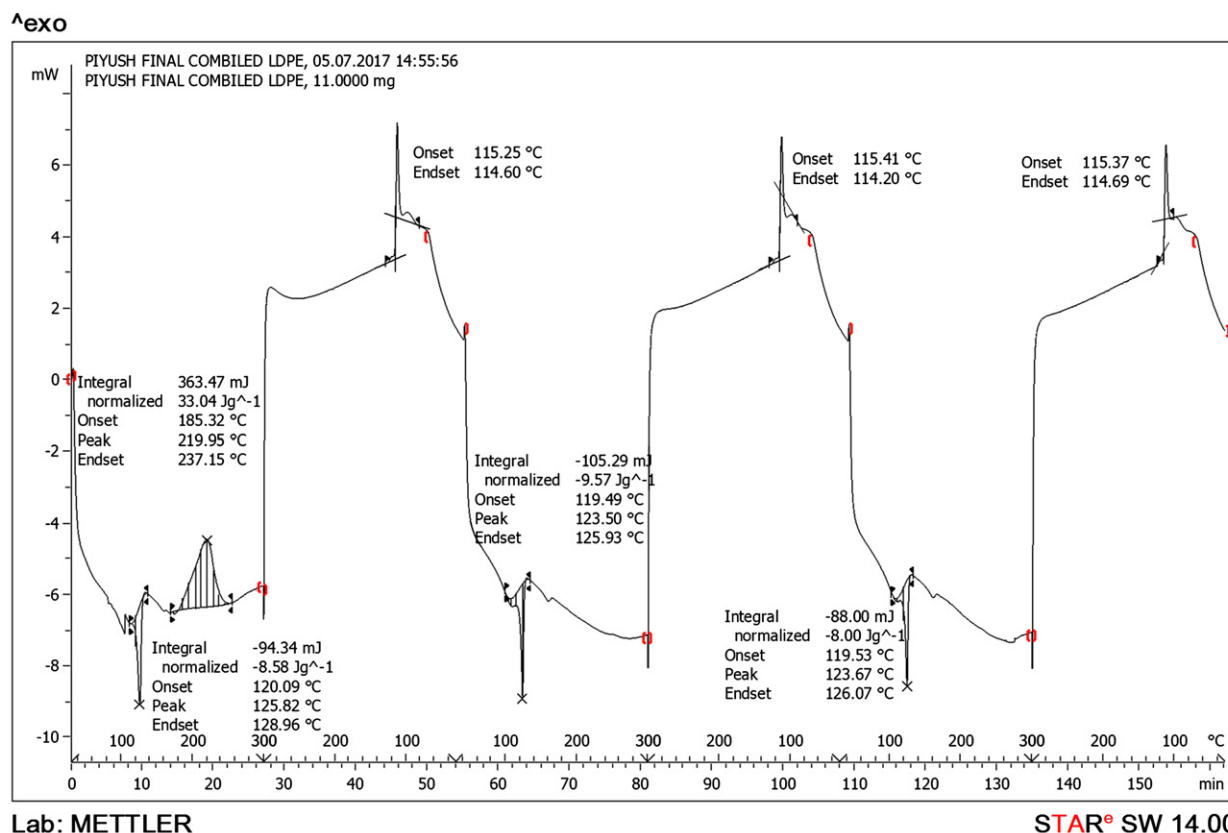


Fig. 14 DSC results of TPS SiC reinforced LDPE sample.

For HDPE:

From Table 2, it can be observed that level 3 for composition (major contributing factor i.e., HDPE as 60% by weight, Al_2O_3 -300G as 13.33% by weight, Al_2O_3 -400G as 13.33% by weight, Al_2O_3 -500G as 13.33% by weight), level 2 for temperature (190°C), level 2 for RPM (40 rpm) and level 1 for load (5 kgf) are the optimized conditions. Hence, it can be concluded that aluminum oxide (Al_2O_3) based TPS reinforcement will exhibit better mechanical properties of the feed stock filament.

For LDPE:

From Table 2, it can be observed that level 6 of composition (i.e., LDPE as 60% by weight, SiC-300G as 13.33% by weight, SiC-400G as 13.33% by weight, SiC-500G as 13.33% by weight), level 2 for temperature (160°C), level 2 for load (10 kgf), level 2 for RPM (40 rpm) are the optimized conditions. Hence, it can be concluded that silicon carbide (SiC) based TPS reinforcement will exhibit better mechanical properties of the feed stock filament.

Various SN ratios of wear as obtained using L9 technique for Al_2O_3 based TPS reinforced HDPE pin and SiC based TPS reinforced LDPE pin are summarized as in Table 3.

Also, percentage contributions of each process parameter on wear properties are summarized in Table 4.

From Table 4, it can be analyzed that for wear of HDPE, load is the major process parameter with 56.49% contribution effecting wear values followed by RPM with 20.42% contribution and time with 13.94% contribution.

Similarly for wear of LDPE, RPM is the major process parameter with 37.57% contribution effecting wear values followed by time with 32.46% contribution and load with 20.17% contribution. After analyzing all SN ratios, the combined effect of all the process parameters on wear properties is shown as in Fig. 15.

The effect of all the process parameters and their ranking for wear of TPS reinforced Al_2O_3 -HDPE pin TPS reinforced SiC-LDPE pin is shown as in Table 5.

Based upon Table 5, it can be summarized that Al_2O_3 based TPS reinforced HDPE pin will exhibit better wear properties at level 3 of load (i.e., 3 kgf load as major factor) followed by level 3 of rpm (500 rpm) and level 1 of time (5 min).

Similarly, from Table 5, it can be summarized that SiC based TPS reinforced LDPE pin will exhibit better wear properties at level 1 of RPM (250) followed by level 2 for time (10 min) and level 2 for load (2 kgf).

The wear tracks for HDPE pins (pure and Al_2O_3 based TPS reinforced HDPE) are shown in Fig. 16, which clearly highlights the extent of wear on pins, when rubbed against the disk. It has been observed that the wear track for the pure HDPE pin is quite sharper than that of tracks for the TPS based HDPE pins.

Table 2 Ranking for different input parameters

Levels	For HDPE				For LDPE			
	Composition	Load	Temperature	RPM	Composition	Load	Temperature	RPM
1	14.23	19.82	19.09	17.88	12.54	11.57	11.48	11.34
2	17.95	18.45	21.69	20.23	13.84	14.75	14.41	12.88
3	22.01	19.09	16.57	19.24	18.38	14.52	13.54	10.47
4	20.49				13.18			
5	19.69				17.55			
6	20.34				18.71			
Delta	7.79	1.37	5.12	2.35	6.35	3.73	5.61	2.11
Rank	1	4	2	3	1	3	2	4

Table 3 SN ratios for wear of TPS HDPE pin (for smaller the better type case)

For HDPE		For LDPE	
SN for wear (HDPE TPS Al ₂ O ₃)		SN for wear (LDPE TPS SiC)	
L1	− 52.6491	L1	− 52.3610
L2	− 50.8814	L2	− 40.3407
L3	− 56.2449	L3	− 62.6516
L4	− 48.0280	L4	− 55.9454
L5	− 54.3866	L5	− 61.6557
L6	− 62.8227	L6	− 59.6905
L7	− 57.8752	L7	− 61.1609
L8	− 56.3645	L8	− 61.5401
L9	− 61.0153	L9	− 61.4229

Table 4 Percentage contribution of process parameters on wear

Parameter	For HDPE	For LDPE
	%age Contribution on wear	%age Contribution on wear
RPM	20.42%	37.57%
Load	56.49%	20.17%
Time	13.94%	32.46%
Error	9.15%	9.80%

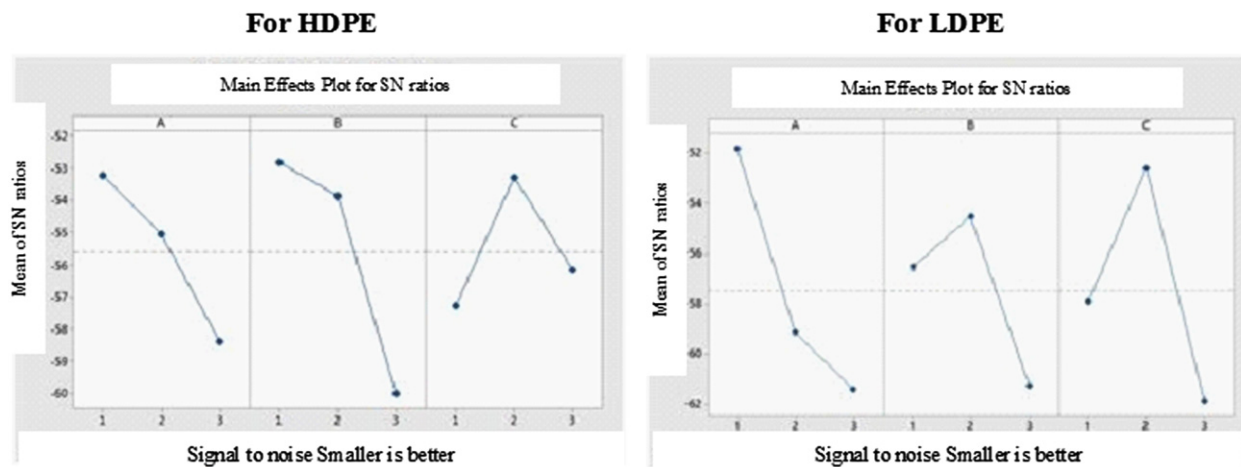
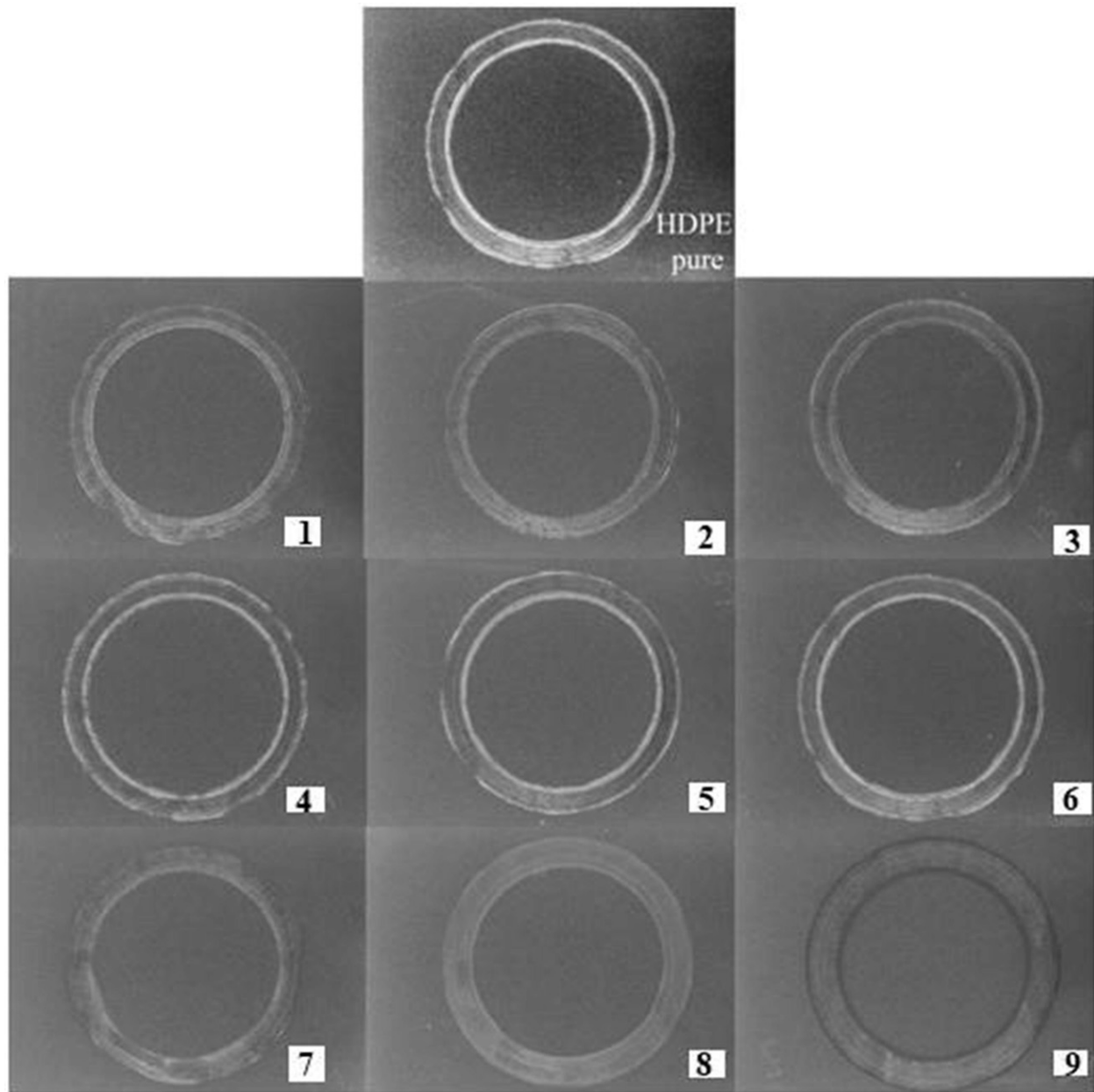
**Fig. 15** SN ratio plot for wear of TPS reinforced Al₂O₃-HDPE pin TPS reinforced SiC-LDPE pin.

Table 5 Ranking of input parameters for wear (smaller the better case)

For HDPE				For LDPE			
Levels	RPM	Load	Time	Levels	RPM	Load	Time
1	− 53.26	− 52.85	− 57.28	1	− 51.78	− 56.49	− 57.86
2	− 55.08	− 53.88	− 53.31	2	− 59.10	− 54.51	− 52.57
3	− 58.42	− 60.03	− 56.17	3	− 61.37	− 61.26	− 61.82
Delta	5.16	7.18	3.97	Delta	9.59	6.74	9.25
Rank	2	1	3	Rank	1	3	2

**Fig. 16** Wear tracks of HDPE pure and HDPE Al_2O_3 TPS pins.

The wear tracks for LDPE pins (pure and SiC based TPS reinforced LDPE) are shown in Fig. 17, which clearly highlights the extent of wear on the pins, when rubbed against the disk. It has been observed that the wear track for the pure LDPE pin is quite sharper than that of tracks for the TPS based LDPE pins.

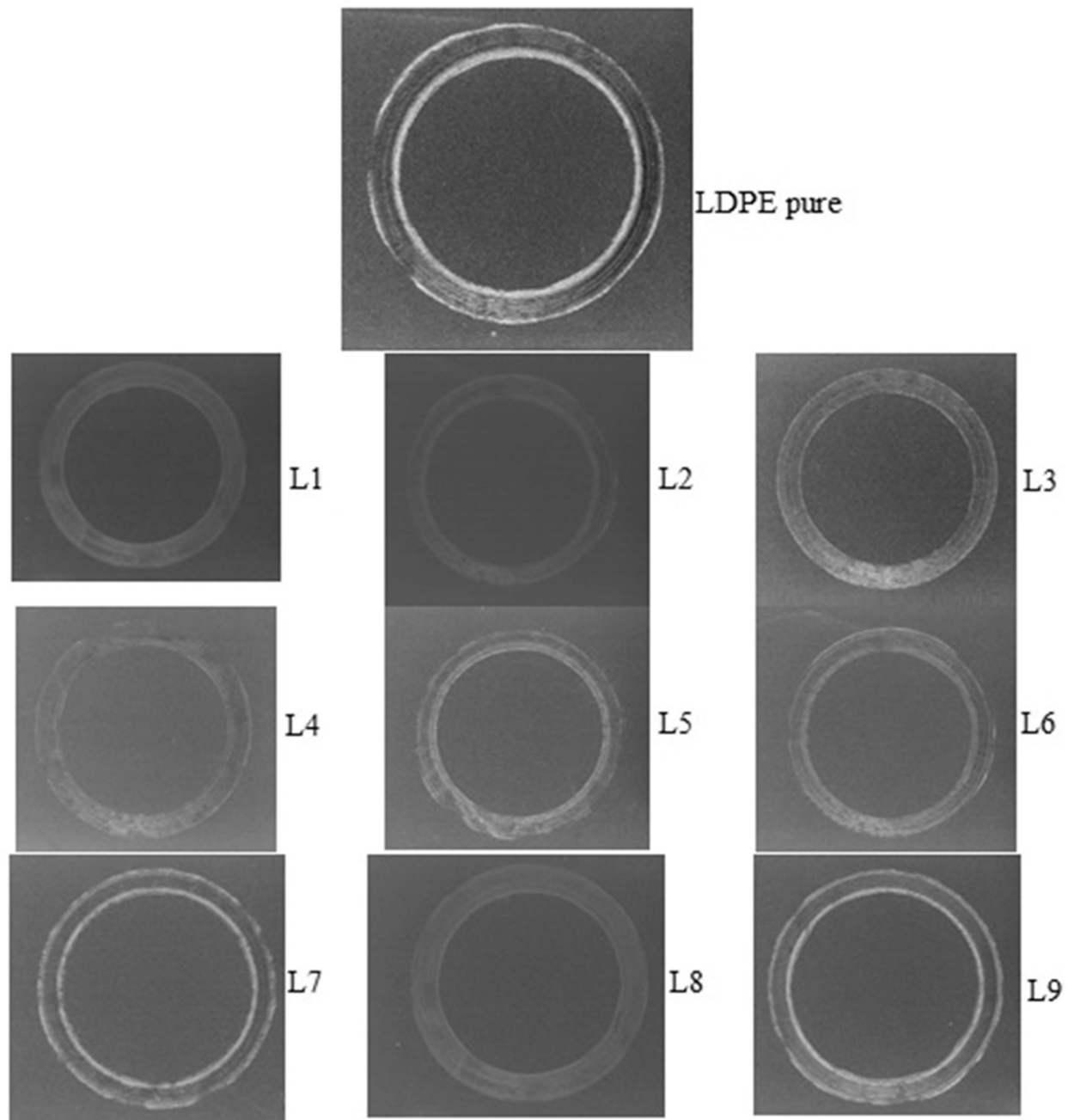


Fig. 17 Wear tracks of LDPE pure and LDPE SiC TPS pins.

Conclusion

The results of study highlights that Al_2O_3 based TPS reinforcement in HDPE matrix and SiC based TPS reinforcement in LDPE matrix resulted in better wear properties under similar service/processing conditions. (See Appendix E at experiment no. 6, wear of pure HDPE was 1244 μm , which was improved as 1120 μm in case of HDPE-TPS-SiC and 1020 μm in case of HDPE-TPS- Al_2O_3). In case of LDPE, (Appendix F) for experiment no. 3, wear of pure LDPE was 1976 μm , which was improved as 1357 μm in case of LDPE-TPS-SiC and 1545 μm in case of LDPE-TPS- Al_2O_3 . Further, results of DSC concluded that the RT prepared from such filament wire will have high thermal stability as there is no evidence of decomposition found after 3 cycles of heating and cooling. Hence the proposed proportion/composition of Al_2O_3 based TPS reinforcement in HDPE (up to 175°C) and SiC based TPS reinforcement in LDPE matrix (up to 125°C) is highly suitable for RT applications.

Acknowledgment

Authors are highly thankful to the Manufacturing Research Lab, Department of Production Engineering, GNDEC Ludhiana, Department of Mechanical Engineering, Punjabi University, Patiala for technical support and Department of Science and Technology, Government of India for its financial support.

Appendix A Different MFIs computed as per pilot study

HDPE (wt%)	Al ₂ O ₃ 300-G (wt%)	Al ₂ O ₃ 400-G (wt%)	Al ₂ O ₃ 500-G (wt%)	MFI g/10 min	LDPE (wt%)	Al ₂ O ₃ 300-G (wt%)	Al ₂ O ₃ 400-G (wt%)	Al ₂ O ₃ 500-G (wt%)	MFI (g/10 min)
50	0	0	50	9.24	50	0	0	50	6.85
50	0	50	0	9.58	50	0	50	0	7.14
50	50	0	0	10.79	50	50	0	0	7.52
50	0	25	25	10.60	50	0	25	25	10.53
50	25	25	0	12.87	50	25	25	0	11.26
50	25	0	25	14.57	50	25	0	25	11.56
50	16.67	16.67	16.66	16.60	50	16.67	16.67	16.66	13.58
60	0	0	40	18.22	60	0	0	40	6.98
60	0	40	0	24.95	60	0	40	0	7.96
60	40	0	0	22.55	60	40	0	0	8.25
60	0	20	20	21.73	60	0	20	20	10.67
60	20	20	0	17.03	60	20	20	0	11.56
60	20	0	20	12.55	60	20	0	20	11.97
60	13.33	13.33	13.34	14.18	60	13.33	13.33	13.34	14.75
70	0	0	30	20.98	70	0	0	30	7.48
70	0	30	0	21.56	70	0	30	0	8.44
70	30	0	0	20.36	70	30	0	0	8.69
70	0	15	15	22.55	70	0	15	15	10.95
70	15	15	0	24.85	70	15	15	0	11.25
70	15	0	15	25.88	70	15	0	15	11.36
70	10	10	10	13.95	70	10	10	10	14.94
80	0	0	20	22.54	80	0	0	20	8.89
80	0	20	0	22.92	80	0	20	0	8.59
80	20	0	0	20.48	80	20	0	0	9.55
80	0	10	10	17.59	80	0	10	10	10.56
80	10	10	0	23.55	80	10	10	0	11.25
80	10	0	10	27.82	80	10	0	10	11.58
80	6.66	6.67	6.67	12.25	80	6.66	6.67	6.67	15.45
90	0	0	10	22.55	90	0	0	10	9.564
90	0	10	0	24.58	90	0	10	0	10.25
90	10	0	0	25.75	90	10	0	0	12.87
90	0	5	5	25.85	90	0	5	5	12.97
90	5	5	0	25.44	90	5	5	0	14.58
90	5	0	5	27.15	90	5	0	5	16.55
90	3.33	3.33	3.34	10.02	90	3.33	3.33	3.34	17.48
HDPE	SiC 300-G wt%	SiC 400-G wt%	SiC 500-G wt%	MFI	LDPE	SiC 300-G wt%	SiC 400-G wt%	SiC 500-G wt%	MFI
50	0	0	50	6.16	50	0	0	50	4.32
50	0	50	0	6.85	50	0	50	0	4.52
50	50	0	0	6.88	50	50	0	0	4.98
50	0	25	25	4.81	50	0	25	25	7.44
50	25	25	0	3.71	50	25	25	0	7.56
50	25	0	25	4.87	50	25	0	25	8.12
50	16.67	16.67	16.66	7.42	50	16.67	16.67	16.66	9.87
60	0	0	40	8.25	60	0	0	40	4.52
60	0	40	0	8.55	60	0	40	0	5.22
60	40	0	0	8.76	60	40	0	0	6.75
60	0	20	20	5.44	60	0	20	20	6.48
60	20	20	0	5.89	60	20	20	0	7.12
60	20	0	20	6.55	60	20	0	20	7.25

60	13.33	13.33	13.34	7.14	60	13.33	13.33	13.34	9.83
70	0	0	30	9.25	70	0	0	30	5.28
70	0	30	0	9.48	70	0	30	0	6.57
70	30	0	0	9.55	70	30	0	0	6.98
70	0	15	15	7.55	70	0	15	15	7.45
70	15	15	0	7.69	70	15	15	0	8.58
70	15	0	15	8.54	70	15	0	15	9.54
70	10	10	10	9.11	70	10	10	10	10.57
80	0	0	20	10.24	80	0	0	20	5.87
80	0	20	0	10.54	80	0	20	0	7.54
80	20	0	0	11.44	80	20	0	0	8.52
80	0	10	10	8.55	80	0	10	10	8.59
80	10	10	0	8.70	80	10	10	0	9.44
80	10	0	10	9.54	80	10	0	10	9.87
80	6.66	6.67	6.67	7.95	80	6.66	6.67	6.67	10.54
90	0	0	10	12.55	90	0	0	10	8.57
90	0	10	0	13.60	90	0	10	0	10.54
90	10	0	0	15.26	90	10	0	0	10.97
90	0	5	5	12.13	90	0	5	5	11.25
90	5	5	0	12.58	90	5	5	0	13.54
90	5	0	5	12.95	90	5	0	5	14.88
90	3.33	3.33	3.34	10.46	90	3.33	3.33	3.34	11.52

Note: G represents grade of abrasives. It should be noted that the SPS represents single particle size (of either 300, 400, 500 American foundry society (AFS) grade), DPS represents two particle sizes in equal proportion by weight (of combination of either of two from 300, 400, 500 AFS grade), and TPS represents three particle sizes in equal proportion by weight (of 300, 400, and 500 AFS grade). It has been observed that in the reported literature, researchers have studied only the effect of SPS and much less exploration is done in the field of study of MFIs considering DPS and TPS. The above stated sizes of SiC/Al₂O₃ are taken, considering the commercial availability of these.

Appendix B Shortlisted proportions of reinforcement for MFI values (for LDPE and HDPE)

S.No.	HDPE	Al ₂ O ₃ 300-G (wt%)	Al ₂ O ₃ 400-G (wt%)	Al ₂ O ₃ 500-G (wt%)	MFI (g/10 min)
1	50	0	0	50	9.24
2	50	0	25	25	10.60
3	90	3.33	3.33	3.34	10.02
S.No.	HDPE	SiC 300-G wt%	SiC 400-G wt%	SiC 500-G wt%	MFI (g/10 min)
4	50	0	0	50	6.16
5	60	25	25	0	3.71
6	60	13.33	13.33	13.34	7.14
S.No.	LDPE	Al ₂ O ₃ 300-G wt%	Al ₂ O ₃ 400-G wt%	Al ₂ O ₃ 500-G wt%	MFI (g/10 min)
1	50	0	0	50	6.85
2	50	0	25	25	10.53
3	50	16.67	16.67	16.67	13.58
S.No.	HDPE	SiC 300-G wt%	SiC 400-G wt%	SiC 500-G wt%	MFI (g/10 min)
4	50	0	0	50	4.32
5	60	0	20	20	6.48
6	60	13.33	13.33	13.33	9.83

Appendix C Detailed input parameters taken for Taguchi L18 array

Levels	Input parameters (for HDPE)				Input parameters (for LDPE)			
	A	B	C	D	A	B	C	D
L1	1	5	185	35	1	5	155	35
L2	1	10	190	40	1	10	160	40
L3	1	15	195	45	1	15	165	45
L4	2	10	185	35	2	10	155	35

L5	2	15	190	40	2	15	160	40
L6	2	5	195	45	2	5	165	45
L7	3	5	190	35	3	5	160	35
L8	3	10	195	40	3	10	165	40
L9	3	15	185	45	3	15	155	45
L10	4	15	195	35	4	15	165	35
L11	4	5	185	40	4	5	155	40
L12	4	10	190	45	4	10	160	45
L13	5	15	190	35	5	15	160	35
L14	5	5	195	40	5	5	165	40
L15	5	10	185	45	5	10	155	45
L16	6	10	195	35	6	10	165	35
L17	6	15	185	40	6	15	155	40
L18	6	5	190	45	6	5	160	45

Note: A is composition, B is load (in kgf), C is temperature (in degree Celsius), D is RPM.

Appendix D Output parameters (mechanical properties) computed as per Taguchi L18 array

Levels	Output parameters (For HDPE)					Output parameters (For LDPE)				
	A	B	C	D	E	A	B	C	D	E
L1	11.8	2.14	10.22	2.04	1.37	9.8	3.04	9.08	2.23	6
L2	13.7	3.42	12.33	3.14	1.51	9.9	4.85	9.19	4.4	7
L3	11.7	3.8	10.53	3.25	1.22	10.2	6.08	10.14	6.06	7
L4	12.7	2.09	12.45	1.95	4.62	8.8	1.23	8.47	1.08	6
L5	16.1	2.47	14.49	2.25	4.88	8.9	2.9	8.88	2.28	6
L6	15.6	1.71	14.04	1.4	2.94	9.4	3.61	9.27	3.46	7
L7	38.1	4.7	25.99	4.25	3.22	7.9	1.71	7.45	1.28	3
L8	20.5	2.66	18.45	2.26	3.65	7.3	3.99	7.14	3.37	4
L9	32.7	5.41	25.13	5.14	2.4	7.8	4.9	7.47	4.09	4
L10	17.1	2.09	15.39	1.85	2.74	5.3	1.09	5.24	0.97	4
L11	21	2.28	18.9	2.08	2.89	6.8	2.09	6.78	2.08	4
L12	21.5	4.75	19.35	4.25	4.93	5.2	3.99	5.04	3.18	5
L13	21	5.7	18.9	5.17	3.66	9.3	2.65	9.22	2.44	7
L14	11.2	1.52	10.08	1.48	2.74	9.3	3.04	9.14	3.03	6
L15	19.6	3.04	17.64	2.48	2.74	9.8	3.8	9.45	3.89	7
L16	12.7	2.66	11.43	2.47	2.89	8.9	2.76	8.36	2.09	10
L17	10.7	2.28	9.63	1.92	4.26	8.3	4.94	8.23	4.46	9
L18	13.7	4.37	12.33	4.06	2.37	9.8	6.08	9.42	6.03	12

Note: A is peak load (N), B is peak elongation (mm), C is break load (N), D is break elongation (mm), E is Young's modulus (MPa).

Appendix E Wear values for pure HDPE,TPS SiC HDPE and TPS Al₂O₃ HDPE as L9 orthogonal array

Material	Levels	RPM	LOAD (in kgf)	TIME (in min)	Wear (in μm)	Original weight (in gm)	Final weight (in gm)	Weight loss (in gm)
HDPE pure	L1	250	1	5	427	3.3685	3.3464	0.0221
	L2	250	2	10	341	3.3464	3.3288	0.0176
	L3	250	3	15	503	3.3288	3.3029	0.0259
	L4	375	1	10	225	3.3029	3.2913	0.0116
	L5	375	2	15	474	3.2913	3.2669	0.0244
	L6	375	3	5	1244	3.2669	3.2028	0.0641
	L7	500	1	15	262	3.2028	3.1895	0.0133
	L8	500	2	5	484	3.1895	3.1646	0.0249
	L9	500	3	10	1099	3.1646	3.1081	0.0565
HDPE TPS SiC	L1	250	1	5	425	1.6699	1.6478	0.0221
	L2	250	2	10	320	1.6478	1.6342	0.0136
	L3	250	3	15	455	1.6342	1.6008	0.0334
	L4	375	1	10	220	1.6008	1.5922	0.0086
	L5	375	2	15	380	1.5922	1.5796	0.0126

	L6	375	3	5	1120	1.5796	1.5555	0.0241
	L7	500	1	15	220	1.5555	1.5153	0.0402
	L8	500	2	5	410	1.5153	1.4319	0.0834
	L9	500	3	10	954	1.4319	1.3741	0.0578
HDPE TPS Al ₂ O ₃	L1	250	1	5	415	5.0898	5.0647	0.0251
	L2	250	2	10	290	5.0647	5.0471	0.0175
	L3	250	3	15	429	5.0471	5.0211	0.0259
	L4	375	1	10	195	5.0211	5.0093	0.0118
	L5	375	2	15	310	5.0093	4.9905	0.0188
	L6	375	3	5	1020	4.9905	4.9287	0.0618
	L7	500	1	15	180	4.9287	4.9178	0.0109
	L8	500	2	5	405	4.9178	4.8933	0.0245
	L9	500	3	10	838	4.8933	4.8425	0.0508

Appendix F Wear values for pure LDPE, TPS SiC LDPE and TPS Al₂O₃ LDPE as L9 orthogonal array

Material	Level	RPM	LOAD (in kgf)	TIME (in min)	Wear (in μm)	Original weight (in gm)	Final weight (in gm)	Weight loss (in gm)
LDPE pure	L1	250	1	5	460	2.6386	2.6149	0.0237
	L2	250	2	10	108	2.6149	2.6094	0.0055
	L3	250	3	15	1776	2.6094	2.5179	0.0915
	L4	375	1	10	867	2.5179	2.4732	0.0444
	L5	375	2	15	1400	2.4732	2.4011	0.0721
	L6	375	3	5	1563	2.4011	2.3206	0.0805
	L7	500	1	15	1376	2.3206	2.2497	0.0709
	L8	500	2	5	1651	2.2497	2.1647	0.0851
	L9	500	3	10	1333	2.1647	2.0961	0.0686
LDPE TPS SiC	L1	250	1	5	415	3.3427	3.3206	0.0221
	L2	250	2	10	104	3.3206	3.2696	0.0511
	L3	250	3	15	1357	3.2696	3.1839	0.0857
	L4	375	1	10	627	3.1839	3.1034	0.0805
	L5	375	2	15	1210	3.1034	3.0436	0.0598
	L6	375	3	5	965	3.0436	2.9684	0.0752
	L7	500	1	15	1143	2.9684	2.9025	0.0659
	L8	500	2	5	1194	2.9025	2.8009	0.1016
	L9	500	3	10	1178	2.8009	2.7181	0.0828
LDPE TPS Al ₂ O ₃	L1	250	1	5	440	4.9861	4.9735	0.0126
	L2	250	2	10	105	4.9735	4.9206	0.0529
	L3	250	3	15	1545	4.9206	4.8581	0.0625
	L4	375	1	10	715	4.8581	4.8053	0.0528
	L5	375	2	15	1215	4.8053	4.7601	0.0452
	L6	375	3	5	1159	4.7601	4.6730	0.0871
	L7	500	1	15	1248	4.6730	4.5976	0.0754
	L8	500	2	5	1286	4.5976	4.4962	0.1014
	L9	500	3	10	1254	4.4962	4.4247	0.0715

Appendix G S-N ratios for each computed mechanical properties

Levels	For HDPE					For LDPE				
	SN peak load	SN break load	SN peak elongation	SN break elongation	SN Young's modulus	SN peak load	SN break load	SN peak elongation	SN break elongation	SN Young's modulus
L1	21.43	20.18	6.60	6.19	2.73	19.82	9.66	19.16	6.19	2.73
L2	22.73	21.81	10.68	9.94	3.58	19.91	13.71	19.27	9.93	3.57
L3	21.36	20.44	11.59	10.24	1.73	20.17	15.68	20.12	10.23	1.72
L4	22.07	21.90	6.40	5.81	13.30	18.89	1.80	18.56	5.80	13.29
L5	24.13	23.22	7.85	7.04	13.77	18.99	9.25	18.97	7.04	13.76
L6	23.86	22.94	4.65	2.92	9.37	19.47	11.15	19.34	2.92	9.36

L7	31.61	28.29	13.44	12.57	10.16	17.95	4.66	17.44	12.56	10.15
L8	26.23	25.31	8.49	7.08	11.25	17.27	12.02	17.07	7.08	11.24
L9	30.29	28.00	14.66	14.22	7.60	17.84	13.80	17.47	14.21	7.60
L10	24.65	23.74	6.40	5.34	8.75	14.49	0.75	14.39	5.34	8.75
L11	26.44	25.52	7.15	6.36	9.22	16.65	6.40	16.62	6.36	9.21
L12	26.64	25.73	13.53	12.57	13.86	14.32	12.02	14.05	12.56	13.85
L13	26.44	25.52	15.11	14.27	11.27	19.37	8.46	19.29	14.26	11.26
L14	20.98	20.06	3.63	3.41	8.76	19.37	9.66	19.22	3.40	8.75
L15	25.84	24.93	9.65	7.89	8.76	19.82	11.60	19.51	7.88	8.75
L16	22.07	21.16	8.49	7.85	9.22	18.99	8.82	18.44	7.85	9.21
L17	20.58	19.67	7.15	5.67	12.59	18.38	13.87	18.31	5.66	12.58
L18	22.73	21.81	12.80	12.17	7.49	19.82	15.68	19.48	12.17	7.49

Appendix H Percentage contribution of different input parameters on mechanical properties

Parameter	For HDPE					For LDPE				
	%age Contribution for peak load	%age Contribution for peak elongation	%age Contribution for break load	%age Contribution for break elongation	%age Contribution for Young's modulus	%age Contribution for peak load	%age Contribution for peak elongation	%age Contribution for break load	%age Contribution for break elongation	%age Contribution for Young's modulus
Composition	74.69%	25.47%	74.95%	25.88%	74.94%	90.03%	34.55%	88.51%	30%	91.8%
Load	5.00%	19.34%	4.74%	16.59%	4.25%	0.6%	56.98%	1.35%	65%	4.32%
Temperature	11.46%	38.92%	11.04%	41.27%	4.74%	0.45%	1.36%	0.26%	0.48%	0.57%
RPM	0.19%	8.58%	0.33%	6.77%	6.35%	3.17%	0.56%	3.25%	0.41%	0.92%
Error	8.65%	7.69%	8.93%	9.48%	9.72%	5.52%	6.54%	6.63%	4.11%	2.3%

See also: Development of HAp Reinforced Biodegradable Porous Structure Through Polymer Deposition Technology for Tissue Engineering Applications. Investigations for Metal Matrix Composites Prepared by Using Waste Polymer-Based Sacrificial Rapid Pattern in Investment Casting

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Large Biomass Burners for Fuel Switch in Existing Fossil Fuel Based Plants

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Introduction

Energy is one of the most fundamental parts for any country and it is known as a strategic commodity. Any uncertainty about its supply can threaten the functioning of the economy, particularly in developing economies.

Energy services could be greatly improved by using agricultural biomass in small-scale combustion units. Wood pellets are a reliable and proven fuel to be used in small-scale combustion units. However, these units should preferably be able to use different types of biomass depending what it is locally available. Therefore, studies have been focused on exploring the suitability of using agricultural residues for small-scale heat and power generation using direct combustion. Steam-treated pellets can help to address technical barriers that limit the uptake of pellets as a fuel for electricity generation, but there is limited understanding of the cost and environmental impacts of their production and use.

A modified Hartmann dust explosion tube was employed to determine the Minimum Explosible Concentration (MEC) and the flame speed for three Pakistani agricultural wastes: bagasse, rice husk and wheat straw (Saeed *et al.*, 2015) where it was shown the lean limits for these pulverized agricultural waste biomasses were comparable to that of pulverized wood but were much leaner than those for coal and hydrocarbon fuels, which indicate that these biomasses are highly reactive. In study (Cardozo *et al.*, 2014) was compared the combustion of different agricultural residues in a single unit designed for wood pellets. In study (McKechnie *et al.*, 2016) was investigated life cycle environmental (greenhouse gas (GHG) and air pollutant emissions) and financial implications of electricity generation from steam-treated pellets, including fuel cycle activities (biomass supply, pellet production, and combustion) and retrofit infrastructure to enable 100% pellet firing at a generating station that previously used coal. Impacts of retrofit infrastructure become increasingly significant at lower generating station capacity factors, further favoring steam-treated pellets for both environmental and financial metrics (McKechnie *et al.*, 2016). In study (Nilsson *et al.*, 2011), the costs and energy requirements for the production of pellets from agricultural raw materials were analyzed. The energy use in manufacturing pellets from air-dried crops was generally no higher than when moist sawdust was used as the raw material. The objective of work (Carvalho *et al.*, 2013) was to evaluate the technical and environmental performance of a 15 kW pellet boiler when operated with different pelletized biomass fuels, namely straw (*Triticum aestivum*), Miscanthus (*Miscanthus _ giganteus*), maize (*Zea mays*), wheat bran, vineyard pruning (from *Vitis vinifera*), hay, Sorghum (*Sorghum bicolor*) and wood (from *Picea abies*) with 5% rye flour. The investigation in the international market shows that mixed biomass pellets are promising fuels and with the appropriate support these fuels have many prospects for the future (Karkania *et al.*, 2012). The use of biomass pellets would not only create new market opportunities for agricultural industries, it would also reduce dependence on coal, as well as the greenhouse gas emissions associated with coal use (Karkania *et al.*, 2012). In paper (Tauro *et al.*, 2018) was examined the potential for biomass pellets to become a sizable low-carbon, renewable energy source that could compete with and substitute fossil fuels in specific economic sectors in Mexico where it was estimated that the market energy potential for pellets from currently available agricultural and forest residues in Mexico is between 131 and 233 PJ/yr, with total costs ranging from 6.3 to 12.8 USD/GJ. In paper (Dai *et al.*, 2015), a ceramic foam burner with embedded alumina pellets was designed, which set different shapes of tubes by taking can advantage of the discrete pellets. An experimental system was built to study the effects of the pellet diameter and pellet location on the combustion of low-concentration coal mine methane (LCM) (Dai *et al.*, 2015). Results indicates that the heat transfer features of 13-mm pellets are more similar to those of 10-PPI ceramic foam compared with 6-mm pellets and 9-mm pellets (Dai *et al.*, 2015). The combustion performance in a double-layer burner packed with alumina pellets of different diameters was experimentally studied in article (Gao *et al.*, 2012). In study (Qu and Feng, 2015), methane/air combustion in a two-zone catalytic alumina pileup-pellets burner with equivalence ratios varying from 0.55 to 0.70 was researched. Torrefied biomass has several benefits, such as higher energy density, good grindability, higher flowability and uniformity (Li *et al.*, 2012). The outlet of a mechanical biological treatment plant for mixed municipal solid waste is further processed to produce RRBf (Refined Renewable Biomass Fuel) within the frame of the EU LifeP project MARSS (Material Advanced Recovery Sustainable Systems) (Schulzke *et al.*, 2017). In paper (Dasappa *et al.*, 2004) addresses case studies of a low temperature and a high temperature industrial heat requirement being met using biomass gasification (Dasappa *et al.*, 2004). In paper (Verma *et al.*, 2017) provides a detail review on the need of drying of biomass before co-firing, different technologies used for biomass drying, biomass co-firing to the existing coal fired power plants and the environmental benefits of biomass co-firing.

In this study is presented burners are based on innovative variant of reciprocating grate. Water cooled double wall construction reducing the overall price of construction. There is high variability of potential fuels to be used (e.g. communal waste, all types of biomass (pellets (wood and agricultural), biomass residues, wood chips, wood debris, coal etc.).

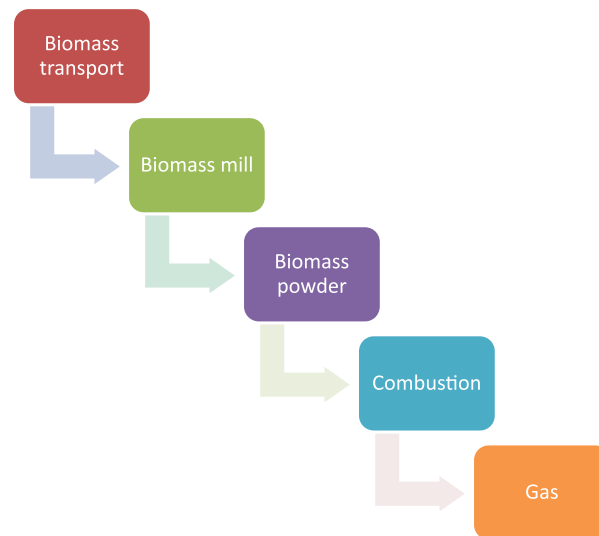


Fig. 1 The biomass treatment process flowchart.

Materials and Methods

Biomass Waste Management

According to the European Union standardization there are six procedures in the biomass waste treatment process:

1. Eco-design,
2. Biomass waste decreasing,
3. Biomass waste reusing,
4. Recycling and making compost,
5. Energy from biomass waste,
6. Biomass waste disposing.

In order to optimize the system for biomass waste management based on decreasing of pollution of life environment and for the cheapest solution there is goal to develop the biomass waste management process. This innovative solution could lead to revolution in the biomass waste issue. By entering of the main data for biomass waste, quantity and composition for the some region, the client could know which is the best solution for the biomass waste treatment and transport for the region. Several biomass waste treatments are included:

- Recycling,
- Combusting,
- Making compost,
- Performing anaerobic digestion, and
- Disposing of biomass waste.

There are several indicators which are calculated according the input data. These indicators are:

- Global warming,
- Heavy metals emission,
- Nitrogen oxide emission,
- Smog formation,
- Water pollution.

Therefore the system has seven modules. These modules

- Calculation of emissions from collection and transport of biomass waste,
- Calculation of emissions from anaerobic digestion,
- Calculation of emissions from combustion,
- Calculation of emissions from recycled waste,
- Calculation of emissions from disposal,
- Calculation of emissions from compost,
- Calculation of cost benefit.

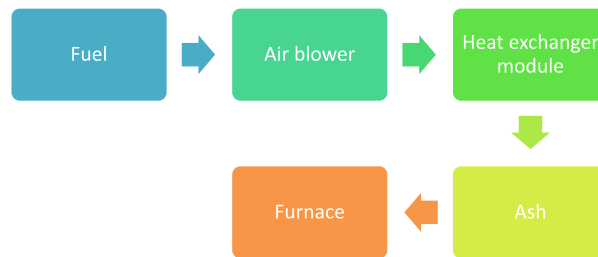


Fig. 2 Process flowchart of the combustion plant with biomass.



Fig. 3 Large biomass burner for fuel switch.

Burner for Agricultural Pellets

Fig. 1 shows the flowchart of the biomass treatment process where it was shown the main process steps. Afterwards process flowchart of combustion plant with biomass is shown in **Fig. 2**.

Burners are based on innovative variant of reciprocating grate. Water cooled double wall construction reducing the overall price of construction. High variability of potential fuels to be used in the burners e.g., communal waste, all types of biomass (pellets (wood and agricultural), biomass residues, wood chips, wood debris, coal etc. The burners have high automation (control of speed of grate, control of emission, temperature, pressure in burner). Burner of 4.5 MW have been produced (assembled) and the models are shown in **Fig. 3**. Additionally, whole boilers can be constructed.

Conclusion

The demand for biofuel has increased considerably in recent years, causing shortage of the traditional raw materials sawdust and wood shavings. Use of biomass fuels for electricity generation can simultaneously contribute to a number of common policy objectives, including: increasing the use of renewable energy; reducing greenhouse gas emissions; compliance with air pollutant emissions regulations; and encouraging economic development in communities dependent on agriculture and forestry sectors.

In this article large biomass burners for fuel switch in existing fossil fuel based plants was used for combustion. The burners have high automation (control of speed of grate, control of emission, temperature, pressure in burner). Burner of 4,5 MW have been produced (assembled).

Small-scale wood combustion systems have been well developed and reached a high quality and performance level. The energy efficiency has increased, the emissions have decreased, fully automatic operation systems have been developed and the combustion technology has been optimized for woody biomass fuels.

See also: Machine for Producing Tablets From Coal Powder. Small to Medium Burners for Agricultural Pellets. Technology for Producing Briquettes From Wet Biomass

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Machine for Producing Tablets From Coal Powder

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Introduction

Energy is one of the most fundamental parts for any country and it is known as a strategic commodity. Any uncertainty about its supply can threaten the functioning of the economy, particularly in developing economies.

Energy services could be greatly improved by using agricultural biomass in small-scale combustion units. Wood pellets are a reliable and proven fuel to be used in small-scale combustion units. However, these units should preferably be able to use different types of biomass depending what it is locally available. Therefore, studies have been focused on exploring the suitability of using agricultural residues for small-scale heat and power generation using direct combustion. Steam-treated pellets can help to address technical barriers that limit the uptake of pellets as a fuel for electricity generation, but there is limited understanding of the cost and environmental impacts of their production and use.

A modified Hartmann dust explosion tube was employed to determine the Minimum Explosible Concentration (MEC) and the flame speed for three Pakistani agricultural wastes: bagasse, rice husk and wheat straw (Saeed *et al.*, 2015) where it was shown the lean limits for these pulverized agricultural waste biomasses were comparable to that of pulverized wood but were much leaner than those for coal and hydrocarbon fuels, which indicate that these biomasses are highly reactive. In study Cardozo *et al.* (2014) was compared the combustion of different agricultural residues in a single unit designed for wood pellets. In study McKechnie *et al.* (2016) was investigated life cycle environmental (greenhouse gas (GHG) and air pollutant emissions) and financial implications of electricity generation from steam-treated pellets, including fuel cycle activities (biomass supply, pellet production, and combustion) and retrofit infrastructure to enable 100% pellet firing at a generating station that previously used coal. Impacts of retrofit infrastructure become increasingly significant at lower generating station capacity factors, further favoring steam-treated pellets for both environmental and financial metrics (McKechnie *et al.*, 2016). In study Nilsson *et al.* (2011), the costs and energy requirements for the production of pellets from agricultural raw materials were analyzed. The energy use in manufacturing pellets from air-dried crops was generally no higher than when moist sawdust was used as the raw material. The objective of work (Carvalho *et al.*, 2013) was to evaluate the technical and environmental performance of a 15 kW pellet boiler when operated with different pelletized biomass fuels, namely straw (*Triticum aestivum*), Miscanthus (*Miscanthus _ giganteus*), maize (*Zea mays*), wheat bran, vineyard pruning (from *Vitis vinifera*), hay, Sorghum (*Sorghum bicolor*) and wood (from *Picea abies*) with 5% rye flour. The investigation in the international market shows that mixed biomass pellets are promising fuels and with the appropriate support these fuels have many prospects for the future (Karkania *et al.*, 2012). The use of biomass pellets would not only create new market opportunities for agricultural industries, it would also reduce dependence on coal, as well as the greenhouse gas emissions associated with coal use (Karkania *et al.*, 2012). In paper Tauro *et al.* (2018) was examined the potential for biomass pellets to become a sizable low-carbon, renewable energy source that could compete with and substitute fossil fuels in specific economic sectors in Mexico where it was estimated that the market energy potential for pellets from currently available agricultural and forest residues in Mexico is between 131 and 233 PJ/yr, with total costs ranging from 6.3 to 12.8 USD/GJ. In paper (Dai *et al.*, 2015), a ceramic foam burner with embedded alumina pellets was designed, which set different shapes of tubes by taking can advantage of the discrete pellets. An experimental system was built to study the effects of the pellet diameter and pellet location on the combustion of low-concentration coal mine methane (LCM) (Dai *et al.*, 2015). Results indicates that the heat transfer features of 13-mm pellets are more similar to those of 10-PPI ceramic foam compared with 6-mm pellets and 9-mm pellets (Dai *et al.*, 2015). The combustion performance in a double-layer burner packed with alumina pellets of different diameters was experimentally studied in article (Gao *et al.*, 2012). In study Qu and Feng, (2015), methane/air combustion in a two-zone catalytic alumina pileup-pellets burner with equivalence ratios varying from 0.55 to 0.70 was researched. Torrefied biomass has several benefits, such as higher energy density, good grindability, higher flowability and uniformity (Li *et al.*, 2012). The outlet of a mechanical biological treatment plant for mixed municipal solid waste is further processed to produce RRBf (Refined Renewable Biomass Fuel) within the frame of the EU Life project MARSS (Material Advanced Recovery Sustainable Systems) (Schulzke *et al.*, 2017). In paper Dasappa *et al.* (2004) addresses case studies of a low temperature and a high temperature industrial heat requirement being met using biomass gasification (Dasappa *et al.*, 2004). In paper Verma *et al.* (2017) provides a detail review on the need of drying of biomass before co-firing, different technologies used for biomass drying, biomass co-firing to the existing coal fired power plants and the environmental benefits of biomass co-firing. In paper Hosier and Svenningsson, (1987) was presented the social and economic analysis of an evaluation of biomass briquettes as a substitute for charcoal.

Coal powder is residue in mines with economic value but is regarded as waste and not used. We have produced machine for binding together the coal powder particles and producing the tablets. Process is completely automatic. Other materials (feedstock) can be used instead the coal. Documentation and machine are available in our lab.

Materials and Methods

Biomass Waste Management

According to the European Union standardization there are five procedures in the biomass waste treatment process:

1. Eco-design,
2. Biomass waste decreasing,
3. Biomass waste reusing,
4. Recycling and making compost,
5. Energy from biomass waste,
6. Biomass waste disposing.

In order to optimize the system for biomass waste management based on decreasing of pollution of life environment and for the cheapest solution there is goal to develop the biomass waste management process. This innovative solution could lead to revolution in the biomass waste issue. By entering of the main data for biomass waste, quantity and composition for the some region, the client could know which is the best solution for the biomass waste treatment and transport for the region. Several biomass waste treatments are included:

- Recycling,
- Combusting,
- Making compost,
- Performing anaerobic digestion and
- Disposing of biomass waste.

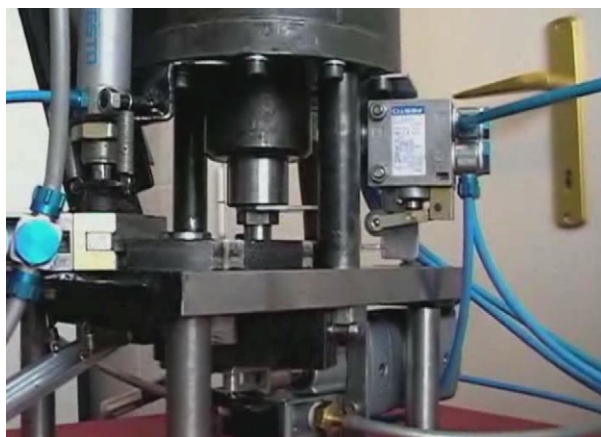


Fig. 1 Machine for producing tables from coal powder (first view).



Fig. 2 Machine for producing tables from coal powder (second view).

There are several indicators which are calculated according the input data. These indicators are:

- Global warming,
- Heavy metals emission,
- Nitrogen oxide emission,
- Smog formation,
- Water pollution.

Therefore the system has seven modules. These modules

- Calculation of emissions from collection and transport of biomass waste,
- Calculation of emissions from anaerobic digestion,
- Calculation of emissions from combustion,
- Calculation of emissions from recycled waste,
- Calculation of emissions from disposal,
- Calculation of emissions from compost,
- Calculation of cost benefit.

Biomass Production

Coal powder is residue in mines with economic value but is regarded as waste and not used. We have produced machine for binding together the coal powder particles and producing the tablets. Process is completely automatic. Other materials (feedstock) can be used instead the coal. Documentation and machine are available in our lab. [Figs. 1–5](#) shows the machine for producing tablets from coal powder.



Fig. 3 Machine for producing tables from coal powder (third view).



Fig. 4 Machine for producing tables from coal powder (fourth view).



Fig. 5 Produced tablets from coal powder.

Conclusion

The demand for biofuel has increased considerably in recent years, causing shortage of the traditional raw materials sawdust and wood shavings. Use of biomass fuels for electricity generation can simultaneously contribute to a number of common policy objectives, including: increasing the use of renewable energy; reducing greenhouse gas emissions; compliance with air pollutant emissions regulations; and encouraging economic development in communities dependent on agriculture and forestry sectors.

In this article technology is proposed for producing tablets from coal powder. We have produced machine for binding together the coal powder particles and producing the tablets. Process is completely automatic. Other materials (feedstock) can be used instead the coal. Documentation and machine are available in our lab.

Small-scale wood combustion systems have been well developed and reached a high quality and performance level. The energy efficiency has increased, the emissions have decreased, fully automatic operation systems have been developed and the combustion technology has been optimized for woody biomass fuels.

See also: Large Biomass Burners for Fuel Switch in Existing Fossil Fuel Based Plants. Small to Medium Burners for Agricultural Pellets. Technology for Producing Briquettes From Wet Biomass

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Manufacturing, Applications and Mechanical Properties of Lightweight Wood-Based Sandwich Panels

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Introduction

Civilizations, irrespective of their temporal locations on the timeline of human existence, strive on the availability of energy in its various guises. As a prime measure of standard of living, the amount of energy consumption typically correlates with the degree of civilization (Holdgate, 1987). It is therefore unsurprising that as civilizations bask in the glory of progress, the progress typically rides on the wave of increased energy usage. The consequence of this state of affairs is the amplification of stress on the environment, the pernicious impact on the ecosystem and the ever increasing pressure on the biosphere (e.g., desertification, water and air pollution, climate variability, global warming etc.). The recognition of these eco-concerns has morphed into global and local policy proposals that: (a) seek long-term global environmental strategies for achieving sustainable development; and (b) intensifies the quest for more sustainable energy systems (Bakshi and Fiksel, 2003; Anon, 2001). Although the recent proliferation of green technologies has been largely driven by the implementation plans for the alternative energy dimensions, a shift in material consumptions offers a promising route for the switch towards low-carbon product designs and development (Anastas and Zimmerman, 2006). In the light of the preceding reasons, the focus of many sustainable development initiatives centres on efficient management of natural resources through the reduction of the environmental impact of materials and manufacturing technologies (Koltun, 2010).

Historically, an array of natural materials such as bone, wood and shell facilitated the survival and development of humanity in early stages. However, these materials were pushed out of fashion by synthetic counterparts that seemingly offered improved performance. Yet, these natural structures, are endowed with distinct combinations of physico-mechano-chemical properties that often surpass those of synthetic counterparts by orders of magnitude. As such, natural materials continue to inspire generations of scientists and engineers. Indeed, in recent years, tremendous research efforts have gone into studying how the design of biological cellular structures of living organisms can influence the design of advanced composite materials for multifunctional capabilities (Chen and Wu, 2013; Verma and Tomar, 2014; Wegst *et al.*, 2015). Along this direction, sandwich composites resembling low-density natural cellular materials have emerged as good candidates for lightweight design technologies with applications in various industries (Schaedler *et al.*, 2011; Zenkert, 1995).

Sandwich structures embody a variant of laminated composites. They comprise three primary parts (a pair of thin skins, a thicker less-dense core, and thin layers of coupling agents) as shown in Fig. 1. In terms of development, wood-based sandwich structures initially lagged behind many of the competing sandwich structures derived from other types of materials. Nevertheless, recent developments have propelled them for use as primary elements in lightweight transport infrastructures, naval shipbuilding, prefabricated shelters, as well as insulation for thermal comfort (Kawasaki and Kawai, 2006; Li *et al.*, 2014). Clearly, the increasing use of these structures hinges on two advantages, among many. First, the use compensates for the scarcity of first-generation raw wood resources as a result of monstrous deforestations. Second, it alleviates the problem of poorer quality of wood products from less mature trees.

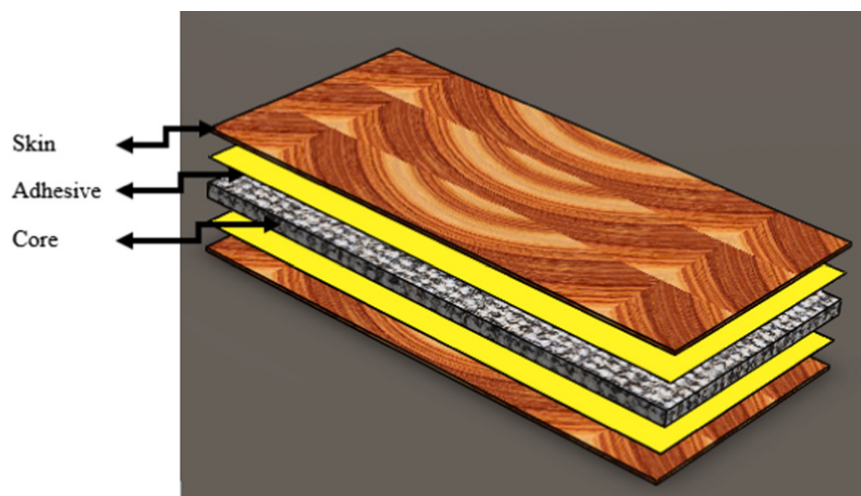


Fig. 1 Schematic of wood-based sandwich structures with wooden skin and wooden core.

The combination of materials for wood-based sandwich structures (WBSS) is diverse, but four broad groups can be defined: (i) WBSS with non-wooden skins separated by a wooden core; (ii) WBSS with non-wooden skins separated by a hybrid wooden composite; (iii) WBSS with wooden skins separated by a non-wooden core; and (iv) WBSS with wooden skins separated by a wooden core. Among these competing types of WBSS, the last group qualifies as the “greenest”. It is therefore the focus of this article to examine the manufacturing, applications and properties of the last group (i.e., the wooden skins/wooden core WBSS).

Lightweight Wood-Based Sandwich Structures

Manufacturing Methods

The manufacturing of sandwich structures is easily influenced by several factors. Structural performance requirement, the volume of production, and the cost of tooling are some of the notable ones. Commercial-grade productions of wood-based sandwich structures rely on a series of proprietary steps and materials. However, the production of prototype sandwich structures routinely embraces the selection of the skin and core materials, the strength requirement of the bonding agent, pressing and finishing. [Fig. 2](#) features some of the common methods of interests in the manufacturing of sandwich structures ([Manalo et al., 2016](#)).

The steam-assisted hot pressing method was used for the construction of wood-based sandwich structures in the earlier studies by [Kawasaki et al. \(2006\)](#).

Skin materials

The top and bottom skins sustain the structural strength and stiffness of the WBSS. The skin materials can be purchased off-the-shelf commercially, since these can often be veneers or products derived from veneers, such as plywood, oriented strand board (OSB), and laminated veneer lumbers (LVL), among the many options that fit this purpose. These products have well-documented methods of productions that are now part of standard literature. For instance, a highlight of the steps in the production of plywood is illustrated in [Fig. 3](#), as expounded in [Hughes \(2015\)](#). A simplified production method of wavy plywood for shipbuilding applications is described by [Francesco et al. \(2011\)](#).

Core materials

The core contributes to the shear rigidity of the WBSS. The core could be random, periodic or hybrid in nature. Random cores are mostly derived from foam-based materials, while periodic cores could take the form of paper honeycomb, or laminated paper (corrugated, or truss). Balsa wood, cork, fibreboard, and many agricultural residues (e.g., flax mat, jute fibres, kenaf fibres etc.) are examples of common materials that have been used for the core of WBSS ([Kawasaki et al., 2003](#); [Dweib et al., 2004](#); [Lakreb et al., 2015](#)). Balsa wood is particularly good for marine applications. For lightweight WBSS, the production of cores derived from fibreboard provides an effective mean of controlling the weight and density of the final product. The construction of WBSS with plywood skins and fibreboard derived from radiata pines was extensively investigated by [Kawasaki et al.](#) in a series of studies that concentrated on their use for in-plane shear loading and thermal insulation capabilities ([Kawasaki et al., 2003, 1998, 1999](#)). With intent on applications for cladding and wind load carrying purposes, [Fernandez-Cabo et al. \(2011\)](#) constructed, simulated and tested specimens of WBSS with OSB skins and fibreboard cores. [Fig. 4](#) portrays a sample industrial set-up for the production of fibreboards. The key raw materials being wood waste, sawdust, recycled wood pellets etc. Other types of agricultural non-wood residues can also be used as demonstrated by [Dweib et al. \(2004\)](#). The resin content in the mixing stage of the production could be polymeric isocyanate. Normally, the quality of the final fibreboard product depends on the processing parameters as enunciated in the comprehensive report by [Kelly \(1977\)](#), of the United States Department of Agriculture (USDA) Forest Services. Nevertheless, fibreboards formed from small fibres have been shown to possess better mechanical and dimensional properties than those made from large fibres ([Kawasaki et al., 1998](#)).

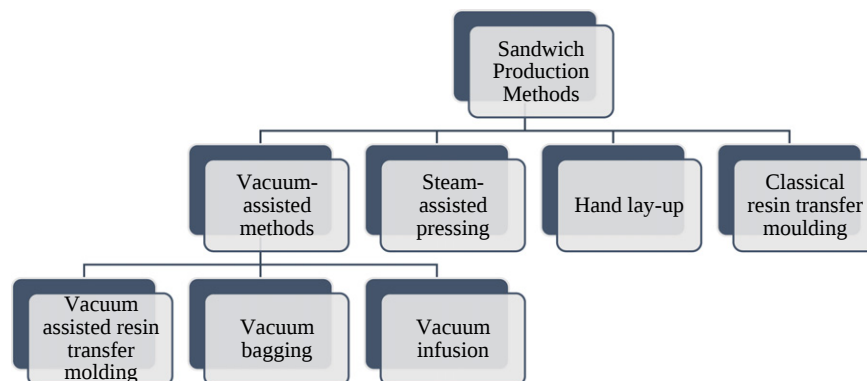


Fig. 2 Methods of manufacturing sandwich structures.

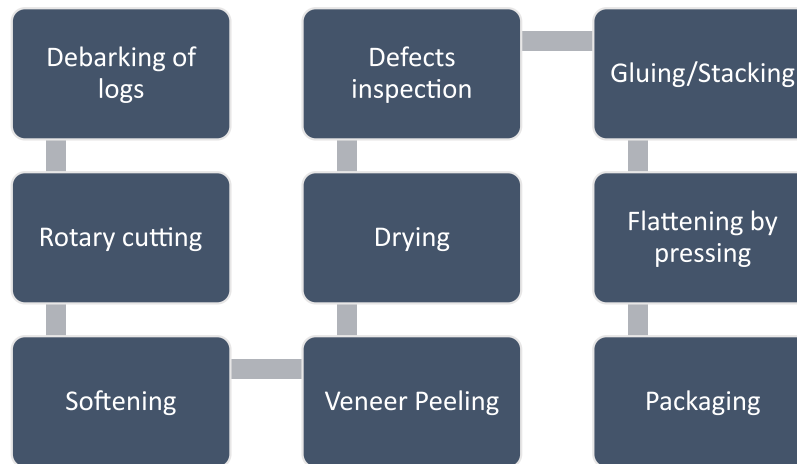


Fig. 3 A summary of key steps in the production of plywood.

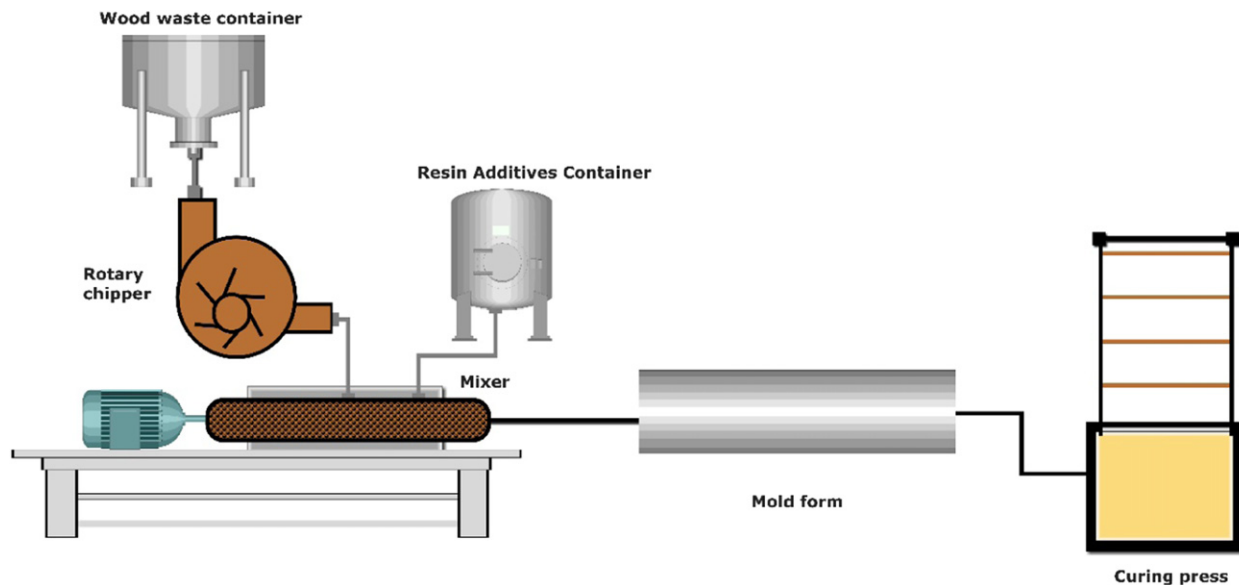


Fig. 4 A simple set-up for the production of fibreboard.

Although fibreboard represents an excellent core material because of its low thermal conductivity and the ability to control its density easily, balsa wood has emerged as another worthwhile alternative for WBSS. Balsa (*Ochroma pyramidale*) is the softest commercial hardwood (EOL, 2018). It is native to South America (Ecuador being the largest commercial supplier), but also found in Solomon Island, Indonesia, Papua New Guinea and Thailand. Osei-Antwi *et al.* (2013) investigated the shear stiffness/strength of panels derived from cubes of South American balsa as core materials for sandwich structures. Kotlarewski *et al.* (2016) compiled the mechanical properties of balsa from Papua New Guinea. A comparative study of the two investigations established that the set of specimens from Papua New Guinea exhibits lower density, better shearing strength as well as better modulus of rupture, making them superior to those from South America.

Bonding

Bonding operation is a major step in the production of the WBSS, and a classic reference on this is the report by Selbo (1975), also of USDA. Although the bonding can be facilitated by a cold or hot pressing process, the injection of steam in the steam-assisted process facilitates a faster operation and high-quality end products. Still, it is advised to abide by the specific recommendations of adhesive manufacturers in applications for sandwich constructions. Some key factors to consider in choosing adhesives include the type of applications (structural/non-structural, interior/exterior), resistance to heat and humidity etc. For laboratory-scale productions of WBSS, means of application of adhesives could be through glue spreader, portable sprayer, precision dispensing kit, and painting brush.

Properties

Investigations into the mechanical behavior of sandwich structures have been dominated by measurements of their flexural and compressive properties, impact and ballistic responses as well as acoustic and shear properties. Assessment of these properties and comparison with conventional materials facilitate the possibility of determining the usefulness of a given sandwich material. In principle, the attendant mechanical properties of a specific WBSS will depend to a large extent on the properties of the components from which it is made. For instance, the density of a WBSS will be a function of the densities of the face skins and the core. It is recommended the measurements of these properties be based on the several international standards developed for this purpose. Among the standards are:

- ASTM Standard C271 for determination of density of sandwich core materials,
- ASTM Standard C273 for determination of shear properties of core materials,
- ASTM Standard C364 for determination of edgewise compressive strength,
- ASTM Standard C393 for determination of core shear properties by beam flexure,
- ASTM Standard D7250 for determination of flexural and shear stiffness,
- JIS A 5908:2003 for testing of fibreboard,
- PN-EN ISO 14125:2001 for flexural test of sandwich panels,
- French standard for bending, shear and compression of particleboard.

These standards stipulate the factors such as shape, dimensions of samples, the essential conditions for conducting the test measurements, and procedures for analysing the obtained results. It is generally common to conduct flexural tests by means of the well-known 3-point or 4-point bending tests. Extensive experimental investigations on WBSS have been performed by [Kawasaki et al. \(2003, 1998, 1999\)](#) and [Fernandez-Cabo et al. \(2011\)](#), who investigated the in-plane shear, bending and thermal insulation properties of WBSS using a variety of standard methods used for testing construction materials. The bending and shear properties of WBSS with marine plywood skins and plywood honeycomb core were reported by [Francesco et al. \(2011\)](#). Two recent studies on the subject matter include [Jin et al. \(2015\)](#) and [Lakreb et al. \(2015\)](#). **Tables 1–3** summarise the range of mechanical properties reported by the aforementioned studies.

Table 1 Shear properties of selected WBSS

Thickness (mm)	Density (kg/m ³)	Shear modulus (MPa)	Shear failure strength (MPa)	Refs.
OSB Skins/Fibreboard core (Test method: NT BUILD 378)				
150	110	0.70	1.94	Fernandez-Cabo et al. (2011)
150	130	1.06	3.11	Fernandez-Cabo et al. (2011)
150	150	3.30	12.30	Fernandez-Cabo et al. (2011)
150	190	5.90	21.80	Fernandez-Cabo et al. (2011)
Plywood skins/fibreboard (Test method: JIS A1414)				
96	350–400	73–89	109 – 125	Kawasaki et al. (2003)
Veneer/cork agglomerates core (Test method: NF T 54–605)				
40	**	2.23	0.15	Lakreb et al. (2015)
Marine plywood/honeycomb plywood core (Test method: EN 789)				
23	205	0.65	–	Francesco et al. (2011)

** (Dash means the value is not available from the reference).

Table 2 Flexural properties of selected WBSS

Thickness (mm)	Density (kg/m ³)	Modulus of elasticity (GPa)	Refs.
Plywood skin/fibreboard core (Test method: JIS A1414)			
100	320	5.1	Kawasaki et al. (2006)
100	350	6.2	Kawasaki et al. (2006)
100	430	5.5	Kawasaki et al. (2006)
LVL skin/wood-based 2D lattice core (Test method: ASTM C393)			
60	–**	4.30	Jin et al. (2015)
Sawn timber skin/wood-based 2D lattice core			
60	–	5.33	Jin et al. (2015)
Veneer/cork agglomerates core (Test method: NF T 54–606)			
40	–	0.053	Lakreb et al. (2015)
Marine plywood/honeycomb plywood core (Test method: EN 310)			
23	205	2.8	Francesco et al. (2011)

** (Dash means the value is not available from the reference).

Table 3 Compressive properties of selected WBSS

Thickness (mm)	Density (kg/m ³)	Modulus of elasticity (MPa)	Refs.
LVL skin/wood-based 2D lattice core (Test method: ASTM C365)			
60	–	28.72	Jin <i>et al.</i> (2015)
Sawn timber skin/wood-based 2D lattice core			
60	–	29.33	Jin <i>et al.</i> (2015)
Veneer/cork agglomerates core (Test method: NF T 54–602)			
40		1.27	Lakreb <i>et al.</i> (2015)

**(Dash means the value is not available from the reference).

Applications

WBSS have applications that are similar to those of the general sandwich structures, especially for use as prefabricated building elements (Davies, 2008). When used as the core materials, the porosity of wood fiber presents acoustic insulation benefits (Fernandez-Cabo *et al.*, 2011), making WBSS suitable in homes and buildings where one wishes to eliminate noise and sound transmission from room to room or as modular separating walls in trade fairs construction. Other potential usages pertains to packaging for flight and cargo containers, furniture, naval shipbuilding, flooring etc.

Further Information

Plywood production

- <http://www.wisaplywood.com/Products/about-plywood/Pages/Default.aspx>
- <https://www.kitronik.co.uk/blog/plywood-production-process/>
- <http://biaform.com.pl/en/about-us/physical-and-mechanical-characteristics-of-plywood/>

Laminated veneer lumber

- <https://www.iso.org/standard/38869.html> (ISO 18776:2008 - specifications)
- <https://www.iso.org/standard/44225.html> (ISO 27567:2009 - methods of tests)

Oriented strand board

- <https://www.iso.org/standard/32475.html> (ISO 16894:2009 - classifications)

Fibreboard production

- <http://www.heat-inc.com/fibreboard-particle-board-3/>
- https://www.egger.com/shop/en_MY/

Balsa wood

- <http://eol.org/pages/584793/overview>

Testing standards

- ASTM Standard
 - <https://www.astm.org/Standards/C271.htm> (Density of core)
 - <https://www.astm.org/Standards/C273.htm> (Shear properties of core)
 - <https://www.astm.org/Standards/C393.htm> (Core shear properties by flexure)
 - <https://www.astm.org/Standards/C364.htm> (Edgewise compressive strength)
 - <https://www.astm.org/Standards/D7250.htm> (Flexural and shear stiffness)
- ISO Standard
 - <https://www.iso.org/standard/32853.html> (ISO 9427:2003 - Density of wood panels)
 - <https://www.iso.org/standard/37996.html> (ISO 16572:2008 -Test method for structural properties)
- Others
 - BIS standard on timber structures (BS EN 408:2003):
 - Japanese Industrial Standard for particleboard: <http://www.jisc.go.jp/eng/index.html>
 - Nordic test methods for timbers: <http://www.nordtest.info/>

Commercial production of WBSS

- a. <http://www.econcore.com/en>
- b. <http://dendrolight.lv/en/>
- c. <http://www.diabgroup.com/>

See also: Characterization of Wood, Cork and Their Composites for Building Insulation. Development of Epoxy Based Composites Using Bamboo and Waste Metal Chips. Investigation of the Fuel Value of Selected Wood Samples Using Artificial Neural Networks. Waste Resources Recycling in Achieving Economic and Environmental Sustainability: Review on Wood Waste Industry

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Materials, Design and Development of Latent Heat Storage Systems for Medium and Large-Scale Applications: Issues and Challenges

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Introduction

Energy plays a vital role in the development of all nations. The majority of the world's current energy consumption is met by the non-renewable energy sources, which occupies a huge proportion of 80.7% (REN21, 2017). If we continue to rely on the non-renewable energy sources at the same pace for another century, we will have exhausted most of these resources. Opting for renewable energy is one of the strategic solutions to avoid the growing imbalance of available resources. Of the several renewable energy sources, solar energy is the best in terms of available energy potential. Traditionally, solar energy is used in heating and drying applications. Nowadays, it finds a remarkable place in the field of electricity generation. Solar energy can be converted to electricity, directly using photovoltaics (PV), or indirectly using concentrated solar power (CSP).

Thermal Energy Storage

Photovoltaics convert the sunlight into electric current using the photoelectric effect. CSP plants use reflective lenses or mirrors and tracking systems to focus a large amount of sunlight into a small point or beam by which the working fluid gets heated to a higher temperature. In direct steam generation (DSG) plants, the working fluid is generally water and the steam produced is directly fed to the turbine for electricity production. In non-DSG plants, the primary working fluid is generally a synthetic oil that gets heated from the concentrated sunlight. Synthetic oil transfers the heat to the secondary working fluid (water/steam), which is then supplied to the turbine for power generation. The major disadvantage with the PV and CSP plants is the inability to generate electricity during night and overcast day, which reduces the operating time. Perhaps this issue can be solved in CSP plants by incorporating thermal energy storage (TES). In addition, TES systems can increase the plant reliability and reduce the levelized cost of energy. Thermal energy can be stored in the form of sensible, latent and thermo-chemical heat. In sensible heat storage (SHS) method, thermal energy is stored in the storage material by raising the temperature. In latent heat storage (LHS), thermal energy is stored by phase change of material, e.g., solid to liquid. In thermo chemical heat storage (THS), thermal energy is stored during the reversible chemical reactions.

TES system employed in CSP plants can be classified as active or passive systems. An active storage system is mainly characterized by the forced convection heat transfer of the storage material. The storage material itself circulates in the main circuit of the CSP plant. This system uses one or two tanks as storage media. Active systems are subdivided into direct and indirect systems. In a direct system, the heat transfer fluid (HTF) serves also as the storage medium, while in an indirect system, a second medium is used for storing the heat. Steam accumulators falls under the category of active storage system and are especially suited to meet the requirements for buffer storage in solar steam systems, providing saturated steam at pressures up to 100 bar. The main disadvantages of active systems are, it requires bulky containers for accommodating the storage materials and necessitates proper control systems to avoid freezing of the storage material during night. Oro *et al.* (2012) reported that the commonly used two tanks molten salts storage system is the one with the higher environmental impact and therefore, should be substituted by the other systems.

In passive heat storage system, the storage material is a fixed entity and HTF passes through the storage medium and exchanges heat during charging and discharging cycles. Passive storage systems are mainly solid storage systems (concrete for SHS, PCM for LHS and metal hydrides for THS). In general, the passive storage system consists of a regenerator type heat exchanger wherein the HTF passes through the storage media for charging and discharging only. During charging, the high-temperature HTF transfers heat to the storage medium. The stored energy is released during discharging as the low-temperature HTF passes through it. Fig. 1 depicts the schematic representation of a CSP plant with TES system.

Phase Change Materials

Phase change materials (PCMs) are a group of families of materials, which will undergo a phase change while heating/cooling it above/below the phase transition temperature. Initially, the PCMs act like SHS materials; their temperature increases as they absorb heat. However, when PCMs reach the phase transition temperature, they absorb a large amount of heat (called as latent heat) at a near constant temperature. The PCM continues to absorb heat without a significant increase in temperature until all the material has transformed to the liquid phase. Once the entire PCM is melted, the temperature of the PCM again increases when heat is supplied to it. PCMs are broadly classified into inorganic, organic and eutectics. Inorganic PCMs generally include hydrated salts and metals, which are suitable for medium to high temperature storage applications such as process industries and thermal power plants. Organic PCMs on the other hand include paraffins and fatty acids, which are normally used in thermal comfort in buildings, preservation of food/medicines, cooling of electronics, etc. Eutectics are compounds formed by mixing two or more

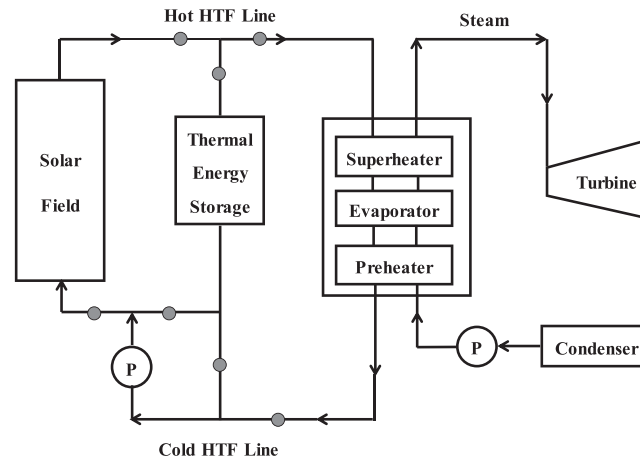


Fig. 1 Schematic view of a CSP plant with TES system.

PCMs (organic or inorganic) which melts/solidifies in the same temperature interval. A large number of PCMs are available in any required temperature range.

The main criteria that govern the selection of PCMs are (Abhat, 1983):

1. Possess a phase transition temperature in the desired operating temperature range.
2. Have a high latent heat of fusion, so that a smaller amount of PCM can store the desired amount of energy.
3. Possess high specific heat to provide additional SHS effects.
4. Have a high thermal conductivity for faster charging and discharging rates.
5. Small volume changes during phase transition, so that a simple type of heat exchanger can be used.
6. Exhibit little or no sub-cooling during freezing.
7. Possess chemical stability, no chemical decomposition.
8. Should not contain poisonous, flammable and explosive elements/compounds.
9. Exhibit little or no corrosion.
10. Available in large quantities at a cheaper cost.

Commercialization of LHS System

The most intensely studied LHS system among various configurations is the shell-and-tube system. In the shell-and-tube configuration, PCM is usually filled in the shell, and the HTF flows through the tubes. Avci and Yazici (2013) performed an experimental study for evaluating TES characteristics of paraffin in a horizontal shell-and-tube storage unit. They found that the temperature field is radially uneven during the melting process in the horizontal annulus due to natural convection. Trp *et al.* (2006) studied the storage phenomenon during melting and solidification of paraffin in a vertical shell-and-tube LHS storage unit. They reported that the temperature distribution in the PCM is non-isothermal during melting and isothermal during solidification. Agyenim *et al.* (2010) experimentally studied the effect of using multiple HTF tubes in shell-and-tube LHS units. The multi-tube system showed superior performance than the single tube system aided with the distribution of heat in multiple layers around each HTF tube to the PCM. Certain numerical studies also portrayed the advantages of using multiple tubes in LHS systems. Esapour *et al.* (2016) developed a 2D numerical model to study the influence of the number of HTF tubes in an LHS system during the charging process. They reported that by increasing the number of HTF tubes, the bottom region of the shell is influenced by the additional heat transfer surface thereby reducing the total melting time by about 29% for the four tubes system. In a more recent experimental work by Allouche *et al.* (2015), the performance of a microencapsulated PCM in a tube-bundle heat exchanger for low-temperature TES was studied. When compared the results with previously published results for other configurations, the tube-bundle storage tank configuration was found to perform better than a coil-in-tank configuration. They also mentioned that shell-and-tube type of heat exchanger has the additional advantage of incorporating fins to the HTF tubes, which can significantly enhance the heat transfer. Though several prototypes of TES were developed across the world, only a few large-scale TES systems have been commissioned in the CSP plants (Gil *et al.*, 2010). There are about 101 operational CSP plants in the world working on technologies such as linear Fresnel reflector, parabolic trough and solar tower. Of these, only 41 CSP plants have added commercial storage systems to the utility. Two-tank molten salt storage system is the highly installed TES system, which has its presence in 31 CSP plants (NREL, 2017). Tables 1 and 2 present the details of the CSP plants with and without 2-tank molten storage system. Though, the passive storage systems have several potential benefits, it has not yet commercialized till date. An attempt has been made in the present work to commercialize the LHS system by studying the performance characteristics of the LHS system through thermal models and experimental investigations using a lab-scale LHS prototype of 10 MJ storage capacity. Based on the results of the thermal model and experimental investigations, the study has been extended to develop an industrial-scale LHS

Table 1 List of CSP plants with 2-tank molten salt storage system

<i>Sl. no</i>	<i>Project name</i>	<i>Country</i>	<i>Sl. no</i>	<i>Project name</i>	<i>Country</i>
1	Andasol-1, 2 & 3	Spain	12	Gemasolar	Spain
2	Archimede	Italy	13	Greenway	Turkey
3	Arcosol 50	Spain	14	KaXu Solar One	South Africa
4	Arenales	Spain	15	La Africana	Spain
5	ASE Demo Plant	Italy	16	La Dehesa	Spain
6	Aste 1A & 1B	Spain	17	La Florida	Spain
7	Astexol II	Spain	18	Manchasol 1 & 2	Spain
8	Bokpoort	South Africa	19	Noor I	Morocco
9	Casablanca	Spain	20	Solana	USA
10	Crescent Dunes	USA	21	Termesol 50	Spain
11	Extresol-1, 2, 3 & 4	Spain	22	Termosol 1 & 2	Spain

Reproduced from NREL, 2017. Concentrating Solar Power Projects [Online], USA. Available: <https://www.nrel.gov/csp/solarpaces/> (accessed 01.01.18).

Table 2 List of CSP plants with their corresponding storage systems

<i>Sl. no.</i>	<i>Project name</i>	<i>Country</i>	<i>Storage</i>
1	Ait-Baha	Morocco	Packed bed of rocks
2	Augustin Fresnel 1	France	Ruths tank
3	Dahan Power Plant	China	saturated steam/oil
4	Jülich Solar Tower	Germany	Ceramic heat sink
5	Khi Solar One	South Africa	Steam drum
6	Lake Cargelligo	Australia	Graphite
7	Planta Solar 10	Spain	Steam drum
8	Planta Solar 20	Spain	Steam drum
9	Puerto Errado 1 & 2	Spain	Single-tank thermocline

Reproduced from NREL, 2017. Concentrating Solar Power Projects [Online], USA. Available: <https://www.nrel.gov/csp/solarpaces/> (accessed 01.01.18).

prototype of 0.25 GJ storage capacity and integrate it with a commercial steam accumulator of 1 GJ storage capacity. This combined storage system has been installed in the LFR based pilot-CSP plant in Vallipuram, Tamil Nadu, India.

Lab Scale Prototype – Design, Thermal Modeling and Numerical Results

Design and optimization of LHS prototypes require an exhaustive analysis of the heat transfer characteristics, between the PCM and HTF. The number of the HTF tubes and fins on the HTF tube's outer surface play a significant role in transferring the heat between them. Un-optimized prototype with more number of the HTF tubes and fins would lead to higher material inventory. Additionally, the overall weight of the system will increase too. Hence, a detailed optimization study is needed to have a cost-effective LHS system. To achieve this, many experiments with different geometric configurations, by varying the number of the HTF tubes and fins, need to be conducted. This approach has two major disadvantages; (i) the development cost of the different prototypes to be tested is high and (ii) for up scaling, new prototypes need to be developed for getting the optimized module. Development of a numerical tool for the optimization of geometric configuration and performance evaluation of LHS prototype is an ideal solution to overcome the above limitations. But the mathematical modeling of the LHS prototypes, especially in the multidimensional case is complex (Bonacina *et al.*, 1973). The major problems involved in the modeling are (i) inclusion of latent heat of PCM, (ii) natural convection of the melt and (iii) conjugate heat transfer between the PCM and HTF. This section presents a 3D transient numerical model, which is developed using the effective heat capacity (EHC) method to study the performance characteristics of a shell-and-tube type lab-scale LHS prototype of 10 MJ LHS capacity. Longitudinal fins adopted for heat transfer enhancement in the experimental studies are also included in the numerical model. Optimization of the number of tubes and fins for the LHS system is performed using a 2D transient model, the output (the number of tubes and fins) of which is used in the 3D model. A eutectic ternary mixture comprising of potassium nitrate, sodium nitrate and sodium nitrite in the weight proportion of 53:7:40, which has the melting point of approximately 142°C is selected as the PCM for the numerical simulation. Hi-Tech Therm 60, a synthetic thermic oil is selected as the HTF. The thermo-physical properties of the selected PCM (Bohlmann, 1972) and HTF are given in Tables 3 and 4.

Design Methodology

The lab-scale prototype is designed for an LHS capacity of about 10 MJ. The volume (V) of PCM required depends on the heat storage capacity (Q), density (ρ) and latent heat of fusion (L_f). For storing a heat of 10 MJ, the PCM volume required is calculated

Table 3 Thermo-physical properties of the PCM

Properties	Values
Latent heat of fusion (kJ kg^{-1})	81.5
Melting point ($^{\circ}\text{C}$)	142
Thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)	0.571
Density (kg m^{-3})	
Solid (122°C)	1996
Liquid (162°C)	1956
Specific heat ($\text{J kg}^{-1} \text{K}^{-1}$)	
Solid	1340
Liquid	1562
Dynamic viscosity (Pa s)	0.02
Thermal expansion coefficient (K^{-1})	3.629×10^{-4}

Reproduced from Bohlmann, e.g., 1972. Heat Transfer Salt for High Temperature Steam Generation. Oak Ridge National Lab., Tennessee.

Table 4 Thermo-physical properties of Hi-Tech Therm 60 at different temperatures

$T (^{\circ}\text{C})$	$\rho (\text{kg m}^{-3})$	$C_p (\text{J kg}^{-1} \text{K}^{-1})$	$k (\text{W m}^{-1} \text{K}^{-1})$	$\gamma (\text{mm}^2 \text{s}^{-1})$	$\mu (\text{Pa s})$
40	860	2081.8	0.1314	20.00	0.017200
100	823	2306.2	0.1238	3.82	0.003144
150	790	2493.2	0.1175	1.75	0.001383
200	755	2680.2	0.1119	0.90	0.000680

Reproduced from Generation Four Engitech Ltd., India. Available at: <http://www.hitechsolution.co.in/product-detail.php?page=hitech-therm-60> (accessed 01.01.18).

using Eq. (1). Based on the volume found, the inner diameter of the shell (D) is calculated using Eq. (2). The outer diameter (d) and thickness of HTF tubes are 12.7 mm and 2 mm. The height (h) and thickness (b) of the longitudinal fins attached to the tubes are 10 mm and 1 mm. The number of HTF tubes and fins were optimized based on the discharging time. The number of HTF tubes (N_T) and fins (N_F) on each tube in the optimized lab-scale LHS prototype are 25 and 4. The HTF tubes and fins are made of copper. The outer shell of the prototype is made of stainless steel (SS304) of diameter 335 mm OD and 5 mm thickness.

$$Q = \rho V L_F \quad (1)$$

$$V = \left[\frac{\pi}{4} (D^2 - N_T d^2) - N_T N_F b h \right] L \quad (2)$$

Model Description

Fig. 2 shows the sectional view of the 3D shell-and-tube type LHS model containing a PCM in the shell region and HTF in the tube region, both separated by HTF tubes. The LHS unit is divided into three cartridges, separated by a thin layer of concrete. To study the thermal storage behavior of a shell-and-tube type LHS prototype, four physical processes have to be simulated, i.e., HTF flow, conduction, convection, and phase change. The thermal model is developed based on following assumptions:

- HTF is incompressible and Newtonian.
- HTF flow is laminar and exhibits negligible viscous dissipation.
- The initial temperature of PCM is uniform.
- Phase change during melting/solidification occurs in a temperature interval.
- Thermal losses through the outer wall of the PCM are negligible.

Governing Equations

The thermal model developed is based on a conjugate heat transfer problem, which simultaneously solves the flow behavior of HTF and phase change behavior of PCM. The biggest problem associated with adapting an existing sensible heat based model for an LHS model is the incorporation of latent heat required to melt/solidify the PCM. This issue is solved by using the EHC method, which includes both specific heat and latent heat of the PCM in a single term called EHC. The EHC method was developed by Bonacina *et al.* (1973) and later used by several authors with slight improvements. The heat capacity of the PCM is modified as shown in Eq. (3) and the EHC is calculated using Eq. (4). Phase change is considered to occur during a temperature interval. Problems of this type are often referred to as mushy region problems. The discontinuous modified heat capacity is implemented in the COMSOL Multiphysics software using a smoothed Heaviside function with a continuous second derivative. Accordingly,

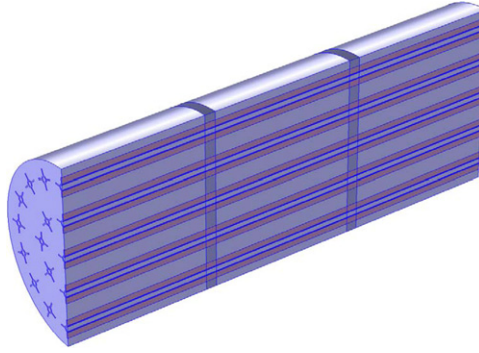


Fig. 2 Computational model of the LHS prototype. Reproduced from Niyas, H., Prasad, S., Muthukumar, P., 2017. Performance investigation of a lab-scale latent heat storage prototype – Numerical results. *Energy Conversion and Management* 135, 188–199.

continuity, momentum, and energy equations are given in Eqs. (5)–(7). The effect of convection heat transfer is taken care by the material derivative term DT/Dt in Eq. (7). To include the effect of buoyancy and reduce the complexity in solving the Navier-Stokes equations, Boussinesq approximation is added to the momentum equation, which is given by Eq. (8). To nullify the velocities in the solid region of the PCM, Darcy law's source term is added to the momentum equation, which is given by Eq. (9).

$$C_p = \begin{cases} C_{p,s} & \text{for } T < T_s \\ C_{p,eff} & \text{for } T_s \leq T \leq T_L \\ C_{p,L} & \text{for } T > T_L \end{cases} \quad (3)$$

$$C_{p,eff} = \frac{C_{p,s} + C_{p,L}}{2} + \frac{L_F}{T_L - T_s} \quad (4)$$

$$\nabla \cdot \vec{v} = 0 \quad (5)$$

$$\frac{\partial \vec{v}}{\partial t} + (\vec{v} \cdot \nabla) \vec{v} = \frac{1}{\rho} (-\nabla P + \mu \nabla^2 \vec{v} + \vec{F} + \vec{S}) \quad (6)$$

$$\rho C_p \frac{DT}{Dt} = k \nabla^2 T \quad (7)$$

$$\vec{F} = \rho \vec{g} \beta (T - T_M) \quad (8)$$

$$\vec{S} = \frac{(1 - \theta)^2}{(\theta^3 + \varepsilon)} A_{MUSH} \vec{v} \quad (9)$$

$$\theta = \frac{T - T_s}{T_L - T_s} = \frac{T - T_M + \Delta T_M}{2 \Delta T_M} = \begin{cases} 0 & \text{for } T < T_s \\ 0 - 1 & \text{for } T_s \leq T \leq T_L \\ 1 & \text{for } T > T_L \end{cases} \quad (10)$$

The mushy zone constant defines the transition of velocity in the mushy region. Mushy zone constant values between 10^3 and 10^7 are recommended for most computations. Here, a value of 10^4 is taken based on the works presented by Kheirabadi and Groulx (2015) on the effect of mushy zone constant. During charging cycle, the Darcy law's source term dominates all other terms in the momentum equations and forces the predicted velocities to near zero before melting of the PCM. Once a molten layer of the PCM is formed, the melt fraction of the PCM increases and hence the source term decreases. After complete melting of the PCM, the melt fraction becomes unity, and therefore the source term becomes zero. The momentum equations then behave normally in terms of actual fluid velocities. Similarly, during the discharging cycle, where the local melt fraction assumes a value of 1 initially, the source term is zero and the momentum equations are in terms of actual fluid velocities. Once the solidification of PCM is started, the source term increases and approximates the Darcy law in the mushy region. Finally, the Darcy law's source term dominates all other terms in momentum equations and forces the predicted velocities to near zero at the end of the discharging cycle.

Performance Parameters

Melt fraction

Most of the PCMs, especially a mixture of salts, often melt over a finite temperature range. The temperature range wherein, the melt exists in both solid and liquid phases is generally called mushy zone. The highest temperature at which, the material is completely in the solid state is called solidus temperature and the lowest temperature at which, the material is completely in the liquid state is called liquidus temperature. Melt fraction is a non-dimensional parameter, which quantifies the percentage of liquid phase in the

marshy region. Melt fraction of the PCM can be calculated based on the lever rule applied between the solidus and liquidus temperatures and it is given by Eq. (10).

Charging/discharging time

Charging/Discharging time of LHS prototype is defined with respect to the temperature rise/decrease of PCM. The LHS prototype is said to be fully charged/discharged when the entire PCM is melted/solidified, i.e., when the melt fraction reaches a value of unity/one. The LHS prototype should be designed and optimized in such a way that, it possess a lesser charging and discharging times.

Energy stored/discharged

Energy gets stored/discharged in the PCM in two forms during charging, viz. sensible and latent heat. Initially, when the PCM is in the solid state, the storage/discharge rate through sensible heat would be greater than that of latent heat, due to the higher temperature difference between the initial temperature and solidus/liquidus temperature of the PCM. Sensible, latent and total heat stored/discharged in the PCM during the charging/discharging process can be calculated using the Eqs. (11)–(16), respectively.

$$E_{S,C} = m [C_{ps} (T - T_m) + C_{pl}(T_m - T_{ini})] \quad (11)$$

$$E_{L,C} = m L_F \theta \quad (12)$$

$$E_{T,C} = m [C_{ps} (T - T_m) + L_F \theta + C_{pl}(T_m - T_{ini})] \quad (13)$$

$$E_{S,D} = m [C_{ps} (T_{ini} - T_m) + C_{pl}(T_m - T)] \quad (14)$$

$$E_{L,D} = m L_F (1 - \theta) \quad (15)$$

$$E_{T,D} = m [C_{ps} (T_{ini} - T_m) + L_F (1 - \theta) + C_{pl}(T_m - T)] \quad (16)$$

Results and Discussions

In the following sub-sections, optimization of the LHS prototype, validation, grid independent test and various results obtained from the numerical simulations of the lab-scale LHS prototype during charging and discharging processes are presented.

Optimization of tubes and fins

The major constraint of PCMs is its lower thermal conductivity, which necessitates the implementation of heat-transfer enhancement techniques such as finned tubes. Increasing the number of tubes and fins on the tubes outer surface increases the overall heat-transfer surface area of the system. To optimize the number of tubes and fins in the LHS prototype, a 2D thermal model is developed based on the governing equations, Eq. (5)–(7) to compare the performances of the selected systems, viz. models with 19, 22, 25 and 28 tubes and 25 tubes model with 0, 2, 4 and 6 fins. To maintain the same PCM volume in the various models, the shell diameter is kept different in the models. The shell diameter values of various models are given in Tables 5 and 6. Figs. 3 and 4 show the various models considered for optimization. The optimization is done based on the discharging time, as

Table 5 Optimization of tubes

No. of tubes	Shell diameter (mm)	Charging time (min)	% reduction in time	Discharging time (min)	% reduction in time
19	318.9	184		262	
22	319.6	166	9.8	210	19.8
25	320.4	151	9.0	180	14.3
28	321.1	138	8.6	165	8.3

Reproduced from Niyas, H., Prasad, S., Muthukumar, P., 2017. Performance investigation of a lab-scale latent heat storage prototype – Numerical results. Energy Conversion and Management 135, 188–200.

Table 6 Optimization of fins

No. of fins	Shell diameter (mm)	Charging time (min)	% reduction in time	Discharging time (min)	% reduction in time
0	320.4	151		180	
2	322.3	117	22.5	127	29.4
4	324.3	93	20.5	100	21.3
6	326.3	78	16.1	91	9.0

Reproduced from Niyas, H., Prasad, S., Muthukumar, P., 2017. Performance investigation of a lab-scale latent heat storage prototype – Numerical results. Energy Conversion and Management 135, 188–201.

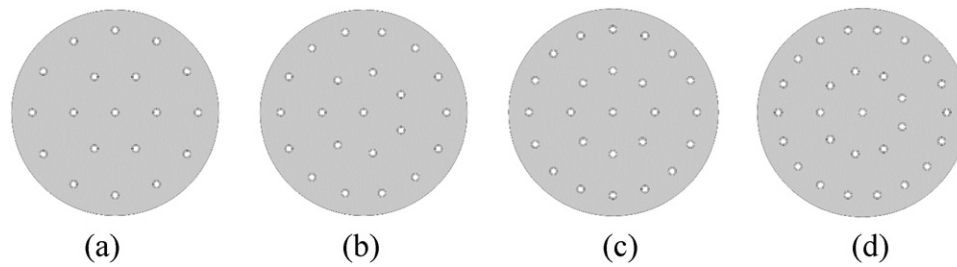


Fig. 3 Optimization of tubes (a) 19 tubes, (b) 22 tubes, (c) 25 tubes and (d) 28 tubes. Reproduced from Niyas, H., Prasad, S., Muthukumar, P., 2017. Performance investigation of a lab-scale latent heat storage prototype – Numerical results. *Energy Conversion and Management* 135, 188–200.

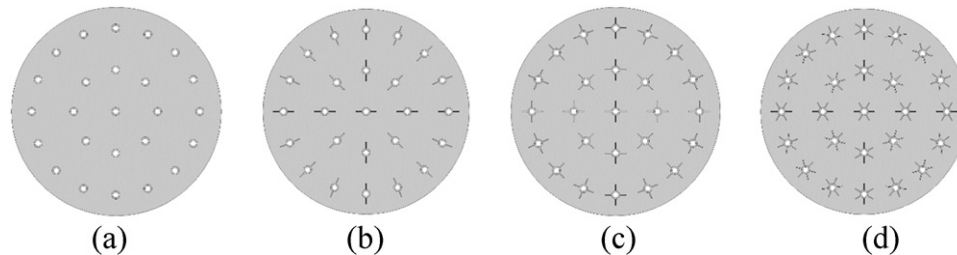


Fig. 4 Optimization of fins (a) no fins, (b) 2 fins, (c) 4 fins and (d) 6 fins. Reproduced from Niyas, H., Prasad, S., Muthukumar, P., 2017. Performance investigation of a lab-scale latent heat storage prototype – Numerical results. *Energy Conversion and Management* 135, 188–201.

discharging is a comparatively slower process than charging. The discharging time of different configurations is given in **Tables 5** and **6**. It can be seen from **Table 5** that there is a vast reduction in the discharging time of LHS prototype (19.8%) with 22 tubes when compared to 19 tubes and 25 tubes when compared to 22 tubes (14.3%). However, there was only a marginal reduction in the discharging time of LHS prototype with 28 tubes when compared to 25 tubes (8.3%). Similarly, it can be seen from **Table 6** that there is a vast reduction in the discharging time of LHS prototype (29.4%) with 2 fins when compared to 0 fins and 4 fins when compared to 2 fins (21.3%). However, there was only a marginal reduction in the discharging time of LHS prototype with 6 fins when compared to 4 fins (9.0%). Hence, shell-and-tube type heat exchanger with 25 tubes and 4 fins attached to each tube is found to be the optimized configuration for the current heat storage/discharge requirement.

Model validation

To validate the developed thermal model for the charging and discharging process, the results obtained for the temperature variation of the PCM at 2 locations in the LHS prototype, viz. middle of 1st and 3rd cartridges [B (–141 mm, 30 mm)] were compared with the corresponding temperature values of the experiments. The thermocouple position selected for validation is point B, which is shown in **Fig. 5(a)**. The PCM is initially at 122/162°C during the charging/discharging process. At any time $t > 0$, the inlet of the tubes is given an HTF flow of 0.3 m³/h and inlet temperature of 162/122°C during the charging/discharging process. **Fig. 5(b)** and **(c)** illustrates the comparison between the experimental and numerical values for the charging and discharging processes. It can be noted from **Fig. 5(b)** and **(c)** that there is a close agreement between the experimental and numerical data. The maximum deviation is about 3.36°C and 2.74°C during the charging and discharging processes, respectively.

Grid independent test

To test the dependency of numerical results on the mesh element size, simulations with different mesh element sizes were run for charging and discharging processes. **Fig. 6(a)** and **(b)** shows the average temperature variation of the LHS prototype with a different number of mesh elements viz. 786,342, 890,548 and 995,643 elements for charging process and 743,148, 842,412 and 944,674 for discharging processes. It can be observed from **Fig. 6(a)** and **(b)** that the charging/melting simulation demands more number of mesh elements, due to the free convective movement of the PCM.

For all the cases of grid independent test, the PCM is initially at 122/162°C during charging/discharging process. At any time $t > 0$, the inlet of the tubes is given an HTF flow of 0.3 m³/h and inlet temperature of 162/122°C during charging/discharging process. It is observed from **Fig. 6(a)** and **(b)** that the models with 890,548 and 842,412 elements are found to be grid independent for charging and discharging processes.

Temperature variation

Fig. 7 depicts the average temperature variation of the LHS prototype during the charging and discharging processes. The average temperature is the volumetric average temperature of all the mesh elements of the numerical model. Initially, the LHS prototype is

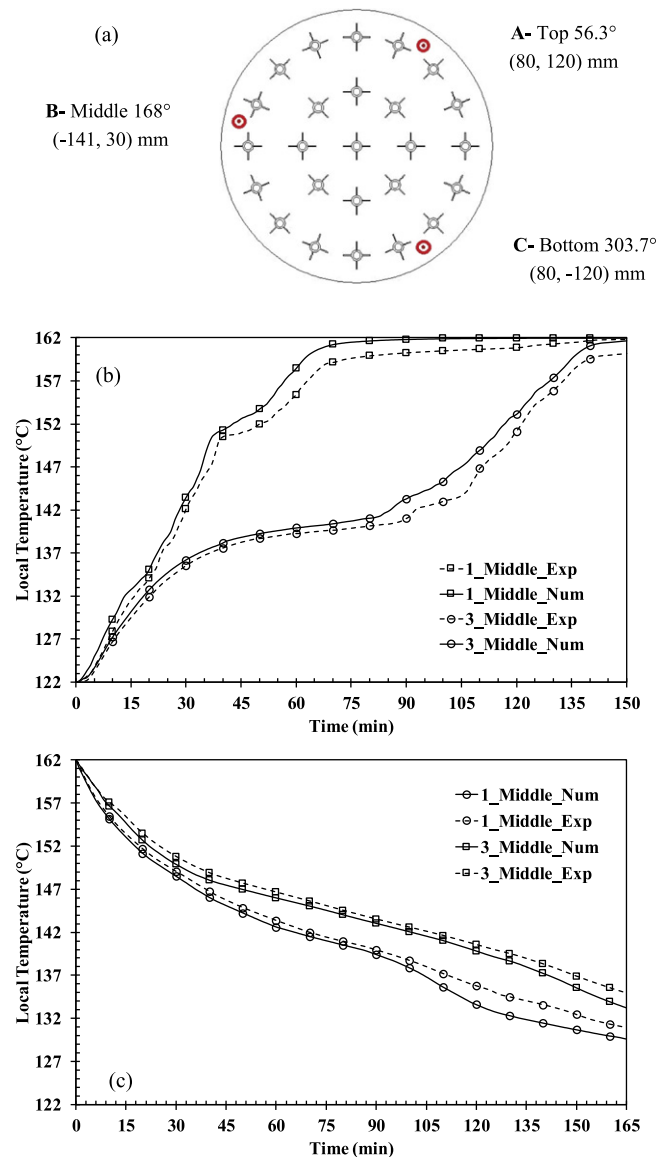


Fig. 5 Model validation (a) thermocouple position, (b) charging and (c) discharging. Reproduced from Niyas, H., Prasad, S., Muthukumar, P., 2017. Performance investigation of a lab-scale latent heat storage prototype – Numerical results. *Energy Conversion and Management* 135, 188–202.

at 122/162°C during the charging/discharging process. When the HTF at 162/122°C is passed through the HTF tubes, heat transfer takes place between the HTF and PCM. It can be noted from Fig. 7 that the initial part of the average temperature variation curve shows a steady increase/decrease of temperature during charging/discharging process. This steady increase/decrease is due to the higher heat transfer potential available during the initial period of the processes. After 30 min, the slope of the temperature variation curve started reducing. During this time, LHS prototype stores/discharges a large amount of latent heat. The PCM average temperature reaches approximately about 161/132.3°C in 150/165 min during the charging/discharging process. The PCM temperature increase during charging is faster than the PCM temperature decrease during discharging. This is mainly due to the additional convective heat transfer that increases the heat transfer rate of the prototype during the charging process.

Charging/discharging time

Fig. 8 shows the average melt fraction variations of the LHS prototype during the charging and discharging processes. Average melt fraction is the volumetric average melt fraction of all the mesh elements of the numerical model. Melt fraction is a critical performance parameter, which depicts only the latent heat storage/discharge characteristics during the charging/discharging process. It can be seen from Fig. 8 that the trend of increase/decrease of average melt fraction during charging/discharging process is initially faster due to the higher heat transfer potential and slower after a certain period due to the lower heat transfer potential

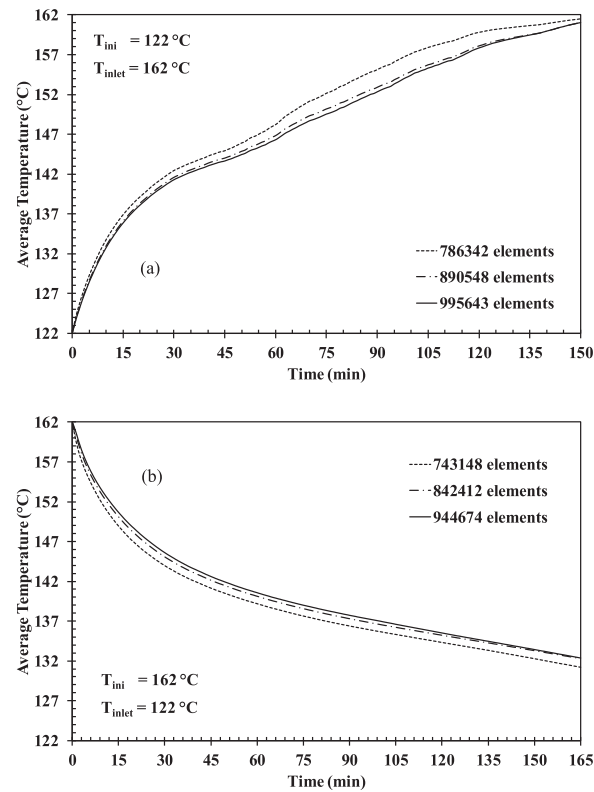


Fig. 6 Grid independent test of the shell-and-tube model (a) charging and (b) discharging. Reproduced from Niyas, H., Prasad, S., Muthukumar, P., 2017. Performance investigation of a lab-scale latent heat storage prototype – Numerical results. *Energy Conversion and Management* 135, 188–203.

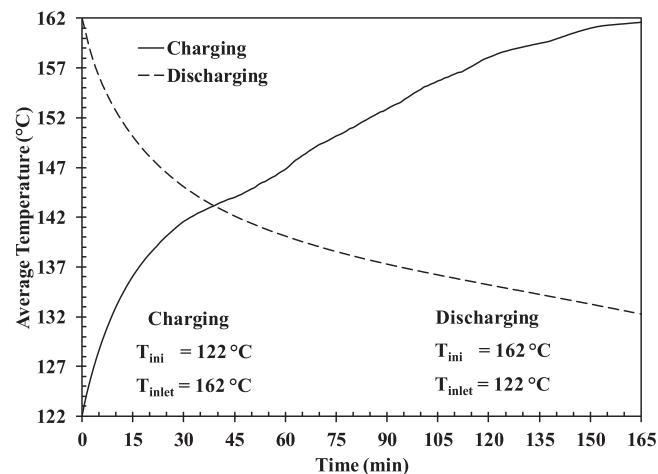


Fig. 7 Average temperature variation of the shell-and-tube LHS model. Reproduced from Niyas, H., Prasad, S., Muthukumar, P., 2017. Performance investigation of a lab-scale latent heat storage prototype – Numerical results. *Energy Conversion and Management* 135, 188–204.

between the HTF and PCM. It took about 137/158 min for the LHS model to get completely charged/discharged. However, the charging/discharging time of the LHS model with respect to the actual thermocouple locations of the prototype is 111/117 min.

Melt fraction

Fig. 9(a) and **(b)** depicts the average melt fraction contours of the LHS prototype during the charging and discharging processes. It can be seen from **Fig. 9(a)** and **(b)** that the average melt fraction of the LHS prototype is 0/1 at the start of the charging/discharging processes ($t=0$ min). At time $t=50$ min, it can be noted that the 1st cartridge is almost fully charged during the charging process. However, during the discharging process at the same time, the 1st cartridge is discharged to a limited extent only and not fully as in the case of charging. Hence, the charging process is faster than the discharging process.

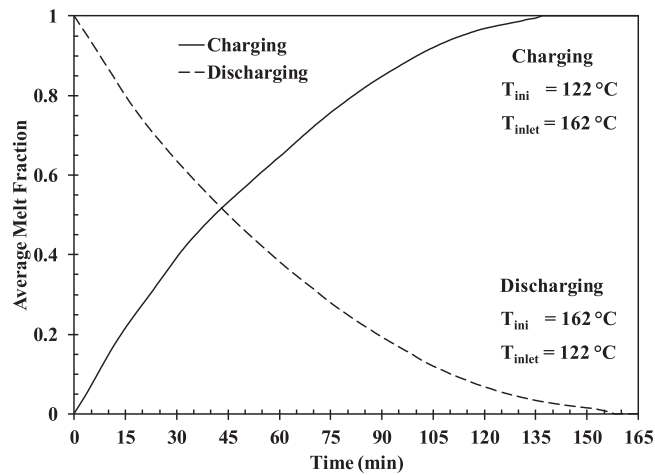


Fig. 8 Average melt fraction variation of the shell-and-tube LHS model. Reproduced from Niyas, H., Prasad, S., Muthukumar, P., 2017. Performance investigation of a lab-scale latent heat storage prototype – Numerical results. *Energy Conversion and Management* 135, 188–205.

This is mainly due to the additional natural convection heat transfer present in the charging process. The effect of natural convection can be clearly seen in the LHS prototype during charging process ($t=50$ min, 100 min) from the asymmetric variation of the melt fraction. Similar melt fraction variation is not noticeable in the discharging process as it is a conduction-dominated process. It can be seen from **Fig. 9(a)** and **(b)** that the LHS prototype is fully charged/discharged at 150/160 min.

Energy storage/discharge rate

Fig. 10(a) and **(b)** illustrates the energy storage/discharge rate of the LHS prototype during the charging/discharging process. When the HTF at 162/122°C is passed through the tubes, heat transfer takes place between the HTF and PCM. Initially, heat gets stored/discharged in the form of sensible heat only. Once the PCM reaches near the phase change temperature (142°C), heat gets stored/discharged in the form of latent heat. Similarly, after phase change of PCM, heat is stored/discharged in the form of sensible heat. When the PCM reaches an average temperature of 161°C in 150 min during the charging process, the amount of sensible, latent and total energy stored in the LHS prototype is 6.94 MJ, 10 MJ, and 16.94 MJ. The range of temperature in which the PCM stores the sensible heat is about 39°C (122–161°C). Similarly, when the PCM reaches an average temperature of 132.3°C in 165 min during the discharging process, the amount of sensible, latent and total energy discharged from the LHS prototype is 5.29 MJ, 10 MJ, and 15.29 MJ. The range of temperature in which the PCM discharges the sensible heat is about 29.7°C (162–132.3°C).

Lab Scale Prototype – Experimental Setup and Performance Evaluation

For any numerical model developed, validation with the real-time experimental data is vital for the practical applicability and further refinement of the model. In this section, details pertaining to the development of a shell-and-tube type lab-scale LHS prototype of 10 MJ capacity with multiple embedded HTF tubes and the corresponding experimental results are presented.

Experimental Setup

The schematic of the experimental setup employed for testing the thermal storage characteristics of the LHS prototype is shown in **Fig. 11**. The experimental setup consists of an oil storage tank, a high-temperature thermic fluid pump, a thermic fluid electric heater, LHS prototype, an expansion tank, a cooling tank, a positive displacement flow meter of the oval gear type, K-type metal-sheathed thermocouples and a data acquisition system. The oil storage tank having a 1000-liter capacity is utilized for storing the HTF. The huge storage capacity of the storage tank is mainly intended for storing the bulk heat, which aids in feeding a nearly constant temperature HTF to the LHS prototype. The HTF is circulated in the experimental loop by a high-temperature thermic fluid pump of single-stage centrifugal and horizontal end suction type. The pump provides enough pressure (about 2 bar) to overcome the pressure drop across the thermic fluid heater/cooling tank, LHS prototype and pipeline. A variable speed drive (frequency controller) is connected to the pump to achieve different flow velocities. The HTF is heated to the required operating temperature using the thermic fluid heater during the charging process.

The heater is of electrical resistance type and has a heating capacity of 72 kW. The electrical load supply to the heater is tuned by a controller, based on the temperature difference between the desired HTF temperature and the heater-exit HTF temperature. The oil volume is generally increased while heating due to the thermal expansion and the excess space needed to accommodate the oil is given by the expansion tank. In addition, the expansion tank serves as a deaerator, i.e., any gases if present in the thermic oil are deaerated. The cooling tank used in the setup is a water based coil-type heat exchanger. The heat exchanger coils are fabricated with

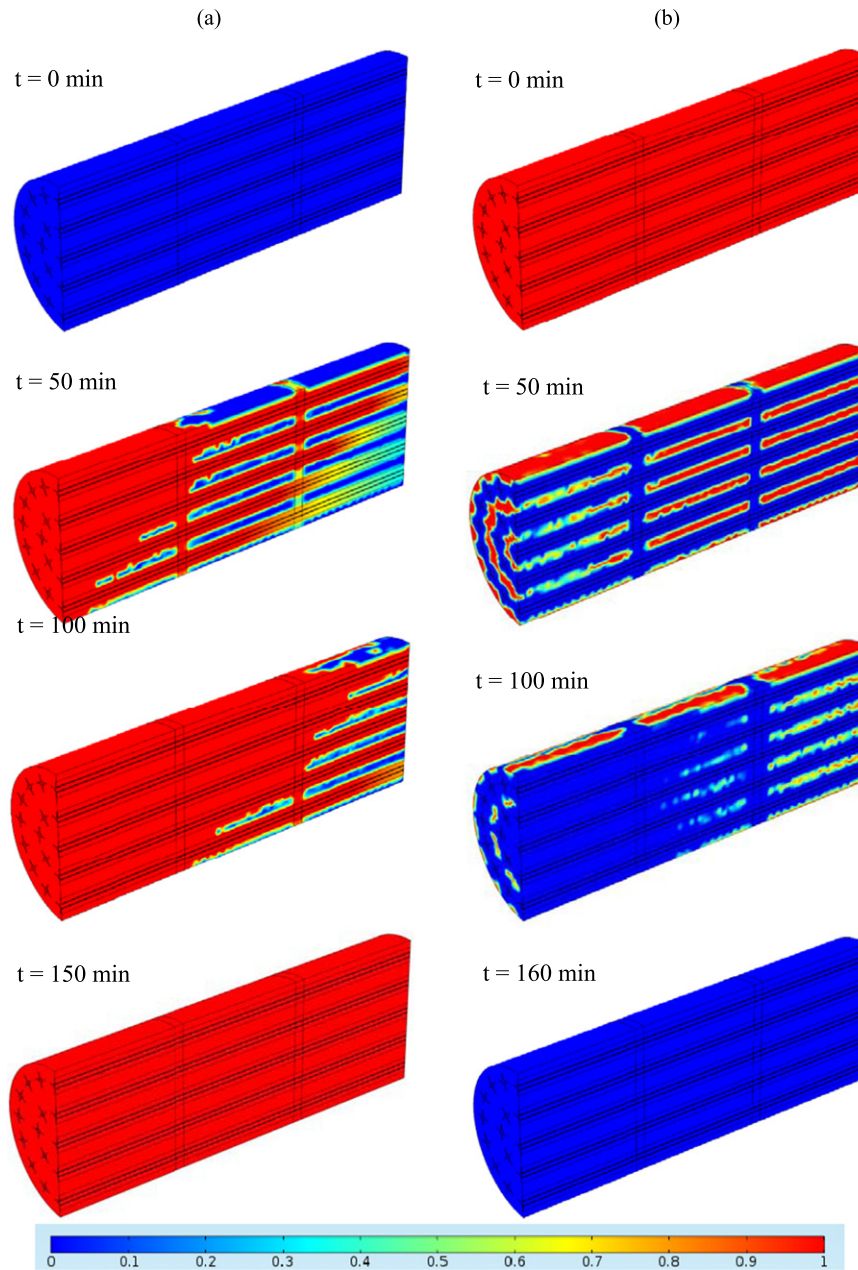


Fig. 9 Average melt fraction contours of the LHS model (a) charging and (b) discharging. Reproduced from Niyas, H., Prasad, S., Muthukumar, P., 2017. Performance investigation of a lab-scale latent heat storage prototype – Numerical results. *Energy Conversion and Management* 135, 188–206.

flexible copper tubes. Water in the cooling tank (about 750 L) serves as the cooling medium, and the temperature of the water is maintained at near room temperature through fresh supply of water. The HTF flows through the copper tubes during the discharging process, and it is cooled down due to the heat transfer between the HTF and water. Single ported, Tee type globe valves (G1–G11) are used to change and divert the flow of HTF during charging and discharging processes. A strainer of Y-type is kept between the expansion tank and storage tank, to filter the circulating HTF from foreign particles. Non-return valves of clapper type are used at certain locations of the fluid line, *viz.* inlet and outlet of the thermic fluid heater and outlet of the storage prototype, to prevent backflow of the HTF. The LHS prototype, oil storage tank and the pipeline are insulated using glass wool of 50 mm thickness for avoiding heat loss to the ambient. The pictorial view of the experimental setup is presented in Fig. 12. During the experiment, temperature of the LHS prototype at various locations, HTF inlet and outlet temperatures and HTF flow rate are measured at a constant time interval of 5 s. A positive displacement flow meter of the oval gear type having an accuracy of $\pm 0.2\%$ is used to measure the HTF flow rate in the circuit. Nine K-type thermocouples having an accuracy of $\pm 0.2^\circ\text{C}$ are fitted to the LHS prototype to measure the temperature. LHS prototype consists of three cartridges for keeping the PCM. In the middle of the three cartridges (0.135 m, 0.435 m, 0.735 m from any side of the prototype), thermocouples are placed at three different locations, *viz.*

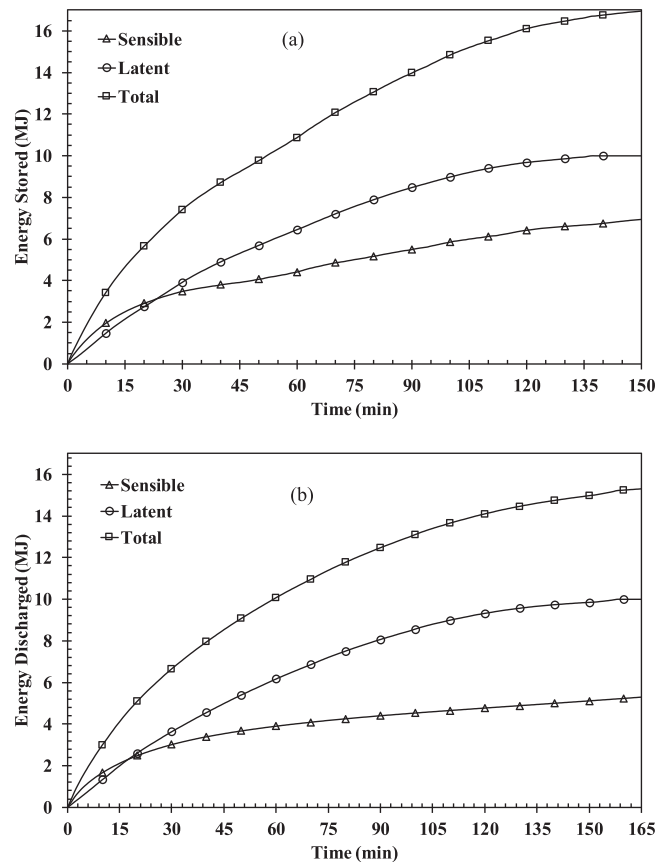


Fig. 10 Energy storage/discharge rate of the shell-and-tube LHS model (a) charging and (b) discharging. Reproduced from Niyas, H., Prasad, S., Muthukumar, P., 2017. Performance investigation of a lab-scale latent heat storage prototype-Numerical results. *Energy Conversion and Management* 135, 188–207.

top, middle and bottom to capture the temperature variations. Details of the thermocouple locations are given in Fig. 5(a). Two K-type thermocouples are fixed, each at the inlet and the outlet of the LHS prototype for measuring the HTF temperature. The thermocouples and the flow meter are connected to a data acquisition system, which in-turn is integrated with a computer for recording the temperature and the flow rate data. The data acquisition system consists of Agilent 34972A data logger (having a precision of $\pm 0.1^\circ\text{C}$) and Agilent 34901A 20-channel multiplexer.

Latent Heat Storage Prototype

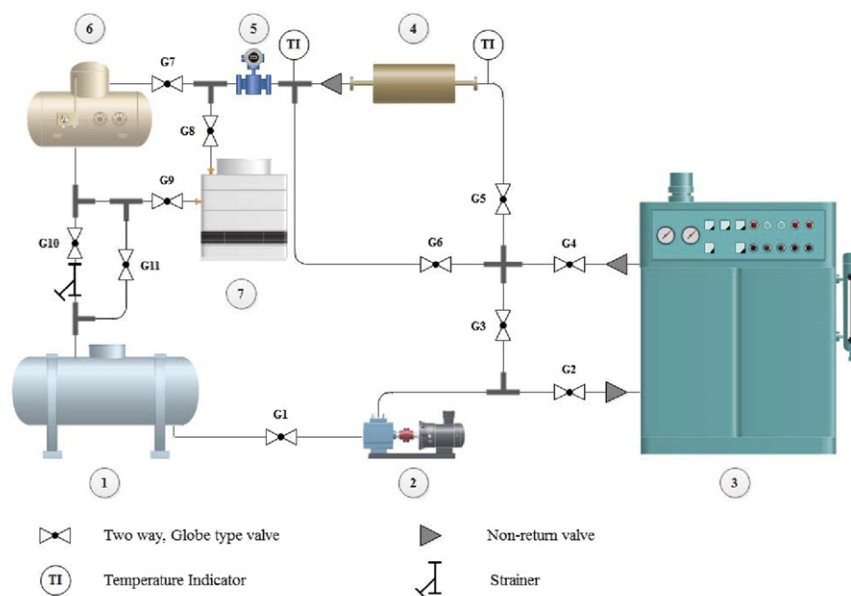
The schematic of the LHS prototype employed for testing the storage characteristics is shown in Fig. 13. A ternary mixture comprising of potassium nitrate, sodium nitrate and sodium nitrite in the weight proportion of 53:7:40 is selected as the PCM. In the current study, the temperature difference between the initial temperature of PCM and the inlet temperature of HTF is fixed as 40°C . As the selected PCM has a melting point of 142°C , the initial temperature of PCM and the inlet temperature of HTF during charging/discharging process are taken as $122/162^\circ\text{C}$ and $162/122^\circ\text{C}$, thereby making a temperature swing of 20°C on both sides of the melting point. The outer diameter (d) and thickness of HTF tubes are 12.7 mm and 2 mm. The height (h) and thickness (b) of the longitudinal fins attached to the tubes are 10 mm and 1 mm. The number of HTF tubes (N_T) and fins (N_F) on each tube in the optimized LHS prototype are 25 and 4. The HTF tubes and fins are made of copper. The outer shell of the prototype is made of stainless steel (SS304) of diameter 335 mm OD and 5 mm thickness. The physical LHS prototype with insulation and temperature sensors is given in Fig. 14.

Experimental Procedure

The entire experimental procedure can be subdivided into four processes, which should be carried out in sequence.

Preheating the oil – Storage prototype bypass

The HTF should be heated up to the desired HTF inlet temperature of the charging process. For achieving this, a bypass line is provided in the experimental loop so that the HTF re-circulates without entering the LHS prototype. Valves G3, G6, G8 and G9 are closed during this process. Once the HTF reaches the desired inlet temperature for charging process, this process is said to be completed.



- 1 – Oil storage tank 2 – Thermic fluid pump 3 – Thermic fluid electric heater
 4 – LHS prototype 5 – Oval gear flow meter 6 – Expansion tank 7 – Cooling tank

Fig. 11 Schematic diagram of the experimental setup. Reproduced from Niyas, H., Rao, C.R.C., Muthukumar, P., 2017. Performance investigation of a lab-scale latent heat storage prototype – Experimental results. *Solar Energy* 155, 971–984.



Fig. 12 Pictorial view of the experimental setup. Reproduced from Niyas, H., Rao, C.R.C., Muthukumar, P., 2017. Performance investigation of a lab-scale latent heat storage prototype – Experimental results. *Solar Energy* 155, 971–984.

Charging

When HTF reaches the desired inlet temperature for charging process, the HTF is passed through the LHS prototype to initiate the charging process. Valves G4, G6, G9 and G10 are closed during this process. The process continues until the prototype is fully charged.

Cooling the oil – Storage prototype bypass

Once the LHS prototype is fully charged, the HTF is then cooled down to the desired HTF inlet temperature for the discharging process. The HTF is made to flow through the cooling tank for achieving the same. Valves G3, G5 and G7 are closed during this process. Once the HTF reaches the desired inlet temperature for the discharging process, this process is said to be completed.

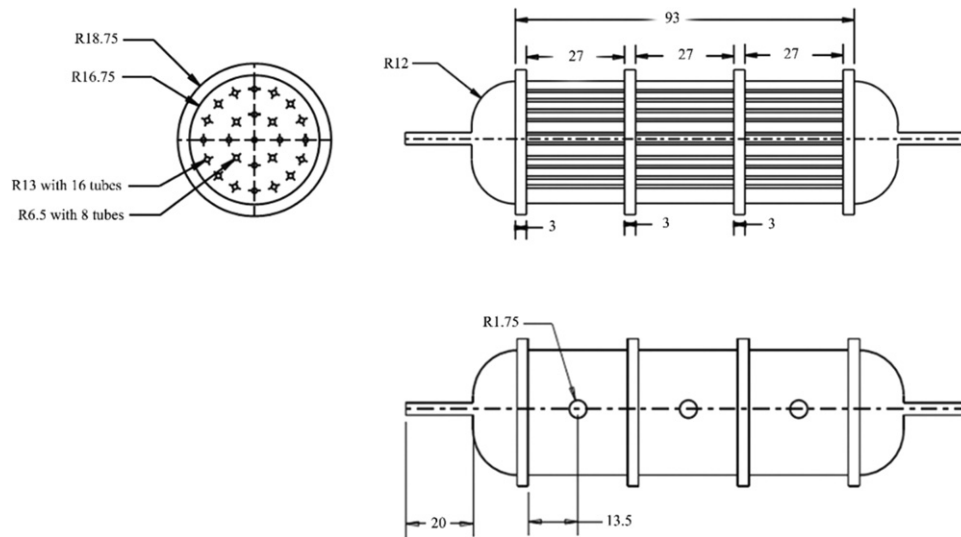


Fig. 13 Schematic of the LHS prototype (all dimensions are in cm). Reproduced from Niyas, H., Rao, C.R.C., Muthukumar, P., 2017. Performance investigation of a lab-scale latent heat storage prototype – Experimental results. *Solar Energy* 155, 971–984.



Fig. 14 Pictorial view of the LHS prototype with thermocouples. Reproduced from Niyas, H., Rao, C.R.C., Muthukumar, P., 2017. Performance investigation of a lab-scale latent heat storage prototype – Experimental results. *Solar Energy* 155, 971–984.

Discharging

When HTF reaches the desired inlet temperature for the discharging process, the HTF is allowed to pass through the prototype and thereby discharging of LHS prototype gets started. Valves G3, G5 and G6 are closed during this process. The process continues until the prototype is fully discharged.

Results and Discussions

In the following sub-sections, various results obtained during the performance testing of the lab-scale LHS prototype during the charging and discharging processes are presented. The major implications of the results are also discussed. The initial average temperature of the LHS prototype during the charging/discharging process is 122/162°C and a comparatively higher/lower temperature HTF at 162/122°C is allowed to pass through the HTF tubes.

Temperature variation

Fig. 15(a) and **(b)** illustrates the local temperature variation of the LHS prototype during the charging and discharging processes. When the high/low temperature HTF is passed through the HTF tubes during the charging/discharging process, heat transfer takes between the high/low temperature HTF and the comparatively low/high temperature PCM through the HTF tubes. It can be noted from **Fig. 15(a)** and **(b)** that the increase/decrease of temperature is faster in cartridge 1 than cartridges 2 and 3 during the charging/discharging process. A similar trend is observed between cartridge 2 and 3. This is due to the fact that there exists a higher heat transfer potential due to more temperature difference in the entry portion than the exit portion of the prototype. It can be seen from **Fig. 15(a)** that the increase in temperature of the PCM in the top region of the prototype is faster than that of middle and bottom regions in all the cartridges. This is due to the buoyancy driven natural convection wherein the high temperature and less dense particles move to the top portion of the prototype. It can be noted from **Fig. 15(b)** that the PCM temperature in the bottom portion decreases slightly faster than the middle and top portions. This is due to the negligible natural convection that exists during the solidification process. In addition, it can be inferred from **Fig. 15(a)** that there is a steady increase in temperature up to a certain point, after that the slope of the curve decreases and finally after a certain interval, the temperature has increased sharply. This transition is due to the melting phenomenon during which a large amount of latent heat gets stored in the PCM. However, a similar trend is not noticeable in the temperature values of the top portion of all cartridges. This is due to the convective

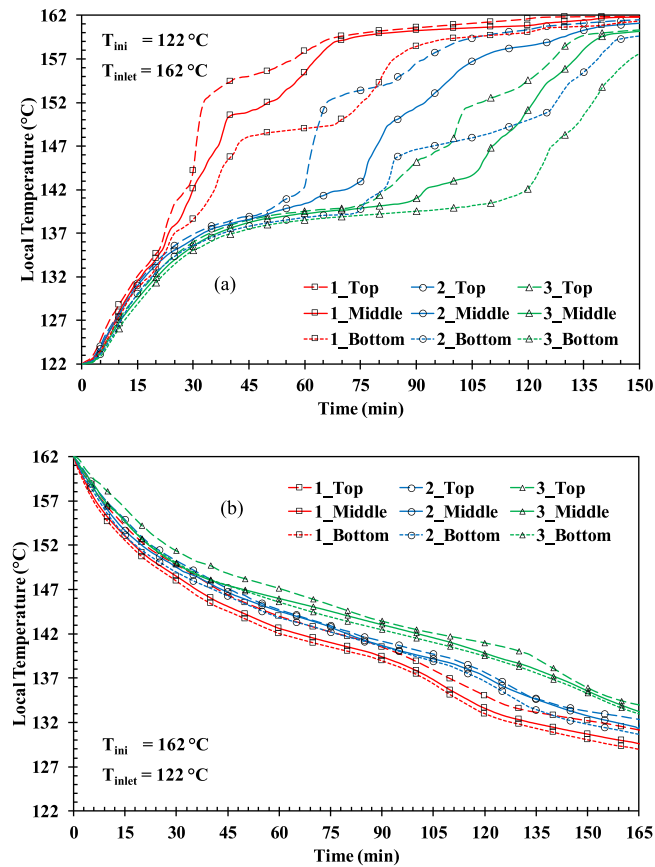


Fig. 15 Local temperature variation of the lab-scale LHS prototype during (a) charging and (b) discharging. Reproduced from Niyas, H., Rao, C.R.C., Muthukumar, P., 2017. Performance investigation of a lab-scale latent heat storage prototype – Experimental results. *Solar Energy* 155, 971–984.

movement of the higher temperature particles in the top portion, by which the temperature has increased sharply. Due to the conduction heat transfer that takes place in the PCM throughout the solidification process, there exists an even temperature distribution in the radial direction of the prototype. Unlike charging process, a sharp plateau is not noticeable in the discharging process. This is because the heat source input during the discharging process is the LHS prototype itself, the potential of which is reduced while exchanging heat with the HTF. In addition, during the discharging process, a thin solid layer of PCM is formed around the HTF tube. Over a period, the thin layer becomes thicker. This increases the thermal resistance and hence, the solidification rate reduces. The uncertainty in the temperature measurements is about $\pm 0.2^\circ\text{C}$. The average temperature of PCM during the charging process is about 160.6°C in 150 min, which is 1.4°C less than the HTF inlet temperature. Similarly, the average temperature of PCM during the discharging process is about 131.6°C in 165 min.

Charging/discharging time

Fig. 16(a) and **(b)** depicts the local melt fraction variations of the LHS prototype during the charging and discharging processes. The local melt fraction is calculated based on the temperature of the PCM (recorded at nine different locations) using the Eq. (10). It is seen from **Fig. 16(a)** that the top portion of the cartridges have a steady increase in melt fraction when compared with the bottom cartridge. This is due to the convection heat transfer occurred during the melting of PCM, wherein the molten PCM moves from the bottom to the top portion of the prototype. On the contrary, it is seen from **Fig. 16(b)** that the top, middle and bottom portion of the cartridges have a steady decrease in melt fraction evenly. This is due to the uniform conduction heat transfer in the PCM. In addition, it can be seen from the above results that PCM in the 1st cartridge has melted/solidified faster than 2nd and 3rd cartridges and similar tendency is observed between 2nd and 3rd cartridges. This is due to the higher heat transfer potential available at the entrance of the LHS prototype than the exit of the prototype. The uncertainty involved in the estimation of melt fraction is about ± 0.061 . It took about 123 min for the LHS prototype to reach an average melt fraction of unity. Similarly, it took about 131 min for the LHS prototype to reach an average melt fraction of zero.

Energy storage/discharge rate

Fig. 17(a) and **(b)** illustrates the energy (sensible, latent and total) storage and discharge rate of the LHS prototype during the charging and discharging processes. Sensible, latent and total heat stored/discharged in/from the PCM are calculated using the

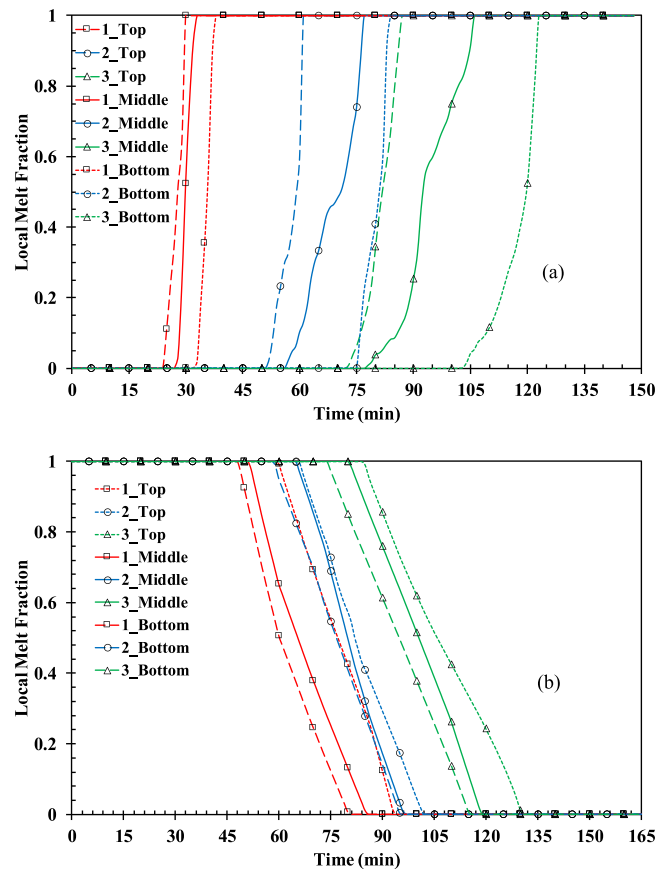


Fig. 16 Local melt fraction variation of the lab-scale LHS prototype during (a) charging and (b) discharging. Reproduced from Niyas, H., Rao, C.R. C., Muthukumar, P., 2017. Performance investigation of a lab-scale latent heat storage prototype – Experimental results. *Solar Energy* 155, 971–984.

Eqs. (11)–(16), respectively. During charging, when the high-temperature HTF at 162°C is passed through the tubes, heat from the HTF is transferred and stored in the PCM. Similarly, during discharging, when the low-temperature HTF is allowed to pass through the HTF tubes, the stored heat from the PCM is discharged to the HTF.

Initially, when the PCM is in the solid/liquid state during charging/discharging, heat gets stored/discharged in the form of sensible heat only. Once the PCM reaches near the phase change temperature (142°C), heat gets stored/discharged in the form of latent heat. Similarly, after melting/solidification of the PCM, heat is stored/discharged in the form of sensible heat. During charging, when the PCM reaches an average temperature of 160.6°C in 150 min, the amount of sensible, latent and total energy stored in the LHS prototype are 6.87 MJ, 10 MJ and 16.87 MJ, respectively. The range of temperature in which the PCM stores the sensible heat is about 38.6°C (122 – 160.6°C). During discharging, when the PCM reaches an average temperature of 131.6°C in 165 min, the amount of sensible, latent and total energy discharged from the LHS prototype are 5.41 MJ, 10 MJ and 15.41 MJ, respectively. The range of temperature in which the PCM discharges the sensible heat is about 30.4°C (162 – 131.6°C). It can also be noted from Fig. 17(a) and (b) that the sensible and latent energy storage/discharge rate curve has a similar trend like average temperature and melt fraction curve. Because, the sensible and latent energy stored/discharged depends only on the average temperature and the average melt fraction of the PCM.

Development of Industrial Scale LHS System

With the expertise and knowledge gained from the experimental and numerical investigations, the studies have been extended to develop an industrial-scale LHS system of 0.25 GJ capacity. The developed LHS module is then integrated with a commercial steam accumulator storage system of 1 GJ storage capacity. This combined storage system has been installed in the LFR based pilot-CSP plant in Vallipuram, Tamil Nadu, India.

Pilot CSP Plant With TES

Fig. 18 shows the pictorial view of the 50-kWth LFR solar collector field with TES system, located in Vallipuram, Tamil Nadu, India. The steam accumulator will maintain the continuous supply of steam when the demand of the power plant is higher than the

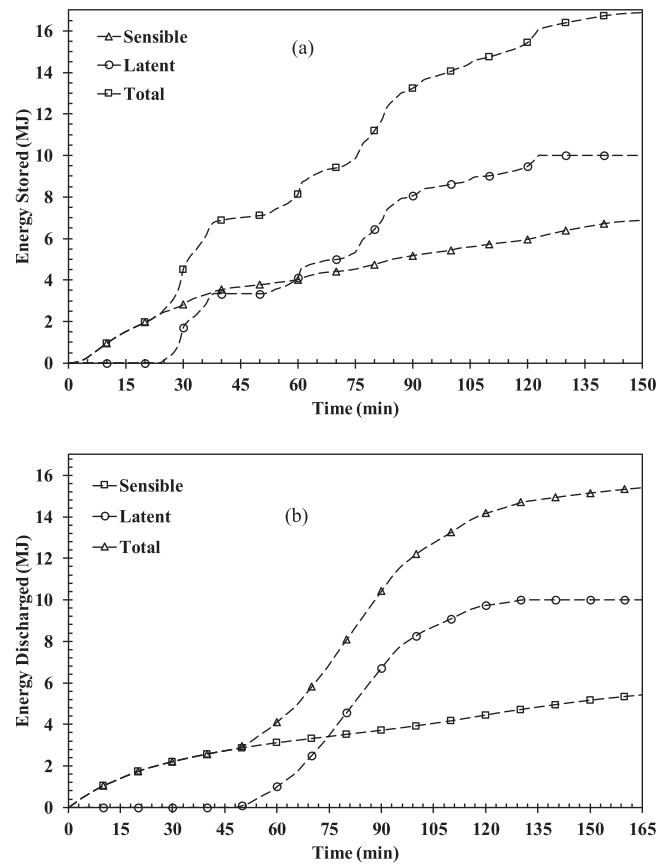


Fig. 17 Energy storage/discharge rate of the lab-scale LHS prototype during the experiments (a) charging and (b) discharging. Reproduced from Niyas, H., Rao, C.R.C., Muthukumar, P., 2017. Performance investigation of a lab-scale latent heat storage prototype – Experimental results. *Solar Energy* 155, 971–984.



Fig. 18 LFR solar collector field with TES.

supply. It also supplies the required amount of steam during the start of the plant. For storing 1 GJ of steam at 55 bar and 270°C, the required volume of steam accumulator has been found to be 16 m³. An industrial-scale LHS module of 0.25 GJ storage having four cartridges of PCM (each of 62.5 MJ capacity with 0.125 m³ volume) in the form of shell-and-tube type heat exchanger has been integrated with the steam accumulator for extended supply of steam and also to compensate the decline in the steam temperature during consumption. The steam accumulator integrated with PCM module is installed between the evaporator and super heater solar field modules. **Fig. 19** shows the schematic layout of the 50-kWth solar collector field with TES system. The steam entering the PCM module gets condensed by supplying its energy to the PCM and the saturated liquid is fed to the

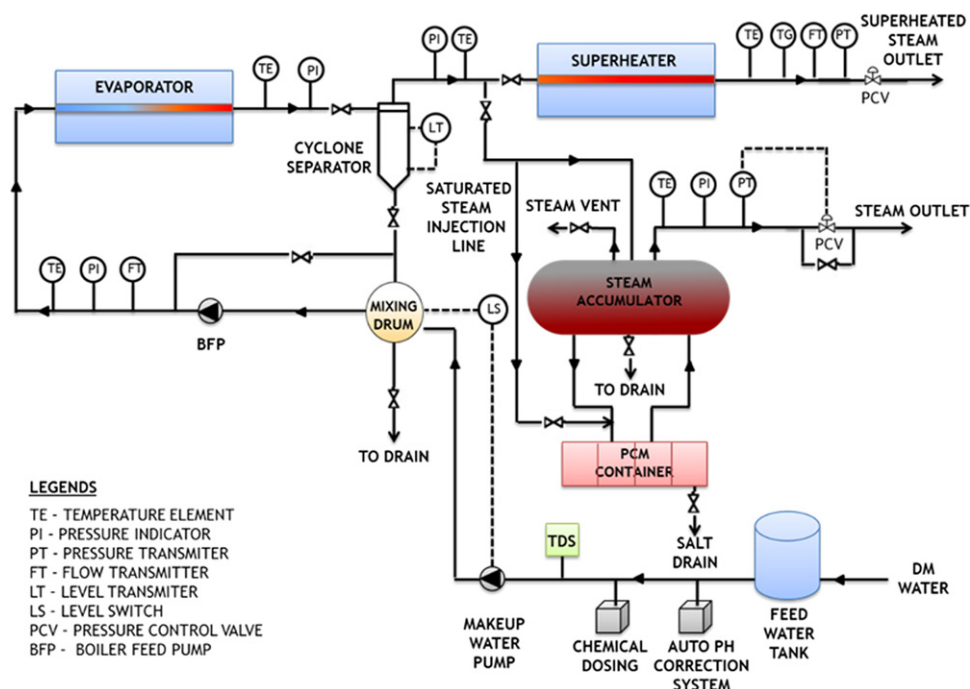


Fig. 19 Layout of solar collector field with TES.

Table 7 Specifications of the steam accumulator

Thermal energy storage capacity	1 GJ
Pressure vessel internal volume	16 m ³
Material of construction	Carbon steel SA516 Gr 70
Maximum allowable working pressure	60 kg/cm ²
Maximum allowable working temperature	280°C
Design (metal) temperature	380°C
Hydrostatic test pressure	90 kg/cm ²
Charging pressure	55 kg/cm ²
Discharging pressure	45 kg/cm ²
Charging maximum steam flow rate	800 kg/h
Discharge steam flow rate	500 kg/h
Total weight	17,500 kg

accumulator unit. During discharging the saturated liquid circulates through the PCM module and generates steam. The selected PCM is a mixture of sodium nitrate (60 wt.%) and potassium nitrate (40 wt.%). The PCM melts at 222°C, stores 0.25 GJ of energy and releases the same amount of energy during solidification when the temperature of the system reduces below 222°C. The PCM containments and fittings occupy about 0.5 m³.

Steam Accumulator

Steam accumulator is an insulated steel pressure vessel containing saturated water and saturated steam under pressure. It is one of the commonly used thermal energy storage devices. It is used to smooth out peaks and troughs in demand for steam. The key purpose of the steam accumulator is to release steam when the demand is greater than the solar boiler's ability to supply at that time, and to accept steam when demand is low. The steam accumulator can be integrated with the steam generating system either in series or in parallel configuration. In our case, series configuration is used. The technical specifications of the steam accumulator are given in [Table 7](#). The steam accumulator installed at the project site is shown in [Fig. 20](#).

Industrial-Scale LHS Module

[Fig. 21](#) depicts the pictorial representation of the CAD and actual industrial-scale LHS module. The industrial-scale LHS module is of square shape (63 × 63 cm) and is segmented into four cartridges of length 50 cm each, which makes the overall length of the



Fig. 20 Steam accumulator.

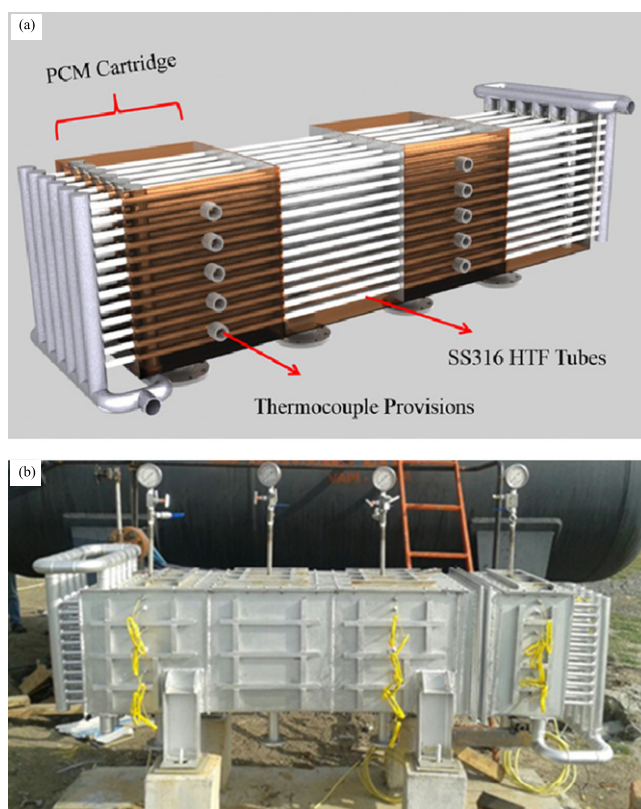


Fig. 21 Industrial-scale PCM module (a) CAD model and (b) actual module.

module to be 2 m. About 121 HTF tubes are arranged in an 11×11 array through which the pressurized water will flow thereby exchanging the heat with the PCM. In general, majority of the PCMs are highly corrosive in nature. Hence, entire LHS module is made up of stainless steel to prevent corrosion. The partition between the cartridges is made of concrete poured between the two plates both of which are machined using laser cutting process. The main advantage of this method is that it ensures a leak proof partition between the PCM cartridges. The inlet and outlet supply of HTF is accomplished by using a header assembly. Six K-type thermocouples are inserted in each cartridge to capture the temperature of the PCM. The specifications of the LHS module and materials used are given in [Tables 8](#) and [9](#).

Binary PCM Mixture Preparation and Filling Process

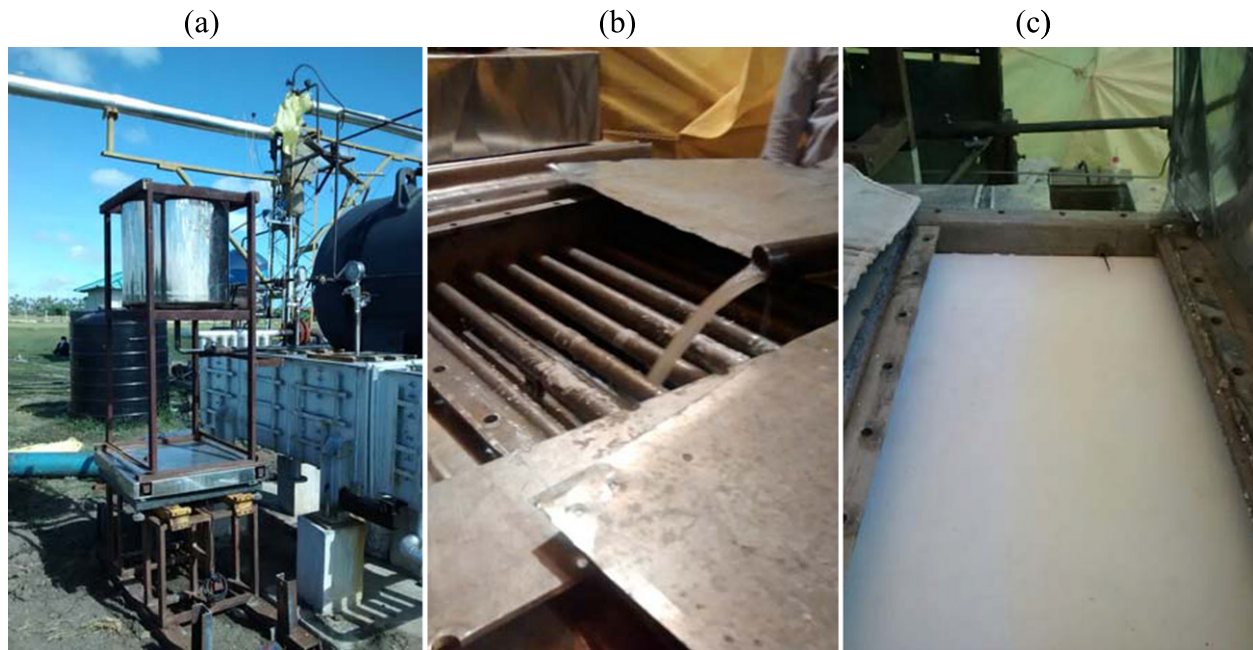
Preparation of a binary mixture from two salts having different melting points is a challenging task. The main strategy in the preparation of the binary mixture is to melt the PCM having lower melting point first. Then add the other PCM to the mixture thus

Table 8 Specifications of the LHS module

<i>Length × Width × Height</i>	<i>2.2 m × 0.63 m × 0.63 m</i>
PCM mixture	NaNO ₃ (60 wt.%) + KNO ₃ (40 wt.%)
PCM volume	0.5 m ³
TES capacity	0.25 GJ

Table 9 Specifications of major materials used in LHS module

HTF pipe	Material	SS316L
	Outer diameter	21.3 mm
	Thickness	2.77 mm
Header pipe	Material	SS316L
	Outer diameter	60.3 mm
	Thickness	5.54 mm
Container	Material	SS316
	Sheet thickness	5 mm

**Fig. 22** Melting and filling of PCM (a) melting setup, (b) filling of PCM and (c) filled PCM.

formed and continuously heating slightly above the melting point of the PCM having the higher melting point. **Fig. 22** shows the pictorial view of the melting and filling of PCM in the LHS module. It was found that the total weight of the PCM required per cartridge is about 302 kg (181 kg of sodium nitrate + 121 kg of potassium nitrate). The following steps have been followed to prepare the binary PCM mixture.

- Initially it was made sure that the mixing vessel was clean.
- The mixing vessel was placed on the support stand with burner underneath.
- Then the entire setup was placed on the weighing machine, this weight was set as tare weight.
- Sodium nitrate was added to the mixing vessel and was heated up to its melting point (306°C).
- It was ensured that the weight of sodium nitrate was about 181 kg after moisture removal.
- Soon after melting sodium nitrate, 121 kg of potassium nitrate salt was added.
- Salt mixture was continuously heated till 334°C (melting point of potassium nitrate).
- The mixture was continuously stirred during the melting process.
- After moisture removal of the salt mixture, the weight of the mixture was ensured for 302 kg and the final weight compensation was done with KNO₃ salt.

- The salt mixture was heated up to 350°C and it was maintained for 6 h.
- The molten salt was drained into one cartridge of the industrial-scale LHS module.
- The same process was repeated for the remaining 3 compartments.

Conclusions

This work presents a detailed study on the various stages involved in development of an industrial-scale latent heat storage (LHS) system. Preliminary studies are conducted in a lab-scale LHS prototype of 10 MJ storage capacity. A ternary salt mixture comprising of potassium nitrate, sodium nitrate and sodium nitrite in the weight proportion of 53:7:40 is used as the phase change material (PCM) in the lab-scale LHS prototype. Hi-Tech Therm 60 is used as the heat transfer fluid (HTF). Performance parameters viz., melt fraction, charging/discharging time and energy storage/discharge rate were evaluated at different operating conditions. It is found from the experimental and numerical studies that the effect of natural convection is very much predominant during the charging process, whereas its effect is negligible during the discharging process. With the expertise and knowledge gained from the experimental and numerical investigations, the studies have been extended to develop an industrial-scale LHS system of 0.25 GJ capacity. A binary salt mixture comprising of sodium and potassium nitrate in the weight proportion of 60:40 is used as the PCM in the industrial-scale LHS module. The developed LHS module is then integrated with a commercial steam accumulator storage system of 1 GJ storage capacity. This combined storage system has been installed in the LFR based pilot-CSP plant in Vallipuram, Tamil Nadu, India. The current study will be helpful in developing large-scale LHS systems for real-time CSP plants.

See also: Eco Friendly Aspects in Hybridization of Friction Stir Welding Technology for Dissimilar Metallic Materials. Sustainable Cutting Fluids: Thermal, Rheological, Biodegradation, Anti-Corrosion, Storage Stability Studies and its Machining Performance

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Metallic Materials From E-Waste

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Nomenclature

ARF Advanced recycling fees is the cost of recycling the product procured by the producer from the consumer during retail selling.

EEE Electrical or electronic equipment utilised by consumers in a market.

EOL End of life is a term denoting the final stage of a product life cycle in the market.

EPR Extended producer responsibility is a strategy designed to promote the integration of environmental costs

associated throughout a products' life cycles into the market price of the products.

E-waste Waste generated by discarding electrical or electronic equipment by a consumer.

MEIS It is a scheme brought by the Government of India to provide incentive for exporting Indian manufactured goods in the world market.

Introduction

The Problem

The problem of recovering metallic materials from e-waste can be best described from the following two comments. "Never mind that it is also an economic stupidity because we are throwing away an enormous amount of raw materials that are essentially re-useable," said Mr. Achim Steiner, Executive Director of the UN Environment Programme (UNEP). "Whether it is gold, silver or some of the rare earths that you have heard about perhaps in recent years, it is still an incredible amount." The emphasis is on the electronic waste, for the current article, which is inexorably rising with time in our contemporary world as subtle consequence of the advent of digitalization. A broader glimpse of the global outline such waste generation can be perceived by the following schematic (Fig. 1).

It is ironic that the boom in advance electronic and electrical technology should bring in its wake a looming danger from the growing pile of electronic waste. The world community, through several authorized bodies, now recognizes that it is necessary to address the dual concerns of recovery of valuable metals from e-waste as well as safe disposal of the hazardous in e-waste. The threat perception by national and international bodies has heightened recently, as the enormity of the problem becomes more clear, aggravated by the accelerated usage of electronic items in the developing countries in Asia powered by improvements in national economy.

The global quantity of e-waste generation in 2014 was found to be around 42 Mt (Million Tons) as reported by the United Nations (see "Relevant Websites section"). To give an idea, a number of 1.15 million trucks with 40-ton (18-wheel) capacity will be completely filled with the e-waste generated in the world, enough to form a line covering 23,000 km, twice the distance between New York and Tokyo. Approximately, 4 billion people in the world are covered by national e-waste legislation, though legislation does not necessarily come together with enforcement. By these national laws, only around 6.5 Mt (16%) of this plethora of e-waste was reported as formally treated by national collection systems. For example, in total, 0.7 Mt of e-waste was thrown into the waste bin by the 28 EU Member States. The amount of e-waste that is disposed of in waste bins is unknown for other regions. The quantities of the collection outside formal take-back systems are not documented systematically. However, they are likely to be a hiatus between e-waste generated, e-waste officially collected and e-waste in the waste bin.

The latest reported accounts of e-waste generation, comprised of 1.0 Mt lamps, 3.0 Mt of Small IT products such mobile phones, calculators etc., 6.3 Mt of screens and monitors, 7 Mt of temperature exchange equipment (cooling as well as freezing), 11.8 Mt large equipment, and 12.8 Mt of small equipment. This amount of e-waste is expected to grow to 49.8 Mt in 2018, with an annual growth rate of 4%–5% (Baldé *et al.*, 2015) (Refer Fig. 2).

To cite an example of e-waste recovery, Teck, a Canadian based company at Trail, British Columbia, became the first metal supplier in Olympic history to include metals recovered from e-waste in the Olympic medals. It developed an e-waste recycling process which maximizes metal recovery, operating its own smelter and refinery. Metals were recovered from cathode ray tube (CRT) glasses, computer parts and circuit boards through separation, segregation and smelting. Over a 77,000 tonnes of e-waste acquired have been processed in between 2006 and 2015 (Mining & Metals in a Sustainable World, 2050, 2015). E-waste constitutes a reliable and rapidly increasing source of metals ensuring the long-term sustainability of Teck's operations. Moreover, the use of e-waste as a source of scrap enables the saving of energy that would have otherwise been used to generate mined resources. For instance, from e-wastes collected in Japan, the "mine" of gold and silver contained in small consumer electronics is equivalent to 16% and 22% of the world's total reserves, respectively. With an eye towards a sustainable future, the 2020 Olympic host has decided to make the medals by tapping the urban mine rather than asking the mining companies for donation (see "Relevant Websites section"), see Figs. 3–5.

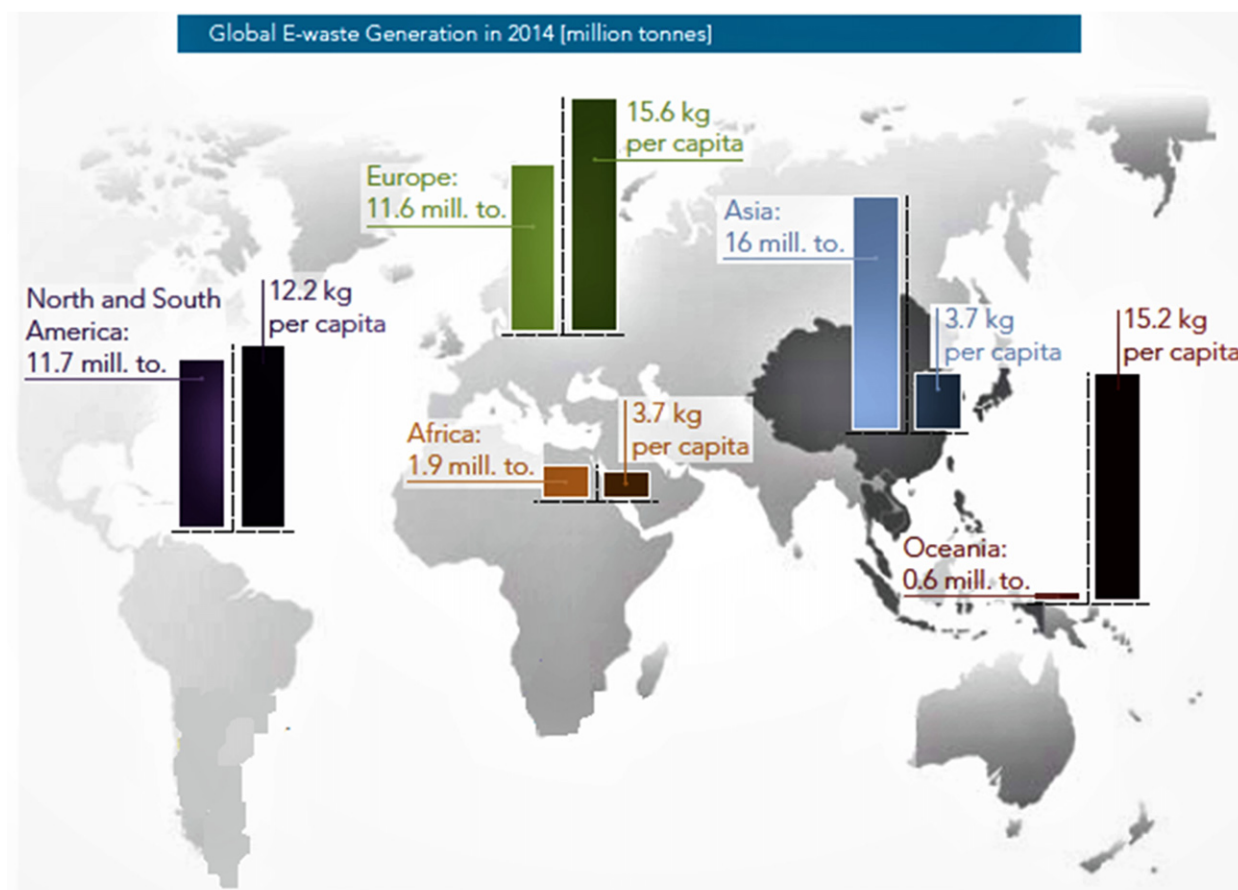


Fig. 1 A global scenario: E-waste generation, 2014. Reproduced from Honda, S., Khetriwal, D.S., Kuehr, R., 2016. Regional E-Waste Monitor: East and Southeast Asia. Bonn, Germany: United Nations University, ViE- SCYLE.

Global Estimated e-waste production

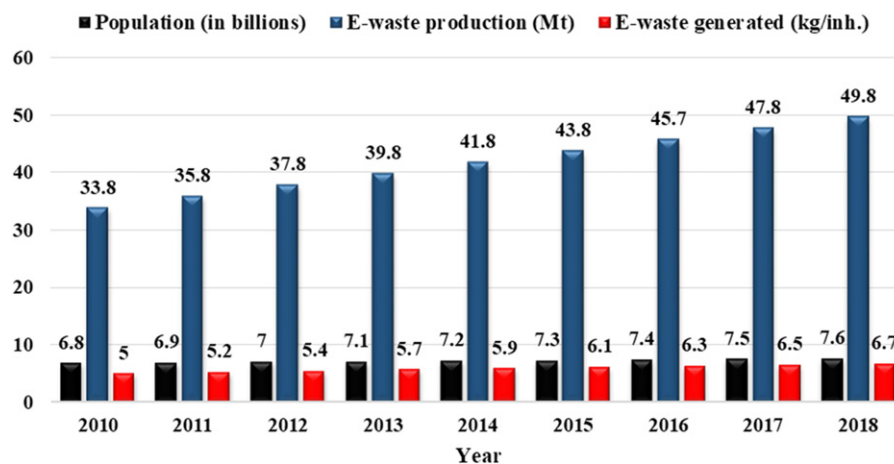


Fig. 2 Global production of e-wastes per year. Reproduced from Baldé, C.P., Wang, F., Kuehr, R., Huisman, J., 2015. The Global E-Waste Monitor – 2014". Bonn, Germany: United Nations University, IAS – SCYCLE.

The above estimation from the monetary evaluation of extractable precious and semi-precious metals does seem lucrative but the bitter truth is that only a fraction of this amount is extracted in the present world scenario. It is just not the economics, but also the potential of mankind to extract using productive technologies without harming the ecological balance. From the resource



Fig. 3 Economic evaluation of e-waste. Reproduced from Baldé, C.P., Wang, F., Kuehr, R., Huisman, J., 2015. The Global E-Waste Monitor – 2014". Bonn, Germany: United Nations University, IAS – SCYCLE.



Fig. 4 Connections made from gold or silver in the cell phone circuit boards discarded as e-waste (<http://www.bbc.com/news/business-37163074>).

perspective, e-waste is a potential “urban mine” which can provide a great amount of secondary resources for remanufacture, refurbishment and recycling of a lot of metals which are very precious, uneconomic in mine extraction and also rare. For instance, the gold content from e-waste generated in the year of 2014 was roughly 300 tonnes, which represents 11% of the global gold production from mines in 2013 (2270 tonnes), reported by the U.S Geological Survey (George, 2014).

Recovery of such valuable materials requires both high collection rate and recycling efficiency. In order to exploit the opportunities, appropriate policies are imperative to facilitate the creation of an infrastructure and ensure that all accumulated e-waste is treated using the state-of-the-art technologies.

Definition

Information and communication technologies; consumer electronics including toys; large household equipment, such as dishwashers and washing machines; medical equipment; and electric tools have become central to our daily lives. People are enjoying



Fig. 5 Japan may use e-waste in making 2020 Olympic medals (<http://www.beebee.info>).

Table 1 Approximate quantification of the types of material found in e-waste

Sr. no.	Type of material	Percentage in e-waste
1	Ferrous	38
2	Non-ferrous	28
3	Plastics	19
4	Glass	4
5	Wood	1
6	Other	10

Plastics – A Material of Choice for the Electrical and Electronic Industry-Plastics Consumption and Recovery in Western Europe, 2004. Brussels, Belgium: APME, p. 1.

what technology provides, surfing the Internet, buying daily merchandise on their smart phones or tablets and watching high-definition movies on their televisions at home. As more and more electronic products are produced to satisfy the demands worldwide, more resources are used to produce these items. Hence, a rapid growth of computing and communication equipment is driving the ever-increasing production of electronic waste (e-waste). As observed by the United Nations, there is a presence of a global inconsistency in the understanding and application of the term “e-waste” in both legislation and everyday use. This had repercussions in the form of many definitions contained within e-waste regulations, policies and guidelines. The term “e-waste” itself is self-explanatory, in the sense that it is an abbreviation of “electronic waste”. A key part of the definition is the word “waste” and what it logically implies – that the item has no further use and is rejected as useless or excess to the owner in its current condition.

“E-waste is a term used to cover items of all of electrical and electronic equipment (EEE) and its parts that have been discarded by the owner as waste without the invention of re-use” (One Global Definition of E-waste, 2014).

The act of discarding an EEE as e-waste is considered when the owner decides the item is no longer useful to them due to any kind of failure, technical capability, cosmetic condition, age, replacement, organizational policy, depreciation, etc. The word “discard” is defined in the Merriam Webster dictionary as “to throw (something) away because it is useless or unwanted”, and in the Cambridge Dictionary as “to throw something away or get rid of it because you no longer want or need it”. There are none requisites for the equipment to be non-functional, to be designated as e-waste by the owner, as it is solely the owner’s discretion, if they so decide.

Constituents of E-Waste

From the point of view of material composition, electronic waste can be defined as a mixture of various metals, particularly copper, aluminium, and steel, attached to, covered with, or mixed with various types of plastics and ceramics (Table 1). Precious and semi-precious metals have a variety of applications in the manufacture of electronic equipment, as contact materials due to their high chemical stability along with good conductivity. The more the electric charge transfer, more is the required nobility of the material, and so is the price. Gold plated contacts in earphone jacks, integrated circuit connectors in smart phones etc., are some examples. Platinum group metals, are used more among other inert metals in integrated circuits (Platinum silicide Ohmic

Table 2 Reported quantitative analyses of important metals present in various e-waste components

<i>Electronic waste (EEE's)</i>	<i>Weight (common metals) (%)</i>					<i>Weight (precious metals) (in ppm)</i>		
	<i>Fe</i>	<i>Cu</i>	<i>Al</i>	<i>Pb</i>	<i>Ni</i>	<i>Ag</i>	<i>Au</i>	<i>Pd</i>
TV board scrap	28	10	10	1	0.3	280	20	10
PC board scrap	7	20	5	1.5	1	1000	250	110
Mobile phone scrap	5	13	1	0.3	0.1	1380	350	210
Portable audio scrap	23	21	1	0.14	0.03	150	10	4
DVD player scrap	62	5	2	0.3	0.05	115	15	4
Calculator scrap	4	3	5	0.1	0.5	260	50	5
PC mainboard scrap	4.5	14.3	2.8	2.2	1.1	639	566	124
Printed circuits scrap	12	10	7	1.2	0.85	280	110	—
TV scrap (CRT's removed)	—	3.4	1.2	0.2	0.038	20	<10	<10
Electronic scrap	8.3	8.5	0.71	3.15	2	29	12	—
PC scrap	20	7	14	6	0.85	189	16	3
Typical electronic scrap	8	20	2	2	2	2000	1000	50
Printed circuit boards	5.3	26.8	1.9	—	0.47	3300	80	—
E-waste mixture	36	4.1	4.9	0.29	1	—	—	—

Note: "—" means not reported.

Cui, J., Zhang, L., 2008. Metallurgical recovery of metals from electronic waste: A review. *Journal of Hazardous Materials* 158, 228–256.

and Schottky contacts), Displays, sensors (MOSFET's, thermocouples), etc., as they are the high temperature coefficient or long term stability (Seymour and Davey, 1985).

Table 2 gives chemical analysis of the metallic metals present in various e-waste divided into two categories; common metals and precious metals. Steel is the most common alloy used for fabrication, signifying the presence of Iron, such as in mobile phone casings, DVD player, PC casings etc., refer **Table 2**. Copper, another most common metal, is extensively used in circuit wires, and substitute for a high conductivity material in the EEE's. It is quite important to recover, copper as much as possible, in the context of augmented demand of copper and dwindling reserves. In few decades, known deposits of copper ores may get completely exploited at the current rate of copper consumption which may lead to a crisis of this crucial metal. Moreover, Nickel similar to Copper is also widely utilised in circuit constructions, batteries (Ni-Cd batteries), and fuel cells, also in various nanoscale application (see "Relevant Websites section"). Aluminium is another metal which is generally found in integrated circuit designed components such as laptops, PCs, smartphone casings etc. Aluminium recovery is of great importance; an analogy can be made by the fact that around 47% of the entire Aluminium in the EU market is obtained from recycling Aluminium components. Aluminium recovery from e-waste shall play a great significance in its global industry. Additionally, other than precious metals like gold, silver and platinum, the presence of semi-precious metals in e-waste such as gallium (Ga), palladium (Pd), tantalum (Ta), tellurium (Te), germanium (Ge) and selenium (Se) makes it attractive for recycling and recovery. E-waste is considered hazardous if the elements like mercury, lead, arsenic, cadmium, selenium, hexavalent chromium and some flame retardants are present beyond permissible amounts.

Disposal of E-Waste

Waste electric and electronic equipment (WEEE); another term which is common for e-waste, has been taken into consideration due to the hazardous material contents of e-waste. Currently, the main options for the treatment of electronic waste are involved in reuse, remanufacturing, and recycling, as well as incineration and landfills. Reuse of end of-life (EOL) electronic equipment is the primary priority in management of electronic waste since the performance life of equipment is extended on a secondary market, resulting in a reduction of actual treatable e-waste. Remanufacturing is a production-batch process where this concept is applied. Used products or cores, are disassembled, cleaned, repaired or refurbished, reassembled and retested to manufacture the original or a similar type of the equipment (Williams and Shu, 2001). Alternatively, recycling is the reprocessing in a production line of the waste materials for the original or other applications. Recovery of the metals are the upshot of this recycling process of e-waste (One Global Definition of E-waste, 2014) (**Fig. 6**).

Hazardous and Toxic Constituents of E-Waste

E-waste is a source of useful as well as toxic materials. Circuit boards and other components can contain arsenic, cadmium, mercury, lead flame retardants containing halide substances etc., some of which become biologically active (Mihai, 2016). These hazardous materials are potential serious environmental and health threat. If burnt, some materials release toxic halogen gases, dioxins and furane. An alarming aspect of such hazardous waste from US and Europe to Asian and African countries, which have been exposed by the Basel Action Network (BAN) a non-governmental watchdog body on disposal of e-waste.

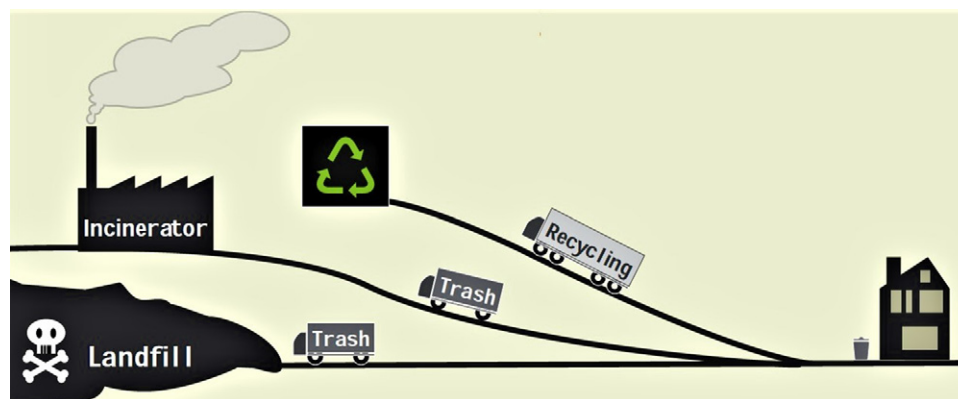


Fig. 6 Steps taken after remanufacturing. Reproduced from Honda, S., Khetriwal, D.S., Kuehr, R., 2016. Regional E-Waste Monitor: East and Southeast Asia. Bonn, Germany: United Nations University, ViE- SCYLE.

Table 3 The terms vis-à-vis steps performed from EEE to E-waste

Step	Description
Manufacture	The phase of the EEE product lifecycle where it is manufactured
Use	First phase of application of the EEE product in its service life
Discard	The decision by the owner to discard or not discard the product. Discarding indicates it becomes e-waste, whereas not discarding and routing to reuse indicates it is not waste. (cf. 1.1)
Reuse	Reuse of electrical and electronic equipment or its components is to continue the use of it (for the same purpose for which it was conceived) Products could be donated or traded before or during this phase (One Global Understanding of Re-Use, Common Definitions, 2009)
Preparation for Reuse	Preparation for reuse comprises any operation performed to bring used EEE or its components into a condition to meet the requirements of a next potential owner (secondary market) (One Global Understanding of Re-Use, Common Definitions, 2009)
Recycle	The phase of the product lifecycle where due to lack of usability, cosmetic condition or age the product is broken down into component materials and recycled to raw materials for the manufacture of new EEE or other products (Recommendations, 2014)
Disposal	Material which cannot be recycled into raw material for further use, would need to be disposed, using methods, such as energy recovery or landfilling. Items that are disposed of in household bins may move directly to this phase avoiding any opportunity of reuse or recycling

One Global Definition of E-Waste, 2014. Solving the E-Waste Problem (Step). Bonn: White Paper, pp. 4–5. ISSN: 2071-3576.

Just “by discarding” an electronic component on personal whims and fancies may have a serious impact when integrated. The e-waste is finally dumped if not recycled, into landfills. Along the passage of time, metallic ions or atoms diffuse to the ground water or gets channelled to water bodies, severely affecting the eco-system and its inhabitants. For example, Lead and Mercury are highly potent neurotoxins, particularly among children, who can suffer from Intelligent Quotient (IQ) deficiency and growth abnormalities even at very low levels of exposure. Cadmium, a toxic metal found in circuit board, is listed by the Environmental Protection Agency (EPA), as a “probable human carcinogen”, and also produces pulmonary damage when burned and inhaled ([Mundada et al., 2004](#)). The environmental issues related with e-waste are aggravated due to the low collection rates of e-waste containing hazardous components as the final owner either hides the equipment in his own house or disposes those via normal unmarked bins, ending up at landfills or incineration setups. Another possibility which is becoming more and more common currently, is where the waste materials reaches developing countries where the treatment processes may not follow the standard practice. For instance, nearly 40% of EEE waste generated in the US lands in developing Asian countries. Nearly all of these exports were illegal under US law. Scale of e-waste exported to Asia has previously been difficult to estimate. According to Jim Puckett, coordinator, BAN, GPS trackers were used inside old printers and monitors sent to recycling centres in the US to enable them to get a clearer picture.

It is true that North America and Europe generate vastly more e-waste per capita than Asia or Africa. Sustainability activists have for years urged the developed world to stop dumping e-waste loaded with heavy metals and toxins in countries like Nigeria or Ghana (see “Relevant Websites section”). The change occurred to the signing of Basel Convention, where these African countries have curbed their e-waste imports. Ideally, optimum efficiency and low environment impacts can be achieved when the e-waste is properly collected and is in the state of art facilities within the boundaries of the same country. Imperfect disposal techniques still prevail, causing e-waste problems.

The EEE goes through a set of stages which are elucidated ([Table 3](#)) using the following flow diagram ([Fig. 7](#)). These are the steps undertaken after an equipment is discarded at the user’s discretion ([Fig. 8](#)).



Fig. 7 E-waste pile at a recycling plant at Hubei, China (<https://www.nature.com/news/take-responsibility-for-electronic-waste-disposal-1.20345>).



Fig. 8 E-waste dump (<https://andrewmcconnell.com/Rubbish-Dump-2-0/6>).

E-Waste Scenarios: Different Landmasses of Our Planet

Asian and Oceanic Countries

China

The top three Asian countries with the highest e-waste generation in absolute quantities are China (6.0 Mt), Japan (2.2 Mt) and India (1.7 Mt). The top three Asian regions or countries having the highest e-waste generation in relative quantities are: Hong Kong (21.5 kg/inh.), Singapore (19.6 kg/inh.) and Brunei (18.1 kg/inh.). A record 16 Million tons of electronic trash, containing both toxic and valuable materials, was generated in 2014, in Southeast Asia. The generation rate soared up by 63% in just five years (Baldé *et al.*, 2015). Due to rapid advancement, the average lifespan of computer has shrunk to less than two years. "Growing incomes, the creation of more and more gadgets and ever-shorter life spans of things like mobile phones are the reasons for this tremendous increase in Asia," said, Ruediger Kuehr, Head of the United Nations University Institute for Sustainability and Peace SCYCLE (Figs. 9 and 10).

In China the mountain of discarded TVs, phones, computers, monitors, e-toys and small appliances grew by 6.7 m tons in 2015 alone, i.e., a 107% increase when compared to that of 2010 data. For an analogy, if every woman, man and child in China had an

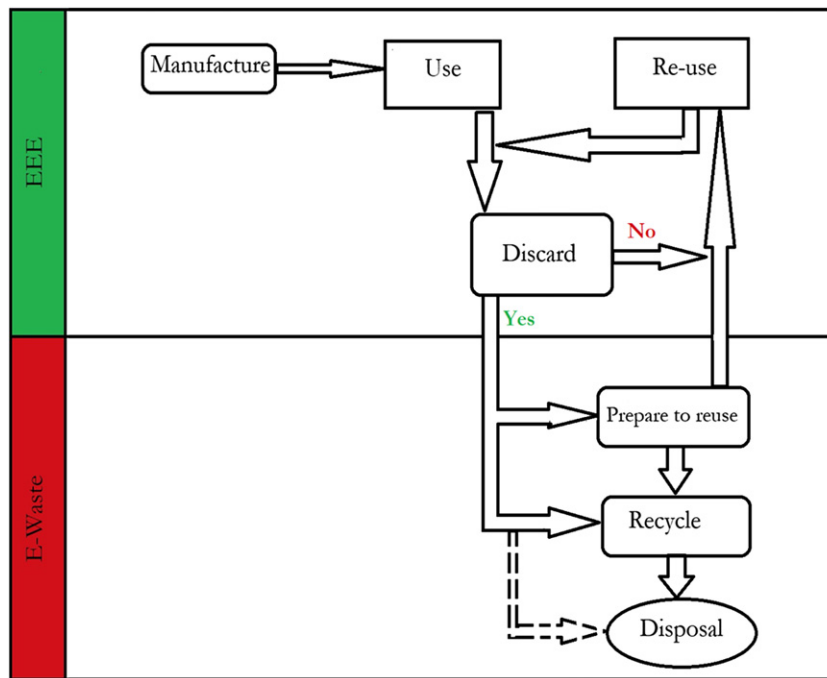


Fig. 9 EEE to E-waste, outcomes of discarding components. Reproduced from One Global Definition of E-Waste, 2014. Solving the E-waste problem (step). Bonn: White Paper, pp. 4–5. ISSN: 2071-3576.



Fig. 10 E-waste distribution over Asian countries (in Kg/inhabitants). Reproduced from Baldé, C.P., Wang, F., Kuehr, R., Huisman, J., 2015. The Global E-Waste Monitor – 2014”. Bonn, Germany: United Nations University, IAS – SCYCLE.

old LCD monitor and accumulated in a pile, it would not equal the 2015 tonnage. Yet, Asia's 3.7 kg per person of waste is still a writ compared to Europe's 15.6 kg per person (see "Relevant Websites section").

Most collection activities in China are carried out in urban areas due to high population density and the availability of large volumes of e-waste. Informal workers perform door-to-door collection and serve as an interface between consumers and medium level scrap dealers, renovators and recyclers. Around 440,000 people are involved in informal e-waste collection. After collection, this e-waste is sorted and usable appliances and valuable components are sold to the second-hand market. Guiyu, which is the largest e-waste recycling site in China and the world, recycles about 1.5 Mt per year, has a population of 150,000 people, nearly 100,000 of whom are migrant labourers engaged in recycling operations. In these informal recycling hubs, the treatment of WEEE is mainly carried out via primitive methods, such as hammering, manual sorting, open burning and acid leaching (Yu *et al.*, 2010; Honda *et al.*, 2016). Apart from domestic generation of e-waste, China remains one of the largest recipients of e-waste from other countries. Despite the fact that Chinese government having banned the import of e-waste (for both domestic reuse and recycling) in 2000 and having ratified both the Basel Convention in 1991 and BAN Amendment in 2001. Scrap dealers and smugglers now use less direct and visible means to import e-waste into China. China has trailed a unique scheme to improve its e-waste recycling system. Given the widespread existence of informal e-waste collectors and recyclers, formal recyclers have difficulty accessing e-waste products, as they are unable to compete on price given higher treatment costs in the formal sector. Consequently, to promote more environmentally sound recycling system, the Chinese government has several policies that provide incentives the channelization of e-waste into the formal sector. As a result, many facilities have cropped up in recent years with additional help from investments by foreign recycling companies, often with state-of-the-art equipment for processing e-waste (Zhong and Zhao, 2012; Honda *et al.*, 2016).

South Korea

The Republic of Korea, also known as South Korea, has a population of around 49 million 27, half of which resides in the metropolitan area surrounding the capital, Seoul. The other populous urban regions include Busan, Incheon, Daegu, Daejeon and Gwangju. Almost 82 per cent of the country's population is urbanized (World urbanization Prospects, 2014). South Korea is a gadget-mad country. It had, for example, worldwide the highest overall mobile ownership of 99 per cent, with 67 per cent owning smart phones, generating slightly over 800,000 tonnes of e-waste through almost all EEE product categories (see "Relevant Websites section"). By the year 2015, the country has managed to recycle 21% of the total 0.8 million tonnes of e-waste generated. The capitol, Seoul, recycles a significant fraction of the e-waste that it produces. It has set up the "Seoul Resource Centre" which receives 20 per cent of the Seoul's generated e-waste for the recovery of valuable metals such as gold, copper, etc. The other 80% of Seoul's e-waste is used entirely for landfilling (see "Relevant Websites section") (Fig. 11).

Management of e-waste was conceptualized in Korea in 1992, with refund of T-V and Washing machine under the Producer Deposit Refund Scheme. The act on the resource circulation of electronic and electrical equipment was constituted by combine efforts from Ministry of Environment, Ministry of Knowledge economy (now Ministry of trade, industry and energy), and the Ministry of Land, Transport and Marine affairs. By law the Ministry of Environment may impose penalties on defaulters (Honda *et al.*, 2016; see "Relevant Websites section").

India

The Indian information technology (IT) industry has played a major role in driving the change in the economy in the last decade along with a significant contribution to the digital revolution, being experienced by the world. India generated about 0.2 million tons of E-waste in 2006 and in 2010 it is about 0.4 million tons (Needhidasan *et al.*, 2014). The figure has soared rapidly to about 1.7 Million Tonnes of e-waste in the year 2014. India, which has emerged as the world's second largest mobile market, is also the

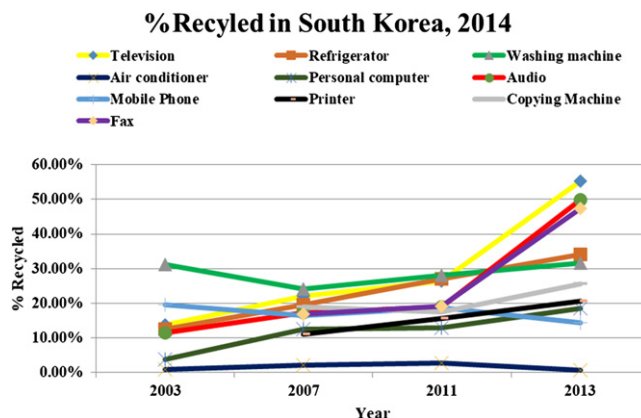


Fig. 11 Augmented Recycled amounts in subsequent years in South Korea. Reproduced from Rhee, S.W., 2016. Beneficial use practice of e-wastes in Republic of Korea. In: Proceeding of the Tenth International Conference on Waste Management and Technology (ICWMT), 31, pp. 707–714. Beijing, China: Procedia Environmental Sciences.

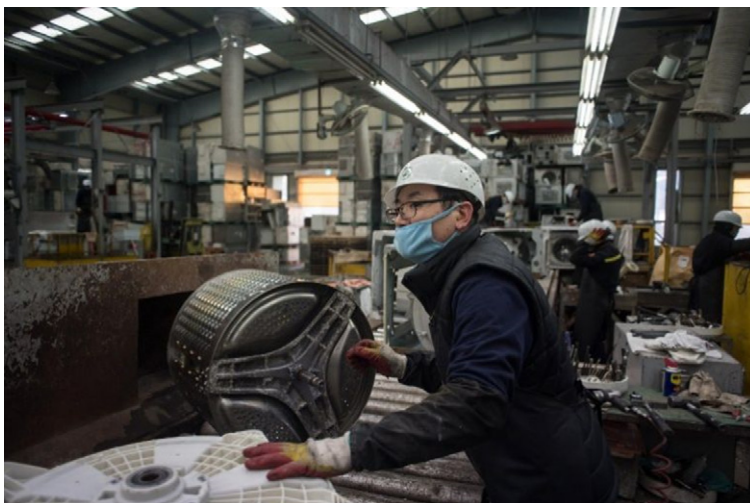


Fig. 12 A worker disassembling a discarded washing machine, Metropolitan Electronics Recycling Centre, Yongin, Seoul (<http://vnews.mv/76670>).



Fig. 13 Workers dismantling Integrated circuit boards from various electronic equipment (<http://www.governancenow.com/views/think-tanks/india-ranks-fifth-in-ewaste-generation-un-report>).

fifth largest producer of e-waste, discarding roughly 18.5 lakh tonnes of electronic waste in the year 2016 which is nearly 12 percent of the global e-waste production, reveals the joint study on 'Rethinking Waste-Scaling Opportunity in India' released at the capital, New Delhi (see "Relevant Websites section").

It has been a level of concern for India in recent years due to rise in levels in e-waste generation. India has emerged as the second largest mobile market with 1.03 Billion subscribers and at the same time 5th largest producer of e-waste in the world. Annually, 18.5 lakh metric tons of e-waste has been discarded. In comparison to the year 2007, by 2020 e-waste from old mobiles and computers will rise by about 1800% and 500% respectively. According an ASSOCHAM-KPMG joint study, 1.5% of the total e-waste generated is recycled by formal recyclers and another 8% of the e-waste is rendered useless and goes to landfills (see "Relevant Websites section").

The Ministry of Environment, Forest and Climate Change rolled out the E-waste Management Rules in 2016 with the goal of reducing e-waste production and increasing recycling in the most efficient and suitable manner. By these rules, the government introduced a similar concept to that in the South-east Asian advanced countries like China, South Korea. The Extended Producers Responsibility (EPR). This makes manufactures liable to collect 30%–70% of the e-waste they produce over a period of seven years (see "Relevant Websites section").



Fig. 14 E-waste transfer from Australia to Asian countries. Reproduced from Baker, E., Bournay, E., Harayama, A., Rekeciewicz, P., 2005. Vital waste graphic. In: Proceeding of the Conference to the Parties of the Basel Convention, pp. 32–33. Arendal, Norway: GRID-Arendal, UNEP.

The policy and target of e-waste collection in Indian market needs to be reviewed with the introduction of new incentive scheme before the industries. On a urgent basis India needs an urgent recycling policy for its mountain of electronic waste. The waste is expected to reach a total of around 30 million tonnes by 2020 in India (see "Relevant Websites section"). Government of Indian has framed a draft proposal which is still under discussion and will be launched very shortly. They are showing already effective, but there is still a pressing need for national policy to alleviate damage to the environment. This will also generate employment and commercial opportunities, address health and safety concerns, and forge a path towards sustainability (see "Relevant Websites section").

Australia

Australia produces substantial amounts of e-waste in the world. In 2007–2008, 0.1 Mt tonnes of e-waste as generated, which are composed of discarded televisions, computers and their products and mobile phones and about 0.47 Million Tonnes in the

year 2014. The estimated production of e-waste in Australia by 2027–2028 will exceed 181,000 tons. The recycling of e-waste in Australia is limited. It is reported that about 10% of e-waste was recycled and 80% was disposed in landfills during 2007–2008 (see “Relevant Websites section”). Australian Bureau of Statistics reported that more than 50% of the e-waste generated in 2010 was either land filled, stored or incinerated (Pink, 2010).

Australia used to save itself by exporting e-waste to Singapore, India and indirectly China for processing (Refer Fig. 12). As per the Basel convention, it has become illegal to export e-waste overseas until the receiving country has the facility to process wastes in eco-friendly manner. Australia, complies with the Basel Convention by controlling the trans-boundary movements of hazardous wastes and their disposal. Keeping in view the strict global legislations, acquiring a permit to export e-waste in Australia is a difficult process. For instance, during 2009–2010, the Department of the Environment, Water, Heritage and Arts processed 14 permits to export hazardous wastes and 20 permits to import hazardous wastes. 16 of the permits were granted and four applications were refused as per their stringent rules (see “Relevant Websites section”). Currently, the export of e-waste to under developed countries is not a viable option (Figs. 13 and 14).

The trend of e-waste recycling is on the rise, yet still lagging behind with respect to Europe or USA. Around 40 collecting centres are working throughout the country (see “Relevant Websites section”). Sims metal management (SIMSMM) and Outotec are some firms which process e-waste for the recovery of metals. SIMSMM is the leading e-waste recycler that has facilities located in New South Wales, Victoria, Queensland and Western Australia. A robust recycling management system is required in Australia to deal with the large quantities of e-waste that will be generated as contemplated, in the future.

European Nations

Waste of electrical and electronic equipment, or EEE's such as computers, TV-sets, fridges and cell phones is one of the soaring waste streams in the countries under EU, with some 9 million tonnes generated in 200 (see “Relevant Websites section”), with an annual growth of 3%–5% per year which is estimated to reach the mark of 12 million tonnes by 2020 (see “Relevant Websites section”).

The European countries with the highest e-waste generation are Germany, the United Kingdom, France and Russia (Table 4). These countries are currently signatories of the Basel Convention and the export of e-waste is strictly curbed in these nations. The e-waste, generally was sent trans-boundaries finally landing in the developing countries of Africa such as Nigeria, Ghana, South

Table 4 Total E-waste collected in the EU in kilograms per capita

GEO/TIME	2012	2013	2014	2015
European Union (28 countries)	5.98	6.06	6.21	:
Belgium	10.06	10.34	9.92	9.67
Bulgaria	5.16	4.67	5.73	8.19
Czech Republic	4.94	4.78	5.23	6.77
Denmark	13.44	12.62	12.33	12.03
Germany (until 1990 former territory of the FRG)	7.72	7.65	7.6	:
Ireland	7.53	7.23	8.07	8.57
Greece	3.25	3.36	4.02	4.42
Spain	3.13	4.33	3.79	:
France	6.92	6.92	7.44	8.63
Croatia	2.27	2.12	2.86	4.76
Italy	3.69	3.47	3.52	:
Lithuania	4.48	5.2	7.16	5.34
Luxembourg	9.38	9.47	9.84	10.22
Hungary	4.28	4.85	5.06	5.26
Netherlands	6.97	6.55	7.95	8.18
Austria	9.09	8.96	8.98	9.14
Poland	4.35	4.3	4.29	4.99
Portugal	4.06	4.74	5.77	6.17
Romania	1.04	1.55	1.5	:
Slovenia	4.3	3.88	4.1	4.41
Slovakia	3.99	3.92	3.89	4.01
Finland	9.25	9.78	11.18	9.84
Sweden	16.58	17.31	13.63	12.2
United Kingdom	7.67	7.4	7.86	10.06
Iceland	6.35	4.97	6.52	:
Norway	15.06	14.19	14.92	14.14

Note: “:” means yet to be updated.

Source: (<http://appsso.eurostat.ec.europa.eu/nui/submitViewTableAction.do>).

Table 5 Collected E-waste recycled in European nations (in tons)

Year	2012	2013	2014	2015
European Union (28 countries)	2,417,464	–	2,845,996	–
Belgium	91,324	95,265	89,284	91,739
Bulgaria	32,282	29,353	35,911	53,085
Czech Republic	43,258	49,402	50,095	61,313
Denmark	64,285	59,513	59,372	61,010
Germany (until 1990 former territory of the FRG)	576,848	602,894	608,587	–
Estonia	4,397	3072	4,382	4,893
Ireland	34,361	35,508	37,584	40,458
Greece	33,578	34,671	38,144	43,888
Spain	133,491	171,769	142,165	–
France	361,127	377,669	422,589	505,466
Croatia	14,942	14,631	14,826	21,987
Italy	397,675	384,578	258,679	–
Cyprus	2,176	1,834	2,049	–
Latvia	3,924	4,359	4,443	4,024
Lithuania	9,794	11,222	16,790	13,120
Luxembourg	4,348	4,533	4,856	5,127
Hungary	36,095	43,637	45,034	43,415
Malta	1,080	1,661	1,791	–
Netherlands	102,614	97,669	116,841	119,448
Austria	61,914	60,698	61,907	65,090
Poland	133,694	129,771	127,190	138,914
Portugal	37,851	43,323	46,470	50,284
Romania	19,459	28,738	28,064	–
Slovenia	7,511	4,359	7,909	9,074
Slovakia	19,896	19,215	20,603	20,258
Finland	47,368	50,925	57,981	57,858
Sweden	142,171	147,860	121,839	120,387
United Kingdom	–	–	420,612	536,580
Iceland	1,827	1,575	2,532	–
Liechtenstein	105	218	231	313
Norway	82,720	84,729	85,857	86,991

Note: “–” means yet to be updated.

Source: (<http://appsso.eurostat.ec.europa.eu/nui/submitViewTableAction.do>).

Africa etc., as a secondary export market. Being in the developing stage, they have under developed technological infrastructure for processing e-waste which severely affect the environment of the vicinity. These countries, after signing the Basel Convention, have strict import regulations, official banning these movements.

Uniform legislation regarding the collection and processing of e-waste has been restored efficiently in the EU by the directive 2012/19/EU of the European Parliament and of the council of 4th July 2012 on waste electrical and electronic equipment (WEEE) (see “Relevant Websites section”). The recast of the WEEE Directive (2012/19/EU), which ended into force on 13th August 2012, proposed an incremental increase in the collection of e-waste from 2016 till 2021. The projected annual collection target should be the relation between the collected amount and the average amount of EEE put on the market in the three preceding years.

In Germany, for instance, a mechanism known as “divided product responsibility” was instituted by the WEEE Directive for electrical and electronic waste disposal operations. This electronic waste disposal responsibility fell into the domains of public sector recycling companies and the EEE manufacturers. Public sector recycling companies were required to establish e-waste recycling centres and to accept such waste at these centres free of charge. This mechanism is currently carried out at around 1500 municipal recycling centres all over the country. Alternatively, manufacturers were free to provide their own recycling mechanisms, and retailers are also allowed to take back electrical and electronic waste. Consumers are subjected by law to take their discarded EEEs to such facilities. The current collection rate targets are set by the WEEE Directive which is currently set to 65%, for the year 2019 (see “Relevant Websites section”).

According to an Ökopol study that was commissioned by the German Environment Agency (Umweltbundesamt or UBA), in 2008 some 150,000 tons of electrical and electronic waste was exported from Germany to Nigeria, Ghana, India, South Africa and other countries. The new WEEE directive enforces the exporters to prove the functionality of devices declared as used prior to export, the purpose is to ensure only intact apparatuses are exported as their reuse shall save resources in the destination countries (see “Relevant Websites section”) (Table 5).

The Balkan region has often been the destination for e-waste disposal from the developed world. The practices of dealing with locally-generated e-waste were not environment friendly, which led to a loss of secondary resources and

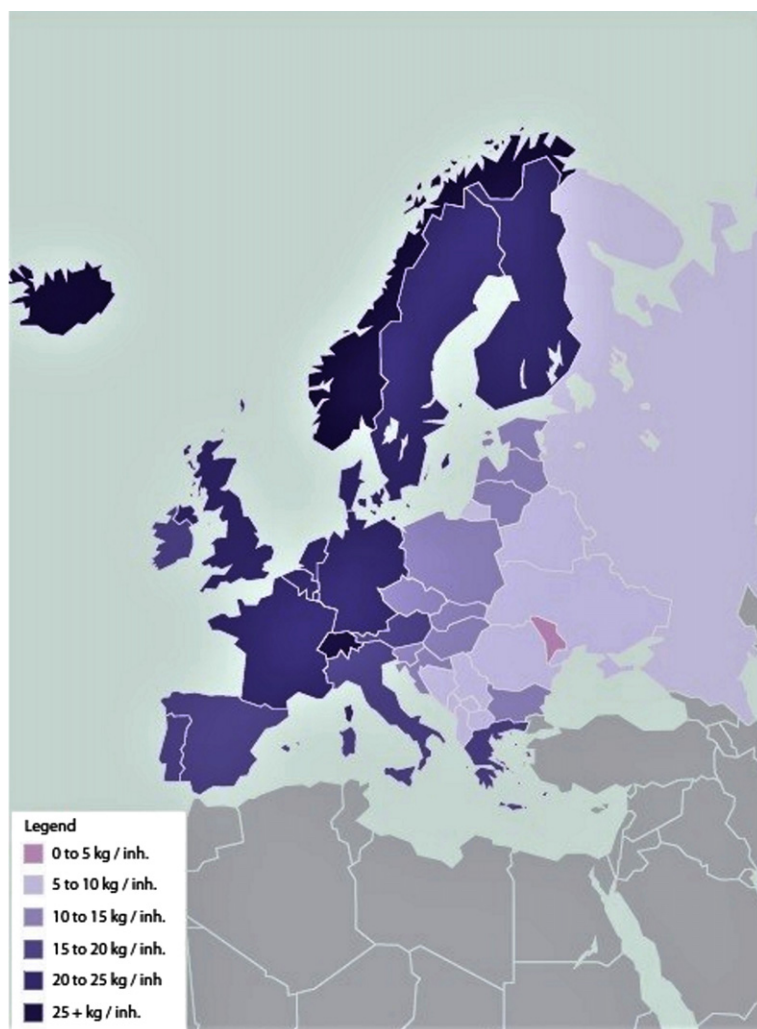


Fig. 15 Distribution mapping of e-waste generation in European nations. Reproduced from Baldé, C.P., Wang, F., Kuehr, R., Huisman, J., 2015. *The Global E-Waste Monitor – 2014*. Bonn, Germany: United Nations University, IAS – SCYCLE.

damage of the environment. The National legislation on e-waste management has been put in force in five countries of this region: Montenegro, Macedonia, Serbia, and Bosnia and Herzegovina. There is no national legislation tackling e-waste in Kosovo, whereas the western Balkans region have not yet implemented an effective e-waste system like the other EU Member States. Further development in collection schemes and recycling infrastructure is of prime requirement in this region.

The situation in Belarus, Armenia, Kirgizstan and Russia is not quite clear. So far, they do not have any e-waste legislation or management system in place. Although, in 2014, Russia introduced EPR (extended product responsibility) as the stepping stone in e-waste management. Various inter-agency groups on regulations are currently active in making the implementation of such laws in the region (Figs. 15 and 16).

United States of America

The United States generated 11.7 million tons of e-waste, around 28% of the entire global production in the year 2014 (see “Relevant Websites section”). Among the world’s e-waste contributors, U.S. is the only country which has generated trash more than that of a few continents, such as South America, Africa Oceania etc. The country either disposes the wastes collected or exports them to the developing nations of Asia and Africa as well as Latin America. Currently, the latter trend is quite compelled by the entire world, as it is the only nation among developed world to sign, yet not ratify the Basel Convention, which restricts the trans-country movements of toxic wastes (see “Relevant Websites section”). The United States currently maintains a multilateral agreement with the members of the Organisation for Economic Co-operation and



Fig. 16 Distribution of e-waste generation per capita in North America. Reproduced from Baldé, C.P., Wang, F., Kuehr, R., Huisman, J., 2015. *The Global E-Waste Monitor – 2014*. Bonn, Germany: United Nations University, IAS – SCYCLE.

Development (OECD), governing transboundary movements of waste for recovery purposes. Moreover, it has established two bilateral agreements, with Canada and Mexico, for importing and exporting hazardous waste. In the end, Costa Rica, Malaysia and the Philippines have entered into separate understanding agreements with the United States, under which, United States may receive waste, but may not export e-waste to these countries respectively (Chapter-V, 2011).

Many states in the U.S. have begun efforts to collect for further processing from the residential and business sources. For instance, the State of California has passed a law in the year 2006, charging consumer fees, called Advanced Recycling Fees (ARFs), at the time of buying the products. The system covered monitors, TVs and laptops, and the ARF was between US\$ 6 and US\$ 10 (Gregory and Kirchain, 2007). Similar steps taken by different states have later helped in collecting e-wastes for recycling. Table 3 describes the data of the recycled e-waste among various states of the United States in the year of 2014 (Fig. 17).

After working systems, valuable components, and hazardous materials are removed from the e-waste, the materials recovery process begins. The primary goal of this process is to separate different types of materials that can be recovered and sold. Residential electronic waste collection programs in the U.S. show that the majority of the items collected consist of TVs, computers and monitors, and other appliances. The flow of materials after discarding the product for the market of USA can be understood from Fig. 18. The letters in the codes in italics in the figure refer to the state of the item, S, the activity, A, or the destination, D.

There are two domestic third party certification systems for e-waste recyclers in the country: R2 and E-Stewards. The electronics recycling industry is increasingly embracing these programs to improve their environmental performances and reduce human health impacts from improper recycling (Baldé et al., 2015).

Continuous and stable supply of materials is still the major challenge for e-waste recycling. Although, the development of cost effective technologies for recycling is of absolute necessity, existing methods have limited ability to handle complex products (Kang and Schoenung, 2005) (Fig. 19).

Whatever system is put in place, it also important that financial responsibility needed is ensured proper management. One issue is the management of the new financial flows. One option – in a strict interpretation of the idea of EPR – is to make manufacturers entirely responsible for collection and disposal. However, other participants in the chain of electronic products, such as consumers and government, should also take partial responsibility for e-waste management.

E-WASTE RECYCLED IN U.S (2014)

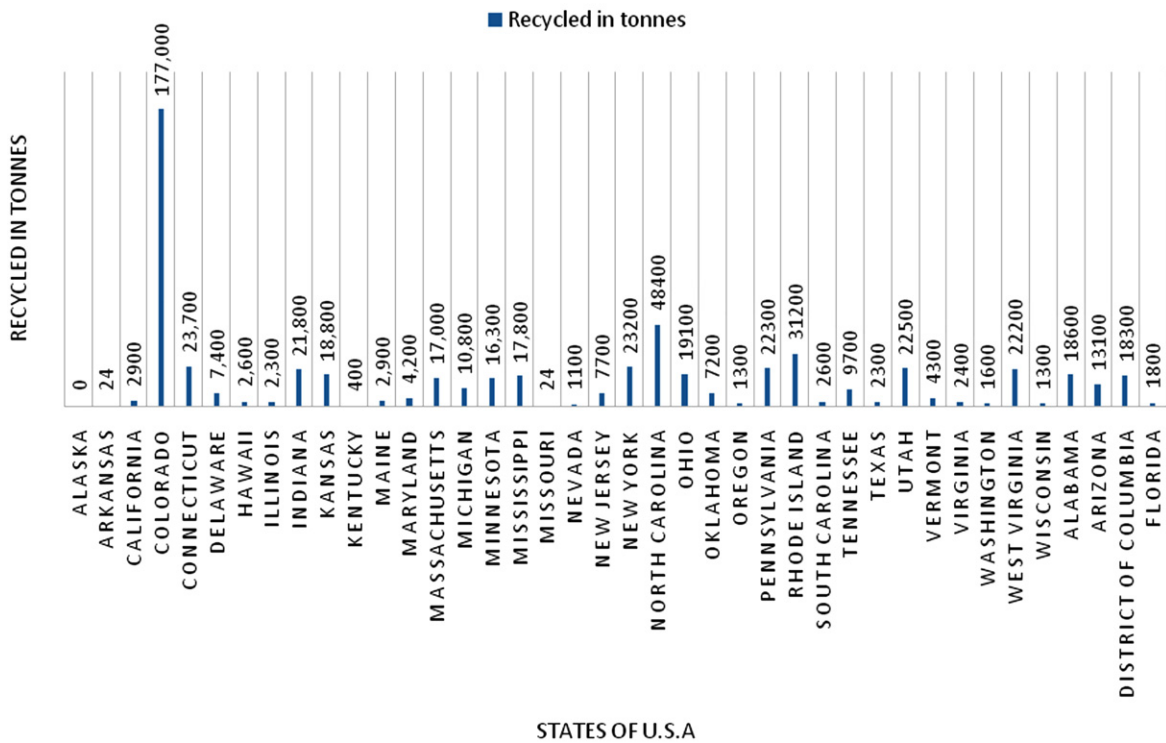


Fig. 17 Recycled e-waste data in USA. Reproduced from Electronic Products Generation and Recycling in the United States, 2013 and 2014, 2016. U.S. environmental protection agency office of resource conservation and recovery.

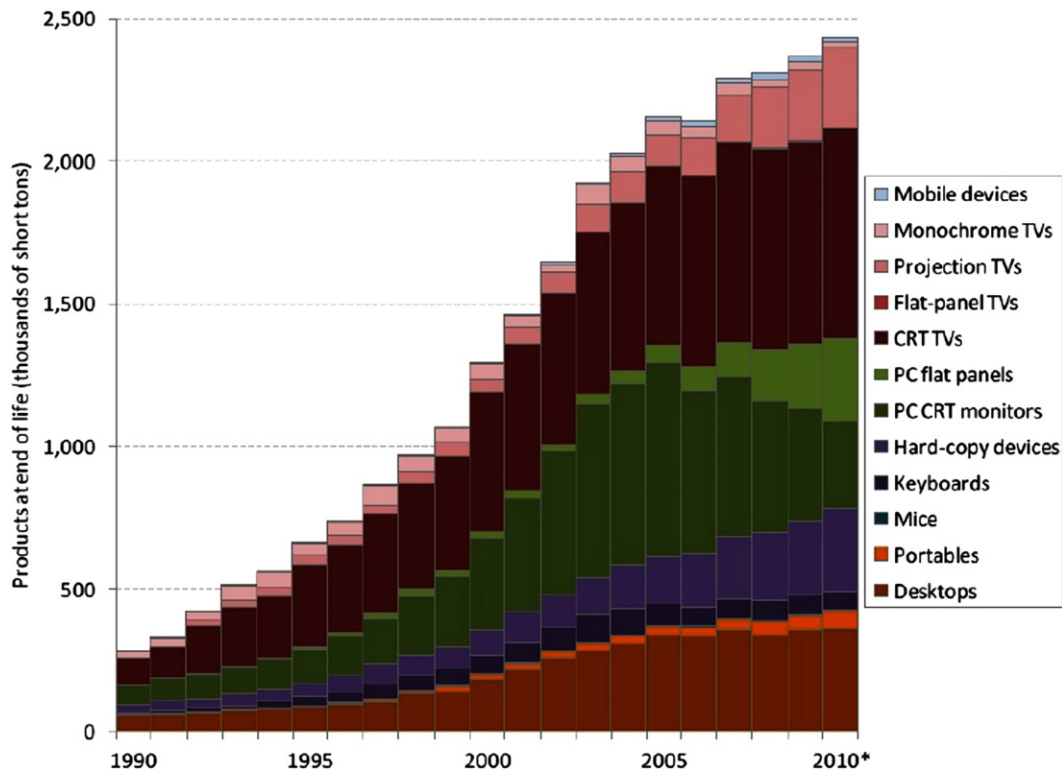


Fig. 18 Distribution of materials within collected residential electronics waste in the U.S. Reproduced from Miller, T., Gregory, J., Duan, H., Kirchain, R., 2012. Characterizing transboundary flows of used electronics: Summary report, MIT Materials Systems Laboratory (MIT MSL) and National Center for Electronics Recycling (NCER), StEP Initiative, p. 28.

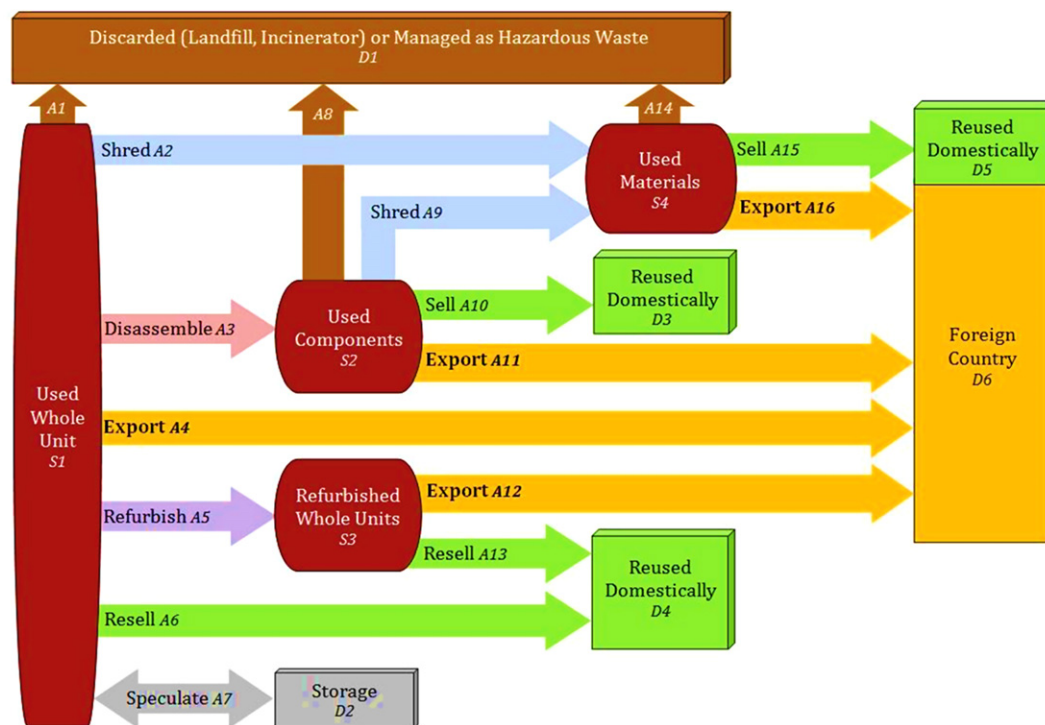


Fig. 19 Used Electronics Flowchart (MIT MSL); Rounded rectangles represent the state of the item (S), arrows represent the activity (A), and boxes represent destinations (D). Reproduced from Miller, T., Gregory, J., Duan, H., Kirchain, R., 2012. Characterizing transboundary flows of used electronics: Summary report, MIT Materials Systems Laboratory (MIT MSL) and National Center for Electronics Recycling (NCER), StEP Initiative, p. 28.

See also: System Optimization for Control of Solid Waste

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Modeling Estimation and Performance Evaluation for Vibration Isolators

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Nomenclature

$\ddot{u}$ Acceleration
 U Complex amplitude
 u Displacement
 F_e Excitation force
 ω Natural frequency

k Stiffness
 T_r Transmissibility
 F_t Transmitted force
 $\dot{u}$ Velocity
 M Working mass

Introduction

Rubber plantation is first introduced in Malaysia even before the country achieved its independence. Rubber seedlings were brought into the country by the British, and were first planted at Kuala Kangsar, Perak. This area was chosen due to the condition of the terrain, which is suitable for rubber trees, and, within a few years, the cultivation of rubber had grown rapidly throughout the Malaysian peninsular.

Since independence in 1957, the Malaysian government has set up many agencies with an objective to modernize the agricultural industries including the rubber plantations. Federal Land Development Authority (FELDA) was given the task of initiating and managing rubber plantations to support the relocation of rural populations. In 1973, the government also established the Rubber Industry Smallholders Development Authority (RISDA). This agency was established with the aim of helping small rubber farmers to increase their income. Until 2010, RISDA brought together the rubber plantations owned by smallholders, and the records showed that the area planted with rubber trees reached up to 587,225 hectares. Moreover, FELDA has managed to open up new land for planting rubber trees, which reached an area of 65,932 hectares. However, several problems were faced by these agencies as well as by the rubber farmers themselves. According to the records, replanting the rubber trees took a long time, and the rubber farmers had to wait for months before they could tap the trees. Furthermore, the farmers were also affected due to the volatile price of rubber in the market. In 2011, Malaysia produced approximately 9% of the total amount of rubber materials produced worldwide which was equivalent to 996,000 metric tonnes of rubber. This number indicated that Malaysia was the third-largest country in the world for rubber production.

Recently, the price of natural rubber (NR) has fallen drastically because of advancements in synthetic rubber. As a result, the rubber farmers must bear huge losses and this situation affects their monthly income. The authorities are demanded to take appropriate action to help the farmers who facing these economic difficulties. Research institutions and universities are also required to participate actively in finding solutions to increase the value and usage of NR. It is also essentially important for more extensive research in finding the use of NR in more appropriate products. This will consequently result in an increase in the price of NR, in line with the main objective, that is to improve the farmers' income. Conservative study needs to be revolutionized with innovative research while maintaining the key characteristics of the NR itself.

Currently, there are over 3500 articles discussing the use of NR as vibration isolators in dissipating energy, by considering various combinations of restoring and damping forces applied on the system. Many researchers are developed an exact solution for vibratory response called symmetric system, which consist of coulomb and viscous damping (Bhuiyan *et al.*, 2010; Carrella, 2011; Burdzik, 2014). Both damping was subjected to a harmonic motion. Based on these two studies, the magnitude of stiffness required in designing the new vibration isolators is found and transmissibility force could be predicted by referring to the resonant amplitudes.

The development of passive mechanical vibration isolator consisting of discrete mass, stiffness, and damping elements have initiated approximately 30 years ago. This system is similar to the lumped parameter system. It was discovered that the effectiveness of the vibration isolators was when the system was subjected to a harmonic excitation in certain frequency ranges. The resonances of the isolator are similar compared to previous researches and the level of transmitted force was further reduced (Chang, 2002; Mitra *et al.*, 2010; Du *et al.*, 2011; Karabork, 2011; Kobayashi *et al.*, 2012).

Vibration isolators have been widely to suppress the level of vibration, especially in building structures for earthquake protection. It is made from layers of rubber with thin steel plates between them, and a thick plate located at the top and bottom of the rubber materials. These vibration isolators are located between the bottom of a building and its foundation. By embedding the metal plates, the combination provides better performance in terms of stress and strain level when a heavy load is applied and prevents a bulging effect in the horizontal direction. It is also designed to be very stiff and strong for vertical load; therefore, it can carry the heavy weight of the building. In addition, this study also investigates the effect of the shape factor on the stress distributions and stress concentration of the NR elastomer subjected to longitudinal load. The finite element analysis (FEA) approach was used to produce an approximated solution. The results obtained from numerical modeling is then compared and validated with an analytical approximated solution (Kobayashi *et al.*, 2012). Based on this correlation study, it was found that a beneficial effect of the shape factor was higher stress distribution and stress concentration parallel with the reduction of edge effects (Kobayashi *et al.*, 2012). This study is in good agreement with past research in the use of rubber bearings to support bridges being built as part of new highway construction in Greece (Ibrahim, 2008). Two samples of

rubber bearings were located at the bridge columns. The test results revealed that the stiffness and damping ratio show a good relationship with longitudinal load as well as the frequency of the horizontal displacement. It was found that by employing the isolation strategy, the superstructure motion was decoupled from the pier's motion during an earthquake. The inertia forces could be reduced and at the same time, energy was dissipated by the vibration isolators, which, finally, reduced the acceleration transmitted into the superstructure.

In addition, in 2007, the model of the hysteretic behaviour of rubber bearings under unidirectional horizontal displacement and constant horizontal compressive load was proposed. Three types of bearing were used in these studies, namely NR bearing, lead rubber bearing and high-damping rubber bearing. Several experiments were conducted to analyse the performance of the bearings, such as basic test, multi-step relaxation, cyclic test and simple relaxation. It was found that the NR bearings gave the best result in terms of the rate-dependent rheology. This represents the typical shear stress-strain responses of high-damping rubber bearings where the strain rate dependency of hysteresis occurs (Bhuiyan *et al.*, 2010).

The new design of vibration isolators is needed to increase the performance of the isolator by shifting the resonance frequency, thus increasing the effectiveness of the isolator. Based on the previous study, the mathematical modeling of the vibration isolator could be derived by using wave propagation approach (Yin *et al.*, 2010; Mishra and Igarashi, 2013; Lee *et al.*, 2014; Salim *et al.*, 2014). The non-dispersive finite rod was chosen as a vibration isolator model, and it was represented as rubber material isolator. Impedance matrix was developed to evaluate and investigate the internal resonance behaviour of the isolator. The waves were propagated from the initial boundary of non-dispersive finite rod, and bounced back to the initial location. It happened due to the natural behaviour of waves. It could not pass the end of the boundary which was fixed.

This phenomenon has also been discussed previously. Researchers agreed that the natural behaviour of the waves could not pass the fixed boundary, and not affecting the vibration isolator performance (Yan *et al.*, 2007; Peng *et al.*, 2010; Sun and Zhang, 2013; Spizzuoco *et al.*, 2014; Sun *et al.*, 2014).

This article focuses on the performance and characteristics of vibration isolator based on the discrete lumped parameter model. This model is adopted from conventional lumped parameter model with some modification. Reynolds and Falkenberg (1984) applied the lump parameter model to evaluate the vibration response characteristics on human hand while operating chipping and grinding process. By using the discrete lumped parameter model in vibration isolator application, it is expected to contribute in characterizing the vibration isolators' performance and transmissibility behaviour subjected to the longitudinal vibration.

Modeling and Prediction Estimation of Discrete Lumped Parameter Model

This section focuses on the development of the discrete lumped parameter model which is adopted from the conventional lumped parameter model. The intention is to model the isolator into discrete springs and masses to take into account the effect of inertial mass. The distributed mass is assumed to have total mass equivalent to the mass of the isolator, and the stiffness value was according to the height of the isolator which was based on the value of the overall stiffness. The excitation force F_e , transmitted force F_t and, finally, displacement u were used in this system.

Distributed parameter model is used as a benchmark to develop the discrete lumped parameter system. Fig. 1 shows the modified distributed parameter isolator compared to the discrete lumped parameter models.

The equation of motion for the discrete lumped parameter system can be given as

$$F_e = M\ddot{u}_1 + ku_1 \quad (1)$$

and

$$F_t = ku_1 \quad (2)$$

In harmonic motion, both equations of motion in Eqs. (1) and (2) become

$$F_e = -\omega^2 MU_1 + kU_1 \quad (3)$$

and

$$F_t = kU_1 \quad (4)$$

where, U is the complex amplitude, ω is the frequency, F_e is excitation force and F_t is transmitted force.

The general transmissibility equation is

$$T_r = \left| \frac{F_t}{F_e} \right| \quad (5)$$

By inserting Eqs. (3) and (4) into (5), the transmissibility equation for the single-degree-of-freedom for the discrete lumped parameter system can be given as

$$T_r = \left| \frac{kU_1}{-\omega^2 MU_1 + kU_1} \right| \quad (6)$$

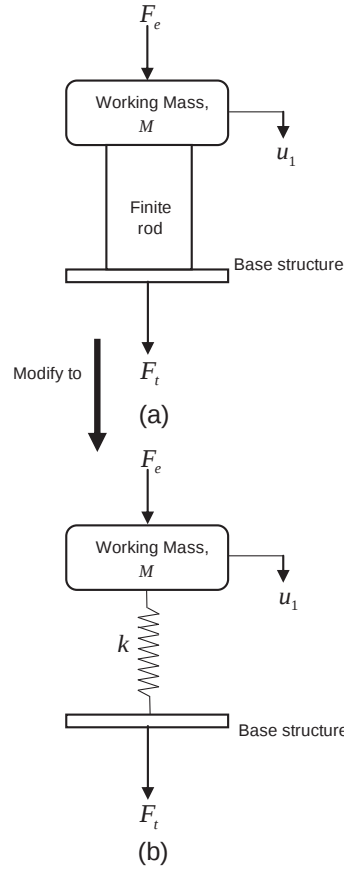


Fig. 1 Discrete lumped parameter models (a) Distributed parameter isolator and (b) Discrete lumped parameter models.

Therefore, the steps from Eqs. (1)–(6) can be used in developing the higher-degree-of-freedom of the system.

Multi-Degree-of-Freedom

In this section, the multi-degree-of-freedom of the discrete lumped parameter model is discussed, and the aim is to develop the internal resonance behaviour. For the two-degree-of-freedom discrete lumped parameter system, the rubber (see Fig. 1(b)) was divided into two spring elements. However, the total value of stiffness and mass remained the same as in the single-degree-of-freedom system. Fig. 2 illustrates the schematic diagram for the two-degree-of-freedom discrete lumped parameter model. The equations of motion for the systems can be derived as

$$F_e = M\ddot{u}_1 + \frac{k}{2}u_1 - \frac{k}{2}u_2 \quad (7)$$

$$0 = m\ddot{u}_2 + \frac{k}{2}u_2 - \frac{k}{2}u_1 \quad (8)$$

and

$$F_t = \frac{k}{2}u_2 \quad (9)$$

In harmonic motion, Eqs. (7)–(9) become

$$F_e = -\omega^2 MU_1 + \frac{k}{2}U_1 - \frac{k}{2}U_2 \quad (10)$$

$$0 = -\omega^2 mU_2 + \frac{k}{2}U_2 - \frac{k}{2}U_1 \quad (11)$$

and

$$F_t = \frac{k}{2}U_2 \quad (12)$$

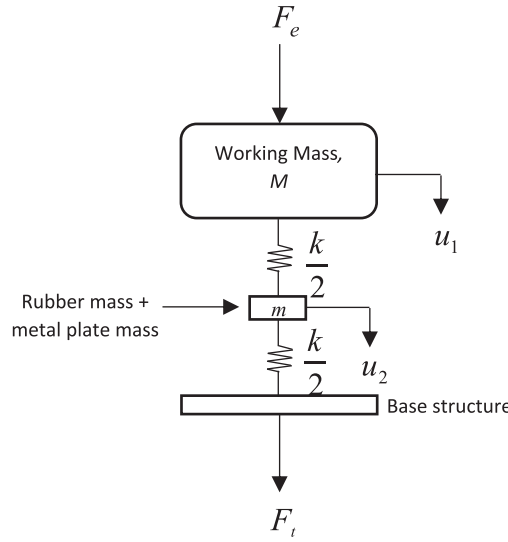


Fig. 2 Two-degrees-of-freedom discrete lumped parameter model.

By simplifying Eqs. (10) and (11), the new equations are given by

$$F_e = \left(\frac{k}{2} - \omega^2 M \right) U_1 - \frac{k}{2} U_2 \quad (13)$$

and

$$0 = \left(\frac{2k}{2} - \omega^2 m \right) U_2 - \frac{k}{2} U_1 \quad (14)$$

By taking U_2 as a reference for U_1 , therefore Eq. (14) can be written and then simplified as

$$U_1 = \left(2 - \frac{2}{k} \omega^2 m \right) U_2 \quad (15)$$

Then, to solve Eq. (13), Eq. (15) is used, and, finally, the new equation becomes

$$F_e = \left(\frac{k}{2} - \omega^2 M \right) \left(2 - \frac{2}{k} \omega^2 m \right) U_2 - \frac{k}{2} U_2 \quad (16)$$

Again, by taking Eq. (5) as a reference, the transmissibility equation for the two-degree-of-freedom discrete lumped parameter of the isolator, is given by

$$T_r = \left| \frac{F_t}{F_e} \right| = \left| \frac{\frac{k}{2} U_2}{\left(\frac{k}{2} - \omega^2 M \right) \left(2 - \frac{2}{k} \omega^2 m \right) U_2 - \frac{k}{2} U_2} \right| \quad (17)$$

For the three-degree-of-freedom discrete lumped parameter system, the stiffness value was divided into three parts of spring element and the mass of the rubber is divided into two. However, the total mass is equivalent to the total mass of the two-degree-of-freedom discrete lumped parameter system. Fig. 3 shows the schematic diagram of the system.

Then, the equation of motion of this system can be given as

$$F_e = M \ddot{u}_1 + \frac{k}{3} u_1 - \frac{k}{3} u_2 \quad (18)$$

$$0 = \frac{m}{2} \ddot{u}_2 + \frac{2k}{3} u_2 - \frac{k}{3} u_1 - \frac{k}{3} u_3 \quad (19)$$

$$0 = \frac{m}{2} \ddot{u}_3 + \frac{2k}{3} u_3 - \frac{k}{3} u_2 \quad (20)$$

and

$$F_t = \frac{k}{3} u_3 \quad (21)$$

For harmonic motion, Eqs. (18)–(21) become

$$F_e = -\omega^2 M U_1 + \frac{k}{3} U_1 - \frac{k}{3} U_2 \quad (22)$$

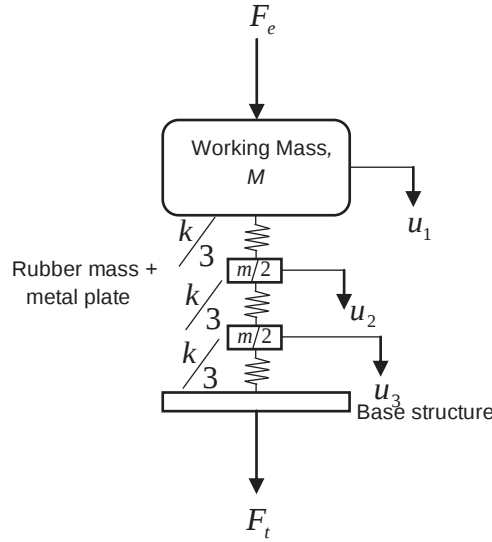


Fig. 3 Three-degree-of-freedom discrete lumped parameter model.

$$0 = -\omega^2 \frac{m}{2} U_2 + \frac{2k}{3} U_2 - \frac{k}{3} U_1 - \frac{k}{3} U_3 \quad (23)$$

$$0 = -\omega^2 \frac{m}{2} U_3 + \frac{2k}{3} U_3 - \frac{k}{3} U_2 \quad (24)$$

and

$$F_t = \frac{k}{3} U_3 \quad (25)$$

By simplifying Eqs. (22)–(24), the equations can be written as

$$F_e = \left(\frac{k}{3} - \omega^2 M \right) U_1 - \frac{k}{3} U_2 \quad (26)$$

$$0 = \left(\frac{2k}{3} - \omega^2 \frac{m}{2} \right) U_2 - \frac{k}{3} U_1 - \frac{k}{3} U_3 \quad (27)$$

and

$$0 = \left(\frac{2k}{3} - \omega^2 \frac{m}{2} \right) U_3 - \frac{k}{3} U_2 \quad (28)$$

By taking U_3 as a reference of U_2 , therefore, the new equation can be derived as

$$U_2 = \left(2 - 3\omega^2 \frac{m}{k} \right) U_3 \quad (29)$$

On the other hand, from Eq. (27), U_2 and U_1 can be written as a reference for U_3 . After rearranging the equation, finally, it can be given as

$$U_3 = \left(2k^2 - \frac{3}{2}\omega^2 mk \right) U_2 - k^2 U_1 \quad (30)$$

By substituting Eq. (30) into Eq. (29), the equation can be written as

$$U_2 = \frac{-k^2}{1 - \left(2 - 3\omega^2 \frac{m}{k} \right) \left(2k^2 - \frac{3}{2}\omega^2 mk \right)} U_1 \quad (31)$$

Then, by inserting Eq. (29) into Eq. (31), the equation becomes

$$\left(2 - 3\omega^2 \frac{m}{k} \right) U_3 = 2 = \frac{-k^2}{1 - \left(2 - 3\omega^2 \frac{m}{k} \right) \left(2k^2 - \frac{3}{2}\omega^2 mk \right)} U_1 \quad (32)$$

By simplifying Eq. (32), it can be written as

$$U_1 = \frac{\left(2 - 3\omega^2 \frac{m}{k} \right) U_3 \times \left[1 - \left(2 - 3\omega^2 \frac{m}{k} \right) \left(2k^2 - \frac{3}{2}\omega^2 mk \right) \right]}{-k^2} \quad (33)$$

By substituting Eqs. (29) and (33) into Eq. (26), it becomes

$$F_e = \left(\frac{k}{3} - \omega^2 M \right) \times \frac{(2 - 3\omega^2 \frac{m}{k}) U_3 \times [1 - (2 - 3\omega^2 \frac{m}{k})(2k^2 - \frac{3}{2}\omega^2 mk)]}{-k^2} - \frac{k}{3} \left(2 - 3\omega^2 \frac{m}{k} \right) U_3 \quad (34)$$

By simplifying Eq. (34), the equation of excitation force becomes

$$F_e = \left(\frac{k}{3} - \omega^2 M \right) \left(2 - \frac{3}{k} \omega^2 m \right) U_3 - \frac{k}{3} U_3 \quad (35)$$

Therefore, the transmissibility equation of the three-degree-of-freedom discrete lumped parameter model can be written as

$$T_r = \left| \frac{F_t}{F_e} \right| = \left| \frac{\frac{k}{3} U_3}{\left(\frac{k}{3} - \omega^2 M \right) \left(2 - \frac{3}{k} \omega^2 m \right) U_3 - \frac{k}{3} U_3} \right| \quad (36)$$

Consequently, by dividing into three parts of the rubber mass, and dividing the stiffness into four parts of spring elements, the system is represented as four-degree-of-freedom discrete lumped parameter system. However, the total value for stiffness and mass remained the same as previous system. Fig. 4 shows the schematic diagram of the system. The equations of motion for the system are as expressed in Eqs. (37)–(41).

$$F_e = M\ddot{u}_1 + \frac{k}{4}u_1 - \frac{k}{4}u_2 \quad (37)$$

$$0 = \frac{m}{3}\ddot{u}_2 + \frac{2k}{4}u_2 - \frac{k}{4}u_1 - \frac{k}{4}u_3 \quad (38)$$

$$0 = \frac{m}{3}\ddot{u}_3 + \frac{2k}{4}u_3 - \frac{k}{4}u_2 - \frac{k}{4}u_4 \quad (39)$$

$$0 = \frac{m}{3}\ddot{u}_4 + \frac{2k}{4}u_4 - \frac{k}{4}u_3 \quad (40)$$

and

$$F_t = \frac{k}{4}u_4 \quad (41)$$

Following this, in harmonic motion, the equations of motion become

$$F_e = -\omega^2 M U_1 + \frac{k}{4}U_1 - \frac{k}{4}U_2 \quad (42)$$

$$0 = -\omega^2 \frac{m}{3} U_2 + \frac{2k}{4}U_2 - \frac{k}{4}U_1 - \frac{k}{4}U_3 \quad (43)$$

$$0 = -\omega^2 \frac{m}{3} U_3 + \frac{2k}{4}U_3 - \frac{k}{4}U_2 - \frac{k}{4}U_4 \quad (44)$$

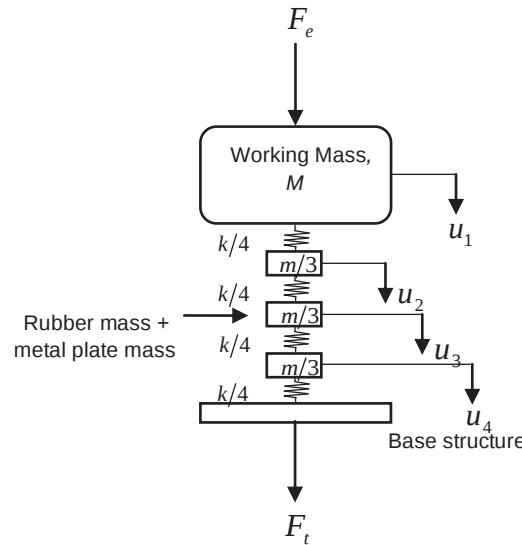


Fig. 4 Four-degree-of-freedom discrete lumped parameter model.

$$0 = -\omega^2 \frac{m}{3} U_4 + \frac{2k}{4} U_4 - \frac{k}{4} U_3 \quad (45)$$

and

$$F_t = \frac{k}{4} U_4 \quad (46)$$

By simplifying Eqs. (42)–(45), the equations are given by

$$F_e = \left(\frac{k}{4} - \omega^2 M \right) U_1 - \frac{k}{4} U_2 \quad (47)$$

$$0 = \left(\frac{2k}{4} - \omega^2 \frac{m}{3} \right) U_2 - \frac{k}{4} U_1 - \frac{k}{4} U_3 \quad (48)$$

$$0 = \left(\frac{2k}{4} - \omega^2 \frac{m}{3} \right) U_3 - \frac{k}{4} U_2 - \frac{k}{4} U_4 \quad (49)$$

and

$$0 = \left(\frac{2k}{4} - \omega^2 \frac{m}{3} \right) U_4 - \frac{k}{4} U_3 \quad (50)$$

From Eq. (49), U_3 and U_4 can be written as a reference for U_2 . Therefore, by rearranging the equation, it then becomes

$$U_2 = \left(2k^2 - 4\omega^2 \frac{m}{3} k \right) U_3 - k^2 U_4 \quad (51)$$

By rearranging Eq. (50), and letting U_3 be a reference value of U_4 , finally, the equation can be expressed as

$$U_4 = \frac{k}{4} \left(\frac{1}{\frac{2k}{4} - \omega^2 \frac{m}{3}} \right) U_3 \quad (52)$$

By substituting Eq. (52) into Eq. (51), it gives

$$U_2 = \left(2k^2 - 4\omega^2 \frac{m}{3} k \right) U_3 - k_2 \left[\frac{k}{4} \left(\frac{1}{\frac{2k}{4} - \omega^2 \frac{m}{3}} \right) \right] U_3 \quad (53)$$

By inserting Eq. (53) into Eq. (49), then the equation becomes

$$0 = \left(\frac{2k}{4} - \omega^2 \frac{m}{3} \right) U_3 - \frac{k}{4} \left(2k^2 - 4\omega^2 \frac{m}{3} k \right) U_3 - k_2 \left[\frac{k}{4} \left(\frac{1}{\frac{2k}{4} - \omega^2 \frac{m}{3}} \right) \right] U_3 - \frac{k}{4} U_4 \quad (54)$$

By rearranging Eq. (54), the equation becomes

$$U_3 = \frac{U_2 + k^2 U_4}{2k^2 - 4\omega^2 \frac{m}{3} k} \quad (55)$$

By inserting Eq. (55) into Eq. (54), the equation can be written as

$$\begin{aligned} 0 = & \left[\left(\frac{2k}{4} - \omega^2 \frac{m}{3} \right) \times \left(\frac{U_2 + k^2 U_4}{2k^2 - 4\omega^2 \frac{m}{3} k} \right) \right] - \left[\frac{k}{4} \left(2k^2 - 4\omega^2 \frac{m}{3} k \right) \times \left(\frac{U_2 + k^2 U_4}{2k^2 - 4\omega^2 \frac{m}{3} k} \right) \right] \dots \\ & \dots - k_2 \left[\frac{k}{4} \left(\frac{1}{\frac{2k}{4} - \omega^2 \frac{m}{3}} \right) \times \left(\frac{U_2 + k^2 U_4}{2k^2 - 4\omega^2 \frac{m}{3} k} \right) \right] - \frac{k}{4} U_4 \end{aligned} \quad (56)$$

By dividing Eq. (56) into small groups, they become

$$G1 = \left(\frac{2k}{4} - \omega^2 \frac{m}{3} \right) \times \left(\frac{U_2 + k^2 U_4}{2k^2 - 4\omega^2 \frac{m}{3} k} \right) \quad (57)$$

$$G2 = \frac{k}{4} \left(2k^2 - 4\omega^2 \frac{m}{3} k \right) \times \left(\frac{U_2 + k^2 U_4}{2k^2 - 4\omega^2 \frac{m}{3} k} \right) \quad (58)$$

$$G3 = k_2 \left[\frac{k}{4} \left(\frac{1}{\frac{2k}{4} - \omega^2 \frac{m}{3}} \right) \times \left(\frac{U_2 + k^2 U_4}{2k^2 - 4\omega^2 \frac{m}{3} k} \right) \right] \quad (59)$$

and

$$G4 = \frac{k}{4} U_4 \quad (60)$$

By substituting Eq. (55) into Eq. (48), the equation can be expressed as

$$0 = \left(\frac{2k}{4} - \omega^2 \frac{m}{3} \right) U_2 - \frac{k}{4} U_1 - \frac{k}{4} \left(\frac{U_2 + k^2 U_4}{2k^2 - 4\omega^2 \frac{m}{3} k} \right) \quad (61)$$

By simplifying Eq. (61), the equation becomes

$$U_2 = \frac{\left(\frac{k^3 U_4}{8k^2 - 16\omega^2 \frac{m}{3} k} \right) - \frac{k}{4} U_1}{\left(\frac{2k}{4} - \omega^2 \frac{m}{3} \right) - \left(\frac{1}{8k^2 - 16\omega^2 \frac{m}{3} k} \right)} \quad (62)$$

By inserting Eq. (62) into Eqs. (57)–(59), the equations become

$$G1 = \left(\frac{2k}{4} - \omega^2 \frac{m}{3} \right) \times \frac{\left(\frac{k^3 U_4}{8k^2 - 16\omega^2 \frac{m}{3} k} \right) - \frac{k}{4} U_1}{\left(\frac{2k}{4} - \omega^2 \frac{m}{3} \right) - \left(\frac{1}{8k^2 - 16\omega^2 \frac{m}{3} k} \right)} + k^2 U_4 \times \left(\frac{1}{2k^2 - 4\omega^2 \frac{m}{3} k} \right) \quad (63)$$

$$G2 = \frac{k}{4} \left(2k^2 - 4\omega^2 \frac{m}{3} k \right) \times \frac{\left(\frac{k^3 U_4}{8k^2 - 16\omega^2 \frac{m}{3} k} \right) - \frac{k}{4} U_1}{\left(\frac{2k}{4} - \omega^2 \frac{m}{3} \right) - \left(\frac{1}{8k^2 - 16\omega^2 \frac{m}{3} k} \right)} + k^2 U_4 \times \left(\frac{1}{2k^2 - 4\omega^2 \frac{m}{3} k} \right) \quad (64)$$

and

$$G3 = k_2 [A \times B + C] \quad (65)$$

where

$$A = \frac{k}{4} \left(\frac{1}{\frac{2k}{4} - \omega^2 \frac{m}{3}} \right) \quad (66)$$

$$B = \frac{\left(\frac{k^3 U_4}{8k^2 - 16\omega^2 \frac{m}{3} k} \right) - \frac{k}{4} U_1}{\left(\frac{2k}{4} - \omega^2 \frac{m}{3} \right) - \left(\frac{1}{8k^2 - 16\omega^2 \frac{m}{3} k} \right)} \quad (67)$$

and

$$C = k^2 U_4 \times \left(\frac{1}{2k^2 - 4\omega^2 \frac{m}{3} k} \right) \quad (68)$$

By simplifying Eqs. (63)–(65), and inserting the simplified group into Eq. (56), and finally transferring the equation into Eq. (45), the excitation force equation becomes

$$F_e = \left(\frac{k}{4} - \omega^2 M \right) \left(2 - \frac{4}{k} \omega^2 m \right) U_4 - \frac{k}{4} U_4 \quad (69)$$

Finally, the transmissibility equation for four-degree-of-freedom discrete lumped parameter system can be written as follow

$$T_r = \left| \frac{F_t}{F_e} \right| = \left| \frac{\frac{k}{4} U_4}{\left(\frac{k}{4} - \omega^2 M \right) \left(2 - \frac{4}{k} \omega^2 m \right) U_4 - \frac{k}{4} U_4} \right| \quad (70)$$

By observing Eqs. (6), (17), (36) and (70), there is a relationship regarding the pattern of the transmissibility equation for two-degree-of-freedom discrete lumped parameter model and onwards. However, it is very hard to derive the discrete lumped parameter model by dividing the mass of rubber at higher number. The general equation of discrete lumped parameter model for higher-degree-of-freedom can be represented as given in Eq. (71).

$$T_r = \left| \frac{F_t}{F_e} \right| = \left| \frac{\frac{k}{N} U_N}{\left(\frac{k}{N} - \omega^2 M \right) \left(2 - \frac{N}{k} \omega^2 m \right) U_N - \frac{k}{N} U_N} \right| \quad (71)$$

where N is a number of degree-of-freedom of discrete lumped parameter system.

Additionally, the stiffness value for the discrete lumped parameter model is obtained from the stiffness value of the non-dispersive finite rod.

Performance Evaluation

This section presents the baseline results and higher order results for discrete lumped parameter models.

Baseline Models

Fig. 5 shows the result for single-degree-of-freedom discrete lumped parameter model. The natural frequency located at 10 Hz, and the graph went below 10^0 . The roll-off rate for the model was recorded at 20 dB per decade, and it was similar to the roll-off rate that was captured in the conventional lumped parameter system Eqs. (11)–(13). Meanwhile, Fig. 6 shows the results for two-degree-of-freedom discrete lumped parameter model. The first natural frequency remained at 10 Hz. The second natural frequency

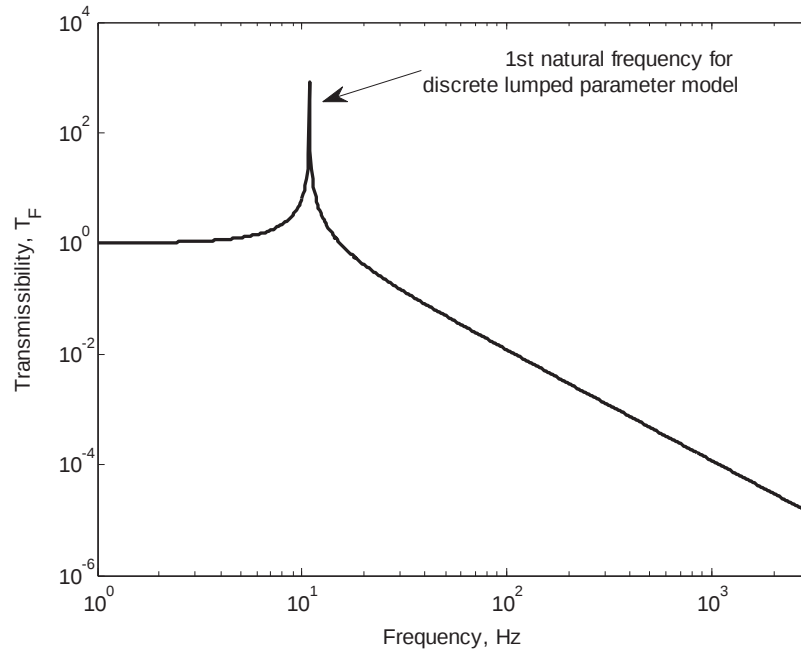


Fig. 5 Transmissibility of one-degree-of-freedom for discrete lumped parameter model.

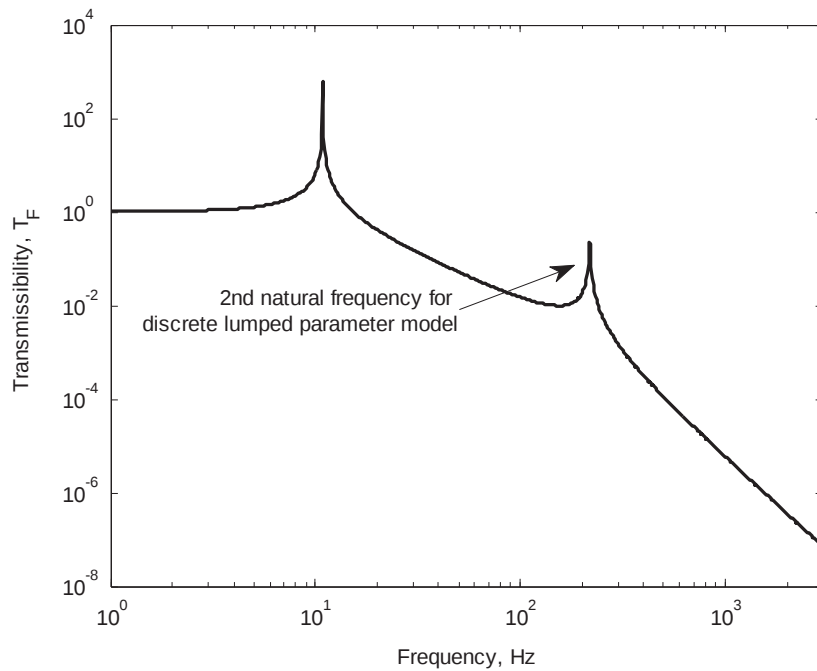


Fig. 6 Transmissibility of two-degree-of-freedom for discrete lumped parameter model.

located approximately at 120 Hz. Figs. 7 and 8 shows the results for three- and four-degree-of-freedom discrete lumped parameter models. The first natural frequency for both models remained at 10 Hz. However, three-degree-of-freedom model showed the second and third natural frequencies at 110 Hz and 125 Hz, respectively. In four-degree-of-freedom model, the second, third and fourth natural frequencies were located at 110 Hz, 120 Hz and 135 Hz. The roll-off rate for both models were same as conventional lumped parameter models Eqs. (11)–(13).

By using this pattern, it is believed that by increasing the number of metal plates embedded in discrete lumped parameter model, the second natural frequency onwards and the internal resonance of the system can be evaluated in higher-degree-of-freedom models.

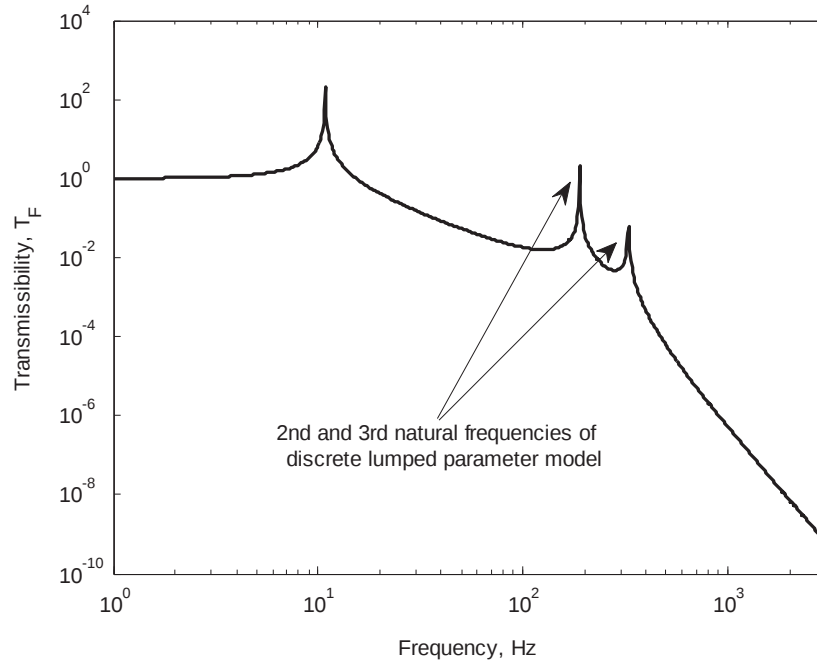


Fig. 7 Transmissibility of three-degree-of-freedom for discrete lumped parameter model.

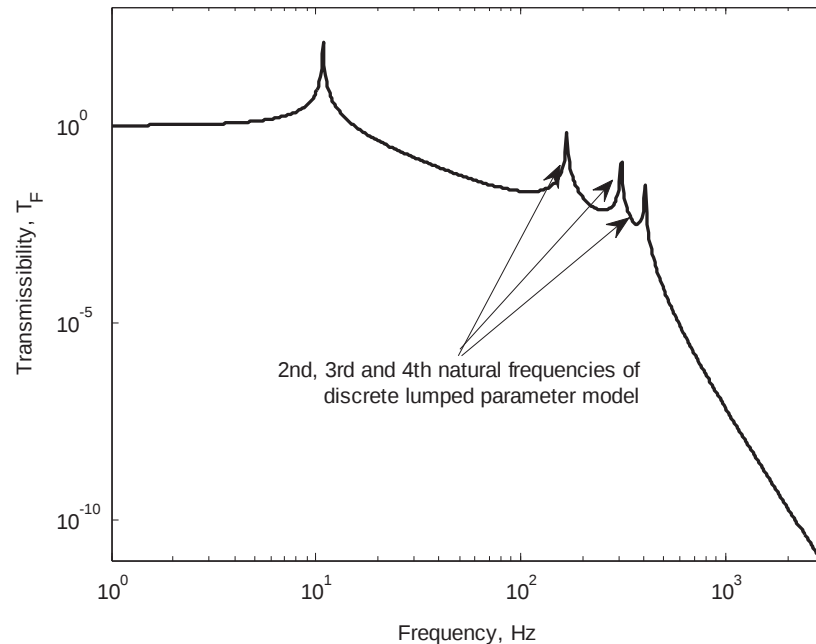


Fig. 8 Transmissibility of four-degree-of-freedom for discrete lumped parameter model.

Higher-Degrees-of-Freedom

The numerical software was used to derive the excitation force of the discrete lumped parameter model when dividing original rubber mass at higher order. Fig. 9 shows the results when dividing the mass of rubber into eight parts. The natural frequency for each graph remained at 10 Hz, and then the graphs went below 10^0 . However, at 900 Hz, the transmissibility increased and was close to unity, where the peaks were obtained at 1380 Hz, and, finally, it refrained below 10^{-2} . Additionally, this only occurred at high frequencies. The roll-off rate was recorded at 20 dB per decade, and it was similar to the roll-off rate that was captured in the conventional lumped

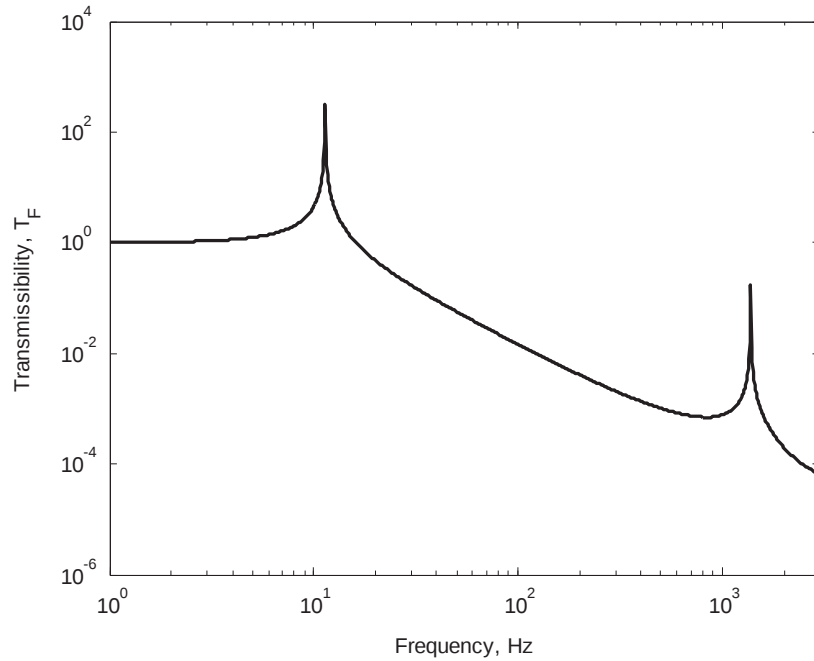


Fig. 9 Result for dividing rubber mass into 8 parts.

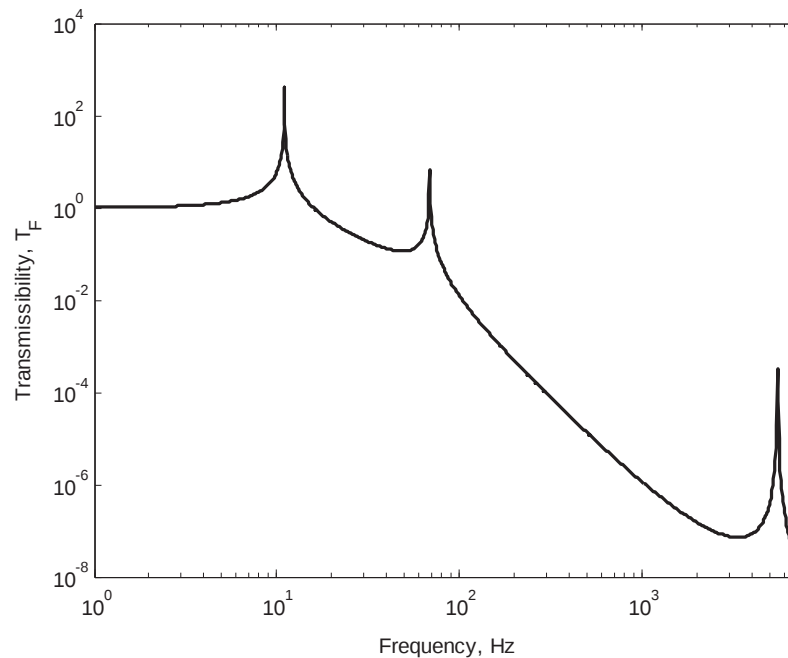


Fig. 10 Result for dividing rubber mass into 12 parts.

parameter system Eqs. (11)–(13). Furthermore, in this model, the second natural frequency can also be recognized as a first peak of the internal resonance, and it will be used as an indicator to investigate the vibration performance in the future.

By dividing the rubber mass of the model into 12 parts, the first and second natural frequencies were positioned at 80 Hz and 6000 Hz, respectively. The internal resonance peaks of the model appeared in high frequency range. Then, rubber mass of the model was also divided into 16 parts, and the fourth natural frequency was located approximately at 10,500 Hz. Next, the rubber mass of the model was divided into more parts which were 20, 32 and 41, and the internal resonance peaks were observed. Therefore, this internal resonance can be used to evaluate and investigate the performance and the characteristics of the discrete lumped parameter models in future. All of the results are shown in Figs. 10–14, respectively.

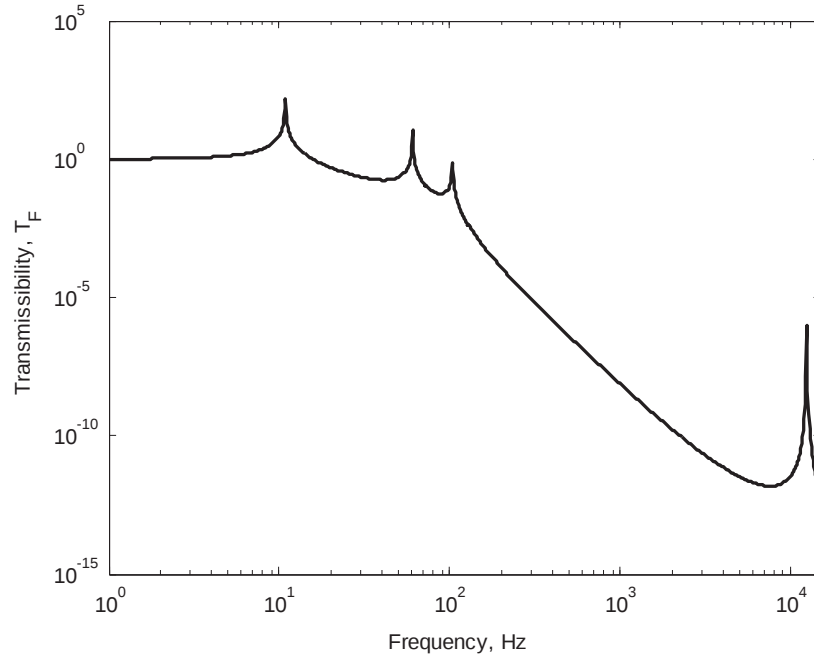


Fig. 11 Result for dividing rubber mass into 16 parts.

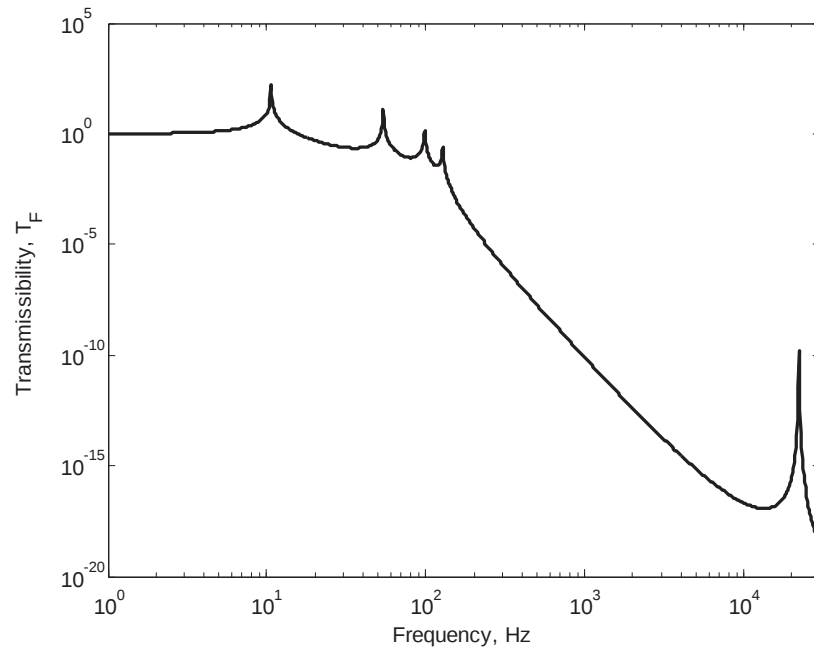


Fig. 12 Result for dividing rubber mass into 20 parts.

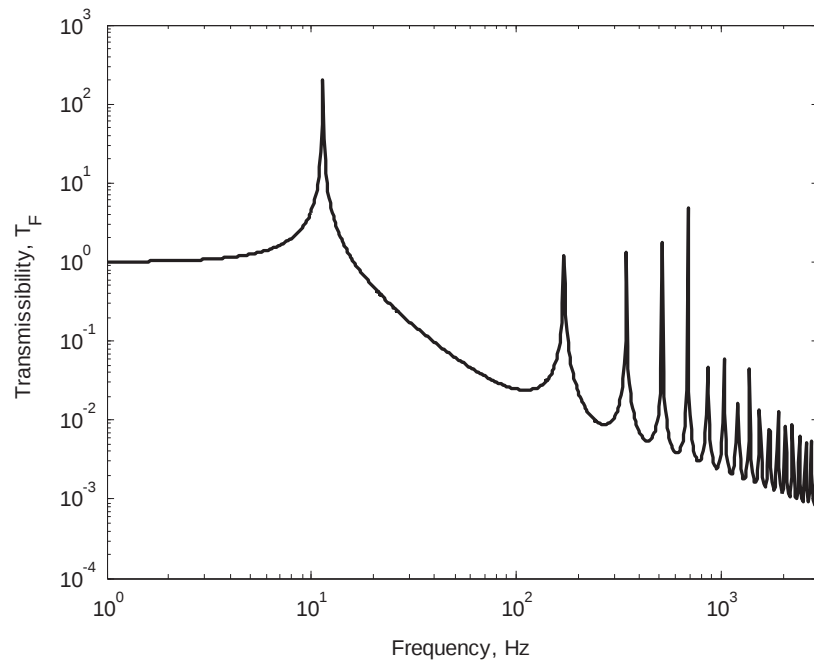


Fig. 13 Result for dividing rubber mass into 32 parts.

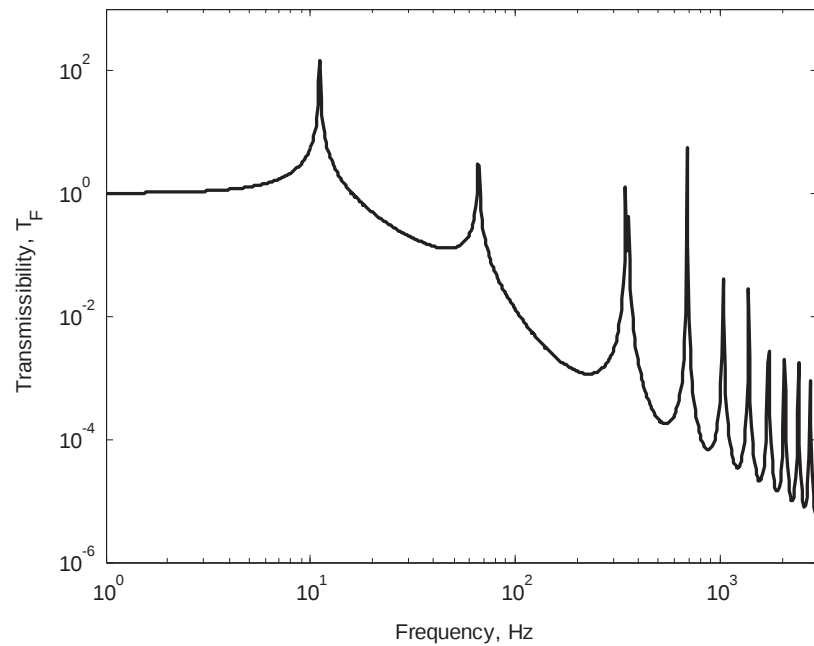


Fig. 14 Result for dividing rubber mass into 41 parts.

Conclusion

In this study, it proves that Natural Rubber (NR) can be used as vibration isolator and the characteristics of specific parameters can be determined. The vibration isolator modeling estimation and performances have been investigated by using discrete lumped parameter model. By dividing the higher number of mass inside the model, the internal resonance behaviour can be evaluated. This behaviour is very critical in determining the overall performance and characteristics of vibration isolator. However, it only appears at high frequency range which is around 400 Hz. There are some assumptions that have been made such as the total mass

of the model is equivalent with the mass of the vibration isolator. The stiffness amount is assumed according to the height of the vibration isolator, and based on the overall stiffness of the isolator. All of these assumptions are very important in order to model the discrete lumped parameter and finally in evaluating the transmissibility results.

See also: Challenges and Developments of Rubber Materials as Vibration Isolator. Rubber Scrap as Reinforced Material in the Production of Environmentally Friendly Brake Lining

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Modeling of Information System for Air Waste Management

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Introduction

The increasing trend in the consumption of various materials has also led to a huge increase in the air waste and the consequent environmental pollutions in particular greenhouse gas emissions. These have made air waste management a significant environmental issue for governments and policy-makers. To address these challenges, developed countries have implemented sustainable material management strategies which have been comprehensively reviewed herein. However, there is need to integrate the strategies in one information system for easy application.

An integrated system for waste reduction, collection, composting, recycling, and disposal is required to tackle the growing challenge of air waste management. Integrated air waste management involves many executive, operational and managerial decisions such as the siting of waste processing and disposal units, selection of waste-treatment technologies and allocation of waste flow to processing facilities and landfills.

Waste management process could be very complex task because of many different suppliers and collectors. Suppliers could be industrial buildings which produce large masses of air waste and collectors should reduce the air wasted. There is need to make optimal route for the most efficient transport of the waste to the collectors. In other word there is need to find the most efficient way to detect and decrease the air wasted. The main problem is suppliers motivation for such a process since they require simple and understandable process for the air waste management. It is suitable to model an software which will make more motivation for suppliers and collectors to make stronger and more uniform connections. The software could determine the optimal routes and treatments for the waste based on locations of suppliers. In this article object orientated approach is used for the software modeling (Lethbridge and Laganier, 2005; Jacobson, 1993).

Object-orientated modeling strategy is an attempt to encapsulate data and process into thing called objects. The data in the objects could be created, deleted or used only by some encapsulated processes or methods. Unified modeling language (UML) is a standard tool for object orientated modeling which could help to developers and engineers to make detailed specification and documentation of any system.

UML (Rumbaugh *et al.*, 2004) is a graphical language which is effective for visualization, specification, construction and documentation of a system's artifact which is software intensive. UML has standard practices for writing a blueprint of system. By using UML one can cover various conceptual things such as functionality by use cases and business processes.

Modeling and analyzing of various activities in any system by UML can help to visualize, specify, constructs and document the system artifact effectively which is helpful for better understanding of the problem and for various stakeholders of the application of the air waste management.

Literature Overview of Air Waste Management

Factors influencing the diurnal atmospheric concentrations and soil-air exchange of polybrominated diphenyl ethers (PBDEs) were investigated at an e-waste recycling site in China during winter and summer (Wang *et al.*, 2017). In study (Giovannis, 2015) was examined the relationship between recycling rate of solid waste and air pollution using data from a waste municipality survey in the state of Massachusetts during the period 2009–2012. The effect of low excess air and high adiabatic combustion temperatures on CO and NO_x formation was investigated on a commercially operated energy-from-waste plant (Strobel *et al.*, 2017). With optimal combination of low O₂ levels and stable combustion control, uncontrolled NO_x levels could be lowered to 100–150 mg/Nm³ (dry, at 11% O₂) while keeping CO emissions at low levels (Strobel *et al.*, 2017). Three pilot-scale lysimeters were operated for 4.5 years to quantify the change in the carbon and nitrogen pool in an old landfill under various air injection conditions and the results indicated that air injection at the bottom layer facilitated homogeneous distribution of oxygen in the waste matrix (Wu *et al.*, 2016). An experiment for five stages of a biofilter-run was performed to investigate the effect of hydrophilic ethanol and hydrophobic toluene on the biodegradation of hydrophobic toluene and hydrophilic ethanol, respectively, when waste-air containing toluene and ethanol was treated by a biofilter (Lim, 2005). In paper (Lin *et al.*, 1994), the feasibility of application of a solid-absorption system using ammonia and chlorides as working pair to automobile air-conditioning system was investigated. This system has the advantages of minimum environmental problem and utilizing waste heat from the automobile engine as thermal energy input (Lin *et al.*, 1994). Hydrogen sulphide, ammonia, nitrogen dioxide, mercaptans and sulphur dioxide (H₂S, NH₃, NO₂, R-SH, SO₂) concentrations were measured at the location in the vicinity of the waste dump to determine the air pollution level of these pollutants prior to the operation of the Mobile Thermal Treatment Plant (Vadić *et al.*, 2000). The accumulation capacity for hydrophobic compounds of absorption agents employed in biological waste air purification was substantially affected by the varnish particles contained in the scrubbing liquid (Feige *et al.*, 1991).

Materials and Methods

Air Waste Management

According to the European Union standardization there are six procedures in the air waste treatment process:

1. Eco-design,
2. Air waste decreasing,
3. Air waste reusing,
4. Recycling and making compost,
5. Energy from air waste,
6. Air waste disposing.

The main activity of the investigation is to develop two separate softwares in order to make sustainable air waste management. In order to optimize the system for air waste management based on decreasing of pollution of life environment and for the cheapest solution there is goal to develop and model the software for the air waste management process. This innovative solution could lead to revolution in the air waste issue. By entering of the main data for air waste, quantity and composition for the some region, the client could know which is the best solution for the air waste treatment and transport for the region. Several air waste treatments are included in the software:

- Recycling,
- Combusting,
- Making compost,
- Performing anaerobic digestion and
- Disposing of air waste.

There are several indicators which are calculated in the software according the input data. These indicators are:

- Global warming,
- Heavy metals emission,
- Nitrogen oxide emission,
- Smog formation,
- Water pollution.

Therefore these software has seven modules. These modules:

- Calculation of emissions from collection and transport of air waste,
- Calculation of emissions from anaerobic digestion,
- Calculation of emissions from combustion,
- Calculation of emissions from recycled waste,
- Calculation of emissions from disposal,
- Calculation of emissions from compost,
- Calculation of cost benefit.

There is also plan to integrate the module for determination of the optimal route of the air waste transport. The optimization of the route is very important since there is constantly changing of the urban parameters: number of residents, waste quantity, type of transport vehicle, transport conditions. Clark and Wright savings algorithm could be applied for the route optimization for the air waste.

This software approach for the air waste management could be very helpful for managers who control waste, companies which produce and transport the waste and for decision makers to select the optimal scenery for the waste treatment and transport for each region. The main goals of the investigation are:

- Removing of the barriers for the decreasing of pollution of life environment by unsuitable treatment of the air waste.
- Increasing of ecological awareness for the importance of regular treatment of waste.
- Solving of problem of air waste collection and transport.

Specific goal of the investigation is:

- Modeling of innovative software as a tool for determination of a right strategy for air waste management.

Software Development for Air Waste Management

Generally, the software development methodology is consisted of procedures, technics, tools and documentation which helps in the software development process. Software development methodology describes all steps and phases of the software development. The methodology suggest tools and technics which should use in the particular step of the software development. Also the methodology could suggest how to plan and track process of the software development and testing as well.

Many companies use the methodologies for software development in order to ensure the consistency of the problem solution, to decrease the possible errors, to acquire the full documentation for current and future projects and to get good final product which could be changeable and adaptable easily since the all steps and phases would be documented in detail and any new changes in the software models could be achieved before software coding.

Models could be describes as simplified presentation of reality. The models could be presented with some standard modeling language. The model presentation could be textual or graphical by diagrams. Each software could be described based on different aspects by structural models in order to show software structure with the main parts and their interconnections and relationships. Also there is behaviour models where one can track the software dynamics.

RUP methodology

Rational Unified Process (RUP) is an iterative methdology for the software development based on architcture and use cases. RUP methdology is based on Unified Modeling Language (UML). UML is used for specification, visualization, construction and documentation of the software development.

RUP methodology has control, key or critical points throught the development. In the other words each phase of the RUP methdology should end by some control, key or critical points where achieved results are summed and future directions are planned based on the results. RUP methodology has artefacts (documents), models i model elements. Project requests are noted in the documents. Models are used to simplify the software architecture without unnecessary details. Model elements could help to visualize, construct and document the main structure and software behaviour.

RUP methodology has four main phases. The first phase is initial phase or idea inception where one needs to understand what should to do and software vision and requirements are identified. This phase includes the identification of key software actors (users) and use cases. Also there is need to identify software domain. Use case defines one sequence of an action which software performs that yields to an observable results. In the other hands one use cass presents result of an action by actor (Fig. 1). Use case presents the main part of some complete software operation from beginning until to the end. It is used to capture the intended behaviour of the system in development. By use cases models desired behaviour of the system could be specified but it is not strictly this desired behaviour to be carried out or implemented in the final product. Use cases models can be developed for whole system or for the part of system. Each part of system or subsystem can be developed by use cases models until the part produces some tangible amount of work and results. System complexity indicates the number of use cases. In the initial stage of system development main use cases are developed and additional use cases can be added or included when there is need for them.

The second phase is project elaboration where one needs to understand how to build the software and basic software architcture is showed in the phase. The third phase presents software construction where software testing is considered. The fourth phase presents software transition where software validation is performed.

RUP models describes software in modeling. RUP models could be business models which describes business processess and business environment, use case models which describes what software doing and software environment, projecting models which describes use cases realization as code abstraction and implementation models which presents collection of components and subsystems.

Software development process could has different problems which needs to be identifies and solved before coding and testing. In order to solve problems there is need to find the problem causes. To remove the problem causes it is suitable to use best practices. For example in order to remove the confusion in communication between team members it is suitable to use standard language UML for the software visualization, specification and documentation. There are different types of UML diagrams which can be used in the software development process. There are two main classes of the ULM diagrams. These are structural and behavioral diagrams. Structural diagram presents structure of the system in passive state and behavioral diagram present the active behaviour of the objects in a system or dynamical state.

Object-orientated modeling of business process

UML is used for object-orientated modeling of business process. As already mentioned there are different UML diagrams for describing of software architecture and software behaviour. UML as standard language is used for modeling, for analyzing, for projecting and for implementation of the software system. Based on the object-orientated modeling all process could be presented by use cases models as rough specification and by structural diagrams and behavioral diagrams as detail specification.

During modeling of the business process it is not recommended to use natural language because of its ambiguity. Also formal programming languages is not understandable for many people in the project team. Therefore it is suitable to organize the natural language to avoid ambiguity. Modeling process is one of the solution for understanding and clear communication between project team members.



Fig. 1 Use case model.

Modeling of the Air Waste Management

Problem Description

The problem is intended for solving of treatment and transport of air waste. The main objects of the model are clients, administrator and module. The clients represent the all possible suppliers of the air waste. Administrator should maintain the software through the process and modules should determine the optimal treatment and transport route of the air waste.

The main goals of the investigation is to decrease the emissions of the greenhouse gasses and generally to decrease global warming and pollution. Also biofuels need to be introduced in the transport as much as it can. The main activity of the investigation should be to develop the GPS system for mapping of the air waste suppliers in order to optimize the transport route.

Object-orientated modeling concepts are used during analyzing and modeling of the air waste management process. Two UML concepts are used for the software modeling like use case models, activity diagrams and scenarios of activities.

Software for Route Optimization for Waste Cooking Oil Transport

Software for route optimization for waste cooking oil transport should be use for organization of the waste cooking oil suppliers and collectors as well. The main advantage of the software for route optimization for waste cooking oil transport in the article is in its universality and in its online usage.

The main feature of the software for route optimization for waste cooking oil transport should be universal application for any subjects and any suppliers and collectors. The software for route optimization for waste cooking oil transport will be framework of the suppliers and collectors of the transport activity.

As users are considered suppliers in different parts of industry and collectors as well. All of the users should have username and password in order to access the waste cooking oil management database.

Collectors should made reports for different statistical analysis of the waste cooking oil. As the main problem of the current software for route optimization for waste cooking oil transport it was identified limitation of unified approach for all subjects. Therefore it is required to develop information system which would allow to users to use the software anytime in order to enter desired data.

Software users

The software users could be divided based on natural basis according to working place, suppliers and collectors. All of the users have equal rights to access and use of the software. Therefore the main users of the software are:

- Client,
- Module,
- Administrator.

Each of the users should have individual username and password in order to access to the software. Administrator of information system who needs to maintain the software and he is responsible for working of computer system and software as well. He gives permission to the staff's access to the waste cooking oil management database, maintains database, maintains web presentation of the waste cooking oil management and makes regular daily reports.

Software Analyzing

Each of the client should have individual username and password to access to the software. Administrator of software should maintain the software and he is responsible for working of computer system and software as well. He gives permission to the access to the database, maintains database, maintains web presentation of the software and makes regular daily reports.

Main use cases diagram of the software

Air waste treatment are depicted by the main use case diagram as it shown in Fig. 2. The main use case diagram has several sub use cases which will be explained in detail. As can be seen, the administrator should perform the main administration process of the air waste treatment in order to ensure smooth working processes by the software. Clients or suppliers record the quantity and composition of the air waste if they are logged in the software database. Based on the records the modules should determine the type of the air waster treatment.

Air waste transport are depicted by the main use case diagram as it shown in Fig. 3. Clients or suppliers record the coordinated of the air waste if they are logged in the software database. Based on the records the modules should determine the optimal route of air waste transport.

Use cases of the software subsystems

Software administration

Administrator performs software administration in order to eliminate all unpredictable errors in the software and system. Administrator has full responsibility for the software maintenance. They will give permissions for other users access to the system, maintains the software, maintains the web pages of the software, maintains the software database, and makes regular daily reports.

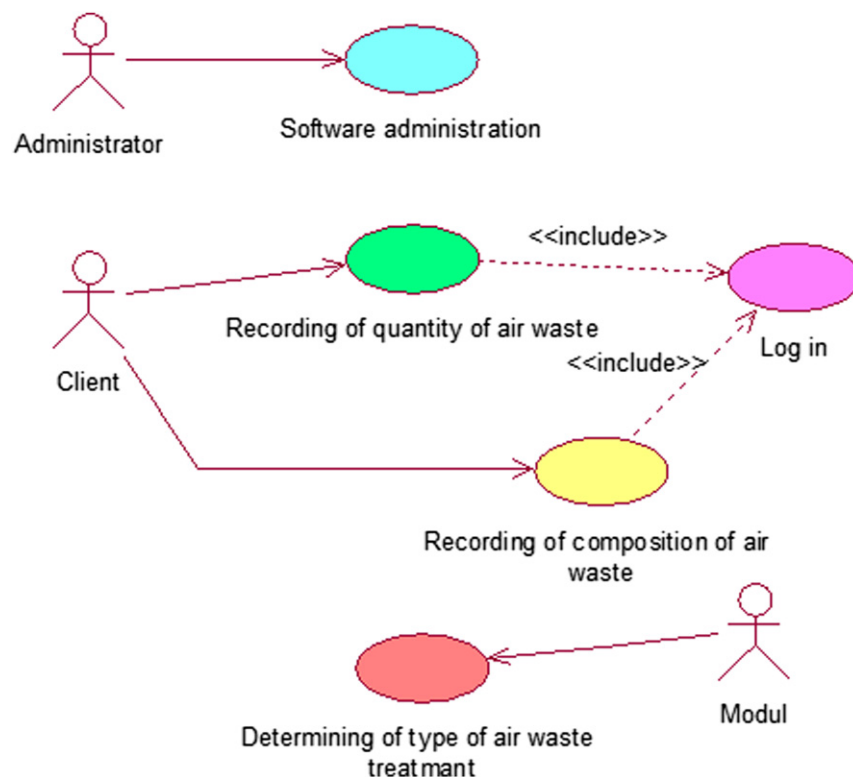


Fig. 2 Main use case diagram of the software for determining of air waste type treatment.

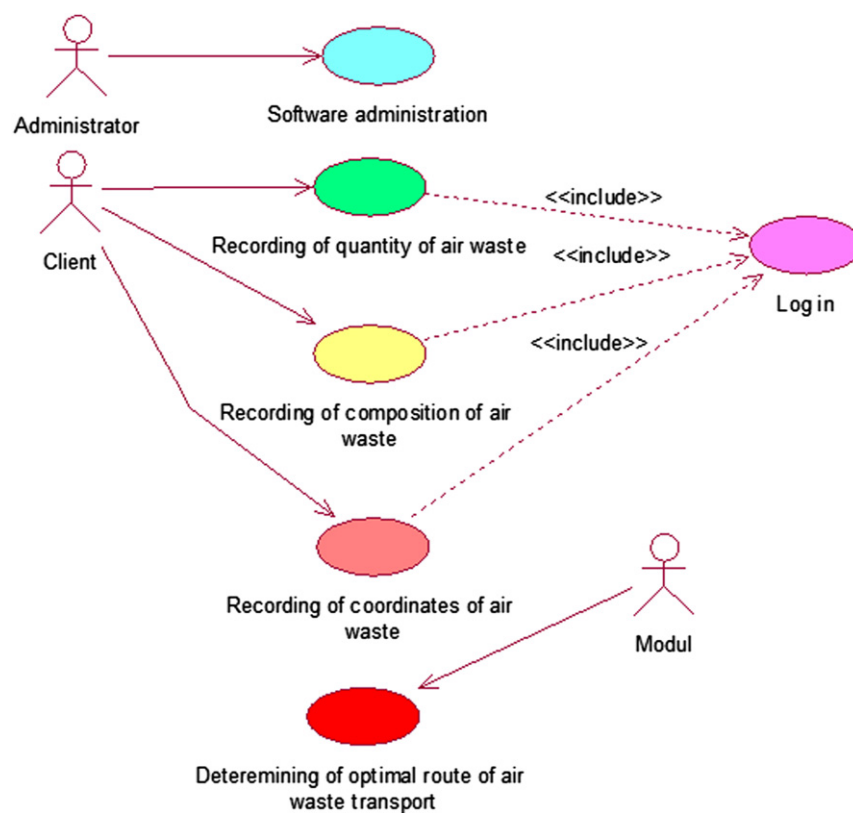


Fig. 3 Main use case diagram of the software for determining of optimal route of air waste transport.

Table 1 shows detailed specification of use case for giving permission for database access of the software by administrator.

Table 2 shows detailed specification of the use case of software maintaining by administrator.

Table 3 shows detailed specification of use case for web pages maintaining of software by administrator.

Table 4 shows detailed specification of use case for database maintaining of software by administrator.

Table 5 shows detailed specification of use case for making of regular reports by administrator.

Table 1 Specification of use case: Giving permission for database access

<i>Title</i>	<i>Giving permission for database access</i>
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the giving permission for database access.
Pre-condition	PC is properly settled. Administrator has needed knowledge for the tasks.
Post-condition	Client received authorization for database access of software
Main scenario	1. Administrator receives the request for the giving permission for database access of software. 2. Administrator checks the request validity. 3. Administrator fills the application form for the giving permission for database access of software. 4. Administrator selects client category based on the quantity of the waste cooking oil. 5. Administrator approves the request. 6. Administrator prints the instruction for the application use. 7. Administrator distributes the instruction to the client as the proof for the successful addition to the users of the waste cooking oil management software for the database access.
Alternative	1. In the case if the request is incorrect filled based on the step 2 of the main scenario the administrator returns the request to the client with the instruction how to correct the errors in the request.

Table 2 Specification of use case: Software maintaining

<i>Title</i>	<i>Software maintaining</i>
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the software maintaining.
Pre-condition	PC is properly settled. Administrator has needed knowledge for the tasks.
Post-condition	Backup of the waste cooking oil management software was made.
Main scenario	1. Administrator checks if there is some large operation on the software. 2. If there is some operation on the software, the administrator waits until the operation ends. 3. If there is not operation on the software, the administrator prepares tools for the software maintaining. 4. Administrator checks if the all functions of the software are proper. 5. If some of the function of the software is not proper than the administrator starts the tool for correction of the function. 6. Administrator starts the backup process of the software. 7. Administrator records the time of the software backup.
Alternative	None

Table 3 Specification of use case: Software web pages maintaining

<i>Title</i>	<i>Software web pages maintaining</i>
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the web pages maintaining of software.
Pre-condition	PC is properly settled. Administrator has needed knowledge for the tasks.
Post-condition	Backup of the web pages of software was made.
Main scenario	1. Administrator checks if there is some large operation on the web pages of software. 2. If there is some operation on the web pages of software, the administrator waits until the operation ends. 3. If there is not operation on the web pages of software, the administrator prepares tools for the web pages of waste cooking oil management software maintaining. 4. Administrator checks if the all functions of the web pages of software are proper. 5. If some of the function of the web pages of education software is not proper than the administrator starts the tool for correction of the function. 6. Administrator starts the backup process of the web pages of software. 7. Administrator records the time of the web pages of software backup.
Alternative	None

Recording of quantity of air waste

Use case recording of quantity of air waste is depicted in Fig. 4. The use case diagram has several sub use cases. Table 6 shows detailed specification for use case recording of quantity of air waste.

Table 4 Specification of use case: Software database maintaining

Title	Software database maintaining
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the database maintaining of software.
Pre-condition	PC is properly settled. Administrator has needed knowledge for the tasks.
Post-condition	Backup of the database of software was made.
Main scenario	1. Administrator checks if there is some large operation on the database of software. 2. If there is some operation on the database of software, the administrator waits until the operation ends. 3. If there is not operation on the database of software, the administrator prepares tools for the database of software maintaining. 4. Administrator checks if the all functions of the database of software are proper. 5. If some of the function of the database of software is not proper than the administrator starts the tool for correction of the function. 6. Administrator starts the backup process of the database of software. 7. Administrator records the time of the database of software backup.
Alternative	None

Table 5 Specification of use case: Making of regular reports

Title	Making of regular reports
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the making of regular reports.
Pre-condition	PC is properly settled. Administrator has needed knowledge for the tasks.
Post-condition	The reposts were printed.
Main scenario	1. Administrator checks if there is some large operation. 2. If there is some operation, the administrator waits until the operation ends. 3. If there is not operation, the administrator prepares tools for the making of regular reports. 4. Administrator selects between standard procedure of the making of regular reports and nonstandard procedure where administrator can adjust the parameters of the reports. If nonstandard procedure was chosen than the administrator adjusts the parameters of the reports. 5. Administrator starts the procedure of the making of regular reports. 6. Administrator saves the backup of the reports. 7. Administrator records the time of the database of making of regular reports.
Alternative	None

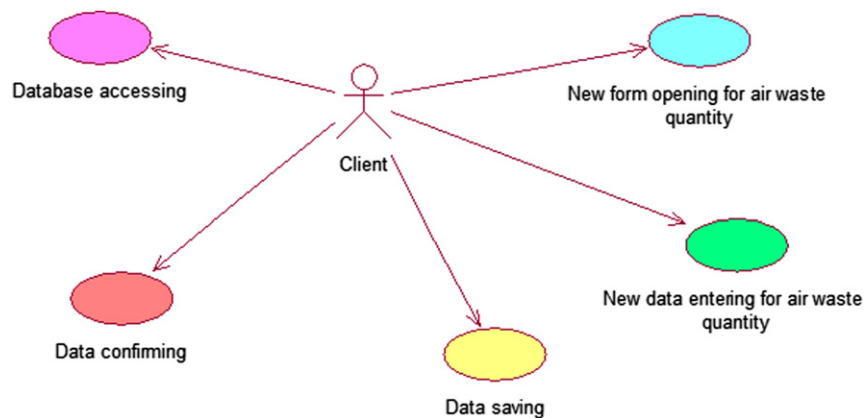
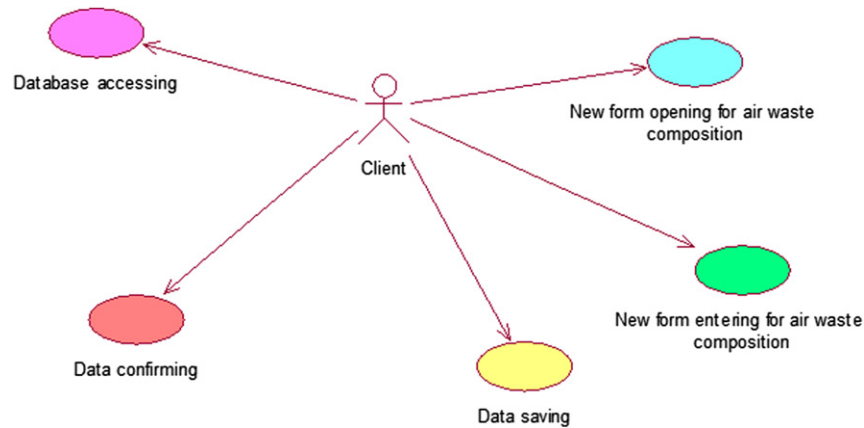
**Fig. 4** Use case diagram – Recording of quantity of air waste.

Table 6 Specification of use case: Recording of quantity of air waste

Title	Recording of quantity of air waste
Actors	Client
Trigger	It starts with the choosing of the option on user interface for the recording of quantity of air waste.
Pre-condition	PC is properly settled. Air waste acquired.
Post-condition	Recorded quantity of air waste.
Main scenario	1. Client starts air waste management software. 2. Client does login into air waste management software. 3. Client records the quantity of air waste. 4. Client confirms the quantity.
Alternative	1. The recording of quantity of air waste is canceled. 2. Due to technical problems the service cannot be made.

**Fig. 5** Use case diagram – Recording of composition of air waste.**Table 7** Specification of use case: Recording of composition of air waste

Title	Recording of composition of air waste
Actors	Client
Trigger	It starts with the choosing of the option on user interface for the recording of composition of air waste.
Pre-condition	PC is properly settled. Air waste acquired.
Post-condition	Recorded composition of air waste.
Main scenario	1. Client starts air waste management software. 2. Client does login into air waste management software. 3. Client records the composition of air waste. 4. Client confirms the composition.
Alternative	1. The recording of composition of air waste is canceled. 2. Due to technical problems the service cannot be made.

Recording of composition of air waste

Use case recording of composition of air waste is depicted in Fig. 5. The use case diagram has several sub use cases. Table 6 shows detailed specification for use case recording of composition of air waste (Table 7).

Conclusion

Air waste management presents a big issue for all countries. One of the most common air waste treatment method is disposal. Illegal air waste disposal and unofficial air waste recycling could produce high pollution of water, air and soil. There is need for systematic sustainable air waste management system in order to preserve natural resources and to keep clean the life environment.

The main innovation of the investigation is analyzing and modeling of new software for air waste treatment. The main suppliers could enter quantity and composition of air waste in the software. Based on the quantity and composition the clients could decide which treatment and transport route is the best for the air waste they collected.

See also: Modeling of Information System for Liquid Waste Management. Modeling of Information System for Nuclear Waste Management. Unified Modeling Language for Cooking Oil Management

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Modeling of Information System for Liquid Waste Management

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Introduction

The increasing trend in the consumption of various materials has also led to a huge increase in the liquid waste and the consequent environmental pollutions in particular greenhouse gas emissions. These have made liquid waste management a significant environmental issue for governments and policy-makers. To address these challenges, developed countries have implemented sustainable material management strategies which have been comprehensively reviewed herein. However, there is need to integrate the strategies in one information system for easy application.

An integrated system for waste reduction, collection, composting, recycling, and disposal is required to tackle the growing challenge of liquid waste management. Integrated liquid waste management involves many executive, operational and managerial decisions such as the siting of waste processing and disposal units, selection of waste-treatment technologies and allocation of waste flow to processing facilities and landfills.

Waste management process could be very complex task because of many different suppliers and collectors. There is need to make optimal route for the most efficient transport of the waste to the collectors. The main problem is suppliers motivation for such a process since they require simple and understandable process for the waste cooking oil management. Because of that it is suitable for the waste transport to model an software which will make more motivation for suppliers and collectors to make stronger and more uniform connections. The software could determine the optimal routes and treatments for the waste based on locations of suppliers. In this article object orientated approach is used for the software modeling (Lethbridge and Laganieri, 2005; Jacobson, 1993).

Object-orientated modeling strategy is an attempt to encapsulate data and process into thing called objects. The data in the objects could be created, deleted or used only by some encapsulated processes or methods. Unified modeling language (ULM) is a standard tool for object orientated modeling which could help to developers and engineers to make detailed specification and documentation of any system.

ULM (Rumbaugh *et al.*, 2004) is a graphical language which is effective for visualization, specification, construction and documentation of a system's artifact which is software intensive. ULM has standard practices for writing a blueprint of system. By using ULM one can cover various conceptual things such as functionality by use cases and business processes.

Modeling and analyzing of various activities in any system by ULM can help to visualize, specify, constructs and document the system artifact effectively which is helpful for better understanding of the problem and for various stakeholders of the application of the liquid waste management.

Literature Overview of Liquid Waste Management

In the article (Robertson *et al.*, 1987) was presented methods of disposal of today's hazardous household chemicals in the United States are frequently not acceptable because of pathways to groundwater, surface water, and the atmosphere and it was identified potentially hazardous liquid waste in the household, notes current disposal practices, and recommends an improved management plan that utilizes consumer education, manufacturer cooperation, and governmental intervention. Managing hazardous household wastes could mitigate potential disposal problems (Robertson *et al.*, 1987). In paper Pires and Martinho (2013) was compared 16 waste lubricant oil (WLO) systems (15 management alternatives and a system in use in Portugal) using a life cycle assessment (LCA). The results shown that mild processing with low liquid gas fuel consumption and re-refining is the best option to manage WLO with regard to abiotic depletion, eutrophication, global warming, and human toxicity environmental impacts (Pires and Martinho, 2013). In study Glazer *et al.* (2017) was compiled and curated data from 2012, 2013, and 2014 on flared gas and generated wastewater associated with hydraulic fracturing operations in seven major shale regions of the USA. In the process, an historical perspective was provided of the management practices of flared gas and wastewater prior to the decline in oil prices in 2015. The seven shale regions were evaluated using mass balances and thermodynamic analysis of the wastewater and flared gas volumes using data compiled from state, federal, and private sources for each region. The findings indicate that novel approaches to managing existing resources and waste streams might have the potential to improve the environmental footprint and economic productivity of select oil and gas sites (Glazer *et al.*, 2017). Marinas are usually located in coastal waters, but can also be found in lakes and rivers. Due to the activities that take place in marinas various contaminants are discharged. Specific measures have to be taken in order to keep the marina environment clean and healthy. Experiences from developed countries have shown that the most effective way to reduce pollution in marinas is the implementation of waste management programs (Dolgen *et al.*, 2003). In article (Dolgen *et al.*, 2003) the importance of management programs towards the mitigation of pollution problems was emphasized. The radiation contamination after the Fukushima Daiichi Nuclear Power Plant accident attracts considerable concern all over the world. Many countries, areas, and oceans are greatly affected by the emergency situation other than Japan. An effective remediation strategy is in a highly urgent demand (Ding *et al.*, 2016). The policy of establishing new universities across Taiwan has led to an

increase in the number of universities, and many schools have constructed new laboratories to meet students' academic needs. In recent years, there is an increase in the number of laboratory accidents from the liquid waste in universities (Ho and Chen, 2018). Therefore, how to build a safety system for laboratory liquid waste disposal has become an important issue in the environmental protection, safety, and hygiene of all universities. In study Ikhlayel (2017) was aimed to evaluate the environmental impacts and benefits of state-of-the-art technologies for proper e-waste handling using Jordan as a case study. Life Cycle Assessment (LCA) was employed to evaluate five advanced management systems represent state-of-the-art treatment technologies, including sanitary landfilling; proper recycling of metals, materials, and precious metals (PMs); and incineration of plastic and the hazardous portion of printed circuit boards (PCBs). The Liquid Waste Management System (LWMS) is a radioactive waste storage and treatment facility equipped in the nuclear power plants to ensure the safe management of radioactive waste generated in the process of operation (Kim and Kim, 2017). An optimization-based supply chain management framework for municipal liquid waste (MSW) to liquid transportation fuels (WTL) processes was presented in article (Niziolek *et al.*, 2017).

Materials and Methods

Liquid Waste Management

According to the European Union standardization there are six procedures in the liquid waste treatment process:

1. Eco-design,
2. Liquid waste decreasing,
3. Liquid waste reusing,
4. Recycling and making compost,
5. Energy from liquid waste,
6. Liquid waste disposing.

The main activity of the investigation is to develop two separate softwares in order to make sustainable liquid waste management. In order to optimize the system for liquid waste management based on decreasing of pollution of life environment and for the cheapest solution there is goal to develop and model the software for the liquid waste management process. This innovative solution could lead to revolution in the liquid waste issue. By entering of the main data for liquid waste, quantity and composition for the some region, the client could know which is the best solution for the liquid waste treatment and transport for the region. Several liquid waste treatments are included in the software:

- Recycling,
- Combusting,
- Making compost,
- Performing anaerobic digestion and
- Disposing of liquid waste.

There are several indicators which are calculated in the software according the input data. These indicators are:

- Global warming,
- Heavy metals emission,
- Nitrogen oxide emission,
- Smog formation,
- Water pollution.

Therefore these software has seven modules. These modules:

- Calculation of emissions from collection and transport of liquid waste,
- Calculation of emissions from anaerobic digestion,
- Calculation of emissions from combustion,
- Calculation of emissions from recycled waste,
- Calculation of emissions from disposal,
- Calculation of emissions from compost,
- Calculation of cost benefit.

There is also plan to integrate the module for determination of the optimal route of the liquid waste transport. The optimization of the route is very important since there is constantly changing of the urban parameters: Number of residents, waste quantity, type of transport vehicle, transport conditions. Clark and Wright savings algorithm could be applied for the route optimization for the liquid waste.

This software approach for the liquid waste management could be very helpful for managers who control waste, companies which produce and transport the waste and for decision makers to select the optimal scenery for the waste treatment and transport for each region. The main goals of the investigation are:

- Removing of the barriers for the decreasing of pollution of life environment by unsuitable treatment of the liquid waste.
- Increasing of ecological awareness for the importance of regular treatment of waste,
- Solving of problem of liquid waste collection and transport.

Specific goal of the investigation is:

- Modeling of innovative software as a tool for determination of a right strategy for liquid waste management.

Software Development for Liquid Waste Management

Generally, the software development methodology is consisted of procedures, technics, tools and documentation which helps in the software development process. Software development methodology describes all steps and phases of the software development. The methodology suggest tools and technics which should use in the particular step of the software development. Also the methodology could suggest how to plan and track process of the software development and testing as well.

Many companies use the methodologies for software development in order to ensure the consistency of the problem solution, to decrease the possible errors, to acquire the full documentation for current and future projects and to get good final product which could be changeable and adaptable easily since the all steps and phases would be documented in detail and any new changes in the software models could be achieved before software coding.

Models could be describes as simplified presentation of reality. The models could be presented with some standard modeling language. The model presentation could be textual or graphical by diagrams. Each software could be described based on different aspects by structural models in order to show software structure with the main parts and their interconnections and relationships. Also there is behaviour models where one can track the software dynamics.

RUP methodology

Rational Unified Process (RUP) is an interactive methodology for the software development based on architecture and use cases. RUP methodology is based on Unified Modeling Language (UML). UML is used for specification, visualization, construction and documentation of the software development.

RUP methodology has control, key or critical points through the development. In the other words each phase of the RUP methodology should end by some control, key or critical points where achieved results are summed and future directions are planned based on the results. RUP methodology has artifacts (documents), models and model elements. Project requests are noted in the documents. Models are used to simplify the software architecture without unnecessary details. Model elements could help to visualize, construct and document the main structure and software behaviour.

RUP methodology has four main phases. The first phase is initial phase or idea inception where one needs to understand what should to do and software vision and requirements are identified. This phase includes the identification of key software actors (users) and use cases. Also there is need to identify software domain. Use case defines one sequence of an action which software performs that yields to an observable results. In the other hands one use case presents result of an action by actor (Fig. 1). Use case presents the main part of some complete software operation from beginning until to the end. It is used to capture the intended behaviour of the system in development. By use cases models desired behaviour of the system could be specified but it is not strictly this desired behaviour to be carried out or implemented in the final product. Use cases models can be developed for whole system or for the part of system. Each part of system or subsystem can be developed by use cases models until the part produces some tangible amount of work and results. System complexity indicates the number of use cases. In the initial stage of system development main use cases are developed and additional use cases can be added or included when there is need for them.

The second phase is project elaboration where one needs to understand how to build the software and basic software architecture is showed in the phase. The third phase presents software construction where software testing is considered. The fourth phase presents software transition where software validation is performed.

RUP models describes software in modeling. RUP models could be business models which describes business processes and business environment, use case models which describes what software doing and software environment, projecting models which describes use cases realization as code abstraction and implementation models which presents collection of components and subsystems.

Software development process could has different problems which needs to be identifies and solved before coding and testing. In order to solve problems there is need to find the problem causes. To remove the problem causes it is suitable to use best



Fig. 1 Use case model.

practices. For example in order to remove the confusion in communication between team members it is suitable to use standard language UML for the software visualization, specification and documentation. There are different types of UML diagrams which can be used in the software development process. There are two main classes of the UML diagrams. These are structural and behavioral diagrams. Structural diagram presents structure of the system in passive state and behavioral diagram present the active behaviour of the objects in a system or dynamical state.

Object-orientated modeling of business process

UML is used for object-orientated modeling of business process. As already mentioned there are different UML diagrams for describing of software architecture and software behaviour. UML as standard language is used for modeling, for analyzing, for projecting and for implementation of the software system. Based on the object-orientated modeling all process could be presented by use cases models as rough specification and by structural diagrams and behavioral diagrams as detail specification.

During modeling of the business process it is not recommended to use natural language because of its ambiguity. Also formal programming languages is not understandable for many people in the project team. Therefore it is suitable to organize the natural language to avoid ambiguity. Modeling process is one of the solution for understanding and clear communication between project team members.

Modeling of the Liquid Waste Management

Problem Description

The problem is intended for solving of treatment and transport of liquid waste. The main objects of the model are clients, administrator and modula. The clients represent the all possible suppliers of the liquid waste. Administrator should maintain the software through the process and modules should determine the optimal treatment and transport route of the liquid waste.

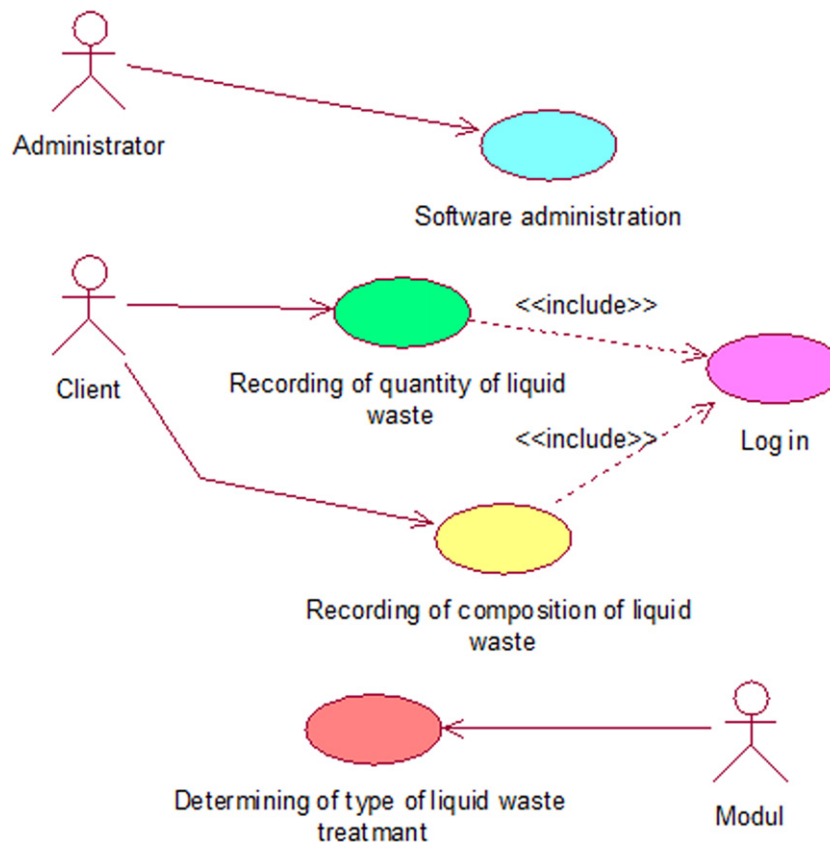


Fig. 2 Main use case diagram of the software for determining of liquid waste type treatment.

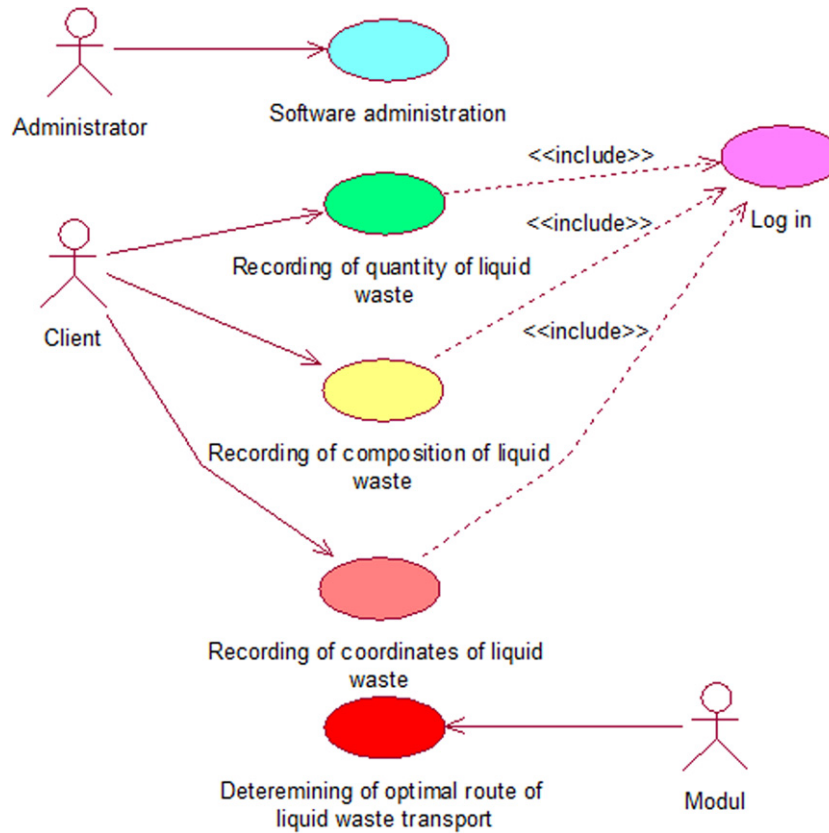


Fig. 3 Main use case diagram of the software for determining of optimal route of liquid waste transport.

Table 1 Specification of use case: Giving permission for database access

Title	Giving permission for database access
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the giving permission for database access
Pre-condition	PC is properly settled Administrator has needed knowledge for the tasks
Post-condition	Client received authorization for database access of software
Main scenario	1. Administrator receives the request for the giving permission for database access of software 2. Administrator checks the request validity 3. Administrator fills the application form for the giving permission for database access of software 4. Administrator selects client category based on the quantity of the waste cooking oil 5. Administrator approves the request 6. Administrator prints the instruction for the application use 7. Administrator distributes the instruction to the client as the proof for the successful addition to the users of the waste cooking oil management software for the database access
Alternative	1. In the case if the request is incorrect filled based on the step 2. of the main scenario the administrator returns the request to the client with the instruction how to correct the errors in the request

The main goals of the investigation is to decrease the emissions of the greenhouse gasses and generally to decrease global warming and pollution. Also biofuels need to be introduced in the transport as much as it can. The main activity of the investigation should be to develop the GPS system for mapping of the liquid waste suppliers in order to optimize the transport route.

Object-oriented modeling concepts are used during analyzing and modeling of the liquid waste management process. Two UML concepts are used for the software modeling like use case models, activity diagrams and scenarios of activities.

Software for Route Optimization for Waste Cooking Oil Transport

Software for route optimization for waste cooking oil transport should be use for organization of the waste cooking oil suppliers and collectors as well. The main advantage of the software for route optimization for waste cooking oil transport in the article is in its universality and in its online usage.

The main feature of the software for route optimization for waste cooking oil transport should be universal application for any subjects and any suppliers and collectors. The software for route optimization for waste cooking oil transport will be framework of the suppliers and collectors of the transport activity.

As users are considered suppliers in different parts of industry and collectors as well. All of the users should have username and password in order to access the waste cooking oil management database.

Collectors should made reports for different statistical analysis of the waste cooking oil. As the main problem of the current software for route optimization for waste cooking oil transport it was identified limitation of unified approach for all subjects. Therefore it is required to develop information system which would allow to users to use the software anytime in order to enter desired data.

Software users

The software users could be divided based on natural basis according to working place, suppliers and collectors. All of the users have equal rights to access and use of the software. Therefore the main users of the software are:

- Client,
- Module,
- Administrator.

Each of the users should have individual username and password in order to access to the software. Administrator of information system who needs to maintain the software and he is responsible for working of computer system and software as well. He

Table 2 Specification of use case: Software maintaining

Title	Software maintaining
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the software maintaining
Pre-condition	PC is properly settled Administrator has needed knowledge for the tasks
Post-condition	Backup of the waste cooking oil management software was made
Main scenario	1. Administrator checks if there is some large operation on the software 2. If there is some operation on the software, the administrator waits until the operation ends 3. If there is not operation on the software, the administrator prepares tools for the software maintaining 4. Administrator checks if the all functions of the software are proper 5. If some of the function of the software is not proper than the administrator starts the tool for correction of the function 6. Administrator starts the backup process of the software 7. Administrator records the time of the software backup
Alternative	None

Table 3 Specification of use case: Software web pages maintaining

Title	Software web pages maintaining
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the web pages maintaining of software
Pre-condition	PC is properly settled Administrator has needed knowledge for the tasks
Post-condition	Backup of the web pages of software was made
Main scenario	1. Administrator checks if there is some large operation on the web pages of software 2. If there is some operation on the web pages of software, the administrator waits until the operation ends 3. If there is not operation on the web pages of software, the administrator prepares tools for the web pages of waste cooking oil management software maintaining 4. Administrator checks if the all functions of the web pages of software are proper 5. If some of the function of the web pages of education software is not proper than the administrator starts the tool for correction of the function 6. Administrator starts the backup process of the web pages of software 7. Administrator records the time of the web pages of software backup
Alternative	None

Table 4 Specification of use case: Software database maintaining

Title	Software database maintaining
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the database maintaining of software
Pre-condition	PC is properly settled Administrator has needed knowledge for the tasks
Post-condition	Backup of the database of software was made
Main scenario	1. Administrator checks if there is some large operation on the database of software 2. If there is some operation on the database of software, the administrator waits until the operation ends 3. If there is not operation on the database of software, the administrator prepares tools for the database of software maintaining 4. Administrator checks if the all functions of the database of software are proper 5. If some of the function of the database of software is not proper than the administrator starts the tool for correction of the function 6. Administrator starts the backup process of the database of software 7. Administrator records the time of the database of software backup
Alternative	None

Table 5 Specification of use case: Making of regular reports

Title	Making of regular reports
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the making of regular reports
Pre-condition	PC is properly settled Administrator has needed knowledge for the tasks
Post-condition	The reposts were printed
Main scenario	1. Administrator checks if there is some large operation 2. If there is some operation, the administrator waits until the operation ends 3. If there is not operation, the administrator prepares tools for the making of regular reports 4. Administrator selects between standard procedure of the making of regular reports and nonstandard procedure where administrator can adjust the parameters of the reports. If nonstandard procedure was chosen than the administrator adjusts the parameters of the reports 5. Administrator starts the procedure of the making of regular reports 6. Administrator saves the backup of the reports 7. Administrator records the time of the database of making of regular reports
Alternative	None

gives permission to the staff's access to the waste cooking oil management database, maintains database, maintains web presentation of the waste cooking oil management and makes regular daily reports.

Software Analyzing

Each of the client should have individual username and password to access to the software. Administrator of software should maintain the software and he is responsible for working of computer system and software as well. He gives permission to the access to the database, maintains database, maintains web presentation of the software and makes regular daily reports.

Main use cases diagram of the software

Liquid waste treatment are depicted by the main use case diagram as it shown in [Fig. 2](#). The main use case diagram has several sub use cases which will be explained in detail. As can be seen, the administrator should perform the main administration process of the liquid waste treatment in order to ensure smooth working processes by the software. Clients or suppliers record the quantity and composition of the liquid waste if they are logged in the software database. Based on the records the modules should determine the type of the liquid waster treatment.

Liquid waste transport are depicted by the main use case diagram as it shown in [Fig. 3](#). Clients or suppliers record the coordinated of the liquid waste if they are logged in the software database. Based on the records the modules should determine the optimal route of liquid waste transport.

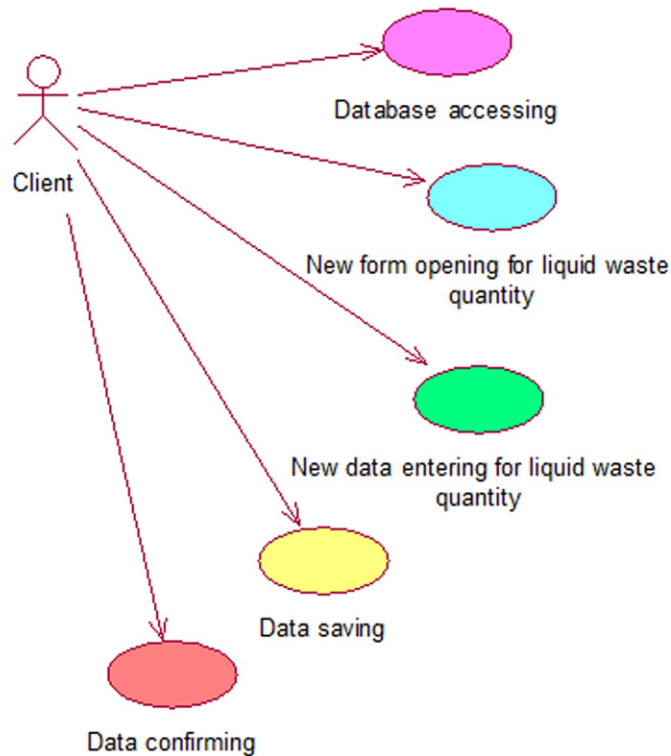


Fig. 4 Use case diagram – Recording of quantity of liquid waste.

Table 6 Specification of use case: Recording of quantity of liquid waste

Title	Recording of quantity of liquid waste
Actors	Client
Trigger	It starts with the choosing of the option on user interface for the recording of quantity of liquid waste
Pre-condition	PC is properly settled Liquid waste acquired
Post-condition	Recorded quantity of liquid waste
Main scenario	1. Client starts liquid waste management software 2. Client does login into liquid waste management software 3. Client records the quantity of liquid waste 4. Client confirms the quantity
Alternative	1. The recording of quantity of liquid waste is canceled 2. Due to technical problems the service cannot be made

Use cases of the software subsystems

Software administration

Administrator performs software administration in order to eliminate all unpredictable errors in the software and system. Administrator has full responsibility for the software maintenance. They will give permissions for other users access to the system, maintains the software, maintains the web pages of the software, maintains the software database, and makes regular daily reports.

Table 1 shows detailed specification of use case for giving permission for database access of the software by administrator.

Table 2 shows detailed specification of the use case of software maintaining by administrator.

Table 3 shows detailed specification of use case for web pages maintaining of software by administrator.

Table 4 shows detailed specification of use case for database maintaining of software by administrator.

Table 5 shows detailed specification of use case for making of regular reports by administrator.

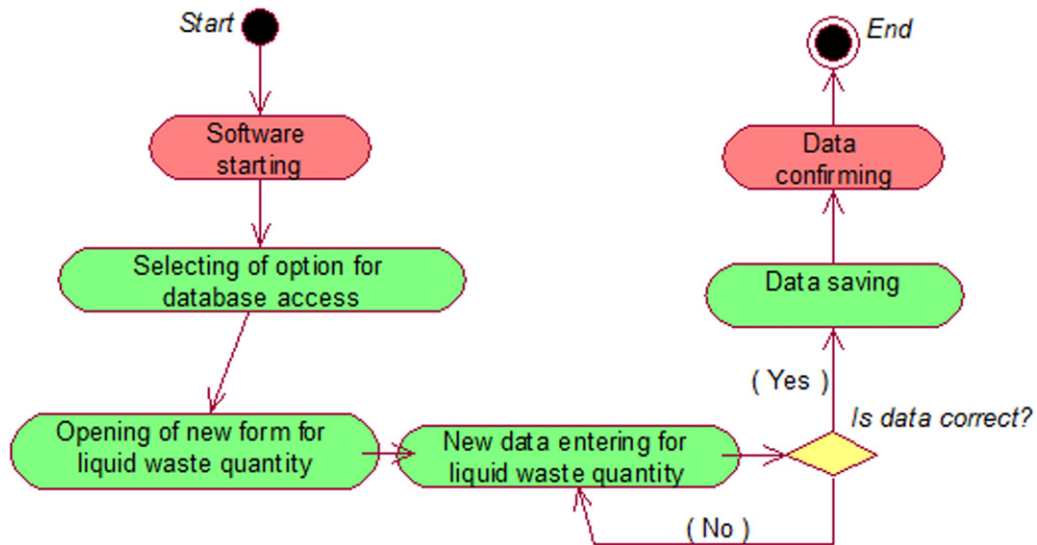


Fig. 5 Activity diagram – Recording of quantity of liquid waste.

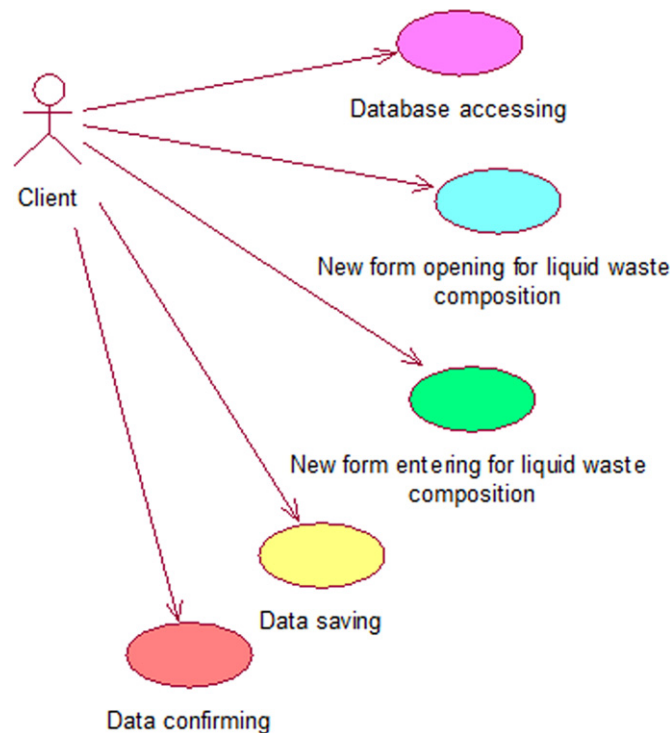


Fig. 6 Use case diagram – Recording of composition of liquid waste.

Recording of quantity of liquid waste

Use case recording of quantity of liquid waste is depicted in Fig. 4. The use case diagram has several sub use cases. Table 6 shows detailed specification for use case recording of quantity of liquid waste. Fig. 5 shows activity diagram for the recording of quantity of liquid waste.

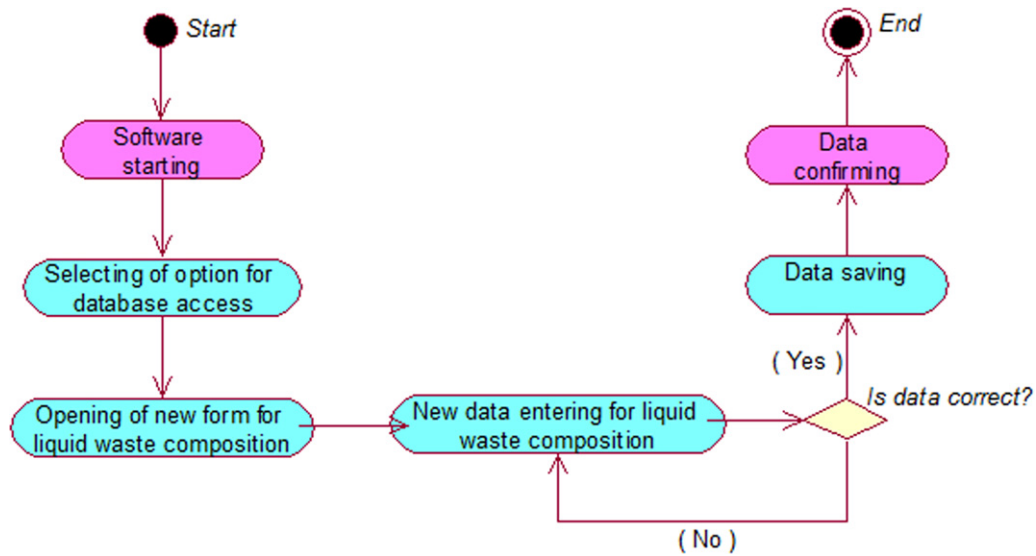


Fig. 7 Activity diagram – Recording of composition of liquid waste.

Table 7 Specification of use case: Recording of composition of liquid waste

Title	Recording of composition of liquid waste
Actors	Client
Trigger	It starts with the choosing of the option on user interface for the recording of composition of liquid waste
Pre-condition	PC is properly settled Liquid waste acquired
Post-condition	Recorded composition of liquid waste
Main scenario	1. Client starts liquid waste management software 2. Client does login into liquid waste management software 3. Client records the composition of liquid waste 4. Client confirms the composition
Alternative	1. The recording of composition of liquid waste is canceled 2. Due to technical problems the service cannot be made

Recording of composition of liquid waste

Use case recording of composition of liquid waste is depicted in Fig. 6. The use case diagram has several sub use cases. Table 6 shows detailed specification for use case recording of composition of liquid waste. Fig. 7 shows activity diagram for the recording of composition of liquid waste (Table 7).

Conclusion

Liquid waste management presents a big issue for all countries. One of the most common liquid waste treatment method is disposal. Illegal liquid waste disposal and unofficial liquid waste recycling could produce high pollution of water, air and soil. There is need for systematic sustainable liquid waste management system in order to preserve natural resources and to keep clean the life environment.

The main innovation of the investigation is analyzing and modeling of new software for liquid waste treatment. The main suppliers could enter quantity and composition of liquid waste in the software. Based on the quantity and composition the clients could decide which treatment and transport route is the best for the liquid waste they collected.

See also: Modeling of Information System for Air Waste Management. Modeling of Information System for Solid Waste Management. System Optimization for Control of Solid Waste

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Modeling of Information System for Nuclear Waste Management

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Introduction

The increasing trend in the consumption of various materials has also led to a huge increase in the nuclear waste and the consequent environmental pollutions in particular greenhouse gas emissions. These have made nuclear waste management a significant environmental issue for governments and policy-makers. To address these challenges, developed countries have implemented sustainable material management strategies which have been comprehensively reviewed herein. However, there is need to integrate the strategies in one information system for easy application.

An integrated system for waste reduction, collection, composting, recycling, and disposal is required to tackle the growing challenge of nuclear waste management. Integrated nuclear waste management involves many executive, operational and managerial decisions such as the siting of waste processing and disposal units, selection of waste-treatment technologies and allocation of waste flow to processing facilities and landfills.

Waste management process could be very complex task because of many different suppliers and collectors. Suppliers could be industrial buildings which produce large masses of nuclear waste and collectors should reduce the nuclear waste. There is need to make optimal route for the most efficient transport of the waste to the collectors. In other word there is need to find the most efficient way to detect and decrease the nuclear waste. The main problem is suppliers motivation for such a process since they require simple and understandable process for the nuclear waste management. It is suitable to model an software which will make more motivation for suppliers and collectors to make stronger and more uniform connections. The software could determine the optimal routes and treatments for the waste based on locations of suppliers. In this article object orientated approach is used for the software modeling (Lethbridge and Laganieri, 2005; Jacobson, 1993).

Object-orientated modeling strategy is an attempt to encapsulate data and process into thing called objects. The data in the objects could be created, deleted or used only by some encapsulated processes or methods. Unified modeling language (UML) is a standard tool for object orientated modeling which could help to developers and engineers to make detailed specification and documentation of any system.

UML (Rumbaugh *et al.*, 2004) is a graphical language which is effective for visualization, specification, construction and documentation of a system's artifact which is software intensive. UML has standard practices for writing a blueprint of system. By using UML one can cover various conceptual things such as functionality by use cases and business processes.

Modeling and analyzing of various activities in any system by UML can help to visualize, specify, constructs and document the system artifact effectively which is helpful for better understanding of the problem and for various stakeholders of the application of the nuclear waste management.

Materials and Methods

Nuclear Waste Management

According to the European Union standardization there are six procedures in the nuclear waste treatment process:

1. Eco-design,
2. Nuclear waste decreasing,
3. Nuclear waste reusing,
4. Recycling and making compost,
5. Energy from nuclear waste,
6. Nuclear waste disposing.

The main activity of the investigation is to develop two separate softwares in order to make sustainable nuclear waste management. In order to optimize the system for nuclear waste management based on decreasing of pollution of life environment and for the cheapest solution there is goal to develop and model the software for the nuclear waste management process. This innovative solution could lead to revolution in the nuclear waste issue. By entering of the main data for nuclear waste, quantity and composition for the some region, the client could know which is the best solution for the nuclear waste treatment and transport for the region. Several nuclear waste treatments are included in the software:

- Recycling,
- Combusting,
- Making compost,
- Performing anaerobic digestion and
- Disposing of nuclear waste.

There are several indicators which are calculated in the software according the input data. These indicators are:

- Global warming,
- Heavy metals emission,
- Nitrogen oxide emission,
- Smog formation,
- Water pollution.

Therefore these software has seven modules. These modules

- Calculation of emissions from collection and transport of nuclear waste,
- Calculation of emissions from anaerobic digestion,
- Calculation of emissions from combustion,
- Calculation of emissions from recycled waste,
- Calculation of emissions from disposal,
- Calculation of emissions from compost,
- Calculation of cost benefit.

There is also plan to integrate the module for determination of the optimal route of the nuclear waste transport. The optimization of the route is very important since there is constantly changing of the urban parameters: number of residents, waste quantity, type of transport vehicle, transport conditions. Clark and Wright savings algorithm could be applied for the route optimization for the nuclear waste.

This software approach for the nuclear waste management could be very helpful for managers who control waste, companies which produce and transport the waste and for decision makers to select the optimal scenery for the waste treatment and transport for each region. The main goals of the investigation are:

- Removing of the barriers for the decreasing of pollution of life environment by nonsuitable treatment of the nuclear waste.
- Increasing of ecological awareness for the importance of regular treatment of waste.
- Solving of problem of nuclear waste collection and transport.

Specific goal of the investigation is:

- Modeling of innovative software as a tool for determination of a right strategy for nuclear waste management.

Software Development for Nuclear Waste Management

Generally, the software development methodology is consisted of procedures, technics, tools and documentation which helps in the software development process. Software development methodology describes all steps and phases of the software development. The methodology suggest tools and technics which should use in the particular step of the software development. Also the methodology could suggest how to plan and track process of the software development and testing as well.

Many companies use the methodologies for software development in order to ensure the consistency of the problem solution, to decrease the possible errors, to acquire the full documentation for current and future projects and to get good final product which could be changeable and adaptable easily since the all steps and phases would be documented in detail and any new changes in the software models could be achieved before software coding.

Models could be describes as simplified presentation of reality. The models could be presented with some standard modeling language. The model presentation could be textual or graphical by diagrams. Each software could be described based on different aspects by structural models in order to show software structure with the main parts and their interconnections and relationships. Also there is behaviour models where one can track the software dynamics.

RUP methodology

Rational Unified Process (RUP) is an iterative methodology for the software development based on architecture and use cases. RUP methodology is based on Unified Modeling Language (UML). UML is used for specification, visualization, construction and documentation of the software development.

RUP methodology has control, key or critical points through the development. In the other words each phase of the RUP methodology should end by some control, key or critical points where achieved results are summed and future directions are planned based on the results. RUP methodology has artefacts (documents), models and model elements. Project requests are noted in the documents. Models are used to simplify the software architecture without unnecessary details. Model elements could help to visualize, construct and document the main structure and software behaviour.

RUP methodology has four main phases. The first phase is initial phase or idea inception where one needs to understand what should to do and software vision and requirements are identified. This phase includes the identification of key software actors (users) and use cases. Also there is need to identify software domain. Use case defines one sequence of an action which software performs that yields to an observable results. In the other hands one use case presents result of an action by actor. Use case presents the main part of some complete software operation from beginning until to the end. It is used to capture the intended behaviour

of the system in development. By use cases models desired behaviour of the system could be specified but it is not strictly this desired behaviour to be carried out or implemented in the final product. Use cases models can be developed for whole system or for the part of system. Each part of system or subsystem can be developed by use cases models until the part produces some tangible amount of work and results. System complexity indicates the number of use cases. In the initial stage of system development main use cases are developed and additional use cases can be added or included when there is need for them.

The second phase is project elaboration where one needs to understand how to build the software and basic software architecture is showed in the phase. The third phase presents software construction where software testing is considered. The fourth phase presents software transition where software validation is performed.

RUP models describes software in modeling. RUP models could be business models which describes business processes and business environment, use case models which describes what software doing and software environment, projecting models which describes use cases realization as code abstraction and implementation models which presents collection of components and subsystems.

Software development process could has different problems which needs to be identifies and solved before coding and testing. In order to solve problems there is need to find the problem causes. To remove the problem cause it is suitable to use best practices. For example in order to remove the confusion in communication between team members it is suitable to use standard language UML for the software visualization, specification and documentation. There are different types of UML diagrams which can be used in the software development process. There are two main classes of the UML diagrams. These are structural and behavioral diagrams. Structural diagram presents structure of the system in passive state and behavioral diagram present the active behaviour of the objects in a system or dynamical state.

Object-orientated modeling of business process

UML is used for object-orientated modeling of business process. As already mentioned there are different UML diagrams for describing of software architecture and software behaviour. UML as standard language is used for modeling, for analyzing, for projecting and for implementation of the software system. Based on the object-orientated modeling all process could be presented by use cases models as rough specification and by structural diagrams and behavioral diagrams as detail specification.

During modeling of the business process it is not recommended to use natural language because of its ambiguity. Also formal programming languages is not understandable for many people in the project team. Therefore it is suitable to organize the natural language to avoid ambiguity. Modeling process is one of the solution for understanding and clear communication between project team members.

Modeling of the Nuclear Waste Management

Problem Description

The problem is intended for solving of treatment and transport of nuclear waste. The main objects of the model are clients, administrator and modula. The clients represent the all possible suppliers of the nuclear waste. Administrator should maintain the software through the process and modules should determine the optimal treatment and transport route of the nuclear waste.

The main goals of the investigation is to decrease the emissions of the greenhouse gasses and generally to decrease global warming and pollution. Also biofuels need to be introduced in the transport as much as it can. The main activity of the investigation should be to develop the GPS system for mapping of the nuclear waste suppliers in order to optimize the transport route.

Object-oriented modeling concepts are used during analyzing and modeling of the nuclear waste management process. Two UML concepts are used for the software modeling like use case models, activity diagrams and scenarios of activities.

Software for Route Optimization for Waste Nuclear Transport

Software for route optimization for waste cooking oil transport should be use for organization of the waste cooking oil suppliers and collectors as well. The main advantage of the software for route optimization for waste cooking oil transport in the article is in its universality and in its online usage.

The main feature of the software for route optimization for waste cooking oil transport should be universal application for any subjects and any suppliers and collectors. The software for route optimization for waste cooking oil transport will be framework of the suppliers and collectors of the transport activity.

As users are considered suppliers in different parts of industry and collectors as well. All of the users should have username and password in order to access the waste cooking oil management database.

Collectors should made reports for different statistical analysis of the waste cooking oil. As the main problem of the current software for route optimization for waste cooking oil transport it was identified limitation of unified approach for all subjects. Therefore it is required to develop information system which would allow to users to use the software anytime in order to enter desired data.

Software users

The software users could be divided based on natural basis according to working place, suppliers and collectors. All of the users have equal rights to access and use of the software. Therefore the main users of the software are:

- Client,
- Module,
- Administrator.

Each of the users should have individual username and password in order to access to the software. Administrator of information system who needs to maintain the software and he is responsible for working of computer system and software as well. He gives permission to the staff's access to the waste cooking oil management database, maintains database, maintains web presentation of the waste cooking oil management and makes regular daily reports.

Software Analyzing

Each of the client should have individual username and password to access to the software. Administrator of software should maintain the software and he is responsible for working of computer system and software as well. He gives permission to the access to the database, maintains database, maintains web presentation of the software and makes regular daily reports.

Main use cases diagram of the software

Nuclear waste treatment are depicted by the main use case diagram as it shown in Fig. 1. The main use case diagram has several sub use cases which will be explained in detail. As can be seen, the administrator should perform the main administration process of the nuclear waste treatment in order to ensure smooth working processes by the software. Clients or suppliers record the quantity and composition of the nuclear waste if they are logged in the software database. Based on the records the modules should determine the type of the nuclear waster treatment.

Nuclear waste transport are depicted by the main use case diagram as it shown in Fig. 2. Clients or suppliers record the coordinated of the nuclear waste if they are logged in the software database. Based on the records the modules should determine the optimal route of nuclear waste transport.

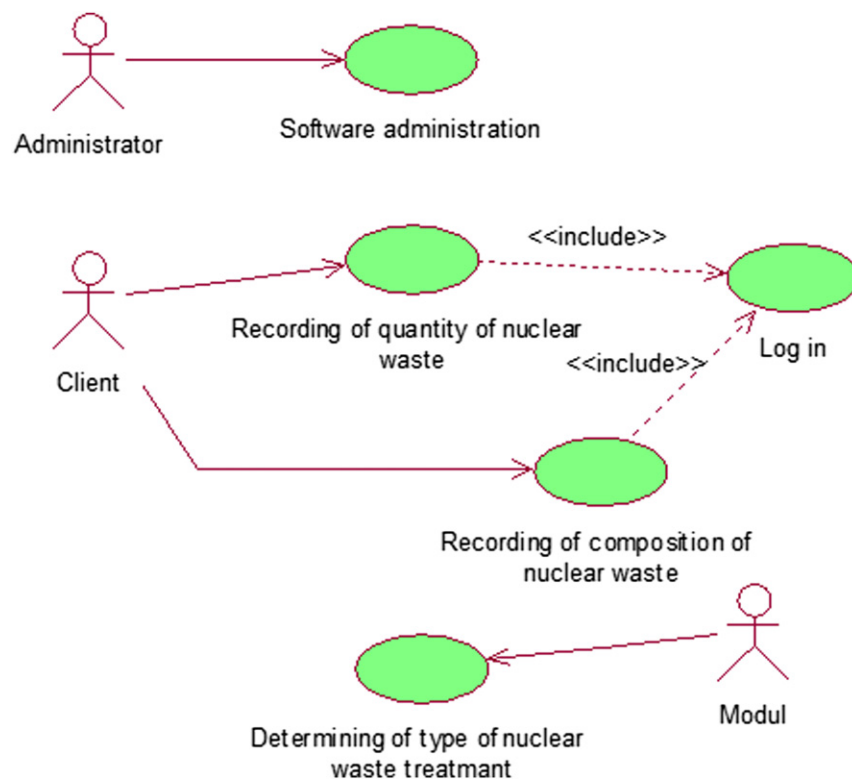


Fig. 1 Main use case diagram of the software for determining of nuclear waste type treatment.

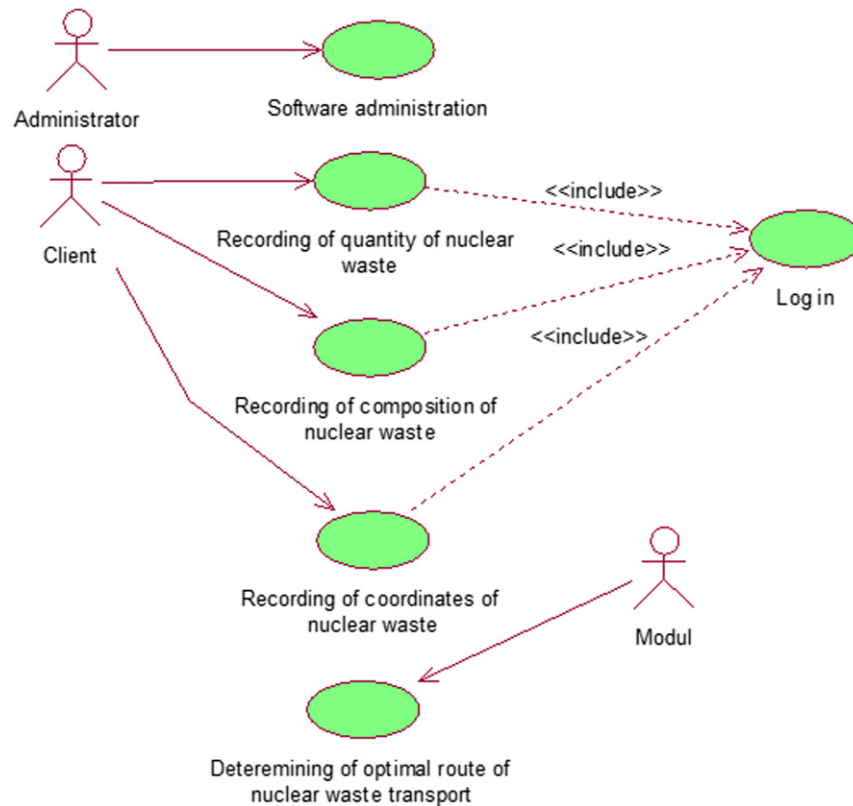


Fig. 2 Main use case diagram of the software for determining of optimal route of nuclear waste transport.

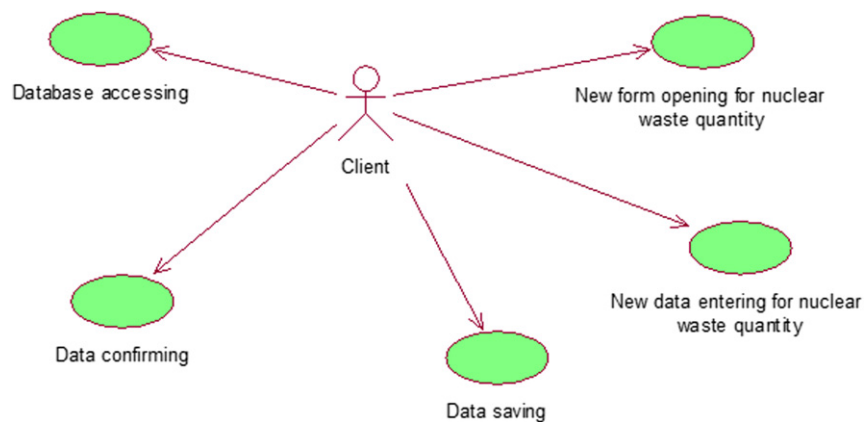


Fig. 3 Use case diagram – Recording of quantity of nuclear waste.

Use cases of the software subsystems

Software administration

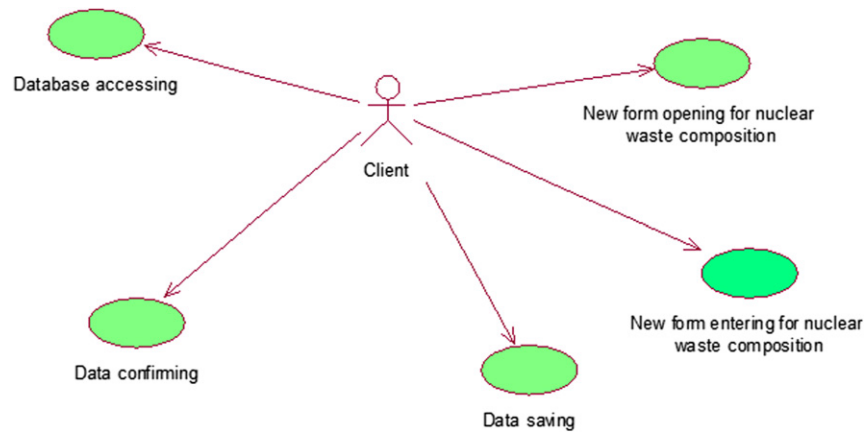
Administrator performs software administration in order to eliminate all unpredictable errors in the software and system. Administrator has full responsibility for the software maintenance. They will give permissions for other users access to the system, maintains the software, maintains the web pages of the software, maintains the software database, and makes regular daily reports.

Recording of quantity of nuclear waste

Use case recording of quantity of nuclear waste is depicted in [Fig. 3](#). The use case diagram has several sub use cases. [Table 1](#) shows detailed specification for use case recording of quantity of nuclear waste.

Table 1 Specification of use case: Recording of quantity of nuclear waste

Title	Recording of quantity of nuclear waste
Actors	Client
Trigger	It starts with the choosing of the option on user interface for the recording of quantity of nuclear waste
Pre-condition	PC is properly settled. Nuclear waste acquired.
Post-condition	Recorded quantity of nuclear waste.
Main scenario	1. Client starts nuclear waste management software. 2. Client does login into nuclear waste management software. 3. Client records the quantity of nuclear waste. 4. Client confirms the quantity.
Alternative	1. The recording of quantity of nuclear waste is canceled. 2. Due to technical problems the service cannot be made.

**Fig. 4** Use case diagram – Recording of composition of nuclear waste.**Table 2** Specification of use case: Recording of composition of nuclear waste

Title	Recording of composition of nuclear waste
Actors	Client
Trigger	It starts with the choosing of the option on user interface for the recording of composition of nuclear waste
Pre-condition	PC is properly settled. Nuclear waste acquired.
Post-condition	Recorded composition of nuclear waste.
Main scenario	1. Client starts nuclear waste management software. 2. Client does login into nuclear waste management software. 3. Client records the composition of nuclear waste. 4. Client confirms the composition.
Alternative	1. The recording of composition of nuclear waste is canceled. 2. Due to technical problems the service cannot be made.

Recording of composition of nuclear waste

Use case recording of composition of nuclear waste is depicted in [Fig. 4](#). The use case diagram has several sub use cases. [Table 2](#) shows detailed specification for use case recording of composition of nuclear waste.

Conclusion

Nuclear waste management present a big issue for all countries. One of the most common nuclear waste treatment method is disposal. Illegal nuclear waste disposal and inofficial nuclear waste recycling could produce high pollution of water, nuclear and soil. There is need for systematic sustainable nuclear waste management system in order to preserve natural resources and to keep clean the life environment.

The main innovation of the investigation is analyzing and modeling of new software for nuclear waste treatment. The main suppliers could enter quantity and composition of nuclear waste in the software. Based on the quantity and composition the clients could decide which treatment and transport route is the best for the nuclear waste they collected.

See also: Analyzing Biodiesel Production From Cooking Oil. Modeling of Information System for Air Waste Management

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Modeling of Information System for Solid Waste Management

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Introduction

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An integrated system for waste reduction, collection, composting, recycling, and disposal is required to tackle the growing challenge of solid waste management. Integrated solid waste management involves many executive, operational and managerial decisions such as the siting of waste processing and disposal units, selection of waste-treatment technologies and allocation of waste flow to processing facilities and landfills.

Waste management process could be very complex task because of many different suppliers and collectors. There is need to make optimal route for the most efficient transport of the waste to the collectors. The main problem is suppliers motivation for such a process since they require simple and understandable process for the waste cooking oil management. Because of that it is suitable for the waste transport to model an software which will make more motivation for suppliers and collectors to make stronger and more uniform connections. The software could determine the optimal routes and treatments for the waste based on locations of suppliers. In this article object orientated approach is used for the software modeling (Lethbridge and Laganiere, 2005; Jacobson, 1993).

Object-orientated modeling strategy is an attempt to encapsulate data and process into thing called objects. The data in the objects could be created, deleted or used only by some encapsulated processes or methods. Unified modeling language (ULM) is a standard tool for object orientated modeling which could help to developers and engineers to make detailed specification and documentation of any system.

ULM (Rumbaugh *et al.*, 2004) is a graphical language which is effective for visualization, specification, construction and documentation of a system's artifact which is software intensive. ULM has standard practices for writing a blueprint of system. By using ULM one can cover various conceptual things such as functionality by use cases and business processes.

Modeling and analyzing of various activities in any system by ULM can help to visualize, specify, constructs and document the system artifact effectively which is helpful for better understanding of the problem and for various stakeholders of the application of the solid waste management.

Literature Overview

A lack of attention to the role of urbanites in municipal solid waste management (MSWM) has contributed to poor state of solid waste management (SWM) (Cobbina *et al.*, 2017). In study (Maalouf and El-Fadel, 2017), the carbon footprint of introducing a food waste disposer (FWD) policy was examined in the context of its implications on solid waste and the sensitivity analyses on processes with a wide range in costs showed an equivalent economic impact thus emphasizing the viability of a FWD policy although the variation in the cost of sludge management exhibited a significant impact on savings. Waste characterization is the first step to any successful waste management policy (Adeniran *et al.*, 2017). Informal waste recycling has become an important activity in the urban regions. Using empirical data collected through the tradition of participatory research, the findings suggest that waste pickers play a vital role in municipal solid waste management and make a significant contribution to the city's economic growth as well as environmental wellness (Simatele *et al.*, 2017). Currently, the overwhelming majority of municipal solid waste (MSW) has been treated in sanitary landfills and incineration plants. In future, with the popularization of separate waste collection, it is logical to treat the biodegradable components using biological treatment technologies (Liu *et al.*, 2017b). Contracting out local solid waste management service is assumed to deliver cost savings without sacrificing the service quality (Zhu and Huang, 2017). The paper (Rajaeifar *et al.*, 2017) was aimed at comprehensively assessing electricity generation potentials from MSW using an integrated solid waste management system (including three different technologies of anaerobic digestion (AD), incineration, and pyrolysis-gasification) while the consequent greenhouse gases emission reduction potentials as a result of their implementation were also explored. In study (Asefi and Lim, 2017) was aimed to satisfy the sustainability requirements for designing an ISWM system by taking economic, environmental and social factors into account. The study (Kumar and Samadder, 2017) was reviewed the current global scenario of waste to energy (WTE) technological options (incineration, pyrolysis, gasification, anaerobic digestion, and landfilling with gas recovery) for effective energy recovery and the challenges faced by developed and developing countries. Ecological-economic evaluation of different treatment technologies is to achieve the maximum practical benefits from investments and to ensure the minimum environmental impacts of waste flows based on variable source-separated collection

and transportation rates were analyzed in paper (Liu *et al.*, 2017a). Municipal solid waste treatment options are not necessarily pragmatic if the stakeholders in the system don't mutually agree on their shares of liabilities (Soltani *et al.*, 2017). With the booming economy and increasing population, the accumulation of waste has become an increasingly arduous issue and has aroused the attention from all sectors of society (Lee *et al.*, 2016).

Materials and Methods

Solid Waste Management

According to the European Union standardization there are six procedures in the solid waste treatment process:

1. Eco-design,
2. Solid waste decreasing,
3. Solid waste reusing,
4. Recycling and making compost,
5. Energy from solid waste,
6. Solid waste disposing.

The main activity of the investigation is to develop two separate softwares in order to make sustainable solid waste management. In order to optimize the system for solid waste management based on decreasing of pollution of life environment and for the cheapest solution there is goal to develop and model the software for the solid waste management process. This innovative solution could lead to revolution in the solid waste issue. By entering of the main data for solid waste, quantity and composition for the some region, the client could know which is the best solution for the solid waste treatment and transport for the region. Several solid waste treatments are included in the software:

- Recycling,
- Combusting,
- Making compost,
- Performing anaerobic digestion, and
- Disposing of solid waste.

There are several indicators which are calculated in the software according the input data. These indicators are:

- Global warming,
- Heavy metals emission,
- Nitrogen oxide emission,
- Smog formation,
- Water pollution.

Therefore these software has seven modules. These modules

- Calculation of emissions from collection and transport of solid waste,
- Calculation of emissions from anaerobic digestion,
- Calculation of emissions from combustion,
- Calculation of emissions from recycled waste,
- Calculation of emissions from disposal,
- Calculation of emissions from compost,
- Calculation of cost benefit.

There is also plan to integrate the module for determination of the optimal route of the solid waste transport. The optimization of the route is very important since there is constantly changing of the urban parameters: number of residents, waste quantity, type of transport vehicle, transport conditions. Clark and Wright savings algorithm could be applied for the route optimization for the solid waste.

This software approach for the solid waste management could be very helpful for managers who control waste, companies which produce and transport the waste and for decision makers to select the optimal scenery for the waste treatment and transport for each region. The main goals of the investigation are:

- Removing of the barriers for the decreasing of pollution of life environment by nonsuitable treatment of the solid waste,
- Increasing of ecological awareness for the importance of regular treatment of waste,
- Solving of problem of solid waste collection and transport.

Specific goal of the investigation is:

- Modeling of innovative software as a tool for determination of a right strategy for solid waste management.

Software Development for Solid Waste Management

Generally, the software development methodology is consisted of procedures, technique, tools and documentation which helps in the software development process. Software development methodology describes all steps and phases of the software development. The methodology suggest tools and technics which should use in the particular step of the software development. Also the methodology could suggest how to plan and track process of the software development and testing as well.

Many companies use the methodologies for software development in order to ensure the consistency of the problem solution, to decrease the possible errors, to acquire the full documentation for current and future projects and to get good final product which could be changeable and adaptable easily since the all steps and phases would be documented in detail and any new changes in the software models could be achieved before software coding.

Models could be describes as simplified presentation of reality. The models could be presented with some standard modeling language. The model presentation could be textual or graphical by diagrams. Each software could be described based on different aspects by structural models in order to show software structure with the main parts and their interconnections and relationships. Also there is behavior models where one can track the software dynamics.

RUP methodology

Rational Unified Process (RUP) is an interactive methodology for the software development based on architecture and use cases. RUP methodology is based on Unified Modeling Language (UML). UML is used for specification, visualization, construction and documentation of the software development.

RUP methodology has control, key or critical points through the development. In the other words each phase of the RUP methodology should end by some control, key or critical points where achieved results are summed and future directions are planned based on the results. RUP methodology has artifacts (documents), models i model elements. Project requests are noted in the documents. Models are used to simplify the software architecture without unnecessary details. Model elements could help to visualize, construct and document the main structure and software behavior. Fig. 1 shows the main elements of the RUP methodology. Each phase of the RUP methodology has iteration where disciplines are considered. The disciplines are described by process flow in details. The process shows activity and roles of everyone in the project. Finally there are artifacts where one can see software documentation, software models and model elements.

RUP methodology has four main phases. The first phase is initial phase or idea inception where one needs to understand what should to do and software vision and requirements are identified. This phase includes the identification of key software actors (users) and use cases. Also there is need to identify software domain. Use case defines one sequence of an action which software performs that yields to an observable results. In the other hands one use cases presents result of an action by actor (Fig. 2). Use case presents the main part of some complete software operation from beginning until to the end. It is used to capture the intended behavior of the system in development. By use cases models desired behavior of the system could be specified but it is not strictly this desired behavior to be carried out or implemented in the final product. Use cases models can be developed for whole system or for the part of system. Each part of system or subsystem can be developed by use cases models until the part produces some tangible amount of work and results. System complexity indicates the number of use cases. In the initial stage of system development main use cases are developed and additional use cases can be added or included when there is need for them.

The second phase is project elaboration where one needs to understand how to build the software and basic software architecture is showed in the phase. The third phase presents software construction where software testing is considered. The fourth phase presents software transition where software validation is performed. The RUP phases are shown in Fig. 3.

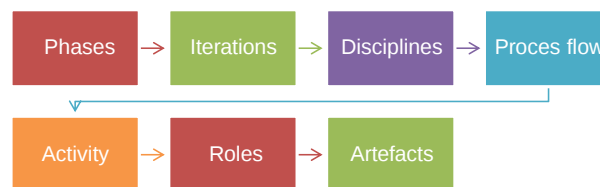


Fig. 1 Elements of RUP methodology.



Fig. 2 Use case model.



Fig. 3 RUP methodology phases.

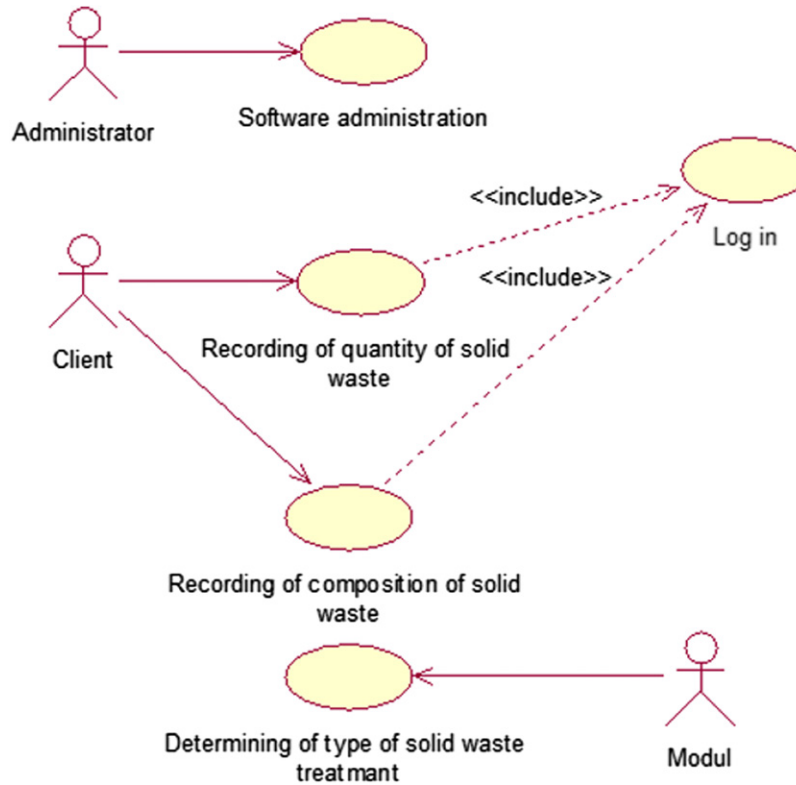


Fig. 4 Main use case diagram of the software for determining of solid waste type treatment.

RUP models describes software in modeling. RUP models could be business models which describes business process and business environment, use case models which describes what software doing and software environment, projecting models which describes use cases realization as code abstraction and implementation models which presents collection of components and subsystems.

Software development process could has different problems which needs to be identifies and solved before coding and testing. In order to solve problems there is need to find the problem causes. To remove the problem causes it is suitable to use best practices. For example in order to remove the confusion in communication between team members it is suitable to use standard language UML for the software visualization, specification and documentation. There are different types of UML diagrams which can be used in the software development process. There are two main classes of the ULM diagrams. These are structural and behavioral diagrams. Structural diagram presents structure of the system in passive state and behavioral diagram present the active behavior of the objects in a system or dynamical state.

Object-orientated modeling of business process

UML is used for object-orientated modeling of business process. As already mentioned there are different UML diagrams for describing of software architecture and software behavior. UML as standard language is used for modeling, for analyzing, for projecting and for implementation of the software system. Based on the object-orientated modeling all process could be presented by use cases models as rough specification and by structural diagrams and behavioral diagrams as detail specification.

During modeling of the business process it is not recommended to use natural language because of its ambiguity. Also formal programming languages is not understandable for many people in the project team. Therefore it is suitable to organize the natural language to avoid ambiguity. Modeling process is one of the solution for understanding and clear communication between project team members.

Modeling of the Solid Waste Management

Problem Description

The problem is intended for solving of treatment and transport of solid waste. The main objects of the model are clients, administrator and modula. The clients represent the all possible suppliers of the solid waste. Administrator should maintain the software throughout the process and modules should determine the optimal treatment and transport route of the solid waste.

The main goals of the investigation is to decrease the emissions of the greenhouse gasses and generally to decrease global warming and pollution. Also biofuels need to be introduced in the transport as much as it can. The main activity of the investigation should be to develop the GPS system for mapping of the solid waste suppliers in order to optimize the transport route.

Object-orientated modeling concepts are used during analyzing and modeling of the solid waste management process. Two UML concepts are used for the software modeling like use case models, activity diagrams and scenarios of activities.

Software for Route Optimization for Waste Cooking Oil Transport

Software for route Optimization for waste cooking oil transport should be use for organization of the waste cooking oil suppliers and collectors as well. The main advantage of the software for route Optimization for waste cooking oil transport in the article is in its universality and in its online usage.

The main feature of the software for route Optimization for waste cooking oil transport should be universal application for any subjects and any suppliers and collectors. The software for route Optimization for waste cooking oil transport will be framework of the suppliers and collectors of the transport activity.

As users are considered suppliers in different parts of industry and collectors as well. All of the users should have username and password in order to access the waste cooking oil management database.

Collectors should made reports for different statistical analysis of the waste cooking oil. As the main problem of the current software for route Optimization for waste cooking oil transport it was identified limitation of unified approach for all

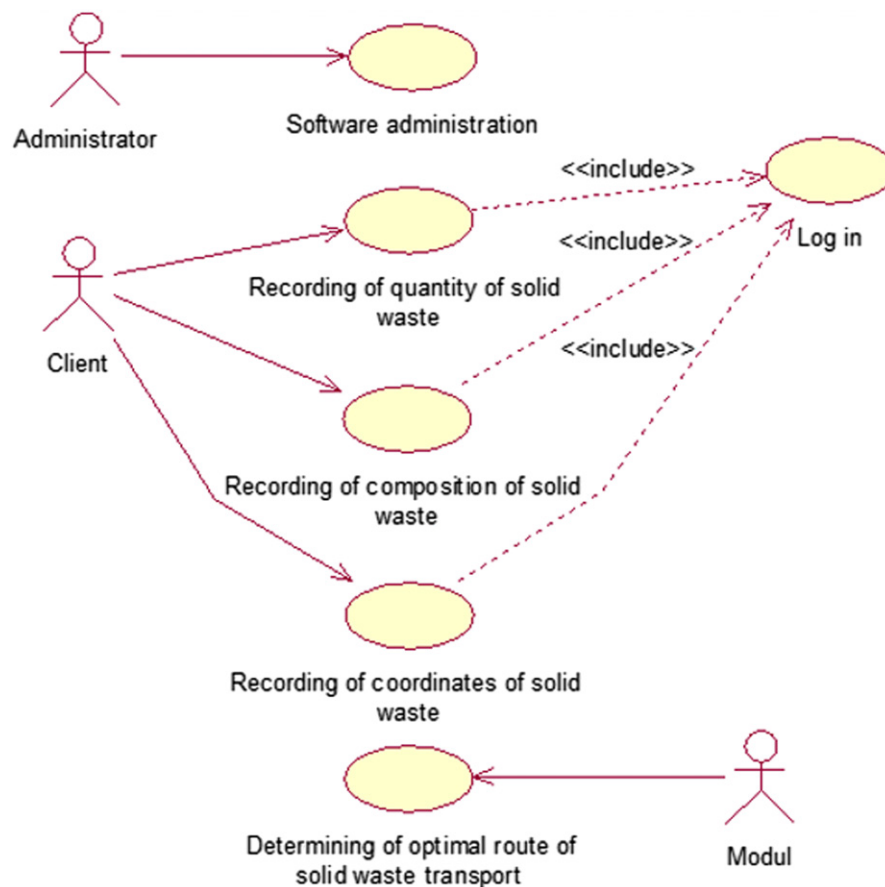


Fig. 5 Main use case diagram of the software for determining of optimal route of solid waste transport.

subjects. Therefore it is required to develop information system which would allow to users to use the software anytime in order to enter desired data.

Software users

The software users could be divided based on natural basis according to working place, suppliers and collectors. All of the users have equal rights to access and use of the software. Therefore the main users of the software are:

- Client,
- Module,
- Administrator.

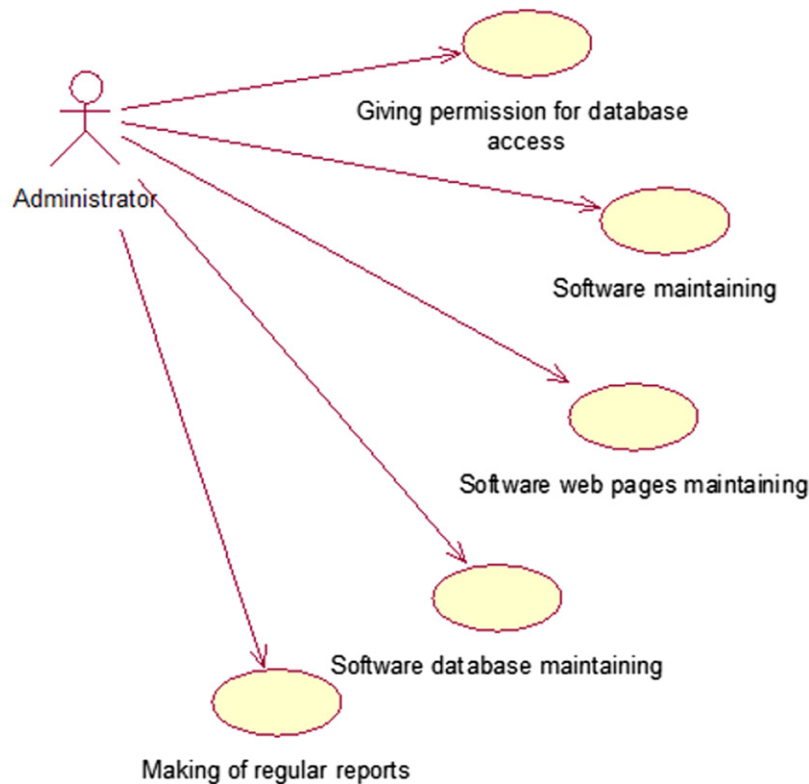


Fig. 6 Use case diagram – Software administration.

Table 1 Specification of use case: Giving permission for database access

Title	Giving permission for database access
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the giving permission for database access
Pre-condition	PC is properly settled Administrator has needed knowledge for the tasks
Post-condition	Client received authorization for database access of software
Main scenario	1. Administrator receives the request for the giving permission for database access of software 2. Administrator checks the request validity 3. Administrator fills the application form for the giving permission for database access of software 4. Administrator selects client category based on the quantity of the waste cooking oil 5. Administrator approves the request 6. Administrator prints the instruction for the application use 7. Administrator distributes the instruction to the client as the proof for the successful addition to the users of the waste cooking oil management software for the database access
Alternative	1. In the case if the request is incorrect filled based on the step 2 of the main scenario the administrator returns the request to the client with the instruction how to correct the errors in the request

Each of the users should have individual username and password in order to access to the software. Administrator of information system who needs to maintain the software and he is responsible for working of computer system and software as well. He gives permission to the staff's access to the waste cooking oil management database, maintains database, maintains web presentation of the waste cooking oil management and makes regular daily reports.

Table 2 Specification of use case: Software maintaining

Title	Software maintaining
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the software maintaining
Pre-condition	PC is properly settled Administrator has needed knowledge for the tasks
Post-condition	Backup of the waste cooking oil management software was made
Main scenario	1. Administrator checks if there is some large operation on the software 2. If there is some operation on the software, the administrator waits until the operation ends 3. If there is not operation on the software, the administrator prepares tools for the software maintaining 4. Administrator checks if the all functions of the software are proper 5. If some of the function of the software is not proper than the administrator starts the tool for correction of the function 6. Administrator starts the backup process of the software 7. Administrator records the time of the software backup
Alternative	None

Table 3 Specification of use case: Software web pages maintaining

Title	Software web pages maintaining
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the web pages maintaining of software
Pre-condition	PC is properly settled Administrator has needed knowledge for the tasks
Post-condition	Backup of the web pages of software was made
Main scenario	1. Administrator checks if there is some large operation on the web pages of software 2. If there is some operation on the web pages of software, the administrator waits until the operation ends 3. If there is not operation on the web pages of software, the administrator prepares tools for the web pages of waste cooking oil management software maintaining 4. Administrator checks if the all functions of the web pages of software are proper 5. If some of the function of the web pages of education software is not proper than the administrator starts the tool for correction of the function 6. Administrator starts the backup process of the web pages of software 7. Administrator records the time of the web pages of software backup
Alternative	None

Table 4 Specification of use case: Software database maintaining

Title	Software database maintaining
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the database maintaining of software
Pre-condition	PC is properly settled Administrator has needed knowledge for the tasks
Post-condition	Backup of the database of software was made
Main scenario	1. Administrator checks if there is some large operation on the database of software 2. If there is some operation on the database of software, the administrator waits until the operation ends 3. If there is not operation on the database of software, the administrator prepares tools for the database of software maintaining 4. Administrator checks if the all functions of the database of software are proper 5. If some of the function of the database of software is not proper than the administrator starts the tool for correction of the function 6. Administrator starts the backup process of the database of software 7. Administrator records the time of the database of software backup
Alternative	None

Software Analyzing

Each of the clients should have individual username and password to access to the software. Administrator of software should maintain the software and he is responsible for working of computer system and software as well. He gives permission to the access to the database, maintains database, maintains web presentation of the software and makes regular daily reports.

Table 5 Specification of use case: Making of regular reports

Title	Making of regular reports
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the making of regular reports
Pre-condition	PC is properly settled Administrator has needed knowledge for the tasks
Post-condition	The reports were printed
Main scenario	1. Administrator checks if there is some large operation 2. If there is some operation, the administrator waits until the operation ends 3. If there is not operation, the administrator prepares tools for the making of regular reports 4. Administrator selects between standard procedure of the making of regular reports and nonstandard procedure where administrator can adjust the parameters of the reports. If nonstandard procedure was chosen than the administrator adjusts the parameters of the reports 5. Administrator starts the procedure of the making of regular reports 6. Administrator saves the backup of the reports 7. Administrator records the time of the database of making of regular reports
Alternative	None

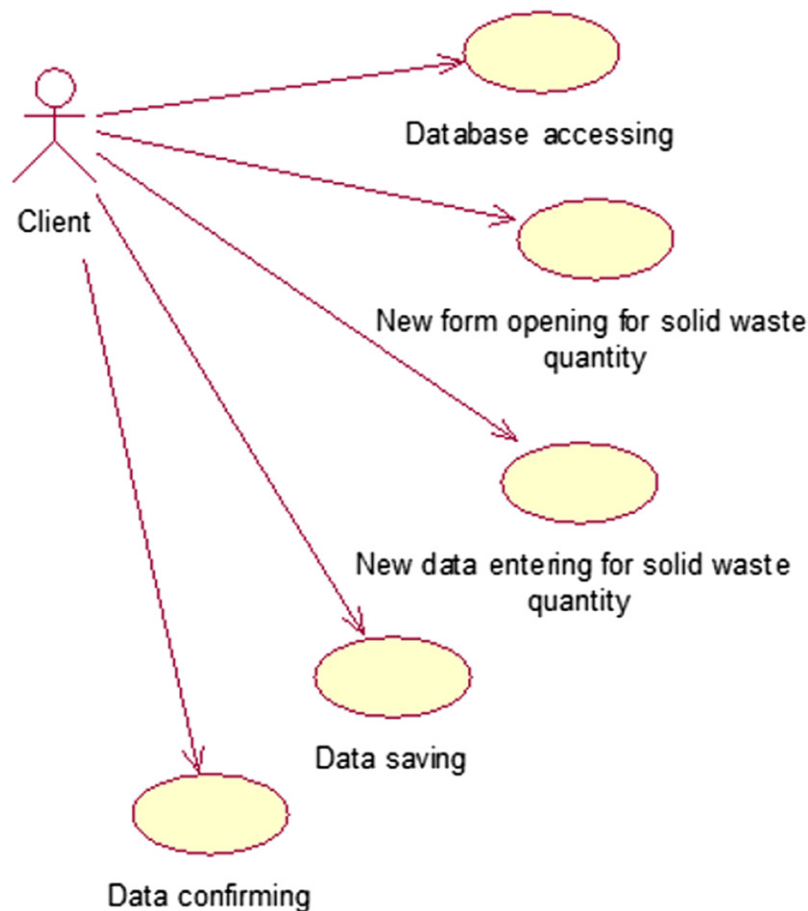


Fig. 7 Use case diagram – Recording of quantity of solid waste.

Main use cases diagram of the software

Solid waste treatment are depicted by the main use case diagram as it shown in Fig. 4. The main use case diagram has several sub use cases which will be explained in detail. As can be seen, the administrator should perform the main administration process of the solid waste treatment in order to ensure smooth working processes by the software. Clients or suppliers record the quantity and

Table 6 Specification of use case: Recording of quantity of solid waste

Title	Recording of quantity of solid waste
Actors	Client
Trigger	It starts with the choosing of the option on user interface for the recording of quantity of solid waste
Pre-condition	PC is properly settled Solid waste acquired
Post-condition	Recorded quantity of solid waste
Main scenario	1. Client starts solid waste management software 2. Client does login into solid waste management software 3. Client records the quantity of solid waste 4. Client confirms the quantity
Alternative	1. The recording of quantity of solid waste is canceled 2. Due to technical problems the service cannot be made

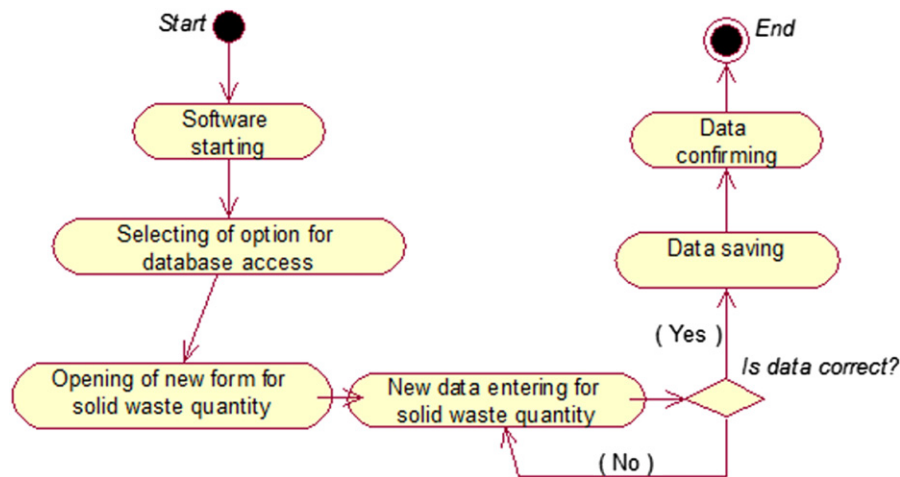


Fig. 8 Activity diagram – Recording of quantity of solid waste.

Table 7 Specification of use case: Recording of composition of solid waste

Title	Recording of composition of solid waste
Actors	Client
Trigger	It starts with the choosing of the option on user interface for the recording of composition of solid waste
Pre-condition	PC is properly settled Solid waste acquired
Post-condition	Recorded composition of solid waste
Main scenario	1. Client starts solid waste management software 2. Client does login into solid waste management software 3. Client records the composition of solid waste 4. Client confirms the composition
Alternative	1. The recording of composition of solid waste is canceled 2. Due to technical problems the service cannot be made

composition of the solid waste if they are logged in the software database. Based on the records the modules should determine the type of the solid waste treatment.

Solid waste transport are depicted by the main use case diagram as it shown in Fig. 5. Clients or suppliers record the coordinated of the solid waste if they are logged in the software database. Based on the records the modules should determine the optimal route of solid waste transport.

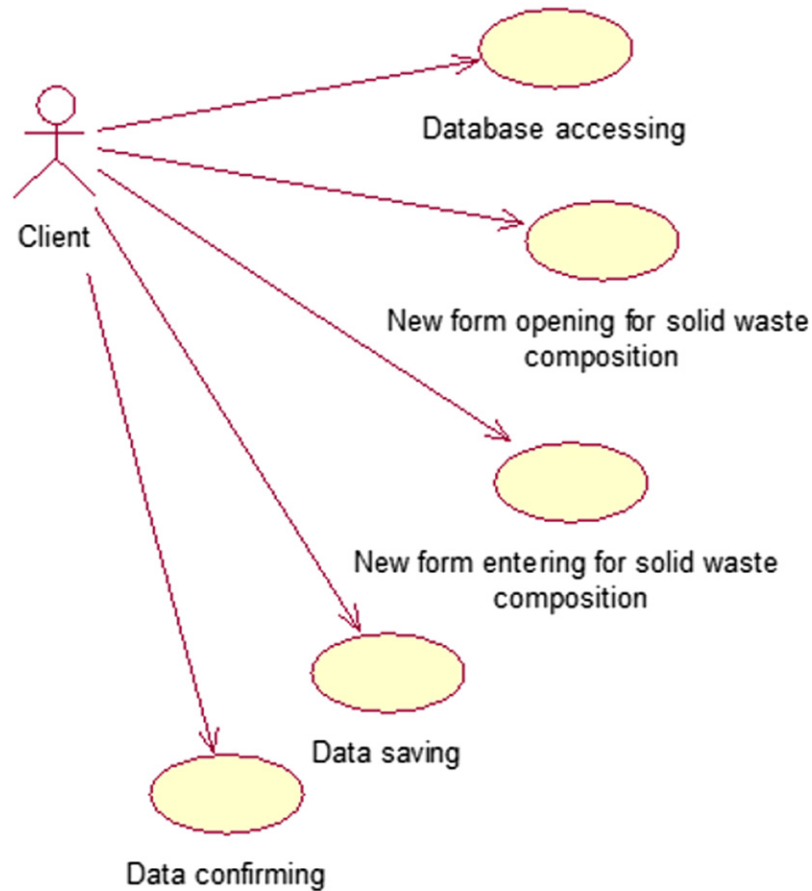


Fig. 9 Use case diagram – Recording of composition of solid waste.

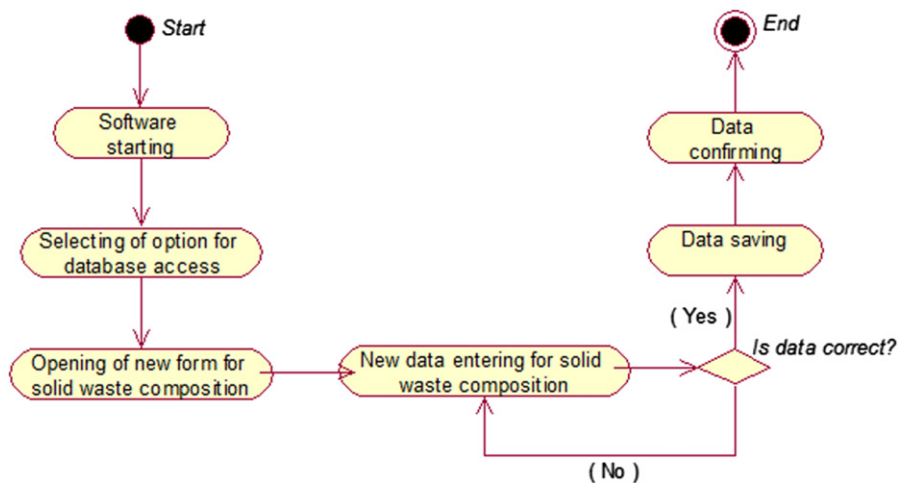


Fig. 10 Activity diagram – Recording of composition of solid waste.

Use cases of the software subsystems

Software administration

Administrator performs software administration in order to eliminate all unpredictable errors in the software and system. Administrator has full responsibility for the software maintenance. They will give permissions for other users access to the system, maintains the software, maintains the web pages of the software, maintains the software database, and makes regular daily reports.

Fig. 6 shows the use case diagram of the software administration. As can be seen there are five functions of the administration which will be explained in details by scenarios.

Table 1 shows detailed specification of use case for giving permission for database access of the software by administrator.

Table 2 shows detailed specification of the use case of software maintaining by administrator.

Table 3 shows detailed specification of use case for web pages maintaining of software by administrator.

Table 4 shows detailed specification of use case for database maintaining of software by administrator.

Table 5 shows detailed specification of use case for making of regular reports by administrator.

Recording of quantity of solid waste

Use case recording of quantity of solid waste is depicted in Fig. 7. The use case diagram has several sub use cases. Table 6 shows detailed specification for use case recording of quantity of solid waste. Fig. 8 shows activity diagram for the recording of quantity of solid waste.

Recording of composition of solid waste

Use case recording of composition of solid waste is depicted in Fig. 7. The use case diagram has several sub use cases. Table 6 shows detailed specification for use case recording of composition of solid waste. Fig. 8 shows activity diagram for the recording of composition of solid waste (Table 7; Figs. 9 and 10).

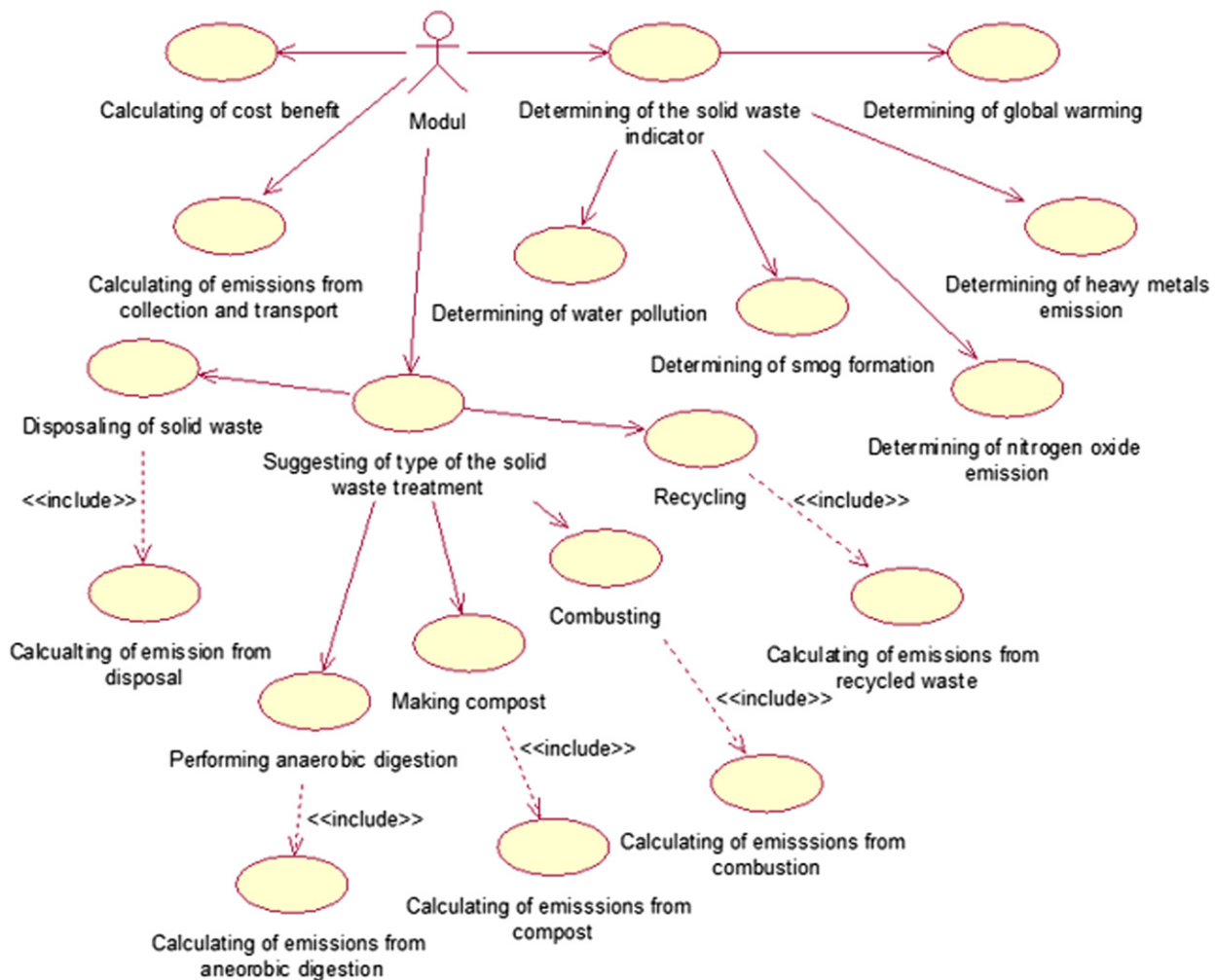


Fig. 11 Use case diagram – Determining of type of solid waste treatment.

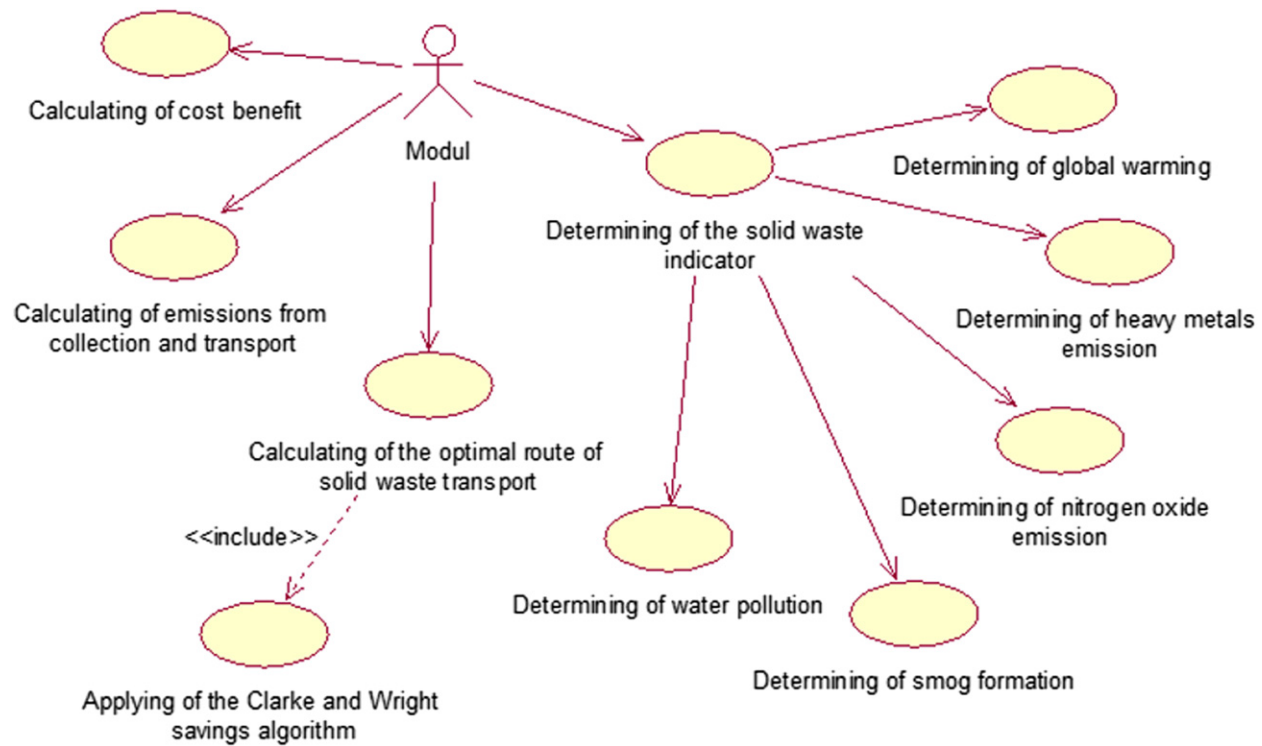


Fig. 12 Use case diagram – Determining of optimal route of solid waste transport.

Determining of type of solid waste treatment

Use case determining of type of solid waste treatment is depicted in Fig. 11. The use case diagram has several sub use cases. As can be seen the module should calculate the cost benefit and emission from collection and transport of solid waste. The module should suggest the type of the solid waste treatment. Also the module should determine the solid waste indicators.

Determining of optimal route of solid waste transport

Use case determining of optimal route of solid waste transport is depicted in Fig. 12. The use case diagram has several sub use cases. The module should calculate the optimal route of the solid waste transport.

Conclusion

Solid waste management present a big issue for all countries. One of the most common solid waste treatment method is disposal. Illegal solid waste disposal and unofficial solid waste recycling could produce high pollution of water, air and soil. There is need for systematic sustainable solid waste management system in order to preserve natural resources and to keep clean the life environment.

The main innovation of the investigation is analyzing and modeling of new software for solid waste treatment. The main suppliers could enter quantity and composition of solid waste in the software. Based on the quantity and composition the clients could decide which treatment and transport route is the best for the solid waste they collected.

See also: System Optimization for Control of Solid Waste

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Multi-Stage Stamping of Lightweight Steel Wheel Disks by Controlling its Wall Thickness Distribution

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Introduction

Lightweight metal parts are strongly demanded by industries due to constraints of economy and environment. Particularly, the reduction in weight of automobile parts has great influence on the fuel consumption of vehicles. The low emission of gas CO₂ from the lightweight vehicles prevents global warming. According to carmakers, there is an increase in mileage of 1 km/L of the fuel consumption for 100 kg of the reduction in weight of an automobile. The reduction in weight of the parts also saves cost of the material. The weight of automobile wheels directly driven by an engine has a great influence on fuel consumption of automobiles. Reduction in weight of wheel lowers the un-sprung weight of a vehicle, leading to improved car's handling, particularly in steering precision. A lighter wheel also makes it easier for the car to accelerate and to stop. Fuel consumption is improved with the lighter wheels.

Although aluminum alloy wheels are attractive for the reduction in the weight, the aluminum wheels produced by casting are costly (Fauth, 1980). Moreover, the shock resistant of cast aluminum wheels is lower than steel wheels (Marron, 2002). The mostly produced steel wheels are two-piece structure composed of the disks and rims welded together, and the disks and rims are formed by multi-stage press forming and roll forming operations, respectively as shown in Fig. 1. Marron and Verrier, (1999) have proposed a new concept of structure of steel wheels to decrease the total weight. For the reduction in weight of wheel disks, the thickness distribution is optimized because of a distribution of required strength, i.e., the wall thickness in the portion of high strength is thick and that of low strength is thin. A significant amount of the reduction in weight of the large stamped parts can be obtained by optimizing its wall thickness distribution for the required strength. Although the strength of the disk is determined by the wall thickness at the inner corner of the disk, the wall thickness at the inner corner tends to decrease in the multi-stage press forming including deep drawing. Abe et al. (2002) have prevented the decrease in wall thickness at the inner corner by optimizing drawing ratio and the punch corner in a two-stage forming process of disks. Mori et al. (2003) have developed a combined forming process of deep drawing and ironing for attaining optimum distributions of wall thickness in the wheel disks. It is desirable in automobile industry to develop forming processes for increasing the wall thickness at the inner corner. For the reduction, the application of high strength steel sheets to steel wheels tends to increase in wheel making industry (Hibon et al., 1996).

The most common type of wheel for passenger cars is made of mild steel due to low cost. According to the rotating bending fatigue test of the steel wheels (Tanaka et al., 1987), cracks tend to occur at the inner corner and the hat portion of the wheel disk as shown in Fig. 2. Since the wall thickness at the inner corner tends to decrease in the conventional multi-stage stamping of the wheel disk, large thickness blanks have been employed in the multi-stage stamping process to satisfy the high requisite strength at the inner corner, and the increase in weight results. Although the wheel disk formed from the circular tailor welded blank has optimum material strength and thickness distribution (Marron and Verrier, 1999), the welding of three or more pieces of sheet for obtaining the local thickening is not practical and costly (see Fig. 3). The control of the wall thickness distribution of the wheel disk by stamping processes is preferred due to high productivity and low cost.

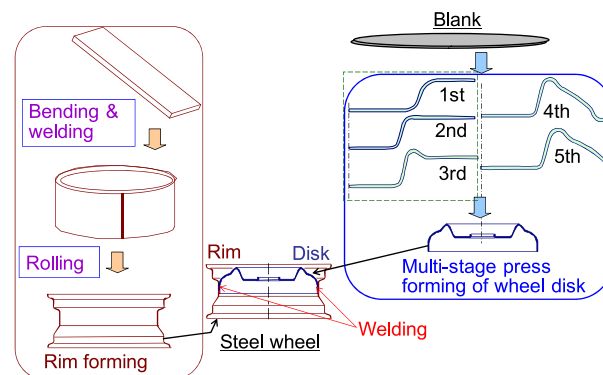


Fig. 1 Forming process of steel wheel.

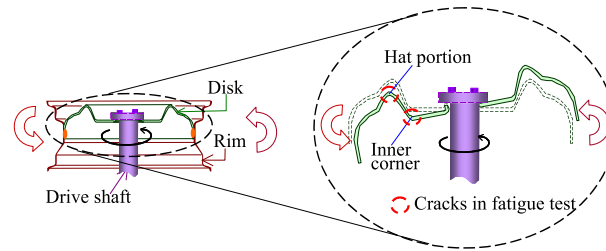


Fig. 2 Locations of cracks in rotating bending fatigue test of steel wheel.

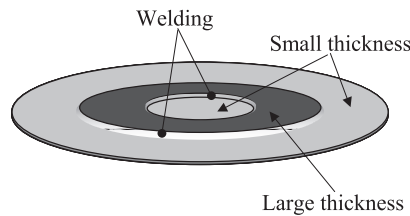


Fig. 3 Tailor blank having local thickening formed from different parts by laser welding.

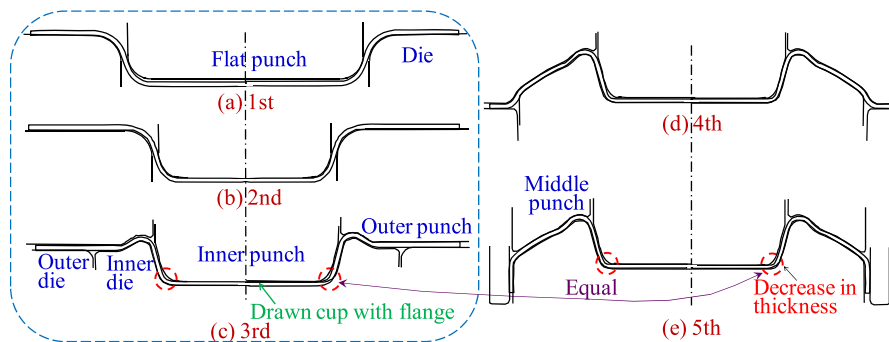


Fig. 4 Conventional multi-stage forming process of wheel disk.

Multi-Stage Stamping of Lightweight Steel Wheel Disk

Conventional Process

The disks in the steel wheels are formed by multi-stage sheet metal forming operation shown in Fig. 4. The blank is deeply drawn in the 1st stage, and then the cup with a flange is redrawn in the 2nd stage. In the 3rd, 4th and 5th stages, the flange of the disk is formed, and the wall thickness at the inner corner of the disk hardly changes in these stages. Since the inner flat region of the disk is connected to the driven shaft, the requisite strength at the inner corner is high, and thus the wall thickness of the corner is set to be large in the design of products. The wall thickness at the inner corner, however, becomes small due to the stretching during the deep drawing and redrawing in the 1st and 2nd stages. To satisfy the requisite strength at the inner corner, the thickness of the blank becomes large, and thus the increase in weight of the wheel disk results.

Increase in Wall Thickness at Inner Corner of Drawn Cup With Flange Using Conical Punches

The increase in wall thickness at the inner corner of the drawn cup with a flange by compression is illustrated in Fig. 5 (Tan et al., 2007). Since the portions in the 1st and 2nd stages equivalent to the inner corner after the 3rd stage are not located near the punch corners, the local thinning in the 1st and 2nd stages is prevented. In the 3rd stage, the side wall and conical bottom of the cup are compressed with the outer punch. Finally, the bottom of the cup is formed with the inner punch into the flat one in the 3rd stage. The wall thickness at the inner corner hardly changes in the 4th and 5th stages. Only the first three-stage forming process is dealt with in the present study.

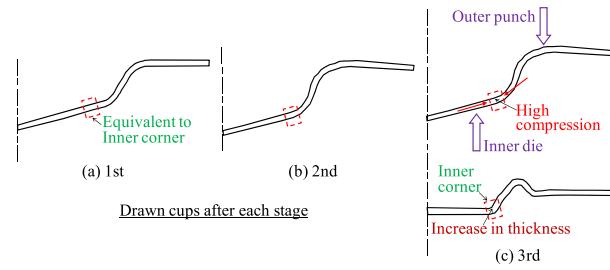


Fig. 5 Increase in wall thickness at inner corner of drawn cup by compression. Reproduced from Tan, C.J., Abe, Y., Mori, K., Nonaka, T., Ebihara, O., 2007. Increase of wall thickness around corner of multi-stage drawn cup with flange using conical punches. *Key Engineering Materials*, 340–341, pp. 761–766.

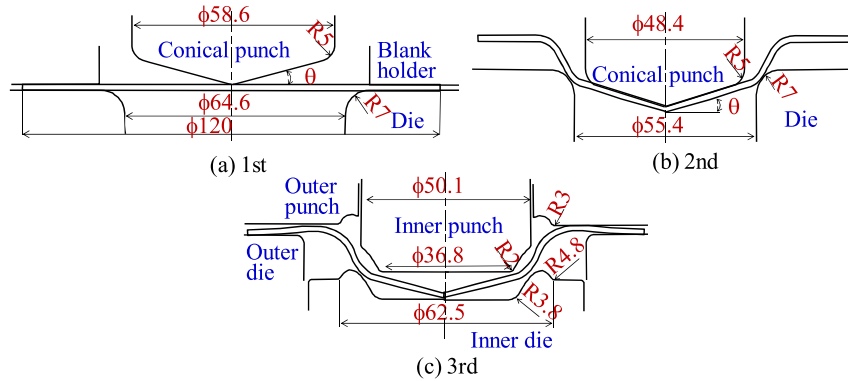


Fig. 6 Conditions for 3-stage forming of drawn cup with flange. Reproduced from Tan, C.J., Abe, Y., Mori, K., Nonaka, T., Ebihara, O., 2007. Increase of wall thickness around corner of multi-stage drawn cup with flange using conical punches. *Key Engineering Materials*, 340–341, pp. 761–766.

The detailed experimental conditions for the 3-stage forming process of the drawn cup with a flange are shown in Fig. 6. The same conical punch angle θ was employed in the 1st and 2nd stages to avoid local thinning around the portion equivalent to the inner corner. The punch angle and stroke in the 1st and 2nd stages were changed in the experiment to increase the wall thickness around the inner corner after the 3rd stage. The experiment of the 3-stage forming process of mild steel blanks having an initial thickness of 1.6 mm was performed. The size of the disk is approximately 1/3.5 of the actual one. All contact surfaces were lubricated with a press oil except the interfaces involving the conical punches were kept dry.

Definition of Drawn Volume

The increase in wall thickness at the inner corner is greatly influenced by the drawn volume into the die after the 2nd stage shown in Fig. 7, because the drawn volume is compressed in the 3rd stage. The drawn volume V after the 2nd stage is approximated by

$$V = \frac{\pi \{D_0^2 - [D_2^2 - (D_{D2} + 2R_{D2})^2]\}t}{4} \quad (1)$$

Where,

D_0 is the initial diameter of the blank, D_2 is the outer diameter of the cup after the 2nd stage, D_{D2} is the diameter of the die in the 2nd stage, R_{D2} is the corner radius of the die in 2nd stage and t_0 is the initial thickness of the blank.

The relationships between the punch angle and the punch stroke in the 2nd stage for maintaining same $V \approx 7700 \text{ mm}^3$ are given in Fig. 8. As the punch angle in the 2nd stage increases, the punch stroke is increased to maintain is at the same drawn volume level. The punch stroke in the 1st stage is approximately 10% less than the 2nd stage.

The wall thickness distributions of the drawn cups with a flange after the 3rd stage for $\theta = 0^\circ$, 15° , 25° and 30° obtained from experiment are shown in Fig. 9. A maximum 12.5% increase in thickness at the inner corner for $\theta = 25^\circ$ was obtained. For the large punch angle, the thinning at the center of the cup occurs. Since the central portion of the cup is punched as a hub hole of the wheel, this thinning is not a defect. In the fatigue test of the steel wheel disk, the crack also occurred at the hat portion (Marron and Verrier, 1999). The fatigue strength of the steel wheel is greatly improved from the increase in wall thickness at the hat portion.

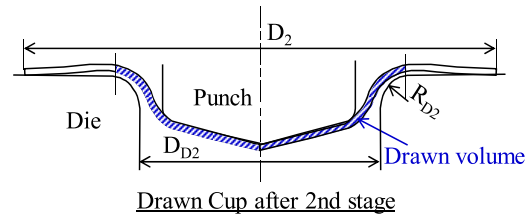


Fig. 7 Definition for drawn volume.

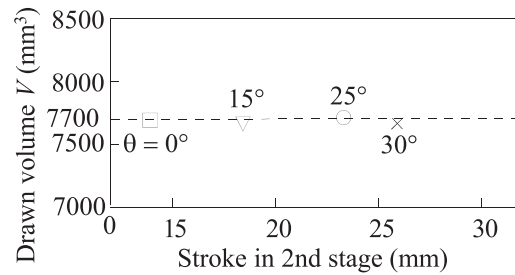


Fig. 8 Relationships between punch angle and punch stroke in 2nd stage for maintaining same $V \approx 7700 \text{ mm}^3$. Reproduced from Tan, C.J., Abe, Y., Mori, K., Nonaka, T., Ebihara, O., 2007. Increase of wall thickness around corner of multi-stage drawn cup with flange using conical punches. Key Engineering Materials, 340–341, pp. 761–766.

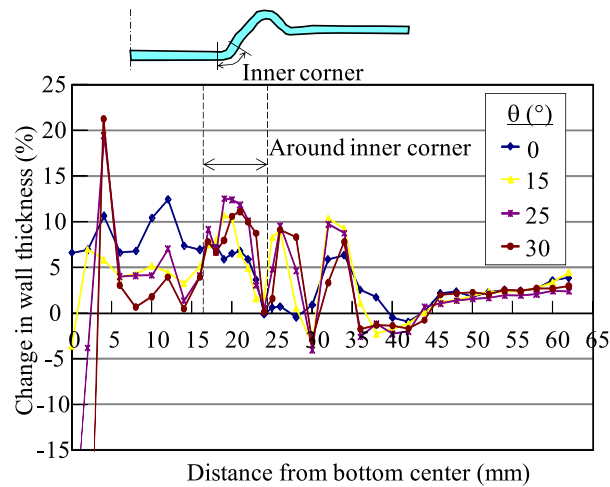


Fig. 9 Wall thickness distributions of drawn cups with flange after 3rd stage for $\theta = 0^\circ, 15^\circ, 25^\circ$ and 30° obtained from experiment.

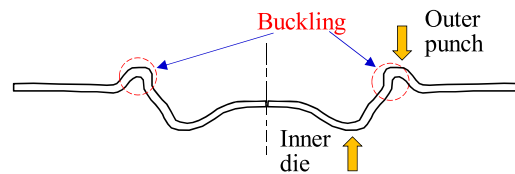


Fig. 10 Buckling at hat portion of drawn cup after 3rd stage for $V \approx 8840 \text{ mm}^3$. Reproduced from Tan, C.J., Abe, Y., Mori, K., Nonaka, T., Ebihara, O., 2007. Increase of wall thickness around corner of multi-stage drawn cup with flange using conical punches. Key Engineering Materials, 340–341, pp. 761–766.

Although it is possible to further increase the wall thickness around the inner corner in the 3rd stage with large drawn volume, buckling was observed in the cup after the 3rd stage for $V \approx 8840 \text{ mm}^3$ due to the excessive compression as shown in Fig. 10. The increase in the drawn volume after the 2nd stage is limited by the occurrence of buckling.

Conclusion

The reduction in weight of automobile parts is strongly demanded to improve fuel consumption of automobiles. Since forming processes are utilized for production of a lot of automobile parts because of high productivity, optimization of forming processes is a key to the reduction in weight. It is increasingly important to control the wall thickness distributions of products by forming. In this paper, the wall thickness at the inner corner of a wheel disk obtained from experiment was successfully increased by 12.5% for the punch angle of 25° in the 1st and 2nd stages. The reduction in weight of the wheel disk can be obtained by decreasing the blank thickness.

See also: A Review on Utilization of Electronic Waste Plastics for Use Within Asphaltic Concrete Materials: Development, Opportunities and Challenges for Successful Implementation

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Nanomaterials

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Introduction

Nanomaterials (NMs) have attracted intense research interests due to their application potential in various fields of science and technology such as health care, food, textile and electronics (OECD Environment Directorate, 2014). As the characteristics of NMs fall between single atom and bulk materials, they generally exhibit unique and significantly improved but sometimes unpredictable physical, chemical, and biological properties which are different from their bulk materials (nanoDE-Report, 2013). The NMs contain at least one structural dimension at the nanoscale (10^{-9} m) and they are classified according to the dimensions of their structural elements like zero (0D), one (1D), two (2D), and three (3D) dimensional. All the 0D, 1D, 2D and 3D nanostructures can be amorphous or monocrystalline. Nanomaterials can also be brittle or ductile. There are various types of NMs and depending on their construction, they are currently classified as (i) carbon-based, (ii) metal-based, (iii) dendrimers, and (iv) composites (Saleh, 2016).

Carbon-based NMs are receiving special attention in the scientific and engineering community because of their multi-faceted superiority in thermal conductivity, flame retardancy, mechanical stability and biocompatibility (Liu *et al.*, 2018). Metal based nanomaterials have drawn significant attention as energy storage devices. These electrochemical energy storage (EES) devices with their high efficiency, versatility and adaptability have emerged as one of the most promising energy storage systems. Batteries and supercapacitors are the two types of EES devices, whose performance is largely dependent on electrode materials (Khaligh and Li, 2010; Beidaghi and Wang, 2012).

Ideally the electrode materials should possess porous structures with high surface area, high electrical conductivity and excellent recycling capability (Yu *et al.*, 2015). Micro-sized EES devices have customized configuration as well as excellent mechanical stability for easy insertion into other micro-electronics (Gogotsi and Simon, 2011; Wang *et al.*, 2014). Moreover, easy ion transport is another requirement with the real capacitance and energy density. However, the bulk form of material with high capacity and energy density exhibits surfaces that are unstable or reactive in electrochemical environment when downsized to nanometer length scales. Hence, the manufacturing strategy and surface engineering play important roles to overcome the bottlenecks of EES from NMs.

Dendrimers are man-sized symmetric molecules. The surface of a dendrimer has many chain ends and as a result there can be change in size, shape, and adaptability to another element (Mendes *et al.*, 2017). Furthermore, three-dimensional dendrimers can have inside cavities into which different particles can be set for different applications in both biological and materials sciences (Mendes *et al.*, 2017). The properties of composite NMs can be designed according to their application or requirement and the properties are dependent on the choice of matrix, curing phase, shape and orientation (Sahay *et al.*, 2014).

However, in this review, we outline the synthesis and production of low cost carbon NMs and their applications, different energy storage devices from NMs and the advances in manufacturing and surface engineering to produce reliable and efficient EES. Such efforts may be helpful for proper expansion of applications and research interest toward further development of nanotechnology.

Carbon Nanomaterials (CNMs)

Carbon is a unique element in the periodic table which acts as the basis of all forms of life on earth. Carbon-based nanomaterials with their exceptional characteristics are promising candidates for future areas of important applications. The dimensionalities in carbon nanomaterials range from zero, one, two and three dimensional structures such as fullerenes, carbon nanotubes (CNTs), nanofibers, graphene and nanodiamond (Ravi and Vadukumpully, 2016). The CNTs were first reported in 1991 (Iijima, 1991) and graphene was discovered in 2004 (Novoselov *et al.*, 2004). Both of them exhibit extraordinary mechanical strength and electrical conductivity, remarkable physical and chemical properties which make them attractive for use as key components in catalysts, biosensors, fuel cells, batteries and electronic devices (Deng *et al.*, 2016; Xu *et al.*, 2014; Avouris and Dimitrakopoulos, 2012; Kumar *et al.*, 2016). Graphene is a flat monolayer of carbon atoms tightly packed into a 2D honeycomb lattice, and it can be considered as the mother form of all the other carbon nanostructures. This can be wrapped up into 0D fullerenes, rolled into 1D tube or stacked into 3D graphite (Fig. 1).

Carbon dots (CDs) and graphene quantum dots (GQDs) are receiving tremendous attention for a wide range of applications due to their attractive properties like chemical inertness, tunable photoluminescence, nontoxicity and excellent biocompatibility (Wang *et al.*, 2016; Zhu *et al.*, 2015; Zhang *et al.*, 2017a; Kozák *et al.*, 2016; Yew *et al.*, 2017). Though there is numerous fabrication

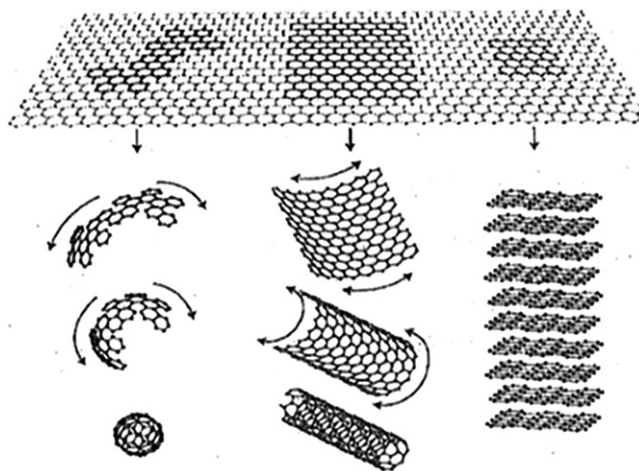


Fig. 1 Graphene as a 2D building material for carbon materials of all other dimensionalities: 0D fullerenes, 1D nanotubes or 3D graphite. Adapted from Ravi, S., Vadukumpully, S., 2016. Sustainable carbon nanomaterials: Recent advances and its applications in energy and environmental remediation. *J. Environ. Chem. Eng.* 4, 835–856.

strategies, the mass production of environment friendly carbon based nanomaterials at low cost is still a major challenge. The high cost of production has restricted the commercialization of these materials. Hence, green fabrication routes to prepare carbon based nanomaterials via cost-effective approaches are of great interest.

Coal and biomass or waste residues have gained momentum in carbon nanomaterial research (Hu *et al.*, 2016). Coal is a heterogeneous material with a three dimensional cross-linked network. It consists of aromatic and hydro aromatic units which are connected by short aliphatic and ether linkages (Ye *et al.*, 2013; Vasireddy *et al.*, 2011).

The carbon concentration varies from 70 wt% in lignite to 75 and 85 wt% in sub-bituminous and bituminous coal respectively, and reaching 94 wt% in anthracites (Vasireddy *et al.*, 2011; Mathews and Chaffee, 2012). In addition, coal is a low-cost resource abundantly available in nature (Hu *et al.*, 2016; Vasireddy *et al.*, 2011; Islam *et al.*, 2017; Dong *et al.*, 2014; Tilman *et al.*, 2006) and, thereby, making coal a promising carbon source for the preparation of nanomaterials.

One of the rich sources of carbon is renewable sources like biomass and waste residues. They are available in plenty and are cost-effective and renewable. Several promising reports have emerged in the recent years on the synthesis of carbon nanomaterials from inexpensive resources through commercially viable and environmental friendly approaches (Hu *et al.*, 2016).

Synthesis and Properties of Carbon Nanomaterials From Coal and Sustainable Resources

Diverse classes of coal and sustainable resources to synthesize carbon based nanomaterials are shown in Figs. 2 and 3 (Ravi and Vadukumpully, 2016; Hoang *et al.*, 2018) along with a discussion on the relevant properties.

Carbon nanotubes (CNTs) from coal

There are various techniques for the production of CNTs of which thermal plasma, chemical vapor deposition (CVD) and arc discharge are noteworthy. Tian *et al.* (2004a) first developed the thermal plasma method for the production of multi-walled CNTs (MWCNTs) by injecting Baode coal fine powders of 5–25 μm size directly into an arc plasma jet. The obtained MWCNTs had interlayer 0.343 nm spacing and length 7 μm . The Raman spectra showed 2 peaks at 1600 and 1291 cm^{-1} , corresponding to G (graphitic order) and D (defect signal) peaks, respectively. The low value of I_G/I_D ratio, illustrates the low-graphitized MWCNTs. However, the addition of 5 wt% Cu powder to coal promoted the yield of CNTs. The effect of three catalysts (Cu, Fe and Co) on the formation of CNTs was found to be significant (Tian *et al.*, 2004b).

Using Cu as catalyst, the diameter of MWCNTs was in the range of 50–70 nm and the yield of CNTs with Cu catalyst (5%) was higher than compared to Fe or Co (1%). Chemical vapor deposition (CVD) is another technique which is widely employed at large-scales to produce CNTs (Moothi *et al.*, 2012). In 2015, Moothi *et al.* (2015) produced CNT from the Bank Colliery-Witbank coal, South Africa at a pyrolysis temperature of 400–750°C and the resultant gases composed of CH_4 and CO were then fed to a vertical reactor tube at 900°C for CNT synthesis with ferrocene as a catalyst. In Fig. 4 the TEM images of CNT at different pyrolysis temperatures are given.

With the increase of pyrolysis temperature, the dimensions of CNT reduce significantly. Song *et al.* (2018) demonstrated the fabrication of MWCNTs from coal tar pitch in an alumina tube furnace with $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as a catalyst. Cobalt accelerated C_2H_4 dissociation via electron donation effect, followed by the formation of straight MWCNTs through diffusion-precipitation mechanism. Ultimately, at the pyrolysis temperature of 1173 K with 0.75 wt% Co clusters, the optimized quality of CNTs ($I_G/I_D = 1.19$) was achieved with diameter of 40 nm and length of 200 μm .

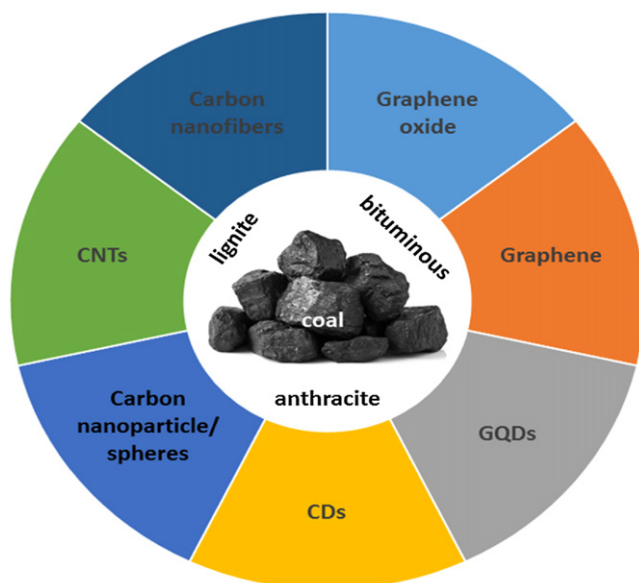


Fig. 2 Various types of coal as precursors for synthesizing carbon based nanomaterials. Reproduced from Hoang, V.C., Hassan, M., Gomes, V.G., 2018. Review coal derived carbon nanomaterials – Recent advances in synthesis and applications. *App. Mater. Today* 12, 342–358.

RAW MATERIALS



WASTE MATERIALS USED AS FEEDSTOCKS FOR CNM GENERATION



Fig. 3 Feedstocks pyrolyzed (from left to right): Corn residue, sugar cane bagasse, waste tyres, postconsumer PE and PET. Reproduced from Ravi, S., Vadukumpully, S., 2016. Sustainable carbon nanomaterials: Recent advances and its applications in energy and environmental remediation. *J. Environ. Chem. Eng.* 4, 835–856.

Carbon nanotubes (CNTs) from sustainable sources

High quality CNTs and related structures can be manufactured from relatively inexpensive feedstock like waste plastics post-consumer PE and PET, agricultural wastes (sugar cane bagasse and waste corn residue obtained after extracting the starch fraction of corn for bioethanol production, scrap tyre chips, etc. (Zhuo *et al.*, 2012)).

The granulated solid feedstocks were first pyrolyzed in a furnace in an inert atmosphere (nitrogen) to generate gaseous carbon containing components. The gases were directed to a venturi where they were mixed with pre-heated oxygen containing gases or with additional inert gases. The fuel to oxygen ratio was pre-adjusted to fuel-rich condition to ensure adequate amount of carbon containing components, hydrogen and water vapor are formed for the growth of CNTs. The partially oxidized effluent was then synthesized in a second furnace synthesis reactor with fixed catalyst substrate for the growth of CNTs. The operating temperatures of both the pyrolysis furnace and the synthesis reactor were in the range 600–1000°C. The shapes and sizes of CNTs from the waste are presented in **Table 1** (Ravi and Vadukumpully, 2016) and TEM images are given in **Fig. 5** (Zhuo *et al.*, 2012).

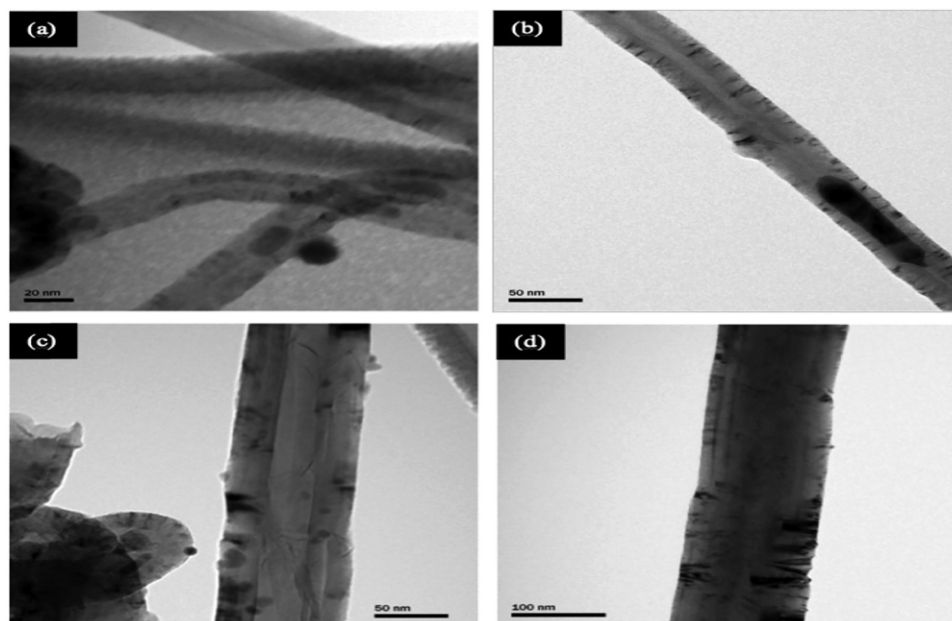


Fig. 4 TEM images of CNTs produced at a temperature of 900°C in the CVD reactor with coal pyrolysis reactor temperatures of (a) 400, (b) 450, (c) 500, and (d) 550°C. Reproduced from Moothi, K., Simate, G.S., Falcon, R., Iyuke, S.E., Meyyappan, M., 2015. Carbon nanotube synthesis using coal pyrolysis. *Langmuir* 31, 9464–9472.

Table 1 CNTs synthesized from waste

Residue source	Shape	Size
Corn	Twisted structure with irregular shape	100–200 nm (width)
Sugar bagasse	Straight, smooth cylindrical shape	~50 μm long, dia 20.8 nm
Waste tyre	Long, entangled braid-like	~40 μm long
PE	Hollow	1–5 μm long, dia 15.8 nm

Raman spectroscopy showed strong peaks of the G-band, indicating the presence of graphitic carbon (Dresselhaus *et al.*, 2010). Besides, there were peaks of 2D and D bands, signifying the presence of parallel graphite layers and disordered structure or impurities respectively. The I_G/I_D ratio was higher for the bagasse and least for tyre waste. The effluents of biomass waste were rich in methane and other light aliphatic compounds. The effluents for PET had high mole fraction of benzene, whereas, PE effluents were rich in ethylene, propylene and acetylene. Hence, biomass waste is a promising source to provide carbon feedstocks for generating various carbon nanostructures and also cogenerate syngas.

Graphene and related structure from coal

There are various techniques to fabricate graphene. Awasthi *et al.* (2015) formed graphene like nanosheets using annealed bituminous coal as an anode under H_2 gas environment using the arc discharge set-up. Graphene in the product was confirmed by the hexagonal pattern in TEM images, together with the evidence of D (1346 cm^{-1}), G (1573 cm^{-1}) and 2D (2688 cm^{-1}) in Raman spectra. In 2014 Graphene nanosheets were also fabricated by Xu *et al.* (2014) through pyrolysis of coal tar pitch at 1700°C using Al powder as a catalyst. The Raman spectrum exhibited a weak D band at 1351 cm^{-1} and strong G band at 1583 cm^{-1} with I_D/I_G of 0.26. A symmetric 2D peak at 2695 cm^{-1} with an intensity ratio of 2D to G (I_{2D}/I_G) bands of 0.82 was also obtained, illustrating that the product comprised few-layer graphene sheets with small amount of defects.

Graphene and related structure from sustainable sources

Wastes with low or negative monetary value like common solid waste, grass blades, dog feces and cockroach legs are used as carbon source. In a tube furnace under H_2/Ar environment, the solid carbon sources are decomposed or diffused to the backside of Cu foil at 1050°C . High quality pristine graphene with few defects and ~97% transparency is confirmed by Raman and UV-vis spectroscopy. In XPS analysis, no heteroatoms were detected (Ruan *et al.*, 2011). High quality graphene was also extracted from hibiscus flowers and lotus petals (Ray *et al.*, 2012) by thermal exfoliation using Ar gas at a temperature of 1600°C . Graphene was also produced from sugar cane. Sugar coated sand was heated in silica crucible in a furnace at 750°C for 3 h in N_2 atmosphere. The composite has application in water purification.

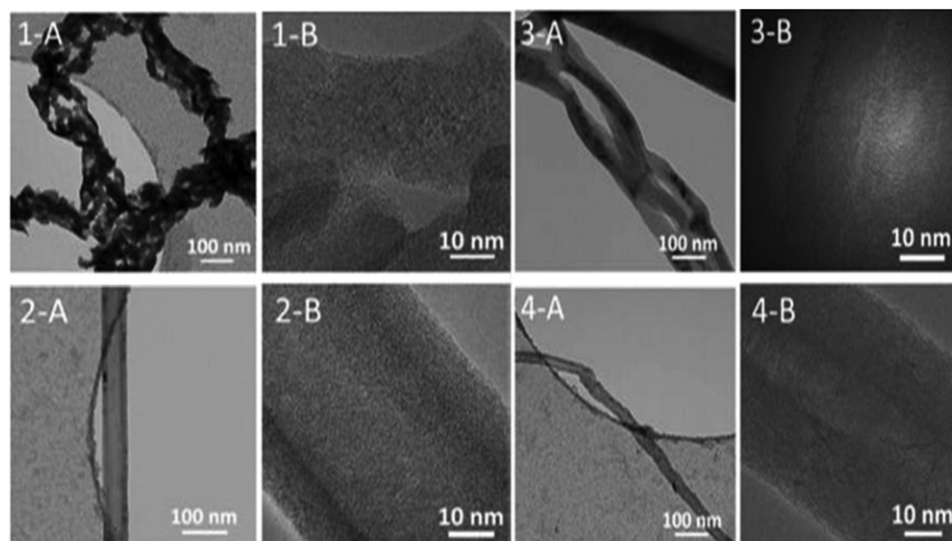


Fig. 5 TEM images taken at low magnification (A) and high magnification (B) of carbon nanomaterials derived at optimum conditions from carbon feedstock such as (1) waste corn residue (2) waste sugar cane bagasse (3) waste tyres, and (4) PE. Reproduced from Zhuo, C., Joner, O. A., Tenorio, J.A.S., Levendis, Y.A., 2012. Synthesis of carbon nanomaterials through up-cycling agricultural and municipal solid wastes. *Ind. Eng. Chem. Res.* 51, 2922–2930.

Many natural products like proteins, vitamin C, glucose, green tea solution (Liu *et al.*, 2010a; Zhang *et al.*, 2010; Zhu *et al.*, 2010; Wang *et al.*, 2011b) are used as reducing agents to produce graphene from GO. The polyphenol (TPs) in green tea is biocompatible and biodegradable and schematic illustration of TP reduced graphene is shown in Fig. 6. The synthesized graphene opens up interesting bio applications.

Graphene quantum dots (GQDs) from coal

GQDs are a new class of materials that have attracted worldwide research attention in the past few years due to exceptional spin (Trauzettel *et al.*, 2007), electronic (Ritter and Lyding, 2009), and optical properties (Ritter and Lyding, 2009). Chemical oxidation is the most widely implemented technique to fabricate GQDs from coal.

The size of GQDs can be easily tuned by the use of different coal precursors and the fluorescence can be varied by the change of temperatures. It was first reported by Ye *et al.* (2013) that GQDs can be fabricated from 3 different types of coals which are bituminous, coke and anthracite in a facile one-step. Bituminous coal is chemically oxidized in a mixture of concentrated H_2SO_4 and HNO_3 acids at 100 and 120°C for a day, followed by neutralization to pH 7 and dialysis for 5 days to obtain b-GQDs. The size and thickness of GQDs were 2.96 ± 0.96 and 2.30 ± 0.78 nm and 1.5–3 nm (Fig. 7(a–d)) respectively. Raman spectra revealed the value of I_D/I_G to 1.55 ± 0.19 . Green and strong blue fluorescence were emitted at 500 and 460 nm respectively at 345 nm UV irradiation.

The size of GQDs was adjusted to 29 ± 11 and 5.8 ± 1.7 nm by choosing anthracite and coke as starting materials and the intensity of D to G peaks I_D/I_G obtained were 1.90 ± 0.22 and 1.28 ± 0.18 respectively. The emitted fluorescence was of yellow and green with maximum emission wavelength at 530 and 480 nm, respectively. By changing the oxidation temperature, the same group produced GQDs of different size ranges and luminescence (Ye *et al.*, 2015).

It was also found that GQDs/PVA composite film emitted white photoluminescence (PL) under UV light and the peak intensity was obtained at 10% loading of GQDs. The quantum yield was obtained at 0.5% (He *et al.*, 2014). The properties of electrospun carbon nanofiber fabrics improved significantly when bituminous derived GQDs was used to a polyacrylonitrile (PAN) solution, followed electrospinning and carbonization at 1000°C under N_2 gas (Zhu *et al.*, 2018).

Graphene quantum dots (GQDs) from sustainable sources

There are various natural sources to produce GQDs but microwave assisted hydrothermal process using glucose as precursor showed promising result (Tang *et al.*, 2012). The authors also suggested that most of the carbohydrates which contain C, H and O in the ratio of 1:2:1 (sucrose, fructose) could also be used as the carbon source to prepare GQDs provided that H and O exist in the form of hydroxyl, carboxyl or carbonyl groups. The size of the GQDs could be tuned from 1.65 to 21 nm by simply extending the heating time from 1 to 9 min, respectively (Fig. 8).

The GQDs display deep ultraviolet emission at 4.1 eV. However, the emission wavelength is independent of the size of the GQDs. Fig. 9 shows the PL properties of the microwave assisted synthesized GQDs.

The emission peak is varied with the excitation frequency. The various functional groups present on the GQD surface acted as “surface state” energy levels between π and π^* states of $\text{C}=\text{C}$. These functional groups possess various energy levels resulting in a series of emissive traps. When a particular excitation wavelength irradiates the GQDs, the surface state emissive trap would dominate the

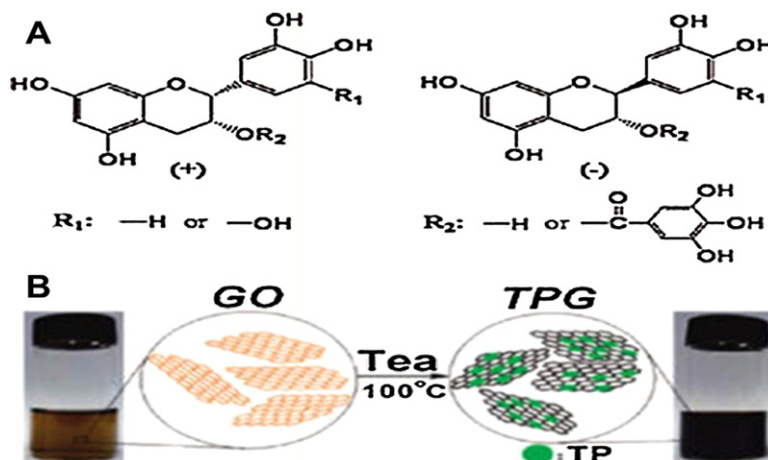


Fig. 6 (A) Chemical structure of tea polyphenols (TPs). (B) Schematic illustration of the preparation of TP reduced graphene. Reproduced from Wang, Y., Shi, Z., Yin, J., 2011b. Facile synthesis of soluble graphene via a green reduction of graphene oxide in tea solution and its biocomposites. *ACS Appl. Mater. Interfaces* 3, 1127–1133.

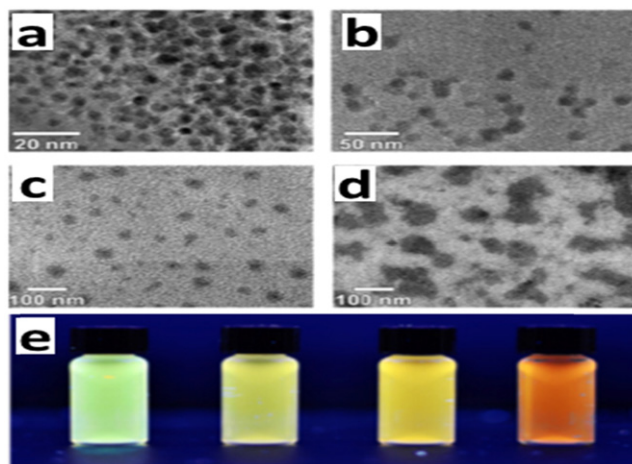


Fig. 7 TEM images of GQDs with size of (a) 4.5 ± 1.2 , (b) 16 ± 1.33 , (c) 41 ± 6.4 and (d) 70 ± 15 nm; (e) solution of GQDs under 365 nm excitation UV lamp. The left-most vial is the GQDs solution with size of 4.5 ± 1.2 nm, then 16 ± 1.33 , 41 ± 6.4 nm and the right-most vial is the GQDs solution with size of 70 ± 15 nm. Reproduced from Ye, R., Peng, Z., Metzger, A., *et al.*, 2015. Bandgap engineering of coal-derived graphene quantum dots. *ACS Appl. Mater. Interfaces* 7, 7041–7048.

emission. With change in excitation wavelength, the surface state emissive trap that dominates the emission would also change. The GQDs are capable of converting blue light into white light when the GQDs are coated onto a blue light emitting diode. Due to the luminescence stability, biocompatibility, low toxicity and high water solubility, these GQDs function as outstanding probes for high contrast bio imaging and sensing applications. Since the PL is tunable, these GQDs find interesting applications in optoelectronics. **Fig. 10** shows the UV-vis absorption spectra and the PL spectra of the GQDs derived from carbon fibers.

It is evident that the reaction temperatures affect the absorption properties of the as synthesized GQDs since there is a clear blue shift from 330 to 270 nm with increasing temperature. The temperature could also change the distribution of emission wavelength of the GQDs.

Carbon dots (CDs) from coal

Carbon nanoparticles less than 10 nm in size are amorphous in nature and are called carbon dots. They have excellent optical properties and fluorescence emissions and are ideal candidates for numerous applications in sensing, bio-imaging and photo voltaic (Wang *et al.*, 2011a). Similar to GQDs, CDs are also produced by a top-down strategy as listed in **Table 2** (Hoang *et al.*, 2018).

Chemical oxidation is simple and effective in large-scale production of CDs from coal. However, the use of strong oxidizing agent (e.g., HNO_3), releases toxic gases, and the removal of excess acid is quite costly. Therefore, green and safe strategies were developed where, Hu *et al.* (2016) employed H_2O_2 to oxidize anthracite at 80°C for only 3 h to produce CDs. The excess hydrogen peroxide could

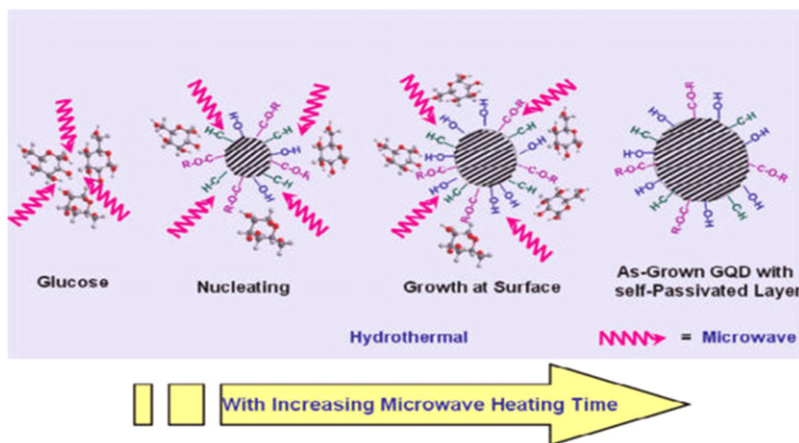


Fig. 8 Schematic representation showing the preparation of GQDs. Reproduced from Gupta, V., Chaudhary, N., Srivastava, R., *et al.*, 2011. Luminescent graphene quantum dots for organic photovoltaic devices. *J. Am. Chem. Soc.* 133, 9960–9963.

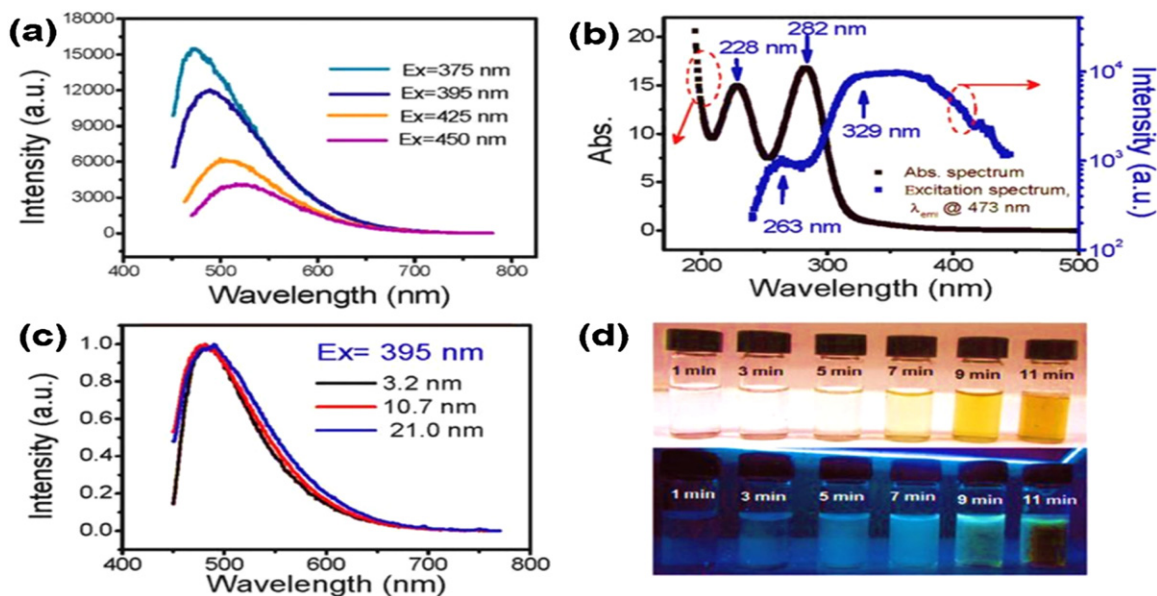


Fig. 9 PL properties of the GQDs. (a) The PL spectra of the GQDs excited by various wavelengths; (b) the absorbance and excitation spectra of the GQDs solution; (c) the normalized PL spectra of the GQDs with various sizes; (d) the GQDs solutions irradiated by ambient light (top) and 365 nm UV lamp (bottom). The GQDs were prepared with 11.1 wt% glucose solution for 5 min (a and b), 5–9 min (c), 1–11 min (d) microwave heating at 595 W. Reproduced from Gupta, V., Chaudhary, N., Srivastava, R., *et al.*, 2011. Luminescent graphene quantum dots for organic photovoltaic devices. *J. Am. Chem. Soc.* 133, 9960–9963.

be removed by simple solution boiling. The fabricated CDs were in size range of 1–3 nm and crystalline structure with (100) lattice spacing of 0.21 nm exhibited a wavelength dependent PL property and emitted cyan fluorescence when excited at 365 nm.

When the CDs were further functionalized with ethylene diamine (EDA), a red shift in the PL emission with emission maxima at ~510 nm and green fluorescence at 375 nm UV irradiation was obtained. [Thiyagarajan *et al.* \(2016\)](#) synthesized CDs of tunable size and surface functionalization by refluxing, microwave irradiation and laser ablation from lignite using an EDA solution. The obtained CDs which were 35–90, 20–50 and 2.5–5.5 nm in size and all had excitation dependent PL behavior with maximum emission wavelength at ~468, 435 and 403 nm, respectively. The CDs were also obtained by refluxing and microwave irradiation methods which exhibited an absorption peak at ~260 nm due to $\pi - \pi^*$ transition of C = C bonds and shoulder at ~325 nm assigned to $\pi - \pi^*$ transition of the surface functional groups whereas the former peak shifted to ~220 nm in the case of CDs prepared by laser ablation strategy. However, low PL quantum yields were achieved ($\leq 6\%$ for all samples).

Carbon dots (CDs) from sustainable sources

Orange juice is a natural bio resource with key components sucrose, fructose, glucose, citric acid and ascorbic acid. Highly fluorescence CDs are obtained by hydrothermal treatment as shown in [Fig. 11](#). It is nontoxic with good stability and of PL

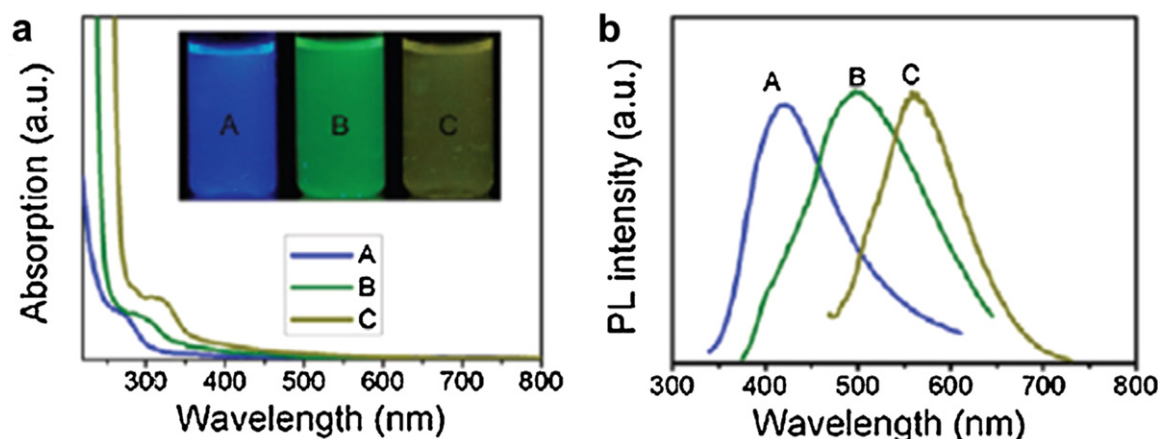


Fig. 10 Optical properties of the GQDs. (a) UV-vis spectra of GQDs A, B, and C, correspond to synthesized reaction temperature at 120, 100, and 80°C, respectively. Inset of panel (a) is a photograph of the corresponding GQDs under UV light with 365 nm excitation. (b) PL spectra of GQDs with different emission color excited at 318, 331, and 429 nm, respectively. Reproduced from Peng, J., Gao, W., Gupta, B.K., *et al.*, 2012. Graphene quantum dots derived from carbon fibers. *Nano Lett.* 12, 844–849.

Table 2 CDs synthesized from different types of coal

Precursor	Product	Fabrication route	Diameter, nm	Yield, %	Quantum yield, %	Optical properties	
						$\lambda_{em, max}, nm$	Color under UV light
Coal	CDs	Chemical oxidation	3–5				
Lignite	CDs	Refluxing	35–90	4.5		468	
		Microwave irradiation	20–50, average 35	5.1		435	
		Laser ablation	2.5–5.5, average 3.5	6		403	
		Laser ablation and dispersion in Na ₂ SO ₄		34.5		493	
Coal tar	CDs	Chemical oxidation and solvothermal	1.5–4.5	29.7		605	Orange (toluene)
	Liposome/CDs composite		50–100	10.7		640	Blue (toluene), white (H ₂ O)
Anthracite	N-doped CDs	Solvothermal	4.7	25.6	47	445	Cyan
Anthracite	CDs	Chemical oxidation	1.96 ± 0.73	7	Relative QY ~0.67	420	
		Calcination at 900°C and Chemical oxidation	2.27 ± 0.74	30	Relative QY ~0.7	420	
		Calcination at 1500°C and Chemical oxidation	3.1 ± 0.8	5	Relative QY ~1	505	
	Reduced CDs	NaBH ₄ reduction of CDs-900			8.8	400	Blue
Anthracite	CDs	Chemical oxidation	1–3	50–60		455	Cyan

quantum yield of 26%. The process is green and cost effective as there is no use of strong acid or passivation agents during synthesis (Bourlinos *et al.*, 2012; Zhang *et al.*, 2012). However, to improve the electronic properties, enhanced surface and local chemical reactivity, Hu *et al.* (2016) doped CDs with ultra-small nitrogen (N) and sulfur (S) (N, S-CDs) which was synthesized from rice and N-acetyl-L-cysteine (NAC) by microwave assisted pyrolysis.

The N, S-CDs had enhanced PL properties compared to undoped CDs. The size was found to be 1.4 nm. The effect of mass ratios of NAC to rice (NAC/rice) on the N, S-CDs were explored using HPLC-FD. The higher NAC/rice ratio aided the synthesis of N, S-CDs with enhanced fluorescence emission as depicted in Fig. 12.

Heteroatoms doped CDs are also synthesized using natural hair (Dong *et al.*, 2013) and goose feathers (Liu *et al.*, 2015b). The obtained S-N-CDs from natural hair retained good biocompatibility, low toxicity and excellent solubility in polar solvents. The CDs obtained from goose feathers had high PL efficiency of 17.1% and demonstrated highly sensitive and selective detection behavior of Fe³⁺ ions with detection limit as low as 196 nm.

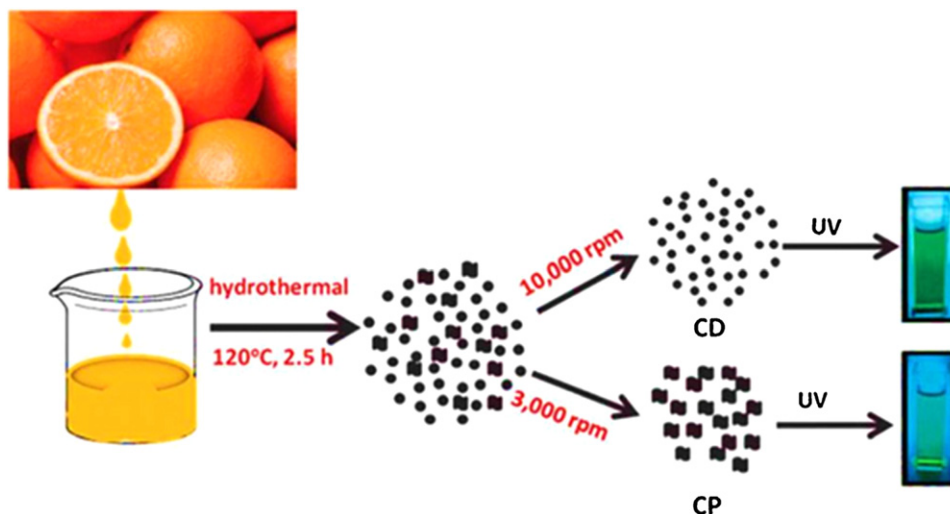


Fig. 11 Illustration of formation of CDs from hydrothermal treatment of orange juice. Reproduced from Sahu, S., Behra, B., Maiti, T.K., Mohapatra, S., 2012. Simple one-step synthesis of highly luminescent carbon dots from orange juice: Application as excellent bio-imaging agents. *Chem. Commun.* 48, 8835–8837.

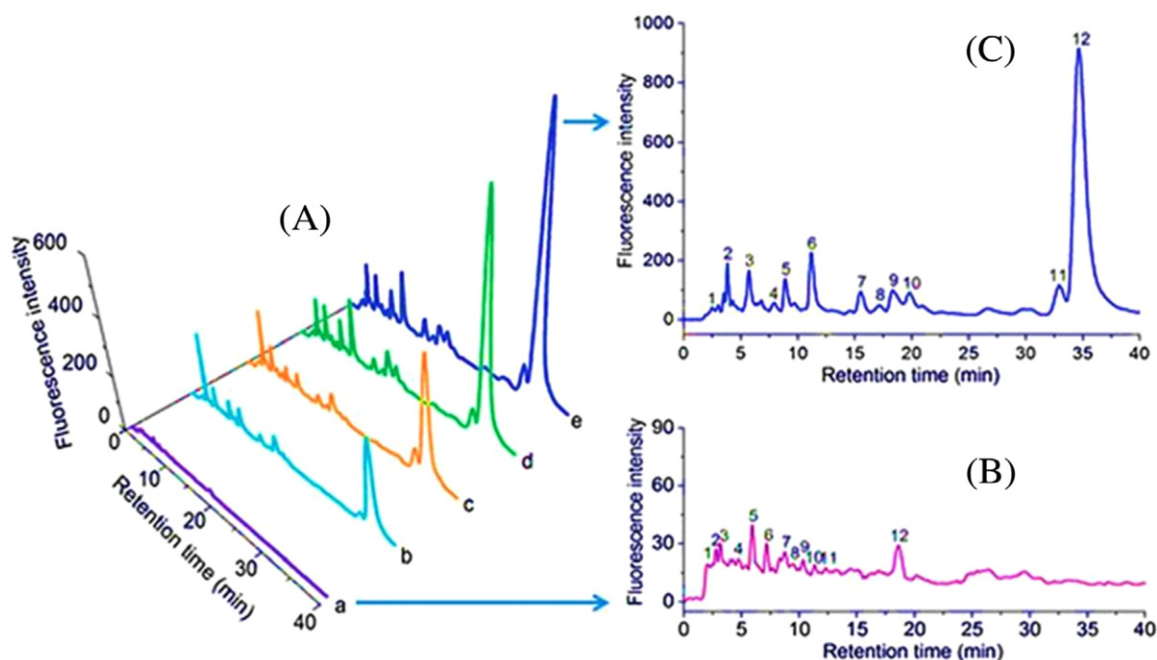


Fig. 12 (A) Chromatograms of aqueous solutions of N, S-CDs (1.0 mg/mL) synthesized with different mass ratios of NAC to rice: (a) 0.00, (b) 0.20, (c) 0.40, (d) 0.60, and (e) 0.80. (B) and (C) are the expanded chromatograms of undoped CDs and N,S-CDs synthesized with the mass ratio of NAC to rice at 0.00 and 0.80, respectively, for clarity and ease of comparison. Reproduced from Hu, Q., Paan, M.C., Zhang, Y., *et al.*, 2014. Green synthesis of fluorescent nitrogen/sulfur doped carbon dots and investigation of their properties by HPLC coupled with mass spectrometry. *RSC Adv.* 4, 18065–18073.

Porous Carbon Nanomaterials

Porous carbon nanomaterials have attracted great research interest in the recent past due to high surface area with open and accessible porosity (Li *et al.*, 2003). As a result, they are the potential candidates for application in separation, electro catalysis and energy storage (Li *et al.*, 2003; Liang *et al.*, 2003; Hyeon *et al.*, 2003). Carbon and natural resources can be used as a precursor to produce carbon nanomaterials.

Carbon source

Lignite, high volatile bituminous, low volatile bituminous and anthracite are four types of coal used by Keller *et al.* (2016) as carbon source for the preparation of thin film of carbon nanoparticles. The coals were ball-milled with isopropyl alcohol (IPA) for 106 h and centrifuged to obtain coal particles with diameters less than 100 nm. The nanoparticles were spin-coated onto a silicon wafer or a quartz substrate to fabricate thin films. It was found that the most uniform thickness with little cracking of the film was achieved from high volatile bituminous coal. Finally, thermal treatment of the film led to a change in sp^2 allotropes and aromatic unit size, allowing the variation of its electrical conductivity in over seven magnitude orders (conductivity $\sim 10^{-6}$ S m^{-1}). The Raman spectra indicated that I_D/I_G ratio increased steadily as the annealing temperature rose from 450°C to 950°C for high volatile bituminous and anthracite films, indicating a remarkable rise in carbon disorder. In addition, the optical gaps associated with $\pi - \pi^*$ transition were found to be 1.8 and 0.68 eV for high volatile bituminous and anthracite films respectively. Interestingly, the gap was reduced to 0 eV at annealing temperature 800°C, indicating the tunability of optical band gaps of the thin films.

Low grade carbon (Das *et al.*, 2016) and carbon tar (Zhang *et al.*, 2017c) were also explored to synthesize carbon nanoparticles. The graphitization level was low for carbon nanoballs from low grade coal which necessitated further purification of nanoballs. Whereas, nanoparticles from tar are very sensitive to calcination temperature where there is gradual collapse of carbon crystal structure with the increase of temperature. Carbon nanofibers have been fabricated from coal of Xinjiang, China by electrospinning (Zhao *et al.*, 2014). The activated carbon nanofibers were treated with a mixture of HNO_3 and H_2SO_4 (1:3, v-v) and polyacrylonitrile (PAN) solution. The prepared sample was further carbonized and steam activated at 800°C to obtain activated carbon nanofibers. Pt/Co carbon nanofibers from coal (Pt/Co-CF) were synthesized from acid treated coal and cobalt acetate which were mixed with PAN and N, N – dimethylformamide (DMF) before electrospinning and carbonization to foster cobalt embedded carbon nanofiber (Co-coal-CF) (Mu *et al.*, 2017). The average crystal size of Pt nanoparticles in Pt/Co-coal-CF was 3.6 nm and the lower I_D/I_G ratio indicated higher degree of graphitization.

Sustainable source

Wood and cotton are suitable precursors for porous carbon structures as they are made of carbon rich organic polymers like cellulose, hemicellulose and lignin. The precursors are loaded with conducting polymer Polypyrrole and Fe catalyst and highly graphitic nanostructures are obtained after microwave treatment. The catalyst Fe was removed by an acid leaching process and nanostructures of 350.95, 431.29 and 293.19 m^2/g were obtained from wood, cotton and filter paper respectively as presented in Fig. 13.

Microporous carbon structure with high specific area of 2511 m^2/g were obtained from EFB of palm oil trees by Parshetti *et al.* HTC method was adopted following activation with KOH (Parshetti *et al.*, 2015). The produced nanoparticles were found to be useful as adsorbents in CO_2 capture applications. A wide variety of diverse sources have been explored as prospective resources for porous carbons which are: cherry stones and olive (Caballero *et al.*, 2011), mangrove charcoal (Liu *et al.*, 2010b), alginic acid (Wu *et al.*, 2010), rice husk (Wang *et al.*, 2013a), banana fibers (Stephan *et al.*, 2006), peanut shells (Fey *et al.*, 2003), waste coffee grounds (Yun *et al.*, 2015), sugarcane bagasse (Wahid *et al.*, 2014) and natural yoghurt (Wahid *et al.*, 2015). Activated graphene also possess outstanding electrochemical performance similar to porous carbon, because of its open and relatively flat adsorption surfaces (Zhu *et al.*, 2011). Wang *et al.* (2013b) have used hemp bast fiber (Cannabis sativa) as the precursor to produce graphene-like nanosheets by combination of hydrothermal and activation processes. Hemp bast fiber has a multilevel layered structure consisting of cellulose, semi cellulose, and lignin. The resulting structure comprised of interconnected 2D carbon nanosheets (CNS) with high degree of mesoporosity. The obtained CNS has high specific surface area in the range of 1505–2287 m^2/g and with good electrical conductivity. The SEM and TEM images of CNS obtained at 800°C activation temperature are presented in Fig. 14.

Applications of Carbon Nanomaterials

The carbon nanomaterials derived from different sources have multitude of applications ranging from environmental (Gong *et al.*, 2015), catalytic (Gao *et al.*, 2015a), electrical (Wang *et al.*, 2013b) and to biological (Sahu *et al.*, 2012). The following section briefly discusses some of the applications of these carbon nanomaterials in environmental and renewable energy related areas.

Adsorbents in Water Purification and Gas Uptake

The adsorbent plays an important role for the elimination of industrial pollutants from waste water. CNTs (Khin *et al.*, 2012), graphene (Li *et al.*, 2011), ordered mesoporous carbon (Zhuang *et al.*, 2009) and activated carbon (Hameed *et al.*, 2007) are used as adsorbents. PCNS derived from waste plastics exhibited superior characteristics as an adsorbents and adsorption capacity was found to be 769.2 m^2/g which was much higher than that of graphene, activated CNT, porous MnO_2 microsphere etc., as demonstrated in Fig. 15. The material also exhibits outstanding recyclability i.e., even after 10 cycles, adsorption capability of 692 m^2/g retained. MG is cationic dye which is widely used in textile, leather and paper industries as a coloring agent. It is extremely toxic and known to cause carcinogenesis and respiratory toxicity (Ahmad and Alrozi, 2011; Scott *et al.*, 2013). The effluent from the industries contain considerable amount of this dye which is difficult to remove. HTC of pine needles at 225°C and subsequent oxidation using H_2O_2 resulted in hydro char that could effectively remove organic dye MG from waste water.

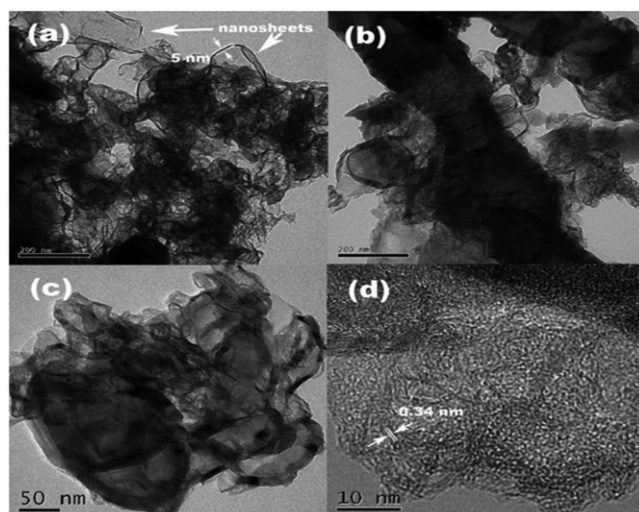


Fig. 13 Typical TEM images of porous graphitic carbon from (a) filter paper, (b) wood, and (c) cotton, and (d) the HRTEM image of the carbon wall microstructures. Reproduced from Wang, C., Ding, M., Bao, X., 2008. Transformation of biomass into porous graphitic carbon nanostructures by microwave irradiation. *J. Phys. Chem. C* 112, 17596–17602.

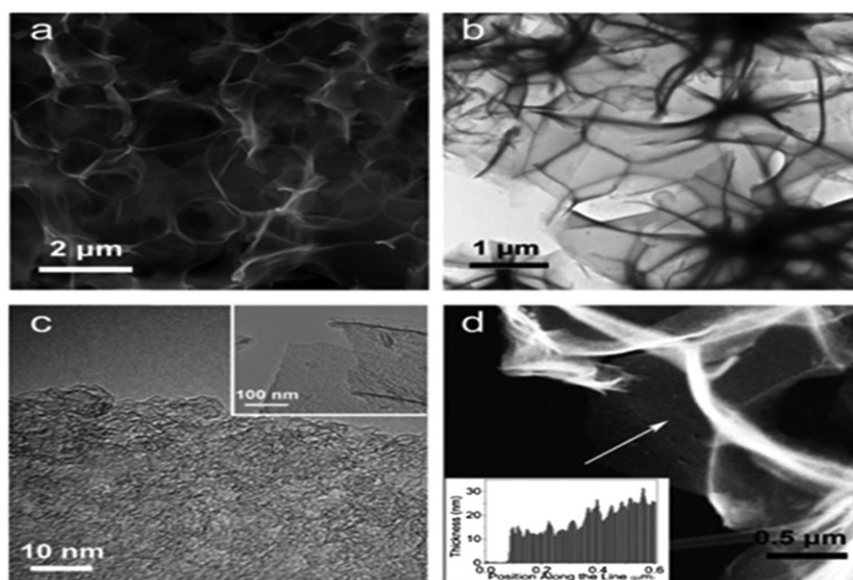


Fig. 14 (a) SEM micrograph highlighting the interconnected 2D structure of CNS obtained at 800°C, (b) TEM, (c) HRTEM micrograph highlighting the porous and partially ordered structure, (d) ADF TEM micrograph and EELS thickness profile (inset). Reproduced from Wang, H., Xu, Z., Alireza, K., *et al.*, 2013b. Interconnected carbon nanosheets derived from hemp for ultrafast supercapacitors with high energy. *ACS Nano* 7, 5131–5141.

One of the major environmental challenges is the global warming and a key factor to this is the emission of greenhouse gases like CO and CO₂ (Scott *et al.*, 2013). Carbon capture and storage is a prospective approach towards lessening the emissions from industrial sources (Haszeldine, 2009). Porous carbon materials are attractive class of adsorbents due to their low-cost, large surface area, better availability, hydrophobicity, resistance to acidic and basic conditions. The microporous carbon from EFB has a CO₂ uptake capacity of 3.71 mmol/g at 25°C and at a pressure of 1 atm (Fig. 16) (Parshetti *et al.*, 2015).

Hydrogen is considered as a clean form of energy and is the fuel for tomorrow. There are various modes of its production, but the major challenge is to store the product. The materials needed for hydrogen storage should have suitable thermodynamics and kinetics for reversible hydrogen sorption and desorption. Porous carbon nanomaterials developed by Cheng *et al.* (2008) from sawdust by a carbonization and chemical activation procedure finds application as sorbents for hydrogen uptake. The experiment was carried out at different carbonization and activation temperatures. A cryogenic hydrogen uptake capacity exceeding 5 wt% at 10 bar and 2.55 wt% at 1 bar was attained with adsorption heat of 4.1–7.5 kJ/mol (Fig. 17).

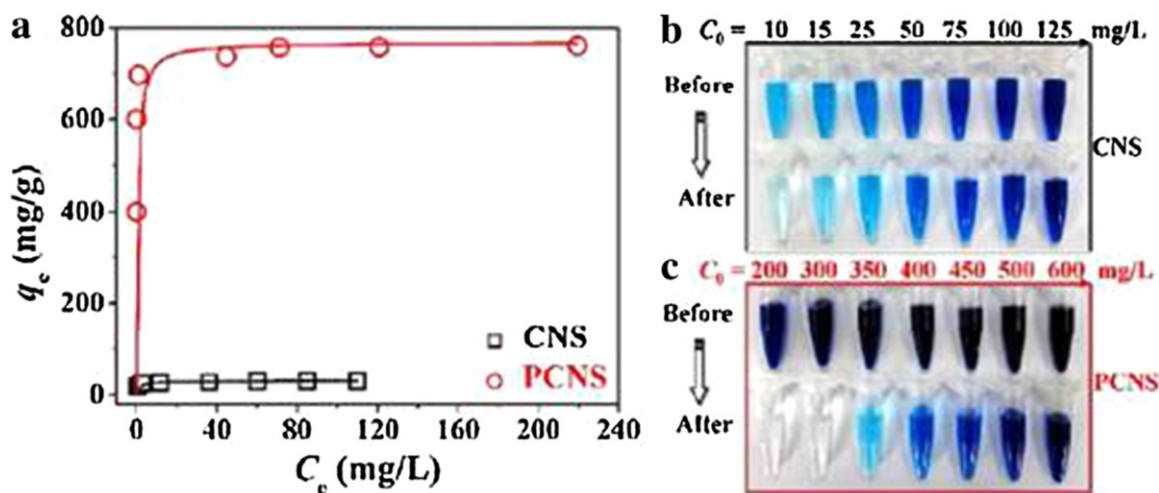


Fig. 15 (a) Equilibrium adsorption isotherms of MB on the CNS before activation and activated PCNS (experimental conditions: MB concentration = 10–125 mg/L for CNS or 200–600 mg/L for PCNS, CNS or PCNS concentration = 0.5 g/L, and 30 adsorption time = 180 min), and the corresponding photos of the MB solutions before and after adsorption by (b) CNS and (c) PCNS. Reproduced from Gong, J., Liu, J., Chen, X., *et al.*, 2015. Converting real-world mixed waste plastics into porous carbon nanosheets with excellent performance in the adsorption of an organic dye from wastewater. *J. Mater. Chem. A* 3, 341–351.

It has been investigated recently, that hydrophobic electrospun carbon nanofiber fabrics (ECNFs) with the water contact angle (WCA) of $142.6 \pm 1.1^\circ$ can separate toluene and water with a separation efficiency of $>99.5\%$ within a few min with a high toluene flux of $324 \text{ L m}^{-2} \text{ h}^{-1}$ (Zhu *et al.*, 2018). High fluxes ($250\text{--}410 \text{ L m}^{-2} \text{ h}^{-1}$) were also observed with other organic solvents such as methylbenzene, ethyl acetate, tetrahydrofuran, petroleum ether, etc., demonstrating that ECNFs are promising candidates for efficient oil/water separation.

Electrocatalysis

As catalyst supports in oxygen electro reduction reactions occurring in fuel cells, the graphitic carbon nanostructures (GCN) have attracted great deal of attention. The performance of fuel cells and metal/air batteries are very much dependent on cost-effective design of electro catalysts.

The sawdust particles impregnated with Ni and Fe salts were carbonized at 900 and 1000°C, respectively to obtain GCNs and that was employed as electro-catalyst support for methanol oxidation reaction (Sevilla *et al.*, 2007). It was also used as a support for making Pt electro catalysts. Nitrogen-doped C_{60} fullerene derived from ginkgo leaves were found to be a prospective cathode catalyst for hydrogen fuel cells (Chen and King, 2005). Nitrogen-doped fullerene-like carbon shells (NDCS) synthesized from fallen ginkgo leaves via pyrolysis in N_2 was also used as an excellent ORR catalyst. The strength of planar bonds in sp^2 hybrids, its rigidity, high elastic recapture, low-friction and resistance to wear offer additional advantages for the NDCS electrode to be used in FCs under both ambient and vigorous conditions (Gao *et al.*, 2015b).

Selective catalytic reduction (SCR) of NO_x (92% NO and 8% NO_2) with NH_3 in a quartz reactor was carried out by using catalyst. The catalyst was produced by using noble metal (Pt, Ru and Pt/Ru) nanoparticles which were deposited on anthracite derived graphene sheet (GS). It was found that the PtRu/GS composite exhibited superior catalytic performance and over 90% conversion of NO at 165°C, which might have resulted from synergistic effect of Ru and Pt.

Sensing Applications

The electro-catalytic property of graphene for caffeine oxidation can be used as a biosensor and Trauzettel *et al.* (2007) could apply the biosensor to detect caffeine in the concentration range of $0.2\text{--}120 \mu\text{mol L}^{-1}$ with a limit of detection of 90 nmol L^{-1} (signal/noise = 3). Bitumen derived graphene was used as an electrode for the biosensor. Anthracite coal derived CDs was successful for Cu (II) analysis due to their selective PL quenching with Cu^{2+} ions as investigated by Hu *et al.* (2014b). The favorable response was attributed to the thermodynamic affinity of Cu^{2+} toward nitrogen and oxygen functional groups of the reduced CDs, and rapid bonding kinetics of copper. As shown in Fig. 18, the response was linear in the range of $0\text{--}0.5 \mu\text{M}$ Cu^{2+} concentration with a limit of detection 2nM and a signal/noise ratio of 3. The interaction between metal ions and reduced CDs was rapid and stabilized within 3 min. Hence, it was revealed that PL sensing had fast response and is a promising candidate for real-time Cu(II) tracking in environmental applications.

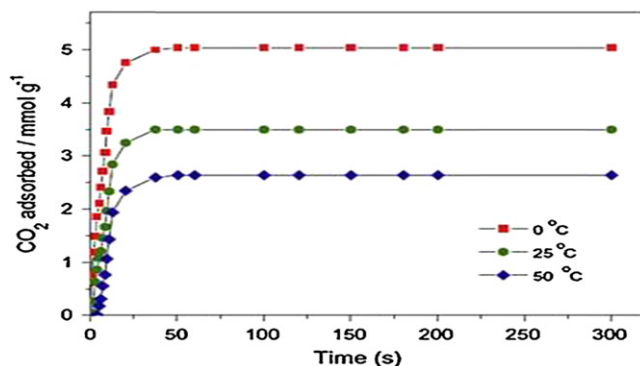


Fig. 16 CO₂ adsorption kinetics for the microporous carbon sample at different temperatures. Reproduced from Parshetti, G.K., Chowdhury, S., Balasubramanian, R., 2015. Biomass derived low-cost microporous adsorbents for efficient CO₂ capture. *Fuel* 148. 246–254.

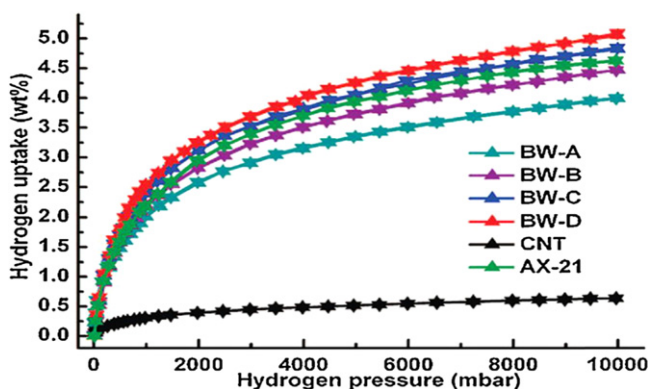


Fig. 17 Comparison of hydrogen sorption isotherms of the obtained carbons (at various carbonization temperatures labeled as BW-A, BW-B, BW-C, BW-D) activated AX-21, and multi-walled carbon nanotubes (CNT) at 196 °C over the pressure range of 0–10 bar. Up-triangles and down-triangles represent H₂ adsorption and desorption isotherms, respectively. Reproduced from Cheng, F., Liang, J., Zhao, J., Tao, Z., Chen, J., 2008. Biomass waste-derived microporous carbons with controlled texture and enhanced hydrogen uptake. *Chem. Mater.* 20, 1889–1895.

Biomedical Applications

Graphene oxide extracted from low grade coal was found to be a potentially suitable vehicle for drug delivery (Pakhira *et al.*, 2015). A GO-DL (donepezil) composite encapsulated with GO was successfully used in the treatment of mild to moderate Alzheimer's disease. The drug molecules were stably entrapped inside the clenched fist of GO in an acidic environment of pH 6.8 but at an alkaline environment of pH 7.4 would trigger the release of DL. Thus, the DL drug could be effectively delivered by closed fist shapes of coal-derived GO with its release depending on pH. The metal contaminants in coal and the difficulty with the removal of acidic species from the synthesized carbon based nanomaterials lower their biocompatibility, which limits their potential application in biomedicine. By encapsulating the CDs in liposomes for in vitro and in vivo bio-imaging applications Geng *et al.* (2017) managed to improve the bio-compatibility of coal-derived carbon quantum dots. The liposome-CD composite was shown to exhibit low cytotoxicity with HeLa cells having viability above 92% after incubation over one day.

Energy Storage

There is an increasing mandate to develop new renewable technologies to meet the increasing energy demands. As an energy storage device, supercapacitors are getting more attention than batteries because of power density, good reversibility and long cycle life (Miller and Simon, 2008). The electrochemical performance of supercapacitor electrode is explored with carbon nanomaterials which are synthesized from biomass (Genovesea *et al.*, 2015). Corn cob (Genovesea *et al.*, 2015), waste coffee ground (Yun *et al.*, 2015), water melon (Wu *et al.*, 2013), hemp fiber (Wang *et al.*, 2013b) have been used to produce supercapacitor based electrodes. The biomass was used to synthesize NCTs, CNS based supercapacitors, and all of them exhibited excellent capacitance value with good electrical transport properties. It was found that biochar electrode produced from corn cob was extremely robust even after 5000 successive cycles, showing only a 3% fading capacitance (Ravi and Vadukumpully, 2016). These behaviors undoubtedly project that the materials are to possess high power-energy characteristics. At a high power density of 20 kW/kg and at 20, 60 and 100 °C, the energy density values were 19, 34, and 40 Wh/kg, respectively (Fig. 19). Thus these high performance carbon nanostructures are promising candidates for usage as electrodes in energy storage devices.

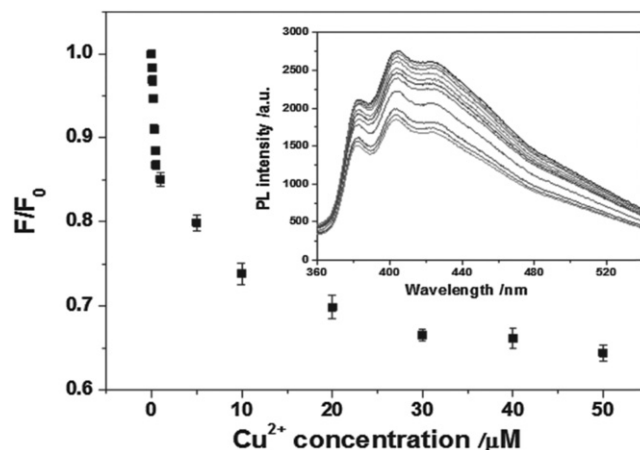


Fig. 18 The dependence of F/F_0 on the concentration of Cu^{2+} in a range of 0–50 μM . Inset shows the corresponding fluorescence response of r-CDs dispersion upon addition of various concentration of Cu^{2+} . Reproduced from Hu, C., Yu, C., Li, M., *et al.*, 2014b. Chemically tailoring coal to fluorescent carbon dots with tuned size and their capacity for Cu(II) detection. Small 10, 4926–4933.

Carbon nanomaterials derived from cost effective sources can act as anode material for Li-ion batteries. Zhang *et al.* reported that rice straw is a good source of carbon nanomaterials to be used as anode in Li-ion battery application (Zhang *et al.*, 2009). The presence of microspores is the limitation and carbon nanostructures alone are not adequate to get good rate of performance at a high current density.

A simplistic and economical route for the preparation of a graphitic material from spongy pomelo peels (SPP) was explored which was found to be an effective anode material for Li ion batteries (Sun *et al.*, 2013). As an anode material, it showed high capacity, outstanding cycling stability and rate capability with a high capacity value of 452 mAh/g at a current density of 90 mA/g and it was retained even after 200 cycles (Fig. 20).

Coal derived carbon nanomaterials are also used in energy applications in Li-ion batteries. CNTs from bitumite coal (Li *et al.*, 2017), N, S-codoped CNTs (Liu *et al.*, 2015a), coal derived graphene/ Mn_3O_4 composite (Gao *et al.*, 2014), 3D hollow porous graphene balls (HPGBS) from coal tar, PAN and coal derived carbon nanofibers (PAN-coal-CFs) (He *et al.*, 2014), bituminous coal derived GQDs (Zhang *et al.*, 2017d) have exhibited high performance as supercapacitor electrode.

Zhang *et al.* (2017d) prepared a high performance supercapacitor electrode based on activated hierarchical porous carbon nanosheets (HPCNs) from bituminous coal-derived GQDs. When the current density increased from 1 to 100 A g^{-1} , the specific capacitance decreased from 230 to 170 F g^{-1} that is by only 26%, implying a superior rate capability of the activated HPCNs. Moreover, the material demonstrated an excellent durability with no obvious fading in specific capacitance after 10,000 galvanostatic charge/discharge cycles at a current density of 10 A g^{-1} . Good electronic conductivity, high surface area ($1450 \text{ m}^2 \text{ g}^{-1}$) and micro/mesoporous distribution in activated HPCNs might be providing more active sites for energy storage and more channels for ionic transport. Meanwhile, a report presented by Guo *et al.* (2017a) used coal based hierarchical porous carbon spheres (PCS) as an electrode active material for supercapacitors. They found that CV plots were in a quasi-rectangular shape with a broad peak between 0.2 and 0.8 V, which was attributed to the surface oxygen pseudo-capacitance. The material exhibited a high specific capacitance of 227 F g^{-1} at 1 A g^{-1} and superior cycle stability in 6 M KOH after 10,000 charge/discharge cycles at 2 A g^{-1} . In addition, a symmetrical device based PCS showed a specific capacitance of 180 F g^{-1} at 0.2 A g^{-1} , which remained at 112 F g^{-1} at 5 A g^{-1} , indicating an excellent rate capability.

Other Nanomaterials for Energy Storage

The energy and environmental crisis is a factor of great concern for sustainable development of human society. Electrochemical energy storage and conversion devices (EESCDs) are emerging as primary power sources for global efforts to shift energy dependence from limited fossil fuels towards sustainable and renewable sources. EESCDs including lithium ion batteries, supercapacitors, alkali ion batteries, alkaline batteries, and photo-electrochemical devices are promising for their high energy or power densities, portability, and long cycle life. However, the promise is often overshadowed by greater surface area and higher reactivity of nanostructured active materials and manufacturing limitations (Zhua *et al.*, 2017; Share *et al.*, 2016). Therefore, electrode materials and components must be appropriately designed and synthesized to enhance the kinetics of ion and electron transport to achieve high-performance EESCDs. In the following sections recent advances in EESCDs, new synthesis approach and control of surface properties are discussed.

Lithium Ion Batteries (LIBs)

Though there is great advancement of LIBs as energy storage devices since 1990s, but till now it is facing great limitations due to limited capacity of electrodes (anode and cathode). Commercial graphite is used as anode materials but it suffers from relatively

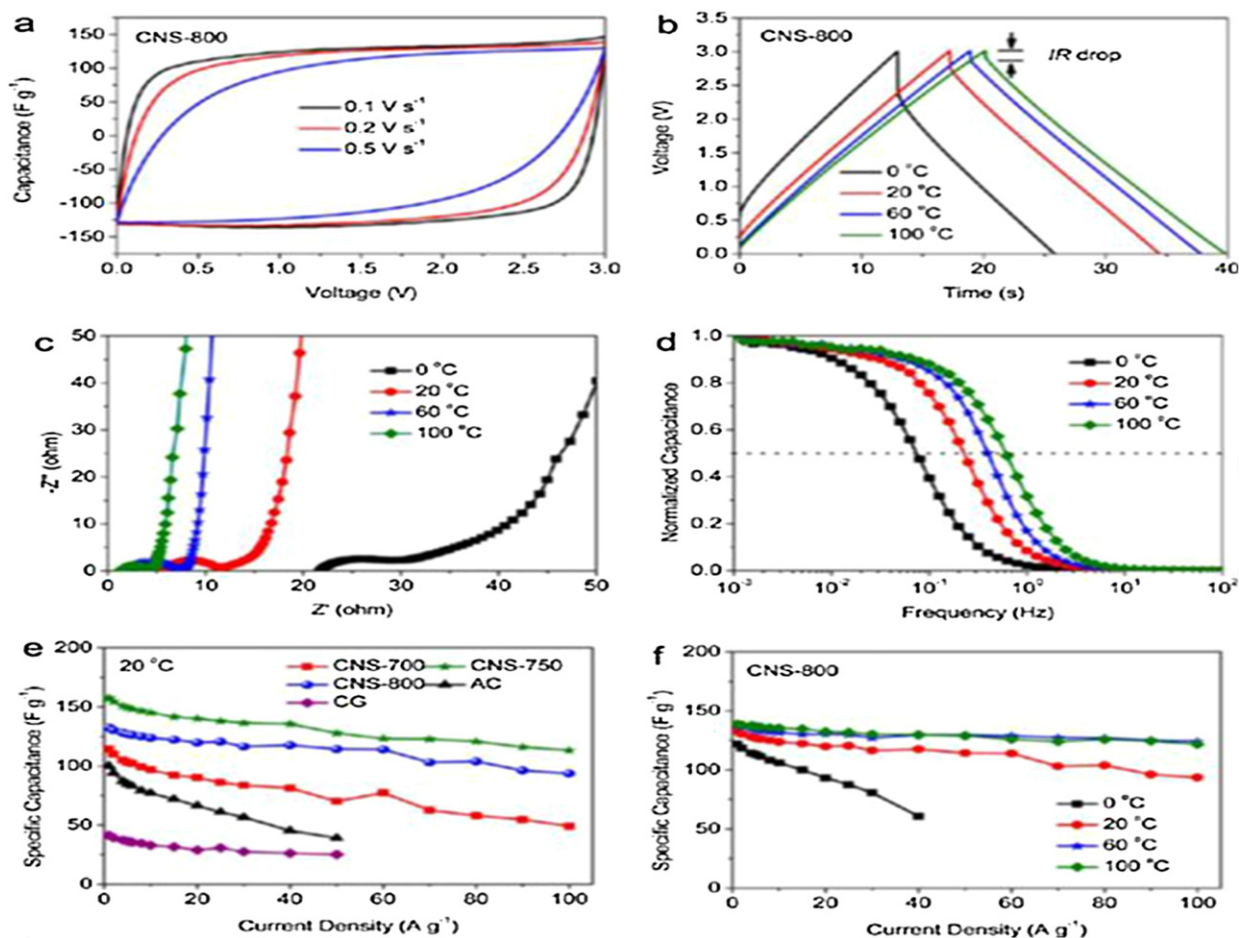


Fig. 19 (a) CV curves of CNS-800 for three different scan rates, tested at 2 °C; (b) galvanostatic charge/discharge profiles of CNS at a current density of 10 A/g; (c) Nyquist plots and (d) frequency responses of CNS measured at 0, 20, 60 and 100 °C. (e) Specific capacitance versus current density, tested at 20 °C for the CNS, baseline commercial activated carbon and baseline graphene nanoplatelets. (f) Specific capacitance versus current density for CNS measured at different temperatures. Reproduced from Wang, H., Xu, Z., Alireza, K., *et al.*, 2013b. Interconnected carbon nanosheets derived from hemp for ultrafast supercapacitors with high energy. *ACS Nano* 7, 5131–5141.

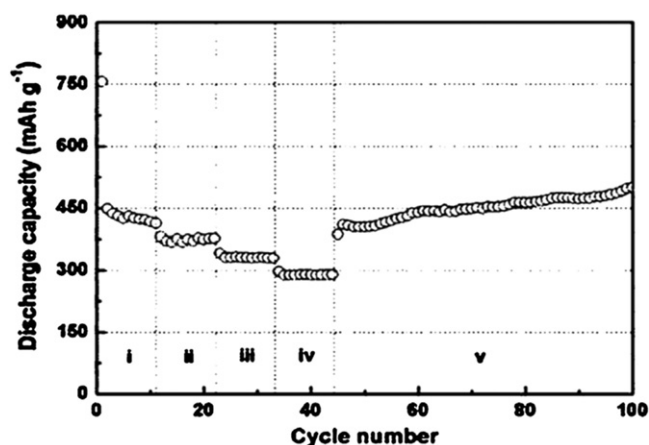


Fig. 20 Rate capability of the carbon at different rates: (i) 40, (ii) 80, (iii) 160, (iv) 320, (v) 40 mA/g, respectively. Reproduced from Sun, X., Wang, X., Feng, N., *et al.*, 2013. A new carbonaceous material derived from biomass source peels as an improved anode for lithium ion batteries. *J. Anal. Appl. Pyrolysis* 100, 181–185.

low capacity. Lithium titanate (LTO), is a typical alternative high rate anode, but the electronic and ionic conductivities are not satisfactory. [Saxena and Sil \(2017\)](#) reported vanadium doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) with enhanced high-rate performance and ion transfer at high working current. [Pan et al. \(2017\)](#) designed integrated graphene foam LTO anode which greatly reinforced the discharge capacity and power density. The LTO based anode showed excellent high-rate capability, about 10 times larger than the commercial graphite, up to 50–200°C. But the higher working voltage in the voltage range of (1–2 V versus Li^+/Li), and lower discharge capacity of LTO ($< 200 \text{ mAh g}^{-1}$) which is higher than the commercial graphite, would result energy and power loss when coupled with the commercial cathode. Hence, the searches for anode for LIBs are still going on.

Silicon based materials are one of the promising successor to commercial graphite as it demonstrated ultrahigh theoretical specific capacity (4200 mAh g^{-1}) and low working potential (0.5 versus Li^+/Li) but due to huge volumetric expansion ($> 300\%$) the columbic efficiency and cyclic life are poor. Moreover, it also exhibits poor electrical conductivity. Biomass derived carbon/silicon three dimensional hierarchical composite or Si as an additive for carbon or graphite anode can enhance the performance of anode remarkably ([Shen et al., 2017b](#)). Exploration with metal oxides such as NiO , MoO_2 and MoO_3 has been widely done by Tarascon group ([Poizot et al., 2001](#)). These metal oxides suffer from some common issues such as poor cycling stability due to large volume and embarrassingly high working voltage which is above 1 V.

Exploration with the cathode is also going on. Tarascon group reported that by doubling the capacity of cathode, the energy density could be increased by 57%, whereas only an increase of 47% can be achieved increasing the capacity of anode by a factor of 10 ([Tarascon, 2010](#)). [Chen et al. \(2017a\)](#) have demonstrated that surface coating of layered $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ for LIBs could improve the capacity significantly for commercial LIBs. But the cycling life should be further enhanced by introduction of different surface coating with the aid of multiscale design. On the other hand, [Cao et al. \(2017\)](#) and [Mao et al. \(2017\)](#) adopted porous design strategy to construct N doped carbon/ LiFePO_4 microspheres and LiMn_2O_4 hollow microspheres as high-performance cathode, respectively. Though the porous design will decrease the tap density of active materials, the transfer kinetics of ions/electrons would be greatly accelerated leading to enhanced high-rate performance.

High Performance Post Lithium Ion Batteries

The high cost and scarcity of lithium have spur in full swing, the search on alternatives to lithium. Sodium ion batteries (SIBs), potassium ion batteries (PIBs), and magnesium ion batteries (MIBs) due to their cost-effective, non-toxic, and larger reserves on earth (about one thousand times more abundant than lithium) are entering into the vision of researchers. Though the performance does not match yet the LIBs, the researchers are optimistic on improvement and these are the hotspots of research ([Chang et al., 2017](#); [Cho et al., 2017](#)).

High Performance Supercapacitors

The higher surface area makes supercapacitor an attractive power solution for an increasing number of applications. [Guo et al. \(2017b\)](#) presented hierarchical $\text{Co}_3\text{O}_4@\text{PPy}$ core-shell composite nanowires for supercapacitors with enhanced electrochemical performance. [Lu et al. \(2017\)](#) reported Bi_2S_3 nanoparticles anchored on graphene nanosheets with superior capacitive performance. The PPy shell and graphene matrix can enhance the electrical conductivity and structural stability, resulting in enhanced capacitance. [Xie et al. \(2017\)](#) designed negative electrode of $\text{Fe}_2\text{O}_3/\text{graphene oxide}$ paper for high energy supercapacitors. Moreover, MnO_2 based cathode such as nanotubes and nanowires are discussed by [Xiao et al. \(2017\)](#) and Kim group ([Tran et al., 2017](#)). It is proven that nano-structuring on MnO_2 is favorable for the fast transportation of ions/electrons, leading to increased utilization of active MnO_2 . However, till to date, the working mechanism on the pseudo capacitive materials is still not clear and controversial.

High Performance Alkaline Batteries

Hybrid alkaline batteries are getting attention as one of the promising energy storage devices as they use battery-type cathode and capacitor-type anode, hence, utilizing the combined advantages of batteries (high energy density) and capacitor (superior power density). Extensive theoretical and experimental studies have demonstrated that the performance of alkaline batteries is mainly determined by the electrochemical activity and kinetic feature of electrodes. [Wu et al. \(2017\)](#), [Chen et al. \(2017b\)](#) and [Ma et al. \(2017\)](#) reported Ni nanoparticles embedded into cross-linked NiO nanoflakes as enhanced cathode, cobalt oxide nanoflakes grown on cobalt nanowires and nickel hydroxide shell on TiO_2 nanorod for alkaline batteries as cathode respectively. These arrays architecture offers shortened ion diffusion paths and facilitates migration of the electrolyte ions, leading to improve high-rate performance. It is noteworthy that these metal oxides/hydroxides cathode must be coupled with capacitive carbon anode to achieve high performance.

High Performance Optical-Electrochemical Energy Storage and Conversion

Solar energy is a clean, abundant and unlimited source of energy which can meet the global energy demand in a green way ([Shen et al., 2017a](#)). It has a wide spectrum of applications of which solar heating, photovoltaics, photo-electrochemical water splitting,

photosynthesis, and photocatalysis are to be mentioned. Shi *et al.* (2017), Zhang *et al.* (2017b), Yadian *et al.* (2017), and Railey *et al.* (2017) have reported the improvements of phototransistors, photocatalytic and photo electrochemical performance respectively with different nanomaterials. These results show that the interface structure is very important to the high absorption/utilization of light energy. All the results indicate that the design/fabrication of interface structure or active materials should be combined with the theoretical calculation results, which can guide the synthesis of efficient photo-electrochemical catalysts and photo anode/photocathode.

3D Printed Nanomaterials for Energy Storage

The micro-sized electrochemical energy storage (EES) devices have customized configurations for easy integration into other micro-electronics (Gogotsi and Simon, 2011; Wang *et al.*, 2014). These configurations must have ultrahigh resolution to shorten transport distances and at the same time should provide sufficient active material to ensure adequate energy output for an extended timeframe. Building of thicker electrodes is the key to further improve the areal capacitance and energy density without sacrificing fast ion diffusion. However, thicker electrodes are associated with reduction of rate capability as the electron transport distances increase with overall increased electrical resistance of electrode. Therefore, fabrication of electrodes or devices involving micro-, meso- and macro-pores via a controllable and scalable method remains a significant challenge (Beidaghi and Gogotsi, 2014). Additive manufacturing (AM) refers to an industrial production technique whereby, 3D objects are created by adding layer-upon-layer of material directly from computer-aid-design (CAD) files. This method is also known as 3D printing which offers the freedom to fast create complex architectures at lower cost than conventional subtractive methods (Gibson *et al.*, 2010). The 3D printing techniques can be divided into several categories: laser deposition of energy fusible powders, photo-polymerization of ultra-violet (UV) sensitive liquids, electrodeposition of surface charged particle-based suspensions, and extrusion deposition of colloidal gels (Gibson *et al.*, 2010; Duoss *et al.*, 2014). Recently, a couple of these 3D printing methods have been applied for electrochemical or energy-related applications (Ambrosi and Pummera, 2016; Fu *et al.*, 2016; Tian *et al.*, 2017), a few of which are discussed in the subsequent paragraphs.

Laser-Based 3D Printing for EES

Laser can consistently and precisely deliver high thermal energy to a target using a highly collimated, coherent beam of light. In a laser-based printing process, the irradiation instantly melts, sinters or chemically converts functional materials into diverse micro-patterns (Gu *et al.*, 2012; Gu, 2015a; Sokolov *et al.*, 2010). Any thermally fusible powder materials can be directly used for laser printing. This is a single-step non-contact and mask-free fabrication which obviates the need for costly, time-consuming, and labor-intensive lithography and related post-processing operations (Gu, 2015b). Laser-based 3D printing has two unique features: (i) a wide selection of materials such as polymers, ceramics, and metals can be made; (ii) no complicated material processing techniques are needed. These advantages make laser-based printing a preferred technique for rapid prototyping of on-chip EES micro-devices (El-Kady *et al.*, 2012; El-Kady and Kaner, 2013; El-Kady *et al.*, 2015; Lin *et al.*, 2014; Li *et al.*, 2016).

Selective Laser Melting

Selective laser melting (SLM) is a specific 3D printing technique, which facilitates specific functions and properties. Near net-shape parts with near full density (up to 99.9% relative density) can be achieved by utilizing high power-density laser. Layer-by-layer scanning and fusion powders are carried on depending on the pre-designed patterns (Fig. 21(a)) (Gao *et al.*, 2011). Ambrosi *et al.* printed helical shaped steel electrodes using SLM (Fig. 21(b)) (Yap *et al.*, 2015). These tailor-made stainless steel electrodes were used as platforms for supercapacitors, catalysts and sensors by means of an effective and controlled deposition of iridium dioxide (IrO₂) films (Fig. 21(c)) which demonstrated excellent capacitive and catalytic properties in alkaline solutions and Nernstian behavior as potentiometric pH sensors.

Direct Metal Laser Sintering

Direct metal laser sintering (DMLS) is another 3D metal printing method, used to build objects out of almost any metal alloy (Ambrosi *et al.*, 2016). In this technique a precise, high-wattage laser is used to micro-weld powdered metals. Objects free from residual stress can be produced by this method.

Template-Assisted Electrodeposition

To obtain electrodes with more complex microstructures, electrodeposition is frequently combined with pre-engineered templates to tune the morphology and structure of deposited films. The 3D ultrafast graphene and silicon (Si) battery electrodes were fabricated by combining electrodeposition with a traditional templating method as mentioned by Zhang *et al.* (2011) and

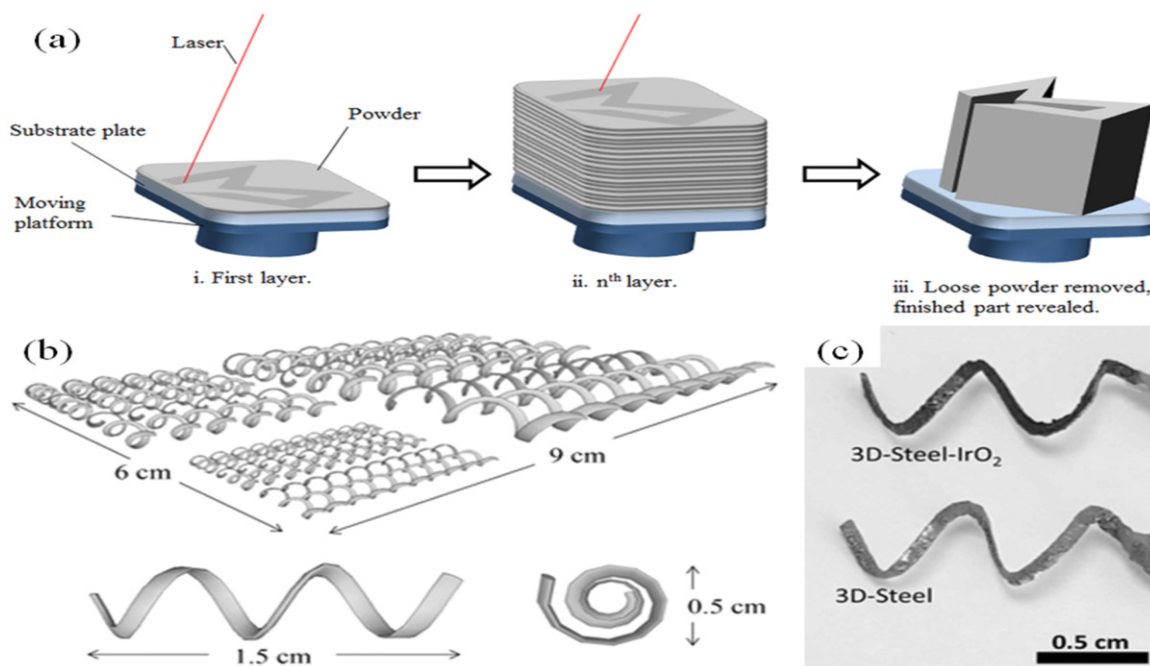


Fig. 21 (a) Schematic illustration of SLM process. (i) High-power laser melts selective areas of the powder bed. (ii) Process is repeated for successive layers. (iii) Loose powder removed and finished part revealed. Reproduced from Gao, W., Singh, N., Song, L., *et al.*, 2011. Direct laser writing of micro-supercapacitors on hydrated graphite oxide films. *Nat. Nanotechnol.* 6, 496–500. Schematic of (b) helical-shaped stainless steel electrodes, and optical image of SLM (c) scaffolds for supporting IrO₂ film. Reproduced from Yap, C., Chua, C.K., Dong, Z.L., *et al.*, 2015. Review of selective laser melting: Materials and applications. *Appl. Phys. Rev.* 2, 041101.

(Zhang and Braun, 2012). As a result rapid ion transport, a short solid-phase ion diffusion length, a large electrode surface area and high electron conductivity were achieved. The schematic of the process is outlined in Fig. 22.

Ultrahigh charge and discharge rates with minimal capacity loss were obtained from the printed device. Rates of up to 400 C and 1000 C for lithium-ion and nickel-metal hydride chemistry, respectively, were achieved (1C rate refers to a current density that can fully charge or discharge a battery in one hour), enabling fabrication of a lithium-ion battery that can be 90% charged in two minutes. Pikul *et al.* (2013) have also achieved similar results by assembling the electrodes into interdigitated 3D lithium ion batteries.

Surface Engineering for Energy Storage Device

In surface engineering the properties of surface is engineered separately from the bulk material to harness the true application potential of heterogeneous material systems. It is a critical component in energy storage applications to design functional electrode with nanomaterials. Commercial scale batteries still use micro-scale materials for electrodes, which may be due to (i) manufacturing challenges of nanomaterials and (ii) the reactive nature of nanoscale materials. Armand and Tarascon (2008). In Fig. 23, control of properties of nanomaterials through surface engineering is presented.

New nanoscale materials have better performance compared to bulk materials but at cell-level the performance is reduced due to consumption of increased electrolyte while forming a stable electrode-electrolyte interface. In energy storage devices, a stable electrode-electrolyte interface is required to prevent Faradic charge transfer reaction and sustain an electric double layer. Moreover, Faradic charge transfer reaction must store and release energy without degradation (Share *et al.*, 2016). Surface engineering offers the scope to identify a material with ideal bulk properties and then independently engineer the surface properties to be stable. A few common surface engineering techniques are highlighted below.

Chemical Vapor Deposition and Atomic Layer Deposition

Chemical vapor deposition (CVD) and atomic layer deposition (ALD) are two processes where the materials in gas phase are used for surface engineering. In CVD the reactions between the gas phase precursor and the substrate are controlled by the precursor partial pressure, the temperature, and the reactivity of the electrode. In ALD the precursors react in a self-limiting process enabling atomic-level control where the alternate pulsing of two or more precursors is needed.

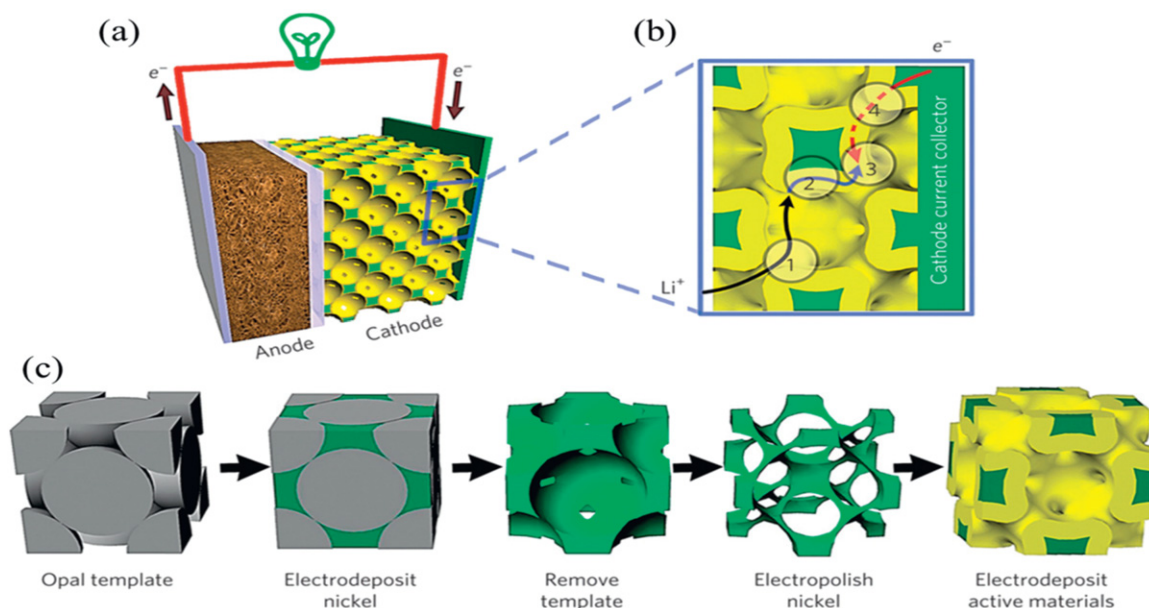


Fig. 22 (a) Schematic of the printed battery with a cathode equipped with a bi-continuous pathway for ions and electrons. (b) Illustration of the four primary resistances in a battery electrode: (1) Ion transport in the electrolyte, (2) ion transport in the electrode, (3) electrochemical reactions in the electrode, and (4) electron conduction in the electrode and current collector. (c) Bi-continuous electrode fabrication process: The electrolytically active phase is yellow and the porous metal current collector is green. The electrolyte fills the remaining pores. Reproduced from Zhang, H., Yu, X., Braun, P.V., 2011. Three-dimensional bicontinuous ultrafast-charge and -discharge bulk battery electrodes. *Nat. Nanotechnol.* 6, 277–281.

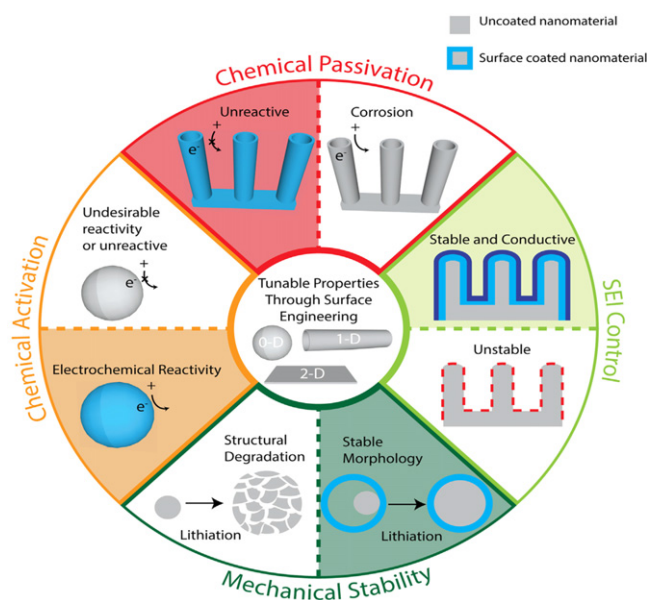


Fig. 23 Schematic representing the different properties of nanostructures that can be controlled through surface engineering. Reproduced from Share, K., Westover, A., Li, M., Pint, C.L., 2016. Surface engineering of nanomaterials for improved energy storage – A review. *Chem. Eng. Sci.* 154, 3–19.

Though CVD is a promising method to engineer the physical, chemical, and mechanical properties of surfaces, precise thickness control can be difficult to achieve. Carbon nanomaterials deposited by CVD on various substrates could improve certain properties of substrate like conductivity (Su *et al.*, 2011), mechanical properties (Taylor, 1991), hydrophobicity (Liu *et al.*, 2004). But the use of high temperatures in CVD process can damage or decompose some materials and limits the choice of stable precursors. Hence, various techniques are employed in CVD to overcome the limitations (Chhowalla *et al.*, 2001). ALD involves a two-step process with an organometallic Precursor and an oxidizing or reducing agent. Inert gas, such as Ar or N₂, carries away the unreacted

residual precursor molecules to avoid a CVD reaction between precursors. Compared to CVD, ALD provides more precise thickness control and can be operated at much lower temperatures. However, only limited materials can be deposited by ALD process mainly because of the high requirement of the precursor, which should have a self-limiting reaction and be volatile.

Mechanism of Surface Engineering for Energy Storage Materials

Surface Engineering has become a critical aspect to design electrodes with nanomaterials for energy storage. By surface engineering the favorable condition of both the bulk materials and electrochemical interphase of electrolyte and bulk materials can be utilized. The complexity of the engineering challenge can be dramatically decreased by utilizing surface engineering which allows a researcher to identify a material with ideal bulk properties, and then independently engineer the surface properties to be stable. In the following section the mechanism of surface engineering is discussed briefly.

Chemical Activation

Pseudocapacitive electrodes and battery electrodes are two different types of energy storage devices. The surface area, electrical conductivity, and/or ionic transport play an important role to engineer independently physical properties and electrochemical properties of the template.

Hybrid supercapacitors and pseudocapacitors

Pseudocapacitors and hybrid supercapacitors are based on a form of Faradaic storage that involves faster charging and discharging rates than typical batteries. A pseudocapacitor can store over a range of voltages instead of at a fixed redox couple like a battery. Ni(OH)₂, cobalt oxides, mixed metal oxides, or organic materials, are hybrid supercapacitors electrodes, while common pseudocapacitor electrodes are MnO₂ and RuO₂ (Share *et al.*, 2016).

Common processing techniques for depositing the faradaic material have advantages and disadvantages but conformal and complete coatings of the substrate by the active material can mitigate capacity fade during cycling (Zilong *et al.*, 2014). Zilong *et al.* (2014) electrodeposited a conformal coating of MnO₂ onto ZnO NWs that was less than 5 nm thick and were able to achieve over 5000 cycles with only 1.5% loss in capacitance.

Separate processing of substrate and surface can optimize the use of active materials during deposition as reported by Ke *et al.* (2015). They investigated TiO₂ NW arrays but with a TiO₂/Ni(OH)₂ core shell as shown in Fig. 24.

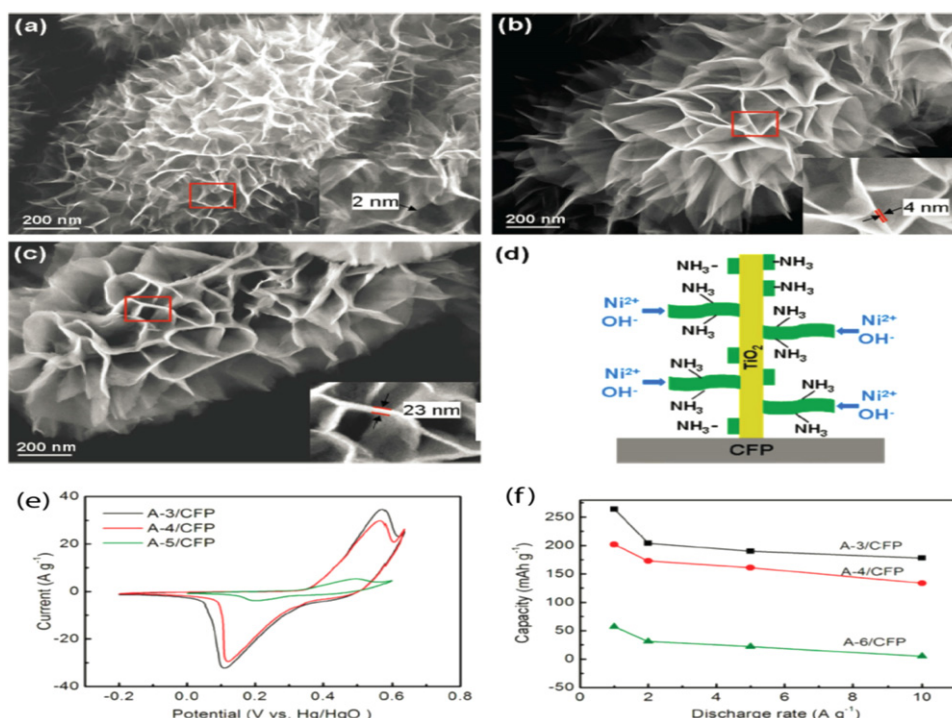


Fig. 24 SEM images of (a) A-3/CFP, (b) A-4/CFP, (c) A-6/CFP and the insets show the high magnified SEM images of Ni(OH)₂, (d) Schematic diagram showing the Ni(OH)₂ nanowalls growth process, (e) CV curves ranging from 0.2 to 0.6 V at a scan rate of 5 mV s⁻¹, (f) Capacity at different current densities.

The $\text{Ni}(\text{OH})_2$ morphology, crystallinity and surface area were optimized during chemical bath deposition process where different amount of ammonia was used. Less ammonia was beneficial in achieving thinner nanowalls with higher surface area but with higher capacities and lower charge transfer resistance. Thus TiO_2 scaffold provided a 3D nanostructure with efficient electron transport while $\text{Ni}(\text{OH})_2$ acted as the optimized active material. This approach was found to be beneficial for graphene and other conductive carbon substrates with a high surface area and the capacitance was increased by $\sim 20\%$ (Share *et al.*, 2016).

Batteries

Batteries are generally optimized for total storage capacity instead of power capacity. Unlike pseudocapacitors, redox reactions in batteries access deep bulk material and not just the surface. Hence, there is a large volume expansion of the electrode. During charging and discharging of batteries solid electrolyte interphase (SEI) is formed, where high surface area is not necessary.

Metal oxides and sulfides like TiO_2 , V_2O_5 , and Cu_2S can be used as active layers in traditional ALD but recent work has focused on lithiated electrode materials such as LiCoO_2 , LiMn_2O_4 , and LiFePO_4 (Share *et al.*, 2016).

Electrode architecture and electrode thickness both can limit the performance, emphasizing the importance of separate optimization. TiO_2 nanotubes with varying aspect ratio but of same surface area were fabricated and it was found that higher aspect ratios have higher capacities, especially at fast rates (30C), due to better electron/ion transport. Some researchers used anodic alumina templates and compared that with a 3D NW template on a Ni current collector with ALD deposited TiO_2 (Fig. 25) (Share *et al.*, 2016).

Due to the unique template, multiple interconnects were formed in the 3D NW network, and thus agglomeration of the NWs was prevented resulting in much higher real capacities and rate capabilities. The TiO_2 thickness was varied during ALD deposition where an 8 nm film had a higher capacity and better rate capability than a 16 nm.

Multi-valent ion batteries such as Al^{3+} and Mg^{2+} bring potential for high capacity batteries. However, due to multivalent state of the ions, the diffusion of these ions through electrodes is particularly limited. Designing electrodes with short diffusion lengths are important to achieve good rate capability, which emphasize the importance of chemical activation process. NW arrays of V_2O_5 and TiO_2 have shown promise as Al ion electrodes. These newer battery technologies still suffer from irreversible reactions between the electrolyte and electrode/current collector but by using techniques discussed earlier could mitigate these issues (Share *et al.*, 2016).

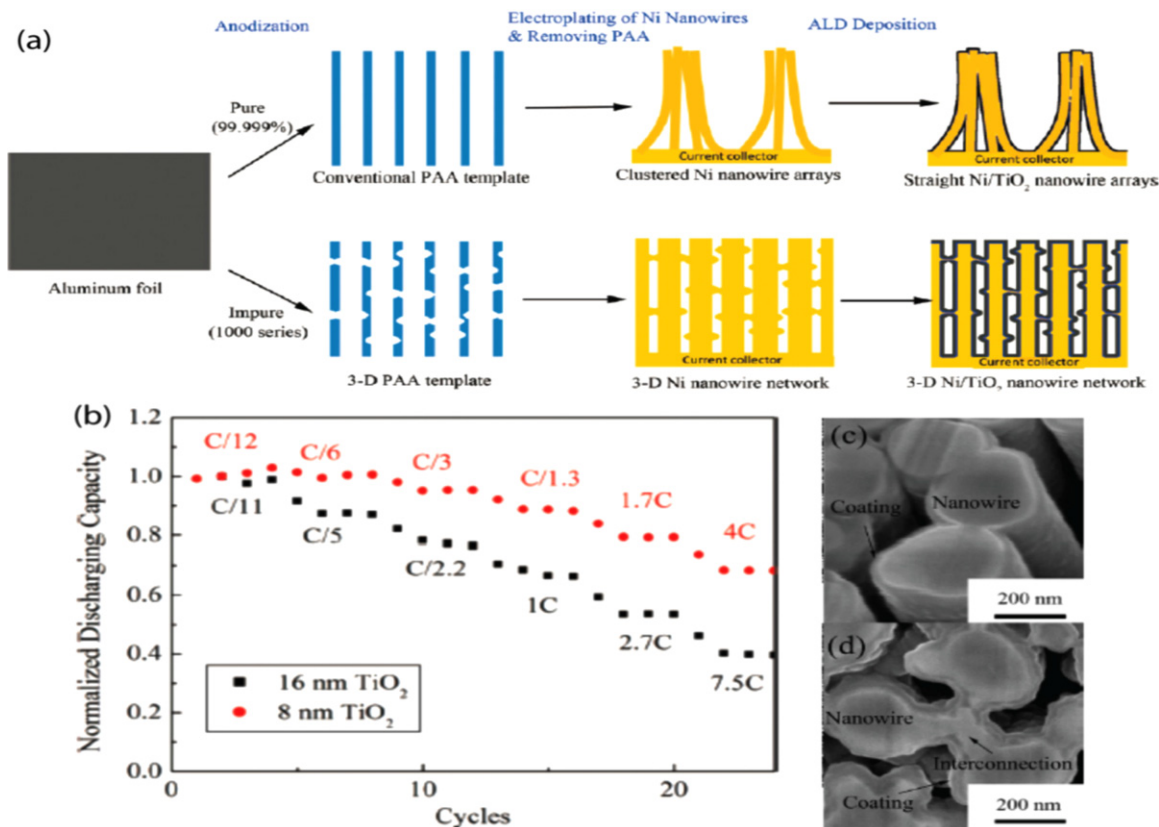


Fig. 25 (a) Schematic fabrication process flow for straight Ni/TiO_2 nanowire arrays (top) and 3D Ni/TiO_2 nanowire network (bottom), which uses Al foils with different impurity. The side holes in the 3D PAA template result in interconnections in 3D nanowire network. (b) Rate capabilities of 32 μm long 3D Ni/TiO_2 nanowire network structure with different TiO_2 coating thicknesses. (c) SEM images of Straight Ni/TiO_2 nanowire arrays and (d) as-prepared 3D Ni/TiO_2 nanowire network.

Conclusions

In this paper the synthesis of nanomaterials is reviewed with a close focus on production of CNMs from different types of coals and sustainable resources through wide range of fabrication routes. An insight on potential applications of CNMs is also provided. The key challenge is to produce high quality CNMs in large scale without causing any major environmental concern, while ensuring better yield and performance. Though coal is mainly used for thermal power generation, coal-based NMs can be harnessed for sustainable energy generation and environmental remediation through electrocatalysis, separation of components through efficient adsorption and in sensing applications. However, care should be taken so that sustainable coal sources do not interfere with food chain. CNMs have potential application as energy storage device. In this regard different active materials of EES including LIBs, SIBs, MIBs, post-LIBs, supercapacitors and their merits and demerits are also highlighted. Though the current LIBs and supercapacitors are still flourishing but their potential alternatives using NMs and nanotechnology are emerging. However, challenges associated with incorporation of nanostructure into high performance EES devices need to be addressed. These challenges can be handled by incorporating 3D printing manufacturing and surface engineering. Surface engineering can be the most relevant theme in energy storage device with respect to cathode design for LIS batteries, dendrite migration in metal anode, and micro-crack prevention in high voltage cathodes. Atomic layer deposition will enable a limitless area of innovation for next generation energy storage technology. Moreover, modifying the surface independently from the bulk materials can add another dimension to unlock the promise of future advance in energy storage systems. Though 3D printing offers tremendous flexibility, there are few limitations with this process in the context of versatility and customizability. But it is envisioned that with the current efforts for continuous development of 3D printing techniques aimed at offering high-speed, low-cost versatile production capability and resolution, 3D printing will eventually become an essential part of future EES manufacturing.

See also: Hydrogen Production Through Water Splitting Using Nanomaterials Under Solar Energy. Semiconductor-Based Photocatalytic Nanomaterials for Environmental Applications

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Nano-Porous Materials for Energy Conversion Using Green Technologies

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Introduction

One of the great challenges in the recent years is unquestionably energy conversion. In response to the recent needs of the world, it is now necessary that new, low-cost and environmentally friendly energy conversion systems are found; hence the accelerating of the development of research in this area. Nanomaterial lies at the heart of the advances that have already been made in energy conversion. Nano materials have various morphology structures based on their structural complexity. [Fig. 1](#) shows nanostructured materials with different morphologies ([Kumar et al., 2017](#)).

Dimensionality of Nanoparticles

They are generally classified based on their dimensionality, morphology, composition, uniformity, and agglomeration.

1D nanomaterials

These are one dimensional in the nanometer scale are typically thin films or surface coatings, and include the circuitry of computer chips and the antireflection and hard coatings on eyeglasses. These have been used in electronics, chemistry, and engineering ([Kumar et al., 2017](#)).

2D nanomaterials

Two-dimensional nanomaterials have two dimensions in the nanometer scale. These include 2D nanostructured films, with nanostructures firmly attached to a substrate, or nanopore filters used for small particle separation and filtration. Asbestos fibers are an example of 2D nanoparticles ([Kumar et al., 2017](#)).

3D nanomaterials

Materials that are nanoscaled in all three dimensions are considered 3D nanomaterials. These include thin films deposited under conditions that generate atomic-scale porosity, colloids, and free nanoparticles with various morphologies ([Kumar et al., 2017](#)).

Porous and Porous Material

Nano-porous materials as a subset of nanostructured materials possess unique surface, structural, and bulk properties that underline their important uses in various fields such as ion exchange, separation, catalysis, sensor, biological molecular isolation, and purifications. Nano-porous materials are also of scientific and technological importance because of their vast ability to adsorb, and interact with atoms, ions, and molecules on their large interior surfaces and in the nano-meter sized pore space.

The presence of pores (holes) in a material can render itself all sorts of useful properties that the corresponding bulk material would not have ([Kresge et al., 1992](#)). Pores are categorized into two types: open pores which connect to the surface of the material and closed pores which are isolated from the outside as shown in [Fig. 2](#).

In [Fig. 2](#), region 'a' represents the closed pores, and regions such as b, c, d, e, and f represent open pores ([Ishizaki et al., 1998](#)).

In functional applications such as adsorption, catalysis, and sensing, closed pores are not of any use. In separation, catalysis, filtration or membranes, often penetrating open pores are required. Materials with closed pores are useful in sonic and thermal insulation, or lightweight structural applications. Pores have various shapes and morphology such as cylindrical, spherical and slit types. There are also pores taking more complex shapes such a hexagonal shape. Pores can be straight or curved or with many turns and twists thus having a high tortuosity ([Shirosaki et al., 2016](#)). Based on the International Union of Pure and Applied Chemistry (IUPAC) the pore size is classified into three types: less than 2 nanometers in diameter (micropores), between 2 and 50 nanometers (mesopores) and more than 50 nanometers (macropores) as shown in [Fig. 3](#) ([Shirosaki et al., 2016](#)).

Nanoporous materials are a subset of porous materials, typically having large porosities (greater than 0.4), and pore diameters between 1 and 100 nanometers. In the field of chemical functional porous materials, it is better to use the term "nanoporous" consistently to refer to this class of porous materials having diameters between 1 and 100 nm. For most functional applications, pore sizes normally do not exceed 100 nanometers anyway ([Lu and Zhao, 2004](#)).

Nanoporous materials classification

Porous materials can be classified according to their materials constituents (such as organic or inorganic; ceramic or metal) or their properties. [Table 1](#) summarizes the available nanoporous materials according to their chemical compositions and their technical characteristics ([Lu and Zhao, 2004](#)).

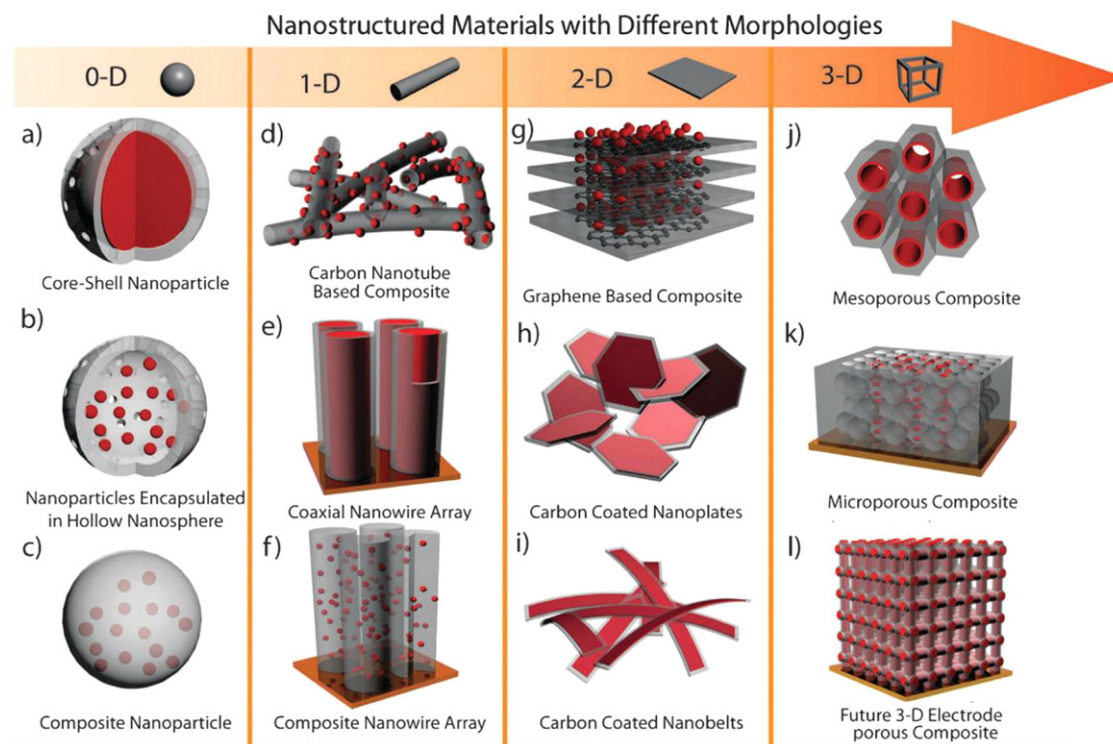


Fig. 1 Different nanostructured materials based on their structural complexity. Reproduced from Kumar, P., Kim, K.-H., Bansal, V., Kumar, P., 2017. Nanostructured materials: A progressive assessment and future direction for energy device applications. *Coordination Chemistry Reviews* 353, 113–141. doi:10.1016/j.ccr.2017.10.005.

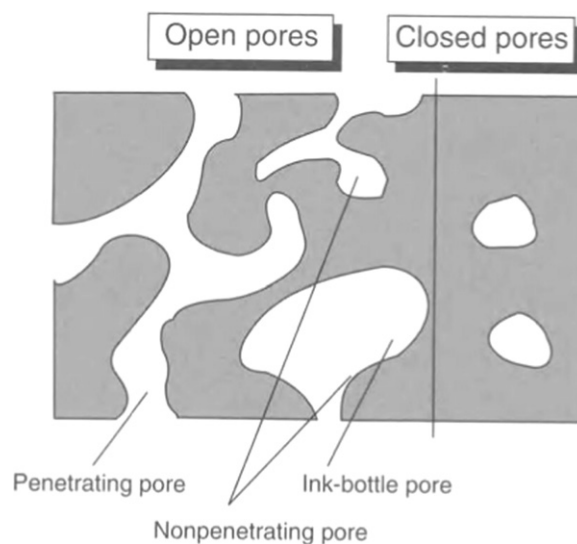


Fig. 2 Classification of pores. Reproduced from Ishizaki, K., Komarneni, S., Nanko, M., 1998. Porous materials. In: *Materials Technology Series*. Springer. (ISBN 978-1-4615-5811-8 (eBook)).

Major applications of nanoporous materials

The applications of the nanoporous materials have not limited to the traditional areas of adsorption separation, catalysis, and membranes; but in the recent years they have expanded into promising applications, which can be summarized as follows (Lu and Zhao, 2004):

- Environmental separations.
- Clean energy production and storage.

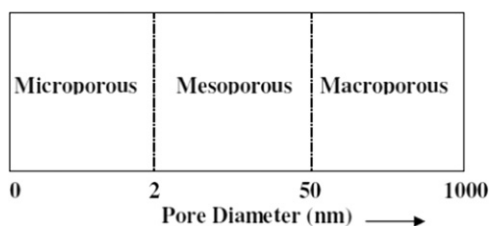


Fig. 3 IUPAC classification of pores. Reproduced from Shirosaki, Y., Nakamura, Y., Yoshioka, T., Osaka, A., 2016. Inorganic-organic hybrids for biomedical applications. In: Klein, L., Aparicio, M., Jitianu, A. (Eds), Handbook of Sol-Gel Science and Technology. Springer: Cham.

Table 1 Nanoporous materials classification

	<i>Polymeric</i>	<i>Carbon</i>	<i>Glass</i>	<i>Alumino-silicate</i>	<i>Oxides</i>	<i>Metal</i>
Pore size	Meso- macro	Micro- meso	Meso- macro	Micro- meso	Micro- meso	Meso- macro
Surface area/Porosity	Low > 0.6	High 0.3–0.6	Low 0.3–0.6	High 0.3–0.7	Medium 0.3–0.6	Low 0.1–0.7
Permeability	Low-medium	Low-medium	High	Low	Low-medium	High
Strength	Medium	Low	Strong	Weak	Weak-medium	Strong
Thermal stability	Low	High	Good	Medium-high	Medium-high	High
Chemical stability	Low- medium	High	High	High	Very high	High
Costs	Low	High	High	Low- medium	Medium	Medium
Life	Short	Long	Long	Medium- long	Long	Long

Note: Lu, G.Q., Zhao, X.S., 2004. Nanoporous Materials: Science and Engineering. Imperial College Press, p. 4. (ISBN: 1-86094-210-5).

- Catalysis and photocatalysis.
- Sensors and actuators.
- Biological applications.
- High-efficiency filtration and separation membranes.
- Catalytic membranes for chemical processes.
- Porous electrodes for fuel cells.
- High-efficiency thermal insulators.
- Electrode materials for batteries.
- Porous electronic substrates for high-speed electronics.

These applications can be summarized in [Table 2](#) ([Sun et al., 2016](#)).

Energy Conversion

Energy conversion concerns the transformation of energy from one form to another, for example, sunlight to chemicals or electricity, electricity to thermal and mechanical energy, chemicals to thermal energy and electricity. Today the sense of energy conversion deals with the conversion of one form of energy to that we can use directly. Energy conversion is a very hot topic and essential to nature and the human society.

Nanoporous materials have played an important role in energy-related applications such as catalysts, and solar energy conversion and chemical energy conversion ([Sun et al., 2016](#)). As one of the clean energy sources with the best potential, solar energy conversion devices, which include commercial silicon solar cells, organic solar cells, quantum dot solar cells, DSSCs, photo-synthetic solar cells, and photocatalytic water splitting systems, have been well studied ([Mor et al., 2006](#); [Liu et al., 1998](#); [Keis et al., 2002](#); [Tennakone et al., 1995](#); [Chappel and Zaban, 2002](#); [Gebeyehu et al., 2001](#); [Reijnen et al., 2002](#); [Sun et al., 2016](#)). Fuel cells (FCs), another potential clean energy sources, have also been widely investigated as chemical energy conversion systems. Considering that there have been many interesting reviews on solar energy conversion, this section only pays attention to the recent progress in typical porous structures for different types of solar cells. The reviews will also focus on the recent developments on fuel cells applications.

Solar Energy

Solar energy is well recognized as one of the most promising choices to meet the predicted energy demand in the near future. This has inspired advances in solar cell research in an attempt to improve the direct conversion of solar radiation energy into electricity. It can be used efficiently in various practical applications like solar power plants, solar cell, seawater desalination, solar collectors, etc. In fact, sunlight falling on Earth offers a solution, since the hourly solar flux incident on Earth's surface is greater than the

Table 2 Applications of hierarchically structured porous materials in energy conversion and storage, photocatalysis, catalysis, adsorption, separation, sensing, and biomedicine

Applications		Types	Structural properties	Positive effects in applications
Energy conversion and storage	Energy conversion	DSSCs Fuel cells	(i) Porous hierarchy	(i) Efficient light-harvesting, especially in biomaterials replica or biocomposites;
		Photocatalytic hydrogen production	(ii) High surface area;	(ii) Fast charge separation and high current density;
	Energy storage	Supercapacitors	(iii) Short diffusion length	(iii) High gas permeability;
		Lithium-ion batteries		(iv) High storage density;
		Lithium-sulfur batteries		(v) Fast electron and ion transport;
		Lithium-air batteries		(vi) Small resistance
		Sodium-ion batteries		
		Magnesium-ion batteries		
Catalysis and photocatalysis	Photocatalysis	Metal catalysts metal oxide catalysts zeolites	(i) Porous hierarchy	(i) High accessibility of bulky molecules;
	traditional catalysis	metals loaded on hierarchically porous inert supports	(ii) High surface area;	(ii) High diffusion rate of reactant and product;
			(iii) Tunable pore size	(iii) Usually, heteroatoms of zeolites or supported nanometal particles as active sites
			(iv) Large pore volume	
Adsorption and separation		Adsorption separation	(i) Homogeneous flow-through pore structure;	(i) High permeability;
			(ii) High surface area;	(ii) Usually, monolithic column used
			(iii) Controlled pore structures and surface properties;	
Sensing		ZnO-based sensors other metal/bimetal oxide based sensors graphene-based sensors	(i) Porous hierarchy	(i) Large surface adsorption positions and reacting areas;
			(ii) High surface area;	(ii) Facile gas diffusion and mass transport
			(iii) Short diffusion length	
Biomedicine		Bone tissue engineering	(i) Porous hierarchy	(i) Improved bioactive behavior and easy for cell penetration, tissue ingrowth;
			(ii) High surface area;	(ii) Enhanced drug diffusion, loading and release;
			(iii) Large pore volume	(iii) High enzyme loadings and quick enzyme immobilization rates

Note: Sun, M.-H., Huang, S.-Z., Chen, L.-H., *et al.*, 2016. Applications of hierarchically structured porous materials from energy storage and conversion, catalysis, photocatalysis, adsorption, separation, and sensing to biomedicine. *The Royal Society of Chemistry* 45, 3479–3563. doi: 10.1039/c6cs00135a.

annual human consumption of energy in a year (Hussein, 2015). That is why the sun so appears in gas an ultimate energy source on the earth. The quantity of solar energy received by the earth is a function of the season, with the highest quantity of incoming solar energy received during the summer months (Hussein, 2015). The big challenge in using these devices is that the clear weakness in the absorption properties of the conventional fluids which lead to reduce the efficiency of these devices. Nowadays, this problem can be solved easily and effectively by using the concept of nanotechnology. The increased surface area to volume ratio of nanoparticles should enhance solar energy collection and efficiency by exposing more conducting surfaces to the sunlight. Another area that nanotechnology will increase solar cell efficiency is by using materials like lead-selenide. These materials cause more electrons (and therefore more electricity) to be released when hit by a photon of light (Hussein, 2015).

Furthermore, the cost is a major factor in the success of any solar technology. Because converting solar energy into electricity occurs at a price comparable with fossil fuel. Semiconductor materials that exhibit a photovoltaic (PV) effect can be used to convert solar radiation into electricity through a photovoltaic process. Photo-voltaics are surfaces typically consisting of a conducting oxide layer and a catalytic platinum layer that directly convert sunlight to electrical energy. A device which converts photons from the solar light into electricity using electrons is called the photovoltaic solar cell. Solar energy is very environment-friendly. For example, if a distributed solar grid meets 1% of the world's electricity demands, approximately 40 million tons of carbon dioxide

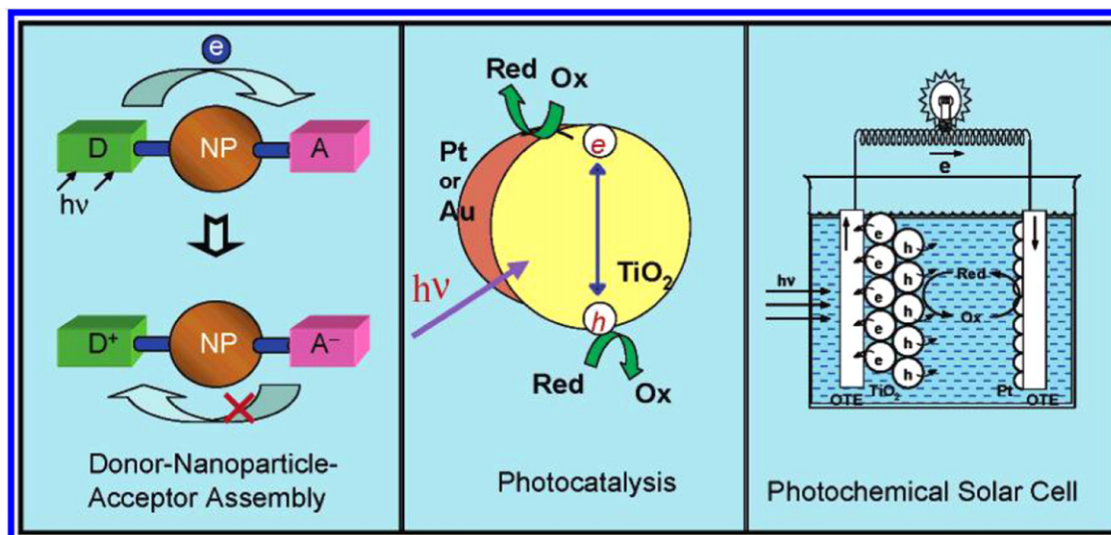


Fig. 4 The major ways that one can utilize nanostructures for the design of solar energy conversion devices. Reproduced from Kamat, P.V., 2007. Meeting the clean energy demand: nanostructure architectures for solar energy conversion. *Journal of Physical Chemistry C* 111, 2834–2860.

emissions can be saved per year (Hussein, 2015). There are three major ways that one can utilize nanostructures for the design of solar energy conversion devices as shown in Fig. 4 (Kamat, 2007).

Solar cells types

There are various types of solar cells which can be described briefly as follows (Hussein, 2015):

- Dye-sensitized solar cell (DSSC):

This type of solar cells enables optical absorption and charge separation/injection by associating a dye sensitizer (a light-absorbing material) with a wide-bandgap semiconductor of nano-crystalline morphology as the photoanode. It is based on the combination of interpenetrating networks of mesoscopic semiconductor materials with electrolytes as alternatives to the p–n junctions of inorganic solid-state semiconductors in conventional solar cells.

Generally, a regular DSSC device consists of a working electrode, dye molecules, electrolytes, a spacer, and a counter electrode as shown in Fig. 5, (Hussein, 2015). The working electrode contains the as-prepared hierarchically porous structured materials, where a great number of dyes can be loaded inside the hierarchically porous structures (Sun *et al.*, 2016). On the other hand, the porous structures are beneficial for light harvesting via multiple light scattering and reflections. It is well known that the macrochannels in hierarchically porous materials play a role as light harvesters, allowing the deep penetration of light in materials due to the scattering effect of the longer pathway length in macrochannels.

The utilization of nanoporous materials improves light absorption, resulting in high power conversion efficiency. So far, the most widely studied hierarchically porous nanostructures are TiO_2 , ZnO and the composites based on them due to their easily controlled porous structures (Mor *et al.*, 2006; Liu *et al.*, 1998; Keis *et al.*, 2002; Tennakone *et al.*, 1995; Chappel and Zaban, 2002; Gebeyehu *et al.*, 2001; Reijnen *et al.*, 2002; Sun *et al.*, 2016), despite many other materials also being used for DSSCs (Sun *et al.*, 2016).

- Organic-polymer-based PV solar cell (OPV):

In this type, excitons are separated in to free electron–hole pairs by the effective field created across the heterojunction between two dissimilar organic materials, known as the donor and acceptor molecules. This type is produced as a result of the increasing requirements for expensive renewable energy sources, as one option for the production of energy from light at very low-cost.

Solar cells based on thin polymer films are particularly attractive because of their ease of processing, mechanical flexibility, and potential for low cost fabrication of large areas. Additionally, their material properties can be tailored by modifying their chemical makeup, resulting in greater customization than traditional solar cells allow. Although significant progress has been made, the efficiency of converting solar energy into electrical power obtained with plastic solar cells still does not warrant commercialization: the most efficient devices have an efficiency of 4%–5% (Askari Mohammad Bagher, 2014). Many crucial studies have been achieved to understand what limits their performance to improve the efficiency of plastic solar cells (Askari Mohammad Bagher, 2014; Antonio Facchetti, 2013; Chiechi *et al.*, 2013; Mayer *et al.*, 2007; Kumar *et al.* 2018; Wang *et al.*, 2018; Chen *et al.*, 2018).

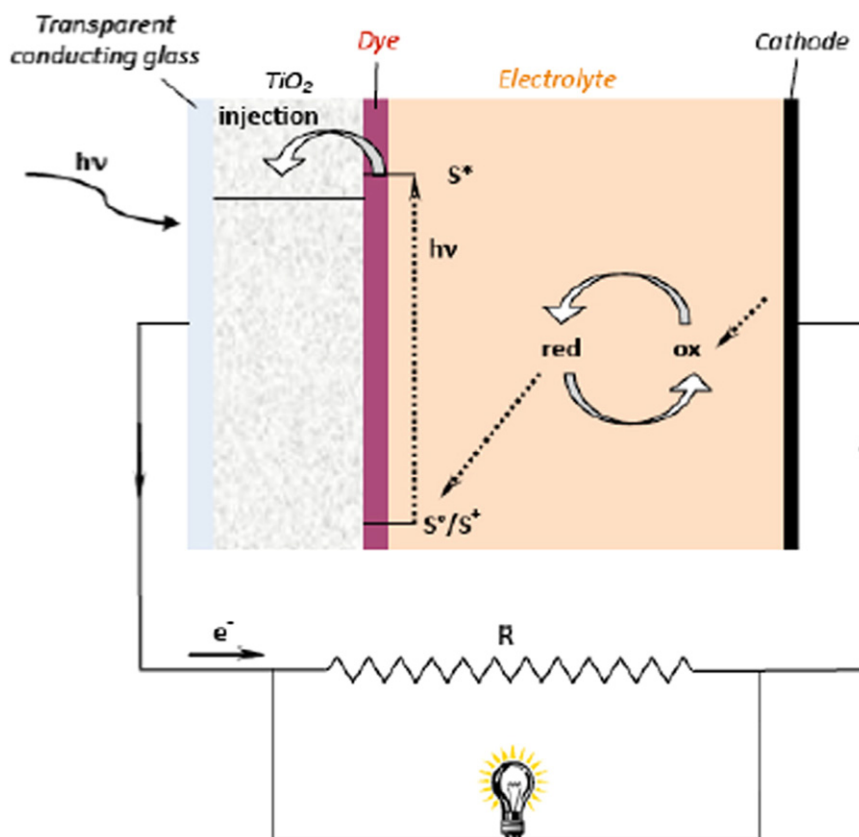


Fig. 5 Schematic principle of a dye-sensitized solar cell. Reproduced from Hussein, A.K., 2015. Applications of nanotechnology in renewable energies – A comprehensive overview and understanding. *Renewable and Sustainable Energy Reviews* 42, 460–476. doi: 10.1016/j.rser.2014.10.027.

- Hot carrier solar cells:

The term hot carrier solar cell (HCSC) was coined by Ross and Nozik to overcome the Shockley-Queisser efficiency limit in simple photovoltaic devices (Farrell *et al.*, 2011). In this type, a free electron is bumped high into the conduction band by a too energetic photon. Therefore, its electronic temperature becomes quite hot (as high as 3000 K). The hot electron will relax to the bottom of the conduction band, typically within a few hundred femtoseconds, imparting heat to the lattice as it does so. This type of solar cells has the following advantages, (Hussein, 2015):

- (1) Using a high-energy electron will increase the photovoltage of the device as well as its efficiency.
- (2) The excess energy will be prevented by heating the device and by lowering its efficiency.

There have been several studies to improve the efficiency of hot carrier solar cells by investigating the following: design and fabrication of HCSC, using different materials, modeling and predictions different parameters (Takeda *et al.*, 2009; Farrell *et al.*, 2011; Yang *et al.*, 2018).

Fuel Cell

A fuel cell is an electrochemical energy conversion device which converts the chemical hydrogen and oxygen into water, and in the process it produces electricity. Most fuel cells today use hydrogen and oxygen as the chemicals (Dzhafarov and Yuksel, 2011).

The fuel can be of fossil origin or come from renewable energy. With fossil origin the primarily of gases produced from natural gas, oil, or coal. They comprise hydrogen, CO, methane or propane, methanol, gasoline or diesel, or mixtures such as syngas or coal gas (both mainly $H_2 + CO$). Fuels from renewables comprise primarily hydrogen, but also some what we may call hydrogen carriers; methanol, ammonia, etc. Recently, the focus has been put on biofuels (alcohols, bio-diesel, etc.) from the organic harvest of sunlight. Fuel cells offer potential advantages in efficiency and environment-friendly operation for all types of fuels (Truls, 2013).

The fuel cell provides a DC (direct current) voltage that can be used to power motors, lights or number of electrical appliances.

Fuel cells are made up of three segments: the anode, the electrolyte, and the cathode, where the catalyst on the anode can oxidize the fuel into a positively charged ion and a negatively charged electron and the catalyst on the cathode turn the ions into

Table 3 Types of fuel cells

<i>Fuel cell types</i>	<i>Fuel</i>	<i>Efficiency (%)</i>	<i>Operating temp. (°C)</i>
PEM	H ₂	40–50	80
Direct Methanol (DMFC)	Methanol	35	80
	Ethanol		
Solid Oxide (SOFC)	H ₂ , CO, CH ₄	45–55	700
Molten Carbonate (MCFC)	H ₂ , CO, CH ₄	50–60	650
Phosphoric Acid (PAFC)	H ₂	40–50	190
Alkaline (AFC)	H ₂	50	50

Note: Dzhafarov, T., Yuksel, S.A., 2011. Nano-porous silicon-based mini hydrogen fuel cells, Chapter 13. In: Manzanera, M. (Ed.), *Alternative Fuel*. InTech, p. 311. (ISBN: 978-953-307-372-9).

waste chemicals. Therefore, the catalysts on both electrodes are very important for a fuel cell (Sun *et al.*, 2016). From the viewpoint of the catalysts used in fuel cells, the high surface areas, large pore volumes and, in particular, interconnected macro-nano porosity of the supports on both electrodes are essential owing to the fact that higher surface areas, larger pore volumes and interconnected macro-nano porosity can allow a better dispersion for the active catalysts and offer an open network around the active catalysts for facile diffusion of fuels and products. So far, porous carbon-supported Pt and Pt-based catalysts have been generally considered to be the most common electrocatalysts for fuel cells (Sun *et al.*, 2016). However, the high cost, quick CO poisoning and slow kinetics of fuel oxidation severely restrict their commercial applications. Pursuing low-cost electrocatalysts with highly improved kinetics is urgent. Great efforts have been made to search for efficient, durable and inexpensive alternatives to Pt-based catalysts, such as Pd-based catalysts and metal-free catalysts.

Types of fuel cells

The existing fuel cells are usually classified by their operating type and the type of electrolyte they use. The main types of fuel cells are given in Table 3, (Dzhafarov and Yuksel, 2011). In this article, the PEM fuel cells type will be focused, for it's a widespread, and its uses and multiple applications.

- Polymer exchange membrane fuel cell (PEM or PEMFC).

The PEM is the most likely candidate for portable and transportation applications. The PEM has a high power density and a relatively low operation temperature (ranging from 80 to 120°C). PEM type fuel cell consists of two electrodes (the anode and cathode) and the electrolyte between them. The electrodes of the fuel cell are thin layers of material, with the platinum catalyst dispersed in carbon, which is applied to each side of the membrane, yielding what is known as a Membrane Electrode Assembly (MEA) as shown in Fig. 6, (Dzhafarov and Yuksel, 2011). The anode, the negative post of the fuel, has several jobs. It conducts the electrons that are freed from the hydrogen molecules so that they can be used in an external circuit. It has channels etched into it that disperse the hydrogen gas equally over the surface of the catalyst. The cathode, the positive post of the fuel cell, has channels etched into it that distribute the oxygen to the surface of the catalyst. It also conducts the electrons back from the external circuit to the catalyst, where they can recombine with the hydrogen ions and oxygen to form water. The electrolyte is the proton exchange membrane. PEM can be made from either pure polymer membranes or from composite membranes where other materials are embedded in a polymer matrix. One of the most common and commercially available PEM material is Nafion, a DuPont product.

The membrane presents a solid polymer having negative ionic sites attached to polymer chains. When such a membrane is hydrated (having water absorbed into it), hydrogen ions (protons) can move among the sites so that the protons can be transported across the membrane. The membrane only conducts positively charged ions and blocks electrons. For a PEMFC, the membrane must be hydrated to function and remain stable. The catalyst (electrode) is a special material that facilitates the reaction of oxygen and hydrogen. It is usually made of platinum nano-particles very thinly coated onto carbon paper or cloth. The catalyst is rough and porous so that the maximum surface area of the platinum can be exposed to the hydrogen or oxygen. When an H₂ molecule comes in contact with the platinum catalyst on the anode side, it splits H₂ into two H⁺ ions (protons) and two electrons (e⁻). The electrons are conducted through the anode, where they make their way through the external circuit (doing useful work such as turning a motor) and return to the cathode side of the fuel cell. On the cathode side of the fuel cell, oxygen gas (O₂) is being forced through the catalyst, where it forms two oxygen atoms. Each of these atoms has a strong negative charge. This negative charge attracts the two H⁺ ions through the membrane, where they combine with an oxygen atom and two of the electrons from an external circuit to form a water molecule (H₂O), (Dzhafarov and Yuksel, 2011).

Problems of performance, reliability, durability, a restricted allowable ambient-temperature range for operation and cost of miniature PEM fuel cells, for portable devices were related with:

- Materials of polymer membrane and the platinum catalyst,
- Poisoning the platinum catalyst by carbon dioxide during fuel cell operation,
- The large resistance drop in the membrane-electrode-assembly,

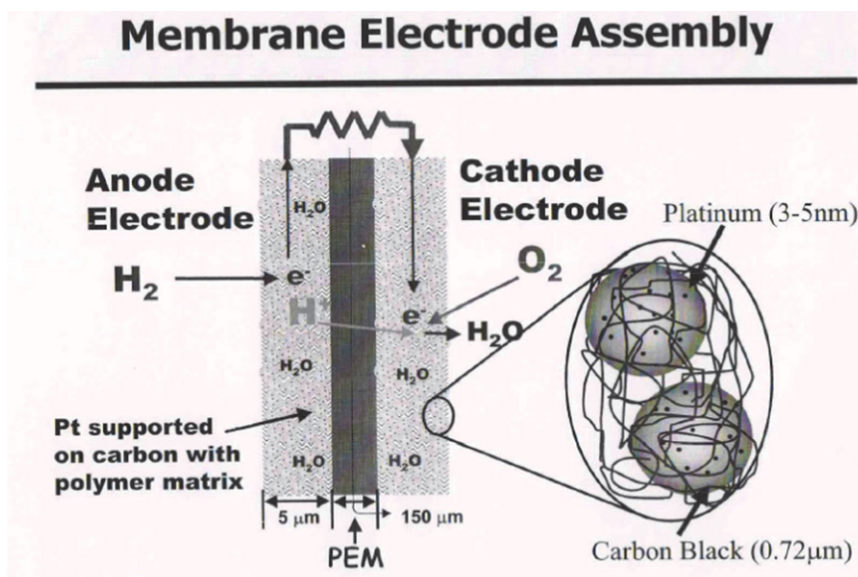


Fig. 6 Proton Exchange Membrane (PEM-type hydrogen fuel cell). Reproduced from Dzhaifarov, T., Yuksel, S.A., 2011. Nano-porous silicon-based mini hydrogen fuel cells, Chapter 13. In: Manzanera, M. (Ed.), *Alternative Fuel*. InTech, p. 311. (ISBN: 978-953-307-372-9).

- Compatibility of DMFC technology fabrication with standard microtechnology.

Many research works have attempted to solve these problems, especially about nonporous materials and their structures (Sun *et al.*, 2016; Dzhaifarov and Yuksel, 2011; Truls, 2013; Candelaria *et al.*, 2012; Wallace *et al.*, 2009; Wolfgang Luther, 2008).

Summary and Remarks

Energy generated via renewable energy strategies is critical to various aspects of global human development, including harmony, equity, employment, ecosystems, and environmental protection. Alternative energy sources should be derived from geothermal, hydrothermal, solar, wind, nuclear and other renewable resources. Several strategies have been attempted to produce a clean energy using green technologies. One of these techniques is using energy conversion forms. This article aims to introduce the Nano-porous materials applications in an energy conversion, particularly in solar cells energy and fuel cells. In spite of the increased efficiency of the conversion of energy using nano-porous particles, by using the green technologies, they still need more research works using new materials with different structures, achieving higher reliability of the system used and more cost reduction and less polluting environment.

See also: Application of Nano Porous Materials for Energy Conservation and Storage. Application of Nano Porous Materials for Energy Conversion Process. Electrochemical Energy Storage Using Batteries, Superconductors and Hybrid Technologies

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Nano-Porous Materials for Use in Solar Cells and Fuel Cells

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Introduction

Nano-structured porous silicon (PSi) has become very attractive for solar cell applications as it can be used for anti-reflection coating to absorb more sunlight, omni-directional Bragg reflector to trap the photons by improving internal reflection, and excellent reusable substrate to reduce the cost of wafer. Besides, through deformation, the porosity of porous Si (PSi) allows Ge, GaN and GaAs to grow in an epitaxial way which was nearly impractical for bulk Si and may bring a paradigm shift in next generation thin film photovoltaic research. On the other hand, Dye Sensitized Solar Cell may surpass all other photovoltaic trends not only for its fascinating state-of-the-art fabrication process but also for the prospect of overall cell efficiency, even though the efficiency of DSSC ($\eta \approx 11\%$) is still far behind of PSi ($\eta \approx 18\%$). These porous ceramic solar cells are beneficial especially for low light environment.

Fuel cells are considered as the most efficient and sustainable tool to combat energy crisis and environment pollution because of their higher efficiency in converting chemical energy into electrical energy directly by a combustion and pollution free operation. Fuel cells generate electricity and heat by electrochemical process of redox reaction between fuel (hydrocarbons, H_2) and oxidant (O_2) through porous electrodes, mostly ceramic, and ion conducting non-porous electrolyte. In this paper, the variety of porous ceramic materials for fuel cell application is reviewed briefly.

Porous Ceramics as Solar Cells

Porous Silicon Solar Cell

In 1956, Uhlir and Uhlir first noticed that electrochemical etching creates round shaped pores instead of polishing the Si and Ge wafers which was then quite unusual (Uhlir and Uhlir, 2005). Porous Si wafers have direct and wide bandgap. Si has indirect type 1.12 eV bandgap which means any electromagnetic (EM) spectrum having energy equal or higher than 1.12 eV, it will be absorbed by the material as well as Silicon in this case. This implies that the absorbed EM spectrum definitely have wavelength equal or less than 1107 nm. Consequently the EM spectrum having energy less than 1.12 eV or wavelength higher than 1107 nm will be reflected by the material.

Therefore, Si should be capable of utilizing almost 60%–70% solar spectra but it fails because it enables the Si solar cell to absorb photons having a wide range of energies associated with the spectra. The photoexcitation creates chaotic electron – hole recombination inside of the depletion zone which is undesirable. It is expected that those electrons, generated by photoexcitation, recombine with holes through some specified paths and the travel of electrons through the paths can be utilized. But this expectation hampers when electrons are excited with photons having higher energy than the required bandgap and as a consequence these excess energy turns into heat followed by decreasing the conductivity and ultimately efficiency of the solar cell. In order to increase the efficiency, we need to narrow the solar spectra transmission since we cannot make the solar spectra monochromatic which means we have to increase the bandgap of Si solar cell.

Porous silicon (PSi) as antireflection coating (ARC)

One of the most important factors which limit the efficiency of solar cell is the reflectance of light from its front surface. Due to the refractive index between air and solar cell material, transmission efficiency is highest when incident angle is lowest and with increase in the incident angle, transmission efficiency decreases. From the concept of refractive index which is basically a measure of how much light has been reflected at incident surface, it can be said that to minimize the reflection, the refractive index needs to be decreased. In this way, more light of specific solar spectra (narrowed by increased bandgap) can be transmitted into the solar cell material which in turn increases the net efficiency.

When a thin layer of antireflection coating is placed on the Si solar cell, light is reflected twice – one from the front surface and another from the bottom of the layer. If these two reflected light waves have equal amplitude but out of phase (180°), then they will cancel out each other by resulting a destructive interference (see Fig. 1(a)). For the amplitudes of two light waves to be equal, the refractive index of the coating layer has to be equal to the square root of the refractive index of the substrate. Single and multilayer porous silicon structure used as an antireflective coating (ARC) are illustrated in Fig. 1.

Although texturizing the front surface has been widely investigated in order to achieve the efficient light trapping, this technique alone could not minimize the reflection below 10% in the wavelength range 400–1000 nm and the reproducibility of state of the art synthesis is another major limiting factor (Dzhafarov *et al.*, 2012; Weiying *et al.*, 2011; Marrero *et al.*, 2009). Hence,

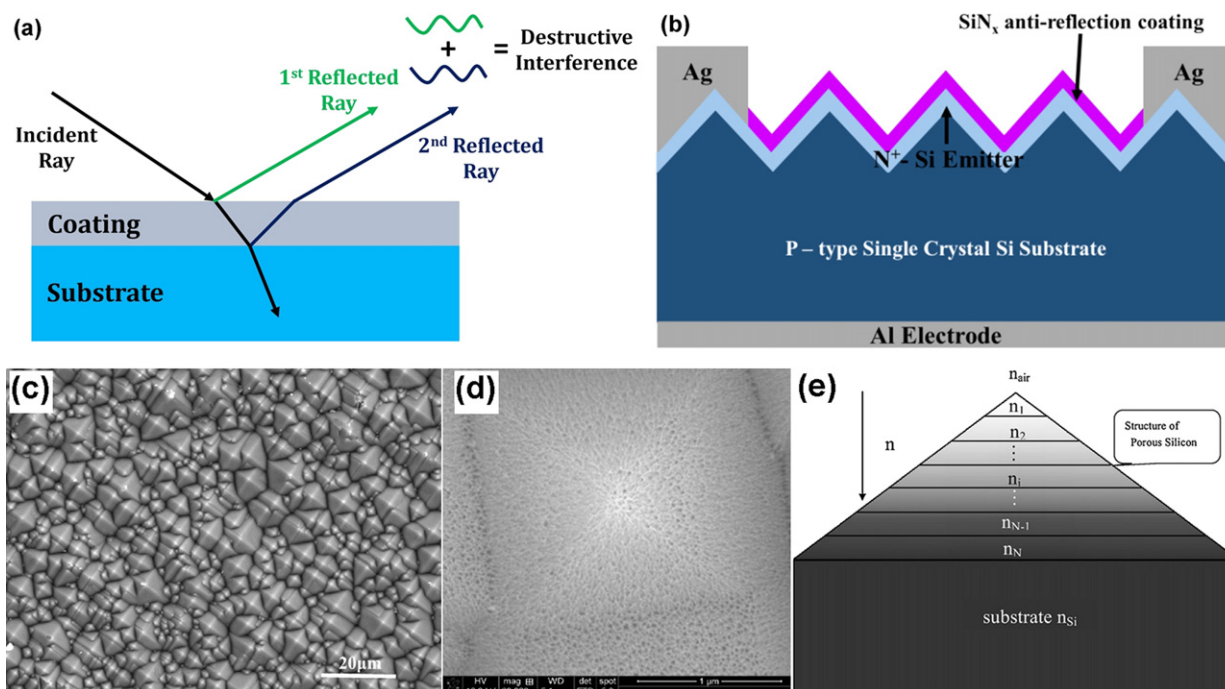


Fig. 1 (a) Schematic diagram of a single layer antireflection coating operation; (b) Schematic diagram of porous Si/textured Si integrated with crystalline Si solar cell; (c) FESEM image of textured Si wafer; (d) FESEM image of one pyramid with porous Si showing uniformity; (e) Schematic multilayer porous Si as ARC, increasing level of darkness and the width of the each film both represent an increasing refractive index (decreasing porosity); $n_{\text{air}} < n_1 < n_2 < n_3 < \dots < n_N < n_{\text{Si}}$. Reproduced from (b) Ho, W.J., *et al.*, 2018. Photovoltaic performance of textured silicon solar cells with MAPbBr₃ perovskite nanophosphors to induce luminescent down-shifting, *Applied Surface Science* 436, pp. 927–933. doi: [10.1016/j.apsusc.2017.12.134](https://doi.org/10.1016/j.apsusc.2017.12.134). (c)–(e) Lv, H., *et al.*, 2012. Porous-pyramids structured silicon surface with low reflectance over a broad band by electrochemical etching, *Applied Surface Science* 258 (14), pp. 5451–5454. doi: [10.1016/j.apsusc.2012.02.033](https://doi.org/10.1016/j.apsusc.2012.02.033).

integration of an antireflection coating has become useful for Silicon solar cell as it reduces the reflectance up to 0.1% and maximizes the efficiency up to 15%–18% (Green *et al.*, 2015; Gao *et al.*, 2018; Kim and Lim, 2015; Silva *et al.*, 2014).

In antireflection coating, the encapsulated and/or front thin layers have refractive index between 1 (air) to 3.84 (bulk Si) which are usually fabricated using plasma enhanced chemical vapor deposition (PECVD) technique. Among them widely investigated Single Layer Antireflection Coatings include SiN_x, Ta₂O₃, ZnS, CeO₂, Al₂O₃ and Double Layer Antireflection Coatings include SiO₂/TiO₂ and ZnS/MgF₂. But it is worth mentioning here that due to state of the art synthesis technique, these ARCs are not cost effective for large scale industrial applications.

While two important pathways – texturizing and vacuum deposited ARCs fade away, integration of porous Silicon as ARC has appeared as a silver lining to reduce the reflection from front surface. Because, the fundamental requirements of antireflection for Single Layer ARC can only be satisfied by one wavelength as well as the light waves reflected from one incident angle and this does not improve much with multilayers introduction on the crystalline Si solar cell. On the other side, refractive index can be easily controlled by varying the porosity in porous silicon (PSi) ARC. Prasad *et al.* (1982) first demonstrated that porous Si as ARC reduces the optical loss from 37% to 8% of silicon solar cell and since then different approaches have been reported by many researchers all around the world. Table 1 lists such kind of studies which have been reported after 2004.

Porous silicon (PSi) as omnidirectional bragg reflector

Like the optical loss, carrier recombination is equally detrimental for solar energy to current conversion in solar devices. Hence, substitution of metal back reflectors, which are highly absorbing and poor reflector, with dielectric materials offered superior advantages by increasing internal reflection to generate more carriers in active cell. However, due to state of the art deposition techniques, the concept of dielectric materials as omnidirectional Bragg reflector recently has been replaced with a concept of using porous Si for its refractive index tuning compatibility and easier fabrication techniques.

Bhandaru *et al.* (2016) demonstrated that using porous amorphous Si back reflector for amorphous Si solar cell, both short circuit current density and overall cell efficiency were improved by 30% compared to flat metal back reflector amorphous Si solar cell device (For metal back reflector: $\eta = 2.7\%$, $J_{sc} = 6.5 \text{ mA/cm}^2$, $V_{oc} = 732 \text{ mV}$, $FF = 0.57$ and porous amorphous Si reflector: $\eta = 3.5\%$, $J_{sc} = 8.66 \text{ mA/cm}^2$, $V_{oc} = 742 \text{ mV}$, $FF = 0.56$).

Ghannam *et al.* (2010) reported a five layered porous Si back reflectors on back of a textured crystalline Si cell where the bottom two layers had 22.5% porosity (each layer thickness was 157 nm) and the rest three layers had 55% porosity (each layer thickness

Table 1 Porous silicon surface improved antireflection properties with different approaches

Approaches	Reflectance (%)	Wavelength (nm)	Ref.
PSi/textured – Si	4.2	400–900	(Xiao <i>et al.</i> , 2010)
PSi/textured – Si	11.34	400–1000	(Chaoui <i>et al.</i> , 2013)
PSi/ (n ⁺ – p) Si	4	400–1000	(Dzhafarov <i>et al.</i> , 2012)
PSi/ textured – Si	3.67–6.15	400–1040	(Weiyang <i>et al.</i> , 2011)
PSi/ textured – Si	< 4	400–800	(Marrero <i>et al.</i> , 2009)
PSi/ textured – Si	7.5	400–1100	(Druzhinin <i>et al.</i> , 2016)
Multilayer PSi/textured – Si	1.9	200–2000	(Lv <i>et al.</i> , 2012)
Multilayer PSi/Si (in air)	3	400–1100	(Selj <i>et al.</i> , 2011)
Multilayer PSi/Si (under glass)	1.4	400–1100	(Selj <i>et al.</i> , 2011)
Multilayer PSi/textured – Si	< 5	400–1000	(Kwon <i>et al.</i> , 2011)
Double Layer ZnO/PSi/Si	< 5	450–850	(Salman <i>et al.</i> , 2012)
Double Layer SiO _x N _y /PSi/ polycrystalline Si	< 5	500–1000	(Marrero <i>et al.</i> , 2009)
Double Layer SiO ₂ /PSi/Si	3.8	400–1000	(Remache <i>et al.</i> , 2010)
Double Layer SiO _x N _y /PSi/ polycrystalline Si	6	450–1100	(Rabha <i>et al.</i> , 2011)
Double Layer Al ₂ O ₃ /PSi/ monocrystalline Si	7	400–1000	(Rabha <i>et al.</i> , 2013)
Double Layer SiO _x N _y /PSi/Si	0.01	430–670	(Search <i>et al.</i> , 2006)
Double Layer SiO _x N _y /PSi/Si	< 7	400–900	(Search <i>et al.</i> , 2006)
Double Layer DLC/PSi/Si	< 2.5	400–850	(Aroutiounian <i>et al.</i> , 2004)
Double Layer DLC/PSi/Si	≈ 1	400 and 700 nm only	(Aroutiounian <i>et al.</i> , 2004)

was 256 nm). The overall cell efficiency (η), short circuit current density (J_{sc}), open circuit voltage (V_{oc}) and fill factor (FF) were found as 12%, 26.99 mA/cm², 609.2 mV and 0.73 respectively.

Kuzma-Filipek *et al.* (2008) showed that low (23%)/high (42%)/low (23%)/.../high (42%) porosity Si layers as back reflector on crystalline Si exhibits internal reflection R_B of 95% in 900–1050 nm wavelength region for 20 bilayers and in 800–1100 nm wavelength region for 60 bilayers. The overall cell efficiency (η), short circuit current density (J_{sc}), open circuit voltage (V_{oc}) and fill factor (FF) for 40 bilayers and 60 chirped bilayers were found as 13.3%, 28.7 mA/cm², 598 mV, 0.78 and 13.9%, 29.6 mA/cm², 605 mV, 0.78 respectively.

Bougoffa *et al.* (2017) investigated the improvement of internal reflection by stacking multiple layers of porous Si as back reflectors on textured crystalline Si solar cell. They showed that for single double-porosity Si layer, internal reflection R_B increases from 18% to 40% due to porosity variation. Again, for three double-porosity Si layers, the porosity variation improved internal reflection R_B from 51% to 80% as depicted in Fig. 2.

Multiple bilayer porous Si back reflectors, improved the internal reflection, have been reported in several literatures i.e., R_B = 62% for multicrystalline Si and more than 90% for single crystalline Si (Ivanov *et al.*, 2013), R_B = almost 100% except for a small dip for p polarized light which can be minimized by chirped like approach and bilayer comprised 70% and 20% porosity Si (Jiang *et al.*, 2014), R_B = 80% for 15 bilayer low and high porosity Si (Kuzma-Filipek *et al.*, 2007), R_B = 86% for single layer Si/PSi comprising 60% porosity and R_B = 83% for Si/PSi/SiN_x (Remache *et al.*, 2016).

Porous silicon (PSi) as a promising substrate for thin film solar cell

Layer transfer process using porous silicon as reusable substrate has raised enormous enthusiasm among researchers since last decade for its promising cost effectiveness and facile state of the art fabrication techniques. In a typical layer transfer process to make thin crystalline Si solar cell as depicted in Fig. 3, a monocrystalline silicon wafer is first electrochemically etched which turns it into a porous Si wafer comprised of two different porosity layers – low (20%–30%) and high (above 50%). Appropriate annealing allows the low porosity layer to act as an excellent monocrystalline ground for growing epitaxial Si on it. Once the epitaxial layer is deposited, the epitaxial layer with low porosity Si layer can be detached through the high porosity layer and thus the remaining high porosity Si wafer becomes further reusable. However, the process sequence i.e., detachment of epitaxial Si layer from high porosity Si substrate, gluing that on a foreign substrate and device fabrication on epitaxial Si layer may vary depending on the research requirements (Solanki *et al.*, 2004).

Brendel *et al.* (2003) achieved 15.4% cell efficiency for 25 μ m thick crystalline Si solar cell where short circuit current density (J_{sc}), open circuit voltage (V_{oc}) and fill factor (FF) were found as 32.7 mA/cm², 623 mV and 0.755, respectively. Later, Reuter *et al.* (2009) fabricated 50 μ m thick crystalline Si solar cell of 17% cell efficiency where short circuit current density (J_{sc}), open circuit voltage (V_{oc}) and fill factor (FF) were found as 36 mA/cm², 634 mV and 0.746 respectively. Petermann *et al.* (2012) improved the cell efficiency to 19.1% for a 43 μ m thick crystalline Si solar cell where short circuit current density (J_{sc}), open circuit voltage (V_{oc}) and fill factor (FF) were found as 37.8 mA/cm², 650 mV and 0.776, respectively. Wang *et al.* (2014) used steel as foreign substrate and achieved 16.8% cell efficiency for 18 μ m thin Si solar cell with short circuit current density (J_{sc}), open circuit voltage (V_{oc}) and fill factor (FF) were found as 34.5 mA/cm², 632 mV and 0.77, respectively.

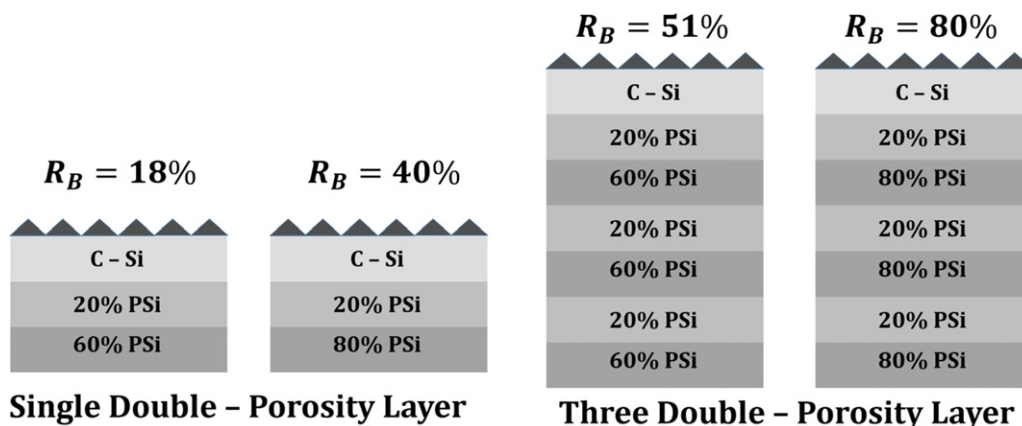


Fig. 2 Multiple stacking of porous Si layers enhanced internal reflection. Reproduced from Bougoffa, A., *et al.*, 2017. Analytical model of front texturization effect on silicon solar cell with porous silicon at the backside, *Optical and Quantum Electronics* 49 (1), pp. 1–13. doi: [10.1007/s11082-016-0864-8](https://doi.org/10.1007/s11082-016-0864-8).

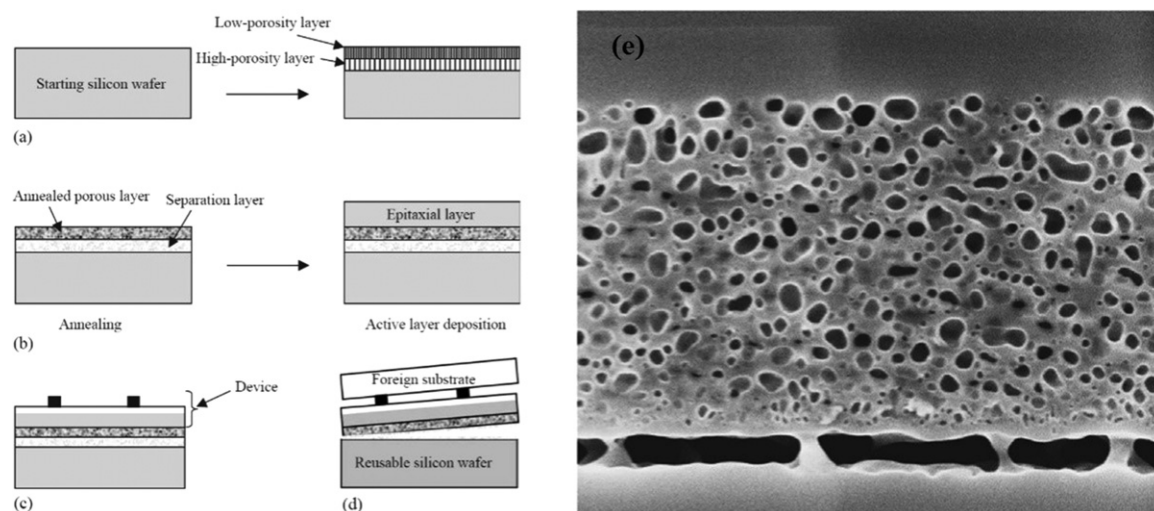


Fig. 3 Steps of porous layer transfer processes using porous silicon as a sacrificial layer for obtaining thin monocrystalline silicon films on cost-effective substrates: (a) a double porosity structure (high-porosity layer beneath low-porosity layer) formation on starting silicon substrate by anodization; (b) thermal annealing of porous silicon and active layer deposition: annealed low-porosity layer acts as a good seeding layer for epitaxial layer deposition and voids with weak silicon pillars form in high-porosity layer acts as a separation layer; (c) Device fabrication; (d) Separation of epitaxial layer from the starting silicon substrate and transfer onto foreign substrate by gluing it with an adhesive layer and applying mechanical force; (e) SEM image showing epitaxial layer/low porosity/high porosity/Si wafer. Reproduced from (a)–(d) Solanki, C.S., *et al.*, 2004. Porous silicon layer transfer processes for solar cells, *Solar Energy Materials and Solar Cells* 83 (1), pp. 101–113. doi: [10.1016/j.solmat.2004.02.016](https://doi.org/10.1016/j.solmat.2004.02.016). (e) Radhakrishnan, H., *et al.*, 2015. Kerfless layer-transfer of thin epitaxial silicon foils using novel multiple layer porous silicon stacks with near 100% detachment yield and large minority carrier diffusion lengths, *Solar Energy Materials and Solar Cells* 135, pp. 113–123. doi: [10.1016/j.solmat.2014.10.049](https://doi.org/10.1016/j.solmat.2014.10.049).

Apart from thin film Si solar cell, porous Si has appeared as a remarkable buffer layer for Ge (Calabrese *et al.*, 2014; Aouassa *et al.*, 2012; Mahamdi *et al.*, 2018; Gouder *et al.*, 2014), GaN (Abud *et al.*, 2016; Wu *et al.*, 2018) and GaAs (Wilkins *et al.*, 2013) epitaxial growth. The compatibility of porosity variation allows PSi to deform during epitaxial growth which is not possible for bulk Si due to its large lattice mismatch with those materials and thus porous Si resembles as a promising substrate for multi-junction solar cell devices.

Dye Sensitized Solar Cell

A dye sensitized solar cell is comprised of four different components: photoanode, dye sensitizer, electrolyte and electrode. Usually porous TiO_2 is used as photoanode which is covered by a thin layer of dye sensitizer materials. When sunlight strikes the surface of the thin layer, dye sensitizers get excited and they pass the photon excited electrons to the TiO_2 film which later travelled through

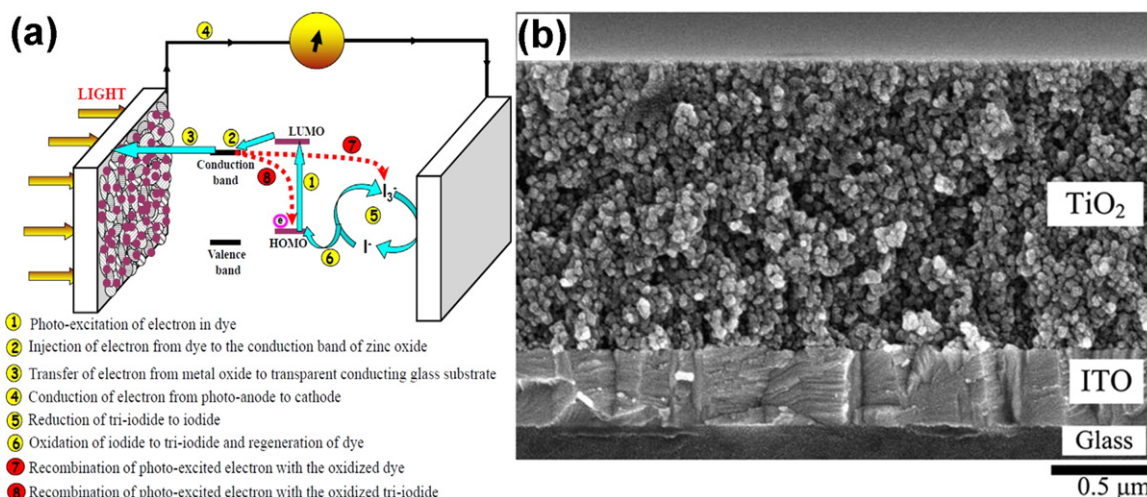


Fig. 4 (a) Schematic working principle of Dye Sensitized Solar Cell (DSSC); LUMO means Lowest Unoccupied Molecular Orbitals and HOMO means Highest Occupied Molecular Orbitals; (b) A cross-sectional photograph of TiO₂ thin film with a film thickness of 1.5 μm. Reproduced from (a) Sengupta, D., *et al.*, 2016. Effects of doping, morphology and film-thickness of photo-anode materials for dye sensitized solar cell application – A review, *Renewable and Sustainable Energy Reviews* 60, pp. 356–376. doi: [10.1016/j.rser.2016.01.104](https://doi.org/10.1016/j.rser.2016.01.104). (b) Kao, M.C., *et al.*, 2009. The effects of the thickness of TiO₂ films on the performance of dye-sensitized solar cells, *Thin Solid Films* 517 (17), pp. 5096–5099. doi: [10.1016/j.tsf.2009.03.102](https://doi.org/10.1016/j.tsf.2009.03.102).

the electrolyte. The redox coupled electrolyte (typically I_3^- and I^-) is attached with a counter electrode to collect the electrons and regenerate the dye. The overall efficiency (η) of DSSC is measured by the following equation:

$$\eta = \frac{V_{oc} J_{sc} FF}{P_{in}} \quad (1)$$

Where, V_{oc} is the open circuit voltage which is actually the measure of the potential difference between TiO₂ and redox potential of electrolyte; J_{sc} is the short circuit current which depends on the light harvesting efficiency of dye sensitizers, electronic conductivity performance of electrolyte and charge collection efficiency of counter electrode; FF (fill factor) represents the ratio of maximum generated power to the product of open circuit voltage and P_{in} is the power of incident light (standard irradiation condition: 100 mW/cm², AM1.5). Working principle of Dye Sensitized Solar Cell (DSSC) is depicted in Fig. 4.

A review on photovoltaic parameters of Dye Sensitized Solar Cell (DSSC) using different approach and photoanode is listed in Table 2.

Porous Ceramics as Fuel Cells

Energy crisis and environmental pollution are the most alarming issues of today's world. Burning of fossil fuels to meet energy requirement have not only reduced the finite reserves of but also caused greenhouse effect by releasing harmful gases. The quest for efficient utilization of renewable energy (like solar, wind energy etc.) and development of sustainable, green energy sources have gathered enormous interest among the researchers. Fuel cells provide a key solution to conversion and storage of energy. In 1838 William Grove invented the first fuel cell by reversing electrolysis of water and named it "wet cell battery" or "Grove cell" (Grove, 1839). Various fuel cells have been developed since then based on electrode and electrolyte types that are listed in Table 3.

Among the varieties of fuel cells, Solid Oxide Fuel Cells (SOFC) and Polymer Electrolyte Membrane (PEM), also known as proton-exchange membrane fuel cell, are most commonly used. In PEM fuel cells, electrolyte material is polymer based, generally PTFE/Teflon and solid (Ni, Ti, stainless steel mesh, porous Carbon) materials are used as electrodes and Pt coated as catalyst on the anode. Each type of fuel cells has its own advantages and limitations. As it can be seen from Table 3 that most of the fuel cells use hydrogen as their fuel which is more costly to produce than other source of energy and it is almost energy neutral (required production energy roughly equal to as it delivers at the end destination). Therefore, the applications of fuel cells are so far very limited. Solid Oxide Fuel Cells (SOFC) has received renewed attention because of hydrogen extraction process. A high operating temperature here allows hydrogen to be extracted directly from natural gas through a catalytic reforming process. Due to the renewed research interest and future prospect, we limit our discussion to SOFC in this paper.

Solid Oxide Fuel Cell

Gauguin first discovered solid electrolyte in 1853 and in 1899 Nernst showed that the conductivity of Y₂O₃ doped ZrO₂ (15 YSZ) rises with increasing temperature (Gauguin, 1853; Nernst, 1899). Baur and Preis finally developed SOFC in 1937

Table 2 Photovoltaic parameters of DSSC using different approach and photoanode

Photoanode	η (%)	V_{oc} (mV)	J_{sc} (mW/cm ²)	FF (%)	Ref.
TiO ₂ nanosphere	8.5	730	17.88	65	(Ye <i>et al.</i> , 2013a)
TiO ₂ microsphere	7.94	690	15.42	66	(Wang <i>et al.</i> , 2013a)
TiO ₂ nanosphere	11.18	846	17.73	75	(Humphry-Baker <i>et al.</i> , 2013)
TiO ₂ nanorod	4.4	739	8.88	67	(Hafez <i>et al.</i> , 2010)
TiO ₂ nanorod	7.91	700	20.49	54.5	(Lv <i>et al.</i> , 2013)
TiO ₂ nanofiber	4.01	770	8.67	60	(Song <i>et al.</i> , 2004)
TiO ₂ nanosphere	8.44	804	14.57	51.9	(Ye <i>et al.</i> , 2013b)
TiO ₂ nanofiber	10.30	640	22.4	72	(Chuangchote <i>et al.</i> , 2008)
TiO ₂ nanofiber	10.20	795	17.48	73.3	(Mukherjee <i>et al.</i> , 2009)
TiO ₂ nanowire	9.95	792	16.22	77.5	(Wang and Bai, 2014)
TiO ₂ nanorods	9.21	750	17.75	70	(Kathirvel <i>et al.</i> , 2016)
Cr doped TiO ₂	8.4	780	15.2	71	(Kim <i>et al.</i> , 2008)
Sn doped TiO ₂	8.31	722	16.01	70.7	(Duan <i>et al.</i> , 2012)
W doped TiO ₂	9.1	610	19.31	77	(Zhang <i>et al.</i> , 2015)
TiO ₂ /Au@GO NPs	9.06	780	17.19	67.6	(Kwon <i>et al.</i> , 2016)
Al ₂ O ₃ – TiO ₂ nanospheres	8.60	730	16.9	70	(Wang and Bai, 2014)
TiCl ₄ treated TiO ₂ nanospheres	10.52	776	19.62	69.1	(Ye <i>et al.</i> , 2013b)
TiO ₂ nanorod/ TiO ₂ nanosphere	10.34	827	18.78	67	(Yan <i>et al.</i> , 2011)
TiO ₂ nanorod/ TiO ₂ nanosphere	7.1	756	14.45	65	(Hafez <i>et al.</i> , 2010)
ZnO nanowire/TiO ₂ nanosphere	8.44	763	16.08	68.8	(Yang <i>et al.</i> , 2017)
TiO ₂ /ZnO nanodonuts	9.0	780	16.70	69	(Li <i>et al.</i> , 2015)

Table 3 Types of fuel cells

	Polymer Electrolyte Membrane (PEM)	Alkaline Fuel Cell (AFC)	Phosphoric Acid Fuel Cell (PAFC)	Molten Carbonate Fuel cell (MCFC)	Solid Oxide Fuel Cell (SOFC)
Fuel	H ₂	H ₂	H ₂ , external reformat	H ₂ , CO, CH ₄	H ₂ , CO, CH ₄
Common Anode	Ni/Pt	Pt	Pt	Ni alloy	Ni/YSZ cermet
Common Cathode	Ni	Pt	Pt	NiO	LaMnO ₃ (LSM)
Common Electrolyte	Perfluorosulfonic acid	KOH (aq)	Phosphoric acid	Molten Li/Na/K carbonates	Yttria Stabilized Zirconia (YSZ)
Operating Temperature	< 120°C	< 100°C	150–200°C	600–700°C	500–1000°C
Electrical Efficiency	60% (direct H ₂) 40% (reformed fuel)	60%	40%	50%	60%

having an operating temperature 1000°C (Baur and Preis, 1937). Most of the SOFCs operate at very high temperature of 800–1000°C, which causes material degradation and, as a result, incur higher maintenance cost. Therefore, researchers, especially in last two decades, focused on developing intermediate (500–800°C) range SOFCs (Mahato *et al.*, 2015; da Silva and de Souza, 2017). The main advantages of SOFC are the lower cost compared to solar and wind energy, less greenhouse gas emission, durability, noise-free power generation, direct conversion of chemical energy to electrical energy and reliability. During 2004–2006 alone, the cost of fuel cell unit reduced from \$8000/KW to \$4800/KW (Shaikh *et al.*, 2015; Shahid Rafique *et al.*, 2018). However, more attention in research is now given to further reduce the unit cost of SOFC by developing new and efficient electrode materials.

Starting from Ni-cermet anodes and LSM (LnSrMnO₃) cathodes, a wide range of ceramic materials has been explored for enhancing the efficiency and lowering the working temperature of Solid Oxide Fuel Cells. Porosity and its characteristics play a major role for efficiency enhancement of SOFC. When porosity is > 25%, gas phase becomes fully in contact with the Triple Phase Boundary (TPB). For effective performance, optimum porosity of the electrodes are estimated to be 36%–48% (Bertei and Nicolella, 2011; Yang *et al.*, 2015). Pore size and distribution are also controlling factors of gas flow inside the electrodes.

Working Principle of SOFC

The main components of SOFC are porous electrodes (anode and cathode) and solid electrolyte that is sandwiched between the two electrodes. Both electrodes and electrolyte are ceramic material. Porous anode and cathode are electronic conductors and the

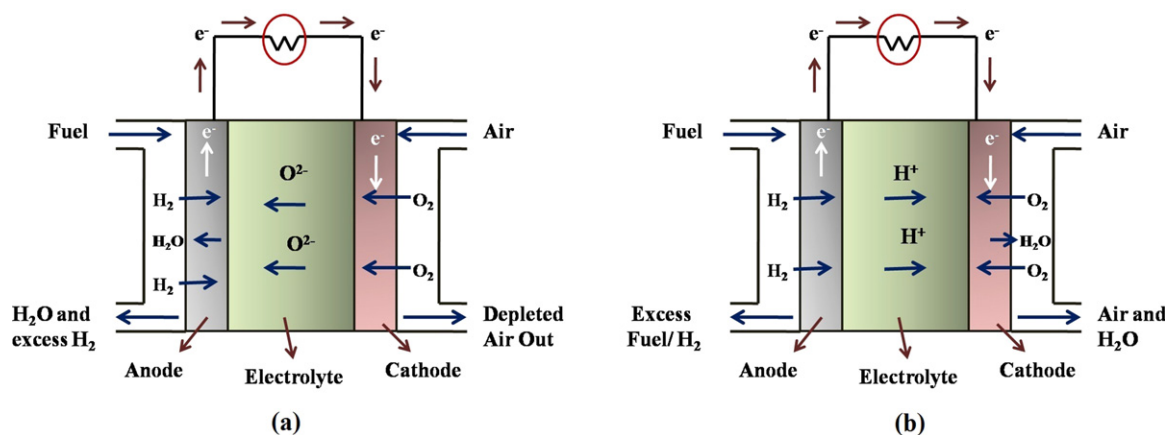


Fig. 5 Schematic diagram of SOFC working principle having (a) oxide ion conducting electrolyte, and (b) proton conducting electrolyte.

Table 4 Evolution of nanoporous anode materials

Material	Processing method	Porosity	Operating temperature (°C)	Electrolyte/Cathode	Maximum power density (mW/cm ²)	Ref.
Ni-YSZ Cermet (50% Ni-50% YSZ)	Tape casting, fired at 950°C	20%–40%	1000	8YSZ/ LSM-8YSZ	1900	(Dees <i>et al.</i> , 1987; Ivers-Tiffée <i>et al.</i> , 1990; Lee <i>et al.</i> , 2002)
Ni-SDC (50%–60% Ni)	Uniaxial pressing, 1200°C	5%–10%	800	YSZ/LSM-YSZ	980	(Chen <i>et al.</i> , 2008b; Mantzouris <i>et al.</i> , 2008)
NiO _{ScSZ} -10Sc-1Ce-SZ	Microtubular design	37%	600	ScCeSZ/LSCF-GDC	200	(Suzuki <i>et al.</i> , 2009)
NiO (nanoporous)	Impregnation, calcination 700°C	Pore dia 40nm	650	LSGM/LSCF-LSGM	1200	(Zhan <i>et al.</i> , 2011)
Ni-CeO ₂ -Ni-Sm ₂ O ₃ -Ni-Eu ₂ O ₃ -Ni-Gd ₂ O ₃	Uniform pressing	~32%–45%	600	Gd _{0.1} Ce _{0.9} O _{1.95} /Sm _{0.5} Sr _{0.5} CoO ₃	600	(He <i>et al.</i> , 2010)
NiO-Gd _{0.1} Ce _{0.9} O _{1.95}	Tape casting, spray coating	~28%	650	GDC/LSCF-GDC	909	(Fu <i>et al.</i> , 2010)
			600		623	
			550		335	
			500		168	
Ag-CGO (Ag 45%)	Pressing, sintering 1500°C	48%	650	CGO (Ce _{0.8} Gd _{0.2} O _{1.9})/LSCF	790	(Wang <i>et al.</i> , 2008)
Pd (nonporous)	DC Sputtering	Pore gap 8 nm	400	YBaZrO ₃ -Pt	72.4 (H ₂) 15.3 (ethanol)	(Li <i>et al.</i> , 2017)
Perovskite Anodes						
La doped STO (La _{0.2} Sr _{0.7} TiO ₃)	Solid state, Sintering 1450°C	40%–60%	750	LSC-YSZ	500	(Savaniu and Irvine, 2011)
Li _{0.33} La _{0.56} TiO ₃ (LLTO) coated SmCeO (SDC)	Solution infiltration, firing 900°C	50%	800	SDC/SDC-BSCF	123–215	(Wang <i>et al.</i> , 2015)
Sm _{0.5} Ba _{0.5} MgO _{3-δ} (SBMO)	Pechini method, Calcination 950°C	High porosity	850	LSGM (LaSrGaMgO)/BSCF (BaSrCoFeO)	150 (H ₂) 415 (methanol)	(Zhao <i>et al.</i> , 2017)

electrolyte is dense, impervious and ion/proton conductor. Anode and cathode are externally connected. The anode side (also called Fuel side) receives H₂, hydrocarbons or methanol as a fuel, oxidizes them and generates electrons that flow through external circuit. Oxygen (or oxidant) is reduced at the triple phase boundary of cathode, gas and electrolyte. Generated oxide ions diffuse through ion conducting electrolyte via vacancy hopping mechanism at high temperature (800–1000°C). High temperature enables and makes the electrolyte ion conductor. At the anode-electrolyte-gas triple phase boundary (TPB), H₂ and O₂⁻ ions react to form H₂O (Mahato *et al.*, 2015; Shaikh *et al.*, 2015; Kee *et al.*, 2008). A schematic diagram of SOFCs operating principle is presented in Fig. 5.

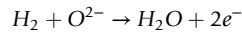
Table 5 Evolution of nanoporous cathode materials

Material	Processing method	Porosity	Operating Temperature (°C)	Maximum Power Density (mW/cm ²)	Ref.
Sm _{0.2} Ce _{0.8} O _{1.9} (SDC) and Sm _{0.5} Sr _{0.5} CoO ₃ (SSC)	Spin coating	Small, inter-connected pores	600	300	(Chen <i>et al.</i> , 2011)
LSM (La _{0.8} Sr _{0.2} MnO _{3-δ}) cathode supporter and LSM-Sm _{0.2} Ce _{0.8} O _{2-δ} (SDC) cathode functional layer (CFL)	Slurry spin coating	23%–33%	850	580	(Chen <i>et al.</i> , 2012)
Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ} (BSCF)	Spray coating	Highly porous cathode, homogeneous pores	800 600	432 145	(Shi <i>et al.</i> , 2012)
YSZ-Mn _{1.5} Co _{1.5} O ₄ (MCO) composite	Pressing 3000 PSI, sintering 1450°C	55%	800	0.15 Ωcm ² (lowest polarization resistance)	(Zhan <i>et al.</i> , 2013)
(La _{0.8} Sr _{0.2}) _{0.95} MnO ₃ (LSM95)	Tape casting	33.76%–45.50%	750	325	(Wang <i>et al.</i> , 2013b)
La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O ₃ and Gd-doped ceria (LSCF-GDC)	Screen printing, sintering 1200°C	Highly porous	750	0.38–0.83 Ωcm ² (polarization resistance)	(Liu <i>et al.</i> , 2013)
Double perovskite SmBaCo _{2-x} Ni _x O _{5+δ} (SBCN _x) (x = 0–0.5)	Screen printing	Porous cathode	800	536	(Xia <i>et al.</i> , 2016)
Sm _{0.5} Sr _{0.5} CoO _{3-δ} (SSC)	Electro spinning	Very porous nano fiber cathode	700	1090	(Chang <i>et al.</i> , 2015)
NdBaFe _{2-x} Mn _x O _{5+δ} (0.0 ≤ x ≤ 0.3)	Citric acid- nitrate process, sintering 1200°C	Porous cathode	500–700	453	(Mao <i>et al.</i> , 2015)
Sr _x Co _{0.7} Nb _{0.1} Fe _{0.2} O _{3-δ} (SCNF, x = 0.95 and 1)	Screen printing	Moderate porosity	700	208–180	(Ding <i>et al.</i> , 2017)

Materials Used in SOFC

Anode

Anode is the most important component of SOFC where the oxidation of fuel takes place. An anode must possess enough porosity, electrical conductivity and chemical compatibility with electrolyte at operating temperature. The following reaction takes place at anode-



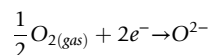
Electro-catalytically active and high electronic conductivity makes cermet based anodes, e.g., Ni-YSZ (8 mol% Y₂O₃ and ZrO₂), most commonly used anode material. However, some limitations associated with Ni-YSZ anode at the SOFC operating temperature are Ni sintering, deposition of Carbon (from hydrocarbon fuels) and Sulfur poisoning. To overcome these drawbacks of Ni based cermets, many studies have been conducted for increasing the stability, durability and electrical conductivity of anodes like: Ni-YSZ anodes modified with Ag (Wu *et al.*, 2016), Al₂O₃ (Song *et al.*, 2016); Ni-SDC (Chen *et al.*, 2008a), Ni-GDC (Fu *et al.*, 2010), Ce based cermets (Ce_xZr_{1-x}O₂) (Kearney and Baker, 2012), LnSTMperovskites (Ln=La, Nd, Sm) (Jeong *et al.*, 2015), PbMO₃ (Pr_{0.5}Ba_{0.5}MnO_{3-δ}) (Sun *et al.*, 2016) etc. Double perovskite based materials have been reported as well and claimed to be exhibited longer life and highest efficiencies. Various anode materials along with their efficiency and porosity are listed in Table 4.

The efficient anode must contain the following chief characteristics:

- High electrical conductivity at operating temperature
- Sufficient electrochemical and catalytic activity for the oxidation.
- Minimal CTE mismatch with other adjacent cell components
- Fuel flexible and able to tolerate carbon deposition and sulfur poisoning.
- Chemical and thermal stability.
- Sufficient mechanical strength to withstand mechanical stress at high operating temperature.
- High porosity (20%–40%) for smooth fuel migration and the reaction product release (Singhal, 2000).

Cathode

Cathode is a porous electrode where reduction of O₂ takes place. Materials selection for cathode should be such that it possesses high electronic conductivity, stability and it remains unreactive to electrolyte materials at high operating temperature. In cathode, the following reaction takes place:



$\text{Ln}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM perovskite) is used as most common cathode material (Chen *et al.*, 2012). Researches have been conducted on LSM/GDC cathodes (Ahmed *et al.*, 2014), $\text{LnBaCoO}_{5+\delta}$ ($\text{Ln} = \text{La, Pr, Nd, Sm, Gd, Y}$) (Xia *et al.*, 2016) and NBCO ($\text{NdBaCu}_2\text{O}_{5+\delta}$) (Kong *et al.*, 2015) cathodes along with $\text{A}_2\text{BO}_{4+\delta}$ ($\text{A} = \text{rare-earth material, B} = \text{Cu, Fe, Ni}$) based composite cathodes (Ferkhi and Ahmed, 2016; Kolchugin *et al.*, 2016). Dependence of Maximum Power Density of SOFC on cathode material and porosity is presented in Table 5.

For an efficient operation of SOFC, the cathode should possess the following functionalities:

- High electronic conductivity (preferably more than 100 S/cm in an oxidizing atmosphere)
- Minimal or no CTE mismatch with other components of the cell
- Chemical compatibility with electrolyte and interconnect materials
- Porous structure to allow fast diffusion of O_2 from cathode to cathode-electrolyte interface
- High ionic conductivity
- Good oxidizing stability
- High catalytic activity during oxygen reduction reaction (ORR)

Conclusions

In this review, the prospect of porosity in nanostructured materials have been summarized particularly for solar and fuel cells. For future photovoltaic research, Porous Si (PSi) can be simultaneously integrated as antireflection coating and Bragg reflector with Si solar cell to improve the overall cell efficiency. Besides, reusability of substrate can highly reduce the cost of solar cell fabrication if Porous Si (PSi) is used as wafer. The use of PSi as substrate for thin film solar cell like Ge, GaAs, GaN requires more focus as it may revolutionize many current research trends which are not limited to solar cell applications. For Dye Sensitized Solar Cell (DSSC), morphology design like Nanorod/Nanosphere, Nanowires/Nanodonuts along with combination of different materials in heterostructured Photoanode has been seen enhancing the overall cell efficiency of DSSC in some recent research. Considering fuel cells, characteristics of pore in electrodes are controlling factor for better performance and efficient Solid Oxide Fuel Cell (SOFC). Among the three components of SOFC, both electrodes are based on porous materials and emphasis has been given by the researchers mostly for the development of electrodes with controlled porosity in order to enhance the durability of electrodes and lowering the operating temperature of SOFCs.

See also: Application of Nano Porous Materials for Energy Conversion Process

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Natural Lignite Resources in Kosovo and Metohija and Their Influence on the Environment

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Introduction

The region of Kosovo and Metohija is rich in mineral resources. Its energy resources and non-ferrous metal resources represent a considerable potential for the overall development. Not all parts of Kosovo and Metohija are equally rich in mineral raw materials. Mineral deposits represent a true natural basis for development of industry, i.e., economy as a whole. Some of the most important resources are lignite, minerals of lead, zinc, silver and gold, silicate minerals of nickel and cobalt, iron – bauxite, manganese and magnesite. Moreover, there are also significant amounts of non-metallic, industrial minerals and geological construction materials. Specified mineral resources and their rational exploitation combined with good management approach represent a solid basis for quick and sustainable economic and social development.

All kinds of existing resources that a country has at its disposal make up a foundation for planning and implementation of development and energy strategy. Each of the specified resources has bigger or smaller resource potential, but planning and strategic exploitation are insufficient. That is why it is necessary to define accurate sector policies and strategies and to select proper mechanisms for their implementation. Regarding Serbia, this goal is extremely difficult to realize at this moment because the region of Autonomous Province of Kosovo and Metohija is a UN protectorate and subject to a Resolution 1244. In fact, at this moment Serbia as a country does not have any mechanisms that could be used to protect those natural mineral resources from exploitation. On the other hand interim institutions in Kosovo and Metohija are doing everything in their power to use those resources for their own development. Pursuant to any natural and international law, including resolution 1244, mineral resources of Kosovo and Metohija should stay in Serbia. Since Serbia has been exposed to double standards by the developed Western countries that recognized unilateral independence of AP of Kosovo and Metohija, the so called independent state of Kosovo was given the opportunity to exploit all of the mineral resources (Figs. 1–3).



Fig. 1 Mineral resources in Kosovo and Metohija. Reproduced from <http://www.nspm.rs/kosovo-i-metohija/u-cijim-rukama-ce-se-naci-prirodna-bogatstva-kosova-i-metohije.html?alphabet=l> (accessed 15.01.18).

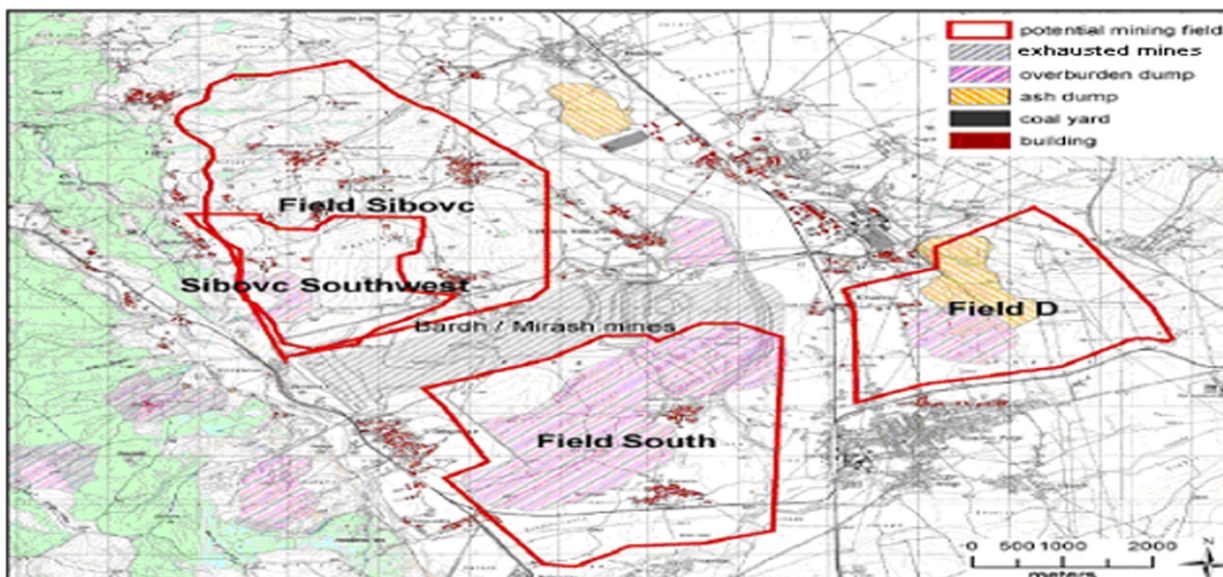


Fig. 2 Mining fields of lignite – Sibovac. Reproduced from Kosovo Power Project, Environmental and Social Impact Assessment (ESIA), Draft Environmental and Social Scoping Study (ESSS) Rev. 2. pp. 21–25.

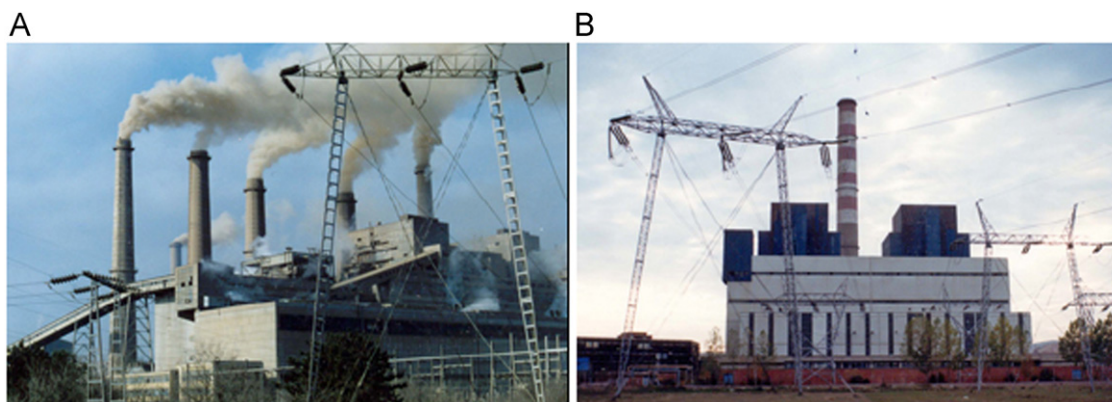


Fig. 3 Thermal power plants “Kosovo A” and “Kosovo B”. Reproduced from <http://www.elektroenergetika.info/te-sr.htm> (accessed 12.02.18).

Lignite Reserves in Kosovo and Metohija

Lignite reserves are by far the most abundant among mineral resources in the region of Kosovo and Metohija. There are still no accurate estimates of the amount of lignite in the region of Kosovo and Metohija. According to Serbian scientists, [Nikolić and Dimitrijević \(1990\)](#), lignite reserves in Kosovo, Metohija and Drenica basin are 7.35 billion tons (Bt). Out of the specified amount, only 1.6 Bt in Kosovo basin are economically exploitable, while 4.8 Bt are non-exploitable (as well as 0.7 Bt in Metohija basin and 0.25 Bt in Drenica basin). As for the thickness of exploitable seam, it is the biggest in Kosovo basin (24–60 meters), then in Metohija basin (36–40 m) and then in Drenica basin (5–18 meters). Only in Kosovo basin is the thickness of overburden smaller than thickness of lignite seam. In Metohija basin that overburden thickness is 2.5 times bigger than thickness of lignite seam. Bigger overburden thickness implies more expensive lignite exploitation and, consequently, smaller profit, i.e., lignite-based wealth of the region. The average overburden to lignite ratio in Kosovo basin is 1.3 m³/t and in Metohija basin 2.4 m³/t.

On the one hand it is positive that there are large amounts of lignite, but on the other hand the negative factor implies high contents of moisture and ash (because of gangues) and increased contents of toxic microelements of Ni and Cr in lignite that are enriched in thermal power plants smoke, so this lignite represents an important but low-budget raw material for exploitation and production of electric energy that pays off only with minimal transport or exploitation on the spot ([Karamata et al., 2006](#)).

According to the data of the interim institution, Ministry of Economic Development, the estimated lignite resources on the entire territory of Kosovo and Metohija are 12.4 Bt ([Anon1, 2012](#)).

In Rainer Hengstmann's report from 2004, the Independent Commission for Mines and Minerals of Kosovo, which was regulated by UNMIK, published that the World Bank estimated the mineral reserves of Kosovo to be worth 13.5 billion euro. The most significant resource is lignite, with geological reserves of about 15 billion tons (Anon2).

This estimate is in line with the estimates by experts from the Faculty of Mining and Geology in Belgrade who also estimated that the lignite potential in Kosovo would be sufficient to supply two thermal power plants and to provide electricity production in a hundred-year period which, according to the estimate of our Ministry of Mining and Energy from 2009, equals the value of 100 billion euro. Therefore, a major part of lignite reserves in the Republic of Serbia (over 76%) is located in Kosovo-Metohija basin (Anon3, 2015) (Tables 1–3).

In one of its reports, the United States' CIA says that, according to international standards, Kosovo is worth 500 billion dollars (estimated reserves of coal, natural gas and metal), and the remaining part of Serbia with Vojvodina only about 200 billion dollars. In line with one study mentioned in that report, the USA experts estimate that in Serbia there are coal reserves for maximum 35–40 years, while in Kosovo there is coal for as much as 16 centuries. Another study estimates that reserves of coal in Serbia are sufficient for 60 years, and in Kosovo for 200 years. They point out that the value of localities of seven strategic ores (lead, zinc, silver, nickel, manganese, molybdenum and boron) was estimated to as much as 1000 billion dollars (Anon4).

It could be concluded that there is enough lignite to last us more than one century, even with the increased exploitation. Importance of lignite for the region of Kosovo and Metohija is supported by the fact that the share of lignite in total electric energy production is about 97%, while hydroelectric power plants account for 3% of production (Anon5, 2013).

Table 1 Lignite reserves in Kosovo and Metohija

Basin	Reserves		
	Geological	Balance reserves ^a	Off-balance reserves ^b
Kosovo	10.09	8.77	1.31
Metohija	2.24	2.04	0.19
Drenica	0.10	0.07	0.03
Total	12.44	10.89	1.54

^aBalance reserves are reserves in which thermal power of coal exceeds 5450 kJ/kg.

^bOff-balance reserves are reserves in which thermal power is smaller than 5450 kJ/kg.

Note: Anon1, 2012. Privremena institucija samoupravljanja – Ministarstvo ekonomskog razvoja, Strategija za rudarstvo Republike Kosovo od 2012–2025. Priština, p. 14.

Table 2 Thermal power plants in the region of Kosovo and Metohija

Thermal power plant name	Thermal power plant Kosovo A		Thermal power plant Kosovo B		Thermal power plant Kosovo C	
Block	Block 3	Block 5	Block 1	Block 2	Block 1	Block 2
Status	existing	existing	existing	existing	new ^a	new ^a
Operating since	1970	1975	1983	1984	2018	2018
Capacity MWe	200	210	339	339	300	300

^aBeginning of operating of new plants is based on estimate.

Note: Holland, M., 2016. Health and Environment Alliance, Tehnički izveštaj: Uticaji termoelektrana na ugalj na zdravlje na Zapadnom Balkanu, mart.

Table 3 Annual numbers of cases of premature death in Europe that can be ascribed to any plant operating with capacity adjusted to loading factor

	Sulphur-dioxide	Nitrogen-dioxide	PM2.5 ^a	Total
Kosovo A, block 3	17	11	21	49
Kosovo A, block 5	36	22	45	103
Kosovo B, block 1	53	38	18	109
Kosovo B, block 2	53	38	18	109
Total	159	109	102	370

^aPM2.5, fraction of "dust" whose diameter is smaller than 2.5 µm.

Note: Holland, M., 2016. Health and Environment Alliance, Tehnički izveštaj: Uticaji termoelektrana na ugalj na zdravlje na Zapadnom Balkanu, mart.

With the estimated lignite value of about 12(Anon6)–15(Anon4) Bt, Kosovo ranks third (after Germany and Poland) in Europe, and fifth in the world regarding established lignite reserves.

Exploitation of Lignite in Kosovo and Metohija

The main energy sources in Kosovo are located in two major lignite basins known as “Kosovo” basin and “Metohija” basin, with usable lignite deposits (Avidiu *et al.*, 2009). Kosovo basin covers the area of 274 km², and Metohija basin the area of 49 km², while the other basins cover 5.1 km² (Bojaxhiu *et al.*, 2009).

The first systematized data on lignite exploitation, i.e., small-scale lignite mining in Kosovo basin, dates back to 1922. More extensive lignite production started with the opening of open-pit mines Miras (1958) and Belacevac (1969) and by application of modern excavators (diggers). Lignite exploitation in those open-pit mines, that represented one collective exploitation area, ended in 2012. Annual production capacity in both mines was 28,000,000 m³ of gangue (solid mass) and about 17,000,000 tons of coal. Since 2010, coal has also been exploited from the so called “New mine” (southwest of Sibovac), and this mine is in the final phase of development.

Among lignite fields in Kosovo and Metohija, Field Sibovac is the largest exploitation reserve. It comprises approximately 330 metric tons of exploitation reserves and has the smallest portion of overburden. Field Sibovac covers the area of 16 km², with maximal depth of 3.8 km and length of about 6 km. In addition to the new mine, Sibovac Southwest, in which lignite is already being exploited, the plan is to start with exploitation of the southeast part of Sibovac field that has been examined, as well as with two alternative fields: Field D and Field South Sibovac (Kosovo Power Project).

In the figure above, potential mining fields of lignite can be observed (Field Sibovac, Sibovac Southwest, Field D and Field South), as well as mines in which exploitable lignite has been exhausted (Miras and Belacevac).

It is important to mention that the prospects of finding new coal localities are very favourable and realistic, due to good geological prerequisites. There are indications that there is coal in many other locations, especially in the south part of the Pec land, in the part of Djakovica and Prizren. Also, one of potential locations is the Neogene basin of Kriva Reka that represents a tectonic basin formed in the cross-border area of a Dardani massif on the east and Vardar zone on the west, whereby the thickness of coal seam in this region reaches 5 m. It would be reasonable to expect intensification of explorations aiming at a discovery of new lignite localities.

Taking into account the specified lignite amounts, it would be reasonable to expect that lignite, as an energy generating product, will continue to be the main source of energy in Kosovo and Metohija. With that in mind, it is necessary to:

- Follow up the developments, in our neighbouring countries and worldwide, related to technology of clean combustion of lignite intended for increased utilization in industry and heating plants and economically justifiable from social and environmental aspect;
- Intensify geologic investigation in order to develop the strategy of lignite exploitation planning;
- Apply economically and environmentally justifiable procedure of lignite refinement in order to comply with modern technological solutions for utilization of lignite in industry and in mass consumption (Mitrović and Kojić-Lekić, 2006).

Thermal Power Plants in the Region of Kosovo and Metohija

In the region of Kosovo and Metohija there are two thermal power plants: “Kosovo A” and “Kosovo B”. Thermal power plant “Kosovo A” consists of five working blocks known as A1, A2, A3, A4 and A5. Block A1 of this thermal power plant was put into operation in 1962 with the power of 65 MWe; A2 in 1965 with the power of 125 MWe; A3 in 1970 with the power of 200 MWe; A4 in 1971 with the power of 200 MWe and A5 in 1975 with the power of 210 MWe. At the moment blocks A3, A4 and A5 are functional. According to the current production plan, two blocks are in use (A3 and A5), while one of them (A4) is a hot reserve because of their low readiness and age. Blocks A1 and A2 are non-functional and are without defined status and according to the current plans they will remain like that until the end, when their decommissioning is expected. The whole thermal power plant “Kosovo A” is in bad condition and is considered to be the worst single pollution source in Europe. Interim institutions in Pristina plan to decommission it, but it cannot be done until sufficient amount of electricity has been provided, which is not feasible at the moment. Annual electric energy production from thermal power plant Kosovo A is around 1500 GWh (Anon7).

In thermal power plant “Kosovo B” Block 1, built in 1983, is active (339 MWe) and so is Block 2, constructed in 1984 (339 MWe), and they are both in need of rehabilitation after being operational for 35 years in order to be aligned with environmental standards of the European Union.

The total capacity of these two thermal power plants (Kosovo A and Kosovo B) amounts to 988 MWe. The plan is to have the thermal power plant Kosovo C, with block 1 (300 MWe) and block 2 (300 MWe), built and put into operation until the end of 2018 (Holland, 2016).

According to the plan, thermal power plant Kosovo A will be decommissioned by the beginning of 2023, when thermal power plant Novo Kosovo, currently under construction, is expected to be put into operation, and after that thermal power plant Kosovo B will undergo rehabilitation (Anon8, 2017).

Environmental Pollution by Thermal Power Plants in Kosovo and Metohija

In this part we shall discuss the environmental pollution related to air emissions of pollutants, created by lignite combustion in thermal power plants in Kosovo and Metohija. As it was already mentioned, in Kosovo and Metohija 97% of electric energy production is based on lignite exploitation. The first step in this process is procurement of raw material for further processing and transformation (Mikić *et al.*, 2017). Large amount of lignite makes possible a certain level of energy independence on the one hand, while on the other hand negative effects of reliance on lignite must be taken into account. Thermal power plants "Kosovo A" and "Kosovo B" operate according to outdated environmental standards, thus producing high emissions of harmful gases which, consequently, greatly affect the environment and human health. In order to reduce harmful gases emission and, consequently, their negative influence, thermal power plant "Kosovo A" needs to be shut down (which is planned to be done until the end of 2023), while thermal power plant "Kosovo B" needs to be improved in order to comply with new legal requirements based on standards that are much stricter than those that currently apply to the existing thermal power plants. Those new standards have been defined by Industrial Emissions Directive (IED) of the EU (European Parliament, 2010).

Regardless of the stricter standards, we have to be aware that the negative consequences cannot be avoided 100%, but at least they can be reduced to a minimum that will not affect environment and human health severely. If the quality of air in a region complies with the requirements, it does not mean that people who live in that region are fully protected from the influence of air pollutants from a certain source. Estimate of pollutants' influence on environment represents a subjective attitude and does not imply the absence of that influence. There are numerous studies of the influence of air pollutants on health, both in our country and worldwide, according to which the risks are not limited to areas in the imminent surrounding of the plants or other combustion objects, but extend to larger areas, sometimes several hundred kilometres away, because the said particles are transmitted by wind and end up deposited on the ground. These harmful substances bring about enormous environmental problems and are a threat to human life and human health (Papadopoulos *et al.*, 2011). What can be done to reduce the harmful consequences of lignite combustion in thermal power plants is to adjust them to the specified standards and to increase the competitiveness of renewable technologies for energy production in relation to exploitation and utilization of lignite in thermal power plants.

By combustion of lignite in thermal power plants harmful particles (sulphur-dioxide SO₂, nitrogen-dioxide NO₂ and particulate matter (PM)) are emitted, which causes pollution of air. Influence of SO₂ and NO₂ is connected not only with exposure to pollutants in the form in which they are emitted, but also to products of their reactions, since they react with other pollutants in the atmosphere forming the aerosol (ammonium-sulphate and ammonium-nitrate in particular) that contributes to the overall particulate loading of air. Nitrogen-dioxide also reacts with volatile organic compounds in the presence of sunlight which results in production of increased levels of ozone, the other pollutant that is considered to be a threat to health (Holland, 2016). Other dangerous substances emitted from flue-gas stacks of coal thermal power plants are heavy metals, e.g., mercury, and persistent organic pollutants such as dioxins and polycyclic aromatic chemicals. High emissions of mercury from lignite-fired thermal power plants raise special concerns about the health of children (Health and Environment Alliance HEAL, 2014).

The influence of air pollutants on health includes death due to respiratory and heart problems, bronchitis, hospitalization and many other negative effects. Exposure to open air contamination is associated with a large number of acute and chronic health conditions, ranging from irritation to death (Anon9, 1996).

The table below shows the annual number of cases of premature death in Europe that can be ascribed to thermal power plants in Kosovo and Metohija.

The latest data, published in HEAL report, show that the influence of harmful particles produced by lignite combustion in thermal power plants on the annual level round the European Union resulted in over 18,200 cases of premature death, around 8500 cases of chronic bronchitis, and over 4 million days of absence from work. Economic costs of coal combustion impact on human health in Europe are estimated as 42.8 billion euro per year (Anon10, 2013).

In addition to negative health consequences, harmful effects caused by air pollution by lignite-fired thermal power plants have financial consequences as well, regarding both population and the state. Monetization of the influence of lignite combustion in thermal power plants is related to several factors: additional health care costs resulting from hospitalization, increased consumption of medicines etc.; lost productivity of workers who take sick leaves because they themselves are ill or to take care of ill family members and; loss of what is labelled as "usefulness" or "pleasure" in economic literature due to pain, suffering and reduced life expectancy (Holland, 2016).

Due to everything aforesaid, air pollution brought about by lignite combustion in thermal power plants is being increasingly acknowledged as a considerable threat to public health.

Conclusion

If a country wishes to plan and realize the energy strategy, it should possess energy resources. It is typical that countries with larger reserves of energy resources have a higher level of energy independence.

The actual lignite reserves in Kosovo and Metohija are still not known as a fact. All lignite localities in Kosovo and Metohija are still not sufficiently known and have not been sufficiently explored. What we do know at the moment is that those reserves are so immense that owing to them Kosovo ranks third in Europe and fifth in the world regarding the amount of lignite.

Big world players have joined the battle for exploitation of Kosovo resources. In addition to American companies, German, British, French and Turkish companies are also interested in investing into mining localities and exploitation of natural resources of Kosovo. It is an interesting fact that the American company "Envidity", run by a retired NATO general Wesley Clark, asked for a licence to explore coal reserves in order to be able to produce synthetic oil from coal, with the production plan of 100,000 barrels of oil per day.

Lignite is the main energy source in Kosovo and Metohija. Its share in total electric energy production is about 97%, while hydroelectric power plants account for only 3% of production. Due to large amount of lignite reserves, the situation is likely to remain the same in the period to come. According to the European Association for Coal and Lignite (EUROCOAL), coal will continue to be important as a factor among energy generating products for a long time for the purpose of electric energy production whose increasing needs are definite and will continue to grow. In order to meet the need for electric energy, it is necessary to modernize the existing and to apply new, technologically innovative processes of obtaining lignite as an energy generating product.

Currently, there are two active thermal power plants in the region of Kosovo and Metohija: thermal power plant "Kosovo A" (blocks A3, A4, A5) and thermal power plant "Kosovo B" (block 1, block 2). These two lignite-fired thermal power plants emit thousands of tons of harmful pollutants every year, thus contributing to air pollution considerably and not only in the region of Kosovo and Metohija, but in the Balkans region and farther, because the pollutants are transmitted by air to a greater distance. Operating of the said thermal power plants is characterized by outdated environmental standards, which contribute to creation of high levels of emission of pollutants that have numerous negative effects on the environment and human health. Therefore, it is necessary to revise the energy production plans in order to reduce reliance on lignite and exclude it in the end and in order to increase investments into renewable energy sources.

See also: High Dynamic Range Imaging and its Use in Daylight and Lighting Design

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New Educational Models to Train Engineers and Executives On Eco Friendly Technologies, Products and Sustainability Policies

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Rationale and Background

The deployment of large-scale renewable resource applications, viewed as a major shift towards the “greening” and sustainability targets, can only be based on the existence of an adequate human capital, which requires efficient information transfer processes, typically associated with education and training schemes. Nevertheless, the complexity and fragmentation of the renewable energy and materials utilization field itself makes such information processes cumbersome and ultimately inefficient, i.e., fluctuating between shallow empiricism and deep theorizing.

In this paper we will survey the 20-long years’ experience of the Bioresource Technology Unit (BTU) of the National Technical University of Athens (NTUA), Greece, in various types of engineering and technology management education and training actions, ranging from the undergraduate and graduate level all the way to lifelong learning schemes, aiming at generating lessons and tools for broader use.

Rationale

There exist several main characteristics of our present era, which should be seriously considered while organizing the education of engineers and executives on “greening”-related subjects and disciplines:

- *The short life cycle of the new knowledge* (Meister, 1998): The knowledge production rate has been accelerated significantly during the last couple of decades thanks to the info-, bio- and more recently nano-based technology revolutions (Gronau *et al.*, 2004) Although a solid background of basic scientific knowledge is always necessary, the current engineering and management portfolios should include specific skills which will facilitate their access to the new knowledge and to the innovation production and use mechanisms.
- *The need for multidimensional sustainability* (Steinbock *et al.*, 2011): The more traditional techno-economic studies carried out for a spectrum of industrial or service sector processes and products should be also increasingly coupled with eco-societal sustainability assessment studies.
- *From process to product and service design*: The saturation of process engineering needs press for a major shift in the global engineering market, where the product, service and system design skills should lead to the desired outlets, especially in the developed economies.

Background

The following is a list of the experimental courses or programs with an innovative structure, form and/or content, all carried out for the several recent years? by the Bioresource Technology Unit of NTUA:

- A sequence of three *Green Engineering* design courses for senior NTUA Chemical Engineering students – as part of the Organic Industries option (elected);
- A freshman NTUA Chemical Engineering elective course aiming at an Introduction to *Information and Knowledge Society* for young engineers;
- A *Bioenergy* course for the post-graduate NTUA’s program on Energy Production and Management – as part of the Renewable Energies option (elected);
- A week-long Advanced Summer School on *Biobased Technologies* for European and Indian Young Researchers, organized by NTUA;
- A training program on *Technology Management* organized by NTUA – a long version for business persons, and a short one for PhD-level researchers; and
- A Master-level program for re-training executives on *Sustainability Policy and Practice*, also organized by NTUA and taking place during summers on Greek islands.

Teaching Approaches and Methodologies

An overview of the long list of innovative elements which have been introduced in the above educational and training schemes follows:

- Project- and group-based learning;
- Individual learning through projects different for each student;
- Balanced group and individual learning activities;
- Thematic character of yearly course runs; e.g., this year, projects on wastes; next year, projects on “green” chemicals;
- Preparation of short “strategic” executive reports, with a set table of contents;
- Oral presentations by groups and individuals under strict time constraints;
- Molecular and other fundamental approaches of the problems addressed;
- Quantitative vs. descriptive solutions to problems, with emphasis in design;
- Product innovation combined with process, service, and system ones;
- Simulation games, e.g., to consider and model stakeholders’ involvement;
- Laboratory work planned and executed by students to fill gaps in their work;
- Optimal use of web-based sources of information and learning methods;
- Feasibility and sustainability criteria systematically searched and applied;
- Courses/programs evaluated by students, educators and other participants, with results communicated to class and discussed on the course final day.

Special attention was given to the exploratory use of a number of Web 2.0-based tools, with emphasis on their smooth potential acceptance by students, educators and administrators; in particular (Kourakos, 2018):

- *Learning styles*, as a class mapping tool for optimal education effects;
- *Mind maps*, as an analysis and synthesis tool especially for complex training landscapes;
- *Wikis*, involving the creation, collaboration and operation of *scoops* by trainees; and
- *Content curation* as a key collective action by all agents of the training processes.

Undergraduate Engineering Courses

Several innovations were integrated to the teaching methodology of the above mentioned four courses in order to provide the necessary tools to the students of NTUA Chemical Engineering School for dealing with the above presented challenges:

- Project based learning through real-life applications (Ribeiro, 2011);
- Multi-disciplinary approach through interactive lectures and experts tutoring on specific project related topics;
- Consecutive semesters coordination for an in-depth optimization of sustainable solutions;
- Shift from process to product design;
- Integration of the new concept of “molecule domestication”;
- Use of multiple research techniques from desk research to experimental data production;
- Design of student experiments according to the needs of each specific project;
- Overviews of the specific scientific fields according to the specific student project needs, provided from a wide spectrum of applications in organic chemical industries;
- Student feedback through evaluation questionnaires, the outcomes of which are used in the continuous improvement process of the courses.

An additional innovation which was integrated into the undergraduate educational process consisted in the profiling of the student learning style that took place in the beginning of each course cycle. According to Felder (Felder and Silverman, 1988), students learn in many ways: by seeing and hearing; by reflecting and acting; by reasoning logically and intuitively; by memorizing and visualizing. However, teaching methods do not take that variety into account and, as a rule, the results of this mismatching have a really heavy negative impact on the efficiency of the whole learning process. Therefore, a fine tuning step guided by the outcomes of the student learning profiling took place, thus affecting the teaching methodology which was followed for each individual group of students in order to minimize the mismatch.

Post-Graduate Technology Courses

The “Biomass” course, which is offered within the frame of the post-graduate program “Energy Production and Management” of NTUA, concerns a more diverse audience, since the attendants of the program, although predominantly engineers, come from different disciplines. The innovative dimensions of the educational methodology applied can be summarized as follows:

- Personalized student projects, which cover the whole range of biomass-to-biofuels and bioenergy applications;
- Region-specific sustainability assessment of each examined application chain;
- Holistic, system approach of the optimization process, instead of the independent process optimization approach;
- Discussion of the non-technological and non-economic dimensions of the feasibility and sustainability assessment; i.e., assessment of social acceptance and environmental impacts;

- Encouragement of the use of Web 2.0 tools for synergistic and group work, which will facilitate the dissemination of the knowledge among the course attendants, as well as the wider community of the bio-based economy;
- More specifically, a digital content curation platform was developed in order to give the opportunity to course attendants to publish online material and to have useful interactions among the web society.

In addition to the above innovative elements, a decision-making simulation game was introduced to this course, inspired by a then ongoing real-life biomass-based energy project. The students, in groups, are asked to represent specific stakeholder categories and to rank their priorities, as a key step towards reaching a final decision on the feasibility and sustainability of the particular project. The framework of the most recent respective project assigned to the students is shown in the following [Box 1](#) (Karaoglanoglou, 2017).

Box 1 Decision making simulation game – Assessment of the stakeholder involvement in a typical Biomass-to-Energy rural project

The municipality of Thermi, in Salonika, is in the process of evaluation of a project according which a biomass gasification unit will be installed in the region. The unit will process non-hazardous residual biomass for the production of Synthesis Gas, which will be used for power generation (498 kWel).

Scope of project: Electricity generation, which will be sold to the Power management authority according to the existing legislative framework.

Feedstock: Wood chips.

Capacity: 5000 t/a wood chips (or 15 t/d), which will be supplied by the local and/or international market, according to the current market prices.

Overall investment: 750.000 Euro to be financed 25% by own sources, and 75% by a loan.

Location: The plant will be installed on a land area of 4800 m², which is located on the North of the National road of Thessaloniki-Polygyros.

For the initial feasibility assessment of the specific project, a stakeholder meeting will be organized, where all the major stakeholders will be represented. More specifically: (a) Biomass producers handling trimmings and other agro-based biomass sources of the region; (b) Companies or individuals managing municipal biomass sources; (c) Bioenergy (gasification) industry; (d) Electricity distribution company; (e) Local community; (f) Local government; (g) Central government; (h) Other stakeholder to be decided following a discussion in the class.

The student groups were asked to represent each of the interest groups during the workshop and to rank its priorities in the following decision-making criteria (where 1: the most important criteria and 9 the least important one), justifying in the meantime their decisions.

Decision criteria: (1). Return on Investment; (2). Annual revenues; (3). National economy; (4). Regional/Local economy; (5). Application of new/innovative technologies; (6). Employment; (7). Environment; (8). Political and institutional benefits; (9). Other criteria.

Until the meeting date the students should:

- (1) Rank their decision priorities, first on a personal basis and then as specific stakeholder group;
- (2) Clarify under which conditions they would be absolutely positive or supportive, absolutely negative or just reluctant about the realization of the project; and
- (3) Assess the potential alliances which can be built with other stakeholder groups.

Life-Long Executive Education

The specific Training Workshop for European and Indian Researchers took place within the framework of the EU-funded FP7 project "SAHYOG." It was the first of two Summer Schools, planned within the project, in order to stimulate research cooperation between Europe and India in the project field, with emphasis on recent developments on environment-friendly biomass and biowaste conversion. The innovative elements of the specific activity can be summarized in the following:

- A multi-national audience, comprised of Indian, Italian, French and Greek students;
- A multi-national and multi-disciplinary teaching team, comprised of specialists for each topic;
- Strict student selection criteria targeting at, among other things, their multi-disciplinarity;
- A multi-level approach, where the socio-environmental aspects were in complete balance with more "traditional" techno-economic aspects;
- The presentation of a very wide range of the available and future biomass-to-bioenergy, biomass-to-biomaterial, and biomass-to-biochemicals chains, with emphasis on the more promising ones;
- Personalized projects aiming at the application of the summer school material on real life cases, deliberating in the meantime the creativeness of the attendants;
- The project topics covered the widest possible range of the relevant production and logistic chains.

The student projects in combination with the whole teaching approach provided the necessary tools for the students' future professional activities, contributing in particular to the process of building a common culture on the specific scientific and technological field.

Content Curation in Education

It is argued that Content Curation (CC) will be a critical strategic option for student-centered engineering and technology teaching in the 21st century (Antonio *et al.*, 2012). CC focuses on the extensive use of any kind of digital material, from whoever has access to the World Wide Web.

Using any kind of digital material is a common place in the current life style. Limiting our scope in the educational activities would further indicate the increasing tendency of saving, uploading on the web and transferring educational material through personal computers, corporate networks and portable devices. To put it bluntly, the conventional printed educational material shows rather insufficient in the digital age. Given that during our educational lifetime the digitalized educational material is almost everywhere, its efficient management, which will render it accessible and usable, is a real necessity. Nowadays, the primarily produced digital material has been being multiplied, whereas material already available in printed form has been being rapidly transformed into digital form (Yakel *et al.*, 2011).

The transition into a model of educational material which will be easily explorable, accessible and reusable is imperative, and it will replace the old, and inactive "dark" material, which offers limited accessibility. In the digitalized world of nowadays, which is also supported using of metadata, reusing any material is a common place. The potential of direct data and information "mining" accelerates the direct access of any student and trainee to material of digitalized format. From the point of view of a user/reader, the easiness of access to the digitally saved Material corresponds to the direct access to the knowledge. On the other hand, the owner/creator of the material is also protected, within the frame of existing technology, ensuring the control of the original creator's identity, as well as, possible corruptions of the original documents (Higgins, 2011).

Eco-Friendly Learning and Other Outcomes

"Green" Engineering Lessons

Throughout the ca. 10-year period of the application of this specific educational approach to the "Green" Engineering courses, more than 50 different student projects were assigned and presented. The distribution of the assigned molecules between the three major product market segments is shown in Fig. 1, whereas the structure of the teaching is shown in Fig. 2:

The surveyed student projects provided some insights both to the trends of modern, "greener" chemical engineering and to the prospects of the applied educational methodology (Seiderand and Widagdo, 2012). Some relevant findings from such a long class experience follow:

- There is a shift in the process technologies from "old school" heavily chemical catalytic processes to bio-catalysed, bioresource based "greener" ones;
- Relocation of production units takes place, especially when the commodities are concerned, from Europe and Western World to Asia. The low labour cost, coupled with a more flexible regulatory framework and environmental tolerance, create the "ideal" investment framework, favouring that part of the world. Quite often this happens without the incorporation of the lessons already learned in the Western World and at the expense of environmental and social sustainability;
- There is also a shift from process to product design due to the fact that the optimization efforts of the former have reached at its limits. Mostly the environmental targets set, in view of stricter regulations, are keeping the process optimization interest still active;
- Products related to quality of life objectives, i.e., food additives, nutritional supplements, and nutraceuticals, do gain an increasing importance in the overall world market. Most of the innovative products proposed by the student groups are somehow related with this product portfolio;
- Even the "hardcore" petrochemical products tend to focus on the research for raw material substitution in order to improve the environmental impact created from their production; i.e., butadiene;
- The product design is the kind of engineering work which can be carried out still in Western world, and not necessarily co-located with the actual production site;
- The proper use of the full set of the chemical engineering tools, requires the proper guidance and tutoring of the students throughout the whole duration of the engineering courses.

The analytic and synthetic skills which are developed step by step seem to be the major benefit of the educational process. Furthermore, the innovative thinking, which is the crucial element of product design, is cultivated during these courses, under the condition that the participating students succeed in overcoming their reluctance concerning "out of the box" creative thinking (Karaoglanoglou *et al.*, 2016).

The continuous improvement of the educational process depends also on measuring the student feedback for certain elements of each course cycle. This is achieved through the use of a tailored questionnaire at the end of each 3-course cycle. The so far

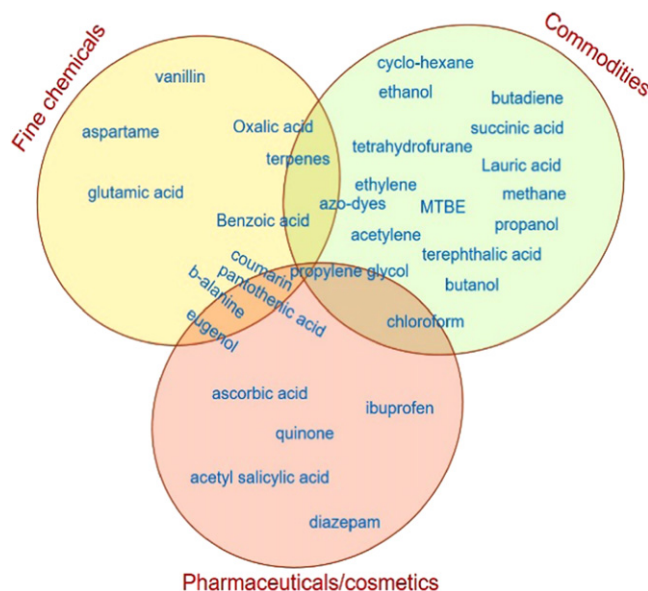


Fig. 1 Studied molecules and their market. *Source:* Karaoglanoglou, L., Kamtsikakis, A., Rigopoulou, M., *et al.*, 2015. Chemical engineering education for dealing with the new challenges: From one-way lectures to project based cognitive learning. In: Proceedings of the 10th Panhellenic Scientific Chemical Engineering Congress.

Structure of Organic Technology Courses

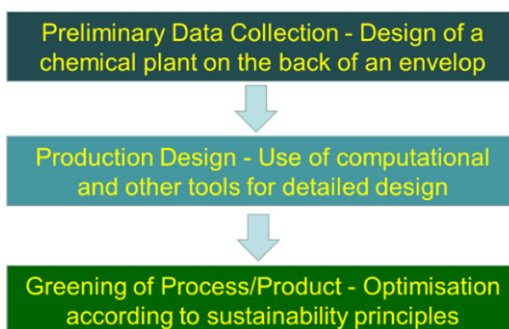


Fig. 2 Structure of Green Engineering Teaching. *Source:* Kourakos, N., 2018. Web 2.0 and Other Digital Tools in Technology Teaching (PhD Thesis). Athens.

outcomes of this questionnaire are presented in [Table 1](#), where the students evaluated the course elements through marks from 1 (worst performance) to 5 (best performance):

“Green” Technology Management Lessons

A Decision-Making Tool: The outcomes of the simulation game, which takes place within the framework of the post-graduate biomass course - see [Box 1](#) - are discussed briefly in this section. The questionnaires which were collected provided data for the determination of the priorities of each interest group (see [Table 2](#)). Grouping the results can give a rough overview of the overall priorities of the region, which will affect the sustainability of a potential plant. The environmental impact of the plant, as well as its effect on the regional development (criteria 7 and 4) seem to play a decisive role according to the stakeholders, followed by the plant microeconomics and its socio-economic impact (criteria 2 and 6).

Further processing of these data can provide indications for the potential alliances and consensus platforms which can be built among several stakeholders and the possible friction points, which could jeopardize the sustainability of the future plants, as well. In particular, the affinity between each couple of interest groups can be assessed using an index which is generated by summing the absolute differences of their responses for all the decision criteria (see [Fig. 3](#)).

The lower this index is, the more easily an alliance between two interest groups can be built. Encouraging such alliances, using the available or new policy tools will be a crucial feasibility and sustainability issue for the implementation of the examined technology. As an outcome of [Fig. 3](#), it can be noticed that the couples of “biomass producers vs electricity distribution company”

Table 1 Student feedback to the educational methodology

Questions	Average score 2013	Average score 2014	Average score 2015
1. The interest of the courses?	4.2	4.1	4,0
2. The utility of the courses?	4.1	4.1	4,1
3. The interconnection of the 3 successive courses?	4.3	4.1	4,3
4. The educational methodology?	3.8	3.5	3,7
5. The course professors?	4.5	4.3	4,4
6. The invited course lecturers	4.0	4.0	4,4
7. The tutors and supporting staff?	4.7	4.6	4,6
8. The supportive course material?	3.2	3.1	3,2
9. The quantity of the lab work?	3.4	3.7	3,9
10. The quality of the lab work?	4.3	4.3	4,0
11. Your choice of the specific specialisation field?	4.7	4.6	4,4
12. Next year continuation of the same methodology?	4.0	4.1	4,1

Source: Karaoglouglou, L., Kamsikakis, A., Rigopoulou, M., *et al.*, 2015. Chemical engineering education for dealing with the new challenges: From one-way lectures to project based cognitive learning. In: Proceedings of the 10th Panhellenic Scientific Chemical Engineering Congress.

Table 2 Priorities set by each interest group/stakeholder

Decision criteria	Ranking of the decision criteria by interest groups/stakeholders								Total	Overall ranking of importance
	a	b	c	d	e	f	g	h		
1	4	6	2	8	7	7	7	3	44	IV _B
2	1	5	1	9	6	8	2	6	38	III _A
3	7	7	8	6	4	3	1	9	45	V
4	2	2	7	7	2	1	4	5	30	II
5	6	9	5	2	5	6	9	1	43	IV _A
6	3	8	9	5	3	2	5	4	39	III _B
7	5	3	3	4	1	4	3	2	25	I
8	8	4	6	3	8	5	6	8	48	VI
9	9	1	4	1	9	9	8	7	48	VI

	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
(a)		28,0	24,0	38,0	22,0	22,5	26,0	22,0
(b)			21,0	25,0	22,0	28,0	24,0	32,0
(c)				30,0	34,0	38,0	28,0	24,0
(d)					32,0	28,0	34,0	28,0
(e)						12,0	20,0	20,0
(f)							20,0	30,0
(g)								30,0
(h)								

Fig. 3 Mapping the potential alliances between socio-economic actors.

and "bioenergy plant vs local government/authorities" present the largest differences. The relatively large index for the couple of bioenergy producer and local community also indicates that work is needed from the producer side in order to gain the confidence of the local community. Especially, the interaction of this couple should be considered as a key success factor for the whole chain. On the other hand, the low value of the index of the pairs of local community with local government, central government and the researchers (who were voted as the 8th stakeholder category by the students), shows that their common basis of understanding can either boost or block the investment.

A Web 2.0 Tool: The outcomes of the digital curation which took place on this course are very interesting and useful, too. In the Fig. 4a and b below, the impact of student scoops in the networked society can be seen. Despite the limited monitoring time for the students' posts in the curation platform, which was only one month, their impact can be considered as promising in terms of the number of both the views for their topics and the followers for their micro sites.

Summer School Toolbox: The initial scope of the SAHYOG Summer School (see above) was to provide the attendants with a overview of the state of the art of biomass related technologies, as well as to supply them with the necessary tools that will let them

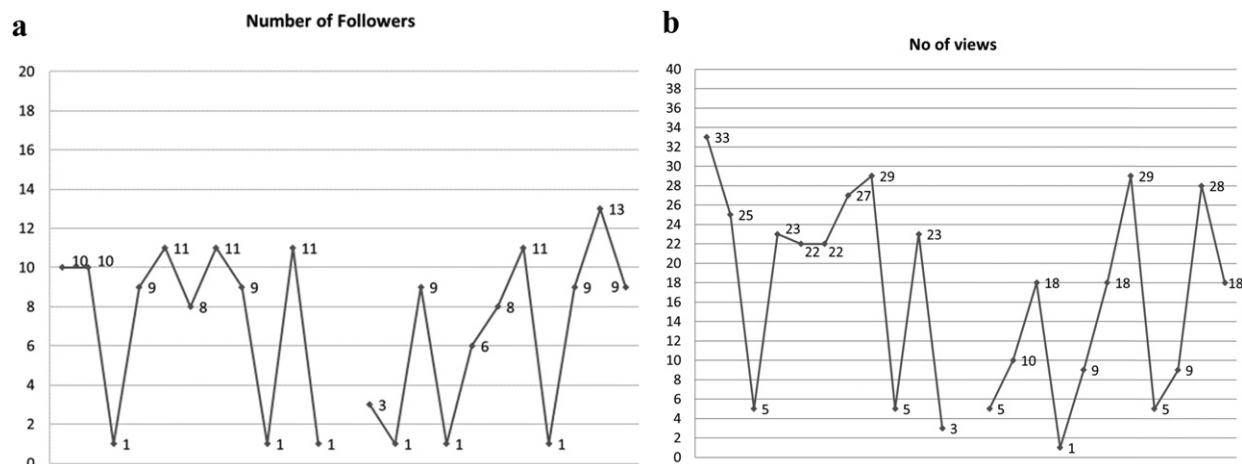


Fig. 4 (a and b) Student scoops impact in the networked society. *Source:* Kourakos, N., 2018. Web 2.0 and Other Digital Tools in Technology Teaching (PhD Thesis). Athens.

Table 3 SAHYOG summer school (S3) evaluation (5 = very positive, 4 = positive, 3 = neutral, 2 = negative, 1 = very negative)

No.	Question	Ranking
1	SUBJECTIVELY: Achievement of your original expectations from S3?	3.8
2	OBJECTIVELY: Achievement of the S3 targets as defined by its organizers?	3.9
3	ON A HINDSIGHT: If you knew what S3 was really about, would you attend it now?	4.1
4	RECOMMENDATION: Would you now recommend S3 to an interested colleague?	4.4
5	COOPERATION: Would you be interested to join a future S3 as an organizer/lecturer?	4.3

assess the applicability of these technologies under different socio-environmental conditions, i.e., the ones in India and in Europe. The results of the course evaluation by the attendants can be seen in [Table 3](#).

During the Summer School the students were also assigned to prepare a short report describing a biomass project of their own interest. In order to do that, the students had to answer briefly 5 questions (A to E) asked by the teaching staff: (A) Biomass feedstock used – (B) Biomass conversion technology applied – (C) Biomass derived product(s) delivered at the end of the pipeline – (D) Location of the “ABC” application – (E) Potential of real-life development of the proposed ABC chain. Moreover, the student project proposals were reviewed by experts, members of the Workshop organizing committee, and the best ones were honoured with a success certificate presented during the closing ceremony of the Workshop.

Concluding Remark

The students who attended any of the above-mentioned dimensions of the educational activities coordinated by BTU were supplied with a toolbox which will be applicable in any future “green” process and product design, or more generally, complexity dealing challenge. During these activities the multiple dimensions of sustainability issues were analysed, beyond the traditional techno-economic feasibility, with an interdisciplinary approach. The students got familiarized with the methodological approaches which should be followed during the data collection and decision-making process, as well as with the productive use of the already available tools; i.e., software, GHG assessment, GIS, etc. In all cases, the students developed skills on how to deal with these complex problems in multidisciplinary way, by not becoming a top expert for every case but by contacting the right expert and through him/her exploiting sustainably the state of the art of science and technology.

Acknowledgements

The present overview of education and training activities by the BTU group of NTUA is based on several reports of individual BTU actions presented at various audiences, mostly as part of the Education Sessions of the National Chemical Engineering Conference Series (2013–2019). Other significant sources of relevant research findings include the Doctoral Theses of two of the co-authors of the present article.

See also: Induction Heating in Sustainable Manufacturing and Material Processing Technologies – A State of the Art Literature Review

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Nuclear Electricity – Renewability, Losses and Recycling

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Introduction

Nuclear reactions are known to have tremendous potential to generate an enormous amount of energy in the form of heat, light, sound etc. Sun being the best example for fusion nuclear reaction, it made clear that controlling the energy produced during fission reaction was practically impossible for the mankind. However, fission energy was viewed to be of human enterprise. The amount of energy produced during a nuclear reaction made it of quiet an importance in the human world. Electricity was first generated using the nuclear reactor on September 3, 1948, at X-10 Graphite reactor in Oak Ridge, Tennessee, United States ([Graphite Reactor](#)). Nuclear fission reactors brought the direct service of the vast majority of the nuclear energy to the humankind with the commencement of Obninsk Nuclear Power Plant in USSR on June 27, 1954 ([Russia's Nuclear Fuel Cycle](#)). Despite all the advantages the nuclear energy could have provided to the human world, its destructive use was first witnessed by mankind during World War II in Hiroshima and Nagasaki of Japan used by the United States of America.

Nuclear power generation has been a huge step in human civilisation. Having known the enormous potential of electricity generation by nuclear fuel, scrutiny instantly turned towards the risks involved during the process and its consequences. The dubiety of nuclear power to be classified as a permanent source of electricity replacing all other alternative source prevails regardless of its extensive prospective. The debate over the nuclear energy being renewable or non-renewable resource hasn't seen a clear side through various sets of belief. Power generation efficiency for nuclear power was found to be around 67%, as discussed in further sections, challenge nuclear powers capability of become the future of power generation. To add to scepticism over the prospect of nuclear power, the waste handling has played an important part. The nuclear waste handling has been one of the biggest road blocks for the development of nuclear power generation infrastructure. The highly radioactive wastes take centuries to get less harmful to the environment. The storage of such wastes for so long time leads to serious criticism of nuclear fuel. However, in modern days, with nuclear reprocessing gaining acceptance, even though its risks, the waste handling is expected to get efficient in next few decades. This article discusses how the nuclear power are getting closer to other alternative sources and claiming to replace them with a lesser risk involved.

Nuclear Energy – Renewable or Non-Renewable Resource?

The Library of Congress defines renewable energy as “a sustainable energy source that is replaced rapidly and indefinitely, by a natural ongoing process.” This creates a debate for the qualification of nuclear energy into a list of Renewable resources, which otherwise is a clean source of energy. The Library of Congress also notes that nuclear fuel sources are “not essentially renewable” since they are liable to be depleted. The U.S. Department of Energy classifies Uranium (U) as a non-renewable source. Experts still question whether the world should call nuclear power “renewable” ([Library of Congress BERA](#)). There are school of thoughts who want to classify nuclear energy as renewable cite the fact that it has low carbon emission, just the way renewable sources such as wind and solar do. Non-renewable fuels, such as natural gas and oil, produce byproducts that harm the environment through global warming emissions. Those opposed to calling nuclear power renewable note that nuclear power plants create harmful waste. According to the ones opposing the idea, if the goal to build a renewable energy infrastructure is to lower carbon emission then there is no reason for not including nuclear energy in that list ([Cohen, 1983](#)).

An interesting argument for including the nuclear energy in renewable source portfolio came from Bernard L Cohen, a former professor at the University of Pittsburg ([Cohen, 1983](#)), USA in the same article. Professor Bernard came up with an interesting definition of the word indefinite, which described the time span required for a source to become renewable in numbers by using an expected relationship between earth and sun. According to Professor Bernard, a source can be said to be renewable if its deposit could prove to last as long as the relationship between earth and the sun is expected to last, i.e., 5 billion years. Hence, according to his argument, the nuclear energy could be declared as renewable if U deposit inside the earth could last for the amount of time span which was indefinite by Professor Bernard's definition. According to the paper by Professor Bernard, using the breeder reactor makes it possible to fuel earth with nuclear energy indefinitely. It was claimed in his paper that although the current supply of U discovered has the capability to fuel earth for 1000 years, but there are still some U deposits available which are yet not extracted. It is mentioned by Professor Bernard in his paper that there are some other deposits of U from which the extraction process could be expensive though. Extraction from sea water and also the depletion of U from the earth crust by sea water has been acknowledged by Professor Bernard. All of those possible U resources if used in a breeder reactor would be enough to fuel the earth for another 5 billion years and hence renders nuclear energy as renewable energy ([Johnson, 2009](#)).

The arguments presented by Professor Bernard left a huge void for reasoning in the debate of renewable and non-renewable nature of nuclear energy. The biggest opposing argument relied on the fact that U deposits tend to end up soon. The claims of Professor Bernard for the indefinite supply of nuclear fuel didn't find an arc since the deposits still are expected to exhaust sooner than what was defined as indefinite. Another major argument was the polluting nature of the nuclear fuel. Although carbon

emission was found to be less in the case of nuclear fuels than the rest of non-renewable fuels, yet the amount of harmful wastes led to a solid argument against its case. Yucca Mountain is one of the examples used quite often to prove this point.

This confusion over the nature of nuclear fuel never could find a shore of settlement. A recent decisive statement by Helene Pelosi, the interim Director General of IRENA (International Renewable Energy Agency), saying IRENA's support won't be extended to nuclear energy program due to its waste production, long and complicated process and higher relative risk (Kanter). The statement proved that the decision over renewability of nuclear fuel has nothing to do with the sustainable supply of fuels. Such a decision has led to the supporters of nuclear energy to look for an efficient way to dispose of wastes before asking IRENA again to tag nuclear energy for a renewable source of energy along with a clean one.

Efficiency

The vastly expanding renewable energy sources like solar, wind, hydro and wave power to replace the current non-replenishing sources are resulting in significant challenges in balancing supply and demand in the smart grid (Lund *et al.*, 2012). Improving resource efficiency is an important factor which can lead to the answers to various challenges. Measurement of Primary Energy Factor (PEF), which describes the amount of energy from primary resources are being used for each delivered unit of energy, is most popularly known method for estimating resource efficiency (Eriksson, 2017). Improvement of energy efficiency on large scale is required, as addressed in e.g., European energy targets (European Commission, 2014), where efficiency measures are targeted to resources which are vast over just electricity.

Primary Energy factor has various flaws in itself. A simple stating of primary energy factor can be a relationship between the total energy input and the final energy used (Russia's Nuclear Fuel Cycle). The aim of PEF to focus on the efficiency relationship of the resource leaving aside its environmental impacts and mankind risks, accounts for a questionable flaw of it. However, its accurate study could serve the purpose of understanding the efficiency of a resource.

Nuclear Power Plant Efficiency

Nuclear energy, famous as one of the clean sources of energy, less is popular about its very low efficiency. At an average, the yield of a nuclear power plant is approximately 30%. In other words, this means 30% of the energy generated by U fission ends up being converted into electricity. The rest is lost or used up during the different steps of the transformation process of potential energy.

In a discussion of Modahl *et al.* (2013), a comparison of primary energy content for hydro, nuclear and wind power is mentioned. The discussion is presented for nuclear energy by two different approaches. In the first approach, power energy is referred as the energy stored in the turbine of the power plant. Here the life cycle efficiency assessment gives nuclear energy to be 33% efficient (International Energy Agency IEA, 2004). In the other approach, the primary energy is defined as "the energy content of the fissile isotope in the natural U extracted from the mines" (Frischknecht *et al.*, 2007). This approach was more realistic, covering the whole life cycle back to the cradle. However, not much of difference was seen from the data obtained in the first approach.

A specific set of directives responsibly appeal to the European standards with a recommendation of PEFs for alternative sources to electricity generation to be established. In Global Emission Model for Integrated Systems (GEMIS), a model and a database both are hosted by IINAS for the life cycle assessment and material flow analysis model, which is used in EU and OCED (Organisation for Economic Co-operation and Development) countries. Table 1 shows a very productive compilation of PEF for nuclear energy from sources which are either taken from GEMIS model or have been found to be consistent with the model.

The fission of one gram of U235 releases approximately 24 MWh or 1 MW day (MWd) of thermal energy. This fact makes it easy to use the concept of combustion rate, also known as "burn-up", which is expressed in MWdays per tonne of heavy metal

Table 1 Compilation of primary energy factors for nuclear power from various sources

<i>Method/Data</i>	<i>Primary energy factor</i>	<i>Degree of efficiency (%)</i>
IEA (2004)	3.0	33
Ecolnvent	3.19–3.58	27.9–31.3
IEA (2009)	3.4975	28.59
Nuclear – DE	3.29	30.4
Nuclear – FR	4.05	24.7
Nuclear – UK	3.15	31.7
Nuclear – SE	2.92	34.2
Partial Substitution	2.5	40
Physical Energy content	3	33
EN 15603: 2008	2.8	35.7

Note: Eriksson, O., 2017. Nuclear power and resource efficiency – A proposal for a revised primary energy factor. Sustainability 9, 1063.

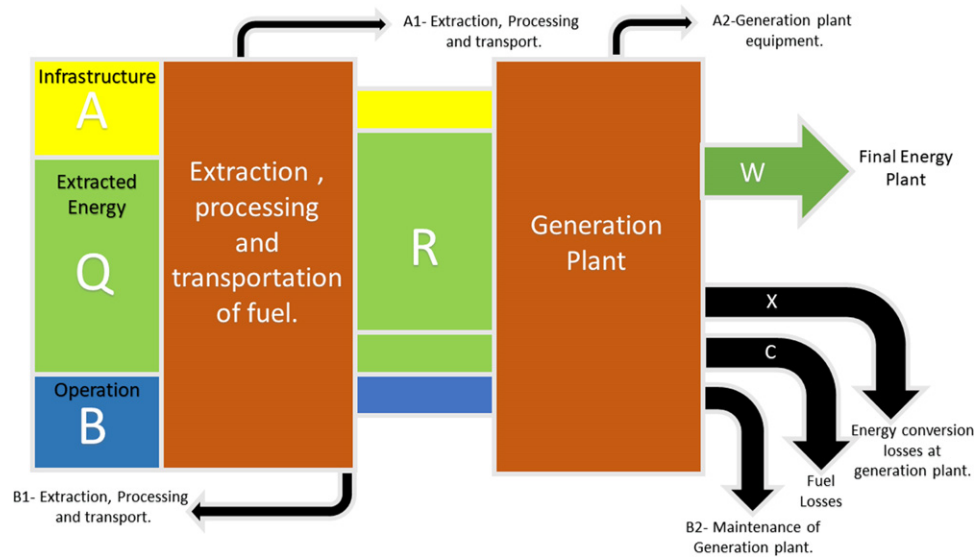


Fig. 1 Life-cycle chain of energy products. Reproduced from Eriksson, O., 2017. Nuclear power and resource efficiency – A proposal for a revised primary energy factor. Sustainability 9, 1063.

Table 2 Calculated PEF for nuclear power (Energy Density = 23.564 GWh/kg)

Scenario	Burn up (GWd/ton)	Power to heat ratio	PEF
Baseline	50	33	60
Conservative baseline	40	27.9	88
Progressive baseline	73	41	32

(The trend and the Benefits of Multi-Energy Services for a New Generation of Industrial and Commercial Customers) (MWd/tHM). The total thermal energy released by nuclear fuel is proportional to the burn-up it reaches at the end of its reactor life (National Strategies for Management of Fluctuations in Wind Power and CHP). The thermal efficiency of a nuclear power station is the efficiency of the thermodynamic cycle by which the heat generated by the fuel is converted into steam through steam generators. The thermal efficiency of a conventional nuclear power station is around 33%–36% agreed through peer review between EUR-ELECTRIC and VGB experts (Efficiency in Electricity Generation, 2003).

In the definition of primary energy, it is vital to consider all pre-combustion losses. In Fig. 1, different types of losses are graphically illustrated.

The prevailing $PEF = 3$ for nuclear power sets the relation between W and the sum of $W + X$. In addition, some data sets considered the contributions of pre-combustion operations shown as A1 and A2, along with the infrastructure losses B1 and B2. Nevertheless, their contributions were found to be minor. Obvious observation shows that losses from the fuel have been neglected in the calculation of prevailing PEF. However, one of the most problematic issues with nuclear power is the problem with radioactive waste. The waste is partly low or medium active (used equipment, clothes, etc.) while the majority of the high active waste is spent fuel. Radioactivity is a form of energy, meaning that radioactive waste contain enormous potential primary energy. This loss is not accounted for in the PEF, which suggests that the energy in spent fuel should be seen as a potential resource that has not been consumed. This means that the current PEF for nuclear power is inconsistent with most current plans for the final disposal of spent fuel. It should also be noted that this circumstance separates nuclear power from the combustion of solid (like coal or biomass) or liquid (e.g., oil, gasoline) fuels, where fuel-related energy losses are moderate due to more or less complete combustion processes.

In the calculations made by Eriksson (2017), PEF values are measured. The reported PEF values demonstrated that the losses which are being considered while considering $PEF = 3$ are very high. In the paper, energy density, burn up value and heat to power ratio led to values which could be used to conclude that “the current values underestimate the poor use of U”. For the calculations

$$PEF = \frac{ED \left(\frac{GWh}{kg} \right) \times 1000 \left(\frac{kg}{ton} \right)}{BU \left(\frac{GWd}{ton} \right) \times 24 \left(\frac{h}{d} \right) \times \eta}$$

Where ED=Energy density, BU=Burn up value and η = heat to power ratio.

Resulting PEFs for the different assumptions on burn-up and power-to-heat ratio are displayed in Table 2 (Eriksson, 2017).

Table 3 Transmission and Distribution losses in various countries

Country	% Losses in 2000	Country	% Losses in 2000
Finland	3.7	Sweden	9.1
Netherlands	4.2	Australia	9.1
Belgium	4.8	U.K.	9.4
Germany	5.1	Portugal	9.4
Italy	7.0	Norway	9.8
Denmark	7.1	Ireland	9.9
USA	7.1	Canada	9.9
Switzerland	7.4	Botswana	10.0
France	7.8	Spain	10.6
Austria	7.8	New Zealand	11.5
Trinidad and Tobago	7.9	Jamaica (2003)	18.8

The table suggests the value of PEF varies with the different reactor scenario. The variation is highly sensitive to actual burn up and may vary between 32 and 88 or more. This implies that PEFs for nuclear power has to be calculated on an individual plant level instead of using the current generic value. So, with 33% efficiency already being too low, it can be said that it still underestimates the amount of wastage of fuel.

Transmission and Distribution Losses

In the previous section, it is already seen that nuclear energy losses are enormous. The conversion of radioactive energy to electrical energy is highly inefficient. In earlier sections, it is illustrated that almost 67% of energy is theoretically already being lost during the generation of electricity from nuclear fuel. To add to this, transmission and distribution losses are a challenge within themselves as well. In India, average Transmission and Distribution losses, have officially been indicated to be 28% of the total energy generated (Singh and Kumar, 2014). India is found to be the country having the highest T&D losses, with almost 30%–50% of the losses coming from eastern India (State Electricity).

The transmission and distribution losses associated with the process of supply of electricity are classified as technical and non-technical losses (Concept notes on T & D losses). The technical losses are almost inevitable, as they arise due to energy dissipated in the electrical system equipment used for transmission, transformation, sub-transmission and distribution of power. The losses can be further sub-grouped depending upon the stage of power transformation & transmission system as Transmission Losses (400kV/220kV/132kV/66kV), as Sub Transmission Losses (33kV/11kV) and Distribution Losses (11kV/0.4kV). Technical Losses generally vary with the square of the load current being distributed. As a result, losses will increase as more capacity is used. Losses are also proportional to the length of the line. These losses consist of both variable and fixed components. Fixed losses comprise of system configuration, the pattern of loading of transmission and distribution lines, magnitude and types of loads, characteristics of equipment etc. While the variable losses arise due to weak and inadequate sub-transmission and distribution lines, inadequate sizing of the conductors used, lengthy transmission and distribution lines and inadequate reactive compensation in the system.

The non-technical losses or commercial losses are a component of distribution system losses that are not related to the physical characteristics and functions of the electrical system. These losses arise due to defective meter, error in meter reading, customer frauds, illegal connections, etc.

In India, transmission and distribution losses have raised from 15% in 1966–67 to 34.33% in 2003–04. However, at present these losses are about 27%. The technical losses in the lost 27% consist around 15% and rest of the 12% are constituted of commercial losses Modahl *et al.* (2013). While comparing this loss with the losses in other countries given in Table 3, it indicates that the losses in other developing countries are around 10% less than India. With India producing around 35 TWh of nuclear energy, it requires the country to build smart grid which can contribute to the infrastructure of nuclear power plants and reduce losses to a minimum amount by avoiding the commercial losses.

In Table 3 (Electric Power in Asia and Pacific, 1997), transmission and distribution losses of various countries are listed in the increasing order during the year 2000.

Nuclear Wastes

Nuclear wastes are the left over materials that nuclear fuels become after being used in the nuclear reactor. Physically nuclear wastes look exactly the same as the loaded fuel – assemblies of metal rods enclosing fuel pellets. Waste materials are generated due to continuous operation of a nuclear reactor or during decommissioning of it. Compared to other power plants, the amount of wastes produced in nuclear power plants are very low (Efremenkov, 1989). It is needless to mention that these waste materials are highly radioactive in nature. Decommissioning of the nuclear power plant is a common practice normally after 20 years of its usage. Nearly 3 power plants in Germany along with a few in France have already been decommissioned (VGB Brochure). During the decommissioning of a nuclear plant, the waste generated can be recycled to give lesser radioactive and constructive products.

Table 4 Heavy metal composition of 4.2% enriched nuclear fuel before and after running for 3 years ([What's about the wastes](#))

<i>Components</i>	<i>Charge</i>	<i>Discharge</i>
Uranium	100%	93.4%
Enrichment	4.2%	0.71%
Plutonium	0.0%	1.27%
Minor actinides	0.0%	0.14%
Fissionable products	0.0%	5.15%

However, there are certain wastes which couldn't be recycled and are to be regarded as radioactive wastes. These wastes are to be properly disposed of, along with the other radioactive products from a nuclear reactor.

The radioactive wastes can be classified by international standards based on the quantum of radioactive nature into Low – level radioactive, Intermediate – level radioactive or High – Level radioactive. Low and Intermediate level radioactive wastes are produced by the contamination of various materials by the radionuclides which are formed as a result of fission in the reactor or released from the reactor walls. Usually, the radionuclides are collected in the reactor coolant system and, to a lower extent, in the fuel storage pool. Low-level radioactive wastes are less on radiations but very high in volume as compared to intermediate and high-level radioactive wastes. Hence, reduction of the volume of low – level radioactive waste is an important measure to reduce the interim disposal costs.

The most important and hazardous waste being produced comprises of components being removed from the reactor during refueling or maintenance or operational wastes such as radioactive liquids, filters, and ion-exchange resins which are contaminated with radionuclides from circuits containing liquid coolant. The chemical composition of a typical US nuclear reactor's waste is given in [Table 4](#).

Liquid Wastes

The wastes streams arising in nuclear reactors can vary depending upon the various reactors operating all over the world. These streams can vary in both in terms of activity and concentration. A reactor whose core is water cooled, produces more wastes than a gas cooled one. Liquid concentrates at Heavy Water Reactors (HWR) is virtually absent due to its clean up system working with ion exchange technique. Moreover, Boiling Water Reactors (BWR) produces more liquid wastes than Pressurized Water Reactor (PWR). Some active liquid wastes are also generated during the clean-up of BWR and PWR and Decontamination of the reactor core ([Efremenkova, 1989](#)).

Wet Solid Wastes

Waste Solids are another major category of produced wastes in nuclear reactors. The principle PWR waste flows include ion exchange resins (bead resins), filter cartridge inserts, metal components, evaporator concentrates, oils, filter concentrates, etc ([Efremenkova, 1989](#)). Spent resins are the most significant part of produced solid wastes. Bead resins are mainly used in the systems such as coolant purification, fuel pool cleaning and coolant preparation. They are mostly seen in deep demineralisers. BWR's have a considerable amount of powdered resins for which a significant source is "condensate polisher" used for further cleaning of water condensed after evaporation from the surface. Filter wastes are produced by the interaction of pre-coated filters with liquid wastes which gives wet solid wastes popularly known as filter sludges. The subsequent drying of the filter concentrates allows interim storage as solids in waste containers.

Gaseous Wastes and Aerosols

Air borne radioactive wastes of either particulate or aerosol type can be generated in a reactor which is gas cooled. The particle size can be of wide range in either solid or liquid form depending on the type of reactor in particulate wastes. These wastes could be a well-formed combination of various components both radioactive and non-radioactive in nature. Three major sources of aerosols are generated by the emission of activated corrosion products and fission products, radioactive decay of gases to in-volatile elements; and adsorption of volatile radionuclides formed in the fission process on existing suspended material ([Efremenkova, 1989](#)). Volatile radionuclides which form radioactive gaseous wastes are halogens, noble gases, tritium, and carbon – 14. These gaseous wastes are of immediate effect to the environment. Hence they are to be treated before releasing to the atmosphere to remove radioactive constituents from the effluents.

Decommissioning and Dismantling of Nuclear Power Plants

An important problem of nuclear energy is that unlike other industrial facilities, nuclear power plants have to be decommissioned at the end of their technical and financial life span leading to its dismantling. These dismantled nuclear reactors are the largest contributors for radioactive wastes. Before dismantling of a nuclear reactor, the plant is converted to a "safe enclosure" for a limited period, where the main radioactive component of the plant is made free from fuel assemblies and other radioactive components. This is left in sealed state until decommissioning. A large number of successfully implemented technologies are available

(Efremenkov, 1989) for dismantling itself, both for decontamination and disassembly and for the disposal of the materials accumulating. In Germany, 19 nuclear power plants and prototype plants of the first construction generation, mainly those with a small and moderate output, had already been dismantled by the end of 2010 (VGB Brochure). In the United States as of 2011, there are 13 plants which are shut down and are in some phase of decommissioning (Sovacool, 2011).

In dismantling of the nuclear section, conventional recycling followed by removal of any surface contamination can be done. With reference to the total mass of nuclear section only 2% is to be transported to the repository as radioactive wastes. Since the waste accumulating during decommissioning of the nuclear power plants are similar to the radioactive waste arising during nuclear power plant operation, the same conditioning methods are used during their treatment.

However efficient it may seem, given the amount of decommissioning of a nuclear plant, challenges for it is very high. "The Yankee Nuclear Power Station in Rowe, Massachusetts, took 15 years to decommission or five times longer than was needed to build it. And decommissioning the plant – Constructed early in the 1960s for \$39 million to cost \$608 million" (Drollette, 2014). For this reason, proper decommissioning and dismantling of nuclear plants are either compromised or delayed which serves to increase of hazard for the environment.

Nuclear Safety Regulations

European Union (EU) is one of the most dependent consumers of nuclear power plants. With 128 nuclear power plants (119 GWe) operating in 14 of the all 28 EU member states has contributed for almost 25% of the total consumption of electricity in the whole of EU (Nuclear Power in European Union, 2018). Major production of nuclear energy takes place in France. These nuclear reactors, although are set up under the legislation of specific countries, but the electricity is distributed throughout the EU. Major concern involved with nuclear energy is the risk relating safety and waste management. A legal framework was set up under The European Atomic Energy Community (EURATOM) set up in 1957, within a treaty named EURATOM treaty which is applicable for all EU members. However, initially, the treaty had an intention for peaceful usage of atomic energy in Belgium, France, West Germany, Italy, Luxembourg, and the Netherlands.

EC deals with 3 major aspects of the nuclear activities:

- Safe operation, radiation protection and radioactive waste management of nuclear installations.
- Nuclear safeguard with a view to ensure the use of nuclear fuels strictly for the constructive user-defined purposes.
- Nuclear security protection by physical protection of nuclear fuel and checking of intentional malicious acts.

A EC nuclear safety directive was released in 2009 with an emphasis on the national liability of ensuring nuclear safety. An amendment in the directive in the year 2014 to ensure high-level nuclear safety by reducing the risks and consequences of nuclear accidents and addressing the safety objective for the entire installation cycle was introduced. The EU prescribed a less controversial set of directives for radioactive wastes and spent fuel management in 2011 (Council Directive 2011/70/Euratom). The salient features indicated for proper legislature throughout the EU through the means of the directives are listed below:

- Establishment of uniform safety standards to protect the health of workers and the general public from ionizing radiations.
- EU countries should have national policies to safeguard the public health and reduce radioactive waste related risks.
- Proper disposal of spent fuel and management of radioactive waste needed to be ensured inside the country by the proper framework and implementation of national programmes in EU countries by providing adequate funds.
- An inventory of future estimates to be prepared with an appropriate discussion about decommissioning, classification and management of spent fuel.
- A proper self-assessment and international peer assessment to be coordinated by EU countries for the national framework of nuclear waste disposal as frequent as every 10 years if not more.
- Transparency to be maintained by the issue of public information for proper knowledge of public in EU countries.
- Export of radioactive wastes for disposal outside EU nations to be allowed only under strict conditions.

Nuclear Waste Management

Effective management of radioactive wastes involves segregation, characterization, handling, treatment, conditioning, and monitoring prior to the final disposal. In Fig. 2, a flow chart depicts the radioactive waste management method being employed in the nuclear commerce.

A radioactive spent fuel constitutes of a mixture which composed of short-lived radioactive wastes and long-lived wastes. The radioactivity of short-lived waste is considerably very small after some time of storage in the deep geological depository (repository). The wastes are treated to reduce its volume to the minimum before permanent storage. The reduction in the volume can be done either by incineration and compaction of the wastes. While incineration of the wastes is performed, the non-radioactive substances like plastics, fabrics, wood, etc. are removed from the wastes. Some of the radioactive components also get transferred into ash, shoot,

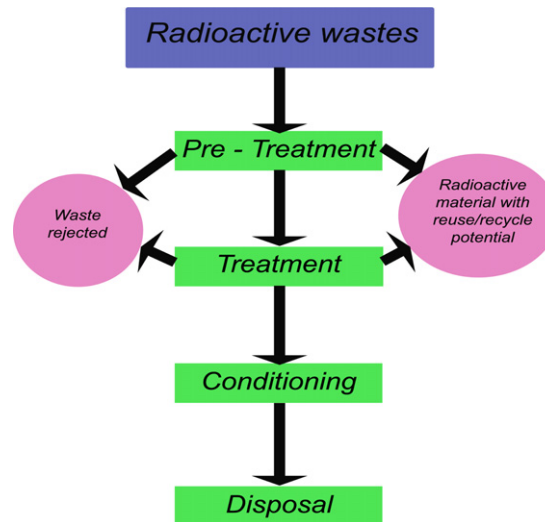


Fig. 2 Management of radioactive wastes.

smoke, etc. generated during the process. These components can again be separated and taken to the compressing unit. During high-pressure compaction, the waste is reduced in volume so that it occupies less space in the repository in which it is stored.

High-level nuclear wastes are generally those wastes that are generated towards the core of the nuclear reactor. These wastes are constituted of certain radioactive isotopes which can be expected to have extremely long half-lives (some even 100,000 years) ([Radioactive Waste Management: Indian scenario](#)). The management of such waste is a three-fold process in the scenario of a country like India. The major steps towards the disposal of high-level nuclear wastes are:

- Immobilisation of high-level liquid waste into vitrified borosilicate glasses.
- Engineered interim storage of the vitrified waste for passive cooling & surveillance over a period of time, qualifying it for ultimate disposal.
- Ultimate storage/disposal of the vitrified waste in a deep geological repository.

Internationally, high-level wastes and heat generating wastes are disposed separately from low-level wastes with negligible heat generation capacity. High-level wastes are suitable to be stored in repositories with salt formation capability which enables heat dissipation easily. Various technical and natural barriers inside the earth surface do not allow the harmful radioactive radiations to return back to the biosphere, hence protecting humans from its exposure.

Nuclear Fuel Cycle

Nuclear fuel cycle, or nuclear fuel chain, is the complete progression of radioactive nuclear fuel in order to extract energy, through a series of different stages. Fuel cycles can have a variety of configurations, depends on various economy, natural resource availability, energy growth projection, and politics. The various configurations are varied by variations in steps in the front end, service period and back end. The front end consists of steps for the preparation of fuel; service period consists of steps in which fuel is being used in the reactor; and back-end consisting reprocessing or disposing of spent fuel.

Nuclear Recycling

A characteristic feature of nuclear energy is the capability to extract energy from the used fuel through a series of recycling processes. In the previous sections, it was seen that the PEF value of nuclear energy was 3 giving a very poor efficiency of 33% for the U fuel ([International Energy Agency IEA, 2004](#)). This indicates that a lot of radioactive energy is contained inside the left over part of the fuel that comes out as wastes from the reactor. This energy can be extracted from the fuel if the concentration of U-235 can be increased to a level where the waste can be again used as a fuel in the reactor. So, nuclear reprocessing is a series of chemical operations that separates Pu and U in the nuclear wastes contained in the spent fuel from the reactor ([Nuclear Reprocessing](#)).

Once Through the Nuclear Fuel Cycle

The simplest and most common form of fuel cycle is the once through the nuclear fuel cycle. This type of cycle finds its popularity due to its economic benefits. U is mined from its ore, enriched to a higher concentration, used as a nuclear fuel in the reactor and then is obtained as a nuclear waste which is stored in a repository until it is no longer dangerously radioactive. The problem with such a cycle is that the decay of radioactivity from the nuclear waste would take thousands of years to disappear. Storage of such radioactive substance for such long duration of time adds to the limitations to such a fuel cycle. Further, U is not abundant in the earth's crust and this kind of a cycle can cause a serious scarcity of U in near future. Fig. 3 shows a typical once through nuclear fuel cycle.

Closed Fuel Cycle

Closed nuclear fuel cycle includes recycling of the nuclear fuel (Fig. 4). As have seen noticed, the nuclear wastes mainly consist of U-238 isotopes along with Plutonium (Pu) and other materials. So, more energy can be obtained from the nuclear wastes if it is properly dealt with. The function of the recycling plant is to separate the radioactive U from the other less radioactive materials. U which could be further used and separated and is concentrated to use again. While the remaining part of the nuclear waste is the one which has been used for the fission reaction. This part is comparatively less radioactive and can reach to a lower radioactivity zone in nearly 300–500 years (Touran, 2009), which is far less than the general radioactive waste.

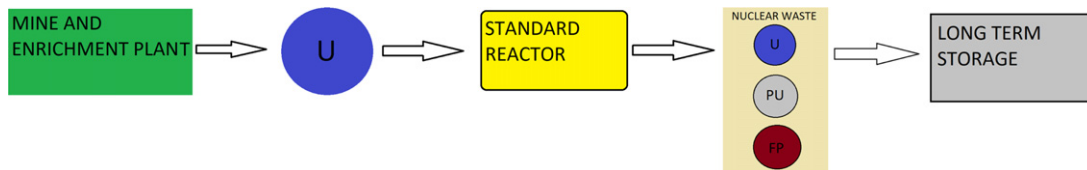


Fig. 3 Once through nuclear fuel cycle. Reproduced from Touran, N., 2009. Recycling Nuclear Waste and Breeder Reactors, © Whatisnuclear.com 2007–2018.

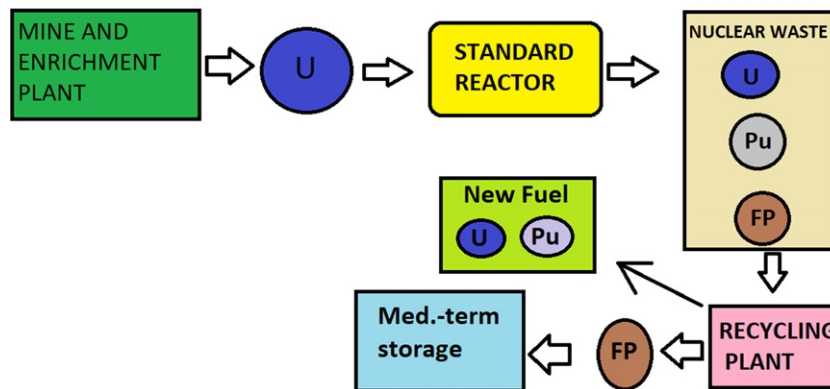


Fig. 4 Closed nuclear fuel cycle. Reproduced from Touran, N., 2009. Recycling Nuclear Waste and Breeder Reactors, © Whatisnuclear.com 2007–2018.

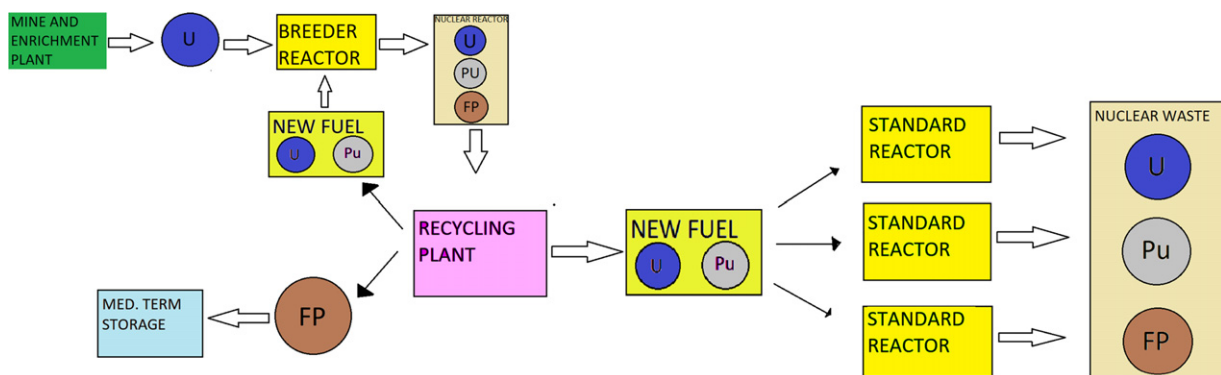


Fig. 5 Breeder nuclear fuel cycle. Reproduced from Touran, N., 2009. Recycling Nuclear Waste and Breeder Reactors, © Whatisnuclear.com 2007–2018.

Breeder Fuel Cycle

Breeder reactors consist of a number of free neutrons which converts the spent fuel content of U-238 into Pu-239 giving more fissile materials. Breeder reactors are fast reactors since the neutrons present in these reactors are very fast moving. Moreover, breeder reactors are nuclear reactors of highest efficiency as very high amount of nuclear fuel is being used inside the reactor and giving a very low amount of radioactive waste. Fig. 5 is a typical example for a Breeder nuclear fuel cycle.

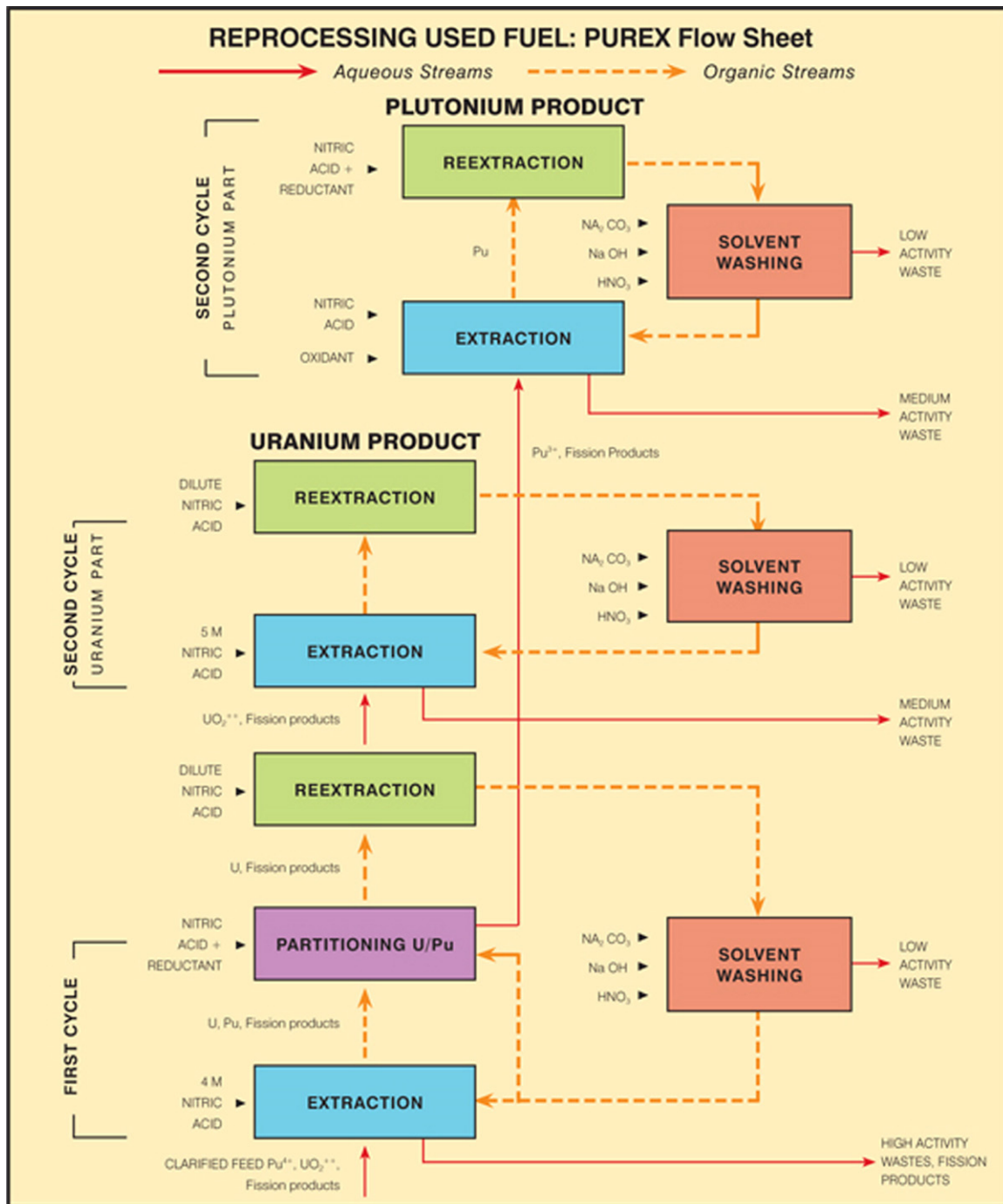


Fig. 6 A Self-explanatory flow chart for PUREX processing (Processing of Used Nuclear Fuel, World Nuclear Association).

Reprocessing of Spent Nuclear Fuels

Reprocessing used fuel to recover U and Pu avoids the wastage of a valuable resource. Earlier, reprocessing of nuclear fuel was done for weapons purposes only. This is the reason for reprocessing being politically controversial for its potential to contribute to nuclear proliferation and potential vulnerability to nuclear terrorism.

Processing used fuel is similar to the processing of concentrate of any metal mineral to recover valuable metals present in it. Instead of an ore, the mineral to process while reprocessing of spent fuel is the hard ceramic uranium oxide. The ore also has a substantial amount of other fission products and actinides for the reactor. The separation techniques can be widely classified into water and organic solvent techniques, electrochemical techniques, pyro-processing, electrolytic separation, and, radio-analytical separation.

An important and commercially most popular reprocessing technique employed for recovery of nuclear fuel by reprocessing of spent fuel is PUREX, which efficiently comes under the category of water and organic solvent technique. All commercial reprocessing plants use the well-proven hydrometallurgical PUREX process, which separates U and Pu very effectively. In the next section, this process is discussed in a better depth.

PUREX

PUREX stands for Plutonium Uranium Redox Extraction ([Choppin et al., 2001](#)). Actually, PUREX is a standard aqueous nuclear reprocessing method to recover Uranium and Plutonium from spent fuel. It is based on liquid-liquid extraction ion-exchange ([Paiva and Malik, 2004](#)). In the primary step, dissolving of spent fuel in nitric acid at a concentration of 7M takes place. Chemical separation of U and Pu is then undertaken by solvent extraction steps. The solid particulates are removed through filtration process. In case of an emulsion formation, the solid is given the reference as a third phase. The organic solvent used includes 30% tributyl phosphate (TBP) in a hydrocarbon. The extraction of Uranium and Plutonium ions take place as a similar complex represented by $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ ([Burns, 1983](#)). Separation of Plutonium from Uranium is done by treating the hydrocarbon solution with reducing agent like ferrous sulfamate, N,N-diethyl-hydroxylamine and hydrazine which converts Pu to Pu^{+3} that passes into aqueous phase. The leftover U is removed from the solution by back-extraction into HNO_3 of concentration of 0.2M ([Greenwood and Earnshaw, 1997](#)).

This process recovers 99.5% of the U and Pu in the spent fuel rod assembly ([IAEA, 2008](#)). The Pu obtained by recovery using PUREX is weapon grade Pu – 240, which is very favorable for use in nuclear weapons. However, PUREX is the most effective method for nuclear reprocessing amongst all other methods. Although the production of a separated pure Plutonium stream remains as a drawback for this process. This drawback encouraged the modification of PUREX process and indicated the virtues of modified processes like UREX. The above portrayal of PUREX operation can be observed in detail in [Fig. 6](#).

There are a number of modifications in the PUREX processing method. Some of the famous processes that are popular in various parts of the world are UREX, TRUEX, DIAMEX, SANEX, etc ([Nuclear Reprocessing](#)). There are some other obsolete methods unpopular due to the quality of reprocessed fuel. Some of the obsolete methods not prevailing in modern industries are Bismuth Phosphate, Hexone or Redox, Pyro-processing, voloxidation, etc. However, the discussion of these methods shall be beyond the attraction of this article.

Summary

- Nuclear energy has tremendous potential for generation of electricity. This potential is utilized in nuclear power plants where inside a reactor the nuclear energy, in the form of heat, is obtained which run the turbine to generate electricity.
- Sustainable nature of nuclear energy has been an argumentative topic. Selecting a side to the debate is a very difficult task given the renewability and replenishment issues of nuclear energy.
- Prevailing PEF value for nuclear power generation is 3. PEF is a measure of resource efficiency of energy sources. However, this value of PEF underestimates the poor efficiency for U fuel in a nuclear power plant.
- Nuclear production losses are found to be very high. Nearly 67% of the nuclear energy is lost during nuclear power generation. Adding to these losses, a further 28% of the produced electricity in a country like India is lost as transmission and distribution losses.
- Nuclear wastes are radioactive substances that are produced either as a result of the operation or decommissioning and dismantling of the nuclear power plant. These wastes comprise majorly of liquid wastes, wet solid wastes and gaseous wastes or aerosols.
- EU directives focus on the establishment of nuclear safety and radioactive waste management.
- Effective management of radioactive wastes involves segregation, characterization, handling, treatment, conditioning and monitoring prior to final disposal.

- Nuclear recycling is a characteristic feature of nuclear energy. A lot of energy gets lost unused from the nuclear fuel which gets removed as nuclear waste. However, transforming U – 238 into radioactive Pu to reuse it as nuclear fuel is done by nuclear reprocessing. This is termed as nuclear recycling process.
- The most popular nuclear reprocessing method is PUREX due to its high recovery. However, production of separate stream of Pu still remains a challenge in the process indicating the virtues of UREX.

See also: Sustainable Materials for Energy Conversion

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Open Volumetric Air Receiver: Current Status, Challenges and Innovative Solutions

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Nomenclature

B' A coefficient in the quadratic pressure difference equation

C_{pf} Specific heat capacity at constant pressure for air ($\text{J kg}^{-1} \text{K}^{-1}$)

d_p Straight channel diameter (m)

H_f Total enthalpy in fluid (J)

I Heat flux along the longitudinal/axial-direction (W m^{-2})

I_o Heat flux on the inner surface of absorber (W m^{-2})

k_f Thermal conductivity of fluid ($\text{W m}^{-1} \text{K}^{-1}$)

k_s Thermal conductivity of solid ($\text{W m}^{-1} \text{K}^{-1}$)

k_p Pressure drop coefficient

$\dot{m}$ Mass flow rate (kg s^{-1})

Q_o Incident power on aperture (W)

q_s'' Concentrated solar irradiance on the OVAR aperture (W m^{-2})

R Gas constant of air ($\text{J kg}^{-1} \text{K}^{-1}$)

Re_p Reynolds number in an absorber straight channel

T Temperature (K)

T_o Temperature of air at the absorber inlet (K)

T_{out} Temperature of air at the absorber outlet (K)

v_p Average speed of air (m s^{-1})

Δp Pressure drop (Pa)

Δp^2 Difference in quadratic pressures (Pa^2)

ε Porosity of absorber

μ_o Reference absolute viscosity of air (Pa s)

ν Kinematic viscosity of air ($\text{m}^2 \text{s}^{-1}$)

ξ Extinction coefficient (m^{-1})

ρ_f Density of air (kg m^{-3})

$\sum$ Emissivity of absorber material

σ Stefan Boltzmann constant ($\text{W m}^{-2} \text{K}^{-4}$)

η_{th} Thermal efficiency

Abbreviations

NDL Non-uniform dust layer

OVAR Open Volumetric Air Receiver

UDL Uniform dust layer

Introduction

In solar power tower plants, the central receiver system is the heat exchanger wherein the concentrated sunlight is absorbed and converted into useful thermal energy in thermodynamic cycles. Because the concentrated heat flux and the resulting temperature are substantially higher than in parabolic trough based system, high-performance materials are needed. A mirror field is used for concentrating the beam solar radiation onto a heat collection element viz. an absorber, which is cooled by a heat transfer fluid like, air, water or liquid metal. Just as cost reduction is the priority for further development in the solar collector field, in solar receivers, the priorities are thermal efficiency and durability. Typical absorber operating temperatures range between 500°C and 1200°C , whereas the concentrated flux covers a wide range between 300 kW/m^2 and 1000 kW/m^2 . Such a high flux concentration is challenging for the design and sustained operation of the central solar receiver based systems.

According to the geometrical configuration, there are basically two design options, external and cavity-type receivers. These can also be directly or indirectly irradiated, depending on the absorber materials used to transfer the energy to the working fluid (Becker and Vant-Hull, 1991). Directly irradiated receivers make use of darkened fluids or particle streams able to efficiently absorb the concentrated flux. The key design element in indirectly heated receivers is the radiative-convective heat exchange surface. Two heat transfer options are typically employed: Tubular panels and volumetric surfaces. In tubular panels, a coolant flows inside the tube and removes the heat collected by the external black panel surfaces by forced convection. It thus operates as a recuperative heat exchanger. Since heat transfer is through the tube surface, the maximum operating peak flux is around 600 kW/m^2 (Romero et al., 2016). In volumetric receivers, highly porous structures operating as convective heat exchangers absorb the concentrated solar radiation. The heat transfer medium (mostly air) flows through the porous structure and is heated by forced convection.

The design of volumetric receivers is one of conjugate heat transfer processes and interconnected optical and thermal requirements where trade-offs are unavoidable. Target operating conditions for their widespread industrial deployment are demanding (Mehos et al., 2016): Working fluid temperatures at receiver exit in excess of 1000 K , thermal conversion efficiencies over 90%, minimum service life of 10,000 cycles and overall costs below 150 USD per kilowatt of thermal power delivered. Operating temperatures play a conflicting role in their performance because thermal losses become significant at the very high levels required for efficient downstream thermochemical or power cycles.

Volumetric absorbers are usually made of thin heat-resistant metal wires (in knitted or layered grids) or either metal or ceramic open-cell matrix structures such, as monolithic honeycombs or reticulated foams. They are generally highly porous, allowing incident radiation to penetrate deep into the structure. Thin substructures (wires, walls, or struts) ensure good convective heat

transfer. A good volumetric absorber produces the so-called volumetric effect, which means that the irradiated side of the absorber is at a lower temperature than the medium leaving the absorber (Boehmer *et al.*, 1991). This minimizes thermal re-radiation loss from the absorber aperture.

There exists, however, scarce experimental evidence of solar receivers achieving a significant volumetric effect. The exception is a double-layer selective receiver composed of an external silica square-channel monolithic honeycomb and an internal layer of silicon carbide particles (Menigault *et al.*, 1991). A similar double-layer configuration where the internal particle layer was replaced by a ceramic silicon carbide monolith concluded otherwise (Pitz-Paal *et al.*, 1992). Comprehensive reviews on solar receivers investigated since the 1980s have been given by Romero *et al.* (2002), Ávila-Marín (2011), and Ho (2017). A detailed one-dimensional analysis has been recently employed to argue that receiver geometry and materials still lack adequate optimization for maximum thermal conversion efficiencies (Kribus *et al.*, 2014).

The current state-of-the-art for OVARs at the pre-commercial industrial scale was achieved by the HiTRec-SolAir receiver configuration (Hoffschmidt *et al.*, 2001). A stainless steel support structure on the back of a set of ceramic absorber modules forms the base of the receiver. Similar to ceramic burner tubes, the absorber modules are separated from the back and allowed to expand both axially and radially during start-up or shutdown. The absorber modules are spaced to avoid contact between adjacent modules. The support structure is a double-sheet membrane, which may be cooled by either ambient or recirculating air. Tubes attached to the absorber cups pass through holes in the front sheet and are welded to the rear sheet. The cooling air circulates between the two sheets and, as it leaves through the sides of the segments, also cools the support structure. The air reaches the absorber aperture through the spaces between the segments. Outgoing air and ambient air are mixed and sucked back into the segments. As they penetrate into the absorber structure, air is heated up by convection. On leaving the absorber structure, the hot air is ducted to the bottom of the cup. There an orifice adjusts the air mass flow rate to compensate the expected solar flux profile over the aperture so as to generate homogeneous outlet air temperatures from the cups. Finally, airflows through the cups, across the holes in the rear sheet of the membrane, and into the downstream power block.

The key advancement of this configuration with respect to previous solar receivers was the introduction of modular ceramic absorbers. This prevented fractures caused by the strong thermal shocks developing over larger absorbers during start up and shut down, whilst allowing for the achievement of higher operating temperatures. Modularity also facilitated cooling of the solar receiver, by means of recirculating air flowing through lateral gaps between adjacent absorber modules. The first HiTRec OVAR reached a maximum average outlet temperature of 980°C with a thermal efficiency of 68% (Hoffschmidt *et al.*, 1999). The next milestone in the development of this type of receiver was the qualification of the 200 kW HiTRec-II receiver. During the course of the test program, the HiTRec-II receiver was operated over a period of 38 days, accumulating a total of 155 operating hours with a thermal efficiency of up to 76% at 700°C (Hoffschmidt *et al.*, 2003). Subsequent developments of this concept led to the SolAir 200 kW receiver, as an intermediate step in the scaling up to the experimental demonstration of a 3 MW OVAR (Téllez, 2003). The SolAir-200 was able to achieve thermal conversion efficiencies of 83% at air outlet temperatures of 700°C (and remains the highest efficiency OVAR tested under fully realistic on-sun conditions).

Eventually, the SolAir 3 MW prototype was developed, installed, and tested at the Plataforma Solar de Almería, connected to a steam generator and a thermocline for heat storage (Téllez *et al.*, 2004). The receiver was composed of 270 ceramic absorber modules and had a total aperture surface of 5.67 m². The honeycomb absorbers were made of recrystallized SiC, with square flow channels and a normal open porosity of 49.5%. During testing, the average incident solar radiation on the ceramic volumetric absorber was 500 kW/m². The SolAir 3 MW receiver system achieved a thermal efficiency of 72% at air outlet temperatures of 750°C, and of 74% at air outlet temperatures of 700°C. Efficiencies were estimated at over 85% (and up to 89%) for air outlet temperatures in the range of 590–630°C and mean incident solar fluxes of 310–370 kW/m².

Although operational flexibility and initial results were satisfactory, it is obvious that open volumetric receiver thermal efficiencies must be still improved to around 90% in order to achieve cost-effective plant designs able to replace tubular receivers. In addition, long-term endurance tests must be conducted, radiation losses must be further reduced, and the radial distribution of recirculating air in operation could be further optimized (Marcos *et al.*, 2004). The thermo-mechanical properties, including corrosion, of the SiC ceramic employed in the SolAir-200 solar receiver were investigated by Agrafiotis *et al.* (2007), who conducted extensive experimentation on both irradiated and non-irradiated samples. The use of siliconized SiC was recommended due to its superior mechanical strength, allowable operating temperatures, and corrosion resistance.

The effects of high temperature cycling on the SiC thermo-radiative properties was researched by Rodríguez-Sánchez *et al.* (2016), who found that absorptivity generally decreased with prolonged cyclical exposures to concentrated solar radiation. Several CFD numerical studies were later conducted both to further explain the aerothermal behavior of the HiTRec-SolAir family of receivers, and to identify ways of increasing their thermal efficiency. Research has focused on the uniformity of air outlet temperatures downstream of absorber modules (Palero *et al.*, 2008); modifications of the honeycomb structure to increase the uniformity of air outlet temperatures and, thus, thermal efficiencies (Fend *et al.*, 2013); the influence of wind velocity and direction on the air recirculation system and air outlet temperatures (Roldán *et al.*, 2016); and the effects of receiver tilt angle, channel aperture size and air inlet speed of volumetric effect and thermal efficiency (Cagnoli *et al.*, 2017). The last study was conducted at the single flow channel level and showed that a trade-off exists between operation under volumetric effect conditions and achieving high thermal efficiencies.

Two recent studies have proposed geometric modifications to the HiTRec-SolAir receiver concept with the objective of increasing overall thermal conversion efficiencies. The first one consists of substituting the ceramic absorber with a cellular metallic

honeycomb built from pairs of flat corrugated metal foils (Pabst *et al.*, 2017). Efficiencies of 80% with air outlet temperatures of 800°C were reported from experiments conducted with an incident radiative power of 500 kW under on-sun conditions. The second study proposed the addition of a staggered pin-shaped micro-structure, additively manufactured in a Titanium-Aluminium alloy, to the aperture plane of the ceramic absorber (Capuano *et al.*, 2017). Operation under volumetric effect conditions was numerically predicted for such geometry, but current manufacturing limitations only allowed for the experimental assessment of a 3:1 scaled-up counterpart.

Another key aspect in the operation of OVARs is the dust deposition in pores or straight channels, which needs to be addressed for their envisaged sustained operation in arid deserts. An open volumetric air receiver design with in-situ cleaning provision is provided by Sharma *et al.* (2015a,b). This assumes that a dust may be deposited or transported through straight channels at a certain mass flow rate of air. A common concern in OVARs is flow instability at a high temperature, which results from local variations of air properties in the receiver flow field. Highly non-uniform heat flux distributions are most likely to promote such a phenomenon. In particular, centrally located absorbers subject to the usual Gaussian type distribution are the most prone to flow instabilities. Moreover, dust deposition may trigger flow instabilities and cause them to occur at a lower radiative heat fluxes. This is attributed to a higher flow resistance causing a lower local mass flow rates of air in the partially blocked channels. The deposited and transported dust may be collected using an external device.

In this paper the aspects of (a) thermal efficiency measurements, (b) flow stability in a straight channel and (b) dust deposition in absorbers are presented. Thermal efficiency measurements conducted on nine monolithic honeycomb absorbers, manufactured in siliconized silicon carbide and with square flow channels, are presented. The effects of two geometric parameters on their thermal conversion efficiency have been investigated: Flow channel width (which affects their cross-sectional porosity as absorber wall thickness is set by the extrusion manufacturing procedure), and absorber length. The results and conclusions later discussed are directly applicable to a modular receiver concept such as that of the HiTReC-SolAir system. Experimental measurements presented here also demonstrate aerodynamically stable flow conditions across the absorbers entire range of operation. For analyzing the flow instability a recently developed pressure-drop correlation for a circular straight channel based absorber is employed. The effects of dust deposition on the heat transfer in circular and square shaped straight channels are also presented.

Aerothermal Experimental Evaluation of Monolithic Honeycombs

Experimental Apparatus

The experimental measurements of thermal efficiency discussed in this paper have been conducted at the IMDEA Energy Institute. The laboratory-scale calorimetric facility and its associated techniques were described by Luque *et al.* (2018). A schematic diagram is given in Fig. 1. Incident radiation is provided by a high flux solar simulator, composed of a single 7 kW_e Xenon-arc lamp (providing 1.2 kW_{th}) and a truncated ellipsoidal reflector that concentrates light onto the test section. The experimental facility, in turn, consists of a radiation homogenizer, a calibrated gas supply system, a working section where absorber samples are housed and instrumented, and inlet and outlet flow conditioning modules. The facility employs a blowing fan upstream of the working section, which avoids the need for a heat exchanger downstream of the absorber sample, and is modular in design, which allows for a rapid interchangeability of test components and instrumentation. Careful alignment of the absorber aperture with the optical axis of the high flux solar simulator is achieved by employing a high precision cross level laser pointer.

A water-cooled radiation homogenizer of square cross section is situated between the inlet module and the working section, exactly at focal point of the high flux solar simulator. This transforms the radiation flux density profile provided by the ellipsoidal reflector (approximately Lorentzian) to a uniform distribution on the absorber aperture, which leads to the homogeneous heating

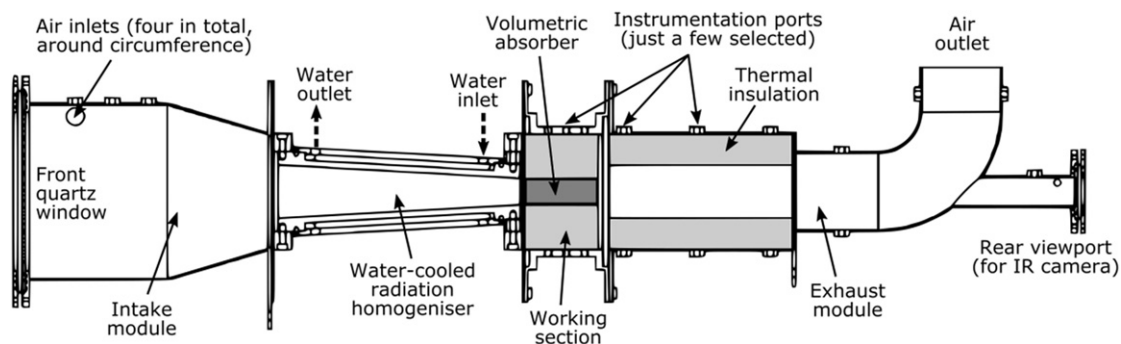


Fig. 1 Schematic diagram of the new experimental facility, with its main constitutive blocks labelled.

of the sample. The intensity of the incident concentrated radiation beam can be adjusted by metal wire grids, employed as attenuators. The inlet module is sealed by a five-millimeter thick quartz glass window.

The facility employs a dedicated instrumentation system with 42 measurement channels, including a mass flow controller, a calibrated 50 mbar differential pressure transducer (measuring between the inlet and outlet of the working section) and a set of 32 K-type thermocouples with 0.5 mm diameter Inconel sheaths. Experimental measurements conducted include absorber solid temperature distributions along its depth, air inlet and outlet temperatures, mass flow rate, pressure drop, incident radiative heat flux distributions and overall thermal efficiency. Heat flux distributions at the homogenizer inlet and outlet planes were measured with a Gardon radiometer, traversing both planes by means of an automated motion control mechanism. To within 95% confidence, the uniformity of the irradiance map at the absorber front face is $1016.4 \text{ kW/m}^2 \pm 20.1\%$, measured over an aperture area of $28 \text{ mm} \times 28 \text{ mm}$, and with an overall power of 782.7 W.

Monolithic Configurations Investigated

Experimental thermal efficiency measurements conducted on nine monolithic absorbers are presented. The effects of two geometric parameters on efficiency were investigated: Porosity and absorber length. Absorbers are grouped into two families of different cross section: Type I and Type II. Four overall absorber lengths were tested within each family, plus a reference monolith which constitutes the ninth sample (Luque *et al.*, 2017). Frontal photographs of absorbers belonging to both Type I and Type II families are shown in Fig. 2, together with a photograph of the baseline geometry. They all consist of square-cell monolithic honeycomb modules, manufactured from siliconized silicon carbide (SiSiC). Absorber lengths tested in both Type I and Type II families were 25 mm, 50 mm, 75 mm and 100 mm. The objective was to measure the influence of flow passage width and overall length on overall thermal efficiency. Wall thicknesses were generally kept as low as possible without compromising structural strength.

Flow channel cross-sectional areas in the Type I absorber family are of approximately $1.16 \text{ mm} \times 1.16 \text{ mm}$ (with a porosity of 67.7%), of $0.56 \text{ mm} \times 0.56 \text{ mm}$ in the Type II family (with a porosity of 41.4%), and of around $2.17 \text{ mm} \times 2.17 \text{ mm}$ in the reference monolith (the porosity of which is 61.4%). All other parameters being equal, absorbers with lower porosity will generally shift the radiation absorption profiles towards the front and will be better at conducting heat due to their increased solid volume. Reynolds number, and thus convective heat transfer coefficients, depends on flow channel width, but for the laminar regimes found in volumetric absorbers, the effect of having larger wetted areas is generally predominant.

Type I and Type II absorber families were manufactured by Ibiden Co., Ltd. (Japan), whereas the reference monolith was manufactured by Saint-Gobain Ceramic Materials (Germany). Besides their geometric differences, it is important to note that, at room temperature, the thermal conductivity of the Type I and II monoliths was around $27 \text{ W m}^{-1} \text{ K}^{-1}$, whereas for the reference monolith it was approximately $160 \text{ W m}^{-1} \text{ K}^{-1}$. In both cases, these values decrease by up to a factor of 4 when the samples reach 1000°C during operation – a feature of the behavior of this material that is detrimental to achieving a volumetric effect in monolithic configurations. The benchmark SolAir 200 absorber aperture, a similar monolithic configuration tested under on-sun conditions (Télez, 2003), is geometrically closest to the Type II absorber family.

Thermal Conversion Efficiency Measurements

Steady-state temperature and mass flow rate measurements were acquired, and thermal efficiency calculated, for the nine monolithic absorbers. In a typical test run, the facility would be operated at a range of decreasing mass flow rates for a given

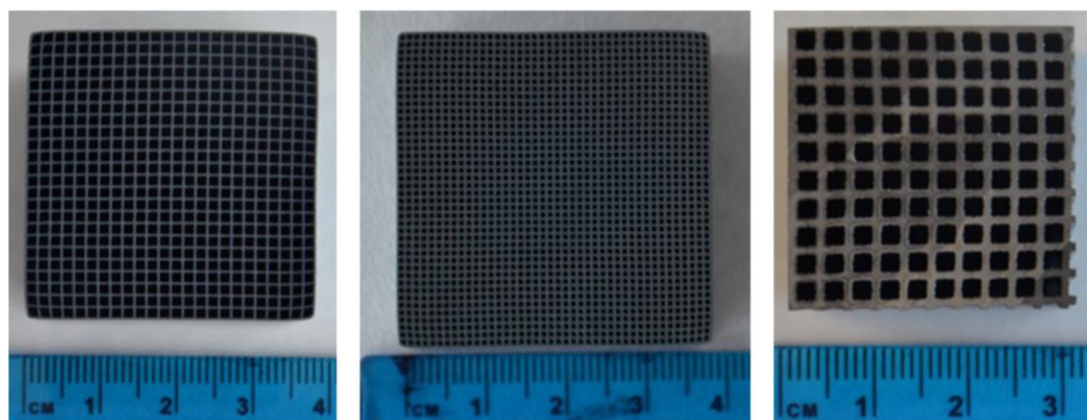


Fig. 2 Frontal photographs of the three types of volumetric absorbers experimentally assessed: Type I (left), Type II (centre), and state-of-the-art reference geometry (right). Reproduced from Luque, S., Bai, F., González-Aguilar, J., Wang, Z., Romero, M., 2017. A parametric experimental study of aerothermal performance and efficiency in monolithic volumetric absorbers. AIP Conference Proceedings 1850 (1), 030034.

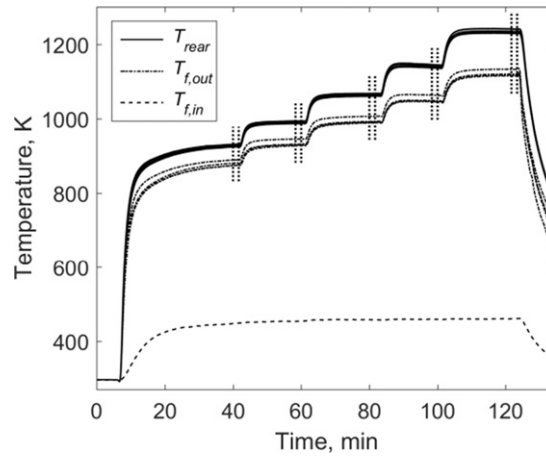


Fig. 3 Typical temperature traces acquired in the experimental facility.

incident power. The flow is allowed to stabilize at each operating condition for around 30 min. **Fig. 3** presents temperature traces in a typical test run at maximum incident power. Reducing the mass flow rate causes all temperatures to rise. Curves presented in **Fig. 3** include temperatures on the absorber rear face (8 thermocouples), and air inlet (1 thermocouple) and outlet temperatures (4 thermocouples). Vertical dotted lines indicate time windows of 100 s during which steady state measurements are time-averaged at each setting for post-processing. The facility is able to produce highly stable, repeatable and well-conditioned experimental conditions.

Absorber thermal efficiencies are calculated as the ratio between the power that is transferred to the working fluid by forced convection and the incident radiative power over the absorber aperture. The amount of heat transferred to the working fluid depends on the convective heat transfer coefficient of the flow (in turn dependent on the internal flow variables and absorber geometrical features). Quantitatively, however, thermal efficiency may be expressed by the rate of enthalpy rise of the working fluid divided by the total incident power:

$$\eta_{th} = \frac{\dot{m}}{Q_0} \int_{T_0}^{T_{out}} C_{pf}(T) dT \quad (1)$$

where $\dot{m}$ is the mass flow rate, Q_0 the overall incident radiative power, C_{pf} the specific heat capacity of air at constant pressure, and T_0 and T_{out} the air inlet and outlet temperatures, respectively. A cubic-spline interpolation of experimental measurements of C_{pf} as a function of temperature has been employed in the integral (Rogers and Mayhew, 1992).

The air temperature increment between the absorber inlet and outlet planes for the Type I family is shown in **Fig. 4**, as a function of incident power per unit mass flow rate. Measurements conducted on the reference monolith are given for comparison. There is a range of $Q_0/\dot{m}$ values in which measurements show an approximately linear behavior, which is a consequence of having low temperatures in the system. As soon as absorber temperatures increase, thermal emissions (the dominant source of heat loss) cause the measured distributions to deviate from the linear behavior.

Air temperature increments are generally higher when the radiative power increases for a given mass flow rate, and vice versa. However, it can be seen that a maximum fluid temperature rise is reached in some configurations. Increases in incident radiative power beyond this maximum do not lead to higher air outlet temperatures. Forced convection is not sufficient in such cases to remove all the additional heat received by the absorber. Thermal energy is instead lost through emission and conduction losses and efficiency decreases sharply.

Corresponding thermal conversion efficiencies for Type I absorbers are shown in **Fig. 5**, as a function of $Q_0/\dot{m}$, together with values for the reference monolith. It can be observed that thermal efficiency increases with mass flow rate in all cases. This is expected as lower mass flow rates lead to lower convective heat transfer coefficients. As a result, less heat is removed from the sample and absorber wall temperatures are higher. Larger thermal emission losses are produced in this situation. For a fixed mass flow rate, efficiencies are higher for lower incident radiation levels for the same reason: The absorber remains moderately cooler and thermal emission losses are less significant.

Air temperature increments for Type II and reference absorbers are shown in **Fig. 6**, with corresponding thermal efficiencies given in **Fig. 7**. Data on both has been plotted with $Q_0/\dot{m}$ on the abscissa. It is immediately clear that Type II configurations, of smaller flow channel width, yield higher efficiencies than any of the other monoliths investigated here. Very high thermal efficiencies (above 90%) are possible, but only when convective heat transfer is significant relative to radiation absorption (and thermal conduction) in the absorber: At low values of incident radiative power per mass flow rate (around 500 kJ/kg). As mentioned before the location of efficiency maxima depends on absorber length. Absorbers shorter than the optimal length do not exploit convective heat transfer to the full, whereas longer ones incur in larger thermal losses once convective heat exchange

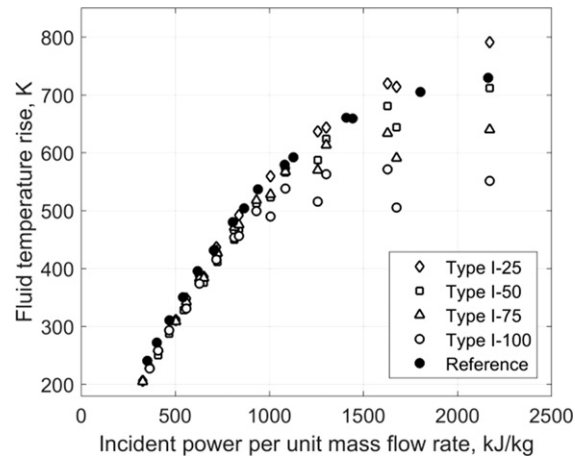


Fig. 4 Air temperature increment between the absorber front and rear faces for Type I and reference absorbers.

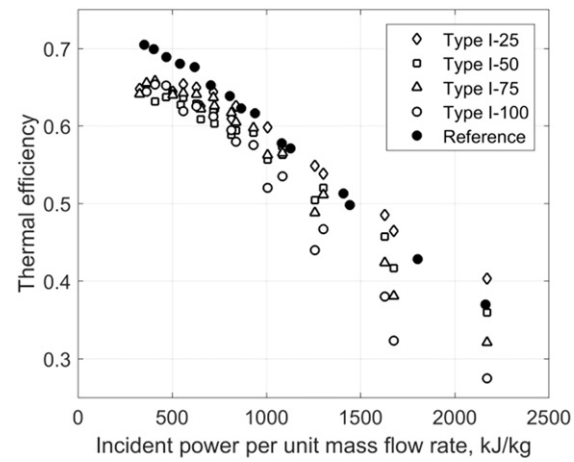


Fig. 5 Thermal efficiency measurements for Type I and reference absorbers.

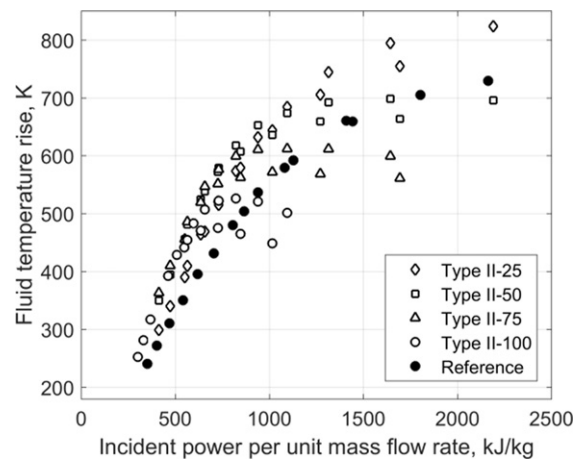


Fig. 6 Air temperature increment between the absorber front and rear faces for Type II and reference absorbers.

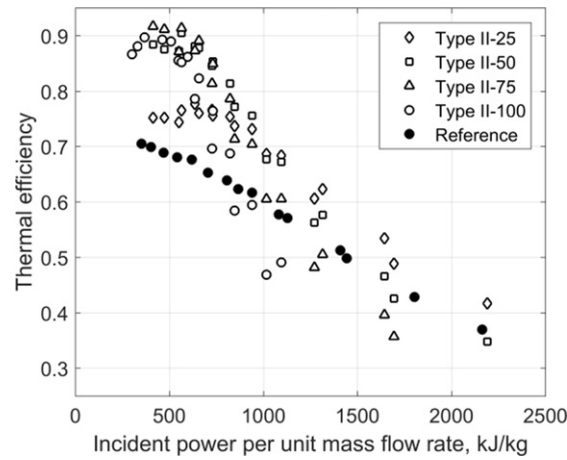


Fig. 7 Thermal efficiency measurements for Type II and reference absorbers.

diminishes as air and wall temperatures equilibrate towards the rear. For absorbers of equal length, reducing the cross-sectional porosity is seen to be beneficial in terms of overall thermal efficiency (this would enhance convective heat transfer).

Although not shown in these graphs, it is worth noting operation under volumetric effect conditions was not achieved with any of the absorbers evaluated in this study. In the best case measured, which was with absorber Type II-75 (of 75 mm length) operating in the low $Q_0/\dot{m}$ regime (at 413 kJ/kg, with a high mass flow rate), the front surface was at approximately the same temperature as the rear surface. In fact, the absorber temperature distribution as a function of depth was fairly flat in this case. Lowering the mass flow rate from this operating condition caused the front surface temperature to become significantly hotter than the rear. The thermal efficiency was 91.7% in this case, air outlet temperature 739.7 K and mean absorber temperature 799.5 K, approximately. Thermal efficiencies of over 90% are obtained with this absorber up to an incident power per unit mass flow rate of 551 kJ/kg.

Numerical Analysis of Flow Instability and Dust Deposition

Even with the volumetric or more so with the non-volumetric heating the desired stable flow limits a high temperature (Kribus *et al.*, 1996; Pitz-Paal *et al.*, 1997; Fend *et al.*, 2005; Becker *et al.*, 2006). This is associated with the local variation of fluid properties and in particular, the offered flow resistance at a high temperature across the different absorber flow paths. The concentrated solar irradiance on the OVAR aperture is known to be quasi-Gaussian and thus centrally located absorbers are more prone to such an unwanted situation. Ways of mitigating this include using high thermal conductivity materials to reduce thermal gradients and employing mechanical flow conditioning devices such as the orifice plates. Another challenge pertaining to the operation of OVARs in arid desert regions is the deposition of dust (with a low thermal conductivity of around $2 \text{ W m}^{-1} \text{ K}^{-1}$) in the absorber channels. This is likely to limit its installation in such areas of high potential, worldwide and in particular the Thar-desert of India and the great desert of Middle-East. The deposition and dust removal process were analyzed by Singh *et al.* (2016). The possible consequences of dust deposition are (a) flow instability even at a low heat flux concentration, (b) local or wide-area hot spots and (c) eventual failure of OVAR. Considering these aspects, this section provides further theoretical insights into the observed stable flow in a straight flow channels, with and without dust deposition, and an analysis of the detrimental effects of the dust deposition in absorber channels.

Flow Instability Analysis

The designed receiver at IIT Jodhpur along with a fabricated absorber is depicted in Fig. 8. The geometrical details and its thermal-hydraulic evaluation is already reported with Sharma *et al.* (2015a,b).

The straight channel based absorbers offer a low pressure-drop and are less prone to the dust deposition, which is adopted in the OVAR reported here. There are a number of correlations to predict the pressure-drop (Δp) across the foam-type absorbers, which may not be applicable for straight channels see e.g., Edouard *et al.* (2008). Therefore, several experiments and detailed analysis are performed (Singh *et al.*, 2018) to deduce a realistic correlation for Δp across the absorber depicted in Fig. 8:

$$\Delta p = k_p \times \frac{\rho_f v_p^2}{2} \text{ with } k_p \approx 179.25 Re_p^{-0.588} \quad (2)$$

where, k_p is the pressure drop coefficient, ρ_f is the density of air, Re_p is Reynolds number based on channel diameter (d_p) and v_p is the average speed of air inside an absorber straight channel. The derived correlation using a least square based curve-fit in terms of Re_p , includes the effect of porosity, flow and fluid properties. The correlation is based on experiments/computations under

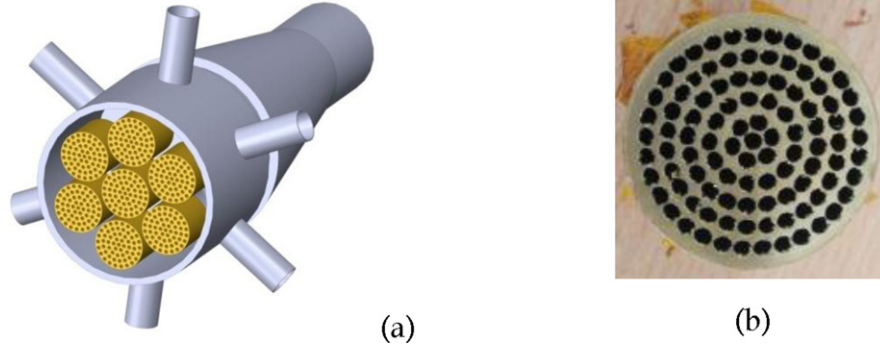


Fig. 8 The open volumetric air receiver at IIT Jodhpur (a) with a fabricated cylindrical absorber (b).

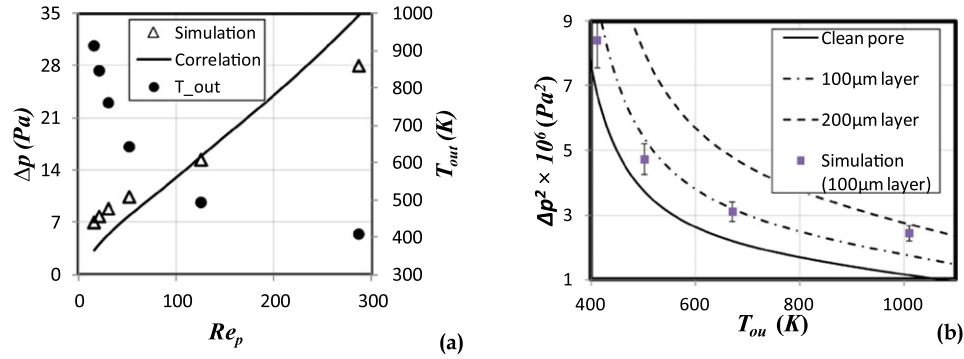


Fig. 9 Comparison between (a) the derived correlation for pressure drop at different temperatures (b) analyzed Δp^2 with clean and partly blocked straight channel.

ambient condition and is validated (Singh *et al.*, 2018). Further, a comparison between the computed and the correlation based Δp is shown in Fig. 9(a) with the applied different uniform heat fluxes as boundary conditions up to a $Re_p < 300$. This shows that (a) the Δp increases and T_{out} decrease at high Re_p , (b) the derived correlation compares within 10%–25% with the performed simulations for a T_{out} up to 900 K, covering the range of interest. Thus, Eq. (2) is realistic and the correlation is used for flow stability analysis at a high temperature and a low Re_p with the circular straight channel based absorber.

For flow stability analysis the quadratic pressure difference across the absorber is deduced following (Becker *et al.*, 2006; Fend *et al.*, 2005) and is presented in Eq. (3). This excludes the presence of dust, but it may be extended with the same in order to investigate whether the deposition of dust will induce flow instability at a lower heat flux.

$$\Delta p^2 = p_{inlet}^2 - p_{outlet}^2 = B' \cdot \left(\frac{q_s'' / \varepsilon T_{out} - (\Sigma) \beta \sigma T_{out}^5}{(T_{out} - T_0)} \right)^{1.412} \quad \text{where } B' = \left(\frac{179.25 R \mu_0^{0.588}}{C_{pf}^{1.412} d_p^{0.588} T_0^{0.412}} \right) \quad (3)$$

Thus, a numerical model is employed and validated with the measured values of T_{out} in the reported experiment with a uniform or volumetric-type heating by Sharma *et al.* (2015a,b). A variation of the derived expression for Δp^2 with respect to T_{out} for the clean and partly blocked straight channels with dust layer thickness up to 200 μm is shown in Fig. 9(b). The increment in T_{out} is attributed to the decreasing mass flow rate of air and thus of Δp^2 . It is inferred that for a given T_{out} , Δp^2 would then increase with dust layer thickness, or with the decreasing effective absorber porosity. Also, the deposition of dust seems not to promote flow instability in the considered absorber. These observations allow expecting a stable operation of such an OVAR in desert regions. This is inferred from Fig. 9(b) in which Δp^2 shows a usual behavior as for a stable flow condition in a partially blocked circular straight channel. Moreover, the simulated value of Δp^2 with the uniform dust layer thickness of 100 μm compares well with that of its analyzed values using Eq. (3), which lends confidence to the numerical results.

Effects of Dust Deposition on Heat Transfer

To analyze the effect of dust deposition on the heat transfer both circular and square shaped straight channels are considered. The parametric investigation includes the (a) deposited dust layer thickness and its distribution along the channel length, (b) heat flux distribution along the channel length, and (c) absorber channel geometry. Two and three dimensional computational fluid

Table 1 The numerical set up for analyzing the heat transfer in absorber straight channels

	Circular straight channel	Square straight channel
Governing equations	Fluid (air) $(\vec{V} \cdot \nabla) \vec{V} = -\frac{\nabla p}{\rho} + (v) \nabla^2 \vec{V} \quad \text{with} \quad \nabla \cdot \vec{V} = 0$ $(\nabla \cdot \rho \vec{V} H_f) = \nabla \cdot \left(\frac{k_f}{C_{pf}} \nabla H_f \right)$ Solid (brass/SiC absorber) $\nabla \cdot (k_s \nabla T) = 0$	
Mesh (structured)	Resolution: 0.015 mm; aspect ratio: 5.5–7.5; orthogonal quality: 0.8–0.99	Resolution: 0.05 mm; aspect ratio: 1.92–2.15; orthogonal quality: 0.98–0.99
Convergence (relative)	10^{-6} – 10^{-5}	
Heat flux (boundary condition)	Uniform: $I(z) = \text{constant}$ Non-uniform: $I(z) = \sqrt{\varepsilon} I_0 e^{-\varepsilon z}$ with porosity ε	

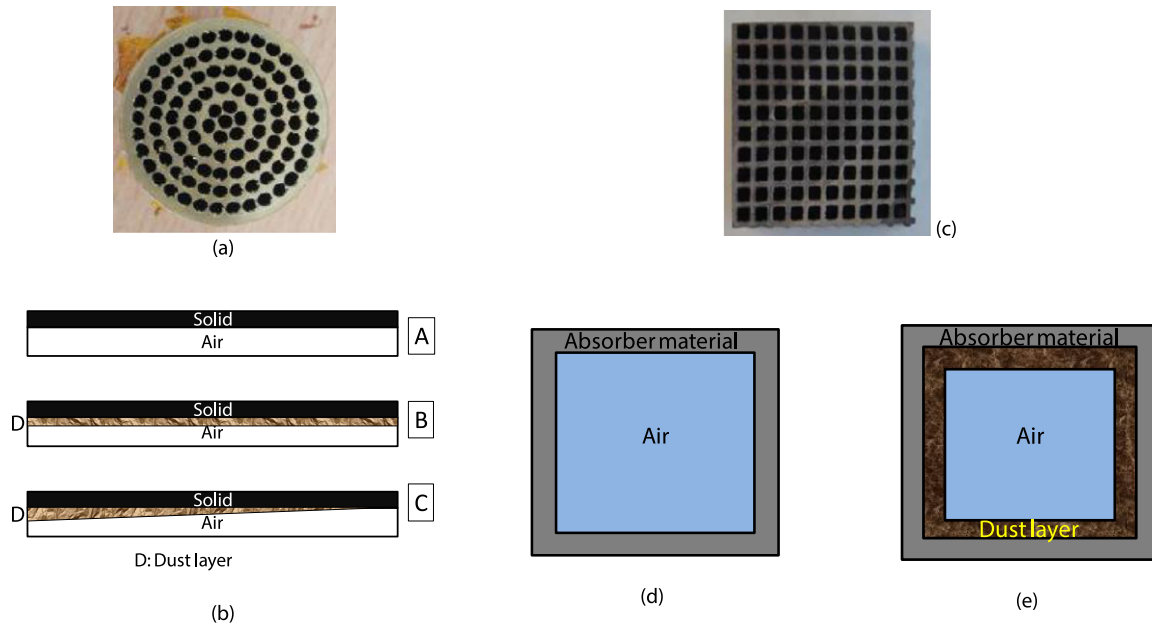


Fig. 10 (a) The circular absorber, (b) the schematic depicting A. Clean straight channel, B. A straight channel with uniform dust layer thickness (UDL), C. A straight channel with non-uniform dust layer thickness; (c) the reference square absorber; The schematic depicting (d) a clean and (e) dust deposited single straight channel. (Reproduced from Luque *et al.* AIP Conference Proceedings 1850 (1), 030034).

dynamics based approaches are adopted for analyzing the effect of dust deposition on the heat transfer in circular and square straight channel based absorbers. The numerical setup is summarized in **Table 1**. This shows the considered property dependent governing equations, the corresponding numerical methods and the convergence criteria. The selected final mesh is based on a grid independence study for heat transfer in a clean straight channel. For a comparative assessment of the dust deposition effect, analyses are performed with the clean and partly blocked straight channels. The deposition of dust, in an ideal case, is treated as uniform along the length, however, in reality, non-uniform profiles are expected. To simulate these different conditions, both a uniform thickness of dust layer (UDL) and a non-uniform thickness of dust layer (NDL) are studied. **Fig. 10** schematically depicts the circular and the square shaped absorbers. An axisymmetric computational model is adopted for the circular absorber, whereas a three-dimensional model is needed for the square absorber. The diameter and length of a circular straight channel are 2 mm and 25.4 mm, whereas the corresponding dimensions in case of a square straight channel are 2.17 mm and 50 mm. The latter is in line with the SolAir 200 geometric configuration (Téllez, 2003).

In **Table 1**, $I(z)$ is the heat flux as a function of axial position along the streamwise direction, I_0 is the irradiance at the front surface ($z=0$), and ε is the porosity of an absorber. The radiation based heat loss from the front surface of absorber is introduced as a boundary condition using user-defined functions.

The schematic in Fig. 11 depicts (a) the volumetric heating with a constant heat flux on the absorber surface and (b) a typical field condition with a non-uniform heat flux along the axial direction, adopted from Roldán *et al.* (2014) and implemented as a user-defined function. Different cases are analyzed with a thickness of dust up to 200 μm , which is equivalent to the four successive dust layers of 50 μm each (Yadav *et al.*, 2014). Both absorber channels are subject to the same Δp as a boundary condition.

Circular straight channel

For the two-dimensional numerical simulations with a circular straight channel, a total pressure of 15.8 Pa is applied at the inlet. This corresponds to a $Q_0/\dot{m}$ of approximately 200 kJ/kg, for a power of 1.03 W in a clean pore. The use of total inlet pressure simulates an operating condition in which all channels are exposed to the same suction. Therefore, the same pressure-drop is maintained even for the simulated partially blocked pore. The calculated Re_p is ca. 175, 70 and 19 for the clean, partially blocked straight channel with uniform dust layer thickness of 100 μm and 200 μm , respectively. Thus, the flow and/or thermal boundary layer development length will be shorter with the partially blocked channels compare to the clean channel. In realistic conditions, however, dust deposition will be generally non-uniform. To estimate the effect of such a distribution, simulations with NDL are also performed. The thickness is maximum (100 μm or 200 μm) at the inlet and linearly reduces to zero at the outlet, as shown in Fig. 10(b).

The simulations are performed with a single clean and partly blocked straight channel. The axial temperature variation of fluid and absorber material is shown in Fig. 12 for the considered straight channels with the uniform and non-uniform heat flux distributions. The deposition of dust on the channel surface will increase both the flow and thermal resistance leading to

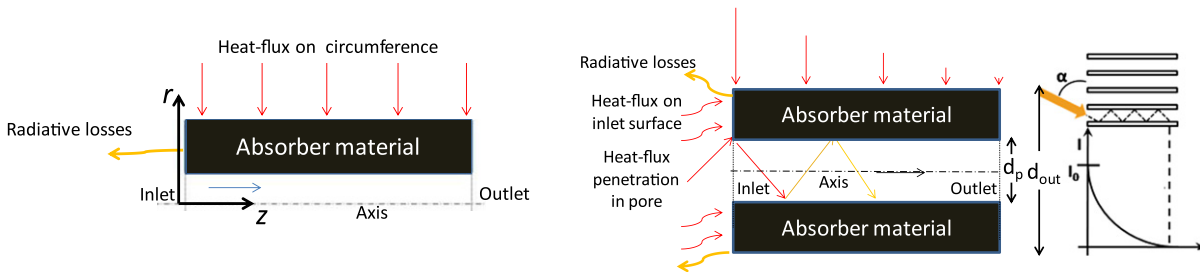


Fig. 11 The schematic showing the applied (a) uniform and (b) non-uniform heat flux. This is depicted by arrows of an equal and the decreasing length along the straight channel-length.

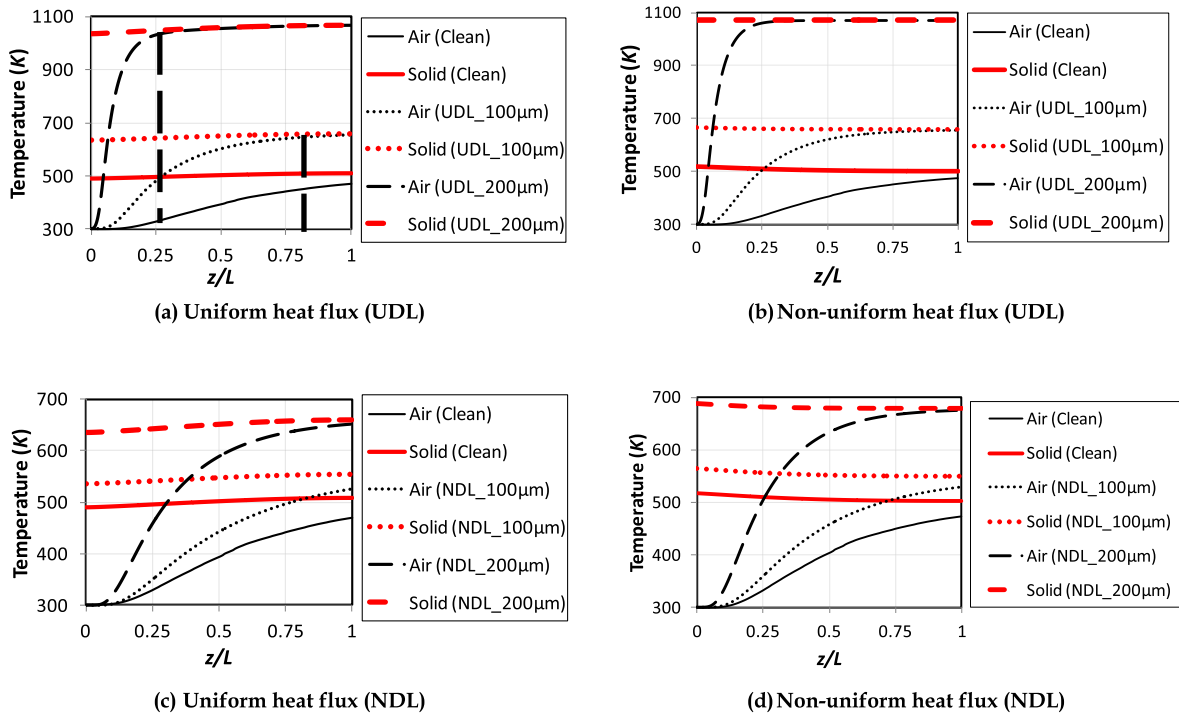


Fig. 12 Axial temperature profile of fluid and solid with uniform dust layer thickness (UDL) and with non-uniform dust layer thickness (NDL) in an OVAR with circular straight channels.

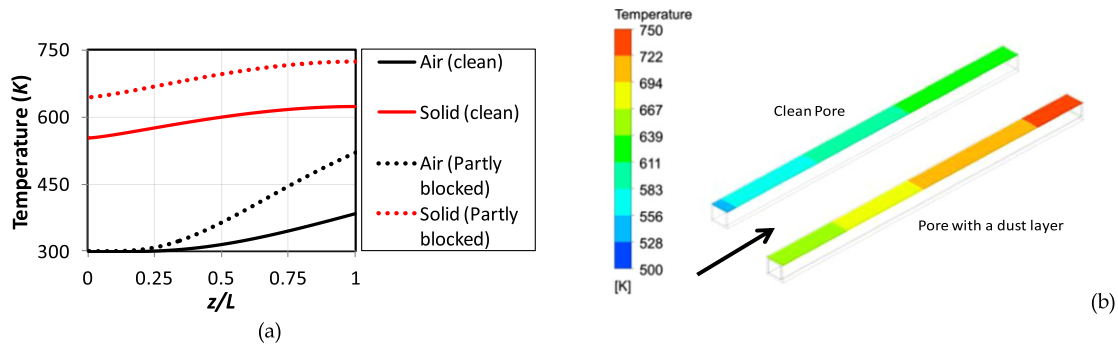


Fig. 13 (a) Axial temperature profile along the centre line of absorber solid and fluid with UDL and a uniform heat-flux distribution with reference square absorber. Reproduced from Luque *et al.* AIP Conference Proceedings 1850 (1), 030034. (b) Variation of solid temperature along the longitudinal direction a clean and partly blocked channel at the central plane.

an elevated air and absorber material temperature. This can be easily inferred from the decreasing Re_p with the increasing thickness of uniform dust layer for the same applied pressure-drop. Therefore, a higher pressure-drop is required to maintain the same flow rate or Re_p in a partially blocked channel in compare to its clean counterpart. This is also evident from the analyses that show substantial rise in temperature with the partially blocked channel in comparison to its clean counterpart. The temperatures of solid and air increase with thickness of the dust layer, as expected. The modeled single circular channel with the applied UDL shows a temperature rise of about 150 K and 580 K for a dust layer thickness of 100 μm and 200 μm , respectively. Whereas with NDL a rise of about 40 K and 150 K is obtained for the deposited dust layers. This is attributed to the decreasing mass-flux for the same pressure-drop, which is confirmed by a shorter thermal development length and is depicted by the dotted vertical lines in Fig. 12(a). Thus, it is concluded that dust deposition is not only detrimental to operation but increases parasitic losses.

Square straight channel

Numerical simulations are also conducted in order to assess the effects of dust deposition on the heat transfer in monolithic absorbers with straight flow channels. The aim was to extend the analysis to a geometrically similar configuration viz. SolAir 200 absorber. The uniform heat flux boundary condition was employed on the absorber surface for simplicity. In this case, an input power of 6 W and a total inlet pressure of 151 Pa leads to the same operating condition viz. $Q_0/\dot{m}$ of 200 kJ/kg. For both the clean and partially blocked absorber channels, the atmospheric pressure is set at the outlet. Also, the radiation based heat loss is incorporated at the front side of the channel using the user-defined functions. Simulations are conducted with a constant heat flux boundary condition with an aim to numerically assess the effect of dust deposition on the heat transport. For a comparative assessment the same $Q_0/\dot{m}$ is maintained for circular and the square shaped channels. In the analysis the uniform dust layer thickness of 100 μm in the square channel is considered for a direct comparison with the circular straight channel.

The comparative assessment between clean and partially blocked square straight channel is given in Fig. 13, where a temperature difference of about 120 K is observed. This demonstrates the increased resistance to heat transfer from solid to air in the partially blocked channels, and the fact that dust deposition may thus limit the operating temperature of OVARs. The temperature rise in the circular and square shaped channels with the uniform dust layer thickness of 100 μm is quite comparable at the same power per unit mass flow rate. Thus, it is concluded that the effects of dust deposition are very similar in these geometrically different flow channels. In the simulations, Reynolds number is about 780 and 500 for the clean and partially blocked square channels. The approximate thermal development lengths are 85 and 50 mm in the clean and partially blocked channels, respectively. Therefore, it is concluded that the effect of dust deposition remains, practically unaffected for a given $Q_0/\dot{m}$, with the different channel geometries and for the developing or developed flow conditions. The fact that partially-blocked absorbers operating at higher temperatures is detrimental in terms of thermal radiation losses (proportional to the fourth power of temperature), which will lower the thermal conversion efficiency of the OVAR in the event of dust storms.

Innovative Solutions

Thermal efficiency measurements presented in this paper have demonstrated that a significantly larger effect of the forced convection heat transfer mechanism is necessary, with respect to the radiative mode, in order to achieve operation under volumetric effect conditions in monolithic absorbers. Some of the major challenges that lie in their operation at high irradiance and high

temperatures include: (a) the transfer of thermal energy from the external radiation-absorbing surfaces to the internal working fluid in a both effective and efficient manner, (b) the minimization of thermal losses throughout the system, (c) the attainment of a stable internal flow field for optimum convective efficiency, and (d) the optimization of the absorber thermo-mechanical behavior, both in transient and steady state conditions.

Variable porosity hierarchically-layered solar receivers (Gómez-García *et al.*, 2015; Alberti *et al.*, 2016) can address the main problems still encountered in monolithic honeycombs, where the incident radiative heat flux is almost completely absorbed in the front region. This enables an enhanced diffusion of incident sunlight and a shift of radiation absorption profiles towards the rear, which reduces thermal emission losses. An additional advantage is the augmentation of internal convective heat transfer in the receiver through a combination of aerothermal mechanisms: A gradually increasing wetted area surface, a reduction of flow cross-sectional areas (increasing flow velocities, Reynolds numbers, and heat transfer coefficients), and the generation and enhancement of turbulent flow structures within the intricate flow channels. Flow instabilities can also be avoided due to the flow field redistribution variable geometry receivers.

A set of fractal-like solar receivers have also been recently proposed, not based on variable porosity concepts, but on the repetition of elementary structures at larger scales: The SCRAP receiver (Lubkoll *et al.*, 2016), the previously cited a pin-shaped external micro-structure of Capuano *et al.* (2017), a bladed receiver (Wang *et al.*, 2016), and staggered rearrangements of tubes along self-repeating patterns (Ortega *et al.*, 2016). The SCRAP receiver is intended as a pressurized air receiver where numerous outward radial spikes are internally cooled by recirculating flow channels. The pin-shaped micro-structure is primarily intended as a frontal add-on to current open volumetric air receivers. The last two have been designed as improvements for current molten salt tubular receivers, however. All are aimed at improving light-trapping performance and move the operating point of solar receivers closer towards volumetric effect situations by minimizing emission losses.

Besides the geometrical and thermal-hydraulic aspects, the dust deposition is a challenge for implementing such a receiver in arid deserts. The analysis demonstrates that the deposition of a uniform dust layer (a) results in an elevated absorber temperature owing to an increased resistance to the flow of heat (b) will lead to a lower thermal efficiency as a consequence of higher radiation based heat losses. A cleaning solution for the in situ removal of dust from the absorber channels is proposed by Singh *et al.* (2016) using a cyclone separator downstream of an OVAR. This will lead to additional parasitic losses, and modified operational strategies are to be established as discussed in Singh *et al.* (2018). Interestingly, a uniform dust deposition is not likely to trigger instability in typical operating conditions of incident power per unit mass flow rate, which is inferred on the basis of the presented computational study. The generalization of this conclusion to arbitrarily non-uniform dust deposition distributions merits a more detailed three-dimensional numerical analysis.

Conclusions

This paper has presented a comprehensive set of numerical simulations and experimental measurements addressing some of the remaining practical challenges that exist in the operation of OVARs at a high irradiance and a high temperature. Stable flow conditions have been demonstrated in siliconized silicon carbide monolithic absorbers for air outlet temperatures in excess of 1000 K. It was shown that reducing flow passage width was clearly beneficial in terms of thermal efficiency in these geometries. Efficiency also generally increased with mass flow rate (for a fixed incident power). Both effects were expected as they lead to higher convective heat transfer coefficients and, as a result, a higher proportion of heat being removed from the sample. Lower thermal emission and conduction losses were produced as a result (forced convection is the only physical mechanism that increases the enthalpy of the working fluid).

With respect to absorber lengths, it was shown that an optimum value generally exists, which may be found by calculating the relative importance of thermal losses with respect to heat exchanged through forced convection. The optimum was typically achieved at low values of radiative power per mass flow rate (around 500 kJ/kg), leading to thermal efficiencies over 0.9. This would require approximately 2 kg/s of air per MW of incident radiative flux for this type of monolithic receivers, which is broadly in agreement with data presented in on-sun experiments for the state-of-the-art SolAir 200 geometry.

Current alternatives being developed as potential replacements of monolithic honeycombs include the use of fractal-like receivers, where structures of different scales are arranged into self-repeating patterns, or variable geometry hierarchically-layered receivers. In both cases, objectives sought include the optimization of radiation absorption and penetration into the solid volume, the achievement of directional thermal conduction, and the introduction of convective heat augmentation features. Additive manufacturing techniques are enabling the design and fabrication of highly creative components of increased functionality.

Such absorbers also mitigate the risk of thermally induced flow instability at the very high operating temperatures that are currently sought. However, special provisions may need to be made for operating such an absorber with in situ cleaning in geographical regions where dust deposition is significant. Numerical simulations presented in the paper showed a temperature increase of about 120–150 K in a single absorber channel at typically low values of radiative power per unit mass flow rate of around 200 kJ/kg (and the effect can be expected to be worse in situations of higher incident power per unit mass flow rate, as found in actual on-sun operating conditions). The analyses revealed that the geometry and flow conditions may increase the heat transfer deterioration on account of the dust deposition. This also has a detrimental impact in terms of increased heat loss and reduced durability.

See also: Multi-Stage Stamping of Lightweight Steel Wheel Disks by Controlling its Wall Thickness Distribution

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Opportunities for Digital Marketing in the Viticulture of Kosovo and Metohija

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Introduction

The culture of cultivating vineyards across the Balkan Peninsula and the Mediterranean Coast was introduced by Thracians, Phoenicians and Greeks. Serbia is among the countries that have vineyards with the ideal conditions for the cultivation of quality wines. Wine experts consider that, depending on the composition of the land, terrain and climate – the Serbian vineyards are among the best in the world. The vineyard region is a broadly defined geographical area with similar climatic and soil conditions that affect organoleptic properties of wines produced on the territory of the country, and with a similar choice of varieties.

According to the written historical data, Orahovac vineyard was known for growing vines even in the Middle Ages. However, the archeological data found indicate that the vineyards existed even before the new era. Numerous archeological finds show that Metohija is one of the oldest wine regions. The cultivation of grapes has always been concentrated in the region of Metohija and Podrimlje, around Prizren, Velika Hoča, Orahovac, Suva Reka, Đakovica and Peć. Viticulture experienced its flourishing in medieval Serbia, during the Nemanjić dynasty. Many Serbian monasteries established their metohos in Metohija ([Fig. 1](#)) (the hilly region of Beli Drim was named Metohija), in which they produced grain, grapes, wine and other products for the needs of churches and monastery fraternity. The highest number of viticulture methos were in the area of Orahovac and Velika Hoča, in which they were produced the famous “Podrumsko crno vino” (engl.Cellar red wine).

Grapes, from which the wine is made, the winemaker produces as an artwork. He designs the taste and is focused on customers who estimate the overall quality of the wine ([Lapsey and Moulton, 2001](#), p. 207). Wine has a great ritual significance in many of the world's largest religions and cultures, and it is an important part of the economy and trade. Wine is one of the oldest fermented products, and it is also a mass-produced, commercialized and studied product of fermentation ([Hutkins, 2006](#), pp. 349–350). Metohija region covers the western and southwestern part of the province, which is surrounded by Mokra Gora from the north, Čakor and branches of Prokletije from the west, Kamnik from the southwest and by Shar mountain from the south. Only one vineyard region was established in the entire territory. This region is known as the Kosovar vineyard region. Within the region, there are two sub-regions: northern and southern. Within the northern sub-region there are vineyards of Pec and Istog. Within the southern sub-region there are the following vineyards: Šakovac, Orahovac, Prizren, Suhareč and Mališevo ([Fig. 2](#)).

Spreading

The South Metohija region extends on the terrain in the southwestern part of Kosovo and Metohija, which is on the territory of South Metohija.

Included Municipalities

The South-Metohija region includes the territory in the municipalities of Djakovica, Orahovac, Prizren and Suva Reka.

Area of the Region

The South-Metohija region occupies an area of 92110.99 ha, where it is the largest.

Spreading

Orahovac vineyard extends into the central part of Metohija from the Beli Drim to Orahovac.

Included Cadastral Municipality

Orahovac vineyard includes parts of the cadastral municipalities of: Kramovik, Petković, Koznik, Pusto Selo, Sanovac, Drenovac, Orahovac, Velika Hoča, Zočište, Opteruša, Zrze, Gedža, Radoste, Ratkovac, Bardosan, Marmule, Doblibare, Meća and Crmljane, as well as cadastral municipalities of Retimlje, Mala Hoča, Nogavac, Velika Kruša, Rogovo II, Poluža, Bratotin, Vranjak, Našpale, Gornje Potočane, Donje Potočane, Stopnić, Bela Crkva, Brnjača, Celina and Brestovac.

There are significant differences in climatic and soil conditions for vineyards or subregions. The largest part of the vineyard area is located around large processing facilities in Orahovac, Prizren, Mala Kruša and Suva Reka.



Fig. 1 The South Metohija region. *Source:* Wine Guide.

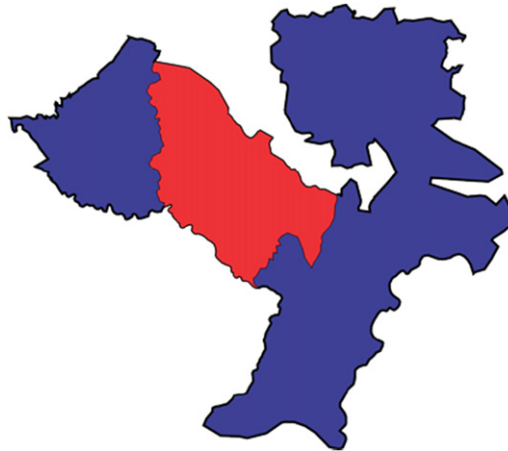


Fig. 2 The Orahovac vineyards. *Source:* Wine Guide.

Starting from Metohija, which is the cradle of Serbian viticulture, the cultivation of the wine was spreading and varieties were transferred to other areas of our country. The wine trade is regulated in the Charter of emperor Stefan Dušan (1355). There is the mention of the villages of Gornja and Donja Hoča (today known as Velika and Mala Hoča) near Orahovac. The production and quality of the wines were famous outside the border of this region. The fullness of this wine is best illustrated by the folk tradition that the wine of this region could be worn in a scarf. Wine intertwines with the history of man from the very beginning. Wine intertwines with the history of man from the very beginning.

At the end of the nineteenth century wine was affected by grape vine parasites – powdery mildew, downy mildew and phylloxera – which at the beginning of the 20th century infected the vineyards of Metohija. The first reconstruction of the destroyed vineyards started around 1920 in Metohija and the utilization of wine rootstock “*riparie portalis*” and “*rupertis du lot*” for grafting grape varieties. Some of these vineyards still exist. Among them, the main variety is Prokupac, and can also be found: smederevka, šasla, plovina, hamburg, afuz-ali, red and black drain, etc.

After the Second World War, viticulture in the Orahovac area was again experiencing its true bloom. Then, in the social and private sector, new vineyards were being erected and they were fundamentally changed a new assortment of varieties. They introduced new methods of cultivation and vineyard cultivation technologies. More and more varieties were produced for quality and top quality wines, such as: game, Italian Riesling, Burgundy, County Riesling, Sauvignon, Semillon, Merlot, Vranac, Cabernet Sauvignon, Cabernet Franc, etc. New substrates are introduced: kober 5BB, ŠxB41B, SO4, etc.

The holder of the grape production in the Orahovac vineyard was a socially-owned enterprise for the production and marketing of alcoholic beverages of PKB “ORVIN” in Orahovac, which had over 1000 ha of modern vineyards. It was equipped with the modern basements with a capacity of 4500 wagons, as well as with highly skilled personnel and workers in the field of viticulture and wine-growing. In these basements were produced table tops, quality and top quality wines, which carry all the quality

characteristics of cultivated varieties and specificities of this region. In these basements were produced table wine, quality and top quality wines, which contain all the quality characteristics of cultivated varieties and specificities of this region.

These wines have gained its reputation with its quality, not only for consumers throughout our country, but they have been highly appreciated and known abroad as well. However, today vine growers in this area are facing enormous problems in the production and marketing of wines. Recently, the hailstorm in the Orahovac area has destroyed about 50% of the grapes, and it will surely cause further increase in production, because it is necessary to extract the vineyards in order to protect them from rot.

Today, one of the more representative wines of this region has a storage capacity of 45,000 L of wine and an annual production of about 15–20,000 L. The winery also has other necessary equipment: crushers, pressing machines, vinificators, pumps, filters and its own laboratory. The winery provides technical assistance in the supply of equipment for use as well as advisory assistance in wine production to small winemakers from the Orahovac and Velika Hoča enclaves. However, the problem of wine placement still remains the imperative for the survival of this and all other wineries of this region.

Given the large number of brands, the selection and purchase of wine is a complex task for the consumer. The quality of the wine is not known until the bottle is opened and the content is tested. Therefore, the moment of selecting a particular wine from the perspective of what is happening in the consumer's mind and what is the main reason for buying a particular wine is a very important in the marketing of wine (Fernandes Ferreira Madureira and Simões de Sousa Nunes, 2013, pp. 75–77). It should be noted that the one-time purchase of a bottle of wine is not the ultimate goal of the manufacturer. Its aim is to obtain loyal customers (Hussain *et al.*, 2007, pp. 49–51).

Small Enterprises and Internet Advertising

The significance of promotion is great nowadays, because it has to radiate diversity and quality service that can compete with all global competitors. The Internet is one of the fastest growing media today. In most European countries, wine production is higher than consumption, which contributes to the imbalance between supply and demand. Companies that appear on the Internet are more seen by customers, they are better targeted, informed, sophisticated and they are better technologically adapted to the younger population (Sutherland and Sylvester, 2000, p. 239).

If we add this information to the primary goal of business communication, we will come to the comprehensive definition of well-known authors, (Kotler and Keller, 2012, p. 478): "Advertising is an audio or visual form of marketing communication that employs an openly sponsored, nonpersonal message to promote or sell a product, service or idea. Sponsors of advertising are often businesses who wish to promote their products or services through various mass media, including printed media, Radio, Television, telephones, cable, satellite and wireless networks, electronic media, billboards, signs and posters." A little later, Kotler and Armstrong (2014, p. 454) represent a slightly different definition, which includes paid advertising components, "Advertising is the communication of the value of a company or brand through the use of paid media and for the purpose of informing, convincing and reminding consumers."

The number of Internet users worldwide and in Serbia is growing rapidly. More than 2.4 million citizens use the Internet on a daily or almost daily, which is 300,000 more in 2012 than in 2012, according to the Statistical Office of the Republic of Serbia (SORS). In Serbia, more than 59.9% of households have a computer, while the Internet connection has 55.8%. The number of households with a computer is 4.7 percentage points higher than last year, and the number of Internet connections increased by 8.3 percentage points.

Enterprises sometimes advertise a product or service, which increases consumer awareness of the company, creating an apparent picture of demand, and thus encourages traders to accumulate stocks or even discourage a certain segment of consumers from purchasing in order to maintain a certain reputation (Brierley, 1995).

When it comes to the enterprises in Serbia, more than 99.6% of them have an Internet connection, which is 1.9 percentage points more than in 2012, according to the Statistical Office of the Republic of Serbia (SORS). According to the survey on the use of information and communication technologies in Serbia, in 2013 the website had almost three quarters of the enterprises with an Internet connection (73.8%). The computer owns 59.9% of households, while the Internet connection owns 55.8%. The analysis of enterprises by size shows that all large and medium-sized enterprises have Internet access, while among small enterprises 99.5% have Internet access.

The definition of micro, small and medium-sized enterprises often changed in the past, so that in different countries there are different definitions and approaches (Kotler and Armstrong, 2014, p. 454). In addition to these two authors, the authors (Bridge *et al.*, 1998) point out that there is no unique, clear definition of small and medium-sized enterprises. Basically at the same time, there are three subgroups of small and medium-sized enterprises: micro, small and medium enterprises. Small enterprises in European Union countries account for 99% of all enterprises (European Commission, 2014).

With the increase of Internet users, the number of the Internet advertising also increases. The Internet offers the market and consumers the possibility of significantly greater interaction and individualization. Individualization refers to the fact that users have control over the flow of information, which leads to opportunities for advertising and promotions that are relevant to consumers. The interaction, which interweaves with individualization, provides the bidder with a choice of information that is significant for him, while the advertising establishes two-way communication with the consumer (Shimp, 2003, p. 394). Advertising on the Internet can be easy, only if we properly use the good and weak sides of that media. Internet advertising allows reaching more people on a global scale, better focus on target groups, lower costs, easier comparison of results, and easier adoption

Table 1 Number and annual growth of Internet users from 2005 to 2014

Year	Number of users	Rate of growth in %	World population	Population growth in %	Penetration(% of internet population)
2014	2,925,249,355	7.9	7,243,784,121	1.14	40.4
2013	2,712,239,573	8.0	7,162,119,430	1.16	37.9
2012	2,511,615,523	10.5	7,080,072,420	1.17	35.5
2011	2,272,463,038	11.7	6,997,998,760	1.18	32.5
2010	2,034,259,368	16.1	6,916,183,480	1.19	29.4
2009	1,752,333,178	12.2	6,834,721,930	1.20	25.6
2008	1,562,067,594	13.8	6,753,649,230	1.21	23.1
2007	1,373,040,542	18.6	6,673,105,940	1.21	20.6
2006	1,157,500,065	12.4	6,593,227,980	1.21	17.6
2005	1,029,717,906	13.1	6,514,094,610	1.22	15.8

of changes (Taylor, 2013, p. 11). At the same time, advertising on the Internet also shows certain weaknesses, such as overcrowding of pages with ads, short lifespan of advertisements, and lower rates of advertising of those ads on Television, because users should not see ads which are not interesting to them (Clow and Baack, 2007, p. 251).

The advantages of small enterprises in comparison with large enterprises and companies are presented below (Bridge *et al.*, 1998):

- Flexibility, which means they are able to respond quickly to new business opportunities, and timely transform innovative ideas into market products.
- Lack of bureaucracy, entrepreneurial managers responds quickly to new opportunities and they are willing to take the risk.
- Efficient and informal communication network that enables quick response in solving internal problems and providing opportunities to quickly adapt to changes in the surroundings.
- Good customer adaptation as well as a good knowledge of their needs and knowledge of problems in a particular working environment and offer them additional services.
- Support for large enterprises.
- Efficient production of goods and provision of services.
- Creating new jobs.
- Small quantities of supplies that are well adapted.
- Increasing efficiency, reducing costs.
- Better information gathering.
- Encouraging competition.
- Possibility of specializing in the market segment of certain products or services.
- Introduction of innovations.

In 1995 access to the Internet had only 1% of the world's population, while nowadays access has about 40% of the world's population. The number of users increased from more than 10 times between 1999 and 2013. Billions of beneficiaries were reached in 2005 and the second billion in 2010. By the end of 2014, Internet access had 3 billion people (Internet Users, 2014).

The rapid advancement of the Internet is reflected in the following numbers. The number of the Internet users reached the first billion in 2005, the second billion in 2010 and the third billion in 2014 (Internet Live Stats – Internet Users, 2016). It is stated in some institutions reports that by 2020, the number of Internet users via mobile devices and tablets will increase to 7.6 billion (International Telecommunication Union, 2014). If these forecasts are made, the number of Internet users will be above the current world population in less than 5 years (Table 1).

More than 3 billion people worldwide are online daily in search for products, entertainment and friends. This brought drastic changes in consumer behavior and in the ways in which organizations perform marketing activities and consumers activities of business marketing (Chaffey and Ellis-Chadwick, 2016). The modern marketing communication approach therefore requires a good knowledge and understanding of the consumers' needs and their habits, as well as understanding of the ways they want to communicate with the organization and the content they want to see (Stone and Woodcock, 2014).

Famous authors, Chaffey and Ellis-Chadwick (2016), are named an approach that enables communication with consumers in the digital world, digital marketing. Digital marketing can be seen as a kind of digital equivalent of the combined marketing communications, which includes all elements of classical marketing. The authors Kotler and Armstrong (2014) emphasize the need for classical advertising on the pages and the demand for communication with clients via e-mail, the use of websites and multimedia presentations of companies, products and services for building relationships and interacting with clients through social media.

Some authors point out that the use of digital technologies for marketing purposes is no longer a choice, but the only way for companies to maintain a competitive advantage, Gartner pointed out already in 2012, when on the basis of several studies he predicted that by 2017, the marketing director will invest more in Technology as IT director (McLellan, 2012). This is confirmed by recent research, which shows that 98% of retailers agree not to talk about digital marketing, but marketing in the digital world

(Gartner, 2015). In addition, experts estimate that marketing has become one of the most technologically dependent business functions (Brinker and McLellan, 2014).

Disadvantages of small businesses compared with large companies are shown below (Bridge *et al.*, 1998):

- Small enterprises run by the owners themselves, who, despite the average higher education, do not have marketing skills. There is also the absence of functional managers and rare creation of specialized departments. This can be a problem, as a leading company usually performs all the work they do in a large company specializing in specific areas, such as financial director, production director, and marketing director.
- Lack of people with appropriate education and work experience is one of the biggest obstacles for the growth and development of small enterprises. Difficulties in hiring skilled workers usually occur because small enterprises generally pay lower wages than large companies and provide fewer extra special benefits, give less social security and job security, and offer few opportunities for advancement.
- Poor use of human resources in the company can be caused by financial concerns for the survival of small enterprises, which do not encourage the creation of training and employee development opportunities.
- Great difficulties in obtaining financial resources, such as loans from banks and other institutions necessary for growth. Some entrepreneurs are sometimes able to cope with the growing challenges of the company. Innovation can be a big financial risk. Small businesses quickly become victims of financial indiscipline because they do not have much capital. Given the limited funding and reserves associated with low borrowing capacity, small enterprises are very vulnerable during the economic downturn.
- Poor conditions with their suppliers for alternative and lesser purchases on the market e.g., lower prices, delivery deadlines, and other terms. At the same time, small enterprises largely depend on their suppliers, among other things, because they can not produce many components and perform all services necessary for their activities.
- Small enterprises are more likely to achieve high economic efficiency, because they can not take advantage of the big company's privileges, which, for example, have a discount for the purchase of large quantities, using a sophisticated marketing and distribution system.
- Obstacles and difficulties in acquisition and exploitation of modern technologies. It is often done with inappropriate or incomplete information. In order not to increase the cost of doing business, it is often saved on the information systems.
- Lack of time or resources to identify and use external sources of scientific and technological knowledge.
- Small enterprises are usually limited to one product or a very narrow range of products and services.
- Problems with patent systems. They can not afford the time or costs that this process requires.
- They can not often deal with complex rules.
- Poor state support and support for small businesses.

Small enterprises with their characteristics are designed and are in a good position to adapt to the needs of consumers and to the new technologies. Compared to larger companies, their flexibility has resulted in easier and faster adaptation for less administrations and hierarchies (Payne, 2005).

In a small company, where the budget for advertising is lower, there are wonderful opportunities for online advertising. Famous author wrote at the time of advanced advertising in traditional media: "If you are in doubt, do it yourself. Be brave! You can not?! Advertisement [...]! Just try! After 4–5 messages, you will see: Advertising is paid off at once!"

As the famous author Neti (2011) presented in his works – about 75% of small enterprises have their own web pages on social networks, of which 69% are regularly updated their website, and 54% monitor consumer responses.

In the European Union countries, small and medium-sized enterprises account for 99% of the total number of enterprises, of which 20% are involved in export activities. Therefore, the internationalization of business for most small enterprises is essential for the survival of the enterprises themselves (Pleitner, 1997; Daily *et al.*, 2000).

Advantages of Online Advertising

Zeff and Aronson (1999, p. 13) have presented four main advantages of the Internet over other media:

- Targeted communication.
- User monitoring.
- Presence and flexibility.
- Interactivity.

In relation to Zeff and Aronson (1999, p. 13), in the literature it can be found that the advantages of the Internet are more analyzed and that other advantages are also added:

- Internet advertising is effective for direct marketing as well as for branding.
- Internet advertising is easy to measure.
- Internet advertising can be improved.
- Internet advertising is "laser" accurate.
- Internet advertising can be monitored and predicted.

- Internet advertising is relatively cheap.
- Internet advertising gives fast and lasting results.
- Internet advertising can be a type of automation.

Disadvantages of Online Advertising

Besides of advantages, we must be aware of some of the disadvantages that the Internet brings us as a medium of advertising. Clow and Baack (2007, p. 251) point to 4 weaknesses.

- Saturation.
- Short lifetime of the ad.
- Limited range.
- Low interruption rate.

In addition to the abovementioned disadvantages, the following shortcomings may also be mentioned:

- Uneven measurement, measured results and campaign efficiency can be different, which makes it impossible to compare data;
- Insufficient information control, because we know that a large amount of online information can be inaccurate or out of date; companies must ensure that their ads are always interesting and current; otherwise they may lose their users;
- Costs that are on a simple internet site and communication channels are relatively low, in more complex solutions can be significantly higher because they require higher maintenance costs;
- Service speed can also be reported as a problem; powerful graphics and applications that a user loads into a computer can lead to slow flow of information, which can dissuade users from browsing the web site;
- The problem is mistrust of users; most users still do not trust electronic business and the Internet does not feel very safe to them;
- A major advertiser problem is a variety of messaging software, which prevents certain ads from appearing on the Internet.

Definition of Online Advertising

Kotler (2003, p. 250) defines advertising as well as any paid form of impersonal presentation and of promotion of ideas, goods or services from a known purchaser. It is a paid form, which means that there must be a place and time for an advertised paid space. As impersonal form, advertising covers mass media (e.g., TV, radio, newspapers) that allow the transmission of messages to a large group of individuals at the same time. Due to the impersonal nature of advertising, advertisers can not receive immediate feedback from the recipients of the message. Advertisers must, before sending the message, predict that recipients will understand and respond to it (Belch and Belch, 2003, p. 16). Richards and Curran (2002) define the notion of advertising as a paid form of communication, the purpose of which is to persuade the recipient to take action now or in the future.

Zeff and Aronson (1999, pp. 11–12) define advertising as an attempt to expand the information in order to influence the transaction between buyer and seller. Internet advertising allows you to display your ads that are tailored to individual users according to their interests. Internet advertising is therefore a convergence between traditional advertising and direct marketing. Internet advertising can be defined as any form of communication that meets the definition of advertising and which can be found on the Internet (McMillan, 2004). At the beginning of the 20th century, it was very important to notify customers with the arrival of new types of products. Today, advertising is an important part of economic activity in all developed economies. In the advertising function, the main goal is to attract the attention of users through any media (Postma, 1999, p. 24).

World's Online Advertising Usage

Today, online advertising is one of the biggest drivers of the European digital economy, promoting industry development and economic growth through accelerated development and innovation. During 2014, 46 billion euros were invested in online advertising, of which 30.4% (30.7 billion euros) went to European publisher's funds. According to IAB data, revenues from Internet advertising in the US in 2013 amounted to 42.8 billion dollars, thus exceeding the revenue from TV advertising, which reached 40.1 billion dollars. In the last quarter of 2013, revenues from the Internet advertising amounted to 12.1 billion dollars, which is 14% more than in the third quarter of the same year, when they amounted to 10.6 billion dollars. Compared to 2012, revenue from Internet advertising grew by 17%.

Internet advertising revenues in 2013 amounted to \$ 12.8 billion, representing 30% of total revenues, which increased by 7% compared to 2012. In this category of Internet ads, banners dominate, which yield 19% of revenues, followed by video ads with 7%, enriched ads with 3%, and sponsorships with 2%. Advertising on search engines still generates the highest revenue, which accounts for 43% of total digital advertising revenue. In 2013, they amounted to \$ 18.4 billion or 9% more than in 2012 (Digital Ad Spending Worldwide to Hit, \$137.53 Billion in, 2014, 2014).

The forecasts indicate that spending on Internet advertising in 2014 amounted to \$ 137.53 billion globally, which means that there was an increase in costs of 14.8% compared to 2013 when they amounted to \$ 119.84 billion (Digital Ad Spending Worldwide to Hit, \$137.53 Billion in, 2014) (Fig. 3).

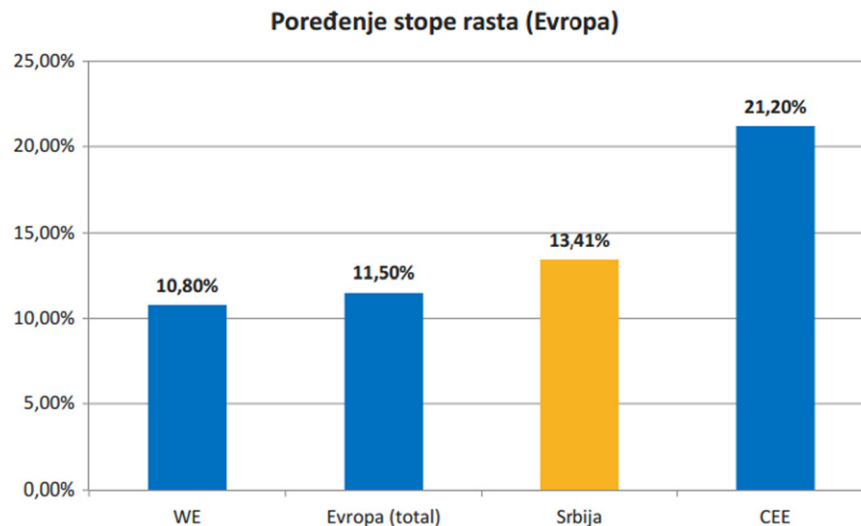


Fig. 3 Serbia within the EU (2012–2013).

In 2013, the largest share in advertising expenditure, which was 40.1%, was still intended for advertising on television. This is followed by mobile advertising with 21%. In 2014, it was mostly spent on internet advertising, which is \$ 55.7 billion dedicated to advertising on the search engines, then on showing ads with \$ 51.8 billion. The data showed that the share of spending on internet advertising would increase to 27.1% by 2016 (Lunden, 2014).

Key data and trends:

- The total value of the digital and interactive advertising market in 2013 was estimated at € 16,320,000, including advertising on mobile devices.
- The growth of the total market value was estimated at 13.41%, which means that the positive trend of double-digit growth was maintained.
- The largest growth in the previous year was due to social networking, or social media marketing (27%).
- The mobile advertising market in 2013 recorded an increase of 150%, which means that the total value of this market segment was € 380,000.
- The total value of the market continues to be the largest contributor to display advertising (50.68%) with a total net value of € 8.230.000.

Internet Advertising Forms

The first forms of internet advertising were the websites themselves. As the Internet soon became crowded with advertising sites, they were no longer enough to attract users. Advertisers needed a tool that would bring more users to the site. The first advertising models were banner and button (Zeff and Aronson, 1999, p. 23). Advertisers are constantly developing new ad formats to attract their desired customers. There are many different forms of internet advertising. Research shows that these are most common: advertising banners, pop-ups, sponsored ads, text ads, comprehensive ads, but also floating ads, wallpaper changes, online games, ad breaks, video ads and screen savers.

Users' Attitudes Towards Online Advertising

Users' attitudes towards online advertising have become a topic of discussion since the mid-1990 (Nasir *et al.*, 2011, p. 61). A study of users' attitudes toward advertising is important because advertising affects the user's attention and responses to specific ads (Alwitt and Prabhaker, 1992, p. 31). Today, most sites are flooded with internet ads, while advertisers have many forms of internet advertising, and are constantly developing new forms and methods of advertising. Site saturation with adverts, the number of existing and new opportunities for expansion and promotion of goods or services offered by the Internet, as well as the forecast that Internet advertising will continue to develop in the future - indicate the need to examine the user's attitude towards online advertising and towards different forms of online advertising (Burns, 2003, p. 18). Famous authors Rodgers and Thorson (2000, p. 43) consider that the user has a great importance in advertising. In order to examine for what purpose people use the Internet and which factors attract users and encourage them to return, they have developed a so-called model of Interactive advertising (Fig. 4).

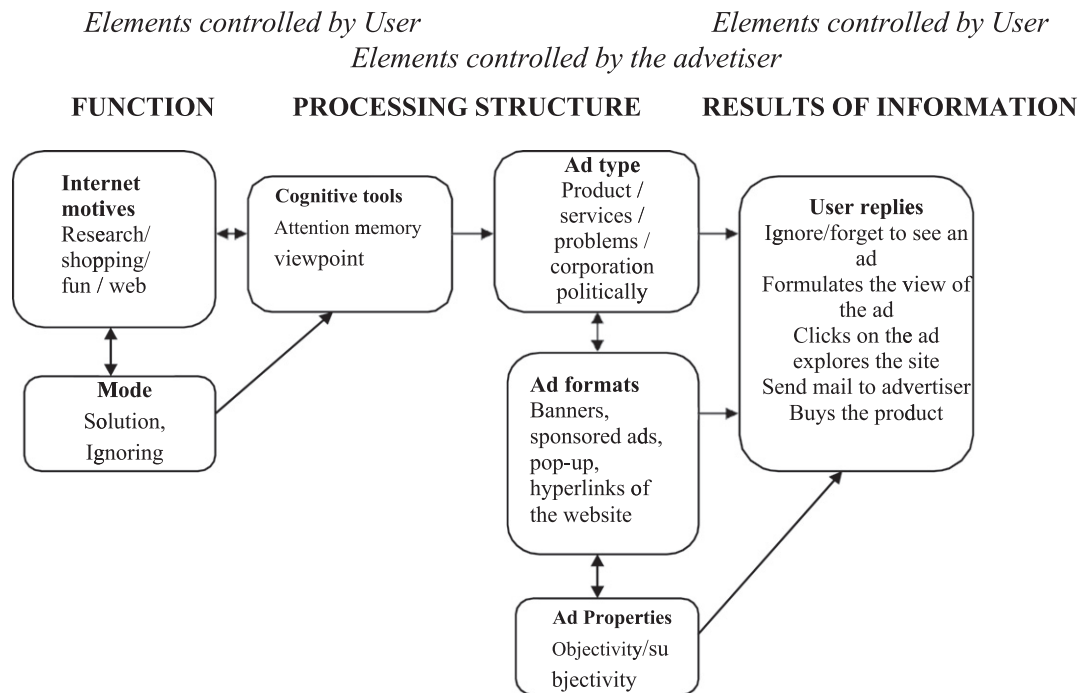


Fig. 4 Interactive advertising model.

Current Research of Users' Attitudes Towards Online Advertising

In his research, Ducoffe (1996, p. 27) found that users perceive advertising as important and informative, not too intrusive, but also not too fun. Other studies have shown that users see online advertising as a pushy (Reed, 1999, p. 25) and intrusive appearance (Li et al., 2002, p. 45). In his study, Schlosser et al. (1999, p. 43) shows a divided opinions on Internet advertising. When they were asked whether they are in favor of advertising or not, 38% of users responded that they are fond of it, 25% that they did not, while the rest was neutral. Most users see internet advertising as informative (62%), while 49% say they do not see all the ads they are exposed to. Less than half of the users (48%) trust Internet advertising. When asked how often they use advertising to help them with the purchase, 67% of users responded with-never.

In the research conducted by Previte (1999, p. 203), users generally consider Internet advertising to be informative. Most users (69%) search for information about products and services via internet ads, 48.9% of users use online ads to find products and services that interest them, while 59.5% think that in Internet advertising there are no current information. Approximately 44% of users think that internet advertising is fun, while 50% of them believe that online advertising is less pleasant than other content on the Internet. Data shows that 54.3% of users believe that internet advertising is a good thing. In general, 46.9% of users have a positive attitude towards Internet advertising.

In a study conducted by Rettie et al. (2003), it was found that users have showed a more negative attitude towards Internet advertising. According to their data, 42% of users believe that Internet advertising is annoying, 45% believe that internet advertising is a waste of time, 63% believe that online ads are boring in terms of control, 62% of them like to visit sites that are not advertised. In contrast, 13% of users never click on an ad, and 69% think that Internet advertising is acceptable when it leads them to the desired content.

Regarding the research on attitudes towards certain forms of online advertising, users perceive web banners as poorly entertaining, unobtrusive and average informative. Users see pop-up windows as boring, disturbing and least informative. On the other hand, users perceive large vertical banners as very entertaining, informative, and unobtrusive. Floating ads turned out to be the funniest, and at the same time the second most striking and least informative form of the advertisement. Advertising breaks are perceived as very entertaining, average informative and average striking (Burns, 2003, p. 162). According to Tutaj and van Reijmersdal (2012, p. 5), users view sponsored links as more informative, more entertaining and less attacking compared to web banners, but they consider web banners more visible than sponsored links.

According to the survey conducted by UK company "Respond", users mostly interfere with video ads that run when websites are loaded, while the second most striking and disturbing factor are pop-ups windows, while the third and fourth-expanding ads and ads that appear when the user sets the mouse on a particular word (Robles, 2012). Adobe's research shows that more than a third of users believe that internet advertising is inefficient, and that advertising on television is more effective than internet advertising (66%). The words boring and striking are also often used to describe online ads (Lomas, 2012).

The research on the relationship between online advertising and Internet advertising was conducted by Gemius in 2006 in some European countries. The results show that in average users consider Internet advertising as an efficient way of advertising

products and services, but also very tedious. More than half of the respondents said that their ads were annoying and that they appeared too frequently when they search the Internet. The most popular forms of internet advertising are banners and sponsored links, which shows that users prefer those types of ads that do not interrupt them and do not interfere with the internet search aggressively. Research shows that the most popular forms of advertising among the users in the Republic of Serbia are web banner ads, followed by a video.

There is also an interesting study conducted by the enterprise Insights One, which, in addition to statistics about the types of ads that are striking to users, shows surprising facts about how users respond on striking ads. Even 60% of users are logged out of receiving promotional mail, 45% ignore e-mails, 36% leave the site, 14% no longer use the advertised product, 13% stop using or buying products from the advertised company (*The Peril of Terrible Ads: Certain Display Ads Draw Ire*, 2013).

To summarize, it can be concluded that the results of individual research in a given period may vary. Some research shows that users consider online advertisements as informative and important, and have a positive attitude about them, while others show a generally negative attitude towards online advertising itself. While a clear conclusion can not be made on the basis of these studies, a self-study on how users perceive the Internet and their views on the forms of online advertising is presented in the text below.

Empirical Research

Analysis of the Research Result

Below is a presentation of the empirical research, which was conducted using the method of quantitative research, i.e., Internet interviewing. The aim of this type of research is to use the questionnaire in order to find out what is the attitude of the users in Serbia towards Internet advertising. We set hypothesis – *H1: Users generally have a negative attitude towards internet advertising.*

The results of the current research generally differ. Some research show that users generally have a positive attitude towards internet advertising (e.g., [Ducoffe, 1996](#); [Previte, 1999](#)), while others have a negative attitude (e.g., [Li et al., 2002](#); [Rettie et al., 2003](#)). As the results of recent research have repeatedly cited the negative attitude of users towards online advertising and because it is possible to notice the saturation of some internet sites with such advertisements, we anticipate that users have a generally negative attitude towards internet advertising.

This research will also reveal what are the factors that help the user when choosing and buying a particular type of wine. At the end of the research common opportunities, weaknesses, opportunities and threats of winemakers in Kosovo and Metohia were summed up through a SWOT analysis.

Sample description

The research was conducted from 01/03/2017 to 01/04/2017. Potential respondents were invited to collaborate via social networks and e-mail and were selected randomly. The poll clicked by 342 users. Of all those who started filling in the questionnaire, the questionnaire was completed by 146 users, while the 57 completed questionnaire only partially. One of the main reasons for a somewhat high number of partially filled questionnaires is probably the occasional irregular work of the 1KA tool in a particular search engine. Due to unknowingly the completion of the questionnaire was interrupted in different steps. The interviewees could not continue filling in because they were again overruled at the beginning of the questionnaire. In the further analysis only the questionnaire filled in is complete. Of all those who started completing the questionnaire, in whole the questionnaire filled 146 users, while 57 questionnaires filled in only partially.

One of the main reasons for, to a certain extent, high number of partially completed questionnaires is probably the occasional irregular work of the 1KA tool in a particular browser. Due to an unknown reason, the questionnaire was interrupted in various steps. The respondents could not continue to fulfill them, as they were again redirected to the beginning of the questionnaire. Only fully completed questionnaires are included in the further analysis.

From the [Table 2](#) it can be seen that out of 146 users, who fully responded to the questionnaire, 65.75% of them were women and 34.25% – men. The largest part of the interviewed users, which is 35.62%, is grouped among people between 30 to 40 years. The second largest age group is comprised of users from 20 to 30 years (26.71%), followed by the age group from 40 to 50 years with 18.49%. A smaller proportion of users, 15.07%, are classified as an age group of 50 years and over, and at least those are up to 20 years old (4.1%). The second largest age group is comprised of users from 20 to 30 years (26.71%), followed by the age group from 40 to 50 years with 18.49%. A smaller proportion of users, 15.07%, is classified as an age group of 50 years and over, and at least those are up to 20 years old (4.1%).

With regard to their education, most users have a completed high school or secondary vocational school (56.85%), and is followed by those with school of higher education (41.78%). The smallest part consists of users with elementary school and less (1.37%). The majority of the surveyed users that is 83.56%, are labor-active, 2.74% are labor-inactive (pensioners, etc.), while 13.70% are unemployed. One third of the respondents (32.19%) have an average net income of 55,001 to 75,000 dinars, followed by those with income of 35,001 to 55,000 dinars (31.51%), followed by those with income of 25,001 to 35,000 dinars (22.60%), while without personal income there is 13.70% of respondents.

As regards the use of the Internet ([Table 3](#)), the majority of users (69.18%) use the Internet several times a day, 16.44% once a day, 11.64% several times a week, 2.74% users several times a month. Of those who use the Internet at least once a day or more,

Table 2 Demographic significance of surveyed Internet users

<i>Demographic variations</i>	<i>Number of users</i>	<i>Percentage (%)</i>
<i>Gender:</i>		
Male	50	34.25
Female	96	65.75
<i>Age:</i>		
Up to 20 years	6	4.1
20–30 years	39	26.71
30–40 years	52	35.62
40–50 years	27	18.49
50 years or more	22	15.07
<i>Education:</i>		
Elementary school or less	2	1.37
High school/secondary vocational school	83	56.85
School of higher education	61	41.78
<i>Employment:</i>		
employed	122	83.56
Inactive, retired, unemployed	4	2.74
	20	13.70
<i>Average, personal, monthly net income</i>		
<i>Income (in dinars):</i>		
25,000 or less	12	8.22
25,001–35,000	33	22.60
35,001–55,000	46	31.51
55,001–75,000	47	32.19
75,000 or more	8	5.48
Without personal income	20	13.70

34.25% of the users use the Internet on average by 1 to 2 hours per day, less than 1 h of Internet use 16.44%, 2 to 3 h use 21.23% of users, 3 to 4 h and more than 5 h 10.96% of users, and 6.16% of those who use the Internet in average for 4 to 5 h a day.

Review of the results and testing of hypotheses

In the second set of questions, users rated 16 claims on the five-step Likert scale, which are related towards user's reactions and attitudes towards Internet advertising and internet advertisements in general. These are the following statements:

Internet advertising is a good form of information

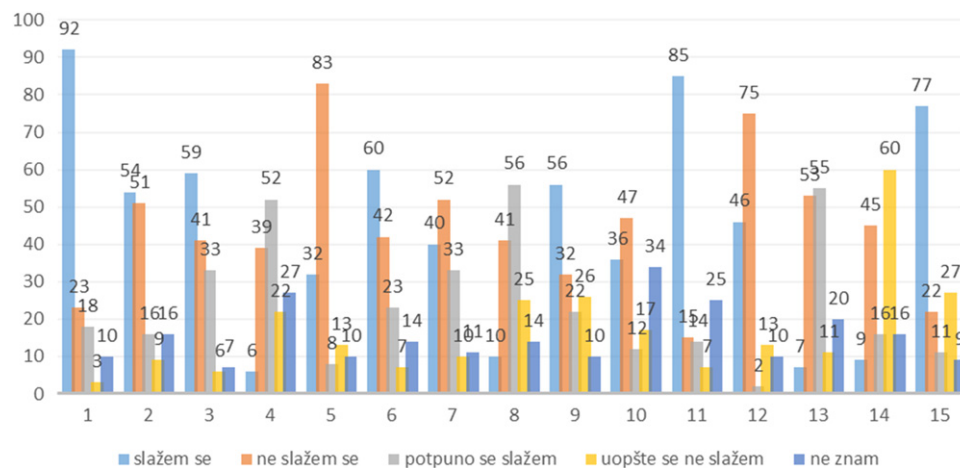
- (1) Internet advertising is mandatory
- (2) There are too many ads on the Internet
- (3) Internet advertising seems deceptive to me
- (4) I am generally fond of internet advertising
- (5) Internet ads are informative.
- (6) Internet ads are useful and fun
- (7) Internet ads are a waste of time
- (8) Internet ads are hindering.
- (9) Internet advertising helps me with purchasing decisions
- (10) I like the web site without ads
- (11) When I see an internet ad, I look closely at it
- (12) When I see an internet ad, I click on it to find more information
- (13) An internet ad often takes me to buy an advertised product/service
- (14) I usually ignore an Internet ad

The results of the research are shown in [Fig. 5](#).

The results of the research showed that out of the 146 respondents, 110 users (75.34%) think that Internet advertising is a good source of information, 83 users (56.85%) also think that Internet ads are informative. On the other hand, 88 users (60.27%) usually ignore Internet ads, 92 users (63.01%) think that there are too many ads, 99 users (67.81%) prefer websites that do not show ads. According to 70 users (47.95%) advertising is mandatory. The claim that Internet advertising helps them with the

Table 3 Internet activity of examined Internet users

<i>Using the Internet</i>	<i>Number of users</i>	<i>Percentage (%)</i>
<i>Frequency of using the Internet:</i>		
Several times a day	101	69.18
Once a day	24	16.44
Several times a week	17	11.64
Several times a month	4	2.74
Less then 1 time per month	0	0
<i>Average number of hours per day</i>		
Less than 1 h	24	16.44
1–2 h	50	34.25
2–3 h	31	21.23
3–4 h	16	10.96
4–5 h	9	6.16
More than 5 h	16	10.96
<i>The needs of the Internet:</i>		
Searching for information	59	40.41
Monitoring news	41	28.08
Job	20	13.70
Fun	13	8.90
Communication	6	4.11
Purchasing	4	2.74
Other	3	2.06

**Fig. 5** Reactions and attitudes of users toward Internet advertising and Internet ads in general.

purchase decision is supported by 40 users (27.40%), while 59 users (40.41%) disagree. 78 users (56.15%) find out that the Internet ads are disturbing.

Before starting to examine the main hypothesis, that is, what are the attitudes of users regarding Internet advertising in general, the direction of the claim first should be consolidated, because in some claims the reverse Likert scale is used. Coefficients of asymmetry and alignment indicate that the data sharing is not normal, for this reason was used the Kolmogorov–Smirnov and Shapiro–Wilk test in order to check the normality of data division. In this case, the null hypothesis states that data is normally distributed. If the P value is smaller than the characteristic rate of 0.05 then the null hypothesis is rejected, and if the P value is greater than the characteristic rate of 0.05 then the null hypothesis can not be rejected. Since both P-values are less than 0.05, this means that data are not normally distributed, so we use the appropriate mean value below. Before calculating the mean value, the variables were adequately decoded. Rating 0 in this example represents a negative attitude. Those ratings are combined with rating 2 (I totally disagree), and 4 (I do not agree). Rating 1 represents a positive attitude. Those ratings are a combined with

Table 4 Mean values for generalized claims about internet advertising and internet ads

Number	General claims about internet ads and internet advertising	Number		Median	Modus
		Valid	Hindering		
1.	Internet advertising is a good form of information	136	10	1000	1.00
2.	Internet advertising is mandatory	130	16	1000	1.00
3.	Too many ads on the internet *	139	7	0000	0.00
4.	Internet advertising seems to me deceptive *	119	27	1000	1.00
5.	I'm generally in favor of internet advertising	136	10	0000	0.00
6.	Internet ads are informative	132	14	1000	1.00
7.	Internet ads are useful and fun	135	11	0000	0.00
8.	Internet ads are a waste of time *	132	14	1000	1.00
9.	Internet ads are hindering *	136	10	0000	0.00
10.	Internet advertising helps me with purchasing decisions	112	34	0000	0.00
11.	I prefer the websites without ads *	121	25	0000	0.00
12.	When I notice an internet ad, I look closely at it	136	10	0000	0.00
13.	When I see an internet ad, I click on it to find the information	126	20	0000	0.00
14.	An internet ad often takes me to buy an advertised product / service	130	16	0000	0.00
15.	I usually ignore an online ad *	137	9	0000	0.00

Appendix: * For these statements was used reverse Likert scale. Rating 0 represents a negative attitude, and the rating 1 is a positive one.

rating 1 (I agree) and 3 (I completely agree). Rating 5 (I do not know) was in this case eliminated because it is neither a positive nor negative attitude.

From the [Table 4](#) it can be seen that 10 claims are negative (66.67% – in the table colored in blue) and only 5 claims (33.33%) are positive. Since users generally show negative attitudes, we can confirm a hypothesis that users generally have a negative attitude towards Internet advertising.

External Evaluation of Small Enterprises for the Production of Wine on the Territory of Orahovac and Velika Hoča

Due to the mild climate, as well as the southern exposure of the terrain around Velika Hoča and favorable soil, and the God-given landscape – is ideal for growing vines and producing excellent wines. This is why vineyards are widespread in large areas. The income from viticulture and wine trade was quite high, so emperor Dušan introduced the customs duty (in 14th century). Almost all the owners in the village had their own cellars (winery) for cultivating grapes, and the arrival of a large number of those who were in the vineyards and produced wine made it possible to raise many residences, cottages and other facilities (Monastery of Dečani, Devič of richer individuals).

Today, there is an active Dečanska vinica (winery), where the monks of the monastery of Dečani make an excellent metohistic wine, and also have private vineyards.

Winery antić-orahovac

- Winery Antić owns 90 acres,
- 50,000 to 55,000 kg of grapes are purchased annually,
- 30,000 to 35,000 L of wine are produced annually,
- 90% are redeemed by Albanians and the remaining 10% of Serbs and others,
- 2/3 black and 1/3 white wine
- the capacity of 35,000 L of wine each year.

Problems in business:

- Double VAT, double excise,
- Kosovo redeemers carry out extortion in price and the money is paid only in May of next year. This could lead to our country being overwhelmed by the fact that this Serbian winemaker is giving money to the producers immediately after the purchase. For this reason Albanians prefer to sell it to a Serbian producer.
- In 2015 the price of grapes purchase was 26–30 cents for the Vranac, which is the most purchased, because it is good for mixing, purchasing, etc.
- The selling price of white and black wine in the plastic bottle is 150–190 dinars per litre,
- The selling price is 4–4.5 Euros for a glass bottle of 0.75 L for black and white wine (38 cents a bottle, cork 50 cents, 10–12 cents labels and transport whose price depends on the destination).

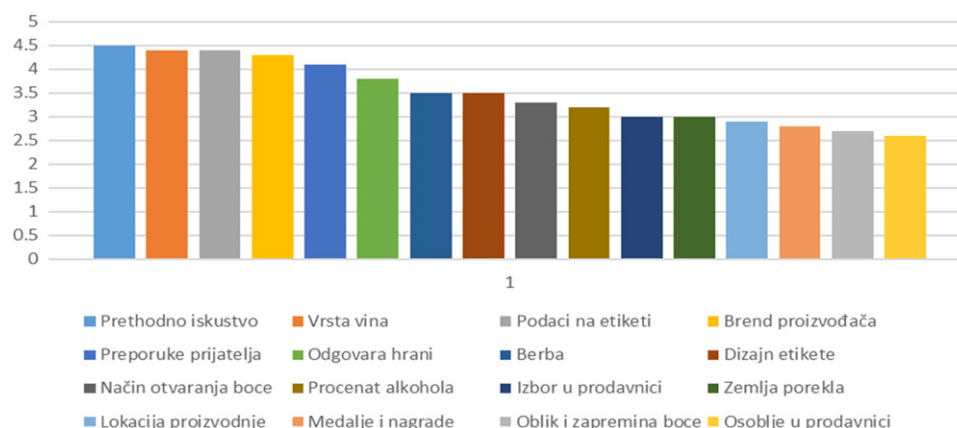


Fig. 6 Significance of different factors in purchasing and selection of wine. Appendix: * 1 means “Not important at all”, 2 means “not important”, 3 represents “not important or unobserved”, 4 means “It’s important” and 5 “very important.”

- The export is mostly done in plastic bottles and glass in small quantities of 20–40 bottles in buses and vans, but not in tanks due to problems on the road by the Kosovo police, sanitary inspection, etc.
- Company “Navip” from Serbia has offered to redeem all wine production, but at 55 cents per liter, but Mr. Antić rejected because it was unprofitable for him.

Winery petrović

- Wine production and wine tourism have 15 sleeping beds that are mostly issued to foreigners because this is a suitable destination for the development of wine tourism.
- The area of the winery Petrović is 2.5 hectares of vineyards,
- Annually produces 50,000 L of wine, šira, grape juice, spirits, grape brandy Lozovača, grape marc Komovica, liqueur....
- 30% of white and 70% of black wine is produced.
- It is exported to Serbia, Montenegro and the Republika Srpska.
- There is a problem with the border, (excise, VAT with double taxation).
- Spirit (rakija) is harder to export than wine
- The export is mostly done in plastic bottles.

According to the manufacturers’ experience – 15,000 Euros is necessary for a hectare of vineyards and another 20,000 euros for a wine cellar, pressing machines, crushers and other equipment.

Winery vinica- the church of Sveti Stefan

Field conditions

The Kosovo government gives 1000 euros per hectare of vineyards annually, while the Serbian government has given loans with incentives and donations in presses, crushers, vats, etc. For now, no incentives have been made for wine production and export, and it should be done, especially in these circumstances where our people live.

Checking the Importance of Various Factors in Purchasing and Selection of Wine

In the previous Fig. 6, it can be clearly seen that the users are paying great attention to the previous experience, the type of wine, the vintage, the brand, while the shape and volume of the bottle and the shop staff are factors that the examined users do not consider decisive when choosing and buying bottles of wine.

All the analyzed wineries gave a much greater emphasis to technical and technological development during the business expansion period, which was not followed by the appropriate marketing activity in order to win and better positioning in the market.

The impression is that this segment was left to the stigma and inertia of the development of the entire sector, which was especially evident in terms of difficulty in the placement, increasing inventory and billing issues.

Previous research has shown that enterprises can increase their marketing activities through Internet advertising without big additional costs and thus mitigate the negative specificities of the living and business environment in Kosovo and Metohija. Based on the SWOT analysis, it can be concluded that even if there are certain weaknesses and threats to the wine production in Kosovo and Metohija, they can gradually be overcome by harnessing opportunities and chances. In this respect, they should also be put

together on the market and use Internet advertising, which, given the specific business conditions, can significantly assist in the placement and sale of wines

Swot Analysis

<i>Strengths</i>	<i>Weaknesses</i>
● Continuously high quality wine quality ● Long tradition of production ● Modern wine facilities and equipment ● High representation of young vineyard seedlings ● Using modern technology ● A wide range of products ● The winemaker belongs to the younger generation of winemakers ● Noteworthy results in wine exhibitions and fairs ● Recognition of the visual identity of the product ● Possibility of independent organization and management of tasting ● Continuous education	● Insufficiently emphasized promotion that is not adapted to the production expansion ● There are no employees who are specialist in marketing and promotion ● Double VAT, double excise, ● Kosovo buyers are blackmailing and the money is paid only in May next year. High selling wine prices ● Insufficient product information ● Product unavailability to potential customers ● Export is done mostly in plastic bottles and glass bottles in small quantities of 20–40 bottles in vans, buses, but not in tanks due to the problems on the road by the Kosovo police, sanitary inspection, etc.
<i>Opportunities</i>	<i>Threats</i>
● Favorable agroecological conditions for the production of quality raw materials ● Development of specific technologies for the production of wines of indigenous grape varieties ● Preservation of the environment and the possibility of ecological production ● Recognition in the domestic market ● Makes it easier to enter foreign markets ● Joining winemakers in the sales segment and the expansion of the direct retail network ● Joint appearance on the market ● Use of the Internet and social networks in promotion of wine	● Capital intensive production and high dependence on the capital market ● Slower turnover (the coefficient of turnover is less than 1) ● Wine prices in catering facilities are not accessible to a wide range of citizens ● Drop in purchasing power, both domestic and foreign markets ● Large producers that have more capital and have a better marketing approach ● International competition with better infrastructure and institutional support

Conclusion

The purpose of this paper is to study the application of new forms of Internet marketing in terms of solving problems of placement of wine of small and medium-sized enterprises, and to investigate and determine the attitude of users in Serbia towards Internet advertising. Nowadays, the survival of a company directly depends on advertising on the web because in this way potential customers can notice them and to get acquainted with their offer at the moment when the company needs it.

People are looking for information about products or services on the Internet, and therefore it is extremely important for small businesses to be present on the Internet.

There should be no sudden change in advertising. Gradually and in small steps, you get the proper ads and the right customers at a reasonable price. The results of the study suggest that European wine production is decreasing and in this way follows the reduction of consumption due to changes in the way of life and the impact of anti-alcohol campaigns. The results of the research in small and medium-sized enterprises in Metohija indicate that the winemakers have huge problems with the placement of wine due to a specific living and business environment, but the owners of the wineries are not fully and sufficiently acquainted with the advantages of the Internet marketing, but also because of poor internet connection they are not able to use these comparative advantages. The results of the survey indicate that online advertising for small enterprises is the most appropriate advertising. It supports a narrowly targeted audience and it has an extremely fast response, which allows continuous, easy adjustment and especially low cost. That is what is needed for small enterprises. Online advertising allows the existence and survival of the rapid growth of the company, and compared with the payment of sales promoters, or preparation and execution of the campaigns, it is far cheaper, faster and more accurate way to target customers.

The greatest potential and challenge for the placement of wines are social media, especially the social network Facebook. What is obvious is that traders will face more competition in the wine market, as wine production from around the world is expected to increase, as well as the introduction of a set of laws on the prevention of alcohol abuse. This gives extra weight to this kind of research among producers and consumers and contributes significantly to increasing enterprise performance and customer satisfaction.

The fact is that society has just passed the threshold of digital transformation and, in this direction before companies in Serbia are new challenges. In the future inexorably comes to linking new technologies and new tools, such as connecting the coffee machines and washing machines to the Internet. There is the period in which advertising will almost completely take care of a multitude of computer algorithms. Internationalization allows us to reach a larger reach and to create a larger market, where online advertising of many audiences is achieved.

In the analysis of users' attitudes towards internet advertising, presented research results in the world generally differ. Some studies have shown that users have a positive attitude towards internet advertising (e.g., Ducoffe, 1996; Previte, 1999), while others show negative attitudes (e.g., Li *et al.*, 2002; Rettie *et al.*, 2003). Most of the research (e.g., Ducoffe, 1996; Brackett and Carr, 2001; Burns, 2003) as the most important factors that will influence the formation of the point of view about Internet advertising or towards the formation of a view on online ads, emphasizes three factors, which are informativity, entertainment and aggressiveness.

Interactivity and credibility factors were also mentioned (e.g., Brackett and Carr, 2001; Wang *et al.*, 2009). Burns (2003) showed in his study that users have different attitudes towards different forms of online advertising. In other words, some forms of online ads are more attractive to users than others. Online advertising is an opportunity that is available to every Internet user for the development of a web browser, but that does not mean that every online advertising user is competitive. It is therefore important to distinguish the benefits and to identify the weaknesses of online advertising business and to take into account its benefits.

Knowledge of certain forms of online advertising affects the viewpoint of users on this form of advertisement. Advertising should attract the attention of the target audience and fulfill the planned objectives. If we want to be contacted by customers, we must be ready for a quick response and quality expert support, advice, things that can be directed, and in the end to solve problems. Users have a more positive attitude towards advanced forms of online ads than on others. Burns (2003) found that users perceived more advanced forms of advertising as entertaining, but at the same time- disturbing. For example, floating ads have proven to be the most fun but also the most annoying form of advertising. The research results show that video ads are the most popular among users in the region. In Serbia, the largest share of advertising costs is still entrusted to television, which is unsustainable for most small enterprises. Therefore, small enterprises are increasingly relying on online pay-per-click advertising, which provides small initial investment and a gradual increase in advertising costs. This is especially important because companies have programs that are strictly focused, because it is absurd to direct ads to the masses.

Large media such as television, radio and print media are not profitable for the company. In this way, you target thousands of clients for just a few responses and you pay are paying too much for that. This can be afforded by large companies that offer consumer goods and well-known brands. On the contrary, online advertising allows low initial costs with narrow targeting to enable us to maintain financial sustainability. Small businesses generally deal with small margins and a limited sales volume, which requires thoughtful consumption for marketing purposes. This can be afforded by large companies which offer consumer goods and well-known brands. In contrast, online advertising allows low initial costs with narrow targeting to enable us to maintain financial sustainability. Small enterprises generally deal with small margins and a limited sales volume, which requires thoughtful consumption for marketing purposes.

Trends in Europe show growth in video advertising. Researchers predict the continued growth of mobile advertising and advertising via social networks. These are advertising potentials. Understanding the success factors of online advertising for entrepreneurs can be of great help if they are aware of the potential effects of individual factors and how to use them.

This is a period in which, according to the forecasts of the research company Gartner, the director of marketing, will invest more in IT, a period in which ICT can not replace marketing experts, but they will have to acquire new skills and to adapt existing business models and to improve IT cooperation. The impact of ICT on marketing communications will be visible, and from year to year, it will be greater. Based on current experience and research, it can be said that online advertising, in combination with personal communication, has been best shown so far because they are complemented very much.

Therefore, it can be concluded that customers can be met via the Internet and confirm our bid, and companies must strive to be at the right time in the right place and offer them what they need, quickly and efficiently, for mutual satisfaction. Although it is difficult for owners of small and medium-sized enterprises in Metohija region to use these sophisticated technologies and advertising tools, it is necessary to include principles and methods of internet marketing in order to solve the problem of placing and selling wine.

See also: Global Economy Increasing by Enterprise Resource Planning

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Optimization of Electrical Energy Usage in Two Secondary Schools Using Different Types of Glass Materials

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Nomenclature

AEC Average energy consumption, kWh

A_f Floor area, m^2

A_g Area of the glass or of the opening in the wall, m^2

$A_{w/r}$ Surface area of the sun-facing wall, m^2

E_c Estimated energy consumption, kWh

E_m Energy consumption per floor area, kWh/ m^2

E_p Energy consumption per person, kWh/person

F_{rc} Reserve factor in cooling

F_t Transmission factor

g_o Outside air moisture content, gkg^{-1}

g_r Room air moisture content, gkg^{-1}

I Solar radiation intensity, W/m^2

N Total number of people present in conditioned space

n Air change rate by natural infiltration, h^{-1}

NP Number of people

P_r Power rating of the equipment, W

P_t Total connected load, W

Q_L Latent heat gain for the occupants, W

Q_{Li} Latent heat gain by natural infiltration, W

$q_{L, person}$ Latent heat gain/person, W

Q_s Sensible heat gain for the occupants, W

Q_{si} Sensible heat gain by natural infiltration, W

$q_{s, person}$ Sensible heat gain/person, W

$Q_{w/r}$ Mean flow of heat through a wall or a roof, W

Q_{window} Cooling load due to solar gains through glass, W

t_o Outside temperature, $^{\circ}C$

t_r Air temperature in the room, $^{\circ}C$

$U_{w/r}$ Thermal transmittance coefficient, $Wm^{-2}K^{-1}$

V Volume of room, m^3

Introduction

Demand and consumption of energy have been increasing drastically due to increasing population, industrial sectors, high-rise commercial buildings, and school buildings. In recent years, Brunei has seen a huge increase in school buildings, where most of these buildings are two stories tall and spaciouly built. Due to this type of building structure, the classrooms and common areas tend to consume significant electrical energy, and this requires architects and civil engineers to revisit the design plan of these buildings to ensure reduced energy consumption. With the aim to assist in efficient building design, monitoring and operation, the relatively new concept of net zero efficient building (ZEB) is getting good attention in the research domain [1]. Energy efficient buildings are often rated better than conventionally designed buildings in indoor climate [2]. Sunikka-Blank and Galvin [3] have investigated energy performance ratings around 3400 German homes. In this research, they found that the occupants consumed, on average, 30% less heating energy than the calculated rating. Marszal *et al.* [4] presented some review-results to facilitate the development of a consistent ZEB definition and a robust energy calculation methodology.

The experience of incorporating energy efficiency, after Hurricanes Katrina and Rita, in four new schools in New Orleans has been discussed in Ref. [5] to help other school districts and design teams with their in-progress and future school building projects in hot-humid climates. The use of Chromogenic in “smart” windows to modify the incoming visible light and solar energy in buildings as well as for other see-through applications has been discussed in Ref. [6], where it has been concluded that the electrochromic (EC) windows seem to be ready for large-scale applications to provide energy efficiency and indoor comfort.

Palmero-Marrero and Oliveira [7] have conducted a general study of the effect of louver shading devices under different climatic conditions, and with the aid of software simulations demonstrated that the use of louver shading devices in the buildings led to comfortable thermal conditions in indoor environment, and might lead to significant energy savings in comparison with the buildings without shading devices.

Zinzi [8] has conducted a study on residential and nonresidential standard building models using cool roof technology. The results demonstrated the potential of this technology to improve the energy performance of Mediterranean residential buildings. Using their analytical model, Wang *et al.* [9] demonstrated that the classroom energy-demands for ventilation and cooling systems could be reduced with the promotion of heat recovery efficiency of the ventilation facility, and in this case, the energy conservation ratio of the air-conditioning unit would decrease with an increase in the temperature of the supplying air.

Santamouris *et al.* [10] dealt with the experimental investigation and analysis of the energy and environmental performance of a green roof system installed in a nursery school building in Athens. The energy performance evaluation showed a significant reduction of the building's cooling load during summer. Moreover, the influence of the green roof system in the building's heating load was found to be insignificant.

Chidiac *et al.* [11] have applied energy retrofit measures (ERMs) to reduce the energy consumption of buildings. They found that heating and cooling loads vary with climate and building characteristics, and react differently to some ERMs. Huang and Niu [12] have studied a superinsulating glazing system, which was formed by two layers of conventional single clear glass panes and a layer of silica aerogel filled in between. Several glazing samples were prepared. The thermal and optical parameters were measured. An annual heating, ventilation, and air-conditioning (HVAC) system energy analysis was also conducted based on the space cooling load simulation. The result indicated that in humid subtropical climates like Hong Kong, the application of silica aerogel glazing system can reduce the annual space cooling load by around 4% in a typical commercial building. They also found that the reduction in envelope heat gain could be around 60%.

Jin *et al.* [13] developed a prototype of phase change material thermal shield (PCMTS) and evaluated its thermal performance in three different locations within the cavity of a typical North American residential wall system using a dynamic wall simulator. The experimental results showed that, compared to a wall without a PCMTS, the peak heat fluxes were reduced by as much as 11%.

In Ref. [14], the authors carried out a survey to gather data that were related to energy consumption in school buildings. The results of this survey were documented in the most diverse fields and units: global energy consumption values, electrical energy consumption, fuel consumption for heating, energy data consumption of schools expressed in annual cost per unit of heated/cooled surface area ($\$/\text{m}^2$) or per unit of heated/cooled volume ($\$/\text{m}^3$) or, finally, as the annual cost per student ($\$/\text{student}$).

Xing *et al.* [15] presented an analysis of energy consumption in 270 schools located in the city of Tianjin, China. The analysis focused specifically on calculating the space heating energy consumption indexes and non-heating energy consumption indexes of different types of schools, aiming at providing reliable and precise data for the government to elaborate policies and measures.

A flexible wireless measurement system for the temperature monitoring of a school building has been proposed in Ref. [16]. Airaksinen [17] studied different schools and day-care centres in southern Finland in terms of their primary energy usage. Here, the author investigated the influence of the design and construction phase to the overall energy performance of the buildings compared to similar existing buildings.

Based on the review works, some alternative glass materials are considered for improving the overall efficiency of the school buildings. As glass materials, Graylite II and Solarcool provide a lower solar heat transmission coefficient and protect the interior including materials, clothes, and their colors from fading by blocking 94% of the sun's ultraviolet energy [18].

In this article, the energy usage by the air-conditioning, lighting, and ventilation systems at two secondary schools in Brunei Darussalam has been investigated, and the results are compared with the standard data sets. In addition, two types of monolithic glass materials have been proposed for windowpanes with the aim to optimize the electrical energy usage.

Climate in Brunei Darussalam

The country Brunei Darussalam is located 4 degrees north of the Equator. Due to this location, the weather is persistently hot and humid as shown in Table 1. The average temperature varies little year to year. The average temperature was found to be 27.6, 28.3, and 26.8°C for the years 2012, 2013, 2014, respectively. The wind direction is generally from south to south west. Since Brunei Darussalam is located near the Equator, the solar radiation remains more or less constant as can be seen in Table 1.

Data Collection

Building Physical Data

The two schools, SA and SB, were selected from the Sengkurong subdivision of Brunei-Muara district of Brunei Darussalam. These two schools are not connected to the local renewable energy system network. Most of the schools have more than two buildings, which consist of the administrative block, multipurpose hall, prayer hall, academic block, and science block. From architectural plans, the data, such as the orientation of buildings, floor space, and wall and window areas, can be found, and the type of materials used for construction can also be obtained. The floor space area used in SB is bigger than SA, and the spaces between the buildings are also roomy. Whereas, SA is confined to a much smaller expanse when compared to SB. Two types of windows along with glass materials are shown in Figs. 1 and 2.

Table 1 Average climatic data

Year	Wind speed (m/s)	Wind direction	Temperature (°C)	Solar radiation W(Kw/m ²)	RH (%)
2012	2.52	South and south west	27.6	5.16	81.3
2013	2.54		28.3	5.17	81.6
2014	2.48		26.8	5.15	81.4



Fig. 1 A first kind of window with a glass material.



Fig. 2 A second kind of window with a glass material.

Table 2 Total connected load for school A (SA) and school B (SB)

<i>Appliances</i>	<i>Connected load (kW)</i>	
	<i>SA</i>	<i>SB</i>
Air conditioning	830.8	2358.92
Lights	157.886	155.5
Ventilation	18.773	21.904

Electrical Power Rating

The power ratings used in the schools can be obtained from the electrical plan layout. The electrical plan layout shows the power ratings for air-conditioning, ventilation, and lighting systems. [Table 2](#) shows the total connected load for SA and SB.

Electrical Consumption

The electrical consumption data were collected from the DES, which are shown in [Tables 3](#) and [4](#) for SA and SB, respectively.

Table 3 Total consumption for school A (SA)

<i>Month</i>	<i>Consumption (kWh)</i>
June-14	11,290
July-14	11,290
August-14	11,290
September-14	11,290
October-14	11,290
November-14	9,150
December-14	9,150
January-15	9,150
February-15	9,150
Total	93,050

Table 4 Total consumption for school B (SB)

<i>Month</i>	<i>Consumption (kWh)</i>
June-14	124,714
July-14	124,714
August-14	124,714
September-14	127,714
October-14	127,714
November-14	127,714
December-14	127,714
January-15	127,714
February-15	124,708
Total	1,137,420

Methodology

Proportion of Energy Used in Schools

The estimated energy consumption can be calculated using the following formula:

$$E_c = \frac{P_r}{P_t} \times \text{AEC} \quad (1)$$

Cooling Load Estimation

The building orientation, weather condition, building spacing, and building materials need to be known to estimate the cooling load of any building. Brunei Darussalam has an equatorial climate characterized by a uniform high temperature, high humidity, and heavy rainfall. Temperatures range from 23 to 32°C, while rainfall varies from 2500 mm annually on the coast to 7500 mm in the interior.

To cool down a room space it is required to remove heat from three main sources. The heat generated by these three sources are, namely, heat gain through wall and roof, solar radiation through windows, and heat generated by the occupants. The heat gains through walls or roofs are assumed to be under steady-state conditions and the heat gain can be calculated as,

$$Q_{w/r} = U_{w/r} A_{w/r} (t_o - t_r) \quad (2)$$

The room air temperature at the air-conditioned space and fans are found to be 25 and 29.1°C, respectively. The outside temperature is found to be 31°C. According to design, the thicknesses of the wall for SA and SB are found to be 120 and 125 mm, respectively. The U-value of the brick wall for both schools is assumed to be 2 W/m²K. The surface area of the wall is calculated after deducting the area occupied by the windows.

The heat gain through windows can be calculated as,

$$Q_{\text{window}} = I \times F_t \times A_g \quad (3)$$

The heat gain from occupancy or people is calculated by the following equations:

Sensible heat gain from occupants is

$$Q_s = q_{s,\text{person}} \times N \quad (4)$$

Latent heat gain from occupants is

$$Q_L = q_{L, \text{person}} \times N \quad (5)$$

Heat gains by natural infiltration may be calculated using the following equations:

$$Q_{si} = 0.33nV(t_o - t_r) \quad (6)$$

$$Q_{Li} = 0.8nV(g_o - g_r) \quad (7)$$

The air moisture content in this equation can be obtained from the psychrometric chart by connecting the wet bulb and dry bulb temperature of the room air and the outside air on the chart to find the specific humidity. The values of the wet and dry bulb temperatures can be obtained from the psychrometer.

To take a reading, the instrument is opened by withdrawing the inner frame from the case. Then it is thoroughly wet by placing the exposed end under cold running water for about 30 s. To take a reading, the psychrometer handle is held vertically and is rotated for about 60 s at a rate of two to three revolutions per second. After the revolution is completed, the wet and dry bulb temperatures are noted.

Consumption per Meter Square and per Person

By calculating energy consumption per meter square and per person, the amount of energy consumption used by air-conditioning, ventilation, and lighting systems for floor space area and per person can be found. These data values help to determine whether the schools use the right amount of energy or more energy. These energy values are calculated using the following equations:

$$E_m = \frac{E_c}{A_f} \quad (8)$$

$$E_p = \frac{E_c}{NP} \quad (9)$$

Results and Discussion

The total consumption of electrical energy used is split into three major divisions. These are air-conditioning, lighting, and ventilation. The air-conditioning system in a building will certainly reduce the effect of heat and produce comfortable dry air. The rate of direct sunlight penetration can be reduced through good orientation of the school building. The intensity of the light entering the building will affect the rate of energy consumption of the building. With no wind movement, the heat will accumulate in the building, thus the heat gains will be more. The percentages of energy used by air-conditioning, lighting, and ventilation (fan) components in SA and SB are shown in Figs. 3 and 4, respectively (from Eqs. (2)–(7)). From Figs. 3 and 4, it is observed that the major contributor of energy consumption is the air-conditioning system. The percentages of energy used by the air-conditioning system are 83 and 93% for SA and SB, respectively.

This is because of the short façades of SA, facing east and west, which enabled less entry of direct sunlight compared to SB. Moreover, since different buildings of SA are in close proximity to each other, direct sunlight rays are mostly blocked by the adjacent buildings, which in turn reduces heat entry to a number of rooms of the buildings in SA. Also, the total sun-facing surface area of the wall, window, and roof for the entire building for SB is greater than SA. It means the heat gains by SB through the wall, window, and roof is greater than SA. Since the air-conditioning system consumes the major portion of the total consumed energy, it is therefore important to look into the operation and maintenance schedule of this system carefully to achieve better efficiency.

Using Eqs. (2)–(7), the cooling load requirement for SA and SB are found to be 773.35 and 1337.25 kW, respectively.

The reserve factor for the cooling system can be calculated as,

$$F_{rc} = \frac{P_t}{P_d} \quad (10)$$

From the cooling load calculation, it is found that the reserve factor for cooling for SA and SB are 1.08 and 1.77, respectively. It means that the reserve factor for SA is reasonable. For SB, the calculated value is found to be very high. From this calculation, it is found that most of the cooling equipment in SB is unutilized. This anomaly needs to be investigated further.

The air-conditioning (AC) power consumption data gathered from SA and SB are compared with similar data collected from schools in Canada (SC) and Ireland (SI), as shown in Fig. 5. The AC power consumption in SA is comparable with SC and SI, whereas, this consumption in SB is much higher than SC and SI as can be seen in Fig. 5. This condition can be explained as follows.

Most of the long façades of the buildings in SA are facing east and west, whereas, the long façades of SB are facing toward north and south. The right orientation for long façades of the building is to face toward east and west. The operation hours of the schools are from 8 am to 4 pm. The average cooling load factors for that time for a building with an orientation with east, west, north, and south are 0.41, 0.34, 0.57, and 0.81, respectively. In view of the above, the cooling load factors for SA are lower than SB. Also, as SB is more spacious, it is possible that the infiltration losses are more in SB when compared to SA. As such, from the above

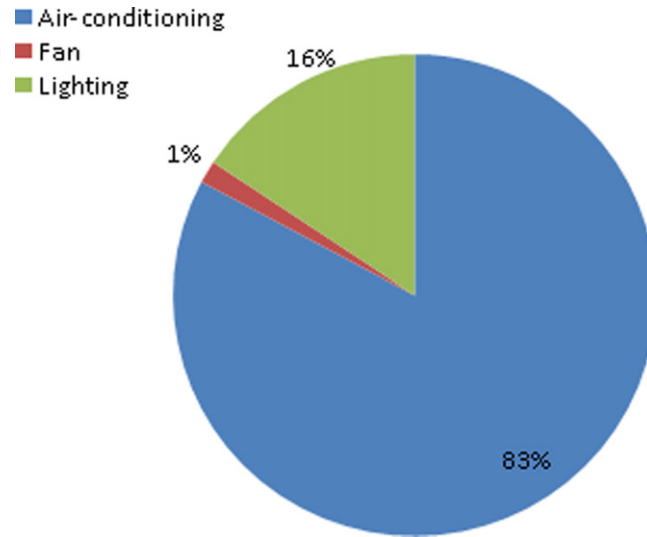


Fig. 3 Energy consumption in school A (SA).

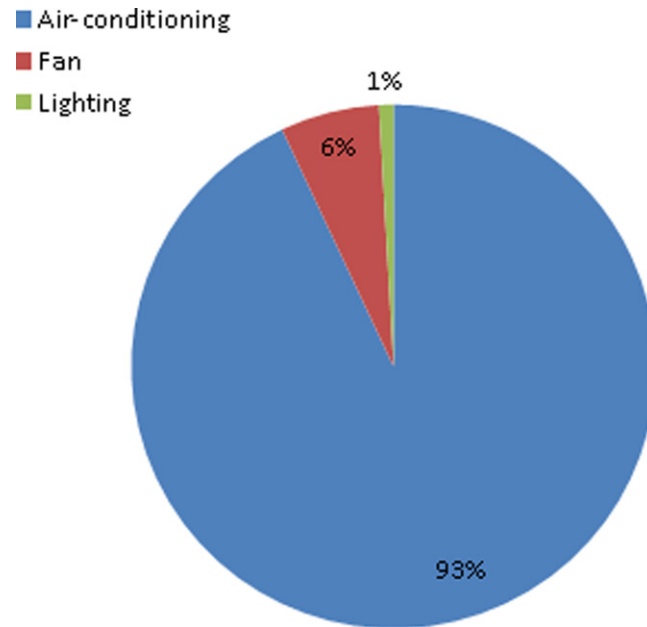


Fig. 4 Energy consumption in school B (SB).

explanation, it is obvious that SA should have a lower AC power consumption than SB. The major contribution toward the heat gain is through the roofs, windows, and the walls of the buildings. The percentage of area for the windows of SA and SB are calculated from Table 5 as,

$$SA = \frac{139.08}{1656.58} \times 100 = 8.40\%$$

$$SB = \frac{427.28}{3270.03} \times 100 = 13.07\%$$

Whereas, with standard glass windows, the percentage of heat gain through the window for SA and SB are calculated from Tables 6 and 7 as,

$$SA_{Normal} = \frac{29532.2}{57725.6} \times 100 = 51.16\%$$

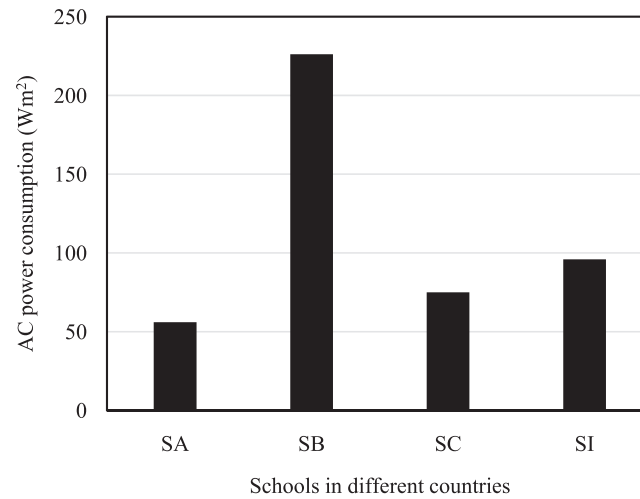


Fig. 5 Comparison of air-conditioning (AC) power consumption in different countries.

Table 5 Area of major contributors for heat gain

Item	School A (SA) (m ²)	School B (SB) (m ²)
Roof	1207.8	2335.75
Window	139.08	427.28
Wall	309.7	507
Total	1656.58	3270.03

Table 6 Heat gain through the major contributing items of school A (SA)

Item	SA (W)		
Window	29,532.2 ^a	5026.94 ^b	2513.47 ^c
Wall	3716.56	3716.56	3716.56
Roof	1811.7	1811.7	1811.7
Infiltration	14,040.14	14,040.14	14,040.14
Occupants	8625	8625	8625
Total	57,725.6	33,220.34	30,706.87

^aNormal glass.

^bGraylite II.

^cSolarcool.

Table 7 Heat gain through the major contributing items of school B (SB)

Item	SB (W)		
Window	90,772.56 ^a	15,442.58 ^b	7721.29 ^c
Wall	6084	6084	6084
Roof	3503.62	3503.62	3503.62
Infiltration	29,195.89	29,195.89	29,195.89
Occupants	9000	9000	9000
Total	138,556.07	63,220.34	55,504.80

^aNormal glass.

^bGraylite II.

^cSolarcool.

Table 8 Energy usages with new glass materials

Glass type (1/4")	Transmission factor	SA (%)	SB (%)
Graylite II	0.08	15.13	24.42
Solarcool	0.04	12.10	13.91

$$SB_{Normal} = \frac{90772.56}{138556.1} \times 100 = 65.51\%$$

Therefore, close attention in choosing the window materials is required for optimizing electrical energy usage. The heat energy gain through the window was calculated using standard windowpanes with a transmission factor of 0.47. In this case, there is a need to search for a glass material with a low transmission factor. Two types of glass materials, namely, Graylite II (1/4") and Solarcool (1/4") [18], with their lower transmission factors are used to optimize the energy usage whose basic characteristics have been outlined below [18].

Graylite II [18] is an uncoated glass with a very low solar heat gain coefficient. It provides ideal brightness control and privacy glazing with visible light transmittance of 12%. This type of glass can be heat-strengthened, tempered, and laminated and is readily available as a standard product. It delivers optimum levels of solar control together with a fashionable, nearly black appearance.

Solarcool glass [18] has been a popular choice for commercial structures because of its cool, light-gray appearance and ability to control solar heat gain and glare. This type of glass may also be combined with other types of glasses to improve the solar heat gain performance and lower U-values. It has light-gray color, which makes it an attractive choice in combination with almost any other exterior cladding material. The properties of Graylite II and Solarcool glasses are mentioned in Table 8 [19,20].

Both of the aforementioned glasses might contain calcium fluoride (CaF₂) and Suprasil (fused silica), which can reduce the ultraviolet ray and physical light transmission significantly.

The heat gain through the windows of SA using Graylite II and Solarcool can be obtained as,

$$Q_{window} = I \sin \alpha \times t_f \times A_{wi} = 493 \sin (66.4) \times 0.08 \times 139.09 = 5026.94 \text{ W}$$

$$Q_{window} = I \sin \alpha \times t_f \times A_{wi} = 493 \sin (66.4) \times 0.04 \times 139.09 = 2513.47 \text{ W}$$

The heat gain through the windows of SB using Graylite II and Solarcool can be obtained as,

$$Q_{window} = I \sin \alpha \times t_f \times A_{wi} = 493 \sin (66.4) \times 0.08 \times 427.28 = 15442.58 \text{ W}$$

$$Q_{window} = I \sin \alpha \times t_f \times A_{wi} = 493 \sin (66.4) \times 0.04 \times 427.28 = 7721.29 \text{ W}$$

The percentage of heat gain through the window for SA with Graylite II and Solarcool can be calculated from Table 6 as,

$$SA_{Graylite II} = \frac{5026.94}{33220.34} \times 100 = 15.13\%$$

$$SA_{Solarcool} = \frac{3716.56}{30706.87} \times 100 = 12.10\%$$

While the percentage of heat gain through the window for SB with Graylite II and Solarcool can be calculated from Table 7 as,

$$SB_{Graylite II} = \frac{15442.58}{63220.34} \times 100 = 24.42\%$$

$$SB_{Solarcool} = \frac{7721.29}{55504.80} \times 100 = 13.91\%$$

The above percentage of heat gain values have been recorded in Table 8.

The intensity of illumination for SA and SB is found to be 720 and 1005.75 lux, respectively. However, according to standard, the intensity of illumination recommended in workspaces is around 250–500 lux/m². Comparing the calculated results with the standard values, it is found that both schools illuminate the workplace using more than the required standard value. This energy wastage in illuminating the school spaces results in a negative impact on the overall energy efficiency of both schools.

The energy usage in ventilation per person for SA and SB is found to be 5.5 and 38.25 W, respectively. According to ASHRAE 62.2 [21], the ventilation requirement is 7 L/s per person. Using standard air pressure of 1 kPa and density of 1.2 kg/m³, the fan power is calculated to be around 7 W. After comparison, it is found that SA uses close to the required calculated power for ventilation, whereas, SB uses 5.5 times more than the required power. Since the air-conditioning system consumes the majority of the energy, it is necessary to look into its operation, maintenance schedule, and user awareness to achieve better efficiency.

A survey comprising 12 questions on energy efficiency and awareness on usage was conducted among the teachers and students of SA and SB. The result from this survey has shown that the majority of the participants agree that energy saving is important. The results also show that the majority of the participants switch off their appliances when they are not in use. However, the majority of the participants reportedly switched off their air-conditioning system only occasionally during the rainy weather when the temperature of the air is usually low. According to the survey, 80% of passage lights including toilets, corridors, etc. were seen to be

Table 9 Properties of Graylite II and Solarcool glass materials

	<i>Transmission factor</i>	<i>Heat gain coefficient</i>	<i>Shading coefficient</i>	<i>Outdoor visible light reflectance</i>	<i>U-value summer</i>
Graylite II	0.08	0.34	0.25	0.04	0.50
Solarcool	0.04	0.58	0.67	0.14	0.50

turned off in SA, whereas that number was found to be 58% for SB. The average power consumptions for SA and SB were found to be 10,338.89 and 126,380 kWh, respectively. The calculated standard deviations for those schools were 106.375 and 1491.458 kWh, respectively. The standard deviations were 1 and 0.1% of the average energy consumptions for SA and SB, respectively. This means that the 95% energy consumption is within a ± 2 and $\pm 0.2\%$ range for SA and SB, respectively. Since the weather conditions in Brunei vary very little throughout the year (see Table 1), it is expected that the variation of electricity consumption over the year will be within a narrow range, which is evident from the aforementioned numbers. The values of the median and the mode for the energy consumptions for both schools were found to be equal. It means that the overall power consumption for both schools is *normally* distributed (Table 9).

Conclusions

Two secondary schools, SA and SB, were considered for investigating the electrical energy usage. It is found that the air-conditioning system consumes the most energy, amounting to 83 and 93% of energy for SA and SB, respectively. Comparing with SA, SC, and SI, it is concluded that SB is using significant power in its air-conditioning system due to its physical orientation. Although the percentage of areas of windows are smaller (8.40 and 13.07% for SA and SB) compared to the other contributing items in the energy consumption, the windows were found to be the major contributing factors toward the air-conditioning load, which was 51.16 and 65.51%, respectively. It has been found that the percentage of electrical energy usage can significantly be reduced to 15.13 and 24.42% using Graylite II for SA and SB, respectively, while these numbers can further be reduced to 12.10 and 13.91%, respectively, with the use of Solarcool glass material. The illumination of the schools is found to be higher compared to the standard values. In addition, it is suggested that a provision can be made to allow sunlight to enter the building through smart electronic glazing, which will further reduce the power used to illuminate both the schools. The energy usage for ventilation in SA is close to the standard value where it is 5.5 times more in SB. The higher energy usage in SB due to ventilation requirements has to be further investigated. Survey results on energy usage show that there is less awareness in the use of lights in the less frequently used areas such as passages, toilets, etc. From the statistical analysis, it is found that the energy consumption for both schools follows the normal distribution.

Acknowledgments

The authors gratefully acknowledge the contribution of all the reviewers, including Sabah Yazdani and Henry Siddiq Lan, for their valuable comments in preparing this article.

See also: 100% Renewable Energy by Renewable Materials. Energy Efficiency Analysis in Building Walls in Tropical Climate Using Thermal Insulation System. Sustainable Materials for Energy Conversion

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An Overview of the Global Ship Recycling Industry

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Introduction

This article presents an overview of the ship recycling industry and the relevant international regulations governing the recycling of end-of-life (EOL) ships. The industry overview is presented by providing insight into three Ws – when, why, and where ship recycling is carried out. This article also provides an insight into the methods used for recycling, transaction terms and conditions, and the historic volumes of EOL ships globally. This discussion is followed by an extensive overview of the material composition of EOL ships. The regulatory overview is presented by discussing the provisions of the Basel Convention, the Hong Kong Convention (HKC), and European Union (EU) ship recycling regulation. The final section of the article explains what green ship recycling is and what criteria, based on the international regulations, can be used to identify a green ship recycling yard.

Industry Overview

When and Why Are Ships Recycled?

The answer to why ship recycling is carried out is rightly put by [Stopford \(2009\)](#) as “scrapping will occur only when the industry’s reserves of cash and optimism have been run down.” Ship recycling is carried out to remove inefficient ships from the market, which in turn generates cash flow for ship owners and tackles oversupply of ships in the freight market. Ship recycling, besides being a business decision for the ship owners, is also necessary for the continued renewal of the shipping fleet. Naturally, the oldest ships are removed first due to their high maintenance costs.

A large-scale scrapping of ships is carried out only when the entire shipping industry does not anticipate any prospects of employing ships profitably in the foreseeable future or when the companies need cash urgently ([Stopford, 2009](#)). According to [Buxton \(1991\)](#), scrapping is the most attractive option for the ship owners when the prospects of anticipated profitability of a ship are poor and the second-hand prices are correspondingly low. If the market is expected to improve before the technical life of the vessels ends, they are usually laid-up in anchorage outside a port instead of recycled.

The decision to recycle a ship is based on the following factors ([Buxton, 1991](#); [Stopford, 2009](#)):

1. obsolescence,
2. current earnings,
3. future market expectations, and
4. scrap prices.

These factors regulate the demand and supply dynamics of both the ship recycling market and the freight market because most ships that are taken out of the freight market are supplied to the ship recycling market. In one way or the other, these factors affect the finances of a shipping company as explained in the subsequent sections.

Obsolescence of ships

Obsolescence of a ship depends on several factors including physical, technical, and regulatory. Therefore, a wide range of ages of the ships sent for recycling can be observed in the datasets recorded for ship recycling. For example, [Buxton \(1991\)](#) observed a minimum age of 8 years and a maximum age of 80 years for the 248 ships scrapped in 1984. The average age of the ships sent for scrapping is generally considered to be about 25–30 years ([Kagkarakis et al., 2016](#)). However, [Knapp et al. \(2008\)](#) determined the average age of ships at which they are recycled as 22 years, based on a dataset of ships over 100 gross tonnage (GT) recycled over a period of 7 years from 2000 to 2007.

Physical obsolescence

The physical deterioration of ships due to aging is a natural process that takes place gradually. As the ship grows old, wear and tear of its hull and machinery increases. Therefore, the ship owners are required to spend an increased amount of money on the routine repair and maintenance of the older ships, making them costlier to operate. The repair and maintenance costs are high especially during the fourth and fifth special surveys of the ships. The special surveys are carried out every 5th year of operation for renewing the class certificate of the ship. It includes in and out-of-water inspection of the ship’s hull to verify its structural integrity and conformance of ship’s systems, machinery, and equipment with the applicable class rules ([IACS, 2011](#)). This docking is usually expensive both in costs and foregone income. The phenomenon of deterioration of a ship’s hull and/or machinery to such an extent that it becomes unworthy of repair is called as physical obsolescence ([Buxton, 1991](#)).

Technical obsolescence

The technical obsolescence is indicated by a ship, which, despite being physically sound, is no longer profitable to remain in service due to increased competitiveness by a more efficient ship type. As a result, such ships are likely to be scrapped. For example, three Batillus class VLCCs (550,000 T deadweight) were scrapped in the mid-1980s at the age of 7–10 years due to the lack of route and trade flexibility available in the smaller vessels, amidst the reduction of parcel sizes well below their maximum capacities due to the fragmentation of crude oil supplies (Buxton, 1991). Similarly, the tankers powered by inefficient steam turbines were gradually replaced by the ships powered by fuel-efficient diesel engines by the 1980s (Buxton, 1991; Stopford, 2009). Some ship owners of container ships even resorted to retrofit the 1970s built container ships with the diesel engines to replace the steam turbines (Evans, 1989). The scrapping of multideckers in the late 1960s due to the containerization is also an eminent example of technical obsolescence (Stopford, 2009).

Regulatory obsolescence

The scrapping of ships due to regulatory requirements can be defined as regulatory obsolescence. For example, a phase-out schedule for single-hull tankers entered into force in 2005 as amendments to Annex 1 of the MARPOL convention (IMO, 2016). It was enforced after a series of accidents involving tankers leading to massive oil spills resulting in irreparable environmental damage, to reduce the risk of oil spills from tankers involved in low energy collisions or groundings. It required the tankers of single-hull construction to phase out or convert to a double hull by a proposed deadline based on their year of delivery. The schedule decided by the International Maritime Organization (IMO) ensured that all single-hull tankers were phased out by the end of 2010.

Port state controls, vetting inspections, statutory surveys, etc. are other such regulatory issues that affect the supply of ships in the demolition market. These issues force ship owners to decide on whether to invest in the maintenance and continue operating a ship or to sell it either for scrapping or in the second-hand market (EC, 2004).

Current earnings and market expectations

Beside the above mentioned clear indicators of low earnings, the market itself can also be depressed. Therefore, the current earnings and future market expectations are two important factors, based on which ship owners decide whether or not to continue trading a vessel in the shipping market. The low earnings either due to high operating costs or due to low freight rates cause a decline in the profitability of running a vessel. This dictates that a ship owner put certain cost-cutting measures in place; for example, slow steaming, laying up ships for a certain period of time, converting ships to suit alternative trades, etc. After exhausting all cost-cutting measures, a ship owner is left with two main options: one, continue to operate in the market incurring losses, expecting freight rates to improve in the near future; and two, sell either in the second-hand market for continued trading by another owner or in the ship recycling market for dismantling and recycling (Buxton, 1991).

A ship owner's decision to continue operating the unprofitable ship during a recession, based on his expectations of higher freight rates in future may be justified because the earnings during a freight rate boom are so great that they can overcome the loss incurred by operating in the market experiencing a slump in freight rates (Stopford, 2009). The ship owner's expectations of lower freight rates for a long period of time may force him to sell his ship. The decision to select the recycling market over the second-hand market to sell a ship is based on its selling ability and market value in the second-hand market. When either the scrap value is more than the market value or there is no buyer in the second-hand market, the ship is likely to be sold in the recycling market (Stopford, 2009).

A low freight rate scenario can be seen during the times of high supply and low demand of ships for transportation. A larger supply of ships than is required by the market always creates pressure on the freight rates. The continued imbalance between the demand and supply of ships brings the freight rates down to such low levels that ship owners cannot operate their ships profitably and resort to scrapping the old ships. This was recently observed in the dry bulk market. During the period from November 2014 to June 2015, Baltic Dry Index (BDI), representing the bulk freight rates, declined continuously from the levels of 1450 to about 580 (Fig. 1), which led to a record ship breaking activity of 10.9 million deadweight tonnes in the second quarter of 2015 (Clarksons, 2016). Similarly, continued depressed levels of BDI from a high of 1200 in August 2015 to a low of 290 in February 2016 (Fig. 1) led to an extensive ship demolition of about 10.1 million deadweight tonnes in the first 3 months of 2016 (Clarksons, 2016). The continued demolition of bulk carriers in 2015 and 2016 led to a reduction in the average scrapping age for bulk carriers from 33 years in 2007 to 24 years so far in 2016 (Clarksons, 2016).

The scenario of the large-scale scrapping of ships can be seen during the times of recession when the economic growth rate is low. In such a scenario, the demand of ships for maritime transportation is low because it is a derived demand and depends largely on the amount of cargo required to be transported, which is affected by the economic growth rate. This means that during a low gross domestic product (GDP) growth rate, a lesser amount of cargo is available for transportation. Therefore, a lower number of ships are required. In such a scenario, more and more ships are available for recycling due to an imbalance created between the demand and the supply of the ships for transportation. This is clear from Fig. 2, which depicts the number of ships recycled every year from 2002 to 2014 superimposed with the GDP growth rates of various countries and the world. The most notable point on the graph (Fig. 2) is 2009 when the world GDP growth rate was negative and the number of ships recycled touched the 1600 mark, which was a record at that time. This record was later surpassed in 2012 due to continued low levels of freight rates and GDP growth rates across the ship types and the countries, respectively. The high amount of ship recycling activity seen in 2009 is partly attributed to the regulatory obsolescence.



Fig. 1 Baltic Dry Index (BDI) from September 2014 to August 2016. Chart courtesy of StockCharts, 2016. Baltic dry index. Available at: [http://stockcharts.com/h-sc/ui?s=\\$BDI](http://stockcharts.com/h-sc/ui?s=$BDI) (accessed 01.09.16).

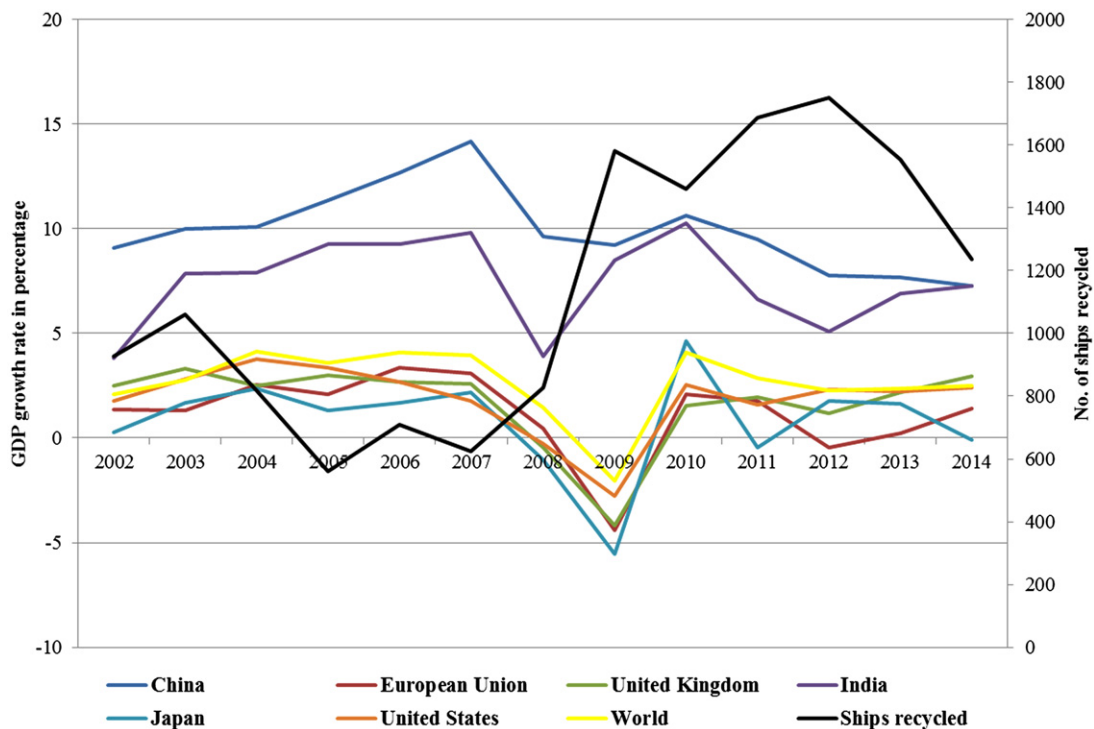


Fig. 2 Gross domestic product (GDP) growth rates of various countries and the world vs. the total number of ships above 100 gross tonnage (GT) recycled globally. Based on the data from World Bank and The Ship Builders' Association of Japan.

Scrap prices

Scrap prices do not play a very important role in the ship owner's decision on when to scrap a vessel as much as in a decision on where to scrap a vessel (EC, 2004). The most important driver, as discussed before, is the operational cost of a vessel at the given level of the freight rates. A ship operating unprofitably with no expectation to be profitable in the near future is likely to end up in a ship recycling yard for scrapping even at a low scrap price. However, the decision to scrap a ship can be delayed slightly if an

increase in the scrap prices is anticipated in the short term. A ship recycling yard offering a high price for buying an EOL ship is always attractive to the ship owners. The offer price of an EOL ship depends on several global, local, and other factors.

The most basic economic concepts of supply and demand form the *global factors* affecting the offer price of EOL ships. In the ship demolition market, the supply of obsolete ships is influenced by the decision of ship owners to scrap their ships, whereas the demand is mainly influenced by the demand for scrap steel in the steel-making industry (Kagkarakis *et al.*, 2016; Sujaudhin *et al.*, 2016). The high supply of obsolete ships in the demolition market coupled with a low demand for scrap steel lowers the offer price, while a low supply of ships during a high demand for scrap steel results in a high offer price (Jain *et al.*, 2016). However, there is a limit to which the offer price responds to the supply and demand forces of the ship demolition market because the demand for EOL ships is an indirect demand that is created due to the demand for scrap steel in the steel-making industry.

The global ship recycling yards are just one source of scrap steel, and contribute only about 1.5% of the global needs of the steel-making industry for scrap steel (Mikelis, 2013b). The demand for scrap steel is also fulfilled by other sources, such as EOL vehicles, construction waste, other obsolete products, and scrap generated at steel mills and factories producing finished goods. Therefore, other markets influence the price of scrap steel much more than the amount of ships offered for recycling mainly due to their relatively small quantity. Hence, the offer price to buy an EOL ship is dictated by the price of scrap steel rather than the demand and supply dynamics of the ship demolition market, as also demonstrated by Kagkarakis *et al.* (2016) in a research on forecasting the scrap price of EOL ships.

The local factors influencing the offer price of EOL ships include health, safety, and environmental standards of a ship recycling yard, end use of scrap steel (melting or rerolling), demand for other recyclable items (nonferrous scrap, used machinery, furniture, etc.) in the market, labor wages, waste disposal costs, taxes, and recycling method employed (beaching, slipway, alongside, drydock) (EC, 2004; Jain *et al.*, 2016; Sarraf, 2010).

The other factors affecting the offer price are distance from the last port of call of the ship and the recycling yard, contractual terms and conditions, such as “on delivery” and “as-is, where-is,” hull configuration in terms of complexity, ship's compatibility with the recycling yard in terms of size and draft restrictions, and items remaining on board, such as bunkers, waste oil, spares, etc. (Jain *et al.*, 2016).

The current average offer prices (March 2017) as obtained by GMS (2017) are in the range of 320 \$/LDT for the Indian subcontinent, while for China and Turkey they are about 270 \$/LDT and 210 \$/LDT, respectively.

Where Are Ships Recycled and in What Quantity?

The ship recycling industry has historically been a mobile industry. It has witnessed a geographical shift through time in the quest for low labor costs and high regional demand for scrap steel (Kagkarakis *et al.*, 2016).

The industry was initially established in the highly industrialized countries, such as the United Kingdom, United States, and Japan when damaged ships were dismantled after the Second World War (Kagkarakis *et al.*, 2016; Stopford, 2009). Subsequently, it moved to Mediterranean countries, such as Spain and Turkey, due to stringent labor safety rules and environment protection laws (Kagkarakis *et al.*, 2016; Sujaudhin *et al.*, 2015). Japan remained a major player till the early 1990s (SAJ, 2009).

In the 1970s, the ship recycling industry started moving to Asian countries, such as Taiwan, China, and South Korea. By the mid-1980s, when scrapping was very high, the industry in these countries peaked with almost three-quarters of the global ship breaking business acquired by them (Stopford, 2009). Although China and South Korea entered the ship breaking business later than Taiwan (in the early 1980s), they quickly became leading buyers of EOL ships for scrap (by the mid-1980s) (SAJ, 2009).

The decline of industry in South Korea started in the late 1980s (Fig. 3) when the wages rose and the shipbuilding industry expanded. At the same time, as the economy grew and labor costs increased in Taiwan, the industry became unattractive and most yards were closed by the early 1990s. China, on the other hand, continued operating its demolition yards albeit with a steady decline in the market share due to government regulations controlling currency for purchasing ships and environmental regulations (Stopford, 2009). Although its market share fell from 23% in 1986 to 9% in 1995 and 3% in 2005, it remained in the top five in most years to date (SAJ, 2009; Stopford, 2009).

The withdrawal of Taiwan, South Korea, and Japan and the decline of China from the demolition business from the late 1980s to the early 1990s moved the industry gradually toward the Indian subcontinent (Fig. 4). The subcontinent countries, such as India, Pakistan, and Bangladesh, had a negligible market share before the 1980s but they witnessed steady growth through the 1980s and 1990s till today (SAJ, 2016). The ship recycling industry flourished greatly in these countries in the last three to three and a half decades.

The growth trends of the global ship recycling industry show that since 1993, the industry is concentrated mainly in five countries, namely India, Pakistan, Bangladesh, China, and Turkey (Fig. 4). The level of activity in these “top five” countries varies from year to year and depends on the number of ships available for scrapping. They have regularly shared 97–98% of the EOL tonnage for the last 15–20 years (Mikelis, 2013b; SAJ, 2016). However, the fluctuations in market share of these countries are highly prominent. Turkey is the smallest of the top five recycling states in terms of the annual tonnage recycled but it recycled almost equal or more tonnage than the rest of the world in the recent past.

The last 5-year trend of the top five countries versus the rest of the world in terms of percentage of total tonnage (LDT) recycled is shown in Fig. 5. An interesting observation from this figure is that subcontinent countries – India, Pakistan, and Bangladesh have invariably accounted for at least two-thirds of the global ship recycling activity.

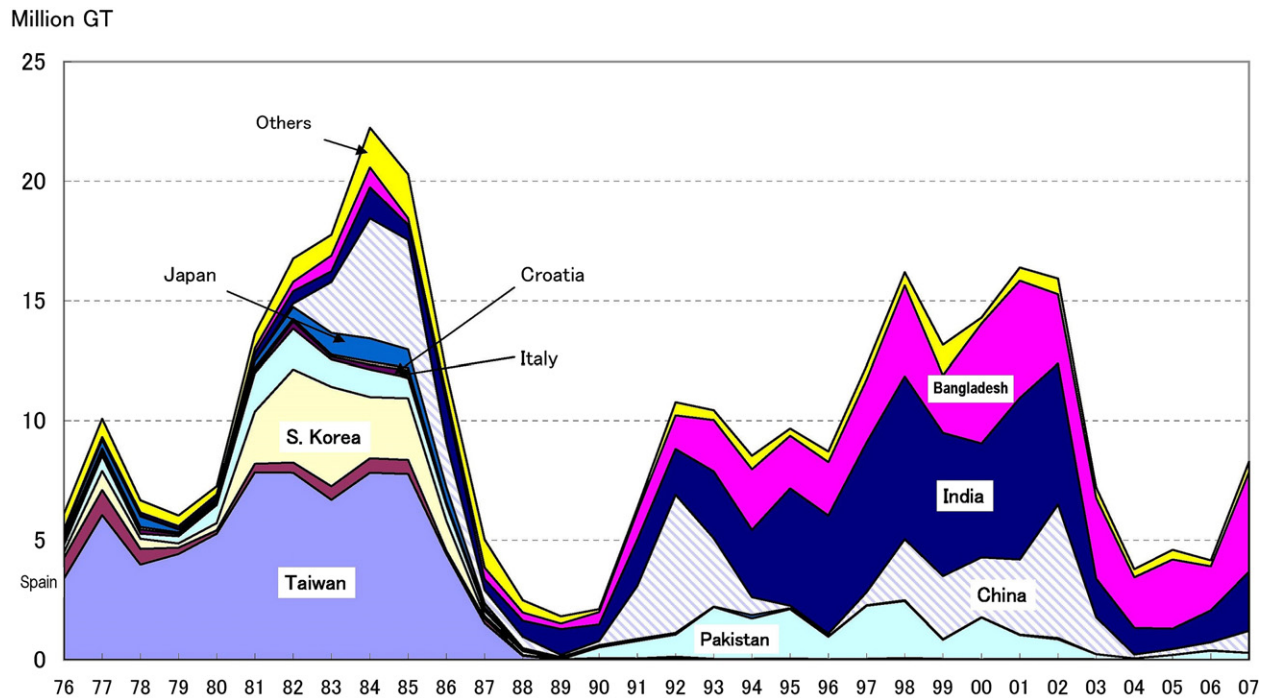


Fig. 3 Growth of ship recycling industry from 1976 to 2007 in various countries in terms of million gross tonnage (GT) of ships recycled. Courtesy of SAJ, 2009. Shipbuilding statistics March 2009. The Ship Builders' Association of Japan.

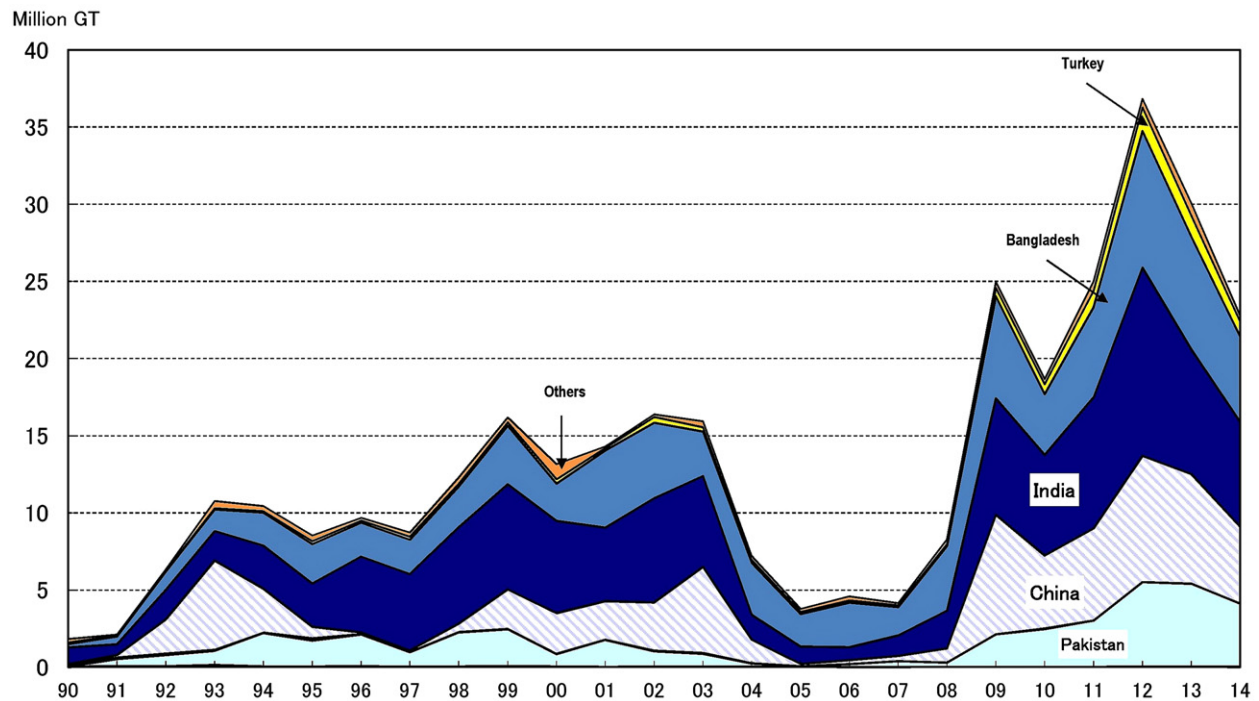


Fig. 4 Growth of ship recycling industry from 1990 to 2014 in various countries in terms of million gross tonnage of ships recycled. Courtesy of SAJ, 2016. Shipbuilding statistics March 2016. The Ship Builders' Association of Japan.

The ship recycling sites in each of the five major countries are clustered in a particular region. The sites in Pakistan are mainly located near Karachi at Gadani Beach situated in Balochistan province, while the sites in Bangladesh are located on the 18-km Sitakunda coastal strip situated north of the port of Chittagong. The Indian recycling sites are located in Alang in the state of Gujarat situated on the west coast, while the Turkish recycling sites are located in Aliaga, a town situated on the Aegean Sea, 60 km

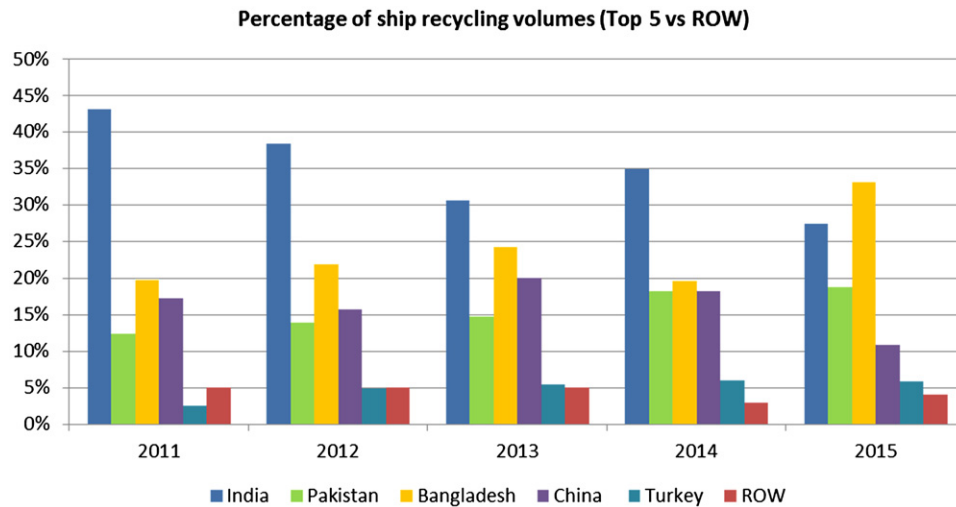


Fig. 5 Ship recycling volumes in the top five countries and rest of the world in percentage of total tonnage (LDT) recycled. Author based on Robin des Bois, 2006–2016. Shipbreaking – Bulletin of information and analysis on end-of-life ships. Available at: <http://www.robindesbois.org/en/a-la-casse-bulletin-dinformation-et-danalyses-sur-les-navires-en-fin-de-vie/>.

north of Izmir port. The ship recycling in China is performed mainly in two locations – yards located along the Yangtze River in North, close to Shanghai and yards located along the Pearl River in South, in Guangdong Province. Some yards are also located close to Tianjin, North of Shanghai.

A small number of shipbreaking companies are also scattered in the United Kingdom, United States, Canada, and European countries, such as Spain, Belgium, The Netherlands, etc. specializing in breaking warships, fishing vessels, and other high value vessels (Abdullah *et al.*, 2013; Kagkarakis *et al.*, 2016; Stopford, 2009) but do not pose any competition to Asian ship breakers due to high labor costs, lack of a ready market for recycled material, and stringent environmental regulations.

The size of a recycling yard is generally determined by its annual dismantling capacity, which varies from one country to another. For example, yard sizes in the Indian subcontinent are in the range of 20,000–150,000 LDT per year. The size of the yards in Turkey is in the range of 50,000–100,000 LDT per year whereas, in China, yard sizes vary from 30,000 LDT to 1.2 million LDT per year (ClassNK, 2017; LR, 2017). In general, the yards operated in Turkey and the Indian subcontinent are small to medium-sized, whereas in China, medium to large-sized yards are operated.

Recycling Methods

Ships are recycled by employing different types of methods in different parts of the world. The methods are similar in most aspects, especially the fact that all ships are cut apart to retrieve materials for recycling, irrespective of the method of recycling employed. The major difference between various methods is the way ships are docked and the level of mechanization used to carry out the recycling process. The difference between various methods depends mainly on the location of the yard and the prevalent practices in the region.

Classification according to the way ships are docked

There are four general methods to dock ships for dismantling, i.e., beaching, slipway, alongside, and drydock.

Beaching

Beaching is the term generally used for dismantling ships at the intertidal zone of a beach (Fig. 6). Ships are run ashore, as far up the beach as possible, at high tide to leave them grounded at low tide (Hougee, 2013). Ships are often unable to travel as far up the beach as desired under their own power and are left stranded on the mudflats. They are then pulled higher onto the beach using chains or heavy steel wires attached to large winches on the beach (LR, 2011). As steel blocks and other equipment of a ship are progressively cut in the intertidal zone using cutting torches, ships become lighter and easy to pull up the beach by winches. Large blocks are often cut from the ship, released onto the mudflats, and dragged individually by the winches onto the shore. Once onshore, everything is cut into smaller pieces as required by end buyers.

The beaching method is used to dismantle about two-thirds of the world's EOL ships, i.e., 66% in terms of GT (Mikelis, 2012) as well as lightweight tonnage (Fig. 5). The main locations include Chittagong in Bangladesh, Alang in India, and Gadani in Pakistan. The large tidal difference and extensive mudflats of these areas are utilized to drive ships up the beach (Lee, 2012). The beach is generally divided into "plots" of about 50 m wide and up to 100 or 150 m deep. A major issue with dismantling ships on tidal mudflats is that any spills of oil or cargo remaining on board are likely to be swept out to sea by the next tide (LR, 2011). However, this can be avoided by taking necessary measures and following the correct procedure.

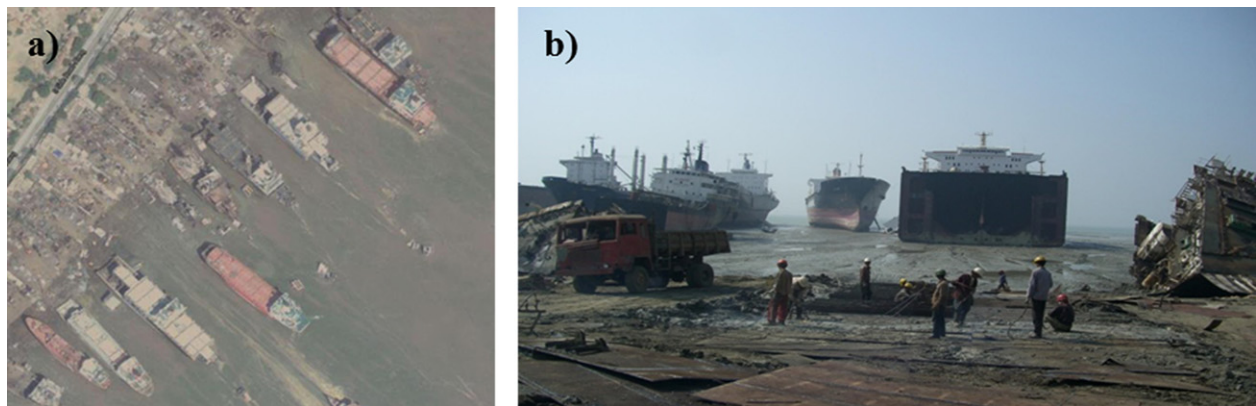


Fig. 6 (a) Satellite image of beach at Alang, India in 2016 (Courtesy of maps.google.com.). (b) Cargo ships beached at Chittagong, Bangladesh in 2009. Courtesy of Mikelis, N., 2012. The emergence of an international regulatory regime for the ship recycling industry. In: Lloyd's Maritime Academy Sale and Purchase Conference, London, reprinted with the author's permission.

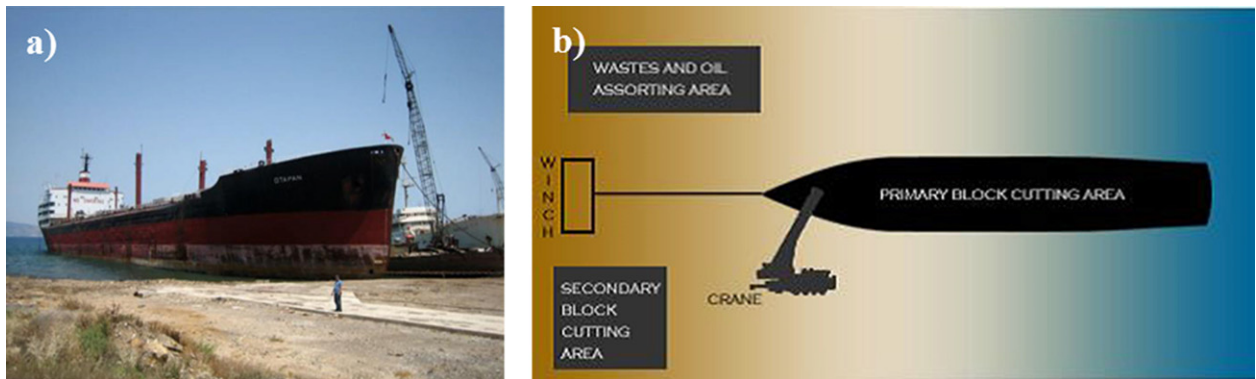


Fig. 7 (a) An end-of-life (EOL) ship beached at a Turkish recycling yard on a slipway (Courtesy of Vardar, E., 2009. Fate of ship breaking waste in Turkey. Brussels: NGO Platform on ship breaking, reprinted with the author's permission.). (b) Pictorial representation of the slipway method. Courtesy of Lee, M.A., 2012. Korean perspectives on ship recycling. MSc Thesis, IIIEE, Lund University.

Slipway

This method is a modification of the beaching method and is also called nontidal beaching (LR, 2011; Mikelis, 2012). The major difference between beaching and the slipway method is that of the tide. It is practiced in areas with a low tidal difference, especially in Turkey (Hougee, 2013). Other than Aliaga in Turkey, slipway recycling is practiced in many small-scale historical recycling locations, such as Inverkeithing in the United Kingdom and other locations in Europe and United States today (LR, 2011). In the United States slipways are generally 400–700 feet long (120–200 m) and 100–120 feet wide (30–36 m) at the entrance (USEPA, 2000). About 4% of the world's recycling capacity uses nontidal beaching method for ship recycling (Mikelis, 2012).

Although, in this method also, the ship is beached either against the shore or, preferably, a concrete slipway extending to the sea, an element of control is available due to the lack of tides. This means that any accidental spillages can reasonably be contained and the lifting and access operation takes place at a predictable and relatively stable waterfront (LR, 2011). Normally, the hull and machinery pieces are removed from the ship by mobile crane working from the shore, as shown in Fig. 7. It is generally acknowledged that the low tidal difference and improved access to the hull and the working area offer advantages for the safe and environmentally sound operations compared to the beaching method (Hougee, 2013).

Alongside

The alongside method, also referred to as quayside, pier side, or floating method, is a method to dismantle ships that are afloat and moored along wharfs, jetties, or quays and/or moored offshore (Hougee, 2013) (Fig. 8). Cranes and either automated cutting gear, such as mechanical shears or gas cutting torches, are used to reduce the ship in a planned and structured manner. The process is "top-down," i.e., the superstructure and upper pieces are removed first, then the work continues along the ship into the engine room until only the double bottom is left (LR, 2011). This last part of the ship, an empty floating hull called the canoe, is reduced to the extent possible, while afloat and then either taken out as a whole or further cut into pieces in a drydock (Hougee, 2013). This method is mainly practiced in China, the United States, and Belgium.



Fig. 8 (a) A ship docked alongside for recycling (Author's personal visit to a ship recycling yard in China.). (b) Pictorial representation of the alongside method. Courtesy of Lee, M.A., 2012. Korean perspectives on ship recycling. MSc Thesis, IIIIEE, Lund University.



Fig. 9 Ship dismantling in drydock. Image reproduced with permission of Harland and Wolff Heavy Industries Ltd., Belfast, Northern Ireland. Available at: www.harland-wolff.com.

During alongside recycling, the local impact of any pollution is likely to be increased since there is no tidal dispersal effect. However, this means that concentrations can be properly monitored, contained, and cleaned if necessary (LR, 2011).

Drydock

In this method ships are dismantled at a drydock, floating dock, or a slipway that has a lock gate and an impermeable floor structure (Hougee, 2013). This method is the safest and cleanest way of recycling a ship because chances of polluting surrounding waters by accident are virtually nil as everything is contained within the dock (Lee, 2012). The dock is cleaned before it is flooded for dismantling the next ship in order to avoid accumulations of contaminants (LR, 2011). The only downside of this method is that it is the most costly method of recycling a ship, which makes it the most scarcely used. In 2011, Leavesley International's facility in Liverpool was reportedly the one of the main drydock recycling locations in the United Kingdom (LR, 2011). Currently, Able UK Limited, Harland and Wolff Heavy Industries Limited (Fig. 9) and Swansea Drydock Limited are reportedly using the drydock recycling method in the United Kingdom (EC, 2016).

Classification according to the level of mechanization

The classification of recycling methods as per the level of mechanization can be carried out into the non-mechanized process, the highly mechanized process, and the intermediate process (Dev, 2010).

The non-mechanized process

This type of process is generally used in the Indian subcontinent yards. It uses a large amount of workforce and a bare minimum of mechanical equipment to carry out the recycling process. It thrives in places where abundant cheap labor is available and low level

of economic development hinders the use of capital intensive mechanical equipment and infrastructure, such as slipways, jetties, waste collection, and treatment technologies, etc. (Dev, 2010). The lack of health, safety, and environmental regulations also encourages this type of process.

The recycling process begins with the beaching of the ship and pulling it on the “plot” using winches. The ship is then taken over by a team of laborers who carry out the cutting operation using the oxy-acetylene blowtorches. Before starting the cutting process, they also carry out the cleaning of the ship’s tanks containing fuel oil, diesel oil, sludge, etc. and ship’s hull by removing insulation, machinery, loose items, such as furniture, etc. without much use of mechanical means. The cleaning of ship tanks and hull sometimes takes place without even using the protective gears, such as helmets, gloves, safety shoes, overalls, etc., while the lifting operations are carried out by bare-handed laborers (Dev, 2010).

The highly mechanized process

This type of process is generally found implemented in European ship recycling yards. It uses very little labor force. It thrives in places where labor is expensive and health, safety, and environmental regulations are in place. The dismantling process takes place either alongside or in a drydock for a greater control of the entire operation. The cutting operation is carried out using mechanical shears. The use of blowtorches is restricted to cutting jobs that are not possible to carry out using mechanical means. The lifting and transferring of large blocks, machinery, and other loose items to the secondary cutting area on the pier is carried out using the quayside gantry cranes. The ship’s hull and tanks are cleaned by using proper equipment and taking required safety precautions. The dismantling process is interrupted whenever required to achieve safe and environmentally sound operation. The process is environmentally and socially reliable because it uses standardized work practices and equipment that are able to control human and environmental risks (Dev, 2010).

The intermediate process

This type of process is generally used in the ship recycling yards located in China, Turkey, and even at some facilities in the United States (Dev, 2010). It uses both labor and mechanical equipment for the dismantling process. Although the cutting operation is generally carried out using gas torches, the lifting operations are carried out using cranes. This prevents harsh working conditions for the workers. The use of infrastructure, such as slipways, floating docks, quays, etc., provides a reasonable control over the recycling process, which ensures better safety of the workers and the environment.

Business Details

Ship owner’s perspective

Once a ship owner decides to recycle a ship, the standard procedure is to choose one of two strategies: either sell the ship directly to a ship recycling yard or sell it through a cash buyer. Most ship owners prefer to choose the latter strategy because cash buyers pay a lump sum to the ship owners in cash in advance, and charge about 3% commission to close the deal (Engels, 2013). The cash buyers are important intermediaries forming a link between the ship owners and the ship recyclers. As they negotiate the price with the owner, they generally negotiate with several recycling yards at the same time. In some cases, they buy a ship without negotiating a firm deal with a yard. In any case, they bear all the financial risk since they sign a contract and pay the owner till they get paid for delivering a ship to a recycling yard (Krishnaraj, 2015; LR, 2011). Therefore, about 80% of the transactions follow the cash buyer route (Alcaide et al., 2016) as it provides ship owners a sense of financial security, contrary to the distress of settling a deal with a letter of credit, while selling a ship directly to a ship recycling yard (Engels, 2013). The price offered to a ship owner is always in terms of USD per light displacement tonnes (LDT).

The cash buyers purchase obsolete ships from the ship owners on one of the two conditions, either “as-is where-is” or “on delivery” (Jain et al., 2016). With the “as-is where-is” contract, the cash buyer takes over the ownership of the ship from its last port of call till it reaches the ship recycling yard. In this case, the cash buyer usually changes the crew, reflags the ship, and subsequently delivers the ship at his risk to the recycling yard (Engels, 2013). In the case of “on delivery” contract, the ship owner is responsible for the delivery of the ship to the recycling yard in lieu of the guidance from the cash buyer on the best available market rate for the given specifications of the ship (Engels, 2013).

The approach of selling an EOL ship directly to a recycling yard may not always deliver the best results for a ship owner. This is firstly because ship owners lack the specific knowledge of the ship recycling market as they do not sell obsolete ships quite often and secondly because not many recycling yards buy ships directly from the ship owners (Ahuja, 2012; Engels, 2013). More importantly, most deals with a ship recycling yard involve a letter of credit as a payment instrument, which is not preferred by ship owners as they seek quick cash for disposing of the EOL ships.

In either case, whether a ship is sold directly to a recycling yard or through a cash buyer, more often than not a ship broker acts on behalf of the ship owner to negotiate the deal and to manage the business transaction. Shipbrokers are different from cash buyers in their mode of operations as they work directly on behalf of the ship owner and negotiate with cash buyers or ship recycling yards to find the best price for the owner (Krishnaraj, 2015). It is customary for shipbrokers and cash buyers to use their own contracts when dealing with ship owners selling vessels for demolition. However, BIMCO, the largest international association of ship owners provides a standard contract for sale and purchase of ships for demolition. It is called DEMOLISHCON (BIMCO, 2016).

In recent years, there is a growing trend among ship owners to use the services of so-called ship recycling consultants, which are companies specializing in monitoring the entire process of ship recycling from the time ship reaches the recycling yard till it is completely dismantled. They act on behalf of ship owners to ensure that a ship recycling yard follows procedures accepted by international regulations governing the ship recycling industry and relevant health, safety, and environmental standards. The use of ship recycling consultants allows ship owning companies to ensure that their corporate social responsibility (CSR) policy is well implemented.

Ship recycler's perspective

As far as business details of a ship recycling yard are concerned, it is important to understand the cost and revenue generating factors of recycling a ship. Beside fixed capital costs and cost of purchasing a ship, a ship recycling yard must pay variable costs like taxes, government duties, premises rent, labor costs, cost of consumables including electricity, waste disposal costs for both hazardous and nonhazardous waste generated in the dismantling process, and so forth (Sarraf, 2010).

The revenue generated by a ship recycling yard depends on what types of materials can be extracted from a ship and out of those extracted, what and how much can be classified and sold as recyclable material and reusable material. Such classification mainly depends on applicable local and international regulations and local market for reusable goods and scrap metals, such as steel, nonferrous metals, etc.

The markets for reusable goods and scrap products differ from one country to another. In the advanced European countries, steel scrap is generally completely melted down to make new steel products whereas in the Far East and Indian subcontinent, steel scrap is sometimes simply heated and rerolled in reinforcing rods for use in the construction industry including sewage projects, metal roads, and agriculture projects (Stopford, 2009; Sujaudhin *et al.*, 2016). In such countries, there is also a very strong demand for equipment and items reclaimed from ships. This includes diesel engines, generators, air compressors, deck cranes, compasses, clocks, and even furniture. They are generally refurbished by specialized firms and sold to other shore-based industries and interested buyers (Rahman and Mayer, 2015).

Material Composition of EOL Ships

An EOL ship is a complex structure comprising of various systems and structures containing numerous materials including ferrous, nonferrous, plastics, wood, oil, gas, chemicals, hydraulics, and hazardous materials. The material streams originating from dismantling an EOL ship can be grouped into three main disposal categories, i.e., materials or products for resale or reuse, materials or products to recycle, and waste (hazardous/nonhazardous).

The assessment of waste streams and their quantity as a result of dismantling a ship can be done by classifying a ship into the following three segments (Andersen *et al.*, 2001):

1. cargo spaces,
2. machinery spaces, and
3. accommodation spaces.

The cargo space is a large low density area of a ship. It is bounded by ships structure containing mostly only pipework and outfit items, such as ladders and hatch covers. Also, a limited amount of cabling, instrumentation, and selected machinery items may be found (Andersen *et al.*, 2001).

The machinery space is represented by steel structure comprising high-density areas containing mainly pipework and heavy machinery, such as main engine, generators, and auxiliary machinery. These areas also contain significant electrical cabling, electronic equipment, instrumentation, insulation, and outfit steel (Andersen *et al.*, 2001).

The accommodation space is also a high-density area. It is surrounded by steel structure comprising outfitting items related to furniture, furnishings, and sanitation within joinery subdivided areas. Electrical and electronic equipment and controls are found in the navigation and domestic areas of the accommodation space. These areas contain complex utility provision involving pipework, electrical cabling, ventilation trunking, and comfort insulation (Andersen *et al.*, 2001).

These areas of the ship, when dismantled for recycling, generate a material stream containing a mixture of materials including the following (UNEP, 2003):

1. ferrous and nonferrous scrap including coatings;
2. components: machinery, electrical/electronic equipment, joinery, minerals, plastics;
3. consumables: oils, chemicals, gases; and
4. hazardous wastes: asbestos, coatings, polychlorinated biphenyls (PCBs), materials, such as electronic waste, which may be hazardous depending on its components.

Every material stream is composed of different products and components that can either be sold for reuse or can be recycled. The products that do not fit in any of this category are usually disposed of either by landfill or incineration. The following is a comprehensive list of item-groups typically sold in the second-hand market for reuse (Andersen *et al.*, 2001; UNEP, 2003; Hjelmeland, 2009):

Table 1 Downstream disposal options of various waste types

<i>Waste types</i>	<i>Treatment/disposal route</i>
Asbestos	Landfill, solidification, vitrification
Polychlorinated biphenyls (PCBs)	High-temperature incineration, chemical, dechlorination
Ozone depleting substances	High-temperature incineration
Antifouling materials	Solidification, landfill
Cadmium	Physiochemical treatment, landfill
Chromium	Physiochemical treatment, landfill
Lead	Chemical treatment, landfill
Mercury	Chemical treatment, landfill
Radioactive substances	Recovery, secure landfill
Paraffin	Incineration
Bilge water	Physiochemical treatment, landfill
Electrical equipment	Recycling, residues to landfill
Fiberglass	Landfill
Fluorescent tubes	Mercury, glass recovery
Lead acid batteries	Recycling and physiochemical treatment, residues to landfill
Waste oil	Incineration
Oily water	Physiochemical treatment
Pyrotechnics	High-temperature incineration
Sludge	Incineration

Source: Watkinson, R., 2012. Waste management in ship recycling yards. In: Seminar on Ship Breaking and Ship Recycling in Bangladesh and Compliance With International Regulations. Dhaka: Department of Naval Architecture & Marine Engineering, Bangladesh University of Engineering & Technology.

1. steel components (anchors, chains, ventilation components, pipework, etc.),
2. pumps, valves, electric motors, machines (compressors, generators, engines, cranes, etc.),
3. navigational equipment,
4. life-saving equipment (rafts, lifebuoys, life-vests, survival suits, etc.),
5. personal protective equipment (helmets, work boots, gloves, goggles, overalls, etc.),
6. sanitary equipment (toilets, sinks, bath tubs, etc.),
7. household appliances (TVs, DVD players, refrigerators, etc.),
8. chemicals and paints,
9. furniture (beds, chairs, tables, etc.),
10. electrical cabling (intact),
11. batteries,
12. insulation material, and
13. lubricants (on drum), oil products (to manufacturing industries).

A major challenge in the ship recycling industry lies in the disposal of hazardous waste, such as asbestos, PCB, heavy metals, etc. Every country has its own national regulations governing hazardous waste disposal. In some countries asbestos, despite being hazardous, is reprocessed by manual crushing and sold to manufacturing industries (UNEP, 2003). The hazardous materials originating from EOL ships are sent to downstream waste disposal facilities, which may or may not be a part of the ship recycling yards. According to Watkinson (2012), likely downstream disposal options of various waste types are summarized in Table 1.

In general, the material composition of an EOL ship can be classified into the following main elements described in the subsequent sections of the article.

Ferrous Scrap Metal

"Ferrous scrap from ships comes from forgings and castings, shell plating, framing, deck plating and beams, bulkheads, pillars and girders, miscellaneous hull steel, foundations, and steel superstructures. In addition, some structural steel outfit, hull attachments, doors and hatches, deck outfit, steward's outfit, hull engineering items, piping, and miscellaneous machinery are ferrous scrap" (USEPA, 2000) (Fig. 10).

Steel scrap represents the largest recyclable fraction from the merchant ships and is commonly classified as ferrous scrap, of which the largest proportion is carbon steel (Andersen *et al.*, 2001), described as the number 1 melting scrap in the scrap trade (USEPA, 2000). The scrapping facility may recycle scrap metal by selling it to a RESM-Selting/erolling company or to a scrap metal broker for remelting.

When dismantling a ship it is possible to separate flat plates, and girders, beams, and angle bars, from smaller and irregular pieces of metal. At present, there is an international standard maximum size for steel scrap of approximately 1.5 m × 0.5 m × 0.5 m (Andersen *et al.*, 2001). The irregular pieces are fed to the electric arc furnace plants for remelting, while flat plates, girders, beams, and



Fig. 10 Pile of steel scrap as a result of ship recycling operation at a ship recycling yard (Author's personal visit to a ship recycling yard in China.).

angle bars can either be used directly in construction or road building, or can be heated and rerolled into bars and rods in rerolling mills (Mikelis, 2013b). Rerolling plates must be cut from between the ribs of the ship, while beams and other rolled sections are also torched. For example, an H-beam can be cut into three long strips, subsequently to be rerolled into reinforcing bars or fencing (Nijkerk and Dalmijn, 2001). About 60–70% of the steel of a tanker and 50–65% of a bulk carrier is rerolling plate (Mikelis, 2012). Rerolled steel is ideal for sewage projects, metal roads, and agricultural needs (Mishra and Mukherjee, 2009).

Machinery from recycled ships, when it is beyond repair and is of no further use, is also cut and sold as steel scrap. Because the chemical composition of the steel used in shipbuilding is controlled by classification society rules and surveys, ship steel has good yield strength, ductility, and impact strength. Ship steel scrap is therefore attractive for steel making (Mikelis, 2013b).

Steel scrap is usually derived from the ship by using oxy-acetylene gas torches to cut ship's structure in top-down sequence. During ship scrapping, the upper decks including superstructure of the ship are cut first, followed by the lower decks and structures. As large parts of the ship are cut away, they are lifted by crane to the ground where they are further cut into the shapes and sizes required by smelter or scrap metal broker.

Nonferrous Scrap Metal

Nonferrous metals are particularly valuable as they can recover a substantial amount of the price paid by the recycler for the ship. While there are many kinds of nonferrous scrap, one of particular interest is copper-yielding scrap, i.e., cuprous scrap. Cuprous scrap can be classified into bronze, brass, and various other copper alloys. Copper is a high value commodity for which recycling markets exist for reclaiming scrap copper.

One of the major sources of copper in a ship is electrical cabling (Fig. 11). According to certain estimates (Mishra and Mukherjee, 2009), on an average sized ship there are about 50,000 m of cables containing about 40,000 kg of copper. Such cable is recycled by stripping off the insulated covering and other layers to recover the copper. The resulting copper can be sold as scrap and the insulation material would add to the relevant waste stream. Alternatively the cable can be sold to an intermediary for such separation.

Another main source of copper is transformers and electric motor windings. Copper may also arrive from the waste stream of electrical and electronic equipment. Copper pipework can be sold directly unless highly contaminated. Special bronze alloys used in the manufacturing of propellers are equally valuable and are sought after in the recycling market.

Other nonferrous metals recovered from scrapping a ship include aluminum and zinc. Anodes, mainly of aluminum and zinc, are fitted to both the vessel's hull and inside tanks in order to protect against corrosion and fouling. Anodes are sacrificed over the lifetime of the ship and the amount of metals left when the ship arrives for scrapping are removed and sorted for reuse/resale (Andersen *et al.*, 2001). The quantities remaining are likely to vary between 30 and 70% of the initial weight, depending on the time spent on the high seas (Mishra and Mukherjee, 2009). Heavily corroded anodes are disposed of as waste, if recycling is not a feasible option.

Machinery

There are many machinery items on board a ship, including large items, such as the main engine, auxiliary generators, air compressors, and boilers, and smaller items, such as pumps, separators, centrifuges, and heat exchangers (Fig. 12). These machines have metal bodies and most ship machinery could be categorized as resaleable to earn revenue. Main engines, owing to their large size, are likely to be dismantled into smaller components. Specialist operators exist that take machinery for recycling (Andersen *et al.*, 2001)



Fig. 11 Cable removal and stripping on an end-of-life (EOL) ship. Courtesy of Rozenveld, W., 2010. Safe & sustainable ship recycling. In: Sustainable Shipping Conference 2010: From the Cradle to the Grave, Miami, reprinted with the author's permission.



Fig. 12 Machinery recovered from ship recycling (Author's personal visit to a ship recycling yard in China.).

but machinery that cannot be sold in the second-hand market either due to its obsolescence or due to its irreparability is considered as ferrous scrap and can be sold to RESM-Selters for melting (USEPA, 2000).

Electrical and Electronic Equipment

There is no existing scrap market for waste electrical and electronic equipment (WEEE) within Europe and its disposal is subjected to EU directive. Equipment that is not built-in, for example, a PC or TV, would be covered and subject to the producer responsibility requirements of the WEEE Directive. However, equipment that is part of another type of equipment not covered by the WEEE Directive (e.g., a ship) is itself not within the scope of the WEEE Directive (DEFRA, 2007). Examples of this are installed lighting or built-in radios/GPS equipment, etc.

On the other hand, light fittings, such as tube lights (more than 500 in number on a ship), heavy electrical equipment, such as generators, transformers, and electrical motors, and light electrical equipment, such as switches, radios, radar, etc. are sold in the second-hand market in subcontinent countries, such as Bangladesh, Pakistan, and India (Mishra and Mukherjee, 2009), where most of the world's ship recycling activity takes place. Resale value of generators derived from ships is about USD 24 per kilovolts (KV) in the second-hand market in India (Mishra and Mukherjee, 2009).

Minerals

A wide range of minerals are found on board including asbestos and mineral wool for insulation, ceramics for domestic sanitary items, concrete, tiles, etc. Certain items, such as intact insulation material, ceramics, crockery, etc., might be sold in the second-hand market as per the demand but most of it is regarded as waste. Specifically there are some mineral wastes, such as asbestos, that are classified as controlled or hazardous wastes for which specialist disposal would be required (Andersen *et al.*, 2001).



Fig. 13 Lifeboats obtained from end-of-life (EOL) ships. Reproduced from Mikelis, N., 2012. The emergence of an international regulatory regime for the ship recycling industry. In: Lloyd's Maritime Academy Sale and Purchase Conference, London, reprinted with the author's permission.

Asbestos, in some facilities, is reprocessed by manual crushing and sold to manufacturing industries (UNEP, 2003). Asbestos-containing material (ACM) may be found in thermal system insulation and on surfacing materials. Some other applications in the form of packing, brake linings, fire blanket, etc. may also be found (USEPA, 2000).

Plastics

Plastic materials used on ships are particularly found in accommodation areas. Plastics used in furniture and fittings are mostly unsuitable for recycling as they are likely to comprise of several polymers or to be contaminated with other materials, such as textiles or metals. Therefore, the majority of the plastic waste streams from vessels generally require disposal. Certain specific items, such as cable coverings, may be suitable for recycling, while lifeboats can be reused thus can be sold as demand exist (Fig. 13).

Liquids, Chemicals, and Gases

As discussed by Andersen *et al.* (2001), "the ship's piping and tank arrangements generally contain some quantities of oil, fuel, sludge and associated residues. Fuel oil may be found in both integrated and free-standing tanks throughout the ship. Lubricating oils may be found in a variety of tanks depending on their individual use. Lubrication oils may also be stored in drums. Tanker ships may arrive at the scrapping facility with a significant quantity of cargo residues. Further, all tanks may contain a certain level of sludge."

Coolants and refrigerants are also found on various systems on board ships (Fig. 14). Chemicals that are generally found on board include glycol, chemicals for injection, AFFF foam, dry powder in fire extinguishers, solvents/thinners, battery electrolyte, evaporator dosing and descaling acids, corrosion inhibitor, fresh paints, oil dispersants, cleaning agents, etc. (Andersen *et al.*, 2001).

Coolants and refrigerants can often be sold for reuse, while oil and oily sludge can be sold to industries where they are required for energy recovery. Chemicals are generally classified as hazardous waste and are disposed as per the local regulations whereas refrigerants are recovered from ship systems by specialized firms. Paints that have second-hand value can be sold to the second-hand market (Fig. 14).

Bilge and ballast water is also part of this material stream coming out of ship dismantling. Bilge water is stagnant mix of fresh water, seawater, and other liquids that are usually drained to the lowest inner part of the ship's hull called bilge (Mishra and Mukherjee, 2009). During ship scrapping, bilge water is created through the accumulation of rain water (because the decks are open) and the collection of water from fire lines that leak, are left open, or are used to wet down compartments (USEPA, 2000). This water often contains oil, grease, and other pollutants, such as inorganic salts, arsenic, copper, chromium, lead, and mercury (Andersen *et al.*, 2001).

Generally, sea/fresh/brackish water is intentionally pumped into a ship's ballast tanks to adjust ship's draft, buoyancy, trim, and list for maintaining the ship's stability. This water is called ballast water. It may contain pollutants, such as metals (e.g., iron, copper, chromium) and chemical constituents, originating from additives (e.g., flocculants that facilitate the separation of suspended silts) or from contact of the water with the piping systems and ballast tank coatings (e.g., epoxy coatings and rust inhibitors containing petroleum distillates) (USEPA, 2000). Sometimes seawater that is pumped into an empty fuel tank to improve a ship's stability is termed "dirty" ballast (USEPA, 2000). Pollutants in dirty ballast may include residual fuel, fuel additives (e.g., biocides), oil, grease, and metals, such as copper, nickel, silver, and zinc (USEPA, 2000).



Fig. 14 (a) Recovery of refrigerants from ship systems (Reproduced from Rozenveld, W., 2010. Safe & sustainable ship recycling. In: Sustainable Shipping Conference 2010: From the Cradle to the Grave, Miami, reprinted with the author's permission.). (b) Paint cans sold in the second-hand market in Bangladesh. Reproduced from Mikelis, N., 2012. Hong Kong Convention: The Origins of a Convention. World Maritime University, Malmo, reprinted with the author's permission.

Bilge and ballast water is often discharged overboard, or transferred to evaporation pits and onshore tanks according to applicable rules on the basis of their pollution concentration (Andersen *et al.*, 2001).

Joinery

Timber, wood, and associated materials derived from an EOL ship can generally be reclaimed and sold to intermediary resellers but in modern ship designs, most of the joinery products are composite in nature and may be contaminated by vinyl, plastics, rubber, etc. rendering them to be disposed of either by landfill or incineration (Andersen *et al.*, 2001). Most of the joinery and related products are found in the accommodation area of the ship.

Hazardous Materials

Hazardous materials can be a part of any of the material streams discussed so far. It depends mainly on the nature of the material derived from an EOL ship. For example, asbestos can be classified as minerals, while ozone depleting substances can be a part of the waste stream liquids, chemicals, and gases.

Components derived from an EOL ship may contain a number of hazardous materials, which poses environmental, health, and safety issues. Such hazardous materials need special attention and techniques to alleviate their harmful effects on environment and workers. Often, their removal is governed by local regulations of the country where ship recycling takes place. International conventions, such as the Basel Convention, are also applicable.

A hazardous material stream as a result of dismantling a ship may contain the following items:

1. asbestos,
2. ozone depleting substances,
3. PCBs,
4. radioactive substances,
5. antifouling compounds, and
6. heavy metals.

Asbestos

Asbestos refers to a group of minerals that occur naturally as masses of long silky fibers (USEPA, 2000). When crushed, asbestos breaks up into fine fibers that are too small to be seen by the human eye, which is a property contrary to most other minerals. These fibers, if inhaled, can easily penetrate body tissues and be deposited and retained in the airways and lung tissue. This may cause diseases, such as asbestosis, lung cancer, or cancers of the esophagus, stomach, colon, and rectum (USEPA, 2000).

"During ship scrapping, the most significant asbestos concerns for workers arise when removing asbestos-bearing thermal insulation; handling of circuit breakers, cable, cable penetrations; and removing floor tiles (from asbestos in the mastic and in the tile). Additional concerns can arise from handling and removing gaskets with piping and electrical systems, as well as molded plastic parts" (USEPA, 2000).

Ozone depleting substances

Ozone depleting substances that may be found on board ships include halons, CFCs, and HCFCs. CFCs are nontoxic, non-flammable, and stable in the troposphere, whereas in the stratosphere, they can be broken down by UV light and deplete the ozone layer (Andersen *et al.*, 2001). CFCs are used as refrigerants, solvents, and foam blowing agents. The use of CFCs, some chlorinated solvents, and halons (chemicals used as fire extinguishing agents) on board ships should become obsolete in the next decade owing to international maritime regulations, such as MARPOL.

PCBs

PCBs belong to a broad family of man-made organic chemicals known as chlorinated hydrocarbons. Due to their physical and chemical properties, such as nonflammability, chemical stability, high boiling point, and electrical insulating properties, PCBs were used in many industrial and commercial applications including electrical, heat transfer, and hydraulic equipment; as plasticizers in paints, plastics, and rubber products; in pigments, dyes, and carbonless copy paper; and many other applications (USEPA, 2000). "PCBs are found in solid (waxy) and liquid (oily) forms in equipment and materials on ships being scrapped. This includes cable insulation, thermal insulation material, transformers, capacitors, oils, paints and coatings, plastics and rubber, etc." (UNEP, 2003).

PCBs are toxic and they remain in the environment persistently. They can cause a number of adverse health effects to workers through skin contact or inhalation. PCBs can spread to the surrounding environment through the ground and/or water if not handled and disposed of properly (UNEP, 2003).

Cable burning for the recovery of copper wire can generate toxic dioxins. PCB concentration in cables taken from vessels during scrapping can be up to 280,000 ppm (28%) (Andersen *et al.*, 2001), which is critically high. Improper processing of cables in order to extract copper by burning off the insulation (commonly used in scrap facilities in Indian subcontinent countries) may lead to the release of particularly hazardous components to the environment (Andersen *et al.*, 2001).

Radioactive substances

As explained by Andersen *et al.* (2001), "radioactive material may be present on board a ship in liquid level indicators, smoke detectors and emergency signs. These sources generate low level radioactive waste, but handling and disposal of such waste is usually strictly regulated. Ionizing radiation is hazardous to human health and the environment and can cause severe forms of cancer and/or damage to genetic material endangering future generations."

Antifouling compounds

Antifouling paints are applied to the ship's hull to avoid marine growth during the operation of the ship. Such coatings are also applied to the ship's ballast tanks. These paints and coatings are harmful to human health and environment as they contain organometallic substances, such as tributyl tin (TBT), and heavy metals, such as lead and chromium (UNEP, 2003). TBT can cause an effect even at very low concentrations and is therefore considered to be one of the most toxic compounds in the aquatic environment (Andersen *et al.*, 2001). Exposure to hazardous paint fumes during metal cutting is an occupational health hazard. Moreover, paint fumes are also dispersed through the air and may be deposited far away from their source (UNEP, 2003). If a ship is recycled by beaching method, paint is removed to the marine environment due to contact between the ship's hull and the beach (Mishra and Mukherjee, 2009).

Heavy metals

Heavy metals, such as lead, cadmium, barium, chromium, zinc, mercury, etc., are found on board ships from various sources, such as paints, coatings, bilge, ballast water, thermometers, electrical switches, batteries, etc. These heavy metals, if not handled properly, are hazardous to health, safety, and environment.

An extensive discussion on the same by Andersen *et al.* (2001) states that "mercury is a toxic heavy metal and a persistent, bio-accumulative pollutant that affects the nervous system. Accidental spills of mercury can lead to dangerous mercury exposure. Consumption of contaminated fish is also an important route of mercury exposure."

The discussion further continues: "lead is toxic, and is found in batteries, paints and in components in motors, generators, piping, cables and others. Long term exposure to low levels can cause irreversible learning difficulties, mental retardation and delayed neurological and physical development in children. In adults, exposure to lead affects primarily the peripheral nervous system and can cause impairment of hearing, vision, and muscle coordination. Lead also damages the blood vessels, kidneys, heart and the reproductive system" (Andersen *et al.*, 2001).

The estimation of material composition of two major ship types (tankers and bulk carriers) carried out by Andersen *et al.* (2001) is depicted by Figs. 15 and 16. These estimates are based on the sampling of few ships of each ship type. An extensive discussion on quantifying the material composition of EOL ships was carried out by Jain *et al.* (2016), where authors suggested a methodology applicable to all ship types. The existing literature on this topic is also discussed in detail.

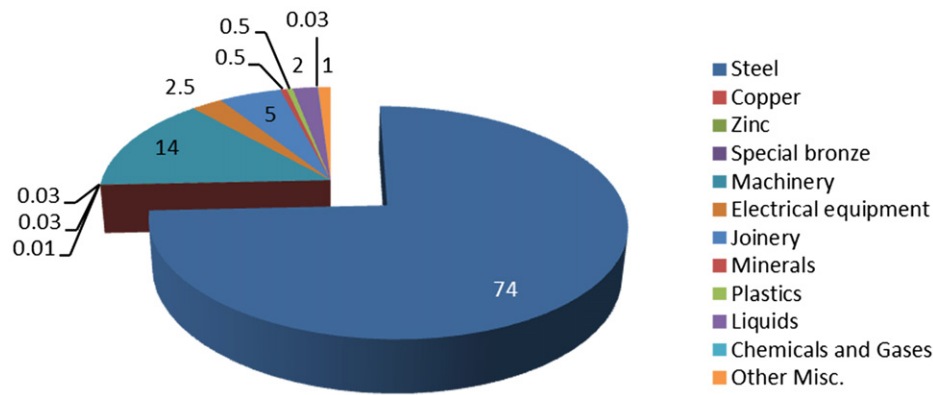


Fig. 15 Fractions of each waste stream in a tanker as percentage of total weight of the ship.

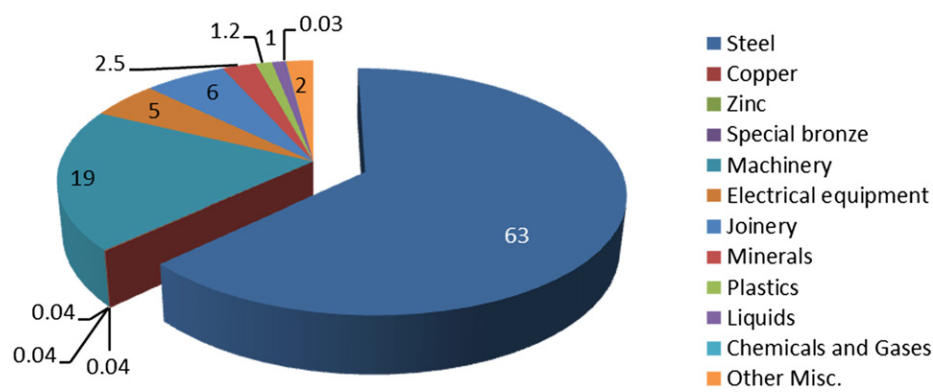


Fig. 16 Fractions of each waste stream in a bulk carrier as percentage of total weight of the ship.

Regulatory Overview

As already mentioned above, ship recycling is considered as one of the most dangerous jobs in the world due to a very high rate of accidents and diseases, compared to other industries (Graham-Rowe, 2004). It also has consistently moved to countries where health and safety regulations are minimal. The governments, nongovernmental organizations, and other international organizations around the world have been putting in their efforts to tackle the social and environmental hazards of the ship recycling industry by means of developing and implementing policies and legal instruments to govern the ship recycling industry on a global level. The relevant international legal regimes governing the global ship recycling industry are discussed below.

Basel Convention

The “Basel Convention on the Transboundary Movements of Hazardous Wastes and their Disposal,” hereinafter called the Basel Convention, was adopted in 1989 and came into force in 1992. It is an international convention that was formed to control the movement of hazardous wastes from the developed countries to the developing countries, so that the illegal dumping of wastes by the operating companies can be prevented (BC, 2011b). A follow-up legislation to this convention is the “Ban Amendment.” It prohibits the transportation of wastes from an Organisation for Economic Co-operation and Development (OECD) country to a non-OECD country (BC, 2011a). Although this amendment has not come into force, several countries including all the EU countries have ratified it (LR, 2011). The legal position of the Basel Convention and the Ban Amendment at the European level is effectively implemented by the European Waste Shipment Regulations (EWSR) (LR, 2011, Mudgal et al., 2010).

The applicability of the Basel Convention to ships sent for recycling rests upon three elements – first, the ships have to be classified as waste; second, they have to be subject to transboundary movement; and third, both the state of export and the state of import have to be parties to the Basel Convention (Engels, 2013). As 179 states including all member states of the EU as well as all the major recycling states are party to the Basel Convention and transboundary movement of a ship is self-evident in its sale and purchase transaction, the only remaining question to answer is whether an EOL qualifies as “waste” or not. Bhattacharjee (2009), Engels (2013), Moen (2008), and several others have extensively discussed the fact that the Basel Convention considers an EOL ship that is meant for export and contains hazardous materials in its structure as “hazardous waste.”

However, due to the global nature of the shipping industry and the practices associated with sending EOL ships for recycling, there has been difficulty in applying the provisions of the Basel Convention to ship recycling and often ship owners are found to circumvent the Convention (BC, 2011b; Bhattacharjee, 2009). Two of the major hurdles to the effective application of the Basel Convention are the challenges in identifying in practice when a ship becomes waste, and identifying which country is to be regarded as the "State of export" under the Basel Convention (Bhattacharjee, 2009). These difficulties in the implementation of the Basel Convention culminated the need for a separate mandatory international regime, specifically designed to meet the unique requirements of the global ship recycling industry, and thus led to the development of the HKC at the IMO.

HKC

The Hong Kong International Convention for the Safe and Environmentally Sound Recycling of Ships, commonly known as the HKC, was adopted at a diplomatic conference held in Hong Kong in May 2009 (IMO, 2009). However, it is not yet in force; to date, only four countries – Belgium, France, Congo, and Norway – have acceded to the Convention. Recently, the Danish, Panamanian, and Turkish governments took necessary legal steps to accede to the Convention (Danish Shipowner's Association, 2016; Green4sea, 2017). The accession by Panama and Turkey would be a big step for the Convention to come into force as per the conditions set out by IMO for its entry into force.

Entry into force criteria

The requirements for its entry into force, as per the Article 17 of the Convention, include the following (IMO, 2009):

"The Convention shall enter into force 24 months after the date on which the following conditions are met:

1. not less than 15 States have either signed it without reservation as to ratification, acceptance or approval, or have deposited the requisite instrument of ratification, acceptance, approval or accession in accordance with Article 16;
2. the combined merchant fleets of the States mentioned in paragraph (1) constitute not less than 40% of the GT of the world's merchant shipping; and
3. the combined maximum annual ship recycling volume of the States mentioned in paragraph (1) during the preceding 10 years constitutes not less than 3% of the GT of the combined merchant shipping of the same States."

These requirements effectively mean that apart from the major shipping states with flags of convenience (Panama, Liberia, Marshall Islands, etc.), ratifications by at least two of the three main recycling countries (India, Bangladesh, China) are required for the Convention to be applicable (Ormond, 2012). The slow progress of the HKC toward attaining its entry into force criteria has created a skepticism amongst the stakeholders about the convention's entry into force in the near future (Cameron-Dow, 2013).

Applicability

The HKC adopts the approach of dual application covering both the ship and the ship recycling facility, which is a comprehensive approach to deal with the problems relating to human health, safety, and environmental protection associated with the process of ship recycling (Jain *et al.*, 2013). The definition of a "ship," as given in the Convention, explicitly includes submersibles, floating crafts, floating platforms, among other offshore and storage vessels including vessels being towed or stripped of equipment. The HKC exempts ships less than 500 GT, ships operating throughout their life only in waters of the state whose flag they are entitled to fly (inland waterway vessels), warships, naval auxiliaries, and other ships not used for commercial purposes from the scope of its application. It defines the ship recycling facility as an area that is a site, yard, or facility used for the recycling of ships.

Key elements and procedures

The aim of the HKC is to ensure that the ships recycled at the end of their operational lives do not pose any unnecessary risk to human health and safety or to the environment. The structure of the Convention is depicted by Fig. 17. It contains 21 articles setting out the general legal provisions and working mechanisms, and an annex containing 25 regulations and 7 appendices, forming the essential requirements and technical details of the Convention (IMO, 2009). The regulations are divided into four chapters, i.e., general provisions (Regulation 1–3), requirements for ships (Regulation 4–14), requirements for ship recycling facilities (Regulation 15–23), and reporting requirements (Regulation 24–25). The appendices contain a list of hazardous materials and a range of forms and checklists, which are supposed to facilitate compliance with the provisions of the Convention (Jain *et al.*, 2013; Ormond, 2012).

It is supplemented by a set of following six guidelines:

1. guidelines for the Development of the Ship Recycling Plan (SRP) (Annex 2) (IMO, 2011b);
2. guidelines for the Development of the Inventory of Hazardous Materials (IHM) (Annex 3) (IMO, 2011a);
3. guidelines for the Safe and Environmentally Sound Ship Recycling (Annex 4) (IMO, 2012a);
4. guidelines for the Authorization of Ship Recycling Facilities (Annex 5) (IMO, 2012b);
5. guidelines for the Survey and Certification of Ships under the HKC (IMO, 2012d); and
6. guidelines for the Inspection of Ships under the HKC (IMO, 2012c).

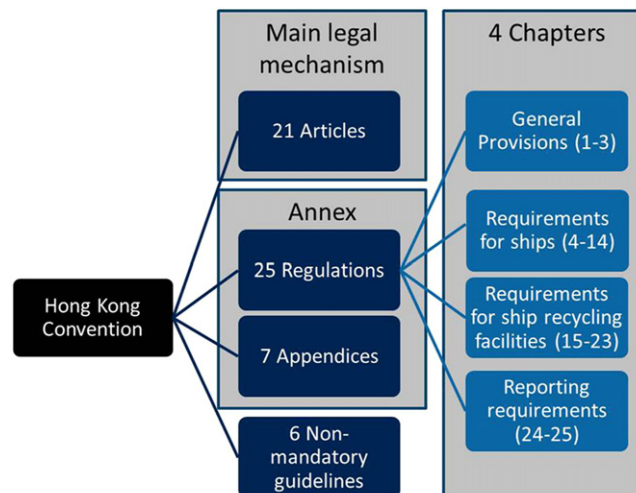


Fig. 17 Structure of the Hong Kong Convention (HKC).

Table 2 Impact of International Maritime Organization's Hong Kong Convention (HKC) on various stakeholders

<i>Recycling state</i>	<i>Ship recycling facility</i>	<i>Ship owner</i>	<i>Flag state</i>
• Authorize the ship recycling facility by issuing Document of Authorization to Conduct Ship Recycling (DASR) • Approve the Ship Recycling Plan • Send a copy of the Statement of Completion to the Flag State	• Prepare a Ship Recycling Facility Plan • Develop a ship-specific Ship Recycling Plan • Notify the Competent Authority (CA) of the planned start of recycling a ship • Notify the CA the completion of the ship recycling by issuing the Statement of Completion	• Always keep an Inventory of Hazardous Materials (IHM) on board the ship • Finalize the ship's IHM before sending it for recycling • Provide ship related information to the ship recycling facility	• Verify IHM, Ship Recycling Plan (SRP), and DASR

These guidelines are designed for proper implementation of the requirements of the HKC unlike other existing non-mandatory guidelines related to ship recycling developed by ILO, IMO, and the Basel Convention.

The HKC, whenever enforced, will create certain obligations for various stakeholders including ship owners, ship recycling yards, flag states, recycling states, port states, etc. as shown in [Table 2](#). It makes mandatory for concerned ships to carry an IHM in accordance with its requirements. It also imposes restrictions on the installation or use of certain hazardous materials (listed in an appendix) in shipyards, ship repair yards, and ships of parties to the Convention. The IHM shall be regularly updated and certified by the Flag State using the International Certificate on Inventory of Hazardous Materials (ICIMH).

The concerned ships are required to be sent for recycling only to the authorized ship recycling facilities. The authorization of the ship recycling facilities is subject to the inspection by the authorities of Recycling State and issuance of a Document of Authorization to Conduct Ship Recycling (DASR). The authorized recycling yards are obliged to develop a Ship Recycling Facility Plan (SRFP) in accordance with the requirements of the Convention. They are also required to develop a ship-specific SRP, specifying the manner in which each ship will be recycled. The SRP shall be developed on the basis of the ship's IHM and other ship related relevant information provided by the ship owner. The responsibility to approve a SRP lies with the Competent Authority (CA) appointed by the Recycling State.

The Flag State is required to issue an International Ready of Recycling Certificate (IRRC) after verifying the ship's IHM, DASR of the recycling facility, and the approved SRP. After the completion of recycling, the Recycling State shall issue a Statement of Completion of Ship Recycling, marking the end of the recycling process in accordance with the HKC. Subsequently, the Recycling State is required to send a copy of the statement to the Administration that issued the IRRC for the ship. The HKC empowers the Port State inspectors to undertake investigations of the ships calling their ports to ensure the adherence to the Convention. They can even detain, dismiss, or exclude a ship from their ports as a result of a violation.

EU Ship Recycling Regulation

The EU Regulation No. 1257/2013 on ship recycling, commonly known as EU Ship Recycling Regulation (EUSRR), was formally adopted by the European Parliament and the Council of the EU on November 20, 2013. It entered into force on December 30,

2013, 20 days after it was published in the *Official Journal of the European Union* (EU, 2013). It is similar to the HKC in most aspects and does not contain any contradictory provisions that could impede the prospects of HKC getting entered into force; in fact, it is likely to support an early implementation of the HKC as this regulation is bound to be applicable by December 31, 2018 at the latest (EU, 2013; Mikelis, 2013a). However, few of its requirements will be applicable only by December 31, 2020, at the latest (EU, 2013).

Unlike HKC, EUSRR has distinct dates for its entry into force and its application. The date of application is the date after which the provisions of the EUSRR are legally applicable. The main provisions of the EUSRR are as under:

1. Its application is restricted to the ships flying the flag of a Member State of the EU and to the vessels with non-EU flags that call at an EU port or anchorage. The ships visiting the EU ports are required to keep an IHM, prepared in accordance with its requirements. The exemptions in this regard are similar to the HKC. It also sets out responsibilities for ship owners and for recycling facilities both in the EU and in other countries.
2. The requirements for the IHM are similar to the HKC except for the inclusion of perfluorooctane sulfonic acid (PFOS) and its derivatives in Annex I and brominated flame retardant (HBCDD) in Annex II of the list of the hazardous materials (EU, 2013; Mikelis, 2013a). Annex I lists the prohibited hazardous materials whereas Annex II lists the hazardous materials which must be included in the IHM.
3. Other requirements related to the SRP, the SRFP, certification (IHM certificate and ready-for-recycling certificate), statement of completion, etc. are similar to the HKC, except that the approved recycling facilities (both EU and non-EU) will be included in the "European List" to be published by the European Council in the *Official Journal of the European Union* no later than December 31, 2016. In fact, first list was published on December 19, 2016 (EC, 2016). This list shall be the first point of reference for the ship owners of EU-flagged ships as they are obliged to recycle their ships only in an approved ship recycling yard. The list will be regularly updated to include or remove ship recycling facilities, as appropriate.
4. To get approved, recycling facilities will have to comply with the provisions of the HKC and also with the following three additional requirements (EU, 2013; Mikelis, 2013a):
 - "operate from built structures";
 - demonstrate "the control of any leakage, in particular in intertidal zones";
 - ensure "the handling of hazardous materials and of waste generated during the ship recycling process, only on impermeable floors with effective drainage systems."

Green Ship Recycling

With the development of international ship recycling regulations discussed above, several recycling yards around the world coined the term "green" recycling to make themselves distinct from other yards. In general, there is a common understanding among the industry stakeholders that recycling a ship with procedures to safeguard the environment and workers' health and safety in place can be called green ship recycling, as discussed by the World Bank (Sarraf, 2010) and the EC (2007). However, using a set of criteria, based on the international ship recycling regulations (HKC and EUSRR), to recognize a green ship recycling yard would be a more pragmatic approach. Therefore, the following criteria, based on Chapter 3 – "Requirements for Ship Recycling Facilities" of the HKC and Article 13 – "Requirements necessary for ship recycling facilities to be included in the European List" of the EUSRR (EU, 2013; IMO, 2009) are identified.

For a ship recycling facility to be called "green,"

1. it should be authorized by the Competent Authority (CA) of the Recycling State to conduct the ship recycling operations;
2. it should prepare a ship recycling facility plan as per the requirements of the HKC;
3. it should operate from the built structures, as defined by the technical guidance note of the EUSRR (EU, 2016);
4. it should establish management and monitoring systems, procedures, and techniques to prevent, reduce, minimize, and to the extent practicable, eliminate health risks to the workers concerned and to the population in the vicinity of the ship recycling facility, and adverse effects on the environment caused by ship recycling (EC, 2013; IMO, 2009), which includes:
 - prevention of fires and explosions by ensuring safe-for-hot-work conditions are maintained and monitored throughout ship recycling;
 - prevention of dangerous conditions by ensuring safe-for-entry procedures are in place to maintain and monitor the atmosphere of confined and enclosed spaces on ship throughout the ship recycling;
 - prevention of accidents, occupational diseases, injuries, spills, or emissions and other adverse effects that may harm human health and environment;
5. it should ensure safe and environmentally sound management and storage of hazardous materials and waste in accordance with the requirements of the HKC and EUSRR, i.e.,
 - containment of hazardous materials present on board during the entire process of recycling;
 - handling of waste and hazardous materials on impermeable floors with effective drainage system;
 - record keeping of the quantity of waste generated during ship recycling and its disposal at authorized waste management facilities only;

6. it should establish and maintain an emergency preparedness and response plan, and ensure rapid access of emergency response equipment, such as fire-fighting vehicles, cranes, ambulances, etc., to ship and all areas of ship recycling facility;
7. it should train the workers and provide them with personal protective equipment; and
8. it should record and report (if required) the incidents, accidents, occupational diseases, and chronic effects causing risks (or have the potential to cause risks) to workers' safety, human health, and the environment.

Concluding Remarks

This article described the current state of the global ship recycling industry. It provides answers to the questions such as, when ships are recycled, why ships are recycled, what are the locations at which ships are generally recycled and in what volumes, what methods are used to recycle ships in various countries, what are the business details of the ship recycling transactions, and which international regulations govern the ship recycling industry. It also described the impact of upcoming international regulations on various stakeholders. The criteria that can be used to identify a green ship recycling yard are also defined in this article.

Acknowledgment and Disclosure

This article is based on Chapter 2 of the first author's PhD dissertation entitled "*Improving the Competitiveness of the Green Ship Recycling*" (<http://doi.org/10.4233/uuid:3e74dea2-c01b-4b23-8194-2faec501a3c7>). The research for the same was carried out at Delft University of Technology, The Netherlands for a project collaboration with Tianjin University, China and International Ship Recycling Association, The Netherlands. The project was funded by Gieskes Strijbis Fonds and Lloyd's Register.

See also: Nuclear Electricity – Renewability, Losses and Recycling

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Plastic Products in Hospitals and Healthcare Systems

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Introduction

Plastic products have significantly impacted applications in hospital and healthcare systems and have made substantial improvements. Plastic is any material that is part of a wide range of semisynthetic or synthetic solids that are used in the manufacture of different products ([Plastic use in Medicine, 2013](#)). The word *plastic* is derived from the Greek *πλαστικός* (*plastikos*) meaning “capable of being shaped or molded” and, in turn, from *πλαστός* (*plastos*) meaning “molded.” ([Lidell and Scott, 2011](#); [Online Etymology Dictionary, 2019](#)).

Plastic has different definitions; one of them is a type of synthetic or manmade polymer, similar in many ways to natural fibers found in trees and other plants. Webster’s Dictionary defines polymer as one of many various organic compounds produced by polymerization, capable of being molded, extruded, cast into shapes and films, or drawn into filaments and then used as textile fibers. ([Life Cycle of a Plastic Product, 2010](#)). While the International Union of Pure and Applied Chemistry (IUPAC) definition of plastic is a generic term used in the case of polymeric material that may contain other substances to improve performance or reduce costs ([Vert et al., 2012](#)).

In many hospitals and medical device applications, materials like metal, wood, glass, and plastics are being used. The 19th and 20th centuries saw an explosion of medical devices, and materials such as stainless steel, titanium, vanadium, ceramic and plastics being used in their manufacturing. The demand for precision instruments for microsurgery in neurosurgery, ophthalmology, and otology was possible, and in the second half of the 20th century, energy-based instruments like electrocauteries, ultrasound, electric scalpels, surgical tools, and surgical robots ([Sastri, 2013](#)).

In general, there are two main types of plastics. The first one is known as natural plastic such as natural rubber, nitrocellulose, collagen, etc. Whereas the second one is the synthetic form such as epoxy, polyvinyl chloride (PVC), Bakelite. Parkesine, the first member of the celluloid class of compound and considered the first manmade plastic, was patented by Alexander Parkes ([UK Patent Office, 2018](#)).

Improvement in chemical technology after World War II led to an explosion in new forms of plastic, with mass production beginning in the 1940s and 1950s ([Richard et al., 2009](#)), and the top 50 plastic companies were in three countries: Germany, Japan, and the United States ([Alexander, 2015](#)). The decades since the 1970s have witnessed the advent of “high-tech” plastic used in demanding fields such as health and technology. New types and forms of plastics with new or improved properties have been created ([American Chemistry Council, 2010](#)). A third of plastic products are used in packaging ([Andrady and Neal, 2009a,b](#)).

The most important advantages of plastic are medical uses and applications for hospitals and public healthcare. Hospitals and healthcare systems see a rich intersection of rigid and flexible plastics and plastic-based medical devices ([Plastic Today, 2017](#)). Plastic are cost-effective, require little energy to produce, and are lightweight and biocompatible ([Proshad et al., 2016](#)). Plastic is soft, transparent, flexible, biodegradable, and many different types of plastics function as innovative materials for use in engineered tissues, absorbed suture, prosthetics, and other medical applications ([Andrady and Neal, 2009a,b](#)).

There are about 20 types of prime plastic in use worldwide ([AMPE, 2006](#)). Plastics play an important role in a more recent, innovative wound care technology: Liquid bandages. These bandages are made from various plastics and a solvent such as water or alcohol.

As the wound heals, the plastic of the liquid bandage sloughs off with the old skin cells. Liquid bandages often are used to replace traditional sutures and staples in surgery – they cause less trauma and do not need to be removed ([American Chemistry Council, 2018a,b](#)). Commodity plastics like PVC, polyethylene (PE), polypropylene (PP), and polystyrene (PS) make up over 70% of the share of plastic used in medical devices ([Sastri, 2010d,e,f,g](#)). Recent advances could lead to even more innovations in healthcare – and help people all around the world. Of these innovation for example the plastic heart (Total Artificial Heart). It is powered by a pneumatic pump that you carry around in a rucksack ([Fong, 2011](#)). A novel use of foam polyurethane plastic may help stabilize trauma patients with serious internal injuries. Painless plastic injections, bacteria-resistant plastics, and plastics could be used to make catheters or medical equipment to help ward off preventable disease. And plastics will continue to help drive innovations in medical care that we only dream about today ([American Chemistry Council, 2017](#)).

General Classification of Plastics

The plastics family is composed of a great variety of materials designed to meet the very different needs of thousands of end products ([Plastic Europe, 2018](#)). So even though the number of plastics is unclear, plastics makers tend to group plastics into two general classes: Thermoplastics and thermosets, as illustrated in [Table 1](#).

Table 1 The two Plastics' family: Thermoplastics and thermosets

<i>Categories of plastics</i>		
<i>Thermoplastics</i>		<i>Thermosets</i>
It is a family of plastics that can be melted when heated and hardened when cooled, and can be reheated, reshaped, and frozen repeatedly.		It is a family of plastics that undergo chemical change when heated, creating a three-dimensional network, and it cannot be remelted and reformed.
Polyethylene	Polycarbonate	Polyurethane
Polypropylene	Poly methyl methacrylate	Unsaturated polyester
Polyvinyl-chloride	Thermoplastic elastomers	Epoxy resins
Fluoropolymers	Polyarylsulfone	Melamine resin
Expanded polystyrene	PEEK	Silicone
ABS	POM	Phenol-formaldehyde
SAN	PBT	Urea-formaldehyde
Polyamides	etc.	Phenolic resins
		Acrylic resins
		etc.

Abbreviations: ABS, Acrylonitrile butadiene styrene; PBT, Polybutylene terephthalate; PEEK, Polyetheretherketones; POM, Polyoxymethylene, or acetal; SAN, Styrene acrylonitrile resin.

Thermoplastics

This family can be remelted and essentially returned to their original sets, sort of like the way an ice cube can be melted and then cooled again. Usually they are produced first in a separate process to create small pellets; these pellets then are heated and formed to make all sorts of consumer and industrial products.

Thermoplastics include PE, PP, PVC, PS, nylon, PC, and others (American Chemistry Council, 2018a,b).

Engineering thermoplastics can be amorphous such as ++ acrylics, PC, and polyurethanes or crystalline such as polyacetals, polyesters, and polyamides (Sastri, 2010a,b,c).

Polyethylene

Polyethylene or polythene (PE), IUPAC name polyethene or poly(methylene), is the most common plastic. As of 2017, over 100 million tons of PE resins are produced annually, accounting for 34% of the total plastics market (Geyer *et al.*, 2017). Many kinds of PE are known, with most having the chemical formula $(C_2H_4)_n$. PE is usually a mixture of similar polymers of ethylene with various values of n .

PE is a thermoplastic; however, it can become a thermoset plastic when modified (such as cross-linked PE) (Plastics Europe, 2017). PE is classified by its density and branching. Its mechanical properties depend significantly on variables such as the extent and type of branching, the crystal structure, and the molecular weight.

There are several types of PE: Ultra high molecular weight polyethylene, Ultra low molecular weight polyethylene, High molecular weight polyethylene, High density polyethylene (HDPE), High density cross-linked polyethylene, Cross-linked polyethylene, Medium-density polyethylene, Linear low density polyethylene (LLDPE), Low density polyethylene (LDPE), Very low density polyethylene, Chlorinated polyethylene. As for sold volumes, the most important PE grades are HDPE, LLDPE, and LDPE. The degree of branching of the different types of PE can be schematically represented as in Fig. 1 (Kaiser, 2011; Panayotov *et al.*, 2016).

Polypropylene

PP is a thermoplastic polymer used in a wide variety of applications. It belongs the group of polyolefins and it has similar properties to PE, but it is slightly harder and more heat resistant. It is white (Whiteley *et al.*, 2005). The global market for PP is about 55 million tonnes (Ceresana, 2019).

There are two main types of PP available: Homopolymers and copolymers. The copolymers family is further divided into block copolymers and random copolymers (McKeen, 2014). Each category fits certain applications better than the others.

They are usually incorporated with anywhere between 1% and 7% ethylene and are selected for applications where a more malleable plastic is needed (Polypropylene PP, 2016). Some of the most common applications are buckets, bowls, crates, toys, medical components, washing machine drums, battery cases, bottle caps, fibers for carpets, and sports clothing (British Plastics Federation, 2019).

Polyvinyl chloride

Polyvinyl chloride or vinyl (PVC) is a polymer in which more than half of the content by weight consists of chlorine (Vesterberg *et al.*, 2005). PVC is produced by polymerization of the vinyl chloride monomer. PVC comes in two basic forms: Rigid (sometimes abbreviated as RPVC) and flexible.

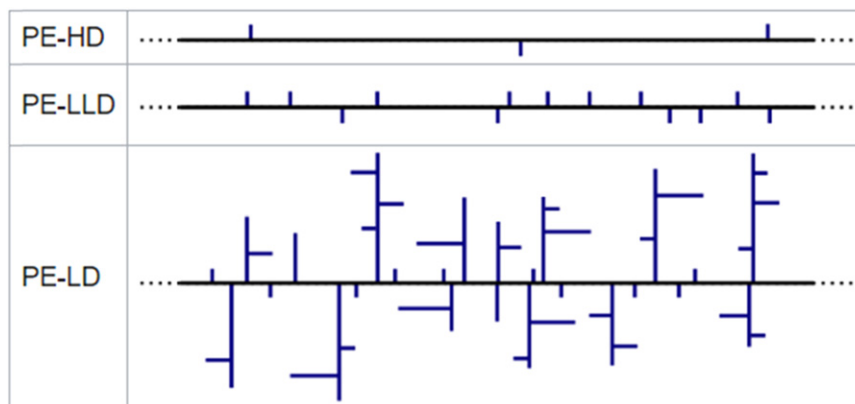


Fig. 1 The figure shows polyethylene backbones, short-chain branches, and side chain branches. The polymer chains are represented linearly. Reproduced from Kaiser, W., 2011. *Kunststoffchemie für Ingenieure von der Synthese bis zur Anwendung*, third ed. München: Hanser.

It is the world's third-most widely produced synthetic plastic polymer, after PE and PP. About 40 million tons are produced per year. Pure PVC is a white, brittle solid (although different PVC variants are designed to be very flexible) and strong (Creative Mechanisms, 2016).

Polystyrene

PS is the simplest plastic based on styrene. PS can be transparent or can be made in various colors. Three general PS types are general purpose or crystal polystyrene, high impact polystyrene, and siderostatic polystyrene.

Nylon

Nylon is a generic designation for a family of synthetic polymers, based on aliphatic or semiaromatic polyamides. Nylon is a thermoplastic silky material that can be melt-processed into fibers, films, or shapes (Kohan, 1995). Nylon polymers can be mixed with a wide variety of additives to achieve many different property variations. Nylon has several types, such as Nylon 66, Nylon 6, and Nylon 510, which have significant commercial applications.

Polycarbonate

PC is a type of polyester but is discussed separately. PC performance properties include very impact resistant, clear as glass, high heat resistance, dimensional stability, resistant to UV light, allows exterior use, and flame-retardant.

Polyacrylate

(Acrylic, Poly methyl methacrylate (PMMA)) While many acrylic polymers are manufactured, PMMA is by far the most common. PMMA has two very distinct properties that set the products apart from others. First, it is optically clear and colorless. They are also highly weather resistant.

Hydrogel (Acrylate)

The acrylic is made from monomers that have hydroxyl (a OH) groups on them that "like" water. One such hydrophilic polymer is poly (hydroxyl ethyl acrylate) or poly (hydroxyl ethyl methacrylate) (PHEMA). Blends of a hydrophobic silicone with a hydrophilic PHEMA produce a lens.

Polysulfone

Polysulfone is a rigid, strong, tough, high temperature amorphous thermoplastic. Its properties are high thermal stability, high toughness and strength, good environmental stress crack resistance, inherent fire resistance, and transparency.

Polyetheretherketone

Polyetheretherketones (PEEK) are also referred to as polyarylktones. It is a thermoplastic with extraordinary mechanical properties. The Young's modulus of elasticity is 3.6 tensile strength is 170 MPa. PEEK is partially crystalline, and melts at around 350°C.

Thermoplastic Elastomers (e.g., Thermoplastic Polyurethane)

An elastomer is a polymer with the property of "elasticity," generally having notably low Young's modulus and high yield strain compared with other materials. The term is often used interchangeably with the term rubber (McKeen, 2014).

Table 2 An example of disposables plastic products in the hospital

Construction products	Doors and windows	Pipes: Water and vent	Roofing membranes
Patient products	Patient ID cards and bracelets	Foot orthoses	Inflatable splints and injury support packs
Furniture products and furnishings	Bed caster, rails, and wheel	Floor covering	Shower curtains
Packaging, medical products	Medical devices	Film wrap	Thermoformed trays for admission and diagnostic kits
Kidney (Renal Disease) therapy products	Hemodialysis: Blood line (tubing) and catheters	Peritoneal dialysis: Dialysate containers (bag) and fill	Peritoneal dialysis Drain lines (tubing)
Entera feeding products	Enteral feeding sets (bags and tubing)	Nasogastric tubes	Tubing for breast pumps
Blood products and transfusion	Apheresis circuits	Blood bags and tubing	Extracorporeal membrane oxygenation circuits
Respiratory therapy products	Aerosol and oxygen masks, tents, and tubing	Endotracheal and tracheostomy tubes	Nasal cannulas and catheters
Office suppliers	Notebook binders	Gloves, examination	Plastic divides in patient charts

Abbreviation: PVC, Polyvinyl chloride.

Thermoset Elastomers

One of the most important thermoset elastomers is silicone, also known as siloxane, polyorganosiloxane, or polysiloxane.

Silicone rubber is a semiorganic synthetic. Its polymer backbone structure consists of a chain of silicon and oxygen atoms rather than carbon and hydrogen atoms, as in the case with other types of rubber.

Poly-*p*-xylylene (Parylene)

Parylene is the generic name for members of a series of polymers. The basic member of the series, called Parylene N, is poly-*para*-xylylene, a completely linear, highly crystalline material. Parylene polymers are not manufactured and sold directly. They are deposited from the vapor phase by a process that in some respects resembles vacuum metalizing.

Fluoropolymers (e.g., PTFE)

Polymer is an example of a linear fluoropolymer. Formed by the polymerization of tetrafluoroethylene (TFE), the (aCF₂aCF₂a) groups repeat many thousands of times. The fundamental properties of fluoropolymers evolve from the atomic structure of fluorine and carbon-carbon bonds and the pendant groups are carbon fluorine bonds. Both are extremely strong bonds (McKeen, 2014).

General Characteristics of Plastics

Each plastic has very distinct characteristics, but most plastics have the following general attributes.

- (1) Plastics can be very resistant to chemicals.
- (2) Plastics can be both thermal and electrical insulators.
- (3) Generally, plastics are very light in weight with varying degrees of strength.
- (4) Plastics can be processed in various ways to produce thin fibers or very intricate parts.
- (5) Polymers are materials with a seemingly limitless range of characteristics and colors.
- (6) Polymers are usually made of petroleum, but not always.

Categories of Plastic Products in Hospitals and Healthcare

Plastic products in hospitals and healthcare can be classified into two major categories. The first category is disposable plastic products such as gloves, blood bags, colostomy bags, bandages, catheters, IV kits, tubing and syringes. The second one is nondisposable plastic products such as devices include machines and instrument, surgical and dental instruments, diagnostic equipment, prostheses, and implants. Table 2 illustrates an example of disposals plastic products in hospitals (PVC products).

Properties of Plastic Products in Hospital and Healthcare Systems

Materials used in nondisposable applications must typically meet long-term durability and stringent physical and mechanical properties. Materials used in machines and diagnostic equipment do not necessarily need to be sterilized or meet specific chemical



Fig. 2 MRI machines. Reproduced from Piedmont Plastics, 2018a. Medical equipment. [Online] (accessed April 2019). Piedmont Plastics, 2018b. What is the best type of plastic for medical equipment? [Online] Available at: <https://www.piedmontplastics.com/blog/82/best-plastics-for-medical-equipment> (accessed April 2019).

resistance or biocompatibility requirements. Examples of diagnostic and surgical equipment are MRI machines (**Fig. 2**), electrocautery devices, and electrocardiogram monitors. Implants on the other hand must meet strict biocompatibility, biodurability, and sterilization requirements to be safe and effective in the body. It is important to know the dimensions, size, and weight requirements for the part or product. Consideration must also be given to the loads, stresses, and impact that the product might see during its use (*Sastri, 2010a,b,c*). Medical devices are getting smaller with more functionality and electronics.

Minimally invasive surgeries, disposables, implants, remote diagnostics, and home healthcare are driving some of these needs. Many additives like fillers, toughness, lubricants, and stabilizers can be used to improve the physical and mechanical properties. Other additives are more specific to medical applications. Radiopaque additives can render plastics visible to X-rays allowing surgeons to view, guide, and place devices in the body. Nanoadditives can be used in small amounts to produce miniature parts and devices that are strong and that incorporate functional characteristics like electrical conductivity, thermal conductivity, barrier properties, and radiopacity and antimicrobial properties. Stabilizers can be used to improve the thermal and radiation stability of plastics. This wide array of additives that can be used in formulating plastics extends the capability of plastics into a wide range of medical device applications (*Sastri, 2010a,b,c*).

The Use of Plastic Products in Hospitals and Healthcare Systems

The most widely used plastic material in medical applications is PVC followed by PE, PP, PS, and PET. PVC most widely used in presterilized single use medical applications. It is a versatile plastic that has been used in medical applications for over 50 years (*Craftech, 2019*). In recent years, PVC has been the major plastics player in the medical market, holding about 40% share. PP came in second, with about 20%–21%. Look for PP's percentage to grow (*Plastic today, 2012*). The two main application areas in healthcare for single-use medically approved PVC compounds are flexible containers and tubing: Containers used for blood and blood components, for urine collection or for ostomy products and tubing used for blood taking and blood giving sets, catheters, heart-lung bypass sets, hemodialysis sets, etc. PVC products are used in hospitals nearly everywhere such as IV bags and tubing, examination gloves, flooring, pipes, carpet backing, wall coverings, plastic food wrap, office furniture and supplies, etc. PVC is used to make a wide variety of plastic products in hospitals, ranging from medical devices to building products to office supplies. PVC is used in both flexible and rigid applications. Most products are not labeled as PVC (*Permanente, 2005*). Medical facilities need building materials with excellent durability, chemical resistance, low maintenance costs, and affordability. The plastic material PVC, also known as vinyl, meets these demands and more. In flooring, ceiling and wall coverings, PVC reduces the need for cleaning and prevents the spread of infection with its smooth hygienic surface. Not only does it last for up to 20 years with intensive use, but PVC also offers the best value for its price. With endless design options, including signage, zone boundaries and even art, PVC makes hospitals more comfortable, energizing, and welcoming for all. As a result, hospital vinyl flooring and other PVC hospital interiors are popular throughout the world (*The European Council of Vinyl Manufacturers, 2019*).

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Choosing the right floor for a hospital can be a bit of a complex endeavor. There are several factors that come into play: What room or rooms in the hospital need flooring, longevity, what is required comfort-wise underfoot, esthetics, point load and rolling load requirements, cleanability, and cost. It's important to take everything into account to make the right decision (*Continental Flooring Company, 2017*). Vinyl flooring is found in hospitals worldwide.



Fig. 3 Vinyl flooring in hospital. Reproduced from The European Council of Vinyl Manufacturers, 2019. PVC in hospital interiors. [Online] Available at: <https://pvcmed.org/healthcare/pvc-hospital-interiors/> (accessed April 2019).



Fig. 4 Operating theater lights.

This is due to a unique combination of properties that make vinyl an ideal material for healthcare facilities, such as hygienic, high durability, safe and shock-absorbent, low total cost of ownership, and providing a more welcoming hospital (**Fig. 3**). PVC wall and ceiling coverings are a favorite in many hospitals thanks to their esthetic, hygienic, and cost-effective qualities. **Fig. 4** shows operating theater lights that are safe and very easy to clean, resist hazardous substances, and are very easy to control during the operation.

Vinyl wall covering is attractive, available in grades of thickness, suited to heavy traffic, and will stand up to many years of heavy use. Also, vinyl wall and ceiling coverings are not only easy to clean, they are also easily repaired should damage occur.

PVC wall and ceiling coverings are fire-retardant, and are easily repaired should damage occur. PVC wall and ceiling coverings can be made shock-absorbent and thus can withstand collisions with beds and other types of hospital equipment. More than 40% of all plastics-based disposable medical devices used in hospitals are made from PVC (PVCMed Alliance, 2019a,b).

Plastic products in healthcare application have achieved very important results and now plastic products are everywhere, from exam gloves to IV tubes or heart valves, Plastic packaging is particularly suitable for medical applications. It safely guards against contamination. Innovations in plastics are making new procedures possible. Just think of an artificial plastic heart, of bacteria-resistant plastics, or of body parts tailored to the needs of the patient and printed in the 3D printer.

Recently, there are effective plastic products in healthcare systems such as unblocking blood vessels: In the latest heart surgery, thin tubes (catheters) are used to unblock blood vessels, while deposits obstructing them can be broken down with a tiny



Fig. 5 Catheters are used to unblock blood vessels and orthopedics device. Reproduced from Plastic Europe, Association of Plastic Manufacturers, 2016. The Plastic Industry Berlin August 2016. [Online] Available at: <https://committee.iso.org/files/live/sites/tc61/files/The%20Plastic%20Industry%20Berlin%20Aug%202016%20-%20Copy.pdf> (accessed April 2019).

spiral-shaped implant, a vessel support. Positioned in the treated artery, it is made of a plastic developed specifically for the medical field and charged with active substances. A second application is known as a prosthesis. Plastics are now being used as orthopedic devices, where they align, support, or correct deformities. Synthetic material also plays a vital role for diseased arteries that cannot be helped via vessel support. An affected section of the aorta is removed, and the gap is bridged by a flexible plastic prosthesis. Thanks to this, the body's lifeline becomes fully functional again **Fig. 5**.

Another innovation is artificial corneas: Eye injuries or chronic inflammation, for example, corneal erosion, can impair sight, and if a transplant has little chance of success, a prosthesis is the only hope. Artificial corneas made from special silicone are now available for treatment. Only 0.3–0.5 mm thick, highly transparent, flexible, and made of biomechanics like a natural cornea, it can restore clear vision again.

Also, hearing aids, one of the most important innovations for people with severely impaired hearing, can now use a plastic implant. It transforms acoustic impulses into electrical ones, bypassing the damaged cells and stimulating the auditory nerve directly (**Fig. 6**) (Plastic Europe, Association of Plastic Manufacturers, 2016).

General application of the most important types of plastic (PE, PP, PVC, PS, and PC) in medicine and medical devices and their products in hospitals and healthcare systems are illustrated in **Table 3**. In medicine and healthcare the diversity of plastics' uses is incredible, and many other sectors of society also have replaced glass, wood, and metal in several products including food packaging, clothing, and even in personal care products by plastic materials.

However, the development of plastic products has led to other disposable objects ubiquitous in hospitals such as IV bags and tubing. So, the importance of IV bags and tubing in caring for hospital patients is clear in the fact that they constitute 20%–25% of hospital waste.

Discussion and Conclusion

Properties of materials and available knowledge and technology are some of the most important factors that can help to find solutions for different healthcare patients. Plastic components have different required characteristics to develop and innovate new products to improve or solve specified medical and technical problems. Plastic components have helped healthcare patients live healthier and happier lives.

Plastic products have revolutionized a lot of industries for several different reasons to include the fact that they resist environmental degradation over time, are generally safe for human beings, are economical and widely available, and are produced with a wide variety of material properties that allow adaptation to many different applications.

According to this study interested in the role and importance of plastic products in the hospital and healthcare systems, and because of analyzing recent studies and topics in using plastic products in hospitals and healthcare systems and depending on the past studies and investigations of the plastic materials and their applications in the mentioned sectors, the following can be concluded:

- The main important innovations were in the past century with the introduction and wide adoption of plastics for many day-to-day applications in all fields.
- Using plastics and related products in a hospital is an increasing trend because of their cost-effectiveness, for their benefit in patients in simple and light tools and instruments, infection control, and wide availability.



Fig. 6 Artificial corneas and hearing aids. Reproduced from Plastic Europe, Association of Plastic Manufacturers, 2016. The Plastic Industry Berlin August 2016. [Online] Available at: <https://committee.iso.org/files/live/sites/tc61/files/The%20Plastic%20Industry%20Berlin%20Aug%202016%20-%20Copy.pdf> (accessed April 2019).

Table 3 Plastic products in hospital and healthcare systems

1	Polyethylene	Containers, packaging films, pouches, lidstock, breather patches, and headers for bags. UHMWPE is used as the wear bearing surface of hip and knee arthroplasty and total joint replacement.
2	Polypropylene	● Homopolymer: Thermoforming, slit film and oriented fibers, high clarity, syringes, and closures, sutures, drapes, and gowns. ● Random copolymer: Food, household chemicals, beauty aid products, clear containers, and hot fill applications.
3	Polyvinyl chloride (PVC)	● Impact copolymers: Film, sheet, profiles, high-pressure resistance, medical trays, and thin wall parts. ● Rigid PVC: Luer connectors and Y-sites. ● Flexible PVC: Secondary packaging, blister packs, solution containers, fluid transport tubes, drip chambers, diaphragms, pull rings, oxygen facemasks, and gloves.
4	Polystyrene	● General purpose: Diagnostic instruments and disposable laboratory ware, Petri dishes, tissue culture components, flasks, and pipettes. ● Oriented: Oriented polystyrene films can be printed and laminated to foams for food service plates and trays offering improved esthetics. The films can also be used as a laminate to polystyrene sheet for a high-gloss shine. ● High impact: Laboratory ware and other medical devices.
5	Nylon	Soft contact lenses, wound dressings, drug delivery.
6	Polycarbonate	Medical apparatus (sterilizable), reservoirs, high-pressure syringes, artery cannulas, stopcocks, luers, centrifugal force separators, blood filter housings, dialyzer housings; glucose meters, pumps, insulin pens; surgical device handles and housings.
7	Polyacrylate	Clear, disposable plastics – only glass transmits light as well; chest drainage units, medical spikes, breathing apparatus accessories, urological accessories, Y-sites, check valves, filter housings, IV adapters, IV pump housings, medical cassettes, blood handling components, and catheter accessories.
8	Hydrogel (Acrylate)	Fittings, valves, pumps, tubing.
9	Polysulfone	Medical equipment that requires repeated sterilization; fluid handling couplings/ fittings.
10	Polyetheretherketone	Reusable medical components including dental syringes and keyhole surgery devices, catheters, disposable surgical instruments.
11	Thermoplastic elastomers (e.g., TPU)	Catheters, valves, needleless syringes, surgical instruments, wound dressing and tape, shunts, drug patches, medical bags, and tubing.
12	Thermoset Elastomers	Catheters, valves, needleless syringes, surgical instruments, wound dressing and tape, shunts, drug patches, medical bags, and tubing.
13	Poly-p-xylylene (Parylene)	Applications and uses: Needles, prosthetic devices, implantable components, catheter, electrodes, stents, epidural probes, cannula assemblies.
14	Fluoropolymers (e.g., PTFE)	Fittings, valves, pumps, tubing.

Abbreviations: PTFE, Polytetrafluoroethylene; TPU, Thermoplastic polyurethane; UHMWPE, Ultra high molecular weight polyethylene.

- Plastic products continue to help scientists find desired solutions for their patients such as unblocking blood vessels, orthopedic device, artificial corneas, hearing aids, and so on.
- Further innovation can improve the quality of plastic products and meet the requirements for sterilization, safety, preservation, etc. of medical equipment used in the healthcare industry. Also, more studies and researches are needed to develop recycling methods and techniques.
- It is important to require the printing of plastic codes for products and packaging.

- Researchers in healthcare continue improve and create new substances to fit and offer newly needed properties.
- The use of plastic products in hospitals and healthcare systems is very important and necessary and this importance will continue to increase.

It is recommended that plastic products manufacturers should be committed and keep working on government and international regulations that concern use of plastic products for healthcare.

See also: Polymer-Recycling of Bulk Plastics. Prospect of Recycling of Plastic Product to Minimize Environmental Pollution

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Post-Processing of HVOF Sprayed WC-Co Coating to Enhance its Performance

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Introduction

Thermal spraying processes are well-known for improving surface properties and can be applied to any components without affecting the bulk material composition (Bolleddu *et al.*, 2014). Thermal spray coating produced by optimized process parameters can extend the service life of the components and improve the performance as well (Hadad *et al.*, 2009). Tungsten Carbide – Cobalt (WC-Co) coatings are widely used in aircraft, textile, automobile, transportation, mining and power generation industries to impede various degradation processes such as wear, corrosion and erosion (Karimi *et al.*, 1993). A proper composition of hard WC phase and Co phase results in favourable combination of high wear resistance, hardness, fracture toughness, etc. (Santana *et al.*, 2008). The WC-Co coatings with nanolevel surface finish find many applications such as main aircraft landing gear cylinders and pistons (Nuse and Falkowski, 2000; Sartwell *et al.*, 2004), diesel engine cylinder (Davis, 2004) and gloss calendar roll of printing industry (Pawlowski, 2008) and many more.

Many thermal spray techniques are available for WC-Co coating on different materials and components. High velocity oxy-fuel spraying (HVOF) technique is extensively used in many industries due to its ability to produce high quality carbide coatings. HVOF technique uses high particle velocity and it leads to the favourable coating properties such as high density, high bonding strength, hardness, etc. (Stewart *et al.*, 2000). During the coating deposition, the Co binder matrix is melted sufficiently and WC particles are dissolved into it. However, the WC particles are subjected to the severe decomposition during coating fabrication and brittle W_2C or W phase are formed around the WC particles. The W phase, free C further reacts with the Co binder and forms a brittle amorphous phase ($Co_xW_yC_z$), which degrade the intersplat bonding, in turn, the mechanical properties of the coatings (Xie *et al.*, 2013; Qiao *et al.*, 2001). Hence, sufficient melting as well as suppression of WC particles decomposition is essential to improve the properties of the coatings. The decomposition can be declined by reducing the flame temperature and exposure time of powders to the high temperature (Karimi *et al.*, 1993).

The coating deposited by thermal spray processes is very rough and not suitable for many applications. Hence, some polishing process needs to reduce the surface roughness of the coating and make it suitable for final usage. Machining and grinding are the some of the preferable processes for finishing of WC-Co coatings (Murthy *et al.*, 2001). Liu *et al.* (2002b) performed surface grinding of nanostructured WC-Co coating deposited by HVOF process. Diamond abrasive based cup-type wheel was used. Surface roughness and grinding forces are studied with the reference to the grinding process parameters. In another work nanostructured coating was finished by grinding and burnishing (Tillmann *et al.*, 2015). From the reported work, it is observed that machining, grinding and ball burnishing are not able to finish the WC-Co coatings to the nanometer scale. This is due to the severe mechanical contact by rigid abrasive tool, very high finishing forces which may result in particle pull out from the coating and low heat transfer from the finishing zone due to the inherent porosity of the coating (Tucker, 1994). Therefore, some gentle finishing process such as shape adaptive grinding (SAG) (Beaucamp *et al.*, 2015; Ghosh *et al.*, 2018) needs to be applied which does not apply very high finishing forces to achieve nanolevel surface finish.

In the recent years, many efforts are made to develop new coating material to enhance the mechanical properties of the WC-Co coating. The grain size of the coating is reduced to nm scale from micron scale and the binders are also being reinforced by some new materials like carbon nanotubes (CNT). An exhaustive research work is continuing to find more suitable fabrication technique and to optimize the process parameters. Furthermore, many post processing techniques are also used and being developed to improve the surface finish as well as surface integrity of the coatings as shown in Fig. 1. In this article, the conventional as well as newly developed coating materials and its various post processing techniques are comprehensively discussed. The mechanical and tribological properties of the newly developed material and processed surfaces are also reported.

Materials

Conventional or Microcrystalline Coating

Conventional WC-Co coatings have been extensively used since the past decades. In this case, the WC grains having size in micron scale (generally 1–20 μm) are embedded into the ductile Co matrix. The percentage of Co content may be varied (generally 10%–23%) to impart different mechanical properties. The decomposition of WC particle during fabrication can hardly be eliminated that leads to the deterioration of the interface bonding. Therefore, the tribological property of the coating is declined. Many literatures are available where the correlations among the process parameters, powder characteristics, coating microstructure and wear resistance of the coatings are studied. It is found that processing condition, initial powder characteristics (i.e., phase content, particle size and grain size) have remarkable effect on the properties of the coatings (Ramnath and Jayaraman, 1989; Voyer and Marple, 1999; Stewart *et al.*, 1999). Yang *et al.* (2003) have studied the effect of WC grain size on the wear behaviour of WC-12Co coating. Higher order decomposition of WC has been observed with the reduction in grain size. It was observed that the specific wear rate of the coatings increases with the increase of carbide grain size. Usmani *et al.* (1997) fabricated

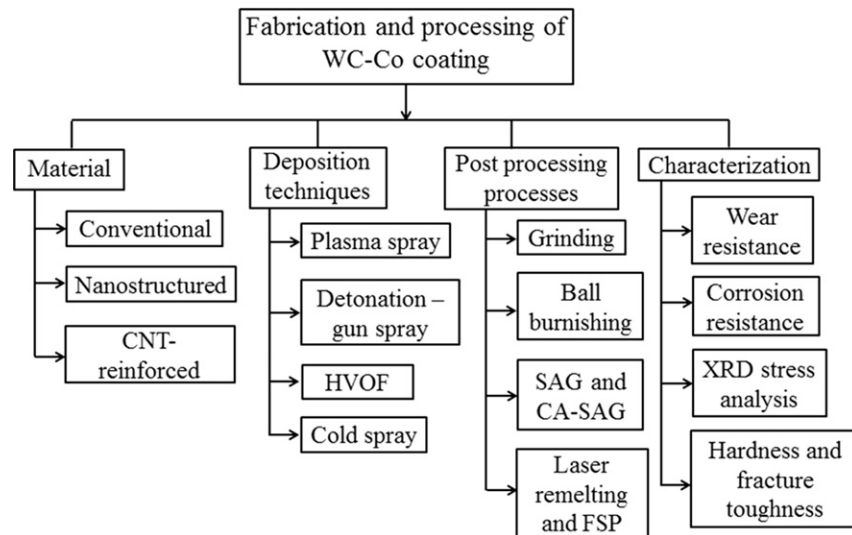


Fig. 1 Fabrication and post processing of WC-Co coating (CNT-carbon nanotube, SAG-shape adaptive grinding, CA-SAG- chemical assisted SAG, FSP-friction stir processing).

WC-17Co coating having different carbide grain sizes. It is observed that the coating with finer grain size possess higher hardness but more prone to decomposition that leads to the lower fracture toughness and abrasion resistance. The decomposition of WC can be significantly inhibited by the addition of chromium (Cr) and it also suppresses the formation of metallic tungsten (W). Moreover, Cr improves the binding strength among the WC phases and the binder and hence, the abrasion resistance of the coating is improved (Karimi *et al.*, 1993). It is also observed that corrosion resistance of the WC-Co coating is lower than the WC-10Co-4Cr coatings owing to the electrochemical properties of cobalt itself (Guilemany *et al.*, 2005). Hence, in the recent days WC-10Co-4Cr coatings are extensively used.

Nanostructured Coating

In the past years, a remarkable progress has been made in the synthesis of nanocrystalline material. Its application has been extended into various fields of science and technology, including coatings. Nanostructured WC-Co coating has been extensively used for its enhanced mechanical properties (He and Schoenung, 2002). The grain size of WC in nanostructured WC-Co coating varies in the range of 10–500 nm. The coating with grain size below 100 nm is called as nanostructured coating and beyond 100 nm is called as near nanostructured coating (Guilemany *et al.*, 2005). Nanostructured coatings experience higher decarburization compared to the coating with micron scale grain size owing to its larger surface-to-volume ratio (Kear *et al.*, 2001; Lekatou *et al.*, 2015). Moreover, nanostructured powder suffer a higher temperature than the conventional one at same spraying parameters and that also leads to the intense decomposition of WC particles (He and Schoenung, 2002). Therefore, the interfaces between the carbides and amorphous Co increase and its characteristics have a significant role to obtain the desired coating properties. However, Stewart *et al.* (1999) have reported that nanostructured coating possesses a lower wear resistance than the conventional one owing to the severe decomposition of WC particles that leads to the reduction in volume fraction of hard WC phase and generation of amorphous phase in binder. Same observations are also made by Dent *et al.* (2002). He *et al.* (2000) performed the characterization of nanostructured WC-12%Co coating and it is observed that the fracture toughness is increased but hardness is not improved remarkably. He *et al.* (2002), Liu *et al.* (2002b) further developed near nanostructured WC-18%Co coatings with a very small amount of non-WC/Co phases. An improvement in both hardness and wear-resistance were observed.

It is also observed that the propylene gas has the ability to retard the decomposition and hence, superior quality coating can be made. Guilemany *et al.* (2005) reported 30% higher hardness of nanostructured WC-12 Co than its conventional counterpart. This is attributed to the finer size carbides distribution in the Co matrix and the hardening effect of W and C in the binder.

Guilemany *et al.* (2006) introduced bimodal WC-Co powder which is a homogeneous mixture of nano-sized and micron-sized WC-Co particles. To reduce the decarburization of WC and associated cost related to nanostructured WC-Co coating, bimodal powder is prepared where nano-sized powder is the minor constituent (approx. 30%). The cross-sectional SEM images of conventional, bimodal and nanostructured coatings are shown in Fig. 2(a–c), respectively. The micron size (1–4 μm) WC particles are heterogeneously dispersed owing to its lower melting and worse deposition as shown in Fig. 2(a). This leads to the higher porosity of conventional coating compared to others. Fig. 2(b) shows the morphology of bimodal coating. Heterogeneity is also observed in the bimodal coating as it is mixture of nanostructured (30–50 nm) and conventional particles (2–3 μm). A homogeneous dispersion of nanoscale (less than 100 nm) WC grain is observed in the nanostructured coating as shown in Fig. 2(c).

The spraying condition is not optimized for bimodal and nanostructured coating and standard spraying condition for conventional coating is used for all the coatings. Therefore, the temperature of the particles depends on its sizes. The nanostructured and bimodal coatings experience more decarburization than the conventional coating. However, the hardness of nanostructured coating is comparatively higher than the other coating. Although nanostructured coating possesses higher hardness, the wear resistance of the bimodal coating is highest. The nano-sized WC particles are dispersed between the gaps of the micron sized WC particles and strengthen the matrix and the presence of hard micron size WC particles in the bimodal coating seems to be the reason of higher wear resistance. [Aw and Tan \(2006\)](#) have also developed a bimodal WC-17Co coating by coupling the very fine nanostructured WC grains with micron-sized grains. They have also observed denser coating than its conventional counterpart.

[Mateen et al. \(2011\)](#) have developed a duplex Co coated near-nanostructured WC-Co powder to impede the decarburization of the WC. **Fig. 3** shows a schematic diagram of a normal carbide particle and a developed particle with the same composition. It is observed that the properties of the near-nanostructured coating such as hardness and wear resistance are better than the conventional one. Moreover, the fracture toughness and wear resistance of the near-nanostructured coating was improved significantly.

[Wang et al. \(2018\)](#) introduced an idea to replace some of the interfaces of WC and amorphous Co (**Fig. 4(a)**) by WC/WC boundaries through near nanostructured WC grains in the coating as shown in **Fig. 4(b)**. In this study, a mechanism of formation of a cluster structure is proposed by bonding WC grains to reduce the intergranular fracture.

In this study, grain growth inhibitors (such as VC and Cr_3C_2) are added to the WC-12 wt%Co powder to reduce the mean grain size of WC from 0.47 μm to 0.22–0.24 μm . **Fig. 5(a)** shows the SEM image of worn surface without grain growth inhibitors (GGI). It is observed that the amorphous Co binder is expelled and WC particles are revealed. Thereafter, the WC particles also get dislodged owing to the removal of binder as shown in **Fig. 5(c)**.

Fig. 5(b) shows the SEM image of worn surface with GGI. The hard WC particles are bonded to each other through the grain boundaries inside the cluster. The thickness of Co binder is significantly reduced. Although, the upper Co binder is expelled, the revealed WC particles are not dislodged owing to the strong binding effect of cluster as shown in **Fig. 5(d)**. Thus the material loss during tribological test is greatly reduced that leads to the remarkable improvement of the wear resistance of the coating.

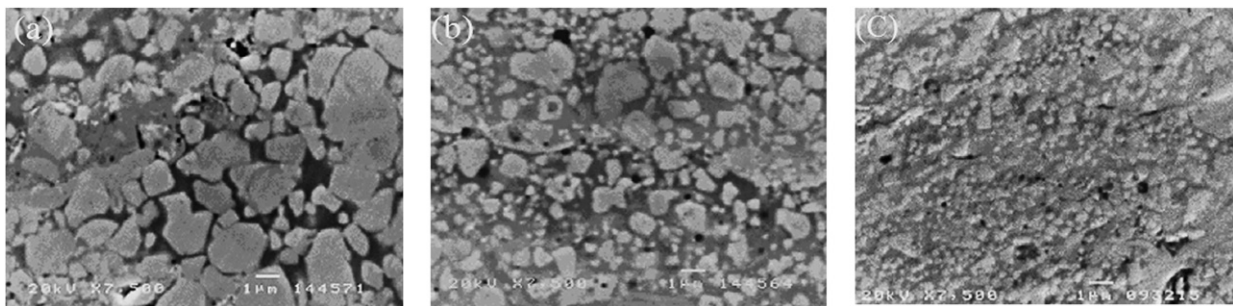


Fig. 2 SEM cross-sectional images of WC-12Co coatings; (a) Conventional, (b) Bimodal and (c) Nanostructured. Reproduced from Guilemany, J. M., Dosta, S., Miguel, J.R., 2006. The enhancement of the properties of WC-Co HVOF coatings through the use of nanostructured and microstructured feedstock powders. *Surf. Coat. Technol.* 201 (3–4), 1180–1190.

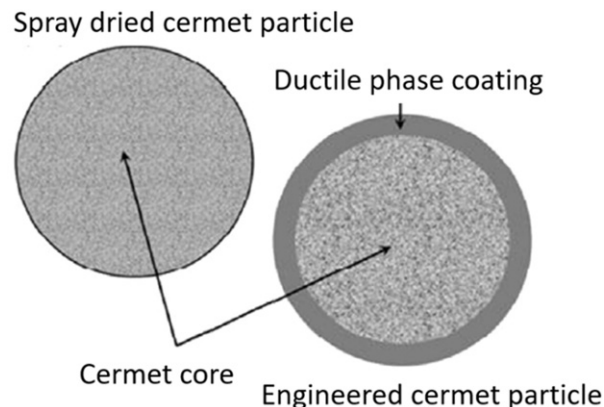


Fig. 3 Schematic of conventional cermet particle and engineered particle. Reproduced from Mateen, A., Saha, G.C., Khan, T.I., Khalid, F.A., 2011. Tribological behaviour of HVOF sprayed near-nanostructured and microstructured WC-17 wt% Co coatings. *Surf. Coat. Technol.* 206 (6), 1077–1084.

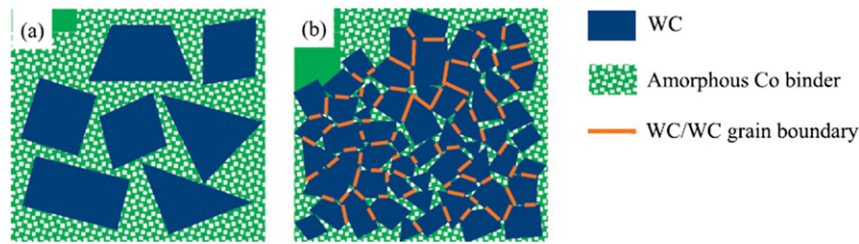


Fig. 4 (a) Schematic of the microstructure of conventional WC-Co coating and (b) the developed microstructure of the coating with fine WC grains. Reproduced from Wang, H., Hou, C., Liu, X., Liu, X., Song, X., 2018. Wear resistance mechanisms of near-nanostructured WC-Co coatings. *Int. J. Refract. Met. Hard Mater.* 71, 122–128.

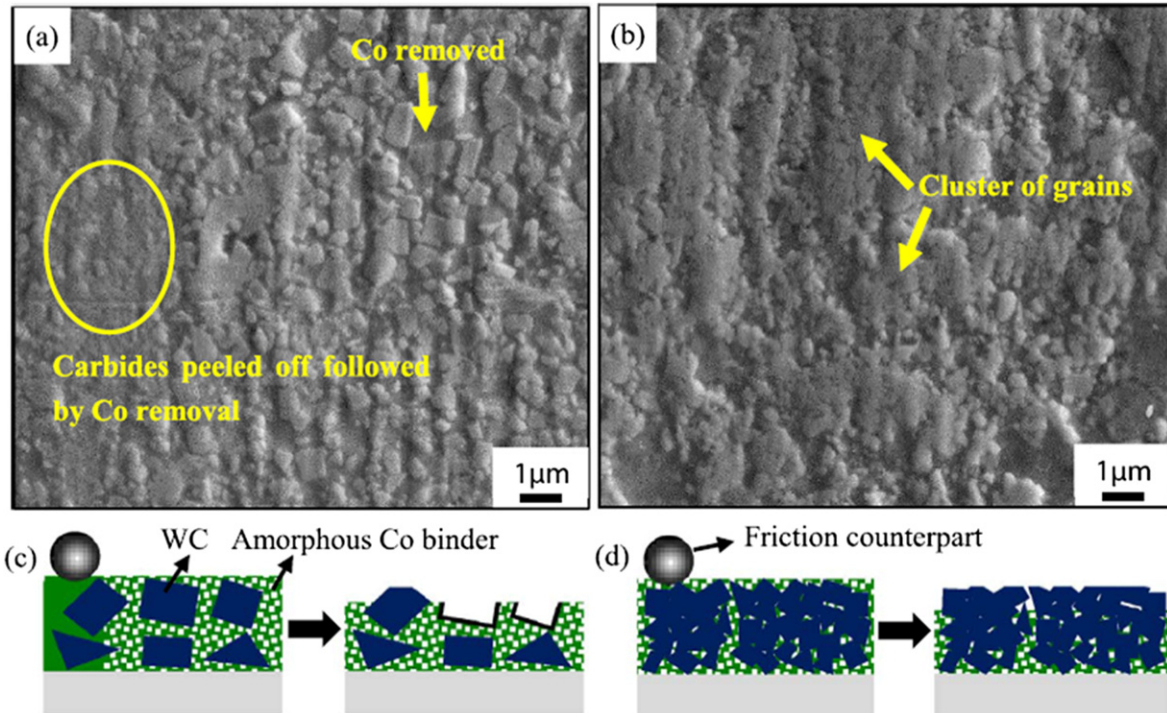


Fig. 5 SEM images of the worn surfaces (a) conventional and (b) with 0.5% VC and 0.5% Cr_3C_2 grain growth inhibitors. The schematics (c) and (d) depicts the mechanism of wear for those coatings. Reproduced from Wang, H., Hou, C., Liu, X., Liu, X., Song, X., 2018. Wear resistance mechanisms of near-nanostructured WC-Co coatings. *Int. J. Refract. Met. Hard Mater.* 71, 122–128.

Coating With the CNT Reinforcement

It is reported that the introduction of multi wall carbon nanotube (MWCNT) can improve the coating properties like hardness, toughness and wear resistance of the composite as well as coating (Xia *et al.*, 2004; Zeng and Lin, 2009; Esawi and Farag, 2007; Balani *et al.*, 2008; Thostenson *et al.*, 2001). This may be attributed to the fiber reinforcement. Rodríguez *et al.* (2014) introduced WC-12 wt% Co conventional coatings with the CNT reinforcement and the tribological and mechanical properties are compared with the coatings without reinforcement. In this study, 0.35 wt% of CNTs (outer diameter=20–40 nm, length=5–15 μm) were mixed with the conventional WC-12% Co powder in ethanol solution by jar-milling for different mixing times. Thereafter, the mixed powder was sprayed using HVOF technique. It is observed that coating fabricated with powder mixed during 36 h reduces porosity and increases hardness. In the case of reinforced coating a higher abrasive wear resistance is observed than the non-reinforced coating. The coating produced from 36 h of mixing possesses an abrasive resistance which is many times higher than the conventional coating as well as the nanostructured coating. This is attributed to the CNTs behaving as bridges and improving the cohesion between lamellas as shown in Fig. 6. As a result mechanical and tribological properties are improved.

Thakur and Arora (2017) developed a CNT reinforced nano-WC-CoCr coating to improve the properties of the coating. It is observed that the introduction of CNTs in the coating enhance the fracture toughness as well as erosion resistance by 'splat-bridging' feature. Moreover, it is also found that the CNT reinforcement favoured the plastic deformation by suppressing the brittle fracture in the coating material.

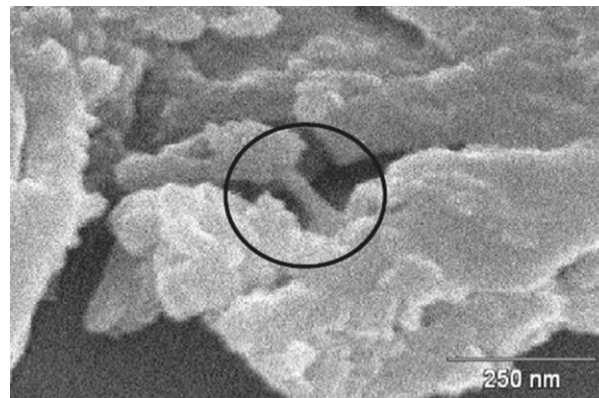


Fig. 6 CNTs bridge in the coating. Reproduced from Rodríguez, M.A., Gil, L., Camero, S., *et al.*, 2014. Effects of the dispersion time on the microstructure and wear resistance of WC/Co-CNTs HVOF sprayed coatings. *Surf. Coat. Technol.* 258, 38–48.

Fabrication Techniques

In the case of thermal spray coating, the coating materials mostly in the form of powder fed to the torch or gun where they are heated around its melting point. Thereafter, the molten or nearly molten droplets of material are accelerated toward the substrate. On impact, the droplets flow into thin lamellar particles and adhere to the surface. The total coating thickness is can be attained by employing multiple passes of the gun. The WC-Co coating can be obtained by various thermal spray processes such as plasma spray, detonation-gun spray, HVOF and cold spray process.

Plasma Spray

In the case of plasma spray process, the temperature of the plasma flame is very high and WC can be easily decarburized (Karimi *et al.*, 1993). Furthermore, cobalt may be evaporated during this process. The microstructure of plasma sprayed WC-Co coating possess many defects such as gas pores, high percentage of porosity, unmelted particles, poor interconnection between the solidified splats (Deen *et al.*, 2017; Afzal *et al.*, 2014, 2015). This may lead to the poorer WC-Co coating properties. Tribological properties and microstructural characterization of plasma spray of WC-Co coating are compared with other coating techniques (Zhu *et al.*, 2001; Al-Mutairi *et al.*, 2015; Sohi and Ghadami, 2010).

Detonation-Gun Spray

In detonation-gun spray process, a high velocity (800–1200 m/s) can be imparted to the spray powders (Du *et al.*, 2005). Therefore, the spraying particles experience a lower temperature and the inflight time is also reduced compared to plasma spray. This leads to the less decomposition of WC phase and hence, better coating properties like higher bond strength, density and lower porosity (Murthy *et al.*, 2001; Wang *et al.*, 2010). However, D-gun spraying may generate high residual stresses in the coating that leads to the formation of cracks (Wang *et al.*, 2010).

High Velocity Oxy-Fuel (HVOF) Spray

High velocity oxy-fuel (HVOF) spraying technique is widely accepted as a most versatile and flexible spraying process for WC-Co coating. The high particle velocities (greater than 500 m/s) and low flame temperatures (lower than 3000°C) reduce the decomposition of the WC phase and that leads to the superior quality of coating (Murthy *et al.*, 2001; Hong *et al.*, 2013). As a result, HVOF sprayed coating possesses better coating properties. The decarburization of WC phase during coating can hardly be eliminated but, it can be reduced by optimizing the process parameters (Thakur and Arora, 2017).

Cold Spray

Cold spraying or called cold gas dynamic spraying process is comparatively new thermal spray process. In this process, spray particles are accelerated to a high velocity (300–1200 m/s) using a supersonic gas flow (Ji *et al.*, 2013). The material is deposited through intensive plastic deformation upon impact at a temperature far below the melting point of spray materials. As a result, the inherent problems to most of the thermal spray process like oxidation, decomposition, etc., can be eliminated. However, the cold spray process is widely used for metallic coating and it possesses very low deposition efficiency in the case of WC-Co coating owing to the lack of ductile phase (Lekatou *et al.*, 2015; Kim *et al.*, 2005).

Post Processing Techniques

Grinding and Ball Burnishing

The as-sprayed WC-Co coating possesses very high surface roughness. The surface roughness of coatings needs to be reduced to make it suitable for end use. Grinding is well accepted and widely used process to reduce the roughness of coating to sub-micron scale from micron scale. Processing of different WC-Co coatings by grinding and major findings are mentioned in [Table 1](#).

Shape Adaptive Grinding (SAG)

Shape adaptive grinding (SAG) is a flexible polishing process where abrasive particles are supported by elastic backing ([Beaucamp et al., 2015](#)). SAG can undergo large deformation of the abrasive tool as compared to conventional grinding. [Ghosh et al. \(2018\)](#) introduced a multistep finishing strategy using conventional grinding, SAG and chemical assisted SAG (CA-SAG) to achieve nanoscale surface finish of WC-12Co coating. Zirconia-alumina polishing pads was used in SAG and CA-SAG. While, Murakami's reagent (potassium ferricyanide ($K_3[Fe(CN)_6]$), KOH and distilled water in 1:1:10 proportion) was selected as a chemical for CA-SAG ([Polini et al., 2006](#); [Peters and Cummings, 1993](#)). From the 3D surface topography of WC-Co coating before finishing, it is observed that it has very high surface unevenness ([Fig. 7\(a\)](#)). After grinding, it is reduced as shown in [Fig. 7\(b\)](#) and grinding marks were clearly visible in 3D topography which are generated by the aggressive interaction of diamond abrasive with the coated surface. SAG ([Fig. 7\(c\)](#)) and CA-SAG ([Fig. 7\(d\)](#)) were applied to reduce the areal surface roughness to nanometer level. Areal surface roughness (S_a) is reduced to 53 nm from initial 5.04 μm .

[Fig. 8\(a-d\)](#) shows the secondary electron images of the as-sprayed and further processed surfaces. Severe plastic deformation was observed on the coating when conventional grinding was used for pre-polishing. The deformed layer consists of plastically deformed and fragmented WC particles (indicated by arrows 1–2) and the relatively soft cobalt binder is smeared out evenly. Using SAG, the deformed surface layer was removed completely from the ground surface and the WC particles and Co phases were revealed. However, few grinding marks were present (indicated by arrow 3) on the surface and the WC particles were protruded slightly above from the relatively soft Co binder. It is observed in [Fig. 8\(d\)](#) that surface of WC particles and Co binders are lying in the same plane as WC was preferentially removed in the presence of Murakami's reagent. All the grinding marks were removed and the whole surface (both WC particles and Co binders) was finished uniformly. In this case also, no fracture or cracks were observed hence material removal takes place through plastic flow.

Laser Remelting of the Coating

[Chen et al. \(2005\)](#) performed laser remelting of HVOF sprayed conventional and nanostructured coating. At first, WC-12 Co coatings with micron-scale and nanoscale WC phases were deposited by HVOF technique. Thereafter, the laser remelting of the coatings is carried out using a 5 kW CO₂ laser of 2.2 kW, beam diameter of 4 mm, scanning speed of 1000 mm/min. re used and nitrogen as a shielding gas. It is observed that the porosity of the coating is reduced little bit by remelting. [Fig. 9\(a, b\)](#) shows the microstructure of as-sprayed and laser remelted coating. Some major cracks are found on the laser remelted coating as shown in [Fig. 9\(b\)](#). Furthermore, significant reduction in carbide size is also observed. The induced high thermal stress and decarburization of WC phases during remelting are responsible for the crack formation and fragmentation of carbides. It leads to the remarkable reduction in microhardness of laser remelted coating. For both type of coating, the hardness is reduced after remelting. The finer size carbides can be easily pulled out and hence, the wear rate of the laser remelted coatings is also higher than the as-sprayed coatings.

Dejun and Tianyuan ([Dejun and Tianyuan, 2017](#)) performed the laser remelting of HVOF sprayed WC-12Co coating using CO₂ laser of 800 W, scanning speed of 500 mm/min and spot size of 15 mm × 2 mm. It is found that the bonding strength of the coating with the substrate become more strong owing to the formation of metallurgical bond in addition to the mechanical bond. [Chikarakara et al. \(2010\)](#) also performed the laser treatment of WC-CoCr coating. It is observed that the higher level of irradiance resulted in poorer roughness and porous surfaces. Moreover, cracks are formed on the coating and microhardness is also reduced. The lower levels of irradiance can produce more uniform microstructures, reduce the porosity and increase the microhardness of the laser remelted coating.

Friction Stir Processing of the Coating

[Rahbar-Kelishami et al. \(2015\)](#) performed friction stir processing (FSP) of WC-12Co coating to improve its wear resistance. The FSP of the sprayed layer was carried out with a 3° tilt tool angle. The tool is made of WC-3%Co. The tool rotation of 600 rpm and the feed rate of 30 mm/min were selected as process parameters. The sliding wear resistance of the coatings was performed using a pin-on-disk type apparatus with alumina ball as a counter body. The 3D topography and 2D surface profile of wear tracks of as-sprayed and FSP processed surface are shown in [Fig. 10\(a,b\)](#), respectively. [Fig. 10\(a\)](#) shows a porous structure of the as-sprayed coating as well as in the wear track. The pits are visible in the wear track which represents the material removal during the wear test. The depth of wear track was around 21 μm . A dense structure is observed in the wear track of the FSP processed surface as shown in [Fig. 10\(b\)](#) and the depth of the wear track was around 5.2 μm . The comparison

Table 1 Grinding and ball burnishing of WC-Co coating

Authors	Coating material	Process parameters**	Major findings
Murthy <i>et al.</i> (2001)	WC-10Co-4Cr (conventional)	$V_s = 25$ m/s, $V_w = 6$ mm/s, $a_i = 10$ μ m, $a_c = 0.75$ mm Grinding fluid -Water soluble oil. Wheel-resin bonded diamond.	- Grinding induces a high compressive residual stress in the coating surface owing to the aggressive interaction of diamond abrasives with the coated surface. - The presence of high compressive residual stress increases the erosion resistance of the ground surface.
Liu <i>et al.</i> (2002b)	WC-12 Co (nanostructured)	$V_s = 33$ m/s, $V_w = 1, 4$ and 8 mm/s, $a_i = 2, 5, 15$ and 30 μ m Wheel-Cup-type diamond bond-vitrified, resin and cast iron fiber grit size-125, 15 μ m grinding fluid-Water based synthetic solution.	- The normal force increases with the increase of depth of cut or feedrate and depth of cut has more influence. - The surface roughness increases with the increase of feed rate and depth of cut. - Both brittle fracture and plastic deformation are observed on the ground surface. - Grinding marks are most significant characteristic under all conditions. - At higher MRR, more brittle fractures are found.
Maiti <i>et al.</i> (2009)	WC-CoCr (conventional)	$V_s = 30$ m/s, $V_w = 5$ mm/s, $a_i = 10$ μ m. Wheel- diamond. Grinding fluid - water soluble coolant.	- The microhardness of the ground surface is increased by 33% at a thickness of 200 μm. This attributed to the incorporation of higher compressive residual stress in the ground surface. - The abrasive wear resistance and erosive wear resistance of the ground surface are increased by 64.3% and 83.4%, respectively. - At the first stage of abrasive wear, plastic deformation and subsequent removal of binder is observed. Thereafter, the WC grains get dislodged.
Masoumi <i>et al.</i> (2014)	WC-10Co-4Cr (conventional)	$V_s = 20, 25, 30$, and 35 m/s, $V_w = 142, 273, 413$, and 550 mm/s. $a_i = 4, 10, 16$, and 22 μ m. Grinding fluid -Water soluble oil. Wheel-resin bonded diamond.	- The depth of cut has a remarkable effect on the cutting forces. - Both plastic deformation and brittle fracture are identified as material removal mechanism. - As the wheel speed increases, plastic deformation becomes the dominant removal mechanism. - At higher MRR, material is removed through brittle fracture.
Tillmann <i>et al.</i> (2015)	WC-12Co (fine powder with a carbide size of 400 nm) (Grinding (1) and ball burnishing (2))	(1) $V_s = 10$ m/s, $V_w = 3.3$ mm/s, $a_i = 10$ μ m Wheel-vitrified bonded diamond. Grain size- 91 μ m. (2) Hydrostatic ball burnishing tools of dia 6.35–12.7 mm and feed rate 83 mm/s.	- The wear resistance of the forming dies can be improved by finishing the components using grinding as well as ball burnishing. - The ground and ball burnished die possess almost same wear resistance. - In ball burnishing, material is not removed. Surface finishing is obtained by plastic deformation of the coating asperities. Hence, it is an economic process.
Zoei <i>et al.</i> (2016)	WC-10Co-4Cr	$V_s = 25, 30$, and 35 m/s, $V_w = 273, 413$, and 550 mm/s, $a_i = 4, 10$, and 16 μ m. Grinding fluid-Water soluble oil. Wheel- resin bonded diamond.	- A higher compressive residual stress is induced in ground surface. - Plastic deformation is found as the dominant removal mechanism in grinding. - The wear resistance of the ground surface is improved.

** V_w is the workpiece/table velocity or feed rate, V_s is the wheel velocity, a_i is the wheel depth of cut or infeed per pass and a_c is the cross feed per pass.

of these two wear tracks clearly indicate that the volume of material removed in the case of as-sprayed coating is many times higher than FSP processed surface.

The SEM micrographs of the wear tracks of as-sprayed and FSP processed surface are shown in Fig. 11(a,c), respectively. Some micro cracks are observed on the wear track of as-sprayed coating as indicated by the arrow in Fig. 11(b). The white region indicates the adherence of alumina to the wear track during wear test. Hence, it can be concluded the microcracking and adhesion are the dominant wear mechanism for the as-sprayed coating. The microcutting marks are visible in the wear track of FSP processed sample as shown in Fig. 11(d) that indicates wear mechanism is mostly abrasive wear.

Characterizations

As mentioned in the earlier section, WC-Co coating has substantial industrial applications for its favourable properties. To evaluate or prejudge the performance of the coating during its actual applications, it is essential to perform the various characterizations of the coating. Moreover, it is generally expected that some of the properties of the coating will be improved after post-processing and that needs to be confirmed by proper characterizations. Among the various characterizations, wear and corrosion resistance,

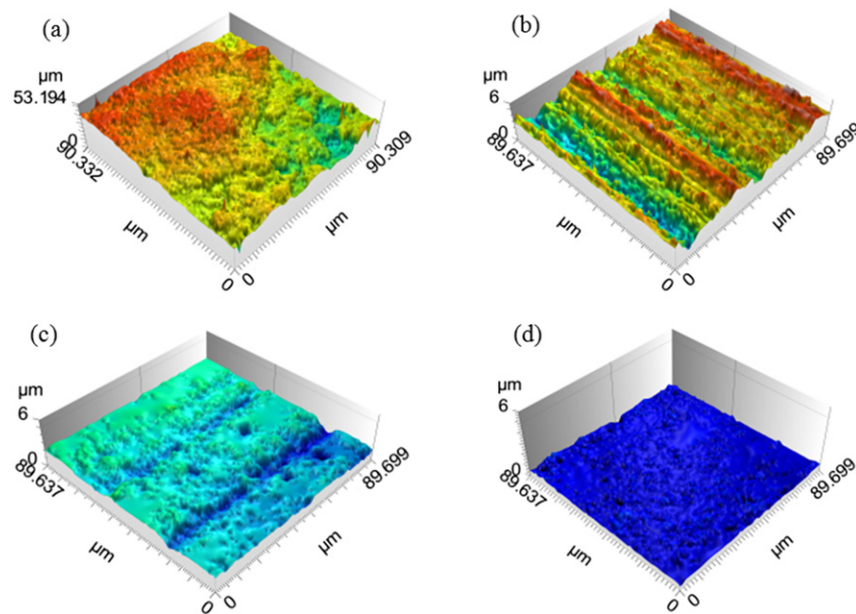


Fig. 7 3D topography of the coated component (a) As-sprayed ($S_a=5.04\ \mu\text{m}$), (b) Grinding ($S_a=0.615\ \mu\text{m}$), (c) SAG ($S_a=266\ \text{nm}$), (d) Chemical assisted SAG ($S_a=53\ \text{nm}$). Reproduced from Ghosh, G., Sidpara, A., Bandyopadhyay, P.P., 2018. High efficiency chemical assisted nanofinishing of HVOF sprayed WC-Co coating. *Surf. Coat. Technol.* 334, 204–214.

residual stress, fracture toughness and hardness measurements are found as essential characterizations of coating. In this section, the reported results of above mentioned characterizations for various coatings are discussed.

Wear Resistance

When the two materials are in a sliding contact, wear or material removal takes place owing to the abrasion, tribochemical reaction, adhesion and surface fatigue. The tribological properties of the coating largely depend on its microstructural properties and type of loading-contact condition (i.e., tribo-system). It is expected that the coating with a higher volume fraction of hard reinforcement phases possesses high wear resistance. Literature related to wear resistance of conventional, nanostructured coatings are presented in the [Table 2](#).

Based on the available literatures, it is perceived that at the initial stage of the sliding wear, the ductile and relatively soft Co binder between the WC phases experience an intense plastic deformation. The deformed Co binder is expelled owing to the development of high compressive stress by the counter body. Under the action of the repeated loads, the fatigue cracks are generated and propagated and that leads to the micro cracking or pull out of WC particles owing to lack of adequate support from the binder. As a result, the wear debris (i.e., Co rich fine WC particles) is formed. Few wear debris are removed and some are trapped between the contacting surfaces. These trapped debris can further degrade both the surfaces as a third body abrasive. Moreover, the debris themselves undergo fragmentation and very fine debris particles are formed consequently. As the finer particles produce less damage to the surfaces, the coating with finer grain size possesses lower wear rate. The finer particles are reattached to each other owing to its large specific surface area and a tribo-film is formed over the surface as shown in the [Fig. 12](#). The ductile and soft Co acts as binder to make a dense tribo-film and facilitates good cohesion of the particles in the film and adhesion to the underlying material. This dense tribo-film protects the surface from further degradation and reduce the initial higher wear rate to a comparatively lower steady wear rate ([Yang et al., 2003](#); [Wang et al., 2013](#); [Guilemany et al., 2001](#); [Magnani et al., 2008](#); [Qiao et al., 2001](#); [Slavin and Nerz, 1991](#)).

Corrosion Resistance

Corrosion can be defined as the deterioration of the material and its functional properties owing to the chemical and electrochemical reaction of the material with its surrounding. The physical state (i.e., solid, liquid and gas), chemical composition and temperature of the environment are significant controlling parameters. Besides, relative velocity of the solution (i.e., environment) and mechanical load (such as residual stress) have also considerable effect on corrosion. Corrosion has detrimental effect on the useful service life of the components. Hence, it is desirable that the corrosion rate of the material should be as low as possible. The corrosion behaviour of WC-Co coating is complex in nature owing to the presence of multiple phases. WC phases possess eminent wear and corrosion resistance owing to its high hardness and the chemical stability. The corrosion resistance of WC-Co coating significantly depend on the properties of binder matrix because Co phase possesses very high corrosion rate ([Neville and Hodgkiess, 1999](#);

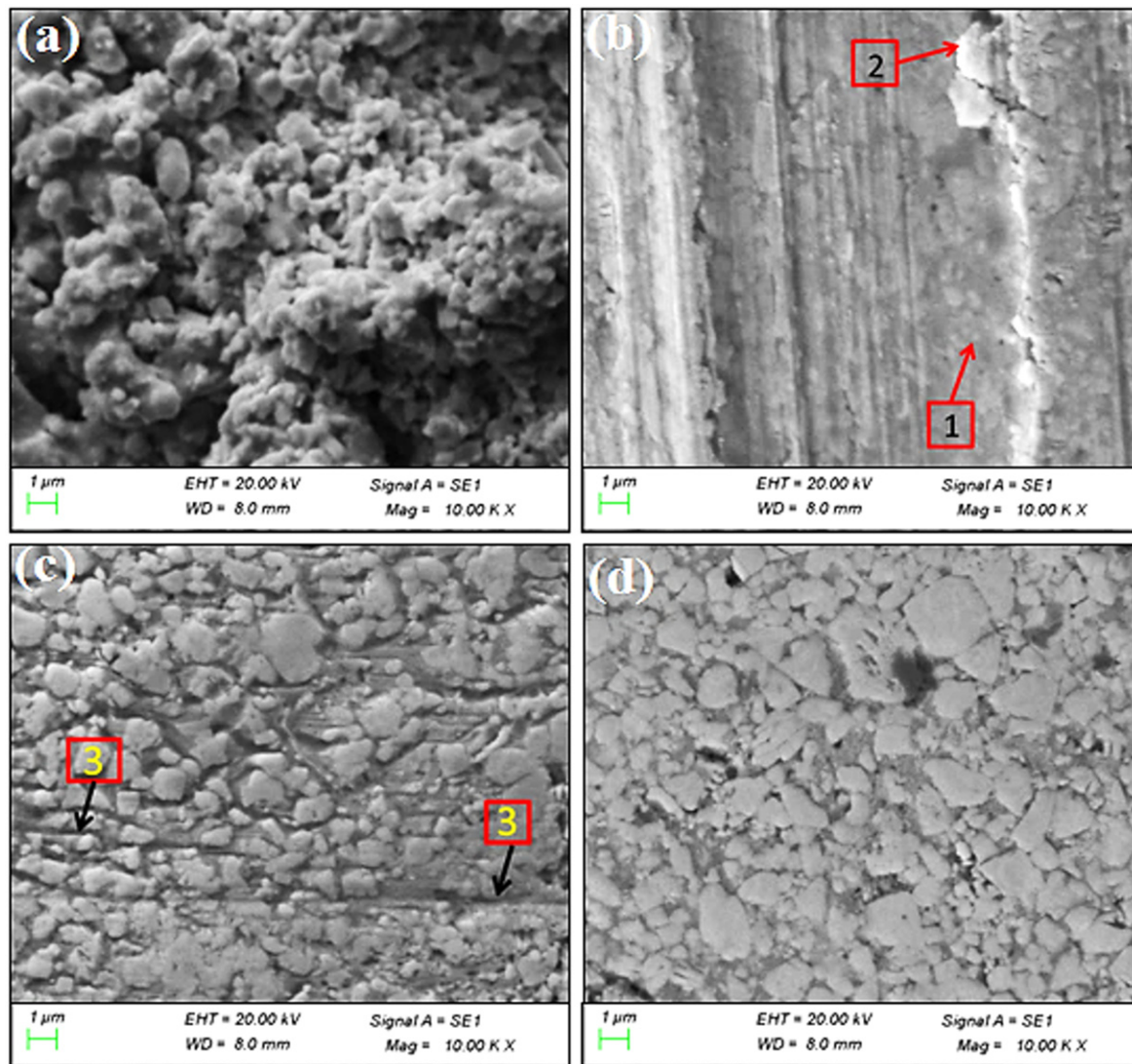


Fig. 8 SEM micrographs of coated component (a) As-sprayed, (b) Ground, (c) After SAG, (d) After CA-SAG. Arrows represents (1) plastically deformed WC, (2) fragmented WC, (3) grinding marks. Reproduced from Ghosh, G., Sidpara, A., Bandyopadhyay, P.P., 2018. High efficiency chemical assisted nanofinishing of HVOF sprayed WC-Co coating. *Surf. Coat. Technol.* 334, 204–214.

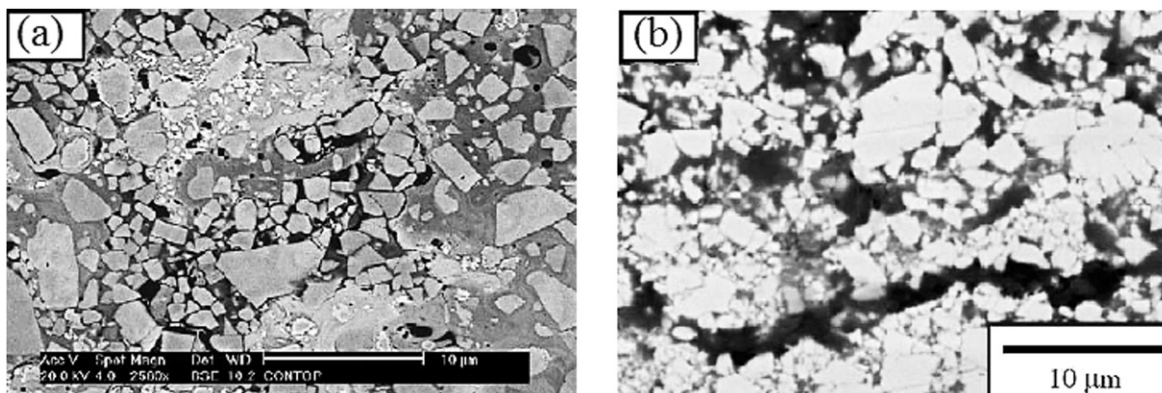


Fig. 9 Backscattered electron SEM images of the coating (a) as-sprayed and (b) after laser remelting. Reproduced from Chen, H., Xu, C., Zhou, Q., *et al.*, 2005. Micro-scale abrasive wear behaviour of HVOF sprayed and laser-remelted conventional and nanostructured WC-Co coatings. *Wear* 258 (1–4), 333–338.

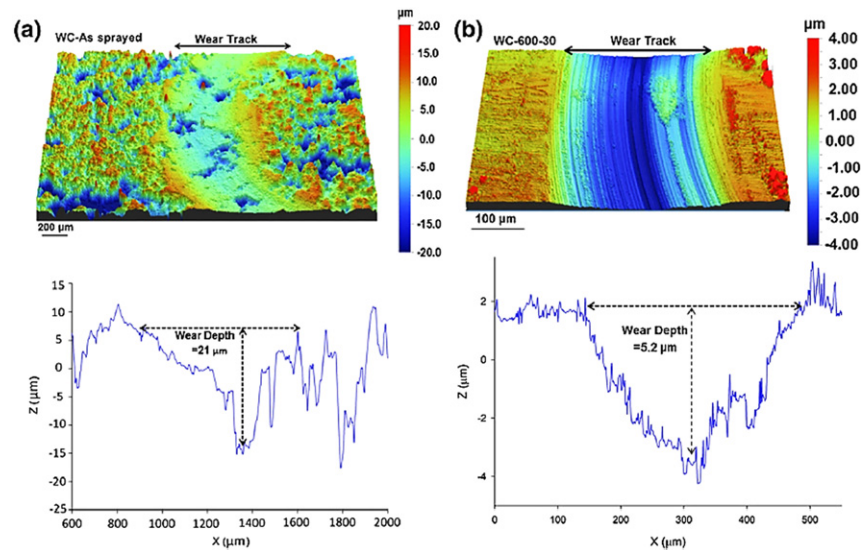


Fig. 10 3D topography and 2D surface profile of wear tracks (a) as-sprayed and (b) FSP processed. Reproduced from Rahbar-Kelishami, A., Abdollah-Zadeh, A., Hadavi, M.M., *et al.*, 2015. Effects of friction stir processing on wear properties of WC-12%Co sprayed on 52,100 steel. *Mater. Des.* 86, 98–104.

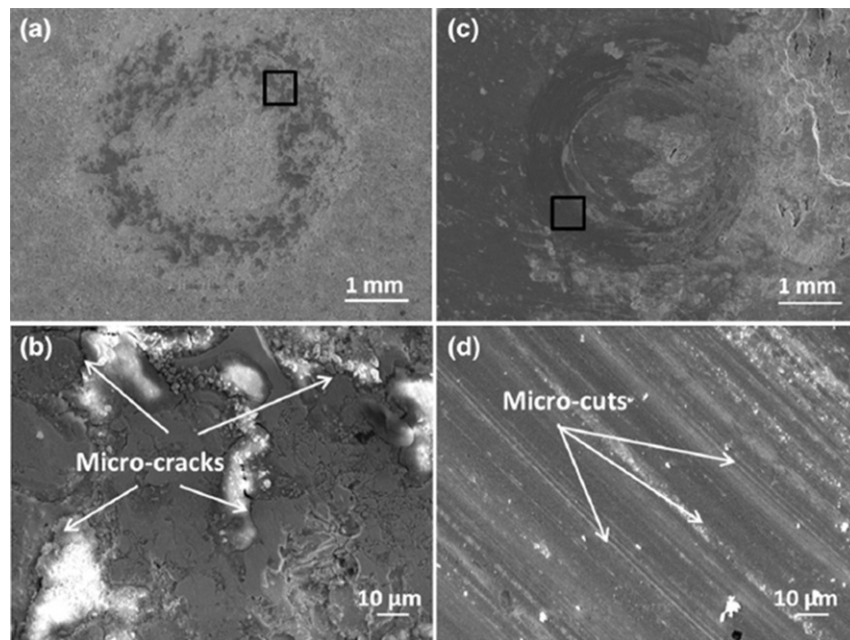


Fig. 11 SEM images of wear tracks (a) and (b) as-sprayed, (c) and (d) FSP processed. Reproduced from Rahbar-Kelishami, A., Abdollah-Zadeh, A., Hadavi, M.M., *et al.*, 2015. Effects of friction stir processing on wear properties of WC-12%Co sprayed on 52,100 steel. *Mater. Des.* 86, 98–104.

Guilemany and De Paco, 1998; Human and Exner, 1997; Berget *et al.*, 1998). The Co binder near the interface of WC phase dissolves owing to micro-galvanic effects that lead to the further pull out of WC particles. The corrosion resistance can be improved by reducing the inter-connected porosities (Wentzel and Allen, 1997, 1995).

The corrosion behaviour of the coating can be assessed by the electrochemical measurements. The measurements are generally performed in the aerated 3.5 wt% NaCl aqueous solution. All the surfaces of the sample for electrochemical test are sealed by epoxy resin except the top surface. Only the top surface will come in contact with the solution. Electrochemical tests are performed in a three-electrode test cell. The sample is treated as working electrode, a saturated calomel electrode as reference electrode and a platinum wire as counter electrode. The test generally includes open circuit potential (OCP) and potentiodynamic polarisation measurements. OCP is performed up to a certain time to stabilize its potential. Thereafter, potentiodynamic polarisation test is

Table 2 Wear resistance of WC-Co coating

Authors	Material	Parameters	Major observations
Wang <i>et al.</i> (2013)	WC-10Co4Cr	● Reciprocating ball-on-block test. ● Zirconia ball of 9.525 mm diameter. ● 50 N load, 0.075 m/s sliding speed and 1800 s time.	● The wear resistance and mechanism of the coatings is affected by both hardness and fracture toughness. ● The presence of zirconia is found in the wear track that indicates the adhesion wear also takes place. ● Decarburisation of the coating affects the wear resistance.
Liu <i>et al.</i> (2002a)	WC-18Co	● Ball-on-disk test. ● Silicon nitride ball. ● 9.8 N load, 30 m/s sliding velocity, 12,000 m sliding distance and 480,000 rotations of the disk.	● Excessive decarburization makes the coating brittle that leads to the higher wear rate. ● The existence of large pits on the wear track indicates that wear occurs mostly owing to the cleavage of the splat boundaries. ● The presence of residual cracks at the splat boundaries of as-sprayed coating increase the wear rate.
Shipway <i>et al.</i> (2005)	WC-12 Co Conventional and nanostructured	● The ball-on-disk test. ● 5000 m sliding, 0.5 m/s sliding speed and 28 mm wear track diameter. ● Alumina ball of 9.6 mm diameter.	● The wear rate of nanostructured coating is many times higher than the conventional coating. ● A few carbide cracking, pull out of WC particles and subsurface cracking are observed in the case of conventional coating. ● Considerable pitting, delamination, intense cracking on the wear track and deep subsurface cracking are found for nanostructured coating. The cracks are formed at the highly decomposed region.
Guilemany <i>et al.</i> (2005)	conventional and nanostructured WC-Co	● Ball-on-disk test. ● 131 rpm velocity, 1000 m testing distance. ● WC-Co ball with 16 mm diameter.	● The friction coefficient of conventional coating is higher than the nanostructured coating. ● The width of the wear tracks of conventional coating was 450–250 μm for the nanostructured coating. ● In spite of having more W_2C phase, higher microhardness leads to the greater wear resistance of the nanostructured coating.
Yuan <i>et al.</i> (2016)	WC-Co with the addition of submicron size WC particles	● Reciprocating wear test. ● 5 mm amplitude, 5 Hz reciprocating frequency, 33 min time, 100 m sliding distance and 5–15 N loads.	● The addition of sub-micron sized WC particles increase both the hardness and wear resistance. ● The addition of submicron size particle transforms the wear mechanism to carbide phase removal instead of splat removal. ● The bonding strength among the splats has significant effect on wear resistance of the coating.
Jacobs <i>et al.</i> (1999)	WC-Co-Cr and WC-Co	● Pin-on-disk test. ● 49 N load, 0.46 m/s linear speed, 28–45 mm track diameter and speed of 313–194 rpm.	● The wear of WC-Co-Cr coatings is mostly three-body abrasion and adhesive wear. ● The softness of Co binder impedes the three body wear in the case of WC-Co coating. The wear particles are smeared over the wear track.
Hong <i>et al.</i> (2014)	WC-10Co4Cr Nanostructured	● Corundum ball of 10 mm diameter. ● Pin-on-disk test. ● 1500 m sliding distance 70 N load and 0.9 m/s sliding velocity.	● The wear resistance of the nanostructured coating can be significantly increased by the optimizing the spray parameters. ● The removal of Co binder followed by the WC particles is observed. The cracks are initiated from the interface of binder and carbides.
Barletta <i>et al.</i> (2010)	WC-CoCr	● Ball-on-disk test. ● 10 N normal load, 0.20 m/s sliding speed and 5000 m sliding distance. ● WC-6%Co balls of 3 mm diameter.	● The wear rate falls on mild wear regime. ● It is observed that the wear resistance increases with the number of torch scan.

performed at fixed scanning rate. The corrosion potential and corrosion current density are evaluated by intersection point of anodic and cathodic polarisation curves. Some reported work related to corrosion study of WC-Co and their main finding are summarized in [Table 3](#).

Residual Stress by X-ray Diffraction (XRD)

X-ray diffraction (XRD) technique using $\sin^2\psi$ method is extensively used for the measurement of the residual stress of the coating. Residual stresses in the thermal spray coating may be compressive and tensile in nature. Compressive residual stress improves the

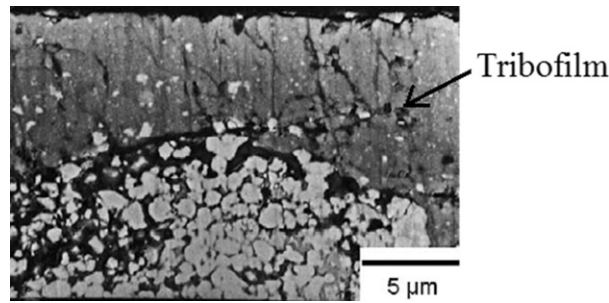


Fig. 12 Cross-section of the wear track. Reproduced from Yang, Q., Senda, T. and Ohmori, A., 2003. Effect of carbide grain size on microstructure and sliding wear behavior of HVOF-sprayed WC–12% Co coatings. *Wear* 254 (1–2), 23–34.

Table 3 Corrosion resistance of WC-Co coating

Authors	Material	Parameters	Major observations
Wang <i>et al.</i> (2013)	WC-10Co4Cr	- Exposed area was 1 cm². - Scanning speed was 0.5 mv/s. 3.5 wt% NaCl solution	- Various cavities or micro-pits are observed owing to the dislodgement of WC phase. - The passive oxide films of CoO, WO₃, etc., are formed and resist further corrosion of the coating.
Hong <i>et al.</i> (2013)	WC-10Co4Cr (Nanostructured)	3.5 wt% NaCl aqueous solution. - Scanning speed was 1 mv/s.	- The presence of nanoclusters and amorphous phase improve the coating corrosion resistance. - The presence of Cr leads to the formation of oxide film and retard further degradation.
Perry <i>et al.</i> (2002)	WC-Co-Cr and WC-Co	- Scanning speed was 0.25 mv/s. - Artificial seawater was used for the test.	- The matrix of WC-Co coating experiences more severe corrosive attack than the WC-Co-Cr coating. - Co matrix possesses more electronegativity than the CoCr matrix that leads to the more intense micro-galvanic corrosion in the case of WC-Co coating.
Guilemany <i>et al.</i> (2006)	WC-Co Conventional and nanostructured	3.4% NaCl solution was used. - Exposed area was 1 cm².	- The nanostructured and bimodal coating possess better corrosion resistance than the conventional one. - The presence of more amorphous phase in the nanostructured coating leads to the better corrosion resistance.

fatigue resistance of the coating. Besides, the tensile residual stress may cause cracking and lead to the fatigue failure (Matejcek and Sampath, 2001). The peening stress, thermal mismatch stress and quenching stress are the responsible to induce residual stress in the HVOF sprayed coating. In HVOF spraying, the semi-molten particles with a very high velocity strike to the substrate and that leads to the formation of peening stress which is compressive in nature. The temperature of the spray particles is rapidly dropped down to the substrate temperature from its melting point. This fast cooling rate during solidification is responsible for the generation of quenching stress and which is always tensile in nature. Moreover, the substrate and coating possess different coefficient of thermal expansion and that leads to the formation of thermal mismatch stress. This stress may be compressive and tensile in nature. However, it is observed that the peening stress and thermal mismatch stresses have dominant effect on the HVOF sprayed WC-Co coating and hence, it possesses residual compressive stress (Lyphout *et al.*, 2008; Takeuchi *et al.*, 1990; Bansal *et al.*, 2007). It is observed that the grinding of WC-Co coating induces high compressive residual stress which may leads to high hardness as well as wear resistance (Murthy *et al.*, 2001; Maiti *et al.*, 2009; Masoumi *et al.*, 2014). Literature related to residual stress measurement and major observations are mentioned in Table 4.

Hardness and Fracture Toughness

Hardness and fracture toughness have significant effect on the wear resistance and failure of WC-Co coatings. Hardness of the coating determines the penetration depth of hard particles when they are in contact. An increase in hardness of the coating indicates higher abrasion resistance. Fracture toughness determine the critical load necessary to propagate a crack in the coating. Hence, it is expected that the coating with higher hardness and fracture toughness leads to higher abrasion resistance. Besides, the size distribution of hard WC has also significant effect on wear behaviour. Hardness and fracture toughness measurement related literature is summarized in Table 5.

Table 4 Residual stress by X-ray diffraction (XRD)

Authors	Material	Parameters	Major observations
Oladijo <i>et al.</i> (2012)	WC-17Co	• X-ray diffraction using Co-Kα radiation having wavelength of 1.79 Å (7 keV). • The shift of the WC (202) Bragg peak was observed at $2\theta = 143.69^\circ$.	• The residual stress of sprayed coating on to three substrates is studied. • The radiation can penetrate up to 4 μm. • The residual stress in brass and aluminium substrates are compressive in nature. In case of super-invar, tensile stress is found.
Nourouzi <i>et al.</i> (2014)	WC-12Co	• Cu-Kα radiation was used. • The strains were evaluated using peak position ($2\theta = 98.7$) of WC in (112) reflection.	• Influences of the process parameters on the residual stress are evaluated. • Stand of distance has significant effect on residual stress followed by oxygen flow and fuel flow.
Zoei <i>et al.</i> (2016)	WC-CoCr	• Cu Kα radiation was used. • Different peak positioning techniques are used.	• Residual stress can be controlled by oxygen and fuel ratio. • The parabolic method is used for the peak positioning as it shows more accurate result. • The compressive residual stress increases after performing grinding operation.
Murthy <i>et al.</i> (2001)	WC-CoCr	• Cr Kα radiation is used. • The Bragg reflection (from WC) utilized for the measurement was from the (256) plane.	• The induced residual stress increases with the increase of depth of cut and feed rate and decrease with the speed. • High compressive residual stress is found after grinding owing to the aggressive interaction of diamond abrasives with the coating. • This attributed to the increase of micro hardness and erosion resistance of the coating.

Table 5 Hardness and fracture toughness of WC-Co coating

Authors	Material	Parameters	Hardness (GPa)	Parameters	Fracture toughness (MPa.m ^{1/2})
Ghosh <i>et al.</i> (2018)	WC-12Co	• Load 300 gm load and dwell time 15 s.	11.02 ± 1.2	• Load 2 kg load and dwell time 15 s are used. • Niihara's equation is used.	7.78 ± 0.9
Mi <i>et al.</i> (2017)	Bimodal WC-Co	• Load 100 gm load and dwell time 15 s.	11.42	• Evans and Charles law is used.	11.5 ± 1.4
Lima <i>et al.</i> (2003)	WC-Co	• Load 29.5–490.5 N.	10.19 ± 0.5	• The Palmqvist coating toughness Niihara's model is used.	4 ± 1
Santana <i>et al.</i> (2012)	WC-12 Co	• 9.8 N load.	7.3 ± 0.9	• The Palmqvist coating toughness Niihara's model is used.	4.56 ± 0.9

Summary

WC-Co coating has many industrial applications as it possesses exceptional tribological as well as mechanical properties. The conventional WC-Co coatings have been widely used since past few decades. However, in the recent years, the conventional WC-Co coatings are being replaced by the nanostructured WC-Co coating. Nanostructured coatings possess better mechanical and tribological properties than its conventional counterparts. Although, there is a serious issue of higher decarburization of nano-sized WC grains during deposition, it can be impeded by optimizing the spraying parameters. The use of bimodal or duplex Co coated powder particles can also improve the coating properties by reducing the decomposition of WC phase. Furthermore, the addition of grain growth inhibitors (such as VC and Cr₃C₂) with the fine powder material leads to the formation of WC grain cluster through the grain boundaries. The wear resistance of the coating is significantly enhanced as the WC grains are strongly bonded and the possibility of grain dislodgement is reduced. The wear resistance of the coating can be significantly improved by MWCNT reinforcement. This is attributed to the CNTs acting as bridges and improving the cohesion between lamellas. Among various fabrication techniques, HVOF spraying technique proves itself as the best process for the economical deposition of WC-Co coating. Although, cold spray process has also ability to produce a superior quality of coating, it possesses very low deposition efficiency in the case of WC-Co coating owing to the lack of ductile phase. The as-sprayed coatings possess very high surface roughness and surface grinding with diamond wheel is widely used to reduce the roughness to sub-micron level. During grinding, high compressive residual stress is induced into the coating surface and that leads to the enhancement of both the microhardness as well as wear resistance. However, to attain nanolevel surface finish of the coating, more gentle and flexible finishing process is

needed. By performing SAG and CA-SAG, sequentially nanolevel surface finish can be achieved. Laser remelted coatings possess low microhardness and wear resistance owing to the crack formation and reduction of carbide size during the remelting. However, the recent study suggest that the lower levels of irradiance can produce more uniform microstructures, reduces porosity and increases microhardness of the laser remelted coating. FSP processed coatings possess better wear resistance. There is a significant lack of literature in finishing of the coating, though nanofinished coatings have significant applications. More emphasis is given to produce different coating material as well as post processing techniques to improve the coating properties as well as surface topography to make them more sustainable and suitable for different applications.

Acknowledgement

The authors acknowledge the funding support from the Indian Institute of Technology Kharagpur under ISIRD grant, Board of Research in Nuclear Sciences (BRNS), India under young scientist research award (34/20/10/2015/BRNS) and Science and Engineering Research Board (SERB), India under young scientist scheme (YSS-2015-001163).

See also: Sustainable Cutting Fluids: Thermal, Rheological, Biodegradation, Anti-Corrosion, Storage Stability Studies and its Machining Performance

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Potential of Co-Fired Fly Ashes as a Construction Material – A Review

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Introduction

In a wide range of fields like electric utility boilers, industrial boilers and kilns, coal is required for heat generation (Tillman and Harding, 2004) which leads to the emission of greenhouse gases (GHG) e.g., NO_x, SO_x and CO₂ (Tripathy *et al.*, 2017). Coal combustion contributes around 41.2% in total global carbon emission (Raghuvanshi *et al.*, 2006; Wu *et al.*, 2015a). Hence, alternate energy sources are being sought in order to meet energy demands and the Kyoto Protocol (Shearer, 2014; Tkaczewska and Małolepszy, 2009).

Co-firing is an emerging method in which the alternate energy options (biomass/non-conventional energy resources) is blended with coal and co-combusted. The inclusion of each ton of biomass reduces one ton of CO₂ emissions (Demirbaş, 2003). In comparison with the pure coal combustion, co-firing reduces the GHG emission as well as the cost associated with it (Doshi *et al.*, 2009; Hein and Bemtgen, 1998; Ipatti, 1988; Senneca, 2008; Wang *et al.*, 2008). Hence, due to its cost-effective and sustainable features, cofiring is gaining popularity among the industries. Countries like Denmark, United States and the United Kingdom have even made biomass inclusion compulsory in the case of electric utilities (Narayanan and Natarajan, 2007). The EU has increased the share of the biomass content from 7.5% (2010) to 14% (2020) in the co-firing process (Kalembkiewicz and Chmielarz, 2012).

Co-fired blended fly ash (CFBA) is a by-product obtained from the co-firing process. Altogether, the above-stated statistics suggest it will lead to increase in the CFBA generation (Kalembkiewicz and Chmielarz, 2012). CFBA generation is of environmental concern as it is different from conventional coal fly ash (CFA) due to the different origin of the secondary fuel and hence, restricts its use in a similar way as CFA (Fuller *et al.*, 2015; Sarabèr, 2012). In the absence of utilization route, CFBA will end up as a landfill which will be a cause of solid waste accumulation.

For the past five decades, CFA was used in the development of various construction material (Doshi *et al.*, 2009; Bouzoubaa *et al.*, 1999; Manz, 1997). Whereas, CFBA is comparatively new and its engineering properties have not been fully explored (Faleschini *et al.*, 2015; Wu *et al.*, 2011). Through literature survey of last two decades, it was observed that the various R&D work was carried out to investigate the effect of co-combustion in greenhouse gases emission trend, chemical and physical characterization of the CFBA generated and the feasibility of CFBA as a construction material. These articles provide the information regarding the available test methods for the characterization of raw material prior to be used in the concrete/mortar, fresh concrete properties and durability of concrete.

The aim of this article is to highlight the research work carried out using different kinds of CFBA as a construction material. Initial section discusses the types of co-firing and available alternate renewable fuels which was used as a secondary fuel for co-combustion with coal. In the proceeding sections, impact of co-firing on chemical (elemental composition, loss on ignition, leaching of metals, radioactivity test), physical (morphology, grain size distribution, bulk density, particle density, specific gravity, activity index) and mineralogical properties of CFBA is discussed. The study was further extended to the effect of CFBA inclusion, as a supplementary cementitious material (SCM), on the concrete/mortar properties. The mortar/concrete properties studied were, fresh concrete properties (hydration kinetics, workability, setting time), hardened concrete properties (compressive strength, water absorbability, resistance against wetting/drying cycles, freezing and thawing, alkali-silica reaction expansion, chemical tests).

Co-Combustion Fuels

Co-firing can be categorized into three types, mainly direct co-firing, indirect co-firing and parallel co-firing. In the process of direct co-firing, biomass and coal are mixed and fed into the furnace and co-combusted. Whereas, in the remaining two methods the fuels do not interact with each other during combustion (Nussbaumer, 2003). Indirect and parallel co-firing generates separate ashes of biomass and coal, whereas the co-fired blended ash (CFBA) obtained from direct co-firing is of hybrid nature, which is focussed in the present study (Narayanan and Natarajan, 2007; Kalembkiewicz and Chmielarz, 2012; Uson *et al.*, 2013). There is a vast variety of biomass type which can be used as a secondary fuel in combination with coal. Saraber (2014), has classified the available biomass which is represented in Table 1.

The number of fuel blends has been reported in the literature (Narayanan and Natarajan, 2007; Fuller *et al.*, 2015; Faleschini *et al.*, 2015; Nussbaumer, 2003; Sarabèr, 2014; Barbosa *et al.*, 2011; Cenni *et al.*, 2001; Grammelis *et al.*, 2006a; Illikainen *et al.*, 2014; Izquierdo *et al.*, 2008; Kosior-Kazberuk, 2013; Shearer *et al.*, 2010; Tkaczewska *et al.*, 2012; Wang, 2014a; Wu *et al.*, 2015b). Table 2 enlists different CFBA, which has been used as an SCM in mortar/concrete to check the feasibility of CFBA as a construction material.

Table 1 Classification of secondary fuel

S. No.	Classification of biomass	Example
1	Wood and woody biomass	Wood pellets, wood waste from commercial logging, harvesting and mill residues
2	Herbaceous and agricultural biomass	Straw, grass, maize and leaves, olive residue, cacao husks and rice husks.
3	Aquatic biomass	Algae
4	Biomass from animal origin	Manure and meat and bone meal
5	Biomass contaminated with mineral matter from anthropogenic origin	Sewage sludge, paper sludge, solid recovered fuel (SRF) and demolition wood.

Note: Reproduced from Sarab  r, A.J., 2014. Co-combustion and its impact on fly ash quality; Full-scale experiments. Fuel Processing Technology 128, 68–82.

Influence of Co-Firing on Ash Properties

CFBA composition and structure are affected by biomass type, biomass property, the proportion of the blend and the combustion conditions (Kalembkiewicz and Chmielarz, 2012; Korpil  rvi *et al.*, 2012; Shearer *et al.*, 2011). To use CFBA as an SCM, it is necessary to characterize its chemical and physical properties. From the literature review, it was observed that there is a lack of availability of the standard codes which lays guidelines specifically for the CFBA or addresses the CFBA. ASTM C 618 prohibits the use of ash in the concrete derived from other than class C and F coals (Wang, 2014a). For concrete production, Indian standard code (IS 3812: 2003) provides standard guidelines for ash obtained from coal. Whereas, EN 450-1:2009 allows fly ash obtained from co-combustion, where the biomass proportion does not exceed 10% of the total blend (Kosior-Kazberuk, 2013). Hence, in order to check the application of CFBA as a construction material, the properties of the CFBA can be compared to the limits set by standard codes for CFA (Korpil  rvi *et al.*, 2012).

Chemical Characterization

To check the feasibility of CFBA in concrete, its chemical, physical and mineralogical characterization is required (Sarab  r, 2012). For the evaluation of the same, various required test methods are enlisted in Table 3. Up to certain limits, an inclusion of biomass does not negatively impact the chemical properties of the CFBA. However, limitations in the chemical properties given in standards need to be specified minutely as some elements present in CFBA in higher quantity, are absent in coal ashes (e.g., phosphorous content, in the case of sewage sludge inclusion as a secondary fuel) (Cenni *et al.*, 2001). Combustion temperature, combustion technology and fuel used plays a major role in the mineralogy and physical properties of the fly ash (Grammelis *et al.*, 2006a; Izquierdo *et al.*, 2008; Koukoulzas *et al.*, 2009).

Elemental composition

Table 4 illustrates the elemental composition of CFBA reported in the literature. From the Table 4, it can be inferred that inclusion of 80% wood pellets did not significantly change the fly ash composition due to its lower ash content i.e., 0.02%–0.5% by weight in comparison with lignite coal, which is 10% by weight (Johnson *et al.*, 2010). Altogether aluminum, silica, potassium and sodium were found to be lesser, whereas, calcium and magnesium content was comparatively higher (Tkaczewska and Ma  lepsz, 2009). Co-combustion results in the ash containing lesser unburned carbon, alkali, magnesium oxide, chlorine and sulfate than CFA (Cenni *et al.*, 2001).

Loss on ignition (LOI)

LOI represents unburnt carbon in the ash (Kalembkiewicz and Chmielarz, 2012) and high LOI value compromises mortar and concrete strength (Sarab  r, 2014). Unburnt particles affect activity index, adsorption of air entrainment additives and workability of the mortar due to their water absorption property (Sarab  r, 2012, 2014; Kosior-Kazberuk, 2013; Foner *et al.*, 1999). Combustion temperature, particle size and moisture content of fuel plays a major role in the LOI value of the ash (Kalembkiewicz and Chmielarz, 2012; Koukoulzas *et al.*, 2009). No linear relation was observed between LOI value and biomass content in the blend (Table 4) which is affirmed by Shearer *et al.* (2011). However, the increasing trend of LOI was observed within the same biomass species. For e.g., LOI value of 15% wood pellets was 0.4, which increased to 0.9 when the wood pellet content was increased to 66% and the same trend was observed in the case of switchgrass.

Leaching of metals

Construction materials have a tendency to leach out environment polluting agents when comes into contact with water (Shaub, 1997; Heasman *et al.*, 1997). Leaching properties of the CFBA was paid less attention (Lopes *et al.*, 2003; Lapa *et al.*, 2007; Steenari and Lindqvist, 1999). Leaching property mainly depends on the composition of the feed fuel (Izquierdo *et al.*, 2008). The inclusion of olive stone and olive pulp, wood pellets and palm pit scales (Table 5) did not cause a marginal difference in leachable elements. Whereas, the inclusion of sewage sludge resulted in the higher amount of Pb, Cu, Zn, P and Sb (Izquierdo *et al.*, 2008). In the study (Grammelis *et al.*, 2006a,b), TCLP was used in the determination of 2 non-metals and 17 metals of CFBA. The inclusion of 19% olive kernels did not cause any alteration in the mobility of elements viz., Sn, Pb, As, Se, Cd and Ag. With the

Table 2 Supplementary fuel used in combination with coal reported in literature

Source	Primary fuel	Secondary fuel	Application (Mortar/Concrete)	Cement replacement (%)	Aim of the study
Izquierdo <i>et al.</i> (2008)	a. Coal tailings b. Coal blend	Wood pellets (45.4%) Sewage sludge (5%) + olive stone and olive pulp (5%)	–	–	Influence of secondary fuel on the fly ash properties (bulk content, mineralogy and leaching of elements)
Sarabèr (2012)	c. Coal blend d. Coal blend	Wood pellets (11%) + palm pit scales (3%) Sewage sludge (5%) + olive pulp (5%)	Mortar	25	Characterization of CFBA and feasibility check of its incorporation in the production of mortars and concrete
Koukouzas <i>et al.</i> (2009)	a. Coal b. Coal c. Coal	Demolition wood (10%–33%) Solid recovered fuel (10%–33%) Poultry dung (10%–33%)	–	–	Chemical, physical, mineralogical and technological property study of CFBA
Kosior-Kazberuk (2013)	a. Polish coal	Wood chips (50%)	Concrete	5, 15, 25	Effect of cyclic freezing and thawing on concrete
Shearer (2014)	a. Bituminous coal a. Bituminous coal b. Bituminous coal c. Bituminous coal d. Bituminous coal e. Bituminous coal f. Bituminous coal g. Bituminous coal	Wood biomass (80%) Clean chipped pine (4%) Pine sawdust (8%) Hardwood, green (10%) Hardwood, green (15%) Whole-tree chipped pine (5%) De-limbed chipped pine (5.5%) Whole-tree chipped pine (5%)	Concrete Concrete	25	Suitability of CFBA as a supplementary cementitious material (SCM)
Wu <i>et al.</i> (2015a)	a. Bituminous coal b. Bituminous coal c. Bituminous coal	Sludge from paper mill pulp process Tire derived fuel (TDF) (18%) Refuse derived fuel (RDF)	Mortar	50 (Binder-GGBS replacement)	Suitability of CFBA as the alkali activators of GGBS
Faleschini <i>et al.</i> (2015)	a. Coal	RDF fly ash	Concrete	20 (volume of cement)	Effect of CFBA on the durability and mechanical properties of concrete, when used as an SCM
Fuller <i>et al.</i> (2015)	a. Hard coal	Wood dust (50%)	Mortar	25	A compliance check of the CFBA containing high percentage of biomass with the EN 450-1
Cenni <i>et al.</i> (2001)	a. Coal	Municipal sewage sludge	–	–	Feasibility of CFBA as an additive to concrete
Grammelis <i>et al.</i> (2006a)	a. Lignite b. Lignite	Olive kernel (5%–20%) Wood (5%)	–	–	Study of fly ash quality and reuse applications
Barbosa <i>et al.</i> (2011)	a. Coal	Sewage sludge (9%) + meat bone meal (22%)	Mortar Concrete	40–43 10–33	Study on the leaching behavior of ash samples and feasibility of the fly ash and bottom ash in mortars and concrete respectively

Johnson <i>et al.</i> (2010)	a. Lignite	Wood pellets (13%–62%)	Mortar	20, 40	Characterization of fly ash and feasibility check to be used as a cement admixture
Tkaczewska and Małolepszy (2009)	a. Bituminous coal	Biomass (not specified) (10%)	Mortar	20, 40	Mechanical behavior of cement with CFBA
Wang (2015)	a. Powder river basin coal	Switchgrass (10%, 20%)	Mortar	15, 25, 35	Study of alkali-silica reaction expansion (ASR) in mortars containing CFBA
	b. Powder river basin coal	Sawdust (20%)	Mortar	15, 25, 35	
Shearer <i>et al.</i> (2010)	a. Bituminous coal	Wood (4%, 5%, 8%)	Concrete	–	Characterization of CFBA and assessment of durability behavior of concrete containing CFBA
Wolski <i>et al.</i> (2004)	a. Coal	Sewage sludge (0%–15%)	–	–	Effect of co-combustion on the fine particulate matter of the ash
Shearer <i>et al.</i> (2011)	a. Eastern bituminous coal	Wood chips (4%–8%)	Mortar	25	Study of the fresh concrete properties (viz. Hydration kinetics, workability and setting time) when CFBA is incorporated as an SCM (focussing mainly on the plastic properties)
Wang (2014a)	a. River basin coal	Sawdust (20%)	Mortar	60, 70, 80 (Binder-Hydrated lime replacement)	Study of mechanical properties of CFBA lime mortar
	b. River basin coal	Switchgrass (10%–20%)			
Tkaczewska <i>et al.</i> (2012)	a. Bituminous coal	Woody biomass (10%)	Mortar	25	A feasibility check of the CFBA in the production of Portland cement type CEM II/A-V 42.5 R

Table 3 Raw material characterization

Characterization	Parameter	Corresponding test	Source
Chemical characterization	Elemental composition	Inductively coupled mass spectrometry (ICP-MS)	Izquierdo <i>et al.</i> (2008), Mellbo <i>et al.</i> (2008), Pettersson <i>et al.</i> (2009)
		Inductively coupled plasma atomic emission spectrometry (ICP-AES)	Grammelis <i>et al.</i> (2006a), Izquierdo <i>et al.</i> (2008), Pettersson <i>et al.</i> (2009), Fryda <i>et al.</i> (2010)
		Mercury Analyser LECO AMA 254, thermal desorption method (TDM)	Izquierdo <i>et al.</i> (2008), Rallo <i>et al.</i> (2010)
		Inductively coupled plasma optical emission spectrometry (ICP-OES)	Fuller <i>et al.</i> (2015), Pettersson <i>et al.</i> (2009), Koukoulzas <i>et al.</i> (2007), Zheng <i>et al.</i> (2007)
		XRF	Illikainen <i>et al.</i> (2014), Shearer <i>et al.</i> (2011), Koukoulzas <i>et al.</i> (2009), Johnson <i>et al.</i> (2010), Yeboah <i>et al.</i> (2014)
	LOI	Thermo gravimetric analysis	Shearer <i>et al.</i> (2011)
	Radioactivity test	–	Grammelis <i>et al.</i> (2006a,b)
	Leaching	Compliance leaching test (EN 12457 Part 2)	Izquierdo <i>et al.</i> (2008), Korpiljärvi <i>et al.</i> (2012)
		Standardized regulatory German test (DIN 38414 part 4)	Cenni <i>et al.</i> (2001)
		Toxicity characteristics Leaching Procedure (EPA TCLP 1311)	Cenni <i>et al.</i> (2001)
Physical characterization	Morphology	NEN 7341	Cenni <i>et al.</i> (2001)
		Scanning electron microscopy (SEM)	Sarabèr (2012), Kosior-Kazberuk (2013), Johnson <i>et al.</i> (2010)
		Scanning electron microscopy-energy dispersive spectra (SEM EDX)	Koukoulzas <i>et al.</i> (2009)
		Quantitative EDS analysis	Tkaczewska and Małolepszy (2009), Faleschini <i>et al.</i> (2015), Sarabèr (2014), Johnson <i>et al.</i> (2010)
	Grain size distribution	Laser granulometry (Malvern)	Sarabèr (2012), Sarabèr (2014), Korpiljärvi <i>et al.</i> (2012), Johnson <i>et al.</i> (2010)
	Particle density	Pycnometer method	Faleschini <i>et al.</i> (2015)
	Specific gravity	Volume displacement of kerosene	Johnson <i>et al.</i> (2010)
	Activity index	As per EN 450-1	Sarabèr (2012)
	Soundness test	Le Chatelier	Sarabèr (2012)
	Surface area	Brunauer, Emmet and teller (BET)	Shearer <i>et al.</i> (2011)
Mineralogical characterization	–	Qualitative X-Ray Diffraction (XRD)	Sarabèr (2012), Koukoulzas <i>et al.</i> (2009)
		Quantitative X-Ray Diffraction (QXRD)	Sarabèr (2012)
Fresh concrete properties	Hydration kinetics	Calorimeter	Tkaczewska and Małolepszy (2009), Shearer <i>et al.</i> (2011)
	Workability	Mortar flow, slump test	Sarabèr (2014), Cenni <i>et al.</i> (2001), Shearer <i>et al.</i> (2011)
	Setting time	Vicats apparatus	Sarabèr (2012), Sarabèr (2014), Shearer <i>et al.</i> (2011)
Hardened concrete properties	Mechanical test		
	Compressive strength	EN 12390-3:2002	Kosior-Kazberuk (2013), Hansen (1986)
	Density	EN 12390-3:2003	Kosior-Kazberuk (2013)
	Splitting tensile strength	ASTM C 496 standard	Nazari and Riahi (2011)
	Flexural strength		Hansen (1986), Nixon (1978)
	Shear strength		Hansen (1986)
	Modulus of elasticity		Hansen (1986), Nixon (1978)
	Bond strength		Knights (1998)
	Drying shrinkage		Ravindrarajah <i>et al.</i> (1987), Sri Ravindrarajah and Tam (1985)
	Durability test		
	Water absorption	EN 12390-3:2004	Kosior-Kazberuk (2013)
	Water penetration depth	–	Faleschini <i>et al.</i> (2015), Kosior-Kazberuk (2013)

Table 3 Continued

Characterization	Parameter	Corresponding test	Source
	Resistance against wetting/drying cycles	–	Faleschini <i>et al.</i> (2015)
	Freezing and thawing	–	Kosior-Kazberuk (2013), Johnson <i>et al.</i> (2010)
	Alkali-silica reaction	–	Shearer (2014), Wang (2015)
	Thermal conductivity	The two-linear parallel-probe (TLPP) method	Morabito (1989)
	Sound absorption	ISO 354 and KS F 2805	Park <i>et al.</i> (2005)
	Chemical tests	Sulfate test	ACI Committee (2001)
		Acid test	ACI Committee (2001)
		Carbonation	ACI Committee (2001)

Table 4 Elemental composition of CFBA

Component	50% wood <i>Fuller et al.</i> (2015)	5% wood pellets <i>Johnson et al.</i> (2010)	66% wood pellets <i>Johnson et al.</i> (2010)	10% biomass <i>Tkaczewska and</i> <i>Małolepszy (2009)</i>	20% sawdust <i>Wang</i> (2014b)	10% switchgrass <i>Wang</i> (2014b)	20% switchgrass <i>Wang</i> (2014b)	50% wood chips <i>Koukouzas et al.</i> (2009)
K ₂ O	4.19	0.7	1.17	2.42	1.89	2.01	2.49	2.23
Na ₂ O	0.94	7.3	7.46	1.48	1.72	1.61	1.39	1.46
CaO	8.72	13.6	14.5	8.7	21.86	20.78	18.28	14.19
MgO	2.49	2.5	2.91	5.4	5.12	5.06	4.65	5
SiO ₂	52.2	45.2	43.6	48.7	35.23	36.22	38.27	28.05
Al ₂ O ₃	23.03	21.5	21	21.2	20.87	20.88	21.1	15.11
Fe ₂ O ₃	5.61	4	3.9	10.1	6.22	6.2	6.33	7.7
TiO ₂	0.86	1	0.89	–	1.42	1.36	1.4	0.48
P ₂ O ₅	1.05	0.6	0.67	0.002	1.73	1.73	1.75	0.73
SO ₃	0.9	–	–	1.1	3.87	3.35	3.64	9.65
Cr ₂ O ₃	–	<0.01	<0.01	–	0.01	0.01	0.01	–
MnO	–	0.02	0.12	–	0.07	0.06	0.06	–
SrO	–	–	–	–	0.33	0.32	0.3	–
BaO	–	–	–	–	0.62	0.59	0.54	–
LOI	–	0.4	0.9	0.9	1.29	1.33	1.81	16.24

increase in the biomass content, the elements Ca and Cr projected a decrease in the leachability. Whereas, elements Si, Ni, Zn, Na, Fe, Cu, Al, Mg, Co and K showed higher leachability with an increase in the higher content of the biomass in the blend. These data suggest that the biomass type and its proportion in the blend plays a major role in the leachability of metals which is found to be in conformance with the statement of *Izquierdo et al. (2008)*.

Radioactivity test

Ash may contain radioactive isotopes such as ²³²Th, ²²²Rn, ²³⁸U, ²²⁶Ra (*Grammelis et al., 2006a,b*). Hence, the radioactive test is required when the ash is used in building materials (*Kalembkiewicz and Chmielarz, 2012*). Three different CFBA were subjected to radioactive tests in the studies conducted by *Grammelis et al. (2006a,b)*. It was observed that the activity of ²³²Th and ²²⁶Ra of CFBA (coal (70%) and biomass (peat 30%)) was 89 and 163 Bq/kg respectively, and the activity for the same was noted as 68 and 123 Bq/kg respectively for CFBA containing coal (50%) and biomass (50%). The activity values for ²³²Th and ²²⁶Ra further decreased to 57 and 140 Bq/kg when the CFBA was obtained from 90% wood content in the fuel mix. It was inferred that the increase in the share of biomass resulted in a decrease of the radioactivity of the ash.

Activity index (AI)

Pozzolanic activity index or activity index (AI) is the measure of the pozzolanic behavior of the ash when used as an SCM (*Sarabèr, 2012*). AI can be defined as the percentage gain in strength of ash mortar (25% cement replacement by ash) in comparison with the standard mortar at the age of 28 and 90 days. As per the EN 450-1, the AI of the ash mortar at the age of 28 and 90 days should be more than 75% and 85% of the cement mortar respectively (*Fuller et al., 2015; Sarabèr, 2012; Kosior-Kazberuk, 2013*). AI does not give information on the role of the ash behavior when used in concrete. Whereas, through this property, use of ash in the lower strength works such as masonry, road repair etc. can be ascertained (*Fuller et al., 2015*).

CFBA containing poultry dung and demolition wood fulfilled AI criteria. At the age of 28 and 91 days, AI was 82% and 90% for CFBA (18% SRF), 76% and 85% for the CFBA (33% SRF). An increase in the SRF content in the coal blend decreased AI

Table 5 Trace elements observed in co-combusted ashes

Component	Wood pellets (45.4%) <i>Izquierdo et al. (2008)</i>	Sewage sludge (5%) and olive (5%) <i>Izquierdo et al. (2008)</i>	Wood pellets (11%) and palm pit scales (3%) <i>Izquierdo et al. (2008)</i>	Sewage sludge (5%) and olive pulp (5%) <i>Izquierdo et al. (2008)</i>	Olive kernel (19%) <i>Grammelis et al. (2006a,b)</i>	Forest residue (19%) <i>Grammelis et al. (2006a,b)</i>
As	0.6	0.03	<0.01	<0.01	–	0.005
Al	–	–	–	–	1.2	0.5
Ag	–	–	–	–	–	0.035
Ba	1.1	7	22	2	–	–
Ca	–	–	–	–	3080	3230
Cd	<0.01	0.02	0.01	0.03	–	–
Cl [–]	368	<40	<200	<80	–	–
Co	–	–	–	–	0.006	0.006
Cr	0.1	1.3	3	3	0.031	0.044
Cu	0.1	0.04	0.02	0.1	–	–
F [–]	80	17	6	6	–	–
Fe	–	–	–	–	0.115	0.1
Hg	80	<0.001	<0.001	<0.001	–	–
K	–	–	–	–	250	165
Na	–	–	–	–	24	12.3
Ni	0.1	0.05	0.2	0.1	0.015	–
Mg	–	–	–	–	12	57
Mo	1	5	3	8	–	–
Mn	–	–	–	–	0.02	0.02
Pb	<0.01	<0.01	<0.01	<0.01	–	–
Sb	0.2	0.5	<0.01	0.01	–	–
Si	–	–	–	–	1	2.5
Se	0.2	0.6	0.3	1.8	–	0.005
SO ₄ ^{2–}	10,302	7852	861	7294	–	–
Zn	0.03	0.03	0.01	0.03	0.12	0.06

(Sarabèr, 2012). CFBA achieved higher AI of 102% and 107% at 28 and 90 days respectively (Kosior-Kazberuk, 2013). The coarser particle size of the CFBA resulted in the lower AI of 13% and hence, suitable as the microfiller instead of SCM (Tkaczewska and Małolepszy, 2009). It can be stated that the particle size of the ash has a major influence on the AI.

Physical Characterization

Ash can be used in concrete in the form of aggregates or binder. In order to be used as aggregates, ash should possess appropriate gradation and in a case of the binder, it should contain pozzolanic properties (Izquierdo *et al.*, 2008). Major physical characteristics are discussed in the below section which needs to be studied, prior to be used in concrete.

Morphology

Morphology of ash can be determined using Scanning electron microscopy (SEM). With the help of SEM, shape and size of grains can be studied. SEM EDX/EDS method provides the location of elements in the ash area subjected to scanning (Koukouzas *et al.*, 2009; Johnson *et al.*, 2010). CFA particles are spherical in shape (Sarabèr, 2014). As per Grammelis *et al.* (2006a,b), CFBA particles majorly consisted of the irregular periphery and the rest were of spherical, elongated and rectangular in shape. The similar kind of morphology was observed by Kosior-Kazberuk (2013). CFBA possessed sub-angular particle shape in comparison with CFA (Koukouzas *et al.*, 2009). Whereas, CFBA particles were found to be spherical in shape as per Faleschini *et al.* (2015). Mixed morphology was observed in CFBA, i.e., long fibrous wood particles along with a glass sphere (Shearer *et al.*, 2011). CFBA was found less spherical and glassy in comparison with the CFA (Tkaczewska and Małolepszy, 2009). In the described investigations, morphological characteristics of the coal ash and biomass ash both have been simultaneously observed in CFBA. Therefore, it is evident that the co-combustion of biomass with coal results in the mixed morphology of the ash.

Grain size distribution

High surface area, high fineness and low particle size are the requirements to achieve pozzolanic activity within the material (Chindaprasirt *et al.*, 2004) as well as for the proper packing within the matrix (Faleschini *et al.*, 2015). Sarabèr (2012), compared the grain size distribution of coal fly ash and two other CFBA samples. It was found that all the three samples showed similar kind of grain size distribution i.e., 4, 14 and 69 µm respectively for D₁₀, D₅₀ and D₉₀. The study (Wolski *et al.*, 2004), implemented that the sampling position also alters particle size. Mean particle size of CFBA (15% sewage sludge) collected at different sections i.e., filter, cyclone and air pre-heater were found to be less than 10 µm, 2–10 µm and 10–200 µm respectively. Smaller particle size of

CFBA was found i.e., 35% of the fly ash particles were less than 10 μm size (Faleschini *et al.*, 2015). The CFBA (15% wood pellets) consisted majorly of particle size greater than 50 μm , whereas CFBA (66% wood pellets) showed the particle size same as the coal fly ash i.e., 14 μm (Johnson *et al.*, 2010). From these values, it was concluded that the variation in the particle size was dominated by the factors combustion conditions (temperature, loading, soot blowers, etc.) rather than the composition of the fuel which is also affirmed by Johnson *et al.* (2010).

Specific gravity

The specific gravity of CFA is in the range of 2.15–2.63 g/cm^3 (Shearer, 2014; Johnson *et al.*, 2010). Whereas for two CFBA (15% biomass, 66% biomass), the obtained specific gravity was 2.361 ± 0.036 and 2.587 ± 0.064 g/cm^3 respectively (Johnson *et al.*, 2010). Eight different CFBA were evaluated for specific gravity, which was found to be 2.20–2.48 g/cm^3 (Shearer, 2014). These values affirm the statement given by Shearer (2014), i.e., the biomass co-combustion with coal does not cause a significant difference in the specific gravity.

Mineralogical Characterization

The nature of macro elements present in the fly ash is estimated through the mineralogical characterization (Sarabèr, 2012). With the help of Qualitative X-ray diffraction (XRD) mineral phases which are present in the ash can be identified (Faleschini *et al.*, 2015; Koukouzas *et al.*, 2009; Jenkins and Snyder, 1996). However, in order to know the percentage of these available mineral phases Quantitative X-ray diffraction (XRD) (e.g., Rietveld's method) is required (Sarabèr, 2012; Koukouzas *et al.*, 2009). Coal fly ash consists of various phases mainly crystalline phases (e.g., mullite and quartz), amorphous (unburnt particles) and glass phase (Koukouzas *et al.*, 2009; Lothenbach *et al.*, 2011; Ball and Carroll, 1999), no matter whether the coal is mono-combusted or co-combusted (Grammelis *et al.*, 2006a).

Minerals which are majorly present in CFA were found to be Quartz (SiO_2), Anhydrite (CaSO_4), Hematite (Fe_2O_3), Illite ($\text{K}_2\text{H}_3\text{O}$) ($\text{Al,Mg,Fe}_2(\text{Si,Al})_4\text{O}_{10}[(\text{OH})_2,\text{H}_2\text{O}]$), Calcite (CaCO_3), Mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), Magnetite (Fe_3O_4), Amorphous material (Koukouzas *et al.*, 2009; Font *et al.*, 2010). Out of the enlisted CFBA in Table 2, common mineral observed in CFA and CFBA were quartz (SiO_2), hematite (Fe_2O_3) and mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$). In addition to these, Sillimanite (Al_2SiO_5) was observed in CFBA (Faleschini *et al.*, 2015). Amorphous phase was found to a large extent in the coal fly ash and two CFBA samples. Minerals observed in all the samples were quartz (SiO_2), periclase (MgO) and in very less amount of anorthite ($(\text{Ca,Na})(\text{Al,Si})_2\text{Si}_2\text{O}_8$), anhydrite (CaSO_4), calcite (CaCO_3), belite (Ca_2SiO_4), gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$), feldspar ($\text{K}_{0.5}\text{Na}_{0.5}\text{AlSi}_3\text{O}_8$), mullite ($\text{Al}_{4.54}\text{Si}_{1.46}\text{O}_{9.73}$), lime (CaO), hematite (Fe_2O_3). Both CFBA samples possessed similar kind of mineralogy as coal fly ash (Johnson *et al.*, 2010). Crystalline phase observed in the CFA were quartz and mullite. In addition to these two phases, free lime and periclase were present in the CFBA (Tkaczewska and Małolepszy, 2009). As per Koukouzas *et al.* (2009), the elemental composition of the fuel is responsible for the minerals found in the ash. For example, anhydrite is a mineral which is found in the ash when calcium is present in the fuel. Hence, CFBA (obtained from either combustion of wood chips or co-combustion of wood chips and coal) possessed was rich in anhydrite due to the presence of calcium in coal and wood chips. Literature survey implements that the mineralogy depends on the composition of the fuel. In all the cases, the minerals which are due to the coal were found common. Whereas, the variation in the mineralogy was majorly due to the composition of the biomass included in co-combustion.

Fresh Concrete Properties

Hydration Kinetics

Mortars were prepared with and without cement replacement as per the standard ASTM C 109 with the proportion 1:2.75 (cement: sand) and $w/c=0.485$. The heat of hydration in mortars consisting of 25% ash as an SCM was observed to be approximately 19% lesser in comparison with the control mortars (Shearer *et al.*, 2011). An experimental study was carried out in order to compare the heat evolved at 24 h and 72 h in the cement mortars. Different types of mortars were cast as control mix (with no cement replacement), with 20% and 40% cement replacement by CFA and with 20% and 40% cement replacement by CFBA. Heat evolution in 20% CFBA replacement at 24 h was 132 kJ/kg and at 72 h was 171 kJ/kg which is 20% less than the control mix. When the same is compared with the specimens with 20% CFA replacement, the heat evolution in the CFBA mortars was found to be 14% and 17% lesser at the end of 24 h and 72 h. The heat of evolution further reduced to 110 kJ/kg and 139 kJ/kg at 24 h and 72 h respectively when the replacement ratio increased to 40% of cement by mass (Tkaczewska and Małolepszy, 2009). It is concluded in the studies that the pozzolanic substitution resulted in the less availability of cement for the hydration and the inert behavior of the CFBA in the initial stages of hydration reaction lead to the decrease in the heat of hydration.

Workability

Factors such as fineness, morphology, LOI, particle size distribution, water demand affect the workability of mixtures (containing ash and cement) (Paya *et al.*, 1996). CFBA inclusion reduced workability up to 50%. Whereas, CFBA (obtained from co-combustion of higher percentages of the biomass with coal) projected the least reduction in the workability, which suggested that the

CFBA does not necessarily have a negative impact on the workability. The angular shape of particles of wood ash did not affect the workability and was stated that the properties like reduced particle size and LOI may be prevailing factors (Shearer *et al.*, 2011). In the experimental study (Johnson *et al.*, 2010), for a particular flow, water demand reduced with the increase in the percentage replacement of cement by CFBA. Hence, it is inferred that the workability is independent of kind of ash and majorly dominated by the physical parameters of the ash, which affirms the statement given by Paya *et al.* (1996).

Setting Time

Setting time of cement mortars prepared by replacing 25% of the cement by the CFBA was tested as per the EN 450-1. Initial and final setting time of the control mix was found to be 271 and 388 min respectively. Initial setting time of the CFBA with 50% poultry dung (PD), 30% demolition wood (DW), 18% solid recovered fuel (SRF1) and 39% solid recovered fuel (SRF2) observed to be 283, 290, 297 and 405 minutes respectively. While the final setting time for the same was observed as 396, 459, 477 and 557 min respectively. Values suggest that there is no co-relation between the setting time and the biomass type in the blend. Whereas, in the case of SRF, the increase in the biomass share in the blend results in a increase in the initial and final setting time with respect to control mix (Sarabèr, 2012). Setting time of plain cement mortar and three types of mortars with 25% replacement (% weight by mass) by CFA, CFBA (4% biomass) and CFBA (8% biomass) was studied. The initial setting of the mortars with and without replacement was found to be similar and the final setting was 6.25 h for all (Shearer *et al.*, 2011).

Mechanical Properties of Hardened Concrete

Above described properties of the material is important to know about the material behavior, when used in concrete. The inclusion of fly ash causes an alteration in the microstructure of the cement matrix (Tkaczewska and Małolepszy, 2009; Wang *et al.*, 2008; Pigeon *et al.*, 1996). The performance of CFBA in concrete is complex (Sami *et al.*, 2001). In order to achieve satisfactory concrete performance, it is mandatory to check the feasibility of concrete composites to sustain environmental exposure (Kosior-Kazberuk, 2013). In this section, physico-mechanical tests performed on concrete (containing CFBA) is discussed.

Compressive Strength

CFBA was used as a partial replacement of Portland cement in the production of concrete. Cement replacement was varied from 0%, 5%, 15% and 25% with a constant w/c ratio of 0.5. Compressive strength at the age of 28 days for 0%, 5%, 15% and 25% was 59.7, 52.2, 49.1 and 45.2 MPa respectively. With the increase in the CFBA %, compressive strength declined as well as initial strength gain was observed to be at a slower rate (Kosior-Kazberuk, 2013). CFBA was also used as an SCM in concrete and the mechanical properties were compared to the control mix and concrete with CFA (20% by volume) with $w/c \leq 0.5$. Compressive strength observed at the age of 28-days were 40.7, 38.97 and 39.80 MPa for control mix, mix with CFA and mix with CFBA respectively. The compressive strength of CFBA mix was 2% less than the control mix and is equivalent to the mix with CFA (Faleschini *et al.*, 2015). In these studies, the decrease in strength is attributed to the lesser availability of active silica and pozzolanic activity of the CFBA. As well as the higher water content was also found responsible for the decrease in the strength.

Water Absorption

The use of the CFBA in concrete did not cause any major change in the water absorption property of concrete. Water absorption of concrete with 0%, 5%, 15% and 25% replacement was found to be 3.50, 3.55, 3.20 and 3.33% which is comparable (Kosior-Kazberuk, 2013). Water absorption observed at the age of 7 days was 4% for control mix, 3.8% for mix with CFA and 2.1% for mix with CFBA which was least (Faleschini *et al.*, 2015). The experimental studies suggested that the inclusion of fly ashes (CFA and CFBA), resulted in a lower porosity matrix which was advantageous for decreasing the water absorption.

Resistance Against Wetting/Drying Cycles

Alternate drying and wetting cause disintegration in the concrete, which results in the decrease in strength. In concrete disintegration, salt crystallization in the conglomerate pores acts as a catalyst by causing thermal stresses (Faleschini *et al.*, 2015). Concrete specimens were subjected to 30 cycles of alternate wetting and drying and then checked for compressive strength. The observed reduction in the strength of the control mix, mix with CFA and mix with CFBA was 20%, 21%, 28% with respect to their 28 days compressive strength. The highest reduction was shown by the mix containing CFBA. Alternate wetting and drying caused the formation of micro-cracks of the width of 2–5 μm on the surface of binder matrix. The cracks were common in all the concrete specimens. The inclusion CFA and CFBA as an SCM was unable to enhance the resistance against the deterioration due to the alternate drying and wetting cycles (Faleschini *et al.*, 2015).

Freezing and Thawing

Concrete specimens containing CFBA was subjected to repeated freezing and thawing. Evaluation of surface scaling due to the freezing and thawing was quantified as per CEN/TS 12390-9:2007 (Kosior-Kazberuk, 2013). For concrete specimens (0%, 5%, 15% CFBA) with an air entraining agent (AEA) content of 0.05% of binder weight, observed scaling was below 0.6 kg/m^2 which is acceptable as per SS 13 72 44 (1995). But concrete (25% CFBA) failed to meet the same. Further, the AEA content was increased to 0.10% of binder weight and the scaling was observed in all concrete specimens after 112 cycles of freezing and thawing. Observed scaled material mass in the concrete (0%, 5%, 15% and 25% CFBA) was $0.09\text{--}0.3 \text{ kg/m}^2$, which is within the permissible limits. For a particular AEA content, an increase in the CFBA content decreased frost resistance (Kosior-Kazberuk, 2013). Mortars with cement replacement 0%, 20% by CFA, 20% by CFBA were cast. All the mortar specimens were subjected to freezing and thawing followed by compressive strength test. After 140 cycles of freezing and thawing, 40%–46% decrease in the compressive strength was observed in all the mortar samples (Johnson *et al.*, 2010). The values from these studies suggested that the inclusion of CFBA and CFA as an SCM did not cause any major alteration in freezing and thawing resistance. As well as the air content plays a major role in the freeze-thaw resistance enhancement.

Alkali-Silica Reaction (ASR) Expansion

CFBA is helpful in the reduction of the ASR expansion (Wang *et al.*, 2007). CFBA has a tendency to adsorb alkali ions and results in products which are non-expansive in nature, unlike expansive alkali-silica gel and stated that the CFBA is feasible to be used in concrete (Sarabèr and van den Berg, 2005). The same was also confirmed by the study (Wang, 2015), which focussed on the ASR expansion of the mortars containing CFBA in the proportion of 15%, 25%, 35% weight of the cement. ASR expansion observed for mortars with 15% CFBA was 0.15%–0.2%, for 25% CFBA was 0.1%–0.15% and for 35% CFBA it was found to be 0.05%–0.1%. With the increase in the CFBA percentage inclusion, ASR expansion decreased. Reduction in the ASR expansion in a mortar containing CFBA at 14 days and 28 days by 78%–94% and 68%–85% respectively lesser than standard cement mortar (Shearer, 2014).

Conclusion

The construction industry is an intensive consumer of energy and natural resources (e.g., cement, aggregates etc.). The ever increasing material demand exerts pressure on the environment, which creates a scope of opting alternate sustainable materials. CFA obtained from combustion of coal is an industrial by-product and is an important asset to the construction industry. It can be used as a binder or as an aggregate in mortar/concrete. CFBA obtained from co-combustion of coal and biomass are comparatively new and were not addressed in American Standard (ASTM C 618) and Indian Standard (IS 3812: 2003) due to its non-coal origin. Whereas, European code (EN 450-1:2009) has permitted CFBA with limitations (i.e., biomass $\leq 10\%$ of coal in the blend).

It can be stated that the biomass inclusion in the process of the direct co-firing with coal, does impact the resultant ash properties (chemical, physical and mineralogical etc.). Following conclusion is drawn from the literature:

- The inclusion of biomass (wood, wood pellets, wood chips, sawdust and switchgrass) did not cause any significant alteration in the elemental composition of the CFBA. But, it was observed in Table 4, that with the increase in the percentage inclusion of particular biomass (wood pellets and switch grass), SiO_2 content in the ash decreased.
- The alteration in the chemical properties is mainly affected by the ash content of the included biomass and its chemical composition.
- These two factors also influence the mineralogy of the CFBA. Mixed mineralogy of CFA and biomass ash was observed in the CFBA.
- Rather than the biomass kind the grain size distribution of CFBA was found to be more dependent on the combustion conditions (temperature, loading and soot blowers) and sampling position (i.e., air preheater, cyclone and filter).

Industrial waste i.e., CFBA has a potential to be used as an alternative raw material in the production of mortar/concrete. But the effect of the CFBA inclusion in the quality of the concrete needs to be assessed through conducting the required tests. Effect of CFBA inclusion, as an SCM, in concrete is

- The heat of hydration decreased when CFBA (obtained from co-combustion of wood chips and coal) was used as an SCM due to its inert behavior in the initial hydration stages.
- CFBA (resultant from co-combustion of wood chips with coal and wood pellets with coal), when used as an SCM reduced the workability. In the case of CFBA (obtained from wood chips and coal co-combustion) reduction in workability was 50%.
- Five different CFBA (with secondary fuel as PD, DW, SRF1, SRF2 and wood chips) were unable to cause significant alteration in the initial and final setting time of the cement.
- CFBA (resultant from co-combustion of wood biomass with coal and RDF with coal), due to its lesser content of reactive silica, decreased the compressive strength of concrete. However, the inclusion of these CFBA caused a decrease in the water absorption by forming the lesser porosity concrete.
- CFBA (obtained from co-combustion of coal-switchgrass, coal-sawdust and coal-pine chips) was found to be beneficial in decreasing the alkali-silica reaction by absorbing alkali-ions and resulting into the non-expansive products.
- Whereas, CFBA (obtained from co-combustion of coal-wood biomass, coal-RDF and coal-wood pellets) was found to be ineffective to enhance few properties like resistance to freezing-thawing and alternate wetting-drying.

The absence of a unique trend in the ash properties was noted. Overall, the study was helpful to assess the suitability of various CFBA as an alternate sustainable construction material and its effect on the concrete properties. The study suggests that there is a scope of consideration of such ashes in existing standard codes.

Future Scope

The aim of the review article was to highlight the feasibility of CFBA as construction material. For the evaluation of the same, various required tests associated with the raw material characterization (i.e., chemical, physical and mineralogical) were enlisted and the effect of co-combustion on these properties was discussed. The article also targets the effect of CFBA inclusion (as an SCM) on the fresh concrete and hardened concrete properties. Through the article, an attempt was made to include maximum possible properties of concrete (containing CFBA) to assess the role of CFBA in concrete quality. Still, through the literature, it is observed that there is a scope of research to evaluate the CFBA effect on the concrete properties such as splitting tensile strength, flexural strength, modulus of elasticity, bond strength, thermal conductivity and sound absorption (enlisted in [Table 3](#)). As well as, the durability of the CFBA-concrete against chemical attack (sulfate attack, physical salt attack, seawater exposure, acid attack and carbonation) needs to be addressed, prior to present CFBA as a practical solution to meet the sustainable raw material demand.

Acknowledgement

The last author gratefully acknowledges the support of Indo-US Science & Technology Forum, Department of Science and Technology for the financial support and to undertake this collaborative study. The author is also thankful to the University of Texas, Arlington, USA and Visvesvaraya National Institute of Technology, Nagpur, India for kindly extending desired facilities to carry out the work.

See also: Technology for Producing Briquettes From Wet Biomass

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The Production of Biogas, Biodiesel as High-Value Bio-Based Product and Multiple Bio-Products Through an Integration Approach of the Anaerobic Digestion and Fermentation Processes

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Introduction

According to the recent projections of the world population, there will be an increase in the population in the coming decades. This increase would be associated with an increase in the world energy demands. Consequently, more depletion of energy sources and more major negative impacts of non renewable energy on the global environment are expected. In terms of minimizing the effects of the projected increase in world energy demand, more investigation on the renewable energy are crucially needed to be good alternatives for non-renewable energy. Biomass is one of these renewable energy resources. It is the fourth largest primary energy resource, renewable, sustainable and a clean resource of energy that has numerous benefits, locally and globally (UN, 2015; Goswami and Kreith, 2015; Saxena *et al.*, 2007; Katuwal and Bohara, 2009). As is well known, lignocellulosic materials are available everywhere in low and stable costs. It is mainly waste materials that are containing in abundance of carbohydrates and non-competitive with food chain (Zabed *et al.*, 2016; Zhao and Xia, 2010). Biomass as an energy resource, requires conversion process to be used as a bio-fuel. AD is one of the most effective biological conversion process of biomass into bio-fuel. It breaks down organic matter by microorganism and enzymes in an oxygen-free environment to produce biogas. Generally, the final output products of AD process are biogas and digestates. Where, the biogas can be directly used in several applications or upgraded and either injected into gas grid or used as a transportation fuel in compressed natural gas (CNG) motor vehicles. While, the digestate generated usually comes in liquid and solids streams and can be further separated. It contains the remained nutrients which did not digested in the digestion process such as; ammonium and phosphates. Liquid stream has the potential to be used in agriculture as a bio-fertilizer and others while, solid stream can be composted, used for dairy bedding or applied directly to cropland. It can be also used in making of high-value bio-based products through bio-refinery concepts i.e., biodiesel (Teater *et al.*, 2011; Yue *et al.*, 2010; De Jong and Jungmeier, 2015; Van Den Hende *et al.*, 2015; Sawatdeenarunat *et al.*, 2016). The production of lignocellulosic biodiesel includes five main stages, are: feedstock pretreatment, carbohydrate scarification, aerobic fungal fermentation, lipid extraction and transesterification. Where, pretreatment is the most important steps as the all following steps in the process are highly depending on its results (Ruan *et al.*, 2013; Agustini *et al.*, 2012). Moreover, although biogas is a promising, sustainable and renewable energy substitute, the sustainable development of AD process primarily depends on the ability to deal with the excessive digestate produced. An improper handling of the digestate would contribute in serious environmental issues. Due to that and to fully utilize the digestate and convert it into useful bio-based products, the attention towards the development of new bio-refining processes, has recently increased. Several recent studies have focused on developing an integrated system including AD and fermentation process to convert various feedstocks into bio-fuel and high-value bio-based products (Wang *et al.*, 2016; Dahlin *et al.*, 2015; Zhong *et al.*, 2015). Successful application of such a system could greatly results in the double benefit of producing renewable energy while adopting a zero waste approach. However, the proposed work aims to present an overview of integration approach of AD and fermentation process to produce biogas, biodiesel and multiple bioproducts such as: livestock food, bio-fertilizer, glycerin in which they can be utilized in many applications and end up with zero waste.

Biodiesel

Biodiesel is a promising form of liquid bio-fuel. It would play a significant role in providing the energy requirements for transportation. Thus, many scientists and researchers have focused recently more on the efficiency and emissions of the biodiesel engine. According to a study on biodiesel engine performances and emissions in 2011 (Jinlin *et al.*, 2011), using of biodiesel may result in considerable drop in particulate matter PM, hydro-carbon HC and carbon monoxide CO emissions and increase in nitrogen oxides NO_x due to the higher amount of oxygen content in biodiesel comparing to conventional diesel. It may result also in reduction in engine power because of the reduction in calorific value of biodiesel compared to conventional diesel. The study has concluded that, the blends of biodiesel with low percentage of petroleum diesel can help in controlling air pollution and easing the pressure on scarce resources without influencing on engine power and economy. In comparison to bio-ethanol as a liquid bio-fuel, biodiesel stands at present in lower position than bio-ethanol because of several factors such as; lower environmental sustainability of raw materials it is obtained from, not as good as bio-ethanol in mitigation of GHG emissions, higher production cost and a less favorable future evolution (Mussatto *et al.*, 2010; Demirbas, 2007, 2011, 2009; Balat and Balat, 2009).

Conventional Diesel Versus Biodiesel

Biodiesel can be used in diesel engines. It can be also blended with petro-diesel and used in standard diesel engines in any percentage i.e.; 1% of pure biodiesel blended with 99% of petro-diesel (Extension, 2013; Sheehan *et al.*, 1998). Biodiesel has lower toxicity compared to conventional diesel. It degrades faster than diesel fuel which significantly helps in reducing the environmental consequences of bio-fuel spills. Where, the biodegradability of biodiesel highly depends on the chemical structure of the fatty acids. Biodiesel is the only alternative fuel can be used in conventional diesel engine. On the other hand, due to the low calorific value of biodiesel in comparison to normal diesel, diesel engine consumes more biodiesel than normal diesel. Biodiesel is not as stable as conventional diesel, therefore the storing of it for longer than six months is inadvisable (Romano and Sorichetti, 2011).

Anaerobic Digestion (AD)

AD is an efficient microbiological conversion process of biomass into biogas. It requires low energy and generally contributes in reducing greenhouse gases. AD has proved its significant performance in converting a wide variety of biomasses such as: edible food (1st bio-fuel generation), LCB's and wastes (2nd bio-fuel generation) and seaweeds (3rd bio-fuel generation). However, AD process breaks down the organic matter by bacteria in the absence of oxygen to produce biogas. The process is carried out in four main stages, pre-treatment, waste digestion, gas recovery or gas upgrading, and residue treatment (Al Seadi *et al.*, 2008; Dutta *et al.*, 2014).

Pretreatment stage is very important stage. The pretreatment method should be carefully selected and implemented, as the other three stages are highly relying on it. The decomposition or digestion process occurs inside the digester in four biochemical reactions. Fig. 1, below illustrates the biochemical reactions. In the hydrolysis step, organic matter is converted into basic monomers by the hydrolytic enzymes. The solubilised monomers are then fermented to organic acids and hydrogen by the fermenting bacteria (acidogens). Following that, the volatile fatty acids (VFA) are converted into acetate, carbon dioxide and hydrogen by the acetogenic bacteria. The results of the previous step are converted then by methanogens bacteria into methane and carbon dioxide. About two-thirds of the methane produced from the digestion process, originates from acetate acids. While, the remaining amount produced are derived from conversion of hydrogen and carbon dioxide. However, the final products of AD are biogas and two by-products (nutrient- rich liquid digestate and the fiber-rich solid digestate) which can be later utilized in several applications (Al Seadi *et al.*, 2008; Kelleher *et al.*, 2002; Parkin and Miller, 1983; Thomas *et al.*, 2013; Al Seadi, 2001).

Biogas

AD biogas is a promising bio-fuel, it contributes in bringing about environmental benefits globally. It is composed of different gases in different amounts. Its composition is varied depending on several factors such as feedstock types, digestion systems, temperature, retention time, etc. It is quite similar to landfill gas composition but varies from the natural gas. In comparison to natural gas, the calorific value of typical biogas (60% CH_4 and 40% CO_2) ranges from 5.5 to 6.5 kWh m^{-3} , while the calorific value of typical natural gas ranges from 5.8 to 7.8 kWh m^{-3} . Thus, biogas has the potential to be a significant alternative to natural gas and can be used in all natural gas appliances. However, biogas is able to be used in different applications, such as; heating, CHP

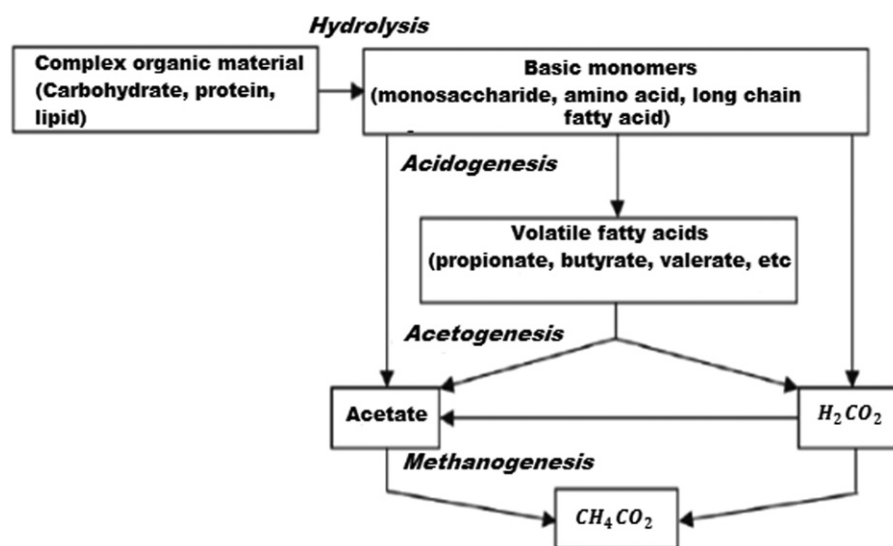


Fig. 1 AD Decomposition steps. Reproduced from Ersahin, M.E., Ovgun, H., Dereli, R.K., Ozturk, I., 2011. Anaerobic treatment of industrial effluents: An overview of applications. In: Einschlag, F.S.G. (Ed.), Waste Water Treatment and Reutilization. Turkey: InTech, pp. 1–28.

and fuel cell or used as chemical feedstock or may be fuel for vehicles (Monnet, 2003; Jensen, 2000; Zorn, 2005; Yu *et al.*, 2010). On the other hand, the biogas contains small traces of different impurities such as; hydrogen sulfide H_2S , ammonia NH_3 , oxygen O_2 and nitrogen N_2 . Due to that and to avoid corrosion and mechanical wear of appliance as well, biogas must be upgraded prior using it (Lamsal and Tyagi, 2010). There are a number of technologies available nowadays for scrubbing contaminants and upgrading gas to the required gas quality (e.g., Carbon dioxide removal, hydrogen sulfide removal and Siloxanes removal technology) (Monnet, 2003). The final product is practically similar to a large extent to the natural gas. It can be blended as bio-natural gas or sold separately (Browne *et al.*, 2011).

AD Digestate

The other end product of AD process is the digestate. Nitrogen, phosphorus and potassium are the three main nutrients conventional fertilizer typically contained. The content of digestate from one or more of these nutrients makes it a substitute for the conventional fertilizer. As aforementioned, digestate is produced in liquid form and can be used as it is or separated into liquid and solid digestate and use each of them separately. The amount of dry matter in both types are different. Usually, liquid digestate contains less than 15% dry matter, while the solid digestate contains more than 15%. The digestion process used and the composition of ingestates are two important factors in determining the quality of a digestate. pH level, macro-element content (such as; N, P and K), micro-element content (such as; copper Cu, zinc Zn) and organic matter content of digestate are another factors to verify the quality and stability of the digestate (Makádi *et al.*, 2012). A study in 2015 (Zhong *et al.*, 2015) claimed that, anaerobic microbes can only convert approximately 40%–60% of carbon into methane in AD of animal manure. However, utilizing the nutrients and lignocellulosic materials in the digestate is critical to significantly improve the efficiency of AD technology and produce multiple products such as: value-added chemical and fuel products from organic wastes (Teater *et al.*, 2011; Yue *et al.*, 2010; De Jong and Jungmeier, 2015; Van Den Hende *et al.*, 2015; Sawatdeenarunat *et al.*, 2016).

Production of Biodiesel

Biodiesel is produced through chemical reaction of a variety of biomass such as; oils, fats, and greases with an alcohol such as; methanol or ethanol and a catalyst like sodium hydroxide or potassium hydroxide. Soybean, rapeseed/canola, used vegetable oils, and tallow (animal fat) are the widely common biomass used in production of biodiesel. The production of biodiesel from lignocellulose biomass can be carried out through three main steps; (1) lignocellulose biomass is converted to fermentable sugar, (2) the sugars are converted to microbial lipids by oleaginous microorganism, and (3) microbial lipids are translated to biodiesel. However, the process of producing biodiesel, separates glycerin from the feedstock used (i.e., oil or fat). Thus, the final biodiesel produced is thinner than the original oil or fat and therefore performs better in a diesel engine. Furthermore, vegetable oils and animal fats used to generate biodiesel come from practically any source. Even cooking oil can be used as well for production of biodiesel. Furthermore, the chemical process applied for making biodiesel called “transesterification” (Gong *et al.*, 2013; Gerpen, 2013). On the other hand, the glycerin extracted from the process of making biodiesel has many uses. It can be used in making soap, food, ink, creams, lubrication of molds, etc. Due to the recent steady growth of using biodiesel, the production of glycerin has increased as well. Currently, there are many academic and industrial research groups for discovering new glycerin uses and applications specifically in polymers and surfactants (Claude, 1999; Gemma *et al.*, 2007).

Integration of Anaerobic Digestion and Aerobic Fungal Fermentation Process

The bio-refinery concept is quite similar to conventional petroleum refinery. It involves making full use of biomass. While, the input of the process is only the biomass, the output can be feed, food, biomaterials and bio-fuel. In other words, the bio-refinery concept is a facility that integrates biomass conversion processes and equipments to produce feed, food, biomaterials, bio-fuel, etc (Sawatdeenarunat *et al.*, 2016). Fig. 2, illustrates a simplified scheme of bio-refinery concept.

Moreover, a study in 2014 (Zhong *et al.*, 2015) was carried out to produce lignocellulosic biogas and biodiesel through an integration approach of AD and aerobic fungal fermentation. Generally, the study has concerned on developing an integrated system including AD and aerobic fungal fermentation in order to convert corn stover, animal manure and food wastes into microbial lipids for production of biodiesel. Fig. 3, below illustrates the integration process of producing biogas and biodiesel. In the production of biogas, the main feedstock was animal manure and a small amount of food wastes which was used to balance nutrient to enhance AD performance. While, in the production of biodiesel, AD fiber was used as the main feedstock for fermentation stage. Corn stover as an agro-industrial waste was used as a solid support, carbon source and nutrient source in the solid state fermentation process. Large amount of agro-industrial wastes are basically composed of cellulose, hemicelluloses and lignin and being called lignocellulose biomass (Zabed *et al.*, 2016). Stalk, leaves, husk, shell, peel, etc. are some types of agro-Industrial wastes. They are mainly contain of water and rich in sugar, minerals and protein which have made them suitable environment for the development of microorganisms, basically fungal strains, which are able to rapidly grow in these wastes. Due to that, they should not be considered as “waste” but lignocellulose raw material for other industrial processes (Mussatto *et al.*, 2012). In the study (Zhong *et al.*, 2015), the combined

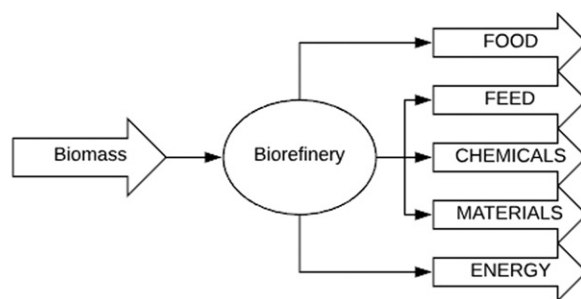


Fig. 2 Simplified scheme of bio-refinery concept. Adapted from Koltuniewicz, A.B., 2014. Bioprocesses. In: Sustainable Process Engineering: Prospects and Opportunities. Berlin: Walter DeGruyter, pp. 269–346.

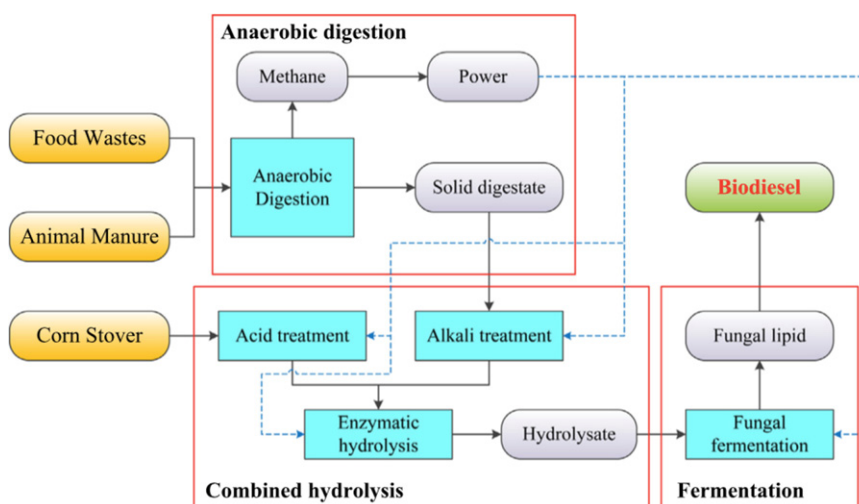


Fig. 3 Flowchart of the integration process. Reproduced from Zhong, Y., Ruan, Z., Zhong, Y., *et al.*, 2015. A self-sustaining advanced lignocellulosic biofuel production by integration of anaerobic digestion and aerobic fungal fermentation. *Bioresource Technology* 179, 173–179.

hydrolysis of corn stover and AD fiber were accomplished by enzymatic hydrolysis of the combined slurry. **Fig. 4**, also shows the mass flow of the integrated system. This integrated process has ended up with producing of 1 L of biodiesel and 1.9 kg CH_4 from (12.8 kg dry dairy manure, 3.1 kg dry food wastes and 12.2 kg dry corn stover) with a positive net energy of 57 MJ. The study has concluded that, combined hydrolysis of alkali treated AD fiber and acid treated corn stover is technically feasible for converting agricultural residues into mono-sugars without neutralization and detoxification.

Moreover, the biodiesel production process begun by separating AD effluent into two streams: nitrogen and phosphorus-rich liquid digestate and fiber-rich solid digestate. Commercial screw press separator with 2 mm screen was used to do so. After that, dilute alkali pretreatment was applied to treat the AD fiber at specific condition (temperature, °C, time, h and NaOH, %). While, corn stover was pretreated at certain condition as well (temperature, °C, time, h and sulfuric acid concentration, %) by dilute acid pretreatment. Total solid concentration of the two pretreated slurries were then adjusted and thoroughly mixed at a ratio of 1:1 (wt/wt) to form combined slurry. For carrying out the enzymatic hydrolysis at certain condition (temperature, °C, rotate speed, rpm), an enzyme mixture was applied on the combined slurry in a shaking incubator. In order to separate the liquid hydrolysate from the residual solids, the hydrolysate was centrifuged. For sugar analysis, about 5 ml of the liquid hydrolysate was taken and filtered through a 0.22 μ m polyether-sulfone membrane filter. The remaining liquid hydrolysate was being used then for fungal lipid fermentation. Beyond that, the right oleaginous microorganism should be carefully selected to be used in accumulation of lipid on the hydrolysate. Where, microorganism which include bacteria, fungi, yeast, mold and microalgae that can accumulate lipids up to 20% or more of their dry weight are considered as oleaginous microorganism (Liang and Jiang, 2013). Fungal lipid accumulation was then fulfilled in Erlenmeyer flask with an amount of medium. Before being sterilized at specific temperature and time, a certain percentage of NaOH was applied to the fermentation medium to adjust the pH level. The fermentation medium was inoculated with a (vol/vol)% seed and cultivated for particular days at certain temperature on a rotary shaker with an agitation speed (rpm). Fungal biomass was collected by filtration and washed twice with distilled water over a Whatman #1 filter paper. In order to obtain a consistent weight, cell mass was determined by drying at certain temperature. Dried mycelia were ground in a mortar and used for lipid extraction. Total lipid was lastly determined gravimetrically (Zhong *et al.*, 2015).

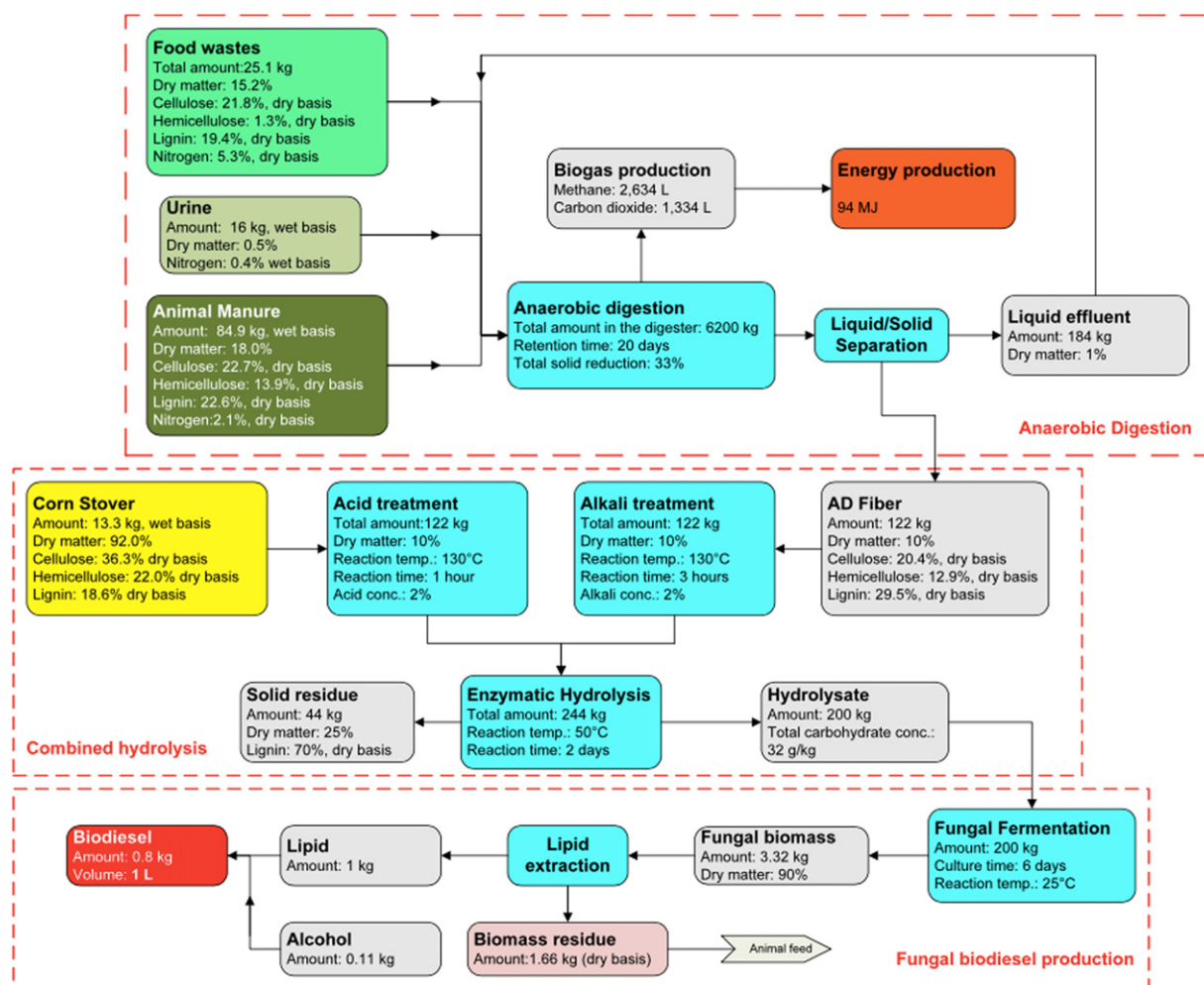


Fig. 4 Mass flow of the integrated process. Reproduced from Zhong, Y., Ruan, Z., Zhong, Y., *et al.*, 2015. A self-sustaining advanced lignocellulosic biofuel production by integration of anaerobic digestion and aerobic fungal fermentation. *Bioresource Technology* 179, 173–179.

However, several previous studies (Teater *et al.*, 2011; Zhong *et al.*, 2015) have confirmed that AD fiber has the potential to provide the same performance as a feedstock for both bio-ethanol and biodiesel productions. Of course, that would greatly contribute in expanding the potential application of AD solid digestate and improving the economical benefits of AD process (Teater *et al.*, 2011; Zhong *et al.*, 2015; Mohan *et al.*, 2010). Zhong *et al.* (2016) have revealed that, although AD consumes a high proportions of organic matter in the waste, AD digestate still contains a significant amount of nutrients as well as lignocellulosic substances. This study (Zhong *et al.*, 2016) has mainly aimed to develop an integrated system that the biogas produced is later used to power fungal fermentation and convert the existed carbon source, nutrients and water in the digestate into bio-fuel precursor-lipid. This would help in developing a fresh-water-free and energy-positive process to simultaneously utilize both solid and liquid digestate in the accumulation of fungal lipid for biodiesel production. The integrated system contains two unit operation, which are, AD and digestate utilization. Digestate utilization includes five main stages, are; digestate pretreatment, enzymatic hydrolysis for mono-sugar release, over-liming detoxification and lastly fungal fermentation for lipid accumulation. In order to release mono-sugar, the mixture of solid and liquid digestate was pretreated at certain conditions and hydrolyzed, by alkali and enzyme respectively. In the pretreatment process, liquid digestate was used as the processing water. After releasing of mono-sugar, over liming detoxification was applied to prepare the hydrolysate for fungal fermentation. The results have indicated that, the studied integrated system has the potential to offer optimal solutions for bio-fuel production and waste management and the fresh-water-free and energy-positive process was significantly developed to utilize solid and liquid digestate to the accumulate fungal lipid and subsequently produce biodiesel.

The Importance of the Pretreatment of Biomass

Pretreatment methods are mainly classified into the following group: physical (mechanical) such as; milling, beating, ultrasonic and collision plate pretreatment, chemical (e.g., alkaline and acid pretreatment), and biological (e.g., fungal pretreatment).

Table 1 Biogas yield from different mechanical pretreatment methods of feedstock

Physical pretreatment	Feedstock	Pretreatment conditions	Results
Comminution	● Agricultural residuals: wheat straw, rice straw, oat, clover, bagasse, coconut fiber, hemp, banana peelings, cauliflower leaves, and digested bio-fibers. ● Forest residuals: mirabilis leaves ● Grass: dump grass and grass hay ● Municipal solid waste (MSW): organic fraction of MSW (OFMSW)	Particle size: 0.003–30 mm	Up to 30% improvement of methane yield. Occasionally, reduced size decreased biogas production
Steam-explosion	● Agricultural residuals: wheat straw, corn stalks, corn straw, citrus waste, potato pulp, rape straw, and digested bio-fibers ● Hardwood: Japanese cedar, willow, and birch ● Grass: bulrush, Miscanthus, and seaweed ● MSW: OFMSW and paper tube residuals ● Softwood: bamboo	160–260°C, 0.7–4.8 MPa, and seconds to a few minutes	Positive effect of up to 40% increase in biogas yield. Occasional zero or negative effect also occurred
Liquid hot water (LHW)	● Agricultural residuals: Wheat straw, rice straw, oil palm empty fruit bunches (OPEFB), sunflower stalks, and sugarcane bagasse ● Grass: Miscanthus and hybrid grass ● MSW: OFMSW and paper tube residuals	100–230°C (0.1–2.8 MPa) for a few minutes to hours	7%–220% increase of methane yield
Extrusion	● Agricultural residuals: barley straw, maize, and solid fraction of manure ● Grass: Lolium multiflorum and pelleted hay ● MSW: OFMSW	0.45–3.5 MPa for a few minutes (e.g., 4–12 min) and typical temperature of 60–90°C	8%–70% improvement of methane yield
Irradiation	● Agricultural residuals: wheat straw, barley straw, spring wheat, winter wheat, oat straw, and rice stalks ● Grass: switchgrass and hybrid grass MSW: OFMSW	115–300°C for a few minutes to hours	4%–28% improvement of methane yield. No or adverse effects were found. Combination with acids or alkali could achieve greater improvement of biogas yield

Note: Zheng, Y., Zhao, J., Xu, F., Li, Y., 2014. Review: Pretreatment of lignocellulosic biomass for enhanced biogas. *Progress in Energy and Combustion Science*, 35–53.

Various types of pretreatment methods have been extensively investigated on the pretreatment of different types of biomass. The effectiveness of the different pretreatment methods on the biomass from even the same pretreatment group is varied from each others. For instance, a study in 2015 (Montingelli, 2015) has compared between three different mechanical pretreatment methods, are; microwave, milling and beating methods on different species of Irish seaweeds. The study has concluded that, the greatest performance in terms of methane production was achieved when a beating pretreatment was applied. Whilst, the other two methods have negatively affected the digestion process, beating pretreatment is relatively a new mechanical pretreatment method was first introduced by the biomass research team in Dublin City University in 2011 based on employing Hollander beater device. This method has proved its performance in pretreatment of only few biomasses such as; seaweed, maize silage, fresh grass and potato wastes, but it is not yet widely applied. Table 1, presents the biogas yields which has been resulted after several mechanical pretreatment methods on different types of biomasses.

However, as the pretreatment is the most important step in the biomass conversion process as it has a major influence on all the other steps in the process. The optimum goal of the pretreatment process is to enhance the enzymatic hydrolysis of carbohydrates (cellulose and hemi-cellulose) therefore increasing the overall bioconversion efficiency for production of sugars. According to some previous studies, Alkaline pretreatment is one of the most viable process options, mainly due to its significant pretreatment effect and relatively simple process scheme. Alkaline pretreatment has a principal feature that, it selectively takes off lignin without degrading carbohydrates, and increases porosity and surface area, thereby improving enzymatic hydrolysis. Table 2, illustrates the difference in effect between several pretreatment methods through showing the extent of the effects of some different pretreatment methods on the compositional and structural alteration of lignocellulosic materials.

Furthermore, as an integrated approach of AD and fermentation process, pretreatment plays a crucial role because the design of the subsequent scarification and fermentation processes highly depending on the result of the pretreatment step. Thus, the following criteria should be considered for selecting the most effective and appropriate pretreatment methods: should require low capital and operational costs, require minimum size reduction of the biomass, toxic compounds produced under the pretreatment conditions should be minimum, etc. However, a pretreatment method should be carefully selected and implemented prior to the combined hydrolysis of agro-industrial wastes and AD fiber which is carried out by enzymatic hydrolysis of the combined slurry (Agustini *et al.*, 2012; Mosier *et al.*, 2005; Alvira *et al.*, 2010; Yang and Wyman, 2008).

Table 2 Illustrates the difference in effect between several pretreatment methods

Pretreatment	Increase of accessible surface area	Decrystallization of cellulose	Solubilization of hemi-cellulose	Solubilization of lignin	Alteration of lignin structure	Formation of furfural/hydroxymethylfurfural (HMF)
Mechanical	✓	✓				
Irradiation	✓	×	×			×
Steam-explosion	✓		✓	×	✓	✓
Liquid hot water	✓	ND	✓	×	×	×
Catalyzed steam-explosion	✓		✓	✓/×	✓/×	✓
Acid	✓		✓	×	✓	✓
Alkaline	✓		×	✓/×	✓	×
Oxidative	✓	ND		✓/×	✓	×
Ionic liquid	✓	✓	×			
Thermal acid	✓	ND	✓			✓
Thermal alkaline	✓	ND	×	✓/×	✓	×
Thermal oxidative	✓	ND	×	✓/×	✓	×
Ammonia fiber explosion	✓	✓	×	✓	✓	×
Biological pretreatment	✓	ND	✓	✓	✓	

Note: ✓ = Major effect, × = Minor effect, ND = Not determined, and blank = No effect.

Hendriks, A.T., Zeeman, G., 2009. Review: Pretreatments to enhance the digestibility of lignocellulosic biomass. *Bioresource Technology* 100 (1), 10–18.

Discussion

As previously mentioned, there will be a number of issues associated with AD when it is applied extensively. These issues have made the investment in AD less attractive or maybe not economically feasible. These issues are categorized into three categories: operational, economical and environmental issues. Generally, there are number of operational factors that must be considered in advance to be avoided. These factors can result in a failure or the poor operational stability of the system such as: inadequate operational management, lack of process control, external disturbances, and others. In addition, personnel qualifications is considered another operational factor should be taken into account to professionally monitor and control the system. Economically, as the biogas is the single main product of AD, the production of AD biogas can be not economically competitive with its counterparts due to: (1) the amount of energy consumed in AD process especially, the energy consumed in the pretreatment and digestion and, (2) the fluctuation of fossil fuel price indexes. The production of more bio-products could be a significant solution for increasing the economical viability of AD. While, the environmental issues lie in the accumulation and the improper handling of the huge the digestate which can lead to serious environmental issues. Practically, there are some ways to overcome the environmental issues, one of these ways is to utilize the digestate in other applications. As mentioned before, anaerobic microbes can convert only from 40% to 60% of carbon into methane. AD digestate contains significant quantity of nutrients and lignocellulose materials which has not been digested in the digestion process. Thus, making a use of the digestate to produce bio-fuel or bio-products would greatly contribute in overcoming the AD economical and environmental issues.

On the other hand, as the digestate still contain undigested materials, it is required to be pretreated. Pretreatment step is the most important step as the other following steps in the biomass conversion processes are relying on its results. Thus, pretreatment method must be selected based on the aforementioned criteria in Section “The Importance of the Pretreatment of Biomass”.

However, the integration approach corresponds to the refinery concept. It is incorporating bioconversion processes to produce multiple bio-products. Many integration approaches of the biomass conversion processes have confirmed their potentials in some previous scientific studies. This approach could help in making a full use of byproducts and biomass, increasing the economical profit, minimizing the wastes, producing bio-fuel and high-value bio-based products simultaneously and improve the industrial values of the production of bio-fuels. Regarding to the production of biodiesel, various studies have proved the capability of the residual biomass to be used as animal feed or feedstock for AD to produce biogas. The glycerin extracted from biodiesel production process can be considered as by products and used further in different applications i.e., soap making. The digestate can be used as bio-fertilizer or soil amendment in agricultural applications. However, much attention have been paid recently towards the development of integrated approaches as it can be a significant and radical solution for AD issues. But, more studies are still required to exploit more biomass other than the conventional ones in order to discover and produce more by products and bio-products. The successful application of the integration approach on the non-conventional biomass would certainly contribute in making AD prosper and the investment in it is much more attractive. A substantial positive changes will be clearly noted when this system proves its effectiveness and capability to prosper.

Conclusion

Biodiesel is a promising form of liquid bio-fuel. Integration approach of producing bio-fuel, bio-products and high-value bio-based products from AD fiber is a new approach. Investigation of the effectiveness of more pretreatment methods on AD fiber prior to the enzymatic hydrolysis is strongly needed for further studies. That can be accomplished by comparing the pretreatment methods which have been applied in previous studies with other methods. However, scientific literatures on the production of lignocellulosic biodiesel through integration system are relatively low. An integration approach has the potential to offer optimal solutions for bio-fuel production and waste management. But, to end up with better integration system, more investigations regarding to several aspects such as; feedstocks used, pretreatment technique, economic analysis, agro-industrial waste applied and others are highly required.

Acknowledgments

The authors would like to gratefully acknowledge Saudi Cultural Bureau for funded this study. Great thanks also express to Dublin City University, Dublin, Ireland for providing the appropriate environment for researchers to do their works and enable them to easy access to the enormous amount of research and scientific publications worldwide.

See also: Analyzing Biodiesel Production From Cooking Oil. Optimization and Kinetic Modeling of Biodiesel Production. Sustainable Biodiesel Production

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Prospect of Recycling of Plastic Product to Minimize Environmental Pollution

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Plastic Recycling

The extreme use of plastic product in the present scenario leads to intense interest in the recycling and reuse of end products (Francis, 2016). Worldwide, the production of plastics was 168 million tons in the year 1999 and approximately 210 million tons in 2010. Since the treatment of plastic wastes has become a serious problem, the development of effective recycling processes is urgently needed (Goto, 2009). The waste management hierarchy indicates an order of preference for action to reduce and manage plastic waste, and is usually presented diagrammatically in the form of a pyramid (Fig. 1). The recycling of plastics products are fit into the waste hierarchy as an efficient and sustainable use of material resources. As per waste management hierarchy, plastic waste can be minimized at the different level following prevention to disposal. The prevention is most preferred, whereas disposal is least (Gertsakis and Lewis, 2003). The society should prefer logically the prevention rather than level of recycling to minimize the chances of pollution spread because it should be noted that reuse, recycle and recovery phase are the energy and resource consuming processes whereas disposal can lead serious hazards. Based upon the waste management concept, plastic recycling can be broadly divided in the four classifications namely: primary, secondary, tertiary and quaternary recycling. Primary and secondary recycling (recycling of clean, uncontaminated and single type waste: extrusion, molding, heat treatment) are actually the mechanical recycling, tertiary recycling are performed by chemical mean (dividing plastic waste into smaller molecules) and quaternary recycling is disposal by thermal utilization specially by energy recovery.

The primary recycling is an uncontaminated process in which only molecular arrangement/behavior are modified to applied the material in different processes (Singh *et al.*, 2017a). Reduction of average molecular weight, increase of average molecular weight, formation of cyclization/unsaturation, remedial combination of molecules, dehydrohalogenation are some of the techniques which termed as the primary recycling process (Kaminsky *et al.*, 1976; See Fig. 2).

The secondary recycling is a mechanical mean of recycling process where polymers like, Polyvinyl styrene (PVS), low density polyethylene (LDPE), high density polyethylene (HDPE), acrylonitrile butadiene styrene (ABS), Polypropylene (PP), Polyethylene terephthalate (PET), Polystyrene (PS), Polycarbonate (PC), polyamides (PA) and etc. are largely modified for preparation of feedstock or useful products (Seike *et al.*, 2018; Soo *et al.*, 2017; Wan *et al.*, 2017; Singh *et al.*, 2017b,c,d,f,e). As reported by the various studies, extrusion is the most effective tool of secondary recycling in which the material are modified as used for the preparation of feedstock (Kumar *et al.*, 2017a,b,c,d, 2018). The metallic/nonmetallic/alloys particle are directly incorporated in the material matrix to modify melt flow behavior, molecular density, tensile properties, hardness, surface, thermal and chemical properties (Maris *et al.*, 2017; Ragaert *et al.*, 2017; Singh *et al.*, 2016a,b). Additive manufacturing/3D printing is also termed under the secondary recycling where useful products are fabricated with provision of recycling. The tertiary recycling process involves various methods of recycling including cracking, gasification, thermolysis and chemolysis (Hahladakis *et al.*, 2017; Horvat and Ng, 1999; López *et al.*, 2013). As the process of polymerization combines the monomer for

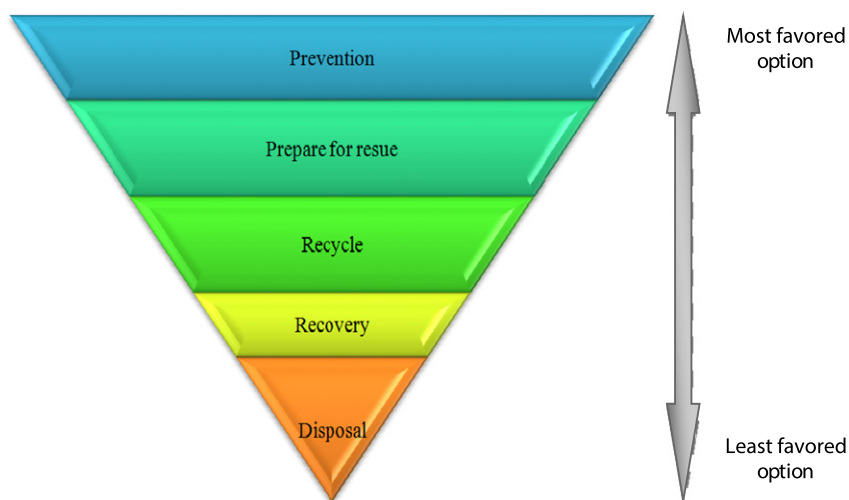


Fig. 1 Waste management hierarchy. Reproduced from Papargyropoulou, E., Lozano, R., Steinberger, J.K., Wright, N., bin Ujang, Z., 2014. The food waste hierarchy as a framework for the management of food surplus and food waste. *Journal of Cleaner Production* 76, 106–115.

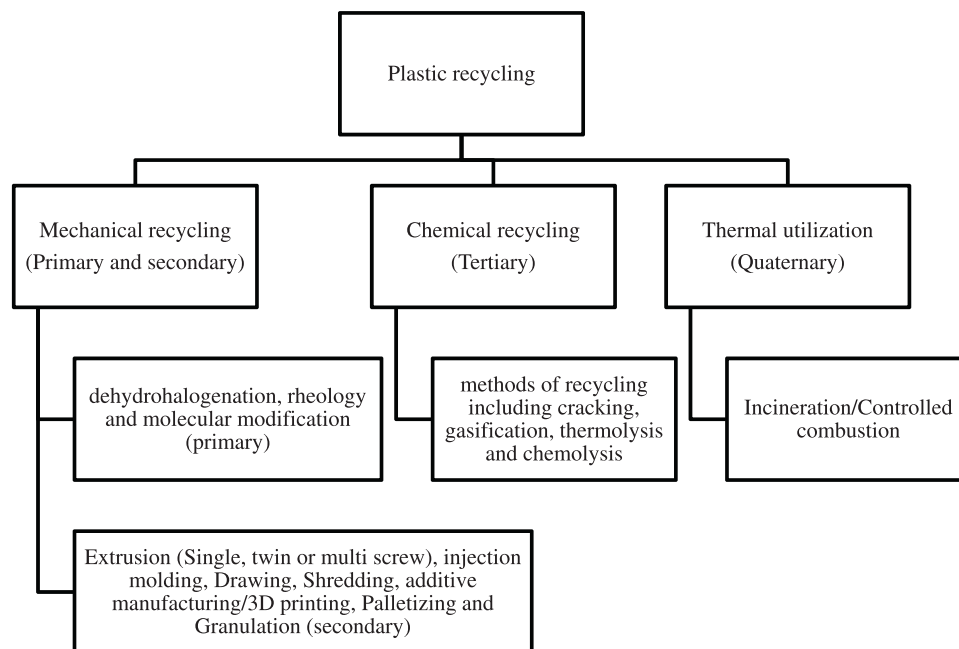


Fig. 2 Recycling techniques for thermoplastic materials.

production of polymer by polymerization, similarly depolymerization is termed under the tertiary recycling process where monomer are formed by breaking chains of polymers. Fourth stage of recycling is also called 'energy recovery', the useful retrieval of the energy content of plastic wastes by its use as an energy source to produce products such as steam and/or electricity. 'Incineration' is the quaternary recycling techniques which is performed under the controlled combustion of the waste polymer. A small amount of the residue is the byproduct of this process which is further landfill or treated for environmental exposure (Gurgul *et al.*, 2018; Hwang *et al.*, 2017; Roes *et al.*, 2012; Taylor *et al.*, 2014). Table 1 shows the categories and their properties of thermoplastics generally used by society.

Case Studies for Recycling of Plastic Product to Minimize Environmental Pollution

The natural fibers are bio-compatible/bio-degradable/renewable/non-abrasive in nature and possess high mechanical and heat capacity values. In this article, sustainable waste management is focused on the development of thermoplastic composite materials reinforced with natural banana fibers (BF). BF is one of the cost effective agricultural waste materials (available in abundance) having high bio-degradability and biocompatibility. Three case studies are being reported in the present article to investigate the effects of BF reinforcement in ABS, PA6, HDPE and LDPE matrix on mechanical, thermal and morphological properties.

Effects of BF on Primary Recycled ABS and PA6 (Case Study: 1)

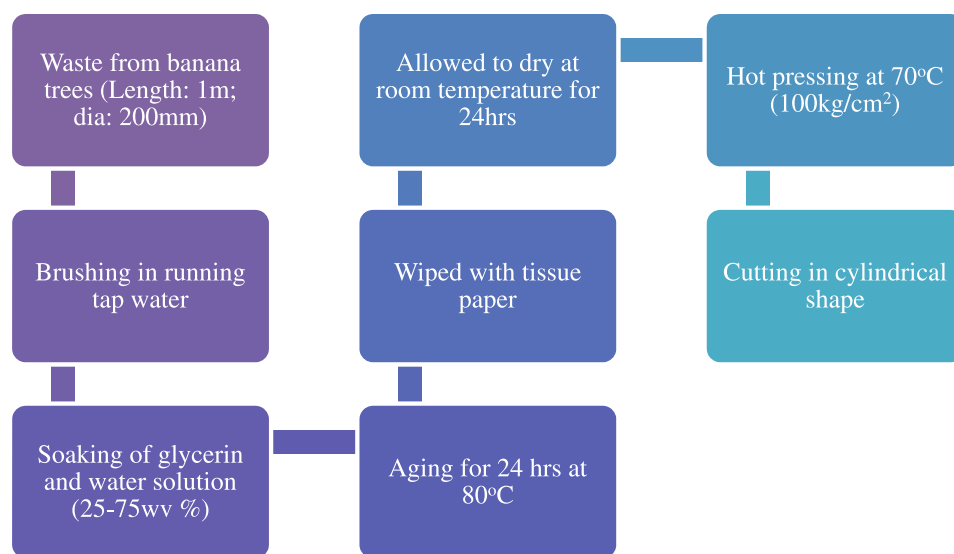
For enhancing the mechanical, thermal and morphological properties in terms of sustainability, primary recycled ABS and PA6 a case study has been taken which was conducted by Singh *et al.* (2018). The BF (size: length 1000 μm and diameter 100 μm ; Shape: cylindrical) were prepared at lab scale by following procedure (See Fig. 3):

A combination of 5% BF has been selected to reinforce with both of the polymer matrix; ABS and PA6 independently. Finally 4 compositions/proportions have been selected for experimentation; (i) recycled ABS, (ii) recycled ABS-5% BF (by weight), (iii) recycled PA6, (iv) recycled PA6-5% BF (by weight).

The recycling of BF reinforced ABS and PA6 have been performed by TSE for producing feedstock filaments for fused deposition modeling (FDM). The pilot experimentation was conducted and input process parameter was decided based upon the uniformity of the filament extruded. Except temperature, nozzle diameter and operating torque were the two other input parameters which have significant effect on the change in the properties of the obtained feedstock filaments. The temperature for extrusion has been selected based upon differential scanning calorimetry (DSC) results obtained (225.01 $^{\circ}\text{C}$ for PA6-5%BF), for better mixing of the BF with PA6 matrix, the extrusion temperature should be greater than the melting point so the temperature of 230 $^{\circ}\text{C}$ has been selected. The acceptable diameter for feedstock filaments to be compatible with FDM is 1.75 mm, so the nozzle diameter has been selected as 1.5 mm. During pilot experimentation it was experienced that the feedstock filaments of PA6-5%BF were obtained

Table 1 Thermoplastics and their properties (www.PolymerProcessing.com, www.engineeringtoolbox.com, www.dynalabcorp.com, www.sigmaldrich.com, www.polymerprocessing.com)

Plastic	Melting point (°C)	Glass transition temperature (°C)	Young's modulus (GPa)	Applications
PC	225	145	2.6	Beverage bottles; baby milk bottles. Non-packaging uses for PC: compact discs; "unbreakable" glazing; electronic apparatus housings; lenses including sunglasses, prescription glasses, automotive headlamps, riot shields, instrument panels
HDPE	130	– 125	0.8	Water pipes, hula hoop rings, five gallon buckets, milk, juice and water bottles; grocery bags, some shampoo/toiletry bottles
LDPE	120	– 125	0.17–0.28	Frozen food bags; squeezable bottles, e.g., honey, mustard; cling films; flexible container lids
PET	250	76	2–2.7	Soft drink, water and salad dressing bottles; peanut butter and jam jars; small consumer electronics
PP	173	– 10	1.5–2	Reusable microwaveable ware; kitchenware; yogurt containers; margarine tubs; microwaveable disposable take-away containers; disposable cups; soft drink bottle caps; plates
PVC	240	85	2.4–4.1	Blister packaging for non-food items; cling films for non-food use. May be used for food packaging with the addition of the plasticizers needed to make natively rigid PVC flexible.
PS	240	100	3–3.5	Nonpackaging uses are electrical cable insulation; rigid piping; vinyl records Egg cartons; packing peanuts; disposable cups, plates, trays and cutlery; disposable take-away containers

**Fig. 3** Steps in BF processing.**Table 2** Processing condition to BF reinforced ABS and PA6

Temperature (°C)	Nozzle diameter (mm)	Torque (N m)
230	1.5	0.10

uniformly at torque of 0.10 N.m, so the levels of all the three parameter have been selected in given range. **Table 2** shows the processing variables for BF reinforced ABS and PA6.

After preparations of the feedstock filament it was fed to the commercial FDM setup to fabricate the parts to check the printing capabilities of the banana reinforced polymers for different engineering applications. The tensile part was fabricated with nozzle diameter of 0.3 mm, filament diameter of 1.75 mm. The other fixed input parameters of FDM were: layer height 0.4 mm, number of perimeter 3 (by adjusting 3 top and 3 bottom layers), fill density 100%, honeycomb fill pattern, perimeter speed 30 mm/sec,

Table 3 Melting points investigation of different samples

<i>Virgin ABS</i>	<i>ABS with 5%BF</i>	<i>Virgin PA6</i>	<i>PA6 with 5%BF</i>
190.12°C	210.35°C	216.69°C	225.01°C

Table 4 Mechanical properties of different samples

<i>Properties</i>	<i>Virgin ABS</i>	<i>ABS with 5%BF</i>	<i>Virgin PA6</i>	<i>PA6 with 5%BF</i>
Load at peak (N)	8.6	10	14.1	18.2
Load at break (N)	7.74	9	12.69	16.38
Peak strength (Kg/mm ²)	3.791	4.208	7.016	9.65
Break strength (Kg/mm ²)	3.412	3.787	6.315	8.685
Peak elongation (mm)	2.85	2.47	6.84	13.11
Break elongation (mm)	3.04	2.47	7.41	37.81
Percentage elongation at peak (%)	4.38	3.8	10.52	20.17
Percentage elongation at break (%)	4.38	3.8	11.4	58.17
Young' modulus (MPa)	55.29	23.1	35.39	126.98

infill speed of 60 mm/sec, travel speed of 130 mm/sec, at extrusion temperature of 250°C and bed temperature of 55°C. All these input parameters are controllable through commercial open source FDM software.

Effects of BF on thermal properties of ABS and PA6

The DSC analysis has been used to check the changes in the thermal behavior of the banana reinforced polymer contributing to the waste management for sustainable development. The DSC was conducted in between temperature range of 30–250°C under heating rate of 10°C/min controlling N₂ gas supply of 50 ml/min in two repeated cycles. Initially sample of recycled ABS (without reinforcement of BF) has been selected for DSC analysis followed by ABS reinforced with 5% BF (ABS-5BF). It is observed that melting point of virgin ABS was 190.12°C and one of the reinforcement can lead to the more thermal stability in the ABS polymer. after 5%BF to their matrix it was shifted to high as 210.35°C. This result shows that reinforcement of BF to ABS results in better thermal stability. Similar melting point of PA6 was shifted from 216.69 to 225.01°C after 5% Bf shows the enhancement of thermal stability. [Table 3](#) shows melting points of different samples.

Effects on BF on mechanical properties of ABS and PA6

To check the durability of the BF reinforced feedstock filaments prepared by the extrusion process, sample feed stock filaments were tested on universal tensile tester in accordance with ASTM D638. The load characteristics (peak load and break load), elongation characteristics (peak elongation, break elongation, percentage peak elongation, percentage elongation at break), tensile strength (peak strength and break strength), and modulus of elasticity (Young's modulus) were calculated/measured to ensure the relative durability comparison of reinforced and un-reinforced feedstock filaments of FDM. The reinforcement of the BF led to the increase in the break load and peak load in the both polymer matrix. It was observed that in case of ABS peak strength was increase from 3.791 to 4.208 kgf after 5% reinforcement where as in PA6 it was increased from 7.016 to 9.65 respectively. Similarly significant rise in the break strength was observed in the case of break strength. Similarly it was observed that in case of ABS the peak and break elongation was reduced after reinforcement of BFs whereas in case of PA6 a significant increase of elongation was observed. As observed in the case of ABS, percentage peak elongation and break elongation was reduced from 4.38% to 3.8%. In case of PA6 it was observed that an excellent rise in the elongation occurred, peak elongation was increased from 10.52% to 20.17% whereas break elongation was increased from 11.4% to 58.17% after 5% reinforcement of BF. After 5% reinforcement of BF, the Young's modulus of the ABS was reduced from 55.29 MPa to 23.1 MPa whereas Young's modulus of PA6 was increased from 35.39 MPa to 126.98 MPa (See [Table 4](#)).

Effects on BF on porosities of ABS and PA6

The micrographic observations have been made with the help of metallurgical image analysis software (MIAS). Porosities on the surface have been checked to understand the reasons for changes in the mechanical strength of the feedstock filaments. All the surfaces of extruded filament have been checked at 200X as per ASTM B 276. Extruded, non-reinforced and recycled ABS and PA6 filaments are having more voids and pores. After the reinforcement of BF at 5% by weight it was observed that a refined surface was obtained in both of the polymer matrix (See [Table 5](#)). Usually extrusion processes are resulted in the creation of voids and pores at the internal as well as external molecular arrangements. The micro-holes presented at the surfaces increases the porosity at the surface. In the present case the impact of the BF has been noted as it perfectly fill the voids and hole during the extrusion process. So the reinforcement of the banana fibers is associated with the enhancement of the porosity at the surfaces.

Table 5 Percentage changes in porosities on surface

Property	Virgin ABS	ABS with 5%BF	Virgin PA6	PA6 with 5%BF
Porosity (%)	48.79	11.3	46.95	24.18

Table 6 Control log of experiment and mechanical properties

Experiment no.	Temperature	Screw speed (RPM)	HDPE:BF	Peak load (N)	Peak strength (N/mm ²)
1	120	20	99:1	24.98	9.82
2	120	25	98:2	25.93	10.23
3	120	30	97:3	27.93	11.01
4	130	20	98:2	22.69	8.56
5	130	25	97:3	23.34	9.20
6	130	30	99:1	26.01	10.25
7	140	20	97:3	26.70	10.52
8	140	25	99:1	29.02	11.44
9	140	30	98:2	31.43	12.39
Unreinforced recycled HDPE				24.20	5.65

Effects of BF on Secondary Recycled HDPE (Case Study: 2)

For enhancing the mechanical, thermal properties in terms of sustainability, secondary recycled HDPE a case study has been taken which was conducted by (Singh *et al.*, 2017b). The BF (size: length 1000 μm and diameter 100 μm ; Shape: cylindrical) were prepared at lab scale by following procedure given in Fig. 3. There are three material (1%, 2% and 3% BF to HDPE), temperature (120, 130 and 140°C) and RPM (20, 25 and 30) combinations have been taken to perform the TSE. A control log based upon the Taguchi L9 orthogonal array has been developed to perform the TSE operation. Thermal (melting point) and mechanical properties (Peak load and peak strength) have been investigated on the experimental run.

Effect of BF on melting points of secondary recycled HDPE

DSC analysis of unreinforced and BF reinforced have been conducted to check the melting points of secondary recycled HDPE. It was observed that unreinforced HDPE resulted in melting point of 121.74°C. Whereas melting point of BF reinforced HDPE observed as 123°C. A little change in the melting point of the samples shows the tendency of the HDPE as the thermally stable material.

Effect of BF on mechanical properties of secondary recycled HDPE

There are three parameter has been taken i.e., temperature, RPM and proportion of matrix material and reinforcement. Feedstock filaments for FDM based on this Taguchi L9 has been prepared and tested on UTM for their mechanical strength. Control log of experiment has been shown in Table 6. Further analysis of this design has been done by Minitab software and results have been obtained for SN ratio and mean values. Analysis for peak strength, peak load has been done. Graphs for the same have also been obtained and shown in Fig. 4. From Fig. 4, it has been observed that increase in temperature resulted into SN ratio up to a certain limit but then after increase in temperature resulted into increase in SN ratio. Further in case of RPM increase in value resulted into increase in SN ratio. Hence it can be concluded that higher temperature and RPM gives the better results. It has been observed that as the temperature increases value of peak load increases. Same trend has been observed in case of RPM. However in case of proportions different trend was obtained as value of peak load decreases.

Here it should be noted that 140°C temperature, 30 RPM and 99:1 HDPE:BF ratio have been mostly contributing for changes in peak load and peak strength. (See Fig. 4).

It was observed that for peak load temperature contributed 64.23%, RPM 34.29% and HDPE:BF ratio 1.37%. Similarly for Peak strength temperature contributed 63.18%, RPM 35.38 and HDPE:BF 1.03% (See Table 7).

Effects of BF on Secondary Recycled LDPE (Case Study: 3)

For enhancing the mechanical, thermal properties in terms of sustainability, secondary recycled LDPE a case study has been taken which was conducted by (Bedi *et al.*, 2017). The BF (size: length 1000 μm and diameter 100 μm ; Shape: cylindrical) were prepared at lab scale by following procedure given in Fig. 3. There are three material combination (1%, 2% and 3% BF to LDPE), temperature (110, 120 and 130°C) and RPM (20, 25 and 30) combinations have been taken to perform the TSE. A control log

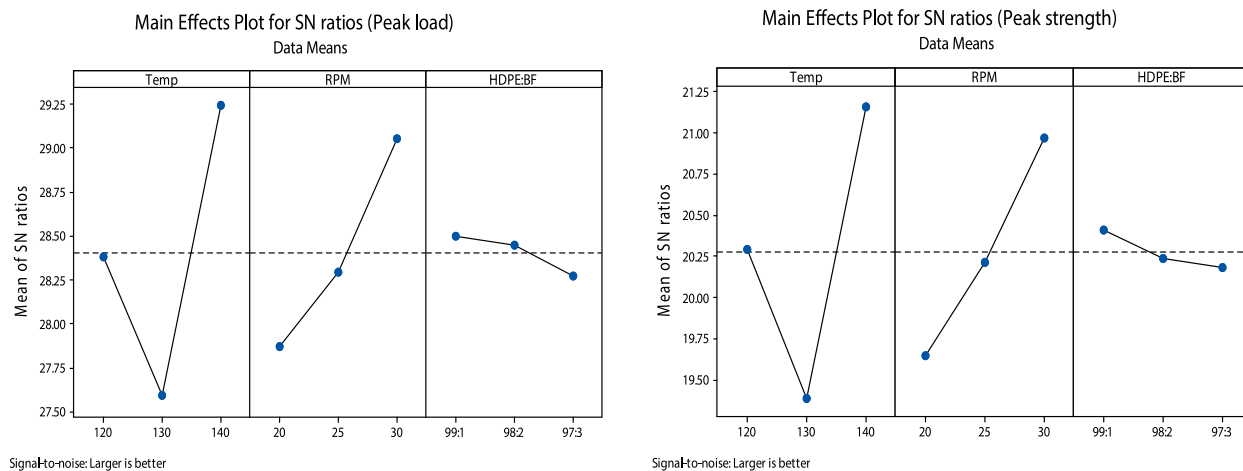


Fig. 4 Linear model for SN ratio of Peak load and peak strength.

Table 7 Percentage contribution of input process parameter

Properties	Temperature	Screw speed (RPM)	HDPE:BF ratio
Peak load	64.23%	34.29%	1.37%
Peak strength	63.18%	35.38%	1.03%

based upon the Taguchi L9 orthogonal array has been developed to perform the TSE operation. Thermal (melting point) and mechanical properties (Peak load and peak strength) have been investigated on the experimental run.

Effect of BF on melting points of secondary recycled LDPE

It clearly depicts the number of cycles of testing on DSC machine. Repetitions were necessary to eliminate any sort of effect arisen due to contamination and pre stored history. First cycle has probably removed the above said effect. Further melting range of the material can be clearly seen in graph in hatched area i.e., 126–129°C. Melting of material starts at 126°C and goes to 129°C. Enthalpy in that melting range was counted to be – 94.34 mJ with a trend. In first cycle of the DSC testing a heaped hatched curve was seen after the melting of LDPE. This shows the decomposition of some substance but surely this is not LDPE, as LDPE decomposes above 300°C. So, this might be decomposition of some of contamination present in the form of the pigment (color). After that, cooling cycle starts and sudden cooling can be seen as straight vertical line. It can be easily observed that there is no evidence of decomposition of LDPE. Some uniformity has been observed in 2nd and 3rd cycle also without any evidence of LDPE decomposition. After 3 cycles of heating, no significant effect was observed in terms of melting and decomposition of material thus it can be concluded that the part prepared from such filament wire will have higher life cycle. It has been observed that melting of the material has occurred at 121.35°C. In case of recycled LDPE, melting temperature was almost same as in case of reinforced LDPE i.e., 123°C.

Effect of BF on mechanical properties of secondary recycled LDPE

There are three parameter has been taken i.e., temperature, RPM and proportion of matrix material and reinforcement. Feedstock filaments for FDM based on this Taguchi L9 has been prepared and tested on UTM for their mechanical strength. Control log of experiment has been shown in Table 8. Further analysis of this design has been done by Minitab software and results have been obtained for SN ratio and mean values. Analysis for peak strength, peak load has been done. Graphs for the same have also been obtained and shown in Fig. 5.

Here it should be noted that 110°C temperature, 30 RPM and 98:2 LDPE:BF ratio have been mostly contributed for changes in peak load and peak strength. (See Fig. 5).

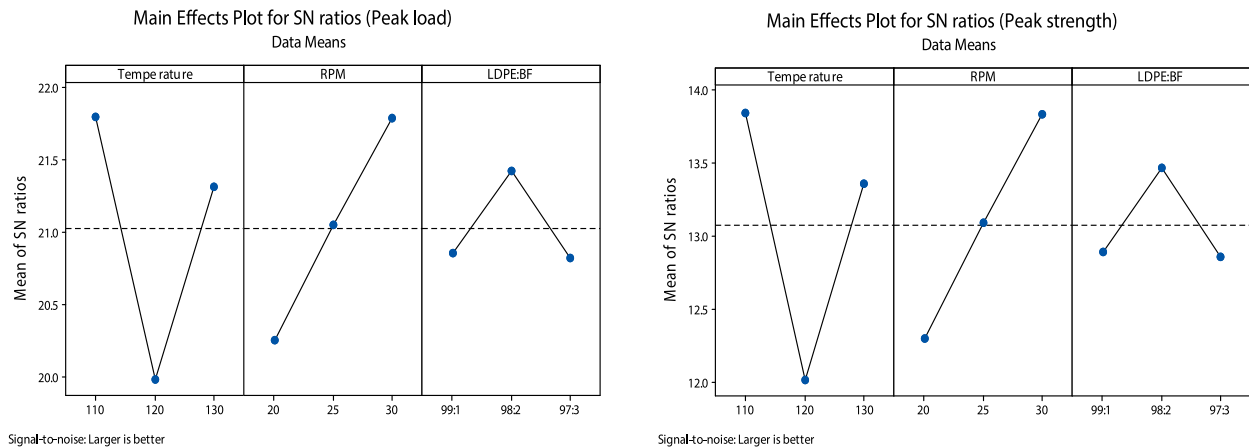
It was observed that for peak load temperature contributed 54.65%, RPM 36.68% and LDPE: BF ratio 7.08%. Similarly for Peak strength temperature contributed 54.95%, RPM 36.35% and LDPE: BF 7.20% (See Table 9).

Summary

The article presents collective case studies for prospect of recycling of plastic product to minimize environmental pollution. The case studies have been reported in the present article to see the effect of BF reinforcement in the primary recycled polymers (ABS,

Table 8 Control log of experiment and mechanical properties

Experiment no.	Temperature	Screw speed (RPM)	LDPE:BF	Peak load (N)	Peak strength (N/mm ²)
1	120	20	99:1	11.25	4.50
2	120	25	98:2	12.79	5.12
3	120	30	97:3	12.94	5.18
4	130	20	98:2	9.42	3.77
5	130	25	97:3	9.97	3.98
6	130	30	99:1	10.58	4.23
7	140	20	97:3	10.29	4.12
8	140	25	99:1	11.28	4.51
9	140	30	98:2	13.57	5.43
Unreinforced recycled LDPE				8.54	3.42

**Fig. 5** Linear model for SN ratio of peak load and peak strength.**Table 9** Percentage contribution of input process parameter

Properties	Temperature	Screw speed (RPM)	LDPE:BF ratio
Peak load	54.64%	36.68%	7.08%
Peak strength	54.95%	36.35%	7.20%

PA6) and secondary recycled polymers (HDPE, LDPE). The following observations have been made from the present study of recycling by mean of extrusion process:

- The BF reinforcement has contributed for improving load resistive capacity of ABS polymer matrix, whereas it has adversely contributed for elongation and Young's modulus. After reinforcement of 5% BF, peak load was increased by 16.27% and peak strength by 10.99%. The elongation was decreased by 13.24%, Young's modulus by 52.22%.
- In the case of recycled PA6 polymer, with the reinforcement MOF 5% BF all mechanical properties have been improved. Peak load was increased by 29.07%, peak strength by 37.52%, elongation at peak by 91.73% and Young's modulus by 258.8%.
- In case of secondary recycled HDPE, it was observed that for peak load temperature contributed 64.23%, RPM 34.29% and HDPE:BF ratio 1.37%. Similarly for Peak strength temperature contributed 63.18%, RPM 35.38 and HDPE:BF 1.03%. Also it was noted that 140°C temperature, 30 RPM and 99:1 HDPE:BF ratio have been mostly contributed for changes in peak load and peak strength.
- In case of secondary recycled LDPE, it was observed that for peak load temperature contributed 54.65%, RPM 36.68% and LDPE: BF ratio 7.08%. Similarly for Peak strength temperature contributed 54.95%, RPM 36.35% and LDPE: BF 7.20%. Also it was noted that 110°C temperature, 30 RPM and 98:2 LDPE:BF ratio have been mostly contributed for changes in peak load and peak strength.

Finally it may be concluded that by reinforcement of BF into various thermoplastics, tailor made mechanical/thermal properties can be attained. Hence for ensuring the recycling of thermoplastics the reinforcement with natural fibers may be one of the cost effective solutions.

Acknowledgement

The authors are highly thankful to Board of research in nuclear science (BRNS) and manufacturing research lab (GNDEC, Ludhiana) for providing financial/technical assistance to carry out the research work.

See also: A Comprehensive Study for 3D Printing of Rapid Tooling From Reinforced Waste Thermoplastics. Food Waste for Sustainable Packaging Materials

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Recent Advancement and Challenges of Additive Manufacturing Geospatial Images Solution Integration

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Introduction

Innovative technology has created a new path of technological application in mainstream market with the promise of environmental sustainability. In order to caution the technology players about this new trend, Malaysian government has announced that 2017 is the starting point of Industrial Revolution 4.0 (IR4.0). IR4.0 can be described as the automation and digitization of industrial processes through robotics and emerging technologies. It includes cyber-physical systems, the internet of things, cloud computing and cognitive computing. It has the ability to disrupt any current industrial processes and moves towards the creation of smart factory. Concurrently, geospatial technology, which is the process of data collection associated with geographic or locational component has gaining huge popularity due to its ability to embrace the emerging technology as described in IR4.0. This technology has rapidly rising in Malaysia since 2010.

Geospatial technology has become an important area to be studied because it involves the aspect of geological analyses, real estate and city planning and educating people (Groger and Plumer, 2012). It means, this technology has become a crucial element in any modern-day system development (Thymianidis, 2015). Most importantly, it helps emergency response and military planning, in which geospatial will generate documentations of location, contour, mapping, environmental condition and many more. All these components cannot be tracked by humans in real time simultaneously due to the lack of transport and communication systems. In Malaysia, there is technological deficiency especially in terms of integrating geospatial with any system that has the ability to print out all the acquired information accurately. This document is very important and acts as information dissemination tool for various agencies in order to plan their strategies in the future (Thymianidis *et al.*, 2012).

This article presents recent advancement and challenges of additive manufacturing (AM) for geospatial images solution. In order to produce the image solution via additive manufacturing, the geospatial image needs to be converted into drawing data without any major changes. It is necessary in order to preserve the originality of the geospatial image. Then, these images can be printed out based on the actual color, contour and mapping condition. The main challenge of this approach is to secure the printing accuracy, precision and tolerance.

Revolution of 3D Printing in Additive Manufacturing

Every technology has their chronological history of development. Additive manufacturing and 3D printing began with the initial commercialization of stereo lithography (SL) in 1987. It can be divided into three developments phases which are the past, current and future. The novel ability of additive manufacturing procedure is the ability to create complex models and irregular shapes with multi-material properties. It has been utilized in various applications such as in automotive, aerospace, defense, restoration, consumer products, architecture, food and many more. The focus of this study is to better understand the recent advanced technology of additive manufacturing for geospatial images data. The importance of geospatial images is to facilitate people who cannot read geographical data in order to extract geospatial information such as politicians, soldiers and many more. This article also describes about the development of 3D printing in converting geospatial data into physical models (Paritala *et al.*, 2017).

Additive manufacturing, also known as layered manufacturing (3D printing, direct digital manufacturing) is an advanced manufacturing technique that replaces process-based job shop operations with product model driven operations based on a 3D CAD model (Holmström *et al.*, 2016). The 3D geometry is converted into a series of motion commands for an additive manufacturing machine by a class of geometric algorithms known as slicers. It starts with digital thread for additive manufacturing (DTAM), a single and seamless of data (Cotteleer *et al.*, 2016) originating from a CAD model in the design environment and moving towards a pre-processing environment to produce the distinct tool paths of making up each layer (Rejeski *et al.*, 2018). It follows by manufacturing environment to fabricate the complex shapes (Steuben *et al.*, 2016). This process is well aligned with additive manufacturing data management, an approach to maintain complex relationship across its lifecycle between the part geometry, material and individual processes to create the final product, known as additive manufacturing Informatics (Mies *et al.*, 2016; Biswal, 2017).

Since 1980s, this innovation showed rapid progression particularly in developed nations. It started in 1987 with the introduction of once well-known SLA (Stereo Lithography Apparatus) 250 machine, which is the main monetary accessible of additive manufacturing framework system in the world. A year later, the first-generation acrylate resin was first commercialized. Japan's NTT Data CMET and Sony/D-MEC commercialized their versions of stereo lithography apparatus, and Asahi Denka Kogyo introduced the first epoxy resin for CMET SL machine. In 1990, German Electro Optical Systems (EOS) sold their first stereo lithography machine namely Stereo and Quadrax presented the Mark 1000 SL system, which used visible light resin (Deshpande and Hsu, 2018). A year later, three additive manufacturing technologies namely fused deposition modeling (FDM) from Stratasys, solid

ground curing (SGC) from Cubital and laminated object manufacturing (LOM) from Helisys were first commercialized. Later on, in 1992, Teijin Seiki introduced Solifrom stereo lithography system and Allied Signal introduced Vinyether Elastomer resin products for SL. In 1993, 3D Systems and Ciba commercialized their first epoxy resin products and proceeded by the commercialization of ModelMaker or Sanders Prototype by Japanese and European companies in 1994. During the same year, Kira Corp commercialized Japan's first non-stereo lithography system called Solid Centre and German's Fockele & Schwarze (F&S) introduced a machine called EOSINT, which was based on laser-sintering technology.

In 1995, Japan's Ushio or currently known as Unirapid Inc sold its first stereo lithography machine. A year after that, Stratasys commercialized Genisys machine, which used an extrusion process that was similar to FDM, Z Corp. launched its Z402 3D printer, which was based primarily on concept modeling and BPM Technology commercially sold Personal Modeler 2100. In 1997, Systems Corp. Company developed a process called laser additive manufacturing (LAM) and Ciba purchased the exactomer resin business from Allied Signal. In 1998, Beijing Yinhua Laser Rapid Prototype Making & Mould Technology Co. Ltd offered similar technology as FDM and other additive processes. Also, Autostrade started introducing its E-DARTS stereo lithography system to companies in Japan and Thermojet 3D introduced faster and less expensive version of Actua 2100.

Innovation of 3D printer became highly sophisticated in year 2000s. LOM machine was produced in Tokyo by Toyoda Machine Company, Sanders Design International announced the development of a machine named Rapid Tool Maker (RTM) and Stratasys introduced a prodigy machine that produced parts in ABS plastic by using FDM technology. In 2001, Objet Geometries began to ship a beta version of its Quadra 3D printer, which combines ultrasonic welding and CNC machining to produce aluminum parts. In the same year, Generis GmbH of Germany commercialized a system used an inkjet-printing technique. Also, Idaho National Engineering and Environmental Laboratory (INEEL) developed a technique for rapid solidification process (RSP).

The technology of lamination, laser sintering, stereo lithography and plaster sintering (similar to FDM) were commercialized by Wuhan Binhu Mechanical & Electrical Co. Ltd of China in 2002. A year later, Z Corp. introduced its ZPrinter 310 system. Meanwhile, North America announced EOSINT laser-sintering, Sony Precision Technology America in US began to market the Sony stereo lithography machines, Envisiontec introduced the Vanquish photopolymer-based system, DSM Somos introduced new resins of SLA/SLS and ProMetal division of Ex One (currently known as Extrude Hone) introduced the small RX-1 metal-based machine (Deshpande and Hsu, 2018). In year 2005, Z Corp. released its latest color 3D-printing system, the Spectrum Z510, 3D Systems unveiled the Sinterstation Pro, a large frame laser-sintering machine with part breakout, powder handling and recycling and Stratasys launched its RedEye RPM and PolyJet machines. On the other hand, Z Corp. commercialized a large powder-based system originally developed based on 3DP technology. In 2006, 3D Systems announced InVision DP (dental professional) system, which includes an InVision 3D printer and 3D scanner for dental market and Somos unveiled NanoTool, a nanoparticle-filled photopolymer for stereo lithography with high heat-resistance capabilities. Two companies introduced new invention of 3D printer in 2007. 3D Systems introduced the V-Flash 3D printer that used film transfer and flash-imaging technology and Z Corp. introduced ZPrinter 450, the first color 3D printer that removed and recycled the loosed powder. In 2008, Stratasys commercialized the FDM 360 to replace Vantage machine and 3D Systems began shipped the first V-Flash desktop modeler. EOS of Germany introduced its high-elongation polyimide PrimePart DC for plastic sintering and Stainless Ph1 for its direct metal laser-sintering platforms. England MTT released a larger selective laser-melting machine, the SLM 250–300, built with automated powder handling and recycling. Mcor Technologies of Ireland officially launched its Matrix 3D printer and Huntsman Advanced Materials introduced the Araldite Digitalis.

In 2009, Dimension 3D Printing Group of Stratasys introduced the uPrint Personal Printer that used the ABS, Objet Geometries announced it Connex 350 system that used ePlyJet Matrix technology to print multiple digital materials with different properties, Lawrenceburg, Tennessee launched its 3D prototype parts service bureau and EuroMold of EOS announced two new plastic laser sintering machines, namely EOSNT P395 and EOSINT P760. A year later, Stratasys and HP signed an agreement for Stratasys to manufacture an exclusive line of HP-branded 3D printers, Optomec released its Aerosol Jet Display Lab System for touch screens and display applications by using direct-write technology and Z Corp. announced a distribution agreement with Envisiontec for its Ultra DLP based machine. Delta Micro Factory Inc. in Beijing, China introduced its extrusion-based portable personal UP! 3D printer and Spanish research centre, IQS announced two new Hydroxyapatite (HA) formulations that can be used in 3D printers. In 2011, MTT Technologies Ltd. (UK) and SLM Solutions GmbH (German) produced a selective laser melting equipment. CRP Technology from Italy introduced carbon-fiber-filled material which is Window XT 2.0 that has greater strength and elongation. In India, 3D Systems acquired Sycode Software Solutions that developed plug-ins for CAD system and Print 3D, which has additive manufacturing quoting plug-in for CAD software. During the same period of time, Object released VeroClear, which was an ABS-like digital, clear and transparent material and New Mexico released Optomec as a new wide-area Aerosol Jet print head to print 3D parts for electronic products.

In 2012, MakerBot in New York released the MakerBot Replicator with larger build volume than its predecessor and EasyClad in France introduced the MAGIC LF600 large-frame additive manufacturing machine. BumpyPhoto in Oregon launched 3D color printed photo relief, Solidscape introduce the 3Z line of high-precision wax 3D printers and Autodesk in California announced a collaboration to create the first 3D bio-printing software. A year later, Arcam in Sweden released its Arcam Q10 machine and 3D Systems acquired the service provider, Rapid Product Development.

Additive manufacturing, especially 3D printing has gone through a lot of different phases of development for more than 30 years. It is an innovative approach of making parts by simply adding the raw materials. It changes the designing, assembling and manufacturing of mass production indistinguishable items to low-volume, innovative, customized and manageable items. One superior characteristic of additive manufacturing is the ability to create intricate shapes with multi-material properties and complex architectures. It can be applied in various fields such as automotive, aerospace, defense, medical, consumer products, food and many more.

Applications of Additive Manufacturing

In automotive industry, the application of additive manufacturing is quite comprehensive. The usage of this safe, smart and sustainable products can be seen in LM3D 3D printed car series from Local Motors, 3D printing of Audi spare parts, new suspension development for Blade, 3D printed supercar by Divergent Microfactories, racing car parts for William F1 team and thumb tool for BMW. The benefits of additive manufacturing in automotive industry can be explained in terms of cutting the time especially during the parts development process and upgrading the quality of the design. These attributes can be achieved with the ability of additive manufacturing in customizing the tooling with reduced cost, producing complex design with decreased weight and reducing assembly and production cost. **Fig. 1** shows the product of additive manufacturing based on automotive application.

Additive manufacturing technologies are also widely used in aerospace and defense industries, which are well-known for their stringent design requirements. The ability of additive manufacturing to manufacture lightweight parts with geometrical and material complexities is very valuable. This technology has been applied in every step of manufacturing process, starts from design concept to end life repairs. Electron Beam Technology (EBM) has been utilized in fabrication process of complex aviation parts. **Fig. 2** shows the aviation part using additive manufacturing system.

The adaptability of 3D printing method with the practicality of producing cost-effective has reformed this technology into new ventures such as kitchenware to nourishment fabrication. 3D printing also incorporates a synthetic chemical design and creates the product by utilizing supercomputers for the purpose of examining the mixture of few substances to produce and assemble of novel chemical compound ([Kurzrock and Stewart, 2016](#)). There is other various application of 3D printing such as in the field of synthetic chemistry for fluidic reactor and reactionware for chemical synthesis. The ability of additive manufacturing processes to manufacture process-dependent of material microstructures demonstrates the flexibility of the technology to be accepted worldwide ([Yalcinkaya and Singh, 2015](#)). **Fig. 3** shows the example of drug printing using additive manufacturing.

In addition to the extensive use of 3D printing in automotive, aerospace and chemical industries, it proves to be beneficial to medical service industry. This industry has seen major transformation especially in biopharmaceuticals, restorative innovation and surgical methods. additive manufacturing is one of the main technology that contributes to this rapid advancement particularly in surgical and diagnostic aids, prosthetic development and tissue engineering. Current research in therapeutic field has fortified the capacity of creating many-sided shapes in the biomedical field such as craniofacial, dental prosthetics and tissue engineering ([Ota et al., 2016](#)).

In food industry, the computerization of manufacturing process increases the productivity and improves quality of products as the food processing involves labor intensive and repetitive operation. The introduction of food printing or digital food manufacturing process allows food to be customized into several colors, shapes, flavors and textures ([Sun et al., 2015](#)). One of the technology that has been widely used in food industry is 3D Foodini printer produced by Natural Machine. This printer can print various sweet and appetizing dishes such as pizza, spaghetti, mini burgers, chocolate, etc.

Current Technology of Additive Manufacturing

Additive manufacturing (AM) processes can be structured from multiple point of views. It is due to the variability of the instrument and material used, high potential to be further improved and their application towards specific industries. additive



Fig. 1 3D printed steering wheel. Retrieved: www.spilaser.com.



Fig. 2 Aviation parts using additive manufacturing system. Reproduced from Coykendall, J., Cotteleer, M., Holdowsky, J., Mahto, M., 2014. 3D opportunity in aerospace and defense. In: Additive Manufacturing Takes Flight. Deloitte University Press, pp. 1–28.



Fig. 3 Drug printing. Retrieved: <https://medtechboston.medstro.com>.

manufacturing can be divided into two categories which are Rapid Manufacturing (RM) and Rapid Prototyping (RP). RM uses different types of materials which can be classified into four material categories, namely polymers, metal, ceramic and composite (Levy *et al.*, 2003).

There are various advantages of using additive manufacturing technology such as the net shape process. It means that less crude or raw materials utilization, which can be up to 25 times less machining process or ability to produce hard to machine products or the combination of both. The net shape ability helps making complex parts with a single step by eliminating multiple operation such as welding and brazing. Moreover, additive manufacturing technology can print a light weight structure, either by the utilization of grid design or by planning a specific placement of the materials without any other constraints. It also has the capability of producing parts which has complex inside channels and multiple sections in one operation. Fig. 4 shows the additive manufacturing processes with large material categories.

The printing rate for each machine is different due to the size, material and type of additive manufacturing used. However, the printing process is generally the same. Normally, low-cost printers utilize plastic fibers such as ABS or PLA with thickness of

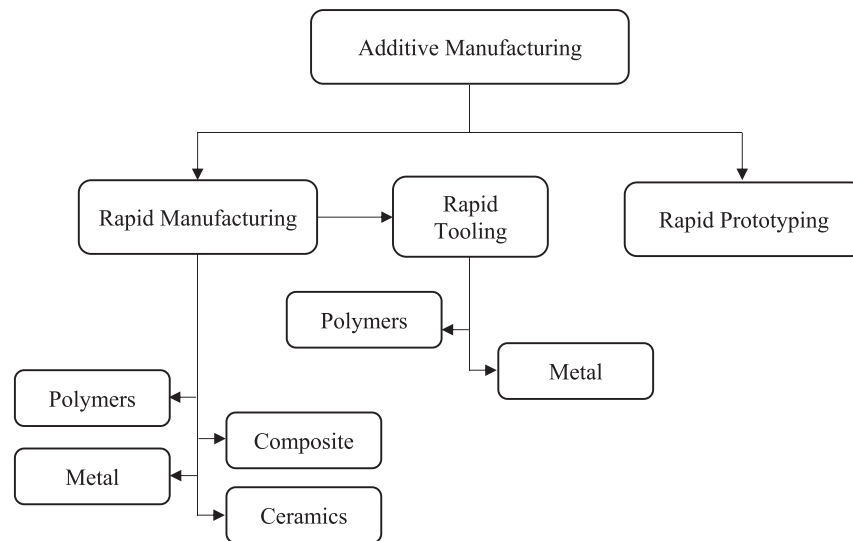


Fig. 4 Additive manufacturing processes with large material categories.

1.75 or 3 mm. It is comparable to hand-work of producing parts by using plywood or acrylic. For open source printers, the software is free such as 3D design apps, slicers, printer control apps and many more. One interesting point to be mentioned is that few printers are technically reproduce themselves, as the fact that some of their components are made from printed parts (Abbott *et al.*, 2018).

Geospatial Images

Geospatial data, or in other word “geographic data” or “spatial data” can be characterized as information represents the location, size and shape of all objects on earth (Lee and Kang, 2015). There are many things that can be considered as geospatial data such as transportation system, property limits, coastlines, aerial imagery and terrain models. Safeguarding geospatial data proves to be a challenge which is similar as protecting all other types of advanced data. There are various technologies that can be used in order to acquire the geospatial data. Nowadays, geospatial data can be obtained by using GPS-enable cellphone and stores in geographic information system (GIS). This system allows the manipulation or visualization of data such as one selected area can be represented in latitude and longitude coordinates, or even a street location. Geospatial information can include various data features such as highway intersection, office structure and political boundaries.

GIS software or Geographic Information Software is a project files consisting of perplexing computerized records that tie together wide assortment of segments, which includes data, instructions on how the data will be displayed, metadata, data models, scripts and other subordinated parts (Eyers and Potter, 2017; Fernandez-Palacios *et al.*, 2017). These documents are blend of information data, which are displayed in a custom-made way that includes grouping, symbolization and annotation based upon the data content. These data can be viewed as maps, charts or tables or some combination of those elements. There are some required processes to render these contents which show the importance of project files, the software that supports the project files, related parts including programming additional items (software add-ons) or extensions and genuine information. The utilization of programming is required for these many-sided qualities of project files to prevent catastrophic failure in the future (Gausemeier *et al.*, 2011).

The development of location-based information technology is the main driver of geospatial digital asset management. Potential industry that can fully utilized these geographical information is insurance industry, especially in determining location or environment that can be exposed to hazardous elements. By exploiting the high-end technology such as multispectral satellite opens up the possibility of acquiring earth perception information, which proves to be valuable for geospatial data analysis. The accessibility of these information expands the usefulness of geospatial technology into new territories such as disaster management, global security and many more. Furthermore, the significance of geospatial technology especially in digital imaginary and its associated products is acknowledged by the public. In 2003, a highly visible conference by GeoIntel appeared to proclaim the importance of geospatial data in US and will generally perceive as an essential component in the commercial sector (Hare *et al.*, 2018).

In order to convert geospatial data to physical or 3D model, it requires a shapefile which comprises of at least three documents, namely a .shp file (feature geometry), a .shx file (list of element geometry) and a .dbf file (a database file that stores the characteristic data of the features). Additional files can be incorporated in this shapefile such as .prj (projection file), .xml (metadata file) and also .sbx and .sbn (index files). Shapefile format presents general guideline for today's standard and widely utilized. Other typical vector format that has been utilized for geospatial data especially in CAD environment is Autodesk DXF, which is a drawing exchange format. There are three stages to convert geospatial data to physical 3D model, which are the input, process and output. All stages are shown in Fig. 5.

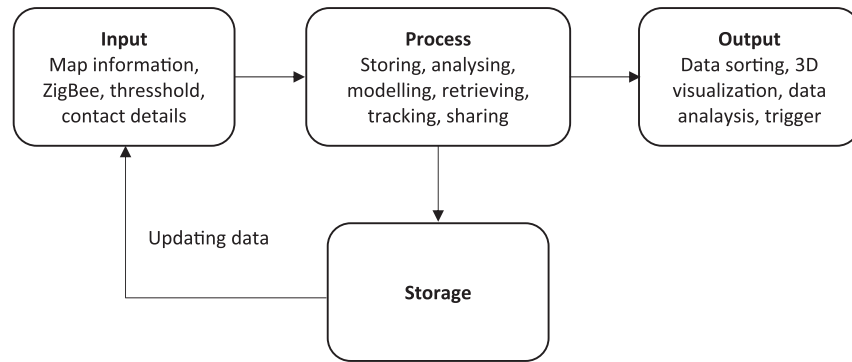


Fig. 5 The procedure to implement geospatial to physical conditions.

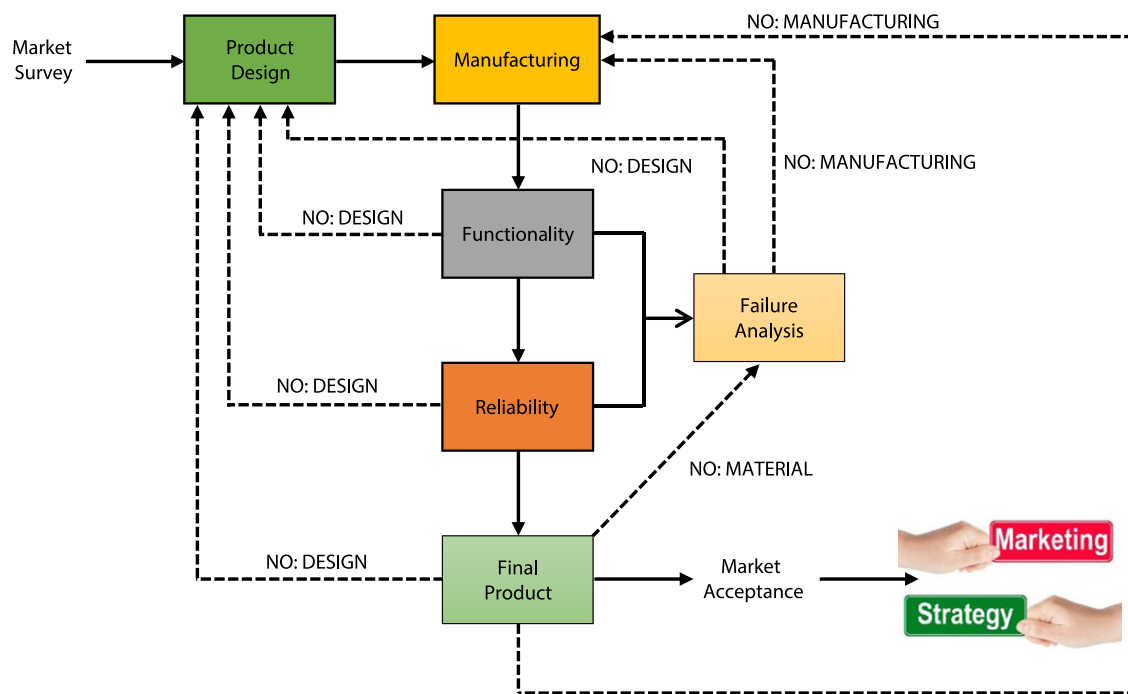


Fig. 6 Flow chart for overall methodology.

The Challenges of Integrated Additive Manufacturing and Geospatial Images

Digital geographical data and geoprocessing have become rapidly important with the advancement of information technology, demanding solution of environmental problems, development of urban and rural planning, development of military strategy and many more (Levy *et al.*, 2003; Janee, 2009; Ghawana and Zlatanova, 2013; Chia and Wu, 2015; Evangelidis *et al.*, 2018). In Malaysia, the number of geospatial technology companies are increasing even though in slower rate. This geospatial technology refers to the technology that is used to acquire, manipulate and store geographical information. It integrates multiple systems such as GIS, GPS, remote sensing and many more. The purpose of a geospatial technology is to share location-based digital geo data that is usually available in public administration based on information technology (Groger and Plumer, 2012; Elberink *et al.*, 2013). Nowadays, due to the rapid changing of information related to the city planning for urban and rural development, and also for military defend strategies, geospatial information has higher demand. It proves to be more effective to get geo data for locations that cannot be tracked by humans.

All geospatial data or documents can be visualized by using digital image. But, most people unable to interpret the data accurately (Evans *et al.*, 2014). It is because, digital image is not representing the actual picture, but it only displays colorful digital bit image (Biljecki *et al.*, 2014). Therefore, in order to represent the data accurately, 3D technology is able to fulfill the demand.

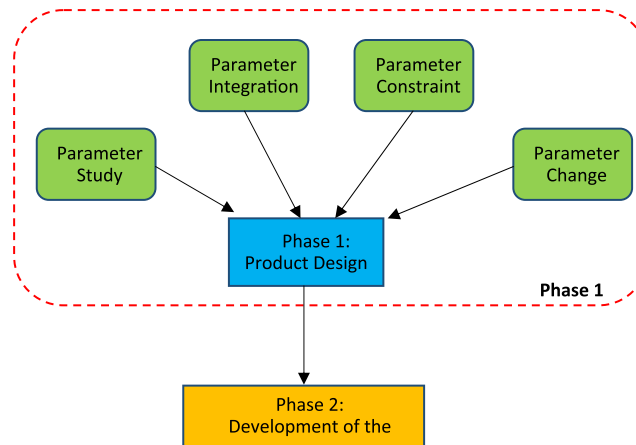


Fig. 7 Flow chart of Phase 1.

But, this technology proves to be too costly. Furthermore, 3D technology to print geospatial data or images is relatively new in Malaysia and most companies send their geospatial data overseas for 3D printing process.

In this section, a new method of printing out geospatial images by using additive manufacturing approach in 3D model is presented. This method allows the integration of geospatial document and data to create 3D environment, which can be zoomed, rotated and viewed from different angles. By concentrating the effort of upgrading the existing additive manufacturing approach, 3D modeling will gain rapid improvement towards creating more realistic model such as urban and rural landscapes equipped with building or forest, topographic variations and location and many more at lower cost.

The flow chart for overall methodology of the solution is shown in [Fig. 6](#). This study is divided into four consecutive phases which starts from product design (Phase 1), development of machine (Phase 2), functionality and reliability (Phase 3) and market acceptance (Phase 4).

The product design phase is consisted of integrating geospatial data or document with additive manufacturing approach. It includes parameter study, parameter integration, parameter constraint and parameter change for different conditions which are before, current after the printing process. In this phase, benchmarking process is also performed by investigating relatively similar approach that has been used or studied in the past. It is also a mode of obtaining baseline and referenced data. The flow chart of product design is shown in [Fig. 7](#).

Phase 2 is focusing on the development of the machine, which includes the modification of existing machine and software development. The main objective is to define the required hardware, software, machine language and module of the additive manufacturing to be fully integrated with the geospatial 3D modeling. For the purpose of market acceptance, this new method of printing geospatial images in 3D modeling must fulfill the requirements established by OGC/ISO1-19128 Web Map Service (WMS) and ISO-19155 Geographic Information Standard. Both standards are used for global geospatial 3D modeling to design high resolution 3D model, which is reliable and conforming the actual landscape or contour. This development process consists of several stages, which are software integration between geospatial raw data or document with additive manufacturing tool, design specifications, design rules and development of 2D and 3D formatting. The flow chart of this phase is shown in [Fig. 8](#).

In printing the 3D modeling of geospatial images, quality is the most important criteria that needs to be accomplished when producing the final product. The quality of 3D modeling can be determined and evaluated based on the functionality and reliability tests of the product. Several test procedures are used such as the logical model test, spatial relationship, visualization, 3D object reconstruction, image texture extraction and image texture mapping. These proposed test procedures are necessary to ensure 3D modeling is accepted by the geospatial industry and adhering to the regulations imposed by international standards ([Fernandez-Palacios et al., 2017](#)).

The 3D modeling of geospatial images is very important for urban and rural planning and in military strategies. Therefore, the demand of this technology is expected to increase in near future especially in the emerging market by 2025. Evidently, there are many studies investigate and evaluate the effectiveness of the additive manufacturing tools to print out 3D modeling of geospatial images. Based on the studies, the utilization of additive manufacturing in geospatial technology is still in early stage. However, the demands are very high especially in United States and Asia. In Malaysia, the demand for geospatial technology comes from state and federal government for the purpose future planning. However, 3D modeling of geospatial images technology is still lacking. Because of that, the geospatial company in Malaysia needs to courier the raw data overseas in order to print them out. This lengthen process inevitably impacting the cost. Therefore, this 3D printer machine will have high demand in the future because of the acceptable high quality with much lower cost. Market acceptance study is needed in order to identify the product attributes and perception among Malaysians towards this technology for both short and long terms. In addition, the market acceptance is also a crucial factor in determining the preference, choice and required trade-offs in fulfilling future demands.

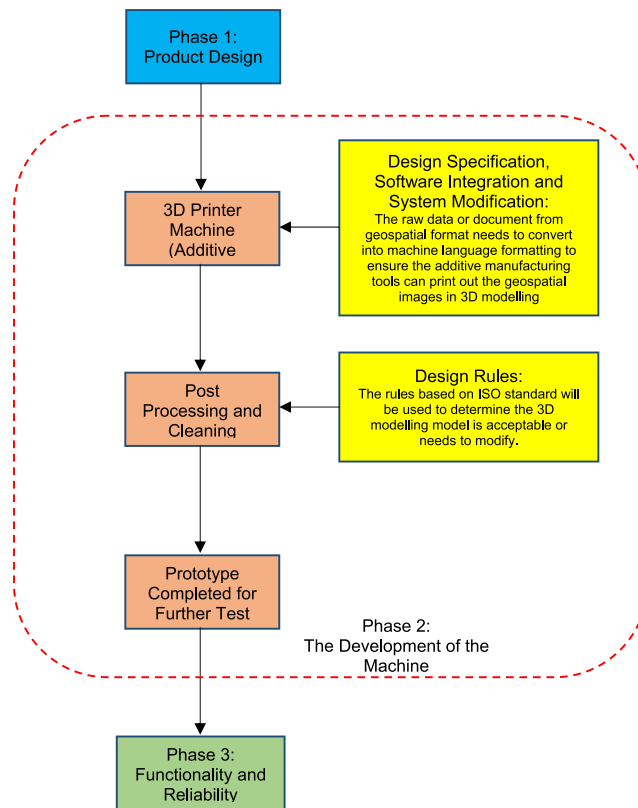


Fig. 8 Flow chart of Phase 2.

Conclusions

This article presents the recent advancement and challenges of additive manufacturing geospatial images solution integration. Basically, additive manufacturing technology shows a great potential to be used in various applications and industries like automotive, aerospace, defense, kitchenware, chemical, food processing and many more. By integrating the additive manufacturing and geospatial technology, the utilization can be infinite. The integrating technologies are totally embracing the new era which is fully supported in Industrial Revolution 4.0 (IR4.0), which is expected to be the future trend on how innovative technology works and delivering the product. This integration technologies have a lot of obstacles that need to be answered in future, and it is also provides opportunity of exploring new technological possibilities. To do that, this article is able to present the detailed procedures of integrating both additive manufacturing and geospatial technology through a structured development process.

See also: A Comprehensive Study for 3D Printing of Rapid Tooling From Reinforced Waste Thermoplastics. Investigations for Metal Matrix Composites Prepared by Using Waste Polymer-Based Sacrificial Rapid Pattern in Investment Casting

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Recycled Clothes With Polypropylene-Nanoclay for Industrial Product via Injection Molding

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Introduction

Typical consumer tend to reuse their clothes through donation or throw away into landfill. Economic growth will increase consumerism, hence lead to more clothes to be used, posing a significant challenge towards waste management and environmental control (Gupta, 2012). One of the possible ways to decipher the reduction of carbon footprint of textiles and clothing sector is to recycle the textile process waste and also to recycle at the end-of-life of textile products. Detailed investigation of the possibilities, barriers, and challenges to recycle textile waste materials with relevant case studies have been discussed (Muthu *et al.*, 2012). Therefore, clothes recycling had become one of the option in order to reduce abundant of waste made from this product. Through recycling, the energy needed to make new products from natural materials could be reduced. For instance, in United Kingdom it was found that the reuse of 1 tons of polyester garments only uses 1.8% of the energy required for manufacture of goods from virgin materials (Woolridge *et al.*, 2006).

In term of polymers, polypropylene was quoted as a semi-crystalline plastic which is tough, stiff, weight to cost effective, balance of strength, modulus and resistance towards creep (Chanda and Roy, 2008). Thus, polypropylene was proposed as thermoplastic composite matrix (Jeencham *et al.*, 2014). As for the filler for composite matrix, clay was chosen to provide a better physical and chemical environment for the polymer (Ramsaroop *et al.*, 2010). A combination of polypropylene-nanoclay had increased more researchers to perform more investigation about the improved properties, the effect of clay content as well as the cost effective-additive utilization (Othman *et al.*, 2014b). Several research have carried out an optimization process towards polypropylene-nanoclay based material at many applications, such as snap fit samples (Othman *et al.*, 2014a), shrinkage and warpage (Othman *et al.*, 2017) and melt flow index (Othman *et al.*, 2018b).

As for exploiting the recycled polymer, a review had been made by Hamad *et al.* (2013), whereby polymers such as polylactic acid (PLA), polyvinyl chloride (PVC), polypropylene (PP), polyethylene (PE), polystyrene (PS), acrylonitrile butadiene styrene (ABS), polyethylene terephthalate (PET) and polyamide (PA) could be recycled through reused, chemical and mechanical recycling. In this article, mechanical recycling through injection molding was chosen because it is a similar process in industry and widely used. Since injection molding is one of the preferred manufacturing process for plastics, then the recycled material that could go through injection molding again would be very beneficial for manufacturing industry. However, the major concern is about the degradation of the mechanical properties. Several studies have been conducted about the properties of the recycled polymer. Table 1 shows some of the findings related to polymer recycling.

Therefore, all of these findings have motivated the use of recycled clothing to be compounded with polypropylene-nanoclay matrix. Thus this compounding can be used as a secondary raw material in the manufacturing process, such as injection molding. By using this approach, the disposal of these clothes that can cause pollution to the environment can be reduced and the plastic manufacturing industries may benefit the applications of this new material in terms reducing the cost and consumption of raw materials.

Preparation of Recycled Clothes With Polypropylene-Nanoclay

To compound the recycled clothes with polypropylene-nanoclay, several processes have to be carried out. First, the clothes have to be shredded into small pieces. It is preferred to use the same clothes material. Then, the shredded used clothes were dried up to remove the moistures by using a drying machine. The recommended temperature was set between 90 and 100°C for 15–18 h. Then, the dried pieces of clothes need to be grind into fibers through grinding machine. These fibers were compounded with polypropylene and nanoclay through a twin screw extruder to make feedstock for injection molding. Polypropylene with 5 wt. % of nanoclay (PPNC-5 wt. %) and 15 wt. % of compatibilizer was used as the polymer matrix. The feedstock need to be crushed into pallets so that it can be injected by using injection molding machines to produce industrial product. The compound could be prepared with three different percentages which were 1%, 2% and 3% of fibers made from recycled clothes.

Properties of Recycled Clothes With Polypropylene-Nanoclay

In this article, injection molding was selected as an approach to recycled clothes into secondary raw material for manufacturing. Injection molding was selected since it is better compared to hot press machine because, injection molding using very high pressure, which can lead to mold better, with a strong pressure molding process to mold than others.

Table 1 Properties studies of recycled polymer

Authors	Recycled Polymer	Properties Studies
Evstatiev <i>et al.</i> (2002)	Poly (ethylene terephthalate)	Elastic modulus, tensile strength and impact strength
Mehat and Kamaruddin (2011)	Polypropylene	Flexural modulus
Rahimi <i>et al.</i> (2014)	Acrylonitrile butadiene styrene	Shrinkage, impact resistance, flexural strength and tensile properties

Note: Evstatiev, M., Fakirov, S., Krasteva, B., *et al.*, 2002. Recycling of poly (ethylene terephthalate) as polymer-polymer composites. *Polymer Engineering & Science* 42 (4), 826–835. Mehat, N.M., Kamaruddin, S., 2011. Investigating the effects of injection molding parameters on the mechanical properties of recycled plastic parts using the Taguchi method. *Materials and Manufacturing Processes* 26 (2), 202–209. Rahimi, M., Esfahanian, M., Moradi, M., 2014. Effect of reprocessing on shrinkage and mechanical properties of ABS and investigating the proper blend of virgin and recycled ABS in injection molding. *Journal of Materials Processing Technology* 214 (11), 2359–2365.

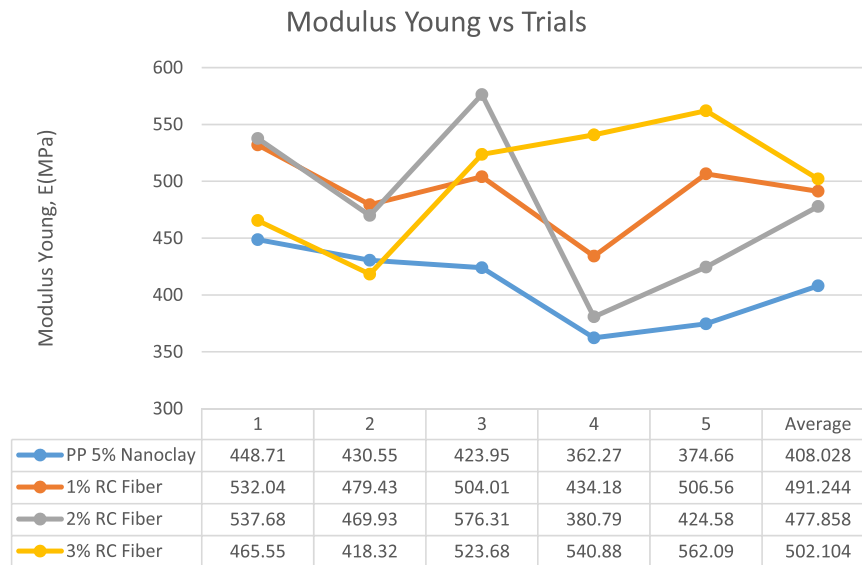


Fig. 1 Young's Modulus vs. Trials for each formulation. Edited from Othman, M.H., Muhammad, A.I., Hassan, S., 2018a. Investigation of clothes recycling as colouring agent for polypropylene-nanoclay nanocomposites. *International Journal of Technology and Engineering Studies* 4 (1), 1–6.

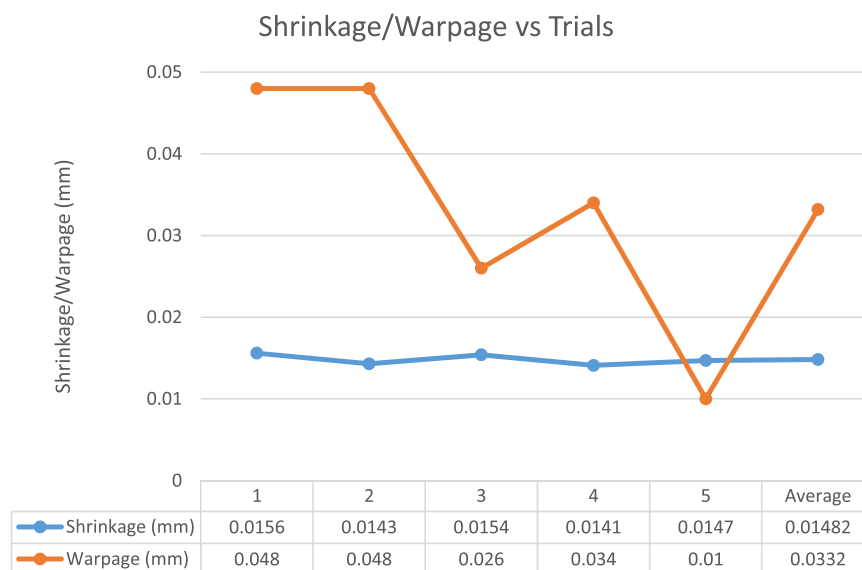


Fig. 2 Young's Modulus vs. Trials for each formulation. Edited from Othman, M.H., Muhammad, A.I., Hassan, S., 2018a. Investigation of clothes recycling as colouring agent for polypropylene-nanoclay nanocomposites. *International Journal of Technology and Engineering Studies* 4 (1), 1–6.



Fig. 3 Example of resin compound made from recycled clothes/polypropylene/nanoclay.

To quote one of the example of material properties for a compound of recycled clothes with polypropylene-nanoclay, the average values of Young Modulus have been summarized and the graph of Young's Modulus versus Trials have been displayed in [Fig. 1](#). Based on the results of tensile test, the highest average Young's Modulus value with the 502.104 MPa for 3% of recycled fiber from recycled clothes. As for the sample mixed with 1% fibers, it recorded the highest value of 491.244 MPa for Young's Modulus. According to [Fig. 1](#), the Young's Modulus value for polypropylene-nanoclay without fiber was lowest as compared with other samples ([Othman et al., 2018a](#)).

Before injection molding was performed, the length of injection-molded cavity was measured before it heat up. After that, the length of produced samples was measured, to analyze the shrinkage. The value of average shrinkage is exemplified in [Fig. 2](#) with the average value of 0.01482 mm. After ejection from the mold, the flashing and runner was removed from the sample. The reading of thickness was measured at 10 different places on the sample by using a micrometer screw gauge. For the maximum height of the sample, the reading was recorded using dial gauges. The value of average warpage is displayed in [Fig. 2](#) ([Othman et al., 2018a](#)). From this figure, it showed that the average warpage was 0.0332 mm. According to [Fig. 2](#), it can be assumed that the product of recycled clothes/polypropylene/nanoclay had a stable shrinkage but could produce variation on warpage values. Hence, more focus was needed to control the warpage value to reduce this defect during manufacturing process.

In present application, the coloring agent that were used in the plastic industries are the dyes and pigments. Both methods are substantially different and produce specific results. Dyes are defined as colorants that are (completely) soluble in a polymer at the processing temperature ([Müller, 2003](#)). In this study, innovation is carried out on recycled clothes as coloring agent for polypropylene injection molding process. As polymer synthetic materials, textile fiber extracted from recycled clothes have potential to be as coloring agent for plastic by compounding the fiber with polymers. As transforming recycled clothes into coloring agent for plastic, the issues of textile waste can be reduced. Undesirable clothes waste was unavoidable by-product in most apparel manufacturing process ([Bhatia et al., 2014](#)). [Fig. 3](#) shows the example of resin compound made from recycled clothes/polypropylene/nanoclay, whereby the colors of black, red and yellow were produced from the recycled clothes with similar colors.

As for the conclusion, it was proven that the approach to recycled clothes by using injection molding has been succeeded. The value of young's Modulus, for the samples recycled clothes (cotton fiber) has higher value compared to sample polypropylene-nanoclay. All the properties of recycled material can be clarified based on graph plotted after testing. The recycled clothes/polypropylene/nanoclay also have a good control on shrinkage. It can be also used as the coloring agent. Based on these findings, these compounded materials can be used in the application of industrial products such as plastic bottle, container, automotive component/cover and more. The outcome of this project should be beneficial in future of plastic manufacturing process; in terms reducing the cost and consumption of raw materials.

See also: Bamboo Fiber as Fillers for Polypropylene-Nanoclay via Injection Molding. Design and Performance Analysis of Small-Scale Parabolic Trough Solar Collectors Using Sustainable Materials. Reuse of Waste Corrugated With Coir Fibers as a Packaging Material. Scaling Up and Intensifying Stakeholders Engagement for Evidence-Based Policymaking: Lessons Learned

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Renewability and Sustainability: Current Status and Future Prospects

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Introduction

With the continuing problems of deforestation, greenhouse emissions, ozone layer depletion, global warming, and overall environmental degradation, it looks like the world is running on a self-destruct mode. In the words of Terry Swearingen, 1997 winner of the Goldman Environmental Prize “we are living on this planet as if we had another one to go to.” Sustainability is one of the top most priorities today. Both recyclable and renewable resources (materials and energies) can help in making the planet better, safer, and greener, for current and future generations. To recycle means to transform waste products into new supplies or products. Resources that are renewable can be naturally and organically replenished over a given time period (Piletic, 2019). For a good “now,” and for a better “future,” it is important to understand and spread awareness about recyclable and renewable materials and energies that work in a sustainable manner. A native American proverb tells us that “we do not inherit the earth from our ancestors; we borrow it from our children.”

There are both positive and negative aspects to renewable and recyclable materials. Knowing how these two types of materials work is critical in trying to make our planet more sustainable. Which is a better option for sustainable living? Let us take logging of timber for the worldwide construction industry as an example. Should we opt for renewables and risk deforestation, or should we go for recyclables and face the hazard of increased pollution if the target of recycling is not met? An optimal solution is quite complex. Another option is ‘recyclable renewables,’ with the possibility of recycling our renewable products. Materials such as renewable plastics (made from cellulosic materials instead of petrochemicals) would be an excellent alternative, and may be a backbone of sustainability in the future (Piletic, 2019).

Some questions in this regard can be quite intriguing and thought-provoking. Let us look at a few more captivating ones. What is the difference between recyclable and recycled? When a material or product has the ability to be recycled, it is *recyclable*. A *recycled* article is made from materials that were part of something else. What is the difference between a circular economy and a linear economy? All over the world, a *linear economy* has been traditionally practiced, which can be summarized as ‘make, use, dispose.’ On the other hand, in a *circular economy*, products are reused instead of being disposed to extract maximum value. The sequence is now ‘make, use, dispose, recover, recycle.’ What is the difference between sustainable and renewable? *Sustainable* relates to a method or resource being maintained, while *renewable* refers to physical reuse of supplies. As an example, plastic is a renewable resource since it can be recycled; while the recycling of plastic is sustainable if the used plastic is recovered and undergoes a recycling process. What is the difference between renewable and sustainable resources? *Renewable resources* can be generated as fast as they are consumed. If this can be maintained, they are also *sustainable*. Again, plastics can be both renewable and sustainable if they are continually recovered and recycled to create new products (Coca-Cola-UK, 2017).

To have an idea of their intertwined nature, let us try to define and briefly discuss the three keywords: renewability, recycling, and sustainability.

Renewability

If an energy (or material) resource can be regenerated at the rate at which it is consumed, it is *renewable*. The word renewable is used mostly in the context of energy, but it can apply to anything that can be replenished. The term renewable is thus applicable to both materials and resources that are not completely depleted at their source, and can be produced at a pace to match the demand. In the energy sector, sources are either renewable (wind, solar, water, thermal) or non-renewable (coal, oil, gas). As for materials, most of the renewable ones are natural (timber, bamboo, cotton, hemp, etc). However, man-made materials such as plastics become renewable through recycling (Coca-Cola-UK, 2017).

If disposed of properly, plastic can successfully go through the three stages of recovery, recycling, and reuse. This can be in the form of the original material (new packaging or can), or as a new product (such as fibers or fabric). So plastic possesses *renewability*, and it is a renewable material. It is reported that recycled plastic consumes about 60% less energy for production compared to new plastic. This helps in sustainability; the higher the recovery and recycling, the more sustainable the source plastic is (Wikipedia, 2019a).

Renewable resources are mostly natural, and they can be replenished, so the portion depleted by consumption is replaced. The mechanism can be natural reproduction or through human intervention. Natural renewable resources are an intrinsic part of our planet's environment and a major component of its ecosystem (Stead *et al.*, 2009). Apart from agricultural production, and renewable energy, water is also a renewable material. The condition is that its usage, treatment, and release are carefully monitored. If not, water would be a non-renewable resource at that locality. For instance, groundwater is generally taken out from an aquifer at a rate much higher than its rather slow natural recharge, making it a non-renewable resource (USGS, 2019). Desalination of seawater also makes water a renewable resource. However, its dependence on energy derived from fossil fuels needs to be reduced for it to be completely renewable (Coleridge, 2008).

Increasing pollution is a major concern for water resources. According to an estimate, at least 22% of water is used by industries the world over (WBSCD, 2012). Bulk of these industrial users are hydroelectric dams, thermoelectric power plants (water as coolant), refineries for oil and mineral ore (water in chemical processes), and a host of manufacturing and chemical plants (water as a solvent). Without efficient chemical treatment, it would lead to severe environment damage and resource depletion (making water a major non-renewable resource).

Sustainable agriculture, as mentioned above, is an important factor in renewability. Coined by the Australian agricultural scientist Gordon McClymont (Rural Science Graduates Association, 2013), it means “an integrated system of plant and animal production practices having a site-specific application that will last over the long term” (Gold, 2009). Expansion of agricultural land reduces biodiversity and contributes to deforestation. The United Nations (UN) Food and Agriculture Organization (FAO) has estimated that farmland will be increasingly lost to industrial and urban development in the coming years. Reclamation of wetlands, and conversion of forest to cultivated land will happen simultaneously, leading to the loss of biodiversity and higher amount of soil erosion (FAO, 2003). Agricultural practices are perhaps the single largest cause for the global increase in soil erosion (Committee on 21st Century Systems Agriculture, 2010). At an estimate, more than a thousand million tons of soil are eroded each year only in the southern part of Africa. Some experts claim that farm yields will be reduced by half within 30–50 years if the current rates of soil erosion continue (South Africa CEP, 2013). Conscious and sustained efforts towards renewability are essential.

Air is one of the primary renewable resources, and it self-replenishes through natural processes such as the nitrogen cycle. All living organisms need oxygen, nitrogen and carbon in a direct or indirect manner, and many other gases. With the ever increasing amount of smog and pollution, this resource is becoming more and more toxic, and is also contributing to global warming. Increased and focused efforts towards renewability of the earth’s atmosphere are an imminent requirement.

Recycling

Recycling is the practice of reusing things that would otherwise be thrown away as waste. It is the process of converting trash materials into new materials and items. In conventional waste disposal, materials and equipment usually end up in a landfill. Recycling, on the other hand, can prevent the waste of potentially useful materials and reduce the consumption of fresh raw materials. This in turn reduces energy usage, air pollution (from incineration), and water pollution (from landfilling). In short, through recycling, rejected materials can be recovered for reuse, helping in lowering greenhouse gas emissions, and thus improving the environment and helping sustainability (Wikipedia, 2019b).

One variation of recycling is *upcycling*, which means adding value to an item so that it can be reused. The other type is called *downcycling*, which is the process of breaking down a product material into its components or elements, with the intent of reusing anything that can be salvaged. The third subclass of *precycling* is a new approach; the idea is to avoid procurement of “unnecessary” items that would have to be recycled in the future, or will be totally wasted. *E-cycling* is a rather new term, referring to the practice of reusing electronic components rather than dumping them at the end of their useful life (Wigmore and Rouse, 2019).

There are various materials that can be recycled, including many types of glasses, paper, cardboard, metals and alloys, plastics, rubbers and tyres, textile products, and electronic components and devices. Composting or other types of salvaging of biodegradable waste (food, garden, or agricultural waste) also comes under recycling. Materials that have to be recycled can be directly deposited at specific collection centers, or can be picked up from domestic or commercial waste bins, and then sorted, cleaned, and reprocessed into new materials, which can be later manufactured into same or different products (Murphy *et al.*, 1993).

There are various standards concerning the process and practice of recycling (Gopalakrishna and Reddy, 2018; Gencer, 2016). Two of the more important ones are ISO 15270:2008 (dealing with plastics waste) and ISO 14001:2015 (regarding control of environmental management for recycling practices).

Sustainability

If a process or state is *sustainable*, it can be maintained at a desired level for as long as it is required. According to the Brundtland Commission (United Nations, 1987), sustainable development “meets the needs of the present without compromising the ability of future generations to meet their own needs.” One dictionary defines *sustainability* as the avoidance of the depletion of natural resources in order to maintain an ecological balance. Sustainable development requires a balance between local and global efforts, such that basic human necessities are met without damaging the natural environment (Kates *et al.*, 2005; IISD, 2019c). However, the term ‘sustainable development’ is itself paradoxical in the eyes of some authors (Williams and Millington, 2004), as development is inherently unsustainable.

Maintaining the health of the environment and the ecosystem is a necessity for the continued survival of humans and other species. Some of the more important means of containing negative human impact are eco-friendly chemical engineering, management of environmental resources, and environmental protection (Bakari, 2017). Sustainability can be thought of as the aim of achieving equilibrium in the human-ecosystem domain (homeostasis). Consequently, sustainable development is a combination of holistic approach and temporal processes that can help us attain the target of sustainability (Shaker, 2015). Though sustainability is a very popular buzz word, the actual possibility that the human civilization will achieve environmental sustainability remains questionable. Climate change, environmental decay, population growth, overconsumption, and the race for uncontained economic growth are a few of the culpable factors (Worldwatch Institute, 2013).

Working towards a sustainable environment also entails a social challenge. It requires changes in national and international legislation, transportation and urban planning, supply chain management, consumer habits and lifestyles, etc (Madiati *et al.*, 2018). Improving of sustainability can be done in many ways: restructuring of living conditions (eco-friendly and sustainable villages, municipalities, etc); reevaluation of economic segments (green building, permaculture, sustainable agriculture); new work practices (ecological architecture); developments in science and technology (renewable energy, green technologies, and sustainable nuclear power); improving flexibility and reversibility in engineering design, (Fawcett *et al.*, 2012; Zhang and Babovic, 2012) and reshaping of individual and group lifestyles targeted at conservation of natural resources (Black and Cherrier, 2010).

The concept of sustainability is composed of three pillars: economic, environmental, and social (Capra, 2015; Scott, 2009); also known informally as the three p's: profits, planet and people. Culture, technology, and politics are considered to be the sub-domains of sustainable development (Magee *et al.*, 2013). Three main goals of sustainable development were agreed upon in the 2005 World Summit on Social Development (UNGA, 2005). These were economic development, social development, and environmental protection. The three pillars are not mutually exclusive, but are inter-dependent, and each can only co-exist with the others (Morelli, 2011). Some experts have added a forth pillar of 'future generations,' highlighting the long-term planning needed for sustainability (Waite, 2013).

Sustainability and the Various R's

According to one study, over 230 million tons of trash go to landfills per year only in the USA. Another study estimated that only 25%–30% of this waste is recycled (Annenberg Learner, 2019). To overcome this increasing problem, various recyclability and sustainability strategies (3R, 4R, 6R) have been proposed and are being promoted, 3R being the most popular.

The 3 R's: Reduce, Reuse, Recycle

The 3R policy (reduce, reuse, recycle) is the most well-known sustainability drive. It is sometimes also called the "waste hierarchy." It is the actions that should be taken, in the order of priority, to reduce the amount of waste generated, and to improve waste management efforts. The target is to bring about a small change in everyone's lifestyle, so that the amount of waste going into landfills is decreased, and the carbon footprint of human beings is reduced. This will help in the conservation of natural resources (materials and energy) and landfill space, and also generate economic savings in terms of money used currently for disposal of wastes in landfills. Putting up the site for a new landfill is becoming more difficult and expensive due to environmental regulations and public opinion.

The first 'R' is *reduce*, the idea of reducing what is produced and what is consumed. The logic is simple: if waste is reduced, then there is less to recycle or reuse. There are three basic questions that need to be assessed. First; can this function be done by using something else? Using the same thing for multiple tasks is an important first step towards reduction. Second; is it something that must be done this way? A large amount of waste material comes from disposable items. Third; is this item really a part of something that is necessary for your life? It is important to ensure that what we consume, or keep as an item to be used some day, actually matches the reality of potential opportunity in our lives (Conserve Energy Future, 2019).

The second R (*reuse*) is again very simple; exactly what it means. Learning to re-use most of our possessions, or using them for a different purpose than initially intended, is another essential in waste hierarchy. One of the best examples today is the modular construction of homes and office buildings, using rejected shipping containers. And if you absolutely do not want an item any more, and it is still usable, it can be donated to others. Some prime examples are old books, old clothes, old electric equipment and rechargeable batteries, etc (Conserve Energy Future, 2019).

The third R of *recycling* is the last stage of the waste hierarchy. After recycling, the item will be transformed again into a raw material that can be used to produce the same or a different new item. There are a lot of materials on earth that can be recycled, and yet it is not a common practice. First, society needs to learn as to what products can be recycled. Second, more efforts are needed in separation and collection of recyclable waste. Third, more progress needs to be made in uniting recycling plants with industries that can process the waste material (Conserve Energy Future, 2019).

The 4 R's: Reduction, Reuse, Recycling, and Recovery

Analyzing a number of the available waste prevention techniques, one group modified the 3R strategy to the so-called 4 R's of "reduction, reuse, recycling, and recovery." More and more businesses today are faced with stricter environmental regulations, public pressure, shortage of landfills, and demand for higher resource efficiency. Many companies are therefore changing their approach from 'waste treatment' to 'waste prevention.' As compared to organizations that focus only on the 3 R's in resolving waste management issues, more innovative companies are adopting 4R solutions being generated as an outcome of industry benchmarking or technological breakthroughs (IISD, 2019a,b).

The approach can be summarized as follows. If possible, waste *reduction* is the first option. If waste is produced, maximum effort should be made to *reuse* it, if practically feasible. *Recycling* is the third step in waste management, which obviously helps in conservation of resources and reduction of wastes. However, waste collection and recycling entail significant economic and environmental costs. That is why, recycling should only be looked into if the waste cannot be reduced or reused. As a further step, it is possible sometimes to *recover* materials or energy from waste that cannot be reduced, reused, or recycled (IISD, 2019a,b).

Empirical studies assert that through the practice of waste prevention, reuse, recycling, and environmentally conscious purchasing, businesses can reduce costs and increase profits. These cost savings include lower costs of waste disposal, waste treatment, energy usage, materials and supplies, regulatory compliance, and storage; and recovery of cost through sale of recyclable materials, and sales of 4R technologies (IISD, 2019a,b).

The 6 R's: Reinvent/Rethink, Refuse, Reduce, Reuse/Repair, Recycle, Replace/Rebuy

The 6R initiative for sustainability is a social drive to motivate and train common consumers to make recycling and sustainability a part of their daily routine. The 6 R's are reinvent/rethink, refuse, reduce, reuse/repair, recycle, replace/rebuy (Alatervo, 2018). *Rethink/reinvent* asks everyone to reconsider and question their daily consumption habits. Do we really need all the things we consume? Can some of these be recycled? *Refuse* means to make a conscious effort to not generate waste, as much as possible. *Reduce* hints at making daily-life decisions that decrease the amount of trash generated. Through buying only what we need, avoiding impulse shopping, and not purchasing more than the amount needed, we can reduce the amount of materials, toxins and waste sent to landfills. The idea of *reuse/repair* is to expand the usable lives of products. By using something again, or by finding new uses for an item, one can extend the product life, and reduce waste. The term *recycle* is rather obvious: at the end of a product's life, reclaim the raw materials for use in a new product. The common person just needs to separate out products such as aluminum cans and plastic (bottles, sheets, etc), and recycling companies can use them again. Recycled materials usually need less energy to process them into products compared to new materials (Recycling Revolution, 2019). Also, these items do not end up in the landfill, resulting in reduced air and water pollution. *Replace/rebuy* wants us to use, on a consistent basis, products made from recycled (or green) materials.

Renewability and Sustainability Practices

Legal reforms and subsidies at the government level play an important role in sustainability and in increasing the market share of renewables. One example is the Non-Fossil Fuel Obligations (NFFO) adopted in the United Kingdom, making it obligatory for the electricity distribution network operators to purchase electricity from nuclear power and renewable energy sectors. Scotland (Scottish Renewable Orders) and Northern Ireland (Northern Ireland Non-Fossil Fuel Obligation) also have similar legislative mechanisms in place. Renewable Energy Certificates (RECs) serve the same purpose in the United States. In Germany, their *Energiiewende* offers subsidies in the form of fed-in tariffs, resulting in increased use of renewable biomass in conventional fossil fuel plants (Clean Energy Wire, 2019).

Renewable Materials

Renewable materials are those which can be manufactured or generated quickly enough to keep pace with how fast they are used up. Non-renewable materials, including materials for energy sources, are those which take a long time to renew and are generally used faster than they can be regenerated. Renewable materials can be made from natural products or synthetically produced, and often include recycled products (Garvin, 2019).

Renewable materials are sustainable materials, which means, according to the Rutgers University Center for Sustainable Materials, these materials do not use up non-renewable resources. They can also be produced in high enough volume to be economically useful. Biopolymers are one such renewable material. A biopolymer is a naturally occurring polymer, such as carbohydrates and proteins. Some examples of biopolymers are cellulose, starch, collagen, soy protein and casein. These raw materials are abundant and biodegradable, and are used to make diverse products such as adhesives and cardboard (Garvin, 2019).

Rapidly renewable materials are plant-based materials that can be replenished within a period of ten years or less. Bamboo and cork are rapidly renewable materials used to create flooring materials for homes and office buildings. Bamboo is commonly used instead of woods such as oak, which is a relatively slow-growing tree. Although oak is technically a renewable resource, it takes many years for an oak tree to mature compared to bamboo (Garvin, 2019).

Biorenewable chemicals are produced through biological organisms, supplying feedstocks for the chemical industry (Nikolau et al., 2008). Instead of the petroleum-based carbon feedstocks that are currently used by the chemical industry, these chemicals are a good alternative as their production is based on solar-energy. There is a huge diversity of enzymes in biological organisms, and synthetic biology has a large capacity for altering these enzymes targeted at new chemical functions, paving the way for the chemical industry to use renewables (Garg et al., 2016; Leber and Da Silva, 2014).

Bioplastics are derived from renewable biomass sources, including vegetable fats and oils, lignin, corn starch, microbiota, etc (CORDIS, 2008). Thermoplastic starch is the most common type, while cellulose bioplastics, biopolyester, polylactic acid, and bio-derived polyethylene are some other forms. In comparison with production of plastics from petroleum derivatives, production and consumption of bioplastics is considered to be more sustainable. However, the issue that needs to be addressed is that petroleum is still used as an energy and materials source for the manufacturing of bioplastics. Compared to the global consumption of all flexible packaging (estimated at around 12.3 million tons) (NNFCC, 2010), worldwide production capacity for bioplastics is around 0.33 million ton (Plastics News, 2008).

One of the biggest construction activities, especially in developing countries, is building of roads and highways. *Bioasphalt* is an alternative type of asphalt, derived from non-petroleum based renewables, such as vegetable oil based waste, sugar, molasses and rice, and corn and potato starches. An asphalt that uses vegetable oil based binders as a source was patented in France in 2004 (Djumari *et al.*, 2017).

Renewable Energy

Renewable energy, as the name implies, is energy provided through renewable resources, which are naturally replenished at the rate at which they are being consumed. Its various forms are sunlight, wind, rain, tides, waves, geothermal heat, and biomass. Renewable energy may either replace or augment energy generated from fossil fuels, such as electricity generation, water heating, automobile fuels, etc (EIA, 2019a).

There are three main types of energy resources: fossil fuels, nuclear power, and renewable energies (Demirbas, 2000). Renewable energy is very attractive for three fundamental reasons. First, it is renewable; sources such as solar energy, wind energy, geothermal energy, marine energy, biomass energy, biofuels, and others can be used to produce energy over and over again (Rathore and Panwar, 1996). Second, these sources are capable of providing energy that is free of air pollutants and greenhouse gasses (Panwar *et al.*, 2011). Third, if developed properly, these technologies can harvest energy in a reliable, affordable, and environmentally sustainable way, especially in rural and small-scale energy sectors (Ravindranath and Hall, 1995). Various renewable energy technologies are already being used, while others are at various stages of development. Hussain *et al.* (2017) have discussed the state of the art for some emerging renewable energy technologies.

Biomass refers to biological material from living organisms, and is mostly plants or plant-derived materials. Sustainable harvesting and use of these renewable sources can reduce air pollution, soil contamination, habitat damage, and degradation of cultivable land (EIA, 2019b). There are six different sources of biomass energy: trash, wood, plants, waste, landfill gases, and alcohol based fuels. Biomass-based energy has been harnessed by humans for a very long time, such as burning of wood and wood-derived coal. Even today, wood is the largest source of biomass energy. Though a significant alternative for fossil energy, this low-tech use of biomass (contributing for more than 10% of world energy requirement) also causes indoor air pollution in developing nations, leading to a staggering 1.5–2.0 million deaths annually (Cheng, 2018).

Biofuels derive their energy from biological carbon fixation. These include fuels derived from biomass conversion, and also solid biomass, liquid fuels, and different types of biogases. For instance, in Brazil, bioethanol made from sugarcane is available in gas stations all over the country, in addition to regular gasoline. Bioethanol is a type of alcohol that is produced through the process of fermentation, using carbohydrates produced in sugar or starch crops such as corn, sugarcane, or switchgrass (Agarwal *et al.*, 2017).

Biodiesel is another biofuel, derived from vegetable oils and animal fats through the mechanism of transesterification. It is the most common biofuel used in Europe. When methane is produced by anaerobic digestion of organic material by anaerobes, the product is biogas. Typically, biogas refers to a mixture of gases that are produced when organic matter is broken down in the absence of oxygen. Apart from anaerobic digestion, the process can also be fermentation of biodegradable resources like manure, sewage, municipal waste, green waste, plant material, and crops. It is mostly methane and carbon dioxide, and may contain small amounts of hydrogen sulfide, moisture, and siloxanes (Knothe and Razon, 2017).

The other side of the coin should not be ignored. Rain forests are home to many species and organisms that are a source of food and other commodities for humans. From this viewpoint, biofuels may not be sustainable if their production causes deforestation.

Threats to Renewable Resources

Industrial development and technological growth, when not regulated in an eco-conscious manner, endangers all renewable resources. There must be a carefully thought out management system in place to avoid exceeding nature's capacity to replenish these sources. Life cycle assessment, at local and global levels, can provide a systematic method of evaluating renewability. World sustainability is intrinsically linked to renewability of natural resources and the environment (Mansson, 2016).

Sustainability mismanagement can take various forms. One is overfishing. National Geographic describes ocean over-fishing as "simply the taking of wildlife from the sea at rates too high for fished species to replace themselves" (National Geographic, 2013). Recently, cod stocks were severely overfished in the Atlantic, leading to abrupt collapse of cod population (Hui, 2006). Demand for tuna meat is increasing its overfishing, and endangering species such as bluefin tuna. Indirectly, overfishing is also resulting in the decline of penguin population, as humans and penguins compete over the same renewable resource (Science Daily, 2010). European Community and other world organizations are trying to bring in fishery regulations in order to protect certain species and prevent their extinction. The UN convention on the Law of the Sea treaty describes various aspects of overfishing (Council Regulation, 2002; UNC, 2012).

Another major threat to sustainability is deforestation. Forests are a major source of fuel and building material. Also, trees protect the environment by producing oxygen and by absorbing carbon dioxide (Mumoki, 2012). Destruction of rain forests (as in portions of Brazil) is a major root cause of climate change. Because of deforestation, CO₂ lingers in the atmosphere, and this accumulation forms a layer in the atmosphere that traps solar radiations. This trapped radiation generates heat, causing global warming. This is commonly known as the greenhouse effect (UNSG, 2001). Deforestation also disrupts the water cycle, decreasing the water content in soil, groundwater, and atmospheric moisture. Also, deforestation is a cause of reduction in soil cohesion, paving the way for soil erosion, flooding, and landslides (Rogge, 2012).

Sustainable Recycling

With the protection of natural resources and the earth's environment becoming a driving concern, many technologies have emerged in the last two decades for recycling of pollutants from water, air, and soil, and reprocessing of wastes (Corder *et al.*, 2015; Colling *et al.*, 2016). Meric *et al.* (2018) discuss various new environmental programs and projects that have been developed, both at national and international levels. These new projects and research studies have one common aim: sustainable technologies for recycling and reuse of various resources. Some of the more prominent ones are techniques for energy recovery from the organic portion of municipal solid wastes (Cesaro *et al.*, 2016), from food wastes (Karmee, 2016), from sludge left after wastewater treatment (Batstone *et al.*, 2015; Colmenar-Santos *et al.*, 2016), reclaiming of compost from solid waste organics (Cesaro *et al.*, 2015), and production of fertilizers from wastewater (Hukari *et al.*, 2016; Puchongkawarin *et al.*, 2015; Shepherd *et al.*, 2016). A few advanced treatment technologies based on the use of membranes have been developed and applied for recycling of urban (Bunani *et al.*, 2013) and industrial wastewaters (Zheng *et al.*, 2015).

Recycling of industrial wastes is another major avenue, either to be reused, or for manufacturing of new products. Some of these new technologies include recycling processes for automobiles (Li *et al.*, 2016), for rejected dry batteries (Lin and Chiu, 2015), for electronic wastes (Awasthi *et al.*, 2016), for waste automotive laminated glass through valorization of polyvinyl butyral (Swain *et al.*, 2015), for blast furnace sludge (Drobikova *et al.*, 2016), and for waste aggregates in concrete used for road pavement (Pasetto and Baldo, 2016). Though valorization of renewable energy sources is a ground-breaking technology in the recycling and reuse domain (Byrnes *et al.*, 2016; Sahoo, 2016), some researchers are of the opinion that is not totally green (Keramitsoglou *et al.*, 2016), and that it can cause negative environmental impact (Sokka *et al.*, 2016).

Renewable Technologies: Present and Future

With the passage of time, renewable energies are becoming more reliable and economically competitive in comparison with conventional energy sources. Until 2012, renewable energy formed about 19% of world energy consumption, but this share increased to 23.7% in 2014 (REN21, 2016). Some of the mainstream renewable energy methods currently in practice are hydropower, wind energy, solar energy, biomass energy, biofuels, and geothermal energy. Hussain *et al.* (2017) have reviewed and analyzed five state of the art renewable energy sources. These emerging technologies are either variants of the typically known energy sources (solar, wind, geothermal, biofuels, biomass, and hydro), or totally new processes. These include marine energy, concentrated solar photovoltaics (CSP), enhanced geothermal energy (EGE), cellulosic ethanol, and artificial photosynthesis (AP).

Marine/Ocean Energy

Marine energy, also known as *ocean energy*, is a highly attractive renewable energy resource. Sub-categories include wave power (wave energy), tidal power, tidal currents, salinity gradients, and temperature gradients. The source is almost infinite, three-quarters of our planet being oceans. Just wave energy has a potential comparable to the sum of nuclear and hydropower (Vining and Muetze, 2009). However, technological challenges have restricted the contribution of marine energy to only a minute proportion of global energy supply (Pelc and Fujita, 2002). For acceleration of marine energy initiatives, various regional governments have announced policies and incentives (Lewis *et al.*, 2011). According to a report published in 2015 by the executive committee of Ocean Energy Systems (OES), tidal power tops the list, followed by tidal currents, and then salinity gradient, as regards installed capacity. Only three countries agreed to the initial OES implementation agreement in 2011, while member countries were 23 by December 2015 (OES, 2014).

Wind that blows across the ocean is the main source of marine *wave energy* (Lewis *et al.*, 2011). Waves can transfer energy efficiently, and can travel long distances with few losses. Some ocean waves even gain energy through wind as they travel across open stretches (Clement and Cullen, 2002). Specialized converters can transform this wave energy into electricity. One major advantage of this form of marine energy is its spatial concentration in comparison with other sources of renewable energy (Titah-Benbouzid and Benbouzid, 2014).

Geographically, the United Kingdom possesses maximum potential for wave energy. Wave energy extraction techniques (WEET) can be classified in terms of location and power take-off (Titah-Benbouzid and Benbouzid, 2014). On the basis of location, WEETs can be divided into onshore, offshore, and near-shore categories. Categories based on power take-off are point absorber, attenuator, oscillating water column, oscillating wave surge converter, submerged pressure differential, and overlapping device, (Titah-Benbouzid and Benbouzid, 2014).

Tidal energy is generated due to the rise and fall of ocean waves, which is a result of rotational and gravitational forces between the earth, sun, and moon. Pattern of tidal currents is regular and predictable (IREA, 2014a). Size and timing of the tides is dependent upon geographical location, shape of the ocean bed, coriolis acceleration, and shape of the shoreline (Lewis *et al.*, 2011). Working principle of tidal power plants is not very different from hydal power plants. However, instead of flowing downhill, the wave masses move back and forth in sync with the tidal flow (Bryden *et al.*, 2006). The hydrokinetic turbines used for extraction of tidal energy can be of different categories: vertical axis turbines, horizontal axis turbines, venture effect turbines, or oscillating hydrofoils. Improvement in these technologies are being considered through the use of gears to allow different rotation speeds for the generator and the turbine, or by increasing the output by better employing the variable frequency generation (Lewis *et al.*, 2011).

Apart from near-shore tidal currents, other significant currents also flow in the oceans, known as ocean currents (Lewis *et al.*, 2011). These ocean currents are slower in rate, but are more consistent as compared to tidal currents. Also, ocean currents are unidirectional, while tidal currents can change direction in line with flood and ebb cycles (IREA, 2014a). Though basic principle of energy capture is the same, some of the infrastructure required for energy from ocean currents is different from tidal current energy extraction (Lewis *et al.*, 2011). Tidal current generators need to operate in both directions, while open-ocean turbines do not require this feature.

Energy derived from the concentration difference between two saline solutions is called *salinity gradient* power. The two possible energy extraction mechanisms are *stand-alone* (plant is located at the river-sea intersection) and *hybrid*. Hybrid processes work in tandem with a desalination or a wastewater treatment system (Scramesto *et al.*, 2009). Harnessing of energy in salinity gradient can be through pressure-retarded osmosis, reversed electro dialysis (RED), or other technologies, using the chemical potential between fresh (river) water and seawater. Also called osmotic power, this potential is captured as a pressure across a semi-permeable membrane (Lewis *et al.*, 2011). As with other osmosis-based technologies, the major issue is cost-effectiveness.

This chemical potential based process, known as pressure-retarded osmosis (PRO) or *osmotic power*, was developed in the 1970s (Loeb and Norman, 1975). In PRO, the salinity difference is between seawater and freshwater. The first prototype osmotic power plant went into operation at Tofte, near Oslo in Norway in 2009 (Van den Ende and Groeman, 2007). An alternate series of cation and anion exchange brings into contact the concentrated salt and freshwater. The reversed electro dialysis process generates electrical voltage across each membrane, utilizing the chemical potential difference (Loeb and Norman, 1975).

Ocean thermal energy conversion (OTEC) depends on solar energy. Due to sunlight falling on the seas, thermal energy is absorbed and stored in the upper layer. Energy is extracted through the OTEC cycle by using the temperature difference between the warm seawater at the ocean surface and the deeper (800–1000 m depth) cold seawater (Kim *et al.*, 2009). Warm seawater is used to produce vapors to drive a turbine, while cold water is used for condensation of vapors, ensuring that there is enough vapor pressure difference to drive the turbine (Yuan *et al.*, 2014). The three types of techniques of energy extraction in OTEC plants are open-cycle, closed-cycle, and hybrid-cycle (IREA, 2014b). In the open cycle, seawater is the working fluid, while it is ammonia, chlorofluorocarbon (CFC), or propane in closed cycle OTEC. Hybrid conversion, as the name implies, is a combination of open and closed cycle schemes (Lewis *et al.*, 2011). Theoretically, OTEC has the highest potential among the different ocean energy sources (IREA, 2014b). For a commercial-scale OTEC power plant to be operational, a minimum temperature difference of 20°C is required. The most optimal locations for OTECs are small islands, which need both power and fresh water. As with many other renewable energy sources, per unit cost is the main obstacle in making OTEC commercially viable.

Challenges and future prospects

For ocean energy to become a major contributor to world energy, innovative improvements are required in the technical, economic, social, environmental, and infrastructural areas. Overall, technical challenges are related to resources, devices, and array configurations. Among ocean energy extraction methods, ocean thermal energy, salinity gradient, and ocean current techniques are the least mature technologies, so they have the maximum potential for improvement. Having a very low environmental impact, and an almost endless source (oceans), policy makers and utility companies should make dedicated efforts to adopt these technologies. The most significant barrier is of course the high cost, significantly higher compared to other renewable energies (Lewis *et al.*, 2011). On the infrastructural side, the main challenges are related to grid issues and the supply chain, for marine energy to be integrated into wider energy networks.

Though ocean energy has a very high potential as a sustainable power source, there are some negatives as well. Marine life may be harmed or displaced, or the marine habitat may be damaged. The large structures housing marine energy extraction equipment and devices may reduce the size of commercial and passenger shipping channels. There will be a major concern of equipment damage through corrosion, and protection against sea storms may also pose a serious challenge.

Concentrated Solar Power/Photovoltaics

In *concentrated solar power* (CSP) technology, electricity is generated through heat produced by concentrating solar radiation on a small area. A combination of mirrors and/or lenses is used to reflect sunlight into a receiver. A primary circuit (thermal energy carrier) collects the heat, and this heat is used directly or thru a secondary circuit for turbine-based electricity generation (Muller-Steinhagen and Trieb, 2014). CSP systems can be equipped with a heat storage device to generate electricity even when skies are cloudy or after sunset. In comparison with wind and photovoltaics, CSP equipped with thermal storage can deliver a significantly higher capacity factor and dispatchability (Greenpeace, 2016).

A major component is the solar energy collector which absorbs and collects the incident solar radiation, and converts it into heat energy. A heat transfer fluid (HTF) that flows through the collector carries away the heat energy, serving as a link between the collector and the power generation system (Scramesto *et al.*, 2009). Obviously, as strong sunlight is a basic requirement, CSP is limited to hot and dry regions of the earth, including the Middle East, North Africa, South Africa, Australia, western US, and some parts of South America.

The first CSP power plant (with no thermal storage) was constructed in California in the 1984–1991 period (IEA-ETSAP and IRENA, 2013). However, there was no major interest in the technology due to abundance of low-cost fossil-fuel energy. By the year 2000, interest in CSP was revived due to energy shortages. A lot of research and development work has been done since then, focusing on collector types, materials, structures, and a variety of heat transport, storage, and electricity conversion systems

(Lorente *et al.*, 2011; Barlev *et al.*, 2011a,b). Major research effort during the last decade has been on increasing the efficiency of solar-to-electric energy conversion, and on making it economically more viable (Madaeni *et al.*, 2012).

Almost all CSP plants (with or without storage) are equipped with backup systems. Transfer fluids/liquids are heated thru fuel burners using fossil fuels, biogas, or solar energy. Because of these fuel-powered backups, as opposed to dependence on solar energy and thermal storage alone, production capacity of these plants can be maintained at a lower cost (Greenpeace, 2016). With these improvements, on-demand energy can be generated by combining CSP technologies with thermal storage. Integrating these systems with conventional energy sources (hybrid mode) can improve the performance of both.

Due to the declining investment and production costs, many new CSP plants have been constructed and commissioned since 2006 (IRENA, 2012). Currently, Spain is considered to be the largest producer of CSP electricity, while several projects are in the planning or construction phases in the USA and North Africa.

Parabolic trough (PT)

In the PT technology, concentration of sunlight is achieved thru heat receivers located on a focal line with parabolic mirrors. These receivers have a special coating that reduces infrared re-irradiation, thereby increasing the energy absorption. Convection type heat losses are minimized by positioning the receivers in a glass envelope under vacuum. Synthetic oil or molten salt is used as the heat transfer liquid, transporting heat to a steam generator for production of superheated steam which runs the turbine for production of electricity (IEA-ETSAP and IRENA, 2013). Heat from the heated fluid can be stored in a thermal storage system for times when sunlight is not available (Sioshansi and Denholm, 2010; US Department of Energy, 2014). PT plants typically generate 14–80 MW of electricity, and are mostly working in Spain and the US (IEA-ETSAP and IRENA, 2013). Total world capacity of installed PTs is around 850 MW. Some notable drawbacks of PT technology are high thermal losses, need for a good heat transfer medium, and requirement of long pipes to join the array and the steam generating plant.

Linear fresnel reflectors (LFR)

Similar to PT collectors, LFRs consist of a series of long, flat, and somewhat curved mirrors. Positioned at different angles, these mirrors can direct the sunlight to both sides of a fixed receiver, which is located a little above the main mirrors field. A single-axis tracking system, optimally installed at each mirror line, concentrates the sunlight on a fixed receiver. Purpose of a secondary reflector is to refocus any missed rays (IRENA, 2012). A newer version, called compact linear Fresnel reflectors (CLFRs), employs two equivalent receivers for every row of mirrors for minimum land usage, and a parabolic trough produces the required output (RENAC Renewables Academy, 2012).

The three operational LFR plants (to date) have been in production since 2008, and are located in California (USA), New South Wales (Australia), and Murcia (Spain). Capacities range from 1.4 to 5 MW (IEA-ETSAP and IRENA, 2013). Major advantages of this technology include readily available materials, lower manufacturing and installation costs (compared to parabolic troughs), direct generation of steam as water is the heat transfer liquid, possibility of hybrid operations, and lower heat transmission losses. On the undesirable side, performance, investment and operation costs are not commercially proven yet, and solar-to-electric efficiency (8%–10%) is lower than that of PT.

Parabolic dishes (PD)

PD collectors are also called solar dish collectors, wherein solar rays are concentrated at a focal point which is supported above the dish center. The dish and the receiver move in tandem to track the sun (Zhang *et al.*, 2013). The receiver can be a Stirling engine or a microturbine, eliminating the need for a heat transfer liquid and cooling water. This guarantees a larger heat-to-electricity conversion ratio. It is anticipated that commercial-scale production of PDs will make them competitive against larger solar thermal systems (Barlev *et al.*, 2011a,b). A 100 MW plant is being considered in Australia, while a few 10 kW or below projects are under development in Europe and USA.

Current energy cost of dish technologies is almost double of parabolic trough systems, so further technological development is definitely needed. Some key advantages of PD technology are 30% or higher conversion efficiency, no cooling requirement, suitability for remote and stand-alone operations, modular system, not limited to flat terrains, good manufacturability, and possibility of mass production due to the use of off-the-shelf existing parts. Major disadvantages include absence of large-scale commercial plants; lack of commercially proven investments, performance and operation costs; and problems in grid-connection.

Solar towers (ST)

ST technology uses various computer-assisted mirrors (heliostats) to track the sun over two axes, concentrating sunlight onto a single receiver. Mounted on the top of a central tower, the receiver utilizes a thermodynamic cycle driven by heat to produce electricity (IRENA, 2012). ST systems provide higher concentration in comparison with other CSP technologies. Steam, synthetic oil, and molten salts are the main heat transfer fluids. Working temperatures in the 250–1000°C can be reached, with proper combination of receiver design and working fluid.

Two 10 MW ST power plants were constructed in California in the 1980s and 1990s. However, both of them were later decommissioned. In recent years, various projects are under development in Spain, USA, Germany, and Israel. Some notable advantages of ST technology are higher efficiencies due to the potential of generating higher temperatures, more suited for dry cooling than PT, and ease of installation in hilly areas. On the other hand, commercially viable operation and consistent performance have not been proven yet.

Challenges and future prospects

It has been estimated that by 2020, total capacity of CSP could grow up to 30 GW in Europe, 50 GW in North America, 23 GW in Middle East and Africa, and that it could reach 337 GW worldwide by 2030 (US Department of Energy, 2014). For commercial viability and reliability, progress would have to be made on various frontiers. These include storage technologies, power blocks, cooling systems, transmission media for heat and electricity, and cost reduction. Potential areas for improvement in PTs and LFRs are solar field elements, replacement of thick glass sheet by less costly material, lower-cost alternatives for heat transfer liquids, and direct steam generators for PT to obtain higher temperatures (more efficiency). For PD and ST technologies, significant improvements could be made by replacement of water cooling with other mature technologies used in fossil fuels (air cooling, pressurized heat, etc), increasing the heat-to-power conversion ratio.

Enhanced Geothermal Energy

Heat energy that is stored in the earth's crust is known as *geothermal energy*. According to earth scientists, 20% of this energy is from the original formation of planet earth, while 80% comes from radioactive decay of different earth materials (Ziagos *et al.*, 2013). Temperature difference between the earth's core and its surface is called *geothermal gradient*, and is the source of the continuous conduction of heat energy from the core to the surface. Kewen *et al.* (2015) present a comparison between wind, solar, hydro, and geothermal energy, and conclude that geothermal energy has a potential which is equivalent to other major renewable energy technologies.

The conventional method of tapping geothermal energy is to locate the naturally occurring reservoirs of superheated steam and hot water. Tectonic and geological phenomena in that region contribute significantly in the sustainability of these naturally occurring reservoirs. That is why, these earlier geothermal technologies can be utilized only in those regions which are rich in natural reservoirs. A new approach, known as *enhanced geothermal system* (EGS), has been developed to overcome these limitations. Also known as *engineered geothermal energy* (EGE) or *hot dry rock* (HDR) energy, this technique is not dependent on the existence of natural geothermal reservoirs. There are two basic sub-categories of EGS techniques: augmentation of traditional geothermal systems by flooding extra fluid using a hydrothermal system, along with the naturally available ground water; and stimulated creation of enhanced permeability, all the way down to hot dry rock (HDR). Key advantages of EGS in comparison with conventional geothermal techniques are longer lifetime, higher productivity, location and sizing flexibility, increased resources, and various environmental benefits.

Performance of EGS power plants depends on various parameters, including reservoir and geological conditions, well drilling, and well completion. Drilling to a depth where rock temperature is high enough to justify total investments is an important consideration for extraction of geothermal energy. The next step is to develop an EGS reservoir in that region. Garman (2004) outlined five essential steps for the optimal construction an EGS reservoir. These are drilling of an injection well into hot basement rock having limited permeability and fluid content; injection of pressurized water for fracturing or reopening of existing fractures; continuous pumping of water to enlarge fractures and re-opening of previous fractures; drilling of a production well in the stimulated fracture area for water circulation aimed at heat extraction from the hot basement rock; and drilling of additional production wells for thermal energy extraction in large volumes from bigger hot basement rocks. Quality of the extracted geothermal energy is a function of temperature gradient, well depth, and rock porosity.

Some authors have investigated different aspects of enhanced geothermal energy, such as assessment of geothermal resource base, estimation of recoverable EGS, development history and current status of EGS related technologies, problems faced in design of subsurface systems, economic aspects of different drilling technologies (MIT, 2006; Blackwell *et al.*, 2006), concerns regarding EGS energy conversion systems, environmental impact assessment of EGS, and economic analysis and sustainability evaluation of EGS projects (Sanyal and Butler, 2005; Vuatez, 2000; Brown, 2000).

Some of the potential detrimental environmental impacts of geothermal energy projects are gaseous emissions, water pollution, land usage, induced seismicity, amount of water usage, stimulated landslides, small earthquakes, etc. Even then, geothermal energy poses much lower environmental hazards in comparison with conventional fossil-fuel and nuclear power units (MIT, 2006).

Challenges and future prospects

On top of economic viability, evaluation and testing of three critical issues is necessary for EGS power plants. First, a practical demonstration of a commercial scale reservoir that will be required for minimization of temperature decline in the reservoir. Second, sustained production from the reservoir. It has been estimated that fluids flowing at a temperature of 200°C and at a flow rate of 80 kg/s are needed to make the EGS power plant economically viable. However, to date, maximum flow rate actually achieved by EGS systems is only 25 kg/s. Third requirement is proof of repeatability; EGS reservoir performance needs to be replicated (Blackwell *et al.*, 2006). Continued judicious R&D investment is needed to make EGS an actual major contributor in pollution-free renewable energy provider.

Cellulosic Ethanol

Ethanol is a type of alcohol and is derived from different plant materials. Ethanol is now being used as an alternate liquid fuel in motor vehicles. The two major agricultural sources for ethanol production are sugarcane and corn starch. As both of these raw

materials are edible, there is a competition between human consumption and fuel production. Emerging non-conventional methods of producing ethanol use wood, grass, or other inedible plant parts as raw material. These new technologies utilize plant cellulose to make ethanol, thus the name *cellulosic ethanol* (Granda *et al.*, 2007). A group of researchers at the University of California at Berkeley has estimated that cellulosic ethanol has the remarkable potential of reducing the emission of greenhouse gasses by 90%, compared to conventional petroleum-based gasoline (Farrell and Plevin, 2006). Another analysis indicates that certain types of cellulosic ethanol are carbon negative, meaning that over the full process life cycle, more CO₂ can be removed from the atmosphere than the CO₂ being emitted into the air. Any technique that can reduce the carbon imprint is of course very environment-friendly and will help long-term sustainability.

Oil, sugar, and starch are first-generation *biofuels*, and it is easy to convert them to ethanol, diesel, or butanol thru conventional techniques. Cellulosic ethanol is a second-generation biofuel, produced from lingo-cellulosic biomasses. Conversion process of second generation biofuels is somewhat more complex. Third-generation biofuels, also known as drop-in fuels, are comparable to petroleum in composition and fuel value, and can be derived from different sustainable sources (cellulose, municipal waste, algae).

Two methods having higher potential for extraction of cellulosic ethanol are *cellulolysis* and *gasification*. Commercial-scale production of ethanol from cellulose has not been achieved yet, but it is considered to be the next generation of renewable energy because of its potential (IEA, 2006; Mabee *et al.*, 2004; US Department of Energy Biomass Program, 2013). There are four major sources of cellulose feedstock: wood residue from the wood industry, saw and paper mills, and furniture market; agricultural waste that comes from straw residues, corn stover, husks, and bagasse; dedicated energy crops, including herbaceous, woody crops, and tall grasses; and municipal solid wastes, which come in the form of paper and other cellulosic material (Nwakaire *et al.*, 2013).

Cellulolysis

The process of *cellulolysis* uses a biological approach. First, size reduction of the biomass takes place. This compaction increases efficiency of the conversion process, and makes it easy to handle. It may consist of grinding of agricultural products, or chipping of wood to achieve size uniformity. Next is the process of pre-treatment, during which the hemicellulose fraction from the biomass is broken down into simple sugars. Then comes the process of hydrolysis (also known as saccharification), where the remaining cellulose is hydrolyzed into glucose. During the next stage of fermentation, glucose is converted into ethanol. After fermentation of glucose and pentose, ethanol is separated from other components. The final step of dehydration is needed to remove residual water from the ethanol. Electricity required for ethanol production can be generated from lignin and other by-products, which are naturally produced during the biomass-to-ethanol conversion.

Gasification

Gasification is based on a thermochemical approach. Rather than breaking cellulose into sugar molecules, the process converts carbon in the raw material to a synthetic gas, using partial combustion. A particular kind of fermenter is then mixed with the produced CO₂, CO, and hydrogen. A microorganism other than bacteria is used for this fermentation. This microorganism ingests the produced gasses, forming ethanol and water. During the final phase of desalination, the produced ethanol is separated from water. New microorganisms are being tested for efficiency enhancement of the conversion process.

Various studies have been conducted for cost estimation of producing ethanol from cellulosic materials. Most of these cost estimates (Von Sivers and Zacchi, 1996; Lynd, 1996) are based on laboratory scale models. Capital cost assessment depends on factors such as raw material cost, cost of hydrolysis, and initial processing costs. This makes the total process cost highly dependent on local conditions and prices (Hahn-Hägerdal *et al.*, 2006).

The US congress enacted the renewable fuel standard in 2005 as a part of US energy policy, and amended it in 2007. Trying to reduce the dependence on fossil fuels, and to encourage the shift towards biofuels, a target was stipulated that by 2022 the volume of cellulosic biofuels should reach 16 billion gallons. This will be on top of 15 billion gallons of conventional corn-based ethanol (Kim and Kim, 2014).

Challenges and future prospects

Support for cellulosic ethanol and other advanced biofuels can be increased by mandating their use at state/provincial and country levels. Major challenges to make cellulosic ethanol widely available and viable are construction of commercial level plants, and various technical issues at the process level (Hahn-Hägerdal *et al.*, 2006). One issue is improving the process of enzymatic hydrolysis. This includes development of efficient enzymes, reduction in enzyme production cost, and devising novel technologies to handle high levels of biosolids. Another challenge is creation of more robust fermenting organisms. These advanced microbes should be more resistant to inhibitors, able to ferment all types of sugars in the raw material, able to work in tandem with concentrated hydrolysis, and should produce high ethanol concentration. One issue is the reduction in the number of process steps through higher levels of process integration.

Though cellulosic ethanol is a high-potential sustainable energy source with various advantages, there are some downsides as well. This fuel is more corrosive and it has the tendency of absorbing moisture from the atmosphere. Contamination can be an issue, making it difficult to ship the fuel through conventional pipelines. Automobile engines would need to be modified, as this biofuel is incompatible with majority of the components in existing auto engines.

Artificial Photosynthesis (AP)

Photosynthesis is a daily occurring natural process, through which plant leaves, green algae, and some other organisms (such as cyanobacteria) convert sunlight into chemical energy that can be later released and used as an energy source. The converted chemical energy is stored in the form of carbohydrates such as sugars, synthesized from carbon dioxide and water. The stored water and CO₂ are then converted into fuel and oxygen gas. This internal fuel is used by the organisms, and the oxygen gas is released into the atmosphere as a byproduct.

The name *artificial photosynthesis* clearly hints at an attempt to biomimic the unique natural photosynthesis process (De Vriend and Purchase, 2013; American Society for Microbiology, 2013). The target, obviously, is to store energy from sunlight in high-energy chemical bonds of a fuel (a solar fuel) (Crabtree *et al.*, 2004), and then decompose water into hydrogen and oxygen efficiently (Liu *et al.*, 2013). Hydrogen is a good energy carrier and can be easily converted to electrical power. This power generation process is environment-friendly, and does not give out harmful byproducts (Kim *et al.*, 2015). In a nutshell, artificial photosynthesis is the process of obtaining energy from sunlight and water. Photocatalytic water splitting separates out hydrogen and oxygen from water. Light-driven CO₂ reduction is another process being attempted to imitate the process of natural carbon fixation.

Research is ongoing in various related areas: design and construction of devices for direct production of solar fuels, photo-electrochemistry and its application in fuel cells, and the engineering of enzymes and photoautotrophic microorganisms for microbial biofuel and biohydrogen production from sunlight. Some of the unique components and devices used in the engineering of artificial photosynthesis and water splitting units include semiconductor particles, electrolyzers, artificial leaf (a solar water-splitting cell), dye-sensitized solar cells, etc (Esswein *et al.*, 2011; Lee *et al.*, 2013).

Challenges and future prospects

Artificial photosynthesis (AP) has a lot of promise as a sustainable energy source, with the possibility of efficiently producing solar fuels. Currently, the main hurdles are the catalytic steps needed for oxidation of water and production of fuels. It is anticipated that small-scale demonstration level systems will be launched within the next ten years (Cogdel *et al.*, 2010). The major driving force in AP research is rapid developments in the area of nanomaterials and nanotechnology, with possible contributions in light capturing, transportation of electrons, water splitting, and hydrogen storage (Nam, 2010). Metals such as hematite, cobalt, and manganese are competing in the production of inexpensive electrodes. Another research stream involves the production of methanol and increasing the capability of the AP system in using hydrogen generated from water splitting and atmospheric CO₂ to store in the form of formic acid (Hull, 2012).

As of now, some laboratory-scale prototypes have been made, using sunlight to split water and produce hydrogen. However, long-term stability has not been proven yet. Which process will come out as the most commercially viable one in terms of efficiency, durability, and cost, is yet to be seen. AP is a high-potential emerging renewable energy source, but this technology has its own drawbacks. There are various safety concerns related to hydrogen storage and transportation, especially because of the low energy density of hydrogen gas. Moreover, the materials used in the AP process get easily corroded in water and cause stability issues (Hull, 2012).

Conclusions

This article discusses the current status and future prospects related to the three interconnected and intertwined issues of renewability, recycling, and sustainability. The three topics are first defined and discussed, briefly touching upon their connectivity. The famous 3R drive of 'reduce, reuse, recycle' is then introduced, later adding 4R and 6R strategies. Renewable practices that can be sustainable are described. Renewable materials are explored, including cutting-edge ones such as rapidly renewable and biorenewable materials, and the more promising class of bioplastics. Renewable energies are described, the more prominent ones being biomass, biofuel, and biodiesel. Major threats to renewable resources are discussed, followed by sustainable recycling practices. In the end, current developments, associated problems, and future outlook of some emerging and state-of-the-art renewable technologies are presented. This includes marine or ocean energy, concentrated solar power and photovoltaics, enhanced geothermal energy, cellulosic ethanol, and artificial photosynthesis.

See also: Induction Heating in Sustainable Manufacturing and Material Processing Technologies – A State of the Art Literature Review. New Educational Models to Train Engineers and Executives On Eco Friendly Technologies, Products and Sustainability Policies

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100% Renewable Energy by Renewable Materials

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Introduction

Energy use is essential to all economic activities and to human well-being. Lack of access to reliable and affordable modern energy represents a constraint to economic and social development in many parts of the world. In the last three decades, the effects of energy consumption on economic growth have become a topic very significant both at the national and international level.

The energy-growth debate has been discussed extensively in the literature. Recent studies have disaggregated the energy data in order to examine, for instance, how electricity consumption is linked to economic growth. Understandably, the electricity-growth linkage merits attention, since most developing countries rely heavily on electricity. Nevertheless, the empirical findings have largely diverged. Thus, policy recommendations emanating from existing studies are often than not conflicting.

The relationship between energy consumption and economic growth has been an active research area. In paper (Alshehry and Belloumi, 2015) was investigated the dynamic causal relationships between energy consumption, energy price and economic activity in Saudi Arabia based on a demand side approach and results indicated that there exists at least a long-run relationship between energy consumption, energy price, carbon dioxide emissions, and economic growth. A better understanding of the relationship between economic growth, energy consumption, and CO₂ emissions is necessary according to study (Wang *et al.*, 2016). The results in Iyke (2015) were shown that there is a distinct causal flow from electricity consumption to economic growth: both in the short run and in the long run. Energy consumption played an important role in the increase of economic growth but with the consequence of high pollution (Saidi and Hammami, 2015). The influence of renewable energy consumption or its share to the total energy mix to economic growth is positive and statistically significant (Inglesi-Lotz, 2016). A strong relation between energy consumption and economic growth was found in study (Kantar *et al.*, 2016). In the long run, there exists also a bidirectional causality between renewable energy consumption and real gross domestic product (GDP) per capita, which argues that renewable energy is a crucial component for economic growth (Saidi and Mbarek, 2016). Results in investigation Nase (2015) of the causal linkage between the variables pointed that energy consumption (i.e., oil or nuclear) has either a predictive power for economic growth, or a feedback impact between with real GDP growth in all countries. Dynamic impacts of GDP growth, energy consumption and population growth on CO₂ emissions using econometric approaches for Malaysia was investigated in (Sohag *et al.*, 2015). The impact of energy consumption and the CO₂ emissions on economic growth using simultaneous-equation models with panel data for 58 countries over the period 1990–2012 was evaluated in Saidi and Hammami (2015) and the empirical results were shown that energy consumption has a positive impact on economic growth. A bidirectional time-varying causality between energy consumption and CO₂ emissions was shown in (Ajmi *et al.*, 2015; Pao and Tsai, 2011). To evaluate the dynamic behaviors of the energy consumption and CO₂ emissions, a few interdisciplinary studies have been conducted (Volker Krey *et al.*, 2012; Chen *et al.*, 2012; Fang *et al.*, 2015).

In this investigation adaptive neuro-fuzzy inference system (ANFIS) (Jang, 1993) was used to detect the influence of energy consumption from alternative, fossil and combustible renewables on the GDP growth rate prediction.

Methodology

Statistical Data and Study Area

One of the most examined issues in growth literature, recently, is the causal linkages between electricity consumption and economic growth. The modern day climate change, energy crises, rising prices of crude oil, and the ever-growing emission of carbon into the atmosphere have added momentum to the debate. The ability to establish the exact causal pattern between electricity consumption and economic growth is of immense relevance for policy formulation. In this study, we analyze the dynamic causal relationships between energy consumption and economic growth. Table 1 shows inputs and output parameters which were used in this study. The dataset was taken from World Bank database for European Union countries.

ANFIS Methodology

In the process of identification of variables in the ANFIS architectures, the hybrid learning algorithms were applied. The functional signals progress until the 4th layer whereby the hybrid learning algorithm passes. Further, the consequent variables are found by

Table 1 Input and output parameters

<i>Inputs</i>	<i>Parameters description</i>
Input 1	Alternative and nuclear energy (% of total energy use)
Input 2	Fossil fuel energy consumption (% of total)
Input 3	Combustible renewables and waste (% of total energy)
Output	Real GDP growth rate

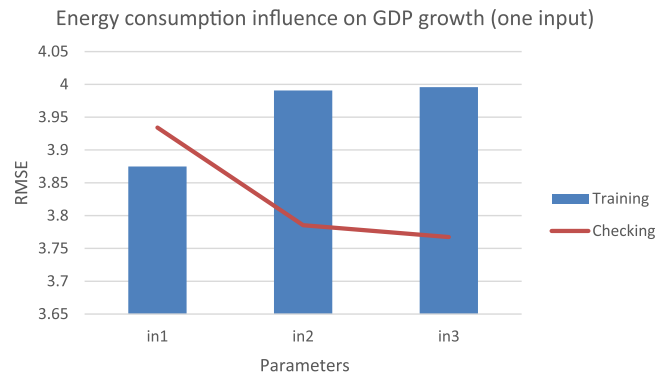


Fig. 1 Parameters influence on GDP prediction for one input.

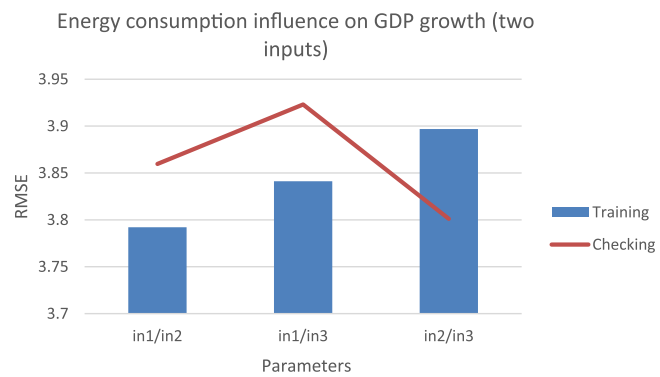


Fig. 2 Parameters influence on GDP prediction for two inputs.

Table 2 Correlation matrix of parameters influence on GDP prediction

	Input 1	Input 2	Input 3
Input 1	trn=3.8748, chk=3.9342	trn=3.7921, chk=3.8596	trn=3.8412, chk=3.9230
Input 2		trn=3.9907, chk=3.7853	trn=3.8968, chk=3.8011
Input 3			trn=3.9958, chk=3.7674

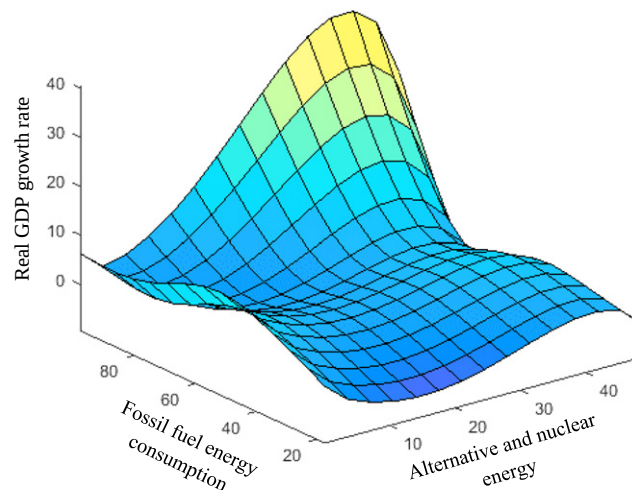


Fig. 3 ANFIS forecasted relationship between alternative and fossil energy consumption and GDP growth rate.

the least squares estimation. In the backward pass, the error rates circulate backwards and the premise variables are synchronized through the gradient decline order.

Results

ANFIS Results

Fig. 1 shows the input 1 (alternative and nuclear energy) has the highest influence on the GDP prediction. Fig. 2 shows the combination of the input 1 and input 2 forms the combination with the highest influence on the GDP prediction. Table 2 shows the correlation matrix of the numerical results for all single parameters and for the two inputs combination influence on the GDP prediction.

Fig. 3 shows the GDP growth rate changing in relation to alternative and fossil energy consumption.

Conclusion

There is a growing literature that examines the relationship between energy consumption and economic growth. The bulk of this literature focuses on developing, developed and emerging countries. It is important for policymakers to understand the relationship between energy consumption and economic growth in order to design effective energy and environmental policies. A general conclusion from these studies is that there is no consensus either on the existence of the relationship or the direction of causality between energy consumption and economic growth in the literature.

In response to growing concerns about energy consumption, numerous energy scenario or computable general equilibrium models have been developed worldwide to provide alerts, mitigation, adaptation, financial and sustainability policy options. However, rigorous evidence-based economic measurement and analysis of the trade-off between energy consumption and economic growth are still limited globally.

Therefore, this study aims at examining the relationship between energy consumption from alternative, fossil and combustible renewables and GDP growth rate prediction in European Union countries. In this study was proposed a new approach to overcome the forecasting difficulties of the growth rate prediction by removing some unnecessary input parameters. The main goal was to analyze the influence of different sectors of energy consumption on the GDP growth rate prediction. Results shown that the energy consumption from alternative and nuclear energy has the highest influence on the GDP growth rate prediction.

See also: Energy Efficiency Analysis in Building Walls in Tropical Climate Using Thermal Insulation System. Optimization of Electrical Energy Usage in Two Secondary Schools Using Different Types of Glass Materials. Sustainable Materials for Energy Conversion

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Reuse of Waste Corrugated With Coir Fibers as a Packaging Material

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Introduction

Coir fiber is a coarse, short fiber naturally obtained from the tissues near the seed of the coconut palm (*Cocos nucifera*). This fiber is the most tough and thick of all natural fibers with low decomposition rate. According to Food and Agricultural Organization (FAO) of the United Nations, coir is one of the future fiber with lots of potential. For instance, this fiber could be used as packaging product such as paper. Typical paper is made of pulps derived from wood. Adding coir fiber with pulp, for example, pulps from waste corrugated, could be a good alternative. However, several mechanical tests should be performed, such as tensile and tear test, so that the mechanical properties of the new composition paper will be at par with current paper product. Certain analysis, such as the behavior of waste corrugated with coir fibers when it is beaten need to be carried out with different formulations. This new composition of paper should be recyclable, degradable and more environmental friendly. There are a number of researches that have been conducted with different composition, analysis, properties and formulation in utilizing coir as packaging material. For instance, [Gurav et al. \(2003\)](#) had studied the mechanical properties of paper-pulp packaging and [Gabriel et al. \(2007\)](#) had removed the ammonia from coir fiber by utilizing gas phase bio-filter and categorized the performance of coir fiber as packaging material. [Monteiro et al. \(2008\)](#) used coir fiber/polyester composites to assess the structural characteristics and mechanical properties, while [Beg and Pickering \(2008\)](#) had utilized beating process to discover their effects towards kraft fiber reinforced polypropylene composites. As an additional information, coir fiber also could be a good sound barrier, as mentioned by [Zulkifli et al. \(2008\)](#) and [Mohd Nor et al. \(2010\)](#). As a wrapped up, a review made by [Sanjay et al. \(2018\)](#) had listed coir as one of potential fibers to be applied for natural fiber-reinforced polymer composites.

Procedure of Paper Making by Using Waste Corrugated/Coir Fiber

Firstly, the waste corrugated and coir fibers need to be cut in small pieces, ranging from 20 to 50 mm. For a weight of 25 grams, 15% of waste corrugated and 85% of coir mixture were prepared for a trial. To produce a mixed pulp, this composition need to be blended for 5 min. Then the mixture was transferred into a container. A deck need to be immersed in this container and then raised up slowly. The screen was shaken for a few minutes to ensure the water had been drained back into the container. After that the screen was flipped on the cotton cloth with a sponge used to squeeze off the water. Slowly the screen was pulled off and finally the sheet of paper was completely prepared. The prepared mixture was dried within the environment temperature for 8 h, and then pressed using a padding machine with 3 kg/cm² of pressure to make sure that all papers have the equivalent thickness.

Mechanical Treatment and Properties of Paper

According to [Casey \(1952\)](#), to make a paper the cellulose fibers need to be treated mechanically. The treatment, such as bruising, rubbing, crushing, refining and beating are essential in the paper making process. Beating time process is the most important treatment, because it will increase the density and strength of the fibers. Therefore, mechanical test such as bursting strength, tensile strength and folding endurance will produce good results. There was a drawback such as decreasing tearing resistance but it will increase smoothness, hardness and amount of bonding fibers.

Common mechanical properties of papers generally measured through tensile and tear strength. Based on [Peperonweb.com](#), tensile and tear relationship was inversely proportional to each other. A paper formed at maximum tear value will be low in tensile strength and the paper with a maximum tensile strength, will be low in tear. The flow of mechanical test was displayed in [Fig. 1](#).

The objective of tensile and tear test towards corrugated waste/coir fibers were to obtain a quality paper with the maximum percentage of coir and minimum beating time. As mentioned before, the mixture of 85% of coir fibers and 15% of corrugated waste was used as a trial. As a pre assumption, higher percentage of coir fiber will produce more lignin, which could weaken the paper's structure. Hence, the increased percentage of waste corrugated could improve the structure of the paper. So it is important to find the optimum formulation. [Table 1](#) shows the result for mechanical test by using 85% of coir fibers as the main raw material. With referred to [Table 1](#), the maximum load that the 85% of coir fibers/15% waste corrugated paper could withstand was 163.47 N for tensile load. As for tear test, the maximum number was 26.95 N. As for extension results, the value of tensile and tear test are 1.95 mm and 1.87 mm respectively. Based on these values, it can be summarized that at the composition is performing their duty as a good paper, and the development of these mixtures as a packaging material product have a potential to be explored.

[Table 2](#) shows the physical properties measurement of sample with 85% of coir fibers/15% waste. The thickness of samples depends on time for pulps were beaten. Then, the weight and area of the sample were measured. After that, the grammage of the sample was calculated, which was approximately between 177 and 178 g/m². These values were significant by comparing with the paperboard's grammage, which is between 120 g/m² to 300 g/m², with +/− 5% of trade tolerance. Hence, this waste corrugated coir fiber can be considered as paperboard.

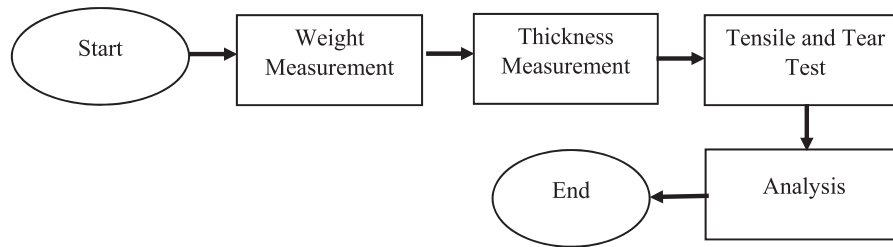


Fig. 1 The flow of mechanical test for paper.

Table 1 The mechanical experiment results for 85% of coir fibers/15% waste corrugated

Test number	Results
Maximum load on tensile test (N)	163.47
Maximum load on tear test (N)	26.95
Extension of tensile test (mm)	1.95
Extension of tear test (mm)	1.87

Note: Othman, M.H., Main, N.M., Mon, S.Z.K., Mohamad, Z., 2013. Development of paper using coir fibers as a packaging product. Asian Journal of Scientific Research 6 (2), 207–216.

Table 2 The physical properties measurement of sample with 85% of coir fibers/15% waste

Properties	Measurement values			
Beating time (min)	5	10	15	20
Thickness, mm	0.980	0.910	0.850	0.920
Weight, g	10.84	10.85	10.83	10.84
Area, m ²	0.061	0.061	0.061	0.061
Grammage, g/m ²	178.00	177.86	177.54	177.70

Note: Othman, M.H., Main, N.M., Mon, S.Z.K., Mohamad, Z., 2013. Development of paper using coir fibers as a packaging product. Asian Journal of Scientific Research 6 (2), 207–216.

Table 3 The preliminary experiment observation

Mixture percentage	Observation
25% coir fibers and 65% waste corrugated	Smooth surface. Nearly same as a normal paper. Gray in color. Easy to beat and blended. Run lightly and noise produced was normal.
45% coir fibers and 55% waste corrugated	Gross surface. Physical color was balance between gray and brown. Hard to beat the raw materials and make noise.
65% coir fibers and 35% waste corrugated.	Rough surface. Brown in color. Hard to blended. Run heavily and lot of noise.

Note: Othman, M.H., Main, N.M., Mon, S.Z.K., Mohamad, Z., 2013. Development of paper using coir fibers as a packaging product. Asian Journal of Scientific Research 6 (2), 207–216.

Table 3 shows the general physical observation when the process of beating was done for another composition of fibers to develop the papers, which were 25% fibers + 65% waste corrugated, 45% coir fibers + 55% waste corrugated and 65% coir fibers + 35% waste corrugated. These samples were prepared to cross-machine direction fiber orientation. Based on the observation, if more coir fiber added in the composition, the paper surface will become rougher and less smooth. Difficulties happened when heavy beating process involved (hard to blend) and causing lots of noise during the process. Papers with more corrugated waste were better in the sense of smooth surface and easy processing.

Fig. 2 shows the orientation of fibers and colors based on coir fiber/waste corrugated percentage. As for 25% of coir fiber samples, the color was gray. When the coir fiber increased to 45%, the color balanced up between gray and brown. At 65% of coir percentage, the color of paper produced was brown. Based on Food and Agricultural Organization (FAO), if the coir was cured in a



Fig. 2 Orientation of fibers and colors based on coir fiber/waste corrugated percentage. Reproduced from Othman, M.H., Main, N.M., Mon, S.Z. K., Mohamad, Z., 2013. Development of paper using coir fibers as a packaging product. *Asian Journal of Scientific Research* 6 (2), 207–216.

brine a longer period of time, the fiber's color will become whiter. Better fiber color and orientation could be produced by using technology such as coconut husk defibering machines. White coir could be manufactured into ropes or fishing nets. However, more robust product could be made from brown coir such as doormat, rugs, and panels for insulation

The most significant findings was the composition of raw materials could be utilized according to their function and economical factor. For example, higher quality of paper could use the treatment for 25% of coir mixed with 75% of waste corrugated with 20 min of beating time. This combination was selected for easier manufacturing process, with desired tensile strength and tear strength. As for the further research, some reference might be useful to mark coir/wasted corrugated paper as a commercially viable, not petroleum dependent and sustainable solution packaging product in future. For instance, other techniques to analyze the findings by Fällström *et al.* (2000). They have established some results that indicated the bending waves were influenced by mechanical properties such as density, thickness, bending stiffness, anisotropy and also by tensile forces in the paper.

See also: Bamboo Fiber as Fillers for Polypropylene-Nanoclay via Injection Molding. Design and Performance Analysis of Small-Scale Parabolic Trough Solar Collectors Using Sustainable Materials. Recycled Clothes With Polypropylene-Nanoclay for Industrial Product via Injection Molding. Scaling Up and Intensifying Stakeholders Engagement for Evidence-Based Policymaking: Lessons Learned

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A Review on Utilization of Electronic Waste Plastics for Use Within Asphaltic Concrete Materials: Development, Opportunities and Challenges for Successful Implementation

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Background

Modification of asphalt binder is not a new concept and has been widely employed to enhance the performance of asphalt mixture, and decrease the problems that are associated with bitumen (Airey, 2002). The mechanical properties of modified asphalt are dependent on the polymer content and the type of polymer used (Ghorbel *et al.*, 2008; Isikyakar and Sengoz, 2008; Lu and Isacsson, 1997). With the addition of polymers, many properties can be improved across the entire temperature spectrum (Kalantar *et al.*, 2012a). Two types of polymers are typically used in the modification of asphalt, namely elastomer and plastomer (Aksoy *et al.*, 2012).

Electronic waste (e-waste) incorporates electronic equipment and products consisting of discarded personal computers, monitors, hard drives, copiers, facsimile machines, cellular phones, and televisions. Processing e-waste materials yields valuable raw materials, but this value is offset by the fact that e-waste generally contains hazardous materials (Khan *et al.*, 2007). E-waste contains potentially hazardous materials along with valuable recyclables (Nagurney and Toyasaki, 2005). E-waste also poses additional recycling challenges, namely its slow decomposition rate and its relatively short life span due to changing or upgraded technology demands. Electronic waste plastics compose approximately 23.3% of the mass of disposed computers (Robinson, 2009). The biodegradation process of e-waste materials can last from 450 years to an indefinite period of time for materials such as glass (Santos *et al.*, 2010). Within the United States, there was an estimated 1.5 billion lbs. of e-waste generated, as of 2006, with only 10% of that amount was actually recycled (Khan *et al.*, 2007). Projections of e-waste estimate that 3 billion tons of consumer electronics will eventually end up as e-waste in the United States (Dawson and Landry, 2004). Fig. 1 shows several stages for the successful implementation of e-waste plastics within bituminous materials.

A driving force behind the concern for the disposal of e-waste is the rapid growth of computer technology and the subsequent amount of obsolete computer technology; it's projected that nearly 1 billion computers are obsolete (Ladou and Lovegrove, 2008). Legislation has been introduced to limit the quantity of e-waste placed within state and local landfill sites due to the potential environmental impact which e-waste could pose to the environment (Dawson and Landry, 2004). Specifically, national and international laws are now only addressing the need to significantly limit and reduce e-waste flowing into limited landfill space (Nagurney and Toyasaki, 2005). New research efforts with various potential applications should be developed and address environmental hazards which e-wastes may pose to society; due to the increasing worldwide production e-waste, and the subsequent legislation limiting the location and quantity of e-waste.

The quantity of e-waste plastics is becoming problematic for the waste management and plastics industry. The sheer amount of e-waste plastics has made disposal difficult and increased the urgency for profitable applications for waste electronic plastics. It is imperative to identify applications where e-waste plastics can be used in a sustainable manner. This paper is intended to be used as an initial effort to identify applications of e-waste plastics within the asphalt industry and highlight its benefits. Potential pitfalls which practitioners and researchers may encounter when using e-waste plastics are also discussed.

Asphalt Modifications

Bitumen has been used for many years as a road paving material as well as other uses. Temperature sensitivity of asphalt binder causes the most frequent deteriorations of road pavement such as rutting, fatigue cracking, and thermal cracking (Kebritchi *et al.*, 2011; García-Morales *et al.*, 2006; Ig, 1999). In asphalt mixture, bitumen acts as an adhesive, which bonds the aggregates together. Loss of bonding influences the performance, it is not only affects the resistance to moisture damage of asphalt mixture, but also the issue of poor temperature susceptibility (Zhang *et al.*, 2012). Asphalt mixture strength is attributed by the cohesive resistance of an asphalt binder, adhesive bond between binder, aggregates, and aggregate interlock as well as frictional resistance between aggregates (Curtis, 1990). At the same time, quality aggregates, and binder bonding are also important aspects to consider as the

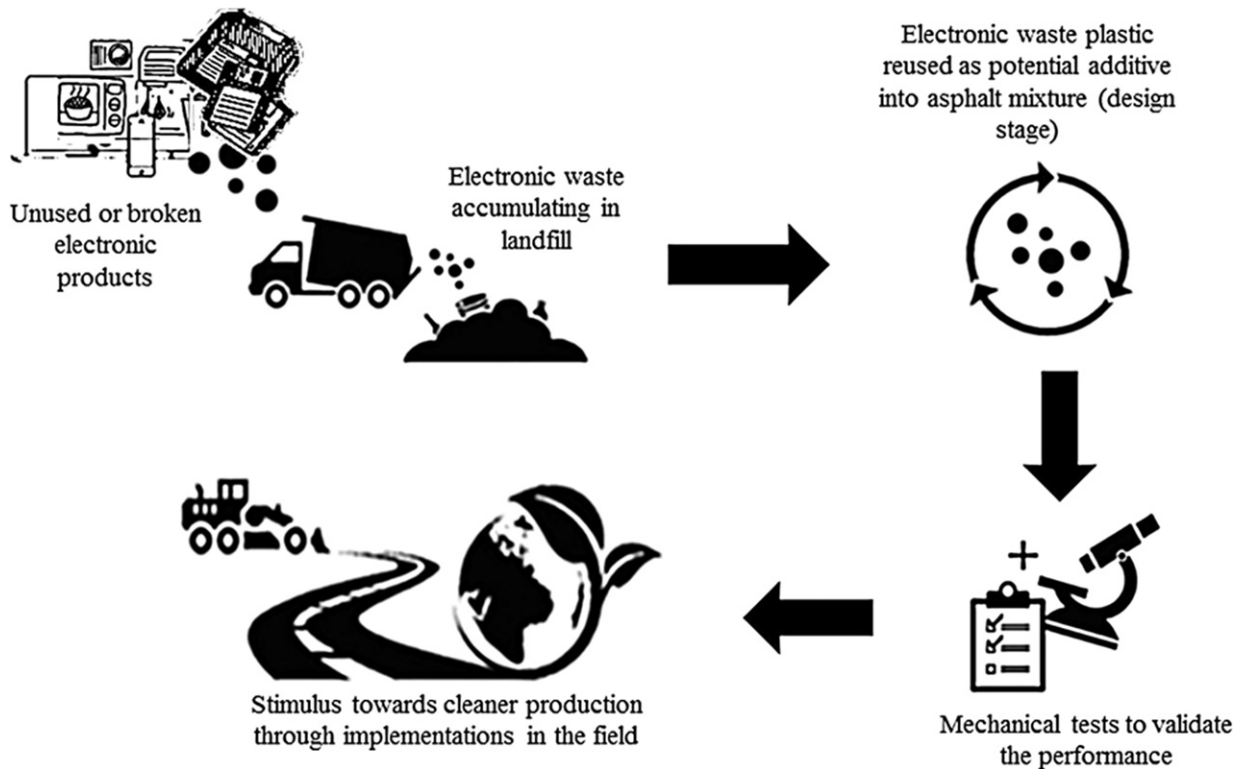


Fig. 1 Applications of e-waste as novel additive in asphalt pavement.

aggregates protects the whole pavement against shear and compression stresses. It also helps to reduce the effect of UV radiation (Estevez, 2009; Dawson *et al.*, 2008; Berdahl *et al.*, 2008; Palmer, 2005). The aggregates connections mainly depend on the cohesive force produced by the binder.

Even though various types of polymers have been used to enhance the performance of asphalt composite, only a few of them are considered as satisfactory based on the performance and economic standpoints (Pinnavaia and Beall, 2000; Jahromi and Khodaii, 2009). You *et al.* (2011) stressed that these challenges became motivation to scientists to reduce the temperature susceptibility at a wide range of temperatures, at the same time maintaining the workability at construction temperatures through asphalt modification.

Applications of Polymer in Asphalt Modification

Various types of polymers have been used to chemically or mechanically improve the properties of asphalt binders, which can be classified into three different categories, elastomer, plastomer and reactive polymers (Brown *et al.*, 2009a; Polacco *et al.*, 2006; Kalantar *et al.*, 2012b). There are different types of rubber (elastomer) materials have been used as asphalt modifiers, such as styrene-butadiene-styrene (SBS) (Alam and Hossain, 2017; Hao *et al.*, 2017), natural rubber (Wen *et al.*, 2017; Al-Mansob *et al.*, 2017), styrene-isoprene-styrene (SIS) (Zhu *et al.*, 2014), polychloroprene latexes as well as grounded waste tires (crumb rubber) (Yang *et al.*, 2017; Zhang *et al.*, 2017; Shirini and Imaninasab, 2016). Meanwhile, the polymers that can be classified as plastic (plastomer) modifiers are polyethylene (Yan *et al.*, 2015), polypropylene (Nekhoroshev *et al.*, 2017), ethyl vinyl acetate (EVA) (Brovelli *et al.*, 2015), poly-vinyl chloride (PVC) (Maharaj and Maharaj, 2015), ethylene propylene (EPDM) (Rahi *et al.*, 2015), epoxy resin (Luo *et al.*, 2017), and poly olefins (Wei *et al.*, 2014). It was found that the rubber modifier is implemented to resist deformation and quick recovery when stress is removed. In contrast, the plastic modifier is exhibited differently by having the asphalt mixture with quick early strength but may fracture under strain (Brown *et al.*, 2009a). According to Polacco *et al.* (2006) the reactive polymers consist of functional group, such as ossiranic ring or succinic anhydride that are capable in forming chemical bonds with asphalt molecules that can be supported by adding on sulfur or mineral acids compound. Table 1 presents some of the major polymers that have been used in studies of polymer modified asphalt.

Elastomers, plastomers, and combinations of the two have properties that can help to remedy different types of asphalt pavement deterioration, such as rutting, moisture damage, as well as fatigue and thermal cracking. Polymer modified asphalt should be produced with a polymer and asphalt that are compatible (Polacco *et al.*, 2005; Jin *et al.*, 2002; Zhang *et al.*, 2009; Polacco *et al.*, 2006). In general, asphalt binders that modified with polymers that have a low compatibility can perform poorly in storage. Additionally, phase separation also might occur, leaving an inhomogeneous material while storing the

Table 1 Common polymers used in polymer modified asphalt

Label/designation	Abbreviation	References
<i>Plastomer</i>		
Ethylene-Vinylacetate	EVA	Airey (2002), Ghorbel <i>et al.</i> (2008), Isikyakar and Sengoz (2008), Fang <i>et al.</i> (2009), Wekumbura <i>et al.</i> (2007), González <i>et al.</i> (2004), Navarro <i>et al.</i> (2009), Upadhyay <i>et al.</i> (2008), Fang <i>et al.</i> (2008c)
High Impact Polystyrene	HIPS	Colbert and You (2012a)
Polyethylene	PE	Fang <i>et al.</i> (2012), Polacco <i>et al.</i> (2005), Punith <i>et al.</i> (2011a), Fang <i>et al.</i> (2008a)
Polypropylene	PP	Al-Hadidy and Yi-qiu (2009a), Giavarini <i>et al.</i> (1996), Yeh <i>et al.</i> (2005)
Polystyrene	PS	Fang <i>et al.</i> (2008c), Jin <i>et al.</i> (2002)
<i>Elastomer</i>		
Acrylonitrile-Butadiene-Styrene	ABS	Colbert and You (2012a), Willard (1998)
Crumb Rubber	CR	Fang <i>et al.</i> (2008a), Amirkhanian <i>et al.</i> (2012), Thodesen <i>et al.</i> (2009)
Natural Rubber	NR	Fernando and Guirguis (1984), Yildirim (2007)
Styrene-Butadiene-Random	SBR	Aksoy <i>et al.</i> (2012), Zhao <i>et al.</i> (2009), Zhang <i>et al.</i> (2009)
Styrene-Butadiene-Styrene	SBS	Isikyakar and Sengoz (2008), Lu and Isacsson (1997), Aksoy <i>et al.</i> (2012), Wekumbura <i>et al.</i> (2007), Navarro <i>et al.</i> (2009), Zhao <i>et al.</i> (2009), Aksoy <i>et al.</i> (2007), Awanti <i>et al.</i> (2008), Chen <i>et al.</i> (2002), Khodaii and Mehrara (2009), Shenoy and Patil (2010), Wu and Han (2009), Zorn <i>et al.</i> (2011)
Styrene-Isoprene-Styrene	SIS	Brown <i>et al.</i> (2009b)

modified binders at high temperatures (Kalantar *et al.*, 2012a; Fang *et al.*, 2009; González *et al.*, 2004; Navarro *et al.*, 2009; Polacco *et al.*, 2005; Jin *et al.*, 2002).

The polymer should be homogeneously dispersed into asphalt to ensure proper adhesion of the asphalt binder. However, incompatibility between the binder and the polymer is sometimes inevitable. As a result, it is difficult to establish and bond, either in terms of a physical or chemical manner (Estevez, 2009; Marzocchi *et al.*, 1981). Prior to gaining a better performance, an application of coupling agent in organic materials or treating inorganic fillers has been used. This enhances the materials cross-linking by means of winding up covalent bonds or molecule chains, thus improving the performance of composites (Hristov and Vlachopoulos, 2007; Liang *et al.*, 2012). It was found that a small amount of coupling agent could increase shear resistance in mechanical properties (Hristov and Vlachopoulos, 2007). There are various types of coupling agents that have been used to improve the bonding of composite materials such as: silane, zirconate, dicarboxylic anhydride, titanates and phosphate ester. However, the most important commercial coupling agents are formed by silane and titanate (Martí-Ferrer *et al.*, 2006).

Application of Plastomers in Asphalt Modification

Plastomer is a type of polymer that typically uses to help remedy problems related to deformation by forming a rigid network to resist distortion (Airey, 2002; Polacco *et al.*, 2005, 2006). In polymer modified asphalt typically the plastomers that are used include polyethylene (PE), polypropylene (PP), ethylene vinyl acetate (EVA), polystyrene (PS), and high impact polystyrene (HIPS). Each form of plastomers has its own level of compatibility with binder, and therefore changes the properties of the binder differently.

Polyethylene (PE) is a plastomer that has a wide range of properties depending on its structure (Polyethylene, 2008). Fang *et al.* (2012) investigated the modification of asphalt with the use of a combination of PE packaging waste and organophilic montmorillonite (MMT), which led to a decrease in penetration and an increase in softening point and ductility. Hence, results in a better resistance to permanent deformation, low temperature cracking, and stability at high temperature. Polacco *et al.* (2005) studied the use of PE based polymers as modifiers for asphalt. It was found that in all cases the PE based polymers did not form a homogeneous structure, however it was found to be stable during storage. Based on a study carried out by Punith *et al.* (2011a) additions of PE has result in a higher asphalt binder viscosity, less susceptibility to damage due to moisture, and an improvement in stripping characteristics. Moreover, Fang *et al.* (2008a) used waste PE as an asphalt modifier, which resulted in an increase in the softening point and ductility.

Polypropylene (PP) has superior performance in stiffness and strength (Khattak *et al.*, 2012). Al-Hadidy and Yi-qiu (2009a) studied the benefits of using polypropylene as a modifier to asphalt. In general, the PP was dissolved completely in the asphalt cement. The addition of PP has resulted in lower penetration, which leads to an improvement in shear resistance and a reduction in temperature susceptibility. A higher PP content indicated a superior resistance of asphalt mixtures to deformation. Giavarini *et al.* (1996) investigated the use of stable polypropylene to modify asphalt. When a poly phosphoric acid treatment was applied there was an increase in softening point and penetration index.

Ethylene-vinyl acetate (EVA) is composed of ethylene and vinyl acetate, which helps to resist deformation with its rigid three-dimensional networks (Brown *et al.*, 2009b). It is used to improve the properties of asphalt binder for pavement applications.

Airey (2002) studied the morphology, thermal properties, and fundamental rheological properties of EVA modified bitumen through a series of test and found that with the addition of EVA to asphalt, there is an improvement in temperature susceptibility and its stiffness. Ghorbel *et al.* (2008) specified that additions of EVA to bitumen have significantly improved the resistance to permanent deformation, softening point and stiffness, with a decrease in the Fraass breaking point and penetration value. González *et al.* (2004) investigated the mixture stability and viscoelastic response of recycled and virgin EVA modified bitumen. The outcome of the study indicated that the addition of EVA has remarkably improved both resistance to thermal cracking and rutting. Zorn *et al.* (2011) also concluded that EVA modified bitumen has improved both behaviors.

Polystyrene (PS) is made up of the monomer styrene that is in solid state at room temperature and will turn to a liquid and eventually will foam when heated (Polystyrene Properties, 2010). PS is ridged and has limited flexibility (Polystyrene Properties, 2010). High impact polystyrene (HIPS) is a tougher version of polystyrene. Jin *et al.* (2002) found that the PS modified asphalt does not store well at high temperatures. The properties of PS modified asphalt can be improved in the presence of sulfur and SBS. At a higher content of PS the softening point is increased, yet resulted in a decrease in penetration. Fang *et al.* (2008c) indicated that a higher ductility can be achieved when using PS as an asphalt modifier. Meanwhile, Colbert and You (2012a) specified that the low temperature performance was improved the most when 5% HIPS (electronic waste composed of HIPS) was added to the binder.

Bulk E-Waste Plastic Considerations for Bituminous Material Modification

When designing long lasting roadways, the pavement engineer should consider the type of e-waste plastic and its behavior, alongside with the design of asphalt pavements and the grade of binder accordingly. Typical e-waste plastics available include ABS and HIPs (Mohd Hasan *et al.*, 2016), PP, PS, styrene acrylonitrile (SAN) (Ali *et al.*, 2015), PE (Wang *et al.*, 2014), polyurethane (PU) (Carrera *et al.*, 2015), polyamide (PA) (Lei and Cao, 2015), acrylonitrile butadiene styrene-polycarbonate (ABS-PC), and polyphenylene oxide (HIPS/PPO) (Santos *et al.*, 2010).

ABS is a heterogeneous multiple phase polymer with a rubber component and a combination of styrene acrylonitrile (Khan *et al.*, 2007). ABS has good impact strength, chemical resistance, and toughness, and rigidity (Achilias *et al.*, 2009). ABS-PC is shown to have good tensile, impact, and strength properties especially during grinding and injecting molding although there are variable ranges of melt flow indices, and poor performances for ultraviolet (UV) susceptibility impact strength, and viscosity for ABS-PC plastics (Dawson and Landry, 2004). Polycarbonate is a common thermoplastic used and has excellent physical and chemical properties, transparency, a high tolerance for heat distortion, high impact properties, and thermally stable (Achilias *et al.*, 2009).

PE and PE-based copolymers have been used to modify the performance of asphalt binder and mixture over many years (Fang *et al.*, 2008c; Polacco *et al.*, 2005; Stastna *et al.*, 2003; Habib *et al.*, 2011; Fang *et al.*, 2008b; Yousefi, 2004). The PE and PP are categorized as elastomers which can bring a high rigidity to the material and improved the resistance to permanent deformation under traffic loads (Polacco *et al.*, 2005; Stastna *et al.*, 2003).

Within the e-waste recycling stream, 33% of the waste stream consists of plastics with 16% composed of computer equipment (Dillon, 1999). The percentages of e-waste plastic resins consist of the following: 31% PS, 16% ABS, and 13% PP (Dillon, 1999). When considering household, e-waste plastics consist of 35% with 3% of the total household waste stream coming from personal computers (Kang and Schoenung, 2004). Typical personal computer plastic waste values consider the amount of impurities within the plastic and type of personal computer component. For instance personal computer circuit boards must have no more than 3% impurities, recycled personal computer plastics must have no more than 4% impurities, hard mix plastic must have no more than 6% impurities (Das and Matthew, 1999). Plastics from external product casings are 20% of the material mass and a valuable end of life recyclable product (Masanet and Horvath, 2007). Numerous researches have been conducted to investigate the applicability of various e-waste plastics. Balart *et al.* (2005) characterized ABS and PC waste plastic properties showing a decrease in mechanical properties versus virgin plastics but favorable to various engineering plastics. Liu *et al.* (2011) conducted an investigation to determine if e-waste plastics particle size affects the bulk properties of the composite material and if there are any agents available which would improve compatibility between the powder and composite matrix. Liang and Gupta (2000a,b, 2001) characterized the properties of typical e-waste plastics for use in recycling applications. Finally Mural *et al.* (2011) characterized polypropylene and waste HIPS blends for use for various packaging applications.

Waste Plastic and E-Waste Plastic Applications for Asphalt Concrete Research

The utilization of waste material in HMA mixtures is a promising way to efficiently use e-waste plastics, but pavement engineers must consider many factors in order to successfully implement these e-waste materials within HMA. Pavement engineers should not sacrifice pavement performance, cost, or contribute to a larger disposal problem (Li *et al.*, 2010). Despite many factors to consider in deciding whether e-waste plastics are appropriate for a given pavement project, the use of waste additives within asphalt concrete mixtures have been shown to bring contractors savings in roadway repair and reconstruction operations. HMA has successfully lined reservoirs within the United States, and chemically restrict waste materials within HMA (Li *et al.*, 2010). Researchers who have been successful in implementing waste plastics within asphalt binder and mixtures include Schroeder (1994). The use of low density polyethylene (LDPE) from waste plastic and sandwich bags were assessed. The LDPE was converted to pellets and mixed into the asphalt binder at a range 4%–7% by weight of asphalt binder (Schroeder, 1994). Hinişliolu and Ağar

conducted an investigation for high density polyethylene (HDPE) to determine if it was possible to successfully integrate HDPE as a polymer modified asphalt concrete mixture. Their results indicated that 4% HDPE modified asphalt mixture had a higher Marshall stability versus virgin mixtures, which presented a higher mixture stiffness and ability to distribute pavement loading (Hinisliolu and Aar, 2004). The long term aging effect of polypropylene modified HMA was investigated by Othman (2010). Whereas, the PP powder was blended into asphalt mixture, and specimens were going through aging process to simulate pavement condition in the field between 5 and 10 years after the placement. The modified mixture was shown to contribute to surface roughness and offset of the hardening effect of aged asphalt concrete mixtures (Othman, 2010).

Agilan (1993) conducted a study using various polymer additives to improve the performance of asphalt mixtures. All tested polymer modified asphalt mixtures has higher mixture stiffness and strength. Whereas the mixture prepared using Kraton has the highest flexibility and strength compared to Elvax and Novophalt modifiers (Agilan, 1993). Jeong *et al.* (2010) conducted a laboratory investigation of waste polyethylene (WPE) film for asphalt pavement mixtures using Marshall Stability test. The result indicated that asphalt mixture modified with 12% WPE provided the best performance compared to the control and polymer modified HMA mixtures. Meanwhile, Morrison *et al.* (1994) who investigated the performance of asphalt mixtures modified using combination of waste plastics and scrap tires (rubber powder), concluded that the combination help improved the high temperature performance in terms of loss moduli, loss tangent, and complex modulus (Morrison *et al.*, 1994). Punith and Veeraragavan (2003, 2010) and Punith *et al.* (2011b) incorporated the LDPE plastic bags for the preparation of asphalt mixtures. Based on the result, it has considerably improved the resistance to fatigue cracking and rutting potential of asphalt mixtures.

Colbert *et al.* (2011) investigated the low temperature performance of asphalt binder at various percentages of e-waste plastics. The preliminary results showed that e-waste modified asphalt binders can meet the low temperature performance criteria of virgin binder. Despite the investigation showing that the e-waste modified binder was stiffer at low temperatures compared to virgin asphalt binders. Lower percentages of e-waste plastics were implied to provide adequate low temperature performance compared to unmodified virgin asphalt binders.

Several research have been conducted (Achilias *et al.*, 2009; Jeong *et al.*, 2010; Anandhan *et al.*, 2002; Li *et al.*, 2007; Yokoyama and Iji, 1995) to improve the impact properties of ABS. Methyl methacrylate butadiene styrene was added to enhance the impact resistance of ABS (Anandhan *et al.*, 2002). Jeong *et al.* presented an attempt to assess the performance of different percentages of WPE film in asphalt mixtures using the Marshall mix design (Jeong *et al.*, 2010). An investigation by Yokoyama and Iji (1995) investigated the use of printed wire boards from electronic materials as filler for resin construction materials. This investigation pulverized printed wire boards into an effective size of 150 μm , and tested versus talc, calcium carbonate and silica powders. Despite the difficulty in pulverizing and re-melting the printed wire boards, it was shown that the printed wire board powder improved mechanical strength and thermal expansion properties versus the talc, calcium carbonate, and silica epoxy resin blends. Finally, it was concluded that it was feasible that printed wire board powder could be used effectively as a construction filler by separating the powder into copper and nonmetallic fiberglass (Yokoyama and Iji, 1995). Using an industrial shredder and a mechanical grinder the authors were able to reduce the size of bulk e-waste plastics into chips and powders (Colbert and You, 2012b). Other research efforts to improve the properties of e-waste plastics was performed by Achilias *et al.* (2009) The research was focused on recycling ABS, PC, and PS through polymer-chemical structure identification and verification using Fourier Transform Infrared Spectroscopy (FTIR) and Differential Scanning Calorimetry (DSC).

Recycled E-Waste Thermoplastic Processing Efforts for Asphalt Pavement Use

Most e-waste plastic recycling efforts focus on high priced plastics such as PC and ABS-PC due to the compounds covering sourcing and processing costs along with competitively pricing the product for resale (Dillon, 1999). Recycling e-waste consists of three steps: (1) recovery of retired electronic devices typically three to five years or longer, (2) pretreatment of e-waste where paints are removed, plastics are reduced in size, washed, sorted, filtered, and dried, then, (3) e-waste components are sorted through froth filtration, density, and or electrostatic means (Flaris *et al.*, 2009).

Obstacles to successful recycling of various e-waste plastics include; enforcement and reliability of the state and national regulations, few specified orders for recycled materials, lack of market forces driving the use of recycled plastics, and perception that recycled plastics are weaker than virgin plastics (Dillon, 1999). The expected cost saving of using processing and recycled resins range from 10% to 30% savings compared to virgin materials (Dillon, 1999). Recycled plastics provide the most salvage value for e-wastes other than metals. Typically, the percentage of plastic in e-waste products range from 15% to 30% (Achilias *et al.*, 2009). E-waste plastics are usually thermoplastics which can be re-melted to make new products that are preferred over thermosetting resins (Kang and Schoenung, 2004). Due to industrial technology advances, the demand to successfully recycle thermoplastics was greatly influenced by the economic, institutional, and political pressures (Dillon, 1999).

In terms of energy consumption, ABS-PC recycling saves roughly 100 MJ of primary energy and 5 kg CO₂ emission per enclosure versus dumping the ABS-PC waste within a landfill (Masanet and Horvath, 2007). One strategy proposed in Khan *et al.* (2007) was to incorporate e-waste plastics into high value products, and use correct quantity of recycled plastic with virgin plastics. For instance, recovery of copper and printer board plastics through pulverization can be performed for a value application. Copper waste printed wire boards were pulverized, and separations of copper, fiberglass, and resin has produced approximately 94% recovery rate for copper, as well as metallic and nonmetallic powder with 100–300 μm in size (Yokoyama and Iji, 1995). Processing techniques used for this investigation included corona separation, grinding, rolling, milling, and pulverizing to reduce

the particle size of the waste circuit board (Yokoyama and Iji, 1995). Recently, Miloudi *et al.* (2011) developed a method to separate and sort granular e-waste plastics such as HIPS, ABS, and PC using electrostatic separation with a propeller driven turbo-charging machine. Dawson and Landry reported a success in recycling HIPS, and ABS-PC that contain several types of flame retardants (Dawson and Landry, 2004). Xia *et al.* (2012) also investigated e-waste modified binders using grounded e-waste plastic polymers and potassium per sulfate as a free radical initiator. The team optimized asphalt binder performance for softening point and ductility using 6% e-waste plastic polymer by weight.

Mohd Hasan *et al.* (2016) conducted a study to evaluate the performance of e-waste modified asphalt binders. E-waste modifiers ABS, ABS-PC and HIPS with 100% of materials passing through 300 μm sieve were studied. The e-waste modifiers were blended with the control binder under two different conditions namely untreated and chemically treated. The chemically treated modifier was processed with cumene hydrogen peroxide before blending into the bitumen to reinforce the molecular bonding between e-waste plastics and asphalt binder. Based on the outcome of the study, the treatment with the initiator has significantly increased the stiffness of the e-waste modified asphalt binders, which attributed to a better integrity between materials and improved the resistance to rutting. In the study, free radical initiator was introduced to enhance the performance of e-waste modified asphalt binders. Free radical initiator was expected to promote covalent bonding between the additive and the binder to promote interfacial adhesion as presented in Fig. 2, and between different parts of the asphalt itself to enhance branching (Fig. 3). Fig. 4 shows the reaction by radical initiator can forms reactive radicals. The new radical ($\text{RO}\bullet$) can abstract an $\text{H}\bullet$, leading to a reactive radical on a polymer backbone on hydrocarbon components that are commonly present in bituminous asphalt leading to new reactive radicals. The coupling of radicals forms an activated styrenic radical from e-waste and a radical on an activated aromatic component of asphalt.

E-Waste Recycling Challenges for Successful Asphalt Pavement Applications

End of life for electronic equipment is the point when electronic product is past its usable life and disposed to landfills (Santos *et al.*, 2010). It was estimated that roughly 48 million personal computers were scrapped in the year 2000 (Anandhan *et al.*, 2002). The amount of e-waste is likely to increase due to rapid innovations in technology and more efficient production systems. Therefore waste management applications and strategies must be developed to meet the goal to lift the burden of disposing solid waste created by the scrapping of e-waste materials (Ismail and AL-Hashmi, 2008). A waste management strategy proposed by Reimer and Sodhi (2001) and Reimer *et al.* (2000) is an electronic recycling network to optimize the network for collecting, processing, and integrating e-waste recycling partners. The utilization of demanufacturing plants is crucial to effectively reduce the amount of e-waste now and in the future.

The main concern on the applicability of waste materials in general is the presence of various hazardous materials contained within e-waste products. Among the major concerns are heavy metals such as cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb), and antimony (Sb) and brominated flame retardants (Santos *et al.*, 2010; Shenoy and Patil, 2010; Li *et al.*, 2007). The potential pollution effects of unmitigated e-waste dumping is the landfill leaching of toxins to water sources, air pollution of toxins from burning e-waste, and the potential exposure hazards that may occur from the manual dismantling of e-waste, along with long periods of biodegrading from e-waste and plastic bags (Li *et al.*, 2007; Ismail and AL-Hashmi, 2008). Several efforts have been taken to address and quantify the amount of hazardous materials present in plastic e-waste components. Dawson and Landry (2004) conducted a toxicological and environmental assessment for flame retardants containing ethane 1,2 bis(pentabromo-

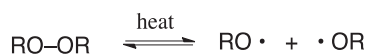


Fig. 2 Free radical initiators decompose to produce alkoxy ($\text{RO}\bullet$) and/or hydroxy ($\text{HO}\bullet$) radicals which can then induce chemical reactions that were expected to promote covalent bonding between the additive and binder to promote interfacial adhesion. Source: Mohd Hasan, M.R., *et al.*, 2016. A simple treatment of electronic-waste plastics to produce asphalt binder additives with improved properties. Construction and Building Materials 110, pp. 79–88.

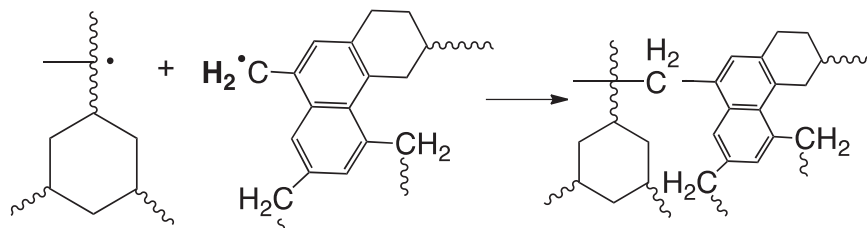


Fig. 3 Radical initiators may lead to increased branching in asphalt components. A representative activated aromatic radical couples with a representative activated saturate radical. Source: Mohd Hasan, M.R., *et al.*, 2016. A simple treatment of electronic-waste plastics to produce asphalt binder additives with improved properties. Construction and Building Materials 110, pp. 79–88.

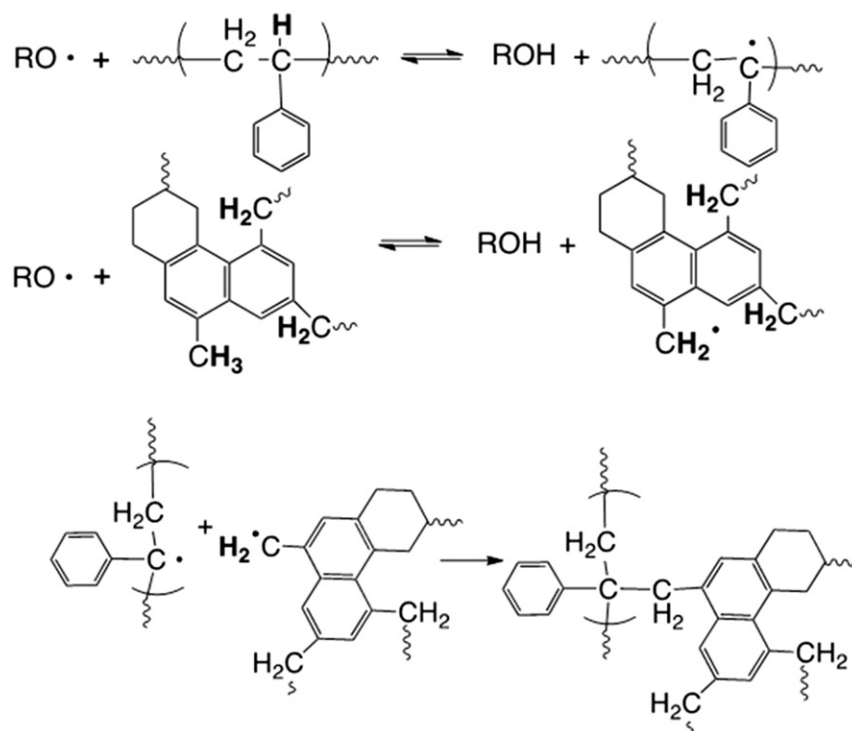


Fig. 4 A reactive radical on a polymer backbone (e.g. a styrene unit in ABS or SBS, with the labile H atom shown in bold), on hydrocarbon components that are typically presented in bituminous asphalt leading to new reactive radicals. The example indicated a representative aromatic component shows seven labile hydrogen atoms. Source: Mohd Hasan, M.R., *et al.*, 2016. A simple treatment of electronic-waste plastics to produce asphalt binder additives with improved properties. *Construction and Building Materials* 110, pp. 79–88.

phenyl) (EBP) and ethylene 1,2 bis(tetrabromophthalimide) (EBTBP) within HIPS. It was shown that there was little environmental or health risk for its use under European Union e-waste regulations (Directive, 2003).

Musson *et al.* used a toxicity characteristic leaching procedure (TCLP) analysis to test e-waste devices for lead leachate and determined that all electronic devices tested failed at least one TCLP test and had lead above the toxicity characteristic (TC) limit in the majority of tests; although the rate of failure was more prevalent for cell phones and remote controls than the personal computers, Central Processing Units (CPUs) and printers (Dawson and Landry, 2004; Musson *et al.*, 2006). Robinson (2009) also reviewed the use of the TCLP analysis for evaluate the heavy metal leaching susceptibility in landfills; the review found that e-waste disposal in modern landfills were not likely to lead significant amounts of plumbum, but the chemical slurry leached from e-waste would likely harm aquatic organisms (Robinson, 2009). Santos *et al.* (2010) also conducted a study quantifying toxic elements within e-waste plastics through slurry sampling by electro thermal atomic absorption spectrometry. Samples tested by Santos *et al.* (2010) originated from cellular phone and personal computer plastics such as PC and ABS blends fully or partially dissolved in dimethylformamide (DMF). Based on outcomes of the study, only ten samples were within values for the European Council (EC) directives for cadmium. Lead and chromium had values in agreement with the EC directives (Directive, 2003).

A study conducted by Colbert and You (2012b) specified that, the pumping difficulty based on viscosity at 135°C is expected to increase when modifying asphalt binder with e-waste plastic powders. But, the viscosity results for the e-waste modified binders have met the Superpave specification. Authors also found that the e-waste modified asphalt binders which can meet the low temperature performance specifications at minimum amount of e-waste plastic. In general, e-waste modified asphalt binders are stiffer compared to virgin asphalt binders. Additionally, it tend to have a greater compaction and mixing temperature versus neat asphalt binders, Incorporations of a higher percentage of e-waste plastic has resulted in a higher compaction temperature as well as raised its viscosity and complex moduli (Colbert and You, 2012b).

Government legislation and the growing numbers of obsolete personal computers has led to the rapid increase in de-manufacturing plants for e-waste (Das and Matthew, 1999). As material purity increases, recycling costs generally decrease, therefore disassembly procedures must be designed to increase purity of recyclables (Das and Matthew, 1999). A major limitation for many recyclables is the amount of impurities for each recycling process can tolerate that directly affects the market price and quality of material. An example of a valuable plastic e-waste recyclable are personal computer enclosures, which disables easily and contains valuable resins making it a likely recycle source (Masanet and Horvath, 2007). A typical personal computer demanufacturing plant has 10–15 employees which process 10 million lbs. within a 5000 m² on a 2000 h/year schedule (Masanet and Horvath, 2007). Although the majority of plastic from e-wastes are recovered in an electronic demanufacturing plant, the various additives within

some plastics prevent the recycled plastic from reentering the original recycle stream and must be used for other applications or burned for fuel (Das and Matthew, 1999). Generally, the percentage of e-waste material which arrives at the recycling plant, and not recycled ranges from 10% to 40% (Das and Matthew, 1999). Demanufacturing of plastic e-waste may include processes such as gravity separation and electrostatic separation (Yokoyama and Iji, 1995). The steps within the demanufacturing process involves three phases: the first phase is to improve accessibility to the various metallic and nonmetallic electronic product parts, the second phase recovers any valuable parts and sub-assemblies, meanwhile the third phase of disassembly further separates e-waste parts for reprocessing within the recycling stream (Das and Matthew, 1999).

E-Waste Compatibility Issues for Asphalt Binders and Mixtures

The issue of compatibility with integrating e-waste plastics with various other nonmetallic materials is crucial for its successful implementation. Yokoyama and Iji (1995) concluded that the compatibility between the e-waste fiberglass powder mixture and epoxy was a factor in improved mechanical performance. Morrison *et al.* (1994) also concluded that compatibility between the low temperature performance of plastic-rubber modified asphalt binders were a factor citing factors such as: interfacial strength between the dispersed and continuous matrix phases of the asphalt mixture. Indications of incompatibility between asphalt binders and e-waste plastics include modified based on the layers of plastic formed on the surface of the asphalt binder. Once the plastic forms a thick layer on the surface, the dispersion of plastic is difficult and may leads to premature failure (Morrison *et al.*, 1994). Cross linking is another indication of incompatibility between e-waste plastics. Anandhan *et al.* (2002) specified that the dynamic crosslinking between rubber and ABS seemed to play a part in preventing oil deteriorating the rubber ABS plastic blend. Small percentages of plastics and mechanical performance were correlated to compatibility and improved phase interaction in an investigation conducted by Balart *et al.* (2005)

Molecular weight of recycled e-waste plastic has an effect upon the compatibility and performance of materials blended with recycled e-waste plastics. Morrison *et al.* (1994) concluded that the high temperature performance of rubber-plastic modified asphalt binders were affected by the amount of dispersion present. Dissolved or fine particles with high weight molecules has great effect on asphalt binder creep properties (Morrison *et al.*, 1994). The author also specified that well dispersed modified asphalt binders provide a better resistance to permanent deformation in asphalt mixtures (Habib *et al.*, 2011). In contrast, asphalt mixture with a lower molecular weight polymer additives can be blended easier, but it does not contribute to the properties of asphalt binder as for high molecular weight additives (Aglan, 1993). In order to control the molecular weight of PP, Das and Patil used free radical initiators to initiate a chain scission process. The free radical initiators are peroxides which are catalyst to the degradation process at controlled rates for plastic palletization and where resin makers can control plastic degradation such as PE (Das and Matthew, 1999). As reaction times increase, it improved the tensile strength and intermolecular interaction along with a likely increase in molecular weight over a period of time (Das and Matthew, 1999). Das and Patil concluded that the reduction in molecular weight of PP was a success using free radical initiators and solvents (Das and Matthew, 1999). Lee and his team also worked with SBS, a common modifier used in polymer modified asphalt, to improve aging resistance using free radical initiators (Li *et al.*, 2010). In the investigation, double bonds in the poly butadiene segment of SBS is susceptible to aging, therefore free radicals formed from antioxidants break the double bonds at high temperatures leading to a cross linking or scission reactions making carbon-peroxide or carbon-carbonyl bonds (Li *et al.*, 2010). Colbert and You (2012b) also conducted an assessment using free-radical initiators to promote compatibility between ABS and HIPS e-waste plastics and asphalt binders. The free radical initiation process is shown in Fig. 5.

Measuring sieves and light microscopy were also used to evaluate the compatibility between asphalt binder and various waste plastics (Al-Hadidy and Yi-qiu, 2009b). FTIR is used to determine compatibility for e-waste plastics by giving information about the composition in differences between the molecular phases and looking at coarse microstructures (Achilias *et al.*, 2009, 2010). Assessment was carried out by Arnold *et al.* using FTIR to determine the compatibility of recycled plastic e-waste materials (Arnold *et al.*, 2010). Table 2 shows the various FTIR frequencies which are used to analyze typical e-waste thermoplastics within asphalt pavement applications.

Recently Mohd Hasan *et al.* investigated the effect of free radical reaction on the e-waste modified asphalt binders using ABS, ABS-PC, and HIPS plastics with cumene hydro peroxide. The result of this investigation indicated that the addition of initiator has significantly improved asphalt mixtures resistance to rutting (Mohd Hasan *et al.*, 2016).

Other Potential of E-Waste Plastic: Flame Retardant

Flame retarder is a typical component used within e-waste product that is designed to promote the use of thin plastic walls in electronic coverings and reduces the overall amount of plastic for electronic equipment, such as ABS and HIPS (Dawson and Landry, 2004). Electronic appliances with flame retardant include personal computer monitor housings, CPU's, circuit boards, plastic parts, printers, copiers, and laser jet printers, to prevent against high temperature spikes which may occur due to the high voltage supply for electronic equipment (Fisher *et al.*, 2005). In an investigation by Fisher *et al.* (2005) it is reported that 30% or all electrical and electronics products have flame retardants and 12% or all plastics used within the electronics industry have brominated flame retardants (BFR). The (BFR) is popular because of the versatility of applications that they can be used for in fire

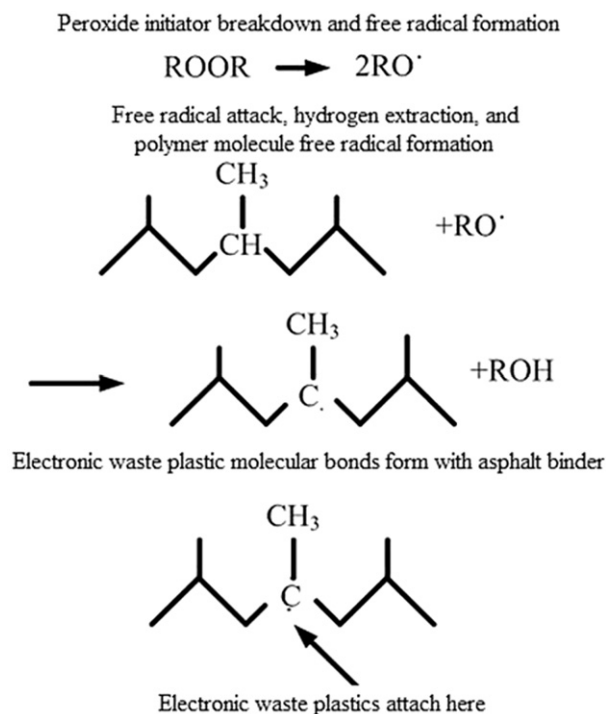


Fig. 5 Hydro peroxide initiator polymerization of electronic waste plastics to asphalt binders.

Table 2 Approximate absorption wavenumbers for FTIR analysis for e-waste plastic modified asphalt binders

Functional group	Formula	Absorption wavenumbers (cm^{-1})
Carbonyl	$\text{C}=\text{O}$	1740–1690 (Stretching) indication of oxidation (Karlsson and Isacsson, 2003)
Aromatic and Hetero-aromatic rings		1600 ($\text{C}=\text{C}$ ring stretching) 900–600 ($\text{C}-\text{H}$ bending) (Karlsson and Isacsson, 2003)
Sulphoxide	$\text{S}=\text{O}$	1055–1030 (stretching) (Karlsson and Isacsson, 2003)
Methyl (aliphatic)	CH_3	2962, 2872 (Stretch), 1450, 1380 (bending) (Karlsson and Isacsson, 2003)
Methylene	CH_2	2926, 2853 (Stretch), 1465, 720 (bending) (Karlsson and Isacsson, 2003)
Hydroxyl	(OH-)	3250 (for indication of possible ABS degradation) (Balart et al., 2005)
Poly-acrylonitrile	$(\text{C}_3\text{H}_3\text{N})_n$	2236 (Arnold et al., 2010)
Poly-butadiene	C_4H_6	967 (Arnold et al., 2010)
Benzene rings		1602 from polystyrene (Arnold et al., 2009)

reduction, recyclability of plastics using BFR's, and the widespread documentation on the material properties and performance (Nnorom and Osibanjo, 2008).

The European Union has instituted regulations in 2006 to reduce the amount of brominated flame retardants to 0.1% of (polybrominated biphenyl (PBB) and polybrominated diphenyl ether (PBDE)) flame retardant types where the majority of these flame retardants occur in older electronic appliances (Khan et al., 2007). The pressure to reduce halogenated flame retardants has led to the increasing use of metal shielding and a shift from using ABS-PC plastics to ABS and HIPS plastics (Dillon, 1999). The PBDE contained within e-waste plastics as flame retardants do not have a strong chemical bond between the flame retardant and plastic matrix posing a leaching concern with disposal of e-waste plastics (Robinson, 2009). Recycling options for brominated flame retardants include mechanically separating e-waste materials containing BFR, or burning these components for energy recovery (Dawson and Landry, 2004). A problem with incineration of BFR is the toxic ash produced into the atmosphere (Santos et al., 2010). A harmful byproduct of waste printed circuit boards which are incinerated is hydrogen cyanide, carbon monoxide, dibenzo-*p*-dioxins and dibenzo furans from incomplete burning of the waste printed circuit boards (Li et al., 2007).

E-Waste Plastic Research Gaps within the Asphalt Pavement Industry

A research gap that needed to be addressed is the use of recycled plastics such as e-waste plastic used along with virgin rubbers to improve the mechanical properties of bituminous materials (Anandhan *et al.*, 2002). Further research are crucial to be conducted include, characterization of e-waste plastics, and quantifying the environmental and economic end of life cost benefits accounting for economic uncertainties using e-waste plastic coverings (Masanet and Horvath, 2007). Future research efforts must identify efficient methods of recycling e-waste plastics, since they are not easily identifiable, although the recovered e-waste plastics have a reduced processing expense versus virgin plastics due to high volume of e-waste (Ching *et al.*, 1996). Other issues which must be taken into consideration for e-waste plastic recycling is to address the various levels of recycling efficiency between various types of e-waste plastics such as, ABS-PC, which is not as advanced as ABS or HIPS plastics, and not as appealing to plastics recyclers economically (Khan *et al.*, 2007). Another research topic that should be taken into consideration prior to other successful applications for recycled e-waste plastics is to evaluate the compatibility between the waste plastics and other raw materials such as asphalt concrete, Portland cement concrete, metals, and future recycled waste plastics (Dillon, 1999; Morrison *et al.*, 1994).

Conclusions and Recommendations

The current state of applications for e-waste plastics was reviewed within this paper and performance results for e-waste modified asphalt binders were discussed. This paper reviewed the current research gaps which researchers should consider in order to successfully integrate e-waste plastics in a sustainable manner for asphaltic concrete materials. Major challenges which hinder the use of e-waste plastics within asphalt pavement materials are e-waste plastic compatibility with asphalt binders and mixtures, the removal or mitigation of hazardous waste materials within e-waste plastic products, and the issue of flame retardants within e-waste. The states of art for recycling e-waste plastics within asphalt pavement applications were discussed. The following issues need to be addressed by future research efforts to successfully implement e-waste plastics within asphalt pavements:

1. The effectiveness of the polymer use to modify asphalt depends on the source and type of polymer and the compatibility that it has with asphalt binder.
2. Despite the many hazardous materials present within e-waste products, utilizing the nonmetallic plastic components of the e-waste avoids the major heavy metal found within e-waste.
3. Economical recycling procedures must be developed to successfully use the thermoplastic components within e-wastes for use as sizes needed for the modification of asphalt binders and for aggregate replacement.
4. Research indicates that the use of e-waste plastics improved the high temperature properties for asphalt binders and mixtures.
5. Low temperature performance of e-waste plastics for asphalt materials is inconclusive and future research efforts must concentrate on appropriate amounts of e-waste material to implement into pavement materials for maximum performance.
6. Future research efforts need to focus on agents or additives which can effectively provide compatibility between various e-waste plastics and bituminous materials.

Acknowledgements

This material is based in part upon work supported by U.S. National Science Foundation under grant 0936726 and the Michigan Space Grant Consortium. Any opinions, findings and conclusions or recommendations expressed in this material are those of the author's and do not necessarily reflect the views of the National Science Foundation nor the Michigan Space Grant Consortium. The authors would like to acknowledge the assistance of former students Julian Mills-Beale, Su Ting Lau, Morgan Hansen, and Shu Wei Goh from Michigan Technological University for their input to this manuscript.

See also: Use of Bio-Fibers in Various Practical Applications

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The Role of Engineering in Mitigating Global Climate Change Effects: Review of the Aspects of Carbon Emissions from Fossil Fuel-Based Power Plants and Manufacturing Industries

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Nomenclature

°C Temperature in degree celsius

CO₂eq Carbon emission equivalent

GHG Greenhouse gas

Gt Giga ton

GW Global warming

GWP Global warming potential

kWh(h)⁻¹ Electricity production per hours

Mt Metric ton

t Aluminum Ton of aluminum

t Ton (1000 kg)

tPOME Ton of palm oil mill effluent

Introduction

This review article presents the research outcomes published in various scientific journals on carbon emission from fossil fuel based power plants and manufacturing industries and targets to share with the concerned stakeholders to speed up R&D work for reducing carbon emission. To achieve the objective, the study is divided into two major parts. Firstly, collecting information on carbon emission paths from fossil fuel based power plants and manufacturing industries. The second part of the study is to collect information on the contribution made by engineering to reduce carbon emission from power plants and manufacturing industries. This study has covered the research papers published in the years between 1990 and 2018 on global carbon emission, global warming (GW) and roles of engineering in developing technology to mitigate climate change effects. Indeed, this document aims at identifying the effective technical measures that have been taken by various organizations to mitigate carbon emissions from those industries, particularly in view of complying with the Kyoto Protocol commitment in achieving economic and environmental sustainability.

Intergovernmental Panel on Climate Change (IPCC), International Energy Association (IEA), United Nation Environment Protection (UNEP) and some other organizations have tried to address this global warming potential (GWP) issue by reducing man-made carbon emission where temperature increase should be limited to well below 2°C above pre-industrial levels, and pursuing a 1.5°C target with aim to mitigate climate change effects. Basically, the efforts of these organizations are limited to developing policy and strategy relating to the reduction of carbon emission and climate change effects. Many modeling studies also covered numerous scenarios of economic, energy and population features relating to carbon emissions and climate science, but the contribution of engineering to this emerging field in reducing carbon emission is not well discussed in published papers. This scenario indicates a gap exists in climate science domain (Henderson *et al.*, 2017) and hence the review work is designed to fill up this major gap.

However, to achieve research goal, this review covers publications made to report on CO₂ and CH₄ emission from fossil fuel based power plant, and as well as major manufacturing industries such as cement, iron, aluminum, palm oil mill, textile, and water treatment industries.

Background of Review on Carbon Emission and Mitigation Technology

Sustainable development strategy has been formulated to meet the needs of the present without compromising the ability of future generations to meet their own needs; this fundamental philosophy is being challenged by current climate change due to higher level carbon density in the atmosphere. The various studies have revealed that in 2016, CO₂ concentration in the atmosphere was 404 ppm, which is about 7% higher than 2007 and even the highest levels in emission history (IPCC, 2014c; UNEP, 2015; Brown *et al.*, 2016). The IPCC states that, if no effective measure is taken to reduce carbon emission, the concentrations would likely to increase 450 ppm by 2050; and between 750 ppm and 1300 ppm by 2100 (Augusta Ayotamuno, 2016; IPCC, 2017a). It was also estimated that by 2100, this planet may experience global mean surface temperature increases of 3.7–7.8°C compared to pre-industrial levels. It is reported that the atmospheric CO₂ concentration must be kept under 450 ppm in order for the global average temperature well below 2°C pre-industrial levels and pursuing a 1.5°C target within 2100 (Henderson *et al.*, 2017).

The broad objectives for reducing carbon concentration within estimated limit is to mitigate climate change effects that can be noticed globally in the form of higher temperature growth, which could lead to greater food insecurity, shortage of potable water (Augusta Ayotamuno, 2016), diseases outbreak and natural disaster (Rogelj *et al.*, 2013). A large body of literature is available on

Table 1 Global GHG emission control in GtCO₂eq at more than 55% probability

2020	2025	2030	2050	2100
56	47	39	8	– 5
53–56	46–48	37–40	4–14	– 5 to – 3

Another path to control temperature increase well below 2°C by 2100 at probability more than 66%.
Note: IPCC, 2017a. 'Intergovernmental Panel on Climate Change'. IPCC, 2017b. 'Intergovernmental Panel on Climate Change Sixth Assessment Report (AR6) Products'. Available at: https://www.ipcc.ch/meetings/session44/l2_adopted_outline_sr15; Sixth Assessment report, 2017.

Table 2 Global GHG emission control in GtCO₂eq at more than 66% probability

2020	2025	2030	2050	2100
52	48	42	23	– 3
49–35	44–53	29–44	17–29	– 11 to 0

Note: IPCC, 2017a. 'Intergovernmental Panel on Climate Change'. IPCC, 2017b. 'Intergovernmental Panel on Climate Change Sixth Assessment Report (AR6) Products'. Available at: https://www.ipcc.ch/meetings/session44/l2_adopted_outline_sr15.

pathways that limit GW to below 2°C within least-cost pathways starting from 2020, which can be divided into two groups (IPCC, 2014c). One is the least-cost pathway of limiting GW to below 1.5°C by 2100 with a probability of more than 55%.

In order to limit temperature increase within 1.5°C through reduction of carbon concentration in the atmosphere, it needs a great deal of innovation in the aspect of low carbon emission technology (Schleussner *et al.*, 2016). It was predicted that carbon emission reduction technology would significantly reduce the risks and impacts of climate change (Peters *et al.*, 2015; UNEP, 2016). Advanced technology development for increasing energy efficiency at consumption point, and both carbon capture for storing (CCS) and carbon capture for usage (CCU) could contribute to reducing carbon concentration in atmosphere significantly (International Energy Agency, 2010; Chapman *et al.*, 2013; Cebrecan *et al.*, 2014; Peters *et al.*, 2015; Schleussner *et al.*, 2016). It was also suggested that a huge amount of inputs from engineering discipline are required to redesign industrial manufacturing process for retrofitting CCS and CCU technology for reducing carbon emission (Hammond *et al.*, 2011; Mukherjee *et al.*, 2014). On this background, this study was designed to collect available information and to disseminate on carbon emission from fossil fuel based power plants, manufacturing industries with emission mitigation technology developed engineers in order to meet goals listed in Tables 1 and 2.

Global Warming and Climate Change Scenario

The Global Warming Potential (GWP) is a measure of GHG's impact on surface temperature (Henderson *et al.*, 2017) where the major GHG are CO₂, CH₄, and N₂O (IPCC, 2014c). The GWP is an indicator used to measure the effect of carbon emission on global surface temperature increase in a scale of 25, 100, and 500 years. In many studies, GWP of CH₄ is considered 25, N₂O is 360 with respect to CO₂. It implies that the effect of CH₄ in climate change is 25 times more than CO₂ (Scheehle and Doorn, 2001; Mukherjee *et al.*, 2014). However, it was reported that carbon concentration (CO₂eq) in the atmosphere is the main cause of increasing surface temperature and climate change (Chapman *et al.*, 2013). The various studies revealed that CO₂ concentrations in the atmosphere were 354.19 in 1990, 365.48 in 2000, 385.34 in 2008, 404 ppm in 2016. And it was also reported that carbon concentration would be 450 ppm in 2050 and 750 ppm in 2100 (IPCC, 2014c; UNEP, 2015), which will contribute to increasing surface temperature (Rogelj *et al.*, 2013; Henderson *et al.*, 2017). The historical data on carbon emission in the atmosphere is presented in Fig. 1 which indicates that carbon emission is increasing with time (EDGAR, 2014; IPCC, 2014c).

The carbon emission is a man-made issue relating to industrial development for economic growth maximization (EPA, 2010; Tol, 2018); which speed up GW. The GW is already underway with consequences that must be faced now, and as well as will appear in future. The GW is already bring changes in the Earth's physical, chemical and biological processes, and now its effect has appeared in every continent of the globe including societies and the natural environment (Georgakakos *et al.*, 2014). However, the climate change indicators stated in published papers are rising sea levels, shrinking glaciers dimensions; increasing surface temperatures, severe rainstorms and frequent droughts globally (IPCC, 2014a). Though it is difficult to quantify the impacts of climate change but it is believed to have major impact on the growth rate of the global economy, which may drag more people into poverty by inflicting severe damage on infrastructure and loss of productivity, in that climate situation, people may be obliged to migrate if they cannot cope with the resulting costs of climate change (Gosain *et al.*, 2006; Baig and Yousaf, 2017).

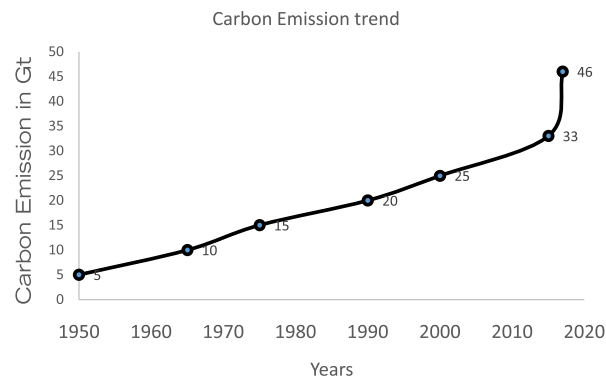


Fig. 1 The historical data on carbon emission. Reproduced from EDGAR, 2014. Emission Database for Global Atmospheric Research (EDGAR), release version 4.2, 2012. Emissions database for Global Atmospheric Research. doi:10.2904/EDGARv4.2; IPCC, 2014c. 'Climate change 2014 synthesis report summary chapter for policymakers', IPCC, p. 31. doi:10.1017/CBO9781107415324.

Global Inventory of Carbon Emission

It is evident that global carbon emission has increased at a steady rate of 1.3% during the period of 1970–2000; 2.2% per year during the period 2000–2010; 3.5% during the year 2010–2011, and 1.8% in the year 2012–2013 (EDGAR, 2014). The major primary sources of the carbon emissions are two: electricity production by the burning of fossil fuels namely coal, oil, gas, and MSW. And manufacturing industries (IPCC, 2007; EPA, 2010). The other sources are the clearing of forests, agricultural practices, transportation which is related to global economic growth (Dahe, 2014; IEA, 2017b). It was also reported that as of 2015, the two largest economies of the world are the major carbon emitters, where China accounted for 6.6 tCO₂eqyear⁻¹ and USA at 15.5 tCO₂eq year⁻¹, which is about 13% higher than 1990 (EPA, 2017). However, to meet the economic growth of these economies, they are planning to set up more power plants and manufacturing industries, which will contribute to increasing emission rate further (Chang, 2010; Habib *et al.*, 2013; Rogelj *et al.*, 2013).

Sources of Global Warming Potential

The major components of GHG are CO₂, CH₄, N₂O and Fluorinated gases (F-gases), which are responsible for global warming and climate change (Ben Abdallah *et al.*, 2013). The sources of these gases are power generation from fossil fuel, decomposition of biomass, deforestation, water treatment industries and agriculture activities (Gschrey *et al.*, 2011; Baig and Yousaf, 2017; IPCC, 2017a).

In GHG, the contents of carbon dioxide in the atmosphere is about 65%. The major sources of CO₂ are the burning of fossil fuels (Gschrey *et al.*, 2011; IEA, 2016). The methane content is the second largest in GHG after CO₂, which accounted for 16% of global emission. The major sources of CH₄ are the agricultural waste, MSW landfilling, waste biomass decomposition, wastewater treatment and animal litter. The effect of CH₄ on GWP and climate change is about 25% higher than CO₂ (IPCC, 2003; Yacob *et al.*, 2006; Liu *et al.*, 2016).

Nitrous oxide is also a part GHG in the atmosphere, and its contribution in GHG is about 6%. The major sources of N₂O emission are agricultural activities, such as fertilizer use, fossil fuel combustion, and wastewater treatment (Debruyne *et al.*, 1994; Wu *et al.*, 2018; Yao *et al.*, 2018). Fluorinated gases have a minor share in GHG. The sources of this gas are Industrial processes, refrigeration, and the use of the variety of consumer products contribute to generating F-gases including hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride SF₆ (IPCC, 2014d; Lee *et al.*, 2017).

However, in a report, IEA stated that the heavy industries like cement, Iron, and Aluminum are significantly responsible for GWP (IAI, 2009a; International Aluminum Institute, 2009b; Liang *et al.*, 2012; IEA, 2016).

Carbon Emission Sources

Begum *et al.* (2015) and fifth assessment report of IPCC (2014) had stated that carbon emission growth is positively associated with global economic growth (IPCC, 2014a). It has been also stated that growth of fossil fuel based power plants for supplying electricity to meet demands from manufacturing industries and other economic activities are the main reasons of global carbon emission growth (Habib *et al.*, 2013; IPCC, 2017a; Ozturk and Acaravci, 2010; Fan *et al.*, 2015). The evidences published in scientific journals show that the growth in world energy demand from fossil fuels has played a key role in the upward trend of CO₂ emissions (IPCC, 2014b).

The Inventory Carbon Emission From Fossil Fuel Based Power Plant

The global total electricity production was 22,433 TWh in 2014; and was 25,570 TWh in 2017, which encompasses the primary energy source (PES) such as coal at 39%; gas at 22%, and oil at 5% (IEA, 2016). Since the Industrial Revolution until 2017, annual

CO₂ emissions from fuel combustion are increasing at a significant rate. Various studies revealed that about 40% of total global GHG have been contributing to electricity production (IPCC, 2003; Henderson *et al.*, 2017). Global energy-related CO₂ emissions rose by 1.4% in 2017, which accounted for 46Gteq (Habib *et al.*, 2013; Le Quéré *et al.*, 2016). The data released by the USA Department of energy show that the share of global GHG emission from energy sector is about 42% (Habib *et al.*, 2013; Moazzem *et al.*, 2013). The EDGA published data, which show that global GHG emission from energy sector was 2.1 GtCO₂eq in 1950; 4.2 GtCO₂eq in 1965, 6.3 GtCO₂eq in 1975, 8.4 GtCO₂eq in 1990, 10.5 GtCO₂eq in 2000, 13.8 GtCO₂eq in 2015 and 19.32 GtCO₂eq in 2017 (EDGAR, 2014; Le Quéré *et al.*, 2016).

Carbon emission from coal-fired power plant

The major percentage of electricity has been produced from this primary energy sources (Andres *et al.*, 1996; IPCC, 2007), while Coal is the least efficient fossil fuel in terms of energy output per unit of CO₂ emission. As stated by U.S. EPA, (2000) that the coal-fired power plants are taking a significant percentage of share in producing electricity where its share in generating CO₂ per kilowatt hour is higher compared to other fossil fuel (Hammond and Spargo, 2014; U.S. EPA, (2000)). IEA stated that coal represented about 28% of the world total primary energy source (TPES), and it accounted for about 15% of the global CO₂ emissions (Ostrowski, 2010; Liang *et al.*, 2012). The average GHG emission rate from burning coal for producing electricity is 0.85 tCO₂eq(kWh)⁻¹ (IPCC, 2007; Lindner *et al.*, 2013). Though by adding CCS and increasing energy efficiency in coal-fired plants, the emission reduced to about 0.5 tCO₂eq/(kWh)⁻¹ (Baig and Yousaf, 2017). The emission history on coal-fired energy revealed that global emission was 8,533 Mt in 2000, 11,360 Mt in 2005, 13,916 Mt in 2010, 114,148 Mt in 2013 (Maryland and Rotty, 1984; IPCC, 2006; EDGAR, 2014). According to the International Energy Agency, the electricity production and GHG emission from coal will increase further about 30% by 2035 due to electricity production capacity increase in this sector.

Carbon emission from biogas fired power plant

Two ways in which natural gas mainly CH₄ is emitted to the atmosphere are through gas transportation and burning of gas for electricity production. However, CH₄ has 25 times higher GWP than compared to CO₂. The CO₂ emission from Gas Turbine Power Plant (GTPP) ranges from 0.4 tCO₂eq(kWh)⁻¹ to 0.6 tCO₂eq(kWh)⁻¹ (Hosseini and Wahid, 2013), which is next higher level of emission compared to coal-fired based energy production (Scheehle and Kruger, 2006). Though by the installation of CCS technology in GTPP, the emission reduced to about 150 gCO₂(kWh)⁻¹ (Hosseini *et al.*, 2013). The emission history on gas-fired energy revealed that total global emission from GTPP was 4712 Mt in 2000, 5416 Mt in 2005, 6233 Mt in 2010, 6222 Mt in 2013, 7.622 Mt in 2015 (Poeschl *et al.*, 2012).

Carbon emission from petroleum oil based power plant

Combustion of petroleum oil for electricity production is one of the top listed sources of CO₂ emissions (Yeh *et al.*, 2017a,b), and estimated emission range is from 3.5 kgCO₂eq(kWh)⁻¹ to 500 kgCO₂eq(kWh)⁻¹ (Burnham *et al.*, 2012; EIA, 2014). The emission history on oil-fired energy revealed that total global emission from oil was 10,425 Mt in 2000, 11,254 Mt in 2005, 11,475 Mt in 2010, 11,793 in 2013, 13.612 Mt in 2015 (EDGAR, 2014).

Emission from municipal solid waste

Municipal solid waste (MSW) is a potential CH₄ emitter, and significantly responsible for enhancing global warming and climate change (Manfredi *et al.*, 2009). Once MSW is disposed into landfills, it undergoes aerobic decomposition process over years, and continue in methanogen activities (Møller *et al.*, 2009; Manfredi *et al.*, 2009). It was reported that CH₄ yield from MSW landfill is up to 0.5 t/t MSW (range 0.1–0.5 t per ton of MSW) (Metz and Davidson, 2007; Møller *et al.*, 2009; Monks *et al.*, 2009; Siddiqui and Khan, 2011; Kumar and Sharma, 2014). A study on MSW reported that CH₄ emission from this sector is a major contributor in GW with a share of about 18% (IEA, 2016; Xydis *et al.*, 2013). In an estimate EPA reported that CH₄ concentration in air was about 68 Mt in 2008, and it would be 130 Mt in 2018, 220 Mt in 2025; 550 Mt in 2030 (Mathews, 2007).

Carbon Emission From Manufacturing Industries

Industrial processes are highly energy intensive and currently account for one-third of global energy use (IEA, 2009; Allwood *et al.*, 2010). It is estimated that around 70% of required energy for industry operations are supplied from the burning of fossil fuels, which make up 40% of total global CO₂ emissions (Allwood *et al.*, 2010). It was also evaluated that emission from the manufacturing process is about 7% (IEA, 2009; Allwood *et al.*, 2010). However, both energy production and manufacturing process are significantly responsible for climate change due to the significant amount of carbon emission.

There are three ways in which carbon is emitted from manufacturing industries. The first route is by the combustion of fuel for producing electricity to operate plant machinery. The second route is by steam production from fossil fuel (IEA, 2017a; IPCC, 2017b). The third route of emission is by the use of carbon-based raw materials for producing product, for example, chemical reaction to convert limestone (CaCO₃) into lime (CaO) (Alsop, 2005; Tol, 2018). The major carbon-emitting industries are Cement, Iron, agriculture, Aluminum, Petrochemicals; and water treatment industries. The estimated GHG from manufacturing industries was about 1.75GtCO₂eq in 2000, 2.33GtCO₂eq in 2015 and 3.22GtCO₂eq in 2017 (EDGAR, 2014); and it would be increased further with manufacturing growth.

Carbon emission from cement industry

Cement production is an energy and carbon-intensive process (Robbie, 2017). In fact, there are two ways by which CO₂ are generated from cement production process. The first one is the burning of fossil fuels to produce electricity and steam for plant operation. The second one is chemical reactions involved in the production of clinker. In the clinker production process, limestone (as MgCO₃ and CaCO₃) disintegrates to produce CaO or MgO, which is known as calcination (Alsop, 2005; Andrew, 2017).

The electrical power consumption of a cement plant is around 1200 kWh t⁻¹ cement (Bakhtyar, 2017; Bakhtyar *et al.*, 2017). This industry emits up to 0.9tCO₂eqt⁻¹ cement [range 0.5–0.9tCO₂eq] (Keeling, 1973; Mahasenan *et al.*, 2003). The global emission data revealed that the contribution to global emission from cement plant was 828.7 Mt in 2000, 1173 Mt in 2005, 1642.82 Mt in 2010, 2031 Mt in 2013, 2213 Mt in 2015 (Keeling, 1973; Tol, 2018; EDGAR, 2014).

Carbon emission from iron and steel industry

International Energy Outlook 2012 reported that the iron and steel industry accounted for about 10% energy consumer of total manufacturing sector (Li *et al.*, 2016). This sector is the second largest industrial CO₂ emitter due to its energy-intensive process and reliance on carbon-based fossil fuels (Yu *et al.*, 2015). Two ways carbon emits from Iron industry such as electricity production for the operating plant machinery, and from Iron production process. Coal and gas-fired power plants are the main sources of electricity and heat supply to Iron and steel process plant (Wou *et al.*, 2015). It is found that from a traditional scrap/electric arc furnace, the carbon emission is about 0.4tCO₂eqt⁻¹ crude steel; and from the integrated blast furnace is up to 1.8tCO₂eqt⁻¹ crude steel. From a basic oxygen furnace process, the emission is up to 2.5tCO₂eqt⁻¹ crude steel (LBNL, 1999). Global carbon emission data shows that the emission from Iron industries was 2.3 Gt in 2016. The projected contribution from this sector to global CO₂ emissions would be about 4.5 Gt in 2050 corresponding to estimate of 3-billion-ton steel production (Allwood *et al.*, 2010).

Carbon emission from aluminum industry

Aluminum processing consumes about 1400 kWh/t Aluminum ingot production (International Aluminum Institute, 2006). The IPCC has marked Aluminum processing as a major GHG emission-intensive industry; and has emphasized to reduce emission from this industry from 50% to 85% by the year 2050 (IAI, 2013; Zeng *et al.*, 2015; Paraskevas *et al.*, 2016). It was estimated that 65% emissions are caused mainly electricity production required for operation of plant machinery. And the other 35% is from aluminum production process (IPCC, 2007; Paraskevas *et al.*, 2016). According to the IEA's indicative statistics, when coal-fired electricity used for Aluminum processing, it contributes about 0.98 kgCO₂eq(kWh)⁻¹ (Paraskevas *et al.*, 2016), whereas during the use of natural gas-fired plants emit 0.54 kgCO₂eq(kWh)⁻¹ (IAI, 2013). Accordingly, emission from Aluminum processing is 1.3CO₂eq/t Aluminum when using coal for energy production; and it could be about 0.73CO₂eq/t Aluminum when using gas for energy production (Zhang *et al.*, 2015). It was also reported that contribution from Aluminum production industry to total global GHG emissions was 0.45 GtCO₂eq in 2007, which was approximately 1.0% of the global GHG emissions (IAI, 2013; Zhang *et al.*, 2015; Paraskevas *et al.*, 2016).

Carbon emission from textile industry

Textile is an important industry in the world economy, and this sector has marked as a medium level energy user and GHG emitter (Clark, 2007; Islam and Khan, 2014). GHG is emitted from this industry to the atmosphere in three different ways. The first route of carbon emission is the production of electricity to operate the process machinery. The second route of emission is textile processing. And the third route of emission is wastewater treatment process (Guleryuz, 2011; IPCC, 2013; Toprak and Anis, 2017). It is estimated that the annual textile production was 60Mt in 2016 and it would be 97.8Mt in 2018 and emission will increase accordingly (Toprak and Anis, 2017). The wastewater treatment is another carbon emission intensive part of the textile industry which emits CO₂, CH₄, and N₂O. The CH₄ emission level depends on COD concentration in wastewater (Scheehle and Doorn, 2001; Shahabadi, 2008; Robbie, 2017) and COD reduction process (El-Fadel and Massoud, 2001; Campos *et al.*, 2016). In major cases, the source of CO₂ emission is from the usage of CaCO₃ in wastewater treatment process which breaks down to CO₂ (Campos *et al.*, 2016).

In knitwear process, about 60% emissions are caused by steam production required in dyeing process (Chen, 2013; Hridam *et al.*, 2016). It has been reported that thermal energy requirement is about 22 MJ m⁻¹ of fabric, and electrical energy consumption in process is up to 0.5 kWh m⁻¹ fabric (range 0.15–0.5 kWh m⁻¹) (Guleryuz, 2011; IPCC, 2013; Toprak and Anis, 2017). The average emission from fabric dyeing process is up to 1.3kgCO₂eq/kg knitted fabric (range 0.8–1.3 kgCO₂eq). It was reported that starting from spinning, knitting, dyeing, finishing, cutting, sewing, plus transportation final products to distributions center, emission could reach up to 12.5 kgCO₂eqkg⁻¹ fabric (Annual report, 2016). However, GHG data from 2012 to 2017 revealed that total emission from textile industry was 8500 Mt year⁻¹ to 1200 Mt year⁻¹ which accounted for 3% of global industrial emission (UNEP, 1993; Annual report, 2016).

Carbon emission from palm oil industry

Increasing palm oil demands in global market is positively associated with GWP due to its carbon emission intensity (Kaewmai *et al.*, 2013; Oosterveer, 2014). Nowadays, this industry becomes a global carbon emission issue. It was reported that CH₄, CO₂, and N₂O have a large share in the total global warming potential (Zutpen and Van, 2005). Palm oil industry emits GHG in three ways. The first route of emission is from burning of fuel in palm oil harvesting machinery. The second route is emission from production of electricity to operate the process. And the third route is emission from wastewater treatment process called POME.

The total GHG emissions from three routes are up to about 30 tCO₂eqt⁻¹ CPO (Zutpen and Van, 2005; Damen and Faaij, 2006); and among this CH₄ emission is significantly harmful (Renewable fuel Agency, 2008; Ng *et al.*, 2011). It has been reported that reported that CH₄ emission potential of POME is about 9 kgt⁻¹ FFB, which equivalent to about 18.3 m³CH₄t⁻¹ POME (Renewable fuel Agency, 2008). It has been also reported that emission rate is about 190 kgCO₂eqt⁻¹ FFB (Ng *et al.*, 2011; The statistics portal, 2018).

In a report, Chynoweth *et al.* (2000) had stated that CH₄ emission could be reduced from 9.0 m³t⁻¹ POME to 5.5 m³t⁻¹ POME by using efficient CCS and CCUS technology (Chynoweth *et al.*, 2000). However, Sridhar and Adeoluwa (2009); and Ng *et al.* (2011) reported that biogas (CH₄, CO₂, and H₂S) yield from POME is up to 28 m³t⁻¹ POME (Sridhar and Adeoluwa, 2009; Ng *et al.*, 2011). Based on (Wicke *et al.*, 2008) and (Zah *et al.*, 2007) estimate, the average emission from palm oil industries found 30 tCO₂eqt⁻¹CPO (Zutpen and Van, 2005; Damen and Faaij, 2006). It was also reported that the contribution of palm industry to global emission was 1569.6 tCO₂eq in 2013, 1680 tCO₂eq in 2014, 1779 tCO₂eq in 2015, 1824 tCO₂eq in 2016 and 1854 tCO₂eq in 2017 (Zutpen and Van, 2005; Wicke *et al.*, 2008).

Carbon emission from water treatment industry

GHG emissions from wastewater and water treatment industries have caused a threat to global sustainable development agenda (Scanlan *et al.*, 2008). The effluent of textile, tannery, POME, chemical, and municipal wastewater are the top ranking carbon emitters. In wastewater treatment process, GHG emits in two ways. The first way of emission is the burning of fossil fuel to produce electricity for the operation of plant machinery (Khandare, 2015). Shaw *et al.* (2008) stated that at the second level, CH₄ and CO₂ emit from treatment process such as from anaerobic reactor (Shaw *et al.*, 2008; Khandare, 2015). A few research reports indicated that wastewater treatment is a potential anthropogenic CO₂ emission source, which is significantly responsible for GWP (Shaw *et al.*, 2008; Khandare, 2015; Hanaki *et al.*, 2001; Sahely *et al.*, 2006). It was also reported that energy consumption in water treatment process is up to 075 kWh t⁻¹ wastewater, which generates up to 1.3 kgCO₂eqm⁻³ water (Choorit and Wisarnwan, 2007; Haridas *et al.*, 2016; Toprak and Anis, 2017).

Engineering in Carbon Emission Reduction From Industries

Engineering contribution in development and implementation of carbon emission reduction technologies have been highlighted in various published papers. It was also stated that a huge amount of inputs from engineering have been employed to develop technologies in order to reduce carbon emission. In this aspect, the major involvement of engineering are: increasing of electricity output efficiency in power plant (Markusson *et al.*, 2012a,b; International Energy Agency, 2017), retrofitting low carbon energy supply to industries (EPA, 2017), using higher energy efficient machinery (Kuo and Wu, 2015), and, using CCS and CUS technologies (Peters *et al.*, 2015) in power plants and manufacturing industries. The cost-effective technologies installation at manufacturing industries for carbon emissions reduction is regarded as a top listed contribution from engineering. The using of low carbon-based raw materials in producing new products, increasing product life cycle, reducing material requirements through efficient product design, and recycling waste materials in new product developed are the key contribution from engineering profession in achieving environmental sustainability (EPA, 2017).

Engineering in Carbon Emission Reduction by Increasing Energy Efficiency

The major involvement of engineering in emission reduction by increasing energy efficiency are: increasing of electricity output efficiency in power plant (Markusson *et al.*, 2012a,b; International Energy Agency, 2017), retrofitting low carbon energy supply to industries (EPA, 2017); and, using the CCS and CUS technologies (Peters *et al.*, 2015) in power plants and manufacturing industries. Developing higher energy efficient machinery and using in industry are recognized as key contribution of engineering to slowdown of GW (Kuo and Wu, 2015).

Engineering in Developing Low Carbon Based Raw Materials for Product Processing

Developing product processing with low carbon-based raw material has appeared a significant contribution to reducing carbon emission (Bakhtyar *et al.*, 2017). For example, Fly-ash or cementations materials or calcination materials have utilized directly in the cement kiln as a replacement of MgCO₃ and CaCO₃, which have contributed to reducing 40% energy consumption in the production process with 50% less CO₂ emissions (Mahasenan *et al.*, 2003; Bakhtyar *et al.*, 2017).

Engineering in Developing Carbon Capturing and Storing Technology

A number of technologies have been developed for carbon emission reduction from power plants and manufacturing industries including CCS, CCU, bio-char techniques, mineral carbonization and biological techniques (Falkowski *et al.*, 1998; Wang *et al.*, 2015). However, CCS/CCUs are engineering-intensive activities, which appeared to be the potential way of reducing GHG emission from power plant and manufacturing industries. The potential routes for CCS from power plant and manufacturing

industries are: capturing from emission sources is the first step. At second step carbon transport to depleted oil and gas fields. The third step and final step is to inject carbon into saline aquifers for storing (Hammond *et al.*, 2011; Henderson *et al.*, 2017). In this process around 90% of operational carbon emissions can be captured; and albeit with an additional energy cost of 16%–20% (Davison, 2007; Hammond *et al.*, 2011; Treasury, 2017). For example, a coal-fired power plant with CCS, the carbon emission rate is about $0.12 \text{ kgCO}_2\text{eq(kWh)}^{-1}$. Whereas, a plant without CCS, the emission rate is about $0.96 \text{ kgCO}_2\text{eq(kWh)}^{-1}$ (IPCC, 2014c, 2017b; Leung *et al.*, 2014; UNEP, 2015).

Engineering in CCS technology implementation at pre-combustion stage of power plant

Three major ways are available for capturing clean CO_2 gas from pre-combustion stage power plants (El-Fadel and Massoud, 2001). The Sorbents and sorbent-enhanced water gas shift technology, Oxy-fuel combustion process, and membrane separation are the proven technologies used in power plants for carbon capturing (ECN, 2013; Spigarelli and Kawatra, 2013). Sorbents and sorbent-enhanced water gas shift technology is a pressure swing cycle and in this technology, hydro-talcite sorbent has appeared as an efficient media (Da Costa *et al.*, 2013). The basic principle of an Oxy-fuel process is of using oxygen in pre-combustion stage of coal fire instead of air. This is an advanced novel technology has the potential to capture over 98% of operational CO_2 emission from power plant (Anderson and Newell, 2004; Bjerger and Brevik, 2014; Lockwood, 2017). Membrane-based CCS is an engineering and cost-intensive process, and dedicated polymer membranes are well suited to separate CO_2 from exhaust gas stream. In this process, about 90% CO_2 retain in high-pressure side of the membrane (Da Costa *et al.*, 2013). This process offers a few advantages including reducing chemical use in water treatment process of power plant (Anderson and Newell, 2004; Lockwood, 2017).

Engineering in CCS technology implementation at post-combustion stage of power plant

Post-combustion carbon capture technique is applied to separate CO_2 from flue gases from the conventional fossil fuel-fired power plant. This technology has reached nearly a mature stage (Inventys, 2009), and could easily be retrofitted at the relatively low cost to existing power plant (ECN, 2013) by keeping combustion process unchanged. In this process, heat from flue gas is recycled to increase thermal efficiency at a CO_2 production cost below $\$30 \text{ t}^{-1}$ (Anderson and Newell, 2004). It was suggested for further R&D to increase performance of CCS technology in order to reduce operating cost (Anderson and Newell, 2004; Lockwood, 2017).

Engineering Efforts for Carbon Reduction From Coal-Fired Power Plants

Cebucean *et al.* (2014) stated that CO_2 emissions from coal-fired power plants are being reduced in three ways, which are engineering-intensive activities. It was reported that the carbon emission from the coal-fired power plant was reduced from $0.9 \text{ tCO}_2\text{eq(MWh)}^{-1}$ to $0.55 \text{ tCO}_2\text{eq(MWh)}^{-1}$ by increasing thermal efficiency from 33% to 40% (Cebucean *et al.*, 2014).

In the coal-fired power plants, CCS technology has also been successfully implemented in both pre and post combustion stages, which contributed to reducing about 90% carbon emission (Inventys, 2009; Liu *et al.*, 2016; Lockwood, 2017). It was reported that in a coal-fired power plant with CCS technology, the emission rate was only $0.12 \text{ tCO}_2\text{eq(kWh)}^{-1}$ (Cebucean *et al.*, 2014; Lockwood, 2017) at a cost of $\$25 \text{ t}^{-1}\text{CO}_2$ (Davison, 2007; Treasury, 2017). It was also reported that application of CCS may increase coal consumption by 25% with electricity production cost up to 50% (Markusson *et al.*, 2012a,b). Arias *et al.* (2013) and Hilz *et al.* (2015) had addressed this issue and reported that they managed to capture CO_2 at a cost of $\$20 \text{ t}^{-1}\text{CO}_2$ by using calcium looping in CCS technology (Arias *et al.*, 2013).

Engineering Efforts for Carbon Emission Reduction From Gas-Fired Power Plant

The carbon emission ranges from a biogas-fired power plant is $0.4 \text{ tCO}_2\text{eq(kWh)}^{-1}$ to $0.6 \text{ tCO}_2\text{eq(kWh)}^{-1}$ (Scheehle and Kruger, 2006; Laboratory, 2015) at a thermal efficiency of 33% to 39%. By installing of waste energy recycling technology, this emission is currently reduced by 27% through increasing thermal efficiency from 39% to 57% (Campanari, 2002; Report, 2012; Hosseini *et al.*, 2013). Molten Carbonate Fuel Cell (MCFC) seems to be another solution to carbon emission problem of the gas-fired power plant. Jarosław Milewski stated that MCFC has effectively used to reduce 73% CO_2 emissions from a Gas Turbine Power Plant (Campanari, 2002; Sánchez *et al.*, 2011; Milewski and Bujalski, 2012) where the recorded emission was only at $135 \text{ kgCO}_2\text{eq(MWh)}^{-1}$ (Report, 2012; Clemente, 2016). However, Carbon capture, use, and storage appeared to be technologically feasible for solving the carbon emission problem though it increases energy production cost by about 25% (Yeh *et al.*, 2017a,b; Cormos *et al.*, 2013; Anderson and Newell, 2004).

Engineering Efforts for Carbon Emission Reduction From Municipal Solid Waste Based Powerplant

Methane emission from MSW is reduced in two ways. One is engineered landfill for optimizing of the CH_4 formation. The second one is landfill gas capturing for WtE technology. It was reported that an engineered WtE plant could successfully reduce CH_4 emission from 0.5 tt^{-1} MSW to 0.2 tt^{-1} MSW (Morselli *et al.*, 2008).

Methane Capturing for electricity production have well established, and globally over 1000 landfills are operating, which contributes to reducing CH_4 emission significantly (IPCC, 2006). The EPA Landfill Methane Outreach Project reported that 2.6 Tg

CH₄ was captured and utilized in power plant for generating 9 billion kWh of electricity in 2005. In another estimate, it was reported that by the year 2030, methane capturing capacity would be 10.3 Tg globally (EPA, 2009). Barnstead and La stated that CH₄ emission reduction capacity through engineered WtE would be about 1800 tCO₂eq(GWh)⁻¹ by 2030 (Bernstad and La Cour Jansen, 2012). It was also stated that if at least 10% MSW is used engineered WtE, it could contribute to reducing about 30% (12 Tg) methane emission by 2030 (Bernstad and La Cour Jansen, 2012). It was also reported that higher CH₄ collection efficiency with CCS technology is economically and environmentally sustainable options but needs quality inputs from engineering (Rajaeifar *et al.*, 2017).

Engineering Efforts for Carbon Emission Reduction From Cement Manufacturing Plant

Carbon emission reduction from cement plant using CCS technology has appeared to be the sustainable procedure for reducing GW (Bakhtyar *et al.*, 2017; Olivier *et al.*, 2017). It was reported that three types of engineering inputs are employed to reduce carbon emission (Bakhtyar *et al.*, 2017).

The first engineering input is the use of indigenous materials and process technology in order to reduce CO₂ emission. For example; the fly-ash or cementations materials or calcination materials are utilized directly in the cement kiln as a replacement for clay or bauxite. This approach contributes to the reduction of 50% CO₂ emissions (Bjerger and Brevik, 2014). Moving from wet to dry process with calciner could also reduce up to 50% of requisite energy and almost 20% of CO₂ emissions in the cement production process (IEA, 2007a,b; Bjerger and Brevik, 2014). The second engineering input is the retrofitting of advanced technology into the existing plants for decreasing the use of MgCO₃ and CaCO₃, this approach contributes to reducing a significant amount carbon emission.

The third engineering inputs are the development and retrofitting of the cost-effective CCS technology in flue gas stream. It was reported CCS technology has been successfully utilized to reduce carbon emission from 0.50 tCO₂eqt⁻¹cement to 0.20 tCO₂eqt⁻¹Cement (Bjerger and Brevik, 2014).

Engineering Efforts for Carbon Emission Reduction From Aluminum Processing Plant

Few ways have been employed by engineers to reduce carbon emission from Aluminum processing. The most popular way is to use advanced technology to reduce energy consumption; in this regards, Norwegian engineering had made a successful progress (Bjerke *et al.*, 2004; Kuo and Wu, 2015). It is reported that carbon emission intensity from Aluminum industry was 4.0 tCO₂eqt⁻¹ in 1993; 1.3 tCO₂eqt⁻¹ in 2014. Indeed, this progress had made by increasing energy efficiency in the production process (Zhang *et al.*, 2015).

The second type of engineering inputs is the use of non-carbon anode which contributes to reducing energy consumption about 25% and resulting in a reduction of over 40% GHG emissions (IAI, 2009a; International Aluminum Institute, 2009b; Bjerger and Brevik, 2014). The third type of engineering inputs was the recycling of waste Aluminum in producing new products which contributed to reducing a significant amount of energy consumption and carbon emission (IAI, 2009a; International Aluminum Institute, 2009b). The fourth type of engineering inputs was the use of low carbon energy in the production process such as hydropower plant. It was reported that a plant with electricity from hydropower plant emission was 0.45 tCO₂eqt⁻¹Aluminum (Argonne, 2009; IAI, 2009a; International Aluminum Institute, 2009b), whereas it was 1.3 tCO₂eqt⁻¹ Aluminum when used coal-fired power plant.

Engineering Efforts for Carbon Emission Reduction From Iron-and Steel Industry

A significant achievement has made by engineers to reduce carbon emission from Iron and steel industry by using three methods; which contributed to reducing from 1.3 tCO₂eqt⁻¹ steel to 0.2 tCO₂eqt⁻¹ (Anderson and Newell, 2004; IEA, 2007a,b; Casillas *et al.*, 2015). Energy efficiency increasing in Iron and Steel production process appeared a significant achievement. In this process, best available technologies had been used for recovering waste thermal energy from flue gas and reused (Kuo and Wu, 2015; Seoane *et al.*, 2015). It was reported that in this process about 30% energy consumption had reduced and net emission appeared about 0.9 tCO₂t⁻¹ Steel instated of 1.3 tCO₂t⁻¹ Steel (LBNL, 1999).

Supplying low carbon energy from hydropower plants to iron and steel industries was considered a successful input from engineering for reducing about 60% carbon emission. The low car carbon energy supply has contributed to reducing emission from 1.3 tCO₂t⁻¹ Steel to 0.45 tCO₂t⁻¹ Steel (LBNL, 1999; UNIDO, 2011).

Another value-added engineering input into Iron and steel production process was of installing CCS technology. The CCS had applied in both pre and post combustion stage of fossil fuel based power plant used in iron and steel industries. The CCS contributed to reduce carbon emission about 90%. It was reported that a plant with CCS technology, the net emission appeared 0.15 tCO₂t⁻¹ Steel instead of 1.3 tCO₂t⁻¹ Steel (IEA, 2007a,b).

Engineering Efforts for Carbon Emission Reduction From Palm Oil Mill

Three engineering activities have recorded in published journals for reducing CO₂ and CH₄ emission from palm oil mills (Ng *et al.*, 2011; The statistics portal, 2018). The total carbon emission from palm plantation; oil refinery at mills for CPO production and

POME processing are accounted for $30 \text{ tCO}_2\text{eqt}^{-1}\text{CPO}$ (Zutpen and Van, 2005; Damen and Faaij, 2006) which reduced to about 40% by using engineered plant machinery (IPCC, 2009).

It has been reported and the using of advanced technology in palm oil industry energy consumption reduced from $90 \text{ (kWh)}^{-1}\text{CPO}$ to $50 \text{ kWh}^{-1}\text{CPO}$ which contributed to reducing 40% carbon emission (Ma *et al.*, 2010). The second and third ways of engineering inputs were of using anaerobic reactor for CH_4 capturing from POME treatment (Kaewmai *et al.*, 2013). The most effective anaerobic reactor developed and used are expanded granular sludge bed reactor (Oosterveer, 2014), up-flow anaerobic Sludge-Fixed film reactor and anaerobic Fluidized Bed single stage reactor (Zhang *et al.*, 2008).

Anaerobic reactor appeared as an efficient technology for methane capturing and using in electricity production. It was reported that CH_4 emission reduced successfully from $9.0 \text{ m}^3\text{CH}_4\text{t}^{-1}$ POME to $5.5 \text{ m}^3\text{CH}_4\text{t}^{-1}$ POME by using efficient CCS and CCUS technology. However, Sridhar and Adeoluwa (2009), Ng *et al.* (2011) reported that CH_4 and CO_2 capturing capacity of an anaerobic reactor is up to $28 \text{ m}^3 \text{ t}^{-1}\text{POME}$, which is high value-added innovation in engineering domain (Annual report, 2016).

Engineering Efforts for Carbon Emission Reduction Water Treatment Industry

Engineering efforts have been deploying in three ways to reduce carbon dioxide, methane, and nitrous oxide (N_2O) emission from water treatment industry (Borja and Banks, 1994; Scheehle and Doorn, 2001). One way of engineering inputs to reduce carbon emission is of increasing energy efficiency by installing advanced technology in water treatment plant. In this way, about 20% carbon emission has reduced from water treatment processing (Choorit and Wisarnwan, 2007). The second way of engineering inputs to reduce carbon emission is of installing anaerobic digester in the treatment process for capturing CH_4 (Seoane *et al.*, 2015). It has been reported that anaerobic reactor has successfully employed to capture over 90% CH_4 from water treatment plant (Hasanbeigi, 2010).

The third way of engineering inputs for carbon capturing is the employment of bio-engineering. Algae production in polluted wastewater has appeared a potential CO_2 sink (Falkowski *et al.*, 1998). It was reported that Algae have the ability to sequester about 40% CO_2 (Hasanbeigi, 2010). It was reported that Algae have the capability of sequestering CO_2 two times higher than terrestrial species.

Conclusion and Summary of Findings

This review article presents the research outcomes published in various scientific journals on carbon emission from fossil fuel based power plants and manufacturing industries. The study aims to share reviewed information with the concern stakeholders for enabling them to make a plan for conducting R&D towards reducing carbon emission for mitigating global warming.

Almost 90% papers studied for this review have stated that fossil fuel burning, energy inefficiency and using of carbon-based raw materials by some heavy industries are the main causes of carbon emission, which contributes to increasing global surface temperature. It was also reported that fossil fuel shall be replaced by low carbon energy in order to maintain carbon density in the atmosphere within 445 ppm for keeping temperature rise well below 2°C compare to pre-industrial development level.

The published papers have indicated that various technologies have developed and retrofitted into fossil fuel power plants and manufacturing industries for capturing carbon aiming to store and use in order to reduce carbon density in the air. It appears that installation of CCS technology is cost and engineering intensive activities, but its contribution to carbon emission reduction is significantly high.

It is also evident that CCS and CCU technologies are contributing to increase energy production cost, but dedicated R&D would be able to reduce cost to an acceptable limit. However, it was stated in various papers that cost of carbon reduction will offset by saving repair cost of infrastructure expected to be damaged due to climate change effects.

Acknowledgement

Authors would like to acknowledge the financial supports received from Ministry of Agriculture, State of Sarawak Malaysia under grant GL/F02/ORSSG/2016. Authors are pleased to offer special thanks to management and academic staff of Engineering Faculty and RIMC, Universiti Malaysia Sarawak.

See also: Waste Resources Recycling in Achieving Economic and Environmental Sustainability: Review on Wood Waste Industry

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Rubber Scrap as Reinforced Material in the Production of Environmentally Friendly Brake Lining

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Introduction

Over the years, asbestos has been used as reinforcement material in brake lining production as a result of its good physical and tribological properties. However, recent studies have shown that asbestos poses a great health hazard which can result from its handling and breathing (NIH, 1989). As a result, it has lost its favor, resulting in the need to explore alternative materials. Hence, efforts by researcher have been geared toward finding a possible replacement for asbestos in the production of brake linings. These were exemplified by the work of several researchers who utilized other materials such as palm kernel shell (PKS), coconut shell, metal fibers, etc., for inclusion in brake lining in order to overcome environmental pollution (Ikpambese *et al.*, 2016; Fono-Tamo and Koya, 2013). Also, a non-asbestos friction lining material was developed by Ibhadode and Dagwa (2008) using an agro-waste material – palm kernel shell, as a reinforcement material. Palm kernel shell (PKS) which was used as a reinforcement material was selected due to its favorable properties which superseded other agro-waste. The developed automobile disk brake pads using the derived friction material and the test results obtained indicated that high wear rate was observed on the PKS pad at high vehicular speeds of 80 km h⁻¹ and above. Zaharudin *et al.* (2012) adopted Taguchi method to carry out a study on the effect of manufacturing parameters on the properties of friction materials. The parameters studied were molding pressure, molding temperature, and the molding time using semi-metallic friction materials and other additives. Physical properties such as hardness and specific gravity as well as tribological properties (wear and fade) were selected as responses and optimized. Molding pressure was observed to be the most significant factor that affected the physical and tribological properties.

Similarly, Bashar *et al.* (2012) carried out a study on the selection and production of composite brake pad by varying constituent compositions. Coconut shell powder was used in the study including other additives such as cast iron fillings, silica, epoxy resin, a catalyst, and an accelerator. Some of the tests conducted in the study included tensile strength, compressive, hardness, impact, wear, and corrosion. Results obtained were in close agreement with commercial-based friction materials and from the results obtained, it was concluded that the developed composite brake pad had much better mechanical properties than the commercial brake pad. Higher content of grounded coconut powder showed a lower braking impact, comprehensive strength, and hardness. Aigbodion *et al.* (2010) also in an effort to find a replacement for asbestos also developed an asbestos-free brake pad using a bio-waste material, bagasses. The bagasses used in the study were sieved into mesh sizes of 100, 150, 250, 350, and 710 μm . The sieved bagasse powder was used to produce brake pad containing of 70% bagasse–30% resin using compression molding machine. The result showed that samples containing 100 μm (70% bagasse–30% resin) gave favorable properties than other brake pad samples which were tested. It was observed that the lower the sieve sizes of bagasse, the better the properties. The results obtained for the 100 μm sieve size, commercially available asbestos-based brake pad and optimum formulation laboratory palm kernel-based pad by Ibhadode and Dagwa (2008) are all in agreement. Ruzaidi *et al.* (2011) studied the morphology and wear properties of brake pad with the view of replacing asbestos with palm ash and polychlorinated biphenyl (PCB) waste mixed together with metal filler and thermosetting resin binder. Five different ratios were examined and the test results showed that the higher the composition of the palm ash, the better wear, and mechanical properties.

In this study, rubber scrap (tire peels) was used as reinforced material instead of asbestos with other constituents in the production of brake lining. Effect of manufacturing parameters on the tribological and physical properties of the formulated brake lining using Taguchi method will be investigated.

Materials and Methods

Materials

The four materials used for the production of brake lining are reinforced material (rubber scrap – tire peels), friction modifier (graphite), binder (phenolic resin), and abrasive (aluminum oxide).

Method

Material preparation

- The rubber scrap (tire peels) used as reinforced material used in this study was sourced from Altimax RT General Automobile Tire (DOT 650F 3T3). It was cut into pieces and washed thoroughly to get rid of dirt which may have possibly combined with the rubber tire powder. The tire pieces was dried in the sun for 1 week and grounded into fine powder using a bench grinding machine (DT 200A, 550 W). The powder was sieved using a sieve size $\leq 100 \mu\text{m}$ to eliminate any fibers that may be present (Ikpambese *et al.*, 2016; Aigbodion *et al.*, 2010).
- Graphite used in this study as friction modifier used was obtained from used 1.5 V dry cell batteries (TIGER HEAD BRAND). The graphite rod was extracted from the used batteries and crushed to smaller sizes using a hammer. It was then pounded using a mortar and pestle and sieved using sieves size $\leq 100 \mu\text{m}$.
- The phenolic resin used as binder in this study was phenol formaldehyde. It was prepared in the Biochemistry laboratory of Federal University of Technology, Minna, using the procedures outlined by Seong Jin Kim *et al.* (2003).
- The aluminum oxide (CAT. NO. 34143; LOT. NO. 44100) used as abrasive for this study was purchased from a chemical store in Kaduna, Nigeria.

Brake lining formulation

The formulation of brake lining sample consists of a series of operations including mixing, cold and hot pressing, cooling, post-curing, and finishing. In the production of the friction lining, the weights of the rubber powder, phenol-formaldehyde resin, friction modifier (graphite), and abrasive (aluminum oxide) was based on 176 g weight of commercial brake pad (Ikpambese *et al.*, 2016). Hence, the following percentage by weight of rubber powder (45), phenolic resin (30), graphite (15), and aluminum oxide (10) were used for the development of brake lining material. Phenolic resin was poured into a container, followed by the addition of small quantity of sulphuric acid (catalyst) and mixed thoroughly. The required quantity of rubber, aluminum oxide and graphite powders were poured into a separate container and mixed thoroughly manually. The mixture was poured into the container holding the resin and further stirred thoroughly to obtain homogeneous mixture. The mixtures were then placed in a mold of size $116 \times 116 \times 10 \text{ mm}$. The compression and curing of the composite samples was carried at the Polymer Workshop of Nigeria Institute of Leather Research and Science Technology, Samaru, Zaria. A compression molding machine (model; 3851-0, CARVER) was used for the compression of each composite sample. The experimental set up was based on design of experiment (DOE) via Taguchi method and three production parameters namely: molding temperature, pressure, and curing time were considered for experimentation. Hence, there were three input parameters and for each parameters, three levels were assumed as shown on Table 1. For a three-factor-three-level experiment, Taguchi had specified $L_9 (3^3)$ orthogonal array for experimentation as shown on Table 2.

Evaluation of Formulated Brake Lining Properties

Impact strength

The impact test was carried out using a Charpy impact testing machine (Norwood instrument, model No.: 412-07-0715269C) with each test sample produced to the size $80 \times 15 \times 5.5 \text{ mm}$ dimensions, 450 notch of 1.5 mm depth, and 0.20 mm root radius machined from different composition. The impact energy of the testing machine ranges from 0 to 25 J with a pendulum striking at a speed of 2.887 m s^{-1} . The testing method involved fixing each test samples on the anvil of the testing machine and then setting the pendulum at a certain height. The pendulum is then released to impact the specimen at the opposite end of the notch in order to produce a fractured surface. The absorbed energy which produced the fractured surfaces for all the test samples were recorded. The impact strength can be calculated using the eq. [1]:

$$\text{Impact strength } (S_i) = \frac{\text{Absorbed energy } (E)}{\text{Thickness of specimen } (t)} \quad [1]$$

Hardness

The hardness test was conducted using a Shore A hardness tester (Durometer) with each samples prepared to size $60 \times 15 \times 5.5 \text{ mm}$. According to ASTM D2240 standard, three prepared specimens from the same sample of different composition were subjected to applied pressure by a calibrated spring to a spherical indenter and an indicating device which measures the depth of indentation.

Tensile strength

The tensile strength test was performed using Tensometer (MONSANTO; Serial No. 05232). The Tensometer consist of two metal fixtures which clamp the test samples prepared to the size $90 \times 16 \times 5.5 \text{ mm}$. The test specimens were prepared and labeled in compliance with ASTM D638 dumbbell parameters. Specimens dimension was measured using a Vernier caliper of accuracy 0.01 mm. With the machine reading set at 0.00 N, the test was performed by clamping each prepared specimen from different

Table 1 Manufacturing parameters and their levels

Factor	Unit	Level 1	Level 2	Level 3
Molding pressure (MP)	MPa	0.6	0.7	0.8
Molding temperature (MT)	°C	130	150	170
Curing time (CT)	Minutes	8.0	10.0	12.0

Table 2 Experimental design layout using Taguchi orthogonal array L₉ (3³)

S. No.	MP (MPa)	MT (°C)	CT (min)
1	1	1	1
2	1	2	2
3	1	3	3
4	2	1	2
5	2	2	3
6	2	3	1
7	3	1	3
8	3	2	1
9	3	3	2

composition between two metal fixtures. A male punch was then forced into a hole in the fixture thereby causing it to shear along the edge of the hole. The Tensometer was used to push the punch until failure occurs. The tensile strength was determined using the relationship in eq. [2]:

$$\text{Tensile strength } (\delta) = \frac{\text{Max force } (P_{\max})}{\text{Area of sheared edge } (A)} \quad [2]$$

Corrosion rate

Concentrated sulphuric acid was used and mixed with distilled water in the ratio of 3 ml/0.5 ml acid to water. Before immersion in the corrosion medium, the weight and dimension of each specimen taken from the different composition was measured using a Vernier calliper and electronic scale of accuracy 0.01 and recorded. Each specimen were cleansed using distilled water and dry cloth and then immersed into the corrosion medium for 72 h with routine removal of specimens for analysis after every 24 h. During the routine removal, the samples were carefully cleaned and weighed before inserting them back into the corrosion medium and the weight loss was noted (Bashar *et al.*, 2012). The corrosion rate (C_r) was calculated using eq. [3]:

$$\text{Corrosion rate } (C_r) = \frac{k \times \Delta w}{\rho \times A \times t} \quad [3]$$

where $k = \text{constant} = 87.6 \text{ (mm year}^{-1}\text{)}$, $w = 1 \text{ g (1000 mg)}^{-1}$, $A = \text{surface area} = 2[(l \times b) + (l \times t) + (b \times t)] \text{ (mm}^2\text{)}$, $l = \text{length}$, $b = \text{width}$, $t = \text{thickness}$, and $\rho = \text{density}$.

Oil and water absorption

A specimen of $90 \times 16 \times 5.5 \text{ mm}$ dimension was prepared from each samples of formulated composite brake lining material. Each sample was dried in an oven to constant weight. The initial weight of each specimen was recorded using a digital weighing balance. The specimens were then immersed in distilled water and brake fluid (oil), respectively, at room temperature for a period of 3 days. After every 24 h, specimens were taken out and the surface water and oil wiped off with a cloth and weighed. The new weight of each sample during the routine removal was recorded. The weighing was done within 30 s in order to avoid any error that may occur as a result of evaporation. The weight change in oil and water were calculated by subtracting initial weight from the new weight after 72 h of soak. The percentage water or oil absorption by weight after 24 h was determined using eqs. [4] and [5]:

$$\text{Percentage water } (\% W_a) = \frac{\Delta w}{w_1} \times 100 \quad [4]$$

$$\text{Percentage oil } (\% O_a) = \frac{\Delta w}{w_1} \times 100 \quad [5]$$

where $\Delta w = \text{change in weight}$ and $w_1 = \text{initial weight of specimen}$.

Co-efficient of friction

The coefficients of friction of samples were determined using an inclined plane (NORWOOD Instrument Ltd., model No. 14678) of angular calibration which can read between 0° and 45°. The weights used during the test vary from 0.1 to 60 N; while the weight of the specimen attached to the steel plate was determined using a spring balance. These different weight sizes were attached with the aid of an adhesive (STICKO, super glue, model No. COCNO011421). The samples were cleaned of any surface dirt using a dry cloth and then attached to a mild steel plate with the aid of an adhesive. The weight of each test sample attached to the steel plate was measured using a spring balance. With the addition of known weights to the test sample which was placed on the smooth surface of the incline plane set at 0°. The incline plane was operated by raising the plane surface from the horizontal position toward the vertical position through various angles. The process was immediately stopped when the sample began to slide down the plane surface and the angle at that particular point recorded. The coefficient of friction was obtained by calculating the tangent of the angle at which the test sample started to slide down the smooth surface of the plane (Fono-Tamo and Koya, 2013). Load of various weights were placed on each sample and the experiment repeated. The average angles at various loads for the nine samples were then calculated and the corresponding coefficient of friction obtained. The coefficient of friction was evaluated using eq. [6]:

$$\mu = \tan \theta \quad [6]$$

where, μ is the coefficient of friction and θ is the sliding angle in degree.

Wear rate

The wear rate test was conducted using the method reported by other researchers (Bashar *et al.*, 2012; Aigbodion *et al.*, 2010). The dimension of each specimen was measured using caliper of an accuracy of 0.01 cm. The test was conducted by placing each sample clamped in a rigid position along the disk of the grinding machine (model: MASTER bench grinder, MD-250; 220 V – 50 Hz of diameter 250 mm, and speed of 2950 rpm for a period of 5 s). The weights of the samples before and after the grinding were recorded. The difference in the weight from each sample was calculated as the loss in weight. The same procedure was repeated for a period of 10, 20, 30, 40, and 50 s for each sample. The wear rate was calculated using the following relation in eq. [7]:

$$\text{Wear rate } (W_r) = \frac{\text{Weight loss } (\Delta w)}{\text{Sliding distance } (S)} = \frac{\Delta w}{S} (\text{g m}^{-1}) \quad [7]$$

where weight loss (Δw) = weight difference before and after the grinding (g), sliding distance (S) = $2\pi D N t$ (m), N = speed of grinding engine (rpm), D = disk diameter (m), t = time of exposure of each sample to grinding machine (s).

Determination of thermal behavior of formulated brake lining

The thermal behavior of formulated brake lining was studied using thermogravimetric analysis. Sample of brake lining for this analysis was prepared with optimal manufacturing parameters for wear rate. The analysis took place under nitrogen environment at a flow rate of 20 ml min⁻¹ and pressure of 2.5 bars using PerkinElmer TGA4000 model.

Experimental Results and Data Analysis

The results for all the properties of formulated brake lining are shown on Table 3 for the nine samples. The significant effect of the manufacturing parameters on each property is shown using analysis of variance (ANOVA) method, while the optimized values of the manufacturing parameters for the properties of the brake lining formulated are shown using the main effect plots in Table 4. In determining the optimized values for the manufacturing parameters signal to noise ratio (S/N ratio) become viable means to achieve that. The S/N ratio has three categories of quality characteristics which includes; larger-the-better, nominal-the-better, and smaller-the-better. Therefore, the S/N ratios for each property (output variable or response) were determined using Minitab 16 software. Therefore, the optimum level of the process parameters is the level which has the highest S/N ratio shown on the main effect plot. The confidence level specified for all the analysis is 95%.

ANOVA

The ANOVA results obtained for all the variables investigated show how each of the manufacturing parameter affect the output variables. For instant, hardness value show that, molding pressure (77.93%) has the most significant effect on the hardness value, while melting temperature (2.99%) has the least significant effect. The influence of manufacturing parameters on impact strength show that curing time (50.43%) has the most influence on the impact strength follow by molding pressure (39.05%) as shown in Table 5.

Table 3 Experimental results for brake lining properties

Exp. No.	Impact strength (J mm ⁻¹)	Hardness (ShoreA)	Tensile strength (MPa)	Corrosion rate (10 ⁻⁵ mm year ⁻¹)	Oil absorption (%)	Water absorption (%)	Co-efficient of friction	Wear rate (mg m ⁻¹)
1	0.647	55.0	55.68	7.606	3.701	1.39	0.64	3.60
2	0.900	52.7	58.30	9.201	3.912	1.48	0.63	3.85
3	1.033	50.3	60.23	4.095	4.571	1.38	0.61	2.76
4	0.888	51.3	51.68	9.214	3.938	2.02	0.58	2.84
5	0.782	57.0	56.82	4.292	3.946	2.88	0.56	2.10
6	0.691	63.0	40.92	6.098	5.645	1.64	0.53	2.52
7	1.152	72.0	36.36	5.841	5.696	2.87	0.52	2.77
8	0.961	75.3	38.64	5.395	5.526	1.67	0.53	1.92
9	0.830	79.3	43.18	6.847	5.765	0.93	0.51	2.24

Table 4 Results of the S/N ratio for brake lining properties

	Impact strength, η (dB)	Hardness, η (dB)	Tensile strength, η (dB)	Corrosion rate, η (dB)	Oil absorption, η (dB)	Water absorption, η (dB)	Co-efficient of friction, η (dB)	Wear rate, η (dB)
1	-3.78	34.81	34.91	82.38	-11.37	-2.86	-3.88	-11.13
2	-0.92	34.44	35.31	80.72	-11.85	-3.41	-4.01	-11.71
3	0.28	34.03	35.60	87.76	-13.20	-2.80	-4.29	-8.82
4	-1.03	34.20	34.27	80.71	-11.91	-6.11	-4.73	-9.07
5	-2.14	35.12	35.09	87.35	-11.92	-9.19	-5.04	-6.44
6	-3.21	35.99	32.24	84.30	-15.03	-4.30	-5.52	-8.03
7	1.23	37.15	31.21	84.67	-15.11	-9.16	-5.68	-8.85
8	-0.35	37.54	31.74	85.36	-14.85	-4.45	-5.51	-5.67
9	-1.62	37.99	32.71	83.29	-15.22	0.63	-5.85	-7.01

Table 5 ANOVA for impact strength

Factor	DOF	SS	MS	F-ratio	p-value
MP	2	0.0576	0.0288	4.6392	39.047
MT	2	0.0031	0.0016	0.2497	2.1015
CT	2	0.0744	0.0372	5.9923	50.435
error	2	0.0124	0.0062		8.4167
Total	8	0.1475	0.0184		100.00

Molding pressure has the most significant effect on the tensile strength of the brake lining material with 75.97% and this is followed by curing time with 10.41% significant effect. The corrosion rate of the brake lining formulated is influenced by curing time (71.56%) and melting temperature (19.21%) as shown in [Table 6](#).

The ANOVA result for oil absorption show that molding pressure (63.28%) has the most significant effect on the oil absorption, followed by molding temperature (23.62%). While curing time (40.88%) has the most significant effect on the water absorption property of the formulated brake lining as shown in [Table 7](#).

It was observed that molding pressure (61.46%) has the greatest effect on the wear rate of the formulated brake lining followed by melting temperature (15.76%). While the result obtained for co-efficient of friction as shown in [Table 8](#), indicate that molding pressure (90.11%) has the most significant effect on the coefficient of friction, follow by melting temperature (7.62%).

Signal-to-Noise Ratio

In order to obtain the optimal value of the manufacturing parameters for different variables, the three categories of quality characteristics of S/N ratio must be applied correctly. Hence, the larger-the-better will be applied for the hardness value as expressed in eqn [8]:

$$S/N \text{ ratio} = -10 \log \frac{1}{n} \left(\sum_{i=1}^n 1/y_i^2 \right) \quad [8]$$

Table 6 ANOVA for corrosion rate

<i>Factor</i>	<i>DOF</i>	<i>SS</i>	<i>MS</i>	<i>F-ratio</i>	<i>p-value</i>
MP	2	1.33	0.665	1.0230	4.670
MT	2	5.47	2.735	4.2072	19.21
CT	2	20.38	10.190	15.675	71.56
Error	2	1.3002	0.650		4.565
Total	8	28.480	3.560		100.0

Table 7 ANOVA for water absorption

<i>Factor</i>	<i>DOF</i>	<i>SS</i>	<i>MS</i>	<i>F-ratio</i>	<i>p-value</i>
MP	2	0.875	0.4375	5.284	24.268
MT	2	1.091	0.5455	6.588	30.259
CT	2	1.474	0.7370	8.901	40.881
Error	2	0.166	0.0828		4.5930
Total	8	3.606	0.4507		100.00

Table 8 ANOVA for coefficient of friction

<i>Factor</i>	<i>DOF</i>	<i>SS</i>	<i>MS</i>	<i>F-ratio</i>	<i>p-value</i>
MP	2	0.0176	0.00881	62.0493	90.1105
MT	2	0.0015	0.00075	5.2465	7.61915
CT	2	0.0002	0.00008	0.5634	0.81816
Error	2	0.0003	0.00014		1.45224
Total	8	0.0196	0.00245		100.000

where γ =responses for the given factor level combination, n =number of responses in the factor level combination. It is observed from the main effect plot using the S/N ratio of hardness values that the optimal manufacturing parameters are molding pressure: 0.8 MPa (level 3), melting temperature: 170 °C (level), and curing time: 8 min (level 1) as shown in Fig. 1.

And for the impact strength, the optimal manufacturing parameters are molding pressure: 0.8 MPa (level 3), melting temperature: 150 °C (level 2), and curing time: 12 min (level 3) using S/N ratio, the larger-the-better quality characteristics. Similarly, the S/N ratio, the larger-the-better quality characteristics was used to obtain the optimized values of the manufacturing parameters for the tensile strength. Fig. 2 shows the optimized values of the manufacturing parameters at molding pressure: 0.6 MPa (level 1), melting temperature: 150 °C (level 2), and curing time: 10 min (level 2).

In the same vein, the optimal values of the manufacturing parameters for corrosion rate are at molding pressure: 0.8 MPa (level 3), melting temperature: 170 °C (level 3), and curing time: 12 min (level 3) using the smaller-the-better S/N ratio quality characteristic as depicted in eqn [9]:

$$\eta = -10 \log \left(\frac{1}{n} \sum_{i=1}^n y_i^2 \right) \quad [9]$$

where η is the S/N ratio for the lower-the-better case, y_i is the measured quality characteristic for the i th repetition, and n is the number of repetitions in a trial.

The optimization values for the oil absorption using the smaller-the-better quality characteristics for the S/N ratio quality characteristics have been determined. The optimal values are: molding pressure: 0.6 MPa (level 1), melting temperature: 130 °C (level 1), and curing time 10 min (level 2) as shown in Fig. 3.

The optimized values obtained for co-efficient of friction are molding pressure: 0.6 MPa (level 1), melting temperature: 130 °C (level 1), and curing time: 10 min (level 2) using the larger-the-better quality characteristics for the S/N ratio quality characteristic. While wear rate as depicted in Fig. 4 show the optimized values at molding pressure: 0.8 MPa (level 3), melting temperature: 150 °C (level 2), and curing time: 12 min (level 3) using the smaller-the-better quality characteristics for the S/N ratio quality characteristic.

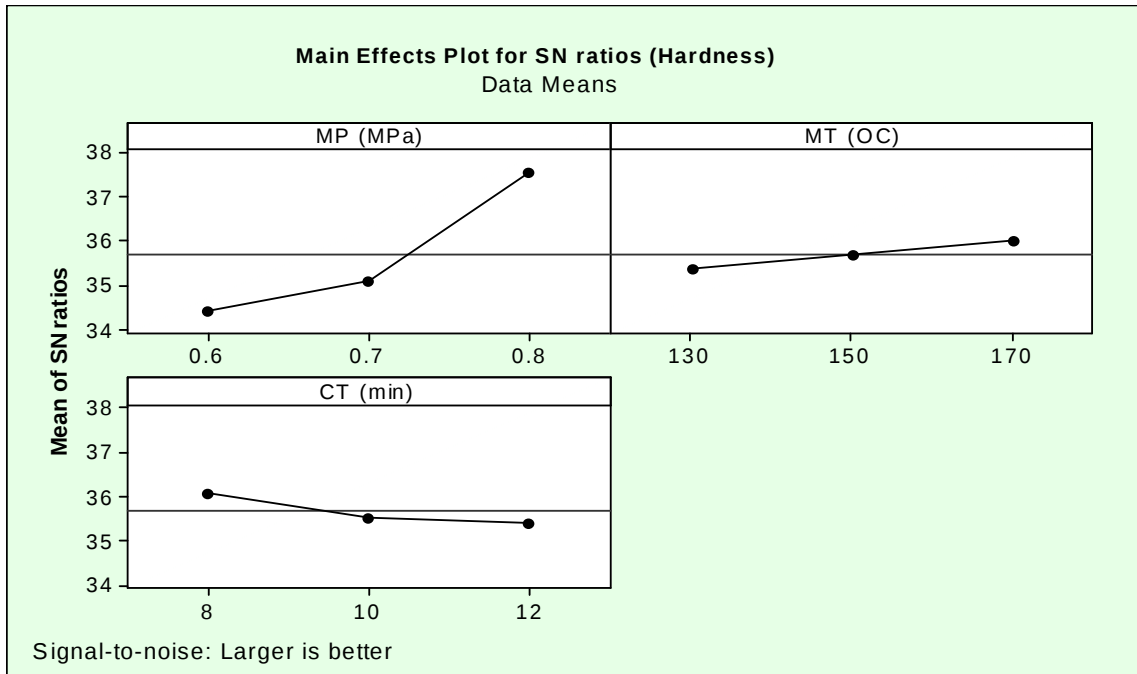


Fig. 1 Main effect plots for hardness.

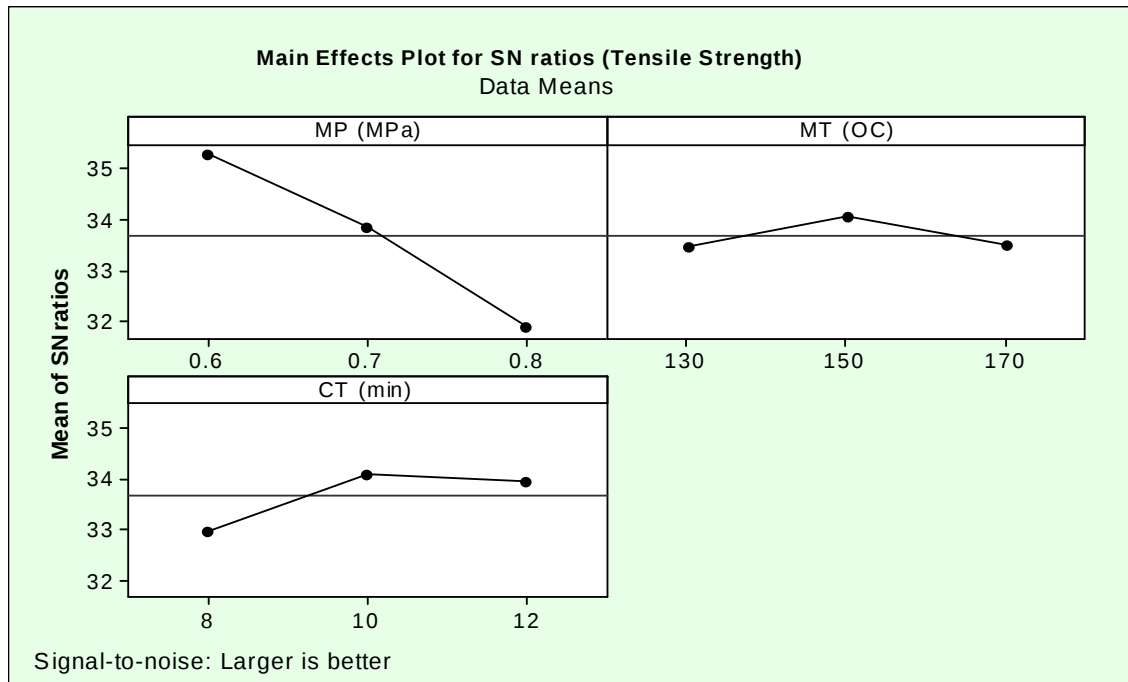


Fig. 2 Main effect plots for tensile strength.

Thermal Behavior of Formulated Brake Lining

The thermal degradation profile of the formulated brake lining is presented in [Fig. 5](#). The sample degraded between 149.89 and 478.36 °C, with a peak degradation at temperature 394.8 °C. This suggest that the formulated brake lining may be used for a system whose braking temperature does not exceed 300 °C.

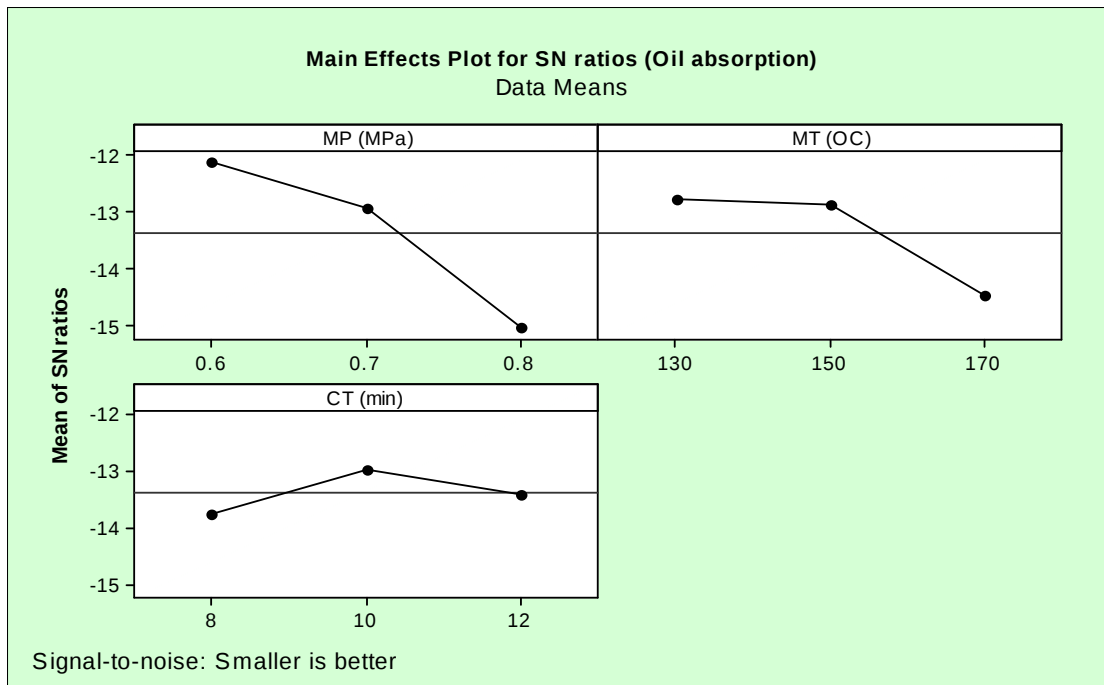


Fig. 3 Main effect plots for S/N ratio for oil absorption.

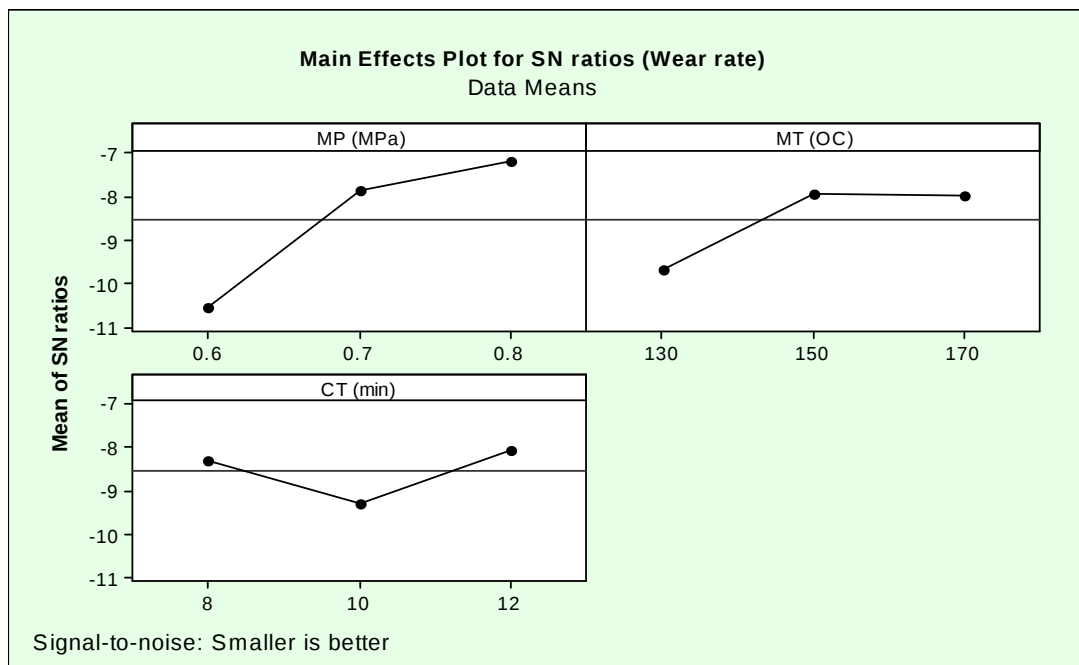


Fig. 4 Main effect plots for wear rate.

Confirmation Test

Regression equations were obtained for all the responses using MINTAB 16 software. The optimized values were used to obtain the experimental values for each of the variable investigated. The same optimized values were used to calculate for each variable.

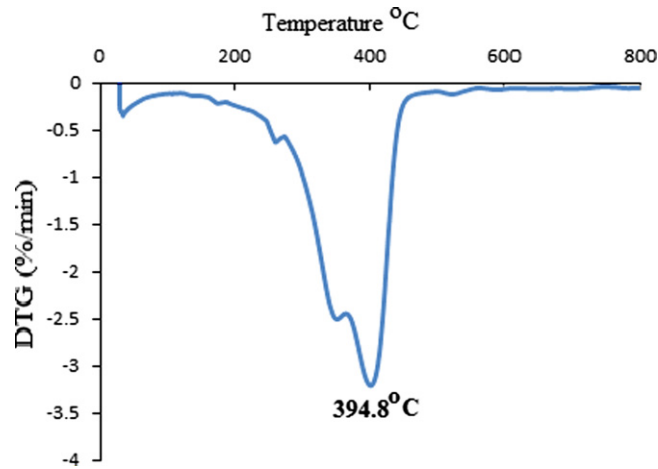


Fig. 5 Thermal behavior of formulated brake lining.

Table 9 Validation test percentage error

Variable	Calculated value	Experimental value	Percentage error (%)
Impact strength	0.93	0.95	2.11
Hardness	77.57	76.85	0.9
Tensile strength	0.82	0.81	1.22
Corrosion rate	4.31	4.29	0.46
Oil absorption	3.93	3.701	5.83
Water absorption	1.22	1.28	4.69
Co-efficient of friction	0.63	0.64	1.56
Wear rate	2.11	1.98	6.16

Table 9 show the comparison of the two values. For each of the variable, the appropriate regression equations used are as follows:

$$\text{Impact strength } (I_s) = 0.062 + 0.605\text{MP} - 0.00111\text{MT} + 0.0557\text{CT} \quad [10]$$

$$\text{Hardness } (H) = -24.5 + 114\text{MP} + 0.119\text{MT} - 1.17\text{CT} \quad [11]$$

$$\text{Tensile strength } (\sigma) = 98.6 - 93.4\text{MP} + 0.0051\text{MT} + 1.51\text{CT} \quad [12]$$

$$\text{Corrosion rate } (C_r) = 20.9 - 4.70\text{MP} - 0.0468\text{MT} - 0.406\text{CT} \quad [13]$$

$$\text{Oil absorption } (O_a) = -3.62 + 8.00\text{MP} + 0.0220\text{MT} - 0.055\text{CT} \quad [14]$$

$$\text{Water absorption } (W_a) = 1.27 + 2.03\text{MP} - 0.0194\text{MT} + 0.203\text{CT} \quad [15]$$

$$\text{Coefficient of friction } (\mu) = 1.06 - 0.533\text{MP} - 0.000750\text{MT} - 0.00083\text{CT} \quad [16]$$

$$\text{Wear rate, } W_r \text{ (mg m}^{-1}\text{)} = 9.01 - 5.47\text{MP} - 0.0141\text{MT} - 0.0342\text{CT} \quad [17]$$

where MP is molding pressure, MT is melting temperature, and CT is curing time.

Conclusions

The study presented Taguchi method as a reliable method of determining the optimal manufacturing parameters for the improved properties of formulated brake lining using rubber scrap as reinforced material. ANOVA shows that the molding pressure (77.93%) has the most significant effect on the hardness value, while melting temperature (2.99%) has the least significant effect. While the influence of manufacturing parameters on impact strength show that curing time (50.43%) has the most significant influence on the impact strength follow by molding pressure (39.05%). It was observed that the molding pressure: 0.8 MPa

(level 3), melting temperature: 150 °C (level 2), curing time: 12 min (level 3) and molding pressure: 0.6 MPa (level 1), melting temperature: 130 °C (level 1), curing time: 10 min (level 2) are the optimal manufacturing parameters respectively for wear rate and co-efficient of friction. The sample formulated from the wear rate optimal manufacturing parameter degraded between 149.9 and 478.4 °C, with a peak degradation at temperature at 394.8 °C. The confirmation tests obtained for all properties investigated shows a close agreement with the calculated results.

See also: Challenges and Developments of Rubber Materials as Vibration Isolators

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Scaling Up and Intensifying Stakeholders Engagement for Evidence-Based Policymaking: Lessons Learned

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Abbreviations

CDM Clean development mechanism
EC European commission
ETS Emissions trading system
EU European union
IEA International energy agency
JRC Joint research centre
NGO Non-Governmental organisation

OECD Organisation for economic co-operation and development
Q&A Questions and answers
QA Quality assurance
RES Renewable energy source
UNFCCC United Nations framework convention on climate change
UPRC University of piraeus research centre

Introduction

Stakeholder consultation is becoming an important component of all policy – and decision – support processes. Dialogue or exchange with stakeholders is a very enriching experience, as it allows scientists or researchers to get exposed to different views, approaches, and expectations on project results. It also enables them to collect feedback and suggestions from a variety of individuals having complementary skills and backgrounds. The involvement of key stakeholders is very useful to get an alternative perspective, which stimulates the scientists or researchers to shift the focus from project activities to intended outcomes in the early stage and to clearly communicate main ideas about the project in terms of objectives, milestones and outputs. However, the involvement of stakeholders with different (and sometimes opposite) views, backgrounds and expectations might increase confusion. Also, dealing with a large number of stakeholders might be an overwhelming exercise and challenges the organisers' capacity.

The present paper addresses these issues so as to share good practices with interested stakeholders and help the policy-makers to achieve concrete and action-oriented results in a more effective way. The methodology was applied within the framework of the POLIMP – Mobilizing and transferring knowledge on post-2012 climate policy implications project (POLIMP is funded by the European Commission under the 7th Framework Programme – Grant Agreement No 603847) and is analytically presented in the following paragraphs.

The remaining paper is structured as follows: Section “Rationale” presents the basic elements of stakeholder engagement process, as well as the levels of POLIMP stakeholders' participation, while Section “Methodological Notes” illustrates the main methodological steps implemented during POLIMP – from the composition and categorisation of stakeholders to dissemination of results – so as to establish an efficient stakeholder engagement. Section “Lessons Learnt” presents the lessons learnt during the POLIMP stakeholder engagement process, as well as the dissemination and communications strategy that was followed, in order to attract more stakeholders to participate actively in POLIMP activities. Finally, Section “Conclusions” summarizes the main points of the paper and provides some concluding remarks.

Rationale

A stakeholder is defined as a person or a group who has a stake or special interest in an issue, policy, or company (Welp *et al.*, 2006). A science-based stakeholder dialogue is defined as a structured communicative process of linking scientists with selected actors who have specialised knowledge and insights that are particularly relevant for the scientific process. In this respect stakeholders are identified based on the relevance of knowledge or certain competencies rather than on the representation of the full spectrum of interests (Welp *et al.*, 2006). This paper addresses both concepts of stakeholders, those with a special interest in climate policy and those in possession of specialised knowledge or competencies, who may be called experts.

Stakeholder engagement is a critical success factor of the POLIMP project (Karakosta *et al.*, 2014, 2015). To engage POLIMP stakeholders sets out two specific objectives:

- 1) To mobilise the collected and processed information to stakeholders, and define suitable formats to that effect; and
- 2) To encourage stakeholders to provide inputs for policy implications and recommendations for the EU and create maximum impacts of these outputs.

First, POLIMP provides stakeholders, such as policy makers, business, NGOs and citizens with a novel and effective opportunity to identify the information needs on the future courses of climate change policy making and their impacts on stakeholders' decisions (Karakosta and Flamos, 2016). It ensures that at different policy- and decision-making levels within the EU, decisions are taken on the basis of the best available knowledge including an increased understanding of opportunities for business and society. Based on

Table 1 Levels of stakeholders' participation

<i>Levels of stakeholders' participation</i>	
Inform	To provide stakeholders with balanced and objective information to assist them in understanding the problem, alternatives, opportunities and/or solutions (e.g., Final Conference, Webinars, Policy Briefs, Climate Change Monitor, Briefing Notes, Climate Policy Database)
Consult	To obtain stakeholders' feedback on policy-makers on analysis, alternatives and/or decisions (e.g., Dialogue, Stakeholder Workshops)
Involve	To work directly with stakeholders throughout the policy-making process to ensure that stakeholder concerns and aspirations are consistently understood and considered in the process (e.g., Dialogue, Stakeholder Workshops, Policy Briefs, Webinars, Expert Response Survey)

the best available knowledge collected and processed on a range of prioritised topics for the current climate policy developments, POLIMP could enhance the insights of policy – and decision-makers on possible courses of climate policy making. This would reduce the uncertainty of policy makers and sector – and company-level decision makers and help them better understand the consequences of different policies and regulatory frameworks on economic sectors and the European society as a whole. Moreover, POLIMP provides stakeholders with ample opportunities to share their experiences and lessons learned with a view to providing targeted input to policy implications and recommendations for the EU and delivering these outputs to a wider range of stakeholders.

Stakeholders can be invited to different levels of participation, depending on the specific purpose that is to be reached: Inform; Consult; and Involve. An overview of the three different levels of stakeholders' participation is given in [Table 1](#).

Below each level of participation is further explained.

a) *Inform*

Dialogue with stakeholders can be purely *informative*: limited in communicating POLIMP results, not requiring further *involvement* of external participants in the research process or seeking to develop a full participatory process ([Dede et al., 2015](#)). In order to raise awareness, POLIMP aims to inform climate policy-makers, researchers and wider stakeholders about the activities and outcomes of the project. All the interested actors continuously benefit from a series of dissemination activities, which aimed to keep them informed for a number of issues concerning POLIMP according to their special nature and interest. The goal is to provide policy-makers and stakeholders with policy implications and recommendations, and to create high impacts, as well as visibility at EU and member state levels.

b) *Consult-Involve*

In the case of full participation, stakeholders may collaborate with POLIMP members, participate in events and provide feedback with a view to contributing in the finalisation of outcomes. The aim of POLIMP is not only to inform policy makers and public, but also to consult, involve and collaborate with stakeholders in order to address knowledge gaps, and further acquire, process and accumulate knowledge for policy debate.

Methodological Notes

In order to establish an efficient stakeholder engagement, it is crucial to:

- Prioritise the main topics/issues that deserve discussion with stakeholders;
- Set the desired outcomes;
- Clarify the right point in time when stakeholders need to be mobilised in order to be more effective and, when needed, maximise the chances of getting valuable inputs;
- Develop a communication strategy, including follow-up;
- Identify the main communication channels for discussing and exchanging ideas with them.

Bearing these points in mind, the purpose of the stakeholders engagement plan is to engage targeted stakeholder groups in POLIMP activities throughout the implementation period and beyond ([POLIMP, 2013, 2016a](#)). A stakeholder engagement process initially contains the identification of suitable stakeholders and relevant information provision ([African Development Bank, 2001; Krywkow and Hare, 2008](#)). The methodological framework, presented in the stakeholder engagement plan, consists of a series of concurrent and consecutive steps to involve stakeholders throughout the process.

Step 1: Composition and categorisation of stakeholders

The element of active involvement in the process of policy– or decision–making constitutes the core characteristic of a stakeholder engagement approach. The composition of a group of stakeholders varies depending on the topic addressed and the group can be comprised by citizens, experts, government members, industry representatives or stakeholders of any kind with an interest in a specific topic ([McTaggart, 1997; Pedrosa and Guimarães Pereira, 2006; Slocum, 2003; Weaver and Cousins, 2004](#)). POLIMP in effect focuses on all those in politics and business who make climate policy-relevant decisions and may have a potential interest in research outcomes addressing knowledge gaps. It recognises a broad sense of stakeholders including both active participants in climate policy (e.g., private or public, regional, national or international organisations/institutions, national ministries, industrial or trade

Table 2 Stakeholder groups

<i>Knowledge functions</i>	<i>Activities</i>	<i>Examples of entities</i>
Knowledge providers	Research-oriented (e.g., desk work, laboratory, field work)	International organisations/institutions (UNFCCC secretariat, OECD/IEA); Joint Research Centre (JRC); national and non-governmental research institutes; business; NGOs
Knowledge users/ implementers	Decision- and implementation-oriented (e.g., management, administration, lobbying/advocacy)	EU institutions (Commission, Parliament, Council, the European Economic and Social Committee, the Committee of the Regions); EU member states (including ministries and political parties); local and regional governments; business sector representatives (trade associations); NGOs; UNFCCC parties (primarily for UNFCCC side-events)
Communicators	Intermediary and catalysing (e.g., networking, mass-mailing)	Media, umbrella organisations in business or NGOs

organisations, NGOs and individual experts) and concerned citizens. For the POLIMP project, its stakeholder engagement activities mainly target the former, a smaller and more specific constituency, while its dissemination and communication activities target the latter, a bigger and broader audience. Between the two are intermediaries and catalysts (e.g., umbrella organisations in business or NGOs), which belong to the former group, but also have leverage and multiplier effects on the latter group.

POLIMP categorises the three stakeholders groups in relation to knowledge function (Table 2).

Regarding the first category, 'knowledge producers', a set of questions remain open, for example:

- What sort of information do we expect from them?
- What incentives do the policy-makers provide?
- What would be their contribution to the results?
- What formal or informal status will they have in relation to the POLIMP project?

These questions are constantly addressed during the designing phase of stakeholder activities, in order to improve the quality of their feedback and to meet expectations from invited stakeholders.

The second category, 'knowledge users', is the main target audience for the processed knowledge, given their capacity as decision makers in policy and business. Questions similar to what are addressed to 'knowledge providers' include:

- What sort of knowledge or information are in demand, and when?
- What incentives do the policy-makers provide?
- What formal or informal status will they have in relation to the POLIMP project?

These categories are function-based, and therefore not mutually exclusive. As indicated above, there might be some overlap between entities identified with respective categories; e.g., umbrella organisations in business or NGOs) provide both the second and third functions (users and communicators). In such a case, the POLIMP researchers would regard entities with multiplier effects as 'knowledge users'.

For POLIMP the stakeholder engagement plan concentrates on the first two categories, 'knowledge providers' and 'knowledge users'. Provided that a dissemination and communication plan would address media to reach out concerned public, the stakeholder engagement plan does not address 'communicators' further on.

Derived from knowledge providers as well as knowledge users, stakeholders were differentiated by region and by sector. This leads to the categorisation of the following three European regions:

- *Western and Northern Europe*, with a proactive attitude and strong capacity to deal with mitigation and adaptation of climate change.
- *Southern Europe* affected by recent financial and economic crisis for which climate policy is currently not a major priority.
- *Central and Eastern Europe* in the transformation from an energy-intensive economy and possibly also affected by the financial and economic crisis for which climate policy is politically challenging and could be undesirable.

Across Europe and inside each Member State, POLIMP recognises the following sectors as climate-relevant:

- Energy production and distribution,
- Energy-intensive industry (e.g., iron & steel, cement, chemical, metal, paper & pulp, glass, lime),
- Mining (hard coal, minerals),
- Other ETS sectors (e.g., aviation),
- Transport (e.g., automobile, rail, shipping),
- Energy end-use (e.g., lighting and heating in buildings, appliances),
- Land-use (e.g., forestry, agriculture, real estate),
- Finance and trading (e.g., private investment banks and funds, pension funds, market traders).

It was assumed to be unlikely that POLIMP project would have a comprehensive coverage of all the above sectors. On the contrary, the consortium would target at, for example, the three most relevant sectors for the selected topic to maximise the impacts. The final selection of the sectors depends on the final choice of the topic and location for a thematic workshop.

Step 2: Stakeholders selection

Next, stakeholders were screened and selected in order to form a database of potential participants in consultation as well as knowledge dissemination. The stakeholders selection process focuses on not only parties to the UNFCCC (e.g., negotiators and policy makers in developed, developing countries and at the EU level), as well as all other non-party actors (e.g., NGOs, academic and corporate sectors both in developed and developing countries, media and the public), who are engaged in UNFCCC negotiations, but also those active in EU-domestic policy processes (e.g., climate change, energy, transport).

The first stakeholder screening was made on the basis of inputs from all project partners about the stakeholders within their home countries and contact networks that, they consider, may be interested in the outputs of the POLIMP project or may provide inputs to POLIMP through stakeholder meetings and workshops. The shortlist of important stakeholders was compiled from this input, including 173 stakeholders from 24 EU countries and from EU institutions (as of July 2013) with countries in Western, Southern and Central/Eastern Europe represented, although with relatively few representatives from Southern countries. The list has been updated with more stakeholders that have been identified in the context of the country preparatory dialogues and through other contact persons of each POLIMP partner on demand. This initial screening provides a good starting point for organising the country preparatory dialogues and for identifying further stakeholders once the topics of the stakeholder workshops are defined. It covers stakeholders from the first two knowledge-based categories as defined earlier in this article.

Potential sources for the identification of stakeholders associated with the relevant member states and topics are the following:

- Outcome of the first screening;
- Preliminary inputs from partners who are responsible to host meetings;
- Inputs from the report on stakeholders mapping;
- Inputs from the report on gap analysis;
- Contributions from stakeholders.

As key ‘knowledge providers’, a limited number of key stakeholders could contribute to the process from early on, especially at the stage of completion of gap analysis across regions/countries or topics. At the beginning of POLIMP, stakeholders were asked to identify priority issues of climate policy in need of additional or new knowledge. The risk is that each stakeholder may have different views about where and to what extent knowledge gap exists. This risk can be reduced by early briefing about the objective, process and expected results of the project.

Step 3: Modes of stakeholder consultation

The POLIMP project has developed a methodology for stakeholder consultation involving physical meetings and online platforms (Fujiwara *et al.*, 2015b). The POLIMP project designed different modes (Table 3) of stakeholder consultation (e.g., workshops, dialogue, events, web-tools) for different objectives (POLIMP, 2015, 2016a, b).

While the project partners hosting events generally have agreed on the basic framework summarised below in each category, it is up to them to select and decide on the specific designs that would suit them best and have maximum impacts.

Step 4: Preparatory dialogues

Preparatory dialogue is one of the main consultation tools to reach out to key stakeholders (e.g., policy-makers, businesses, researchers and NGOs) in EU member states (Fujiwara *et al.*, 2015a). Because bi-directional stakeholder participation is desired, the POLIMP consortium listened to their opinions, and gathered their feedback.

POLIMP initially envisaged to establish a clear link between dialogue and the workshop, calling the dialogue as preparatory to the meeting. It was expected to lay a ground before entering into discussion at the workshop, to have common understanding and perception about the policy framework, policy objectives, or policy instruments. It was expected that dialogue participants could further influence other stakeholders through their own connections (cf. ‘entities with multiplier effects’). Hosting organisations agreed on the basic framework in the stakeholders engagement plan including the timing and targeted countries, examples of different patterns to conduct dialogue and a guideline to structure the dialogue process. Further detail about the format and modality of dialogue can be made flexible and tailored to interests, priorities or needs of regions and countries hosting dialogue. In principle participation in dialogue are limited on an invitation only.

Table 3 Modes of consultation

<i>Modes of consultation</i>	<i>Location</i>	<i>Objectives</i>	<i>Main target groups</i>
Workshops	BE, UK, DE	Presentation of knowledge gaps; preparation for recommendations	Knowledge producers and users
Dialogue	NL, AU, PL, GR	Identification of knowledge gaps	Knowledge producers and users
UN-Side events	PL, Peru, FR	Presentation of research outcome	Stakeholders registered at UNFCCC
Web-Tools	n.a.	Sustainable and long-term engagement	All stakeholders

The ETS dialogue has been implemented throughout the period October 2013–March 2015. By the end of March 2015, more than 70 stakeholders from five countries (Greece, Poland, Austria, Hungary and the Netherlands) in total have participated in the dialogue processes. (The process was organised by four POLIMP partner organisations (University of Piraeus Research Centre (UPRC), Instytut Badan Strukturalnych, (IBS), University of Graz and JIN Climate and Sustainability) and coordinated by the Centre for European Policy Studies (CEPS).) Each dialogue organiser selected the topics corresponding to the most immediate stakeholder workshop, but allowed some variation in its interpretation of topical questions depending on the national circumstances or priorities, and developed its own method in accordance with the basic framework that is common to all dialogue processes. The POLIMP research team aimed at an iterative process of stakeholder consultation through a series of interviews or/and group discussions that enable the stakeholders to make contributions. The example of a methodology adopted in Greece is presented below.

Example of Preparatory Dialogues in Greece

For preparatory dialogue the University of Piraeus Research Centre (UPRC) in Greece held two sets of interviews a questionnaire with follow-up interviews. The first round focused on the role of carbon markets mechanisms in climate negotiations (market mechanisms, renewables, Article 9 Renewable Energy Directive), targeting 19 experts from academia, research institutes, the business-private sector, the public sector and NGOs. Questions concerned carbon markets, the Clean Development Mechanism (CDM) and the EU ETS, inter alia (Karakosta *et al.*, 2011, 2010). The second round focused on the ETS, consulting 12 stakeholders in Greece from academia as well as from research institutes and businesses in the energy sector. Questions focused on the assessment of economic impacts on the cost-effectiveness of the EU ETS, increasing harmonisation in the implementation of the EU ETS, and national stakeholders' views on how the 2030 framework will influence the political support for the EU ETS.

Several steps were taken for the dialogue process. Input elicitation began with the identification of key stakeholders for participation, followed by a personal invitation that was sent to the identified stakeholders. After receiving a positive answer, UPRC conducted interviews with them based on a questionnaire developed for this purpose. Preparatory material was subsequently developed in the form of a questionnaire, in order to be completed individually by stakeholders and also to facilitate discussion during interviews. Stakeholders were then invited to participate in the procedure and their interest was confirmed. Self-filling in of questionnaires and conduction of interviews took place in parallel.

Then UPRC analysed their feedback and identified the key outcomes. Feedback analysis provided preliminary results that were presented to selected stakeholders during thematic workshops conducted within the framework POLIMP (see step 5). Results of dialogue were reported in a common template used by hosting organisations. The template include basic sections in order to present key concepts and related policy questions in need of preparatory discussions, the main discussion points on which participants agreed or disagreed, as well as the key findings. The process of the dialogue preparation and implementation was completed in consecutive steps, as diagrammed in the Fig. 1 below.

Step 5: Thematic workshops

Thematic workshops, aim at engaging stakeholders in consultation with researchers from the early stage. This approach enables stakeholders to provide researchers with early feedback to preliminary analysis on knowledge gaps and to help them further develop evidence-based policy recommendations. The main target groups of these workshops were knowledge providers and users. In principle participation in the workshops was limited to invitation only. A list of invited participants consists of EU and member states policy-makers, industry and business representatives, researchers from academia and think-tanks, representatives of NGOs and other stakeholder groups.

The size of workshops varied, largely depending on the timing and topics to be discussed. For selecting invited participants, organisers took account the geographic and sector groupings that are most relevant to the chosen topic on the one hand, and representation of knowledge providers (mainly technical experts and researchers) and knowledge users (mainly policy makers and market participants) on the other hand. On the average, 20–30 stakeholders are expected to participate in a full day workshop. Within POLIMP duration, four Stakeholder Workshop were implemented, enabling stakeholders to provide researchers with early feedback to preliminary analysis on knowledge gaps and to help them further develop evidence-based policy recommendations.

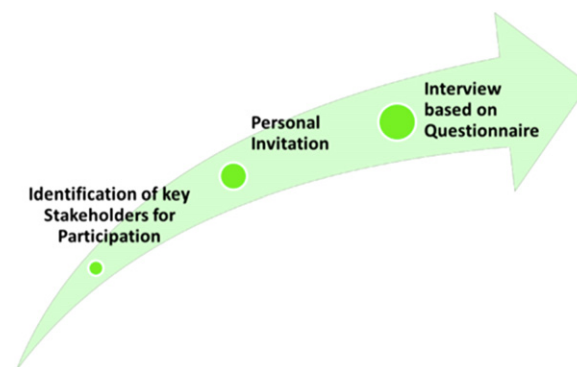


Fig. 1 UPRC dialogue process.

Scheduling the 'preparatory' dialogue at national or regional levels prior to the workshop in major capitals such as Brussels and London would better inform EU and national policymakers and stakeholders. Some of the dialogue participants could directly present to or share their experiences with stakeholders from other countries or the EU policy circle.

The hosting organisation ensures that discussion with stakeholders should be well-structured and evidence-based, presentation be short and concise and comments be kept even shorter (Karakosta and Fruhmenn, 2014). The purpose of this approach is to leave sufficient time for stakeholders to have clear understanding, exchange ideas and contribute to findings and, eventually, recommendations. The workshop programme consisted of several sessions moderated by session chairs and introduced by short presentations and interventions. For the ETS workshop, one session focused on the design issues in the context of the ETS reform debate and another on the implementation issues particularly relevant to groups of countries characterised by weak economic performances or other national circumstances, Central and Eastern Europe and Southern Europe.

In order to structure discussions for the thematic workshop on the EU ETS, key findings and messages of dialogue outcome were communicated in a background paper to speakers. This required focusing on topical policy issues related to the background research to be undertaken by the POLIMP team and expanded for discussion with external speakers and stakeholder participants. Prior to each workshop, a draft Policy Brief or a background paper was circulated. After the workshop, this draft Policy Brief or a background paper was finalised, incorporating feedback from stakeholders and preliminary suggestions for policy implications and recommendations. Three Policy Briefs were published after three workshops and circulated to a broader group of interested citizens beyond the workshop participants. Such feedback includes preliminary suggestions for policy implications and recommendations to policymakers (Fujiwara and Hofman, 2016; Fujiwara *et al.*, 2015b; Hofman and Van der Gaast, 2014; Michaelowa and Tuerk, 2014). In each Policy Brief, messages and recommendations are supported by the key outcomes of the project and tailored to policy- and decision-makers' priority issues.

Step 6: Dissemination of results

Based on a Dissemination and Communication Plan, POLIMP consortium members collected information targeted on priority issues in need of additional or new knowledge, and processed the information into integrated packages for decision makers. The processed information is presented in various formats, which are considered to be user-friendly and accessible, to reach target groups and a wider public. The tools for spreading excellence, exploiting results and disseminating knowledge are the following:

Targeted materials

- Policy-oriented publication series (e.g., Policy Briefs, Working Documents laying a sound basis on which policy options can be formulated, detailing methodologies, tools or indicators and presenting empirical data, Climate Change Monitor reports which focus on development in the UNFCCC negotiations as well as the EU climate change policy, and Briefing Notes which contain general conclusions from the knowledge collection and procession work, regarding policy implications).
- Collaboration with relevant European Initiatives.
- POLIMP Climate Policy Database, an ontology for annotating and structuring the knowledge related to climate policies.
- POLIMP Webinars Series, where stakeholders were actively engaged, enriching with their experience the discussion on climate policy.
- Bilateral contact (email and in person) with targeted audience for the provision of feedback.
- POLIMP Expert Response Survey Series, which engaged a targeted group of stakeholders and experts on matters relating to EU and international climate and energy policy.
- POLIMP Climate Policy Database, that allows stakeholders to explore, edit and extend the concentrated knowledge.
- Providing access to POLIMP data for stakeholders closely involved.
- Acknowledging stakeholders in all deliverables & POLIMP results where they provide feedback.

Workshops and events

- Presentations into events, dialogues and press conferences, as well as interventions/announcements at international conferences/forums/events of on-going initiatives in the same area etc.
- POLIMP final conference. In those events climate policy and other experts provided input on the results of POLIMP.

Distribution of promotional materials

- Production and distribution of promotional material e.g., brochure, flyer/leaflet, etc. The promotional material informs the wider audience about POLIMP goals and objectives and directed interested parties to sources of more detailed information.

Scientific publications

Articles to engage academia and researchers promoting the research conducted.

E-activities

- POLIMP website presenting the POLIMP results and containing useful dissemination material.
- POLIMP online knowledge platform "Climate Policy Info Hub", exploring impacts and implications of international and EU climate policy for decision-makers in policy, business and civil society and supporting informed science-based EU climate policy-making.
- POLIMP Climate Change Monitor Series focus on development in the UNFCCC negotiations, as well as the EU climate change policy and provides a regular stream of most updated information in a concise form.

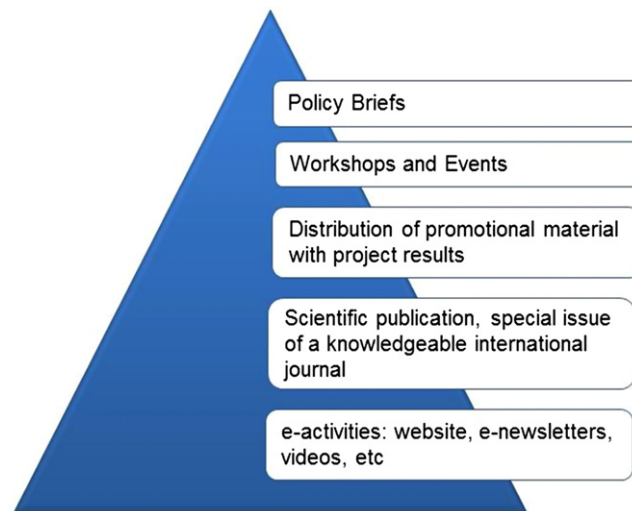


Fig. 2 Different dissemination means for different needs.

- POLIMP Briefing Notes containing general conclusions from the knowledge collection and procession work, regarding policy implications: socioeconomic aspects, technology transfer, land use, market mechanisms and other policy options.
- Web-based tools (e.g., QA forms-through which questions and comments were send during the webinars).
- Newsletters, Press Releases, Videos.
- Announcements & discussions in social media and EC platforms.

The pyramid dissemination structure finally reached policy makers and related stakeholders by producing policy briefs (Fig. 2).

Lessons Learnt

Stakeholders Engagement

The POLIMP project identified three main lessons learned from stakeholders' engagement activities. Sharing lessons from a methodological perspective, POLIMP could help policymakers improve the process for EU climate policy-making and invite researchers to future EU-funded projects, especially those aimed at coordinating and supporting action.

First, the portfolio approach based on combination of different modes of stakeholder consultation to fit for different purposes and for different target groups enabled the POLIMP team to have an extensive coverage of regions/countries as well as sectors. It is significant that most of the consortium members were involved in more than one consultation process. Consequently, POLIMP succeeded in reaching out stakeholders in the EU, three European regions (Western, Central and Eastern, and Southern Europe), seven countries (Poland, Greece, Austria, Hungary, the Netherlands, UK and Germany) as well as international negotiators and observers of climate policy.

It was assumed that the team would target at the most relevant sectors for the selected topic to maximise the impacts. Reflecting on the original focus of POLIMP and the composition of the its team, most of the stakeholders invited to the POLIMP consultation process were based on climate change mitigation policy: sectoral orientation towards 'energy production and distribution', 'energy-intensive industry (e.g., iron & steel, cement, chemical, metal, paper & pulp, glass, lime)', and to a less extent 'Finance and trading (e.g., investors and market traders)'. The format of regional or national dialogue allowed the team to complement the above sectoral coverage with those sectors that are of strategic importance to the targeted countries (e.g., mining in Poland and shipping in Greece).

Second, while it is crucial to narrow down the focus of interview questions and workshop sessions to facilitate interaction between policymakers and stakeholders, it was difficult to identify the topics and sub-topics in advance. Although the work plan developed a methodology on how to determine the topics in a systematic way, policy issues tend to be time-sensitive. More specifically, there was time lag between selection of the topics and discussion of the topics, and between the discussion in preparatory dialogue and the discussion in a stakeholder workshop. In effect timely transition from physical meetings (preparatory dialogue and stakeholder workshops in M6-29 (October 2013 – September 2015)) to online consultation (surveys and webinars in M27-36 (July 2015 – April 2016)) ensured that the topics selected earlier (e.g., financing renewable energy and the ETS reform) would remain on the table throughout the POLIMP period.

Third, among other modes of consultation, preparatory dialogue turned out to be methodologically effective but at the same time particularly challenging for implementation. There were practical issues related to planning and implementation at regional/national levels: e.g., selection of topics, contacts with stakeholders, scheduling meetings or interviews. Although it was envisaged to

hold preparatory dialogue before the first stakeholder workshop, in effect the process started after the first workshop (April 2015) and lasted longer until the third workshop (February 2015). Thus, real feed-in from regional/national levels to the European level was realised at the third workshop.

Another challenge to dialogue implementation was the need to coordinate a largely decentralised approach. In the preparation stage, although the coordinator circulated the guidelines for dialogue (see Annex 1 of D2.2) specified indicative elements (with optional ones), it was left to the hosting organisation to decide the format of dialogue. Even though the guidelines also suggested likely steps to implement the dialogue process, this required a series of bilateral briefing and interaction (Q&A), in some cases bilateral elaboration on designing the questionnaire. In the implementation stage, it was difficult to have an overview of progress being made at regional/national levels, particularly to support the hosting organisation in reaching out stakeholders at the minimum level that is required in each country for analytical purposes. In the analysis stage, diverse circumstances and interests across countries and sectors, which was the case for the EU ETS dialogue, made it impossible to summarise or draw common messages.

These three lessons, the portfolio approach, selection of policy-relevant topics, and a decentralised approach, are related and complementary to each other. Sharing these lessons and exchanging experiences from the POLIMP project with ongoing and future EU projects (e.g., CARISMA for the former) would contribute to maximising the impacts beyond the end of the project.

Dissemination and Communication

Within the POLIMP duration, and more particular during the implementation of POLIMP dissemination strategy several challenges were faced and addressed. The main challenges are presented in this document.

To begin with, one of the main POLIMP objectives was to achieve the vast communication and dissemination of the POLIMP achievements, but also their sustainability, ensuring the dissemination to the wider possible range of stakeholders groups. The main challenge to the effective, efficient and tailor-made diffusion of POLIMP message was the selection of the appropriate means and ways to address the communication of each POLIMP activity, knowledge produced and publication to the targeted stakeholder group. The process started with the appropriate selection of the information and experience from a wide range of research findings and activity results shared in POLIMP. The promotion and further facilitation of knowledge exchange on key policy issues was initially challenging and finally was elaborated through a target-oriented Dissemination and Communication Plan. By finalising and updating the POLIMP communication and dissemination strategy, the project team made it sure that the appropriate measures are used for the efficient and effective information transfer while the desirable message is shared among the appropriate audiences.

In order to meet the needs of different stakeholder groups, the POLIMP team developed and presented a series of publications with specific guidelines, in order to reach targeted group of stakeholders and experts on matters relating to EU and international climate and energy policy, as well as to present the methods used towards the outreach of the POLIMP results and progress. POLIMP publications contain general conclusions from the knowledge collection and procession work implemented during POLIMP, regarding policy implications: socioeconomic aspects, market mechanisms and other policy options.

Another challenge to the POLIMP team was creating the maximum impacts of the findings. Within the POLIMP duration information and data were collected to identify where knowledge gaps exist, provide insights and raise awareness on the implications of possible directions of international climate policies and a future climate policy regime. In order to ensure and increase the POLIMP visibility, a variety of targeted events, stakeholder consultation workshops and side events were implemented, communicating POLIMP progress and outcomes and engaging the stakeholder target groups in an ongoing direct consultation process. Thus, many stakeholders showed interest to cooperate with POLIMP and actively participate in its events and provide their feedback on the activities and progress of POLIMP.

The third challenge was the level of expectation from stakeholder engagement. Although an important number of experts were attracted to participate to POLIMP events, some of them were not further committed to providing feedback on policy implications and recommendations or exchanging knowledge and experience on the topics of discussions and outcomes of the events. In addition, despite the constant efforts of the POLIMP team to engage into POLIMP network a wide range of different stakeholders by presenting POLIMP activities and disseminating informational material, many policy makers, experts and stakeholders were not willing to participate to POLIMP activities, although their work was associated with climate and energy policy issues and with POLIMP objectives in general.

For a success factor, through the POLIMP dissemination and communication plan, the association between objectives, targets and message to disseminate has been thoroughly considered. The entire communication and dissemination strategy was based on a solid foundation comprised by clarity, transparency and honesty in order to support information availability and open access. All the stakeholders and policy makers were continuous recipients of a series of dissemination activities, which aim to keep them informed for a number of issues concerning POLIMP progress, concept and activities, through awareness raising, knowledge sharing, interest creation, mobilization and various other activities.

Future climate policy initiatives, both at an EU and at a global level are encouraged to follow the POLIMP dissemination plan, which contains tailor-made communication activities aiming at target groups with specific objectives and direct messages, and to implement the effective policies and practices that were proved to be particularly successful during the POLIMP

dissemination efforts. It remains challenging to further address the recognized aforementioned issues, regarding the wide variety of source information and key conclusions, target groups, types of events, and the effective and constant stakeholder engagement.

Conclusions

POLIMP identified key lessons learned from stakeholder engagement and the respective dissemination activities. The POLIMP team managed to have an extensive coverage of regions/countries as well as sectors, following a portfolio approach based on combination of different modes of stakeholder consultation to fit for different purposes and for different target groups. In addition, the format of regional or national dialogue allowed the team to complement the sectoral coverage with those sectors that are of strategic importance to the targeted countries. Thus, among other modes of consultation, preparatory dialogue turned out to be methodologically effective but at the same time particularly challenging for implementation. There were practical issues related to planning and implementation at regional/national levels concerning the overall portfolio approach, the selection of policy relevant topics and the need to coordinate a largely decentralised approach. However, as the ETS publication process highlighted, a decentralised approach was suitable in topics with wide difference and diversity of interests among stakeholders. This is less clear in case of RES publication which was presumably based on literature review.

The dissemination and communication strategy developed to mobilise stakeholders engagement thoroughly considered the association between objectives, targets and message to be disseminated. Tailor made communication activities were successful in supporting knowledge sharing concerning POLIMP progress, concept and activities. However, important issues emerged regarding the dissemination and communication strategy, particularly the wide variety of source information, key conclusions, target groups, types of events, in addition to the need of effective and constant stakeholder engagement. Finally, exchanging knowledge and experience acquired through POLIMP could support ongoing and future EU projects on achieving concrete and action-oriented results in a more effective way.

Acknowledgement

We acknowledge our receipt of support within the POLIMP project “Mobilizing and transferring knowledge on post-2012 climate policy implications” funded within the 7th Framework Programme of the European Union (grant agreement No 603847). The content of the paper is the sole responsibility of its authors and does not necessary reflect the views of the EC.

See also: Bamboo Fiber as Fillers for Polypropylene-Nanoclay via Injection Molding. Design and Performance Analysis of Small-Scale Parabolic Trough Solar Collectors Using Sustainable Materials. Recycled Clothes With Polypropylene-Nanoclay for Industrial Product via Injection Molding. Reuse of Waste Corrugated with Coir Fibers as a Packaging Material

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Simulation and Modeling of Vehicle Emissions – A Review

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Introduction

The emissions from cars can have a deadly consequence on human life, as seen with the CO emission, which has been proven to be fatal to human life in a confined space. In addition, research has shown that exposure to fuel emissions can have a carcinogenic effect on humans. This is a huge concern for people as the number of vehicles hitting the road increases globally. Car manufacturers and drivers can help reduce these harmful emissions in three separate ways: increasing engine efficiency, increasing vehicle efficiency and finally; standardized driving technique, unobstructed traffic conditions, cruising at an optimum speed for the vehicle and the reduction of cold starts which is the research interest in this paper. [Fig. 1](#) points out the world approaches in reducing transport emissions, where the green area is the paper's interest.

Models for emissions and fuel consumption factor estimations can be broadly divided into two categories: Average Speed Model and Instantaneous Emission Model.

Average Speed Model

The average speed approach is commonly used to estimate emissions from road traffic. This approach is based on aggregated emission data for various driving patterns. Driving patterns are represented by their mean speeds alone ([Wielenmann et al., 2005](#)). The average speed, vehicle class, size and year are used to obtain a derived speed emission function. This function fails to consider that using different cycles (i.e., with different driving behaviours and vehicle dynamics) with the same average speed will obtain different emissions and fuel consumption factors ([Myung et al., 2004](#)). This approach is limited to regional and national estimates ([Wielenmann et al., 2005](#)).

The MODEM project, in an attempt to overcome the average speed model limitations, established a set of 14 realistic driving cycles from a set of on-street measurement exercises ([Pang and Brace, 2004](#)). Emission data for the 14 cycles were then obtained from a range of vehicles using chassis dynamometer tests. A set of charts relating the emissions CO, HC, NOx and CO₂ and fuel consumption to second by second speeds for the driving cycles were then produced.

[Ryu et al. \(2015\)](#) have proposed and developed a corrected average emission model. This is an improved average speed model that accurately calculates CO₂ emissions on the road. When emissions from the central roads of a city are calculated, the existing average speed model only reflects the driving behaviour of a vehicle that accelerates and decelerates due to signals and traffic. Their results showed that the average speed model underestimated CO₂ emissions with an increase in acceleration and idle time for a speed range of 20 km/h and below, which is the speed range for traffic congestion. Based on these results, they

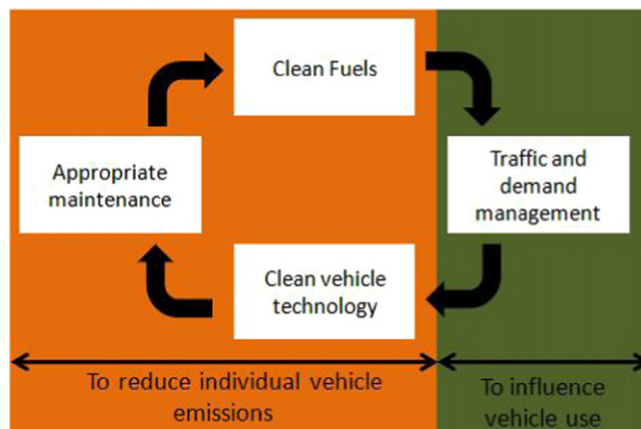


Fig. 1 Emission reduction approaches.

analysed the relationship between average emissions and instantaneous emissions according to the average speed per link unit, and they developed a model that performed better with improved accuracy of calculated CO₂ emissions for 20 km/h and below.

Instantaneous Emissions Model

The use of instantaneous emission models was introduced to overcome the limitations of the average speed model. This model measures emissions continuously at the exhaust during chassis dynamometer tests and stores the data at a particular time interval (typically 1 s) (Wielenmann *et al.*, 2005). An averaged emission value is assigned to every pair of instantaneous speed and acceleration values (measured simultaneously). The emission function can then be defined as a two-dimensional matrix of speed and a product of speed and acceleration. This modal method still has limitations in estimating transient, high acceleration emissions since these matrices are derived solely from chassis dynamometer tests (Myung *et al.*, 2004). Mera *et al.* (2019) have reported that in real-world driving, most Euro 5 and 6 diesel passenger cars exceed the nitrogen oxides (NOx) emission limits of type approval procedure. The emission factors of the fleet of Euro 6 vehicles show high variability, irrespective of the NOx control technology. It was concluded that high instantaneous NOx emissions represent a large number of total NOx emissions, although they are produced in a small percentage of driving time. A theoretical constraint of these high NOx emissions could reduce emission factors by 30%–82%. The emission of high instantaneous NOx emission is related to characteristic speed modes of urban, rural and motorway sections, and is primarily produced in a narrow engine speed range of approximately 700 rpm. In general, the probability of producing high instantaneous NOx emission increases as the engine speed, the exhaust gas temperature or the vehicle speed is increased.

Comparison of Vehicle Emissions Measurement Technique

Regulatory testing includes a pre-scale vehicle certification testing as the manufacturer should prove their vehicles to be under emissions standards (type approval tests) which are being carried out on chassis dynamometer emissions test equipment. Another procedure is in-service inspection and maintenance. This procedure is an idle test used without a load applied to the engine where a gas analyser probe is inserted into the tailpipe to measure the concentration of vehicle emissions (Vehicle & Operator Services Agency (VOSA), 2006). Sometimes, a load can be applied to the engine for more representative measurements (Wenzel *et al.*, 2000), but that can lead to excessive costs (Wenzel, 2003). Present, built-in, on-board diagnostic (OBD) systems can identify faulty parts in a car (Baltusis, 2004). In terms of on-road emission monitoring, there are two types of emission tests as below.

Monitoring Equipment

This method is used to measure the emission concentrations in ambient air (Fuller, 2006), this type uses a pump to sample the ambient air and sometimes samples of PM or HC emissions collected and analysed in a laboratory (Harrison *et al.*, 2003). This type of technology is considered to be good in measuring the in-use vehicle fleet rather than single vehicles measurements (Fuller, 2006). One of their applications is in Tunnel studies, where this equipment is placed inside the tunnel in order to measure the emissions factors for CO, CO₂, NOx, and HC (Hausberger *et al.*, 2003).

On-Road Remote Sensing

This method involves some tools set up on a roadside to measure the emissions from a single car when it passes (Achour, 2012). These tools have been developed by researchers for a better understanding of emission factors CO, NO, HC and PM (Bishop and Stedman, 1996; Jimenez *et al.*, 1999; Moosmuller *et al.*, 2003). On-road remote sensing was successfully used in many regions to specify vehicle fleet emissions (Bishop *et al.*, 1997; Bradley *et al.*, 2000; Stephens *et al.*, 1997). Fuel consumption has been improved for emissions factors using this technique (Pokharel *et al.*, 2002). However, there is no direct method to determine the details of the mode of operation such as gear, engine speed, etc., at the moment of measurement (Wenzel *et al.*, 2000).

Results from regulatory measurements methods are not sufficient. Chassis dynamometer testing must be carried out (North, 2006) and can be carried out in parallel by either instantaneous or modal emissions with the aggregate bag measurements required for certification (Sturm *et al.*, 1998). Using drive cycles in chassis dynamometer testing is not always representative of real drive cycles (Samuel *et al.*, 2002; Färnlund and Engström, 2001; Esteves-Booth *et al.*, 2001). Its usage covers only a limited area of driving modes (Younglove *et al.*, 2005). As a result of this, much research has been carried out in developing realistic driving cycles. Comparing these drive cycles showed differences in the measured emissions (De Haan and Keller, 2001; André, 2004). Since using the on-board emission monitoring for measuring instantaneous emissions makes data acquisition relatively quick, cost-effective and allows the drive cycles as well as emission factors to be evaluated (Rakha and Ahn, 2004; Ensfield, 2002; Hart *et al.*, 2002; Davis *et al.*, 2005). A correlation between measured and estimated emissions was found to be within 5% for CO₂ and NOx (Kihara *et al.*, 2000) and within

10% for HC and CO (Frey *et al.*, 2001). Much research has been conducted using emission analysers in order to calculate instantaneous emissions. For example, Ayala *et al.* identified the different hydrocarbon species emitted from the tailpipe (Ayala *et al.*, 2002).

As it was mentioned previously that vehicle emission estimation conducted on a single car requires validation by using measuring equipment fitted to the car under test (Cadle *et al.*, 2004, 2003). One of the parameters has been found to affect emissions levels is driver behaviour (Holmen and Niemeier, 1998; Nam *et al.*, 2003). Traffic jams have also been studied as one of the parameters that affect emission levels (Daham *et al.*, 2005; Unal *et al.*, 2004). Bishop *et al.* (2019) have mentioned that data from portable emissions measurement systems (PEMS) and other sources have allowed the discrepancy between type approval and real-world fuel economy and nitrogen oxides (NOx) emissions to be both identified and quantified. However, a gap in the knowledge persists because identifying this discrepancy does not allow us to predict real-world fuel economy and emissions accurately.

Comparison of Vehicle Emissions Modeling Technique

Many modeling methods have been developed in estimating the emission factors in the transport sector (Latham *et al.*, 2000; Düring *et al.*, 2005). National emissions inventories in areas (such as a country or a state) are important to assess the emissions levels, identify the air quality and help reduce the hazardous emissions affecting human health and environment.

Studies have been done in developing these modeling methods to estimate the emission factors CO, CO₂, HC, NOx and PM (Latham *et al.*, 2000). This study also investigated other factors such as evaporative emissions and PM emissions of brake dust (Düring *et al.*, 2005). The standard method in Europe and US is the average-speed models. The most useful data set for the work carried out for Europe is COPERT (Computer Programme to estimate Emissions from Road Transport) (Ntziachristos and Samaras, 2000) or the TRL (Transport Research Laboratory) emissions factors. Both can describe emissions in terms of grams per kilometre travelled [g/km] and are functions of vehicle speed (Edward and Bright, 2008), such that for the TRL factors:

$$EF_{i, m, n} = k + ax + bx^2 + cx^3 + \frac{d}{x} + \frac{e}{x^2} + \frac{f}{x^3}$$

where a, b, c, d, e, f and k are coefficients specific to a given engine size, m and technology level, n, x is the average vehicle speed in kilometres per hour (g/km) EF_{i, m, n} is the emissions value, in grams per kilometre travelled (g/km) for a given species i, of age m and engine size, n.

Emissions calculations exist for each of carbon dioxide (CO₂), carbon monoxide (CO), particulate matter (PM), oxides of nitrogen (NOx) and unburned hydrocarbons (HC) (Ekström *et al.*, 2004). COPERT4.V9 has recently been made available (Düring *et al.*, 2005). Validation studies for COPERT as well as method comparison studies are still on-going. Ekstrom *et al.* found an agreement in NOx emissions between COPERT and on-road sensing measurements, while a weaker agreement was noticed for CO and HC (COPERT was overestimated) (Ekström *et al.*, 2004). Another programme MOBILE6 has been compared with on-road sensing measurements. Noticeable differences have been found between the two methods (Pokharel *et al.*, 2002). Smit *et al.* presented a new modeling approach for dealing with road traffic emissions: VERSIT+. When compared to COPERT, higher accuracy was noticed with VERSIT+ with respect to emission estimations (Smit *et al.*, 2007).

Although average-speed models have world-wide use in the transport sector, there are some difficulties facing this method. Difficulties include fleet test data, fleet activity patterns, acceleration issues and identifying of local emissions (Wenzel *et al.*, 2000). However, good correlations between the predicted results of the modeling packages and the actual data obtained by direct measurement are still maintained.

Achour *et al.* have utilized COPERT and the combination of On-board diagnostic data extraction incorporated in all modern passenger cars. COPERT emission factors have been employed to allow for the real-world vehicular activity in order to better estimate the contribution of private cars to local emissions inventories (Achour *et al.*, 2011). A built-in data acquisition package has been developed in LabVIEW to log and save the data extracted from the OBD system. This data is then analysed to obtain driving cycles of specified routes which have been plotted so that emission factors could be obtained, Fig. 2 (Achour *et al.*, 2011).

Advantages of this method are: easy to follow, inexpensive and the results are in a good fit to the estimated values. Achour *et al.* also used the gas analyser, which measures resultant emissions directly from the exhaust manifold for the validation of the results for Dublin City, Ireland, Fig. 3. Good correlations between the predicted results of the modeling packages and the actual data that is obtained by direct measurement are still maintained (Ekström *et al.*, 2004). The same method has been employed in Aleppo city, Syria to establish a representative tool for the local authority in identifying the air quality caused by traffic emissions (Achour *et al.*, 2012).

Discussion and Conclusion

With respect to controlling air pollution, specifically from transport, there is a need to establish a method quickly and effectively to estimate on-road vehicle emissions. There are many methods to measure harmful emissions that are being produced by vehicles into the earth's atmosphere. However, with few methods that have been presented and discussed in this paper, it is now possible to monitor a range of engine signals such as drive cycles, emissions and fuel consumption in real time. Some data can be visualized

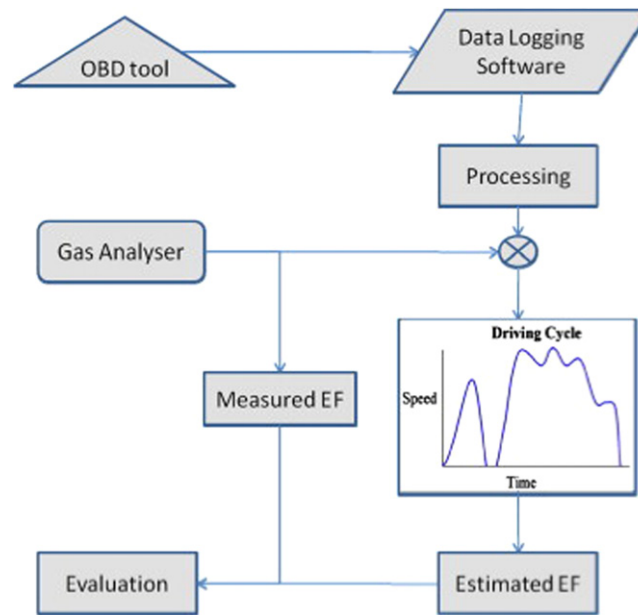


Fig. 2 Flow chart of development of driving cycle. Reproduced from Achour, H., Carton, J.G., Olabi, A.G., 2011. Estimating vehicle emissions from road transport, case study: Dublin city. *Applied Energy* 88 (5), 1957–1964.

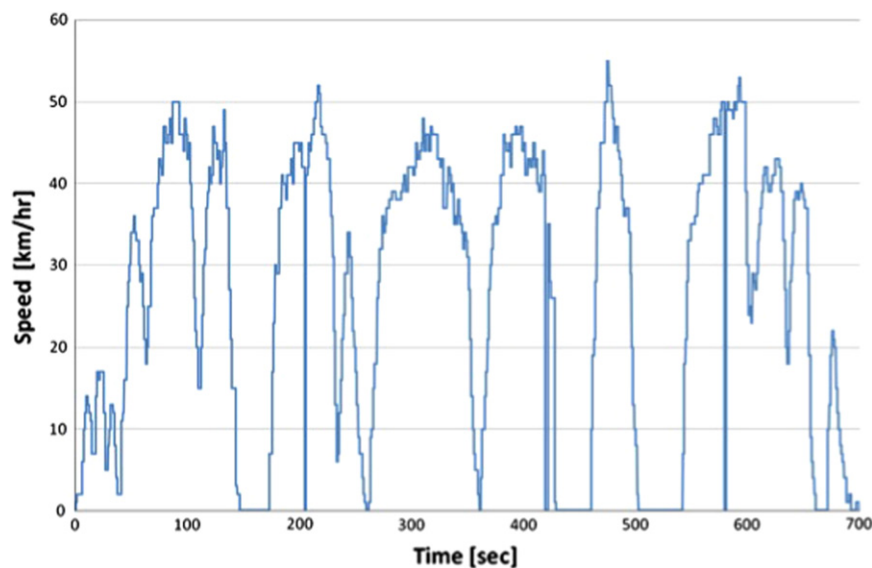


Fig. 3 Dublin driving cycle (DDC). Reproduced from Achour, H., Carton, J.G., Olabi, A.G., 2011. Estimating vehicle emissions from road transport, case study: Dublin city. *Applied Energy* 88 (5), 1957–1964.

via a PC attached with the tools in the form of graphed data plots. The results pertained from such packages estimate these plots in real time using OBD signals. The use of computer software reduces the need for bulky expensive analysis equipment and provides quick and accurate emissions estimates of the European regulated emissions (CO, HC, NO_x and particulate matter). The main two advantages of these methods are: user-friendly and can be used anywhere using portable equipment that can fit easily in the back seats of the car without affecting driver's behaviour or opposing people's life to any danger.

In conclusion, as each country has a unique driving cycle which represents the characteristics of the driving and the real amount of emissions from vehicles, individual testing is necessary for each region. An overall review of the most common emission modeling techniques is presented in this study with the purpose of being considered by future researchers as a primarily database in vehicle emission modeling techniques for further work in this field.

See also: Modeling Estimation and Performance Evaluation for Vibration Isolators

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Small to Medium Burners for Agricultural Pellets

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Introduction

Energy services could be greatly improved by use of agricultural biomass in small-scale combustion units. Wood pellets are a reliable and proven fuel to be used in small-scale combustion units. However, these units should preferably be able to use different types of biomass depending what it is locally available. Therefore, studies have been focused on exploring the suitability of using agricultural residues for small-scale heat and power generation using direct combustion. Steam-treated pellets can help to address technical barriers that limit the uptake of pellets as a fuel for electricity generation, but there is limited understanding of the cost and environmental impacts of their production and use.

A modified Hartmann dust explosion tube was employed to determine the Minimum Explosible Concentration (MEC) and the flame speed for three Pakistani agricultural wastes: bagasse, rice husk and wheat straw (Saeed *et al.*, 2015) where it was shown the lean limits for these pulverized agricultural waste biomasses were comparable to that of pulverized wood but were much leaner than those for coal and hydrocarbon fuels, which indicate that these biomasses are highly reactive. In study (Cardozo *et al.*, 2014) was compared the combustion of different agricultural residues in a single unit designed for wood pellets. In study (McKechnie *et al.*, 2016) was investigated life cycle environmental (greenhouse gas (GHG) and air pollutant emissions) and financial implications of electricity generation from steam-treated pellets, including fuel cycle activities (biomass supply, pellet production, and combustion) and retrofit infrastructure to enable 100% pellet firing at a generating station that previously used coal. Impacts of retrofit infrastructure become increasingly significant at lower generating station capacity factors, further favoring steam-treated pellets for both environmental and financial metrics (McKechnie *et al.*, 2016). In study, (Nilsson *et al.*, 2011) the costs and energy requirements for the production of pellets from agricultural raw materials were analyzed. The energy use in manufacturing pellets from air-dried crops was generally no higher than when moist sawdust was used as the raw material. The objective of work (Carvalho *et al.*, 2013) was to evaluate the technical and environmental performance of a 15 kW pellet boiler when operated with different pelletized biomass fuels, namely straw (*Triticum aestivum*), *Miscanthus* (*Miscanthus* _ giganteus), maize (*Zea mays*), wheat bran, vineyard pruning (from *Vitis vinifera*), hay, *Sorghum* (*Sorghum bicolor*) and wood (from *Picea abies*) with 5% rye flour. The investigation in the international market shows that mixed biomass pellets are promising fuels and with the appropriate support these fuels have many prospects for the future (Karkania *et al.*, 2012). The use of biomass pellets would not only create new market opportunities for agricultural industries, it would also reduce dependence on coal, as well as the greenhouse gas emissions associated with coal use (Karkania *et al.*, 2012). In paper (Tauro *et al.*, 2018) was examined the potential for biomass pellets to become a sizable low-carbon, renewable energy source that could compete with and substitute fossil fuels in specific economic sectors in Mexico where it was estimated that the market energy potential for pellets from currently available agricultural and forest residues in Mexico is between 131 and 233 PJ/yr, with total costs ranging from 6.3 to 12.8 USD/GJ. In paper (Dai *et al.*, 2015), a ceramic foam burner with embedded alumina pellets was designed, which set different shapes of tubes by taking can advantage of the discrete pellets. An experimental system was built to study the effects of the pellet diameter and pellet location on the combustion of low-concentration coal mine methane (LCM) (Dai *et al.*, 2015). Results indicates that the heat transfer features of 13-mm pellets are more similar to those of 10-PPI ceramic foam compared with 6-mm pellets and 9-mm pellets (Dai *et al.*, 2015). The combustion performance in a double-layer burner packed with alumina pellets of different diameters was experimentally studied in article (Gao *et al.*, 2012). In study (Qu and Feng, 2015), methane/air combustion in a two-zone catalytic alumina pileup-pellets burner with equivalence ratios varying from 0.55 to 0.70 was researched.

Conventional small to medium burners for agricultural pellets can be used for combustion of agricultural pellets. Main problem is low ash melting temperature for biomass from agriculture. After the burner finish combustion as it cool down ash is transformed from liquid to solid state and layer of ash block the wholes on grate for provision of air in combustion chamber. In this article was presented and conventional small to medium burners for agricultural pellets.

Materials and Methods

Biomass Waste Management

According to the European Union standardization there are six procedures in the biomass waste treatment process:

1. Eco-design,
2. Biomass waste decreasing,
3. Biomass waste reusing,
4. Recycling and making compost,
5. Energy from biomass waste,
6. Biomass waste disposing.

In order to optimize the system for biomass waste management based on decreasing of pollution of life environment and for the cheapest solution there is goal to develop the biomass waste management process. This innovative solution could lead to revolution in the biomass waste issue. By entering of the main data for biomass waste, quantity and composition for the some region, the client could know which is the best solution for the biomass waste treatment and transport for the region. Several biomass waste treatments are included:

- Recycling,
- Combusting,
- Making compost,
- Performing anaerobic digestion, and
- Disposing of biomass waste.

There are several indicators which are calculated according the input data. These indicators are:

- Global warming,
- Heavy metals emission,
- Nitrogen oxide emission,
- Smog formation,
- Water pollution.

Therefore the system has seven modules. These modules

- Calculation of emissions from collection and transport of biomass waste,
- Calculation of emissions from anaerobic digestion,
- Calculation of emissions from combustion,
- Calculation of emissions from recycled waste,
- Calculation of emissions from disposal,
- Calculation of emissions from compost,
- Calculation of cost benefit.

Burner for Agricultural Pellets

Fig. 1 shows the flowchart of the pelletizing process where it was shown the main process steps. Afterwards each pellet boiler has own process flowchart as it shown in Fig. 2.

Conventional small to medium burners for agricultural pellets can be used for combustion of agricultural pellets. Main problem is low ash melting temperature for biomass from agriculture. After the burner finish combustion as it cool down ash is transformed from liquid to solid state and layer of ash block the wholes on grate for provision of air in combustion chamber. In our construction this kind of problems are eliminated and burner is applied with mechanical system for eliminating the ash from grate. Burner of 120 kW have been produced (assembled) and is in operation today (Fig. 3).

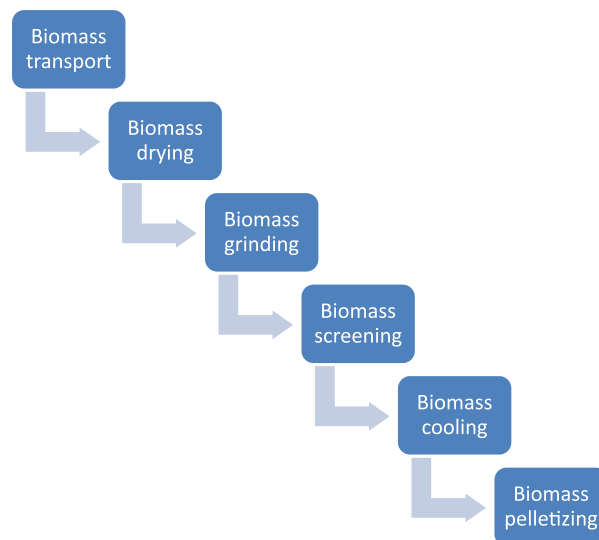


Fig. 1 The pelletizing process flowchart.

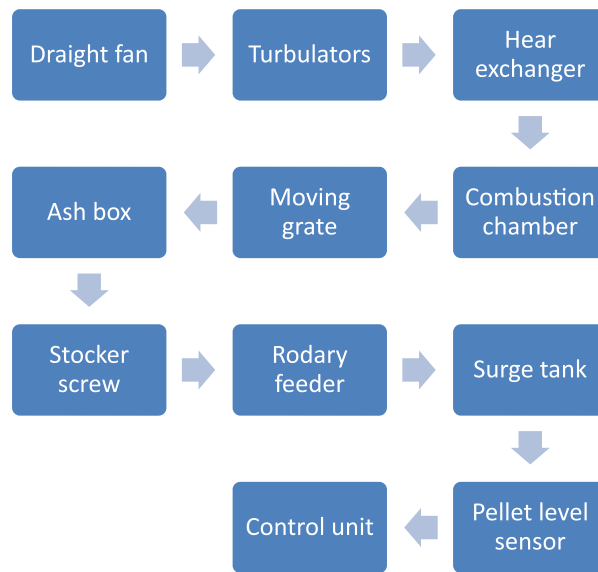


Fig. 2 Process flowchart of the pellet boiler.



Fig. 3 Pellet burner for agricultural biomass.

Conclusion

The demand for biofuel pellets has increased considerably in recent years, causing shortage of the traditional raw materials sawdust and wood shavings. Use of biomass fuels for electricity generation can simultaneously contribute to a number of common policy objectives, including: increasing the use of renewable energy; reducing greenhouse gas emissions; compliance with air pollutant emissions regulations; and encouraging economic development in communities dependent on agriculture and forestry sectors.

In this article conventional small to medium burners for agricultural pellets was used for combustion of agricultural pellets. Main problem is low ash melting temperature for biomass from agriculture. After the burner finish combustion as it cool down ash

is transformed from liquid to solid state and layer of ash block the wholes on grate for provision of air in combustion chamber. In this article was presented and conventional small to medium burners for agricultural pellets.

Small-scale wood combustion systems have been well developed and reached a high quality and performance level. The energy efficiency has increased, the emissions have decreased, fully automatic operation systems have been developed and the combustion technology has been optimized for woody biomass fuels.

See also: Large Biomass Burners for Fuel Switch in Existing Fossil Fuel Based Plants. Machine for Producing Tablets From Coal Powder. Technology for Producing Briquettes From Wet Biomass

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Small to Medium Scale Gasification Plant

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Introduction

Biomass is going to play an increasing role in the energy supply of the future, as it is an important renewable source of energy and the only source of renewable carbon. The efficient use of biomass is currently receiving increasing attention. Gasification – as an innovative and viable technology for the thermal conversion of biomass – has been the focus of considerable research for a number of decades.

Gasification is recognized as one of the most promising technologies to convert low quality fuels into more valuable ones. The principal problem related with the use of biomass in gasification processes is the high amount of tar released during the pyrolysis step. However, biomass is a low-grade energy fuel and has limited uses as a direct feedstock to produce energy. For this reason the study of innovative thermochemical processes, such as gasification and pyrolysis, to transform the solid biomass into more valuable fuels is of fundamental importance for the success of biomass exploitation. Gasification converts the low-grade solid biomass under high temperature into gaseous fuel called syngas.

A modified Hartmann dust explosion tube was employed to determine the Minimum Explosible Concentration (MEC) and the flame speed for three Pakistani agricultural wastes: bagasse, rice husk and wheat straw (Saeed *et al.*, 2015) where it was shown the lean limits for these pulverized agricultural waste biomasses were comparable to that of pulverized wood but were much leaner than those for coal and hydrocarbon fuels, which indicate that these biomasses are highly reactive. In study (Cardozo *et al.*, 2014) was compared the combustion of different agricultural residues in a single unit designed for wood pellets. In study (McKechnie *et al.*, 2016) was investigated life cycle environmental (greenhouse gas (GHG) and air pollutant emissions) and financial implications of electricity generation from steam-treated pellets, including fuel cycle activities (biomass supply, pellet production, and combustion) and retrofit infrastructure to enable 100% pellet firing at a generating station that previously used coal. Impacts of retrofit infrastructure become increasingly significant at lower generating station capacity factors, further favoring steam-treated pellets for both environmental and financial metrics (McKechnie *et al.*, 2016). In study, (Nilsson *et al.*, 2011) the costs and energy requirements for the production of pellets from agricultural raw materials were analyzed. The energy use in manufacturing pellets from air-dried crops was generally no higher than when moist sawdust was used as the raw material. The objective of work (Carvalho *et al.*, 2013) was to evaluate the technical and environmental performance of a 15 kW pellet boiler when operated with different pelletized biomass fuels, namely straw (*Triticum aestivum*), Miscanthus (*Miscanthus _ giganteus*), maize (*Zea mays*), wheat bran, vineyard pruning (from *Vitis vinifera*), hay, Sorghum (*Sorghum bicolor*) and wood (from *Picea abies*) with 5% rye flour. The investigation in the international market shows that mixed biomass pellets are promising fuels and with the appropriate support these fuels have many prospects for the future (Karkania *et al.*, 2012). The use of biomass pellets would not only create new market opportunities for agricultural industries, it would also reduce dependence on coal, as well as the greenhouse gas emissions associated with coal use (Karkania *et al.*, 2012). In paper (Tauro *et al.*, 2018) was examined the potential for biomass pellets to become a sizable low-carbon, renewable energy source that could compete with and substitute fossil fuels in specific economic sectors in Mexico where it was estimated that the market energy potential for pellets from currently available agricultural and forest residues in Mexico is between 131 and 233 PJ/yr, with total costs ranging from 6.3 to 12.8 USD/GJ. In paper, (Dai *et al.*, 2015) a ceramic foam burner with embedded alumina pellets was designed, which set different shapes of tubes by taking can advantage of the discrete pellets. An experimental system was built to study the effects of the pellet diameter and pellet location on the combustion of low-concentration coal mine methane (LCM) (Dai *et al.*, 2015). Results indicates that the heat transfer features of 13-mm pellets are more similar to those of 10-PPI ceramic foam compared with 6-mm pellets and 9-mm pellets (Dai *et al.*, 2015). The combustion performance in a double-layer burner packed with alumina pellets of different diameters was experimentally studied in article (Gao *et al.*, 2012). In study (Qu and Feng, 2015), methane/air combustion in a two-zone catalytic alumina pile-up-pellets burner with equivalence ratios varying from 0.55 to 0.70 was researched. Torrefied biomass has several benefits, such as higher energy density, good grindability, higher flowability and uniformity (Li *et al.*, 2012). The outlet of a mechanical biological treatment plant for mixed municipal solid waste is further processed to produce RRBf (Refined Renewable Biomass Fuel) within the frame of the EU Lifeþ project MARSS (Material Advanced Recovery Sustainable Systems) (Schulzke *et al.*, 2017). In paper (Dasappa *et al.*, 2004) addresses case studies of a low temperature and a high temperature industrial heat requirement being met using biomass gasification (Dasappa *et al.*, 2004). In paper (Verma *et al.*, 2017) provides a detail review on the need of drying of biomass before co-firing, different technologies used for biomass drying, biomass co-firing to the existing coal fired power plants and the environmental benefits of biomass co-firing. In paper (Perna *et al.*, 2015) conventional and advanced biomass gasification power plants designed for small cogeneration application were defined. A techno-economic feasibility study of liquid bio-fuel production from biomass to meet the demand for public transport in small communities was presented in article (Mustafa *et al.*, 2017).

In this study is presented small gasification plant (downdraft Imbert type). Different biomass fuels have been successfully tested. There is possibility to expand the idea and to use produced syngas for powering the gas motor and produce heat and power in the same time (small cogeneration plant).

Materials and Methods

Biomass Waste Management

According to the European Union standardization there are six procedures in the biomass waste treatment process:

1. Eco-design,
2. Biomass waste decreasing,
3. Biomass waste reusing,
4. Recycling and making compost,
5. Energy from biomass waste,
6. Biomass waste disposing.

In order to optimize the system for biomass waste management based on decreasing of pollution of life environment and for the cheapest solution there is goal to develop the biomass waste management process. This innovative solution could lead to revolution in the biomass waste issue. By entering of the main data for biomass waste, quantity and composition for the some region, the client could know which is the best solution for the biomass waste treatment and transport for the region. Several biomass waste treatments are included:

- Recycling,
- Combusting,
- Making compost,
- Performing anaerobic digestion and
- Disposing of biomass waste.

There are several indicators which are calculated according the input data. These indicators are:

- Global warming,
- Heavy metals emission,
- Nitrogen oxide emission,
- Smog formation,
- Water pollution.

Therefore the system has seven modules. These modules

- Calculation of emissions from collection and transport of biomass waste,
- Calculation of emissions from anaerobic digestion,
- Calculation of emissions from combustion,
- Calculation of emissions from recycled waste,
- Calculation of emissions from disposal,
- Calculation of emissions from compost,
- Calculation of cost benefit.

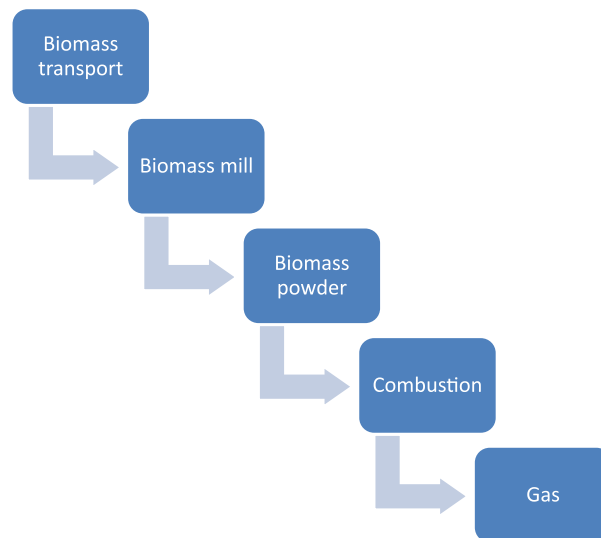


Fig. 1 The biomass treatment process flowchart.

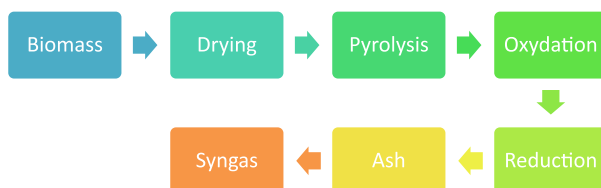


Fig. 2 Process flowchart of the gasifier.

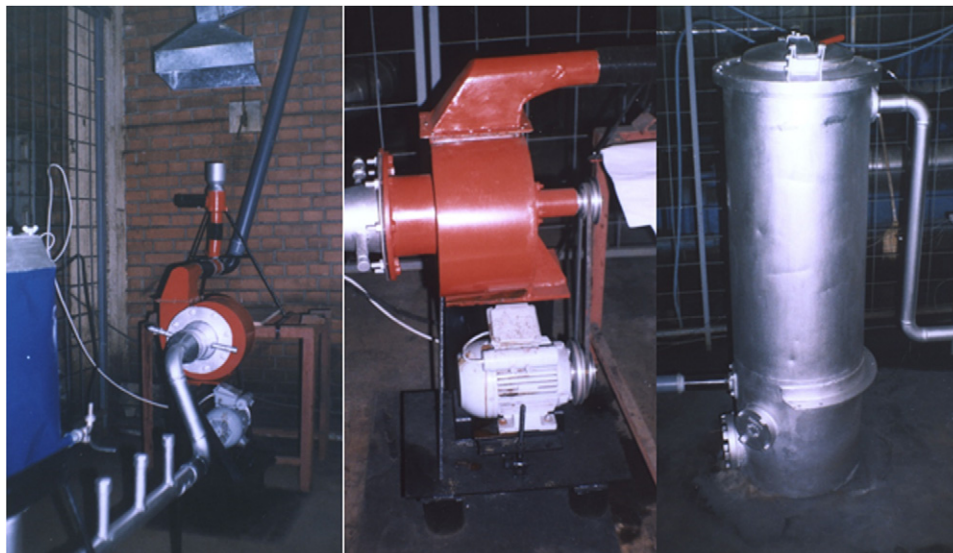


Fig. 3 Gasification plant.

Burner for Agricultural Pellets

Fig. 1 shows the flowchart of the biomass treatment process where it was shown the main process steps. The gasification process is presented in **Fig. 2**.

In this study small gasification plant (downdraft Imbert type) have been constructed and tested. Different biomass fuels have been successfully tested. There is possibility to expand the idea and to use produced syngas for powering the gas motor and produce heat and power in the same time (small cogeneration plant). The gasification plant is presented in **Fig. 3**.

Conclusion

The interest on the exploitation of biomass as source of energy has continuously increased in the last decade. Biomass has been recognized as one of the most attractive alternatives to fossil fuel, even if is not yet competitive. Many research efforts have been successfully made to develop efficient and convenient process for biomass exploitation. However, biomass is a low-grade energy fuel and has limited uses as a direct feedstock to produce energy. For this reason the study of innovative thermochemical processes, such as gasification and pyrolysis, to transform the solid biomass into more valuable fuels is of fundamental importance for the success of biomass exploitation.

In this study small gasification plant (downdraft Imbert type) have been constructed and tested. Different biomass fuels have been successfully tested. There is possibility to expand the idea and to use produced syngas for powering the gas motor and produce heat and power in the same time (small cogeneration plant).

See also: Sustainable Materials for Energy Conversion

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Sustainable and Environment Friendly Power Sources for Long Duration Environment Monitoring

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Introduction

Field sensor networks have many important modern-day applications and have been deployed for environmental monitoring, particularly forest management, wildlife-preservation, air quality, water quality and soil erosion monitoring (Fig. 1; Akyildiz *et al.*, 2002). These devices are also emerging as important tools in disaster prediction, including measuring winds in a hurricane, measuring rising seawater from storm surges, inland flooding, sea-erosion, monitoring spread of forest fires, monitoring avalanches, earthquakes, volcanoes and tsunamis. Field sensor networks play an important role in monitoring critical variables from the environment. They are also feeding complex computer models used to perform advanced prediction and planning.

This has all been made possible thanks to rapid miniaturization of low-cost electronics (particularly micro-computers), sensors, actuators and radios into ever-smaller packages that consume low average power of 5 W or less. An example field sensor network module architecture is shown Fig. 2. The micro-computers are typically combined into a single System on a Chip (SoC) that enables mass-manufacturing and customization. System on a Chip contains all the components of a typical computer including input/output ports, CPU, memory, storage and some peripherals such as Graphics Processing Units (GPUs) and short-range 2.4 Ghz wireless radio (Wi-Fi). Integration of these components onto a single chip, lowers the cost of production making the cost of a micro-computer a few dollars and increases power efficiency. The sensor networks in turn communicate to other nodes via radio. The SoC in turn is connected to a sensor payload that monitors the environment and stores data typically on a solid-state data storage system. The entire system is powered with an onboard power supply that provides power to the SoC which in turns power all the connected peripherals.

To be practical, once deployed, field sensor network modules need to operate unattended, ideally for years. A key to making these sensor systems practical and ready for wide-scale use is the need for high-energy power supplies. Power supplies, including power generation and storage technologies have been slow to advance compared to electronics, sensors, actuators and radios. This is principally due to the limitations with the material used in power supply components.

Photovoltaics and Wind Generators

Photovoltaics are a common power source used to power sensor networks. They are composed of single-junction amorphous silicon or triple-junction Gallium-Arsenide semi-conductor cells. The cells absorb insolation (in the form of photons) and produce electricity. Single junction cell range in efficiency from 5% to 20% while triple junction cells reach 25%–35%.

However, photovoltaic panels are bulky, requiring regular cleaning and need to be actively pointed towards the sun for best results. Plummeting market prices of solar panels from the late 1990s onwards make them one of the leading options for powering environmental sensors. The challenges remain in powering the sensor when sunlight is not available, including during inclement weather and night time. Another alternative is a wind generator. Wind generators consist of a dynamo connected to a wind turbine. The turbine spins producing current which is rectified using power electronics. Although wind-generators contain many moving parts and can be large, they have become attractive due to their low-cost from mass-production. Wind generators are well



Fig. 1 Field sensor networks have ever-growing applications in environmental monitoring. They are playing a critical part in continuous observation of water ways (left), <http://eurogoos.eu/member-product/real-time-data-oceanographic-buoy-vida/> forests (center), <https://blog.adafruit.com/2016/10/25/using-circuits-sensors-to-study-dendrometry-dimensions-of-trees-in-alaska-citizenscience/> and in precision agriculture (right), <http://www.projectwatersense.nl/>.

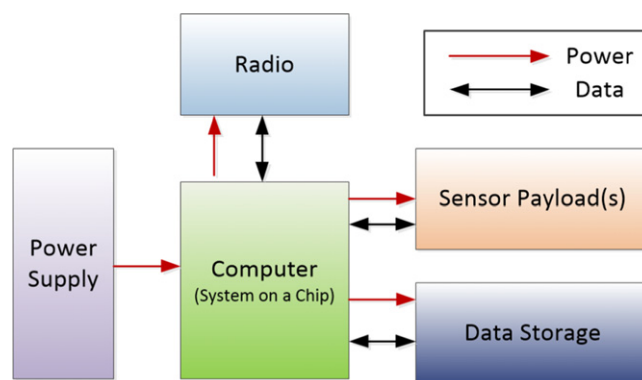


Fig. 2 A Field sensor network module architecture. Drawn for the encyclopedia article by Jekan Thangavelautham.

sited in certain natural environments such as coastlines, mountain passes and flat plains. Due to their large footprint and need for periodic maintenance, they are only promising for large field applications.

Batteries

Daily variabilities experienced by both photovoltaic systems and wind power generators, mean that these power sources need to be coupled with a battery to store excess capacity and kick-in when there is an input power shortage. Batteries are electro-chemical devices that store electricity in chemical bonds. Current battery technology typically serves as a limiting factor in terms of life and performance of field sensors. This is due to low specific energy of batteries. This is despite the fact that rechargeable batteries have made substantial improvements over the past 30 years in terms of specific energy, overall reliability and power density. 30 years ago several battery technologies were promising including lead-acid, nickel metal hydride, silver-zinc and lithium-ion batteries. Since then lithium ion batteries, particularly containing lithium cobalt oxide (LiCoO_2) or lithium iron phosphate (LiFePO_4) have surpassed these other battery technologies to permit higher specific energy, fast-charge, large number of charge-discharge cycles, long cycle and shelf-life. For the lithium cobalt oxide chemistry, the overall reaction is the following:



However, for long life applications, batteries need to be recharged or replaced often. In some instances, they are ideally coupled with photovoltaics. In other instances, this presents a major challenge in remote environments with limited accessibility. Significant work is being done to address the energy limits of current batteries (Ritchie, 2006; Tarascon and Armand, 2004) but current trends show that batteries cannot meet the high-energy requirements of long-life field sensor networks.

Rechargeable batteries still trail behind non-rechargeable batteries that have higher specific energy and shelf-life. Non-rechargeable batteries can be designed to be the only power source for field sensors, provided the field sensors operate periodically and for low-power. In particular, communication from a remote environment over long distances in the range of kilometres requires direct satellite communication or the cell phone network taking up significant power. Continuous advancement in communication devices are reducing these power demands but still require high-energy power sources.

Batteries can be sized to be larger to make-up for their low-specific energy, but they contain cathode, anode and electrolyte material that do not bio-degrade and are harmful if dispersed into the environment. High-energy batteries such as lithium thionyl chloride (LiSOCl_2) batteries (500–700 Wh/kg) requires even more care in terms of use and disposable as they are highly reactive and susceptible to explosion from shock and vibration. The reaction is given as follows:



Other non-rechargeable batteries such as lithium manganese dioxide (LiMnO_2) have higher specific energy compared to rechargeable batteries at 280 Wh/kg, and are well protected from damage and leaks, but still face the environment disposal problem. Alkaline batteries are common for use in consumer electronics, have excellent shelf-life and competitive specific energy of 200 Wh/kg however they contain chromium in their electrolyte which is a major environmental hazard. Another promising new technology is the lithium-air battery. Lithium air batteries have specific energy of 12,000 Wh/kg and in theory they are rechargeable. These batteries in the laboratory have achieved 50–100 charge/discharge cycles however run into challenges with reliability. The challenges are with the cathode that result in build-up of irreversible Li_2O that translates into steady loss of lithium.

Fuel Cells

An alternative to batteries are fuel cells. Fuel cells are electrochemical energy conversion devices that convert chemical energy directly into electrical energy (Barbir, 2005). Table 1 shows common fuel cell technologies. Unlike a battery, fuel cells must be constantly fed with fuel and oxidizer to produce electricity. There are different fuel cell technologies based on operating temperature, chemistry of electrolyte, fuel and oxidizer used. Some of the fuel cells listed utilize low-cost fuels such as natural gas,

Table 1 Fuel cell technologies

<i>Fuel Cell</i>	<i>Electrolyte</i>	<i>Operating temperature</i>	<i>Electrical efficiency</i>	<i>Fuel oxidant</i>
Alkaline fuel cell –AFC	Potassium hydroxide solution	15–90°C	20%–60%	H ₂ O ₂
Proton exchange membrane fuel cell PEMFC	Proton exchange membrane	15–80°C	40%–70%	H ₂ O ₂ /Air
Direct methanol fuel cell (DMFC)	Proton exchange membrane	15–130°C	20%–40%	CH ₃ OH O ₂ , Air
Phosphoric acid fuel cell PAFC	Phosphoric acid	160–220°C	55%	Natural gas, bio gas, H ₂ , O ₂ , Air
Molten carbonate fuel cell MCFC	Molten mixture of alkali metal carbonates	620–660°C	65%	Natural gas, bio gas, gasoline, H ₂ , O ₂ , Air
Solid oxide fuel cell SOFC	Oxide ion conducting ceramic	800–1000°C	60%–65%	Natural gas, bio gas, gasoline, H ₂ , O ₂ , Air

methanol and gasoline. However, they operate at high temperatures and produce CO₂. This makes them unsuitable for use in pristine environments.

Solid-Oxide and Molten Carbonate fuel cells can utilize a range of fuels including hydrocarbons and hydrogen and are strongly immune to poisoning from impurities such as sulphur. However, they require high operating temperatures, have long start-up times and produce CO₂ when using hydrocarbons.

Alkaline, Polymer Electrolyte Membrane (PEM) and Direct Methanol Fuel Cells (DMFC) all operate at low temperatures. Alkaline fuel cells operate at lower efficiencies and require an electrolyte which requires relatively large containers/casing. However, Alkaline fuel cells are known to be reliable having been used as a power source on several space crafts and on the International Space Station. It is the bulky size and low-operating efficiencies that makes Alkaline fuel cells less attractive for sensor networks.

However, two of the remaining technologies including, PEM fuel cells and direct-methanol fuel cells are both attractive for sensor networks. Both operate at low-temperatures and are quiet.

Overall, PEM fuel cells are mature amongst fuel cell technologies and can operate at cell efficiency as high as 60%–65%. They react with hydrogen and oxygen to produce electricity and water. Their overall reaction is given below:



The storage and release of hydrogen is typically a challenge. However, there are new practical solutions that are simple, that offer high specific-energy and low-temperature solutions. Oxygen is obtained directly from the air or pressurized storage tanks or chemical sources. Air-based PEM fuel cells have reduced power density, but are convenient avoiding bulky, pressurized oxygen tanks.

Direct methanol fuel cells use methanol and oxygen from the air to produce electricity. The overall reaction for the direct methanol fuel cell is given below:



DMFCs tend to have lower efficiencies than PEM, longer start-up times and produce carbon dioxide and water. However, direct methanol fuel cells are attractive, because methanol is relatively easy to produce, store and has higher energy densities than conventional hydrogen storage methods. The main challenge with direct methanol fuel cells is an inherent limitation with the fuel-cell design compared to PEM. Direct methanol fuel cells produce CO₂ as a waste product. This requires an effective ventilation system to prevent build-up of CO₂.

Carbon dioxide can build-up in the fuel cell and dissolve in the water to form carbonic acid (H₂CO₃), a mild source of corrosion and degradation of fuel cell components including the membrane and carbon support layer. A second source is the formation of carbon-monoxide, (CO) an intermediary in the generation of CO₂. Carbon monoxide can poison the platinum catalyst, resulting in irreversible damage to the cell. Together, these sources can cause high rates of unreliability, lower operating efficiencies and, worse reduced performance or poisoning resulting in significant loss of power.

PEM Fuel Cells

PEM fuel cells using hydrogen and oxygen is more attractive compared to the other fuel cell technologies for sensor network applications. However, PEM fuel cells are not widely used in field applications because they face significant hurdles. Firstly, PEM fuel cells are faced with the problem of degradation of their components that result in shortened lives and lower reliability compared to batteries. A second major challenge is the storage of hydrogen. Conventional methods of hydrogen storage are bulky and inefficient, providing only a marginal advantage over current batteries. A third major challenge is that the fuel cell produces lower power compared to batteries. A fourth challenge is that PEM fuel cells have high capital and operating costs. Significant progress is being made in all these areas. Our research addresses the first three challenges.

PEM Fuel Cell Overview

PEM fuel cells became the focus of our interest in high-energy power supplies because it is one of the more mature technologies and shows significant potential for both high-energy and long-life applications (Barbir, 2005). A PEM fuel cell Membrane Electrode Assembly (MEA) has several major components that are all subject to degradation (Fig. 2). They are the Gas Diffusion Layer (GDL), bi-polar plates, the membrane and catalyst layers. The GDL facilitates transfer of input gasses to the anode and cathode. The bi-polar plates have an important role in distributing the reactant gases to the anode and cathode, conduct electrical current within the cell and help to remove heat from the active area, while preventing leakage of gasses. The anode catalyst layer facilitates the oxidation of hydrogen molecules into protons while the membrane allows for the transport of protons from the anode to the cathode. The cathode catalyst layer facilitates the assembly of protons and oxygen molecules into water via a reduction reaction.

Component Degradation

Extensive research has been done to identify the mechanisms that degrade fuel cell components, including the Gas Diffusion Layer (GDL), membrane and catalyst layers. Gas Diffusion Layer (GDL) degradation affects the ability of the cell to absorb reactants. This degradation includes loss of hydrophobicity from corrosion of Polytetrafluoroethylene (PTFE) in the cathode. This can result in flooding causing loss in performance (Kandlikar *et al.*, 2011). Degradation of the GDL can reduce or block gas passageways resulting in choking of the fuel cell. A major source of GDL degradation has been due to mechanical compressions resulting in stress and strains that reduce the micropore regions. This reduces gas transport and thus reduces the effectiveness of the GDL. Freeze thaw cycles are well known to damage the GDL as freezing water expands and damages the micro-pores. Another source of damage to the GDL is corrosion of carbon layers and dissolution of platinum catalyst layers (Barbir, 2005; Wu *et al.*, 2008). However, it should be noted that many of these sources of GDL degradation can be prevented by avoiding such conditions as structural damage, flooding or freezing.

Membranes are also subject to degradation and can be classified into three categories, thermal, mechanical and chemical (Wu *et al.*, 2008). An important source of membrane degradation is due to mechanical stress and strain. The root cause of this degradation is flooding. Membranes once weak are prone to formation of pinholes that result in fuel cross-over and significant reduction in power generated. This is followed by catastrophic failure of the fuel cell (Liu *et al.*, 2001). Mechanical stress and strain is known to occur due primarily to humidity and temperature cycling. Humidity is known to impact the mechanical properties of the membrane. With too high a humidity, the membrane curls up and with too little humidity the membrane hardens and dries out. The impact of relative humidity cycling can be severe. It has been shown that a membrane cycled between a Relative Humidity of 30% and 80% faces structural failure after only 100 cycles (Huang *et al.*, 2006). A second source of membrane degradation is due to chemical attack. The result from chemical attack is reduced strength of the membrane leading to structural failure.

In many cases, platinum catalyst degradation in the cathode is an important factor in fuel cell durability and life (Liu *et al.*, 2001). One cause of catalyst degradation is the dissolution of the platinum particles into ions. The ions either redeposit on large platinum particles or dissolve and migrate away from the catalyst layer and into nearby regions (Kandlikar *et al.*, 2011). Sustained degradation reduces the available catalyst surface in the anode and cathode resulting in loss of power. It also weakens the carbon support structure that holds the platinum and vice-versa through carbon corrosion.

Carbon corrosion is another important source of degradation in a fuel cell. The carbon structure breaks into particles that migrate into the membrane and GDL. The migrating platinum catalyst and carbon particles weakens the membrane structure as discussed above, causing irreversible structural damage ultimately resulting in tears and pinholes. The fuel cell catalyst is impacted by the oxidation of the platinum particles. Oxidation of the platinum particles results in the formation of surface films of platinum oxide that effectively reduces the available catalyst surface area resulting in loss of power. While oxidation of platinum reduces the surface area, it is also known to protect platinum particles beneath the oxide layer from dissolution.

Fuel Cell Life Time Prediction & Degradation

Based on results from several degradation models (Bi and Fuller, 2008; Thangavelautham and Dubowsky, 2013; Darling and Meyers, 2003; Fowler *et al.*, 2002) we produce a combined equation to predict the effect of fuel cell catalyst life. The inputs to the model include voltage V , temperature T , humidity, h and voltage oscillation amplitude, λ . This equation for τ_{clife} in years presumes each operating variable has an independent effect on the life of the fuel cell catalyst. The equation is given below:

$$\tau_{clife} = a_V e^{-k_V V} a_T \cdot e^{-k_T T} \cdot (a_h \ln h + k_h) \cdot (1 - a_\lambda \lambda) \quad (5)$$

The equation considers the effect of operating voltage, operating temperature, operating humidity and voltage oscillations. The list of variables used and their respective values are shown in Table 2.

For field applications, ambient temperature and humidity may change over the course of a day and over the seasons. Next, we model the impact of humidity and temperature oscillations on the life of the fuel cell membrane. A second degradation phenomenon modelled is degradation of the membrane due to humidity cycling given below. Based on the experiments from Huang *et al.* (2006) and others, the PEM fuel cell membrane can only withstand a finite number of humidity cycles that result in

Table 2 Constant value for fuel cell life prediction model

Variable	Value
a_v	3.11×10^{14}
a_T	7.67 years
a_h	-3.37×10^{-1}
a_λ	4.173 V^{-1}
k_h	2.77
k_v	-4.48 V^{-1}
k_t	$-3.75 \times 10^{-2} \text{ C}^{-1}$

Note: Drawn by Thangavelautham, J., Strawser, D., Dubowsky, S., 2017. The design of long-life, high-efficiency PEM fuel cell power supplies for low power sensor networks. International Journal of Hydrogen Energy 42, 20277–20296.

Table 3 Fuel cell catalyst life comparison for field sensor network

Conditions	Predicted fuel cell life
Operating voltage 0.78 V, 0.2 V oscillation, no environment control	0.27 years
Operating voltage 0.78 V, 0.2 V oscillation, 15% humidity, +5°C dew point	2.2 years
Operating voltage 0.78 V, 0.02 V oscillation, 15% humidity, +5°C dew point	12.2 years

Note: Drawn by Thangavelautham, J., Strawser, D., Dubowsky, S., 2017. The design of long-life, high-efficiency PEM fuel cell power supplies for low power sensor networks. International Journal of Hydrogen Energy 42, 20277–20296.

stress loading culminating in mechanical failure of the membrane.

$$\tau_{mlife} = \Delta t_{hosc} \cdot \frac{b_{memb}}{RH_{max} - RH_{min}} \quad (6)$$

where Δt_{hosc} is the humidity cycling period, b_{memb} is a membrane specific constant and is 0.02 for Nafion NR111, RH_{max} and RH_{min} is the maximum and minimum relative humidity.

The total life of the fuel cell is then modelled as the following:

$$\tau_{life} = \min(\tau_{clife}, \tau_{mlife}) \quad (7)$$

where τ_{life} is the expected life of the PEM fuel cell. In summary, the expected life is the minimum of the catalyst life presented earlier and life of the membrane due to humidity cycling. These factors independently impact the fuel cell. Catalyst degradation begins with performance degradation of the catalyst and finally results in catastrophic loss, while membrane degradation results in mechanical damage to the membrane that results in the formation of pinholes and ends up in catastrophic loss.

Using annual temperature and humidity conditions of a location such as Negev, Israel, we can predict the net effect on life of a fuel cell power supply in the field. We presume the fuel cells operating at 0.78 V and voltage oscillations are at 0.2 V. Using ambient temperature and humidity (in other words no environment control) the expected fuel cell life is 0.27 years (Table 3).

Next, we set the fuel cell to operate at 10% humidity and operate the power supply 5 degrees above dew point. The annual maximum and minimum dew point in Negev, Israel. By effectively lowering the operating temperature and humidity, we expect to increase the life of the fuel cell. In addition, lower operating humidity also reduces the chances of flooding. The resultant fuel cell life is 2.2 years (Table 3).

Furthermore, we can reduce voltage oscillations experienced by the fuel cell system to 0.02 V. Our studies show that we can minimize oscillations to 0.02 V further extending life to 12.2 years (Table 3). By effectively controlling the humidity, temperature, operating voltage and voltage oscillations we can extend the operating life of the fuel cell.

Fuel Storage

Another major challenge as noted earlier is hydrogen storage. High pressure and cryogenic storage of hydrogen are clearly impractical for small, low power applications such as sensors networks. A third practical option is the use of chemicals including metal hydrides and hydrocarbons. Conventional reversible metal hydrides release hydrogen through changes in pressure or temperature. Reversible hydrides are valued because of their ability to be recharged with hydrogen, they are not ideal for long-life field applications because they normally have low hydrogen storage densities (defined as the weight of hydrogen divided by the total weight of the hydride) on the order of 1%–2%. However, there exists other higher hydrides with much higher yield but they require much higher temperatures, in the order 200–700°C. Achieving such high temperatures for small, low-power devices limits the potential field applications and increases complexity. An alternate option is the use of chemical hydrides that release hydrogen through chemical reaction (Kong *et al.*, 1999). This include hydrocarbons, but they also contain trace amounts of sulphur that can poison a PEM fuel cell.

Hydrolysis is the reaction of chemical hydride with water to produce hydrogen. However, popular water activated metal hydrides including sodium borohydride (NaBH_4) and magnesium hydride (MgH_2) have low hydrogen content, low-reliability and require expensive catalysts. Alternatives such as calcium hydride do not require catalyst but have low yield. Our research has focused on lithium hydride (LiH) which has higher net hydrogen content by mass than calcium hydride. Hydrogen can be released by exposing lithium hydride to water releasing the hydrogen from the hydride and stripping water of its hydrogen. Lithium hydride unlike other water activated hydrides requires no complex mechanisms or catalysts to start, control and complete the hydrogen release reaction. Our experimental studies show that water activated lithium hydride can achieve 95%–100% reaction completion rates with excess of water (Fig. 4) (Strawser *et al.*, 2014).

Fuel Cell Operations

Power Management

The proposed fuel cell power supply consists of a fuel cell-battery hybrid system (Fig. 3). The fuel cell constantly charges a battery and the battery/fuel cell system periodically powers an electrical load. By having several fuel cells in series, the net voltage can be set high enough to charge a battery without use of additional electronics. Otherwise, a step-up DC-DC convertor is required. The DC-DC typically introduces voltage oscillations that can by our analysis result in degradation of the fuel cell power supply (Thangavelautham and Dubowsky, 2013). It also decreases the efficiency of the system due to voltage conversion losses.

Without the DC-DC convertor, the system is simpler and more efficient. In addition, a variable resistor circuit is included in the circuit. This variable resistor circuit is activated and used during start-up and shutdown, to ensure the fuel cell is at proper voltages at all times and to avoid fuel starvation. The variable resistor ensures the fuel cell maintains a constant voltage during start-up and shutdown. Finally, an electrical load is connected to the circuit and periodically turned on at a set duty cycle or on-demand. For sensor network applications, we wish to maximize both the life and fuel cell conversion efficiency to minimize hydrogen fuel consumption. The operating efficiency of a fuel cell given as a function of voltage is (Barbir, 2005):

$$\lambda_{FC} = 0.81V \quad (8)$$

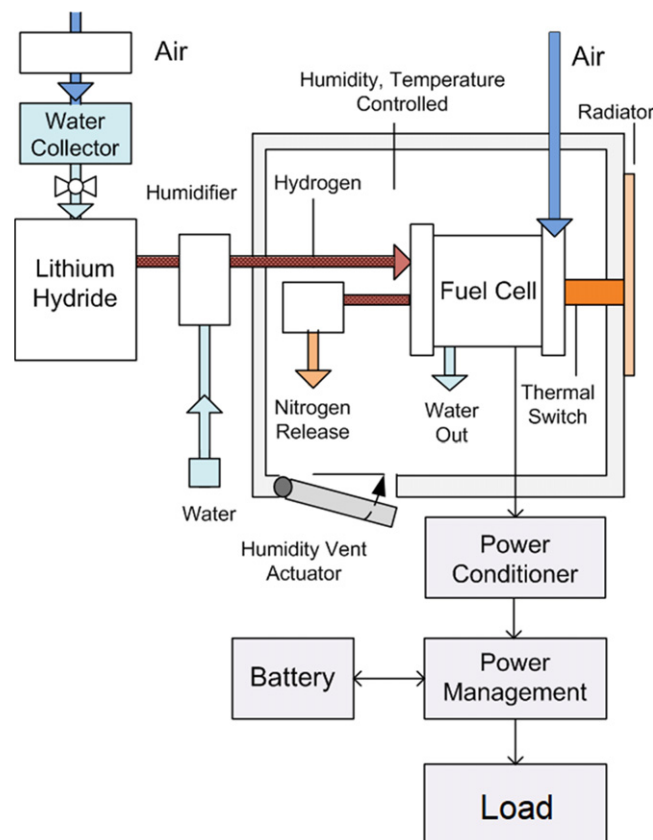


Fig. 3 PEM fuel cell power supply for sensor networks. Drawn by Thangavelautham, J., Strawser, D., Dubowsky, S., 2017. The design of long-life, high-efficiency PEM fuel cell power supplies for low power sensor networks. *International Journal of Hydrogen Energy* 42, 20277–20296.

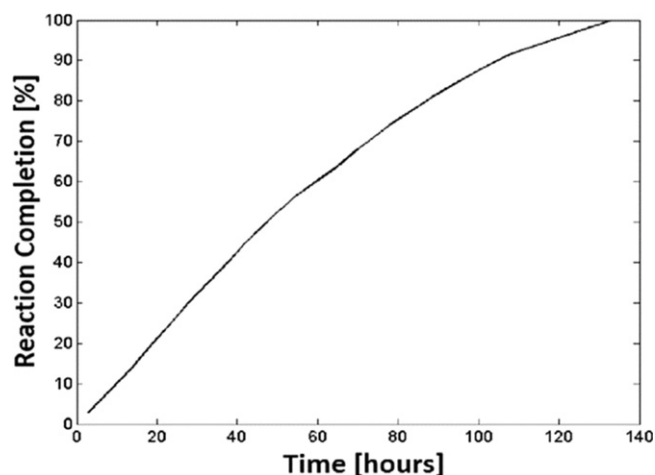


Fig. 4 Lithium Hydride Hydrolysis reaction with excess water. Credit from Strawser, D., Thangavelautham, J., Dubowsky, S., 2015. A passive lithium hydride based hydrogen generator for low-power fuel cells for long-duration applications. *International Journal of Hydrogen Energy*, 1–36.

A third constraint is that the fuel cells need to have matching output voltage to charge the battery. This is to avoid a specialized battery charging circuitry. A battery charging circuitry would add additional complexity to the system, and be a source of voltage oscillations and it will further reduce system efficiency due to conversion losses. A battery needs to be selected that has enough capacity so that when the load is powered, it does not result in a substantial voltage drain from the battery. This is once again to avoid voltage oscillations that degrade the fuel cell. This expected change in voltage due to loss of charge can be calculated from integrating a voltage-battery charge curve.

A power control system monitors the fuel cell output voltage and the battery. Once the voltage drops just below operating voltage range, the control system would divert output power from the fuel cell to charge the battery until the net voltage reaches the upper boundary of the operating voltage range. However, these rechargeable batteries increase the cost, complexity and reduce system robustness. These rechargeable batteries cannot provide power when there is a prolonged power shortage. Hence, the system needs to be designed to predict these shortages and have sufficient battery capacity to handle them.

Air, Water and Humidity Management

The purpose of the air and water management system is to ensure oxygen is delivered to the fuel cell cathode and ensure inert gasses such as nitrogen don't build-up in the anode. We assume that air-breathing PEM fuel cells are used; hence the oxygen is freely extracted from the air. However, it is critical that the air entering the cathode maintains a proper humidity to ensure smooth operation of the fuel cell. This requires that the air humidity not be too low or too high. Improper water management can result in loss of performance, prolonged flooding and shortened life (Kandlikar *et al.*, 2011). The results show that humidity needs to be well above 10% to avoid accelerated degradation. However, input humidity also cannot be too high, otherwise this might cause flooding that blocks pores in the GDL and cathode and result in reduced power output due to fuel starvation, oxygen starvation or both.

We can control the humidity of the fuel utilizing a feed-back control system. Once the humidity reaches beyond a set-point threshold, a vent opens to release the excess humidity into a dry environment. Furthermore, this controls approach can be made passive utilizing humidity sensitive material that can expand or contract (i.e., open or close) a vent. However, our laboratory studies shown these methods are unable to achieve humidity control within $\pm 10\%$ relative humidity.

A second objective as noted earlier is to prevent build-up of inert gasses such as nitrogen in the anode. The fuel cells as noted earlier are configured in a dead-end anode mode. This typically maximizes fuel utilization, but at a cost of build-up on nitrogen on the anode. If this is left unattended, a fuel cell will starve of hydrogen and drop in voltage. The net effect is that this degrades the fuel cell catalyst and limits life. A conventional method of removing the nitrogen is using a purge valve or material to release nitrogen upon build up.

Fuel Management

Here it is shown that lithium hydride is ideal for storage and release of hydrogen. Hydrogen can be released by exposing the hydride to water, releasing the hydrogen from the hydride and stripping water of its hydrogen according to the following reaction:



Lithium hydride unlike other water activated hydrides requires no complex mechanisms or catalysts to start, control and complete the reaction (Kong *et al.*, 1999; Strawser *et al.*, 2014). Our experimental studies show that water activated lithium hydride can achieve 100% reaction completion rates (see Fig. 4). Another appealing feature of water activated lithium hydride, for PEM fuel cells is that in theory, it produces enough waste water for activating the lithium hydride. When exhaust water from a fuel cell is

reused for producing more hydrogen using a lithium hydride generator, the reaction achieves a theoretical 25% hydrogen storage efficiency or 5000 Wh/kg specific energy (Strawser *et al.*, 2014) (40 folds higher than lithium ion batteries).

Several control strategies have been developed to produce the required hydrogen at high operating efficiencies. The passive hydrogen generator is designed not to carry water on board. Instead, it extracts water vapour from its surroundings and can work for humidity 15% and higher. This design is tested for long duration to produce hydrogen for a fuel cell power supply in (Strawser *et al.*, 2014; Thangavelautham *et al.*, 2017). The generator was designed to not carry water on-board. While passive lithium hydride generators relying on liquid water have been developed, this generator is unique in its ability to use water vapour from the atmosphere or fuel cell exhaust (Strawser *et al.*, 2014). Additionally, lithium hydride generators have not been experimentally validated for long periods of time or with a hybrid PEM fuel cell system. Based on the lessons learned, an experimental system was built to demonstrate the fuel cell power supply for field sensor networks.

The waste product from the lithium hydride hydrolysis reaction is lithium hydroxide. Lithium hydroxide is typically used as a CO₂ scrubber and the following reaction results in environment friendly lithium carbonate (Li₂CO₃) and water. Lithium carbonate exists as a natural mineral form called zabuyelite.



Applications

Consider a spherical sensor network node (Fig. 5) with a 10 cm radius. The node consists of 4 interchangeable modules, a central System on a Chip microcontroller module containing electronics, a wireless-radio, a power module consisting of either fuel cells or batteries and a payload module to house sensors. The payload module may contain temperature, humidity/moisture, vibration, accelerometers, chemical, light sensors and cameras. These nodes periodically communicate to neighbouring nodes and a central base station. Hence, they will be low-power devices that intermittently operate at high power to operate their payloads or communicate data. Each node will require a minimum 10 mW for standby power.

It is assumed the sensor modules consume 500 mW average. These nodes need to operate for 3–5 years unattended, without any periodic maintenance and have a mass less than 30 kg, so that it may be easily carried and deployed on site.

It is assumed that the field sensor is deployed in a temperate, desert or tropical location, operating continuously, where the temperature stays between 15 and 40°C and humidity varies between 0.15 and 0.9. In colder climates, the sensor node will require heaters to maintain the fuel cell temperature at 15°C or higher.

For environmental monitoring, the duty cycle can be low, utilizing environmental sensors (air, CO₂, temperature, humidity, soil moisture) that are typically low power devices with data being gathered periodically at duty cycles of 10% or less.

Battery Sizing

First batteries are considered as power supplies for these nodes. Batteries self-discharge, where stored energy is lost as heat and is modelled as a geometric series. It is further assumed that the last 20% of the stored energy cannot be used. The mass of a battery power supply required is:

$$M_{bat} = \frac{\alpha E(T)(1 - r^T)}{\rho_{bat}(1 - r)} \quad (11)$$

Where, M_{bat} is the total mass of the battery power supply required for T years of life, α is the capacity margin, r is the self-discharge rate, ρ_{bat} is the energy density of the battery, $E(T)$ is the energy required to power a payload device for T years according

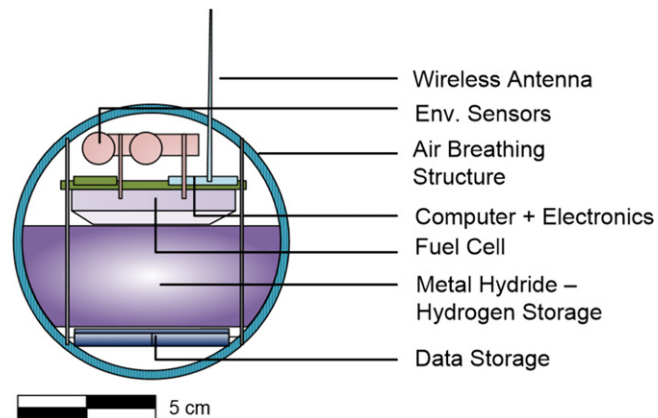


Fig. 5 A sensor node for environmental monitoring of air quality and pollution readings. Drawn for the encyclopedia article by Jekan Thangavelautham.

to a given duty cycle. The energy densities, self-discharge rates and mass of the battery power supplies are shown in Table 4 (Thangavelautham and Dubowsky, 2013).

A sensor module weighing more than 30 kg or more lacks scalability to hundreds or even thousands of modules owing to the high cost and logistics required for transporting and installing them. Ideally, the sensor module and power supply needs to have low-mass that enables them to be carried in backpacks, mules and be readily deployed in off-grid environments.

Fuel Cell Sizing

Next, the proposed PEM fuel cell power supply concept is compared against batteries (Thangavelautham and Dubowsky, 2013). The mass of the fuel for the PEM fuel cell power supply is given by:

$$M_{fuel} = \frac{E(T)}{\rho_{fuel} \cdot r} \cdot \ln \left| \frac{0.5 - \frac{1}{r}}{T + 0.5 - \frac{1}{r}} \right| \quad (12)$$

where M_{fuel} is the total mass of the fuel for T years of life, ρ_{fuel} is the specific energy of the fuel, $E(T)$ is the energy required to power a payload device for T years for a given a power profile, r is the power degradation rate of the fuel cell power supply for a specified operating point. In addition, the dry mass of the power supply excluding the structural shell is given in Table 5. The lithium hydride fuel has a volume of 0.7 g/cm^3 . Based on these factors, the shell consists of an aluminium spheres, 1 mm thick, each with enough internal volume to hold the lithium hydride fuel.

The energy density of the fuel is given as follows:

$$\rho_{Fuel} = \rho_{LiH} \cdot \lambda_{FC_EH2} \cdot \eta_{LiH_RC} \quad (13)$$

Where, σ_{LiH} is the usable quantity of hydrogen energy released from the lithium hydride hydrolysis reaction (presuming water reuse), η_{LiH_RC} is the percentage reaction completion of the lithium hydride reaction and λ_{FC_EH2} is the efficiency of the fuel cell system.

The total efficiency of the fuel cell is calculated from the following:

$$\lambda_{FC_EH2} = \lambda_{FC} \cdot \lambda_{FC_Stack} \cdot \lambda_{Purge} \quad (14)$$

Where λ_{FC} is the chemical to electrical efficiency of the individual fuel cells and is related to the operating voltage of the cell, V/V_{LHV} , where V_{LHV} is 1.23 V, λ_{FC_stack} is the fuel cell stack efficiency and is 0.95, λ_{purge} is the losses due to nitrogen purging and is 0.95. Our work shows that operating each cell at 0.78 Volts, giving it a $\lambda_{FC}=0.63$ is a good trade-off between efficiency, life and power output. To supply peak system power and avoid oscillatory voltage seen by the fuel cell, the battery handles the high and varying power of the load.

To generate the average power required this requires 5 fuel cells or more. This design vastly simplifies the fuel cell control electronics. The fuel cells are assembled in this configuration to avoid a DC-DC convertor. With each fuel cell operating at 0.78 volts, 5 are assembled in series to obtain a nominal volt of 3.9 Volts. Note, that the mass calculated accounts for the extra fuel required due to losses from degradation and to ensure the fuel cell provides the energy required at the end of T years. Table 5

Table 4 Power supply technology characteristics

Technology	Specific energy (Wh/kg)	Self-discharge/degradation (% per month)
Alkaline	110	0.5
Lithium ion	140	5
Lithium CR	270	0.17
Lithium thionyl chloride	420	0.08
LiH fuel cell	5000	0.12

Note: Drawn by Thangavelautham, J., Strawser, D., Dubowsky, S., 2017. The design of long-life, high-efficiency PEM fuel cell power supplies for low power sensor networks. International Journal of Hydrogen Energy 42, 20277–20296.

Table 5 Dry mass of sensor module

Component	Mass [g]
Fuel cell and electronics	100
Sensor payload	80
Computer	50

Note: Drawn by Thangavelautham, J., Strawser, D., Dubowsky, S., 2017. The design of long-life, high-efficiency PEM fuel cell power supplies for low power sensor networks. International Journal of Hydrogen Energy 42, 20277–20296.

shows the mass breakdown of the fuel cell power supply. The power supply consists of the fuel cell, lithium hydride fuel storage system, power control electronics and other components for air and water management. The lithium hydride fuel produces hydrogen with the addition of water extracted from the air.

System Comparison between Battery and Fuel Cell

We first compare the proposed system with batteries. Fig. 6 shows the mass of the power system vs. average power of 0.5 W for 5 years of operation at 100% duty cycle. For very low power, batteries provide an advantage, because of the additional overhead mass required for the fuel cell power supply. The advantage for the fuel power supply is apparent when the system requires high-energy. Fuel cells using lithium hydride shows a 50-fold advantage in terms of mass compared to lithium ion batteries, a 7-fold advantage over Lithium CR batteries and a 3-fold advantage versus lithium thionyl chloride batteries. It should be noted that the rechargeable batteries weigh tens or hundreds of kilograms. For a network of hundred or thousand nodes, most of the batteries considered are not feasible. We also compare the proposed fuel cell power supply with previously reported fuel cell storage technologies (Fig. 7). These previously reported numbers are extrapolated to the required energy for mission lifetime.

This includes a PEM fuel cell powered using sodium borohydride and Direct Methanol Fuel Cells (DMFC). For these comparisons, the dry mass for these fuel cell configurations is assumed to be the same as the concept fuel cell system presented here. In addition, the operating efficiency of DMFC is lower at 40% and it outputs carbon dioxide that needs to be vented. DMFC offers a simpler approach to fuel storage, however, challenges exist with fuel cell life, due to build-up of carbon monoxide and low operating efficiencies. We presume these challenges have been overcome. The major difference is the mass and volume of the fuel and container.

Overall, for high duty cycle applications (see Fig. 8 left), the proposed fuel cell power supply offers a compelling advantage over other energy storage technologies. A LiH fuelled PEM fuel cell power supply of 78 kg can be fully operational for 5 years at 100% duty cycle and supply 2 W of power. In comparison, a lithium thionyl chloride primary battery system would weigh 360 kg. Overall, the proposed power supply offers a 4.6-fold mass advantage over the best battery technology and 5.25-fold advantage over DMFC.

In another scenario (Fig. 8 right), we consider powering a field sensor at 5% duty cycle for 5 years. This is equivalent to operating a sensor for 3 s every minute. The proposed fuel cell power supply can power a 20 W field sensor and have a total mass of 51 kg. In comparison, the lithium thionyl chloride battery would have a mass of 173 kg. The advantage of the lithium hydride fuel cell system is reduced mass for long duration missions.

Summary

Overall, the presented lithium hydride fuelled PEM fuel cell offers a substantial advantage over conventional batteries and other fuel cell and hydrogen technologies. These results present a promising pathway towards field testing and evaluation of the

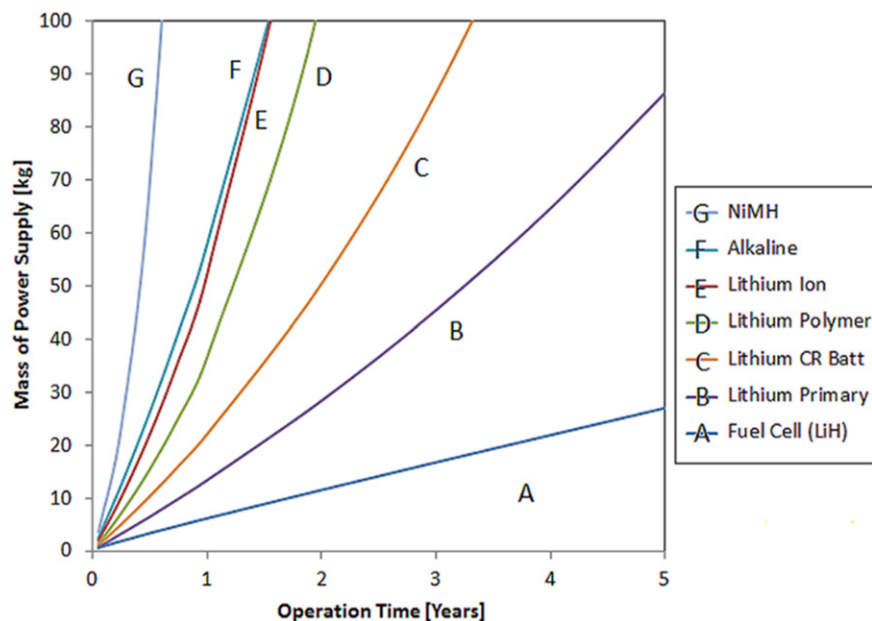


Fig. 6 Comparison of field sensor power supply technologies for up to 5 years of operation, 0.5 W and 100% duty cycle. Results generated by author Jekanthan Thangavelautham for this entry.

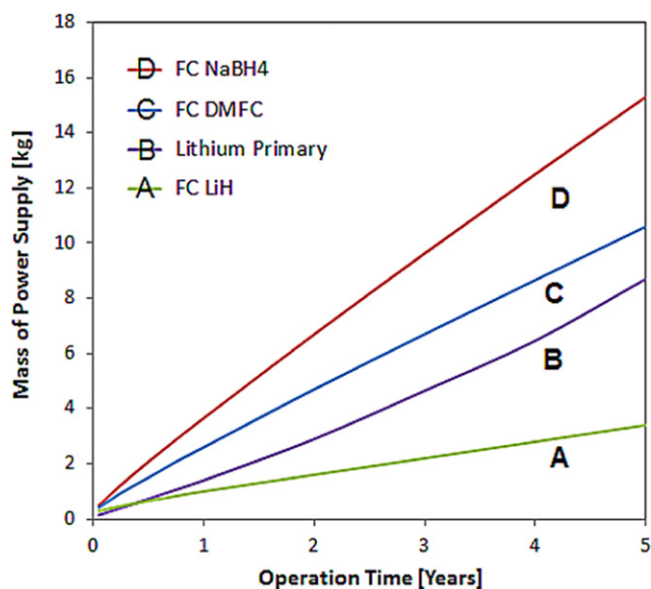


Fig. 7 Comparison of fuel cell and battery technologies for field sensor power supply. The system is compared for up to 5 years of operation, 0.5 W and 10% duty cycle. Results generated by author Jekanthan Thangavelautham for this entry.

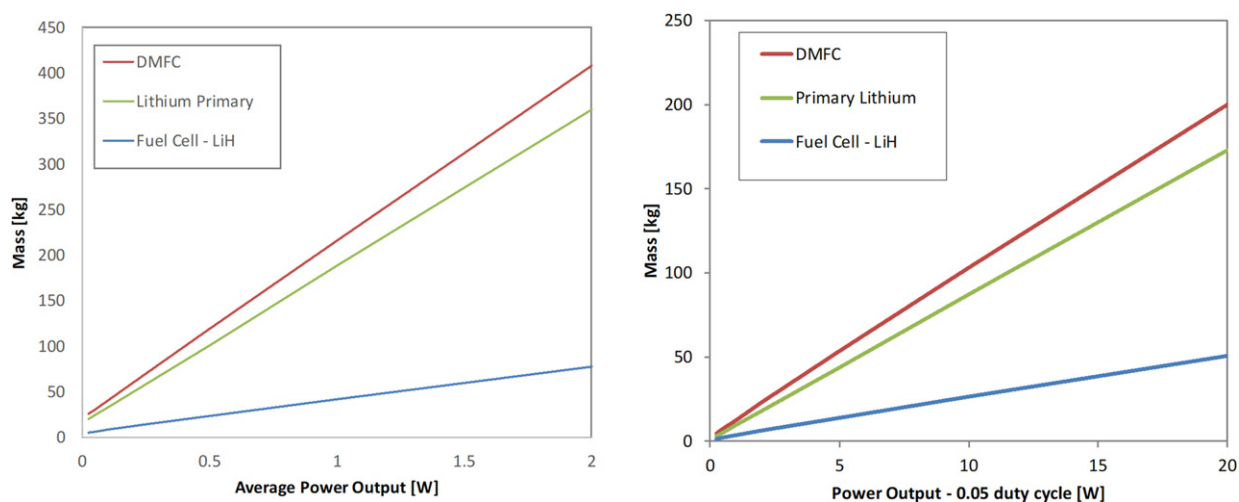


Fig. 8 Comparison of leading fuel cell and battery technologies for field sensor power supply. The system is compared for up to 5 years of operation with 100% duty cycle (left) and 5% duty cycle (right). Results generated by author Jekanthan Thangavelautham for this entry.

proposed concept. For higher duty cycle applications, the proposed system shows an increased advantage over conventional technology. The mass advantage approaches nearly 5-folds over lithium primary batteries. This shows the promise in this technology for high-energy, remote, off-grid applications.

See also: Treatment and Recycling of Domestic and Industrial Wastewater

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Sustainable Biofuels for Automotive Applications

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Nomenclature

(C_p)_{water} specific heat of water = 1 Kcal/Kg.

(CV)_{fuel} Calorific value of the fuel.

(CV)_{thread} Calorific value of thread = 4.18 Kcal/Kg.

(CV)_{wire} Calorific value of Nichrome ignition wire = .355 Kcal/Kg.

M_{fuel} Mass of the sample or biodiesel in grams.

M_{thread} Mass of the cotton thread in grams.

M_{water} Mass of the water in Kg.

M_{wire} Mass of the wire in grams.

ΔT Increase in the temperature of the surrounding water jacket.

Introduction

During the last century, the consumption of energy has increased substantially due to change in the life style and significant growth of population. This increase of energy demand has been supplied using fossil resources, which caused the crisis of fossil fuel depletion, the increase in the price and serious environmental impacts such as global warming, acidification, deforestation, ozone depletion, and photo chemical smog. As fossil fuels are limited sources of energy, the increasing demand of energy has led to a search of alternative sources of energy that would be economically efficient, socially acceptable, and environmentally sound. Petroleum based fuels consist of blends of hundreds of different chemicals of varying hydrocarbon chains, many of these are hazardous. Carbon monoxide (produced when combustion is incomplete), nitrogen oxides (produced when combustion occurs at very high temperature), sulphur oxides (produced when elemental sulphur is present in fuel), and particulates that are generally produced during combustion are other specific emission concern. So, it is time to search for its alternative fuels. There are several alternative sources of fuel like vegetable oils, biogas, biomass, primary alcohols which are all renewable in nature. Among these fuels, vegetable oils appear to have an exceptional importance as they are renewable and widely available, biodegradable, non-toxic and environmental friendly. Biodiesel refers to a family of products made from vegetable oil or animal fats and alcohol, such as methanol called mono alkyl esters of fatty acids. Study shows on the mass basis; biodiesel has energy content of about 12% less than petroleum based fuel. It reduces unburned hydrocarbons (HC), carbon monoxide (CO), and increase oxides of nitrogen (NO_x) than diesel fueled engine (Ayhan-Demirbas, 2007). Gas chromatographic system is widely applied technique in many branches of science and technology. For over a century, GC has played a fundamental role in determining how many components and in what proportion they exist in nature. In a gas chromatographic system, the ability to establish the nature and chemical structure of these separated and quantified compounds is ambiguous and reduced, and requires a spectroscopic detection system. In this system, the sample to be analyzed may be liquid solution or a collection of molecules adsorbed on a surface. During the transfer into the GC, the sample is volatilized by rapid exposure to a zone kept at relatively high temperature and mixed with a stream of carrier gas (Stashenko and Martínez, 2014). Biodiesel is a clean burning alternative fuel, produced from renewable resources like pure or used vegetable oil, both edible and non-edible. It can be used in compression-ignition (diesel) engines with little or no modification. Biodiesel is simple to use, biodegradable, nontoxic, and essentially free of sulphur and aromatic. It can be stored just like petroleum diesel fuel and hence does not require a separate infrastructure. The use of biodiesel in conventional diesel engines results in substantial reduction of unburned hydrocarbon, carbon monoxide and matter. Its high cetane number improves the ignition quality even when blended in petroleum diesel. Indian plants like *Jatropha* (*Atrophy curcas*), *Mahua* (*Madhuca Indica*), *Karanja* (*Pongamia pinnata*), and *Neem* (*Mellia* are widely used). In India, as edible oils are in short in supply, non-edible tree borne oilseeds of *Karanja*, *Jatropha*, *Mahua*, *Neem* are being considered as sources of straight vegetable oil and biodiesel (Radha and Manikandan, 2011). Plant species, which have 30% or more fixed oil in their seeds or kernel, have been identified. In India, edible oils are in short supply, and country must import up to 40% of its requirement. Hence prices of edible oils are higher than that of petroleum diesel. Most of the edible oils used currently for manufacture of Biodiesel, are stable. These do not decompose much on storage. Hence these are preferred for Transesterification process. Non-edible oils are not that stable, and need a lot of pre-treatment adding to the cost of manufacture of biodiesel. Government policy is also very important in production of biodiesel in India. Government of India started biodiesel mission in 2003, but it announced biodiesel policy on 11 September 2008. As per government policy, an indicative target of 20% by 2017 for the blending of biodiesel in diesel fuel and proposed biodiesel production will be taken up from non-edible oil seeds grown in waste, degraded, marginal lands. Biodiesel plantations on community, Government, forest waste lands would be encouraged while plantation in fertile irrigated lands. It was experimentally examined the Performance, emission and combustion characteristics of methyl esters of Punnai, Neem, Waste Cooking Oil and their diesel blends in a C.I. engine. For their study, Punnai oil methyl esters, neem oil methyl esters, and Waste Cooking Oil Methyl Esters were prepared by transesterification process. The Bio diesel-diesel blends were prepared by mixing 10%, 20%, 30%, and 40% of bio diesel with diesel. The effects of three methyl esters and their diesel blends on engine performance, combustion, and exhaust emissions were examined at different engine loads. Experimental results concluded that up to 30% of methyl esters did not affect the performance, combustion, and emissions characteristics

(Subramaniam *et al.*, 2013). On the other hand, above B30 (30% Biodiesel with 70% diesel) are reduction in performance, combustion, and emission characteristics were clear from the study. It was evident in the study that for all test fuels the brake thermal efficiency increased with increase in brake power. Among B10, B20, B30, B40, and B100 biodiesel, bio diesel blends up to B30 has a maximum brake thermal efficiency. With an increase in bio diesel blends the value of BSFC also increased. CO, CO₂, HC, NO_x, and smoke are the major exhaust emissions from C.I. engines. The diesel engine produces lesser amount of CO and HC emissions than spark ignition engines. Moreover, in case of bio diesel fueled engines, presence of airborne oxygen as well as its presence in the molecules of bio-diesel aids nearly complete combustion of fuel. The emission of diesel at maximum load was noted to be 960 ppm, whereas for B100 NOME it was noted to be 890 ppm. This reduced NO_x emission for B100 bio diesel when compared to diesel may be due to the reduced premixed combustion rate leading to lower NO_x emissions for B100 bio diesel operation. The experimental results proved that up to B30 blend of bio diesel-diesel blends, the performance and emission Characteristics were not much affected. When the blend ratio increased, incomplete Combustion takes place because of less time available for mixture formation, which leads to a reduction in the brake thermal efficiency of the engine as well as an increase in the emission level. The combustion analysis revealed that the overall combustion characteristics of B30 biodiesel blends were closer to diesel than pure bio diesel. Overall, the methyl esters of waste cooking oil proved improvements in performance and emission characteristics than the methyl esters of Punnai and Neem due to its closer physical and thermo-chemical properties to neat diesel (Liaquat *et al.*, 2013). It was studied the effect of storage on the physio-chemical properties of biodiesel produced from *Ricinus communis* (Castor), *Heavea brasiliensis* (Rubber), *Gossypium hirsutum* (Cotton), *Azadirachta indica* (Neem), *Glycin max* (Soyabean), and *Jatropha curcas* (Jatropha oils) stored in an open-air environment for a period of ten months. The peroxide value was found to be increasing with storage. However, since peroxide value is an index of oxidation of vegetable oil or its derivatives, it is obvious that oxidation of biodiesel takes place at rapid rate due to in built oxygen and unsaturated fatty acids (Muralidharan and Vasudevan, 2011). It has been conducted experiment with different blends (B10, B20) of neem oil and diesel at various loads. The results showed that the brake thermal efficiency of diesel is slightly higher at all loads followed by blends of neem oil and diesel, it has been established that 20% of neem oil biodiesel can be used as a substitute for diesel without any engine modification thus neem oil as non-edible oil can be a good renewable raw material for biodiesel production. From the experimental analysis, it was found that the blends of neem oil and diesel could be successfully used with acceptable performance up to a certain extent. Based on the result of this study properties of neem oil suggest that it cannot be used directly as CI engine fuel due to higher viscosity, density which will result in low volatility and poor atomization of oil during oil injection in combustion chamber causing incomplete combustion and carbon deposits in combustion chamber. Biodiesel blends produce lower brake thermal efficiency and higher brake specific fuel consumption than diesel because of low calorific value. The properties results of all blends show that blends up to 20% straight neem oil have value of viscosity and density equivalent to specified range for CI engine fuel, therefore it can be concluded that up to 20% blends can be used to run the CI engine at short term basis (Anbumani and Singh, 2010). It has been experimentally examined properties, performance and emissions of different blends (B10, B20, and B40) of PME, JME and NME in comparison to diesel. Results indicated that B20 have closer performance to diesel and B100 had lower brake thermal efficiency mainly due to its high viscosity compared to diesel. However, its diesel blends showed reasonable efficiencies, lower smoke, CO and HC. Jatropha and Neem based methyl esters (biodiesel) can be directly used in diesel engines without any engine modifications. Brake thermal efficiency of B10, B20 and B40 blends are better than B100 but still inferior to diesel. Properties of different blends of biodiesel are very close to the diesel and B20 is giving good results. It is not advisable to use B100 in CI engines unless its properties are comparable with diesel fuel. Smoke, HC, CO emissions at different loads were found to be higher for diesel, compared to B10, B20, B40 blends (Kumar *et al.*, 2013).

Methodology

Production of Biodiesel

To produce biodiesel from crude oil four process such as oil filtration, acid esterification, alkaline Transesterification and washing process, are used (Figs. 1–3).

Crude oil production

Coconut crude oil:

Seed = 22 kg, Extracted oil = 12.5 kg, Waste = 9.5 kg.

Yield = 56.81%

Castor crude oil:

Seed = 25 kg, Extracted oil = 9.5 kg, Waste = 15.5 kg.

Yield = 38%

Neem crude oil:

Seed = 25 kg, Extracted oil = 10 kg, Waste = 15 kg.

Yield = 40%

Mahua crude oil:

Seed = 23 Kg, Extracted oil = 9 Kg, Waste = 14 kg.

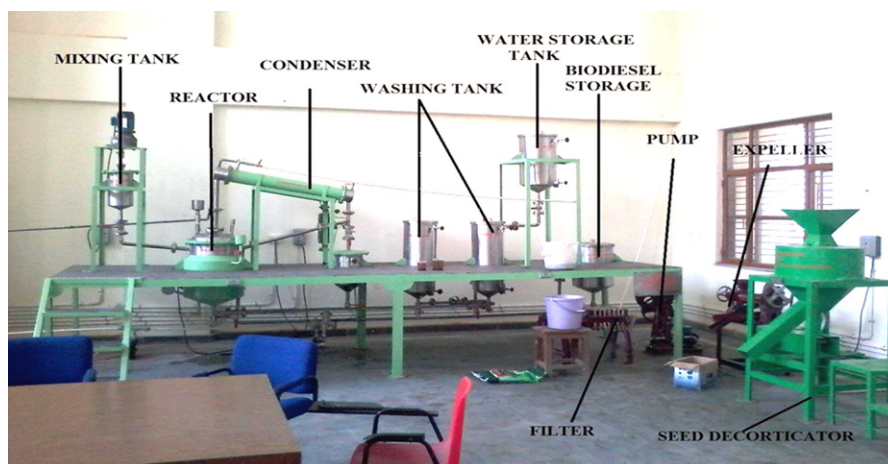


Fig. 1 Biodiesel Transesterification unit.



Fig. 2 Neem biodiesel.

Biodiesel production

Coconut biodiesel:

Crude Oil=12,300 ml, Produced Biodiesel= 11,380 ml, Yield=92.52%
Produced Glycerine= 2400 ml.

Castor biodiesel:

Crude Oil=8000 ml, Produced Biodiesel=7300 ml, Yield=91.25%
Produced Glycerine=750 ml.

Neem biodiesel:

Crude Oil=8500 ml, Produced Biodiesel=7700 ml, Yield=90.58%
Produced Glycerine=950 ml.

Mahua biodiesel:

Crude oil=7700 ml, Produced Biodiesel=6800 ml, Yield=88.31%
Produced Glycerine=700 ml.



Fig. 3 Neem biodiesel with glycerine.

Oil Filtration

Crude oil has higher moisture content and some other impurities. So in order to remove moisture and impurities oil is refined. The purification is done by boiling oil with 20% water. The boiling is continued until no bubble of water vapor anymore. After one hour the oil becomes clear. This refined crude oil is taken as raw material for esterification process.

Acid Esterification

This step is used for only those oils that have free fatty acids (FFA) more than 2%. Since Mahua, neem, castor oil have FFA about 9.4%, so this process is also used for these biodiesel. The crude oil is poured into a flask and heated up to 60°C. The 45% v/v methanol is added with preheated crude oil and stirred for few minutes, 0.5% of sulphuric acid is added with mixture. Heating and stirring is about 45 min at atmospheric pressure. Then the mixture is poured in to a separating funnel for separating excess methanol, impurities and sulphuric acid. The excess methanol, sulphuric acid and impurities move to the top layer and it is discarded. The lower layer is separated for transesterified it into methyl ester (Biodiesel). This process reduces the acid value of oil to 1% of FFA.

Alkaline Transesterification

Now esterifies oil is taken in flask and heated up to 60°C. 1% NaOH is dissolved in 30% methanol and dissolved solution is poured into flask. The mixture is heated and stirred about 750 rpm for one hour. Now the mixture is poured into separating funnel and left for 2 h. The glycerol and impurities are settled in lower layer by the gravity. The impure Biodiesel remain in upper layer. After discarding lower layer impure biodiesel drawn off which contain some trace of catalyst, glycerol, and methanol, this impure biodiesel is purified by washing process.

Washing Process

Purification of biodiesel is done by adding 3/4th of distilled hot water with impure biodiesel and shaking gently. The upper layer is of biodiesel and impurities collected into lower layer.

Experimental Setup

Castor, Coconut, linseed, mahua and neem biodiesel was used as a fuel with different blending ratios of B10, B20, B30, B40 and pure diesel (B00). For performance and emission testing of variable compression ratio (VCR) engine (**Fig. 4**) which has following



Fig. 4 Experimental setup.

specifications (**Table 1**): single cylinder 4-stroke multi-fuel water cooled engine, bore 87.5 mm, a stroke of cylinder 110 mm, the capacity of engine 661 cc, diesel power 3.5 kW, speed 1500 rpm, compression ratio range 12.1–18.1. Eddy current type dynamometer was connected to the engine for loading. Emission and performance test were conducted at different compression ratios of 15, 16, 17 and 18 under constant engine speed of 1500 rpm. We have used engine performance analysis software “Engine Soft.” For measuring the temperature at different zones, three types of sensors are used like RTD, PT 100 and Thermocouple, Type K. Digital voltmeter of range 0–20 V was used for display voltage, Strain gauge type load sensor was used of range 0–50 kg. A pipe type calorimeter was used for measuring the heat taken from exhaust gas with water flow rate of 25–250 lph. Engine cooling was done with water flow rate of 40–400 lph. To circulate water in engine and calorimeter self-priming pump was used. Starter motor was used for starting. Portable AVL digas 444 gas analyzer was used (**Table 2**). It measures the different constituents in exhaust gas like CO (vol %), CO₂ (vol %), NO_x (ppm), unconsumed oxygen O₂ (vol %) in the exhaust and unburnt HC (ppm). Setup of VCR engine consists of stand-alone type independent panel box consisting of fuel tank, fuel measuring unit, digital speed indicator, air box, manometer and digital temperature indicator (**Table 3**). Air box measured air flow rate. The cylinder pressure was recorded at the crank angle for each 1-degree increment. Two types of tests i.e., leakage test and hydrocarbon residue test were conducted before measurement of exhaust gas constituents. Leakage test was performed for 24 s, if the result is ok then no problem, but in any case, the test fails means leakage is found then the whole test has to be conducted again. Similarly, hydrocarbon residue test was conducted for 80 s.

Properties Measurements

Calculation of Lower Calorific Value

Calorific value is the amount of heat energy released by the combustion of a unit value of fuel (**Table 4**). Calorific value of biodiesel is calculated by bomb calorimeter (**Fig. 5**) present in IC engine laboratory. It is a constant volume calorimeter used in measuring the heat of combustion. In the present calorimeter design, the bomb is pressurized with pure oxygen at 25–30 bar, containing a known mass of fuel. It submerged under the known volume of water. The bomb forms a closed system. The bomb is ignited electrically. The energy released by the combustion raise the temperature of the bomb and the surrounding water jacket.

Calorific value is calculated by the following formula:

$$M_{\text{fuel}} * (CV)_{\text{fuel}} + M_{\text{thread}} * (CV)_{\text{thread}} + M_{\text{wire}} * (CV)_{\text{wire}} = M_{\text{water}} * (C_p)_{\text{water}} * (\Delta T)$$

Where: M_{fuel} = Mass of the sample or biodiesel in grams.

M_{thread} = Mass of the cotton thread in grams.

M_{water} = Mass of the water in Kg.

M_{wire} = Mass of the wire in grams.

$(CV)_{\text{fuel}}$ = Calorific value of the fuel.

$(CV)_{\text{thread}}$ = Calorific value of thread = 4.18 Kcal/Kg.

$(CV)_{\text{wire}}$ = Calorific value of Nichrome ignition wire = .355 Kcal/Kg

$(C_p)_{\text{water}}$ = specific heat of water = 1Kcal/Kg.

ΔT = Increase in the temperature of the surrounding water jacket.

Table 1 Engine specification

<i>S.No</i>	<i>Specification</i>	<i>Details</i>
1.	Model	TVI 4stroke, water cooled
2.	Make	Kirloskar oil engine
3.	Number of cylinder	1
4.	Bore/Stroke	87.5/110 mm
5.	Connecting rod length	234 mm
6.	Rated power	3.5 Kw
7.	Rated speed	1500 rpm
8.	Peak pressure	77.5 kg/cm ²
9.	Injection timing	23° BTDC
10.	Capacity	661 cc
11.	Sump capacity	2.7 liter
12.	Compression ratio	12:1 to 18:1
13.	Loading	Eddy current dynamometer
14.	Cooling	Water
15.	IVO/IVC	4.5° BTDC/35.5° ATDC
16.	EVO/EVC	35.5° BTDC/4.5° ATDC
17.	Valve clearance inlet	.18 mm
18.	Valve clearance exhaust	.20 mm

Table 2 Range and accuracy of gas analyzer

<i>Emission</i>	<i>Range</i>	<i>Methods</i>	<i>Accuracy</i>
Carbon monoxide	0–15% vol.	Filter paper methods	<10% vol.: ± .02% vol. ± 3% °M ≥ 10.0% vol.: ± 5% °M
Carbon dioxide	0–20% vol.	Filter paper methods	< 16.% vol.: ± .3% vol. ± 3% °M ≥ 16.0% vol.: ± 5% °M
Carbon hydroxide	0–30000 ppm vol.	Filter paper methods	<2000 ppm vol.: ± 4 ppm vol. ± 3% °M ≥ 5000 ppm vol.: ± 5% °M
Nitrogen oxides	0–5000 ppm vol.	Filter paper methods	≥ 10000 ppm vol.: ± 10% °M ± .02% vol. ± 1 % °M

Table 3 Ranges and Accuracy of Instrument

<i>S.No</i>	<i>Specification</i>	<i>Range</i>	<i>Accuracy</i>
1.	Engine speed rate	1200–1500 rpm	± 5 rpm
2.	Temperature	0–1200°C	± 2°C
3.	Load	0–50 kg	± .1 kg
4.	Water flow	25–400 lph	± 2 lph
5.	Pressure	0–5000 psi	± 2 psi

Table 4 Calorific value of different biodiesel (measured)

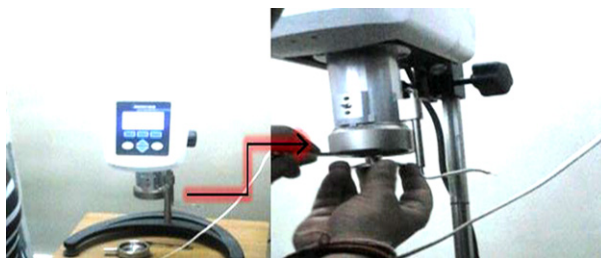
<i>S.No</i>	<i>Biodiesel</i>	<i>Calorific value (kj/kg) DEC.</i>				<i>Calorific value(kj/kg) JUN.</i>			
		B10	B20	B30	B40	B10	B20	B30	B40
1.	Castor	35,486	35,225	33,184	34,580	34,416	35,110	32,184	34,875
2.	Linseed	31,686	34,871	34,332	35,664	31,686	34,871	34,332	34,314
3.	Mahua	31,552	33,444	33,398	34,396	31,552	33,445	33,398	34,396
4.	Neem	34,328	33,971	34,089	35,664	34,328	33,971	34,089	35,664
5.	Coconut	33,017	33,259	33,106	33,883	32,830	32,910	32,890	33,125

Table 5 Viscosity of different crude oil and biodiesels (measured)

S.No.	Oil	Crude oil (cSt)	Biodiesel (cSt)
1.	Castor	45.83	6.52
2.	Coconut	35.23	4.50
3.	Linseed	22.63	3.32
4.	Mahua	32.23	5.58
5.	Neem	38.89	6.02

Table 6 Flash and Fire point of different Biodiesel (measured)

S.No	Name of Oil	Crude oil Flash point (°C)	Fire point (°C)	Biodiesel Flash point (°C)	Fire point (°C)
1.	Castor	298	335	260	302
2.	Coconut	235	265	205	242
3.	Linseed	225	255	215	270
4.	Mahua	285	328	248	292
5.	Neem	260	290	240	280

**Fig. 5** Bomb calorimeter.**Fig. 6** Brook field viscometer.

Viscosity

Viscosity is the property of fluid by which it offers resistance to flow (Table 5). It affects the injector lubrication and fuel atomization. Fuel with low viscosity may not provide sufficient lubrication for the precision fit of fuel injector pumps resulting in leakage or increased wear. Fuel atomization is also affected by fuel viscosity. Fuel with low viscosity tends to form smaller droplets on injection which cause good combustion and vice-versa. Through transesterification and washing process it is decreased and comes very close to diesel. Viscosity of crude oil and biodiesel is measured by Brookfield viscometer (Fig. 6) present in fluid mechanics laboratory.

Flash Point and Fire Point

The flash point temperature of a fuel is the minimum temperature at which the fuel ignites (flash) on application of an ignition source under specific condition. Flash point varies inversely with the fuel volatility. Minimum flash point temperature is required for proper safety and handling of fuel. The fire point of a fuel is temperature at which the vapor produced by the test

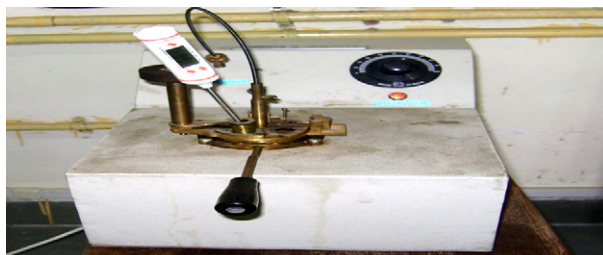


Fig. 7 Flash point and Fire point tester.

fuel continues burning for at least 5 s after ignition by an open flame. At flash point which is lower than fire point (**Table 6**), a fuel ignites briefly but vapor might not at sufficient rate to sustain the fire. These values have observed by performing experiment on flash and fire point tester (**Fig. 7**).

Gas Chromatography

Gas chromatography (GC) is a common type chromatography used in analytical chemistry for separating and analyzing compounds that can be vaporized without decomposition. Typical uses of GC include testing the purity of a particular substance, or separating the different components of mixture (relative compounds of such components can also be determined).

Structure of Gas Chromatography

In gas chromatography, the mobile phase or moving phase is a carrier gas, usually an inert gas such as helium or nonreactive gas such as nitrogen. Helium remains the most commonly used carrier gas in about 90% instrument although hydrogen is preferred for improved separations. The stationary phase is a microscopic layer of liquid or polymer on a inert solid support inside a piece of glass or metal tubing called column, through which different chemicals constituents of a sample pass in a gas stream (carrier gas, mobile phase) at different rates depending on their various chemical and physical properties and their interaction with a specific column filling called stationary phase. The function of the stationary phase in the column is to separate different components, causing each one to exit the column at a different time (retention time).

Principle of Working of Gas Chromatography

Flame ionization detector (FID)

Flame ionization detector is a scientific instrument that measures the concentrations of organic species in a gas stream. It is a frequently used as a detector in gas chromatography. The operation of the FID is based on the detections of the ions formed during combustions of organic compounds in a hydrogen flame. The generations of these ions are proportional to the concentrations of organic species in the sample gas stream.

Thermal conductivity detector (TCD)

Thermal conductivity detector is a common detector relies on the thermal conductivity of matter passing around a tungsten filament with a current travelling through it. In this set up helium or nitrogen serve as the carrier gas because of their relatively high thermal conductivity which keeps the filament cool and maintain uniform resistivity and electrical efficiency of the filament. However, when analyze molecules elute from the column, mixed with carrier gas, thermal conductivity decreases and this causes detector response. The response is due to the decreased thermal conductivity causing an increase in filament temperature and resistivity resulting in fluctuations in voltage.

Parameters of GC for FAME Analysis

Analytical Method Parameter:

Column: SUPELCOWAX 10 (30 × .25 mm inner diameter × .25 μm film).

Injection Volume: 1 μL

Split ratio: 10:1

Inlet temperature: 250°C

Constant flow: 1 mL/min helium

Oven temperature: 100°C for 1 min, 25°C/min up to 200°C and hold for 1 min, 5°C/min up to 250°C and hold for 7 min.

FID: 280°C

Fame sample: Fame mix C8–C24.

Result and Discussions

Performance Characteristics

Brake thermal efficiency (BTE)

Figs. 8–15 show the variation of brake thermal efficiency to different blending for different biodiesel and pure diesel for different loading conditions at compression ratio of 18. It has been observed that brake thermal efficiency increases with increasing load. From the figure it has been observed that brake thermal efficiency is lower at minimum load. This is due to high fuel-air ratio which leads to incomplete combustion and most of the fresh charge remains unburnt. At higher loads brake thermal efficiency is continuous increasing. This is due to complete combustion of fuel; lower losses are encountered at higher load and brake thermal efficiency increases with load (Liaquat *et al.*, 2013; Muralidharan and Vasudevan, 2011). Brake thermal efficiency is directly proportional to the compression ratio. Brake thermal efficiency is obtained maximum 43.04% for castor biodiesel at full load at B20 and its obtained minimum 1.58% for Neem biodiesel at zero load at B40 in December month. Brake thermal efficiency is obtained maximum 46.52% for neem biodiesel at full load at B40 and its obtained minimum 2.08% for Mahua biodiesel at zero loads at B30 in June month. It observed from figure of December and June that brake thermal efficiency increases for all blending. This may due to blends fuel density, heating value, viscosity of the fuel (Liaquat *et al.*, 2013).

Variation of brake thermal efficiency with load in the month of December:

Variation of brake thermal efficiency with load in the month of June:

Brake power

Figs. 16–23 show the variation of brake power at a different load of different blending of castor, coconut, linseed, mahua, neem biodiesel and pure diesel at compression ratio 18. It indicates that brake power increases linearly with increasing the load and maximum at full load. Brake power decreases at high compression ratio due to the conversion of chemical energy to mechanical energy (Subramaniam *et al.*, 2013). Due to lower heating value of blends of biodiesel, brake power decreases (Liaquat *et al.*, 2013). Brake power is obtained maximum 3.66 kW for Mahua biodiesel at full load at B10 and its obtained minimum .5 kW for Neem biodiesel at zero loads at B40 in December month. Brake power is obtained maximum 3.56 kW for coconut biodiesel at full load at B20 and its obtained minimum .06 kW for Linseed biodiesel at zero loads at B30 in June month. It concluded from graph of December and June month brake power decreases with storage time of biodiesel blends.

Variation of brake power with load in the month of December:

Variation of brake power with load in the month of June:

Mechanical efficiency

Figs. 24–31 show the variation of mechanical efficiency at different load for different blending for castor, coconut, linseed, Mahua, Neem biodiesel and pure diesel at compression ratio 18. It has been observed that mechanical efficiency increases with increasing load for all blends B10, B20, B30, B40, and pure diesel. It has been observed that mechanical efficiency increase with increasing the proportion of blends in the diesel. Mechanical efficiency is obtained maximum 58.42% for linseed biodiesel at full load at B30 and its obtained minimum 2.04% for linseed biodiesel at zero loads at B10 in December month. Mechanical efficiency is obtained maximum 78.65% for coconut biodiesel at full load at B30 and its obtained minimum 1.6% for Neem biodiesel at zero loads at

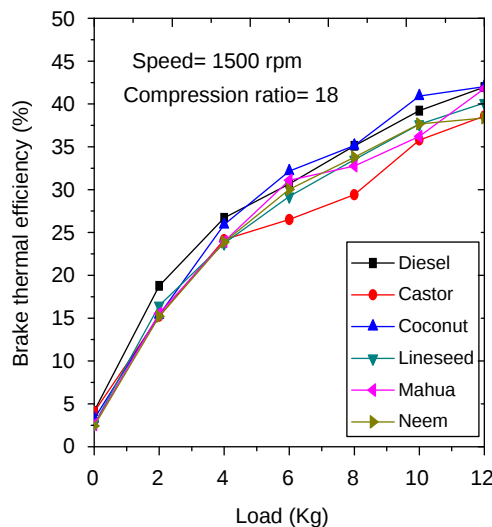


Fig. 8 BTE vs. Load at B10.

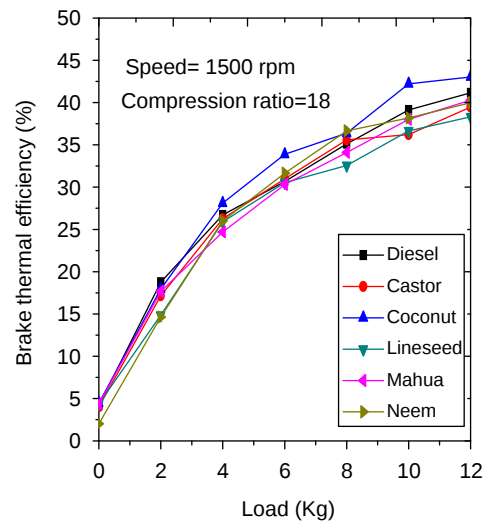


Fig. 9 BTE vs. Load at B20.

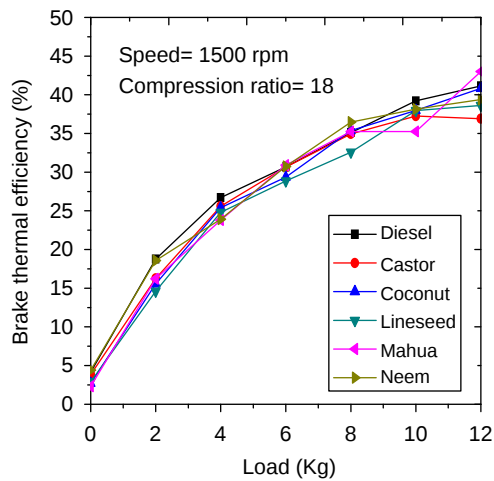


Fig. 10 BTE vs. Load at B30.

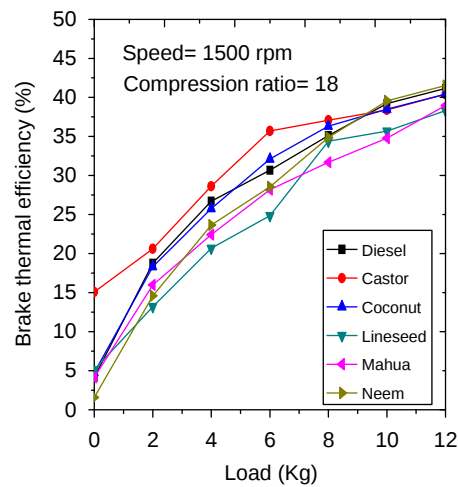


Fig. 11 BTE vs. Load at B40.

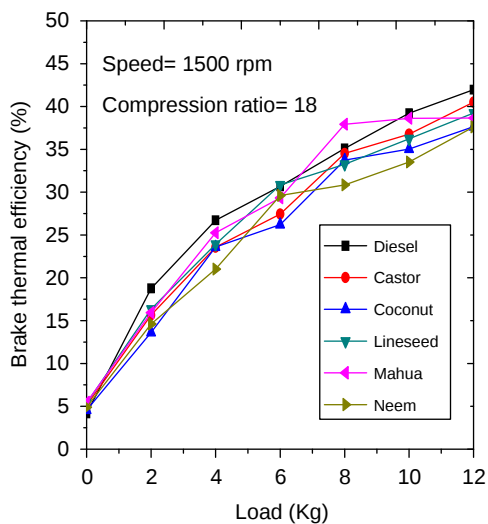


Fig. 12 BTE vs. Load at B10.

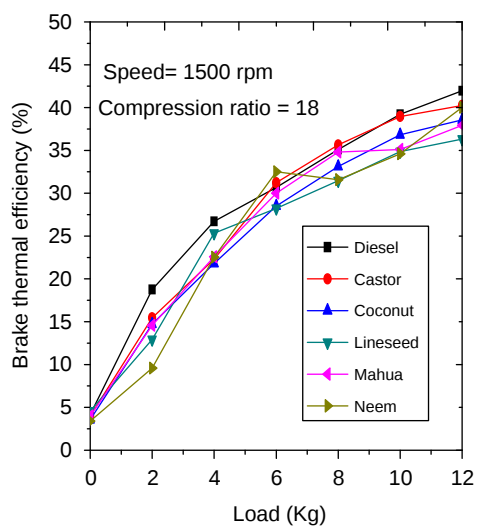


Fig. 13 BTE vs. Load at B20.

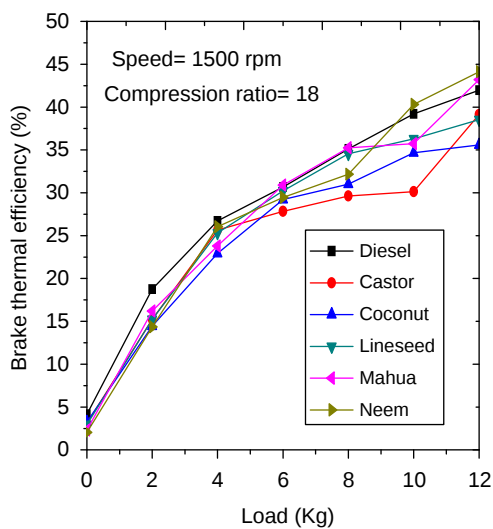


Fig. 14 BTE vs. Load at B30.

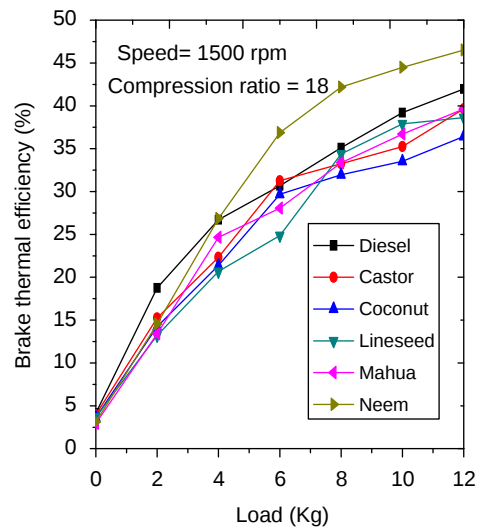


Fig. 15 BTE vs. Load at B40.

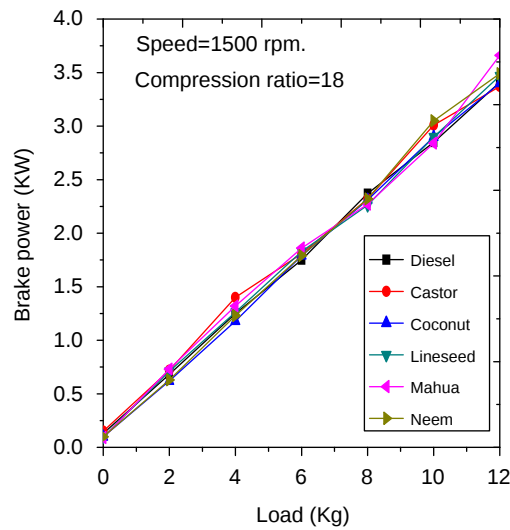


Fig. 16 BP vs. Load at B10.

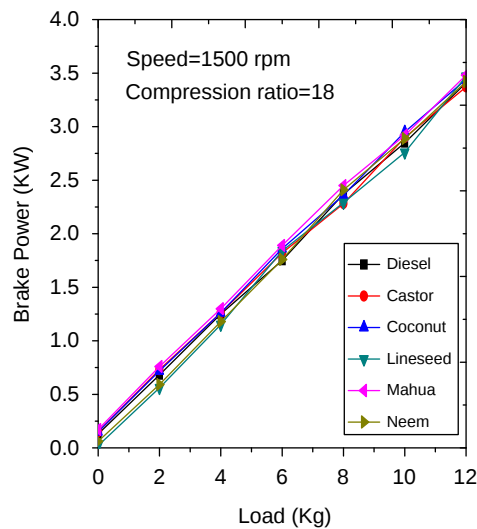


Fig. 17 BP vs. Load at B20.

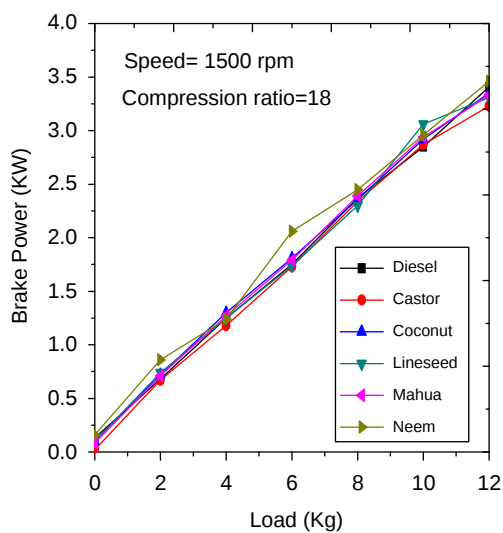


Fig. 18 BP vs. Load at B30.

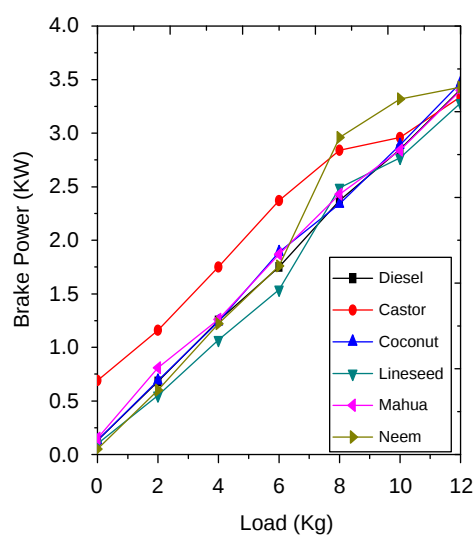


Fig. 19 BP vs. Load at B40.

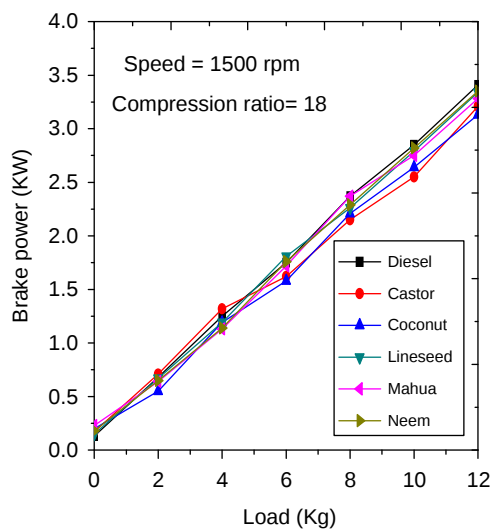


Fig. 20 BP vs. Load at B10.

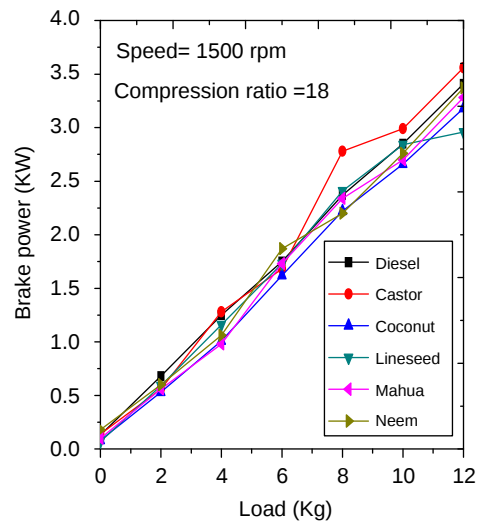


Fig. 21 BP vs. Load at B20.

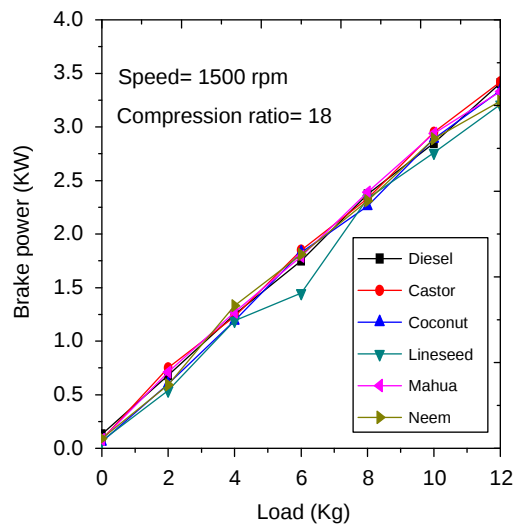


Fig. 22 BP vs. Load at B30.

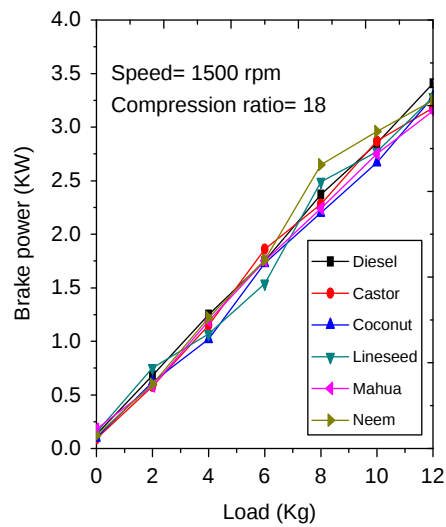


Fig. 23 BP vs. Load at B40.

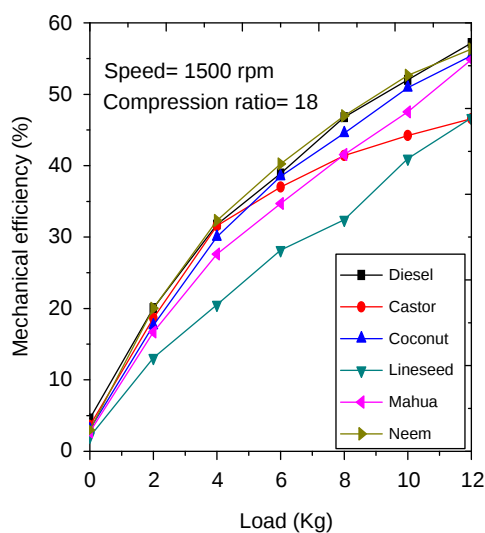


Fig. 24 ME vs. Load at B10.

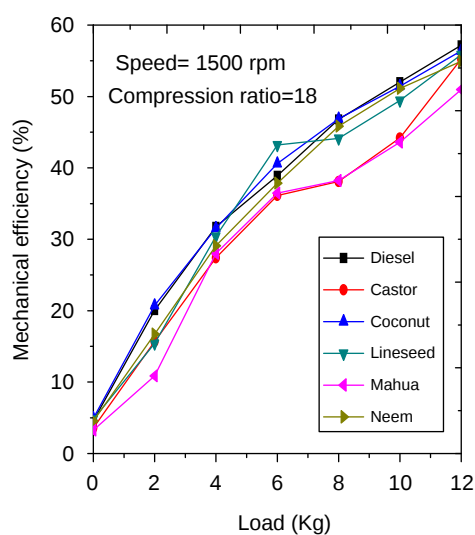


Fig. 25 ME vs. Load at B20.

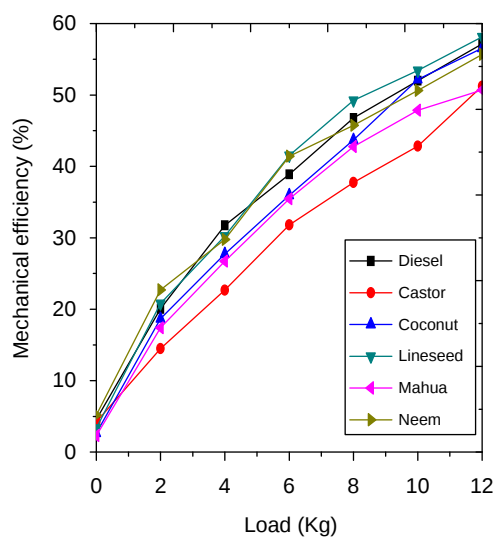


Fig. 26 ME vs. Load at B30.

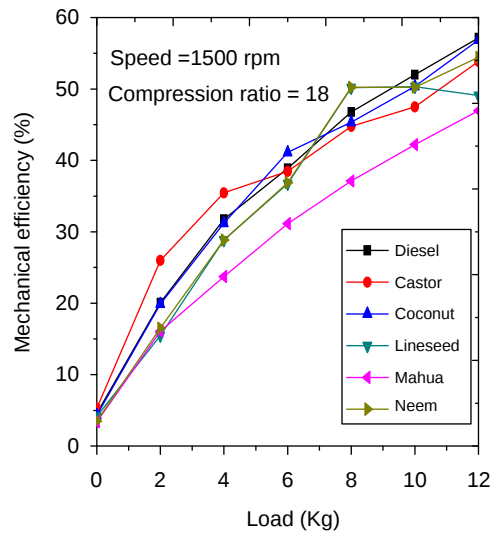


Fig. 27 ME vs. Load at B40.

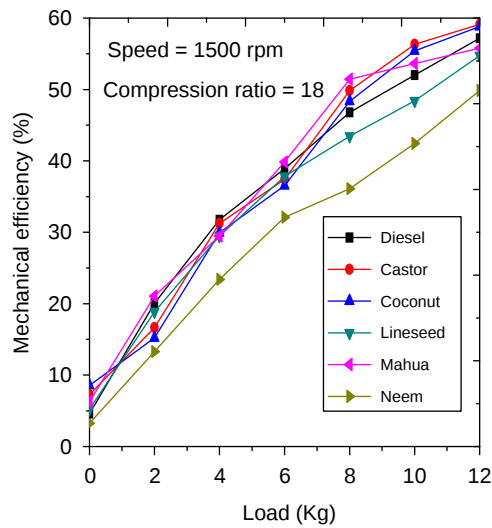


Fig. 28 ME vs. Load at B10.

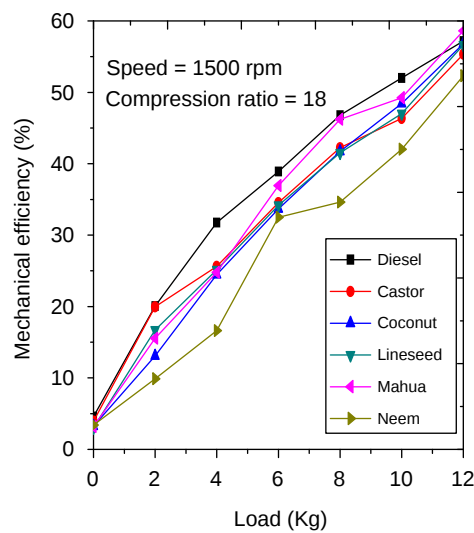


Fig. 29 ME vs. Load at B20.

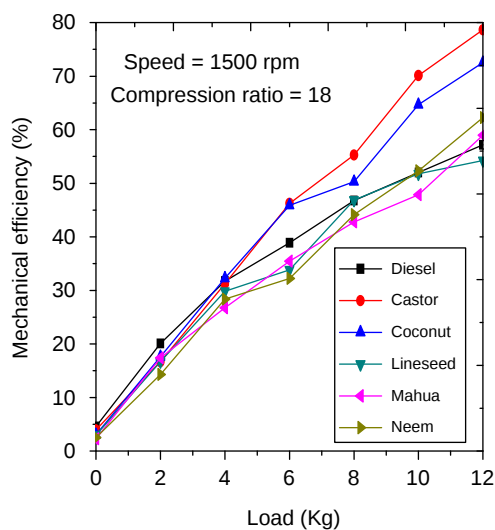


Fig. 30 ME vs. Load at B30.

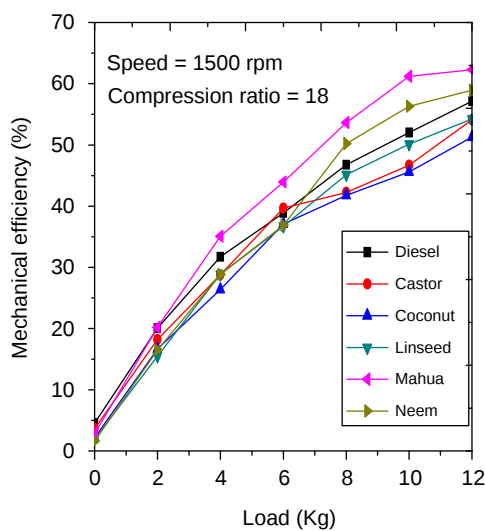


Fig. 31 ME vs. Load at B40.

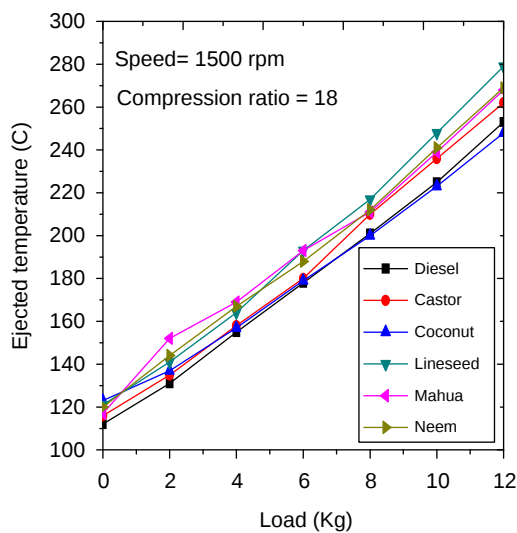
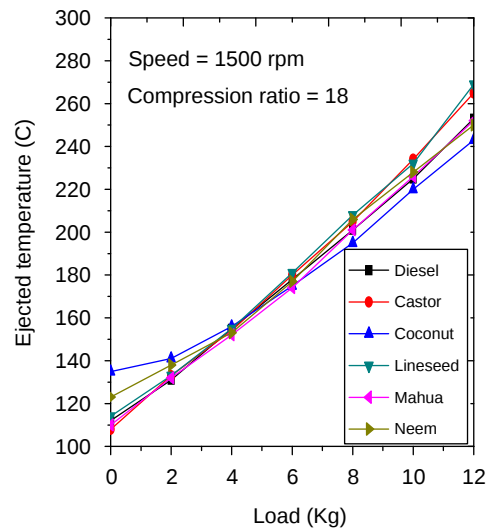
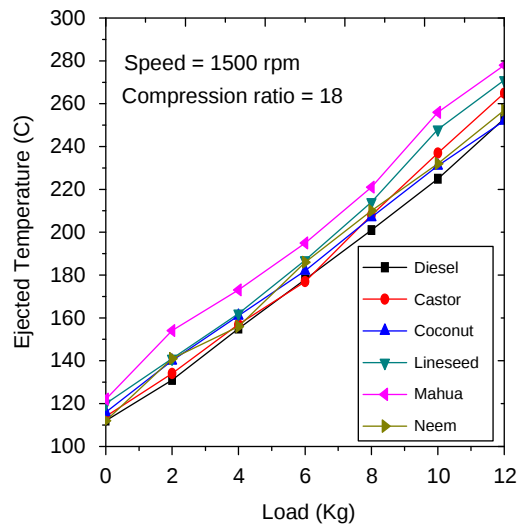
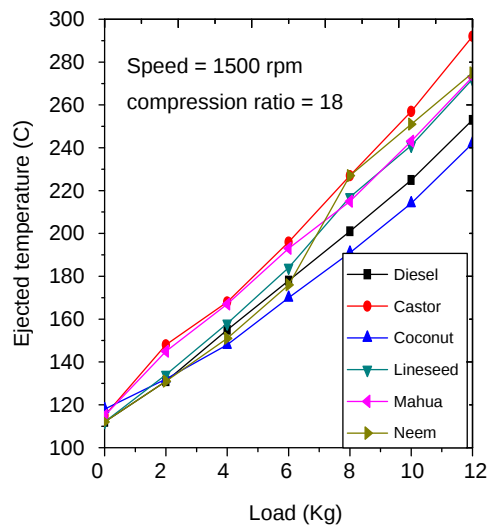


Fig. 32 EGT vs. Load at B10.

**Fig. 33** EGT vs. Load at B20.**Fig. 34** EGT vs. Load at B30.**Fig. 35** EGT vs. Load at B40.

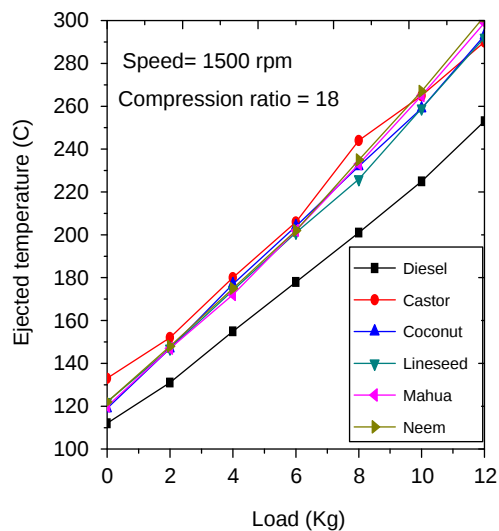


Fig. 36 EGT vs. Load at B10.

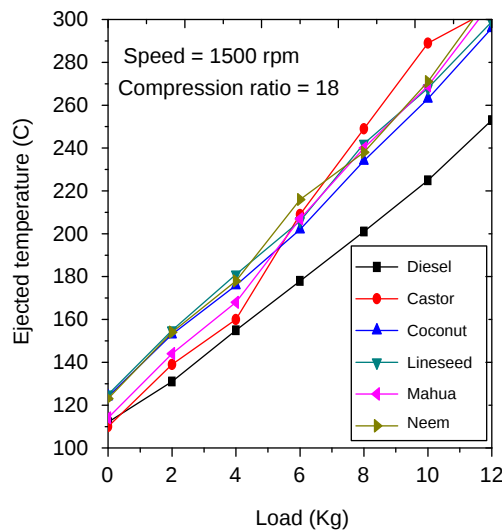


Fig. 37 EGT vs. Load at B20.

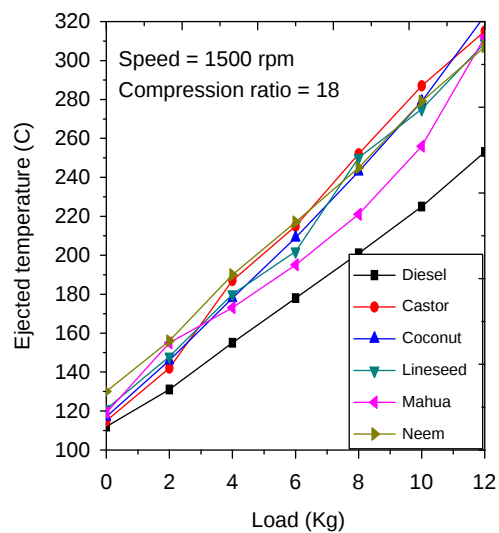


Fig. 38 EGT vs. Load at B30.

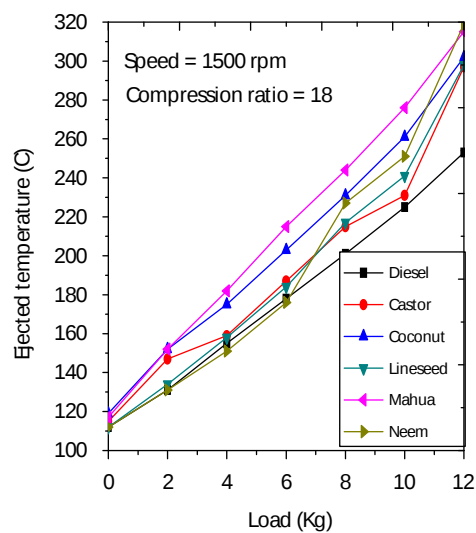


Fig. 39 EGT vs. Load at B40.

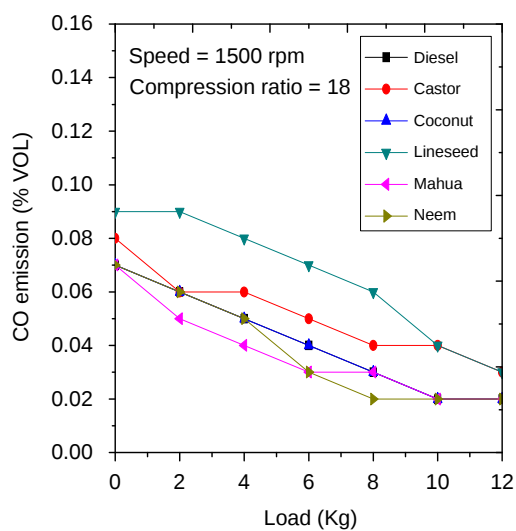


Fig. 40 CO vs. Load at B10.

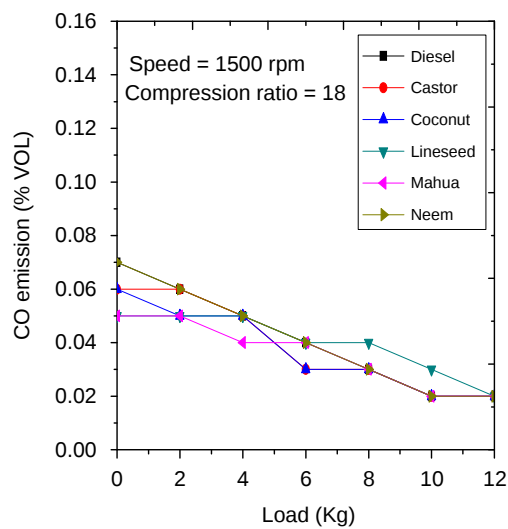


Fig. 41 CO vs. Load at B20.

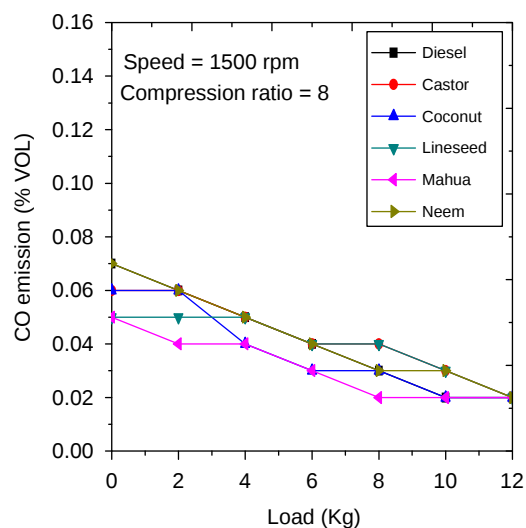


Fig. 42 CO vs. Load at B30.

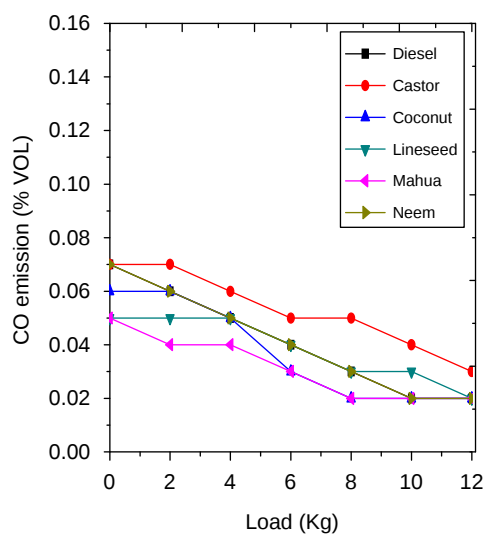


Fig. 43 CO vs. Load at B40.

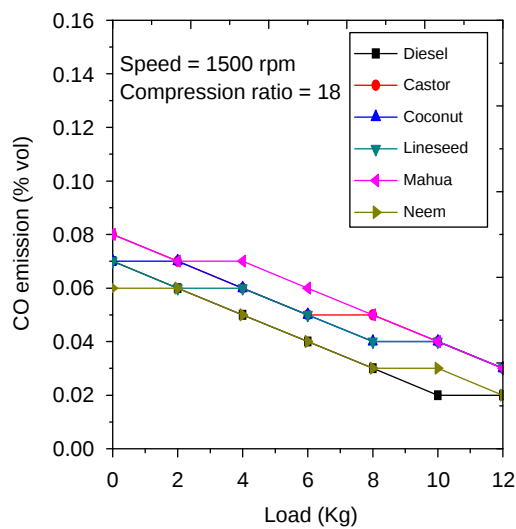


Fig. 44 CO vs. Load at B10.

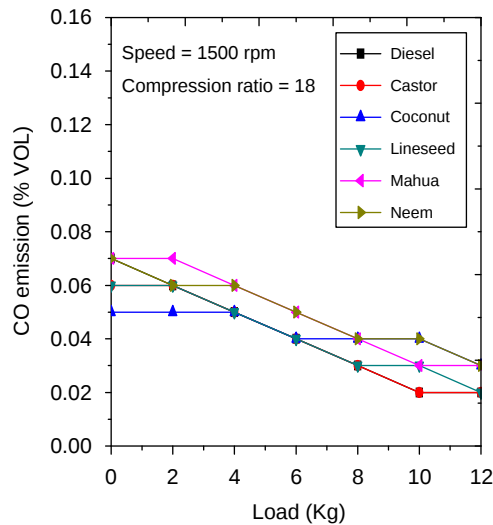


Fig. 45 CO vs. Load at B20.

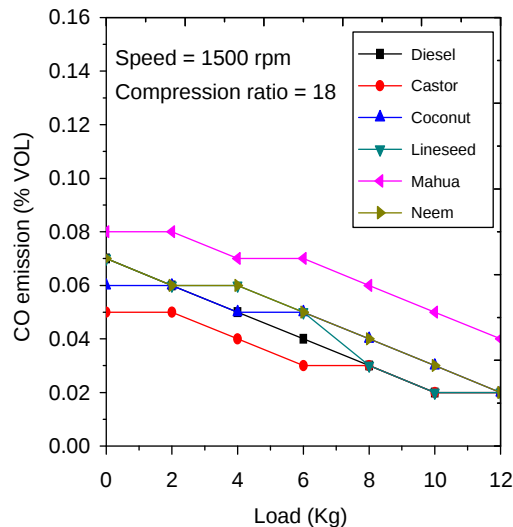


Fig. 46 CO vs. Load at B30.

B40 in June month. It is concluded from the results of December and June month mechanical efficiency increases with storage time of biodiesel blends.

Variation of mechanical efficiency with load in the month of December:

Variation of mechanical efficiency with load in the month of June:

Exhaust Gas temperature

The Exhaust Gas Temperature (EGT) is an indication of effectiveness of utilization of heat energy produced by combustion of fuel. Figure shows that the Exhaust gas temperature increases as load increases for both diesel and biodiesel blending because increase in load increases amount of fuel supply which leads to high exhaust gas temperature. It is observed that the exhaust gas temperature for biodiesel blends is lesser than diesel. Figs. 32–39 show that exhaust gas temperature of biodiesel blending decreases with increasing blending due to increasing viscosity which leads to poor atomization, vaporization and therefore exhaust gas temperature of biodiesel decreases. Exhaust gas temperature obtained maximum 279°C for linseed biodiesel at full load at B10 and obtained minimum 112°C for pure diesel at zero load in December. Exhaust gas temperature obtained maximum 323°C for coconut biodiesel at full load at blending B30 and obtained minimum 110°C for castor biodiesel at zero load at blending B20 in June.

Variation of Exhaust gas temperature with load in the month of December:

Variation of Exhaust gas temperature with load in the month of June:

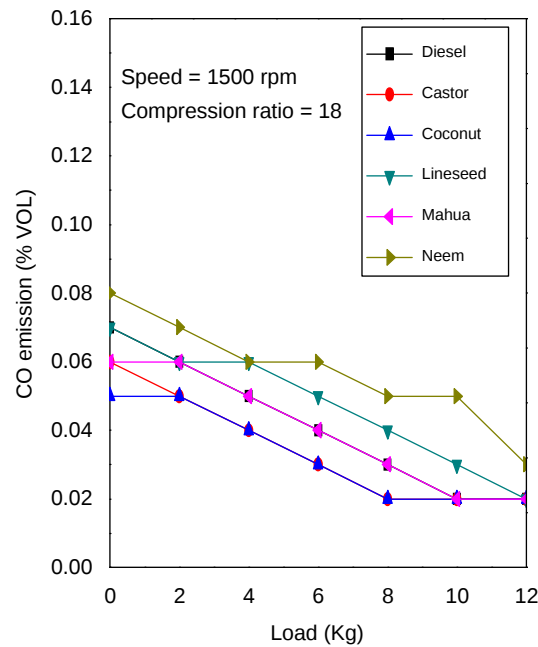


Fig. 47 CO vs. Load at B40.

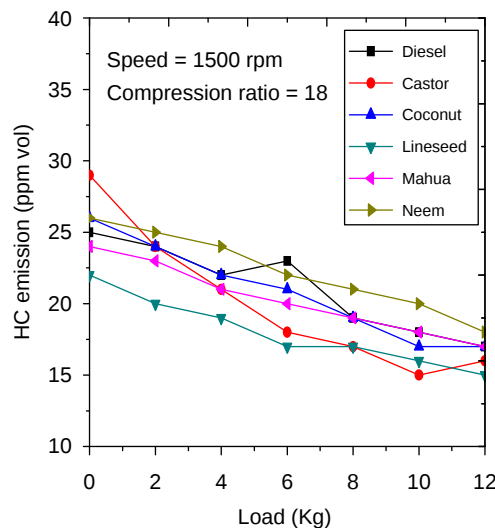


Fig. 48 HC vs. Load at B10.

Emission Characteristics

Carbon monoxide (CO)

Figs. 40–47 show the variation of carbon mono oxide emission with castor, coconut, linseed, Mahua and neem biodiesel blends and pure diesel at different load at compression ratio 18. It forms due to incomplete combustion of fuel, which is caused by lack of oxidants, residence time, and mean temperature. The percentage of CO decrease with increasing load and compression ratio due to rising temperature in combustion temperature, physical and chemical properties of the fuel, air-fuel ratio, shortage of oxygen at high speed, lesser time available for the combustion of the fuel (VenkateswaraRao *et al.*, 2008). CO emission is obtained maximum .08 vol% for castor biodiesel at zero. Load at B10 and its obtained minimum .02 vol% for coconut biodiesel at full loads at B10 in December month. CO emission is obtained maximum .09 vol% for castor biodiesel at zero loads at B20 and its obtained minimum .02 vol% for linseed biodiesel at full load at B30 in June month. It concluded from results of December and June month CO emission almost remains constant with storage time of biodiesel blends.

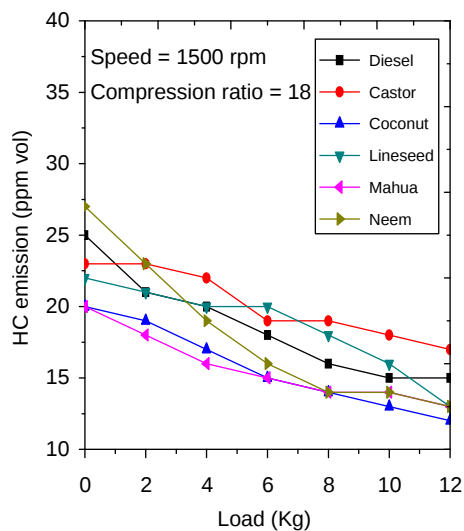


Fig. 49 HC vs. Load at B20.

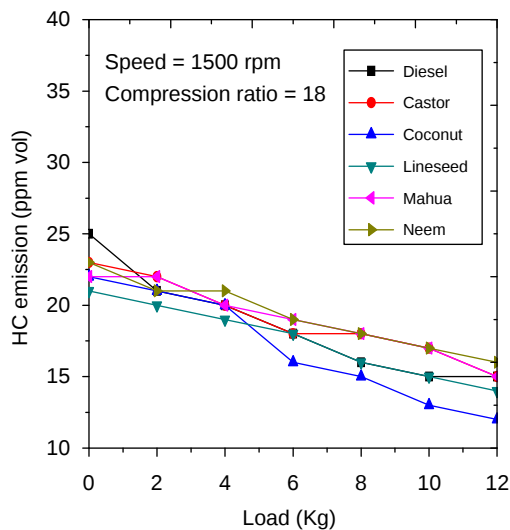


Fig. 50 HC vs. Load at B30.

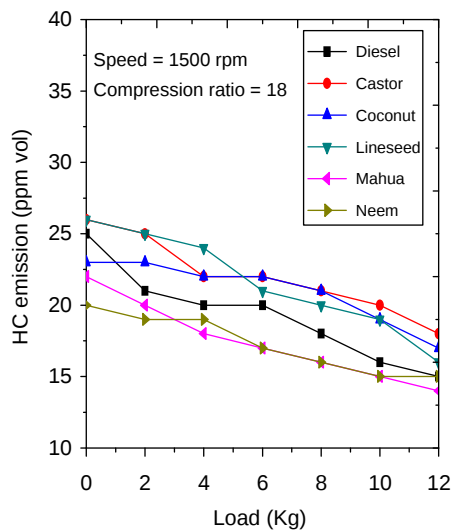


Fig. 51 HC vs. Load at B40.

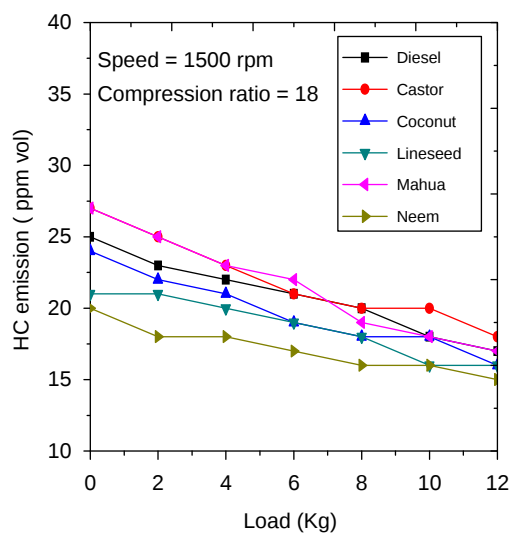


Fig. 52 HC vs. Load at B10.

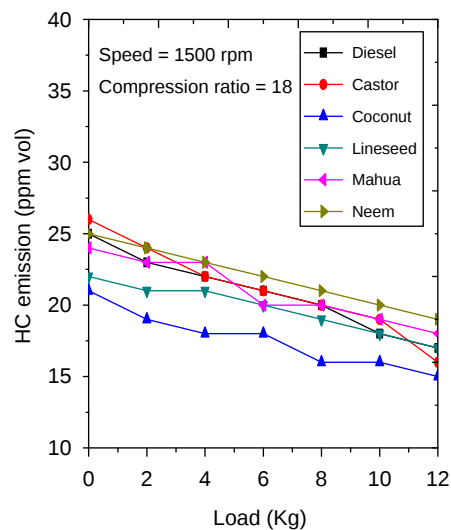


Fig. 53 HC vs. Load at B20.

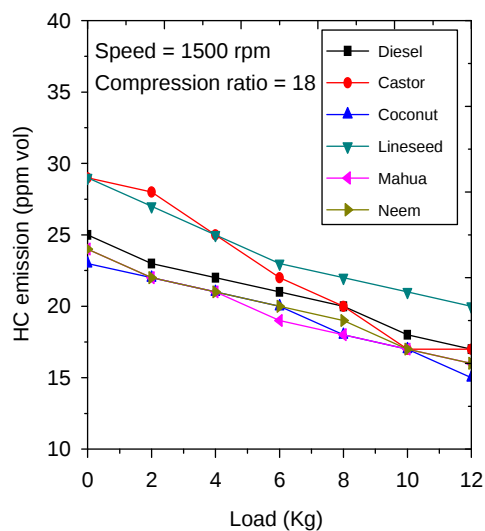


Fig. 54 HC vs. Load at B30.

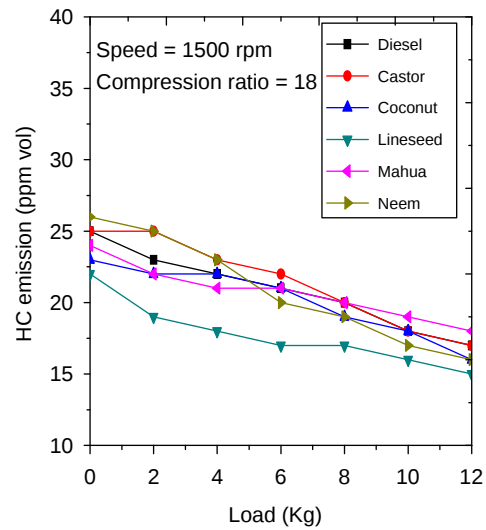


Fig. 55 HC vs. Load at B40.

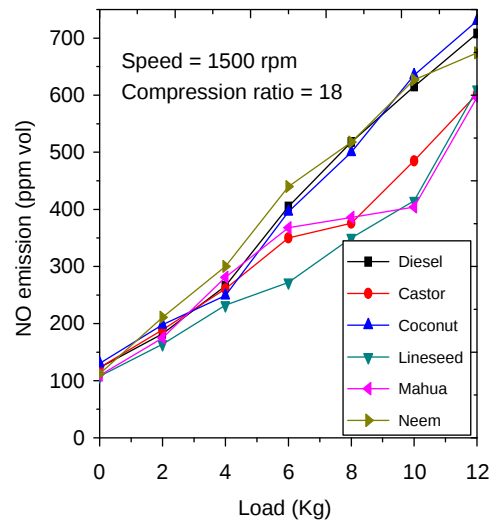


Fig. 56 NO vs. Load at B10.

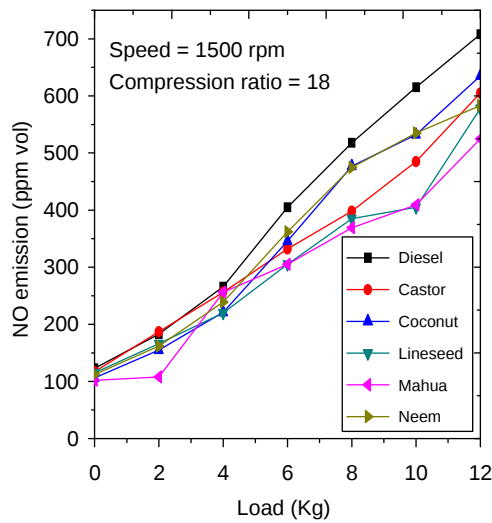


Fig. 57 NO vs. Load at B20.

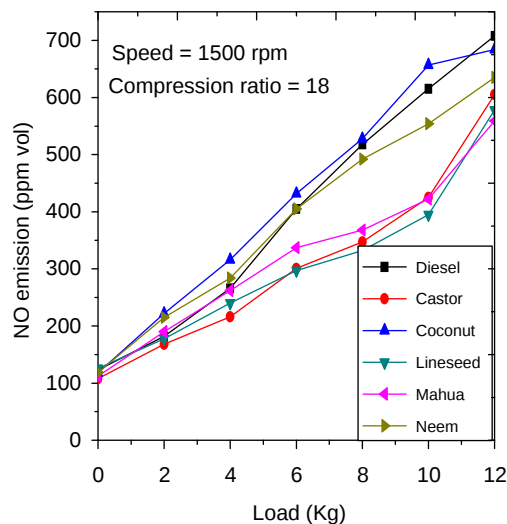


Fig. 58 NO vs. Load at B30.

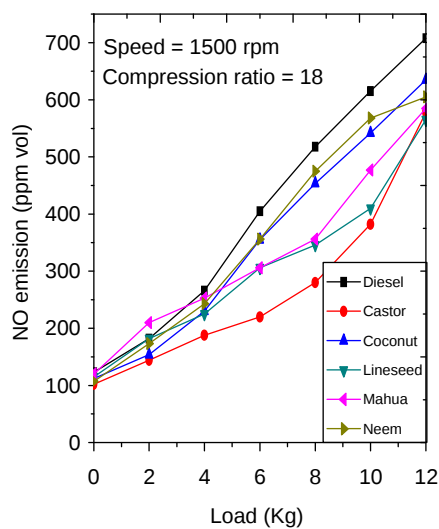


Fig. 59 NO vs. Load at B40.

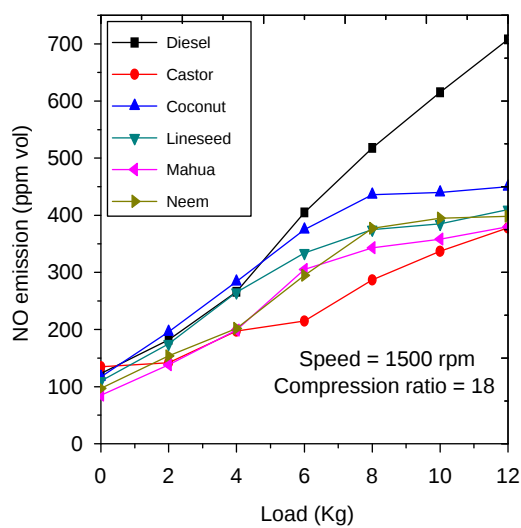


Fig. 60 NO vs. Load at B10.

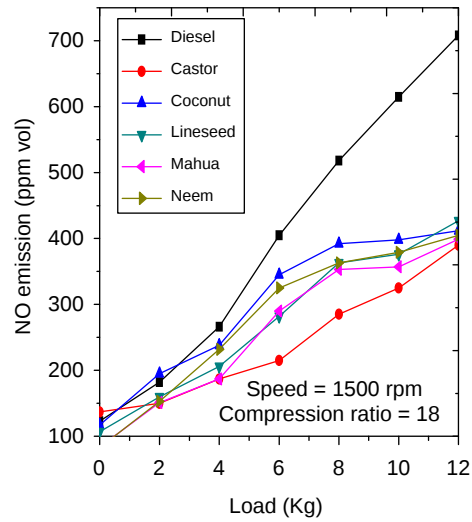


Fig. 61 NO vs. Load at B20.

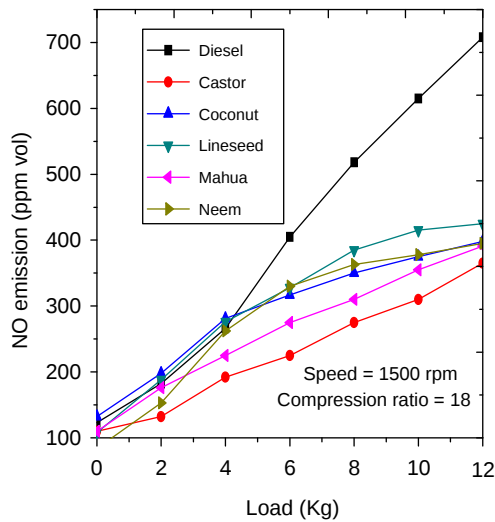


Fig. 62 NO vs. Load at B30.

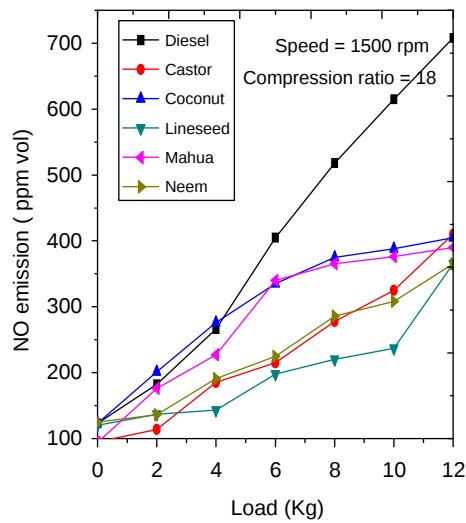


Fig. 63 NO vs. Load at B40.

Variation of CO emission with load in the month of December:

Variation of CO emission with load in the month of June:

Hydrocarbon (HC)

Figs. 48–55 show the variation of HC emission of castor, coconut, linseed, Mahua and neem biodiesel blends and pure diesel at varying load at compression ratio 18. It has been observed from graph that as load increases, HC emission decreases and as compression ratio decreases, hydrocarbon emission decreases, this is due to the fuel consumption increases with load and more fuel injected in the cylinder, temperature increases and complete combustion takes place. The unburnt hydrocarbon is the product of incomplete combustion. As load increases the temperature inside the cylinder increases which helps in complete combustion of fuel and unburned hydrocarbon decreases. HC emission is obtained maximum 29 ppm vol. for castor biodiesel at zero loads at B10 and its obtained minimum 12 ppm vol. for coconut biodiesel at full load at B20 in December month. HC emission is obtained maximum 29 ppm vol. for castor biodiesel at zero loads at B40 and its obtained minimum 15 ppm vol. for neem biodiesel at full load at B40 in June month. It is concluded from results of December and June month, CO emission almost remains constant with storage time of biodiesel blends.

Variation of HC emission with load in the month December:

Variation of HC emission with load in the month of June:

Oxides of nitrogen (NOX)

Figs. 56–63 exhibits the variation in NO emission with load at the different blending of castor, coconut, linseed, Mahua and neem biodiesel and pure diesel at compression ratio 18. From the literature, it is revealed that NO is directly proportional to the power output of the engine because NO emission increased with increase in combustion and exhaust temperature (Yogesh Tamboli *et al.*, 2013). The present test results shows that NO emission increase almost linearly with increasing load because of higher cylinder pressure and higher temperature (ADemirbas, 2003). NO emission increase with average of 1.2% for diesel and for biodiesel blends increases with 2.25% with compression ratio. NO_x emission is obtained maximum 730 ppm vol. for coconut biodiesel at full load at B10 and obtained minimum 106 ppm for coconut biodiesel at zero loads at B20 in December month. NO_x emission is obtained maximum 450 ppm vol. for coconut biodiesel at full load at B10 and its obtained minimum 83 ppm vol. for neem biodiesel at zero loads at B40 in June month. It concluded from graph of December and June month oxides of nitrogen decreases with storage time of biodiesel blends.

Variation of NO emission with load in the month of December:

Variation of NO emission with load in June month:

Conclusion

During the present investigation, several tests were carried out on four strokes single cylinder water-cooled direct injection diesel engine using diesel, castor, linseed, mahua, neem biodiesel with different volume proportion. The experimental results confirm that brake power, mechanical efficiency, brake thermal efficiency, carbon monoxides, oxides of nitrogen are functions of biodiesel blends, and compression ratio. From the experiment following conclusions were drawn:

- Brake Power decreases with increasing the compression ratio, and it is maximum 3.47 kW for pure diesel. Minimum brake power for biodiesel blends and minimum obtained 3.25 kW linseed biodiesel at compression ratio 18.
- It was observed that the brake thermal efficiency was maximum for B20 and increases as load increases at compression ratio 18.
- Mechanical efficiency is also increasing with load. Diesel has the better mechanical efficiency compare to all blends of the coconut biodiesel but blend B50 shows the ME near to pure diesel at CR 18.
- Increasing compression ratio there was a significant reduction in the CO. CO emission increases with increasing the blending. Minimum for linseed biodiesel at B20 is .05% at compression ratio 18 and maximum for diesel is .22% at compression ratio 15.
- NO_x emission increases with increase in compression ratio. For higher blending proportions NO_x emission were also higher. Maximum NO_x emission was obtained 403 ppm for castor biodiesel at compression ratio 18 at B10, and minimum emission was obtained 145 ppm for diesel at compression ratio 15.

See also: Sustainable Materials for Energy Conversion. System Optimization for Control of Solid Waste

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Further Reading

Anon. Wikipedia castor oil, linseed oil, Mahua oil, neem oil Fatty acid composition.

Sustainable Cutting Fluids: Thermal, Rheological, Biodegradation, Anti-Corrosion, Storage Stability Studies and its Machining Performance

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Introduction

The demand for energy is increasing day by day due to ever-going development, modernization and industrialization. The energy consumption by world is estimated to increase by 33.5% from 2010 to 2030 (Saidur *et al.*, 2011). Fossil fuels are one of the most commonly used sources of energy. In general, fossil fuels are used in the form of fuel and lubricant to fulfil soaring energy demand. Survey estimation says that 30–40 million tons of lubricants are used every year. Out of these, 20 million tons come back to the environment after usage (Mang and Dresel, 2017). Most of these lubricants (over 95%) that end up in the environment are based on petroleum products (Schneider, 2006).

Petroleum-based cutting fluids are subdivided into two categories; straight oils and neat oils. Both consists performance enhancer additives to improve its various properties. Additives such as fatty material, free sulphur, chlorinated paraffin, sulphurized oils and phosphorus compounds are present in petroleum-based cutting fluids (Dixit *et al.*, 2012). At higher temperature these additives react with work material and form metal chloride, phosphates as well as sulphides, which are hazardous and harmful to the environment (Trent, 2000; Gajrani and Sankar, 2017a). In long run, inappropriate disposal of used petroleum-based cutting fluids can cause serious damage to environment. Moreover, prolong exposure to emissions of the cutting fluids causes several types of cancers as well as respiratory diseases (Sankar and Gajrani, 2017). Also, petroleum-based lubricants are non-renewable. A global concern has aroused due to environmental hazard and gradual depletion of petroleum source.

Nowadays to minimize these concerns, several alternative measures such as development of environment friendly cutting fluids and green energy systems are focused (Nagendramma and Kaul, 2012; Bart *et al.*, 2013; Somashekaraiah *et al.*, 2016). Therefore, bio-based cutting fluids or bio-cutting fluids (BCF) are derived using bio-based raw materials such as animal fats, vegetable oils, unsaturated acids, etc., (Salimon *et al.*, 2010). From recent past, BCF production is growing with agricultural advancement. As per the estimation of United States Department of Agriculture (USDA), 185.72 million metric tons vegetable oil will be produce in 2016/17 (USDA, 2016). Most BCF have almost similar molecular structure. They mainly consist of triglycerides. Triglycerides have number of long unsaturated fatty acids chains (Fox and Stachowiak, 2007; Mongkolwongrojn and Arunmetta, 2002), which are renewable and readily biodegradable. In addition, BCF have high viscosity index and high flash point than that of petroleum-based mineral oils (MO) (Soni and Agarwal, 2014). High viscosity index of BCF ensures better stable lubricity, which means with the increase in temperature viscosity of BCF drops slowly as compared to petroleum based MO (Woods, 2005). Also, high flash point of BCF reduces possibilities of fire hazard and smoke formation. Moreover, BCF have higher boiling point and heavier molecular weight that reduces vaporization and mist formation (Khan and Dhar, 2006). Further, BCF is capable of reducing friction and wear between two mating surfaces. It is due to ability of polar and long carbon unsaturated acid chain to strongly interacting with intermetallic surface. Apart from above mentioned characteristics, BCF is sustainable, biodegradable and highly renewable source. Therefore, BCF can be a viable alternative to petroleum-based cutting fluids. Fig. 1 illustrates life cycle of renewable resources based products (Willing, 2001).

In spite of numerous merits, usage of BCF is still limited today. It is due to major issues regarding their cost and performance. However, most of the researchers have used BCF with minimum quantity lubrication (MQL) also known as minimum quantity cutting fluid (MQCF) technique to reduce cost by minimizing its consumption (Boswell *et al.*, 2017; Khandekar *et al.*, 2012; Heinemann *et al.*, 2006). As per the performance is concern, these insufficiencies can be improved by the addition of proper additives and chemical modifications. These additives and modification changes the properties of BCF. With proper knowledge, BCF properties can be altered and controlled in a desired way. Therefore, it is necessary to investigate various properties of BCF. Furthermore, constant activities among government organizations, environmental agencies and manufacturer will results in development of procedures for the implementation of bio-technologies that can benefit ecological, social and economic aspects. In long run, there hard work can lead in sustainable environmental management and assessment (Walters, 1986).

In this study, physical properties of BCF are characterized. Also, thermal, rheological, apparent activation energy, biodegradable potential, anti-corrosion and storage stability characteristics of BCF are investigated. For comparison, similar studies are also conducted with MO. Afterwards, machining experiments using minimum quantity cutting fluids (MQCF) technique are carried out to examine the relative machining performance of both cutting fluids in terms of cutting force, feed force, coefficient of friction and surface roughness.

Physical Characterization of Cutting Fluids

The cutting fluids used for this study are petroleum-based MO and sustainable BCF. The MO used in this study was supplied by Servo Lubricants and Greases, Indian Oil Corporation Limited, India and BCF by CORTEC Corporation, India. BCF and MO are

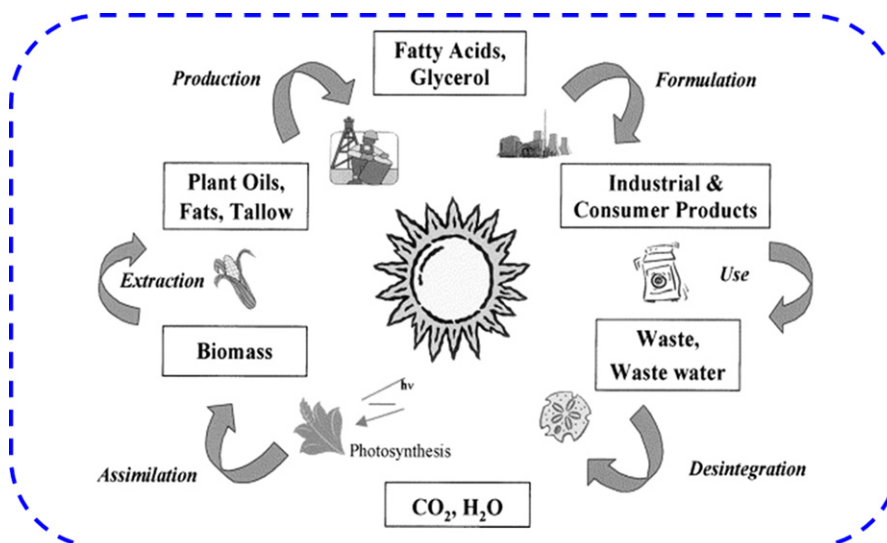


Fig. 1 Life cycle renewable resources based bio-cutting fluids. Reprinted with permission from Willing, A., 2001. Lubricants based on renewable resources – An environmentally compatible alternative to mineral oil products, *Chemosphere* 43, 89–98. Copyright [2001], Copyright holder [Elsevier].

Table 1 Physical properties of bio-cutting fluid and mineral oil

<i>Metal cutting fluid</i>	<i>Density (g/mL)</i>	<i>pH</i>	<i>Flash point (°C)</i>
Bio-cutting fluid	0.9420 ± 0.04	8.65 ± 0.06	310 – 320
Mineral oil	0.890 ± 0.07	9.05 ± 0.08	206 – 214

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characterized. Flash point of cutting fluids are measured using Pensky-Martens open cup setup in accordance with EN ISO 2719 (ECS, 2003) standard (Janes and Chaineaux, 2013). A Varian digital pH meter is used to measure pH of the cutting fluids.

Both BCF and MO are characterized and their physical properties are illustrated in Table 1 (Gajrani *et al.*, 2017b). BCF have more density and less pH as compared to MO that suggest that BCF is less basic among them. BCF have high flash point, which suggests that it can be used even for higher temperature applications and it is safer during hard machining as compared to MO.

Thermal Stability of Cutting Fluids

Stability of the molecule at high temperatures is known as thermal stability; i.e., molecule which offers more resistance to degradation at higher temperature is termed as more stable molecule. Cutting fluid thermal stability is the measure of its mass loss with varying temperature, which can be investigated using thermal gravimetric analysis (TGA).

Twenty mg of each cutting fluids in alumina crucible are tested for thermal degradation studies using thermal gravimetric analysis setup (Make: NETZCH Instruments, Model: STA F4913). Samples are tested in the range of 50–700°C with heating rate of 10°C min⁻¹. Tests are carried out under argon atmosphere (argon flow rate=60 mL min⁻¹).

Fig. 2 illustrates the thermal degradation behaviour of BCF and MO with respect to temperature (Gajrani *et al.*, 2016). The result shows that both cutting fluids have similar behaviour in terms of mass loss. However, they have different starting degradation temperature. BCF degradation starts at 118°C, which shows a better thermal stability as compared to MO whose degradation starts as 51°C.

In case of BCF, upto 100°C no mass loss was observed, which shows the absence of water in it. BCF degrades $13.33 \pm 1\%$ of its mass up to 200°C, which is much lower than MO mass degradation ($28.54 \pm 2\%$). After 466°C, mass almost become constant. This is attributed to already decompose higher molecular mass components of BCF. Maximum mass loss of $91.2 \pm 2\%$ was observed for BCF. Mass loss with temperature is due to the combination of both degradation and volatilization.

In case of MO, over 10% mass degrades before 100°C, which confirms the presence of small carbon chain groups and moisture in it. Up to 460°C, around $90 \pm 3\%$ mass loss was observed. After experiment, around $4 \pm 3\%$ mass was still remaining, which

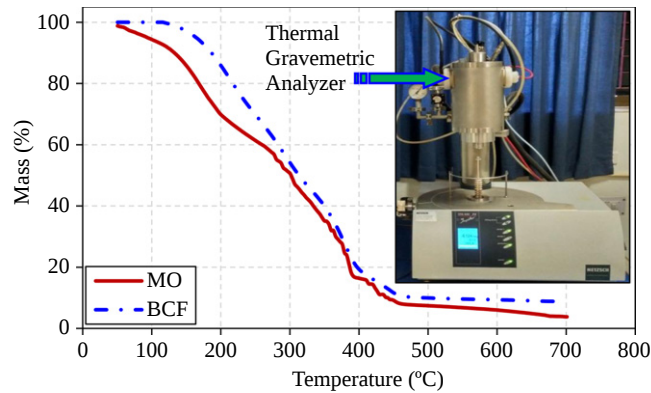


Fig. 2 Mass loss of bio-cutting fluid and mineral oil with respect to temperature. Reprinted with permission from Gajrani, K.K., Suvin, P.S., Kailash, S.V., Sankar, M.R., 2016. Comparative studies on thermal, rheological behaviour of eco-friendly cutting fluids and their machining performance. In: Proceedings of the 6th International and 27th All India Manufacturing Technology Design and Research (AIMTDR) Conference, pp. 674 – 678. Pune: COEP. Copyright [2016], Copyright holder [AIMTDR].

indicates the presence of formation of coke (carbon derived from pyrolysis of organic compound) or inorganic compound. MO has lower thermal stability as compared to BCF. Therefore, BCF can be used at high temperature application like hard machining.

Shear Stress and Viscosity of Cutting Fluids

The flow and lubricant behaviour of cutting fluid depends on its shear stress and viscosity. Therefore, shear stress and viscosities of cutting fluids are measured as a function of shear rate using a rheometer (Make: ANTON PAAR[®], Model: MCR-101) with a coaxial cylinder tool master. To obtain shear flow conditions, experiments are conducted under steady flow state. Measurements were carried out by linear increase in shear rate from 1 – 1000 s⁻¹ at four different temperatures of 20°C, 50°C, 80°C and 100°C. Average values of three tests are reported.

It is obvious that BCF cannot follow the same mechanism for lubrication as MO. Lubrication depends on various properties such as viscosity, density, composition, etc. However, cutting fluid viscosity is the most important among them. Cutting fluids having higher viscosity are believed to have better lubricating properties.

Apparently viscosity can decrease, remain unchanged or increase with respect to shear rate for time dependent fluids. These fluids are known as pseudoplastic ($n < 1$), Newtonian ($n = 1$) and dilatant ($n > 1$), respectively. It is important to know the behaviour of cutting fluid because various metalworking processes involve different operating range of temperature and shear rate.

Fig. 3(a – d) shows the effect of shear rate on shear stress of BCF and MO at 20°C, 50°C, 80°C and 100°C, respectively (Gajrani *et al.*, 2016). Even though the chemical composition of BCF and MO is different, their rheological behaviour is similar. Both cutting fluids shows near Newtonian behaviour ($n = 1$) at 20°C (**Fig. 3(a)**) and 50°C (**Fig. 3(b)**). Newtonian behaviour can be confirmed by the linear variation of shear stress with shear rate. However, at the higher temperature of 80°C (**Fig. 3(c)**), only BCF shows near Newtonian behaviour. At higher shear rate, MO exhibits the dilatant behaviour. With the further increase in temperature at 100°C (**Fig. 3(d)**) both cutting fluids exhibits dilatant behaviour after shear rate of 500 s⁻¹. Therefore, it can be said that BCF is able to maintain Newtonian behaviour at higher temperature as compared to MO.

Fig. 4(a–d) illustrates the effect of shear rate on viscosities of BCF and MO at 20°C, 50°C, 80°C and 100°C, respectively (Gajrani *et al.*, 2016). At 20°C, viscosities of BCF and MO are 0.12 Pa.s and 0.05 Pa.s, respectively. However, due to high heat and temperature during metalworking operations, cutting fluids mostly operate much above 20°C. Therefore, viscosities of BCF and MO at higher temperature are also reported. At 50°C, viscosities of BCF and MO are 0.03 Pa.s and 0.015 Pa.s, respectively. Furthermore, with increase in temperature, the viscosities of BCF and MO are 0.011 and 0.007 Pa.s, respectively at 80°C as well as 0.007 and 0.004 Pa.s, respectively at 100°C. With increase in temperature, viscosity of both cutting fluid reduces. It is attributed to molecules that overcome a threshold energy barrier and occupy the adjacent vacant site due to thermal activation. For varying temperature range, BCF has more viscosity as compared to MO that enables it to lubricate better as compared to MO.

Apparent Activation Energy of Cutting Fluids

Flow of molecules is a thermally activated process. In any liquid, molecules need to overcome an energy barrier to flow to the nearby vacant site. With the increase in temperature, the number of vacant sites in the liquid increases as well as molecules own thermal energy also increases. The dependence of the reaction rate on the temperature indicates the apparent activation energy. The term activation energy is defined as minimum necessary energy required for the occurrence of a specific chemical reaction. Arrhenius type equation relates the viscosity (μ) and the activation energy (E_a) as follows:

$$\mu = A \exp\left(\frac{E_a}{RT}\right) \quad (1)$$

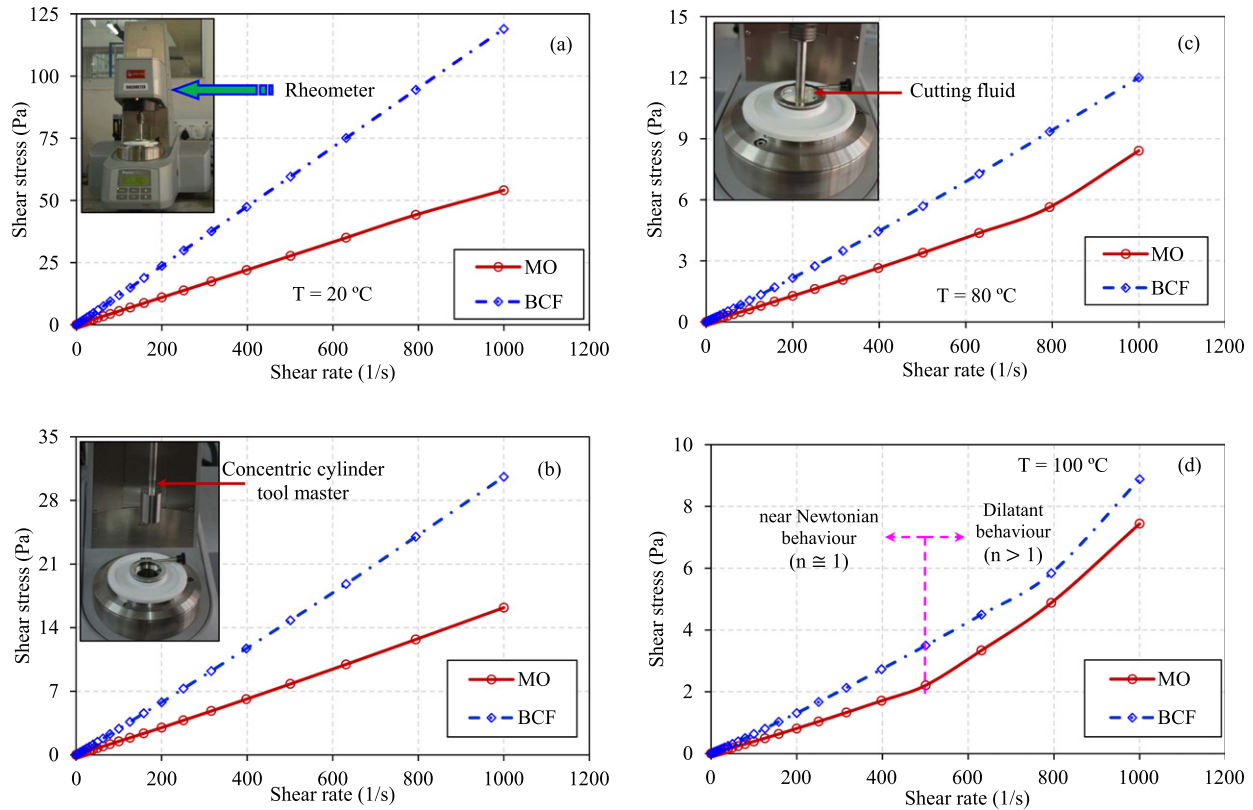


Fig. 3 Effect of shear rate on shear stress of mineral oil and bio-cutting fluid at (a) 20°C, (b) 50°C, (c) 80°C and (d) 100°C. Reprinted with permission from Gajrani, K.K., Suvin, P.S., Kailash, S.V., Sankar, M.R., 2016. Comparative studies on thermal, rheological behaviour of eco-friendly cutting fluids and their machining performance. In: Proceedings of the 6th International and 27th All India Manufacturing Technology Design and Research (AIMTDR) Conference, pp. 674 – 678. Pune: COEP. Copyright [2016], Copyright holder [AIMTDR].

where T is the absolute temperature, R refers to real gas constant and A is a constant. Activation energy is determined using temperature dependence of viscosity with the help of Eq. (1) (Moraes *et al.*, 2011; Qi-Wei *et al.*, 2003). Eq. (1) can be rewritten as:

$$\ln(\mu) = \ln(A) + \left(\frac{E_a}{R}\right) \frac{1}{T} \quad (2)$$

Fig. 5 shows the variation of viscosities with respect to temperature for BCF and MO. Viscosity of both cutting fluid reduces with increase in temperature. It is attributed to reduction in intermolecular forces between molecules with increase in temperature. Using Eq. (2) and data from Fig. 5, a relation between $\ln(\mu)$ against T^{-1} is plotted as shown in Fig. 6 (Gajrani *et al.*, 2016). From the slopes of $\ln(\mu)$ against T^{-1} , apparent activation energy is calculated and reported in Table 2 (Gajrani *et al.*, 2016). BCF have high activation energy that means BCF is less sensitive and more stable with increasing temperature as compared to MO.

Biodegradability of Cutting Fluids

The term biodegradation represents breakdown of any substance by micro-organism such as enzymes, fungi, bacteria etc. and the substance own ability to biodegrade is called biodegradability. Biodegradation is classified into two categories: Primary biodegradation and ultimate biodegradation. Primary biodegradation means change in physical and chemical characteristics of the matter or substance due to activities of micro-organism. Further, ultimate biodegradation is described as total (full) conversion of matter or substance into biomass, water, carbon dioxide, methane and mineral salts.

The aim of cutting fluid biodegradation study is to measure ultimate biodegradability. In general, ample amount of oxygen and water (aerobic aquatic biodegradation environment) is needed for biodegradability test of cutting fluids. For measuring life cycle of any liquid matter or substance, its dissolved oxygen (DO) is an important element. To measure the oxygen demand for degradation of both non-biodegradable oxidisable matter/substance and biodegradable matter/substance, chemical oxygen demand (COD) tests are carried out. However, biological oxygen demand (BOD) test give only measure of oxygen demand for degrading organic matter in cutting fluid (only cutting fluid's biodegradable portion). Therefore, the ratio of BOD/COD quantifies the biodegradable potential of cutting fluids.

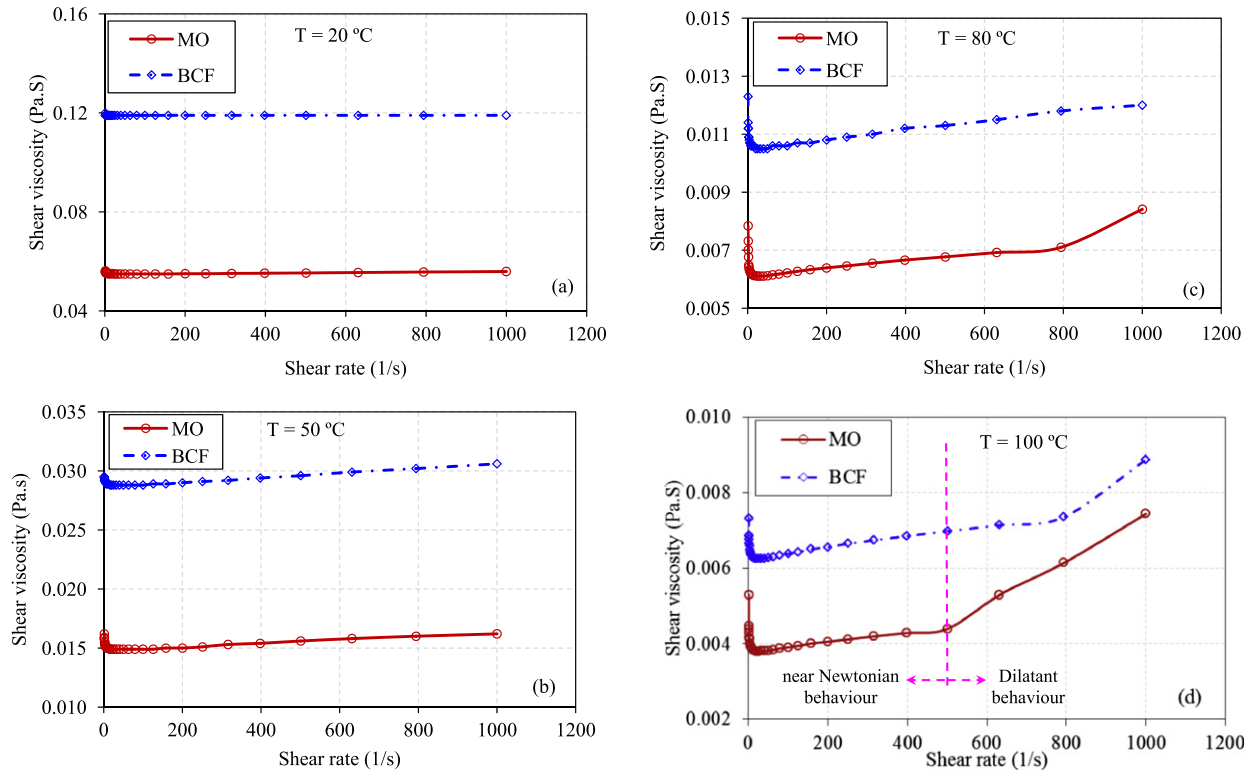


Fig. 4 Effect of shear rate on shear viscosity of mineral oil and bio-cutting fluid at (a) 20°C, (b) 50°C, (c) 80°C and (d) 100°C. Reprinted with permission from Gajrani, K.K., Suvin, P.S., Kailash, S.V., Sankar, M.R., 2016. Comparative studies on thermal, rheological behaviour of eco-friendly cutting fluids and their machining performance. In: Proceedings of the 6th International and 27th All India Manufacturing Technology Design and Research (AIMTDR) Conference, pp. 674 – 678. Pune: COEP. Copyright [2016], Copyright holder [AIMTDR].

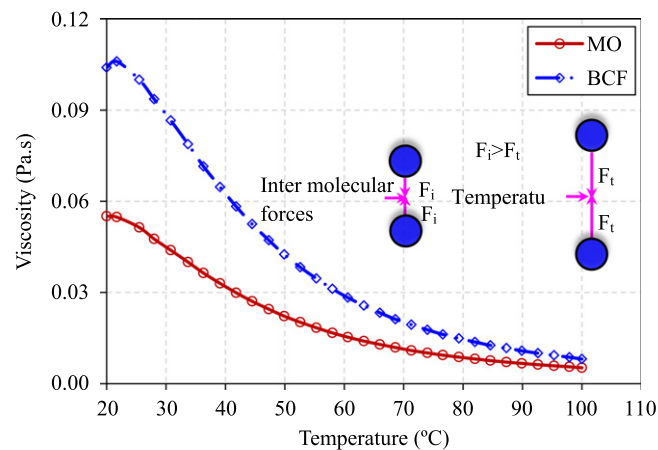


Fig. 5 Effect of temperature on viscosity of mineral oil and bio-cutting fluid.

For primary biodegradation, five days BOD and COD tests are carried out using 1:100000 (lubricant: Aerated water) diluted samples of BCF and MO. Afterwards, least square method is used to calculate ultimate BOD (BOD_u) for complete biodegradation information in accordance with *Standard Methods 2005* (American Public Health Association) (APHA, AWWA, WPCF, 2005).

BOD test for a period of five days is known as BOD_5 . The degradation potential of biodegradable substance is indicated by BOD_5/COD ratio. Therefore, BOD_5/COD ratios of BCF and MO at different times are used to assess the biodegradation potential of cutting fluids (Fig. 7) (Gajrani et al., 2017b).

It is well known that the cutting fluids biodegradability primarily depends on organic content and their chemical structure. It is observed that over the five days, MO degraded around 10%; however, BOD_5/COD ratio for BCF is well over 40%. This is attributed to composition of BCF. BCF consist high amount of organic matter which degrades easily. However, MO is mostly made up of fixed solids or non-degradable volatile solids. For five days biodegradability test, BOD_5/COD ratio over 0.4 for any chemicals/

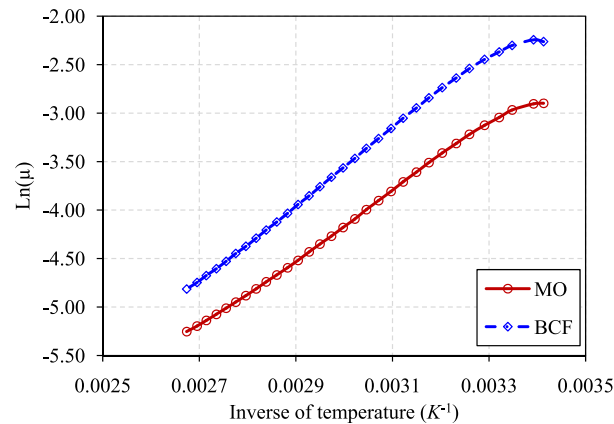


Fig. 6 Variation of $\ln(\mu)$ with respect to variation of temperature for apparent activation energies. Reprinted with permission from Gajrani, K.K., Suvin, P.S., Kailash, S.V., Sankar, M.R., 2016. Comparative studies on thermal, rheological behaviour of eco-friendly cutting fluids and their machining performance. In: Proceedings of the 6th International and 27th All India Manufacturing Technology Design and Research (AIMTDR) Conference, pp. 674 – 678. Pune: COEP. Copyright [2016], Copyright holder [AIMTDR].

Table 2 Apparent activation energies of bio-cutting fluid and mineral oil

Metal cutting fluid	Apparent activation energy E_a (kJ/mol)
Bio-cutting fluid	31.23 ± 0.5
Mineral oil	28.50 ± 0.8

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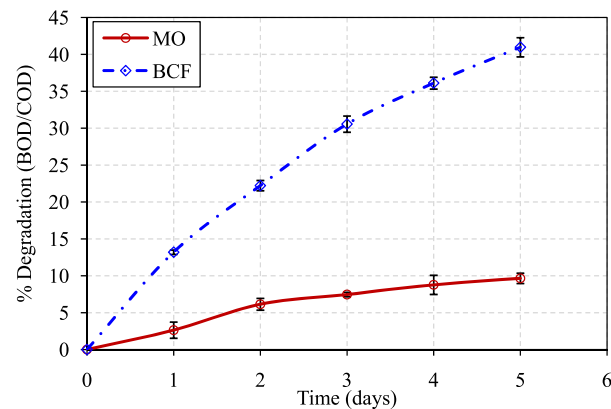


Fig. 7 Biodegradability of bio-cutting fluid and mineral oil over five days. Reprinted with permission from Gajrani, K.K., Ram, D., Sankar, M.R., 2017b. Biodegradation and hard machining performance comparison of ecofriendly cutting fluid and mineral oil using flood cooling and minimum quantity cutting fluid techniques. Journal of Cleaner Production 165, 1420–1435. Copyright [2017], Copyright holder [Elsevier].

waste water/substance is considered completely degradable (Adams *et al.*, 1979). In contrast, BOD_5/COD ratio under 0.2 falls under the category of highly non-degradable in nature due to presence of unoxidisable organic matter in high amount. However, BOD_5/COD ratio only provides preliminary information about cutting fluids biodegradability.

For total biodegradation, ultimate BOD (BOD_u)/COD ratio provides complete information. As per *Standard Methods 2005*, least square method is used for calculating BOD_u (APHA, AWWA, WPCF, 2005). Table 3 shows the calculated ultimate aerobic biodegradability of BCF and MO (Gajrani *et al.*, 2017b). BOD_u for BCF is 1392 g/L; however, BOD_u for MO is only 417.8 g/L. In contrast, COD for BCF is only 1440 g/L while for MO is 2280 g/L. From Table 3, it is observed that BOD_u/COD ratio for BCF is well over 0.8 that is considered readily and highly biodegradable for any matter (Adams *et al.*, 1979). The atmospheric present natural bacteria can easily oxidised cutting fluids containing organic matter which is shown by high BOD_u value.

Table 3 Ultimate aerobic biodegradability of mineral oil and bio-cutting fluid

Metal cutting fluid	BOD_u ultimate (g/L) (least square method)	COD (g/L)	BOD_u/COD	Final degradation (%)
Mineral oil	417.8	2280	0.1832	18.32
Bio-cutting fluid	1392	1440	0.9667	96.67

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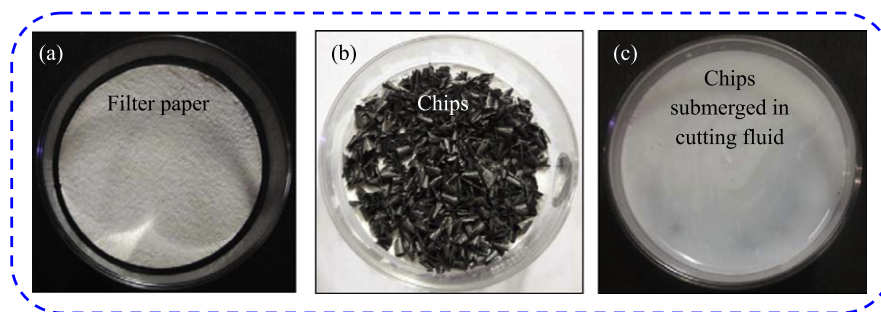


Fig. 8 Overview of corrosion test method setup (a) filter paper with petri dish, (b) grey cast iron chips on the filter paper and (c) cutting fluid poured into petri dish.

MO exhibits very low biodegradation. MO based cutting fluids are more inclined towards metallic cations. Those are hazardous to sewage micro-organism, which further reduces the plant disposals efficiencies. Ultimate biodegradability predicts the capacity of natural water bodies/sewage micro-organism to degrade BCF without any external factor. However, during incubation time, MO does not show satisfactory degradation. Therefore, un-decomposed matter of MO may appear as pollutants in the environment.

Anti-Corrosion Properties of Cutting Fluids (ASTM D 4627)

Cutting fluids corrosion tests are performed in accordance with ASTM D 4627 standard (ASTM D, 4627, 2012). **Fig. 8(a)** illustrates 47 mm diameter filter paper made of glass fiber (1.5 μ m particle retention) placed inside the petri dish. Cutting fluid with ten different oil concentration (0.5, 1, 1.5, 2, 2.5, 3, 4, 5, 7 and 10%) of each BCF and MO were mixed with synthetic hard water (calcium chloride dehydrate in distilled water). As per the standard, grey cast iron chips are selected for corrosion tests. Chips were sieved using 18 mesh screen. **Fig. 8(b)** illustrates 4 g of chips sprinkled on the top of glass fiber filter paper. Afterwards, different petri dishes were filled with 25 mL of ten varying oil concentration of BCF and MO each. **Fig. 8(c)** shows chips submerged in cutting fluids. All petri dishes were covered with top lid. After incubation time of 24 h, cutting fluids were drained from petri dish. Afterwards, corroded chips were collected separately. Chips were cleaned by sonication using acetone for 20 min and dried. Chip weight loss due to its corrosion was also calculated. Moreover, glass fiber filter paper was rinsed. The amount of rust stain over the filter paper gives measure of cutting fluid anti-corrosion properties that helps in identifying breakpoint. ASTM D4627 defined breakpoint as the weakest concentration of cutting fluid tested, which shows no rust stain on the glass fiber filter paper.

As per ASTM D 4627 standard, the rate of corrosion is graded from 1 to 10, where ten is highly corrosive, five represent medium corrosion and one stands for non-corrosive cutting fluids (ASTM D, 4627, 2012). After corrosion test, rusted filter paper with several concentrations of BCF and MO is shown in **Fig. 9(a-b)**. Results shows that the amount of rusting reduces with the increase in concentration of cutting fluids. For BCF less rusting was observed as compared to filter paper of MO for all concentrations. Breakeven point of 8 and 9 are exhibited by BCF and MO, respectively, where no further rust is observed by naked eyes. It confirms that the BCF has better anti-corrosion properties with respect to MO based cutting fluids.

Moreover, the chips weight loss was also measured and reported as shown in **Fig. 10**. It is observed that chips weight loss and rate of corrosion reduces with the increase in concentration of cutting fluids. This is attributed to anti-corrosion properties of cutting fluids that slow the reaction of oxygen and iron in its presence. Even though BCF and MO have different composition, they follow similar behaviour in case of chips weight loss after corrosion tests.

Storage Stability of Cutting Fluids (ASTM D 3707)

During machining, generated heat and friction is reduced with the help of cutting fluids in the form of emulsions. Therefore, storage stability of cutting fluid emulsions is one of the important parameter to select cutting fluid for particular application. Cutting fluid emulsions storage stability tests are performed in accordance with ASTM D 3707 standard (ASTM D, 3707, 2010). As

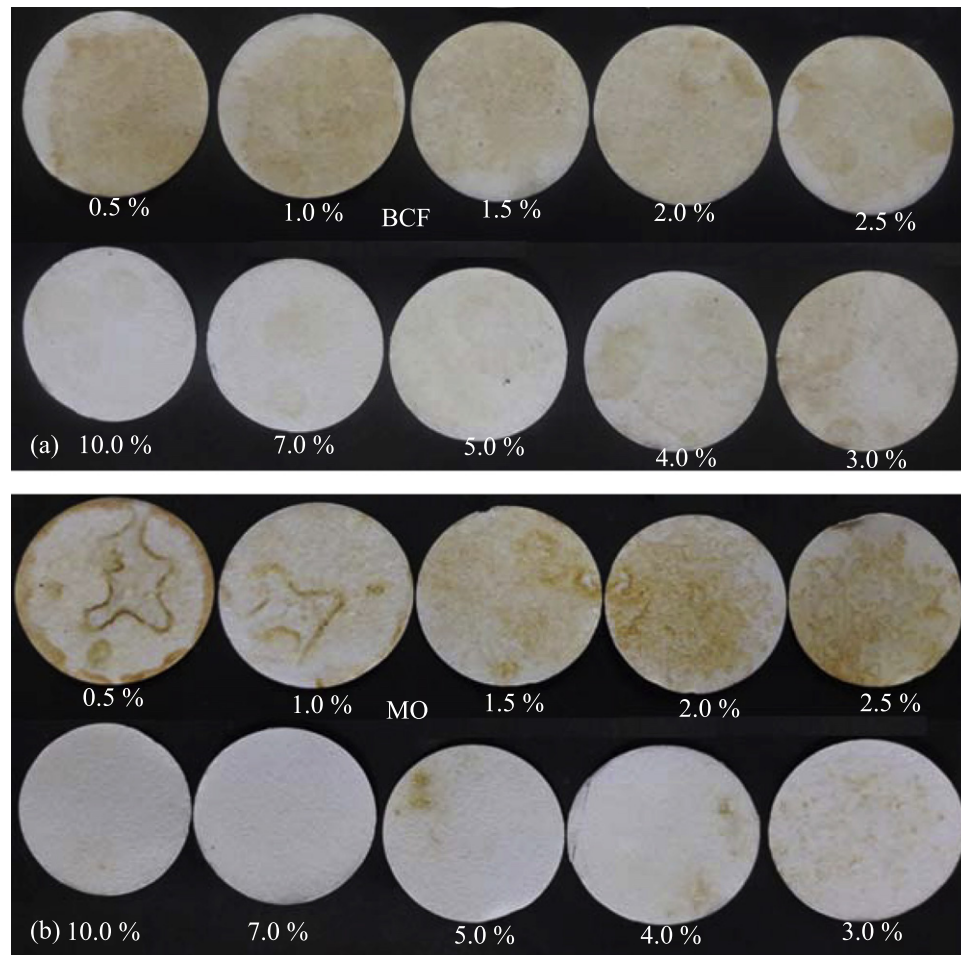


Fig. 9 Rusty filter paper after corrosion test with several concentration of (a) bio-cutting fluid and (b) mineral oil.

per the guidelines, 50 mL of cutting fluid emulsions with ten varying oil concentration (1:2–1:20, 1 part of oil for 2–20 part of water) for both BCF and MO were prepared and kept in glass graduated cylinder (**Fig. 11(a)**). For storage stability tests, prepared samples were kept inside convection oven for 48 h at $85 \pm 1^\circ\text{C}$. After test, samples were kept at room temperature for an hour. Afterwards, amount of separated water, oil and remaining emulsions were measured in glass graduated cylinder (**Fig. 11(b)**).

In accordance with ASTM D3707 standard, storage stability of the emulsion was assessed by measuring separated oil and water from intact emulsion after tests. After tests, amount of sample evaporated was considered as separated water. Amount of initial sample minus measured separated oil and separated water was considered as an intact emulsion after tests. **Figs. (12–14)** illustrates the effect of emulsion concentration on separated oil, separated water and remaining emulsions, respectively for BCF and MO after oven tests. The result shows that separation of oil increases with the increase in concentration of water in emulsions (**Fig. 12**) for both cutting fluids. However, in case of BCF, the amount of separated oil is less as compared to MO. Moreover, the amount of separated water reduces up to 1:16 emulsion concentration while afterwards it starts increasing for both cutting fluids (**Fig. 13**). In the similar way, the amount of remaining emulsion increases up to 1:16 emulsion concentration while afterwards it starts increasing for both cutting fluids (**Fig. 14**). However, in all cases, the amount of separated oil and separated water is less for BCF as well as the amount of remaining emulsion is high for BCF as compared to MO. The emulsion type and composition showing the least separation (most remaining emulsion) after oven test is considered as the most stable composition. Therefore, based on the measured parameters, the storage stability of 1:16 BCF emulsion composition is proved to be better among others.

Machining Experiments Using Cutting Fluids

Machining experiments are carried out using a lathe (Make: HMT[®], Model: NH 26) equipped with a tool holder (Make: Sandvik[®], Model: PTG NR 2525 M16) and tungsten carbide tool insert (Make: Sandvik[®], Model: TNMA 220412). Machining experiments are carried out at MQCF environment using sustainable BCF and MO. Cutting tool insert was TiN coated on flank face. This inserts were selected as during machining MQCF spray was only injected in-between workpiece and cutting tool rake face. AISI H-13 steel

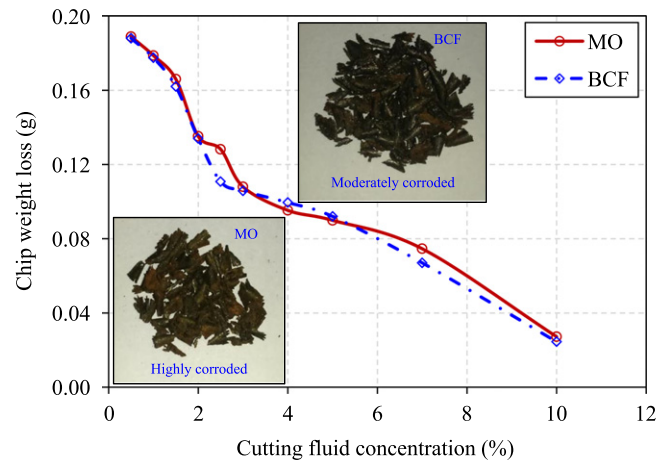


Fig. 10 Effect of bio-cutting fluid and mineral oil on weight loss of chips due to corrosion at varying concentration.

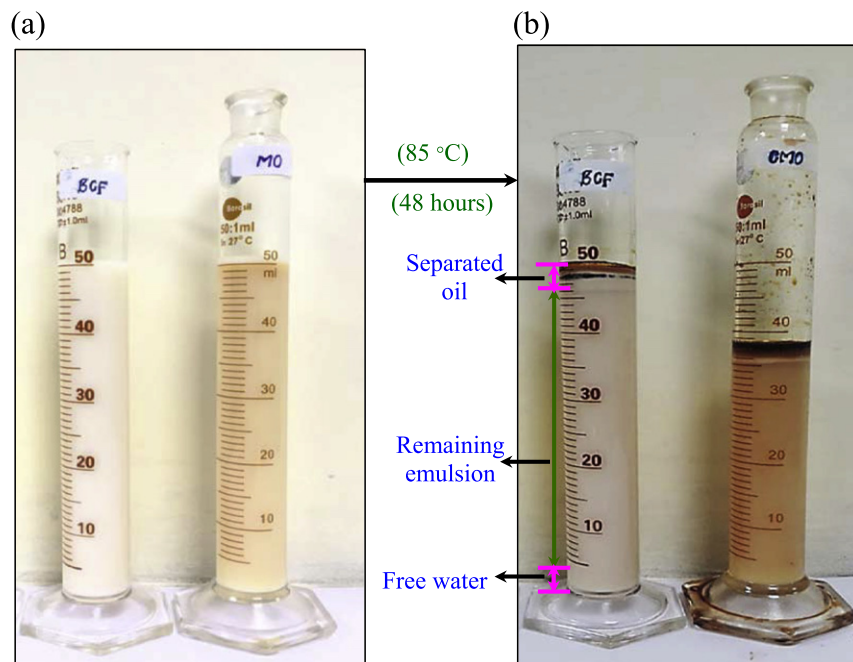


Fig. 11 Bio-cutting fluid and mineral oil emulsions (1:16) for the storage stability test (a) before and (b) after 48 h at 85°C.

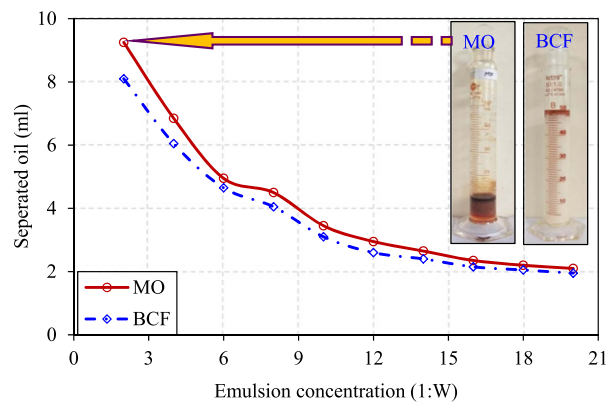


Fig. 12 Assessment of separated oil from the emulsion after oven test with respect to emulsion concentration (1:W represents 1 part of oil in W part of water).

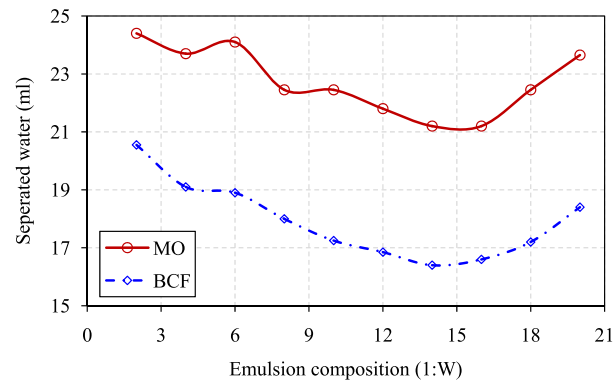


Fig. 13 Assessment of separated water from the emulsion after oven test with respect to emulsion concentration (1:W represents 1 part of oil in W part of water).

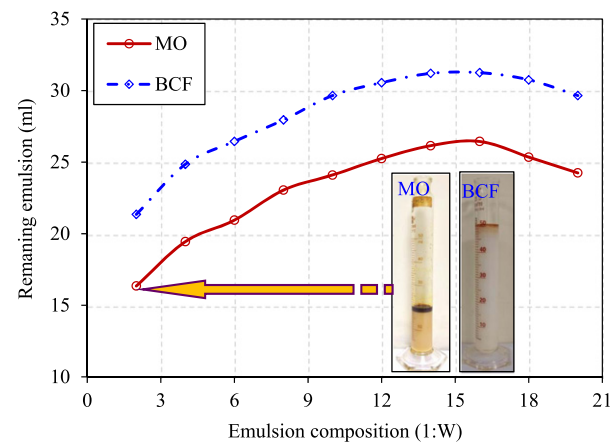


Fig. 14 Assessment of remaining emulsion after oven test with respect to emulsion concentration (1:W represents 1 part of oil in W part of water).

Table 4 Machining conditions

Parameter	Values
Depth of cut	0.5 mm
Feed	0.16 mm/rev
Cutting speed	90 m/min
Environments	MQCF
Cutting fluid	Bio-cutting fluid and mineral oil
Air pressure	5 bar (0.5 MPa)
MQCF flow rate of oil	35 mL/h
Oil concentration	1:16 (1 part oil, 16 part water)

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were chosen as workpiece material due to its various applications and high average hardness (56 ± 2 HRC). Workpiece material has C 0.32%–0.4%, Mo 1.33%–1.4%, Cr 5.13%–5.25%, Si 1%, V 1% and Fe remaining. **Table 4** shows the machining conditions (Gajrani *et al.*, 2017b).

Fig. 15 illustrates machining experimental setup with MQCF technique. The average cutting and feed forces are measured using a Kistler® make piezoelectric quartz dynamometer (Model: 9272B). Mahr® make contact type surface profilometer was used to measure the workpiece surface roughness. All experiments are repeated thrice and average values are plotted.

Both BCF and MO are applied using MQCF technique for enhanced lubrication with minimum amount of cutting fluid during hard turning of AISI H-13 steel. Effect of both cutting fluid viscosity on the cutting and feed forces are illustrated in **Fig. 16(a-b)**.

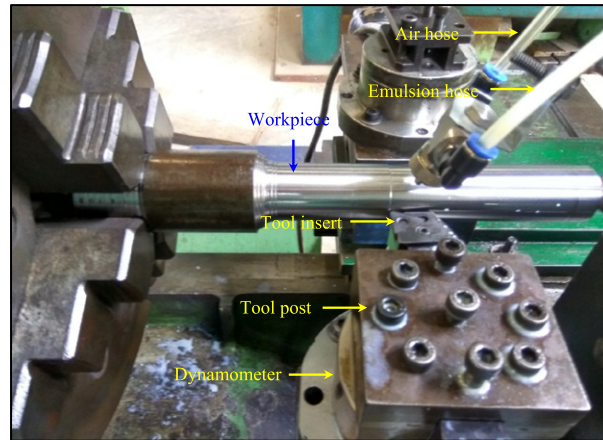


Fig. 15 Tool-workpiece-mist interaction region during machining with minimum quantity cutting fluid technique.

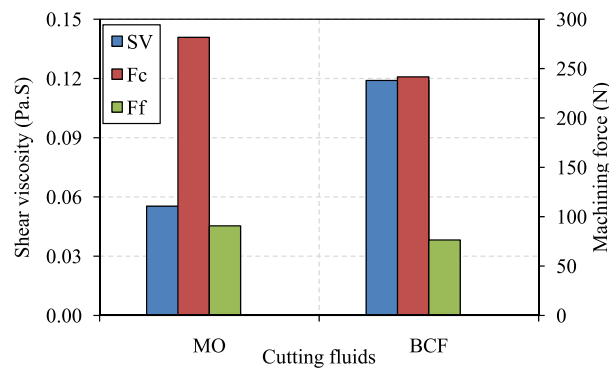


Fig. 16 Effect of cutting fluid viscosity on cutting and feed forces.

Result shows that the performance of BCF is superior to that of MO in terms of both cutting and feed forces. This is attributed to better lubricating ability of BCF because of its high viscosity as compared to MO.

In general, low viscosity cutting fluids are preferred for better flow ability and cooling properties. However particularly with MQCF technique, cutting fluid lubricating property should dominate rather than its flow ability. The relation between cutting fluid viscosity and machining force is complex. Even though the flow ability of cutting fluid is compromised by higher viscosity cutting fluid but machining forces reduces. This is mainly because of MQCF technique. In this technique, cutting fluid is mixed with air and atomized in the form of mist/spray, which is directly focused in between tool-chip interface. Therefore, flow ability of cutting fluid is not that much important as compared to its viscosity which provides better lubrication. Apart from high viscosity, BCF has a better thermal property, thermal conductivity and specific heat capacity that also help in improving its machining performance (Gajrani *et al.*, 2017b).

The tool-chip interface coefficient of friction is calculated as follows (Ernst and Merchant, 1941):

$$\mu = \tan(\alpha) = \tan(\lambda + \tan^{-1}(F_f/F_c)) \quad (3)$$

where F_f and F_c represents the feed and cutting force, λ and α represents the friction and rake angle, respectively. The effect of both cutting fluid viscosity on the tool-chip interface coefficient of friction is illustrated in Fig. 17.

Result shows that the tool-chip interface coefficient of friction is less for machining with BCF as compared to MO. This is due to reduced total tool-chip contact length using BCF (Fig. 18) (Gajrani *et al.*, 2017b). In another study, similar behaviour was also observed during machining with green cutting fluid (Gajrani *et al.*, 2017c). Fig. 18(a-b) illustrates the tool rake face morphology showing tool-chip interface region after machining with BCF and MO using MQCF technique. Tool rake face after machining with MO shows severe adhered material from workpiece (Fig. 18(b)) (Gajrani *et al.*, 2017b). In contrast for tool rake face after machining with BCF, fewer workpiece adhered material was observed (Fig. 18(a)) (Gajrani *et al.*, 2017b). Fig. 18(c) shows the elemental composition of adhered material (Area A), which is similar to the composition of workpiece material (Fe in bulk). This evidence supports the adhesion of workpiece material on the tool rake face. Also, the overall tool-chip contact length is lower for the cutting tool after machining with BCF as compared to MO (Fig. 18(b)) (Gajrani *et al.*, 2017b). This is attributed due to high viscosity of BCF, which creates better lubricating film in between tool-chip interface and it does not allow chip material to slide directly over the cutting tool rake face for more length. Therefore, with increase in viscosity of cutting fluid, the tool-chip contact length decreases that lead to the reduction of friction force which ultimately lower friction coefficients.

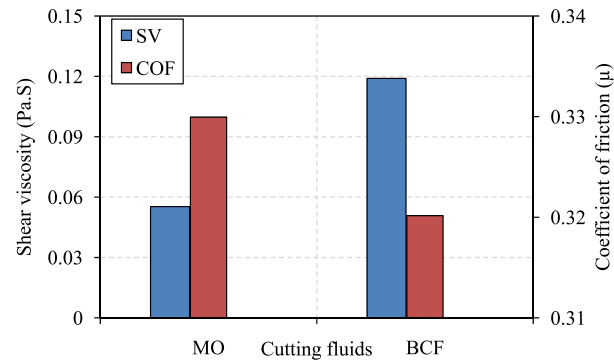


Fig. 17 Effect of cutting fluid viscosity on tool-chip interface coefficient of friction.

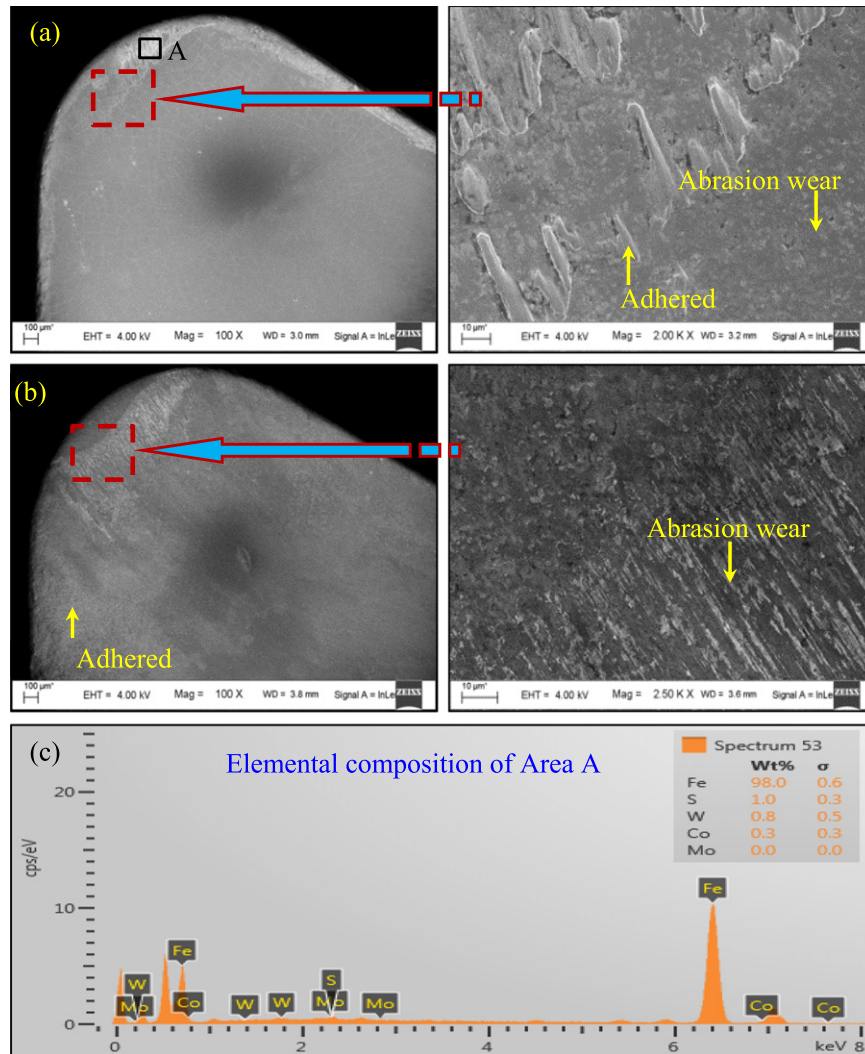


Fig. 18 Tool rake face morphology showing tool-chip interface region after machining with (a) bio-cutting fluid, (b) mineral oil showing adhesion and abrasion wear and (c) elemental composition of adhered material (Area A, Fig. 18 a). Reprinted with permission from Gajrani, K.K., Ram, D., Sankar, M.R., 2017b. Biodegradation and hard machining performance comparison of ecofriendly cutting fluid and mineral oil using flood cooling and minimum quantity cutting fluid techniques. *Journal of Cleaner Production* 165, 1420–1435. Copyright [2017], Copyright holder [Elsevier].

Afterwards, the effect of both cutting fluid viscosity on the surface roughness is shown in **Fig. 19**. The result shows that workpiece surface roughness after machining with BCF is lower as compared to MO. This is attributed to lower machining forces with BCF due to which tool chatter also reduces. Thus, it leads to the better workpiece surface finish.

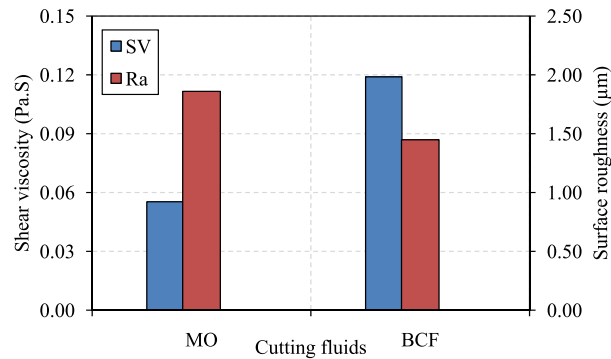


Fig. 19 Effect of cutting fluid viscosity on workpiece surface roughness.

Concluding Remarks

The physical, thermal, rheological, biodegradation, anti-corrosion and storage stability properties of sustainable BCF and petroleum-based MO are assessed and compared. Machining experiments were conducted with BCF and MO using MQCF technique. The salient findings are as follows:

- The flash point of BCF is higher as compared to MO that allows its use for high temperature hard machining.
- BCF exhibits less variation from Newtonian behaviour even at higher temperature. Also, its sensitivity to temperature is lower as compared to MO.
- As per *Standard methods 2005*, ultimate biodegradability of BCF and MO is found to be 96.67% and 18.32%, respectively.
- BCF showed corrosion breakpoint of 8; whereas MO exhibits corrosion breakpoint of 9 as per ASTM D 4627 standard.
- As per ASTM D 3707 standard, BCF shows more remaining emulsion as compared to MO after storage stability test.
- Sustainable BCF showed better machining performance as compared to MO in terms of cutting force, feed force, tool-chip interface coefficient of friction and surface roughness due to its high viscosity and better lubricating properties.

Acknowledgement

Authors are thankful to “ELSEVIER (Licence numbers: 4300100119334 and 4300100926374)” for providing the copyright permission of various figures and tables in the current manuscript. Authors are also thankful to the organiser of “6th International and 27th All Indian Manufacturing Technology, Design and Research Conference (AIMTDR-2016)” held at Pune, India on 16-18 December 2018 for providing copyright permission of various figures and tables used in this manuscript. The authors are also thankful for the financial support provided by the Board of Research in Nuclear Sciences (Project Number: ME/P/MRS/02), Department of Science and Technology for their TSDP (DST/TSG/AMT/2015/619), Defence Research Development & Development Laboratory (CARS Project). Authors also acknowledge Central Instrumentation Facility, IIT Guwahati for providing FESEM and EDS facility for this work.

See also: Sustainable Biofuels for Automotive Applications

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Sustainable Machining With Self-Lubricating Coated Mechanical Micro-Textured Cutting Tools

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Introduction

Main purposes of cutting fluids are to cool and lubricate machining region as well as to flush away the chips produced. Cutting fluids have various merits over dry machining. During machining, use of cutting fluids improves machined surface finish and reduces cutting tool wear. In general, cutting fluids also have anti-corrosion properties, which protect machined surfaces from corrosion. Cutting fluids also save power consumption by reducing the machining forces. In few applications, the associated costs of cutting fluids are higher than tool related costs (Astakhov, 2008). However, apart from merits, cutting fluid also possess various detrimental effects on the environment and health hazard to the operators (Gajrani and Sankar, 2017a).

Cutting fluid associated diseases to operators are mainly caused due to direct contact or inhalation of its fumes, which produces during machining. Dermatitis, skin irritation, folliculitis and allergic reaction are caused due to direct contact of cutting fluids. However, hypersensitivity pneumonitis, bronchitis and asthma are few examples of diseases caused due to inhalation of cutting fluids fumes (Sankar and Gajrani, 2017). Most of the chemicals present in petroleum-based cutting fluids are suspected carcinogens (Dixit *et al.*, 2012). Moreover, due to prolonged exposure to cutting fluids; machine and materials are also affected. For example, water-based cutting fluid emulsions cause corrosion and stains on machined surface.

Disposal of cutting fluids after its usage is a major concern. In general, waste cutting fluids are dumped either in water bodies or landfill. Thus, it can pollute groundwater, surface water as well as can cause soil contamination, which ultimately affects agriculture and contaminate food (Dixit *et al.*, 2012). Therefore, use of cutting fluids need to be minimized or eliminated.

Few researchers have reduced amount of cutting fluid usage by adopting minimum quantity cutting fluids (MQCF) (Gajrani *et al.*, 2017a). In MQCF, a combination of pressurized air is mixed with cutting fluids to form a mist, which is directly injected at the tool-chip interface to reduce heat and to lubricate sliding interface (Gajrani *et al.*, 2017b). However, due to mist nature of MQCF mixture, cutting fluid mix with atmospheric air and easily inhaled by operators working in its vicinity, which may lead to indirect diseases caused by cutting fluids. Thus, it is recommended to totally avoid usage of cutting fluids. Keeping in mind the safety of environment and operators, one of the viable solutions is dry machining (Sreejith and Ngoi, 2000).

Dry machining has several merits such as safety of operators and environments as well as no issue of cutting fluid disposal. However, alternatives to the function of cutting fluids need to explore to reduce heat from machining region and to lubricate tool-chip interface. Researchers have tried various different methods to reduce heat from machining zone such as the use of heat pipe (Jen *et al.*, 2002), internal cooling (Sanchez *et al.*, 2011), cryogenic cooling (Yildiz and Nalbant, 2008), thermoelectric refrigeration (Sreejith and Ngoi, 2000). Researchers have also tried to lubricate machining zone during dry machining using various techniques such as trilayer and multilayer hard coating of various substances on the surface of cutting tools (Kustas *et al.*, 1997; Koshy, 2008). One such technique to enhance tribological properties in-between tool-chip interface is to fabricate controlled surface textures on the rake of cutting tools (Gajrani *et al.*, 2016; Gajrani and Sankar, 2017b).

Controlled engineered modification of surfaces by fabricating micro to nano patterns using various techniques is known as surface textures. Surface textures have the ability to reduce friction between two sliding pairs due to which it is getting wide attention. Optimized textures can improve various functions of surfaces. Engineered surface textures have the variety of applications in industries such as medical implants, to create hydrophobic surfaces, microfluidics, MEMS components, piston rings, bearings, acoustics, etc., (Coblas *et al.*, 2015). Micro-textures can be fabricated using a variety of techniques including both conventional and unconventional methods in varying geometry, shape and size (micrometre to nanometre level). Unconventional texturing methods such as laser (Li *et al.*, 2014), electrical discharge machining (Wenlong *et al.*, 2011), focused ion beam (Kawasegi *et al.*, 2017), etc. have been employed to fabricate micro-textures on the number of various previous studies. In past decade, surface textures are introduced on the tool rake and flank surface to reduce frictional heating at the machining region.

Due to the presence of micro-textures, the actual contact length of tool-chip interface reduces, which in turn reduces sliding friction (Jianxin *et al.*, 2009). Another study reported lesser tool-chip contact length up to 30% due to the presence of micro-textures (Lei *et al.*, 2009). This also favours lesser workpiece material adhesion on the surface of the cutting tool, which leads to stabilize the built-up edge formation (Kummel *et al.*, 2015). Sugihara and Enomoto (2012) have also reported the reduction in adhesion of aluminium workpiece on the tool surface due to the presence of nano/micro textures. Sharma and Pandey (2016) have filled surface textures using calcium fluoride (CaF₂) solid lubricant. Result shows that CaF₂ was able to reduce friction heat generation from machining zone. Deng *et al.* (2013) carried out machining experiment using molybdenum disulphide (MoS₂) coated micro-textured cutting tools and it was found that cutting temperature and cutting force was reduced as compared to machining with convention tool.

As discussed above, surface textured cutting tools have several benefits; however, in most of the studies, thermal-based texturing techniques have been used to fabricate micro-textures. There are several issues with thermal-based texturing techniques such as the formation of recast layer, formation of heat affected zone, development of thermal stress and formation of cracks (Gajrani *et al.*, 2018b).

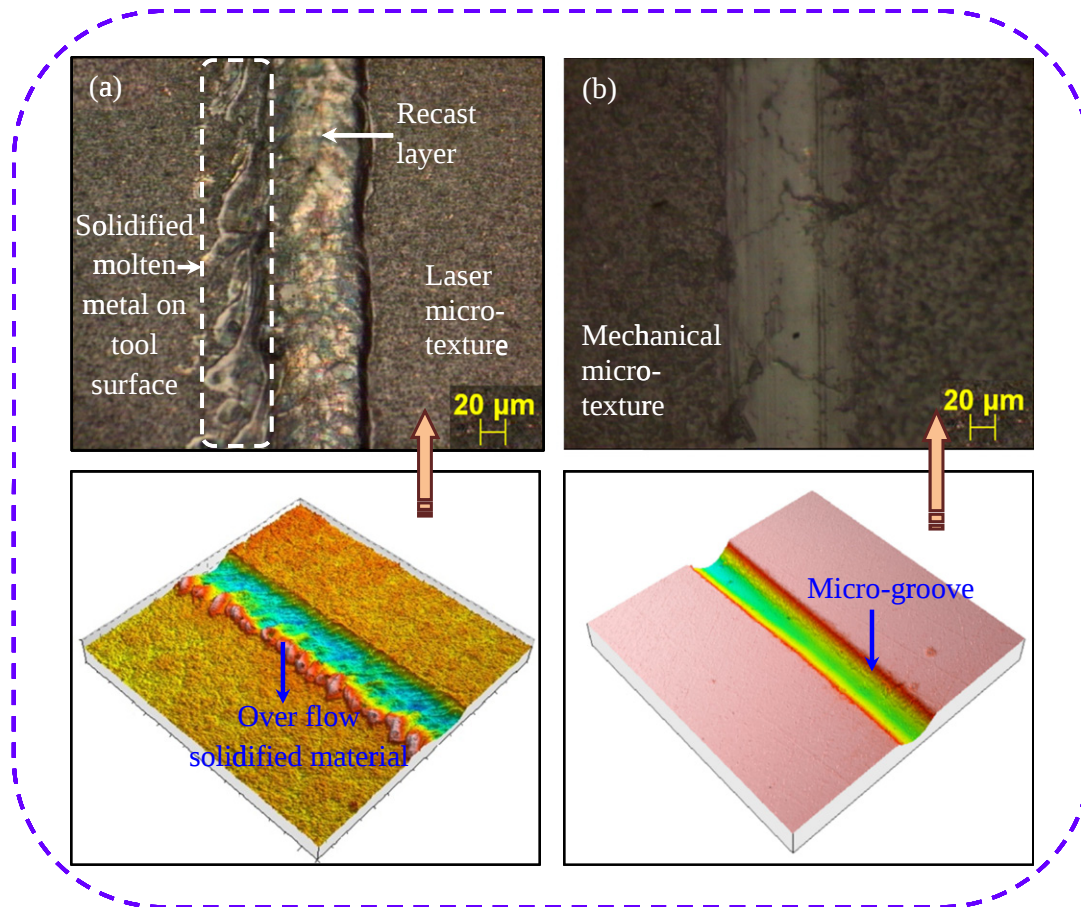


Fig. 1 Micrograph and corresponding 3-d surface profile of (a) single micro-groove fabricated using CO₂ laser and (b) single micro-groove fabricated using scratch tester. Reproduced from Gajrani, K.K., Suresh, S., Sankar, M.R., 2018a. "Environmental friendly hard machining performance of uncoated and MoS₂ coated mechanical micro-textured tungsten carbide cutting tools". *Tribology International* 125, 141–155. doi:10.1016/j.triboint.2018.04.031.

These issues can be eliminated by fabricating surface textures using conventional mechanical techniques. Mechanical micro-textures (MμTs) can be fabricated using the scratch tester, Rockwell hardness tester, nano-indenter and Vicker hardness tester. A typical example of fabricated micro-groove using CO₂ laser and scratch tester is shown in Fig. 1 (Gajrani *et al.*, 2018a). MμTs are easy to fabricate, accurate, repetitive, less time consuming and free from heat affected zone, recast layer as well as thermal stresses.

In this work, three different geometric types of MμT cutting tools were fabricated using mechanical texturing technique. Afterwards, another set of MμT cutting tools were coated using MoS₂ solid lubricant. Hard machining experiments were conducted using six different type of cutting tools while machining of hardened AISI H-13 steel. Machining performance of those cutting tool was compared in terms of machining region temperature, machining forces, coefficient of friction (COF), machined surface finish and tool surface morphology. For comparison purpose, hard machining experiments were also conducted using conventional untextured (UT) cutting tool.

Selecting Area for Texturing and Fabrication of Micro-Textures on the Cutting Tool Rake Face

Preliminary experiments were conducted using UT tool for 15 minutes to select area for texturing on the cutting tool rake face ($f=0.28$ mm/rev, $v=125$ m/min, $\alpha=0.5$ mm). Fig. 2(a) illustrates maximum affected UT tool rake face morphology after preliminary experimentation (Gajrani *et al.*, 2018a). Also, UT rake face was identified for abrasion and adhesion worn areas as well as notch wear as shown in Fig. 2(b-c) (Gajrani *et al.*, 2018a). Texturing area was selected such that it can encompass abrasion and adhesion worn areas with adequate margin as shown in Fig. 2(d) (Gajrani *et al.*, 2018a).

Vicker hardness tester and Ducom[®] make scratch tester (Model: TR-101) were used to fabricate MμTs on the tungsten carbide cutting tool rake face. Three different type of cutting tools were fabricated named VT, PT and PDT cutting tools. VT cutting tools have an array of micro-dimple on its rake face fabricated using Vicker hardness tester. PT and PDT cutting tools have an array of

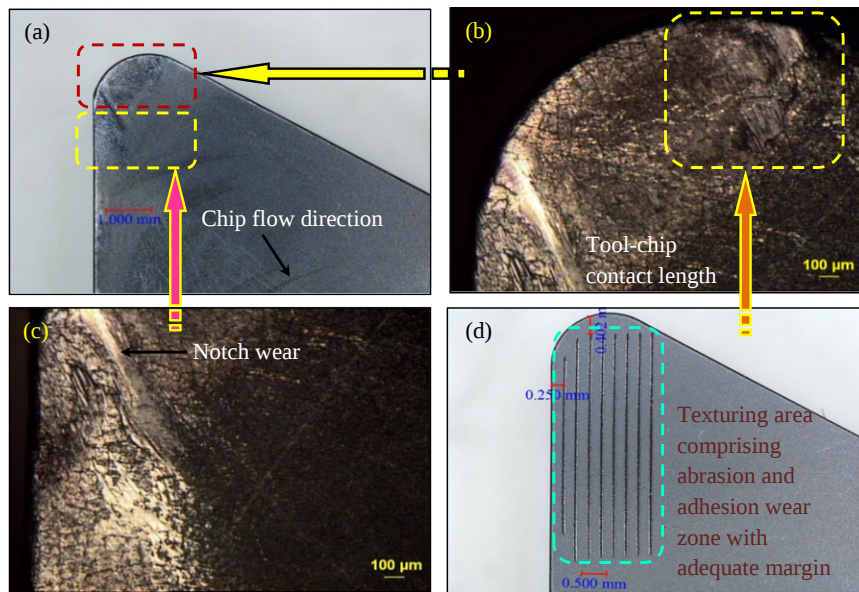


Fig. 2 (a) Micrograph showing worn out zones on the un-textured cutting tool rake face, (b) tool-chip contact length region, (c) notch wear formation and (d) selected area for fabrication of micro-textures and (d) fabricated textured tool. Reproduced from Gajrani, K.K., Suresh, S., Sankar, M.R., 2018a. "Environmental friendly hard machining performance of uncoated and MoS_2 coated mechanical micro-textured tungsten carbide cutting tools". *Tribology International* 125, 141–155. doi:10.1016/j.triboint.2018.04.031.

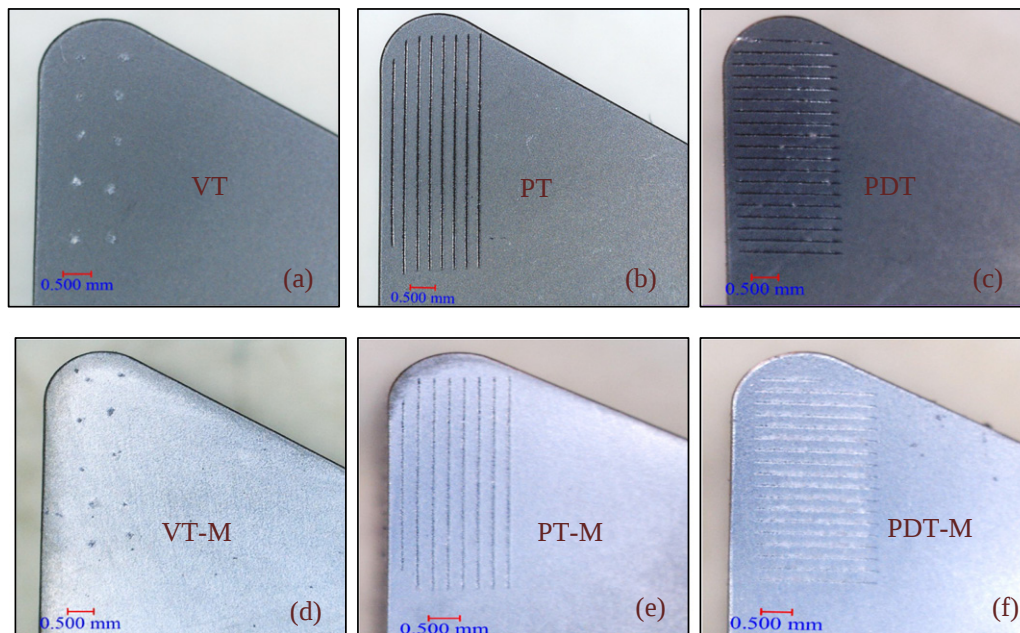


Fig. 3 Surface micrograph of fabricated: (a–c) uncoated textured tools and (d–f) MoS_2 coated self-lubricating tools. Reproduced from Gajrani, K. K., Suresh, S., Sankar, M.R., 2018a. "Environmental friendly hard machining performance of uncoated and MoS_2 coated mechanical micro-textured tungsten carbide cutting tools". *Tribology International* 125, 141–155. doi:10.1016/j.triboint.2018.04.031.

micro-groove that are parallel and perpendicular to the tool principle cutting edge, respectively. Both are fabricated using the scratch tester. **Fig. 3 (a–c)** illustrates fabricated VT, PT and PDT cutting tool (Gajrani *et al.*, 2018a). Afterwards, $\text{M}\mu\text{T}$ cutting tools were smeared and compacted with MoS_2 solid lubricant having an average particle size of 300 nm. MoS_2 coated $\text{M}\mu\text{T}$ self-lubricating cutting tools were entitled as VT-M, PT-M and PDT-M, respectively. Fig. 3 (d–f) illustrates coated $\text{M}\mu\text{T}$ cutting tool (Gajrani *et al.*, 2018a). **Fig. 4** illustrates surface morphology and transmission electron microscopic image of commercial

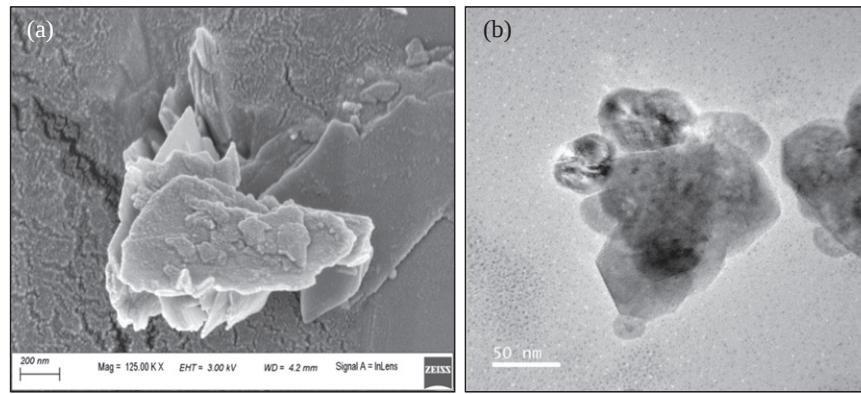


Fig. 4 (a) Surface micrograph of commercial molybdenum disulphide nano-platelet and (b) transmission electron microscopic image of molybdenum disulphide nano-platelet.

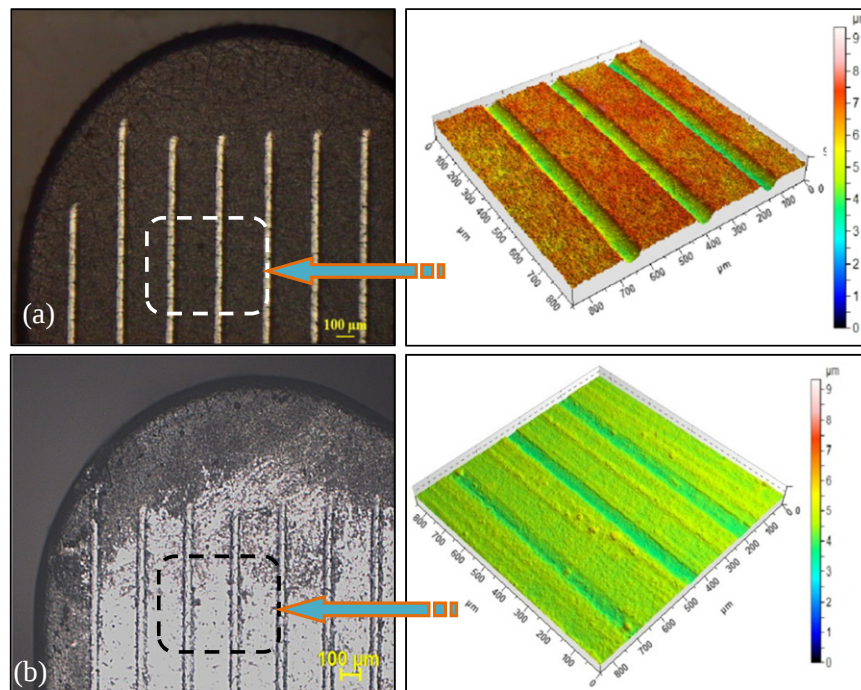


Fig. 5 Surface micrograph and corresponding 3D profile of fabricated (a) uncoated parallel micro-textured cutting tool, (b) MoS_2 coated parallel micro-textured cutting tool. Reproduced from Gajrani, K.K., Suresh, S., Sankar, M.R., 2018a. "Environmental friendly hard machining performance of uncoated and MoS_2 coated mechanical micro-textured tungsten carbide cutting tools". *Tribology International* 125, 141–155. doi:10.1016/j.triboint.2018.04.031.

molybdenum disulphide nano-platelet. **Fig. 5** illustrates surface micrograph and corresponding 3D profile of fabricated uncoated PT cutting tool and MoS_2 coated PT-M cutting tool.

Experimental Design

An efficient technique for determining the correlation between control parameters and output parameters by conducting least number of experiments is known as experimental design or design of experiments. One such technique is central composite rotatable design (CCRD). As per CCRD, for n number of inputs, the total numbers of experiments are $2^n + 2n + \text{central run}$ (Cochran and Cox, 1968). For two control parameter (feed and cutting speed) with five central runs (for better repeatability and assessment), $4 + 4 + 5 = 13$ experiments are required with each type of cutting tool. Feed and cutting speeds were selected based on the preliminary experiments. Depth of cut (0.5 mm) was kept constant during experiments. **Table 1** shows the original and coded value of control parameters (Gajrani et al., 2018a).

Table 1 Machining input parameters actual and CCRD coded values

CCRD coded values	Cutting speed (m/min)	Feed (mm/rev)
−1.414	55	0.04
−1.000	65	0.08
0.000	90	0.16
1.000	115	0.24
1.414	125	0.28

Note: Reproduced from Gajrani, K.K., Suresh, S., Sankar, M.R., 2018a. "Environmental friendly hard machining performance of uncoated and MoS₂ coated mechanical micro-textured tungsten carbide cutting tools". Tribology International 125, 141–155. doi:10.1016/j.triboint.2018.04.031.

Table 2 Hardened AISI H-13 steel workpiece and tungsten carbide tool material properties

Material	AISI H-13 steel	WC + CO
Density (g/cm ³)	7.8	14.5
Young's modulus (GPa)	210	550
Flexural strength (MPa)	950	2000
Hardness (HRC)	56 ± 2	89 ± 3
Poisson's Ratio	0.3	0.23
Co-efficient of thermal expansion μm/(m.°C)	7.42	4.51

Note: Reproduced from Gajrani, K.K., Suresh, S., Sankar, M.R., 2018a. "Environmental friendly hard machining performance of uncoated and MoS₂ coated mechanical micro-textured tungsten carbide cutting tools". Tribology International 125, 141–155. doi:10.1016/j.triboint.2018.04.031.

Materials and Machining Experiments

Hardened AISI H-13 steel was chosen as workpiece material due to various applications such as stamping dies, hot shear blades, forging dies, extrusion tools, casting tools, pressure die, plastic moulds, etc. The workpiece was in the form of a cylindrical rod having 250 mm length and 50 mm diameter with the average hardness of 56 ± 2 HRC. The chemical composition of hardened AISI H-13 steel is Mo 1.33%–1.4%, V 1%, Si 1%, Cr 5.13%–5.25%, C 0.32%–0.4% and Fe remaining. Tungsten carbide Sandvik Coromant[®] insert (Model: TNMA220412) was selected as cutting tool insert along with PTG NR 2525 M 22 tool holder. Table 2 illustrates the workpiece and cutting tool inserts material properties (Gajrani *et al.*, 2018a). Commercial tool holder has nose radius (r_n) of 1.2 mm, angle of approach (K_r) of 9°, inclination angle (λ_s) of −6°, clearance angle (α_o) of 0° and rake angle (γ_o) of −6°. Machining experiments were carried out with all six uncoated and MoS₂ coated MμT cutting tools. Machining with UT tool was also conducted for reference and comparison purpose. Kistler[®] dynamometer (Model: 9272 B) and Infratech[®] thermal infrared camera (Model: VARIOCAM hr-400) was used to measure machining force and temperature of the machining region, respectively. Afterwards, Zeiss[®] optical microscope (Model: AxioCam MRc) and Zeiss[®] field emission scanning electron microscopy (FESEM, Model: Sigma) were used to characterized surface morphologies of worn out cutting tool rake face. Overview of machining experimental setup with the dynamometer, tool post, workpiece and magnified view of micro-textured tool insert is illustrated in Fig. 6 (Gajrani *et al.*, 2018a).

Temperature of Machining Region

Tool life and machined surface finish highly depends upon the temperature of machining region. Thermal infrared camera was used to measure the temperature of machining region. Experiments were carried out in accordance with CCRD. Plan of experiments and output temperature of machining region with various cutting tools are illustrated in Table 3 (Gajrani *et al.*, 2018a).

As per CCRD, the obtained correlations for the temperature of machining region in terms of control parameters for various cutting tools are as follows (Gajrani *et al.*, 2018a):

$$T_{PDT-M} = -417.81 + 2814.03f + 7.418v + 3.642vf - 5709.36v^2 - 0.03512f^2 \quad (1a)$$

$$T_{PT-M} = -441.766 + 2952.04f + 8.33v + 3.522vf - 6001.79v^2 - 0.0374f^2 \quad (1b)$$

$$T_{VT-M} = -496.375 + 3271.73f + 9.18v + 3.41vf - 6451.13v^2 - 0.0401f^2 \quad (1c)$$

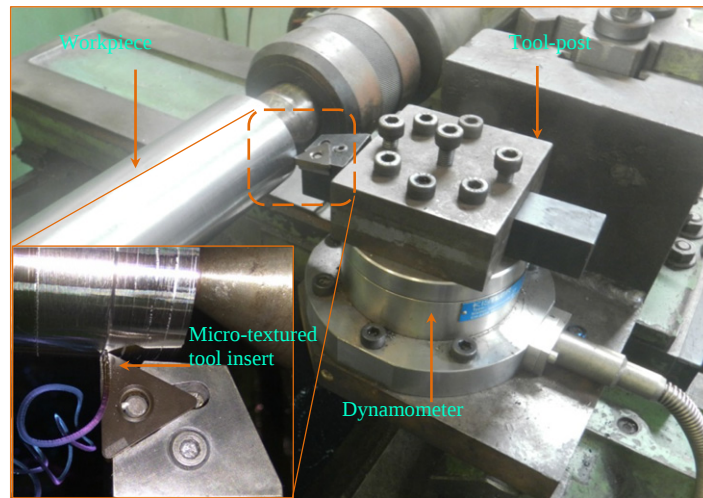


Fig. 6 Machining experimental set-up showing dynamometer, tool post, workpiece and magnified view of micro-textured tool insert. Reproduced from Gajrani, K.K., Suresh, S., Sankar, M.R., 2018a. "Environmental friendly hard machining performance of uncoated and MoS₂ coated mechanical micro-textured tungsten carbide cutting tools". Tribology International 125, 141–155. doi:10.1016/j.triboint.2018.04.031.

Table 3 Temperature of machining region during machining using various cutting tools

S. No.	Feed (mm/rev)	Cutting speed (m/min)	T _{PDT-M} (°C)	T _{PT-M} (°C)	T _{VT-M} (°C)	T _{PDT} (°C)	T _{PT} (°C)	T _{VT} (°C)	T _{UT} (°C)
1	0.24	115	417	441	488	502	555	590	615
2	0.16	90	358	377	412	429	466	498	513
3	0.16	90	357	372	415	424	469	492	509
4	0.16	125	411	454	504	529	578	612	636
5	0.28	90	431	470	528	514	619	655	695
6	0.08	115	199	212	241	260	297	319	342
7	0.24	65	326	357	390	417	461	490	537
8	0.16	90	359	378	415	427	472	535	510
9	0.04	90	133	145	153	149	133	141	159
10	0.16	55	225	247	271	297	332	358	382
11	0.16	90	358	375	411	426	466	496	512
12	0.08	65	144	157	169	184	192	211	232
13	0.16	90	360	375	413	429	469	494	508

Note: Reproduced from Gajrani, K.K., Suresh, S., Sankar, M.R., 2018a. "Environmental friendly hard machining performance of uncoated and MoS₂ coated mechanical micro-textured tungsten carbide cutting tools". Tribology International 125, 141–155. doi:10.1016/j.triboint.2018.04.031.

Table 4 MoS₂ coated perpendicular self-lubricating tool temperature ANOVA

Source	Model	A-Feed	B-Speed	AB	A ²	B ²	Lack of Fit
F-Value	8.75	18.32	29.41	0.09	16.41	34.72	1.05
p-value Prob > F	0.0004	0.0036	0.0048	0.9412	0.0036	0.0007	0.5128
Percentage contribution		18.51	29.72	0.09	16.59	35.09	

Note: Reproduced from Gajrani, K.K., Suresh, S., Sankar, M.R., 2018a. "Environmental friendly hard machining performance of uncoated and MoS₂ coated mechanical micro-textured tungsten carbide cutting tools". Tribology International 125, 141–155. doi:10.1016/j.triboint.2018.04.031.

$$T_{PDT} = -437.045 + 3891.67f + 7.13v + 1.085vf - 7766.81v^2 - 0.026f^2 \quad (1d)$$

$$T_{PT} = -531.119 + 4462.911f + 8.23v - 1.44vf - 7772.55v^2 - 0.0292f^2 \quad (1e)$$

$$T_{VT} = -449.96 + 4658.13f + 6.6831v - 4.06752vf - 7058.24v^2 - 0.018f^2 \quad (1f)$$

$$T_{UT} = -572.39 + 4809.86v + 9.029f - 1.0012vf - 8672.6v^2 - 0.03346f^2 \quad (1g)$$

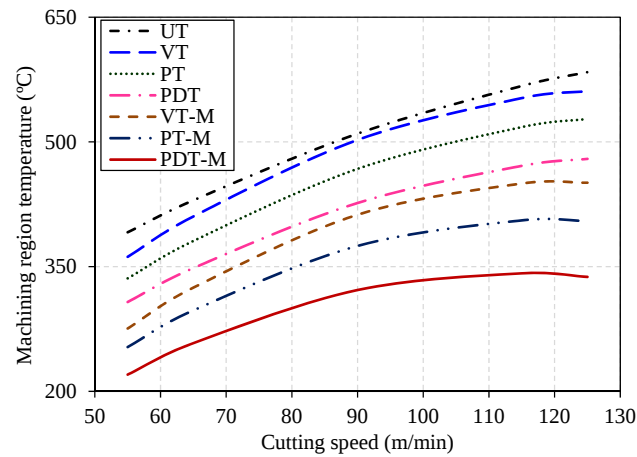


Fig. 7 Influence of cutting speed on machining region temperature. Reproduced from Gajrani, K.K., Suresh, S., Sankar, M.R., 2018a. “Environmental friendly hard machining performance of uncoated and MoS₂ coated mechanical micro-textured tungsten carbide cutting tools”. *Tribology International* 125, 141–155. doi:10.1016/j.triboint.2018.04.031.

where f and v are the feed (mm/rev) and cutting speed (mm/rev), respectively. Machining region temperature (T) subscript represents the cutting tool type.

Analysis of variance (ANOVA) was carried out for the temperature of machining region while PDT-M self-lubricating tool being used (Table 4; Gajrani *et al.*, 2018a). From the table, it was observed that the temperature of machining region was mostly influenced by cutting speed terms (B and B^2), which have around 64.72% contribution. However, feed terms (A and A^2) have around 35.1% influences on it. ANOVA was also carried out with all other cutting tools and coefficient of determination (R^2) was more than 0.92.

Influence of cutting speed on the machining region temperature is illustrated in Fig. 7 (Gajrani *et al.*, 2018a). It is observed that machining region temperature is greatly affected by cutting speed. With the increase in cutting speed increases, the material removal rate (MRR) also increases. Therefore, the per unit interaction time in-between tool-workpiece is less for the same amount of MRR, which results in rising temperature as shown in Fig. 7 (Gajrani *et al.*, 2018a).

Machining region temperature during machining with UT tool is high among all. This is attributed to higher tool-chip contact length on the rake face of the tool. Higher contact length results in the high frictional force that leads to rise in temperature. However, during machining with M μ T tools, because of the presence of an array of micro-textures on the cutting tool rake face, the actual tool-chip contact length reduces. Lesser contact length causes less friction force, which in terms reduces machining region temperature as compared to UT cutting tools. Actual tool-chip contact length is given below:

$$l_f' = l_f - n.d \quad (2)$$

where d denotes the average width of M μ T, n represents the number of M μ T in-between contact length, l_f represents apparent tool-chip contact length and l_f' denotes real tool-chip contact length.

In case of MoS₂ coated M μ T tools, when machined chips travel on the cutting tool rake face, temperature rises, which causes to semi-solidifying solid lubricant. Further, MoS₂ sticks on the back face of machined chips and slides over the tool rake face in chip flow direction. Released MoS₂ from M μ T spread over the tool rake face and create a thin self-lubricating film.

In general, the shear strength of MoS₂ is in the range of 30–35 MPa, whereas tungsten carbide shear strength is about 700–800 MPa. Therefore, due to the presence of MoS₂ solid lubricant layers in-between tool-chip interface, the overall frictional force reduces, which further leads to the reduction in temperature. Therefore, in case of machining with MoS₂ coated M μ T tools, the machining region temperature is less as compared to M μ T and UT tools. Fig. 8 shows schematic representation of the tool-chip interface for UT tool and M μ T tool showing plucked out tungsten grains and iron-molybdenum sulphide-bridge formation, respectively that helps in the formation of MoS₂ self-lubricating film (Gajrani *et al.*, 2018a). Fig. 9 illustrates the thermal micrograph of machining region temperature during machining with UT, PDT and PDT-M tools (Gajrani *et al.*, 2018a).

Machining Forces

As per CCRD, the empirical models of feed force and cutting force for various different cutting tools are as follows:

$$F_{NT} = -10.73 + 663.99f + 1.018v - 0.79vf - 699.61f^2 - 0.006v^2 \quad (3a)$$

$$F_{PT} = 11.01 + 658.89f + 0.62v - 1.08vf - 665.30f^2 - 0.004v^2 \quad (3b)$$

$$F_{PDT} = 35.74 + 649.27f - 0.25v - 1.58vf - 415.84f^2 + 0.0016v^2 \quad (3c)$$

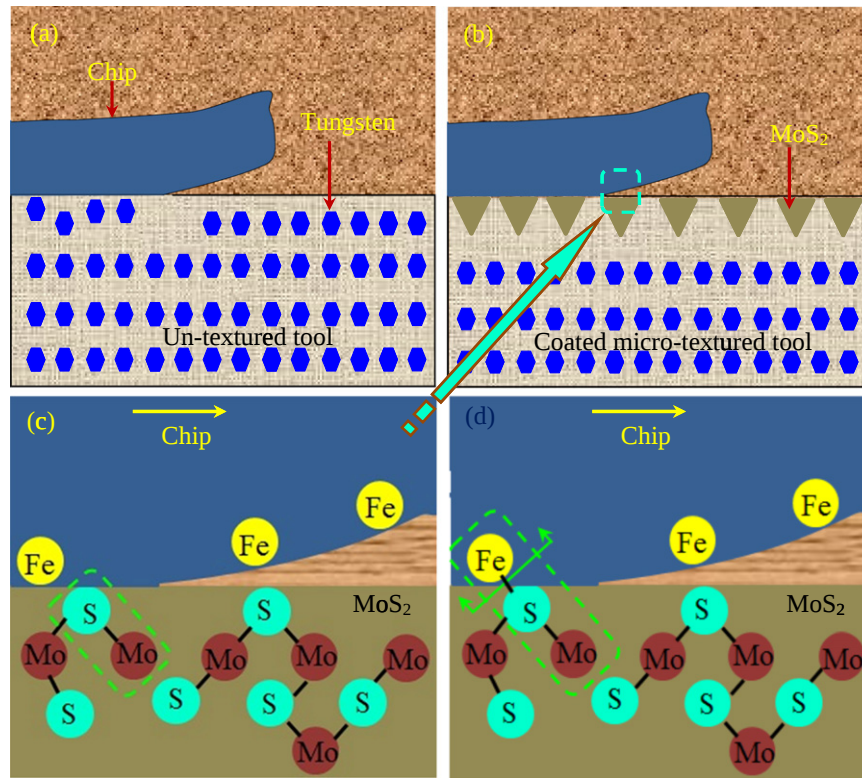


Fig. 8 Tool-chip interface schematic representation: (a) Un-textured tool showing plucked out tungsten grains, (b) MoS₂ coated self-lubricating textured tool, (c) MoS₂ formation and (d) iron-molybdenum sulphide-bridge formation. Reproduced from Gajrani, K.K., Suresh, S., Sankar, M.R., 2018a. "Environmental friendly hard machining performance of uncoated and MoS₂ coated mechanical micro-textured tungsten carbide cutting tools". Tribology International 125, 141–155. doi:10.1016/j.triboint.2018.04.031.

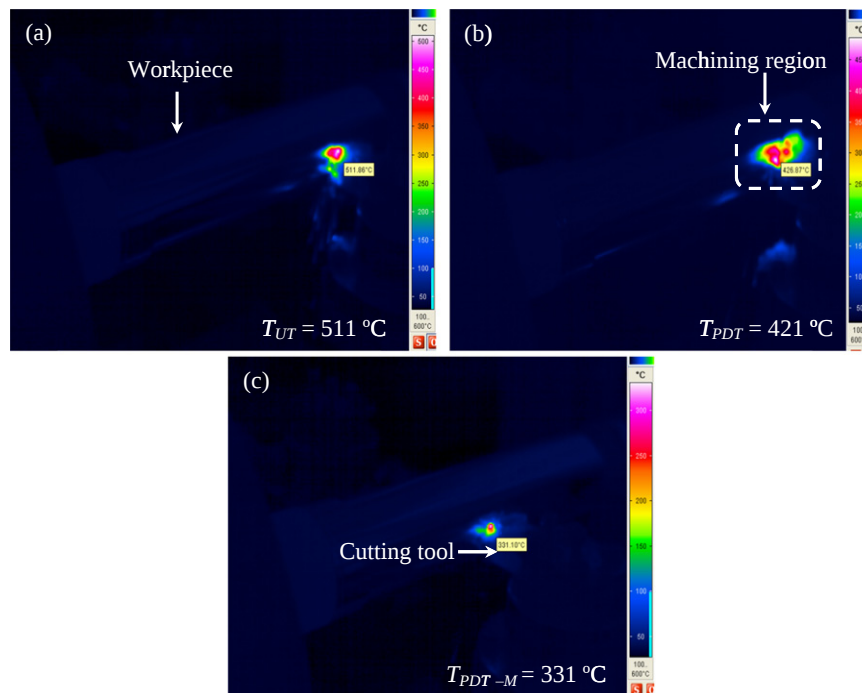


Fig. 9 Thermal images showing temperature while machining using: (a) Un-textured tool, (b) uncoated perpendicular textured tool and (c) MoS₂ coated perpendicular self-lubricating tool. Reproduced from Gajrani, K.K., Suresh, S., Sankar, M.R., 2018a. "Environmental friendly hard machining performance of uncoated and MoS₂ coated mechanical micro-textured tungsten carbide cutting tools". Tribology International 125, 141–155. doi:10.1016/j.triboint.2018.04.031.

$$F_{fVT-M} = -4.19 + 608.64f + 0.759v - 1.75vf - 439.64f^2 - 0.003v^2 \quad (3d)$$

$$F_{fPT-M} = 13.78 + 556.17f + 0.41v - 1.51vf - 406.09f^2 - 0.00226v^2 \quad (3e)$$

$$F_{fPDT-M} = -9.79 + 471.38f + 0.79v - 1.50vf - 296.95f^2 - 0.0035v^2 \quad (3f)$$

$$F_{fCT} = 18.61 + 637.72f + 0.55v - 0.695vf - 643.79f^2 - 0.004v^2 \quad (3g)$$

$$F_{cVT} = 521.43 + 1436.19f - 7.79v - 1.79vf + 207.5f^2 + 0.05v^2 \quad (4a)$$

$$F_{cPT} = 502.42 + 1556.00f - 7.72v - 2.97vf + 222.97f^2 + 0.03v^2 \quad (4b)$$

$$F_{cPDT} = 323.66 + 2220.36f - 5.85v - 7.67vf - 254.61f^2 + 0.03v^2 \quad (4c)$$

$$F_{cVT-M} = 400.29 + 1918.84f - 6.35v - 3.62vf - 602.4f^2 + 0.03v^2 \quad (4d)$$

$$F_{cPT-M} = 308.17 + 2284.53f - 6.17v - 9.96vf + 325.61f^2 + 0.03v^2 \quad (4e)$$

$$F_{cPDT-M} = 264.46 + 2301.38f - 5.65v - 10.295vf + 484.361f^2 + 0.03v^2 \quad (4f)$$

$$F_{cCT} = 529.18 + 1302.57f - 7.45v - 2.48vf + 644.81f^2 + 0.03v^2 \quad (4g)$$

where the F_f and F_c represent feed force and cutting force and the subscripts show the tool type.

The influence of cutting speed on the feed force and cutting force with different types of tools is illustrated in Figs. 10 and 11, respectively (Gajrani *et al.*, 2018a). With the increase in cutting speed, keeping the constant interaction time between workpiece and tool, the MRR increases. Increase in MRR causes rise in primary and secondary shear zone temperatures. As the workpiece

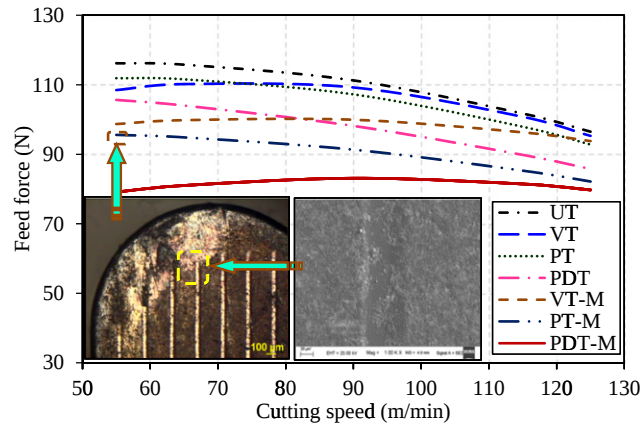


Fig. 10 Influence of cutting speed on feed force. Reproduced from Gajrani, K.K., Suresh, S., Sankar, M.R., 2018a. "Environmental friendly hard machining performance of uncoated and MoS₂ coated mechanical micro-textured tungsten carbide cutting tools". Tribology International 125, 141–155. doi:10.1016/j.triboint.2018.04.031.

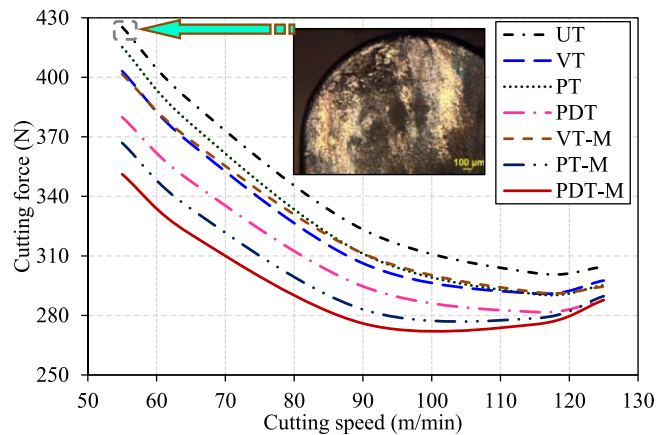


Fig. 11 Influence of cutting speed on cutting force. Reproduced from Gajrani, K.K., Suresh, S., Sankar, M.R., 2018a. "Environmental friendly hard machining performance of uncoated and MoS₂ coated mechanical micro-textured tungsten carbide cutting tools". Tribology International 125, 141–155. doi:10.1016/j.triboint.2018.04.031.

thermal conductivity is high, the temperature ahead of tool-workpiece interaction region also increases. This, preheating of the machined zone is known as thermal softening of the workpiece, which helps to decrease workpiece flow stress leading towards the reduction of feed force and cutting forces with increase in cutting speed. Results show that the feed force and cutting force while machining with uncoated and MoS₂ coated M μ T tools is lower as compared to UT tool. Two main reasons explain this behaviour. First, while machining with M μ T tools, the actual contact length reduces leading towards the lesser frictional force. Thus, machining force reduces. In case of MoS₂ coated M μ T tools, the formation of self-lubricating film in-between sliding interfaces is another reason (Gajrani *et al.*, 2018c).

Tool-Chip Interface Coefficient of Friction

COF was calculated using the concept of Merchant circle with experimental feed force and cutting force data. As per Ernst and Merchant (1941), tool-chip interface COF is as follows:

$$\mu = \frac{F_c \sin \alpha + F_f \cos \alpha}{F_c \cos \alpha - F_f \sin \alpha} \quad (5)$$

where μ represents the COF and α denotes the cutting tool rake angle.

The influence of cutting speed on the tool-chip interface COF for various tools is illustrated in Fig. 12 Gajrani *et al.* (2018a). As discussed above in the previous section, due to the presence of M μ T on the tool rake face, the contact length reduces. Thus, frictional force reduces, which leads to reduction in coefficient of friction. Moreover, in case of MoS₂ coated M μ T tools, the presence of MoS₂ in-between tool-chip interfaces further reduces the coefficient of friction.

MoS₂ coated PDT cutting tool perform best among all uncoated M μ T and UT tools concerning machining region temperature, cutting force, feed force and tool-chip interface COF. This is attributed to the lowest tool-chip contact length with PDT tool. Fig. 13 illustrates the typical representation of chip flow direction over various uncoated M μ T tools (Gajrani *et al.*, 2018a). For constant feed (0.16 mm/rev), cutting speed (90 m/min) and depth of cut (0.5 mm), the experimentally measured chip flow direction from tool principal cutting edge is at 18°. From Eq. 2, actual contact length depends on n and chip flow direction. For this particular case, keeping chip-flow direction constant as shown in Fig. 13, n will be maximum for PDT cutting tool ($n_{VT} < n_{PT} < n_{PDT}$). Therefore,

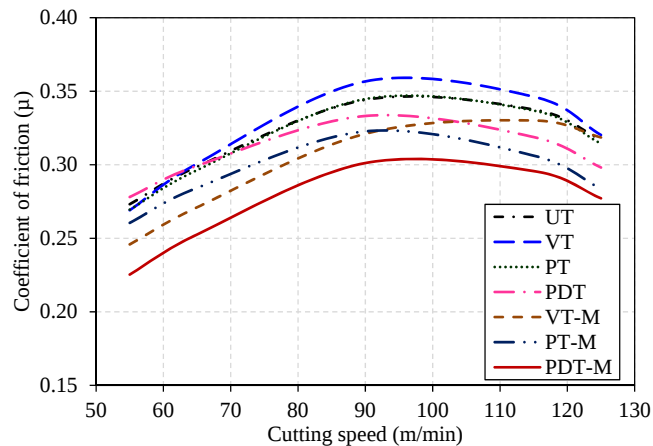


Fig. 12 Influence of cutting speed on the tool-chip interface coefficient of friction. Reproduced from Gajrani, K.K., Suresh, S., Sankar, M.R., 2018a. "Environmental friendly hard machining performance of uncoated and MoS₂ coated mechanical micro-textured tungsten carbide cutting tools". Tribology International 125, 141–155. doi:10.1016/j.triboint.2018.04.031.

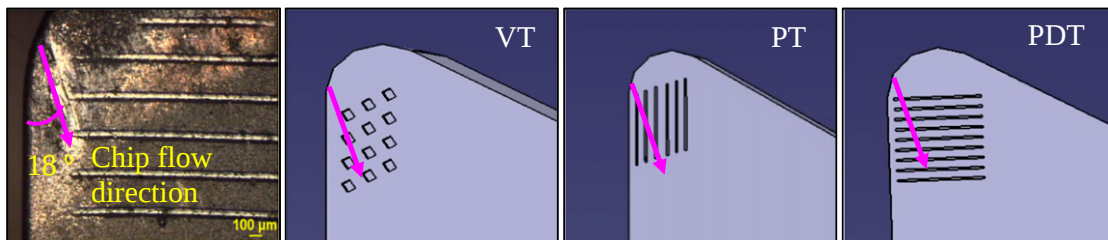


Fig. 13 Representation of chip flow direction over various mechanical micro-textured cutting tools. Reproduced from Gajrani, K.K., Suresh, S., Sankar, M.R., 2018a. "Environmental friendly hard machining performance of uncoated and MoS₂ coated mechanical micro-textured tungsten carbide cutting tools". Tribology International 125, 141–155. doi:10.1016/j.triboint.2018.04.031.

contact length is least for PDT tools. Thus, PDT performs better among all uncoated M μ T and UT tools. Further, PDT-M tool performs best among all tools due to least contact length as well as the formation of MoS₂ self-lubricating film on the tool rake face.

Tool Rake Face Morphology

Tool rake face morphology after machining is an important parameter to understand the performance of cutting tool at the particular condition. After 15 min of machining ($f=0.16$ mm/rev, $v=90$ m/min, $a_w=0.5$ mm), cutting tool rake face surface morphology was characterized using FESEM. Corresponding elemental maps and elemental composition micrographs were also characterized using elemental dispersive spectroscopy (EDS). UT tool rake face surface morphology is illustrated in Fig. 14 (Gajrani *et al.*, 2018a).

As discussed in previous sections, machining region temperature is high while machining with UT cutting tool, which also causes rise in workpiece temperature. Thus, due to preheating of workpiece material and continuous chip flow over the cutting tool rake face, adhesion wear is predominant. Due to repetitive tool adhesion on the back side of the machined chips, tungsten carbide material plucks out from the UT cutting tool that leads to its catastrophic failure (Fig. 14(a-b); Gajrani *et al.*, 2018a). Fig. 14(c) illustrates the UT rake face fractured surface and its interface with parent tool (Gajrani *et al.*, 2018a). Fig. 14(d) shows the tungsten carbide tool material shredding from the UT tool rake face due to tool adhesion on the back side of the machined chips (Gajrani *et al.*, 2018a).

After 15 minutes of machining ($f=0.16$ mm/rev, $v=90$ m/min, $a_w=0.5$ mm), VT-M, PT-M and PDT-M M μ T tool rake face surface morphology, corresponding iron (Fe), molybdenum (Mo) as well as sulphur (S) elemental maps and elemental composition is shown in Figs. 15–17, respectively (Gajrani *et al.*, 2018a). Worn out VT-M tool rake face morphology is illustrated in Fig. 15(a) (Gajrani *et al.*, 2018a). Corresponding to VT-M tool rake face, Fe, Mo and S elemental maps are shown in Fig. 15(b–d) (Gajrani *et al.*, 2018a). Elemental map of Fe confirms the workpiece material adhesion on the VT-M tool rake face. Further, elemental maps of Mo and S shows that MoS₂ solid lubricant was able to spread out over the cutting tool rake face and has created a thin self-lubricating film. Further, elemental composition analysis of point U and V (points in Fig. 15(a)) is shown in Fig. 15(e–f) (Gajrani *et al.*, 2018a). Point U is chosen near the vicinity of VT-M tool cutting edge while point V is chosen on the M μ T. From the elemental analysis, it is confirmed that Fe weight percentage is high near the cutting edge. This is attributed to predominant adhesive wear near tool cutting edge.

Similar to VT-M tool, surface morphology, elemental maps and elemental composition analysis of PT-M tool as well as PDT-M tool rake face confirms the formation of the thin self-lubricating film as shown in Figs. 16 and 17, respectively (Gajrani *et al.*, 2018a).

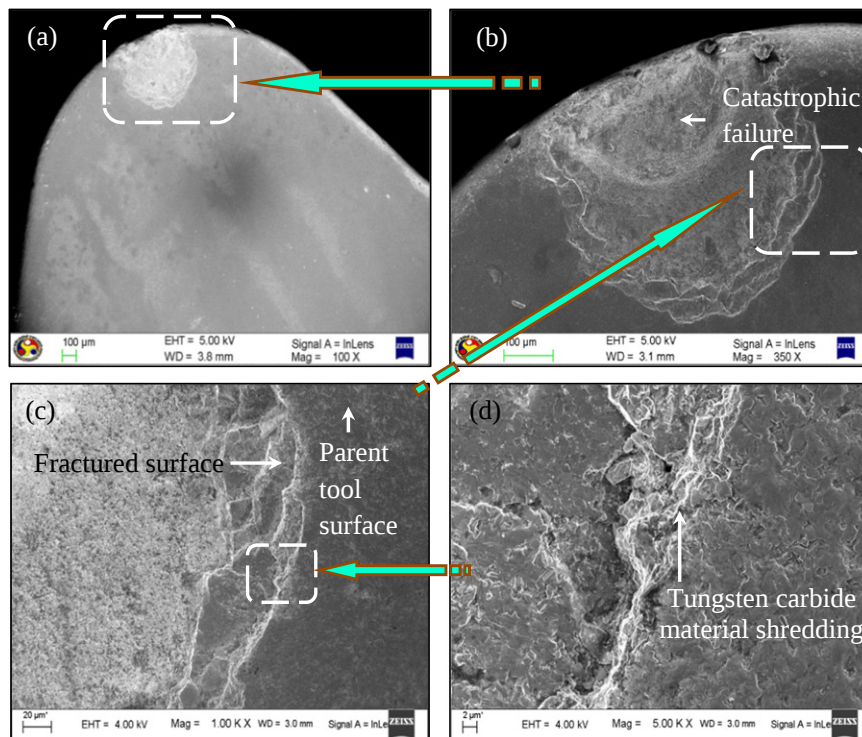


Fig. 14 After 15 minutes of machining: (a) Rake face micrograph of untextured tool, (b) tool catastrophic failure, (c) tool fractured surface and (d) tungsten carbide material shredding from parent tool. Reproduced from Gajrani, K.K., Suresh, S., Sankar, M.R., 2018a. "Environmental friendly hard machining performance of uncoated and MoS₂ coated mechanical micro-textured tungsten carbide cutting tools". *Tribology International* 125, 141–155. doi:10.1016/j.triboint.2018.04.031.

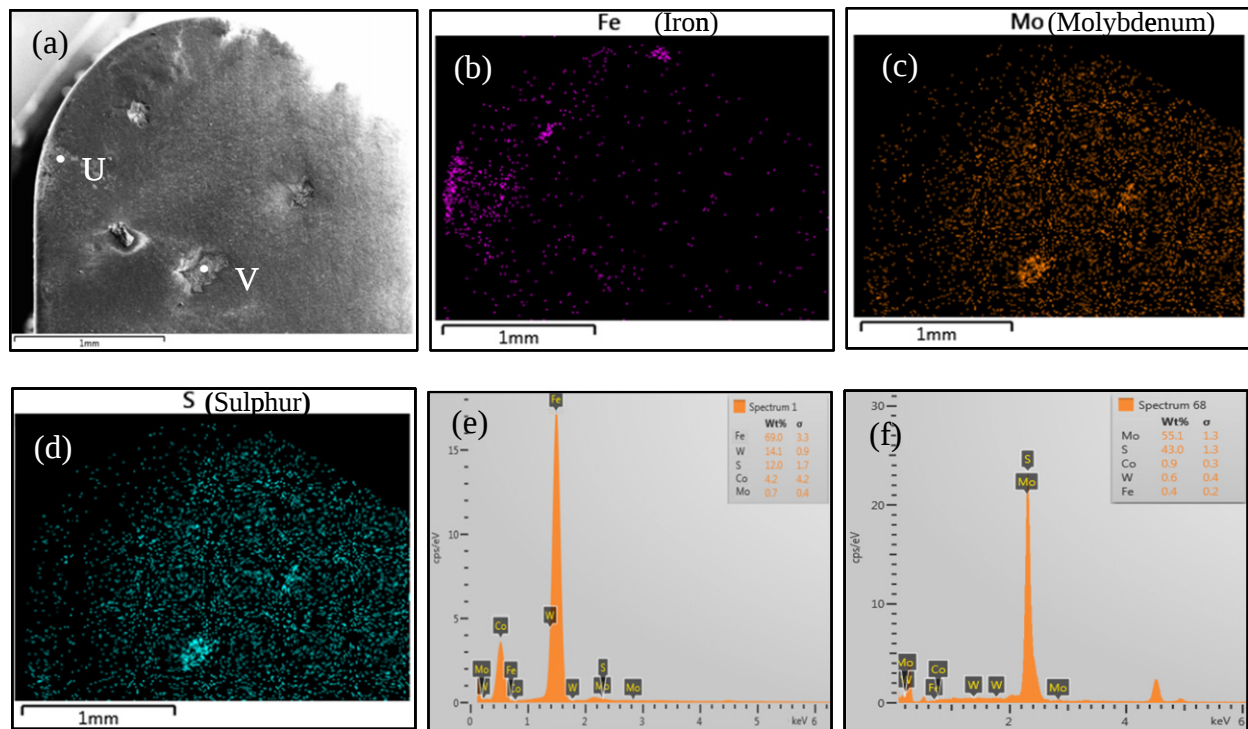


Fig. 15 After 15 minutes of machining: (a) Rake face micrograph of Vickers textured self-lubricating tool, (b) corresponding elemental map showing iron distribution, (c) corresponding elemental map showing molybdenum distribution, (b) corresponding elemental map showing sulphur distribution, (e) elemental composition corresponding to point U and (f) elemental composition corresponding to point V. ; Reproduced from Gajrani, K.K., Suresh, S., Sankar, M.R., 2018a. "Environmental friendly hard machining performance of uncoated and MoS₂ coated mechanical micro-textured tungsten carbide cutting tools". Tribology International 125, 141–155. doi:10.1016/j.triboint.2018.04.031.

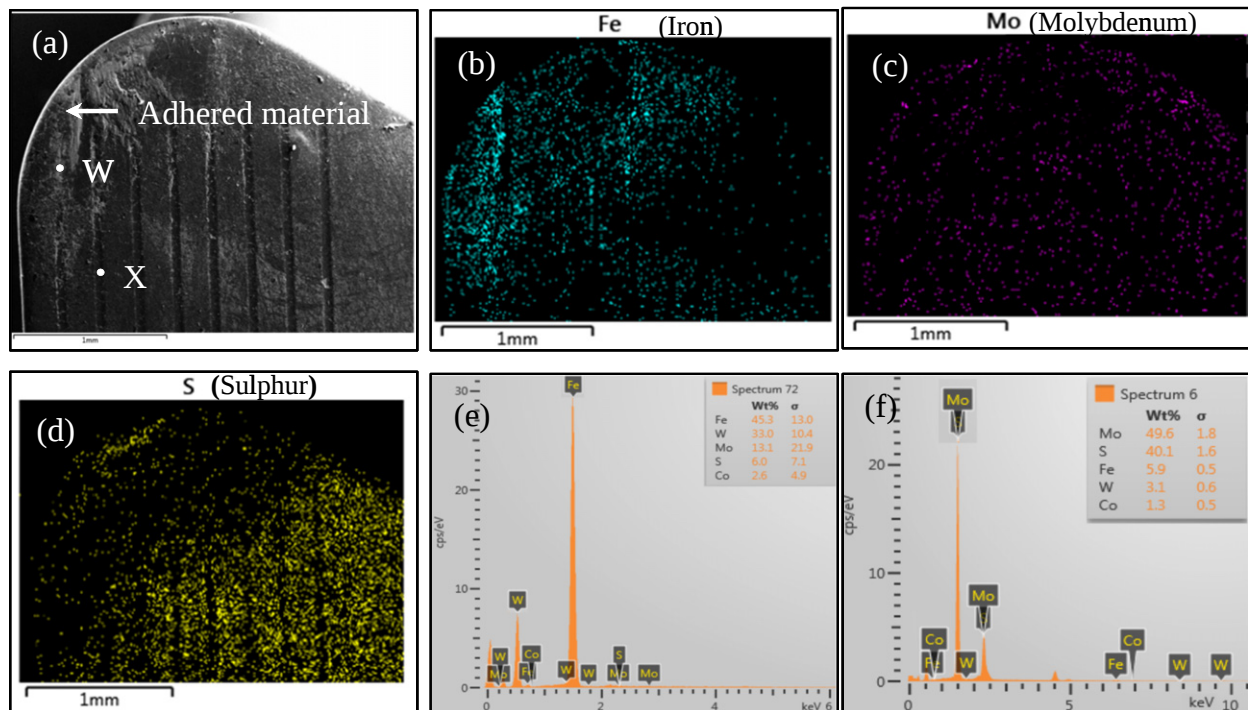


Fig. 16 After 15 minutes of machining: (a) Rake face micrograph of parallel textured self-lubricating tool, (b) corresponding elemental map showing iron distribution, (c) corresponding elemental map showing molybdenum distribution, (b) corresponding elemental map showing sulphur distribution, (e) elemental composition corresponding to point W and (f) elemental composition corresponding to point X. ; Reproduced from Gajrani, K.K., Suresh, S., Sankar, M.R., 2018a. "Environmental friendly hard machining performance of uncoated and MoS₂ coated mechanical micro-textured tungsten carbide cutting tools". Tribology International 125, 141–155. doi:10.1016/j.triboint.2018.04.031.

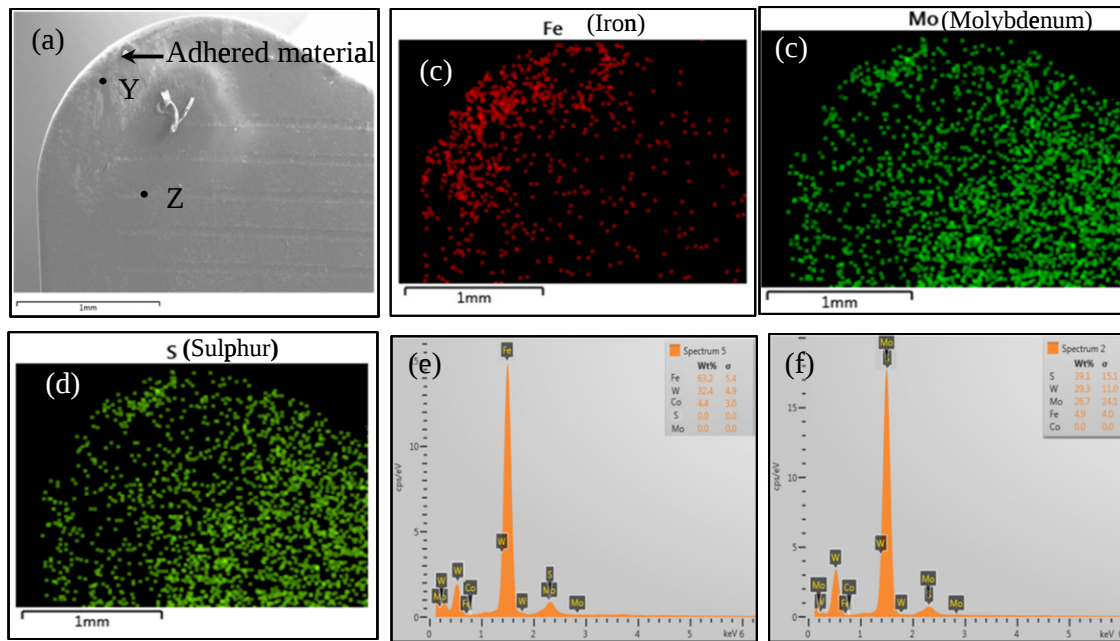


Fig. 17 After 15 minutes of machining: (a) Rake face micrograph of perpendicular textured self-lubricating tool, (b) corresponding elemental map showing iron distribution, (c) corresponding elemental map showing molybdenum distribution, (b) corresponding elemental map showing sulphur distribution, (e) elemental composition corresponding to point Y and (f) elemental composition corresponding to point Z ; Reproduced from Gajrani, K.K., Suresh, S., Sankar, M.R., 2018a. "Environmental friendly hard machining performance of uncoated and MoS₂ coated mechanical micro-textured tungsten carbide cutting tools". Tribology International 125, 141–155. doi:10.1016/j.triboint.2018.04.031.

However, regarding PDT-M tool, the tool-chip contact area is smaller as compared to PT-M tool. Further, workpiece material adhesion is lesser as compared to other cutting self-lubricating tools. Elemental maps of Mo and S illustrates uniform lubricating film formation. Therefore, it can be confirmed that PDT-M M μ T cutting tool performs best among all other cutting tools in terms of machining region temperature, cutting force, feed force, tool-chip interface COF and tool rake face morphology.

Concluding Remarks

M μ T cutting tools having three different geometries were fabricated for machining. Another set of M μ T cutting tools were coated using MoS₂ solid lubricants. Hard machining experiments were conducted using uncoated, coated M μ T and UT cutting tools. Machining performance was compared and their salient findings are as follows:

- (1) Uncoated and MoS₂ coated self-lubricating tools reduce machining region temperature, cutting force, feed force and tool-chip interface COF as compared to UT tools.
- (2) MoS₂ coated PDT-M tool performs best among all. It is due to the least tool-chip contact length and formation of MoS₂ self-lubricating film over the cutting tool rake face.
- (3) As compared to UT tools, PDT-M tool reduces tool-chip interface COF in the range of 11.73%–17.42%.

Acknowledgement

The authors are also thankful for the financial support provided by the Board of Research in Nuclear Sciences (Project Number: ME/P/MRS/02), Department of Science and Technology for their TSDP (DST/TSG/AMT/2015/619), Defence Research Development & Development Laboratory (CARS Project). Authors also acknowledge Central Instrumentation Facility, IIT Guwahati for providing FESEM, EDS and TEM facility for this work.

See also: Experimental Investigations for Development of Aluminum MMC With Hybrid Reinforcement and Vacuum Molding. Experimental Investigations for Development of Conductive Ceramic Composites with Microwave Sintering and Their Electric Discharge Machining. Investigations for Barium Titanate and Graphene Reinforced PVDF Matrix for 4D Applications

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Sustainable Materials for Energy Conversion

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Introduction

Sustainability issues are a major concern in our modern life. Energy and materials are important aspects to be considered. The current need for enhancement in energy efficiency technologies is driven by an urgency of maximizing the moderate global energy efficiency to match the increasing demand. It has been shown ([Exxonmobil's, 2017](#); [International Energy Agency, World Energy Outlook, 2016](#)) that improvements of energy efficiencies resulted in a significant cut to the global energy demand by two-thirds over the past decades, as shown in [Fig. 1](#). Many approaches could be adopted for energy efficiency enhancement, amongst which energy conversion and storage are the least developed. The main reasons for this may be due to lack of appropriate economic, sustainable and eco-friendly materials.

Sustainable materials for waste energy recovery and conversion are currently exploited for new trending applications. Fields of solar energy conversion into thermal energy and waste heat recovery/electrical energy generation are amongst the hot topics for new environmentally friendly and sustainable sources of green energy. Most of the research efforts are conducted towards developing new sustainable materials for energy conversion applications. Polymer base materials have recently proven to be excellent candidates and good alternatives for other metallic and ceramic-based energy conversion materials.

Energy Conversion Applications

Energy conversion from one form to another has been known through all human ages. This work focuses on conversion of solar energy and waste heat to useful energy forms for modern applications. Solar energy is harvested by photovoltaic materials (for electric energy generation) and selective absorber materials (for thermal energy generation). The idea of converting waste energy to useful heat or energy fits well within sustainability requirements. Waste heat is defined as the generated heat as a by-product of daily and industrial process ([Viklund and Johansson, 2014](#)). Different technologies and materials have been developed over the past decades to harvest as much as possible of the waste heat considering it as a primary source of energy. Thermoelectric generation, solar thermal collectors, phase change materials, thermoacoustic materials, organic rankine cycles are the most trending technologies for waste heat recovery ([Anon, 2015](#)). The sources of waste heat have extended to include any activity, which results a temperature 10 k higher than the room temperature, such as human activities, vehicles exhausting systems, electrical utilities, etc. However, this small temperature difference is only compatible with the low temperature energy conversion/storage polymeric based materials. Though metal based and ceramic based materials have reached a mature stage of development relative to energy conversion and storage applications, polymeric based materials have great options for expanding the range of applications due to their large sensitivity over a narrow range of temperature difference.

Materials Requirements for Energy Conversion

The choice of a material for energy conversion applications is governed by a set of its physical properties; mainly electrical, thermal and optical properties. The basics and fundamentals of these properties for different types of engineering material is discussed in this section.

Electrical Properties of Materials

The electrical or electronic properties of materials describe the response of the material in the presence of an applied electric field. Although electricity concepts can seem complicated, an electric current is just the flow of electrons from one atom to the other and this flow is dependent on the type and the structure of the material. Solid metals are characterized by their metallic bonds, where the atoms form a tightly packed structure with a positive cationic core soaked in a negative loose electron cloud characterized by the delocalized nature of the valence electrons, which makes metals excellent conductors of electricity. Ceramics are characterized by ionic bonding, which usually forms between metals and nonmetals. The ionic bond is characterized by electrical neutrality and the electrons are firmly kept inside the bond, which makes ceramics excellent insulators. Generally, in polymers and nonmetals, which are considered to be insulators too, the electrons are held tightly to the nucleus preventing their free movement as they are usually shared in the covalent bond ([Smith and Hashemi, 2011a](#)).

The transistors were invented in 1947–1948 at Bell Telephone laboratories; which opened a new field of technology that led to advancement in electronic devices and machines. All the computers, mobiles and other electronic devices contain thousands but millions of different types of transistors. This invention was possible because of the semiconducting behaviour of certain metals

and alloys. What makes semiconductors so special is the ability of altering their conductivity through adding impurities in a process called doping. Semiconductors with excess electrons are called n-type semiconductors and the ones with shortage in electrons or more specifically the ones with excess holes are called p-type semiconductors. Different combinations and configurations of n-type and p-type semiconductors result in numerous electronic devices starting from diodes and transistors (Hu, 2009). Another important aspect of semiconductors that distinguishes them is that they have an almost empty conduction band and an almost filled valence band, which are separated by a specific band gap. When an electron from the valence band receives in any way an amount of energy bigger than the energy of the band gap it will be excited to the conduction band which will in return increase the conductivity. In fact, this special characteristic is utilized in lots of interesting technologies such as solar cells and photoconductors. Examples of semiconducting metals are the group-4 elements with silicon and germanium being the most famous. Group3-Group5 compounds, such as GaAs, are also famous for their semiconducting properties. Actually, there are also a number of famous ceramics that are considered semiconductors such as SiO_2 , TiO_2 and ZnO_2 (Hu, 2009; Ross, 2006). Indeed, each semiconductor is characterized by its own band gap energy, carriers' distributions and the electrons and holes mobilities; which set the basis for the comparison between them in a theoretical level for any application. However, when it comes to real world devices and applications, availability, costs and environmental effects are also considered.

Despite the fundamental fact that metals are good conductors and far better than polymers, this idea changed when Hideki Shirakawa pioneered the field of conductive polymers. In 1977, Shirakawa, MacDiarmid and Heeger, who shared the noble prize in chemistry in 2000, discovered that oxidation with chlorine or bromine vapor raised the conductivity of polyacetylene films by a factor of 10^9 to reach 10^5 Siemens per meter, which means that the conductivity of polyacetylene increased to a level that approached that of copper (Shirakawa *et al.*, 1977). Although, metals are the best conductors known, they are associated with many problems such as the costs and environmental impacts of both mining and preparation stages. Therefore, conductive polymers has introduced a functionally available alternative and consequently the research on them has increased exponentially in a pursuit to understand their full potentials and to implement them in the development of technology.

In general, the electrons in polymers are not delocalized like in metals. However, the conducting organics are distinguished by their alternating single and double bonds that forms a conjugated structure as shown in Fig. 2. These molecules can be either polymers or smaller molecules that conduct electricity through delocalized pi-electrons, which can move easily within a molecule and can tunnel between molecules. This kind of conduction is called hopping and relies on the match between the highest occupied molecular orbitals HOMO and the lowest unoccupied molecular orbitals LUMO in the adjacent molecules. In fact, HOMO and LUMO are the analogies to the valence band and the conduction band respectively and they are also separated by a band gap (Solymar *et al.*, 2014).

The conjugated structure is not enough to guarantee a conductive polymer, as it also depends on the doping level. Dopants act as donors or acceptors to provide electrons or holes, respectively. An undoped conjugated polymer is considered to be an insulator. With more doping, the conjugated polymer becomes an organic semiconductor and finally with a large extent of doping it can reach remarkably high values of conductivity. In fact, organic semiconductors are progressively utilized in a wide range of technologies. What makes them attractive is that their band gaps can be tuned by adjusting the structure of the molecules and then they can be engineered to meet specific demands (Ross, 2006; Saleh and Teich, 2007).

In conducting polymers, the carriers move via hopping as they are localized to some extent. In fact, the carriers are present in the form of excitons, where an exciton is the bound state of an electron and a hole attached to each other by electrostatic force (Solymar *et al.*, 2014). Excitons diffuse in the material but they do not drift and they won't convey current till they split to separate

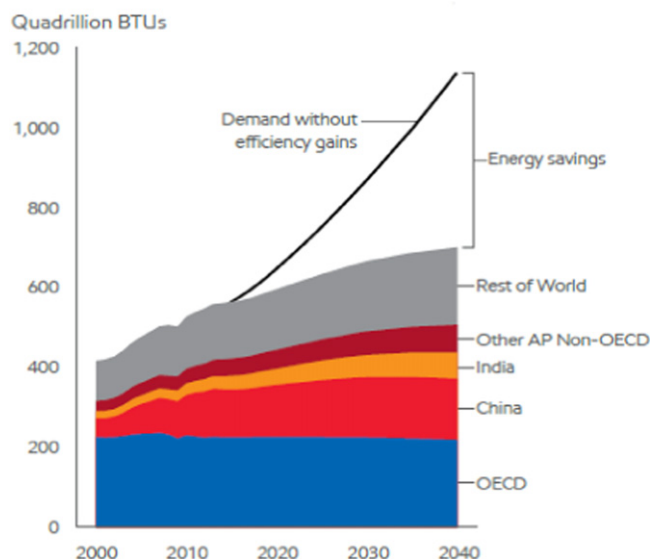


Fig. 1 Energy consumption with/without efficiency enhancement. Reproduced from Exxonmobil's, 2017. Outlook for energy: A view to 2040.

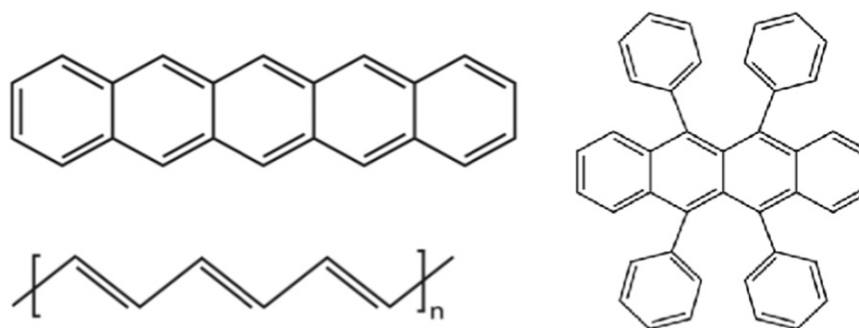


Fig. 2 Conjugated structure of conducting polymers. Reproduced from Ross, C., 2006. 3.15 electrical, optical & magnetic materials and devices. Fall 2006. Massachusetts Institute of Technology: MIT OpenCourseWare, License: Creative Commons BY-NC-SA. Available at: <https://ocw.mit.edu>.

electrons and holes by strong electric fields. Therefore, the carrier mobilities in most organic materials are typically low which results in apparent slow responses in the devices they are used in. For instance, the crystalline organic semiconductors with the highest mobilities can reach the 0.1–20 cm²/V·s range (Coropceanu *et al.*, 2007), which is very small compared to semiconductors such as silicon with an electron mobility of about 1500 cm²/V·s and a hole mobility of around 450 cm²/V·s (Ross, 2006).

In contrast, there are certain organic materials, graphene and carbon nanotubes being the most well-known, where carriers reach very high mobilities and thus are characterized by very high electrical conductivity. Graphene is an extended sheet of carbon that forms a 2D crystal, which is the first of its kind to be observed in science. Through this 2D crystal, electrons and holes can move freely as the delocalized π -orbital extends over the whole sheet. Carbon nanotubes are just rolled graphene sheets, which have very interesting technological applications. One interesting prospective application of graphene is to use a few nanometres graphene strip to replace the 50 nm electrical channels of silicon in transistors (Ross, 2006; Fuchs and Goerbig, 2008).

Optical Properties of Materials

Photovoltaics, LEDs and transmitting signals through optical fibres are all high technologies that depend on the optical properties of materials. The optical properties of materials are the set of characteristics that define the material's response to electromagnetic radiation including: colour, absorbance, transmission reflection and luminosity. Electromagnetic radiation, along with its wave like characteristics, consists of photons, which are packets of energy that can behave like particles. Optical properties are concerned in particular with the visible light, which extends from about 0.4–0.75 μ m in the electromagnetic spectrum (Smith and Hashemi, 2011b).

Metals are opaque to the radiation from the middle of ultraviolet radiation to the low energy radiation. Therefore, they are opaque to visible light, which indicates that all the visible light photons are absorbed by metals. Absorption happens when a photon excites an electron from the conduction band to the valence band and this happens when the incident photon has equal or higher energy than the band gap. However, this doesn't apply on high frequency photons. Naturally, this gives the impression that metals are dark black. However, energized electron falls back to their equilibrium original state by emitting a photon with the same wavelength it absorbed making it reflective and the distribution of these wavelengths gives the metal its colour. On the other hand, nonmetallic materials can be transparent, where the characteristic colour of a transparent surface is determined by the distribution of wavelengths of the non-absorbed light radiation that is transmitted through the material (Callister and Rethwisch, 2015a).

Photoconductivity is the electrical conductivity that rises from the increased number of electrons that are induced and excited by photons absorption in semiconducting materials. Electroluminescence is the emission of light due to the recombination between electrons and holes, which occur in light-emitting diodes (LEDs). In fact, the reverse of LEDs are solar cells where sunlight is converted to electrical current (Callister and Rethwisch, 2015a). The elemental semiconductors, semiconductor compounds and semiconductor ceramics show significant electrical and optical properties, however, they are difficult to handle and many of them show considerable environmental issues and undeniable toxicity. For example, according to CES EduPack 2018, 2018 Gallium requires appreciable care in handling, Indium compounds are highly toxic and Tin is carcinogenic (CES EduPack 2018, 2018).

Organic photovoltaics and LEDs have gained wide attention lately. When an organic semiconductor absorbs a photon, an exciton is classically formed, which can be split apart by an electric field, causing the electrons and holes to move in different directions away from each other's. A bilayer structure is needed to make an organic photovoltaic where holes are transported in a p-type layer, and electrons are transported in an n-type layer. In the case of an organic LED, electrons and holes are injected from opposing electrodes. Holes are injected by a high work function electrode, while electrons are injected by a low work function electrode. These electrons and holes recombine via excitons by emitting photons. Excitons exist in two forms according to their spin either singlets where the electron and hole have opposite spin or triplets where the electron and hole have the same spin. For every singlet produced, three triplets are formed. Actually, in LED only singlets contribute to photon formation, which means that just quarter of the carriers injected into organic materials can generate photons (Solyman *et al.*, 2014).

Table 1 Thermal properties of materials

Tabulation of the thermal properties for a variety of materials

Material	C_p (J/kg-K) ^a	α_1 [(°C) ⁻¹ × 10 ⁻⁶] ^b	k (W/m-K) ^c	L [Ω-W/(K) ² × 10 ⁻⁸]
<i>Metals</i>				
Aluminum	900	23.6	247	2.20
Copper	386	17.0	398	2.25
Gold	128	14.2	315	2.50
Iron	448	11.8	80	2.71
Nickel	443	13.3	90	2.08
Silver	235	19.7	428	2.13
Tungsten	138	4.5	178	3.20
1025 Steel	486	12.0	51.9	—
316 Stainless steel	502	16.0	15.9	—
Brass (70Cu-30Zn)	375	20.0	120	—
Kovar (54Fe 29Ni 17Co)	460	5.1	17	2.80
Invar (64Fe-36Ni)	500	1.6	10	2.75
Super Invar (63Fe 32Ni 5Co)	500	0.72	10	2.68
<i>Ceramics</i>				
Alumina (Al ₂ O ₃)	775	7.6	39	—
Magnesia (MgO)	940	13.5 ^d	37.7	—
Spinel (MgAl ₂ O ₄)	790	7.6 ^d	15.0 ^e	—
Fused silica (SiO ₂)	740	0.4	1.4	—
Soda lime glass	840	9.0	1.7	—
Borosilicate (Pyrex) glass	850	3.3	1.4	—
<i>Polymers</i>				
Polyethylene (high density)	1850	106–198	0.46–0.50	—
Polypropylene	1925	145–180	0.12	—
Polystyrene	1170	90–150	0.13	—
Polytetrafluoroethylene (Teflon)	1050	126–216	0.25	—
Phenol formaldehyde, phenolic (Bakelite)	1590–1760	122	0.15	—
Nylon 6,6	1670	144	0.24	—
Polyisoprene	—	220	0.14	—

^aTo convert to cal/g-K, multiply by 2.39 × 10⁻⁴; to convert to Btu/lb_m-°F, multiply by 2.39 × 10⁻⁴.

^bTo convert to (°F)⁻¹, multiply by 0.56.

^cTo convert to cal/s-cm-K, multiply by 2.39 × 10⁻³; to convert to Btu/ft-h-°F, multiply by 0.578.

^dValue measured at 100°C.

^eMean value taken over the temperature range 0–1000°C.

Note: Callister, W., Rethwisch, D., 2015b. Thermal properties. In: Materials Science and Engineering, ninth ed. New York: John Wiley & Sons.

Thermal Properties of Materials

Thermal properties refer to the response of a material to the application of heat represented mainly by heat capacity, thermal expansion and thermal conductivity. **Table 1** presents typical thermal properties for some well-known engineering materials where the great differences between the thermal properties according to material type is evident (Callister and Rethwisch, 2015b).

Heat capacity is one of the important properties that qualify the material for energy conversion or storage applications. When a solid material is heated, it experiences a rise in temperature indicating absorption of energy. Heat capacity is a property that represents the material's ability to store thermal energy by the absorption of heat from the surroundings. Therefore, it represents the amount of energy needed to cause a unit temperature rise.

The Specific heat expresses the heat capacity per unit mass. Heat capacity is expressed in two ways based on maintaining either the specimen volume or the pressure constant but the difference is very insignificant for most solid materials at and below room temperature. Indeed, the energy is mainly absorbed by the increase of the vibrational energy of atoms along with the increase of the kinetic energy and the randomization of the electron spin in some special cases. Exchange of electrons is very limited in covalent bonds compared to metallic bonds. Consequently, polymers show the highest heat capacity as they are covalently bonded, followed by ceramics then metals (Callister and Rethwisch, 2015b).

Transport of thermal energy may be caused by the migration of free electrons and lattice vibrational waves. Phonons are considered to be the lattice vibration quanta. The electrons role to conduction heat transfer dominates in pure metals, while the contribution of phonons dominates in semiconductors and non-conductors (Incropera et al., 2017). The transport of heat energy by phonons is not as effective as free electrons due to the very efficient scattering of phonons by lattice imperfections

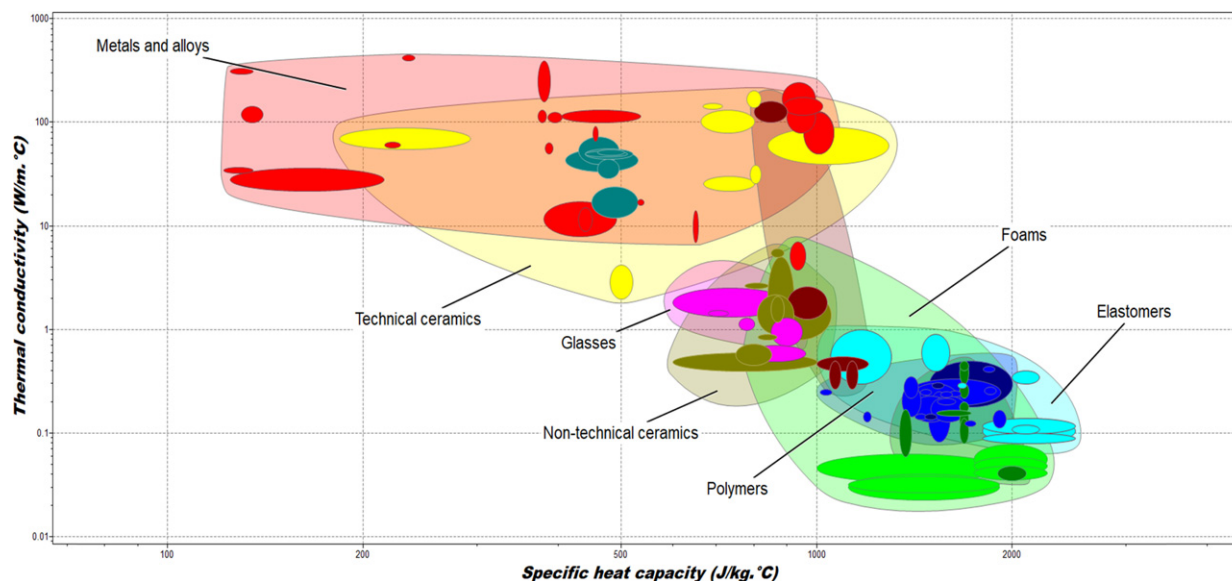


Fig. 3 Thermal conductivity vs specific heat capacity. Produced using CES EduPack 2018, 2018. Cambridge: Granta.

(Callister and Rethwisch, 2015b). The thermal conductivity is a property that represents the ability to conduct heat. In fact, the thermal conductivity is the proportionality constant between the heat flux and the temperature gradient along the direction of flow in steady-state heat transfer. The large numbers of free electrons and their efficiency to transport thermal energy in pure metals make them efficient thermal conductors. However, ceramics and polymers have low thermal conductivity due to phonon conduction domination and the low concentration of free electrons (Callister and Rethwisch, 2015b; Cengel, 2002). Crystalline solids and semi-conductors show high heat conductivity but poor electrical conductivity (Cengel, 2002). For thin films, the thermal conductivity is the lowest in the thin direction due to the effect of the physical boundaries (Incropera *et al.*, 2017).

Although polymers have high specific heat values, they are poor thermal conductors. In contrast, metals are efficient thermal conductors but have poor to modest specific heat values while ceramics shows modesty and moderation in both properties relative to metals and polymers. A graph between thermal conductivity and specific heat values is generated by CES EduPack and is shown in Fig. 3 (CES EduPack 2018, 2018). This raises the need for the thermal diffusivity property, which represents the ratio of thermal conductivity of the material to the heat stored per unit volume and measures the capability of conducting thermal energy relative to storing it. Therefore, materials of large thermal diffusivity such as metals reach equilibrium conditions in shorter period than materials with small thermal diffusivity as they respond quickly to thermal variations (Incropera *et al.*, 2017; Cengel, 2002).

Heating solid materials causes them to expand. Thermal expansion is the constant of proportionality between relative change in length to the temperature change. In fact, the increase in the average interatomic separation causes thermal expansion which is a result of the uneven nature of the potential energy versus the trough of the interatomic spacing curve. Therefore, the low coefficient of thermal expansion indicates a large interatomic bonding energy and vice versa. The values of thermal expansion for polymers are typically higher than metals and metals have higher thermal expansion coefficients than ceramic materials. Therefore, energy absorbance increases the interatomic distance in polymers rather than raising the temperature. Actually, Linear and branched polymers have higher thermal expansion coefficients than polymers with intercrossing (Callister and Rethwisch, 2015b). When the non-crystalline solids reach the glass temperature, it undergoes a transition to very viscous liquid (Ashby *et al.*, 2007). Table 2 shows a summary of the variation among the thermal properties of metals, polymers and ceramics.

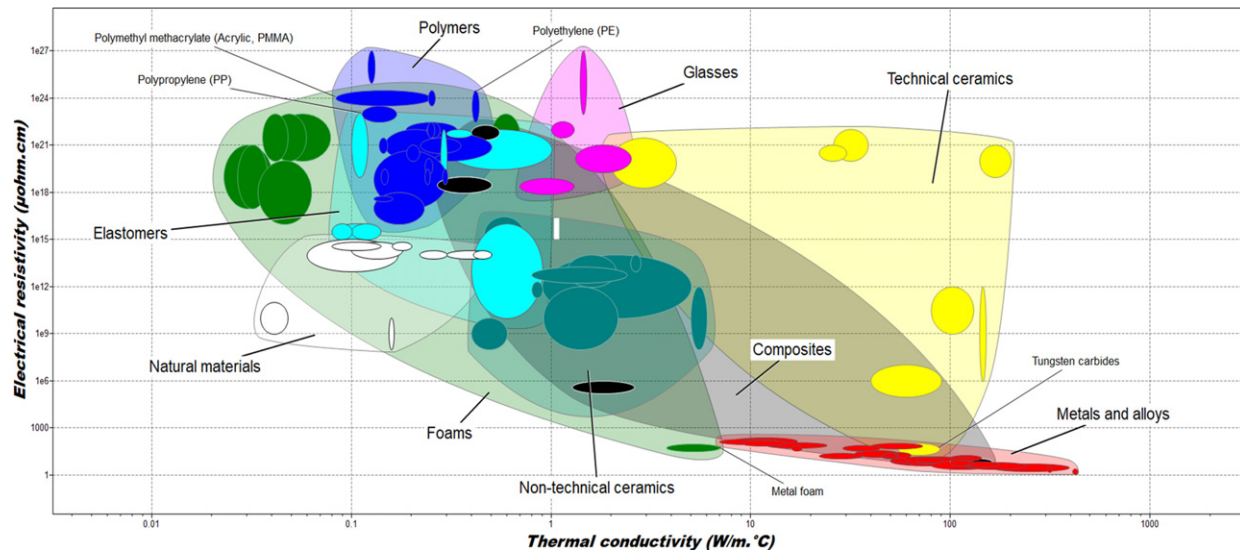
The relation between thermal and electrical conductivity properties is behind the thermoelectric devices whose efficiency is measured by the figure of merit (ZT) which is a ratio between the electric conductivity to the thermal conductivity (Moriarty *et al.*, 2012). A graph between electrical resistivity and thermal conductivity is generated by CES EduPack and is shown in Fig. 4 (CES EduPack 2018, 2018). Therefore, for proper thermoelectric device, a material with low thermal conductivity and low electrical resistivity is needed. In other words, the materials which exist to the lower left of the graph in Fig. 4. Polymers have low thermal conductivity but high electrical resistivity while conductive polymers have low electrical resistivity, which makes them prospective candidates for thermoelectric devices.

Materials Requirements for Sustainability

Significant work has been conducted by Cambridge University, Materials research Society (MRS), the Metals Society (TMS) and European Union on defining sustainability challenges and concepts related to materials development and consumption (Allwood, 2012; Green *et al.*, 2012; Ashby, 2012). Sustainability concepts include Zero emission, industrial environmental sustainability, legislation, economics, sustainable technologies, renewable energy resources and energy efficiency of the technology processes.

Table 2 Thermal properties of metals, polymers and ceramics

	<i>Metals</i>	<i>Polymers</i>	<i>Ceramics</i>
Heat capacity	Low	High	Moderate
Thermal expansion	Moderate	High	Low
Thermal conductivity	High	Very low	Low

**Fig. 4** Electrical resistivity vs Thermal conductivity. Produced using, CES EduPack 2018, 2018. Cambridge: Granta.

Though difficult to include all concepts in one application, at least one or two concepts should be verified when issues of sustainability are considered. Surely, integrating renewable energy sources and energy efficiency concepts are amongst the important concepts of sustainability.

Applying sustainable energy concepts include a wide spectrum of concerns. First, energy is a major component in the process of exploiting resources and transformation of raw materials and ores into useful metallic forms. This concern is becoming more significant with the status of shortages in resources and the need to exploit less convenient ore sites. The increased formation of greenhouse gases with the relevant material processing activities is a major concern. In this context, it should be noted that the more the amount of material needed for an application, the higher will the penalty be on the energy consumption side. Second, sustainable energy concepts include harvesting energy from sustainable and green resources.

The term “embodied energy” refers to the energy consumed in processing and manufacturing of a final engineering part. **Fig. 5** (Ashby, 2012) shows the breakdown of the total life-energy demands of engineering products, from which it is suggested that materials have significant impact. In applications where high strength is a requirement, though the family of composite materials can meet the strength criterion, but their embodied energy is higher than metals and they are not recyclable. The research team from Cambridge University (Ashby, 2012) has presented tables for the embodied energy of conventional key materials being transformed to useful form. For example, the embodied energy of concrete is 1.9 MJ/kg, the embodied energy of plastic is 90 MJ/kg and the embodied energy of steel and aluminum are 20 and 160 MJ/Kg, respectively. However, the situation is not similar for harvesting-green-energy applications, as the strength is not the major requirement. Energy harvesting materials are selected owing to specific physical properties (electrical, optical or thermal). The embodied energy of mono-crystalline silicon solar cells is identified (Holst) to be 1656 MJ/Kg in addition to 432 MJ/m² for wafer processing, 684 MJ/ m² for assembly and 720–1800 MJ/m² for installation. Emerging technologies such as perovskites and organic solar cells often have much lower embodied energies than their silicon counterparts.

The development of materials in modern world for energy applications have opened the door for the inclusion of many types of materials, some of which are known to be toxic and environmentally unfriendly. Moreover, the processing stages of some of these metals or elements from their raw state may include the use of toxic chemicals or the production of environmentally unfriendly by-products. The CES EduPack Sustainability database presents materials data-table containing data for the embodied energies and carbon footprints of materials and processes (Ashby, 2012).

Compared to metals and ceramics, polymers are known to possess low thermal conductivity (0.17–0.23 Wm-1K-1) and relatively high specific heat capacity (polyethylene 1800 Jkg-1 K-1). Those properties, combined with lightweight and low cost, have opened the doors for polymers to be used as low-cost alternative materials for thermal energy conversion and storage

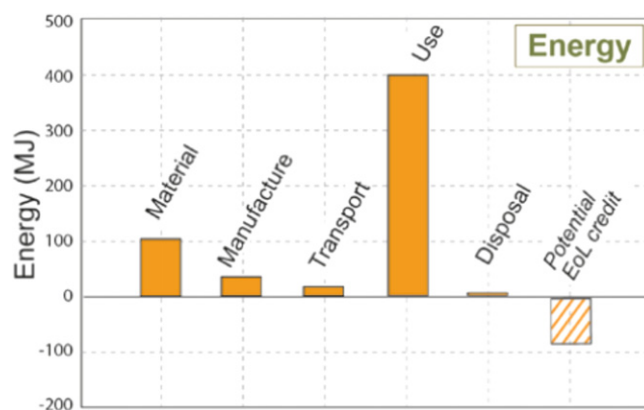


Fig. 5 Breakdown of energy associated to each life-phase. Reproduced from Ashby, M., 2012. The CES EduPack Eco Audit Tool – A White Paper. Version 2.1 © Granta Design Ltd.

applications (El-Mahallawi *et al.*, 2018). The major drawback of the low thermal conductivity of polymers has been resolved in the last decade owing to nanoparticles, nanoplatelets, nanodots and nanofibers.

Polymers in Thermoelectric Applications

Overview of Polymers

The unique material properties of polymers and the versatility of their processing methods are attributed to their molecular structure, which is composed of large molecules (macromolecules) arranged in chains. Polymers have gained their industrial significance from their ease of fabrication, relatively low density, and their ability to be shaped and molded at relatively low temperatures compared to traditional metallic materials. However, the properties of a finished product depend not only on the choice of material and additives but also on the process used to manufacture the part. The relation that exists between the material and product performance is referred to as the 6 P's: Polymer Process, Product, Performance, Post-consumer Life, and Profit (Tim and Osswald, 2010).

Polymers can be classified in many different ways. The most obvious classification is based on the origin of the polymer, i.e., natural vs. synthetic. Other classifications are based on the polymer structure, polymerization mechanism, preparative techniques, or thermal behaviour.

Polymers may be either naturally occurring or purely synthetic. Starch, cellulose, and natural rubber are examples of naturally occurring polymers of enzymes or proteins or plant origins.

Alternatively, polymers are well known among polymers community by their classification according the polymerization mechanism. There are two major methods of polymerization used to convert small molecules (monomers) into polymers. These methods were referred to as addition and condensation polymerization. Addition polymerization is now called chain, chain-growth, or chain reaction polymerization. Condensation is now referred to as step-growth or step-reaction polymerization. The major distinction between these two methods is a result of the differences in the kinetics of the polymerization reaction (Harris, 1981).

Condensation polymers are formed from a series of reactions, often of condensation type, in which any two species (monomers, dimers, trimers, etc.) can react at any time leading to a larger molecule. In condensation polymerization, the stepwise reaction occurs between the chemically reactive groups or functional groups on the reacting molecules. In the process, a small molecule, usually water or ammonia, is eliminated. Addition polymers are produced by reactions in which monomers are added one after another to a rapidly growing chain. The growing polymer in addition polymerization proceeds via a chain mechanism. Like all chain reactions, three fundamental steps are involved: initiation, propagation, and termination. Monomers generally employed in addition polymerization are unsaturated (usually with carbon-carbon double bonds) (Ebewele, 2000).

On the other side, the engineering community distinguishes two classes of polymers, which are thermoplastics and thermosets (Allwood, 2012). Thermoplastics can be melted and reformed several times, while thermosets cure irreversibly upon being heated or treated and cannot be recycled. The basic structural difference between thermoplastics and thermosets is that thermoplastic polymers are composed mainly of linear and branched molecules, whereas thermosets are made up of cross-linked systems. Linear and branched polymers consist of molecules that are not chemically tied together, thus it is possible for individual chains to slide past one another. For cross-linked systems, however, chains are linked chemically; consequently, chains will not flow freely even under the application of heat and pressure. The main thermoplastics and their applications are presented extensively in literature (Allwood, 2012).

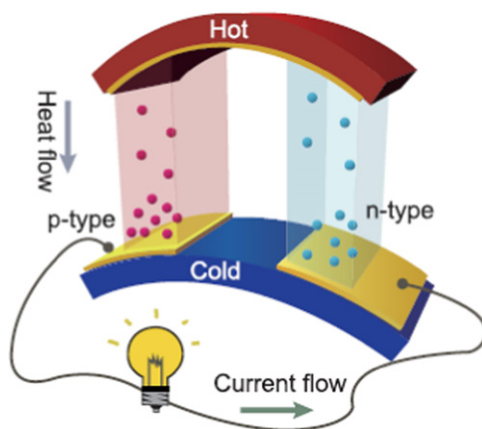


Fig. 6 Schematic of direct thermal/electrical energy conversion. Reproduced from Di, C.-A., Xu, W., Zhu, Z., 2016. Organic thermoelectrics for green energy. *National Science Review* 3 (3), 269–271. Available at: <https://doi.org/10.1093/nsr/nww040>.

Recycling and post-consumer life is a major topic within the scope of this article. In this context, the current state of art has reached a satisfactory level for polymer recycling (Allwood, 2012). Reprocessing of plastics has an effect on both flow and mechanical properties of the material, as the molecular weight is reduced each time the material is heated and sheared during the pelletizing and manufacturing process. The reduction in molecular weight is reflected by increases in the melt flow index (MFI), a common technique used to detect degradation (Tim and Osswald, 2010).

Thermoelectrics

Around 90 % of the energy used all over the world is produced by thermal processes which consequently deliver 40% as useful energy and the rest is considered as waste heat (Di *et al.*, 2016), hence waste heat recovery became of interest over the past decades. Waste heat is the generated heat as a by-product of industrial processes, vehicle exhausting systems, housing glass windows and even from human's body skin (Viklund and Johansson, 2014).

Different technologies have been developed over the past decades aiming to harvest as much as possible of the waste heat considering it as a primary source of energy. Thermoelectric generation, solar thermal collectors, phase change materials, thermoacoustic materials, organic rankine cycles are the most trending technologies for waste heat recovery (Oluleye *et al.*, 2016). Thermoelectric generation shows large findings in the field of waste heat recovery and conversion as it enables the direct thermal/electrical energy conversion with no moving parts and robustness device (Fig. 6).

A thermoelectric material is a solid state device that directly converts thermal energy to electrical energy. Its energy conversion efficiency is determined in terms of figure of merit (ZT) which is defined by the relation $ZT = \frac{S^2 \sigma}{\kappa} T$, where S , σ , T and κ are the Seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity, respectively.

Thermoelectric Materials

Conventional thermoelectric materials have been extensively studied along the past decades to show a deep understanding of their electrical, thermal, thermoelectric behaviour especially for the tellurides and selenides. Tellurium based materials such as Bi_2Te_3 , PbTe and Sb_2Te_3 are characterized to show high ZT (larger than unity) that's why they represent more than 37% of the thermoelectric technologies nowadays as shown in Fig. 7 (Chen *et al.*, 2015; Chhatrasal Gayner and Kar, 2016). Unfortunately, these materials have limited applications in real products as their main building elements are toxic, rare earth and expensive in addition to their processing difficulties and high thermal conductivity (Chen *et al.*, 2015).

On the other hand, though organic based materials have limited contribution to the thermoelectric market, they show an emerging trend in thermoelectric applications (4% of the total thermoelectric technologies) during the last few years with an increasing number of published items and citations as shown in Fig. 8 (Di *et al.*, 2016; Chhatrasal Gayner and Kar, 2016). That's owed to their remarkable advantages of low thermal conductivity, ease of manufacturing and processing, low cost, lightweight, versatility, recyclability, in addition to that, they are considered sustainable and eco-friendly materials (Yao *et al.*, 2010). Organic based thermoelectric materials, that have limited working temperature up to 300°C, target around 89% of the total wasted heat as reported in 2008 based on industrial case study (Fig. 9; Haddad *et al.*, 2014).

Over the past two decades, a large number of polymer based materials and/or composites are reported to be successfully developed for thermoelectric applications. Seeking higher thermal to electrical energy conversion efficiency, large efforts are conducted into fabrication and improvement of novel polymers especially the class of conducting polymers. These developments are performed along variant structure doping, morphological tuning and/or nano-structuring that directly affect the materials' thermoelectric behaviour by manipulating the charge carrier concentration and mobility (Di *et al.*, 2016). Developing

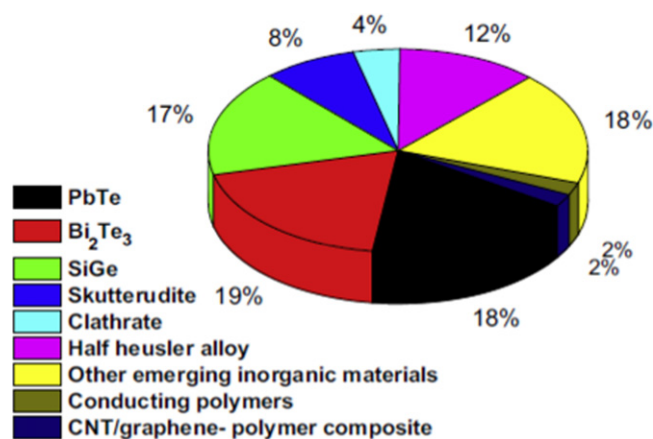


Fig. 7 Different materials research and development in thermoelectric application. Reproduced from Gayner, A.C., Kar, K.K., 2016. Recent advances in thermoelectric materials. *Progress in Materials Science* 83, 330–382.

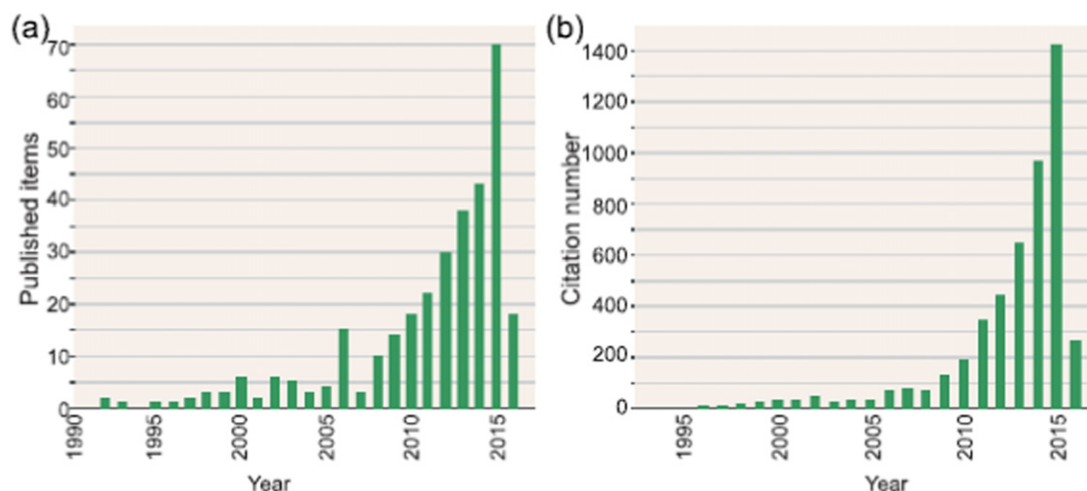


Fig. 8 The trend of research in thermoelectrics over the past two decades (a) number of published items. (b) Number of citations. Reproduced from Di, C.-A., Xu, W., Zhu, Z., 2016. Organic thermoelectrics for green energy. *National Science Review* 3 (3), 269–271. Available at: <https://doi.org/10.1093/nsr/nww040>.

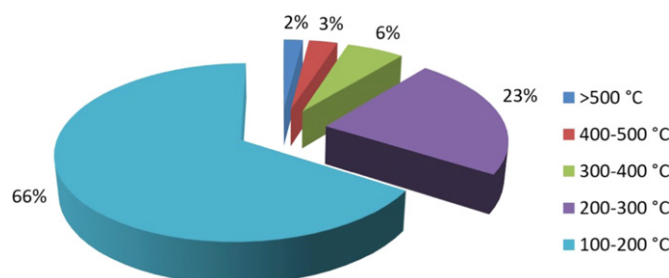
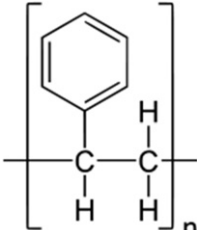
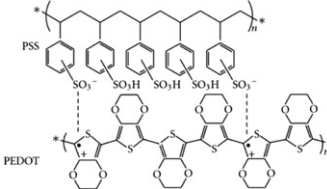
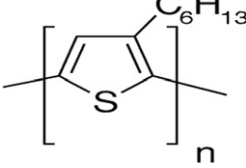
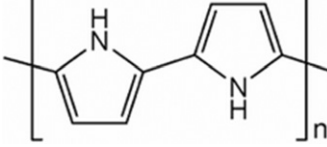
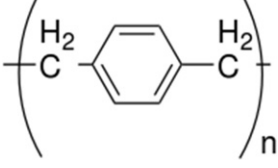
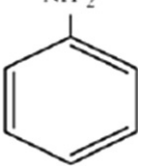


Fig. 9 Waste heat temperature distribution in different industrial processes (60TWh). Reproduced from Haddad, C., Périllon, C., Danlos, A., François, M.-X., Descombes, G., 2014. Some efficient solutions to recover low and medium waste heat: Competitiveness of the thermoacoustic technology. *Energy Procedia* 50, 1056–1069.

thermoelectric nanocomposites is the second approach to be adopted. This occurs by incorporating inorganic nano-particles with large thermopower into these enhanced semiconducting polymers to result in superior thermoelectric properties (Di *et al.*, 2016). Table 3 shows the most important organic polymers used in this context.

It is shown from Table 3 that the most common polymers in thermoelectric applications include both conducting and insulating polymers. Polyvinyl acetate and polystyrene are commercial polymers that are used only for hosting highly designed

Table 3 Organic polymers names and their chemical formulas

	Polymer type	Polymer name	Chemical formula
Organic polymers	Insulating polymer	polyvinyle acetate (PVAc)	$\left[\text{CH}_2 - \underset{\begin{array}{c} \\ \text{O} \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_3 \end{array}}{\text{CH}} \right]_n$
		Polystyrene (PS)	
	Conducting polymer	Poly (3, 4-ethylenedioxythiophene): (poly(styrene sulfonate) (PEDOT:PSS)	
		Poly (3-hexyl)thiophene (P3HT)	
		Polypyrrole	
		Parylene	
		Polyaniline	

thermoelectric nanoparticles with some contribution to the composite thermoelectric behaviour while the rest are the inherent conducting polymers that are either used stand-alone or incorporated in composites for the purpose of higher thermal/electrical conversion efficiency (Anon, 2015). Despite their inherent low electrical conductivity, all insulating polymers are characterized by low thermal conductivity that offers a great potential for the field of thermoelectrics. Incorporating highly electrical conductivity nano-filler materials; carbon nanotubes (CNTs) or graphene to these polymers can effectively transform the insulating polymer into semiconducting and conducting composites with desirable thermoelectric properties as shown in Fig. 10 (Moriarty *et al.*, 2012; Yu *et al.*, 2011; Badr *et al.*, 2017; Suemori *et al.*, 2013, 2015). Fig. 10 reports the state of art, showing power factor values of

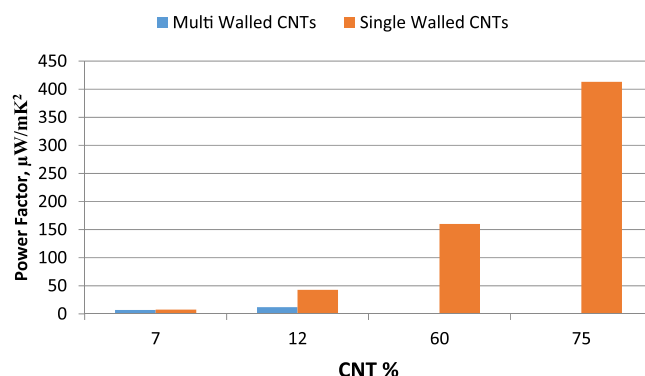


Fig. 10 Thermoelectric behaviour of carbon nanotubes/insulating polymer composites. Produced using data from Moriarty, G.P., Wheeler, J.N., Yu, C., Grunlan, J.C., 2012. Increasing the thermoelectric power factor of polymer composites using a semiconducting stabilizer for carbon nanotubes Carbon 50, 885–895. Yu, C., Choi, K., Yin, L., Grunlan, J.C., Light-weight flexible carbon nanotube based organic composites with large thermoelectric power factors ACS NANO 5 (10), 7885–7892. Badr, H., Youssef, M.A., Elsalam, H.S.A., *et al.*, 2017. Thermoelectric behaviour of polyvinyl acetate/CNT composites. In: Proceedings of the TMS 2017 146th Annual Meeting & Exhibition Supplemental. Suemori, K., Watanabe, Y., Hoshino, S., Carbon nanotube bundles/polystyrene composites as high-performance flexible thermoelectric materials Applied Physics Letters 106 (11), 113902. Available at: <https://doi.org/10.1063/1.4915622>.

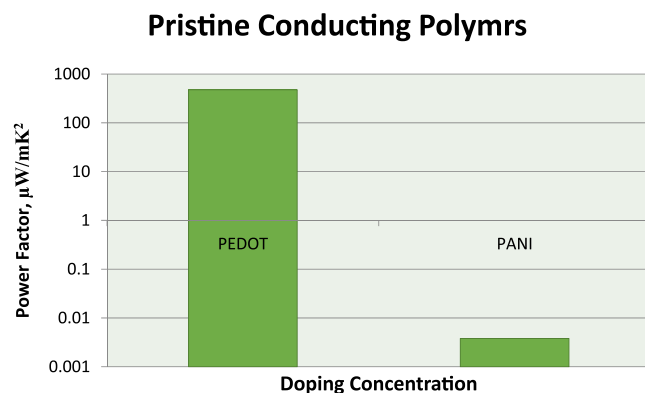


Fig. 11 Power factor of Ethylene glycole doped PEDOT: PSS, (Produced using data from Kim, G.-H., Shao, L., Zhang, K., Pipe, K.P., 2013. Engineered doping of organic semiconductors for enhanced thermoelectric efficiency Nature Materials 12, 719–723). And HCl doped PANI with Ferric Chloride initiator.

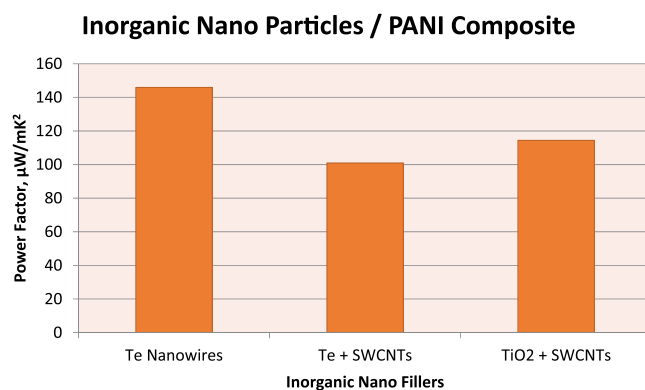


Fig. 12 Power factor of binary and ternary PANI based composites (A) tellurium nanowire, (B) SWNTs / Te and (C) CNTs / TiO₂ produced using data from Wang, Y., Zhang, S.M., Deng, Y., 2013. Flexible Low-Grade Energy Utilization Devices Based on High Performance Thermoelectric Polyaniline/Tellurium Nanorods Hybrid Films. The Royal Society of Chemistry. Wang, L., Yao, Q., Shi, W., Qu, S., Chen, L., 2016. Engineering carrier scattering at the interfaces in polyaniline based nano composites for high thermoelectric performances Materials Chemistry Frontiers 4 (1), 741–748. Erden, F., Li, H., Wang, X., Wang, F., He, C., 2018. High-performance thermoelectric materials based on ternary TiO₂/CNT/PANI composites. Physical Chemistry Chemical Physics 20, 9411–9418.

these composites to range from 0.001 to 100 $\mu\text{W}/\text{mK}^2$ or higher according to the different sorts of the used CNTs (single, double and multi walled) and the used stabilizers as reported by Yu *et al.* (2011).

Poly (3, 4-ethylenedioxythiophene), polystyrene sulfonate (PEDOT), PSS and polyaniline are the most common polymers in electronics and optoelectronics applications. Kim *et al.* (2013) reported that the most efficient polymer in thermoelectric applications (EG doped PEDOT: PSS) show a power factor that exceeds 450 $\mu\text{W}/\text{mK}^2$ with specific doping concentration as shown in Fig. 11. The previously reported power factor values of CNTs based composites are also achieved by polymers with conjugated nature that possess semiconducting/conducting characteristics. Badr *et al.* (2017) recently reported the chlorine doping effect on thermoelectric characteristics of pristine PANI as shown in Fig. 11.

In 2012, Lu *et al.* (2012) prepared a hybrid composite of graphene nano sheets (GNs) incorporated into HCl protonated polyaniline by in situ polymerization for thermoelectric use. This composite showed a dramatic increase of the power factor from the pristine materials to that with 30% GNs to reach 2.6 $\mu\text{W}/\text{mK}^2$. In the same year, Yong Du *et al.* (2012) adopted another method of preparation to result in simultaneous increase in both Seebeck coefficient and electrical conductivity by wisely controlling the charge carriers' mobility without affecting their concentration. This occurred by incorporating graphene nano sheets (GNs) in polyaniline (PANI) matrix to reach a higher power factor of 5.6 $\mu\text{W}/\text{mK}^2$ at GNs:PANI ratio of 1:1 at room temperature.

For further improvement of PANI based materials, the ternary composite approach is adopted to reach dual electrical conductivity and thermopower enhancement. Wang *et al.* (2013) achieved the greatest power factor of 146 $\mu\text{W}/\text{mK}^2$ by hosting tellurium nanowires into camphor sulfonic acid (CSA) secondary doped PANI. This large PF is attributed to the energy filtering effect between PANI and Tellurium. Further additions of SWNTs/Te and TiO_2 nanoparticles resulted into 101 and 114.5 $\mu\text{W}/\text{mK}^2$ as reported by Wang *et al.* (2016) and Erden *et al.* (2018) (Fig. 12).

Conclusion

The previous discussion reveals that organic based polymeric materials are promising candidates for future sustainable energy harvesting applications and continuous scientific and technical development will result tuning and development of their properties to meet functional and sustainability challenges.

See also: 100% Renewable Energy by Renewable Materials. Analyzing Biodiesel Production From Cooking Oil

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Sustainable Materials for Tribological Applications

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Background and Challenges

Technology has gone far beyond the thought of an ordinary person and it looks almost casual to handle many of the problems which were too complex to understand just few decades back. Many of such issues will be resolved satisfactorily in years to come relevant to interacting surfaces of different component systems. However, many of the problems remain unresolved mysteries like dolphins avoiding turbulence and maintaining fully laminar flow to move faster than the theory predicts. Even, it is difficult to explain logically the reduction of drag force in pipelines on application of certain polymers and additives. Additives are also used in many more applications such as firefighting, torpedo designing etc. There are many applications for which as tribologists, we need to provide a proper design of component and material which can avoid skidding of automobiles in wet zones, minimise slippage of drive wheels while accelerating, etc. There is virtually endless list of applications posing challenges to tribologists (Moore, 1975).

Further, relentless pressure to develop automobiles, aircrafts etc. with ever increasing fuel efficiency, compact design of engines and stringent environment norms has been another challenge. Looking at it from tribologist point of view, it becomes imperative to design parts as well as materials with capability to bear high specific loads, speeds and temperatures for the major engine components. However, it may not be possible to discuss many aspects in one chapter so, I will be restricting myself only to sustainable materials. In last few decades, advanced composite materials have presented significant benefits and their sustainability has made them accepted engineering materials in many applications. The polymer, metal, or ceramic based composites with different kind of reinforcements, and exceptional tailoring capabilities, can be made suitable for wide range of applications.

Composites as Sustainable Materials

The capability of composites can be clearly understood from few examples of AMCs showing much superior mechanical and tribological properties. These examples clearly show that composites with different reinforcements have superior strength parameters while comparing with corresponding metal/alloy systems. It has been observed that mechanical properties such as ultimate tensile strength, yield strength and hardness improve continuously with increasing amount of reinforcement unless and until clustering of reinforcement takes place due to some reason (Figs. 1–3). It is also interesting to observe many times that ductility also improves with reinforcement (Fig. 4), whereas, in alloy systems with improvement in hardness, ductility is compromised. It is well said that properties of composites can be tailored as per need (Figs. 5 and 6) and these can be designed to meet the requirement i.e., composites can be designed with low coefficient of friction and high wear resistance and also with high coefficient of friction and high wear resistance (Gautam and Mohan, 2016; Kumar *et al.*, 2015; Gautam and Mohan, 2015; Srivastava and Mohan, 2011; Sarkar *et al.*, 2014; Mohan *et al.*, 2002; Pathak *et al.*, 2006; Deppisch *et al.*, 1997; Miranda *et al.*, 2016; Karantzalis *et al.*, 1997; Tee *et al.*, 1999; Kalaiselvan *et al.*, 2011; Gautam *et al.*, 2016a,b; Kumar *et al.*, 2016; Gautam *et al.*, 2016a,b; Mohan *et al.*, 2016a; Agrawal *et al.*, 2014; Mohan *et al.*, 2016b).

Composite Materials

There exist natural composite materials such as timber, bone, tooth etc., but among man made composites the glass reinforced plastic (GRP) was the first composite to be used as an industrial material. However, its potential for aircraft applications could be established only in 1940s, when first time reinforced composite airframe structures were showcased. Tests showed that, it was nearly 50 percent stronger than metallic or wooden structures which were earlier used. Since then such composites have gone long way, and are used in numerous applications related to aircrafts, spacecrafts, sports and recreation goods, marine, automobiles, etc. Infrastructural applications are opening new avenues for composites as commodity material. Metal-matrix are much newer but have found some specialty applications of space shuttle, Hubble telescope etc. and now aluminium matrix composites being very cost effective, are widely in use as automotive material in brakes, drive shafts, and cylinder liners etc. They are also used in electronic packaging and thermal-management applications. Another class with ceramic matrix find applications in cutting tool inserts, wear-resistant parts, aerospace and defense, engines, etc. These have high potential for high performance applications, but due to high cost their applications are limited. However, their high temperature stability, corrosion resistance, and toughness make

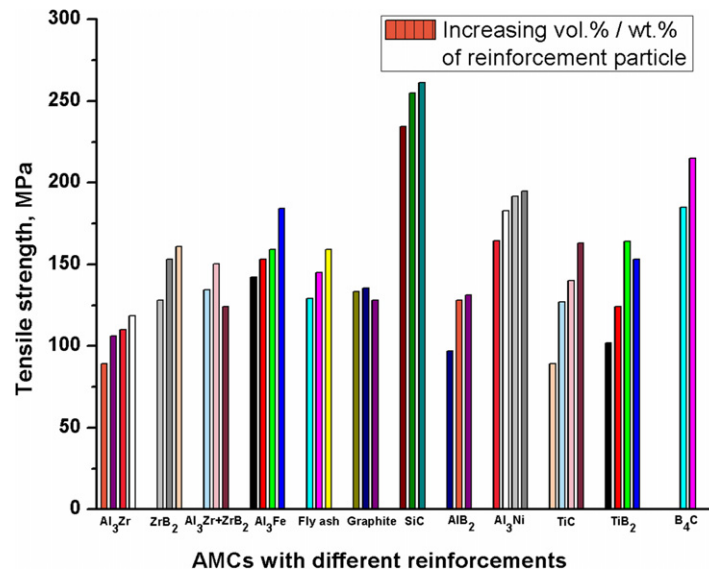


Fig. 1 Tensile strength of AMCs with different reinforcements. Reproduced from Gautam, G., Mohan, A., 2015. Effect of ZrB₂ particles on the microstructure and mechanical properties of hybrid (ZrB₂ + Al₃Zr)/AA5052 in situ composites. *Journal of Alloys and Compounds* 649, 174–183, Gautam, G., Mohan, A., 2016. Wear and friction of AA5052-Al₃Zr in situ composites synthesized by direct melt reaction. *Journal of Tribology ASME* 138, 021602-1–021602-12, Kumar, N., Gautam, R.K., Mohan, S., 2015. In-situ development of ZrB₂ particles and their effect on microstructure and mechanical properties of AA5052 metal matrix composites, *Materials and Design* 80, 129–136, Srivastava, S., Mohan, S., 2011. Study of wear and friction of Al–Fe metal matrix composite produced by liquid Metallurgical method. *Tribology of Industry* 33, 128–137, Sarkar, S., Tripathy, S., Mohan, S., 2014. Effect of Si and Mg addition on dry sliding wear of Al–Fly ash metal matrix composite. *International Journal of Material and Mechanical Engineering* 3, 31–37, Mohan, S., Pathak, J.P., Gupta, R.C., Srivastava, S., 2002. Wear behaviour of graphitic aluminium composite sliding under dry conditions. *Zeitschrift für Metallkunde* 93, 1245–1251, Pathak, J.P., Singh, J.K., Mohan, S., 2006. Synthesis and characterisation of aluminium-silicon-silicon carbide composite. *Indian Journal of Engineering and Materials Sciences* 13, 238–246, Deppisch, C., Liu, G., Shang, J.K., Economy, J., 1997. Processing and mechanical properties of AlB₂ flakes reinforced Al alloy composites. *Materials Science and Engineering A* 225, 153–151, Miranda, G., Carvalho, O., Soares, D., Silva, F.S., 2016. Properties assessment of nickel particulate-reinforced aluminum composites produced by hot pressing. *Journal of Composite Materials* 50, 523–531, Karantzalis, A.E., Wyatt, S., Kennedy, A.R., 1997. The mechanical properties of Al–TiC metal matrix composites fabricated by a flux-casting technique. *Materials Science and Engineering A* 237, 200–206, Tee, K.L., Lu, L., Lai, M.O., 1999. In situ processing of Al–TiB₂ composite by the stir-casting technique. *Journal of Materials Processing Technology* 89–90, 513–519, Kalaiselvan, K., Murugan, N., Parameswaran, S., 2011. Production and characterization of AA6061–B₄C stir cast composite. *Materials and Design* 32, 4004–4009.

them attractive for a wide range of applications. It may not be feasible to discuss all applications due to limitation of a chapter, however, it will be tried to cover few important ones (Hunt, 2011).

Industry-Based Applications

Automotive

Way back in 1940s, Henry Ford introduced an environment friendly car, having body panels made of soybean-resin matrix reinforcement with cellulose-fibers. This car had capability of withstanding high impact loads, with 900 kg less curb weight. Just after few years flying car was presented by Convair. It's body and chassis were of glass-epoxy structural composite. Thereafter, in 1950s, Chevrolet Corvette used body panels of fiberglass reinforced composites. Since then composites are being used in various parts of different automotive vehicles. Today, through structural polymer matrix composites vehicles can be designed to achieve certain goals. The energy crises leading to corporate fuel economy regulations and high rate of taxes on fuels made it imperative to improve efficiency of the automotive engines through more aerodynamic design and weight reduction. Studies have shown that 30% mass reduction in the automobile can reduce fuel consumption by 30%. The potential regions for mass reduction are chassis area which includes the suspension, driveline, braking, and steering components, body and underbody structural systems. The high strength-to-mass ratio of composites makes them suitable to achieve mass reduction. Comparatively higher cost of composites is the main reason that these materials are not dominating automotive industry. Hence, design and property optimization will allow structural composites to be successful in automobiles, pick-up vans, SUVs, etc. in a cost-effective manner (Gianaris, 2001; Musselman, 1997).

Composite materials are engineered and optimized to be fit for structural applications. These materials have high-strength to weight ratio, intermediate to high apparent modulus, and high aspect ratio of fiber with a coherent matrix. They are also

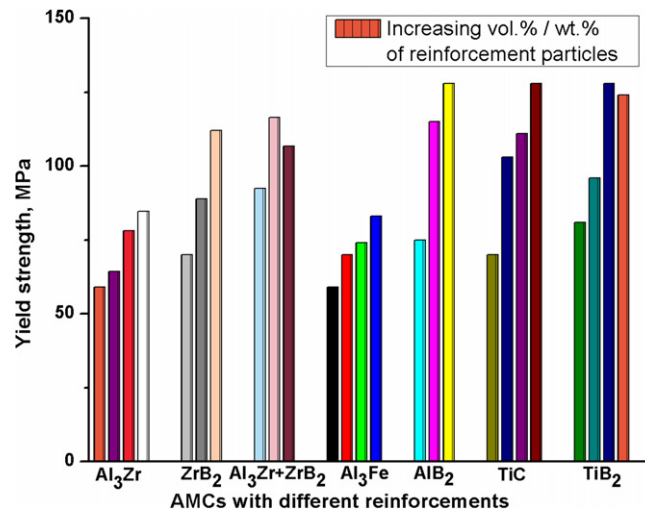


Fig. 2 Yield strength of AMCs with different reinforcements. Reproduced from Gautam, G., Mohan, A., 2015. Effect of ZrB₂ particles on the microstructure and mechanical properties of hybrid (ZrB₂ + Al₃Zr)/AA5052 in situ composites. *Journal of Alloys and Compounds* 649, 174–183, Gautam, G., Mohan, A., 2016. Wear and friction of AA5052-Al₃Zr in situ composites synthesized by direct melt reaction. *Journal of Tribology ASME* 138, 021602-1–021602-12, Kumar, N., Gautam, R.K., Mohan, S., 2015. In-situ development of ZrB₂ particles and their effect on microstructure and mechanical properties of AA5052 metal matrix composites, *Materials and Design* 80, 129–136, Srivastava, S., Mohan, S., 2011. Study of wear and friction of Al–Fe metal matrix composite produced by liquid Metallurgical method. *Tribology of Industry* 33, 128–137, Deppisch, C., Liu, G., Shang, J.K., Economy, J., 1997. Processing and mechanical properties of AlB₂ flakes reinforced Al alloy composites. *Materials Science and Engineering A* 225, 153–151, Tee, K.L., Lu, L., Lai, M.O., 1999. In situ processing of Al–TiB₂ composite by the stir-casting technique. *Journal of Materials Processing Technology* 89–90, 513–519, Kalaiselvan, K., Murugan, N., Parameswaran, S., 2011. Production and characterization of AA6061–B4C stir cast composite. *Materials and Design* 32, 4004–4009.

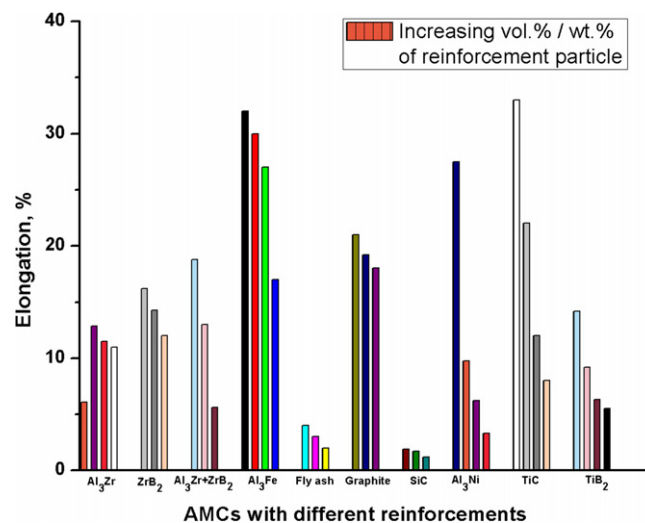


Fig. 3 Brinell hardness of AMCs with different reinforcements. Reproduced from Gautam, G., Mohan, A., 2016. Wear and friction of AA5052-Al₃Zr in situ composites synthesized by direct melt reaction. *Journal of Tribology ASME* 138, 021602-1–021602-12, Kumar, N., Gautam, R.K., Mohan, S., 2015. In-situ development of ZrB₂ particles and their effect on microstructure and mechanical properties of AA5052 metal matrix composites, *Materials and Design* 80, 129–136, Gautam, G., Mohan, A., 2015. Effect of ZrB₂ particles on the microstructure and mechanical properties of hybrid (ZrB₂ + Al₃Zr)/AA5052 in situ composites. *Journal of Alloys and Compounds* 649, 174–183, Sarkar, S., Tripathy, S., Mohan, S., 2014. Effect of Si and Mg addition on dry sliding wear of Al–Fly ash metal matrix composite. *International Journal of Material and Mechanical Engineering* 3, 31–37, Mohan, S., Pathak, J.P., Gupta, R.C., Srivastava, S., 2002. Wear behaviour of graphitic aluminium composite sliding under dry conditions. *Zeitschrift für Metallkunde* 93, 1245–1251, Pathak, J.P., Singh, J.K., Mohan, S., 2006. Synthesis and characterisation of aluminium-silicon-silicon carbide composite. *Indian Journal of Engineering and Materials Sciences* 13, 238–246, Kalaiselvan, K., Murugan, N., Parameswaran, S., 2011. Production and characterization of AA6061–B4C stir cast composite. *Materials and Design* 32, 4004–4009, Gautam, G., Kumar, N., Mohan, A., Gautam, R.K., Mohan, S., 2016a. Synthesis and characterization of tri-aluminide in situ composites. *Journal of Material Science* 51, 8055–8074, Gautam, G., Kumar, N., Mohan, A., Gautam, R.K., Mohan, S., 2016b. Tribology and surface topography of tri-aluminide reinforced composites. *Tribology International* 97, 49–58, Kumar, N., Gautam, G., Gautam, R.K., Mohan, A., Mohan, S., 2016. Wear, friction and profilometer studies of in situ AA5052/ZrB₂ composites. *Tribology International* 97, 313–326.

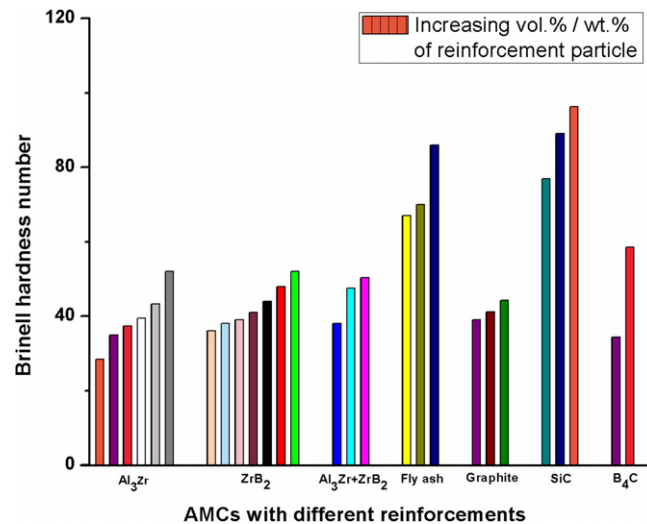


Fig. 4 % elongation of AMCs with different reinforcements. Reproduced from Gautam, G., Mohan, A., 2015. Effect of ZrB₂ particles on the microstructure and mechanical properties of hybrid (ZrB₂ + Al₃Zr)/AA5052 in situ composites. *Journal of Alloys and Compounds* 649, 174–183, Gautam, G., Mohan, A., 2016. Wear and friction of AA5052-Al₃Zr in situ composites synthesized by direct melt reaction. *Journal of Tribology ASME* 138, 021602-1–021602-12, Kumar, N., Gautam, R.K., Mohan, S., 2015. In-situ development of ZrB₂ particles and their effect on microstructure and mechanical properties of AA5052 metal matrix composites, *Materials and Design* 80, 129–136, Srivastava, S., Mohan, S., 2011. Study of wear and friction of Al–Fe metal matrix composite produced by liquid Metallurgical method. *Tribology of Industry* 33, 128–137, Sarkar, S., Tripathy, S., Mohan, S., 2014. Effect of Si and Mg addition on dry sliding wear of Al–Fly ash metal matrix composite. *International Journal of Material and Mechanical Engineering* 3, 31–37, Mohan, S., Pathak, J.P., Gupta, R.C., Srivastava, S., 2002. Wear behaviour of graphitic aluminium composite sliding under dry conditions. *Zeitschrift für Metallkunde* 93, 1245–1251, Pathak, J.P., Singh, J.K., Mohan, S., 2006. Synthesis and characterisation of aluminium-silicon-silicon carbide composite. *Indian Journal of Engineering and Materials Sciences* 13, 238–246, Miranda, G., Carvalho, O., Soares, D., Silva, F.S., 2016. Properties assessment of nickel particulate-reinforced aluminum composites produced by hot pressing. *Journal of Composite Materials* 50, 523–531, Karantzalis, A.E., Wyatt, S., Kennedy, A.R., 1997. The mechanical properties of Al–TiC metal matrix composites fabricated by a flux-casting technique. *Materials Science and Engineering A* 237, 200–206, Tee, K.L., Lu, L., Lai, M.O., 1999. In situ processing of Al–TiB₂ composite by the stir-casting technique. *Journal of Materials Processing Technology* 89–90, 513–519, Kalaiselvan, K., Murugan, N., Parameswaran, S., 2011. Production and characterization of AA6061–B₄C stir cast composite. *Materials and Design* 32, 4004–4009.

engineered to withstand static and dynamic structural requirements and environmental issues. Further, in case of automobiles appearance, noise level, vibrations of body, process drivers, cost, and safety standards are also very important and must be considered during designing.

Stiffness, strength to weight ratio and weight reduction are treated as design drivers for PMCs in automobiles. Mass reduction in a vehicle system improves fuel economy. The rotating unsprung mass at the hub, wheel, and brake system is very important. Body and the chassis are also mass sensitive regions for vehicle dynamics and performance. The reductions made in unsprung mass improves the performance of vehicle to a much larger level as compared to reduced mass in sprung mass. Hence, mass reduction made in the chassis region, especially the braking/suspension systems improves vehicle dynamics more effectively than reduction in body mass. Additionally, overall mass distribution is very important for dynamics. Any kind of unbalanced reduction is likely to affect dynamics and performance very badly, hence, vehicle dynamics is very crucial. PMCs have inherent advantage of increasing natural frequencies of noise, vibration, and harshness (NVH) in a vehicle while driving. The high stiffness to mass ratios and good damping properties of PMCs increase these frequencies to indistinguishable levels for driver and passenger, hence, these also eliminate the need of additional bushings, other damping materials, and spot welds that are added solely to increase structural stiffness and reduce noise transmission. Therefore, total vehicle mass and cost is further reduced (Gianaris, 2001).

The advantages of structural composites can only be appreciated if we give adequate attention to design principles, process limitations and materials. Engineers need to understand that simply substituting the materials is not enough to have a successful product. Polymer-matrix composites have great potentials for automotive, but the most common mistake made is “direct substitution of materials”. Suppose, a component was originally designed for steel or cast iron, and now it is manufactured with PMCs without any design change, then it will lead to underutilization of PMC capabilities. The specific need of an application must be considered while selecting the material and process, instead of just using a specific material for change. Another critical design driver is related to safety of the vehicle during a crash. The automobile must meet vehicle dynamic and performance expectations that differentiate it from its competition. The reliability and service costs are also quite important (Gianaris, 2001).

Unlike aerospace, applications of structural composites have been limited only to secondary structures in the automotive sector. In aerospace primary and secondary structure are well connected and structural composites have been used extensively for both structures. Role of computer aided engineering (CAE) is very important in automotive design with PMCs. CAE models have been widely used for conventional materials but for PMCs resources are required to develop CAE models. It is also important to

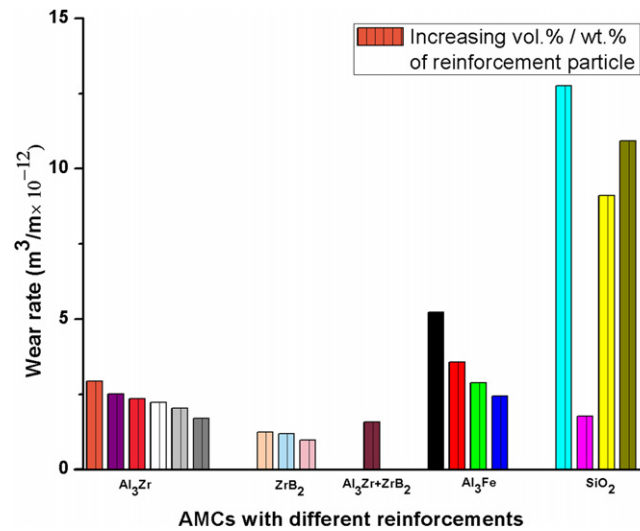
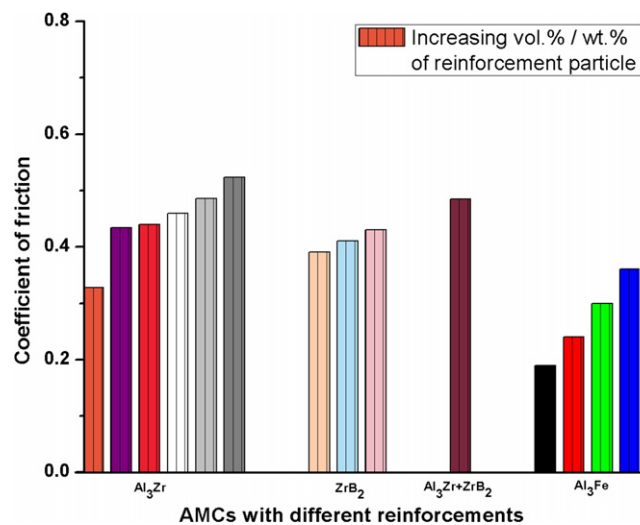


Fig. 5 Wear rate of AMCs with different reinforcements. Reproduced from Gautam, G., Mohan, A., 2016. Wear and friction of AA5052-Al₃Zr in situ composites synthesized by direct melt reaction. *Journal of Tribology ASME* 138, 021602-1–021602-12, Kumar, N., Gautam, G., Gautam, R. K., Mohan, A., Mohan, S., 2016. Wear, friction and profilometer studies of insitu AA5052/ZrB₂ composites. *Tribology International* 97, 313–326, Gautam, G., Kumar, N., Mohan, A., Gautam, R.K., Mohan, S., 2016a. Synthesis and characterization of tri-aluminide in situ composites. *Journal of Material Science* 51, 8055–8074, Gautam, G., Kumar, N., Mohan, A., Gautam, R.K., Mohan, S., 2016b. Tribology and surface topography of tri-aluminide reinforced composites. *Tribology International* 97, 49–58, Mohan, A., Gautam, G., Kumar, N., Mohan, S., Gautam, R.K., 2016a. Synthesis and tribological properties of AA5052-base insitu composites. *Composite Interfaces* 23, 503–518. Mohan, S., Gautam, G., Kumar, N., Gautam, R. K., Mohan, A., Jaiswal, A.K., 2016b. Dry sliding wear behavior of Al–SiO₂ composites. *Composite Interfaces* 23, 493–502, Agrawal, R., Mohan, A., Mohan, S., Gautam, R.K., 2014. Synthesis and characterization of Al/Al₃Fe nanocomposite for tribological applications. *Journal of Tribology ASME* 136, 012001-1–012001-9.



though the need to increase the use of composites to meet fuel economy and safety goals for these vehicles production volume is required. To achieve production volume and to take full advantage of composite material cost, tooling, design optimization, and ownership costs needs to be addressed. Optimized design tools and practices and cost of materials is likely to counterbalance overall cost (Gianaris, 2001).

Solectria Sunrise electric vehicle has been manufactured by stitched woven and braided composite fibers. The entire structure for the body and chassis consists of six separate parts. These were assembled at a cost comparable to conventional structures. Composites have also been used in fuel storage chambers for natural gas storage. These are lighter and more durable

Carrigan *et al.* (2000) and Koppert and Beukers (2000). Development of hydrogen fuel-based powertrains will provide another opportunity for hydrogen storage. High volume production of superior quality low modulus carbon will provide low cost composites which could be used in high stiffness applications like driveshafts (Gianaris, 2001).

Natural fibers like leaf and flax seeds are ecologically friendly and are suitable alternatives for interiors of automobiles. These fibers are lighter with renewability and recyclability properties. Further, low cost, and good thermal and acoustic properties make them more attractive. However, these have certain disadvantages like low strength, limited temperatures of processing, quality variations, absorption of moisture, poor fire resistance, and variable prices. Advancements in these fibers will make them attractive in automotive applications (Brouwer, 2000; Gianaris, 2001).

Metal-Matrix Composites (MMCs) have been in commercial use in number of the automotive applications for several decades because of their low density, high specific stiffness, better high cycle fatigue (HCF) resistance and superior wear resistance (Gianaris, 2001). Though the raw material cost of steel and cast iron is lesser than discontinuously reinforced aluminium (DRA) but it weighs less by 45% which nullifies the cost part. However, wider applications require improvement in performance coupled with innovations in process to bring down the overall cost drastically. But with all these limitations, MMCs have taken over a large share in several engine applications such as pistons, cylinder liners, cylinder blocks, intake and exhaust valves, pushrods, connecting rods, driveshafts, brake system, gears, brake calipers, valves, pump housings, suspension components, supercharger compressors, pulleys, turbocharger, and brackets of certain automobiles. In addition, MMCs are also the candidates for suspension pushrods and rockers, clutch parts, and other gearbox and engine parts (Hunt, 2011; Allison and Cole, 1993; Rittner, 2000; Kevorkian, 1999; Donomoto *et al.*, 1983; Harrigan, 1994; Hamajima *et al.*, 1990; Saito, 1995; Hurley, 1995; Nussbaum, 1997). These applications are already have detailed discussion in another chapter by my colleague so these don't find scope here.

Space

Low coefficient of thermal expansion (CTE), high stiffness, and lifetime dimensional stability are typical requirements of space structures. Hence, these require light weight and high-performance composites. From the beginning of space program solid-fuel rocket motor cases of composites have been used. Continuous developments are being made for launch vehicles, aircraft, spacecraft structures, and missiles. Fiber reinforced laminated composites are very much different in strength, failure mode, elastic response, and damage tolerance properties from metals and alloys. PMCs are also different from metals and alloys in respect to space environment, sensitivity to temperature, and moisture. These things cannot be ignored while choosing designing, manufacturing and test techniques for composites. There have been continuous advancements in manufacturing methods, design & analysis techniques, and fiber quality in last few decades. This has increased composites use in structural and other applications of spacecraft (Lubin, 1982; Policelli and Vicario, 1987; Griffin, 2004; Larson and Wertz, 1992; Rittenhouse and Singletary, 1968; Sarafin, 1995; Schmidt *et al.*, 1999; Strong, 1989; Silverman, 1999; Rule, 1990; Dodson and Rule, 1989; Vicario, 2000; Rawal and Goodman, 2000). The non-structural applications have an extensive list and to name few are optical benches, antenna reflectors, antenna masts, equipment-panel structure, truss structure, electronic enclosures, radiators, engine shields, and solar array support structures. In missiles applications and space launch vehicles composites are used in inter stage structures, payload support structures, rocket motor cases, payload fairings, nozzles, and igniters etc. (Rawal, 2001).

Composites properties such as low density, reduced part count and structural complexity, improved specific strength and stiffness, better dimensional stability, high thermal conductivity, and potentially lower cost than conventional materials make them design drivers for space applications. In space applications, major challenges faced by design engineers are due to allowables limits of properties, manufacturing and testing expenditure, and uncertainty when going for composites. One has to depend on recurring data in the absence of available data for different characteristics of composites. Environment is another major issue because spacecraft are subjected to various environments during various stages starting from fabrication to service life. Designing of structures is mostly governed by earth and space environment. Spacecraft environments include acoustic, transient/steady state, thermal, handling, pyro-shock, vibration, transport, and pressure. Further, structural design is also likely to be affected by other factors like space environment, humidity, ambient temperature, salt-fog etc. The space environment has atomic oxygen (AO), very low-density atmospheric density, ionizing radiation, plasma, charged and neutral particles, micrometeoroids, and anthropogenic debris. Significant change is observed in pressure conditions with altitude in space and it may be about 1.3×10^{-13} Pa for geosynchronous spacecraft, compared to atmospheric pressure of 101.3 kPa at sea level. Exposure to space vacuum, including temperatures variations, PMCs may outgas i.e., release gases. This outgassing causes deterioration of mechanical properties. It is also likely that these gases may condense on critical regions of sensors, lenses, and mirrors, which may influence optical performance (Sarafin, 1995; Vicario, 2000; Rawal and Goodman, 2000; James *et al.*, 1994; Belk *et al.*, 1997; Anderson and Smith, 1994; Dooling and Kinckenor, 1999; Adams *et al.*, 1986; Rawal, 2001).

Composites do offer significant performance improvements in the form of mass reduction, which amounts to \$20,000 for every kilogram of weight saving resulting in reduced launch cost. But choosing constituent materials requires to understand the system in depth. Material choice for spacecraft surfaces is crucial because prevailing temperature and pressure conditions make them prone to atomic oxygen attack. Atomic oxygen has very high percentage in lower earth orbit region (James *et al.*, 1994; Belk *et al.*, 1997; Anderson and Smith, 1994; Dooling and Kinckenor, 1999; Silverman, 1996). The spacecraft material not only faces atomic oxygen erosion, but it also, bears with adverse conditions of solar ultraviolet and high-energy radiation, micrometeoroid and man-made debris impacts, vacuum, cycling of temperature in orbit, and volatilizing condensed organics particles from the surface of spacecraft. The combined effect can cause severe damage to surface's optical, thermal and, mechanical properties. Careful selection and designing of materials can ensure satisfactory performance of the system over a period of time (Rawal, 2001).

Carrying payload is the defined mission of spacecraft and the bus holds components of different subsystems. The bus is the main load path between launch vehicle and components of the spacecraft. The instrumentation part is stationed in bus. Some spacecrafts are using C-C composite nozzle/exit cone parts in the propulsion system. Bus is the main body and it attaches all other parts. Composites provide minimum weight for a particular application and these have to be tailored for high strength/modulus to weight ratio. Composites with carbon/graphite fibers produced from pitch contain highest stiffness and elastic modulus of about 900 GPa. Highly thermally conductive stiff fibers fail at relatively low compressive strength and low strain to failure and are used in applications related to thermal management both structural and non-structural (Rawal, 2001).

Sandwich and isogrid constructions are used in platform structures. Even with low density, both the constructions have high strength to buckling and high stiffness. A composite laminate has adhesively bonded light honeycomb core of aluminium sandwiched between two thin face sheets of composite. Core bears the out-of-plane flexure shear loads while bending moments, axial loads, and in-plane shear loads which act on the panel are dealt by the face-sheets. Bus modules using panel structure have been used in several spacecraft. Taking care of load path, composite bus structures can be designed using simple cylinders, moulded tubes, etc. Most of the bus structure panels are made out of graphite/cyanate or graphite/epoxy composite, but C-C composite has been used in high-temperature structural panels. C-C composite panel, with aluminium core exhibits higher thermal conductivity as well as stiffness while comparing with baseline aluminium panel. This C-C panel has been successfully used as a structural radiator on an operational spacecraft (Vaughn *et al.*, 1998). Aramid and graphite/cyanate esters are used to develop reflectors. These composites materials provide quite high stiffness to weight ratio while coefficient of thermal expansion approaches almost zero. But the laminates and sandwiches of these materials have surprisingly high CTE and coefficient of moisture expansion (CME) through the thickness. It is important to determine CTE and CME to predict as well as to control surface accuracy while fabricating these composites and also when these are in use. PMCs are widely used in many other space applications such as solar array support structures, reflector, avionics boxes/enclosures, attachment fittings, heat sinks for circuit cards, heat sinks for components generating too much heat, radiator fins, and antenna including waveguides (Rawal, 2001).

Though most of the structure related applications are dealt by PMCs, whether, it is structural or non-structural but certain untouched regions have been successfully covered by MMCs and carbon-carbon composites like space shuttle. In space shuttles unidirectional B-Al tubular struts are used as rib truss members and frame in mid fuselage section and also as link of landing gear for space shuttle. These B-Al save about 44% weight from existing ones. Hubble space telescope high-gain antenna boom requires low CTE and high stiffness where diffusion bonded AMC reinforced with graphite fiber has been used. Carbon-carbon composites are used in structural as well as non-structural applications such as radiator, engine shield, thermal doublers, thermal planes, etc. (Anonymous, 1983; Krumweide and Chamberlain, 1988; Rawal, 2001).

Composites are used in various components of space launch vehicle and missile, such as aerodynamic fairings, nozzles, rocket motor cases, launch canisters and control surfaces. Since the early days of lunar missions, fuels and pressurized gases have been stored in the tanks of filament wound composites. Composites have been used in solid rocket motors of nearly all expendable launch vehicles. In the solid-propellant-type motor, fuel burns inside the case and generates moderately high pressures, which is controlled by the large case wall. Low density composites with high tensile strength offer an excellent materials solution. Filament-wound solid rocket motor casings have been extensively used in almost all missile systems, including strategic, ballistic and defensive missile systems that forms the primary system in which Kevlar-49 aramid-fiber/epoxy and standard modulus carbon fiber/epoxy composites are used in different sections. The major composite components of the missile include 1st to 3rd stage rocket motors, equipment section, igniters, etc. (Rawal, 2001).

Aerospace

MMCs are widely used in components related to structural, propulsion, thermal management systems and facing wear problems of commercial as well as military aircrafts. The main motivating factor for MMCs in aeronautics application is their excellent combination of stiffness and specific strength. Due to anisotropic nature, properties of MMCs are limited and generally inferior to organic matrix composites. But discontinuously reinforced aluminium (DRA) with isotropic nature has much superior specific stiffness while comparing with conventional metals and alloys used in such applications. Highest values of specific stiffness are achieved by large volume of particulates but to have good combination of toughness, ductility, and fatigue one needs to limit reinforcement within 25%. These DRAs are isotropic in nature and have nearly 1.5 times higher specific stiffnesses to respective alloys and comparable to most widely used 7075-T6 aluminium alloy as well as Ti-6Al-4V titanium alloy. Discontinuously reinforced titanium (DRTi) has very good structural properties among MMCs. Though, these are new but they find applications in

intake and exhaust valves of automobiles. Efforts have been made to fabricate fiber reinforced metal-matrix composites suitable for aircraft components but with a little success. Many matrices have been used but focus remains on α -, β -, $\alpha + \beta$ titanium alloys and aluminides. Alumina fibers and SiC monofilaments have been common choice but number of problems faced create barrier to their use. Different means have been used to develop these composites. Significant resources have been applied to develop these materials for compressor components of gas turbine engines. In one case, such efforts are still underway, and it is not certain whether a successful insertion will result. Titanium reinforced with fiber has been used for actuator piston rod. Manufacturing of parts with simple shape is easier and due to axial loading material properties are fully utilized. Discontinuously reinforced iron is used in industrial rollers and extrusion dies for wear resistance. Most significant progress has been made in DRAs because of flexible material system where matrix can be cast or wrought alloys while reinforcements can be such as SiC, Al_2O_3 , B_4C . Hence, these are used in wide range specifically in cylinder liners, snow tire studs etc. and in broader prospective in application related to space, automotive, thermal management etc. (Miracle, 2001).

Aero-structural

During flight ventral fins are subjected to unexpected turbulence situations. The turbulent air originates in the front engine intake and propagates along fuselage. Ventral fins observe rolling effect causing bending movement. In this process bolt holes are elongated and eventually failure takes place. Though there is no life risk for pilot or damage to aircraft, but it leads to heavy cost as well as repair time. High strength and stiffness of the material is very important (Miracle, 2001). 2024-T4 aluminium alloy has been a choice for ventral fin structure. The inner structure comprises of a central root rib projecting normal to skin of fuselage while front and rear spar are in parallel direction to the fuselage skin. Honeycomb core and sheet complete the assembly. Design trade studies have been used to find the solution to ventral fin failure. These studies show that critical designing requires strength to high cycle fatigue (HCF) and excellent stiffness. Initial solution suggested to use graphite/epoxy skin above spar to increase thickness of the original 2024-T4 aluminium alloy, and a discontinuously reinforce sheet above Al-alloy spar. However, it failed due to cost issues. 6092 age hardenable aluminium alloy was optimized as matrix alloy for 17.5pSiC reinforced DRA. This material showed 40% higher specific stiffness over the baseline design. It removed torsional load on fin and restricted elongation of bolt hole. About 50% reduction in peak tip deflection was also observed. Ventral fins of DRA reduced the downtime as well as inspection and maintenance cost. It results in overall life cycle cost. Further, this composite has also been used to tackle the problem of cracking in fuel access door covers near the vertical tail root. In order to reduce stress at opening door fasteners were re-designed. Changed design was more compatible with improved HCF resistance. This design with changed material also provided improved bearing properties, higher strength and stiffness. Improved designing of doors and fasteners by DRA reduced the peak skin stress by 38%, and average skin stress by 10% and cracking issue was completely resolved (Miracle, 2001).

The helicopter blade sleeve has an important function of supporting centrifugal load of rotor blades to drive shaft. Hence, it requires a set of properties like excellent resistance to fretting fatigue, high specific strength, good fracture toughness and endless fatigue life. Rotating mass is key to performance and durability of Helicopter so reduction in rotating mass is likely to improve life and performance. If the original material is titanium alloy cost also becomes important. It has been replaced by forged DRA (2009/SiC/15p-T4). DRA has a fatigue strength of 270 MPa. The excellent strength, good fracture toughness, comparable specific strength to titanium alloy along with weight reduction of about 14 kg in rotating mass has made the DRA front runner. Lastly, it also reduces the cost of the part (Miracle, 2001).

Aero-propulsion

It is important to get maximum thrust from redirected air to move forward. The fan exit guide vane (FEGV) of high-bypass gas turbine engines has an important role of removing swirl component of bypassing air which may cause hinderance in forward motion. The primary design in commercial engines requires excellent resistance to air erosion due to particles, high specific stiffness, and ballistic response, however, support cost part is also important and cannot be ignored. The graphite/epoxy used for the application did not have adequate ballistic response, had poor performance due to airborne particulates erosion and rain. It increased service cost and even flight safety was at stake. Though, Ti-alloy foil on leading edges provided slight improvement on erosion aspect but no change in ballistic performance could be bought with highly expensive Ti-alloy. Finally, billets of P/M produced 6092/SiC/17.5p DRA were used as replacement. Its proper particle distribution after extrusion improved fracture properties. The DRA design exhibited seven times reduction in erosion and remarkable improvement in resistance to ballistic damage. This composite reduced the unit cost and increased the service life by three times, and also reduced repair and maintenance (Miracle, 2001).

Direction and velocity of exhaust gases is very important in efficiency of gas turbine engines and both of these are controlled by engine nozzle flap position through actuator and linkage devices. The actuator assembly consisting of a hydraulic cylinder and a metallic piston with linkage mechanism, drives the all divergent nozzle flaps. The piston must support large axial loads and also possess high stiffness. Precipitation hardened 13-8 Cr-Ni stainless steel solid rod has been the specified material. The piston rod operating temperature is about 450°C and it requires good fatigue strength, specific strength and stiffness. It has been replaced by MMC containing titanium alloy reinforced with SiC fibers. Titanium matrix composite (TMC) saves about 13.4 kg of weight and this being in aft end counter weights so it can also be removed/minimized which provides further weight saving. F110 engine nozzle has 24 nozzle flaps around the exhaust periphery. Every second nozzle flap requires one actuator via a nozzle link which amounts to total 12 nozzle link actuators of TMC for an engine. Inconel 718 was used for original link from a square tube. The TMC link saves weight by 2 kg per shipset and improves buckling resistance as compared to Inconel 718 component (Miracle, 2001).

6091/SiC/25p DRA has been the first composite to be used in the history of military aircraft application as avionics support racks. The primary requirements for the application is high electrical conductivity, good bearing strength, and isotropic stiffness. The graphite/epoxy replaced original structure was an aluminium alloy for weight saving, but this also lacked isotropic stiffness and bearing properties. Issue was tackled by several modes but other problems arose and success was not achieved. Finally, DRA solved the issue with minimum gage thickness extruded tubes. It provided good bearing strength along with the high intrinsic electrical conductivity and weight saving of 20% as compared to graphite/epoxy and 34% to original aluminium design. Reduced material costs led to reduced component cost (Miracle, 2001).

DRA's are used in naval aircrafts for hydraulic manifolds. These manifolds redistribute hydraulic fluid with high pressure of about 70 MPa to flight controlling surfaces. In addition, manifolds are subjected to impulse loading at an operating temperature of about 100°C. Material used should have near net shape processing capability, good resistance to HCF due to impulse loading and high specific strength. The initial material i.e., 7050 aluminium was not successful due to failing in burst tests so as replacement 2009/SiC/15w DRA with whisker reinforced was successfully used satisfying service requirements, but high cost due to whiskers and machining remained bottleneck. Alternatively, A206/SiC/40p DRA produced through pressure infiltration casting was also used. This can be produced with near net shape capability with 30%–70% vol. fractions SiC. The component produced by DRA provides weight saving, with lower CTE, superior wear resistance, and much better fatigue properties which is unique because in general Al-alloys have poor fatigue response in hydraulic fluid for pressures exceeding 34 MPa. Hence, DRA components are becoming replacement to titanium alloys in such applications due to much lower cost (Miracle, 2001).

Size-based

FRPs have replaced existing materials in many components in aircraft related applications. Composites are strong, fatigue resistant, damage tolerant, and have been shown to be very durable when the design of the component includes proper consideration for the operating environment common to the component. They satisfy designing and certification compulsions with mass reduction. Cost reductions, especially in aircraft life-cycle makes them ahead of other materials. Fibers or filaments are common reinforcements in composites which are used in aircrafts related components. Carbon, glass, aramid are common fibers but carbon is used most widely among these. These are generally used in epoxy base resin matrix (Wilhelm, 2001).

Composite components are used extensively on current commercial aircrafts weighing about 1500 kg, while smaller planes use approximately 680 kg. The vertical fin of the Airbus A310 was produced from carbon-reinforced epoxy as a production commitment and certified. A twin jet Boeing aircraft contains approximately 7450 kg of carbon- and fiberglass-composite material; 71% of this amount is carbon reinforced and it doesn't include the payload interiors. The majority of the carbon/epoxy quantity is an intermediate modulus fiber impregnated with a toughened epoxy base matrix used in floor beams, the horizontal stabilizer, and the vertical fin. On the 737, composites are used for control surfaces, fairings, and nacelle components for about 3% of the total structural weight of the aircraft. Individual composite parts are 20%–30% lighter than their metallic counterparts. Small, general aviation airplanes make extensive use of advanced carbon-, glass-, and aramid-fiber based composites up to 820–1360 kg per aircraft. Honeycomb sandwich structure is most common except for few parts. Structures like fairings, fixed wings, trailing edge panels are mostly sandwiched structures. Face sheets for panels are produced by only carbon or hybrid fibers. Composites are becoming important even in interiors applications. Apart from other requirements, now it is mandatory pass flammability resistance test and smoke and toxic-gas emission guidelines. Additionally, visible portions of interior components must meet stringent aesthetic requirements to satisfy the airlines and their customers. Most of the interior region like luggage bins, walls, ceilings, floors, lavatories, etc. are made of composite. Either, fiber reinforced epoxy or phenolic resin honeycomb sandwich structures are used. Apart from fire resistant properties interior components are required to have impact resistance, stiffness, and surface smoothness (Wilhelm, 2001).

Composites are most widely (about 40%) used in U.S. military related programs. Most military aircrafts use carbon-fiber-reinforcement in epoxy. Carbon fiber reinforced composites constitute about 26% of the structural weight of the U.S. Naval AV-8B aircraft. Components using composites are forward fuselage, wing box, elevators, horizontal stabilizer, rudder & other control surfaces, and over wing fairings. The wing skins is single piece laminate, mechanically fastened composite. AV-8B uses nearly 590 kg of carbon-fiber epoxy and reduces the weight almost by 225 kg. Carbon fiber composites constitute about 10% of F-18 aircraft structural weight and about 50% of surface area. These are used in wing skins, tail boxes, control surfaces, speed brake, doors and leading-edge extensions. At a production rate of four aircraft per month, the B-1B uses 127,000 kg per year of composite structure, i.e., 3040 kg per aircraft that results in weight savings of approximately 1360 kg on each bomber (Wilhelm, 2001).

Marine

FRP composites use started in boat building due to increasing timber cost. Seawater and marine organisms degrade the timber hulls and that ends up with high maintenance and repairing cost (Buermann and Della Rocca, 1960; Spaulding, 1966; Heller, 1967). It led to the use of composites in different marine crafts, and with time it got extended to lightweight structures on warships. Composites have large number of application in leisure craft, yachts, boats, ships, submarines, and offshore structures (Mouritz, 2001; Greene, 1990; Graner, 1982; Smith, 1990; Mouritz *et al.*, 2001).

Naval

The main objective to use FRP composites was to have lightweight, strong, corrosion resistant, and durable naval boats. US Navy used composites in large ships deckhouses, pipes, fuel and water tanks, submarines fairwaters and mast shrouds (Buermann and Della Rocca, 1960; Spaulding, 1966; Heller, 1967). Later, navies of many other countries also started using composites and just in decades time their use increased several folds in marine applications (Henton, 1967; Mäkinen *et al.*, 1998).

The problem of stiffness for low hull girder for small warships was resolved in early 1970s with the construction of the Royal Navy minesweeper HMS Wilton (Dixon *et al.*, 1972; Chalmers *et al.*, 1984). A thin FRP laminate shell stiffened with longitudinal and transverse frames, mostly of sandwiched structure solved the problem and hull girder with high stiffness was achieved. It's frame was single-skin design of composite construction. Other requirements of naval ships like good impact strength and underwater blast damage resistance were also fulfilled (Mouritz *et al.*, 2001). Apart from single skin hull, two other hull forms of composite have also been developed which consist of thick laminate hull and sandwich construction hull (Smith, 1990). FRP patrol boats became popular mainly due to reduced maintenance cost because of excellent corrosion resistance and light weight resulting in high speed and improved fuel economy. Composite reduces 10% weight as compared to aluminium and 35% as compared to steel (Goubalt and Mayes, 1996) but major drawback is nearly 30% higher cost. Composite propellers, propulsors, and propulsion shafts are also being worked out. Composites are expected to offer several benefits over metals in propulsion systems like low cost, reduced weight, lower magnetic signature, improved damping properties, and superior corrosion resistance. It is important to understand switching over from steel to composite in propulsion shafts because it will reduce weight by 25%–80% with same size and life-cycle costs will reduce at least by 25% due to lesser corrosion and fatigue problems. Though, at present the use is very limited but with time it is expected to increase several folds in applications including funnels, bulkheads, decks, watertight doors, machinery foundations, pipes, ventilation ducts, and components for diesel engines, pumps, and heat exchangers on large warships (Mouritz *et al.*, 2001; Goubalt and Mayes, 1996; Horsman, 1994; Kane and Dow, 1994; Macander, 1994; Foxwell, 1999; Womack, 1993; Pegg and Reyes, 1987; Searle and Shot, 1994; Wilhelmi *et al.*, 1986; Gagorik *et al.*, 1991; Phelan, 1995; Bhasin *et al.*, 1998; Suitt and Girona, 1993; Wilhelmi and Schab, 1977).

Offshore

Offshore drilling platforms are using FRP composites for quite some time, though these are used only in niche applications (Williams, 1990). Apart from cost cutting and outstanding corrosion resistance, composites also provide opportunity to reduce topside weight of offshore platforms. The important applications are accommodation modules, helicopter landing pads, and decks, where, weight saving of 30%–50% can be achieved. Currently, FRPs are used in low pressure pipes, diesel storage-, lube-, and utility tanks, walkway gratings, stair steps, handrails, cable ladders, fire protection panels, strengthening of primary steel structures, helicopter landing decks, etc. Composites use is expected to increase with time once economic and technical issues are resolved (Williams, 1990; Barnes, 1996; Mouritz, 2001; McConnell, 1996; Goldsworthy and Wiernicki, 1990; Godfrey and Davis, 1990; Gibson, 1993).

Thermal Management and Electronic Packaging

Advanced composites provide many advantages over traditional materials in thermal management and microelectronic packaging such as thermal conductivity more than double of copper, low CTE with tailorable capability, 80% weight saving, about 65% reduction in size, excellent strength and stiffness, less thermal stresses, increased reliability, simple thermal design, potential elimination of heat pipes, reduced cost and net-shape fabrication capabilities (Zweben, 2001a,b). Combining two or more constituents creates material with unique set of properties for which no example can be better than printed circuit boards (PCBs) for which dielectric properties are very critical. The most common PCB material, E-glass fiber-reinforced epoxy, was first developed over a half century ago. In addition to microelectronic packaging, composites are also suitable in other applications including optoelectronics and microelectromechanical systems (MEMS) (Schmidt and Zweben, 1989; Kelly, 1988).

Packaging parts are produced from several hundreds to thousands per annum. Copper- and aluminium based composites are most common, however, discontinuous thermally conductive carbon-fiber-reinforced polymers are also not far behind. Microelectronic packaging components include carriers, hermetic microwave packages, power semiconductor packages, liquid cooled PCB cold plates, heat sinks, thermal straps, enclosures, and support structures (Sangha *et al.*, 1997; Thaw *et al.*, 1987a,b,c; Zweben, 1988; Schmidt and Zweben, 1988; Zweben, 1992; Miller, 1995; Shih *et al.*, 1994b; Montesano, 1996; DiNardo *et al.*, 1990; Zweben, 1995; Fleming *et al.*, 1995; Chung, 1995; Zweben, 1998a,b,c,d,e; Chung and Zweben, 2000; Zweben, 1999a,b). Spacecraft applications include radiators, radiator panel thermal doublers, and battery sleeves. The composite electronic packaging components are being used in commercial and aerospace such as electric vehicles, motor controllers, cellular telephone ground stations, laptops, and also in microwave and power supply subsystems. Composites are key to integrated multifunctional structural/electronic systems (Kuhn *et al.*, 1999; Zweben, 1999a,b; Rawal and Goodman, 2000; Rawal, 2000; Zweben, 2001a,b).

Sports and Recreation

The advantages of composite construction have been applied to equipment for a wide range of sports and recreation activities. These advantages include strength, ductility, stiffness (modulus), and low density (Easterling, 1993). Laminated wood construction or plywood, was later used in various forms for sport and pleasure boating, as well as in tennis rackets and the delicate

glued flyrods constructed of tapered bamboo sections. More recently, the term composite has been associated with such materials as fiberglass, carbon fibers, silicon carbide platelets and whiskers, and aramid fibers. These materials have greatly broadened composite use in sports and recreational equipments by introducing filamentary materials whose tensile strength to weight and stiffness properties are far superior than those of wood, steel, and other more common materials.

Bats, rackets, and clubs

Nowadays softball teams and college baseball teams are generally using composite bats. These bats are made of a graphite-reinforced polycarbonate. The graphite-reinforced bat is lighter and durable just like aluminium and has sound of wood. The bat is extremely resistant to impact which is very important property of a bat. It has been tested against air cannon which rockets balls at 290 km/h. The graphite-reinforced resin shell is light, strong, and stiff. The weight savings allows greater options in the placement of the urethane filler. Graphite also helps to reduce vibrations as well as shock and tingling feeling in hands given by ball. The centre of gravity of the bat also can be moved down the handle which allows the hitter to generate more bat speed. With a larger sweet spot and greater bat speed, sports person can hit the ball to far more distance (Anonymous, 2001).

Many professionals smash the tennis balls over 160 km/h speed. It is a game of speed as well as control. Hitting and receiving ball at high speeds requires high level of concentration and great degree of control over racket. Rackets made of graphite-fibers composites provide better control of ball without using excessive physical energy. The graphite rackets are much stronger and stiffer while comparing with metal or wood. These rackets also have lesser head torque that provides a solid feeling over a larger area of the racket head to a player. A graphite racket dissipates less energy, allowing the player to hit the ball with greater speed. Weight and balance of the racket can be tailored according to individual player's needs. The endurance life of a graphite racket is also more than that of conventional rackets. Composite rackets can also be made with a combination of unidirectional and braided carbon fibers. Braided carbon fibers restricts twisting of racket. Rackets are made of about 65% carbon, 30% glass, and 5% aramid. Graphite provides stiffness with brittleness; fiberglass provides flexibility with toughness. Rackets are also made out of 84% carbon, 12% aramid, and 4% alumina fibers. It provides the comfort of ceramic and performance of carbon. Carbon provides controlled power with good combination of stiffness and strength. Aramid provides damping property and prevents "tennis elbow" (Anonymous, 2001).

Composite golf shafts, reinforced with graphite fibers, helps golfer to have better control over the game. It is 40% lighter than conventional one, hence, allows weight to be added to the club head, while still have lesser overall club weight. Larger head weight ball is driven farther while lighter side of the club helps the golfer to remain accurate with his shots. These golf shafts are usually produced by either roll wrapping or filament winding. Golf club shafts are made of combination of carbon- and boron-fiber reinforcement. Larger fiber diameter of boron as compared to carbon helps to serve better when used longitudinally (Anonymous, 2001).

Bicycling

Cycling need training, endurance, strategy, and well-designed equipment. Bike racing also need high level of concentration. Energy should not be wasted in unnecessary moves. During pedalling, power should be transmitted all the way, and it is obvious that lighter the bicycle faster it will go. Carbon-fiber-reinforced bicycle frames are lighter than aluminium and stiffer than steel. Hubs and wheels are designed from glass fiber reinforced nylon. Normal drive plates and drive chains have been replaced by PMC. Bicycle frames are composed of G/epoxy composite allowing flexibility in designing with reduced drag. They also provide damping against vibrations. The suspension system is made of graphite and glass which reduces shock. Graphite braided bicycle frames are used to achieve high level of strength and torsion resistance or twisting. In another design with carbon/epoxy frame there is no seat tube. This single-piece frame with integrally moulded tubes uses a passive suspension system that provides smooth and aerodynamic ride. In another single-piece design, true airfoils are used to reduce the drag. It has hybrid reinforcement of carbon and polyethylene (PE). Carbon fibers provide stiffness, and PE is responsible for lightweight strength. PE fibers resist shocks and fatigue. Stress concentration regions are absent due to unavailability of bonded joints. Composite frames are more flexible and easier on bumps, so helpful in long races. It is also important that composite frames provide three to four times better fatigue and crushing strength than steel. Air resistance is the major cause to slow down the speed of cyclist and it amounts to 90% of the total force. C-C composite tubes are used to provide airfoil shape to bicycle frame which helps to reduce the drag. Boron-reinforced aluminium is also used for frame and these are lighter, stiffer and stronger than aluminium. Composite spoke and disc wheels are also used. Carbon- fiber-reinforced polymer composites in combination with titanium, have been used (Anonymous, 2001).

Carbon-fiber reinforced nylon has been used for spin bicycle wheels. The spin wheel three-spoke is a one-piece hollow construction. It is stronger and lighter with half the cost of traditional carbon/ epoxy wheel. Aramid-fiber composites are used in disc wheels. The aramid wheels reduce the wind resistance of a normal bicycle wheel. Aramid-reinforced tires are lighter than 0.1 kg and these feather-light wheels and tires help to reduce rolling friction to a large extent (Anonymous, 2001).

Environment-Based Applications

High Temperature

High temperature polymers are being used in applications such as aerospace, electronics, and other applications demanding elevated temperature, physical and mechanical properties. Major product forms of such polymers include fibers, coatings,

adhesives, foam, film, insulating paper laminating resin solutions, wire enamels and moulding powders. In the beginning, PMCs with fiber reinforcement were used only in high temperature non-structural (non-load bearing) components. However, with in situ polymerization of monomer reactants (PMR) polyimides (Serafini *et al.*, 1972; Serafini *et al.*, 1973; Serafini, 1976) and their commercialization, the fiber-reinforced PMR polyimide based on PMR-15 became increasingly acceptable as high-performance engineering material for structural applications. Other resins that have found use in composites for high-temperature applications include phenolics and bismaleimides (Serafini, 2001).

In a composite, matrix must bind the fiber reinforcement for a material to function as a viable matrix. It should also be transferring load, provide processability and environment stability. Organic polymers generally melt below 200°C. Preparing high-temperature polymers requires incorporation of structural units of high stability in the polymer chain. These structural units absorb thermal energy and contain minimum oxidizable hydrogen atoms. Apart from high temperature capabilities polymers are also resistant to processed into structural components. Composites prepared from these polymers exhibit too much voids, poor translation ability of fibers, poor high-temperature mechanical properties, as well as thermo-oxidative stabilities. Though thermal ability could be improved but processing part remained neglected (Serafini, 2001).

High-temperature condensation-type polyimides commercialized in 1960s and became single competitor for resin-matrix applications. These materials had processing problems but these had very good high-temperature properties, easy availability and low cost. The initial applications these fiber-reinforced polyimides were radomes for advanced aircraft (Poveromo, 1983) and for sound-suppression panels in the engine nacelles of subsonic commercial transports. Both were secondary structural applications. It was observed that high void content of such polyimides could be desirable for the sound-suppression panels (Serafini, 2001). Major breakthrough in high-temperature resins was to develop polyimides that could be cured by an addition reaction (Lubowitz, 1970; Burns *et al.*, 1968). Earlier studies (Serafini *et al.*, 1972; Delvigs *et al.*, 1972) have shown ability and versatile nature of the PMR approach. Fiber-reinforced PMR composites have been fabricated by high pressure as well as low pressure moulding cycles (Vannucci, 1977).

The development of PMR-15 resin increased the number of applications of composite components for high-temperature. Earlier resin systems had serious size and thickness limitations for potential applications; however, development of PMR-15 opened-up large avenues for design engineers for large, complex and thick sections components. PMR-15 became interesting material for military propulsion community, due to the high operating temperatures within the low-pressure system. Its high weight savings led its use in both rotor blades and stator vanes. The blade was the first structural airfoil component which could be developed with PMR-15 and could be reinforced with high tensile strength graphite fiber. The blade was designed and developed for ultrahigh-speed fan stage (Halle *et al.*, 1977; Cavano, 1974). The thickest section of the composite consisted of 77 plies of arranged in different fiber orientations. The torsional stiffness requirements could be met with different orientation of fibers with height. Although some internal defects were observed in the blade while going for LCF and HCF but PMR-15 got established as a processible matrix resin. Another application of PMR-15 composites in rotating components was the fourth-stage compressor blade shells and spacers of supersonic wind tunnel. Almost 11,000 kg fiberglass-PMR-15 were used for the application and total amount was equally divided for 360 blade shells and 600 blade spacers. The success with small airfoil components created interest to use PMR-15 in large static structures. The most aggressive use of composite was to apply it in propulsion system. To achieve the goals for low weight, low noise, clean emissions, and improved efficiency, composites were extensively used in the vane frame, fan blades, integrated nacelle, external flaps, containment, inlet, and inner core cowl. The blades, frame, and nacelle components were produced out of carbon- epoxy tape and fabric; the containment with aramid fabric; and the inner core cowl with graphite-PMR-15 fabric. The high-temperature at core cowl was due to radiant heating at shutdown. The absence of airflow raised the temperature approximately to 315°C. The core cowl was a honeycomb sandwich structure. Polyimide reinforced with fiberglass has been used for core. To control acoustic emissions, the flowpath of the core cowl was perforated with 0.5 mm holes to have 10% porosity level. The use of cowl for 300 h without any degradation established the feasibility of using graphite-PMR-15 composites in large structures (Adamson, 1979; Stotler, 1979; Serafini, 2001).

Material-Based Applications

Carbon–Carbon Composites

Carbon–carbon composites have been utilized for applications requiring ablation and high temperature stability (i.e., rocket nozzles and exit cones) or wear resistance at moderate temperatures (i.e., aircraft brakes). In mid-1980s, these were considered stiff thin walls. This interest has led to the investigation into other properties of carbon that could be exploited in a carbon–carbon composite. One area that has been explored is carbon–carbon for thermal management. Many systems require heat control, either by rejecting or by absorbing “waste heat energy.” This has led to much interest in carbon–carbon for such applications as electronic thermal planes; thermal doublers, radiators, and thermal and shields; and heat exchangers. Carbon has many characteristics that are appealing for many different thermal management applications. It's very low density, a tailorable thermal conductivity, and very low CTE with acceptable mechanical properties has made it important in large number of applications. This implies that a carbon composite can be fabricated with high specific thermal conductivity and low CTE. These properties are very desirable for many different thermal management applications (Kearns, 2001).

Thermal planes for electronics is one among many thermal management applications of C–C composites. Electronic board need to maintain a temperature at which they can properly operate, so the thermal plane should be capable of dissipating heat i.e.,

it should have good thermal conductivity. The thermal plane should also have low CTE so that it doesn't expand much under heat loads. Otherwise wearing of board may attach the chips to electronic board. High stiffness of material is important to restrict transmission of vibrations to electronic board that reduces fatigue load on the joints and also reduces deflections. Electronic boards having less deflection under load can be easily packed together without impact risk. This allows a designer to provide more electronic capability within small volume. C-C is very suitable for such application with low CTE and high thermal conductivity. It reduces electronic packaging temperature by 4–16°C, as compared to conventional aluminium thermal plane. This temperature reduction increases the reliability of packaging. Further, its high stiffness restricts the deflections during vibrational loading. Its low density also suits electronic thermal planes.

Spacecraft thermal doublers have same function as that of thermal planes, but it has different mechanical requirements. The thermal doubler removes the heat from different parts of spacecraft and allows its radiation to space that requires material with high thermal conductivity. A light weight thermal doubler is needed to be attached to components requiring low stiffness to reduce vibration. The weight of spacecraft considerably affects the cost of launching a spacecraft. Hence, designers need a low-density material to meet the performance. C-C composite fulfils all the requirement of a thermal doubler properties. Choosing a low-modulus fiber of high conductivity with appropriate architecture, composite can be prepared with low-modulus. C-C thermal doublers have been used on some spacecraft. Spacecraft thermal shields constitute a different type of thermal management application. Its shields rest of the spacecraft from useless heat of the propulsion system. Hence, it requires high-temperature stability, low density, and high stiffness. It also requires stability at high temperatures to take care of heat which is generated by the propulsion system. It should also be able to respond well to high vibrational loading from the acoustics. C-C composites provide a thermal shield almost with 50% weight reduction over metallic ones. These composites have proven record to maintain temperature stability and stiffness which ensures their successful performance in thermal shields. Spacecraft radiators also need a material with ability to conduct waste heat from a source to space. Its function is to maintain all attachments cool enough to operate properly, hence, high thermal conductivity, good strength & stiffness, and low density are the main requirements of a material. A carbon-carbon composites possesses most of the needed properties (Kearns, 2001).

Different heat exchangers are used on different systems in an aircraft. The operating conditions touch temperature as high as 650°C with low to high fluid pressures. The specific conditions depend on the location and functioning of heat exchanger in the aircraft. The function of the heat-exchanger material is basically to dissipate heat from the hot fluid to the cold. The material requires high thermal conductivity, good corrosion resistance, reasonable strength, stiffness, with low permeability, and moderate temperature capability depending on location and functioning of heat exchanger. Corrosion resistance is needed to take care of the fluids running through heat-exchanger channels. For aircraft flying over the oceans ingests salt spray, therefore, resistant to saltwater corrosion or maintenance costs will be high. For the lower-temperature heat exchangers with air fluids, carbon-carbon may be the ideal material due to its unique properties. Corrosion doesn't bother at temperatures below 370°C. In higher-temperature heat exchangers weight savings and high thermal conductivity of carbon-carbon offers the payoff of a higher-performance. But many issues need to be addressed in having a C-C carbon-carbon heat exchanger. The core consists of parting plates and fins which is a delicate design for composites. The core structure with carbon-carbon must be highly automated for better reproducibility, quality and low cost. Carbon starts oxidizing in the presence of oxygen at high temperature which require oxidation protection schemes for heat exchangers working above 370°C (Wilhelm, 2001; Schmidt *et al.*, 1999; Shih *et al.*, 1994a; Rawal, 2000; Kearns, 2001).

Ceramic-Matrix Composites

Ceramic-matrix composites' (CMCs) applications fall in four major groups (Davis, 1995, 2001; Abraham, 2000):

- Cutting tool
- Wear
- Aerospace and military parts
- Other applications

CMCs involves discontinuous reinforcement of particles, whiskers, chopped fibers, etc. into polycrystalline ceramic, glass, or glass-ceramic matrix. From industrial application viewpoint, alumina (Al_2O_3) is the most important matrix material, though, such composites have also been produced from silicon carbide (SiC), silicon nitride (Si_3N_4), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), and aluminosilicate matrices while important reinforcements have been SiC, zirconia (ZrO_2), and titanium carbide (TiC) etc. (Davis, 2001).

Cutting tools

Both particulates and whiskers are widely used as reinforcements. Al_2O_3 is used in cutting tool inserts. The development of these composites as tool materials has been based on high temperature ceramics as well as on process developments for applications related to automobile gas turbine and high temperature structural applications. Al_2O_3 -TiC Composites can produce a cutting tool with superior hardness and fracture resistance if these are hot-pressed or hot isostatically pressed consisting of approximately 70%

Al_2O_3 with 30% TiC particulate. These are known as black ceramics due to their dark colour, which is due to the presence of TiC (Davis, 2001).

The hard-refractory particles when dispersed increase the hardness of these composites for the temperature up to 800°C comparing to monolithic oxide ceramics. Further, impediment, deflection, and/or branching of cracks due to dispersed hard particles increase the fracture toughness and bending strength. Combination of higher hardness with high toughness improves the resistance to abrasion and erosion considerably. High thermal conductivity combined with low CTE of composites exhibits improved thermal shock resistance as compared to monolithic oxide ceramics. TiC particles oxidize and lose reinforcing properties as the temperature exceeds 800°C, which weaken the composite. This phenomenon needs to be taken into account while selecting cutting conditions like speed, depth, and feed rate. The HIPed Al_2O_3 -TiC composite tool grades are used for interrupted cutting, finishing etc. of high-temperature superalloys, hardened steels up to 50 HRC, chilled irons with hardness up to 60 HRC and gray and ductile cast irons with high hardness. Al_2O_3 -SiCw is the recent alumina base tool material. In these 20–45 vol% SiC whiskers are added and subsequently it is hot-pressed which provides good toughness. The whiskers have high thermal conductivity and low CTE than Al_2O_3 . It leads to improved thermal-shock resistance. The SiC whiskers improve fracture toughness. High level of energy is required to pull out the whiskers, and this greatly inhibits crack propagation (Wei and Becher, 1985; Tieg and Becher, 1986; Jun and Smith, 1994; Davis, 2001).

The Al_2O_3 -SiCw tool grades composite are used for rough turning of alloys, hardened steels etc. Their main primary application is roughing, finishing, and milling of difficult-to-machine alloys and superalloys parts. They provide much higher cutting speeds and longer tool life. Si_3N_4 -base particle-reinforced and whisker-reinforced composites have also been tested as cutting tool materials (Buljan and Sarin, 1981, 1982; Sarin and Buljan, 1983; Baldoni and Buljan, 1986; Hampshire, 1991). The addition phases such as TiC, TiN, and HfC to a Si_3N_4 matrix improves hardness. Hot-pressed composites, reinforced with 10–30 vol% SiC whiskers exhibit higher fracture toughness than their unreinforced parts. Despite many advantages, Si_3N_4 -base composite tool materials are yet to reach commercial viability (Davis, 2001).

Wear-resistant

Ceramic toughened through zirconia particulate are finding applications in bushings, bearings, precision balls, valve seats, die inserts etc., where both friction and wear resistance are improved. One example is zirconia-toughened alumina, or ZTA, where Al_2O_3 is continuous phase with 70–95 vol%. Zirconia particulate additions from 5% to 30% represent the second phase (Davis, 2001).

The microstructure and mechanical properties can be tailored for particular application. High ZrO_2 content improves strength and fracture toughness, but hardness and elastic modulus are slightly reduced. Strengths of 1050 MPa and fracture toughness of 8.0 MPa are achievable. Wear properties also find improvement in certain applications. Such compositions of ZTA have been used in transportation applications because these can withstand erosion, abrasion, corrosion, and thermal shock. ZTA are also used in cutting tool inserts and abrasive grinding medium. ZTA have also shown important properties related to thermal shock applications (Davis, 2001).

Coarse SiC particles reinforcement Al_2O_3 matrix composite have shown good slurry erosion resistance (Weinstein and Rossing, 1990; Rossing and Rocazella, 1990), hence these are used in slurry pump components, hydro-cyclone and chute liners, and also in materials handling systems. A similar type of composite is also used in armor applications. SiC particle reinforced Al_2O_3 matrix composite has also been optimized for sliding and rolling contact wear application (Urquhart, 1991). It has fine SiC particles with modifications in Al_2O_3 ceramic matrix. Favourable prototype test results have been observed for piston, engine cam, follower, rollers (Davis, 2001). CMC has also been accepted in aluminium can-making equipment and associated tooling. Products made from CMCs include punches, redraw dies, ironing dies, pressure rings, domer tooling, cupper tooling, stripper tooling, necker tooling, trimmer blades, etc. Materials used for these applications include transformation-toughened zirconia, Al_2O_3 -SiCw, and Si_3N_4 -SiCw (Davis, 2001).

Aerospace

Most of the CMCs which are in developing stage for aero-structural applications, are using continuous fiber. However, attempts have been made for discontinuously reinforced CMCs. ZrB_2 platelet reinforced ZrC composite is one such example. It forms by reaction of Zr with B_4C powder in a graphite mould at about 1850–2000°C (Johnson *et al.*, 1989; Davis, 2001).

Composite with 3–12 vol% Zr has high flexural strengths of 800–900 MPa, Weibull moduli of 20–30, and fracture toughness of 12–15 (Claar *et al.*, 1989). Platelet toughening mechanisms leads to toughness values of 10–12 MPa with very low metal content. The increase in metal content increases the toughness in which ductile rupturing of metal ligaments during crack propagation also contributes. This composite has been successful even at very high temperature i.e., > 2700°C, definitely for a short time application like in rocket engines. The high refractory nature of the ZrB_2 and ZrC phases and the excellent thermal shock resistance of the composite has contributed to these excellent results. These materials have limited resistance to high-temperature oxidation and creep, hence, long term application is not feasible. These composites are also being under evaluation for prosthetic devices based on their strength, fracture toughness, wear resistance, and biocompatibility. Mechanical seals and other special wear parts are other prospective applications (Davis, 2001).

Space shuttle

Success of the space shuttle orbiter need development of a fully reusable thermal protection system (TPS) which should be capable of being used for up to 100 missions. During re-entry of the shuttle into the earth's atmosphere, surface goes up to 1260°C, where, tiles of ceramic are used. The nose tip and the wing leading edges, where reinforced C–C composites must be employed because it has to bear even higher temperature of 1650°C. The tile, coated with a high emittance layer of glass functions to dissipate heat and also acts as an insulator to block heat to the structure. The felt mounting pad i.e., the strain isolator pad (SIP) isolates the tile from the thermal and mechanical strains. The filler bar, also a nylon felt material coated with silicone rubber, protects the structure under the tile- to-tile gap from overheating. The substructure consists of aluminium alloys or graphite-epoxy composites (Korb *et al.*, 1981; Davis, 2001).

Heat-resistant

This CMC also uses direct metal oxidation to form composite of SiC particles in Al₂O₃ matrix. It has been used in high temperature components of furnace and heat exchanger. It uses very fine SiC particles and parent metal. Processing criterion is such that optimizes mechanical properties and high temperature stability. High temperature strengths tests have exhibited that holding at 1500°C even for thousand hours hardly affects properties (Davis, 2001). Continuous fiber ceramic composites (CFCCs) are the most recent advanced ceramic. The continuous fibers improves fracture toughness by overcoming brittle nature of the composite. The operative mechanisms to resolve the problem are namely, deflection and bridging of cracks through fibers and pull-out of fiber from the matrix. Though, the cracks may generate in the matrix, but the fibers continue to carry the load and avoid the catastrophic behaviour that is familiar in ceramic materials (Davis, 2001).

The most common matrix materials for CFCCs are SiC, Al₂O₃, Si₃N₄, mullite, and aluminosilicates and the fiber is SiC, although Al₂O₃ and carbon fibers are also used. Fiber may be as high as 35–50 vol%. The high-temperature stability, corrosion resistance, and toughness of CFCCs make them suitable for a wide range of applications in both the aerospace and industrial sectors (Craig, 1999; Wessel and Long, 2000; Effinger *et al.*, 2000; Davis, 2001). The major applications include:

Turbine engine components in which SiC–SiC and Al₂O₃–SiC composites industrial, and aeronautical engine applications. Radiant burner screens use SiC–SiC reverberatory screens for natural gas burners. Immersion heater tubes also use SiC–SiC composite burner tubes. The CFCC is not wetted or chemically attacked by the molten aluminium. Hot gas filters use Al₂O₃–Al₂O₃ composites in advanced coalfired energy applications. Turbine disks for rocket engines use integrally bladed disks for rocket engine turbopumps of carbon fiber reinforced SiC. Other potential applications for CFCCs include heat exchanger tubes, armor, pipe hangers for petroleum refining, submersible pump housings for chemical processing, etc.

Conclusion

Industrial use of composites started nearly fifty to sixty years back with very limited applications of polymer-based composites. With time it has gone far off in the form of variety as well as applications. Organic, metal and ceramic matrix composites are being used in almost all avenues of life due to tailorable capability. Though, comparing with organic and metal matrix composites, ceramic matrix composites have lesser applications due to brittle nature and limitations of processing routes. In time to come with innovative processing techniques, CMCs growth is likely to increase due to its high temperature capabilities.

See also: Sustainable Cutting Fluids: Thermal, Rheological, Biodegradation, Anti-Corrosion, Storage Stability Studies and its Machining Performance

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System Optimization for Control of Solid Waste

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Introduction

The issue of climate change has become a subject of intense worldwide interest. Previous studies showed that the most significant increase of energy consumptions and carbon dioxide (CO₂) emissions is taking place in cities, where rapidly expanding populations enjoy higher living standards and material affluence (Fong *et al.*, 2009; Sethi, 2015). Urban building system assumes significant environmental and ecological implications in terms of a contribution of emissions of CO₂ and other greenhouse gases (Atmaca and Atmaca, 2015). Thus, dealing with the issue of CO₂ emissions, it is vital to focus on reducing emissions from the cities. In spite of the fact that cities are the main sources of CO₂ emissions, presently there are still no specific measures directly addressing the global warming issue in the urban planning process. Urban trees are important components of the landscape and offer numerous benefits. Urban trees act as a sink for CO₂, helping to offset carbon emissions from urban areas by removing the greenhouse gas from the atmosphere through photosynthesis (Zheng *et al.*, 2013; Ren *et al.*, 2012). In order to effectively quantify CO₂ fluxes from urban forests, future research needs to integrate data from a combination of methodologies collected at a range of scales (Weissert *et al.*, 2014). Annual CO₂ exchanges are significantly different between sites, demonstrating the impacts of increasing urban density on the CO₂ flux to the atmosphere (Ward *et al.*, 2015).

The expansion of urban agriculture assists in reducing CO₂ emissions not only by producing food but also by reducing the amount of food transported from farming areas and therefore reducing the food mileage. The largest CO₂ reductions can be achieved by giving preference to the crops that are conventionally grown in energy intensive greenhouses or air-freighted before reaching the end-user (Kulak *et al.*, 2013). From the perspective of CO₂ reduction effects in the transportation sector, urban agriculture is expected to produce a considerable effect in diverse aspects such as the habituation of green growth, self-sufficiency, and food security (Lee *et al.*, 2015).

To evaluate the dynamic behaviors of the energy consumption and CO₂ emissions, a few of interdisciplinary studies have been conducted (Krey *et al.*, 2012; Chen *et al.*, 2012; Fang *et al.*, 2015). In study (Sun and Xu, 2016) was examined the carbon dioxide emissions and its influential factors through the proposed algorithm and the statistical method, providing a theoretical support for further measures to reduce emissions. The aim of the study (Russo *et al.*, 2015) was to develop a method to calculate carbon dioxide storage and sequestration at the streetscapes level using field data, an existing tree inventory and available region-specific allometric equations. Rich households generate more emissions per capita than poor households via both their direct energy consumption and their higher expenditure on goods and services that use energy as an intermediate input (Golley and Meng, 2012). The results revealed that human disturbance played the dominant role in influencing the carbon stock and density of forest patches close to the locations of human activities. In forest patches far away from the locations of human activities, natural forest regrowth was the dominant factor affecting carbon stock and density. Rapid urbanization increases carbon dioxide emissions both in the short-run and in the long-run (Sheng and Guo, 2016).

In this investigation adaptive neuro-fuzzy inference system (ANFIS) (Meng *et al.*, 2014) was used to detect the influence of population growth, urbanization, forest and agriculture land areas on the CO₂ emission prediction. The main goal is to estimate CO₂ emissions where there are lack of data. It can be challenge when developing inventory method for local communities, due to limited data. Therefore in this study the main aim is to detect which energy source has the most influence on the CO₂ emission prediction.

Methodology

Statistical Data and Study Area

Currently, the increased greenhouse gas concentrations in the atmosphere are one of the most pressing environmental problems. CO₂ is an important green-house gas and a major driver of climate change effects, as a result the predicted global temperature rise will be proportional to the total amount of CO₂ emitted. In recent years, increases in carbon dioxide concentrations are mostly due to rapidly increasing population energy use, and emissions from vehicular traffic. In fact, half of the world's population is living in cities and in Europe alone, it is estimated that around 70% of the EU population – approximately 350 million people live in urban agglomerations of more than 5000 inhabitants.

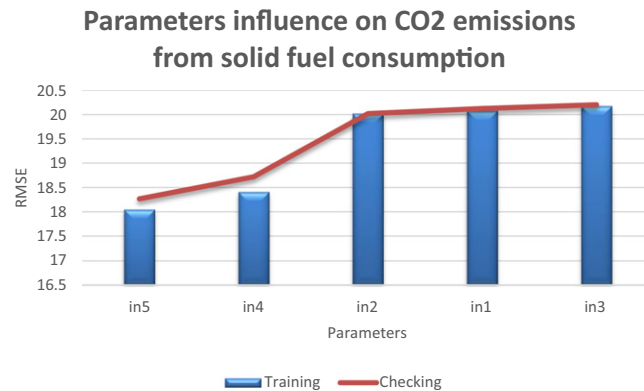
Table 1 shows inputs and output parameters which were used in this study. The dataset was taken from World Bank database for European Union countries. CO₂ emission is analyzed separately for solid fuel consumption.

ANFIS Methodology

Fuzzy inference system in MATLAB software is employed in the whole process of the ANFIS training and evaluation. In the process of identification of variables in the ANFIS architectures, the hybrid learning algorithms were applied. The functional signals progress until the 4th layer whereby the hybrid learning algorithm passes. Further, the consequent variables are found by the least squares estimation. In the backward pass, the error rates circulate backwards and the premise variables are synchronized through the gradient decline order.

Table 1 Input and output parameters

Inputs	Parameters description
Input 1	Rural population growth (annual %)
Input 2	Agricultural land (% of land area)
Input 3	Forest area (% of land area)
Input 4	Population growth (annual %)
Input 5	Urban population growth (annual %)
Output	CO ₂ emissions from solid fuel consumption (% of total)

**Fig. 1** Parameters influence on CO₂ emission prediction.**Table 2** Parameters influence on CO₂ emissions prediction from solid fuel consumption

Input 1	Input 2	Input 3	Input 4	Input 5
Input 1 trn=20.0839, chk=20.1240	trn=19.2803, chk=19.4741	trn=19.3473, chk=19.7549	trn=17.1679, chk=17.7554	trn=17.4268, chk=17.9994
Input 2	trn=20.0249, chk=20.0172	trn=16.6917, chk=16.7652	trn=17.4772, chk=17.7721	trn=16.6956, chk=16.9941
Input 3		trn=20.1805, chk=20.1998	trn=18.2306, chk=18.5132	trn=17.7790, chk=17.8881
Input 4			trn=18.4111, chk=18.7195	trn=17.3881, chk=18.6605
Input 5				trn=18.0497, chk=18.2643

Results

A searching procedure was performed in order to choose the inputs with the most impact and influence on the output parameters (CO₂ emission prediction). **Fig. 1** shows the urban population growth is the most influential parameter for CO₂ emission prediction from solid fuel consumption.

Table 2 shows the numerical results for all single parameters influence on the CO₂ emission prediction. Also the **Table 2** show the combinations of the two parameters influence on the CO₂ emission prediction. The bolded numbers represent the parameters with the highest influence on the CO₂ emission prediction. For example the combination of agricultural area and forest area form the most influential combination for the CO₂ emission prediction from the CO₂ emission prediction from solid fuel consumption. Generally the agricultural area is the most important parameter for the CO₂ emission prediction.

Conclusion

The global warming, mainly sourced from the human induced emission of CO₂, is one of the major environmental threats that we are facing in the 21st century. Therefore, this study aims at examining the relationship between rural population growth, urban population growth, population growth, agricultural land and forest area and CO₂ emission in European Union countries. Prediction of the future CO₂ emission is complex due to the many indicators and factors. Therefore in this study was proposed a new

approach to overcome the forecasting difficulties of the CO₂ prediction by removing some unnecessary input parameters. The main goal was to analyze the influence of different energy sources on the CO₂ prediction.

Results shown that for the CO₂ emission prediction from solid fuel consumption the most influential parameter is urban population growth.

See also: Metallic Materials From E-Waste. Modeling of Information System for Solid Waste Management

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Technology for Producing Briquettes From Wet Biomass

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Introduction

Energy is one of the most fundamental parts for any country and it is known as a strategic commodity. Any uncertainty about its supply can threaten the functioning of the economy, particularly in developing economies.

Energy services could be greatly improved by use of agricultural biomass in small-scale combustion units. Wood pellets are a reliable and proven fuel to be used in small-scale combustion units. However, these units should preferably be able to use different types of biomass depending what it is locally available. Therefore, studies have been focused on exploring the suitability of using agricultural residues for small-scale heat and power generation using direct combustion. Steam-treated pellets can help to address technical barriers that limit the uptake of pellets as a fuel for electricity generation, but there is limited understanding of the cost and environmental impacts of their production and use.

A modified Hartmann dust explosion tube was employed to determine the Minimum Explosible Concentration (MEC) and the flame speed for three Pakistani agricultural wastes: bagasse, rice husk and wheat straw (Saeed *et al.*, 2015) where it was shown the lean limits for these pulverized agricultural waste biomasses were comparable to that of pulverized wood but were much leaner than those for coal and hydrocarbon fuels, which indicate that these biomasses are highly reactive. In study (Cardozo *et al.*, 2014) was compared the combustion of different agricultural residues in a single unit designed for wood pellets. In study (McKechnie *et al.*, 2016) was investigated life cycle environmental (greenhouse gas (GHG) and air pollutant emissions) and financial implications of electricity generation from steam-treated pellets, including fuel cycle activities (biomass supply, pellet production, and combustion) and retrofit infrastructure to enable 100% pellet firing at a generating station that previously used coal. Impacts of retrofit infrastructure become increasingly significant at lower generating station capacity factors, further favoring steam-treated pellets for both environmental and financial metrics (McKechnie *et al.*, 2016). In study (Nilsson *et al.*, 2011), the costs and energy requirements for the production of pellets from agricultural raw materials were analyzed. The energy use in manufacturing pellets from air-dried crops was generally no higher than when moist sawdust was used as the raw material. The objective of work (Carvalho *et al.*, 2013) was to evaluate the technical and environmental performance of a 15 kW pellet boiler when operated with different pelletized biomass fuels, namely straw (*Triticum aestivum*), Miscanthus (*Miscanthus _ giganteus*), maize (*Zea mays*), wheat bran, vineyard pruning (from *Vitis vinifera*), hay, Sorghum (*Sorghum bicolor*) and wood (from *Picea abies*) with 5% rye flour. The investigation in the international market shows that mixed biomass pellets are promising fuels and with the appropriate support these fuels have many prospects for the future (Karkania *et al.*, 2012). The use of biomass pellets would not only create new market opportunities for agricultural industries, it would also reduce dependence on coal, as well as the greenhouse gas emissions associated with coal use (Karkania *et al.*, 2012). In paper (Tauro *et al.*, 2018) was examined the potential for biomass pellets to become a sizable low-carbon, renewable energy source that could compete with and substitute fossil fuels in specific economic sectors in Mexico where it was estimated that the market energy potential for pellets from currently available agricultural and forest residues in Mexico is between 131 and 233 PJ/yr, with total costs ranging from 6.3 to 12.8 USD/GJ. In paper (Dai *et al.*, 2015), a ceramic foam burner with embedded alumina pellets was designed, which set different shapes of tubes by taking can advantage of the discrete pellets. An experimental system was built to study the effects of the pellet diameter and pellet location on the combustion of low-concentration coal mine methane (LCM) (Dai *et al.*, 2015). Results indicates that the heat transfer features of 13-mm pellets are more similar to those of 10-PPI ceramic foam compared with 6-mm pellets and 9-mm pellets (Dai *et al.*, 2015). The combustion performance in a double-layer burner packed with alumina pellets of different diameters was experimentally studied in article (Gao *et al.*, 2012). In study (Qu and Feng, 2015), methane/air combustion in a two-zone catalytic alumina pileup-pellets burner with equivalence ratios varying from 0.55 to 0.70 was researched. Torrefied biomass has several benefits, such as higher energy density, good grindability, higher flowability and uniformity (Li *et al.*, 2012). The outlet of a mechanical biological treatment plant for mixed municipal solid waste is further processed to produce RRBf (Refined Renewable Biomass Fuel) within the frame of the EU Life project MARSS (Material Advanced Recovery Sustainable Systems) (Schulzke *et al.*, 2018). In paper (Dasappa *et al.*, 2004) addresses case studies of a low temperature and a high temperature industrial heat requirement being met using biomass gasification (Dasappa *et al.*, 2004). In paper (Verma *et al.*, 2017) provides a detail review on the need of drying of biomass before co-firing, different technologies used for biomass drying, biomass co-firing to the existing coal fired power plants and the environmental benefits of biomass co-firing. In paper (Hosier and Svenningsson, 1987) was presented the social and economic analysis of an evaluation of biomass briquettes as a substitute for charcoal.

Main cost in pelleting and briquetting are associated with expenditures related to feedstock provision and drying material. Innovative technology is proposed for producing the briquettes from wet biomass without the necessity for drying, thus reducing the overall price of produced briquettes.

Materials and Methods

Biomass Waste Management

According to the European Union standardization there are six procedures in the biomass waste treatment process:

1. Eco-design,
2. Biomass waste decreasing,
3. Biomass waste reusing,
4. Recycling and making compost,
5. Energy from biomass waste,
6. Biomass waste disposing.

In order to optimize the system for biomass waste management based on decreasing of pollution of life environment and for the cheapest solution there is goal to develop the biomass waste management process. This innovative solution could lead to revolution in the biomass waste issue. By entering of the main data for biomass waste, quantity and composition for the some region, the client could know which is the best solution for the biomass waste treatment and transport for the region. Several biomass waste treatments are included:

- Recycling,
- Combusting,
- Making compost,
- Performing anaerobic digestion and
- Disposing of biomass waste.

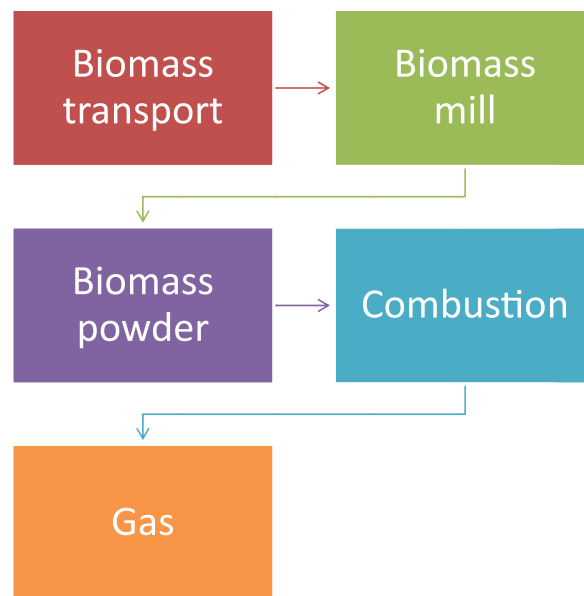


Fig. 1 The biomass treatment process flowchart.

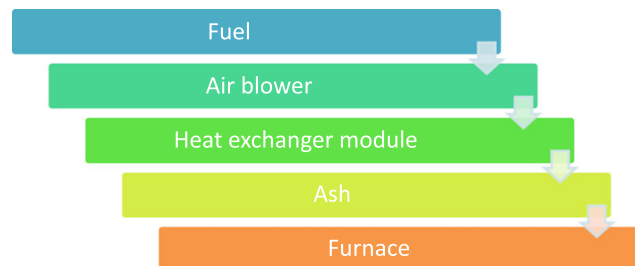


Fig. 2 Process flowchart of the combustion plant with biomass.

There are several indicators which are calculated according to the input data. These indicators are:

- Global warming,
- Heavy metals emission,
- Nitrogen oxide emission,
- Smog formation,
- Water pollution.

Therefore the system has seven modules. These modules

- Calculation of emissions from collection and transport of biomass waste,
- Calculation of emissions from anaerobic digestion,
- Calculation of emissions from combustion,
- Calculation of emissions from recycled waste,
- Calculation of emissions from disposal,
- Calculation of emissions from compost,
- Calculation of cost benefit.

Burner for Agricultural Pellets

Fig. 1 shows the flowchart of the biomass treatment process where it was shown the main process steps. Afterwards process flowchart of combustion plant with biomass is shown in **Fig. 2**.



Fig. 3 Cherry pits briquettes.

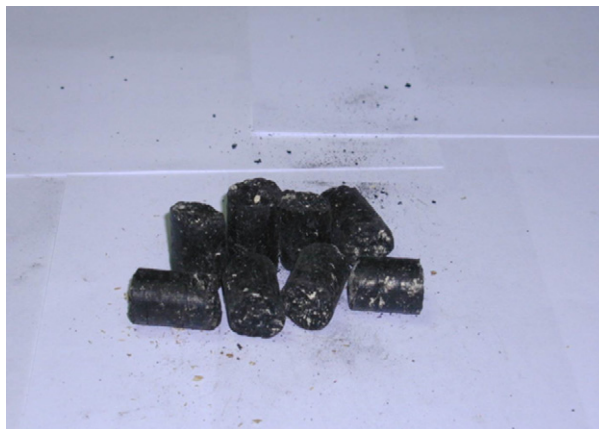


Fig. 4 Coal powder pellets.



Fig. 5 Corn cob briquettes.



Fig. 6 Grape residues briquettes.



Fig. 7 Locust tree branches briquettes.

Main cost in pelleting and briquetting are associated with expenditures related to feedstock provision and drying material. Innovative technology is proposed for producing the briquettes from wet biomass without the necessity for drying, thus reducing the overall price of produced briquettes. Additionally, great number of innovative binders are proposed for compacting the biomass materials which are hard of impossible to bind together (rice husk, sunflower husks, grape seeds and residues, cherry and pitch pits etc.). [Figs. 3–11](#) shows the produced briquettes.



Fig. 8 Peach pit briquette.



Fig. 9 Rice husk briquettes.



Fig. 10 Sunflower husk pellets and briquettes.



Fig. 11 Wheat straw pellets.

Conclusion

The demand for biofuel has increased considerably in recent years, causing shortage of the traditional raw materials sawdust and wood shavings. Use of biomass fuels for electricity generation can simultaneously contribute to a number of common policy objectives, including: increasing the use of renewable energy; reducing greenhouse gas emissions; compliance with air pollutant emissions regulations; and encouraging economic development in communities dependent on agriculture and forestry sectors.

In this article innovative technology is proposed for producing the briquettes from wet biomass without the necessity for drying, thus reducing the overall price of produced briquettes.

Small-scale wood combustion systems have been well developed and reached a high quality and performance level. The energy efficiency has increased, the emissions have decreased, fully automatic operation systems have been developed and the combustion technology has been optimized for woody biomass fuels.

See also: Large Biomass Burners for Fuel Switch in Existing Fossil Fuel Based Plants. Machine for Producing Tablets From Coal Powder. Small to Medium Burners for Agricultural Pellets

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Treatment and Recycling of Domestic and Industrial Wastewater

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Introduction

The availability of clean water is vital for life. With increasing human activity, droughts, floods and an overall reduction of new sources of fresh water, water pollution is becoming more common. Therefore, technologies for both protecting the water resources we do have and proper treatment and recycling of domestic and industrial wastewater are becoming essential. In the same way as processing any material, (in this case wastewater), there are a number of factors that need to be considered to ensure the material (ie the wastewater) is processed effectively so that the treated product is fit for purpose on completion. In the case of processing wastewater, the factors that need to be considered include:

- The quality of the source water (e.g., heavily polluted industrial wastewater, storm water, greywater, agricultural runoff, sewage etc).
- The quality of the treated water required to prevent pollution (e.g., for drinking, removal of pollutants from water before discharge to the environment, reuse etc).
- The treatment technologies available (primary, secondary, tertiary or quaternary) and therefore the types of materials required for the treatment of the water.
- The legislative requirements (can be country specific).

The focus of this article is on the treatment technologies and associated materials commonly used in the processing of wastewater. It is possible that some contaminants are incompletely degraded or removed by regular water and wastewater treatment, while other contaminants are discharged to water bodies directly from agricultural land field runoff and industrial sources without any treatment which could end up in drinking water sources (Fig. 1). This adds further complications to the water treatment process. To this end, there is a growing body of research on finding new materials as well as improving the performance of existing materials (such as activated carbon) to do this. Most of the applications of these emerging technologies such as nanotechnologies and advanced oxidation processes as well as those technologies using novel compounds such as graphene are in the tertiary/quaternary stage of wastewater treatment.

Management of Wastewater

Until the end of the third quarter of the 19th century, the main way for treating domestic and industrial wastewater was to simply move it from the place where it was generated out of population centres and into the nearest river or water body without any further treatment (Abellan, 2017). In certain parts of the world, especially in developing countries, this is still the case. In other countries, a lack of investment in adequate wastewater treatment infrastructure or poor maintenance of the infrastructure that does exist, means that partially treated wastewater can be discharged to the environment with the obvious resulting impacts on health, the environment and the supply of potable water. For example, figures from the World Health Organisation show that about 842,000 people die each year (globally) from diarrhoeal disease mainly caused by poor or no treatment of human wastewater, while at least 2 billion people use a drinking water source contaminated with faeces (WHO, 2018). While acknowledging that this is still a problem in certain parts of the world, the focus of this article is on how to successfully treat domestic and industrial

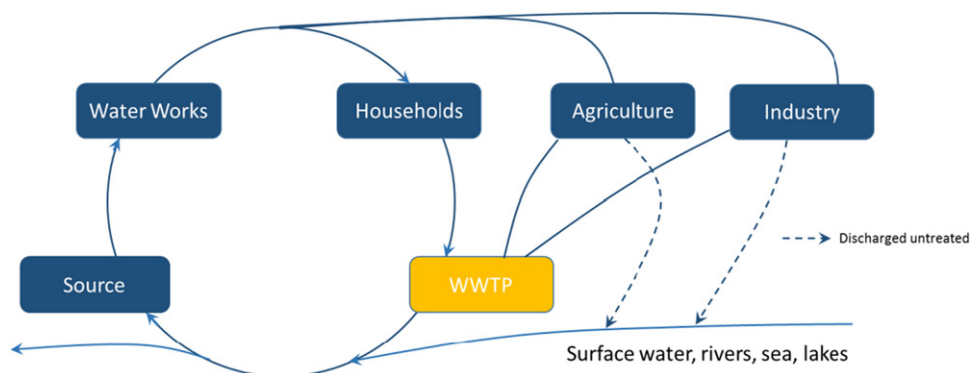


Fig. 1 Simplified Water and wastewater treatment cycle.

wastewater using the best available technologies most commonly used, thereby avoiding water pollution, health problems and water security issues. To this end, it is important to consider a number of technical questions in addition to the broader factors raised above before deciding on the best approach. These questions include, but are not limited to:

- Can the treated wastewater be disposed of directly to land, also known as on-site subsurface disposal, e.g., septic tanks or spray irrigation?
- Will secondary treatment of the wastewater (which can remove at least 85% of biodegradable products) be sufficient to avoid water pollution, or will some form of advanced treatment, such as ultra violet disinfection or advanced oxidation processes, be required?
- What method will be used to dispose of the treated sludge or biosolids? For example, is the level of pathogens in the sludge sufficiently low so that the treated sludge can be disposed of to land as a fertiliser without causing a pathogen problem in the food chain?

The above points will be described in more detail in the following sections as well as the materials required, particularly at the tertiary and quaternary treatment stages. In addition, using processed wastewater as a resource or material will be examined because if properly captured and treated, treated wastewater can be reused for irrigation and agriculture and the biosolids can be used as a fertiliser or treated by anaerobic digestion for the generation of biogas.

Wastewater Treatment

The processes involved in a typical wastewater treatment plant are shown in Fig. 2, and an aerial view of a wastewater treatment plant is shown in Fig. 3. The influent to a wastewater treatment works is made up of untreated domestic and industrial sewage as well as treated industrial wastewater which was not reused within the industrial plant itself and is below the standard permissible for direct discharge to surface waters. The steps of a wastewater treatment process are usually divided into preliminary, primary, secondary, tertiary and more recently quaternary. Large materials, such as paper, plastics and other large solids ranging in size from 5 or 6 mm and above depending on the specific facility, are removed in the *preliminary screening step*. This solid material is then washed, shredded in a *comminutor* and dewatered. The wastewater then passes through a centrifugal grit removal process, which removes coffee grinds, egg shells, sand and other relatively inert material. The material and grit are collected and sent to landfill for proper disposal, or used for road construction. The wastewater then flows by gravity to the *Primary Settling Tanks* which are also known as *clarifiers*.

Primary Treatment

Primary treatment is mainly a physical process to separate the solids in the wastewater from the liquid. Depending on local plant conditions and requirements, this step may also include fat, oils and grease removal, pH and temperature adjustment. These primary clarifiers, of which there should be at least two in a treatment works, can be circular or rectangular in shape. In some treatment plants, where space can be a problem, primary settling takes place in *Lamella Plate* settlement tanks in a tiered system, which are specially designed to maximise surface area for settlement, rather than in conventional settling tanks. The settled sludge is continuously scraped away for further treatment (Fig. 2), while the primary effluent (Liquid) is pumped to the secondary

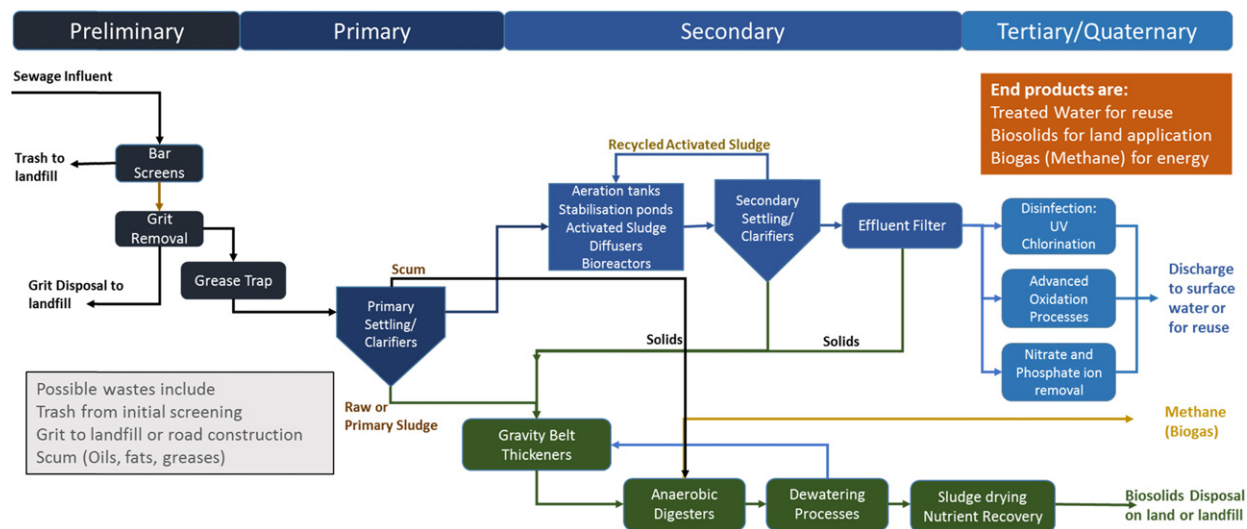


Fig. 2 A modern sewage treatment plant showing wastes and products produced.

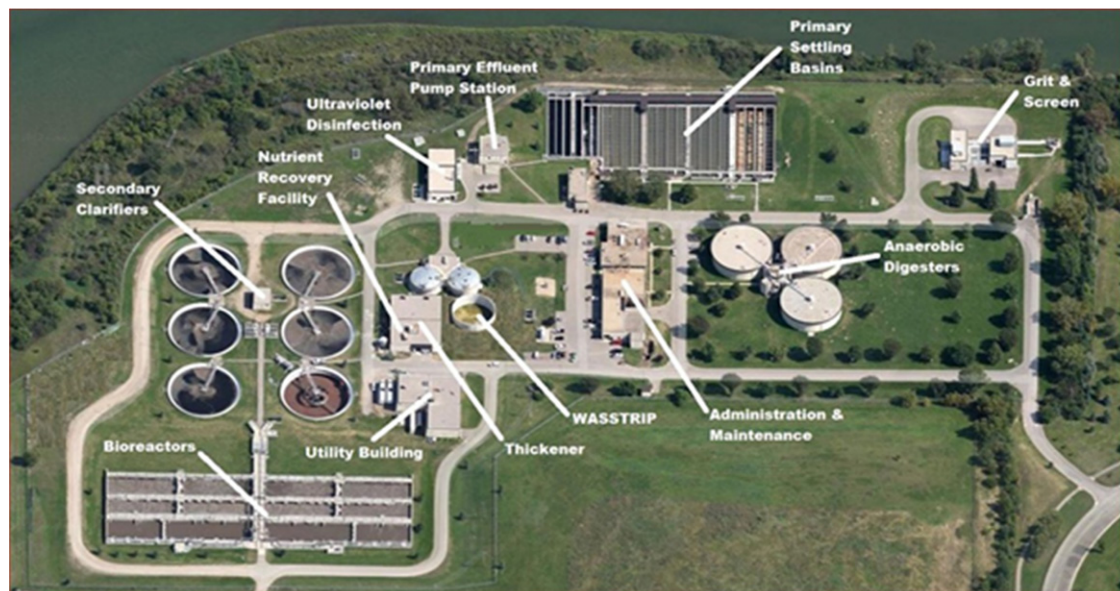


Fig. 3 Aerial view of a wastewater treatment plant, Canada (<https://www.saskatoon.ca/services-residents/power-water-sewer/sanitary-sewer/wastewater-treatment-plant>).

treatment stage. Scum from the top of the settling tanks is also pumped to the anaerobic digesters for further treatment. Primary treatment typically removes about 60% of the suspended solids and only 35% of the Biological Oxygen Demand (BOD) from wastewater, which is insufficient to meet most regulatory requirements. Hence the need for further treatment to remove those pollutants that did not settle in the primary clarifiers and the dissolved BOD that was not removed by physical treatment.

Secondary Treatment

Secondary Treatment is mainly an *aerobic biological* process. There are a large number of technologies that can be used depending on the size of the water treatment plant (single houses, small groups of houses, towns and cities), its location (near an aquifer, river, sea), the age of the treatment works etc. Two of the most common types of biological secondary wastewater treatment are the relatively newer *suspended growth systems* such as Activated Sludge (AS) and the older, more stable *fixed growth systems*, such as Trickling Filters, (TF) (also known as biofilters, trickle biofilter and biological filter among other variations) and constructed wetlands. Both suspended and fixed growth systems work in the same way by using microbes to “eat” the organic matter in the sewage. The difference between the systems is that the microbes in the AS system are suspended in the water, whereas in the TF systems, the microbes are fixed to a substrate such as crushed rock, corrugated plastic, coke or sand with the wastewater flowing over the surface to provide contact with the organic material. Both AS and TF systems are still being used, and the choice of which to use in a particular situation depends on factors such as cost, location, availability of space, sludge management requirements etc. A brief description of each is given below and further details on these technologies can be found in any number of books on wastewater treatment such as Metcalf and Eddy Inc. *et al.* (2014) and Nathanson and Schneider (2015).

The *Activated Sludge* process uses an aeration tank containing the primary treated sewage combined with microorganisms, (mainly saprotrophic bacteria and some protozoa) that degrade the organics or carbonaceous material in the wastewater (Fig. 4(a)). The diffused air also has the effect of thoroughly mixing the microorganisms and wastewater together to ensure consistency in the tanks. At the same time, the microorganisms grow in conglomerates or *flocs*, (Activated Sludge), which combined with the wastewater is known as *mixed liquor*. After about 6 h of aeration (depending on the system), the mixed liquor flows to *secondary clarifiers* where the flocs settle to the bottom of the tank and are either removed as excess sludge (about 70% of the AS) or re-circulated back into the aeration tank (about 30% of the AS). This sludge is called Activated because the microorganisms are acclimated to the wastewater and will continue to absorb and metabolise fresh sewage; hence this process can be maintained continuously without the addition of fresh microbes. The excess sludge is processed further, along with the primary sludge, in the anaerobic digesters (Fig. 2). The supernatant from the settling tank can be discharged to surface waters (river, lakes or sea) without further treatment or can be processed further in a tertiary treatment step where nutrients and/or micro-pollutants are removed. In poorly managed activated sludge systems, a range of *mucilaginous filamentous bacteria* can develop which produces a sludge that is difficult to settle and which can flow into the secondary clarifiers contaminating the final effluent quality.

A *Trickling Filter* (TF) type system is usually circular in shape, about 2 m deep and 50–60 m in diameter (Fig. 4(b)). Sometimes the TFs are covered for odour and/or temperature control, as the efficiency of a TF system is reduced in cold weather. The effluent from the primary clarifiers is sprayed over the surface of the filter bed by a rotating distributor arm (Fig. 4(b)). The filter medium

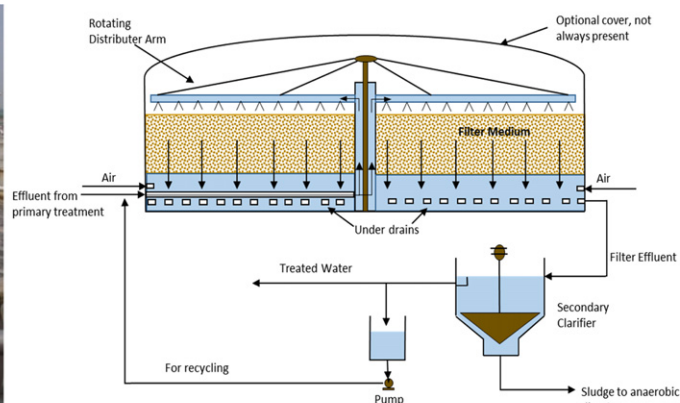


Fig. 4 (a) Aeration tank in a wastewater treatment plant (By SuSanA Secretariat [CC BY 2.0 (<http://creativecommons.org/licenses/by/2.0>)], via Wikimedia Commons) (b) Schematic of Trickling Filter plant system (not to scale).

used should have a very high surface area to volume to maximise the opportunity for biological growth while at the same time, porous enough to allow the air to circulate. As the primary effluent flows through the filter medium, a biological slime (also called a *biofilm*) starts to grow and thicken. The microorganisms in the biofilm absorb the dissolved organic compounds in the effluent being treated, thus lowering the BOD of the wastewater. As the microorganisms multiply, the biofilm thickens until a point where the flowing wastewater *sloughs* i.e., washes off the biofilms from the surfaces of the filter medium. This water containing the sloughed off biofilm trickles by gravity to the bottom of the filter and is collected in underdrains for discharge to a secondary clarifier. The biofilm containing the microorganisms is allowed to settle out in the clarifier, which is collected and sent to an anaerobic digester for further treatment. The air being circulated through the filter medium provides oxygen for the stabilisation of the organics, with the release of carbon dioxide, water and other products. Some of the treated water may be pumped back into the trickling filter inlet for a second pass through the filter medium for two reasons: (a) As a means of keeping the flowrate constant through the trickling filter and (b) to improve the pollutant removal efficiency.

Both secondary treatment methods described above produce sludge as a by-product that needs to be treated further before final discharge, in order to reduce its volume, stabilise it and ensure that there are no pathogens left in the digested sludge. The main sludge treatment process used is *Anaerobic Digestion (AD)* followed by pasteurisation or thermal drying to remove all pathogens. This process can provide useful products in the form of biogas (which can be used to generate energy as it typically contains 55%–75% methane) and nutrient rich biosolids which can be used as a fertiliser. Further details on the anaerobic digestion process can be found in many sources such as Caruana and Olsen (2012).

While the Trickling Filter and Activated Sludge systems are the most commonly used secondary treatment systems, there are a number of other processes in use particularly for smaller scale or rural communities. Of these, Biodiscs also known as rotating biological contactors (a fixed growth system) and the wastewater treatment pond or constructed wetlands (a suspended growth system) are the most commonly used. A *rotating biological contactor (RBC)* system consists of packs of closely spaced, parallel discs (known as media and typically made from polyethylene or PVC) on a rotating shaft, on which the microorganisms grow. As the shaft rotates, the discs are alternately submerged in wastewater and then exposed to the atmosphere above the liquid, allowing a layer of biofilm to grow on each disc. The microbes contained in the biofilm biodegrade the pollutants in the wastewater in a process similar to the TF system. There is no need to recycle the sludge in a RBC system but a secondary clarifier is needed where the sloughed off sludge can settle.

A *wastewater treatment pond system* is a low cost, energy efficient, natural water purification system and is usually used in rural areas where land is available. Typically, about one hectare of land is needed to treat the wastewater generate by 1000 people. There are many types of ponds depending on whether they are aerobic, anaerobic or a mixture such as in a *Facultative lagoon* (Fig. 5). The general approach to the operation of a treatment pond system is that the wastewater to be treated is held in a depression or pond in the ground, and through a combination of microbes, sunlight and oxygen, the biological pollutants in the water are degraded. The bacteria degrade the pollutants in the wastewater producing carbon dioxide, methane (if anaerobic) and other compounds such as ammonia and hydrogen sulphide. These compounds are then degraded by algae contained in the pond, as they consume the compounds released by the bacteria to produce oxygen, which is then used by the aerobic bacteria to further decompose the pollutants in the wastewater. It should be noted that a problem can arise, particularly in warm weather, if the algae grow too much and are carried out in the effluent, thereby exceeding the allowable suspended solids limits in the effluent from secondary treatment. This problem can be eliminated with the construction of a number of ponds in series to control the flow of the effluent.

Tertiary Treatment

The wastewater treatment industry today is moving towards high added value resource recovery, from waste and wastewater, offering new technological options and opportunities to address modern societies and to protect the environment

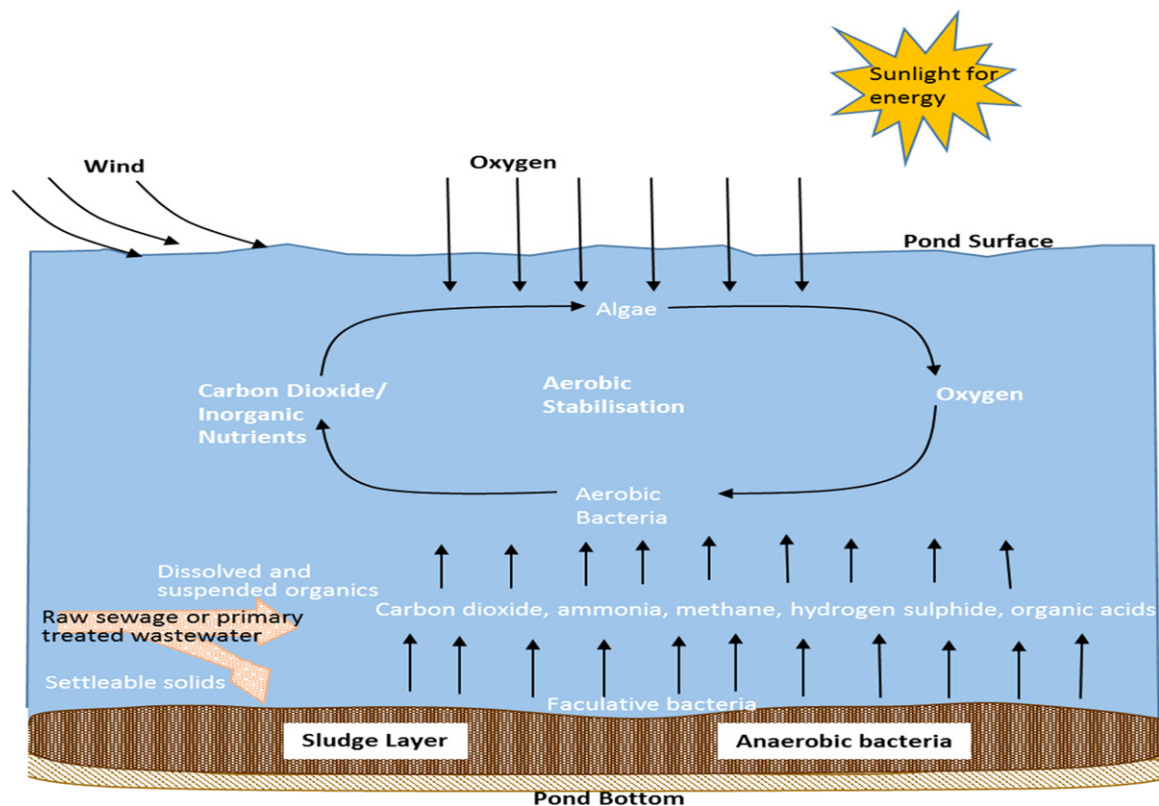


Fig. 5 Schematic of a Facultative Lagoon as an example of a wastewater stabilisation pond.

(Curl *et al.*, 2014; Moustakas *et al.*, 2018). As seen above, secondary treatment can only remove about 85% of the BOD and TSS and 30% of the phosphorus from the sewage. In addition, pharmaceutical residues, personal care products (PCPs) and antibiotics that are being used in increasing amounts, are not removed by traditional water treatment systems and are entering waterways in volumes not seen in the past (Gholamvand, 2015). Furthermore, the more prevalent use of antibiotics has resulted in their presence in increasing concentrations within activated sludge systems, resulting in a rise of antibiotic resistant bacteria and their spread into the environment through the water course (Wang and Wang, 2016). As a result, tertiary treatment that can remove up to 99% of pollutants, including bacteria, from raw sewage and is becoming the norm. While the cost of doing so can be as much as the cost of secondary treatment, tertiary treatment is being increasingly applied in developed countries due to increasingly stringent water quality standards.

The most common type of tertiary treatment is *disinfection*, either by chlorination or with Ultra Violet (UV) light, which kills off any remaining pathogens in the water. In some wastewater treatment plants, this is the only form of tertiary treatment present and may or may not be used all the time. Disinfection is particularly important if the treated water is being discharged to an area in the sea frequented by swimmers, where shellfish and other microorganisms live or where sources of drinking water supplies may be contaminated by wastewater effluent. *Chlorination* is the more common process of the two and is known to be effective in destroying a variety of bacteria, viruses and protozoa, including *Salmonella*, *Shigella* and *Vibrio cholera*. The concentration of chlorine supplied must be tightly controlled: It should be sufficient enough to kill off any pathogens, but not too much to cause an adverse environmental impact, such as fish kills. To avoid problems with chlorination, newer wastewater treatment plants use Ultraviolet light rather than chlorine for disinfection. The UV light kills any pathogens by blocking the DNA required for cell division and can kill up to 99.99% of any remaining pathogens. At the same time undesirable by-products such as Trihalomethanes, a by-product of chlorination, are less likely to be produced and the quality of water remains unchanged. The addition of an effluent filter (Fig. 2) upstream of UV in a tertiary treatment process is an optional additional process to improve water quality to a standard sufficient for water reclamation or reuse.

Other situations where tertiary or advanced treatment is required are in situations where there is insufficient removal of nitrogen and phosphorus in the secondary treatment to prevent *eutrophication*, *algal blooms* and other environmental problems. Secondary treatment is usually only effective in removing Carbonaceous BOD and additional treatment is needed to remove Nitrogenous BOD. Furthermore, nitrogen in sewage effluent is mostly present in the form of ammonia compounds, which are not only toxic to fish in high concentrations but which can cause *nitrification*. Finally, both nitrogen (Ergas and Aponte-Morales, 2014) and phosphorus (Goel and Motlagh, 2014) are valuable resources known as macronutrients and the recovery of these from wastewater is becoming increasingly important.

Phosphorus in sewage is present as organic phosphorus or phosphate and can be removed in two ways. One is a physical-chemical process using a precipitating agent such as Aluminium Sulphate (Al_2SO_4) also known as alum, Ferric Chloride, FeCl_3 or Calcium Oxide (CaO) to the sewage. In the precipitation method, the cation in the agent reacts with the phosphorous ions in the sewage to form an insoluble precipitate, which then forms a floc and settles to the bottom of the clarifier. The precipitating agent or coagulant can be added at any point in the treatment process (e.g., after primary settling or after secondary treatment), but if added after secondary treatment, additional settling tanks and filters are required, thereby increasing the quantity of sludge generated. However, in line with making wastewater treatment plants more sustainable, the phosphorus contained in the sludge can be extracted (Egle *et al.*, 2016; Cieřlik and Konieczka, 2017).

The second method for removing phosphorus from wastewater is through modifying the activated sludge process so that it operates as an enhanced biological phosphorus removal (EBPR)- activated sludge plant (Goel and Motlagh, 2014). In an EBPR process, heterotrophic bacteria, called polyphosphate-accumulating organisms (PAO) not only consume phosphorus as food, but also accumulate large quantities of polyphosphate within their cells thereby enhancing the removal of phosphorus from the wastewater. This biomass settles out in the sludge from which the phosphorus can be removed.

The most common method to remove nitrogen from sewage is to use a biological nitrification-denitrification process. A schematic of the process is shown in Fig. 6, and an animated description of the process can be found at website provided in “Relevant Websites section”. In the nitrification step of this process, the ammonia nitrogen (either NH_3 or NH_4^+ , depending on the pH of the system) is converted to nitrite (NO_2^-) and then to nitrate (NO_3^-) by nitrifying or autotroph bacteria such as *Nitrosomonas* and aeration. As the nitrogen is still present in the water, it can be removed by the addition of denitrifying or heterotroph bacteria such as *Pseudomonas* to the sewage and methanol as a source of food for the bacteria. It is crucial to keep conditions in the tank anoxic, otherwise, the bacteria will use the dissolved oxygen in the water instead of the nitrate oxygen in their metabolic process. One product of the process is molecular nitrogen which escapes into the atmosphere as a gas.

Quaternary Treatment

Pharmaceuticals are designed so that they are chemically stable and they have a biological effect on many cells and organisms. As a result, excreted or unused pharmaceuticals can be persistently present in the environment and act as a contaminant with hazardous effect on living organisms (Joss *et al.*, 2005). Furthermore, the removal of pharmaceuticals and other emerging pollutants from the wastewater is more difficult due to their small molecule size, persistence and a lack of knowledge of what exactly is in any specific wastewater stream (Byrne *et al.*, 2017; Sweetman *et al.*, 2017). As a result, even more advanced treatment is required to achieve this. These advanced treatments include physio-chemical treatments such as biodegradation, adsorption to activated carbon, air stripping, incineration, ion-exchange, reverse osmosis, coagulation-precipitation, membrane separation and oxidation reactions including thermal and catalytic oxidation, oxidation by permanganate, chlorine, ozone and hydrogen peroxide (Gholamvand, 2015). While not normally used for wastewater treatment, some of these are becoming more commonly used at the quaternary treatment stage to remove emerging pollutants. This is an additional step following mechanical removal of solids (primary treatment), using microorganisms to degrade organic matter (secondary treatment) and disinfection, phosphorus and nitrate removal (tertiary treatment). Nevertheless, each of the advanced treatment processes has shortcomings and is not fully effective at removing these persistent pollutants completely (Gholamvand, 2015). For example, the air stripping process, which is commonly used for the removal of volatile organic compounds for aqueous media, merely transfers the pollutants from liquid phase to gaseous phase rather than destroying them completely. In the process of adsorption to activated carbon, the spent carbon must be either regenerated or incinerated, which converts the adsorbed pollutant to by-products, which may be worse for the environment than the original compound. Membranes such as those used for reverse osmosis, nanofiltration and ultrafiltration can be an effective method for the removal of both potential pathogens and chemical contaminants, but

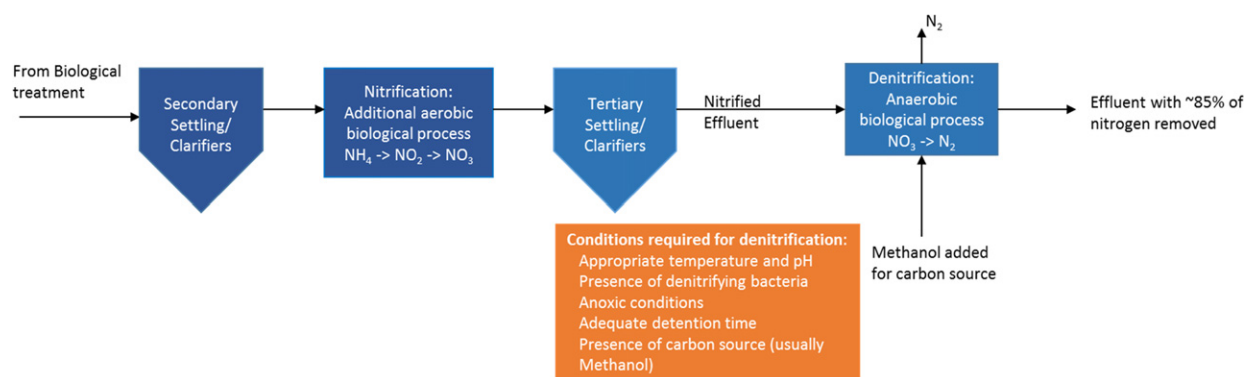


Fig. 6 Biological Nitrification – Denitrification process in wastewater treatment.

filtration systems are susceptible to fouling and do not make the microorganisms inactive. Chlorination and ozonation are two water disinfection and destructive oxidation technologies in water treatment process, but as seen earlier, chlorine-based water disinfection processes may form potentially toxic and carcinogenic disinfection by-products (DBPs) such as trihalomethanes.

As a result of these shortcomings, there is a growing area of research to find new ways to ensure that the discharged wastewater is properly treated to the standard required, particularly if the water is to be reused. One such quaternary process is *Advanced Oxidation Processes* or AOPs. Advanced Oxidation Processes rely mainly on the formation of short-lived oxygen containing intermediates, non-selective reagents, such as hydroxyl radicals ($\text{OH}^\bullet$) or superoxides ($\text{O}_2^{\bullet-}$). These are produced, separately or in combination, with the help of strong oxidising agents such as ozone or hydrogen peroxide, irradiation, such as UV light and a catalyst such as titanium dioxide, which then react unselectively with contaminants, such as pesticides and pharmaceutical molecules, to form smaller inorganic molecules. While the goal of the oxidation of compounds is complete mineralization to carbon dioxide and water if the treatment time is sufficient, it is usually not necessary to operate the processes for this long and therefore the target pollutants are usually degraded to biodegradable intermediates. The chemical reactions involved are essentially the same as if the pollutants were slowly oxidised in the environment, but the oxidation rate is considerably faster (Gholamvand, 2015). The main advantage of AOPs over chemical and biological processes is that they neither transfer pollutants from one phase to the other (as in chemical precipitation, adsorption and volatilization) nor produce massive amounts of hazardous sludge (as in activated sludge processes) and hence have a lesser impact on the environment (Deng and Zhao, 2015). Titanium dioxide (TiO_2) is the most popular photocatalyst due to its low cost, nontoxicity and high oxidising ability, even though there has also been considerable research into other photocatalysts such as ZnO , ZnS , perovskites, Semiconductor-Graphene composites, MoS_2 , WO_3 and Fe_2O_3 . Moreover, titania photocatalysts can easily be immobilized on various surfaces and be scaled up for large scale water treatment (Byrne *et al.*, 2017).

The oxidation potential of various oxidising agents is compared in Table 1, while the most common AOPs developed for wastewater treatment are presented in Table 2. Some of these, such as photolysis have been commercialised, while others (such as photocatalysis and ultrasound) are still at the lab or prototype stage. Processes that are at a more advanced stage of development and which have been used at full scale include combinations of H_2O_2 , O_3 and UV, Fenton's reagent, super-critical water oxidation and ionizing radiation. The focus of the remainder of this section of this article is on the most common classes of materials used in quaternary treatment of wastewater, which include adsorbents, photocatalysts and oxidising agents.

Classes of Materials Used in Wastewater Treatment

Adsorbents

Adsorption is the most common physical process for quaternary treatment to remove trace organic compounds from water (Wang and Wang, 2016). One of the most commonly used adsorbents in wastewater treatment is *Activated Carbon* which is usually made from the pyrolysis and chemical treatment of an organic material such as coal, coconut shells and wood. AC is typically used in granular form (GAC) in a packed or adsorption bed following the activated sludge step, but sometimes as a powdered feed (PAC) to remove odours and taste. Other carbon based adsorbents such as Graphene and carbon nanotubes are being widely researched in order to enhance the adsorption capacity for the micro pollutants. The advantages of adsorption especially, by activated carbon, is the simplicity and applicability for wide range of compounds, but the removal efficiency of each compound depends on different parameters such as solubility, $\text{P}k_{\text{a}}$, chemical properties of the compound, acidity, porosity, chemistry and surface properties of the adsorbent and operating parameters such as contact time (Wang and Wang, 2016). However, for efficient performance, regular regeneration of the carbon is required which is expensive. In the case of PAC, the long contact times and possible need for a batch system/coagulation and in separating the powdered carbon from the water also adds to system

Table 1 Comparison of oxidising potential of various oxidising agents

Oxidising species	EOP (V)	EOP relative to chlorine
Positively charged hole on TiO_2	3.20	2.35
Fluorine	3.06	2.25
Hydroxyl radical	2.80	2.06
Atomic oxygen	2.42	1.78
Ozone	2.08	1.52
Hydrogen peroxide	1.78	1.30
Chlorine	1.36	1.00
Oxygen (molecular)	1.23	0.90

Source: Adapted from Pelaez, M., Nolan, N.T., Pillai, S.C., *et al.*, 2012. A review on the visible light active titanium dioxide photocatalysts for environmental applications. Applied Catalysis B, Environmental 125, 331– 349.

Table 2 Most common AOPs for water and wastewater treatment

<i>Photochemical processes (Light driven AOPs)</i>	<i>Non-photochemical processes (Dark AOPs)</i>
UV oxidation processes	Ozonation
UV/H ₂ O ₂	Fenton
UV/O ₃	Ultrasound (US)
UV/H ₂ O ₂ /O ₃	US/H ₂ O ₂ , US/O ₃ , US/Fenton
UV/Ultrasound	Electrochemical oxidation
Photo-Fenton	Supercritical water oxidation
Photocatalysis	Ionizing radiation
Sonophotocatalysis	Electron-beam irradiation
Vacuum UV (VUV)	Wet-air oxidation
Microwave	Pulsed plasma

Note: Gültekin, I., Ince, N.H., 2007. Synthetic endocrine disruptors in the environment and water remediation by advanced oxidation processes. *Journal of Environmental Management* 85, 816–832.

complexity. Furthermore, dissolved organic compounds, surfactants and humic acids compete with binding sites of the activated carbon and can block pores within the AC structure. In addition, during chemical regeneration, adsorbed compounds are released to a regenerating medium that will have to be disposed of in landfill or released to the air in the form of CO₂ during incineration.

One way that is widely researched to improve the performance of Activated Carbon is to incorporate specific chemical functionality onto the AC surface, e.g., to target specific pollutants (Sweetman *et al.*, 2017), with the addition of a photocatalyst such as Titanium Dioxide. Composites based on activated carbon and titanium dioxide are a new material in their own right, known as Integrated Photocatalysts (IPCA). Another way to improve the performance of Activated Carbon is to improve the AC regeneration techniques, by using electrochemical regeneration rather than thermal regeneration, which was first studied by Narbaitz and Cen in 1994 (Narbaitz and Cen, 1994). Finally, there is a growing body of research on developing new materials for water treatment, the most promising of which are advanced nanomaterials including graphene, carbon nanotubes (CNTs), and composite materials.

Most research to date in relation to the removal efficiencies of *Graphene and Graphene Oxide* has been completed at laboratory scale using synthetic water (Wang and Wang, 2016), with very few commercial applications for water treatment reported so far. Nevertheless, graphene and its precursor graphene oxide are showing promise for use in water treatment due to the relatively low quantity of these materials required to achieve high adsorption or filtration capacity and easier regeneration of the graphene based materials compared to activated carbon (Sweetman *et al.*, 2017). Recent lab-based research has also shown that porous graphene nanosheets (Tabish *et al.*, 2018) and membranes made from graphene oxide (GO) (Abraham *et al.*, 2017), rather than pristine Graphene which is hydrophobic, allow water to permeate, while at the same time blocking materials like gases and solvents. This makes them ideal candidate materials for water treatment. Scaling up this technology for commercial applications remains the challenge. While a separate issue, an additional concern is the fate of wastes that contain these nanomaterials that enter the wastewater treatment system is that while they can be removed from the water if quaternary treatment is used, they will end up in the sludge (Suárez-Iglesias *et al.*, 2017). It was also noted that graphene oxide has a negative effect on the biological treatment in the activated sludge process due to the biocidal ability of graphene materials (McGlade, 2017). So, on the one hand, graphene related materials have the potential to greatly improve the quality and the efficiency of water treatment particularly if used as a tertiary or quaternary treatment, while on the other hand, cause their own problems by entering the sewage system as nanomaterials from the environment.

Photocatalysts

The most common photocatalyst used as part of an Advanced Oxidation Process (AOP) is Titanium Dioxide (Byrne *et al.*, 2017). Titanium Dioxide is the naturally occurring oxide of titanium, with its use as a white pigment being its most widely used application. The TiO₂ crystal structure can occur in several polymorphs: Anatase, rutile, brookite and TiO₂ (B), with the rutile and anatase phases being of most use commercially. As the rutile form is the most stable and the anatase form is the most photoactive, commercially available TiO₂ used for photocatalysis usually contains a mixture of the two forms. For example, Evonik (Degussa) P25 contains ~80% anatase and ~20% rutile and is often used as a reference to which the performance of other photocatalysts are compared (Pelaez *et al.*, 2012; Byrne *et al.*, 2017). The photocatalytic properties of titanium dioxide were first published in 1972 (Fujishima and Honda, 1972), with the original research focussing on water splitting using an electrochemical photocell with TiO₂ and platinum electrodes. Since Carey *et al.* (1976) first reported the photocatalytic degradation of organic molecules (biphenyl and chlorobiphenyl derivatives) numerous works have been published demonstrating the efficiency of the use of TiO₂ in photocatalytic processes as a mean of wastewater detoxification (Deegan, 2011). Titanium Dioxide has the potential to mineralize pollutants, including pesticides, pharmaceuticals and other organic chemicals in water for drinking and industrial

purposes, without generating a waste disposal problem (Byrne *et al.*, 2017). Further advantages of TiO_2 include its very high photoactivity compared to alternatives (Table 1), stability, chemical inertness and relatively low cost. However, the full commercial application of TiO_2 mediated photoreactions is subject to a series of technical challenges including:

- TiO_2 is a nanoparticle powder and therefore the successful separation of the TiO_2 catalyst after water treatment is considered a major obstacle. In addition, its presence in the treated water stream after the photocatalytic degradation can cause genotoxicity and cytotoxicity to aquatic and human lives (Srikanth *et al.*, 2017).
- TiO_2 as a catalyst works best in the UV light range, which greatly adds to the cost of treatment.
- The photocatalytic efficiency of the TiO_2 catalyst is poor at low concentration of pollutants.

To overcome these shortcomings, much research is ongoing to find ways to immobilise TiO_2 (Gholamvand, 2015; Byrne *et al.*, 2017; Srikanth *et al.*, 2017), doping TiO_2 with a metal such as Zinc, or non-metals such as Nitrogen, to bring the working range of TiO_2 into the visible range to create Visible Light Active TiO_2 (VLA- TiO_2) (Pelaez *et al.*, 2012) and the development of a new class of TiO_2 catalyst combined with an efficient adsorbent (Gholamvand, 2015). TiO_2 has been immobilised on numerous surfaces including glass and stainless steel (Byrne *et al.*, 2017), adsorbents such as activated carbon or zeolites, also known as Integrated Photocatalytic Adsorbents, or IPCAs (Basha *et al.*, 2015) and blends of Graphene Oxide/ TiO_2 nanocomposite and polysulfone (Kumar *et al.*, 2016). Most research is still at laboratory or pilot scale using synthetic water, with no commercial applications reported to date. Whatever immobilised photocatalyst is developed will need to be photoactive in the visible light range and also be recycled many times without significant loss in its photocatalytic activity (Srikanth *et al.*, 2017). In all cases, an effective assessment of these nanomaterials is needed to address several issues regarding test protocols, ensure true photocatalytic activity, and explore future commercialisation of the materials (Pelaez *et al.*, 2012).

In addition to TiO_2 photocatalysis, photo-Fenton is another popular photochemical advanced oxidation process. Fenton's chemistry involves reactions of hydrogen peroxide in the presence of iron to generate hydroxyl radicals. Ultraviolet light enhances this generation by the photo reduction of Fe(III) to Fe(II) . Since iron is abundant and non-toxic and Fenton's reactions operate at room temperature and normal pressure, it is seen as a viable option for wastewater treatment. However, the strong dependence on the aqueous solution pH (optimum pH 2–4 for the production of OH radicals) and on the concentrations of hydrogen peroxide and ferric/ferrous ions and the disposal of the iron sludge are factors that have limited its commercialisation to date.

Sludge Management

The discussion in this paper so far has been on the treatment of the aqueous stream of the wastewater to ensure that when the treated wastewater is discharged to the environment, it meets national standards with minimal impact on the environment. However, in treating the water, the removed contaminants have to go somewhere and usually end up in a sludge in a more concentrated form than in the original untreated wastewater. As a result, the sludge must be treated properly to avoid any environmental problem; otherwise, the original treatment processes are pointless (Dentel and Qi, 2014). The costs of sludge management can be up to 50% of the cost of wastewater treatment (Nathanson and Schneider, 2015), but some of these costs can be recovered, e.g., by using the treated sewage sludge as a fertiliser or recovering the energy from the sludge through anaerobic digestion. As a result of this, sludges are more generally referred to as biosolids to emphasise its potential as a natural resource (Nathanson and Schneider, 2015).

The treatment of the biosolids is complicated by the fact that their composition depends on the composition of the original wastewater, which can vary considerably, leading to a wide variation in sludge characteristics. A typical wastewater sludge will contain organics, microbes, nutrients and a wide variety of household chemicals and pharmaceuticals. Indeed, it is likely that a typical sludge will also contain illicit drugs as well (Yadav *et al.*, 2017), as very little is known about the environmental fate and toxicity of these drugs. The amount of sludge generated depends on the type of treatment provided and on the amounts of chemicals added. Primary sludge from the primary settling tanks (Fig. 2) typically has a solids concentration of about 7%, which can go septic and odorous if not properly handled, while the sludge from the activated sludge tanks containing about 2% solids or less. Therefore, the main objectives of sewage sludge treatment are volume reduction and stabilisation of organics prior to disposal. Several processes are typically used for these purposes including gravity belt thickeners, anaerobic digesters, sludge dewatering and sludge drying with nutrient recovery (Fig. 2). Alternatives to anaerobic digestion include incinerating or composting the sludge with municipal waste, following a dewatering process.

The main purpose of sludge dewatering and thickening is to increase the solids concentration in the sludge; otherwise the sludge is very difficult to manage. Sludge Thickening is a physical process that is usually carried out using a Gravity Thickener, Dissolved air Floatation (DAF) or centrifuge, in which sludges can be thickened to more than 10% solids, thereby reducing the sludge volume by half or more. This process is used before or after the dewatering process, and/or before or after digestion on any of the sludges generated in the WTP. Details on how the process works can be found in any number of text books (for example, Metcalf and Eddy Inc *et al.*, 2014), or on various websites such as provided in "Relevant Websites section" or "Relevant Websites section"

The next step in the process is sludge digestion in which biochemical decomposition of the sludge occurs, converting the organics into simpler more stable substances, reducing the total mass of the sludge solids and destroying pathogens. In most

wastewater treatment plants, digestion is carried out anaerobically with the production of a biogas (a mixture of methane, carbon dioxide and other gases), which helps make the wastewater treatment plant energy neutral. The biochemical reactions that take place during the anaerobic digestion process are quite complex, starting with the breaking down of insoluble organic polymers into soluble derivatives such as sugars and amino acids with one set of bacteria and then further decomposition of these chemicals into carbon dioxide, hydrogen and organic acids, with a second set of bacteria. These organic acids are converted into acetic acid and gases such as ammonia, hydrogen and carbon dioxide and finally, another set of bacteria convert these products into methane and carbon dioxide. The quantity of methane produced is an indicator of how well the plant is operating and is tightly monitored. Typical detention times are between 15 and 40 days depending on the characteristics of the sludge.

In sludge dewatering, the sludge is dewatered or dried to the consistency of moist earth. Even though this dewatered sludge can contain as much as 70% moisture, it now appears more akin to a solid than a liquid and so is easier to handle. This process typically takes place using a sludge drying bed if there is enough land on which to spread the sludge or with a vacuum filter, centrifuge or belt press filter, if not. Further details on the process can be found in any text book on wastewater management, such as the previously mentioned [Metcalf and Eddy Inc. et al. \(2014\)](#) or [Nathanson and Schneider \(2015\)](#).

The final step in the process is sludge disposal, which can range from dumping in the sea, landfilling, incineration or sale as a fertiliser. In most developed countries, dumping sludge at sea is no longer permitted, while landfill disposal is severely restricted. Therefore, the two most commonly used routes for disposal are thermal treatment and land application. Thermal treatment is an expensive option, because the exhaust from the incinerator must be scrubbed to remove pollutants to adhere to the relevant national "Clean Air Acts" and so is really only an option where the land disposal is not available. Therefore, the most sustainable option is to use the treated sludge (biosolids) as a fertiliser, if properly treated to standards ([DELG, 1999](#)) as it can contain large amounts of nitrates and phosphates. The sludge can be applied as ground cover or mixed into the ground during placement. Liquid digested sludge in the form of a slurry, can be spread directly onto land, but only at certain times of the year. In the EU, the application of treated municipal sewage sludge to agricultural land is governed by EU Directive 86/278/EEC ([EU, 1986](#)), which requires that sewage sludge undergoes biological, chemical or heat treatment, long-term storage, or any other process to reduce the potential for health hazards associated with its use.

Wastewater Recycling and Reuse

As noted in the Introduction, due to increasing human activity, droughts, floods and an overall reduction of new sources of fresh water, water is becoming a limited resource. Water recycling and reuse of treated wastewater for applications such as agricultural irrigation and street cleaning, or for household uses like toilet flushing and watering lawns are becoming more common. In many countries, reuse of treated wastewater has been proven as a reliable alternative water resource and an effective solution for coping with water scarcity conditions.

Of the two types of domestic wastewater, greywater is easier to recycle than blackwater. If Greywater (wastewater produced from showers, baths and washing machines) is collected separately to Blackwater, (wastewater generated from toilets, kitchen sinks and dishwashers), it could be reused for watering gardens, washing cars or flushing toilets. While the reuse of greywater within a household is becoming more common, its rollout is hindered by the relatively high cost of the systems especially if retro-fitting, the need for careful maintenance of the system and concerns that the quality of the water may pose a health risk. A more sustainable and cost effective approach, is to reduce water usage by fitting more water efficient appliances and changing habits than going to the expense with possible operational complications of recycling greywater within a household.

Reusing Blackwater within a home is not possible and must be sent for biological or chemical treatment and disinfection in a wastewater treatment plant before reuse or treated on site in a septic tank arrangement, for example. Once treated to a sufficient standard, treated effluent can be, and is being reused all over the world as in the "toilet to tap" initiatives. As a result of growing populations and drought, recycled water is being incorporated into the water supply in places such as Singapore, California and Australia and is slowly gaining acceptance. However, the biggest problem will be for people to accept that the treated water is not only potable, but can sometimes contain less contaminants than raw water. This is an ongoing challenge, and not only is recycling water becoming a necessity, a sustainable water future will demand it.

Conclusions

Treating wastewater to the standard required for discharge to the environment is becoming increasingly expensive and more complex, with tertiary treatment and in a growing number of situations, quaternary treatment, becoming the norm. However, if wastewater is being treated to almost potable standards, then the onus is on society to recycle and reuse this water as is the case for any scarce resource and not to discharge it to the environment as a waste product. One of the main limiting factors of reusing water is the concern that it could be contaminated or could cause a public health issue, and so policies will need to be put in place to ensure that this is not the case as well as promoting water conservation.

See also: Sustainable and Environment Friendly Power Sources for Long Duration Environment Monitoring

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Unified Modeling Language for Cooking Oil Management

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Introduction

Biodiesel is considered to be a good alternative in renewable energy generation. Therefore it is well studied throughout for its efficient, economic and greener production. Biodiesel production stands out on an international level because of its environmentally sustainable characteristics and the potential to promote rural development in developing countries. Introducing waste cooking oil into the biodiesel chain holds the potential to promote social inclusion in urban areas in all countries.

There is a need for recyclers to convince the food establishments and users of cooking oil of the benefits of recycling cooking oil, which in turn obtains a steady source of waste cooking oil as feedstock for biodiesel production. In addition, as the biodiesel life cycle defined is very much dependent on waste cooking oil as a feedstock, it is recommended to optimize the waste cooking oil collection network.

In this article we recommend research into the collection of waste cooking oil, such as a pilot-scaled collection and production scheme in large estates. The government should provide outlets for biodiesel, for instance electricity in estates or a subsidy for drivers choosing to use environmentally friendly biodiesel as fuel. For such a purpose we modelled a waste cooking oil management software which will help in the collection of waste cooking oil. Biodiesel is conventionally produced by alkaline-catalyzed transesterification, which requires high-purity oils. However, low-quality oils can be used as feedstocks for the production of biodiesel by enzyme-catalyzed reactions.

Therefore it is essential to model an waste cooking oil management software which will be acceptable for all users in the process of the waste cooking oil management. Moreover it is more important the software would be universal and can be applied in all suppliers and all collectors of the waste cooking oil. Also the software should be understandable and easy in application for anyone. In order to make such a software it is important to analyze and model the structural and dynamical characteristics of the software. One of the best solution for analyzing and modeling of the software is object-orientated approach (Lethbridge and Laganier, 2005). This approach is used at the beginning of the software life cycle (Jacobson, 1993).

The object-orientated strategy is focused on assembly of the system from a library of reusable objects. By assembling the objects the useful computer application could be made which represents one system. Although there are different methodologies for the object-oriented modeling it is very difficult for beginners to understand and to model some systems. Unified modeling language (UML) is object orientated modeling tool based on use cases, architectures, iterations and increments.

UML (Rumbaugh *et al.*, 2004) is used as the standard tool for software development in early stages. UML is no a programming language but resided at a higher conceptual level than programming languages. Since it is standard tool for software development it was used in various applications for system modeling ranging from engineering modeling to business processes. The main purpose of the UML is system documentation and specification.

Various activities could be modelled by using UML diagrams. In this paper the waste cooking oil management software is analyzed and modelled with help of use case diagrams along with scenarios of activities and activity and state diagrams.

Literature Overview

The intention of study in Muralidharan and Vasudevan (2015) was to predict the performance, emission and combustion characteristics of a single-cylinder, four-stroke variable compression ratio engine fuelled with waste cooking oil methyl ester and its blends – standard diesel with the aid of artificial neural network (ANN) and this study was shown that there is a good correlation between the ANN-predicted values and the experimental data for different engine performance, emission parameters and combustion characteristics. Biodiesel from waste cooking oil (WCO) and soybean oil (SO) mixture was produced by changing the alkali catalyst (NaOH) content and the WCO to SO ratio in the feedstock (Primata *et al.*, 2013) and conclusion was implied that the waste cooking oil mixture, which contains 40 wt% fresh soybean oil, could be treated like the fresh soybean oil to produce biodiesel, and that this behaviour would be helpful to reduce the biodiesel production cost when waste cooking oil used as feedstock. There has been an alarming increase in the dumping municipal solid waste (MSW), predominantly food waste. One way of promoting an environmentally friendly method of minimizing food waste is to turn the waste into energy by producing biodiesel from waste cooking oils. Biodiesel is a biodegradable fuel that can be manufactured from food waste with a low price and sustainable supply. The purpose of research in Li and Yu (2015) was to produce biodiesel from waste cooking oils in the laboratory and compare the quantity and quality of products made from domestic waste cooking oil, restaurant cooking oil and fresh cooking oil. The feedstocks used were domestic deep-frying canola oil, domestic lard, deep-frying oil obtained from a restaurant and fresh canola oil. In a comparison of biodiesel yield and quality, household waste cooking oil was a better feedstock than restaurant waste cooking oil (Rumbaugh *et al.*, 2004). Waste cooking oils should be used for biodiesel production to turn waste into energy (Rumbaugh *et al.*, 2004). An acid–base-catalyst-based two-step biodiesel production experiment from soybean waste cooking oil was carried out to identify which parameter is the most influential among the experimental parameters by using the Taguchi method (Fajriutami *et al.*, 2013) and under the optimum conditions, waste

cooking oil was converted into crude biodiesel by a two-step process with fatty acid methyl ester content without any further post-purification. Physiochemical properties of biodiesel, a sustainable and green alternative fuel produced from renewable resources, are greatly influenced by the structural features of polyunsaturated, monounsaturated and saturated fatty acids. Two feedstock oils, potentially contribution to cleaner technologies, refined cooking oil and waste cooking oil derived from palm olein have been studied in article (Chuah *et al.*, 2017). Fatty acid compositions of the refined cooking oil and waste cooking oil were analyzed and confronted with other literature sources. With the proposed triangular chart for biodiesel properties prediction, potential biodiesel fuels from various feedstock oils can be analyzed (Chuah *et al.*, 2017). Growing demand for fuel in the industrialized and urbanized era coupled with the skyrocketing oil prices and growing concern over the adverse impacts on climate necessitate use of eco-friendly energy sources and recycling of wastes (Anitha, 2013). Article (Anitha, 2013) presented the results obtained from experiments on conversion of waste cooking oil into bio-diesel where the fuel properties of biodiesel obtained were found to be in agreement with standards. The use of metakaolinite as a catalyst in the transesterification reaction of waste cooking oil with methanol to obtain fatty acid methyl esters (biodiesel) was studied (Ramirez-Ortiz *et al.*, 2012) where results showed that metakaolinite is a prominent, inexpensive, reusable and thermally stable catalyst for the transesterification of waste cooking oil. Nano MgO is not capable of catalyzing the transesterification by itself, because it has a much weaker basic affinity but when used with Nano CaO due to its surface structure, the basic properties increase and it becomes a proper base for the catalyst so that CaO contact surface increases and transesterification reaction yield significantly increases as well (Tahvildari *et al.*, 2015). In study (Sodhi *et al.*, 2017), biodiesel was produced using waste cooking oil that was discarded as a waste in the environment. The properties of the feedstock were determined using standard methods. The transesterification process was implemented to extract the biodiesel, and this process was optimized and standardized by selecting three different parameters: molar ratio (methanol:oil), catalyst concentration (KOH) and reaction temperature. The study concluded that waste cooking oil has a great potential for waste to energy process (Sodhi *et al.*, 2017). The aim of the life cycle assessment study (Chua *et al.*, 2010) was to compare the environmental performances of biodiesel derived from WCO and low sulphur diesel in terms of global warming potential, life cycle energy efficiency (LCEE) and fossil energy ratio (FER) using the life cycle inventory where the results of this study would serve as a reference for energy policy makers and environmental agencies. The emission results and the life cycle energy efficiencies have indicated that the replacement of low sulphur diesel with biodiesel derived from WCO as a transportation fuel is favorable (Chua *et al.*, 2010). In study (Hosseini and Ju, 2015), the feasibility of pretreatment and/or upgrading of waste cooking oil (WCO) using the microalga *Ochromonas danica* was investigated where contacting the WCO with the phagotrophic *O. danica* cells was found to decrease the acid values of the remaining oil by 2.8 and 2.4 mg KOH/g WCO, respectively. The *O. danica*-pretreated WCO, with lower acid values, are potentially better feedstock for biodiesel production (Muralidharan and Vasudevan, 2015). The use of enzymes has several advantages, such as the absence of saponification side reactions, production of high-purity glycerol co-product, and low-cost downstream processing. In work (Vescovi *et al.*, 2016), biodiesel was produced from lipase-catalyzed hydrolysis of waste cooking oil (WCO) followed by esterification of the hydrolyzed WCO (HWCO) where it was found reuse hydrolysis and esterification assays showed that the immobilized enzymes could be recycled five times in 10-h batches, under the conditions described above. The results showed that WCO is a promising feedstock for use in the production of biodiesel (Vescovi *et al.*, 2016). A reactor has been developed to produce high quality fatty acid methyl esters (FAME) from waste cooking palm oil (WCO) (Buasri *et al.*, 2012) where continuous transesterification of free fatty acids (FFA) from acidified oil with methanol was carried out using a calcium oxide supported on activated carbon (CaO/AC) as a heterogeneous solid-base catalyst. The results showed that the FFA conversion increased with increases in alcohol/oil molar ratio, catalyst bed height and temperature, whereas decreased with flow rate and initial water content in feedstock increase. High quality waste cooking palm oil methyl ester was produced by combination of heterogeneous alkali transesterification and separation processes in a fixed bed reactor. In sum, activated carbon shows potential for transesterification of FFA (Buasri *et al.*, 2012). In the study (Farid *et al.*, 2017), a bioadsorbent produced from pressed-shredded oil palm empty fruit bunch was used to remove impurities from crude biodiesel derived from waste cooking oil. In comparison to commercial adsorbents and the water washing method, purification using the oil palm empty fruit bunch derived bioadsorbent resulted in higher removal of free fatty acids, potassium, water impurities and a smaller loss of fatty acid methyl esters. It was found that the use of the bioadsorbent improved the biodiesel quality besides its benefits of ease of operations and avoidance of waste water production (Farid *et al.*, 2017). The use of waste cooking oil and dimethyl carbonate (DMC) as a reactants was illustrated in article (Panadare and Rathod, 2017), enzyme as catalyst that facilitated the biodiesel production by providing low cost reactant, ecofriendly methodology and glycerol carbonate as marketable by-product. It is found that, about 94% conversion was obtained in just four hours using microwave irradiation when operated at optimized parameters which include temperature, enzyme loading, water content, molar ratio reactants and addition of surfactant. Lipase 435 used as a catalyst was found to recover 88% of its activity after catalyzing six successive reaction cycles. Biodiesel obtained was observed to fit ASTM D 6751 standards after least downstream steps (Panadare and Rathod, 2017). Improving the flow ability at a low temperature is vital for the utilization and popularization of biodiesel. The cold flow properties of waste cooking oil biodiesel-0# diesel blends with poly-alpha-olefin (PAO) pour point depressants were studied in Xue *et al.* (2016). Viscosity-temperature curves, polarized optical microscopy, low-temperature X-ray diffraction, and differential scanning calorimetry were used to explore the performance mechanism of PAO in biodiesel blends; and results presented that PAO could effectively lower the low-temperature viscosity, delay the aggregation of wax crystals and modify their crystallization behaviour by transforming the shape of crystals and depressing the formation of large wax crystals (Xue *et al.*, 2016). The International Maritime Organization (IMO) has enacted the Maritime Agreement Regarding Oil Pollution (MARPOL) VI to regulate the ship emissions. In the large ocean-going ship, the

marine auxiliary diesel engine is widely used to produce electricity, and it could also generate large amounts of harmful emissions (Geng *et al.*, 2017).

Methodologies for Software Development

Software development is very complicated and sensitive process. There are many subjects into the process with different tasks and goals. Since software could be very complex system there is demand to model different functions of the software separately to simplify the software development. Software could have dynamic and unstable nature since there are different technical and business aspect to model in the same time.

Early software developers did not use any specific methodology for software development for analyzing and modeling until for implementation and testing. In the meantime software developers were concluded that there are needs for software analyzing and modeling based on specific methodology. In other words it was established the concept of highly integrated software. It was lead to accept the methodology for general framework for software development. Accordingly the methodology could lead to better final result.

The models have to be created in order to understand the software behaviour and structure. Software modeling process shows the software visualization where one can see the software in graphical representation for easier observation.

RUP Methodology

Rational Unified Process (RUP) methodology has four main phases. The first phase is initial phase or idea inception where one needs to understand what should to do and software vision and requirements are identified. This phase includes the identification of key software actors (users) and use cases. Also there is need to identify software domain. Use case defines one sequence of an action which software performs that yields to an observable results. In the other hands one use cass presents result of an action by actor (Fig. 1). Use case presents the main part of some complete software operation from beginning until to the end. It is used to capture the intended behaviour of the system in development. By use cases models desired behaviour of the system could be specified but it is not strictly this desired behaviour to be carried out or implemented in the final product. Use cases models can be developed for whole system or for the part of system. Each part of system or subsystem can be developed by use cases models until the part produces some tangible amount of work and results. System complexity indicates the number of use cases. In the initial stage of system development main use cases are developed and additional use cases can be added or included when there is need for them.

The second phase is project elaboration where one needs to understand how to build the software and basic software architecture is showed in the phase. The third phase presents software construction where software testing is considered. The fourth phase presents software transition where software validation is performed. The RUP phases are shown in Fig. 2.

RUP models describes software in modeling. RUP models could be business models which describes business processes and business environment, use case models which describes what software doing and software environment, projecting models which describes use cases realization as code abstraction and implementation models which presents collection of components and subsystems.

Software development process could has different problems which needs to be identifies and solved before coding and testing. In order to solve problems there is need to find the problem causes. To remove the problem causes it is suitable to use best practices. For example in order to remove the confusion in communication between team members it is suitable to use standard language UML for the software visualization, specification and documentation. There are different types of UML diagrams which can be used in the software development process. There are two main classes of the ULM diagrams. These are structural and

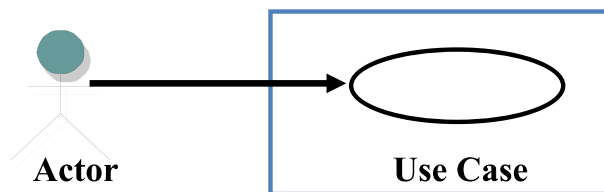


Fig. 1 Use case model.



Fig. 2 RUP methodology phases.

behavioral diagrams. Structural diagram presents structure of the system in passive state and behavioral diagram present the active behaviour of the objects in a system or dynamical state.

Business Process Modeling

Business Process

Business process presents all operative procedures, rules, data and technologies of the companies. However mostly business processes are not optimized nor documented properly and therefore the processes are prone to errors and they are not understandable to all people. Business process enables goal fulfillment by transformation of inputs to outputs through producing some worth in the companies. The inputs and outputs could be information or products. People and machines transform the inputs to the outputs. The most known business process are operative process, support process and control process.

Business process are made as results of company project. Business process needs to be optimized in the mostly cases in order to improve the company efficiency. Also there is need to enable control and adaptation of the business process in order to track new trends and solutions. Fig. 3 shows the most important rules of the business process modeling. In the top there are standards which must be followed during the process modeling. The standards should answer to question what should one do. The second level is best practices where there are presented completed solutions of the some process. The second level answer to question how to work. In the other hand there is no need to develop solutions of product or process if there is already developed solutions of the product or process. The third level presents the software application in the some field of company in order to increase company efficiency. The last level represents the rules and procedures where it is described how software should implement in the particular organization.

Business process modeling should enable the specification of the all activities in the company in order to analyze, improve and automatize the processes. The models define users of the process, inputs and outputs, activities, etc. In order to model the business processes it is required to identify and describe the all processes which leads to the process complexity problem. To make easy understanding and analyzing of the business process it is required to perform software decomposition up to software components. Each of the software component is analyzed separately and the components interactions and relationship as well.

Object-Orientated Modeling of Business Process

UML is used for object-orientated modeling of business process. As already mentioned there are different UML diagrams for describing of software architecture and software behaviour. UML as standard language is used for modeling, for analyzing, for projecting and for implementation of the software system. Based on the object-orientated modeling all process could be presented by use cases models as rough specification and by structural diagrams and behavioral diagrams as detail specification.

During modeling of the business process it is not recommended to use natural language because of its ambiguity. Also, formal programming languages are not understandable for many people in the project team. Therefore it is suitable to organize the natural language to avoid ambiguity. Modeling process is one of the solutions for understanding and clear communication between project team members.

Rough software specification

Use case model could represent rough software specification, desirable software behaviour and activity sequence of the software which describes what software could do from the point of actors or users. The actor could be external user, internal user, another software or hardware. During modeling of use cases one can use standard specifications and relations like associations, generalizations, inclusions and extensions between actors and use cases and between two use cases as well.

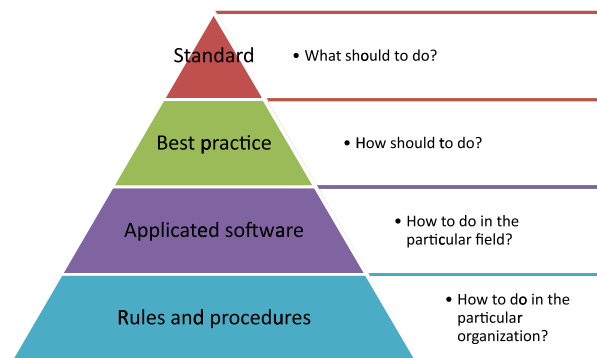


Fig. 3 Rules of business process modeling.

Use case model should identify software users and what software should do. Also use case model should verify all requirements and to ensure communications with end users and experts. The main use case presents main functions of the software with main actors and software domain.

Detailed software specification

The next step after use case modeling is detailed software specification. This specification could be made by UML diagrams by software decomposition which shows use cases realization.

Each use case should be explained in detail. The first step is to describe normal and alternative activity flows in order to cover all predictable and unpredictable cases of the business process. One use case presents activity sequence. One sequence presents a scenario. There is normal scenario and an alternative scenario. The both of the scenarios should be written explicitly. Scenarios are instances of use cases. A scenario is systematic description of sequence of messages sent between actors and the system. Although there is large number of possible scenarios corresponding to a single use as it is important to write at least one non-trivial or normal scenario.

There is need to document each use case separately in order to specify use case. Activity flow and scenario should show what software should do but not how to do. Activity flow writing for particular use case needs to be done iteratively. In the other hand normal activity steps are written at first. Afterwards alternative activity step should be written as well in the next iteration.

There are different diagrams to explain use cases in detail like activity and state diagrams. Activity diagram is used for software modeling on different levels for business process, activity flows, procedure logic and etc. Activity diagrams is used for modeling software dynamical aspects based on activities.

State diagrams is used to describe behaviour of one object through several use cases. In the other hand state diagrams show life span of one object or several similar objects (class). State diagram is focused on object behaviour for particular activities. It describes how one object transform from one state to another by some activity. Each object should be in some state through its life span. This object state is changable through time or by some activity action. For example faculty teacher could change his state from assistant through assistant professor and docent until regular professor state. For each of the state there is need time and some activity to perform by object or candidate.

Waste Cooking Oil Management Software Modeling

Problem Description

The investigation is intended for the problem solving of collection and acquiring of waste cooking oil which is cancerogenic. The main objects of the suppliers which are implemented in the software of the waste cooking oil management are market objects, touristy industry, catering industry and industry objects. The main problems in collecting and acquiring of the waste cooking oil are:

1. Suppliers are not identified,
2. There is no technical support for the waste cooking oil management,
3. Insufficient usage of fuel in transport from renewable energy sources,
4. Insufficient education of the main suppliers of the waste cooking oil about the main problem of the waste cooking oil and suggestions for the problem solution.

The main goals of the investigation is to decrease the emissions of the greenhouse gasses and generally to decrease global warming. Also biofuels need to be introduced in the transport as much as it can. The main activities of the investigation should be:

1. To identify all waste cooking oil generators which are the most relevant,
2. To analyze the potential of the waste cooking oil generators,
3. To analyze quantity of the potential waste cooking oil,
4. To model software for waste cooking oil management.

Object-orientated modeling concepts are used during analyzing and modeling of the waste cooking oil management software. Two UML concepts are used for the software modeling like use case models, activity diagrams, state diagrams and scenarios of activities.

Waste Cooking Oil Management Software

Waste cooking oil management software should be use for organization of the waste cooking oil suppliers and collectors as well. The main advantage of the waste cooking oil management software in the article is in its universality and in its online usage. In the other hand it is possible to access to the software from any place and anytime.

The main feature of the waste cooking oil management software should be universal application for any subjects and any suppliers and collectors. The waste cooking oil management software will be framework of the suppliers and collectors of the waste cooking oil management activity. Also this software could be adapted based on new subjects or new material.

As users are considered, suppliers in different parts of the industry are collectors as well. All of the users should have username and password in order to access the waste cooking oil management database.

Collectors should made reports for different statistical analysis of the waste cooking oil. As the main problem of the current waste cooking oil management software it was identified limitation of unified approach for all subjects. Therefore it is required to develop information system which would allow to users to use the software anytime in order to enter desired data.

Waste cooking oil management software users

The waste cooking oil management software users could be divided based on natural basis according to working place, suppliers and collectors. All of the users have equal rights to access and use of the software. Therefore the main users of the software are:

- Suppliers (market objects, touristy industry, catering industry and industry objects),
- Collectors,
- Administrator.

Each of the users should have individual username and password in order to access to the software. Administrator of information system who needs to maintain the software and he is responsible for working of computer system and software as well. He gives permission to the staff's access to the waste cooking oil management database, maintains database, maintains web presentation of the waste cooking oil management and makes regular daily reports.

Waste Cooking Oil Management Software Analyzing

Each of the users should have individual username and password in order to access to the software. Administrator of information system who needs to maintain the software and he is responsible for working of computer system and software as well. He gives permission to the staff's access to the waste cooking oil management database, maintains database, maintains web presentation of the waste cooking oil management and makes regular daily reports.

Analyzing of the current state of waste cooking oil management software is crucial in order to get knowledge about advantageous and drawbacks of the current state and to find potential spaces to make the software better. The main goal of the article is analyzing and modeling of the waste cooking oil management software.

During analyzing process of the current waste cooking oil management software it is concluded that the suppliers and collectors of the waste cooking oil have the have universal software to improve the efficiency of the waste cooking oil acquiring. This software needs to have online and offline working regime since there is no need to be always online to track desired materials. The software should enable fast searching procedure for the material.

Main use cases diagram of the waste cooking oil management software

Waste cooking oil management processes are depicted by the main use case diagram as it shown in Fig. 4. The main use case diagram has several sub use cases which will be explained in detail. As can be see administrator should perform main administration process of the waste cooking oil management process in order to ensure smooth working processes by the software. Waste

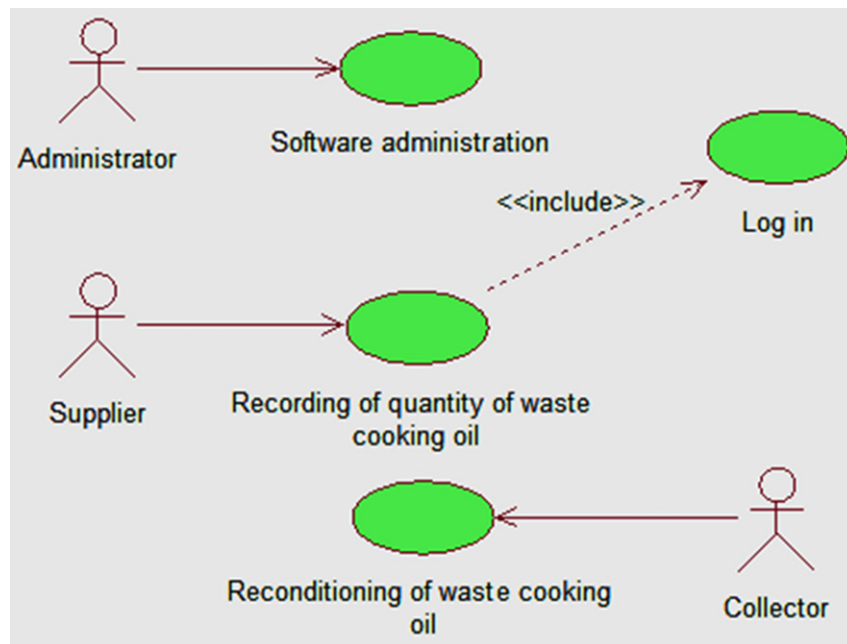


Fig. 4 Main use case diagram of the waste cooking oil management software.

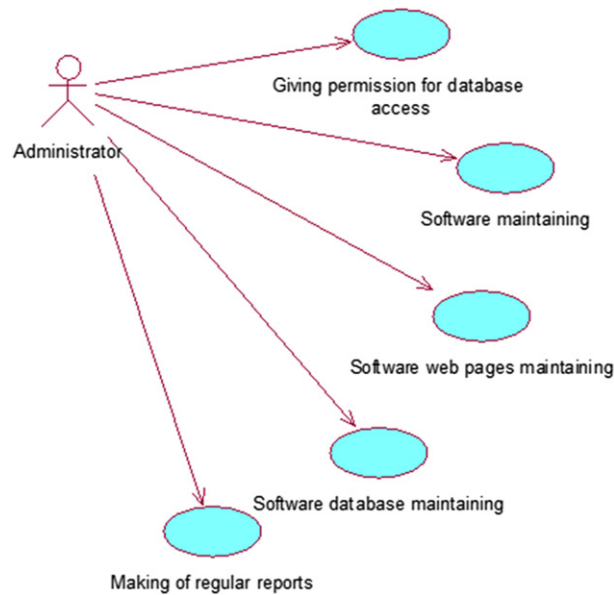


Fig. 5 Use case diagram – Software administration.

Table 1 Specification of use case: Giving permission for database access

Title	Giving permission for database access
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the giving permission for database access
Pre-condition	PC is properly settled Administrator has needed knowledge for the tasks
Post-condition	Client received authorization for database access of waste cooking oil management software
Main scenario	1. Administrator receives the request for the giving permission for database access of waste cooking oil management software. 2. Administrator checks the request validity 3. Administrator fills the application form for the giving permission for database access of waste cooking oil management software 4. Administrator selects client category based on the quantity of the waste cooking oil 5. Administrator approves the request 6. Administrator prints the instruction for the application use 7. Administrator distributes the instruction to the client as the proof for the successful addition to the users of the waste cooking oil management software for the database access
Alternative	1. In the case if the request is incorrect filled based on the step 2 of the main scenario the administrator returns the request to the client with the instruction how to correct the errors in the request

Table 2 Specification of use case: Software maintaining

Title	Software maintaining
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the waste cooking oil management software maintaining
Pre-condition	PC is properly settled Administrator has needed knowledge for the tasks
Post-condition	Backup of the waste cooking oil management software was made
Main scenario	1. Administrator checks if there is some large operation on the waste cooking oil management software 2. If there is some operation on the waste cooking oil management software, the administrator waits until the operation ends 3. If there is not operation on the waste cooking oil management software, the administrator prepares tools for the software maintaining 4. Administrator checks if the all functions of the waste cooking oil management software are proper 5. If some of the function of the waste cooking oil management software is not proper than the administrator starts the tool for correction of the function 6. Administrator starts the backup process of the waste cooking oil management software 7. Administrator records the time of the software backup
Alternative	None

Table 3 Specification of use case: Software web pages maintaining

Title	Software web pages maintaining
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the web pages maintaining of waste cooking oil management software
Pre-condition	PC is properly settled Administrator has needed knowledge for the tasks
Post-condition	Backup of the web pages of waste cooking oil management software was made
Main scenario	1. Administrator checks if there is some large operation on the web pages of waste cooking oil management software 2. If there is some operation on the web pages of waste cooking oil management software, the administrator waits until the operation ends 3. If there is not operation on the web pages of waste cooking oil management software, the administrator prepares tools for the web pages of waste cooking oil management software maintaining 4. Administrator checks if the all functions of the web pages of waste cooking oil management software are proper 5. If some of the function of the web pages of education software is not proper than the administrator starts the tool for correction of the function 6. Administrator starts the backup process of the web pages of waste cooking oil management software 7. Administrator records the time of the web pages of waste cooking oil management software backup
Alternative	None

Table 4 Specification of use case: Software database maintaining

Title	Software database maintaining
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the database maintaining of waste cooking oil management software
Pre-condition	PC is properly settled Administrator has needed knowledge for the tasks
Post-condition	Backup of the database of waste cooking oil management software was made
Main scenario	1. Administrator checks if there is some large operation on the database of waste cooking oil management software 2. If there is some operation on the database of waste cooking oil management software, the administrator waits until the operation ends 3. If there is not operation on the database of waste cooking oil management software, the administrator prepares tools for the database of waste cooking oil management software maintaining 4. Administrator checks if the all functions of the database of education software are proper 5. If some of the function of the database of waste cooking oil management software is not proper than the administrator starts the tool for correction of the function 6. Administrator starts the backup process of the database of waste cooking oil management software 7. Administrator records the time of the database of waste cooking oil management software backup
Alternative	None

Table 5 Specification of use case: Making of regular reports

Title	Making of regular reports
Actors	Administrator
Trigger	It starts with the choosing of the option on user interface for the making of regular reports
Pre-condition	PC is properly settled Administrator has needed knowledge for the tasks
Post-condition	The reposts were printed
Main scenario	1. Administrator checks if there is some large operation 2. If there is some operation, the administrator waits until the operation ends 3. If there is not operation, the administrator prepares tools for the making of regular reports 4. Administrator selects between standard procedure of the making of regular reports and nonstandard procedure where administrator can adjust the parameters of the reports. If nonstandard procedure was chosen than the administrator adjusts the parameters of the reports 5. Administrator starts the procedure of the making of regular reports 6. Administrator saves the backup of the reports 7. Administrator records the time of the database of making of regular reports
Alternative	None

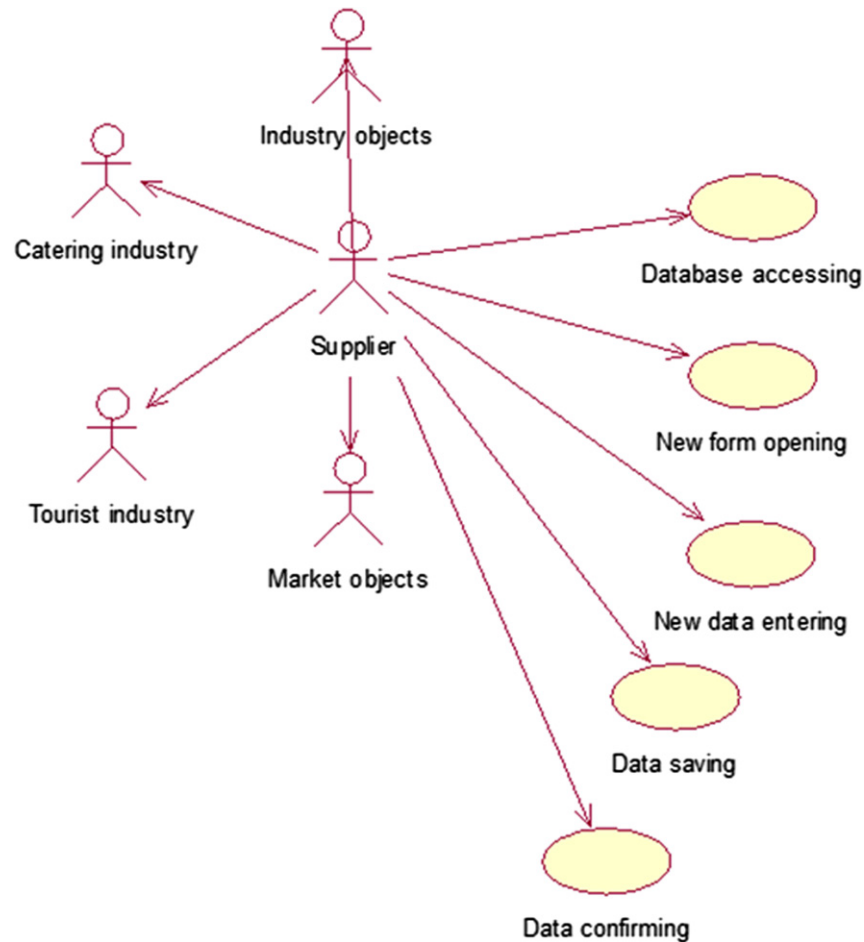


Fig. 6 Use case diagram – Recording of quantity of waste cooking oil.

Table 6 Specification of use case: Recording of quantity of waste cooking oil

Title	Faculty or school selecting
Actors	Suppliers
Trigger	It starts with the choosing of the option on user interface for the recording of quantity of waste cooking oil
Pre-condition	PC is properly settled Waste cooking oil acquired
Post-condition	Recorded quantity of waste cooking oil
Main scenario	1. Client starts waste cooking oil management software 2. Client does login into waste cooking oil management education software 3. Client records the quantity of waste cooking oil 4. Client confirms the quantity
Alternative	1. The recording of quantity of waste cooking oil is canceled 2. Due to technical problems the service cannot be made

cooking oil management clients or suppliers could record the quantity of the waste cooking oil if they are logged in the software database. Collectors will perform reconditioning of the waste cooking oil only after clients or suppliers confirmed the recorded quantity of the waste cooking oil.

Use cases of the waste cooking oil management software subsystems

Software administration

Based on the analyzing of cooking oil management process it is noted there is need for new computer system for the sector. Accordingly there is need for person who will maintain administration of the software and the computer system. Therefore there is need for a software administrator.

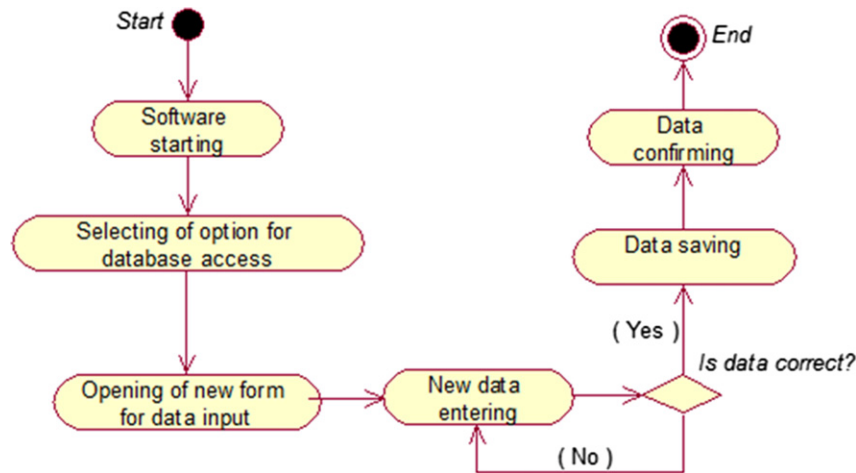


Fig. 7 Activity diagram – Recording of quantity of waste cooking oil.

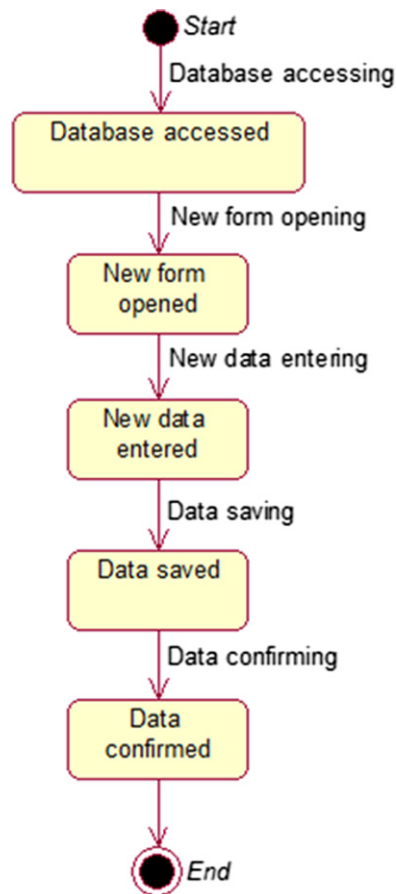


Fig. 8 State diagram – Recording of quantity of waste cooking oil.

Administrator performs software administration in order to eliminate all unpredictable errors in the software and system. Administrator has full responsibility for the software maintenance. They will give permissions for other users access to the system, maintains the software, maintains the web pages of the software, maintains the software database, and makes regular daily reports. Fig. 5 shows the use case diagram of the software administration. As can be seen there are five functions of the administration which will be explained in details by scenarios.

Table 1 shows detailed specification of use case for giving permission for database access of the waste cooking oil management software by administrator.

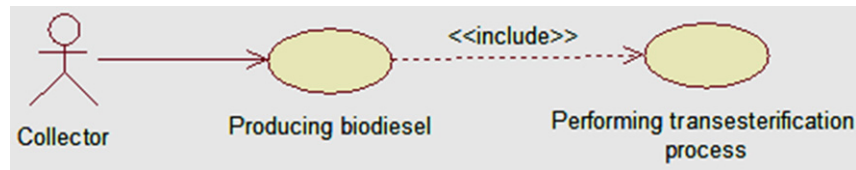


Fig. 9 Use case: Reconditioning of waste cooking oil.

Table 7 Specification of use case: Reconditioning of waste cooking oil

Title	Reconditioning of waste cooking oil
Actors	Collector
Trigger	It starts with the choosing of the option on user interface for the reconditioning of waste cooking oil
Pre-condition	PC is properly settled Recorded quantity of waste cooking oil
Post-condition	Produced biodiesel
Main scenario	1. Collector receives quantity of waste cooking oil 2. Collector performs transesterification process of the waste cooking oil
Alternative	1. The reconditioning of waste cooking oil is canceled 2. Due to technical problems the service cannot be made

Table 2 shows detailed specification of the use case of waste cooking oil management software maintaining by administrator.

Table 3 shows detailed specification of use case for web pages maintaining of waste cooking oil management software by administrator.

Table 4 shows detailed specification of use case for database maintaining of waste cooking oil management software by administrator.

Table 5 shows detailed specification of use case for making of regular reports by administrator.

Recording of quantity waste cooking oil

Use case diagram for recording of quantity waste cooking oil in the software is shown in **Fig. 6**. As can be seen the use case has several activities in order to record the quantity waste cooking oil. These activities are database accessing, new form opening, new data entering, data saving and data confirming. Login into the software is necessary action before perform other main activities. As can be seen suppliers (market objects, touristy industry, catering industry and industry objects) and are the main users of the use case.

Table 6 shows detailed specification for use case recording of quantity of waste cooking oil. **Fig. 7** shows activity diagram for recording of quantity of waste cooking oil. **Fig. 8** shows state diagram for recording of quantity of waste cooking oil.

Reconditioning of waste cooking oil

Use case for reconditioning of waste cooking oil by the software will be explained by sub activities in the use case as can be seen in **Fig. 9**. As can be seen the use case is composed of two activities. The main activity is biodiesel production from the waste cooking oil. In order to perform the main activity one sub activity needs to be established. The sub activity is performing transesterification process of the waste cooking oil. As users of the use case there are collectors.

Table 7 shows detail specification of use case for reconditioning of waste cooking oil.

Conclusion

An attempt for modeling of universal waste cooking oil management software was expressed in this paper by applying object-orientated modeling approach by using unified modeling language (UML) which is standard language for software visualization and modeling. The main concepts of the object-orientated modeling was described in the article. Generally, the waste cooking oil management software development was done by UML approach. Use case diagram and UML diagram was used for the waste cooking oil management software development and modeling. Afterward the main and alternate scenarios were written for each set of activity.

Since the UML has become a standard modeling language accepted widely by the industry leaders and a tool of communication between system users, analysts and programmers it is beneficial to develop models by using the UML. The UML developed models could be implements in any object-orientated language to become platform independent.

Visual modeling is a way of thinking about the problems from reality. The models are used for problems understanding, for communications between team members which are included in the project, for modeling of company, for documentation

preparation and for program and database design. Modeling enable better understanding of requirements, clean design and better support and maiming of the systems.

UML has become standard language for software modeling. ULM enables full tracking of project development process through fill life cycle. Because of the analysis through UML programming time is significantly reduced since mostly problems are identified in initial stage by modeling in UML. Programmers get full documentation and specification and new team members could be easily added in the project.

We develop all use cases of the waste cooking oil management software in the article. Also all scenarios are written for the all activities. The way of modeling could enable easy further development for the software.

See also: Analyzing Biodiesel Production From Cooking Oil

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Use of Bio-Fibers in Various Practical Applications

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Introduction

The life on earth today is combating the worst effects of environmental degradation brought about by human exploitation. Environmental degradation has directly reduced the quality of life on earth and also resulted in producing extreme scarcity of resources. Polymers which were once believed a boon to mankind, over the years have turned out to be environment's primary bane. To counter this condition, there is an immediate need to make these polymers environment-friendly. Governments around the world are imposing strict norms and are calling for stringent adaptation of 3Rs: Reduce, Reuse and Recycle. Industries are now searching for alternatives to comply with regulations and come up with products that are more 'green'. Thus, polymer composites are fabricated by incorporating organic, biodegradable natural fiber reinforcements instead of the most widely used synthetic fibers such as glass, aramid and carbon fibers. Bio/Natural fibers are derived from plants, animals and other geological processes. Natural fibers are made up of clusters of microscopic cells and possess a negligible diameter in comparison to their length. Polymer matrix composites reinforced with nature-derived fibers exhibit excellent strength-to-weight ratio, superior mechanical properties such as elastic modulus, flexural strength, and shear strength (Tajvidi *et al.*, 2006). Due to these inherent properties, the natural fiber reinforced composites find a wide-spread application. The use of locally available natural fibers also help to bring down the cost of the composites by a greater extent, alternatively helping the agriculture sector to find a means for sustainable income.

Classification

Bio fibers are classified based on the source from which they are derived from such as plant, animal and mineral derivatives. Fig. 1 illustrates the classification of bio fibers.

Application

The most primitive application area of bio-fibers is textile (Robinson, 1969). Since ages man has clothed himself in the cloth weaved from threads spun from various bio-fibers such as cotton, silk and wool. To make the fabric look attractive the bio-fibers of cotton, wool and silk are dyed in an array of colors. Both natural and synthetic dyes are used to beautify the fabric (Cristea and Vilarem, 2006). But technological advancements have led to the use of many bio fibers in various industrial applications. The following sections highlight the use of some of the most abundantly available bio fibers throughout the world.

Banana Fibers

Banana which is rich in nutrition is the world's fourth most important food (Reddy and Yang, 2015). Fibers derived from the stem of the banana plant has grabbed the attention of several researchers due to its attractive tensile strength (458 MPa) and tensile modulus (17 GPa) (Pappu *et al.*, 2015). Banana fibers are derived through mechanical means from the stem of the banana plant. The long fibers thus extracted are subjected to enzymatic treatment under optimized conditions to produce yarns (Ortega *et al.*, 2016). The treated banana fibers are used as reinforcement for polymeric composites. The treatment of banana fibers is needed to reduce the hygroscopicity by eliminating lignin, pectin, waxes and other such water soluble substances. Fiber treatment also improves the wetting of the fiber with the polymer matrix resulting in a composite with superior properties such as tensile, impact and flexural strength (Venkateshwaran and Elayaperumal, 2010). Banana fibers are used not only in cottage industry to produce

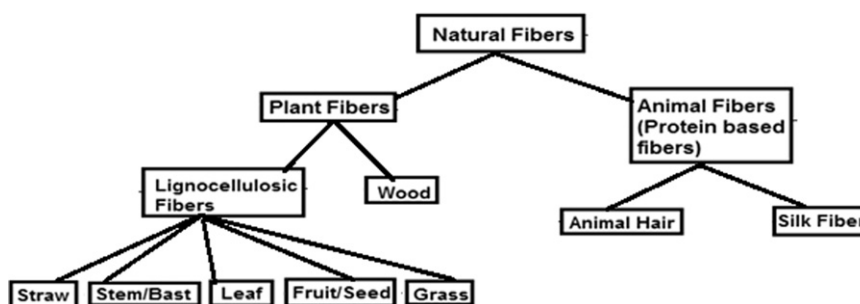


Fig. 1 Classification of bio-fibers.

ropes, floor mats, carpets and bags, but are also used extensively in paper and textile industries across the globe (Ray *et al.*, 2012). Banana fiber yarn can be spun to a scale as small as 10 nano-meter making it the most sought after material to produce summer wears, textured apparels, socks, cushion covers, rugs, neckties, curtains and table cloth. Banana fibers

Jute Fibers

Jute is known as the 'golden fiber' due to its silky texture and golden sheen. It is majorly extracted from the hard bark of *Corchorus capsularis* plant grown mainly in south Asian countries. India is the largest producer of jute in the world. Jute is harvested annually and the crop takes approximately four months to grow with almost nil application of fertilizers and/or pesticides making it the most affordable. It is one of the most widely used natural fiber with application areas spanning from textiles to automotive fields. Sacks woven from jute fibers were extensively used during the period of industrial revolution in 18th century. Till date, jute fibers are primarily used for sacking simple agricultural produce to rigid packing. Jute fibers are woven to produce strong ropes owing to their superior strength. Various cottage industries thrive by producing textiles woven from jute which are used to produce curtains, carpets, cushion coverings and rugs. Jute, when treated through the application of caustic soda, is rendered soft and pliable making it easy to blend with wool. Blended fibers are then used to produce clothing and furnishings that have huge market worldwide. Jute is one such natural fiber which imparts excellent tensile strength to epoxy composites and can be used directly without any prior treatment as the strength imparted to the composites through untreated jute fiber does not show significant variation with the incorporation of treated jute fiber (Rashed *et al.*, 2006). This brings down the cost of composite fabrication by a greater level. The improve in various mechanical properties of jute reinforced polymer composites is due to the fact that jute contains very high proportion of cellulose which renders excellent stiffness to the fibers. Studies have indicated that jute fibers can effectively replace glass fibers as composite reinforcements in the production of automobile component such as bonnet (Alves *et al.*, 2010). Jute fiber reinforced concrete is found to exhibit superior flexural, compressive and tensile strength over unreinforced concrete, thus increasing the scope for inclusion of jute fibers for structural applications (Zakaria *et al.*, 2017). This scenario would enable the surge of low cost, sustainable housing solutions worldwide.

Coconut Fibers

'Coir' is the tradename given for coconut fiber which is derived from the inner husk of coconuts. Cellulosic fibers bonded together with lignin and hemicellulose constitute coir. The proportion of lignin in the coir is very high as compared with the proportion of cellulose. This renders coir with a low tensile modulus and strength. Coir also possesses very high elongation at break which renders coir most suitable for cushioning applications such as seating for automotive (Nam *et al.*, 2011). The high lignin content makes coir more moisture resistance thus reducing the adverse effect of fungus and bacterial decay (Khedari *et al.*, 2004). Traditionally, coir is used to produce mats, ropes, blinds, mattresses and decorative items. Coconut producing countries like India have setup coir boards exclusively to develop and promote value addition to coir. In India coir pith is a waste that is generated from numerous coir processing industries. This large amount of waste in the form of coir pith is used to produce activated carbon through chemical treatment economically (Namasivayam and Kadirvelu, 1997). It is also used to adsorb dyes from aqueous solution resulting from textile industries. Coconut fiber mats are employed as an underlayment for floor covering for indoor sports arena owing to their superior elasticity, resistance to wear and moisture (Schomerus, 1981). Densified coir dust briquette has excellent calorific value of around 4000 kcal/kg and can be effectively used as energy source (Hamidul Islam *et al.*, 2014). Coir finds its extensive use in the field of agriculture due to its inherent characteristics such as high water retention, resistance to fungus and bacterial attack. Due to its extremely high lignin content (approx. 40%), coir decomposes very slowly and hence does not rot quickly. 'Coir dust' which is traded in the name of 'Coco peat', a byproduct of short coir fiber production, is considered a boon to the farming community. It has been proven that through the addition of as less as two percent of cocopeat to loamy soil, the moisture-retention of the soil increased to 40% from 24.3% (Hume, 1949). Coconut fiber reinforced polymer composites have gained the attention of researchers and industries throughout the globe as coconut fibers possess a natural wax layer that aids in the promotion of a strong interfacial bonding between the polymer resin and the fiber (Brahmakumar *et al.*, 2005). Coir reinforced polymer composites indicate good flame retardancy and such composites qualify as good materials for automobile interior applications (Ayrlimis *et al.*, 2011).

Bamboo Fibers

Bamboo is an evergreen plant belonging to Poaceae grass family. Bamboo possesses superior compressive strength which is greater than that possessed by concrete, brick or wood. It has a tensile strength value which is almost exceeding the steel's tensile strength (Amatosa Jr. and Loretero, 2017). Bamboo is a tropical plant which thrives in the hot and humid regions of the world. Bamboo is the fastest growing evergreen plant with growth rate ranging from 300 to 1000 mm per day and is known to reach maturity in as little as five years. The traditional applications of bamboo include structural constructions, furniture, weapons, tools, utensils, textiles and musical instruments due to their extremely high strength to weight ratio. The fibers extracted from bamboo are almost equivalent to glass fibers in their strength and modulus (Osorio *et al.*, 2011). This is mainly due to the fact that bamboo fibers are composed of cellulose (60%) coupled with higher concentration of lignin and a small micro-fibril angle. Cross-ply poly-lactic acid

laminates reinforced by bamboo fiber can suitably replace glass fiber based composites used as skins for sandwich structures. Carbonized bamboo fibers molded into sheets have been successfully employed as a gas diffusion layer of proton exchange membrane fuel cells which is a greener and sustainable step towards reducing the usage of carbon fibers (Kinumoto *et al.*, 2015). Woven bamboo fiber reinforced composites possess excellent mechanical properties and are found to be a good substitute for cotton and nylon fiber based composites in orthotic and prosthetic devices (Kramer *et al.*, 2015). Epoxy composite reinforced with bamboo fiber performs better than conventional aramid fabric plies in multilayered ballistic armors with nearly 22% superior ballistic performance, ensuring both safety and cost effectiveness (Cruz *et al.*, 2015). Bamboo fiber reinforced nano-hydroxyapatite/poly (lactic-co-glycolic) composite scaffold exhibit the required porosity and porous structure coupled with compressive strengths that are extremely superior to the conventional n-HA/PLGA composite scaffold indicating that bamboo fiber reinforced composites are the candidate materials for bone tissue engineering scaffold (Jiang *et al.*, 2017). Bamboo fibers are a rich source of dietary fibers possessing good hygroscopic properties, excellent stability to emulsification and compatibility of color for meat based products. Hence, bamboo fibers can be applied in the formulation of chicken burger acting as a substitute for animal fats (Huber *et al.*, 2016). Bamboo fibers have been successfully incorporated in 'Amaretti cookie', an Italian food. Bamboo fiber incorporation resulted in an enhanced textured, flavorful and tastier cookie (Farris and Piergiovanni, 2008). The use of bamboo fiber based biofilm carrier for bio-contact oxidation reactor employed for waste-water treatment is proven to be far superior in effluent removal under fluctuating loads as compared to the prevalent activated sludge system (Xiao and Chu, 2015). Bamboo fiber are candidate materials for providing low-cost, sustainable buildings and houses. Bamboo fiber reinforced concrete beams have performed well under cracking as the bamboo fibers tend to reduce the width of the crack and arrest beam deflection, thereby enhancing the beam's load-carrying ability post cracking (Dewi and Wijaya, 2017). Bamboo fibers have been employed in the production of Wood-free material for paperboard packaging (Shi *et al.*, 2018). Bamboo fiber reinforced composites possess good fire retardant characteristics enabling their application in the field of automotive. Technological enhancements in injection molding process has enabled the incorporation of bamboo fiber based polymeric structures for automobiles (Partanen and Carus, 2016). The excellent strength and wear resistance possessed by bamboo fibers have led to their incorporation in semi-metallic matrices to produce composites for brake friction materials employed in automotive applications (Talib *et al.*, 2016). Bamboo fibers are mixed with polylactic acid resin along with a natural binder to produce a speaker diaphragm which can produce high quality rich sound with enhanced audio experience for electronic devices (Jin *et al.*, 2015).

Flax Fibers

Flax, also called as linseed plant belonging to Linaceae family, is a very versatile food plant cultivated originally for its fibers and recently for its oilseeds which are known to be a rich source of ω -3 and α -linolenic fatty acids that are essential to prevent cardiovascular diseases. Fibers from the stem of the flax plant are derived through the process called 'retting'. The flax fibers are extensively used for the production of linen garments and is one of the oldest known luxury fiber (Farrer and Watt, 2015). Long length flax fibers are used to produce superior quality linen garments such as bed spreads, inner wears, table cloth, bathrobes, hand towels, lace, socks and stocking, while the short flax fiber is utilized for the production of ropes and twines. Flax fibers are extensively used for the production of superior grade paper employed for printing currencies, production of tea bags and cigarette rolls. Apart from its traditional use in textile industry, flax fibers, off late are being incorporated as reinforcements for production of variety of composite materials having innumerable applications. This in turn possess challenges for flax cultivators and breeders to produce flax fibers with specific characteristics in large quantities. Flax fibers have excellent specific tensile modulus (20×10^3 to 50×10^3 mm²/s²) coupled with extremely good tensile strength of 1500 N/mm² for single fiber to 800 N/mm² for fiber bundle (Sojoudiasli, 2017). Due to such superior properties, flax fibers are considered to be the best replacement for glass fibers. Long, unidirectional, nonwoven flax fiber reinforced composite panels employed for load bearing floor panels in a passenger vehicle compartment resulted in a drastic reduction in the total weight of the vehicle coupled with extreme durability under the applied load (Akampumuza *et al.*, 2017). Automobile giant such as Mercedes have incorporated flax fiber reinforced polyester composite for encapsulating their bus engines which resulted in a 5% reduction in the total weight of the buses, thereby improving the fuel economy (Koronis *et al.*, 2013). This prompted the manufacturers to incorporate flax fiber reinforced composites in shelving for parcels and coverings for the rear trunk in the 2006 Mercedes Benz S-class luxury car (Wallenberger, 2001). Another auto-giant, Audi, in its 2000 model of A2 car utilized the flax/sisal fiber reinforced polyurethane door trim composite panels. Flax fiber reinforced polymer sandwich panel exhibited superior impact resistance and thus are successfully used for building cladding and roof slabs (Betts *et al.*, 2018). Light weight, ventilated facades for buildings made out of nonwoven flax fiber reinforced Portland cement are considered to be apt replacement for the current heavy building materials such as ceramics and stones due to their superior strength to weight ratio, high durability, ductility, insulating capacity and ease of incorporation of required aesthetic features (Claramunt *et al.*, 2016). Flax fiber composites are extremely resistant to the formation of molds and fungal attacks (Segovia *et al.*, 2016) making them candidate building construction materials. Flax fibers are very good insulators and are ideally used to provide thermal insulation for the buildings. Flax fiber composites find their use in the field of medicine. Flax fiber reinforced Polycaprolactone composites are beneficial for accelerated bone regeneration (Gredes *et al.*, 2016). Efforts have been made to come up with disposable wet wipes for removable dental appliances incorporating nonwoven cellulosic fiber such as flax fiber (Tricca *et al.*, 2018). Modified flax fibers with induced polyhydroxybutyrate gene are considered to be

exceptional biomedical materials that promote proliferation of human fibroblast coupled with high antimicrobial properties and such fibers are successfully utilized for the production of wound-dressing gauze (Kulma *et al.*, 2015). Knitted flax fiber mesh is a new class of implantable structures in surgical procedures such as for the repair of the incisions of the abdominal wall due to hernia (Michel *et al.*, 2014).

See also: A Review on Utilization of Electronic Waste Plastics for Use Within Asphaltic Concrete Materials: Development, Opportunities and Challenges for Successful Implementation. Energy Efficiency Analysis in Building Walls in Tropical Climate Using Thermal Insulation System

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Use of Clayey Salty Soils and its Composite Derivatives for Construction and Ceramics for Household Use in the Thar Desert in India

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Introduction

Soil is a valued commodity for use in household construction in rural Rajasthan, India (Niroumand *et al.*, 2013). Soil and carbonaceous material blends have been used in the manufacture of ceramics for water storage and cooking (Roux, 2015). The skills to cast clayey soils and spin wheel are vital in cruse manufacturing. These cruse are manufactured from local soil, small pebbles and organic material such as wood waste, donkey dung etc. (Roux, 2015). Cruse manufacturing can be traced back to the Mesolithic period in this region. The importance to pottery, settlements and domestication of animals towards the west of the Vindhya in India were observed during this period (Agrawal, 2007). Arid areas of the Thar lie to the West of the Vindhya Ranges in India.

Western Rajasthan is arid and has desert loam soils. Soil should have adequate fertility in order to be utilized for production of crops. Generally dung or ordure is added to enhance soil fertility (Chandra, 2005). Compost of plant materials is also added to attain similar fertility enhancements (Haug, 1980). It is advantageous, if the soil and carbonaceous mixtures are pressed together, organically protected and into arid soils (Satankar *et al.*, 2017). This hybrid composite plays an important role in soil quality revival and waste management. Apart from ecological advantage, such hybrid composites enhance the value of animal waste (Thakur *et al.*, 2013).

Ceramics from mud and organic materials are also used to produce functional ceramics which help water filtration (Plappally and Lienhard, 2013). Similar ceramic devices namely the G filter is also molded and baked by local hereditary potter families of this region. Further they also manufacture the cruse for water storage.

This article discusses the soil based blends or immingles specific to western Rajasthan, India. It is important to know the geographic location where these materials are used. For clarity, the geographical position in focus is bounded on the east and west between latitudes 26°48' 56.42"N and 27° 25' 15.18"N and longitudes 69°33' 18.95"E and 74°42'2.02"E. Further latitudes 28°31' 38.65 N and 23° 40'11.013"N and longitudes 72° 17'36.98" E and 73°33' 13.91"E respectively bound the region in the north and south.

It is said that accumulation of sea water occurred in this area during the post tertiary era (CGWB, 2008). Recent report confirms that Pachpadra town in this area was one of the three major salt lakes in Western Rajasthan (CGWB, 2008). Specific conductance of soil here ranges between 385 to 46,580 micro mhos/cm. at 25°C (CGWB, 2008). Luni river which disappears into the Rann of Kutch in Gujarat, India flows through the Thar Desert in Rajasthan. Luni (in local Marwari dialect) means salt and thus reverberates presence of salt in the region.

Soil-Carbonaceous Matter Immingle (SCMI)

The soils with clayey nature are appended with carbonaceous matter for utility in different traditional products, devices, practices, and processes. Most of the compositions are heterogeneous. In Rajasthan, the soil-carbonaceous matter immingle (SCMI) finds its use in household construction, soil and water use management. A similitude in the compositional ratio of composites and ceramics thus manufactured from these immingles are shown in Fig. 1.

SCMI for Surface Finish

Traditionally, soil-cow dung paste is applied on walls, floors, kilns, and earthen stoves as a finishing coat or cleansing coat across households in India. This coat is considered as a benchmark of daily cleaning activity of rural households in India. The wall finishing process shown in Fig. 2 is a low cost operation usually performed by local women. They incorporate aesthetic design using red mud and charcoal.

Cow dung is used for the finishing purpose due to its fine texture. Small size of plant based particulates suspended within cow dung is responsible for its fine texture and hence suitability for finishing application. Particulates within horse dung are comparatively large compared to cow dung. Size of particulates plays an important role in animal dung use (Satankar *et al.*, 2018).

Fresh cow dung and red soil taken in ratios of 1:2 by volume is uniformly mixed for producing the finishing paste. Further water equal to the volume of cow dung is added to provide coat consistency adhering to the spatula test. The paste is manually applied on the dry surface of the wall as per aesthetic requirements of the household.

While performing wall finish, paste is applied from bottom to top. The patches and cracks on the walls are also repaired using this paste. Finally a tint of water is also applied to obtain a smooth finish.

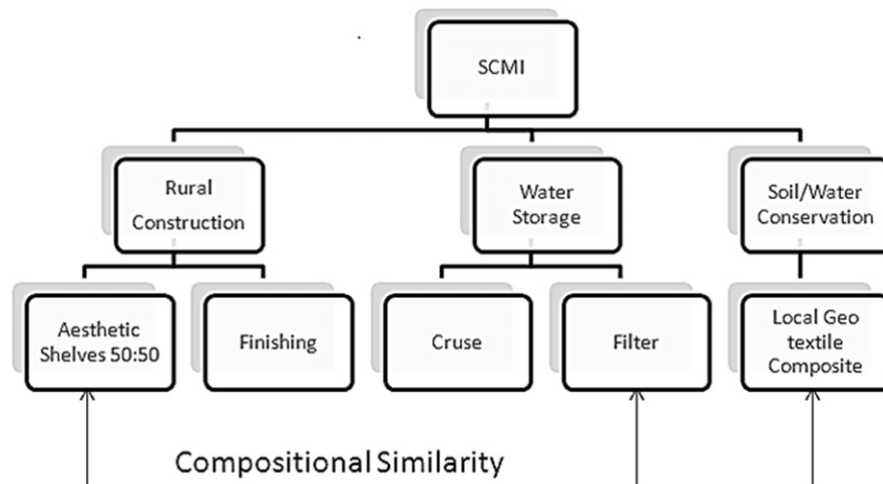


Fig. 1 SCMI based products and processes.



Fig. 2 Local women folk performing periodic finishing on mud structure.

The wall depicted in [Fig. 3\(a\)](#) is manually finished by hand. The saturated red coarse-cow dung soil immingle is impressed with a design shown in [Fig. 3\(b\)](#). The design is made by smallest fingers of both hands joined together at their tips. This in turn results in the formation of the crests and troughs. Once plaster saturates, the water flows down the crests and passes along the troughs to reach the bottom without harming the underlying immingle plastered on to the stone walls. This patterning prevents wear due to precipitation.

SCMI for Rural Household Construction

Composites manufactured from horse dung (*Equus* family) and local clayey soil is used to manufacture low load bearing structures (such as shelves as shown in [Fig. 4](#)) within households. Here the composites contain equal quantities of horse dung and soil. This technology is inherited by local “Santhi” tribal women of this region under study. The technology is limited and performed within the areal expanse of Marwar within which Marwari breed horses sustain ([ICAR-NRCE, 2017](#)).

The existence of this local *Equus* breed provides an insight that people from ages were aware of the properties of Marwari equine ordure. The Santhi community people believe that ordure have medicinal properties which prevent respiratory, microbial and other contagious diseases. The similar mixture also finds its application in manufacturing grain storage containers. *Equus* dung thus finds its application in manufacture of load bearing structures and flexural members.

The horse dung composites also have clayey soil in them. These soils are excavated from local ponds. These water harvesting structures deposit materials due to chemical weathering of rocks. The soil is thus characterized by high content of MgO , SiO_2 and Na_2O ([Satankar et al., 2017](#)).

Found in large chunks, the pond soil is soaked in water for a day. The aged slurry of pond soil and horse dung is mixed uniformly to make the wet mass. An equal volume of pond soil and horse dung is considered the correct ratio for manufacturing



Fig. 3 (a) Rural stone wall building finished with red soil and cow dung immingle (b) The crest and trough impressions.



Fig. 4 Aesthetic household shelf of soil-horse dung composite.

aesthetic shelves. This wet mass is spread on a bamboo cantilever structure protruding from the stone walls and pressed manually. The structure shown is then allowed to cure for sufficient time before use.

SCMI for Fertilization

About 40% of the arid areas of India (49.5 mha) is composed of Thar Desert in Rajasthan (Narayan and Kar, 2006). Sandy soils, negligible precipitation, and mining resulted in erosion, salinity of soils and degradation of vegetation cover. Dumping of stone, mine and industrial wastes also contribute to desertification in this region (Kaurwar *et al.*, 2018). SCMI composites with any animal dung can be used for fertilization (Dave *et al.*, 2017).

SCMI for Making the Cruse

Earthen cruse is used across the world for storing and cooling water especially during summer. These may vary in size, shape and color with geographical variability. The baked ceramic off-white pots are manufactured by local potters of Thar desert region using different material composition and firing techniques.

Potters in this region used donkey dung as a pore forming material in manufacturing of cruse (which is uncommon from other parts of world). The use of animal dung as pore former has now been replaced by sawdust due to decline in population of donkeys (*Equus* family) in this region (Satankar *et al.*, 2018). The cruse manufactured with soil-donkey dung immingle is

found to be comparatively weightless and compressively stronger than the cruse manufactured using soil-sawdust immingle (Satankar *et al.*, 2018).

Traditionally three ingredients salty clay, sawdust and granite gravels are used as base materials for cruse manufacturing. The clay can be procured from Pachpadra and Pokhran, Rajasthan. The working immingle must contain 45 liter equivalent of clayey soil. Water equal to one-third the volume of soil is used to produce wet mix. The other constituents are 9 liter equivalent of wood waste (collected from nearby timber businesses) and 2 kg of Saltpetre respectively. The women potters' helps in preparation of raw material and mixture while men potters cast the cruse on wheel.

SCMI for Making the Water Filter

The potters in Western Rajasthan are acquainted with rotating wheel based pottery. The clay ceramic water filter receptacle is shaped with a frustum shaped mold. Salty clay is mined from Raital and Mokalsar near Jodhpur, Rajasthan. The women folk (irrespective of the location of potter across India) powder and sieve the clay using a household sieve (3 mm $\times$ 3 mm).

Traditionally potter interprets the salinity of clay by tasting. If the desired salinity is missing rock salt equivalent to 0.02% by volume of soil is added to it. Addition of salt is considered to make the clay ceramics more load bearing, and functionally better in cooling characteristics. Local artisans believe that addition of salt in clay influence the sintering rates of clay ceramics. Sieving of sawdust is performed with the same sieve used for the powdered clay. This is analogous to the Potter for Peace method of preparing the clay-sawdust mixture for manufacturing of the frustum shaped ceramic water filter (Gupta *et al.*, 2018).

Composite for Rural Construction and Fertilizers

Composite Preparation Analysis

It is important to retrodict the technical reason behind sustainable use of equal volumes of soil and horse dung for constructing aesthetic shelves. Therefore clayey soil (C) and horse dung (H) in volume fractions of 30:70, 40:60, 50:50 and 60:40 respectively were mixed, shaped and analyzed. The analysis elaborates study of curing, flexural strength and fracture toughness property of C-H composites.

Equal volumes of the horse dung (H) & pond soil (C) were manually powdered and sieved (Satankar *et al.*, 2017). Local pond soil was soaked in sufficient quantity of water for 24 hours and then next day stabilized with powdered horse dung (Satankar *et al.*, 2017). The resulting dough was then formed into a rectangular shape (of size 250 mm $\times$ 50 mm $\times$ 20 mm). The resulting shapes were exposed to open environment (temperature of 35°C, humidity of 42%) for about 28 days. The change in weather parameters, composite weight and its dimension were noted during this 28 day curing period (Satankar *et al.*, 2017). The raw material volume, the immediate environment, and time play an important role in defining the weight of the cured sample (Satankar *et al.*, 2018).

The scanning electron image analysis of horse dung shown in Fig. 5 indicates calcium richness. The white flakes adhering onto the base are nanoparticles of calcium carbonate (Satankar *et al.*, 2017). Nanoparticles of CaCO_3 adhered to cellulose content provides horse dung composites with characteristics of a bio cement (Satankar *et al.*, 2017). An increase in horse dung would prevent C-H composite failures due to bending. The presence of calcium carbonate will also influence surface finish

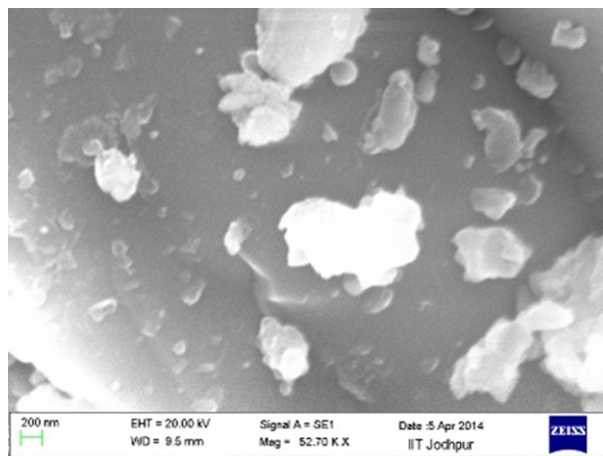


Fig. 5 Scanning electron imagery of soil-horse dung C-H composites.

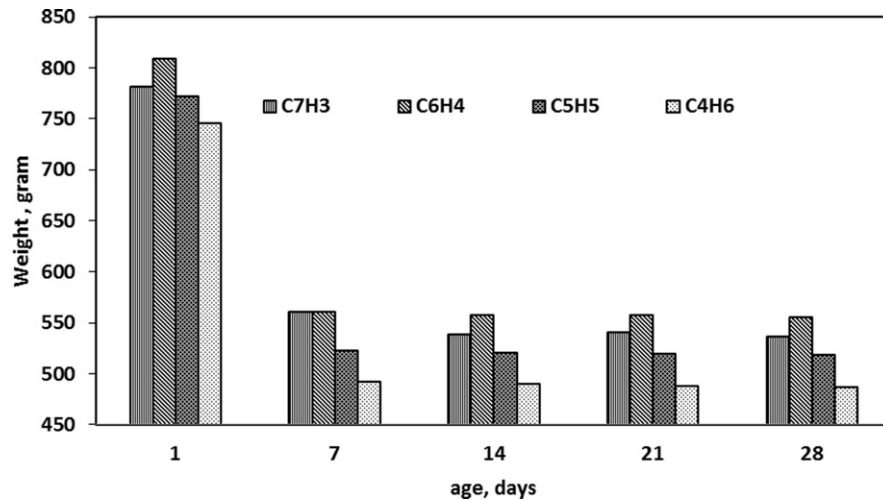


Fig. 6 Curing of composite samples.

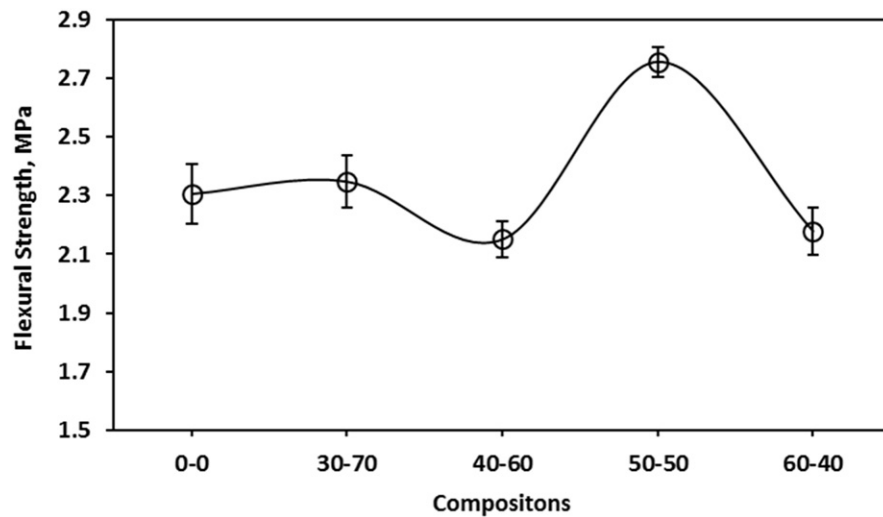


Fig. 7 Flexural strength as a function of volume of horse dung in the C-H composite.

and thus surface energy of C-H composite (Satankar *et al.*, 2017). The low surface energy help in production of structurally strong manure cakes which disintegrate slowly in soil. A novel way of manufacturing slowly disintegrating fertilizer materials is thus envisaged.

Composite Curing Studies

Weight loss gradient was large during first week for all C-H composite samples. The weight loss varied from 25% to 39% in the different C-H composites tested. Curing rate hence is considered to peak during the first week while it petered after the second week. The samples containing more volume fraction of horse dung comparatively weighed less. Fig. 6 below indicates weight loss of C-H composites during curing. Density of the 28 day cured sample varies from 1120 to 1980 kg/m³ (Satankar *et al.*, 2018). Stability in weight of C5H5 is observed after the second week of curing.

Mechanical Strength of C-H Composite

C-H composite structure built with C5H5 composition is a flexural member. From Fig. 7 it is evident that flexural strength of C5H5 is better than any other composition of C-H composites. Flexural strength follows a quotient response based multiplicative distribution as a function of curing age (Satankar *et al.*, 2018). M5H5 samples were found to have visually uniform surface compared to all other compositions (Satankar *et al.*, 2018).

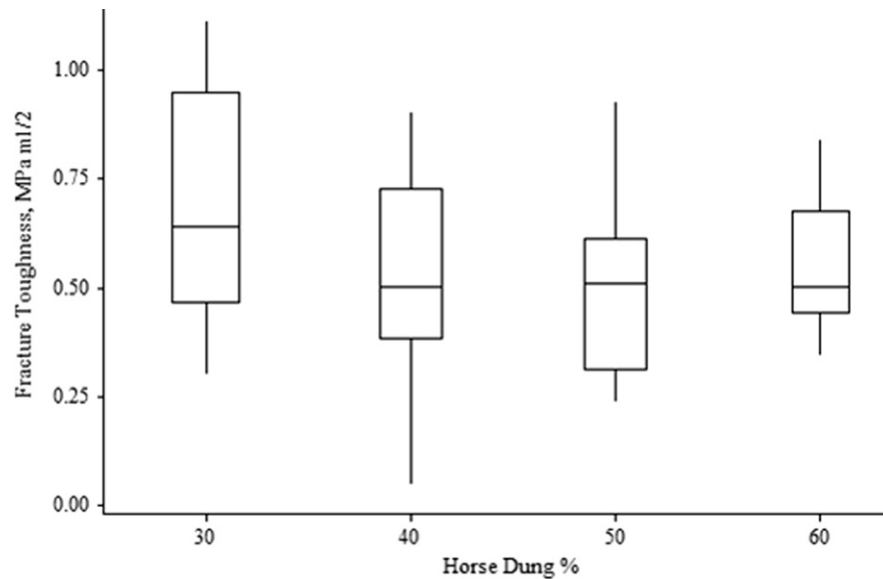


Fig. 8 Fracture toughness of C-H with varying volume fractions of horse dung.



Fig. 9 Geotextiles of *Leptadenia Pyrotechnica* (left) and *Crotalaria Burhia* (right) embedded with C-H Composite.

The property of fracture toughness in C-H composites follow a cyclic pattern as illustrated in **Fig. 8**. Fracture toughness values of the traditional C-H composites follows a generalized three parameter pareto model (Satankar *et al.*, 2018).

The packaging of such composites within geotextile mats is used in managing soil quality and productivity (Dave *et al.*, 2017). The packaged hybrid composite is shown in **Fig. 9**. The hybrid composites are embedded in the arid sandy loam soil in wet saturated condition as shown in **Fig. 9** to trap moisture for a long time beneath the soil surface.

SCMI Ceramics for Water Storage

Cruse manufactured in western Rajasthan is off-white in color (Roux, 2015; Kaurwar *et al.*, 2017a,b). The process of cruse manufacturing has not varied across India since ages (Satankar *et al.*, 2018). The off-white color is due to high content of MgO and CaO oxides on the cruse outer surface (Kaurwar *et al.*, 2017a,b). The non oxidative and oxidative sintering on the inside and outside of the cruse is evident with the color differentiation between the two surfaces. The internal wall of the cruse is red in color. This distinctiveness is supported by comparatively high percentage of Ca and Fe on the internal wall of the cruse.

The selection of clay is very important and depends on potters experience in cruse manufacturing. The excavated clay is collected at a specified location where it is exposed to the open atmosphere. The degeneration process that occurs during this period makes the soil better to work. A clay ball is shaped manually by placing it at the center of the spinning wheel.

Further the shaped vessel is preheated under sunlight during winter and in shade during summer. Preheating process provides optimum hardness and plasticity for further processing. Then hand building of the shaped vessel is performed. This provides the



Fig. 10 (a) Thrown cruse (b) Paddled cruse.

required shape and size for the cruse as shown in **Fig. 10(b)** (Kramer, 1997). The product dried in open for a week is then fired using up draught kiln to around 550–750°C (Kaurwar *et al.*, 2017a,b).

Baking

The manufacturing of pots is a seasonal process and is not carried out during rains and summers (Vincentelli, 2000). Baking has been performed using two firing techniques open firing and firing in a kiln (Ravi *et al.*, 2007). Out of these two techniques open firing is oldest and still popular among potters of different parts of India (Ravi *et al.*, 2007). The kiln preparation and loading requires 2–3 h while firing time depends on the type of the method used. The firing is usually done at night. The sintered products are allowed to cool in the furnace till next morning (Roux, 2015).

Baking preference is a procedural choice rather than thought of design for the potter (Guo, 2017; Roux, 2015). These procedural choices correspond to the culture, climate, traditional knowledge inertia, and social narratives related to local deities (Guo, 2017; Roux, 2015). The technological changes are more resistant to adoption in domestic manufacturing than decorative styles (Habicht-Mauche *et al.*, 2006).

The open firing process is usually performed on flat surface where the raw products are arranged in circular pattern over a bed of dried chopped grass or materials from agriculture residue. Agriculture waste, animal dung, twigs and leaves are used as a fuel (Roux, 2015).

Open firing provides temperatures of 500–850°C (Vincentelli, 2000). This technique does not leave waste and hence less technological evidence of its practice (Vincentelli, 2000). The open firing process does not need infrastructure but requires great technical expertise and observational skills to obtain required results (Perryman, 2008). Potters practice transfer of this technology within their household (Perryman, 2008). By 1970s, potters of this region shifted to kiln based baking (Roux, 2015). The use of open firing has petered since then. Technological knowledge transfer related to soils and blends are performed by potter women (Kramer, 1997; Satankar *et al.*, 2018).

Material Properties and Physical Properties

X-Ray fluorescence analysis of the cruse illustrates SiO₂(57.87%), Al₂O₃(17.55%), CaO(2.25%) and Fe₂O₃ as major constituents of the off-white cruse. High Na₂O content in off-white cruse supports the salty nature of the soil used in off-white pot manufacture. MgO is about 3.14% in off-white cruse compared to 2.82% in red cruse imported from neighboring state of Gujarat due to aesthetic appearance.

Fourier Transform Infrared (FTIR) spectra in **Fig. 11** showed the appearance of quartz (794, 690 and 460 cm⁻¹), iron oxides (583 cm⁻¹–521 cm⁻¹) and Si-O stretching (1019 cm⁻¹) off white water cruse. The pronounced character of calcite spectra (1440 cm⁻¹) in the IR curve indicates that cruse was not fired above 800°C. The presence of salt in local soil helps the cruse to be baked at comparatively low temperature.

From **Fig. 12**, a non-linear variation of compressive strength as a function of cruse height is observed. The shape of the cruse can be modeled using the information of cruse height. Further the cruse thickness would vary as an antithesis to shape of the cruse (Satankar *et al.*, 2018).

Cooling Studies

The graph in **Fig. 13** shows water cooling studies with the off-white cruse and red cruse during the first week of August (with a outside dry bulb temperature of 36°C). Considerable cooling is obtained while using fully filled off-white cruse as compared to red cruse.

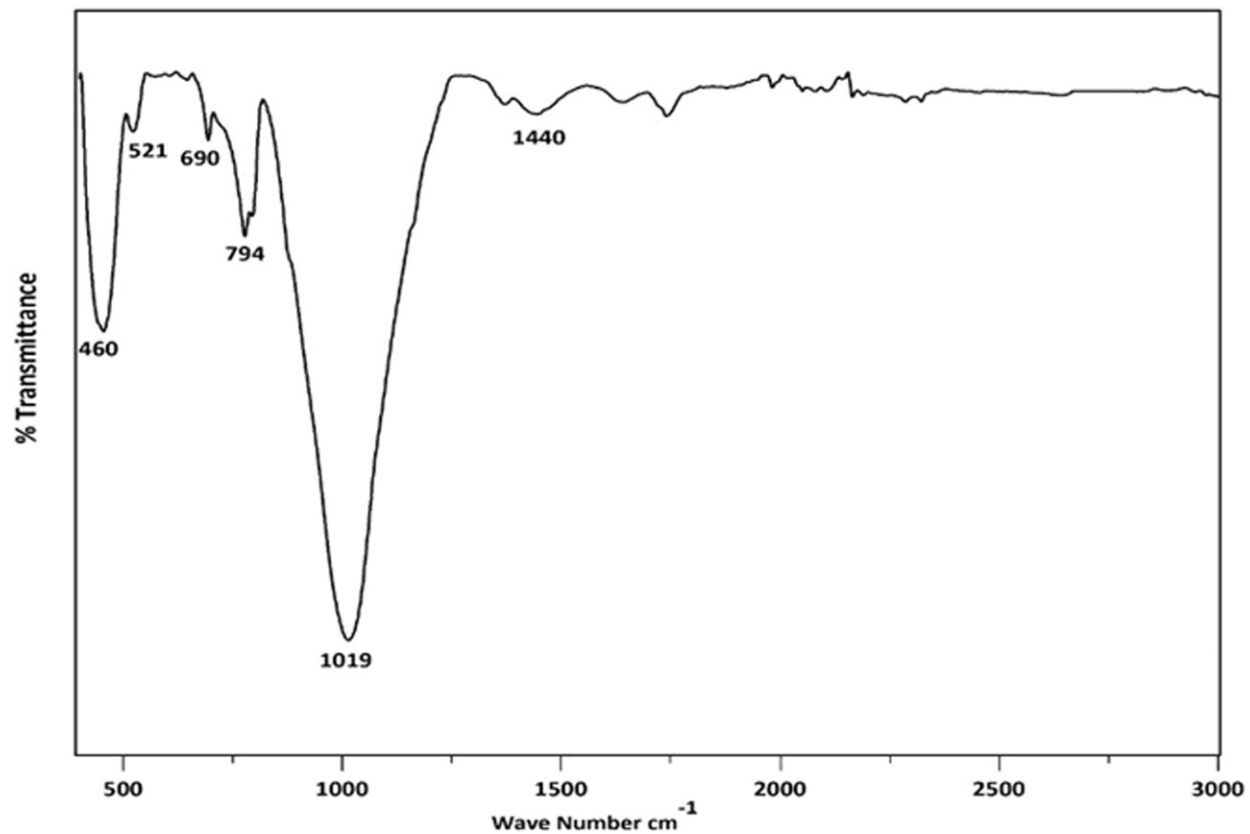


Fig. 11 FTIR Spectra of off-white water cruse.

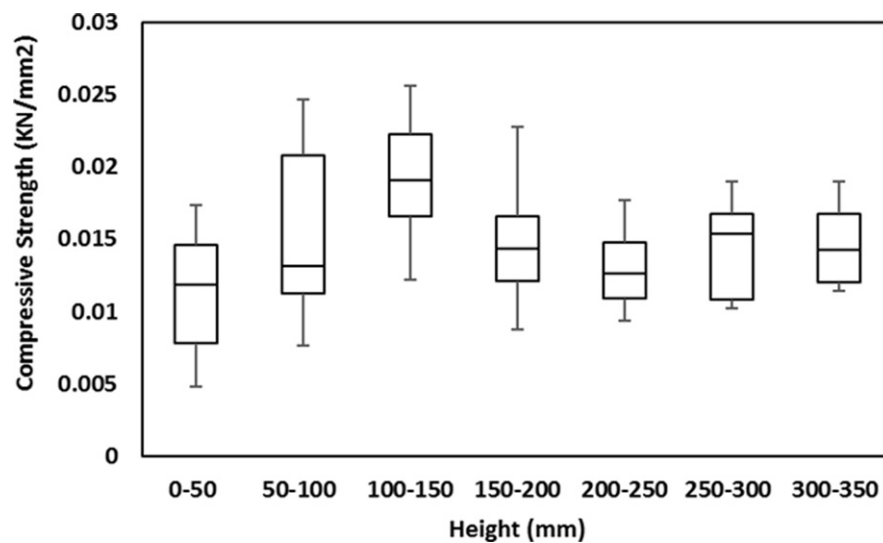


Fig. 12 Strength as a function of the height of the off-white cruse.

SCMI Ceramics for Water Filtration

A uniform mix of sawdust and salty clay is taken in equal volumes to form the basic mixture required for manufacturing ceramic water filters. Water equal to seventy percent by volume of imingle is added and manual mixing is performed to form the green composite which is further shaped as disks as shown in [Fig. 14\(d\)](#). The disks are kept overnight in a moist cloth covering. The disks are press-formed to frustum shape using a 30 ton press.

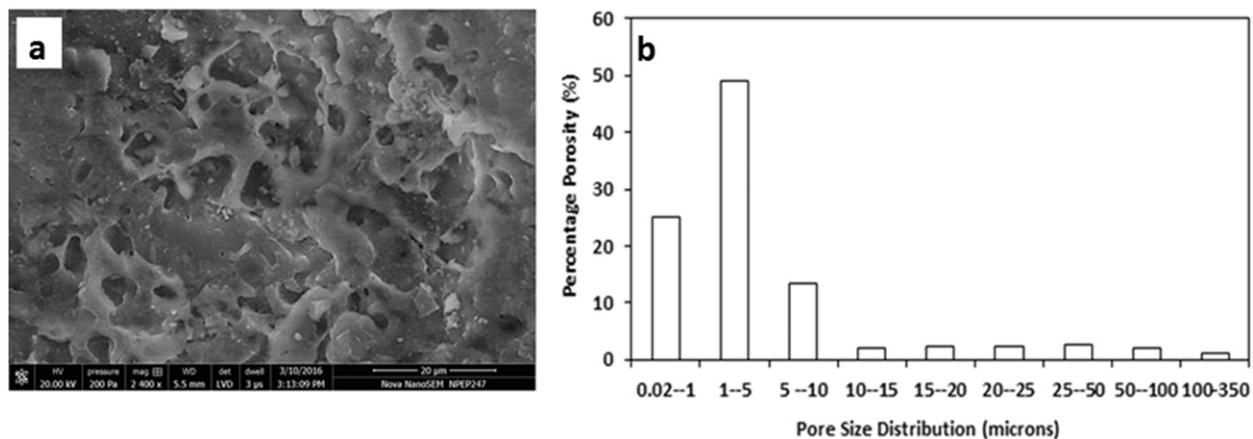


Fig. 13 Water temperature profiles within the distinct cruse during August at Jodhpur.



Fig. 14 Steps for the manufacture of the ceramic water filter at Banad village, Rajasthan.

The dimensions of the green ware thus formed were set according to a commercially available plastic bucket of 38 cm height. The green ware thus formed has to be kept for 2 days in ambient conditions and then cured under direct sunlight for 3 days.

Once cured, the green ware is baked in a vertical open hearth furnace (circular shape) of a minimum 5 ft radius and 5 ft height (Roux, 2015). This updraught baking furnace was introduced in Jodhpur in 1960s (Roux, 2015). The green wares were kept 2 ft above the ground in inverted position while baking (Roux, 2015; Ravi *et al.*, 2007). The local potters informed that pure clay flower vases were baked at very high temperatures (800–900°C) using a similar arrangement. These temperatures are similar to those set in factory mode sintering of ceramic water filters (Yakub and Soboyejo, 2013; Plappally *et al.*, 2011a,b). The ceramic water filters thus baked are locally named G Filters (Gupta *et al.*, 2016).

Characterization of Ceramics

Fig. 15(a) shows the microstructure of fired ceramics for water filtration. The scanning electron microscopic image Fig. 15(a) showcases the presence of heterogeneous pore distribution over the clay matrix. The pore size distribution range and porosity

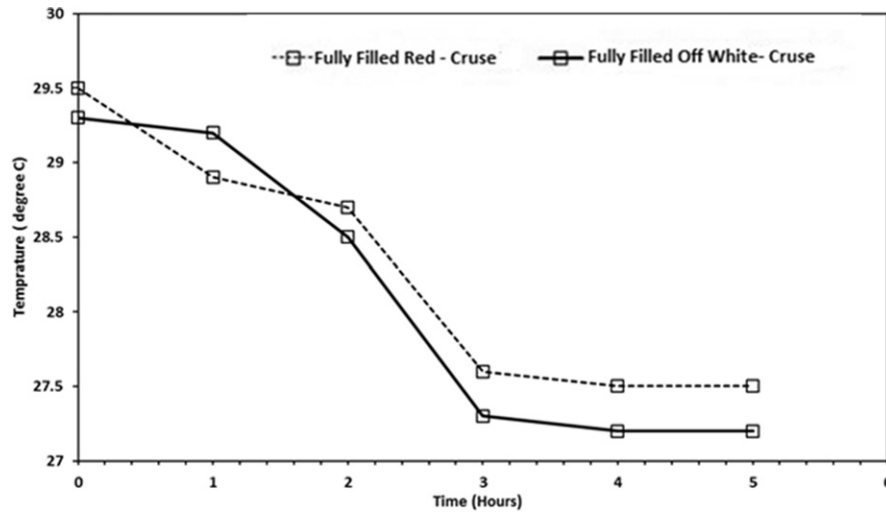


Fig. 15 (a) Surface morphology of Ceramics and (b) Pore size distribution in the Ceramics.

correlations are shown in [Fig. 15\(b\)](#). It can be inferred that the high frequency of porosity is contributed by the pores in the range between 0.02 and 5 microns. This porosity range is at par with the average porosity values of frustum shaped ceramic water filters manufactured at other parts of the globe using a factory mode.

Microbial Removal Efficacy

E. coli (*Escherichia coli*) is an indicator bacterium for occurrence of bacterial pathogens and for fecal contamination ([Brown et al., 2008](#); [Plappally et al., 2011a,b](#)). The *E. coli* filtration experiments were performed on the three separate ceramic water filters manufactured at Banad, Sar and Salawas in Jodhpur District, Rajasthan. Locally these water filters are known as G Filter. The contaminated water when filtered through these devices provided a log removal in the range 2.5–2.8 ([Gupta et al., 2018](#)). These tests adhered to ISO 9308–1:2014 framework ([Paulinus Chigbu, 2007](#)). The contaminated water suspension was similar to the contamination level (10^6 – 10^8 cells/ml) observed in the Yamuna river, India ([CPCB, 2012](#)).

Predicting Flow Through Frustum Shaped Ceramic Water Filters

Using geometrical extension of Darcy's porous flow model

For any porous media, Darcy's Law states that flow rate (Q) is directly proportional to change in pressure head (ΔP), cross-section area of flow and inversely proportional to the thickness t of the media. The law is valid as long as flow is laminar. The Darcy's law may be expressed as

$$Q = -kA\Delta P / \mu t \quad (1)$$

Here k is the intrinsic permeability of the porous media, A is the surface area (of porous media of thickness t) through which the transport of water or fluid may occur and ΔP is the head of water or fluid column above the percolating surface. The Darcy's law for water flow through porous media will change with temperature. At 25°C the density of water is 999.041 Kg/m³ and viscosity takes value 8.935e–4 Pa.s while at 40°C, density of water will be 989.418 Kg/m³, and viscosity will become 6.533e–4 Pa.s.

The flow rate through such a porous media with a frustum shape as shown in [Fig. 16](#) will be expressed as

$$Q_{total} = Q_{base} + Q_{sides} \quad (2)$$

Flow through the surface with radius R_2 and a base thickness of t_{base} is expressed as

$$Q_{base} = \frac{k}{\mu t_{base}} \pi R_2^2 \rho g h \quad (3)$$

The variable flow through the sides of the slanted side frustum surface with a length l and thickness t_{side} is expressed as

$$Q_{side} = \frac{k}{\mu t_{side}} \int_0^h \rho g (h - z) \times 2\pi(R_1 + z \tan \theta) \frac{dz}{\cos \theta} \quad (4)$$

Using information on constituent raw materials

Percolation through frustum shaped ceramic water treatment filters had been theoretically analyzed by several authors ([Plappally et al., 2009](#)). [Plappally et al. 2009](#) outlined a simple multi-parameter empirical model to characterize the percolation

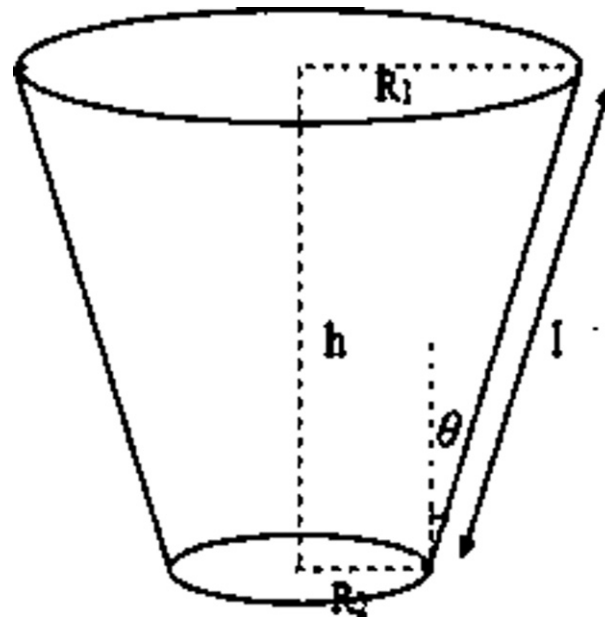


Fig. 16 Schematic of the geometry frustum shaped water filter.

through the filter manufactured with known volume of material constituents. This prediction model is given by

$$G = \frac{X_a}{Z} = 11.4 \times X_a^{0.32} X_b^{-3.02} \quad (5)$$

Here, X_a and X_b represent time and volume fraction of sawdust respectively. Z is the cumulative discharge at any time t .

Using information of electro-kinetic parameters

The electro-kinetic properties of drinking water are important since solute fluxes travelling across frustum shaped ceramic water filter depend on thermo-osmosis, capillary osmosis, electro-osmosis, and time. Percolation flux Q (l/h) may be expressed in terms of these parameters (Plappally *et al.*, 2010),

$$Q = a + bp_1 - cp_2 - dp_3 - ep_4 - fp_5 \quad (6)$$

where p_1 is the ratio of change of turbidity and pH at a specific time before and after a filtration event, p_2 is the change of turbidity before and after the filtration event, p_3 is the change in temperature before and after filtration event, p_4 is the change of electrical conductivity measured before and after the filtration event, and p_5 is the time. This provides a non-equilibrium thermodynamic viewpoint to prediction of flow (Plappally *et al.*, 2010).

Strength of Ceramics

The compressive strength of the G Filter material is a polynomial function of density of the material (Gupta *et al.*, 2018). The density of the material ranges between 2.5 and 2.7 gm/cm³. Compressive strength of the filter material ranges from 5.5 to 9.5 MPa (Gupta *et al.*, 2018). The strength of the material does not diminish during point-of-use water filtration for a continued use of more than 3 months (Gupta *et al.*, 2016).

Local potters also add marble powder in small volume to improve the compressive and flexural strength of these filtration materials. Marble mines are spread all across western Rajasthan which are the source of powdered marble. It is found that this modification to G filter makes them efficient in removing arsenic from contaminated drinking water apart from bacterial contaminants (Kaurwar *et al.*, 2018).

Conclusion

The sustainable use of clayey soils and carbonaceous matter found in Western Rajasthan has been discussed. The blend of equal volume fraction of clayey soils and carbonaceous matter (horse dung) is used in construction of traditional aesthetic shelves within households of this region. The development of flexural strength for such an immingle when saturated with water was found to improve with time. Composites of equal volume fraction of clayey soils and carbonaceous matter (animal dung) can therefore be considered good candidates for use as a medium to fertilize the soil.

Cruse used in this region for water storage have comparatively better water cooling characteristics that imported cruse from neighboring states. Salty soils of this region abundant in Mg and Ca compounds help in production of sustainable off-white cruse covered with amorphous off-white Mg and Ca oxides. Compressive strength of the cruse is a function of its shape.

Another sintered product analyzed in this article is the local ceramic water filter named the G filter. The immingle of equal volume fraction of clayey soils and carbonaceous matter (sawdust) is used as raw materials. Local potter household processes and sinters this device at their premises. Flow through these devices can be modeled geometrically, electro-kinetically and also as a function of constituent raw materials. The water filters showcased good bacterial contaminant removal.

Acknowledgement

The authors deeply acknowledge the DST grant no. YSS/2014/00576 for supporting the research.

See also: Design and Performance Analysis of Small-Scale Parabolic Trough Solar Collectors Using Sustainable Materials

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Use of Novel Nanostructured Photocatalysts for the Environmental Sustainability of Wastewater Treatments

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Introduction

The term, 'sustainability' means conservation of an ecological balance by avoiding depletion of natural resources, i.e., it is the endurance of systems and processes. In ecology, sustainability is the property of biological systems to remain diverse and productive indefinitely. Sustainable development is the organizing principle for meeting human developmental goals without affecting/harming the natural systems upon which the economy and society depend. The preferred result is a state of society where the resources continue to meet human needs (for healthy living) without undermining the integrity and stability of the natural systems. We all know that water is the most important element for the survival of living beings; life on earth cannot exist without water. While nearly 70% of the earth's surface is covered with water only 2.5% of it is in the form of fresh water. Fresh water contains very low amount of dissolved salt and is naturally occurring water on earth's surface in ice caps and glaciers (constitutes over 68% of fresh water), ponds, lakes, rivers and swamps (constitutes about 0.3% of fresh water) and around 30% is found in the form of ground water. Even less than 3% of the water on the earth is in the form of fresh water, most of that are inaccessible. Of all the water on earth, more than 99% is unusable by humans and many other living things (Shiklomanov, 2000; Korzoun and Sokolov, 1978). Hence, it is crucial to utilize the accessible fresh water in a sustainable manner. However, one of the most badly affected from human action is water resources. There are numbers of human activities which are continuously destroying the ecological balance and polluting the water resources; industrial runoff, landfills, construction runoff, dumping of waste materials are some of them.

Due to their good solubility in water, synthetic dyes are one of the most common water pollutants that are found in industrial wastewater. Synthetic dyes are extensively used in many industries including paper, textile, plastic, cosmetic, food, concrete etc. More than 10,000 different dyes and pigments are used industrially and 0.7 million tons of synthetic dyes are produced each year all over the world (Meyer, 1981; Zollinger, 2003). In India, about 80% of the total 130,000 tons of dyestuff production is consumed by the textile industry alone (Naik *et al.*, 2013). These industries release wastewater containing residual dyes which are not biodegradable. During dyeing process around 10%–15% of the dye lost in the effluent (Guivarch *et al.*, 2003; Bandara *et al.*, 1996). With the increased use of a wide variety of dyes, pollution by dye wastewater is becoming increasingly alarming. Around 60% of the dyes are used in textile industry and most of them are based on azo dyes. Some of their precursors and reaction products are carcinogenic (e.g., benzidine, 3,3'-dimethoxybenzidine, 3,3'-dimethylbenzidine based azo dyes) (Guivarch *et al.*, 2003; Golka *et al.*, 2004; Brown and De Vito, 1993), therefore treatment of the effluent containing these are very important as they can create serious health issues for humans as well as for aquatic species. Most of effluent wastewater is coming from textile industries due to a more consumption of water for its different wet processing operations, e.g., for an average sized textile mill 200 L water is required for processing 1 kg of fabric per day. According to the World Bank assessment, around 20% of the industrial effluents are generated during textile dyeing and finishing treatment given to a fabric (Kant, 2012).

Color is the first contaminant recognized in wastewater. This discharged wastewater is the origin of some serious environmental problems (e.g., destruction of various life forms, consumption of dissolved oxygen in the water sources etc.). These color effluents also limit the photosynthetic action by restricting the sunlight penetration. Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD) was established in the year 1974 with an aim to minimize possible negative impacts of the use of synthetic organic colorants on health and environment. According to the ETAD survey more than 90% of over 4000 tested dyes had LD₅₀ (a lethal dose that kill 50% of the test population) value greater than 2×10^3 mg/kg (Shore, 1996). International organization for standardization has made rules more stringent. For the removal of organic pollutants such as dyes, technological systems have been developed. ISO 14001, October 1996 and the latest environmental management systems is guided in ISO 14001:2015.

Water is a finite and irreplaceable resource that is fundamental to human well-being. It is only renewable if well managed and having a balanced ecosystem. Hence, we need to come up with alternative methods in which we can treat the waste water released from the different sources. Photocatalysis is one of the ways which can help us in the waste water treatment in an efficient way. In this article, we aim to discuss the pathways/solutions that have been carried out for the treatment of waste water and pollutants (which are directly or indirectly affecting the environment and all the living beings).

Methodology for Waste Water Treatment

Several methods which have been used for the wastewater treatments can be broadly classified in three categories (i) chemical (ii) physical (iii) biological (Robinson *et al.*, 2001). The detailed branching and sub-divisions has been schematically shown in Fig. 1.

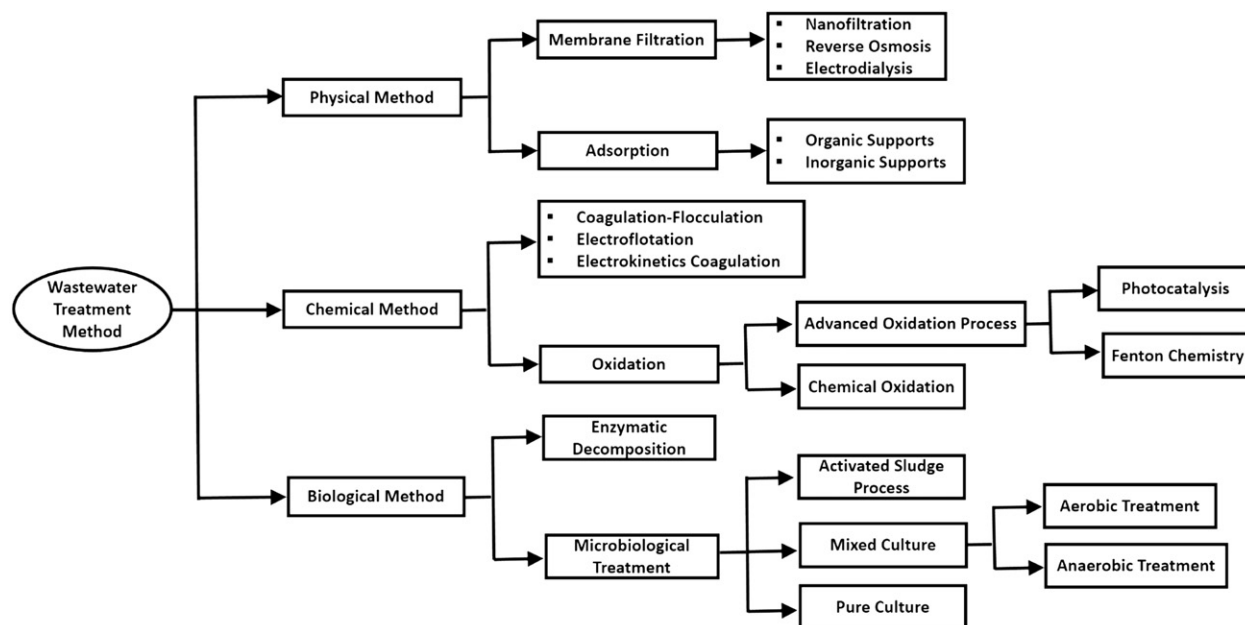


Fig. 1 A flow chart illustrating various methods used in the wastewater treatment.

Chemical Process: Chemical methods include coagulation or flocculation techniques combined with flotation and filtration, electroflotation, electrokinetic coagulation, oxidation methods (Gupta *et al.*, 2012; Holkar *et al.*, 2016; Robinson *et al.*, 2001) etc. This is often considered as one of the robust ways of removing color from the wastewater. Amongst all chemical processes, oxidation method is the most commonly used chemical decoloration process owing to its easy application process. This method is further categorized into chemical oxidation and advance oxidation process (AOP). Both these methods has the ability to degrade chemical dyes, pesticides etc. either partially or completely under ambient conditions (Holkar *et al.*, 2016). These AOP process can further be classified into photocatalytic oxidation (use of light for activation of catalyst) and fenton chemistry suitable for treating wastewater which are resistant to biological treatment (Holkar *et al.*, 2016).

Physical Process: Physical methods widely used for wastewater treatments include membrane-filtration processes (nanofiltration, reverse osmosis, electrodialysis etc.) and adsorption techniques (Gupta and Suhas, 2009; Robinson *et al.*, 2001; Holkar *et al.*, 2016). The major disadvantage of the membrane processes is that they have a limited lifetime before membrane fouling occurs and the cost of periodic replacement must thus be included in any analysis of their economic viability. Adsorption method provides an alternative way and is superior and efficient than any other physical technique especially if the sorbent is inexpensive and does not require an additional pre-treatment step before its application. Activated carbon is the most efficient adsorbent for a wide range of dyes. Due to difficulty in its regeneration and its high cost makes it less attractive (Robinson *et al.*, 2001) for its utilization at industrial scale.

Biological Process: It is often considered as the cheapest method used for wastewater treatment compared to the chemical and physical methods. Many microorganisms like yeasts, fungi, bacteria and algae are capable to degrade different pollutants and therefore, used for the treatment of industrial effluents (Satyawali and Balakrishnan, 2008; Robinson *et al.*, 2001). On the basis of working environment, biological method can be categorized into aerobic, anaerobic, anoxic, facultative or a combination of these. Their application is often restricted because of technical constraints. Biological treatment requires a large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals and limited flexibility in design and operation (Bhattacharyya and Sarma, 2003). Biological treatment is incapable of obtaining satisfactory color elimination with current conventional biodegradation processes. Moreover, although many organic molecules are degraded, many others are recalcitrant due to their complex chemical structure and synthetic organic origin (Robinson *et al.*, 2001; Kumar *et al.*, 1998).

Existing waste water treatment technology such as electrochemical oxidation, coagulation or adsorption do not completely eliminate the pollutants and lead to creation of a more concentrated pollutant-containing phase (Padmanabhan *et al.*, 2006). Other water treatment methods such as filtration, sedimentation, membrane and chemical technologies involve high operating costs and has the potential risk of generating toxic secondary pollutants into the ecosystem (Gaya and Abdullah, 2008). Chlorination has been the most commonly and widely used disinfection process. The disinfection by-products generated from chlorination are mutagenic and carcinogenic to human health (Yang and Cheng, 2007). These have led to the rapid research and development in the field of advanced oxidation process to make improvement in oxidative degradation of the organic compound dispersed or dissolved in aqueous media. Among them heterogeneous photocatalysis is attracting researchers because of its high efficiency in degrading most of the organic pollutants, an exhaustive list has been illustrated in the report by Blake (2001).

Photocatalysis

Photocatalysts are the materials which promote reaction in the presence of light and not get consumed in the overall reaction. Some of the characteristics of a good photocatalysts are (a) being photoactive (preferably visible light active) (b) chemical/biochemical inertness, (c) photostability (i.e. not liable to photo-corrosion), (d) nontoxicity (Bhatkhande *et al.*, 2002) etc. The possible reasons which may be assigned to photocatalysis gaining high importance in wastewater treatment are as follows (Bhatkhande *et al.*, 2002):

- (1) Illustrating total mineralization of most of the organic pollutants,
- (2) Ability to operate in ambient temperature,
- (3) No disposal issues (in water),
- (4) Pathways for an economic and environmentally-friendly solution.

Fundamentals and mechanism of photocatalysis

Photocatalysts in general operate through the principal of band gap (and interactions involving the same), i.e., different classes of semiconductor materials cater to the need of various photocatalytic applications. Traditionally, semiconductors exhibit an empty energy region in which no energy levels are available to promote the recombination of an electron and hole produced by photoactivation in the solid which is unlike metals, i.e., having a continuum of electronic states. For a semiconductor to be a photo-chemically active, the redox potential of the photogenerated conductance band electron must be sufficiently negative and photogenerated valence band must be sufficiently positive so that electron can reduce the adsorbed O_2 to superoxide and hole can generate the OH radicals (most potent oxidizing agents) which will then subsequently oxidize the organic pollutants (Gaya and Abdullah, 2008; Bhatkhande *et al.*, 2002; Mills and Le Hunte, 1997; Chong *et al.*, 2010).

On irradiation of light (Ultraviolet or Visible) absorption of photon takes place in semiconductor materials and excites an electron (e^-) from the valence band to the conduction band if the photon energy ($h\nu$), equals or greater than the band gap of the semiconductor/photocatalyst. During excitation of an electron (e^-), simultaneously, a hole (h^+ , positive charge) is generated in the valence band (schematically shown in Fig. 2).



On the generation of electron-hole (e^-h^+) pair, mainly two possibilities exists (i) recombination of electron and hole pair producing thermal energy in the absence of suitable scavenger or surface defect state to trap the electrons (ii) prevention of recombination and participation in redox reactions with the compound adsorbed on the photocatalyst. Although, the lifetime of an e^-h^+ pair is few nanoseconds (Bussi *et al.*, 2002), it is still long enough for initiating/promoting redox reactions. Generally, the electron can be offered to an electron acceptor like a metal ion whose redox potential is more positive than the photocatalyst band gap or to an oxygen molecule to form a superoxide radical. In the same way, a hole oxidizes water to form hydroxyl radicals (which subsequently initiate a chain of reactions leading to the oxidation of organics). The same can also combine with the electron from a donor species, depending on the mechanism of the photoreaction. Thus, the series of chain oxidative reductive reactions that occur at the photon activated surface can be postulated as follows (Chong *et al.*, 2010):

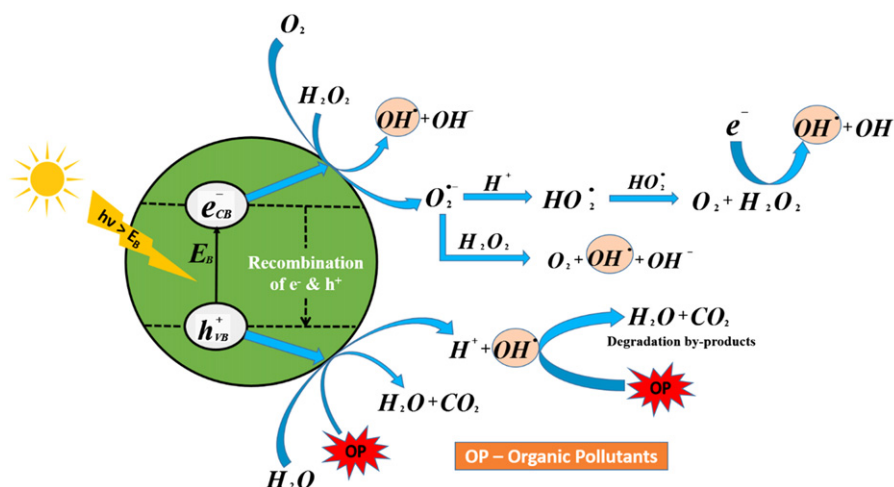
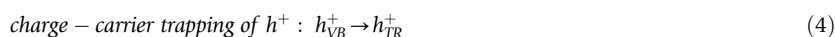
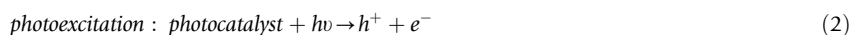
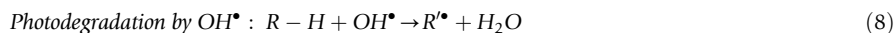
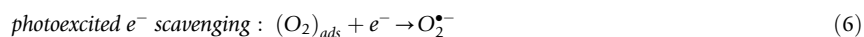
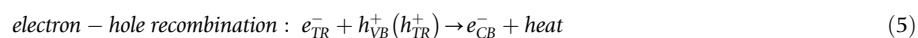


Fig. 2 Schematic diagram depicting mechanisms that take place during photocatalysis.



Here, e_{TR}^- and h_{TR}^+ in Eq. (5) represent the surface trapped conductance band electron and valence band hole respectively. Furube *et al.* (2001) worked on TiO_2 and reported that these trapped carriers are surface bound and do not recombine immediately after photon excitation. For the successful functioning of photocatalysis, recombination of electron-hole needs to be delayed. In the absence of an electron scavenger, they recombine (Eq. (5)) in nanoseconds and negatively affects the efficiency of photocatalytic reaction. Eq. (6) depicts prevention of recombination of electron-hole pair in the presence of oxygen and allowing the formation of superoxide radical ($O_2^{\bullet -}$) further lead to the formation of $HO_2^\bullet$; a radical with scavenging property (Chong *et al.*, 2010).

Kinetics of photocatalytic degradation

For the industrial need of scaling up of the process, it is crucial to study the kinetics and mechanisms of the photodegradation and/or photo-disinfection rate of the water contaminants. Proper operation of kinetic models for the elucidation of experimental data allows the design and optimization of photoreactor framework with adequate capacity and minimal non-illuminated reactor volume. Most of the kinetic studies have been performed for the TiO_2 materials in the past (Okamoto *et al.*, 1985; Fox and Dulay, 1993; Robert and Weber, 1998; Khanchandani *et al.*, 2016; Xu *et al.*, 1999); some of them have been highlighted here (in Section "Recent Research Works in Related Field" and Table 1). Most of these studies concluded that, the initial rate of degradation of pollutants fits a Langmuir-Hinshelwood (L-H) model. Generally, two main reaction mechanisms have been proposed for heterogeneous catalysis, namely Langmuir-Hinshelwood and Eley-Rideal (Ertl, 1994; Rademann, 1990). Baxter and Hu (2002) studied CO oxidation on Pt(111) and investigated the suitability of L-H mechanism over Eley-Rideal ones. The authors concluded that reaction barriers for Langmuir-Hinshelwood mechanisms actually tend to be higher than those for Eley-Rideal ones. They also provided an explanation of why the Langmuir-Hinshelwood is preferred in the vast majority of surface catalytic reactions, despite its higher energy barrier.

The L-H model is strictly surface area dependent and works on the following basic assumptions (Fox and Dulay, 1993):

- (1) Number of surface site is fixed at equilibrium;
- (2) Only one substrate may connect at each surface site;
- (3) Heat of adsorption by the substrate is same for each site and is independent of surface exposure;
- (4) There is no interaction between adjacent adsorbed molecules;
- (5) The rate of surface adsorption of the substrate is greater than the rate of any succeeding chemical reactions;
- (6) No irreversible blocking of active sites by binding to product occurs.

With all these assumptions L-H kinetic scheme can be shown as (Mills *et al.*, 1993; Fox and Dulay, 1993);

$$r_t = \frac{-dC}{dt} = \frac{k_r K_{ads} C}{1 + K_{ads} C} \quad (9)$$

where C is the initial concentration of pollutant, r_t is the rate of reaction (changes with time), k_r is the reaction rate constant ($\text{mg L}^{-1} \text{min}^{-1}$), K_{ads} is the equilibrium or Langmuir adsorption constant of the pollutant molecule on the catalyst surface (L mg^{-1}). The initial rate of reaction as a function of C_0 can be given by:

$$r_0 = \frac{k_r K_{ads} C_0}{1 + K_{ads} C_0} \quad (10)$$

Values of K_{ads} and k_r can be obtained by linearizing the Eq. (10) as follows:

$$1/r_0 = 1/k_r + 1/k_r K_{ads} C_0 \quad (11)$$

On integrating Eq. (9) between the limits: $C=C_0$ at time, $t=0$ and $C=C$ at $t=t$, we will get:

$$\ln \frac{C_0}{C} + K_{ads}(C_0 - C) = k_r K_{ads} t \quad (12)$$

If $K_{ads} C \ll 1$, then integrating Eq. (9) between the limits: $C=C_0$ at $t=0$ and $C=C$ at $t=t$, L-H expression can be reduced to

$$-\ln \frac{C}{C_0} = k_{app} t \quad (13)$$

When the organics concentration is low (in mM), an "apparent" first-order rate constant Eq. (13) could be expressed where (apparent rate constant, $k_{app}=k_r K_{ads}$). The term k_{app} (min^{-1}) is only served as a comparison and description for the photocatalytic reaction rate in the reactor system (Chong *et al.*, 2010). The linearity of a plot of $1/r_t$ versus $1/C$ of the Eq. (9) tests the validity of the L-H model, where $1/k_r$ can be taken as the 'Y-intercept' and $1/k_r K_{ads}$ is the slope (Fox and Dulay, 1993).

The popularity of the L-H model is clearly evident by the number of research papers used this model over the years; a histogram depicting the trend is shown in Fig. 3. Around 4400 papers have appeared (1970–2016) out of which around 3600 have appeared in last 20 years (1996–2016). Many works have shown good linearity (Cunningham and Al-Sayyed, 1990; Al-Ekabi and Serpone, 1988;

Table 1 Degradation of pollutants using photocatalysts

Photocatalysts	Pollutants	Operating Conditions	Highlights of work	Ref.
TiO ₂ (Degussa P-25)	Alizarin S (AS) Crocein Orange G (OG) Methyl Red (MR) Congo Red (CR) Methylene Blue (MB)	● NaOH and HNO₃ were used for pH adjustment ● UV light for excitation source	Feasibility of TiO ₂ was tested successfully for complete degradation of structurally different dyes either anthraquinonic (AS), or azoic (OG, MR, CR) or heteropolyaromatic (MB).	Lachheb <i>et al.</i> (2002)
TiO ₂ /Carbon fibers (T/CF)	Acid Orange 7 (AO7)	● working pH – 7 ● UV light was used as an excitation source	Low exciton recombination, numerous activated sites, high surface areas and hydroxy content of T/CF demonstrated functional property with enhanced degradation efficiency.	Lin <i>et al.</i> (2015)
TiO ₂ /CuS core/shell nanostructure	Methylene blue	● Visible light was used as an excitation source	Broad potential in the photocatalysis domain for the design of a visible light functional and reusable core/shell nanostructures photocatalyst.	Khanchandani <i>et al.</i> (2016)
Poly(diphenylbutadiyne) (PDPB)	Methyl Orange Phenol	● Both Visible and UV light were used as an excitation source ● Solution was bubbled with oxygen at fixed flow rate	PDPB nanofibres exhibited excellent photocatalytic activity compared to bulk PDPB. First experimental evidence of the photocatalytic activity of conjugated polymer nanostructures under visible light for water decontamination.	Ghosh <i>et al.</i> (2015)
BiPO ₄	Methylene blue	● UV light was used as an excitation source	BiPO ₄ photocatalytic activity was found twice better than that of Degussa P-25 TiO ₂ . The inductive effect of PO ₄ ^{3–} helped the e [–] /h ⁺ separation, leading to its excellent photocatalytic activity.	Pan and Zhu (2010)
ZnS-GR (Reduced grapheme oxide)	Organic compounds (alcohols or alkenes)	● Visible light was used as an excitation source	The ZnS/GR nanocomposites were confirmed to work for selective aerobic oxidation of alcohols and alkenes under ambient conditions.	Zhang <i>et al.</i> (2012)
Ag ₂ O	Methyl Orange	● Visible light was used as an excitation source	The Ag ₂ O photocatalyst was reported as a new candidate the removal of hazardous organic materials from wastewater; issues persisted with its preparation (with large specific surface areas and high pore volumes)	Wang <i>et al.</i> (2011)
Sb ₂ S ₃	Methyl Orange	● Visible light was used as an excitation source	Photodegradation ratio of methyl orange was up to 97% after 30 min of irradiation, which was much better than that of CdS and TiO _{2-x} N _x under the same condition	Sun <i>et al.</i> (2008)
Ag-AgBr	Methyl Orange	● Visible light was used as an excitation source	The as-prepared Ag-AgBr photocatalyst was reported for methyl orange dye degradation (more than 83% within 2 min of sunlight irradiation)	Kuai <i>et al.</i> (2010)
CNT-pillared graphene oxide (GO) and reduced graphene oxide (RGO)	Rhodamine B (RhB)	● Visible light was used as an excitation source	3D CNT-pillared GO and RGO nanostructures exhibited an excellent visible light photocatalytic performance in degrading RhB dye in water	Zhang <i>et al.</i> (2010)
g-C ₃ N ₄ /Ag ₃ PO ₄	Methyl Orange	● Scavengers for [•]OH, h⁺ and O₂^{•–} introduced ● Visible light was used as an excitation source	The as-prepared graphitic-C ₃ N ₄ /Ag ₃ PO ₄ hybrids exhibited excellent photocatalytic activity on the decolorization of methyl orange, which was superior to those of pure g-C ₃ N ₄ and Ag ₃ PO ₄ under visible-light irradiation (> 440 nm)	Katsumata <i>et al.</i> (2014)
BiOCl/BiOI	Methyl Orange Rhodamine B (RhB)	● Visible light was used as an excitation source	20% BiOCl/BiOI composite illustrated highest photocatalytic activity for the decomposition of MO and the 70% BiOCl/BiOI composite exhibited the highest photocatalytic activity on the degradation of RhB.	Li <i>et al.</i> (2011)
ZnS-GR (Reduced grapheme oxide)	Organic compounds (alcohols or alkenes)	● Visible light was used as an excitation source	The ZnS/GR nanocomposites were reported promising photocatalysts for selective aerobic oxidation of alcohols and alkenes under ambient conditions.	Zhang <i>et al.</i> (2012)
Co ₃ O ₄ /BiVO ₄	Phenol	● Visible light was used as an excitation source	The composite photocatalyst exhibited highest efficiency at 0.8 wt% cobalt content, 96% reduction in the concentration of phenol was noted in 180 minutes.	Long <i>et al.</i> (2006)

(Continued)

Table 1 Continued

<i>Photocatalysts</i>	<i>Pollutants</i>	<i>Operating Conditions</i>	<i>Highlights of work</i>	<i>Ref.</i>
ZnO	Acetaldehyde	● Hg–Xe lamp ($\lambda=365$ nm) was used as an excitation source	Photocatalytic activity noted to be strongly dependent on powder crystallinity than the surface area.	Li and Haneda (2003)
TiO ₂ (Degussa P-25)	Pesticide derivative triclopyr and daminozid	● Medium pressure mercury lamp was used as an excitation source	The pesticide derivative triclopyr was found to degrade faster as compared to daminozid. Addition of electron acceptors enhanced the degradation rate of the pollutants.	Qamar <i>et al.</i> (2006)
Graphitic carbon nitride	4-chlorophenol and phenol	● Visible light irradiation from a 300 W Xe lamp	The photocatalysts could induce the formation of reactive oxy-species such as H ₂ O ₂ , ·OH and O ₂ ^{·-} /OOH under visible light irradiation, while keeping a high photocatalytic reactivity during recycling operations.	Cui <i>et al.</i> (2012)
CuO	4-Nitrophenol	● No external source of light, normal light only	Remarkable activity was shown by CuO nanorods (in presence of sodium borohydride) as the complete degradation of 4-NP was observed in just fifteen minutes.	Kumar and Chowdhury (2017)

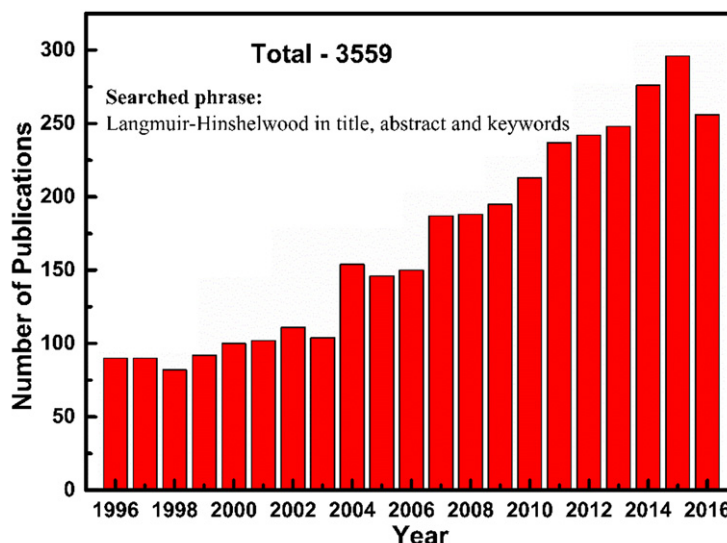


Fig. 3 Histogram showing number of papers published related to Langmuir-Hinshelwood (Year 1996–2016). (Searched phrase: Langmuir-Hinshelwood).

Hsiao *et al.*, 1983) in such plots but unfortunately, this fit cannot be taken as a guaranteed proof of pre-adsorption since an identical analytical formulation of the rate law can be obtained even for reactions occurring entirely within a homogeneous phase (Turchi and Ollis, 1990). These cases pose restrictions and associated concerns for overall general applicability of L-H kinetics to any given photocatalytic degradation process. Cunningham and Al-Sayyed (1990) have measured dark Langmuir adsorption isotherms for TiO_2 , for a variety of different organic pollutants and found them to be significantly smaller than the values of K_{ads} obtained from plots $1/r_v$ versus $1/[C]$. It appeared more likely that the value of K_{ads} derived from a kinetic study was not directly equivalent to the Langmuir absorption coefficient (for pollutants on TiO_2). Alternative kinetic approaches/models have been worked out by researchers; some of the important ones are discussed below:

(1) Pseudo steady-state approach:

Ollis (2005) has also shown that reactant adsorption is not constant in photocatalytic reaction. This is contrary to one of the assumptions of the L-H kinetic approach. As photocatalysis routinely involves the initial generation of reactive intermediates like holes, free electrons and hydroxyl radicals; their reactivity with reactants in the solution cannot expect reactant adsorption to be equilibrated. Hence, the slow rate controlling surface step inherent in the original L-H formulation is not valid in photocatalysis. So, a pseudo-steady state approach was suggested by the author to be utilized in the kinetic equation for reactant itself, not just for the active intermediates (Ollis, 2005).

(2) Direct-Indirect (D-I) model:

K_{ads} is dependent on the illumination flux (ϕ , i.e., photons per unit time reaching a surface). This also contradicts the L-H model premise according to which adsorption/desorption of reactants is maintained at equilibrium under illumination. The L-H model does not define the k_r dependence on ϕ , so that by itself is unable to predict any existing relationship between ϕ and the reaction rate. To alleviate such problems, an alternative kinetic approach was given by Monllor-Satoca *et al.* (2007). This is known as the "Direct-Indirect" (D-I) model, which is based on the degree of electronic interaction of the semiconductor surface with dissolved reactant molecules. Since a primary assumption of the L-H kinetic model is the requirement for surface pre-adsorption, a broad range of reaction rates can be expected from differences in adsorptive affinity of different substrates on a given semiconductor surface.

(3) Chemometric approach:

This approach was suggested by Sleiman *et al.* (2007) specifically for TiO_2 and its related systems based upon the surface response modeling. In this, two-step process, the first step involved investigation and establishment of the relative influence of the experimental factors (TiO_2 and dye concentration, pH, temperature, light flux and oxygen concentration) and their possible interactions. The second step was left for the identification of possible degradation products as well as the evaluation of the total mineralization during the process.

Kinetics of water purification photosensitized by photocatalyst is dependent on many factors as discussed below in the following section.

Effect of operating parameters on photocatalysis reactions

- Intensity and Wavelength of Light:

The photocatalytic reaction rates are dependent on the intensity of the light; an enhanced response with increase in light intensity during photocatalytic degradation was reported (Qamar *et al.*, 2006). The nature or form of the light did not seem to affect the reaction pathways (Stylidi *et al.*, 2004). In other words, the band-gap sensitization mechanisms do not seem to influence the photocatalytic degradation pathways, as a whole. Rincón and Pulgarín (2003) reported that the residual disinfecting ability of the photocatalyst largely depends on the duration of light intensity (without any temporal pauses). The authors examined the effect of light intensities (at 400 and 1000 W/m²) on bacterial mortality and regrowth, and found that the higher intensity (without any breaks) can cause irreversible damage to the *E. coli* bacteria's. In the sporadic light irradiations with constant interruptions, the bacteria were noted to regrow during the subsequent 24 or 48 h. Light sources emitting different range of wavelength was reported to have significant impact on the photocatalytic response rate and also noted to depend upon the type of photocatalysts utilized, crystalline phase, anatase-to-rutile phase transitions (in case of TiO₂) etc. (Chong *et al.*, 2010).

- Photocatalyst Loading:

Heterogeneous photocatalytic responses are known to demonstrate corresponding increment in photodegradation with catalyst loading. In any given photocatalytic application, optimum catalyst concentration must be determined, as over-abundance have a negative impact on the activity of the photocatalytic process due to unfavorable light dispersing and decrease of light infiltration (Gaya and Abdullah, 2008). The assurance of photoreactor distance across is critical in retaining the optimum photons successfully; the water stream hydrodynamics is also noted to be crucial for efficient working of the photocatalytic system (Malato *et al.*, 2009).

- Effect of pH:

pH is one of the most important operating parameters in heterogeneous photocatalytic water reactions that control the charge on the catalyst particles, size of catalyst aggregates and the positions of conductance and valence bands (Haque and Muneer, 2007; Chong *et al.*, 2010). The pH of a system has the potential to influence the surface charge and also the ionization state of the substrate (and hence the adsorption) (Kosmulski, 2006).

- Effect of Anions and Cations:

Abdullah *et al.* (1990) carried out a thorough investigation on the impact of anions on the rate of photo-mineralization of organic pollutants (salicylic acid, aniline, and ethanol) in the presence of TiO₂. The authors concluded that perchlorate and nitrate ions have little/no impact, while sulfate, chloride, and phosphate (at fixations > 10⁻³ mol dm⁻³) could diminish the rate of photomineralization by 20%–70% because of their retention at the oxidation locales on the TiO₂. Wei *et al.* (1990) examined the impact of cations, for example, Fe³⁺ and Cu²⁺ on the photocatalytic degradation of phenol. Fe³⁺ depicted an enhancement in initial phenol removal from 23% to 33%, whereas a negative impact was observed for Cu²⁺ case. However, in the presence of H₂O₂, an increase in the rate of phenol oxidation was noted for both the cases.

- Effect of Surface Area:

Photocatalytic degradation process is influenced by adsorption of pollutants on the catalysts, thus the impact of surface area is critical in entire process. As the particle size diminishes to nanoscale, the increase in the surface area foster the adsorption activities thereby improving the photocatalytic degradation rate. Degan and Tomkiewicz (1993) showed that TiO₂ aerogels with a surface area of 600 m² g⁻¹ depicting superior activity than commercial Degussa P-25 (with surface area of 55 m² g⁻¹).

- Effect of Reaction Temperature:

Generally, the increase in temperature enhances recombination of charge carriers along with the desorption of adsorbed reactant species, thereby resulting in a decrease of photocatalytic activity (Gaya and Abdullah, 2008). For a TiO₂ system at a reaction temperature (for photocatalytic activity) greater than 80°C, the adsorption of the reactants was disfavored, leading to the reduction of photocatalytic activity. At a very low reaction temperature (down to 0°C), increase in the apparent activation energy was noted. As a consequence, the optimum reaction temperature for photo-mineralization is reported to be in the range 20–80°C (Malato *et al.*, 2009).

- Effect of Dissolved Oxygen:

A critical part in TiO₂ photocatalysis response is to ensure adequate electron scavengers are present to trap the energized conduction-band electron from recombination (Chong *et al.*, 2009). The oxygen does not influence the adsorption on the TiO₂ catalyst surface as the reduction response happens at an alternate location from where oxidation occurs (Malato *et al.*, 2009). The presence of dissolved oxygen is needed for degradation of hydroxyl byproducts, and in the cleavage mechanism of aromatic ring (Wang and Hong, 2000).

Recent Research Works in Related Field

The interest in the area of photocatalysis started with the pioneering work by Honda–Fujishima on water splitting by using TiO₂ electrode in early 1970s (Fujishima, 1972). Plethora of initiatives were taken by the research community during the 1970 and 1980s in the development of semiconductor photochemical cells (Heller, 1981). This is also clearly evident from the number of publications in

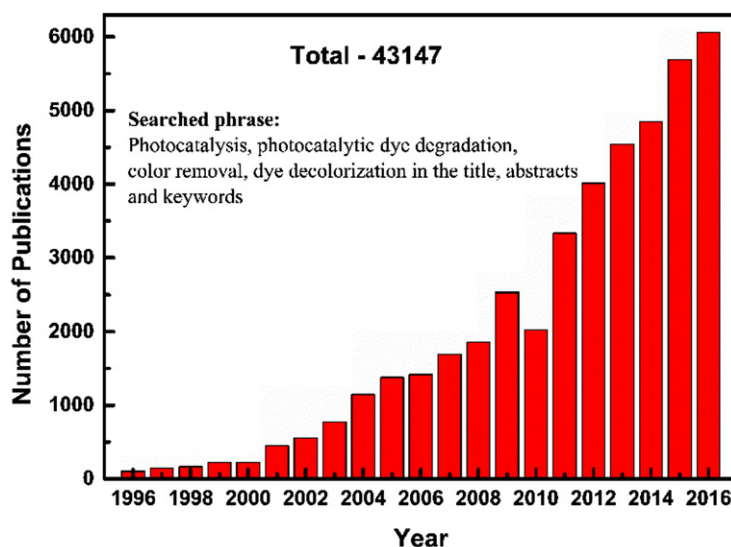


Fig. 4 Histogram for number of papers published related to photocatalysis during the period 1996–2016.

the recent years as shown in Fig. 4. Around 43,600 papers have been published (1970–2016); out of which around 43,000 in just 20 years from 1996 to 2016. Some of the important materials that have been explored for the photocatalysis are listed below as follows:

- Titanium dioxide (TiO₂):

TiO₂ has been the most-investigated system for all such cases involving photocatalysis, removal of organic pollutants etc. Frank and Bard (Steven and Bard, 1977; Frank and Bard, 1977) were the first to examine the use of TiO₂ for the environmental application and reported on the decomposition of cyanide (CN[−]) and sulfite (SO₃^{2−}) ions in aqueous solution with the help of xenon light source. TiO₂ emerged as the superior one and the possible reasons were assigned to various factors, e.g., highly oxidizing photogenerated holes, high chemical stability, low cost etc. (Fujishima *et al.*, 2000). The use of TiO₂ (in powder form) for photocatalysis requires its separation from the solution. To immobilize these TiO₂ particles, researchers started using it in thin film form. Sopyan *et al.* (1996) investigated the photocatalytic activity of TiO₂ thin film (on a glass substrate) for the degradation of gaseous acetaldehyde. Larger number of adsorption sites per unit of (true) surface area was traced for the thin film (analyzed in powder form) compared to the degussa P-25 TiO₂ powders, thereby confirming superior photocatalytic activity for film (w.r.t. the powder form). Lin *et al.* (2015) worked on the synthesis of ordered mesoporous titania on carbon fibers via liquid crystal template technique under supercritical conditions. The authors concluded on achieving high photocatalytic activity under UV light (for acid orange 7 degradation) and attributed the same to numerous factors, viz., high surface area, high hydroxyl content, numerous activated sites and low exciton recombination rate. One major disadvantage of TiO₂ system lies in its ineffectiveness in visible light. Anatase TiO₂ bandgap is around 3.3 eV and requires an excitation wavelength, $\lambda < 376$ nm. This spectral regime constitute less than 5% of the solar flux incident at the earth's surface (In *et al.*, 2007). To eliminate this drawback, TiO₂ has been frequently doped with other elements like boron, sulfur nitrogen etc. (Ho *et al.*, 2006; Asahi *et al.*, 2001; In *et al.*, 2007). However, doped TiO₂ materials has their own issues, viz., requirement of an expensive ion-implantation facility, an increase of carrier-recombination centers, thermal instability etc. (Choi *et al.*, 1994; Anpo, 1997).

Hence, the present day goal for researchers is focused on finding more stable, cost effective and industrially viable efficient photocatalysts which can be activated by natural sunlight. Till date, numerous system (Pan and Zhu, 2010; Asahi *et al.*, 2001; Ghosh *et al.*, 2015; Lin *et al.*, 2015; Zhang *et al.*, 2010, 2012) have been tried, some of the important materials are discussed below and other relevant data are compiled in Table 1.

- Zinc oxide (ZnO):

Apart from TiO₂, ZnO is one material which has been heavily explored for photocatalysis (Quintana *et al.*, 2017; Chakrabarti and Dutta, 2004). The greatest advantage of ZnO is that it absorbs large fraction of the solar spectrum and higher quanta of light than TiO₂ (Sakthivel *et al.*, 2003). Although, it is relatively cheaper material than the TiO₂ but belong to the same class of wide band gap semiconductor and also suffers from photo-corrosion upon UV irradiation in solution. To alleviate these issues, number of modifications (e.g., rare earth and/or cationic/anionic doping etc.) has been carried out in ZnO (Lee *et al.*, 2016). Pd doped ZnO (Zhong *et al.*, 2012) has been reported for increased adsorption ability of light and high separation rate of photoinduced charge carriers. Similarly, stronger ultraviolet as well as visible light absorption was induced by the C, N doping and discouragement in e-h pair recombination was reported on doping of C, N and S in ZnO (Yu *et al.*, 2016).

- Bismuth oxyhalide:

Bismuth oxyhalide-based nanomaterials is another system which has received huge attention (Xiao *et al.*, 2012; Song *et al.*, 2010; Jiang *et al.*, 2010; Chang *et al.*, 2010; Zhang *et al.*, 2008; Guan *et al.*, 2013) recently because of their unique layered

structures which endow them with excellent physicochemical properties. Li *et al.* (2014) have worked on bismuth oxyhalide and highlighted some crucial issues in tailoring the layered structure mediated properties of bismuth oxyhalide photocatalysts (such as pH-dependent crystal facet exposure and allied phase transformation mechanisms, facet-dependent molecular oxygen activation pathways etc.). The authors also recommended exploratory suggestions for future research for increasing the photocatalytic performance, as (i) crystal facet engineering to tune the internal electric field intensity in bismuth oxyhalide nanomaterials (ii) controlled synthesis measures to expose high energy crystal facets (iii) investigations on the facet-related redox behavior of bismuth oxyhalide nanomaterials.

- Graphene-based composites/carbon nanotubes (CNTs)/fullerenes:

Graphene, known as the “wonder” material among the research community, has also been used as a grapheme/semiconductor composite photocatalyst (Zhang *et al.*, 2009; Xiang *et al.*, 2012); the main advantages have been highlighted as superior electrical conductivity, large specific surface area and high adsorption rates (Xiang *et al.*, 2012). Zhang *et al.* reported enhanced photocatalytic activity for TiO₂ (P25)-graphene composite under both UV/Visible light in degrading methylene blue compared to the bare TiO₂ (P25) and P25-CNTs with the same carbon content. The authors assigned the performance credit to the synergistic effects of extended light absorption range and efficient charge separation properties (Zhang *et al.*, 2009). Graphene-Bi₂WO₆ composite (synthesized via in-situ hydrothermal reaction using ethylene glycol as a reducing agent) was noted for enhanced photocatalytic activity; complete degradation of rhodamine-B dye was observed in eight (08) minutes in visible light (Gao *et al.*, 2011). No doubt that graphene based composites are promising candidates suitable for designing and fabricating advanced photocatalysts for various applications. However, there are many open issues (e.g., fabrication of large scale defect-free single layer pure graphene sheets, synthesis of high-quality graphene-based nanomaterials, composites etc.) which need considerable attention by the research community, at large. Also, due to the lack of hydrophilic functional groups on the pure graphene sheets, preparation of semiconductor/pure graphene composites has been reported to be challenging (Li *et al.*, 2016). CNTs and fullerenes have been used as a promising adsorbents for the treatment of aqueous solutions contaminated by metals ions as well as reported to be good in treating organic and inorganic pollutants. However, further research is needed to understand and improve the absorption mechanism in these materials (Gupta and Saleh, 2013).

- Other materials for pollutant removal:

α -Fe₂O₃ has been noted for absorption of visible light (~ 560 nm), but the electron-hole (e^- - h^+) charge separation is very short-lived and limits its use as a photocatalyst/photoelectrode (Cherepy *et al.*, 1998). Plasmonic photocatalysts like nanostructured Ag, Au or Cu supported on metal oxides have been reported for broader scope for treatments of pollutants. However, they are considered as expensive options and mechanistic insights are still lacking (Lang *et al.*, 2014). In one of our recent work (Kumar and Chowdhury, 2017), we have tested the applicability of high aspect ratio (nanorods length greater than 100 nm having diameter of 10 nm) copper oxide (CuO) nanorods (synthesized without using any surfactants or templates) for treatments of water pollutants. We chose 4-Nitrophenol (4-NP), one of the most common pollutants traced in industrial effluents usually originating from various chemical plants, e.g., units manufacturing explosives, products for leather treatment, dyestuffs, and agricultural irrigation effluents etc. Remarkable activity was shown by CuO nanorods (in presence of sodium borohydride) as the complete degradation of 4-NP was observed in just fifteen minutes; Fig. 5. Similarly, in another work we illustrated the efficacy of the La³⁺-doped-CeO₂ nanoparticles for the degradation of methylene blue (MB) dye as pollutant. MB is one of the commonly used staining agents that portrays strong resistance to biochemical oxidation. The catalyst nanoparticles degraded MB dye completely in three hours under artificial visible light (shown in Fig. 6).

Nanostructures involving conducting polymers have also been used under visible light for photocatalysis. Ghosh *et al.* (2015) reported good photocatalytic activity for poly-(diphenylbutadiyne) nanostructures prepared by photo polymerization using a soft templating approach; the synthesis process did not involve any sacrificial reagents or metal co-catalysts. They have reported 75% photodegradation of methyl orange in the presence of poly (diphenylbutadiyne) nanostructures after 240 min visible light irradiation. It was shown that the polymer fiber remained stable and retained the morphology and structure even after five photocatalytic cycles. The authors claimed usefulness of this system for the development of semiconducting-based polymers for applications in photovoltaics, self-cleaning surfaces and hydrogen generation.

Issues With the Use of Dye as Model Pollutant

Most of the research works have used dyes as a model for testing the potential of the photocatalytic material. Dyes are commonly used as model pollutants, not only because they are used by numerous industries (Tanaka *et al.*, 2000) but also their degradation concentration can be easily monitored using a spectrophotometer. Table 1 shows the works that have used dye as a pollutant to study the photocatalytic activity. But dye decolorization test for visible light active photocatalysts have number of serious concerns as discussed below,

- (1) Dye sensitization effect:

Dyes can absorb visible light and many of them have an ability to inject an electron into the conduction band of the semiconductor photocatalytic material. This property is widely exploited in dye-sensitized solar cells (DSSC), where dyes are used together with a photocatalyst that is usually a semiconductor oxide such as TiO₂ (Grätzel, 2009). Design of DSSCs

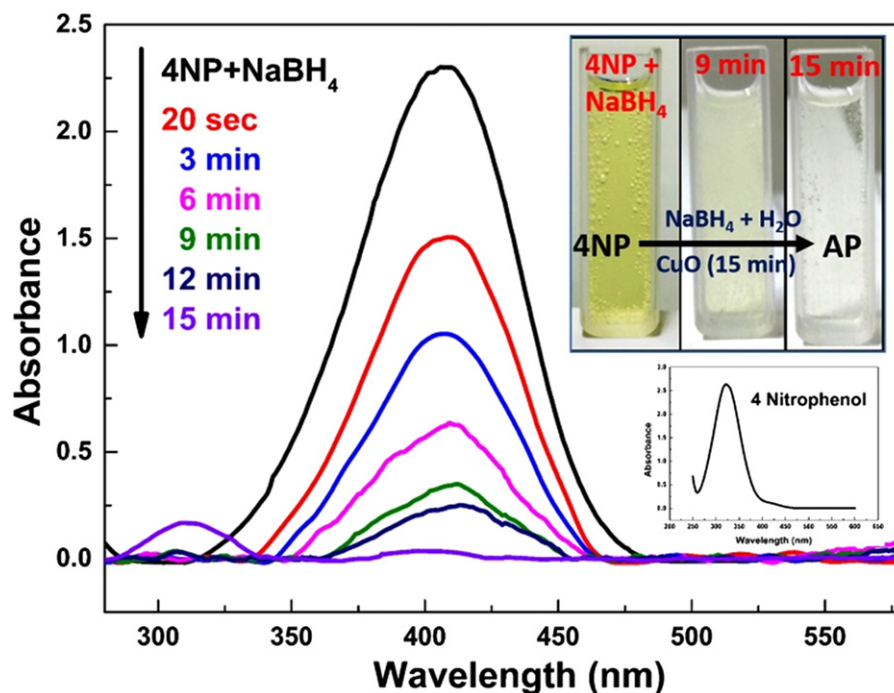


Fig. 5 UV-vis spectra of 4-nitrophenol reduction with NaBH_4 in absence and presence of CuO nanorods (from zero to 15 min); the inset plot depicts the UV-vis spectrum of 4-nitrophenol. The color changes of the mixture (confirming the degradation of 4-nitrophenol) solution over time is also shown. Reproduced by Kumar, K., Chowdhury, A., 2017. Facile synthesis of CuO nanorods obtained without any template and/or surfactant. *Ceramics International* 43 (16), 13943–13947.

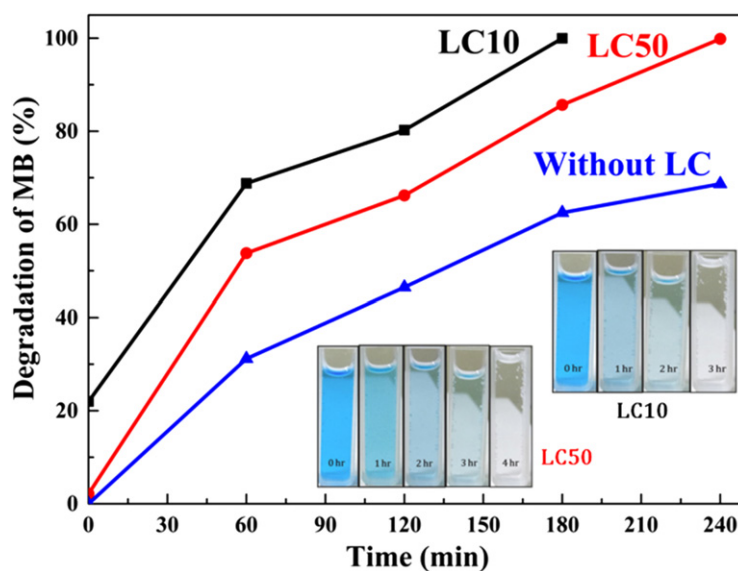


Fig. 6 Photocatalytic degradation kinetics plot of MB dye under visible light under different loading of catalysts (0%, 10% and 50% as denoted by the trend lines with 'triangle', 'square' and 'circle' legends). The color change of the solution with continuous decrease in the MB concentration is shown for LC10 and LC50 in the inset images. For the case of LC10 sample, more than 20% degradation was observed within 30 s justifying a non-zero Y-axis start value. Reproduced by Singh, K., Kumar, K., Srivastava, S., Chowdhury, A., 2017. Effect of rare-earth doping in CeO_2 matrix: Correlations with structure, catalytic and visible light photocatalytic properties. *Ceramics International* 43, 17041–17047.

prevents the degradation of dye but this may not be in the case of aqueous suspension of dye and photocatalyst. Hence, it would be difficult to know, whether dye has degraded itself through dye sensitization or by a photocatalyst or under the influence of both the factors (Kamat *et al.*, 1991; Kamat, 1990).



Fig. 7 Photograph of the photocatalytic pilot plant installed in the Wolfsburg factory of the Volkswagen AG (Photo: J. Lohmann, ISFH). Reproduced by Bahnemann, D., 2004. Photocatalytic water treatment: Solar energy applications. *Solar Energy* 77 (5), 445–459.

(2) Dye concentration effect:

Generally, higher the dye concentration higher the adsorption and this may lead to high photocatalytic degradation. But when both the dye and photocatalyst can absorb the light (in visible range) in the same wavelength range, the effect of dye concentration on degradation becomes complex and the photocatalytic degradation may be retarded. Excess dye may shield the photocatalyst from irradiation as they may attenuate the incident light flux available to the system during visible light absorption. This may underestimate the intrinsic visible light activity of the photocatalysts (Bae *et al.*, 2014).

(3) Dye decolorization and mineralization:

Generally, dye decolorization indicates the destruction of chromophore group (the structure which is responsible for the appearance of color in dyes) and may not guarantee the complete mineralization as there is poor correlation between decolorization and total organic carbon removal (TOC) (Vautier *et al.*, 2001). The absorbance monitoring at a single wavelength can be inaccurate as any other compound/s may form during reaction (having a different absorbance wavelength) and that will be reflected in TOC measurement test. Bae *et al.* (2014) have reported similar color removal efficiency for TiO_2 based catalyst on UV and visible light irradiation but TOC removal efficiency was different and it was much higher under UV than the visible light for the same sample.

Despite of numerous advantages and high potential of photocatalysis in waste water treatment, very few photocatalytic reactor has been commercially installed (or in use). Nearly twenty years ago a review by Goswami (1997) discussed on the matter of only two engineering scale demonstrations, one for groundwater treatment in the U.S. and the other for industrial wastewater treatment in Spain. But more installations have recently been put up, mainly based on nonconcentrating collectors. In laboratory and bench-scale experiments, Dillert *et al.* (1999b) have treated biologically pretreated industrial waste water from the Volkswagen AG factories in Wolfsburg (Germany) and Taubaté (Brazil). The results of the experiments, which were executed using the Double Skin Sheet Reactor (DSSR), were promising enough to install a pilot plant in the Wolfsburg factory (shown in Fig. 7) during the summer of 1998 (Dillert *et al.*, 1999a). The flowsheet of a more recent version of this pilot plant which was installed in 2000 is given by Bahnemann (2004). Since 2007, a homogeneous solar photocatalytic CPC plant (100 m^2) for the pretreatment of saline industrial wastewater containing bio-refractory pharmaceuticals is in operation at a Spanish pharmaceutical company (DSM DIRETIL) as shown in Fig. 8. The system is reported to be able to remove 50% of the initial dissolved organic carbon; the remaining 45% can be removed by an aerobic biological treatment (Oller *et al.*, 2007).

One of the primary inclination behind the development of visible light-mediated photocatalytic processes is the need for more environmental friendly chemical processes. The work that has been carried out in this area till date is neither very much economically viable nor so much eco-friendly.

Future Challenges and Prospects

Use of photocatalysts (preferably under visible light) has become more prominent owing to its simplicity in operation and efficiency in removing disinfectants and mineralization aspects. As many other methods transformed the recalcitrant organics to other phases, photocatalysis helps in complete mineralization. All these attributes make them a viable option for waste water treatments. Although some photocatalytic applications (portable depollution systems, self-cleaning windows etc.) are already in the market, it is understandable that development of photocatalysts with improved capability and efficiency will continue to be a trending topic of research in the near future. Titania-based materials seem to dominate this field because of its relatively superior performance and economic factors.

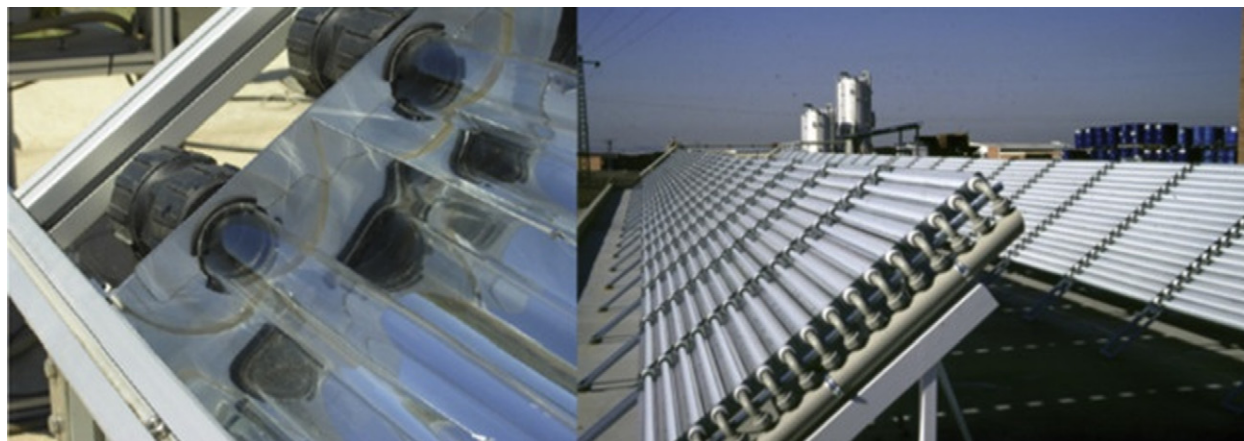


Fig. 8 Partial views of a solar photocatalytic plant used for solar photocatalytic water detoxification. Reproduced by Spasiano, D., Marotta, R., Malato, S., Fernandez-Ibañez, P., Di Somma, I., 2015. Solar photocatalysis: Materials, reactors, some commercial, and pre-industrialized applications. A comprehensive approach. *Applied Catalysis B: Environmental* 170–171 (0), 90–123.

In today's time the use of photocatalysis under visible light faces serious challenges in various directions. The first concern involves the choice and find of a suitable material/s which can prove its versatility for the degradation of a range of hazardous dyes and pigments. Although the initial research in this field started with TiO_2 ; a lot of other materials and composites are being reported on a daily basis as suitable photocatalysts. The main philosophy behind such new materials mostly relates to their suitable band gap (comparable in the visible light wavelength) and its kinetics of degradation. It needs to be realized that both these factors and their assessment may be seriously flawed due to the assumptions or errors in measurements. As discussed before, both the degradation kinetics and band gap measurements need crucial modifications. While the synthesis of new composites (e.g., graphene based) involves serious dispersibility issues; the photocatalysts involving bismuth-based systems poses serious environmental concerns (for it to be used in a large industrial scale). The band gap engineering of these photocatalysts can also be achieved via microstructural modifications (size, shape, texture etc.) and therefore remains as an open arena for further research. At present it seems that, photocatalysts alone may not be able to serve as the panacea for the degradation of dyes, pigments and pollutants since the lists for these hazardous species is long and ever increasing. However, the photocatalysis method may come handy as a quick fix solution at industrial scale where degradation can be monitored visually by the change in color.

The rate of degradation (kinetics) is another area which needs serious attention for the purpose of defining authentic rate equations. Many previous reports have pointed out serious concerns over the use of L-H based models. The alternative ones are also under investigation and still not widely accepted as a universal model equation. At one end, while the revised rate equations need pragmatic assumptions to begin with; the final form of the equation should be more holistic to encompass all crucial variables, viz., synthesis parameters, reaction conditions etc. The approach towards photocatalysis for the degradation of dyes and pollutants hence need an out of box thinking for the solutions of novel and economic materials with innovative microstructure and properties; the process kinetics and scaling up issues (at industrial scale) need further monitoring for a benign solution.

For application purposes, one also needs to consider whether photocatalysis will be used as a stand-alone system or as a pre-treatment step and then further treated by other method (like physical or biological) for effective wastewater treatment. As photocatalysis requires continuous light irradiation for its operation, it would be advisable to use it as a pre-treatment step. It seems more logical to use it in combination with biological or physical method for its cost effectiveness and improved performance. In order to promote the feasibility of photocatalytic water treatment technology in the near future, several key technical constraints ranging from catalyst development to reactor design and process optimization have to be addressed. Some of these issues include its operating ability in the solar light, wide pH ranges for operation, minimizing the use of oxidant additives and sacrificial reagents etc.

Conclusion

Photocatalysis has the signature of a promising technology that has a number of applications in environmental systems such as air purification, water disinfection, hazardous waste remediation, and water purification. In addition, the basic research that underlies the application of this technology is promoting a new understanding of the complex heterogeneous photochemical process of metal oxide systems in different environments. The continuous exploration of new phases and materials as potentially improved photocatalysts will most likely provide exciting results in the coming years. However, a more integrated use of theoretical and advanced experimental techniques will be crucial for achieving a rapid and significant enhancement of the performance.

Giacomo Luigi Ciamician, a pioneering photochemist, presented his remarkable vision of “The Photochemistry of the Future” (Ciamician, 1912) at the International Congress of Applied Chemistry held in New York in 1912. He expressed his views that photochemistry, which was an entirely solar discipline at that time, could be an essential component of industry in the future: “On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains, and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them even more abundant fruit than nature, for nature is not in a hurry and mankind is”.

Although solar photocatalysis has produced significant interest in research, it is still too young for commercialization: there are only a few examples of medium and large-scale solar photocatalytic chemical processes in industries around the globe. However, these few validate that solar photochemical production of selected fine chemicals and solar photocatalytic wastewater treatment (particularly for tropical regions), may be environmentally-benign alternatives to the existing traditional processes. The application of heterogeneous solar photocatalysis with TiO_2 (in particular) is expected to have a future beneficial impact on the environment, public health and society at large.

Finally, a particularly important long-term goal of visible-light photocatalysis will be the utilization of large-scale photochemical processes in commercial applications. The environmental benefits envisaged by Ciamician cannot be achieved if photochemical synthesis remains a largely academic assignment. Thus, the development of increasingly efficient, pragmatic and synthetically useful photocatalytic materials and their efficient degradation for the construction of fine and commodity chemicals should be an enduring goal for academic researchers and we anticipate that this will remain as an exhilarating task for many years to come.

See also: Eco Friendly Flocculants: Synthesis, Characterization and Applications

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Waste Resources Recycling in Achieving Economic and Environmental Sustainability: Review on Wood Waste Industry

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Nomenclature

σ Bending strength

$^{\circ}\text{C}$ Temperature in degree celsius

C&DW Construction and demolition waste

E Young modulus

GWP Global warming potential

LLS Laminated strand lumber

LVL Laminated veneer lumber

MOE Modulus of elasticity

MOR Modulus of rupture

PLS Parallel strand lumber

WtE Waste to energy

Background of Literature Review on Wood-Waste Recycling

The broad objective of this review article is to present the published research findings on wood-waste recycling with aiming to support on going global sustainable development activities. This review has been designed for answering a few questions on problems relating to the effect of wood-waste recycling on mitigating climate change through reducing carbon emission, how timber industries meet required mechanical and chemical properties for achieving higher lifecycle of wood-waste based new materials. The other emerging issues this review article has addressed are the supply chain of collecting wood-waste, the major uses of wood-waste recycling, the contribution of engineering for developing new products from wood-waste, and the cost benefits analysis of wood-waste recycling. However, the total number of papers reviewed in this work is 139 and are all published in the year 1997–2018. The 10% of the papers outlined the potentials and the need for recycling of wood-waste. The uses and recycling of wood in building & construction, paper and furniture industries have been explained in more than 14% of the papers reviewed. The mechanical and chemical properties have been studied in 18% while in-depth analysis of the engineering contributions and its positive implication on the value chain of the recycled wood-waste has been analyzed in 25% of the papers reviewed. The remaining 33% of papers outlined the importance of wood recycling on the economic and environmental sustainability.

Historical evidence has shown that deforestation has been the primary source of raw materials for timber industries (Sun *et al.*, 2004; Köhl *et al.*, 2015). The raw wood supply to timber industries for producing building materials, furniture and other purpose has been formulating in line with the aim to achieve global economic growth (ISWA, 2010; Pirard *et al.*, 2016). A unit of United Nations (UN) subdivision: Food and Agriculture Organization (FAO) have made a forest Assessment Report (FAR) on forest resources, which indicated that wood-based manufactured products add more than \$450 billion to the world market economy annually (Köhl *et al.*, 2015; Moellendorf, 2015). This amount is equivalent to a total of 530.5 billion m^3 timber in 2015, and it has increased by 3.6 billion m^3 (0.7%) more than the total growth reported in 1990 (Gurnell, 2002; Ulubeyli *et al.*, 2017). However, this huge amount of wood sourcing from the forest is one of the main reason of deforestation and is responsible for about 20% of global carbon emissions (Gregory, 2008; Maratovich *et al.*, 2016), and it was 9Gt CO_2eq in 2017 (Yargicoglu *et al.*, 2015; EPA, 2017; Gregory, 2008; Maratovich *et al.*, 2016). In addition, there is a significant amount of carbon and CH_4 emit due to landfilling of wood-waste into the soil for decomposing in an anaerobic environment (Gregory, 2008). It has been stated that construction demolition waste alone generates an estimated 70.62 million metric tons of wood-waste material and disposable solid wood products per year in the united states (Falk and McKeever, 2004; Bratkovich *et al.*, 2014). However, the research published papers on wood-waste mainly focused on economic and engineering aspect in-line with sustainable development; but wood-waste recycling in-line with carbon emission linking with global warming potential (GWP) and climate change effect was not much; it indicates that a research gap exists in wood waste recycling domain. To fill up this gap, this study was designed for addressing all these mentioned issues. In that aspect, this review paper is novel as this work has addressed the contribution of wood-waste recycling to reduce carbon emission and GWP. Indeed, this review article has been written to provide adequate information on wood-waste processing for developing value-added new materials with higher lifecycle by improving required mechanical properties such as durability and modulus of elasticity. With this celebration, wood recycling article has been authored to provide data that will serve as a necessary guideline for future research in wood-waste management for contributing to achieving economic and environmental sustainability.

The Wood Waste Recycling Scenarios

Wood-waste can be regarded as a non-hazardous material that originates from household and commercial consumption of wood products such as furniture, demolition of buildings, refurbishment and renovation waste from construction sites, industrial packaging wood, and wood pallets (FWPA, 2008; EPA, 2014). The source of the wood-waste material is also very important as it

determines the processing method required to produce a value-added engineering material. It has been reported that wood-waste have a very diverse used in the economy for sustainable development activities. Indeed, the use of wood-wastes have been increasing in various uses because of its durability; and improvement in engineering design to make it environmentally friendly (Gurnell, 2002; Ulubeyli *et al.*, 2017). Some of the products that produce from wood-waste are animal bedding, equestrian surfaces, mulch, landscaping, as a bulking agent in composting and particleboard (Wilk *et al.*, 2010), and building materials. It must also be emphasized that different uses of wood-waste require the different level of purity and engineering properties that must take into consideration while designing new materials from wood waste (Yargicoglu *et al.*, 2015; EPA, 2017).

Global Wood Waste Recycling Scenario

The need for recycling wood-waste for producing new materials with required mechanical strength and higher lifecycle has become research interest area among engineers specialized in the field of material science (Defra, 2012). The commercial and research activities with wood-waste have focused into two streams; one is wood-waste from municipal solid wastes and another one is the demolition of old building (Defra, 2012). According to a study conducted by the Waste & Resources Action Programme (WRAP), some of the largest sources of wood-waste come from three areas (Defra, 2012).

(a) Municipal waste that consists of disposed items such as furniture, packaging and other wood related to waste from households. (b) Industrial and commercial waste that consists of wood waste come from wood products manufacturers and construction materials. (c) Construction and demolition waste that are made up of surplus structural timber unable to be used further, torn down structural wood and unwanted furniture from the demolition industry (Tolvic, 2011).

However, literature revealed a few ways of using wood-waste but the major ways are two. One way of using is recycling to produce new materials for building and manufacturing industries, and another way of using is to producing energy inline with the concept of waste to energy (WtE) (Clegg, 2017; Ramage *et al.*, 2017).

Recycled Waste-Wood for Energy and Fuel

The wood-waste which cannot be recycled in developing new materials are converting to energy in line with the concept of WtE (Clegg, 2017). Studies revealed that wood-waste are also used as a substitute for fossil fuels in the form of WtE (Rawat *et al.*, 2009; In-HO Choi *et al.*, 2013). In WtE process, wood-waste is used as boiler fuel for producing steam for turbine (Scotland, 2003; Shaw and Moore, 2011). It is reported that the wood-waste in the WtE application is positively associated with higher GHG emission and accounted for 55% higher than the burning of biogas for electricity production; in this aspect, wood-waste is not recommended for WtE (Clegg, 2017). It was also reported that between 2009 and 2013, there is the spontaneous increase of more than 20% wood-waste application in WtE and in globally this figure is quite higher. It is observed that the WtE application has been in use in European countries (EU) for electricity production (Canam and Campbell, 2009).

However, two categories of wood-wastes recommended for WtE: (1) Clean wood-wastes that are uncontaminated by harmful substances, and (2) wood waste contaminated with hazardous substances. Those uncontaminated are usually burn and used directly in power stations and private stoves, while those wood or chipboards containing adhesives and paints are used for WtE in specialized combustion equipment (Shaw and Moore, 2011).

A significant amount of Timber wastes are using in energy industries; for example, in the Netherlands, the huge amount of wood waste generated from C&D activities (Tam and Tam, 2006), most of these wood waste have used in power plants and hot water generation purpose.

It was reported that more than a million tons of Canadian waste wood pellets have been exported to the EU for using in power plant as substituted of fossil fuel (Northwoods *et al.*, 2008; European Commission, 2014; Edo *et al.*, 2016).

Recycled Wood Waste for Landfill

The last alternative at the end-of-life cycle scenario of wood-waste is the use as a landfill materials (Joely *et al.*, 2005). Landfill option is a costly practice compare to other available options as well. The practice of using wood waste for the landfill has been restricted in some part of Europe including Sweden, Austria, and Germany through the United Kingdom has allowed to a certain limit (Kale *et al.*, 2002). However, it has been reported that wood-waste containing some hazardous materials, which appeared as the main barrier to using wood waste for landfilling purpose (Shaw and Moore, 2011). It was reported that there are a few disadvantages associated with landfill, which are the slow biodegradation process that takes a longer time to decompose wood-waste. The lignin present in wood which is very resistant to decompose and this might take a very long period of time especially if the biodegradation is to take place in anaerobic conditions (Kale *et al.*, 2002). The wood waste also responsible for GHG emission which includes methane, nitrogen, and CO₂, (Kale *et al.*, 2002).

Recycled Wood Waste for Developing New Products

Development longer lifecycle materials from wood waste is a challenge due to composition of various quality of wood (Ramage *et al.*, 2017). The major challenge is the sorting of waste wood into different categories in order for the quality of the new materials.

The need to develop an efficient waste wood sorting is therefore very crucial to develop the quality product from the recycling process. The second step is pre-treatment for waste-wood prior to process for new material (Farsi, 2010). The third steps are selecting recycling process for developing new material as in this aspect process conditions, temperature, pressure and process duration are vital parameters. It has been reported that sorting process is not able to separate 100% impurities from wood waste, and a significant percent of other materials remain in the bulk wood waste such as metals and plastics that may affect the final product (Tsuchimoto *et al.*, 2016).

Recycling wood waste for developing building and construction materials

A large quantity of timber waste have been generated from construction and demolition works (C&DW). The United Kingdom produced more than 2.5 million tons of timber wastes each year (Tam and Tam, 2006). The reason for the higher quantity Timber in C&DW is of using these materials as a preferred quality structural material compares to concrete and steel (Forestry Commission, 2016). It has been reported that sawn wood waste is the major percent in C&DW (Chen, 2008).

However, the method of C&DW conversion to new materials is still new in the most of countries and even technology is costly. It is reported that 50%–95% of C&DW can be recycled for developing new value-added materials (Ulubeyli *et al.*, 2017). For example, Turkey established her first C&DW recycling industry in 2006 and this is continually been developed. Recently the EU (Directive 2008/98/EC) has set a target of recycling 70% C&DW materials in development activities (Ulubeyli *et al.*, 2017). The statistics of C&DW show that Netherland is successfully used 98.1%, Denmark 94.9%, Estonia 91.9%, Germany 86.3%, and Ireland 79.5%. Similarly, the U.S.A has achieved 73.5% of C&DW in recycling process.

Environmental benefits of recycling wood waste from construction and demolition waste

Today, the reduction of GHG emission has been achieved to a significant level through the recycling of C&DW (Ulubeyli *et al.*, 2017). A study jointly conducted by Columbia, British and Canada in 2017, the findings demonstrated that the use of wood-waste for developing new products is positively associated with mitigating climate change (Xu *et al.*, 2017). This study influenced several countries on data collection of wood waste (Werner *et al.*, 2010; Lundmark *et al.*, 2014; Nordström *et al.*, 2016; Russell and Kumar, 2017), and to investigate on the necessary parameters need to higher utilization of wood-waste for developing new products to mitigate climate change. The results obtained from various studies has been recommended for further applications on a global scale so as to exploit the potentials of C&DW that would contribute to restore the conservation forest resources through wood-waste management (Shahiduzzaman and Layton, 2015).

Recycling wood waste with concrete materials

It has been stated that structural efficiency of wood sometimes better than concrete and steel, though the structural efficiency of wood may reduce to a greater extent due to the unfavorable environment (Jeffrey, 2011). Based on this properties, wood waste chips mixed with cement has seen to increase the compressive strength of building materials. In an experiment, Thandavamoorthya (2015) found that 15% wood chips with 85% concrete produce higher strength cement, and its estimated value was about 32 Mpa; whereas cement produced from only concrete the compressive strength was only 25 Mpa. This experiment concluded that wood-waste could be a good choice in cement production (Thandavamoorthya, 2015). Mehmood stated that the hardwood is significantly stronger and can be used in some structure conveniently as a replacement of reinforced concretes (Mehmood *et al.*, 2010). Similarly, Timber has a higher stiffness than reinforced concrete, which makes it feasible to use as building materials (Oriyomi *et al.*, 2011). The low-density timber appeared a better choice for building due to its higher load-bearing strength, and higher strength-to-weight ratio. Sometimes timber is better building materials compare to concrete due to its higher elastic modulus-to-weight ratio. In all these aspects mentioned, wood-waste appeared a good option for converting it to building structural materials for increasing strength of building at a lower weight.

Recycling wood waste for developing industrial products

Wood waste from C&DW and furniture manufacturing can be reused after reprocessing through hydrolysis, gasification, pyrolysis, heat treatment, chipping and pulping process (Hendriks, 2000). After Cleaning, de-nailing and sizing, waste timber reused for making a plank, beam, door, floorboard, rafter, panel, balcony parapet and pile (Hendriks, 2000). In 2004, Japan developed a new technology in turning timber waste into furniture, wood bench, and timber stair (Tam and Tam, 2006). Wood waste from C&DW is also used to produce paper and recycled board. Clipped timber is recycled by spraying them onto sloped soil surface in Japan, which is called “fiber (Hiramatsu *et al.*, 2002)”. It has been reported that Japan developed a new technology to paving material timber chip, which is regarded as a high value-added product from waste (Tam and Tam, 2006).

Wood waste from C&DW is also recycled to develop building materials like wood-based panel for the roof, ceiling, floor, cladding, hoarding, as a packaging substitute and sound barrier for building (Tam and Tam, 2006). Woodchip of C&DW is also using to improve soil texture by mixing with topsoil. I has been reported that Timber waste is also used to produce insulation board, kitchen utensil and furniture (Sheidaei and Serwanja, 2016).

Recycling wood based waste furniture

Quality of new materials that produce from wood waste depends on from which quality of timber the original furniture was produced (Kaplinsky *et al.*, 2003). Australia is successfully utilizing her potentials in the recycling of furniture waste at a larger scale; it was reported that six companies currently in operation for recycling furniture wastes to produce various high-value-added

new products (Daian and Ozarska, 2009). The size of these companies is medium to large with yearly revenue about 7.3 million Euro per (Bruns, 2017). Different kinds of wastes used by these companies namely solid wood offcuts, sawdust, engineered wood offcuts and shavings (Bredemo and Mäkelä, 2008). They used both clean and contaminated furniture wastes for producing new products. The offcuts are usually clean and are free from contaminants such as dirt, chemical impurities, rock, and metal, while the mixture streams consist of shaving trims and sawdust (Liang *et al.*, 2012).

Different valued-added products are manufactured from waste timber including Veneers flakes, wood chips, and fibers (Mercer and Frostick, 2012). By using these waste wood elements, variety of building materials are produced such as plywood, laminated veneer lumber (LVL), glued laminated lumber, particleboard and medium density fibreboard (MDF) (Sinha and Miyamoto, 2014; Davids *et al.*, 2017).

Laminated veneer lumber from waste furniture

Laminated Veneer Lumber (LVL) has been producing from wood waste. The thickness of LVL product is from 2.5 to 4.8mm with significantly higher compressive and tensile strength (Book, 1997; Liang *et al.*, 2012). Studies show that the base wood of this product are pine, poplar, birch, or eucalyptus (Janowiak *et al.*, 2001; Kiliç, 2012). In product processing, the LVL fibers are arranged in a parallel way with the homogeneous mixture in order to increase its strength; and the strength-to-weight ratio (Ayrilmis *et al.*, 2009). The veneer is glued with melamine-formaldehyde and phenol-formaldehyde adhesives at required temperature and pressure in order to increase stability of product structure (Wang *et al.*, 2015; Sasaki and Abdullahi, 2016).

Parallel strand lumber from waste furniture

The Parallel Strand Lumber (PLS) is a building materials produces from different kinds of waste timber's chips, mostly pine, poplar, and Douglas. These strands are usually positioned in parallel length-wise manner (Clouston, 2007). PLS elements are about 3 mm thick, 20 mm wide, and 0.6–3.0 m long, and manufactured by cutting of the veneers (Hockey *et al.*, 2000). PLS is predominantly used as columns and beams, reaching up to 30 meters, as well as in frame construction (Donaldson, 2008; Huang *et al.*, 2012). Phenolresorcinol-formaldehyde glues adhesive are used to bond the strands together in order to increase its strength (Kurt *et al.*, 2013).

Laminated strand lumber from waste furniture

Laminated Strand Lumber (LSL) is a composite timber materials produced from waste furniture; and used in building structure (Mahdavi *et al.*, 2012). The production technology used to produce LSL is very similar to LVL, but the final product is thicker compared to LVL (Tannert and Lam, 2007). The standard size of strands are 0.8 mm thick, 20–50 mm wide, and 300 mm long. The strands are usually bonded at high pressure with polyurethane adhesives and steam (Nugroho and Ando, 2001). Initially, the strands are laid in parallel or crosswise before it cuts into desired and acceptable size. The orientation of the strands affects the strength of the material (Ma and Young, 2010). However, these strands are used as beams, rafters, or columns of a building. Sometimes it uses in building walls, ceilings, and floors (Çolak *et al.*, 2007; Ardalany *et al.*, 2010).

Research in Improving Chemical and Mechanical Properties of Wood Waste Based New Materials

A huge number of researches have been conducted on wood waste based materials to improve its mechanical properties, and to limit its recycling potentials (Hossain *et al.*, 2014). The major researches have been focused on various physical and chemical treatments, which contributed to prevent biological deterioration products and also improve its service life (Mohareb *et al.*, 2012).

Chemical Modification of Wood Waste Based Products for Improving Quality and Lifecycle

After chemical and heat treatment two types of inspection have been using; X-ray fluorescence (XRF) and laser-induced breakdown spectroscopy (LIBS) (Janin *et al.*, 2011). These characterization processes are capable of identifying two chemicals: chrome copper arsenate (CCA) and alkaline copper quat (ACQ). Both of them contain metals that contaminate recycled wood products (Conard Holton, 2001; Love, 2003; Yasuda *et al.*, 2006). The LIBS equipment is usually fixed in an air-conditioned room and connected by fiber optics to the wood waste recycling processing area. The LIBS laser beam is directly focussed on the shredded wood chips in order to identify chromium contamination (Rahman *et al.*, 2001).

There are various types of chemical modification process have been using in wood waste recycling process for improving mechanical properties of wood waste based products (de Guimarães *et al.*, 2015). Aside from the changes in mechanical properties, chemical modification process also used, which contribute to improve physical dimensions, increase resistance to fungi and moisture. The chemical modification of wood waste recycling process usually involved the adjustment of temperatures, the use of catalysts, water vapor, organic solvents and chemicals reactive (Bodirlau *et al.*, 2008). Therefore, the effect of chemical and heat treatment of wood is very important in determining the quality of new material (Epmeier *et al.*, 2004). The mechanical properties of the new products also determine whether it will be sustainable to use wood as an engineering material (Stoeckel *et al.*, 2013).

Table 1 Different mechanical properties of wood species before and after heat treatments

Wood species	Media	Moisture Content		Changes in mechanical properties Static bending (Fresh)		Changes in mechanical properties Static bending (Recycled)	
		Fresh	Recycle	MOE	MOR	MOE	MOR
Softwood	–	12.2	5.3	–	– 15	–	4.0
Hardwood	–	10.5	6	–	– 20	–	3
Pine 1	Air	0	0	– 32	– 33	0	0
Pine 2	Steam	12.6	4.5	– 40	– 5	0	–
Beach	Gas	11.3	4.9	11	– 26	10	–

Heat Treatment of Wood Waste Based Products for Improving Quality and Life Cycle

Heat treatment of wood is usually conducted within the ranges of 150–230°C in a shield media such as steam, nitrogen gas, vegetable oils or under a vacuum; and it would apply for both fresh wood and recycle wood processing (Martin *et al.*, 2013). The report of various studies demonstrated that heat treatment had played a vital role in improving mechanical properties of materials developed from waste wood. Indeed, heat treatment is also contributed to reducing hydrophobicity and greater dimension stability (Tascioglu *et al.*, 2003; Service, 2010). The mechanical properties modulus of elasticity (MOE) and the modulus of rupture (MOR) of wood are highly affected by heat treatment, but the effect of heat on MOE and MOR is less effective on wood products developed from wood waste (Tiryaki and Hamzaçebi, 2014). This scenario is presented in Table 1.

The effect of heat treatment on mechanical properties is significantly good as stated by Hein *et al.* (2013); he demonstrated from his study results that load-deflection properties had appeared better for wood-waste based new materials compare to fresh wood (Hein *et al.*, 2013). The general effect of the different kinds of media on the mechanical properties of a different kind of fresh and recycled wood after heat treatment represented in Table 1 Hein *et al.*, 2013; Tiryaki and Ha. For example, Beach wood treated at 220°C for 4 h in Gas media exhibited an improvement of approximately 11% in MOE but a reduction of more than 26% in MOR when tested after conditioning at 20°C.

Improvement Mechanical Properties in Wood Waste Based New Materials

The mechanical properties of timber are the determinants of using this material in construction industry. The required properties that consider are bending strength (σ_b ; Pa), bending stiffness (MOE, modulus of elasticity; Pa) compression strength (σ_a ; Pa) and compression stiffness (E, Young's modulus; Pa) (Xie *et al.*, 2013). However, mechanical properties improvement of new materials made from wood waste would be enhanced by chemical and heat treatment (Service, 2010). In chemical modifications process, solvents, organic compounds, water vapor and reactive chemicals are extensively used. It has also been reported that Acetylation, Furfurylation, Resignation, Wax treatment, and Grafting methods are the proven ways that have been used in wood treatment for improving mechanical properties (Belgacem and Gandini, 2008).

Mechanical properties improvement by using waxing method

The treatment by waxing has been established to increase mechanical properties of wood. It has been reported that MOR, MOE, and bending strength of wood waste materials can be increased up to 25%, 11%, and 31% respectively by Using Waxing Method (Scholz *et al.*, 2012).

Mechanical properties improvement by using grafting method

Grafting modification process, Vinyl Monomers is used. It has been reported that the treatment sugar maple wood with vinyl monomers has increased MOE and MOR by 20.0% and 28.0% respectively (Rowell, 2012). This process is also contributed to increase tensile strength and compression strength in wood waste based new materials (Scholz *et al.*, 2012).

Mechanical properties improvement by using furfurylation method

The chemical modification of wood product by using Furfurylation is positively associated with mechanical properties. It has been reported that while pine species sap wood treated with Furfuryl alcohol (FA) contributed to increase MOR and MOE by 6% and 38% respectively (Esteves *et al.*, 2011). In addition, the chemical modification of wood by using FA also contributed to improving dimensional stability, reduced water uptake capacity, and increase resistance to biological deterioration.

A Short Inventory on Research for Improving Wood Waste Recycling Performance

A large number of engineers have intensified their researches for optimizing wood-waste recycling in producing higher value-added materials for the economy (Sui and Chen, 2014). It has been suggested that to improve mechanical behavior of waste

timber-based products, need for an in-depth study on basic parameters such as physical, mechanical and chemical characteristics of wood waste-based materials (Donaldson, 2008). Inputs from engineering to recycling of wood-waste processes is essential for improving the quality of products as well as process performance. It has been reported that to achieve desired quality products from wood waste, process parameters namely compression time, temperature and pressure need to control precisely; in this aspect, R&D is essential (Hiramatsu *et al.*, 2002; Stelte, 2013).

Other aspects of researchers that getting attention and have been well documented in the published literature are the enhancement of mechanical properties including improvement of the strength and stiffness (Burgert *et al.*, 2002). In various studies, a few indicators have used to evaluate the properties of products developed from wood waste. The indicators are Knots, annual ring width, modulus of elasticity (MOE) and density of timber (Institute, 2005; Tabet and AbdulAziz, 2013).

For enhancing research towards improving mechanical properties of wood waste-based materials, Cave (1997) suggested that the coefficient of quality determinant could be compared with the mechanical properties indicators as independent variables (such as knot, annual ring width, density, and MOE) and tensile and bending strength could be the dependent variable (Cave, 1997; Huang *et al.*, 2012; Toolbox.com, 2015).

Effects of Recycling Wood-Waste on Environmental Sustainability

The estimated carbon density in the air was 405 ppm as of 2017. In future, it would be 450 ppm in 2050, and 750 ppm in 2100 (IPCC, 2017). It has also been reported that the Global carbon was 45GtCO₂ in 2017. Various studies reports demonstrated that about 20% of this carbon is emitted from deforestation process, while wood collect from the forest. It is saying that wood waste recycling will definitely contribute to reduce deforestation and reduce GHG emission (Nzeadibe, 2009; Song and Li, 2014). It has been reported that recycling wood waste for developing new materials will contribute to conserving natural resources (Nzeadibe, 2009; Yau, 2012). With the development of a market for wood-waste, overall health of the forests would improve (Song and Li, 2014). It has been reported that the efficient use of wood waste has a multiplier effect on the conservation of forest resources with a very appreciable reduction in GHG emissions and biodiversity loss (Spittlehouse and Stewart, 2003).

Recycling Wood Waste for Saving Carbon Sink

Forest is proven carbon sink, which could be saved by efficient utilization of wood-waste is to contribute to reducing deforestation, carbon emission by protecting carbon sink (Huron *et al.*, 2017). In this concern, Tsunetsugu and Tonosaki, (2017) reported that the utilization of wood-waste in the construction industry would contribute to reducing a significant amount of GHG emission due to saving carbon sink deforestation. It was also reported that this kind of wood-waste utilization for construction purposes and other uses would definitely reduce climate change due to reducing of GHG emission (Soimakallio *et al.*, 2016; Wang and Chen, 2016).

Economy of Waste Wood Recycling

It has been reported that wood-waste recycling for producing new products is an economically viable project because it conserving natural resources (Laurijssen *et al.*, 2010; Carpio *et al.*, 2013). Recycling of wood-waste has been regarded as a source of renewable material supply for economic development (Greyson, 2007). The indirect contribution of Wood Waste recycling is to establish supply chain network for collecting wood waste which would enhance economic growth and create employment opportunity (Björklund and Finnveden, 2005). The wood-waste recycling effort has also guaranteed the continued sustainability of the forest reserve in the emerging economies (Chen *et al.*, 2012; Bergeron, 2014). Wood brings ecological balance in the environment, which has a wider economic benefit in terms of achieving higher agriculture productivity. In the report, Ramage *et al.* (2017) stated that the utilization of wood-waste in the construction industry would be contributed to increase various activities, which would be enhanced the growth of local economy (Ramage *et al.*, 2017).

Supply Chain and Economic Benefits for Wood Waste Recycling

The degree of supply chain strength for collecting, transporting and processing has a positive effect on wood waste recycling performance (Kassim and Ali, 2006; Das and Bhattacharyya, 2015). In a study, Asif (2009) found that reuse of wood-waste in developing new materials and other economic use depends on the cost-effectiveness of wood waste collection (Asif, 2009).

It has been reported that the volume-based fee for disposal system has appeared an effective method for promoting wood-waste recycling (Hong, 1999; Lee and Paik, 2011). It has been observed that the quantity of wood-waste recycling has increased significantly as people are asked to pay for disposing of their waste (Wath *et al.*, 2010). It has been also reported that the amount of wood-waste collection from apartments is higher compared to detached single houses due to the availability of strong supply chain system (Tan and Tracey, 2007).

The existence of recycling bins close to residences and the availability of waste management staff has also contributed to the increasing wood waste supply chain network. However, wood waste recycling performance depends on a few factors such as the availability of lobby for collection, specific space in community for disposing off waste wood; affordable technology for converting

waste to value-added materials, and finally government support for establishing strong supply chain net (United Nations, 2011; Australian Government, 2012).

The immediate benefits of recycling wood waste are the avoidance of landfill cost and saving of space costs (Atkinson and Mourato, 2008). In an estimate Merry *et al.* (2009) has shown that benefits cost ratio of wood waste recycling is more than one, which indicate that wood waste shall recycle project is economically feasible (Merry *et al.*, 2009).

Conclusion

This review presents the research outcomes published in various scientific journals on wood-waste recycling. This paper outlined the potentials of wood waste recycling in developing new materials to be used in building & construction, paper and furniture industries. This review listed the research outcomes published relating to mechanical and chemical properties of wood waste based materials, which revealed that wood waste recycling for developing new materials would contribute to reduce deforestation and carbon emission. This paper discussed the major challenges and opportunities of wood waste recycling industries; and contributions of engineering to address the challenges. Lastly, this review disclosed that wood waste recycling is positively associated with reduction of global carbon reduction and climate change. This review concludes that engineers and scientist shall conduct further R&D on wood waste value chain for increase recycling performance for achieving sustainable development through economic and environmental sustainability.

Acknowledgment

Authors would like to acknowledge the financial support received from Ministry of Agriculture, State of Sarawak Malaysia under grant GL/F02/ORSSG/2016. Authors are pleased to offer special thanks to the management and academic staff of Engineering Faculty and RIMC, Universiti Malaysia Sarawak.

See also: Characterization of Wood, Cork and Their Composites for Building Insulation. Investigation of the Fuel Value of Selected Wood Samples Using Artificial Neural Networks. Manufacturing, Applications and Mechanical Properties of Lightweight Wood-Based Sandwich Panels. The Role of Engineering in Mitigating Global Climate Change Effects: Review of the Aspects of Carbon Emissions from Fossil Fuel-Based Power Plants and Manufacturing Industries

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Water Resource Management for Renewable and Sustainable Hydro Energy in Turkey

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Introduction

Because of social and economic development, the demand for energy and particularly for electricity is growing rapidly in Turkey. The main indigenous energy resources are hydro and lignite. Turkey has no big oil and gas reserves but it has a large potential for renewable energies. Turkey's geographic location has several advantages for extensive use of most of the renewable energy sources. It is on the humid and warm climatic belt, which includes most of Europe, the near East and western Asia (Yuksel *et al.*, 2005; Paish, 2002).

Owing to Turkey's regions, most of which are hilly, it is possible to develop relatively higher heads without expensive civil engineering works, so relatively smaller flows are required to develop the desired power. In these cases, it may be possible to construct a relatively simple diversion structure and to obtain the highest drop by diverting flows at the top of a waterfall. There are intensive investigations to improve small and large hydropower development in Turkey and some small hydropower plants are still under construction.

The development of hydro-electricity in the 20th century is usually associated with the building of large dams. Hundreds of massive barriers of concrete, rock and earth were placed across river valleys world-wide to create huge artificial lakes. While they created a major, reliable power supply, plus irrigation and flood control benefits, the dams necessarily flooded large areas of fertile land and displaced many thousands of local inhabitants. In many cases, rapid silting up of the dam has since reduced its productivity and lifetime. There are also numerous environmental problems that can result from such major interference with river flows (Yuksel *et al.*, 2016).

Small, mini and micro hydro plants (usually defined as plants less than 10 MW, 2 MW and 100 kW, respectively) play a key role in many countries for rural electrification. Small-scale hydro is mainly 'run of river,' so does not involve the construction of large dams and reservoirs. Small hydro currently contributes over 40 GW of world capacity. The global small hydro potential is believed to be in excess of 100 GW. The industry believes that small hydro will have a strong resurgence in Europe in the next 10 years, after 20 years of decline (Yuksel *et al.*, 2016).

Turkey's energy demand is met through thermal power plant consuming coal, gas, fuel oil and geothermal energy, wind energy and hydropower. Because Turkey does not own any nuclear power plant yet, the installation of the first nuclear power plant with a capacity of 1000 MW is on the schedule as a plan for the near future. In 2008, the energy consumption of Turkey was about 106,525 kilo tons of oil equivalent (ktoe) as shown in Table 1 (DPT, 2010).

Turkey's installed generation capacity is also 41.818 GW and electricity generation is 198.418 GWh in 2008. According to Turkey's Ninth Plan, 66% of Turkey's generated electricity is supplied from thermal power plants. Contribution of wind and hydro power plants are 0.2% and 32.20%, respectively. 49% of Turkey's electricity is generated by Electricity Generation Incorporation (EUAS), 39.70% is generated by auto-producers, and 9.5% is generated by affiliated partnerships of EUAS and 1.8% by distribution of electricity generation by primary resources by 2007 is given in Fig. 1 (DPT, 2010; TEIAS, 2007; Yuksel, 2015; DSI, 2010; MENR, 2008; WECTNC, 2008; EIE, General; RTLED, 2004; Yuksel, 2012).

Table 1 Primary energy consumption (ktoe)

Energy sources	2008	2009	2010
Hard coal	16,427	16,165	16,861
Lignite	15,217	15,031	15,891
Petroleum products	31,784	27,652	29,312
Natural gas	33,807	30,764	33,603
Hydroelectricity	2,861	3,121	3,354
Renewable energy	1,645	1,910	2,102
Wood	3,679	3,610	3,591
Animal waste and plant residue	1,134	1,150	1,120
Total primary energy consumption	106,525	99,360	105,791
Per capita consumption (kgoe)	1,423	1,312	1,381

ktoe: Kilo tons of oil equivalent; kgoe: Kilo gram of oil equivalent.

Note: DPT, 2010. State Planning Organization Ninth development plan 2007-2013. In: Proceedings of the Prime Ministry of Turkey, Ankara, Turkey.

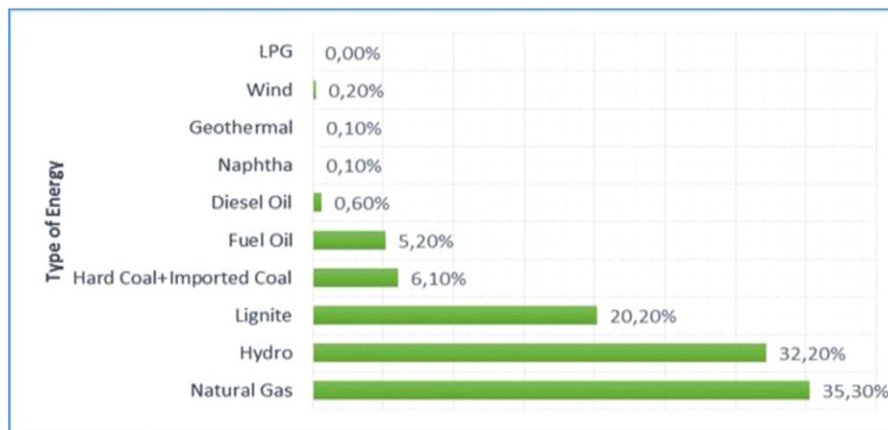


Fig. 1 Percentages of electricity generation by primary energy resources in Turkey. Data from TEIAS, 2007. Turkish electricity transmission company. In: Proceedings Percentages of Electricity Generation by Primary Energy Resources, Ankara, Turkey.

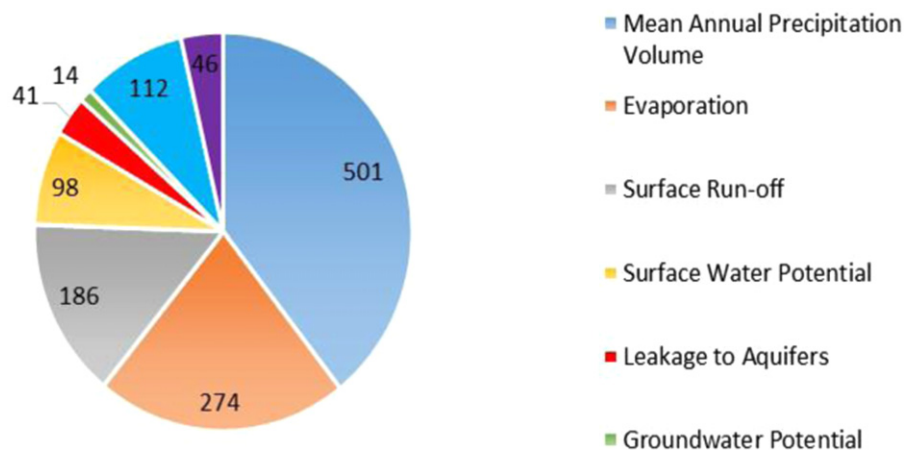


Fig. 2 Annual water budget in Turkey. Reproduced from DSI, 2009. State hydraulic works. Turkey Water Report. Ankara, Turkey.

Water Budget and Consumption

There are 25 hydrological basins in Turkey. The rivers in these basins often have irregular regimes. The basins have a total surface water run-off of 193 billion $\text{m}^3 \text{ year}^{-1}$ 31% of the potential is constituted by the Euphrates (Fırat) and the Tigris (Dicle) Rivers both of which have their sources in the eastern part of the country. Fig. 2 shows, annual water budget, Tables 2 and 3 show domestic and industrial water use in Turkey respectively (DSI, 2009).

Energy Situation in Turkey

A demand prediction model, called “Model for Assessment of Energy Demand” (MAED) was used to predict Turkey’s long term electric energy demand. This model, prepared by International Atom Energy Agency (IAEA), is a simulation model which evaluate mid and long term energy demands. MAED evaluates future energy needs based on medium to long term scenarios of socio-economic, technological and demographic development in a country or region.

The electric energy demand varies according to various parameters. The main parameters to affect the energy demand are: Gross National Product (GNP); population and demographic variations; development in housing, industry, agriculture and transportation sectors; income per capita; climatic conditions; employment, technological development, etc. Three kinds of planning scenario were applied in the model and MAED Model was executed for three scenarios and Turkey’s annual electric energy demand values were predicted from 2004 to 2020. According to the results of the study, Turkey’s annual electric energy demand in 2020 is predicted between 407 and 571 TWh (Paish, 2002; Kaygusuz, 2009).

For any analysis of the future demand for energy in Turkey to be accurate, it has to be grounded in the understanding that rapid and continued economic growth are and will remain the single most important national aspirations. According to 2005 figures,

Table 2 Domestic water use in Turkey

Year		1990	1999	2002	2008	2023*
Total water use	Million m ³	30,600	38,900	39,300	46,000	112,000
	%	27	35	36	41	100
Domestic water use	Million m ³	5,141	5,700	5,800	7,000	18,000
	%	17	10	15	15	16

*projected.

Note: DSI, 2009. State hydraulic works. Turkey Water Report. Ankara, Turkey.

Table 3 Industrial water use in Turkey

Year		1990	1999	2002	2008	2023*
Total water use	Million m ³	30,600	38,900	39,300	46,000	112,000
	%	27	35	36	41	100
Industrial water use	Million m ³	3,443	4,000	4,200	5,000	22,000
	%	11	11	11	11	20

*projected.

Note: DSI, 2009. State hydraulic works. Turkey Water Report. Ankara, Turkey.

Table 4 Turkey's population, economy, and energy

Year	Population (000s)	GNP (per capita)	Total GNP	Total energy demand (Mtoe)	Energy/Capita (KEP)	Energy intensity
1973	38,072	1,994	75,915,568	24.6	646	81
1990	56,098	2,674	150,006,052	53.7	957	50
1995	62,171	2,861	177,871,231	64.6	1,039	44
2000	67,618	3,303	223,342,254	82.6	1,218	40
2010	78,459	5,366	421,010,994	153.9	1,962	35
2020	87,759	9,261	812,736,099	282.2	3,216	33

Mtoe, Million ton oil equivalent; KEP, Kilogram of oil equivalent.

TUBITAK, 2003. Turkish scientific and technical research council. In: Proceedings of the Vision 2023 Technology Project: Energy and Natural Resources Panel, Ankara, Turkey.

Turkey has a population of 72.6 million. This translates to a per capita GNP of \$4900 and per capita energy consumption of 1.2 million ton oil equivalent (Mtoe), placing Turkey last in both categories among OECD countries (Yuksel, 2010). The projection of Turkey's population, economy, and energy is given in the Table 4 (TUBITAK, 2003). It is worth emphasizing that, even if both population and economic output were to grow more slowly than projected, it is almost certain that energy demand will increase.

Two factors critical to sustainable energy development in Turkey, however, are harder to predict. The first is the energy intensity of the economy. While the reported and predicted decreases seem impressive, it is by no means clear from this table whether this is the best that can be achieved in Turkey. If even sharper reductions are possible, increased economic growth could be delinked from energy consumption. The second is the type of primary and secondary energy sources that are required to fulfill future energy needs.

In other words, the decision on the mix of energy production technologies and primary sources needs to be considered carefully, as certain combinations of technologies and primary sources are likely to result in more sustainable outcomes. It is important, therefore, to understand the determinants of energy intensity and energy supply (Yuksel, 2010).

In Turkey, energy intensity has been relatively steady for the last two decades. Total final consumption (TFC) was 64 Mtoe in 2003, up by 54% from the 1990 level. In 2003, oil accounted for 41% of TFC, electricity 15%, coal 21%, combustible renewables and wastes 9%, natural gas 12%, geothermal 1.2% and solar and wind 0.5%. The share of oil and the combustible renewables and waste (largely non-commercial energies) has declined since 1990 whereas the use of gas, electricity and to a smaller extent coal has increased (IEA, 2005).

The structure of industry in Turkey is energy-intensive. The iron and steel sector is the biggest energy consumer among the industrial sectors (3.3 Mtoe in 2003), textile and leather industries (1.5 Mtoe) and chemicals and petrochemicals (2.2 Mtoe excluding feedstock); the cement industry is also among the largest industrial energy consumers. Industrial energy consumption (including non-energy use) more than doubled between 1990 and 2003 reaching 29 Mtoe. Industrial production grew over the same period by 49.5%. The government estimates that industrial energy consumption will increase by 53% from 2003 to 2010. The sector consumes large amounts of coal (39.5% of sectoral demand) and oil (29.6%) followed by electricity (15.4%), gas (15.1%) and other fuels (0.4%) (IEA, 2005). Energy consumption in the transport sector grew by 29% between 1990 and 2003, reaching 12.4 Mtoe. For the period from 2003 to 2010, the government expects a 61% increase in energy use in this sector. There

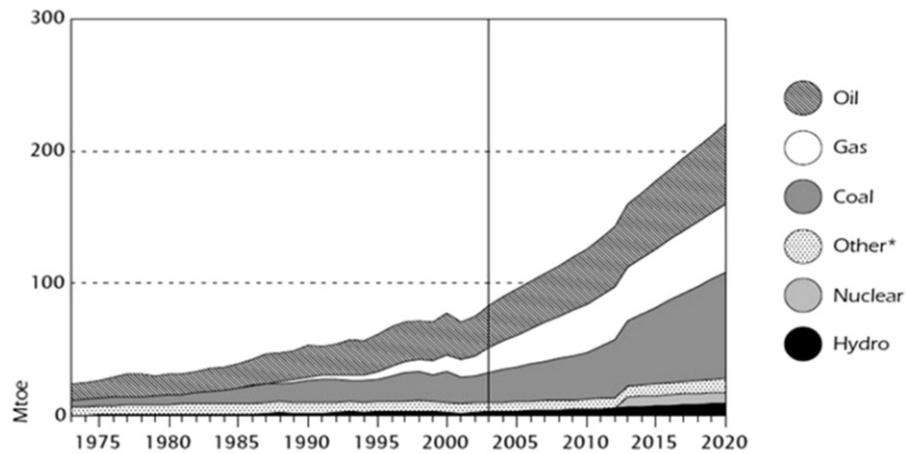


Fig. 3 Between 1973 and 2020, total primary energy supply in Turkey. Reproduced from IEA, 2005. International energy agency. In: Proceedings of the Energy Policies of IEA Countries: Turkey 2005 Review, Paris, France: IEA. *Includes geothermal, solar, wind, combustible renewables and waste.

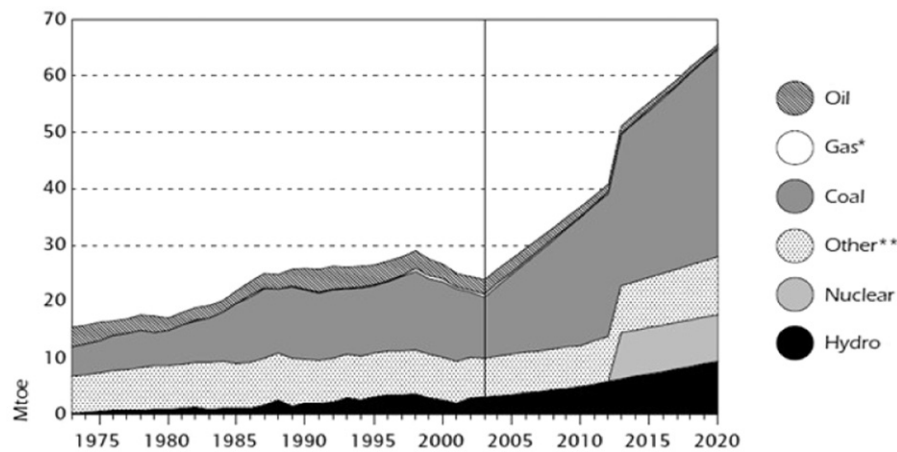


Fig. 4 Between 1973 and 2020, energy production by sources in Turkey. Reproduced from IEA, 2005. International energy agency. In: Proceedings of the Energy Policies of IEA Countries: Turkey 2005 Review, Paris, France: IEA. *Negligible, **Includes geothermal, solar, wind, combustible renewables and waste.

are about 67 cars per 1000 inhabitants in Turkey but regional variations are large; whereas, for example, in the Marmara Region the car density is 90 per 1000 people, in Eastern and South-Eastern Anatolia the density is only 20 per 1000 people. Road has been the dominant means of transport for decades; during 1996–2000 about 96% of passenger transport occurred on roads. The share of road in freight transport is about 90% and rail 5%. Freight transport volumes have been increasing by almost 8% per year. Detailed statistics and trends for the number of vehicles, mileage and the share of different modes of transport are not available because statistics in the transport sector are not carried out regularly. The last statistics on the transport sector were issued in 1998 but the quality was so poor that they were not published (IEA, 2005).

Along with the economic growth and population increase, significant increases were observed both in primary energy and electricity consumption during the 8th Plan period (DPT, 2010; Yuksel, 2009). Consumption of primary energy reached 94.3 Mtoe as of the end of 2005 with an annual average increase of 2.8% while electricity consumption reached 165.3 billion kWh with an annual average increase of 4.6% during this period. These increases are more evident in the period following 2003, since the impact of the 2001 economic crisis was alleviated, and the economy stabilized. Between 1973–2020, Figs. 3, 4 and 5 show total primary energy supply, energy production, final energy consumption in Turkey respectively (IEA, 2005).

As a Renewable Energy Hydropower

Hydropower is the largest renewable resource used for electricity. It plays an essential role in many regions of the world with more than 150 countries generating hydroelectric power. About 10 countries obtain essentially all their commercial electricity

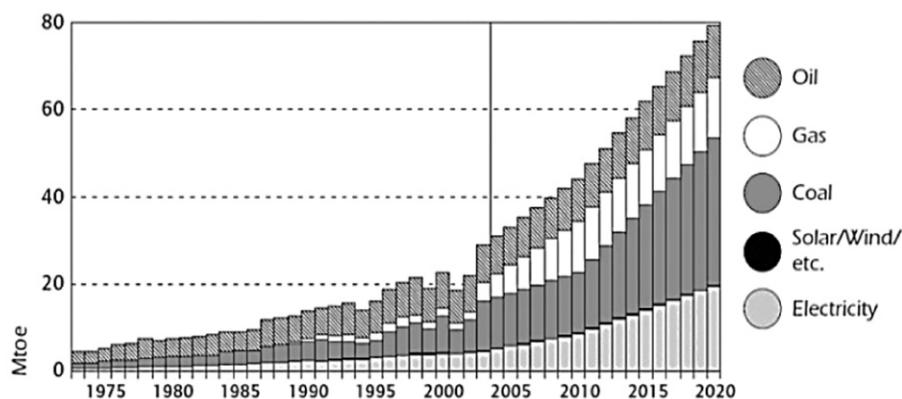


Fig. 5 Between 1973 and 2020 total final energy consumption in Turkey. Reproduced from IEA, 2005. International energy agency. In: Proceedings of the Energy Policies of IEA Countries: Turkey 2005 Review, Paris, France: IEA.

from hydro, including Norway, several African nations, Bhutan and Paraguay. There is about 700 GW of hydro capacity in operation worldwide, generating 2600 TWh year⁻¹ (about 19% of the world's electricity production). About half of this capacity and generation is in Europe and North America with Europe the largest at 32% of total hydro use and North America at 23% of the total. However, this proportion is declining as Asia and Latin America commission large amounts of new hydro capacity (Herzog *et al.*, 2012).

In the last decades, hydropower continues to be the most efficient way to generate electricity. Modern hydro turbines can convert as much as 90% of the available energy into electricity. The best fossil fuel plants are only about 50% efficient. In the U.S., hydropower is produced for an average of 0.7 cents kWh⁻¹. This is about one-third the cost of using fossil fuel or nuclear and one-sixth the cost of using natural gas. Hydro resources are also widely distributed compared with fossil and nuclear fuels and can help provide energy independence for countries without fossil fuel resources.

There is also significant, widespread activity in developing small, mini and micro hydro plants. At least forty countries, particularly in Asia and Europe, have plants under construction and even more have plants planned. China, Brazil, Canada, Turkey, Italy, Japan and Spain all have plans for more than 100 MW of new capacity (Herzog *et al.*, 2012).

It is well known that the hydropower industry is closely linked to both water management and renewable energy production, and so has a unique role to play in contributing to sustainable development in a world where billions of people lack access to safe drinking water and adequate energy supplies. On the other hand, approximately 1.6 billion people have no access to electricity and about 1.1 billion are without an adequate water supply.

However, resources for hydropower development are widely spread around the world. Potential exists in about 150 countries, and about 70% of the economically feasible potential remains to be developed – Mostly in developing countries where the needs are most urgent (EIA, 2006; AR American Rivers, 2004). Fig. 6 shows the estimated hydropower development by region in the world (IHA, 2003).

Water Management for Renewable and Sustainable Energy in Turkey

The role of energy utilities to deliver energy savings should not be underestimated in Turkey-planned measures to allow energy efficiency measures to be bid into energy pools on an equal basis to energy supply options should be implemented, or other relevant policy measures should be considered.

Although Turkey has an adequate amount of water in general, it is not always in the right place at the right time to meet present and anticipated needs. As regards hydrology, Turkey is divided into 26 drainage basins. The rivers in general have irregular regimes, and natural flows cannot be taken directly as usable resources. The average annual precipitation, evaporation and surface runoff geographically vary greatly (DPT, 2010; Yuksel, 2015, 2008a; DIE, 2004; DSI, 2004; MENR, 2005).

Turkey has 665,000 ha of inland waters, excluding rivers and small streams. There are 200 natural lakes, with a total area of 500,000 ha, and 775 dam lakes and ponds with a total surface area of 165,000 ha (DPT, 2010; Yuksel, 2015; DIE, 2004). With the projects developed primarily by DSI and other institutions engaged in water resources development, water consumption in Turkey reached 39.3 billion m³ by 2000, corresponding to only 36% of the economically exploitable water resources.

During water consumption estimates on a sectoral basis, it is accepted that all of the economically irrigable land will be irrigated with irrigation schemes constructed by the year 2030 and water consumption for irrigation will be 71.5 billion m³. Hence, while its share in the total consumption was 75% in 1999, the share of irrigation water in the total water consumption will be decreased to 65% by the year 2030, through the utilization of modern irrigation techniques (DPT, 2010; Yuksel, 2015; MENR, 2005; Ozturk *et al.*, 2009).

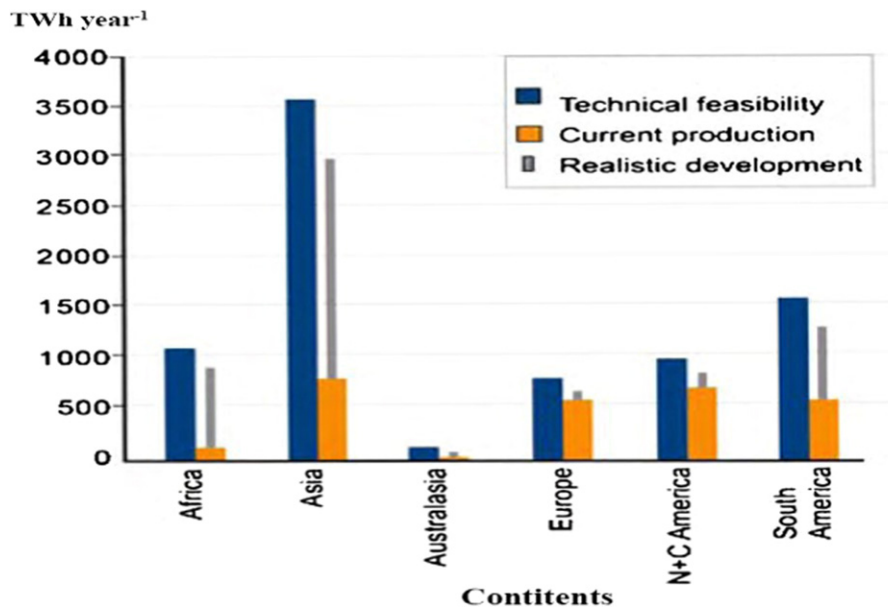


Fig. 6 Estimated hydropower development by region in the world. Reproduced from IHA, 2003. International Hydropower Association. In: Proceedings of the Role of Hydropower in Sustainable Development, pp. 1–140. IHA White Paper.

According to Chambers of Turkish Electrical Engineers, Turkey has 259 billion kWh energy potential, but only 35% of this potential can be used. Nowadays, Turkey's electricity generation is approximately 176 billion kWh per year and will be 400–500 billion kWh per year by year 2020. Turkey does not have enough primary energy sources, but has a tremendous hydropower potential.

Nowadays, hydropower is recognized as the most important kind of renewable and sustainable energy sources. The position of hydro power plants (HPP) becomes more and more important in today's global renewable technologies. The small-scale renewable and distributed generation may be the most cost-effective way to bring electricity to remote villages that are not near transmission lines (DPT, 2010; Yuksel, 2015; DSI, 2010, 2009; Alboyaci and Dursun, 2008). In terms of hydropower potential, with 440 TWh year⁻¹, Turkey is the second richest country after Norway in Europe. This potential can be used technically 215 TWh year⁻¹ and economical potential 128 TWh year⁻¹ in accordance with the predictions of General Directorate State Hydraulic Works (DSI). Table 5 shows the status of economically feasible hydropower potential in Turkey (DSI, 2009).

GAP Factor on Hydro Energy for Renewable Energy in Turkey

Water and hydropower potential in Turkey are distributed into 26 basins and the total flow rate of water sources for energy production is 186 km³ years⁻¹. The biggest five basins of Turkey are Euphrates, Tigris, Eastern Black Sea, Coruh and Seyhan as shown in the Fig. 7 (DSI, 2006).

On the other hand, 27 billion kWh of electricity will be generated annually over an established capacity of 7460 MW. The area to be irrigated accounts for 19% of all the economically irrigable area in Turkey (8.5 million hectares), and the annual electricity generated will account for 22% of the country's economically viable hydroelectric power potential, 118 billion kW by 2006. At the present the Ataturk and Karakaya dams, the most important investments of the GAP, had generated about 175 billion kWh energy. Table 6 shows the energy production in GAP (Southeastern Anatolia Project GAP, 2004).

Turkey has made some progress in implementing energy efficiency policies since the 2009 Evaluation. In the industrial sector, for example, between 2009 and 2010, Turkey trained and certified 1525 energy managers. The total number of certified energy managers in Turkey reached more than 4200 in mid-2011. It also hosted the 9th international energy manager course in June 2010. Measures and voluntary agreements, begun in 2009, to encourage energy efficiency in industrial establishments were continuing in 2010 (DPT, 2010; DSI, 2010; Kavak-Akpinar and Akpinar, 2004).

Turkey is attempting to improve methods to ensure both voluntary and mandatory energy efficiency policies are adequately monitored, enforced and evaluated. For example, a new Division of Monitoring and Evaluation was established in the General Directorate of Electrical Power Resources Survey Administration (EİE) at the end of 2010. A new project is planned for 2011 to establish a comprehensive monitoring and evaluation system and infrastructure (DPT, 2010; DSI, 2010; Kavak-Akpinar and Akpinar, 2004).

On the other hand, the second prong of the criticisms launched by the Greens is that Turkey has abundant potential for alternative energy sources. Recently, a spate of studies by Turkish scientists has demonstrated that significant unexplored renewable energy potential exists in wind, biomass, geothermal, and solar (Kavak-Akpinar and Akpinar, 2004; Kaygusuz and Turker, 2002;

Table 5 The status of economically feasible hydropower potential in Turkey

Project	Number of project	Total installed capacity (MW)	Annual average energy (TWh year ⁻¹)	Ratio (%)
In operation	172	13,700	48	35
Under construction	148	8600	20	14
In program	1,418	22,700	72	51
Total	1,738	45,000	140	100

Note: DSI, 2009. State hydraulic works. Turkey Water Report. Ankara, Turkey.

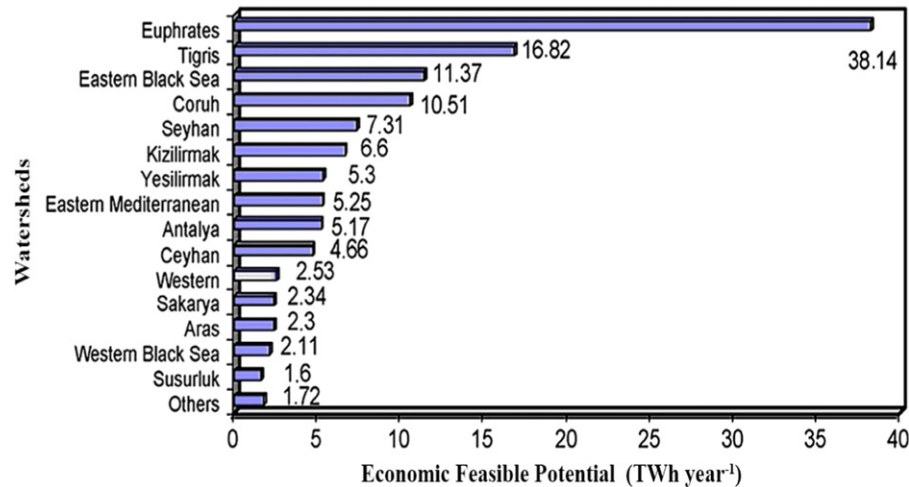

Fig. 7 Distribution of Turkey's hydropower potential on basin level. DSI, 2006. State hydraulic works. In: Proceedings of the Statistics on Hydropower, Ankara, Turkey.

Table 6 Energy production in GAP

Name of dam	Yearly energy production (kWh)
Karakaya dam and HPP	106.8 billion
Ataturk dam and HPP	74.5 billion
Kralkızı dam and HPP	0.3 billion
Karkamış dam and HPP	0.6 billion
Dicle dam and HPP	0.1 billion
Birecik dam and HPP	1.6 billion
Total	183.9 billion

Note: Southeastern Anatolia Project (GAP), 2004. Energy and water in the GAP region. Available from: <http://www.gap.gov.tr>.

Kose, 2005; Oğulata and Oğulata, 2002; Kaygusuz, 2002). These alternative energy sources support the general tendency of the Greens to favor small-scale and alternative technologies.

These studies make it clear that, especially when combined with efficiency gains, renewable energy sources stand to meet a significant proportion of the future energy need of Turkey (Yuksel *et al.*, 2005; TUBITAK, 2003; Yuksel, 2006; Kaygusuz and Kaygusuz, 2004; Evrendilek and Ertekin, 2003; Balat, 2004; Hepbasli and Ozgener, 2004; Yuksek and Ucuncu, 1999). **Table 7** shows the energy potential of the Southeastern Anatolia Project (GAP), in Turkey (DSI, 2009).

In Turkey, the hydropower industry is closely linked to both water management and renewable energy production and thus has an important role, in cooperation with the international community, and in striving for sustainable development in a world where billions of people still lack access to safe drinking water and adequate energy supplies.

The Role of Small Hydropower on Energy Demand

At the beginning of 2000s, the Turkish government began privatizing some of its electricity generating and distribution networks, and allowing for more private construction and ownership in the sector. The annual average precipitation in Turkey is nearly 643 mm, corresponding to a volume of 500 km³. The average runoff coefficient is 0.37, and the annual runoff is 186 km³ (2400 m³ ha⁻¹).

Table 7 The energy potential of the GAP

	<i>Installed capacity (MW year⁻¹)</i>	<i>Generation (GW year⁻¹)</i>	<i>Capacity project value (Million \$)</i>
In operation	4,214	16.296	4,779
Euphrates basin	4,214	16.296	4,779
Tigris basin	0	0	0
In installation	632	1.703	1,412
Euphrates basin	230	7.76	798
Tigris basin	402	9.27	614
Others	2,664	9.385	4,459
Euphrates basin	874	3.068	1,656
Tigris basin	1,170	6.317	2,803
Total	7,490	27.384	10,650

Note: DSI, 2009. State hydraulic works. Turkey Water Report. Ankara, Turkey.

Subtracting from this figure the estimated water rights of neighboring countries, minimum stream flow requirements for pollution control, aquatic life and navigation, and topographic and geologic constraints; bringing the total consumable potential to 107 km³ (Bakir, 2005). Taking into consideration the electric energy demand predictions and the hydropower potential according to the new criteria, it can be easily predicted that, Turkey's hydropower potential can meet nearly 33%–46% of its electric energy demand in 2020, depending on the energy demand scenario.

Moreover, in these calculations, many of small hydro power (SHP) plants are not taken into consideration. By evaluating these resources, of which potential may be in the order of some tens of TWh year⁻¹, it is obvious that, Turkey will provide important part of its electric energy demand from its own hydro power resources. The findings of two case projects strongly support this opinion. SHP is especially very important in the Eastern Black Sea Region, which has abundant SHP capacity due to its meteorological and topographic properties, and this potential can be easily and economically developed. By doing this, the economical status of the rural people, most of whom are unemployed and poor, will be significantly improved.

According to findings of a study carried out (Bakir, 2005), in which a new criterion was developed related to key concept of “the economical feasibility”, by taking into consideration some undervalued benefits of hydro plants and some overvalued benefits of thermal power plants; economically feasible hydropower potential goes up 188 TWh year⁻¹, with an increase ratio of 47% compared to DSI value.

Prices and Competition on Energy Sector in Turkey

Retail electricity prices are relatively high in Turkey, at approximately USD 0.163 kWh⁻¹ for households and USD 0.1 kWh⁻¹ for industrial consumers. Turkey currently has implicit cross-subsidies between regions and for certain subcategories of consumers. The government is considering a transition period, with a tariff equalization method, to reduce cross-subsidies and progressively introduce cost-effective tariffs in the medium term. Differences in energy prices are mainly due to tax differentiation by fuel types: The special consumption tax on natural gas is much lower than on fuel oils. However, no special consumption tax is applied to coal (DSI, 2006).

The development of nominal electricity prices for industrial and residential customers over the last two decades in US cents per kWh, respectively. Note that following rapid increases between 1985 and 1993, prices have fallen again. This is partly because of insufficient inflation adjustment and falling real prices. Note also that prices for industrial consumers are almost exactly as high as for residential consumers.

Turkish Electricity Generation-Transmission Corporation (TEAS) publishes its end-1999 direct sales prices per kWh for industrial customers as US cents 6.87 for high-voltage customers and US cents 7.15 for intermediate and low-voltage customers, whereas its sales prices to distributors are in the range of US cents 4 per kWh and sales prices to Turkish Electricity Distribution Corporation (TEDAS) are around US cents 3.5 per kWh (IEA, 2001).

However, the gap between cost and prices is likely to be much larger than suggested by these data. Whereas TEAS states that its average net generating costs are as indicated in Table 6, the cost of purchasing additional electricity from build-own-transfer (BOT), build-own-operate (BOO) and Transfer of Operating Right (TOOR) generators (see below) is much higher (except for diesel peaking plants), and can reach US cents 11–12 per kWh. Since these plants are urgently needed because of the lack of supply capacity, and are therefore dispatched frequently, TEAS's full costs are likely to be significantly higher than the average cost listed in Table 8 (IEA, 2001).

As a consequence, TEAS's income statements have long shown significant losses; in 1999, losses amounted to more than 61 billion Turkish lira. These losses are eventually borne by TEAS's shareholder, the Republic of Turkey, thus contributing to the government budget deficit and, eventually, to inflation. The developments described so far were superseded by the adoption of the new Electricity Market act on 20 February 2001 by the Turkish Grand National Assembly. This Act fundamentally changes the structure of the Turkish power industry and ends the use of BOT and TOOR schemes in Turkey. The Electricity Market Act of 2001 is to come into force in early 2003, following a two-year transition period. It aims at creating a competitive, transparent and financially strong electricity market that encourages private investment without government guarantees, provides sufficient,

Table 8 Net power generating cost by energy input, TEAS and DSI

Fuel input	Cost (US cents per kWh)
Hard coal	4.37
Lignite	2.99
Fuel oil	3.14
Diesel	16.24
Geothermal	2.46
Natural gas	3.86
Average thermal (TEAS)	3.56
Dam	0.14
Lake	1.11
Run-of-river	0.68
Average hydro (DSI)	0.16
Average TEAS + DSI	1.96

Note: IEA, 2001. International Energy Agency. In: Proceedings of the Energy Policies of IEA Countries Review, Paris, France: IEA.

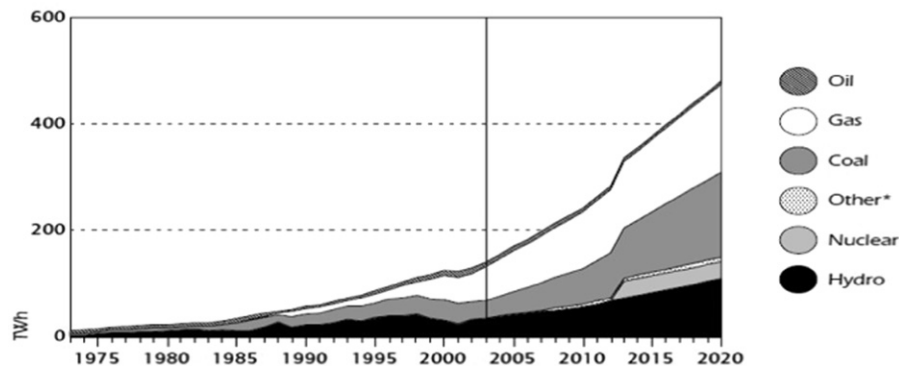


Fig. 8 Between 1973 and 2020, Electricity of Generation by sectors in Turkey. Reproduced from IEA, 2005. International Energy Agency. In: Proceedings of the Energy Policies of IEA Countries: Turkey 2005 Review, Paris, France: IEA. *Includes geothermal, solar, wind, combustible renewables and waste.

reliable and low-cost electricity to consumers and is compatible with the European Union Electricity Directive. Between 1973 and 2020, **Figs. 8** and **9** show electricity of generation and final conception by sectors in Turkey respectively (IEA, 2005).

A competitive electricity market is to be established, based on bilateral contracts between market participants. Within two years of entry into force of the act, i.e., in March 2003, customers consuming more than 9 GWh will be eligible for competition. A short-term market will be created to allow system balancing. If market conditions permit, distribution and retailing activities will be separated. TEAS will be divided into three different companies: A generation company, an independent transmission operator, and a wholesale trading company. The establishment of the three companies had already been provided for by Decree No. 310 of 3 March 2000 and will now be put into effect. The electricity generation company is to retain all power plants not yet transferred from TEAS via the TOOR procedure. It will also operate the nuclear power plants that the government still expects to come on stream by 2008, as well as "strategic" power plants (IEA, 2001).

The transmission company will be responsible for transmission and nondiscriminatory dispatch of all power plants. The wholesale trading company is to be responsible for buying and selling electricity at wholesale level. It will succeed TEAS in the power purchase agreements concluded with the BOT and BOO facilities under the old system, as well as with the one TOOR plant. It will also take TEAS's place in the power supply contract concluded between TEDAS and the TOOR distributors. Other market participants will include private-sector generators, industrial auto producers, private wholesale and retail traders, and eligible consumers. A new regulatory framework will be put in place to allow the market to function properly. An independent regulatory authority is to be established, governed by its own board, to apply non-discriminatory, transparent, stable and consistent regulation without day-to-day interference by the government. The regulatory authority will have the following functions (IEA, 2001):

- It will determine eligible consumers within the framework set by the act.
- It will apply and oversee a new licensing framework for market participants.
- It will enforce regulated third party access to transmission and distribution grids and develop and apply a new transmission and distribution code.
- It will regulate prices for any remaining captive consumers and oversee the transition towards the competitive market.

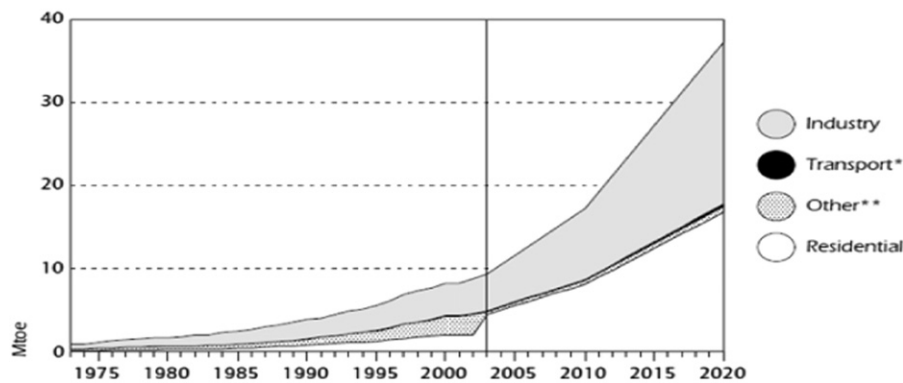


Fig. 9 Between 1973–2020, Final Consumption of Electricity by sectors in Turkey. Reproduced from IEA, 2005. International Energy Agency. In: Proceedings of the Energy Policies of IEA Countries: Turkey 2005 Review, Paris, France: IEA. *Negligible, **Includes commercial, public service and agricultural sectors.

Conclusion

From the viewpoint of energy sources such as petroleum and natural gas reserves, Turkey is not a rich country, but has an abundant hydropower potential to be used for generation of electricity.

Turkey must base its energy strategy on developing the whole hydroelectric potential as soon as possible. Turkey's main indigenous energy resources are hydro and almost all oil natural gas and high quality coal are imported. Therefore, in order to avoid foreign dependency both in sources and funds, Turkey must discover new and renewable energy resources.

Water and energy are the two important engines of sustainable development. In the energy sector, the basic policy of Turkey is the provision of cheap electrical energy on time and in sufficient quality and quantity. Investments in hydropower deserve special support as they are clean and have a long economic life-span.

It is important to point out the restructuring policies that are directing the development of new and renewable energy, and giving special emphasis to socio-economical bodies, laws and legal regulations. In this respect, particular attention and priority should be given to the development of the hydroelectric in Turkey, since it is the most important natural renewable resource and only 35% of the technically and economically utilizable hydro potential has been developed so far.

On the other hand, hydropower emits very few greenhouse gases in comparison with other large-scale energy options and thus helps slowing down global warming. In addition, by storing water in rainy seasons and releasing it in dry ones, dams and reservoirs help control water during floods and droughts. These essential functions, protecting human lives and other assets, will be increasingly important in the context of climate change is expected to give rise to even greater variability in the frequency and intensity of rainfall.

See also: 100% Renewable Energy by Renewable Materials. Energy Efficiency Analysis in Building Walls in Tropical Climate Using Thermal Insulation System. Sustainable Materials for Energy Conversion

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A Numerical Approach to Simulating Oxidation in Thermal Barrier Coatings

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Introduction

Today's thermal barrier coatings (TBCs) are mainly manufactured with two different techniques. The first coatings brought into service were plasma sprayed coatings which are still in service. These coatings were first tested on commercial aircraft and owe their acceptance to success in this field. However, this success brought up a demand for research to achieve pioneer coatings that can serve in higher temperatures and more severe conditions. In cases where thermal cycle may happen, use of zirconia-based coating with high amount of monoclinic phase was proven to be inappropriate for structures (due to high volumetric change when transforming to martensitic phase). Porous atmospheric-pressure plasma-sprayed (APPS) zirconia-yttria ($\text{ZrO}_2\text{-Y}_2\text{O}_3$) on a plasma sprayed NiCrAlY bond-coat was introduced by NASA Lewis Research Center as an alternative way to overcome this handicap. This new technology is considered to be the onset of the thermal barrier coating research era (Miller, 1995; Toriz *et al.*, 1988).

Using yttria as a stabilizer for zirconia, using an oxidation resistant material (NiCrAlY) as bond-coat for base metallic material and lastly using the bond-coat system to eliminate the layer between ceramic and the base metal have been the most critical developments for the success of new coatings. Using metallic bond-coat as a replacement for the intermediate layer reduces stresses induced by material mismatch in thermal loading. However, mitigation of stresses due to material mismatch was not significant when exposed to higher temperatures since oxidation of the metallic bond-coat would be highly accelerated (DeMasi-Marcin *et al.*, 1990).

A new type of coating which was deposited using electron beam was developed in the late 1980s and became commercial in 1990s. Electron beam-physical vapor deposited (EB-PVD) zirconia-yttria coating was first used and tested in the burner rig lives and performance was reported to be much better than the performance of plasma sprayed entirely zirconia-yttria coatings (Sumner, 1980) and modifications in topcoat material made it possible to use these systems at higher temperatures (Bratton *et al.*, 1982; Stecura, 1979). Coatings deposited by electron beam technique owe their long life and durability to flexible columnar and porous structure, which makes it more strain tolerant. There are two types of porosities reported for these coatings, intra columnar and inter columnar vacancies. These porosities may disappear by sintering mechanism during service at high temperatures, but it is efficient enough to extend coating life by a considerable time.

Oxidation of the bond coat is often considered as one of the prime mechanisms that can lead to failure of TBC systems. Evans *et al.* (2001, 2008) claimed that due to anisotropic swelling of thermally grown oxide layer and uneven development of TGO layer residual stresses can rise and lead to nucleation of micro-cracks and thus become the dominant failure mechanism which can affect long-term durability of TBC systems. However, the mechanism through which oxidation occurs and different species travel through materials and meet to form TGO is pretty complicated and significant amount of research have been conducted to clarify this problem. For bond-coat alloys containing yttrium, diffusion of aluminum is affected by this reactive component, which decelerates diffusion of Aluminum cations, thus oxide components meet in the regions closer to substrate material (Balmain *et al.*, 1997). Consequently, presence of Yttrium leads to the formation of oxide mainly on the oxide-bond coat interface Fig. 1.

In contrast to classical models, where phase interface of a multi-phase system was investigated using discrete solutions with possessing severe computational challenges, Cahn-Hilliard (Cahn and Hilliard, 1958) and Ginzburg-Landau models treat these systems as continuous domains which brings certain ease to implementation of the model. In those approaches, free energy is defined to be a function of either species concentration or order parameter generally represented by ϕ and gradients of these parameters along with any other thermodynamic variable may also be included in the model. According to these theories, a previously predetermined interfacial energy for a restricted thickness is taken into account. It is also noted that the existence of free energy due to non-equilibrium of phases in the diffuse interface of two-phase system was not considered at the time. The treatment proposed by Cahn-Hilliard, Allen-Cahn, and Ginzburg-Landau are general equations that can be used in the fields with spatial variation of a parameter (Composition, density, etc.). Simulation of oxide formation process TBC systems has been a hot topic in the past decade and an extensive variety of models are available in the literature, and only few of them are tackling coupled multi-physics oxidation and failure problem in the same numerical framework. Ammar *et al.* (2009) have used Allen-Cahn phase field model to simulate oxidation and oxide propagation in the bulk metal. This model has the nature of flattening initial phase interface undulations. In the case of oxidation of bulk metal, initial surface undulation smoothing is observed in time. In contrast, when the coating is present on the metal, interface undulations maintain their shape during oxide growth due to material mismatches (He *et al.*, 2000). The most recent and inclusive model available is proposed and implemented by Loeffel and Anand (2011); Al-Athel *et al.* (2013), where a modified version of classical Fick's law for diffusion of oxygen through ceramic is used and thus the model generates a sharp interface of diffusing oxide in the bond coat.

In this work, a comprehensive model based on Allen-Cahn theory, which can retain undulations during growth of oxide through modifying a gradient term in the diffusion and phase field equation is proposed. The model is implemented in finite strain framework using ABAQUS user element subroutine (UEL) for finite element analysis (Fig. 1).

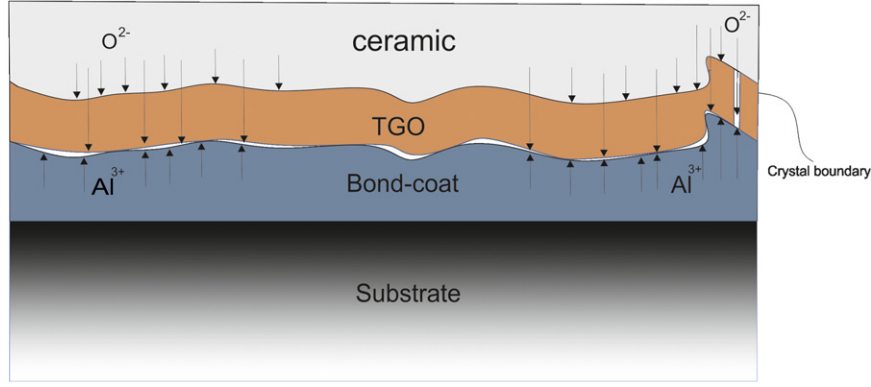


Fig. 1 Schematic diagram for diffusion of paths of components for formation of Alumina.

Balance Laws and Constitutive Equations

For an arbitrary material point with volume V and surface ∂v the coupled balance equations are presented at specific time t . Neglecting inertia effects, balance of momentum and forces, in current configuration for a spatial region can be expressed as,

$$\int_{\partial v} \mathbf{T} \mathbf{n} dS + \int_V \mathbf{b} dV = 0$$

Where $\mathbf{b}$, $\mathbf{T}$ and $\mathbf{n}$ represent body force, Cauchy stress and surface normal respectively. Thus, using divergence theorem for local balance, it can be written in the form below,

$$\text{Div} \mathbf{T} + \mathbf{b} = 0$$

Kröner's decomposition is initially used for the deformation gradient.

$$\mathbf{F} = \mathbf{F}^e \mathbf{F}^p$$

Where $\mathbf{F}^e$ is the elastic distortion which represents stretch and rotation and $\mathbf{F}^p$ is plastic distortion which is invariant with rigid body motions. From right polar decomposition $\mathbf{F}^e$ can be decomposed into right stretch $\mathbf{U}^e$ and rotation tensor $\mathbf{R}^e$

$$\mathbf{F}^e = \mathbf{R}^e \mathbf{U}^e$$

In this model the main strain measure is chosen as Hencky's strain due to good agreement with experiments for moderate deformation.

$$\mathbf{E}^e = \ln(\mathbf{U}^e)$$

Finally, Piola stress is expressed as

$$\mathbf{T}^e = 2G\mathbf{E}^e + K\text{tr}(\mathbf{E}^e)\mathbf{1}$$

Where G and K are shear modulus and bulk modulus respectively. Mandel stress which is the driving stress for plastic flow and the deviatoric part $\mathbf{M}_0^e$ are as below,

$$\mathbf{M}^e = \mathbf{F}^{eT} \mathbf{F}^e \mathbf{T}^e$$

$$\mathbf{M}_0^e = \mathbf{M}^e - \frac{1}{3} \text{tr}(\mathbf{M}^e) \mathbf{1}$$

Then using volume ratio which is expressed as

$$J = \det \mathbf{F}$$

Cauchy stress can be recalculated as follows

$$\mathbf{T} = J^{-1} \mathbf{R}^e \mathbf{M}^e \mathbf{R}^{e-T}$$

Equivalent tensile stress and plastic strain rate are,

$$\bar{\sigma} = \sqrt{\frac{3}{2}} |\mathbf{M}_0^e|, \quad \dot{\bar{\epsilon}}^p = f(\bar{\sigma}, S)$$

Parameter S is known as material resistance with initial value S_0 is defined to be a saturating type of function. Function g is defined to satisfy viscoplastic behavior for bond-coat and oxide material with $\dot{\bar{\epsilon}}_0$ and m defined as material parameters.

$$\dot{S} = g(\bar{\sigma}, S) = S \left(\frac{\dot{\bar{\epsilon}}^p}{\dot{\bar{\epsilon}}_0} \right)^m$$

For ceramic layer, it is assumed to have no plastic deformation due to brittleness of the material.

Phase change is tracked using a phase field parameter $0 < \phi < 1$, where 0 and 1 values for ϕ indicate un-oxidized metal and totally oxidized material respectively. Inelastic part of velocity gradient can be found as,

$$L^i = \dot{F}^i F^{i-1}$$

An inelastic stretch tensor can be expressed as,

$$D^i = D^s + (1 - \phi) D_{bc}^p + \phi D_{ox}^p$$

D_{bc}^p and D_{ox}^p represent stretching due to viscoplastic flow taking place in bond-coat and oxide respectively. As stated before $0 < \phi < 1$ is a function characterizing the relative extent of plastic flow at the interface. Plastic behavior of multi-phase materials is not well understood yet, thus a homogenization technique was used similar to Reuss/Sachs model for multiphase regions but in finite strain formulation.

Oxide growth is anisotropic process, for the reason that oxide tends to grow faster on metal interface approximately a hundred times faster than transverse direction. Consequently, D^s will be an anisotropic swelling tensor can be calculated using oxidation rate $\dot{\phi}$.

$$D^s = \dot{\phi} S$$

Swelling strain of the TGO can be defined as,

$$S = B_l m \otimes m + B_t (1 - m \otimes m)$$

S (Swelling concerning the principal direction of stress) is calculated using PBR (Pilling-Bedworth Ratio) (Chunhua and Wei, 2000) value with B_l for lateral and B_t for vertical growth direction with respect to interface normal vector m and $\otimes$ stand for dyadic of two vectors. For the numerical example demonstrated in Fig. 2, m is directly calculated from interface profile. Then, total inelastic deformation gradient is found to be

$$\dot{F}^i = D^i F^i$$

In Allen-Cahn theory it is assumed that local energy depends on, regional composition and interfacial composition of the environment as well as phase field. Cahn-Hilliard assumed that gradient of c (If the non-uniform field is chosen to be molar fraction of a definite phase) is small enough with respect to reciprocal inter-molecular distance that can be accounted to be an independent variable. The present model considers the gradient of the field variable ϕ , which leads to the definition of a free energy based on phase field and its gradient and additionally concentration of species, $\psi(c, \phi, \nabla \phi)$. Applying divergence theorem on Taylor expansion of the free energy function and neglecting species inlet from boundary surface one can write a specific form Helmholtz free energy as below,

$$\psi(c, \phi, \nabla \phi) = n \int_V \left(\psi_0(c, \phi) + \frac{1}{2} \alpha \nabla \phi \nabla \phi \right) dV$$

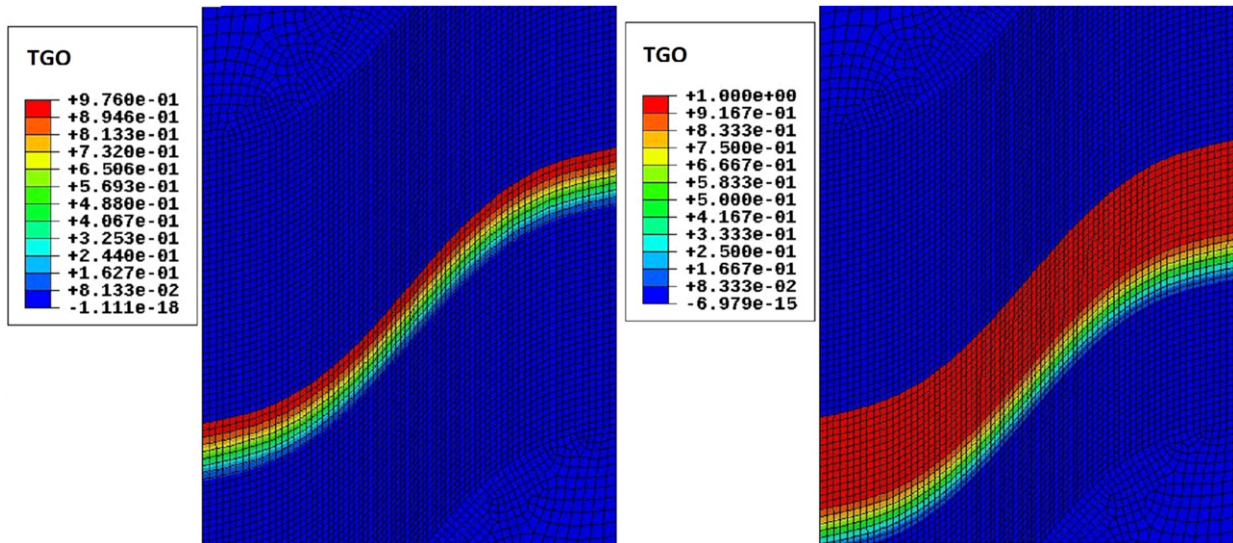


Fig. 2 TGO growth after 10 h (left) and 100 h (right).

ψ , c and n are free energy, normalized species concentration, number of molecules per unit volume respectively. Time evolution of phase field is expressed as

$$\beta \dot{\phi} = \alpha \Delta \phi - \frac{\partial \psi_0}{\partial \phi}$$

Where α and β are parameters used to control interface thickness and velocity. Chemical potential μ and species flux j are defined as below,

$$\mu = \frac{\partial \psi_0(c, \phi)}{\partial c}$$

$$j = -M(\phi) \nabla \mu$$

With M defined as mobility of the species. Then classical Fick's law for diffusion of species can be written as,

$$\dot{c} = \text{div}(M(\phi) \nabla \mu)$$

Coupling between diffusion of oxygen and deformation should be a two-way coupling in order to deaccelerate diffusion in compressed medium and vice versa. The oxide diffusion-imposed bulging is performed by adding a swelling stretch term D^s into inelastic stretch tensor D^i . Strain induced diffusion coupling is defined to be sensitive to the magnitude of $\text{tr}(\epsilon)$. Adding this term to the free energy of the system as an independent variable requires the calculation of gradient of this term. The gradient is calculated through the solution of the following trivial balance law, where a scalar variable P is defined as a new degree of freedom.

$$P = \text{tr}(\epsilon)$$

A specific form of free energy is assumed to have the following form,

$$\psi_0(c, \phi) = \phi^2(3 - 2\phi)\psi_1 + (1 - \phi^2(3 - 2\phi))\psi_2 + \chi\phi^2(1 - \phi)^2 - KP(c - c_0)$$

$$\psi_i(c) = \frac{1}{2}k_i(c - c_i)^2 \quad i = 1, 2$$

k and χ are material phase curvature and a parameter relate to free energy function respectively. Material properties are also defined to be dependent on phase field variable.

$$K(\phi) = K_{ox}\phi + K_{bc}(1 - \phi)$$

$$G(\phi) = G_{ox}\phi + G_{bc}(1 - \phi)$$

$$M(\phi) = M_{ox}\phi + M_{bc}(1 - \phi)$$

Numerical Implementation

The theory and model presented, are implemented as an implicit user element subroutine (UEL) code in ABAQUS finite element software. The element was designed as a two dimensional four-noded linear isoparametric element. Balance equations solved through the numerical process are presented below.

$$\text{Div}T + b = 0$$

$$\dot{c} = \text{div}\left(M(\phi) \nabla \left(\frac{\partial \psi_0(c, \phi)}{\partial c}\right)\right)$$

$$\beta \dot{\phi} = \text{div}(\alpha \nabla \phi) - \frac{\partial \psi_0}{\partial \phi}$$

M and α are written in tensorial form and transverse components are defined to be zero in order to prevent lateral propagation of oxide. This modification supports the experimental results claiming negligible growth in lateral direction against rapid vertical growth of TGO.

$$P = \text{tr}(\epsilon)$$

Defining,

$$a = k_1\phi^2(3 - 2\phi) + k_2(1 - \phi^2(3 - 2\phi))$$

$$b = k_1(c - c_1) - k_2(c - c_2)$$

And choosing N^A as a shape function for interpolation in node A, residual vectors for phase field and diffusion equations are expressed as,

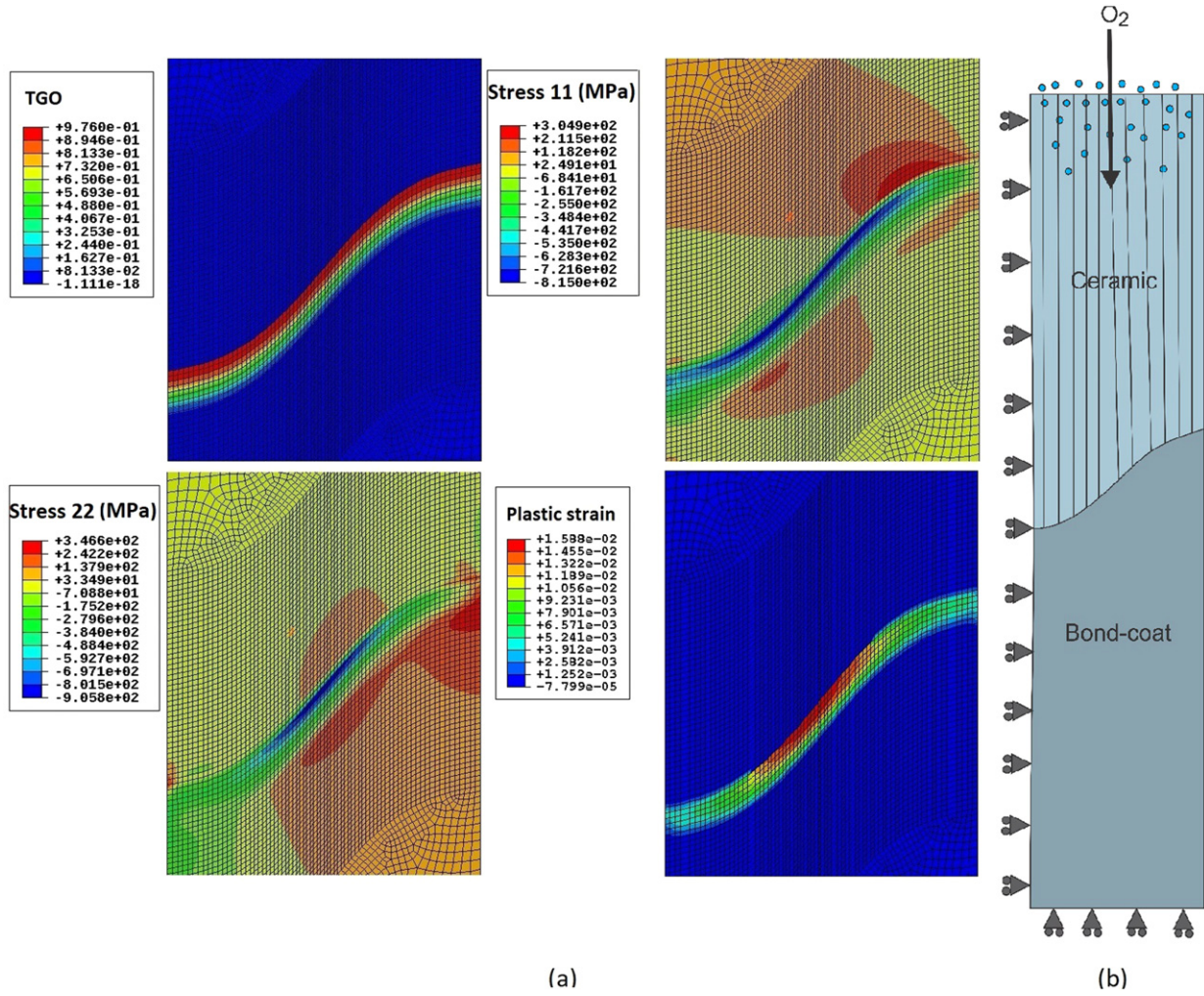


Fig. 3 (a) Results for (top-left) thermally grown oxide (top-right) stress in x direction (bottom-left) stress in y direction and (bottom-right) Plastic strain after 10 h of oxidation (b) Boundary conditions and schematic of the geometry.

$$R_c = \int_e \left(N_A \dot{c} - a \nabla N_A \cdot M(\phi) \nabla c + 6M(\phi)b(1-\phi) \nabla N_A \nabla \phi + 3KN_A P \right) dV - \int_{\partial e} N_A \mathbf{j} \cdot \mathbf{n} dS$$

$$R_\phi = \int_v \left(N_A \beta \dot{\phi} + \nabla N_A \cdot \alpha \nabla \phi + N_A (3\phi(1-\phi)C + \chi D) \right) dV + \int_{\partial e} N_A \epsilon \cdot \mathbf{n} dS$$

$$R_e = \int_e N_A (P - \text{tr}(\epsilon)) dV$$

Where ϵ is an energy conjugate for $\nabla \phi$ and scalar values C and D are defined as,

$$C = k_1(c - c_1)^2 - k_2(c - c_2)^2$$

$$D = 4\phi^3 - 6\phi^2 + 2\phi$$

Dominant terms of the global tangent tensor is also found to be in the following form.

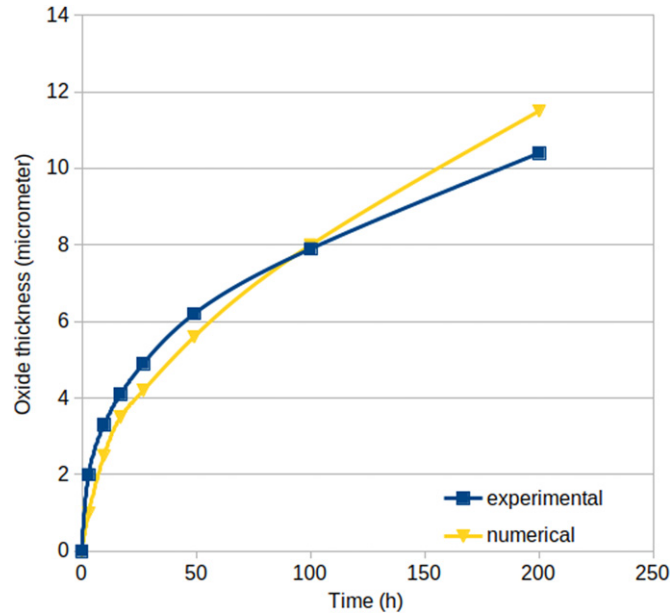
$$K_{cc}^{AB} = - \int_e \left(\frac{N_A N_B}{\Delta t} + aM(\phi) \nabla N_A \nabla N_B + N_B 6M(\phi)b(1-\phi) \frac{\partial b}{\partial c} \nabla N_A \nabla \phi \right) dV + \int_{\partial e} N_A N_B \frac{\partial \mathbf{j}}{\partial c} \cdot \mathbf{n} dS$$

$$K_{\phi\phi}^{AB} = - \int_e \left(\beta \frac{N_A N_B}{\Delta t} + \alpha \nabla N_A \nabla N_B + N_A N_B \left(3(1-2\phi)C + \chi \frac{\partial D}{\partial \phi} \right) \right) dV - \int_{\partial e} N_A N_B \frac{\partial \epsilon}{\partial \phi} dV$$

Table 1 Material and diffusion parameters used in the analysis

Top-coat (Elastic)			
C_{11}	500e9 (Pa)	C_{44}	175e9 (Pa)
C_{12}	113e9 (Pa)	C_{13}	500e9 (Pa)
C_{33}	200e9 (Pa)	M	$9e - 16 \text{ (m}^5 \text{ s mol J}^{-1}\text{)}$
Bond-coat (Viscoplastic)			
G	88.46e9 (Pa)	β	$1.0e6 \text{ (J m}^{-3}\text{)}$
K	191.66e9 (Pa)	χ	$3.916e - 1$
S	460.0e6 (Pa)	B_l, B_t	0.005, 0.5
M	$4e - 17 \text{ (m}^5 \text{ s mol J}^{-1}\text{)}$	$k_1 \text{ \& } k_2$	$6.0e9 \text{ (J mol}^{-1} \text{ m}^{-3}\text{)}$
S_0	300.0e6 (Pa)	m	0.25
α	$3.62e - 7 \text{ (J m}^{-1}\text{)}$	$\dot{\epsilon}_0$	$1e - 4$
Oxide (Viscoplastic)			
G	132.0e9 (Pa)	β	$1.0e6 \text{ (J m}^{-3}\text{)}$
K	172.0e9 (Pa)	χ	$3.916e - 1$
S	2500.0e6 (Pa)	$k_1 \text{ \& } k_2$	$6.0e9 \text{ (J mol}^{-1} \text{ m}^{-3}\text{)}$
D	$4e - 17 \text{ (m}^2 \text{ s}^{-1}\text{)}$	B_l, B_t	0.005, 0.5
S_0	2400.0e6 (Pa)	m	0.25
α	$3.62e - 7 \text{ (J m}^{-1}\text{)}$	$\dot{\epsilon}_0$	$1e - 4$

* C_{ij} parameters are related to stiffness of transversely isotropic material.


Fig. 4 Comparison of results for oxide growth with experimental data.

$$K_{ee}^{AB} = - \int_e (N_A N_B) dV$$

Analysis and Results

A medium with two distinct material properties was modeled with a sinusoidal interface to resemble ceramic top-coat and bond-coat alloy. Layers are designed to have 150 μm thickness (average ceramic coating thickness) and 30 μm width. 0.5 μm size meshes were chosen for TGO propagation around the interface and coarser meshes were used in distant regions. Mechanical boundary conditions are presented in Fig. 3 for an isothermal analysis at 1423 K. Bond-coat material is assumed to be FeCrAlY. Parameters utilized for different material layers in the analysis can be found in the Table 1.

As illustrated in the figure below transverse isotropy is assumed for top-coat due to the special columnar structure of the EB-PVD coating. A $\tanh$ type function was given as initial condition for phase field in the interface with $\phi = 1$ in ceramic and

$\phi = 0$ in bond-coat. Initial concentration was defined to be zero in bond-coat and one in ceramic. As interface propagates into bond-coat region, actual new phase with distinct material properties will start to grow. Analysis results for TGO growth, stresses (MPa) for 10 h of service can be found in the flowing figure.

Growth of oxide phase with a definite interface thickness can also be clearly observed in the figure below. Interface thickness is defined to be approximately 4 μm but it will be physically more feasible to reduce it to a smaller region to mimic a sharp interface in oxidation process. In order to satisfy mesh independency of the problem a certain number of elements should be used. For this analysis an interface with 5 elements with 2.5 μm width is used.

The model validation is performed through comparing numerical and experimental results available for EB-PVD oxidation (Tolpygo *et al.*, 1998) (Fig. 4).

Concluding Remarks

In this study, development and growth mechanism of thermally grown oxide resulting local inelastic deformation is modeled on the base of Allen-Cahn phase field model. A fully coupled formulation in finite deformation framework is implemented using ABAQUS finite element program and validated for EB-PVD FeCrAlY type thermal barrier coatings. The model parameters are calibrated for experimental results available for TGO thickness evolution in time. The stress contours are observed to be in good agreement with other studies showing concentration of stress in uphill and downhill regions of the undulations. Moreover, the magnitude of internal stress generated in the bond-coat exceeds GPa level after a certain service time as reported in the literature (Al-Athel *et al.*, 2013). A considerable amount of plasticity generated in the bond-coat region due to growing oxide is demonstrated in Fig. 2. It is considered that those results could be a good base for an additional step of including a failure mechanism to the model for the life time estimation of the coating system.

See also: Advanced Polymeric Coatings and Their Applications: Green Tribology. Particulate Composite Protective Coating Using Conventional Melting Approach. Post-Processing of HVOF Sprayed WC-Co Coating to Enhance its Performance. Processing of Ceramic Composite Coating via TIG Torch Welding Technique. Tribological Interactions of Advanced Polymeric Coatings

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Library of Congress Cataloging-in-Publication Data

A catalog record for this book is available from the Library of Congress

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library

ISBN 978-0-12-813195-4

For information on all publications visit our
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PREFACE

The *Encyclopedia of Renewable and Sustainable Materials* is a novel initiative, launched to cater for researchers, industrial practitioners and environmental conservationists to bring to the fore the issues of renewability, regeneration, recyclability and sustainability of natural material resources for the greater good of the environment, society and renewable resources. With these objectives the project was constituted of 11 sections, led by one Section Editor each. There are about 4,000 printed pages, accommodated in five volumes ranging from 600 to 1000 pages each.

This encyclopedia is the primary reference source for researchers at different levels and stages in their career in academia and industry and those with an interest in environmental protection and sustainability, including re-use and recycling of natural and synthetic materials and regeneration of natural materials. The work encompasses the knowledge and understanding of many experts into a single, comprehensive work of about 370 articles comprising a combination of review articles, case studies and research findings resulting from research and development activities in both industrial and academic domains. The encyclopedia, focuses on how some of these topics bring advantages for a broad range of technologies and environmental protectionists. These include harnessing existing materials both natural and synthetic, their re-usability and regeneration possibilities for the greater good of society and the environment. The aspects of feasibility, conservational objectives and practicability of implementation have been addressed through a number of relevant articles.

As Editors in Chief of this five-volume comprehensive publication, a truly collaborative work, we are greatly indebted to the 11 Section Editors who are internationally renowned experts in their fields, for guiding and selecting the topics for their respective sections which constitute the five volumes, commissioning authors and reviewing the contents so meticulously. Their true dedication to the scientific community and society is reflected in the time and energy they have given to this project. My sincerest thanks are due to all the authors – researchers, environmental protectionists and practitioners who have contributed extensive coverage of literature review as well as recent works of research to this substantial five volume encyclopedia. The excellent insight and specialist knowledge in their respective fields is reflected in the high quality content of this unique work.

Both of us and all the section editors are greatly appreciative of all the hard work undertaken by all concerned to turn this concept of the *Encyclopedia of Renewable and Sustainable Materials* into a publishable work. Our special thanks go to Ruth Rhodes and Michael Nicholls, the Project Manager, along with Kshitija Iyer and the rest of the team at Elsevier who served successively to keep the project on track through friendly nudges in order to ensure timely completion. We are also hugely grateful to other colleagues at Elsevier production unit for the coordination of the proofs.

The extensive research treatment of core ethos of renewability, recyclability and regeneration, supplemented by applied case studies has drawn together many areas of research and we sincerely hope that this work will prove to be of great help to both the young and experienced members of the international research community, academics and industrial practitioners associated with sensible utilization of natural and synthetic materials for many years to come.

Saleem Hashmi and Imtiaz Ahmed Choudhury
Editors in Chief – *Encyclopedia of Renewable and Sustainable Materials*

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Bamboo Versus Tubular Steel Scaffolding in Construction: Pros and Cons

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Introduction

Structural scaffold is a temporary structure used during building construction or repair of exteriors or interiors to support movement of people and materials. In most nations of the world, the construction industry is a booming sector of the economy and the demand for scaffolding formwork for the maintenance of existing building stocks and construction of new low-rise and high-rise buildings is high. It is estimated that scaffolding works normally share about 1% of a construction project budget, which can be a considerably high in large projects.

Scaffolds perform an important role in ensuring the process of different works in a construction project. Thus, owing to the significance of scaffolding in buildings, it therefore becomes essential to know the nitty-gritty of the various materials mostly used for this purpose.

There are a multiplicity of scaffolding systems, both traditional imported ones, with each system having its pros and cons in terms of cost and safety performances. The three prevailing scaffolding systems established internationally are bamboo scaffolding, metal (steel) scaffolding, and mixed scaffolding.

Good use of metal scaffolds applies structural design principles for spacing, layout of components, and foundation stability in relation to the self-weight of structural elements to be supported, and environmental and operation loads imposed on the falsework system. In scaffolding, we are concerned with combined stresses of bending and buckling for which the cross-sectional shape becomes of overriding concern. All steel scaffolding has always been made from tubes, same as bamboo, though the shape of steel is fixed, while that of bamboo is adaptable. The multidirectional resistance of tube to buckling is excellent. Favorably, in a scaffolding, cross-bracing is an extra usual means of preventing buckling. Moreover, bamboo supports its own weight and resists bending loads from wind. These similarity in shape and resistance have contributed to the use of bamboo for scaffolding.

Over the years, both bamboo and the tubular steel scaffolding have been used during construction of buildings, and as such, there are various experiences that constructors have while using these materials. Therefore, this article focuses on exploring the application of both scaffolding materials with emphasis on their pros and cons.

Overview of Scaffolding Materials

Basic Components of Scaffolding

During construction of buildings, irrespective of the height, scaffolding is mostly used to provide external structural support for both the building-in-progress and the people working on it. Different materials, such as metal piping, tubes, and bamboo, are used for scaffolding, in addition to couplers and boards. However, regardless of type and quality of material, scaffolding must satisfy the standards for performance requirements and structural design methods. The scaffolding member needs to be compatible with a wide array of buildings and structures, because there are various kinds of scaffolds that fit specific building requirements.

The scaffolding materials can vary based on building type or constructor choice, however, the scaffolding process is comprised of the same basic elements. Only the manner in which the elements are designed and coupled together may vary.

There are three basic scaffolding components, these include standards, ledgers, and transoms. The standard is usually a long pipe, tube, or bamboo that connects the mass of the scaffold directly to the ground, this runs through the length of the scaffolding. The base of each standard is connected to a base plate that aids distribution of the overburden weight resisted by each standard across the ground. The ledger runs horizontally in between each standard, which further support weight distribution. Lastly, the transom is usually connected on top of the ledgers at a right angle; this may come in several different forms. The transom holds the standards in position as well as supporting the boards. [Fig. 1](#) shows the basic components of a scaffolding system.

There are other smaller supportive components used in scaffolding besides standards, ledgers, and transoms. These elements include braces (cross braces and façade braces) and couplers, which serve to reinforce the basic scaffolding members. The braces are used to hold ledgers diagonally (cross braces). The braces are securely attached to the standards to increase the overall rigidity of the structure and also prevent the structure from swaying.

The couplers are used to connect the structural elements, whether to connect a ledger or transom to a standard, a right-angle coupler, just as the need may be.

Metal Scaffold or Tubular Scaffold

Metal scaffolds are formed by steel tubes joined by couplers and the most common type is the tubular scaffold. The Hong Kong Code of Practice for Metal Scaffolding Safety given by the [Labour Department \(2001\)](#), stipulates that steel tubular scaffolds be constructed in tubes and couplers based on the design and drawings of professional engineer. A steel tube is expected to have a

yield stress equal or greater than 235 N/mm^2 with an outside diameter of 48.3 mm and a wall thickness of 4 mm. Steel scaffold can be properly engineered, accurately designed and effectively tested for the envisaged height and load. It has the advantage of being properly planned for safety with less risk of cost cutting and it requires far less skilled labor. It has customized accessories like wheels and ladders that fasten securely to the frame system and the walk boards are hooked securely as well.

Several forms of tubular scaffolds are in use, but the most common is the single-pole scaffold or putlog scaffold and the independent tied scaffold (Pallett and Nicoll, 2015).

Putlog scaffold

This single-pole scaffold system consists only of a single row of vertical standards tied parallel to the face of the building. The standards are set away from the building façade at a distance so that working platforms can be accommodated in the space between the row and the building façade, with its inner edge as close to the façade as practicable. The scaffolds shown in Fig. 2 are held to the building structure by horizontal members called putlogs. This form is usually used for light duty.

Independent tied scaffold

This form has two rows of standards parallel to the building. Boards and toe boards are accommodated in between the rows to form a working platform. This type of scaffold does not rely on the building for support and is therefore suitable for use in conjunction with frame structures.

A structure of an independent tied scaffold is shown in Fig. 3.

Typical Design Consideration for Steel or Bamboo Scaffolding

Generally, the design of a scaffold should normally take into consideration:

- Strength, stability, and rigidity of the supporting structure;
- Handling normally associated with scaffolding; and
- Safety of persons engaged in the erection, alteration, use, and dismantling of the scaffold.

However, scaffolding design should involve consideration for load support or access by construction workers, based on the design standard.

Similar to the case of building design, the design of scaffolding can be categorized into load estimation, assessment of components, and provision for support. The load consideration for scaffolding includes:

- Dead loads – these loads are permanent on the scaffold through its service life. They include self-weight of the scaffold structure and components including working platforms, catch platforms, access platforms, stairways, ladders, screens, sheeting, platform brackets, suspension ropes, secondary ropes, traversing ropes, tie assemblies, scaffolding hoists, electrical cables, and any other permanent attachments.
- Live loads – these are moving loads on the scaffold, including weight of persons, weight of materials and debris, weight of tools and equipment, and impact forces.
- Environmental loads – these include loads impacted on the scaffold due to the effect of wind, snow, earthquake, rain, and ice.

Thus during design, scaffolding should be loaded for the most adverse combination of dead loads, live loads, and environmental loads that can reasonably be expected during the period that the scaffold is expected to be in service. This is done by introducing a minimum factor of safety, which is usually four. That is, the design load is multiplied by a factor of 4, before and determining limiting strength and yield stress of the metal used in the engineering design of scaffolds and their components. Using the factor of safety ensures that scaffolds and their components can support four times the maximum design load without experiencing failure.

Generally, design of scaffolding should take into consideration the following conditions:

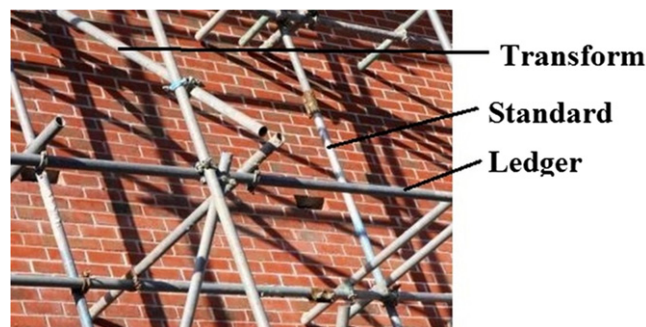


Fig. 1 Basic components of scaffolding.



Fig. 2 Structure of metal putlog scaffold. Reproduced from The Constructor, 2017. Types of scaffolding in construction. Available at: <https://theconstructor.org/building/types-of-scaffolding-in-construction/11845/> (accessed 05.06.17).



Fig. 3 Structure of independent tied scaffold. Reproduced from Penketh, C., 2014. Scaffold management and update. Available at: <http://www.ncsg.org.uk/> (accessed 05.06.17).

1. Adequate estimation of the loading conditions or combination of different loads on the structure (dead, live, wind, and snow load).
2. Scaffolding elements must be checked to ensure they can sustain the required loads.
3. Both the stability or rigidity of the scaffold system must be ensured by adopting a standard safety factor.
4. Adequate foundation must be installed for the scaffolding elements. A timber sole plate, not less than 200 mm × 38 mm × 500 mm long, can be used as foundation support for scaffolds. However, materials, such as bricks and blocks, are not suitable for this purpose because they are loose material that can easily crumble or be driven into the ground.

Design fundamentals

There is currently a standardized design approach for steel scaffolding as a result of rapid development in its usage. However, the unavailability of standard design codes for bamboo scaffold has created limitations in this regard. As a result, the majority of bamboo users mostly rely on their previous experience with the material during practice. In this section, a typical design consideration of a tubular steel scaffolding is presented.

Load estimation is an integral part of scaffolding design. Two major load types to be considered in scaffold design are:

- Steadily applied load, such as scaffold self-weight, dead load from permanent structures, wind load, access load, and thermal load.
- Dynamic load, such as vibration, surge, or impact resulting from pouring of concrete, plant movement, or vehicles.

British standard (BS 5973, 1993) provides a detailed loading specification to be considered for a steel tubular scaffolding design. The equivalent uniformly distributed load for a metal scaffolding ranges from 0.72 kN/m² for class 1 to 6.0 kN/m² for class 6. However, classes 4 or 5 are for operational load (such as one worker, concrete or 9-inch brick), which is 3.0 kN/m².

Wind load is represented in the form of pressure exerted on the scaffolding system. The code specifies maximum design wind pressure as 770 N/m², while a working wind is 200 N/m².

For example, the wind pressure exerted per unit length of a 48.4-mm-diameter tubular steel is taken as 37.0 N/m² from the code.

The safe strut permissible stress can be determined using the Perry–Robertson formula (see Eq. 1) provided in appendix B of BS 449-2 (1969). Thus, for a tubular mild steel of grade 43, having 48.4 mm outer diameter and 4.08 mm thickness and a Young's modulus of 206 kN/mm², the safe strut load for an effective length of 1.8 m is 36.5 kN.

$$K_2 \times P_c = \frac{Y_s + (\eta + 1)C_o}{2} - \sqrt{\left[\left\{ \frac{Y_s + (\eta + 1)C_o}{2} \right\}^2 - Y_s \times C_o \right]} \quad (1)$$

where P_c is the permissible average stress (in N/mm²). K_2 is a coefficient to allow for lack of straightness in addition to h , together with lack of square ends and some corrosion. Y_s is the minimum yield stress (in N/mm²). C_o is the Euler critical stress (in N/mm²).

$$C_o = \frac{\pi^2 E}{\left(\frac{l}{r}\right)^2} = \pi^2 \frac{210,000}{\left(\frac{l}{r}\right)^2} \quad (2)$$

where η is a constant. l is the effective length (in m). r is the effective radius of gyration (in m). l/r is the slenderness ratio.

For instance, in fittings and auxiliaries, such as the base, a safe working load of 65 kN is recommended by standard.

According to BS 5973 (1993), parameters required for an elastic design of scaffold are given as follows, using Eqs. (3)–(5):

$$n = \frac{2P - W}{s} \quad (3)$$

$$h = n \times \text{the lift height} \quad (4)$$

$$H = \frac{h}{C} \quad (5)$$

where s is the self-mass of the scaffold per lift/bay (in kg). w is the extra mass on all the working lifts in a single bay (in kg). W is the total extra mass of all the working lifts (in kg). P is the allowable load in a standard (in kN). n is the number of lifts. h is the calculated height of the scaffold (in m). C is the safety coefficient. H is the recommended height of the scaffold after the application of the factor C (in m). $W + ns$ is the required strength for two standards, which is equivalent to $2P$.

As an example, the height of scaffold required for a three lengths of bay, 2.1, 2.4, and 2.7 m, of a very light duty scaffold, having one working platform that is rated at 0.75 kN/m² with three boards wide and in 2-m lifts, is estimated as shown in Table 1.

Bamboo Scaffold

Bamboo scaffolding is a type of scaffolding made from bamboo and has been widely used in building work for ages. It is an ancient structural system, having been used in China for a few thousand years, and in more recent decades it has been well developed in Hong Kong. Bamboo scaffolding is a slender structure of natural bamboo pieces (Shing, 2009).

Bamboo is the fastest growing grass and it grows in large quantities in the tropical regions of Asia and in Africa. It is cheap in regions where bamboo plant is locally available. It is the cheapest scaffolding material and is readily available in the tropical regions and a few well-developed nations in Asia. It requires a special skill by cheap semiskilled labor to place it properly and is suitable for small projects. Good-quality bamboo can be used multiple times, which reduces the cost of construction. It has been

Table 1 Design results

Bay length (m)	S (Kg)	W (Kg)	P (kN)	n	h (m)	C	H (m)
2.1	76	182	24.9	64.4	128.8	1.64	78.54
2.4	78	205	24.9	62.5	125.0	1.62	77.16
2.7	81	229	24.9	59.8	119.6	1.60	74.75

Source: Adapted from BS 5973, 1993. Code of Practice for Access and Working Scaffolds and Special Scaffold Structures in Steel. London: British Standard.

verified that quality bamboo has a good tensile strength, which makes it comparable to the steel used in most scaffolding, but that inconsistent bamboo quality can cause problems. Bamboo is also cheaper, which has made it more attractive in most developing nations and advanced nations where the use is permitted. Bamboo is a fibrous material too, so it makes sense that it can be as strong as many other natural fibers. It has been verified that bamboo has tensile strength in the range of 156–185 N/mm², which is impressive and certainly implies a greater strength to weight ratio than steel, and it is flexible. It's half the weight of steel. Despite being lightweight, some stronger species of bamboo will actually compete favorably with steel. Bamboo scaffold design is highly approximate and based more on the experience of the fabricator. With a bamboo scaffold, the ladders are tied to it and the walk board RESM-S are just laid unfastened on the cross beams and can easily slip off leading to great safety risk. It is cost effective and quite safe if properly built. But for it to be safe, it must be over designed to consume more materials, therefore tending to be expensive, while the realities of cost cutting and lax oversight can lead to severe fatalities. Bamboo is a viable choice where highly skilled workers are cheap. It is not easily reusable, actual strength varies with great uncertainty, it is not suitable for big projects, and is less trustworthy than metal scaffolding. During arrangement of bamboo scaffolds, strong nylon fiber straps are used to tighten bamboo shoots together, thereby forming a solid and secure scaffold structure using no screws. Bamboo scaffold does not have a solid foundation and anchorage base on the ground, thereby creating a great risk for instability.

There are two common types of bamboo scaffolding systems in the building industry, one of the most developed in the world: the single-layered and double-layered bamboo scaffolds.

Components, selection, erection, maintenance, and dismantling of bamboo scaffolds

Bamboo scaffolding system is used in similar manner as the steel scaffold, so the components are similar, however there is variation in terms of coupling of bamboo members. The traditional means of coupling bamboo members is by tying using strong nylon, but steel scaffolds are developed with the use of standard couplers at joints. Recent advancement in technology is providing solutions that can ensure a more systemic coupling of bamboo members.

The selection of bamboo for scaffolding is primarily based on its strength development at maturity, although this property can vary among different species. The strength of bamboo comes from its vascular bundles within the main matrix of the culm. Bamboo tends to perform poorly, when loaded perpendicularly to its grain direction, and its strength diminishes with increasing moisture content.

The erection process of bamboo scaffolds in building is slightly different compared to steel scaffolds. In the case of bamboo, the bracings are extended from the base to the top of the scaffolds. This helps to ensure that bamboo scaffolds are effectively braced and tied back to ascertain overall stability of the structure. Also, knotting between bamboo members must be tight and secure.

Safety during construction is a concern to building workers, so there must be a periodic inspection and maintenance of bamboo scaffold during construction. Bamboo, being a natural material, can expand and contract as the moisture content changes. Therefore, close supervision and frequent inspection is required in order to ensure the structural integrity of the bamboo scaffolds. The inspection is more needed when there is rainfall or wind at the building site. This procedure can help to prevent unnecessary accidents during construction.

Immediately after a project has been completed, it is important that the bamboo scaffold be dismantled to avoid exposing it to deterioration as a result of changing weather conditions. Normally, dismantling of the scaffold should start from the building's topmost level and downward, first removing the noncritical members before the critical ones. Bamboo must be stored appropriately after dismantling, in a place free from moisture.

Bamboo scaffolding: A case study from Hong Kong

Regardless of Hong Kong's predominantly modern architecture, it still sticks with bamboo scaffolding over steel counterparts in new construction or renovation of high-rise residential blocks or commercial buildings. The attractive factors that have made bamboo scaffolding an overwhelming choice in Hong Kong over steel materials are cost, time, and durability. Bamboo is locally available and cheap. Time is very important in Hong Kong and bamboo scaffolding has great advantage over steel for putting up and for taking down by the Hong Kong scaffolder specialists. This time savings is attributed to the presence of skilled bamboo scaffolders. As of 2013, there were 1751 registered bamboo scaffolders and roughly 200 scaffolding companies in Hong Kong, many of whom are members of the Hong Kong & Kowloon Scaffolders General Merchants Association Limited.

In Hong Kong, building construction crews use bamboo instead of steel to construct scaffolding up to 50 stories high (Chavan, 2001). Bamboo scaffolding is being used to build apartment blocks, repair walls, and refurbish neon signs because bamboo is cheaper, lighter, more flexible, and takes less time to erect and dismantle than steel scaffolding. Scaffolders in Hong Kong are of the opinion that properly erected and maintained bamboo scaffolding can be as strong and as safe as steel or aluminum structures. But construction workers here have one of the highest fatality rates in the developed world.

Bamboo scaffolding was first introduced into the modern building industry in Hong Kong prior to British colonization in the 1800s. The three major types of scaffolding in Hong Kong are double-row scaffold, extended bamboo scaffolding, and shop signs of bamboo scaffolding. The success story of bamboo scaffolding in Hong Kong can be attributed to the government regulation of the bamboo scaffolding trade and abundance of skilled bamboo scaffolders.

Trend of gradual decline of bamboo scaffolding in Hong Kong

Of the more than 1751 registered bamboo scaffolders and roughly 200 scaffolding companies recorded in Hong Kong in 2013 (Saurin and de Macedo Guimarães, 2006), the use of bamboo scaffolding in Hong Kong is beginning to diminish due to safety risks, as well as shortages in labor and material. Safety risks of bamboo scaffolding are very high due to so many variabilities and

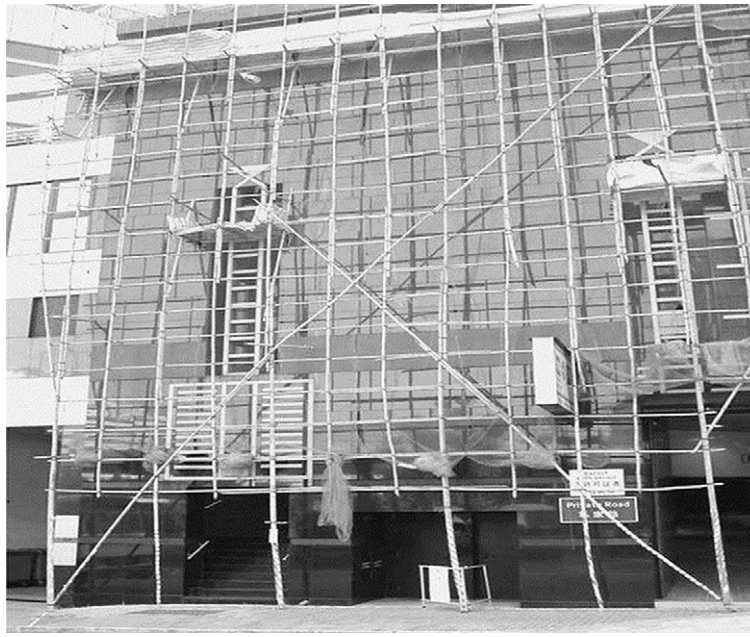


Fig. 4 Structure of single-layered bamboo scaffold. Reproduced from Yu, W.K., Chung, K.F., Chan, S.L., 2003. Column buckling of structural bamboo. *Engineering Structures* 25 (6), 755–768.

uncertainties in bamboo material, accessories, design approach, and fabrication methods. The labor shortage may be due to the unwillingness of younger generations to take up the scaffolding trade due to high accident risk, unsafe work environment, and unwillingness to procure professional license from the Hong Kong Construction Industry Council. Actual and future bamboo material shortage is also a contributing factor to the decline bamboo scaffolding in Hong Kong. The bamboo scaffolding material is imported to Hong Kong from mainland China. The fear of uncertainties related to possible blocked supplies due to export embargoes and environmental concerns remain high.

Single-layered bamboo scaffold

This is made up of a single plane of framework (Wang, 1998), which is commonly known as the working scaffolds. It is usually erected at about 750–900 mm from the building face. This type of scaffold is shown in Fig. 4. Single-layered bamboo scaffold is mainly used for light site works, such as exterior decoration, platform for rebar workers, and for boundary fencing during the construction stage. It is highly flexible for sites, cheaper, causes less obstruction to work in progress, and easy to mount and dismantle. However, it poses high safety challenges due to high risk of instability. For instance, in Hong Kong, the use of single-layered scaffolds has been banned in the construction stage of buildings (Shing, 2009), due to its associated safety concerns.

Double-layered bamboo scaffold

This type of bamboo scaffold consists of two layers: the inner layer or the finishing scaffold, which is usually erected at about 150–300 mm from the building face, and the outer layer or working scaffold, erected at about 600–700 mm from the inner layer, as can be seen in Fig. 5. Double-layered scaffolds permit more complex jobs to be executed at greater heights more safely (Shing, 2009). This is the Hong Kong Government's approved bamboo scaffold since it offers greater safety for the workers and a means to reduce the rate of accidents and fatalities (Wang, 1998).

Life cycle of bamboo scaffold

Bamboo scaffolding systems, as a renewable resource, are used during construction in most developing countries. They can be easily assembled using a simple repetitive design, and can be used effectively for up to a five-story building. Just like a steel scaffold, bamboo scaffold is also recyclable. A typical life cycle of a bamboo scaffolding system is shown in Fig. 6. There is need to periodically inspect and maintain bamboo scaffold when it is in use until when the project is completed. At the end of a particular project, it can be possible to reuse bamboo scaffold for another project, if it is assessed and found suitable, i.e., showing no significant sign of deterioration.



Fig. 5 Structure of double-layered bamboo scaffold. Reproduced from European Commission, 2016. New bamboo engineered biomaterial sustainable building components. Available at: <http://europa.eu/geninfo/query/resultaction.jsp?QueryText=bamboo&swlang=en&x=0&y=0> (accessed 23.05.17).

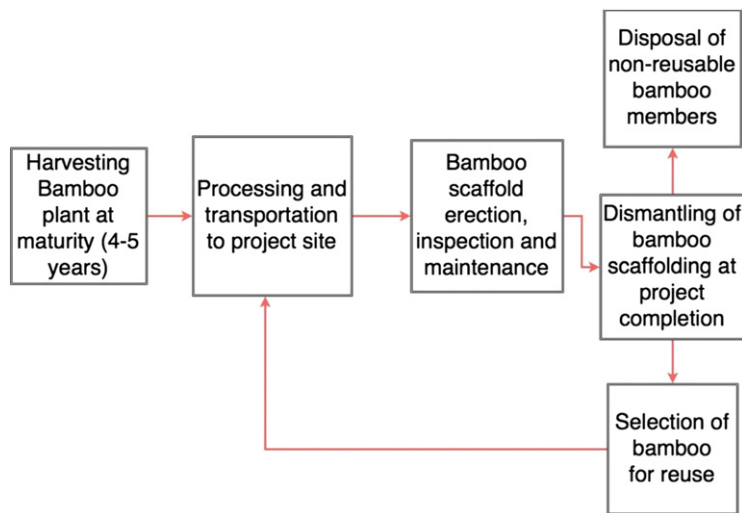


Fig. 6 Life cycle of bamboo scaffolding system.

Pros and Cons of Bamboo and Tubular Steel Scaffolds

Uses and Associated Building Failures

There is an open competition that is common with bamboo and many metal scaffolding systems, mostly imported from different countries all over the world. Users of these materials consider a number of factors before making a choice on what material to be used for scaffolding.

In most developing countries of the world, mostly where there are abundant bamboo plantations, bamboo scaffold has been one of the most preferred access scaffolding systems during building construction. Apart from Hong Kong, bamboo scaffolding is mostly seen in many developing Asian countries, such as India, Bangladesh, Sri Lanka, Indonesia, and most of the nations of Africa, such as Nigeria, Cameroon, and Ghana. Tropical rain forest regions of African and Asia countries are the home of bamboo,



Fig. 7 Partial collapsed of a building under construction in Ikeja, Nigeria. Reproduced from Akoni, O., Olowoosopejo, M., 2012. 5 Escape Death as Building Collapses in Lagos. Valley Forge, PA: Vanguard.

which matures after 3 years to the required wide thickness and dense skin perfect for scaffolding. The supply of bamboo is highly sustainable in the tropical regions as long as a replanting strategy is in place to replace the harvested stock. In many African countries, notably Nigeria, bamboo scaffolding is commonly used in large-scale construction in rural and urban areas. In fact, bamboo is an essential building and construction commodity in Nigeria due to the abundance from the tropical rain forest, thus there is no shortage of bamboo, and its sustainability is not an issue, since new bamboo trees are continually being planted. Meanwhile, tubular steel scaffolds are mostly used in developed nations of the globe, due to their advancement or because they have no bamboo availability. There is increasing growth in tubular steel scaffold all over the world, however, pressure to clear vegetation to make room for more habitation for the teeming population and the trend to build high in developing nations with low-skilled manpower could reduce the use of bamboo scaffolding in future.

It is well known that a typical height of bamboo scaffolds is about 15 m, but on the other hand the installation of steel bracket supports at regular intervals is able to cover the full height of the building. Although the tubular steel scaffolds are erected based on technical design specifications, erection of bamboo scaffolds is generally done by scaffolding practitioners, mostly without using any technical details but based on their intuition and experience.

As a result of certain shortcomings during construction, there have been a number of associated building failures that may or may not be attributed to the type of scaffolding employed in building construction.

On a general note, column buckling is the only associated deficiency of any scaffolding materials that may eventually contribute to a partial or total collapse of a building system. Column bulking is considered to be one of the critical modes of failure in bamboo scaffolds (Yu *et al.*, 2003), which often leads to their overall collapse. Unfortunately, outside Hong Kong and in many developing nations like Nigeria, there is currently no regulation of the bamboo scaffolding trade, opening doors to all forms of quackery and of course frequent fatal accidents and rampant failure of structures under construction. Failure of poorly erected bamboo scaffolding in Nigeria, though rarely researched or properly investigated, remains one of the significant causes of structural collapse, thereby propping up the nation's construction industry as one of the most dangerous in the world. Scene of some of the building collapse sites in Nigeria is displayed in Fig. 7. The failure in buildings was insinuated to be due to improper scaffolding systems.

Tubular steel scaffolds usually don't fail due to column buckling, except if they have been used beyond specification limits. Such limits include general preservation procedures, aging, and loading specifications.

Apart from column buckling, the effect of high wind is another factor that often leads to the failure of scaffolding systems. A typical failure scene of scaffolding, which was due to high wind, is shown in Fig. 8.

Safety Challenges of Scaffolding Systems

Safety of scaffolding will depend on how it is assembled, though it is obvious that steel has a definite advantage due to regular shape, trusted fabrication process of steel tubes in the factory with all the accessories, such as collars, T-joints, etc., fabricated to fixed sizes. A steel tube can be clamped into the end of a collar by a bolt that bears directly onto it. Bamboo, on the other hand, has



Fig. 8 Failure in building due to tubular steel collapse. Reproduced from Booth, S., 2017. Scaffolding collapses at Croydon building site during high winds. Available at: <http://www.croydonadvertiser.co.uk/scaffolding-collapses-at-croydon-building-site-in-high-winds/story-30158667-detail/story.html> (accessed 01.06.17).

inherent size variability with anisotropic behavior and a bolt bearing onto it can cause it to splinter and split. This requires more care and effort in adapting bamboo to stable scaffolds. Bamboo scaffolds stand a risk of being brought down more easily by high winds and turned at lethal speeds to spears.

Cost Variation of Scaffolding Materials

Cost effectiveness of construction materials, among other building expenses, is usually given due focus in a construction project. Building owners, constructors, and other stakeholders in the built environment give cost of construction a priority, after safety considerations have been made.

Attempts made to compare the price of a typical piece of bamboo in comparison with tubular steel scaffold has shown that it is only about 6% the cost of a similar length of a steel scaffolding (Jiang, 2008). It is obvious that the key reason why bamboo is selected for scaffolding in certain developed countries is due to this wide variation in cost. Generally, considering total cost of bamboo with steel scaffold in a large building, bamboo is considerably cheaper than tubular steel scaffolding system.

In a complete analysis of scaffolding requirements for a seven story building, Jiang (2008) compared the cost of bamboo to tubular steel. The analysis has shown that bamboo scaffolding could save about \$20,000 over steel scaffolding requirements in the same building. In other words using bamboo scaffolds would save close to \$5.91 per square meter of the building. Consequently, when cost is a major concern, then using bamboo scaffolds can be extremely advantageous.

Summary and Conclusions

In this article, various pros and cons that are associated with the use of either bamboo or tubular steel scaffolding for building construction have been explored. From the two materials, bamboo has been the most innovative patented scaffolding system so far around the world (Poon, 2007), at the rate of 60% bamboo and 40% steel. The choice of bamboo scaffold for construction dwells entirely on its availability and accessibility, and ultimately the cost. Bamboo is a renewable resource; it is easy and quicker to assemble, as it is tied with strong material straps at the joints; and the design is simple and repetitive. The poles, beams, or cross braces of bamboo can be utilized for up to 7 years, after which it can still be cut into material for making walk boards, finally ending up as a firewood on site once the walk boards are damaged.

On the other hand, tubular steel scaffolds are mostly used in developed nations, but often imported to other developing countries. There are standard technical details for using steel scaffolds, which makes it the more preferred all over the globe. Bamboo is much cheaper when compared with tubular steel scaffolds; however, there are more safety concerns associated

with bamboo scaffolds. Steel scaffold has locks and pins to ensure good connection where bamboo does not. With bamboo the connection points are tied straps that can be subject to wear and loosening.

In case of steel scaffolds, there are accessories, such as wheels and ladders, that fasten securely to the frame system. Also, the walk boards are hooked on securely as well. However, with bamboo scaffolds, the walk board RESM-S are just laid unfastened on the cross beams and ladders.

Steel scaffold can be engineered and tested for height and load capabilities. Steel scaffold members don't have an age limit like bamboo does. There is no way to know for sure how old the poles and cross braces are. I did not see any date stamps on them in my inspections.

It is also interesting to note that steel scaffold is as recyclable as bamboo. It can be melted and its by-products are used to make asphalt.

See also: A Comparative Life Cycle Assessment for Utilising Laminated Veneer Bamboo as a Primary Structural Material in High-Rise Residential Buildings. Bamboo Fiber as Fillers for Polypropylene-Nanoclay via Injection Molding. Bamboo Structural Technology. Bamboo: The Emerging Renewable Material for Sustainable Construction. Constructing a PV-Integrated Permanent Bamboo Building – An Experience. Development of Epoxy Based Composites Using Bamboo and Waste Metal Chips. Development of Self-Adhesive Products Using Only Bamboo Fibers Extracted With a Machining Center. Structural Integrity Assessment of Bamboo for Construction Purposes. Study of Junctions With Bamboo: An Attempt Towards Their Classification. Sustainability and Recycling of Bamboo for Engineering Applications

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Biogas Production From Solid Waste Landfill

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Introduction

The generation of waste in a region tends to rise with its economic growth. One of the options less costly and more used throughout the world for the disposal of urban solid waste are the landfills. These landfills are widely used in developing countries and consist of large anaerobic reactors where the input of solid waste and the output of biogas and slurry. The biogas is produced by anaerobic digestion of organic matter and has high energy potential (due to its high percentage of methane) and therefore can be used in various applications such as heat generation, electricity or production of fuel for vehicles. The energy use of biogas from landfill contributes to the reduction of environmental impacts of this structure because it employs the best land used for the construction of the landfill and reduces the emission of greenhouse gases into the atmosphere. These benefits are due either by reducing emissions of methane in the landfill or by energy production with lower carbon emissions from fossil fuels.

Municipal Solid Waste

Increasing industrial production, population growth and urbanization have increased the consumption of goods and services. This has resulted in increased solid waste generation, specifically in urban areas, in which waste includes public and household solid waste and is called municipal solid waste (MSW) (Barros *et al.*, 2014). This growth can be seen in the projections presented by Hoornweg and Bhada-Tata (2012), which predicted urban solid waste generation growth, from 1.3 billion tonnes/year in 2012 to approximately 2.2 billion tonnes/year in 2025. This makes MSW management one of the greatest challenges faced by most developing countries (Chhabra *et al.*, 2016).

According to estimates by Hoornweg and Bhada-Tata (2012), 44% of all waste is generated in the 34 developed countries participating in the OECD. The average MSW generation rate in these countries is around 2.2 kg per inhabitant per day, which contrasts with average values of 0.65 kg per inhabitant per day of underdeveloped and developing countries of the African continent. Therefore, waste generation is related to each population's economic power as a country or region and, as each group develops economically, it will have to invest more intensely in appropriate waste treatment.

Sanitary Landfills

Sanitary landfills are an improvement of one of the oldest techniques used by humankind to dispose of solid waste generated by anthropic activities. Nowadays, engineering leads the way in restricting solid wastes to a minimum space, ideally causing the smallest amount of damage to the environment or public health. This technique is carried out through solid waste compacting in the soil in the form of layers that are periodically covered with dirt or other inert materials (Environmental Protection Agency of the State of São Paulo – CETESB, 2018). This method is usually chosen by developing countries because of its lower costs. However, many developed countries still employ landfills as an integral part of their solid waste management infrastructure (as noted by Cuartas *et al.*, 2018).

According to the US Environmental Protection Agency (USEPA, 2018) US federal law (revised 09/2018) places the following requirements for construction of MSW landfills:

- (1) Fulfillment of location restrictions: Set distances from wetlands and plains, among other landforms;
- (2) Use of geomembranes to cover the sides and back of the landfill;
- (3) Slurry collection and removal systems for further treatment and disposal;
- (4) Groundwater quality monitoring systems;
- (5) Criteria for landfill coverage and care after closure;
- (6) Corrective action devices for control and treatment of the landfill and nearby groundwater;
- (7) Guarantee of financial security for environmental protection during and after landfill closure.

The ISWA (2010) states that a complete and regular application of soil coverage on the landfill is a fundamental control mechanism for effective management of a modern and well-designed landfill. This coverage can be done using inert materials (various types of soils), artificial or synthetic materials (geotextile blankets or plastic films) or even by means of reuse of materials present in the waste (wood or shredded plastics).

Also according to ISWA (2010), ease of application is a factor that needs to be considered when choosing the daily coverage for use on any given site. When selecting natural soil coverage, dry and brittle soils should be considered easier to handle than damp clays. However, each type of soil has advantages and disadvantages and the reality is that most landfills tend to use the material that is available in the most feasible form.

Table 1 Advantages and disadvantages to landfill usage. Elaborated by the authors based on Cheremisinoff, Tansel *et al.* and Kalyany and Pandey

Advantages	Disadvantages
Lower disposal costs	Older sites built before leachate collection and gas production are now sources of difficult-to-control pollution
Alternative that can be used for a wide variety of wastes	Risk of soil and groundwater contamination
Often found as the only final disposal route for wastes from other MSW management options such as incineration	Decrease in available areas near urban centers
The gas produced in the landfill can be used for thermal and electric energy generation	Landfills reach a lower waste conversion rate for energy than other or MSW management options
Restored land can provide valuable space for wildlife habitat or for leisure	The convenience of landfills tends to discourage the development of innovative waste management strategies
Waste decomposes in the soil, which leads to the replacement of valuable natural resources	Explosion hazards in cases of gas leakage
No need for skilled labor	Leakage costs
Use of the available area upon closing the power plant for implantation of photovoltaic panels	The landfill causes sound pollution, odors and, the frequent traffic of heavy vehicles, increasing problems related to regional air pollution

Note: Cheremisinoff, N.P., 2003. Handbook of Solid Waste Management and Waste Minimization Technologies. Butterworth-Heinemann. 477. doi:10.1016/B978-0-7506-7507-9.X5000-1. Tansel, B., Varala, P.K., Londono, V., 2013. Solar energy harvesting at closed landfills: Energy yield and wind loads on solar panels on top and side slopes. Sustainable Cities and Society 8, 42–47. doi:10.1016/j.scs.2013.01.004. Kalyany, K.A., Pandey, K.K., 2014. Waste to energy status in India: A short review. Renewable and Sustainable Energy Reviews 31, 113–120. doi:10.1016/j.rser.2013.11.020.

Municipal Solid Waste disposal costs in landfills vary between 10 and 30 USD t⁻¹ for low-income countries and between 40 and 100 USD t⁻¹ for high-income countries (Hoornweg and Bhada-Tata, 2012).

The advantages and disadvantages of the use of landfills are described in Table 1.

Biogas Production in Sanitary Landfills

The production of biogas in landfills occurs through anaerobic digestion. According to Leonzio (2016), biogas composition is approximately 55%–70% methane (CH₄) by volume; 30%–45% carbon dioxide (CO₂); 80–100 ppmV ammonia (NH₃), 1000–3000 ppmV hydrogen sulfide (H₂S) and other hydrocarbons (<100 ppmV). Traces of siloxines can also be found.

Upon introducing MSW into the landfill, the organic components begin to undergo a series of chemical reactions. In the presence of atmospheric air near the landfill surface, natural organic components are oxidized aerobically, producing CO₂ and H₂O. However, the main reaction in landfills is anaerobic digestion. This occurs in three main stages (according to Themelis and Ulloa, 2006).

- (1) Fermentative bacteria perform hydrolysis of complex organic matter in soluble molecules;
- (2) These molecules are converted into simple organic acids, CO₂ and H₂ by acid-producing bacteria. The main acids produced are: Acetic acid (CH₃COOH), propionic, butyl and ethanol;
- (3) Fermentative bacteria carry out hydrolysis of complex organic matter, transforming it into soluble molecules;
- (4) These molecules are converted into simple organic acids, CO₂ and H₂ through acid producing bacteria. The main acids produced are: acetic acid (CH₃COOH), propionic, butyl and ethanol;
- (5) Finally, CH₄ is formed by methanogenic bacteria, both by breaking down these acids in CH₄ and CO₂ (Eq. 1) and by the reduction of CO₂ by H₂ (Eq. 2) (Themelis and Ulloa, 2006).



Landfill gas production passes through four phases listed by Farquhar and Rovers (1973) as described below. All phases are shown in Fig. 1.

- Phase I – First aerobic phase: Aerobic decomposition occurs with oxygen consumption present in the waste at the time of disposal. At this stage the production of CO₂ is verified.
- Phase II – Non-methanogenic anaerobic: Anaerobic activity becomes predominant. During this period, a peak occurs in the concentration of carbon dioxide and hydrogen production is relevant. At this stage, there is still the substitution of N₂, which can, however, be reproduced in smaller quantities by means of denitrification.
- Phase III – Unstable methanogenic anaerobic: An increase is seen in CH₄ concentration and stabilization at a very high value. At this stage, the concentrations of CO₂ and N₂ are reduced to final concentrations.

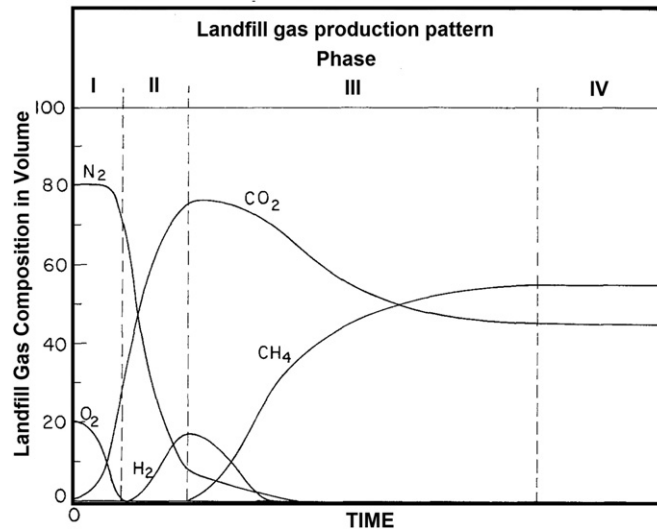


Fig. 1 Variation of gas composition produced in landfills throughout the various phases of microbiological activity. Source: Farquhar, G.F., Rovers, F.A., 1973. Gas production during refuse decomposition. *Water, Air, Soil and Pollution*. 2, 483–495. doi:10.1007/BF00585092.

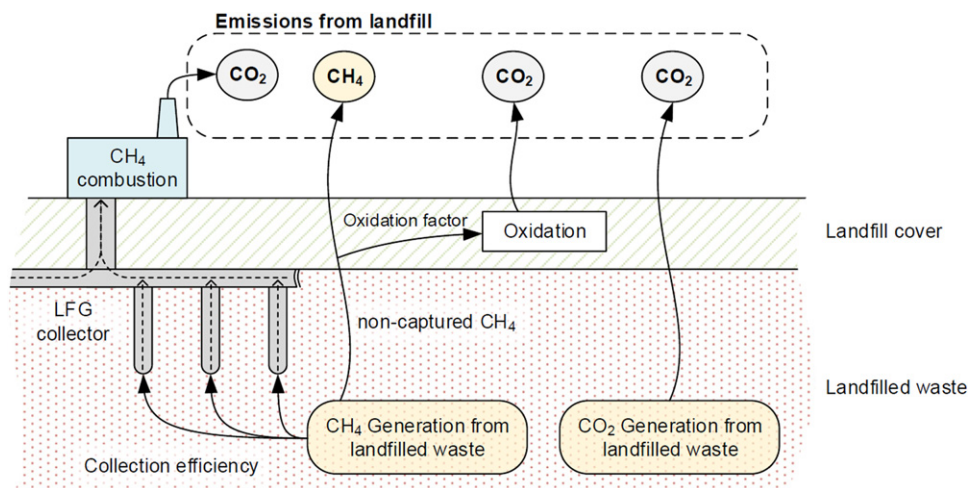


Fig. 2 Biogas processing path through anaerobic digestion in landfills. Reproduced from Lee, U., Han, J., Wang, M., 2017. Evaluation of landfill gas emissions from municipal solid waste landfills for the life-cycle analysis of waste-to-energy pathways. *Journal of Cleaner Production* 166, 335–342. doi:10.1016/j.jclepro.2017.08.016.

- Phase IV – Stable methanogenic anaerobic: At this stage, gas composition and production rates reach constant levels. This does not exclude the occurrence of abrupt variations in gas production due to changes in environmental conditions, nor long-term variations caused by nutrient depletion.

Fig. 2 Summarizes all possible landfill gas emissions (obtained in Lee *et al.*, 2017). See below:

- (1) CO₂ emission due to the combustion of captured CH₄;
- (2) CH₄ uncaptured emissions;
- (3) CO₂ emissions due to the oxidation of CH₄ as it passes through the landfill cover layer;
- (4) CO₂ emissions due to waste decomposition.

Methane must be captured and conducted using collection devices, as shown in Fig. 2. When not used, this gas must always be burnt to convert to CO₂, a gas with a much lower global warming potential.

There are many potential biogas applications for landfills. Chen *et al.* (2010) cites landfill biogas applications which are already in place in China including: Power generation in internal combustion engines; power generation in Stirling engines; the production of steam and heated water in gas boilers; production of vehicular fuel after enrichment to increase the content of CH₄; use as an auxiliary fuel in furnaces and incinerators; for treatment of landfill leachate via combustion and evaporation

and for flushing of hospital waste. Biogas can also be used to produce other chemicals such as methanol, gasoline, and even hydrogen (Yang *et al.*, 2014) in domestic stoves (not necessarily with the same yield, as shown by Grima-Olmedo *et al.* (2014) and even for the supply of desalination plants (Silva *et al.*, 2018).

Estimation Models for Biogas Production in Sanitary Landfills

The equations for estimation of gas production in sanitary landfills are generally based on first-order kinetic reactions, such as those seen in Eq. 3, used in LandGEM® software developed by the US Environmental Protection Agency (USEPA, 2005), and Eq. 4 presented by IPCC (1996).

$$Q = \sum_{i=1}^n \sum_{j=0,1}^1 k \cdot L_0 \cdot \left(\frac{M_i}{10}\right) \cdot e^{-kt_{ij}} \quad (3)$$

$$Q = L_0 \cdot R(e^{-kc} - e^{-kt}) \quad (4)$$

Where: k = decay rate for methane production in y^{-1} , L_0 = Methane gas generation potential $m^3 t^{-1}$, M_i = residual mass in the landfill in year i in t (USEPA, 2005), Q = annual methane flow in $m^3 y^{-1}$, R = residue flow per year in $t y^{-1}$, c = landfill useful life and t = time since the landfill's opening (IPCC, 1996).

Methane generation potential L_0 refers to the total amount of methane that could be produced per one ton of solid waste. This parameter is almost entirely dependent on the type of waste in the landfill. Table 2 presents L_0 values suggested by Conestoga-Rovers & Associates (2004), depending on the type of waste.

Climatic aspects such as precipitation and temperature are among the factors that influence the constant methane production rate (k) in a landfill, which has been studied by several authors. The k values obtained in the literature are highly variable, ranging from 0.02 (in arid areas) to 0.7 (in wet bioreactors, according to USEPA, 2005). Ishii and Furuichi (2013) obtained values of 0.05 and $0.062 y^{-1}$ for paper and food waste for the region of Hokkaido, Japan (cold weather region). Maciel and Jucá (2011), by means of an adjustment of the experimental data to simulation data using the LandGem software, obtained a value of k equal to $0.8 y^{-1}$ in an experimental cell of a landfill in the state of Pernambuco, Brazil. Amini *et al.* (2012) studied landfills in Florida (American region with high summer temperatures) and obtained k values ranging from 0.04 to $0.131 y^{-1}$. Table 3 presents the suggestions of the k values given by the Conestoga-Rovers & Associates (2004).

Another estimate which involves a mass balance considering degradable organic carbon can also be found in IPCC (1996), as presented in Eq. 5.

$$Q_{CH_4} \left[\frac{ton}{ano} \right] = MSW_T \cdot MSW_f \cdot MCF \cdot DOC \cdot DOC_F \cdot F \cdot \left(\frac{16}{12} \right) \cdot (1 - OX) \quad (5)$$

Table 2 Suggested Values for L_0

USW Category	Minimum value for $L_0 \text{ m}^3 \text{ t}^{-1}$	Maximum value for $L_0 \text{ m}^3 \text{ t}^{-1}$
Relatively Inert	5	25
Highly Degradable	140	200
Altamente degradável	225	300

Source: Conestoga-Rovers & Associates, 2004. Handbook for the Preparation of Landfill Gas to Energy Projects in Latin America and the Caribbean. Energy Sector Management Assistance Programme paper series. World Bank, Washington, DC. © World Bank. Available at: <https://openknowledge.worldbank.org/handle/10986/18081>. (License: CC BY 3.0 IGO).

Table 3 Suggested values for k in y^{-1}

Annual Precipitation in mm	Relatively inert	Moderately degradable	Highly degradable
< 250	0.01	0.02	0.03
250–500	0.01	0.03	0.05
500–1000	0.02	0.05	0.08
> 1000	0.02	0.06	0.09

Source: Conestoga-Rovers & Associates, 2004. Handbook for the Preparation of Landfill Gas to Energy Projects in Latin America and the Caribbean. Energy Sector Management Assistance Programme paper series. World Bank, Washington, DC. © World Bank. Available at: <https://openknowledge.worldbank.org/handle/10986/18081>. (License: CC BY 3.0 IGO). Cuartas, M., López, A., Pérez, F., Lobo, A., 2018. Analysis of landfill design variables based on scientific computing. Waste Management 71, 287–300. doi:10.1016/j.wasman.2017.10.043.

Where MSW_T = Total waste generated annually in tonnes, MSW_f = fraction of solid waste sent to the landfill, MCF = Methane correction factor, DOC = Degradable organic carbon fraction, DOC_f = Degraded DOC fraction, F = Methane fraction in biogas and OX = the oxidation fraction of methane (Generally equal to 0) (IPCC, 1996).

The methane correction factor (MCF) is related to the type of landfill operation and can be obtained through the use of Table 4; these data are provided by the IPCC (1996). The fraction of degradable organic carbon (DOC) is based on the composition of the residue and can be obtained through Eq. 6. The fraction of this carbon converted to biogas (DOC_f) can be obtained by means of Eq. 7 (IPCC, 1996).

$$DOC = 0,4.A + 0,17.B + 0,15.C + 0,3.D \quad (6)$$

$$DOC_f = 0,014T + 0,28 \quad (7)$$

Where: A = Percentage of paper and textile material in the waste; B = Percentage of pruning waste, gardening or other organic putrescible material other than leftover food; C = Percentage of food debris, D = Percentage of wood or straw and T = Temperature ($^{\circ}\text{C}$). Variables A, B, C, D can be obtained through analysis of gravimetric composition of the city or region where the landfill will be implanted. This composition varies from region to region. Table 5 shows the differences in the gravimetric composition of solid waste between South, Central and North America. In it, it is possible to observe that when economic conditions increase, organic material in MSW reduces.

Other estimates can be found in the literature. Das *et al.* (2016) presented a first order multiphase model developed by the Agricultural University of Wageningen which considers eight different types of waste with three types of degradation rates which are differentiated by index i, according to Eq. 8.

$$Q = \varepsilon \cdot \sum_{i=1}^3 c \cdot MSW_T \cdot C_0 \cdot k_{1,i} \cdot e^{-k_{1,i} \cdot t} \quad (8)$$

Where: ε = Dissimilation factor; i = Fraction of the residue degradation rate of $k_{1,i}$; c = Biogas conversion factor per kg of degraded C; MSW_T = Residue mass, in t; C_0 = Concentration of organic carbon in the residue in KgC t^{-1} residue, k_1 = Rate of degradation of the residues in y^{-1} , t = Time in y, i = Index of each type of residue (varying between 1 and 3, since this model adopts 3 degradation rates) and Q = Biogas flow in $\text{m}^3 \text{y}^{-1}$.

Table 4 Landfill classification and MCF parameter determination

Type of sanitary landfill	MCF
Controlled	1
Uncontrolled – Deep (>5 m)	0,8
Uncontrolled – Shallow (<5 m)	0,4
Unclassified Landfills – Default Value	0,6

Source: IPCC, 1996. Intergovernmental panel on climate change. In: IPCC Guidelines for National Greenhouse Gas Inventories: Reference Manual. Chapter 6: Wastes. (accessed on 02.06.2015).

Table 5 Differences between gravimetric composition (in %) in South America, Central America and North America. Translated by Hoornweg and Bhada-Tata

Region	South America	Central America	North America
Leftover food	44.9	43.8	33.9
Paper	17.1	13.7	23.2
Wood	4.7	13.5	6.2
Textiles	2.6	2.6	3.9
Leather/Rubber	0.7	1.8	1.4
Plastic	10.8	6.7	8.5
Metal	2.9	2.6	4.6
Glass	3.3	3.7	6.5
Others	13	12.3	9.8

Note: Hoornweg, D., Bhada-Tata, P., 2012. What a Waste: A Global Review of Solid Waste Management. Urban development series; knowledge papers no. 15. World Bank, Washington, DC. © World Bank. Available at: <https://openknowledge.worldbank.org/handle/10986/17388>. (License: CC BY 3.0 IGO).

A specific model for the Indian reality as a function of temperature was developed by Kumar *et al.* (2016), described in Eq. 9. According to the authors, this model can be used by local authorities to plan methane recovery in sanitary landfills.

$$CH_4 = \alpha (MSW_T)^{0.179} \cdot e^{0.0069 \cdot T + E} \quad (9)$$

Where: CH_4 = Methane flow rate; MSW_T = Total mass of waste per year per ton; α = Model parameter (estimated at 2.33, varying between 0.8 and 7.05); E = Error associated with the model; and T = Temperature in °C (Kumar *et al.*, 2016).

The uncertainties related to landfill gas generation is the greatest difficulty in estimating the gas flow rate collected there and its eventual use for energy generation (Amini *et al.*, 2012). Since first-order models are extremely dependent on their input parameters, they must be carefully chosen to ensure the model's effectiveness. Factors such as precipitation, mean temperature and residue composition can be used to aid in the selection of these parameters. A detailed comparison with rich discussions among several methods of prediction of biogas production in landfills can be obtained in Scharff and Jacobs (2006).

Biogas Utilization in Sanitary Landfills for Electrical Energy Generation

Biogas produced in landfills can be considered a renewable fuel and stands out as an excellent energy generator, by contributing to distributed generation. In this form of generation, energy is produced close to consumer centers, reducing the risks and losses which can be characteristic of the centralized generation of extensive transmission lines. As the results of Leme *et al.* (2014) show, environmental performance of landfills performs better on issues such as global warming emission reductions, ozone layer depletion, human toxicity, acidification and abiotic depletion, when using biogas from this type of electrical generation.

The power levels, P_{el} and energy, E , which can be generated each year through energy conversion of the biogas is calculated using Eqs. 9 and 10.

$$P_{el} = Q \cdot LHV \cdot \eta \cdot E_c / 1000 \quad (10)$$

$$E = P_{el} \cdot 8,760 \cdot C_F \quad (11)$$

Where: P_{el} = Electric power in kW; Q = Biogas flow to be used in $m^3 s^{-1}$; η = Energy conversion efficiency; E_c = Landfill gas collection efficiency; LHV = Lower calorific value of biogas = $22 \times 10^6 J m^{-3}$ (Guerini Filho *et al.*, 2018); 8760 = Number of hours per year; C_F = Capacity factor; E = Energy available annually in $kWh y^{-1}$.

The E_c value varies with the characteristics of the landfill. The value suggested by USEPA (2005) is 75%, while used a value of 55.5%. A representative schematic of a biogas plant installed in a landfill is presented in Fig. 3. As shown in the figure, the components required for the plant are:

- (1) Gas collection drains;
- (2) Piping to transport the collected gas;

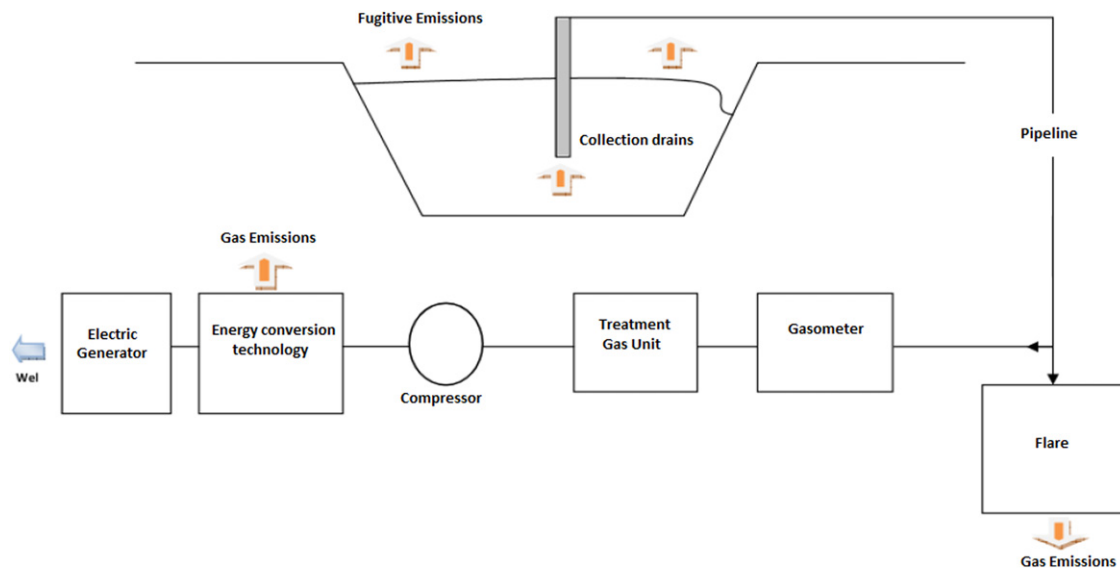


Fig. 3 Diagram of electrical energy power plant in a sanitary landfill. Adapted from Santos, I.F.S., Barros, R.M., Tiago Filho, G.L., 2018a. Economic study on LFG energy projects in function of the number of generators. Sustainable Cities and Society 41, 587–600. doi:10.1016/j.scs.2018.04.029.

- (3) Combustion burner for unused biogas;
- (4) Gasometer for storage and gas flow control;
- (5) Gas treatment unit, which can be dispensed at the cost of further damage to energy conversion technology;
- (6) Compressor for pumping and raising gas pressure;
- (7) Energy conversion unit for the conversion of the biogas chemical energy into mechanical energy. **Table 6** shows a comparison of the yields and emissions associated to the two main biogas energy conversion technologies of landfills; and finally
- (8) Electric generator for conversion into electric energy.

The costs of a biogas-fueled thermoelectric plant can be estimated using aggregate cost, which are given in terms of installed power. **Table 7** presents estimates in the literature that can be used to plan the energetic use of landfill biogas and for economic viability analyzes.

Chen et al. (2010) cite some of the problems commonly encountered in landfills in China: (i) Gas collection is less than estimates (due to errors in estimates or structural problems); (ii) problems with gas emission limits; and (iii) wear and tear

Table 6 Characteristics of the energy conversion technologies in sanitary landfills. Obtained in Bove and Lunghi

Technology	NO_x Emissions $\mu g\ kJ^{-1}$	Electrical energy yield with generator	CO emissions $\mu g\ kJ^{-1}$
Internal combustion engines	56.6	33%	56.6
Gas turbines	15	28%	19

Note: Obtained Bove, R., Lunghi, P., 2006. Electric power generation from landfill gas using traditional and innovative Technologies. *Energy Conversion and Management* 47, 1391–1401. doi:10.1016/j.enconman.2005.08.017.

Table 7 Estimates of the costs of electricity generation from landfill gas present in the literature

Description	Equation
Capital, operation and maintenance costs estimate.	$I = 11,550.P^{0.78}$ (12)
Considers a plant operating 8000 h per year with an electrical efficiency conversion of 33%. Presented by Gómez et al. (2010)	$C_{om} = 115.P$ (13)
	Where: I = Capital cost, in €; P = power, in kW; and C_{OM} = operation & maintenance cost, in $€\ y^{-1}$
Aggregate estimate developed by Santos et al. (2015) without considering gas treatment using data of Brazilian reality. Given as a function of electrical power and efficiency of the adopted conversion technology	$I = \beta.P + 0.52$ (14)
	Where: I = Capital cost, in 10^6 USD; P = power, in kW; and β = constant given depending on the efficiency conversion technology. For the Brazilian internal combustion engines $\beta_{ICE} = 0.008$; and for gas turbines $\beta_{GMT} = 0.012$
Estimate presented by USEPA (2016)^a of a complete co-generation plant using reciprocating engine. Includes gas treatment (dehydration equipment and filtration). Gross capacity factor of 93%	$I = 1.900.P + 250,000 + 355.P + 63.L + 106.\lambda + 12,000$ (15)
	Where: I = Capital cost, in USD; P = Power, in kW; 250,000 = Connecting cost to the grid system; L = Piping length, in ft; λ = Trench for the steam piping length, in ft; and 12,000 = Recirculating pump cost.
Estimate presented by USEPA (2016) of a complete co-generation plant using gas turbine. Includes gas treatment (dehydration equipment, siloxane absorbers, and filtration). Gross capacity factor of 93%	$I = 2,340.P - 0.103.P^2 + 250,000 + 355.P + 63.L + 106.\lambda + 12,000$ (16)
	Where: I = Capital cost, in USD; P = power, in kW; 250,000 = Connecting cost to the grid system; L = Piping length, in ft; λ = Trench for the steam piping length, in ft; and 12,000 = Recirculating pump cost.

^aMore information about these costs can be found in **USEPA (2016)**.

Table 8 Energy potential of biogas through municipal solid waste in multiple countries

Country	Energy potential	Reference
Mexico	Theoretic Potential: 30.2 TWh y^{-1} Economically viable potential: 1.1 TWh y^{-1}	(Rios and Kaltschmitt, 2016)
Uruguay	30–45 GWh y^{-1} of electrical energy and 108–162 TJ y^{-1} of heat	(Moreda, 2016)
Brazil	Between 6.9 and 11.8 TWh y^{-1}	(Santos et al., 2018b)
Serbia	49.72 Mtoe y^{-1} (equal to 578.24 GWh y^{-1})	(Cvetković et al., 2014)
Urban Regions of Africa	62.5 TWh in 2012 and 122.2 TWh in 2025	(Scarlát et al., 2015)
Poland	82 million $m^3\ y^{-1}$ just in organic material, equal to 115 GWh y^{-1}	(Igliński et al., 2015)
Turkey	4.85 TWh y^{-1}	(Ozcan et al., 2015)
China	418.5 MW in the case of installation in all sanitary landfills (2010) for the generation of energy	(Chen et al., 2010)
Spain	Electrical energy potential 4.02 TWh y^{-1}	(Gómez et al., 2010)

on the combustion engines due to impurities present in the biogas which make gas treatment necessary. Despite these difficulties, the use of biogas improves the environmental impact of landfills and has a very high potential for worldwide application.

Table 8 Presents data on the energy potential that can be obtained through municipal solid waste biogas in several countries available in the literature.

Conclusion

Economic and population growth have paved the way for growing rates of waste generation. Inadequate and uncontrolled waste disposal generates significant impacts on the environment, such as greenhouse gas emissions, soil contamination and water sources (surface and groundwater).

Landfills, while having drawbacks in some respects, are still widely used for the disposal of municipal solid waste in developing countries and are still an essential part of waste management in developed countries. In sanitary landfills the decomposition of organic matter in anaerobic environment generates biogas. This gas has several applications, such as the generation of heat, electric energy and the production of vehicular fuels. Among the difficulties in the application of this gas are the correct prediction of the gas collected and the presence of impurities in its composition.

Great potential lies in electric energy generation from biogas in several countries. When harnessed, this significantly improves the environmental performance of landfills and reduces the energy liabilities of the goods and products that generated the waste sent to the landfill.

See also: Modeling of Information System for Solid Waste Management. Plasma Arc Driven Solid Waste Management: Energy Generation and Greenhouse Gases (GHGs) Mitigation. Reducing Greenhouse Gas Emission From Waste Landfill. System Optimization for Control of Solid Waste. The Production of Biogas, Biodiesel as High-Value Bio-Based Product and Multiple Bio-Products Through an Integration Approach of the Anaerobic Digestion and Fermentation Processes

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Biopolymer-Based Composites for Medical Applications

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Introduction

In recent years, the benefits of biopolymer research and biopolymer-based composites (predominantly derived from proteins and polysaccharides) have attracted considerable attention for use in medical applications. The usage of biopolymer-based composites is increasing considerably owing to their high biocompatibility, optimal mechanical properties, ease of availability from natural sources, low immunogenicity, non-mutagenic, non-carcinogenic, and non-irritating properties, hemocompatible nature, biodegradable and edible nature, and ability to adsorb bioactive molecules (Jacob *et al.*, 2018). Biopolymers are successfully applied in various medical applications due to their biomimetic functions, which are similar to native extracellular matrix (ECM) systems (Velema and Kaplan, 2006). Biopolymer-based biocomposite materials are prepared using the beneficial features of two or more different biopolymers while maintaining their unique physicochemical properties to improve positive outcomes for medical applications (Dhillip Kumar *et al.*, 2018b). Biopolymer-based composites provide numerous advantages in medical applications such as the ability to act as a carrier molecule for targeted delivery of bioactive compounds, high level of biocompatibility within tissues, cells and cell compartments, good degradation kinetics and efficient antibacterial activity (Nitta and Numata, 2013; Nguyen *et al.*, 2013).

The physicochemical properties of biopolymers such as structure, morphology, solubility, tensile strength, chemistry modification with suitable molecules, and biomimicry of the ECM aids to control the mechanical properties of biopolymer-based products such as scaffolds, tubes, porous sponges, electrospun fibers, sponges, films, sheets, microbeads, membranes, dressing materials, microcapsules and hydrogels. The schematic illustration of various forms of biopolymer-based composites are given in Fig. 1.

This article is organized into five different sections. Section "Introduction" deals with an introduction of the biopolymer-based composites and their medical applications in brief. Section "Types of Biopolymers Derived from Natural Sources" describes the different types and sources of biopolymers and their functional role in medical applications. In Section "Biopolymer-Based Composites for Medical Applications", biopolymer-based composites and their application in tissue engineering, medical implants, drug delivery and wound healing is discussed in detail. Section "Fabrication Methodology of Biopolymer-based Composite" explains the different methodology available to fabricate biopolymer-based composites for medical applications, and finally in Section "Clinical Application and Major Global Clinical Trial Status of Biopolymers in Medical Applications" clinical applications and major global clinical trial status of biopolymers in medical applications are given.

Types of Biopolymers Derived From Natural Sources

There are several types of biopolymers derived from natural sources which have been widely prepared and used as a functional biomaterial for different medical applications. They are predominantly derived from proteins and polysaccharides which include collagen, gelatin, silk fibroin, keratin, natural rubber latex, chitin and chitosan, starch and its derivatives, pullulan, alginate, cellulose and its derivatives, albumin, casein, hyaluronic acid, chondroitin sulfate, laminarin, fucoidan, sargassum, carrageenan, agar, ulvan, dextrans, levan, curdlan, arabic gum, kondagogu gum, tragacanth gum, xanthan gum, gellan gum, and guar gum. Detailed information on different types and sources of biopolymers and their functional role in medical applications are listed in Table 1.

Biopolymer-Based Composites for Medical Applications

Tissue Engineering

Tissue engineering combined with biopolymer-based composites offers a promising approach for the treatment of damaged cartilage and bone tissues (Moreira *et al.*, 2018). Biopolymer-based nanoparticles has successfully been used to deliver drugs and genes to achieve good therapeutic efficiency in tissue engineering (Nitta and Numata, 2013). Kaczmarek *et al.* (2018) prepared a novel 3D porous scaffold (chitosan, collagen and hyaluronic acid) through the lyophilization process for tissue engineering and regenerative medicine. The scaffolds showed good mechanical properties, and thermal stability, as well as enhanced cellular adhesion with increased proliferation rate of osteosarcoma SaOS-2 cells (Kaczmarek *et al.*, 2018). A silk fibroin based bilayer nanobiocomposite scaffold showed excellent biocompatibility, good hydrophilicity, and superior osteogenic potential with cord blood derived mesenchymal stem cells, and it has been developed as a potential graft for bone tissue for clinical applications (Singh and Pramanik, 2017). Hyaluronic acid (oxidized) functionalized gelatin microcarriers were tested in both *in vitro* and *in vivo*

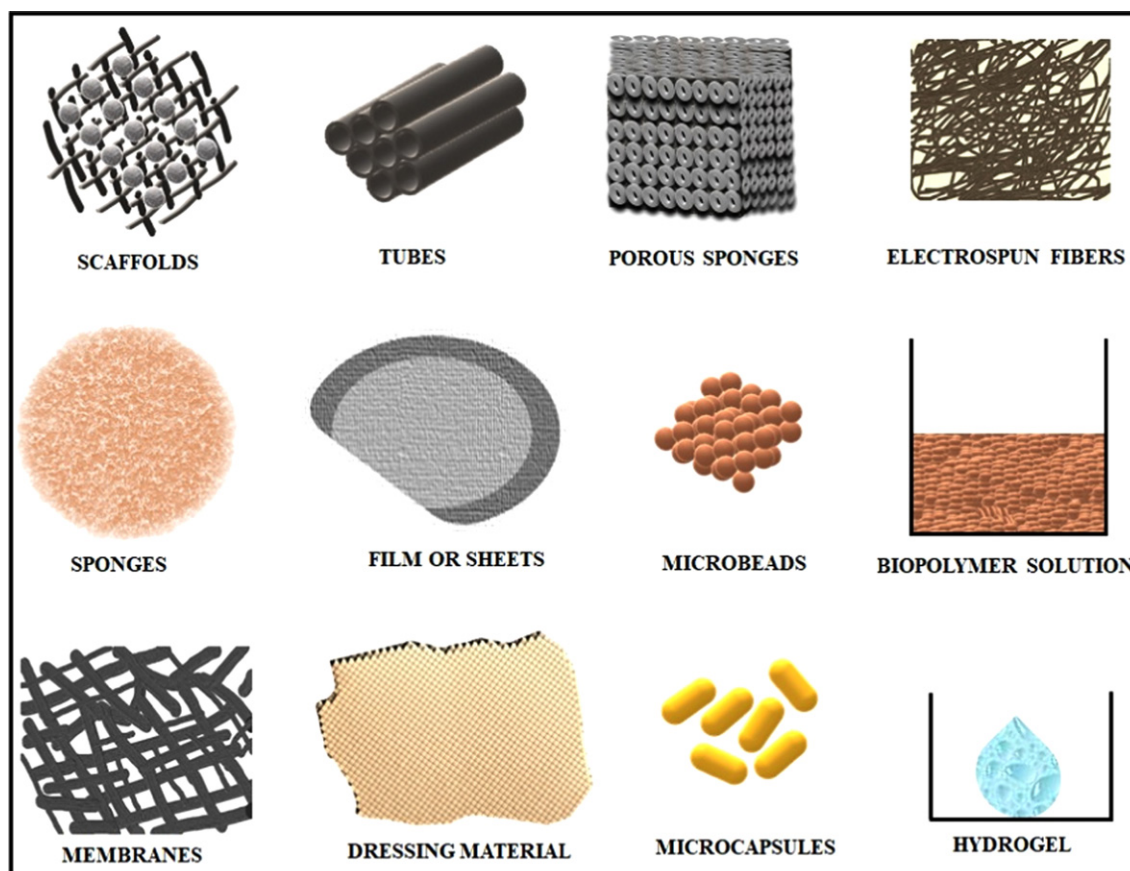


Fig. 1 Schematic illustration of various forms of biopolymer-based composites used for medical applications.

models, and the test material showed a high level of viability with all types of corneal cells (epithelial, stromal and endothelial). It can potentially be used for the development of microcarriers for applications in tissue engineering (Lai and Ma, 2017).

Medical Implants

In general, implantable devices or biomimetic devices are used to replace a damaged organ or structure to facilitate the normal function in the body. Heart, bones, eyes, ears, knees, breasts, hips and cardiovascular system implants are considered the most used implants in medical applications (Rebelo *et al.*, 2017). Some of the well-known advantages associated with biopolymers make this material more feasible for the preparation of biopolymer-based implants. Gelatin, chitosan polyurethane based electrospun materials showed exceptional biocompatibility and cell retention ability, and it can be used in implants for heart valves (Wong *et al.*, 2010). Chitosan, gelatin based composite films showed an improved water absorption and solute permeability rate. It is a transparent and flexible film and can potentially be used for contact lenses (Xin-yuan and Tian-wei, 2004). In another study, chitosan and gelatin blends were cross-linked with genipin and the optimized concentration of the blends showed good cell adhesion and proliferation properties with neuroblastoma cells. This material can be used in the field of nerve regeneration (Chiono *et al.*, 2008).

Drug Delivery Systems

Biopolymer-based composites show numerous advantages in drug delivery owing to their biocompatibility and biodegradability. They function as an excellent carrier molecule for both hydrophilic and hydrophobic drugs in order to achieve sustained drug release. These biopolymers have been shown to possess excellent biocompatibility, hemocompatibility, stability in physiological conditions and are non-immunogenic, they are also considered as a safe material in drug delivery systems. The complexity and structure of the biopolymer facilitates to protect the nativity of the drug and improve their stability in biological conditions. The surface chemistry of biopolymers can be functionalized with specific ligands to achieve targeted drug delivery (Sundar *et al.*, 2016). Hyaluronic acid functionalized gold nanoparticles were conjugated with the drug metformin to target CD44 receptors in HepG2 cells for the treatment of liver cancer (Kumar *et al.*, 2015). Kondagogu gum capped gold nanoparticles were synthesized using sunlight mediated green synthesis; here the anionic polysaccharide based kondagogu gum acted as a reducing, stabilizing and

Table 1 Types, sources, functional role and medical applications of biopolymers

Types of biopolymer	Sources	Functional properties	Various forms of biopolymer in medical applications	References
Collagen	Animals (e.g., fish)	Collagen based materials act as a good carrier molecule and helps to extend the shelf-life of the products	Scaffolds, sheets, tubes, sponges, films, membranes, and composites	(Bhagwat and Dandge, 2018)
Gelatin	Derived from hydrolysis of collagen	It exhibits both positively and negatively charged amino acids, and it facilitates surface modification of gelatin with new functional materials	Microcapsules, microspheres, sealant for vascular prostheses, absorbent pads and dressings	(Han and Lv, 2018)
Silk fibroin	<i>Bombyx mori</i>	It has been integrated with different materials via chemical modification	Films, gels, membranes, powders, porous sponges, wound dressings, matrices, prostheses and implants	(Kim <i>et al.</i> , 2015)
Keratin	Epidermal skin, hair, nails, bird feathers and mammalian hooves	It is a fibrous protein and possesses high physical and chemical stability due to their disulphide bonds	Hydrogels, films, and biomaterials	(Mori and Hara, 2018)
Natural rubber latex	<i>Hevea brasiliensis</i>	It aids to stimulate different cellular processes which includes adhesion, formation of ECM, and promotion of tissue regeneration	Dermal wound dressing materials	(Dhilip Kumar <i>et al.</i> , 2018b; Wattanakaroon <i>et al.</i> , 2017)
Chitin and Chitosan	Animals (e.g., shrimps, crabs)	Chitin and chitosan based biomaterials possess unique properties including hemostatic, solubility, antioxidant, and antibacterial	Wound dressings, coatings (antibacterial and stent), scaffolds, membranes, sensors, carrier molecules, and nanomaterials	(Usman <i>et al.</i> , 2016)
Starch and its derivatives	Plants (stem, tuberous tissues, seeds) and algae	It is composed of glucose units and is semicrystalline in nature	Fibers, films, powders, hydrogels, and sponges	(Hemamalini and Dev, 2018)
Pullulan	Extracellular microbial polysaccharide (<i>Aureobasidium pullulans</i>)	It is highly soluble in water and exhibits very good structural flexibility	Capsules, gels, films, and nanoparticles	(Han and Lv, 2018)
Alginate	Algae	Acts as scaffolds for cell growth in tissue engineering	Hydrogels, microbeads, fibers, and nanomaterials	(Wongkanya <i>et al.</i> , 2017)
Cellulose and its derivatives	Plants (cotton, oat husk, sugarcane bagasse, and peels of bananas, and oranges) and microorganisms (bacteria)	It is a water-insoluble, stable, fibrous polysaccharide. Engineered cellulose aids excellent drug release properties	Hydrogels, and beads	(Gopinath <i>et al.</i> , 2018)
Albumin	Animals (bovine, rat chicken eggs, etc.)	The chemical modification of albumin is easy for drug delivery applications and it shows high binding capacity with different types of drugs	Nanostructures	(Karimi <i>et al.</i> , 2016)
Casein	Whole milk	It possesses a unique amphiphilic nature which contains both hydrophilic and hydrophobic ends. The amphiphilic surfaces has been employed in surface modification	Nanowhiskers, composites, and films	(Gu and Catchmark, 2013)
Hyaluronic acid (HA)	Animals (synovial fluid, vitreous body of the eye and umbilical tissue)	It is a linear polysaccharide and one of the essential components of the extracellular matrix, and HA-based medical products are clinically available for the past three decades	Hydrogels, matrix, films, scaffolds, electrospun fibers, non-woven meshes, sponges, sheets, and nanoparticulate fluids	(Burdick and Prestwich, 2011; Park <i>et al.</i> , 2017)
Chondroitin sulfate	Bovine trachea, and fish (shark)	Used as a therapeutic intervention for osteoarthritis and cartilage damage	Matrix	(Henrotin <i>et al.</i> , 2010)
Laminarin and Fucoidan	Brown seaweed	It aids certain biological functions, which includes the activation of immune cells, and enhances antiviral and antitumor responses	Solution	(Song <i>et al.</i> , 2017)
Sargassum	Brown macroalgae	It is identified as a nutritious seaweed and a rich source of different bioactive compounds. The extracted compounds are functionally used for various therapeutic applications	Medicinal food	(Yende <i>et al.</i> , 2014)

Table 1 Continued

Types of biopolymer	Sources	Functional properties	Various forms of biopolymer in medical applications	References
Carrageenan	Red algae	It is a sulphated polysaccharide and serves numerous applications in tissue engineering (bone, cartilage), wound healing, and drug delivery (antifungal, oral, nasal, ophthalmic, vaginal, and transdermal)	Different forms of hydrogels which include photocrosslinking hydrogels, gradient hydrogels, floating hydrogels, micropatterned hydrogels, hydrogel scaffolds, interpenetrating polymer network, nanogels, and bioinks	(Yegappan <i>et al.</i> , 2018)
Agar	<i>Gelidium cartilagineu</i> , <i>Gracilaria confervoides</i> or related red algae (Class Rhodophyceae)	It is a hydrophilic thermoreversible polysaccharide which acts as a stabilizer, and is widely used as a thickening, water holding and gel forming agent	Beads	(Yin <i>et al.</i> , 2018)
Ulvan	Green algae	It is a water-soluble sulphated polysaccharide and can be applied in both pharmaceutical and food industries	Biomaterials, wound dressings, and hydrogels	(Alves <i>et al.</i> , 2012)
Dextrans	Derived from bacteria	It is a homopolysaccharide and is extensively used as a coating material to improve the biocompatibility in biomedical and pharmaceutical applications	Scaffolds	(Sun and Mao, 2012)
Arabic gum	<i>Acacia senegal</i> and <i>Acacia seyal</i>	It is an edible gum that has the therapeutic efficacy to treat chronic kidney diseases, and is also used in the food industry	Due to their emulsifying, stabilizing, and binding properties, it has numerous applications in the food and medical industries	(Patel and Goyal, 2014)
Kondagogu Gum	<i>Cochlospermum gossypium</i> tree	It is an anionic polysaccharide from the bark and used as an additive material in the pharma industry	Reducing, capping and stabilizing agent for the production of gold and silver nanoparticles	(Dhilip Kumar <i>et al.</i> , 2018a)
Tragacanth gum	Bark of 15 different species of <i>Astragalus</i>	It is an anionic polysaccharide, with a high molecular weight and is soluble in water. It shows excellent structural stability under heat, acidity and long-term storage	Green synthesis of nanoparticles, nanofibers, hydrogels, burn wound dressings, and carrier molecules to achieve controlled release of drugs in drug delivery	(Ranjibar-Mohammadi <i>et al.</i> , 2013)
Xanthan gum	Derived from <i>Xanthomonas</i> bacteria	It is a high molecular weight exo-polysaccharide and is highly water-soluble. It shows a promising beneficial role in tissue engineering due to their shear-thinning and gelling behavior	Biomaterials, hydrogels, wound dressings, scaffolds, and synthesis of nanomaterials	(Kumar <i>et al.</i> , 2018)
Gellan gum	Derived from <i>Sphingomonas elodea</i> bacteria	It is an anionic linear expolysaccharide and has numerous applications in the pharmaceutical industry and medicine. Gellan gum is abundantly used to prepare oral, ophthalmic and nasal formulations	Oral formulations, capsules, beads, gels, granules, tablets, macrobeads, ophthalmic solutions, bioadhesives, and nasal gels	(Osmalek <i>et al.</i> , 2014)
Guar gum	Seeds of <i>Cyamopsis tetragonoloba</i>	It has a wide range of applications in different areas and facilitates surface chemistry functionalization	Nanocomposites, and films	(Auddy <i>et al.</i> , 2013)

capping agent for the production of gold nanoparticles. It facilitated the coupling of folic acid and fluorescein isothiocyanate on the surface of the gum in order to achieve better cellular imaging and folate receptor targeting efficiencies in MCF-7 cells (Dhilip Kumar *et al.*, 2018a).

Wound Healing

Biopolymers play a functional role in wound healing, and biopolymer-based composites are actively used for different types of wounds, which include diabetic wounds, thermal burn injuries, infected wounds, chronic wounds, and normal wounds. Kumar *et al.* (2018) studied the preparation, antimicrobial activity and clinical and commercial application of different types of biopolymer-based biomaterials in wound healing, which include collagen, gelatin, silk, keratin, natural rubber latex, chitin and chitosan, starch, pullulan, alginate, cellulose and hyaluronic acid. These materials are easy to apply on the wound site, are

Table 2 Number of clinical trials, generated from the “<https://clinicaltrials.gov>” database using the keywords (different types of biopolymers)

Keywords used	No. of studies found
Collagen	632
Gelatin	75
Silk fibroin	2
Keratin	16
Chitin	6
Chitosan	44
Starch	127
Pullulan	2
Alginate	41
Cellulose	23
Albumin	347
Casein	95
Hyaluronic acid	341
Chondroitin sulfate	34
Laminarin	1
Fucoidan	5
Sargassum	0
Carrageenan	14
Agar	4
Ulvan	0
Dextrans	26
Levan	13
Curdlan	1
Arabic gum	6
Gum kondagogu	0
Tragacanth gum	0
Xanthan gum	2
Gellan gum	0
Guar gum	5

inexpensive to fabricate and fulfil the needs of clinical expectations (Dhilip Kumar *et al.*, 2018b). Silver nanoparticle loaded chitosan, silk fibroin based biocompatible dressings showed excellent physicochemical characteristics for wound healing, and an *in vivo* mouse study revealed a positive outcome for the treatment of infected wounds (Liu *et al.*, 2017). Polysaccharide alginate, hyaluronic acid based composite materials displayed excellent wound healing effects *in vitro*, and efficiently controlled bacterial growth (Tarusha *et al.*, 2018). Cellulose matrix based nanocomposites have successfully been used for the treatment of acute and diabetic wounds. The nanocomposite based topical dressing facilitated complete wound closure with enhanced tissue repair in an *in vivo* mouse model (Singla *et al.*, 2017).

Fabrication Methodology of Biopolymer-Based Composite

There are different types of methods available to fabricate biopolymer-based composites for medical applications such as casting/solvent evaporation, freeze-drying, electrospinning, 3D printing, deposition-precipitation, nanoprecipitation, film casting, forspinning and gelation. Biofibers (chitosan solution, potato starch solution, long keratin, and ground rachis) were synthesized using the casting/solvent evaporation method. Synthesized bio composites exhibited good compatibility and the mixture of different biopolymers produced strong interactions in the matrix (Flores-Hernandez *et al.*, 2014). Nanotube-biopolymer composite scaffolds (chitosan-gelatin-agarose hydrogels doped with halloysite) were prepared by freeze – drying methods. The study showed excellent *in vitro* cell adhesion and proliferation on the synthesized material without affecting cellular viability and cytoskeleton formation. An *in vivo* rat study proved that the material promotes the formation of new blood vessels (Naumenko *et al.*, 2016).

In another study, room temperature ionic liquids was used to prepare cellulose and heparin-based composite fibers by electrospinning, and the material showed excellent anticoagulant activity (Viswanathan *et al.*, 2016). Chitosan biopolymers showed more favourable outcomes in electrospinning compared with silk, cellulose, collagen, gelatin and hyaluronic acid (Qasim *et al.*, 2018). Lam *et al.* (2002) explained the synthesis procedure of 3D porous starch-based scaffolds (cornstarch, dextran, and gelatin). The 3D printing method allows us to fabricate well-constructed novel biopolymer-based composites with good interconnected porosity (Lam *et al.*, 2002). Biopolymer-based core-shell nanoparticles were successfully synthesized using the

Table 3 Some of the major global clinical trial status of different biopolymers

<i>Name of the Biopolymer</i>	<i>ClinicalTrials.gov Identifier</i>	<i>Condition or disease</i>	<i>Intervention/treatment</i>	<i>Phase</i>	<i>Reference</i>
Collagen	NCT02767817	Brain injury	Injectable collagen scaffold with mesenchymal stem cells transplantation	Phase 1	(Injectable Collagen Scaffold™ Combined With MSCs Transplantation for Brain Injury)
Silk fibroin	NCT02091076	Impaired wound healing	Silk fibroin with bioactive coating layer dressing, Bactigras wound dressing	Phase 1 and 2	(Efficacy and Safety of Silk Fibroin With Bioactive Coating Layer Dressing)
Keratin	NCT02896725	Varicose ulcer	Keratin dressings	NA	(Wool-derived Keratin Dressings for Venous Leg Ulcers (Keratin4VLU))
Chitin	NCT01508039	Health	Chitin micro particle	NA	(Immunological Effects From Intranasal Chitin Micro-Particles (INCA))
Chitosan	NCT01278784	Dry eye syndrome	0.05% Chitosan-N-Acetylcysteine eye drops and 0.1% Chitosan-N-Acetylcysteine eye drops	Phase 1	(Local Tolerability of Chitosan-N-acetylcysteine Eye Drops in Healthy Young Volunteers)
Starch and gelatin	NCT03674684	Coagulopathy	Hydroxyethyl starch	NA	(ROTEM Assessment of Modern Crystalloid, Hydroxyethyl Starch and Gelatin Effect on Coagulation)
Pullulan	NCT00106158	Neoplasms	Protein vaccination	Phase 1	(Safety Study of NY-ESO-1 Protein Vaccine to Treat Cancer Expressing NY-ESO-1)
Alginate	NCT01338077	Gastroesophageal reflux disease	Sodium alginate	Phase 3	(Efficacy and Safety of Sodium Alginate Oral Suspension to Treat Non-erosive Gastro-esophageal Reflux Disease)
Cellulose	NCT00947089	Infections	Oxidized regenerated cellulose (Fibrillar SURGICEL)	Phase 4	(Role of Oxidized Regenerated Cellulose (ORC) Applied to “Dirty” Surgical Wounds (ORC))
Hyaluronic acid	NCT02534415	Wound healing complications – gingival graft donor site	Periodontal dressing material	Phase 4	(Effect of Topically-Applied Hyaluronic-Acid on Palatal Epithelial Wound Closure)
Chondroitin sulfate	NCT00669123	Osteoarthritis, psoriasis, joint diseases, musculoskeletal diseases, and skin diseases	Chondroitin sulfate	Phase 4	(Chondroitin Sulfate Efficacy/Safety in Patients With Knee Osteoarthritis and Psoriasis)
Fucoidan	NCT01399216	Low basal body temperature	Supplement containing fucoidan, EPA, and DHA	NA	(Effects of a Supplement Containing Fucoidan on Basal Body Temperature)
Carrageenan	NCT02382419	Healthy subject human papillomavirus infection	Carrageenan-containing gel	Phase 2	(Carrageenan-Containing Gel in Reducing the Rate of HPV Infection in Healthy Participants)
Agar	NCT02012543	Constipation	Dietary supplement: Agar jelly	NA	(Effect of Agar Administration on Defecation and Fecal Condition in Chronic Constipated Patients)
Dextrans	NCT03070353	Cirrhosis, and liver and acute kidney injury	Dextran 40	Phase 2, 3	(Dextran, a Plasma Expander, Offers New Hope for Patients With Decompensated Liver Cirrhosis and Acute Kidney Injury)
Curdlan	NCT00002100	HIV infections	Curdlan sulfate	Phase 1	(Phase I/II Study of Curdlan Sulfate)
Arabic gum	NCT03348241	Chemotherapy-induced oral mucositis	Arabic gum	Phase 2	(Using Gum Arabic for Cancer Patients to Protect From Oral Mucositis Caused by Chemotherapy: An Experimental Study)
Xanthan gum	NCT01959854	Dry eye	Carboxymethyl cellulose, xanthan gum	NA	(Efficacy of Topical 0.2% Xanthan Gum in Patients With Dry Eye)
Guar gum	NCT01779765	Irritable Bowel syndrome	Hydrolyzed Guar gum (PHGG)	Phase 4	(The Efficacy of Hydrolyzed Guar Gum (PHGG) in the Treatment of Patients With Irritable Bowel Syndrome (IBS))

deposition-precipitation method for the delivery of bioactive molecules in food and pharmaceutical formulations. The material showed good thermal stability at neutral pH, and displayed good stability free from aggregation in the pH range of 3–8 (Hu and McClements, 2015). Starch-based nanospheres was prepared using nanoprecipitation, whereby the size of the nanospheres can be easily controlled by this methodology using simple and efficient modifications. These types of nanospheres aid to load hydrophobic drugs (Tan *et al.*, 2009).

Biocomposite films (chitosan, sago starch, and silver nanoparticles) were synthesized using the method of film casting and was used as a wound dressing material. An *in vivo* wound healing study showed a faster healing pattern compared with untreated controls (Arockianathan *et al.*, 2012). Xu *et al.* (2015) developed a biocompatible biopolymer-based composite nanofiber membrane using the forspinning technique, and the materials showed synergistic antibacterial activity against *Escherichia coli*. The nanofiber membrane enhanced cell attachment and cell growth and mimics the ECM in skin. It can potentially be used for the treatment of deep and intricate wounds (Xu *et al.*, 2015). Metformin loaded bionanofiller composites were produced via the green synthesis ionotropic gelation technique using zinc acetate (cross-linker). The novel material was found to be a suitable carrier molecule for the delivery of metformin for the treatment of type 2 diabetes. An *in vivo* study in streptozotocin-induced diabetic rats showed a substantial hypoglycemic effect (Bera *et al.*, 2018).

Clinical Application and Major Global Clinical Trial Status of Biopolymers in Medical Applications

The research on biopolymer-based composites for clinical applications is considerably increasing, and the detail of the number of studies found from the “<https://clinicaltrials.gov>” database using the keywords (different types of biopolymers) are listed in Table 2. Some of the major global clinical trial status of different biopolymer-based composites are listed in Table 3.

Conclusion

Biopolymer-based composites has numerous advantages in medical applications such as the ability to act as a carrier molecule for bioactive compounds to deliver in a targeted region, high levels of biocompatibility with tissues, cells and cell compartments, good biodegradability, low immunogenicity and efficient antibacterial activity. Biopolymers derived from natural sources offers great opportunities to develop novel biopolymer-based composites and their functional applications in tissue engineering, medical implants, drug delivery systems and wound healing. Recent research and development of biopolymer-based composites has shown successful outcomes by reducing drawbacks associated with biopolymers for their use in medical applications.

Conflict of Interest

The authors confirm that this article content has no conflict of interest.

Acknowledgements

Sathish Sundar Dhillip Kumar is supported by funding from the Claude Leon Foundation, South Africa. This work is based on the research supported by the South African Research Chairs Initiative of the Department of Science and Technology and National Research Foundation of South Africa (Grant no 98337), as well as grants received from the University of Johannesburg (URC), the National Research Foundation (NRF), and the CSIR (Council for Scientific and industrial Research) – NLC (National Laser Centre) Laser Rental Pool Programme.

See also: Biopolymers in the Synthesis of Different Nanostructures. Characterization of Wood, Cork and Their Composites for Building Insulation. Experimental Investigations for Joining of 3D Printed PEEK Substrates for Biomedical Applications. Injected Mold HDPE/Nanoclay Composite Products: Mechanical Properties and Quality. Kenaf Fiber Based Bio-Composites: Processing, Characterization and Potential Applications. Materials Selection Charts for Designing Products With Biocomposites. Performance of Cork and Composites Joints. Polyhydroxyalkanoate and Polylactic Acid Composite. Processing, Properties and Prospects of Nano-Biocomposites. Recycling of Flax Fiber Towards Developing Biocomposites for Automotive Application From a Life Cycle Assessment Perspective

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Biopolymers in the Synthesis of Different Nanostructures

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Introduction

Polymers or so-called macromolecules are known as large molecular structures that contain one or more units, which are repeated within the molecule. The term 'polymer' has its origin in Greek and is derived from the term 'poly' that means many and 'mer' meaning unit. Polymers are usually prepared by a reaction between identical or similar molecules in order to produce a theoretically infinite chain. In reality, reactions usually result in a range of long chains as they are hindered by molecular motions and side reactions. Biopolymers stand among the kinds of polymers, which are generated through the means of living organisms and can be acknowledged as polymeric biomolecules. The term "Biopolymer" stands for a biodegradable polymer, which is recognized as a biodegradable chemical compound and considered the most organic composite throughout the ecosphere. All of the existing biopolymers (DNA, proteins, carbohydrates, lipids, polysaccharides, polyphenols, and nucleic acids) hold a great portion of the human body and ecosphere. Since the whole structure of body and genetic behaviors that is transported from parents to children is based upon DNA biopolymer, they are quite significant for mankind. Representing the most frequently utilized biopolymer, Cellulose contains the greatest abundance as an organic compound on earth, which consists 33% of all the plant components on this particular planet. One of the objectives of biology has been the production of polymers for as long as life has existed. Biopolymers form the basis of genetic encoding, cell structures, and extracellular matrices, while their biodegradability is evident throughout the cycle of life. Among these polymers, the two main classes that are employed nowadays are proteins and polysaccharides. Silk and cotton are excellent examples of biodegradable natural polymers that are used on daily basis. Silk is a protein-based material whereas cotton is known as a polysaccharide-based material and they have been both utilized by humans for millennia to cause great effects. The existing interest in these materials is due to their relative stability in abiotic hydrolysis when compared to relatively rapid biotic degradation. The genesis of biopolymers can be performed by using renewable sources while their biodegradable procedure can be easily achieved due to the presence of oxygen and nitrogen atoms throughout their structural backbone. Biodegradation can alter biopolymers into CO₂, water, biomass, humide matter, and other natural substances, which indicates that they are capable of being naturally recycled through the means of biological methods.

Considering how nanoparticles accommodate specific physicochemical qualities and practical attributes, their utilization as ingredients in food industry is notably expanding. The utilitarian operation of biopolymer particles can be changed by their various dimensions. To be stated as an example, the effects of particle size has been observed on the bulk physicochemical qualities of foods (Optics, rheology, and stability), encapsulation characteristics (e.g., loading, retention, and release), and behavior throughout the gastrointestinal tract (GIT; e.g., transport, degradation, interactions, and penetration). In addition, the significance of surface molecules over the bulk molecules can be intensified by the high ratio of surface/volume that seems to cause an impression on the induced phenomena at the interfaces, such as oxidation or digestion (Matalanis *et al.*, 2012; Li *et al.*, 2011). We have distinguished the data in correlation with the employed monomeric unit and the structure of produced biopolymer (Table 1) (Kaewkannetra, 2012).

The United States Congress Office of Technology Assessment has categorized them into five groups (Ramesh *et al.*, 2010) as the following:

- Nucleic acids
- Proteins
- Polysaccharides
- Polyhydroxyalkanoates
- Polyphenols

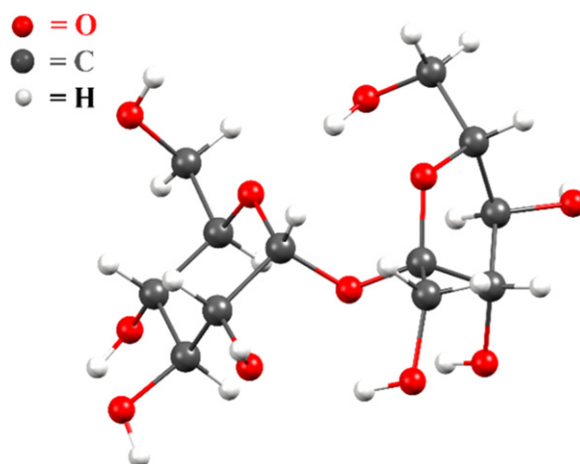
Biopolymer can be also distinguished (Table 2) (Yadav *et al.*, 2015) as the following by considering their origins:

Table 1 Classification of biopolymers in accordance with the utilized monomeric unit and structure

Classification	Description
Polynucleotides	DNA and RNA which are long polymers composed of 13 or more nucleotide monomers
Polypeptides	Short polymers of amino acids
Polysaccharides	Linear, bonded polymeric carbohydrate structures

Table 2 Classification of biopolymer based on their origin

Type	Example
Polyesters	Polyhydroxyalkanoates, Polylactic Acid
Proteins	Silk, Collagen, Elastin, Resilin, Adhesive, Polyaminoacid, Soy, Zein, Wheat Gluten, Casein, Serum Albumin
Polysaccharides	Plant/Alga Starch, Cellulose, Agar, Alginate, Carrageenan, Pectin, Konjan, Various Gums Animal Chitin, Hyaluronic Acid, ... Bacterial Xanthan, Dextran, Gellan, Levan, Curd Lan, Polygalactosamine, Cellulose Fungal Pollulan, Elsinan, Yeast Glucans
Lipids/Surfactants	Acetoglycerides, Waxes, Emulsion
Polyphenols	Lignin, Tannin, Humic Acid
Specialty Polymers	Shellac, Poly Gamma Glutamic Acid, Natural Rubber, and Synthetic Polymers from Natural Fats and Oils

**Fig. 1** Structure of sucrose showing the glycoside bonds.

Sources and Structure of Some Natural Polymers

All of the existing proteins can be classified as biodegradable. The cycle of life relies on the ability of breaking down and reusing the amino acids of proteins in order to construct cells, enzymes, and many other building blocks of complex organisms. Their structures are commonly complex, not just in their chemical make-up, but also throughout their exact structure. The process of folding and coiling proteins into specific geometries can influence their properties and functionalities. At elevated temperatures, the thermal disruption of these complex structures usually results in spelling the end of life for most organisms. The degradation procedure of proteins is dependent on some specific enzymes, while the simple chemical degradation seems to be generally slow without enzyme intervention. Throughout this particular section, we aim to briefly discuss the chemistry and properties of some natural polymers.

Polysaccharides

Polysaccharides are capable of forming a massive class of natural polymers, which are often modified before being utilized. They can compose some of the first polymeric materials that are used by humans for manufacturing applications, along with nitro-cellulose which was once employed for the production of films and gun cottons. The polysaccharide class of natural polymers is based upon polymers with repeat units which are founded by sugars. The sugar repeat units that exist on the backbone of polysaccharides contains many chiral centers that determine the exact saccharide. For example, all of the available saccharides carry the same nominal formula, $C_6H_{12}O_6$; however, each one is distinctly different due to their particular chiral nature. Within a polysaccharide, the saccharide repeat units are apparently connected via the oxygen of carbon 1, which forms a glycosidic bond with carbon 4 in another molecule, subsequent to the elimination of water. Fig. 1 illustrates an example of this process, while the source structure can be also observed.

Cellulose

There is a large number of polysaccharides that are being employed as degradable polymers, while cellulose (Fig. 2) probably stands as the most commonly utilized, which is the general component of cotton. This substance is acknowledged as a significant and captivating biopolymer and contains an exceptional position throughout daily life and industrial applications since next to

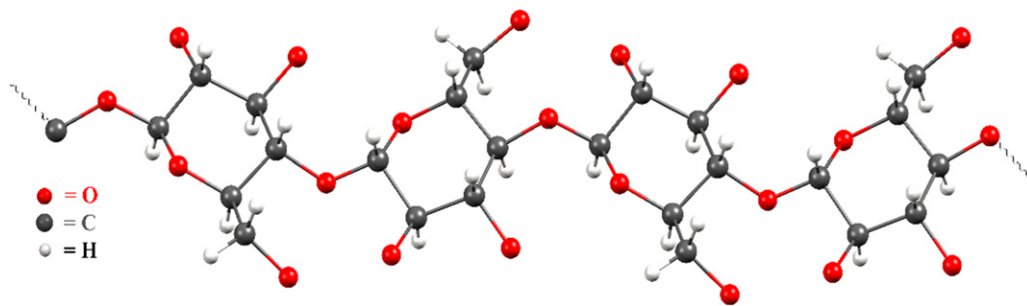


Fig. 2 Molecular structure of Cellulose.

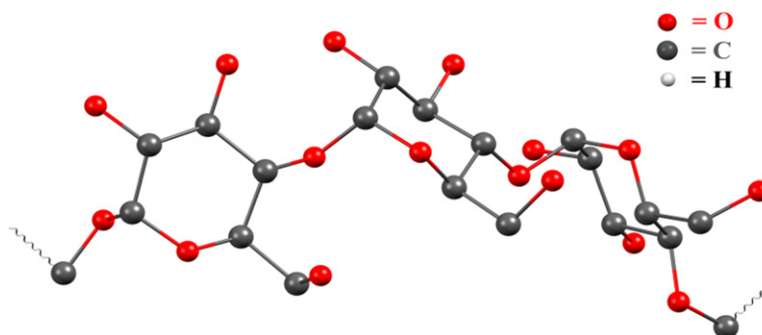


Fig. 3 Molecular structure of Starch.

being a sustainable natural raw material, it is almost impossible to exhaust cellulose. It should be mentioned that this particular substance is a promising pyrolysis precursor for providing carbon's species (Ruan *et al.*, 2018), which can be discovered within the cell walls of superior plants. Cellulose accommodates various favorable qualities, including mechanical robustness, hydrophilicity, biocompatibility, biodegradability, relative thermostability, high sorption capacity, and alterable optical appearance, and is known to be the most plentiful and copious biomass material that nature has to offer (Hu *et al.*, 2014).

The alteration process of a polymer usually involves the modification of OH groups that exist on the backbone of the designated polymer by the utilization of an acid anhydride. The performance of this sequence can result in various degrees of substitution in order to obtain ester functionalized celluloses (Edgar *et al.*, 2001). It must be noted that similar modifications have been attempted with other polysaccharides as well (Campoccia *et al.*, 1998). Although the amazing features of cellulose have given it the potential to be employed throughout a wild range of fields, yet from the Approximately 5×10^{11} metric tons of this substance that is produced yearly, only 2% is apparently recovered industrially (Qiu and Hu, 2013).

Other polysaccharides that build the different parts of this group of degradable polymers include starch, larch gum, alginic acid, agar, carrageenan, chitin, hyaluronic acid, dextran, gellan gum, and pullulan. Most of these polysaccharides structures are complex and a full discussion on their topic is available in the literature (Mano *et al.*, 2007). Among the mentioned substances, starch, cellulose and larch gum are plant derived (although cellulose may also be obtained from microbial sources), while alginic acid, agar, and carrageenan are commonly obtained from algae, chitin and hyaluronic acid are procured from animal sources or microbial sources, and the others are achieved from microbes.

Starch

Being formulated by linear amylose and branched amylopectin chain (Fig. 3), starch is known to be a genuinely plentiful polymeric carbohydrate (Finkenstadt and Willett, 2004).

The available semi-crystalline starch granules can be altered into an amorphous state through the utilization of gelatinization method (Ai and Jane, 2015). The observation of water molecules that seemed to be tightly and loosely bounded as an effect of the starch chain network throughout the procedure has been quiet fascinating, which can force reasonable ionic conductivity out of starch and label it as a solid polymer electrolytes (SPEs) (Shukur *et al.*, 2014; Liew and Ramesh, 2015; Raeis-Hosseini and Lee, 2016). The origin qualities of starch need to be improved for the purpose of achieving practical materials, since this substance contains high water sensitivity and poor mechanical features when it is contrasted with those of synthetic polymers (Mourya *et al.*, 2010). Starch and biopolymer have been chemically modified in synthetic polymers (Mohanty *et al.*, 2000). Plants such as potato, rice, maize (corn), and cassava are the utilized raw materials for the production of biopolymers. The main component of these specific plants is starch, which is capable of being employed in biodegradable materials due to being cheap, available, and

produced from renewable resources. Starch is known to be the mixture of two D-glucan homo polymers, is composed of α -D-glucopyranosyl units (AGU) that includes amylose and amylopectin. The molecular weight of amylose relies on the starch origin (Patil, 2010), which generally contains a lower molecular weight if it has been extracted from cereals. Considering its abundant and being a polysaccharide that is naturally induced, starch has been commonly utilized for the preparation and evaluation of edible biodegradable films (Tuil *et al.*, 2000).

Chitin

poly (-(1-4)-N-acetyl-D-glucosamine) that is acknowledged as chitin has been initially discovered in 1884 and recognized as a significant and vital natural polysaccharide. The synthesizing process of this particular biopolymer is achieved by the employment of a vast number of living organisms, while this substance has occupied the second position after cellulose in regards to the portion of its annual production as well as its abundance as a polymer. Chitin is generally perceived throughout the nature in the shape of ordered crystalline microfibrils that produce structural components within the exoskeleton of arthropods or cell walls of fungi and yeast. It can be also composed through different other living organisms that exist in the fields of lower plant and animal kingdoms and diversely operate upon the requirement of reinforcement and strength. Chitosan stands as the most notable derivative of chitin, which is procured either through the application of (partial) deacetylation of chitin within the solid state and under alkaline circumstances (concentrated NaOH) or by enzymatic hydrolysis in the appearance of chitin deacetylase. The achieved chitosan by the means of solid-state reaction seem to contain a heterogeneous distribution of acetyl groups along the chains, which is apparently caused by the semi-crystalline morphology of chitin. Chitin and chitosan have proved to be biocompatible, biodegradable, and non-toxic polymers (Jayakumar *et al.*, 2010).

Proteins

Considering how proteins can be applied for enhancing new blend and/or composite materials, they seem to be more practical than the other natural polymers. The structural form of proteins has been observed to be either globular or fibrous when they are stabled in their natural state. A sphere-shaped structure has been perceived in globular folded proteins, which are held mutually through the existing disposition of hydrogen, ionic, hydrophobic, and covalent (disulfide) bonds. On the other hand, the structure of fibrous proteins seems to be completely extended and coupled quiet strongly together in the form of parallel constructions, which are generally induced by the means of hydrogen bonds for the purpose of developing fibers. The chemical and physical qualities of these specific proteins apparently rely on the comparative portion of amino acid resultants, along with their position next to the polypeptide chain. The chemistry and science of polymers can be improved by the utilization of amino acid sequence and other organic and synthetic polymers. Moreover, this assessment can be more profiting if there are adjustments in chemical and protein engineering in order to obtain a novel design of polymers from proteins. Several scientists have performed investigations on the blends of protein with nonprotein, natural, and synthetic molecules including keratin-chitosan (Tanabe *et al.*, 2002), glutenmethyl-cellulose (Zuo *et al.*, 2009), keratin-polypropylene, keratin-cellulosepolypropylene (Bullions *et al.*, 2003, 2004; Schuster, 2000), and keratin-polyethylene (Barone and Schmidt, 2005) etc., and it has been suggested from their observations that the features of native protein film has been enhanced to some extend (i.e., film strength, flexibility, and water vapor permeability, etc.). The application of gluten (Mojumdar *et al.*, 2011), milk protein (Ramos *et al.*, 2013; Bahram *et al.*, 2014), and soy protein (Su *et al.*, 2010) has been employed for the production of edible film, while keratin implementation for the growth of nanofiber (Aluigi *et al.*, 2008), film (Barone *et al.*, 2005), and composites (Bertini *et al.*, 2013) in the field of material industries has been evident. Protein based natural polymers are intensely getting involved throughout the various fields of biomaterials (Xing *et al.*, 2011), packaging material, and coatings industries (Scheller and Conrad, 2005). Throughout the present article, we have facilitated the featured of protein within its native state in regards to the genesis of bio-based polymer and polymer reinforcement methods in order to upgrade the characteristic/qualities of peptide polymer, which will probably lead to novel designs of polymers. An inclusive analysis has been presented in regards to the implementation of mentioned protein blends and composites, which are ranging from micro to macro structural level.

Silk

Silk is known as a protein that is based upon the large extent of the fragment Gly-Ala-Gly-Ala-Gly-[Ser-Gly-(Ala-Gly) n]8-Ser-Gly-Ala-Ala-Gly-Try (Lucas *et al.*, 1962). This specific substance has caught the attention of many due to its high tensile strength and excellent mechanical properties. The high performance of silk is thought to be a result of the large numbers of ordered sheets that is caused by the folding of proteins. Silk itself is obtained from the cocoons of mulberry silkworm (*Bombyx mori*) and is generally procured by unravelling the fibers that enwrap the cocoon. Nowadays, the larvae themselves are particularly farmed. The ease of obtaining silk with little processing has explained its prevalence since ancient times.

Collagen

The quaternary structure of collagen is acknowledged to be composed of three lefthanded helices that are deformed into a right-handed coil. Collagen is formed by a cluster of naturally induced proteins that can be discovered within animals and due to its un ordinary features including biodegradability and weak antigenicity (Lee *et al.*, 2001), it has been labeled as a significant biomaterials in regards to tissue engineering implementations. The fibers of collagen are generally observed to be a white, opaque, and viscoelastic matter, which

usually demand a high tensile strength along with less extensibility. This specific material contains the role of biomaterial throughout the fields of drug delivery systems (Friess, 1998) and tissue engineering (Pachence, 1996). In accordance with the analysis of a scientist, the Young's modulus of the rat tail collagen Type I seem to vary between 3.7 and 11.5 GPa (Wenger *et al.*, 2007). In order to be utilized for fabricating practical biomaterials that can be employed in clinical application, a sequence of investigations has been targeted on the structural and tensile qualities of collagen scaffolds (Chen *et al.*, 1995; Matsuda *et al.*, 1993; Yannas and Burke, 1980).

Keratin

Being the kind of a protein that holds bonds of disulfide, Keratin contains an array of features that varies from a structurally robust, impact-resistant substance (horn) towards an uncomplicated waterproof layer (turtle shell). It is known that this material is mechanically functional in both tension (wool) and compression (hooves) circumstances (Feughelman, 1959). Keratins can be discovered within hair, wool, claws, nails, skin, fur, hooves, beaks, feathers, horns, scales, and actin, while the myosin protein is commonly observed in muscle tissues. The difference in content of sulfur is the principal reason behind the existence of various keratins. The appearance of lots of cysteine disulfide crosslinks will result in decreased flexibility, as it can be perceived in claws, hooves, horns, and nails, while in regards to textures such as wool, skin, and muscle proteins, there are apparently less disulfide crosslinks and although a bit of stretching is possible, yet it will return to the normal position as the tension is reduced.

Synthetic Biopolymers

Unlike natural polymers, degradable synthetic polymers may be readily mass produced on a multi-ton scale and contain properties that are similar to nondegradable polymers. There is a vast range of degradable polymers and many others are being discovered and appended to this list on a daily basis; however, they may be divided into several classes since each one can contain specific properties. The properties of a degradable polymer depend on the ability in its manufacturing procedure and its components without significant degradation, as well as accommodating a suitable lifetime for the final material to fulfill its role. The challenge of balancing these factors has driven continued research towards this area. Moreover, the wide range of applications for degradable polymers usually dictates the type of polymer that is required to be used. To be stated as an example, a degradable polymer for human implant, which functions as a slow release mechanism, must not degrade into toxic or irritating components that could cause an inflammatory response. There are three main classes of degradable synthetic polymer, including polyesters, polycarbonates, and polyanhydrides, and in addition to these, a different range of polymers exists that involves other degradable groups including amino acids and phosphates.

Polyesters

Polyesters contain the ester linkage between monomer units. This type of bond is usually, but not exclusively, formed via either a trans-esterification reaction or a ring opening reaction. There are five main polyesters which are considered to be biodegradable: polyglycolic acid (PGA), polylactic acid (PLA), poly-*ε*-caprolactone (PCL), polyhydroxybutyrate (PHB) and polyhydroxyvalerate (PHV). PGA, PLA and PCL are all readily prepared via ring-opening polymerizations (Labet and Thielemans, 2009). Typically, polymers are composed in the molten monomer by using a catalyst (octanoate) for the purpose of promoting the ring opening process. Tin octanoate is known as a traditional catalyst and due to the hazards of its usage and associated toxicity, there have been several other catalysts developed over the recent years, whereas in this respect, the production of catalysts for controlling the chiral centers in PLA has been of particular interest (Thomas, 2010).

Polycarbonates

Polycarbonates are a similar class of polymer to polyesters and can be prepared through a similar ring opening polymerization process to that of the mentioned polyesters (Rokicki, 2000). The examples of polycarbonate-based degradable polymers have been restricted within the main to poly (trimethylene) carbonate.

Polyanhydrides

The polyanhydrides are perhaps some of the least hydrolytically stable degradable polymers. There are many examples that hold the anhydride group as part of their repeat unit. Poly(1,3-bis-*p*-carboxypheloxypropane anhydride) is probably one of the best representatives of the degradable polyanhydrides that are currently being utilized (Kumar *et al.*, 2002), as well as being generally prepared by the means of condensation reactions.

Biopolymer Nanofibrils

Biopolymer nanofibrils stand as the universal nano-building blocks throughout the field of natural materials (Neville, 1993; Meyers and Chen, 2014; Naleway *et al.*, 2015), such as cellulose nanofibrils (CNFs) that exist within plants and bacteria, chitin nanofibrils (ChNFs) in animals, and silk nanofibrils (SNFs) existing in spider and silkworm cocoon silks, as well as collagen nanofibrils (CoNFs) that can be discovered in ligaments, mammalian tendons, and bones. Being constructed from various biopolymer molecules, biopolymer nanofibrils

seem to contain different chemical reactivities such as cellulose, chitin, silk fibroin, and collagen; nevertheless, at higher structural levels they apparently possess similar properties. In addition, CNFs, ChNFs, SNFs, and CoNFs represent the four most plentiful biopolymer nanomaterials that nature has to offer and considering how they contain fascinating mechanical qualities, wide-availability, sustainability, biocompatibility and biodegradability (ChNFs, SNFs, and CoNFs), many scientific and commercial interests have been focused on these materials over the past years (Xiong *et al.*, 2018; Chen *et al.*, 2018; Kumar, 2000). Nonetheless, it is of great value to perform qualified investigations on these particular biopolymer nanofibrils since beside being the most plentiful among their kind on earth, they also stand as the four prototypes that have demonstrated the nature capability in producing similar constructions with the utilization of different elements (Ling *et al.*, 2018). A sequence of top-down and bottom-up tactics have been arranged and done for the purpose of procuring biopolymer nanofibrils. Considering the prospects of biopolymer nanofibril implementations, CNFs, ChNFs, SNFs and CoNFs seem to accommodate various significant and typical characteristics that rise from their nano-size influences, which involves ultra-high specific surface areas and length to diameter ratios (Liu *et al.*, 2014; Wu *et al.*, 2016), nanoporous structure (Ling *et al.*, 2016, 2017), nano-confinement effects (Giesa *et al.*, 2014), and optical transparency (Ling *et al.*, 2014). The existence of these specific features that are quiet common in biopolymer nanofibrils has created the possibility of inventing and employing these substances in similar procedures.

Cellulose Nanofibrils

Nanocellulose is known to be the most plentiful biopolymer nanomaterial that can be discovered in the living world (Moon *et al.*, 2011), which is commonly formed through plants, marine animals, algae, fungi, and amoeba. The functionality of CNFs in most of the existing organisms is to be the structural components within the cell walls. We can distinguish and place Nanocellulose in the group of cellulose nanocrystals (CNCs) and CNFs, which would be in correlation with their morphology. CNFs can be alluded to nanofibrils that hold long lengths and high aspect ratios and on the other hand, the nanofibrils that accommodate high crystallinity and relative shorter lengths along with lower aspect ratios are acknowledged as CNCs or cellulose nanowhiskers. In addition, the expression of cellulose nano-objects has been utilized for describing both CNFs and CNCs. Being directed to nanostructured cellulose that are generated by bacteria, bacterial cellulose (BC) is recognized as another kind of CNFs (Wu *et al.*, 2015). Four various crystalline conditions have been perceived for cellulose, cellulose I, II, III, and IV, which promotes dissimilarities upon the position of hydrogen bonds between and within strands. Being interpreted as the native nanocrystal structure, cellulose I contains two allomorphs, i.e., I α and I β . The I α crystalline seem to have bacteria and algae under its influence, while the I β crystalline is apparently abundant in plants (Oehme *et al.*, 2015). Being the principal element of wood, crystalline cellulose is the key factor in figuring the stiffness and strength of a wood. This particular substance has not been observed to exist alone within most of the biological material throughout the nature, but congregates with various kinds of organic materials for the purpose of shaping composites. To be stated as an example, CNFs can be discerned in the wrappings of soft matrixes that are formulated by hemicellulose and lignin within wood (being the most plentiful resources of cellulose). The vast employment of CNFs for developing optoelectronic, energy, and environmental devices throughout scientific and commercial fields has been quite evident. The global manufacturing capacity of nanocellulose (involving CNFs and CNCs) has been approximately on the order of 600 metric tonnes/year throughout 2013, while the capability of future global market has been estimated to be 35 million metric tonnes/year (Arvidsson *et al.*, 2015). The evolution of many innovative CNF/CNC-based nano-composites have been arranged upon the different methods of coordination hybridizing (Saito *et al.*, 2014; Hamed *et al.*, 2014; Malho *et al.*, 2015). A flexible procedure for the production of polymer nano-composites has been invented, which involves the application of tunicate CNCs as its building blocks (Capadona *et al.*, 2007). Additionally, CNFs are known to be fascinating raw materials for the construction of practical aerogels/foams as well (Svagan *et al.*, 2008; Kettunen *et al.*, 2011; Khan *et al.*, 2016; Tian *et al.*, 2015a). In order to produce magnetic aerogels, freeze dried BC aerogels have been employed in the role of templates that were further compacted to turn into a stiff magnetic nanopaper (Olsson *et al.*, 2010). The slender size (smaller than the wavelength of visible light) along with high mechanical- thermal- performances can be considered as some of the rare features of CNFs that can finance its auspicious implementations throughout the optical fields. It has been proved that the CNF-based optical materials can accommodate high optical transparency, superb flexibility, and reduced thermal expansion. Although CNFs are not capable of conducting electricity on their own, yet their combination with other electrically conductive substances can be well situated for establishing electronic materials. By the application of vacuum filtration, different conductive materials have been formed and deposited on the CNF-derived nano-papers, which includes silver nano-wires, graphene, and carbon nanotubes (CNTs) (Koga *et al.*, 2014; Yan *et al.*, 2014). As there are many requests for CNFs in regards to the electronic devices, it must be noted that a combination with functional electrochemistry substances is needed for the utilization of CNFs in energy-related applications, such as graphene (Zheng *et al.*, 2017; Gao *et al.*, 2013) and conductive polymers (Wang *et al.*, 2015, 2013). Recently, the assessment of CNF-based substances throughout the field of solar cells is becoming quiet apparent (Zhou *et al.*, 2013; Nogi *et al.*, 2015). An intensifying light absorption within the active layer can be caused by CNF nano-papers, since they contain large forward light scattering that can extend the length of light path (Hu *et al.*, 2013). CNF films can be employed without being altered as filtration membranes throughout the relative procedures of environmentally-related purification, due to their intertwined and packed CNF networks. The usage of CNF membranes for the task of filtering nanoparticles (including inorganic nanoparticles, bacteria, and viruses) has been determined due to their size exclusion, considering how CNF membranes contain smaller pore sizes in comparison to most of the other nanoparticles (Metreveli *et al.*, 2014).

Chitin Nanofibrils (ChNFs)

Being a derivative of glucose in chemical terms, chitin can be generally acknowledged as a cellulose analog –, which is a long-chain polymer of (1,4)- β -N-acetylglucosamine (Fig. 1) (Ogawa *et al.*, 2016). The advantageous features of chitin has been preserved by ChNFs while demonstrating a fascinating biocompatibility, biodegradability, reduced immunogenicity, and antibacterial functionality, which is quite different from CNF-based materials that are fabricated from top-down approaches and commonly result in deficient biocompatibility and biodegradability (Jayakumar *et al.*, 2010; Muzzarelli, 2011; Anitha *et al.*, 2014; Rinaudo, 2006). The appealing chemical, morphological, and mechanical benefits of ChNFs have been evident throughout their implementations in the field of tissue engineering (Islam *et al.*, 2017; Kiroshka *et al.*, 2017). Moreover, for the enhancement of strength and cell adhesion of the designated materials, ChNFs have been merged with different synthetic polymers and biopolymers, including polyglycolide, polycaprolactone, polylactic acid, collagen, cellulose, silk, and chitosan (Siró and Plackett, 2010; Fernandez *et al.*, 2005). It is apparent that the deacetylated ChNFs have advanced the proliferating process of fibroblasts that has led to the creation of proliferation and re-modeling phases throughout the procedure of wound healing (Izumi *et al.*, 2015). In contrast to the mentioned fact, chitosan is known to be a little bit soluble within acidic aqueous media and as a derivative of chitin, it has the potential to turn into nanofibrils if certain circumstances are facilitated (Ding *et al.*, 2014). Functioning as a substrate has been another application of CNFs for the purpose of keeping the companion of other components, such as gold nanoparticles, which results in the manufacturing of biosensors (Gomathi *et al.*, 2011). Considering its position as the most plentiful natural nitrogen-containing biomacromolecule, chitin has the capability of being modified into N-doped carbon-based materials and utilized in the role of electrocatalysts for the reactions of oxygen reduction (Borghei *et al.*, 2018). In accordance with the reported observations, Chitosan nanofibril-based materials are capable of displaying fascinating features in adsorbing multiple cations, anions, and radionuclides within air and aquatic habitat pollutants (Bhatnagar and Sillanpää, 2009; Jiuhui, 2008; Haider and Park, 2009).

Silk Nanofibrils (SNFs)

SNFs stand as the most essential nano-elements within the structures of spider and silkworm cocoon silk fibers, which have been perceived to contain some similar constructional characteristics in various species. To be stated as an example, a beaded topological construction has been promoted by all of the single SNFs, which are apparently linked by homogeneous nano-globules that have a diameter fluctuation within the range of 3–5 nm. In the cases of spiders and silkworm cocoon silks, these particular nanofibrils can be bundled into 20–200 nm thick fibrils (Also expressed as microfibrils) and be further processed to turn into silk fibroin filaments (Nguyen *et al.*, 2015). With regards to the appealing features of Silk fibroin, which include biocompatibility, tunable biodegradability, and adaptable processability, a great amount of investigation has been performed on this topic in biomedical fields (Vepari and Kaplan, 2007). Nevertheless, it must be noted that in comparison with silk fibroin, SNFs have shown more different properties for biomedical implementations. Generally, SNF hydrogels and scaffolds can be discovered within hierarchical micro- and nanoporous constructions, which have proved to be beneficial in regards to cell adhesion/migration and nutrient transmission (Liu *et al.*, 2014). It has been suggested by some of the past reports that in order to achieve the effects of nano-size and high specific surface area of single nanofibrils, the pore size of SNF elements should be adjusted towards the range of designated nanometer scale (Ling *et al.*, 2017, 2014). The biominerals (e.g., calcium carbonate (Bai *et al.*, 2014) and hydroxyapatite nanocrystals (Mi *et al.*, 2016)) or inorganic nanomaterials (e.g., silver and gold nanoparticles (Dong and Lu, 2014; Lv *et al.*, 2017)), which had been fabricated through the course of the procedure, seemed to be confined in the networks of SNF and therefore ended up in a stabilized situation in the form of a suspension within the solution.

Collagen Nanofibrils (CoNFs)

Collagen contains the largest quantity of protein that exists in the body of mammals, which is approximately 25%–35% of their protein content (Di Lullo *et al.*, 2001). Until now, Type I, II, III, IV, and V stand as the most general kinds of collagen in between the 28 types that have been discovered, while type I, II, III, V, and XI are known to be built of fibrillar constructions (Cen *et al.*, 2008). Consisting 90% of all the existing collagen in the body, type I collagen has been identified as the principal collagen that can be observed in bones, tendons, corneas, and ligaments (Di Lullo *et al.*, 2001). CoNFs have caught the attention and interest of many, especially for biomedical implementations, due to containing fascinating biological qualities that include high biocompatibility, biodegradability, and weak antigenicity (Lode *et al.*, 2016; Shen *et al.*, 2014). In regards to biomedical applications, CoNFs have been utilized in massive quantities for cartilage repair, considering how the existence of non-vascularized tissues results in reducing the potential of cartilage for intrinsic regeneration and thus, cause this procedure to be quiet challenging (Rosenzweig *et al.*, 2017; Lode *et al.*, 2016). The compatibility of CoNFs with a series of biopolymers and inorganic materials, such as chitin/chitosan, (Shen *et al.*, 2014), silk fibroin (Vepari and Kaplan, 2007), silver nanoparticles (Srivatsan *et al.*, 2015), minerals (Maté-Sánchez de Val *et al.*, 2014), ceramics (Brodie *et al.*, 2005) have been approved, while this harmony can be further processed into versatile composites in order to fulfill the necessities of their applications throughout blood vessels, heart valves, and nervous and bone tissue engineering. On account of their unique hemostatic and antibacterial features, low antigenicity, and biocompatibility, the application of CoNFs can be considered for composing mechanically robust and biodegradable materials, which can be utilized for wound sutures and reconstructive surgeries (Maffia *et al.*, 2004; Huang *et al.*, 2009). Next to being beneficial throughout the treatment of idiopathic pulmonary fibrosis immunotherapy (Wilkes *et al.*, 2015), arthritis, and rheumatoid

arthritis (Woo *et al.*, 2017), collagen has been recognized as a natural nutrient (a cholesterol-lowering food) (Sun *et al.*, 2011) that is capable of performing a well-organized dermal matrix synthesis. Regarding the application of CoNFs in food industry, this substance is commonly provided as edible meat casings, binders, emulsifiers and extenders in sausages and hams, next to being employed in the role of additives for advancing the capacity of water holding and enriching the tastes of meats (Schilling *et al.*, 2003). The health of humans has been severely threatened by the effects of induced amassing within the living organisms, which is caused by environmental contamination and specifically heavy metal ion pollutants (Maffia *et al.*, 2004), while as it has been previously noted, most of the discovered ultrafiltration membranes and adsorbents are either incompetent or can only partially discard and eliminate the heavy metal ions of contaminated solutions. The vast utilization of CoNFs for the production of heavy metal ion adsorptive materials has been quiet evident throughout the past decade (Huang *et al.*, 2009; Sun *et al.*, 2011). Additionally, this substance is capable of displaying integrating behaviors with other materials for water treatment purposes, which is similar to the features of CNFs, ChNFs, and SNFs; some of the examples of this procedure would be the processing of CoNFs into composite systems with Zr (IV) to obtain fluoride adsorption (Liao and Shi, 2005), Fe(III) and Al(III) to discard and eliminate phosphate (Huang *et al.*, 2009), and tannins to achieve uranium adsorption (Liao *et al.*, 2004).

Application of Biopolymer in the Synthesis of Nano-Structures

In accordance with the available data, there are lots of metal and metal oxide nanoparticles that are capable of functioning as sorbents, catalysts, sensors, reducing agents, and bactericides due to their rare and specific qualities (Yazdi *et al.*, 2018a,b; Charbgoor *et al.*, 2017; Hasanazadeh *et al.*, 2018; Khorrami *et al.*, 2018; Moghaddasi *et al.*, 2018). Although these particular nanoparticles can provide fast kinetics and improved sorption capacity because of their high surface to volume ratio, yet the existing disadvantages, including propensity to aggregation, exceeding reduction of high pressure in the course of flow-through systems, the absence of specificity throughout reactions in complex systems, and deficient mechanical strength, have usually terminated their chances of constant real-life applications. Acknowledged as a whole different kind of organic materials, functionalized polymers and biopolymers have been approved of being robust, chemically stable, and amenable to chemical adjustments, which are dependent on the requirements of the designated implementation. The sudden progress of these synthetic and semi-synthetic functionalized materials, which are in many cases expressed as reactive polymers or ion exchangers, can be clearly perceived throughout the course of the last five decades by their existing reports of multitude scientific attempts that varies from mining to microelectronics, deionization to decontamination, synthesis to sensing, drug delivery to desalination, and etc (Zagorodni, 2006). This project aims to portray polymer-supported metal or metal oxide nanoparticles as a novel type of hybrid polymeric/inorganic materials, which are capable of presenting features and application opportunities that have not been observed by solitary polymeric host materials or inorganic nanoparticles. We have labeled these particular classes of hybrid materials as polymer supported nanoparticles (PSNPs) in our context for the readers convenience. The distribution of metal and metal oxide nanoparticles throughout the PSNPs within the polymer phase has been performed in conformity with in-situ and ex-situ procedures. Despite the constant presence of metal and metal oxides as nanoparticles in PSNPs, yet there is a vast range of possibilities in regards to the morphology or physical arrangement of polymeric materials, which could differ from spherical beads to granules, membranes, fibers, and other structures. It can be stated from the observations that although polymer and metal/metal oxide nanoparticles can preserve their intrinsic qualities at the level of nano-scale, yet it is effortlessly possible to make modifications to supplement the overall features of PSNPs in different ways.

Metal Nanoparticles

Gold (Au)

The interest of many scientists has been captured by gold nanoparticles (Au-NPs), which is probably due to their fascinating qualities including simple synthesizing process and functionalization, chemical stability, low inherent toxicity (biocompatibility), and tunable optical and electronic properties (absorption, fluorescence, and conductivity) (Eustis and El-Sayed, 2006). There are three ways that the polymer scaffold in AuNPs–polymer composites can be utilized: (1) congregating the NPs and turning them into composite materials, (2) being modified as a matrix that can cause ordering and anisotropic orientation in clusters and on surfaces, and (3) taking the role of a functional element (e.g., possess an electronic property). In order to manufacture novel materials, the Polymer-mediated self-assembly of AuNPs can facilitate a flexible and practical method for this purpose. This “bottom up” technique can result in coupled AuNPs that contain varied nano-sized building blocks, such as linear, branched, and block copolymers, along with biopolymers that include proteins and DNA. The flexibility and reversibility of self-assembly procedures, which are conveyed through the means of certain molecular interactions, can provide the genesis of defect-free superstructures, while having the potential of being further studied throughout different fields varying from electronics and materials science to molecular biology (Ofir *et al.*, 2008). The modification of AuNPs is also possible by the utilization of carbohydrates or carbohydrate derivatives. Combemale *et al.* have demonstrated the production of AuNP neoglycoconjugates, which were decorated with mannose-6-phosphate (Man6P) analogues and procured through various synthetic methods (Combemale *et al.*, 2014). In order to evaluate their angiogenic activity, we have tested the AuNPs that had been functionalized with Man6P analogues through the usage of chorioallantoic membrane (CAM) assay, while the obtained results have indicated the

existence of anti-angiogenic activities in all the samples via the Man6P receptor, along with the lack of any apparent toxicity. Hyaluronic acid (HA) has been employed for the purpose of decorating AuNPs. A novel polysaccharide-Au nano-cluster supra-molecular conjugates has been fabricated by the usage of AuNPs, which bear adamantane moieties and β -cyclodextrin-grafted HA (Li *et al.*, 2014). Various anticancer drugs have been injected into the porous structure of the nanoparticle conjugates.

Silver (Ag)

The different and upgraded physicochemical qualities of silver nanoparticles (AgNPs), in comparison to the bulk silver, have been announced by various reports. The utilization of Silver nanoparticles in a vast range of applications have been evident, such as drug delivery and molecular imaging of cells, while various reports have emphasized their anti-inflammatory, anti-microbial, and wound healing activities (Braydich-Stolle *et al.*, 2005; Alt *et al.*, 2004; Kandamchira *et al.*, 2013). Different biopolymers, such as chitosan, alginate, etc., have been widely employed throughout the synthesizing procedures of nanoparticles. It has been observed in a particular research that the curcumin caged AgNPs were capable of causing an upgrade in the viscosity and self-assembly procedure of collagen, while advancing its mechanical and thermal qualities as well. Curcumin caged silver stabilized collagen stands as an exemplary candidate for biomedical implementations (Srivatsan *et al.*, 2015). In addition, the capability of AgNPs in being notable antimicrobial agents have been confirmed by several studies that had been carried out throughout the recent years, since these specified nanoparticles can counter different infectious diseases and take the role of a novel nano-medicine (Vellasamy *et al.*, 2014; Yazdi *et al.*, 2018c). The aim of the studies that have been carried out on bioconjugation of AgNPs were mostly pointed towards antimicrobials. The production of AgNPs decorated with proline-rich peptide C-Bac3.4 has been achieved in the course of a successful approach and thus, the bioactivity of these bioconjugates has been assessed in contrast to the functionality of their constituents such as bare nanoparticles and peptide (Golubeva *et al.*, 2012). In conformity with the obtained outcomes, the peptide-conjugated nanoparticles have exhibited pronounced antimicrobial activity in opposition to both 9 standard and multidrug-resistant bacteria.

Other metals

A great deal of investigations has been performed on synthesizing metal nanoparticles through the utilization of polymer networks as controlled environments (Caseri, 2000), which can provide an accurate control on the size and shape of nanoparticles, as well as three-dimensional organizations (Zhang *et al.*, 2004). Alginate has proved to be a successful polymer in controlling the progress of monometallic and bimetallic metal nanoparticles (Brayner *et al.*, 2007). Metal cations contain the ability to function as cross-linkers in order to produce a gel network and apparently get caught up within the specific cavities where they get positioned in a close proximity. Once a reduction is induced, these particular cavities can be perceived in the role of confined media that can restrict the development of metal nanoparticles. Based upon the alginate composition, we have observed the varying particle sizes, structures, and magnetic qualities of Ni and Co nanoparticles (Brayner *et al.*, 2007). It is possible to decorate PtNPs with the usage of nucleic acids, since this method has been employed as a label for the amplified biorecognition of DNA hybridization and aptamer-protein recognition events (Gill *et al.*, 2006). In the company of H_2O_2 and luminol, nucleic acid functionalized PtNPs can operate as catalysts in order to create chemiluminescence. Among the many types of catalysts, supported molybdenum catalysts are active and widely used for oxidative desulfurization (ODS) (Zhang *et al.*, 2004; Brayner *et al.*, 2007). SiC can be considered as a fine material for catalytic applications due to its defects and intrinsic structure. The main advantages of utilizing these bio-SiCs as catalyst supports include containing a low synthesis temperature and excellent catalytic properties, as well as being inexpensive and environmentally friendly raw material precursors.

Throughout the last few decades, an exceeding development in polymer nano-composites has happened due to their exceptional accreditations in structural, electrical, and mechanical utilizations. The incorporation of nano-fillers with polymer host can be quiet practical in the fields of biosensors, energy storage devices, photo catalysts, drug delivery, and etc (Gill *et al.*, 2006). The attributions of nano-structured materials in regards to miniaturized and smart futuristic technology have been acknowledged as a class of materials in the range of nanoscale, which can be disperses into polymer matrixes for intensifying the efficiency of high aspect ratio and load the potential of transferring. Through the employment of ultrasonication method, we have supplemented the production of polymer nano-composite in order to carry out the dispersing procedure of nanofillers; nevertheless, the controlled numbers of weight and size of the nanomaterials have been taken into account throughout the whole process. The main obstacle of this approach appears itself when the agglomerated formation has to be eradicated as the nano-filler confronts the host polymer. For the purpose of achieving a uniformed dispersion, we have adopted several techniques to functionalize the surface of nano-filler. Nowadays, various kinds of structures, including nanotubes, nanofibers, nanoribbons, and nanoparticles, have been discovered that can fulfill the demands for specific and required properties (Faupeil *et al.*, 2010). The utilization of conventional fillers, such as carbon black, silicates, and calcium carbonates along with lots of other reinforcing agents, have been perceptible in industrial applications, while their academic scale has faced a decrease (Muccini, 2006). A wide range of investigations has been performed on various polymers including conducting polymers (Polyaniline, polypyrrole, polythiophene, and polyfuran), since due to their high optical and conductive features, their applications in different fields of sensors, fuel and solar cells, EMI shielding, and supercapacitors have given fascinating results (Sharma *et al.*, 2018). The focus of scientific society has been pointed towards the augmentation of biopolymers-based nanocomposites due to the existing population, global changes in climate, and industrial pursuits. For the purpose of inventing new applications based on environmental implications, a lot of interest has been invested in the usage of various thermoplastic biopolymers and their nano-composites. The companion of nano-fillers can effortlessly improve the mechanical strength, electrical conductivity, anti-corrosion, thermal qualities, and etc of biopolymers and when the

high fabrication costs and inadequate characteristics of biopolymers are considered, their integration becomes a necessity (Lau and Hui, 2002; Tran *et al.*, 2010). Most of the biopolymers are known to be biodegradable and since they are derived from renewable resources, they have been labeled as harmless materials for the environment. The origins of natural and synthetic biopolymers are known to be living organisms, polynucleotides, polysaccharides, and biomass production, while the integration of a small portion of nano-fillers, e.g., polyethylene, polystyrene, etc. can be a replacement for many other utilized thermoplastics (Zhao *et al.*, 2005). In accordance with a review from literature, the interest of many scientists has been turned towards the various types of metal and carbon based nano-fillers, since these particular elements are capable of improving the qualities of biopolymer matrixes. Most of the reports have principally categorized carbon based nano-composites, while significant investigations has been performed on graphene and carbon nanotubes and the optimization of dispersion has been kept as a major concern. The motivation behind the attempts for enhancing the fabrication of metal-based polymer nano-composites is to surpass the disadvantages of polymer matrixes and thus, upgrade the biomedical implementations, environmental decontamination, edible packaging applications, and many other intentions that has been previously noted. Some of the methods that have been carried out for the synthesis of metal nanoparticles would be chemical vapor deposition (CVD), spray pyrolysis, electrodeposition and chemical procedures, sol gel process, rapid solidification, etc (Kumar *et al.*, 2002; Neville, 1993). To state some of the characteristics of metal nanoparticles, one can name their features of antibacterial agents, electrical conductivity, optical polarizability, and fine chemical qualities. In the course of their procedure, metal based nanocomposites encounter a decrease in their size and functionalization of surface which can apparently be utilized in plasmonic and sensing implementations (Faupel *et al.*, 2010). An opportunity for evolving bio-organic electronics has been created in the last decades by synthesizing polymer matrixes through the integration of nano-structured metal reinforcements (Muccini, 2006). Polymer nanocomposites have appeared in the position of new ingenious complexes that are constructed by layered nanomaterials including silicates or nano-clay. Nevertheless it must be mentioned that these particular elements contain deficient electrical and thermal conductivities and for the purpose of surpassing these drawbacks, the usage of carbon based nano-fillers, e.g., carbon black, carbon nanotubes, graphene oxide and its derivatives, is quite necessary. Carbon nanomaterials have displayed notable properties, such as containing high surface area, noncorrosive feature, light weight, and exceptional mechanical strength, which have labeled this substance as an appealing absorbent; however, the application of these specific materials has been restricted due to their expensive production costs (Sharma *et al.*, 2018). Throughout the different members of nano-fillers category, carbon nanotubes (CNTs) seem to contain the propensity for causing agglomerations within polymer matrixes to destroy their surfaces, which is treated with functionalizing agents in order to obtain homogeneous dispersion. The CNTs have been discovered by Iijima, which are graphite sheets that have been rolled into tube-like forms for the purpose of facilitating high strength composites, energy storage devices, biosensors, etc (Lau and Hui, 2002).

Metal Oxide Nanoparticles

Magnetite (Fe_3O_4)

Magnetite (Fe_3O_4) has been observed to be a common ferrite that contains a cubic inverse spinel construction. This particular compound has demonstrated rare electric and magnetic qualities, which are based upon the movements of electrons between Fe^{2+} and Fe^{3+} within the octahedral sites. The attraction that has been captured by magnetite is mainly focused on applications such as the removal of heavy metal (Tran *et al.*, 2010), electrocatalytic (Zhao *et al.*, 2005), and drug carriers (Liu *et al.*, 2009). Commonly, the synthesis of magnetite nanoparticles is carried out by utilizing the coprecipitation of ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions which involves a base as well. Green and generic techniques are environmentally utilized through the composition of Fe_3O_4 nanoparticles while their potential applications are facilitated as well. As a biopolymer, sodium alginate can function as a reducing and stabilizing agent throughout the fabricating procedure of Fe_3O_4 nanoparticles (Gao *et al.*, 2008). The results of preliminary magnetic measurements have proved the existence of apparent ferromagnetic qualities that have the potential of being practical for high-density recording media in the upcoming nano-devices.

Zinc oxide (ZnO)

Throughout the metal oxide nanoparticles, ZnO nanoparticles (ZnO-NPs) have been selected to be utilized as a potential material for biosensing purposes, due to their exceptional features such as high surface area, high catalytic efficiency, non-toxicity, chemical stability, and strong adsorption capability (high isoelectric point ~ 9.5). The competence of Nano-porous ZnO in exceedingly improving the active surface area has been proved, which can be employed for strong adsorption of biomolecules (Singh *et al.*, 2007). The uniformly dispersed ZnO-NPs in chitosan (CHIT) have been employed through an examination for the purpose of modifying a hybrid nanocomposite film into indium-tin-oxide (ITO) glass plate. Moreover, Cholesterol oxidase (ChOx) has been inactivated onto the designated nano ZnO-CHIT composite film. ChOx/NanoZnO-CHIT/ITO bioelectrode has been applied to approximate the cholesterol that exists within the solution and the blood serum samples, which will also help in perceiving the other metabolites such as urea, glucose, uric acid that includes toxicants, etc (Khan *et al.*, 2008).

Cerium oxide (CeO_2)

A great amount of interest has been invested in CeO_2 nanoparticles (CNPs) throughout nanotechnology that has been caused by their beneficial applications including catalysts, fuel cells, and antioxidants in biological systems (Gagnon and Fromm, 2015; Tian *et al.*, 2015b; Arya *et al.*, 2016). Predominantly, cerium is capable of existing in two specific oxidation states, which are

Ce^{3+} and Ce^{4+} , and for this very reason, cerium dioxide can accommodate two varying oxide forms (Beaudoux *et al.*, 2016). The production of CNPs have been carried out by the employment of various routes and synthesis techniques including solution precipitation (Chen and Chang, 2005), sonochemical (Jimmy *et al.*, 2003), and sol-gel procedures (Darroudi *et al.*, 2014a). Nevertheless, the utilization of toxic solvents and reagents, high temperature and pressure, and the necessity of external additives as stabilizing or capping agents in the course of the reaction, can be counted as some of the disadvantages of exploiting the noted methods. Similar to the existing relationship between the physiochemical qualities of NPs and their synthesis method, the significance of NPs synthesizing procedure in biological applications is quite evident as well and for this very reason, the green synthesis of CNPs has attracted the attention of many researchers in recent years. In the role of macromolecules, natural polymers can also function as templates through the bio-directed synthesizing procedure of CNPs. Different reports have labeled egg white protein and honey as nutrients and natural materials for the green synthesis of CNPs (Kargar *et al.*, 2015b; Darroudi *et al.*, 2014b). On the topic of CNPs development, Kargar *et al.* (2015b) have suggested that the two substantial proteins of egg white, which are ovalbumin and lysozyme, are capable of operating as green binder/stabilizing agents. They have also announced the successful green synthesis of small CNPs, which had been stabilized by the means of agarose polymers via a sol-gel procedure (Kargar *et al.*, 2015a). When agarose powder is heated up to $>90^{\circ}\text{C}$, it commonly dissolves in water and as the temperature is lowered to $35\text{--}40^{\circ}\text{C}$, the formation of a semisolid gel can be observed that seems to be stable in a vast range of pH (from 3 to 9). In a comparable situation, Darroudi *et al.* have had synthesized CNPs through the utilization of starch, which has functioned in the role of a capping biopolymer (Darroudi *et al.*, 2014a). This starch-based mechanism has suggested that subsequent to dissolving starch in water, metal cations seem to get drawn towards the oxygens of existing OH branches. Darroudi *et al.* have also utilized Gum Tragacanth for the purpose of developing CNPs, which involved both chemical and biological procedures (Darroudi *et al.*, 2014c).

Other metal oxide nanoparticles

Chitosan and CNPs, which were based upon nano-biocomposite film and had been deposited onto the substrate of indium-tin-oxide coated glass, have been employed to co-immobilize rabbit immunoglobulin (r-IgGs) and bovine serum albumin for the purpose of detecting food borne mycotoxin (Kaushik *et al.*, 2009). The application of copper oxide NPs (CuO-NPs) can be regularly observed, which is probably due to their antimicrobial and biocidal features (Ren *et al.*, 2009). Due to their antimicrobial qualities, these particular CuO-NPs are often utilized in paints or fabrics in a polymer-coated form (Perreault *et al.*, 2012). In accordance with the available studies, chitosan has displayed exceptional antibacterial abilities for food packaging applications, which is probably due to being a biomaterial based nano-composite film that contains silver oxides (Tripathi *et al.*, 2011).

Silicon carbide materials have captured the interest of many due to their exceptional qualities, which includes semiconducting properties, excellent mechanical strength and thermal conductivity, chemical inertness, and outstanding thermal shock resistance (Zagorodni, 2006; Eustis and El-Sayed, 2006). Nano-structured SiC have proved to contain superior electrical, optical, and mechanical features, when compared to their bulk form, and seem to stand as an appealing candidate for various applications such as catalyst support, drug delivery, and hydrogen storage (Ofir *et al.*, 2008; Combemale *et al.*, 2014). The available synthesizing procedures for these materials involve various disadvantages such as the requirement of high-temperature synthesizing method and expensive raw precursors, as well as not being environmentally friendly (Li *et al.*, 2014; Braydich-Stolle *et al.*, 2005). Typically, surfactants or polymers are utilized as the templates for the production of porous materials, since the template method can be practical for regulating the structural properties, including surface area, internal porosity, and external shape (Alt *et al.*, 2004). However, it must be noted that many surfactants can cause toxic effects in animals, humans, and ecosystems while intensifying the propagation of environmental pollution as well (Kandamchira *et al.*, 2013; Vellasamy *et al.*, 2014). Even though the utilized polymers as templates are not fitted for biological applications next to containing petrochemical structures and requiring a large budget, yet natural biopolymers have proved to be inexpensive, nontoxic, and environmentally friendly materials that can be appointed as carbon templates (Yazdi *et al.*, 2018c). In addition to the mentioned advantages, natural biopolymers contain an uncountable number of structures. In a previous report, tragacanth, guar, xanthan, and Arabic gums with cellulose-like backbone had been utilized in the synthesizing procedure of nanostructured silicon carbide. Throughout this specific method, most of the sulfur compounds have been detached under a mild condition (Golubeva *et al.*, 2012; Caseri, 2000).

Perspective and Future Study

In recent years, the attention of many researchers has been focused on the natural biopolymer-based materials that are mainly due to their possession of desired features, which include biodegradability, biocompatibility, nontoxicity, and antimicrobial properties. The utilization of biopolymers by mankind is majorly involved in food applications or the production of clothing and furniture. Fossil fuel, oil for example, have been the dominant source for developing and fabricating almost every commercial product since the industrial time, such as plastic that is being utilized in an enormous scale at the present time. The requirements for these novel materials throughout the future of biopolymers will be massive and irresistible for manufacturers. Nevertheless, it is necessary to enhance the cost-effectiveness of these materials while specifically contributing to their sustainable advancement. The exceptional features of these polymers must be employed in their applications and it is quite vital that the constructed products would be developed based upon those properties. The recent appearance of bio-based products have been noticed and preferred over the petroleum or natural gas based products due to the uprising concern for tending and looking after the world we live in. There are several motivations behind the performed researches and developments of Biopolymers. By producing more

durable versions of biopolymers, their utilization can be remarkably intensified while the fabrication costs of these bio-plastics proceed to fall. Bio-plastics stand as an outstanding replacement for conventional plastics throughout their fields of applications, as well as other various sectors such as food packaging, plastic plates, cups, cutlery, plastic storage bags, storage containers or other plastic or composite material items that are available for sale; therefore, this evolution can be considered as a big step in having a more sustainable environment. The substitution of conventional polymers with biopolymers has never been this close to reality throughout its history. Nowadays, due to the induced progress in biotechnologies and the increased public awareness, bio-based polymers can be regularly perceived in many different fields that vary from commodity to hi-tech applications.

Throughout the performed examinations for discovering novel nanomaterials while concerning the goal of sustainable production and consumption, biopolymers have proved to contain several (potential) advantages including the employment of renewable resources to manufacture bio-based materials as the fundamental factor for expanding resource efficiency, the possibility of cultivating resources on a (at least) yearly basis, making the principle of cascade use possible since biomass is capable of generating energy after being utilized for fabricating materials, diminishing the footprints of carbon and GHG emissions that exist in different materials and products – resulting in saving fossil resources and thus, progress by gradually replacing them.

See also: Eco Friendly Flocculants: Synthesis, Characterization and Applications. Natural Fiber Reinforced Composites in the Context of Biodegradability: A Review. Synthesis of High Grade Activated Carbons From Waste Biomass. Use of Novel Nanostructured Photocatalysts for the Environmental Sustainability of Wastewater Treatments. Vegetable Oil-Based Polymeric Materials: Synthesis, Properties, and Applications

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Characterization of Wood, Cork and Their Composites for Building Insulation

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Introduction

Nowadays, there is a rapid growth in the building sector worldwide. Due to rapid urbanization, a significant part of total energy consumption and greenhouse gas emission is attributed to the building sector. Worldwide, one-third of the total energy is consumed for heating or cooling the buildings. The predicted demand for energy consumption is increasing 8% annually due to sharp income and population growth around the country. Recently, the European Union and developing country administration have introduced building energy efficiency program and regulation for commercial and residential buildings to mitigate the requirement of energy consumption. These kinds of program will be helpful for the planet by reducing greenhouse gas emissions. The energy consumption for heating or cooling the building is strongly dependent on the properties of building envelope. The appropriate selection of design and components of building envelope as per surroundings climate are the key factors for reducing the space heating and cooling (Al-Homoud, 2005). In a broader context, insulation is an efficient tool to reduce energy consumption in the building sector. Therefore, the optimum thickness of insulation and type of insulation materials for building envelope are the key points for the subject of investigation. The insulation thickness is mainly dependent on construction materials, shape of the building, insulation material, energy category and its cost and the efficiency of heating and air-conditioning system. Hence, the optimum thickness of insulation is the function of the cost of insulation materials and energy saving during the service time of insulation material, illustrated in Fig. 1. These kinds of investigations help us to estimate the demand for energy usage, size of heating and air-conditioning system as well as desirable thermal comfort of residents.

The adequate choice of building insulation is not only to fulfill the criterion of thermal performance but also to consider some other non-thermal features such as fire resistant, water vapor permeability, acoustic insulation, and impact on occupant's health etc. This is a holistic approach to choose the insulation material for the improvement of the building envelope.

Historical Development of Wood and Cork-Based Building Insulator

The study of historical development viewpoint is necessary to understand the requirement of different characterization for building insulation. In ancient civilization, wooden houses had been used for the residing purpose. But the peoples were not aware that the insulation was carried out by wood-based structure. In the early ninetieth century, concrete and cement materials had been adopted due to structural stability and mechanical properties enhancement. At the same time, energy consumption and environmental pollution were raised by the building sector. Just then, the researchers and scientist have shown their interest to save the earth. There are few reports based on thermal insulation in early 1970. The biobased building insulation was a new area intended towards research. In the mid-nineties, some researchers had worked on building insulation. Previously, the objective of the building was just for living and staying purpose, nobody was concern about environmental performance and energy conservation. Afterward, a storm had come in this precise space of investigation due to numerous regulations in the field of energy conservation and pollution. Consequently, attention was paid towards renewable insulation materials as well as conventional insulation materials. The research interest in the direction of biomaterial-based building insulation increases from the year 2010 due to economic crises. Environmental protection and energy conservation laws were taken worldwide. On the other hand, there

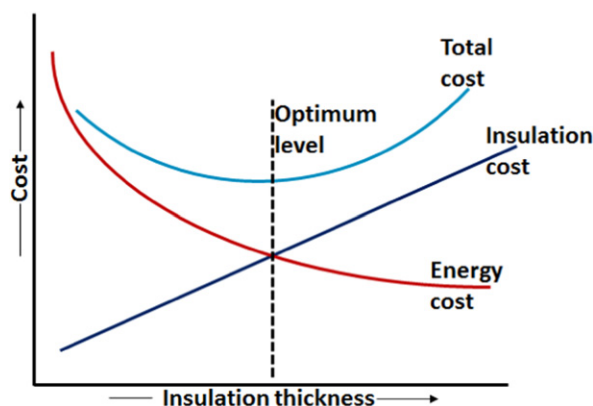


Fig. 1 Optimum thickness of insulation. Reproduced from Kaynakli, O., 2012. A review of the economical and optimum thermal insulation thickness for building applications. *Renewable and Sustainable Energy Reviews* 16 (1), 415–425.

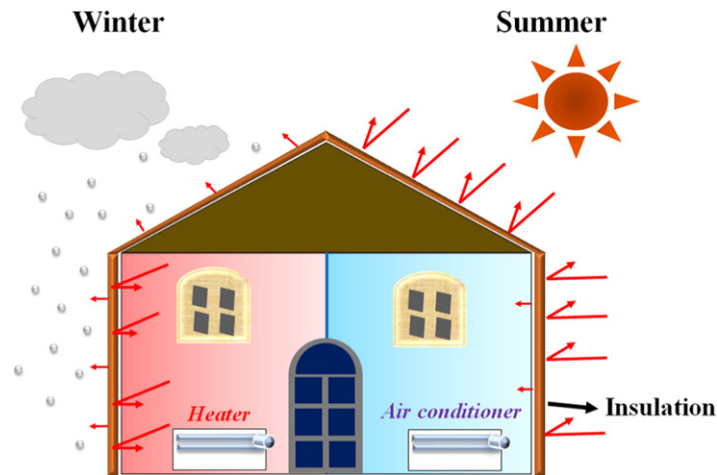


Fig. 2 Thermally comfort building.

was a rapid growth in the demand for indoor air quality, which leads towards the air-conditioning system and furthermore energy consumption (Liu *et al.*, 2017). Hence, the demand for energy conservation was moved towards the search for an eco-friendly way to fix a barrier against heat flow. Thus, Bio-based insulation material was drawn into attention to keep the heat flow from space to surroundings or vice-versa. In the current time, widely the people want to keep calm in the workplace as well as in the home, hence noise reduction or soundproof insulation system are also utilized as an acoustic insulation system. The objective of building insulation is building energy savings and environmental protection which moves towards the study of characterization of bio-insulation materials for building application.

Importance of Insulation In Building Sector

Building insulation is considered as a simple and highly efficient technique for energy saving, which can be applied in the residential, industrial and commercial division. Thermal insulation technique reduces energy utilization and thus protects our environment as well as enhances the lifecycle of the building by protecting from the weather. A building with seamless insulation is depicted in Fig. 2. It is quite clear in the image that, during winter season insulation keep the space warm and heat is not dissipated from space to surroundings. Whereas, in the summer season the outside heat cannot pass through the insulation and air-conditioning make a thermal comfort without wasting the energy. The key features of building insulation are listed here.

Thermal Comfort

Thermally comfortable feelings are strongly dependent on space air temperature and surroundings surface temperature. In a non-insulated space, a draft is created between space and surroundings due to huge temperature differences. Hence, an enormous amount of energy is required to create a thermally comfortable zone. Whereas, a small temperature difference in the air is maintained between the system and surroundings by applying insulation with wall, roof, and floor in the building. This helps to reduce the reliance on energy consumption and also extends the periods of thermal comfortable conditions.

Environment Protection

Building insulation leads to cost saving by reducing fuel consumption, which is also associated with less CO₂ emission. Less energy consumption leads to less environmental pollution. According to a report, insulated building panel reduced 45% environmental pollution as compare to non-insulated building panel.

Acoustic Insulation

Apart from thermal insulation, the insulation materials should be able to absorb intruding sound waves and contrast sound transmission. Acoustic insulation is the capability of insulation material to dissipate the sound energy due to resonance or thermal and friction loss (Schiaivoni *et al.*, 2016). Generally, sound absorption materials are good thermal insulator but vice-versa is not true. Because sound absorption requires open cell porous structure and the open porous cell captures the heated air molecules is also a good condition for thermal insulation. Closed cell porous structure is good for thermal insulation but it does not work for acoustic insulation because it requires movement of air inside the insulation material.

Fire Retardant

Building insulation materials should be a flame retarder. If the building insulation is made up of chemically treated flame retardant materials, it will play a crucial role during flame devastation and prevent the flame propagation from outside to inside space.

Vapor Condensation Prevention

The proper design of insulation material assisted to reduce water vapor condensation in case of low temperature.

Working Principle of Building Thermal Insulator

The aim of insulation is to keep a hygienic climate and comfortable temperature of the space by preventing the heat flow between the building and surroundings. All the insulation materials work on the basic principle that heat always flows from warmer to a colder place. Hence in the winter season, building insulation prevents heat flow from inside to outside areas and vice versa for the summer season. The strategy of thermal insulation is to achieve low thermal conductivity. The low thermally conductive material demonstrates the ability to use a thin building envelope. The insulation material must reflect high thermal resistance (R -value) and low thermal transmittance (U -value). The thermal conductivity of a system depends on several factors (Eq. (1)), which is as follows:

$$\lambda_{\text{total}} = \lambda_{\text{conduction}} + \lambda_{\text{convection}} + \lambda_{\text{radiation}} \quad (1)$$

In order to achieve low total thermal conductivity (λ_{total}) of insulation material, each of the contributions should be as low as possible. Thermal conduction of a material is based on two factors i.e., solid conduction and gaseous conduction. In the case of insulation, solid conduction is devoted to phonon phenomenon. Thermal energy transports through solid by lattice vibration with the help of chemical bonds between atoms. Whereas gaseous conduction takes place through the collision of gas molecules with each other and thermal energy transfer through one molecule to another (Jelle, 2011). Thermal convection drives via thermal mass transport of air or moisture between the pores. One of the best ways to decrease thermal convection is to reduce the pore size of insulation material. Hence, the air molecules are entrapped within the pores and interacted within the pores walls. The phenomenon is termed as Knudsen effect. Thermal radiation is based on the emittance of electromagnetic radiation within the infrared region.

All these thermal contributions basically depend upon the temperature difference. Building insulation materials have to fulfill a series of requirements. Some other requirements such as low density, high porosity, resistant to fire as well as low thermal conductivity restrict the selection of material and solutions for building insulation.

Manufacturing Process of Building Insulator

There are several preparation methods described by numerous authors according to raw material and end-user application (Liu *et al.*, 2017). Some of the common methods are as follows.

Bonding

The binding agents such as glue, starch, aluminum sulfate and some other resins are used to combine loose raw material like jute, flax, hemp and cellulose in the form of board or slab.

Pressing

A press based on high pressure at ambient condition is utilized to combine loose fill fibers and particles by compressing the material in the form of the homogeneous body. This particular method reduces voids without adding supplementary material.

Hot Pressing

In this method, high temperature and high pressure are applied to bound the particles and form a solid board.

Injection Molding

The composites slab is prepared by molding process. In this method, the polymer melt and reinforcing materials are mixed at certain pressure and temperature. Then the solution is injected in the definite shape and size of the mold.

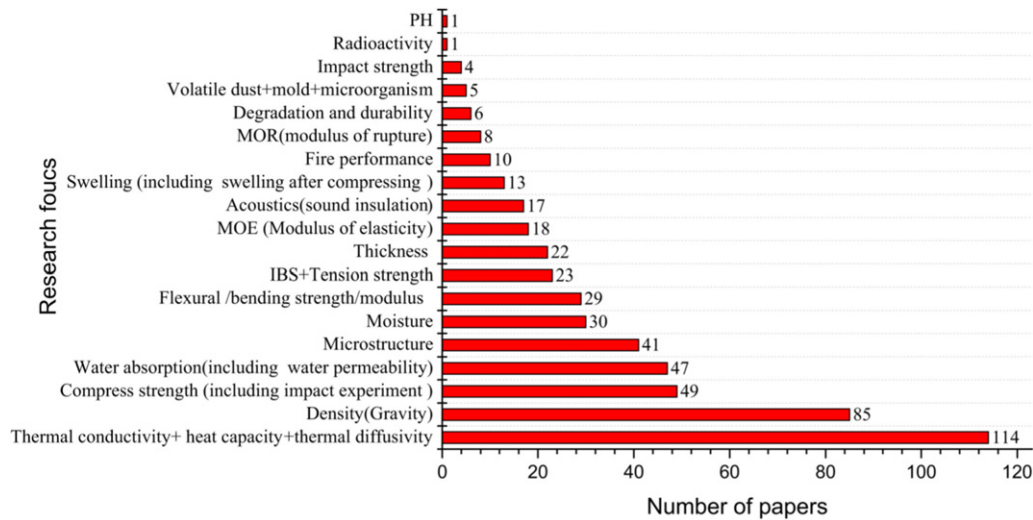


Fig. 3 Recent publication based on different characterizations for building insulation application. Reproduced from Liu, L., Li, H., Lazzaretto, A., *et al.*, 2017. The development history and prospects of biomass-based insulation materials for buildings. *Renewable and Sustainable Energy Reviews* 69, 912–932.

Foaming

The homogeneous porous structure in solid material is generated by the physical or chemical foaming process. Initially, the polyurethane and polystyrene based composites foams are prepared by chemical and physical foaming process. In the recent scenario, most researchers and scientists have worked on wood and cellulose-based thermal insulation system. The authors basically focused on nano-technological synthesis routes like freeze drying or supercritical drying for the preparation of bio-based thermal insulator. These kinds of drying processes are costly and can not be adopted for commercial purpose. According to a survey, the foaming molding process has a strong potential towards bio-insulations despite very few research group have been carried the work out up to now. The foaming molding process can reduce density significantly, while porosity can be highly enhanced. Moreover, the mechanical properties such as compressibility, bending strength, etc. can be improved as well by properly tuning the processing conditions.

Natural Form

Wood and cork based biomass can be used the same as the raw form.

Others

Some other processes such as punching and hydroentanglement etc., can be used for the preparation of building insulation materials according to end use application.

Basic Criterion for Selection of Building Insulator

There are several characterizations to validate the ability of building insulator like thermal characterization, acoustic characterization, life cycle assessment, resistant to fire and moisture resistant etc. Thermal properties such as thermal conductivity, thermal resistivity, thermal diffusivity, heat capacity and coefficient of thermal expansion are mostly explored (Fig. 3) for building insulation application. Table 1 shows various characterization, method and criteria.

The properties are described as follows:

Thermal Insulation

Thermal insulation is the ability of the material or a system to resist against heat flow for the system to surroundings or vice-versa. Thermal insulation hinders the heat flow through conduction, convection, and radiation. The researchers mainly focused on thermal conductivity of building insulation material.

Table 1 List of characterizations, method and specimen criterion

Characterization	Method	Criteria
Conditioning	ASTM C 870	Conditioning prior to testing
Thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)	EN 12664	Low thermal resistance
	EN 12667	High thermal resistance
	EN 12939	Thick material
	ASTM C 518	Heat flow meter apparatus
	ASTM C 177	Guarded hot plate apparatus
Thermal diffusivity ($\text{m}^2 \text{s}^{-1}$)	ISO 8990	Hot box method
	ASTM E 1269	Differential Scanning Calorimetry
	ISO 22007-3	Temperature wave analysis method
	ISO 22007-2	Transient plane heat source(hot disc)method
	ISO 22007-4	Laser flash method
Density (kg m^{-3})	EN 1602	Apparent density
	ASTM C 303	Board and block type insulation material
Specific heat capacity ($\text{J kg}^{-1} \text{K}^{-1}$)	ISO11357	Differential Scanning Calorimetry
Acoustic insulation (dB)	ISO 717-1	Weighted sound reduction index, R_w
	ISO 16283-1	Apparent sound reduction index, R_0
	ISO 10140	Normalized impact sound pressure level, L_n
	ISO 717-2	Normalized impact sound pressure level, L_n
	ISO 354	Sound absorption coefficient
	ASTM C 42309a	Noise reduction coefficient, NRC
	ASTM D 3801	Burning characteristics of solid plastics in a vertical position
	ASTM D 5048	Comparative burning characteristics and resistance to burn
Flame retardancy	UL 94	Flammability of Plastic Materials
	ISO 5660	Reaction to fire test
	ASTM E 1354	Heat and smoke release rate using calorimeter
	ASTM C 356	Linear shrinkage
Coefficient of thermal expansion ($^{\circ}\text{K}$)	ASTM C 356	Linear shrinkage
Vapor retention capacity	ASTM E 96	Water vapor transmission rate

Note: Schiavoni, S., Bianchi, F., Asdrubali, F., 2016. Insulation materials for the building sector: A review and comparative analysis. Renewable and Sustainable Energy Reviews 62, 988–1011.

Thermal conductivity

Thermal conductivity is “the time rate of steady state heat flow through a body of per unit area (1 m^2) by inducing per unit (1K) thermal gradient in the perpendicular direction of isotropic substance”. The thermal conductivity of wood and cork is affected by various factors such as density, porosity, extractive content, moisture content, grain direction, structural irregularities, and temperature. Generally, Thermal conductivity is directly proportional to density, moisture content, and temperature.

Thermal diffusivity

Thermal diffusivity is an important criterion to measure how rapid a system absorbs energy from surroundings. It is the ratio of thermal conductivity of a substance to its heat capacity and density.

Thermal resistivity

Thermal resistivity is associated with R -value of insulation. Thermal resistivity is the capability of a substance to resist the conduction, convection, and radiation by opposing the heat flow. It is the ratio of the thickness of insulation materials to its thermal conductivity.

Thermal transmittance

Thermal transmittance is associated with U -value of multi-layered insulation material. Thermal transmittance is the heat flow through per unit area of anisotropic and non-homogeneous insulation material due to increment of 1°K temperature.

Coefficient of thermal expansion

The coefficient of thermal expansion is the change in the dimension of substance due to change in temperature.

Density

Density is the most important factor which influences the thermal conductivity of insulation material. The density of any specimen affects the heat flow due to solid conduction.

Porosity

The porosity of any specimen is affected by the particle size of raw material and size of voids. Porosity is the void fraction of specimen with respect to their total volume. It is calculated by Eq. (2)

$$\epsilon = 1 - \frac{\rho}{\rho_s} \quad (2)$$

where, ϵ = porosity of insulator (%), ρ = density of final product (i.e., weight with respect to their volume), and ρ_s = skeleton density of the product.

Life Cycle Assessment

The environmental impact of building insulation is an important criterion for the selection of material. Global warming and energy consumption are the basis for the life cycle assessment of insulation material. The direct or indirect burden on the environment due to energy consumption influences towards eco-design and energy efficiency building insulation. Cork, wood and other valuable natural material for building applications have shown great ecological value. It is also very interesting from a sustainability perspective because, in addition to its low emissions and the great potential for capturing CO₂, it generates economic revenues, provides jobs and development in rural areas, and allows many environmental services such as forest preservation, biodiversity conservation, and wildfire prevention.

Mechanical Properties

Mechanical properties are secondary characterizations in building insulator sector, that does not affect the performance of insulation, but it varies the credibility of insulation material in the presence of the external load. The common mechanical properties for building insulation application are as follows.

Modulus of elasticity

Modulus of elasticity is the ratio of stress to the strain of specimen in the elastic zone. It is also termed as elastic modulus or Young's modulus.

Modulus of rupture

Modulus of rupture is the ratio of maximum sustainable load and the fracture cross-section area of the specimen. It is calculated from maximum tensile strength or maximum shear strength up to the failure of a sample.

Flexural strength

Flexural strength is the ability to sustain bending without breakage of the specimen.

Internal bonding strength

The bonding strength is the ability to sustain load in the lateral dimension of the specimen.

Tensile strength

Tensile strength measures the ability to sustain longitudinal stress without breaking the specimen.

Compression strength

Compression strength is defined as the bearing capacity of the specimen under the action of pressure or compressive stress along the axis of the applied load.

Impact strength

Impact strength is the toughness of specimen or energy-absorbed per unit cross-section area. It is defined as breakage under impact or sudden load.

Durability

Durability is the ability of bio-based insulation material to resist the corrosion or environmental damage during long term application.

pH

pH is the hydrogen ion concentration present in a specimen. The pH value of insulation explains the microbial contamination of bio-insulation material, which refers to the long term durability of the specimen.

Antimicrobial activity

Wood and other biomaterials are prone towards several microbes like termite. In recent time, bio-insulation materials are present in the market with an antimicrobial coating to prevent mold and microbial proliferation that enhances long term durability of insulation material.

Microstructure

The morphology and structural characteristics show strong relation with the thermal and mechanical properties of insulation material. The microstructural characterization will contribute to justify and correlate structure and properties relationship. Several analyses like scanning electron microscope, X-ray microtomography, scanning probe microscopy, and optical microscopy has been reported for microstructural characterizations by several authors.

Volatile Organic Compound

If the insulation material is made by adding an artificial binding agent, then it may be a possibility that binding agent leached out some organic volatile compound in the environment during installation period or during the whole service life of the building.

Moisture Absorption Behavior

The biomaterials like wood, hemp, flax, bamboo, and cellulose etc., are susceptible to moisture. If the insulation materials are used in the interior or exterior side of walls instead of a sandwich panel, hence a hydrophobic coating is required to maintain the mechanical and thermal properties of insulation material.

Swelling thickness

Swelling thickness is determined by water absorption performance and expansion ratio of insulation material while immersing the specimen in water for 24 h.

Coefficient of moisture absorption

It is the amount of moisture absorbed per unit volume by exposing the specimen in the air at atmospheric condition.

Water vapor permeability

It is the ability to transmit the moisture through the specimen. The bio-insulation materials are made up of the porous structure and suitable to make desirable moisture in the space and comfort for the occupants.

Moisture content

Moisture content is also an important factor for wood-based insulation materials. Several authors have already discussed the variation in the thermal conductivity at a different moisture content of the specimen. The probable fact is that the thermal conductivity of water is higher than air and that is why thermal conductivity increases by varying the moisture content.

Several Types of Wood and Cork-Based Insulation System

Thermal insulation is playing an important role in the building sector. Several types of conventional materials such as glass wool, mineral wool, vermiculite, expanded perlite, phenolic foam, polyurethane are also considered as building insulation materials. The main drawbacks of conventional insulation materials are the depletion of nonrenewable sources and environmentally hazardous. Apart from that, several authors have reported building insulation materials based on renewable and natural sources. For the reference purpose for the current situation of research, hemp is considered as the most explored biomaterial for building insulation application. Around 17.4% of publications are on hemp, however; sunflower, cork, corn, wood, coconut, straw and flax cover 74% of total research interest. Some other biomaterials are not explored yet, for instance, durian, pineapple, sisal, reed, bamboo, olive and grass covers 8.3%. Some common bio insulation materials are as follows.

Cork

Cork is used for several applications by mankind from the last 5000 years. Cork is extracted from the outer bark of Oak "*Quercus suber L.*" tree. Cork is a natural, sustainable and renewable material because it does not damage the tree. The oak tree bark regenerates every 10–12 years depending upon the region until the 180–200 years age of the tree. Cork consists of ligno-cellulosic structure and 30%–50% suberin as an aliphatic polyester. The unique properties of the bio-derived material are its visco-elasticity and hydrophobicity. The cellular structural cork demonstrated as versatile acoustic, vibration, electric and thermal insulator, flexible, and a dielectric material. Cork depicted the extra-ordinary properties due to its closed cell wall structure ([Fig. 4](#)).

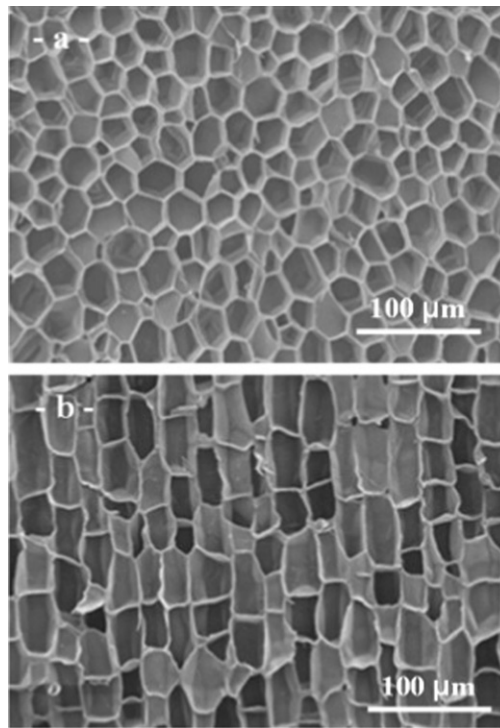


Fig. 4 Cellular structure of cork (a) transverse (b) longitudinal direction. Reproduced from Fernandes, E.M., Correlo, V.M., Chagas, J.A., Mano, J.F., Reis, R.L., 2010. Cork based composites using polyolefin's as matrix: Morphology and mechanical performance. *Composites Science and Technology* 70 (16), 2310–2318.

Basically, cork is a collective unit of approximately ten million cell walls per cubic centimeter, bounded by resin. The maximum percentage of cork is generated in southern Mediterranean countries especially Portugal. The cork forest rises environmental advantageous such as carbon-dioxide consumption, hydrological cycle, prevent desertification and maintains the habitat for several plant and animal species (Gil, 2015). There are four different types of building material produced from cork. The first one is obtained as steam treated thin and fine laminates from natural cork. The second one is produced by hot pressing of agglomerated cork at 350°C and 300 kPa. The final color is brown and is used for thermal and acoustic insulation (Hernández-Olivares *et al.*, 1999). As a substitute for building materials, cork-rubber and granules are used as a reinforcing agent in composites.

Wood

Basically, wood is collected from ecological forestry system. Wood is a natural thermal insulator consist of ligno-cellulosic masses. Wood is basically subdivided into two categories; softwood and hardwood. The main difference between the trees is based on the way to reproduce. Softwood trees are gymnosperm and reproduced by uncovered seed. Pine, cedar and other conifers are the examples of softwood trees. While, hardwood are angiosperms and reproduced from covered seed such as fruit, acorns, and nut. Mostly, hardwood drops their leaves in the fall season. The selection of wood is based on the characteristics, easiness, the ability to sustain load and climatic conditions etc. Several types of woods and its characteristics are briefly described here,

Softwood

- *Cedar*

Cedar is lightweight and low-density wood with excellent resistant towards decay. The aromatic oil wards of cedar show outstanding resilient against microbial growth and insects.

- *Cypress*

The specialty of cypress is its sustainability against extremely wet conditions. Hence, it can be used in the outer most structure of building, docks, and decks.

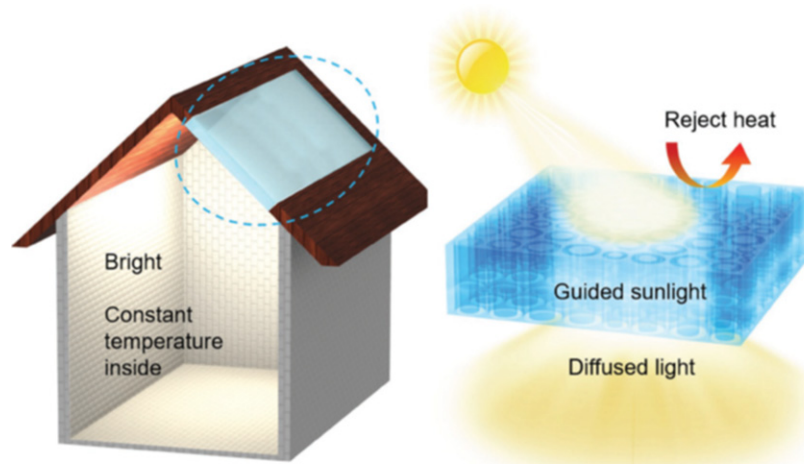


Fig. 5 Transparent wood based rooftop. Reproduced from Li, T., Zhu, M., Yang, Z., *et al.*, 2016. Wood composite as an energy efficient building material: Guided sunlight transmittance and effective thermal insulation. *Advanced Energy Materials* 6 (22), 1601122.

Hardwood

- *Balsa*

Balsa is mostly harvested from South America and Ecuador. It is a lightweight and durable wood with exceptional strength.

- *Birch*

The thin paper bark of the birch tree makes it superior for insulation purpose. Birch is massively found in Canada and northern America.

The cellulose is basically provided low thermal conductivity and lignin acts as a binder in wood. Due to excellent mechanical strength, wood-based panel and the pillar are already used in construction from the decades. Most of the cases, wood fiber based panel or board is used for building insulation. Hence the sawmill industries residue and another type of wood waste can be utilized in the preparation of insulation materials. Instead of lignin, different kind of binders such as aluminum sulfate is applied as a binder, which also acts as a pesticide and wood preservative. The thermal conductivity of wood-based material depends upon temperature, humidity, moisture, density, and microstructure. In a recent report by Li *et al.* (2018), transparent wood based structure was prepared as energy efficiency and light harvested building material. The transparent wood based system is shown in Fig. 5.

Hemp

Hemp is harvested from "*Cannabis sativa L.*" and mostly used as textile fiber. Hemp consists of a surface layer, 20–50 bundles of bast fiber, a wood-based core and a central lumen. The bundles of bast fibers utilize as a raw material for the preparation of thermal insulator. The hemp can be used as a loose fill insulator or as a board with the binder, which is advantageous on different raw materials.

Kenaf

Kenaf is a potential material for developing low-density boards which can be further used for thermal insulation products. The Kenaf plant comprises of long outer bast fibers with an inner core suitable for wide range applications. Kenaf is usually free from insects and rodents attack as it lacks protein. These fibers are usually supplied with fire retardants and polyester.

Flax

Flax (*Linum usitatissimum*) is already utilized by the Egyptian since 5000 BCE. The flax plant consists of 70% cellulose, having the ability to hold air. Hence, Flax is shown excellent thermal insulation properties over other materials.

Coir Fiber

A natural fiber isolated from the husk of coconut or collected as a waste product from the coconut industry constitutes the term coir. This fiber is one of the few natural fibers resistant to deterioration caused by saltwater. These fibers have inherent high mechanical strength. These fibers also act as a good sound absorber when compressed in bales.

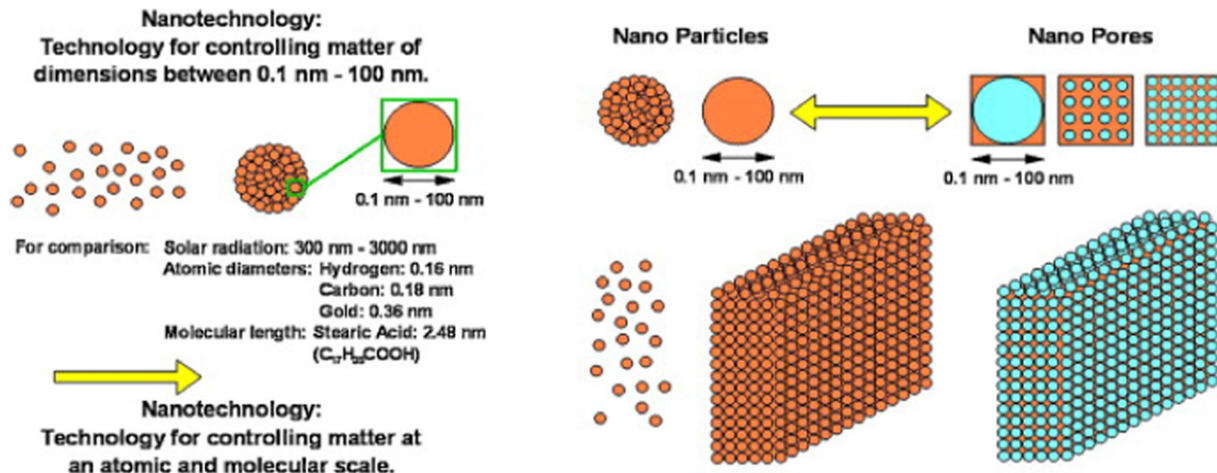


Fig. 6 Nanotechnological control arrangement of building insulation. Reproduced from Jelle, B.P., 2011. Traditional, state-of-the-art and future thermal building insulation materials and solutions – Properties, requirements and possibilities. *Energy and Buildings* 43 (10), 2549–2563.

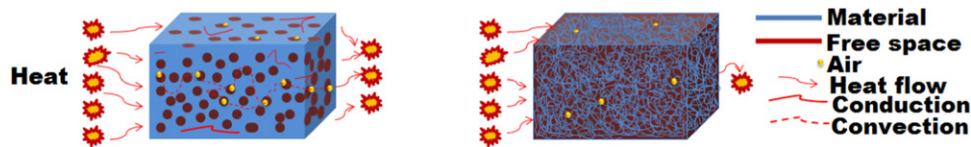


Fig. 7 Comparison between conventional foam and aerogel for thermal insulation application. Reproduced from Gupta, P., Singh, B., Agrawal, A.K., Maji, P.K., 2018. Low density and high strength nanofibrillated cellulose aerogel for thermal insulation application. *Materials and Design* 158, 224–236.

Jute

India and Bangladesh are the leading producers of jute. Jute fibers are less expensive and highly elastic in nature showing excellent resilient property which is utilized in floating floors. These fibers can be utilized as sound, electrical or thermally insulating material.

Cellulose

Cellulose acts as an environmentally friendly material for application in building insulation having suitable acoustic properties and low embodied energy per kg of material. Cellulose fibers used for insulation mainly comprise of recycled paper fibers having certain drawbacks like hygroscopic nature of cellulose and fungal growth and combustibility and are hence are treated with additives like fire retardants and fungal growth inhibitor. Mainly cellulose fiber utilized for insulation is available in two forms one is a prefabricated panel in which fibers are bound using polyester resin and second where fibers are supplied for ceiling and walls application as loose fibers (Hurtado *et al.*, 2016).

Nanotechnological Revolution in Wood and Cork-Based Composites

Nanotechnology is a scientific tool, which enhances the performance of thermal insulation material. The basic criteria of nanotechnology is that the dimension of material should be between 0.1 and 100 nm (Jelle, 2011). Nowadays, the energy efficiency building regulations and nation-wise standards are more rigid. The primary objective is to diminish the heat flow through the walls. It can be done either by means of increasing the thickness of wall insulation or enhance the performance of insulation material. In the case of insulation, the void space of material should be in nano-range (Fig. 6). The nano insulation material is based on the fact that heated molecules collide with pore walls instead of other molecules follow the Knudsen effect. The elimination of molecular collision lowers the thermal conductivity and enhances the efficiency of nanotechnological insulating materials.

The nano-insulating materials are basically vacuum insulation panel, gas insulating panel, phase change material and aerogel. The low density and highly porous structure with pore size between 2 and 50 nm is termed as “aerogel”. The building insulation based on aerogel is the current subject of investigation. Several researchers have reported cellulose,

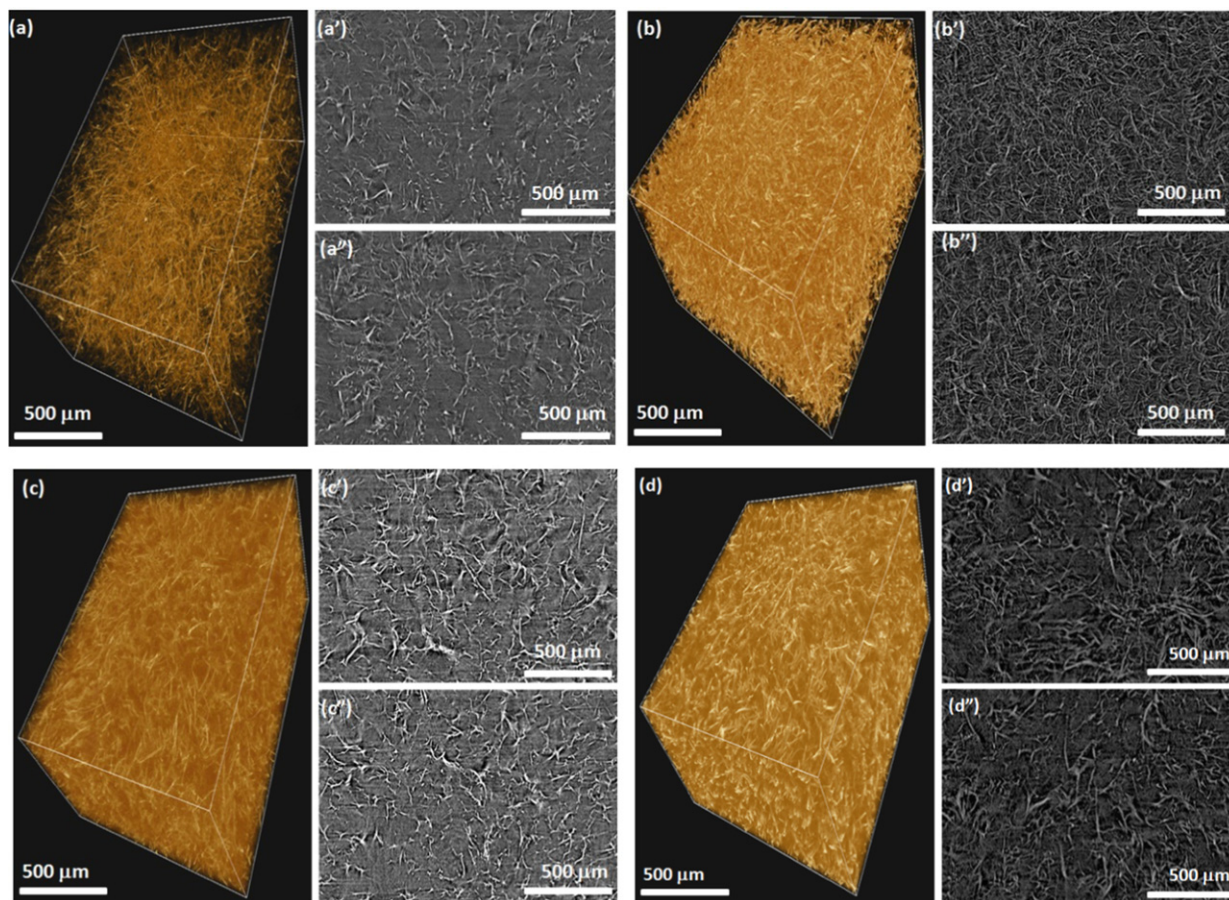


Fig. 8 X-ray tomographic analysis of nanofibrillated cellulose aerogel by varying concentration, (a) 3 Dimensional view of low density aerogel similarly for (b), (c) and (d); (a' and a'') local density distribution of aerogel similarly for other images. Reproduced from Gupta, P., Singh, B., Agrawal, A.K., Maji, P.K., 2018. Low density and high strength nanofibrillated cellulose aerogel for thermal insulation application. *Materials and Design* 158, 224–236.

pectin, starch etc., for super thermal insulation application. Different kinds of additives such as nanoparticles, clay, graphene, and specialty polymers can be added as a reinforcing agent to enhance mechanical properties as well to decrease flame susceptibility and brittleness of bio-based aerogel. Gupta *et al.* (2018), had worked on cellulose nanofibers based aerogel for thermal insulation application. The authors explained the difference in the thermal conductivity phenomenon between conventional foam and aerogel via pictorial view (Fig. 7). It is clear in the picture that more solid content enhances the density of structure, which boosts the solid conduction. While due to large particle size of primary materials generate large voids in the specimen that helps to enhance gaseous conduction as well as convection phenomenon. Whereas, in the case of aerogel, the diameter of fibers is in nano-range having a low radius of curvature that assisted to squeeze the fibers and compresses the pores of structure within 2–50 nm range. The phenomena advantageous to capture the heated air in the pores and the air molecules crashed within the internal cell wall without transmitting the heat conductivity.

X-ray micro-tomographic analysis is basically performed to evaluate the three dimensional and homogeneous structure of any porous material. The analysis facilitated to investigate local density distribution and cracks in the microstructure, which help to correlate the thermal conductivity and mechanical properties of specimen. Fig. 8 shows the x-ray micro-tomographic images at a different density of cellulose nanofibers based aerogel. The top view and bottom view of local images (Fig. 8) depicted that aerogel was homogeneous throughout, while the three dimensional images are self-explained; that is by varying the solid content, the void space is reduced and aerogel should be more homogenous which accelerate to reduce the thermal conductivity of aerogel. The authors reported that thermal conductivity of insulation depends on the amount of solid material, moisture content, density and pore size of aerogel. The optimum thermal conductivity was reported to be $0.0255 \text{ W m}^{-1} \text{ K}^{-1}$ at aerogel density of 11.9 kg m^{-3} . A comparative study between thermal conductivity vs. density in addition to constituent of aerogel (Fig. 9) was reported by Gupta *et al.* (2018).

The exploration of thermal conductivity of aerogel is predominantly dedicated to the energy efficient building insulation application. Nanowood based anisotropic, lightweight and super thermal insulation materials were also explored by Li *et al.* (2018). Wood-based nano-insulation material had revealed four main characteristics to explain the super thermal insulation performance. Primarily, the porosity of nanowood was increased to 91% while pristine wood has 60% porosity. The higher porous nanowood

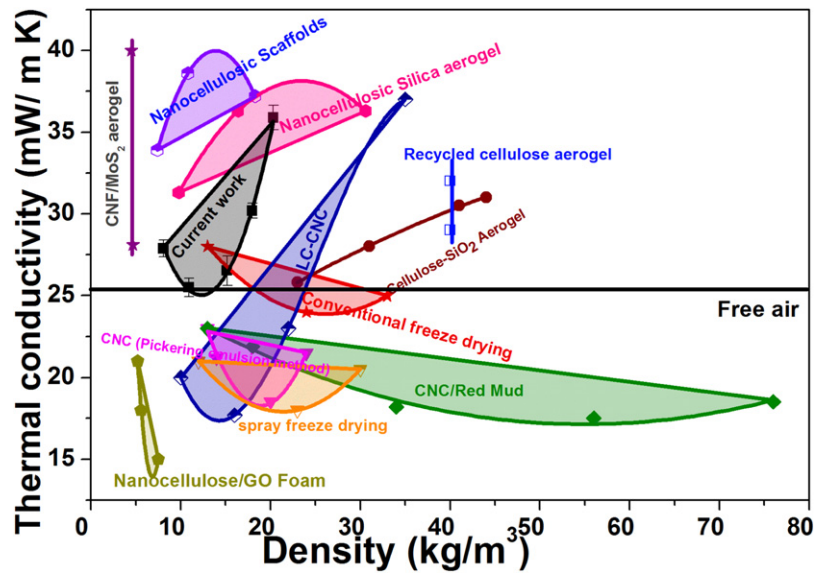


Fig. 9 Comparative study between numerous reports on aerogel for thermal conductivity as a function of density. Reproduced from Gupta, P., Singh, B., Agrawal, A.K., Maji, P.K., 2018. Low density and high strength nanofibrillated cellulose aerogel for thermal insulation application. *Materials and Design* 158, 224–236.

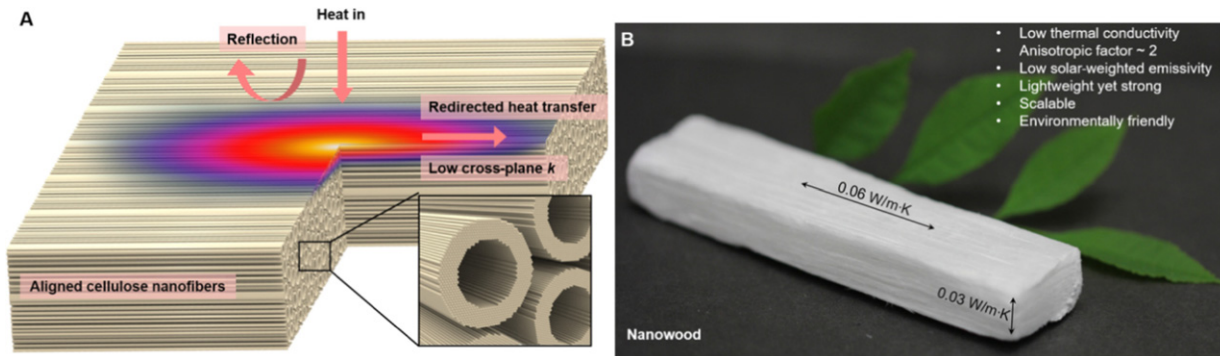


Fig. 10 Wood-based nano-insulation material: (A) Schematic representation of thermal conducting phenomenon, (B) Digital photograph and its corresponding properties. Reproduced from Li, T., Song, J., Zhao, X., *et al.*, 2018. Anisotropic, lightweight, strong, and super thermally insulating nanowood with naturally aligned nanocellulose. *Science Advances* 4 (3), eaar3724.

lowers the thermal conductivity. Secondly, the elimination of undesirable components of wood such as lignin and hemicellulose reduce the aggregates by weakening the interaction between cell wall fibrils that lowers the heat conductivity in lateral dimension (Fig. 10). The aggregated nanowood resulted in the anisotropic heat flow in the direction of fibers alignment. While the concluding remarks to lower the thermal conductivity of nanowood was described by several authors that pore size below mean free path of air predominately reduces the thermal conductivity of nano insulation materials.

Survey on Wood and Cork-Based Building Insulation

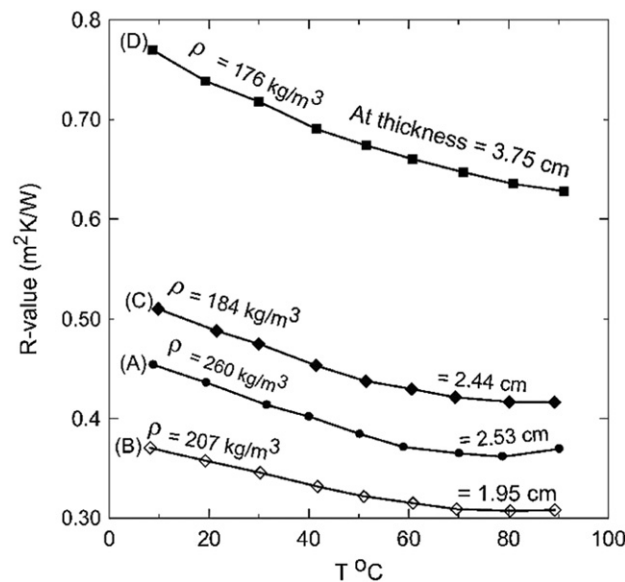
As a building insulation material, thermal conductivity is one of the most important criteria of subject of the investigation to evaluate the performance. The quantitative evaluation of thermal conductivity permits the assessment of the effectiveness of different insulation material (Al-Homoud, 2005).

Influence of Density on the Thermal Conduction

Thermal conductivity and diffusivity of birch (hardwood) had been investigated by Suleiman *et al.* (1999) via transient plane source method. The density and thermal conductivity are shown in Table 2. By varying the density, date palm fibers based board was prepared by Ali and Alabdulkarem (2017). The date palm fibers board was prepared by using corn starch binder. The authors

Table 2 Density and thermal conductivity of several biomaterials

Specimen	Density (kg m^{-3})	Temperature ($^{\circ}\text{C}$)	Thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
Birch (Hardwood)	680	21	0.323
	567	21	0.293
	543	21	0.291
	680	100	0.370
	567	100	0.309
	543	25	0.318
Mixed cork	162	25	0.045
Gypsum/ palm (10%)	753	25	0.15–0.17
Gypsum/cork (20%)	578–864	25	0.12–0.19
Concrete/cork (10%)	2100	25	0.96
Cement/hemp shives (40%)	1040	25	0.11
Plaster/Wheat fiber (25%)	1699	25	0.33
Plaster/Barley fiber (25%)	1617	25	0.29
Plaster/Wood shaving (25%)	1605	25	0.28
Concrete/durian (30%)	950	25	0.18
Concrete/coconut (30%)	770	25	0.17
Cement/coconut coir fibers (5%)	2100	25	0.41
Cement/coconut coir fibers (10%)	19,801	25	0.38
Cement/coconut coir fibers (15%)	1800	25	0.37
Cement/oil palm fibers (5%)	2030	25	0.40
Cement/oil palm fibers (10%)	1990	25	0.30
Cement/oil palm fibers (15%)	1970	25	0.27

**Fig. 11** *R*-value of date palmwood-based insulation material. Reproduced from Ali, M.E., Alabdulkarem, A., 2017. On thermal characteristics and microstructure of a new insulation material extracted from date palm trees surface fibers. Construction and Building Materials 138, 276–284.

had reported that thermal conductivity of boards is a function of temperature and density. The value of thermal conductivity increases by increasing the density and specimen temperature. The increment in the density enhances conduction as the solid transports the heat by phonon scattering due to lattice vibration of atoms and several authors have reported the same fact.

The date palm fibers based board has thermal conductivity between 0.0475 and $0.0697 \text{ W m}^{-1} \text{K}^{-1}$ with respect to density between 176 and 260 kg m^{-3} at 20 – 70°C (Ali and Alabdulkarem, 2017). Different varieties of date palm wood based materials for heat insulation is reported by Agoudjil *et al.* (2011). The mean thermal conductivity value is reported to be $0.083 \text{ W m}^{-1} \text{K}^{-1}$ at atmospheric condition.

Thermal resistance (*R*-value) of insulation measures, the effectiveness of insulation. The *R*-value of insulation depends on the thickness of insulation materials, thermal conductivity at a specified temperature and density. *R*-values of date palm fiber at different densities are shown in Fig. 11. The variation in the *R*-value of date palm fiber-based insulation with respect to temperature is reported as 18.49% for 176 kg m^{-3} , 18.32% for 184 kg m^{-3} , 18.61% for 260 kg m^{-3} and 16.91% for 207 kg m^{-3} (Ali and Alabdulkarem, 2017).

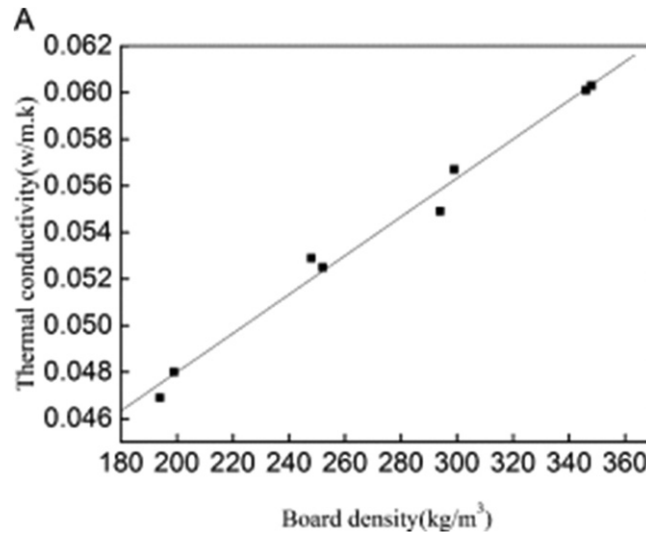


Fig. 12 Thermal conductivity of rice straw based board by varying density. Reproduced from Wei, K., Lv, C., Chen, M., *et al.*, 2015. Development and performance evaluation of a new thermal insulation material from rice straw using high frequency hot-pressing. *Energy and Buildings* 87, 116–122.

R -value of insulation had been investigated for waste cork based mortar and cement composites. The authors reported huge enhancement in R -value of insulation by incorporating waste cork. Different composition based on particle size and content of mortar, cement, and the waste cork had been prepared for characterization. The thermal conductivity of composites is reduced by 16% and 30% after addition of 10% and 20% waste cork as a reinforcing agent (Panesar and Shindman, 2012). The R -value of insulation increased from 0.059 to 0.086 m² K W⁻¹ and thermal conductivity decreased from 1.14 to 0.79 W m⁻¹ K⁻¹ by incorporating 20% waste cork. A 46% increment in the thermal resistivity was found after the addition of 20% waste cork in the composite. The oil palm fibers and coconut coir fiber reinforced cement composites also demonstrated a significant reduction in thermal conductivity coefficient with respect to control cement specimen (Lertwattanakul and Suntijitto, 2015). The incorporation of natural fibers had shown a positive effect on the thermal insulation performance of composites. The density and thermal conductivity are shown in Table 2. The thermal conductivity of pure natural particleboard based on different composition had been investigated by Khedari *et al.* (2004). The conductivity of composites with respect to density is demonstrated in Fig. 12. The authors described that density of fiberboard is directly proportional to the thermal conductivity because high dense packing of natural fibers shrinkages the voids and spaces and enhances the solid conduction which is the main factor of thermal conductivity. The authors also explained that, at the particular density, the thermal conductivity is varied due to different types of fibers used during sample preparation. The high amount of coconut fibers increases thermal conductivity as compared to durian fiber. This is due to the shape and size of the fiber which affects the porosity and structure of fiberboard.

Another insulation material based on rice-straw was prepared by Wei *et al.* (2015) by the hot pressing method. The authors also correlated the variation in the thermal conductivity with density and particle size. They had prepared a 40 mm thick sheet based on rice straw with a density in the range of 200–350 kg m⁻³. The thermal conductivity of rice straw based board is demonstrated between 0.051 and 0.053 W m⁻¹ K⁻¹. Rice straw is agricultural waste residue that is very lightweight and porous material with a significantly lower value of thermal conductivity. The authors reported a linear relationship of thermal conductivity with respect to density, which is shown in Fig. 12.

The thermal conductivity increases with density as the amount of solid content increases, heat conduction by solid also increases. So, the pore size of the solid board also decreases significantly with the increment in density, and thermal conductivity of rice straw is higher than the air which is also a responsible factor for the enhancement in thermal conductivity.

The density of any porous structure depends upon particle size and void space. For a specified density of board, if the particle size of raw materials decreases, it decreases the pore size of the board. The small pores capture the heated air due to the scattering effect of phonon and lower the thermal conductivity, whereas, in case of larger pores the heated air pass throughout the board following the law of thermal convection and increases the quantitative thermal conductivity (Niemz and Sonderegger, 2011). Due to the variation in the particle and pore sizes of the board, the thermal conductivity of rice straw based board is varied between 0.0498 and 0.0543 W m⁻¹ K⁻¹ (Wei *et al.*, 2015).

Influence of Temperature on the Thermal Conduction

The thermal conductivity of rice straw based board was also evaluated by varying the temperature. It is observed that there was a 20% increment in the thermal conductivity of 250 kg m⁻³ board by varying the temperature from 10°C to 50°C. The results have shown strong agreement with the temperature-dependent thermal conductivity of birch wood. The thermal conductivity

of wood-based specimens had demonstrated 14% and 24% increment in the longitudinal and transverse direction respectively in the temperature range of 20–100°C (Suleiman *et al.*, 1999). This is due to the fact that temperature increment enhances the thermal motion of solid molecules. The total thermal conductivity is also dependent on heat transfer due to radiation. Another fact of increment in the temperature-dependent thermal conductivity is the basis of the composition of bio-originated products i.e., ligno-cellulosic materials. At the micro level, the crystallinity of cellulose structure deviated at higher temperature and resulted in loss in their mechanical properties and also altered their ability of heat conduction.

Influence of Moisture on the Thermal Conduction

Besides all other factors, humidity is also an important factor for bio-originated insulation materials. The natural materials are sensitive to moisture but some natural materials like jute, hemp, cork, rice straw have shown excellent result against moisture. The influence of the moisture on the wood-based fiberboard had been investigated by Troppová *et al.* (2015). The thermal conductivity was calculated in the temperature range of –10 to 60°C at different moisture content. It is quite clear in the results that moisture content enhances the thermal conductivity of wood-based composites. Hence a hydrophobic coating would be a great idea to improve the insulation performance of wood-based board.

Mechanical Properties of Building Insulation Materials

Most of the authors devoted to the thermal insulating properties of materials, while very few researchers have shown their concern about the mechanical properties of insulation. Wei *et al.* (2015) have reported the influence of moisture content on the mechanical properties of rice straw based hot pressed board. The relationship between pressing temperature vs. internal bonding strength and modulus of rupture was estimated for coconut husk and bagasse based insulation board. The board was prepared by hot pressing technique without using the artificial binding agent. Modulus of rupture was increased by varying the hot pressing time and temperature. Modulus of rupture was not only dependent on the internal bonding strength of fibers but also act as a function of geometry, orientation and individual strength of fibers. The modulus of elasticity followed the same trend as the modulus of rupture. Most of the specimen was found to behave as an open cell porous structure and follows the power law of density. The bulk moduli of bagasse based insulation board were found to be 102 MPa, 392 MPa and 957 MPa at a density of 250 kg m⁻³, 350 kg m⁻³ and 450 kg m⁻³ respectively. While the moduli of rupture of coconut husk based board were 88 MPa and 365 MPa at 350 kg m⁻³ and 450 kg m⁻³ respectively.

Conclusions

Characterizations of wood and cork based building insulation is an intense area of research nowadays. Environmental protection and energy conservation are the two most prominent areas of exploration due to several regulations and country policies. The optimum thickness of insulating materials depends on the cost of energy consumption and the cost of insulation. The increment in the cost of energy increases the demand for insulation material. The insulating material saves energy utilization by the act as a barrier between system and surroundings. The preparation methodology and several characterizations techniques of wood and cork based composites for building insulation system has been discussed in this article. The effect of density and porosity of specimen is clearly visualized in recent investigations. The high-density wood-based composites range the thermal conductivity between 0.12–0.98 W m⁻¹ K⁻¹, whereas, the wood-based nanocomposites aerogel shows around 0.008–0.040 W m⁻¹ K⁻¹. The influence of moisture and temperature variation plays an important role in the thermal conductivity of wooden composites. Mechanical properties such as bonding strength, modulus of rupture and compression strength depend on the size of particles, density and preparation methodology. This article covers the importance of insulation in the building sector, several primary and secondary characterization etc.

See also: Bio-Based Materials in Sportswear Applications. Energy Efficiency Analysis in Building Walls in Tropical Climate Using Thermal Insulation System. Insulation Materials for the Building Sector: A Review and Comparative Analysis. Investigation of the Fuel Value of Selected Wood Samples Using Artificial Neural Networks. Manufacturing, Applications and Mechanical Properties of Lightweight Wood-Based Sandwich Panels. Performance of Cork and Composites Joints. Waste Resources Recycling in Achieving Economic and Environmental Sustainability: Review on Wood Waste Industry

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Dry/Solid-State Fermentative Ethanol Production

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Introduction

The necessity of replacing fossil fuels by renewable energy resources is not deniable. Fossil fuels release carbon dioxide, nitrous oxide, methane, and other pollutants that have greenhouse gas (GHG) effect. GHGs concentrations in the atmosphere have enormously increased during the last century (Metz, 2007). The increasing trend of GHG emissions draws serious negative effects on world climate. Increases in GHG emissions mostly caused by human activities. It is required to decrease GHG emissions to minimize the future climate change. A part of this goal can be achieved by substituting fossil fuels with biofuels. Other motivations to develop renewable energy resources are the wide fluctuations in the oil price as well as the security of energy supply. In addition, local production is a specific feature of bioenergy, which can help rural development.

Biofuels

Biofuels, as fossil fuels substitutes, have the potential of improving the energy security and quality together with reducing the global warming (Chum and Overend, 2001). Biofuels are produced from biomass, e.g., agricultural material, wood, energy crops, organic fraction of municipal solid waste, manure, and algae. In other words, biofuels are produced from recently living biomass as opposed to ancient biomass in fossil fuels. Biofuels are divided to solid, liquid, and gaseous forms and include wood pellets, bioethanol, biodiesel, and biogas. The global biofuels production increased from 37 to 84 million tons oil equivalent from 2007 to 2017, annually. The European Union planned a proportion of 10% for renewable resources in final energy consumption in the transport sector by 2020.

First generation biofuels, which is prepared from food and feed crops containing sugars, starch, and vegetable oils, have been widely investigated to this point. These crops are available in limited quantities, and their use as biofuel substrates make a direct competition between food and fuel. Second-generation biofuels can be produced from different types of non-food biomass, including animal waste and plant residue, which are mostly lignocellulosic biomass. Second-generation biofuels are more favorable than first-generation biofuels because of lower GHG emissions, in addition to being non-food resources (Fig. 1).

The most widely applied biofuel is bioethanol with an approximate portion of 90% of total biofuels consumption, mostly in Brazil, the United States, and some European countries. It can be produced from different substrates, including corn (maize), cereal crops, potatoes, sugar cane, sugar beets, cassava, sorghum, and lignocellulosic materials.

Ethanol can be used alone or as a blend with gasoline for transportation applications. However, it is usually blended with gasoline to increase the octane number of gasoline, improve cold start of the engine, decrease the gasoline consumption, improve engine performance, and reduce air pollution. Ethanol combustion produces carbon dioxide which can be consumed by biomass during the growth cycle. Therefore, there is no net increase in the CO₂ emissions (Wyman, 1994).

Bioethanol Production

Second-generation bioethanol, produced from lignocelluloses, is one of the most promising renewable energy resources and the main topic in this article. Lignocelluloses are mainly composed of cellulose, hemicellulose, and lignin. The lignocellulose cell wall

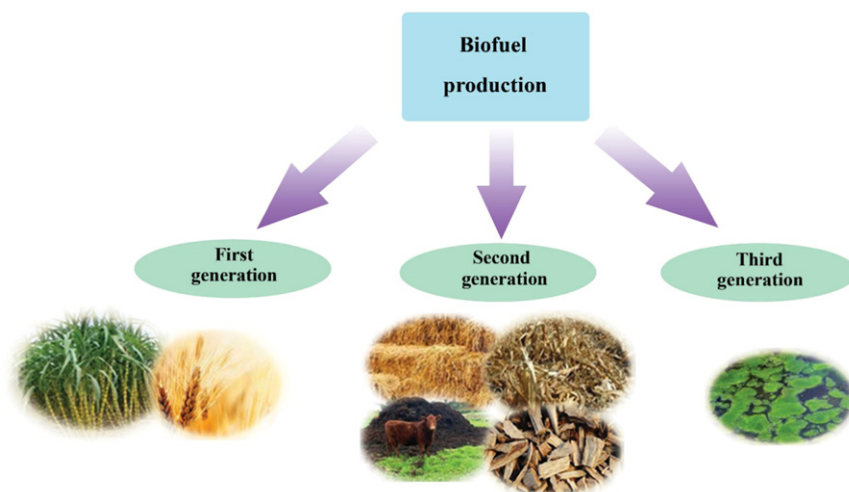


Fig. 1 Different generation of biofuels.

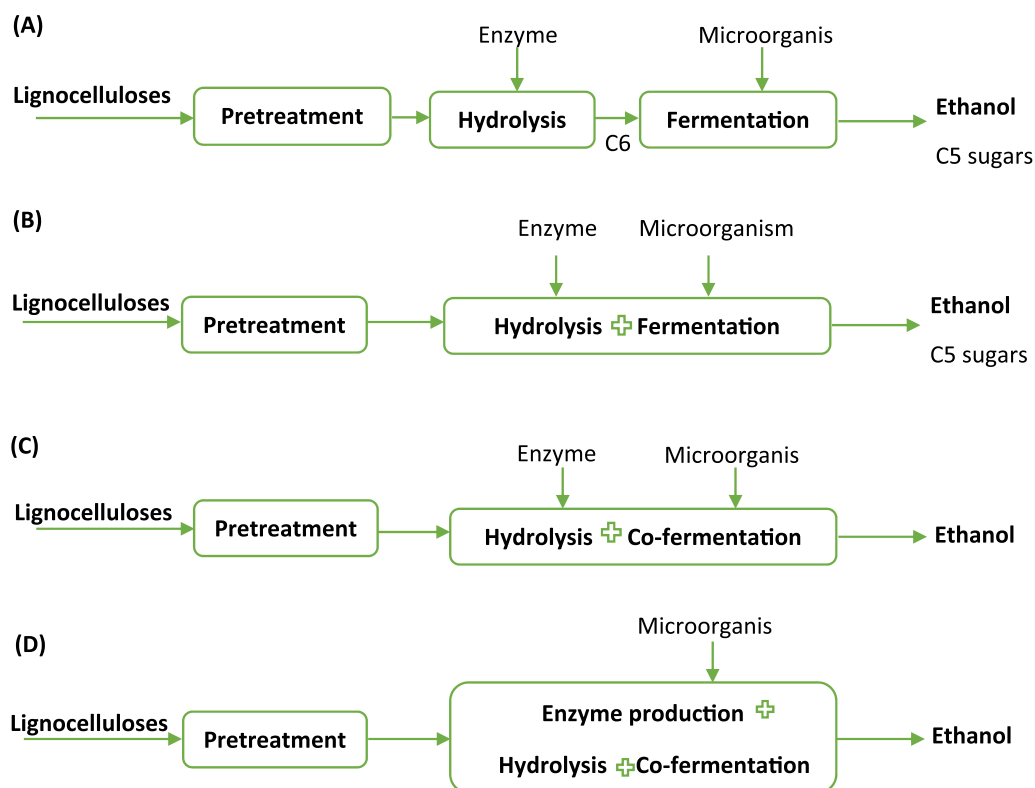


Fig. 2 Different methods for bioethanol production from lignocelluloses: (A) Separate hydrolysis and fermentation, (B) simultaneous saccharification and fermentation, (C) simultaneous saccharification and co-fermentation, and (D) consolidated bioprocessing.

has a highly complex and compact structure and acts as a barrier to enzymatic/microbial hydrolysis and the following fermentation. Therefore, a substantial pretreatment is essential to make lignocelluloses degradable. Different pretreatments aim at increasing the accessibility of the polysaccharides to hydrolytic enzymes. Discarding pretreatment step, enzymatic hydrolysis can only release less than 20% of the sugars. Comprehensive reviews and book articles have been focused on the pretreatment methods for lignocellulosic substrates (Mood *et al.*, 2013). This topic is not within the purpose of this article; thus, the interested readers can refer to the related references.

Hydrolysis

In hydrolysis stage, polysaccharides are depolymerized and converted into oligosaccharides and monosaccharides. Enzymatic hydrolysis is known as the most effective process to liquefy polysaccharides. Cellulases and hemicellulases are used simultaneously for the hydrolysis of cellulose and hemicellulose, respectively. The conjugated action of these two enzymes yields higher sugar production (Talebnia *et al.*, 2010). Cellulose is converted to glucose and hemicellulose is depolymerized to glucose, galactose, mannose (C6 sugars), as well as xylose and arabinose (C5 sugars). Hydrolysis of lignocelluloses for ethanol production was also presented in the literature (Sun and Cheng, 2002).

Fermentation

The sugar-rich hydrolysate from hydrolysis stage can be fermented by microorganisms to produce ethanol. The theoretical yield of ethanol production is 0.51 g ethanol per kg of glucose (Hamelinck *et al.*, 2005). In the fermentation stage, it is very important that the operational conditions, such as temperature and pH, be maintained in the optimum range for the growth of microorganism (Aditiya *et al.*, 2016). An important factor preventing industrial utilization of lignocelluloses for bioethanol production is the lack of microorganisms able to efficiently ferment (with high yield and high rate) all sugars (both pentoses and hexoses) released during pretreatment and hydrolysis stages.

Different Approaches for Bioethanol Production

Different approaches are used to produce ethanol from lignocelluloses via enzymatic hydrolysis and fermentation, depicted in Fig. 2. Hydrolysis (saccharification) and fermentation of pretreated lignocellulose can be performed at separate reactors or at the same reactor. When hydrolysis and fermentation are performed at separate steps, the process is called separate hydrolysis and fermentation. This approach makes the possibility of performing each step at its optimum conditions. The common

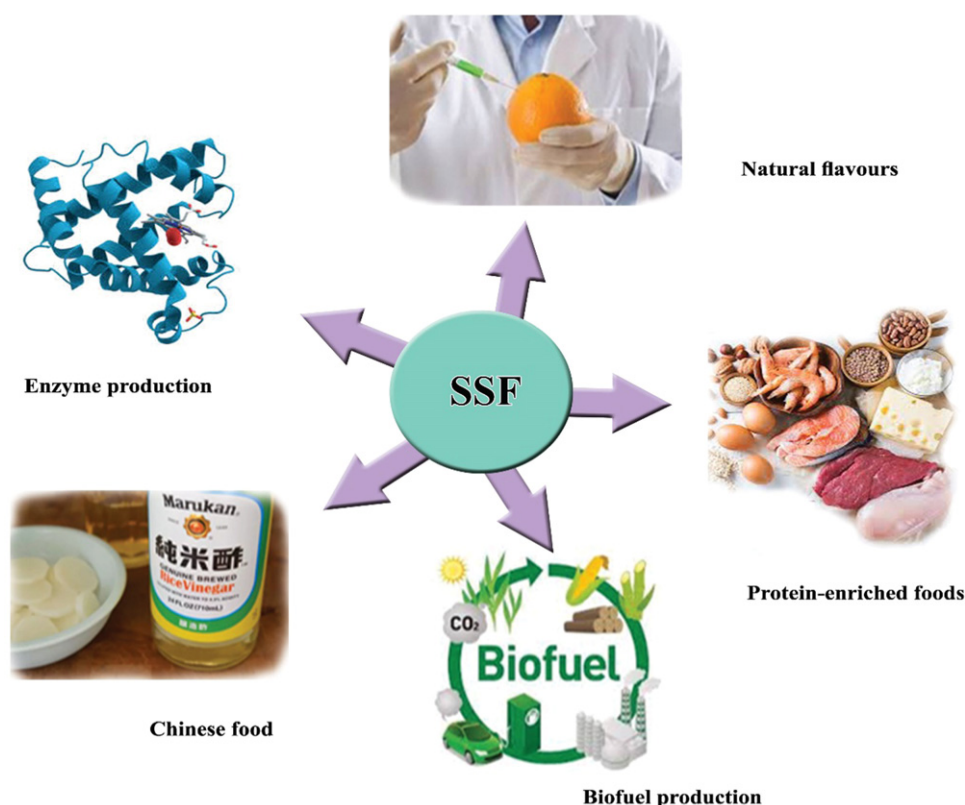


Fig. 3 Production of different biochemical/bioproducts by SSF.

microorganism applied in this approach, *Saccharomyces cerevisiae*, is only able to ferment C6 sugars. Therefore, C5 sugars should be fermented at a separate stage using another microorganism. Also, the hydrolysate needs to be squeezed in this process to be feed to fermentation step, which requires energy and water input. Another approach is simultaneous saccharification and fermentation, which hydrolysis and fermentation are combined in one stage. In this approach, the microorganism consumes glucose as soon as it is produced. Therefore, the inhibitory effect of glucose on enzymatic hydrolysis is reduced. Simultaneous saccharification and fermentation process has other advantages over separate hydrolysis and fermentation, including less energy requirement, lower enzyme need, less contamination potential, and higher ethanol yields (Olofsson *et al.*, 2008). When the microorganism applied in SSF is able to ferment both C6 and C5 sugars, the process is called simultaneous saccharification and co-fermentation. In this process, the inhibitory effect of xylose is also eliminated with its consumption, which leads to the increase of ethanol yield. Consolidated bioprocessing includes the biological conversion of lignocelluloses into bioethanol in a single step without adding enzymes and has been attracted numerous researches in recent years. In consolidated bioprocessing, enzyme production, hydrolysis, and fermentation are performed by a single strain or a group of microorganisms in one step (Olson *et al.*, 2012).

In addition, the process of ethanol production can be performed in submerged or solid-state approaches. When the substrate and microorganisms are floated in free water during the process, it is called submerged fermentation (SmF). And, if the process is performed in the presence of no or only a few free water molecules, it is called solid-state fermentation (SSF). The water content in SmF process is 90%–95%, and some solids are suspended in liquid phase. In contrast, the moisture content in SSF is typically in the range of 12%–70% (Chen, 2013). The SmF is well established, while SSF is still the topic of intensive research in recent years.

Solid-State Fermentation

SSF process is conducted in the absence or near absence of free liquid phase, unlike SmF (Pandey, 2003). However, the presence of enough moisture (usually around 60%) in the system is necessary for microorganisms to grow and metabolize the substrate. In recent decades, SSF in biological processes, specifically in biofuel production, is considered as the least expensive process and the most environmentally friendly (Zhou *et al.*, 2018).

SSF has been used for production of traditional foods and mould-ripened cheese since a long time ago. This method has been widely used for different purposes such as production of secondary metabolites, enzymes, Chinese food, natural flavors, protein-enriched foods, and bioconversion of lignocelluloses (Olofsson *et al.*, 2008), Fig. 3. SSF is commercially applied for some purposes, e.g., bread making, and enzyme and biogas production. However, its application in ethanol production is still in the research phase.

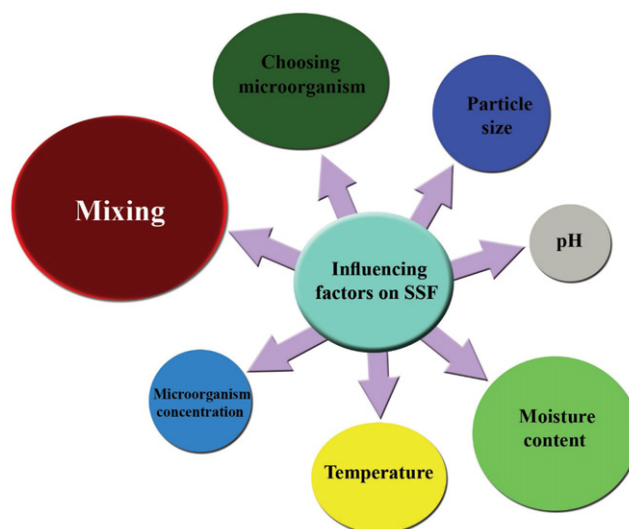


Fig. 4 Different factors affecting ethanol production by SSF.

Influencing Factors on SSF

The selection of microorganism, substrate, and operational conditions are the most influencing factors in SSF, which are explained in this section (Fig. 4).

Microorganism for SSF

The selection of microorganism is one of the most important factors that influences ethanol production through SSF. The desired water activity for the growth of bacteria, yeasts, and fungi in solid-state environment is different. Bacteria and yeast typically grow at water activity values about 0.9 and 0.8, respectively. Whereas, the desired value of water activity for fungi is between 0.6 and 0.7. The microorganisms adapted to environments with lower water activity values are more suitable for SSF. The industrial microorganism for applying in an SSF process of lignocelluloses should have a high ethanol yield and productivity, high resistance to sugars, ethanol, and salts, high specific growth rate, the ability of utilizing different substrates, low nutrition needs, and thermal and shear tolerance. Such a microorganism with all these features is not known in nature. However, the yeast *Saccharomyces cerevisiae* has been successfully applied in industrial scale. Some microorganisms, including *Mucor indicus*, *Zymomonas mobilis*, and Thermotolerant *Issatchenkia orientalis*, has also been studied for SSF ethanol production and showed acceptable ethanol yields.

Some anaerobic bacteria have also the ability to produce ethanol from lignocelluloses, but the process has a very slow rate, low ethanol yield, high production of byproducts, and very low tolerance to ethanol. One of the features of anaerobic bacteria, like *Z. mobilis*, is low production of biomass, and thus converting the majority of carbon source to ethanol. *Z. mobilis* metabolizes glucose to ethanol using the Entner-Doudoroff pathway and shows high ethanol yield and tolerance. However, it could not occupy the position of *S. cerevisiae* in industrial applications until now.

In nature, fungi usually live on moist solid substrates such as wood, roots, seeds, stems, and excrement of animals. Filamentous fungi are thought to be the best options for SSF because of their physiological, biochemical, and enzymological characteristics. These characteristics include hyphal tip growth and high tolerance to high osmotic pressure and low water activity. Therefore, solid-state fermentation offers the greatest potentials with the presence of filamentous fungi (Manan and Webb, 2017).

Moisture content

The moisture content, as one of the most influencing factors on the enzyme stability, microbial growth, and ethanol yield, should remain constant at its optimum value during SSF process. The optimum amount of water for microbial activity of different microorganisms is presented based on the water activity (a_w) of the culture, which indicates the amount of water in the substance. Too low moisture contents lead to the decrease of microbial growth, nutrition diffusion, enzyme resistance, and substrate swelling, and finally result in the process cessation. On the other hand, the high moisture contents of substrate result in agglomeration of particles, decrease in the surface area of substrate, limitations in oxygen transfer, and great decrease in ethanol production. A method to provide enough moisture is adding the desired amount of water during the process. Feeding with saturated air is another common method to avoid substrate drying in designated fermenters. The moisture content in the range of 70%–80% is shown as the optimum value for ethanol production from lignocelluloses by SSF process (Molaverdi et al., 2013).

Microorganism concentration

The initial inoculation is another important parameter that its value should be optimized to improve the rate of ethanol production in SSF. Increasing the inoculation concentration up to a special point increases the ethanol yield. After that point, the ethanol yield decreases because of overusing sugars by microorganisms for their growth and maintenance (Kwon *et al.*, 2011).

Particle size

The particle size of substrate is another factor, influencing ethanol production by SSF. The particle size with effects on the shape, porosity, and accessible surface area of substrate can interfere the rates of heat and mass transfer and microbial growth. Smaller particle size of substrate can increase the initial rate of hydrolysis and degradation by providing larger accessible surface area to the hydrolytic enzymes. However, too small particle size would cause geometric limitations of mycelia growth, and heat and mass transfer limitations, especially for oxygen diffusion, which can be mentioned as steric hindrance. An optimum particle size can provide adequate oxygen diffusion, nutrients accessibility, and mycelia growth. Particle size and the related properties may change during fermentation (Karimi *et al.*, 2014).

Temperature

Each microorganism has an optimum temperature for maximum metabolite production. The microbial activity generates heat, which can be accumulated in bioreactor and leads to the temperature increase due to the heat transfer limitation in SSF. Overheating the bioreactor disturbs the microorganisms' growth, the synthesis of enzymes, and the production of ethanol. Also, overheating in large-scale bioreactors results in moisture loss, which in turn, disturbs the growth of microorganisms. To avoid this problem, design of SSF bioreactors is performed with a focus on maximizing heat transfer. On the other hand, temperature control causes temperature variations, which can produce a large amount of water condensed and dropped back to fermenter, and consequently creates a heterogeneous environment. To maintain the temperature within the ideal range, an air inlet is usually applied to make the system cool. To maintain the required moisture in the system, the loss of moisture by the air outlet must be considered (Nee'nigam and Pandey, 2009).

Mixing

Mixing or agitation can disrupt gradients and improve homogeneity in SSF systems, in addition to helping aeration. However, continuous or severe mixing can disturb the microorganism cells, particularly the mycelium of filamentous fungi. Slow and irregular agitation may be applied to avoid cells damage. However, the mixing of SSF process is not always preferred. Generally, it is suitable when yeasts or bacteria are used, because they are not tightly attached to the substrate (Mitchell *et al.*, 2011; Zhao *et al.*, 2017).

pH

The measurement and control of pH in SSF is too difficult due to the absence of free water, the system heterogeneity, and the lack of pH electrode in the solid media. Using the microorganisms with the ability of growing at wide ranges of pH is usually preferred. Different groups of microorganisms prefer culture environments at different pH values. In general, the favorite environment for bacteria has almost neutral pH, that of fungi and yeasts has poor acidic pH, and actinomycetes mostly prefer basic environment. Applying the usual electrodes for the substrate suspended in water or potentiometric electrodes are available methods for measuring pH value in SSF process (Behera and Ray, 2016).

Advantages and Disadvantages of SSF

Application of SSF instead of SmF offers from several advantages, as listed in Table 1. An important advantage of SSF rather than SmF is its resistance to catabolite repression of enzyme synthesis. Catabolite repression is a system of gene control which causes quick adaptation of microorganism to a preferred carbon and energy resource (mainly glucose). This phenomenon suppresses the metabolism of other carbon resources in the presence of glucose, usually through inhibiting the synthesis of enzymes involved in catabolism of other sugars. Catabolite repression does not occur in SSF even in the presence of 100 gL⁻¹ sugar, whereas severe repression happens in SmF at sugar concentrations higher than 10 gL⁻¹. Some hypotheses were introduced to explain the resistance of SSF to metabolite repression, including the presence of sugar gradients inside the aggregate of microorganisms and changes in sugars permeability of microorganisms grown by SSF (Viniestra-González and Favela-Torres, 2006). This feature can effectively modify the performance of SSF consolidated bioprocessing, since enzyme production happens in the same step of hydrolysis and fermentation.

The interesting point is that most microorganisms, e.g., filamentous fungi and most actinomycetes, naturally live on the wet surfaces, considered as natural SSF (Carlile *et al.*, 1994). Therefore, the natural strains mostly have been adapted to SSF conditions.

In addition, lower water activity in SSF leads to lower demand on sterility (Hölker *et al.*, 2004). Low water content also results in lower probability of contaminations. Downstream processing, including ethanol distillation, is easier and less energy demanding because of the higher concentration of ethanol (Canabarro *et al.*, 2017). One of the main problems in SmF is foam production that prevents oxygen mass transfer, especially in the case of using filamentous fungi. However, foam is not produced in SSF process. Generally, SSF is proved as an economically feasible process (Manan and Webb, 2017). Also,

Table 1 Advantages and disadvantages of SSF process

<i>Advantages</i>	<i>Disadvantages</i>
– Lower catabolite repression	– Existence of temperature gradient
– lower water demand	– Mass and heat transfer limitations
– Less liquid waste production	– Substrate and moisture gradients
– Lower demand for sterility	– Steric hindrance
– No rigorous process control requirement	– Bed caking
– No foam production	– Difficulty in handling solids in reactor
– Absence of anti-foam chemicals	– Difficulty in mixing
– Easier aeration	– Difficulty in pH control
– Higher volumetric productivity	– Difficulty in biomass measurement
– Higher concentration of ethanol	– Difficulty in scale-up
– Lower capital investment	– Lack of kinetic and design data
– Lower operating costs	– Loss of moisture
– Lower energy requirements	
– Lower cost for ethanol recovery	

traditional applications of SSF in food processes shows tremendous potential of this promising process for industrial applications.

Although SSF offers some unique advantages, it undergoes some operational disadvantages which needs further attempts to overcome. Mixing/agitation is a challenge in SSF, as it is difficult or impossible. The absence of mixing can restrict the growth of microorganism due to limited nutrient diffusion and also inhibit the growth of some microorganisms. Also, SSF process suffers from some engineering problems, such as temperature build-up, the presence of gradients in concentrations of substrate, moisture, and products as well as pH, which all are due to the limited mass and heat transfer. Besides, heat, accumulated during the growth and metabolism of microorganism, leads to the moisture loss.

Difficulties in biomass measurement have limited the available information on microbial growth, and kinetics data in SSF. Moreover, the lack of data causes difficulties in scaling up of laboratory results. Another important factor for scaling up a SSF bioreactor is finding the operating conditions that yield constant values of water and energy balances with increasing scale. However, several bioreactors have been recently made to overcome the scaling up problems (Singhania *et al.*, 2009).

Low biomass concentration and low density of mycelia can occur for cellulolytic fungi in SSF of lignocelluloses, which are due to the steric hindrance of the growth of filamentous fungi. The term “steric hindrance” refers to the combined effect of geometric limitations of mycelia growth, especially in substrate pores, mass transfer limitations, and low substrate availability (Laukevics *et al.*, 1985).

Bed caking is another common problem in SSF, which occurs due to the changes in substrate during the fermentation. This phenomenon makes some problems in process control and downstream treatments.

Despite the problems that exist in performing SSF and its scaling up, this process is considered advantageous in competition with SmF.

SSF Bioreactors

Bioreactors are responsible for providing a sealed and proper medium for microorganism to grow and produce ethanol. As it was discussed in Section “SSF Bioreactors”, the optimization and control of influencing factors, including moisture content, temperature, oxygen content, mixing, pH, are very important in SSF bioreactors. Some operating parameters like cooling system, the heat transfer coefficient of fermenter wall, aeration, and oxygen diffusion in gas phase needs careful consideration in the design of SSF bioreactors.

Improper oxygen transfer can often occur in some designs of SSF bioreactor, affecting the moisture content and temperature of medium. An appropriate design of bioreactor leads to high rates of bioreactions, which consequently results in high rates of microorganism growth, substrate consumption, and ethanol synthesis.

To design a special SSF bioreactor for a specific biological process (ethanol production), many parameters, including mixing, moisture gradients, aeration, oxygen transfer, temperature control, stability, reliability, scale-up, and costs, should be considered. Different types of bioreactors have been developed and used for SSF process, and different researchers named them differently. However, Mitchell *et al.* (2002, 2011) classified SSF bioreactors into four groups based on mixing and aeration, Fig. 5:

- *Un aerated and unmixed bioreactors*: In this group of bioreactors, air stream is not blown forcefully through the bed, but it is circulated around the bed, and they have a static or occasionally mixed (e.g., twice a day) bed. Tray bioreactor is another name of this group.
- *Forcefully-aerated bioreactors without mixing*: In these bioreactors, air stream is blown forcefully through the bed, and the bed is static or mixed occasionally (e.g., once a day). *Packed-bed bioreactor* is the typical name of this group.

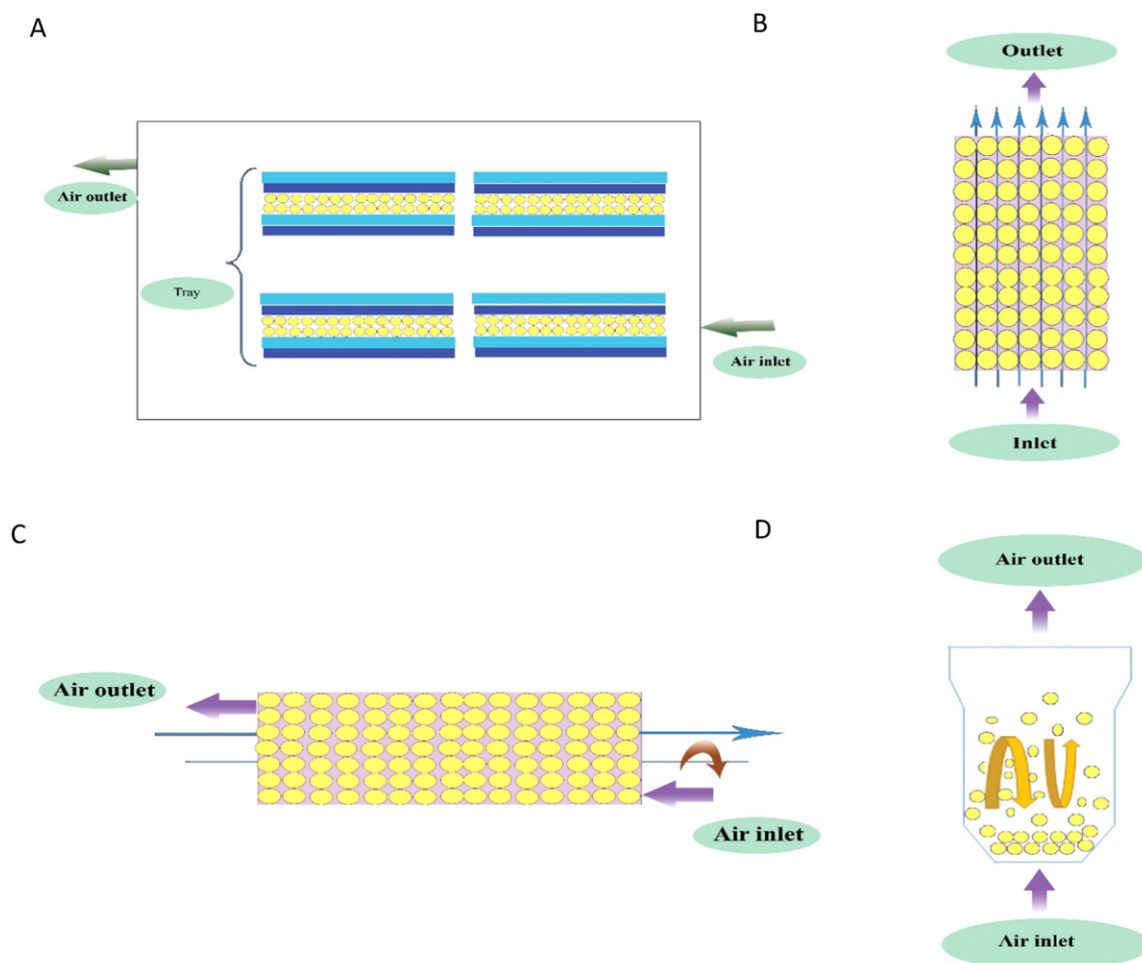


Fig. 5 Classification ofSSF bioreactors: (A) Tray bioreactor, (B) packed bed, (C) rotating drum, and (D) gas-solid fluidized bioreactors.

- *Unaerated, continuously/intermittently mixed bioreactors*: In this group, air stream is not blown forcefully through the bed, but circulated around it, and the mixing is performed continuously or intermittently with intervals of minutes to hours. Stirred-drum bioreactors and rotating drum bioreactors are two type of bioreactors in this group, having different mechanisms for mixing. This type of bioreactor can be used for batch or continuous operation.
- *Forcefully-aerated, continuously/intermittently mixed bioreactors*: In these bioreactors, air stream is forcefully blown through the bed, and the mixing is performed continuously or intermittently with time intervals of minutes to hours. Selecting continuous or intermittent mixing is dependent to the microorganism sensitivity to shear stress and the physical properties of the substrate. Different designs belong to this group, such as gas-solid fluidized bed bioreactors, stirred-aerated bioreactors, and rocking drum.

Conclusions

Ethanol, the most widely applied biofuel, can be produced through different approaches from various substrates. A promising approach is SSF that has interested many researches during the past few years. It is because of many technical advantages of SSF in comparison with SmF, including less water requirement, higher volumetric productivity, less liquid waste production, easier downstream processing, less capital investment, and less operating costs. SSF has been widely used at industrial scale for other products. However, its application for ethanol production has been recently started and is mostly still performed at laboratory scale. The main challenges of SSF, including mass and heat transfer limitations, can be solved by an appropriate design of bioreactor and are still at development stage.

See also: Fermentative Production of Optically Pure Lactic Acid From Renewable Materials. Plasma Arc Driven Solid Waste Management: Energy Generation and Greenhouse Gases (GHGs) Mitigation. Solid Polymer Waste Materials for Repairing of Heritage Composite Structure: An Additive Manufacturing Approach

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Effect of Temperature Dependence of Sorption on Hygrothermal Performance of a Hemp Concrete Building Envelope

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Nomenclature

Latin symbol

C	Energy constant of GAB model
C_p	Specific heat at constant pressure ($J.kg^{-1}.K^{-1}$)
C_{p0}	Specific heat of dry material at constant pressure ($J.kg^{-1}.K^{-1}$)
C_{p1}	Specific heat of water at constant pressure ($J.kg^{-1}.K^{-1}$)
D_T	Mass (vapor and liquid) transport coefficient associated to a temperature gradient ($m^2.s^{-1}.K^{-1}$)
$D_{T,v}$	Vapor transport coefficient associated to a temperature gradient ($m^2.s^{-1}.K^{-1}$)
D_θ	Mass (vapor and liquid) transport coefficient associated to a moisture content gradient ($m^2.s^{-1}$)
$D_{\theta v}$	Vapor transport coefficient associated to a moisture content gradient ($m^2.s^{-1}$)
E_1	Monolayer enthalpy of adsorption ($kJ.mol^{-1}$)

Greek Symbol

ϕ	Relative humidity (%)
π	Water vapor permeability ($kg.m^{-1}.s^{-1}.Pa^{-1}$)
θ	Moisture volumetric content ($m^3.m^{-3}$)

E_m	Multilayer enthalpy of adsorption ($kJ.mol^{-1}$)
g	Gravity acceleration ($m.s^{-2}$)
h_M	Convective mass transfer coefficient ($m.s^{-1}$)
h_T	Convective heat transfer coefficient ($W.m^{-2}.K^{-1}$)
K	Energy constant of GAB model
Le	Lewis number
L_v	Heat of vaporization ($J.kg^{-1}$)
M_w	Molecular weight ($g.mol^{-1}$)
P_v	Vapor pressure (Pa)
P_{vs}	Saturation pressure of water vapor (Pa)
R	Ideal gas constant ($J.mol^{-1}.K^{-1}$)
T	Temperature (K)
t	Time (s)
w	Moisture content ($kg.kg^{-1}$)
w_m	Monolayer moisture content ($kg.kg^{-1}$)
x	Abscissa (m)

λ	Thermal conductivity ($W.m^{-1}.K^{-1}$)
ρ_l	Mass density of water ($kg.m^{-3}$)
ρ_v	Mass density of water vapor ($kg.m^{-3}$)

Introduction

Temperature and relative humidity are important parameters influencing perceived indoor air quality and human comfort. High moisture levels can damage construction and inhabitant's health. High humidity harms materials, especially in cases of condensation and it helps moulds development increasing allergic risks. The use of various hygroscopic materials is a passive way to moderate indoor humidity levels. The material that adsorbs and desorbs water vapor can be used to moderate the amplitude of indoor relative humidity and therefore to participate in the improvement of the indoor quality and energy saving (Hameury, 2005; Shea *et al.*, 2012; Maalouf *et al.*, 2014; Samri and Moujalled, 2014; Olalekan and Simonson, 2006; Tran Le *et al.*, 2010). The use of vegetable particles (such as flax shives, straw bales, etc.) as building material aggregates is an interesting solution as they are eco-friendly materials and have low embodied energy. Among these vegetable particles, hemp shives have been extensively studied in many researches (Li *et al.*, 2017; Gurlay *et al.*, 2017; Amziane *et al.*, 2016). Hemp shives can be used as particle boards, biodegradable plastics, building materials for thermal and acoustic insulation products (Li *et al.*, 2013; Pantawee *et al.*, 2017), etc. Hemp concrete which is one of these materials is more and more recommended by the eco-builders for its low environmental impact. The physical properties (thermal conductivity, heat capacity, sorption isotherm, water vapor permeability, etc.) of hemp concrete have been measured by many authors (Collet *et al.*, 2008; Rahim *et al.*, 2015) showing that it presents high moisture buffering capacity and a good compromise between insulation and inertia materials.

The knowledge of hygrothermal profile of materials is very important in order to evaluate the performance and the durability of building envelope. For studying the hygrothermal behavior of a hemp concrete wall, a simulation should be done because it is cheaper and able to give more detailed results than a test in situ. For this purpose, many simulation tools have been developed and hygrothermal properties are required for all Heat, Air and Moisture transfer (HAM) models. Many models and simulation tools are represented in the Annex 41 of the International Energy Agency's (Woloszyn and Rode, 2008). For the building envelope, the main difference in HAM-transfer modeling is made by the dimension of represented phenomena and they can be categorized by the

granularity and complexity. Up to now, most hygrothermal tools have used the isothermal sorption curves that express the equilibrium between the moisture content and relative humidity in the representative elementary volume at a constant temperature.

A detailed parametric study of hygrothermal behavior of a wall made of hemp concrete subjected to hygrothermal shocks was carried out and showed that temperature and relative humidity variations in the wall are very sensitive to thermal properties, moisture transport coefficient and sorption isotherm (Tran Le *et al.*, 2014). However, few works studied the effect of temperature dependence of sorption on hygrothermal behavior of building envelopes (Carsten and Clorius, 2004; Poyet and Charles, 2009; Ait Oumeziane, 2014). Concerning hemp concrete, some studies showed a significant difference between numerical and experimental results when neglecting the effect of temperature on the sorption curves (Samri and Moujalled, 2014; Tran Le *et al.*, 2016; Colinart and Glouannec, 2017). In contrast to hemp concrete, a recent study that focuses on the prediction of the evolution of sorption curves with temperature on earthen plasters and compacted earthen samples, concluded that *"if the choice of taking into account the temperature dependency of sorption curves will depend on the required precision, the assumption that $w=w(\varphi)$ seems quite acceptable for moderate variations of temperature"* (Fabbri *et al.*, 2017).

This article aims to study the effect of the temperature-dependent sorption on the prediction of hygrothermal behavior of a hemp building envelope subjected to variations of temperature and relative humidity. First, details for the mathematical physical models are presented to investigate the influence of non-isothermal conditions. The models were elaborated and implemented in the Simulation Problem Analysis and Research Kernel (SPARK), which is adapted to the complex problems. Then, the simulation tools are validated by experimental results obtained from a tested wall conducted in our laboratory, in which the relative humidity and temperature in the middle of the hemp concrete wall were measured for 5 days. After being validated, a parameter sensitivity analysis will be discussed. In the next part, a mathematical model for the coupled heat and moisture transfer in building materials will be presented.

Mathematical Models

Heat and Moisture Transport in Porous Building Materials

Mechanisms of moisture transport in a single porous building material have been extensively studied (Philip and De Vries, 1957; Kunzel, 1995; Mendes *et al.*, 2003). Most of the models have nearly the same origin; the main difference among them is related to assumptions used. In this article, the model that takes into account liquid and vapor moisture transport is used (Mendes *et al.*, 2003). Forms of moisture transport depend on the pore structure as well as on the environmental conditions. The liquid phase is transported by capillarity whereas the vapor phase is due to the gradients of partial vapor pressure. With these considerations, the mass conservation equation becomes:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left(D_T \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial x} \left(D_\theta \frac{\partial \theta}{\partial x} \right) \quad (1)$$

with the following boundary conditions respectively for the external ($x=0$) and internal ($x=L$) surfaces of the wall:

$$-p_l \left(D_T \frac{\partial T}{\partial x} + D_\theta \frac{\partial \theta}{\partial x} \right) \Big|_{x=0,e} = h_{M,e} (p_{v,a,e} - p_{v,s,e}) \quad (2)$$

$$-p_l \left(D_T \frac{\partial T}{\partial x} + D_\theta \frac{\partial \theta}{\partial x} \right) \Big|_{x=L,i} = h_{M,i} (p_{v,s,i} - p_{v,a,i}) \quad (3)$$

where the subscript *a* represent the adjacent air and *s* the solid surface of the material, while the subscripts *e* and *i* correspond respectively to the external and internal neighbouring environment (*a*) or solid surface (*s*).

One dimension of the energy conservation equation with coupled temperature and moisture for a porous media is considered and the effect of the adsorption or desorption heat is added. This final one is greater than the heat of vaporization of free water L_v (J/kg), and the difference is expressed as the net isosteric heat (q_{st}). This value depends on the moisture content. The energy conservation equation is written as:

$$\rho_0 C_{p_m} \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(\lambda \frac{\partial T}{\partial x} \right) + Q_{st} \rho_l \left(\frac{\partial}{\partial x} \left(D_{T,v} \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial x} \left(D_{\theta,v} \frac{\partial T}{\partial x} \right) \right) \quad (4)$$

where C_{p_m} is the average specific heat which takes into account of the dry material specific heat and the contribution of the specific heat of liquid phase:

$$C_{p_m} = C_{p0} + C_{p,l} \frac{\rho_l}{\rho_0} \theta \quad (5)$$

λ is thermal conductivity depending on moisture content.

Q_{st} is the isosteric heat which can be calculated using Powers and Brownyard (1948):

$$Q_{st} = L_v + \frac{a}{(b + w)^c} \quad (6)$$

where a , b and c are the fitting parameters.

Boundary conditions take into account of convective heat transfer, radiative heat transfer and heat associated to phase changes, as expressed in the right hand side of Eqs. (7) and (8) for the external and internal surfaces respectively.

$$-\lambda \frac{\partial T}{\partial x} - L_v p_l \left(D_{T,v} \frac{\partial T}{\partial x} + D_{\theta,v} \frac{\partial \theta}{\partial x} \right)_{x=0,e} = h_{T,e} (T_{a,e} - T_{s,e}) + L_v h_{M,e} (p_{v,a,e} - p_{v,s,e}) + \Phi_{ray,e} \quad (7)$$

$$-\lambda \frac{\partial T}{\partial x} - L_v p_l \left(D_{T,v} \frac{\partial T}{\partial x} + D_{\theta,v} \frac{\partial \theta}{\partial x} \right) \Big|_{x=L,i} = h_{T,i} (T_{s,i} - T_{a,i}) + L_v h_{M,i} (p_{v,s,i} - p_{v,a,i}) + \Phi_{ray,i} \quad (8)$$

In the case lacking a data base of moisture transport coefficients, simplified models should be used. The use of simplified mathematical models has varying effects on accuracy and has been discussed by Mendes *et al.* (2003). The moisture diffusion coefficient related to moisture content gradient is evaluated as:

$$D_\theta = \pi \frac{P_{vs}(T)}{P_l} \frac{\partial(\varphi)}{\partial \theta} \quad (9)$$

The equations contain several parameters that are themselves function of the state variables. The special interests of the model are the dependencies of moisture content, moisture transport coefficient, thermal conductivity etc., upon the relative humidity and temperature. This makes possible to take into account of the temperature-sorption dependence into the model, which will be presented in the next sub-section.

Effect of Temperature on the Sorption Characteristics

The moisture sorption isotherm of material describes the relationship between relative humidity and moisture content. The knowledge of sorption isotherm of hemp concrete is important to predict its hygrothermal behavior (Carsten and Clorius, 2004; Ait Oumeziane, 2014; Dubois *et al.*, 2016; Tran Le *et al.*, 2016; Colinart and Glouannec, 2017; Costantine *et al.*, 2018; Moujalled *et al.*, 2018). Up to now, many studies have been carried out to measure the general shape of the isothermal sorption characteristic. However, the physics related to the isothermal sorption curves are still disputed. Some studies indicated that the sorption capacity of hygroscopic materials depends on temperature (Carsten and Clorius, 2004; Ait Oumeziane, 2014; Colinart and Glouannec, 2017). Increasing temperature will entail that the moisture content is in equilibrium with a higher relative humidity. Studies of temperature-effect on the hygrothermal behavior of bio-based materials are highly appreciated. Concerning hemp concrete, some studies (Ait Oumeziane, 2014; Tran Le *et al.*, 2016; Colinart and Glouannec, 2017) showed that taking into account of its influence is necessary. In this article, the Guggenheim-Anderson-deBoer (GAB) model (Timmermann, 2003) which is extended from Langmuir and BET theories (Langmuir, 1918; Brunauer *et al.*, 1938) of physical adsorption, is used to describe the relation between sorption characteristics at different temperatures. Using the GAB model has many advantages such as having a viable theoretical background and giving a good description of the sorption behavior of hemp concrete (Andrade *et al.*, 2011; Collet *et al.*, 2008).

The GAB model can be written as follows:

$$w = \frac{w_m C K(\varphi)}{(1 - K(\varphi))(1 + K C(\varphi) - K(\varphi))} \quad (10)$$

where w_m is the monolayer water content value, C and K are energy constants.

To model the temperature-dependent sorption curves using the GAB model, two energy constants C and K are defined as:

$$C = C_0 \exp\left(\frac{E_1 - E_m}{RT}\right) = C_0 \exp\left(\frac{\Delta H_C}{RT}\right) \quad (11)$$

$$K = K_0 \exp\left(\frac{M_w L_v - E_m}{RT}\right) = K_0 \exp\left(\frac{\Delta H_k}{RT}\right) \quad (12)$$

where:

M_w : is the molecular weight [g.mol⁻¹];

R : ideal gas constant [J.mol⁻¹.K⁻¹];

E_1 and E_m are monolayer and multilayer enthalpies of adsorption, respectively.

In order to solve the above-mentioned equation system, the numerical solution is based on the finite difference technique with an implicit scheme. We used the Simulation Problem Analysis and Research Kernel (SPARK) which is especially suited to efficiently solve differential equation systems (Sowell and Haves, 2001; Wurtz *et al.*, 2006; Mendonça *et al.*, 2002; Tran Le *et al.*, 2010).

Experimental Set-Up, Model Validation and Discussions

Experiment Set-Up

To study the hygrothermal behavior of a hemp concrete building envelope (HC wall), an experimental facility has been developed at "Ecole Nationale des Travaux Publics de l'Etat (ENTPE)" in France (see Fig. 1). The experimental setup consists of a climate chamber to simulate outdoor climate conditions, a test wall and hygrothermal sensors for measuring temperature and relative humidity. More details of this facility can be found in Samri (2008). One side of the test wall was subjected to various outdoor conditions of temperature and relative humidity using the climate chamber, while other side of the wall was in contact with the laboratory ambient where temperature and relative humidity are relatively constant. The test wall was instrumented with sensors which are connected to an acquisition system to measure the hygrothermal profiles (see Fig. 1(b)). This study concerns a 30 cm of thick hemp concrete wall and only the results obtained in the middle of the wall (point C) will be presented in order to facilitate the investigation (see Fig. 1(a)).

In this article, the studied wall was subjected to simulated hygrothermal conditions in summer as presented in Fig. 2. It can be seen that the climate conditions in the laboratory are relatively constant while the outdoor temperature and the

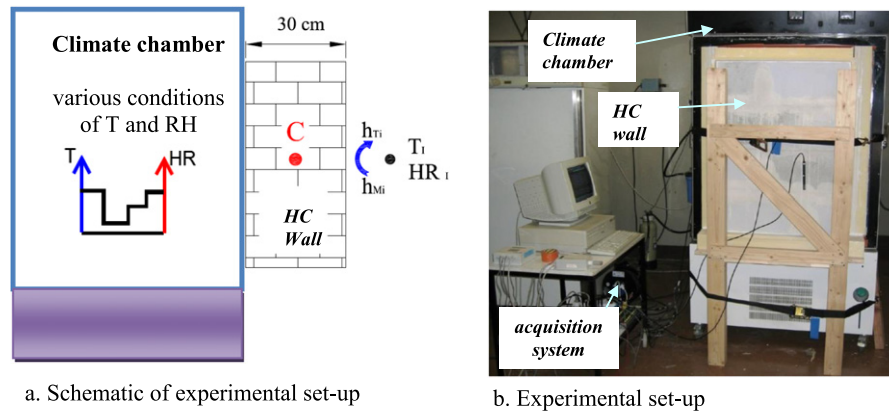


Fig. 1 Experimental set-up for studying hygrothermal behavior of the hemp concrete building envelope developed by Samri. Reproduced from Samri, D., 2008. Analyse physique et caractérisation hygrothermique des matériaux de construction: Approche expérimentale et modélisation numérique, Thèse ENTPE de Lyon, France.

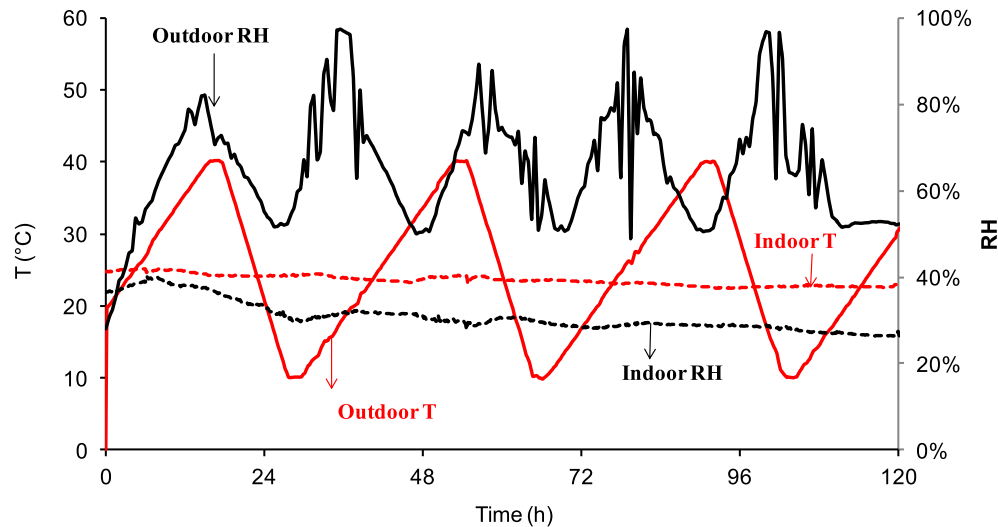


Fig. 2 Hygrothermal conditions in the climate chamber and the laboratory ambient for modeling summer conditions.

outdoor relative humidity (simulated by the climate chamber) vary between 10°C and 40°C; 52% and 97% RH, respectively.

Materials Properties

The hygrothermal properties of hemp concrete measured by Collet (2004); Ait Oumeziane *et al.* (2016); Colinart and Glouannec, (2017) are used for the simulation. The basic hygrothermal data of hemp concrete is given in Table 1. Concerning ΔH_c and ΔH_d , they are set to 4.25 and 0.25 MJ/mol for both adsorption and desorption as recommended by Colinart and Glouannec (2017).

Fig. 3 provides the sorption curves at different temperatures (10°C, 23°C, 40°C and 50°C) and experimental data at 23°C. As one can see from this figure, the moisture content decreases when the temperature increases and the GAB model can predict accurately the sorption curves at 23°C by comparing with the experimental data.

Concerning the isosteric heat Q_{st} (see Eq. 6), the fitting parameters a , b and c ($a=0.697$ J/kg; $b=0.0886$ kg/kg; $c=6.443$) recommended by Ait Oumeziane *et al.* (2016) are used. Fig. 4 shows the variation of the isosteric heat of hemp concrete when the water content varies between 0.01 and 0.2 (kg/kg). It can be observed that the isosteric heat decreases with increasing water content and tends to the latent heat of condensation (L_v); when water content increases from 0.01 to 0.2 kg/kg, Q_{st} decreases from 4.57 to 2.45 MJ/kg.

Table 1 Hygrothermal properties of hemp concrete

Density	Dry thermal conductivity	Specific heat capacity	Water vapor permeability	GAB coefficient w_m	GAB coefficient $C_{23^\circ C}$	GAB coefficient $K_{23^\circ C}$
kg/m ³	W/(m.K)	J/(kg.K)	Kg/(m.s.Pa)	–	–	–
425	0.124	1000	$2,3 \cdot 10^{-11}$	Ad:0.025 Des:0.055	Ad: 7 Des:23	Ad:0.82 Des:0.68

Note: Collet, F., 2004. Caractérisation hydrique et thermique de matériaux de génie civil à faibles impacts environnementaux, Thèse de Doctorat, INSA de Rennes. Colinart, T., Glouannec, P., 2017. Temperature dependence of sorption isotherm of hygroscopic building materials. Part 1: Experimental evidence and modeling. Energy Build. 139, 360–370.

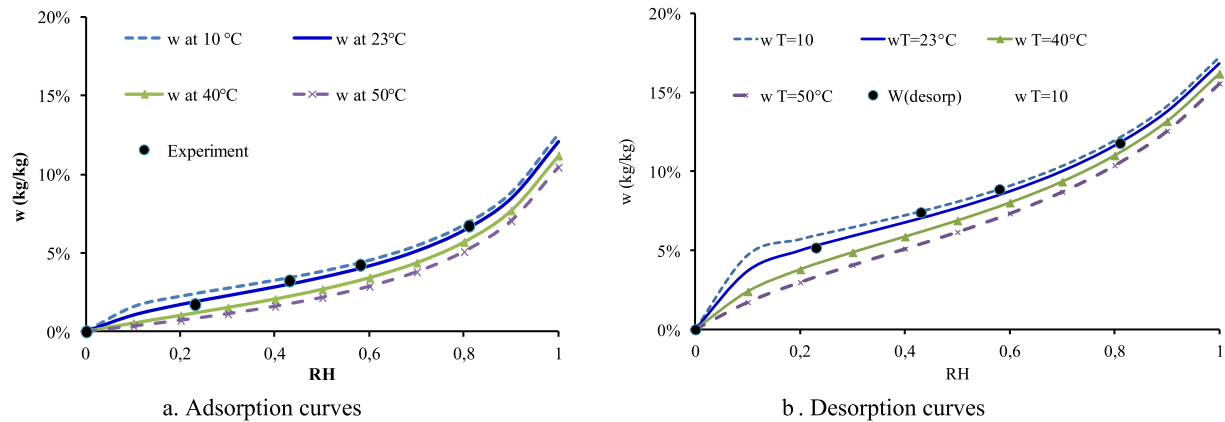


Fig. 3 Sorption curves of hemp concrete at different temperatures.

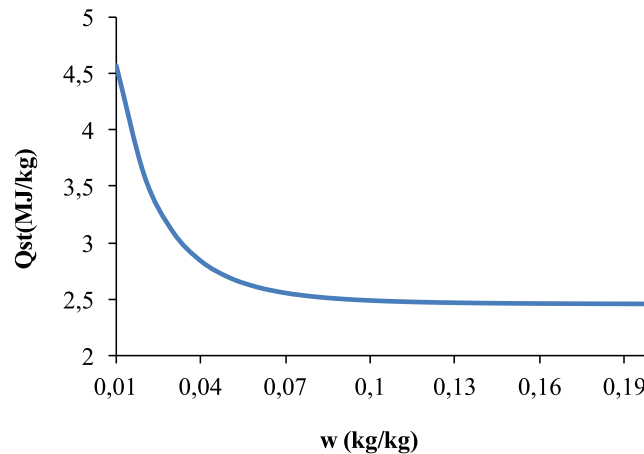


Fig. 4 Isosteric heat Q_{st} of hemp concrete as a function of water content.

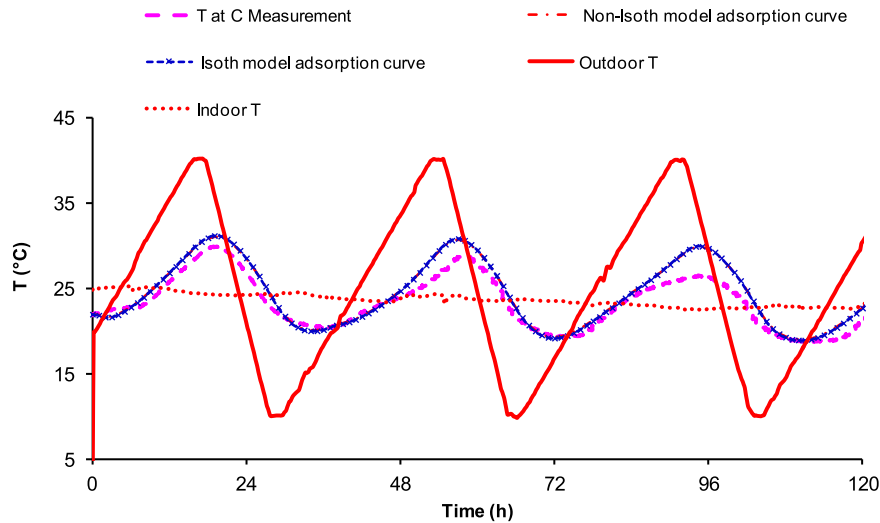


Fig. 5 Variation of temperature at point C – Numerical models and experimental measurement.

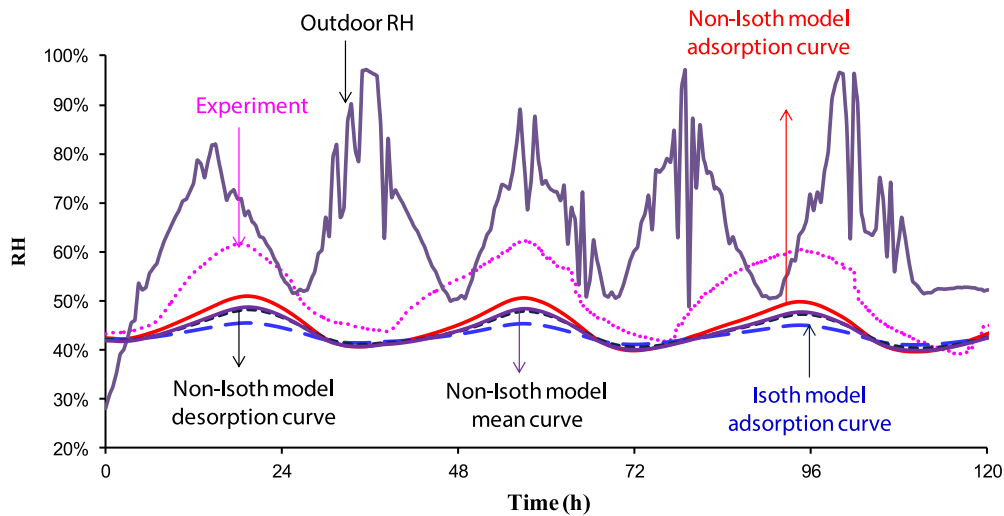


Fig. 6 Variation of relative humidity at point C – Numerical models and experimental measurement.

Model Validation

This article focuses on a more completed model that takes into account the effect of the temperature-dependent sorption characteristics on the hygrothermal response of the hemp concrete building envelope. Two following models are used for the simulation:

- *Isoth* model: Using the isothermal sorption characteristics measured at 23°C in the simulation.
- *Non-Isoth* model: Taking into account the effect of temperature on the sorption curves using the GAB model with the fitting parameters obtained from the literatures (Collet, 2004; Colinart and Glouannec, 2017).

In addition, for each model, three cases have been considered: The adsorption curve, the desorption curve and the mean sorption curve which is obtained from the average of the adsorption and desorption curves.

For both indoor and outdoor surfaces, the heat and mass transfer coefficients are $6 \text{ W.m}^{-2}.\text{K}^{-1}$ and 0.003 m.s^{-1} , respectively. The time step is 240 sec and the wall was discretized into 25 nodes according to recommendations from a sensitive study conducted by Tran Le et al. (2009). Based on initial measured values, the initial relative humidity and temperature in the hemp concrete wall are set to 43% and 21.9°C, respectively.

The simulated temperature and relative humidity at point C obtained from the simulation using the numerical models (*Isoth* and *Non-isoth* models) were compared to those obtained from the experimental measurement and the results are presented in Figs. 5 and 6.

The temperature variations at point C for three cases (adsorption, desorption and mean sorption curves) are very close to each other, only the ones used in the adsorption curve are presented. One can observe that the variation of temperature given by the two

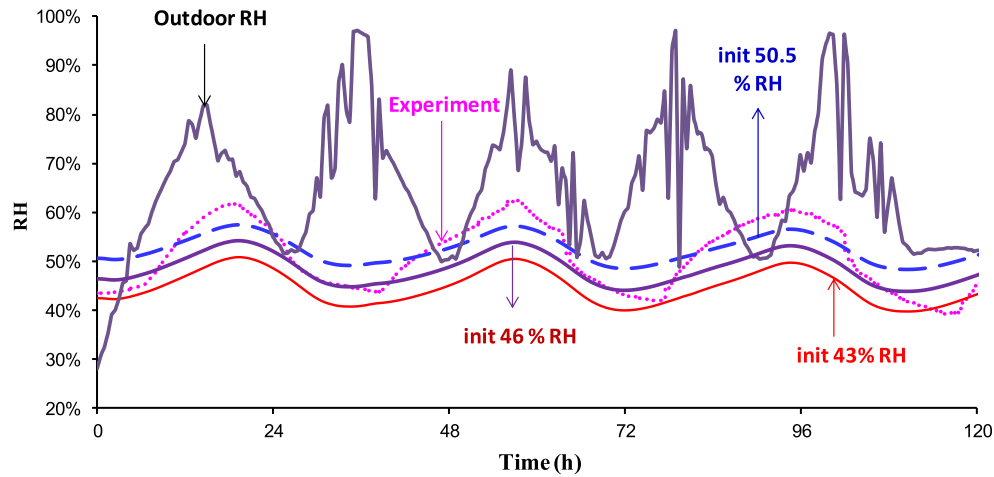


Fig. 7 Effect of initial relative humidity (43%, 46% and 50.5% RH) on the relative humidity profile at point C for the Non-isoth model with adsorption .

numerical models is very similar. Compared to outdoor temperature, temperature in middle of the test wall is dampened and phase shifted. While outdoor temperature varies between 10°C and 40°C, the temperature at point C varies from 20°C to 31.5°C. The time lag (at point C) is around 3.5 h. In summer conditions, the time lag is important and should be increased to shift daily outdoor conditions propagation to the night when outdoor air is colder and night cooling is efficient. The model gives a quite satisfactory prediction of the temperature within the wall, despite the underestimation of the minimum temperature and the overestimation of the maximum temperature.

Regarding the variations of relative humidity, the computed results of the *Isoth* model did not fit the experimental ones (see Fig. 6). In Fig. 6, only the result obtained by the *Isoth* model using the adsorption curve is presented because the ones of three cases (adsorption, desorption and mean sorption curves) are very similar to each other. The relative humidity at point C of the *Isoth* model varies between 43% and 46.3% (so an amplitude of 3.3% RH) while the experimental one varies between 43% and 62.3% (an amplitude of 19.3% RH). This should be explained by the fact that the *Isoth* model neglects the effect of temperature on the moisture sorption capacity of material, in which increasing temperature results in an increase of the relative humidity at a given water content. This explanation is confirmed by the results obtained by the *Non-isoth* model that provides a much better prediction of relative humidity compared to the *Isoth* model (see Fig. 6). Comparing the three cases investigated for this model, the results are dependent on which the sorption curve is used for the simulations. The predicted values calculated with the adsorption curve allow a better prediction of the relative humidity variation than those of the model that uses the average sorption curve or the desorption curve. The predicted relative humidity variations at C are more dampened compared to the experimental ones. Numerically, it varies from 43% RH to 50.9% RH so an amplitude of 7.6% RH of the *Non-isoth* model with adsorption compared to an amplitude of 19.3% of the experiment.

The fact that *Non-isoth* model with adsorption allowed the best prediction compared to the ones obtained by using desorption and mean sorption curves is interesting and in line with the results of some studies focussing on hysteresis effect (Lelièvre et al., 2014; Promis et al., 2018). These studies confirmed that the main adsorption curve is close to the moisture sorption hysteresis in the range of relative humidity in this study.

For this model validation, the initial relative humidity and temperature in the hemp concrete wall are set with respect to initially measured values. Fig. 7 shows the relative humidity variations at point C of the *Non-isoth* model with adsorption when initial relative humidities are 43%, 46% and 50.5%. As expected, the initial conditions have a significant effect on the relative humidity profile at point C because the test was only run for a short time. Increasing initial value of RH results in an increase of the relative humidity value at point C. This conclusion is in accordance with a study performed by Osanyintola et al. (2006) showing that the hygric performance of plywood depends on the initial conditions of relative humidity. Note that moisture transport is slow and consequently this effect should be neglected for a test which is run for a very long time. Concerning the effect on temperature variations at point C, it is very small and not presented here.

Indeed, under the hygrothermal conditions of this study, the *Non-isoth* model showed much better performance compared to the *Isoth* model. However, some discrepancies between predicted and measured values were still observed. This difference should be due to uncertainties of fitting parameters of the GAB model and it will be discussed in the following subsection.

Effect of Energy Constant K on the Hygrothermal Behavior of Hemp Concrete

One of the reasons to explain the discrepancies which still remain between predicted and measured relative humidity within the hemp concrete wall is the non-homogeneous properties and the difference between actual hygrothermal properties and the ones used as input data in the simulation due to the manufacturing process itself. Due to the difficulty or impossibility of verifying

actual properties of the test hemp concrete wall, the validated numerical model is a powerful tool that can be used to overcome this limitation by doing a sensitivity study.

It is noticed that the BET model can predict only the sorption of hemp concrete when relative humidity is lower than 50%. To overcome this limitation, the GAB model is used for describing the sorption isotherm of hemp concrete. When K of the GAB model is equal to 1, the GAB model becomes the BET model. Therefore, to facilitate the investigation, this sub-section focuses only on the effect of energy constant K of the *Non-isoth* model with adsorption curve on the prediction of hygrothermal profile of the hemp concrete building envelope by considering three values of K at 23°C: 0.8 (reference case), 0.6 and 0.5.

Concerning the temperature profiles at point C, they are not depicted and presented here because the results obtained for three cases (reference case, $K_{23^\circ\text{C}}=0.6$ and $K_{23^\circ\text{C}}=0.5$) are very close to each other. The result confirmed that the effect of K value on temperature profile at point C is very small. Regarding the relative humidity profile, the result is presented in Fig. 8. One can observe that the energy constant K has a significant influence on the hygric behavior of the hemp concrete wall. The results obtained by the model with $K_{23^\circ\text{C}}=0.5$ are in good agreement with the experimental results. This energy constant value gives a satisfactory prediction of relative humidity within the tested wall. The maximum difference between the computed values for the

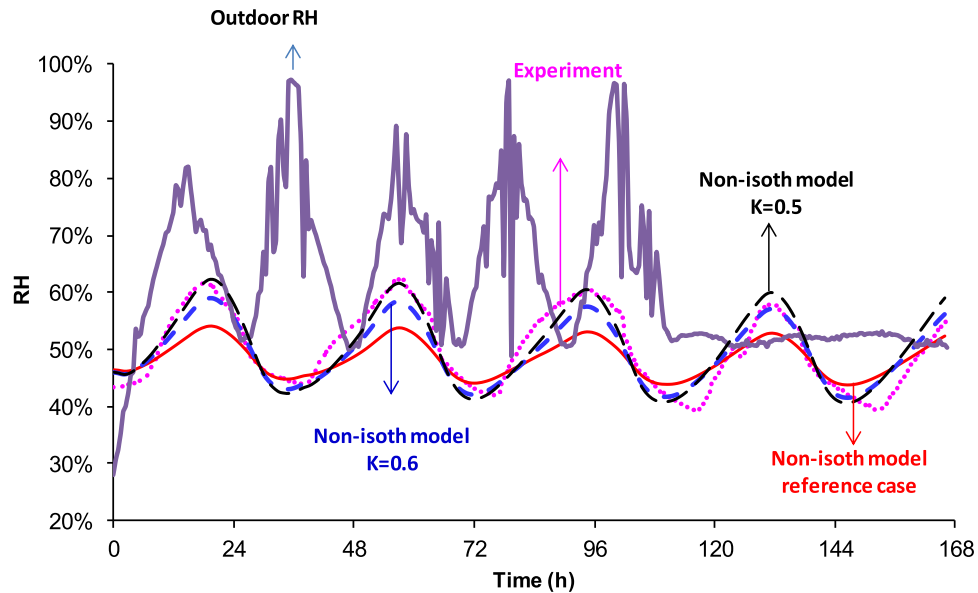


Fig. 8 Variations of relative humidity at point C obtained from numerical models and measurement.

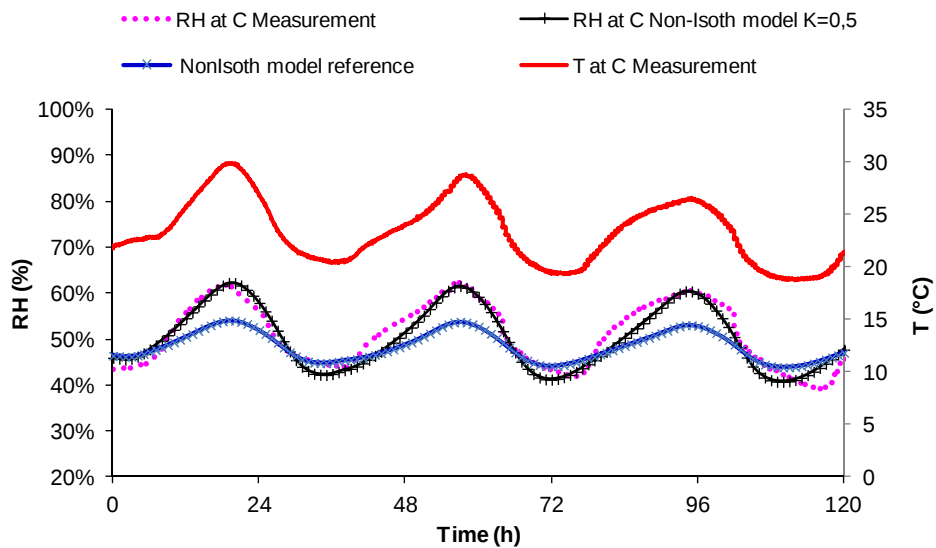


Fig. 9 Predicted relative humidity (Non-isoth model), measured temperature and relative humidity variations measured at point C.

model with adsorption curve and the experimental ones is 3% RH. This value is small compared to the accuracy of sensor inserted in the tested wall, which is $\pm 1.5\%$ of RH.

Based on the obtained results, it can be concluded that it is necessary to take into account the non-isothermal conditions on the sorption curves to predict the hygrothermal behavior of a hemp concrete building envelope subjected to the dynamic conditions of temperature and relative humidity. For better prediction, the parameter $K_{23^\circ\text{C}}$ can be empirically determined and justified using experimental data.

Correlation Between Local Temperature and Relative Humidity Variations in the Test Wall

The predicted relative humidity (*Non-isoth* model with adsorption curve: reference case and the case $K_{23^\circ\text{C}}=0.5$), the measured temperature and relative humidity variations at point C are presented together in Fig. 9. Note that similar behavior for both RH and T profiles is observed. Due to the temperature dependence of the sorption isotherm, relative humidity profile in the hemp building concrete wall is strongly correlated to the local temperature variations. This conclusion is in accordance with the experimental studies carried out by Colinart and Glouannec (2017).

Conclusions

This article presents the development and the use of a numerical model that takes into account of the temperature dependency of the moisture sorption characteristics on the hygrothermal response of a hemp concrete building envelope under dynamic conditions of temperature and relative humidity. Two models named the *Isoth* and the *Non-isoth* have been presented and implemented in the simulation environment SPARK which is suited to solve efficiently the differential equation systems. For each model, three cases that use adsorption or desorption or mean sorption curves have been considered. In addition, to validate the proposed models, an experimental facility has been developed. These results obtained in this study are useful in experimental design and HAM-tools development. With respect to the comparison of measured and modelled temperature and relative humidity profiles in the test wall, the following conclusions are drawn:

- Temperature in the middle of the hemp concrete wall is dampened and phase shifted compared to outdoor temperature.
- Taking the influence of temperature on the sorption curves into account is necessary to predict the hygrothermal behavior of the hemp concrete wall.
- Initial conditions have a significant effect on the relative humidity profile at point C in this study (short-time test).
- Both the *Isoth* and the *Non-isoth* models can be used for predicting the variation of temperature. However, only the *Non-isoth* model is adapted to study the variation of the relative humidity. In addition, this study confirmed that the use of adsorption curve is recommended because it is close to the moisture hysteresis curves.
- Relative humidity profile in the hemp concrete wall is strongly correlated to the local temperature variations. The correlation can be determined from the sorption curves at different temperatures.
- Predicted values exhibit smaller relative humidity fluctuations than the measured values. This deviation of the modeling may be explained by fitting parameters used for the GAB model and can be remedied by changing $K_{23^\circ\text{C}}$ value which can be easily justified by experimental data.

See also: Analysis of the Thermal Performance and Comfort Conditions of Vernacular Rammed Earth Architecture From Southern Portugal. Evaluation of Sustainability Indicators of Buildings. Improving Building Technologies With a Sustainable Strategy. Improving Energy Efficiency in Buildings Through Responsible Design: Optimizing use and Careful Selection of Building Materials. Insulation Materials for the Building Sector: A Review and Comparative Analysis. LCCA and Environmental Impact of Buildings. Leadership in Energy and Environmental Design Rating System: A Global Tool to Assess Sustainability in Buildings, Communities and Cities. Understanding High Performance Buildings: The Link between Occupant Knowledge of Passive Design Systems, Corresponding Behaviors, Occupant Comfort and Environmental Satisfaction. Use of Lime Mortar and Post-Occupancy Thermal Performance Analysis of Buildings. Using Construction and Demolition Waste as Construction Materials for New Buildings

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Energy and Acoustic Performances of Timber in Buildings

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Introduction

Nowadays timber buildings are present worldwide and their construction market is growing, because the use of sustainable materials is encouraged both from governments and from public opinion. CO₂ is stored, renewable and environmentally friendly raw materials are used and commonly a very good thermal insulation is provided. Timber elements are produced within industry plants where costs are optimized in advance and where very little waste is produced, according to Kyoto protocol purposes.

Ramage *et al.* (2017) demonstrated how wood for construction is one of the many forest products around the world. It is understood that timber has very good mechanical properties such as high strength to weight ratio, a good service life and high specific heat values. For this reason, gradually the edifices are moving from one or two floors to six or seven multi-story. Furthermore, wastes from wood modification and transformation could become secondary products like chipboards, sand sawdust panels, biomass for conversion or gasification and so on.

Additionally, the introduction of environmental certifications of buildings, requiring high energy savings, high standards of indoor comfort and large usage of ecofriendly materials, raise the need of timber building diffusion.

Wood could be used for almost every requirement, from structural beams to containers, from thermal and acoustic insulation panels to component elements. It could be used for precast products, meaning high repeatability of performances and characteristics.

As an example, CAD-CAM technologies used for the building production permit a wide range of possibility including traditional or new and complex architectural shapes, concepts and tendencies. For every product, the final CE certifications are needed, to ensure its quality.

As a matter of fact, every building component could be made of wood parts, ensuring the same final performances of other materials like metals or plastics. Granzotto *et al.* (2017) clearly demonstrated that timber windows frames could provide same thermal and acoustic insulation properties in comparison with other materials. The research, based on more than 45 laboratory tests, highlighted that no single windows element could define alone final performances, but all constituents participate to final insulation effect. The windows thermal transmittance is the result of the superposition of all single contributions and the frame material is just a link in the chain.

On the other hand, acoustic insulation has shown a full dependence on single parameters, such as PolyVinylButyral for coincidence reduction, overall glass and gas gap(s) thickness to improve middle and, in some case, low frequencies insulation, but no correlation between material frame composition was found.

Both thermal and acoustic best performances can be obtained with all available material frames. So when choosing the best one, wood is the less environmental impactful, with higher insulation values.

On a building scale, wood could provide very good specific heat values, suitable for the insulation from hot climate, but insufficient protection from cold ones.

From the acoustic point of view, Caniato *et al.* (2017a) demonstrated how performances are not always at the top range. For example, impact noise in timber constructions is the most common cause of complaint on the part of inhabitants because in this kind of lightweight buildings the usual impact reduction methods would not properly work.

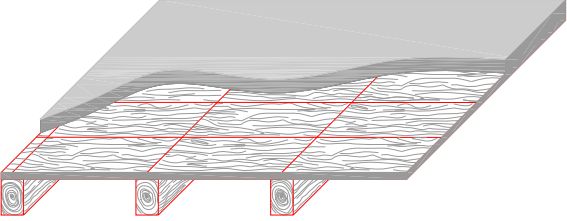
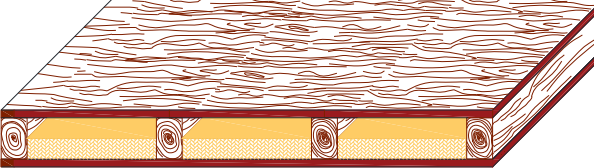
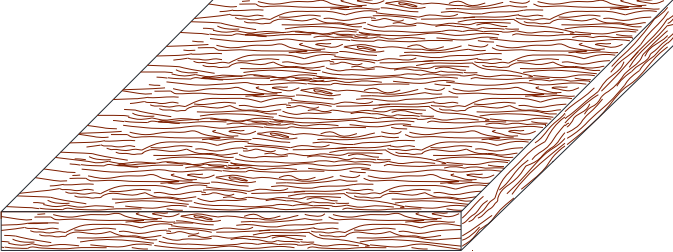
Technological diversity distinguishing wooden constructions (frame, cross laminated timber, etc.) makes homogenization of forecasting calculation methods more difficult compared to traditional massive buildings (concrete, masonry, etc). Furthermore, applying the same prediction methods or analysis used for heavy weight constructions could lead to misleading results. Nevertheless, prediction methods developed for traditional structures are frequently applied to wooden ones, which is obviously questionable. How many types of wooden structure have been studied? How many of them accurately and satisfactorily?

In this work, energy and acoustic performances of timber in building are described, focusing on thermal and acoustic insulation.

A graphical summary of possible structures is summarized in Table 1. There are three main categories grouping different structures as follows:

- type A: wood structure not included in plaster or fiber board;
- type B: glulam beams with boards screwed on top;
- type C: homogenous wooden structure.

Table 1 Types of lightweight bare partitions included in literature

Code	Description	Scheme
A	Timber-concrete floor. It consists of timber structure with an additional layer of concrete on top of it	
B	Particle or gypsum board on top of wooden glulam beams with screw attaching the boards to the beams. Fibrous layers between beams is often present. These structures could be both walls and floors	
C	Cross laminated timber These structures could be both walls and floors	

Energy Performance of Timber Envelope and Layer

Timber structures could be personalized for every necessity since the precast process ensure the application of different layers and different thicknesses. The most used are rockwool, wood, paper or cellulose waste, and wood wool. Often, a combination of them is used in order to better adapt to diverse climate.

Since type A (Table 1) is only used for internal floors, type B and type C (or a combination of them) are the only possible solutions for vertical walls.

Glulam technology provides the best possibility of potential combinations with different materials and layers, because gaps between beams leave hollow spaces, which could be filled either with panels or by insufflated flakes or particles (Fig. 1). Nevertheless, beams provide thermal bridges, so an additional layer is needed in order to limit this problem. Usually this last stratum is composed by wood wool in order to enhance impact and hot climate insulation performance, whether the inner one is usually softer and lighter, suitable for the cold weather.

For opaque components, transmittance U and periodic transmittance Y_{ie} are the main significant parameters; the first one is described by Eq. (1):

$$U = \frac{1}{\frac{1}{h_e} + \sum_{i=1}^n \frac{d_i}{\lambda_i} + \frac{1}{h_i}} \quad (1)$$

where d_i is the thickness of the layer [m], λ_i is the thermal rated heat conductivity of the material [W/m K], h_e is the heat exchange surface coefficient of the external surface [W/m² K] and h_i is the heat exchange surface coefficient of the internal surface [W/m² K].

This property identifies the thermal insulation from cold external environment in a static condition. The second one is used in order to evaluate the protection from hot climate since in this case the outer temperature could vary a lot during the day.

In case of inhomogeneous structures (e.g., type B), as a first approximation it can be taken into account the percentage of wooden beams in respect with the insulating material laid in the hollow spaces. Since structural elements acts as thermal bridges compared to insulating material, their influence should be considered in final transmittance results (Fig. 2).

In Table 2, beam influence (glulam) on final transmittance value is reported. In the first step, the standard beam dimension of glulam external wall construction (Fig. 3) is calculated (6 cm × 16 cm) and increased by 20%, 50% and 100%. In the second, an external insulating layer constituted by wood wool of 6 cm thickness is applied. It is evident how it reduces the thermal bridge caused by beams.



Fig. 1 Glulam external wall production with cellulose fiber insufflation.

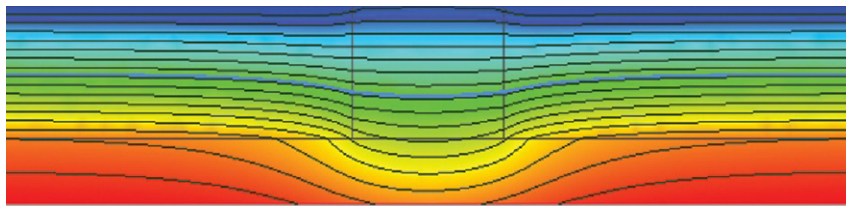


Fig. 2 Wooden beam thermal bridge within glulam structure.

Table 2 Influence of the beam width on final transmittance values

	$U_{first\ step} [W/m^2\ K]$	$U_{second\ step} [W/m^2\ K]$
Standard	0.29	0.20
Standard + 20%	0.30	0.20
Standard + 50%	0.32	0.21
Standard + 100%	0.35	0.22

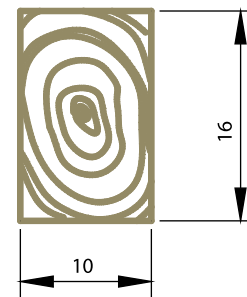


Fig. 3 External glulam beam construction (a) and beam scheme (b).

The calculation of the periodic transmittance Y_{ie} of a non-homogenous structure is not an easy task, because it depends on thermal conductivity, thickness, specific heat and density of all materials constituting the partition and on the external force (heat flux).

The analytical model is based on transfer matrix solutions combining the described parameters. Since the first hypothesis is that the external temperature is sinusoidal, the solution will be a complex number. For this reason the general numerical model is reported in Eq. (2) (source: ISO 13786:2017):

Table 3 Thermal proprieties of common construction materials

Material type	Conductivity [W/m K]	Specific heat [J/Kg K]	Density [kg/m ³]
Masonry	0.78	940	1700
Concrete	1.6	1000	2300
Wood wool	0.044	2100	200
Rock wool	0.038	840	175
EPS	0.036	1480	35

Table 4 Periodic transmittance and time shift variation for bare structures (20 cm) and additional layers (10 cm)

Material type	Periodic transmittance [W/m ² K]	Time shift [h]
Masonry	1.27	6.5
Masonry + EPS	0.06	8.92
Masonry + wood wool	0.05	12.04
Wood	0.11	12.31
Wood + EPS	0.01	15.48
Wood + wood wool	0.01	16.10

Table 5 Comparison of time shift value within glulam structure of the same thickness (16 cm)

Structure description	Periodic transmittance [W/m ² K]	Time shift [h]
Beam portion	0.24	9.46
Thermal insulator portion	0.21	3.2

$$\begin{pmatrix} \vartheta_2 \\ q_2 \end{pmatrix} = \begin{pmatrix} Z_{11} & Z_{12} \\ Z_{21} & Z_{22} \end{pmatrix} \cdot \begin{pmatrix} \vartheta_1 \\ q_1 \end{pmatrix} \quad (2)$$

The periodic transmittance Y_{ie} is the inverse of the Z_{12} term as reported in Eq. (3) (source: ISO 13786:2017):

$$Y_{ie} = -\frac{1}{Z_{12}} \quad (3)$$

The argument normalized on the time period of Z_{12} represent the time shift imposed by the materials at the sinusoidal external heat as reported in Eq. (4) (source: ISO 13786:2017):

$$(\varphi) = \frac{T}{2\pi} \arg\left(\frac{1}{Z_{12}}\right) \quad (4)$$

where T is time within the sinusoidal variation is present [s].

As a matter of fact, insulation from hot climate will strongly depend on density and on specific heat (comparing materials with same thickness) since this two parameters strongly influence the reactive properties layers.

Wood and wood products have very high specific heat compared to tradition heavyweight materials (masonry, concrete) and lightweight insulators (EPS, XPS, rock wool etc.). They are very useful to rise time shift and periodic transmittance values. In Table 3 A comparison between thermal proprieties of common construction materials is provide and in Table 4 standard construction with additional wooden or non-wooden layers are reported.

Wood products provide higher time shift and lower periodic transmittance values compared to masonry and EPS. The difference is bigger on the traditional heavyweight structures, because no wood product is present in the bare structure.

On the other hand, for periodic structure (glulam) no calculation is possible because of the non-static approach of this phenomenon.

As a matter of fact, the timber beams provide better time shift value compared to thermal insulator as reported in Table 5.

In order to determine the external and internal temperatures, the only possibility, as described by Pernigotto *et al.* (2015) and Pajek *et al.* (2017), is to perform simulations and laboratory experiments; these results could then be used to calculate the correct value of periodic transmittance.

Acoustic Performance

Acoustic performances of timber in buildings could be divided into two main items: airborne sound insulation and impact noise reduction. As a matter of fact, both of them are analyzed at present and every years many researchers and technicians write several papers on these topics. As highlighted by [Simmons et al. \(2011\)](#) and by [Ljunggren et al. \(2014\)](#), noise inside a wooden construction is one of the most complained issue since both users and designers at first steps of planning and construction do not pay attention to this topic.

After an international subjective survey performed by [Caniato et al. \(2017a\)](#), sent to both designers and lay people, it could be concluded that acoustic design and acoustic final performances are the less considered issue but the first cause of indoor discomfort. This could be essentially explained by two alternative scenarios. On one hand, the acoustic insulation is related to wood. On the other hand, since timber buildings are felt like the stereotype of perfect constructions where to live in, it is believed that the whole wall layering could provide some kind of “standard protection”.

In the next paragraphs a dissertation on recent researches is reported and divided into two parts: impact noise and airborne noise.

Impact Noise

The impact noise depends on two independent parameters: impact noise level of the bare floor and sound reduction provided by the chosen insulating technology (floating floor, resilient layers, suspended ceiling)

according to [Eq. \(5\)](#):

$$L_{n,w} = L_{n,w,eq} - \Delta L_w(\text{dB}) \quad (5)$$

where $L_{n,w}$ is the resulting impact noise (dB), $L_{n,w,eq}$ is the impact noise of the bare floor (dB), ΔL_w is the impact sound pressure level reduction (dB).

It is evident that the bare floor acts as starting point and so the type of partitions is the primary source. In timber structures there are many different technologies.

The A technology (Ref. [Table 1](#)) is widely studied and used in Mediterranean countries. [Bettarello et al. \(2010\)](#), performed on field measurement of bare floors, providing an empirical model ([Eqs. \(6\) and \(7\)](#)) describing the frequency trend of the bare floor impact noise.

$$L_{n,eq,avg} = 10.4 \log(f) + 50(\text{dB}) \text{ for } f < 1600 \text{ Hz} \quad (6)$$

$$L_{n,eq,avg} = -6.1 \log(f) + 129(\text{dB}) \text{ for } f > 1600 \text{ Hz} \quad (7)$$

The B technology is the most studied and presents a great number of variants. Since this type of construction performances could be influenced by many parameters such as dimensions and periodicity of the beams, presence, thickness and density of sound absorbing materials in void spaces, stiffness, thickness and number of upper and lower layers etc., parameter studies were carried out by [Brunskog and Hammer \(2003\)](#), in order to determine single components influence. The conclusions report the following considerations:

- Sound absorbing material (with different flow resistivity) in void spaces reduces the impact noise for frequency above 250 Hz,
- Different mass of upper and lower layers provide better performances than a single heavy one,
- Periodic beams displacement influences low frequency range,
- Sound absorbing material could represent up to 15 dB reduction.

The most interesting aspect is that the low frequency effect is caused by the structure itself and it does not significantly vary if big changes (high density added layer, very thick suspended ceilings, etc.) are not applied on it. On the other hand, the wooden structures could better insulate in middle and high frequency range than the heavy weight ones.

Laboratory measurements of glulam floor are very few and not always available. For this reason field measurements could provide missing information about the frequency behavior of the bare floor and the influence of the floating floor and the suspended ceiling as impact noise reduction technologies.

Tests were performed in a three – story construction where floors were tested by [Caniato et al. \(2017c\)](#), on different receiving rooms ([Fig. 4](#)). Panels were constituted of glulam beams (18 cm thickness) connected with wooden chipboard screwed on top of them (2.2 cm thickness), mineral wool between them (10 cm thickness, 55 kg/m³ density) and laterally fastened with wooden closures ([Fig. 5](#)). These panels were laid in order to match the external border, so it was possible to find an air gap between them. This was filled using high sound insulation foam.

Different bare floors results are very similar due to industrial production, so only average final values are worthy of being presented. In [Fig. 6](#) the bare floor impact noise trend is reported both without and with insulating foam inserted inside the air gap between panels. The green trend reports the impact noise level of the separated panels while the red curve represents the impact sound of the sealed panels. It is evident how the insertion makes the pieces work together, thus providing more energy (more excited area) at low frequencies.

After these steps, a first floating floor was posed by the authors using the following layers ([Fig. 7](#)), where s' is the apparent dynamic stiffness per unit area, d the thickness and m' is the mass per unit area of the massive slab:



Fig. 4 Multi-storey glulam with top boards building. Source: Caniato, M., Bettarello, F., Patrizio, F., *et al.*, 2017c. Impact sound of timber floors in sustainable buildings. *Building and Environment* 120, 110–122. Available at: <http://dx.doi.org/10.1016/j.buildenv.2017.05.015>.

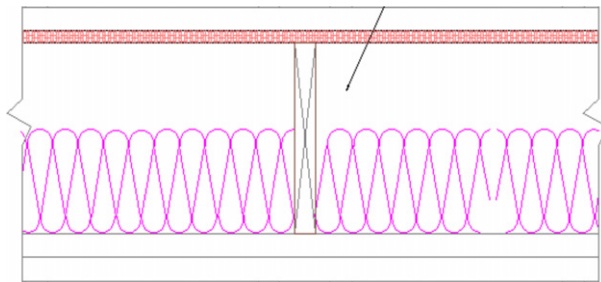


Fig. 5 Floor assembly scheme. Source: Caniato, M., Bettarello, F., Patrizio, F., *et al.*, 2017c. Impact sound of timber floors in sustainable buildings. *Building and Environment* 120, 110–122. Available at: <http://dx.doi.org/10.1016/j.buildenv.2017.05.015>.

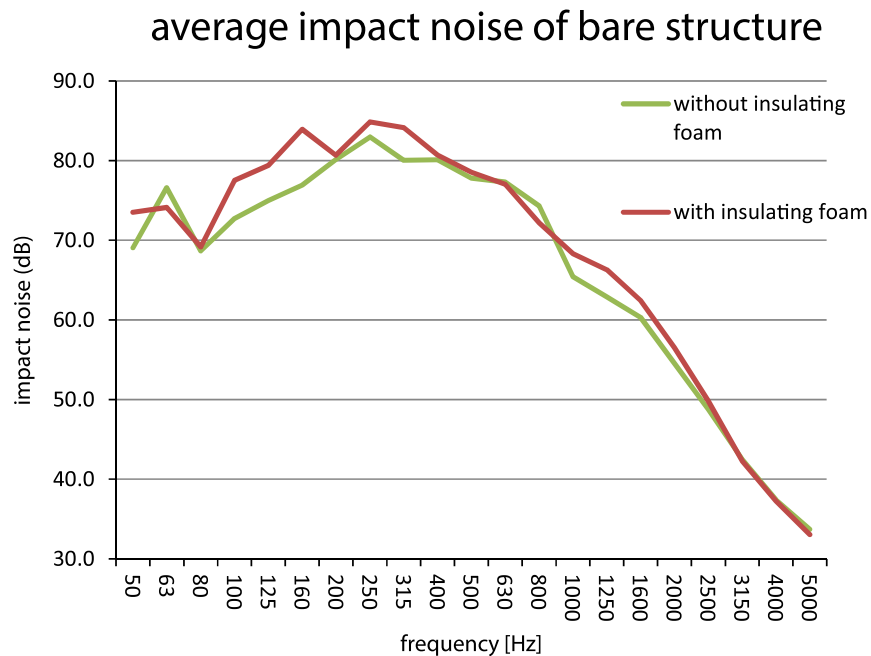


Fig. 6 Bare floor impact noise. Source: Caniato, M., Bettarello, F., Patrizio, F., *et al.*, 2017c. Impact sound of timber floors in sustainable buildings. *Building and Environment* 120, 110–122. Available at: <http://dx.doi.org/10.1016/j.buildenv.2017.05.015>.



Fig. 7 First floating floor realization. Source: Caniato, M., Bettarello, F., Patrizio, F., *et al.*, 2017c. Impact sound of timber floors in sustainable buildings. Building and Environment 120, 110–122. Available at: <http://dx.doi.org/10.1016/j.buildenv.2017.05.015>.



Fig. 8 Second floating floor realization. Source: Caniato, M., Bettarello, F., Patrizio, F., *et al.*, 2017c. Impact sound of timber floors in sustainable buildings. Building and Environment 120, 110–122. Available at: <http://dx.doi.org/10.1016/j.buildenv.2017.05.015>.



Fig. 9 Location of tapping machine during tests: Bare floor (left) and first floating floor (right). Source: Caniato, M., Bettarello, F., Patrizio, F., *et al.*, 2017c. Impact sound of timber floors in sustainable buildings. Building and Environment 120, 110–122. Available at: <http://dx.doi.org/10.1016/j.buildenv.2017.05.015>.

- Recycled cotton waste resilient layer ($s' = 32 \text{ MN/m}^3$, $d = 8 \text{ mm}$),
- Marble powder (5 cm) in honeycomb paper panels ($m' = 45 \text{ kg/m}^2$).

Then a second floating floor was laid upon the first one using the following coatings (**Fig. 8**):

- Recycled cotton waste resilient layer ($s' = 32 \text{ MN/m}^3$, $d = 8 \text{ mm}$),
- Two gypsum fiberboards (2.5 cm, $m' = 35 \text{ kg/m}^2$).

Impact noise tests using an ISO tapping machine were carried out (**Fig. 9**) and the influence of these sound reduction solutions is reported in **Fig. 10**. The red line represents the bare floor trend, whether the light blue and purple lines highlights the impact noise reduction provided by the two floating floor layers. The contribution offered by these technologies is evident from 80 Hz.

average impact noise of bare structure

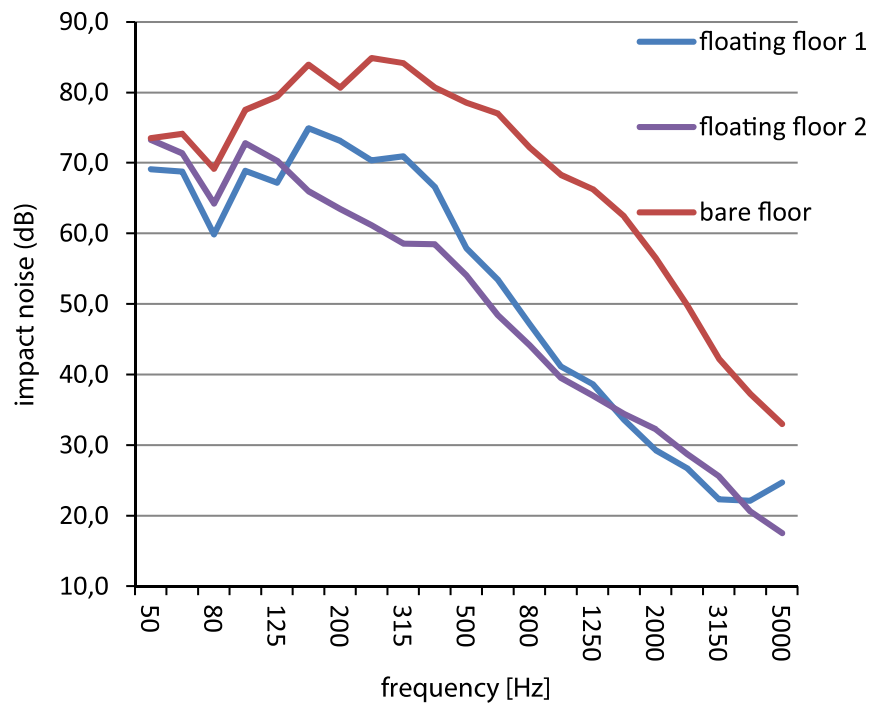


Fig. 10 Floating floors influence. Source: Caniato, M., Bettarello, F., Patrizio, F., *et al.*, 2017c. Impact sound of timber floors in sustainable buildings. Building and Environment 120, 110–122. Available at: <http://dx.doi.org/10.1016/j.buildenv.2017.05.015>.

average impact noise of bare structure

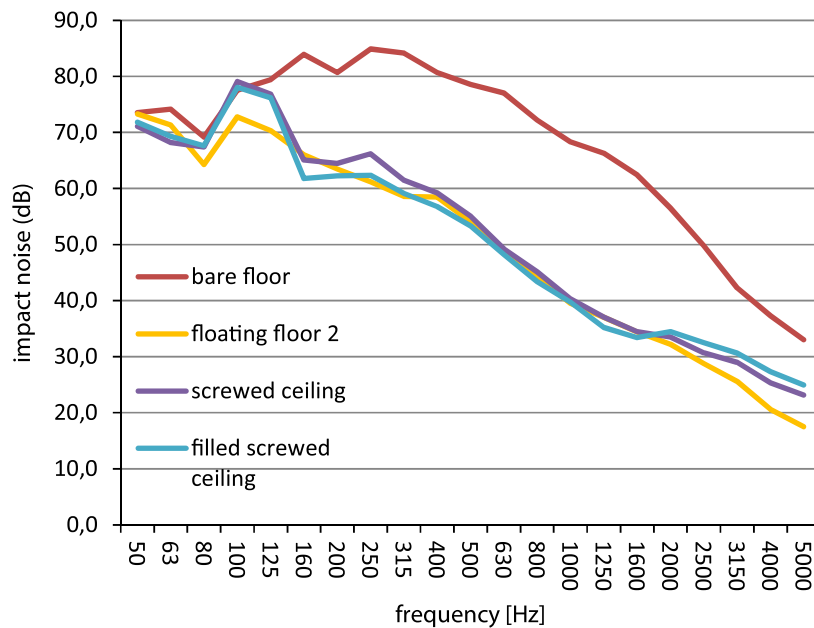


Fig. 11 Screwed ceiling effect. Source: Caniato, M., Bettarello, F., Patrizio, F., *et al.*, 2017c. Impact sound of timber floors in sustainable buildings. Building and Environment 120, 110–122. Available at: <http://dx.doi.org/10.1016/j.buildenv.2017.05.015>.

Table 6 Floating floors normalized impact sound pressure index prediction for glulam bare floor. Single number identification

TIMBER	Mass per unit area [kg/m ²]	Measured Normalized Impact sound pressure index $L'_{n,w}$ (dB)	Predicted Normalized Impact sound pressure index $L'_{n,w}$ (dB)	Difference (dB)
Bare floor	130	76	–	–
Floating floor 1	45	64	54	10
Floating floor 1 + 2	80	58	46	12

Source: Caniato, M., Bettarello, F., Patrizio, F., *et al.*, 2017c. Impact sound of timber floors in sustainable buildings. Building and Environment 120, 110–122. Available at: <http://dx.doi.org/10.1016/j.buildenv.2017.05.015>.

Table 7 Floating floor effect on same thickness different bare floor technologies using frequency Cremer's relation. Frequency trend calculation

	Mass per unit area [kg/m ²]	Measured Normalized Impact sound pressure index of bare floor $L'_{n,w}$ (dB)	Predicted Normalized Impact sound pressure index reduction of floating floor $\Delta L_{n,w}$ (dB)
Glulam	130	76	14
Concrete	600	81	33
Beam and pot	340	87	41

Source: Caniato, M., Bettarello, F., Patrizio, F., *et al.*, 2017c. Impact sound of timber floors in sustainable buildings. Building and Environment 120, 110–122. Available at: <http://dx.doi.org/10.1016/j.buildenv.2017.05.015>.

Afterwards, a screwed ceiling was posed. This setup implies an additional plasterboard (1 cm thick) underneath the timber floor. It was screwed on wooden beam (50 mm thick) with a resulting air gap of 50 mm. In Fig. 11 the influence of the screwed ceiling is reported. In comparison with Fig. 10, it is here evidenced how the screwed ceiling worsen the situation at middle frequencies (purple line), because of the rigid connections.

The worsening caused by the presence of this element is evident. At around 100 Hz its resonance frequency increases the impact noise, according to Eq. (8):

$$f_0 = \frac{60}{\sqrt{\frac{m'}{d}}} [\text{Hz}] \quad (8)$$

where m' is the mass per unit area [kg/m²] of the plasterboard (6.5 kg/m²) and d is the distance (0.05 m) from the floor structure [m].

In order to reduce this effect, the air gap was filled with mineral wool. This operation slightly lowered the middle frequencies, but did not change the resonance influence on the impact noise.

For glulam beams with top boards, in Table 6 the comparison between ISO 12354-2 normalized impact sound pressure index models and measured values is shown. Presented results were calculated using the average of all tests. In order to compare results with predicted ones, Eq. (9) is used to forecast final values

$$\Delta L_{nw, \text{single number}} = 30 \cdot \log(500/f_0) + 3(\text{dB}) \quad (9)$$

where f_0 is the resonance frequency of the floating floor.

It is clear that the relation is not applicable with timber structures since the bare floors are not of infinite mass in comparison with the floating layers. The difference in mass is reduced ($m'_{\text{bare floor}} = 130 \text{ kg/m}^2$ whether $m'_{\text{overall floating floor}} = 80 \text{ kg/m}^2$) in comparison with a concrete bare floor ($m'_{\text{concrete}} = 600 \text{ kg/m}^2$) or beam and pot ($m'_{\text{beam and pot}} = 340 \text{ kg/m}^2$). The focus is the impact of the traditional floating floor; since the flanking transmission values are constant from bare floor to covered floor, the measured final outcomes are influenced only by the additional floating layer.

In Table 7 A comparison of the sound reduction index of an ideal floating floor, used as example, on different structures is presented, using the frequency of Cremer's relation (Cremer, 1942).

The floating floor is composed of a high density coating (90 kg/m², 50 mm thickness) and a resilient layer ($s' = 16 \text{ MN/m}^3$).

Here, it is evident how the same impact sound reduction solution provides very diverse performance, depending on the type of bare horizontal partition. This result depends on the different distribution of the exciting energy coming from the ISO tapping machine and on the specific limit of floating floor technology: low frequency reduction.

The cross-laminated timber (CLT – Type C) panels are constituted of thin beams or planks laid on the top of each other and high pressure glued in order to form a solid uniform board. Therefore, the horizontal (as well as vertical) partitions seem to behave like homogenous slab. Very few studies are present in literature for this kind of structure. Nevertheless, this technology is commonly used in Europe, North America, Australia, New Zealand, etc.

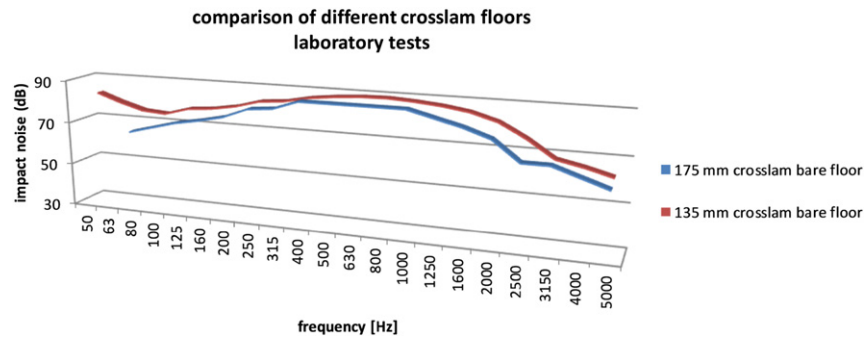


Fig. 12 Laboratory and field measurements of CLT floor. Source: Caniato, M., Bettarello, F., Patrizio, F., *et al.*, 2017c. Impact sound of timber floors in sustainable buildings. Building and Environment 120, 110–122. Available at: <http://dx.doi.org/10.1016/j.buildenv.2017.05.015>.



Fig. 13 Field measurements of CLT floor.

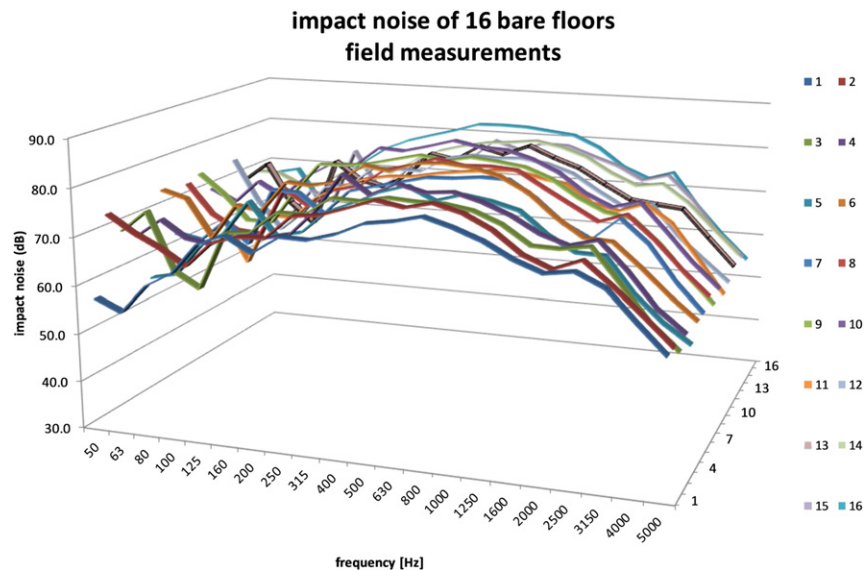
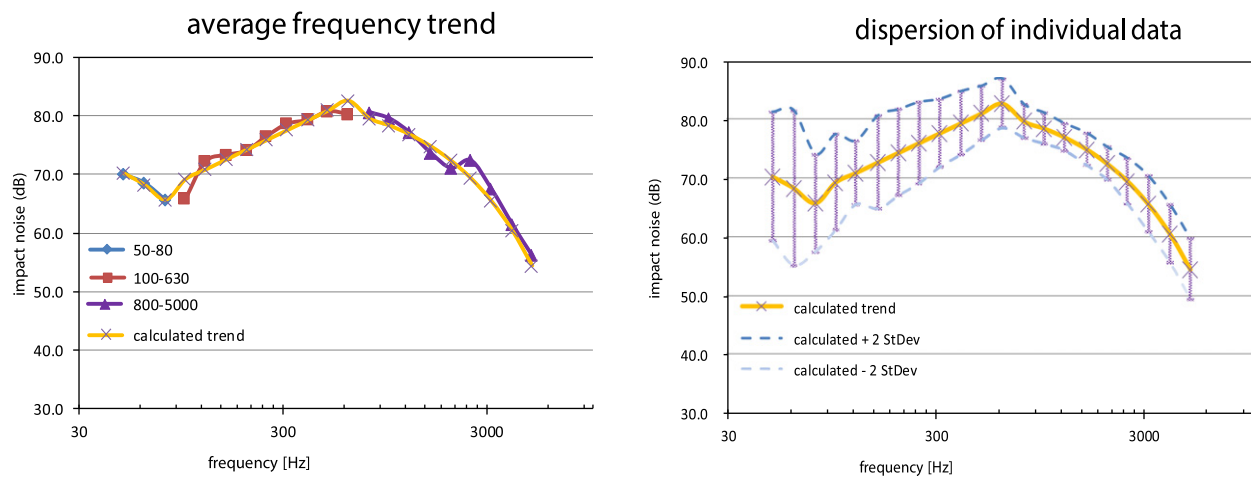


Fig. 14 Frequency trends for impact noise of 16 floors. Source: Caniato, M., Bettarello, F., Patrizio, F., *et al.*, 2017c. Impact sound of timber floors in sustainable buildings. Building and Environment 120, 110–122. Available at: <http://dx.doi.org/10.1016/j.buildenv.2017.05.015>.

Table 8 Normalized impact sound pressure index values and $C_{l, 50-2500}$ factor for Cross Laminated Timber bare floors of every tested room. Similar receiving room volumes are compared

Measurement number	$L'_{n, w}$	$C_{l, 50-2500}$	Measurement number	$L'_{n, w}$	$C_{l, 50-2500}$
1	79	-7, 6	11	78	-7
2	79	-5, 6	12	79	-6, 3
3	80	6, 6	13	80	-6, 9
4	80	5, 7	14	81	-7
5	78	-5, 8	15	80	-7, 3
6	81	-4, 3	16	81	5, 3

Source: Caniato, M., Bettarello, F., Patrizio, F., *et al.*, 2017c. Impact sound of timber floors in sustainable buildings. Building and Environment 120, 110–122. Available at: <http://dx.doi.org/10.1016/j.buildenv.2017.05.015>.

**Fig. 15** Average frequency trends for impact noise, calculated linear regression and dispersion of individual data. Source: Caniato, M., Bettarello, F., Patrizio, F., *et al.*, 2017c. Impact sound of timber floors in sustainable buildings. Building and Environment 120, 110–122. Available at: <http://dx.doi.org/10.1016/j.buildenv.2017.05.015>.

Laboratory tests show the effect of the bare slab reacting to heavyweight impact noise (ISO tapping machine) highlighting the typical “bell-like” frequency trend on middle high frequencies (Fig. 12). The red and blue lines represents different bare floor impact noises with respectively 135 mm and 175 mm thickness. It is evident how the two trends are very similar in the frequency domain; it could be concluded that only the thickness parameter has an influence on final results.

In order to understand if the real acoustic behavior was similar, field measurements were carried out in 16 different bare floors (Figs. 13 and 14).

The increase in frequency at about 2500 Hz could be ascribed to the resonance caused by the ISO tapping machine laid directly on the wooden floor.

In order to compare only single index results, the weighted sound reduction index $L'_{n, w}$ determined by ISO 717-2 method as well as $C_{l, 50-2500}$ factor were calculated (Table 8). It is possible to understand once more that the single number differences are caused by low frequency range.

Linear regression was calculated in order to obtain a possible predicting equation of the impact noise of bare floor.

The mean value of the frequency spectrum trend can be represented with the following equations:

$$L_{n,eq,avg} = -0.15(f) + 77.7(\text{dB}) \text{ for } 50 < f < 80\text{Hz} \quad (10)$$

$$L_{n,eq,avg} = 7.26\log(f) + 35.6(\text{dB}) \text{ for } 100 < f < 630\text{Hz} \quad (11)$$

$$L_{n,eq,avg} = -0.006(f) + 84.4(\text{dB}) \text{ for } 800 < f < 5000\text{Hz} \quad (12)$$

The calculated linear regression coefficient is $R^2=0.99$ for Eq. (10), $R^2=0.89$ for Eq. (11) and $R^2=0.97$ for Eq. (12) and represented in Fig. 15 where 95% of the measured values are situated inside the yellow lined zone.

From the single index point of view, in Table 9, the normalized impact sound pressure index values, calculated according to ISO 12354-2 are described. The first line reports the single index value calculated using ISO 717-2 methods; for the 250 mm bare floor the frequency trend provided by Eqs. (8–10) was used for calculation. No flanking transmissions were taken into account since the L_{nw} parameter was analyzed (laboratory tests).

Table 9 Normalized impact sound pressure index values for Cross Laminated Timber bare floors

	135 mm bare floor Laboratory test	175 mm bare floor Laboratory test	250 mm bare floor
Measured L_{nw} (dB)	88	85	80
$L_{n,w}$ standard model (dB)	98.5	94.6	89.2
$L_{n,w}$ modified model (dB)	87.7	84.9	81.0

Source: Caniato, M., Bettarello, F., Patrizio, F., *et al.*, 2017c. Impact sound of timber floors in sustainable buildings. Building and Environment 120, 110–122. Available at: <http://dx.doi.org/10.1016/j.buildenv.2017.05.015>.

Table 10 Result summary of airborne laboratory test on glulam partitions

Description	R_w (dB)
(1) Single leaf wall with wooden structure (140 mm thickness), rock wool between beams (140 mm thickness), external wooden chipboards (15 mm thickness)	39
(2) Single leaf wall with wooden structure (140 mm thickness), rock wool between beams (140 mm thickness), external wooden fiberboards (15 mm thickness)	44
(3) Single leaf wall with wooden structure (140 mm thickness), rock wool between beams (140 mm thickness), external wooden fiberboards (15 mm thickness). Additional layer constituted by mineral wool (40 mm thickness) and external fiberboard (15 mm thickness)	48
(4) Vertical wall with double timber structure containing rock wool. Air gap filled with rock wall between the structures, inner wooden chipboards (10 mm thickness) and external single plasterboard	55
(5) Single leaf wall with wooden structure (140 mm thickness), rock wool between beams (140 mm thickness), external double fiberboards (15 + 15 mm thickness). Additional separated layer constituted by rock wool (40 mm thickness) and external fiberboard	62
(6) Single leaf wall with wooden structure (140 mm thickness), rock wool between beams (140 mm thickness), external double fiberboards (15 + 15 mm thickness). Double additional separated layer constituted by rock wool (40 mm thickness) and double external fiberboard	65

It is evident that the standard method does not provide reliable results. In fact it is suggested for homogeneous bare concrete floor with a mass per unit area $100 \text{ kg/m}^2 < m' < 600 \text{ kg/m}^2$. The provided results differ from the measured values up to 10.5 dB. Nevertheless, since this is the only available method, a correction is proposed according to Eq. (13):

$$L_{n,w,eq,corrected} = 134.5 - 25 \cdot \log(m') \text{ (dB)} \quad (13)$$

where m' is the mass per unit area [kg/m^2] of the CLT floor. Using this method, the measured and predicted results agree very well.

Airborne Sound Insulation

For A typology, laboratory tests show how for the bare structure the mass law (Eq. (13)) could be very useful to predict final single index airborne sound insulation value. Furthermore, the addition of a suspend ceiling could be easily calculated and predicted using Eqs. (14) and (15):

$$R_w = 20 \log(m') \quad (14)$$

$$\Delta R_w = 73 - \frac{R_{w,m1}}{2} - 20 \log(f_0) \quad (15)$$

where $R_{w,m1}$ is the sound insulation index of the concrete slab (dB), m' is the mass of the concrete slab [kg/m^2], and f_0 is the resonance frequency of the system [Hz], which can be calculated using Eq. (16):

$$f_0 = 160 \sqrt{\frac{0.1}{d} \left(\frac{1}{m'} + \frac{1}{m''} \right)} \quad (16)$$

Where m'' is the mass of the additional layer [kg/m^2].

For the B typology the airborne sound insulation is generally less investigated than the impact sound pressure level reduction.

Comparing the same structure, the influence of the external massive layer does influence final sound insulation. This final material could vary from wooden chipboard (30 kg/m^2) to plaster or fiber board (from 45 to 50 kg/m^2). As a consequence, sound insulation index could vary between 39 and 45 dB for a traditional 16 cm thickness vertical wall.

As a matter of fact, 7.5 cm plasterboard walls provide sound insulation values from 46 dB to 47 dB. This is due to the fact that timber junctions transmit the airborne sound through the partition, while the steel does not. In order to raise final wooden partitions performances, it would be necessary either to add a double leaf external additional layer ($R'_w > 53 \text{ dB}$) or to split the wall in to two different and separated structures ($R'_w > 55 \text{ dB}$).

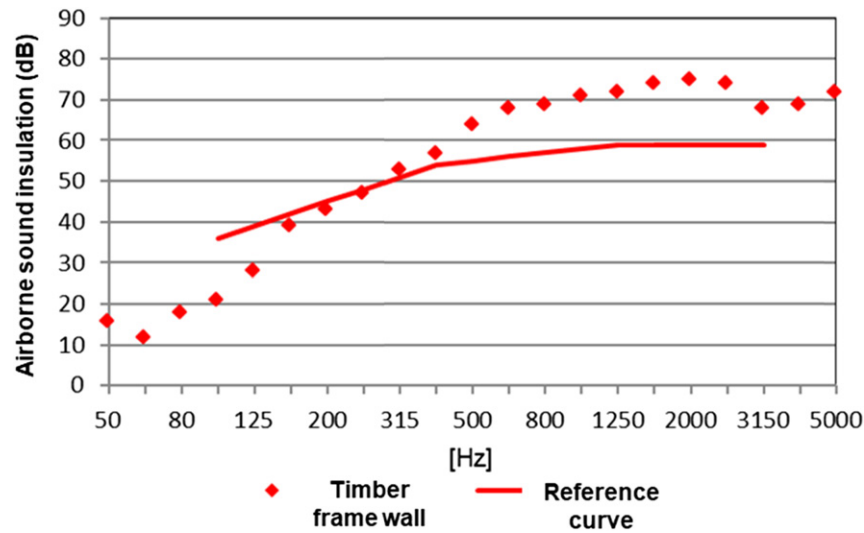


Fig. 16 Typical frequency trend of a double structured vertical partition with fibrous material in the middle air gap.

Table 11 R_w values obtained using mass law method and laboratory measurement

Description	Mass law (dB)	Measured R_w (dB)
CLT floor. 175 mm thickness	40.1	39
CLT floor. 135 mm thickness	38.2	39

If the external layers are fixed, the influence of additional inner massive panels (wooden chipboards, plaster or fiber boards) or the insertion of additional fonoabsorbing layer between the two structures will rise the sound insulation performances. A typical frequency trend of a double structured vertical partition with fibrous material in the middle air gap is reported in Fig. 16 where the resonance (63 Hz) and coincidence (3150 Hz) are highlighted. As a matter of fact, even if at middle and high frequency range the partition performance is high, in the low range (<250 Hz) sound insulation values are far from being suitable for a good noise protection.

In order to determine the influence of single parameter on this kind of construction, a very complete work was conducted by Quint *et al.* (2006), where an in-depth laboratory measurement campaign was performed. Starting from the bare partition, it could be concluded that the additional layer could or could not have a real influence on final performances. Results may be summarized as in Table 10.

For C typology, the bare CLT airborne sound insulation performances are not focus of particular studies or researches since, as type A, final values depend only on the mass and thickness of the partition (Eq. (13)). The model agrees with the provided measurement, as highlighted in Table 11.

Conclusions

The use of timber in buildings is described and critically analyzed. Energy and acoustic performances of timber in constructions were described, focusing on thermal and acoustic insulation. Three main typologies of structures were studied: (i) Timber concrete floors, (ii) glulam and (iii) crosslam walls and floors.

Thermal and periodic transmittance numerical models were depicted and adapted for timber structures, focusing on periodic structures (glulam) and homogeneous ones (crosslam). Results evidenced how the influence of beams width in glulam constructions leads to thermal bridges and worsens the overall thermal insulation up to 18%. The use of an external insulating layer could solve the problem limiting the energy transmission at about 2%. On the other hand, wood products like wood fibers provide up to 100% higher specific heat value compared to rockwool or masonry, demonstrating how their use is to prefer in term of external hot climate insulation.

Airborne and impact sound insulation were approached either by field and laboratory measurements of bear constructions. Numerical models were presented and deeply analyzed highlighting the difference between traditional heavyweight and timber

constructions. New equations and simulation-based approaches were presented and validated. For timber concrete buildings, the new formula show how medium low frequencies rises up to 30% in comparison of concrete structures. For glulam structures, parameters studies report that sound absorbing material (with different flow resistivity) in void spaces reduces the impact noise for frequency above 250 Hz sound absorbing and could represent up to 15 dB reduction. Furthermore, the use of floating floor(s) may provide up to 16 dB extra reduction, while the use of rigid fastened suspended ceiling will worsen the results in dependence of its resonance frequency.

The crosslam technologies provided a “bell-like” frequency trend centered on middle high frequencies and a dependency of the floor thickness was highlighted as the more important parameter.

See also: Analysis of the Thermal Performance and Comfort Conditions of Vernacular Rammed Earth Architecture From Southern Portugal. Bio-Based Materials in Sportswear Applications. Characterization of Wood, Cork and Their Composites for Building Insulation. Energy Efficiency Analysis in Building Walls in Tropical Climate Using Thermal Insulation System. Environmental Assessment of Green Buildings. Improving Energy Efficiency in Buildings Through Responsible Design: Optimizing use and Careful Selection of Building Materials. Insulation Materials for the Building Sector: A Review and Comparative Analysis. Investigation of the Fuel Value of Selected Wood Samples Using Artificial Neural Networks. LCCA and Environmental Impact of Buildings. Manufacturing, Applications and Mechanical Properties of Lightweight Wood-Based Sandwich Panels

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Environmental Assessment of Green Buildings

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Introduction

The building industry poses significant impact on environment, social, economic, and health conditions at global level due to one-third energy consumption [1]. The growing population and economy have drastically increased the demand for construction of buildings. In addition, most of the users spend much of their time, approximately 90% in these buildings [2]. Thus, the buildings require comfort level for the occupants, and ultimately entails huge amount of energy, about 30% of total energy demand [3]. Moreover, the building's energy performance is required to operate typical domestic appliances, such as heating, cooling, ventilation, artificial lighting, and mechanical devices etc. for attaining the desired comfort level.

The era of 1960s and 1970s has primitively emerged for green buildings movement. This countercultural movement raised the concerns for the usage of resources, waste, environmental sabotage and intensity of energy uses in building [4]. Several policies and plans have been devised to enhance the sustainability of buildings for curbing the severe impacts of above-mentioned challenges. The development of such buildings paves the way to use energy efficient materials and plays prominent role in energy saving by utilizing renewable energy resources [5], reducing greenhouse gas (GHG) emissions, improving health and comfort levels etc. These buildings are often termed interchangeably as green buildings (GB), high performance buildings, sustainable buildings, and sustainable construction. Confering to the American Society for Testing Materials (ASTM) standards E2114-08, the sustainable buildings are the ones that provide the performance requirements of specified buildings curtailing disturbance and improve the functioning of buildings at local, regional, and global ecosystems. It is considered at both during and after its construction and specified service life [6]. The buildings are neither considered as monolithic school of architecture, nor the practitioners controvert over trade-off between various objective functions. There remains a sufficient unique collection of predominant values, ideas and practices that are determined with socio-technical niche [7].

The buildings pose great impact on society and economy and is considered as the major sector in producing monetary values [8]. The buildings emit huge amount of carbon dioxide and consumes most of the energy in the United Kingdom out of many sectors of the economy as reported by the European Information service commission, 2012. About 26% of waste is being contributed by the building construction, besides emitting greenhouse gases which are detrimental to environmental impacts [9]. Therefore, the sustainable measures have to be devised to establish the construction industry and building sector to gain momentum for green buildings [10].

The Fig. 1 shows that there should be a balance between environment, orientation or ventilation and energy use within the green building. Green Building should focus on the cycle of use and reuse of the resources within its system boundary. With global

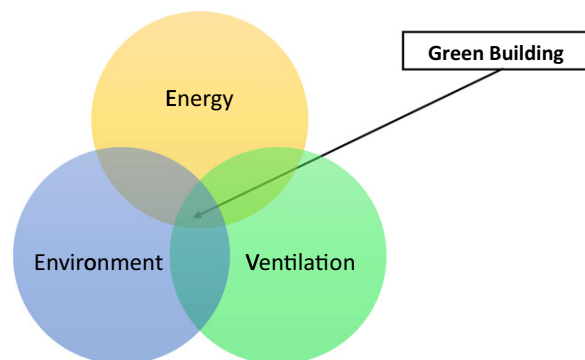


Fig. 1 Green building rating concept.

reference, it has been defined that there are various indicators used for the green building. However, through intensive analysis, it is concluded that these three parameters are the main indicators for sustainability assessment of green buildings.

The environmental performance of the buildings is assessed based on the GB assessment methods. These are referred as an instrument to assess and evaluate that the building is green and efficient which is to be ranked accordingly [11]. The environmental performance of the buildings is to be enhanced with assessment techniques that may go beyond measuring energy use in buildings. The GB tool serves as guideline or management tool to address environmental apprehensions over the scheme, design, development and construction and operation of the buildings [12]. These assessment tools provide an opportunity for appraising environmental concerns to stakeholders, promoting sustainable practices, besides playing crucial role for their effectiveness.

Environmental Assessment

The environmental assessment is a process which ensures the estimation and evaluation of short-term and long-term effects of buildings in the surrounding environment. The assessment also involves identifying the ways and means to alleviate, mitigate and eliminate the adverse environmental impacts and or compensate otherwise. The study is required prior to the project to establish all positive and negative environmental impacts constituting technical, economic and social outcomes. The environmental assessment undertakes the following:

- (1) Potential of adverse environmental effects from buildings.
- (2) Measures to mitigate, eliminate or compensate adverse effects.
- (3) Predicts after the measures have been implemented.
- (4) Designs a follow-up program for effective mitigation measures.

It is significant to emphasize the environmental audits that can evaluate the regulatory compliances and management of building operations, which may not be used to identify the nature and extent of contaminants.

The purpose of an environmental assessment is to incorporate design, maintenance, operation and demolition with eco-friendly planning and decision making of green buildings. This would advocate the analysis at each stage for mitigation measures and address adverse effects. The mitigation measures for planning the building environmental assessment may result in various benefits that includes minimizing adverse environmental effects, human health, project cost and delays, risk of environmental disasters, increased awareness for harmonization, probability of transboundary environmental challenges along with contribution for development of natural resources [13].

The environmental assessment framework for buildings have been devised in Fig. 2. The building tools are developed and designed to assist the environmental assessment measures and rate the environment friendliness. These tools are available in different countries and regions that vary from each other due to their databases, users, life cycle assessment, certification and quality. Besides, different types of buildings can be assessed such as, residential (single family and multi-unit), commercial, office, industry, institutional, and hospitals etc. [14,15]. Moreover, it can also be classified as new buildings, existing or under renovation. This criterion categorizes the environmental assessment based on different standards, benchmarks and indicators. The qualitative and quantitative criteria and indicators vary with different tools available, which can be scaled from the

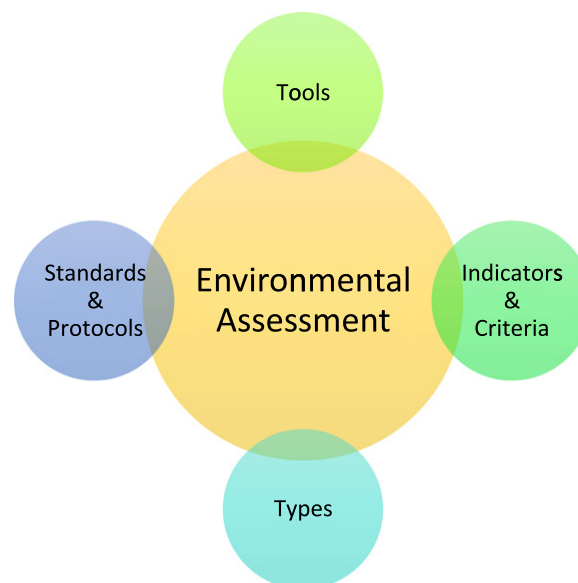


Fig. 2 Framework design for environmental assessment of buildings.

Table 1 Green building rating tools globally

<i>Sr. no.</i>	<i>Green building rating tool</i>	<i>Country</i>	<i>Region</i>
1	ARZ rating system	Baabda-Lebanon	Middle East
2	BERDE	Philippines	Asia
3	BREEAM-NOR	Norway	Europe
4	Casa (Colombia)	Colombia	South America
5	CEDBIK-Knut Green building certification system	Turkey	Europe/ Asia
6	EDGE	United States	America
7	Greenship	Indonesia	Asia
8	Green Key	Canada	North America
9	Green Star	Australia	Australia
10	Green Star SA	South Africa	Africa
11	GRESB	Netherlands	Europe
12	HQE	France	Europe
13	IGBC	India	Asia
14	LOTUS	Vietnam	Asia
15	LEED	United States	America
16	OMIR	Kazakhstan	Europe
17	PEARL (Abu Dhabi)	Abu Dhabi	Middle East
18	Singapore Green Building Product/Services Certification	Singapore	Asia
19	TARSHEED	Egypt	Africa
20	The WELL Building Standard	United States	America
21	BEAM Plus	Hong Kong	Asia
22	BREEAM-LV	Latvia	Europe
23	CASBEE	Japan	Asia
24	DGNB System	Germany	Europe
25	GBC Brasil CASA	Brazil	South America
26	Green Building Index	Malaysia	Asia
27	GreenSL	Sri Lanka	Asia
28	Homestar	New Zealand	Zealandia
29	Green Star SA Kenya	Kenya	Africa
30	Home Performance Index	Ireland	Europe
31	ICP	United States	America
32	Korea Green Building Certification	South Korea	Asia
33	NABERSNZ	New Zealand	Zealandia
34	Parksmart	United States	America
35	PEER	United States	America
36	SITES	United States	America
37	Swiss DGNB System	Switzerland	Europe
38	Verde	United States	America
39	Zero Waste	United States	America
40	BREEAM	UK	Europe

buildings assessment to urbanization and its development. Furthermore, the standardization plays vital role in categorizing all the available tools for environmental assessment. These standards set the norms and regulations for attaining the framework of indicators. These various tools are neither integrated nor adaptive to the changing dynamics for social transformation of buildings. This poses a future challenge, since the later the environmental assessment in the design process, fewer the options would influence the design.

Assessment Methods

The environmental assessment methods in buildings are powerful and effective means for the improvement of performance during its life cycle [16]. Over the past decade, various types and number of assessment tools have been emerged. There are approximately forty (40) assessment tools that have been identified worldwide. Different tools belong to different country and region as shown in Table 1.

The Building Research Establishment's Environmental Assessment Method (BREEAM) among the GB assessment tools is the first and leading method developed in 1990 in United Kingdom (UK). In 1998, Leadership in Energy and Environmental Design (LEED) has been established in the United States. LEED has been widely recognized and dominant building assessment method worldwide and implemented in more than 41 countries [17]. Other popular assessment tools have been listed in the Table 1. Some of these tools are accepted and recognized, however, new assessment dimensions are still significant for countries depending on

their local environmental conditions and types of buildings. The assessment tools may also be unable to reflect building sustainability, refinement and evolution objectively or accurately [18]. The incorporation of cutting-edge technologies, conventions and proficiencies in practice would be refined and evolved with time.

Despite of this situation, there are various possible techniques to establish latest and up-to-date assessment process to enhance existing tools with their strengths and weaknesses. These transformations could be based on statistical database formed with green building practices [19], feedback of GB professionals [20,21], equate the assessment techniques with popular ones and human behavioral and climatic change indicators. Besides all, the approach of equating and analyzing is generally used to drive convenient, accessible and reliable intuitions of green building within the least time [22].

Green Economy in Buildings

The concern over the environmental assessment of green buildings depends on the economic and social development. The integrated development of society, economy and protection of environment has evolved the term green economy [23]. The green economy can be defined as, efficient resource utilization, least carbon emissions, and socially inclusive which drives through public and private investments to enhance income and employment. It also deals to reduce environmental emissions and pollutions, and enhance energy resources efficiency along with the prevention of biodiversity and ecosystem services loss [24]. Thus, creation of green economy is not only promoting environmental protection but also establishing closed-loop ecological alternatives in building sector that can contribute to detoxification and dematerialization of the economy.

The notion of green economy development has been trending since it transforms ecological modernization, environmental improvements and economic development. Developing green economy can also be viewed as to tackle global temperature rise, climatic variations and rise of sea level. Whereas, in narrow concepts, green economy can be understood as low carbon economy that aims to diminish carbon emissions as a part to stabilize carbon index levels [25]. Furthermore, enhanced performance of energy, water and other resources can contribute in green economy that can also raise the building asset value for resale and rental markets. These benefits may act as hedge against climatic, regulatory and environmental risks and make less reliance on inputs with volatile prices that reduces the firms risk exposure.

Sustainability of Assessment Methods

The building project can be considered sustainable if economic, environmental, social and cultural dimensions have been dealt with. The sustainability assessment methods of buildings consider optimization of site potential, regional and cultural identity perpetuation, water resource conservation and reuse, environmental friendly products and materials, maintain optimal indoor climatic conditions, health and safety practices, optimal operation and maintenance and renewable energies supply etc. [26,27]. The sustainability assessment should ensure the practitioners, engineers, scientists and stakeholders for judgement during the building construction, design, use and demolishing of buildings. In such a scenario, a multi-criteria decision method could possibly be devised in decision making for energy efficient and sustainable solution [26]. The building profiles or scores sustainability is dependent on indicators, process results in which the pertinent phenomena are recognized, analyzed and valued.

The sustainability assessment methods are effective and compelling for the enhanced performance of the buildings [16]. The existing and new buildings sustainability benchmarks are assessed differently and each assessment tool may have the capability to rate the building. Although, the accurate and objective reflection of these assessment tools may not be sustainable always, the development, refinement and evolving of the assessment item is therefore the need of an hour [18]. Since, most of the aforementioned assessment tools incorporate new and artificial technologies, principles, regulations and expertise in practice. There would be several ways to develop and evolve sustainability assessment methods, which are to analyze through: (a) Statistical data obtained through green building practices [19]; (b) professionals feedback and experience; (c) comparing the widely used and most recognized assessment methods.

The sustainable environmental issues share common concerns that includes reduction in the use of non-renewable materials, water, emissions, wastes and pollutants reductions. The building sustainability assessment policies may affect the entire life cycle from planning, design, construction to the operations in buildings. The green building and sustainability policies seem to be instrumental in analyzing the challenges, like market failure, information asymmetries, economic externalities. The policy of assessment methods for green building considers the entire life of the assessed building from its planning, design and construction to its operation and demolition. These methods and policies seem to be an influential in analyzing the problems, like market failures, information asymmetries and economic externalities. In order to develop any type of sustainability policy, the identification of challenges which may threat to the development of green building, is very essential. These challenges involve lack of understanding, updated knowledge and awareness, funding, insufficient incentives, uncertainty and risks. The process-related barriers involve lack of measurable requirements, team coordination and collaboration. However, the organizational and personal challenges include commitments from building administration, cooperation between public and government, and incentives availability. The approach to counter these challenges is to propose a uniform policy throughout the world, which is implemented through government to encourage green buildings [28].

Conclusion

The building sector has received much consideration over a couple of decade from engineers, environmental economists, scientists and policy makers that tend to accentuate the resource efficiency within the buildings and reduce its impact on human health and environment. This article has made an effort to encapsulate the theoretical motivation for environmental and economic assessment impacts of buildings. Since, the building industry is considered as one of the main sectors in generating economic value addition and poses a huge impact on the environment, economy and society. An environmental assessment incorporates design, maintenance, operation and demolition with eco-friendly planning and decision making for buildings to be green. These assessments would impose low carbon emission, efficient resource utilization, prevent loss of biodiversity, inhibit ecosystem services and socially inclusive where the growth in income and employment can be driven with public and private investments.

Acknowledgement

The authors are thankful to Mehran University of Engineering and Technology Jamshoro for the motivation to conduct this research work.

See also: Environmental Life Cycle Analysis of Earthen Building Materials. Green Buildings: Risk Factors and Mitigation Measures/Emerging Urban Green Spaces in Dhaka: Planning and Analysis. LCCA and Environmental Impact of Buildings. Retrofitting of Buildings/Built Environment – A Sustainable Development Model. Sustainability and Green Building Rating Systems: A Critical Analysis to Advance Sustainable Performance. Understanding High Performance Buildings: The Link between Occupant Knowledge of Passive Design Systems, Corresponding Behaviors, Occupant Comfort and Environmental Satisfaction. Wind Farm Repowering Using WASP Software – An Approach for Reducing CO₂ Emissions in the Environment

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Green Buildings: Risk Factors and Mitigation Measures/Emerging Urban Green Spaces in Dhaka: Planning and Analysis

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Introduction

A city is built of public and private spaces. But it's the public space which envelopes with uniqueness and presents a statement of the city (Lopes and Camanho, 2012). Generally speaking, public space includes – “All those parts of the built and natural environment where the public have free access. It encompasses: all the streets, squares and other rights of way, whether predominantly in residential, commercial or community/civic uses; the open spaces and parks; and the ‘public/private’ spaces where public access is unrestricted (at least during daylight hours)” The public space includes the Urban green spaces like- parks, recreational spaces, graveyards, and open spaces. Dhaka, the capital city of Bangladesh, is in acute shortage of public spaces or urban green spaces. The city has been expanding to the north since the Mughal period, but it has a limited scope to create new green spaces in the existing context.

United Nations (UN) stated in ‘Concise Report on the World Population Situation in (2014)’, Dhaka is the eleventh most populous megacity in the world with 17 million people. The increasing population has put an immense pressure to the urban settlement of Dhaka and the green spaces are engulfed day by day to meet the urban sprawl (Nilufar, 1999). So this paper aims to point out the potential lands that can be converted into urban green spaces for the wellbeing of the city and make it a livable and sustainable city for the future.

A minimum of 25% open space (plantation and water body combined) of a city, is required to endure a sustainable environment, declared by United Nations Environment Programme (UNEP). In Dhaka, open space area is only about 14.5% (Byomkesh *et al.*, 2012). In another study by Nilufar (1999), shows that, the total amount of open space in Dhaka include- roads, footpaths, parks, playgrounds tracts, lakes, ponds etc. which is about 17%–18% of city area. According to Nilufar (1999), the total land of Dhaka City Corporation (DCC) area and its population ratio, is only 0.12 acres per thousand of population. In the ‘Draft Dhaka Structure Plan Report 2016–2035’, it is mentioned that 0.07 acre/1000 population is the current ratio of recreational areas in Dhaka. With fewer parks and open spaces, the city is facing gradual encroachment of the open spaces both by private and public bodies. Fig. 1 shows, how in 28 years the majority of urban lands, that were previously agricultural land, vegetation, water bodies or low-lying areas were converted due to the increasing demand for urban land. This process put an immense pressure on natural resources in Greater Dhaka (Dewan and Yamaguchi, 2009). These unplanned land use changes has an adverse effect on the present lifestyle and the flooding events, unbearable air pollution, flash flood, water pollution, loss of biodiversity etc. are taking places as a result.

The study conducted by Nilufar (1999), identifies that the precious open spaces of Dhaka are highly used and there also remains a great demand of more open spaces in our urban life. In spite of growing densification of built-up areas in newer parts of Dhaka, a number of medium and large scale open spaces are scattered in the city. The stock of public open spaces under DCC (previously Dhaka City Corporation) control is approximately 190 acres and under Public Work Department (PWD) is 302 acres. These two authorities cover 0.768 sq. miles of area, which is only 1.4% of Dhaka's land.

The southern part, the older part of the city offers more large public spaces which is more culturally active and historically significant, like – Ramna Park (established during British period in 1908), Sohrawardy Uddayan in 1972 (as Habib (2010) stated, Sohrawardy Uddyan was a Mughal Garden until 1825 and later it was turned into a race course under British Rule), Osmani Uddyan, Dhaka university open areas, Shahid Minar, Majar of Three Leaders (beside Sohrawardi Uddayan), Dhanmondi lakes - Nilufar (1999) estimates the plausibility of their diminished value due to over utilization and rapid urban growth. Unless they can be replicated these valuable assets will permanently be impoverished. But the northern part of the city has South Plaza of National Assembly Building, (which is restricted of public entrance) and Chandrima Uddayan are only large scale urban green spaces available for public gathering. Fig. 2 illustrates the existing open spaces of the Dhaka city.

This research aims to identify the potential lands which exist in use as parks, liner green space like lake brims, but absence of landscape quality, inadequate accessibility and vacant/preserved lands which are under different authorities other than Public Works Department (PWD) and Rajuk, can increase the livability of the city.

The aim of this paper is (1) to locate the potential vacant lands or under-utilized Government lands to be converted into urban green spaces. (2) To identify the criteria or attributes necessary to select an urban green space in city scale and (3) to review the current standard of recreational space ratio to population of Dhaka city and analyze the increased ratio due to the selected land. In achieving the objectives, it is necessary to determine which undeveloped/vacant land and under-utilized government land within Northern Dhaka can be converted fully into or at partially to urban green space respectively. It is imperative to identify the criteria or attributes to select an urban green space in city scale. The question to be addressed in this respect is what are the current standard of recreational space ratio to population of Dhaka city and how the newly selected land through LSA (Land Use Analysis) will help improve this ratio.

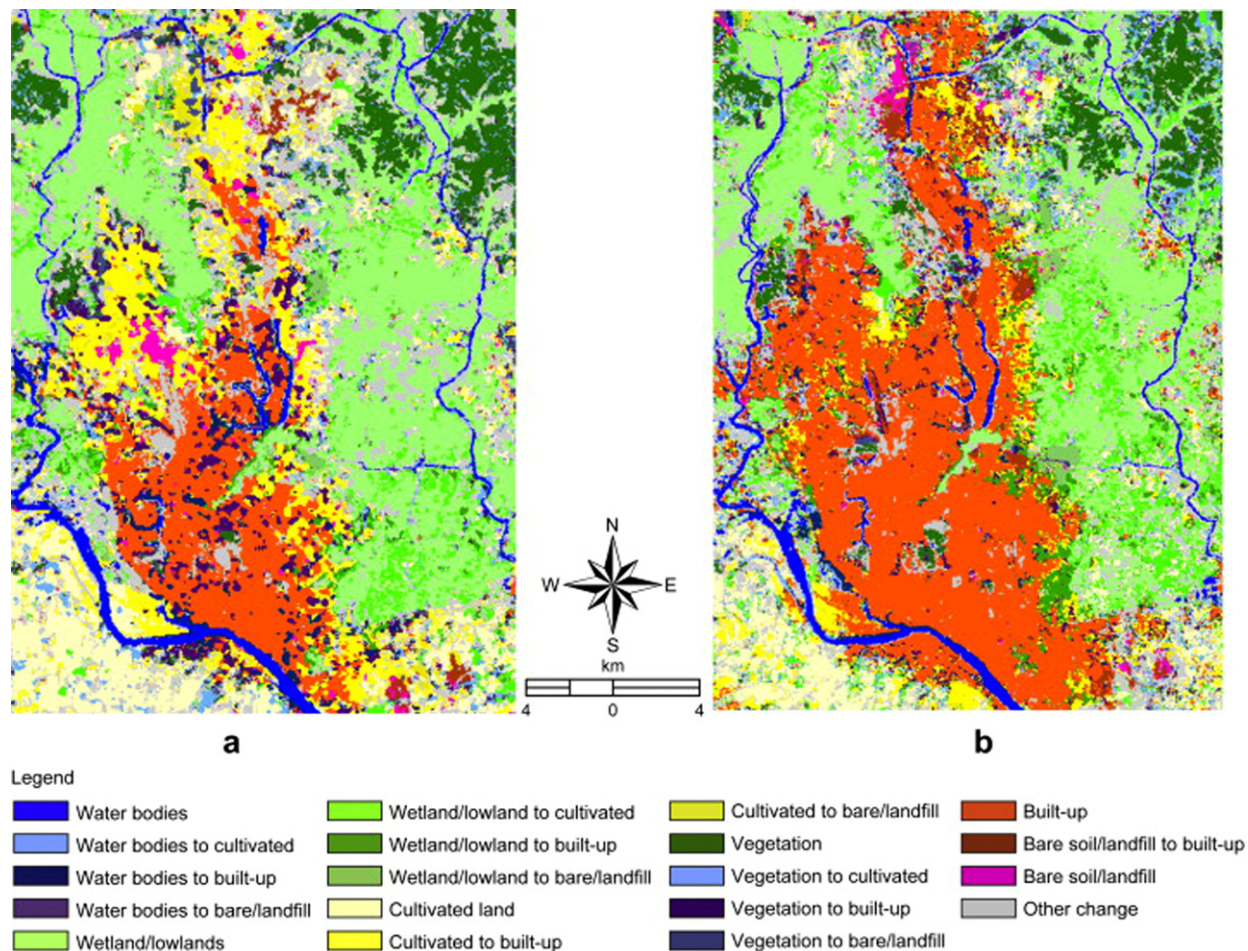


Fig. 1 Major land use conversion of Dhaka, (a) 1975–1992 (b) 1992–2003. Reproduced from Credit line: Dewan, A., Yamaguchi, Y., 2009. Land use and land cover change in Greater Dhaka, Bangladesh: Using remote sensing to promote sustainable urbanization. *Applied Geography*, 398. doi:10.1016/j.apgeog.2008.12.005.

Green Space

Urban green space: This is defined as land that consists predominantly of unsealed, permeable, 'soft' surfaces such as soil, grass, shrubs and trees. These green spaces may also include other facilities and hard surfaced areas. For instance – All areas of parks, play areas and other green spaces specifically intended for recreational use, as well as other green spaces with other origins (Dunnett *et al.*, 2002). In this paper it is aimed to follow the definition of *urban green space* (Table 1).

The following table discusses the typology of urban green spaces of UK that will help to determine the type of urban green space to be selected-

Open space: The terms *green space* and *open space* are often used as synonyms. According to Dunnett *et al.* (2002), the external environments between buildings are composed of two distinct spaces: Grey space and green space. Grey space is land that comprises of primarily impermeable, 'hard' surfaces such as concrete or tarmac. Green space land, whether publicly or privately owned, consists of primarily permeable, 'soft' surfaces such as soil, grass, shrubs, trees and water.

Public open space: Is defined as *open space*, both green spaces and hard 'civic' spaces, to which there is public access, even though the land may not necessarily be in public ownership. In other definitions also includes publicly accessible green space without any formal facilities for recreation provision.

Different Zones

Dhaka, a 400 year old megacity, expanded with the context of history. The morphological changes in the growth of the city can be divided into five stages, which show the gradual evolution of the city from southern river bank to the north. The growth and development of Dhaka can be categorized into six periods (Fig. 3), viz. the pre-Mughal period (1205–1610), the Mughal period

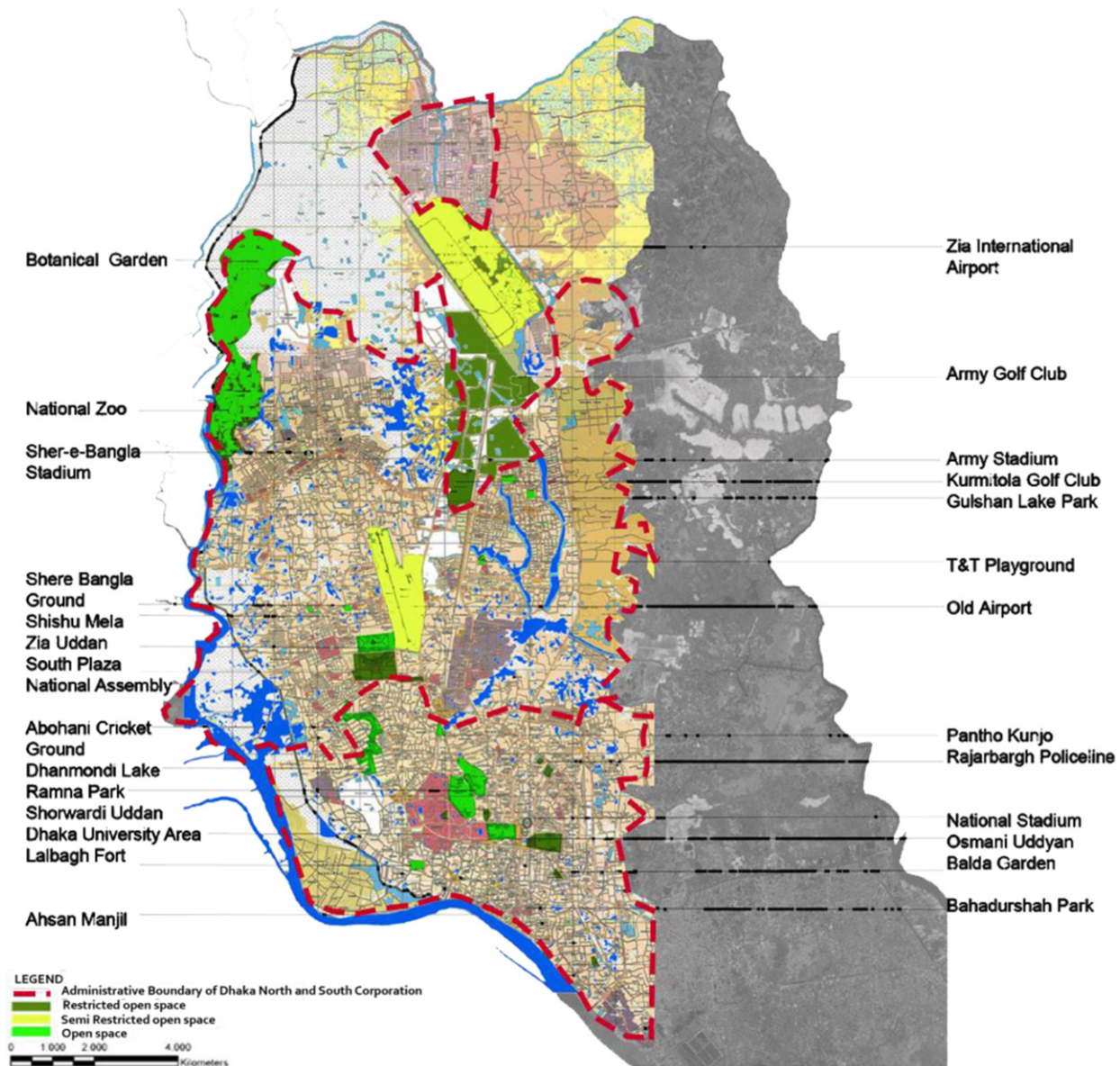


Fig. 2 Major existing open spaces of Dhaka city. Modified from: Habib, K., 2010. The post-colonial public spaces and its cultural diversity: The case of national-cultural representative public spaces of Dhaka. Master thesis, Katholieke Universiteit Leuven, Department of Architecture, Urbanism and Planning (ASRO), Leuven, Belgium.

(1620–1757), the East India Company period (1758–1858), the British colonial period (1858–1947), the Pakistan period (1947–1971), and the Bangladesh period (from 1971 onwards) (Ahmed *et al.*, 2014).

The climate is tropical wet and dry. But due to global warming a lot of changes has occur in the natural cycle of seasons. The monsoon season brings nearly 80% of the annual average rainfall of 1854 millimeters (73 in). Southwest monsoon occurs from June till September during the summer months (Wikipedia, 2015).

The city has a distinct monsoonal season, with an annual average temperature of 25°C (77°F) and monthly means varying between 18°C (64°F) in January and 29°C (84°F) in August.

The Local Government (City Corporation) Amendment Act (2011) divided DCC as Dhaka South City Corporation (DSCC) and Dhaka North City Corporation (DNCC) on 4 December 2011. Because of this amendment, DCC was divided into two parts: DNCC and DSCC (Ahmed *et al.*, 2014, c.f. Ahmed, 2012). This study is based on DNCC and will call it *North of Dhaka* (Fig. 4).

North of Dhaka is situated within Longitude 90°20' to 98°28' and Latitude within 23°44' to 23° 54'. Its total area covers 82.638 sq. kms which consists of five zones including 36 Wards (Dhaka North City Corporation, 2014).

The major zones, the areas, and existing number of parks and playground under DNCC authority are enlisted in the Table 2.

Table 1 Typology of urban green spaces in UK*Urban green space*

1. Amenity green space ● All land which is designed primarily for amenity, both visual amenity and enjoyment for access and recreation. ● It consists mainly of publicly owned land but also includes private land like Domestic gardens.			
Parks and gardens ● Areas of green publically owned ● Variety in landscape and horticulture element ● Facilities included like- buildings, sports, playing area.	Outdoor sports areas ● Accommodate sports; including sports pitches, playing fields, golf courses, and other outdoor activities ● Often occurs within parks, except golf course occurs independently.	Play areas ● Designed specifically for children's play ● Occur separately but also often incorporated within parks.	Incidental green space ● Minimal landscape values ● 'left over' green spaces within housing and other forms of development.
2. Functional green space Green space which has a primary function other than amenity or recreation, although some of these areas may also be publicly accessible and available for people's enjoyment. For instance- Nursery, Burial grounds and Institutional grounds.			
3. Semi-natural green space ● A green space that is made up of semi natural habitat. ● It may have been formed by the natural processes of colonisation and succession on abandoned or disturbed ground or by deliberate creation of new habitat. ● Such as- Wetlands and disturbed grounds.			
4. Linear green space ● Occurs in association with linear features, especially transport routes such as roads, railways and canals, but also rivers and streams. ● These spaces are, however, distinguished by their linear character and are often an important part of strategic green space designations such as green links and green corridors.			
River and canal banks ● Green space occurring along the margins of canals or rivers and forming part of the river or canal corridor.	Transport corridors ● Green space associated with transport, includes: the variety of habitats, associated with railways. ● Along roads, and especially the large areas of grassland, scrub, trees ● And woodland found along major roads and motorways.		

Source: Modified from: Dunnett, N., Swanwick, C., Woolley, H., 2002. Improving Urban Parks, Play Areas and Green Spaces. London: Queen's Printer and Controller of Her Majesty's Stationery Office.

Open Space Provision Standard for Dhaka Metropolitan Development Plan (DMDP) Area

Dhaka Metropolitan Development Plan (DMDP) (2010), Detailed Area Plan (DAP) only suggested standards for parks and play-grounds at only neighbourhood level in Dhaka city. A standard of recreational open spaces within RAJUK area that requires 0.86 acre/1,000 population, thereby 22,360 acre (90.46 sq.km) for 26 million populations which will be 6% of total area is proposed in DMDP. The following [Table 3](#) shows the breakdown of the suggested open spaces criteria and their land cover.

Open Space Provision Standard in Other Countries

The standards approach for parks and open space provision dates back to the early twentieth century. The park reformers sought to establish minimum acceptable park allocations for urban residents. Recreational standards are affected by the cultural background, age, socio-economic status and demographic structure. The following [Table 4](#) discusses the evolved standard of recreational spaces per 1000 residents in the developed countries-

It shows that the required provision for urban recreational spaces in Dhaka city is even bear than minimum in comparison to other developed countries.

Categorization of Existing Green Spaces in North of Dhaka

There are indigenous urban open spaces of Mughal period, still thrives with social activity in Old Dhaka. For instance – *Uthan-mohalla-gali*, are semi- private and public spaces, attributed to rural spatial layout, whereas, [Habib \(2010\)](#) also referred *Bazar and Chouk* (square) as the larger public spaces in Indigenous Dhaka and used for commercial propose as well as a central place for gathering.

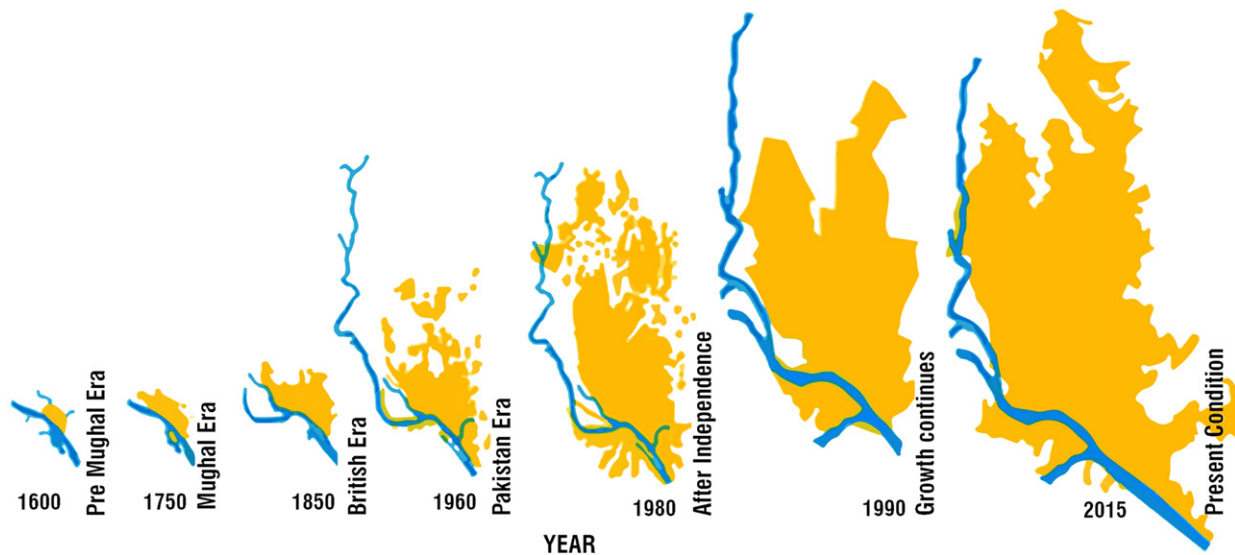


Fig. 3 Historical growth of Dhaka, 1600–2015. Modified from: Ahmed, B., Hasan, R., Maniruzzaman, K., 2014. Urban morphological change analysis of Dhaka city, Bangladesh, using space syntax. *International Journal of Geo-Information*, 1412–1444.

The colonial urban open spaces were the cultural landscape for British and local elites. These spaces later on became the post-colonial urban spaces which served during the 1971 liberation war of Bangladesh and incorporated a new symbol to nationalism. Later on as the city developed to the North, more planned pattern of settlement appeared but the provision of urban green spaces were meagre.

The western standard of urban green space is not applicable to Dhaka city, in terms of hierarchy. Based on nature of the land and the type of open space use, Nilufar (1999) categorized urban green spaces in four types. Here, it is aimed to sort urban green spaces in Northern Dhaka, based on the classification of Nilufar (1999).

This paper aims to select the land for 'Urban Green Parks' typology to increase the percentage of the green open space ratio of Dhaka city.

The Table 5 shows 652.75 acre area is dedicated for 3,957,302 people of North of Dhaka city. From the data in the table, the current provision of recreational spaces in the northern part of the city is about 0.16 acres.

DMDP (Dhaka Metropolitan Development Plan) Structure Plan Policies of Open Spaces

Dhaka City Structure Plan, Vol-I, 1995 [1995–2015] depicted vision regarding city's open spaces but unfortunately they could not meet up the proposal (Nilufar, 1999). The proposed policies are, in brief, as follows:

- POLICY SE/10- Augmenting city open space:
The Municipal Planning Authority [MPA] will seek to augment the City's existing stock of major recreational facilities by means of exploiting the resource of vacant and/or under-utilized Government land within the established urban areas.
- POLICY SE/11- Securing future open space:
It is the MPA's intention to identify and secure sites for major recreational use in the DMDP Structure Plan's all the priority new development areas. It is also recommended that necessary land for flood retention ponds may be assessed to combine them with the recreational open spaces.

However, those policies have not been implemented due to unconcerned and unwilling authorities and lack of awareness and coordination among the implementing agencies. DMDP (1995–2015) standardized 0.16 acres as parks/open space per 1000 populations which is equivalent to 4 acres of open space as parks as part of community services for 25,000 populations as specified in Urban Area Plan (1995–2005).

Methodology of Suitability Analysis

The Landuse Suitability Analysis (LSA) was supported by the spatial analysis functions of GIS through steps including: Identification and collection of spatial data, maps, scoring, weighting and, data integration and GIS analysis, and output evaluation. In

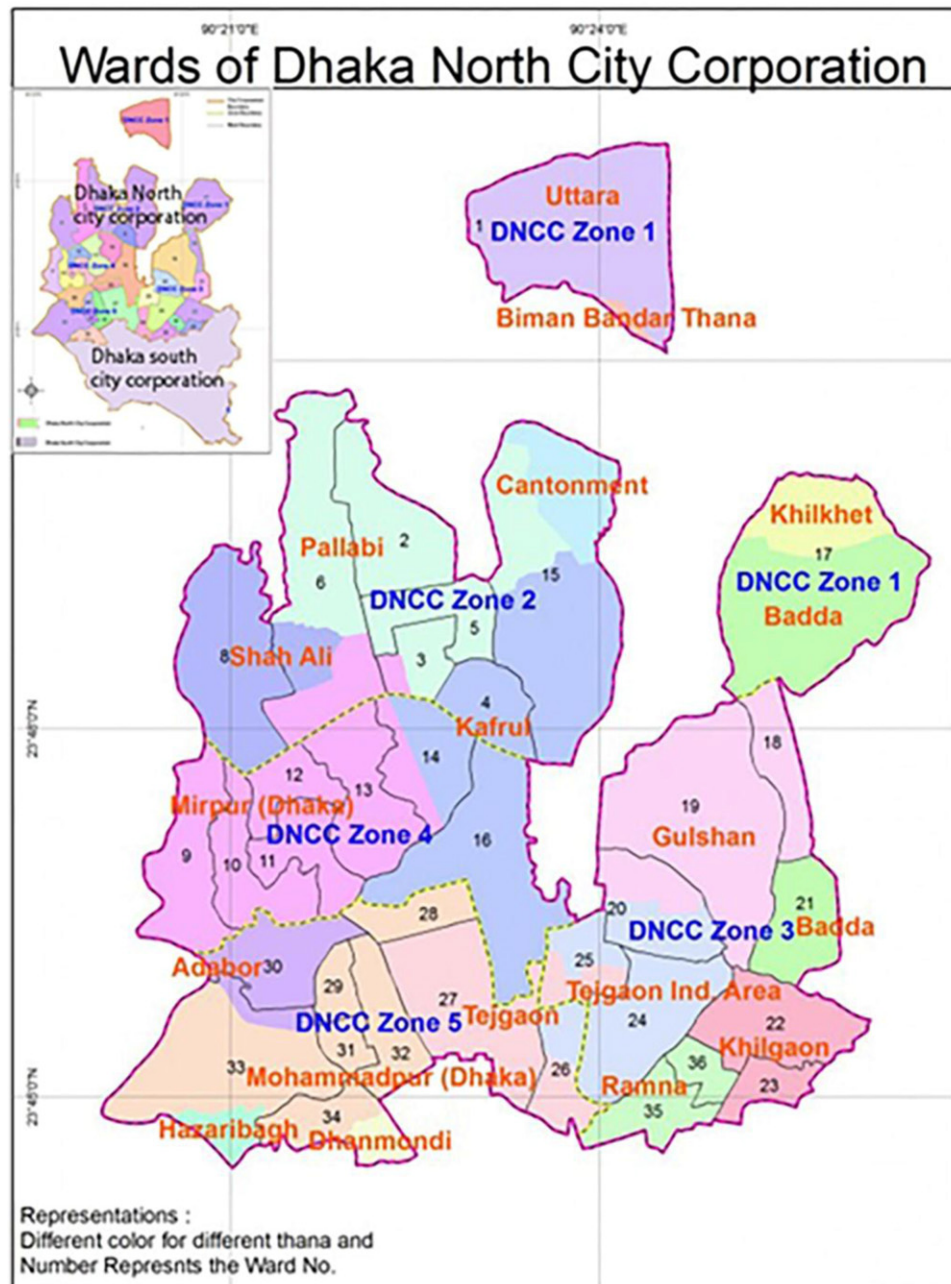


Fig. 4 North of Dhaka, DNCC. Modified from: Iqbal, M.J., (n.d.), 2015. Centre for Urban Studies (CUS), Dhaka. Available at: <http://cusdhaka.org/maps/598/attachment/dcc-north-new> (Retrieved 03.06.15).

LSA, determining the suitability scores for each factor is a compulsory step, and in this study they were regulated from 1 to 4 where a higher score indicates an area more suitable for developing urban green open spaces. Once combined, the resulting map provides a visual tool useful in understanding which areas of Dhaka have superior probability to convert into quality green space and which have lower levels of access. Fig. 5 demonstrates the algorithmic flow of all the necessary steps taken.

Limitations

There are very few previous studies available on suitability analysis of urban green spaces of Dhaka city. So, the current study faced difficulties to enrich the analysis of the findings. The base map used in the current study is 2006 GIS map is from Dhaka City Corporation (DCC). Moreover, the changing rate of infrastructure in the study areas is very high. And also the limited time frame and availability of information over internet are to be considered as limitations.

Table 2 Major zones and existing urban open spaces

Zone	Area name	Area (Sq km)	Population	Parks	Playground
Zone-1 (Uttara)	Uttara Model Town, Kuril, Khilkhet, Nikunjo.	11.570	379,777	6	2
Zone-2 (Mirpur-Pallabi)	Mirpur section-12, Mirpur Ceramic, Mirpur section-10, Mirpur section-14, Byshteki, Mirpur section-11, Bawneabad Area, Mirpur section-6 & 7, Pollabi, Mirpur section-2, Rupnagar, Govt. housing Estate, Mirpur section-1, Box Nagar, Zoo and Botanical Garden, Vasantek, Maticata Manik Dey, Barentek.	21.317	1,002,501	— ^a	5
Zone-3 (Gulshan)	Baridhara, Shahjampur, Gulshan, Banani, Mohakhali, Niketan, Badda, East Rampura, Ulon, West Haji Para, Khilgaon B Zone, Purbo Haji Para, Chowdhury Para, Tejgaon I/A, Kunipara, Arzat Para, Rasul bag, Tejgaon, Boro Maghbazar, Eskaton, Neyatola.	18.987	926,769	14	8
Zone-4 (Mirpur-Kazi Para, Gabtoli)	Golartek, Bagbari, Gabtoli Bus Terminal, Gabtoli, Mirpur Colony, Darus Salam, Paikpara, Ahmed Nagar, Monipur, Parer Bagh, Kazipara, Sawrapara, Senpara-parbata, Ibrahimpur, Kafrul.	11.962	836,132	2	4
Zone-5 (Kawranbazar)	Kawranbazar, Tegturipara, Tejkunipara, Razabazar, Monipuripara, Indira Road, Agargaon, Taltola Staff Quarter, Mohammadpur, Shamoli Ring Road, Adabor, Shakertek, Mohammadpur Azam Road, Jakir Hossain Road, Nazrul Islam Road, Lalmatia, Asad Gate, Khilji Road, Babar Road, Iqbal Road, Aurangzeb Road, PC Culture, Basila, Katasur, Mohammadia Housing, Basbari, Jafrabad, Sultanganj, Rayer Bazar, Bibir Bazar, Madhu Bazar	18.802	812,123	13	20
		3,957,302			

^aAll the open spaces are under Housing and Settlement Directorate and less than 5 acre in total.

Source: Modified From: [Dhaka North City Corporation \(2014\)](#). From Dhaka North City Corporation Web site: Available from: <http://www.dncc.gov.bd/dncc-setup/geographical-location-area-of-dncc.html>. (retrieved 3.06.15).

Table 3 DMDP area for each 1000 people in Dhaka city

Facility Open space	Standard acres/population	Size Acre
1 Park/children's park (local park/mini park within neighbourhood)	1.5 acre/12,500 i.e., 0.12 acres/1000	Under 2 acres & avg. 0.25 acre
2 Play field (local play area)	3 acre/12,500 i.e., 0.24 acre/1000	3–10 acres
3 District park (within city, intermediate scale)	25 acre/100,000 i.e., 0.25 acres/1000	50–75 acres
4 Metro park (urban forests/natural parks out city or on edge, large scale)	25 acre/100,000 i.e., 0.25 acres/1000	150 + acres
Total	0.86 acres/1000	

Source: Modified from: Nilufar, F., 1999. Urban life and use of public space in Dhaka. Report Submitted to Asiatic Society of Bangladesh.

Table 4 Standard area for each 1000 people in around the world

Country	Year	Size	Distance
U.S	1970s	10 acre/4 ha	¼ mile/400 mtrs
U.K	1920s	6 acres/2.4 ha	Unspecified
U.K	1950s	4 acres/1.6 ha	½ mile/800 meters
Australia	1940s	7 acres/3 ha	Unspecified

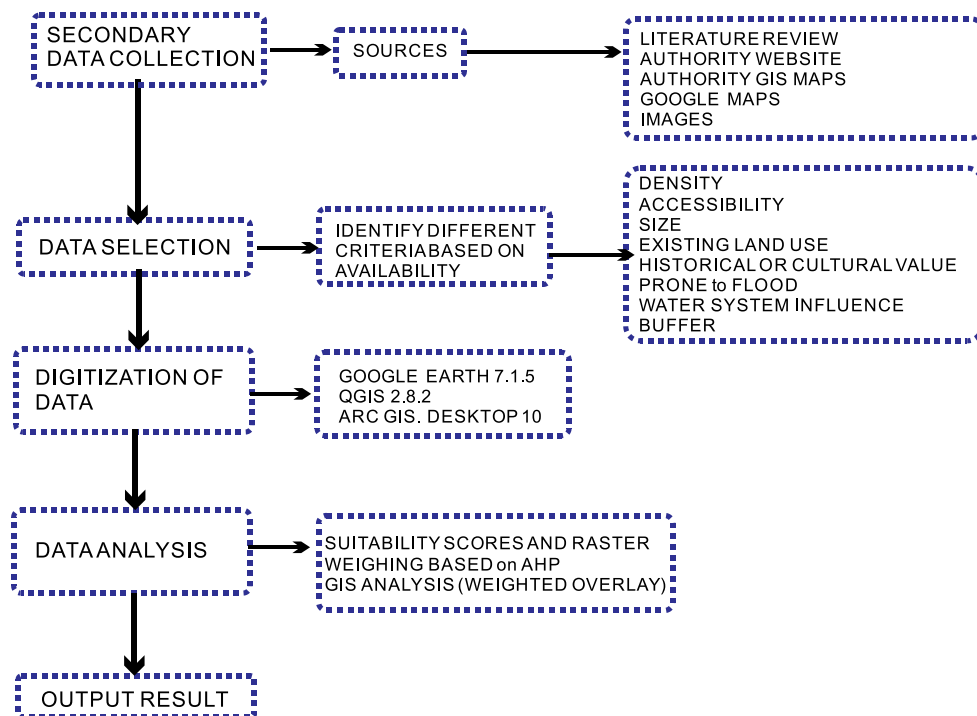
Source: Modified from: Byrne, D.J., Sipe, N., 2010. Green and open space planning for urban consolidation, a review of the literature and best practice. Urban Research Program(11). (retrieved November 2017).

Criteria of Suitability Analysis

Suitability Analysis is defined as the most appropriate spatial analysis for land uses, identified by land use suitability analysis based on specific requirements, preferences, and predictor of some activity (Malczewski, 2004). Generally a myriad of data set can be used for the land suitability analysis of urban green spaces based on ecological, economic and social demands. Previously discussed in [Table 4](#) which has been adopted from C, the open green space of Dhaka city categories into three basic typologies and “Urban Green Parks” is the major park type. But further liner green areas beside lakes or wetlands have also been enlisted in as semi natural green corridors which may host any large public activity; they also fall into the ‘Urban Green parks’ type of open space. The identified open green spaces are shown in the following [Fig. 6](#).

Table 5 Types of urban green spaces in dhaka

Type of open space	Criteria	Standard area (Acre)	Existing example	Zone	Area (Acre)	Desistance from home
Urban green parks	Large open spaces, may include semi-natural or liner green space that accommodates any activity and large group of user	30–120	Chandrima udyan North and South Plaza of National Assembly Building [including National Graveyard, Officers housing & Lake]	5 5	77 95	1.2–1 km
Urban development open spaces	Urban plazas/parks of various size in commercial and institutional areas which has historic, cultural or political importance	2–8	Mirpur Intellectual's Memorial with Park Shishu Mela Shere Bangla Nogar Park National zoo Botanical Garden Pantha kunja	4 5 5 4 4 5	11.6 1.43 6.16 186 208 0.96	800 m
Urban recreational areas	Open spaces developed and assigned for residential outdoor recreational activities	0.5–9	Uttara Sector 3 Park Uttara Sector 4 Park Uttara Sector 6 Park Uttara Sector 07 Park Uttara Sector 13 Park Gulshan Taltala Park Gulshan Park at Road no 103 Gulshan Ladies Park Gulshan Tank Park Baridhara Park Khilgaon Chowdhury para children's park Dr. Fozle Rabbi Park Play Field of PC Culture, Shamoli Khilji Road Children's Park [PC Culture, Shamoli]	1 1 1 1 1 3 3 3 3 3 3 5 5	3.28 3.2 5.75 11.44 6.16 4.2 7.3 5.7 7.5 2.14 4.97 2.1 2.86	400 m
Functional open spaces	Serves functions other than recreation in residential, commercial, industrial area	Variable	Banani grave yard Mirpur Graveyard Kazipara Graveyard Graveyard in Section 13 and 11. Total area	3,4	Variable 652.75	Wherever feasible

**Fig. 5** Methodological flowchart indicating the land suitability analysis (LSA) for urban green space development in North of Dhaka.

Hence, the potential land and liner green spaces have been included in proposed [Table 6](#) with their existing physical, meta-physical criteria, which are 30–120 acre in size and able to host large public gathering. They are as follows:-

The suitability factors accessibility, Historic-cultural value, flooding and water body are taken into consideration other than size, buffer or distance from locality, existing land use and density.

- **Size:** Size is a prime factor for the urban green space in Northern Dhaka. So that it can accommodate the cultural festivals like Pahela Baishakh (Bengali new year), National events like Independence day, Fairs, Dhaka Art and Architecture Biennale etc. all the part and parcel of Bengali life style. It is also vital for the ecology and to enhance a sustainable city for living.
- **Accessibility:** Using space syntax analysis ([Khan, 2014](#)) showed that the use of parks can be augmented by making their accessibility better i.e., by providing entrances from other adjacent roads of parks in Dhaka city. Ease of access of any system of public space depends on the number of alternative access roads. More favorable are major roads, as they ensure more easy accessibility. A large space like Botanical Garden at Mirpur in Dhaka is underutilized, because the road network does not offer a clear approach.
- **Land Use:** Land use includes how people use and manage the land ([Wikipedia, 2015](#)). The economy is interrelated to land-use. The mixed use offers- commercial, residential, institutional uses existing in a particular area that can bring an array of users from different socio-cultural background. Otherwise a specific area can be comprised of dedicated commercial, residential, institutional, industrial users.

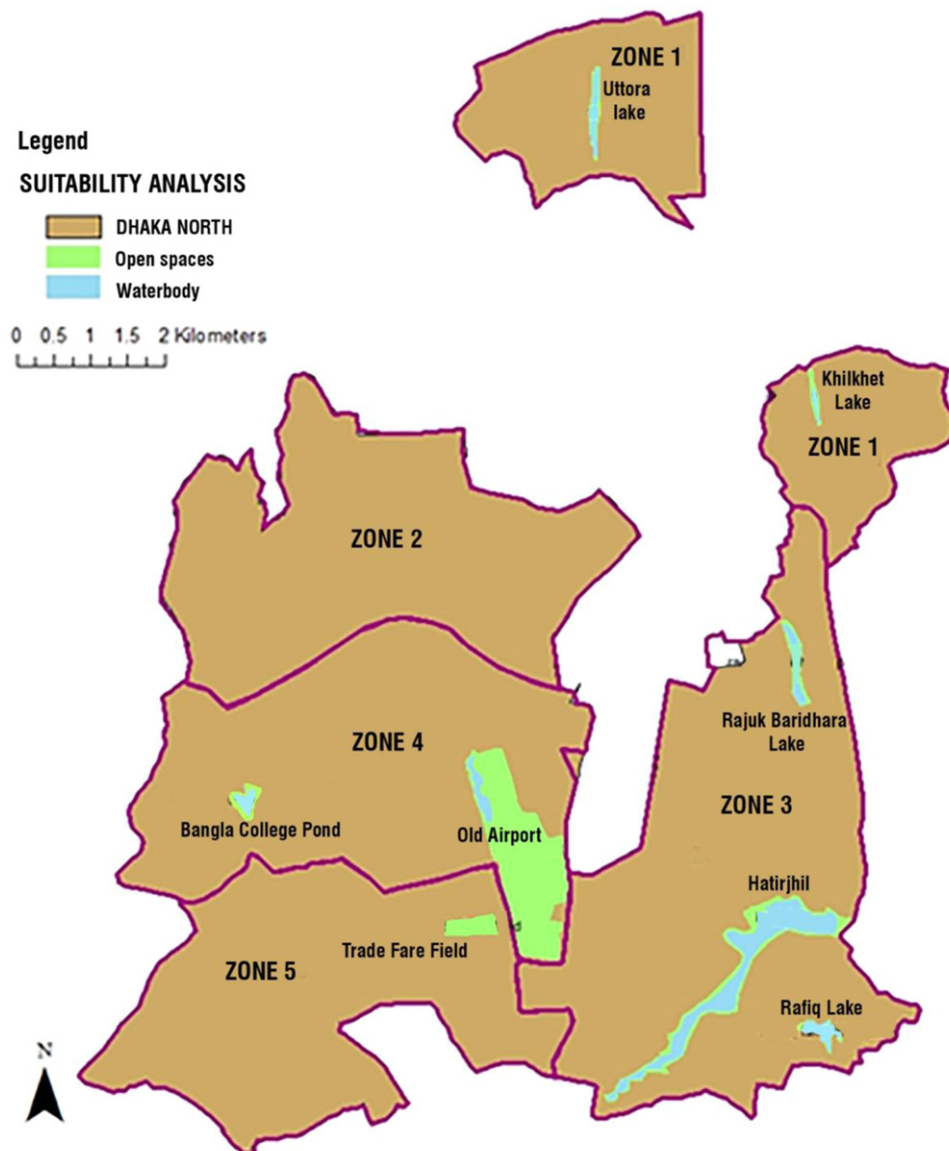


Fig. 6 Proposed lands for urban green space in North of Dhaka.

Table 6 Proposed land criteria

<i>Proposed lands in 5 DNCC zones^a</i>	<i>Area (Acre)</i>	<i>Land use</i>	<i>Buffer of 1.2 km covering maximum DNCC zone (nos)</i>	<i>Accessibility</i>	<i>Historical or cultural value</i>	<i>Flood prone</i>	<i>Water system influence</i>
National Parade Ground zone 4	435	Institutional restricted in nature	4	Bounded by arterial road at west, two major road on south and east, no access from north and eastern corner	Historical site Runway was built during 1942 world war II	Low risk High land	Water body within the site
Hatir jheel lake (INCLUDING WATERBODY) infrastructure Zone 3	302	Mixed use	2	Bounded by major traffic loop	Recreational/tourist spot – Thousands of people gathers at weekends	Low risk New developed	Surrounding a lake or waterbody
Baridhara Lake side Rajuk park Zone 3	41.73	Mixed use	2	Bounded by two major roads at north- south, secondary road at the east and west	Recreational/tourist spot, daily users like joggers	high risk	Surrounding a lake
Uttara Sector Lake Zone 1	29.84	Residential	1	Bounded by two major road at north- south, one secondary road at east and alley on the west	Recreational spot- daily users like joggers	Very high risk With low land	Surrounding a lake
TRADE fare field Zone 5	32.09	Institutional Occasionally used	2	Only accessible from secondary road at north	Culturally active- once a year a trade fair takes place for one month	Low risk With high land	No water feature
Rafiq lake Zone 3	23	Residential	1	Only accessible from few alley of the neighbourhood	Neither culturally nor historically significant	Very High risk with low land	Surrounding a lake
Bangla college Pond Zone 4	23	Mixed use	3	Only accessible from the alley	Historical site Genocide spot during 1971 liberation war	High Risk with low land	Surrounding a lake
Khilkhet Lake Zone 1	20	Mixed use	1	Bounded by major high way at west, and 2ndary road at east	Neither culturally nor historically significant	Moderate risk	Surrounding a lake

^aThe demographic data or density is already mentioned in [Table 2](#), that's why it's not been repeated in the [Table 5](#).

Table 7 Suitability classes and scores

<i>Factor</i>	<i>Suitability class</i>	<i>Class description</i>	<i>Score</i>
Density	High	699,910/sqkm	4
	Moderate	48,828–47,028/sqkm	3
	Low	43,198/sqkm	2
	No	33,024/sq km	1
Accessibility	High	Bounded by four major rd.	4
	Moderate	Bounded by one major rd. two secondary rd.	3
	Low	Bounded by two secondary rd.	2
	No	Bounded by Alley	1
Size	High	≥ 120 acre	4
	Moderate	< 120 but ≥ 40acre	3
	Low	< 40 but ≥ 30 acre	2
	No	30 acre <	1
Existing land use	High	Mixed use	4
	Moderate	Institutional	3
	Low	Commercial	2
	No	Residential	1
Historical or cultural value	High	Historic site	4
	Moderate	Culturally active site	3
	Low	Tourist area	2
	No	Other areas with potential of high historic value	1
Flood prone	High	Low risk	4
	Moderate	Moderate risk	3
	Low	High Risk	2
	No	Very high Risk	1
Water system influence	High	Besides waterbody or lake	4
	Moderate	Water within site	3
	Low	Distance to main reservoir, lake is < 10 m	2
	No	No waterbody within 50 m or vicinity of site	1
Buffer of 1.2 Km radius	High	Covers 4 or all zones	4
	Moderate	Covers 3 zones	3
	Low	Covers 2 zones	2
	No	Cover the only zone it belongs to	1

- *Density*: Population size is an important factor to be considered. Different countries around the world have their own standard of green space ratio per 10,000 people. Even it may vary from city to city within a country, for instance – In US, Boston offers 7.9 acres per 1000 population, whereas New York offers 4.7 acre per 100 ([Harnik et al., 2012](#)). Densely populated Dhaka is unable to meet this bear minimum ratio. In zone 2 and 4 there is a serious lack of large or even neighbourhood scale urban green space, but it has the highest population density among 5 zones. Therefore, it will help to decide which land is more vital.
- *Historical and cultural values*: History and cultural values is another social factor which will include value to the urban green spaces. [Uy and Nakagoshi \(2008\)](#), [Manlun \(2003\)](#) selected this criterion to preserve the site for future generations and by using the space. In the current study, few selected sites have significant historical value – Liberation war genocide field or first establishment of an airport in Dhaka city.
- *Water system influence*: In the densely populated area, it is difficult to find vacant lands, so the existing lakes and lake side have been also included as potential green space. Because Dhanmondi Lake (showed in [Fig. 1](#)) development in Dhaka South city corporation is a successful example of urban space of 15 acre which consist of the soft and hard space excluding waterbody area. And it will also help to terminate encroachment of wetlands caused by urban sprawl and may play a major means of flood and storm water runoff mitigation. In Vietnam, the Hanoi masterplan includes green spaces beside water bodies as valuable landscapes in lieu of strategic planning ([Uy and Nakagoshi, 2008](#)).
- *Flood*: Flood is a form of natural hydro-meteorological phenomenon and very common in Dhaka due to heavy rain, dense settlement and poor drainage network. [Sarker and Sivertun \(2011\)](#) studied various factors of flood and produced a flood prediction mapping of the city, which is used as reference of areas to flood risk.
- *Distance or Buffer*: As it is aimed to propose urban green proto type of “Urban green parks”. Of which accessibility radius of 1.2 km is acceptable. The proximity analysis by [Etingoff \(2014\)](#) determined access to green space outside of the immediate area. In this study, the outer ring of each zone has been buffered to 1.2 km, and then it is identified which land falls in the strategic location to be covered by maximum number of zones.

Table 8 Weighing sub categories (a) Size, (b) landuse, (c) historic cultural values, (d) flood risk, (e) population, (f) population (g) buffer (h) water system influence by applying online AHP calculator

Resulting Priorities				Resulting Priorities				Resulting Priorities			
Category	Priority	Rank		Category	Priority	Rank		Category	Priority	Rank	
1 >150 Acre	45.7%	1		1 Mixed use	51.0%	1		1 Historic site	49.9%	1	
2 120 acre	33.5%	2		2 Institutional	27.1%	2		2 Culturally active	31.3%	2	
3 50 acre	14.5%	3		3 Commercial	15.2%	3		3 tourist area	12.0%	3	
4 30 acre	6.3%	4		4 Residential	6.7%	4		4 other areas	6.8%	4	

Resulting Priorities				Resulting Priorities				Resulting Priorities			
Category	Priority	Rank		Category	Priority	Rank		Category	Priority	Rank	
1 Very high risk	49.5%	1		1 699910/ sqkm	53.9%	1		1 >1.2 Km	5.6%	4	
2 High risk	31.0%	2		2 48828/ sqkm	26.0%	2		2 1.2- 1 km	57.4%	1	
3 moderate risk	13.4%	3		3 43198/sqkm	13.9%	3		3 >800 m	23.9%	2	
4 low risk	6.1%	4		4 33024/ sqkm	6.2%	4		4 >400 m	13.1%	3	

Resulting Priorities			
Category	Priority	Rank	
1 Beside water-body	50.2%	1	
2 water within site	26.3%	2	
3 10 m but 400 m	17.8%	3	
4 no water within or vicinity	5.7%	4	

Source: Created through: Goepel, K. D. (18 May, 2014). BPMSG AHP Online System. Retrieved 20 June, 2015, from Business Performance Management website: <http://bpmsg.com/academic/ahp-hierarchy.php>.

Data Analysis

The proposed lands have been drawn in polygon in Google Earth 7.1.5 and saved as .kml file. Then this .kml file has been converted into shape files using QGIS Desktop 2.8.2 and projected in ArcGIS 10 by using WGS_1984_UTM_Zone_46N projected co-ordinate system for Bangladesh.

In LSA, determining the suitability scores for each factor is a compulsory step, and in this study they were regulated from 1 to 4 of scale. Here a higher score indicates an area more suitable for developing urban green space. In the Size map, for instance, greater than 120 acre in size spaces receive the score 4 (highest suitability), < 120 but ≥ 40 acre in size score 3 (moderate suitability), < 40 but ≥ 30 acre in size achieves 2 (low suitability) and smaller than 30 acre in size score 1 (no suitability). The following Table 7 describes the suitability classes and scores for every criteria. They are illustrated in map. They have been converted to raster image for the weighed overlay in ArcGIS 10.

Analytical Hierarchical Process is a mathematically multi-criteria decision making process. Pairwise comparison method can exchange subjective measurements of comparative importance into a linear set of weights that is developed by Prof. Saaty (1980) known as Analytical Hierarchical Process (AHP). An online AHP Calculator created by Goepel (2014), has been used to obtain AHP of four degree and pairwise comparison matrix for both factors and sub category and define each criteria's relative importance by weighted score. It precisely influences the result, and is complicated by interacting of factors with each other (Uy and Nakagoshi, 2008).

Table 9 Priorities of Criteria

Resulting Priorities			
Category		Priority	Rank
1	Size	32.1%	1
2	Density	9.5%	4
3	Accessibility	22.9%	2
4	Existing Land Use	8.5%	5
5	Historical or Cultural Value	4.8%	6
6	Water System Influence	17.6%	3
7	Buffer	2.8%	7
8	Flood	1.8%	8

Source: Generated through: Goepel, K. D. (18 May, 2014). BPMSG AHP Online System. Retrieved 20 June.

Consistency ratio (CR) for the above weights have been tried to maintain fewer than 10% and this consistency is acceptable. Because, it is less than 0.10 which means the subjective judgments need not to be revised.

Finally the weight has been normalized and the spatial analysis tool has been used in ArcGIS 10 to overlay the previously rasterized maps to obtain the final composite map.

Results and Discussions

The priority of each Criterion contributes to the priority of the Goal. The priority of each Subcriterion contributes to the priority of its parent; the AHP software (Goepel, 2014) calculated the global priority of each Subcriterion. The Table 8 shows the priority of each sub-criterion. The local priorities throughout the hierarchy will add up to 1.000, like this:

Based on the entered judgments the AHP has derived the priorities for the factors against which each of the eight lands will be compared. The consistency ratio (CR) is 7.4%. They are shown in the Table 9 below.

The next step is to evaluate each of the lands with respect to these factors. These evaluations are done in ArcGIS 10 by normalizing the weights. The spatial analysis tool produces the rasterized images (Fig. 7) which show the suitability of each land with respect to each category. Then these rasterized maps are then overlaid with derived priorities for the factors. Final overlay of all the maps has produced the desired map (Fig. 8) and the most suitable land has been selected for conversion which is the old airport at Tejgaon.

The map in Fig. 8 clearly depicts the most suitable vacant or underutilized land, suitable for converting into new Urban Green Space in North of Dhaka. The current condition of urban green open space is dire and inadequate urban recreational spaces initiated this research. However the selected criteria are unique to the lands but not limited to the scope.

These physical attributes have helped to define the ultimate land which used to be the Old Airport of Dhaka. It has received the highest scores in all criteria except the existing land use criteria. The area is used as Base Bashar by BAF (Bangladesh Air Force) and is a highly restricted area. It covers the densest catchment area, bounded by major road for ease of accessibility, and has the biggest area. It was the first international airport of Bangladesh, so it has historical-cultural value and the site is located on the high plane of Dhaka which is less prone to flood and has water body inside the area. Also the site covers 4 zones of DNCC in 1.2 km radius. By critically fulfilling highest scores in most of the criteria, old airport of Dhaka is certainly suitable for converting into urban green space. The 435 acre of area will also increase the provision of the recreational area per 1000 population in the north of Dhaka city.

The current ratio is only 0.16 acre/1000 population. This is also below the standard of DMDP standard 0.86 acre/1000 population. If Old Airport at Tejgaon can be converted into the green area of the city, which is also proposed in the Draft Dhaka Structure Plan (2016–2035), the ratio will increase to 0.27 acre/1000 population.

Followed in order of importance comes in second- Hatir jheel, which is a lake side corridor and needs landscape planning to overcome its current issues. It has received highest scores in accessibility, size and existing land use. It's a low land and prone to flood, that's why received the lowest score in flood prone criteria. It's also less suitable in terms of buffer and existing landuse.

In third-Rajuk Baridhara Park and Rafiq Lake Khilgaon are suitable to become the urban green space, but these sites received the highest scores only in exiting land use criteria, and are less suitable in terms of size, density, accessibility,

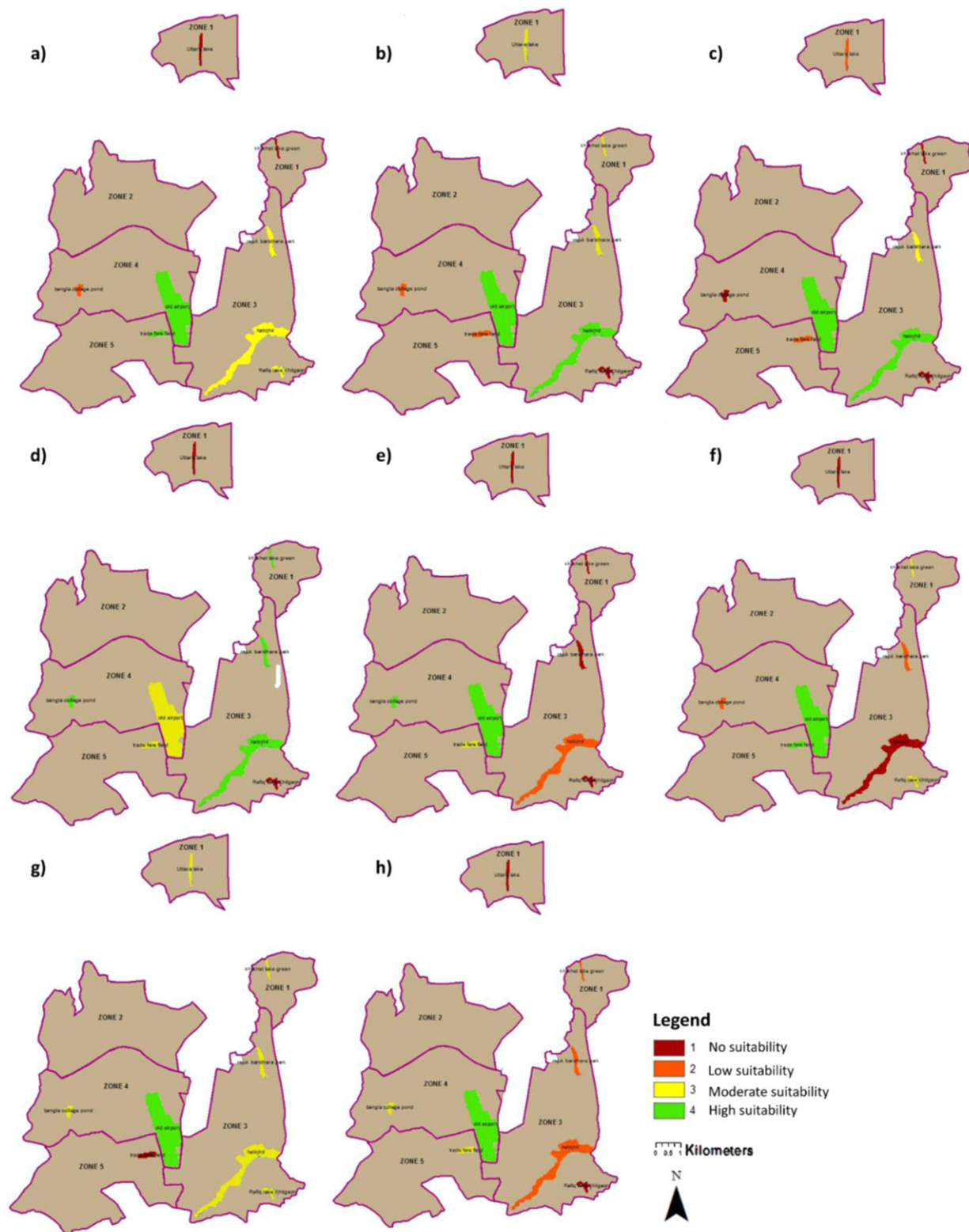


Fig. 7 Suitability scores for (a) density, (b) accessibility, (c) size, (d) existing land use, (e) historical and cultural value, (f) flood prone (g) water system influence (h) buffer.

SUITABILITY ANALYSIS OF PROPOSED URBAN GREEN SPACES IN NORTH OF DHAKA

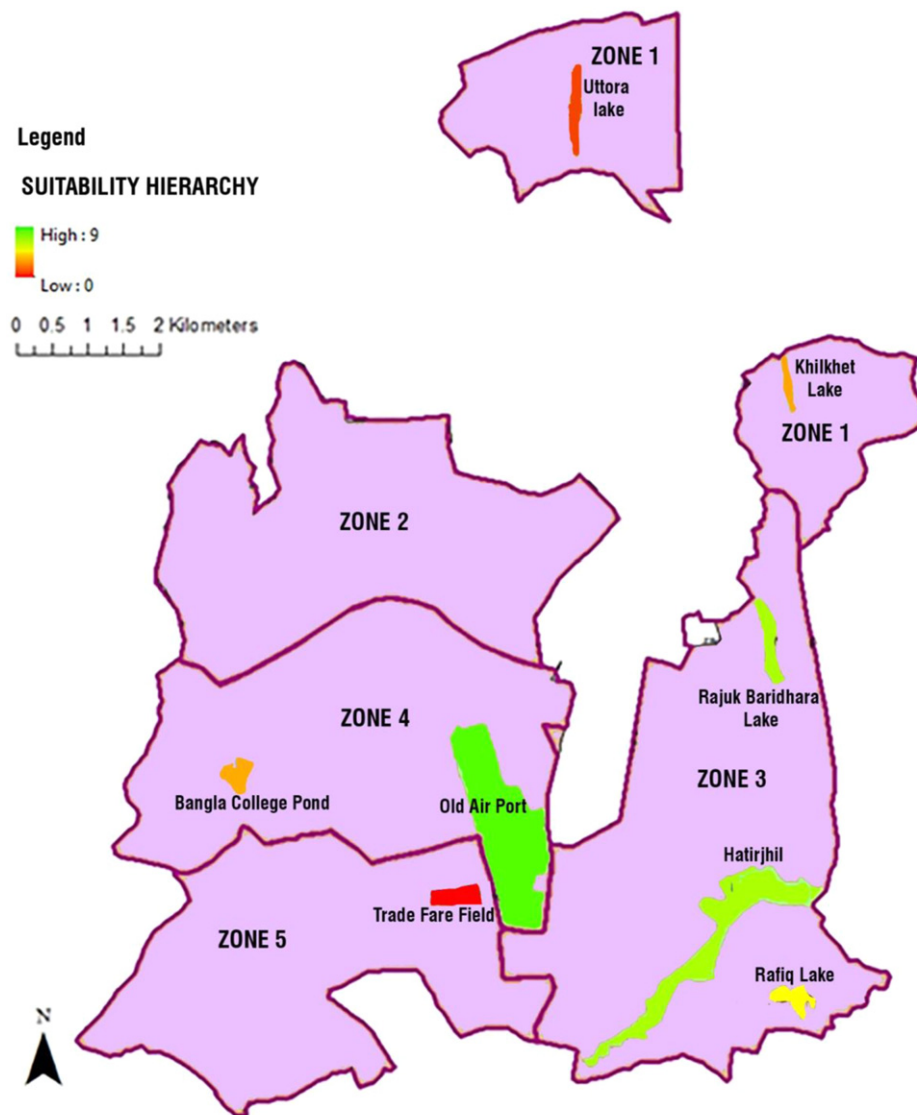


Fig. 8 Generated Composite map of proposed lands with highest suitability.

historical-cultural value, buffer and flood prone criteria. But these lands can be protected and converted into community scale green spaces.

In fourth place come- Bangla college pond and Khilkhet Lake, in fifth- Uttara Lake Park and in the last- trade fare field. The trade fare field shows no suitability at all for future development of urban green space. To enhance Trade fair field's viability it can become an extended part of Chandrima Udyan to increase the provision for recreational area.

Conclusion

The research has led to identify the most appropriate vacant land of North of Dhaka which will serve to all most all zones, except zone 1. In terms of landscape architecture, the Old Airport can contribute to increase the green space ratio from 0.016 to 0.27 per acre after the development of the site. Diverse flora and fauna habitat can be introduced in the heart of the city. In identifying the desired land physical and meta physical attributes were identified that helped to select plot. The establishment of an urban green space in the congested area of North dhaka will not only increase the land value in terms of aesthetics and landscape but it will also help to take steps to build sustainable city." Policy se/10- augmenting city open space" of Dhaka Metropolitan Development plan (DMDP) structure plan can be implemented to take over the viable land.

It will also help to develop economy and new users. The habitants of North dhaka will not have to travel down to south for any urban gathering if this land is established as an urban green space at the heart of the city.

But further research is necessary for better understanding and social criteria like users should be included for more accurate outcome of results. For more intense results, if funding are available, more land should be identified to develop community parks and greenbelts surrounding the city. Previously Nilufar (1999) suggested to convert the Old Airport into urban green spaces and resemble it's potential with the Central Park of New York. This heuristic research will certainly create a new horizon in the field of landscape architecture in Bangladesh. To develop a more sustainable city we must understand the growing needs and pressing problems of the current lands. Multi criteria sutability analysis is surely an important tool, only used by the planners in Bangladesh. But it's the first time it has been used to identify lands for landscape planning purpose.

See also: Environmental Assessment of Green Buildings. Leadership in Energy and Environmental Design Rating System: A Global Tool to Assess Sustainability in Buildings, Communities and Cities. Sustainability and Green Building Rating Systems: A Critical Analysis to Advance Sustainable Performance

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Green Energy Fuel From Biomass and Sea Water

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Introduction

In this modern era of the 21st century, the need of energy as fuel has been increased from two decades. Human life has become only dependent on energy carrying resources. Without energy, the life seems dull and colorless (Kumaravel and Abdel-Wahab, 2018). From the chores of a peasant to the patients in the hospitals, from transport to vehicles to aircraft purposes, from cooking to meals to pressing dresses, even from conversion of energy from one form to another including mechanical, chemical, electrical, solar, cell, etc., the energy sources are required. This energy is obtaining from the sun, earth, water, air, waste products of animals and dead plants. Greater than 70%–80% of energy is utilized by the non-renewable resources like fuel, oil, coal and in the form of natural gas. But, renewable energy sources like solar (Vanderhulst *et al.*, 1990), wind (Kempton and Tomić, 2005), geo-thermal (Banerjee *et al.*, 2015), biomass (Sriram and Shahidehpour, 2005), tidal (Twidell and Weir, 2015) and hydro power (Akhtar *et al.*, 2018) are used to produce only 15%–20% energy carrying devices utilizing for human objectives. If we take command over the production of energy releasing from the sea water (Ferreira and Estefen, 2011), that is, abundance in quantity all over the earth, then, the need of energy may be minimized, so that development rate can also be increased. Therefore, to quench the thirst for production of energy is now under considerable view at a large scale. To discuss these energy resources, we perform a comparison between the basic energy resources is given in this article. To meet favorable methods to overcome the restricted aspects that are becoming the hurdles among the existing methods, different modern technologies have identified (Ellabban *et al.*, 2014). The difference in the renewable and non-renewable energy resources is also described in this review. These energy carriers are useful in the form of light and heat in the building, offices, hospitals, schools, public stations, at work-shops, ware houses, hotels, libraries at shopping malls and market centers as well agricultural and industrial field of life is equally important. All these energy carriers including domestic, commercial, industrial and agricultural objectives are obtained from the sustainable as well as non-sustainable energy resources. It is also seen that the renewable energy resources are in abundance and natural occurring without any cost. Out of all over world research on the energy, there are 20% sources for Bio-chemical, 21% for microbial desalination, 10% for photocatalysis, 12% for seawater batteries, 9% for petrochemical industries, 4% for electro dialysis and 24% for others. As with the increasing population, energy has become the primary block for diversity in every walk of life. Since, all the set-up round the world depends upon the energy. The energy utilization is taken as the backbone for its progress. Out of all the energy usages there are 40% sources used it for industries, 24% for globalization consumption, 30% for domestic chores and commercial objectives and remaining part is used for other applications including agricultural.

In developing and under-developed countries, there exists opponency between energy usage appliances. Since, there are 2 billion citizens in developed countries. There is deficiency in achieving the suitable amount of power suppliers. Above three million people's lives in the under-developed countries depend upon the wood, kerosene, coal, charcoal and dung for their domestic purposes. Contrary to it, urbanized locations accounted for seventy percent (70%) of energy consumption at commercial scale. Pakistan, with 13% of the world's population used only 2% of world energy. If American society uses the 100 units for conveyance and only 1.5 units are used by Pakistanis. Pakistan as an agricultural country, majority peoples used dry wood, livestock wastage and agricultural wastes for their heating and cooking purposes. The minority of the peoples who lives in urban areas are facilitated with industries, free transport, technology availability and home appliances. This energy is obtained from renewable as well as non-renewable sources. The energy share in each walk of life is the result of commercial resources as petroleum, coal, charcoal, sun energy, etc.

Main Energy Resources

Among the efficient energy resources, solar and sea water can play significant role to numerous energy harvesting applications. The energy produced by them is used in the industries at commercial as well as at agricultural level. Solar energy; with each day of the rising sun, provide us heat and light. This solar energy when reaches the earth in the form of light and heat, some fraction of its energy is reflected back to the space and some fraction is absorbed through plants by the process of photosynthesis. These are divided in two categories as;

- (1) Renewable energy resources and
- (2) Non-renewable energy resources

Renewable Energy Resources

Renewable energy resources are biomass energy resources available in the naturally in abundance and exist everywhere around the world. These sources are unlimited, i.e., they can be recycled for many times to obtain the energy. They consist of dry fuel wood in

forests, Petro-plants and trees, biomass base plants, livestock dung, solar energy, wind power, water energy, and geothermal energy. These energy resources can be recycled under viewing and taking some suitable steps in nature. Renewable energy sources produce eco-friendly and pollution free environment. These energy resources are widely using in all over the world. The advanced countries are using the sun light and wind with hydra power to produce heat and warmly environment. In Pakistan, a place called Sui; there is a big power plant for natural gas where sulfur di-oxide and other odor gases are treated to generate the smelt gas. Consequently, the gas leakage can be realized and can be safe from a serious accident. The solar energy in solar panel has become a forceful mean to day at every place round the world. The solar plate absorbs the ultraviolet rays from the sun and converts it to electricity by using in home appliances. There is not too much cost consumption for the purposes of wind producing setup than other sources producing energy. The wind energy rotates the turbine and thus the generator produced electricity through wind-mills. And further by the transformer it is facilitated to domestic areas by grid stations and used. Geothermal energy, another renewable energy source, used to produce energy in the form of fuel and electricity. Natural heat from the earth core is used to turn the turbines planted in remote areas, resulting in the production of energy as heat and electricity. However, a small amount of geo thermal energy is used and consequently a huge amount of electricity, about 10,000 times more energy is generated.

Water, a natural gift, has enough pressure to create the energy of several Giga voltages. The small amount of kinetic energy of river water is utilized, and as a result, the energy about the amount of country requirements can be achieved. The dams all over the world are using the same principle and producing the energy as heat as well as electricity, a biggest need for energy requirements, and removing the thirst for energy. The energy producing by the hydra power is at the higher level all around the world. Now a day, it has become the biggest source of electricity. Biofuel is conversion of biomass, including the livestock wastage with plants and the animal's fossils are treated to combustion under the high heat that convert the waste products to steam and this steam is used to rotate the coil and produce electricity.

In the developing countries, the biomass-based energy generation methods are efficiently used due to its versatile properties. The biomass based waste-materials have to be crushed through machine and then to be processed by grinding to form the required fine form of material. This material is then ionized under pressure to turn it into heat and consequently this heat is used to generate electricity by the turbine (Boyle, 2004). Thus, the electricity is produced in remote areas. In this way, fuel crisis, energy crisis, water purification problems have been overcome up to 70%. In the future, if the energy necessities would be control over if the struggle will continue. However, these methods are producing a high amount of energy and are utilizing energy in the world, but there are some drawbacks of them. However, they are eco-friendly, but they are polluted to some extent as well. Due to un-advancement in some countries, the availability of the material is uncertain for many countries. Even the advanced countries are also facing these adverse defects (Johansson *et al.*, 1993). The death rate of the world population has been increased up to 30% due to polluted environment. Among 5 men of the world each three men had fallen prey into serious disease.

Non-Renewable Energy Resources

Non-renewable energy resources that are produced for long a time and are accessible in controlled amount. Due to control utilization, they are fatigued for a limited time. Non-renewable energy resources are petroleum based, coal, natural gas, nuclear energy fossil fuels, etc. These sources are obtained by the cracking and reforming of by-products.

Nuclear energy is obtained by the nuclear fission reaction of uranium and thorium. In this reaction, the neutron with its sufficient energy strikes to the uranium atoms and, as a result, and adduct of the reactant with the catalyst is obtained for a short period of time, this adduct is unstable and get stability by the emission of krypton and barium with extra three neutrons and an amount of energy of mega voltage range is obtained. If the neutrons are controlled then the reaction is controlled, but, if the neutrons are not captured, they further react with other uranium atom to do a reaction and thus continued the reaction as shown in Eq. (1).



As a result, the fission chain reaction takes place. That is a function of the atom bomb. Fossil fuels; dead plants and animals are buried under the ground for a long period of time. Due to global warming and increasing temperature and pressure on earth, these decay objects are converted into fuel. This fuel contains coal, petroleum including carbon. These compounds are organic compounds found also in proteins, carbohydrates, enzymes, lipids, vitamins and nucleic acids. Energy is obtained by the petroleum, coal and natural gas reservoir contains organic compounds. The dead plants and animals, due to bacterial and chemical reactions are converted into peat resulting into the coal under high temperature and pressure.

These sources have shorter duration to sustain themselves. Fractional energy achieved by petroleum is given by the following Table 1:

These gasoline products are found from the biomass material with the help of some renewable energy resources. Non-renewable energy sources are the carriers of polluted environment and the poisoned air. These energy carriers are the greatest source of disease, causing death (Han *et al.*, 2015). Thus, the death rate has been increased from last decades. The polluted air has created a number of patients suffering from asthma, serious flue, chest attack diseases and many other diseases.

Table 1 The table shows the fractional volume of non-renewable energy resources

<i>Fraction</i>	<i>Boiling point range (°C)</i>	<i>Uses</i>
Natural gas	<20	Fuel, petrochemicals
Petroleum ether	20–60	Solvent
Gasoline	40–220	Motor fuel
Kerosene	175–325	Heating fuel
Gas oil	> 275	Diesel and heating fuel
Lubricating oil	Viscous	Lubricants
Asphalt	Solids	Paving and fuel reducing

Sea Water Abundancy

Sea-water found on the earth is in abundance and is about 90% in nature. This sea-water contains NaCl, MgCl₂, MgSO₄, CaSO₄, k₂SO₄, Ca₂CO₃, and some MgBr₂. In order to meet the progress in each field of life, the production of energy as a fuel has now become basic requirements throughout the world. Since, the temperature at near the earth surface is about high of 26°C. A current is, like a vast river in the ocean, transferring fluid from one place to another. The differences in temperature, wind and salinity cause current. These currents are responsible for the movement of water in the ocean and sea. Moreover, the earth water is also found in the form of salinity at greater amount. Due to such a marvelous amount of water there is a need to produce electricity at such higher level. Suitable steps are followed by various companies to promote their countries and states.

Hydro-Electric Power

Sea power is another superb source of the renewable energy as a fuel for the human being's benefits (Ferreira and Estefen, 2011). The energy released by the sea water can be converted into the electric power by turbines. This electrical or mechanical energy can also be used as water purification for home appliances and other commercial chores. The solution was separated and air was passed through alloy, water reactor and fuel cell. The whole mixture was then reacted with water and converted it into hydrogen by catalysis process. Owing the efficient hydroelectric energy, the world's maximum energy shortage has been sustained (Estefen *et al.*, 2007). The other method that can play significant role to generate electricity through hydraulic energy conversion is ocean energy converters (OEC). It converts the seawater into electricity which then converts it into mechanical energy. The energy generated through these sources was found to be effective for domestic, industrial as well as agricultural requirements.

Wave Energy Converter

According to Brooke (2003) and (Liu *et al.*, 2014), wave energy converter (WEC) is managed by remote areas of the seashore, the coastline and offshore devices. This process is based on the ultra-pressurized chamber that has the ability to store the wave energy though the fast movement of water. The pressurized water is then accumulated into low-vacuum and ultra-high vacuum system. The water is stored in hyperbaric chamber and ultrahigh pressurized pneumatic chamber. These chambers worked as a hydraulic press. When the pressure of the press has reached at its critical operational value, the water is driven through the valve which is directly connected to a generator that rotates the turbine and as a result, electricity is produced. The power obtained by ocean is converted into electrical/mechanical energy. This kind of energy is then treated through desalination of water. Consequently, obtained water is used for cooking, drinking and many domestic tasks, industries suppliers and agricultural cultivation.

Hydro Power

Water is the most conventional renewable means of energy. Energy is obtained when water flows or falls off from a height. Hilly and highland areas like mountains and springs are suitable for this objective, where water flows in large continuous sequence falling from slopes. Dams and power plants are built over rivers. Falling rain water with river water is stacked in dams to fall from heights. This stored water flows out through pipes in specific directions inside the dam, which drives turbine blades placed at the bottom of the dam. Thus, the speedy rotating blades then turn the generator to produce electricity. This energy is called hydro-electricity. The water is used in crops and fields for irrigation after the generation of electricity.

Pressure Retarded Osmosis (PRO)

The pressure between the river and sea water at the height is used to change the SGE (salinity level) to mechanical/electrical energy. Water flows with the chemical potential from river water with low pressure to the higher level in the seawater. The mechanical power is utilized to expand the volume level in the higher concentration region. This pressurized water is used to turn the turbine

Table 2 The PRO result for energy generation with natural and commercial sea salty water in draw solution form

Membrane	HC	LC	Pressure	Power density (W/m)	References
SiO ₂ /polyacrylonitrile	Seawater brine	80 mM NaCl	15.2	15.2	(Song <i>et al.</i> , 2013)
Hollow fiber membrane	Seawater brine (1000 mM NaCl)	10 mM NaCl	20	7.0	(Zhang and Chung, 2016)
Thin film composite-polyethersulfone	Sea water brine	Wastewater concentration	20	4.6	(Wan and Chung, 2015)
Thin film composite-polyethersulfone	Sea water brine	Deionized water	20	21.7	(Wan and Chung, 2015)

resulting in the generation of electricity. In the chemical format, higher and lower concentrations are used to draw and feed solid solutions. **Table 2** shows the PRO result for energy generation with natural and commercial sea salty water in draw solution form.

The experimental results revealed that the energy production is strongly affected by using membrane characteristics and quantity of LC/HC (light chains (LC)/heavy chains (HC)), that is, feed and drawn solutions. Further, membrane efficiency is also influenced by reverse solution permeation instead of forward solute permeation. At the same time, the inside concentration polarization and outside concentration polarization was found to be 95% and 96%, respectively. The treated wastewater, being a feed solution, has also become an attractive choice for energy production using PRO. Pretreatment of wastewater by ultrafiltration and nano-filtration are getting higher efficiency and more advantageous when compared to other conventional techniques.

Electricity From Biomass

Biomass is the organic material generated by dead plants and animals waste that are buried underground for a long period of time. After many years due to global warming and high temperature of the earth these waste materials are converted into the organic products like oil, petroleum, coal etc. These materials that are combustible are also called biomass. Biomass having organic compounds comprises of carbon, hydrogen, and oxygen. Biomass with plant and animal's excreta are used as fuel energy and for nourishing and growth of plants and seeds (Liu *et al.*, 2013). There are some important kinds of biomass such as: wood, livestock waste, bagasse, human waste, etc. However, coal is the main part of biomass containing hydrocarbon. In spite of this, it contains the waste product but it is considered more efficient source of energy throughout the world. There are many applications in the society in which biomass are used. It is considered more important than other energy source. Biomass can be oxygenated to produce heat and electricity and because of this, it is widely used in combined heat and power plants (CHP). It also can be used in combined state with fossil fuels to improve the characteristics of combusted residues. Biomass can replace the petroleum as fuel. Biomass with fossil fuels can also be used to generate electricity.

Organic waste products in the form of hydrocarbons such as dead plant and animal products, animal dung and food waste are converted into gaseous fuel called biogas. This organic waste is decomposed by bacterial microorganisms in biogas tankers to emit biogas which contains mixture of methane CH₄ and carbon dioxide CO₂ gases. Biogas is a conducting fuel for cooking and lighting houses and building and produces huge amount of organic manure annually. Energy is everywhere in nature, but the harnessing of this energy is difficult as well as costly. Each one of us can make a competitive arrangement by not wasting energy.

Methods of Extracting Energy From Biomass

Thermal energy, liquid, solid and gaseous fuels with other chemical products can be extracted from biomass by any processes. In the United States, the bio energy also called bio power is used for the energy generation in the form of electricity at the rate of 10 GW capacities. But now a days, majority of technical sources focus on the direct-combustion based technologies. The future performance will be better by co-firing the biomass with coal and invention of new methods like gasification, the combined system of heat and fuel, fuel cell arrangements and modulated systems. The basic bio-power technologies are based on the process of direct combustion, alcoholic fermentation, anaerobic digestion, pyrolysis and gasification. Specific sources of energy are given in **Table 3** as follows:

Direct Combustion

It is the simplest method for energy evolution from biomass. The industrial oxygenated availabilities can combust many ionized biomass products like biomass fuel, wood, crops residues, wood pulping, municipal wastage and livestock wastage as animal dung. The biofuel is burned to generate steam and the steam at high pressure rotates the turbine. As a result, the turbine rotates the generator and electricity is produced.

Gasification

Gasification is another process for the generation of energy from biomass in which, a solid fuel is combusted at high temperature and insufficient oxygen to generate gaseous fuel. It contains the mixture of gases, including carbon monoxide (CO),

Table 3 Specific sources of energy

<i>Field and plantation biomass</i>	<i>Industrial biomass</i>	<i>Forest biomass</i>	<i>Urban waste biomass</i>	<i>Aquatic biomass</i>
Agriculture crops residues: Cobs, stalks, straw, cane etc.	Agro-industrial processes: Husk, whey hides and skin waste.	Timber.	Municipal solid wastes.	Microalgae blooms.
Edible matters from crops: Pulses, fruits nuts, spices, lint	Oil cakes, Sugar molasses, Sugar bagasse.	Log residues forest floor debris.	Sewage sludge.	Sea weeds.
Dedicated energy crops: Bamboo, willow, poplar etc.	Fruit and pulp debris saw dust.	Animals carcass	Kitchen and canteen wastes.	Fresh water weeds.
Plantation debris: Leaves, barks, trunks, etc.	Shavings, Fermented, Microbial mass.			Dead fishes.
Livestock wastes: From fields, slaughter houses.				

carbon dioxide (CO₂), nitrogen (N₂), hydrogen (H), and methane (CH₄). The gas is used to drive the turbine and electricity is produced. This process has many advantages than combusted solid fuels. One of them is used for the convenience and other is used for resultant. Methane can be used as natural gas for burning purposes. Another advantage for the gasification process is to burn many polluted impurities and becomes a source for some removal of pollution free particles (Kubacka *et al.*, 2012). Under some specific conditions, it can also be used to produce the hydrocarbons by mixing of carbon monoxide and hydrogen and can be replaced by fossil fuels. Hydrogen is also a fueling agent used to produce methanol and ethanol.

Pyrolysis

The simplest method, the pyrolysis method, includes heating the biomass material to draw the volatile matter that is not in liquid form but directly sublimates, leaving behind charcoal. This process has doubled the production of energy density of original material because, charcoal is ½ the weight of the original biomass, having the same amount of energy. The charcoal, containing hydrocarbons that burn with black fumes and dirt smelt at much higher temperature than the original biomass, turning it more useful for manufacturing processes, especially in the road engineering. Specialized pyrolysis techniques have been developed to store the volatiles that may be dangerous to the remaining setup. These collections of volatile product generate enriched hydrogen (H₂) gas, a potential fuel and carbon monoxide (CO). These compounds are then commercialized into methane, methanol, and other hydrocarbons in alcoholic form.

Digestion

Biomass digestion works by using biological anaerobic bacterial micro-organisms. The micro-organisms live at the bottom of swamps or at places having no supply of air. These are overwhelming dead organic matter used to produce methane gas (CH₄) and hydrogen (H₂) gas. These bacteria are then fed by organic material like wastage such as, animal dung or human sewage into tanks, called digesters.

The emitted gas is used to store for its utilization as an energy carrier. This process is a very resourceful means of emission of usable energy from such biomass. Generally, up to 2/3 part of fuel energy of the animal dung could be recycled. Another important technique that is related to this process is to collect methane gas from landfill regions. A large quantities of household biomass waste are the kitchen leftovers, lawn cutting and trimming, leaves the wastage materials. After a long life of decades, anaerobic bacterial organisms at the bottom of the tips of digesters could decompose organic matter, including the hydrocarbons and emit methane gas. This gas is then extracted from digester tanks and is used by covering the landfill site with a strong layer of clay. When perforated pipes are injected, then these pipes would collect the gas and bring it to the surface.

Biomass Energy

Advantages of Biomass Energy

There are certain advantages that encourage the bio-mass to be used for further processes. Biomass energy is an eco-friendly and pollution free source of energy. It does not emit CO₂ gas that causes global warming. The same amount of CO₂ is absorbed as the same is released. The main advantage of biomass energy is the use of the same apparatus to produce electricity. It does not affect the environment as the other conventional methods have adverse effects like oil spillage, acid rain, mine spillage, open spitting, radioactive disposal and other wastage produced. Bio-fuels are sustainable. The green methods are used to produce the bio-fuels. So, the rate of carbon is not increasing in the atmosphere. These biomasses are not costly and easily available. They can be grown easily in any area of the world. Alcohol obtained by this process is reliable and can be produced easily.

Disadvantages of Biomass Energy

The cost of construction of the biogas power plant is high, so only advanced cities can utilize them. Continuous supply of biomass is required to generate biomass energy. Biogas plant requires space and produces dirty smell. Transportation of bio-fuel through the long pipes is difficult. Due to improper construction, many biomasses plants are working inefficiently. It leads to the increasing rate of deforestation, soil erosion and desertification.

Conclusion

In this review article the energy resources, types and methodology and their advantages and drawbacks have been discussed. The energy generated from biomass and sea water in the form of electricity is also discussed. The energy production from the biomass and removal of waste materials from the polluted environment is an eco-friendly process. The methods of digestion, pyrolysis, gasification, etc., are described for the electricity generation from seawater. Moreover, hydro process by utilizing sea water for electricity production is also discussed and their advantages and disadvantages have been highlighted.

See also: Biochar Production From Biomass Waste-Derived Material. Biomass Conversion to Selected Value-Added Chemicals Using Zeolites: A Review. Biomass for CO₂ Sequestration. CO₂ Sequestration Using Algal Biomass and its Application as Bio Energy. Co-Firing of Biomass to Reduce CO₂ Emission. Large Biomass Burners for Fuel Switch in Existing Fossil Fuel Based Plants. Renewable Biomass: A Candidate for Mitigating Global Warming. Synthesis of High Grade Activated Carbons From Waste Biomass. Thermophysical and Adsorption Characteristics of Waste Biomass-Derived Activated Carbons. Traditional Biomass: A Replacement for Petro-Fuels

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Green House Effect and Carbon Foot Print

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Introduction

In this age of globalization, media communications and social media, almost everyone is well familiar with the concept of greenhouse effect. The natural process that warms the earth's surface is known as greenhouse effect. The enhanced greenhouse effect is likely to boost the earth's average temperature by 1.0–3.7°C during the next century, leading to changed regional climates, increased global rainfall and a rise in sea levels [1]. There are certain gases, such as water vapor (H_2O), carbon dioxide (CO_2), methane (CH_4), and ozone (O_3), which actively contribute in the process of greenhouse effect. Few more gases and compounds such as nitrous oxide (N_2O) and artificial chemicals such as chlorofluorocarbons (CFCs), also take part in greenhouse effect. The range of share of individual gases causing the greenhouse effect is given in Table 1.

While the share of N_2O and CFCs can reach maximum value of 11%. The share of each contributor gas varies in certain ranges, and probably there is no exact percentage of the share of each gas contributing in the greenhouse effect. This is because of the reason that few gases absorb and emit the radiations at same frequencies and other gases. So, it cannot be said that the total greenhouse effect is the addition of the share of each gas [2]. The issues we are facing nowadays is an increase in the negative effects of greenhouse gases and the volume of these gases generated by human activities. The human activities mainly include but not limited to the burning of fossil fuels, agricultural activities, industrialization, transportation, etc. The increase in the emission of greenhouse gases substantially increases the effects on the earth's ecosystem, thereby creating the disturbance in the normal equilibrium life on the earth at website provided in "Relevant Websites section". Since, the greenhouse gas, especially CO_2 is emitted from various man-made activities, and it is difficult to determine the amount of these gases emitted by individuals, organization or a group of people. Carbon footprint is a term that can be used to measure the total amount of CO_2 released by individual's activities. In this way, the carbon emissions can be measured from individual sources [3]. Once the sources of CO_2 emission can be identified and measured, the values obtained can be used to develop the future energy plans. In this way, the greenhouse gases and carbon footprint can be reduced significantly, which is also an intention of this module.

Greenhouse Effect: Is it an Unending Process?

It is well known process of warming up the earth surface temperature by some of the radiations which are reflected to the space back and trapped into the greenhouse gases. Although this subject was discovered a long time ago, even though it has been the topic of much discussion nowadays. This is owing to the deleterious effects of global warming due to the greenhouse effect [4]. This reference module's intention is to make aware of all the communities of society regarding the understanding of greenhouse gases, their sources, effects and remedies. Therefore, it is of utmost importance to know how this process takes places and affects the climate of the earth. The step-wise process of greenhouse effect is illustrated in Fig. 1.

The greenhouse gases trap the extra heat and warm the global temperature and cause the global warming. These gases are listed in Table 1 along with their individual range of share contributing to global rise of temperature. There are various sources of greenhouse gases, such as CO_2 emitted from combustion of fossil fuels (natural gas, oil, coal and wood), solid waste incineration, production of cement, fertilizers, decay of biomass, forest fires, and deforestation, etc., at website provided in "Relevant Websites section". The sources of methane emissions are production, transport and distribution of natural gas and oil, mining of coal, agricultural activities, and decomposition of organic solid waste. Similarly, nitrous oxide and CFCs are also emitted from agricultural and industrial practices respectively. Among these greenhouse gases, CO_2 is a major cause of global warming even though the range of contribution is lower than that of water (Table 1). Water is available in larger quantities as compared to CO_2 . However, the residence time of water vapors in the atmosphere is quite weak. Therefore, water vapors are not considered when measuring greenhouse emissions. On the contrary, CO_2 emitted from variety of sources remains for a very long time, therefore considered as a major source of greenhouse effect at website provided in "Relevant Websites section". The topic of CO_2 emission as a source of global warming has remained a burning issue since long time. It is evident from the literature that a lot of efforts have been continuously carried out to minimize the CO_2 emission. Until today, it is not clear that how much amount has been spent for the alleviation of CO_2 emissions. This implies that the communities are aware of the harmful effects of greenhouse in the form of global warming. Some of the most understood effects are climate change which leads to the potential ecological, physical and health impacts, including extreme weather conditions, floods, storms, droughts, heatwaves etc. These effects have also been noticed recently in various countries including United States of America, United Kingdom,

Table 1 Range of contribution of various gases in greenhouse effect

Greenhouse effect contributor gas/compound	Range of contribution (%)
H ₂ O	36%–72%
CO ₂	9%–26%
CH ₄	4%–9%
O ₃	3%–7%

Note: Kiehl, J.T., Kevin, E., 1997. Trenberth Earth's annual global mean energy budget (PDF). Bulletin of the American Meteorological Society 78 (2), 197–208.

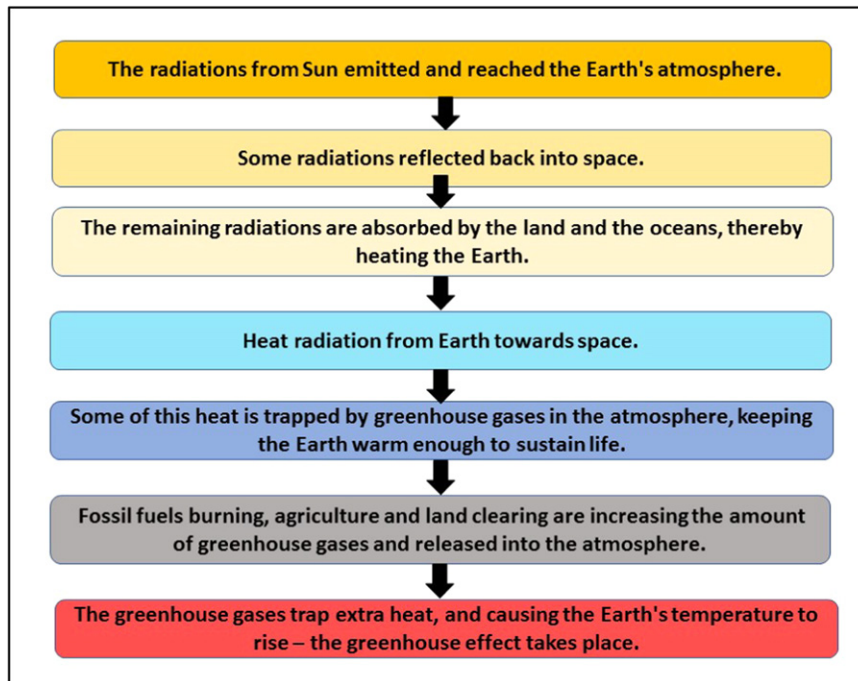


Fig. 1 Step-wise process of greenhouse effect. Data used from Australian Government, Department of the Environment and Energy. Available at: www.environment.gov.au/climate-change.

Ireland, Indonesia, China, etc. Other notable effects are sea level rise, disruption of carbon cycle and water systems, and irregular growth of crops, etc. [5,6]. Despite the enormous efforts made by government organizations, private firms, stakeholders and public for the reduction of CO₂ emissions, still it is not clear how long it will take to completely combat this issue. To date, no time line is suggested or recommended for its complete remediation.

Greenhouse Gases: Timeline Matters

The different greenhouse gases have different timeline to stay in to the atmosphere once these are emitted from any source. The gases that have weak residence time, contribute lower in the greenhouse effect as compared to the gases with higher time of residence in the atmosphere. This is because of the reason that the heat trapped by those gases stays longer time in the atmosphere, thereby warming it extensively at website provided in “Relevant Websites section”. The timeline or residence time of various greenhouse gases ranges from few years to thousands of years and is portrayed in Fig. 2.

No gas remains forever in the atmosphere. This is because of various physical, chemical and physico-chemical processes are continuously undergoing in the complex atmospheric system. The details on these systems can also be found elsewhere in the literature. It is obvious from Fig. 2 that the water vapors and ozone stay less time in the atmosphere. CO₂ is third long lived gas in the atmosphere following nitrous oxide and CFCs, therefore, the contribution of these gases is according to their time span in the atmosphere. Based on the above facts, it can be said the CO₂ and other long-lived gases emitted by any individuals or organizations and industries in a day can sustain the environment and remain for too long time. This long time of greenhouse gases remain in the atmosphere and causes the global warming, which can be very dangerous for us and our future generations at website provided in “Relevant Websites section”. Therefore, it is essential to investigate, how to reduce the release of these gases along with their residence time in the atmosphere, so that the effects of global warming can be minimized.

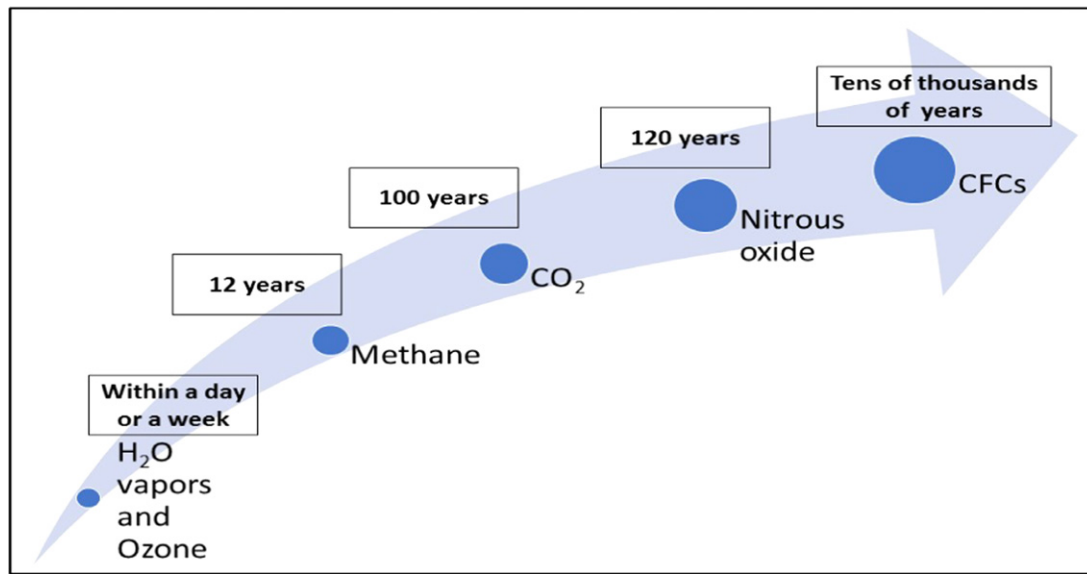


Fig. 2 Timeline of greenhouse gases in atmosphere. Data used from Jean-Marc. Jancovici. Available at: www.jancovici.com/en/climate-change.

Table 2 Greenhouse gases and their respective GWP values

Name of gas	Relative GWP/CO ₂
CO ₂	1
CH ₄	25
N ₂ O	298
Hydrofluorocarbons	120–14800

Source: Intergovernmental Panel on Climate Change, 2007, 2007. Climate Change.

Global Warming Potential

Another most important factor that can be used to understand and control the greenhouse gases is the term Global Warming Potential (GWP). After the lifetime of greenhouse gases, this is very crucial way to measure the radiative power of a gas and its radiation efficiency. In its simplest form, how much the power of the greenhouse gas for emitting the radiation back to the ground. GWP also varies with respect to the type of greenhouse gas. Water vapors, CO₂, methane, nitrous oxide, ozone and CFCs, all these gases have different GWP value. The different values of GWP for various greenhouse gases provide a relative contribution of each gas in global warming at website provided in “Relevant Websites section” [5]. These values can be very useful to establish the policies and strategies to overcome or control the emission of such toxic gases. Similar to the lifetime of greenhouse gas, larger the values of GWP, the larger will be the contribution of that gas to the global warming at website provided in “Relevant Websites section”. The GWP values of various greenhouse gases are given in Table 2. It is obvious from Table 2 that the GWP of CO₂ is quite lower than that of methane gas. As an example, it can be stated that the methane gas has 25 times more potential than that of CO₂. The other relative comparison can also be made based on the values given in the table.

Based on the GWP values, an assessment can be made on what sources of these high potent greenhouse gases that can be controlled and or minimized.

Carbon Footprint

The contribution in the emission of greenhouse gases at individual level is best described by the term carbon footprint. It is a notion that describes a person's each activity that generates greenhouse gases. The emission of these gases varies greatly from one individual to another depending upon the activities carried out by them [3]. The routine activities of every individual greatly vary, so does their carbon footprint. These activities range from driving a car, travelling in the fossil fuel vehicles, aero planes to the use of domestic equipment at home. Other important factors which reduce the amount of individual's carbon footprint are habits of people, their culture, choices and geographical locations, etc. Like the GWP, carbon footprint is also very important notion of measuring the individual's emissions and contribution to the global warming because it helps to identify the exact sources of populations from where the gaseous emissions are generated in bulk quantities [3] at website provided in “Relevant Websites section”. Once, those sources are identified, the control and mitigation strategies are easier to implement at website provided in “Relevant Websites section”.

Table 3 Categorical ways of reduction of greenhouse gases and carbon footprint

<i>Reduction category</i>	<i>Ways of reduction</i>
Energy	● Sensible use of energy ● Change the light bulbs to LEDs ● Unplug unused electronic appliances ● Turn off the pilot flame of gas furnace in summer ● Turn off lights when you leave the room ● Buy energy efficient appliances ● Clean fridge and freezer coils ● Low wattage equipment/appliances ● Use rechargeable batteries ● Use of renewable energy resources ● Clean AC filters regularly ● Conceal your cooling/heating rooms ● Insulate the walls where necessary ● Operate AC at 26°C ● Use sleep mode on computers when inactive
Water	● Use a reusable water bottle ● Take shorter showers ● Use less hot water ● Limit the water for garden ● Installation of drip irrigation system ● Don't let your water running continuously ● Install low flow rate water sinks ● Use less detergent for washing etc. ● Wash your car in the garden ● Limit your water games/water plays etc. ● Don't defrost food with running water ● Harvest rain water
Food	● Buy food from local sources ● Limit your groceries as per your needs ● Prepare your own compost ● Grow your own gardens ● Buy seasonal food/vegetables and fruits ● Donate excessive/leftover food ● Lower the use beef/lamb and dairy ● Be more vegetarian ● Eat at sustainable restaurants ● Store the food properly to avoid spoilage ● Cooking more at home ● Eat less/as per health requirement
Travelling	● Use mass transit/carpool/public transport ● Combine trips and travelling ● Take fewer long way travels ● Use video conferencing/distance learning where possible ● Avoid flying on private jets ● Avoid flying for short distances
Driving	● Drive smartly and smoothly ● Go for scheduled tuning of engines ● Try driving low carbon vehicle ● Walk or ride bicycle when possible ● Buy low power vehicle or as per need ● Avoid unnecessary speeding ● Use properly inflated tires ● Try avoiding traffic routes ● Try driving on highways/fast routes ● Remove excessive weight from your car ● Limit unnecessary trips and car races ● Avoid unnecessary long mileages ● Prefer hybrid fuel cars ● Prefer to use bikes in bike-friendly routes ● Limit the purchase of unnecessary cars

Table 3 Continued

<i>Reduction category</i>	<i>Ways of reduction</i>
Clothing	● Use a sun light to dry your cloths ● Use full load of cloth cleaning in machines ● Recycle old cloths where possible ● Donate old clothes to charity ● Buy sustainable manufactured clothes ● Avoid over purchasing of clothes
Living style at home	● Chopping by hand ● Avoid minimum use of electronic appliances ● Use environment-friendly colors at home ● Sensible use of air conditioning and heating ● Keep ice maker turned off when not in use ● Avoid too many decorative lighting ● Avoid putting hot objects in fridge/freezer
Community/public	● Attend events that support environment ● Join a club for environmental grooming habits ● Support local environmental legislation ● Contact elected officials ● Awareness workshops ● Plant maximum trees ● Support local business
Education	● Educate yourself ● Teach/educate others regarding the environmental issues ● Introduce educated documentaries for all aged population ● Provide training for environment-friendly practices at home, offices, etc.
Miscellaneous	● Use email instead of paper mail ● Mechanical pencil usage ● Recycle your papers mails ● Print both sides of paper ● Use recycles paper where possible ● Try using non-toxic products everywhere ● Use wash cloths instead of paper towels ● Use hand kerchiefs in place of tissues ● Use digital books and reading materials ● Purchase recyclable toys ● Don't use bad chemicals on your garden ● Use refillable containers ● Use white/chalk boards which are erasable ● Refill the lighters ● Recycle ink jet cartridges ● Upgrade your computer instead new buying ● Buying and consuming needful stuff

Source: Data taken from Carbon offsets To Alleviate Poverty (COTAP). Available at: www.cotap.org/reduce-carbon-footprint, www.conserve-energy-future.com/carbon-footprint.php, www.theguardian.com/environment/2017.

Ways to Reduce Greenhouse Gases and Carbon Footprint

There are so many ways to reduce, minimize and alleviate the emissions of greenhouse gases, suggested by various researchers, scientists and engineers. Also, the ways are suggested to implement the policies and strategies for the same purpose. This module consolidates various ways categorically in a tabular form to reduce the toxic emissions of greenhouse gases.

When we Get Rid of all This?

Knowing the history of greenhouse gases and its effects in terms of global warming since very long time, it can be concluded that the reduction in greenhouse gases at significant levels (250–350 ppm) may not be possible for few more centuries. A marginal reduction may be noticed in recent future only if the appropriate remediation measures would be exercised at every stage of emission source. However, since the data varies from time to time, and from region to region, therefore, it is hard to predict the time when the earth will stop overheating by greenhouse gases. This is because of the technological advancements, social, cultural and regional changes in the inhabitants of earth.

It is mentioned elsewhere that if the use of fossil fuels stops today, it would still take many decades to level off the concentrations of greenhouse gases [7]. Although, much efforts are taken to exercise and implement the ways of reduction of greenhouse gases mentioned in Table 3, however, it is still difficult to balance the situation. Therefore, the ultimate recommendation is to continuously optimize the efforts that are made for the minimization of greenhouse gases emissions as much as possible. This is to ensure that the future generations would be able to live happy and safely without the bad consequences of our today's activities that increases the greenhouse gases emissions [8,9].

Judgements and Future Directions for Mitigation of Greenhouse Gas Emissions

The effect of greenhouse and carbon footprints can be limited and mitigated with certain measures. These measures have a certain cost which can constitute the economic value in reducing impact of greenhouse gases. The best and wise decision would be to reduce energy consumption which has been utilized in various forms from electricity generation, transportation, industrial zones, commercial and residential sectors. This could be possible with the transformation of lifestyle and behavioral change of human beings that favors the resource conservation. In addition, the reduction in wastage would greatly contributes in mitigating the release of greenhouse gases. The physical products that are being consumed requires the primary energy to produce and dispose. Therefore, limiting needless products and processes should be encouraged. Besides, plantation would be the great way to revive the natural life cycle. Since, plants absorbs CO₂ gas and help reduce earth's surface temperature. The promotion of mitigation measures can be exercised through carbon price that can establish incentives for producers and consumers to invest in products, processes and technologies notably which may limit emissions below the current levels.

Above all, the first and foremost step toward the mitigation of the greenhouse gases emissions should be the strict implementation of related policies. All the stakeholders, including government, industrialists, practitioners, engineers, scientists, social workers, law makers, and public should involve themselves extensively in the practices that reduces the emissions. The people of all age groups should be trained to exercise the environmentally friendly activities at all walks of life. They should be realized that this globe is not only for you and your kids, rather it is also for your future generations. Furthermore, the extensive attention should be given on the conservation of nature such as plants and forests because of their good capacity to provide carbon sinks. Besides, the global coordination regarding the mitigation of carbon emissions need to be enhanced to support the underdeveloped and developing countries to implement the strategies and exercise the policies and norms. Based on the above judgements and future directions, it would be manageable to find a way out of the serious issues of global warming caused by greenhouse gas emissions.

See also: Carbon Footprint Reduction Instrument. Challenges of Employing Renewable Energy for Reducing GreenHouse Gases (GHGs) and Carbon Footprint. Innovations in Variable Frequency Drives and its Implication in Reducing Carbon Footprint. Plasma Arc Driven Solid Waste Management: Energy Generation and GreenHouse Gases (GHGs) Mitigation. Power and Other Energy Utilities From Low Grade Waste Heat – Novel Technologies to Reduce Carbon Footprint. Utilizing the Greenhouse Effect as a Source to Produce Renewable Energy

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 Jean-Marc. Jancovici.

Hydrogen Evolution Using Advanced Technologies Based on Photocatalysis and Plasma

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Introduction

Our earth is one part of the universe that occupies seventy-one percent of water and only twenty-nine percent of land, where human life exists. The water part of earth exists in the form of oceans, sea, rivers, glaciers, lakes, canals and for domestic purposes. Out of seventy-one percent of earth water, only nine percent is used for domestic chores (Granovskii *et al.*, 2008). Most of the ocean and sea water is salty. To utilize this sea water there are many different methods including reforming of fossil, cracking of gasoline products, and electrochemical processes etc., Dincer and Acar (2015). These methods are cost effective and power consuming in the range of mega volts. The hydrogen evolved by these processes was used for conversion of unsaturated hydrocarbons into saturated hydrocarbons like vegetable ghee to vegetable oil. Hydrogen produced from the photocatalysis and plasma is not costly. Further, it provides more energy and fuel that has become the need of every person in this modern era of life. The hydrogen gas at cathode is collected by using catalyst. On the other hand, chlorine gas is toxic for human life, plants and animal (Jiang *et al.*, 2010; Madsen *et al.*, 1996). The reaction of oxygen with chlorine gives rise to chloride oxides, being toxic and injurious, it could cause of air pollution (Mizeraczyk and Jasiński, 2016; Vos *et al.*, 2018). The technology of hydrogen energy production is divided into three categories: at small level availability of hydrogen, at medium level availability and at large level availability of hydrogen production and consumption (Bergman, 2010). It is based on the quantity of hydrogen produced during a process. When natural gas reacts with plasma path, it changes to hydrogen and coal. The formed coal was found in the form of carbon black, composed at the surface, while hydrogen is in gaseous state (Yu *et al.*, 2012). The Table 1 shows some reactions of hydrogen synthesis method to change the renewable fuel sources and production of higher energy means by using the various methods of green synthesis for evolution of hydrogen. The different energy sources are strongly dependent on thermal and/or solar. The hydrogen evolution based on photocatalysis is measured in g/(Wh) to kg/(kWh) at the cost of one dollar to two dollars (Chaubey *et al.*, 2013). In this method, the photocatalyst is added in salty water with particular amount, in the presence of photovoltaic light and under some typical condition of temperature and pressure, which results in the formation cations (sodium ions) and anion (chloride ions). The chlorine gas may react with aqueous solution of hydrogen and form hydrochloric acid. To overcome these kind of problems, the metal oxide catalysts could be used. The manganese oxide is used as an anti-oxidizing agent to shield out the chlorine gas and thus on the other electrode hydrogen gas has to evolve. The reaction of hydrogen evolved by the processes is treated with nitrogen to form ammonia and this ammonia when reacted with carbon dioxide turn it into hydrocarbons, that is, in the form of fuel as given by the reaction. When the evolved H₂ gas is treated at high temperature, it changes into ionic form (plasma formation), which exhibits temperature of millions kelvin.

Significance of Hydrogen Plasma Evolved From Seawater

The fuel cells may be upgraded to hydrogen-based plasma fuel cells and could be useful in the engines of vehicles and many other combustion applications. The price, now a day, for hydrogen fee kilogram is about 2\$ in America and 3\$ in developing countries. The cost of the hydrogen-based plasma produced from seawater is around 1\$/kg. Therefore, the need to find out hydrogen sources

Table 1 Some useful methods to create hydrogen

Energy sources	Hydrogen generation method	Sources	Overview of the methods
Electrical energy	Electrolysis	Water	By electro chemical reaction the water decomposition takes place, thus, by passing electric current the O ₂ and H ₂ are evolved
	Plasma arc decomposition	Natural gas	Cleaned methane gas is passed through electrical discharge plasma to produce hydrogen and carbon soot
Biochemical energy	Dark fermentation enzymatic	Biomass	Anaerobic fermentation in the absence of light
Electric + Photon	Photo-electrolysis	Water	Photo electrodes + electric energy

Note: Kalamaras, C.M., Efstathiou, A.M., 2013. Hydrogen production technologies: Current state and future developments. In: Proceedings of the Conference Papers in Science, vol. 2013. Hindawi.

has increasing day by day. Numerous efforts are in process and plasma researchers are finding the more resources for evolution of plasma hydrogen (Hsu *et al.*, 2018). Energy produced by this method can work at 6 K and is useful in any environment because as it has no toxic or hazardous effect on environment (Nicoletti *et al.*, 2015).

Methodology for Generation of Hydrogen From Sea Water

There is variety of processes that are for hydrogen production and limited methods for production of hydrogen-based plasma and only a few are finding the hydrogen plasma by the sea water. The hydrogen evolved by these processes is utilizing indifferent domestic chores and different energy producing and utilizing sectors. The methods and techniques are given as:

- (1) Hydrogen-based plasma releasing by vaporization of fuels in the form of liquid and gases.
- (2) The production of hydrogen through Au@ZnO zinc oxide composites incorporating different amounts of gold nanoparticles.
- (3) Tentative results are obtained by using experimental findings and observations.
- (4) The process of electrolysis using nickel iron carbide by salty water.
- (5) Plasma hydrogen producing by using catalyst of Bismuth vanadium oxalate in the presence of sunlight.
- (6) Various techniques used for hydrogen evolution by plasma characterization.
- (7) Hydrogenated plasma by green synthesis.
- (8) Other experimental methods-based on hydrogen-based plasma.

Hydrogen-Based Plasma Evolution by Volatizing Substances

The strength of energy for a plasma reaction is defined as the minimum power consumed in equilibrium in a method under considerations. Total heat content known as enthalpy of the system is denoted by ΔH . The rate of this reaction is determined by the consumption rate of reactants. 100% efficient material corresponds to low consumption rate. The strength of partial equilibrium for plasma discharge is less than 20% (Nicoletti *et al.*, 2015). This system of plasma production Consist of different parts i.e., apparatus to get rid of combustion elements, a gas discharge source, plasma producing device for phase of matter transfer to the ionization source, annealing process device and a fuel jet assembly for evolution of plasma into blister assembly. In addition to above parts a secondary gas source takes exhaust and optical detecting device is also part of this system. The oxygen and hydrogen through SEM or TEM is observed. The process is carried out in the presence of hydrogen or carbon with low value dielectric materials. This process is carried out for different exhausting gas for example:

- (1) The exhaust gas of hydrogen and oxygen from combustion burner in plasma gadget are conducted. The noble gas that is non-reactive is introduced at the level of 7000 cm range at typical atmospheric pressure is introduced. The photoresist on the substrate is heated at temperature of 300°C. The hydrocarbon material is combusting ionized at the preheating temperature. in early stage no plasma formation takes place. Oxygen gas is evolved at 1000 cm supply. But it does not take place in the glass chamber. The exhaust of hydrogenated plasma with hydroxide ion takes place after a long time and it is occurring within vacuum chamber. This experimental result is drawn by the plasma slag process. The resulting peaks represents that the different hydrocarbons are combusted with different behavior. But, this hydrogen can be utilized into the chamber and cannot be exhaled from the system to be used for other applications.
- (2) Using the above apparatus set up the carbon dioxide gas is observed by using an enduring gas inventor like plasma invention in burner.

Hydrogen Generation Using Catalyst Under UV-Technique

The production rate for hydrogen may increase by adding the amount of Au in catalytic material, at the cathode. The evolution of hydrogen depends on the amount of gold and surface area of the catalyst when it was irradiated at 400 nm UV radiation. The solution was characterized by 100 mL of salty water including the brine solution into a reactor beaker. As a catalyst, 50 gm of Au was added to this flask. For opposing the corrosion, the sacrificial reagents were used in the form of Na₂S and Na₂SO₃ in adequate amounts. The resulting solution is heated at 20°C, with magnetically focalized nitrogen at 20 rpm. The prepared solution can be irradiated by the UV-light for two hours under suitable wavelength. The hydrogen may be produced at the nitrogen electrode and is demonstrated by gas chromatography. If the amount of gold is increased, then the production of hydrogen can be increased. In collaboration of the USA, Japan and many European countries, better result is expected in the coming days. Table 2 illustrates the weight percent of Au@ZnO corresponding to surface area.

The maximum amount of hydrogen by this process was determined to be 550 $\mu\text{mol/hg}$ under UV-radiation of 320 nm with gold weight of 10%. Thus, the evolution of hydrogen was 6 times higher than the commercial hydrogen. But, when it is irradiated at 400 nm wavelength of light, then the production of hydrogen is 8 times higher than the commercial generation of hydrogen. The production of hydrogen at the wavelength of 400 nm is higher than the wurtzite gold particles with 10% weight of gold (Wu *et al.*, 2014; Chen *et al.*, 2012; Flis-Kabulska *et al.*, 2015). The hydrogen-based plasma evolution from fuels can derived by using various methods such as using electron beam having specific aperture lenses, creating barrier of dielectric igniting discharges,

Table 2 Characterized surface area of Au@ZnO catalyst for the experiment

Catalysts	ZnO commercial scale ($\text{m}^2 \text{g}^{-1}$)	ZnO nanoparticles ($\text{m}^2 \text{g}^{-1}$)	ZnO nanowires ($\text{m}^2 \text{g}^{-1}$)
Bare catalyst	18	67	167
1% Au	22	70	174
3% Au	23	73	183
5% Au	25	77	184

Note: He, W., Kim, W.K., Wamer, W.G., *et al.*, 2014. Photogenerated charge carriers and reactive oxygen species in ZnO/Au hybrid nanostructures with enhanced photocatalytic and antibacterial activity. *Journal of the American Chemical Society* 136, 750–757.

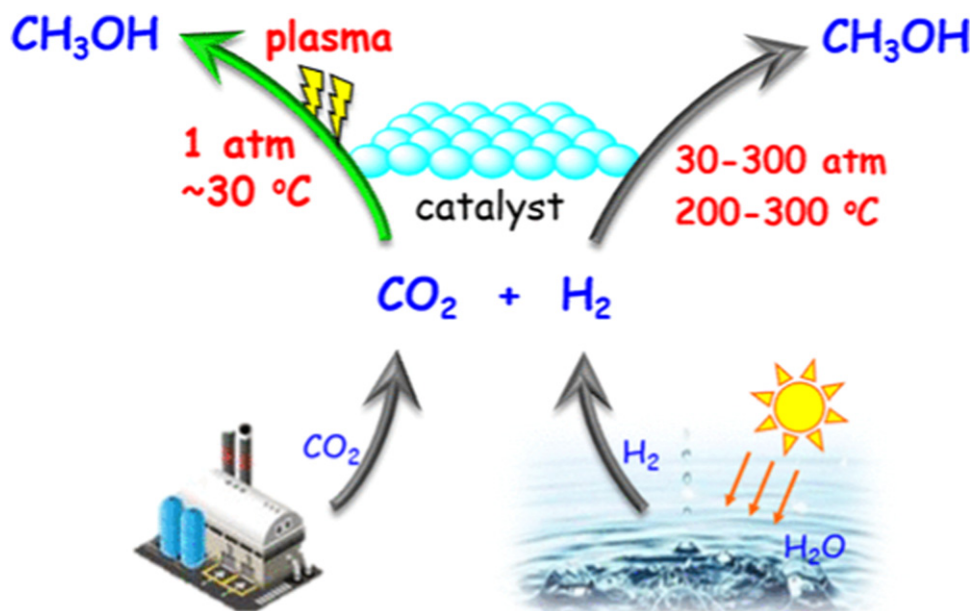
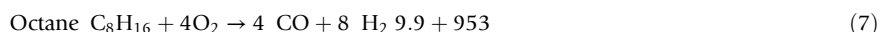
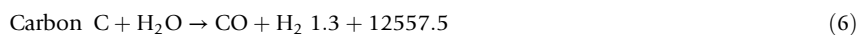
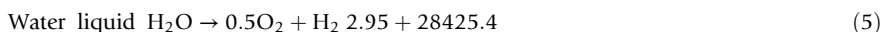
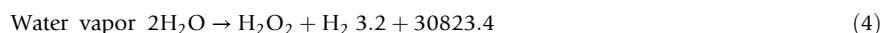
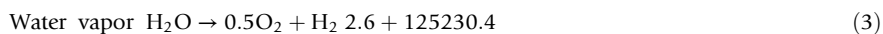
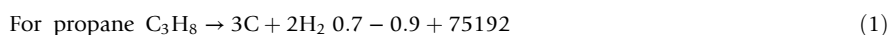
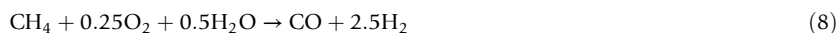


Fig. 1 Two steps for hydrogen generation using catalyst and plasma. Reproduced from Wang, L., Yi, Y., Guo, H., Tu, X., 2017. Atmospheric pressure and room temperature synthesis of methanol through plasma-catalytic hydrogenation of CO₂. *ACS Catalysis* 8 (1), 90–100.

skating, Laval nozzle devices and microwave. There are some reactions that results in plasma production as shown in Eqs. (1)–(8). The energy drawn during these reactions in eV/(molecule's. KJ/mol g (H₂)/kWh) is shown in following reaction (1)–(8).



Auto thermal reforming Methane



The first two steps for the evaluation of hydrogen are shown in Fig. 1. The most important task is to find out the hydrogen-based plasma from hydrocarbons reforming. The plasma produced by methane reforming is analyzed over electron beam radiolysis spark igniters microwave gas ionization. Methanol and ethanol are used as a feedback with dielectric discharges, surface ion discharges in the form of Aurora Borealis. The cost of energy based on hydrogen production yield is 2\$/kg of hydrogen. These technologies are widely used for production of hydrogen.

The energy production rate will be higher when the liquid fuel is used as source of hydrogen production. When the catalyst used there are many chances to produce other processes energy rather, but it is just a prediction not an experimental proof

(Jones *et al.*, 2010). Since, plasma method is suitable for production of hydrogen under low cost rate. The plasma generating 5 years ago, yields the energy power of about 60 g H₂/kWh. But, this method requires high energy requirements with high relying. So, possible advancement in the producing of hydrogen-based plasma is a necessary step to produce high yield at low cost.

Nickel Iron Carbide as Electrolysis Process From Seawater

In this process, aluminum matrix with electron deposits is used. The hydrogen evolution process in Ni-Fe-C is measured in the form of current density of the order of 200 A/m². At the evaluation point the potential observed is about only 65 mV at the pH 12. The rising demand of amount of fuel, the hydrogen can be suitable for energy in the next few years (Winand, 1994). The electrolysis process is still considered an effective method for Hydrogen production. Sea water that is consisting of NaCl in the form of brine is an electrolytic solution. The ions that are, sodium ion Na⁺ and Cl⁻ ions are responsible for electrolysis process. The tides in sea water are providing the power for electrolysis and thus for evolving of hydrogen. For this mechanism the cost is higher, due to this reason use of catalyst to improve the electrolysis process is mandatory. For this a transition metal like nickel is used. Ni is best for its usage in hydrogen evolution system due to low price and a reactive transporter in the reaction of hydrogen evolution. Since all the requirements of good catalyst are found in nickel (Kim *et al.*, 2014; Cullity and Stock, 2001). At different pH values of solution different I value shows the electrolysis process for brine solution. The hydrogen concentration is 3.5% weightage in the salty solution at 65 mV at pH value of 12 at temperature about 90°C in 60 min.

Generation of Hydrogen From BiVO₄ under Solar Energy

The method to produce hydrogen from sea water, that is, solution of brine that contains NaCl is an interesting and vast field of plasma science. Since, there is no device that can measure the energy at high scale which is one of the requirement of the process. To fulfill this demand, BiVO₄ was used as a source of energy. Bismuth vanadate is nanomaterial derived from the Bismuth related particle. The hydrogen that may be used as an energy source, can be used as a fuel in the future at low cost. The natural sun source and natural water are the greatest source for production of energy at large scale. Different resources used to synthesize the other artificial materials and the purpose of catalytic reactions was achieved. The abundance of seawater and the presence of high level salinity is the main motivation behind the process of production hydrogen by using the salty (Bakony *et al.*, 1996; Santato *et al.*, 2001). There is not any stable process yet available to split up water in the sea by absorption of photo light beside the process of bismuth vanadium (BiVO₄) oxide and poly metal oxide element. The current density of light for this process is used in the order of 2.16 mA, and the solar energy of the order of 1.5 g. The photo anode is operated in the visible region. BiVO₄ based solar system have been invented in which, BiVO₄ is doped with molybdenum transition metal. The resistivity of molybdenum metal is lower due to which it is used to increase the photo current and enhanced dispersion. When RhO₂ is used as catalyst with it, it increases further the photo current and increases the stability of light in saline water containing 3.5% NaCl. This catalyst is necessary to encourage the usage of molybdenum impurities with BiVO₄. There are bubbles of hydrogen and chlorine gas at the cathode and

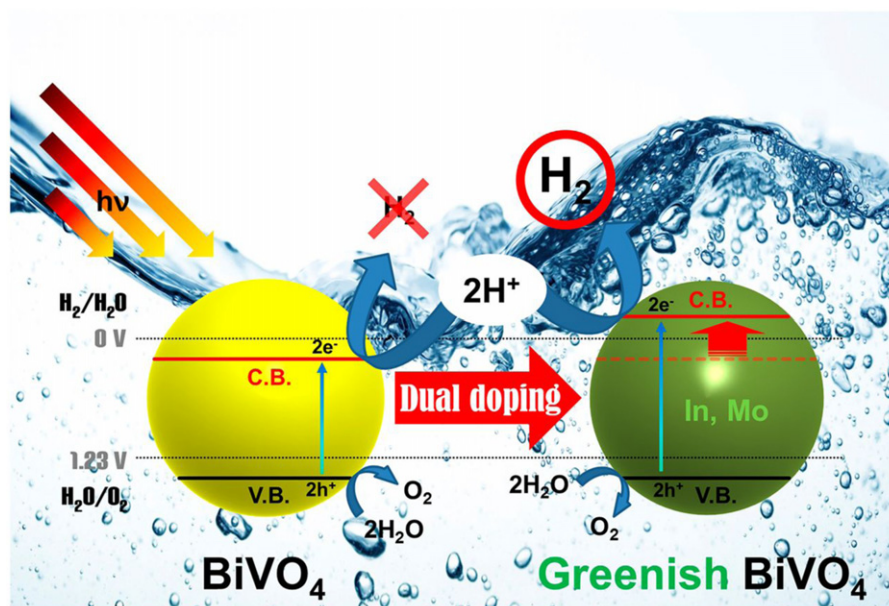


Fig. 2 BiVO₄ nanophotocatalysts dual doping for hydrogen evaluation. Reproduced from Jo, W.J., Kang, H.J., Kong, K.J., *et al.*, 2015. Phase transition-induced band edge engineering of BiVO₄ to split pure water under visible light. *Proceedings of the National Academy of Sciences of the United States of America* 112 (45), 13774–13778.

anode since chlorine gas is more absorbed in water than hydrogen. Chlorine gas is highly oxidizing than hydrogen and it has more pH than hydrogen of the order of 6–7. When chlorine gas interacts with water, hypo chloric ion is formed. Due to smaller conductivity of BiVO_4 , a doping process is used that enhances its photocurrent and photochemical efficiency for production of hydrogen through saltwater. The nano particles for BiVO_4 are very stable and are widely used to remove the impurities from the waste water emitted by the industrial terrestrial sources contaminated with toxic impurities (Long *et al.*, 2008; Wang *et al.*, 2013; Zhou *et al.*, 2008; Sarkar and Chattopadhyay, 2012; Mitev *et al.*, 2015). Fig. 2 shows the dual doping of bismuth vanadate nanoparticles used for hydrogen evaluation.

Hydrogenated Plasma by Green Synthesis

Hydrogen evolution is necessary tool overcome the limitations of the greenhouse gases, that's why, it is called green synthesis (Ambrosio *et al.*, 2018; Lin *et al.*, 2013; Gharbi *et al.*, 1982). Recently, methane gas is characterized to produce hydrogen resulting in emission of greenhouse gases. Steam reforming also produces about 30% hydrogen gas from oil and 18% from coal. Water electrolysis also yields 3.8% hydrogen gas. In future, the green methods will be applicable to produce hydrogen on commercial scale. This hydrogen may be useful in producing artificial fuel, NH_3 and fertilizers with saturated hydrocarbons (Yu and Kudo, 2005; Nagabhushana *et al.*, 2013).

Conclusion

Here, numerous methods were investigated for the production of hydrogen-based plasma as a green energy using biological, chemical and physical approaches. However, each method has its merits and demerits that limit their frequent use to produce hydrogen at industrial scale. The hydrogen produced from photocatalysis and plasma based seawater is pollution free and non-toxic. The fuel derived by this method can be extended its limit up to 70%. The significance of hydrogen plasma evaluated by seawater, hydrogen evaluation under UV and solar light in the presence of catalyst is also reviewed.

See also: An Assessment of Hydrogen Energy Utilization for Sustainable Development. Clean Energy Technologies: Hydrogen Power and Fuel Cells. Semiconductor-Based Photocatalytic Nanomaterials for Environmental Applications. Utilization of Bio-Hydrogen in HCCI Engines as a Most Renewable Fuel for Sustainable Transportation – A Thermodynamic Analysis

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Hydrogen Production Through Water Splitting Using Nanomaterials Under Solar Energy

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Introduction

Fresh and clean energy is the basic need of our era but due to the rapid increase of population and industrialization of the globe, it would be very difficult to provide the energy equally. The demand of energy has increased from 17 TW to 27 TW within the last 30 years (Huang *et al.*, 2013). In the near future, it would be a challenging task to fulfill these requirements of energy because resources of fossil fuels are decreasing and may cause a pollution in air and environment. Since hydrogen energy was found to be efficient and clean, numerous sources have been adopted for hydrogen evolution including fossil fuels, fractional oxidation, coal-gasification, auto thermal reforming, electrolysis and by consuming the steam reforming through natural gas (Tahir *et al.*, 2017a). The hydrogen generated from fossil fuels and others may cause emission of harmful gases like CO₂, CO, etc (Xia *et al.*, 2014). Practically 85% energy can be exchanged by the fossil fuels which, disturbs our atmosphere and assets also. It also changes the configuration of our atmosphere upsetting weathers and human health (Mai *et al.*, 2013). Therefore, the production of green energy has become thrilling need to modern era of technology. Photocatalysis was found to be more efficient approach to produce hydrogen through splitting of water.

Photocatalytic Hydrogen Evolution Through Water Splitting: Mechanism

In this method, due to the presence of sunlight, water molecule breaks into the hydrogen and oxygen. The general form of water splitting reaction is given as



A large amount of energy is absorbed to perform this reaction that is $\Delta G = 237.1$ kJ/MOL at the STP and at the 1.23 V of thermodynamic potential (Tahir *et al.*, 2017c). Previously, different devices were in use for the advancement reaction of hydrogen and oxygen, however currently a single device involves with both evolution reactions; one is at cathode and other is at anode. The evolution reactions for hydrogen and oxygen are given as (Amoo and Fagbenle, 2014):



The above reactions cannot take place without photo-catalysts.

Hydrogen-Evolution Reaction (HER)

The hydrogen evolution reaction involves many steps given by the following equations:



Eq. (1) is Volmer step, Eq. (2) is a Heyrovsky step and the Eq. (3) is known as Tafel step. There are two cases for the evolution reaction of hydrogen; in the 1st case, Volmer and Heyrovsky steps are involved while in the 2nd case, Volmer and Tafel steps are involved. In both cases, the amount of energy that is ΔG is absorbed to perform this reaction and hydrogen is absorbed by the electrodes that release it in the form of hydrogen gas. The rate of this reaction directly changes with bonding strength of atoms and ΔG . As the surface bonds are weak, less amount of energy is required and reaction would occur rapidly but in the case of strong surface bonding large amount of energy is needed that slows down this reaction (Tang *et al.*, 2011). That's catalyst was used to enhance the evolution of hydrogen and these catalyst decreases the value of ΔG . The materials that may be used as catalysts for this hydrogen evolution reaction may be alloys of nickel (Ni), oxides and phosphides of metals.

Catalytic Requirement for HER

Hydrogen production and evolution reactions are usually slow types of reactions. It means that it takes long period of time (Wang *et al.*, 2017). To increase the rate of reaction and to decrease the time of these reaction occurrences, different types of

catalyst such as molybdenum sulphides, molybdenum carbides, molybdenum nitrides and molybdenum phosphides etc, were used (Yan *et al.*, 2013). However, here the effect of molybdenum sulphides catalyst due to its outstanding activity and constancy on hydrogen evolution reaction in their nanoparticles form has been reviewed. Nanoparticles are the microscopic particles that have dimensions in the range of 100 nm or less than 100 nm (Duan *et al.*, 2015). Most of the time, the properties of nanoparticles are different as compared to their bulk molecules form. Molybdenum sulphides catalysts are regularly manufactured at a high temperature and particular optimal experimental conditions (Gholamvand *et al.*, 2016). The procedure could be exorbitant and vitality escalated. The undefined MoS_x (x = 2, 3) films were incredible hydrogen development catalysts. As for the MoS_x films created, the manufacture technique represents a limitation in the functional usage of these impetuses: the layers must be prepared by electrode position at 0.3–0.8 V versus SHE (Standard Hydrogen Electrode). Anodes and cathodes which are not stable in such an electro-chemical gap are subsequently not appropriate substrates (Zheng *et al.*, 2014). Numerous semiconducting and non-directing substrates can-not be utilized not one or the other. The weaknesses of the MoS_x thin films can be survived if the nebulous MoS_x impetuses can be delivered artificially and in a huge amount. Different affidavit techniques would then be able to be connected to gather the impetuses onto an extensive variety of substrates. In this, the compound readiness of shapeless MoS₃ nano-particles and their reactant movement for hydrogen evaluation reaction have been discussed (Seo *et al.*, 2015).

MoS₂ as a Photocatalyst

MoS₂ has many interesting characteristics like it can be used as a lubricant, as a catalyst for HE reaction and as a transistor in two dimensions. Tributsch was the first person who worked on the catalytic effect of MoS₂ in its bulk form and he observed that this is not energetic in its bulk structure. After that by using the suggestions of their colleagues, they utilized the MoS₂ in the form of nanoparticles and then they observed that it was very reactive at its smaller level (Yang *et al.*, 2016). Molybdenum disulphide is highly closely packed structure like graphite. It has large number of surfaces inside it with the distance of 6.5 angstrom and providing the path for the motion of electrons and holes. The sheets of Molybdenum disulphide are perpendicular to each other (Dong *et al.*, 2015). Due to its large number of sheets and surfaces in its bulk structure, it has expressed inertness towards the reaction. But due to its activity even as nanoparticles, it was used as a catalyst to speed up the hydrogen evaluation reaction.

Molybdenum Tri-Sulfide as a Catalyst

The properties of molybdenum trisulphide, its production and comparison with molybdenum disulphide have been discussed.

Production of MoS₃ and Their Characteristics in Amorphous Form

Indistinct MoS₃ particles are regularly arranged via fermentation of tetrathiomolybdate resolutions. It was observed that MoS₃ can be of endless supply of MoO₃ and Na₂S making the combination more practical (Zhou *et al.*, 2016). For typical synthesis of material, molybdenum trioxide MoS₃ (1.0 g, 6.95 mmol) was dissolved in distilled water and sodium sulfide (8.34 g, 34.74 mmol of Na₂S·9H₂O in 250 mili-Litter of water) for the preparation of gel like solution. That arrangement was then held below enthusiastic mixing while the 6.0 mole solution of HCl was added gradually (approximately 10-min) until-the solution reached a value of pH 4. Then the prepared solution was placed under observation for an optimal time and it was found that significant amount of H₂S has been produced in vapor form (Mahler *et al.*, 2014; Zhao *et al.*, 2013; Hosseini *et al.*, 2017). After this, the whole suspension was bubbled for 30-min to remove the H₂S and to enhance the filtration-step. The solution was then cooled at room temperature and washed with water and ethanol. The glue like suspension obtained was mixed with 1.0 L of (CH₃)₂CO in an Erlenmeyer cup and stirring was performed for 30-min. After this, it was sonicated for 5-min through ultrasonic-horn at 20 kHz. A very clear dark solution was obtained and placed 3 days for precipitation (Tahir *et al.*, 2017b; Zhang *et al.*, 2014). It was then dried for 12 h at 80°C after purification and crushed MoS₃ was formed.

Production of Molybdenum Sulphides C-Paste Electrodes

The terminal of carbon's surface was cleaned by testing paper. The prepared powdered MoS_x particles were squeezed at carbon glue terminal and were extended equally by utilizing paper (MoS_x incorporates MoS₃, MoS₃-350, MoS₂-650, and MoS₂). The commercial MoS₂ particles were observed to be crystal-like. There are some specific conditions which make it (MoS₃) possible to utilize as a catalyst for the given reactions (Benck *et al.*, 2014). The electrode of carbon paste was prepared with 80:20 ratios of graphite and paraffin wax respectively and was not found to be able for the performance of hydrogen evolution until by taking composition with thin film of molybdenum trisulphide nanoparticles (Vrubel *et al.*, 2012). This kind of reaction was found to occur at the 17 mA cm⁻² current density within 60 min. It shows the excellent activity and stability of molybdenum trisulphide.

Activity of Crystalline Molybdenum Sulphides as a Catalyst

By using the chemical reduction process, molybdenum trisulphide cannot be directly reduced into the molybdenum disulphide. There are different methods that are used to form the molybdenum disulphide (Yan *et al.*, 2014). At the temperature of 350°C, the molybdenum trisulphide is converted into the MoS₃-350 by increasing the 1 µm size of the material within the time of 60 min. By using the same techniques, MoS₂-650 was obtained at 650°C within the time of half an hour. For the reaction of hydrogen evolution, these MoS₃-350 and MoS₂-650 are passed through the carbon-blank-paste. Both of these are least reactive catalysts (Zhang *et al.*, 2015). But the molybdenum disulphide does not activate in the reaction even when the potential is greater than two hundred million volts. But there is no such type of condition with molybdenum trisulphide; it is very reactive even at its lower potential. Here it was found that the activity of molybdenum trisulphide is payable to the occurrence of sulphur atoms in the material. These sulphur atoms make bonds with hydrogen atoms in the evolution reaction of hydrogen and separate it from the hydrogen to form the hydrogen gas H₂. As the molybdenum trisulphide has crystalline structure, so by increasing the particles number in the crystals, crystallinity of the material is increased. The activity of molybdenum trisulphide has inverse relation with concentration of particles in the crystals. Therefore, by increasing the particles' numbers, reactivity of molybdenum trisulphide catalyst decreases and vice versa (Benck *et al.*, 2014).

Cobalt as a Co Catalyst for Molybdenum-Trisulphide

It was revealed that shapeless MoS_x layers were stored on an operational anode, e.g., ITO or lustrous carbon, only when a watery arrangement of (NH₄)₂[MoS₄] was focused to successive repeated voltammetry experimentations. The MoS_x layers were dynamic hydrogen evaluation reaction impetuses. It was observed that a thin film was likewise saved from a fluid arrangement of (NH₄)₂[Co (MoS₄)₂] in a comparative electro-polymerization system (Wang *et al.*, 2012). Complex-1 is a very much characterized Cobalt complex that was recently prepared as a nitrogenase enzyme model. Investigation by XPS revealed that the film surrounds Co, Mo, and S. In this manner, complex-1 fills in as an atomic antecedent for the ternary metallic sulfide-layering. Moreover, it is conceivable to practice in situ arranged 1, framed promptly upon the blending of CoCl₂ with (NH₄)₂[MoS₄], as the antecedent. The proportion of Cobalt to Mo isn't restricted to 1:2 in the statement shower. The Co– Mo– S films are dynamic hydrogen evaluation reaction impetuses. To recognize the ideal proportion of Co to Mo in the affidavit shower, various films were set up on a polished carbon anode from arrangements in which the fixation proportions of CoCl₂ to (NH₄)₂[MoS₄] shifted between 1:200 and 1:2. At the point when the proportion surpassed 1:2, a precipitation was seen after blending of CoCl₂ and (NH₄)₂[MoS₄], so no endeavor was made to store films from such blends. The polarization bends of the Co–Mo–S films at pH equal to 7 and 0 can be demonstrated. The Co²⁺ particle advances the reactant action of nebulous MoS₃ (Zhang *et al.*, 2015).

Conclusion

In the current article, the detailed description on the green approach of hydrogen evolution, its fundamental aspect and mechanism and hydrogen-evolution reaction has been discussed. Comparing with the pristine molybdenum sulphides based nanoparticles, the modified nanostructures were observed to be more efficient and showed an outstanding photocatalytic hydrogen efficiency. Further, the improved efficiency could be attributed to the upshifted conduction band edge, higher surface area, narrowed bandgap and efficient transfer and separation of charge-carriers. The newly developed photocatalytic nanomaterials will be more beneficial for energy harvesting potential application.

See also: Green Energy Fuel From Biomass and Sea Water. Nanomaterials. Semiconductor-Based Photocatalytic Nanomaterials for Environmental Applications. Water Resource Management for Renewable and Sustainable Hydro Energy in Turkey

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Jute Pulping: Opportunities and Challenges

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Introduction

Pulping and Pulping Processes

Pulping is a process of defibration of lignocelluloses into individual fibres. It is done by mechanical and or chemical processes. Chemical wood pulping involves the extraction of cellulose from lignocelluloses by dissolving the lignin that binds the cellulose fibres together. Four processes principally used in chemical pulping are kraft, sulfite, neutral sulfite semichemical (NSSC), and soda. The kraft process is the predominant process in the world. In the kraft process, sodium hydroxide and sodium sulfide used in water as cooking chemicals at higher temperature. The cooking chemicals are known as white liquor. This process is flexible to raw materials.

Pulping and papermaking process includes: Raw material preparation and handling, Pulp manufacturing, Pulp Washing and Screening, Chemical recovery, Bleaching, Stock Preparation, and Papermaking.

Pulp is produced from lignocellulosic biomass, which includes hardwood, softwood, non-wood and recycle fibres. Hardwood and softwood are the dominant raw materials for pulping.

What is Jute?

Corchorus sp is a bast fibre obtained from dicotyledonous plants of the Genus *Corchorus* and family Tilaceae. It is an annual renewable fibre crops grown mainly in Bangladesh, India and other Asian countries. Conventionally, the bast fibre is extracted from plants by a natural microbial process known as retting. Retting has been used for a long time in case of extraction of fibres from jute plants. In general, the practice of retting jute plants in the jute growing regions is to immerse the jute bundles in clear slow flowing water in canals, tanks, ponds or ditches. The minimum ratio of plant material to water in stagnant water should be 1:20. Retting and extraction processes have a profound effect on the quality of fibre produced, and on the cost of fibre production. It affects the efficiency of manufacturing, the quality of the end products and their competitiveness in the market. The conventional retting requires 14–28 days to degrade the pectic materials, hemicellulose, and lignin (Paridah *et al.*, 2011). Conventional retting process is not environmental friendly and requires large amount of water. Therefore, Bangladesh Government has introduced ribbon retting method in different areas of the country to ease peeling of jute fibre. Fig. 1 shows conventional and ribbon retting of jute.

Jute is one of the cheapest textile fibres and used widely in the manufacture of different types of packing materials for various agricultural and industrial products. Once it was known as “Golden fibre of Bangladesh”. The export of jute and related products accounts for a significant portion of total export in Bangladesh. In addition, it provides considerable employment opportunities to the country's work force. Traditionally, jute is being used in sacking, gunny bag, hasein, etc. In recent years, jute has faced hard competition from synthetics. Therefore, traditional uses of jute have declined. As a result, its demand in local and overseas markets has declined. Therefore, diversified usage is needed to regain the lost glory of jute.

In this article, evaluation of jute pulping in respect to raw material handling, process selection, and product development is discussed.

Chemical Composition

Jute fibres have three principal chemical components, namely, α -cellulose, hemicelluloses, and lignin. The lignin can be almost completely removed by chlorination, and the hemicelluloses are then dissolved out of the remaining holocellulose by treatment with dilute alkali. The final insoluble residue is the α -cellulose constituent. Many research papers have been published on the chemical constituents of jute. Jahan *et al.* (2007a,b) showed that retted jute fibre constituted with 63.1% α -cellulose, 13.5% pentosans, 12.7% Klason lignin along with minor amount of extractives and ash. As shown in Table 1, jute fibre is characterized with higher α -cellulose and lower lignin than hardwood and softwood. The α -cellulose and lignin content in jute stick is close to softwood. The hemicelluloses consist of polysaccharides of comparatively low molecular weight built up from hexoses, pentoses, and uronic acid residues. In jute, *Corchorus capsularis* and *Corchorus olitorius* have similar analyses, although small differences occur between different fibre samples. The average molecular weight of the hemicelluloses is in the range of 24,000–27,000. Jute fibres contain a proportion of acetyl groups, which are readily hydrolyzed by dilute alkali to acetic acid. Soutar and Bryden (1955) have reported acetyl contents averaging 110 for hibiscus, 89 for *C. capsularis*, and 76 for *C. olitorius*, all expressed in milliequivalents of acetic acid per 100 g of dry fibre. The higher acetyl content of *capsularis* than *olitorius* has since been confirmed by Manzoor-i-Khuda *et al.* (1970). Acetyl content is a very important parameter for prehydrolysis step in producing dissolving pulp (Li *et al.*, 2010). Acetyl content generates free acetic acid during prehydrolysis process, which facilitates hemicelluloses dissolution (Saeed *et al.*, 2012; Jahan and Rahman, 2012; Jahan *et al.*, 2013a,b).



Fig. 1 Conventional and ribbon retting of jute (a) conventional retting, (b) ribbon extraction, (c) ribbon retting.

Table 1 Chemical constituent of jute along with hardwood and softwood

Raw material	α -cellulose (%)	Lignin (%)	Hemicellulose (%)	Reference
Jute fibre	63.1	12.7	13.5	Jahan <i>et al.</i> (2007a,b)
Jute stick	39.6	25.9	18.2	Rahman <i>et al.</i> (2016)
Hardwood (Sugar maple)	45.0	22.0	17.0	Pettersen (1984)
Softwood	37.2–41.5	29.1–32.6	18–21.9	Mcdonough <i>et al.</i> (2001)

The chemical composition and fibre properties of different parts are different. Different stages of the growing season also affect the chemical composition and fibre properties of the plant tissue. It was seen that the fibre length at the middle part of both the bastfibre (bark) and core (stick) was longer than the top and bottom part. Shafi *et al.* (1993) showed that jute bast fibre was longest at a distance of about 75 cm from the bottom of jute plant. With increasing height from bottom to top lignin content

decreased and α -cellulose content increased. Consequently, the paper making properties of the pulp obtained from jute at different portions of jute is expected to vary. Jute follows the same morphological pattern as in the case of wood/tree. It is well agreed that wood exhibits the longest fibres at a distance of about one-third to one-half of the tree height (Panshin and Zeeuw, 1980). The bottom and the top of the tree possess the shortest fibres (Hale, 1969).

The jute bastfibre has higher α -cellulose and lower lignin than core (Jahan *et al.*, 2008b). Rowell and Stout (1998) noted in his book article that the University of Manchester, the Shirley Institute and the British Textile Technology Group in the United Kingdom have spent years working on jute. While some of the research findings have been published, the results relating to the changes in the properties of jute fibre as a function of the growing season were done for the International Jute Organization in Bangladesh, but were not published. Personal communications concerning these results indicate that juvenile jute fibre looks and feels like silk, but this has never been documented in print. Chatterjee, working at the Technological Jute Research Laboratories in Calcutta, India, first reported the changes in chemical composition at different stages of jute plant growth (Chatterjee, 1959). These results show that there is little difference in cellulose, holo-cellulose, and the lignin content, but the content of xylan, ash, and iron decreases as the plant matures.

Mukherjee *et al.* (1986) also studied characteristics of the jute fibre at different stages of growth. It was observed that there was an incomplete formation of the middle lamella in the cell wall at the early stages of growth and the parallel bundles of fibers were oriented at an angle with respect to the fibre axis that gradually decreased with growth. After about 35 days of growth, the fibrils run parallel to the fibre axis. In the mature plant, a few helically oriented fibrils were observed in the 2-direction just below the primary cell wall layer. Clark and Wolff (1969) found that the pentosans, lignin, and α -cellulose content increases with age. Data taken from the top part of the plant shows similar trends; however, the top part has less cellulose, pentosans and lignin.

Effect of ribbon retting on the chemical properties of jute fibre and jute stick was studied by Jahan *et al.* (2016). Pentosan, extractive and ash content in ribbon retted jute fibre and jute stick were higher and lignin and α -cellulose content were lower than the conventional retted jute fibre and jute stick. These differences were pronounced for jute stick. The differences in chemical characteristics of core and bark fibre of jute at different position -top, middle and bottom were studied (Jahan *et al.*, 2008a). With increasing height from bottom to top lignin content decreased and α -cellulose content increased. The bark (fibre) had higher α -cellulose and lower lignin than core (stick) (Table 1). The bark produced nitrobenzene oxidation products with larger syringaldehyde/vanillin (S/V) ratios than the core. The yields of nitrobenzene oxidation products in bark were higher than core. The analysis of neutral sugars suggested that xylose is the predominant sugar of hemicellulose in both bark and core. The bark had higher glucose and lower xylose as compared to core.

Pulp Making

A brief description on pulping has been mentioned in Section 1.1., it is done by mechanical and or chemical processes. Most of the studies of jute pulping were carried out on chemical processes. Therefore, in this article, pulp making is discussed on chemical process only.

For chemical pulp, logs are first chopped into wood chips which are then cooked with chemicals under high pressure. Cooking removes lignin and separates the wood into cellulose fibres. The resulting slurry contains loose but intact fibres which maintain their strength. During the process, approximately half of the wood dissolves into what is called black liquor. The cooked pulp is then washed and screened to achieve a more uniform quality. The black liquor is separated out from the pulp before the bleaching process. Black liquor is evaporated and burnt in recovery boiler and generates heat and recover cooking chemical by causticizing. Bleached pulp is sent to paper machine. The detail process flow diagram is shown in Fig. 2.

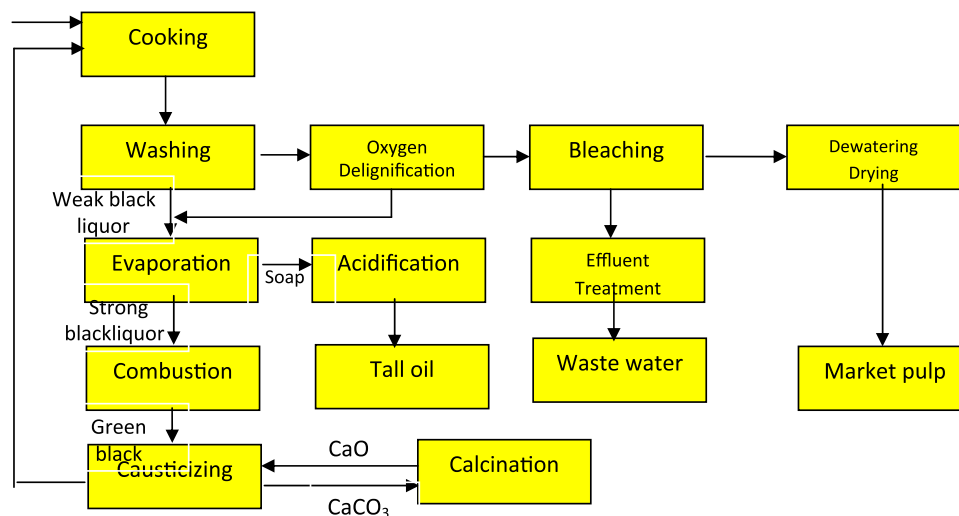


Fig. 2 Pulping process flow diagram.

Table 2 Properties of pulp from jute and other raw materials

Raw material	Process	Pulp yield (%)	Kappa number	oSR	Tensile index (N m/g)	Tear index (mN m ² /g)	Burst index (kPa m ² /g)	Reference
Jute fibre	Soda-AQ	64.2	10.7	31	53.1	21.2	5.5	Jahan <i>et al.</i> (2013a,b)
	AS-AQ	65.5	16.9	31	53.5	22.2	6.3	
	NS-AQ	66.1	11.1	24	73.7	23.9	6.6	
Whole jute plant	ASAM	56.6	39.2	30	100.0	11.3	6.9	Jahan <i>et al.</i> (2005a,b)
Hardwood (red maple)	Kraft	50.6	16	2000	78	7.0	—	Watson <i>et al.</i> (2003)
Softwood (pine)	Kraft	46.6	35	383	119	11.7	10.3	Hatton and Gee (1994)

Pulping for Papermaking

The basic density of wood influences the pulp production. The density of jute fibre is 1400–1500 kg/m³. The density of jute fibre is higher pulpwood (Casey, 1980). As for example, wood density of mangrove species was within the range of 562–643 kg/m³ (Al-Maruf and Jahan, 2015). The higher wood density certainly produces more pulp produced per digester (Goyal *et al.*, 1999). This result indicates that jute fibre gives a significantly higher packing factor, producing more pulp per digester.

Chemical constituents of jute indicate suitability for pulping. Therefore, many studies have been carried out on jute fibre, jute stick and whole jute plant pulping in different processes conventional kraft and soda processes as reviewed by Akhtaruzzaman *et al.* (1991), Akhtaruzzaman (1994), Akhtaruzzaman and Shafi (1995), Akhtaruzzaman (1998), Shafi (1994) in home and abroad. The conventional kraft and soda processes produce pulp with low yield with inferior strength with several processing problems. There have been attempts in the manufacturing of chemical grade pulp from jute by the conventional soda process in Sylhet Pulp and Paper Mills since seventies. But it failed due to severe lumping of pulped material in the digester, difficulties in washing and screening and more seriously due to drastic loss in pulp strength on bleaching. The process also leads to low pulp yield (Anon, 1988). Studies were then conducted with conventional kraft process. But the situation did not improve to a noticeable extent (Bhowmick, 1988).

Jute fibre produced higher yield and lower kappa number than whole jute plant and jute stick (Table 2). This is due to higher α -cellulose content and lower lignin content in jute fibre (Rahman *et al.*, 2006). Alkaline sulfite anthraquinone methanol (ASAM) process showed very high pulp yield (61.5%) and low kappa number (7.6) from retted jute fibre (Jahan *et al.*, 2005a,b). The papermaking properties and bleachability of the produced pulp was very good. But the process needs high pressure vessel, which will increase capital investment. This will also increase operating cost (Table 2).

Akhtaruzzaman *et al.* (1991), Akhtaruzzaman (1994), Akhtaruzzaman and Shafi (1995), Akhtaruzzaman (1998), Bose *et al.* (1999), Shafi (1994) conducted extensive studies and reported on the suitability of jute in respect pulping process, economics, problems of jute pulping etc. The authors showed that the neutral sulfite anthraquinone (NS-AQ) process was very promising for jute fibre pulping. It eliminates the problems encountered in the alkaline processes. In addition, this economically feasible process produces pulp with higher yield and conifer-like kraft pulp, with regard to physical strength properties. These append that despite higher cost of jute, highly demanding costly pulp can be produced from retted jute fibre. But little studies were conducted on bleaching.

Jahan *et al.* (2013a,b) re-verified soda- anthraquinone, (soda-AQ), alkaline sulfite- anthraquinone (AS-AQ) and neutral sulfite-anthraquinone (NS-AQ) pulping processes for jute cutting and caddis. The jute mill do not use bottom part of jute fibre (due to inferior properties), this part is called jute cuttings; in addition, jute caddies obtained as rejects in jute mill. A photograph of jute cutting and jute caddis is shown in Fig. 3. The NS-AQ process showed favorable pulp yield and kappa number for both these raw materials: 66.1% for jute cutting and 59.9% for caddis at a kappa number of about 11. The physical properties of NS-AQ pulps were also better than those of soda-AQ and AS-AQ pulps. At °SR 44, the tensile index of NS-AQ pulp was about 100 N m/g for jute cuttings and 70 N m/g for caddis, while their tear index was almost similar. All these pulp were bleached by D₀E_pD₁ bleaching sequences. The NS-AQ pulp showed excellent bleachability and its brightness reached to 89% for jute cutting and 85% for caddis using a total chlorine dioxide of about 15 kg per ton. After bleaching, the strength properties of NS-AQ pulp were slightly better compared to soda-AQ and AS-AQ pulps. The differences in pulpability of core and bark fibre of jute at different position were studied (Jahan *et al.*, 2008a). Under identical conditions of pulping, bark gave higher pulp yield and lower kappa number than core. Lower kappa number signifies higher delignification degree. The bark pulp showed better bleachability than core pulp. The higher tensile index in core pulp and higher tear index in bark pulp were observed.

Effect of ribbon retting on kraft pulping was studied (Jahan *et al.*, 2016). Pulp yield of conventional retted jute fibre and jute stick was higher at any kappa number. The variation of papermaking properties of the produced pulp on retting process was insignificant. The bleachability of jute fibre pulp was better than that of jute stick pulp. Conventional retted fibres showed slightly better bleachability. Jute fibre pulp consumed 15 kg ClO₂/MTof pulp to produce brightness of 81%–86%, while jute stick consumed 30 kg ClO₂/MTof pulp to produce brightness 85%.

Organic acid pulping of jute has also been evaluated for papermaking. It was observed that pulp yield was very good and easy to bleach by total chlorine free bleaching, but papermaking properties were not acceptable level (Jahan *et al.*, 2007a,b; Sahin and Young, 2008). It was also seen that hemicelluloses were dissolved along with lignin in the pulping, causing reduced fibre bonding during sheet formation. Acetylation and formylation of hydroxyl group of cellulose were another possible reason of lower papermaking properties (Jahan *et al.*, 2007a,b). Sahin (2003) pulped jute fibres by ethanol-alkali (EtOH-NaOH) process. The

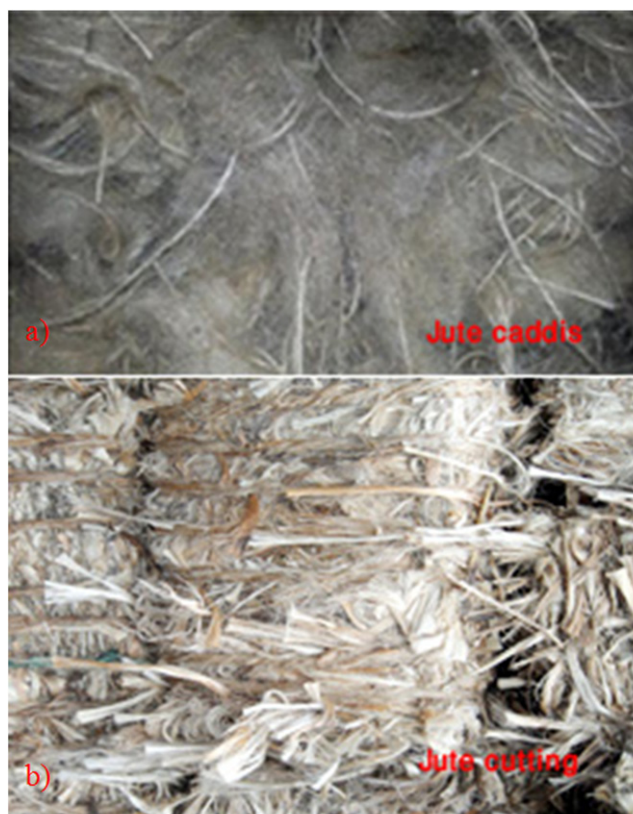


Fig. 3 Photograph of (a) jute caddis, (b) jute cutting.

Table 3 The possible uses of jute pulp

<i>Kind of jute fibre</i>	<i>Type of paper to be made</i>	<i>% Jute fibre in furnish</i>	<i>Fibre forming balance of furnish</i>
Jute bast	● Cigarette paper ● Security paper, bonds, and ledgers ● Currency paper ● Tea bag, sausage skin ● LW printing and writing ● Tag, wrapping and bag	30–50 Adj Adj Adj 20–80 60–80	Hemp pulp Cotton pulp/wood pulp Cotton pulp Flax pulp Wood pulp, bamboo pulp Wood pulp, bamboo pulp
Jute whole plant core and	● Printing and writing ● Newsprint with TMP/CTMP	Adj Adj	Wood pulp, bamboo pulp Long fibred chem. pulp

Note: Hurler, A.M., 1991. Nonwood plant fiber progress Report No.19, Tappi Press. Quoted by Akhtaruzzaman, A.F.M., 1994. Market Prospect for Pulp and Paper from Jute, Kenaf and Sisal and Appropriate Technology and Marketing Strategies FAO These Products, ESC: JU/EGM 94/5. Rome: FAO.

delignification proceeded more rapidly and selectively with ethanol-alkali than alkali alone. Pulp yield and strength properties were better than soda alone.

Pulping of whole jute plant also has been studied in different processes (Jahan and Farouqui, 2000; Jahan *et al.*, 2000; Jahan and Farouqui, 2001; Jahan *et al.*, 2005a,b). Pulp yield obtained was 51% at kappa number 28 in kraft process (Jahan and Farouqui, 2000). In that study ethylenediamine (EDA) or monoethanolamine (MEA) was used as additive with soda liquor. The pulp yield is considerably higher than for the control soda and kraft pulps. Pulps obtained are better in physical properties compared to kraft and soda pulps. As shown in Table 1, pulp yield in ASAM process was 56.6% with kappa number 39.2, but the papermaking properties was very good (Jahan *et al.*, 2005a,b).

Jute fibre pulp bleached to very high brightness (88%–90%) with the consumption of 7.6 kg ClO₂/ton of pulp (Jahan *et al.*, 2010).

The papermaking processes from jute in some cases are superior to conifer pulps (Akhtaruzzaman and Shafi, 1995). Such pulp can be used to make specialty papers that cannot be readily produced from wood pulps. This can also be used as additives to impart some special characteristics that cannot be used by wood pulp alone. The possible end uses of jute pulp are noted in Table 3.

Blending of Nonwood Pulp With Wood Pulp

In papermaking, it is very often that more than one type (or grade) of pulps are used to develop paper sheet properties necessary for both machine runnability and requirement of the end users. In many paper grades, long fibres from softwood bleached kraft pulp are often used in combination with short fibre from hardwood bleached kraft pulp (HBKP). In this combination, the long fibre component provides the strength (especially tear resistance) to the paper sheet, while the short fibre helps to improve the paper functional properties, such as sheet smoothness and formation. It is generally accepted that fibres such as straw are not likely to be used on a 100% basis for paper manufacturing. Particularly their poor drainability and low tearing strength make it necessary to use furnish mixtures containing a certain amount of long fibres. Jute has longer fibres and other non-wood in Bangladesh have shorter fibres. A very good tensile-tear ratio is observed in case of jute pulp. Whereas corn stalks, kash, dhanicha, straw, etc. produced pulp of high tensile strength. So jute pulp can be used as reinforcing fibre for other nonwood pulps. Jute fibre provides long fibre furnish, where cotton stalks, corn stalks, straw and other nonwood fibres available in Bangladesh provide short fibre furnish. It was observed that the blending of corn stalks pulp with jute pulp increased tear strength (Islam and Jahan, 2001). Tschimer *et al.* (2003) showed that a significant increase in tensile and burst strength with an addition of soda-AQ wheat fibre to the hardwood/softwood mixture typically used in printing and writing grades. The tear index of dhaincha pulp was improved with adding jute pulp (Jahan *et al.*, 2007c). Therefore, there is a good possibility in Bangladesh to set up integrated pulp (separate fibre line for different characters of fibres) mills based on nonwood fibres, which will solve the scarcity of fibrous raw materials and contributes an environment friendly atmosphere.

Dissolving Pulp

Jute fibre is an expensive lignocellulosic fibre. Its α -cellulose content is very high and lignin and pentosan content are low (Table 1). These are advantageous for producing dissolving pulp production.

Jute fibre, jute cutting and jute caddis were evaluated in producing dissolving pulp by prehydrolysed kraft process (Jahan *et al.*, 2007a,b). In that study it was observed that rayon grade pulp could be produced from jute fibre, cutting or caddis. Jute fibre produced dissolving pulp having 90%–97% α -cellulose (Jahan, 2009). Organic acid process dissolved both lignin and hemicellulose simultaneously (Jahan *et al.*, 2007c). Therefore, jute fibre, jute cutting and jute caddis were also evaluated for dissolving pulp production in organic acid process (Jahan *et al.*, 2008b). The α -cellulose of the produced pulp in organic acid process was 90%–97%. The pulp bleached up to 87% brightness in total chlorine free bleaching. High purity dissolving pulp were also produced from jute fibre by prehydrolysed kraft pulping followed by fractionation and alkali extraction (Nayeem *et al.*, 2017). Fock reactivity increased with decreasing fibre size, but α -cellulose content in long fibre fraction was higher than that of short fibre fraction. Fock reactivity of pulp indicates its ability in xanthation reaction. Alkaline extraction further removed pentosans resulting in increased α -cellulose content in the pulp. Fock's reactivity also increased after reduction of hemicelluloses by weak alkaline extraction. Formic acid treatment followed by alkaline extraction and $D_0E_pD_1$ bleaching produced pulp of 94.3% purity with Fock's reactivity of 63.2%. Alkaline extraction of the bleached pulp increased purity to 97% with Fock's reactivity of 72%–73% (Nayeem *et al.*, 2017).

Dissolving pulp was also produced from jute stick by pre-hydrolysis kraft process (Matin *et al.*, 2015). The pulp yield was 36.2% with kappa number 18.5 at the cooking conditions of 16% active alkali as Na_2O for 2 h of cooking at 170°C. The prehydrolysis was carried out at 170°C for 1 h of pre-hydrolysis. Final pulp was produced with 92% α -cellulose and 89% brightness after $D_0E_pD_1$ bleaching, which could be used in rayon production.

Supply and Storage of Jute for Pulp Making

Jute is a non-conventional raw material for pulping. Therefore, for the development of jute pulp mill, it is immense attention on jute supply and its delivery is very vital. Jute pulp mills project needs to know the growth, harvesting, collection, transportation and storage aspects of jute. Thus, critical analysis of supply and storage of jute has enormous importance in setting a jute based pulp mill.

A sustained supply of fibrous raw material (FRM) to the mill site and its effective storage are important parameters for consideration of setting a pulp mill. Akhtaruzzaman (1998) extensively discussed on the storage and supply of jute for pulping. In case of jute, it is altogether different from round wood and saw mill chips that it is a seasonal crop. Jute is traditionally cultivated by the farmers in the land which cannot normally be used for other crops. It is mainly grown for the retted bastfibre which brings immediate cash to the farmers during the lean period. In extracting the bast fibre on retting, the woody core is obtained as the by-product. The core is largely used by the villagers as fuel and in making thatched house and for fencing. As a result, the value of the core is in no way less important than the bast fibre. Thus, use of jute stem or core may create social problems in countries where there is an acute scarcity of fuel and thatching materials, unless alternatives are given to the villagers. Jute is cultivated in small patches of land scattered at different localities. Its stem and core are very bulky.

Conventionally, they are costly to transport over long distances. The situation is further aggravated because the harvesting time falls in the monsoon when normal vehicular transportation in many jute growing areas becomes more difficult and expensive. The odd harvesting time also makes drying of the stem in the field impossible in many cases.

In this situation when the stem is collected and transported in the green condition with approximately 70% moisture, the transportation cost can be a large component of the total cost of production.

Conventionally, a pulp mill does not own a large area of land to grow jute. Then naturally the mill may not have a direct control over the cost of fibrous raw material (FRM). This situation may become worse in case of crop failure due to perennial weather changes. In order to avert these problems in the supply position, the mill may plan to grow jute itself in leased land in adjoining areas to meet the mill demand. It seems to be too optimistic. Jute cultivation by the mill authorities using hired land and labour, management and inputs, etc., may turn it into an expensive venture.

Therefore, the supply situation of jute stem and core must be seriously taken into account in considering them as pulping FRM. It is a fundamental problem that has to be overcome for the viability of a mill.

Jute stem and core are susceptible to rapid fungal decomposition causing severe damage to the fibre. Because of their high bulk, they are difficult to store. It is reported that kenaf stem (a material similar to jute stem) even if compressed to high density bales of 500 kg/m³, the volume of storage for one year supply of the stem is about 217,000 m³ for a 50,000 ton/year chemical pulp mill (Wong, 1991). With a stacking height of 3 m, a stacking width of 3 m and a stacking space of 3 m, the estimated storage yard needs a space of 150 hectares (373 acres). This space should be under cover. Many developing countries may not afford to arrange such a large space under cover for storage. Even then there remains the chance of hazardous attack by termite and powder post beetles. Thus, the storage problems alone can act as a cognizable limitation and demand a serious consideration in pulping of jute stem and core. The problems must be scientifically assessed and solved if these materials are used as the FRM. With such multiples of problems in the supply and storage of jute stem and core, naturally the question arises whether jute has at all any prospect to be used in pulp industry. The situation is entirely different when the bast fibre is considered. The collection and transportation mechanisms of retted jute bast fibre are well accepted by the jute fabric mills. The farmers bring the dried material in hand-pressed bundles to the selling centers or markets. The practice continues for months together after harvesting. So the problem of patch collection from the farmer's field or home immediately after harvesting as is usual for the stem or core is done away with. The density of the retted bast fibre is reported to be 1500 kg/m³ (Joseph, 1980) against 185 kg/m³ for the stem (Islam and Khan, 1984). This means a large advantage in transportation and storage of the bast fibre. The dried fibre is resistant to micro-organisms and insects (Joseph, 1980). Thus its storage has been well practiced in sheds by the jute fabric mills with no serious problems. Therefore the supply and storage problems of the FRM with the bast fibre are substantially minimized. This is a strong point in favor of its use as a pulping raw material. However, the cost of the material may be questionable. The lower grades of jute (bast fibre) and jute cuttings which are low priced have little use and can serve as the FRM in pulp making. These grades of jute amounted to about 250,000 tons annually in Bangladesh (Akhtaruzzaman and Shafi, 1995). Encouragingly, these fibres can yield pulp superior to conifers (Akhtaruzzaman and Shafi, 1995). The pulp can then be used in making specialty papers (Akhtaruzzaman, 1994). The FAO expert group meeting on diversified application of bio-resources (FAO, 1994) also concluded that jute bast fibre has the potentiality of making pulp for value-added specialty papers.

Conclusion

Jute fibre is characterized with high α -cellulose (>60%) and low lignin (<15%) content consequently easier to delignify. A very high pulp yield (above 60%) is obtained from jute fibre with low kappa number (10–15). Papermaking properties of jute fibre pulp were exceptionally good. Tensile index of jute pulp reached to 100 N m/g at tear index of about 20 mN m²/g. Jute pulp need less chlorine dioxide to get desired pulp brightness (90% ISO). Neutral sulphiteanthraquinone (NS-AQ) and alkaline sulfite anthraquinone (AS-AQ) processes showed best results in terms of pulp yield, kappa number, bleachability and papermaking properties. Dissolving pulp can also be produced from jute fibre with good purity and reactivity. For dissolving pulp production, organic acid process showed the best results in terms of yield, bleachability (84%), purity (97% α -cellulose) and reactivity (73% fock reactivity). Jute fibre is a seasonal crop, therefore, a good transportation and storage strategies are needed for jute based pulp production.

See also: An Overview on the Development of Natural Renewable Materials for Textile Applications. Opportunities With Renewable Jute Fiber Composites to Reduce Eco-Impact of Nonrenewable Polymers. Rice Straw as a Raw Material for Pulp and Paper Production

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Life Cycle Assessment of Sisal Fiber

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Introduction

Although sisal plant is found across the world, it grows mostly in the regions of Brazil, Tanzania, Mexico, Africa and china. Normally, sisal plants are not planting in systematic way. It grows along the railroad pathways and beside the water flowing areas of farming fields (Chand and Fahim, 2008). Numerous types of sisal plants are identified all over the world. Agaves are large plants in the sisal fiber family of Agavaceae in which it contains about 300 species such as Agave cantala, Agave guiengola, Agave americana, Agave angustifolia, Agave flexispina etc (Yu, 2005).

Initially, Sisal plant was found in South American and Middle African countries. In 1930s, the Brazil is the first country for harvesting and cultivating the sisal plants, commercially. Later, the other African, European and Asian countries initiated the sisal fiber cultivation and harvesting. Also, the first sisal fiber trading was made in the year 1948 by Brazil. In 1960s, India also joined to cultivate and extract fibers from the sisal plants from southern east states such as Orissa, Andhra Pradesh and Tamil Nadu (Saxena *et al.*, 2011).

The sisal fibers and their products are consumed in the period of 1960–1970 since the production reached 800,000 tonnes. In the recent years, due to the challenge of the man-made fibers and their products, there is reduction in the production and exports. Even though, the sisal fibers are sustaining their direct and indirect products in the real time markets. The major sisal fibers consuming countries are the United States of America, Canada, France, Germany, China and Belgium. These countries are using the sisal fibers in various applications such as high quality papermaking, mining, forestry, metallurgical industries, composite materials, floor casing mattresses, buffs and construction materials (Yu, 2005).

The necessities of research on sisal fiber are (a). It possesses high strength, attraction to dyes and resistance to weakening in sea water, (b). Sisal is the one of the best among all other natural fibers which is simply cultivated, (c). It has excellent recyclability and less renewable times and (d). Sisal fiber and products are eco- friendly.

Properties of Sisal Fibers

Physical Properties

The sisal plant normally yields 50–150 mm thick, sharp, long and closely arranged leaves and is prepared to get yield merely after 2 years of planting (Laxmikanta Nayak *et al.*, 2011). However, the plant matures fully after 3–4 years of growth. The matured sisal leaf is to be identified by the accomplishment of leaf length of about 1 m and also the leaf spike attains the angle of 60° in which the colour of the end spike changed to pale brownish. Typically, a well grown up sisal plant produces 200–250 usable leaves in its entire lifespan of about 12 years. Also, the leaf encloses with 1000–1200 fibers (Yu, 2005).

Sisal plant

The schematic diagram of sisal plant is shown in Fig. 1(a). Sisal plant (Agaves) has a central stem on which the leaves grow up. Their leaf physically appears like a sword and dark green colour. The edges of the leaves are covered with teeth. When it attains maturity period, these teeth will disappear. A typical length and width of the sisal leaf is 1.5 m and 15 cm respectively. Usually, it can be extracted from the fibers which is equal to length of the leaves. That is, the length of sisal fiber is approximately equal to the length of the leaf and the diameter of the fiber is in between 100 and 300 μm (Naveen *et al.*, 2019). The dried fiber weight is just 3%–4% of the leaf weight.

Sisal leaf

The schematic diagram of a sisal leaf is shown in Fig. 1(b). A sisal leaf has 15 cm length and average thickness is 5 cm. A cut section of sisal leaf is shown in Fig. 1(c). The leaf consists of the fiber and moisture. There are three kinds of fibers such as mechanical fiber, ribbon fiber and xylem fiber.

Mechanical Fiber: The fiber is attached to the sisal leaf's periphery. When the leaf is crushed, the moisture in the fiber is removed and fibers are separated. This fiber is called mechanical fiber. It appears like thick-horseshoe shape after the extraction. This fiber will have good strength and can be used for all commercial purpose.

Ribbon fiber: The fiber occurring in the mid span of the leaf is called ribbon fiber and its cross-sectional view is shown in the Fig. 1(c). This ribbon fiber offers mechanical strength to the sisal leaf. This fiber is the longest one compared to other type of the fiber. It can be fragmented longitudinally according to the process requirement.

Xylem fiber: The fiber present at middle of the leaf is called Xylem fiber. It is arranged in irregular manner. It occurs along the latitudinal direction to the ribbon fibers. This fiber gives the shape to the leaf. Since these fibers are arranged in irregular manner, it may be broken while extracted.

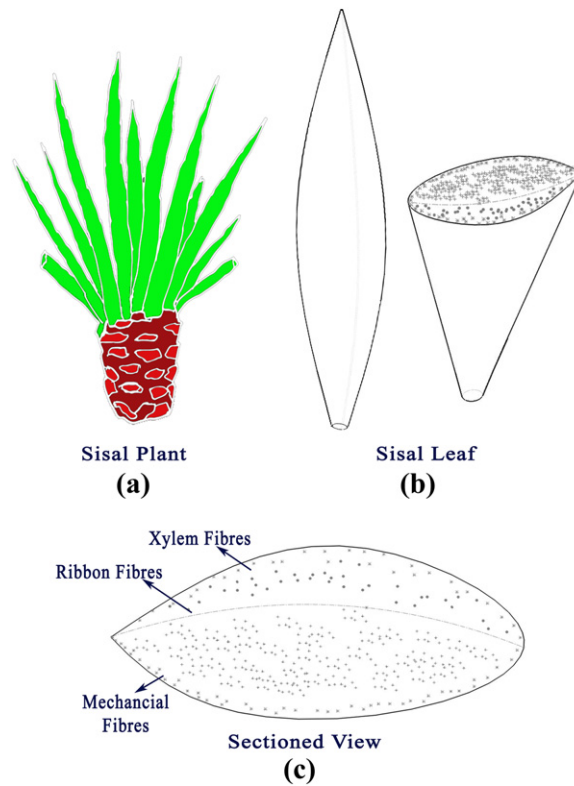


Fig. 1 The schematic diagram of (a) sisal plant, (b) sisal leaf and (c) sectioned view of the sisal leaf.

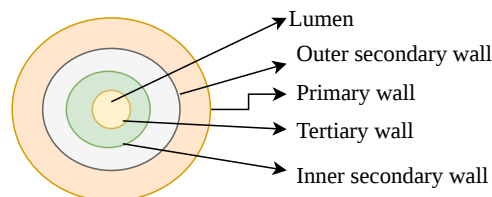


Fig. 2 A cross sectional view of a sisal fiber cell.

Sisal cell

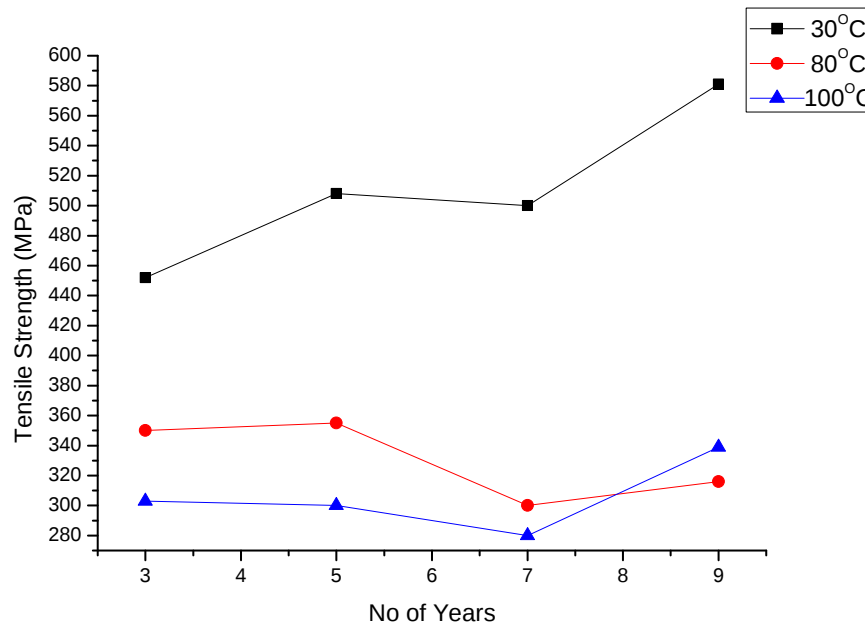
A sisal fiber has more than 100 cells and every cell has a length of 2–5 mm (Naveen *et al.*, 2019). The cross sectional view of a sisal fiber cell is shown in the Fig. 2. Every single cell is linked with other cells through the middle lamellae. The Lamella consists of hemicellulose, lignin and pectin. A sisal fiber cell consists of lumen, tertiary wall, inner secondary wall, outer secondary wall and primary wall. Lumen, the smallest inner part of the sisal cell, is positioned at the centre of the cell (as shown in Fig. 2). The diameter of the lumen is 9–12 μm . The lumen is covered by tertiary wall. The fibrillae is irregularly arranged over the tertiary wall. This tertiary wall is covered by inner secondary wall with a slope of 18° . These walls are attached with hemi-cellulose and lignin matrix in spiral orientation manner. The outer secondary wall lies between the primary wall and inner secondary wall. This outer secondary wall is covered by primary wall with a slope of 40° . This wall is also covered by the cellulose with spiral shape direction. However, cellulose presents on the outer secondary wall is opposite direction to the inner secondary wall.

Chemical Composition

The chemical composition of sisal leaf is shown in the Table 1. It has 60% cellulose, 10% hemi-cellulose, 9% lignin, 7% pectin, 10% moisture content, 2% waxes and 2% ash (Saxena *et al.*, 2011). The sisal fibers have the similar composition of cellulose level with other natural fiber. Alternatively, the presence of lignin content in the sisal fiber is higher than the other natural fiber plants such as jute, pineapple fiber etc. Also, the sisal fiber is stronger and coarser than other natural fibers. It is because of high pectin and lignin content presence in the sisal leaf.

Table 1 The chemical composition of sisal leaf in percentage

Constituents	Values (%)
Cellulose	66
Hemicellulose	10
Lignin	10
Pectin	10
Waxes	2
Ash	2
Moisture absorption	10

**Fig. 3** Tensile strength of the sisal fiber after the aging at different temperature. Reproduced from Chand, N., Fahim, M., 2008. Tribology of Natural Fiber Polymer Composites, first ed. India: Woodhead Publishing.**Table 2** Mechanical properties of sisal fiber

Mechanical Property	Sisal
Specific modulus (approximate)	18
Stiffness (kN mm^{-1})	30–40
Tensile modulus (GPa)	10–40
Tensile strength (GPa)	540–720
Young's modulus (GPa)	13
Elongation at break (%)	2.2–3.3
Maximum elongation (mm)	5–10

Mechanical Properties Sisal Fiber

The sisal fiber bundles have the greater lignin content. This lignin content in the sisal fiber bundles provides high rigidity and exhibit excellent tendency of strength when compared to other natural fibers. The sisal fibers have the highest stiffness, low density and low compressibility ratio when associated with other natural fibers. Chand and Fahim (2008) evaluated the sisal fiber tensile strength after the different aging treatment. The graphical representation of this result has been given in the Fig. 3. It reveals that the strength of the sisal fiber remains almost equal even after 7 years treatment. The Table 2 provides the mechanical properties of a typical sisal fiber.

Extraction of Sisal Fiber

Usually, ample quantities of fiber exist on the surface of the sisal leaves. These fibers are rooted longitudinally in the leaves. The average weight of a standard leaf is about 600 g and individual leaf has more than 1000 fibers. After the harvesting of the sisal plant, the useful fibers are extracted from the leaves. The process involved for extracting fibers are (1). Retting, (2). Boiling and (3). Decortication.

Retting

It is a method that divides the fiber packs from the leaf stem. In this process, the fibers are released from the fiber crop tissues (Ramesh, 2018).

Boiling

The functional fibers are obtained from the sisal plant by bleaching, boiling, beating, washing and drying with sunlight. This method is suitable only for smaller quantity.

Decortication

It is the mechanical technique for extracting sisal fiber. During this process, the leaves are crumpled between smooth-edged blades. While it is crushed the moisture and the fleshy pastes are eliminated from the fiber. The fiber quality remains the same and it is suited for large scale operations. The residues exist after the fiber extraction can be used as raw material for biogas plant, paper board, wax, polymers and preparing paper.

Sisal Fiber Treatments

Sisal fiber treatments facilitate the adhesion at the interphase between fiber and matrix resin. It increases strength of the sisal fiber embedded in the composites. It also impacts the mechanical and frictional properties of the sisal fiber reinforced composites.

Physical Treatment

A physical treatment changes the structural and superficial properties of the fiber. This treatment affects the other properties of composites. The various methods of physical techniques are heat treatment, plasma treatment, fiber surface coating, electric discharge method, and gamma radiation treatment. These methods are employed to increase the interface bonding and adhesion.

Heat treatment

The sisal fibers will be immersed in the boiling water either with pressure or without pressure for stipulated time period. This treatment helps to improve the cleaning of sisal fiber. Only if the fiber surface is in clean condition, it can react with resin and exhibit strong interface bonding.

Surface coating

Normally, polymeric coating will be done for improving reinforcing character. It enhances flexural strength and thereby flexural modulus. These coating improves the fiber-resin matrix bonding (Venkateshwaran *et al.*, 2013).

Plasma treatment

The plasma treatment primarily causes chemical embedding, engraving, and change of crystal structure. The adhesive property of the fiber is increased by the etching process which enhances physical property like surface roughness. This modified surface roughness aids the adhesion at the inter-phase. The modification of the cellulose fiber carried out by the electric discharge method increases the melt viscosity of the fiber and enhances the other related properties.

Chemical Treatment

The chemical treatments are used to alter the fiber external modification and their interior structure. Some important chemical treatments are (1). Treatment with sodium hydroxide (2). Treatment with salt water and (3). Permanganate treatment.

Treatment with sodium hydroxide

This treatment is a kind of purifying process. The sisal fiber cellulose constituent is not affected by the treatment of Sodium hydroxide. This treatment removes the non-cellulosic constituents like hemi-cellulose, pectin and water solvable constituents. The

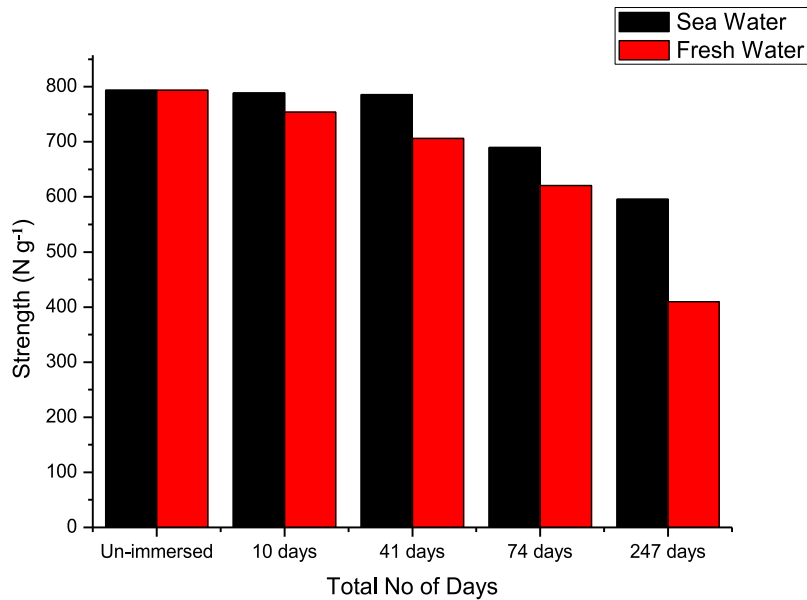


Fig. 4 A bar chart represents the strength of the sisal fiber after the sea water treatment. Reproduced from Yu, C., 2005. Sisal. In: Franck, R.R. (Ed.), *Bast and Other Plant Fibers*, first ed. United Kingdom: Woodhead Publishing, pp. 84–107.

ultimate aim of this treatment is to reduce the quantity of gums and lignin in the fibers. It improves their elasticity, quality and elongation at break (Saravanan and Devaraju, 2018). This will increase the spin-ability of the fiber.

Treatment with sea water

To understand the reaction of sisal fiber with salt water, the fibers are immersed in the sea water and fresh water for the different time periods. Fig. 4 represents the strength of the sisal fiber after the sea water treatment. The result reveals that strength of sisal fiber immersed in fresh water decreased drastically. Whereas sisal fiber maintains its almost full strength even after 45 days immersed in sea water (Yu, 2005).

Permanganate treatment

Alkali treatment alters the superficial structure and tensile strength of sisal fiber. The permanganate treatment improves the tensile strength of the sisal fiber. Whereas some other treatment (acetone) decreases its strength because of water absorption.

Bleaching

It is the method of removing non-cellulosic compounds by chemical treatment. Normally, the bleaching is done with sodium chlorite solution about 60°C for 1.5–2 h. This treatment improves the mechanical and physical characteristics. Although the bleaching treatment reduces the tensile strength of the sisal fiber, it exhibits huge bonding strength while preparing the sisal based composite. It improves flexural strength and impact strength. Since lignin is removed due to bleaching process, it exhibits less stiffness and hence it can be rolled easily.

Sisal Fiber Composites

The natural fiber composites play important role in recent decades. Although the research on jute, hemp, banana and palm leaf based composite started long back, the attention on sisal fiber based composites started very recently. The sisal fiber composite replaces a synthetic fiber material in all day to day life. Moreover, the hybridisation of the sisal fiber with other natural fiber such as jute, hemp, and banana, gives the excellent mechanical and tribological properties.

Sisal Fiber Reinforced Polymer

The sisal fiber, normally, absorbs a large amount of water which leads to delaminate failure. Alternatively, when the sisal fiber is reinforced with hydrophobic polymer matrices, it becomes Sisal Polymer Composite (SPC). And this SPC will have poor resistance to water absorption. The SPC can be classified as thermo-set and thermo-plastic.

Table 3 Comparison of thermo-plastic Sisal Polymer Composite and thermo-set plastic Sisal Polymer Composite for different properties

S.No	Properties	Thermo-plastic SPC	Thermo- set SPC
1	Tensile strength	Low	High
2	Flexural strength	High	Low
3	Fatigue strength	Low	High
4	Stiffness	Low	High
5	Toughness	High	Low
6	Water resistance	High	High
7	Synthesis	Addition polymerisation	Condensation polymerisation
8	Reusability	Recyclable, remould /reform after heating	Can not be recyclable and remoulded since it retains the rigidity at high temperatures.
9	Brittleness	Low	High
10	Temperature stability	Low	High,
11	Cost	Moderate	Cheaper
12	Density	Low	High
13	Common resins	PET, polypropylene, polycarbonate, PBT, Vinyl, polyethylene, PVC, PEI, nylon	Polyester resin, Vinyl ester resin, Epoxy, Phenolic, Urethane
14	Melting point	Low	High
15	Rigidity	Low	High
16	Solubility	Soluble in some organic solvents	Insoluble in organic solvents
17	Durability	Low	High
18	Processing methods	Injection moulding, extrusion process, blow moulding, thermoforming process, and rotational moulding	Compression moulding, reaction injection moulding
19	Molecular weight	Low	High

Thermo-set SPC

The thermo-set SPC is fabricated with the resin such as polyester, epoxy and phenol-formaldehyde. It can be prepared by hand lay-up followed by hot compression moulding. This is simple and effective method. The strength of this composite depends on sisal fiber length, percentage of fiber weight, fiber orientation and kind of resins. Addition of nano particles plays important role in mechanical properties of SPC (Devaraju and Sivasamy, 2018). Among aforementioned resin, the phenol-formaldehyde provides better tensile, toughness and flexural properties because of strong interfacial bonding. And also it can be heat treated between 100 and 250°C so that its tensile strength and elongation at break will be improved.

Thermo-plastic SPC

The thermo-plastic SPC normally, is fabricated by extrusion compounding or injection moulding. Since it is fabricated under pressure, sisal fiber length may be reduced due to breakage in the intermediate steps. There are four thermoplastic matrices such as Poly Lactic Acid (PLA), Low-Density PolyEthylene (LDPE), High-Density PolyEthylene (HDPE) and Poly Vinyl Chloride (PVC). The major advantage of thermo-plastic SPC is recyclability. The thermo-plastic SPC can be fabricated with lesser time than thermo-set SPC. The waste products of natural cellulosic fillers are shell flour, wood flour, and pulp. These cellulosic fillers can be used as reinforcement for thermo-plastic SPC (Table 3).

Hybrid Sisal Fiber-Based Polymer

Hybrid composite consists of two or more fibers. Adding sisal fibers into synthetic fibers partially replace synthetic fibers in the Hybrid Sisal based Polymer Composites (HSPC). The HSPC provides the combined properties of their individual constituents. While sisal fibers hybrid with other natural or synthetic fibers, it significantly enhances their tribological and mechanical properties by taking the advantage of their individual constituents. It also reduces the water absorption. Since HSPC have superior properties, it can be used in many applications of engineering and technology.

Tribological Behavior of Sisal-Polymer Composites

Tribological behaviors of sisal fiber are quite interesting. However, a very few researchers (Chand and Fahim, 2008) have attempted to evaluate the friction and wear behaviors of different sisal fiber based composite.

Sisal – Epoxy Composite

Sisal- Epoxy Composites (SEC) are used in car interiors. The tribological test on SEC reveals that abrasive wear takes place when sisal fiber is placed parallel to the sliding direction. Whereas when the sisal fiber is placed perpendicular to the sliding direction, less surface damage occurs. However, SEC exhibits better wear resistance than epoxy composite.

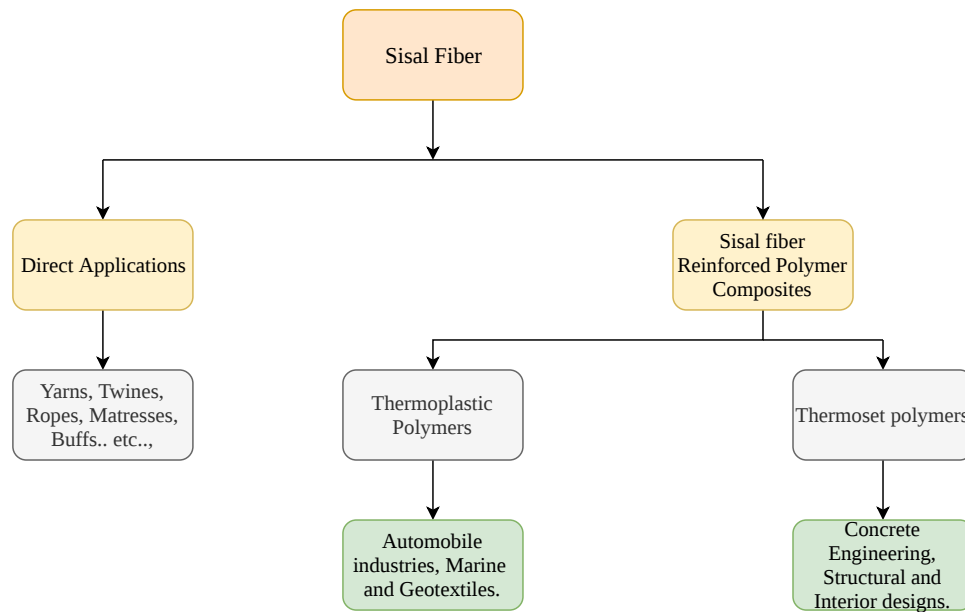


Fig. 5 Various applications of sisal fiber.

Sisal – Phenolic Composite

Sisal- phenolic composites are used in automobile brake pads, linings and couplings. Normally, sisal fiber will easily decompose at higher temperature. But, when sisal fiber is reinforced with phenolic, it withstands the higher temperature applications. Because of that, the sisal- phenolic composites exhibit better friction and wear behaviors at 150°C and 250°C. Furthermore, when sisal fiber content is increased, Sisal- phenolic composites performs much better.

Application of Sisal Fiber-based Composites

Sisal fiber can be used directly as twines, ropes etc. and indirectly, it can be used as sisal embedded composites. **Fig. 5** shows the different applications of the sisal fiber.

Direct Applications

Sisal fibers are directly used in the form of yarn, twine, rope, fabrics, buffs, mattress and floor coverings (Yu, 2005). Sisal yarns are used to make rope or cables. Sisal twines are used for weaving carpets. Ropes are prepared by twisting the twines. Since sisal ropes have anti-slipage properties, cold resistance, abrasion resistance and chemical resistance, it can be used in chemical, mechanical and shipping industries. Sisal buffs are produced from yarns. These buffs are used for polishing the shoes and hand bag design. Sisal fiber can be used as mattress since it has good permeability with moist air and water. Mosquito net can be produced from sisal twine. Also it can be woven as floor and wall covering cloths.

Indirect Applications

The sisal fibers are used in composite. The sisal embedded composite can be used as noise absorber, insulator and impact load absorber. Sisal fiber based composites can be used in construction materials, automobiles, rail engines, and aerospace applications. It is also used in packing and binding material for construction and agriculture industries. Sisal based composites are used as insulating materials in the electrical applications. Since sisal fiber has high specific strength, and processing advantages, it replaces synthetic fibers such as asbestos and glass fiber.

Inorganic fibers (glass, asbestos etc.) have several disadvantages such as (1). Non-bio degradability, (2). Abrasion when it rubs with other parts, and (3). Human health problems during processing, and handling of these fibers. Whereas sisal fibers are biodegradable, it is eco-friendly and less abrasive. Hence, sisal fiber based composites are used as computer casing, cabin lining, acoustic insulation, seat cushions, geo textiles, personal safety equipment, bio gas applications, paper making, sun helmets etc.

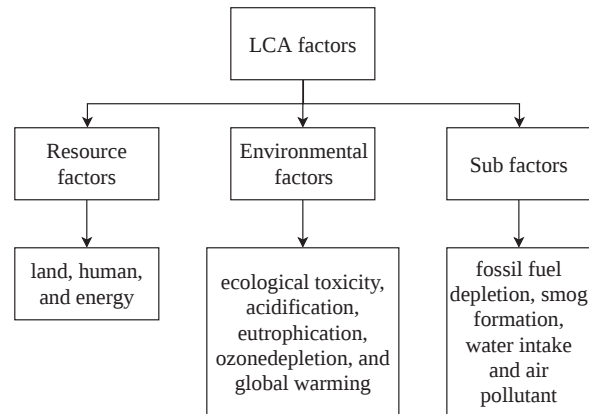


Fig. 6 The different types of impact factors of the LCA.

Life Cycle Assessment

Life Cycle Assessment (LCA) is a method to analyse the impact of environmental issues and energy requirements for the different stages of a product (raw material to end life) (Jane Bare, 2009). LCA can be implemented for the various part of the product's life cycle.

Need of LCA

LCA report should be prepared before the start of any factory or introduction of a new product. The different LCA factors have been presented in Fig. 6. This LCA report contains the details of resource requirements such as land, human, energy etc and environmental impacts such as ecological toxicity, acidification, eutrophication, ozone depletion and global warming (Guinee *et al.*, 2011). In addition to that, some sub factors such as fossil fuel depletion, smog formation, water intake, air pollutant etc., are also considered for this analysis. Based on this report only, the appropriate governing body will recommend to the government to start a factory or to permit to introduce a product to the society. Moreover, the LCA will give the detailed knowledge to the manufacturer about the different stages of the life cycle of the product (Young Song *et al.*, 2009).

Methods of LCA

LCA is broadly divided as cradle to grave assessment, cradle to gate assessment and gate to gate assessment (Young Song *et al.*, 2009). These assessments are explained based on the life cycle of the sisal fiber product. As shown in the Fig. 7, the life cycle of the sisal fiber product can be divided into nine stages such as cultivation, harvesting, fiber extraction, treatments, products, composites, applications, decomposing and disposal (Edgar Hertwich *et al.*, 2008).

The *cradle to grave* assessment of sisal fiber is the full life cycle assessment (stage 1 to stage 9). This assessment studies from the sisal plant cultivation to the disposal of the sisal products to the earth. The *cradle to gate* assessment is a partial life cycle analysis. In this assessment, the analysis is done between initial stage (cultivation of sisal plant) and product at the factory gate (yarns, twines, ropes etc). That is in the stage between 1 and 5. The *gate to gate* assessment is the analysis of any one specific stage of a product. For example, fiber extraction (3) is a stage.

Standards of LCA

The LCA study was introduced in the year of 1960s. The main objective of this study was initially limited to the energy analysis. In the period of 1970s, this was broadly extended into the departing approaches, interpretations, terminologies and outcomes. And then, in the 21st century onwards, the LCA was fixed as a mandatory assessment for every product to review the environmental impact analysis and to know the resource requirement. To avoid the confusion and variations among the different methods of the LCA, the ISO introduced a standard during the year 1997, called ISO 14040. Later, after some modifications ISO 14044 was introduced during the year 2006 (Finkbeiner *et al.*, 2006). This standard will give the assessment results of the cradle to grave analysis, cradle to gate analysis and gate to gate analysis. The ISO standards suggested four stages of LCA studies. They are goal definition and scoping, inventory analysis, impact assessment and interpretation of results (Mansor *et al.*, 2019). Guinee *et al.* (2011) suggested that, in addition to the LCA, the Life Cycle Sustainability Analysis (LCSA) will also be done to know the complete details about the technical relations and product associated difficulties including environmental impact analysis.

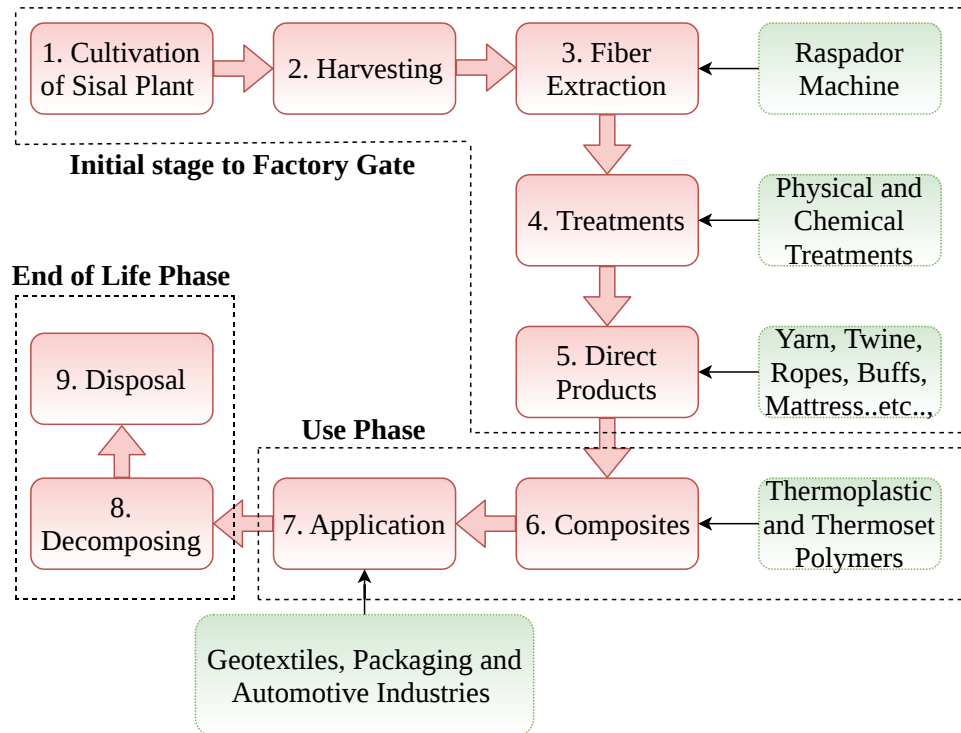


Fig. 7 The different stages of the life cycle of the sisal fiber.

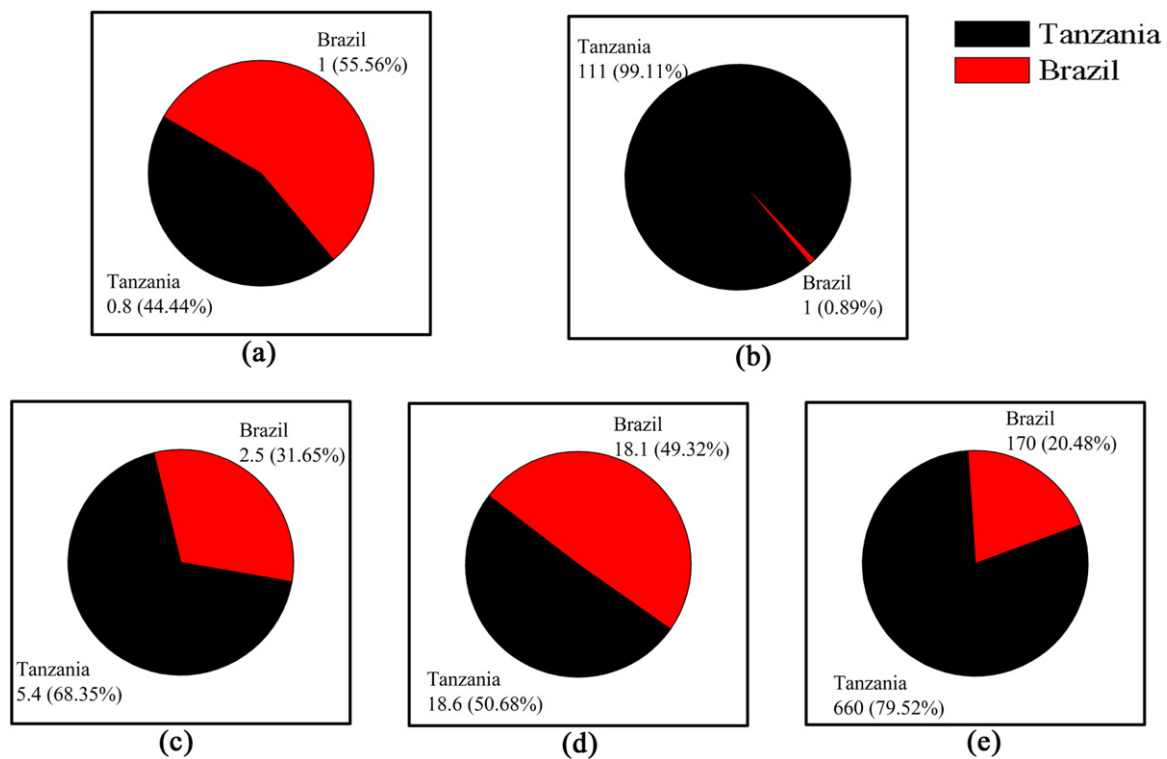


Fig. 8 Comparison of different LCA factors between Tanzania and Brazil (a) land occupied (ha yr^{-1}), (b) Depletion of fresh water ($\text{m}^3 \text{t}^{-1}$), (c) Depletion of Non-Renewable Energy (NRE) (GJ t^{-1}), (d) percentage sisal plant used as Renewable Energy (RE) (GJ t^{-1}), and (e) emission of Greenhouse Gas (GHG) ($\text{kg CO}_2 \text{eq. t}^{-1}$) Reproduced from Broeren, M.L.M., Dellaert, S.N.C., Cok, B., *et al.*, 2017. Life cycle assessment of sisal fiber – Exploring how local practices can influence environmental performance practices can influence environmental performance. Journal of Cleaner Production 149, 818–827.

LCA on Sisal Fiber

Many researchers have evaluated the LCA study in different natural fibers such as hemp, flax, banana, cotton, china reed, jute and kenaf fibers (La Rosa *et al.*, 2013; Finnveden *et al.*, 2009; Zhou *et al.*, 2018; Venkateshwaran and Elayaperumal, 2010). However, as far as current researcher knowledge is concerned, no researcher has attempted for the complete LCA study (cradle to grave approach) on sisal fiber and its products. Broeren *et al.* (2017) conducted the cradle to gate LCA analysis on the sisal fiber. The outcomes are compared to the glass fiber and other natural fibers.

The land occupied, depletion of fresh water, depletion of Non-Renewable Energy (NRE), percentage sisal residues used as Renewable Energy (RE) and emission of Greenhouse Gas (GHG) are compared between Tanzania and Brazil. These data are presented in the Fig. 8. The occupation of the agricultural land in Brazil is higher than Tanzania for same quantity of sisal fiber production (Fig. 8(a)). Since the essential soil nutrients such as potassium, magnesium and urea are naturally present in the Tanzanian soil, Tanzania occupies lesser land than Brazil. Normally, African countries are lacking with water resources and rainfall. In this situation, if the fresh water is used further for irrigation and cultivation of sisal plants, water resources will deplete in Tanzania. Because of this, Tanzania will have huge depletion of fresh water (Fig. 8(b)). Generally, the wastage of Non-Renewable Energy (NRE) is caused by the fiber processing (i.e. decortication, scrubbing and treatments). In Brazil, the NRE wastage is reduced due to the suitable practices and fiber treatments when compared to Tanzania (Fig. 8(c)). Majority of the sisal residues are used as biomass. The biomass is the excellent Renewable Energy (RE) resource which is used as various forms of energy. The sisal residues are used as RE almost equally for both countries (Fig. 8(d)). The Greenhouse Gas (GHG) can be calculated in terms of weight of the CO₂ equivalent emission. The GHG mainly influencing the global warming leads to the drastic climate change. It is found that the emission of GHG in Tanzania is three times higher than Brazil (Fig. 8(e)). This reveals that Tanzania does not properly maintain the residue disposal patterns.

Conclusion

It is concluded that the usage of sisal fiber reinforced composites have increased more than 30% in the past 25 years because of their economic and environmental benefits. This study on life cycle assessment of the sisal fiber provides knowledge for selecting right methods, treatments and product for right applications. In current scenario, the sisal fiber based products also increased tremendously in various applications due to their unique properties.

In some developing countries, most of the researchers are giving more importance to the natural fiber reinforced composites since the natural fibers are having low cost, high specific strength with low density and sustainability. The real time applications of the sisal fiber based products are reasonably low because of their misunderstanding of the physical, chemical and mechanical behaviors due to the environmental effects. These behaviors are highly sensitive to the matrix types, fiber lengths and orientations, manufacturing methods, physical and chemical treatment methods and strain rate. Since the sisal fibers are having excellent mechanical and tribological properties, it plays a vital role in defence and automotive industries.

The future scopes of the sisal fiber are given below.

- To maintain the consistent properties of the sisal fiber, there is a necessity to examine and manipulate the properties of the sisal fiber because it is ultimately depending on the sources, processing and nature of the environment.
- The complete study of the sisal fiber will give the knowledge about the thermal and tribological properties. Based on this study, the applications of the sisal fiber can be extended.
- Since the sisal fibers are discontinuous and have rough surface, the twist is mandatory for making the products such as ropes, fabrics and mattresses. In order to increase the natural fiber products, still there is adequate research required on the proper twisting and non-twisting of the sisal fiber.
- The researchers are promoting the usage of the biodegradable and eco-friendly fibers. In the same way, there is a research gap in the recyclability and repeatability of the sisal fiber products and their composites.
- The cradle to gate LCA analysis on sisal fiber gives the complete information about the environmental impacts of the sisal fiber from initial stage to the product stage.

See also: A Comparative Life Cycle Assessment for Utilising Laminated Veneer Bamboo as a Primary Structural Material in High-Rise Residential Buildings. Bio-Waste Based Nanofiber Materials. Jute/Coir/Banana Fiber Reinforced Bio-Composites: Critical Review of Design, Fabrication, Properties and Applications. Kenaf Fiber Based Bio-Composites: Processing, Characterization and Potential Applications. Life Cycle Assessment Methods and Procedures and Their Role in Measuring the Sustainability Component of a Construction Technology. Natural Fiber and Synthetic Fiber Composites: Comparison of Properties, Performance, Cost and Environmental Benefits. Natural Fiber Reinforced Composites in the Context of Biodegradability: A Review. Recyclability of Natural Fiber-Filled Thermoplastic Composites. Sustainable Construction Achieved Through Life Cycle Assessment: Methodology, Limitations and the Way Forward. The Utilization of Vegetable Fibers in Cementitious Materials

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Nanocellulose Based Aerogels for Varying Engineering Applications

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Introduction

Our society are increasingly demanding products made from renewable and sustainable resources that are biodegradable, non-petroleum based and have low environmental, animal/human health and safety risks. There is a growing trend to use bio-fibers as fillers and/or reinforces in plastics composites ([Abdul Khalil *et al.*, 2012](#); [Jawaid and Abdul Khalil, 2011](#); [Abdul Khalil *et al.*, 2014](#); [Abdul Khalil *et al.*, 2016b](#); [Fatah *et al.*, 2014](#); [Abdul Khalil *et al.*, 2016a](#); [Abdul Khalil *et al.*, 2017](#)). In recent years, there is increasing interest in the development of biodegradable and/or plant derived composite materials which sometimes referred to as “green composites because of the strong global demand for creating renewable sources. In this context, cellulose and its nanostructures have gained considerable interest among the scientific community due to its inherent fascinating properties like high specific surface area, aspect ratio, mechanical properties etc., ([Gopakumar *et al.*, 2017](#)). Cellulose is a homo polysaccharide consisting of a linear chain of linked anhydroglucose units. The three hydroxyl groups on each anhydroglucose units enable the cellulose chains to assemble with each other. Nanocellulose in the form of cellulose nanocrystals and cellulose nanofibers has been the focus of a significant research interest during the last two decades. Nanocellulose is an abundant and renewable nanomaterial flexibility with chemical inertness and possibility to modify the surface chemistry. Now a days, the innovative nanocellulose aerogels have gained substantial attention in the scientific community due to their renewability, good mechanical properties, low density, high porosity, natural biodegradability, and environmental friendliness [Lavoine and Bergström \(2017\)](#). These attractive properties facilitate the use of nanocellulose aerogels in various environmental and engineering applications. This article reviews recent advancement of nanocellulose aerogels and discusses about its possibility for sustainable future materials. These materials can be applied for environmentally friendly engineering composites that surpass current technological limits of composite materials.

Extraction of Cellulose Nanofibers (CNfs) and Cellulose Nanocrystals (CNCs)

Mainly nanocelluloses are classified into (1) cellulose nanofibers (CNFs) (2) cellulose nanocrystals (CNCs) and (3) bacterial nanocellulose (BNC). The CNCs have nano dimension in both length and diameter wise, whereas CNFs have length in micro dimension and diameter is in the nano dimension is shown in [Fig. 1](#). Isolation of nanocellulose from renewable source is becoming an important area for the researchers all over the world. A lot of procedures have been reported for the extraction of CNFs from the plant cell wall. There are several mechanical treatments have been used to extract CNFs from various sources. These processes mainly include high pressure homogenization, grinding, cryocrushing and high intensity ultrasonic treatments which led to the transverse cleavage of the cellulose fibers.

Chen *et al.* reported a method to fibrillate the raw dried cotton fibers into individual cellulose nanofibers by chemical purification and pre-treatment by a high-speed blender combined with high pressure homogenization ([Chen *et al.*, 2014](#)). Abe *et al.* obtained CNFs with a uniform width of 15 nm from wood by the grinding treatment in an undried state ([Abe *et al.*, 2007](#)). Cryocrushing combined with a high-pressure fibrillation process was used by Wang & Sain for the isolation of CNFs with diameters in the range of 50–100 nm from soyabean stock ([Wang and Sain, 2007](#)). CNFs were individualized from poplar wood by explosive chemical pre-treatment and high-intensity ultrasonic treatment by Chen *et al.* When the output power of ultrasonic treatment was greater than 1000 W, CNFs were 5–20 nm in width and several microns in length were obtained ([Chen *et al.*, 2014](#)). Deepa *et al.* reported the extraction of CNFs from the banana plant by the steam explosion process in an autoclave ([Deepa *et al.*, 2011](#)). Cellulose acetate (CA) nanofibers with fiber diameter ranging from 200 nm to 1 μ m using electrospinning technique was reported by Ramakrishna *et al.* and the solvent employed was acetone/DMF/Trifluoroethylene (3:1:1) mixture ([Ma *et al.*, 2005](#)). Tibolla *et al.* isolated CNFs from banana peel bran using chemical treatment and enzymatic treatment (alkaline treatment and hydrolysis with xylanase). Nanofibers produced from enzymatic treatment had an average diameter of 7.6 nm and length in the range of 2889.7 nm ([Tibolla *et al.*, 2017](#)).

CNCs are typically prepared by acid hydrolysis of the cellulose nanofibers shown in [Fig. 2](#). The amorphous portion in the cellulose microfibrils could be hydrolysed by the strong acid treatment and resulting a rod like crystalline structures are known as cellulose nanocrystals (CNCs) or whiskers. Several types of acids have been employed for the acid hydrolysis of cellulose microfibrils that includes sulphuric acid, hydrochloric acid, oxalic acid, hydrobromic acid (HBr) and nitric acid

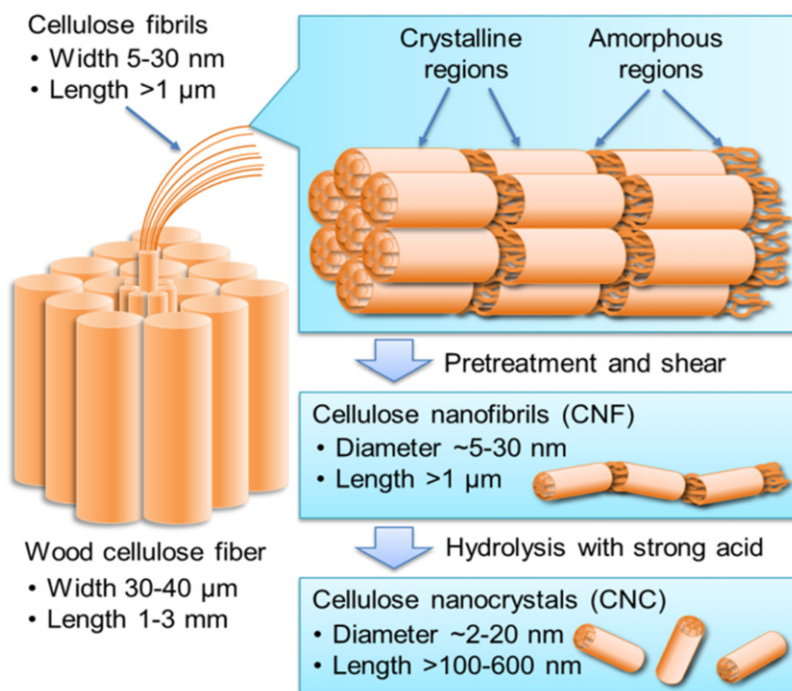


Fig. 1 Schematic representation of nanocelluloses obtained from wood cellulose fibers. The cellulose fibers are first deconstructed into microfibrils and after various processing steps into cellulose nanofibrils (CNF). Cellulose nanocrystals (CNCs) can be further obtained by using acid hydrolysis. Reproduced from Rajala, S., Siponkoski, T., Sarlin, E., *et al.*, 2016. Cellulose nanofibril film as a piezoelectric sensor material. ACS Appl. Mater. Interfaces 8, 15607–15614. doi:10.1021/acsami.6b03597. Reproduced with permission from American Chemical Society.

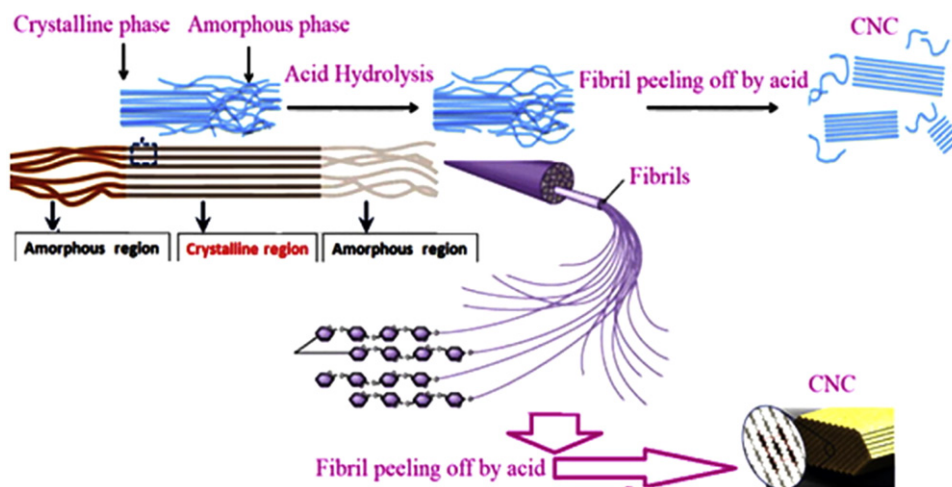


Fig. 2 Scheme illustrating the extraction of cellulose nanocrystals. Reproduced from Mishra, R.K., Sabu, A., Tiwari, S.K., 2018. Materials chemistry and the futurist eco-friendly applications of nanocellulose: Status and prospect. J. Saudi Chem. Soc. 22, 949–978. doi:10.1016/j.jscs.2018.02.005. Reproduced with permission from Elsevier Ltd.

(Maiti *et al.*, 2013; Sonia *et al.*, 2013) Among the acid hydrolysis treatments, sulphuric acid treatment of cellulosic material has been widely used to extract CNCs. Recently Danial *et al.* extracted the CNCs from waste paper by acid hydrolysis using 60% (V/V) sulphuric acid solution at 45°C with constant stirring. They obtained the CNCs with length ranged in 100–300 nm (Danial *et al.*, 2015).

Extraction processes of nanocellulose plays an important role to tune the surface chemistries of nanocellulose and in turn for enhancing the adsorption efficiency towards various viruses in the water via electrostatic attraction. Tempo mediated oxidation is another method of extraction of cellulose nanofibers, where the 2,2,6,6-tetra methyl piperidine – 1-oxyl radical (TEMPO)-mediated oxidation of celluloses for regioselective conversion of the primary hydroxyl groups to carboxylate ones. In Tempo mediated oxidation the significant amounts of carboxylate and aldehyde groups were introduced into the native cellulose fibers,

maintaining their fibrous morphologies and crystallinity (Saito *et al.*, 2007). Ma *et al.* removed the virus from aqueous solution using Tempo oxidized cellulose nanofibers. From the TEMPO/NaBr/NaClO treatment, C6 positioned hydroxyl groups of cellulose molecules were partially oxidized into carboxylate/aldehyde groups, resulted in coverage of a negatively charged surface, which was effectively adsorbed positively charged virus via electrostatic attraction (Ma *et al.*, 2011). In summary it has been showed that by changing the surface charge densities of cellulose nanofibers by different extraction process, could possible to remove various pollutants in water via electrostatic attraction.

Nanocellulose Based Aerogels and its Applications

Aerogels are ultra-light weight materials with exceptionally high porosity within their network structure. Aerogels were first reported by Kistler (1931). They prepared aerogels by subjecting a wet gel precursor to Critical Point Drying (CPD) or lyophilization (freeze drying) to remove the solvent. They had been pursued for a multitude of applications due to their combination of feasible properties such as extremely low density, low mean free path of diffusion, high specific surface area, low dielectric constant and slow speed of sound. However, their inherent fragility limited their use in various fields where mechanical robustness is needed.

The nanocellulose aerogels can be fabricated via three steps: Dissolving/dispersing cellulose or cellulose derivatives, forming cellulose gel by the sol-gel process, and drying cellulose gel while basically retaining its 3D porous structure (Moon *et al.*, 2011). Nano cellulose aerogels could be prepared by dispersing nano cellulose in water using ultrasonic or mechanical methods, followed by subsequent drying with or without solvent exchange. Pääkkö *et al.* demonstrated the formation of MFC aerogel formation using either rapid freeze drying and drying by vacuum freezing, followed by sublimation. The MFC aerogels exhibited high porosity, with nanoscale pores in sheets of agglomerated MFC and macroscale pores between the sheets. The densities ranged to 0.020 g cm^{-3} (Pääkkö *et al.*, 2008). Shamskar *et al.* obtained NCC aerogels from raw cotton and cotton stalks by freeze drying method (Rahbar Shamskar *et al.*, 2016). Jin *et al.* reported highly porous nano fibrillated cellulose aerogels, of density approximately 0.02 g cm^{-3} , by the dissolution of cellulose in aqueous calcium thiocyanate solution followed by regeneration and freeze drying. Jin *et al.* (2004) Hoepfner *et al.* reported the same dissolution method, however, super critical CO_2 drying was utilized, which lowered the density to 0.010 g cm^{-3} (Hoepfner *et al.*, 2008). Nano cellulose-based aerogels exhibits densities ranging from 1 to 200 Kg m^{-3} and their porosity can be higher than 99%. The thermal and mechanical properties of aerogels are much influenced by their pore size and morphology. The particle size and shape and interactions and their processing routes accounts for the porous architecture.

Nanocellulose Aerogel as Efficient Media for Water Purification

Water pollution has drawn much attention now-a-days because of its disastrous effect on the environment and ecosystem. Industrial wastewater often contains broad ranges of chemical pollutant species including heavy metal ions, such as Cr^{6+} , Pd^{2+} and Hg^{2+} , dyes, organic solvents, pesticides, herbicides and the like. Lack of proper treatment results in the leakage of chemical species into the groundwater, generating harmful diseases. Various techniques including chemical precipitation, biological treatment, membrane technology, electrolytic reduction, ion exchange and adsorption have been adopted to tackle this problem. Among these approaches, adsorption is the most convenient method. The emergence of nanocellulose as potential adsorbents for environmental remediation replaced the conventional waste water treatment technologies in an environment friendly manner. This method involves removal of chemical species from wastewater including heavy metal ions, pesticides, herbicides and dissolved organic pollutants. Owing to the large surface area and excellent adsorption capacities, nanocellulose, especially Cellulose nanofibers (CNFs), have been employed for the removal of pollutants from water (Mahfoudhi and Boufi, 2017).

Heavy metal removal

Kardam *et al.* prepared Cellulose nanocrystals (CNCs) from rice straw by acid hydrolysis to use them as adsorbents for Pb^{2+} , Ni^{2+} and Cd^{2+} . The adsorption capacities were relatively low reaching about 9.7 mg g^{-1} Cd^{2+} , 9.42 mg g^{-1} Pb^{2+} and 8.55 mg g^{-1} Ni^{2+} ions from 25 mg l^{-1} of metal solution (Kardam *et al.*, 2014). In addition, Yu *et al.* studied the effect of CNC modified with succinic anhydride on the adsorption properties of nanocellulose for Pb^{2+} and Cd^{2+} . Although CNCs demonstrated interesting capacities to adsorb heavy metal ions, their strong tendency to aggregate has seriously affected their practical applications in water treatment (Yu *et al.*, 2013).

Ion exchange and chemical complexation were the main two mechanisms evoked in heavy metal adsorption. The functional groups of the adsorbent surface in chemical complexation have site interactions with specific kinds of metal ions. For this reason, surface modification is necessary to increase or introduce ionizable, ionic or complexing sites on the surface of the nanocellulose on which the metal is adsorbed. Hokkanen *et al.* reported the removal of heavy metals by using amino modified nanostructured Microfibrillated nanocellulose aerogels. Carboxylic sulfate and amine were among the most prevalent groups generated to boost the adsorption capacity. They modified CNFs with 3-aminopropyltriethoxysilane (APS) which successfully adsorbed Ni^{2+} , Cu^{2+} and Cd^{2+} heavy metal ions from water (Hokkanen *et al.*, 2014).

Xu He *et al.* demonstrated for the first time, freeze dried and quaternary ammonium-functionalized aerogels from soft wood CNFs, as excellent candidates for the removal of heavy metal ion pollutants, such as those of Cr (VI) from water. The low density,

high porosity of aerogel together with its large specific surface area enabled fast and efficient removal of Cr(VI) from water. CNFs Quaternary ammonium-functionalized CNFs were prepared through a chemical reaction between CNFs and 2,3-epoxypropyl-trimethylammoniumchloride under an alkali environment. The aerogel was covalently crosslinked to stabilize the 3D structure. The aerogels retained a large specific surface area in combination with the unique porous structure leading to the rapid and efficient removal of Cr (VI) from water. With only 1 g of aerogel, more than 99% of Cr (VI) in 1 L of 1 mg/L solution could be removed in 50 min. Besides, the aerogel also exhibited excellent reusability with a decrease in the percentage adsorption from 90.9% to 84.9% (He *et al.*, 2014).

Removal of dyes

Synthetic dyes have a profound use in many large scale as well as small scale industries such as textile, paper, leather, food and cosmetic goods. Organic dye molecules chelate strongly to various metal ions which imparts toxicity to fish and other aquatic organisms. Furthermore, dyes in water bodies absorb light to impede light penetration and reduce photosynthetic activities where by inhibiting growth of aquatic flora. Dye removal from wastewater is achieved through adsorption, sedimentation, filtration, chemical coagulation, and oxidation or treatment with microorganisms. Malachite green (MG), an N-methylated diaminotriarylmethane, is a cationic dye, which has been widely used as a parasiticide, fungicide and antiprotozoan in aquaculture, medical disinfectant and anthelmintic. Accumulation of MG in living organisms can become cytotoxic, mutagenic, teratological and carcinogenic.

Jiang *et al.* fabricated an ultralight weight aerogel from TEMPO oxidized CNFs via a three-step freezing-thawing induced hydrogel formation, tert-butanol exchange and freeze-drying to a honeycomb cellular structure consisting of a few hundred μm wide irregularly shaped open cells surrounded by mesoporous (8–60 nm) thin walls of self-assembled CNFs. The macro- and meso-porous structure along with high specific surface (193 m^2/g) and negatively charged surface effected the removal of cationic dye. The MG adsorption on CNF aerogels exhibited a monolayer Langmuir adsorption isotherm with maximum adsorption of 212.7 mg/g, corresponding to participation of 46% of the total surface carboxyl's. The CNF aerogel showed over 92% MG removal efficiency in a single batch adsorption at 10:5 mg/mL aerogel/MG ratio and 100 mg/L dye concentration (Jiang *et al.*, 2017).

Removal of oil from water

Like other industrial wastes, oil leakage has also added much to the issue. Several physical, chemical and biological methods such as *in situ* burning, chemical treatments, bioremediation have been developed to tackle with this problem. Among these, physical absorption via absorbents is considered the most promising way as it is cost-effective and does not generate by products. For an effective sorption to occur, the sorbents should possess high sorption capacity and porosity, oil/water selectivity, and a fast sorption rate. Conventional oil and chemical sorbent materials can be grouped into three major classes: Inorganic mineral sorbents, synthetic polymer sorbents, and natural organic sorbents. Inorganic mineral sorbents and synthetic sorbents are highly oleophilic and hydrophobic. However, they degrade or disintegrate very slowly. Natural sorbents on the other hand, have moderate sorption capacity, comparable or sometimes lower density than inorganic and synthetic sorbents, and excellent biodegradability. Currently, research has been focused on developing novel, high quality materials with low density and high sorption capacity, that are bio-degradable and ecofriendly.

Nanocellulose aerogels as absorbents have attracted considerable research interests due to their high absorption capacities (more than 40 times by weight), environmental friendliness, biodegradability and sustainability. In addition, their high compression strength and high flexibility, which accounts for their reusability, also makes them suitable for absorption of oil and other organic pollutants. Yet, the inherent high hydrophilicity of the nanocellulose surface, reduces the oil/water selectivity and destroys the porous structure of the cellulose aerogels (Jin *et al.*, 2011). Hydrophobization of the nanocellulose surface is being done to address the above difficulty.

Korhonen *et al.* demonstrated such a material, based on functionalized cellulose nanofibrils, where cellulose is natural, renewable and the most abundant polymer. They prepared highly porous nanocellulose aerogels via vacuum freeze drying from microfibrillated cellulose hydrogels. They showed that by functionalizing the native cellulose nanofibrils of the aerogel with a hydrophobic titanium dioxide oleophilic coating to selectively absorb oils from water. Because of the low density and ability to absorb non-polar liquids and oils up to nearly all of its initial volume, the surface modified aerogels could remove organic contaminants from the water surface as shown in Fig. 3. They showed that the absorption was close to the overall volume of the aerogel (80%–90% vol/vol) and the mass-based adsorption capacity varies from 20 to 40 (wt/wt) depending on the density of the liquid. They concluded that the nano cellulose based aerogels will be a good promising candidate as oil absorbents for future sustainable applications (Korhonen *et al.*, 2011).

Another work was done by Jin *et al.* and they demonstrated the super hydrophobic and super oleophobic nanocellulose aerogels, consisting of fibrillar networks and aggregates with structures at different length scales, support considerable load on a water surface and on oils. They showed that the load carrying capacity of the aerogels might be a few orders of magnitude larger than the weight of the aerogel itself. They suggested that this would open up a new platform for carriers or for coatings that have large load bearing capability on various organic and aqueous liquids including oil-polluted water (Jin *et al.*, 2011). Another interesting work was done by Meng *et al.* and they reported a sponge-like nanocellulose-based carbon aerogels for oil absorption. They prepared carbon aerogel material via heat treatment of cellulose microfibril aerogel. They showed that this aerogel was useful as a highly porous oil absorbent (99% of porosity) with ultra-light density (0.01 g/cm^3), hydrophobic properties (144° static

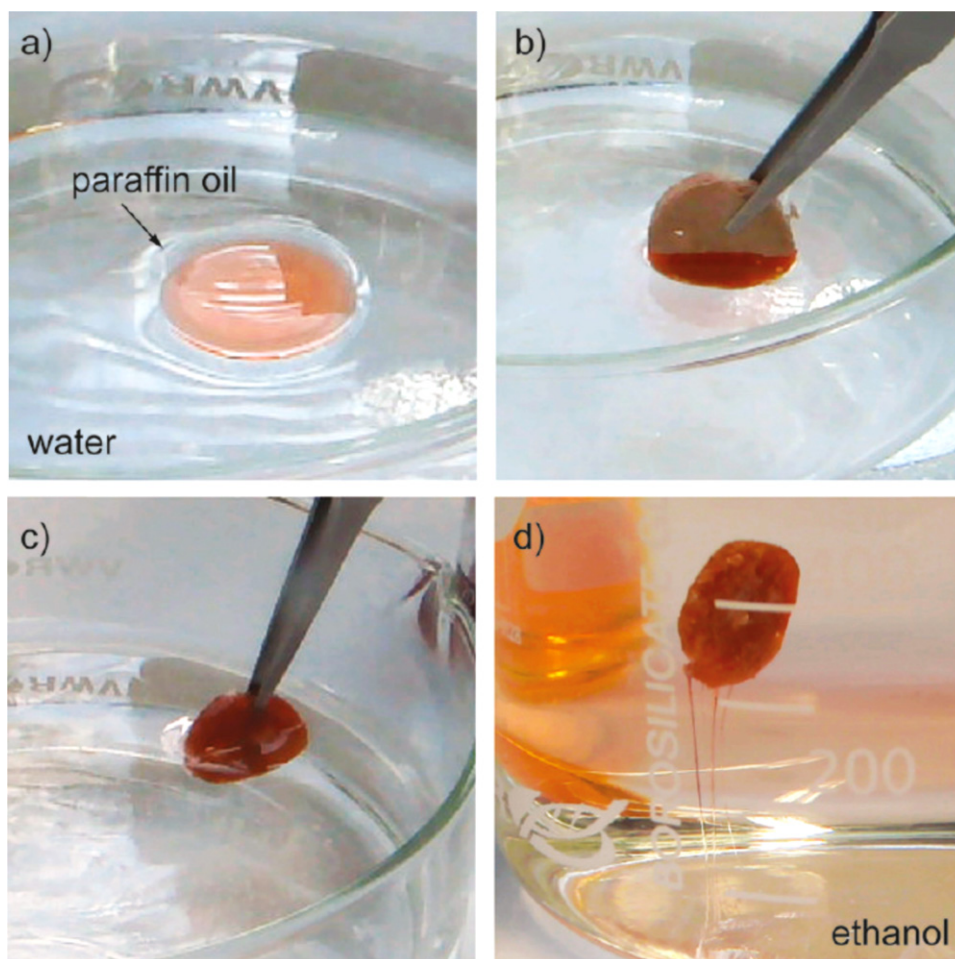


Fig. 3 Oil spill removal from water. (a) Paraffin oil (colored for clarity) floating on water; (b) the oil being absorbed into the aerogel; and (c) all of the floating oil has been absorbed. (d) The oil-filled aerogel can be washed simply by immersing it in a solvent, such as ethanol. The oil gets removed as shown by the red streaks. Reproduced from Korhonen, J.T., Kettunen, M., Ras, R.H.A., Ikkala, O., 2011. Hydrophobic nanocellulose aerogels as floating, sustainable, reusable, and recyclable oil absorbents. *ACS Appl. Mater. Interfaces* 3, 1813–1816. doi:10.1021/am200475b. Reproduced with permission from American Chemical Society.

contact angle), fast absorption rate and multiple reusability as shown in the Fig. 4. Their investigations revealed that carbon aerogel which was heat treated at 700° C had higher oil absorption capacity of various types of oils. This was due to the fact that 3D-network structure formed by the entanglement of carbonized cellulose fibrils and the large surface energy of carbonized fibers. They concluded that the unique properties of carbon aerogel from nanocellulose, along with the advantages of using a natural renewable, low cost and sustainable material, recommend carbon aerogel for a wide range of oil-spill clean-up applications (Meng *et al.*, 2015).

Feng *et al.* reported about the advanced fabrication and oil absorption properties of super-hydrophilic recycled cellulose aerogels. They coated the recycled cellulose aerogels with methyl/trimethoxysilane (MTMS) via chemical vapour deposition yielded, a very stable super hydrophobicity for over five months and excellent oil absorption capacities upto 95 gg⁻¹ with the 0.25 wt% cellulose aerogel. It was shown that the initial cellulose fiber concentration significantly affects the oil absorption capability of the developed cellulose aerogels. They concluded that the demonstrated super-hydrophobic recycled cellulose aerogels could be one of the very promising sorbents for oil spill cleaning as shown in the Fig. 5 (Feng *et al.*, 2015).

Zhang *et al.* fabricated a highly efficient cellulose based aerogel with high mechanical strength via novel method. The prepared aerogel possessed perfect 3D skeleton and interconnected pores similar to the honey comb, exhibiting excellent oil/water selectivity. In addition, the demonstrated aerogels exhibited stable super hydrophobic and superoleophilic properties even towards a strong mechanical abrasion. Moreover, they showed that demonstrated cellulose aerogels can be reused up to 30 cycles (Zhang *et al.*, 2016). Wang *et al.* reported an ultra-weight; elastic, cost-effective, highly recyclable super absorbent from microfibrillated cellulose fibers for oil spillage cleanup. They demonstrated a simple method to produce a low cost highly recyclable super absorbent from renewable cellulose fibers via simple and environmentally friendly microfibrillation treatment and freeze drying. The demonstrated

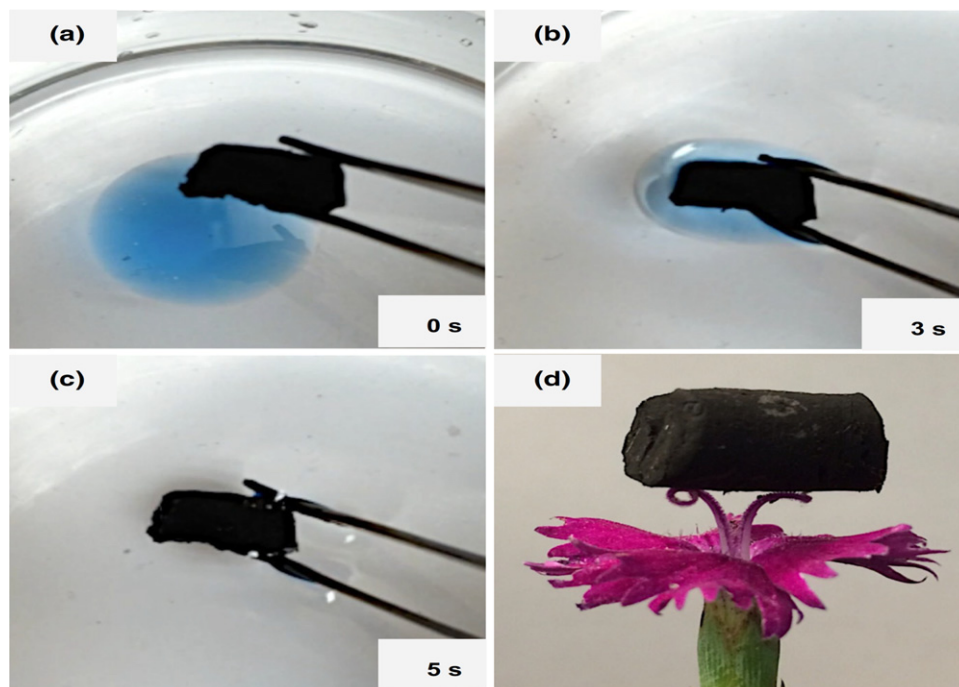


Fig. 4 (a–c) Removal of engine oil from the water surface using nanocellulose carbon aerogel. d Ultralight carbon aerogel sitting on a flower. Reproduced from Meng, Y., Young, T.M., Liu, P., *et al.*, 2015. Ultralight carbon aerogel from nanocellulose as a highly selective oil absorption material. *Cellulose* 22, 435–447. doi:10.1007/s10570-014-0519-5. Reproduced with permission from Springer.

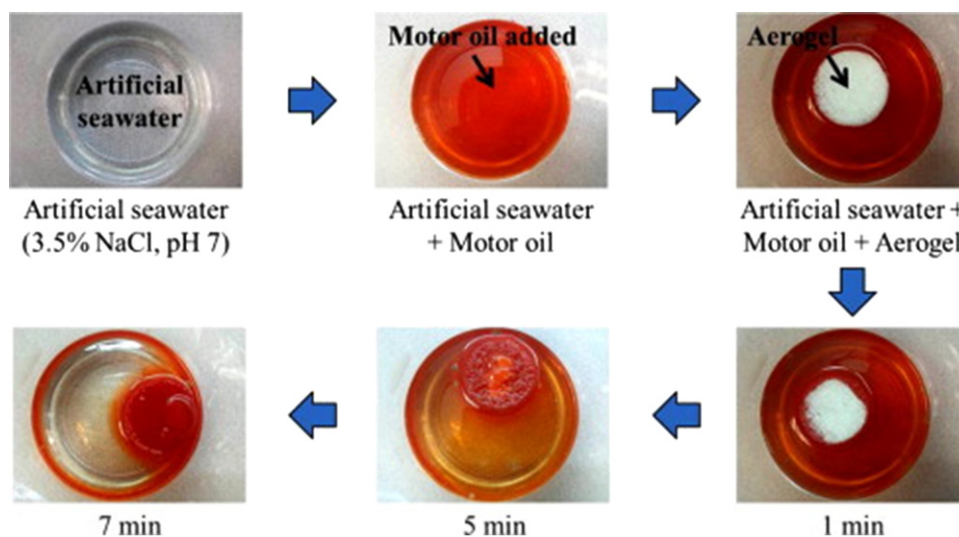


Fig. 5 Oil absorption process of the recycled cellulose aerogel having 5.0 wt.% of the cellulose fibers in the artificial seawater (3.5% NaCl and pH=7) mixed with the 5w40 motor oil and dyed with Sudan Red G before testing. Reproduced from Feng, J., Nguyen, S.T., Fan, Z., Duong, H.M., 2015. Advanced fabrication and oil absorption properties of super-hydrophobic recycled cellulose aerogels. *Chem. Eng. J.* 270, 168–175. doi:10.1016/j.cej.2015.02.034. Reproduced with permission from Elsevier Ltd.

hydrophobic superabsorbent could selectively absorb oil from an oil-water mixture and showed an ultra-high absorption capacity of 88–228 mg/g, which was comparable to those of other novel carbon-based super absorbents. More importantly, the superabsorbent showed excellent flexibility and could be repeatedly squeezed without structure failure (more than 30 times) (Wang *et al.*, 2015).

Nanocellulose Aerogels as Air Filters

Nano celluloses can be used as components in porous materials with large specific surface areas to create high performance products such as filters, adsorbents, catalyst supports, cell culture substrates, thermal insulators, and drug carriers (Metreveli *et al.*, 2014).

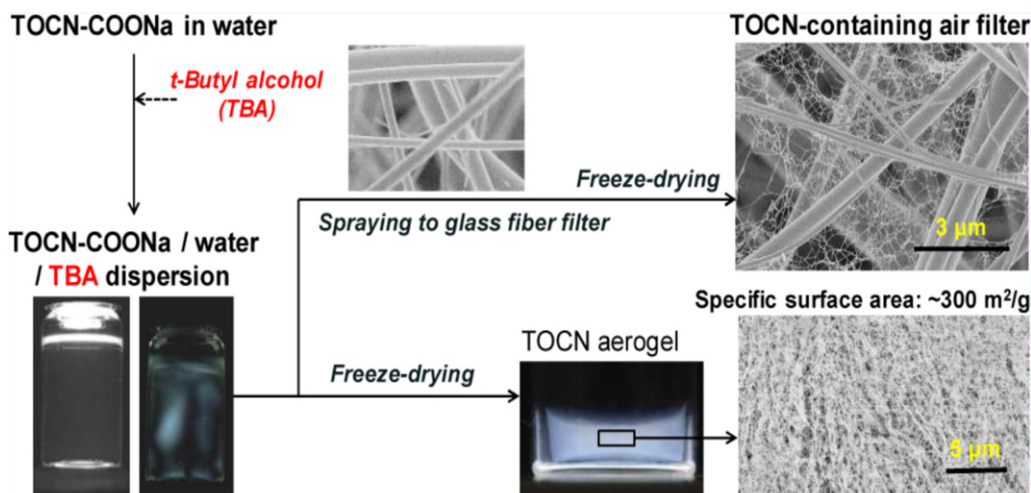


Fig. 6 Strategy for the preparation of TOCN aerogel. Reproduced from Nemoto, J., Saito, T., Isogai, A., 2015. Simple freeze-drying procedure for producing nanocellulose aerogel-containing, high-performance air filters. *ACS Appl. Mater. Interfaces* 7, 19809–19815. doi:10.1021/acsami.5b05841. Reproduced with permission from American Chemical Society.

Generally good air filters have high air permeability (i.e., low pressure drop), and large surface areas that can capture more particles (Podgórski *et al.*, 2006). Nano celluloses are a promising candidate for air filter applications due to its fibrous nature which reduce the resistance in filters and thereby enhance the frequency of collision of particles with the fibers (Mao *et al.*, 2008).

Nemoto *et al.* reported a (2,2,6,6-tetramethylpiperidine-1-oxyl) TEMPO oxidized nanocellulose aerogel for the high-performance air filtration application (Nemoto *et al.*, 2015). They prepare TEMPO oxidized aerogel freeze drying of the TEMPO-oxidized cellulose nanofibril (TOCN) dispersions with tert-butyl alcohol (TBA) mixture as shown in the Fig. 6. They observed that the TOCNs were homogeneously dispersed in the water/TBA mixtures at TBA concentrations up to 40% w/w. They found that when a commercially available, high-efficiency particulate air (HEPA) filter was combined with TOCN/water/TBA dispersions prepared using 30% TBA, and the product was freeze-dried, the resulting TOCN aerogel-containing filters showed superior filtration properties. They concluded that the enhanced filtration efficiency of the demonstrated TEMPO nanocellulose aerogels was due to its nanoscale, spider-web-like networks of the TOCNs with large specific surface areas as shown in the Fig. 7.

Another work was reported by Lu *et al.* and they fabricated a novel air filter with spider-web-like structure based on renewable and biodegradable fibrillated cellulose fibers. They demonstrated an effective strategy for network structure regulation during freeze-drying process. Their results showed that the air filter with spider-web-like structure, whose filtration efficiency for model PM particles with the diameter of 300 nm could exceed 99%, was obtained from a fibrillated cellulose fiber/water/Tert-Butyl Alcohol (TBA) mixture by freeze-drying. They concluded that the demonstrated work paved a way to fabricate high-performance air filters based on renewable materials (Lu *et al.*, 2018).

Nanocellulose Aerogel for Flame Retardant Applications

Cellulose aerogels are ultralight three-dimensional porous materials, which combine the excellent properties of highly porous aerogels such as high specific surface area, low density, low thermal conductivity, and high insulation, with the fantastic properties of sustainable biopolymers such as biodegradability and biocompatibility. Cellulose aerogel is considered one of the most promising heat insulating materials due to its abundant internal pores and good thermal insulation performance. However, nanocellulose aerogels are easy to ignite, which is the main limitation to its wide applicability in many commercial applications. In this context, the researches have been more focused to develop the flame retardant nanocellulose aerogels while maintaining their unique properties for varying technological application. He *et al.* reported a facile strategy to construct flame retardant, sound-adsorption and mechanical enhancement cellulose-based composite aerogels by the incorporation of aluminum hydroxide nanoparticles (AH NPs) into cellulose gels via an in-situ sol-gel process followed by freeze-drying to coat AH NPs on cellulose composite aerogels (AH NPs@cellulose composite aerogels) as shown in the Fig. 8.

The prepared composite cellulose aerogels showed excellent flame retardancy, the peak of heat release rate (PHRR) of the composite aerogels decreased significantly from 280 W/g of the control sample to 22 W/g, and total heat release (THR) of the composite aerogels decreased remarkably from 13.2 kJ/g to 1.6 kJ/g as shown in the Fig. 9.

Moreover, the incorporation of AH NPs composite aerogels exhibited remarkable mechanical properties, the compressive strength of the composite aerogels increased significantly from 0.08 to 1.5 MPa. In addition, AH NPs composite cellulose aerogels have excellent sound absorption at high frequencies with a maximum sound absorption coefficient of 1. In summary, they concluded that the demonstrated work was a facile strategy to rationally construct flame retardant, mechanically robust,

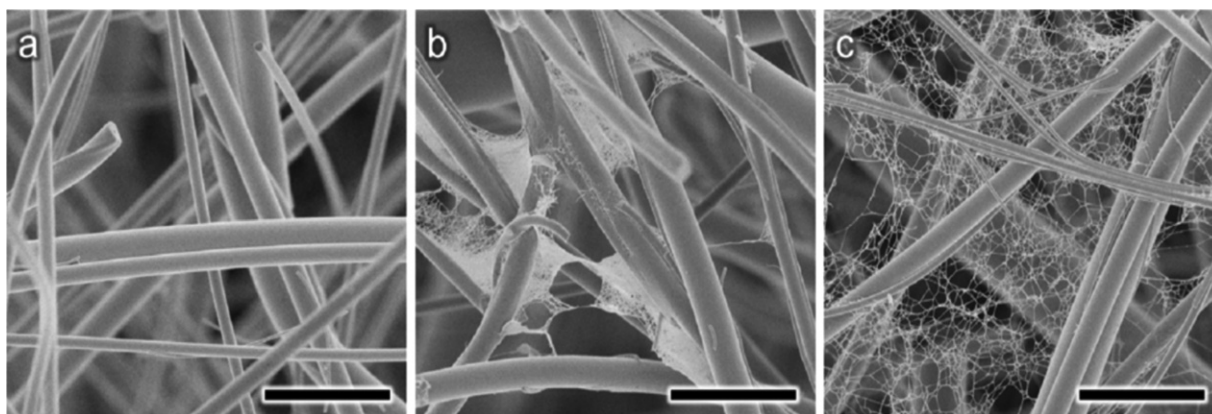


Fig. 7 SEM images of the surfaces of the base filter (a), the TOCN aerogel-containing filters prepared with TOCN/water dispersions (b), and TOCN/water/TBA dispersions (c). The scale bar represents 3 μm . Reproduced from Nemoto, J., Saito, T., Isogai, A., 2015. Simple freeze-drying procedure for producing nanocellulose aerogel-containing, high-performance air filters. *ACS Appl. Mater. Interfaces* 7, 19809–19815. doi:10.1021/acsami.5b05841. Reproduced with permission from American Chemical Society.

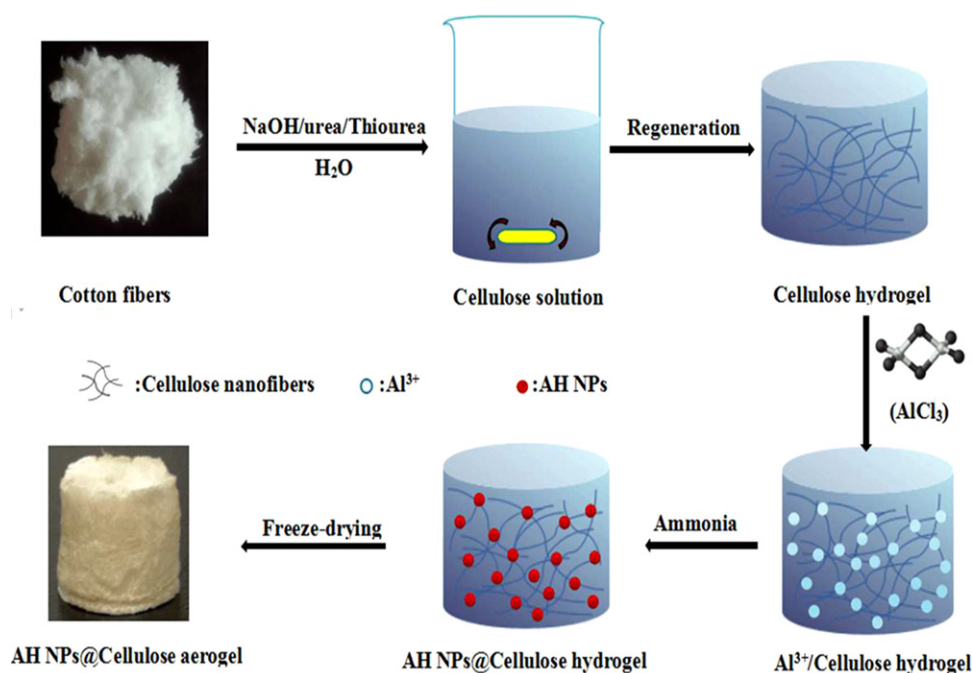


Fig. 8 Schematic illustration of the in-situ synthesis of AH NPs@cellulose composite aerogels. Reproduced from He, C., Huang, J., Li, S., *et al.*, 2018. Mechanically resistant and sustainable cellulose-based composite aerogels with excellent flame retardant, sound-absorption, and superantwetting ability for advanced engineering materials. *ACS Sustain. Chem. Eng.* 6, 927–936. doi:10.1021/acssuschemeng.7b03281. Reproduced with permission from American Chemical Society.

high-efficiency sound-adsorption and superamphiphobic cellulose-based composite aerogels, which have promising applications in the future as green engineering materials (He *et al.*, 2018).

Yuan *et al.* prepared cellulose-silica composite aerogels by in situ formation of silica nanoparticles via a two-step sol-gel process in cellulose gel, which was prepared by dissolving cotton pulp in 1-allyl-methylimidazole chloride ionic liquid (AmimCl) and then regenerating from AmimCl/water bath. The results showed that the composite aerogels displayed an enhanced transparency, compressive properties, and thermal and thermal-oxidative stability with increasing of silica content. They found that the incorporation of silica nanoparticles also improved the mesoporous characteristics of aerogels including specific surface area and mesopore volume, and significantly delayed the decomposition of cellulose, suppressed the heat release during combustion. The composite aerogels with high silica content (33.6% or more) exhibited good transparency with light transmittance as high as 78.4% at 800 nm, even higher than the neat cellulose aerogels, and presented excellent flame-retardant performance, achieving self-extinguishment after ignition. They conclude that the transparent cellulose-silica composite aerogels with enhanced

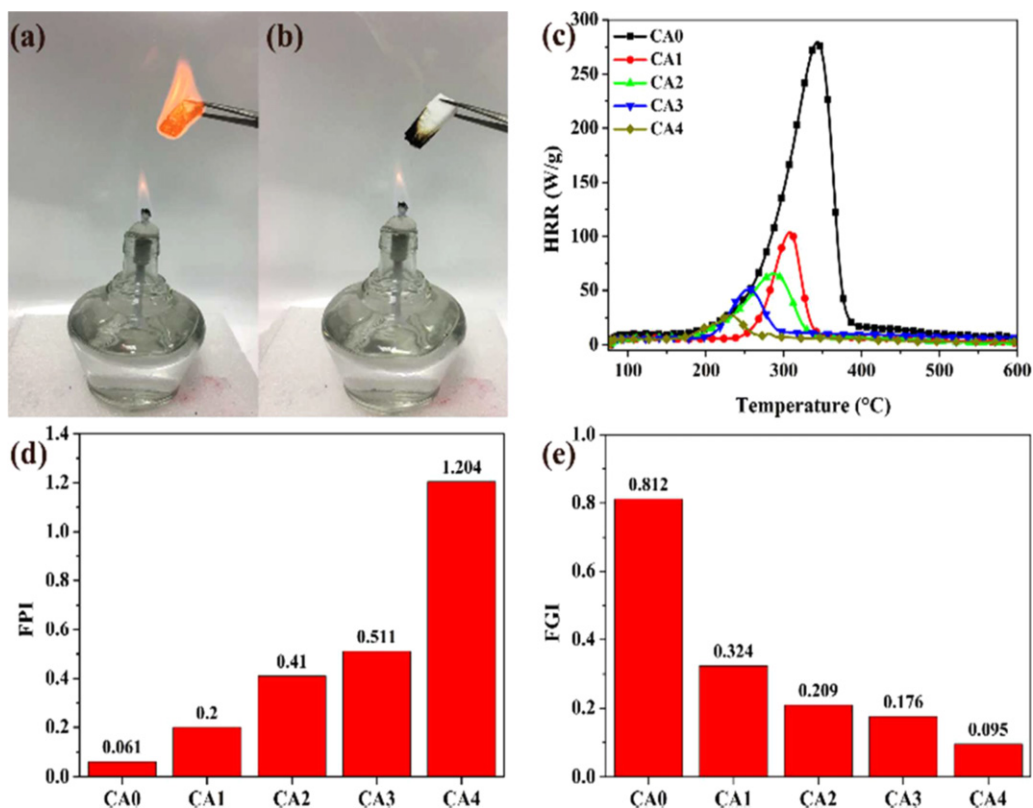


Fig. 9 Optical images of cellulose aerogels (a) and AH NPs@cellulose composite aerogels (b) captured after ignition by an alcohol burner. HRR curves (c) of cellulose aerogel and AH NPs@cellulose composite aerogels measured by MCC. MCC fire performance index (d) and fire growth index (e) for all samples. Reproduced from He, C., Huang, J., Li, S., *et al.*, 2018. Mechanically resistant and sustainable cellulose-based composite aerogels with excellent flame retardant, sound-absorption, and superantitwetting ability for advanced engineering materials. ACS Sustain. Chem. Eng. 6, 927–936. doi:10.1021/acssuschemeng.7b03281. Reproduced with permission from American Chemical Society.

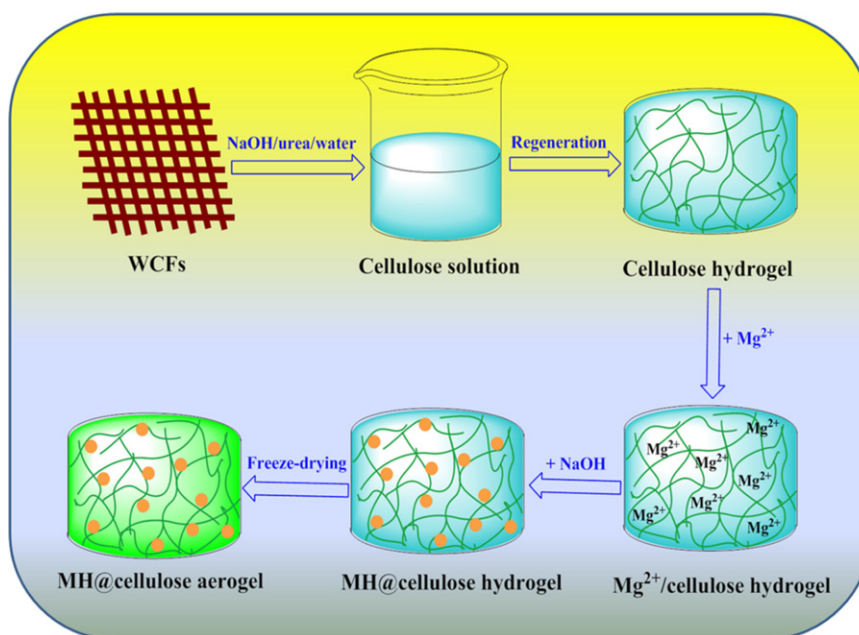


Fig. 10 Schematic illustration of the in-situ synthesis of MH NPs@ cellulose composite aerogel. Reproduced from Han, Y., Zhang, X., Wu, X., Lu, C., 2015. Flame retardant, heat insulating cellulose aerogels from waste cotton fabrics by in situ formation of magnesium hydroxide nanoparticles in cellulose gel nanostructures. ACS Sustain. Chem. Eng. 3, 1853–1859. doi:10.1021/acssuschemeng.5b00438. Reproduced with permission from American Chemical Society.

mechanical performance and improved flame retardancy might show great potential in a wide variety of applications (Yuan *et al.*, 2017).

Another interesting work was reported by Han *et al.* and they fabricated flame retardant cellulose aerogels from waste cotton fabrics by in situ synthesis of magnesium hydroxide nanoparticles (MH NPs) in cellulose gel nanostructures, followed by freeze-drying as shown in the Fig. 10. They also found that the three dimensionally nanoporous cellulose gel prepared from the NaOH/urea solution could serve as scaffold/template for the non-agglomerated growth of MH NPs (Han *et al.*, 2015).

Conclusion

Nanocellulose has gained considerable attention in last 10 years among the scientific community due to its fascinating properties and sustainable nature. Among the nanocellulose, cellulose nanofibers and cellulose nanocrystals has been becoming very popular due to its ease of preparation and fabrication methods. Cellulose aerogels are ultralight three-dimensional porous materials, with excellent properties like high specific surface area, low density, low thermal conductivity, and high insulation, with the fantastic properties of sustainable biopolymers such as biodegradability and biocompatibility. These properties make nanocellulose aerogel as efficient substrate for various engineering applications. Nanocellulose possesses a blend of properties suitable to produce ultralight, strong and flexible foams and aerogels for various technological applications. Numerous processing procedures have been established that enabled the production of nanocellulose-based foams and aerogels with a tunable porosity and pore architecture. The recent advances in nanotechnology have proved that, the research on nanocellulose-based foams and aerogels will be continued to grow. Future focus will be on designing of the novel methodologies to fabricate light weight materials with fascinating properties from nanocellulose for specific engineering applications

See also: Bacterial Cellulose Based Nanocomposites for Electronic and Energy Applications. Cellulose Nanocrystal as a Prospective Reinforcement for Polymer Matrix Nanocomposites. Green Composites From Sustainable Cellulose Nanofibrils

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Natural Fiber Composites: Review of Recent Automotive Trends

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Introduction

Plastic waste is a growing concern in today's society, well-acknowledged by both government and private sectors. Waste disposal and recycling are simply not enough to manage completely the enormous volume of waste produced. Moreover, petroleum product demand is increasing while supply is uncertain.

The industrial sector has responded by looking for new material substitutes that reduce dependence on petroleum and fossil fuels (Salazar *et al.*, 2011; Faruk *et al.*, 2012; Al-Oqla and Sapuan, 2014). Natural fiber composites (NFCs) present an excellent solution to this problem. Composites are made from two or more constituent materials – matrix and reinforcement fiber – with significantly different physical or chemical properties to produce a new material, which has better properties than the individual components alone. NFCs consist of natural fiber reinforcement (made from fibers such as kenaf, flax, hemp, coir or cotton) incorporated into a (typically) polymer- or ceramic-based matrix (Taj *et al.*, 2007; Smitthipong *et al.*, 2013).

NFCs have become an exciting selection for the automotive industry because of their numerous advantages. Many researchers have demonstrated the mechanical, economic, and environmental benefits of NFCs (Mueller *et al.*, 2001; Kalia *et al.*, 2011; Savage and Evans, 2014; Mitschang and Hildebrandt, 2012). Natural fibers have been shown to enhance composite mechanical performance, reduce weight and processing time, decrease production cost, and improve passenger safety and shatterproof performance (Chen, 2005). They are also biodegradable, nonabrasive to processing equipment, and can be used as acoustic and thermal insulators (Alves *et al.*, 2010). Moreover, the combination of thermoplastic matrix and natural fiber can provide other desirable properties such as high resistance to adverse environmental conditions (moisture and UV radiation), as well as providing significant stiffness and hardness (Salasinska and Ryszkowska, 2012) and superior vibration damping characteristics. The latter is significant as the addition of damping materials to address noise, vibration and harshness is an increasing percentage of vehicle mass (National Research Council, 2011).

The aim of this article is to review the current state of NFC technology and its level of implementation in the automotive sector. In so doing, it is hoped that the work will stimulate innovation and development in these new environmentally responsible products while at the same time spur further adoption of the technology in the automotive industry.

Background

Natural Fiber Properties and Potential

Natural fibers are generally classified into two broad categories: wood fibers and nonwood fibers (see Fig. 1). The most extensively studied and used fibers in automotive applications are nonwood fibers, especially those collected from the bast of plants (e.g., flax, hemp, jute and kenaf) and from leaves (e.g., sisal and henequen) (Faruk *et al.*, 2014; Mohanty *et al.*, 2002). However, researchers and industry proponents have also given significant attention to seed fibers (e.g., cotton, coir and coconut) as well as straw and grass fibers (e.g., wheat straw, bagasse, and bamboo) as viable options for composites.

Natural fibers offer environmental, economic and technical advantages when compared to synthetic fibers. Table 1 summarizes general attributes of various bast, leaf and seed fibers, side-by-side with traditional reinforcement fibers, glass and carbon. In this broad comparison, plant fibers show advantages in terms of cost and density but they especially stand out in terms of environmental benefits. Unlike synthetic fibers, they are biodegradable, carbon sequestering, and cause no human health concern during production. Also, natural fibers are not just renewable, but rapidly renewable with some species capable of being harvested up to six times per year (Beda Ricklin, 2015). Indeed, sustainability is one of the main drivers behind the eco-car trend and as public awareness increases on the sustainable aspects of plant fibers, they will likely gain more attention for commercial use.

Generally, natural fibers have high aspect ratios while the structure of the fiber is hollow and laminated with molecular layers in an integrated matrix. This anatomical structure results in excellent technical capabilities with low density and consequently, high strength-to-weight ratios. The specific mechanical properties are comparable with that of glass fibers. Fig. 2 compiled from published values in the literature (Koronis *et al.*, 2013; Dittenber and Gangarao, 2012; Shah, 2013; Yan *et al.*, 2014; Dicker *et al.*, 2014; Zini and Scandola, 2011; Bismarck *et al.*, 2006) provides a visual comparison of the range and potential of specific stiffness and strength for many commercially used fibers. The comparison is favorable for several types of natural fibers. Most species have higher potential specific stiffness than glass and for many, the specific strength is quite comparable to glass. While the wide range of properties is relective of the well-known inherent material variability of natural fibers (ie, quality of fiber varies due to growing climate or processing methods), it is also partially due to differing conditions between studies, such as different fiber moisture content or test methods employed (Faruk *et al.*, 2014).

It is important to note that in order to improve the mechanical properties of the composite, modification of the natural fiber surface is necessary. Almost all natural fibers are hydrophilic and, generally, polymer matrixes are hydrophobic so the compatibility of the two materials is poor. Therefore, modification is an important step prior to mixing them. Commonly, research interests lay in modification



Fig. 1 Examples of raw natural fibers: (A) rice straw, (B) wood, (C) kenaf, (D) flax, (E) sugar cane and (F) cotton ball.

Table 1 Broad comparison of natural and synthetic fiber attributes

Attributes	Plant fibers	Glass fibers	Carbon fibers
<i>Environmental</i>			
Renewable	Yes ^a	No	No
Biodegradable	Yes ^a	No	No
Carbon sequestering	Yes ^a	No	No
Human health safe	Yes ^a	No	No
Recyclable	Yes ^a	Partly	Partly
<i>Economic</i>			
Cost of raw fiber (USD/kg)	Low (~0.3–4.5) ^a	Low to moderate (~2–32)	High (>100)
<i>Technical</i>			
Density (g/cm ³)	Low (~1–1.6) ^a	High (2.5–2.7)	Low (1.7–2.2)
Tensile stiffness (GPa)	Moderate (~10–100)	Moderate (70–85)	High (15–500) ^a
Tensile strength (MPa)	Low (~250–1500)	Moderate (2000–3700)	High (1300–6300) ^a
Specific tensile stiffness (GPa/g · cm ³)	Moderate (~10–100)	Low (27–34)	High (68–290) ^a
Specific tensile strength (MPa/g · cm ³)	Moderate (~200–1400)	Moderate (700–2250)	High (600–3700) ^a
Strain at tensile failure (%)	Low (~1.2–3.5)	High (2.5–5.3)	Low (0.3–2.2) ^a

^amost desirable.

Source: Adapted from Shah, D.U., 2013. Developing plant fibre composites for structural applications by optimising composite parameters: A critical review. Journal of Materials Science 48(18), 6083–6107. Available at: <http://link.springer.com/10.1007/s10853-013-7458-7> (accessed 7.05.15).

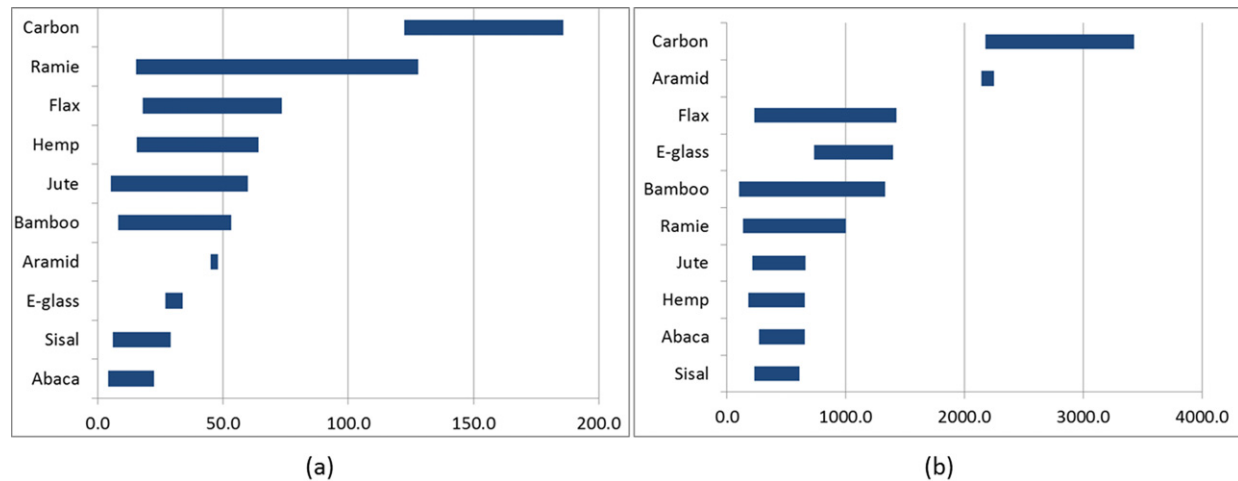


Fig. 2 Broad comparison of specific tensile properties of various reinforcing fibers: (a) Young's modulus (GPa) and (b) tensile strength (MPa).

Table 2 Pros and cons of NFC in automotive applications

Pros	Cons
Low density and lightweight leading to the weight reduction of 10%–30% in comparable parts	Concerns over the unevenness of the fiber supply and long term availability of fiber
Sustainable and renewable resource	Could be more expensive if fully bio-based and biodegradable
Good mechanical and manufacturing properties	Extremely sensitive to moisture and temperature
Relatively good impact performance	Uncontrolled biodegradable can occur
Occupational health advantages in assembly and handling compared to glass fiber	High variability properties
Biodegradable (if proper matrix is used)	
Good thermal and acoustic insulation properties	
Relative cost advantages compared to conventional constructions	
Low energy consumption	

of the natural fiber more than in the polymer matrix. Modification depends on either chemical or physical techniques, mainly focused on grafting between the natural fibers and the matrix to improve interfacial interaction (La Mantia and Morreale, 2011). For example, coupling agents (trichloro-s-triazine and di-methylol melamine) can create covalent bonds between the cellulose and the polymer matrix (Zadorecki and Flodin, 1986), or chemical treatment with sodium hydroxide, isocyanate and peroxide can increase bonding between sisal and a PE matrix thereby enhancing mechanical properties of the composite (Joseph *et al.*, 1996).

It is speculated that the next generation composite will be a hybrid consisting of two or more fiber types in a polymer matrix (Sathishkumar *et al.*, 2014). Possible combinations of hybrid composites include natural/natural, natural/synthetic and synthetic/synthetic fibers. Hybrid composite materials have wide applications in the field of engineering due to low cost, strength-to-weight ratio and ease of manufacturing (Nunna *et al.*, 2012). They provide the possibility of achieving a blend of properties (such as stiffness, ductility and strength), which cannot be achieved by single fiber-reinforced composites. Hybrid composites also possess increased fatigue life, better fracture toughness and lower notch sensitivity compared to single fiber-reinforced composites. Research on various combinations of synthetic fiber-based hybrid composites revealed that they had certain advantages like high specific strength, high toughness, and high impact resistance (Shahzad, 2011).

Challenges of Using Natural Fibers

Although there are many positive aspects of using NFCs, there are also negative factors that prevent a more widespread adoption of the technology. Advantages and disadvantages are summarized in Table 2 (Fung and Hardcastle, 2001; Bledzki *et al.*, 2006). For example, sensitivity of the natural fiber to moisture and temperature currently restricts most NFC applications to interior parts (e.g., trim in dashboards, door panels, parcel shelves, seat cushions, backrests, and cabin lining).

It should also be noted that the challenges that NFCs have in becoming more broadly adopted by the automotive industry are in many ways representative of the challenges faced by composite materials in general, and are not exclusive to NFCs. For example, the BMW i3 and i8 are being touted as the first mass production automobiles based upon a composite architecture. Nonetheless, the increase of public awareness of environmental problems about what to do with nondegradable, nonrecyclable contents at

the end of product life is having an impact on the industry to favor switching from synthetics to natural fibers. To this end, the United States and Europe have both issued specific directives on end-of-life vehicles. The European Commission implemented a "European Guideline 2000/53/EG" that set a goal of improving automotive recyclability to 85% of a vehicle (by weight) being recyclable for 2005. This percentage will be increased to 95% by 2015 (European Parliament and Council of the European Union, 2000). Such legislation is a significant driving factor toward the adoption of NFCs. It also represents a broader accounting of the environmental and social cost of industrial production.

Commercial Implementation

Processing Techniques and Products

In general, production technologies for NFCs are similar to those for the production of glass fiber composites. During processing, temperatures must not exceed 200°C, and the time that the material is exposed to high temperature should not be too long, to avoid destruction of the fibers. Compression molding, injection molding, extrusion, thermoforming, resin transfer molding and sheet molding are common processes used to manufacture NFCs.

Table 3 presents some popular NFC products: their trade names, constituents, processes, and applications that are produced by automotive interior companies, Johnson Controls and FlexForm Technologies. The properties of these materials are summarized

Table 3 Commercial NFCs products and their respective constituents, fabrication process and applications

Product trade name	Fibers/polymer	Process	Automotive applications
Fibrit (in production since 1954)	Wood fiber (offcuts from sawmill processing)/acrylic resin	Wet forming process of wood fiber (94%)/acrylic resin mat Compression molded at 230–250°C	Carrier for covered door panels Covered or foamed instrument panels Covered inserts (currently in production for Mercedes-Benz, Opel)
Fibrowood (in production since 1998)	Wood fiber/acrylic resin, synthetic fiber	Preimpregnated needled wood fiber felt (wood fiber (70%) mixed with acrylic resin and synthetic fiber binder) Compression molded at 220°C	Carrier for covered door panels Covered or foamed instrument panels Covered inserts and components Covered seat back panels (currently in production for BMW, Ford, Mercedes-Benz, Opel, Hyundai)
PP-NF for injection molding	Fibrowood recycles/polypropylene granules, thermoplastic	Compounded shredded fibrowood recycles with PP → injection molding	Plastic retainer for seat back panel
Wood-stock (in production since 1982)	Wood flour/polypropylene or polyolefin	Extruded of thermoplastic sheet based on polyolefin and wood flour → the mat is heated in an infrared oven → compression molded in a low-temperature tool (coupling of the coverstock, additional inserts and cutting of holes as well as perimeter is carried out in a one-step process)	Carrier for covered door panels Carrier for armrest Carrier for covered inserts (currently in production for FIAT, Lancia, Alfa Romeo)
EcoCor (in production since 2000)	Bast fibers (flax, hemp, kenaf, etc.)/polypropylene	Bast fibers (50%)/PP fiber felt → heated to over 200°C → compression molded in a low-temperature tool (<40°C) → the coverstock can be applied in a one-step manufacturing process	Carrier for covered door panels Covered components for instrument panels Covered inserts Carrier for hard and soft armrests Seat back panels (currently in production for Dodge, Ford, Mercedes-Benz, Opel, Porsche, Volkswagen)
Natural mat with epoxy resin (NF-EP) (in production since 2003)	Natural fiber mat (flax or hemp)/epoxy resin	A natural fiber mat (flax or hemp) is imbued with epoxy resin (natural fiber content of NF-EP is 70%) → compression molded using a high-temperature tool (150°C) → the carrier can be laminated with TPO, textile or leather	Carrier for covered door panels (currently in production for BMW)
FlexForm	Bast fibers (flax, hemp, kenaf, jute and sisal)/polypropylene and polyester	50% bast fiber/50% PP non-woven mat → thermoformed at 200°C and 0.379 MPa using matched metal tooling	Door panels, door bolsters, headliners, side and back walls, seat backs, rear deck trays, pillars, center consoles, load floors, trunk trim (currently in production for Mercedes-Benz, Chrysler (DCX), Ford, GM, Honda, and Nissan)

in **Table 4** and some examples of these products are shown in **Fig. 3** (Bledzki *et al.*, 2006; Johnson Controls Inc., 2015; Promper, 2010; Flexform, 2015).

Applications

Automotive applications of NFCs can be traced as far back as the 1940s, when Henry Ford developed the first composite car using hemp fiber. The next occurrence was in the 1950s, with the production of the body of the East German Trabant. Other manufacturers followed suit Daimler-Benz (1994), Mercedes (1996), but NFCs only really began to play an important role in the

Table 4 Physical and mechanical properties of commercial NFC products

Trade name	Density (g/cm ³)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (kJ/mm ²)
Fibrit	0.75–0.80	30–45	3000–3300	20–30
Fibrowood	0.85–0.95	50–60	3000–3800	12–20
PP-NF	1.14	57	3800	12
Wood-stock	1.1	40	18	–
EcoCor	0.7–1.0	45–55	2300–2700	25–35
NF-EP	0.75–0.85	55–70	4500–5800	25–35
FlexForm	0.9	21–67	1793–3792	–

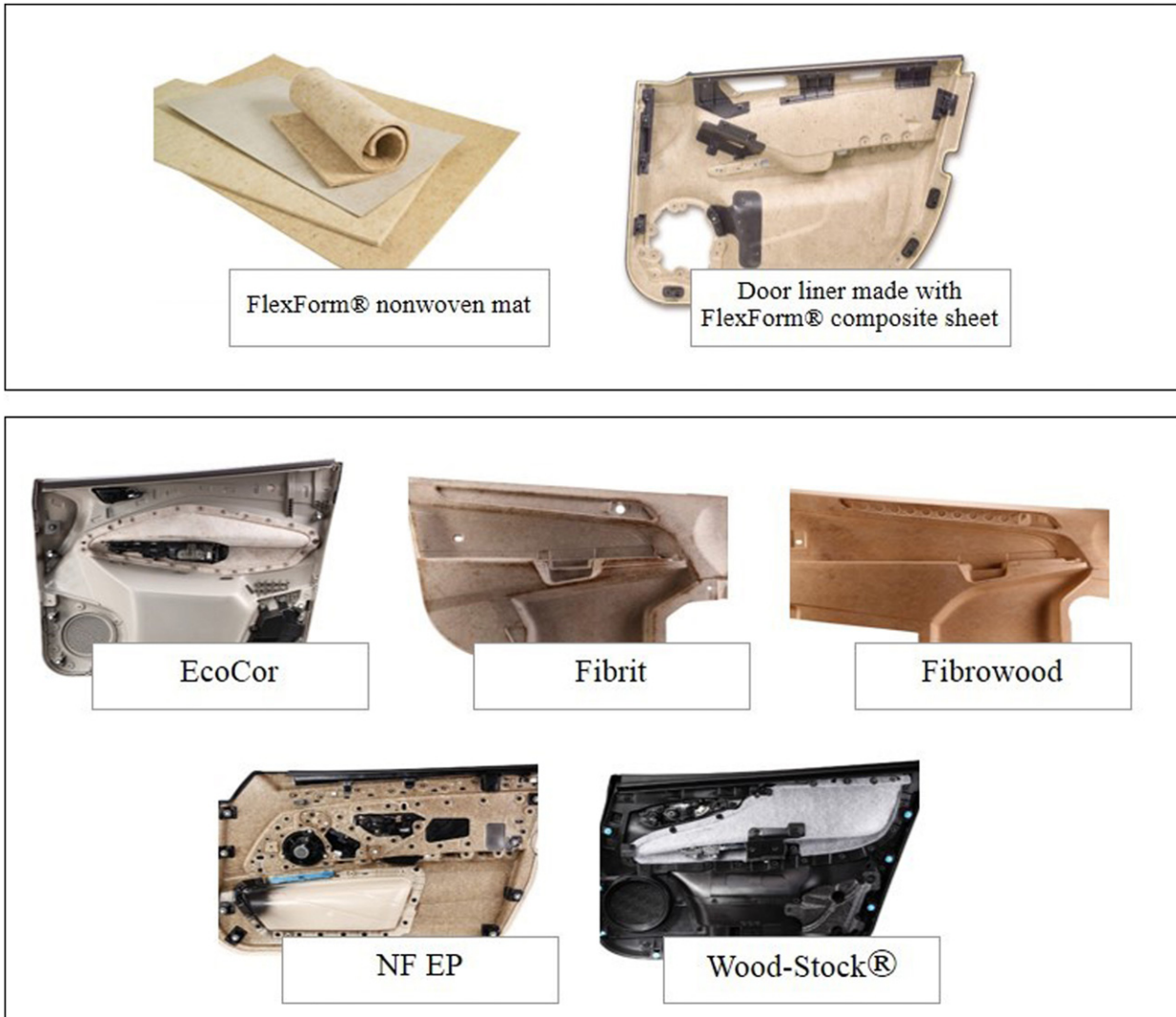


Fig. 3 Interior applications of natural fiber composites products by FlexForm Technologies (above) and Johnson Controls (below).

Table 5 Natural fiber composites applications by manufacturer

Manufacturer	Automotive parts	Car models
Audi	Seat back, hat rack, boot lining, spare tire lining, side and back door panel/flax, sisal	A2, A3, A4, A4 Avant, A6, A8, Roadstar, Coupe
BMW	Door panels, headliner panel, boot lining, seat back/sisal	3, 5 and 7 series and others
Citroen	Interior door panel/flax, jute	C5
Daimler-Chrysler	Windshield/dashboard, door panels, business table, pillar cover panel; A class, Travego bus: exterior under body protection trim; M class: Instrumental panel; S class: 27 parts manufactured from natural fibers/sisal, flax, coir, hemp, cotton	A, C, E and S class, Travego bus, Sebring convertible, Stratus
Dodge	Door panels, center console	Viper
Fiat	Door panels	Alfa Romeo 159
Ford	B-pillar, boot liner, door panels, seat backs/kenaf	Mondeo CD 162, D219, Focus, Freestar, all-new Ford Escape, Expedition
General motors	Cargo area floor, seat backs, tire cover, package trays, door panels/hemp, kenaf, flax	Chevrolet TrailBlazer, Cadillac DeVille, Daewoo Lacetti, Regal, Grand Prix, Monte Carlo
Honda	Cargo area	Pilot
Lotus	Interior carpets, body panels, seats, spoiler/hemp	Eco Elise (July 2008)
Mercedes-Benz	Door panels (flax/sisal/wood fibers with epoxy resin/UP matrix), seat backrest panel (cotton fiber), glove box (cotton fibers/wood molded, flax/sisal), instrument panel support, seat surface/backrest (coconut fiber/natural rubber), insulation (cotton fiber), molding rod/apertures, trunk panel (cotton with PP/PET fibers)	C, S, E, and A classes, 2004 Mercedes 164/251
Mercury	Door inserts	Cougar
Mitsubishi	Colt: instrumental panel; space star: door panels	Space star, Colt
Nissan	Trunk divider/flax	Sentra
Peugeot	Front and rear door panel	406
Opel	Instrumental panel, door panels, pillar cover panel, headliner panel	Zafira, Vectra, Astra
Renault	Rear parcel shelf	Clio, Twingo
Rover	Rear storage shelf or panel, insulation	Rover 2000 and others
Saab	Door panels	–
Saturn	Door panels, package trays	L300, LS
SEAT	Door panels, seat back	–
Toyota	Raum: cargo area floor, door panels, instrumental panel; ES3: pillar garnish and other interior parts/kenaf	Raum, ES3,
Volkswagen	Door panel, seat back, boot lid finish panel, boot line	Golf A4, Passat Variant, Bora
Volvo	Cargo floor tray, seat padding, natural foams	C70, V70

automotive industry in 1999, when Morassi produced seats made of coir with latex for trucks and top-of-the-line cars for Mercedes-Benz. Today, all of the major car manufacturers, including Daimler-Chrysler, Mercedes, Volkswagen, Audi Group, BMW, Ford, Opel, Toyota, Nissan, and Mitsubishi, use NFCs in various applications as summarized in [Table 5](#) ([Bledzki et al., 2006](#); [Dai and Fan, 2014](#); [Huda et al., 2008](#)).

NFCs are used mostly for interior parts such as dashboards, door panels, parcel shelves, seat cushions, backrests and cabin linings ([Bledzki et al., 2006](#); [Huda et al., 2008](#)). So far, there are only a few examples of exterior parts made from NFCs due to their high moisture absorption behavior: an example is the exterior under floor paneling on the Mercedes A-class made with abaca fiber-reinforced composite and other nonspecific exterior parts for Travego and Top Class models by Mercedes-Benz used flax fibers.

Automotive applications of NFCs have proven themselves very well, especially in the German automotive industries. Germany holds a dominant market position in terms of product innovation, research, and commercially available products; laying claim to two-thirds of all plant fibers consumed in the European automotive industry. In Germany, car manufacturers are aiming to make every component of their vehicles either recyclable or biodegradable ([Bruijn, 2015](#)).

In 2013, the nova-Institute (Germany) in cooperation with Asta Eder Composites Consulting (Austria/Finland) conducted a market study about biocomposites produced in the European Union (EU) ([Carus et al., 2013](#)). The report showed that the total volume of biocomposites, including wood and other NFCs, produced in the EU in 2012 was 352,000 t. Wood–plastic composites accounted for 260,000 t while the remaining amount represented other NFCs. Wood–plastic composite production for decking (174,000 t) and automotive (60,000 t) are the most important application sectors, followed by siding and fencing (16,000 t). Only the automotive sector was relevant for other natural (nonwood) fiber composites (90,000 t).

In the automotive sector, NFCs have a clear focus on interior trims for high value doors and dashboards. Wood–plastic composites are mainly used for rear shelves and trims for trunks and spare wheels, as well as in interior trims for doors. The total volume of wood and natural fibers used in the production of biocomposites for passenger cars and lorries produced in Europe in 2012 was 80,000 t ([Fig. 4](#)). Recycled cotton fiber composites were mainly used for the driver cabins of the lorries.

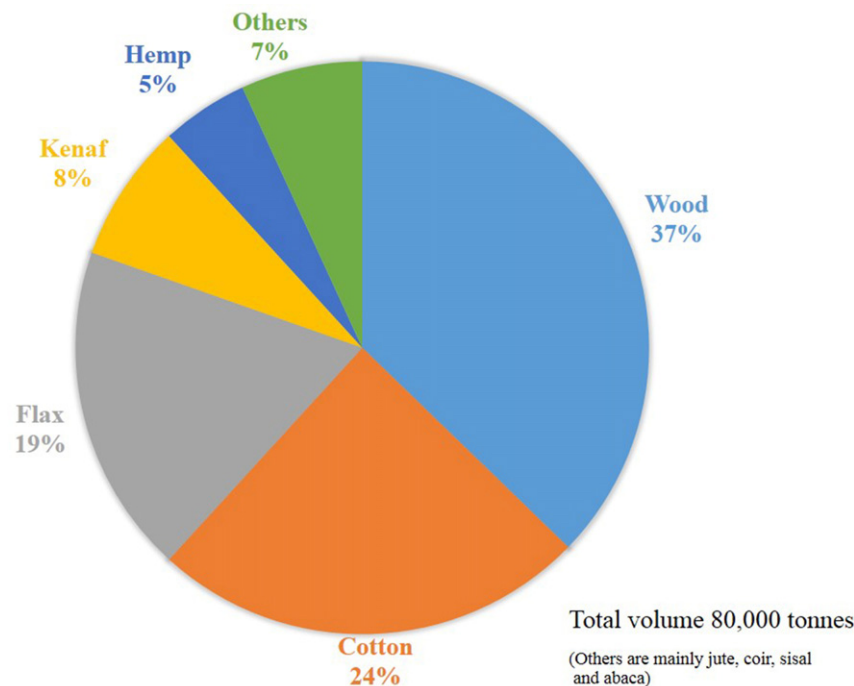


Fig. 4 Use of wood and natural fibers for composites in the EU automotive industry in 2012.

Future Directions and Challenges

While the share of biocomposites in today's total composite market in the EU (including glass, carbon, wood and natural fiber composite) is already an impressive 15%, even higher shares are expected in the future. NFCs are starting to enter other markets such as consumer goods, although they are still at a very early stage. In the EU, the production and use of 150,000 t biocomposites (using 80,000 t of wood and natural fibers) in the automotive sector in 2012 could expand to over 600,000 t of biocomposites in 2020, using 150,000 t of wood and natural fibers each along with some recycled cotton. Yet this fast development will not take place if there are no major political incentives to increase the bio-based share of the materials used in cars.

Besides the EU, according to a Food and Agricultural Organization survey, Tanzania and Brazil produce the largest amount of sisal. Henequen is grown in Mexico. Abaca is grown mainly in the Philippines. The largest producers of jute are India, China and Bangladesh. Presently, the annual production of natural fibers in India is about six million tons as compared to worldwide production of about 25 million tons. In temperate climate countries, flax and hemp are the most representative plants. Cultivation of kenaf has recently been introduced in several countries, and is now grown in places such as the United States, Malaysia, Bangladesh, Thailand, among others (FAO, 2012).

Since 2009, improved compression molding technology has shown impressive weight reduction characteristics of auto parts based on NFCs. Currently, it is possible to get area weight down to 1500 g/m² (with thermoplastics) or even 1000 g/m² (with thermosets), which are outstanding properties when compared to pure plastics or glass fiber composites. In addition, in 2012, three big paper companies in Europe and the United States recently introduced cellulose-based PP granulates for injected molded parts to the automotive market. The cellulose-based PP granulates have fiber shares of between 20 and 50% for new and interesting applications such as furniture, consumer goods and automotive parts. This technology is still small in volume but strong in innovation (Carus *et al.*, 2013). Recently, Johnson Controls developed a "visible natural fiber surface material" concept used for the instrument panel and door panels of the Johnson Controls re3 interior demonstrator (Johnson Controls Inc., 2015). This innovation enables a unique eco-fashion vehicle interior that shows natural wood fibers as a structural, visible surface material.

Today, many studies focus on the development of fully biodegradable green composites – those made from natural fibers and bio-based resins derived from soybeans, pure cellulose acetate, citrate-based plasticizer, and polylactic acid (PLA), for example. It is expected that the future will see increased use of these green composites due to their renewable and environmentally benign constituents (Bogoeva-Gaceva *et al.*, 2007). Research suggests that these are producible with competitive properties (Schuster *et al.*, 2014; Liu *et al.*, 2007).

Toyota has, in fact, begun producing Eco Plastic such PLA, Bio-PET, which is used for automotive applications (Boshoku, 2014). They substituted the PP used in the kenaf-based material with PLA resin and developed spare tire covers and door trim using 100% plant-derived kenaf-PLA that is more environmentally friendly. In 2011, Bio-PET derived from sugar cane and new ecological plastic were used in the CT200h and SAI, respectively. In cooperation with the Aichi Industrial Technology Institute,

Mitsubishi Motors developed an automotive interior material that uses a novel plant-based resin polybutylene succinate (PBS), combined with bamboo fiber for reinforcement. Parts made from the material was used in the interior of a revolutionary minicar launched in Japan in 2007 (Mitsubishi, 2006). Recently, Mitsubishi filed the patent about the method of producing automobile interior boards based on green composites. The composite material is comprised of bamboo, cotton, hemp and a mixture of cotton and hemp in decreasing order of content together with a biodegradable resin (PBS) (Terasawa *et al.*, 2009).

Conclusions

NFCs have good potential for both interior and exterior automotive applications. Their advantages include having low density and cost, high specific strength, and being sustainable and environmentally friendly. The resulting products from those composites can be both reused and incinerated and do not have to be land filled as glass fiber compounds, which can help in developing cars according to the EU end-of-life directive. Consequently, these composites are becoming attractive alternatives to glass and carbon fiber-reinforced polymer composites for automotive components; however, further research is necessary to overcome challenges such as moisture absorption, to instead enhance mechanical properties for use as exterior parts. In addition, the current intensive development of bio-based resin could provide fully bio-based composite options to future automotive designers. Market developments of NFCs also depend on the political framework: any political incentives for the use of natural fibers in the automotive industry could help increase existing volumes of natural fibers used. The future looks very bright for NFCs; in addition to the automotive industry, other markets, such as consumer goods and furniture, are beginning to incorporate NFCs into their products.

See also: Kenaf Fiber Reinforced Composite in the Automotive Industry. Natural Fiber and Synthetic Fiber Composites: Comparison of Properties, Performance, Cost and Environmental Benefits. Natural Fiber Reinforced Composites in the Context of Biodegradability: A Review. Recyclability of Natural Fiber-Filled Thermoplastic Composites. Recycling of Flax Fiber Towards Developing Biocomposites for Automotive Application From a Life Cycle Assessment Perspective. Renewable and Sustainable Materials in Automotive Industry

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The Nexus Between Biomass – Footprint and Sustainable Development

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Introduction

Over a half century, the burden of human activities, especially economic ones, on the environment has dramatically exceeded regenerative and absorptive capacity of the biosphere and environmental degradations have become socio-ecological crisis that is firstly remarked by [Craig \(2016\)](#). Although many scholars and international organizations have tried to take attention to this deterioration and its detrimental impacts on the life for so long, policy makers have lately recognized that traditional economic development policies are not sustainable, and sustainability has been crucial to survive in development strategies. The definition of sustainable development, as is given in the Brundtland Report (1987), is “to meet the needs of the present without compromising the ability of future generations to meet their own needs”. Therefore sustainable development path consists of interconnected and interrelated systems in which the intergenerational/overlapping generational welfare is optimized ([Bhinge et al., 2015](#); [Kannegiesser and Günther, 2014](#)). Three dimensions must be followed closely in this course ([Basiago, 1998](#); [Stoddart, 2011](#); [Emas, 2015](#)). (i) *The Economic Dimension* (Economic Sustainability) in which human well-being is treated economically in terms of various conditions and indicators, (ii) *The Environmental Dimension* (Environmental Sustainability) considering health, depletion of natural resources, quality environment, and, biodiversity, and, (iii) *Social Dimension* (Socio-Sustainability) paying attention to human capital, cultural capital, social reconciliation and peace, the existence of socio-political institutions, equality, and, justice eventually.

In recent times, the increasing negative impacts of global warming and/or climate change have shown that environmental dimension is much more important for a thriving future. It is crucial to state that environmental sustainability is also a prior condition to be able to manage economic and social sustainable policy implementations ([Pearce and Barbier, 2000](#)). In this respect, environmental sustainability has become an important research topic from various perspectives.

These perspectives mainly consider (i) observing management side of sustainable development ([Durach and Wiengarten, 2017](#); [García-Onetti et al., 2018](#); [Virapongse et al., 2016](#); [Mikulčić et al., 2017](#)), (ii) designing environmentally sustainable products ([Diego-Mas et al., 2016](#); [Delmas and Burbano, 2011](#); [He and Gu, 2016](#); [He et al., 2017](#)), (iii) focusing on environmental awareness ([Iosifidi, 2016](#); [Deniz, 2016](#); [Simsekli, 2015](#); [Mei et al., 2016](#)), (iv) investigating whether renewable material usage contributes to reduce environmental pollution ([Bilgili et al., 2017](#); [Choudhury, 2016](#); [López and Yoon, 2016](#); [Dogan and Inglesi-Lotz, 2017](#)), and, (v) attempting to develop an indicator or index ([Faulkner and Fazleen, 2014](#); [Butnariu and Avasilcai, 2015](#); [Moria and Christodoulou, 2012](#); [Esty et al., 2005](#); [Wackernagel and Rees, 1996](#)) to monitor environmental sustainability by combining many environmental metrics at plant or country level.

In empirical analyses, researchers in general need to employ an environmental indicator or an index within their relevant models to observe environmental changes ([Brambila and Flombaum, 2017](#); [Dong and Hauschild, 2017](#)).

One of those indicators developed by [Wackernagel and Rees \(1996\)](#) which can observe environmental changes is ecological footprint (EF hereafter). The EF indicator refers to how much of environment is demanded by people ([Wackernagel, 2002](#)) and how much the regenerative biological capacity of the planet is demanded by human activities ([Kitzes and Wackernagel, 2009](#)). Thereby, EF has been widely accepted in the environmental literature as an important sustainability indicator ([Gu et al., 2015](#); [Wiedmann and Barrett, 2010](#); [Collins et al., 2018](#); [Zhang et al., 2017](#); [Ulucak and Lin, 2017](#)). This indicator, then, has become one of the most prominent indicators throughout theoretical and empirical researches of environmental issues in recent years ([Ding and Banihashemi, 2017](#); [Zhang et al., 2017](#); [Wang et al., 2018](#); [Li et al., 2017](#); [Gu et al., 2015](#); [Bartelmus, 2008](#); [Lu and Chen, 2017](#); [Chakraborty, 2018](#); [Rashid et al., 2018](#); [Ulucak and Apergis, 2017](#)). Additionally, The European Environment Agency (EEA, 2010, 2015) the European Parliament, the European Commission ([Best et al., 2008](#)), and the United Nations Development Program (UNDP, 2014) consider the EF a useful tool for measuring environmental performance since it provides a framework of setting goals, identifying options for action, and tracking progress toward stated goals ([Borucke et al., 2013](#)).

The EF consists of six elements (cropland footprint, carbon footprint, grazing land footprint, built-up land footprint, fishing grounds footprint, forest footprint). When these elements are examined, one may indicate that the carbon footprint caused by fossil energy sources has the largest share in increasing ecological footprints (see “Relevant Website section”). Therefore, renewable material usage will contribute to the sustainability by reducing carbon footprint. Due to technical and economic feasibilities, biomass can be an efficient tool for environmental sustainability as well as sustainable development ([Bilgili et al., 2017](#); [Bilgili and Ozturk, 2015](#); [Ozturk and Bilgili, 2015](#)).

Accordingly, this paper aims at investigating the effect of biomass usage on sustainable development by observing the potential impact of biomass consumption on EF and Greenhouse Gas Emissions (GHG). This paper also examines the interaction of EF and GHG variables to observe their roles in environmental degradation.

Eventually, this paper is expected to provide researchers and policy makers with possible energy policies to mitigate the negative impact of global warming in the World for environmental sustainability. Remaining of the study is organized as follows: Section “Environmental Sustainability and Sustainability Indicators” explains environmental sustainability and its indicators, Section “Literature Review” follows relevant empirical literature, Section “Data, Model and Methodologies” presents the data, model and methodologies, Section “Estimation Output” reveals empirical results, and, Conclusion section yields the highlights of this research.

Environmental Sustainability and Sustainability Indicators

Although sustainable development has economic, social and environmental dimensions, the environmental dimension needs to be given more priority since the origin of the sustainability issue mainly stems from rising environmental problems (Kidd, 1992; Dong and Hauschild, 2017; Goodland, 1995). Additionally, the aim of protecting the environment might improve the human welfare by providing societies with numerous materials for economic activities and by preventing human from environmental harms (Goodland, 1995).

This point of view has emerged a new paradigm called ‘ecological economics’ based on the framework of “limits to growth (Olafsson *et al.*, 2014). Holdren *et al.* (1995) underlined the requirements for environmental sustainability, and, they remarked “maintenance of essential ecological processes and life-support systems; preservation of genetic diversity; and sustainable utilization of species and resources” (p. 7). To be able to stay within these sustainable environmental frontiers (i) renewable resources should be used at a rate which do not exceed regeneration rates, (ii) nonrenewable resources usage should be less than development of alternative substitutes, and, (iii) pollution level should be within the absorptive capacity of the environment (Daly, 1991). These three items stated by Daly (1991) are underlined also by Organization For Economic Co-Operation and Development. OECD (2001) classifies the relevant items into three principles; *regeneration*, *substitutability*, and *assimilation*. Besides, OECD introduces a fourth principle, *avoiding irreversibility* principle, implying that irreversible adverse effects of human activities on the environment should be avoided. These principles are proposed to design policies for environmental sustainability. However, relevant environmental indicators are required to monitor and assess the aims and success of policies towards sustainability and to know whether things are getting better or worse (Dong and Hauschild, 2017). To this end, several environmental sustainability indicators are proposed by international organizations and/or non-governmental organizations. These indicators are *Key and Core Environmental Indicators* by OECD, *Convention on Biological Diversity Framework Indicators* by United Nations Environmental Programme (UNEP), *Sustainable European Biodiversity Indicators* by European Union European Environment Agency (EEA), *Environmental Performance Index (EPI)* by Yale and Columbia Universities, *Environmental Vulnerability Index* by Secretariat of the Pacific Community, *Living Planet Index* by World Wildlife Fund, *Happy Planet Index* by New Economics Foundation and *Ecological Footprint (EF)* by Global Footprint Network, respectively.

Among others, EPI and EF have become more prominent indicators in terms of their more comprehensiveness (Moria and Christodoulou, 2012; Wilson *et al.*, 2007; Olafsson *et al.*, 2014; Strezov *et al.*, 2017). At this juncture, sustainability issue in its entirety is discussed in two forms based on substitutability of capitals. Accordingly, capital is considered as the sum of natural capital that represents nature resources and man-made capital. Strong sustainability argues that natural capital and man-made capital cannot be substituted by following irreversibility principle, while weak sustainability states that decrease in natural capital can be compensated by increase in man-made capital (Pearce and Barbier, 2000). Hence, EPI and EF have stood out as an environmental sustainability indicator (Wilson *et al.*, 2007; Moria and Christodoulou, 2012; Strezov *et al.*, 2017).

EPI has been calculated by Yale and Columbia universities and biennially published since 2006. it includes nine issue areas (climate & energy, biodiversity & habitat, fisheries, forests, agriculture, water resources, water & sanitation, air quality, health impacts) focusing on ecosystem vitality and environmental health to score country performance (Hsu *et al.*, 2016; Emerson *et al.*, 2010; Esty *et al.*, 2008). Countries are ranked till 100 as 100 denotes best performance in the method of EPI aggregation and their performance may change over time. One may visit at website provided in “Relevant Websites section” address to have more details on the EPI’s calculation methods. The countries’ EPI scores of 2006, 2008, 2010, 2012, 2014 and 2016 have been calculated and published so far. One of the main objectives of EPI is to provide empirical data for long term analyses and to facilitate analytical assessments (Haberland, 2008). However, current available time dimension of EPI may not be sufficient in order to make long term analyses and policy implications. In this respect, EF may be an alternative sustainability indicator that enables long term analyses to investigate stochastic properties of environmental performance since it has annual data spanning from 1961 to 2013 and it is widely preferred for econometric analyses in the literature. Therefore, this study focuses on EF as environmental sustainability indicator.

EF developed by Wackernagel and Rees (1996) aims at observing the fact that how much the regenerative biological capacity of the planet is demanded by human activities. These activities are basically consumption and production of goods and services (Kitzes and Wackernagel, 2009). The biologically productive areas are considered in EF computations and the cropland, forest, and fishing grounds are included into calculations while deserts, glaciers, and the open oceans are excluded. In these frontiers, EF is an aggregation of six components: *cropland footprint*, *grazing land footprint*, *fishing grounds footprint*, *forest land footprint*, *built-up land footprint*, and, *carbon footprint*. *Cropland footprint* computes the area required to grow all crop products, including livestock feeds, fish meals, oil, crops and rubber. *Grazing land footprint* estimates the area of grassland used in addition to crop feeds to support livestock. *Fishing grounds footprint* quantifies the annual primary production required to sustain a harvested aquatic species. *Forest land footprint* measures the annual harvests of fuelwood and timber to supply forest products. *Built-up land footprint* takes into account of the area of land covered by human infrastructure: transportation, housing, industrial structures and reservoirs for hydroelectric power generation and *carbon footprint* represents the forest lands required for anthropogenic CO₂ absorption (Ewing *et al.*, 2010). Combining these six components, EF answers how much nature countries/regions have and how much they use it in terms of biologically productive areas. Biocapacity (BC), on the other hand, represents biologically productive areas of countries to be able to reproduce all resources demanded from nature.

EF accounts and calculations at country level are undertaken by Global Footprint Network (GFN) and these calculations for each country are released under the name of National Footprint Accounts (NFA). Several statistical databases, i.e., International Energy Agency (IEA), International Panel on Climate Change (IPCC) database, United Nations (UN) commodity trade statistics Database, Food and Agricultural Organization (FAO) production database, FAO trade database, FAO technical conversion factors, FAO fisheries statistical database, FAO ForeSTAT statistical database, Global Forest Resources Assessment, Global Agro-Ecological Zones (GAEZ), FAO ResourceSTAT statistical database, and, Global Land Use Database might be followed in NFA calculations.

Latest two versions of NFA calculations are explained in detail by Lin *et al.* (2016) and Lazarus *et al.* (2014). Having calculated each land use footprint through related data, yield factor (YF), intertemporal yield factor (IYF) and equivalence factor (EQF), the total footprint for a country or region is obtained by summing them as given in Eq. (1).

$$EF = \sum_k Footprint_k \quad (1)$$

Following Eq. (1), EF is firstly produced based on production, export and import activities and sum of them yields EF for consumption as shown in Eq. (2).

$$EF_{consumption} = EF_{production} + (EF_{import} - EF_{export}) \quad (2)$$

EF_c represents biologically productive areas consumed by people in a country and it depends on people's consumption behaviors while EF_p indicates some part of it stemming from production activities that can be used as a reflection of gross domestic product (GDP). The sum given in parenthesis is net EF of trade. If export based EF is higher (lower) than import based EF in a country, that country is an exporter (importer) of its own biologically productive areas. The basic procedures to calculate total ecological footprint and biocapacity are depicted in Lin *et al.*, (2016).

YF and EQF become important in relevant calculations to capture differences in land types of countries. More precisely, they are balancing factors that standardize land use types. YF, implying relative productivity, is a ratio of national productivity to World average for a given land type and country while EQF is measured by using GAEZ suitability indexes of the World in terms of land types as average hectares. Thus, EQF allows any area used in EF calculation to be converted into common unit of biologically productive area called a global hectare (gha). On the other hand, IYF is considered to reflect changes in the World average yield over time. In this direction, EF related with a product(EF_p) and BC can be calculated by following Eqs. (3) and (4).

$$EF_p = \frac{P_i}{Y_N} * YF * EQF * IYF \quad (3)$$

$$BC = A * YF * IYF * EQF \quad (4)$$

P_i , Y_N and A notations given in Eqs. (3) and (4) indicate amount of product, national average productivity and area of a given land use type within a country, respectively. EF and BC can be measured as per capita dividing it by total population for a given country as well. Positive or negative difference between BC and EF refers ecological reserve or deficit. According to NFA calculations, more than 80% of world's population experiences ecological deficits. Ecological deficit threatens sustainability and it is considered an unsustainable situation for countries (Pearce and Barbier, 2000).

According to NFA calculations, most recent data shows that demand for nature is 70% more than what the biosphere can regenerate. There is no doubt that this situation mostly arises from non-renewable energy resources since carbon footprint, calculated by CO₂ emissions which are caused by their combustions, forms approximately 60% of humanity's ecological footprint. In this regard, it can be asserted that the best choice to decrease ecological footprint and to contribute sustainability is to meet energy needs through renewable sources. Moreover, considering economic pillar of sustainability and investments costs for renewable energy, biomass may be an efficient tool for sustainable development since it is technically and economically feasible (Bhattacharya *et al.*, 2003; Whalley *et al.*, 2017; Hendricks *et al.*, 2016) as well as an alternative policy that may contribute to increase income and to reduce poverty in developing countries (Demirbas *et al.*, 2009; Bildirici, 2014; Bildirici and Ozaksoy, 2017) and that might help to lessen energy dependence and trade deficits by reducing energy imports (Chalvatzis and Ioannidis, 2017; Ozturk *et al.*, 2017). More importantly, biomass usage, as an alternative to fossil fuels, helps in preventing the environmental threats (such as global warming and climate change) stemming from CO₂ emissions (Dogan and Inglesi-Lotz, 2017). So, it is one of the most prominent renewable energy sources and it is proved that biomass is an effective tool to be able to meet clean energy demand for sustainable development (Sansaniwal *et al.*, 2017).

Literature Review

Especially, in terms of economic and ecological considerations, the substantiality of biomass energy has been an important research topic in the literature (Paine *et al.*, 1996; Caputo *et al.*, 2005; Whalley *et al.*, 2017; Liu *et al.*, 2017). Therefore, based on a great variety of methodologies and observed experiences of countries, biomass energy can be examined from several respects within the frame of sustainable development in the available literature. Some of the relevant literature analyzes efficiency or

potential cost of biomass while some others investigate the role of biomass on CO₂ emissions. On the other hand, some studies focus on growth effect of biomass usage as an alternative energy input and they statistically confirm that biomass usage lead to increase in economic growth (Bildirici, 2013, 2014; Bildirici and Ersin, 2015; Adewuyi and Awodumi, 2017; Bildirici and Ozaksoy, 2017; Aslan, 2016; Shahbaz *et al.*, 2016; Bilgili and Ozturk, 2015; Ozturk and Bilgili, 2015). Eventually, these works highlight that renewable materials, such as biomass, might be imperative to reach sustainable growth. However, the relationship between biomass and emission mitigation is more prior subject in terms of environmental sustainability.

Although some studies notice that bioenergy policies may lead to increase in CO₂ emissions by focusing land use change, carbon leakage, green paradox and some minor adverse effect of biomass on the environment (Piroli *et al.*, 2015; van der Ploeg, 2016; Quentin Grafton *et al.*, 2012; Searchinger *et al.*, 2008; Grafton *et al.*, 2014; Schulze *et al.*, 2012; Repo *et al.*, 2015) the biomass energy is one of the best alternative tools to economically mitigate carbon emissions (Fontaras *et al.*, 2012; Demirbas, 2009; Pradhan and Mbohwa, 2014; McCarl *et al.*, 2010; Liu *et al.*, 2017; Whalley *et al.*, 2017). In this direction, Reinhardt and von Falkenstein (2011) underlined that biofuels are favorable in comparison with fossil alternatives although biofuels might have some negative effect on the environment. However, efficiencies of biofuels and their potential costs for energy conversion may vary from region to region (Fischer *et al.*, 2010; Rogers and Brammer, 2012; Khanna *et al.*, 2011; Furubayashi and Nakata, 2018).

Some econometrical models, as well, have been estimated by several studies to measure the statistical significances of biomass energy on CO₂ emissions in the literature. Based on their sample selections and methodologies, they found negative or positive impact on CO₂ emissions. Ma and Stern (2008) reached important increases in CO₂ emissions in case a shift from biomass to commercial energy by using decomposition analysis for China during 1971–2013. Joelsson and Gustavsson (2010) showed that biomass usage considerably reduces the CO₂ emissions. Bilgili (2012) investigated whether or not biomass consumption can mitigate CO₂ emissions in U.S. for the period 1990:1 and 2011:11 by employing cointegration analyses with unknown regime shifts and confirmed the negative impact of biomass on CO₂ emissions. Taking attention on green paradox, Grafton *et al.* (2014) obtained positive impact on CO₂ emissions for biomass subsidies and biomass production by applying ordinary least squares on the United States' data ranging from 1981 to 2011. Piroli *et al.* (2015) employed a structural VAR approach to analyze the impact of biomass on CO₂ emissions at global level for the period 1961–2009 and they yielded that biofuels significantly reduce global CO₂ emissions. Katircioglu (2015) analyzed Turkey's data from 1980 to 2010 to determine the impact of biomass consumption on CO₂ emissions by conducting bounds test and conditional error correction model and found negative impact. Following the wavelet coherence approach to examine the impact of biomass consumption on CO₂ emissions, Bilgili *et al.* (2016) revealed that biomass consumption improves the quality of environment by reducing CO₂ emissions. For selected European countries, Ahmed *et al.* (2016) obtained positive but insignificant relationship between biomass energy usage and CO₂ emissions by conducting PMG, MG and DFE estimators. Adewuyi and Awodumi (2017) established a simultaneous equation model estimated by three stage least squares for 11 West African countries' data spanning from 1980 to 2010 to investigate the effect of biomass consumption on carbon emissions and their estimations exhibited positive coefficients for 7 out of 11 countries, while negative relationship was obtained just for 4 countries. Dogan and Inglesi-Lotz (2017) employed biomass energy consumption to observe its effect on CO₂ in the panel of biomass-consuming countries by applying panel cointegration and FMOLS estimation techniques for the period 1985–2012 and they concluded that biomass energy consumption mitigates CO₂ emissions. Shahbaz *et al.* (2017) reached the evidence that biomass consumption lowers CO₂ emissions in United States over the period 1960–2016 through ARDL cointegration and VECM Granger causality approaches.

Data, Model and Methodologies

In order to investigate the effect of biomass on proxy indicators of environmental sustainability, this paper mainly follows the models given in Eqs. (5–7) with or without deterministic (or fixed) variables employing annual data spanning from 1990 to 2015 for the UK, Turkey and EU 16 countries:

$$LGHG_{it} = \beta_0 + \beta_1 LEF_{it} + \beta_2 LBiomass_{it} + \beta_3 LFUEL_{it} + \beta_4 LGAS_{it} + u_{it} \quad (5)$$

$$LGHG_{it} = \beta_0 + \beta_1 LEF_{it} + \beta_2 LBiomass_{it} + \beta_3 LGDP_{it} + u_{it} \quad (6)$$

$$LEF_{it} = \beta_0 + \beta_1 LGHG_{it} + \beta_2 LBiomass_{it} + \beta_3 LGDP_{it} + u_{it} \quad (7)$$

The variables LGHG, LEF, LBiomass, LFUEL, LGAS, and LGDP represent the logarithms of Greenhouse Gas Emissions (LGHG), Ecological Footprint (LEF), Biomass energy consumption (LBiomass), fuel consumption (LFUEL), natural gas consumption (LGAS), and GDP (LGDP), respectively.

EF data (1990–2013) is obtained from The Global Footprint Network GFN (2017) as other variable's data are extracted from Eurostat (2018). Additionally, the trend simulations of EF for 2014 and 2015 are also conducted in order for this research to be able to analyze a larger time period.

Since the aim of this study is to examine mainly the interaction between LEF, LBiomass, and LGHG, one might prefer to have a visual inspection of variables that are of primary interest before proceeding to relevant model analyzes.

The Fig. 1 represents the panel data line graph for ecological footprint (EF), which is presented in natural logarithms (LEF). The country level of EF indicates the demand for nature (i.e., demand for land, forest, water sources) within the borders of the country. In other words, the EF of a country, as we underlined before in the text, is an indicator of amount of surface needed by people of

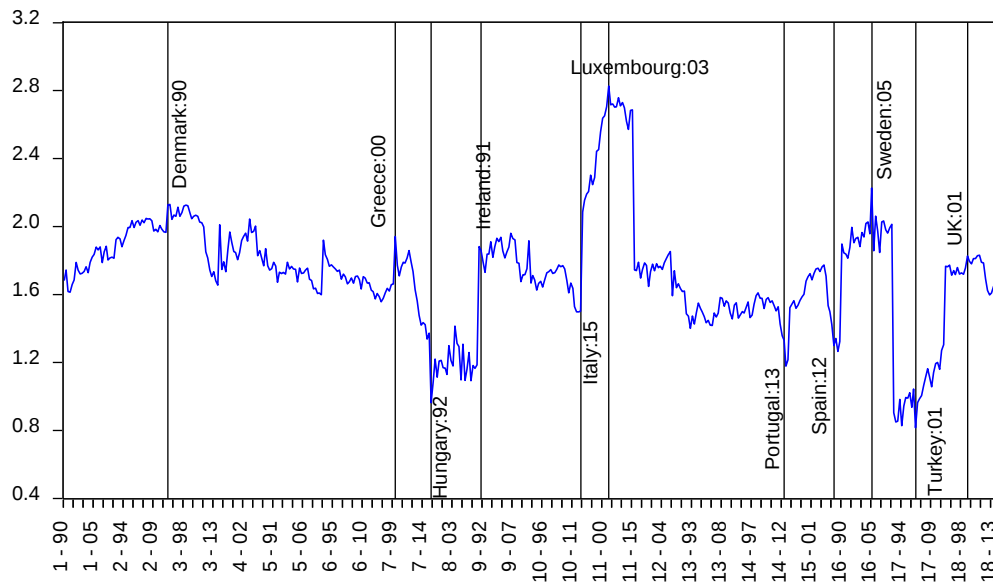


Fig. 1 The movements of LEF panel data: 1990_2015.

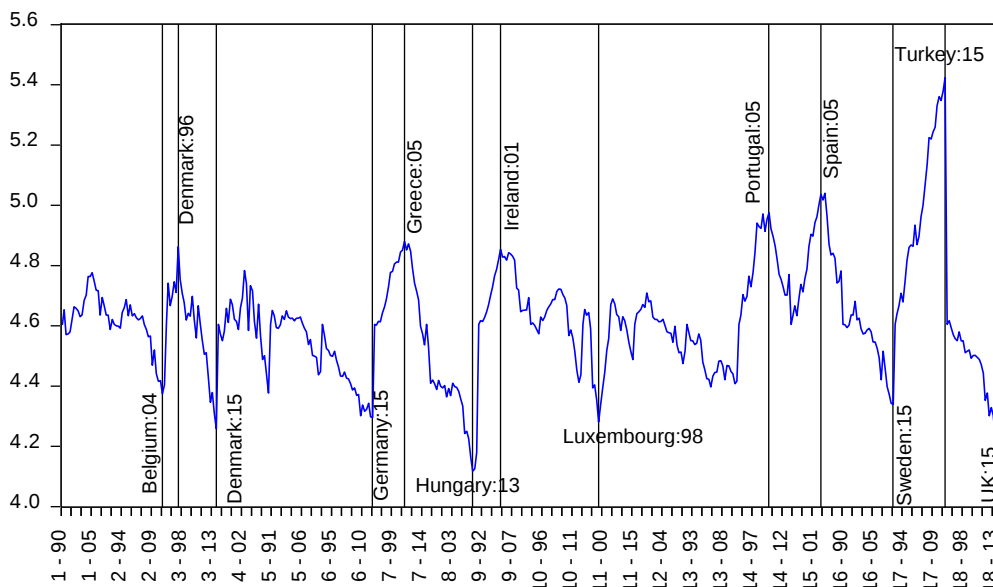


Fig. 2 The movements of LGHG panel data: 1990_2015.

relevant country to survive by employing her current technology. Considering 18 countries' panel data for EF, Denmark in 1990, Luxembourg in 2003, Sweden in 2005, and UK during 2001 have relatively greater EF values as Hungary (1992), Italy (2015), Portugal (2013), Spain (2012) and Turkey (2001) have relatively less EF measurements. The panel data reaches the highest peak in 2003-EF value of Luxembourg while the data reaches its lowest value at 2001-EF observation of Turkey.

Fig. 2 plots the line graph for greenhouse gas emissions in logarithmic values (LGHG) within panel data. As is seen from the graph, one might assert that the LGHG spikes up relatively more sharply in observations of Denmark:96; Greece:05; Ireland:01; Portugal:05; Spain:05; and Turkey:15, and that LGHG scales down prominently during 1998 (Luxembourg), 2004 (Belgium), 2013 (Hungary), and, 2015 (Denmark, Germany, Sweden, and, UK).

Fig. 3 depicts the natural logarithms of biomass consumption in panel countries. It appears that the biomass consumption reaches its relatively higher values in 2011 (Netherlands), 2012 (Belgium, Poland and Spain), 2013 (Austria and France) and in 2015 (Germany, Hungary, Italy, Sweden and UK). The biomass consumption, on the other hand, seems to be relatively lower in 1990 (UK), 1991 (Poland and Luxembourg), 1993 (Ireland), and, in 1994 (Belgium).

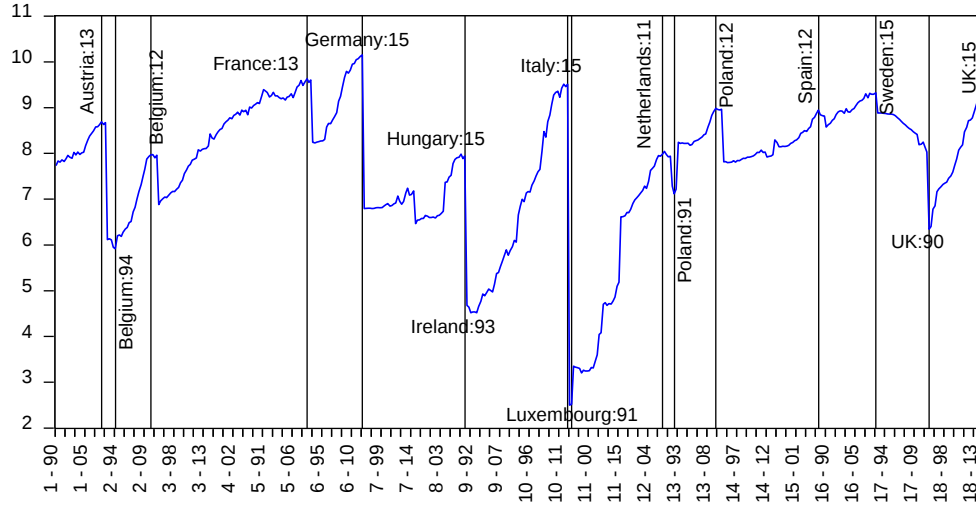


Fig. 3 The movements of LBiomass panel data: 1990_2015.

After some preliminary graphical observations, several panel data estimation techniques are followed to consider cross-section (i) and time dimensions (t) of the variables. Panel data analyses enable us to control for individual heterogeneity, to give more informative data, more variability, less collinearity, more degrees of freedom and more efficiency (Hsiao, 2003).

Considering panel regression equation, $y_{it} = X'_{it}\beta + u_{it}$, most of the panel data applications utilize one-way error component model for residuals as $u_{it} = \mu + v_{it}$. The first term in this residual component represents unobservable individual specific effects while the second one denotes the remainders that are independent and identically distributed IID $(0, \sigma_v^2)$. Fixed effect and random effect estimators might be launched to estimate panel regression equations. In fixed effect estimations, the μ_i are assumed to be fixed parameters while they are assumed random variables in random effect estimations. However, the variables with large time dimensions included into panel models should be stationary and cross-sectionally independent to be able to reach unbiased and efficient outcome (Baltagi, 2015). Hence, the first step is to check the possibility of cross-correlation of variables. Pesaran *et al.* (2008) proposed a bias adjusted LM test given below for cross-correlation by following Breusch and Pagan (1980).

$$LM_{adj} = \sqrt{\frac{2}{N(N-1)}} \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{(T-k)\hat{\rho}_{ij}^2 - \mu_{Tij}}{v_{Tij}} \quad (8)$$

Where $\hat{\rho}_{ij}$ denotes sample estimate pair-wise correlation of the residuals, μ and v are the exact mean and variance of $(T-k)\hat{\rho}_{ij}^2$ respectively. The null hypothesis of the test states “no cross-sectional dependence”. Having applied bias adjusted LM test on the variables, the null hypothesis was strongly rejected for each variable. Results are not presented here to save space, they are, however, available upon request from the authors. The second step is to run the stationarity tests. Under the null hypothesis of non-stationary, Pesaran (2007) proposed cross sectionally augmented Dickey-Fuller test (CADF) in order to take into account the cross-sectional dependence. CADF statistics are obtained by following pth order cross-section/time-series augmented regression.

$$\Delta x_{it} = \psi_i + \zeta_i x_{it-1} + (\phi)_i \bar{x}_{t-1} + \sum_{j=0}^p \phi_{ij} \Delta \bar{x}_{it-1} + \sum_{j=1}^p \beta_{ij} x_{it-1} + \varepsilon_{it} \quad (9)$$

Pesaran (2007) also used IPS test procedure proposed by Im *et al.* (2003) to obtain cross-sectionally augmented IPS test statistics (CIPS) based on the average of CADF statistic for each i . The critical values of CIPS are given by Pesaran (2007). CADF and CIPS statistics of the variables used in this study show that the null of non-stationary cannot be rejected. In the case of non-stationarity, one would get spurious results from the regression equations. Results are not presented here to save space; they are, however, available upon request from the authors. Although the variables of interest might be individually nonstationary, one or more linear combinations of those variables might be stationary (Bai *et al.*, 2009). The next step is, then, to observe if one or more linear combinations of the variables are stationary. To this end, Westerlund (2008) considered two statistics based on the Durbin-Hausman (DH) principle, which takes dependence into account by using common factors. These statistics are calculated through following formulas.

$$DH_g = \sum_{i=1}^n \hat{S}_i \left((\tilde{\varphi})_i - (\hat{\varphi})_i \right)^2 \sum_{t=2}^T \hat{\varepsilon}_{it-1}^2 \quad DH_p = \hat{S}_n \left((\tilde{\varphi}) - (\hat{\varphi}) \right)^2 \sum_{i=1}^n \sum_{t=2}^T \hat{\varepsilon}_{it-1}^2 \quad (10)$$

DH_g and DH_p denote the group mean statistic and panel statistic respectively. $(\tilde{\varphi})_i$ and $(\hat{\varphi})_i$ represent coefficient for one lagged series of error term obtained from the lagged regression of error term (ε_{it}) through OLS and instrumental variables estimators

respectively. $\hat{S}$ depicts variance ratios calculated by Kernel estimator based on OLS residual to variance of OLS estimation. The null hypothesis of DH_g and DH_p tests states "no cointegration". In estimating panel cointegrated regressions Pedroni (2001a,b) and Kao and Chiang (2001) suggested FMOLS and DOLS estimators as given in Eqs. (11) and (12).

$$\hat{\beta}_{FMOLS} = \left[\frac{1}{N} \sum_{i=1}^N \left(\sum_{t=1}^T (x_{it} - \bar{x}_i)^2 \right) \right]^{-1} \times \left[\left(\sum_{t=1}^T (x_{it} - \bar{x}_i) \dot{y}_{it} - T \hat{\Delta}_{eu} \right) \right] \quad (11)$$

Δ_{eu} is a member of covariance matrix to consider serial correlation in interpretation of the asymptotic covariance matrix and $\hat{\Delta}_{eu}$ is kernel estimate of Δ_{eu} . $\bar{x}_i$ refers to the individual specific means. On the other hand, DOLS parameters can be estimated through the regression equation below.

$$\hat{\beta}_{DOLS} = \left[\frac{1}{N} \sum_{i=1}^N \left(\sum_{t=1}^T A_{it} A'_{it} \right) \right]^{-1} \left(\sum_{t=1}^T A_{it} \dot{y}_{it} \right) \quad (12)$$

A_{it} is the $2(K+1) \times 1$ vector of regressors $A_{it} = (x_{it} - \bar{x}_i, \Delta x_{it-K}, \dots, \Delta x_{it+K})$. FMOLS and DOLS estimators are also modified by Kao and Chiang (2001) for heterogeneous panels and they can be used in case there are substantial heterogeneities in cross sections. As a cointegration estimator, Autoregressive Distributed Lag (ARDL) procedure can be used as well. In general framework proposed by Pesaran *et al.* (1999), it is formulated as follows.

$$\Delta y_{it} = b_1 y_{i,t-1} + \tau_i x_{i,t} + \sum_{j=1}^{p-1} \theta_{ij} \Delta y_{i,t-j} + \sum_{j=0}^{q-1} \xi_{ij} x_{i,t-j} + \mu_i + \varepsilon_{it} \quad (13)$$

Besides, the causal interactions among the variables can be estimated by establishing vector error correction model (VECM) based on two-step procedure, that firstly obtains residuals from long run estimation and then includes these residuals as error correction term (ECT) into the VECM, suggested by Engle and Granger (1987). The VECM specification in a bivariate framework can be constructed for panel data as follows.

$$\begin{aligned} \Delta y_{it} &= \theta_{1i} + \gamma_1 ECT_{it-1} + \sum_{p=1}^k \theta_{11p} \Delta y_{it-p} + \sum_{p=1}^k \theta_{12} \Delta x_{it-p} + \varepsilon_{1it} \\ \Delta x_{it} &= \theta_{2i} + \gamma_2 ECT_{it-1} + \sum_{p=1}^k \theta_{21p} \Delta x_{it-p} + \sum_{p=1}^k \theta_{22} \Delta y_{it-p} + \varepsilon_{2it} \end{aligned} \quad (14)$$

where Δ is the first difference operator, k is the optimal lag length(s) proposed by information criteria, p is the lag number. ECT represents error correction term and it is the residuals of long run estimation. The coefficient of ECT (γ_1) is considered as speed of adjustment in correcting disequilibrium for reaching long run equilibrium as well as long run causality.

However, under the heterogeneities and dependencies among cross-sections, bivariate Granger causality analysis proposed by Dumitrescu and Hurlin (2012) may yield more reliable results. Having applied the following equation, Dumitrescu and Hurlin (2012) observed Wald statistics with bootstrap critical values in order to consider dependence.

$$y_{it} = a_i + \sum_{k=1}^K \tau_i^{(k)} y_{i,t-k} + \sum_{k=1}^K \delta_i^{(k)} x_{i,t-k} + e_{i,t} \quad (15)$$

where K is lag order, $K \in N$ and $\delta_i = \delta_i^1, \dots, \delta_i^{(K)}$. It is assumed that lag orders are identical for all cross-sections while $\tau_i^{(k)}$ and $\delta_i^{(k)}$ are allowed to differ across units. The null and alternative hypotheses are defined as:

$$H_0 : \delta_i = 0, \forall i = 1, \dots, N \quad H_1 : \begin{cases} \delta_i = 0 \forall i = 1, \dots, N \\ \delta_i \neq 0 \forall i = N_1 + 1, N_1 + 2, \dots, N \end{cases} \quad (16)$$

The null hypothesis states that the variable x does not granger cause the variable y for all individuals of the panel and rejection of the null ($N_1=0$) implies that x Granger causes y for all units of the panel. Employing the average of Wald statistics for all units $i=1, \dots, N$, the existence of no Granger causality for all sections is tested under the null hypothesis against the alternative meaning that at least one causal relationship exists ($N_1 > 0$) in the panel data. If $N_1 > 0$, the causality relationship between x and y differs from one cross-section to another and the alternative hypothesis yields heterogeneous results.

Estimation Output

This research paper mainly considers analyzing the data for 18 European Countries to observe (i) the impact of biomass energy source on Greenhouse Gas emissions, (ii) the influence of biomass energy consumption on ecological footprint, (iii) the effect of ecological footprint on Greenhouse gas emissions, and, (iv) the impulse of Greenhouse gas emissions on ecological footprint. The regarding results are obtained through MATLAB and RATS program's lines.

Table 1a Dumitrescu-Hurlin panel causality tests from X to Y ($X \rightarrow Y$)^{*, **}

	$\bar{W}$	$\bar{Z}$	<i>p value</i>	$\tilde{Z}$	<i>p value</i>
LEF $\rightarrow$ LGHG	2.5723	4.7168	0.0000	3.7598	0.0002
LGHG $\rightarrow$ LEF	3.6337	7.9012	0.0000	6.4618	0.0000

*T=26, N=18, Total number of panel observations=468, Lag order K=1.

**H₀: The null is the Homogenous non Causality (HNC) hypothesis from X to Y.

Table 1b Dumitrescu-Hurlin cross unit individual causality tests from X to Y ($X \rightarrow Y$)

Country	LEF $\rightarrow$ LGHG		LGHG $\rightarrow$ LEF	
	Wald	<i>p value</i>	Wald	<i>p value</i>
Austria	2.8782	0.0898	0.9696	0.3248
Belgium	4.7628	0.0291	0.8999	0.3428
Denmark	10.2839	0.0013	3.1730	0.0749
Finland	1.0401	0.3078	9.1300	0.0025
France	0.0053	0.9421	12.4574	0.0004
Germany	0.3518	0.5531	3.5644	0.0590
Greece	3.3729	0.0663	1.7263	0.1889
Hungary	4.9651	0.0259	0.4623	0.4965
Ireland	0.2357	0.6273	0.6098	0.4349
Italy	5.4284	0.0198	0.8188	0.3655
Luxembourg	2.3435	0.1258	4.4387	0.0351
Netherlands	0.8485	0.3570	2.3389	0.1262
Poland	1.6049	0.2052	0.3293	0.5661
Portugal	0.0518	0.8200	0.0456	0.8310
Spain	4.1701	0.0411	2.4559	0.1171
Sweden	1.9365	0.1641	1.5172	0.2180
Turkey	2.0208	0.1552	17.8472	0.0000
UK	0.0003	0.9865	2.6233	0.1053

Table 2a Dumitrescu-Hurlin panel causality tests from X to Y ($X \rightarrow Y$)^{*, **}

	$\bar{W}$	$\bar{Z}$	<i>p value</i>	$\tilde{Z}$	<i>p value</i>
LBiomass $\rightarrow$ LEF	4.2911	9.8732	0.0000	8.1351	0.0000
LEF $\rightarrow$ LBiomass	2.4916	4.4747	0.0000	3.5544	0.0004

*T=26, N=18, Total number of panel observations=468, Lag order K=1.

**H₀: The null is the Homogenous non Causality (HNC) hypothesis from X to Y.

In this paper, all estimations are conducted by launching logarithmic forms of the relevant variables. The paper first analyzes the Dumitrescu-Hurlin panel causalities (a) from LEF to LGHG, (b) from LGHG to LEF, (c) from LBiomass to LEF, (d) from LEF to LBiomass, (e) from LBiomass to LGHG, and, (g) from LGHG to LBiomass.

$\bar{W}$ depicts the mean value of the N individual Wald statistics. Wald statistic follows asymptotically χ^2 (chi-squared) distribution. Under some circumstances, individual Wald statistics may not follow standard χ^2 distribution. However, Dumitrescu and Hurlin (2012) showed in general that individual Wald statistics are independently distributed with finite second order moments. The $\bar{Z}$ and $\tilde{Z}$ statistics denote standardized statistic and approximated standardized statistic, respectively, for the mean value of the N individual Wald statistics.

Table 1a reveals the output of Dumitrescu-Hurlin panel causality tests from Ecological Footprint (LEF) to Greenhouse Gas Emissions (LGHG). The null hypothesis (H₀) is the Homogenous non Causality (HNC) hypothesis from LEF to LGHG. According to $\bar{W}$, $\bar{Z}$ and $\tilde{Z}$ statistics, there exists significant causality from LEF to LGHG. The statistics of $\bar{W}$, $\bar{Z}$ and $\tilde{Z}$ are significant at 1% level. Hence, one can claim that LEF causes LGHG significantly. The LEF is found significant in determining the LGHG values. Then, one can argue that LEF should precede the future values (leads) of LGHG. **Table 1a** also depicts that there exists also significant causality from LGHG to LEF. The statistics of $\bar{W}$, $\bar{Z}$ and $\tilde{Z}$ explored that LGHG causes LEF. **Table 1a** eventually indicates that there exists bilateral causality from LEF (LGHG) to LGHG (LEF). This result confirms the expectation that carbon emission (LGHG) and environmental degradation (LEF) are closely associated.

Table 2b Dumitrescu-Hurlin cross unit individual causality tests from X to Y ($X \rightarrow Y$)

Country	$LBiomass \rightarrow LEF$		$LEF \rightarrow LBiomass$	
	Wald	p value	Wald	p value
Austria	1.1805	0.2773	1.2536	0.2629
Belgium	0.6620	0.4158	3.8527	0.0497
Denmark	4.5388	0.0331	1.0764	0.2995
Finland	0.1991	0.6554	0.9042	0.3417
France	14.1096	0.0002	0.3229	0.5699
Germany	5.1652	0.0230	9.6116	0.0019
Greece	4.5299	0.0333	0.0248	0.8749
Hungary	0.2291	0.6322	5.8996	0.0151
Ireland	0.2165	0.6417	0.1228	0.7260
Italy	4.2568	0.0391	2.5299	0.1117
Luxembourg	0.3159	0.5741	0.4083	0.5228
Netherlands	2.7739	0.0958	7.5179	0.0061
Poland	2.2059	0.1375	0.2236	0.6363
Portugal	3.4910	0.0617	0.2051	0.6506
Spain	7.9867	0.0047	10.5990	0.0011
Sweden	6.7521	0.0094	0.0975	0.7548
Turkey	16.8175	0.0000	0.1166	0.7327
UK	1.8087	0.1787	0.0816	0.7751

Table 3a Dumitrescu-Hurlin panel causality tests from X to Y ($X \rightarrow Y$)*, **

	$\bar{W}$	$\bar{Z}$	p value	$\tilde{Z}$	p value
$LBiomass \rightarrow LGHG$	8.9338	23.8013	0.0000	19.9532	0.0000
$LGHG \rightarrow LBiomass$	2.9604	5.8813	0.0000	4.7479	0.0000

*T=26, N=18, Total number of panel observations=468, Lag order K=1.

**H₀: The null is the Homogenous non Causality (HNC) hypothesis from X to Y.

Table 1b yields significant the individual effects of LEF on LGHG in Austria, Belgium, Denmark, Greece, Hungary, Italy and Spain. **Table 1b**, then, exhibits the outcome that the variable LEF can predict significantly the future values of LGHG in these countries. The **Table 1b** also depicts the individual results that the past values of LGHG can forecast significantly the future values of LEF in Denmark, Finland, France, Germany, Luxembourg and Turkey.

Table 2a shows the outcome of Dumitrescu-Hurlin panel causality tests among the pairs of variables LBiomass and LEF. The **Table 2a** indicates that LBiomass (LEF) causes LEF (LBiomass). The $\bar{W}$, $\bar{Z}$ and $\tilde{Z}$ statistics have the p values of 0.000 verifying the bivariate significant causalities between LBiomass and LEF.

The **Table 2b** presents the significant individual country impact of LBiomass on LEF in Denmark, France, Germany, Italy, Netherlands, Portugal, Spain, Sweden and Turkey. In other word, the effect of renewable energy of biomass consumption on ecological footprint is found considerable in 10 out of 18 countries in European continent. **Table 2b** shows, on the other hand, the significant cross section impact of LEF on LBiomass in the countries of Belgium, Germany, Hungary, Netherlands and Spain. **Table 2b**, then, confirms relatively more the influence of biomass energy usage on ecological degradation than the impulse of ecological degradation on biomass consumption in Europe.

Table 3a reveals the significant causalities between LBiomass and LGHG. The relevant $\bar{W}$, $\bar{Z}$ and $\tilde{Z}$ statistics are found significant at 1% level. **Table 3b** gives the conclusion of Dumitrescu-Hurlin cross unit individual causality tests from LBiomass to LGHG and the individual causality tests from LGHG and LBiomass. The table exhibits that the 13 countries out of 18 countries in Europe experience statistically significant causality from biomass consumption to carbon emission. These countries in which LBiomass consumption causes LGHG emissions are Belgium, Denmark, France, Germany, Greece, Hungary, Ireland, Italy, Netherlands, Portugal, Spain, Sweden, and UK, respectively.

The following **Tables 4, 5, 6** and **7** yield the sign of the causalities between the pair of variables. **Table 4a** and **Table 4b** give the output from panel regression estimation by fixed effects and panel regression estimation by random effects. According to **Table 4a**, LBiomass has negative impact on LGHG as LEF, LFUEL and LGAS have positive influences on LGHG. Considering long run fixed effect output, one may state that as LBiomass increases 1 percent, the LGHG will decrease by 0.0382 percent.

The long run biomass elasticity of Greenhouse gas emissions is statistically significant, has expected negative sign and is less than unity. The long run LEF, LFUEL and LGAS elasticities of LGHG are 0.5304, 0.1384 and 0.0671, respectively. In the long run, 1% increase in LEF variable causes LGHG to increase by 53.04%. Fuel energy consumption has also considerable positive impact on carbon emissions (0.1384). In the short run, the error correction term (EC) is found significant and negative. The EC term denotes one period lagged residuals (u,t-1) from the relevant long run equilibrium. The coefficient of EC is expected to be

Table 3b Dumitrescu-Hurlin cross unit individual causality tests from X to Y ($X \rightarrow Y$)

Country	LBiomass $\rightarrow$ LGHG		LGHG $\rightarrow$ LBiomass	
	Wald	p value	Wald	p value
Austria	1.2760	0.2586	1.8003	0.1797
Belgium	16.2208	0.0001	5.4018	0.0201
Denmark	12.5905	0.0004	0.0117	0.9138
Finland	2.6333	0.1046	0.3355	0.5625
France	20.5933	0.0000	9.9972	0.0016
Germany	12.1296	0.0005	1.7579	0.1849
Greece	29.4066	0.0000	0.0012	0.9720
Hungary	15.1396	0.0001	0.4414	0.5064
Ireland	4.8040	0.0284	2.4040	0.1210
Italy	7.2564	0.0071	3.5970	0.0579
Luxembourg	0.3160	0.5740	5.6790	0.0172
Netherlands	15.5870	0.0001	3.7823	0.0518
Poland	0.5964	0.4399	0.7487	0.3869
Portugal	7.3639	0.0067	3.4231	0.0643
Spain	4.9610	0.0259	9.2036	0.0024
Sweden	5.4508	0.0196	2.2137	0.1368
Turkey	0.7268	0.3939	1.7583	0.1848
UK	3.7559	0.0526	0.7310	0.3926

Table 4a Panel regression estimation by fixed effects

Dependent variable LGHG						
Long-run ^{a,b,c}	LEF*	LBiomass*	LFUEL*	LGAS*	Constant	
	0.5304 (0.0294)	− 0.0382 (0.0073)	0.1384 (0.0107)	0.0671 (0.0049)	0.0000 (0.0000)	
Dependent Variable Δ LGHG b						
Short-run ^d	Δ LEF*	Δ LBiomass ^e	Δ LFUEL*	Δ LGAS*	Constant	EC*
	0.1620 (0.0178)	0.0016 (0.0107)	0.2002 (0.0092)	0.0820 (0.0080)	0.0000 (0.0000)	− 0.1453 (0.0205)

^aTotal number of panel observations = 468.^b $\bar{R}^2 = 0.8832$.^cLog Likelihood = 594.2669.^dTotal number of panel observations = 450.^eEstimation is not significant.

*depicts 1% statistical significance. (Standard errors are given in parentheses).

Table 4b Panel regression estimation by random effects

Dependent variable LGHG						
Long-run ^{a,b,c,d}	LEF*	LBiomass*	LFUEL*	LGAS*	Constant*	
	0.5324 (0.0292)	− 0.0397 (0.0071)	0.1337 (0.0103)	0.0660 (0.0049)	2.2255 (0.1649)	
Dependent variable Δ LGHG						
Short-run ^e	Δ LEF*	Δ LBiomass ^f	Δ LFUEL*	Δ LGAS*	Constant	EC*
	0.1607 (0.0178)	0.0061 (0.0115)	0.1981 (0.0093)	0.0841 (0.0082)	− 0.0015 (0.0014)	− 0.1466 (0.0204)

^aTotal number of panel observations = 468.^b $\bar{R}^2 = 0.6778$.^cLog Likelihood = 529.3409.^dHausman Test(4) = 14.974, Significance Level = 0.0047.^eTotal number of panel observations = 450.^fEstimation is not significant.

*depicts 1% statistical significance. (Standard errors are given in parentheses).

significant and negative in order for LGHG to be able to restore its equilibrium. For instance, the residual in 2014 of cross section UK is -0.061887 . It means that LGHG is below its long run equilibrium value. Then LGHG will increase by 0.008992181 [$= (-0.1453) \times (-0.061887)$] in UK to restore its long run equilibrium. In the short run, all variables, except Δ LBiomass, are significant and affect Δ LGHG positively.

Table 5a Panel regression estimation by fixed effects

Dependent variable LGHG					
Long-run ^{a,b,c}	LEF [*]	LBiomass [*]	LGDP [*]	Constant	
	0.4474 (0.0411)	− 0.1102 (0.0103)	0.1894 (0.0331)	0.0000 (0.0000)	
Dependent variable ΔLGHG ^b					
Short-run ^d	ΔLEF [*]	ΔLBiomass ^e	ΔLGDP [*]	Constant [*]	EC [*]
	0.1547 (0.0285)	0.0104 (0.0167)	0.3249 (0.0668)	− 0.00841 (0.00230)	− 0.1586 (0.0225)

^aTotal number of panel observations = 468.^b $\bar{R}^2 = 0.8012$.^cLog Likelihood = 475.9779.^dTotal number of panel observations = 450.^eEstimation is not significant.

*depicts 1% statistical significance. (Standard errors are given in parentheses).

Table 5b Panel regression estimation by random effects

Dependent variable LGHG					
Long-run ^{a,b,c,d}	LEF [*]	LBiomass [*]	LGDP [*]	Constant [*]	
	0.4407 (0.0410)	− 0.1048 (0.0101)	0.1739 (0.0327)	2.8690 (0.2885)	
Dependent variable ΔLGHG					
Short-run ^e	ΔLEF [*]	ΔLBiomass ^f	ΔLGDP [*]	Constant [*]	EC [*]
	0.1539 (0.0285)	0.01082 (0.0168)	0.32610 (0.0669)	− 0.00844 (0.00230)	− 0.1569 (0.0226)

^aTotal number of panel observations = 468.^b $\bar{R}^2 = 0.8138$.^cLog Likelihood = 530.1004.^dHausman Test(4) = 13.4420, Significance Level = 0.0037.^eTotal number of panel observations = 450.^fEstimation is not significant.

*depicts 1% statistical significance. (Standard errors are given in parentheses).

Table 4b indicates that the output of panel regression estimation by random effect methodology is similar to that of panel regression estimation by fixed effect methodology. The random effect results, hence, yield that biomass consumption has negative influence on emissions whereas EF, fuel and gas have positive impact on emissions in the long run. In the short run, the error correction term is significant and has negative sign. This output underlines the statistical evidence that the deviation from long run equilibrium will be restored by the amount of $[(- 0.1466) \times (u, t-1)]$. In the short run, Δ LEF, Δ LFUEL, and Δ LGAS have positive impulses on Δ LGHG. The Δ LBiomass' standard error value of 0.0115, hence, t value of 0.53 reveal that Δ LBiomass appears to be insignificant in the short run.

Tables 5a and **5b** follow fixed effect and random effect estimations, respectively, to observe the effects of log of biomass and log of ecological footprint as log of GDP is added into model. **Table 5a** explores that (i) as LEF goes up by 1%, the LGHG goes up by 0.4474%, (ii) when LBiomass increases 1%, the LGHG diminishes by 0.1102%. The results of **Table 5a** and **Table 5b** are very close to each other. **Table 5b** yields the LEF (0.4407) and LBiomass (– 0.1048) elasticities of LGHG.

The EC term is significant with the values of – 0.1586 (**Tables 5a**) and – 0.1569 (**Table 5b**). As Δ LBiomass happens to be insignificant in the short run as given in **Tables 5a** and **5b**, (i) the LEF and LGDP have positive significant impacts on LGHG in both **Table 5a** and **Table 5b**, (ii) the short run slope coefficient estimates of LEF and LGD are 0.1547 and 0.3249, respectively (**Table 5a**), (iii) the short run slope coefficient estimates of LEF and LGDP are 0.1539 and 0.32610, respectively (**Table 5b**).

Table 6 shows the panel cointegration regression estimations through FMOLS and DOLS models. The upper part of the table yield the estimation with deterministic variables of constant, LFUEL and LGAS, while lower part of the table gives the estimated coefficients through deterministic variables of constant, LFUEL, LGAS, and, LGDP.

In upper part, the regression output from FMOLS models indicate that a unit % expansion in LEF advances LGHG by 0.2857% and a unit % increment in LBiomass lowers the LGHG by 0.0515%. The relevant DOLS estimations for LEF and LBiomass are 0.2843 and – 0.0712, respectively. The below part of the table exhibits the outputs of FMOLS and DOLS that are similar to those of upper part of the table in terms of signs. The magnitudes of estimations are close to each other.

Table 7a and **Table 7b** depict the significant impulses of LEF and LBiomass on LGHG through ARDL estimations. As in previous tables, **Tables 7a** and **7b** confirm as well, that biomass usage decreases carbon emissions whereas ecological footprint boosts the emissions. The long run equilibrium estimated coefficients of LEF and LBiomass are 0.23401 and – 0.0730, respectively (**Table 7a**). The short run estimations reveal that EC term is found significant and that, among other short term changes, only the

Table 6 Panel cointegration regression estimation by FMOLS and DOLS

Dependent variable LGHG					
FMOLS ^{a,b}	LEF*	LBiomass*	DOLS ^{a,c}	LEF*	LBiomass*
	0.2857 (0.0399)	– 0.0515 (0.0089)		0.2843 (0.0525)	– 0.0712 (0.0088)
FMOLS ^{d,e}	LEF*	LBiomass*	DOLS ^{d,f}	LEF*	LBiomass*
	0.2053 (0.0377)	– 0.0377 (0.0109)		0.3146 (0.0560)	– 0.0444 (0.0120)

^aDeterministic variables: Constant, LFUEL, LGAS.^b $\bar{R}^2 = 0.9612$.^c $\bar{R}^2 = 0.9771$.^dDeterministic variables: Constant, LFUEL, LGAS, LGDP.^e $\bar{R}^2 = 0.9740$.^f $\bar{R}^2 = 0.9844$.

*depicts 1% statistical significance. (Standard errors are given in parentheses).

Table 7a Panel regression estimation by ARDL^{a,b}

Dependent variable LGHG					
Long-run	LEF*	LBiomass*			
	0.23401 (0.02686)	– 0.0730 (0.0031)			
Dependent variable Δ LGHG					
Short-run	Δ LEF ^c	Δ LEF(– 1) ^c	Δ LEF(– 2) ^c	Δ LBiomass*	Δ LBiomass(– 1) ^c
	– 0.0074 (0.03433)	– 0.0159 (0.0258)	– 0.0124 (0.0248)	0.0760 (0.0218)	0.0459 (0.0283)
	Δ LBiomass(– 2) ^c	EC*			
	0.0051 (0.0235)	– 0.6622 (0.0785)			

^aFixed variables: Constant, LFUEL, LGAS.^bLog likelihood = 1204.753.^cEstimation is not significant.

*depicts 1% statistical significance. (Standard errors are given in parentheses).

Table 7b Panel regression estimation by ARDL^{a,b}

Dependent variable LGHG				
Long-run	LEF*	LBiomass*		
	0.1536 (0.0308)	– 0.0802 (0.0077)		
Dependent variable Δ LGHG				
Short-run	Δ LEF ^c	Δ LEF(– 1) ^c	Δ LBiomass**	Δ LBiomass(– 1) ^c
	0.0430 (0.0311)	0.0428 (0.0355.)	0.0567 (0.0174)	0.0334 (0.0230)
	Δ LGHG(– 1)**	Δ LGHG(– 2) ^c	EC*	
	– 0.1125 (0.0594)	– 0.0012 (0.0460)	– 0.6648 (0.0578)	

^aFixed variables: Constant, LFUEL, LGAS, LGDP.^bLog likelihood = 1262.469.^cEstimation is not significant.

*depicts 1% statistical significance.

**depicts 10% statistical significance. (Standard errors are given in parentheses).

short term change in biomass (Δ LBiomass) variable is significant at 1% level. In the short run, biomass usage appears to affect the greenhouse gas emissions positively (Table 7a). Employing the fixed variables of constant, LFUEL, LGAS, and LGDP, Table 7b explores the positive consequences of LEF and LBiomass on LGHG in the long run at 1% level, and positive consequence of Δ LBiomass and negative power of Δ LGHG(– 1) on Δ LGHG in the short run at 10% significance levels.

From the output of Table 4a to the output of Table 7b, this paper concludes that LEF deepens LGHG whereas LBiomass declines LGHG. Since this paper also considers the causalities from GHG and Biomass to EF, the following Tables 8a, 8b, 9, 10a and 10b give the sequences of greenhouse gas emissions and biomass consumption on ecological footprint.

In Table 8a, the panel regression estimations by fixed effects reveal that there exist significant positive effects of logs of greenhouse gas emissions and GDP on log of ecological footprint both in the long run and short run. The log of biomass consumption is found insignificant in determining the long run and short run values of log of ecological footprint.

Table 8a Panel regression estimation by fixed effects

Dependent Variable LEF					
Long-run ^{a,b,c}	LGHG [*]	LBiomass ^e	LGDP [*]	Constant	
	0.4889 (0.04497)	− 0.0094 (0.0121)	0.1836 (0.03480)	0.0000 (0.0000)	
Dependent Variable ΔLEF ^b					
Short-run ^d	ΔLGHG [*]	ΔLBiomass ^e	ΔLGDP [*]	Constant [*]	EC [*]
	0.4477 (0.0692)	0.0113 (0.0254)	0.8487 (0.0962)	− 0.0147 (0.0034)	− 0.3179 (0.03328)

^aTotal number of panel observations = 468.^b $R^2 = 0.9328$.^cLog Likelihood = 456.3249.^dTotal number of panel observations = 450.^eEstimation is not significant.

*depicts 1% statistical significance. (Standard errors are given in parentheses).

Table 8b Panel regression estimation by random effects

Dependent Variable LEF					
Long-run ^{a,b,c,d}	LGHG [*]	LBiomass ^{**}	LGDP [*]	Constant [*]	
	0.4600 (0.0439)	− 0.0196 (0.0115)	0.2147 (0.0333)	− 2.4749 (0.3043)	
Dependent Variable ΔLEF					
Short-run ^e	ΔLGHG [*]	ΔLBiomass ^f	ΔLGDP [*]	Constant [*]	EC [*]
	0.4407 (0.0691)	0.0108 (0.0254)	0.8517 (0.0962)	0.0147 (0.0034)	− 0.3169 (0.0332)

^aTotal number of panel observations = 468.^b $R^2 = 0.7375$.^cLog Likelihood = 399.0725.^dHausman Test(4) = 12.0903, Significance Level = 0.0070.^eTotal number of panel observations = 450.^fEstimation is not significant.

*depicts 1% statistical significance.

**depicts 10% statistical significance. (Standard errors are given in parentheses).

Table 9 Panel cointegration regression estimation by FMOLS and DOLS

Dependent variable LEF					
FMOLS ^{a,b}	LGHG*	LBiomass ^g	DOLS ^{a,c}	LGHG*	LBiomass ^g
	0.6613 (0.0945)	– 0.0122 (0.0137)		0.7303 (0.1020)	0.0061 (0.0166)
FMOLS ^{d,e}	LGHG*	LBiomass*	DOLS ^{d,f}	LGHG*	LBiomass*
	0.5265 (0.0969)	– 0.0797 (0.0160)		0.5285 (0.1001)	– 0.1135 (0.0198)

^aDeterministic variables: Constant, LFUEL, LGAS.^b $R^2 = 0.9640$.^c $R^2 = 0.9674$.^dDeterministic variables: Constant, LFUEL, LGAS, LGDP.^e $R^2 = 0.9726$.^f $R^2 = 0.9795$.^gEstimation is not significant.

*depicts 1% statistical significance. (Standard errors are given in parentheses).

In **Table 8b**, the panel regression estimations through random effects yield positive influences of LGHG and LGDP on LEF at 1% levels, and, negative impulse of LBiomass on LEF at 10% level. **Table 8b** verifies **Table 8a** in terms of statistical significances and signs of LGHG, LGDP and EC term in the short run.

Table 9 shows the panel cointegration regression estimation by FMOLS and DOLS models. The outcome indicates that LGHG affects significantly and prominently the LEF when constant, LFUEL and LGAS are employed as deterministic variables. On the other hand, LGHG intensifies LEF and LBiomass lessens LEF in the long run, when the constant term, and LFUEL, LGAS and LGDP variables are considered deterministic variables within the models of FMOLS and DOLS. The estimated significant parameters of LGHG and LBiomass from FMOLS are 0.5265 and – 0.0797, respectively. The estimated significant

Table 10a Panel regression estimation by ARDL^{a,b}

Dependent variable LEF					
Long-run	LGHG [*] 0.9449 (0.0229)	LBiomass [*] − 0.0126 (0.0022)			
Dependent variable ΔLEF					
Short-run	ΔLEF(− 1) ^c 0.0669 (0.1816)	ΔLEF(− 2) ^c 0.0527 (0.1244)	ΔLEF(− 3) ^c 0.2228 (0.1371)	ΔLBiomass ^c 0.0604 (0.0568)	
	ΔLBiomass(− 1) ^c 0.0424 (0.0784)	ΔLBiomass(− 2) ^c − 0.0916 (0.0689)	ΔLBiomass(− 3) ^c − 0.0280 (0.0594)	ΔLGHG ^c 0.1576 (0.2601)	
	ΔLGHG(− 1) ^c − 0.1828 (0.2531)	ΔLGHG(− 2) ^c − 0.2617 (0.1767)	ΔLGHG(− 3) ^c − 0.1626 (0.1717)	EC [*] − 0.6444 (0.2134)	Constant [*] − 1.6456 (0.5331)

^aWhen fixed variables (Constant, LFUEL, LGAS) are added, only constant is found significant.^bLog likelihood = 876.716.^cEstimation is not significant.

*depicts 1% statistical significance. (Standard errors are given in parentheses).

Table 10b Panel regression estimation by ARDL^{a,b}

Dependent variable LEF					
Long-run	LGHG [*] 0.8578 (0.0237)	LBiomass [*] − 0.0226 (0.0029)			
Dependent variable ΔLEF					
Short-run	ΔLEF(− 1) ^c 0.1982 (0.2131)	ΔLEF(− 2) ^c 0.1468 (0.1378)	ΔLEF(− 3) ^{**} 0.28304 (0.1684)	ΔLBiomass ^c 0.0521 (0.0588)	
	ΔLBiomass(− 1) ^c 0.04805 (0.0800)	ΔLBiomass(− 2) ^c − 0.0662 (0.0751)	ΔLBiomass(− 3) ^c 0.0086 (0.0770)	ΔLGHG ^c − 0.0117 (0.2827)	
	ΔLGHG(− 1) ^c − 0.3190 (0.2540)	ΔLGHG(− 2) ^{**} − 0.3385 (0.1831)	ΔLGHG(− 3) ^c − 0.2766 (0.1891)	EC [*] − 0.8610 (0.2430)	Constant [*] − 2.6531 (1.0548)

^aWhen fixed variables (Constant, LGDP) are added, only constant is found significant.^bLog likelihood = 923.492.^cEstimation is not significant.

*depicts 1% statistical significance.

**depicts 10% statistical significance. (Standard errors are given in parentheses).

coefficients of LGHG and LBiomass from DOLS are 0.5285 and – 0.1135, respectively. Regarding DOLS results, one can indicate that the LEF increases by 0.5285% in response to one percent increase in LGHG, and, reduces by 0.1135% in response to one percent increase in LBiomass.

Table 10a exhibits the output from panel ARDL regression estimations and states that LGHG affects positively the LEF with the estimated coefficient of 0.9449 and LBiomass affects negatively LEF variable with the estimated parameter of – 0.0126. In the short run equilibrium, only EC and constant terms appear to be significant.

Table 10b demonstrates the positive impact of LGHG on LEF and negative effect of LBiomass on LEF in the long run. The estimated cointegration equilibrium coefficients of LGHG and LBiomass are 0.8578 and – 0.0226, respectively.

If EC term is not significant and not negative, there exists no long run relationship between LEF, LGHG and LBiomass. In the short run, Δ LEF responses significantly to lagged variables of Δ LEF, Δ LGHG [Δ LEF(– 3), Δ LGHG(– 2)], and EC and constant terms.

The EC term is significant at 1% level and has the value of – 0.8610. One may observe, for instance, the residual from Swedish data estimation in 1994 (= – 0.028751), among 18 European countries' panel data, and indicate that the LEF long run equilibrium will increase in 1995 by 0.02475 percentage [– 0.028751 $\times$ – 0.8610] to restore its cointegrating relationships with LGHG and LBiomass. Or, again, let one observe, by coincidence, the residual from Turkish data estimations in 2014 (= – 0.003132). It would mean that the LEF was below its cointegrating equilibrium level in 2014 by 0.003132 units and that, hence, LEF would increase in 2015 by 0.002696 units to keep its long run equilibrium.

Conclusion

This paper mainly aims at estimating the determinants of environmental degradation by analyzing the panel data for 18 European Countries. The paper, then, observes (i) the impact of biomass energy source on Greenhouse Gas emissions, (ii) the influence of biomass energy consumption on ecological footprint, (iii) the effect of ecological footprint on Greenhouse gas emissions, and, (iv) the impulse of Greenhouse gas emissions on ecological footprint.

To this end, the paper follows panel data methodologies. The paper first analyzes the Dumitrescu-Hurlin panel causalities (a) from LEF to LGHG, (b) from LGHG to LEF, (c) from LBiomass to LEF, (d) from LEF to LBiomass, (e) from LBiomass to LGHG, and, (g) from LGHG to LBiomass.

The output, for instance, exhibits that the 13 countries out of 18 countries in Europe experience statistically significant causality from biomass consumption to carbon emission. These countries in which LBiomass consumption causes LGHG emissions are Belgium, Denmark, France, Germany, Greece, Hungary, Ireland, Italy, Netherlands, Portugal, Spain, Sweden, and UK, respectively.

Fixed and random effect models indicate that log of biomass consumption has negative influence on log of emissions whereas logs of EF, fuel and gas have positive impact on log of emissions in the long run.

FMOLS models indicate that 1% expansion in LEF advances LGHG by 0.2857% and 1% increment in LBiomass diminishes the LGHG by 0.0515%. The relevant DOLS estimations for LEF and LBiomass are 0.2843 and -0.0712 , respectively.

ARDL estimations confirm the previous estimation and yield that biomass consumption lowers GHG emissions whereas ecological footprint boosts the emissions. The long run equilibrium estimated coefficients of LEF and LBiomass are 0.23401 and -0.0730 , respectively.

The panel regression estimations through random effects reveal positive impacts of LGHG and LGDP on LEF at 1% levels, and, negative impulse of LBiomass on LEF at 10% level.

FMOLS and DOLS estimations exhibit the output that LGHG increases LEF and LBiomass diminishes LEF in the long run. The DOLS results, for instance, indicate that the LEF increases by 0.5285% in response to 1% increase in LGHG and decreases by 0.1135% in response to 1% increase in LBiomass.

ARDL output verifies FMOLS and DOLS results by stating that long run impacts of LGHG and LBiomass on LEF are 0.8578 and -0.0226 , respectively.

Throughout the panel estimations, this paper suggests that policy makers support more biomass energy production and consumption in EU-18 countries to mitigate greenhouse gas emissions and hence environmental degradation. This possible action that might be taken by EU administrators might enable EU societies to reach sustainable growth.

See also: An Assessment of Hydrogen Energy Utilization for Sustainable Development. Low Carbon Economy for Sustainable Development. Retrofitting of Buildings/Built Environment – A Sustainable Development Model. Sustainable Future Alternative: (Bio)degradable Polymers for the Environment

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Relevant Website

- www.epi.yale.edu
Environmental Performance Index.
<https://www.footprintnetwork.org>
Global Footprint Network.

Optimization and Kinetic Modeling of Biodiesel Production

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Introduction

Energy is an essential requirement for human in the current scenario to sustain the living standards and to enhance the economics of the nation. So far, the energy need was fulfilled by the fossil based fuels like petroleum products, natural gas and coal etc. Due to rapid industrialization and population growth the demand for the energy is increased more whereas energy supply from fossil fuels is decreased since it is non-renewable resource. The alternate renewable sources have been gaining interest to overcome the energy crisis due to the exhaustion of fossil fuels. Biodiesel is mainly focused as an alternative fuel source since it possesses serial advantages like less carbon dioxide emission, non-toxic and better efficiency. Mono-alkyl esters of fatty acid obtained from the transesterification reaction of oil and alcohol in the presence of catalyst is known as biodiesel. It shows similar properties of the conventional petroleum fuel and it is produced mainly from the edible oils. Use of edible oils for large scale biodiesel production is limited since it imbalances the global food demand. Non-edible oils were employed as an alternate source to edible oils because they are economic, easily available and do not affect the food industrial demand. Various non-edible oils such as jatropha, karanja, palm, mahua, moringa and rubber seed etc were used for production of clean, eco-friendly biodiesel nowadays.

Optimization is one of the key steps in any process since it directly influences the product yield and economics. The variables or conditions involved in the process should be optimized to get maximum yield with optimal resources. Previously, conventional one-variable at a time (OVAT) method is preferred for optimization studies but it lacks to provide the details of interaction effect of variables, require more time and experiments. Statistical experimental designs are very effective for multivariate optimization which gives better insight about the variables interaction and its optimal levels. Response Surface Methodology (RSM) is a most widely used successful statistical optimization tool to make experimental design, model the process, study the combined effects of variables and identify the optimum levels. In this report, utilization of RSM for optimization of biodiesel production from Jatropha oil was discussed.

The kinetics of the reaction is very important to determine the rate constant and the mechanism which are useful for designing an appropriate reactor for production. For biodiesel production, transesterification is an important reaction for the synthesis of alkyl ester from the reaction of oil and solvent in the presence of catalyst. The reaction rates were highly influenced by the type of catalyst involved in the reaction. For homogeneous catalyzed transesterification, usually the kinetics followed first or second order models. In case of heterogeneous catalyst reaction rate follows different mechanism. The study of different kinetic models for biodiesel production provides the details about the reaction mechanism and rate controlling step in transesterification. In this chapter, different kinetic models used to determine the reaction rate for biodiesel production was also discussed.

Jatropha Oil

Jatropha curcas (Linnaeus) belongs to Euphorbiaceae family and widely planted as an economic crop. Jatropha is easy to grow and it is tolerant to stress and drought. Different parts of the plant such as bark, fruit and seeds were used for several applications in medicine and energy production. *Jatropha curcas* seeds are found to be the richest source of oil provides the highest productivity of biodiesel. Moreover, American and European standards organisation confirmed the quality of jatropha biodiesel and they are very well comparable with the commercially available fossil fuels. The productivity of biodiesel from crude jatropha oil can be improved by optimizing the conditions required for the conversion of seed oil to methyl ester of fatty acids.

Response Surface Optimization of Jatropha Oil Based Biodiesel Production

Yee *et al.* (2011) reported a maximum biodiesel yield of 90.32 wt% produced by optimizing the process variables such as reaction temperature, time, molar ratio of methanol to jatropha oil and concentration of catalyst: alumina loaded with sulphated zirconia. The optimization study was conducted using Design Expert software to analyse the process variables based on Response Surface Methodology. The coefficient of variation decides the quality of the model and it was found to be 98.66% with a confidence level of 95% analysed through ANOVA. The study on influence of interaction effects of process variables on biodiesel yield was conducted with fixed catalyst loading of 6 wt% and methanol to oil ratio at 8. It was observed that on increasing the temperature from 90°C to 150°C there is a gradual increase in the yield of biodiesel from 25.59% to 60.21% and with the same trend the duration time increased to 4 h the biodiesel yield was shoot up to 74.74%. Hence it was concluded that the reaction duration have more impact on the biodiesel yield at higher temperature rather than at lower temperature. Similarly at higher reaction

temperature of 150°C, the raise in methanol to oil ratio from 6 to 10 leads to increase the biodiesel yield from 57.19% to 75.05%. The characterization studies proved that the fuel properties of Jatropha biodiesel met with the standards as per ASTM D 6751.

A two step processes for biodiesel production using crude jatropha oil was experimented by [Gandhi and Kumaran \(2014\)](#). The first step involves the acid treatment to reduce the free fatty acid content from 6.85% to 1.12% and the second step comprised of RSM based optimization to the transesterification process of pretreated jatropha oil. A central composite rotatable second-order design was implemented to analyse the process variables with three factors at 5-levels to derive the ANOVA report and interaction effects via response surface plots. The results of ANOVA suggested that the model is significant as the p-value obtained is below 0.0001 with R^2 value of 0.9722. The 3-D plots depict the effects of interaction of process variables on biodiesel yield. The interaction effects were demonstrated by changing two process variables by keeping one as constant value to predict the biodiesel yield. In this way the experiments were conducted by changing the reaction temperature and methanol to oil ratio with the fixed concentration of catalyst (0.55%). The results suggested that the reaction temperature was found to be reciprocal with the methanol to oil ratio. By increased methanol to oil ratio at lowest temperature the yield of biodiesel was found to be high and vice versa. Similarly the interaction effects were studied for the change in catalyst concentration and reaction temperature with fixed concentration of methanol to oil ratio (1:5.41). These results depicts that the biodiesel yield was increased till 62°C and 0.58% of catalyst concentration and beyond that there was a decline in the biodiesel yield. A highest yield of 92.5% was achieved under the reaction temperature of 61.5°C, catalyst concentration of 0.58% w/w and 1:5.93 molar ratio of oil to methanol.

Jatropha biodiesel production up to 98.3% with reduced free fatty acid from 14.6% to 0.34% was produced by [Goyal et al. \(2012\)](#). To achieve this yield, four process variables such as methanol/oil molar ratio, reaction time, reaction temperature and catalyst concentration at five level was employed using central composite design (CCD) of RSM. The optimization of the experimental conditions using RSM was performed with two-step processes. In the first step, optimization involves the reduction of free fatty acid content to 0.34% achieved at optimum temperature of 50°C for 125 min reaction with 1.5% v/v sulphuric acid as catalyst and methanol/oil in 6.5:1 molar ratio. The ANOVA table was framed for the esterification process and it was showed with the p-value less than 0.0001, which indicated that the model was significant. The model also proved as goodness of fit, as the regression co-efficient value for the experimental model was found to be 0.96 and which was near closer to the model predicted value of 0.92. The impact of the catalyst concentration, temperature, time and methanol/oil ratio on FFA content was demonstrated by calculating the deviation of the coded value from the middle point of the respective process variables. It was observed that increase in concentration of catalyst decreases the FFA content and whereas, the methanol/oil ratio have no effect on the change in FFA content. The FFA was found to be decreased with increase in time and temperature till middle point after that it was increased. These results indicated that longer incubation time and exposure to higher temperature leads to inhibition of FFA reduction. The effect of process variables in esterification process was demonstrated that the second step optimization is yield improving step, includes the optimum range of process variables such as 11.1 methanol/oil molar ratios, 1% w/w of sodium hydroxide reacted for 110 min at reaction temperature of 55°C. This trans-esterification step also showed a p-value lower than 0.0001 with a goodness of fit regression values of 0.945, which was greater than the model predicted value of 0.890 indicated that the model is more significant. To determine the efficiency of trans-esterification process for biodiesel production, a similar kind of deviation with coded value of process variables from the middle point was studied. It was understood that the biodiesel productivity was increased with increase in concentration of methanol and time, indicated that increasing the processing time along with methanol ratio ensures the complete transformation of the fatty acid esters to biodiesel. At initial stage the increase in temperature decreases the biodiesel yield but after the reaction proceeds the production of jatropha biodiesel was improved with increasing temperature. This results suggested that initial period the viscosity of the oil decreases the biodiesel productivity and later on the viscosity decreases with time and hence the productivity of the biodiesel improved with higher temperature. A maximum yield of 98.3% of jatropha biodiesel was produced and it was confirmed with ASTM standard requirements.

Microwave assisted biodiesel yield improvement was demonstrated by [Jaliliannosrati et al. \(2013\)](#). The parametric variables include particles seed size, irradiation time, stirrer speed and catalyst loading. Response Surface Methodology (RSM) based Central Composite Design (CCD) was used to design the experimental variables. The reaction was induced by using 5N potassium hydroxide solution as base catalyst. Initially the free fatty acid present in the oil was reduced to 1% from 14% by treating with catalyst, sulphuric acid and the reduced free fatty acid was subjected for optimization to yield 97.29% of fatty acid ethyl esters. The RSM design was generated by incorporating four independent variables such as irradiation time, agitation speed, catalyst loading and size of the particles. The experimental results were analysed by ANOVA report and response surface plots to justify the significance of the model. A smaller p-value of 0.005 indicated that the model is significant but the value of 'lack of fit' was found to be 0.2870 revealed the insignificant of the model. The surface and contour plots were used for determining the interaction effects for irradiation time versus agitation speed and catalyst loading versus agitation speed against the conversion of free fatty acid. To study the interaction effect, irradiation time was fixed at constant up to 20 min; the agitation speed and catalyst loading varied from 150 to 350 rpm and 8–10 mL respectively. It was found that beyond 300 rpm speed and 9 mL of catalyst loading there is no improvement in the FFA conversion. Similarly 9 mL of catalyst loading was fixed with varying the irradiation time and speed of 12–28 min and 150–350 rpm respectively. The results suggested that lesser the irradiation time for 10–12 min and agitation speed about 300 rpm is sufficient for the successful conversion of FFA. The optimum conditions for the process include less than 0.5 mm of seed size, time of irradiation 12.21 min. with 110 W microwave power, potassium hydroxide catalyst loading of 8.15 ml and stirrer speed of 331.52 rpm.

Calcium oxide coupled with magnesium oxide was employed as synergetic catalyst for transesterification of jatropha plant oil in production of biodiesel. The novel catalyst has proved its incredible effect in improved production of biodiesel of 93.55%. A highest order polynomial with greater significant, a quadratic model suggested by CCD based RSM was utilized for the determination of interaction effects by surface and contour plots. A 95% of confidence level with p-value less than 0.0001 depicted that the model suggested was statistically significant. The ANOVA results suggested that time of reaction (A), Methanol to oil ratio (B), Temperature (C) and Catalyst concentration (D) are the variables having significant influence in conversion of fatty acid methyl esters. The interaction terms such as AD, AC and CD have major impact on increasing conversion of fatty acid demonstrated by 3-D surface plots. The p-value obtained for the lack of fit test is greater than 0.05 indicated that the model is not significant but the coefficient of variation and R^2 value is 3.99% and 98.9% respectively, and this suggested that the model possess high degree of precision and reliability. The combined catalysts along with the following optimum conditions generated by CCD, such as methanol to oil molar ratio of 38.67, catalyst loading of 3.7% w/w along with 115.87°C temperature and 3.44 h of reaction time respectively contributed high production of biodiesel. Lee *et al.* (2011), has proved that the high yield of biodiesel is due to the synergetic effect of the coupled active catalysts CaO-MgO.

The CCD based optimum conditions with 0.62% v/v of ethanol to oil molar ratio, 1.7% v/v of acid catalyst using sulphuric acid, 79 min of processing time and operating temperature at 54°C was provided to reduce the FFA from 14% to 1%. A quadratic polynomial model was utilized to relate the reaction variables with the FFA reduction showed better coefficient of determination $R^2=0.893$. Suwito *et al.* (2012) proved that these results were comparable with transesterification process utilizing a base catalyst. According to the ANOVA results it was noted that the ethanol to oil ratio one exhibited the significant effect on reduction of FFA at confidence level of 95%. The interaction effects of process variables on the biodiesel productivity suggested that the catalyst concentration between 1% and 3% with increase in ethanol to oil concentration greatly increases the FFA reduction. Another interactions between time and ethanol to oil ratio indicated that the concentration of ethanol beyond 0.5% and time of 90 min enhances the reduction of FFA.

Kombe and Temu (2017), utilized two process variables to optimize the deacidification efficiency of jatropha oil up to 98.74% using CCD based RSM. The two independent process variables employed in the study were amount of steam and reaction temperature which yielded a 13 runs of CCD based RSM design. The steam distillation efficiency for the conversion of free fatty acid into biodiesel was determined from the results of surface plots and the ANOVA. The p-value less than 0.005 and the coefficient of determination $R^2=0.9563$ highly supports the model is statistically significant. The 3-D surface plots results suggested that the interaction effect of amount of steam and reaction temperature 3.4 wt% and 235°C yielded a maximum transesterification of free fatty acid. The optimized conditions reduce the high FFA of crude jatropha oil to a value near to 0.09% from 4.54%. The deacidified jatropha oil was transesterified by homogenous base catalyst to produce biodiesel of 97.45%. The fuel produced was tested for the viscosity, acid value, total calorific value, FAME, density and iodine value to prove that the biodiesel obtained from jatropha oil through this optimization study was very well comparable with the EN14214 and ASTM D6751.

Kinetic Modeling of Biodiesel Production

Transesterification Reaction

Transesterification is a chemical reaction where alkoxy group of an ester and alkoxy group of an alcohol is exchanged in the presence an acid or a base catalyst. In the case of biodiesel production, three moles of triglycerides (TG) in animal fats or vegetable oil reacts with alcohol (methanol or ethanol) to yield one mole of glycerol and three moles of fatty acid methyl ester (FAME) or fatty acid ethyl ester (FAEE) (Fig. 1). If methanol is used as alcohol in biodiesel production, the product is methyl esters (ME); likewise, if ethanol is used as alcohol, the reaction product will be ethyl esters (EE). But, in both, glycerin is the co-product of transesterification. The reaction are shown below,

Generally, transesterification reaction consists of three successive reversible reactions; in each step one mole of ME is generated along with monoglycerides (M) and diglycerides (D) as intermediates during first and second steps respectively (Fig. 2). Transesterification of TG with methanol is catalyzed by acid or base catalyst, where acid and base catalyst could be either homogenous or heterogeneous catalyst.

Transesterification, catalyzed by heterogeneous catalyst is more complex reaction (reaction proceed on the surface of solid catalyst) since it is three phase liquid-liquid-solid reaction. Therefore, rate of biodiesel depends on seven steps such as,

- (1) External diffusion of reactant,
- (2) Internal diffusion of reactant,
- (3) Adsorption of reactant on the catalyst surface,
- (4) Surface reaction,
- (5) Desorption of product,
- (6) Internal diffusion of product and
- (7) External diffusion of product.

Kinetics for transesterification reactions of TG are examined by numerous researchers. Theses researches mainly focused to generate equation for rate of reaction. These developed rate kinetics are very much useful in the design of reactors in the biodiesel

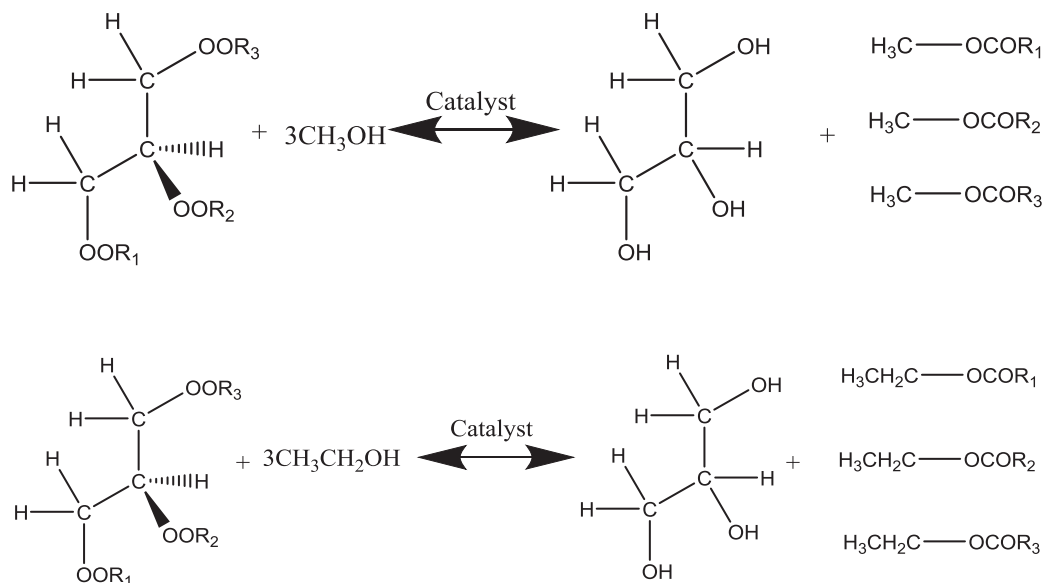


Fig. 1 Scheme of transesterification reaction.

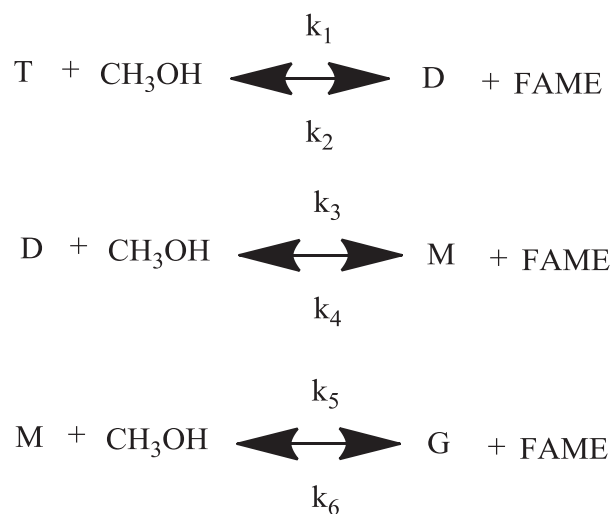


Fig. 2 Three steps involved in Transesterification of TG and methanol.

production. Different rate equation has been developed by various scientists depends on the types of catalyst used in the transesterification reaction. For Homogenous catalyst, generally, first order and second order kinetics are developed. On the other hand, for heterogeneous catalyst Eley-Rideal kinetics and Langmuir- Hinshelwood-Hougen-Watson (LHHW) are developed. In the case of catalytic reaction, controlling step could be surface chemical reaction or adsorption of reactants or desorption of reactants or internal diffusion or external diffusion.

Kinetic Models for Homogeneous Catalyzed Transesterification

Pseudo-First Order Kinetics Model

This kinetic model rests on the following assumptions

- (1) The transesterification reaction occurs in the oil phase. i.e., oil is the limiting reactant,
- (2) Transesterification reaction is carried out in the presence of large quantity of methanol (excess reactant),
- (3) The slowest step (rate limiting step) is reaction between TAG and one mole of methanol.

Table 1 Summary of pseudo-first order rate constants for transesterification of TG

Oil	Catalyst	Rate constant (min^{-1})	Activation energy (kJ mol^{-1})	References
<i>Bombax ceiba</i> oil	CaO-NPs	0.031	35.99	Hebbbar <i>et al.</i> (2018)
<i>Madhuca indica</i> oil	KOH	0.011	22.31	Muthukumaran <i>et al.</i> (2017)
Sunflower oil	Al-Sr NPs	0.012	72.86	Feyzi and Shahbazi (2017)
Soybean oil	H ₂ SO ₄	0.003	27.53	Parkar <i>et al.</i> (2012)
Waste cooking oil	NaOH	0.078	88.76	Jain <i>et al.</i> (2011)
Rapeseed crude oil	NaOH	0.696	85.4	Wang <i>et al.</i> (2007)

Based on the assumption stated above the following rate equation could be written as:

$$-r_{TG} = -\frac{dC_{TG}}{dt} = kC_{TG}C_{MOH} \quad (1)$$

Since, methanol is added into reaction mixture as excess reactant, the simplification could be made,

$$k' = kC_{MOH} \quad (2)$$

Substituting Eq. (2) into the Eq. (1) result to,

$$-r_{TG} = -\frac{dC_{TG}}{dt} = kC_{TG} \quad (3)$$

Conversion (X_{TG}) with respective TG could be defined as,

$$X_{TG} = \frac{C_{TG0} - C_{TG}}{C_{TG0}} \quad (4)$$

$$\therefore dC_{TG} = -C_{TG0}dX_{TG}$$

Substituting the Eq. (4) into (3) and integrating with the boundary condition as when time=0 $X_{TG}=0$ and when time=t; $X_{TG}=X_{TG}$

$$-1n(1 - X_{TG}) = k't \quad (5)$$

Further, the activation energy necessary to proceed with the transesterification reaction could be calculated using Arrhenius equation as given below (Table 1),

$$k = k_0 e^{-E_a/RT} \quad (6)$$

Second Order Kinetics

Transesterification of TG could be modelled with second order differential equation based on the elementary reaction mentioned in the stoichiometry represented in Eq. 7–12. Table 2 showed second order the rate constants reported in different studies on biodiesel production.

$$-r_{TG} = \frac{dC_{TG}}{dt} = k_1 C_{TG} C_{MOH} - k_2 C_{FAME} C_{DG} \quad (7)$$

$$-r_{DG} = \frac{dC_{DG}}{dt} = k_2 C_{FAME} C_{DG} - k_1 C_{TG} C_{MOH} + k_3 C_{DG} C_{MOH} - k_4 C_{FAME} C_{MG} \quad (8)$$

$$-r_{MG} = \frac{dC_{MG}}{dt} = k_4 C_{FAME} C_{MG} - k_3 C_{DG} C_{MOH} + K_5 C_{MG} C_{MOH} - k_6 C_{FAME} C_G \quad (9)$$

$$r_{MOH} = \frac{dC_{MOH}}{dt} = k_1 C_{TG} C_{MOH} - k_2 C_{FAME} C_{DG} + k_3 C_{DG} C_{MOH} - k_4 C_{FAME} C_{MG} + K_5 C_{MG} C_{MOH} - k_6 C_{FAME} C_G \quad (10)$$

$$r_{FAME} = \frac{dC_{FAME}}{dt} = k_1 C_{TG} C_{MOH} - k_2 C_{FAME} C_{DG} + k_3 C_{DG} C_{MOH} - k_4 C_{FAME} C_{MG} + K_5 C_{MG} C_{MOH} - k_6 C_{FAME} C_G \quad (11)$$

$$r_G = \frac{dC_G}{dt} = K_5 C_{MG} C_{MOH} - k_6 C_{FAME} C_G \quad (12)$$

Table 2 Summary of second order rate constant for transesterification of TG

Oil	Catalyst	k_1 (L mol ⁻¹ min ⁻¹)	k_2 (L mol ⁻¹ min ⁻¹)	k_3 (L mol ⁻¹ min ⁻¹)	k_4 (L mol ⁻¹ min ⁻¹)	k_5 (L mol ⁻¹ min ⁻¹)	k_6 (L mol ⁻¹ min ⁻¹)	Reference
Crude sunflower	NaOH	0.0895	0.0094	0.3480	0.1285	0.4884	0.0380	Bambase <i>et al.</i> (2007)
Sunflower	KOH	0.08	0.02	0.97	0.00	0.01	0.88	Klofutar <i>et al.</i> (2010)
Canola	KOH	0.09	0.05	1.56	0.01	0.07	0.61	Klofutar <i>et al.</i> (2010)
Waste sunflower	KOH	0.0247	0.0558	0.0703	0.0015	0.0394	0.0042	Klofutar <i>et al.</i> (2010)

Table 3 Kinetic rate equations for Eley-Rideal mechanism ($K=k_i/k_{-i}$)

Elementary reaction	Rate equation
$3S + 3MOH \leftrightarrow 3S.MOH$	$\frac{k_1 C_S^3 - k_{-1} \left(\frac{k_3 C_D C_{FAME}}{k_2} \right)^3}{\left(1 + \frac{k_3 C_D C_{FAME}}{k_2} + K_3 C_D + K_5 C_M + K_7 C_G \right)^3}$
$S.MOH + T \leftrightarrow S.D + FAME$	$\frac{k_2 C_T - k_{-2} C_D C_{FAME}}{1 + K_1 C_{MOH} + K_3 C_D + K_5 C_M + K_7 C_G}$
$S.D \leftrightarrow S + D$	$\frac{k_{-3} \left(\frac{k_2 K_1 C_T C_{MOH}}{C_{FAME}} \right) - k_3 C_D}{1 + K_1 C_{MOH} + \frac{k_2 K_1 C_T C_{MOH}}{C_{FAME}} + K_5 C_M + K_7 C_G}$
$S.MOH + D \leftrightarrow S.M + FAME$	$\frac{K_1 k_4 C_{MOH} C_D - k_{-4} K_5 C_M C_{FAME}}{1 + K_1 C_{MOH} + K_3 C_D + K_5 C_M + K_7 C_G}$
$S.M \leftrightarrow S + M$	$\frac{k_{-5} \left(\frac{k_4 K_1 C_D C_{MOH}}{C_{FAME}} \right) - k_5 C_M}{1 + K_1 C_{MOH} + \frac{k_4 K_1 C_D C_{MOH}}{C_{FAME}} + K_5 C_M + K_7 C_G}$
$S.MOH + M \leftrightarrow S.G + FAME$	$\frac{K_1 k_6 C_{MOH} C_M - k_{-6} K_7 C_G C_{FAME}}{1 + K_1 C_{MOH} + K_3 C_D + K_5 C_M + K_7 C_G}$
$S.G \leftrightarrow S + G$	$\frac{k_{-7} \left(\frac{k_6 K_1 C_M C_{MOH}}{C_{FAME}} \right) - k_7 C_G}{1 + K_1 C_{MOH} + K_3 C_D + K_5 C_M + \frac{k_6 K_1 C_M C_{MOH}}{C_{FAME}}}$

Modified from Kapil, A., Wilson, K., Lee, A.F., Sadhukhan, J., 2011. Kinetic modeling studies of heterogeneously catalyzed biodiesel synthesis reactions. *Industrial & Engineering Chemistry Research* 50 (9), 4818–4830.

Kinetic Models for Heterogeneous Catalyzed Transesterification

Eley-Rideal Kinetics

The elementary step involved in the Eley-Rideal model shown in **Table 3**. In this, methanol is adsorbed on (M) on the vacant site of catalyst(S), these adsorbed methanol subsequently interact with T, D, M (which are in the bulk fluid) and results adsorbed diglyceride (S.D), monoglyceride (S.M), and glycerol (S.G) respectively, along with FAME in each step. Each of the above step can be considered as rate controlling step. The kinetic expressions given in **Table 3** was developed by making the following assumptions.(i) Surface of catalyst is homogenous without the inert species on the surface and (ii) Slowest reaction is considered as rate controlling step (Kapil *et al.*, 2011).

Langmuir-Hinshelwood-Hougen-Watson (LHHW)

In addition to assumption made in Langmuir model, Langmuir-Hinshelwood model assumed that both methanol and triglyceride are adsorbed on the adjacent active sites of catalyst. In the first two steps both methanol and triglyceride are adsorbed adjacently on the catalyst surface, subsequently, the adsorbed methanol (S.MOH) and triglyceride (S.T) resulted to S.FAME and adsorbed diglyceride. Consequently these adsorbed diglyceride (S.D) reacts with adsorbed methanol (S.MOH) to give fatty acid methyl esters (S.FAME) and adsorbed monoglyceride (S.D). Then adsorbed monoglyceride reacts with adsorbed methanol (S.MOH) to produce S.FAME and glycerol (S.G). Each of the following steps could be a rate controlling step. **Table 4**. shows the generalized rate equation for each elementary reaction (Kapil *et al.*, 2011).

Table 4 Kinetic rate equations for Langmuir- Hinshelwood-Hougen-Watson mechanism ($K=k_i/k_{-i}$)

Elementary reaction	Rate equation
$3S + 3MOH \leftrightarrow S.MOH$	$\frac{k_1 C_{MOH}^3 - K_{-1} \left(\frac{K_6 K_7 C_D C_{FAME}}{K_3 K_2 C_T} \right)^3}{\left(1 + \frac{K_6 K_7 C_D C_{FAME}}{K_3 K_2 C_T} + K_2 C_T + K_6 C_{FAME} + K_7 C_D + K_8 C_M + K_9 C_G \right)^3}$
$S + T \leftrightarrow S.T$	$\frac{k_2 C_T - K_{-2} \left(\frac{K_6 K_7 C_D C_{FAME}}{K_3 K_1 C_{MOH}} \right)}{\left(1 + K_1 C_{MOH} + \frac{K_6 K_7 C_D C_{FAME}}{K_3 K_1 C_{MOH}} + K_6 C_{FAME} + K_7 C_D + K_8 C_M + K_9 C_G \right)}$
$S.MOH + S.T \leftrightarrow S.FAME + S.D$	$\frac{k_3 C_{MOH} C_T - K_{-3} C_{FAME} C_D}{(1 + K_1 C_{MOH} + K_2 C_T + K_6 C_{FAME} + K_7 C_D + K_8 C_M + K_9 C_G)^2}$
$S.MeOH + S.D \leftrightarrow S.FAME + S.M$	$\frac{k_4 C_{MOH} C_D - K_{-4} C_{FAME} C_M}{(1 + K_1 C_{MOH} + K_2 C_T + K_6 C_{FAME} + K_7 C_D + K_8 C_M + K_9 C_G)^2}$
$S.MeOH + S.M \leftrightarrow S.FAME + S.G$	$\frac{k_5 C_{MOH} C_M - K_{-5} C_{FAME} C_G}{(1 + K_1 C_{MOH} + K_2 C_T + K_6 C_{FAME} + K_7 C_D + K_8 C_M + K_9 C_G)^2}$
$3S.FAME \leftrightarrow 3.S + 3 FAME$	$\frac{K_{-6} \left(\frac{K_1 K_2 K_3 C_{MOH} C_T}{K_7 C_D} \right)^3 - K_6 C_{FAME}^3}{\left(1 + K_1 C_{MOH} + K_2 C_T + \frac{K_1 K_2 K_3 C_{MOH} C_T}{K_7 C_D} + K_7 C_D + K_8 C_M + K_9 C_G \right)^3}$
$S.D \leftrightarrow S + D$	$\frac{K_{-7} \frac{K_1 K_2 K_3 C_{MOH} C_T}{K_6 C_{FAME}} - K_6 C_D}{\left(1 + K_1 C_{MOH} + K_2 C_T + K_6 C_{FAME} + \frac{K_1 K_2 K_3 C_{MOH} C_T}{K_6 C_{FAME}} + K_8 C_M + K_9 C_G \right)}$
$S.M \leftrightarrow S + M$	$\frac{K_{-8} \frac{K_6 K_9 C_{FAME} C_G}{K_5 C_{MOH}} - K_8 C_M}{\left(1 + K_1 C_{MOH} + K_2 C_T + K_6 C_{FAME} + K_7 C_D + \frac{K_6 K_9 C_{FAME} C_G}{K_5 C_{MOH}} + K_9 C_G \right)}$
$S.G \leftrightarrow S + G$	$\frac{K_{-9} \frac{K_1 K_5 K_8 C_{MOH} C_M}{K_6 C_{FAME}} - K_9 C_G}{\left(1 + K_1 C_{MOH} + K_2 C_T + K_6 C_{FAME} + K_7 C_D + K_8 C_M + \frac{K_1 K_5 K_8 C_{MOH} C_M}{K_6 C_{FAME}} \right)}$

Modified from Kapil, A., Wilson, K., Lee, A.F., Sadhukhan, J., 2011. Kinetic modeling studies of heterogeneously catalyzed biodiesel synthesis reactions. Industrial & Engineering Chemistry Research 50 (9), 4818–4830.

External Diffusion

In the case, when external diffusion of oil is the slowest step, then the rate equation can be calculated using the following equation (Fogler, 2005),

$$r = k(C_{TG_B} - C_{TG_S}) \quad (13)$$

Where, k is mass transfer coefficient, C_{TG_S} is concentration of TG on the surface, C_{TG_B} is concentration of TG on the bulk
The mass transfer co-efficient of TG in reaction mixture can be calculated using Frossling correlation

$$Sh = 2 + 0.6 \times Re^{1/2} \times Sc^{1/3} \quad (14)$$

Where,

$$Sh = \text{Sherwood number} = \frac{k d_p}{D_{AB}}$$

$$Re = \text{Reynolds number} = \frac{\rho d_p \omega D}{\mu}$$

$$Sc = \text{Schmidt number} = \frac{\mu}{\rho D_{AB}}$$

Where

d_p – Diameter of the particle (m)

ω – Angular velocity (rad/s)

ρ – Density (kg/m³)

μ – Viscosity (kg/m s)

D_{AB} – Diffusivity coefficient (m²/s)

Internal Diffusion

If the internal diffusion of TG is rate controlling step, the actual rate of reaction can be determined using Thiele modulus (ϕ_n^2)

$$\phi_n^2 = \frac{k_n \rho_c S_a C_{TGS}^{n-1} R^2}{D_e} = \frac{\text{surface reaction rate}}{\text{Diffusion rate}} \quad (15)$$

where,

k_n – Reaction rate constant for n^{th} order of reaction

ρ_c – Density of catalyst (kg/m^3)

S_a – Surface area of the catalyst per unit mass of catalyst (m^2/g)

C_{TGS} – Surface concentration of TG (kg/m^3)

R – radius of catalyst particle (m)

D_e – Effective diffusivity (m^2/s)

- (1) Small values of the Thiele modulus indicates that the surface reaction is controlled and a significant amount of the reactant diffuses well into the pellet interior without reacting.
- (2) Large values of the Thiele modulus indicates that the surface reaction is rapid and that the reactant is consumed very close to the external pellet surface with very little penetration into the interior of the pellet (Fogler, 2005).

Further, the actual reaction rate is calculated using the following equation

$$r = \frac{3}{\phi_n^2} (\phi_n \coth \phi_n - 1) k C_{AS}^n \quad (16)$$

C_{AS} can be calculated using the following equation

$$k_c (C_{A0} - C_{AS}) A_p = \eta k C_{AS}^n A_s \quad (17)$$

where,

k_c = mass transfer coefficient

$A_p = 4\pi R^2$

$A_s = S_a \cdot (\text{mass of the catalyst})$

Conclusion

Optimization studies on biodiesel production from non-edible jatropha oil using RSM was reported in this chapter. The application of RSM was highly useful for identifying the optimal levels of the selected factors and also it illuminates the interaction of each variable on the biodiesel production. Further, the kinetic models for homogeneous and heterogeneous catalyzed transesterification reaction was also discussed which would be helpful in designing a suitable reactor for biodiesel production.

See also: An Assessment of Hydrogen Energy Utilization for Sustainable Development. Analyzing Biodiesel Production From Cooking Oil. Is the Production of Biofuels Environmentally Sustainable?. Performance and Emission Characteristics of Biodiesel–Diesel Blend. Renewable and Sustainable Materials in Automotive Industry. Sustainable Biodiesel Production. The Production of Biogas, Biodiesel as High-Value Bio-Based Product and Multiple Bio-Products Through an Integration Approach of the Anaerobic Digestion and Fermentation Processes. Utilization of Bio-Hydrogen in HCCI Engines as a Most Renewable Fuel for Sustainable Transportation – A Thermodynamic Analysis

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Performance and Emission Characteristics of Biodiesel–Diesel Blend

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Introduction

World Energy Scenario: Transportation Sector

Energy consumption is an indicator of economic growth and standard of living in any civilization. After the Industrial Revolution in the late 18th and early 19th century, the energy consumption of the world has increased exponentially over the years. According to the prediction in a U.S. Energy Information Administration (2017) report, the total energy consumption of the world will increase from 575 quadrillion British thermal units (Btu) in 2015 to 663 quadrillion Btu by 2030 and then to 736 quadrillion Btu by 2040. Thus, the world will need around 30% more energy in 2040 compared with 2015. Most global primary energy is produced from the conventional energy sources (fossil fuels). As shown in Fig. 1, oil, coal, and gas remain the dominant resources with 86% contribution of total world energy, while hydro, nuclear, and other renewable energy account for 7%, 4%, and 3% of the total primary energy consumption, respectively (British Petroleum Company, 2017). The transport sector, which includes automobiles, ships, trains, and airplanes, is the second largest global energy consumer after the industrial sector (Fig. 2). This sector accounts for 25% of world's total energy consumption, of which 80% is used for road transport (U.S. Energy Information Administration, 2017). Around the world, the vehicle fleet (both commercial vehicles and passenger cars) is growing rapidly. There were about 1.1 billion total global vehicles on the road in 2013 and this is projected to be around 2.3 billion (which is more than double) by 2035. In India and China, projected vehicle density per 1000 population is expected to grow from 20 to 130 (8.4% p.a.) and 80 to 360 (6.9% p.a.),

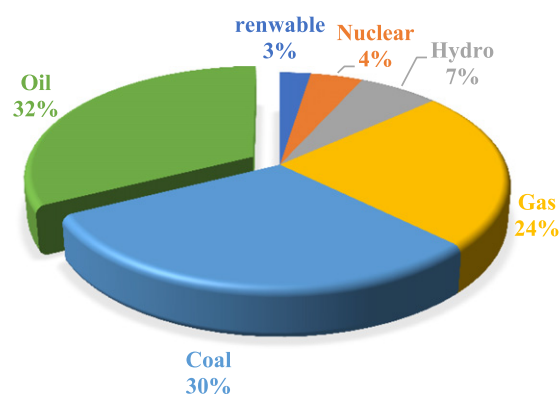


Fig. 1 Global primary energy production in 2015. Source: British Petroleum Company, 2017. BP Energy Outlook 2017. Retrieved from <https://www.bp.com/content/dam/bp/pdf/energy-economics/energy-outlook-2017/bp-energy-outlook-2017.pdf>.

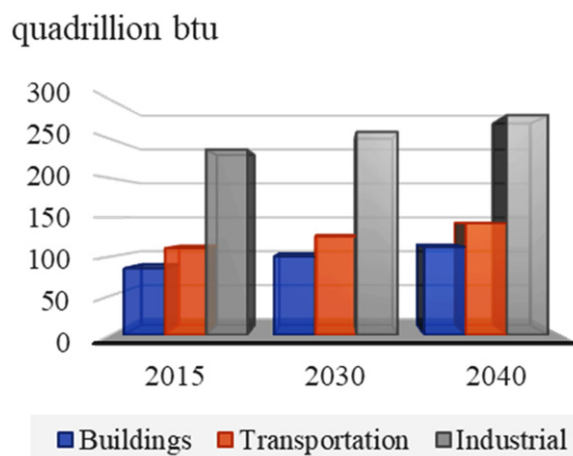


Fig. 2 Global primary energy consumption. Source: U.S. Energy Information Administration, 2017. International Energy Outlook 2017. International Energy Outlook (vol. IE02017). Retrieved from [https://www.eia.gov/outlooks/ieo/pdf/0484\(2017\).pdf](https://www.eia.gov/outlooks/ieo/pdf/0484(2017).pdf).

respectively, between 2012 and 2035 (British Petroleum Company, 2014). The transport sector is currently consuming around 60% of world oil demand and will be the largest growing energy sector in the coming days. This sector consumes nearly all conventional fuel energy that comes from oil (97.6%) and a small amount from natural gas (Atabani *et al.*, 2012). But transport demand for oil is decelerating with significant improvement of fuel efficiency and increase in use of nonoil fuels (electricity), biofuels, coal, and natural gas. Total oil demand for this sector is expected to fall gradually from about 1 Mb/d p.a. in 2015 to about 0.4 Mb/d p.a. by 2035 (British Petroleum Company, 2017).

World Emission Problem

Climate change is currently the most irresistible world environmental problem. If world's average temperature increases by 2°C from the preindustrial revolution era, more than one million species may become extinct and hundreds of millions of humans may lose their lives (Atabani *et al.*, 2012).

Environmental scientists have noticed that carbon dioxide (CO₂) concentration in the Earth's atmosphere has been increasing significantly over the past century. The average concentration of CO₂ was 399 parts per million (ppm) in 2015, which was about 40% higher than in the mid-1800s (280 ppm). The average growth of CO₂ was 2 ppm/year over the last ten years (IEA, 2016). It is expected that about 6.2 billion metric tons of carbon dioxide will be released into the atmosphere between 2015 and 2035 (EIA, 2017). The levels of methane (CH₄) and the oxides of nitrogen (NO_x) have also increased significantly. Electric utility sector (42%) and transport sector (23%) together produced two-thirds of global CO₂ emissions from fossil fuel combustion in 2014 (Fig. 3) (IEA, 2016). In 2014, three-quarters of the transport sector emission was driven from the road sector, which was increased by 71% since 1990 (Fig. 4). About 95% greenhouse gas (GHG) emission from transportation is of CO₂ and only 1% is of methane (CH₄) and nitrous oxides (N₂O). The transportation sector also emits carbon monoxide (CO), ozone, and hydro fluorocarbons (HFCs) from the cooling system of the vehicles (Atabani *et al.*, 2012). Such a fast growth of emissions will directly affect the stable ecosystem and thus the global climate. In this context, the renewable and nonconventional fuels, such as biofuel, biogas, and biodiesel, can be used as alternative sources of energy. So, there is a growing need to focus on developing suitable biofuels to reduce the dependency on fossil fuels.

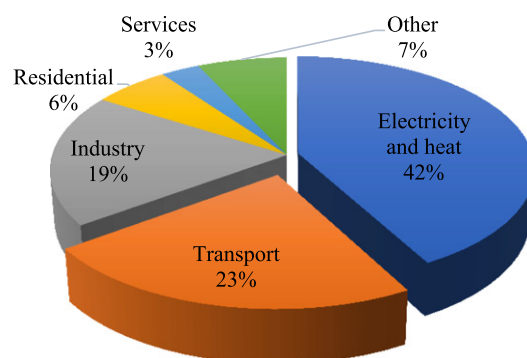


Fig. 3 World CO₂ emissions from fuel combustion by sector in 2014. Source: IEA, 2016. CO₂ Emissions from Fuel Combustion 2016. OECD/IEA. Available at: https://doi.org/10.1787/co2_fuel-2016-en.

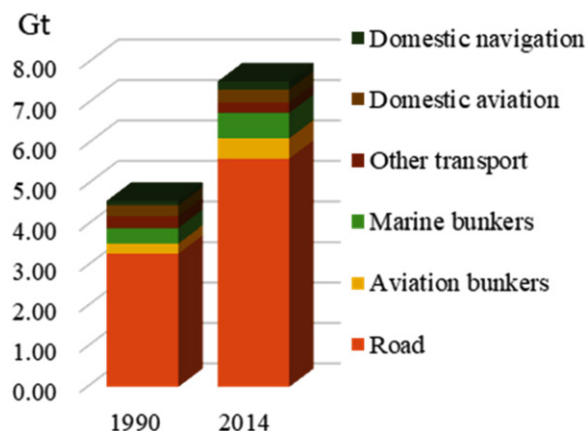


Fig. 4 World CO₂ emissions from transport. Source: IEA, 2016. CO₂ Emissions from Fuel Combustion 2016. OECD/IEA. Available at: https://doi.org/10.1787/co2_fuel-2016-en.

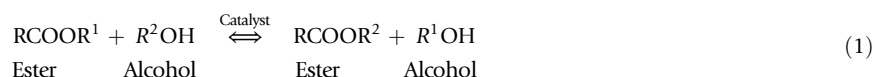
Biodiesel as an Emerging Energy Resource

The biofuels, mainly produced from biological resources, are available in both liquid and gaseous states for transportation purposes. Various types of fuels can be produced from bioresources, which include liquid fuels, such as bioethanol, biomethanol, biodiesel, and gaseous fuels, such as producer gas and biogas. Among all these fuels, biodiesel is one of the most reliable options as an alternative to the base fuel, diesel. It is highly biodegradable, has lower sulfur content, lower aromatic content, and minimal toxicity (Balat and Balat, 2010). Biodiesel has higher cetane number (CN) and higher flash point (FP), which offers safety benefits over diesel fuel (Demirbas and Balat, 2006). It generally contains 10%–11% oxygen by weight, which improves combustion efficiency and also minimizes CO and unburned hydrocarbon emissions (Atabani *et al.*, 2012). It produces no net carbon dioxide (if the whole life cycle of the tree is considered) and less particulate matter (PM) and smoke (Atabani *et al.*, 2012). Therefore, biodiesel–diesel blends can be used as fuel in internal combustion engines without major modifications.

Biodiesel is commercially available in many countries such as the United States, Brazil, Germany, Argentina, France, Thailand, and various European countries (Sawin *et al.*, 2017). Fig. 5 shows the amount of biodiesel production in 2016 of some of the top biodiesel producing countries, and shows that the United States was the highest biodiesel producer, with 5.5 billion liters, in 2016. Worldwide annual biodiesel production increased from 7 billion liters in 2006 to 31 billion liters in 2016 (Sawin *et al.*, 2017). In the last decade, the growth rate of biodiesel production was around 35% per annum. Therefore, biodiesel has a massive capability to be a part of sustainable energy source in the future.

Biodiesel Production Potential: Feedstock and Availability

The use of vegetable oil in an engine is not a new idea and the concept of using vegetable oil as fuel dates back to 1895. In fact, when Rudolph Diesel developed the first engine in 1900, he ran it on peanut oil (Srithar *et al.*, 2013). However, vegetable oil has several drawbacks as engine fuel, the major of which are its very high viscosity and pour point (PP), low calorific value (CV), and low volatility (Rakopoulos, 2013). The highly viscous vegetable oil leads to difficulty in pumping, causes poor atomization, and also poor combustion in a diesel engine. This can be improved by preheating the oil, blending it with a base fuel, and transesterification or pyrolysis. The most popular method of decreasing the viscosity of vegetable oil is transesterification (Prabhu *et al.*, 2013; Prakash *et al.*, 2013; Sivalakshmi and Balusamy, 2013). Transesterification (also called alcoholysis) is the displacement of alcohol from an ester by another alcohol (Meher *et al.*, 2006). The transesterification reaction is represented by the general equation [Eq. (1)] as follows:



It is a reversible reaction and proceeds essentially by mixing the reactants. However, the presence of a catalyst (a strong acid or base) accelerates the conversion process. Transesterification of triglycerides (as found in vegetable oils) produces fatty acid (FA) alkyl esters and glycerol. The heavier glycerol layer settles down at the bottom of the reaction vessel. The upper layer of (m)ethyl ester forms the raw biodiesel. Diglycerides and monoglycerides are the intermediates in this process. The mechanism of transesterification is described in Eq. (2) (Sivakumar *et al.*, 2015), where R^i represents a mixture of various FA chains. The major components of vegetable oils and animal fats are triacylglycerols or, in short, triglycerides. The triglycerides of oils or fats primarily contain several different FAs, which can be attached to one glycerol backbone. The vegetable oil or animal fat is reacted in the

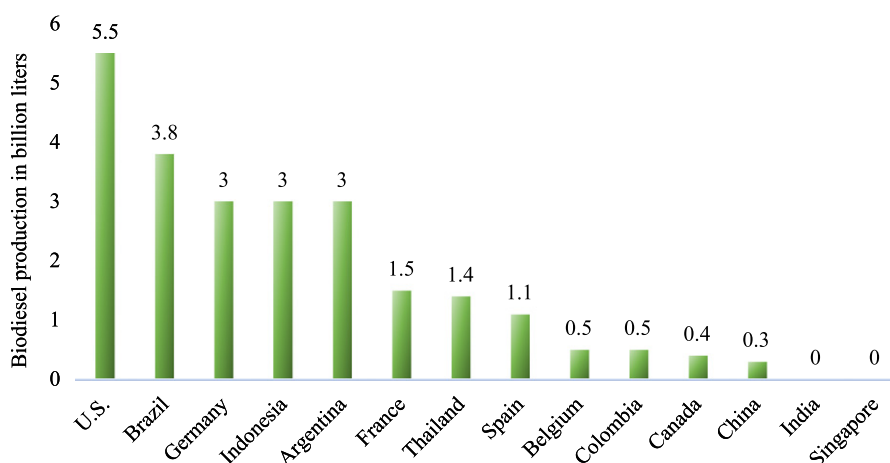
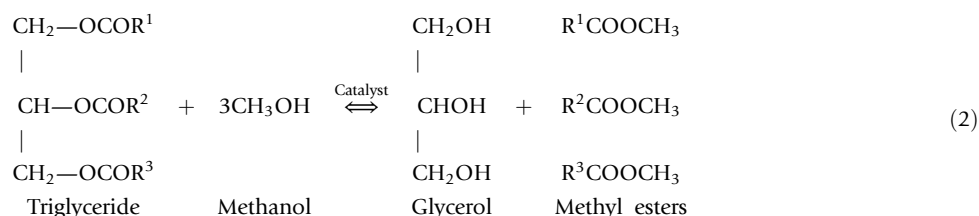


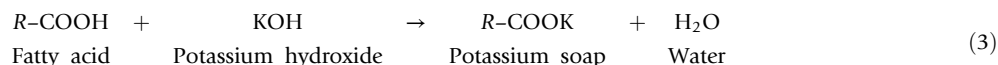
Fig. 5 Leading biodiesel producers worldwide in 2016, by country. Source: Sawin, J., Seyboth, K., Sverrisson, F., 2017. Renewables 2017 Global Status Report. Retrieved from http://www.ren21.net/wp-content/uploads/2017/06/17-8399_GSR_2017_Full_Report_0621_Opt.pdf.

presence of a catalyst (usually a base) with alcohol (usually methanol) to give the corresponding alkyl esters (or for methanol, the methyl esters) of the FA mixture that is found in the parent vegetable oil or animal fat. This alkyl ester is known as biodiesel.

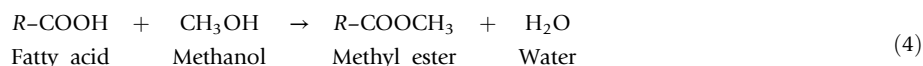


Acid-Catalyzed Pretreatment

If the oil or fat contains significant amounts of free fatty acid (FFA), acid-catalyzed pretreatment process is required. Usually, nonedible oil or animal fat contains 2%–30% FFA (Knothe *et al.*, 2010). The high FFA feedstock reacts with the alkali catalyst and generates soap and water as shown in the reaction [Eq. (3)] below:



In general, the reaction is catalyzed with an alkali catalyst for less than 2% FFA in oil or fat, but up to ~ 5% FFA can be possible to complete reaction in the presence of alkali catalyst (Knothe *et al.*, 2010). When the FFA level is > 5%, the soap resists the separation of glycerol from alkyl ester and emulsion formation take place during water wash. For these cases, an acid catalyst (such as H_2SO_4) is used to esterify the FFA to alkyl ester. The reaction is shown in Eq. (4).



This process is normally used as a pretreatment to convert the FFA to methyl esters, thereafter the alkaline transesterification is applied to produce biodiesel. The complete biodiesel production process is shown in Fig. 6.

Biodiesel Resources

The selection of vegetable oil used in transesterification for the production of biodiesel varies from region to region, depending upon the climate and soil conditions (Karmakar *et al.*, 2012). For example, in the United States soybean oil is widely used for the preparation of biodiesel, while in Europe rapeseed and sunflower oils are more popular for the same. Similarly, palm oil is used in southeast Asia, coconut oil in the Philippines, animal fat in Japan, and canola oil in Canada (Murugesan *et al.*, 2009; Karmakar *et al.*, 2012).

In general, biodiesel feedstock can be divided into four types (Kumar *et al.*, 2013):

- (1) *Edible vegetable oil*: Rapeseed, soybean, sunflower, rice bran, coconut, palm, corn, olive, sesame seed, palestine, peanut, safflower oil etc.
- (2) *Non-edible vegetable oil*: Neem, mahua, jatropha, pongamia, jojoba, cottonseed, orange, linseed, kusum, sea mango, halo-phytes, algae etc.
- (3) *Animal fats*: Chicken fat, tallow, yellow grease and fish oil (from byproducts), etc.
- (4) *Waste cooking or recycled oil*.

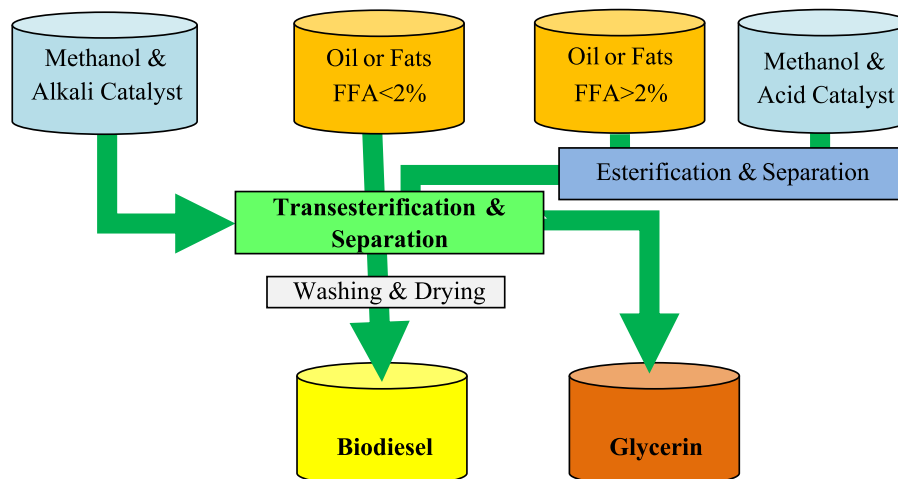


Fig. 6 The flowchart of biodiesel production process.

Table 1 Maximum allowed quantities of physicochemical properties for diesel and biodiesel according to ASTM/EN standards

Property	Unit	Diesel	Biodiesel	
		ASTM D975	ASTM D6751	EN 14214
Density at 15°C	kg/m ³	850	Max. 880	860–900
Kinematic viscosity at 40°C	mm ² /s	2.0–4.5	1.9–6.0	3.5–5.0
Cetane number	–	40–55	Min. 47	Min. 51
Iodine value	mg I ₂ /g	–	–	Max. 120
Calorific value	MJ/kg	42–46	–	Min. 35
Acid number	mg KOH/g	–	Max. 0.5	Max. 0.5
Pour point	°C	–15 to 5	–15 to –16	–
Flash point	°C	60–80	Min. 100–170	> 120
Cloud point	°C	–35 to 15	–3 to –12	–
Cold filter plugging point	°C	–25	19	Max. 5
Copper strip corrosion (3 h at 50°C)	–	1	Max. 3	–
Carbon	wt%	84–87	77	–
Hydrogen	wt%	12–16	12	–
Oxygen	wt%	0–0.31	11	–
Sulfur content	%(m/m)	0.05	Max. 0.05	–
Sulfate ash content	%(w/w)	0.01	0.02	0.02
Oxidation stability at 110°C	h	–	Min. 3	Min. 6
Lubricity	–	685	314	–

Note: Dharma, S., Ong, H.C., Masjuki, H.H., Sebayang, A.H., Silitonga, A.S., 2016. An overview of engine durability and compatibility using biodiesel–bioethanol–diesel blends in compression-ignition engines. *Energy Conversion and Management* 128, 66–81.

Characteristics of Biodiesel

Biodiesel is one of the best alternatives to diesel and can be used as alternative fuel in compression ignition (CI) engines. The engine injection, combustion, performance, and emission characteristics are influenced by biodiesel properties, which depend on the FA compositions and types of feed stocks (Dharma *et al.*, 2016; Sakthivel *et al.*, 2017). In many countries, biodiesel has been successfully introduced and commercialized. Hence, some biodiesel standards, like ASTM D6751 and the European standard EN 14214, have been developed to certify high product quality and to improve user confidence. The biodiesel is characterized by determining its different physicochemical properties like density, viscosity, FP, cloud point (CP), pure point, CV, volatility, etc. ASTM and EN standards of maximum allowed quantities of different properties for diesel and biodiesel are shown in Table 1. The important properties of different biodiesels are given in Table 2.

Density

Density is an important property for liquid fuels used in engines. This is because the liquid fuels are generally sold in volume quantity while their heating values are expressed on a gravimetric basis. Therefore, the heat content in a certain volume of diesel depends on its density. There is evidence showing that the ignition delay in diesel engine is sensitive towards the density of the fuel (Ra *et al.*, 2008). Measurement of density follows the ASTM Standard D1298 and EN 3675 test methods (Zaharin *et al.*, 2017). Table 2 indicates that biodiesel density is higher compared with base fuel diesel as the molecular weight of biodiesel is higher (Zaharin *et al.*, 2017). It can be clearly seen that density of most of the biodiesels lie in the range of 850 kg/m³ to 930 kg/m³. Among them, biodiesel from jatropha has the minimum density value around 857 kg/m³ whereas castor oil biodiesel shows the maximum with 928.7 kg/m³.

Kinematic Viscosity

Kinematic viscosity is an important property of fuel, which directly influences the fuel atomization quality and size of the fuel droplet in the spray. In general, kinematic viscosity is measured using the ASTM Standard D445 and EN 3104 test methods. Low viscous fuel may lead to leakage in the fuel system and high viscosity may disturb the fuel flow rate during intake stroke, which delays the mixing of air and fuel in the combustion chamber (Dharma *et al.*, 2016). Kinematic viscosity for most of the biodiesels ranges between 3 mm²/s and 5.5 mm²/s at 40°C, but for castor oil biodiesel it is exceptionally high (16.67 mm²/s).

Cetane Number

CN indicates the knocking tendency of diesel in a CI engine. High CN fuel tends to ignite early in the engine cylinder, which decreases the knocking tendency of the engine. The CN depends on the presence of saturated molecules and the length of FA carbon chains in the

Table 2 Physiochemical properties of different biodiesels

Fuels	Density (kg/m ³)	Kinematic viscosity (40 °C) (mm ² /s)	Cetane number	Calorific value (MJ/kg)	Cold filter plugging point (°C)	Flash point (°C)	Carbon content (wt%)	Hydrogen content (wt%)	Oxygen content (wt%)	Surface tension (40°C) (mN/m)
Diesel	814	2.95	45	46.273	−16	66.5	80.97	12.62	—	28
Sunflower	862	4.49	—	40.25	—	141	75.18	11.44	12.88	25.4
Canola	880	4.29	61.5	43.96	—	182	—	—	10.8	—
Rapeseed	883.7	4.53	54.7	37.8	—	—	77.09	12.07	10.84	—
Neem	860	4.5	51	41	—	172	77	11.6	11	26
Mahua	860	3.1	53	40	—	—	—	—	10	25
Karanja	893.6	5.4	57	41.5	−2	158	75.04	12.76	11.62	30
Castor	928.7	16.67	48.9	37.63	—	—	73.48	11.69	14.83	—
Jatropha	857	4.57	58.2	41.3	—	158	72.5	12.8	11.8	31
Microalgae	912	5.06	46.5	39.86	4	95	78.41	11.12	10.47	—
Animal fat	877	5.23	70	37.2	10	—	76.46	12.4	11.14	—
Waste cooking oil	866	4.07	66	38.03	8	170	71.26	—	9.81	32

Note: Sundarapandian, S., Devaradjane, G., 2007. Performance and emission analysis of bio diesel operated CI engine. *Engineering, Computing and Architecture* 1 (2), 1–22. Lapuerta, M., Rodríguez-Fernández, J., Oliva, F., Canoira, L., 2009. Biodiesel from low-grade animal fats: Diesel engine performance and emissions. *Energy & Fuels* 23 (1), 121–129. Sharma, Y.C., Singh, B., Korstad, J., 2010. Application of an efficient nonconventional heterogeneous catalyst for biodiesel synthesis from *Pongamia pinnata* oil. *Energy and Fuels* 24 (5), 3223–3231. Sivalakshmi, S., Balusamy, T., 2011. Experimental investigation on a diesel engine fuelled with neem oil and its methyl ester. *Thermal Science* 15 (4), 1193–1204. Sukjit, E., Herreros, J.M., Piaszyk, J., Dearn, K.D., Tsolakis, A., 2013. Finding synergies in fuels properties for the design of renewable fuels -hydroxylated biodiesel effects on butanol-diesel blends. *Environmental Science and Technology* 47 (7), 3535–3542. Ge, J., Yoon, S., Choi, N., 2017. Using canola oil biodiesel as an alternative fuel in diesel engines: A review. *Applied Sciences* 7 (9), 881. Silitonga, A.S., Hassan, M.H., Ong, H.C., Kusumo, F., 2017. Analysis of the performance, emission and combustion characteristics of a turbocharged diesel engine fuelled with *Jatropha curcas* biodiesel-diesel blends using kernel-based extreme learning machine. *Environmental Science and Pollution Research* 24 (32), 25383–25405. Karmakar, A., Karmakar, S., Mukherjee, S., 2012. Biodiesel production from neem towards feedstock diversification: Indian perspective. *Renewable and Sustainable Energy Reviews* 16 (1), 1050–1060. Das, M., Sarkar, M., Datta, A., Santra, A.K., 2018a. Study on viscosity and surface tension properties of biodiesel–diesel blends and their effects on spray parameters for CI engines. *Fuel* 220 (January), 769–779.

fuel (Zaharin *et al.*, 2017; Sakthivel *et al.*, 2017). High CN fuels provide significant advantages in terms of engine performance and emission characteristics, which allow the engine to run smoothly with less tendency of knocking and noise disturbance (Zaharin *et al.*, 2017). The CN of biodiesel fuel is measured by ASTM D613 and EN 5165 test methods. Table 2 shows that most of the biodiesels have higher CN than base fuel diesel. It may be due to the presence of long FA carbon chains in the biodiesel (Ashraful *et al.*, 2014).

Calorific Value

CV denotes the energy content in a fuel. High calorific value of fuel is the most desirable as releasing more heat during combustion improves the engine power output (Hasan and Rahman, 2017). CV of biodiesel has been prescribed in EN 14213 standards with a minimum value of 35 MJ/kg. Biodiesels usually have lower CV than diesel fuel (see Table 2) because of the higher oxygen content in them (Ashraful *et al.*, 2014).

Cloud Point and Pour Point

The information regarding CP and PP of fuels is essential for low temperature operation of the engine. The CP is the temperature at which a cloud of wax crystals first becomes visible when the fuel is cooled. The PP of a fuel is the temperature below which the fuel loses its flow characteristics. CP and PP are measured following ASTM D2500 and D97 standards. In general, these two points for biodiesels are higher than the base fuel diesel (Atabani *et al.*, 2013). Cold filter plugging point (CFPP) is used as an indicator of low temperature operability of fuels. At this temperature, the test filter starts to plug due to gel formation or crystallization of fuel components. Usually, the CFPP of a fuel is lower than its CP. The CFPP is measured by ASTM D6371 standard. It has been found from Table 2 that the highest CFPP is found for animal fat oil biodiesel with temperature of 10°C while karanja oil biodiesel has the lowest CFPP temperature of −2°C.

Flash Point

FP is another important property for a liquid fuel. FP is defined as the temperature at which the fuel flashes when exposed to a flame or a spark. FP varies inversely with the fuel's volatility. FP is measured according to ASTM D93 and EN ISO 3679 standard. Biodiesel has a high FP, which is normally more than 150°C, while generally diesel fuel has a flash point of 55–66°C (Atabani *et al.*, 2013).

Elemental Analysis

Using elemental analyzer, the composition of fuel is measured according to ASTM D3176 standard, which is a measure of carbon, hydrogen, nitrogen, sulfur, and oxygen content in a fuel. The main components of diesel are carbon and hydrogen but no oxygen, whereas biodiesels have generally 10–15 (wt%) oxygen ([Table 2](#)).

Surface Tension

Surface tension is also an important fuel property, which affects the characteristics of the spray issued from a fuel nozzle. Higher surface tension value of a fuel results in coarser droplets in the spray ([Das et al., 2018a](#)) because of the increase in the cohesive force, resisting disintegration. The surface tension of fuel is measured following ASTM D971 standard. Generally, biodiesel has higher surface tension than conventional diesel fuel ([Table 2](#)). Higher molecular weight and unsaturation in the molecular structure of the biodiesel increases the viscosity and surface tension of biodiesel compared with diesel.

Engine Performance and Emission Characteristics

The performance and emission characteristics of a diesel engine mainly depend on fuel properties and the engine operating variables such as compression ratio, injection pressure, ignition delay, and other factors. The biodiesel–diesel blend can be directly used in a CI engine. The effect of the biodiesel on an engine can be investigated by the analysis of the engine performance characteristics like brake thermal efficiency (BTE), brake specific fuel consumption (BSFC), and emission parameters such as CO, carbon dioxide (CO₂), unburnt hydrocarbon (HC), smoke, and NO_x. In the following sections, a detailed discussion has been carried out on the performance and emission parameters of various biodiesel–diesel blends.

Brake Thermal Efficiency

BTE is defined as the ratio of the useful work obtained by an engine to the fuel energy supplied to the engine. Most of studies reported higher BTE for biodiesel–diesel blends related to base diesel fuel ([Table 3](#)). [Teoh et al. \(2014\)](#) reported 2% higher BTE for B50 (jatropha biodiesel) compared with mineral diesel. Researchers suggested that oxygen content of the biodiesel enhanced the burning rate during the combustion. [Mathimani et al. \(2017\)](#) also found better BTE for B30, B40, and B50 of *Chlorella vulgaris* BDUG 91771 biodiesel–diesel. It was due to shorter ignition delay of the biodiesel. [Rakopoulos et al. \(2008\)](#) ran a Mercedes-Benz minibus diesel engine using biodiesel of sunflower and cottonseed oil and their blends with diesel. BTE of blends of these two biodiesels was similar to the base fuel diesel. [Das et al. \(2018b\)](#) was also obtained similar or slightly higher BTE for castor oil biodiesel–diesel blends (B05, B10, and B20). On the other hand, BTE was reduced up to 4.2% with 20% blend of canola biodiesel at higher load as the calorific value of the biodiesel was 9.6% less than diesel ([Can et al., 2017](#)). [Santhosh and Padmanaban \(2016\)](#)

Table 3 Comparative changes of engine performance and emission parameters for biodiesel blends with respect to diesel

Feed stock of biodiesel	Performance		Emission				Reference
	BSFC	BTE	CO	HC	Smoke	NO _x	
Sunflower oil (B10, B20) Cottonseed oil (B10, B20)	Increase	Similar	Decrease	Slightly increase	Decrease	Slightly increase	(Rakopoulos et al., 2008)
Jatropha oil (B10, B30, B50)	Increase, ↑6% (B50)	Slightly reduced ↑2% (B50)	Decrease ↓11.9, 30, 49.9%	–	Decrease ↓20.9 (B10), 69.5 (B50)	Decrease ↓20.2% (B30)	
<i>Citrullus colocynthis</i> L. oil (B30, B100)	↓B30↑B100	Increase	–	↓20 (B30), 50 (B100)	Decrease, ↓22%	Increase	(Alloune et al., 2018)
Algal oil (<i>Chlorella vulgaris</i> BDUG 91771) B30, B40, B50, B60	Increase	↑B30, B40, B50 ↓B50	Decrease	Decrease	–	Marginally lower or equal	(Mathimani et al., 2017)
Canola oil (B05, B10, B15, B20)	↑up to 6.56%	↓ up to 4.2%	↓32% (max)	↓30.3% (max)	↓24.5 (ML), 53.5 (FL) for B20	↑3%–9%	(Can et al., 2017)
Sal oil (B10, B20, B30, B40)	↓1.84 % (B10), 2.09% (B20) at 80% load, ↑< B20	↑2.3 % (B10), 2.4% (B20) at 80% load, ↓< B20	↓at full load	Decrease	↑ at 0%–40% load, ↓50% at 90% load	Increase	(Pali and Kumar, 2016)
Cottonseed oil (B15, B30, B45, B60, B75, B90, and B100)	Increase	↑for lower blends	↓B15–B60	Decrease	Decrease	Increase	(Santhosh and Padmanaban, 2016)
Rapeseed oil (B5, B20, B70, B100)	↑2.5%, 3%, 5.5%, 7.5%	Decrease	Decrease	Decrease	Decrease, ↓45% for B70	Increase	(Buyukkaya, 2010)
Soya bean oil (B30, B50, B80, B100)	Increase	Decrease	Decrease, ↓0.05%	Decrease	Decrease	Increase	(Qi et al., 2010)

investigated that at high compression ratio (22.1:1), BTE could be improved using lower percentage blends of cottonseed biodiesel and diesel. This was due to the better spray characteristics in the lower biodiesel–diesel blends and hence better combustion.

Brake Specific Fuel Consumption

BSFC is defined as the ratio of the total fuel consumption rate to the brake power output of the engine. It is one of the most important parameters for evaluating the effects of fuels on an engine performance. Generally, higher BTE outcomes in lower BSFC and lower calorific value of fuel enhance the BSFC. Most researchers (Table 3) reported that BSFC increased when biodiesel–diesel blends were used as fuels in the engine. When the engine is fueled with 50% blend (B50) of jatropha biodiesel and diesel, Teoh *et al.* (2014) observed that the engine consumed more B50 fuel compared with mineral diesel for same power output. This was because of the lower calorific value of the biodiesel, approximately 6% less than that of diesel fuel. The higher specific fuel consumption (SFC) was obtained with increase of the cottonseed biodiesel concentration in the blend (Santhosh and Padmanaban, 2016). The percentage increment in SFC for B15, B30, B45, B60, B90, and B100 were 4.06%, 0.41%, 4.54%, 8.19%, 8.76%, 14.76%, and 16.71%, respectively, at medium load. 30% blend (B30) of the *Citrullus colocynthis* L. biodiesel and diesel reduced BSFC compared with diesel as higher CN with lower viscosity of B30 fuel (Alloune *et al.*, 2018). Pali and Kumar (2016) observed that for up to 20% blend of sal oil biodiesel, BSFC was reduced about 2% compared with diesel. However, BSFC was enhanced for more than 20% blends.

Carbon Monoxide

CO, an intermediate combustion byproduct of burning fuels, is produced by different factors like absence of oxidant, non-uniformly mixing of air–fuel mixture, lack of time for postoxidation, etc. (Sakthivel *et al.*, 2017). In Table 3, we observe that most studies found lower CO emission in an engine fueled with biodiesel or its blends. Many researchers suggested that this was mainly due to the oxygen content in biodiesel enhancing to complete combustion of the fuel. CO emission was decreased with the use of jatropha oil methyl ester (biodiesel) in the blend and in fact, it consistently reduced with the increase of biodiesel proportion in the blend (Teoh *et al.*, 2014). Buyukkaya (2010) noticed that CO emission was reduced at low engine speed for rapeseed oil biodiesel–diesel blended fuel. The CO emissions of the B5, B20, B70, and B100 were 12%, 25%, 31%, and 35%, respectively, lower than that of diesel fuel.

Hydrocarbon

HC emissions indicate the incomplete combustion of fuel inside the combustion chamber of an engine. Combustion chamber construction, engine operational conditions, fuel type or structure are the main constraints that influence on the HC emissions (Sakthivel *et al.*, 2017). The Table 3 conclusively shows that HC emissions from engines with the use of biodiesel or its blends are lower than baseline diesel. Alloune *et al.* (2018) found that the reduction of HC emissions was obtained for pure *C. colocynthis* L. biodiesel and its 30% blend compared with diesel fuel. This was due to the presence of oxygen in biodiesel, which improved combustion quality of the fuel. Authors explained furthermore that the higher CN of biodiesel and its blend reduced the ignition delay, and as a result, had a substantial effect on the lower HC emission. Rakopoulos *et al.* (2008) observed that HC emissions from B10 and B20 blend (sunflower or cottonseed biodiesel–diesel) fueled Mercedes-Benz, minibus diesel engine were slightly higher than that of diesel fuel.

Oxides of Nitrogen

Formation of NO_x, the most toxic pollutants, in CI engines is dependent on in-cylinder peak temperature, type of the fuels, oxygen availability in the high temperature zones, and reaction time. In biodiesel–diesel blends, different parameters such as chemical composition of the fuel and concentration of oxygen in the high temperature reaction zone are changed, which may directly affect NO_x emission (Agarwal *et al.*, 2017). Pali and Kumar (2016) found higher NO_x with the use of sal oil biodiesel and its blends as compared with diesel fuel. They suggested that higher combustion temperature and excess oxygen were the predominant factor for higher NO_x emissions. In the case of pure rapeseed biodiesel, the enhance of NO_x emission was about 12% compared with the base fuel (Buyukkaya, 2010). Similarly, 6% and 9% higher NO_x emissions were found for B20 and B70, respectively. Mathimani *et al.* (2017) noticed that NO_x emissions from all algal biodiesel blends fueled engine were slightly lower or equal to the corresponding base fuel at all loads. This was due to the shorter ignition delay and lower exhaust gas temperature.

Smoke and Particulate Matter

Smoke and PM are the unwanted byproducts of combustion in a diesel engine, and are primarily produced from incomplete combustion of fuel. The formation of smoke or PM mostly depends on the type of fuels, operating conditions of the engine, and carbon residue of the fuel (Teoh *et al.*, 2014). Pali and Kumar (2016) observed that smoke opacities for sal oil biodiesel and its blends were higher at part loads (up to 40%). This was because of higher viscosity of the biodiesel and lower in-cylinder

temperatures at these low loads, leading to poorer spray along with locally rich fuel mixtures and generating more smoke. However, smoke was significantly reduced at higher loads. PM emission from pure algal oil biodiesel fueled engine was lower than that of diesel fuel, as the biodiesel supplied extra amount of oxygen in the premixed reaction zone and reducing PM emission (Alloune *et al.*, 2018). The reduction of PMs for the biodiesel is about 22% as compared with base fuel. However, B30 and diesel generated the same amount of PM.

Conclusion

With recent increase in prices of crude petroleum-based fuels and uncertainties of the availability of these fossil fuels, there is renewed interest in alternative ecofriendly and easily available fuels. Biodiesel is the most promising alternative to the fossil diesel fuel. Biodiesel can be produced from any type of vegetable oils, animal oil/fats, tallow, and waste cooking oil. Transesterification is the most popular method to produce biodiesel from different feedstocks. Biodiesel or its blends can be directly used in existing CI engines without any modification or with minor modification, mainly compression ratio, fuel injection timing or exhaust gas recirculation, etc. In general, the BTE of an engine with the use of biodiesel–diesel blends is similar or slightly reduced (about 4%) as compared with mineral diesel. On the other hand, BSFC is normally increased for biodiesel–diesel blends. All types of emissions except nitrogen oxides are significantly decreased (about 20%–50%) by using biodiesel or its blend as fuel instead of base diesel fuel. Finally, biodiesel has emerged as an alternative environment-friendly fuel, which can be partially mixed with diesel and easily used in existing engines with great reduction of pollution but with minor loss in power output.

See also: Co-Firing of Biomass to Reduce CO₂ Emission. Overview of CCS: A Strategy of Meeting CO₂ Emission Targets. Renewable Electricity Generation – Effect on GHG Emission. Renewable Jet-Fuel (RJF): Mitigation of Aviation-Related GHG Emission. Simulation and Modeling of Vehicle Emissions: A Review. The Role of Engineering in Mitigating Global Climate Change Effects: Review of the Aspects of Carbon Emissions from Fossil Fuel-Based Power Plants and Manufacturing Industries

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Performance of Cork and Composites Joints

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Nomenclature

λ Thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)

ρ Apparent density (kg m^{-3})

E Thermal effusivity ($\text{J K}^{-1} \text{m}^{-2} \text{s}^{-0.5}$)

a Thermal diffusivity ($\text{m}^2 \text{s}^{-1}$)

ξ Spherical parameter

Subscripts

co Granular cork

c Clay

c+co Composite clay-cork

MC+co Composite cement mortar-cork

Wc+co Composite white cement-cork

y Volume fraction cork

ϕ Heat flow (W)

ΔT Variation of the temperature (K)

Introduction

Cork is a natural additive combining to different binders presents composites of a very good thermal performance, using in building it reduces a lot the energy consumption due to the energy necessary of heating or cooling in summer. Authors in this work try to present the different performance of cork, to describe the characteristics of the materials cement mortar, clay and white cement used to produce the composites clay-cork, cement mortar-cork and white cement-cork. Two kinds of studies were done: the variation of the size of cork and its volume fraction to show the influence of the form of cork and the volume fraction on thermal properties of the composites produces. Thermal characterization of materials: clay, cement-mortar and white cement combining with this additive were done using the hot plate and flash methods in both regimes under steady state and transient conditions. The physical–chemical description of cork was done.

Molina *et al.* (2018) studied the fire response and flammability of cork using bench and field scales. The paper treats the oak tree cork flammability using a set comprised of 120 cork specimens and 120 cork pieces to test the cambial temperature and lethal temperature rate according to cork bark roughness, cork thickness, cork porosity and cork quality and results reveal that those characteristics influence the vulnerability of cork oak forests to wildfires and a thickness of over than 3.7 cm prevented reaching lethal cambial temperature.

Sarasini *et al.* (2019) studied the impact of green sandwich structures made of agglomerated cork encapsulated between two thin flaxes/epoxy face sheets compared to a traditional synthetic foam core, the results reveal that the cork based structures exhibited a higher perforation threshold than foam sandwiches (94.41 J instead of 79.71 J) for the foam synthetic core.

Kaczynski *et al.* (2019) assessed the capability of five different types of cork agglomerates to withstand 500 J impact according to different temperature conditions, the results indicate that the capability of absorbing energy depends on the density of cork and the temperature, the grain size of cork influence the value of absorbed energy, a mathematical cork agglomerated model for energy absorption was formulated and the cork agglomerates performance is significantly affected by the temperature.

Tártaro *et al.* (2017) calculated the carbon footprint of insulating cork board following the life cycle thinking approach and the ISO/TS 14067. The authors have compared the carbon footprint of the insulating cork board to other insulating material such as the expanded polystyrene ($59 \text{ kgCO}_2 \text{ m}^{-3} \text{ ICB}^{-1}$), the extruded polystyrene ($94.4 \text{ kgCO}_2 \text{ m}^{-3} \text{ ICB}^{-1}$), the polyurethane ($127.7 \text{ kgCO}_2 \text{ m}^{-3} \text{ ICB}^{-1}$), the stone wool ($34.35 \text{ kgCO}_2 \text{ m}^{-3} \text{ ICB}^{-1}$), the lightweight expanded clay aggregates ($53.77 \text{ kgCO}_2 \text{ m}^{-3} \text{ ICB}^{-1}$), However the ICB present a negative carbon footprint of $-116.229 (53.77 \text{ kgCO}_2 \text{ m}^{-3} \text{ ICB}^{-1})$.

Şen *et al.* (2014) treated the role of chemical components on the thermal degradation of cork using coupled differential scanning calorimetry-thermogravimetical analysis. The thermal decomposition of corks and phloem occurred at temperature above 200°C and increased at higher temperatures until about 485°C where the material becomes ash. The Fig. 1 of thermogravimetical analysis of the untreated Q.cerris and Q.suber corks showed quite a similar thermal degradation, however TGA curve of phloem differs from cork, mass loss below 250°C is higher than corks due to the higher percentage of polysaccharide content in phloem.

Physical–Chemical Characterization of Cork

The cork is known by its low density, high compressive characteristics, high elasticity, high adherence and high impermeability properties.



Fig. 1 Granular cork.

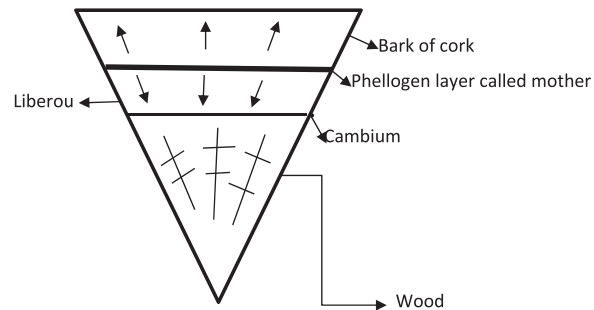


Fig. 2 Transversal section of oak cork trunk.

Cork is the parenchyma Suber created by the meristem suberophelo-dermic oak cork as shown in [Fig. 1](#).

Taxonomy of Oak Cork

The taxonomy of oak tree is described as below:

- Species; Suber L
- Kind: Quercus
- Family: Fagaceae
- Order: Fagale
- Class: Dicotyledonous
- Under branch lines: Angiosperm
- Branch: spermatophyte

Biology of Oak Cork

This tree essence can survive for 300 years. It is mainly calcifuge and siliceous and does not support cold. [Fig. 2](#) describes the different part of an oak cork trunk which consists of the bark of cork, the phellogen layer, the liberou, the cambium and finally the wood.

[Fig. 3](#) shows the microstructure of cork which seems to be like cells, things which prove the best properties in term of impermeability to gases and liquids, lightness, thermal and acoustic insulations.

Properties of Expanded Granular Cork

[Table 1](#) shows the thermal, the acoustic and the ant vibration characteristics of expanded granular cork in term of density, thermal conductivity and flexure strength. Acoustic expanded granular cork has the light and the most insulating characteristics but it possesses a low mechanical characteristic of low flexure strength. However, the ant vibration expanded cork possesses the low thermal properties and the high mechanical characteristics. This table gives an idea about the different kind of expanded granular cork and their characteristics according to the utilization.

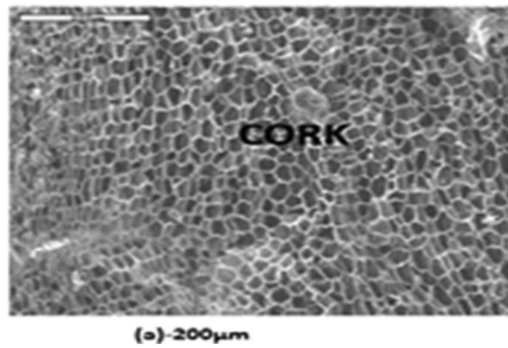


Fig. 3 Scanning electron microscopic analysis of structure of cork which is a honeycomb.

Table 1 Characteristic of expanded granular cork

Kind of expanded granular cork	Density (kg m^{-3})	Thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)	Flexure strength (MPa)
Acoustic	80–100	0.037	1.4–1.6
Thermal	100–130	0.039	1.4–2
Antivibration	175–190	0.048	2.7–3.2
	210–225	0.051	3.9–4.5
	245–255	0.052	5–5.7
	290–320	0.057	7.4–8.2

Note: Amine, M., 1980. Les industries du liège au Maroc.



Fig. 4 Composites clay-cork with different fraction of cork.

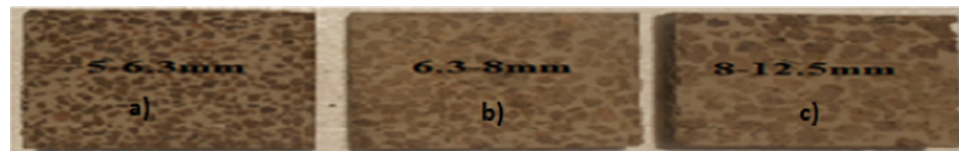


Fig. 5 Composites cement mortar-cork at different sizes of cork.

Composites Cork Joints

The composites studied in this work are: (i) clay-cork, (ii) cement mortar-cork, and (iii) white cement-cork. **Fig. 4(a)–(d)** shows composite clay cork with various fractions of cork. **Fig. 5(a)–(c)** shows composite cement mortar-cork with various sizes of cork. **Fig. 6(a)–(c)** shows white cement-cork with various sizes of cork

Preparation of Samples

Cement mortar cork

The procedure of preparing samples of cement mortar-cork (MC-co) and cement mortar (MC) is described in this paragraph. A mold of dimensions $100 \times 100 \times 20 \text{ mm}^3$ was filled with cork until it was full. Then the volume of mold filled entirely by cork was considered as the 100% of cork's size (5–6.3 mm, 6.3–8 mm, 8–12.5 mm). The cement mortar was then added in a manner such that it fills in all the void existing between the grains of cork. At the same time samples of cement mortar alone were prepared to

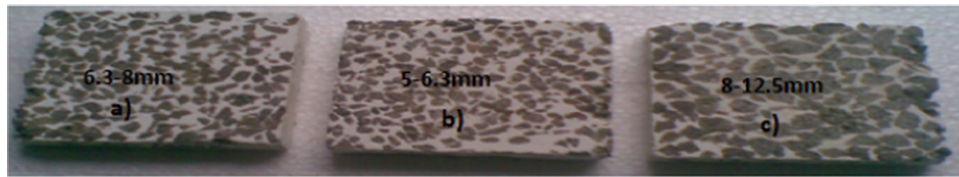


Fig. 6 Composites white cement-cork with different sizes of cork. Reproduced from Cherki, A., Khabbazi, A., Mounir, S., Maaloufa, Y., 2014. Thermal properties of a new ecological building material/granular cork embedded in white cement. In: Proceedings of the MATEC Web of Conferences 11, p. 01017. doi:10.1051/mateconf/20141101017.

compare the thermal properties of the composites cement mortar-cork and cement mortar alone (50% cement-50% sand and 0.5 ratio of water per binder). After these all samples were put in a stove to remove the moisture from it. Finally samples were preserved in plastic bags to prevent it from absorbing moisture.

Knowing the densities of each material, mortar cement and granular cork and that of the mixture and depending on the law of mixture, the granular cork volume fraction was deduced for each sample of the composite material according to the formula given in Eq. (1). The volume fraction is:

$$\gamma = \frac{\rho_{c+co} - \rho_c}{\rho_{co} + \rho_c} \quad (1)$$

where, ρ_{c+co} is the apparent density of the composite binder-cork, ρ_c is the apparent density of the binder and ρ_{co} is the apparent density of the cork.

White cement cork

The samples were fabricated in a mold of dimensions $100 \times 100 \times 20 \text{ mm}^3$ in which, different sizes of cork (a) 5–6.3 mm, (b) 6.3–8 mm, (c) 8–12.5 mm were filled up to 100% mold volume and then the space between grains were filled by the white cement. Also samples of white cement were prepared at a ratio of water to binder equal to 0.5. Finally, all samples were put in a stove and weighing their masses each time until it became constant.

Clay cork

The study of the composites clay-cork was treated differently from the composites of cement mortar-cork and white cement-cork. To see the effect of the variation of the volume fraction in the binder, the mold dimensions ($100 \times 100 \times 20 \text{ mm}^3$) was filled with granular cork of size 6.3–8 mm. After it was totally full, the mass was considered 100% volumes of cork and the mass equal to 80% and 60% were calculated. Then the voids were filled with clay with a ratio of water to binder of 0.5. Also samples of clay alone were prepared to compare both samples (with and without cork). Then all samples were put in a stove to remove the moisture from the samples. Mass was controlled regularly until it became constant. Apparent density was measured according to the formula given by Eq. (1).

Description of the Used Materials

Cement mortar

The cement used was CPJ45 in accordance with the norms NM 10.1.004. The proportion of cement on the mortar was 50%. The percentage of water in binder (W/g) used was 0.5. The sand was taken according to the proportion of sand on the mortar as 50%. The fineness modulus of used sand was 2.15. The absolute density was 2.65 g cm^{-3} , the intergranular porosity was 46.58% and the equivalent sand was 92.3%.

White cement

The white cement used was the CEM II A-I-42.5N according to the norms NF EN197-1 and NFP 15-318 was used according to the NM 10.1.004. The percentage of water in the binder (W/g) used was 0.5.

Clay

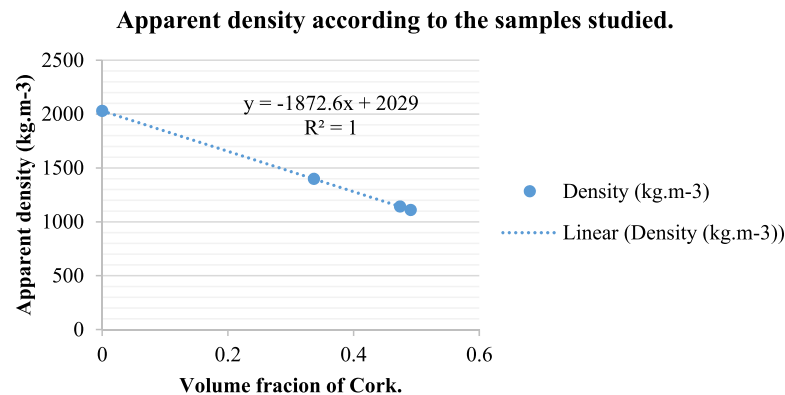
The chemical composition of is given in Table 2.

Description of the Thermal Characterization Methods

The asymmetrical hot plate (Mounir *et al.*, 2019; Yves, 2011) was used to determine thermal conductivity and thermal effusivity under steady state and transient conditions. Flash (Degiovanni and Laurent, 1986) method was used to determine thermal diffusivity by sending a laminar flow in a very short time. The methods used for the thermal characterization had proven their efficiency using just one sample contrary to the old method which consists of two samples.

Table 2 Chemical composition of clay

Chemical element	Percentage of chemical element (%)
SiO ₂	59.6
Al ₂ O ₃	22.4
Fe ₂ O ₃	6.69
CaO	0.0777
MgO	0.97
K ₂ O	2.53
TiO ₂	0.832
P ₂ O ₅	0.458
P.a.f	5.34

**Fig. 7** Apparent density of the composites clay-cork according to the volume fraction of cork.

Results and Discussions

The apparent density was calculated according to the dimensions and masses of samples and the thermal properties were measured using the Hot plate and Flash methods. The results are described as below.

Composites Clay-Cork

Density of composites clay cork

Fig. 7 shows the apparent density of clay cork versus the volume fraction of cork. The curve indicates that for the highest volume fraction of cork, the density is 1114 kg m^{-3} . However, the density of clay alone is 2029 kg m^{-3} which proves a gain in term of lightness for the composites clay-cork of 45%. The decrease of density is explained by the porosity created by cork inside the matrix clay. As a conclusion of these results, the insulator material cork introduces the air inside the matrix clay and become lighter in weight.

Thermal conductivity of composites clay cork

Fig. 8 below shows the plot of thermal conductivity versus volume fraction of cork. As the volume fraction of cork in the composite increases, the composite thermal conductivity decreases. At the highest volume fraction of cork, thermal conductivity of the composite is $0.24 \text{ W m}^{-1} \text{ K}^{-1}$, while, the thermal conductivity of clay is $0.51 \text{ W m}^{-1} \text{ K}^{-1}$. This proves an improvement of the insulating properties by 50%.

Thermal diffusivity of composites clay cork

Fig. 9 shows the relationship between thermal diffusivity and volume fraction of cork. Analysis of this curve indicates that the thermal diffusivity decreases from $5.10^{-7} \text{ m}^2 \text{ s}^{-1}$ to $3.10^{-7} \text{ m}^2 \text{ s}^{-1}$ by adding cork. This is a reduction of 39% thermal diffusivity which improves the thermal inertia of the clay. A linear fit was made to calculate thermal diffusivity according to the volume fraction of cork.

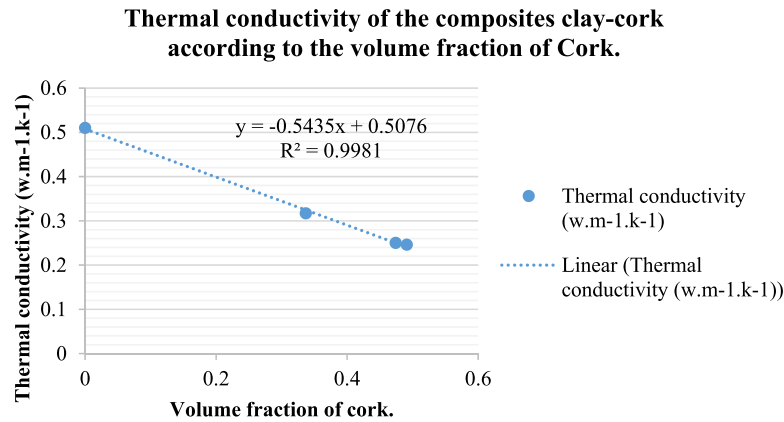


Fig. 8 Thermal conductivity of the composites clay-cork according to the volume fraction of cork.

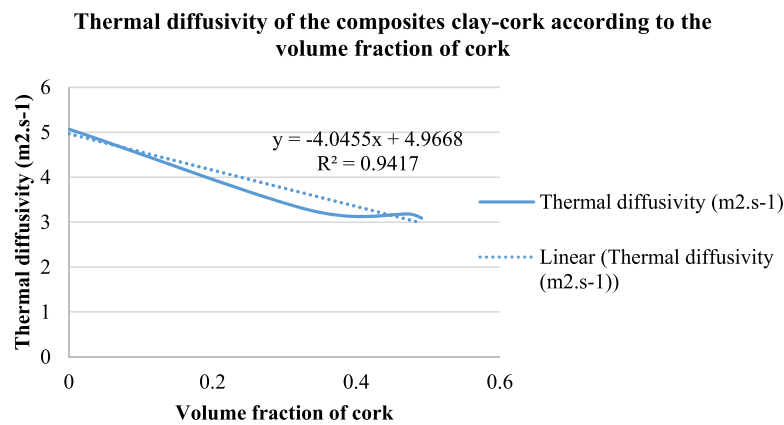


Fig. 9 Thermal diffusivity of the composites clay-cork according to the volume fraction of cork.

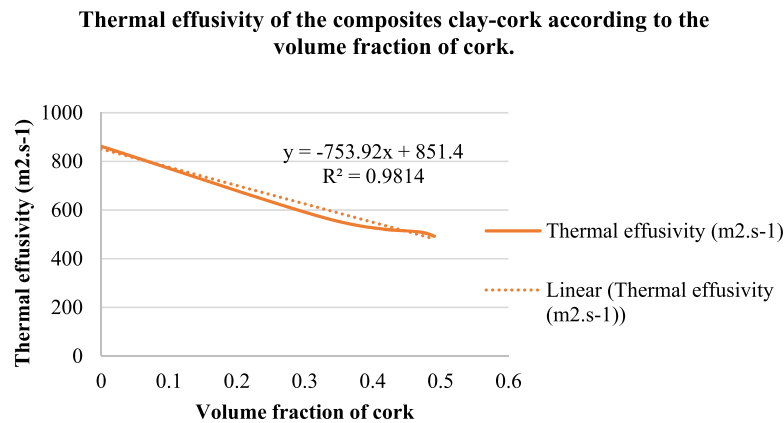


Fig. 10 Thermal effusivity of the composites clay-cork according to the volume fraction of cork.

Thermal effusivity of composite clay cork

Fig. 10 shows thermal effusivity as a function of volume fraction of cork. Analysis of the curve demonstrates that thermal effusivity of clay is reduced by 40% when the volume fraction of cork is the highest. As a conclusion, granular cork minimizes heating of the superficial area of clay combined by cork.

Comparison and discussion of results using different methods

Fig. 11 shows the plots of thermal conductivity versus cork volume fraction of composite for different theoretical models. According to the results of thermal conductivity of the composite clay-cork as illustrated in the **Fig. 11**, the equivalent thermal

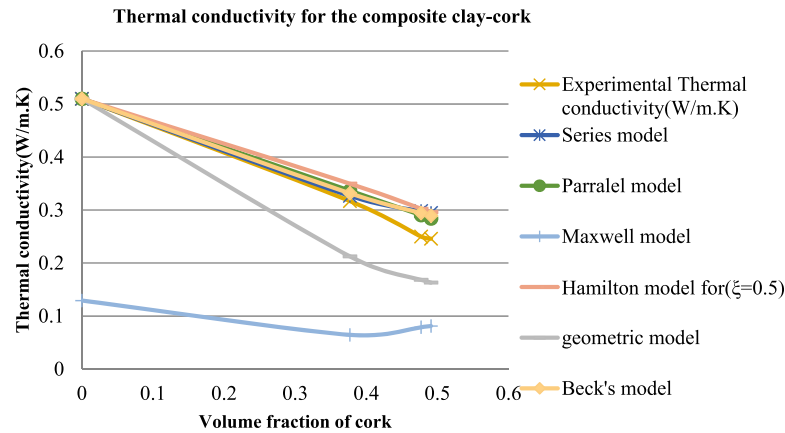


Fig. 11 Graphical representation of the different theoretical models of the equivalent thermal conductivity of the composite clay-cork.

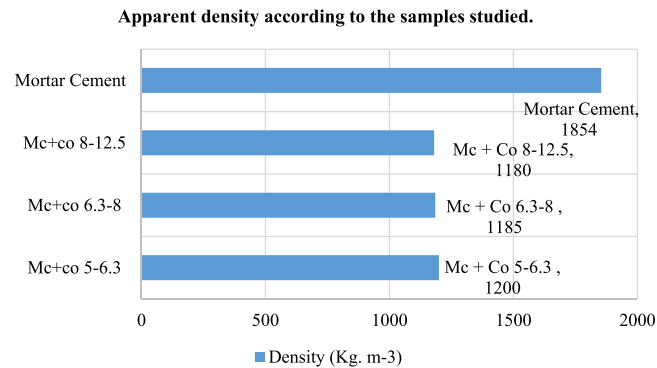


Fig. 12 Apparent density according to the size of cork.

conductivity is between the lower limit (series model) and the upper limit. However, the experimental data is more representative by the geometric model which estimates that the particular cork possesses a preferred orientation according to their natural segregation. Also, they have a special geometrical form between a spherical and cylindrical with a spherical value $\xi = 0.5$. The Hamilton model is more close to the experimental results. The Beck model is in the center of the equivalent thermal conductivity. In reality the real distribution of this composite is between the series and the parallel model.

Composites Cement Mortar Cork

Density of composites cement mortar cork

Fig. 12 shows apparent density of materials based on mortar cement and cork. The results demonstrate that cork has a significant effect in reducing the density of mortar. The density decreased from 1854 to 1180 kg m^{-3} when cork was added to mortar cement. The different volume fraction of cork has insignificant effect on the density of the composite cement mortar. The reduction of density is due to the creation of porosity inside the matrix mortar cement.

Thermal effusivity

Fig. 13 illustrates a clear impact of cork in decreasing the thermal effusivity by 60% compared to mortar cement alone. Different sizes of cork are showing approximatively the same impact.

Thermal conductivity

Fig. 14 shows the thermal conductivity mortar cement with various cork sizes in the composite. The composites cement mortar-cork possesses high insulating properties in comparison with cement mortar alone. Thermal conductivity decreases from 0.703 to 0.207 $\text{W m}^{-1} \text{K}^{-1}$ as the cork sizes changes and a reduction of 70% was obtained. Another observation made is that the variation of cork sizes does not influence significantly on the value of the thermal conductivity. The decrease of this property for the composites cement mortar-cork is due to the creation of air inside the matrix cement. The thermal conductivity of the air in

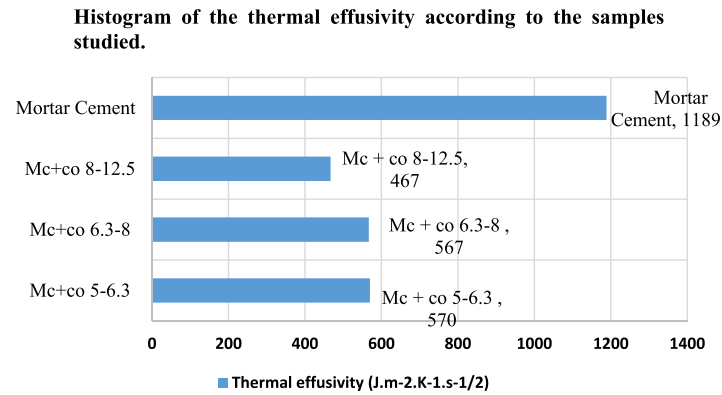


Fig. 13 Thermal effusivity according to the size of cork.

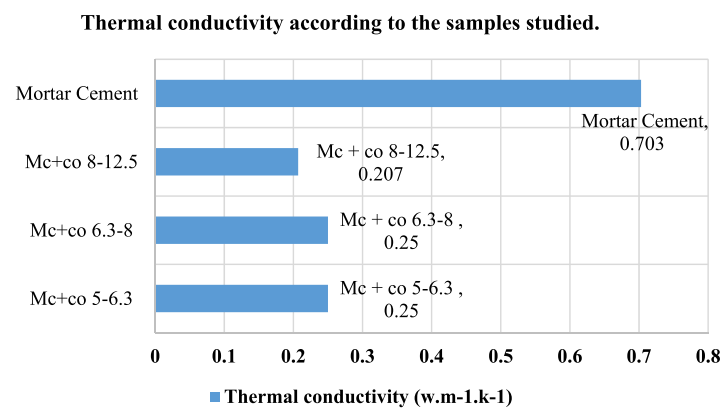


Fig. 14 Thermal conductivity according to the size of cork.

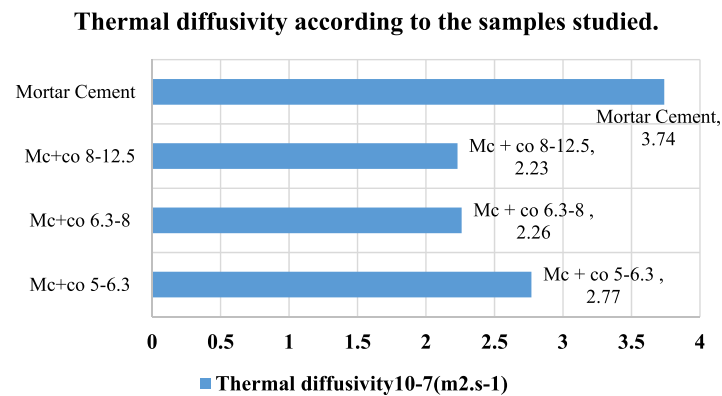


Fig. 15 Thermal diffusivity of the composites cement mortar-cork according to the size of cork.

ambient temperature is $0.025 \text{ W m}^{-1} \text{ K}^{-1}$. [Bachar et al. \(2015\)](#) also got similar findings in their investigation to determine the effect of porosity of cork on mortar cement.

Thermal diffusivity

Fig. 15 shows thermal diffusivity of the composite with various cork sizes in it. When the corks size is 8–12.5 mm, thermal diffusivity decreases to $2.23 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ from that of cement mortar only. This gives a reduction of 40% compared to thermal diffusivity of mortar cement $3.74 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$. This proves that the highest size of cork retards best the acceleration of heat flow inside the matrix mortar cement.

Comparison of results with literature

The results obtained were compared with that of [Borges et al. \(2018\)](#) to compare the effect of cork on cement mortar composite. [Borges et al. \(2018\)](#) prepared two varieties of twenty samples of composites made of cement-expanded cork and cement-expanded clay and studied the effect of various cork sizes on the thermal and mechanical properties of the composites. Their results have shown that mixture of cement and expanded cork gave the lowest bulk density (52 kg m^{-3}) and the mixture of cement and expanded clay produced the highest bulk density (431 kg m^{-3}). Also, they explained that mortars with expanded cork granules presented the lowest thermal properties with a reduction of 93%–94% while the highest values were achieved by mortars with expanded clay and this result can be explained by the best thermal behavior of cork due to its uniform closed cells structure that hinders the heat transfer by convection.

Composites White Cement Cork

Density of composites white cement cork

Fig. 16 shows apparent density of composites white cement cork for various cork sizes. The results demonstrate that cork has a significant effect in reducing the density of white cement. The density decreased from 1571 to 821.5 kg m^{-3} when cork size was 8–12.5 mm. The different volume fraction of cork has insignificant effect on the density of the composite white cement. The reduction of density is due to the creation of porosity inside the matrix of white cement.

Thermal conductivity of composites white cement cork

Fig. 17 shows the thermal conductivity white cement cork with various cork sizes in the composite. The composites of white cement cork possess high insulating properties in comparison to white cement alone. Thermal conductivity decreases from 0.86 to $0.207 \text{ W m}^{-1} \text{ K}^{-1}$ as the cork size is 8–12.5 mm changes and a reduction of 76% was obtained. The corks sizes of 5–6.3 mm and 6.3–8 mm in the composite yielded the same thermal conductivities.

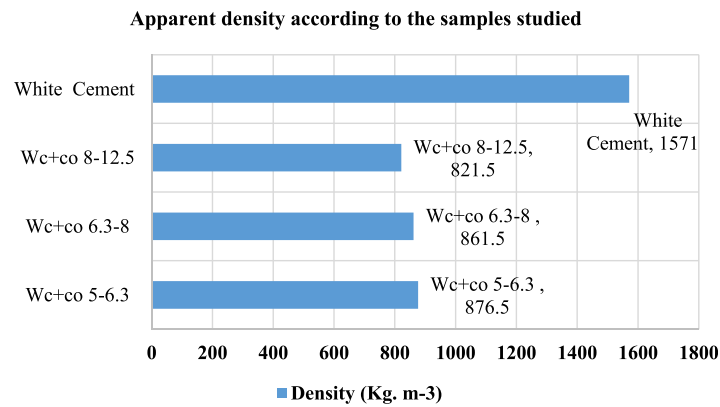


Fig. 16 Apparent density of the composites white cement-cork according to the size of cork.

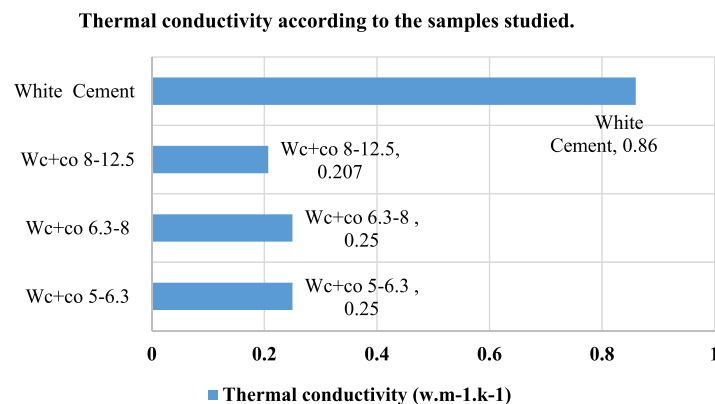


Fig. 17 Thermal conductivity of the composites white cement-cork according to the size of cork.

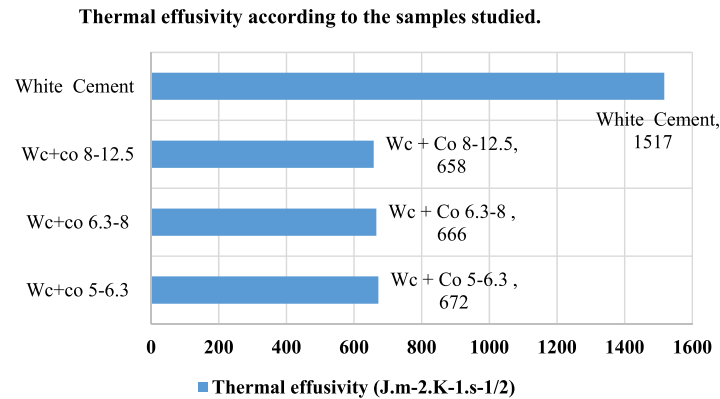


Fig. 18 Thermal effusivity of the composites white cement-cork according to the size of cork.

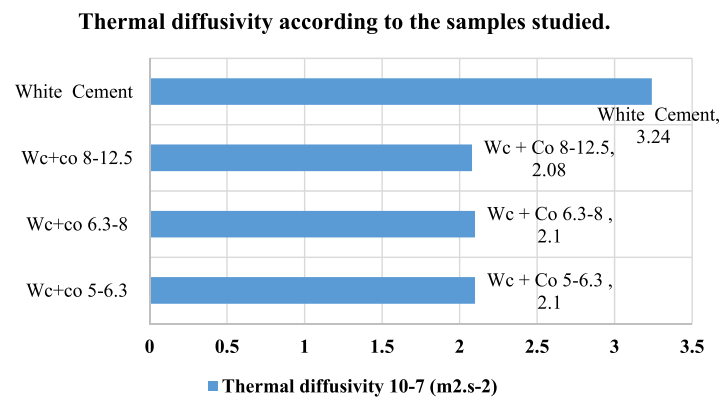


Fig. 19 Thermal diffusivity of the composites white cement-cork according to the size of cork.

Thermal effusivity of the composites white cement cork

Fig. 18 shows thermal effusivity of composites based on white cement and various cork sizes. There is a distinct effect of cork in decreasing the thermal effusivity by 57% compared to white cement alone. Different sizes of cork have approximatively the same effect on thermal conductivity.

Thermal diffusivity of composites white cement cork

Fig. 19 shows thermal diffusivity of white cement composite with various cork sizes in it. Thermal diffusivity decreases from 3.24×10^{-7} to $2.08 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ from white cement to white cement composite when the cork size is 8–12.5 mm. This gives a reduction of 36% compared to thermal diffusivity of white cement of $3.24 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$. This proves that the highest size of cork retards best the acceleration of heat flow inside the matrix mortar cement. The cork sizes do not have an influence on thermal diffusivity of the composite white cement cork.

Comparison of results with literature

A comparison of this result was made with the work of [Mounir et al. \(2015\)](#). They studied the effect of composites white cement-cork, mortar cement cork and plaster-cork on the thermal inertia of building by analyzing the thickness of heat diffusion according to a time interval of 3 h, 6 h, and 12 h. Their results showed that the thickness decreased from 5.82 to 5.32 cm at 3 h, 8.24–7.52 cm at 6 h, and 11.65–10.18 cm at 12 h. This proves the improvement of thermal inertia characteristics using cork in the composite.

Conclusion

This work is divided in two main sections: physical-chemical characteristics of cork and thermal performance of material clay, mortar-cement and white cement joints to cork. A lot of parameters such as apparent density using the weight and the dimensions of samples, thermal conductivity, thermal effusivity using the asymmetrical hot plate method and thermal diffusivity using flash method were studied. With regard to the material clay, the study was focused on the variation of the volume fraction of cork and

its effect on the thermal performance and density. Results show that at the highest volume fraction (0.491), a reduction of weight by 45%, a gain on insulating properties by 51%, and an improvement of thermal inertia by a ratio of 40% was obtained. Also, equivalent thermal conductivity was studied to see the most representative model. It was observed that the geometric model was close to the experimental results which, proves that granular cork is well distributed inside the matrix clay. For the mortar cement and white cement composites, the effect of the cork sizes cork was studied. Results showed that cork possesses some important characteristics in reducing lightness. Thermal properties and thermal inertia of these composites materials, the composite mortar cement-cork showed a reduction of lightness of 36%, a reduction of 76% on thermal characteristics and an improvement of 40% of thermal inertia parameter. Although, for the composite white cement-cork, lightness was improved by 47%, insulating properties was improved by 76% and the thermal inertia parameters were reduced by 40% compared to white cement alone. The variation of the cork sizes does not have any influence on the lightness and thermal performance of the mortar cement and white cement cork composites.

Acknowledgments

National School of Architecture Fez and EMDD-CERNE2D-EST SALE presents a special thanks to LEMTA INPL NANCY for their help so as to realize this work.

See also: Biocompatible Thermoplastic Composite Blended With HAP and CS for 3D Printing. Characterization of Wood, Cork and Their Composites for Building Insulation. Jute/Coir/Banana Fiber Reinforced Bio-Composites: Critical Review of Design, Fabrication, Properties and Applications. Kenaf Fiber Based Bio-Composites: Processing, Characterization and Potential Applications. Manufacturing, Applications and Mechanical Properties of Lightweight Wood-Based Sandwich Panels. Natural Fiber and Synthetic Fiber Composites: Comparison of Properties, Performance, Cost and Environmental Benefits. Natural Fiber Composites: Review of Recent Automotive Trends. Opportunities With Renewable Jute Fiber Composites to Reduce Eco-Impact of Nonrenewable Polymers. Processing, Properties and Prospects of Nano-Biocomposites. Recycling of Flax Fiber Towards Developing Biocomposites for Automotive Application From a Life Cycle Assessment Perspective

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Polyhydroxyalkanoate and Polylactic Acid Composite

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Introduction

Plastics have become an indispensable part of our daily life. Since the 1950s, the production of plastics has shown a steady increase with about 9% per year. Global production reached 335 million tons in 2016. The production of plastics is so far mainly based on fossil fuels and takes place through energy intensive petrochemical processes. The environmental impact of these conventional fossil-based plastics is not associated only to their production process, but also to their non-biodegradability, making them persistent to the environment. They are therefore becoming a serious pollution issue. The world's growing environmental awareness and limited fossil fuels reserves have directed research and industrial attention towards the production of bioplastics as alternatives for petrochemical based synthetics plastics. Bioplastics encompass the materials which are either biobased or biodegradable or both. They can be produced fully or partially from biomass and can be tailored to be fully or partially biodegradable (Table 1).

The market of biopolymers is growing every year and demands can be expected from the applications of biopolymers-based product which offer clear benefits for customers and environment. A report published by BCC Research (a market research company) has estimated that in 2014 the global bioplastic demand was more than 1400 kt (metric kilo tonnes), whereas it was predicted an increasing to about 6000 kt in 2019, which represents a CAGR (compound annual growth rate) of 32.7% for the five-year period; from 2014 to 2019 (Chen, 2014). Furthermore, from the correlation of the demand of bioplastics, it is expected that the global production capacities will be increased to more than 7.8 million tonnes in year 2019. At that time, within the bio-based polymer the biodegradable part will be only 16%.

The rapid emergence of bioplastics is one of the major stories of the last decade (Chen, 2014). Unfortunately, for certain requirements such as in packaging or engineering sectors, the biopolymers cannot be fully competitive with polymers from the category of commodity or engineering thermoplastics (e.g., PS, PE, PP, PET, etc). In order to maximize the impact of biopolymers, there is a growing trend to combine bio-polymers, a key-approach allowing to extend their consumption and market as durable products used in cars, electronics, and elsewhere. The focus has shifted to the total "carbon footprint", and the bio-based polymers not only can replace existing polymers in various sectors but can also provide new combinations of properties and extended applications.

Polyhydroxybutyrate (PHB) being considered as bio-plastics, has the potential to substitute the conventional plastics as it has the similar material properties of polypropylene (PP). But till PHB has not been used on a large scale to replace conventional polymers because of its drawbacks in mechanical properties. It is hard to process PHB due to its high melting temperature of approximately 170°C, which is very near to its degradation temperature (Hazer and Steinbuchel, 2007). Therefore, a solution to these drawbacks could be the copolymerization of hydroxybutyrate with other monomers or making composite with other polymer that confer less stiffness and tougher properties (which bestow greater flexibility and lessen breakage) and to reduce the melting point.

Polylactic acid (PLA) has good mechanical properties particularly, high tensile strength, young's modulus and good flexural strength, which are even higher than those of polystyrene (PS), PP, polyethylene (PE), or other conventional polymers (Hamad et al., 2015). The tensile strength and elastic modulus of PLA are comparable to those of polyethylene terephthalate (PET), but unfortunately PLA is very brittle, with less than 10% elongation at break and low toughness, which limits its use in applications that need plastic deformation under high stress (Rasal et al., 2010). For packaging applications, it is stated that PLA films have mechanical properties comparable to those of PET, whereas the lower glass transition temperature is considered a disadvantage,

Table 1 Classification of plastics based on source and biodegradability

	Fully petroleum based	Partially biobased	Fully biobased
Fully biodegradable	● PBS ● PCL	● Starch blends ● PLA blends	● PLA ● PHA ● PLA/PHA composites
Non biodegradable	● PE ● PP ● PET ● PVC	● PA ● PET from biobased ethylene ● PVC from biobased ethylene ● SBR from biobased succinic acid	● Biobased PE ● Biobased PB

Source: PA = Polyamide, PB = Polybutadiene, PBS = Polybutyrate succinate, PCL = Polycaprolactone, PE = Polyethylene, PET = Polyethylene terephthalate, PHA = Polyhydroxyalkanoate, PLA = Polylactic acid, PP = Polypropylene, PVC = Polyvinyl chloride, SBR = Styrene butadiene rubber.

especially in applications (e.g., hot packaging) requiring resistance at high temperature. Regarding the characteristics of films, the gas permeability coefficients to CO₂, O₂, N₂ and H₂O(g) have been reported as being higher than for PET, therefore these properties need further improvement.

Polyhydroxyalkanoates (PHAs)

Structure, Properties and Sources

Among the alternatives of different bioplastics, an interesting bioplastic are the fully biobased and biodegradable polyhydroxyalkanoates (PHAs). It is synthesized by a number of microorganisms as intracellular storage material. PHAs constitute an attractive alternative to petrochemically synthesized plastics due to their comparable physical and chemical properties, and because of their biodegradability and biocompatibility as additional advantages.

PHAs are polyesters of hydroxyalkanoic acids, composed of hydroxy fatty acids with the most common structure shown in Fig. 1. The side group (R in Fig. 1) varies from methyl (C₁) to tridecyl (C₁₃). PHAs are termed polyhydroxybutyrate (PHB) if R is a methyl (-CH₃) group, polyhydroxyvalerate (PHV) if R is an ethyl (-CH₂CH₃) group, and polyhydroxyhexanoate (PHHx) if R represents a propyl (-CH₂CH₂CH₃) group.

Polyhydroxybutyrate (PHB) is the most common and well-studied PHA which was first isolated and characterized by Lemoigne in 1925. Since then, a number of studies have been performed with various bacterial strains such as Gram-positive bacteria, Gram-negative bacteria, photosynthetic bacteria including cyanobacteria which one has identified the highest PHA production capacity. The microorganisms are stimulated to produce PHAs when the ratio of substrate to nutrients in the culture medium is high, but intracellular degradation of PHAs occurred in absence of carbon and energy sources. By the year 1973 it was well recognized that the storage material PHAs fulfilled a similar role for bacteria as starch and glycogen for higher organisms i.e., eukaryotic (Dawes and Senior, 1973).

At the beginning of the invention, it was thought that the produced PHA was a homopolymer, comprising hydroxybutyrate (3HB or 4HB) as the sole monomer. Later, it was discovered that PHA also contained other types of monomers besides the already present 3HB or 4HB such as hydroxyvalerate (HV), hydroxyhexanoate (HHx), hydroxyheptanoate (HHp), hydroxyoctanoate (HO) to produce co-polymers such as P(3HB-co-3HHx), P(3HB-co-4HB), P(3HB-co-3HV) etc. Besides, a large variety of monomers with straight, branched, saturated, unsaturated and also aromatic structures were also found as a constituent in copolymers of PHB. The presence of various monomers in the copolymer appeared to be dependent on the substrate used as carbon and energy source.

Production Process of Polyhydroxyalkanoates (PHAs)

Pure-culture PHAs production processes

Pure culture PHAs production process is conducted either non-growth associated or growth associated. Due to higher productivity, most of the cases it followed non-growth associated process which consists two phases; first one is biomass growth under favourable condition especially at optimal level of carbon, nitrogen and oxygen concentration and second phase is PHAs accumulation under nutrient limiting condition (Fig. 2(a)). The process is either in batch or fed-batch. The growth associated PHAs production is a single stage process in which growth and production is conducted at same time (Fig. 2(b)).

PHAs production through microbial fermentation takes place under heterotrophic and/or autotrophic conditions. While most works were carried out using organic substrates as carbon source, i.e., heterotrophic PHAs production. There are also some attempts to produce PHAs from carbon dioxide (CO₂), i.e., autotrophic or heterotrophic-autotrophic PHAs production, using hydrogen (H₂) as an energy.

Heterotrophic process

Heterotrophic PHAs production is a bioprocess that uses an organic substrate as carbon and energy source. The provided substrate is able to support bacterial growth, maintenance functions and reserve polymer synthesis.

Pure culture heterotrophic PHAs production was mainly focused in most of the research and industrial production. Under optimal process conditions, the microorganisms have the ability to accumulate PHAs until 80% of the cell dry mass (CDM) (Posada *et al.*, 2011).

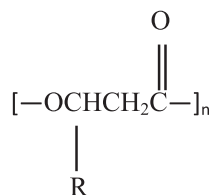


Fig. 1 General structure of a polyhydroxyalkanoate (PHA).

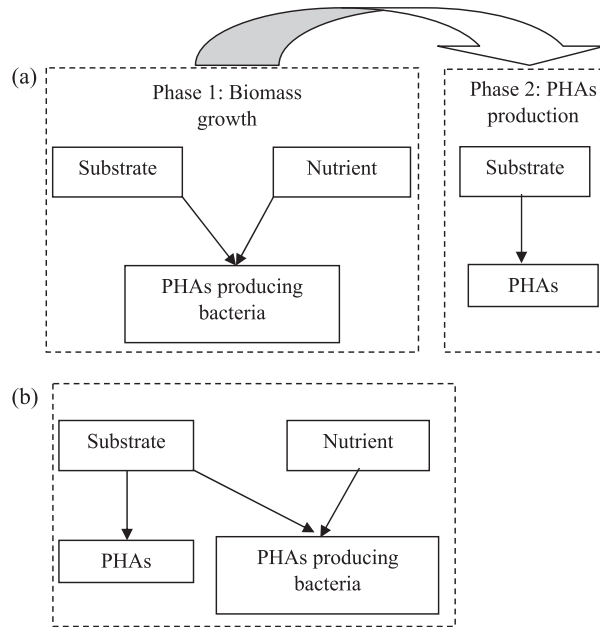
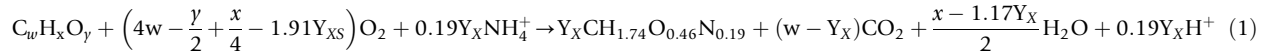


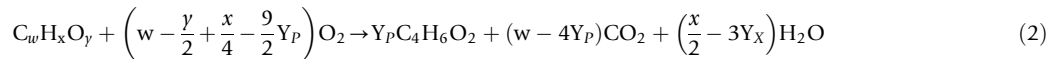
Fig. 2 Schematic presentation of PHAs production in a pure culture system (a) non-growth associated and (b) growth associated.

Heterotrophic biomass growth on an organic substrate proceeds mostly according to the following equation:



In Eq. 1, $C_wH_xO_y$ denotes the organic substrate, and $CH_{1.74}O_{0.46}N_{0.19}$ is the chemical composition of *Cupriavidus necator* biomass (without PHAs), a model organism for PHAs production (Ishizaki and Tanaka, 1990). Y_X is the yield of biomass over organic substrate. During cultivation, oxygen (O_2) and NH_4^+ as a nitrogen source are mandatory for bacterial growth as an electron acceptor and as a nutrient source respectively and CO_2 is produced as a side-product. PHAs production is suppressed due to excess of NH_4^+ -N.

Heterotrophic PHB (one of the most common PHAs) production from an organic carbon source is represented according to the Eq. 2.



Here $C_4H_6O_2$ is the chemical composition of PHB monomer. Y_P is the yield of PHB over organic substrate.

Most lab-scale studies and established industrial processes for PHAs production work with pure sugars such as glucose, fructose, sucrose etc. as carbon source, ensuring high productivity and proper metabolic functioning of the strain. Nevertheless, these substances are expensive and several efforts have been developed to identify low cost carbon sources, namely industrial and agricultural waste substrate such as waste glycerol, molasses, dairy whey, corn syrup, starch residues etc. There are still some concerns about the final PHAs content as well as a high productivity.

Two prevalent cultivation methods are employed for pure culture PHB production, depending on the microorganism used; growth associated and non-growth associated mode.

Growth associated PHAs production

Growth associated PHAs production is a one step process, in which PHAs production is conducted in parallel with bacterial growth. In this case there is low nutrient inhibition effect on the PHAs production. Organisms like *Bacillus mycoides*, *Azohydromonas lata* etc., are able to produce PHAs in growth associated mode with high productivity in a nutrient rich medium.

Non-growth associated PHB production

The non-growth associated manner consists of two phases. First, biomass is grown under favourable conditions especially at optimal level of carbon, nitrogen and oxygen (O_2) concentration. The second phase is PHB accumulation under nutrient limiting conditions namely nitrogen or oxygen limitation. Due to the higher productivity, the pure culture non-growth associated process to produce PHAs attract major attention.

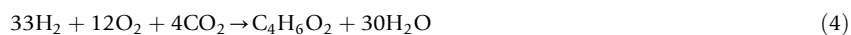
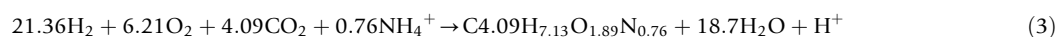
Table 2 Comparison of PHB production and productivity using *Cupriavidus necator* (formerly known as *Ralstonia eutropha* and *Alcaligenes eutrophus*) as an organism in a fed-batch fermentation process in order of increased PHB concentration

Substrate	Strain and mutant	Feeding of organic substrate	CDM concentration (g/L)	PHB production (g/L)	PHB content (%)	PHB productivity (g/L/h)	Reference
Heterotrophic-heterotrophic process							
Corn syrup	<i>C. necator</i> DSM 545	–	16.57	10.75	65	0.22	Daneshi <i>et al.</i> (2010)
Waste glycerol	<i>C. necator</i> DSM 545	Pulse addition	30.19	10.9	36.1	0.17	Cavalheiro <i>et al.</i> (2012)
Fructose	<i>R. eutropha</i> B-5786	Continuous	18	15.5	86	0.22	Volova and Kalacheva (2005)
Waste glycerol	<i>C. necator</i> DSM 545	–	76.2	38.1	50	1.1	Cavalheiro <i>et al.</i> (2009)
Pure glycerol	<i>C. necator</i> DSM 545	–	82.6	51.2	62	1.52	Cavalheiro <i>et al.</i> (2009)
Pure glycerol	<i>C. necator</i> JMP 134	–	102	57.1	56	1.31	Posada <i>et al.</i> (2011)
Glucose	<i>C. necator</i> DSM 545	Mixed feeding strategy	164	127.7	75.8	2.03	Mozumder <i>et al.</i> (2014)
Soybean oil	<i>C. necator</i> DSM 545	Pulse addition	83	67	80	2.5	Pradella <i>et al.</i> (2012)
Waste potato starch	<i>R. eutrophus</i> NCIMB 11599	–	179	94	53	1.31	Haas <i>et al.</i> (2008)
Glucose	<i>A. eutrophus</i> NCIMB 11599	CO ₂ evolution rate	164	121	74	2.42	Kim <i>et al.</i> (1994)
Autotrophic-autotrophic process							
H ₂ :O ₂ :CO ₂ =60:20:10 vol%	<i>C. eutrophus</i> B 10646	–	30	22	75	0.314	Volova and Voinov (2003)
H ₂ :O ₂ :CO ₂ =70:20:10 vol%	<i>C. eutrophus</i> B 10646	–	48	40.8	85	0.583	Volova <i>et al.</i> (2013)
H ₂ :O ₂ :CO ₂ =85:5:10 vol%	<i>C. necator</i> ATCC 17697	–	69.3	56.4	81.4	0.61	Taga <i>et al.</i> (1997)
H ₂ :O ₂ :CO ₂ =85.2:6.3:8.3 vol%	<i>C. necator</i> ATCC 17697	–	91.3	61.9	68	1.55	Tanaka <i>et al.</i> (1995)
Heterotrophic-autotrophic process							
Acetic acid + H ₂ :O ₂ :CO ₂ =86.5:4.9:9.8 vol%	<i>C. necator</i> ATCC 17697	–	22.9	12.6	55	0.224	Sugimoto <i>et al.</i> (1999)
Fructose + H ₂ :O ₂ :CO ₂ =86.5:4.9:9.8 vol%	<i>C. necator</i> ATCC 17697	–	26.3	21.6	82.1	0.556	Tanaka and Ishizaki (1994)
Glucose + H ₂ :O ₂ :CO ₂ =86.5:4.9:9.8 vol%	<i>C. necator</i> DSM 545	–	46	28	61	0.168	Garcia-Gonzalez <i>et al.</i> (2015)

Various bacteria have the ability to synthesize PHAs such as *Cupriavidus necator*, *Alcaligenes latus*, *Azotobacter vinelandii*, certain *Pseudomonas* as well as genetically modified *Escherichia coli* strains etc. Among them *C. necator* (also named as *A. eutropha*, *C. eutropha* or *R. eutropha*) is the most extensively studied micro-organism due to its high productivity (Ashby *et al.*, 2002). It can produce significant amounts of PHAs from different carbon substrate such as glucose, fructose, glycerol, oil and even waste substrate (Table 2).

Autotrophic process

The autotrophic process is the process at which CO₂ is used as carbon source. In this process a gas mixture of CO₂, H₂ and O₂ is used for cell growth and PHAs production. Hydrogen oxidizing bacteria such as *C. necator* have the ability to grow and produce PHAs through autotrophic metabolism, using CO₂ as carbon source and H₂ as energy source (Table 2). CO₂ is a greenhouse gas of which the concentration in the atmosphere is related with the global warming phenomenon. In attempts to counteract climate change, emitted CO₂ can be a valuable source of carbon which can be utilized in the production of commercially valuable products such as PHAs. Autotrophic biomass growth (Eq. (3)) and PHB production (Eq. (4)) are described by the following equations.



Until now autotrophic PHAs production has only been conducted in pure culture non-growth associated manner using *C. necator* as organism. The gas composition which attains sufficient cell growth has a ratio of $H_2:O_2:CO_2=7:2:1$ (Mozumder *et al.*, 2015). Such a gas composition lies completely within the gas-explosion range and is therefore too dangerous to work with. Considering safety issues, the O_2 concentration in the gas phase should be kept below the lower level of explosion (LEL) for O_2 , between 6 and 6.9 vol% (Takeshita and Ishizaki, 1996). However, under those low O_2 concentrations, limited growth as well as low PHAs production were achieved.

Heterotrophic-autotrophic process

The heterotrophic-autotrophic process consists of a heterotrophic phase for exponential growth using an organic substrate promoting a high cell density culture followed by an autotrophic phase for PHAs production using a gas mixture of CO_2 , O_2 and H_2 at an O_2 concentration under the LEL. The advantage of this cultivation system is that a high cell concentration can be obtained as O_2 can be supplied under non-limiting conditions during the heterotrophic cell mass growth phase, while in the autotrophic phase PHAs biosynthesis will be triggered when the O_2 concentration is below its critical value of LEL.

Two organism cultures of PHAs production

In pure culture it was proven that *C. necator* was an efficient microorganism for PHAs production, but it cannot easily metabolize sucrose. This limitation can effectively overcome using the two-organism culture method by a two-reactor system; in first phase sucrose was converted to lactate by lactate producing organism (such as *Lactococcus lactis*) and then followed PHAs production by *A. eutropha* (Tanaka and Ishizaki, 1994). The overall process flow is shown in Fig. 3. The process has mainly three phases; (1) conversion of sucrose or higher hydrocarbon to easily metabolite form of hydrocarbon; for example, production of Lactate through lactate producing bacteria, (2) growth of PHAs producing organism under sufficient Lactate and nutrient conditions and (3) PHAs production under nutrient stress condition. Although in literature the process was called a mixed culture, two pure microorganisms are used and followed nutrient stress condition to stimulate the PHAs production, same as the mechanism of pure culture. There is also possible to use single bioreactor instead of two for this two-organism system; initially inoculated pure *L. delbrueckii* to ensure the sufficient conversion of lactate and then pure *C. necator* was injected to same bioreactor for the synthesis of PHAs. However, the competition between both organisms is not still clear.

Mixed culture PHAs production

Mixed culture operation had been evaluated aiming to conversion of waste material to valuable product like PHAs and to reduce the capital and operational expenses. The process is known as 'feast and famine'; in which substrate availability alternated periodically, explained in Fig. 4. In feast famine process, the substrate uptake rate reaches its maximum value after the addition of substrate, as well as the cell growth rate slowly reached to the maximal level. In the transient period the excess of substrate was taken up and stored into the cell as PHAs. After depletion of the external substrate, the stored PHAs is used for cell growth. The most accepted explanation, PHAs synthesis occurred when the growth was limited by internal factors such as insufficient amount of RNA or enzymes required for growth. Feast famine process also implemented in aerobic activated sludge system where sludge is submitted periodically as an external carbon source for PHAs storage. Indeed, the intracellular PHAs content was reached around 70% of the cell dry weight, suggesting that this process could be competitive with pure culture PHAs production when fully developed (Dias *et al.*, 2006).

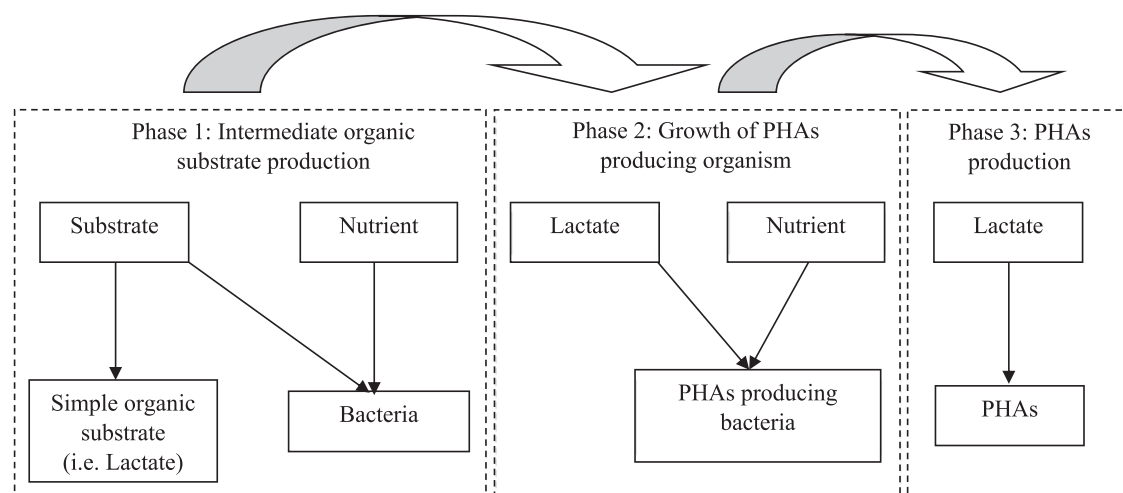


Fig. 3 Stoichiometric representation of PHAs production by a two-organism mixed culture system.

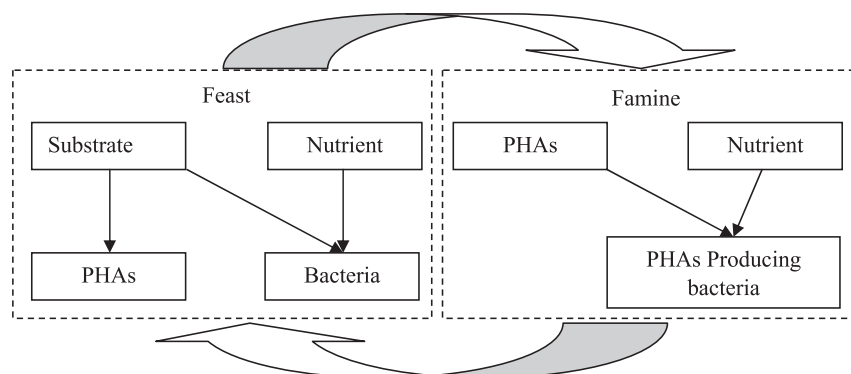


Fig. 4 Schematic representation of PHAs production through mixed culture feast famine process.

Application of PHAs

The wide range of properties of PHAs and its copolymers make it an attractive biopolymer for various applications involving packaging, medical and coating materials. However the main obstacle behind the limited application of PHAs is to produce a specific copolymer with desired properties.

Industrial applications

PHAs is used to make small disposable articles such as shampoo bottles and packaging materials including food packages. It is also used for bags, paper, disposable utensils, cups etc. Foils, films and diaphragms can also possible be made with PHAs (Lauzier *et al.*, 1993). PHAs latex can be used as water-resistance surface of cover paper or cardboard. Hard articles such as combs, pens etc., are made of P(3HB) because of its high crystallinity (Chen and Wu, 2005). The copolymer P(3HB-co-3HHx) is used to make flushable, nonwovens, binders, flexible packing, thermoformed articles, synthetic paper and medical devices. P(HB-HV) has gas barrier properties and is useful for food packaging, plastic beverage bottles, coated paper milk cartons etc. PHB blend with polyhydroxyoctanoate (PHO) is also known as an elastomer for the production of food additives (Clarival and Halleux, 2005).

Medical applications

PHB and its copolymers are extensively used as pharmaceutical products in surgery, transplantology, tissue engineering, pharmacology etc. In tissue engineering, the cells are grown *in vitro* on PHAs to construct "tissue" for implantation purposes (Shinoka *et al.*, 1998). PHB and P(HB-co-HHx) are the most extensively studied biopolymers for tissue engineering and controlled internal drug delivery system. PHB has also been found to be a suitable scaffold for preparing autologous cardiovascular tissue (Shangguan *et al.*, 2006).

PHB is frequently used as bone plates, osteosynthetic materials and surgical sutures. Hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) incorporated into PHB can be used in hard tissue regeneration (Doyle *et al.*, 1991). The combination of hydroxyapatite with PHB and P(HB-HV) leads to similar mechanical strength as that of human bones which is beneficial for bone tissue engineering (Galego *et al.*, 2000). The graft copolymer of methyl methacrylate and PHB blocks can be used as bone cement in orthopaedic applications. Moreover, the biocompatible property of PHB makes it well-suited for skincare products (Chen and Wu, 2005).

Polylactic Acid (PLA)

Production of Polylactic Acid (PLA)

The synthesis of PLA polymers can be performed by direct polycondensation of lactic acid as well as by ring-opening polymerization of lactides, a cyclic dimer of lactic acid. Before the production reaction to PLA, either lactic acid or lactides are needed to produce.

Synthesis of lactic acids

Stereoisomers of lactic acid

Lactic acid chemically named as 2-hydroxypropanoic acid, is the simplest 2-hydroxycarboxylic acid with a chiral carbon atom. There are two optically active stereoisomers of lactic acid namely L and D enantiomers; L- and D-lactic acid, respectively (Fig. 5). These L- and D-lactic acids are generally synthesized through fermentation using organic carbon source and suitable microorganisms. Racemic DL-lactic acid is also existing which consist equimolar mixture of D- and L-lactic acids, shows different characteristics from original single lactic acids and synthesized by chemical method rather than fermentation.

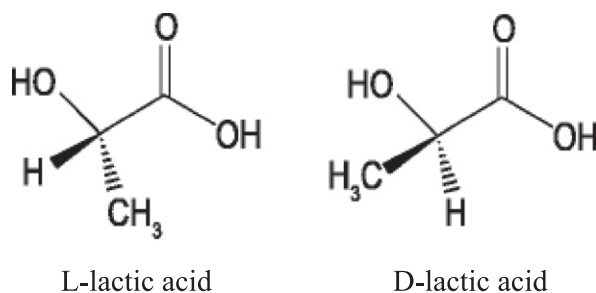


Fig. 5 Structure of L-, D-lactic acids.

Lactic acid production through fermentation

Lactic acid is mainly produced through fermentation using lactic acid bacteria. Worldwide it is counted that around 90% lactic acid is produced through fermentation. The fermentation process has attracted interest because of its numerous advantages compared with chemical synthesis, such as production of pure isomers, the use of renewable resources as substrates etc. Several microorganisms and raw materials can be used in the production of lactic acid. Using pure substrate such as sucrose from sugarcane and sugar beet etc. produce highly pure Lactic acid, results in a reduction in the cost of purification. Unfortunately, the high cost of pure substrate such as sugar makes it unfeasible for industrial application. The waste products from food industries, agricultural industries, sugarcane mills, and biomasses can be used, which is advantageous from an environmental and economic standpoint.

Lactic acid bacteria are generally divided into several classes in terms of cell morphology, i.e., *Lactobacillus*, *Streptococcus*, *Pediococcus*, *Aerococcus*, *Leuconostoc* and *Coryne* species. Most of them produce L-lactic acid and few of them are able to produce D- or DL-lactic acids. The species belonging to the same *Lactobacillus* genus can produce either L- or D-lactic acid. *Lactobacillus helveticus* and *Sporolactobacillus* produce DL- and D-lactic acids, respectively, however, depending on operating conditions, sometimes small amounts of both L- and D-lactic acid also can be produced.

Chemical synthesis of lactic acid

Racemic DL-lactic acid can be synthesized by fermentation using appropriate bacteria, but it is more easily to synthesize it by following the chemical process shown in Eqs. (5) and (6). Here, the DL-lactic acid is produced by hydrolysis of lactonitrile that is generally formed by the addition reaction of acetaldehyde and hydrogen cyanide. Industrially, the lactonitrile is obtained as a by-product of acrylonitrile production. The reactions involved for DL-lactic acid production are described in Eqs. (5) and (6).



At first hydrogen cyanide (HCN) is added to liquid acetaldehyde (CH_3CHO) in presence of a base catalyst under high pressure to produce lactonitrile (Eq. (5)). The lactonitrile is then recovered, purified by distillation, and hydrolyzed using sulphuric acid (H_2SO_4) to produce lactic acid ($\text{CH}_3\text{CHOHCOOH}$) (Eq. (6)).

Although there are many possible routes for the production of lactic acid by chemical synthesis, none of these routes are technically and economically feasible, except for the routes that use lactonitrile as the raw material.

Separation and purification of lactic acids

The fermenting liquor obtained from fermentation process contains lactic acid with various impurities such as un-reacted raw materials, cells and culture media-derived saccharides, amino acids, carboxylic acids, proteins and inorganic salts. Therefore, the isolation and purification of Lactic acids are needed for obtaining a highly pure product as well as polylactic acid (PLA) synthesis. Effective separation and purification of lactic acid from fermentation broth is extremely important for economic viability. Although the difference between the boiling point of lactic acid and water is relatively large, it is almost impossible to obtain pure crystalline lactic acid. This is due to a high affinity of lactic acid to water and formation of a dimer lactate at high concentration of lactic acid.

The separation and purification of Lactic acid involves a series of downstream process such as precipitation, conventional filtration, acidification, carbon adsorption, evaporation, crystallization, etc (Pal et al., 2009). The number of steps involved in downstream processing, strongly influences the quality and the price of the product.

Every purification technologies have several advances, but many drawbacks are still reported. In precipitation process, the reagents cost is very high and necessity of filtration and other separation processes, while high product purity is required. It generates large amounts of waste water which is a major drawback. Furthermore, to produce one ton of lactic acid, approximately one ton of calcium sulphate is needed (Pal et al., 2009), which poses serious problems in treatment of produced waste. In solvent extraction process, a high surface area is necessary for the efficient separation – make the process expensive. The in-situ application of solvent extraction process is not possible due to limited solvent recovery and toxicity to microorganisms (Gao et al., 2009). The membrane separation processes are promising technologies for the efficient separation, but its application in large scale is limited by its high cost of membranes and polarization and fouling problems.

In recent years, a number of studies have been completed to solve the problems by improvement of traditional separation process, such as applying reactive distillation (Kumar *et al.*, 2006; Lunelli *et al.*, 2010) and molecular distillation (Chen *et al.*, 2012; Komesu *et al.*, 2014). In this process lactic acid is first esterified with methanol (CH₃OH) to produce methyl lactate (CH₃CHOHCOOCH₃) (Eq. (7)). The produced methyl lactate is recovered, purified by distillation, and hydrolyzed in an acidic medium to produce lactic acid and methanol (Eq. (8)). Methanol is separated by distillation and recycled.



Furthermore, more studies on lactic acid recovery processes are required to develop a more efficient and economically attractive process for industrial applications.

Synthesis and purification of lactides

Lactides is the cyclic dimer of lactic acids. It is usually synthesized by depolymerization of corresponding lactic acid that is obtained by polycondensation of relevant lactic acid. At first water is removed by a continuous condensation of aqueous lactic acid to produce low molecular weight oligomers or prepolymers. The oligomers or prepolymers is then catalytically converted to lactides through an internal transesterification reaction. Because of the ring-chain equilibrium between lactide and oligomers or prepolymers, unzipping depolymerization generates lactide through the back-biting mechanism involving the -OH terminals as the active site. This reaction is well catalysed by metal compounds involving Sn, Zn, Al and Sb ions, etc. The crude lactide can be purified by melt crystallization or ordinary recrystallization from solution or distillation under vacuum.

There are three potential forms of lactides: D,D-lactide called D-lactide, L,L-lactide called L-lactide and L,D- or D,L-lactide known as meso-lactide (Fig. 6). Only D- and L-lactide are optically active stereoisomers. The meso-lactide is up to two times more susceptible to reactions than L-, D-, or racemic lactides, which can mean less catalyst usage, lower processing temperatures, or both for meso-lactide.

Polymerization of lactic acids and lactide monomers

There are two major routes to produce polylactic acid (PLA) at industrial scale:

- (1) Direct polycondensation of lactic acid (LA)
- (2) Ring-opening polymerization (ROP) via lactide

In direct polycondensation of lactic acids, at first water was removed by condensation and then used solvent under vacuum pressure and high temperature to produce PLA. There are several disadvantages of this process such as, only low to intermediate molecular weight PLA can be produced due to the difficulties of removing water and impurities, relatively large reactor required, the need for evaporation, recovery of the solvent, significant change of colour and racemization (Farrington *et al.*, 2005). Using chain-extension method with low or intermediate molecular weight PLA high molecular weight PLA is possible to produce, but the properties of PLA obtained in this way can be affected. Azeotropic distillation using a high boiling solvent to remove the water from lactic acids before polymerization is another alternative to produce high molecular weight PLA (Murariu and Dubois, 2016).

Industrial production of PLA mostly based on ring-opening polymerization (ROP), the main way to obtain high molecular weight PLA. It is carried out by commonly using a stannous octoate based catalyst. Currently, industries focusing on a multi-step procedure involving the ROP of lactide without using any solvents. It starts with the condensation reaction of aqueous lactic acids to produce low molecular weight PLA prepolymer followed the conversion into a mixture of lactide stereoisomers using tin (Sn) catalysis to enhance the rate and selectivity of intramolecular cyclization reactions. The impurities are removed in a distillation step, and the meso-lactide is separated. The "meso" fraction is then combined with the low D-lactide fraction and high L-lactide fraction to produce a large portfolio of PLA grades. The high molecular weight PLA is produced using an organo-tin catalyst. It is also help to eliminate the use of costly and environmentally unfriendly solvents (Farrington *et al.*, 2005). After polymerization, the residual lactide monomer is recycled within the process.

Recently another catalytic process has developed to make the process economically viable (Jacobsen and Fritz, 1999). In this new catalytic system, an equimolar amount of triphenylphosphine and stannous octoate is used for the polymerization of lactide by reactive extrusion. It has the advantages of low residence time and specific features, especially where is used the twin-screw extruder as "reactor" equipment.

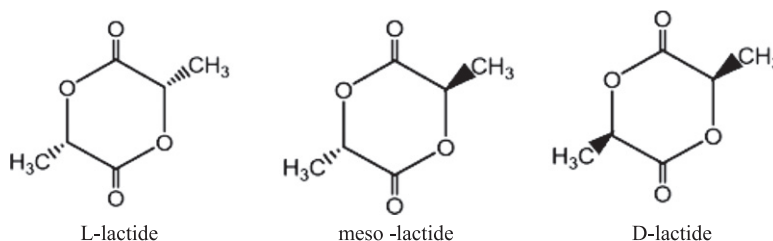


Fig. 6 Stereoisomers of Lactides.

Properties of PLA

The polymerization of pure L- and D-lactides gives isotactic homopolymers of Poly(L-lactide) (PLLA) and Poly(D-lactide) (PDLA), respectively. Both of them are crystalline with a melting temperature 180°C and decrease with decreasing optical purity (OP) of the lactate (Liu *et al.*, 2013). Poly(DL-lactide) (PDLLA), prepared from meso-lactides, is an amorphous polymer, having an atactic sequence of D and L- units. Stereo-block copolymers of PLA diversities of PLA polymers provide a broad range of physicochemical properties for PLA materials when processed.

Generally, PLA is thermoplastic polyester which has a good mechanical, thermal and optical properties with elastic modulus 3000–4000 MPa and tensile strength in the range 50–70 MPa (Murariu *et al.*, 2010; Sodergard and Stolt, 2002; Urayama *et al.*, 2001). But they have very poor elongation at break (2%–10%) and restricts the application potential of pure PLA. PLA has the glass transition temperature (T_g) between 55 and 65°C and brittle at room temperature (Anderson and Hillmyer, 2006; Bao *et al.*, 2012; Liu *et al.*, 2013). The impact resistance of PLA is about 13–20 kJ/m² for low crystallinity and 18–35 kJ/m² for high crystalline grades – very poor or low impact resistance (Anderson *et al.*, 2008; Grijpma *et al.*, 2002). The chemical stability of PLA can be adversely affected at processing temperatures. The commercially available PLAs are typically stabilized against thermal degradation. The presence of water in PLA processing have a significant effect of PLA characteristics, a large amount of hydrolysis occurs when PLA with high moisture. The appearance of PLA is affected by the crystalline content; amorphous or low-crystalline PLA is a clear material with high gloss while highly crystalline PLA is an opaque white material.

Applications of PLA

PLA is a high-strength and high modulus polymer with acceptable barrier properties and easy processing with conventional machinery. However, PLA applications are still limited due to its higher cost with respect to conventional materials, but also for its brittleness and low thermal stability (Huneaul and Li, 2007).

From the beginning of the PLA production, it has been used in medical applications such as biodegradable scaffold, catheter, tissue regeneration and many other devices where biodegradability and biocompatibility are important. PLA shows attractive results in regulation of angiogenic factors or gene transfer in growing tissues (Sheridan *et al.*, 2000), biodegradation in regeneration tissue, control of drug delivery systems to target organs and tissues etc.

Using of PLA in packaging industry, particularly food packaging, plays a fundamental role to reduce the disposal waste mainly non-renewable and non-biodegradable packaging materials. Food with PLA packaging is safe with no health risks to consumers under glass transition temperature (T_g). PLA shows better behavior than classical materials like polystyrene, cellophane, PET or LDPE in terms of barrier properties against radiation, water vapor, atmospheric which increase its potential to use in food packaging (Oliveira *et al.*, 2004).

PLA, due to its low cost and its fibre properties, is now considering one of the most promising bio-polymers for textile applications. It is used in knitted fabrics, non-woven textiles, headrest covers, vehicle seats, tarpaulins non-woven wipes, car and household wipes, personal care towels, diapers, napkins etc. PLA is also used in the home/office furnishing sector such as carpets, tiles and rugs, draperies, curtains, pillows cushions, mattresses, sofas etc.

Fibrous reinforcements within PLA decrease the overall cost and improve mechanical properties, while powdered fillers are used. PLA formulations by using natural fibre reinforcements improve its thermal properties and it can be used to make the objects that can use at high temperature such as applications in the automotive industry; Toyota and Ford have used PLA/fibre composites for the interior parts of their cars i.e., canvas roof, carpet mats etc. (Serizawa *et al.*, 2006). Moreover, Samsung and Toshiba used PLA for remote control and phone chassis, Sanyo for CD/DVD discs and cases and Fujitsu used for the hard-shell case of notebooks.

Polyhydroxyalkanoates and Polylactic Acid Composites

Although polyhydroxyalkanoates are biodegradable polymers and synthesized from renewable resources, their potential applications are hampered due to brittleness and formation of very large spherulites. The polyhydroxybutyrate (PHB) and polylactic acid (PLA) composite is one of the most studied composites, which exhibits mechanical properties that are intermediate between the individual components. The PHA/PLA blends were studied mainly to explore their miscibility, crystallization, morphology, mechanical properties and degradation behavior. The composites of PHA and PLA not only improve the performance and offset the high price of PHAs but also offer more scope to expand their range of applications.

Production of Polyhydroxyalkanoates and Polylactic Acid Composites

The production of PHA and PLA composites is realized using the following techniques:

(1) Melt-compounding:

Melt compounding is a typical procedure in which dry mixing of all or some of the components with high speed mixers is conducted that followed by compounding in a wide range of melt-blending equipment such as internal mixers, single- or twin-screw extruders, Buss kneaders, etc. The processing conditions such as shear stress, temperatures, mixing time, etc. are

determined by the types of equipment, nature of dispersed phase(s), blend composition, desired end-use product properties, etc. The polyester-based matrix (i.e., PLA, PHA) is very sensitive to temperature, shearing and hydrolysis, so that all precautions should be applied to avoid its degradation. To avoid hydrolysis the limit of the water content in PLA for all compositions is around 50–250 ppm independent of processing conditions. Reinforcements or fillers containing crystallization water also make problem in the process.

In the preparation of a PHA and PLA composites using a co-rotating twin-screw extruder; the melt mixing is carried out above the glass transition temperature (T_g) as amorphous polymer. The reason for using a twin-screw extruder is to ensure that all the specimens undergo the same thermal–mechanical history. After processing the polymers is dried in a vacuum prior to use.

The melt-compounding method is highly preferred in the context of sustainable development. It has several advantages such as it avoids the use of organic solvents which are not eco-friendly and can alter the life cycle analysis of PLA. It is easy to up-scale to larger-scale and to industry, whereas the twin-screw extrusion is the preferred method for polymer modification or for the addition of masterbatches, impact modifiers, fibres, fillers, additives, or of selected polymers, which can increase the performances of PHAs/PLA composites.

(2) *Solvent-based methods (e.g., solvent-casting):*

This process mostly used at small laboratory scale. Due to low quantities of active pharmaceutical ingredients, this technique is attracting the interest for the biomedical sector. The composite produced through this approach lead some differences in proprieties compare to those obtained using melt compounding. The film form of PHA/PLA blends is generally produced by solvent casting using a common solvent mainly chloroform, at room temperature. The solvent-casted film is inserted between two Teflon sheets and compression-molded by heating at 200°C for 1 min under a pressure of 75 kg/cm². After melting, samples are kept at a given crystallization temperature and isothermally crystallized for 3 days. Thermo-compression together with solvent-casting methods, showed better thermal stability and higher tensile strength (increased to 44 MPa from 17 MPa) than those obtained by solvent-casting. However, solvent-cast films were very ductile (elongation at break of 203%) compared to the films by compression-moulding (elongation of only 3%). The condition of thermo-compression such as heating temperature, pressure, compression time are differ based on application of the end product (Murariu and Dubois, 2016).

(3) *Other methods:*

Other possible methods for the production of PLA based composites are (i) polymerization of lactide on the surface of dispersed phases of PHA for better compatibility or higher performances, (ii) the physical blending of PLA (as fibres) with PHA fibres, (iii) co-extrusion (fibres, films, sheets), (iv) hot pressing using the film stacking method etc.

Characterisation of PHAs/PLA Composites

The PHAs/PLA composition and types of PHAs within the composite have a significant effect on the toughness, miscibility, crystallization, mechanical properties and hydrolytic degradation of PHA/PLA composites.

Physical properties

The composites prepared through the solvent-casting method is immiscible in amorphous state but blends prepared through the melt-compounding method showed greater miscibility due to the trans-esterification of PHAs and PLA at high temperatures in the formation of PHAs/PLA block (Zhang *et al.*, 1996). The composition of P(3HB)/PLA: 50/50 wt% blend reveals a separate phase while the P(3HB)/PLA: 30/70 wt% blend is a compatible one-phase system (Vogel *et al.*, 2008). The miscibility of the P(3HB)/PLA composite is strongly influenced by the molecular weight of PLA component; the PLA of molecular weight values below 18,000 exhibited greater miscibility (Koyama and Doi, 1997). P(3HB) is highly crystalline polymer, addition of PLA decreases its crystallinity and the P(3HB)/PLA composites with 80% PLA do not show any crystallinity at all (Zhang *et al.*, 1996). There is a contradictory finding as in most cases, the crystal growth rate of crystallisable component is depressed by mixing amorphous components; the addition of the completely amorphous P(3HB) component has accelerated the growth rate of PLA spherulites. However, PLA is a transparent polymer and increasing HV in the composites, decrease the transparency. P(3HB-co-3HV) copolymer has a dense structure that does not allow light to pass through it and decrease the transparency in the P(3HB-co-3HV)/PLA composites (Nanda *et al.*, 2011). The P(3HB-co-4HB) copolymer is found evenly distributed in the PLA matrix. With an increase in the P(3HB-co-4HB) copolymer content, the average particle size, indicated by the P(3HB-co-4HB) copolymer pores, is also increased; make completely an immiscible system.

Mechanical properties

The P(3HB)/PLA composites show a reduction in modulus and stress at break and an enhancement of the elongation at break. P(3HB)/PLA blend films were more hydrophilic than P(3HB) films and PLA component; shows faster hydrolytic degradation. The elongation at break of P(3HB)/PLA composites are intermediate between pure P(3HB) and pure PLA. PLA dominated composites shows better mechanical deformation properties (Vogel *et al.*, 2008). The addition of PLA to P(3HB-co-3HV) copolymer gradually increase the tensile strength and modulus due to low tensile strength of P(3HB-co-3HV) and higher tensile strength and modulus of PLA. The strain at break increases as the P(3HB-co-3HV) copolymer is incorporated into the PLA. The impact strength of neat

PLA is 30 J/m and for neat P(3HB-co-3HV), it is 49 J/m (Zhao *et al.*, 2013). Although the elongation at break for the P(3HB-co-3HV)/PLA composites are higher than the individual polymers, the impact strength is nearly equal to that of the PLA and the Young's modulus decreases as the amount of PLA increase (Nanda *et al.*, 2011; Zembouai *et al.*, 2013).

Addition of P(3HB-co-4HB) copolymer in PLA composites increase elongation at break, decrease of modulus and tensile strength. 20% P(3HB-co-4HB) content increase the elongation at break to a maximum value of 317% (Han *et al.*, 2012).

Thermal properties

The PLA was more thermally stable than the P(3HB-co-3HV) copolymer. The thermal degradation of P(3HB-co-3HV) copolymer occurred through a random chain scission at ester groups whereas the thermal degradation of PLA occurred through the cleavage of a bond on the backbone to form a cyclic oligomer (McNeill and Leiper, 1985). Therefore, the thermal stability of the P(3HB-co-3HV)/PLA composites can be improved by increasing the amount of PLA however, the decomposition temperature for all the composites are between the PLA and P(3HB-co-3HV) copolymer.

Some report says that the degradation of each polymer occurred separately in PHAs/PLA composites. For the P(3HB-co-3HV)/PLA composites, two weight loss peaks were observed, one at 290°C and the other at 375°C represent individual degradation of P(3HB-co-3HV) and PLA. The melting temperature do not correlate with the miscibility of the PHAs/PLA composites. The melting temperature (T_m) of P(3HB-co-3HV) copolymer is 152°C and for PLA, it is 170°C and the T_m for the composites was found to be in between these two polymers. Miscibility of any polymer can be determined by evaluating the glass transition temperature (T_g). A single T_g indicates the miscibility of the polymer. One single T_g for both PLA and P(3HB-co-3HV) copolymer was poorly observed. However, increasing P(3HB-co-3HV) copolymer in PLA reduce the T_g from 60 to 45°C (Nanda *et al.*, 2011). The T_g for P(3HB-co-4HB) copolymer is higher than that of PLA; P(3HB-co-4HB) composite with PLA reduce the T_g , with an unchanging T_g for the PLA.

The degree of crystallinity of any polymer composites depends on the orientation, the flexibility of the polymer chain and nucleation. Crystallization temperature (T_c) of PLA from decrease from 119 to 83°C with an increase of P(3HB-co-3HV) copolymer content due to the presence of PLA prevent the crystal growth of P(3HB-co-3HV) copolymer in the composites (Nanda *et al.*, 2011). The P(3HB-co-4HB) copolymer component in the composites shows lower T_g values as compared to the neat P(3HB-co-4HB) copolymer; with increasing P(3HB-co-4HB) content in P(3HB-co-4HB)/PLA composite decreases the T_g . This is due to the immiscibility, resulting in the existence of a phase interface between PLA and P(3HB-co-4HB) copolymer (Shibata *et al.*, 2006).

The chain end's enriched surroundings therefore enhanced the chain's mobility near the interface. P(3HB-co-4HB) enhance chain mobility near the interface and thus enhance the cold crystallization of PLA by enhancing the nucleation of PLA; results a decrease in cold crystallization temperature.

Application of PHAs PLA Composites

The composites of PHAs and PLA can advance and extend the applicability of PHAs as well as PLA. Depending on the specific properties required, the composites can be tailor-made to incorporate some extra features or to improve the material properties currently present in particular PHAs and PLA, make a wide application.

The pure PHAs and PLA have some common limitations, such as brittleness, difficult heat-sealing ability, high oxygen and vapor permeability, poor mechanical strength, thermal instability etc. and hamper their applicability. These drawbacks can be overcome by making composites such as PHAs/PLA composites. It is very feasible and versatile in food packaging applications. P(3HB)/PLA: 75/25 wt% composite using polyester plasticizer to create a new type of eco-friendly material suitable for single-use applications, such as fast food packaging (Abdelwahab *et al.*, 2012). Besides food packaging, the PHAs/PLA composites can be used in general purpose such as packaging household items that are a part of daily consumerism. It is a promising material for making kitchen films, cups, coats and sanitary napkins (Reddy *et al.*, 2013).

PHAs/PLA composites are attracting attention for making various electrical and electronic products, such as display panels, sensors and solar cells. These composites can also be used for a large range of products, including, scientific, medical, military and security products (Reddy *et al.*, 2013).

The composites of PHAs/PLA are also applied to medical and biopharmaceutical applications. It plays a vital role in creation of tissue engineering scaffolds and as a material for drug delivery.

However, the properties developed through making composites of PHAs/PLA are more favourable for environmental or food preservation or household applications but limited success in biomedical scenarios. Intensive research is required to improve compatibilizing mechanisms, surface modification and advanced processing techniques to produce novel materials suitable for specific applications mainly in biomedical issue.

Summary

Bioplastics are nowadays attracting a lot of attention due to the growing importance to sustainable development. Polyhydroxyalkanoates (PHAs) and polylactic acid (PLA) are the biodegradable bioplastics that have the potential to substitute the conventional plastics. PHAs are known as a complete bio-plastics; produced by bioprocess using microorganism from renewable

resource. Polyhydroxybutyrate (PHB) has the similar material properties of polypropylene (PP) but PHB is hard to process due to its high melting temperature – limits its application. PLA is produced through a mixed process; lactic acid by fermentation using renewable resource and then to PLA through polymerization reaction. PLA has good mechanical properties particularly, high tensile strength, young's modulus and good flexural strength, which are even higher than those of polystyrene (PS), PP, polyethylene (PE) and/or other conventional polymers. But PLA is very brittle that hamper its wide applications.

Although, both PHAs and PLA are biodegradable and produced from renewable resource, their potential applications are hampered due to the limitations of several properties. These drawbacks could be overcome by producing PHAs/PLA composites. The composites have the improved properties such as miscibility, crystallization, morphology, mechanical properties and degradation behavior. The composites of bio-based polymers not only can replace existing polymers in various sectors but also can provide new combinations of properties and extended its applications. The composition and types of PHAs within the composite have a significant effect on the toughness, miscibility, crystallization, mechanical properties and hydrolytic degradation. Melt compounding, among the different methods for the production of PHAs/PLA composites, is the most suited one due to its high production capacity, environmentally friendly process and better properties of the produced composites. The use of PHAs/PLA composites in various sector such as environmental, food preservation, electronics, packaging, commercial purpose, household applications etc are increasing day by day but still it has very limited success in desired medical application. Intensive research is required to improve the properties of PHAs/PLA composites for the specific application in biomedical issue.

See also: Bioresorbable Polymers for Surgical Suture Applications. Microbial Production of Polyhydroxyalkanoates From Plant Oils: Renewability and Biodegradability. Polyhydroxyalkanoates (PHA) Production. Polysaccharide-Based Flocculants for Industrial Effluents. Properties and End-of-Life of Polymers From Renewable Resources

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Polyhydroxyalkanoates (PHA) Production

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Glossary

ACP	Acyl carrier protein	PET	Polyethylene terephthalate
CoA	Coenzyme A	PHA	Polyhydroxyalkanoates
DCW	Dry cell weight	PHB	Polyhydroxybutyrate
DSC	Differential scanning calorimetry	PHBV	Polyhydroxybutyrate copolymer valerate
EPS	Extracellular polysaccharide	PHD	Polyhydroxy hexadecanoic acid
LDPE	Light density polyethylene	RAF	Rigid amorphous fraction
MCL	Medium chain length	SCL	Short chain length
		T_g	Glass transition temperature

Introduction

In the present era of modern industrialization, numerous sophisticated materials and products with high-end applications are manufactured in large scale employing plastics as raw materials. A view from the lens of sustainability supports the paradigm that bioplastics can be an alternative to the conventional petrochemical-based polymers. The total global bioplastic production capacities are forecasted to stand at 6.1 million tons in 2021, approximately 1.45 times higher than the production capacity in 2016. The biobased durable plastic productions are expected to increase by over 80% in 2019, compared to 60% in 2014 (Fig. 1). Though future prospects highlight the scope for increased bioplastics productions, currently their productions are limited to a mere 1% of the total production volume (300 million tons). Due to increase in demand, the supply of bioplastics is recording a growth of 20%–100% per year with bio-based/non-biodegradable plastics such as biobased Polyethylene and biobased Polyethylene Terephthalate (PET) being the main drivers for this growth.

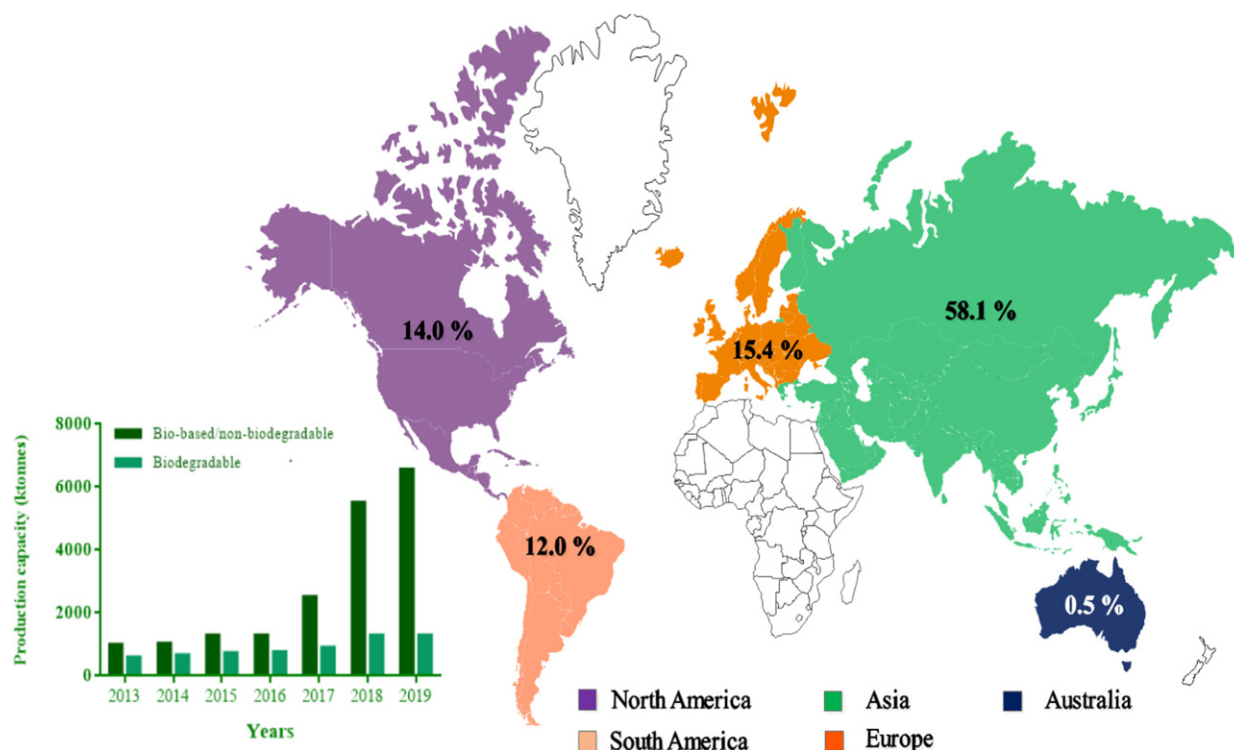


Fig. 1 Global production capacities 2013–2019 and production capacities of bioplastics by region. Reproduced from Sumathi, S., Chai, S.P., Mohamed, A.R., 2008. Utilization of oil palm as a source of renewable energy in Malaysia. *Renew. Sustain. Energy Rev.* 12, 2404–2421. doi:10.1016/j.rser.2007.06.006.

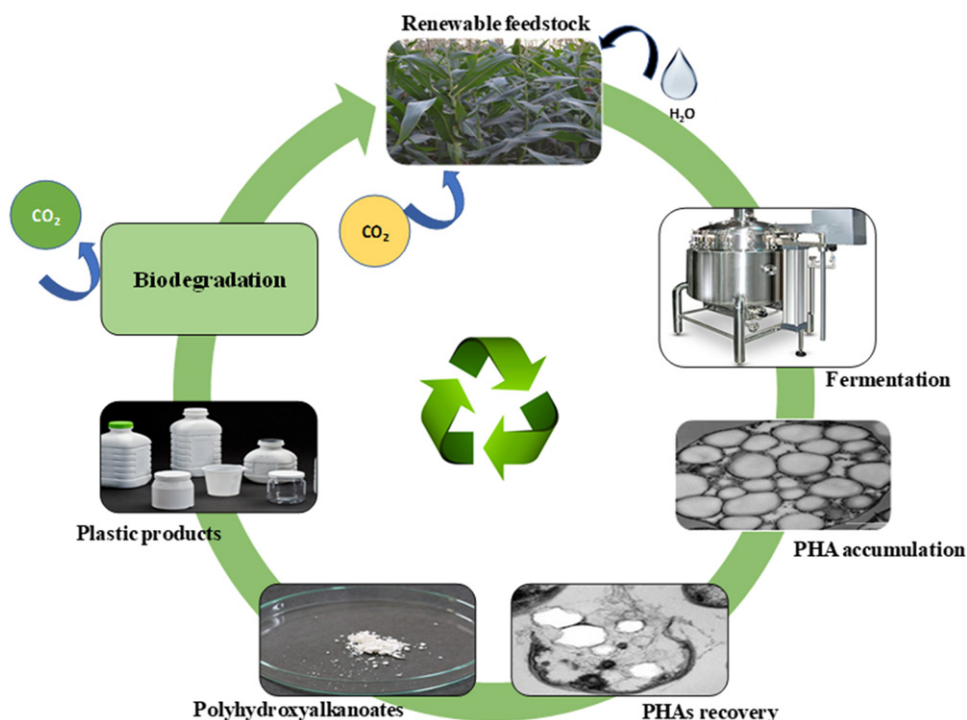


Fig. 2 Biodegradation cycle of PHAs. Reproduced from Altaee, N., El-Hiti, G.A., Fahdil, A., Sudesh, K., Yousif, E., 2016. Biodegradation of different formulations of polyhydroxybutyrate films in soil. Springerplus 5 (1), 762. doi:10.1186/s40064-016-2480-2.

This trend is supportive in developing regions, where Asia accounts for 58.1% of the total global production of bioplastics. Polyhydroxyalkanoates (PHA), the most researched biopolymers in the present century, are expected to have a production rate of over 1.2 million metric tons by 2019, due to the ramping up of old and new capacities in Asia and the USA.

During the forecast period, the highest growth rate of the projected areas for packaging, chemicals, and biomedical are estimated to encompass the wide application of the PHA copolymer type. This, besides offering similar benefits as other PHA types, manifests cost-effectiveness and thus makes it facultative to lead the global PHA market mainly segmented into Africa, European Union, North America, South America, Middle East, and Asia-Pacific region. The demand for PHA in the key regions of the Asia-Pacific market is projected to grow to the highest by the end of 2021 in light of expected escalated growth in the pharmaceutical, agro-industries, and packaging sectors. Finding innovative ways and processes to produce bio-plastics are the present focus of the research and development segment of companies. The high cost of production relative to the conventional plastics have been the major bottleneck in its growth despite fluctuating oil prices leading to the hunt for stable raw material for plastic production, tax subsidies, taxes on conventional plastics, and government policies for the cleaner environment being major reasons for driving their market.

There has been a search of nucleating agents and plasticizers that are capable of improving the flexibility of the polymer and improve its crystallinity. This confines the focus in compounding PHB as there is inconsistency in its mechanical properties leading to fragility, attributed to its extensively reported recrystallization at room temperature.

PHAs are a class of natural esters secreted by microorganism as intracellular granules under nitrogen limiting condition along with excess carbon source. Around 30% of natural soil microbial flora can produce this polymer with some producing upto 90% of its dry weight. This class of natural esters exhibits high variability by encompassing more than 150 monomer types and weighing up to 100,000 Da (Dalton). The polymer remains amorphous inside the cells due to its stability contributed by phospholipids while it turns crystalline after extraction. Its composition was enunciated by Lemoigne in 1925, though Beijerinck reported its occurrence back in 1888 (De Koning, 1993; Pal *et al.*, 1999). It took several years to recognize PHA as a natural polymer because of refusals from some organic chemists regarding its existence hovered through the scientific community. After successfully establishing its identity as a natural polymer, it took a multidimensional evolution in different fields for various applications such as medical implants, cosmetics, and more importantly as bioplastics used for various packaging applications (Pal *et al.*, 1999).

Production and utilization of synthetic plastics come with a cost for both environment and health hazards. The depleting fossil reserves pose serious constrictions on the large-scale production and consumption of plastics. PHAs can address this problem and also meet consumer demands if produced in large amounts as they are hydrophobic, thermoplastic, biodegradable, and impermeable to gases and water. It exhibits high crystallinity and high melting point when compared to LDPE. These physical properties make it a substitute for conventional plastics. Moreover, PHA producing micro-organisms help in carbon sequestration, by utilizing renewable feedstock, which in turn utilize the atmospheric carbon-di-oxide, following a carbon cycle (Fig. 2).

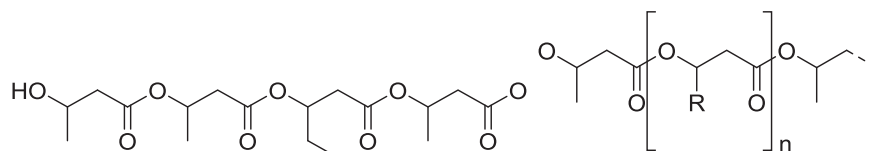


Fig. 3 Repeating units of the monomer of Polyhydroxyalkanoates. Reproduced from Koller, M., Vadjla, D., Braunnegg, G., Atlic, A., 2017. Formal- and high-structured kinetic process modeling and footprint area analysis of binary imaged cells: Tools to understand and optimize multistage-continuous PHA biosynthesis. *The EuroBiotech. J.* 1 (3), 203–211. doi:10.24190/ISSN2564-615X/2017/03.01.

At the global level, 24 companies produce PHA and the number is expected to increase further. Studies suggest that the demand for bioplastics can shoot up to 20% by 2020. Increasing the PHA production coupled with affordable prices can boost its potential as an alternative to synthetic plastics. This can be done by utilizing cheap carbon sources that can reduce the price of PHA produced at the process end. Some cheap carbon feedstocks that can be utilized for PHA production are lignocellulosic biomass, oils, and glycerol. These low-cost substrates are metabolized in the microorganisms involving various pathways to yield PHA as the end product of the metabolism. Oils follow fatty acid metabolism and beta-oxidation whereas lignocellulosic biomass and glycerol follow different pathways ultimately synthesizing Acetyl-CoA for PHA production.

A wide variety of methodologies are available at different stages of the production process starting from pretreatment of feedstocks to the recovery of PHA from biomass. Pretreatment of biomass is an essential role to obtain the required simple utilizable units for microorganisms to synthesize PHA. For example, enzymatic hydrolysis of starch is required to produce two molecules of a monosaccharide, which is taken up by the microorganism for producing PHAs. Fermentation conditions depend upon the strains being employed in the process along with the physical and chemical properties of the medium. For example, *Cuprividus necator* is the most commonly used microorganism which can grow in both aerobic and anaerobic conditions. After fermentation, the recovery of PHAs from the cells requires special unit operations. Cell disruption, solvent extraction, digestion using a surfactant, and enzymatic digestion are some of the commonly used methods to recover PHAs from cell biomass.

Structure of PHAs

The basic structural backbone of PHAs contains repeating units of aliphatic polyesters (As shown in Fig. 3) ranging from 600 to 35,000 (Albuquerque and Malafaia, 2018).

PHA with $n=1$ represents a class of poly(3-hydroxyalkonates) while $n=2$ represents poly(4-hydroxyalkonates). The type of derivate attached to the side chain (R) of the unit determines the functionality of the monomer. Depending on the number of carbon atoms in a monomeric unit of the chain, PHAs are classified into three types: Short chain-length monomers (3–5 carbon atoms), Medium chain length monomers (6–15 carbon atoms) and Long chain-length monomers (more than 15). The type of PHA produced depends upon the biochemical pathways inherently (or genetically modified) present in the microorganism.

Thermal and Mechanical Properties of PHAs

Despite exhibiting numerous properties like high melting temperature (175°C) and relatively high tensile strength (30–35 MPa) as to petroleum-based polymers (e.g., polypropylene), the curbed usage of isostatic PHB pertains mainly to the narrow processing window of this plastic and its internal brittleness (El-Hadi *et al.*, 2002). The proximity of the glass transition temperature (T_g) of PHB to the room temperature inciting secondary crystallization of the amorphous phase at room temperature has been exhibited by several authors (Steinbüchel, 1991; de Koning and Lemstra, 1993); its low nucleation density, justifying the inter-spherulitic cracks in large spherulites, has been a major antecedents for the brittleness exhibited by PHB and PHB/V.

The rigid amorphous chains coupled with the crystals are expected to be affected by the slow crystallization kinetics of the PHB which is attributed to its homogeneity emanated from the natural origin of the polymer is by tuning the crystallinity level. The homogeneity of PHB rules out the presence of impurities or catalyst residues that can act as heterogeneous nuclei (Di Lorenzo *et al.*, 2001). The heterogeneous nuclei promote crystallization onset by increasing the number of small spherulites, thereby disrupting its crystallization kinetics.

The influence by the physical state of the amorphous layer in contact with the growing crystals on the mechanism of crystallization of PHB was established in a recent study that expounds the crystal growth being hampered by the Rigid Amorphous Fraction (RAF) establishment during the heating of initially amorphous PHB coordinating with crystal formation at the first stage of cold crystallization (Androsch, 2008). This could only proceed on the achievement of complete mobilization of the RAF upon further temperature increase that can also be enhanced by the addition of plasticizers and thus, lowering the glass transition.

Upon quasi-isothermal cold crystallization of PHB at 22.8°C, the quantification of the kinetic vitrification of the rigid amorphous fraction RAF of the amorphous phase that exhibits reduced molecular mobility when connected with the crystalline phase covalently which are reported to be around 20%–30% of the overall sample mass, connoted the establishment of whole RAF of PHB during crystallization (Schick *et al.*, 2002).

In addition to morphology, the lowering of glass transition temperature (T_g) to the testing temperature mitigates higher flexibility and high elongation at break for the formulated/modified PHB. Faster cooling after melting is observed to affect the

nucleation rate and spherulite size, thereby adding to nucleation density and increasing the crystallization rate in the blends. This alleviates crystallinity due to the formation of fine spherulites that is cardinal in achieving central mechanical properties.

As evident from the random chain scission reaction of crotonic acid and various oligomers involving a cis-elimination reaction of β -CH and a six-member ring transition, a severe degradation of the PHB along with the degraded products of olefinic and carboxylic acid and reduction on the melt velocity observed on a short exposure of PHB to temperatures near 180°C, just above its melting point, poses a serious problem in processing of PHB due to a rapid molecular weight decrease with the most common mechanisms (Grassie *et al.*, 1984). The addition of lubricant during the processing at 170–180°C prevents the thermal degradation of the chains and delays crystallization by decreasing the crystallization temperature.

At higher temperatures, random cleavage of PHB chains occurs, decreasing the resultant molecular weight. This can be observed in the Differential Scanning Calorimetry (DSC) data where a bimodal distribution of crystallite size is seen as a double peak (Erceg *et al.*, 2005).

The non-conventional irregularly shaped DSC exotherms under given crystallization conditions characterized by spikes are related to the non-monotonous development of latent heat with a sudden increase and decrease in the crystallization.

Synthesizing copolyesters containing other hydroxyalkanoates groups is one of the main approaches being investigated extensively (Zhang *et al.*, 1997; Ahmed *et al.*, 2010). This process involves a mixture of groups in different molar ratios and is very effective in improving the mechanical properties as it lowers the melting point of the polymer thereby reducing its degradation (Qiu *et al.*, 2005). A decreased processing temperature can be achieved by blending plasticizers with polymers and modifying its physical properties. Thus, PHB is commonly blended with plasticizers and nucleation agents that lead to a lower glass temperature and lower crystallinity as it forms numerous, small and imperfect crystallites.

Synthesis of PHAs

Chemical Synthesis of PHAs

Chemical synthesis of PHA was proposed in 1998 where propiolactones are substituted using aluminum or zinc alkyl catalysts and water being the cocatalyst (Bastioli, 1998). Biodegradable PHBV has been successfully produced from butyrolactone and valerolactone with an oligomeric aluminoxane catalyst and achieved an almost identical resemblance to the biopolymers (Hocking and Marchessault, 1998). The stereochemistry plays an important role in the biodegradability of the polymer and also decides its structural integrity. However, the biologically produced polymers have the same stereochemistry and thereby replacing the highly priced lactone monomer.

Biological Synthesis of PHAs

Lignocellulosic biomass consists of cellulose, hemicelluloses, and lignin. Each of these components follows different biochemical pathways for PHA production. Fig. 4 shows an overview of the biochemical pathways in the production of PHA from different sources. The action of laccase and other enzymes degrade lignin to cinnamate, coumarate, ferulate, and methyl-(phenyl). Except for methyl phenyl, other components are converted to 3-oxodipate following a series of enzyme-mediated conversions. 3-oxodipate is converted into 3-Keto-adipyl CoA, and finally into Acetyl CoA. The biochemical pathway indicates the role of acetyl-CoA for the production of PHB. Degraded lignin products are metabolized by the microorganism to increase the acetyl-CoA concentration, which is further used for the production of PHB. Degradation of hemicelluloses yields xylose, arabinose, mannose, and glucose. Xylose and arabinose produce xylulose-5 Phosphate which is finally converted into fructose-6 Phosphate that enters into glycolysis pathway to generate acetyl-CoA for production of PHB. Mannose is converted to Mannose-6 Phosphate by the enzyme hexokinase. Mannose-6 Phosphate is converted to Fructose-6 Phosphate which further enters into glycolysis pathway. Glycerol kinase and glycerol dehydrogenase convert glycerol into glycerol-3 Phosphate and dihydroxyacetone, which are in turn converted into dihydroxyacetone phosphate that is used for the synthesis of pyruvate. The conversion of fatty acids present in oils to PHA takes place via different biochemical routes. R-3 hydroxylacyl CoA synthesized from beta-oxidation pathway results in the production of P3HA. Production of P(3HB-CO-3HA) SCL-MCL-PHA is achieved through conversion from primary precursor malonyl ACP through a series of steps (As depicted in Fig. 4). When, containing a high amount of lactose is converted into phosphoenol pyruvate to produce PHB via glycolysis pathway. Molasses is a rich source of sucrose that can be converted to glucose and fructose which enters the glycolysis pathway to produce PHB.

Microorganisms

Diverse groups of micro-organism are found to accumulate PHAs under nitrogen depleting conditions (Fig. 5). Both gram positive and gram negative bacteria's were found to accumulate PHAs well. Some common examples include *Rhodobacter sp* (Kim *et al.*, 2011; Gabrielyan *et al.*, 2015; Ali Hassan *et al.*, 1997), *Cupriavidus necator* (Arikawa *et al.*, 2017; Martino *et al.*, 2014; Gahlawat and Soni, 2017), *Bacillus sp* (Chandani Devi *et al.*, 2018; Reddy *et al.*, 2009; Venkateswar Reddy *et al.*, 2014; Singh *et al.*, 2009; Sreekanth *et al.*, 2013; Kynadi and Suchithra, 2017) and *Pseudomonas sp* (Qiu *et al.*, 2005; Liu *et al.*, 2011; Costa *et al.*, 2009; Gumel *et al.*, 2012;

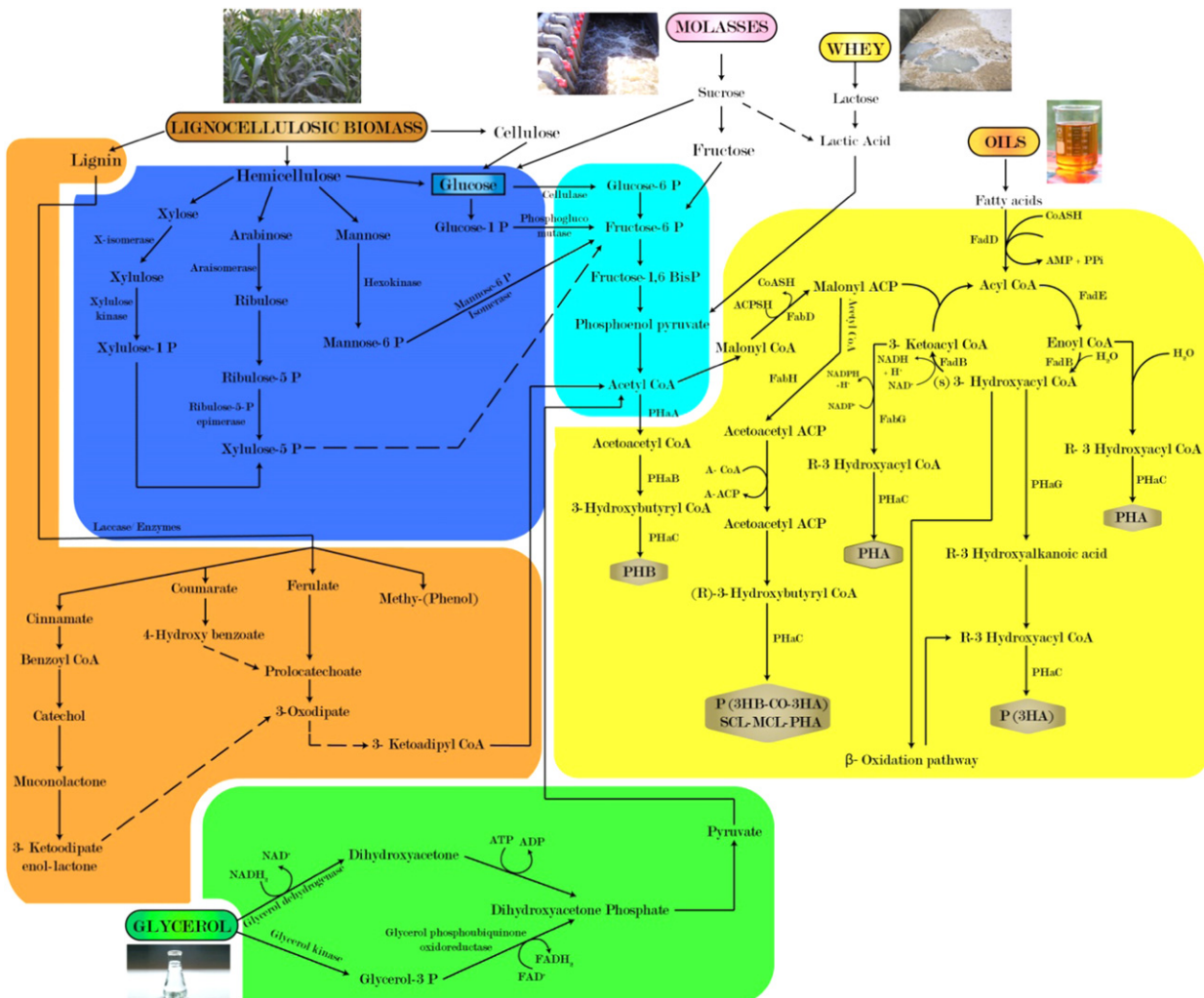


Fig. 4 Overview of the biosynthetic pathway involved in the production of PHAs from various biomass sources. Reproduced from Srirangan, K., Liu, X., Tran, T.T., Charles, T.C., Moo-Young, M., 2016. Engineering of *Escherichia coli* for direct and modulated biosynthesis of poly (3-hydroxybutyrate-co-3-hydroxyvalerate) copolymer using unrelated carbon sources. *Nat. Publ. Gr.*, 1–11. doi:10.1038/srep36470. Mozejko-Ciesielska, J., Kiewisz, R., 2016. Bacterial polyhydroxyalkanoates: Still fabulous *Microbiol. Res.* 192, 271–282. doi:10.1016/j.micres.2016.07.010. Pisco, A.R., Bengtsson, S., Werker, A., et al., 2009. Community structure evolution and enrichment of glycogen-accumulating organisms producing Polyhydroxyalkanoates from fermented molasses. *Appl. Environ. Microbiol.* 75 (14), 4676–4686. doi:10.1128/AEM.02486-08.

Poblete-castro *et al.*, 2014; Soberón-Chávez *et al.*, 2005). With the advent of genetic engineering, a powerful tool to alter the base sequence to impart or enhance a particular characteristic, microorganisms have been mutated to enhance their production capacity. *Pseudomonas sp* is one of the most researched organisms to enhance the production of PHA by using genetic engineering.

Biomass Feedstocks for PHA Production

Industrial Waste

Carbon feedstocks are the basic raw materials utilized by microorganisms as a source to carry out their regular metabolisms. Experimenting with different carbon feedstocks has been a great topic of interest among researchers. Apart from conventional high glucose/cellulose-containing agricultural feedstocks, several industrial wastes are being alternatively explored as well as used at industrial scale for PHA production. Waste effluents from fruit processing industries, paper, and pulp industries and sugar industries are rich in carbon sources that can be tapped by PHA producing microorganisms for efficient conversion to PHA (Pakalapati *et al.*, 2018). Whey produced from the cheese industry was used as a carbon source for the growth of PHA producing microorganism (Oliveira *et al.*, 2017). Several other interesting non-agricultural feedstocks used in PHA production are Biodiesel waste (glycerol) (Ray *et al.*, 2016), municipal solid waste (Korkakaki *et al.*, 2016), food waste (Wen *et al.*, 2018), slaughtering wastes (Shahzad *et al.*, 2017) and waste animal fats (Riedel *et al.*, 2015).

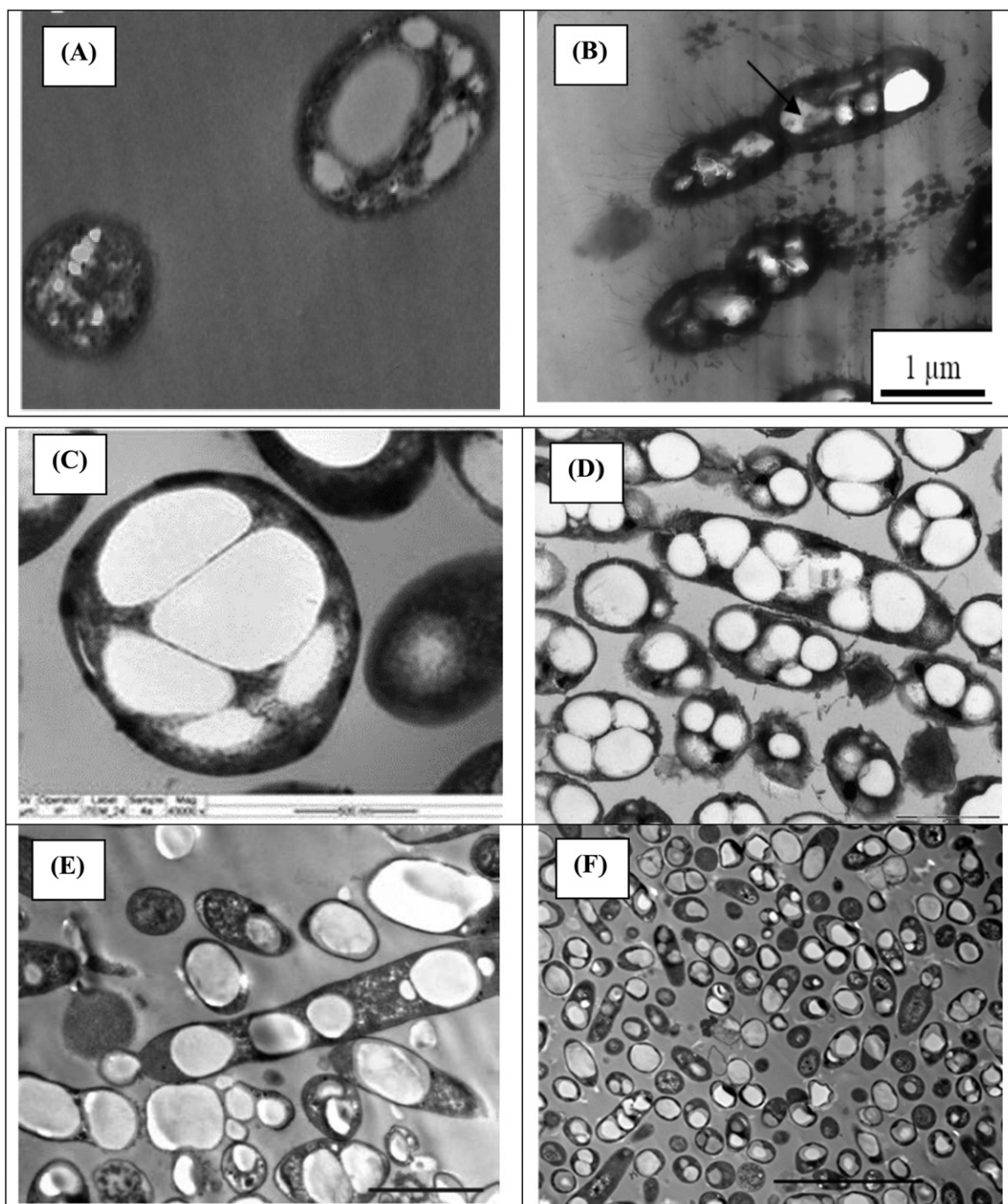


Fig. 5 (A) TEM image of *Pseudomonas putida* Bet001 cells. Reproduced from Kim, M.S., Kim, D.H., Son, H.N., Ten, L.N., Lee, J.K., 2011. Enhancing photo-fermentative hydrogen production by *Rhodobacter sphaeroides* KD131 and its PHB synthase deleted-mutant from acetate and butyrate. *Int. J. Hydrogen Energy* 36, 13964–13971. doi:[10.1016/j.ijhydene.2011.03.099](https://doi.org/10.1016/j.ijhydene.2011.03.099). (B) *B. megaterium* MC1. Reproduced from Legat, A., Gruber, C., Zangger, K., Wanner, G., Stan-Lotter, H., 2010. Identification of polyhydroxyalkanoates in *Halococcus* and other haloarchaeal species. *Appl. Microbiol. Biotechnol.* 87 (3), 1119–1127. doi:[10.1007/s00253-010-2611-6](https://doi.org/10.1007/s00253-010-2611-6). (C) Transmission electron micrographs of *P. putida* KT2440. Reproduced from Borrero-de Acuña, J.M., Hidalgo-Dumont, C., Pacheco, N., Cabrera, A., Poblete-Castro, I., 2017. A novel programmable lysozyme-based lysis system in *Pseudomonas putida* for biopolymer production. *Sci. Rep.* 7, 4373. doi:[10.1038/s41598-017-04741-2](https://doi.org/10.1038/s41598-017-04741-2). (D) *Cupriavidus necator* H16. Reproduced from Mravec, F., Obruca, S., Krzyzanek, V., *et al.*, 2016. Accumulation of PHA granules in *Cupriavidus necator* as seen by confocal fluorescence microscopy. *FEMS Microbiol. Lett.* 363 (10), 1–18. (E) *E. coli* genetically modified organism accumulating PHB (scale – 10 μm). Reproduced from Wu, H., Fan, Z., Jiang, X., Chen, J., Chen, G.-Q., 2016. Enhanced production of polyhydroxybutyrate by multiple dividing *E. coli*. *Microb. Cell Fact.* 15, 128. doi:[10.1186/s12934-016-0531-6](https://doi.org/10.1186/s12934-016-0531-6). (F) Electron micrographic image of the genetically modified *E. coli* accumulating PHB. Reproduced from Chen, G., Jiang, X., Guo, Y., 2016. Synthetic biology of microbes synthesizing polyhydroxyalkanoates (PHA). *Synth. Syst. Biotechnol.* 1, 236–242. doi:[10.1016/j.synbio.2016.09.006](https://doi.org/10.1016/j.synbio.2016.09.006).

Food Wastes

Two fermented cheese whey's composed of lactic, acetic and butyric acids (FCW1) and acetic, propionic, butyric, lactic and valeric acids (FCW2) were subjected for production of PHA using a preselected mixed microbial culture (MMC) (Colombo *et al.*, 2016). Cassava has an excellent nutritional profile with a high amount of carbohydrates. It can be grown in areas where water stress is commonly making them a preferable option for food industries. Cassava starch wastewater was used for producing PHA from sequencing batch reactor (SBR) treatment system seeded with *Bacillus tequilensis* MSU 112, a PHA-producing bacterial strain (Chaleomrum *et al.*, 2014).

Pseudomonas pseudoflava produced PHA using synthetic wastewater as a carbon source. The carbon concentration was varied from 5 g L⁻¹ to 60 g L⁻¹ and 20 g L⁻¹ was identified as the optimum concentration for PHA production (57%). It produced P3HB when acetate was used as a sole carbon source and produced P(3HB-co-3HV) by addition of propionate as a cosubstrate. Furthermore, PHA synthase was extracted from *P. pseudoflava* and *P. pallero* which are vital for PHA synthesis (Venkateswar Reddy *et al.*, 2017).

MMC was used to produce PHA using hardwood spent sulfite liquor (HSSL) as a feedstock under aerobic dynamic feeding (ADF) conditions. It was found that acetic acid was utilized completely by the consortia leaving behind partially consumed xylose and lignosulphonates (Queirós *et al.*, 2014). Also, there are studies reporting the production of PHA from the organic fraction of municipal solid waste (OFMSW) leachate (Korkakaki *et al.*, 2016).

Biodiesel production units generate a large amount of glycerol as a waste by-product during the transesterification process. Some bacterial strains use glycerol as a carbon source for the synthesis of PHA.

A novel strain isolate named *Pandoraea sp.* MA03 was used for the production of PHA from glycerol. It was found that 10–50 g L⁻¹ of carbon source was found to be the most optimal concentration of carbon source required for maximal production of P3HB (de Paula *et al.*, 2017). *Bacillus sphaericus* NII 0838 exhibited the potential to produce PHB (31%) by utilizing the crude glycerol from biodiesel industry under nitrogen limiting conditions (Sindhu *et al.*, 2011).

Pseudomonas oleovorans was able to produce PHA by metabolizing alkanolic acids from hexanoate to decanoate. The maximum yield of 30% DCW with octanoate or nonanoate was obtained and the molecular weights of PHA produced by this bacterium range from 90,000 to 370,000 (Brandl *et al.*, 1988). Sugar mill waste generates a large amount of molasses and bagasse during sugar production process from cane juice. *Sphingo bacterium sp.* isolates served the dual purpose of decolorizing Direct Red 5B (DR5B) and synthesizing polyhydroxyhexadecanoic acid (PHD) in medium containing a significantly high amount of molasses as a carbon source (Tamboli *et al.*, 2010).

Previously, these industrial wastes were released into the environments, causing environmental pollution with irreversible damages to the surrounding niche. Industrial waste can be sustainably disposed of safely as well as utilized for production of high-value low volume products (Koller *et al.*, 2017).

Algae

Algal biomass can be subjected to degradation using microorganisms for producing simple carbon sources that act as a substrate for PHA production. Microalgae (Ghosh *et al.*, 2019) and *Gelidium amansii* red algae (Sawant *et al.*, 2018) are some of the algal biomass used in PHA productions. *Saccharophagus degradans*, a bacterium used to degrade the *Gelidium amansii* for the production of PHA by utilizing algae as its carbon source. The yield was reported in the range of 17%–27% of P(3HB). *Haloferax mediterranei* was used to produce PHA by utilizing micro-algae as a carbon source. The total production was found to be 2.2 ± 0.12 g/L (Ghosh *et al.*, 2019). Algal biomass has gained popularity in environmental aspects due to their photosynthetic ability. Moreover, unlike agricultural feedstocks, algae do not require farmlands for cultivation. These advantages make algae the most suitable candidate for the production of PHA aided by a microbial consortium.

Vegetable Oils

In the modern world, million tons of cooking oils are being disposed of directly into the wastewater stream. It is reported that around 1 million tons of cooking oils are being generated annually in Europe alone; suggesting that cooked oils can be available around the year without any hindrance in the supply chain. Low-cost factor coupled with high fatty acid contents and conversion ratio with stable supply make cooking oils as a best alternative carbon source for producing PHA, even at industrial scale.

Cooked oils are recognized as the low-cost carbon source with the potential to support the growth of the microorganism. It contains a high amount of unsaturated fatty acids rendering them unsafe for human consumption. This scenario is exactly opposite for microorganism, which metabolizes fatty acids through the beta-oxidation pathway and synthesizes valuable PHA without undergoing any significant inhibitory effects (Riedel *et al.*, 2015). A study reported the production of PHA from waste frying oil with a yield of 1.2 g L⁻¹ equivalent to the yield obtained when pure glucose was used as a carbon source (Verlinden *et al.*, 2011). This suggests that cooking oils can be a cost-effective carbon substrate in the long run. If further research is made to maximize the fatty acids uptake rate by genetically engineering the microorganism, a better yield can be expected. A study reported that a strain of *Pseudomonas sp.* has the potential to produce PHA from vegetable oils with a high propensity for linoleic acids as a carbon source (Tufail *et al.*, 2017). This opens the possibility of research to find or engineer suitable strains capable of selectively depleting the components present in the oils for efficient conversion to PHAs.

Many other oils such as *Calophyllum inophyllum* oils, canola oils, rubber seed oils, and palm oils are utilized for production of PHA. Around 604 mg g^{-1} (On dry weight basis) of PHA was produced using *Bacillus cereus* in the media containing low-cost rubber seed oil (RSO) as a carbon source. The result was obtained based on a full factorial design indicating an optimized RSO of 1.5% (v/v). The total yield was found to be 2.16 g L^{-1} under a growth period of 3 days (Kynadi and Suchithra, 2017). MCL-PHA was produced by *Wautersiae utropha* using fructose as carbon and ammonium sulfate as a nitrogen source. The process was carried out in three stages, starting from batch to fed-batch achieving up to a final cell density to 4.36 g L^{-1} and PHA to 0.36 g L^{-1} respectively. The yield was found to increase from 4.36 g L^{-1} to 18.27 g L^{-1} (with 90% PHA) with the addition of canola oil in the last stage. The presence of 3HV, 3HO, 3HDD, and 3HB were found analytically using ^1H and ^{13}C NMR (López-Cuellar et al., 2011). *Burkholderia* sp. was used to produce 70% and 60% P(3HB) using 0.5% (v/v) crude palm kernel oil and glycerol respectively (Chee et al., 2010). *Calophyllum inophyllum* oil was used for producing PHA using *Cupriavidus necator* by Arumugam and his co-workers and effective value for a carbon source, nitrogen and size of inoculum was studied (Arumugam et al., 2018). A maximum PHA yield of 10.6 g L^{-1} was produced under optimized conditions.

Agricultural Feedstocks and Waste

With the increasing demand for food and fodder due to the population surge, a large amount of agricultural residues are being generated from the agricultural processes. Some commonly generated agriculture wastes are husk, hull, peel, leaves, offals, stem and stalks. At the global level, six main crops such as wheat, rice, soybean, maize, sugarcane, and barely generate 3.7 pentagrams (in dry weight) of agricultural residues on yearly basis (Bentsen et al., 2014). It is estimated that 146,000 kilotons of dry matter can be produced annually in Europe alone (Monforti et al., 2015). Agricultural residues are rich in glucose, sucrose, fructose, cellulose, hemicellulose, starch, arabinose and mannose which can be successfully tapped by microorganism for PHA production. *Haloferax mediterranei*, a halophile, utilized starch, dextrose and whey to produce P(3-HB-co-3-HV), whose composition and the molecular weight was found to be changing depending on the substrates used in the production process. Among the reported yields in the literature, *Halomonas boliviensis* tops the leader board with the capacity to produce a high yield of PHA. Hemicellulosic hydrolysate of sugar maple containing xylose (71.9 g L^{-1}) was used as an inexpensive carbon source to synthesize PHAs using *Burkholderia cepacia*. Fed-batch fermentation resulted in a maximal yield of 8.72 g L^{-1} with 51.4% CDW (Pan et al., 2012). Grasslands covering 30 million square kilometers over the earth possess the potential to act as biomass for PHA production. A fed-batch fermentation of grass juice containing a high amount of mannitol was used as the sole carbon source for the production of PHA using *Burkholderia sacchari*. Under the same experimental setup, *Pseudomonas chlororaphis* synthesized MCL-PHA (Cerrone et al., 2015).

Co-Production of PHA With Other Products

Co-production of PHA with other valuable products have been sought after to create an economic balance under optimized conditions recently. Synthesis of PHB positively induced the accumulation of many other value-added products (Zhang et al., 2006; Liu et al., 2007). Many small molecules that exploit intra and extracellular products such as hydrogen, L-tryptophan, methanol, succinate, amino levulinic acid, and rhamnolipids can be produced. In the context of balancing the *in vivo* metabolism, molecules such as L-arginine, succinate, and L-glutamate are produced. In addition to these features, synthesis of microbial PHA facilitates proper recombinant protein folding (Grage et al., 2011).

Several attempts to coproduce PHA with large molecules mainly α - amylase, recombinant proteins like tissue Plasminogen activator, antibody fusion with PHA proved successful. Shamala and his co-workers produced PHA and α - amylase from unhydrolyzed corn starch supplemented with wheat bran and rice bran using *Bacillus* sp. The PHA produced was 5.9 g L^{-1} and enzyme activity showed to be $2\text{--}40 \text{ U mL min}^{-1}$. Furthermore, Sreekanth and his co-workers studied the carbon to nitrogen ratio of the substrate for producing the enzyme and polymer using the same species. Glucose and sucrose as a carbon source and Yeast extract and ammonium acetate as nitrogen source yielded maximum PHA and α - amylase (Sreekanth et al., 2013).

Several proteins like tissue plasminogen activator and antibodies are expressed with the Phasins and PHA synthases to reduce the purification cost protein loss during downstream processing (Grage et al., 2011; Geng et al., 2010; Barnard et al., 2005; Peters and Rehm, 2005). Extracellular polysaccharides help in the growth and sustainability of cells during adverse growth conditions and nutrient limitation. Lama et al., studied the effect of growth condition on endo and exopolymer biosynthesis in *Anabena cylindrica* in the synthetic medium (Lama et al., 1996). It was reported that 0.3 g L^{-1} of extracellular polysaccharide along with 0.01 g L^{-1} of PHB-co-PHV was produced. Similarly, Pal and his co-workers produced 1.5 g L^{-1} of exopolysaccharides and 2.7 g L^{-1} of PHB using synthetic media (Pal et al., 1999). The coproduction of PHB and EPS was studied in *Ralstonia eutropha* in different glucose and nitrogen concentration. Under optimized condition, 12 g L^{-1} of PHB and 0.1 g L^{-1} of EPS were obtained. Recently Devi et al. (2012) used *Sinorhizobium meliloti* for producing EPS and PHB using rice bran and obtained a yield of 3.6 and 11.8 g L^{-1} of EPS and PHB respectively. *Azotobacter chroococcum* was used for producing EPS and PHB from various carbon sources and was found to produce a comparable amount of PHB and EPS under nitrogen limitation condition (Quagliano and Miyazaki, 1999). Furthermore, *H. boliviensis* and other *Halomonas* species are able to co-produce PHA and osmolytes, i.e., ectoines and hydroxyectoine, in a single process (Quillaguamán et al., 2010).

Alginates find themselves useful in the food and pharmaceutical industries as a stabilizer and gelling agent. Guo and his co-workers produced Alginate oligosaccharides and medium chain length PHA using *Pseudomonas mendocina* in a 200 L fermentor in a medium supplemented with glucose. The yield of 0.57 and 0.316 g L⁻¹ of alginate and PHA was obtained (Guo *et al.*, 2011). Similarly, glycerol was used as carbon source for production of mcl-PHA and alginates using *Pseudomonas mediterranea* and obtained a yield of 6.93 and 0.52 g L⁻¹ of alginate and mcl-PHA respectively. Overexpression of alginate, genes were observed during PHA production.

Pseudomonas aeruginosa has found an important place in co-production of PHA and Rhamnolipids. Coupled production of rhamnolipid and PHA were carried out effectively using variety of microorganisms on substrates like waste glycerol, glucose, decanoate, palm oil, hexadecane, cassava wastewater and waste cooking oil in single stage batch reactors and obtained sizeable yield (Costa *et al.*, 2009; Soberón-Chávez *et al.*, 2005; Hori *et al.*, 2002; Marsudi *et al.*, 2008; Chayabutra and Ju, 2001). Furthermore, owing to its opportunistic pathogenicity there is a quest for the non-pathogenic strain that can utilize complex substrates to produce both the products. Recently, nonpathogenic strains *Burkholderia thailandensis* and *Thermus thermophilus* were used in waste cooking oil and sodium gluconate to yield 60.0% and 34.8% of PHA and 2.2 and 0.2 g L⁻¹ of Rhamnolipid respectively (Kourmentza *et al.*, 2018; Pantazaki *et al.*, 2011). Substrate channelization plays a major role in co-generation of PHA and rhamnolipid as to maintain a balance between fatty acid β – oxidation pathway and fatty acid *de novo* biosynthetic pathway. Rhamnolipid as an extracellular product can easily be extracted than PHA. The rhamnolipid is extracted using a phase separation method and the lower phase containing PHA is extracted using the solvent method as described by Kourmentza *et al.* (2018).

Mothes and his co-workers reported the feasibility of coproduction using glucose and glycerol as substrates. Under fed-batch conditions, the glycerol showed more yield than glucose indicating the complex metabolism involved in the utilization of glycerol by the organism (Mothes *et al.*, 2008). High saline concentration plays a vital role in co-synthesis. A salt concentration of 7.5% yielded a highest ectoine level at 7.3% and 68% of PHB on a weight basis. Further increase in salt concentration, however, lowered the PHA synthesis and increased the ectoine (Guzmán *et al.*, 2009). Chen and his co-workers found that the organism *Halomonas salina* was effective in utilizing monosodium glutamate as a substrate and with an enriched medium, could produce a higher yield of PHB (35.3 g L⁻¹) and ectoine (8.6 g L⁻¹) respectively. Aqueous extraction and recovery of PHB are also optimized to obtain a better yield. This organism is found to utilize all the complex substrates ranging from polyols to sugars, aromatic compounds, and organic acids, proving it to be a potent organism for co-production (Chen *et al.*, 2014a,b).

Co-production of PHA with carotenoids has been an interest in recent years. Among several carotenoids such as astaxanthin, zeaxanthin, β - carotene, adonixanthin, cataxanthin, astaxanthin and aadonixanthin plays a major role in the food and pharma industries. These are much costlier than the normal pigments and hence methods for cogeneration with other products prove to be a better option. Although few reports on dark and photo fermentation on simultaneous production with PHA and hydrogen are available co-productions of pigments are always a topic of interest recently (Eroğlu *et al.*, 2004; Kumar *et al.*, 2018; Ramachandran and Amirul, 2012). Eroglu and his co-workers produced PHA, Hydrogen and carotenoids from *Rhodobacter sphaeroides* cultivated on oil mill wastewater and were able to obtain a yield of 60 mg/L of PHB, 40 mg/L carotenoids and hydrogen. Later large scale cultivation in an 8L photobioreactor by varying carbon sources by Eroglu and his coworkers showed that a satisfactory yield of PHB and carotenoids could be obtained, indicating the feasibility of large-scale co-generation (Eroğlu *et al.*, 2008). Recent works of Kumar *et al.* used glycerol as a substrate to yield astaxanthin (7.14 mg mL⁻¹) and PHB (9.52 g L⁻¹) using a methylotroph *Paracoccus sp.* Using the same species in glucose as a carbon source yielded 0.8 mg L⁻¹ of Astaxanthin and 41% PHA. The downstream process in regard to this organism is found to be very easy as they are known to accumulate carotenoids in the vesicles (Kumar *et al.*, 2018). Combining PHA with hydrogen production is of interest lately. Many types of research have been carried out to optimize the conditions required for simultaneous production of hydrogen and PHA. Under dark and photofermentation, the potential of *Calophyllum inophyllum* oil cake in biohydrogen and polyhydroxyalkanoates production simultaneously using mixed/ cultures of *Enterobacter* and *Rhodobacter* was elucidated by Arumugam *et al.* (2014). High biodegradable organic contents and nutrient-rich compositions made *Calophyllum inophyllum* oil cake as an attractive feedstock for the fermentation process. Higher yield of hydrogen (7.95 L H₂/L) and PHA (10.73 g/L) was observed under alternate dark and photo fermentation compared to complete dark fermentation which could only yield 3.23 L H₂/L and 5.6 g PHA/L collectively. Apart from the normal strains, an attempt was made to use the genetically modified *E. coli* to produced hydrogen and PHA in excess by Wang *et al.* (2012). The photofermentative bacteria are also found to produce hydrogen along with the accumulation of PHA in the presence of excess acetate and butyrate (Kim *et al.*, 2011). These studies show that highly potent bioenergy source hydrogen can also be produced with PHA simultaneously.

Pilot Plant Studies

Production of PHB/PHA at a pilot scale using conventional carbon feedstocks is reported in many studies. *Synechocystis sp.* CCA1A192 was used for the production of PHB in a 200 L tubular photobioreactor semi-continuously for 75 days. In this study, two levels for the cultivation of *Synechocystis sp.* were performed. The first stage lasts for 5–7 days within which the nitrogen source is depleted, a condition that favors PHB production. The biomass production attained 1 g/l containing PHB around 12.5% of cell dry weight under non-sterile conditions (Troschl *et al.*, 2018). Wastewater from ice and milk processing industries were used for the production of PHA in a continuous mode. The process contains a series of reactors namely, the anaerobic acidogenic reactor

(AAR), activated sludge production reactor (ASPR) and PHA synthesis reactor (PHAR). Around 43% of the sludge (on a dry weight basis) contains PHA. The process reduces the volume of disposable sludge as well produce a considerable amount of PHA (Chakravarty *et al.*, 2010). A similar study, using sludge fermentation liquid (containing a high amount of volatile fatty acids) as a carbon source for PHB production was performed using bacterial consortia was done. The PHA content was found to be 59.47% of dry cell weight with a yield of 0.17 gPHA/gCOD (Jia *et al.*, 2014). Concentrate from wastewater treatment plant was used for the production of PHA up to 0.39 gPHA/gVSS (Morgan-Sagastume *et al.*, 2015) and nitrogen removed wastewater gave up to 49% of PHA (In volatile suspended solids) (Bengtsson *et al.*, 2017). Wastewater from candy bar factory was utilized at pilot scale for culturing consortia, mainly containing *Plasticumulans acidivorans*. It produced 0.70 ± 0.05 gPHA/gVSS compared to 0.90 gPHA/gVSS at lab scale (Tamis *et al.*, 2014). A two-stage pilot plant was designed for the production of PHA from olive oil mill wastewater using *Pseudomonas* was achieved with a yield of 25% (Ntaikou *et al.*, 2014). These studies show the real-time pilot scale experiments using wastewater as a potential carbon source for PHA production.

Downstream Processing

Despite the availability of numerous methods for isolation of PHA, such as microbial, enzymatic and plant-based sources, obtaining of maximum yield out of the process still remains a challenge. Several investigations on PHA purification and extraction were carried out recently aiming to optimize downstream process at the industrial scale keeping its composition, purity, and properties as priority parameters (Koller *et al.*, 2013; Fernández-Dacosta *et al.*, 2015; Hajnal *et al.*, 2016). PHA extraction and purification follow two main strategies: solvent extraction and using strong oxidants. In the former method, where a suitable solvent is used to dissolve the cell membrane and other proteins to release the polymer from the cell. Fig. 6 shows an overview of various strategies in downstream processing of PHA. Strong oxidants like acids or surfactants are used to dissolve biomass and separate PHA granules (Kosseva and Rusbandi, 2018).

PHA is recovered from the fermented biomass mainly by digestion (enzymatic or acid), mechanical disruption, compromising the cell membrane during its growth, supercritical fluid extraction and solvent extraction. Digestion dissolves other cell mass, disintegrates the cells containing PHA and conserves the polymer granules. Enzymes, acids and alkali, surfactants and strong oxidizing agents like sodium hypochlorite are widely used for solubilizing non-PHA cellular components (López-Abelairas *et al.*, 2015; Chen *et al.*, 1999). Kim and his co-workers extracted PHB from *Ralstonia eutropha* using sodium dodecyl sulfate surfactant without any pre-treatment steps. 97% of the polymer was extracted without much reduction in the molecular weight of the

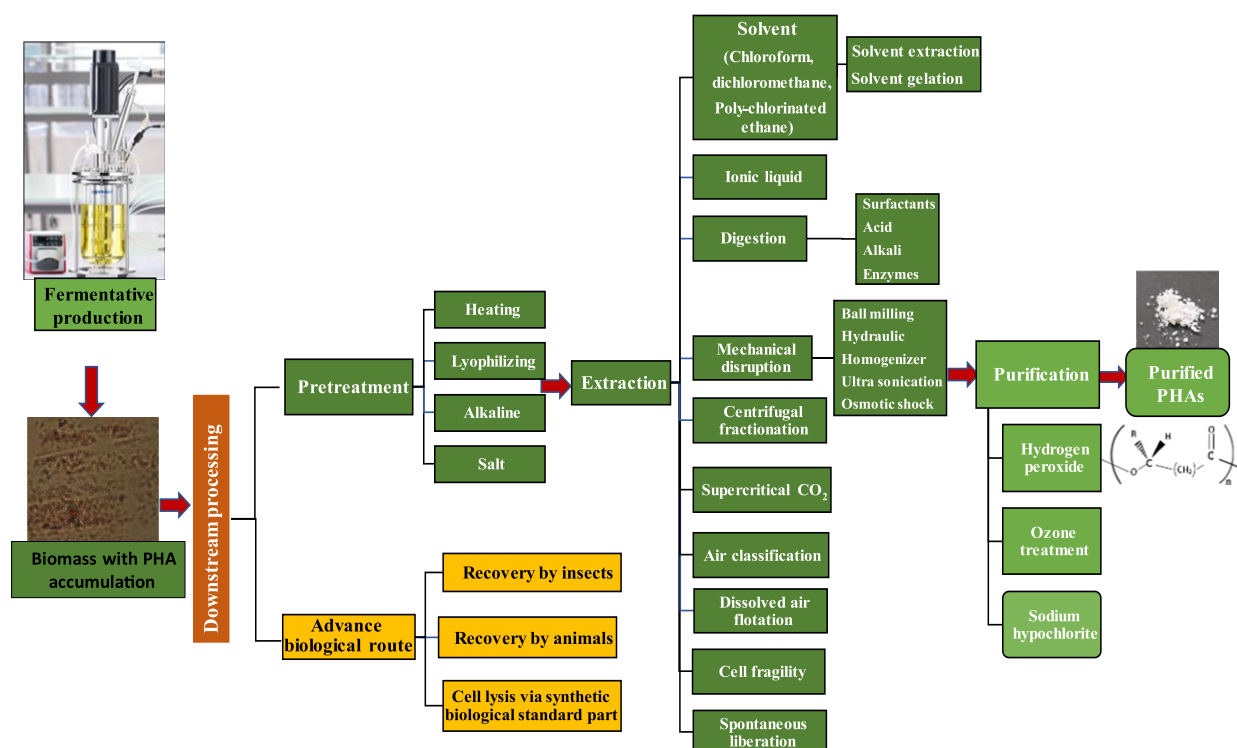


Fig. 6 Recovery and purification strategies for PHA from microbial biomass. Reproduced from Koller, M., Niebelschütz, H., Braunnegg, G., 2013. Strategies for recovery and purification of poly[(R)-3-hydroxyalkanoates] (PHA) biopolyesters from surrounding biomass. Eng. Life Sci. 13, 549–562. doi:10.1002/elsc.201300021. Kosseva, M.R., Rusbandi, E., 2018. Trends in the biomanufacture of polyhydroxyalkanoates with focus on downstream processing. Int. J. Biol. Macromol. 107, 762–778. doi:10.1016/j.ijbiomac.2017.09.054.

polymer. Lee *et al.* (1993) used a surfactant palmitoyl carnitine for extracting PHA from *Alkaligenes latus* and *Alkaligenes eutropus* and recorded an extraction rate of 85 and 70% respectively.

Posada *et al.* studied various recovery methods from the glycerol fermentation medium. Among the three methods viz., solvent extraction, combining chemical with surfactant and chemical with enzyme, enzyme alkaline digestion process showed more polymer yield and was also economic (Posada *et al.*, 2011). Lopez and his co-workers evaluated different combinations of treatments for the biomass using chlorinated solvents, alkaline and acid digestions for PHA extraction from *Cupriavidus necator* grown in a synthetic medium. Hypochlorite and dichloromethane treatment yielded higher product purity and a sizeable recovery but acid treatment was preferred considering the polymer degradation, economic and environmental aspects (López-Abelairas *et al.*, 2015). Yu (2008) reported PHA extraction by acid subsequently purifying it with hydrogen peroxide or chloroform with a 97% pure polymer. Studies claimed that the concentration of acid used has a greater impact on the mechanical strength of PHA. Use of Sodium hypochlorite has been attempted by several researchers aiming for a high purity polymer product (Berger *et al.*, 1989; Hahn *et al.*, 1994). Berger and his co-workers used hypochlorite solution to extract polymer from *R. eutropha* and recombinant *E. coli* and obtained purity of 86% and 93% respectively (Berger *et al.*, 1989). Yet another similar study by Hahn *et al.*, yielded 94% of 99% pure PHA from *Cupriavidus taiwanensis* (Hahn *et al.*, 1994).

Mechanical disruption of cell mass to obtain the polymer seems to be an easy and effective method in terms of scale-up, environmental and purity aspects (Tamer *et al.*, 1998). This method can be widely followed in larger scale industrial production having a very less environmental impact, with the only disadvantage having long processing time and sequential treatment (Jacquel *et al.*, 2008). Combining mechanical methods like high-pressure homogenization, ultrasonication with chemical treatments prove a greater recovery than the methods as such (Ghatnekar *et al.*, 2002; Van Wegen and Ling, 1998; Ling *et al.*, 1997).

High-pressure homogenization assisted with an anionic surfactant was used for isolation of polyhydroxybutyrate from the *Methylobacterium sp.* and 95% pure polymer was obtained with a yield of 98% (Ghatnekar *et al.*, 2002). Hwang and his co-workers claimed ultrasonication to be a better method for cellular disruption and PHA separation from the cellular biomass and could attain 80% of the pure polymer (Hwang *et al.*, 2006). Van Wegen and Ling (1998) studied PHA recovery on a large scale using the model suggested by Ling *et al.* (1997). Prior to NaOCl treatment, the biomass was homogenized followed by centrifugation that increased the yield up to 80% recovery. Bead milling was proved to be more effective in recovering PHA from the fermented biomass comparing the high-pressure hydraulic homogenizer (Tamer *et al.*, 1998).

Solvent extraction of PHA is one of the oldest methods used (Baptist, 1962). This method is being preferred widely to suppress the endotoxins and other cellular materials and to yield a polymer with intact structure (Jacquel *et al.*, 2008; Lee *et al.*, 1999). Baptist and his co-workers demonstrated the feasibility of several chlorinated solvents such as chloroform, dichloromethane and methylene chloride to estimate the yield of polymer from *Rhodospirillum rubrum* (Baptist, 1962). Trausnigg and his co-workers used diols, acetalized triols, tricarboxylic acid esters, and lactones to extract PHA from biomass where the highest yield (diethyl succinate- 100% purity) of the polymer was obtained in tricarboxylic acid esters. Kinoshita *et al.* claimed that addition of precipitating solvent to extractant separates PHA crystals with a fluidity more than 97% pure (Kosseva and Rusbandi, 2018). Lee *et al.* (1999) demonstrated effective endotoxin elimination from fermented *E. Coli* biomass while extracting PHA using chloroform indicating the possible use of solvents for gram-negative cellular biomass.

Although the solvents prove to be a convenient method for PHA extraction, it compromises the natural morphology of the polymer and poses a hazard for both the environment and the user at industrial scale. However, this method is suitable in the lab scale owing to the contained environment and scale down approach (Gorenflo *et al.*, 2001). This problem can be overcome by the use of nonchlorinated solvents like ketones, amides, esters, and alcohols at high temperature as claimed by Kurdikar and his co-workers (Kurdikar *et al.*, 2000). The solubility of PHA in different solvent plays a vital role in determining the proper use of solvents for extraction (Terada and Marchessault, 1999).

Owing to exceptional physicochemical properties of the supercritical solvents, they are much sought for the extraction process. Use of carbon dioxide as an extractant was proposed by Castor and his co-workers (Castor and Hong, 1995). Hejazi *et al.*, formulated optimized condition for extraction of PHB (Hejazi *et al.*, 2003). Taking it as a lead, many works that combine the pretreatment process with supercritical extraction process has been proposed (Darani and Mozafari, 2009).

PHA can also be extracted using the fragility of cells where the cells accumulate large fractions of the polymer (Lee *et al.*, 1994; Page and Cornish, 1993). The integrity of the cells are compromised when the PHA is overproduced and on treating the cell mass with either NH_3 (Page and Cornish, 1993), bacteriophage lysis (Fidler and Dennis, 1992) or NaOH (Choi and Lee, 1999), the polymer is recovered.

Economics of PHA Production

The cost of producing PHAs at the industrial scale is mainly based on the cost of fermentation, nature of carbon source, polymer yield from the selected carbon source and downstream processing (Lee and Na, 2013). The cost of the carbon substrate alone tends to contribute to 50% of the total cost (Kim *et al.*, 2000). Based on the use of the polymer in different fields, the cost of downstream processing is also taken into account. High purity products for medical purposes look into more purity than the cost of extraction. While disposable products require cost-effective processing rather than purity of the product (Koller *et al.*, 2013). The extensive study of sustainability of bio-based plastics in terms of environmental and social basis has always been a gap owing to the small number of published studies. Also due to the lack of standardized methods for estimation, there has been less data for estimating

Table 1 The comparison of polyhydroxyalkanoates production from various biomass sources reported in the literature

Authors	Carbon source	Reaction type	Microorganism	Yield
Industrial waste				
Wen <i>et al.</i> (2018)	Food waste fermentation leachate	Anaerobic digestion	<i>Paracoccus</i> sp.	33.40%
Venkateswar Reddy <i>et al.</i> (2017)	Synthetic waste	Sequencing batch reactor	<i>P. pseudoflava</i> and <i>P. palleronii</i>	20 g/L
Oliveira <i>et al.</i> (2017)	Cheese whey	anaerobic membrane bioreactor	Mixed microbial culture	6.09 g/L/day
Ray <i>et al.</i> (2016)	Glycerol waste	Optimization by central composite design	<i>Pannonibacter phragmitetus</i>	1.36 g/L
Korkakaki <i>et al.</i> (2016)	Organic fraction of municipal solid waste	Sequencing batch reactor	Mixed microbial culture	78 wt%
Colombo <i>et al.</i> (2016)	Fermented Cheese whey's	Sequencing batch reactor	Mixed microbial culture	70 g/Kg substrate
de Paula <i>et al.</i> (2017)	Crude glycerol	Shake flask	<i>Pandoraea</i> sp.	49%–63% cell dry weight
Riedel <i>et al.</i> (2015)	Low quality waste animal fats	An emulsification strategy, without any mechanical or chemical pre-treatment,	<i>Ralstonia eutropha</i> (recombinant strain)	0.4 g/L
Chaleomrum <i>et al.</i> (2014)	Cassava starch wastewater	Sequencing batch reactor	<i>Bacillus tequilensis</i>	79.2% per DCW
Queirós <i>et al.</i> (2014)	Hardwood spent sulfite liquor	Aerobic dynamic feeding	Mixed microbial culture	67.60%
Devi <i>et al.</i> (2012)	Rice bran hydrolysate	Shake flask fermentation	<i>Sinorhizobium meliloti</i> MTCC 100	3.6 g/L
Tamboli <i>et al.</i> (2010)	Textile dye Direct red 5B	Static fermentation	<i>Sphingo bacterium</i> sp.	64% DCW
Eroğlu <i>et al.</i> (2004)	Olive mill wastewater	Glass-column photobioreactors	<i>Rhodobacter sphaeroides</i>	60 mg/L
Vegetable oil				
Arumugam <i>et al.</i> (2018)	<i>Calophyllum inophyllum</i> oil	Batch fermentation	<i>Cupriavidus necator</i>	10.6 g/L
Kourmentza <i>et al.</i> (2018)	Used cooking oil	Batch fermentation	<i>Burkholderia thailandensis</i>	60% DCW
Kynadi and Suchithra (2017)	Rubber seed oil	Shake flask method	<i>Bacillus cereus</i>	2.5 g/L
Verlinden <i>et al.</i> (2011)	Waste rapeseed oil	Batch fermentation	<i>Cupriavidus necator</i>	1.2 g/L
López-Cuellar <i>et al.</i> (2011)	Canola oil	Fed batch cultivation	<i>Wautersia eutropha</i>	18.27 g/L
Chee <i>et al.</i> (2010)	Palm oil products	PHA accumulation condition	<i>Burkholderia</i> sp. USM (JCM15050)	60 wt%
Marsudi <i>et al.</i> (2008)	Palm oil	Batch cultivation	<i>Pseudomonas aeruginosa</i>	0.11 g /g oil
Algae				
Sawant <i>et al.</i> (2018)	Red seaweed <i>Gelidiummamsii</i>	Batch fermentation	<i>Saccharophagus degradans</i>	17%–27% DCW
Agricultural wastes				
Kumar <i>et al.</i> (2018)	Glycerol	Batch fermentation	<i>Paracoccus</i> sp.	39.3% w/w
Cerrone <i>et al.</i> (2015)	Mannitol rich ensiled grass press juice	Fed batch cultivation	<i>B. sacchari</i> IPT101	33% DCW
Arumugam <i>et al.</i> (2014)	<i>Calophyllum inophyllum</i> oil cake	Dark and photo fermentation	<i>Enterobacter aerogenes</i> and <i>Rhodobacter sphaeroides</i>	603% DCW
Chen <i>et al.</i> (2014b)	Glucose and monosodium glutamate	shake flask and batch fermentation	<i>Halomonas salina</i>	35.3 g/L
Sreekanth <i>et al.</i> (2013)	Hydrolysates of rice bran and wheat bran	Submerged fermentation	<i>Bacillus</i> sp. CFR 67	444 mg/L
Pan <i>et al.</i> (2012)	Detoxified sugar maple	Fermentation and detoxification	<i>Burkholderia cepacia</i> ATCC 17759	8.72 g/L
Ramachandran and Amirul (2012)	Glycerine pitch	–	<i>Cupriavidus</i> sp.	6.0 g/L
Pantazaki <i>et al.</i> (2011)	Sodium gluconate or glucose	–	<i>Thermus thermophilus</i>	308 mg/ L
Costa <i>et al.</i> (2009)	Cassava wastewater	–	<i>Pseudomonas aeruginosa</i>	39% DCW
Guzmán <i>et al.</i> (2009)	Glucose and monosodium glutamate	Fed batch cultivation	<i>Halomonas boliviensis</i>	68.5% DCW
Mothes <i>et al.</i> (2008)	Mineral medium	–	<i>Halomonas elongata</i>	50% wt/wt
Hori <i>et al.</i> (2002)	Glucose medium	Batch cultivation	<i>Pseudomonas aeruginosa</i>	23% CDW
Chayabutra and Ju (2001)	Hydrocarbons	Hexadecane Fermentation	<i>Pseudomonas aeruginosa</i>	7.5 g/L
Pal <i>et al.</i> (1999)	Glucose agar medium	N-free condition with excess carbon	<i>Azotobacter beijerinckii</i> WDN-01	2.73 g/L

the Life Cycle Assessment of the polymer. Spierling and his co-workers estimated that 35% of bio-based plastics have already taken over the conventional plastics in terms of Global Warming Potential (Spierling *et al.*, 2018). However, the claim was based only from the average industrial data and lacks all the highlights of both plastics.

Large-scale production of biobased plastics faces a major setback from inadequacy of large volume feedstock that is cheap and readily available. Levett and his co-workers studied PHA production from methane and evaluated the economic design for the production of 100,000 tons per annum of PHB from methanotrophic fermentation. Reduction in the cost of feedstock for production was observed from 30% to 50%. Cost of production was reduced in case of thermophilic conditions that could be a potential novel method for producing PHB. The cost of the polymer was in range from 4.1 to 6.8\$ kg⁻¹ of PHB (Levett *et al.*, 2016). Sagastume *et al.* studied the production of PHB using mixed microbial culture from the municipal waste water treatment plant based on mass and energy balances. The model was evaluated for four configurations among which the integration of PHB production with biogas yielded a stable polymer production (Morgan-Sagastume *et al.*, 2016). Leong and his co-workers concluded that aqueous two phase extraction method was best in terms of economical and environmental aspects consuming upto 5.77.

USD Kg⁻¹ of PHA (Leong *et al.*, 2017). Shahzad and his co-workers studied PHA production from waste streams of animal processing industry. It was estimated that 1.41–1.64 £ Kg⁻¹ of PHA was produced from high protein content offal. The transportation cost was about 61 tons of waste biomass and with the input cost of 13.88 million Euros per annum for PHA, the total revenue was 67.5 million Euros per annum (Shahzad *et al.*, 2017). Suwannasing *et al.* (2015) compared pineapple and sugarcane waste as raw material for producing PHA from *Bacillus* strain and claimed pineapple waste to be a better source for polymer production. Furthermore, the substrates did not contain any inhibitors and sugar content was found to be simple. However, they failed to perform a detailed cost analysis in the industrial scale (Suwannasing *et al.*, 2015). Fernandez and his co-workers performed techno-economic analysis on PHB production from waste water and compared three downstream process involving solvent, alkali and hypochlorite treatment. Alkaline treatment found to be most promising in terms of economic and environmental aspects (Fernández-Dacosta *et al.*, 2015). Table 1 summarizes the reports on polyhydroxyalkanoates produced from various carbon sources.

Conclusion

Increased food and fuel demand due to ever growing human population has led the world to look for an alternative to plastics. Conventional plastics derived from petroleum tend to cause pollution with the risk of survivability. Hence, an alternative that solves pollution hazards and mitigates the demand for polymer is of current interest. The production of PHA in sustainable manner is still a burgeoning field where plethora of ideas for parameter optimization and cost cutting strategies are available. Though the methods listed in the chapter are available for producing PHA through an ecofriendly manner, the production cost, raw material expenses and the nature of downstream processing plays a vital role in its side chain grafting and material strengthening. The utilization of the well-defined carbon rich substrates calls for its careful choosing such that the food versus fuel conflict should be resolved. In other words, the substrates should not contain any components that are edible and nutritious. Also, the substrate chosen should be perennially available. Several wastes from fruits, agro industries, offals (Intestinal part of dead meat) and kitchen are used extensively for combined production of PHA and other value added products. Adding to this, the sewage wastes are also extensively used for PHA production. Their ecofriendly nature and flexible modulation properties have put PHA research on a pedestal. Current trend mainly involves producing PHA from defined bacterial cultures and enriched medium that require a lot of process monitoring and control protocols. This results in higher cost of the polymer production alone excluding its polishing process. Technically, downstream processing and increasing the durability of the polymer for public usage makes it even more inaccessible financially. Entry of PHA into the market on a larger scale depends on materials and methods that are economically feasible, socially acceptable and environmentally viable. Through optimizing the bacterial accumulation of PHA, using mixed culture process with low cost substrate and reducing the polishing cost to highly functional polymer, the market demand of PHA can be increased over conventional polymers. The scientific fraternity and industrialists should move hand in hand towards promoting a sustainable way for production of bioplastics.

Conflict of Interest

The authors declare no conflicts of interest.

Acknowledgment

The authors gratefully acknowledge the financial support provided by SERB (Science and Engineering Research Board), INDIA (Grant no. ECR/2017/001038/ES) to carry out this work.

See also: Bioresorbable Polymers for Surgical Suture Applications. Microbial Production of Polyhydroxyalkanoates From Plant Oils: Renewability and Biodegradability. Polyhydroxyalkanoate and Polylactic Acid Composite. Polysaccharide-Based Flocculants for Industrial Effluents. Properties and End-of-Life of Polymers From Renewable Resources

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Properties and End-of-Life of Polymers From Renewable Resources

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Introduction

In this natural world, polymers have been found everywhere, since the beginning of time. It is one of the highly functional materials, which forms an inextricable part of human civilization. Generally polymers are light-weight but possess excellent mechanical properties, environmentally superior, renewable, inexpensive and can be easily processed by different methods. Nowadays, polymers are commonly used in thousands of products as foams, clothing, adhesives, fibers, molding, composites, films, plastics, biomaterials, etc. Current applications extend from pharmaceutical, medical, electronic, chemical, health and food industries. More recently, significant developments have occurred in the area of flexible electronic devices based on the useful piezoelectric, semiconducting, optical and electro-optical properties seen in some polymers.

Polymer, a chain like macromolecule, consists of a sequence of various types of monomer units. There can be infinitely many types of polymers depending on the combination and sequence of those monomer units along the chain. The classification of polymers is given in **Table 1** (Sabbatini, 2014; Raju and Kumar, 2016; Robert and Rawn, 2015).

Polymers From Renewable Resources (PFRR)

Polymers from renewable resources have received greater attention over the past two decades. Increasing environmental compatibility, providing additional income to those involved in agriculture and realization of global petroleum resources are finite, have given significant opportunities for improved materials from renewable resources with enhanced support for global sustainability. Biodegradability is an additional benefit of polymers that are degraded and catabolized, eventually to CO₂ and H₂O, by naturally occurring microorganisms such as bacteria, fungi or algae. In addition, when they are degraded, these polymers should not generate any substances that are harmful to the natural environment. At present, high performance plastics, one of the major environmental pollutants around the world, are the outcome of continuous research over the last few decades. The real challenge of renewable polymers lies in finding application, which will result in man production research and price reduction. This can be attained only by improving the end performance of environmental friendly polymers.

Table 1 Classification of polymers

S. No.	Classification	Types of polymers	Examples
1.	Based on origin of source	1. Natural 2. Synthetic 3. Semi Synthetic	Rubber, Wool, Cellulose, Starch and Proteins Nylon, Terylene, PVC, Bakelite, Teflon Cellulose acetate, cellulose nitrate
2.	Based on Structure	1. Linear 2. Branched 3. Cross-linked 4. Network	HDPE, Nylons LDPE, LLDPE Bakelite, Melamine, Formaldehyde resins Epoxies, polyurethanes and phenol-formaldehyde
3.	Based on Molecular Forces	1. Elastomers 2. Fibers 3. Thermoplasts 4. Thermosets	Natural Rubber, buna-S, buna-N, neoprene Cellulosic, animal and synthetic fibers Commodity Plastics (LDPE, HDPE, PVC, PP) Engineering Plastics (Poly acetol, poly carbonate) Epoxy, Urea Formaldehyde, ABS,
4.	Based on method of synthesis	1. Addition or chain growth 2. Condensation or step growth	Polyethylene, Polypropylene, PVC, Teflon Polyamides, Polyesters
5.	Based on backbone of polymers	1. Organic 2. Inorganic	Hydrogen, Oxygen, Nitrogen Glass, Silicon rubber
6.	Based on difference in configuration	1. Isotactic 2. Syndiotactic 3. Atactic	Polypropylene Guttapercha Polyvinyl chloride
7.	Based on composition	1. Homopolymers 2. Copolymers	Polyethylene, Polypropylene, Nylon 6 Nylon 6, 6
8.	Based on atoms	1. Homochain 2. Heterochain	Polyethylene, vinyl polymers, polyacetylene Polyethers, polyesters, polyamides
9.	Crystallinity	1. Crystalline 2. Amorphous 3. Semi-crystalline	HDPE, LDPE, cellulosic fibers Synthetic rubbers, poly (vinyl acetate), polystyrene Polybutene, Gutta percha (1, 4 trans polyisoprene) etc.

Classification of PFRR

PFRR can be classified into three groups: they are (i) the natural polymers most commonly available are extracted from marine, agricultural animals and plants. Examples are polysaccharides (cellulose, starch, chitin, pectin, natural gums), proteins (collagen, soy, whey, casein), polyisoprenes, etc., (ii) polymers produced from chemical synthesis from bio-derived monomers such as polylactic acid (PLA), propanediol; and (iii) polymers produced directly by natural or genetically modified bacteria such as polyhydroxyalkanoates (PHA), dextran, xanthan, gellan, etc.

In this article, polymers from renewable resources such as PLA, PHA and polysaccharides, in particular those which have been used as or have been shown to have potential for use as polymeric materials are briefly reviewed. Physical properties of polymers include molecular weight, density, degree of polymerization, crystallinity of material and so on. Chemical properties such as solubility and permeability, thermal properties like melting, glass transition, crystallization temperature were discussed. Life cycle assessment (LCA) is a powerful and valuable tool for measuring the environmental optimization of the products which was taken into the account as the end-of-life options such as landfills, incineration, composting and recycling.

Polylactic Acid (C₃H₄O₂)_n

Poly lactide or PLA is a kind of biodegradable, hydrolysable aliphatic polyester, commodity polymer derived from 100% renewable agricultural resources such as corn starch, tapioca roots, cassava roots or sugarcane. It has a potential industrial application as packaging materials and also a leading biomaterial for numerous applications in medicine such as controlled drug delivery systems, surgical sutures, bone tissue engineering scaffolds (Chaozong *et al.*, 2004) and healing dental extraction wounds. PLA has stereoisomers of D-Lactic (produced by microorganisms) and L-Lactic acid (natural and biologically important isomer). The major limitation of PLA is the low molecular weight (M_w), which was first synthesized by Wallace Carothers in 1932. Later he developed the high M_w PLA by preferring the ring opening polymerization process (ROP). Various methods could be adopted to prepare PLA, which includes polymer through lactide formation, ROP and DCP (direct condensation polymerization process like azeotropic dehydration and enzymatic polymerization). Extrusion, casting, injection molding, thermoforming and fiber spinning are the different methods to prepare PLA into useful and versatile products (Lim *et al.*, 2008). The production of PLA has number of advantages compared to other polymers. The advantages are a) ecofriendly b) biocompatibility c) processability d) significant energy savings e) improvement of farm economy f) reduction of landfill volumes g) fixation of significant quantities of CO₂, the leading greenhouse gas (Dorgan *et al.*, 2000). On the other hand, this polymer has some drawbacks like, a) poor impact resistance, b) slow degradation rate c) moisture sensitivity, d) lack of reactive side chain groups and relatively expensive.

Properties of PLA

The characteristic features of PLA closely resemble polystyrene and are comparable to many petroleum based products; PLA produces an excellent ecofriendly polymer during polymerization. The physical, thermal and mechanical properties of PLA and its copolymers are very dependent on the molecular weight, M_w distribution, and composition. Generally the properties of composites are greatly influenced by the crystallinity of PLA used. The structure of PLA was shown in Fig. 1 (Aliotta *et al.*, 2019).

PLA is very clear and colorless thermoplastic which is soluble in dioxane, chloroform, acetonitrile, methylene chloride dichloroacetic acid etc. At the same time, it is not soluble in water, some alcohols and alkanes. The density of amorphous and crystalline PLLA has been reported as 1.248 kg L⁻¹ and 1.290 kg L⁻¹, respectively. The density of solid PLA was reported as 1.36 g cm⁻³ for L-lactide, 1.33 g cm⁻³ for meso-lactide, 1.36 g cm⁻³ for crystalline and 1.25 g cm⁻³ for amorphous PLA, respectively (Auras *et al.*, 2004). Moreover, PLA specimens sinks in a liquid column, has the density of 1.240 ± 0.002 kg L⁻¹ for poly (98%) L-lactide and 1.243 ± 0.002 kg L⁻¹ for poly (94%) L-lactide.

The thermal properties of PLA were determined by Ahmed *et al.* (2009) based on the number of average molecular mass (M_n) and the nature of the isomer. Glass transition temperature (T_g) and degree of crystallinity ($\chi_c\%$) was increased as a function of M_n . The melting temperature (T_m) and enthalpy (H) of L isomer increased, as M_n was increased from 1100 to 27,500. No crystallization peak was observed in lower M_n range from 550 to 1400. Auras *et al.* (2004) observed that PLA films undergo an endothermic curve superimposed on T_g during the first scan of DSC heating. A relaxation enthalpy of 1.4 Jg⁻¹ for PLA (98%L-lactide) and 2.9 J g⁻¹ for (94%L-lactide) is noticed resulting a secondary molecular reordering in the amorphous phase of

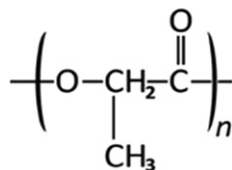


Fig. 1 Structure of PLA.

semi-crystalline polymers. Moreover, *Tabi et al. (2010)* used different temperatures (60–140°C) and time intervals (10–60 min) for the investigations of crystallization of injection molded amorphous and pure PLA specimens in a vented oven. It was verified by wide angle X-ray diffraction (WAXD) spectrometry and the results predicted that the un-annealed PLA had no crystallinity, but one significant peak appeared at 16.3° for the specimens annealed at 80°C. Also the intensity of the peak increases as annealing time increases. The WAXD results showed that in an annealing temperature range of 100–140°C, 10 min were enough to achieve as high crystallinity, as possible for injection molding grade PLA (crystalline content around 40%). The DSC results showed a significant exothermic peak in the temperature range of 80–140°C which is related to cold crystallization. The exothermic peak decreased with increasing crystallinity, thus no exothermic peak could be observed for the fully annealed specimens (specimens with around 40% crystalline content).

The melt behavior (Pseudoplastic, non-Newtonian behavior) of PLA is similar to the polystyrene. Semicrystalline PLA has a higher shear viscosity than amorphous PLA at these elevated temperatures (150°C and 170°C) and at various shear rates (30, 50, 70, 90, 110, 130 and 150 rpm screw speeds). The decrement in shear viscosity is noticed for both this type of PLA, as the temperature increased (*Fang and Hanna, 1999*). Melt viscosities of high M_w PLA were reported as 5000–10000 poise (500–1000 Pas) at 10–50 s⁻¹. The average molecular weight of PLA used for injection molding was around 100,000 Daltons and approximately 300,000 tons for cast-extruded film grades (*Garlotta, 2001*).

PLA has an approximate tensile modulus (TM) of 3500 MPa, a maximum tensile strength (TS) of 50 MPa and a low elongation at break of 4% (*Jacobsen and Fritz, 1999*). An improved TM and TS has been obtained with the crosslinking of PLA via the chemical treatment by adding small amount of triallyl isocyanurate and dicumyl peroxide (*Sen-lin et al., 2008*). The mechanical properties like tensile strength, elastic modulus and elongation at break for poly (98%L-lactide) were 72 MPa, 2.11 GPa and 11% respectively, and for poly (94%L-lactide) it was 84 MPa, 2.31 GPa and 7.8% respectively. The higher content of L-lactide present in the PLA film contributes a higher tensile strength. Both PLA films have lower mechanical characteristics, when compared to polyethylene terephthalate (PET), under the same testing conditions.

The CO₂ permeability coefficient of PLA has lower value of 2.77 ± 0.05 for poly (98%L-lactide) at 25°C and higher value of 15.65 ± 0.63 for poly (94%L-lactide) at 45°C. The permeation activation energy, calculated by using Arrhenius equation, has lower value for poly (98%L-lactide) resin. Similarly a significant increase in the O₂ permeability coefficient was noticed as the temperature increases in the range of 5°C (3.5×10^{-18} kgm m⁻² s⁻¹ Pa⁻¹) to 4°C (11×10^{-18} kgm m⁻² s⁻¹ Pa⁻¹) at 0% relative humidity. As water activity level ($A_w = 0.9$) increases, there is a reduction in the O₂ permeability coefficient of 8.2×10^{-18} kgm m⁻² s⁻¹ Pa⁻¹ at 40°C. Nitrogen barrier properties of PLA films are 1.21×10^{-17} kgm m⁻² s⁻¹ Pa⁻¹ with activation energy of 11.2 kJ mol⁻¹ at 30°C.

End-of-Life of PLA

The most economic and feasible method for handling municipal solid waste (MSW) is landfilling. It has lot of environmental impacts primarily due to gas and leachate formation, including health hazards, fires and explosions, vegetation damage, unpleasant odors, landfill settlement, ground water pollution, air pollution, and global warming. The major disadvantage of disposing plastics in landfills lied in the fact that most plastic materials do not degrade in a practical period of time and end up accumulating. Landfills usually do not provide the appropriate environment to promote degradation, and their conditions vary considerably by geographical locations. On the other hand, PLA biodegradation is highly dependent on temperature and moisture since these two factors promote hydrolysis of the polymer chains, and in turn accelerate biodegradation. At mesophilic temperatures little or no degradation of PLA is observed.

Composting provides a viable option for recovering waste packages by returning them to nature. Biodegradability of these biodegradable polymers in composting conditions and soil burial condition are affected by two factors: i) exposure conditions (water or moisture, acidity, temperature, aerobic or anaerobic, enzyme specificity) and ii) polymer factors (polymer structure, chain flexibility, crystallinity M_w , copolymer composition, size and shape). Commercial Composting (CC) or municipal composting is a faster process than backyard or home composting as it managed more intensively and optimal conditions are maintained. For commercial composting, three types of waste are used: a) Yard waste: vegetative waste from leaves, grass, clippings, tree trunks and pruning wastes, b) Food waste: uneaten food or waste from domestic, commercial or institutional sources such as restaurants or cafeterias (*Rynk et al., 1992*), and c) Manure waste: waste from fecal and urinal excretion of livestock and is usually rich in N₂. Commercial composting is a large scale operation, which generally employs turning and active aeration, except for static pile (*Matthew and John, 2018*) and some in-vessel composting system, whereas, home composting is a small scale using small piles or composting bins, usually occurs at lower temperatures. Yard waste and food waste were going into this system, but improper management of food scraps can cause odors and attract unwanted insects or animals. The conversion of organic matter into compost may take 2 years but manual turning can decrease this time to 3–6 months (*EPA, 2006*). This composting are either can be open or closed cylinders revolving drums or orbs that can be rolled along the ground to turn the pile.

Kale et al. (2007) determined the rate at which 473 ml PLA bottles with and without caps (HDPE) and polypropylene (PP) labels decomposed in an industrial compost pile. A 94% of reduction in mass and molecular weight is noticed at the week 2. PLA bottles alone decomposed completely by week 4 while bottles with the caps and labels decomposed are at the week 8. Within 35–45 days, PLA bottles can be composted with the caps and labels (barrier of biodegradation). From their results it was concluded that, in order to reduce the municipal solid waste, a proper infrastructure should be put in place to allow large scale

composting of PLA. Similarly PLA bottles biodegradation tests were carried out in real and simulated (Cumulative Measurement Respirometric, CMR and Gravimetric Measurement Respirometric, GMR) composting conditions. During these two conditions day to day observations were recorded by [Kale et al. \(2007\)](#). With a small increase in M_w (+11, 400 Da), changes in shape and color was noted in the very first day. On the 15th day, a few pieces of bottle were seen, after that no bottle residues could be located through visual inspection. M_w of 4100 Da was obtained on the 30th day. PDI was reduced from 1.84 to 1.04 due to the polymer fragmentation. At the end of the 58th day, the mineralization was $84.2 \pm 0.9\%$ and $77.8 \pm 10.4\%$ respectively for both CMR and GMR systems, which showed similar trends on biodegradation of PLA bottles. The variation in degradation time frame between these two composting conditions (CMR and GMR) depends upon many variables such as size of the polymer sample, sample/compost ratio and nature of the compost material.

A natural way of recycling the polymer is biodegradation and it takes place in two steps: primary biodegradation where the fragmentation of the polymer chain occurs due to hydrolyzes (CO_2 and H_2O) and ultimate biodegradation where the microorganisms assimilate the low M_w chains formed. Recycling is the process of recovering waste or reprocessing the material into new and useful products. Even though PLA is a biodegradable polymer and thus supposed to finish its life in compost, it was interesting to analyze its recyclability. Lack of suitable infrastructure for sorting, recycling and composting these products at their end-of-life are the major constraints. The four level waste management hierarchy (1) source reduction (reuse), (2) recycling (including composting), (3) combustion and (4) disposal through landfill were introduced by European Commission and US Environmental Protection Agency (EPA). Among 100% PLA waste generated mostly from plates, cups, packaging and other durable goods, only a negligible amount i.e., 10% was recovered through recycling and composting. Mechanical recycling (MR) involves recovering, sorting, regrinding and reprocessing the waste PLA. According to [NatureWorks \(2009\)](#), near infrared or black light illumination technology is used to facilitate the sorting of PLA from the waste stream. Due to the contamination of this stream, PLA can be successfully recycled in the current plastics recycling infrastructure. The eminent and inexpensive disposal route to recover the post-consumer PLA is by mechanical recycling. A commercial grade of PLA undergoes melt processing and compression molding methods. Then it was subjected into two different recycling processes. The first process is accelerated aging and melt processing, while the other is accelerated aging, washing and second melt processing step. A decrease of intrinsic viscosity and molecular weight was noticed for PLA. This is because the generation of shorter polymer chain as a result of degradation of PLA during ageing of the polymer. Chemical recycling, a complex and expensive process, where the PLA is hydrolyzed at a high temperature to yield lactic acid, can be readily polymerized to high M_w PLA. Thus if there are sufficient PLA containers entering the waste stream, recycling entrepreneurs may explore means of recovering and recycling PLA in a cost effective fashion.

Polyhydroxyalkanoates (PHA)

A family of biodegradable polyesters is produced in microorganisms as intracellular storage compounds of energy and carbon nutrient deficiency (lack of Nitrogen, phosphate, sulfur, potassium, tin iron, magnesium and carbon). Beijerinck in 1888 (reported in [Chowdhury, 1963](#)) first observed the occurrence of PHA as granules of 0.2–0.5 μm in the bacterial cells, which are 100% biodegradable. Later, it was described as homopolymer containing 3-hydroxybutyric acids (3-HB) by French bacteriologist [Lemoigne \(1926\)](#). The structure of PHA ([Jiang et al., 2016](#)) is shown in [Fig. 2](#).

Production of PHA involves three steps: (i) preprocessing of biomass into reduced sugar, which are easily fermentable in a nutrient broth (ii) optimization of the fermentation process and (iii) extraction and purification of PHA through cell lysis. 250 different microorganisms are reported to produce PHA, out of these, very few microbes have been studied for industrial production. PHAs are natural, biodegradable, non-toxic, hydrophobic, optically active, biocompatible, and synthesis from renewable resources. Due to this behavior, it has a wide range of applications in various fields such as drug delivery, tissue engineering, surgery, wound dressing, water resistant coatings on cardboard or paper, and additives in cosmetics and in food processing industries. Based on the number of C_2 atoms present in the monomer units of PHA, it is classified as (i) short chain length (scl) consisting of 3–5 carbon monomers obtained from bacteria such as *Cupriavidus necator* and *Alcaligenes latus* (ii) medium chain length (mcl) consisting of 6–14 carbon atoms obtained from *Pseudomonas Putida* and *Pseudomonas Mendocina* and (iii) long chain length (lcl) containing more than 14 carbon atoms obtained from *Shewanella oneidensis* and *Aureipira Marina*. The typical examples of scl PHAs are poly 3-hydroxybutyrate (PHB), poly (3-hydroxyvalerate) (PHV) and their copolymers poly (3-

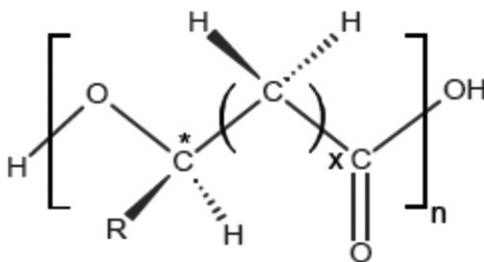


Fig. 2 Structure of polyhydroxyalkanoate.

hydroxybutyrate-co-3hydroxyvalerate) (PHBV). Similarly mcl PHAs have poly 3-hydroxyhexanoate (P3HH₆C₆), poly-3-hydroxyheptanoate (P3HH₇C₇) and poly-3-hydroxyoctanoate (P3HOC₈) etc. The commercial name of PHB is Biogreen and Biomer, and for PHBV it is Biopol. Several methods such as batch, fed-batch and continuous process could be adopted for the production of PHA. Unfortunately, there is a constraint of the production of PHA because it needs special microbial growth condition and expensive raw materials such as the microorganisms, culture condition, fermentable process etc. PHB, the most commonly seen polymer in PHA was first characterized by French Microbiologist Lemoigne (1925). Maximum production of PHB (46.2% per mg cell dry matter) was obtained by *Bacillus Megaterium* strain using sugarcane molasses (2%) and corn steep liquor as sole carbon sources (Gouda *et al.*, 2001). PHA copolymer of PHB/HV with a 3-hydroxyvalerate content of about 11% may have an optimum balance of strength and toughness for a wide range of possible applications (Pachence *et al.*, 2007). The application of PHAs includes as (i) an environmental remedy for packaging industries and biofuels (ii) valuable industrial raw material for synthesis of drugs and chiral compounds, protein purification and (iii) biomedical application for skin, tissue, heart valve, nerve, bone cartilage engineering, therapeutic as implant material regenerative medicine (Masood *et al.*, 2014).

Properties of PHA

The properties of the PHA polymer varied depending on the growth conditions (inoculum, microbial), bacterial strains used for fermentation, optimization of the purification process and carbon source. PHAs are water-insoluble but soluble in halogenated solvents such as chloroform, dichloromethane or dichloroethane, ethyl acetate or methyl tert butyl. The M_w of these polyesters can range from tens into the hundreds of thousands (Pachence *et al.*, 2007). Using Sterical Exclusion Chromatography SEC, the M_w of raw PHA were found between ranges from 2.9 to $604 \times 10^5 \text{ g mol}^{-1}$ and the poly disperse index PDI ranges from 1.52 to 2.53 respectively. The densities of crystalline and amorphous PHA are 1.26 and 1.18 g cm^{-3} respectively. The PHAs become highly crystalline (range of a few to 70%) and shows material properties similar to polypropylene (PP), polyethylene (PE), polystyrene (PS). Normally, the production of PHAs is carried under moderate temperature range of $30\text{--}35^\circ\text{C}$ and at pH $6.5\text{--}7.0$.

PHAs structure is composed of a monomer of 3-hydroxyalkanoic (HA) acid. The general formulae of the monomer unit is $[-O-CH(R)-CH_2-CO-]$. The (R)-3HA monomer units are all in the *R* configuration due to stereospecificity of polymerizing enzyme PHAs synthase. PHAs are resistant to hydrolytic degradation, exhibit a high degree of polymerization ranging from 10^5 to almost 10^7 Da. Short chain length PHA such as PHB are isotactic in structure, with a T_m of $\sim 75\text{--}180^\circ\text{C}$, T_g of $\sim 4^\circ\text{C}$ and crystalline temperature (T_c) $\sim 102\text{--}106^\circ\text{C}$ respectively. The mechanical characteristics exhibit a higher tensile strength at $\sim 43\text{MPa}$ and are highly brittle and stiffer with $\sim 5\%$ reduction in elongation at break. Medium chain length (mcl) PHA is flexible and elastic, having low tensile strength, low crystallinity, low temperatures (T_m , T_g) and higher elongation at break. Depending on the branched length of the hydroxyalkanoic (HA) acid or from the distance between the ester linkages in the polymer backbone, the mechanical properties of PHA ranges from brittle to flexible, and elastic. Typically, PHAs with short pendant groups are hard crystalline whereas longer pendant are elastomeric. In contrast to other polymeric materials, PHB possesses excellent natural resistance to UV weathering but far inferior solvent resistance. Using diluted solution viscometry, the average viscosity molecular weights (M_v) were determined and the value was around 110 kDa . Here the chloroform is used as a solvent. The intrinsic viscosity is $\eta = kM_v^\alpha$, where $k = 1.21 \times 10^{-4}$ and $\alpha = 0.75$ (Thara and Shawapun, 2010). The neat PHBV exhibit a non-Newtonian flow profile and zero shear viscosity is 1990 pa s . Water contact angle (WCA) is an important parameter to measure the work of adhesion, surface tension and interface free energy. The polymer P (3HB) has the highest value of WCA (70.0 ± 0.4) and interface free energy (7.9 erg cm^{-2}) whereas the copolymers P (3HB-co-3HV), P (3HB-co-3HH) and P (3HB)c-4HB have the lowest values. The surface tension (43.1 erg cm^{-2}) and work of adhesion ($112.0 \text{ erg cm}^{-2}$) are higher for P (3HB-co-4HB) (Volova *et al.*, 2013). Wide angle X-ray scattering (WAXS) analysis was used to determine the crystalline structure and crystallinity index of the PHBV. Two strong diffraction pattern peaks located at $2\theta = 13.5^\circ$ and 17° were observed corresponding to the (020) and (110) planes of orthorhombic unit cell and small peaks at $2\theta = 20, 25.5, 27$ and 30.4° . The crystalline index for PHBV is 47.8% , calculated by using the formula $CI = \frac{I_c - I_a}{I_0} \times 100$ where I_a is the area of the amorphous peaks and I_0 is the total intensity. Oxygen barrier properties of PHA were $23\text{--}29$ (O_2 in cc-mil ($100 \text{ cm}^2 \text{ day}^{-1}$) at 25°C $0\% \text{ RH}$) and water barrier was $5\text{--}19$ (in g-mil ($100 \text{ cm}^2 \text{ day}^{-1}$) at 38°C , $90\% \text{ RH}$). These properties and better environmental performance create a bright future for PHA and expected to be a good candidate to substitute PP and PE, but also PET in certain applications.

End-of-Life of PHA

Biodegradation was measured for PHA when it was exposed to aerobic (ASTM 5338), anaerobic (ASTM 5511), marine (ASTM 6691), soil burial (En 13432) and industrial (ASTM D6400) composting conditions. ASTM represents the Standard Test Method for determining the environmental conditions used. PHAs are fully biodegradable in both aerobic and anaerobic, whereas a slower rate in marine environmental conditions was observed. (Joseph, 2018). The biodegradation of PHB and PHBV were evaluated by the loss of mass, tensile strength and roughness of the polymer. Both PHB and PHBV showed biodegradation in soil composting medium at 46°C and at room temperature 24°C respectively (Rosa *et al.*, 2004). After aging in soil composting for 86 days, PHB and PHBV showed a decrease in tensile strength at break (76% for PHB and 74% for PHBV). Weng *et al.* (2011) studied the PHAs with different copolymer content ($40 \text{ mol}\%3\text{HV}$, $20 \text{ Mol}\%3\text{HV}$, $3 \text{ mol}\%3\text{HV}$ and $40 \text{ mol}\%4\text{HB}$) under controlled composting conditions in accordance with ISO 14855-1. The decrease in thermal stability and MW was noticed and

the chemical structure of PHA was unchanged. The order of biodegradability was as follows: P (3HB-co-40mol%4HB) > P (3HB-co-40mol%3HV) > P (3HB-co-3mol%3HV) > P (3HB). Proper management of municipal solid waste (MSW) is an important parameter for environment and economic issues. Approximately 250 million tons of MSWs are generated in USA and only 85 million tons of these materials are recycled or composted (US EPA, 2011). About 55% of MSW is deposited in landfills and about 13% is incinerated (Barlaz *et al.*, 2010). Landfills, a significant source of greenhouse gas emissions and require a lot of land. Incineration of MSW generates air pollutants as well as and a lot of ash requiring landfilling as hazardous waste. The conversion of MSW into paperboard, wood, yard trimmings, food scraps contain biodegradable organic matter. Furthermore, 53% of MSW can be transformed into valuable products instead of landfilling or incineration. Zaverl *et al.* (2012) determined that there was some loss of M_w and mechanical properties when it went through mechanical recycling. The reprocessing cycles did not significantly affect the properties of PHBV (up to 5 cycles). After reprocessing, the mechanical properties were maintained for 4 cycles; however they showed a slight decrease after the fifth cycle (7.1%). Also a slight decrement in M_w by GPC and a drop were noticed after the 3rd, 4th and 5th cycles (8.7%, 13.5% and 16.6% respectively). Chemical recycling has been tried for other biopolymers as well. The chemical recycling of PHAs by thermal degradation resulted in transformation into vinyl monomers, and enzymatic transformation into an oligomer has been reported by Azadeh and Ignacy (2013).

Polysaccharides ($C_6H_{12}O_6$)

Polysaccharides (also known as Glycans) are complex, high molecular weight biological molecules that are almost pure carbohydrate. It consists of repeating units either monosaccharide or disaccharides joined together by glycosidic linkages. They mainly occur in nature as functional and structural components of cells (e.g., glycoproteins and glycolipids), or merely as non-informational storage forms of energy (e.g., glycogen). The structure of repeating unit of the marine bacterial polysaccharide is shown in Fig. 3 (Senni *et al.*, 2011). Commonly found monomer units in polysaccharides are glucose, fructose, mannose, galactose and aminouronic acids. The various polysaccharides differ from one another not only in the composition of the constituent monosaccharide but also in the molecular weight, degree of branching, glycosidic linkage pattern and type of configurations involved in the respective monosaccharide units.

Commercially available polysaccharides used in food and nonfood industries as stabilizers, thickness and gelling agents, crystallization inhibitors and encapsulating agents etc., are also called hydrocolloids or gums. Additionally, polysaccharides exhibited various pharmaceutical fields, papermaking, biological activities such as antitumor, anti-inflammatory, anti-bacterial and immunologic activity as well as anti-mutagenic activity. Table 2 (Stiger-Pouvreau *et al.*, 2016; Verbeke *et al.*, 2003; Alphons *et al.*, 2009; Choudhary and Pawar, 2014) shows the source, sugar presents and linkages in some naturally occurring polysaccharides. Polymer derived from 100% renewable agricultural resources can be depolymerized by acids and heat, specific enzymes and high pH. In order to reduce the amount of non-biodegradable plastic waste (a serious environmental problem), polysaccharides serves as an alternate for its biodegradability. One of the drawbacks is, it has poor mechanical properties due to its hydrophilic behavior which causes earlier rupture. At the molecular level, the polysaccharides structuring are encountered with either ordered or disordered conformations. Polysaccharides may adapt secondary structures because of sugar residues linked through glycosidic linkages. More than 20 several monosaccharide units are combined through glycosidic linkages form polysaccharides. Based on the number of different monomer units in the structure, polysaccharides can be divided into homo polysaccharides (has single sugar unit on the backbone) and hetero polysaccharides (more than one sugar unit). Storage polysaccharides such as starch and glycogen, and structural polysaccharides such as cellulose and chitin, were mainly found in the nature.

Properties of Polysaccharides

Polysaccharides contain a large number of hydroxyl groups, oxygen atoms, and other groups that may interact with water molecules mainly through hydrogen bonding. These interactions control the mobility of water in food systems, affect ice crystal formation and growth, and thus may exert a particular influence on the textural and functional properties of foods. According to solubility (Murray, 2009), some polysaccharides insoluble in water or organic solvents, (e.g., cellulose), some are soluble in hot

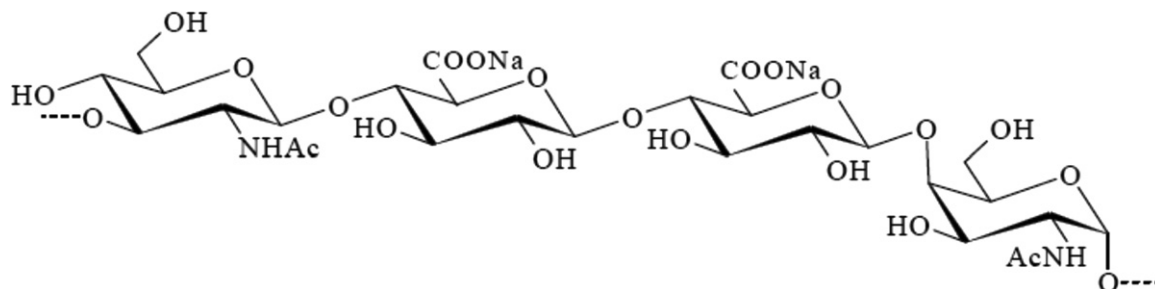


Fig. 3 Structure of marine bacterial polysaccharides.

Table 2 Classification of Naturally occurring Polysaccharides

Polysaccharides	Source	Sugar present and linkages
I Sea weeds		
1. Agar	Red algae (Gelidium species)	D-Galactose β -(1 $\rightarrow$ 4), 3,6-anhydro – L-galactose α -(1 $\rightarrow$ 3), + sulfate acid ester groups
2. Algin	Brown algae (Macrocystis pyrifera)	D-Mannuronic acid β -(1 $\rightarrow$ 4), L-guluronic acid β -(1 $\rightarrow$ 4), Na salt
3. Carrageenan	Red algae (Chondrus crispus, Gigartina stellata)	3-linked β -D-galactose 4-sulfate and 4-linked 3,6-anhydro- α -D-galactose.
4. Fucoidan	Brown algae (Fucus sp., Laminaria sp.)	L-Fucose + sulfate acid ester groups
II Plant exudates		
1. Gum Arabic	Acacia sp.	L-Arabinose, D-Galactose, L-rhamnose, D-glucuronic acid
2. Ghatti	Anogeissus latifolia	L-Arabinose, D-xylose, D-galactose, D-mannose, D-glucuronic acid
3. Karaya	Sterculia urens	D-Galactose, D-xylose, D-glucuronic acid
4. Tragacanth	Asteragalus sp.	D-Galactose, L-rhamnose, D-galacturonic acid
III Plant extracts		
1. Pectin	Cell walls and intracellular spaces of all plants (commercial source, citrus waste)	D-Galacturonic acid α -(1 $\rightarrow$ 4) partially esterified, L-arabinose, α -(1 $\rightarrow$ 5) and α -(1 $\rightarrow$ 3) branches, D- galactose β -(1 $\rightarrow$ 4)
2. Larch	Western larch	D-Galactose, L-arabinose
IV Plant seeds		
1. Corn-hull	Corn seed coat	D-Xylose, L-arabinose, galactose and glucuronic acid
2. Guar	Camposia tera gonolobus endosperm	D-Mannose β -(1 $\rightarrow$ 4), D-galactose α -(1 $\rightarrow$ 6) branches
3. Locust bean	Carob tree (Ceratonia siliqua) Endosperm	D-Mannose β -(1 $\rightarrow$ 4), D-galactose α -(1 $\rightarrow$ 6) branches
4. Quince seed	Cydonia vulgaris	L-Arabinose, D-xylose, hexuronic acid, monoethyl, hexuronic acid
5. Psyllium seed	Plantago sp.	D-Xylose, L-arabinose, D-galacturonic acid, L-rhamnose, D-galactose
6. Flax seed	Linum usitatissimum	D-Galacturonic acid, D-xylose, L-rhamnose, L-arabinose, L-galactose, D-glucose
7. Tamarind	Tamarindus Indica	D-Glucose, D-Galactose, D-xylose
8. Wheat gum	Wheat	D-Xylose β -(1 $\rightarrow$ 4), L-arabinose branches
1. Cellulose Derivatives	Plant cell walls, wood pulp and cotton	D-Glucose β -(1 $\rightarrow$ 4)
2. Starch Amylose Amylopectin	Cereal grains and tubers	D-Glucose α -(1 $\rightarrow$ 4), D-glucose α -(1 $\rightarrow$ 4), α -(1 $\rightarrow$ 6), at branch points
3. Dextran	Bacterial action on sucrose	D-Glucose α -(1 $\rightarrow$ 6) and α -(1 $\rightarrow$ 3)
4. Chitin	Exoskeleton of animals of the phylum Arthropoda	N-Acetyl, D-glucosamine β -(1 $\rightarrow$ 4)

water (e.g., starch) and some are soluble in cold water (e.g., pullulan or gum arabic). Highly branched polysaccharides are easily dissolved in water due to the irregularity of molecular structure which prevents the formation of a closely packed structure and allows many polymers to hydrate. On the other hand, linear polysaccharides with regularity in molecular structure are insoluble in water. Natural polysaccharides are less soluble than the charged ones (polyelectrolytes) (Wang and Cui, 2005).

The functional properties of various natural polysaccharides like flow, solubility, water holding capacity (WHC), oil holding capacity (OHC), angle of repose, and bulk and true density were studied and the results were summarized by Sarkar *et al.* (2018). Babchi gum has 1% outstanding flow ability and Piyaar gum (Buchanania lanzan) has the highest bulk density of 1.25 g mL⁻¹ and true density of 1.66 g mL⁻¹. The solubility index is higher for Khair gum (83.65%), the WHC for Psyllium gum (1024.66) and tamarind gum showed the highest OHC (214.66 g oil 100 g⁻¹ gum⁻¹). Guar gum showed increase in the angle of repose (39.80°). One of the direct methods to determine the molecular weight of polysaccharide is osmotic pressure (π). It is calculated by using the formula $\pi = \Delta h \rho g$ (where Δh is the difference in heights of the liquid in the column, ρ is the density of the solution and g is the acceleration due to gravity) through static membrane osmometer. This method is less sensitive to high molecular weight polysaccharides. Also, for neutral and charged polysaccharides, the measurement can be made in water and 0.1M-1M NaCl solutions respectively. The weight-average molecular weight (M_w) of native kondagogu gum and deacetylated gum were determined to be 8.5×10^6 and 2.5×10^7 g mol⁻¹, respectively, by 'Static Light Scattering' experiments.

Viscometry is the most widely used and another straight forward method to determine the molecular weight of polysaccharides. Intrinsic viscosity can be measured with the help of relative viscosity (η) and the concentration (c) of the polymer taken. Using Mark-Houwink equation, $\eta = kM_v^\alpha$, the viscosity is measured. The parameter k and α are primarily dependent on the geometry of the inter-residue linkages within the polymer chain. α values for various gums were given by Vinod *et al.* (2008) and it can be used to distinguish, if a polymer has a compact (close to 0.5 and has lower intrinsic viscosity) extended (close to 0.8 or higher intrinsic viscosity) conformation. On the other hand polysaccharide with expanded coil conformation gives high values of k values and low k values for compact coil conformation. Conformation of the polysaccharides gives the idea of 3D orientation of a specific polysaccharide in space, and the orientation of the glycosidic groups presents the projections of sugar moieties in the chain. The traditional method (Ubbelohde Viscometer) is used to find the relative viscosity of polysaccharides $\eta_{rel} = \frac{t}{t_s}$ where t is the time period for solution and t_s is for solvent. The intrinsic viscosities $[\eta]$ of native and deacetylated gum kondagogu were observed to be

$32.68 \pm 0.23 \text{ dL g}^{-1}$ and $59.34 \pm 1.38 \text{ dL g}^{-1}$, respectively in 1.0 M aqueous NaCl. The zero shear specific viscosity, for polysaccharides, was found to be close to 10 mPa·s at critical concentration.

There are various techniques to analyze the thermal property of polysaccharides such as dynamic mechanical analysis (DMA), differential thermal analysis (DTA), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). But the distinguished and common technique is used to characterize the polysaccharide gel is DSC. The cooling curve of 3.2% and 1% of gellan gum exhibited a sharp exothermic peak at $\sim 40^\circ\text{C}$ (T_s) while the heating curve has a sharp endothermic peak at temperature (t_m) slightly greater than T_s (Miyoshi *et al.*, 1996). Gum tragacanth and hydroxyethyl cellulose exhibited the highest (258 kJ mol^{-1}) and the lowest (121 kJ mol^{-1}) activation energy of thermal decomposition, respectively. Most of the DSC traces indicated a major intense exothermic transition (around 300°C) followed by weaker exotherm(s). TGA showed two phase of weight loss, one is due to the desorption of moisture as hydrogen bound water to the saccharide structure and the second phase is due to the polysaccharide decomposition. Furthermore, the initial decomposition temperature (IDT) and integral procedural decomposition temperature (IPDT) was calculated for the seed polysaccharides such as gum Arabic (IDT 274.6°C and IPDT 375°C), gum tragacanth (IDT 252.3°C and IPDT 366°C), xanthan gum (IDT 266.4°C and IPDT 383°C), sodium alginate (IDT 225.1°C and IPDT 381°C), Chitosan (IDT 293.0°C and IPDT 417°C), *D. melonoxylon* (IDT 221.21°C and IPDT 563.3°C), *B. lanzan* (IPDT 170.4°C and IPDT 598.1°C) and *M. zapota* (IPDT 178.6°C and IPDT 600.6°C) respectively. The presence of certain percentage of carbon, nitrogen, sulfur and hydrogen are identified through the elemental analysis (Bothara and Singh, 2012). Similarly gum kondagogu has revealed the contents of carbon, hydrogen, nitrogen and sulfur to be 34.97, 5.58, 0.229 and 0.128 (w/w %), respectively.

Polysaccharides based films are poor barrier against water vapor permeability coefficient (WVPC) and other polar substance at high relative humidity (RH), whereas at low to intermediate RH, the films has good barrier against O_2 and other non-polar substances. According to starch based films, the water vapor transmission rate (WVTR) is 4–6 times greater than the conventional films made from synthetic polymers (Dole *et al.*, 2004). Arabinoxylan films have low O_2 and CO_2 permeability but high water vapor permeability coefficient (Grondahl *et al.*, 2006).

End-of-Life of Polysaccharides

Polysaccharide based end products show better environmental profiles than their conventional counterparts in terms of non-renewable energy use (NREU) and greenhouse gas (GHG) emissions. Starch, a degradable polymers have lower calorific values than non-degradable LDPE, hence by incineration, less energy could be recovered from thermoplastic starch (TPS). This implies that for the system cradle-to-grave, the inclusion of waste incineration with energy recovery could invert the energy saving benefit for starch polymers. TPS leads to lower GHG emissions than petrochemical LDPE or HDPE. The value of GHG emission saving of TPS was $1.2\text{--}3.7 \text{ kg CO}_2 \text{ eq kg}^{-1}$, $\pm 15\%$ (Patel *et al.*, 2003) and $1.1\text{--}2.1 \text{ kg CO}_2 \text{ eq kg}^{-1}$ was reported by James and Grant (2005). Due to its better biodegradability and biocompatibility, the polysaccharides were not accumulated in the environment. However, when it was chemically treated or modified or blended with high melting temperature oil based polymers, the disposability can create issues. The goal for new products is to design in such a way that after their period of service they can be reused, recycled or disposed of, without negative impact on the environment. Options for disposal at the end of the product life cycle require that the materials can be fully degraded by environmental influences such as temperature, UV light, water and microbial attack. Most polysaccharides are known to degrade under conditions where bacterial and enzymatic degradation can occur. Mineralization of polysaccharide derivatives may proceed substantially slower by different composting routes (Persin *et al.*, 2011). Starch were added to polyethylene (PE) to enhance degradation under natural environments resulting the disintegration of 6% starch added PE bags in soil was complete within 3–6 years. 40% starch blends with PE and copolymer of PE and acrylic acid (PEAA) partially disintegrated and lost a substantial amount of starch when exposed to pond and river water. Also, the chemical structures of the PE and PEAA polymers were unchanged. Starch-added products may disintegrate as litter in natural environments, but are probably not effective in reducing accumulation of landfill solid waste after municipal disposal (Hamilton *et al.*, 1995).

Polysaccharides such as cellulose and hemicellulose are a principal biodegradable polymer in MSW and could be degraded under the aerobic conditions found in landfills. It has been estimated (Barlaz *et al.*, 1990) that 41% of municipal refuse is composed of paper and paperboard, 7.9% is food waste, and 17.9% is yard waste. The majority of cellulose and hemicellulose in landfills therefore originate from forest products.

Conclusions

The present article briefly reviewed the works related to polymers from renewable resources. The properties such as solubility, poly disperse index, molecular weight, viscosity, density, DSC, barrier properties (O_2 , CO_2 , WVPC), tensile strength, modulus etc., and EOL like disposal, recycling, incineration, composting and landfills etc. were discussed. Polymers (PLA, PHA and polysaccharides) from renewable resources have received greater attention because of its biodegradability, the environmental compatibility. The production of PLA has number of advantages compared to other polymers. PLA produces an excellent ecofriendly polymer during polymerization. PLA biodegradation is highly dependent on temperature and moisture since these two factors promote hydrolysis of the polymer chains, and in turn accelerate biodegradation. Recycling entrepreneurs may explore means of recovering and recycling PLA in a cost effective fashion. PHAs are natural, biodegradable, non-toxic, hydrophobic, optically active, biocompatible,

and synthesis from renewable resources. Due to this behavior, it has a wide range of application. These properties and better environmental performance create a bright future for PHA and expected to be a good candidate to substitute PP and PE, but also PET in certain applications. PHAs are fully biodegradable in both aerobic and anaerobic. Commercially available polysaccharides used in food and nonfood industries. Polysaccharide based end products show better environmental profiles than their conventional counterparts in terms of non-renewable energy use (NREU) and greenhouse gas (GHG) emissions. Hence, it can be concluded that the PFRR have better physical properties that make it as a suitable material to replace conventional materials as reinforcement in the existing polymer industry. As a major source of indigenous raw material in polymer industry not only provides a biodegradable resource, but also provides a chance for economic development in rural areas.

See also: An Overview on the Development of Natural Renewable Materials for Textile Applications. Bamboo: The Emerging Renewable Material for Sustainable Construction. Opportunities With Renewable Jute Fiber Composites to Reduce Eco-Impact of Nonrenewable Polymers. Renewable Energy Production From Environmental Hazardous Palm Oil Mill Waste Materials: A Review

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Properties of Coconut Fiber

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Introduction

Coconut trees ([Fig. 1](#)) are grown in the coastal regions in the wet tropical areas of India, Sri Lanka, Philippines, Indonesia, Malaysia, Fiji Islands, Vietnam, Hawaii Islands, Papua New Guinea, and Solomon Islands mainly. It is grown for the high oil content of the endosperm (copra), which is widely used in both food and non-food industries (e.g., margarine and soaps). The coconut trees are having a life span of about 80 years. Coconut is the seed of a species of palm, *Cocos nucifera*, and its fiber is the fibrous husk of the coconut shell ([Fig. 2](#)). The most suitable soil for the coconut is rich alluvial or loam having adequate soil moisture either through well-distributed rainfall, percolation of soil moisture, and drainage system alongside the backwater. The coconut also yields well in lateral loamy or black clayey soil. It generally grows in an atmosphere of saline moisture, light wind with heavy and well-distributed rainfall and high-humidity and moderate climate ([John, 1970](#)). Large-production areas, in particular, are found along in these countries millions of people make a living from the coconut palm and its many products. Total world productivity has increased substantially from 35 MT around 1980 to almost 50 MT today ([John, 1970](#); [FAO, 2004, 2008](#)). These palms flower on a monthly



Fig. 1 Coconut trees on the shore of backwater lagoon.

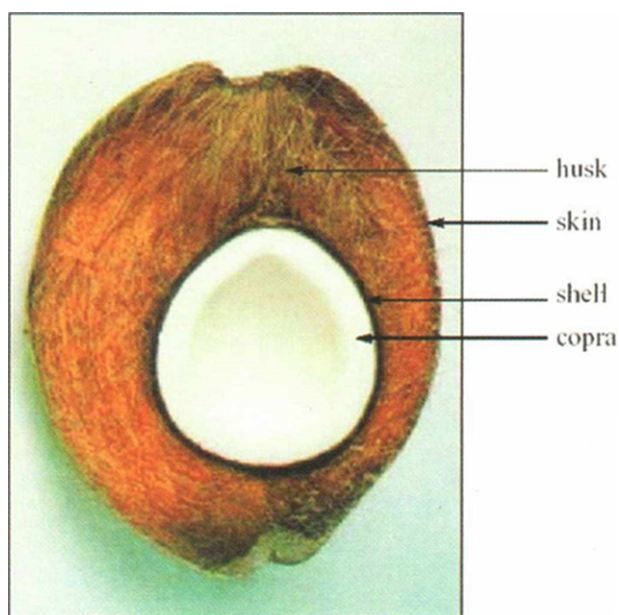


Fig. 2 Cross section of matured coconut fruit.

basis and the fruit take 1 year to ripen after 3–5 years of plantation. A palm tree may have fruit in every stage of maturity. A mature tree can produce 50–100 coconuts per year. Generally, a coconut weighs 1.0–1.2 kg per nut of which, weight of husk is around 300–400 gms (NRDC, 2009). This husk contains about 30% of textile quality fiber and rest small fibers (Pits) and small fragments (Pith). Green coconuts, harvested after about 6–12 months on the palm, contain pliable white fibers to dehydrated rigid brown fibers. These fibers are mainly used for making ropes/twines, carpets, furnishings, floor matting, wall decorative, fancy bags, etc.

The quality of coconut fiber depends upon several factors, viz., agro-ecological conditions (rainfall, humidity, soil, etc.), variety of seedlings and most importantly on stage of harvesting and process employed for extracting the fiber. A good-quality fiber can be obtained from the green coconut husk when they are in naturally hydrated condition. The fiber at this stage found to be whiter, flexible, softer, and easy for chemical processing. However, as copra is the prime product of coconut, hence the dehusking is generally done when the coconut reached to its full maturity after 9 months and fibers are matured, dehydrated, and yellow to brown in color. Raw fibers (Fig. 3) are retted conventionally in backwater for about 6–12 months (Manilal *et al.*, 2010) to make it softer. Recently, chemical retting has been proposed by Basu *et al.* (2015) using a combination of Na_2S , Na_2CO_3 , and NaOH ; which can improve fiber property after 2 h of treatment (Fig. 4).

Fine Structure of Fiber

Scanning Electron Microscopy

The observation of the scanning electron micrographs of the raw fiber surface (Fig. 5(a)) reveals cracks, voids, and parallel ridges, which are further connected with intermediate nodes perpendicular to fiber length forming more or less rectangular indentation. The non-uniformity seen in this fiber is probably caused by heterogeneous distribution of impurities, fat and waxy substances, and

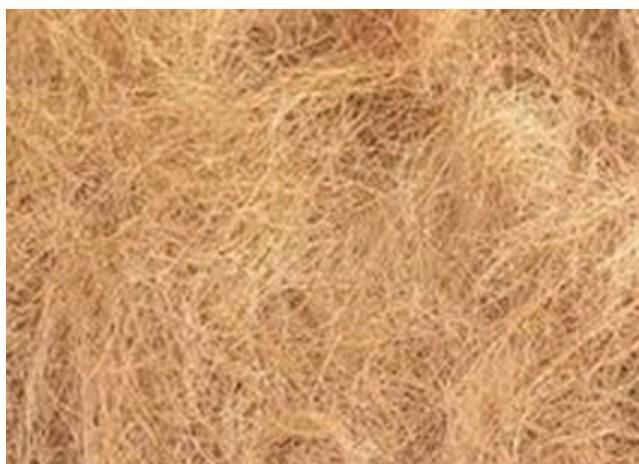


Fig. 3 Raw fiber.



Fig. 4 Retted fiber.

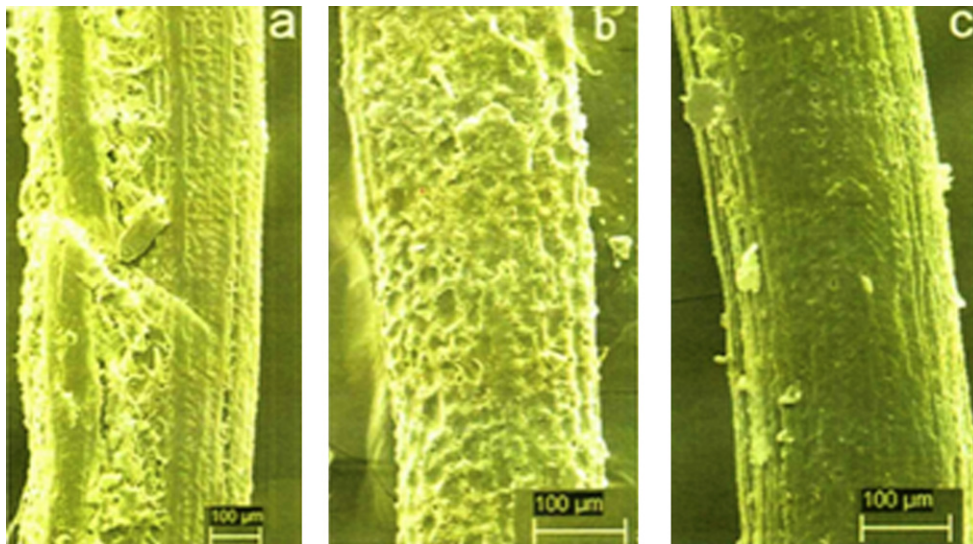


Fig. 5 SEM view of coconut fibers (a) raw, (b) backwater retted, and (c) chemically retted. Reproduced from Basu, G., Mishra, L., Jose, S., Samanta, A.K., 2015. Accelerated retting cum softening of coconut fibre. *Industrial Crops and Products* 77, 66–73.

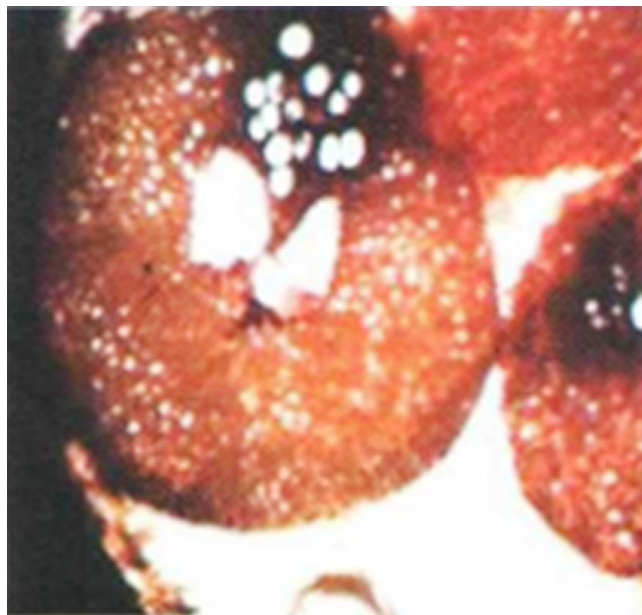


Fig. 6 Cross section of a coconut fiber. Reproduced from Mishra, L., Basu, G., 2013. Coconut fibre – Journey from food to fibre. In: Satapathy, K.K., Ganguly, P.K. (Eds.), *Diversification of Jute and Allied Fibres: Some recent Developments*. Kolkata: ICAR-National Institute of Research on Jute and Allied Fibre Technology, pp. 335–348.

globular protrusions. The surface morphology of backwater retted fiber (**Fig. 5(b)**) has more irregularities and impurities than the raw fiber, which might be due to formation of an additional salt coating through its backwater retting followed by air drying without washing. Comparing to raw and backwater retted coconut fibers, treated fibers appeared to be clean, with a smoother surface and it is possible to observe a reduction on fats and waxes (**Fig. 5(c)**). Alkali treatment removes the surface adhered impurities leading to formation of rough surface with pits which were not revealed on the surface of raw and backwater retted fibers.

Cross-Sectional View

The cross-section of fiber (**Fig. 6**) is circular having central lumen. Presence of numerous voids around central lumen indicates its multi-fibrillar structure. The scanning electron micrograph shows the micro-fibrills by longitudinal parallel ridges. Uneven fiber surface with prominent cracks and micro-pores are detectable. Irregular wax-like deposition on the fiber surface masking the cracks,

and micro-pores in places, is visible in the micrograph. In this context, it may be noted that the fats and wax contents was found to be 1.03% as estimated by solvent extracted method.

Physical and Mechanical Properties of Fiber

Mechanical and physical properties of coconut fiber are shown in Table 1 where it is being compared with two allied popular lignocellulosic fibers viz., jute and sisal.

Length and diameter

Coconut fiber is notably thicker than sisal and jute. The diameter and length of coconut fiber, both are highly variable having range values 100–795 μm (average being 183 μm) and 44–305 mm (average being 320 mm), respectively. Linear density (59.2 tex) of coconut fiber is much higher as compared to jute (3.8 tex) and sisal (29.67 tex). However, apparent density and true density are 1.17 and 1.40 g cm^{-3} respectively comparable to jute and sisal. High linear density along with low length–diameter ratio (750) of coconut fiber indicates its suitability for coarse textile applications.

Mechanical property

Table 3 shows that, breaking tenacity (11.25 cN/tex) and initial modulus (200 cN/tex) of coconut fiber are notably lower than those of other two natural fibers. This may be due to its lower degree of crystallinity (45%) as compared to jute (58.7%) (Samanta *et al.*, 2008) and sisal (71.7%) (Kalia *et al.*, 2011). Coconut fiber showed relatively high extensibility of even up to over 21%, in contrast to the other natural fibers, jute (1.8%) and sisal (2.76%). High extensibility ultimately resulted in high-specific work of rupture (13.4 mJ/tex-m) of coconut fiber as compared to jute (2.8 mJ/tex-m) and sisal (4.41 mJ/tex-m). The extension of coconut fiber indicates spiraled cellulosic macro-molecular arrangement in the fiber having high angle of orientation (Stern and Stout, 1954). The fiber is having much higher degree of flexural rigidity (1473 mN-mm²) as compared to jute and sisal, may be attributed to its high-lignin content, coarseness, and

Table 1 Physical and mechanical properties

Property parameter	Coconut	Jute	Sisal
<i>Physical parameters</i>			
Diameter (μm)	320 ^a (50.5)	60 (32.1)	190 (36.9)
Length (mm)	183 ^b	60 ^c	770
Length–diameter ratio	750	1000	4052.6
Linear density (tex)	59.2	3.8	29.67
True density (g cm^{-3})	1.40	1.48	1.45
Apparent density (g cm^{-3})	1.17	1.23	1.2
Bulk density	0.43	0.48	0.45
<i>Mechanical behavior</i>			
Breaking tenacity (cN/tex)	11.25 (54)	33.2 (45.7)	28.2 (40.05)
Breaking extension (%)	21.5 (51)	1.8 (41.3)	2.76 (48.01)
Initial modulus (cN/tex)	200	1900	1100
Specific work of rupture (mJ/tex-m)	13.4	2.8	4.41
Flexural rigidity (mN-mm ²)	1100	22.1	284.1
Coefficient of friction	0.35	0.45	0.56
<i>Moisture relationship</i>			
Moisture regain at 65% RH (%)	11.7	13.5	10.92
Longitudinal swelling (%)	0.6	0.07	0.08
Transverse swelling (%)	15	25	15
Water imbibition (%)	58	92	64
Vertical wicking length after 24 h (mm)	2	7	17
<i>Electrical properties</i>			
Mass specific resistance ($\Omega\text{-kg m}^{-2}$)	4.0	1.83	2.96

^aRange 100–795 μm ;

^bRange 44–305 mm;

^cModal value of filament.

Figure in parentheses indicates coefficient of variation of the corresponding parameter.

Note: Bhattacharya, G.K., Basu, G., Chattopadhyay, S.K., *et al.*, 2009. Coconut Fibre and Its by Products: Present Status and Potentiality. Kolkata: ICAR-National Institute of Research on Jute and Allied Fibre Technology.

nearly circular cross-section. Coconut fiber showed 59.3% instantaneous recovery and in total 81.5% recovery at 2 h on removal of compressive load. High-flexural modulus along with good resiliency indicates its high-shock resistance property.

Frictional property

Coefficient of friction for coconut fiber (0.35 in parallel direction and 0.30 in perpendicular direction) is lower with respect to jute (0.45 in parallel and 0.40 in perpendicular) and sisal (0.56 in parallel and 0.51 in perpendicular). This indicates its lack of inter fiber cohesiveness. This may be attributed, to the much less area of contact between the coconut fiber surfaces due to (1) more circularity in its cross-section as compared to jute and sisal, (2) hardness of fiber surface, (3) irregular fiber contour, and (4) high-flexural rigidity of coconut fibers, ultimately resulting in less welding effect.

Electrical resistance

It shows the maximum resistance of $4 \Omega\text{-kg m}^{-2}$, while sisal and jute show 2.96 and $1.83 \Omega\text{-kg m}^{-2}$, respectively. In semi-crystalline polymers, current flows mainly through the crystalline regions (Pathania and Singh, 2009). Hence coconut fiber, which is a low crystalline fiber, compared to jute and sisal, shows higher resistance. Additionally, presence of lignin up to 45%, which is hydrophobic in nature, inhibits the flow of current through the fiber matrix. High insulation property indicates its potentiality in use of electrical insulating materials.

Microbial decomposition

Accelerated testing for microbial decomposition reveals that coconut fiber retained 60% of its original strength even after 75 days, while, jute and sisal lost their strength within a period of 21 days. High durability of coconut fiber may be attributed to its higher lignin and much lesser hemicellulose and pectin content as compared to jute and sisal (Bhattacharyya and Paul, 1980; Rosa Medeiros *et al.*, 2010).

Moisture

Coconut fiber showed good moisture regain (11.7%) and moderate to high water absorbency (63%). Moisture absorption resulted in moderate swelling of coconut fiber up to 50%. On the contrary, sisal despite having greater amount of cellulose (67–78%) in its macromolecule (Rahman and Khan, 2007), has low absorbency mainly due to its higher degree of crystallinity and wax content (Basu *et al.*, 2011). It was observed that coconut fiber shows an apparent hydrophobic nature with water. This may be attributed to high carbon to carbon (C–C) and carbon-to-hydrogen (C–H) bonds of surface lignin (Mahato *et al.*, 2009), which initially hinder the aqueous treatment.

Distribution of Different Properties of Coconut Fiber

Wei and Gu (2009) analyzed length and fineness characters of coconut fibers (Table 2) from a bunch of randomly taken from a fiber stack. The fiber-length distribution is given below. It is found that longer fibers usually have higher diameters.

Table 3 summarizes the statistical distribution data, viz., extreme values, mean, median, mode, coefficient of variation (CV), skewness, standard error of skewness, kurtosis and standard error of kurtosis, of property parameters of coconut fiber. It is clear from the table that all the physical properties have high variation. Majority of the fibers are lying in the range of 4–12 cm length, 100–200 μm diameter, and 10–20 tex linear density. This is mainly attributed to their natural inheritance. In coconut fiber, this variability is much higher due to poor extraction process and unorganized collection which mixes fibers of different maturity and varieties. To test the normality of all the characteristics, its skewness and kurtosis were evaluated. All the properties were shown to have skewed asymmetric curve. Similarly, kurtosis values, which are not zero, indicate that none of the characteristics follow normal distribution; either it is leptokurtic (positive value) or platykurtic (negative value). The distribution curves are shown in Fig. 1. Since, it is evident that all the characteristics are asymmetric in nature; Kolmogorov–Smirnov (K–S) goodness-of-fit test (Massey, 1951; Miller, 1956) is applied at a significance level $\alpha \geq 0.5$ to ascertain the best-fit curve, where highest K–S probability value represents the best asymmetric curve. Table 4 shows the K–S distribution and K–S probability values of fiber length for different probability density functions. The highest K–S probability value of 0.199 for Weibull function indicates the best-fit function for that property. All other properties of coconut fiber were tested likewise and the best-fit functions of different properties along with its K–S probability value are listed in Table 5.

An extensive work (Sengupta *et al.*, 2014) deals with variation in different physical properties within a lot of coconut fibers randomly selected from mixture of fibers taken from a specified agro-ecological region in India. Natural fibers inherently differ

Table 2 Length and fineness distribution

Parameters	Fiber-length distribution	
	Range of fiber length, mm	% of Fiber
No of fibers	15–145	81.95
Weight of fibers	35–225	88.34

Table 3 Property parameters of various physical characteristics of coconut fiber

<i>Characteristics</i>	<i>Sample size</i>	<i>Minimum</i>	<i>Maximum</i>	<i>Mean</i>	<i>Median</i>	<i>Mode</i>	<i>Coefficient of variation</i>	<i>Skewness</i>	<i>Standard error of skewness for normal distribution</i>	<i>Kurtosis</i>	<i>Standard error of kurtosis for normal distribution</i>
Length (cm)	102	3.8	26.4	14.08	12.9	5.8	50.9	0.221	0.239	−1.328	0.473
Diameter (μm)	102	83.3	550	244.6	200	166.6	52.9	0.818	0.233	−0.445	0.463
Linear density (tex)	102	4.6	140	36.8	25.2	Multiple	80.4	0.993	0.23	0.05	0.469
Breaking tenacity (cN/tex)	62	3.85	47.1	14.1	11.8	10.3	47.3	1.65	0.3	3.12	0.61
Breaking extension (%)	62	7.7	51.6	28.2	28.3	Multiple	37.5	0.19	0.31	−0.66	0.6
Specific work of rupture (mJ/tex-m)	62	7.1	172.4	57.6	51.3	Multiple	56.6	0.92	0.31	0.99	0.6
Flexural rigidity (mN-mm ²)	33	36.8	2084.3	811.4	864.1	1121.4	69.7	0.68	0.42	−0.08	0.82
Specific flexural rigidity (mN-mm ²) × 10 ⁴	34	500.3	15343.6	3524	2554.5	Multiple	94.3	2.58	0.4	7.1	0.78

Note: Sengupta, S., Basu, G., Chakraborty, R., Thampi, C.J., 2014. Stochastic analysis of major physical properties of coconut fibre. Indian Journal of Fibre and Textile Research 39(1), 14–23.

Table 4 Estimation of goodness of fit of different distribution curves for some physical property parameters of coconut

Property parameter	Probability density function (PDF)	K-S d^a	K-S p^b
Length	Weibull	0.1012	0.1993
	Extreme	0.108101	0.145378
	Rayleigh	0.116818	0.094139
	Lognormal	0.119202	0.083099
	Exponential	0.2	<0.05
	Gamma	0.102	<0.05

^aK-S d =Kolmogorov–Smirnov distribution^bK-S p =Kolmogorov–Smirnov probability

Note: Sengupta, S., Basu, G., Chakraborty, R., Thampi, C.J., 2014. Stochastic analysis of major physical properties of coconut fibre. Indian Journal of Fibre and Textile Research 39(1), 14–23.

Table 5 Relations of different physical characteristics

Variable X	Variable Y	Correlation coefficient	Best-fit equation	Degree of freedom	Calculated t-value	p-Value
Length	Diameter	0.759	$y = 0.533x^2 - 5.525x + 153.1$	60	8.4	0.00001 ^a
Length	Linear density	0.799	$y = 0.180x^2 - 2.679x + 23.12$	60	7.48	0.0001 ^a
Length	Breaking tenacity	0.293	$y = -0.030x^2 + 1.037x + 5.720$	60	0.592	0.555
Length	Breaking Load	0.834	$y = 1.809x^2 - 19.31x + 208.8$	60	10.2	0.00001 ^a
Length	Breaking extension	-0.272	$y = -0.451x + 33.26$	60	-2.44	0.017 ^a
Length	Specific work of rupture	-0.743	$y = 115.2e^{-0.07x}$	60	-6.56	0.0002 ^a
Length	Flexural rigidity	0.423	$y = -31.21x^2 + 1146. x - 9295$	30	0.634	0.53
Length	Specific flexural rigidity	-0.07	$y = -84.74x + 4948$	30	-0.4	0.69
Diameter	Linear density	0.893	$y = 0.255x - 21.31$	60	15.38	0.00001 ^a
Diameter	Load	0.785	$y = -0.001x^2 + 3.360x - 226.0$	60	11.5	0.0001 ^a
Diameter	Breaking tenacity	-0.122	$y = 13.83e^{-8E-04x}$	60	-1.24	0.219
Diameter	Breaking extension	-0.437	$y = 12.45e^{0.005x}$	60	-2.94	0.0045 ^a
Diameter	Specific work of rupture	-0.826	$y = 190.3e^{-0.00x}$	60	-7.07	0.00001 ^a
Diameter	Flexural rigidity	0.764	$y = 117.3e^{-0.07x}$	30	6.27	0.00003 ^a
Diameter	Specific flexural rigidity	-0.33	$y = -87.82x + 4951$	30	-1.99	0.054
Linear density	Breaking tenacity	-0.207	$y = -0.045x + 14.07$	60	-1.91	0.06
Linear Density	Breaking Load	0.804	$y = -0.066x^2 + 15.83x + 0.656$	60	8.7	0.0001 ^a
Linear density	Breaking extension	-0.316	$y = 29.00e^{-0.00x}$	60	-3.42	0.0011 ^a
Linear density	Specific work of rupture	-0.934	$y = 90.86e^{-0.02x}$	60	-7.78	0.00001 ^a
Linear density	Flexural rigidity	0.739	$y = 87.72e^{0.034x}$	30	7.98	0.00002 ^a
Linear density	Specific flexural rigidity	-0.302	$y = -36.43x + 5457$	30	-1.79	0.082

^adenotes the insignificance of value.

Note: Sengupta, S., Basu, G., Chakraborty, R., Thampi, C.J., 2014. Stochastic analysis of major physical properties of coconut fibre. Indian Journal of Fibre and Textile Research 39(1), 14–23.

from each other to a great extent. Information on average values of various property parameters and variability of each property parameters is essential to a processor to identify or to design processing machines to convert the fiber to value-added products. For any industrially processable fiber crop, an evenly distributed property parameter is most desirable to the processor. The results (Table 3) show that all the major property parameters of coconut fiber are highly variable and follows asymmetric distribution curve. It indicates the chance of coming out with highly variable textile products from processing machines in spite of taking all the possible measures to produce regular thread-like materials (twines and cordages) and any finer sheet-like materials. High variability in fiber length (Fig. 7(a)) causes high hairiness protruded from thread surface. It becomes difficult to engineer finer materials if the diameter is highly variable. High variability in diameter and linear density indicates that coconut fiber may be used in making much coarser materials like household ropes and cordages. However, length-wise segregation of fiber would solve the problem to a considerable extent. Considering the asymmetric distribution (Fig. 7(a)), the fibers may be segregated in following three major length-groups, namely (1) long, (2) medium, and (3) short. Figures reveal that number of medium length fiber is substantially higher than short followed by long fibers. The distribution of diameter as well as linear density values also shows nearly similar trend. In this case number of coarse fiber is substantially higher than medium followed by fine fibers. So, the fiber mix may also be sorted by diameter or linear density (Figs. 7(b))

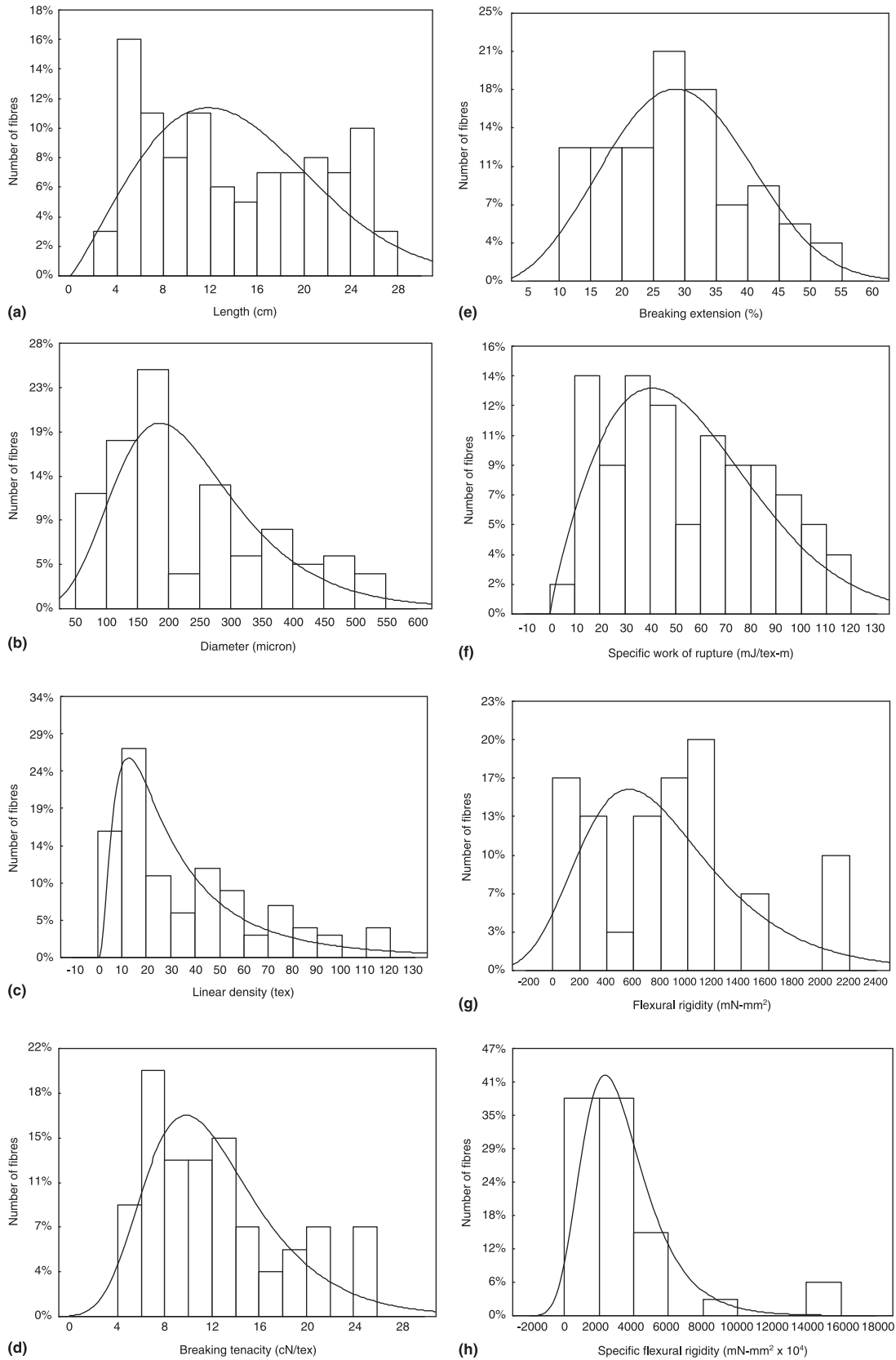


Fig. 7 (a) Length distribution of coconut fiber. (b) Diameter distribution of coconut fiber. (c) Linear density (fineness) distribution of coconut fiber. (d) Strength distribution of coconut fiber. (e) Breaking extension distribution of coconut fiber. (f) Specific work of rupture distribution of coconut fiber. (g) Flexural rigidity distribution of coconut fiber. (h) Specific flexural rigidity distribution of coconut fiber.

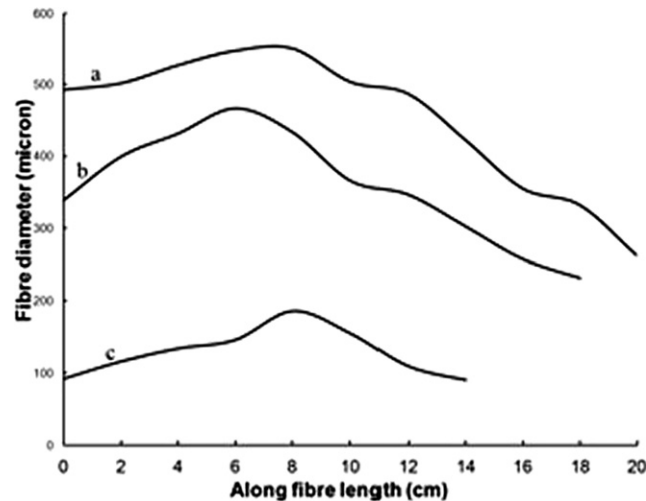


Fig. 8 Diameter distribution along the fiber length; (a) coarse fiber (62 tex), (b) medium fiber (25 tex), and (c) fine fiber (9.5 tex). Reproduced from Sengupta, S., Basu, G., Chakraborty, R., Thampi, C.J., 2014. Stochastic analysis of major physical properties of coconut fibre. *Indian Journal of Fibre and Textile Research* 39(1), 14–23.

and 7(c)). Due to differences in linear densities, segregation may be done by centrifugation or winnowing the fiber mix. The segregated fibers may be used for producing three different groups of materials. Long and coarse fibers may be used for producing conventional ropes and coarse RESM-S, while medium length and fine fiber may be used for making finer textiles materials with improved property parameters, either elementarily or in blends with other fibers. Short fibers may be used in making flexible or semi-rigid composites and also used as geofibre (Balan, 2004) for soil stabilization.

It may be worth noting that distribution of mechanical property parameters (viz., breaking tenacity and elongation) are much less asymmetric (Figs. 7(d) and 7(e)) as compared to the dimensional property parameters. The coefficient of variation of breaking tenacity (47.3%) and breaking extension (37.5%) is lower than the CV of length (50.9%) and diameter (52.9%). Distribution of specific work of rupture and flexural rigidity has been shown in Figs. 7(f) and 7(g), respectively. Specific flexural rigidity values were highly asymmetric with CV, 94.3% (Fig. 7(h)). The increased coefficient variation, in this case, may be attributed to the combination of the two highly variable physical parameters, flexural rigidity and linear density. The problem has been further aggravated due to variation in diameter along the length of individual fiber.

Diameter Distribution along the Fiber Length

Fig. 8 shows variation in fiber diameter along the fiber length. Sixty fibers were selected randomly and divided into three equal parts as fine, medium, and coarse according to its linear density. Diameter of all the fibers was measured from base to tip in 1 cm interval. The diameter of different fibers gradually increases from base to a mid-point, and then starts decreasing till the tip ends. The diameter of coarse fiber changes from 493 to 263 μm having the highest diameter at 550 μm with the coefficient of variation of 21.2%. The diameter of fine fiber changes from 93 to 91 μm having the highest diameter of 187 μm with the coefficient of variation of 25.6%. This may be one of the major reasons for high coefficient of variation of different fiber properties. Fig. 2 reveals that individual fiber possesses variable diameter along its length tapering off at both the ends.

Inter-Relation between Two Fiber Properties

Among the fiber properties studied, length, diameter, and linear density can be studied easily. A rough estimation of these parameters can be done without any sophisticated instrument. A simple stainless steel scale graduated in 10 divisions of a centimeter and an ordinary magnifying glass may be used to measure length and diameter, whereas a simple weighing balance may be used to get linear density. Therefore, it has been tried to understand the relationship (Table 5 and Figs. 9(a)–9(c)) between these three parameters individually with other fiber properties (Sengupta *et al.*, 2014) so that those properties can be predicted from these three primary parameters. The properties which are poorly correlated and insignificant with fiber length are not shown graphically.

Length is the most important primary parameter to judge fiber quality. This study shows a good correlation of fiber length with diameter (0.759), linear density (0.799), braking load (0.834), and specific work of rupture (0.743), out of which first three are positively correlated, whereas specific work of rupture is negatively correlated, i.e., with increase of length, it decreases. The significance of these relations has also shown by student *t*-test (significance level $\alpha \geq 0.5$) and corresponding *p*-value. Tenacity, breaking extension, flexural rigidity, and specific flexural rigidity are poorly correlated with length and this is supported by the

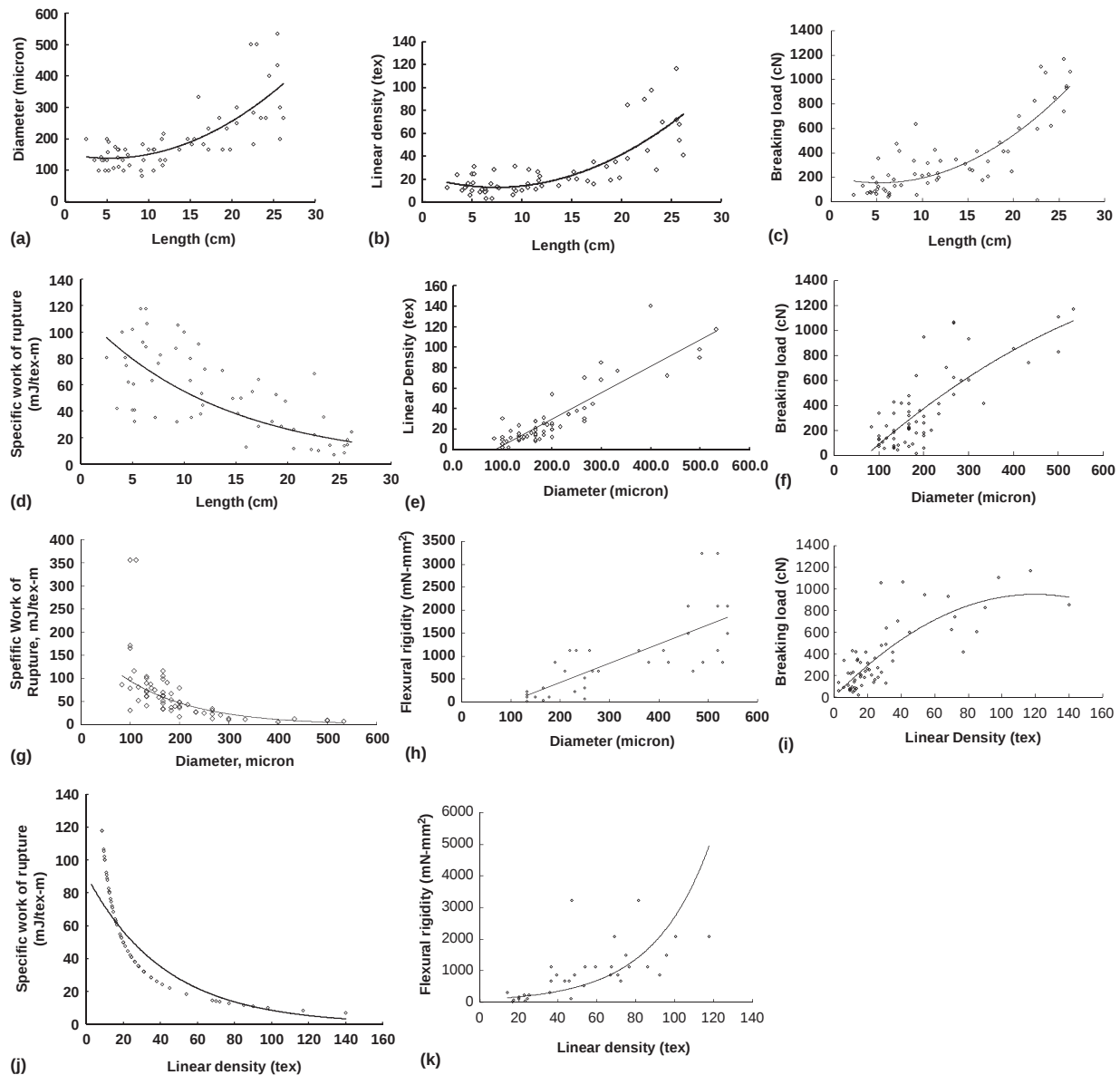


Fig. 9 (a) Effect of fiber length on diameter. (b) Effect of fiber length on linear density. (c) Effect of fiber length on breaking load. (d) Effect of fiber length on specific work of rupture. (e) Effect of diameter on linear density of fiber. (f) Effect of diameter on breaking load of fiber. (g) Effect of diameter on specific work of rupture of fiber. (h) Effect of diameter on flexural rigidity of fiber. (i) Effect of linear density on breaking load of fibers. (j) Effect of fiber linear density on specific work of rupture. (k) Effect of fiber linear density on flexural rigidity.

t -test and p -values. **Table 5** shows the best-fit equations for each relation. Diameter, linear density, and braking load follow the second order polynomial, whereas specific work of rupture follows exponential curve. **Figs. 9(a)–9(d)** show the effect of fiber length on diameter, linear density, braking load, and specific work of rupture of fibers.

Diameter is another important primary parameter for fiber quality assessment. This study shows a good correlation of fiber diameter with length (0.799), linear density (0.893), braking load (0.785), specific work of rupture (0.826), and flexural rigidity (0.764) out of which first three are positively correlated. The significance of these relations is also shown by student t -test (significance level $\alpha \geq 0.5$) and corresponding p -value. Tenacity, breaking extension, and specific flexural rigidity are poorly correlated with diameter and this is supported by the t -test and p -values. **Table 5** shows the best-fit equations for each relation. Diameter is related with linear density by linear equation and load by second order polynomial, whereas other properties exponentially. **Figs. 9(a)** and **9(e)–9(h)** show the effect of diameter on length, linear density, braking load, specific work of rupture, and flexural rigidity of fibers.

Linear density is an important primary fiber quality for processability point of view. This study shows a good correlation of linear density with length (0.799), braking load (0.804), specific work of rupture (0.934), and flexural rigidity (0.739), out of which length, braking load, and flexural rigidity are positively correlated, i.e., with increase of linear density other parameters increases, whereas

specific work of rupture is negatively correlated, i.e., with increase of linear density it decreases. The significance of these relations is also shown by student *t*-test (significance level $\alpha \geq 0.5$) and corresponding *p*-value. Tenacity, breaking extension, and specific flexural rigidity are poorly correlated with linear density and this is supported by the *t*-test and *p*-values. Table 5 shows the best-fit equations for each relation. Diameter and braking load follow the second order polynomial, whereas others are related exponentially. Figs. 9(b) and 9(i)–9(k) show the effect of linear density on length, braking load, specific work of rupture, and flexural rigidity of fibers.

In all the cases, it is apparent that the relations of easily measurable parameters (length, diameter, and linear density) with breaking tenacity and specific flexural rigidity are very poor due to the combined effect of very high variability of linear density as well as basic parameter, i.e., breaking load or flexural rigidity. High linear density variation may be due to the age of the fibrous elements within or between the nuts. On reaching the maturity level, deposition of biological elements increases in both longitudinal and radial directions of the individual fibrous element as duration increases before harvesting. Furthermore, the diameter as well as linear density also varies along the length of fiber. The breaking extension is always poorly correlated, as it is mainly governed by weak places and structural defects of fibers and not by the basic fiber parameters. That is why the extensibility of fibers is unpredictable by length, diameter, and linear density.

The best-fit equations with significant correction coefficient help to predict major fiber quality parameters (linear density, breaking load, specific work of rupture, and flexural rigidity) by easily measurable parameters (length and diameter). Since, the grading is generally done at growers' field or at the market yard, our aim is to assess the quality characteristics of fiber in shorter period of time adopting minimum number of easily measurable parameters. The predicted values will help to grade the coconut fiber lot in farmers' field by measuring length and diameter using ordinary scale and magnifying glass. By this process the farmer will fetch good economic return from the fiber.

Textile and non-textile products prepared from the fibrous materials depend on fiber property and structural parameters of end product (Goswami *et al.*, 1977). The major dimensional and mechanical property parameters of fibers include length, diameter, linear density, strength, elongation, work of rupture, and flexural rigidity. Longer and finer (lower linear density) fiber produces stronger, regular, and less hairy products. Soft fiber (low flexural rigidity) requires much less energy to twist a fiber bundle to make thread-like material. Soft fiber also yields stronger and softer textile materials. The increase in linear density, caused due to increased deposition of lignocellulosic matters, restricts intermolecular movements during bending, resulting in high rigidity. Toughness (specific work of rupture) depicts the combined effect of fiber strength and elongation, and it indicates end use performance of the product. The stated fiber parameters also decide some other important product functional parameters, i.e., handle, insulation, etc.

Defects in Fibers

Four main defects are identified namely (1) coconut peat, a dust-like matter of small particle size (10.64%); (2) mid-joint, a sticky bark-like matter at the middle of fiber (6.03%), (3) branched fiber, branching out from the main fibrous element (2.35%), and (4) insect bite (2.31%). On physical verification, it is found that the coco-peat would be removed from the fibers during their mechanical processing, such as opening, cleaning, and drawing. Similarly, the mid-joints would also be opened up during the same processing machines. So, coco-peat and mid-joints may be considered as minor defects. Though, weight loss to an extent of 10% (or more) may cause monetary loss to the fiber processing units. Some branched fiber and insect bitten may be remained in the fibers even after initial mechanical processing and this would not be suitable for mechanical conversion to finer or value-added end products. So, branched fiber and insect bite may be considered as the major defect. Different defects are shown in Figs. 10(a)–10(d) (Sengupta *et al.*, 2014).

Defects in fiber are one of the major parameters of fiber quality in terms of its processability, generation of waste and quality of the output of the machine. Minor defects are generally eliminated during processing of fiber and most of them are generally dropped down during processing in the machines and do not affect the end product quality. However, minor defects have some economic importance due to the waste generated from fiber lot. Among the major defects, branched fiber may cause generation of hairiness on the yarn surface. Insect bitten fiber may affect strength and appearance properties of the intermediate or of the end product.

Chemical Properties of Raw Coconut Fibers

Chemical Composition

The chemical composition of coconut is given in Table 6, which shows that brown coconut fiber contain relatively low amounts of cellulose but have high-lignin content. The exceptionally high-lignin content implies that the available dyeing and bleaching techniques for textile fibers cannot simply transferred to coconut fibers/products.

Treatment with Water

Treatment with water (Table 7) at boil and steaming for 2 h causes weight loss of 2.6 and 7.2% respectively in raw coconut fiber. Water treatment at boil leaches out part of the water soluble matters. However, under steaming, water insoluble matter including pectin, low-molecular-weight hemicellulose fraction apparently gets leached out contributing to additional weight loss. The flexural rigidity value of 1273 cN mm² of the raw coconut fiber has lowered to 1235 and 1177 cN mm² on boiling and steaming the fiber for 2 h respectively (Basu *et al.*, 2015).



Fig. 10 (a) Branched fiber. (b) Insect bite. (c) Coconut pit. (d) Mid-joint.

Table 6 Chemical composition of raw coconut fiber (% of bone dry weight)

<i>Constituent</i>	<i>%</i>
α -Cellulose	38.4
Lignin	31.8
Hemicelluloses	24.5
Pectin	0.5
Ash	1.6
Fats and waxes	1.1

Treatment with Sulphuric Acid

The treatment (Table 7) using H_2SO_4 (40% and above) at ambient temperature, results in surface carbonization with gradual solubilization (complete or partial) of the fiber. However, for concentration of 30% and below for H_2SO_4 , the fibers resist the treatment for 1 h without any surface carbonization. The action of HCl is milder than H_2SO_4 , which shows no surface carbonization under the

Table 7 Effect of treatments on physical and mechanical properties of coconut

Expt. no.	Treatment	Physical property				Mechanical property			
		Weight loss(%) ^a	Diameter (μ n)	Linear density (tex) ^b	L/D ratio	Flexural rigidity (cN mm ²)	Breaking tenacity (cN/tex)	Breaking elongation (%)	Specific work of rupture(mJ/ tex-m)
1	Control	–	345 (57)	53 (58)	695 (61)	1273 (49)	11.3 (67)	21.5 (33)	12.1 (42)
2	Backwater retted	–	282 (37)	44 (49)	748 (58)	613 (57)	14.0 (53)	27.1 (39)	12.0 (58)
3	Water at boil for 2 h	2.60 (10)	381 (55)	52 (46)	689 (48)	1235 (64)	12.1 (46)	18.8 (27)	13.9 (43)
4	Steaming at 121°C for 2 h	7.20 (7)	347 (56)	48 (58)	712 (62)	1177 (67)	12.2 (56)	19.2 (41)	14.5 (42)
5	20% NaOH at boil for 2 h	12.2 (13)	341 (53)	45 (67)	789 (73)	1034 (49)	13.8 (39)	24.7 (36)	19.3 (48)
6	40% Na ₂ S at boil for 2 h	17.6 (8)	227 (57)	41 (47)	917 (54)	731 (76)	13.4 (41)	27.8 (29)	18.1 (41)
7	15% Na ₂ CO ₃ at boil for 2 h	11.5 (9)	359 (54)	49 (57)	742 (63)	1084 (49)	11.9 (46)	22.4 (42)	12.5 (56)
8	40% Na ₂ S, 20% NaOH at boil for 2 h	21.7 (9)	249 (52)	43 (59)	898 (72)	893 (56)	11.8 (87)	21.5 (37)	18.2 (56)
9	40% Na ₂ S, 15% Na ₂ CO ₃ at boil for 2 h	20.1 (11)	255 (57)	48 (47)	915 (59)	921 (64)	12.1 (65)	21.2 (35)	17.4 (47)
10	40% Na ₂ S, 15% Na ₂ CO ₃ , 20% NaOH at boil for 2 h	28.4 (13)	225 (41)	34 (52)	991 (63)	361 (55)	14.2 (59)	21.3 (33)	21.6 (43)
11	3% H ₂ O ₂ for 2 h at 80°C(pH-11)	13.6 (9)	251 (59)	39 (39)	891 (48)	890 (53)	11.7 (57)	19.9 (36)	17.5 (39)
12	2% NaIO ₄ at boil for 2 h	6.40 (7)	276 (63)	52 (46)	734 (49)	1062 (48)	8.4 (51)	14.3 (45)	9.5 (47)
13	HCl (35%) at 30°C for 1 h	37.4 (23)	250 (64)	35 (57)	1073 (64)	745 (67)	2.9 (167)	3.90 (98)	0.5 (99)
14	H ₂ SO ₄ at 30°C for 1 h	Immediate surface charcoaling at and above 30% concentration and fiber became brittle during storage even after alkaline neutralization							

^aResults shows the mean value of ten repeat tests.^bTex is the weight of 1000 m long fiber in gram.

The figures in the parenthesis indicates CV% of the corresponding value.

Note: Basu, G., Mishra, L., Jose, S., Samanta, A.K., 2015. Accelerated retting cum softening of coconut fibre. Industrial Crops and Products 77, 66–73.

treatment conditions. However, both the treatments made the fiber brittle during storage even after alkali neutralization, probably due to hydrolysis of cellulose polymers by the acids (breakage of the β -1,4-glycosidic bonds of cellulose) (Huang and Fu, 2013).

Treatment with Oxidizing Agent

The treatment (Table 7) of strong oxidizing agent NaIO₄ with coconut fiber (alkaline pH) results in more reduction in tensile properties than in flexural rigidity. This may be due to possible chain scission of 1,2-diols linkages of cellulose to form aldehydes and ketones (Hong *et al.*, 2009). Oxidizing agent, H₂O₂ (alkaline pH) is also not found to be sufficiently suitable to reduce the fiber flexural rigidity, though there is no adverse effect observed on the tensile properties of the fiber.

The treatment with Na₂S (Treatment No. 6), showed high weight loss (17.6%) and larger reduction in flexural rigidity, diameter, linear density and thereby increased the length to diameter ratio, improving the mechanical properties of coconut fiber. The reaction of Na₂S can be explained on the basis of its hydrolysis to convert into NaHS and finally to NaOH. The high alkalinity at elevated temperature of the treatment partially hydrolyzes the components of coconut fiber. Apart from this, NaHS reacts with lignin to introduce -SNa group which increases its acidity and solubility in alkaline medium. The Na₂S being a reducing agent retards the rate of hydrolysis and oxidation of cellulose (Tomlinson, 1950) causing lower damage to the fiber structure. Treatment of coconut fiber was also carried out using alkaline aqueous solution of NaOH and Na₂CO₃ separately. The individual treatment of NaOH and Na₂CO₃ has moderate reducing effect on fiber flexural rigidity.

The combination of Na₂S with NaOH reduces the flexural rigidity and breaking tenacity more than that of combination of Na₂S with Na₂CO₃. However, the binary treatments (Treatment No. 8 and 9), show lesser effect on fiber softening properties than the individual treatment of Na₂S (Treatment No. 6).

The ternary combination of Na_2S , Na_2CO_3 , and NaOH treatment (Treatment No.10 of Table 7) is found to be most effective in all respect. The combination of 40% Na_2S , 15% Na_2CO_3 , and 20% NaOH causes highest weight loss (about 28%) without affecting the tensile property. The treatment also reduced flexural rigidity, linear density, and diameter significantly resulting in enhancement of length to diameter ratio (Table 1). It is assumed that the combination of alkalis (NaOH , Na_2CO_3) might enhance the effect of Na_2S . Alkalis swell the structure of the fiber causing easy penetration of Na_2S for disruption of internal fiber structure. Further, in any natural fibers, the addition of alkali reduces the surface negative ion concentration by the excessive supply of Na^+ ion, which facilitates better reaction of the chemical with the fiber. Alkalis also tend to reduce the surface tension of the natural fibers and helps in saponification and emulsification of fat and wax (present on fiber surface of most natural fibers), which otherwise hinders the water based treatments. Besides pure cellulosic components, hemicelluloses and alkali soluble lignin part are solubilised or precipitated out by alkalis. The presence of Na_2CO_3 provides some action of detergency to the treatment solution and thus helps in holding the dirt and other insoluble impurities in the suspension from depositing on the fiber surface.

Chemical Properties of Retted Coconut Fibers

The change in major constituents of raw coconut fibers, due to backwater and newly developed chemical retting is given in Table 8. The chemically retted fiber shows considerably higher α -cellulose (54.2%) than both backwater retted (39.6%) and raw (38.4%) coconut fiber. The increase in cellulosic content is also evident in FTIR and XRD of chemically retted fibers. Chemical treatment resulted in reduction of lignin content of raw coconut fiber from 31.8 to 26.3%. The reduction of lignin content possibly decreases the flexural rigidity of the fiber up to a certain extent. The analysis also reveals notable reduction in other constituents of the fiber like hemicelluloses, pectin, fats, and waxes, and ash content due to chemical treatment. The removal of constituents other than cellulose (viz., lignin, hemicelluloses, pectin, fats, and waxes), which are not contributing toward the tensile parameters probably cause much better mechanical properties in terms of higher breaking tenacity, and work of rupture in chemically retted fiber. The trend of removal of constituents like, hemicelluloses, pectin, and fat and wax matters is also evident in backwater retting, but the extent of removal is trivial.

Infrared Spectrum Analysis

Fig. 11 shows the FTIR spectra of the (a) raw (b) conventionally backwater retted, and (c) accelerated chemically retted coconut fiber. It can be seen from the three spectra that, no considerable change occurs either in position or in appearance/disappearance of the peaks. However, there was a change in intensity of some of the peaks, such as 1250 , 1332 , and 1513 cm^{-1} observed. The broad and intense peak at $\sim 3340\text{ cm}^{-1}$ suggesting OH stretching vibrations from cellulose and lignin intensified in chemical retted fibers. The characteristic bands of hemicelluloses and lignin observed around 1741 cm^{-1} due to the conjugated $>\text{C}=\text{O}$ stretching of ester and aldehyde reduced more in chemically treated coconut fiber than the conventionally backwater retted fiber. No change is observed in β -glucosidic linkage peak of celluloses at 897 cm^{-1} in backwater retted and raw fiber. However the same peak intensifies slightly in case of chemically retted fiber. The C–O–C stretching absorption peak of cellulose at 1038 cm^{-1} remain similar in the three fibers (Samal *et al.*, 1995; Samanta *et al.*, 2008). This proves backwater retting and chemical retting do not affect the celluloses part of coconut fibers. However, the absorption peaks at 1250 cm^{-1} correspond to CO– stretching of esters, ethers and phenols groups attributed to the presence of waxes in the epidermal tissue (Brigida *et al.*, 2010) and at 1513 cm^{-1} correspond to lignin aromatic ring stretching (Mahato *et al.*, 2009), both drastically reduced in the chemically retted fiber due to the removal of wax and lignin respectively during chemical retting/softening of fiber.

Crystalline Structure Analysis

Fig. 12 shows the radial X-ray diffractogram of the three coconut fiber samples. Crystallinity Index (C.I.) of the chemically treated coconut fiber (54%) is much higher than the C.I. of the raw fiber (37%) and retted fiber (42%) as estimated by amorphous subtraction method. The diffractogram peaks (mainly peak 002) for the chemically retted fiber intensified considerably and got sharpened than the others indicating an enhancement of crystalline perfection due to removal of non-crystalline material like lignin, hemicellulose, pectin, etc., by the chemical treatment. Similar results were also reported by different authors (Varma *et al.*, 1984; Sreenivasan *et al.*, 1995) while discussing the effects of alkali treatments on coconut fibers.

Table 8 Chemical composition of coconut fiber (weight % on oven dry basis)

Components	Raw/unretted	Backwater retted	Chemically retted
α -Cellulose	38.44 ± 0.7	39.64 ± 0.21	54.16 ± 0.13
Lignin	31.84 ± 0.48	31.95 ± 0.02	26.29 ± 0.05
Hemicelluloses	24.54 ± 0.15	22.73 ± 0.9	14.04 ± 0.01
Pectin	0.5 ± 0.01	0.37 ± 0.03	0.00
Ash	1.41 ± 0.03	1.46 ± 0.06	0.76 ± 0.03
Fats and waxes	1.12 ± 0.001	1.09 ± 0.07	0.75 ± 0.01

Note: Basu, G., Mishra, L., Jose, S., Samanta, A.K., 2015. Accelerated retting cum softening of coconut fibre. *Industrial Crops and Products* 77, 66–73.

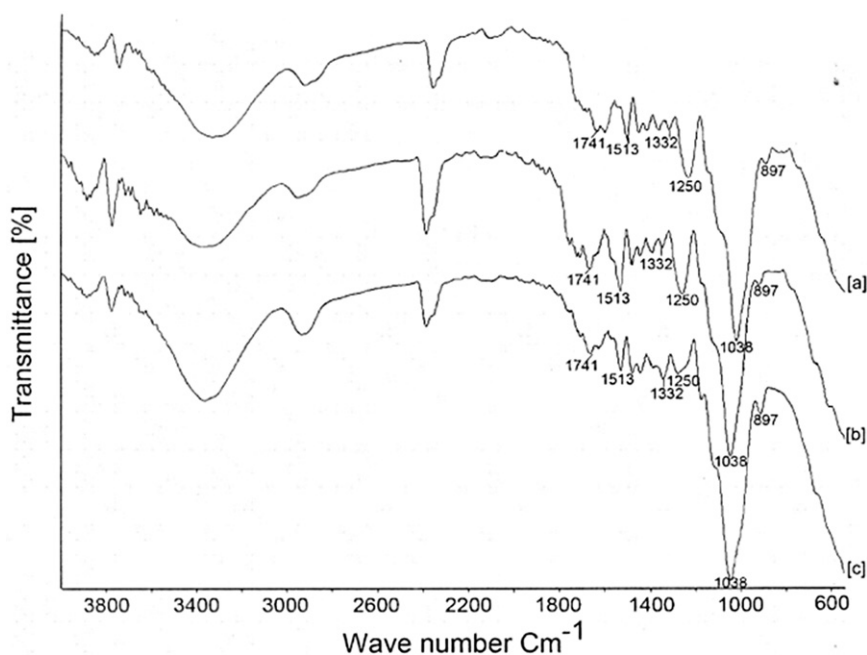


Fig. 11 FTIR Spectra of coconut fiber (a) raw, (b) backwater retted, and (c) chemically retted. Reproduced from Basu, G., Mishra, L., Jose, S., Samanta, A.K., 2015. Accelerated retting cum softening of coconut fibre. *Industrial Crops and Products* 77, 66–73.

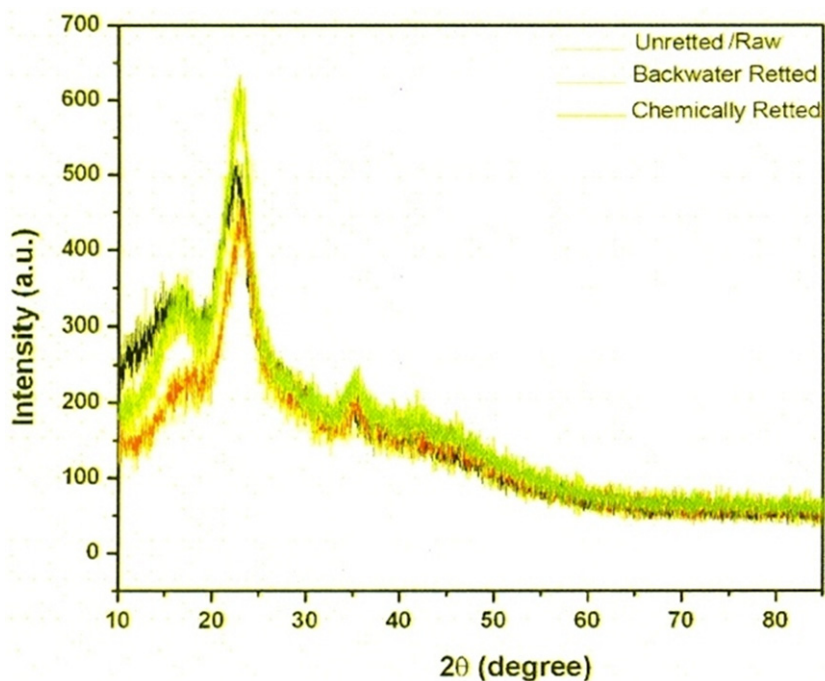


Fig. 12 XRD curves of coconut fiber. Reproduced from Basu, G., Mishra, L., Jose, S., Samanta, A.K., 2015. Accelerated retting cum softening of coconut fibre. *Industrial Crops and Products* 77, 66–73.

Thermal Analysis

The results of thermogravimetric analyses for raw, backwater retted and chemically retted coconut fibers are shown in [Fig. 13](#) and summarized in [Table 9](#). It can be seen that, decomposition of fibers are characterized by the temperature range. The initial decomposition of fiber takes place for evaporation of water and volatile substances (low-molecular-weight waxes and fats) occurs

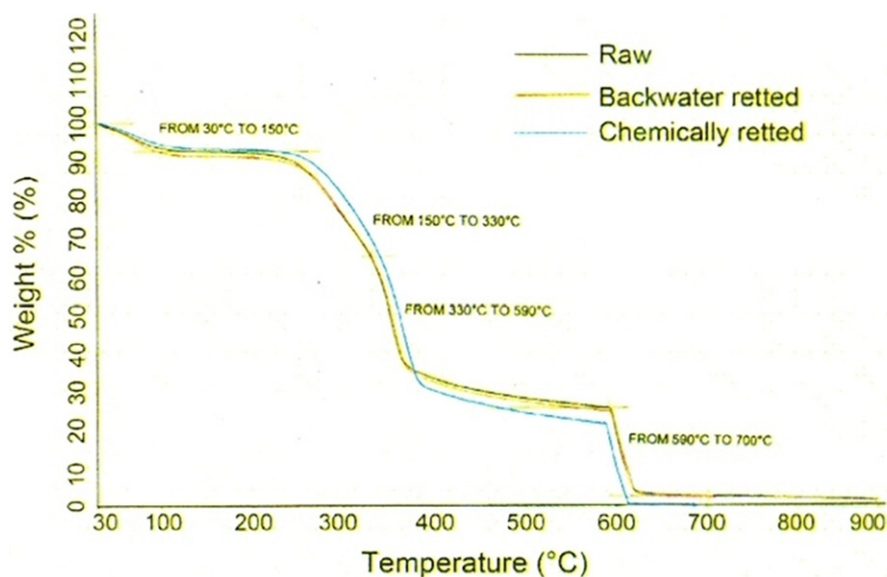


Fig. 13 TG curves of coconut fiber. Reproduced from Basu, G., Mishra, L., Jose, S., Samanta, A.K., 2015. Accelerated retting cum softening of coconut fibre. *Industrial Crops and Products* 77, 66–73.

Table 9 Thermogravimetric results of coconut fibers

Coconut fiber	Transition temperature range (°C)	Weight loss (%)	Residue ^a left (%)
Raw	30–150	7.39	2.8
	150–330	27.13	
	330–590	39.24	
	590–690	23.43	
Backwater retted	30–150	8.46	2.6
	150–330	26.77	
	330–590	39.12	
	590–690	23.02	
Chemically retted	30–150	6.84	0.7
	150–330	21.82	
	330–590	49.07	
	590–690	21.54	

^aDegradation residue at 700 °C.

Note: Basu, G., Mishra, L., Jose, S., Samanta, A.K., 2015. Accelerated retting cum softening of coconut fibre. *Industrial Crops and Products* 77, 66–73.

between room temperature and 150°C. The second weight loss corresponds to hemicelluloses degradation, starts at about 190°C. Weight loss occurs between 290 and 360°C mainly corresponds to cellulose degradation. Lignin degradation starts at about 280°C and continues even above 500 °C (Rosa *et al.*, 2009).

The chemical treatment have a considerable change on the thermal degradation behavior of coconut fibers as compared to raw and backwater retted fibers, which possess resembling profile of weight loss. The initial weight loss attributed to evaporation of water and volatile substances was found to be lowest (6.8%) for chemically retted fibers due to removal of some easily hydrolyzed substances (waxes and fats) during chemical treatment. The comparatively higher weight loss (8.5%) for evaporation of water observed in backwater retted fibers than raw (7.4%) fiber possibly due to the extra moisture adsorbed by the salty layer present on fiber surface (as constituent analysis reports similar content of fats and waxes). Chemically treated fiber showed markedly lower weight loss of 21.8 and 21.5% under the transition temperature range of 150–330 and 590–700°C respectively, as compared to raw and backwater retted fiber. The comparatively lower weight loss occurred in chemically treated fiber for the temperature range, is indicating the reduction in hemicelluloses and overall lignin content than the other two fibers. Chemically retted fiber showed notably higher weight loss (49.1%) in the temperature range of 330–590 °C as compared to weight loss observed for raw (39.2%) and backwater retted (39.1%) fiber. The higher weight loss for the said region is indicative of the degradation of notably higher amount of cellulosic material present in chemically retted fiber. Chemically retted fibers are left with much less residue of 0.7% as compared to residue left in case of raw (2.8%) and backwater retted (2.6%) fiber.

Differential Scanning Calorimetry

Fig. 14 shows DSC thermogram of coconut fiber. The relatively low temperature wide endothermic peak at 84.17°C is attributed to the evaporation of absorbed moisture and volatile substances (low-molecular-weight waxes and fats) of the fiber (Samanta *et al.*, 2008). The second weight loss corresponds to hemicelluloses degradation at temperatures 241.01°C (long). Degradation at 284.11°C (small) may be due to pectin (Ali *et al.*, 2009) and hemicellulose (Samanta *et al.*, 2008) jointly. Among the two major constituents of coconut fiber, an endothermic peak at 364°C is representative of cellulose degradation while, lignin, being the most resistant, shows an exotherm peak at 390.7°C and its degradation still continued till 497°C.

Quality Specifications

Retted Coir Fiber/White Fiber

Retted coir fiber, also called white fiber, is extracted from green natural coconut husks after retting in flowing, circulating or changed water for a period of minimum 3 months. However, if the fiber is made out of pre-crushed husks the retting period could be reduced suitably. The fiber shall be free from moisture and impurities. Grading has been shown in **Table 10**.

Brown Fiber

Brown fiber is mechanically extracted from the dry husks of matured and ripe coconut after soaking these husks in water. The fiber shall be free from moisture and impurities.

Length of fiber: The mechanically extracted coir fiber shall be grouped based on the length

Long fibers above 20 cm

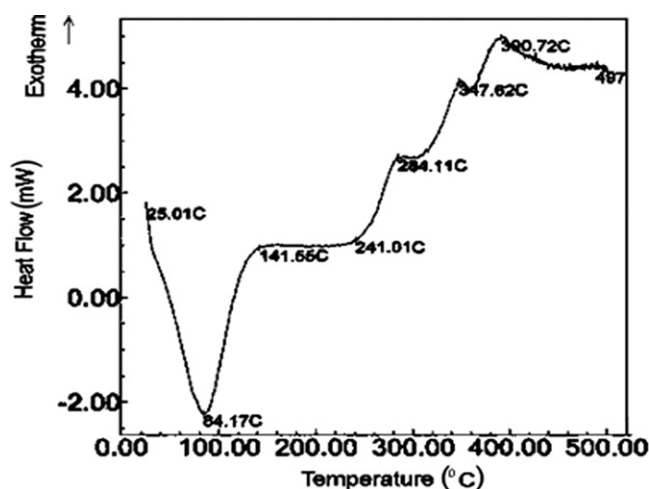


Fig. 14 DSC curve for coconut fiber. Reproduced from Basu, G., Mishra, L., Jose, S., Samanta, A.K., 2015. Accelerated retting cum softening of coconut fibre. *Industrial Crops and Products* 77, 66–73.

Table 10 Grading of retted/white coconut fibers

Grade	Color	Maximum impurities percent by weight
1	Natural bright	2.0
2	Natural light brown and/or light gray	3.0
3	Natural brown and/or gray	5.0
4	Natural dark brown and/or dark gray	7.0

Length of Fiber: The length of fibers shall be designated as follows:

'Long' over 15 cm.

'Medium' over 10 and up to 15 cm.

'Short' over 5 and up to 10 cm.

'Bit' up to and including 5 cm.

Source: Quality specifications. Available at: <http://coirboard.gov.in> (accessed 22.11.15).

Table 11 Percent by mass of 'Long,' 'Medium,' and 'Short' fibers and impurities in bristle coconut fiber

<i>Grade</i>	<i>Long Fibers Min.</i>	<i>Medium Fibers Max.</i>	<i>Short Fibers Max.</i>	<i>Impurities Max.</i>
Bristle fiber				
Grade I	50	30	20	4
Grade II	40	25	35	5

Source: Quality specifications. Available at: <http://coirboard.gov.in> (accessed 22.11.15).

Table 12 Percent by mass of 'Long,' 'Medium,' and 'Short' fibers and impurities in Mattress coconut fiber

	<i>Long/Medium Fibers Min.</i>	<i>Short Fibers</i>	<i>Impurities Max.</i>
Mattress fiber	110	90	20

Source: Quality specifications. Available at: <http://coirboard.gov.in> (accessed 22.11.15).

Table 13 Percent by mass of 'Long,' 'Medium,' and 'Short' fibers and impurities in decorticated coconut fiber

<i>Grade</i>	<i>Long Fibers Min.</i>	<i>Medium Fibers Max.</i>	<i>Short Fibers Max.</i>	<i>Impurities Max.</i>
Grade I	20	30	50	7
Grade II	20	25	55	12

Source: Quality specifications. Available at: <http://coirboard.gov.in> (accessed 22.11.15).

Medium fibers above 15 and up to 20 cm

Short fibers above 5 and up to 15 cm

Grading of bristle, mattress, and decorticated coconut fibers have been shown in **Tables 11–13**, respectively.

Conclusions

- Property-based advantages of coconut fibers:
 - Resistant to fungi and rot.
 - Provides excellent insulation against temperature.
 - Not easily combustible.
 - Flame-retardant.
 - Resistant to moisture and dampness.
 - Tough and durable.
 - Resilient; springs back to shape even after constant use.
 - Totally static free.
 - Easy to clean.
- Coconut fibers are multi-cellular, lignocellulosic, hard, a very coarse, and rigid variety of natural fruit fiber.
- The quality of coconut fiber, depends upon agro-ecological conditions (rainfall, humidity, soil, etc.), variety of seedlings and most importantly on stage of harvesting and process employed for extracting the fiber.
- A good-quality fiber can be obtained from the green coconut husk when they are in naturally hydrated condition. The fiber at this stage found to be whiter, flexible, softer, and easy for chemical processing.
- Scanning electron micrographs of the raw fiber surface reveals cracks, voids, and parallel ridges, which are further connected with intermediate nodes perpendicular to fiber length, forming more or less rectangular indentation. The cross-section of fiber is circular having central lumen.
- Distribution of all the physical properties such as length, diameter, linear density, breaking tenacity, breaking extension, specific work of rupture, flexural rigidity, and specific flexural rigidity of the raw coconut fibers are of asymmetric nature with high coefficient of variation.
- Diameter of a fiber varies along its length with tapering shape at the both ends.
- Length, diameter, and linear density – three dimensional properties are positively correlated among themselves. All these dimensional parameters are positively correlated with breaking load and negatively correlated with specific work of rupture. Flexural rigidity is positively correlated with diameter and linear density.

9. The major defects of coconut fibers are branched fiber, short and weak fiber, whereas, minor defects are coconut pect and mid-joint.
10. Softening treatment of raw coconut fiber with combination of Na_2S , Na_2CO_3 , and NaOH decreases the flexural rigidity value of raw fiber by 75% without any deterioration of desirable properties viz., strength and elongation.

See also: Jute/Coir/Banana Fiber Reinforced Bio-Composites: Critical Review of Design, Fabrication, Properties and Applications. Kenaf Fiber Based Bio-Composites: Processing, Characterization and Potential Applications. Natural Fiber and Synthetic Fiber Composites: Comparison of Properties, Performance, Cost and Environmental Benefits. Properties and End-of-Life of Polymers From Renewable Resources. Renewable Agricultural Fibers as Reinforcing Fillers in Plastics: Mechanical Properties of Kenaf Fiber-Polypropylene Composites

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Further Reading

Available at: www.coirboard.gov.in (accessed 22.11.15).

Recycling of Polylactide

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Circular Economy and Valorization of Bioplastics

Due to their high potential of replacement of petroleum-based polymers, the design, use, and disposal routes of bio-based polymers must be carefully strategized to ensure appropriate service conditions and adequate valorization and/or elimination means after their service-life. The balance between the long-term properties and the end-of-life of bio-based polymers is key to set up a design for sustainability (Badia *et al.*, 2017).

Poly (lactic acid) is the polymer resulting from the polycondensation reaction of its monomer, lactic acid. In contrast, the ring-opening polymerization of the cyclic lactide dimer brings up polylactide, which usually results in a polymer with higher molar mass than that of poly (lactic acid). Both are usually termed as PLA in literature and care must be taken to understand its origin previously to its transformation. PLA is an aliphatic polyester and biocompatible thermoplastic, currently considered a promising material with an outstanding development prospect and highlighted as a green eco-friendly material. A review on the properties, origin, applications, and market of PLA is reported by Madhavan Nampoothiri *et al.* (2010). The carbon source for microbial production of lactic acid can be either sugar in pure form such as glucose, sucrose, lactose, etc. or sugar-containing materials such as molasses, whey, sugar cane, and cassava bagasse, or starchy materials from potato, tapioca, or wheat, among others. PLA-based materials are essentially referenced on three different markets: Biomedical, agricultural, and packaging, in the last case mainly for food-contact applications. Manufactured products are blow-molded bottles, injection-molded cups, spoons and forks, thermoformed cups and trays, paper coatings, fibers for textile industry or sutures, films and various molded articles. These applications have a short life and most of the time the goods are discarded leaving their properties intact. One might think that there is a lot of invested time, intellectual effort, and economical resources to create high-tech packages with outstanding properties just to be used and discarded within a few short minutes.

A smart combination of the routes of production, valorization, and disposal might therefore lead to reduce the environmental impact and gear bio-based polymers towards added-value applications.

There are several routes to valorize plastics: (1) material valorization, which considers the obtaining of material from another material, by means of reusing, mechanical recycling or chemical recycling, which is also termed as feedstock recycling; (2) energy valorization, which is aimed at obtaining energy from thermal treatments such as pyrolysis or gasification; (3) biological valorization, which comprises the natural reincorporation of plastics into the carbon cycle, by means of biotic agents such as microorganisms or enzymes. The initial trends of research on bioplastics were focused on their biodegradability, and therefore their end-of-life was designed to be treated in biological valorization facilities such as composters. However, from a circular economy perspective (Spierling *et al.*, 2019), it is advisable to explore the possibilities of potentiating the recovery of plastics towards downgraded, similar, or upgraded applications, by means of material valorization routes, previous to final biological or energy valorizations. The key is to enlarge the path of bioplastics along the cradle-to-cradle journey, and avoid the cradle-to-grave shortcuts.

Among the aforementioned valorization routes, mechanical recycling represents one of the most cost-effective methodologies, since they are economically affordable, the technology is ready, and the know-how is well-established along the transformation pathway. This fact offers discarded bioplastics a new chance to perform at good level of conditions. Therefore, a revision of the most relevant works on the mechanical recycling of PLA is performed in this article. The influence of degradation is evaluated in terms of structural and morphological changes, in close connection with the performance of recycled PLA on its processability, thermal and mechanical properties, and mass transfer capabilities. PLA-based blends and PLA-based nanocomposites are also considered, since they are close to real applications in market.

Mechanical Recycling of PLA

Simulation of Mechanical Recycling

Mechanical recycling is a type of material valorization that uses thermo-mechanical means to produce a new product from another used product. This new product is usually affected by degrading conditions during the whole life cycle of the material, from production to discarding, in addition to the effects of environmental solicitations during their use. Therefore, a new production cycle will affect on their performance and thus usually leads to downgraded applications. In the near future, PLA will probably compete with the commodities' market, and therefore the society must start wondering how to manage the inherent new source of bioplastics waste, since nowadays there are not specific routes for its recovery and valorization at industrial scale. This issue has brought attention to scientists to perform simulations of mechanical recycling and subsequently understand the impact of these processes on its structure and correlated performance.

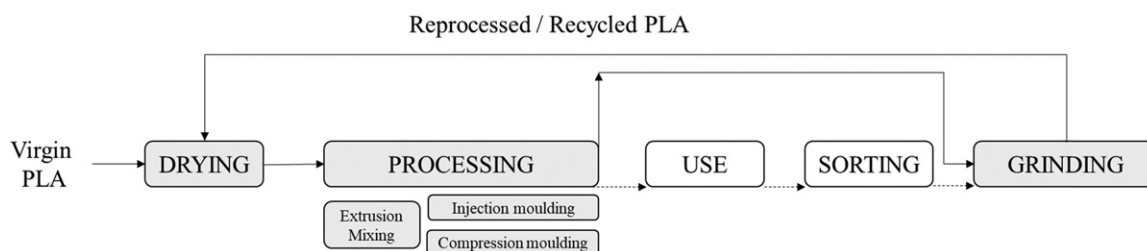


Fig. 1 Scheme of common experimental approaches to the simulation of mechanical recycling of PLA.

The common experimental approaches to simulate the mechanical recycling of PLA are shown in **Fig. 1**. It usually considers a prestage of drying, due to the high hygroscopicity of PLA, which may lead to hydrolytic reactions during subsequent processing at relatively high temperatures. It is followed by processing, by means of extrusion or mixing and ulterior shaping by injection or compression molding. At lab conditions, it is usually driven to a grinding process, to granulate the material to feed the process again.

It is important to remark that the results in literature concerning recycled PLA have to be taken with care, since it might not be representative of the same recycling route. For instance, during the processing stage, some materials are just taken from the extruded fraction to the subsequent grinding. In these studies, injection or compression molding are used for shaping the probes for mechanical or viscoelastic tests but, in essence, they account for another processing cycle in its lifetime, which is not usually considered in terms of reprocessing cycles. In contrast, in other studies, the grinding is performed after the injected or compressed cycles, and therefore the reprocessing cycle considers both processes in the cycle. Therefore, the comparability of data is somehow compromised. Nevertheless, the trends of the evolution of properties gathered in this article permit to understand in broad terms the influence of recycling on the performance of PLA.

As the reader might wonder, reprocessing and recycling do not essentially represent the same concept, though in literature there is a risk to confuse them. Reprocessing does not take into account the stages of use and sorting, and therefore this simulation is relevant to understand the reuse of leftover flakes in the industry. This is the case of most of the studies found in literature. In contrast, studies that account for the use or sorting of PLA are hard to find. At lab conditions, the use has been simulated by thermo-oxidative aging, usually maintaining the PLA probes in contact with air at high temperature, close to the glass transition temperature. However, no relevant studies have been found simulating recycling of PLA with other plastics in semireal conditions, where the influence of contamination of other fractions could be analyzed.

Under these conditions, the most relevant studies to date that approach the reprocessing of PLA have been gathered in this article, and summarized in **Table 1**. The numbers of reprocessing cycles and the type of main processing stage have been considered, along with the most relevant analytical techniques and specific indicators of quality of the key aspects of PLA, for example, structure, processability, mechanical properties, and mass transfer, which are tackled in the following subsections.

Degradation Mechanisms of PLA Induced by Mechanical Recycling

Thermo-mechanical degradation induced by mechanical recycling of PLA considers the impact of degradation agents such as temperature, oxygen, humidity, mechanical stresses, or light, individually or in combination. Even if technical measures are taken to prevent the contact of PLA with the environment at high temperatures, oxidation, and hydrolysis end up in chain scission reactions; while transesterifications modify the molar mass distributions of the polymers and therefore affect to their morphological properties in terms of amorphous-to-crystalline ratio, chirality, or steric rearrangements. The temperature of many PLA processing routes should not exceed 230°C to avoid thermal degradation via nonradical reactions, which would lead to a significant decrease in molar mass that has an important effect on the performance of PLA.

A particular analysis of the macromolecular species that take place during mechanical recycling of PLA was carried out by *Badía et al. (2011)*. The postulated mechanistic routes, as obtained from MALDI-TOF-MS analysis, along with the evolution of oligomeric species encountered after up to five injection-grinding cycles is shown in **Fig. 2**. The main reactions are hydrolysis (route I), which provoke the formation of hydroxyl and carboxyl linear oligomers with shorter chain length. In addition, esterification and intra- and intertransesterifications (routes II, III, and IV, respectively) occur by backbiting, that is, from the end of the chain, and at the middle of the chain, which leads to the formation of cyclic oligomers and linear species with shorter length, modifying the molar mass distribution. The most remarkable changes were those occurring for linear $H-[LA_L]_n-O-CH_3$ species, which presented a noticeable increase, being the most predominant species after three processing cycles, and achieving a proportion of up to 40% for the fourth recycle.

Structural and Morphological Changes Induced by Mechanical Recycling on PLA

The impact of mechanical recycling on the structure and morphology of PLA will directly determine its final behavior in terms of processability, performance, and durability. Therefore the application of specific techniques to establish proper indicators of degradation is a fundamental step in the design context, as highlighted in **Table 1**.

Table 1 Summary or relevant studies in literature on the reprocessing of PLA

	References	Żenkiewicz et al. (2009)	Pillin et al. (2008)		Brüster et al. (2016)	Scaffaro et al. (2011)	Cruz Sanchez et al. (2017)	Beltrán et al. (2016)	Carrasco et al. (2010)
Mechanical recycling simulation	PLA trade	PLA2002D Natureworks	PLLA L9000 Biomer	PLA2002D Natureworks	PLA4042D Natureworks	PLA3001D Natureworks	PLA4043D Natureworks	Ingeo 2003D Natureworks	PLA2002D Natureworks
	D-PLA content	4.20%	8%	4.20%	4.20%	—	—	—	4.20%
	Procedure	Extrusion + grinding + [injection]	Drying + injection + [compression]	Drying + injection + grinding	Predrying + extrusion + grinding + compression + grinding	Injection + extrusion + grinding	Injection + extrusion + 3D printing + grinding	Annealing + drying + extrusion + [compression] + previous UV-aging or H ₂ O-T-aging	Injection + annealing + extrusion + grinding
	Recycling cycles	10	7	5	5	3	4	1	1
Processability	Differential scanning calorimetry	$T_{g0}, T_g, T_{cc0}, T_{cc}, \Delta h_{cc}, T_{m0}, T_m, \Delta h_m$	$T_g, T_{cc}, \Delta h_{cc}, T_m, \Delta h_m$	$T_g, T_{cc0}, T_{cc}, \Delta h_{cc}, T_m, \Delta h_m$, Melting peak separation	$T_g, T_{cc0}, T_{cc}, \Delta h_{cc}, T_m, \Delta h_m$, Melting peak separation	$T_g, T_{cc}, \Delta h_{cc}, T_m, \Delta h_m$	—	$T_g, T_{cc}, \Delta h_{cc}, T_m, \Delta h_m$, Melting peak separation	$T_g, T_{cc}, \Delta h_{cc}, T_m, \Delta h_m$
	Thermogravimetry	T_d	—	—	—	—	—	TG profiles	T_5, T_{50}, T_{95}, T_p
	Rheometry	—	—	—	η	η_0	—	—	—
	Viscometry	—	η_0	—	—	—	—	$[\eta]$	—
	Melt-flow index	<i>MFI</i>	—	—	—	<i>MFI</i>	—	—	<i>MFI</i>
Chemical structure, Macromolecular arrangement	Size exclusion chromatography	—	THF-solvent UV-detector PS-calibration M_n, M_w, PDI	—	CHCl ₃ -solvent RI-detector PS-calibration M_n, M_w, PDI	—	—	—	HFIP-solvent RI detector PMMA calibration M_n, M_w, PDI
	Viscometry	—	—	η, MV	—	—	—	—	—
	Microscopy	—	—	SEM	SEM, AFM	SEM	—	—	—
	Spectroscopy	—	—	FTIR-ATR, $I_{C=O}$	FTIR-ATR	—	—	UV-vis-Haze, FTIR-ATR, $I_{C=O}$	FTIR-ATR
	MALDI-TOF-MS	—	—	$[LAC]_n, [LAL]_n$	—	—	—	—	—
	Differential scanning calorimetry	—	X_c	X_c	X_c	—	—	X_c	—
	Nuclear magnetic resonance	—	—	—	CH ₃ , CH chemical shifts	—	—	—	C=O, CH ₃ , CH chemical shifts
	X-ray diffraction	—	—	—	—	—	—	—	$2\theta, X_c$
Performance - Mechanical properties	Tensile testing	$E, \sigma_T, \epsilon_T, \sigma_B, \epsilon_B$	E, σ_B, ϵ_B	E, σ_B, ϵ_B	$E, \sigma_y, \sigma_B, \epsilon_B$	E, σ_T, ϵ_B	$E, \sigma_T, \epsilon_T, \sigma_B, \epsilon_B$	—	E, σ_y, ϵ_B
	Impact testing	σ_C	—	IC	IC	IC	—	—	—
	Flexural testing	—	—	—	—	G, σ_G	—	—	—
	Thermo-mechanical test	—	—	DMTA: $E', E'', tg(\delta), \Delta E_{GR}, \Delta E'_{RC}, D, B, m, Ea_{GT}, \Phi$	DMTA: $E', E'', tg(\delta)$	HDT	—	—	—
	Hardness	—	Nanoindentation, H, E	—	—	—	—	Micro-hardness, H, E	—
Performance- Mass transfer	Permeability gases	O ₂	—	—	—	—	—	N ₂ , O ₂ , CO ₂	—
	Permeability water vapor	H ₂ O	—	—	—	H ₂ O	—	—	—

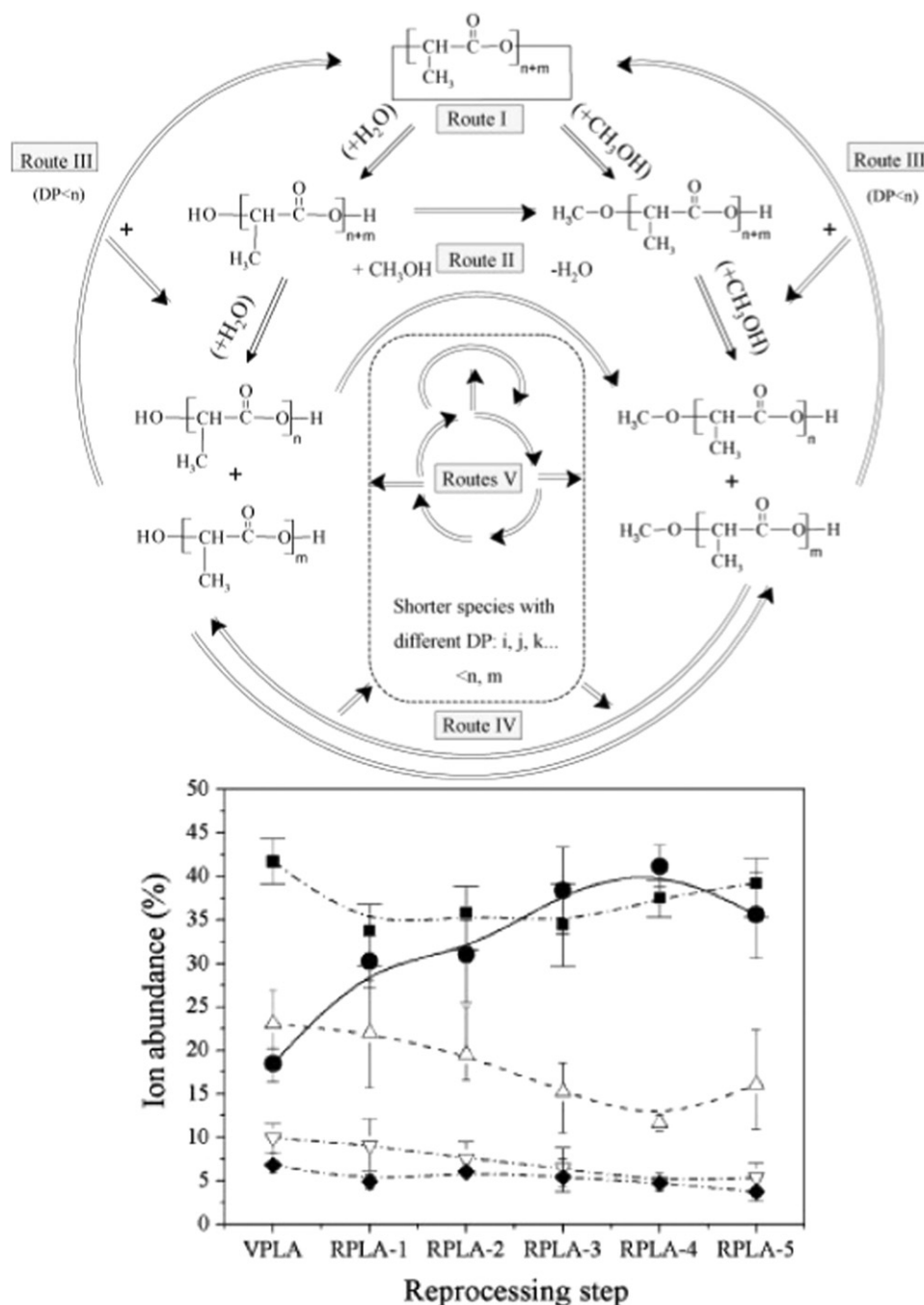


Fig. 2 Degradation pathways (up) and evolution of oligomers (down) as a result of the application of 5 successive thermo-mechanical cycles. Legends: square: $[LA]_n$; circle: $CH_3-O-[LA]_n-H$; up-triangle: $HO-[LA]_n-H$; down-triangle: $CH_3-O-[LA]_n-CH_3$; diamond: $CH_3-CO-O-[LA]_n-CH_3$, where LA stands for lactic acid repeating unit, L stands for linear and C for cycling oligomeric species. Reproduced from Badía, J.D., Strömberg, E., Amparo, R.G., Karlsson, S., 2011. Assessing the MALDI-TOF MS sample preparation procedure to analyze the influence of thermo-oxidative ageing and thermo-mechanical degradation on poly (Lactide). *European Polymer Journal* 47 (7), 1416–1428. doi:10.1016/j.eurpolymj.2011.05.001.

In this sense, among other techniques, size exclusion chromatography (SEC) permits to determine the molar mass distributions, Fourier-transform infrared spectroscopy (FT-IR) permits following the relative intensity of absorbance of specific functional groups, mass spectrometry (MS) and nuclear magnetic resonance offer the identification of macromolecular distribution of species in the polymer, differential scanning calorimetry (DSC) offers information about the relative amorphous-to-crystalline ratio, and X-ray diffraction (XRD) points out the degree of crystallinity.

To picture the impact of thermo-mechanical degradation on the structure and morphology of PLA, three analyses by means of SEC, FT-IR, and DSC have been selected in Fig. 3.

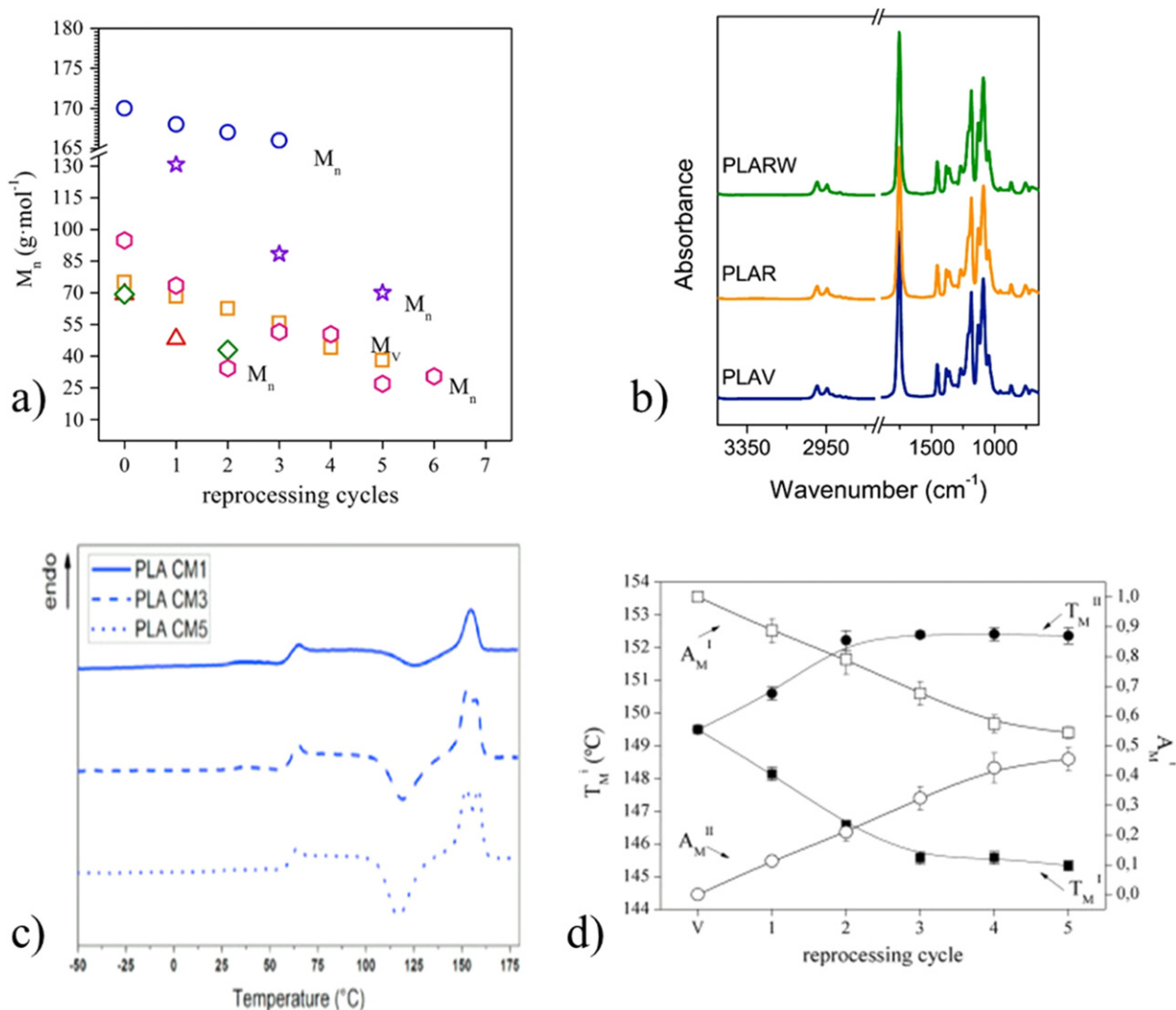


Fig. 3 Structural impact of mechanical reprocessing on PLA. (a) Molar mass (number- M_n , viscous- M_v) decay after several processing steps. Reproduced from Badia, J.D., Ribes-Greus, A., 2016. Mechanical recycling of polylactide, upgrading trends and combination of valorization techniques. *European Polymer Journal* 84, 22–39. doi:10.1016/j.eurpolymj.2016.09.005; (b) FTIR-ATR spectra of PLA subjected to different simulated mechanical recycling processes (V=virgin; R=recycled; RW=recycled with washing step). Reproduced from Beltrán, F.R., Ortega, E., Solvoll, A.M., *et al.*, 2018. Effects of aging and different mechanical recycling processes on the structure and properties of poly(lactic acid)-clay nanocomposites. *Journal of Polymers and the Environment* 26 (5), 2142–2152. doi:10.1007/s10924-017-1117-z; (c) Representative DSC curves of (a) PLA after 1, 3, and 5 processing cycles. Reproduced from Brüster, B., Addiego, F., Hassouna, F., *et al.*, 2016. Thermo-mechanical degradation of plasticized poly(lactide) after multiple reprocessing to simulate recycling: Multi-scale analysis and underlying mechanisms. *Polymer Degradation and Stability* 131, 132–144. doi:10.1016/j.polymdegradstab.2016.07.017; (d) Evolution of partial melting areas (A_M^I) and partial melting temperatures (T_M^I) obtained from the DSC analysis of the effect of five successive reprocessing cycles on PLA. Reproduced from Badia, J.D., Strömberg, E., Karlsson, S., Amparo, R.G., 2012d. Material valorization of amorphous polylactide. Influence of thermo-mechanical degradation on the morphology, segmental dynamics, thermal and mechanical performance. *Polymer Degradation and Stability* 97 (4), 670–678. doi:10.1016/j.polymdegradstab.2011.12.019.

Badia and Ribes-Greus (2016) reviewed the trends of molar mass evolution of different studies and found a general reduction of the molar mass in number M_n and the viscous molar mass M_v , regardless the molar mass of the virgin PLA, the type of processing or the number of reprocessing cycles, which meant that the PLA backbone suffered from scissions induced by mechanical recycling (Fig. 3(a)).

The most relevant functional group affected by degradation, observed by FT-IR, as shown by Beltrán *et al.* (2018) for PLA, reprocessed PLA and reprocessed PLA with a washing step, is that of the increase of the band related to the stretching vibration of C=O bonds, around 1750 cm^{-1} , which permits tracking degradation by the apparition of new carbonyl-linked species (Fig. 3(b)).

Concerning the amorphous-to-crystalline ratio, the impact will be different depending on the D-isomers of PLA, which induce its intrinsic semicrystalline or amorphous nature. As an example, the DSC traces of the second calorimetric scan, that is, after

erasing the thermal history and applying a controlled annealing ramp, are shown in Fig. 3(c), for PLA reprocessed up to five successive times. In this study, Bruster *et al.* (2016) analyzed a PLA that remained completely amorphous regardless the number of reprocessing cycles. In fact, the melting events at temperatures near 150°C correspond to the fusion of the crystallites formed during the DSC experiment at the so-called cold-crystallization, around 120°C. The assignation of the melting to a real crystalline fraction is, however, one of the main mistakes in literature and therefore the analyses must be taken with care and counterchecked, in case of doubts, with techniques such as XRD.

Nevertheless, it is still possible to establish patterns of degradation by means of indicators taken from DSC, as shown by Badia *et al.* (2012d) from the deconvolutions of the melting event and the proposal of monitoring of T_M^I and A_M^I , that is, the partial melting temperature peak and the partial area of the melting curve, respectively. As can be seen in Fig. 3(c), the shape of the endotherms showed a change from a monomodal to a bimodal distribution, which was attributed to a superimposed melting–crystallization–melting process, dependent on the kinetics of the DSC temperature program. A deconvolution process by means of Gaussian or Lorentzian curves would be helpful to discriminate between low-T and high-T pseudocrystalline populations. As pointed out in the study by Badia *et al.* (2012d), the melting peaks were progressively detached until the second reprocessing step, where the position of the endotherms, characterized by its peak temperature, held unmoved. The evolution of A_M^I decreased progressively reaching almost equal proportions as that of A_M^{II} , as shown in Fig. 3(d). The effect of the thermo-mechanical degradation could be ascribed to the variation of the first area A_M^I , which would be indicative of the promoted tendency of crystals to melt, and thus for molten shorter chains to recrystallize. Both overall decreases of $\sim 5^\circ\text{C}$ in T_M^I and $\sim 47\%$ in A_M^I suggested the presence of weaker cold-crystallized domains along the injection cycles, corresponding to the crystallization of scissored macromolecular chains.

Processability of Reprocessed PLA

The influence of mechanical recycling on the structure in terms of diminution of molar mass or modification of its molar mass distribution will affect the further possibilities of PLA to be reprocessed under similar and standardized technological conditions. It is, in fact, one of the key pillars to ensure a well-established industry of PLA worldwide. In this sense, the thermal stability and the flowing rates of the polymer shall be known and controlled. In this framework, as highlighted in Table 1, among other techniques, DSC and thermogravimetric analysis (TGA) permit to find out the thermal properties in inert or oxidative conditions and therefore determine the thermal ranges of operation and security (Badia and Ribes-Greus, 2016). Glass transition temperature, melting temperatures and enthalpies, onset temperature of decomposition, and mass-loss are the common indicators. Concerning flowability, rheometry (RH) and simpler but effective, viscometry (VISC), and melt-flow index (MFI) assessment are usually considered to assess viscosity or melt-flow rate.

To illustrate the effect of reprocessing on the thermal and thermo-oxidative stability of PLA, along with the impact on the flowability, three analyses by means of TGA, MFI, and RH have been brought to Fig. 4.

Fig. 4(a) shows the thermogravimetric (TG) curves for both virgin and fifth reprocessed polylactides analyzed under inert and oxidative atmospheres (VPLA, RPLA5, VPLA-O₂, and RPLA5-O₂, respectively) at the heating rate $\beta = 5^\circ\text{C min}^{-1}$ (Badia *et al.*, 2012a,c). The region for the induction of thermal and thermo-oxidative decompositions is zoomed in the upper-right region. The recyclates showed similar trends like those revealed by virgin PLA, with no relevant impact on the onset of decomposition. Since the results of thermogravimetry might be dependent on the technique and heating rate, a further analysis in terms of the temperature decomposition behavior (TDB) model and the zero-decomposition temperature (ZDT), which would prevent the results from having kinetic bias, can be found in literature (Badia *et al.*, 2012a,c).

Zenkiewicz *et al.* (2009) performed the measurement of MFI for PLA subjected to 10 successive extrusion–grinding cycles, as shown in Fig. 4(b). The simplicity of this technique allows the plastic industry to perform fast quality control checks and detect unexpected deviations from the desired specifications of thermoplastics. The chain scission induced by thermo-mechanical degradation provokes a reduction of molar mass, which turns evident in terms of increase of the MFI. Therefore, the higher the number of reprocessing steps was applied, the larger the MFI was, and therefore a closer inspection on the rheological behavior at different shear rates is advisable.

Scaffaro *et al.* performed rotational RH to PLA upgraded by an elastomeric impact modifier, and analyzed the evolution of viscosity as a function of frequency. RH permits identifying the flowing behavior at low, medium, and high shear rates and therefore adjust the technological processing parameters to give a new life to the downgraded PLA after recycling. In general, the decrease of the molecular weight was related to a decrease in the viscosity (Scaffaro *et al.*, 2011).

Influence of Recycling on the Mechanical Performance of PLA

Mechanical properties are, along with mass transfer barrier properties, the main issues raised by plastic producers when they face the challenge of using recycled material in their formulations. The capability of plastics to withstand the mechanical solicitations in service has to be therefore ensured in a routinely based manner. Literature frequently refers to mechanical properties of recyclates as better as or worse than those of the virgin polymer. This description of course discusses the resistance properties, but there are other mechanical properties that have to be taken into account such as flexibility, stiffness, toughness, or viscoelasticity, among others. Therefore, more specific descriptions must be detailed when reporting mechanical properties of polymers.

The most used techniques are tensile testing and flexural testing for resistance and flexibility, Charpy impact test to measure toughness, indentation to determine stiffness, or dynamical-mechanical-thermal analysis to understand viscoelasticity. The most

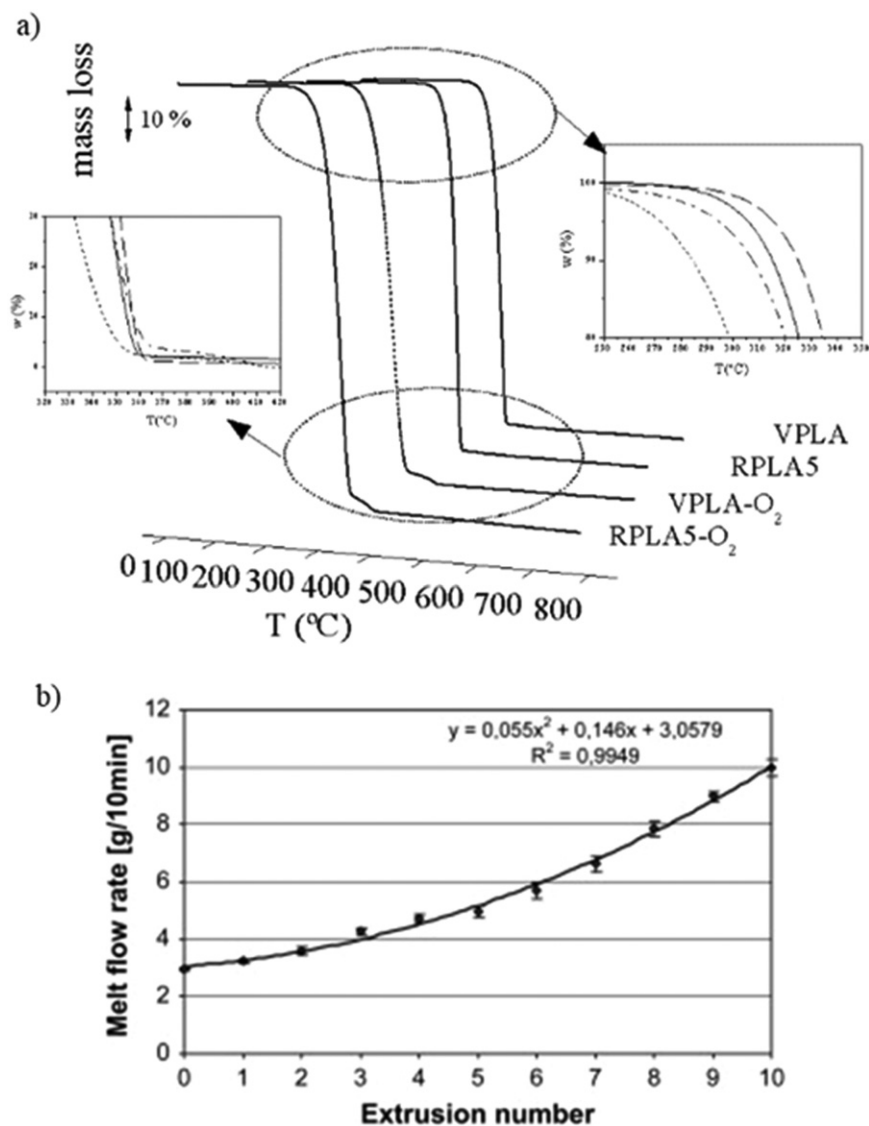


Fig. 4 Effects of reprocessing on the processability of PLA. (a) Comparison of thermal and thermo-oxidative stability of virgin PLA (VPLA) and PLA reprocessed five cycles (RPLA-5), as observed by thermogravimetry under inert and oxidative (O₂) conditions. Reproduced from Badia, J.D., Santonja-Blasco, L., Martínez-Felipe, A., Ribes-Greus, A., 2012a. A methodology to assess the energetic valorization of bio-based polymers from the packaging industry: Pyrolysis of reprocessed polylactide. *Bioresource Technology* 111, 468–475. doi:10.1016/j.biortech.2012.02.013. Badia, J.D., Santonja-Blasco, L., Martínez-Felipe, A., Ribes-Greus, A., 2012c. Reprocessed polylactide: Studies of thermo-oxidative decomposition. *Bioresource Technology* 114, 622–628. doi:10.1016/j.biortech.2012.02.128; (b) Evolution of the melt-flow index of PLA subjected to 10 successive extrusion cycles. Reproduced from Żenkiewicz, M., Richert, J., Rytlewski, P., Moraczewski, K., 2009. Characterisation of multi-extruded poly(lactic acid). *Polymer Testing* 28 (4), 412–418. doi:10.1016/j.polymertesting.2009.01.012.

relevant indicators are summarized in Table 1. To explain the effects of reprocessing on the mechanical properties of PLA, three studies have been highlighted in Fig. 5.

A general decrease in the resistance properties was registered by Żenkiewicz *et al.* (2009) in terms of tensile stress and stress at break, as a function of 10 successive extrusion–grinding cycles, as shown in Fig. 5(a). Consequently, the structural changes observed at the macromolecular level have an impact on the endurance of the newly formed crystallites.

Concerning flexibility, Pillin *et al.* (2008) reported the evolution of the ductility, in terms of elongation at break, of PLA reprocessed up to seven cycles, as shown in Fig. 5(b). The steep decrease during the initial reprocessing cycles showed that one of the main problems of recycling is the loss of ductility, which in turn corresponds with an increase of brittleness that reduces its applicability in similar markets.

The influence of thermo-mechanical degradation induced by successive reprocessing in the viscoelastic behavior of PLA was reported by Badia *et al.* (2012d), as shown in Fig. 5(c). The viscoelastic spectra showed different relaxation zones. At temperatures

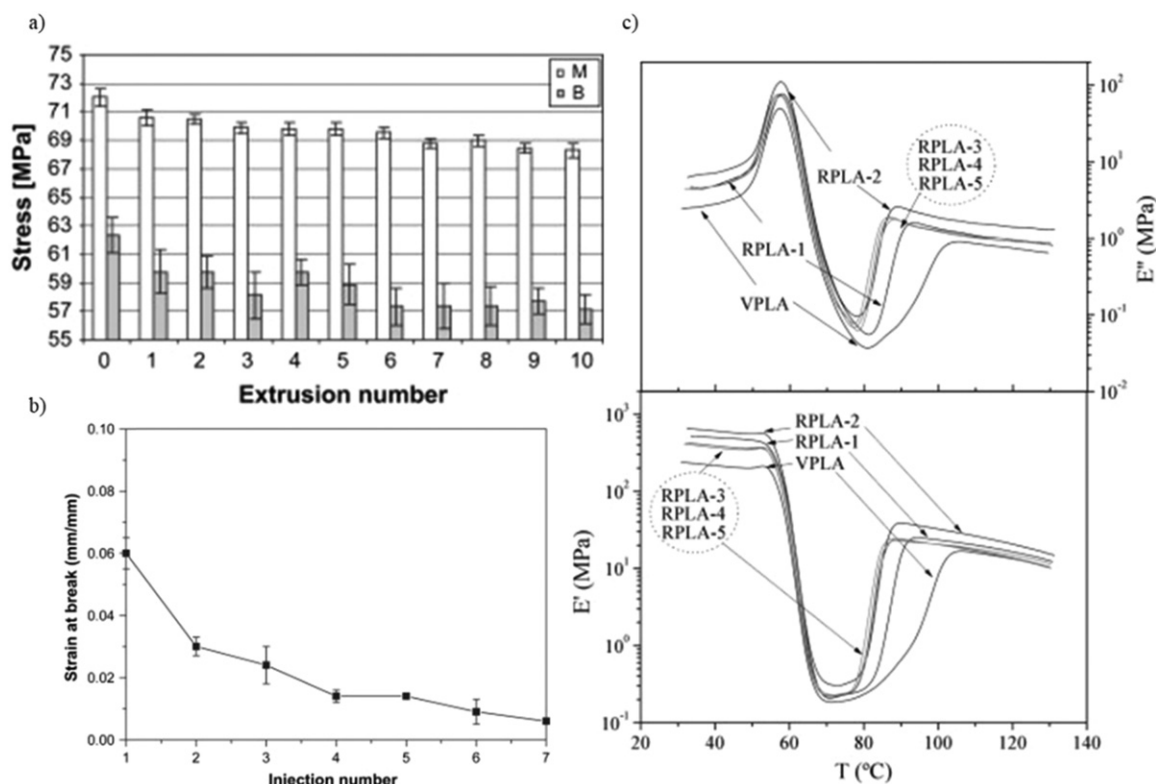


Fig. 5 Effects of reprocessing on the mechanical properties of PLA. (a) Evolution of tensile stress (M) and stress at break (B) of PLA subjected to 10 successive extrusion-grinding cycles. Reproduced from Żenkiewicz, M., Richert, J., Rytlewski, P., Moraczewski, K., 2009. Characterisation of multi-extruded poly(lactic acid). *Polymer Testing* 28 (4), 412–418. doi:10.1016/j.polymertesting.2009.01.012; (b) Variation of ductility of PLA subjected to seven successive injection-grinding cycles. Reproduced from Pillin, I., Montrelay, N., Bourmaud, A., Grohens, Y., 2008. Effect of thermo-mechanical cycles on the physico-chemical properties of poly(lactic acid). *Polymer Degradation and Stability* 93 (2), 321–328. doi:10.1016/j.polymdegradstab.2007.12.005; (c) Dynamical-mechanical-thermal analysis traces of storage and loss moduli for virgin PLA (VPLA) and PLA reprocessed by injection-grinding up to $i=5$ cycles (RPLA- i). Reproduced from Badia, J.D., Strömberg, E., Karlsson, S., Amparo, R.G., 2012d. Material valorization of amorphous polylactide. Influence of thermo-mechanical degradation on the morphology, segmental dynamics, thermal and mechanical performance. *Polymer Degradation and Stability* 97 (4), 670–678. doi:10.1016/j.polymdegradstab.2011.12.019.

reaching the glass–rubber relaxation around 55°C, all materials showed a drop in the storage modulus of nearly 99% of the initial value that after a rubbery plateau increased until 5%–8% of the modulus. This behavior may be due to the formation of crystalline phases in the rubber state, regardless the reprocessing cycle or frequency analyzed. Regarding the evolution of the initial storage moduli along the reprocessing cycles, an initial increase up to the second recycle was shown, and afterwards the values decreased to nearly equal values for RPLA-3,4,5. The origin of these results can be understood in terms of cooperative movements within the amorphous phase throughout the glass–rubber relaxation and thus a deeper inspection into the influence of reprocessing into the glass-forming behavior of PLA was performed. A closer inspection on the segmental dynamics and macromolecular cooperativeness of relaxations can be found in literature (Badia *et al.*, 2012d).

Influence of Recycling on the Barrier Properties of PLA

One of the key properties of the polymers in the field of food packaging is their permeability against different gases, such as oxygen, water vapor, nitrogen, or carbon dioxide, among others, in terms of diffusion rate or permeability coefficients. Therefore, the control of the mass transfer behavior of the recyclates represents one of the main focuses of optimization routes in the design of products from recycled fractions.

A relevant report by Żenkiewicz *et al.* (2009) showed that the water vapor and oxygen transmission rates increased by 39% and 18.3%, respectively, in a PLA subjected to 10 reprocessing steps, as shown in Fig. 6.

Impact of Mechanical Recycling of PLA to Subsequent Valorization Routes

Recycled PLA is a source of material that should not be wasted without further valorization. Indeed, there are particular studies that address the possibilities to consider recycled PLA as a new input for material valorization, in the form of blends with virgin PLA

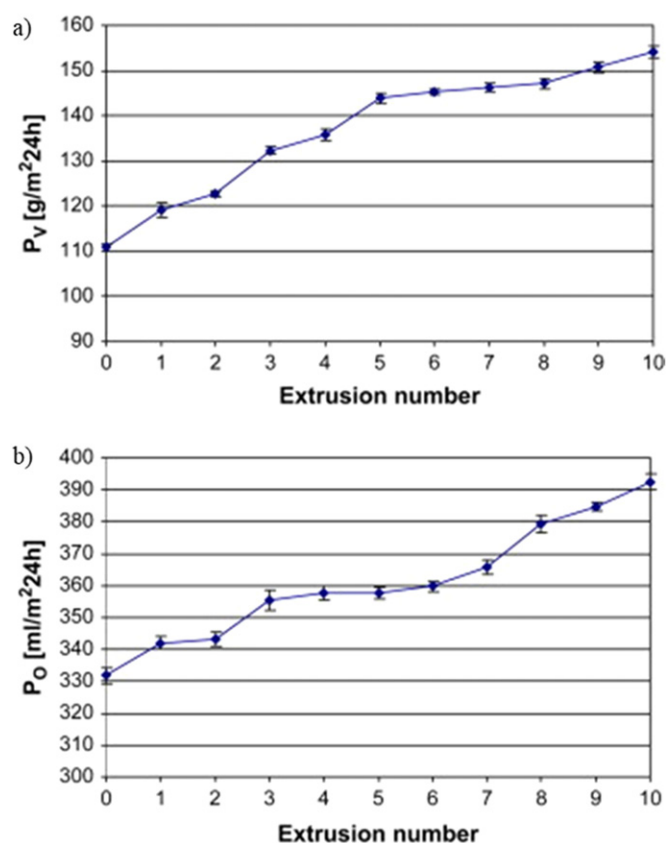


Fig. 6 Effects of reprocessing on permeability of polylactide films: (a) water vapor transmission rates (P_v), (b) oxygen transmission rates (P_o). Reproduced from Żenkiewicz, M., Richert, J., Rytlewski, P., Moraczewski, K., 2009. Characterisation of multi-extruded poly(lactic acid). *Polymer Testing* 28 (4), 412–418. doi:10.1016/j.polymertesting.2009.01.012.

(Hopmann *et al.*, 2015; Gil-Castell *et al.*, 2018b), a source for energy valorization, both considering pyrolysis or controlled combustion (Badia *et al.*, 2012a,c; Gil-Castell *et al.*, 2018b), or biodegradation by composting (Sikorska *et al.*, 2012). A selection of results of these studies in these fields has been included in Fig. 7, and described in the subsections hereby.

Material Valorization of Mechanically Recycled PLA

The combination of reprocessed and virgin polylactide is considered as a good alternative not only to reduce the material cost at the industrial level, but also as a contribution to further plastic waste management solutions. The incorporation of recycled PLA into virgin/recycled PLA blends (V/R-PLA) has to take into account the structural-to-performance approach presented in the present article for the evaluation of materials. In this sense, the first analysis must be focused on the structural effect, and take into account that, necessarily, at least one more processing step is needed to obtain V/R-PLA blends, which inherently affects the molar mass distribution of polymers. For example, Hopmann *et al.* (2015) evaluated the incorporation of different quotas of recycled PLA on the performance of blends for packaging applications. The reduction of the molar mass of the blend was marginal regardless of the quota of recycled PLA that was present in the formulation up to 50%, for two types of PLA, amorphous and semicrystalline. These researchers also evaluated the impact on the processability by means of the assessment of the viscosity, which suffered from degradation in a higher extent than the molar mass. The study reports that, by using recycled PLA, the viscosity dropped with increasing recycling quota. Due to the low difference of the absolute recycled PLA content, the difference in the range of a recycling quota of 10%–50% was low. Up to a recycling quota of 50%, the average viscosity decreased a 15% for amorphous or a 13% for semicrystalline recycled PLA. Further on, by recycling 100% recycled PLA, the average viscosity drop accounted for 28% for amorphous and 24% for semicrystalline recycled PLA, respectively.

Another study by Gil-Castell *et al.* (2018b) reported the performance of blends prepared from virgin polylactide and polylactide mechanically reprocessed up to two cycles (V/R-PLA), at quotas of 20%, 40%, and 60%, which was assessed in terms of thermo-oxidative stability, morphology, and viscoelasticity. V/R-PLA blends showed appropriate thermo-oxidative stability. The amorphous nature of polylactide was maintained after blending, without relevant modification of the glass transition temperature. Higher rigidity was found for all compounded blends regardless of the composition of recycled PLA, reaching similar values between ~2800 and ~3000 MPa, representing a ~33% of increase with respect to virgin PLA. The viscoelastic properties showed an increment of the

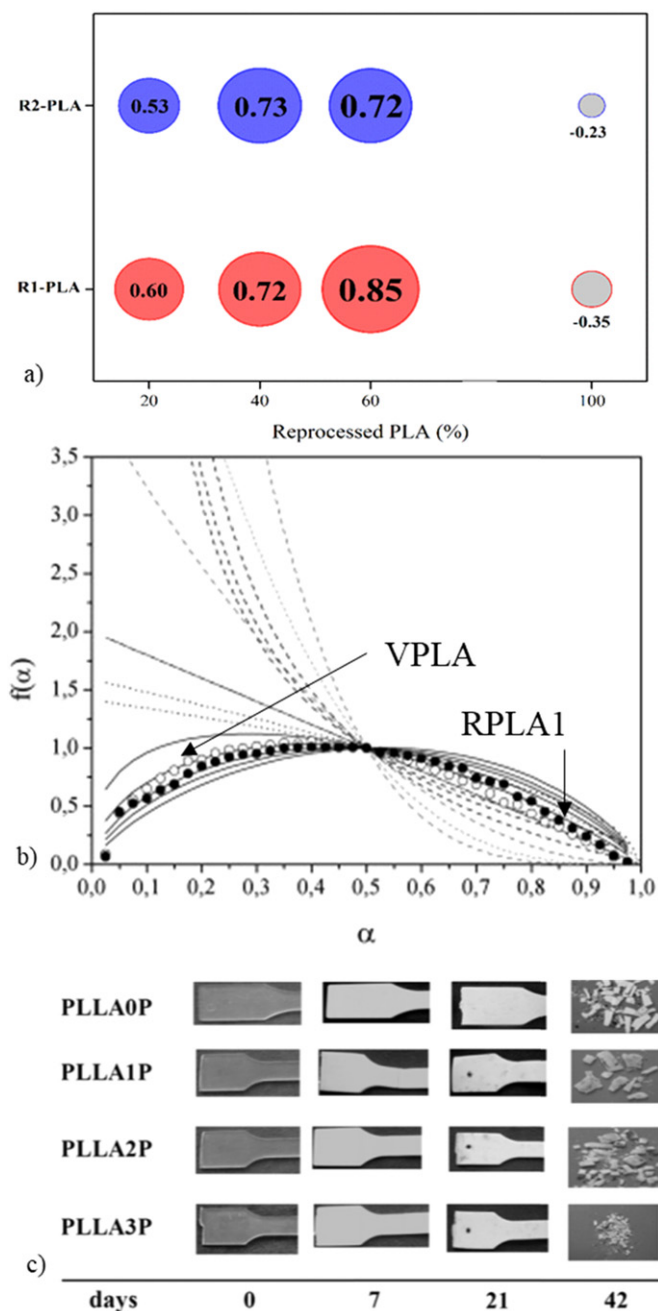


Fig. 7 Combination of mechanical recycling of PLA with further valorization routes. (a) Material valorization: Mechanical blending effectiveness values (MBE), considering the measured E' at 35°C and 100°C at 1 Hz as E'_g and E'_r , respectively, for virgin/reprocessed PLA blends. Reproduced from Gil-Castell, O., Badia, J. D. and Ribes-Greus, A., 2018b. Suitability of blends from virgin and reprocessed polylactide: Performance and energy valorisation kinetics. *Journal of Renewable Materials*, 6(4), 370–382; (b) Energy valorization: Master plots based on the differential form of the general kinetic law compared to experimental data obtained for thermo-oxidative decomposition of VPLA (hollow circles) and RPLA-1 (full circle). Kinetic models: A_n (nucleation and growth, solid black lines), F_n (n -order reactions, solid gray lines), R_n (reaction-controlled, pointed lines), D_n (diffusion-controlled, dashed lines). Badia, J.D., Santonja-Blasco, L., Martínez-Felipe, A., Ribes-Greus, A., 2012c. Reprocessed polylactide: Studies of thermo-oxidative decomposition. *Bioresource Technology* 114, 622–628. doi:10.1016/j.biortech.2012.02.128; (c) Biological valorization: Influence of recycling on the biodegradation of PLA under industrial composting conditions. Reproduced from Sikorska, W., Richert, J., Rydz, J., Musioł, M., 2012. Degradability studies of poly(L-lactide) after multi-reprocessing experiments in extruder. *Polymer Degradation and Stability* 97 (10), 1891–1897. doi:10.1016/j.polymdegradstab.2012.03.049.

mechanical blend effectiveness (MBE), as shown in Fig. 7(a). This increment was similar regardless of the type of reprocessed PLA incorporated in the blend. The increase of the MBE was more relevant for higher contents of reprocessed PLA in the blend. These results suggested the feasibility of V/R-PLA blends to be used under similar mechanical conditions to those of virgin PLA goods.

Energy Valorization of Mechanically Recycled PLA

Valorization by energy recovery through technological means such as pyrolysis or controlled combustion implies burning waste to produce energy in the form of heat, steam, and electricity. This is only considered a very sensible way of waste treatment when material recovery processes fail due to economical constraints. Plastic materials possess a very high calorific value when burned, especially considering that they are derived from crude oil. Producing water and carbon dioxide upon combustion makes them similar to other petroleum-based fuels.

Badia *et al.* (2012a,c) assessed the impact of five mechanical reprocessing steps on the energy valorization of PLA under inert and oxidative conditions by TGA. The study of the evolved gases, the changes in thermal stability, and the kinetics of decomposition pictured the behavior of recyclates under both thermolytic processes. PLAs, as well as their successive five recyclates, described a mass loss driven by one decomposition stage in inert conditions and two in oxidizing conditions. A first step is ascribed to the pyrolysis of the backbone. A second mass-loss step under O₂ was related to the decomposition of the remaining char (~2%), regardless of the number of reprocessing cycles.

The kinetic model that mathematically described the thermal and thermo-oxidative decompositions of PLA and their recyclates was of the type Avrami–Erofev A_n ; nucleation and growth, which gave importance to the formation of gas bubbles in the melt, as shown in Fig. 7(b). From the second to the third reprocessing cycle, a change in tendency was shown by thermal stability and thermal activation parameters for PLA recyclates. Focusing on each process, under argon the recyclates needed more energy and temperatures to decompose than virgin materials, whereas under oxygen the decomposition of all recyclates was overcome at lower apparent activation energy E_a than that of virgin materials. Thus controlled combustion could be an option to valorize recycled PLA energetically.

Concerning the energy valorization of V/R-PLA blends, it was shown by Gil-Castell *et al.* that the energetic demand for the thermo-oxidative decomposition of V/R-PLA blends was lower and varied in a narrower margin than that of virgin or reprocessed PLA. In particular, the apparent activation energy E_{a_x} increased from ~80–110 kJ mol⁻¹ at low conversions to ~150–200 kJ mol⁻¹ at the end of decomposition. Blending provoked similar E_{a_x} values to reprocessed PLA at low conversion degrees whereas showed lower activation energy at high conversion degrees. In general, V/R-PLA blends showed E_{a_x} values lower than those given by virgin PLA. Therefore, from a cost-effective point of view, considering the energetic demand of each material, the combustion of V/R-PLA blends would result in an advantageous energetic process, thus highlighting the feasibility of the energetic demand for the valorization process (Gil-Castell *et al.*, 2018b).

Biological Valorization of Mechanically Recycled PLA

Biological valorization is the natural route to treat wastes of biodegradable bioplastics, focusing on the reincorporation of the material into the carbon cycle without environmental impact, as raised up by the circular economy philosophy. Within this strategic expression of the eco-effective industrial approach, cradle-to-cradle design defines a framework for designing products and industrial processes that turn materials into nutrients in the carbon cycle.

PLA is not easily biodegraded at service conditions, but is highly liable to composting conditions due to the temperatures close to the glass transition of PLA (Gil-Castell *et al.*, 2018a). Reprocessed PLA is more susceptible to hydrolysis at high temperatures (Badia *et al.*, 2012b). PLA degrades rapidly in the composting atmosphere of high humidity and temperature but at lower temperatures and/or lower humidity, the storage stability of PLA products is considered to be acceptable. In this sense, it would advisable that reprocessed PLA would not introduce complications in the management of their wastes and could be therefore treated without further modification of the already defined technological parameters of composting.

Sikorska *et al.* (2012) evaluated the degradation profiles of multireprocessed PLA under industrial composting conditions at the static composting open-air pile. The progress of the degradation process was monitored by surface changes and measurements of sample weight loss and changes in the molecular weight of the PLA samples. As shown in Fig. 7(c), the repetitions number of the processing experiments of PLLA in the extruder only slightly affected the disintegration progress of the PLLA samples, without further effect on the biodegradation rates. Nevertheless, there were not produced new constraints to disintegration and therefore the same valorization routes could be applied for virgin and recycled PLAs.

Mechanical Recycling of PLA-Based Blends and Nanocomposites

To prevent the problem of degradation during reprocessing, different strategies can be followed, from the incorporation of specific additives to minimize degradation, to the incorporation of PLA into blends or the reinforcement of PLA by different nanoloads to give nanocomposites (Badia and Ribes-Greus, 2016).

Concerning additives, there are antioxidants and stabilizers such as dianthraquinone, benzoyl peroxide, dycumil peroxide, tropolone, or quinine, among others that act by neutralizing the radicals and preventing degradation in properties such as

resistance, flowability, or UV protection. In addition, the use of chain extenders based on acrylates or phosphites can prevent PLA from degradation during reprocessing (Badia and Ribes-Greus, 2016).

Regarding blends and nanocomposites based on a PLA matrix, some selected studies have been brought to this section, to picture the advantages and drawbacks of each option. Blends of PLA with polyethylene glycol (PEG), thermoplastic starch (TPS), or poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) have been considered (Sirin *et al.*, 2014; Zembouai *et al.*, 2015; Brüster *et al.*, 2016). For the case of nanocomposites, PLAs reinforced by nanoceramic fillers of clay and chalk, lignocellulosic loads of cellulose nanocrystals (CNCs) and wood flour, or carbon-based graphene nanoplatelets (GnP) (Bhattacharjee and Bajwa, 2017; Fazelinejad *et al.*, 2017; Beltrán *et al.*, 2018; Botta *et al.*, 2018; Dhar *et al.*, 2018) are summarized hereinafter.

Mechanical Recycling of PLA-Based Blends

The use of plasticizers to improve the processability and versatility of performance of PLA is of relevant importance. The mechanism of degradation of PLA-based blends during mechanical recycling was investigated by Brüster *et al.* Multiple reprocessing of a plasticized PLA grade obtained by grafting poly(ethylene glycol) methyl ether acrylate (acryl-PEG) within PLA via reactive extrusion was reported (Brüster *et al.*, 2016). As can be seen in the DSC curves in Fig. 8(a), in contrast to the behavior shown in Fig. 3(c), the presence of acryl-PEG hindered cold-crystallization and offered nucleation sites to increase the crystallinity of the blends. In addition, the mechanical resistance properties strongly worsened from the first processing to the third processing and the material became brittle since it markedly lost tensile ductility and its toughness dropped. As a result, the authors concluded that at the actual state, plasticized PLA by reactive extrusion could not be recycled and reused for the same application.

Blends of PLA and TPS have been also subjected to four extrusion and injection processing cycles by Sirin *et al.* (2014). The thermal stability of the blends decreased as the TPS content increased in the blend. Multiple recycling negatively influenced the thermal transition temperatures of the blends, such as T_g and T_m . Owing to the presence of starch particles in the PLA matrix, heterogeneous nucleation occurred in the PLA phase for the blends, and was followed by the reduction of the cold-crystallization of the blends. As a general conclusion, PLA/TPS blends were more sensitive to recycling in comparison with neat PLA.

Zembouai *et al.* (2015) reported the mechanical recycling of blends based on PLA and PHBV 50/50 wt% by subjecting them to six extrusion and injection cycles. It was concluded that the thermo-mechanical PHBV degradation was significantly reduced in the presence of PLA. Consequently, the mechanical properties of PLA and PHBV/PLA blends were less affected after six cycles contrary to neat PHBV, which exhibited a reduction.

Mechanical Recycling of PLA-Based Nanocomposites

It might be generally expected that PLA-based reinforced composites have less recyclability than their neat thermoplastic matrix, because composites are more sensitive to thermo-mechanical degradation. Thus, recycling is usually guaranteed up to several reprocessing cycles until the mechanical properties are conserved and then they are discarded for biological or energy valorization. Several nanofillers can be considered for the preparation of nanocomposites, such as nanoparticles or nanofibers, from synthetic or natural origin, which will affect their assimilability once their service lives are covered and they are discarded. Some examples have been chosen to picture the main effects of reprocessing on nanocomposites for PLA reinforced with ceramic nanoparticles such from clay (Beltrán *et al.*, 2018) or chalk (Fazelinejad *et al.*, 2017), lignocellulosic compounds like CNCs (Dhar *et al.*, 2018) or wood fiber (Bhattacharjee and Bajwa, 2017), or carbon nanosources such as GnP (Botta *et al.*, 2018).

Beltran *et al.* (2018) studied the influence of recycling on PLA/nanoclay composites by means of an extrusion–compression–grinding process that also included accelerated thermal and photochemical aging steps to simulate the degradation experienced by postconsumer plastics during their service-life. Mechanical recycling caused an improvement in the dispersion of the clay

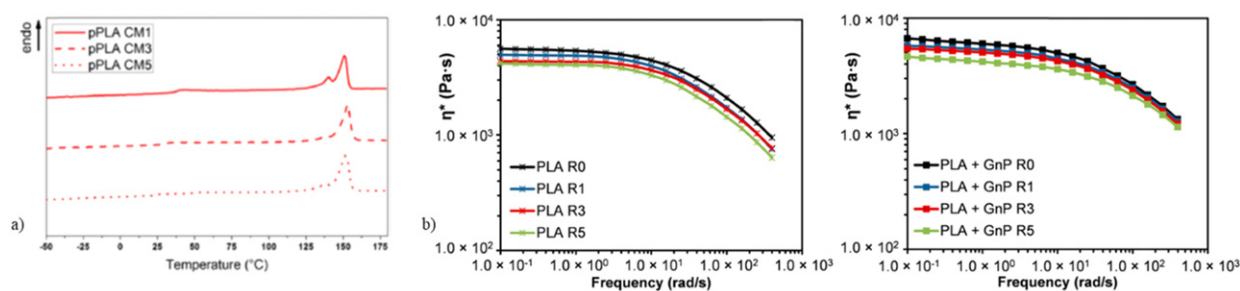


Fig. 8 Examples of effects of recycling on PLA-based blends and nanocomposites. (a) DSC second heating trace of PLA plasticized with poly(ethylene glycol) subjected to 1, 3, and 5 processing cycles. Reproduced from Brüster, B., Addiego, F., Hassouna, F., *et al.*, 2016. Thermo-mechanical degradation of plasticized poly(lactide) after multiple reprocessing to simulate recycling: Multi-scale analysis and underlying mechanisms. *Polymer Degradation and Stability* 131, 132–144. doi:10.1016/j.polymdegradstab.2016.07.017; (b) Influence of the addition of graphene nanoplatelets (GnP) into PLA on the rheological viscosity after 1, 3, and 5 recycling cycles. Reproduced from Botta, L., Scaffaro, R., Sutera, F., Mistretta, M.C., 2018. Reprocessing of PLA/graphene nanoplatelets nanocomposites. *Polymers* 10 (1). doi:10.3390/polym10010018.

nanoparticles into PLA. It was concluded that the effect of accelerated aging and the mechanical recycling processes on the properties of the nanocomposite were not extremely aggressive. In the case of permeability to gases such as O₂, N₂, or CO₂, it clearly decreased as a result of the mechanical recycling, being less relevant for N₂ and O₂. This behavior was explained considering two interesting opposite effects. On the one hand, the polymer degradation during service and the recycling process, which might favor the permeation because of the increase of the free volume related to a molar mass decrease in glassy polymers. On the other hand, the tortuosity brought by the nanoplatelets, which may prevent the mass transfer and therefore limit the permeability of these gases. Nonetheless, in general terms, the recycled nanocomposites had similar or even better properties in some cases than those of the virgin material, so the use of recycled nanocomposites in demanding applications could be guaranteed, and even in the same applications as the virgin material is achievable.

Another study performed with a load of 30% of chalk into a PLA matrix, conducted by Fazelinejad *et al.* (2017) revealed promising conclusions for the recycling industry. It was concluded that PLA/chalk nanocomposites could be recycled up to six times without being subjected to any significant change in the mechanical and thermal properties, analogous to that of the virgin PLA matrix.

When it comes to the recycling of PLA reinforced by lignocellulosic loads, Dhar *et al.* (2018) studied the mechanical recycling of PLA filled by CNCs. Like most users, CNCs are usually added to the PLA matrix to improve structural and gas barrier properties, and also to enhance biodegradability, in contrast to other fillers. However, due to the hydrophilic nature of CNCs and the presence of sulfate groups, it results in agglomeration and provokes the initiation of hydrolytic degradation of the PLA backbone. The use of dicumyl peroxide at low content (1 wt%) as crosslinking agent was reported to maintain and even increase by 6%–10% the molar mass after three recycling processes. In addition, the reinforcing effect of CNCs and the action of DCP to ease extrudability was also prevalent by the recycled PLA/CNC films due to the presence of high fractions of grafted PLA/CNC gel-like structures, which showed improved tensile strength by ~16%–30%, increased the maximum degradation temperature by ~7–12°C, and enhanced the viscosity of polymer nanocomposite melts by ~10 times and the storage modulus by ~50 times after the third recycling step.

Bhattacharjee and Bajwa (2017) focused on the effect of six successive mechanical recycling steps on PLA reinforced by oak wood flour, coupled by maleic acid. The results showed how composites experienced a decrease in tensile modulus, flexural modulus, and storage modulus with successive recycling, while they exhibited an increase in failure strain, coefficient of thermal expansion, and melt flow index. With consecutive reprocessing, composite thermal stability increased, while polymer crystallinity decreased.

Regarding the use of nanocarbon sources on PLA, Botta *et al.* (2018) reported the effects of five extrusion recycling cycles on PLA reinforced by GnP. They consist in stacked nanosheets of graphene with relevant electrical, thermal, or resistance properties, and good biocompatibility and innocuous environmental effect after discarding, due to its carbon–carbon nature. A relevant effect of the addition of GnP is pictured in Fig. 8(b), which compares the rheological behavior of PLA and PLA/GnP after 1, 3, and 5 extrusion cycles. The viscosity of nanocomposites was slightly higher than that of neat PLA. Even more, the viscosity of PLA/GnP after five reprocessing cycles was still similar to that of neat PLA. It was attributed to the interaction of the disperse filler with the matrix, which restricted polymer chain displacements. At low frequencies, the behavior of PLA/GnP was more similar to non-Newtonian than unfilled PLA. At high frequencies, the drop was less pronounced if compared with that of unfilled PLA, which was attributed to the positive effect of GnP to reduce degradation phenomena. In addition, improved dispersion of GnP due to reprocessing further increased the nucleating role of the nanofiller. Also the stiffness of the PLA filled with GnP increased as a function of the reprocessing cycles for all the extrusion steps and did not modify the ductility to a high extent.

Conclusions: The Challenge of Mechanical Recycling of PLA

The future presence of PLA in the fractions of polymer waste encourages technologists to ascertain its valorization at the best quality conditions. Mechanical recycling of PLA represents one of the most cost-effective methodologies, but the recycled materials are usually directed to downgraded applications, due to the inherent thermo-mechanical degradation affecting its mechanical, thermal, and rheological performance. During mechanical recycling, PLA is subjected to the influence of degrading agents such as oxygen, light, mechanical stresses, temperature, and water, which, separately or in combination, during its material loop (synthesis–processing–service life–discarding–recovery), results in chemical and physical changes that alter their stabilization mechanisms and long-term properties. In particular, it mainly induces hydrolytic chain scissions and inter/intramolecular transesterifications, affecting the molar mass distribution and subsequently the performance of PLA. A set of opportunities for the field of recycling of PLA was given by Badia and Ribes-Greus, focusing on aspects such as (1) the investment in sorting technologies, to obtain relevant homofractions of polymers; (2) the closer knowledge of the structure-to-performance relationship, with special focus on the influence of the enantiomeric nature of PLA; or (3) the research to potentiate the studies of additives such as stabilizers and chain extenders to lengthen the service life and enlarge the recycling capability of PLA, among others (Badia and Ribes-Greus, 2016). Despite the fact that the focus is already moving from lab scale to pilot scale, the technological challenge will come in the near future when PLA is implemented in the market and suffers from degrading conditions during storage and use at different environments, mixing during discarding, and cross-contamination with other plastics during sorting and valorization. Therefore, larger investments should be considered to bring PLA from an alternative to a reality, within the cradle-to-cradle perspective of the circular economy of bioplastics.

Acknowledgements

The authors appreciate the support of the Chilean Government through the project CEN LEITAT Chile, with reference 13CEI2-21839.

See also: Internet of Things Platform to Encourage Recycling in a Smart City. Polymer-Recycling of Bulk Plastics. Prospect of Recycling of Plastic Product to Minimize Environmental Pollution. Recycling Approaches, Policies and Regulations on Electronic Waste With Special Focus on India. Recycling of Flax Fiber Towards Developing Biocomposites for Automotive Application From a Life Cycle Assessment Perspective. Recycling of Plastics for Low Cost Construction. Smart Contract for Monitoring and Control of Logistics Activities: Garbage Utilities Case Study in a Smart City. Sustainability and Recycling of Bamboo for Engineering Applications. Worldwide Research Trends in the Recycling of Materials

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Rice Straw as a Raw Material for Pulp and Paper Production

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Introduction

Rice straw is an agricultural byproduct even it could be considered as a waste, rice straw could be utilized as a raw material for pulp and paper production. The chemical composition of rice straw varies from season to season and depends on species. The chemical analysis of an Egyptian rice straw sample is given: Alpha cellulose 41.8%, Pentosans 21.6%, Lignin 13.6%, Ash 18.4% and Silica 16.7% (Elhelece, 2010).

The advantages of rice straw for paper and board production could be summarized as; Rice straw found in abundant amount, rice straw are found in a steady and continuous supply over the years. Also, rice straw is easily collectable, easy of baling and easy of transportation to the factory site. Rice straw is cheap and have no more valuable or profitable use. Rice straw is capable of being stored for at least one year without deterioration. Storage and protection means for storage should be not costly.

It should be noted that rice straw due to its open structure is easily pulpable and does not require hard pulping conditions. Moreover, the price of rice straw is much cheaper than other agricultural residues. Even without recovery of chemicals, production of chemical pulp from rice straw was economically feasible (Raafat *et al.*, 2009).

The disadvantages of rice straw for pulp paper production could be summarized as follows:

High ash content (mainly silicon dioxide) is particularly harmful to cutting tools and to chemical recovery systems in the pulp and paper industry. This difficulty could be overcome, the silica content has been removed simply by an immersion process in a sodium hydroxide solution to obtain desilicated rice straw. However, production of pulp consumes about 500 tones water based on the weight of raw material. The disposal of this great water amount directly into water stream causes environmental pollution. Other alternatives were proposed. The spent liquor instead of being discharged in a body of water can be used, as it is, for different purposes. One of the uses is the direct application of the lignin in the liquor as adhesive in brick industry (El-Kassas and Mourad, 2013).

Also, the strength properties of straw pulp are relatively poor compared to wood pulp and therefore, application to produce brown grades such as sack Kraft, bag Kraft and liner board is generally avoided.

Rice straw must undergo several operations in order to produce paper. These operations are:

- (1) Preparation of the raw material,
- (2) Pulping procedure will be done to separate and clean the fibers,
- (3) Bleaching procedure will be followed after pulping processes,
- (4) Dilution process to form a thin fiber mixture,
- (5) Screening formation of fibers on a thin screened,
- (6) Pressurization to enhance the materials density,
- (7) Drying to eliminate the density of materials,
- (8) Finishing procedure to provide a suitable surface for usage.

Pulping

Rice straw had to be dried and cut into pieces. Lignin molecules and other impurity molecules present in rice straw could be eliminated through mechanical, semi-mechanical and chemical treatments.

In mechanical pulping, the lignin cementing the fibers is destroyed but not removed. The fibers are separated from each other but they still retain the lignin.

In semichemical pulping mild, reduced pulping conditions are used. About 70% of the lignin is dissolved out and the separation of the fibers is not enough. Therefore, the pulp is mechanically treated in refiners in order to liberate more and more fiber. The obtained pulp still contains around 7% lignin based on pulp.

In chemical pulping, more severe pulping conditions are applied. These conditions result in removal of over 95% of the lignin. In the case of easy bleachable pulps, the lignin left in the pulp amounts to not more than 2% based on pulp. Consequently, chemical pulping can be safely termed as "Delignification". These pulps are classified as "soft" pulps when well-cooked and are of high purity and have good tearing strength. When pulps are not well cooked, they are classified as "hard" and are of lower purity and have high bursting strength and high bleach consumption. Chemical pulps do not need further mechanical treatment in fibrators or refiners to complete the liberation of the individual fibers. Sometimes such treatment might be necessary, but only for a short period. For chemical pulping there are two major processes in use. Both processes depolymerize and solubilize the lignin (Evon *et al.*, 2010a).

Semichemical Pulping Process

All processes of semichemical pulping deliver high yield pulp. In semichemical pulping a mild or reduced chemical treatment is applied to the raw material. This treatment is just capable of dissolving lignin partially, and leads to incomplete release of individual fibers. We get rather fiber aggregates. However the remaining lignin in the treated raw material becomes sufficiently soft to be destroyed by a further mechanical treatment. Semichemical pulping is economical because of the high yield it delivers, and the low chemical consumption. In semichemical pulping only 30%–50% of the lignin and 35%–40% of the hemicellulose is removed. On the other hand, in ordinary chemical pulping 90%–95% of the lignin is removed and 60%–68% of the hemicellulose is removed. The yield of semichemical pulp varies between 65% and 85% compared to less than 50% or 40% in the case of chemical pulping. The properties of semichemical pulp are intermediate between whole fibers (e.g., mechanical pulp) and full chemical pulp. Any of the pulping reagents used in chemical pulping can be applied for semichemical pulping but under much reduced conditions of concentration, temperature, pressure and pulping time. However, there are some chemical reagents used specifically for semichemical pulping, namely sodium sulfite alone or in mixture with sodium hydroxide and/or sodium sulfide. The neutral sulfite method uses sodium sulfite and some sodium hydroxide which acts as a buffer to neutralize the organic acids which are formed when the raw material is heated at 120°C and more. When making a bleachable pulp, the yield should not exceed 70% by semichemical pulping. This assures that a sufficient amount of lignin is dissolved out. Thus, the bleaching process can be effective and a degree of brightness of 70% could be achieved. The conditions of semichemical pulping are adjusted according to the type of pulp which has to be produced, the coarse-grade pulp or high-grade pulp. After chemical treatment, the cooked mass is then refined without washing in a disc refiner. For semichemical pulping, batch cooking in rotary digesters can be used. Continuous cooking equipment is preferable. This has the advantage of continuous operations and the great advantage of delivering the cooked raw material quickly to the refiner at high temperature. An example of such equipment is the defibrator chemipulper. A reaction chamber is used which consists of a series of closed, horizontal stainless steel screws. This equipment embodies a combination of continuous digestion and continuous mechanical refining under pressure. In the case of coarse pulps, the most desirable combination of high yield and acceptable strength is obtained in the yield range 70%–80%. The obtained coarse pulp is suitable for making corrugating medium, coarse wrapping paper, liner board, hardboard, insulating board etc.

Pulps for the finer grade of paper (e.g., book, bond, glassine waxing and tissue paper) have to be produced in lower yields. Bleachable grades are made by adjusting cooking conditions to a lignin of about 10% content. This pulp can be bleached in a single hypochlorite stage to give a brightness of 70%–75% without appreciable loss in strength. Even it was possible to obtain pulps at atmospheric pressure, low temperature and low chemicals concentration. Semichemical pulp when used alone in the paper furnish, it produces paper with high bursting strength but with low tear strength, and the paper tend to be too stiff and ratty. When blended with chemical pulp in small ratio, paper acquires good properties (Evon *et al.*, 2010b).

Chemical Pulping

Chemical pulping means cooking rice straw with chemicals on heat. Pulping was done by using classic reagents as soda (with anthraquinone and parabenzoquinone as additives), potassium hydroxide, formic acid and Kraft process. Pulping with NaOH in different concentrations is the easiest method. The heating is done for different time periods until the boiling solution and the straw feels soft or easy to break with your hands and feels sticky, indicating that the straw is ready to be mechanically destroyed. Lignin lost or dissolved in water can be characterized by a brown solution, solution chocolate formed due to lignin and other pollutants dissolved in NaOH, after washing with clean water for several times to keep the straw clean and mechanically destroyed by using a blender. Straw that has been in the blender is dried and ready for use.

The sulfite process makes use of a buffered acid solution of calcium bisulfite or magnesium bisulfite. The sulfur dioxide and bisulfite convert the lignin into soluble lignosulfonic acid and consequently lignosulfonate.

The other process is the alkaline process namely the soda process and it makes use of NaOH solution which reacts with the free –OH groups in the lignin molecules and converts it into sodium ligninate (alcoholate). This is soluble in the cooking liquor i.e., NaOH solution. However a part of NaOH is replaced by Na₂S in order to lower the degradation effect of NaOH on cellulose. Usually Na₂S enhances the delignification due to its reaction with lignin. Accordingly the duration or temperature of pulping can be reduced. This results in stronger pulp and paper and hence the process is called the “Kraft” process referring to the German word “Kraft” means strength. It is called also the sulfate process because sodium sulfate is added in the chemical recovery system where it is reduced to Na₂S (Evon *et al.*, 2012).

The degree of cooking is generally measured by methods which are related to the lignin content of pulp. These are bleachability tests such as permanganate number. Complete purification is not necessary to be achieved in the cooking process, since final purification can be obtained in the bleaching process under milder conditions which are not so degrading on the fiber as pulping.

The acid sulfite process is not suitable for pulping agricultural wastes since these wastes contain a substantial amount of minerals especially silica. These substances cannot be dissolved out in acid medium. On the other hand silica is easily dissolved in alkaline medium. Therefore, for agricultural wastes the alkaline process is recommended. It is also worth mentioning that the Kraft process, which is an alkaline process, accounts for greater than 90% delignification of wood into bleachable grade pulp (Evon *et al.*, 2014).

Variables in Alkaline Pulping

The variables in alkaline pulping are: Composition of cooking liquor i.e., sulfidity etc., concentration of cooking liquor, chemical-to-raw material ratio, temperature and time of cooking. It is important that the liquor penetrates the raw material easily in order to reach the innermost layers of the raw material. The reagent molecules must reach the middle lamella where lignin is located. Thus, the reagent could dissolve the lignin cementing the fibers together, and defibrize the raw material. Fortunately, due to the open supermolecular structure of the cell wall of straws, bagasse and other agricultural wastes, there is no problem facing the penetration of the reagent molecules.

The concentration of the cooking liquor is of prime importance for the rate and extent of delignification. The maximum temperature of cooking (also termed digestion) plays also a great role together with the chemical concentration. These are followed by the time duration of the cooking process. In all cases the alkali is consumed in the early stages of cooking. The mechanism of cooking is not only restricted to delignification but a great part of the carbohydrates fraction especially the hemicellulose is dissolved out. The cellulose also becomes partially degraded as seen by the drop in the molecular weight i.e., degree of polymerization (D.P.) of cellulose. Therefore, the time of pulping or cooking should be adjusted to prohibit substantial cellulose degradation. The cellulose degradation leads to yield loss and decrease in pulp and paper strength. It is well known that D.P. of cellulose is one of the main factors affecting paper strength (Evon *et al.*, 2015).

In contradiction to wood, agricultural wastes are easily penetrable by cooking chemicals and are easily delignifiable. Summing up they are easily pulpable. It is the duty of the chemist in charge of the cooking operation to stop the reaction and blow the digesters at the proper time. The rest of lignin not removed during cooking is removed safely during bleaching. Bleaching is carried out under more mild conditions than pulping. Thus there is no fear to degrade cellulose during bleaching if certain precautions are taken especially pH.

The alkali respectively the sulfate or Kraft process are old processes but they are still being used all over the world, sometimes with minor modifications.

Several chemical additives have been suggested to accelerate delignification and to decrease degradation of the carbohydrate fraction, hemicellulose and cellulose itself. Anthraquinone and polysulfide have been successively used. Polysulfide also reduces the amount of toxic sulfur compound and reduces odor emission. The addition of surfactant-based additives reduces surface tension and improves wetting of the raw material resulting in a quick penetration or diffusion of the chemical reagent used in cooking. Under certain precautions oxygen can be used for partial delignification. Peroxyacids have been used for pulping. Preparation of peroxy carboxylic acids, its use in pulping and properties of obtained paper have been reviewed. Peroxy mineral acids were also successfully used for pulping (Evon, 2008).

Another group of pulping processes is organosolv pulping. The advantages of organosolv pulping over conventional methods have been reported by many authors including ourselves. Organosolv pulping by different alcohols have been extensively studied in the cellulose and paper department in N.R.C., Cairo, to delignify bagasse, cotton stalks and wheat straw. Uncatalyzed ethanol and methanol pulping of bagasse resulted in a suitable pulp provided that a proper washing procedure is applied to the pulp. Alkali addition to ethanol pulping leads to an easily bleachable pulp. Bagasse pulping by butanol gave comparable results. We have studied Organosolv pulping of wheat straw using aqueous ethanol and alkali ethanol. Best results obtained in the alkaline ethanol process gave a pulp yield of 56.5% and chlorine number 3 by using 8.4% NaOH on raw material, 0.05% anthraquinone and ethanol concentration 50% at 150°C for 90 min. Cotton stalks can be partially pulped by aqueous ethanol process while the alkali process constitutes possibilities for chemical pulp quality. Screened yield was 41%, and reject was 1.5% (FAOSTAT, 2016).

Biopulping process also could be described as; Enzymes from wood destroying fungi are used to degrade lignin selectively. This biochemical process operates at low temperature and at atmospheric pressure but requires very long time. It can, then, be used as first step as partial pulping that must be then followed by mechanical or chemical pulping, but using reduced conditions (FAOSTAT, 2016).

Bleaching

Organosolv pulping using acids are the prominent choices of researchers to convert this residue into valuable pulp but in developed countries only. Developing world favours the soda and soda-AQ processes as these are economical. As a virtue of rice straw contains less lignin than wood so, rice straw requires less harsh conditions for cooking and can be easily pulped. Bleaching is a crucial step of paper making but also responsible for causing water pollution. Many studies revealed that during the process more than 500 chlorinated compounds are released that are highly toxic, bio-accumulative and carcinogenic in nature. Most of the industries over the globe switch on to the elemental chlorine free short sequence bleaching methods using chlorine dioxide, hypochlorite and hydrogen peroxide. There is an effective need of ecofriendly, economically reliable pulping and bleaching sequences in case of rice straw to eliminate the problems of chlorinated compounds in wastewater of paper mills. Such approach of using waste as a raw material with its environmentally safe processing for making paper can prove to be valuable towards sustainable growth.

Mechanical pulp which contains almost the whole amount of lignin as in the original raw material, is bleached with peroxide. Chemical and semichemical pulps are usually bleached with chlorine compounds either directly with chlorine or by hypochlorites

in one or more steps. Chemical pulps are usually bleached by a multistage process. Usually chlorine is applied in the first step followed by alkali wash then hypochlorite in the third step. This is the most conventional sequence. The hypochlorite can be divided into two steps. Before bleaching, it is necessary to determine or measure the bleachability of the pulp. Bleachability can be measured by several methods e.g., chlorine number, permanganate number and hypochlorite test. According to the result we can estimate the amount of chlorine or hypochlorite necessary for bleaching to attain a certain degree of brightness. Usually degree of brightness from 70% to 80% is required for average and high-grade paper. 85% degree of brightness or more could be also necessary in some paper types. In newsprint on the other hand even 60% brightness is sufficient.

Generally speaking, pulps from agricultural wastes, even semichemical pulps are easily bleachable. This is due to the lower lignin content in these pulps compared to wood pulps and to their open fibrous structure. Such pulps require less chlorine than wood pulps. Bleaching with chlorine and hypochlorite takes place at normal pressure and at temperatures varying from 20 to 40°C.

Environmental legislation has forced the pulp and paper industry to reduce or eliminate chlorinated organic compounds in water effluents. To satisfy this governmental demand, elemental chlorine is substituted by chlorine dioxide. This is called elemental chlorine free process or (ECF) process. Some factories have completely dispensed with chlorine and chlorine compounds bleaching and shifted to the total chlorine free process. This is abbreviated as (TCF) bleaching process. Several studies have shown that the effluents are similar in ECF and TCF especially in toxicity tests. The ECF bleaching process is preferred because of its lower capital cost compared to TCF process (Li *et al.*, 2010).

Another method for bleaching is oxygen bleaching. In fact oxygen has been used since long time for partial delignification of wood and other raw materials as a stage in the pulping process. It cannot achieve more or less complete delignification because the pulp will be excessively degraded.

Hydrogen Peroxide Bleaching

Hydrogen peroxide is a mild oxidant, which has been applied since long time in the industry especially for bleaching of mechanical pulps. It is now applied to bleach chemical pulp in order to reduce the use of chlorine in bleaching. Additives, temperature etc. play a big role in peroxide bleaching (Pan *et al.*, 2010).

Ozone Bleaching

Ozone is another oxygen-based agent producing no chlorinated organic materials in the bleaching effluent. However cellulose is susceptible to oxidation and can be easily degraded during oxygen bleaching or ozone bleaching. Several measures have to be taken to prohibit or reduce this degradation (Theng *et al.*, 2015a).

Other Bleaching Processes

These include peracids bleaching, bleaching with activated oxygen, and catalytic oxidative bleaching.

Biobleaching

This process represents a new biotechnological approach to reduce toxic effects of conventional chlorine bleaching processes. Biobleaching can be classified in two categories.

- Microbial bleaching in which growing cells are used (bacteria, yeast, fungi or algae).
- Enzymatic bleaching in which preformed enzymes are employed.

However, biobleaching has not been solely used for pulp bleaching. It should be fortified by a previous or a following chemical bleaching step (Theng *et al.*, 2015b).

Additives in Papermaking

These are the non-fibrous part in the paper furnish. In ancient days of paper making, mineral matter was added to pulp prior to sheet formation in order to increase the weight of paper. This process has been considered as adulteration. Later on it was realized that the addition of certain minerals to paper is highly beneficial. These added minerals are termed as fillers.

The process itself is called filling or loading. Fillers, when added in certain amounts, improve the opacity of paper and increase the smoothness of paper surface. Thus it improves the suitability of paper for printing. The most popular filler is kaolin or clay. Another important group of additives are the sizing agents.

Sizing makes the paper resistant to liquid penetration, e.g., writing inks. Unsized paper could not be suitable for writing. The oldest sizing agent used is rosin size. There is a lot of other additive such as dry strength and wet strength additives. Attention must be paid, that pulp alone does not make paper. Other components are needed.

Due to the high ash content in rice straw, one can more or less dispense with fillers. Due to the closed surface of paper sheets produced from this raw material, only slight sizing is needed to improve the writability. Besides using additives in paper making, the agricultural wastes pulps have to be blended with other pulp sorts, preferably soft wood pulp to ensure reasonable speed of the paper machine, and to compensate some defects in the paper (Theng *et al.*, 2017).

According to stricter environmental legislation nowadays, factories utilizing rice straw for pulp manufacture are reducing their dependence on this raw material and shift to other cellulose materials, so far that the problem of silica is not solved (Wu *et al.*, 2011).

Blending

Mixing of different pulps together is termed as blending. Addition of minerals is termed as filling. All these processes i.e., blending, and filling as well as sizing and applying other types of additives are carried out in the beater or in an extra chest. The produced mixture is called "paper furnish". This can be charged directly to paper machine.

Paper Coating

Many types of paper need to be surface sized or coated in order to modify some of paper properties or to implement new properties.

Pigment coating is one of the most important coating processes. It is used mainly for the production of printing papers for magazine, catalogues etc. Usually an aqueous mixture of pigments (e.g., clay) and an adhesive (e.g., starch) is applied to the surface of paper. When this coat is applied to a cheap dark rough-surfaced paper, one can get a paper of high brightness. In other words, the paper defects are overcome by an economic process, and the paper becomes suitable for fine printing.

Other types of coating make paper resistant to water vapor and air as required for packaging of food and beverages etc (Zhang and Hu, 2014).

The Present Status of Production of Paper and Board From Agricultural Wastes in Egypt

Rice straw was the first agricultural waste used for production of paper and board in Egypt. In the thirties cheap packaging and wrapping paper was produced from rice straw. Production of stationary paper from rice straw has begun in the early sixties. The amount of rice straw used in this industry increased steadily since that time till it reached more than 60,000 tons of pulp and more annually. However due to more and more strict environmental legislation, the utilization of rice straw has decreased.

Experimental work on laboratory scale and pilot scale has shown that difficulties, encountering chemicals recovery from black liquor could be overcome, to a great extent. Nevertheless, realization on industrial scale has not yet taken place. Apart from chemicals recovery, treatment of black liquor to decrease the (B.O.D.) before disposal in water stream has not been seriously considered up till now.

Solving the Most Difficult in Pulp and Paper Production

Recovery of Pulping Chemicals

The first step in recovery is to concentrate the dilute black liquor in order to increase its solid content. This is done by evaporation. There are several types of evaporators. Usually the liquor passes upward in vertical tubes countercurrent to the flow of steam. Vacuum also could be applied in one step or more. The concentration of the black liquor rises to about 50% solid content. The liquor is further concentrated in direct contact evaporators to a solid content more than 55% and could reach 70%. At this concentration, the liquor can be burned easily with stable combustion in the recovery furnaces. The presence of much silica in rice straw black liquor causes severe difficulties during this process. Silica precipitates at the surface of the evaporating tubes and in the nozzles leading to low heat exchange and even clogging. Therefore, desilication of the black liquor is necessary before sending the liquor to the evaporators. Several experiments and designs have been proposed for desilication.

The results were promising but the project was not completed. It should be noted that rice straw due to its open structure is easily pulpable and does not require high sodium hydroxide liquor concentration. Moreover, the price of rice straw is much cheaper than other agricultural residues. Even without recovery of chemicals, production of chemical pulp from rice straw was economically feasible. For instance rice straw cost represents one sixth of the total production cost of pulp while wood cost represents up to one-third of the cost of production.

However, production of pulp consumes about 500 tones water based on the weight of raw material. The disposal of this great amount of water directly into water stream causes environmental pollution. Other alternatives were proposed. The spent liquor instead of being discharged in a body of water can be used, as it is, for different purposes. One of the uses is the direct application of the lignin in the liquor as adhesive in brick industry.

The black liquor can also be treated easily in special installations to lower its B.O.D. demand. Then it can be safely discharged in water stream without causing pollution (Nassar *et al.*, 2017).

Recovery Furnace Operations

As seen before we have discussed each industrial operation during pulp manufacture in order to assess the suitability of agricultural wastes for full industrial manufacture of pulp. Now in the following a brief account of recovery furnace operations is given.

At first, the remaining water in the heavy liquor, coming out from the evaporators is further evaporated. The organic part of the solid matter is ignited and burnt in the recovery furnace. This part includes lignin, and its degradation products, as well as hemicellulose and its degradation products. The sodium in the liquor is converted into sodium carbonate because of the excess carbon dioxide evolving during burning. It should be mentioned that in factories using sugar cane bagasse as pulping raw material, the concentration of the black liquor charged in the furnace is usually less than average values of black liquor concentration of wood pulp.

This, however, does not affect much the profitability of the production. Many burner types are used in the furnace. The recovered chemical is discharged from the furnace bottom as a melt or smelt consisting of sodium carbonate in the case of soda process, or a mixture of sodium carbonate and sodium sulfate in the case of sulfate process. This smelt, after partial dissolution in weak dissolving liquor, is sent to the recausticizing department.

The heat generated from burning black liquor is recovered by passing hot gases into a boiler to generate steam. The amount of recovered heat is usually sufficient for all the heat requirements of the pulp factory and there could be still some heat for other uses. The recovered chemicals from the furnace are dissolved in water. The resulting liquor is known as green liquor. This color is imparted by iron compounds (Fahmy *et al.*, 2017).

Causticization of Green Liquor

This operation consists of reacting lime with green liquor after clarification. Lime reacts with sodium carbonate to produce sodium hydroxide and calcium carbonate. The causticizing reaction proceeds to about 85%–90% completion. In continuous causticizing systems the causticized liquor containing the suspension of calcium carbonate is pumped to decanters, and the clean liquor called white liquor is sent to storage tanks. From there it is pumped to the digesters for further pulping.

Land Filling

This involves the discharge of the black liquor in the earth and then covers the waste with earth.

Designating an area for land fill is an engineering project. The geological features of the area are considered, since there will be a certain amount of settling. Minimum pulp washing is necessary. Also partial evaporation to reduce water content should be considered.

The Biological Oxygen Demand (B.O.D.) must be reduced before discharging the black liquor into the sewer or water stream, the B.O.D. has to be reduced. In a primary treatment the liquor can be partially neutralized, then clarified. This takes place in big basins. The liquid is then pumped to large lagoons. The natural self-cleaning process is enhanced by aeration or by pumping oxygen in the liquid (Nassar *et al.*, 2015).

Paper Types and Properties of Paper

These are divided into physical, optical, chemical, electrical and microscopical properties. Physical properties include thickness, basis weight, tensile strength, tear strength, etc. Agricultural wastes pulps can possess high tensile strength but usually low tear strength. Optical properties include brightness and opacity. These can be tailored by bleaching ...etc. Agricultural wastes paper can be made equal in this respect to paper produced from hard woods.

Agricultural wastes are suitable for producing almost all types of packaging and wrapping paper except the Kraft liner in corrugated board as well as cement bags.

Agricultural wastes are more or less suitable for producing many types of fine paper as middle grade printing or writing paper. There are some limitations for producing newsprint from agricultural residues. Cotton linter is suitable for producing security paper such as currency and bond paper.

Paper Types

There are enormously many types of paper including the examples given before. The most common paper types are:

Newsprint, stationery papers (printing and writing), lightweight coated paper for magazine, currency paper, hygienic tissue paper (sanitary and household), paper card, solid board for boxes, wrapping and packaging paper, corrugated board. In the following some paper types are discussed in details (Anapanurak and Pisuthpichet, 1997).

Newsprint

All daily newspapers use this type because it is the most economical. All newsprint is almost made of mechanical softwood pulp. Up till now only one factory in the whole world is producing newsprint from agricultural residues. This kind of paper is lower in quality and cannot be accepted by some consumers.

Offset Paper

This is the printing paper and uncoated. This paper type is about three times expensive than newsprint. The reason is that this paper should be chemical free. It requires extensive washing during the manufacturing process as well as extensive bleaching. Filling, sizing, and other additives are required.

Opaque Paper

This is used for high quality printed paper as annual reports.

Tablet Paper

For school purposes, cheap paper with a partial ground wood content is produced for maximum economy.

Bond Paper

This paper should be durable and resistant to aging. It is usually made of rags or cotton linters.

Manifold

It is a light-weight paper used for snap-out forms.

Coated Paper

Mentioned before.

Glassine Paper

Highly beaten paper is almost non-porous and transparent. This is called (in Arabic) butter paper and is used for packaging fatty and greasy food materials.

Paper sheet formation in the laboratory involves simple operations. On the other hand, in the industry, the situation is completely different. In fact, the paper machine used in the industry represents one of the most complicated and sophisticated continuous machinery. As being reported, it consists of different parts applying different techniques for removal of water from stock. The stock flows from the headbox to the wire in a consistency of about 1%–2% fibers, i.e., about 98% water, and paper leaves the end of the machine at only 6% water or moisture content. As paper machine runs at speed of up to 2000 m/min and at a machine width up to 6 m or more, it becomes evident that production under such conditions necessitates highly technological devices to synchronize sheet transfer from each part of the machine to the next part. Any slight misfit causes the paper sheet to tear either on the wet or on the dry state.

Before going up from the laboratory scale to full industrial scale, it is advisable to carry out pilot plant scale experiments.

After call for tenders in the late fifties different pulping processes were proposed by different participants. Comparison was made between the different processes on full industrial scale regarding easier production, less technical difficulties and economic feasibility. On basis of all these steps of the study the most suitable process and most suitable conditions were chosen.

As mentioned before the presence of high amount of silica in rice straw, and consequently in black liquor, prohibits the recovery of chemicals from black liquor. Therefore, no recovery unit was established.

Despite the disposal of black liquor containing the pulping chemicals in water stream yet the process was used, and is still economic. Due to its open microporous structure and low lignin content, rice straw is easily pulpable and bleachable. In other words, the consumption of sodium hydroxide is less than half as in the case of other raw materials.

In order to find a solution for water stream pollution several experiments were undertaken. One is the desilication of black liquor before pumping to the evaporators. Pilot plant equipment has been designed and tried experimentally. Another trial was based on new design for recovery furnace. Till now neither was realized industrially.

According to stricter environmental legislation nowadays, factories utilizing rice straw for pulp manufacture are reducing their dependence on this raw material and shifting to other cellulose materials, so far that the problem of silica is not solved.

Characterization of the Rice Straw Pulp

Dry matter content of pulp was determined according to the standard method given below and cooking yield was calculated and followed by a screening process. Kappa number and the other pulp properties were measured according to the standards given (Kaur *et al.*, 2017).

<i>Analysis</i>	<i>Method</i>
Kappa Number	TAPPI T 236 cm-85
Ash (%)	TAPPI 211
α -Cellulose (%)	TAPPI 203 os-61
Pulp Dry Matter Content (%)	SCAN-C 3:78
Raw Material Dry Matter Content (%)	SCAN-CM 39:94

Physical Properties of the Pulp

- Breaking length
- Burst factor
- Folding endurance
- Brightness

Mechanical Properties of Paperboard

Strength properties: Strength properties were estimated according to the Tappi Standard Methods.

Tensile strength (Kg/mm): Tensile strength was conducted according to Tappi standard (T 494 om-01). Tensile index, the tensile strength in N/m divided by grammage.

Stiffness strength: Stiffness was conducted according to Tappi standard (T 489 om-08) This procedure is used to measure the stiffness of paper and paperboard by determining the bending moment in gram centimeters necessary to deflect the free end of a 38-mm wide vertically clamped specimen 150 mm from its center line when the load is applied 50 mm away from the clamp.

Taber Stiffness: Units are defined as the bending moment of 1/5 of a gram applied to a 3.81 cm wide specimen at a 5 centimeter test length.

The Present Status of Production of Paper and Board From Agricultural Wastes in Egypt

Rice straw was the first agricultural waste used for production of paper and board in Egypt. In the thirties cheap packaging and wrapping paper was produced from rice straw. Production of stationary paper from rice straw has begun in the early sixties. The amount of rice straw used in this industry increased steadily since that time till it reached more than 60,000 tons of pulp and more annually. However due to more and more strict environmental legislation, the utilization of rice straw has decreased.

Experimental work on laboratory scale and pilot scale has shown that difficulties, encountering chemicals recovery from black liquor could be overcome, to a great extent. Nevertheless, realization on industrial scale has not yet taken place. Apart from chemicals recovery, treatment of black liquor to decrease the (B.O.D.) before disposal in water stream has not been seriously considered up till now.

Future Prospects

The present annual consumption of different paper and board types in Egypt is till now much higher than the amount produced locally and has surpassed 500,000 tons annually. The utilization of more rice straw in future depends upon finding a suitable solution for the disposal problem of black liquor. It is possible to fulfill the environmental requirements by one or more methods. Lowering the B.O.D. before disposal of the black liquor in water stream might be reasonable. However, desilication of the black liquor before combustion in chemicals recovery furnace may be the best method. This needs further research.

Conclusion

Rice straw was transformed into pulp and paper through semichemical pulp in high yield easily. Either coarse grade pulp or fine grade pulp can be obtained by semichemical pulping. As shown earlier, the lignin content of these residues is low and much lower than lignin of wood, this facilitates delignification i.e., pulping. Moreover, the open structures of agricultural residues make them more accessible to the chemical reagents used in cooking. The reagent molecules diffuse and penetrate quickly and deeply in the cell wall fine structure. Thus, this makes agricultural residues more pulpable than wood.

See also: Expediting Faster Housing Supply in India Using Straw Bale as Prefab Building Material. Jute Pulping: Opportunities and Challenges. Lignin: A Renewable Raw Material

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Role of Green Polymers in Food Packaging

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Introduction

The environmental impact of plastic wastes has been recently put on the top of the agenda of each government politics. There are different ways by which the challenges related to plastic waste can be significantly overcome. These approaches include: innovative design for recycling process that makes us sure even more sophisticated packaging are appropriately recycled, development of new packaging materials which have higher efficiency to protect products while are still easily recyclable, development of biodegradable packaging materials which meet all the requirements of conventional materials, improving the collection strategies to reach more reliable techniques for handling plastic wastes, and encouraging use of recycled polymers by setting new standards development (Ragheb and Miller, 2018). Biodegradable materials are attracting much attention due to polysaccharides environmental issues and the fact that petroleum resources are finite. Food packaging is considered the main application of green polymers (Oever *et al.*, 2017). This article focuses on three various types of bio-based polymers having unique properties in order to efficiently discuss the suitability of these polymers as food packaging materials.

An Overview of Polymers

Fossil-Based Polymers

A chemical compound synthesized from repeating structural units through polymerization is called a polymer (Mirabal *et al.*, 2013). Petroleum and natural gas as fossil feed-stocks are used to produce fossil plastics or petrochemicals. The formation of fossil feed-stocks takes millions of years (EIA, 2018). About 7% of these resources are converted into polymers like polypropylene (PP), polyethylene (PE), polystyrene (PS), polyethylene terephthalate (PET), and others. Although these materials are presently and predominantly produced from fossil feedstocks, they can also be bio-based which are made from biomass (Oever *et al.*, 2017). Fossil-based polymers known as conventional polymers exhibit excellent properties like high transparency, barrier, and mechanical characteristics. Their production causes the environment to be disturbed due to increasing the effect of gases like methane, SO₂, nitrous oxide, and raising the level of CO₂ in the ecosystem which finally results in disbalance in climate pattern and subsequently, devastating disasters will occur. Various harmful gases including alkenes, alkanes, aromatic and chlorinated hydrocarbons are emitted during incineration of synthetic polymers (Ghuttora, 2016; Ashok *et al.*, 2016; Mirabal *et al.*, 2013).

Green Polymers, an Alternative to Fossil-Based Polymers

Green polymers or environmentally friendly polymers can be produced from renewable or synthetic materials (Fig. 1).

There is a false controversy between green polymers and petroleum-based polymers. According to several incorrect arguments, oil-derived polymers are environmentally unfriendly while polymers produced by organisms are considered as green. It has to be noticed that petroleum-based polymers can move towards a sustainable situation raising petroleum-derived compounds like aliphatic, aromatic copolymers can also be considered a starting point to produce biodegradable polymers which have technical properties similar to those of polyethylene (Belgian Plastics & Rubber Institute, 2006), and can be synthesized through altering the microstructure and composition to fulfill particular requirements. These materials offer an alternative to the conventional polymers used in various applications (Chauhan *et al.*, 2013). Green polymers cause no disadvantage to the environment since no hazardous substances like chemical residues or toxins are produced as byproducts (Ghuttora, 2016). Green polymers are categorized into Synthetic polymers and bio-based polymers which are totally or partially produced from natural polymers such as proteins, polysaccharides, and lipids; and poly-blends made from a mixture of bio-based and synthetic polymers, or biopolymer blends (Cheng *et al.*, 2013; Weber *et al.*, 2002).

Renewable and Bio-Based Materials

Renewable feedstock refers to the provision of feedstock collected from natural resources which are replenished rapid enough as being used. It means unlike petroleum that forms after millions of years, the resources of bio-based feed-stock renew very fast as new crop plantation balances harvesting, which means they have a high regeneration rate (Oever *et al.*, 2017; Ivankovic *et al.*, 2017).

There is contradictory and unclear information regarding biodegradable and/or bio-based materials. The term bio-based relates to the source of the material whereas the term biodegradable shows the material can be decomposed depending on its chemical structure. In fact, materials considered as bio-based are not necessarily biodegradable or compostable. A bio-based material is defined

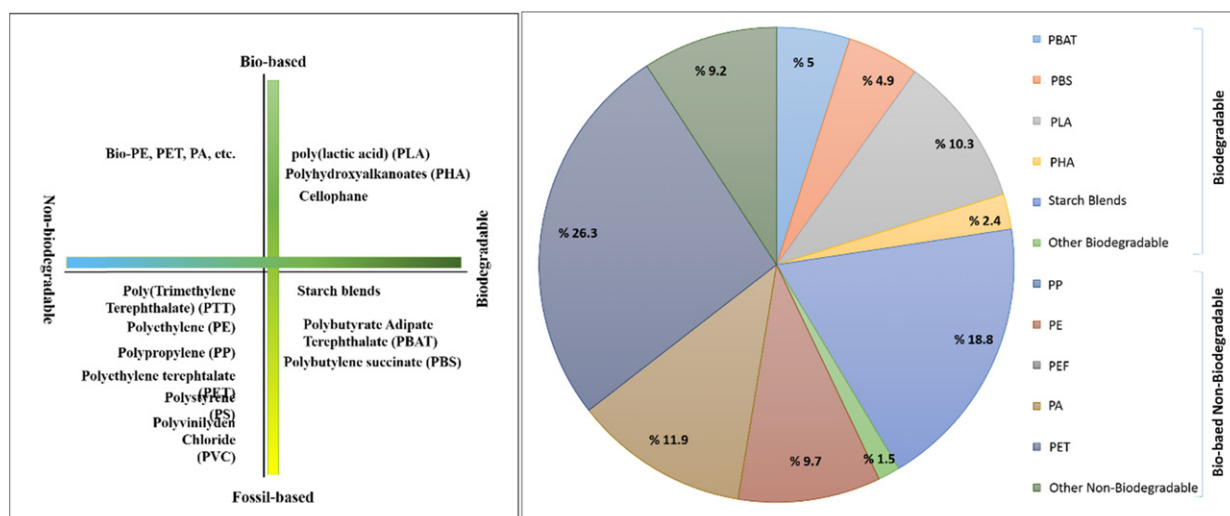


Fig. 1 Different categories of biopolymers (left), and Global production capacities of biopolymers 2017 (right) (by material type).
Source: European Bioplastics, nova-Institute (2017).

Table 1 Certification schemes and labels for biodegradable polymers

Country	Organization	Standards compliance	Symbol
USA	Biodegradable Products Institute	ASTM D6400	
Finland	Jatelaito Syhdistys	EN 13432 and ISO 14851 ff.	
Germany	International Biodegradable Polymers Association and Working Groups	DIN V 54900 or EN 13432 or ASTM D6400	
Belgium	AIB Vincotte	EN 13432 and ISO 14851 ff.	
Japan	Biodegradable Plastics Society	ISO 14851 ff. moreover, OECD 301C and JIS K 6950 ff.	

Note: Published with permission from Krzan, A., Hemjinda, S., Miertus, S., Corti, A., Chiellini, E. 2006. Standardization and certification in the area of environmentally degradable plastics. *Polymer Degradation and Stability* 91, 2819–2833. Copyright 2006 Elsevier.

as a product partly or wholly obtained from biomass, a material of biological origin. However, some polymers like PLA containing building blocks derived from sugars are also considered as bio-based products. Most of these bio-based materials have certificates proving they can be utilized in food-contact applications (Ivankovic *et al.*, 2017). The carbon content of bio-based materials and the bio-based content of a product can be measured according to the standard methods, e.g., the EU or ASTM standards (EN 16640 (2015), and D6866 respectively), which are based on ^{14}C (Carbon-14, or radiocarbon, as a radioactive isotope of carbon) content measurement to evaluate the biogenic carbon content (Oever *et al.*, 2017). This measurement is based on the fact that petroleum-based materials like gas and oil do not contain ^{14}C due to radioactive decay, while bio-based materials take up ^{14}C from the atmosphere and therefore contain this component (Bradley, 2010; Guzman *et al.*, 2011; Ivankovic *et al.*, 2017).

Biodegradability and or compostability or even disposing of procedure after use can be made clear to the consumer using labels and logo's, by linking a certification system (Table 1).

Environmental Impact

Conventional polymers, although very useful, cause damage to water resources, environment, and the whole ecosystem. Accumulation of conventional polymers has led to the mitigation of arable land and releasing gases by burning, which induced researchers to develop biodegradable polymers (Ghuttora, 2016; Ivankovic *et al.*, 2017). Many economic and social benefits will be brought by reducing the environmental cost of packaging waste. Substitution of petroleum-based polymers with bio-based polymers leads to the reduction of greenhouse gas emission and non-renewable energy use. However, land-use change may have a negative influence on reducing greenhouse gas emission (Oever *et al.*, 2017).

End-of-Life Options

The type of polymers and the processing infrastructure determine the end-of-life solution. Certified biodegradable polymeric materials can be digested on agricultural land and even can be industrially or home composted (Oever *et al.*, 2017). The end-of-life options are entirely dependent on the region where these materials are recovered. According to the type of biodegradable and bio-based materials and the application they are used for, the most appropriate end-of-life solution is determined. Apart from all the options reported for conventional polymers, various biodegradable and bio-based polymers can also be composted. Some of the biodegradable polymers are appropriate for domestic composting, and through industrial or home composting they will be decomposed by 90% within a maximum of 6 months. According to EN 13432 (2000) standard, these biopolymers qualify as compostable polymers (Belgian Plastics & Rubber Institute, 2006). Compostable packaging materials have a potential to collect food waste which is converted to compost through the composting route (Ghuttora, 2016; Lucas *et al.*, 2008; Shah *et al.*, 2008).

Sustainability

Sustainability is the requirement to manage the resource base, by which we assure ourselves of sharing the average quality of life by future generations. Therefore a sustainable material involves a non-subtractive quality of life (Oever *et al.*, 2017). The major aspects required to design a sustainable product are outlined in Fig. 2.

The term sustainability is meaningful when all sustainability aspects have been considered, and the specific product has been clearly compared to other products (Oever *et al.*, 2017). In the case of biopolymers, the plants are grown by farmers. After polymerization, biopolymers are converted to final products which are eventually transported to the wholesalers, retailers, and consumers. After all, composting or recycling are the end-of-life options which do not leave any toxins and nature's balance for sustainability is maintained (Ghuttora, 2016).

Durability

Durability refers to the power of a product to keep its efficiency for a long period without remarkable deterioration. The durability of a polymer depends on its chemical structure and the conditions the polymer is going to be subjected. Opposite to biodegradable materials, petroleum-based materials are considered durable. However, the lifespan of some biodegradable materials such as PLA can be as long as 10–20 years at indoor conditions, although they are biodegradable at industrial conditions via composting process. Some bio-based polymers like bio-PET and bio-PE also indicate the same durability as a petroleum-based PET and PE (Oever *et al.*, 2017).

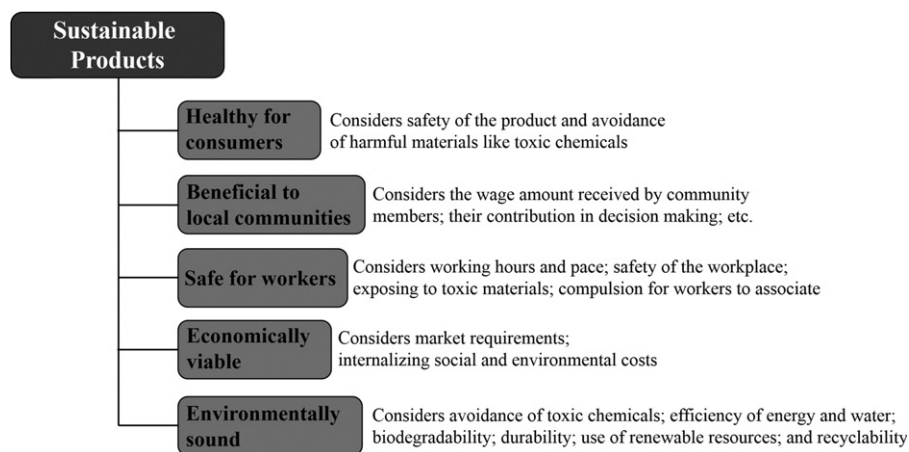


Fig. 2 Major aspects to design a sustainable product.

Costs

In general, biodegradable and bio-based polymers are high-priced on a weight basis compared to petroleum-based polymers. This higher price can be due to a higher density of most bio-based polymers. However, there are still exceptions like PLA for which the thickness of the polymer can be reduced due to the higher stiffness of PLA compared to PS, which causes the price of this material to decrease. Moreover, unlike the price of petroleum-based polymers which changes by oil price fluctuations, the price of bio-based polymers are more stable. It is foreseen that bio-based polymers prices will drop under the effect of economy of production scale, conversion and logistics (Oever *et al.*, 2017).

Food Packaging

Packaging is defined as a product used to protect, hold and deliver goods. Packaging materials should be carefully selected to meet legislation, safety, and functionality conditions and other requirements determined for various food packaging applications. The main task of food packaging is protective against microbial, chemical and mechanical impact. Moreover, packaging keeps the freshness and nutritional value of the product. The main application field of biodegradable and bio-based polymers is for food packaging (Bradley, 2010; Ivankovic *et al.*, 2017; Oever *et al.*, 2017).

Bio-based polymers which are identical to petroleum-based polymers such as bio-PE and bio-PET are applicable for the same applications. Cellophane, PLA, and Starch-based polymers with unique properties are the most common bio-based polymers used for food packaging. These kinds of materials same as petroleum-based polymers have to comply with the regulations related to food safety and have a certificate proving they are allowed to be used for food packaging especially in food-contact applications (Ivankovic *et al.*, 2017; Oever *et al.*, 2017; Siracusa *et al.*, 2008).

Type of Bio-Based Polymers Suitable for Food Packaging

As shown in Fig. 3 bio-based polymers suitable for food packaging are categorized based on their resource and production method. Commercial bio-based food packaging applications are also presented in Table 2.

Polymers directly isolated from biomaterials

These polymers comprise polysaccharides, proteins, and lipids, which are frequently presented on the market. The main feedstock used to extract these polymers are plants, domestic and marine animals. Polysaccharides like starch, cellulose and chitin; and proteins like

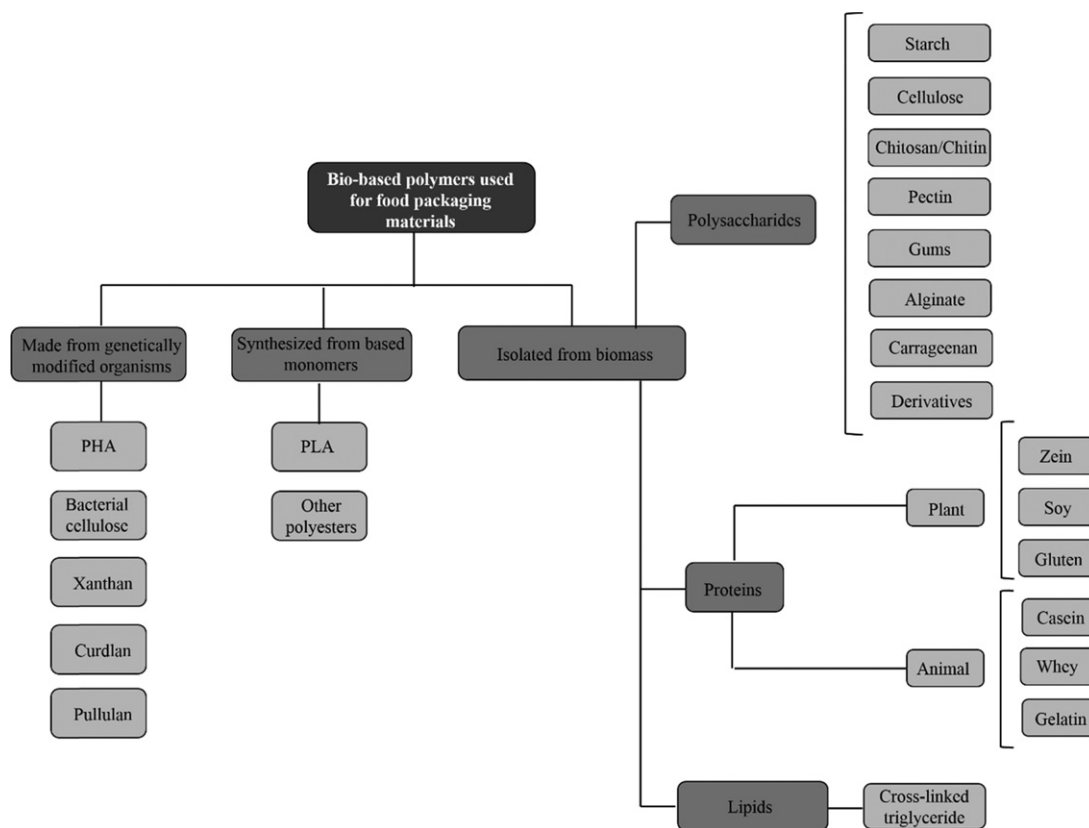


Fig. 3 An overview of bio-based polymeric materials.

Table 2 Commercial bio-based food packaging applications

	<i>Food packaging applications</i>		
	<i>Cups and Trays</i>	<i>Bottles</i>	<i>Films</i>
<i>Starch blends</i>	Fruits and vegetables, cups used for coffee	N. A	Fruits and vegetables, grocery bags
<i>Biodegradable polyesters</i>	Fruits and vegetables	N. A	Frozen foods, grocery bags, fruits and vegetables
<i>Cellulose</i>	N. A	N. A	Candy wrapping, fruits, and vegetables (e.g., tomatoes and peppers), meat, fish, cheese, butter, bread, coffee
<i>Starch PLA</i>	N. A	N. A	Fruits and vegetables (e.g., potatoes and carrots)
	Fruits and vegetables, bakery, salad, dairy products, meat drinking cups, ice cream	Wine bottle capsules, short shelf life products and juices	Fruits and vegetables, bread bags, using barrier laminates can be used for long shelf life products
<i>PHA</i>	Frozen foods	N. A	Fresh meat

Note: Oever, M., Molenveld, K., Zee, M., Bos, H., 2017. Bio-based and biodegradable plastics: Facts and figures: Focus on food packaging in the Netherlands. Wageningen Food & Biobased Research, Institute Within the Legal Entity Stichting Wageningen Research. Report 1722.

casein, whey, collagen, and soy protein are the most common biopolymers listed in this category which are used alone or mixed with poly(lactic acid) or other synthetic polyesters. The cellulose-based paper is the most prevalent packaging type used in the food industry, although cellophane as regenerated cellulose film and cellulose acetate are used for this purpose as well (Ivankovic *et al.*, 2017).

Polysaccharides

Polysaccharides may contain two or more sugar diagnosed as hetero-polysaccharides or may be composed of a single monosaccharide considered as homo-polysaccharides. Pullulan, curdlan, levan, and bacterial cellulose are homo-polysaccharide comprising linear chains, whereas gellan, and xanthan is hetero-polysaccharides (Oner, 2013). It has to be noticed that acyl groups, inorganic residues, and amino acids are other elements which may be attached. There are nearly 40 different monosaccharides which produce polysaccharides through making a wide variety of structures (Ghuttora, 2016). The main structural polysaccharides playing an effective role in biopolymer production are described in this section.

Starch

The most common new materials used to produce starch biopolymer are green plants such as wheat, rice, corn, and potato. Availability and low cost of starch make it the most acceptable biopolymer. Different types of bags and sacks, hot-formed containers, and trays are made using starch-based biodegradable polymers. Polystyrene and polyethylene are successfully replaced with starch-based materials (Bradley, 2010; Ghuttora, 2016). Starch can be blended with other materials in a proportion of about 30%–80% based on its application. Fossil-based biodegradable polymers like PLA or PHA/B (polyhydroxyalkanoate/butyrate) are used as the most common copolymers. These starch blends are fully biodegradable however partially bio-based. Besides, the starch may be blended with fossil-based polymers like polypropylene to produce durable polymers. Starch-based plastics have a higher density than conventional plastics which makes them less price competitive (Bradley, 2010; Ghuttora, 2016; Ivankovic *et al.*, 2017).

Pulping native starch with cellulose fibers is performed to make compostable cups and trays through the hot-pressing method. The melting point of starch is higher than the temperature in which starch decomposition occurs, which causes this polymer not to be thermally processed. In order to make thermoplastic starch (TPS), an extruder is used to process native starch under controlled conditions of pressure, temperature, shear, and water content, during which crystalline structure melts, an inter-molecular rearrangement happens by swelling granules, and semi-crystalline polymer transforms to the amorphous structure with highly enhanced processability. The final resin composition can be provided through integration of additives. Plasticizers are used to mitigate intermolecular hydrogen bonding and subsequently to stabilize the product. However, there are still limitations with TPS including limited mechanical properties and a high level of hydrophilicity that should be improved (Ivankovic *et al.*, 2017).

Biodegradable starch-based plastics

Starch-based plastics are made from starch and compostable polyesters (PLA, PBS (polybutylene succinate), PCL (polycaprolactone)). The blending of polyesters with starch caused water resistance and improved mechanical and processing properties. Starch-based plastics usually contain less than 50% of starch and are applied where biodegradability is important such as service ware, garbage bags, and agricultural products. These products can provide feedstock while containing organic waste. These materials can also be biodegraded in the soil, freshwater, marine environment, and anaerobic digestion. The main factor determining whether these materials can be used for food contact applications is the type of component blended with starch because some of these components can easily migrate (Bradley, 2010; Ghuttora, 2016; Ivankovic *et al.*, 2017; Oever *et al.*, 2017).

Starch-based films

Starch-based films are used as a monolayer or in combination with barrier films as laminates for packaging applications. These films can be translucent, but they are not a good option for applications where transparency is required. Combination of starch films with flexible polyesters like PBAT (polybutyrate adipate terephthalate) results in the high flexibility of these materials. These films are appropriate for grocery bags in which barrier properties are not required, and starch-based films are good alternatives to PE. BOPP (biaxially oriented polypropylene) can be replaced with starch-based films if an outer layer made from PLA is used. Starch-based films can also be used in barrier laminates made from cellophane in order to make them heat stable (Oever *et al.*, 2017).

Starch-based trays and other thermoformed products

Starch-based trays are structured as a rigid foam which is not transparent and only used for the applications where barrier properties are not required. Mechanical properties and the end-of-life options are important for these trays. In order to improve thermoforming properties and rigidity, the addition of PLA in blend composition can be effective; whereas, in order to increase flexibility, application of biodegradable polyesters is useful (Oever *et al.*, 2017).

Cellulose

Cellulose is a highly polar polymer composed of glucose units with strong mechanical properties. Polymer chain configures in a different way than what is observed in starch, which provides an opportunity to make this polymer stronger because of forming strong hydrogen bonds. Hydrolysis resistant of cellulose is higher than starch due to the mixed morphology of cellulose. Cellulose extraction was a difficult process with expensive pre-treatment which caused alternative extraction methods to be developed. Enzymatic hydrolysis process is used to isolate cellulose from biomass with the help of genetically modified hydrolysis enzymes (SB), such as exoglucanases, endoglucanases, and β -glucosidase. (Chee *et al.*, 2010; Ghuttora, 2016). After cellulose purification, it can be chemically modified to manufacture cellulose derivatives having improved properties (Bradley, 2010; Ivankovic *et al.*, 2017). However, bulk production of cellulose derivatives costs much. Uncoated cellulose films are a good barrier to aromas, flavor, and bacteria, and highly permeable to water vapor. Natural attributes of cellulose films can be refined through coating, metalizing, and laminating processes which cause them to be prepared for specific applications. The most effective coatings are synthetic coatings. However, bio-based coating materials can also be used (Ivankovic *et al.*, 2017).

Cellophane films

Cellophane film is produced through acetate substitution which reduces moisture sensitivity and increases transparency and gloss, while results in less biodegradability (Shen *et al.*, 2009). Different cellulose esters can be manufactured, but only cellulose acetate is currently used for food applications like fresh products and baked goods (Bradley, 2010; Oever *et al.*, 2017). Rather stiff, and highly transparent cellophane films have a small share in the market, however, for decades, they have been used especially as candy wrapping. They are also used as the glossy transparent cover on tea boxes. Cellophane as a biodegradable barrier film is suitable to be applied for manufacturing laminates (Oever *et al.*, 2017).

Chitin and chitosan

Chitin as the second most abundant polysaccharide is found in marine invertebrates such as shrimps, crabs, shellfish, insects, and some fungi and yeasts. Chitin contains units of N-acetyl-D-glucosamine. Deacetylation of chitin results in chitosan production. Chitin and chitosan are non-toxic and eco-friendly renewable polymers with no solubility in water, due to the formation of intermolecular hydrogen bonds, and no antigenic properties; besides they have excellent biocompatibility (Cheba, 2011; Ghuttora, 2016). Both are utilized to manufacture biodegradable food packaging and an edible coating which prolong the shelf life of products especially fresh fruits and vegetables (Zhao and Mc Daniel, 2005). Chitosan has poor water resistance and mechanical properties which make producers to blend chitosan with other polymers like starch in order to improve these properties. Good antimicrobial properties of chitin and chitosan make them useful as a biodegradable food packaging in order to prolong the shelf life of foods (Chiellini, 2008; Ivankovic *et al.*, 2017).

Proteins

Proteins are divided into two categories based on their origin including plant proteins (such as soy, gluten, zein, potato, and pea) and animal proteins (like collagen, casein, whey, and keratin). Numerous functionalities of proteins make them proper to be modified to create a polymer. Protein-based polymers, except for keratin, are sensitive to humidity which can be solved by blending or lamination. To date, there was no protein-based plastic commercially utilized for food contact applications. Isolated soy protein is the most common plant protein applied to produce biodegradable food packaging (Bradley, 2010).

Soybeans

Isolated soy protein-based films are weak and moisture sensitive which can be improved by incorporation of stearic acid in a proportion of about 25% (Lodha and Nteravali, 2005). It has been recently reported that blending soy protein with glycerol, K-carrageenan, or gellan gum is useful to produce biodegradable or edible soy protein-based packaging trays (Mohareb and Mittal, 2007). Barrier properties, especially to moisture, have to be considered to produce such packaging before coming across a great application in the future, due to the hydrophilicity biopolymers mostly have. Protein-based films are expected to be extensively applied as edible films in the future (Ivankovic *et al.*, 2017).

Lipids

Lipid compounds like glycerides and wax are mainly used to supply hydrophobicity in food coating structures. They efficiently prevent water-vapor transition through edible films. The functional properties of packaging films contained lipids are extensively influenced by lipid characteristics including the degree of saturation, physical state, structure, chain length, the shape of crystals, and distribution (Aydin *et al.*, 2017).

Polymers produced by chemical synthesis using bio-based monomers

In theory, all polymer materials previously used for packaging can be substituted with the types synthesized from renewable monomers. However economic viability can be a question (Kobayashi, 2010). Poly(lactic acid) (PLA) is the most prevalent polymer synthesized using bio-based monomers. Bio-based sources can also be used to prepare monomers applied for conventional petroleum-based polymers (Ivankovic *et al.*, 2017).

Poly(lactic acid) (PLA)

Polymerization of 2-hydroxypropionic acid (lactic acid) leads to produce an aliphatic polyester named poly(lactic acid). Synthesis of lactic acid is conventionally performed using acetaldehyde and hydrogen cyanide. However anaerobic fermentation of carbon substances by certain fungi or bacteria can be an alternative to this process. The new materials used for this fermentation is foreseen to move towards agricultural waste. Low and high molecular weight PLA can be produced through lactic acid condensation and ring-opening polymerization of lactide, respectively. However, the low-molecular-weight PLA is not used commercially. Utilizing racemic lactide leads to produce an amorphous structure which is unsuitable for packaging (De Vlieger, 2003). Two forms of D- and L-lactic acid naturally exist. The optically-pure monomer can be provided by fermentation using a suitable lactobacillus, which subsequently allows producers to enhance the properties of PLA polymer by controlling the combination of D-PLA with L-PLA. The best combination for packaging application is the proportion of 90% from L-lactide and 10% racemic D, L-lactide (De Vlieger, 2003). The application of PLA can be extended by blending with other polymers (Bradley, 2010).

Some specific properties which make PLA attractive for food packaging applications are its stiffness, transparency, gloss, processability, printability, and excellent aroma barrier. Moreover, mechanical properties of PLA as a rigid material is comparable with polyethylene terephthalate (PET) and polystyrene (PS) (Ashok *et al.*, 2016; Bradley, 2010). There is no food safety concern about PLA used for food contact applications. Therefore it can be used in a wide range of packaging products (NatureWorks, 2016). Stiffness and strength of PLA can be improved through combination with other biodegradable or bio-based polymers which causes cost reduction as well (Ivankovic *et al.*, 2017).

PLA can be used to package different type of products including aqueous, fatty, and acidic foods below 60°C, and acidic drinks below 90°C. Besides, considering that PLA is grease resistant, it is suitable to pack viscous and oily liquids. Moreover, dry products and those having limited shelf life can be preserved using PLA. Although PLA is appropriate for beverages, it has to be noticed that PLA is not a good barrier to oxygen, water vapor, and carbon dioxide which makes it unsuitable for carbonated drinks (Shen *et al.*, 2009). PLA is fully compostable and biodegradable. PLA is not home compostable and does not degrade in a landfill, sea water, and soil. Besides, if sorting facilities are available, PLA can be converted back to its monomer lactic acid. It can also be physically recycled (Shen *et al.*, 2009).

PLA film

PLA can be used as a homo-material or as laminates (barrier film) for food packaging. However it is not flexible and besides is rather sensitive to tearing. BOPLA films can be used as an alternative to biaxially oriented PP (BOPP) films. In this application, BOPLA is more advantageous due to its higher water vapor permeability; and they are industrially composted with vegetable and fruit waste. Without barrier materials added to the PLA layer, this bio-based polymer cannot be used to pack water sensitive products stored for a long period. These sensitive products are currently packed in films made from PE. By application of PLA mixed with barrier materials in laminates and/or using AlOx or SiOx technologies, other compostable materials holding good barrier properties will be constructed which are used for a wide range of applications. These methods cause the industry to be able to use PLA for rather a long shelf life foods (Oever *et al.*, 2017).

PLA trays

PLA trays can be used as an alternative to PS trays to pack fruits. Moreover, thermoformed cups made from PLA are varied suitably for dairy products instead of PS cups. The thickness of the cup can be significantly reduced because of the high stiffness of PLA and besides it can be composted without the need to separate its remaining content. Foamed PLA trays are also useful where reduction of cup weight is the main issue. The appearance of the bottles produced from PLA is similar to PET bottles. However high water permeability of PET does not allow the PET to be replaced with PLA in applications needing long shelf life (Oever *et al.*, 2017).

Other PLA packaging products

PLA teabag is an innovative product which does not need to be separated from tea waste for being industrially composted. Conventional paper-based teabags contain up to 30% PP fibers to facilitate heat sealing, which is not compostable. Today, most of the compostable coffee capsules are made from PLA. EPLA as a foam structure is used for various applications and is industrially compostable and safe to use for food contact applications (Ivankovic *et al.*, 2017; Oever *et al.*, 2017).

Biodegradable polymers made from genetically modified organisms

Genetic engineering and genetic modification are generally employed to improve fruit yield, alter the composition of the plant, and/or enhance plant resistance to insects or pesticides (Gould *et al.*, 2016). However, some environmental groups believe that genetically modified organisms (GMO) can be harmful to human health, conventional crops; and therefore its application has to be abandoned (Oever *et al.*, 2017).

Various types of microorganisms including *Alcaligenes*, *Bacillus*, *Azotobacter*, *Rhizobium*, *Halobacterium* produce large quantities of renewable materials. These materials are accumulated by bacteria as a carbon reserve and source of energy. PHAs and bacterial cellulose are two main polymers produced through this route (Ivankovic *et al.*, 2017).

Polyhydroxyalkanoates (PHA)

Polyhydroxyalkanoates (PHAs) are hydrophobic polyesters which may have different properties depending on the monomer building blocks that result in a wide variety of PHA. PHA may be rigid, brittle or rubber-like polymer depending on the carbon source and the bacteria type (Ashok *et al.*, 2016). The bacteria type and the feed are the main factors determining the general structure of monomer units repeated in polyesters like PHA. – (CH₃)-CH₃ is the most prevalent unit repeated in the structure of naturally-occurring PHA. Poly (3-hydroxybutyrate), PHB, is a semi-crystalline linear bio-polymer recognized as a biodegradable PHA. PHB produced by bacterial fermentation of lipid or sugar is useful for food packaging. Biodegradation of PHB takes about 5–6 weeks under optimum conditions (Botana *et al.*, 2010; Ivankovic *et al.*, 2017). PHA can be an elastomeric or a thermoplastic material. Therefore its melting point alters between 40 and 180°C (Yalcin *et al.*, 2006). PHA characteristics depend on the technique used for microbial fermentation, and monomer composition (Ashok *et al.*, 2016; Kumar *et al.*, 2011; Modi *et al.*, 2011).

PHAs, like PLA, are kind of aliphatic polyesters manufactured via fermentation, however, in contrast to PLA, PHAs are synthesized directly within the microorganism. The composition and final properties of PHA polymer are associated with bacteria strain and feedstock type. Moreover, copolymerization can modify PHA characteristics. PHA as the most common polymer of this group is synthesized by polymerization of 3-hydroxybutyrate monomer.

Poly hydroxybutyrate-co-hexanoate (PHBH), and poly (3-hydroxybutyrate-co-valerate) are two main copolymers. These copolymerizations improve processability, ductility, toughness, and flexibility in the finished product (Noda *et al.*, 2004). PHAs can be converted into molded articles, films, fibers, laminates, coatings, and foams. using a conversion process. PHAs are good barriers to water vapor, which makes them appropriate for food packaging applications. PHAs are mostly applied as alternatives to PVC, PP, LDPE, and HDPE. Moreover, bio-PHAs can be utilized for food service ware (Shen *et al.*, 2009; Bradley, 2010).

Bacterial cellulose

Bio-cellulose (bacterial cellulose) is very strong and pure with good mechanical and barrier properties; however, its low yield and high cost prevent large-scale production and application of this material for bulk products (Bradley, 2010).

Conventional polymers from bio-based monomers

Different types of fossil-based conventional polymers can be made using renewable monomers which are indistinguishable from their oil-derived counterparts. One of these polymers is poly (trimethylene terephthalate) (PTT) synthesized through condensation of PDO (1,3-propanediol), and either PTA (terephthalic acid) or DMT (dimethyl terephthalate). PTT characteristics are similar to PET, and the same facilities can be used for its production (Ivankovic *et al.*, 2017; Shen *et al.*, 2009).

Polyurethanes

Polyol and isocyanate are used to synthesize polyurethane. Polyol component can be acquired from vegetable oils, while to date, isocyanate was exclusively obtained from petroleum-based feedstock (Ivankovic *et al.*, 2017).

Polyamides

Bio-based polyamides which are currently available include PA610 and PA11, both synthesized from monomers derived from castor oil. Other monomers partially acquired through fermentation of sugar can be utilized to manufacture partially bio-based PA66. Moreover, azelaic acid as a bio-based monomer derived from oleic acid is used to produce PA69 (Shen *et al.*, 2009).

Polyolefin

Bioethanol produced via fermentation process is used to manufacture polyethylene. In fact, ethylene is produced from bioethanol which is then applied to make polyethylene (LDPE, LLDPE, HDPE), PVA, PET, and PS. As the characteristics of bio-based PE are identical to the properties of fossil-based PE, conventional PE can be totally substituted with its bio-based counterpart. A proportion of about 57% of PE used in Western Europe, is applied for packaging (Schut, 2008; Shen *et al.*, 2009). As previously mentioned different types of conventional polymers are synthesized from renewable resources, among which bio-based PE is the main polymer commercially available for food packaging applications (Bradley, 2010; Shen *et al.*, 2009).

Bio-Based Food Packaging Forms

Several different forms of biodegradable packaging are produced to meet the requirements to pack various products. The most commonly used forms include edible coatings, biodegradable gels, films, bags, trays, and boxes (Ivankovic *et al.*, 2017).

Edible coatings

One of the green food packaging application is an edible coating formed directly on the surface of the food product. Edible polymers are considered as polymeric materials easily consumed by human beings or animals through oral cavity which do not give harmful effect to the health. Direct utilization of edible polymers on the product surface can provide additional protection to retain the quality and stability of the product. The requirements of edible polymers are defined according to the specific characteristics of the product feedstocks, and the alterations may occur in these properties throughout the production and storage (Kokoszka and Lenart, 2007). The loss of nutrients is prevented using edible polymers which control the transportation rate of molecular components from inside of the packaging. Moreover, these coatings slow down harmful reactions and cause the prevention of unpleasant changes in food products. Mass transport properties are measured to determine the efficiency of edible coatings (Buonocore *et al.*, 2003; Kokoszka and Lenart, 2007). The possibility of edible polymer consumption with food products is their main advantage over conventional synthetic polymers, which eliminates residues needing to be disposed of and consequently contributes to decrease the environmental effect. Edible polymers are exclusively manufactured from edible, renewable ingredients (Dhanapal *et al.*, 2012). Organoleptic properties of food products can be expanded by using edible polymers containing various ingredients such as colorings, flavorings, and sweeteners. The coating is usually performed by spraying or dipping which create a thin film on the surface of food that suppresses the gas transfer and controls the moisture loss (Dhanapal *et al.*, 2012). Four different component categories including hydrocolloids, lipids, polypeptides, and composites can be used to prepare edible polymers. Hydrocolloid films are good barriers to carbon dioxide, oxygen, and lipids, while are an unsuitable barrier to water vapor. Hydrocolloid polymers are quite advantageous to use for fragile food products because they possess great mechanical properties. Protein-based edible films are the most attractive ones due to their superb gas barrier properties compared to the polymers prepared from polysaccharides and lipids. At a very low proportion of humidity, the oxygen permeability of the films prepared from soy protein has been measured about 540, 500, 250, and 670 times less than what was reported for LDPE, starch, methylcellulose, and pectin, respectively (Akbari *et al.*, 2007).

Moreover, numerous linkages at different positions can be formed in protein-based edible films. Some requirements need to be fulfilled by edible polymers including mechanical efficiencies, high barrier properties, microbial, physicochemical, and biochemical stabilities, and nontoxicity and non-polluting effects (Bergo *et al.*, 2010; Shit and Shah, 2014). Edible films can be commercially produced through several techniques like extrusion process, compression molding, and novel electrospinning process. Different approaches like using natural extracts, modified polymers, and nanocomposites can be applied to improve the functionality of edible film coatings (Ashok *et al.*, 2016).

Active packaging

Considering demand for green packaging materials is growing, novel technologies and novel green packaging materials have been developed. Active packaging is produced by preparing composites which are blends of polymers and specific additives having various geometries like spheres, fibers, and particulates. Edible polymers can be utilized as active packaging by which consumer demand for elevated retention freshness and quality of foods will comply. Active packaging preserves the product quality by altering the surrounding conditions of the food (Ashok *et al.*, 2016).

Biodegradable gels

The extremely hydrated gels as hydrogel polymeric networks are generally applied to prevent microbial contamination (Farrisa *et al.*, 2009). Impregnating gel may show positive effects on the quality of food products and maintain specific components like beta-carotene inside the fruits. However, it has been figured out that a mixture of hydrogels diminishes the service life of some fruits, may be due to moisture migration through the surrounding area (Ivankovic *et al.*, 2017). Numerous water absorption capacity of hydrogels causes fast decay of product to be avoided because packaging material absorbs the moisture released from food products. Flexibility and brittleness of the gels should be at a certain level which makes it possible to fold these materials as desired during packaging.

Bio-based polymers used for food packaging can be produced through the approach of poly-ion complex hydrogels. Introducing mainly charge interactions instead of hydrogen bonding strengthens polymer-polymer interactions which subsequently improves the mechanical properties of biopolymer films (Farrisa *et al.*, 2009, 2011).

Biodegradable films

Biodegradable films are manufactured with the intention of substitution of polyethylene film utilized for various applications including packaging products, industrial films, and collection of organic waste. The quality of some fruits and vegetables like tomatoes will be affected by the permeability of film to oxygen and carbon dioxide. Low permeability adversely affects fruits quality. Although, when the permeability of packaging films and respiration of the fruits are compatible, the durability and quality of the product will be positively affected through prevention of contamination by insects and microorganisms (Ivankovic *et al.*, 2017;

Muratore *et al.*, 2005). The flexibility of composting programs will be increased using biodegradable films, and no harmful residues are left after composting.

Biodegradable bags

Biodegradable bags are flexible, strong, resistant to damage and breakage, and resistant to temperature and moisture alterations. The notable applications of these bags in the hydroxybutyrate food industry can be correlated with the composition of raw materials used for this production. The application of these bags can be extended to other industrial branches by using incorporation of certain additives. Moreover compared to the traditionally used polyethylene, biodegradable bags are more sustainable because upon completion of their use as packaging, they are exposed to a composting process which decomposes them to water, and carbon dioxide and no harmful or toxic substances will be created (Ivankovic *et al.*, 2017; Nampoothiri *et al.*, 2010).

Biodegradable boxes and trays

Corn is used to producing bi-oriented polystyrene with the intention of manufacturing biodegradable boxes with lids. These bags are temperature resistant (between -6°C to $+80^{\circ}\text{C}$), grease resistant, and crystal clear which provides good visibility of content (Alemar *et al.*, 2008). Biodegradation of such packaging happens after 47 days during which no harmful substances will be released in the environment.

Various fresh food products like sliced broccoli, sweet corn, tomatoes, salad, and blueberries are successfully kept inside biodegradable trays, which are brittle and resistant to moisture (Ivankovic *et al.*, 2017).

Bio-Based Polymers Challenges

There are several problems related to the commercial performance of bio-based materials compared with their fossil-based counterparts, which limit the application of these polymers for food packaging. The poor performance of bio-based materials associated with their processability, hydrophilicity, barrier properties, resistance to breakage, the properties of raw materials, and high production cost are the main challenges associated with these materials (Jang *et al.*, 2011; Ramos *et al.*, 2018). The degradation rate of bio-based polymers, alteration of their mechanical properties by time, possible interactions with food compounds, and their potential to develop microorganisms are other concerns that have to be noticed regarding bio-based polymers (Rhim *et al.*, 2013). Moreover, the use of bio-based polymers for a broad range of applications is also restricted by their inherent properties like brittleness, vapor and gas permeability, melt viscosity, and thermal stability (Ramos *et al.*, 2018).

Barrier properties

Packaging used for many foodstuffs must meet the barrier requirements especially moisture and gas resistant. Permeation capacity of bio-based polymers determines their barrier properties. Permeation capacity means the capacity of exchanging low molecular weight articles through the polymer (Kumar *et al.*, 2011). Most of the used biomaterials possess poor barrier properties which makes it necessary to apply synthetic polymers (such as EVOH) in laminate or blend films to achieve the desirable barrier characteristics. Polysaccharide-based materials are sensitive to humidity and exchange a large amount of water vapor and other polar substances when exposing to a large portion of moisture. While barrier properties to oxygen and non-polar substances like oils and flavors are acceptable at the low or middle level of humidity, water vapor permeability of starch-based materials is about 4–6 times higher than what is measured for conventional polymers. The surface hydrophilicity of these materials can be reduced through fluorinating them. The water vapor transmission rate of PLA is 3–5 times bigger than that of LDPE, PET, and HDPE. While oxygen barrier properties of PLA is better than PS but less than PET, the water vapor transmission rate of PHA is similar to the petroleum-based materials. Oxygen barrier properties of PHB is greater than PET and PP and is adequate when the film comes to fragrances and fat. Gas barrier properties in most biomaterials are dependent on the ambient humidity (Ivankovic *et al.*, 2017). Various techniques can be applied to achieve high moisture barrier properties like an external coating of water-resistant material, blending with moisture resistant materials, crosslinking using inorganic fillers, or reinforcement using natural fibers like sisal, jute (Ashok *et al.*, 2016).

Mechanical properties

One of the features distinguishing polymers from small molecules is mechanical property. The mechanical properties of biopolymers are frequently similar to the petroleum-derived polymers (Table 3).

The molecular weight, orientation, and crystallization degree are the main parameters defining the properties of biopolymers. For example, regarding PLA, heat stability and mechanical strength are improved by the orientation of biopolymer. Moreover, different proportions of crystallinity and various molecular weight result in a wide range of materials characterized from hard and strong to soft and elastic. The poorly crystallized and amorphous PLA has a shiny and transparent surface, while highly crystallized PLA indicates an opaque surface. The properties of PHA is dependent on the molecular structure and the composition of the copolymer. PHB as a thermoplastic polymer is generally hard and highly crystalline which cause its mechanical properties to resemble the isotactic PP (Ivankovic *et al.*, 2017).

Table 3 Typical mechanical properties of some bio- and petroleum-based polymers

Polymer	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	References
<i>Biopolymer-based polymers</i>				
Poly(lactic acid) PLAs	3600	49.6	2.4	Mathew <i>et al.</i> (2005)
Poly(hydroxyalkanoates) PHAs	200–3500	17–40	5–680	Sudesh <i>et al.</i> (2000)
<i>Petrochemical based polymers</i>				
Low-density Polyethylene (LDPE)	210	11,000	190	Zhao <i>et al.</i> (2008)
High-density Polyethylene (HDPE)	911	20.3	380	Zhao <i>et al.</i> (2008)
Poly(ethylene terephthalate) (PET)	2700	55	130	Zhao <i>et al.</i> (2008)

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PLA is reasonably transparent and has acceptable mechanical properties which are comparable with those measured for fossil-based thermoplastic polymers. PLA films can also hold twists or creases which make them a good alternative to fossil-based plastics (such as LDPE, PP, HDPE, PET) in different applications. The most promising applications are rigid containers, high-value films, and expanded foams (Bradley, 2010; Shen *et al.*, 2009).

Techniques for Improving Functionality

Lamination

The properties of single biopolymers are improved by producing laminates or multilayer films. Generally, biopolymers are susceptible to brittleness, drying and mechanical forces which can be overcome by developing multilayer films based on conventional and bio-polymers. Laminate films are extensively useful to extend the shelf life of food products like fresh pasta, meats and cut vegetables (Fang *et al.*, 2005; Chiellini *et al.*, 2008). Multilayer films used as food packaging materials mostly contain several thermoplastic polymer layers to provide a combination of moisture- and oxygen-barrier, and mechanical properties. Therefore, natural packaging biopolymers are now considered to be used as a barrier layer especially to oxygen and aroma. For example, chitosan films, relative to commercial polymers, indicate a superior oxygen barrier properties while water vapor barrier property is measured low for chitosan. Therefore improvement of mechanical and barrier properties are the main advantages of these films. These multilayers easily separate in a solvent, which makes them recyclable (Shin *et al.*, 2002).

Nanotechnology

There are many reports indicating the properties of bio-based packaging materials can be enhanced using new techniques like nanotechnology as the most effective technique showing unique advantages (Armentano *et al.*, 2015; Cerqueira *et al.*, 2012; Ramos *et al.*, 2014). Nanotechnology has recently attracted considerable attention to be used to improve bio-based polymers and develop novel polymeric materials (Jochen Weiss and McClements, 2006). Nanotechnology as a new technique is used to develop bio-nanocomposites which improve mechanical performance, barrier properties, and even thermal properties of bio-based polymers (Table 4; Chiellini, 2008).

Bio-based reinforcement agents for bio-nanocomposites

Cellulose nanowhiskers

The main types of nanoscale materials obtained from cellulose and used to reinforce bio-nanocomposites are nano-fibrillated cellulose, cellulose nanowhiskers, and nanocrystalline (Velásquez-Cock *et al.*, 2014). Cellulose nanofibrils contain a bunch of molecules elongated and stabilized through the formation of H-bonds (Reddy *et al.*, 2013). Both crystalline and amorphous regions are found in these fibrils. Crystalline part of this structure can be isolated using various techniques and is known as a whisker. Amorphous region is removed through acid hydrolysis in order to extract cellulose nanowhiskers (Azizi Samir *et al.*, 2005). Incorporation of cellulose nanofibrils into bio-based polymer matrices like chitosan creates new materials with superior transparency and mechanical properties (Fernandes *et al.*, 2009). Mechanical properties of PLA films can be improved by the production of PLA-based nanocomposite films using lignin nanoparticles and cellulose nanocrystals (Yang *et al.*, 2016). Moreover biopolymers these structures cause oxygen and water vapor barrier properties to be improved as well.

Bacterial cellulose nanofibrils/nanoribbons

Although the chemical composition of bacterial cellulose synthesized by bacterial species is identical, its structure and mechanical properties are different to those of plant cellulose. Generally, bacterial cellulose possesses higher crystallinity, superior mechanical properties, moisture-barrier properties, water holding capacity, and purer nano fibrillar structure compared with plant cellulose (Fernandes *et al.*, 2009; Velásquez-Cock *et al.*, 2014). Therefore nanoribbons and nanofibrils prepared from bacterial cellulose are excellent reinforcement agents used for various polymeric matrices (Wan *et al.*, 2009; Velásquez-Cock *et al.*, 2014).

Table 4 Effect of bio-reinforcement agents on bio-nanocomposite properties

Bio-based continuous phase	Bio-based reinforcement agent	Modified properties	References
PLA	Cellulose nanowhiskers	Oxygen and water vapor barrier	Sanchez-Garcia and Lagaron (2010)
PLA	Cellulose nanocrystals and lignin nanoparticles	Mechanical and antimicrobial	Yang <i>et al.</i> (2016)
Starch	Chitin whiskers	Mechanical, water vapor barrier, and antimicrobial activity	Qin <i>et al.</i> (2016)
Starch	Chitin nanoparticles	Mechanical and water vapor barrier	Chang <i>et al.</i> (2010b)
Potato starch	Starch nanocrystals	Mechanical and thermal	Sessini <i>et al.</i> (2016)
Cassava starch	Starch nanocrystals	Mechanical and water vapor barrier	Garcia <i>et al.</i> (2009)
Waxy maize starch	Starch nanocrystals	Mechanical	Garcia <i>et al.</i> (2011)
Whey protein isolate	Zein nanoparticles	Mechanical, hydrophilicity, water vapor barrier	Oymaci and Altinkaya (2016)
Chitosan	Bacterial cellulose micro- and nanofibers	Mechanical, water vapor barrier, bacteriostatic, and bactericidal	Fernandes <i>et al.</i> (2009)
Chitosan	Bacterial cellulose nanoribbons	Mechanical	Velásquez-Cock <i>et al.</i> (2014)
Chitosan	Chitin whiskers	Mechanical and water vapor barrier	Rubentheren <i>et al.</i> (2015), Sriupayo <i>et al.</i> (2005)
Chitosan	Cellulose micro- and nanofibers	Mechanical and transparency	Fernandes <i>et al.</i> (2009)

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Starch nanocrystals

Starch nanocrystals as new reinforcement materials are produced by acid hydrolysis. The conditions under which hydrolysis occurs including temperature, starch, and acid concentrations, stirring speed, and hydrolysis duration should be strictly controlled (Le Corre *et al.*, 2010). Three-dimensional architecture and semicrystalline nature of these reinforcement agents make them susceptible to hot water which can result in disruption of starch nanocrystals by exposing to hot water that subsequently limits their use to prepare starch-based nanocomposites (Xie *et al.*, 2013). However, in general, it has been reported that the application of starch nanocrystals leads to improve thermal stability, mechanical performance, and barrier properties of nanocomposite structures prepared using nanocrystals are likely due to strong interactions between matrix and nanocrystals through H-bond formation (Sessini *et al.*, 2016; Garcia *et al.*, 2009, 2011).

Chitin nanowhiskers/nanoparticles

Different chitin sources can be used to prepare chitin nanowhiskers through deproteinization in a boiling potassium hydroxide solution which is followed by using a boiling hydrochloric acid solution to do hydrolysis step (Gopalan Nair *et al.*, 2003; Sriupayo *et al.*, 2005). Considering acid hydrolysis causes some of the crystalline part to convert into amorphous regions, utilization of alternative production methods of chitin reinforcement agents and the use of other techniques like sonication, ionotropic gelation, can lead to developing chitin nanoparticles having different crystallinity level (Chang *et al.*, 2010b). Moreover, these new methods may avoid unsuitable conditions like the toxicity of substances (Chang *et al.*, 2010a; Tsai *et al.*, 2008). Mechanical properties and water sensitivity of biopolymer films are improved by incorporation of chitin whiskers to biopolymer matrices (Rubentheren *et al.*, 2015; Sriupayo *et al.*, 2005). Besides, the presence of chitin nanowhiskers provides a good antimicrobial activity against *Listeria monocytogenes* (Qin *et al.*, 2016; Chang *et al.*, 2010b).

Zein nanoparticles

Various types of protein including gliadin, lectins, zein and soy proteins can be successfully applied to synthesize polymeric nanoparticles used for food applications. However, among these protein-based nano-reinforcement agents, zein is especially interesting to be used to produce nanoparticles. Zein nanoparticles can be produced through different procedures like liquid-liquid dispersion method which results in the formation of zein nanoparticles with diameter sizes less than 200 nm. It has been reported that these particles enhance nanocomposite properties including barrier and mechanical properties (Oymaci and Altinkaya, 2016).

Future Trends

Development of bio-based packaging materials depends on different factors such as the global demand for energy and food resources and legislative and political changes. However bio-based materials will be increasingly used for food packaging applications because of the environmental issues, cost of petroleum-based polymers, etc.

Next generation of bio-based materials used for food packaging applications is likely to be bio-nanocomposites. Development of bio-nanocomposites is a route to create innovative materials in the area of bio-based polymers. Nowadays a new group of

edible polymers was being developed using nano-technological procedures such as nano-encapsulation structures with the goal of the introduction of controlled release systems protecting bioactive compounds from extreme heat and humidity conditions. These systems enhance the viability and stability of susceptible active compounds. Moreover, nutritional properties of food products can be enhanced using nanoscale nutrients and additives, and delivery systems applied for bioactive compounds (Jochen Weiss and McClements, 2006). Various functional agents such as antioxidants, antimicrobials, enzymes, colorants, and anti-browning agents can be incorporated into the nano-laminate structures coating food products. In general, most of these nanocomposite materials prepared using bio-based polymers can compete both in performance and price with fossil-based polymeric materials (Shit and Shah, 2014; Akbari *et al.*, 2007).

Conclusion

According to the literature review, it can be concluded that green polymers have a great role in the food packaging industry. Biodegradable polymers are increasingly used to produce packaging materials partly due to the new strategies used to improve their properties, and partly because the price of bio-based polymers is getting more acceptable over time. Moreover, it must be noticed that novel techniques, especially nanotechnology, extensively affect the future of green packaging by improving its performance. These approaches have not only the potential to enhance biodegradation, barrier, thermal, and mechanical properties but also create new functionalities like antimicrobial properties. However, more researches need to be done in order to use these methods to tailor advanced packaging materials.

Acknowledgement

Amin Mousavi Khaneghah likes to thank the supports Azerbaijan State Oil and Industry University, Baku, Azerbaijan.

See also: Bio-Nanocomposites for Food Packaging Applications. Bio-Polymeric Packaging Material for Packaging of Raw Food. Eco-Innovation Options in Food Processing. Food Waste for Sustainable Packaging Materials. Tailor-Made Bioplastics for Environmentally Friendly Food Packaging: A Methodological Approach to a Challenging Problem

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Semiconductor-Based Photocatalytic Nanomaterials for Environmental Applications

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Introduction

Water is an essential part of our life on the earth and to sustain life every human being takes several liters' of water daily. All the aquatic life is dependent on water (Luo *et al.*, 2014). With increasing population day by day, the freshwater resources are decreasing quickly. Among many reasons of decline in freshwater resources, polluting of water is one of them. Surface and ground water are resources of fresh water and are vulnerable to contamination. There are various ways to make toxic and impure water. One of them is wastewater flowing out through industries. The industries like textile industries, ceramics industries, auto industries, leather tanneries, oil refineries, paper industries, cosmetic industries are draining the wastewater in the rivers, sea, canals that consist of many by-products and waste effluents (Deblonde *et al.*, 2011). The industrial waste pollutants also accompanied by some organic chemicals contain highly toxic organic byproducts, heavy metals, oils, and mineral acids. This contaminated water which is polluted by toxic hydrocarbons compound, heavy metals, toxic dyes, and metalloids is the main cause of polluting the surface as well as groundwater. For removal of these toxic materials, different methods are adopted including membrane filtration, electrodialysis, photocatalysis, adsorbent process, and nanomaterials catalytic activities.

The contaminated water discharge through industries and factories are polluted and toxic to our health as well as for agriculture and marine life. It is also the cause of irreversible degradation of the atmosphere resulting in serious health problems (Deblonde *et al.*, 2011). The leather industries, fertilizers tanneries, oil refineries, textile, paper, rubber, and agrochemicals etc. are producing wastewater that contains pollutants such as highly toxic synthetic organic compound (O.C), oils, greases and mineral acids. These compounds are very dangerous and injurious to all living organisms.

Heavy Metals and Their Toxicity

Heavy Metals

Heavy metals have a density greater than water and are easily dissolved in water and produce positive ions in the solution. Usually, the heavy metals have atomic number greater than 23 and density higher than 5 gm/cm³ (Deblonde *et al.*, 2011). Heavy metals are Cadmium (Cd), Arsenic (As), Mercury (Hg), Chromium (Cr), Lead (Pb), Nickel (Ni), Uranium (U), Aluminum (Al), and Thorium (Th). Under the controlled condition, these are useful in chemical analysis. The higher quantity than cellular metal accomplished value, these metal especially cadmium, silver, and nickel cause the toxic effects on the environment (Sheoran and Sheoran, 2006). The toxicities of three heavy metals named cadmium, mercury, and lead are very high even though their presence of 0.05 mg m⁻³ can become serious problems such as Pulmonary Edema, vomiting, nausea and affects directly to the gastric system of the humans. The specific limits of heavy metals are in different quantities.

Sources of Heavy Metals

There are two types of sources of heavy metals like primary and secondary. In nature, these heavy metals are found in the earth crust. The secondary sources of heavy metals are industry, medical and domestic wastage of water. Heavy metals primary sources summary is shown below in Table 1.

Toxicity of Heavy Metals

Out of 80 metal elements throughout the 118 recognized elements, the more toxic elements are heavy metals. These metals are soluble in the water and in food nutrients. When industrial waste water leaches into the soil and flows out through rivers and sea,

Table 1 Primary sources of heavy metals (Pb, Ar, Cd, Hg)

Heavy metals	Primary and secondary sources
Lead	Fuel combustion, oil refinery, petroleum and gasoline, auto-exhaust, lead solder food can lead plumbing pipes, lead storage paints, lead storage batteries, electrical equipment
Mercury	Antiseptic, refinery system, scientific devices, glowing light, plastic and as paints
Cadmium	Scrubber, battery, tannery system, mining equipment, electroplating machines, dyes
Arsenic	Insecticide and pesticide, wood preservative, combustion fuel, copper smelter

it turns the fresh water into polluted water. The annual casting amount of lead is 3 million tons. A controlled amount of lead is used in lead storage batteries, gasoline refineries, sanitary system and cable coatings. Cadmium is used in the electroplating system, dyes and pigments, transport objects, television equipment, a nickel-cadmium battery and solar systems (Naja and Volesky, 2009). Chromium salts and chromium-VI are very serious and injurious elements for plants and water living things. The mg/L values of toxicity for heavy metals are given in Table 2.

Heavy Metals and Their Impact on the Environment

The water extracted from industry contains polluted contamination including the heavy metals and other toxic synthetic organic compounds (Gadd and Griffiths, 1977). The origin of heavy metals is ores like iron sulfide, arsenic sulfide, lead sulfide, aluminum sulfide, selenium sulfide and gold sulfide. This metal contamination is becoming very serious now-a-days in every country especially in Asian countries like Pakistan. These heavy metals consist of cadmium (Cd), copper (Cu), lead (Pb), chromium (Cr) and their oxides. The mercury from industry reacts with dyes and chemical and converts into methyl and dimethyl mercury resulting in the cause of the toxic component. These transition rare metals exhibit biotic, aquatic, agricultural toxic and hazardous effect on human beings. The resulting symptoms cause many diseases in living organisms because of wastewater polluted water usage air spoliation, and land waste materials leaching (Barakat, 2011). The numbers of patients had been increasing in hospitals during the last 5 years. Sudden death has now become common.

Effect of Heavy Metals on Aquatic Life

Marine and other living organisms in the ocean and rivers are dependent on the water. Without water, their lives would be impossible. The wastewater including dangerous toxic metals, extracted from hospitals, industry and chemical laboratories flow through rivers, canals, oceans and as a result in sea leach out. This water in oil spillage converts definite dyes into acids. The heavy metals also present in this wastewater are soluble in water, resulting in an acidic solution. The solubility of mercury is due to its compound formation (Tyagi *et al.*, 2017).

The mercury elements leach out from industry waste effluents are deposited in rivers reacted directly to microorganism anaerobic reparations of marine. Consequently, the dimethyl mercury and methyl mercury result in marine life to toxic food web and affects the ocean life. Likewise, mercury the other heavy metals are soluble in water and becomes the sources of acidic salt solution in water and when this water is used by the fishes, amphibians, brush, and plants even for man chores is also dangerous to their health. Thus, the food chain of marine life is also poisoned and toxic (Wang *et al.*, 2008).

Effects of Heavy Metals on Human Beings and Agriculture

Overdose of heavy metals leads to hazardous and poisoned impacts on human beings. Within limit these metals are suitable for human, the excessive and recess amount can also become the cause of even the death of human (Jeong *et al.*, 2013). The symptoms to the food web of man are peptide disarrangement, diarrhea, tremor, haemoglobinuria and many other serious diseases as discussed and shown in Fig. 1.

The agricultural uses of this wastewater that flow out through the rivers and canals toxins the fertility of soil which leads the fresh water into an acidic solution that is to irrigate the fields by the peasants. The highly poisoned metals are absorbed in soil and water and ultimately injected into the grains during their development (Khulbe and Matsuura, 2018). As a result, when the water is planted to crops most of the plants are dead and some of them go through the growth process. These are deadly harmful to health and to pollute the environment. High blood pressure, Anemia, Vomiting, Irritation, Gastric system, Immune system disorders, Blindness, Headache, Nausea, Asthma like diseases are increasing day by day due to drinking the wastewater and by taking the poison food.

Table 2 Representation of toxicities of heavy metals in Mg/L

Heavy Metal	Mg/L	Toxicities
Arsenic (Ar)	0.05	Skin infection, cancer, vascular diseases
Cadmium (Cd)	0.01	Headache, renal and cortex problems
Chromium (Cr)	0.05	Headache, diarrhea, dermatitis
Copper (Cu)	0.25	Liver diseases, insomnia
Nickel (Ni)	0.20	Asthma, coughing, carcinogen, nausea
Zinc (Zn)	0.80	Thirst increasing, neurological disease, headache and anxiety
Lead (Pb)	0.06	Destruction of brain nerve, kidney, and nerve related diseases
Mercury (Hg)	0.0003	A cause for kidney, circulatory, nervous problems

Note: Naja, G.M., Volesky, B., 2009. Toxicity and sources of Pb, Cd, Hg, Cr, As, and radionuclides in the environment. In: Wang, L.K., Chen, J.P., Hung, Y.-T., Shammash, N.K. (Eds.), Heavy Metals in the Environment, vol. 8.

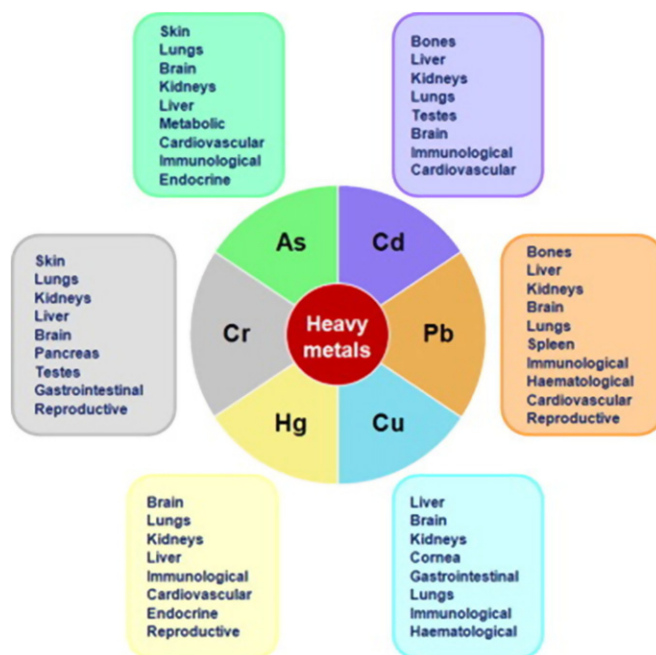


Fig. 1 Illustrates the effects of heavy metals on the human beings resulting in diseases. Reproduced from García-Niño, W.R., Pedraza-Chaverri, J., 2014. Protective effect of curcumin against heavy metals-induced liver damage. *Food and Chemical Toxicology* 69, 182–201.

Conventional Process for Removal of Heavy Metals

The adsorption process, chemical decomposition, ion exchange, electroplating, floatation is the conventional process to remove the heavy metals effluents. The chemical precipitation process, as described in Eq. (3.1), is a process using at a large commercial scale.



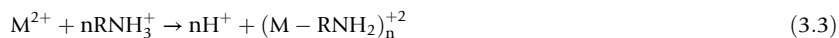
where the ions M^{2+} and (OH^{-}) are dissolved in the solution to form the impure $M(OH)_2$ that are insoluble in water. This reaction is strongly dependent on the pH level of the solution. Lime water consists of calcium hydroxide, due to low cost and high facilitated it is used frequently. It is used in excessive amounts as in 1000 mg/L. but, it requires the high availability of metal. The low amount cannot perform the mechanism. Another method like electroplating is used to pass the current to flow through the hydrous solution. The resulting ions move towards their respective electrodes like cathode and anode. Consequently, the resulting products in the form of metals crystal formed. But, it is a corrosive method. Ion exchange is a process to exchange the cations and the anions in the atmosphere. The ions, that are transferred to air is in the form of hydrocarbons.

Filtration Process

Membrane filtration, based on the ultra-filtration, nano-filtration and reverse process of osmoregulation, are the processes to remove the heavy metals effluents from the contaminated wastewater. The ultra-filtration uses the semi-permeable membrane to separate all pollutants having size up to 5–20 nm. In literature measured values of free-pollutants by this process is up to 95% especially for Cu and Zn. The filtration process is repeated to 5–6 times. It is done by the amino group that is present in the resulting suspension. The amino group action is presented in Eq. (3.2).



The functional group with donor atom is attracted towards the metals. By reacting with metals, the product is the formation of a complex structure which is strongly dependent on pH as shown in Eq. (3.3).



To remove the cadmium and chromium metals, the $ZnAl_2O_3-TiO_2$ is being used widely and attained the precipitation of 93% of Cd and 86% of Cr. This can filter by the ultra-filtration membrane. The membrane filtration can pull the metals up to 80%–90% removal from wastewater at a concentration rate of 10–12 mg/L with pH value level of 5–9.5. Due to fouling it has a hazardous effect on the membrane caused by the turgor pressure, and flux low rate. The process is also performed for reverse osmosis and

nano-filtration for copper and cadmium. The osmosis process is suitable to achieve 98%–99% concentration of free metals (Sivakumar *et al.*, 2015).

Electrodialysis

Electrodialysis is another process in which current is passed through the solution to separate the ion from the membrane. Membranes are the ionic solution comprising of the ion species. When the current passes through the solution, the ions move to their respective electrodes. Polyvinyl fluoride-membrane and perfluorosulphonic-Nafon-117 membranes are used as cations. When flow rate is increased, the separation rate decreased. At more than 500 ppm concentration, separation is ceased. The Electrodialysis (ED) process was established in chemistry to remove the toxic metals from solution. This process requires the precautionary measurements like contaminated air avoidance, specific temperature, voltage and pressure control.

Photocatalysis

In photocatalysis, the sunlight falls on the aqueous solution of the semiconductor. This light energy is converted into the charged particle if the band-gap is less than the light energy. These charges are removed by the semiconductor wafers like TiO_2 , ZnO , CdO , etc., responsible for oxidation and reduction as shown in Eqs. (3.4–3.6) as an example.



The UV-light has to irradiate on the prepared solution to transform it into ionic solution and then the redox reaction started (Hashmi *et al.*, 2013).

The chromium reduction is possible by using the UV-radiation on titanium dioxide catalyst in combination with Neodymium catalyst. The Nd ions that make a layer on the TiO_2 surfaces act like a layer deposited on the electrons. The separation of positive and negative charges increases the oxidation-reduction reaction and the recombination reaction does not take place. The electron acts like donor and chromium as an acceptor to the TiO_2 . Powder TiO_2 limitation is improved by the process of immobilization. The immobile process converts the toxic chromium Cr(VI) to non-toxic chromium (III) under UV-characterization.

Adsorption Process

The adsorption process is a mass exchange mechanism between solution (water) and soil/surface. Different agricultural waste adsorbents, industrial by-product adsorbents, natural material, synthesized biopolymers, and less-cost adsorbents are used to remove the heavy metals from wastewater. The sorption method consists of three basic processes: (1) transfer of pollutant on the adsorbent substrate/surface, (2) adsorption on the surface and (3) transport within the adsorbent molecule (Tchounwou *et al.*, 2012).

The zeolite material is a natural ion-exchange particle. Among the zeolites, the clinoptilolite is used for selection of Pb, Cd, Zn, and Cu. Cation ability for this zeolite is dependent on the pre-treating conditions. The pH factor is very important in the selection of adsorption of the heavy metals. For removal of Cr, NaA zeolite is used at pH 7. The copper and zinc are absorbed by the 4A-zeolite at neutral and basic pH values. Manganese is adsorbed at the alkaline pH. Magnetically modified zeolite (MMZ) adsorbs the Pb(II) and Zn(II) at pH 5–10.

Research revealed that rice husk, pecan shells, jackfruit, maize cob, and hazelnut cover have properties of the removal of heavy metals. The process to remove heavy metal using agricultural products is called bio-sorption. Rice shells are used to extract the heavy metal Cr(VI) at pH 2, Potato peel charcoal adsorbed the Cu(II) and Zn(II), and coconut shell charcoal is used to remove the Cr(VI) (Bourke *et al.*, 1995).

Remedies of Heavy Metals Using Nano-Particles

Carbon and oxide-based nano-particles have the capability to adsorb the heavy metals from the aqueous solution. The carbon nanotubes (CNT's) are the nano-range materials that are widely used in different fields of life. To remove pollutants from the wastewater, the nanotechnology is playing a vital role. The adsorption, redox, photo-catalyzation, and size exclusion process are the widely used processes to remove the heavy metals ions from the solution. Size exclusion is one of the processes used to remove the impurities in the form of filtration as discussed before. The adsorption processes the nano-particles such as CNT's, FeO_3 , charcoal, graphene, MnO_2 , TiO_2 , ZnO_2 are being used to remove the heavy metals. These particles are present in the form of particles, tubes, powder etc. These nanomaterials are low cost and reliable particles to eradicate the heavy metals (Borchers *et al.*, 2013). Recent research has shown that the nanomaterials as adsorbents are used in the purification of water. The polluted particles that are characterized are Ni^{2+} , Cr^{3+} , Cr^{6+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Hg^{2+} , Pb^{2+} , As^{3+} , As^{2+} , Th^{2+} , Eu^{3+} , Sr^{2+} , Zn^{2+} and U^{6+} . Moreover, adsorption capacity of different nanomaterials shown in Fig. 2. These materials like carbon active, CNT's, graphene, with oxide materials like ferric oxides, manganese oxide.

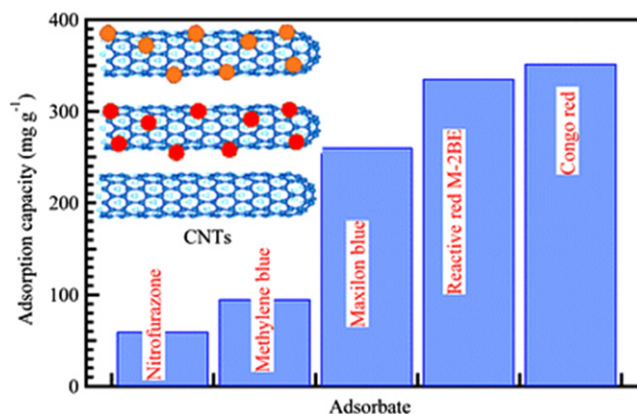


Fig. 2 Graphical review of the adsorption capacity of different material. Reproduced from Sadegh, H., Ali, G.A., Gupta, V.K., *et al.*, 2017. The role of nanomaterials as effective adsorbents and their applications in wastewater treatment. *Journal of Nanostructure in Chemistry* 7 (1), 1–14.

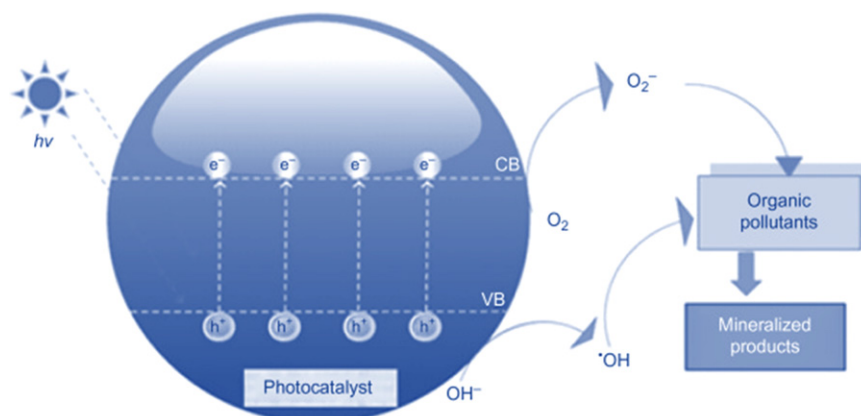


Fig. 3 Hydroxyl ion reaction mechanism for the removal of pollutant. Reproduced from Ameta, R., Solanki, M.S., Benjamin, S., Ameta, S.C., 2018. *Photocatalysis Advanced Oxidation Processes for Waste Water Treatment*. Elsevier, pp. 135–175.

Bismuth Nano-Particles

The bismuth nanoparticles show the electrical, optical and non-resistive properties (Soltani and Entezari, 2013). These are Bismuth vanadate, Bismuth oxyhalides, and Bismuth chalcogenides. Bismuth Chalcogenide is photoelectric compound with 6th group elements. These are represented as Bi_2E_3 (O, O, S, Se, Te, O, S, Se, Te, Te) and consist of bismuth oxide (Bi_2O_3), bismuth sulfide (Bi_2S_3), bismuth selenide (Bi_2Se_3) and bismuth telluride (Bi_2T_3). These materials are semiconductor materials with specific bandgap. When the sunlight or the electrical light source falls on the polluted water, these are converted into ions to extract heavy metals from aqueous solution.

BiVO_4 exists in three stages namely; monoclinic scheelite, tetragonal scheelite, and the tetragonal zircon. Through the photocatalytic process, the harmful products are removed. Photodegradation of hydrocarbons occurs when a photocatalyst absorbs the light of suitable wavelength and converts the substrate into the cation and anions. Hydroxyl ion in water then reacts to remove the pollutants. The mechanism is shown in Fig. 3.

Strategies to Increase the Photo Catalytic Properties of BiVO_4

To improve the efficiency of BiVO_4 nanoparticles, there are three methods. These are (1) doping, (2) heterojunction and (3) catalyst deposition. These methods are performed by the earth-crust elements that are in abundance (Niu *et al.*, 2015). When these three processes are performed for hexavalent heavy metals ion like Mo^{6+} , Cr^{6+} , W^{6+} , then the doping of Mo^{6+} is found to be more significant at photo-current generation and 2-times higher than electrode potential. Further, the resistance is decreased and an increase in efficiency is observed to be about 25%. To increase the efficiency of Mo^{6+} - BiVO_4 , the WO_3 was deposited on the layer of BiVO_4 . This has to increase the photocurrent about 50% with 3 times higher generation of photocurrent. The observed photocurrent for this heterojunction was 2.4 mA/cm² with weight 60%–90% (Asghar *et al.*, 2013).

Conclusion

Herein, numerous sources of wastewater including industries, factories, mining and tanneries in the form of organic compounds, heavy metals, dyes, and chemical textures have been reviewed and discussed. The heavy metals like Pb, Zn, Cr, Hg etc. were found to be more hazardous for human livings, aquatic system, wild animals, plants and crops. With the passage of time, numerous techniques like filtration, electrolysis, electrodialysis were used to treat the hazardous wastewater that contain heavy metals. However, high cost and low efficiency limited their wide use. The photocatalysis, being a green approach, was observed to be the most efficient and stable technique to completely degrade the heavy metals present in wastewater.

See also: Hydrogen Production Through Water Splitting Using Nanomaterials Under Solar Energy. Nanomaterials. Natural Fiber and Synthetic Fiber Composites: Comparison of Properties, Performance, Cost and Environmental Benefits. Optimal Operation of Renewable Distributed Generators (DGs) and its Environmental Benefits. Renewable Energy Production From Environmental Hazardous Palm Oil Mill Waste Materials: A Review. Wind Farm Repowering Using WAsP Software – An Approach for Reducing CO₂ Emissions in the Environment

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Structural Integrity Assessment of Bamboo for Construction Purposes

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Introduction

With the possibility of using different materials to support loads, it is essential to assess the structural integrity of the materials so as to prevent failure. Structural integrity of a material can be defined as the capacity of the material to withstand a predetermined load without failure during its service life. The loss of structural integrity in a material leads to failure of the material. Failure of the material can be as a result of deformation, fatigue, and fracture.

Assessment of the structural integrity of materials used for construction applications is very essential, as this would help the designer in making appropriate material selection for specific uses. Structural integrity assessment can be carried out on building materials, such as concrete, steel, wood, and bamboo.

Generally, the structural integrity of a material depends mainly on its mechanical properties, such as strength, elasticity, and durability. Assessment of this integrity is based on the specific application of the materials, as this varies depending on the estimated load the material would carry. For instance, the mechanical properties of concrete to be used for a rigid pavement are different from the properties of the concrete that would be used for a column of a high-rise building. For safety reasons, the maximum load carrying capacity or stress of a material should be higher than the design load or stress. The ratio of maximum load capacity or stress of the material to the design load or stress is called safety factor.

This article focuses on the structural integrity assessment of bamboo for construction purposes. Bamboo is one of the most frequently used materials in the field of construction; it is used in very sensitive areas, such as scaffolding and making concrete formworks. However, due to the significance of the support that bamboo provides during construction, its failure can result in structural collapse or leaving the structure in an unserviceable state.

Bamboo can compete with building materials, such as concrete, wood, and brick, and can be used for several structural applications (Sá Ribeiro *et al.*, 2004). Therefore, its properties and performance must be determined, to ensure proper application.

Significance of Bamboo as a Construction Material

Bamboo is a plant in Plantae kingdom, and it's one of the world's fastest growing plants. Bamboo grows in areas around the equator as shown in Fig. 1.

On the other hand, owing to the clamor to reduce the CO₂ footprint caused by the production of other building materials, such as steel and concrete, bamboo is a good material in this regard. As can be observed in Fig. 2, bamboo requires about one-eighth of the energy required to produce concrete of the same strength, about half that of wood, and one-fiftieth that of steel. Therefore, the use of bamboo is a great way to reduce the construction industry's CO₂ footprint, and its strength and application flexibility also complement this advantage.

Not only is the strength and sustainability of bamboo a great choice for structural construction purposes, the plant can be harvested every year, which gives it an edge over wood, which requires an average age of 15 years to be harvested.

The properties of bamboo vary based on the type of species and climate of where they were grown (Ghavami, 2008), and assessing their structural integrity would help to determine their suitability for structural application. The parts of bamboo play a critical role in its properties, when using it for structural application.

Common Uses of Bamboo in Construction

Bamboo can be used for a variety of application, and construction has been its primary application (Lobovikov *et al.*, 2007). However, most of these applications have been limited to nonengineered construction, leading to inappropriate structural applications. A few examples of structural applications are briefly elaborated.

The use of bamboo for scaffolding over decades is common in Southeast Asian countries, such as China, India, and Thailand (Janssen, 2000). A typical bamboo scaffolding is shown in Fig. 3. The ability of bamboo to resist winds caused by hurricane (Chapman, 1996) has been one of the reasons why the scaffolding application is more common. However, its durability and lack of standards has limited the broad adoption of using bamboo for scaffolding (Jayanetti and Follett, 2008).

Bamboo has been used in the construction of simple suspension bridges. A study concluded that the best way to use bamboo for bridge construction is by using a short trestle framework (Jayanetti and Follett, 2008). However, Laroque (2007) suggested the possibility of using bamboo for girder and suspension bridge construction in his study. A sample pedestrian bridge built using bamboo is shown in Fig. 4.

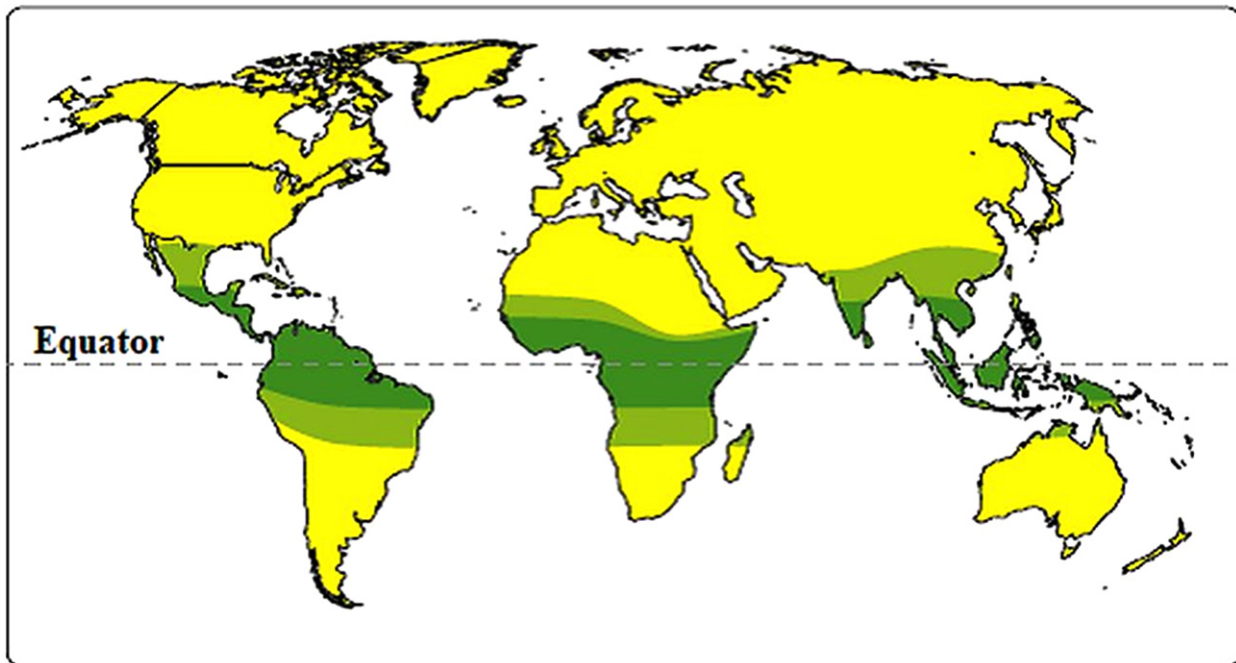


Fig. 1 Bamboo grows in areas around the equator, with about 1.4 billion tonnes annual worldwide production, resulting in \$2.5 billion in international trade in 2005. Reproduced from Lobovikov, M., Paudel, S., Piazza, M., Ren, H., Wu, J., 2007. World bamboo resources: A thematic study prepared in the framework of the global forest resources assessment 2005. In: Food and Agriculture Organization (FAO) of the United Nations, Rome, Italy.

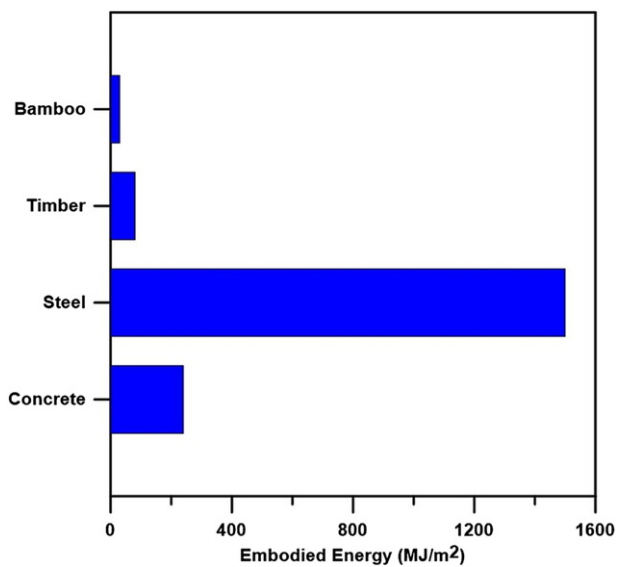


Fig. 2 Embodied energy of bamboo and other building materials. Data from Salcido, J.C., Raheem, A.A., Ravi, S., 2016. Comparison of embodied energy and environmental impact of alternative materials used in reticulated dome construction. *Building and Environment* 96, 22–34.

The use of bamboo has been limited to construction of mostly small houses and community buildings, such as schools and community centers. These houses are found in rural communities, and are of simple design as the construction is by locals (Jayanetti and Follett, 2008). An example is shown in Fig. 5.

However, in the urban areas, there are large structures built with bamboo. A good example is the Church without Religion in Colombia, shown in Fig. 6, which was designed by Simon Velez, a famous Colombian architect. Velez also designed other bamboo structures, such as a bamboo bridge in China and the ZERI Pavilion.

Bamboo can also be used as a roofing member for a building. It can be employed in different ways, such as using it for making truss systems, rafters, tiles, or as covering (Jayanetti and Follett, 2008). Fig. 7 shows a roof made using bamboo.



Fig. 3 Bamboo used for scaffolding in building. Photograph by Clément Bucco-Lechat, distributed under a CC-BY 2.0 license.



Fig. 4 Pedestrian bridge made with bamboo. Photograph by Gibson, K. Bamboo pedestrian bridge. Available at: https://commons.wikimedia.org/wiki/Main_Page (accessed 11.06.17), distributed under a CC-BY 2.0 license.

Structural Integrity of Bamboo

Failure of bamboo structures can lead to several devastating situations, such as injuries or economic losses. This failure would be as a result of bamboo being stressed beyond its strength limit. Bamboo being a natural material makes its properties vary from one sample to another. Therefore, it is essential to determine the factors that affect its strength limit and overall structural application.

These factors can be classified into physical properties and mechanical properties; the physical properties directly affect the mechanical properties of bamboo. However, it should be noted that it is difficult to compare bamboo based on these properties, as there may be difference in the composition of samples, and testing methods.

On a general note, one study (Kaminski *et al.*, 2016) has shown that the bamboo plant will possess good structural integrity if it tends to:

- grow locally in abundance,
- be stronger than other local species,
- have a large diameter (50–200 mm),



Fig. 5 House made with bamboo. Photograph by Kubo, B. Housing with bamboo. Available at: https://commons.wikimedia.org/wiki/Main_Page (accessed 11.06.17), distributed under a CC-BY 2.0 license.



Fig. 6 Church without Religion in Colombia. Reproduced from Vélez, S. Arquitectura vegetariana. Available at: <http://www.simonvelez.net/> (accessed 11.06.17).

- grow relatively straight,
- mature quickly (3–5 years),
- be slightly more resistant to insects and fungi, having lower starch content, although bamboo may also be cured in boron mix to enhance its resistance to attacks, and
- be less susceptible to splitting.

These attributes form the basis for selection of a particular species of bamboo for traditional construction works.

Bamboo Plant Parts and Features

Canes and nodes

The cane is the long tubular part of the bamboo plant, and this has been used for various applications, such as beams and columns. It has been used effectively for these applications by filling the first node with concrete or cement to ensure it stays fixed in the ground to prevent splitting of the cane (Minke, 2012). The node also has a huge influence on the structural integrity of bamboo, because it increases the capacity of the bamboo to resist buckling or splitting. As a result, it is necessary to perform



Fig. 7 Bamboo used for roofing purposes. Reproduced from CLC Construction. Earth and bamboo. Available at: <https://www.bamboo-earth-architecture-construction.com/> (accessed 11.06.17).

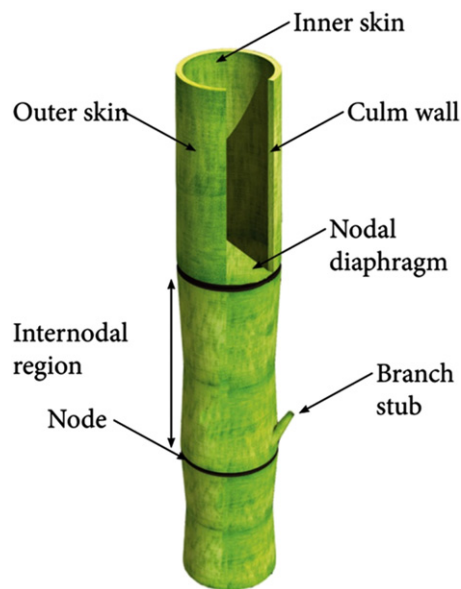


Fig. 8 Bamboo culm. Reproduced from Kaminski, S., Lawrence, A., Trujillo, D., 2016. Structural use of bamboo. Part 1: Introduction to bamboo. *The Structural Engineer* 94 (8), 40–43.

compression tests on a complete section of bamboo, with the load being situated between two nodes. There are short fibers in the bamboo nodes (Richard, 2013), which are responsible for its rigidity.

Culms

The culm of a bamboo is the hollow part; a typical structure of the culm is shown in Fig. 8. However, not all bamboo species have hollow culm. Fiber density of bamboo increases from the inner wall of the culm to the outer part. The high density and presence of silica in the outer wall of the culm serve as a protection for bamboo, but can lead to construction tools getting blunt when used on it (Janssen, 2000).

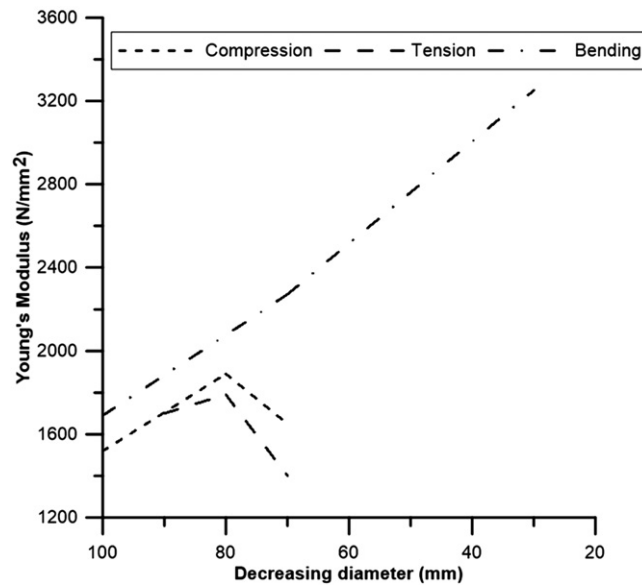


Fig. 9 Relationship between diameter and elastic modulus of bamboo. Reproduced from Laroque, P., 2007. Design of a low-cost bamboo footbridge. MSc Thesis, Massachusetts Institute of Technology.

The culm normally serves as a structural support, and pathway for water and sap movement in bamboo. The culm is made up of 10% vessels, 40% cellulose fibers, and 50% parenchyma tissue (Janssen, 2000). As the bamboo grows, the parenchyma tissue hardens, and the fibers are responsible for the strength development in the culm (Richard, 2013).

Properties of Bamboo

Physical properties

The age of bamboo significantly affects its strength, and the optimum age is between 3 and 4 years, therefore bamboo younger than 3 years or older than 5 years should not be used for structural construction purposes. Liese and Weiner (1996) also observed that there are lesser strength properties in bamboo when it is older than 5 years.

The size of bamboo plant is another factor that can influence its strength characteristics. In terms of structural applications, the slenderer the bamboo is, the better are its mechanical properties. Therefore, the thinner bamboo canes would have better mechanical properties compared to the bigger ones. This would be as a result of the microstructure of the bamboo, as the proportion of the silicate external skin is greater in thinner bamboo canes than bigger ones (Laroque, 2007). An illustration of how the size affects the strength properties is shown in Fig. 9.

The size of a bamboo can also be described using the outer diameter, as it determines whether the bamboo is slender or not. As can be seen in Fig. 9, the diameter is very essential when using bamboo for structural application, as there is an optimum cross-section for elastic modulus, when the bamboo is in tension or compression.

Bamboo fiber density is another important property. The thickness of the cell wall and fiber diameter determines the fiber density of the bamboo. This can equally be quantified by the specific gravity of the bamboo, and it has been found to affect its mechanical properties (Janssen, 2000). The density of bamboo is between 700 and 800 kg/m³, and approximately 60%–70% of the culm tissue, with 60% at the outer wall of the culm, and between 10 and 15% at the interior wall (Richard, 2013). The bamboo fiber density increases with the culm's height (Amada et al., 1996).

Janssen (2000) shows the relation between stiffness and strength of some building materials to their density. It can be seen in Fig. 10 that, compared to other building materials, bamboo has a high and similar value for both ratio of strength and stiffness to density. The optimal density for bamboo has been found to be between 520 and 820 kg/m³, but outside this limit, there would be a significant reduction in its compressive strength (Laroque, 2007).

Mechanical properties of bamboo

The mechanical characteristic of bamboo is mostly influenced by its physical properties. However, the level of effect may vary depending on the type of physical properties. Bamboo is a good structural material used for construction; it is strong in both tension and compression (Laroque, 2007), unlike a building material, such as concrete, which is strong in compression only, but weak in tension.

Compressive strength

The compressive strength of the bamboo is essential in assessing whether it can be used for construction purposes. There are various factors that determine the strength of a bamboo plant. For instance, strength properties are higher in bamboo between

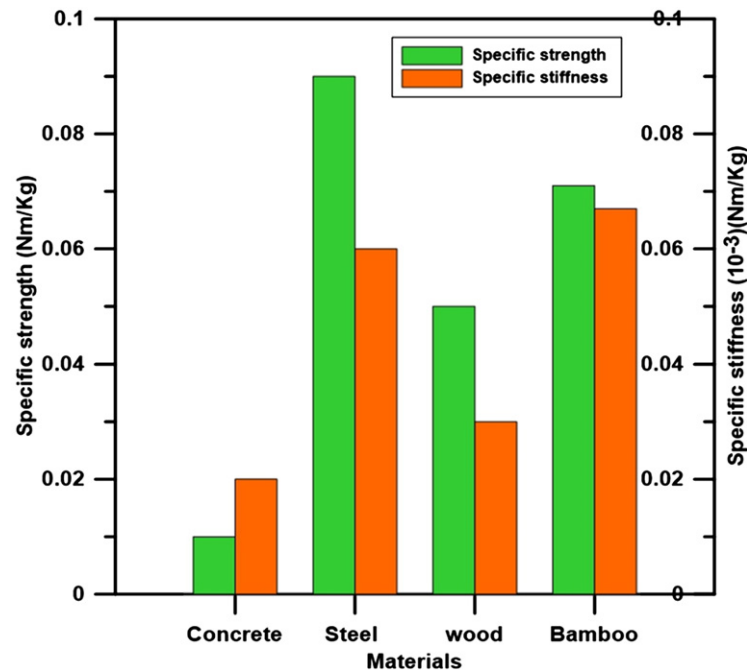


Fig. 10 Effect of material density on the strength and stiffness. Reproduced from Janssen, J., 2000. Designing and building with bamboo. INBAR Technical Report 20, Beijing, China.

3 and 4 years old, but outside this age bracket, bamboo is found to possess a lesser strength characteristic (Sattar *et al.*, 1990), and it was also reported that the compressive strength of bamboo increases with culm height.

The compressive strength of bamboo is estimated to be 30.7–42.2 MPa (Tomak *et al.*, 2012) or 0.094 times the density (Janssen, 2000). The accompanying failure pattern during compression test is lateral bulges and vertical cracks. Lignin has been found to have a huge effect on the failure resistance of bamboo under compression, because it provides rigidity in the bamboo cell wall and it does not rot easily. So, it will require much energy and time before the tangential expansive forces generated could lead to critical tangential strains on the bamboo (Arce-Villalobos, 1993).

Modulus of rupture

Also, another important characteristic to be assessed in bamboo is the modulus of rupture. It should be noted that modulus of rupture is not the same as modulus of elasticity. Compared to modulus of elasticity, modulus of rupture is the amount of a material's strength before it ruptures. In bamboo, the modulus of rupture (bending stress) is related to the fiber length (Janssen, 2000), and it decreases with the culm height (Tomak *et al.*, 2012). The modulus of bamboo was reported to be between 69.5 and 102.7 MPa (Tomak *et al.*, 2012), and also estimated to be 0.14 times its density (Janssen, 2000). Also, Fig. 11 shows the relationship between flexural strength and modulus of different wood products.

Young's modulus

In addition, there is need to evaluate the Young's modulus of bamboo, which helps to measure how stiff a particular bamboo sample is, and it can also be used to determine elastic properties of bamboo when it is in compression or tension. The Young's modulus along the fibers depends to a large extent on the number of vascular bundles per area (Janssen, 2000). Therefore, the Young's modulus of bamboo can be determined by measuring the fraction of fibers across the bamboo wall thickness (Janssen, 2000), and then using the fraction (Ghavami *et al.*, 2003; Li and Shen, 2011). The relationship between the Young's modulus and the density of bamboo and some other building materials is presented in Fig. 12.

Tensile strength

Bamboo is known to possess a good tensile strength, but it is necessary that this property be examined in a species before being used. Just like in a typical wood, the direction of force application on the fiber affects its strength properties. The fibers present on the outer part of the bamboo have high tensile strength compared to other parts of the bamboo (Laroque, 2007). Compared to the compressive strength, the tensile strength of bamboo is almost the same for its entire service life. However, the tensile strength of bamboo has been found to differ widely between different species. The nodes of the bamboo exhibit lower tensile strength compared to other parts due to their twisted fiber (Amada *et al.*, 1997).

The tensile strength of bamboo varies, depending on whether it is assessed along fiber length or across the fiber.

When the tension force is applied across the fibers, just the lignin matrix withstands the stress, which results in cracking and splitting failures (Richard, 2013). Bamboo tends to fail at a specific transverse strain of approximately 0.001 (Arce-Villalobos, 1993) when loaded transversally.

Shear strength

Shear strength is the property of a material to resist the forces that cause the internal structure of material to move or slide against itself. Bamboo, having a hollow cross section, has less cross-sectional area to resist shear force compared to similar building material, such as timber. There are two shear planes in bamboo: shear plane parallel to the fibers and shear plane across the cross section of the culm (Richard, 2013). Bamboo exhibits a critical shear stress of 2.2 N/mm^2 (Janssen, 2000) at the neutral axis.

Fire resistance

Though this is not a strength property, it is essential to understand the fire resistance of any construction material, because it is a norm that a material tends to diminish in strength after being exposed to fire. So, fire resistance can be indirectly related to strength. Bamboo canes have a good fire resistance capacity, because of their high density and presence of high silicate acid content in its outer skin (Laroque, 2007). Large-scale tests have shown that bamboo is able to last longer compared to a wood system that is unprotected but loaded the same way. Bamboo has also been graded as hardly combustible but flammable by DIN 402 (building behavior of building materials).

Method of Making Bamboo Joints

One of the challenges associated with the use of bamboo as a structural construction material is designing for joints (Laroque, 2007) that are capable of transferring forces in the whole structure effectively, without bulging at the joint. The method of joining bamboo together or with other material is critical. Therefore, the most accurate technique must be employed to ensure the resulting bamboo structure is capable of carrying its designed load, throughout its entire service life.

The cylindrical shape of bamboo and presence of nodes at different intervals makes the design of connections and joints for bamboo difficult. An ideal joint for bamboo members must take into account the geometric form of bamboo and also the varying size of the bamboo among culm of various species and along the culm itself.

Traditional methods

These types of connections involve the use of available natural materials, such as bamboo stripes, palm or coconut fibers, and rattan, to join the bamboo components together (Laroque, 2007). When these natural materials are used to join bamboo together, it is referred to as lashing. Lashing is the most commonly used method of joining bamboo members, as it is cheap, easy to use, and takes minimal time to do (Jayanetti and Follett, 2008). The fibers can be used by passing it through drilled holes in the members, or by simply knotting the members together (Laroque, 2007). However, most of the existing traditional joint methods lack strength and deform easily (Janssen, 2000). Therefore, depending on the bamboo application, careful selection of the type of joint to be used has to be determined.

Since joining bamboo effectively requires much consideration during construction, more research and development of existing methods of bamboo jointing, can enhance the possibility of a wider adoption of bamboo for construction purposes.

However, it is important to avoid using a fresh cut bamboo for construction. Bamboo needs to be completely dry before it can be used; this will ensure there is no shrinkage of its diameter when used in joinery. Otherwise, using a fresh cut bamboo can cause loss and weak joints after a few weeks of erection. The drying process of bamboo can best be done in air, and not in the sun, because sun drying bamboo could create cracks in its wall due to the rapidity of drying.

Bamboo Failure Modes

The common failure modes in bamboo include fracture, fatigue, tensile tearing, and creep. When bamboo is subjected to loading, it fails by fracture of the fibers connecting the weaker lignin, thereby resulting in longitudinal splitting of the bamboo (Janssen, 2000). However, bamboo possesses excellent elastic properties (Sá Ribeiro *et al.*, 2004), such that when it is subjected to bending, it tends to return back to its original straight form, despite being fractured. This ultimately shows that there is enormous benefits to bamboo over other building materials, and this can be an advantage for ensuring structural stability during hurricanes or earthquakes.

Fatigue failure can set in when a bamboo member resists higher load than the design load, which leads to cracks forming at the stress points along its length. However, when an axial load is imposed on a weaker bamboo cane, this could result in bamboo tensile tearing.

Bamboo has a better resistance to creep loading than materials like timber. When loaded with its outer culm-wall in tension, bamboo exhibits a larger modulus of rupture, lower apparent modulus of elasticity, and a lower residual strength when compared to specimens with their outer culm-wall in compression (Gotttron *et al.*, 2014).

Enhancing Resistance of Bamboo to Failures

To ensure that forces and stresses are transferred within the structure appropriately, proper joints, and end caps must be used. Improper transfer of forces and stresses in the structural system can lead to cracks and possibly failure of the bamboo

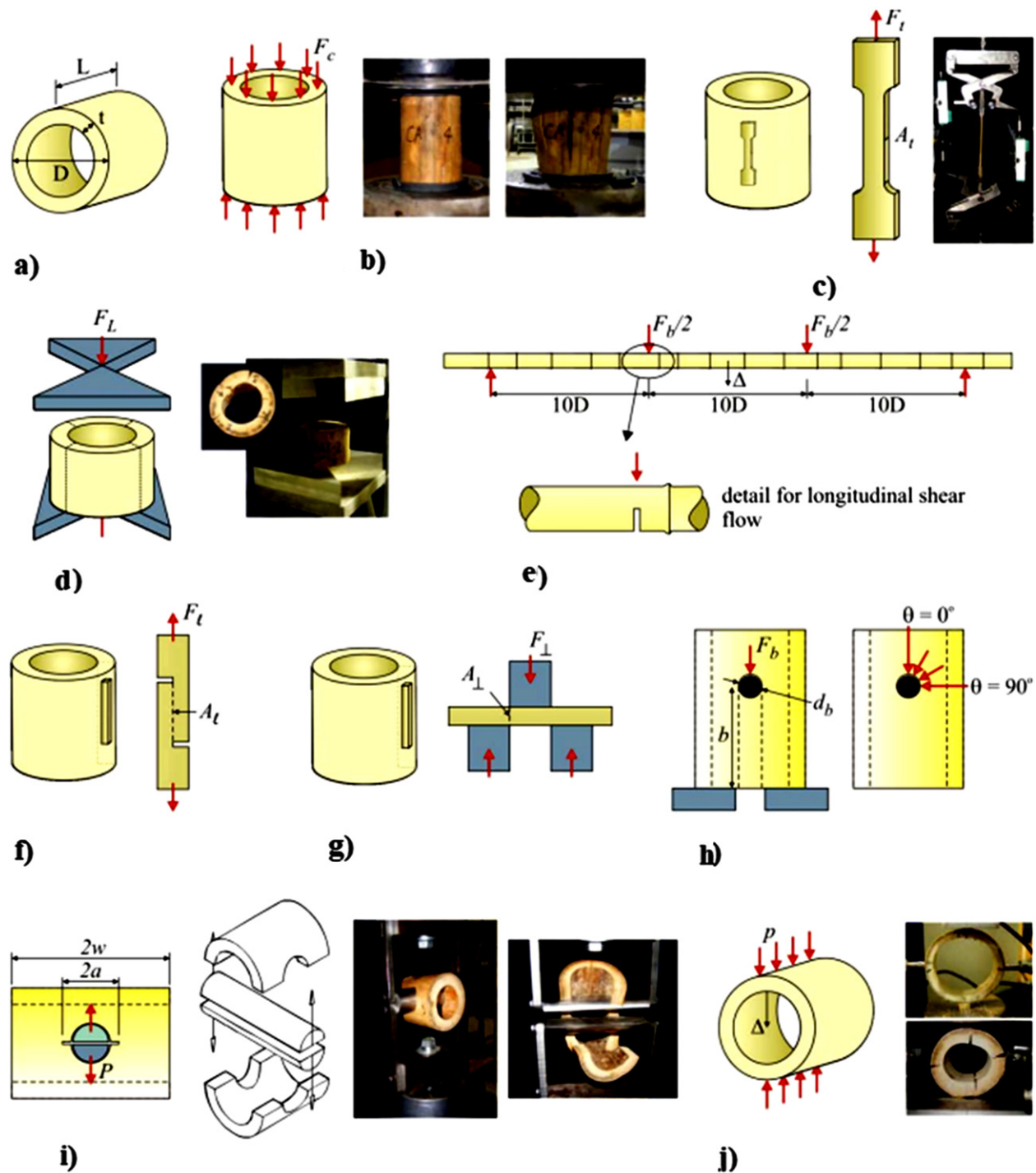


Fig. 13 Current tests that are standardized for testing bamboo properties. (a) Culm dimension. (b) Compression. (c) Tension. (d) Parallel shear. (e) Bending and longitudinal shear. (f) Interlaminar shear. (g) Perpendicular shear. (h) Pin shear. (i) Transverse tension split-pin. (j) Edge bearing. Reproduced from Harries, K., Sharma, B., Richard, M., 2012. Structural use of full culm bamboo: The path to standardization. *International Journal of Architecture, Engineering and Construction* 1 (2), 66–75.

structure. Therefore, to ensure a safe connection between the bamboo members or the foundation, the first node of the bamboo can be filled with cement with a metal rod attached to the end of the bamboo (Minke, 2012). On the other hand, it was also suggested that the end of the cane can be reshaped into cone, using cement or epoxy to wrap a steel wire around it.

Need for Bamboo Standard Regulations

Compared to building materials, such as concrete and steel, bamboo is less regulated, and this has made its acceptance and usage very low. Due to these shortcomings, the technicalities of bamboo usage are not well understood by constructors, and consequently, bamboo is mostly referred to as an inferior building material (Richard, 2013). Therefore, the development of standards for testing and design of bamboo for structural construction can promote its acceptance and also ensure that it is used properly and safely. Standards ensure the protection of the users, environment, and regulation of the production, and also serve both the social and technical contexts. Current tests that have been standardized for bamboo properties are shown in Fig. 13.

Summary and Conclusion

Assessing the structural integrity of bamboo for construction purposes is essential to ensure that its usage aligns with the required applications. This gives an indication of the whether bamboo is capable of carrying its current design loads and future loads without failing or bending redundantly during its service and functional life. This assessment can also lead to potential cost savings and better application of bamboo for construction purposes.

Not only is bamboo suitable for structural application because of its strength and light weight, its esthetic, cost, low environmental impact, and accessibility makes it a great choice for construction purposes. Bamboo being a natural material is both its greatest asset and weakest point, as it is sustainable but the properties of similar bamboo are not generic.

Though the mechanical properties of bamboo are above par, it is necessary to treat bamboo against fire, and attacks from termites, beetles, and fungus. Bamboo is more susceptible to attacks than common building materials like concrete and steel.

More research and development is still needed in the field of bamboo technology to understand its properties more and its effective uses for structural purposes.

See also: A Comparative Life Cycle Assessment for Utilising Laminated Veneer Bamboo as a Primary Structural Material in High-Rise Residential Buildings. Bamboo Structural Technology. Bamboo: The Emerging Renewable Material for Sustainable Construction. Bamboo Versus Tubular Steel Scaffolding in Construction: Pros and Cons. Constructing a PV-Integrated Permanent Bamboo Building – An Experience. Study of Junctions With Bamboo: An Attempt Towards Their Classification. Sustainability and Recycling of Bamboo for Engineering Applications

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Further Reading

Bucco-Lechat, C., 2012. Dismantling of bamboo scaffolding. Available at: https://commons.wikimedia.org/wiki/Main_Page (accessed 11.06.17).

Sustainability and Recycling of Bamboo for Engineering Applications

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Introduction

Bamboo, also known as *Bambusa vulgaris*, is a general nomenclature for various types of giant grasses. There are nearly 1500 species under 87 genera of bamboos worldwide (Ohnberger, 1999), and these species can exist in diverse forms and shapes (see Fig. 1). Bamboo grows mainly in the tropics especially in regions like Africa, Asia, and Latin America. It has a height ranging from some centimeters to above 30 m and stems ranging from 3 mm to above 25 cm.

Ashby and Ashby (2016) described bamboo as an exceptionally fast-growing plant, allowing harvesting within 4–7 years for construction purposes. Its stem usually collapses and decays after reaching its longevity, but this depends on the climate conditions as well as the species of the plant. However, no matter the conditions of the environment, the bamboo plant still tends to survive. Interestingly, bamboo is one of those rugged plants that can grow in poor soils, and as a result it is a useful plant for degraded soils (Hunter, 2003). In the same vein, bamboo forests have ecological and environmental functions, in terms of soil erosion control, land rehabilitation, water conservation, and carbon sequestration (Tu *et al.*, 2013). However, various species of bamboos affect soil characteristics in various ways. Arunachalam and Arunachalam (2002) reported that bamboo increases the microbial biomass in the rhizosphere zone by providing a large root surface, which significantly helps in increasing the fertility of the soil. Meanwhile, aside from enriching the soil fertility, bamboo also reduces microbial activities and soil enzyme activity (Tu *et al.*, 2013).

There are significant roles that bamboo plays in terms of climate change adaptation and mitigation, in addition to safety net provision to forest-dependent communities vulnerable to the effects of climate change (Kumar, 2014). The bamboo plant is able to act as cover for soil, and also stabilizes riverbanks and reduces soil erosion.

The Japanese, Chinese, West Indian, and Indo-Chinese communities, use bamboo for different daily activities, because it is a strong plant, and also due to its hollow stems, excluding the nodal partitions. Also, in a developing country like Nigeria, there is spatial distribution and availability of bamboo in various localities, only that the quantity is yet to be ascertained. The versatility, beauty, and strength of bamboo, both in its natural and finished states, are enormous. This makes it one of the most consumed plants all over the world. Studies have shown that bamboo is a useful raw material for the production of original items for domestic and commercial uses (Xiaobo, 2002; Bansal and Zoolagud, 2002). Fig. 2 shows parts of a bamboo plant and some of their common uses.

Some of the unique attributes of bamboo are that it is fast growing and attains maturity in a short period, and in fact, its fiber is stronger than that of wood fiber. These characteristics make bamboo an important tree for solving wood shortage problems in developing countries. The problem of wood shortage in some developing countries has been solved via the use of bamboo on a small-scale for furniture making, fencing, and shed construction, just to mention a few. However, despite the use of bamboo in most rural settings, the paramount use of bamboo is for making scaffolds during building construction. When bamboo is used as scaffolds in building, it tends to provide structural support for the building, so, it is very important for the bamboo plant to attain maturity before it can be used for making scaffolds. The more mature a bamboo plant is, the more strengthened it becomes (Chung and Yu, 2002).

Bamboo has many benefits, which include its ease of cultivation and harvesting, as well as its renewable resource nature. It equally has a very high tensile strength that can be compared to mild steel, since it can withstand forces as great as 231 kN (Environmental Bamboo Foundation, 2011).



Fig. 1 Various species of bamboo. Adapted from Von Vegesack, A., Kries, M., 2000. Grow Your Own House. Balingen: Vitra Design Museum.

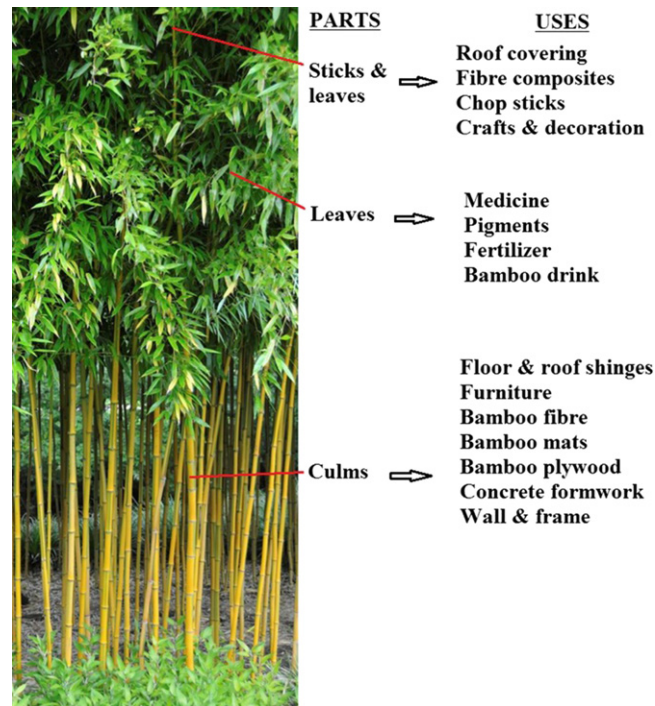


Fig. 2 Bamboo plant parts and some common uses.

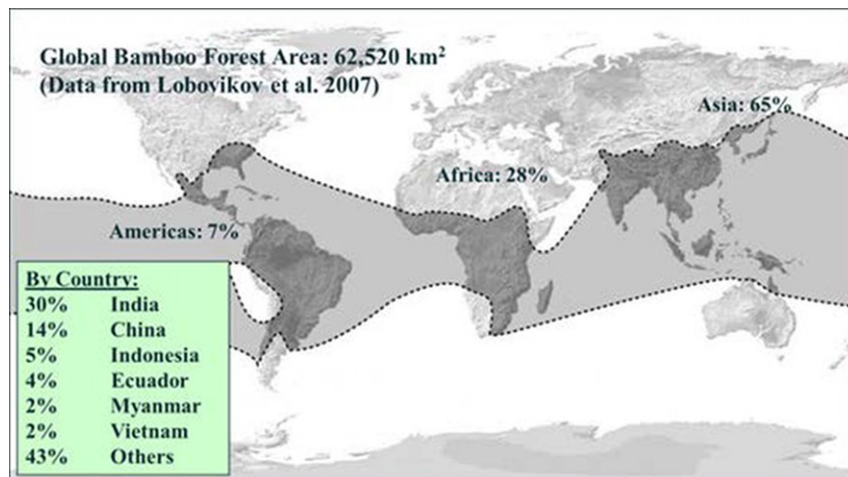


Fig. 3 World bamboo habitat. Adapted from Richard, M., 2013. Assessing the performance of bamboo structural components. Doctoral Thesis, University of Pittsburgh.

Background to the Use of Bamboo in Construction

The use of bamboo as a construction material began many centuries ago. However, despite the popularity and continuous usage of bamboo, it is still regarded as a nonengineered construction material. There is a wide availability of bamboo across the globe, due to its rapid growth and regeneration; this makes it a potential sustainable alternative to the conventional engineered building materials, especially in the regions where it is readily available.

Bamboo is known to be one of the oldest construction materials, used since ancient times. The incorporation of bamboo as a construction material started in the regions where plant growth is abundant, including Africa, South America, and most especially Southeast Asia. The worldwide bamboo habitat is shown in [Fig. 3](#).

Buildings using bamboo look back on an ancient tradition. Since ancient times, bamboo material has been used in a surprisingly large number of applications. For instance, in building architecture, there are numerous applications of bamboo in



Fig. 4 Bamboo used as a skeletal building. Reproduced from KATI, 2012. Uses for bamboo in sustainable building. Available at: <http://www.greenbuild.org/new-construction/uses-for-bamboo-in-sustainable-building/> (accessed 04.06.17).

several types of construction. There are skeletal buildings that are strictly bamboo houses as shown in Fig. 4. These buildings are just raised floors having main posts that are anchored firmly to the ground. This ensures the stability of the bamboo building. Generally, the structural stability of the skeletal bamboo building is extensively provided by its posts, which are anchored in the ground. Thus the only loading considerations for its construction are mainly the vertical and horizontal forces that are acting on the building; these forces include wind load or pressure, load resulting from rainfall on the roof, live loads from moving objects in the building, and lastly the dead load from the weight of material used for its construction.

The increasing world population, which is still estimated to attain 9.7 billion people by 2050 (United Nations Department of Economic and Social Development, 2015), creates a notion for natural material like bamboo to be adequately utilized in construction, as a measure to sustain the convention materials. Bamboo is obviously a much needed alternative to a variety of construction materials. Over the years, the application of bamboo for structural purposes across the globe has ensured a lot of development and sustenance in areas, such as:

- using bamboo to construct small houses for homeless people or internally displaced people from war zones and natural disasters;
- reducing the effect of natural disasters and their resulting damages; and
- helping to sustain the growing socioeconomic gap in populations around the world.

Although, despite the visible impact of bamboo as a tool for ensuring sustainability in the construction field, it is still mostly regarded as an inferior material by stakeholders in the built industry. However, Richard (2013) attributed this assertion to a lack of understanding, as well as a lack in engineering standardization among the users.

Also, since ancient times, the simplest roof covering has been formed using bamboo shingles that are as long as the rafters. An example of such roofing system is presented in Fig. 5. The shingles are produced by splitting bamboo canes into halves along their length, while the diaphragms are removed. As shown in the figure, the bamboo cane halves are threaded to the ridge and positioned, such as in the “Roman tile fashion.” The shingles are not fixed at the eaves and are held in position by their own weight.

Notably, from the ancient times until now, bamboo has mostly been used as a scaffolding member, even before the introduction of the tubular steel scaffolding system. A multistory building under construction having bamboo scaffolding system is shown in Fig. 6. Bamboo has an excellent load-bearing capacity, coupled with its relationship with its weight, so this has made it a suitable material for the construction of safe scaffoldings, in buildings ranging from medium height to high-rise buildings. In the same vein, ladders are also made from bamboo stems, often found in India. In addition to the use of such ladders for climbing high places, it is also used in India to make small carriers for transporting the dead from one place to another.

A variety of footbridges and bridges have also been constructed over the years from bamboo material. Bamboo has a good elastic property even more than timber or any similar material, which ensures its usefulness for this purpose. Although, it will require some structural expertise before it can be used for large bridges, mainly because there is need to put into consideration measures that takes care of its side effects, such as vibration, bending, and at times twisting. As it is commonly known, footbridges



Fig. 5 Roof covering formed by bamboo shingles. Reproduced from European Commission, 2016. New bamboo engineered biomaterial sustainable building components. Available at: <http://europa.eu/geninfo/query/resultaction.jsp?QueryText=bamboo&swlang=en&x=0&y=0> (accessed 23.05.17).



Fig. 6 Bamboo scaffold. Reproduced from European Commission, 2016. New bamboo engineered biomaterial sustainable building components. Available at: <http://europa.eu/geninfo/query/resultaction.jsp?QueryText=bamboo&swlang=en&x=0&y=0> (accessed 23.05.17).



Fig. 7 Qian-Xian bamboo suspended bridge. Reproduced from BambooBlankets, 2013. Historic uses of bamboo in construction. Available at: <http://bambooblankets.net/2013/02/22/historic-uses-of-bamboo-in-construction/> (accessed 06.06.17).

and bridges are structures that are exposed to the weather, no matter how they are covered. As a result, they tend not to last long, like bamboo skeletal buildings. The applications of bamboo as a material for footbridges and bridges range from its usage as poles that are placed across a ditch to the twin suspended framed truss that spans over a river about 30–50 m wide, or as tied battens that hold poles together and also act as a load distributor so that the load on a single pole is transferred to its surrounding members. In such bridges, the ends of the poles are pinned to the ground, thereby ensuring that they are secured against turning and displacement. In China, bamboo has been a popular material for the construction of suspended bridges. An example is the Qian-Xian suspended bridge (Fig. 7), which was constructed before AD 960 and it is still standing today. Although, it has been continually maintained to keep it in use to date.

In a more advanced application, bamboo was used for construction of the world's largest dome in India. The dome was built in 2010, and has a diameter of 34 m. This dome is an illustration of the interaction existing between the urban and the rural areas of India, thereby showcasing the various sections of the Indian culture, like the faith, language, and culture. The dome structure, during and after construction, is presented in Figs. 8 and 9, respectively. Also, in modern construction, bamboo has been used as a flooring material (see Fig. 10).

Bamboo is a naturally existing resource, and it is therefore essential to ensure its sustenance and standardization, in order to foster a better performance of its structural components. As a material, bamboo has unique and promising attributes that can lead to its general acceptance and consumption in the construction industry.

Uses, Recycling, and Sustainability of Bamboo

Bamboo as Reinforcing Member in Concrete

Due to the increasing cost of steel reinforcement bars, and coupled with a bid to reduce the persistent reliance on conventional reinforcement used in concrete, bamboo is currently one of the considered alternative materials used in place of steel. In recent years, bamboo has been processed into typical reinforcement bar sizes, which are systematically arranged and embedded in concrete instead of the conventional steel bars. A comparative evaluation of the flexural behavior and deformation pattern of concrete members reinforced with bamboo, rattan, and twisted steel rebars was performed by Adewuyi *et al.* (2015). From that study, it was reported that the bamboo bars are suitable rebars for non-load-bearing and lightweight-reinforced concrete flexural members. Bamboo has even been used as concrete reinforcement in various studies. An investigation by Ikponmwosa and Fapohunda (2015) explored the behavior of foamed aerated concrete beams that were reinforced with bamboo strips. According to the study, the deflection of beams decreased with increasing area of the bamboo splints, and it was also reported that the failure load decreased with an increase in area of bamboo at the tension zones. Another related study (Karthik *et al.*, in press) has indicated that bamboo strips could be a good alternative to steel bars in structural beams. Similarly, other studies (Ikponmwosa and Adegbite, 2011; Ghavami, 2005; Terai and Minami, 2011) have also evaluated the behavior of bamboo-reinforced concrete; it



Fig. 8 World's largest bamboo dome in India during construction. Reproduced from Fang, Y., 2010. World Expo 2010 Shanghai: World's largest bamboo dome in India. Available at: http://www.china.org.cn/travel/expo2010shanghai/2010-07/09/content_20461115.htm (accessed 06.06.17).



Fig. 9 World's largest bamboo dome in India after construction. Reproduced from Fang, Y., 2010. World Expo 2010 Shanghai: World's largest bamboo dome in India. Available at: http://www.china.org.cn/travel/expo2010shanghai/2010-07/09/content_20461115.htm (accessed 06.06.17).

was yet suggested that bamboo has the most potential to be used as a viable replacement for steel as reinforcement in structural members.

Also, bamboo fiber has been tested on how its inclusion in concrete affects the strength characteristics of concrete (Awoyera *et al.*, 2015; Ramaswamy *et al.*, 1983). Reports from these studies indicated that bamboo fiber has no significant effect on the strength of concrete when compared with the conventional concrete.

However, it is important to ensure that bamboo does not absorb mixing water when used in concrete. At the same time, bamboo must not swell or cause any form of crack in the concrete. Therefore bamboo must be subjected to some treatment processes before being used for construction. Such treatments are mostly done to ensure that the bamboo is prevented from attacks from insects, or even deterioration. As a result, a lot of techniques have been developed to ensure that construction work done with bamboo will last for any extended period of time. Such treatments include using a solution composed of borax and boric acid, which can effectively protect bamboo against attack. There is another option of boiling the bamboo that is to be used for construction, so that starches are removed from it, because starches can attract insects to bamboo, which can cause subsequent deterioration (Fig. 11).



Fig. 10 Bamboo flooring in modern construction. Reproduced from KATI, 2012. Uses for bamboo in sustainable building. Available at: <http://www.greenbuild.org/new-construction/uses-for-bamboo-in-sustainable-building/> (accessed 04.06.17).

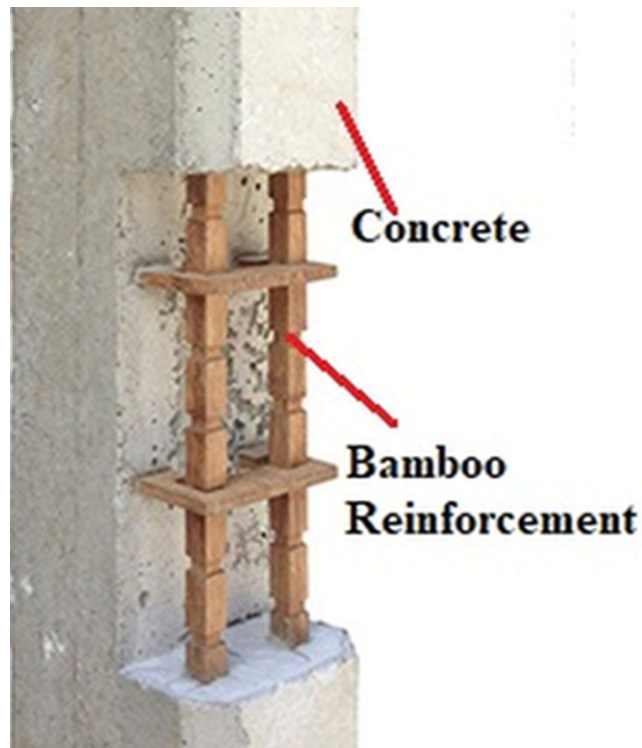
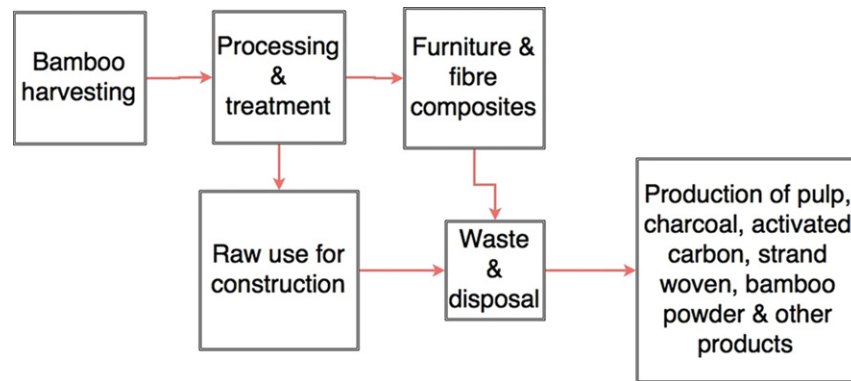


Fig. 11 Bamboo-reinforced concrete column. Adapted from Cardno, C.A., 2014. Bamboo reinforcement could help developing cities. The Magazine of the American Society of Civil Engineers. Available at: <http://www.asce.org/magazine/20140708-bamboo-reinforcement-could-help-developing-cities/> (accessed 06.06.17).

The mechanical properties of bamboo are presented in [Table 1](#). However, the mechanical properties of bamboo are mostly influenced by factors, such as harvesting age, species, climatic and soil conditions, moisture content, presence or absence of nodes, and location of the sample with respect to the length of the culm ([Asif, 2009](#); [Correal, 2016](#)).

Table 1 Mechanical properties of bamboo

S/N	Mechanical properties	Correal (2016)	Amada et al. (1997)	Janssen (2000)	Sá Ribeiro et al. (2017)
1	Specific gravity	0.64–0.79			
2	Compressive strength (N/mm ²)	64–75		0.094 times its density	
3	Bending strength (N/mm ²)	88–137		0.14 times its density	88
4	Shear stress (N/mm ²)			2.2	
5	Tensile strength (N/mm ²)	127–156	140–230		
6	Elastic modulus (GPa)	9.8–21.5	2		9.6

**Fig. 12** Schematic bamboo recycling process.

Recycling of Bamboo

Over the years, bamboo has been recognized as a potentially sustainable alternative to conventional materials. This is because bamboo is a rapidly growing plant, which has a rapid renewability, material strength, and most importantly, a variety of species across the globe.

Bamboo can be recycled for different uses. Activated carbon can be produced from bamboo for heavy metal removal from water or wastewater. Activated carbon otherwise known as activated coal or activated charcoal is a form of carbon that has been processed to make it extremely porous, thereby having a wider surface area that is suitable for adsorption or chemical reaction (Okada et al., 2003). Carbon has been produced from bamboo plants, which have attained a 5-year maturity period, through a process of pyrolysis. It has been suggested by Lobovikov et al. (2012) that increasing the stands of bamboo culms could serve as a means of biomass carbon sinks in some regions. A schematic recycling process of bamboo is shown in Fig. 12.

Bamboo has the capacity to purify water, owing to its extraordinary microstructure. It can also be used in many applications, from very traditional handicraft (such as baskets) to products that are completely industrialized (van der Lugt et al., 2006). Recycled bamboo is also used in furniture production.

Cao et al. (2016) developed a new combination of corncob carbon source and bamboo charcoal filter for effective nitrogen removal. From the study, bamboo charcoal served as an ideal filter material for denitrification, and it also played a role in the storage and supply of the organic matter. Similarly, lignin from bamboo shoot shells is an activator and novel immobilizing support for α -amylase (Gong et al., 2017), which is an indication that the addition of bamboo sawdust has a synergetic effect on metal immobilization in sewage sludge during copyrolysis.

Disposable bamboo chopsticks are very useful in the development of a novel type of self-supported binder-free carbon fibers/MnO₂ composite electrode. According to Wen et al. (2017), the application of bamboo for a well-designed nanostructured carbon fiber/MnO₂ composite proved suitable in the development of a sustainable and environmentally friendly energy storage device.

Apart from the use of bamboo for construction purposes, this article has also shown that bamboo can be recycled for other numerous applications, such as food production and water treatment.

Environmental Impacts of Bamboo

Bamboo in itself is mostly regarded as an environmentally friendly material. Considering the fact that it has a naturally waxy surface, which normally does not require painting, this even makes the environment safe from any health hazard that could arise from toxic substances that are present in paints. Also, there is a significant reduction in pollution with bamboo cultivation, because the plants absorb up to 35% carbon dioxide from the atmosphere – more than any other plant – and release more oxygen.

Before bamboo is used, it can be smoked in its own resin, which makes its surface stiff enough to resist the penetration of insects; this normally will protect it from insect infestation. Bamboo is one of the plants than can be grown in a variety of climates,

and as such its sustainability is also ensured. The process of cultivating bamboo is environmentally friendly, because it does not require the use of pesticides and other harmful chemicals, normally used to grow some other plants.

Furthermore, the roots in bamboo, like in some other plants, help to control soil erosion as they create a water barrier. As a result, some developing countries use bamboo to protect their crops and villages from serious climatic problems (Ataur Rahman and Rahman, 2015). According to Atanda (2015) bamboo is known to have the ability to consume a high amount of nitrogen, and this subsequently could aid drastic reduction in water pollution.

This suggests that bamboo can be grown alongside industrial areas, where there is usually a persistent pollution of water bodies due to effluent ejections. Thus it will help to convert the wastewater into nutrients normally required for its own growth. In the same vein, bamboo also has the capability to desalinate sea water.

On the other hand, studies (Joseph and Retsiakova-McNally, 2010; Suhaily *et al.*, 2013) have shown that of all the building materials that are used in construction, bamboo is the least hazardous in terms of waste, because it can easily be recycled and at the same time, it is not associated with any disposal problems.

However, despite the huge benefits accruing from bamboo trees, in some settings bamboo may have negative environmental impacts that offset the positive benefits (Yuen *et al.*, 2017). It has been accompanied with so much environmental impact. This has equally created serious detrimental effects on local ecosystems, which have been of much concern to scientific and environmental observers. Hence, there is reduction in the biodiversity of the ecosystem as well as species in bamboo forests. Most ecosystems encounter a decrease in their ability to withstand external threats, such as harsh weather conditions, attacks from diseases and pests, as well as a decrease in their ability to offer some vital supports like nutrient cycling and erosion control, which in turn affects the productivity of bamboo forests. Bamboo plantation not only brings about loss in biodiversity but also soil erosion, which in the long run leads to eutrophication at downstream as well as surface water pollution. Some environmental impacts arising from management of bamboo stands and bamboo stem harvesting as well as recycling of the product include effects on nutrient supply to ecosystem and contamination. Many species of bamboo generate natural herbicides that retard the growth of other species of plant in the underlying layer of bamboo shrubs and thereby affect the ecosystem. As a result, forages for wildlife are depleted, which in turn affects the growth of wildlife.

Sustainability of Bamboo

Being a grass, it is almost impossible to kill an entire bamboo plant by harvesting of a single culm. This is because the culms continue to grow from the underground rhizome system through vegetative reproduction (Richard, 2013). This feature makes bamboo more unique than timber, which can easily be eliminated. According to Janssen (2000), bamboo rarely flowers over its lifetime, and therefore its natural propagation takes time. Meanwhile, the vegetative reproduction is also used to expand a plantation through both horizontal and vertical cuttings.

Bamboo's sustainability may be ensured through a number of methods, such as layering, macroproliferation, and tissue cutting; all these are sustainable methods to ascertain the propagation of bamboo. For instance, during the cutting process, the typical vertical cuttings are from 2 to 3 internodes in length, which are planted in the ground much like a tree sprout. The rhizomes will first begin to grow downward from the buried bottom node, and later sprouts grow from the top nodes (Richard, 2013). While the horizontal cuttings involve burying a certain length of a green bamboo culm and trimming off the branches horizontally in the ground. Hence, the new sprouts and rhizomes will then start to grow at their nodes where branches have been cut off. A good practice is to obtain cutting material from various sources in order to reduce the impact of expansive blooming and die-off of the bamboo stock (Janssen, 2000).

It is important to note that the largest stock of bamboo in the world is mostly found in the natural forests (Janssen, 2000). Although, there are also privately owned homesteads, which are usually only for private use, with little or no material being sold. The homestead mode usually turns out to be less profitable, except if the owners would like to sell the bamboo in the market. However, in the major bamboo plantations that are owned by companies and cooperatives, the bamboo product is often sold for use in the pulp and paper manufacturing industries. Meanwhile, a huge amount of bamboo is usually required by the companies in order to ensure their continuous production.

Therefore a more sustainable measure for bamboo lies in creating more local bamboo plantation cooperatives. The yield of bamboo can be improved through the use of chemical fertilization (Liese, 1987), of which bamboo yields can increase by more than 50%, and a sustained plantation can yield an estimated amount of 5–12 t of air-dried material per hectare.

Similarly, Janssen (2000), in his estimate, reported that a well-managed plantation could yield as much as 20–30 t of the air-dried bamboo per hectare per year. Therefore bamboo is notably a renewable material, and bamboo forests could be grown in just a few years.

Summary and Conclusions

This article has briefly reviewed the sustainability and recycling of bamboo for engineering applications. The properties that are uniquely behind the choice of bamboo for some sensitive construction applications were explored. A wide range of application of bamboo for construction works were listed; these include making scaffolding for medium to tall buildings, construction of bridges and, on some occasions, for roofing applications. This study has shown that bamboo is a sustainable material, that it is one of the fastest growing plants in the world, and besides, it can be planted using various chemicals or other agricultural plant growth enhancement. In addition, another good attribute associated with bamboo is its appreciable economic importance. Private farmers and foresters are able to generate resources from bamboo plantations.

The typical bamboo elements that are mostly used include canes, halved canes, laths, beading, bamboo boards, and rope ties. So, the sustenance of bamboo for construction application offers benefits, such as prefabrication, simple assembly, simple replacement of structural parts, and moreover, the bamboo elements could easily be dismantled and reused for another application.

See also: A Comparative Life Cycle Assessment for Utilising Laminated Veneer Bamboo as a Primary Structural Material in High-Rise Residential Buildings. Bamboo Fiber as Fillers for Polypropylene-Nanoclay via Injection Molding. Bamboo Structural Technology. Bamboo: The Emerging Renewable Material for Sustainable Construction. Bamboo Versus Tubular Steel Scaffolding in Construction: Pros and Cons. Constructing a PV-Integrated Permanent Bamboo Building – An Experience. Development of Epoxy Based Composites Using Bamboo and Waste Metal Chips. Development of Self-Adhesive Products Using Only Bamboo Fibers Extracted With a Machining Center. Study of Junctions With Bamboo: An Attempt Towards Their Classification

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Sustainable Biodiesel Production

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Introduction

The increased growth rate of human population and advancements in the sciences and technology has resulted the enhanced energy demands, which is expected to increase by 50% or more than it by the year 2030. The fossil fuels cannot fulfill the current energy demands, which are already expected to be 105 times faster than nature available resources. Moreover, the use of petro-fuels is damaging the environment through greenhouse gas emissions and the consequential global warming. Therefore, the search for 'clean' energy has become one of most overwhelming challenges (Shuba and Kifle, 2018; Shah *et al.*, 2018). In current era enormous global carbon dioxide (CO₂) emissions from organic fuels sectors i.e., petroleum fuels, along with greenhouse gases has resulted environmental degradation and accelerated the climate changes. Transport sector is one of the potential contributors which is uplifting the atmospheric CO₂ levels on every second on the planet earth and its share is about 20% among other sources. It is estimated that by the year 2050 over 2 billion vehicles will be contributing towards global warming and climate change (Rawat *et al.*, 2013b). Biofuels are the organic substances that contain energy from the last carbon fixation. Biofuels are derived in the form of starch, animal fats, vegetable oils, remaining biomass and algal biomass. They are biodegradable, nontoxic and robust. Biofuels are classified into first, second and third generation biofuels based on their feedstocks used and their current of future availability (Kumar *et al.*, 2018). This can bring environmental benefits because it reduces carbon dioxide, hydrocarbons and particulate emissions, reduces SO_x, and also reduces inefficient greenhouse gases. The burning of biofuels results less toxic gases emissions and reduces the carbon load in the atmosphere, as a part of carbon cycle (Jiaqiang *et al.*, 2017).

Unfortunately, current biofuel predictions are based on raw materials and are also suitable for the production of food and resources in traditional agriculture systems. Alternatives to petro-diesel i.e., biodiesel fuel include the use of land for food production and fiscal incentives to reduce food production (Jiaqiang *et al.*, 2017). To this end, in recent years, microalgae have caused the world's attention to valued natural products, their aptitude to reduce the amount of wastewater and their potential as energy crops (Satyanarayana *et al.*, 2011). Algae based fuels (biodiesel or biogas) are biofuels derived from algae. Algae is a suitable solution for the production of biofuels in renewable energy sources because of its very high potential (e.g., low input and enhanced performance) (Shuba and Kifle, 2018). Therefore, this potential can entirely substitute the fuel used to transportation oil without the need for undeniable discussion of "food versus fuel". Today, microalgae biofuels are attracting attention due to increasing interest in fossil fuels, energy security, greenhouse gas emissions and other biofuels. To commercialize microalgae cultivation and biofuels production, it is constantly being worked out by combining accumulated knowledge, legislative measures and past market demands knowledge (Stavrakas *et al.*, 2018). Therefore, the purpose of this dialogue is to summarize previous tests and results, discuss future commitments and issues in the biofuel industry, and demonstrate the differences. However, biodiesel is saturated in all soils, but it is not toxic. Biodiesel does not provide a carbon dioxide or sulfur exhausts compared to petro-diesel fuel and typically provides low pollution. These factors play an important role in the acceptability of biodiesel, which is a more serious environmental problem (Hasan and Rahman, 2017).

The first generation of biofuels have been used in transport and industrial sector around for more than a century. Biodiesel is presently produced from seed oil in the United States of America (USA). Commercially available sources of biodiesel include animal fat, rapeseed oil, corn oil, palm oil, edible oil and jatropha oil. However, the use of vegetable oils for fuel production is controversial and cannot be fully utilized to meet fuel needs in specific regions, which may have major impacts over food security and the resources like farmland and water are needed. About 1% of the world's cultivated land is used for first-generation biofuels. Only this fuel can meet 1% of the world's demand. Biodiesel production studies from the alternative sources of biodiesel from microalgae are the most suitable alternatives for petroleum and diesel fuels (Naik *et al.*, 2010).

Feed Stocks for Biodiesel Production

In 2006, world biodiesel production was estimated at 580 billion liters. Different countries have different potential for biodiesel production i.e., Germany has 48%, European countries have 30%, USA has 15%, and other countries like Brazil, China and India have 7% of this share. According to estimates for 2007, the 7% of the world's vegetable oil production was comprised by the EU. In 2006, the world's vegetable oil production was about 6000 tons. Brazil, the PR-China, Pakistan, India, Indonesia, Nigeria, the Philippines, Thailand, the United States and Uzbekistan are the main participating countries, with approximately 115 million tons. It accounts for 80% of the total output (Shah *et al.*, 2018).

Around for more than a century the first generation of biofuels have been used in energy sector. Currently, in the United States, biodiesel is formed from the oil of soybeans. Commercially, animal fat, rapeseed oil, corn oil, palm oil, jatropha oil and vegetable oil are the available sources of biodiesel (Qin *et al.*, 2012). In 2006, world biodiesel production was estimated at \$580 billion. Participation in global biofuel production and biofuel production varies from country to country. The United States and Brazil are the largest manufacturers. In the same year, 8 million tons of fat were produced. It is the most important food item used among meals. Biofuel production has a long history. In recent years, the performance of biofuels produced from various

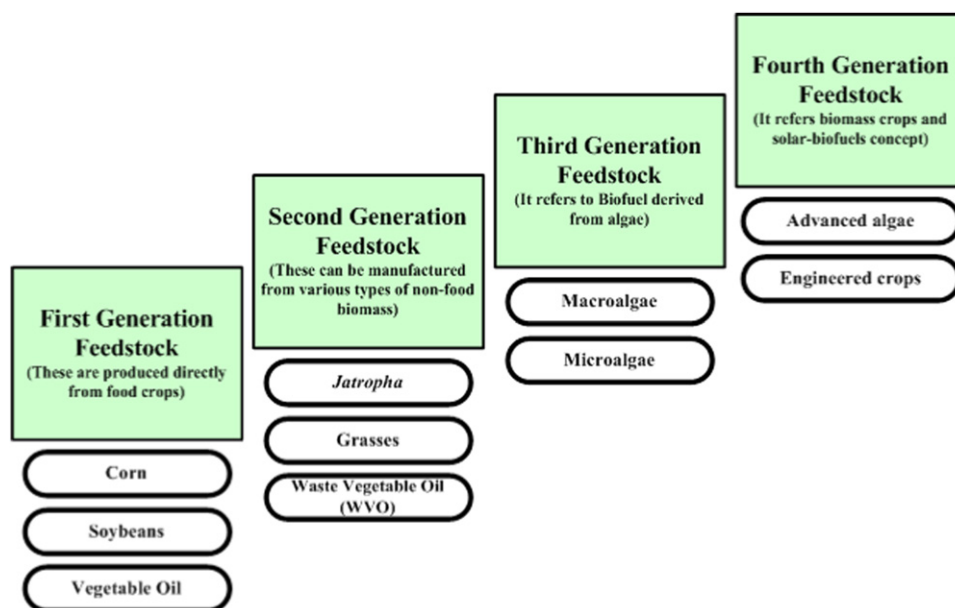


Fig. 1 Categorization of different feedstocks for biofuels production.

raw materials has been studied. For biodiesel production, the feedstocks are divided into first generation (G-1), second generation (G-2) and third generation (G-3). In the following sections the details of these feedstocks have been studied (Shah *et al.*, 2018). The categorization of different feedstocks for biofuels production has been summarized in Fig. 1.

First Generation Feed Stocks

The first generation of biofuel feedstocks are mainly oilseeds and food crops. Beans, rapeseed, sunflower oil, palm oil and other products are mainly used in biofuel production. The first generation of raw materials consisting of vegetable oil and animal fat is based on a bio-polymer component and is mainly composed of triglyceride, diglyceride and a small amount of monoglyceride. Therefore, the first generation of raw materials is included. Since biodiesel can be obtained by simply extruding oil-containing biomass, it can be easily manufactured from previous generations of raw materials. Energy production is technically limited, but can be increased by increasing the availability of food based feedstocks. Vegetable oils contain long chain molecules with several alkyl branches and higher molecular weights. The relative molecular weight of vegetable oil varies between 850 a.m.u. to 995 a.m.u., and therefore it is much higher than diesel (average is 168 a.m.u.) (Shah *et al.*, 2016, 2018). To improve national energy security, first-generation biofuels can provide several advantages associated with carbon sequestration. G-1 biofuels can be classified according to their ability to mix with fuel oil can be burned directly from the engine. It can be installed through existing infrastructure or using alternative transportation technologies such as Flexible Fuel Vehicle or alternative fuel transport vehicles (FFV) and liquefied or compressed natural gas (LNG or CNG).

Second Generation Feed Stocks

Second-generation biofuel feedstocks include intact plant tissues such as energy crops, agricultural waste and residual wood waste. Examples of second-generation secondary sources such as *Jatropha*, *Madhuca longifolia*, tobacco seeds, jojoba oil, salmon oil, and marine mango are potential sources of the feedstocks. Waste oil, restaurant fat, animal fat, fat and pig lard are the raw materials for second-generation biofuels. In recent years, the issue of large-scale production of non-edible oilseed biodiesel has also been studied. The second generation of raw materials is more effective and environmentally friendly as compared with the first generation of raw materials. Methyl esters of animal-based fats have several advantages over primary feedstocks, such as non-corrosiveness properties, higher octane numbers, purity and continuity. Thereover they reduce and eliminate competition or crises between food and feed (Shah *et al.*, 2018). A small land area is required for their plantations and can be grown using mixed crops. Oil bearing seeds can be grown on non-agricultural land that is not suitable for the production of food crops and irrigation with wastewater side by side. Nonedible oil is not suitable as a human food item because it contains a small amount of toxic substances. The problem with G-2 feedstocks are the lack of effective technology for the commercial development of waste to biofuels production. In addition, most animal fats contain high levels of saturated fatty acids, making transesterification difficult. Therefore, because of the relatively low yield of biodiesel at low temperatures, it is not possible to completely replace current transportation fuels. Biodiesel from animal's resources using infected animals can also cause bio-protection problems. Forest biodiversity is greatly affected by the widespread cutting of trees for wood and forest residues, removing and decreasing nutrients from the soil and causing wastewater drainage. This may affect the supply of water. If the biomass resources are excepted from the

Table 1 Advantages and disadvantages of G-1, G-2 and G-3 feed stocks for biodiesel production

<i>Feed stock for Biodiesel</i>	<i>Advantages of feed stocks</i>	<i>Disadvantages of feed stocks</i>	<i>References</i>
G-1 Corn oil, Vegetable oils, sunflower oil etc.	● Economic and social security ● Environmentally friendly	● First-generation biofuels are generally edible oils ● They have limited feed stocks, i.e., possess food vs. fuel crises ● Generally, they are blended with petro-diesel, i.e., B5, B10 etc.	(Naik <i>et al.</i> , 2010; Vanthoor-Koopmans <i>et al.</i> , 2013; Ziolkowska, 2014)
G-2 Aquatic biomass, grass, agriculture and forest remains, Waste Vegetable Oil, water hyacinth and Jatropa	● Environmentally friendly ● Do not compete with food ● Less conversion cost ● Perennial plants ● Fast growing and can frequently be harvested ● Low needs for fertilizer ● Marginal land could be used ● Biomass could directly be used	● For biodiesel production grasses are not appropriate ● Require extensive processing ● Several years are needed for harvesting to obtain biomass ● Early investment in culture is considerable ● Since the seeds are weak competitors with weeds although they can be cultivated on borderline land ● They are cultivated in moist soils and do not grow fit in arid environments ● If biodiesel is not properly refined, then waste vegetable oil can reduce the engine life	(Naik <i>et al.</i> , 2010; Hou <i>et al.</i> , 2011; Ziolkowska, 2014)
G-3 (Chen <i>et al.</i> , 2011) Algal biomass, (Microalgae and macroalgae)	● Microalgae can be grown on diverse types of carbon sources ● The total carbon emissions can potentially be reduced ● Scale up technologies are easy ● In closed photobioreactors they have low water use and many strain can be utilized ● Organic solvents are used to extract lipids from microalgal biomass (dry and wet).	● A minor limitation is that microalgal biodiesel is less stable and could be vulnerable to biodegradation ● The presence of unsaturated fatty acids among extracted lipids can have more volatile nature than saturated lipids ● At elevated temperatures they are less stable and more vulnerable to degradation ● The cost of microalgal biofuel is moderately higher than other feedstocks ● In case of different photobioreactors the microalgal cultivation rates and biomass productivity are variable ● The technology appears to be costly for commercial scale	(Stephens <i>et al.</i> , 2010; Brennan and Owende, 2010; Oncel, 2013)

likelihood of bioenergy, the energy potential of second generation biofuels will be greatly reduced (Naik *et al.*, 2010). The advantages and disadvantages of different feedstocks for biodiesel production are summarized in **Table 1**.

Third Generation Feed Stocks

Microorganisms are potential feedstocks as third-generation biodiesel feedstocks (G-3) for biodiesel production. A variety of microorganisms can be used for this need. Microalgae are considered as the most promising opportunity for biodiesel production. Algae are roughly divided into two groups according to its size and shape i.e., large algae (macroalgae) and microalgae. For example, large seaweeds with more plants resembling roots, stems and leaves can produce more biomass. In contrast, microalgae are common in freshwater, wastewater and seawater (Shuba and Kifle, 2018). Microalgae are photosynthetic organisms, also found as mixotrophic and heterotrophic microorganisms. Because their lifestyles are aquatic, colonial or free, and due to photosynthesis properties, these are suitable for the production of specific chemicals as feedstocks for the synthesis of biofuels products in industrial processes. Autotrophic algae use inorganic carbon sources, heterotrophic organisms use organic carbon sources. The production of biodiesel from these two microalgae (autotrophic and heterotrophic) is different. They require less surface area for their growth and have high oil content as a part of their biomass. Microalgae do not require large area for their cultivation as required by food crops and similar plants (Shah *et al.*, 2016, 2018).

Microalgae as Emerging Feed Stock for Biodiesel Production

Microalgae are by far the only organisms known to show photosynthesis and production of oxygen. Microalgae grow in natural and artificial environments as well. Microalgae are simple microorganisms having the growth requirements that need light, carbon

dioxide and other inorganic nutrients, and have the ability to grow in a variety of environments. Microalgae also can reduce air pollution by reducing atmospheric carbon dioxide levels. They use carbon dioxide which is a greenhouse gas in the atmosphere. Approximately it takes 1.8 kilograms of carbon dioxide to produce 1 kilogram of algal biomass. Some microalgae contain more than 80% of dry biomass. According to Oilgae report (2010), some microalgae have about 15%–40% (dry weight). However, the palm oil content is about 50%. Beside this the coconut oil content is 60% and sunflower oil content 55%. In actual fact, microalgae possess highest yield compared with many other vegetable oils. Palm trees, coconuts, castor and sunflowers produce 5950, 2689, and 1413, and 552 L respectively of oil per hectare per year.

Microalgae can be used to get a variety of biofuels. They can produce methane (CH_4), bioethanol, hydrogen, and biodiesel through a variety of processes. Microalgal biofuels could be used without changing existing fuel engines structures. The properties of petro oil-based diesel fuel such as cold filter point, calorific value, density, flash point, viscosity and condensation point are like those of biodiesel derived from microalgae. Mostly the parameters meet the requirements of the American Society for the Testing and Materials (ASTM). Microalgal biodiesel also meets the requirements of the international automotive biodiesel standard. A comparison of petro-oils and bio-based oils obtained by rapid pyrolysis of wood and microalgae shows that microalgae have a higher calorific value, lower density and lower viscosity than bio-oil (derived from wood). Due to its high quality, microalgae oil is better than bio-oil from lignocellulosic oil. The presence of high content of polyunsaturated fatty acids present in the microalgal oil leads to oxidation during storage and limits the use of oils for vegetable oils (Shuba and Kifle, 2018).

Microalgae primarily multiply their cells by the uptake of nitrogen (N_2) and phosphorus (P) present in the wastewater. Microalgae tend to remove inorganic nutrients from the wastewater and produce more oil containing biomass. Of course, this process is very expensive at the industrial level. Finally, microalgal biomass can be collected for lipid extraction and biodiesel production. The possibilities of cyanobacteria and microalgae-based biofuels are economic and ecological. They can reduce the dependence on fossil fuels as an energy basis. Many eukaryotic microalgal strains can synthesis and store a large quantity of energy enriched compounds, i.e., starch and triacylglycerol (TAG), which can be used to make biofuels, including biodiesel and bioethanol. The combination of cultivation and wastewater treatment can result a large amount of biodiesel amounts to reduce the impacts of energy crisis (Mubarak *et al.*, 2015).

There are few fresh water microalgal species that are investigated for wastewater treatment i.e., *Scenedesmus* sp. and *Chlorella* sp. They can potentially remove excess of nitrogen and phosphorus from wastewater. Microalgae have many advantages over other feed stocks, in the removal of nitrogen and phosphorus. There are many advantages of microalgae, i.e., *Scenedesmus* sp. and *Chlorella* sp. are used to treat wastewater. They remove excess of nitrogen and phosphorus from the wastewater. Microalga have many advantages over other feedstocks, beside removing nitrogen and phosphorus from the wastewater (Rawat *et al.*, 2013a; Shuba and Kifle, 2018). They have the following benefits:

- Increase the oxygen concentration in the water i.e., dissolved oxygen.
- Solar photobioreactors make the downstream process efficient for algae biomass production
- Reduce carbon dioxide from the atmosphere at the same time.
- Additional supply of organic carbon is not needed as compared with biological nitrification and denitrification.

Compared to diesel, biodiesel is like ordinary diesel. Therefore, it can be used to directly reduce carbon monoxide (CO) or sulfur oxides (SOx) emissions in diesel engines. In addition, microalgae have high photosynthetic capacity and can efficiently produce high quality of oil. The lipid productivity of microalgae dry biomass is an approximate unit. It is 15–300 times more than a traditional crop. Therefore, microalgae is considered a promising alternative to petroleum fuels (Jiaqiang *et al.*, 2017).

Downstream Processing for Microalgal Biodiesel Production

Light and nutrients are the essential components of microalgal growth. Microalgae consume nutrients in the presence of light and convert them into organic compounds. Microalgal cultivation is affected by aeration, carbon source, light, nutrients composition, temperature, pH and photoperiod. A number of culture media have been introduced for microalgal cultivation. Nutrients pose high cost on microalgal cultivation. Alternatively, wastewater can be used as a growth medium for microalgae cultivation and growth (Halim *et al.*, 2012).

Light and nutrition (C:N:P:K) are the important elements in the growth of microalgae. Microalgae slightly utilize the nutrients to form organic compounds. By aeration the culture of microalgae are affected, and the other impacting parameters are light intensity, carbon source, nutrients, pH, temperature and photoperiod. Many experiments have been carried out for the culturing variations for microalgae and biomass production. Nutrients can cause significant costs for the growth of microalgae. And wastewater can also be used as a means of growing and reproducing microalgae for biodiesel production (Demirbas, 2011; Liang *et al.*, 2009).

The cultures of microalgae can use wastewater as a source of nutrients, and its use can achieve two goals, i.e., removing pollutants and producing biofuels. Seawater is one of the economic methods among others for growing microalgae. In sea water the essential nutrients for growth are present and for mass cultivation the nutrients concentration may be varied. There are more than 70 elements in seawater, but 6 elements account for 99% or more of completely dissolved salts. These salts are present in ionic form in their aqueous solution, i.e., Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , CO_3^{2-} and SO_4^{2-} (Ahmad *et al.*, 2012). Biodiesel production from algae biomass by adopting downstream processing has been summarized in Fig. 2.

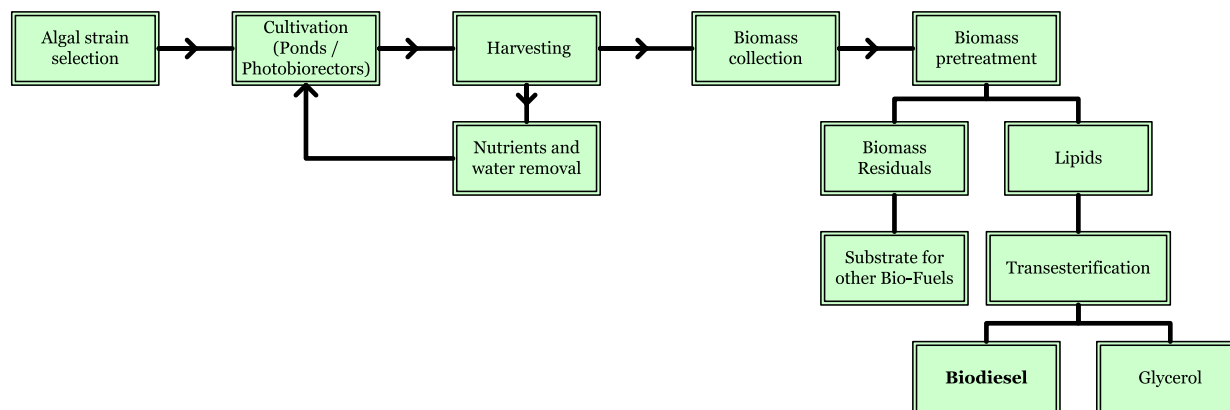


Fig. 2 Biodiesel production from algae biomass by adopting downstream processing.

Microalgal Cultivation

Apart from nutrients supplement, microalgae cultivation system also plays an important role to determine the success of the industry. An effective culture system should consist of the following criteria: (1) effective illumination area, (2) optimal gas–liquid transfer, (3) easy to operate, (4) low contamination level, (5) low capital and production cost and (6) minimal land area requirement. Apparently, only raceway pond is implemented in commercial scale for microalgae cultivation to produce high-value nutritious products for animal feed. The system consists of a paddle wheel to avoid microalgae biomass sedimentation and CO_2 is sparged at the bottom of the raceway as carbon source. In addition to the nutrients requirements for microalgal growth, the cultivation systems also play an important role in the success of the industry. Effective planting systems are (1) effective lighting areas, (2) optimal transport of gases and liquids, (3) simple use, (4) less pollution, and (5) cost effectiveness. It is evident that at commercial scale microalgal biomass production can produce high value oil for the biodiesel production. The raceway ponds for the cultivation consists of paddle wheels and homogenizers, that prevents microalgal biomass from precipitating and introduces CO_2 as a carbon source during the growth phase (Rawat *et al.*, 2013b).

There are many types of closed photobioreactor structures, such as gas lifts, flat plates, bubble column and vertical column. The key benefit of cultivating microalgae in a closed photobioreactor is that the single strain cultures are maintained at the optimal conditions without being contaminated and can result the improved consistency of biomass production and lipid accumulation. Therefore, closed photobioreactors are of great interest to researchers to further improve commercial scale operating conditions. In addition, it can further enhance the mass transfer of carbon dioxide to the medium and increase the growth of microalgae cells. Alternatively, the deflector system can be easily installed on the current set of tracks without any significant changes. However, the efficiency of photobioreactors could be evaluated on the basis of lattice cell deflection systems, fluid dynamics, mass transfer, efficiency of CO_2 transfer, turbulence effects of on microalgal growth, energy balance and scalability (Demirbas, 2011; Shah *et al.*, 2016).

Microalgal Biomass Harvesting

When the microalgal culture reaches at the stationary phase, the next stage is to separate or harvest the fresh biomass from the nutrients solution and to get seed for the next cultures. However, the microalgae are microorganisms (usually 1–20 microns) and are suspended in the liquid, so it is difficult for the skilled person to recover the microalgae. Currently, there are several ways for microalgal harvesting, i.e., sedimentation, filtration, floatation, centrifugation and flocculation (Pragya *et al.*, 2013).

Recent research on LCA has emphasized the harvesting and drying of microalgal biomass to provide considerable energy for biodiesel production from microalgae. In this case, the results indicate that a large number of collection methods can play an important role in reducing the energy demands during concentration of the microalgae suspension. Therefore, the energy consumption during the extraction and drying of microalgal biomass cannot be exempted. In fact, microalgae may have a significant negative impact on the overall energy balance of biofuel production (Taher *et al.*, 2014). Centrifugation and filtration have not been a viable method for harvesting microalgae on an industrial scale. Alternatively, flocculation provides a relatively low energy form for the concentration of microalgae. In fact, since microalgal cells are always negatively charged, they stay in the liquid for a long time and repel without mixing. The negative charge around the cells with fine elements is neutralized by introducing a coagulant in the medium. Simultaneously, the coagulant can be added to the agglomerated bridge between the aggregate and the neutralizing cells, and becomes clustered and settled flock due to gravity (Anthony *et al.*, 2013). Another probable way for microalgal harvesting is by immobilization technologies, as microalgae are continuously deposited in the matrix i.e., by the captured matrix. When the microalgae reached the fixed bed and the mixture was completed, the microalgae biomass immediately settled to the bottom of the medium. Therefore, relatively large

micronutrients can be easily separated from water by a simple filtration process (e.g., screening) that is not so much energy intensive (Pragya *et al.*, 2013).

Biomass Drying and Lipids Extraction

Unlike energy crops on the ground, biofuel production requires large amounts of dry particulate biomass, because the presence of water can restrict the subsequent downstream processes i.e., lipid extraction and transesterification for biodiesel production. However, this issue is not a big issue. This is because after the harvesting, solar drying is considered to be the best way to dry wet microalgal biomass. However, due to limited sunlight, it is important to have research on the areas where the day light duration is less throughout the year (Shah *et al.*, 2018).

In this case, in order to ensure optimal biomass production, heat must be generated from fossil fuels to continuously dry the microalgal biomass in the cultural cycle. However, recent LCA studies indicate that if natural gas is used to dry biomass, it will consume about 69% of the total energy input and produce a negative energy balance when microalgae produce biofuels. Alternatively, the high dependence of dry microalgal biomass on fossil fuels significantly impairs the commercial viability of microalgal fuels and new technologies or methods, such as the efficient development of dryers. Therefore, it confirms that the biofuel sector of microalgae is sustainable. Other strategies are also used, such as in situ partial transesterification and partial or non-drying treatment of microalgal biofuels by hot water liquefaction (hydrothermal) (Patil *et al.*, 2011).

Once the microalgal biomass is collected and dried, the next step is to extract the lipid. The energy required to extract lipids from dry particulate dry biomass accounts for a relatively small percentage (about 5%–10%) of the total energy of the biofuel-containing algae, but this method is still very significant. In the case of low lipid microalgae, loss of lipids during extraction may have a significant impact on the production of biodiesel, therefore, effective lipid extraction is necessary. Unlike terrestrial energy crops, the extraction of lipids from microalgal biomass is relatively difficult due to the presence of thick-walled cell walls that prevent lipid release. Therefore, the mechanical pressure to effectively release oil from terrestrial energy crops is generally not applicable to microalgal biomass. The subsequent sections describe two methods of lipid extraction: (1) solvent extraction for dried microalgal biomass and (2) lipids extraction from wet microalgal biomass through supercritical fluid extraction (Park *et al.*, 2015).

The most common method of extracting lipids from dried microalgal biomass is by chemical solvent extraction i.e., Bligh and Dyer methods. In fact, chemical solvents have high lipid selectivity and solubility, and even the solvents can diffuse and extract lipids on the cell walls of microalgae. In this method the organic solvents such as ethanol, methanol, n-hexane, and methanol-chloroform mixtures (2:1 v/v) can effectively extract lipids from microalgae (Mubarak *et al.*, 2016). For chemical solvent extraction, diffusion is always a limiting factor in the overall lipids extraction mechanism. But, it becomes more difficult in case of microalgae because the rigid cell wall prevents the solvent from diffusing into the cell content to extract lipids. Therefore, in order to increase the diffusion efficiency of the solvent, beads beating method can accelerate the lipid extraction rate from microalgal biomass. There are several pretreatment methods to disrupt the cell walls of microalgae, such as bead-beater, autoclaves, ultrasound, and osmotic shock and microwave (Iqbal and Theegala, 2013; Araujo *et al.*, 2013).

In recent years, the introduction of supercritical fluid extraction technology has made a new, dynamic era of lipids recovery and biodiesel production from oleaginous biomass. The fundamental principle of the method is to reach a specific stage (supercritical) other than the critical point of the liquid, and the meniscus of the separated liquid phase separated by evaporation and leaving only the homogeneous phase. In the supercritical phase, thermal and physical properties such as diffusion coefficient, viscosity, fluid density and dielectric constant vary greatly with temperature and pressure (Mubarak *et al.*, 2015).

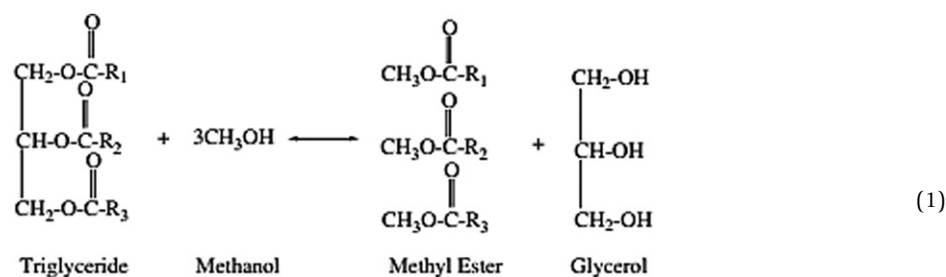
Thus, changes in thermophysical properties turn the liquid into a super solvent and increase the efficiency of the extraction and reaction. Currently, supercritical fluids such as ethylene, ethane, ethanol, carbon dioxide, methanol, toluene, benzene and water are being studied. Among them, supercritical extraction by carbon dioxide generally employed on the products recovery i.e., of drugs or health-related products from microalgae. Recently, in order to produce biodiesel, it has been studied to extract lipids from microalgae using supercritical carbon dioxide extraction method (Mouahid *et al.*, 2013).

Biodiesel Synthesis Though Transesterification

Lipids extracted from microalgal biomass can be converted to biodiesel. In the following several possible methods for obtaining biodiesel from microalgal lipids using homogeneous and heterogeneous catalysts for the transesterification are discussed. The common method used for preparing biodiesel is the transesterification of a triglyceride (e.g., vegetable oil) with a short chain alcohol (e.g., ethanol or methanol) by adding a suitable catalyst in the reaction medium. Common base catalyst such as NaOH and KOH are used for the transesterification of triglycerides (Baskar and Aiswarya, 2016).

The inclusion of high free fatty acid (FFA) content (greater than 0.5% w/w) in microalgal lipids prevents the use of homogeneous basic catalysts in the transesterification reaction. In fact, free fatty acids react with the main catalyst to form soap, reduce the production of biodiesel, and complicate the separation of glycerol (by-product) and biodiesel (Jin *et al.*, 2014; Zhang *et al.*, 2015). Acid catalysts such as sulfuric acid (H_2SO_4) are more suitable because the catalyst is not sensitive to the FFA level of the oil. Thus, esterification (the conversion of FFA to alkyl ether) and transesterification proceed simultaneously. Based on modern

technology, a two-step process involving acidic and basic catalysts is the best alternative to converting microalgae-based biodiesel (Eq. (1)) (Shah *et al.*, 2016, 2018)



The microalgae lipids are pretreated with acid to reduce FFA levels prior to transesterification with a base. These two stages of process are successfully applied to high FFA biodiesel feedstocks (such as jatropha oil and vegetable oils) and can be simply extended to industrial applications based on scale up techniques. However, the main disadvantage of these two processes is the additional cost of neutralizing the acid catalyst and biodiesel using an additional basic catalyst while transesterification process (Park *et al.*, 2015). To date, in the literature, the conversion process of microalgae biodiesel with alkaline catalysts or homogeneous acids is still very limited. Heterogeneous catalysts (acids or bases) are also widely used in transesterification reactions to produce biodiesel. Different homogeneous and heterogeneous catalysts can be regenerated and recycled in subsequent transesterification cycles to increase the profitability of biodiesel production (Pawera *et al.*, 2017). Further, the catalyst can easily be removed by filtration at the end of the reaction, thereby minimizing product contamination and cleaning cycle time (washing). To date, research on heterogeneous catalysts for the production of microalgae for biodiesel has been limited because it is a relatively new raw material and cannot be used. The commonly used heterogeneous base catalyst; CaO supplemented with Al₂O₃ have been studied in transesterification of oil derived from *Nannochloropsis oculata* (Mohamad *et al.*, 2017; Steriti *et al.*, 2014).

Quality and Application of Biodiesel

Microalgae are acceptable as an alternative to fossil diesel fuel and is highly dependent on compliance with applicable standards. Generally, the physical properties of finely derived biodiesel are comparable to those of diesel. The current references are the American Society for Testing and Materials (ASTM D 6751 07 b) and the European Union (EN 14214:2008). Many researchers compared the properties of biodiesel and compared ASTM standards for cetane number, viscosity, cold filters, calorific value, viscosity, density, flash point, hot spots, freezing points and few other parameters as well. Biodiesel derived from microalgae has a low plugging point temperature of $-11\text{ }^{\circ}\text{C}$, which is considerably lower than petro diesel (Ejim, 2015; Oasmaa *et al.*, 2009). The use of chemical transesterification and feedstock production of biodiesel is a simple and straightforward process by which glycerol is produced as a by-product. The biodiesel or fatty acid ester extracted after the reaction is mixed with contaminants such as alcohol and soap, and thus can be considered wet and impure. Therefore, to eliminate these contaminants, high concentrations and processes are required to ensure that biodiesel fuel quality meets the requirements of the American Society for Testing and Materials (ASTM) Standard. Biodiesel of poor quality and grade is harmful to diesel engines and may void the engine manufacturer's warranty (Mohamad *et al.*, 2017; Oasmaa *et al.*, 2009). The comparison of the properties of biodiesel standards with Petro-diesel are summarized in Table 2.

Table 2 Comparison of properties of microalgal biodiesel and petro-diesel with ASTM biodiesel standard

Properties	Biodiesel from microalgal oil	ASTM D6751 07b	Diesel fuel (EN 590:1999)	EN 14214:2008
1. Density (kg/l)	0.864	–	0.838	0.86–0.90
2. Viscosity (mm ² /s, cSt at 40 °C)	5.2	1.9–6	2.0–4.5	3.5–5
3. Flash point (°C)	115	> 93	> 55	> 101
4. Solidifying point (°C)	12	–	50 to 10	–
5. Cold filter plugging point (°C)	11	^a	^a	^a
6. Acid value (mg KOH/g)	0.374	Max 0.5	Max 0.5	–
7. Heating value (MJ/kg)	41	–	40–45	–
8. H/C ratio	1.81	–	1.81	–
9. Cetane number		47 min	51 min	51 min

^aCountry specific.

Note: Rawat, I., Ranjith Kumar, R., Mutanda, T., Bux, F., 2013b. Biodiesel from microalgae: A critical evaluation from laboratory to large scale production. Applied Energy 103, 444–467.

Sustainability Perspectives of Biodiesel Production

Since algae biomass has the potential to accumulate lipids in cells, algae biomass produces biodiesel with a yield of more than 100 times per acre, and is therefore one of the most important alternative fuels. The chemical method for enhanced lipid extraction is promoted by supercritical fluid extraction, Soxhlet extraction and organic solvent extraction. Mechanical methods include hydrothermal extraction, ultrasonic extraction and microwave assisted extraction. Compared to diesel fuel, biodiesel can be used directly in diesel engines to reduce carbon monoxide (CO) or sulfur oxide (SOx) emissions, unlike conventional diesel fuels. In addition, microalgae have a high photosynthetic capacity and can effectively accumulate the lipids content. Microalgae have lipid productivity per unit dry biomass 15–300 times more than conventional cultivation of terrestrial crops. Therefore, microalgae are considered a promising alternative to petroleum fuels.

Biofuels and bioethanol are undeniable issues for the World Trade Organization (WTO), complicating product transactions. According to experts, some energy producers have become WTO members and have never studied energy issues. Biofuels are no longer guaranteed because they are only a small part of the world's energy supply. Biodiesel is still classified as an industrial product. However, the use of bioethanol is uncertain (Shah *et al.*, 2018; Florentino de Souza Silva *et al.*, 2014).

The WTO classified bioethanol as an agricultural product. This is due to the different materials used to produce bioethanol for bioethanol and biodiesel according to different classification methods. In addition, the use of bioethanol has many advantages, including reducing greenhouse gas emissions from automobiles and improving vehicle efficiency and economy. Biodiesel is exempted from fuel taxes in European countries such as France and Germany. Europe is a leader in biodiesel production, i.e., France, Germany and Italy being the most important countries. In Europe, Spain is a leader in bioethanol production. In addition to these countries, countries from other continents such as Brazil, North America and Southeast Asia have also introduced new policies (Ziolkowska, 2014).

Therefore, the scientists are getting more opportunities for projects scale-up and commercialization. The infrastructure development, commercialization, education and outreach programs, public awareness, monitoring, subsidies, government participation, technology transfer and adoption, evaluation and lack of appropriate policies should be the hallmark of the mentioned technologies and recommendations. As a result, researchers have more opportunities to develop and commercialize projects. Infrastructure development, marketing, education and public relations programs, public awareness, monitoring, subsidies, technology transfer, country participation, and implementation, appropriate assessment policies and lack of appropriate policies must be the characteristics of above mentioned technologies and recommendations (Pragya *et al.*, 2013).

Conclusions

Due to the drastic consequences of fossil fuels burning and greenhouse gases emissions, there is dire need to promote and utilize the renewable energy resources. Solar energy, wind energy, tidal energy, geothermal energy and bioenergy (biofuels) are the main sectors of renewable energy options. Microalgal biodiesel is a promising biofuel which has multiple benefits, i.e., CO₂ sequestration, nutrients removal from water, efficient conversion of solar energy into chemical energy and lesser emissions of toxic and greenhouse gases. Several achievements have been made for sustainable biodiesel production and scale-up technologies. Microalgae used for biodiesel production has eliminated the use of food oil and minimized the demands to large land areas for cultivating feedstock (jatropha and oil seed crops) and water demands for irrigation. Additionally, many technical sides have been upgraded during algal biomass production and biomass processing techniques to yield more oil than terrestrial crops. Still the cost effectiveness is a great challenge. But by the improvements in downstream processes i.e., cultivation, harvesting, biomass processing, lipids extraction and transesterification the microalgal biodiesel production could be scaled up and commercialized.

See also: An Assessment of Hydrogen Energy Utilization for Sustainable Development. Analyzing Biodiesel Production From Cooking Oil. Is the Production of Biofuels Environmentally Sustainable?. Optimization and Kinetic Modeling of Biodiesel Production. Performance and Emission Characteristics of Biodiesel–Diesel Blend. Renewable and Sustainable Materials in Automotive Industry. The Production of Biogas, Biodiesel as High-Value Bio-Based Product and Multiple Bio-Products Through an Integration Approach of the Anaerobic Digestion and Fermentation Processes. Utilization of Bio-Hydrogen in HCCI Engines as a Most Renewable Fuel for Sustainable Transportation – A Thermodynamic Analysis

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Yield and Fiber Quality of Cotton

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Introduction

Classification of Cotton

Cotton is classified in the genus *Gossypium* of the mallow family, *Malvaceae*. According to Fryxell (1992), the genus *Gossypium* consists of 4 subgenera and 50 species. Among these, *G. herbaceum*, *G. arboreum*, *G. hirsutum* and *G. barbadense* are the four cultivars widely grown. *Gossypium hirsutum*, also called New World or upland cotton, and *G. barbadense*, the source of Egyptian cotton and Sea Island cotton, supply most (98%) of the world's cotton fiber. Levant cotton (*G. herbaceum*) is native to southern Africa and the Arabian Peninsula. Asian cotton (*G. arboreum*) is native to India and was first cultivated and spread in Asia. Both *G. herbaceum* and *G. arboreum* are diploid and are known as Old World Cotton.

Cotton fiber is most often spun into yarn or thread and used to make a soft, breathable textile, which is a renewable natural resource. The use of cotton for fabric is known to date to prehistoric times. Currently, more than half of the clothes people wear are made of cotton fiber, hence the cotton plant has gained the reputation of "clothing the world".

Cotton Production in the World

Cotton has a long history of cultivation, being globally distributed across Asia, North America and Western Africa. According to data from the International Cotton Advisory Committee in 2015 (the annual report of the international organization), more than 80 countries around the world plant cotton, mostly in Asia and America. Cotton production in these two continents accounts for more than 80% of the world's total. Asia is the world's largest cotton producing continent, accounting for 70% of global production. The leading cotton producing countries are China, India, Pakistan, Uzbekistan and Turkey, which together account for half of the world's and 95% of Asian production. North America is the second largest cotton producing continent, accounting for 18% of the world's total. The major cotton producing countries are the United States and Mexico.

Growth and Development Habit

Cotton was originally a perennial plant. After long-term planting, domestication, artificial selection and cultivation, it evolved into an annual plant. Therefore, it not only follows the general growth pattern of annual crops, but also has the following characteristics:

Firstly, cotton has an indeterminate growth habit and can grow continuously under conditions of unrestrained growth.

Secondly, the plant has great plasticity. The height and vegetative growth are affected by environmental conditions and cultural practices.

Thirdly, cotton can adapt to different environmental stresses to some extent. It can survive when soil moisture (10–30 cm) is reduced to 8%–12%. At low and moderate salinity, its growth and development are almost unaffected. After 3–4 days of waterlogging, cotton could still return to normal growth.

Fourthly, the plants grow vegetative at the early stage of development, and then transit to reproductive stage until senescence and maturity. However, there is a long-term overlap between vegetative growth and reproductive growth, accounting for almost 4/5 of the whole growth period.

Fifthly, cotton has the ability to compensate for damage. It has a potential to compensate for loss of the fruiting structures. For example, cotton can sustain relatively high levels of first position square loss with negligible yield loss.

Growth Stages of Cotton

Cotton requires a relatively long season (from 180 to 200 days) with sunny and warm weather and plenty of water during growth and development. The growth stages of cotton consist of emergence, seedling, squaring, flowering, boll-setting and maturity (boll opening) stages.

With good soil moisture and warm temperature at planting, cotton usually emerges 5–7 days after planting, with a full stand establishment at about 11 days. The seedling stage usually lasts approximately six weeks, and then squares or flower buds begin to form and enter the squaring stage. The squares mature in three weeks and then blossom into creamy yellow flowers, which turn pink, then red, and finally fall off three to four days after blossoming. After the flower falls off, a tiny ovary is left on the cotton branch. This ovary ripens and enlarges into a green pod called cotton boll; the boll matures (opening) in 55 to 80 days.



Fig. 1 Cotton seedlings. (a) Pre-emerged seedlings from the soil; (b, c) seedlings at 18 days after planting.

Cotton Growth and Development

Germination and Emergence

Germination begins as the seed absorbs water through its chalaza after seeding. The water swells the dormant tissues, and cell growth and division begin to take place. The radicle emerges through the micropyle, turns downward, and grows deeper into the soil as the taproot that will supply water and nutrients throughout the whole life of the plant. The hypocotyl elongates from the radicle and forms a hook that begins to push up through the soil. Seedling emergence normally takes place 4–14 days after seeding. At the soil surface, the hypocotyl straightens and pulls the folded cotyledons out of the soil. After the cotyledons are pulled through the soil surface, they unfold and expose the epicotyl and the apical meristem. At this point, germination and emergence have been completed and the plant begins its active vegetative growth (Ritchie *et al.*, 2004) (Fig. 1).

Root Establishment

Cotton has a straight root system, which is in a net-like inverted conical shape in the soil. It consists of the main root, lateral roots, small roots, hairy roots and root hairs. The depth of the main root can be more than 2 m in the soil, and the extension of the lateral roots can reach 0.6–1 m horizontally. The establishment of the root system includes four stages: root development stage (from seed germination to squaring), root growth stage (from squaring to flowering), peak root absorption stage (from flowering to initial boll-opening) and root activity declining stage (during boll opening). The root growth stage is the key growth period of the main and lateral roots, and the number of active roots in the plough layer is greatly reduced and the ability for absorbing minerals is also significantly decreased at the root activity declining stage.

Stem and Branch Growth

Stems and branches are the skeleton of cotton plants. The main stems are gradually formed by the growth point of the stem through cell proliferation, differentiation and growth. The growth of cotton main stem is slow at the seedling stage. It grows faster at the squaring and flowering stages, and peaks at the initial flowering stage. After peak flowering, the growth of the main stem slows and stops after the boll-opening stage. The branches on a cotton plant can be classified as vegetative branches (*monopodia*) and fruiting branches (*sympodia*) (Ritchie *et al.*, 2004). The fruiting branches are generally formed in the middle and upper parts of the main stem, and the branches stretch outward horizontally, so they exhibit axis branching. The squares and bolls are directly formed on the fruiting branches. Because vegetative branches have only one meristem, they grow straight and erect, much like the main stem. Vegetative branches are produced after fruiting branches and below the node at which the first fruiting branch was developed.

Leaf Growth

Cotton leaves are heart-shaped, lobed, and coarse veined, somewhat resembling a maple leaf. After a cotton seed has sprouted (about four to five weeks after planting), two “seed” leaves provide food for the plant until additional “true” leaves appear.

As the cotton plant develops, new leaves appear and expand, increasing sunlight interception (Ritchie *et al.*, 2004). Initially the carbohydrates produced by the leaves are used to produce roots and more leaves. This production of new leaves causes the leaf area of the cotton plant to increase rapidly. Leaf photosynthesis does not remain constant as the leaf grows and develops. A cotton leaf reaches its maximum photosynthetic capacity at about 20 days of age, after which it declines.

Squaring, Flowering, and Fertilization

Cotton seedlings begin to differentiate into squares at the 2 or 3 true leaves stage. Based on the structure of floral organ, flower and square differentiation begins in an outside-in pattern. The 6 periods of the differentiation are flower primordium elongation, temporal primordium differentiation, square primordium differentiation, petal differentiation, stamen differentiation and pistil differentiation. After squaring, the primordium continues differentiation; the filaments are elongated, the ovules protrude from the pistil, the septum is formed, and the ovules are formed. The stamens form pollen mother cells 7–10 days before flowering, and form a tetrad by meiosis. The isolated single cells form pollen grains.

Flower buds protected by a fringed, leafy covering develop a few weeks after the plant starts to grow, and then bloom a few weeks later. The flower usually blooms in the morning and then withers and turns color within two to three days. The bloom falls off the plant, leaving a ripening seed pod.

Pollination must occur before the flower falls off. The entire pollination process is completed within 24–48 h after blooming. Pollen from the stamens (male part) is transferred to the stigma (female part) by insects or wind, and travels down the stigma to the ovary. It takes about 8 h for the pollen tube to reach the ovary. The ovary contains ovules, which become seeds if fertilized. The ovary swells around the seeds and develops into a boll (Fig. 2).

Boll Development

After pollination the boll begins to develop. Under optimum conditions it requires approximately 50 days for a boll to “open” after pollination. Boll development can be characterized by three phases: enlargement, filling, and maturation. The enlargement phase lasts approximately 3 weeks. During this time the fibers produced on the seed elongate and the maximum volume of the boll and seeds contained therein are attained. The filling phase begins during the fourth week after flowering. At this time, fiber elongation ceases and formation of secondary wall on the fiber begins. The filling phase continues into the sixth week after pollination. The boll maturation phase begins as the boll reaches its full size and maximum weight. During this phase, fiber and seed maturation takes place and boll dehiscence occurs. The capsule walls of the boll dry out, causing the cells adjacent to the dorsal suture to shrink unevenly. This shrinking causes the suture between the carpel walls to split, and the boll opens (Ritchie *et al.*, 2004).

Seed Development

Cotton seeds are endosperm-free seeds developed from ovules after fertilization. The development of seeds corresponds with the development of bolls. The ovules begin to expand after fertilization and reach the peak volume 20–30 days after flowering. The fertilized eggs began to divide 4–5 days after flowering. After 15–20 days, cotyledons, germs, hypocotyls and radicles are clearly visible, and the seeds acquire germination ability. At the same time, nutrients in the endosperm are gradually absorbed and utilized by the embryo, and become enveloped in a film outside the embryo, while the embryo is full of seed shell.

Fiber Development

Cotton fibers are developed from epidermal cells of ovules after fertilization. The shape, structure and formation process of fibers are closely related to their quality and economic value. Mature cotton fibers have good consistency in structure, fineness and strength, and thus have ideal spinning and dyeing properties. A mature cotton fiber can be roughly divided into base, middle and tip parts. The cross section of mature fibers is mostly elliptical or circular, consisting of many concentric circles, which can be further divided into primary wall, secondary wall and central cavity. The primary wall is the primary cell wall of fibroblasts, which



Fig. 2 Parts of a mature cotton flower.

is composed of pectin and cellulose. Externally, waxes, pectin, fat and resin form a very thin cuticle. The secondary wall is the main part of cotton fibers, almost all of which are composed of cellulose. It is a wheel-like layer. The thickness of the secondary wall is related to fiber strength. The secondary wall of mature fibers is thicker, the middle cavity is smaller, and the strength of the fibers is higher. The innermost layer of the fibers is the lumen, which is left when the cell wall stops thickening.

The morphogenesis of cotton fiber is comprised of four developmental stages: initiation, elongation, secondary wall thickening, and maturation. The formation of fiber initials is observed as balloon-like protrusions on the ovule surface at anthesis. After initiation on the day of anthesis, single-celled fibers undergo the second stage called fiber elongation. Fiber elongation occurs over a period of approximately 21 days, with accelerated growth, reaching peak levels at approximately 5 to 20 days post-anthesis (DPA). This period is critical for fiber elongation. If the plant is exposed to drought stress at this period, the fiber would not elongate sufficiently. Under normal circumstances, cells initiated within about 3 DPA can form long fibers; cells initiated from 4 to 10 DPA can only form short fibers (fuzz) (Wilkins and Arpat, 2005).

Termination of fiber elongation is accompanied by a corresponding thickening of the cell wall, which lasts for 25–35 days. At 5–10 DPA, the cell wall thickens and the middle cavity becomes smaller due to the deposit of cellulose in the centripetal layer of the primary wall (Wilkins and Arpat, 2005). The maturity starts from boll cracking to full opening, which lasts about 5 days. With the cracking of bolls and fiber-dehydration, the residual protoplasm in the cavity dries up gradually, causing the fibers to shrink into flat tubes. Due to the spiral arrangement of small fibers and changes in spiral direction, an internal stress occurs that twists the fibers.

Yield and Yield Components

Biological and Economic Yields

The biological yield of cotton refers to the total amount of dry matter that cotton absorbs and synthesizes during its lifetime after subtracting the consumption of respiration. The economic yield refers to the seed cotton yield or lint yield. Of the total dry matter of cotton, 90%–95% comes from photosynthesis, and only 5%–10% comes from the absorbed mineral nutrients. Therefore, the biological yield depends on the amount of photosynthetic products. However, whether high economic yield can be achieved also depends on the harvest index which is the ratio of economic yield (seed cotton) to biological yield.

Yield Components

Cotton yield is formed through fruiting (boll setting). The basic components of lint yield are the number of bolls per unit land area (fruiting sites and boll retention), weight per boll (cotton weight per boll seed) and lint percentage. The relationships between cotton lint yield and its components are complex (Constable, 2012). They are dependent on genetic and environmental variation and their interactions. The primary yield components that contribute to seed cotton yield are the number of bolls per unit area and boll weight. Thus the most commonly used yield component equation for cotton is the geometric model proposed by Kerr (1966):

$$\text{Seed cotton yield} = \text{bolls/unit area} * \text{average single boll weight}$$

Boll density

The number of bolls is determined by fruiting sites and fruit retention, which can be monitored during early boll development and possibly manipulated by field management to maximize yield. Different yield components contribute to lint yields at varying degrees. Increases in yield are generally associated with the number of bolls per unit ground area (Pettigrew, 1994; Wells and Meredith, 1984). The number of bolls/m² is affected by soil fertility level, soil water content and planting density.

Boll weight

The boll weight may be more genetically determined than boll density. Boll weight is the main determinant of yield when the number of bolls is the same. In addition to the genetic characteristics of the varieties, the boll weight is affected by temperature and heat accumulation. The optimum temperature for boll development is 25–30°C. When the active accumulated temperature (> 15°C) is between 1300 and 1500°C, cotton bolls can crack and open normally; when the active accumulated temperature (> 15°C) is less than 1100°C, most of the bolls cannot open normally. The boll weight decreases as the effective accumulated temperature decreases. The boll weight is also affected by fertilizer and water supply.

Lint percentage

Lint percentage is an important yield component and is also correlated with fiber development. It is indicated by the weight of fibers (lint) accounting for the percentage of cotton weight. Thus, it is the relation between the weight of the fiber and the weight of the seeds from which the fiber is obtained in the process of ginning. The lint percentage of mid-maturing upland cotton varieties is 36%–40%. Lint percentage is mainly determined by genetic characteristics of varieties, and is less affected by environmental conditions than boll density and boll size.

Fiber Quality

Main Quality Indexes of Cotton Fiber

Fiber length

Fiber lengths of cotton can be determined by hand-stapling or photoelectrical measurement (Munro, 1987; Behery, 1993) while the fibers are still attached to the individual seed (Munro, 1987) or after ginning. Traditionally, staple lengths have been measured and reported to the nearest millimeter. There are four upland staple classes: Short (<21 mm), Medium (22–25 mm), Medium–Long (26–28 mm), and Long (29–34 mm). Pima staple is classed as Long (29–34 mm) and Extra-long (> 34 mm) (Bradow and Davidonis, 2010).

Fiber strength

The inherent breaking strengths of the individual cotton fibers are considered the most important factor in determining the strength of the yarn spun from those fibers (Munro, 1987; Patil and Singh, 1995; Moore, 1996).

Fiber fineness

Fiber 'fineness' has long been recognized as an important factor in yarn strength and uniformity, properties which largely depend upon the average number of fibers in the yarn cross-section (Bradow and Davidonis, 2010). Micronaire is an indirect estimate of fiber fineness and maturity.

Factors Affecting Fiber Quality

The fiber quality of cotton is a composite property determined by complex interactions among (1) the genetic potential of the genotype, (2) the environmental fluctuations experienced by the maternal plant from planting through harvest, and (3) the genetically controlled responses of the genotype to the environmental fluctuations (Bradow and Davidonis, 2010). As do all metabolizing plant cells, a cotton fiber cell responds individually to fluctuations in the macro- and micro-environments so that the fibers on a single seed constitute a continuum of fiber lengths, shapes, cell-wall thicknesses, and maturities (Bradow *et al.*, 1997a,b). Environmental changes among plants, and within and among the fields assure that each bale of cotton contains a highly variable fiber population that contains a wide range of fiber-quality characteristics. Therefore, the natural genetic and physiological changes in fiber cell shape, size, and maturity are regulated by fluctuations in the growth environment (Bradow and Davidonis, 2010).

Traditional Field Management for Cotton Production

Pre-Sowing Preparation

Pre-sowing preparation for cotton includes preparation of land, seed and other materials for production, and determination of sowing date. Land preparation includes deep tillage, leveling and irrigation; seed preparation includes selecting good seeds, doing germination test and solar drying of seeds before sowing. Sowing date should be determined comprehensively according to soil temperature and moisture.

Sowing and Plant Density

Cotton is planted by machines or manually. The planter opens a small furrow in each row, drops in seed, covers them, and then packs more dirt on top. Seed may be deposited in either small clumps (referred to as hill-dropped) or singularly (called drilled). The seed is placed 2–3 cm deep, depending on the soil type.

Plant density is an important factor influencing cotton yield and yield components. Lint yield is relatively stable across a wide range of plant densities. The planting density should be determined according to plant and ecological condition, planting methods and cotton varieties.

Fertilizer Use

Nitrogen (N), phosphorus (P) and potassium (K) are the essential nutrients required most consistently for cotton production. The absorption of N, P and K is 4.5, 3.0 and 4.0% of the whole growth period at the seedling stage; 28%–30%, 25%–29% and 28%–32% at the squaring stage; 60%–62%, 64%–67% and 62%–63%, at flowering and boll-setting stage which is the key period for yield formation; and 3.0%–8.0%, 1.0%–7.0% and 1.0%–6.0%, at the boll-opening stage. Thus, rational use of basal fertilizer and moderate topdressing is an important measure to improve cotton yield and fiber quality.

Irrigation

Cotton is one of the most tolerant crops of drought stress, but it responds well to water application. Timing of drought stress appears to be more important than total amount of water available to the crop. During early seedling growth, cotton can withstand long periods with minimal water and growth and yield will not be greatly affected. However, once squaring begins, drought stress will cause square and boll abortion and dramatically affect its growth and yield. Square and boll shedding is especially important in areas with short growing seasons since the plants may not have enough season left to develop more bolls at the top of the canopy. Severe soil water deficit can reduce fiber length and micronaire value. Since cotton responds to water stress by abscising squares and bolls, few bolls develop under severe water stress conditions. Thus, the impact of water stress on fiber properties appears to be smaller than that on lint yield (Bauer, 1994).

Water requirement

Water requirement refers to the amount of water consumed in the field during the growth and development of cotton. It is the total amount of water used by cotton and the amount of transpiration and evaporation during the whole growth period. The required amount of water at different growth stages varies with environmental conditions. The water requirement at the seedling stage is less than 15% of the total requirement for the whole growth period; it is 12%–20% at the squaring stage, 45%–65% at the flowering and boll stage and 10%–20% at the boll opening stage.

Irrigation techniques

The predominant methods for application of supplemental water to cotton are furrow irrigation, overhead sprinkler irrigation and drip irrigation. In furrow-irrigation systems, water is applied through gated pipes from one end of the field and allowed to flow down row middles. Overhead sprinkler systems travel through the field applying water above the canopy. Micro-irrigation pipe, which can be buried or placed on the surface, places small amounts of water in the rooting zone of the plants, eliminating water loss through evaporation and through leaching.

Plant Growth Regulation

The cotton plant can produce excess vegetative growth under high soil moisture and fertility. Excess growth can lead to boll and square shedding. Plant growth regulators are organic compounds other than nutrients that affect physiological processes of plants when applied in low concentrations. For cotton, growth regulators are used to control vegetative development and to improve maturity in the late season. For example, Mepiquat chloride has been widely used to regulate cotton growth and development.

Harvesting and Processing

For centuries, cotton harvesting was done by hand. Cotton had to be picked several times in the season because bolls do not completely ripen at the same time. Today, more and more cotton is mechanically harvested.

Cotton plant should be defoliated if it is to be machine harvested. Defoliation (removing the leaves) is often accomplished by spraying the plant with a chemical. It is important that leaves not be harvested with the fiber because they are considered “trash” and must be removed. In addition, removing the leaves minimizes staining the fiber and eliminates a source of excess moisture. Without defoliation, the cotton must be picked by hand.

Harvested cotton needs to be cleaned before ginning. Often, it is dried before being put through the cleaning equipment which removes leaves, dirt, twigs, and other unwanted materials. After cleaning, the long fibers are separated from the seeds with a cotton gin and then packed tightly. Cotton is classified according to its staple (length of fiber), grade (color), and character (smoothness). In the textile mill, cotton fibers are spun into yarn and then woven or knitted into cloth. The seeds, still covered with linter, are sent to be pressed in an oil mill (Fig. 3).



Fig. 3 Cotton harvesting (*Left*) manual picking; (*Right*) mechanical harvesting.

Specific Cultural Practices for Improved Yield and Fiber Quality

Intensive Culture

Intensive farming technologies and cultural practices in cotton are widely adopted in China and some other developing cotton growing countries. They mainly include seedling transplanting, plastic mulching, plant pruning and super-high plant density technique (Dai and Dong, 2014).

Seedling transplanting

The seedling transplanting process mainly consists of three steps: raising of seedlings in nursery beds, transplanting seedlings to the fields, and field management after transplanting (Dong *et al.*, 2007). Generally, transplanting is carried out when the mean soil temperature at the 5 cm depth reaches 17–19°C and cotton seedlings have 2–4 true leaves on the main stem. Soon after transplanting, the field is watered to let seedlings recover normal growth quickly.

Plastic mulching

Plastic mulching is usually done soon after sowing. Seedlings are freed from mulching cover by cutting film above hills at emergence, and thinned to the planned population density by leaving one vigorous plant per hill at the two-leaf stage (Dong *et al.*, 2009). Generally, the polythene mulch can be retained during the whole growth season, especially in arid and special early maturing cotton areas to improve soil temperature and decrease moisture evaporation. In areas with ample water and heat sources, plastic film should be removed at full squaring.

Plant pruning

Plant pruning mainly involves removal of vegetative branches, plant topping, and excising old leaves and empty fruit branches. It can efficiently coordinate the relationship between vegetative and reproductive growth by adjusting the distribution of nutrients in plant tissues, and reducing the nutrient consumption by surplus organs. Plant pruning could also improve the microclimate of the cotton field, reduce boll abscission and boll rot (Li *et al.*, 2007) and increase cotton yield and fiber quality (Zhou and Yang, 1999).

Light and Simplified Culture

During the last two decades of the 20th century, the adoption of intensive cultivation technologies has helped China to enhance yields and emerge as the world's largest cotton producer. But this approach is being debated now because of the increasing labor costs which are linked to the rapid economic development and urbanization of the country. A new approach called 'light and simplified cultivation' (LSC) has been initiated to respond to the new context. This approach has become more relevant to the small-scale farming systems of China as opposed to the complete mechanization observed in developed countries. The approach of LSC aims to reduce labor intensiveness. It simplifies field management, diminishes the frequency of field operations, and adjusts techniques that blend with their implementation by machines (Dai *et al.*, 2017). The key technologies of LSC in cotton cropping include precision mono-seeding technology, light and simplified seedling nursery technology, non-pruning technology, one-time fertilization technique, fertigation technology and technology for plant population management (Dong and Fok, 2018).

Precision mono-seeding is based on using high-quality seeds sown as single-seed per hill on finely prepared soil-beds, at row spacing defined for mechanical sowing (Kong *et al.*, 2018). This technique is applied through diverse modalities depending on regions.

The non-pruning technology consists of setting up a large population of small individual plants whose growth is properly regulated. By LSC approach, the development of vegetative branches can be greatly inhibited by increased plant population density instead of traditional plant pruning.

One-time fertilization technique in the LSC approach refers to a reduction in the number of fertilizer applications and the amounts of fertilizers under various conditions, depending on regions and yield targets.

In short, the development and application of LSC are indispensable for sustainable cotton production in China in view of the scarcity and higher cost of labor. For the techniques already operational, the shift from the intensive cultivation system to LSC is significant. LSC technology is believed to provide a solid support for sustainable production of cotton in China and holds tremendous promise for field-enhancement in the small-scale farming systems in Africa (Fig. 4).

Distinctive Cotton

Organic Cotton

Organic cotton is generally understood as cotton from non-genetically modified plants, which is certified to be grown without the use of any synthetic agricultural chemicals such as fertilizers or pesticides. Its production also promotes and enhances biodiversity and biological cycles. In the United States, cotton plantations must also meet the requirements enforced by the National Organic



Fig. 4 Non-pruning cotton field under high plant density and chemical topping.



Fig. 5 Colored cotton and white cotton.

Program (NOP), from the USDA, in order to be considered organic. This institution determines the allowed practices for pest control, growing, fertilizer use, and handling of organic crops.

Colored Cotton

Nearly all of the cotton fiber used for textiles is white; consequently, dyes are required during the processing of fibers to color cloth. The enormous consumption of dyes has resulted in environmental pollution and has thus negatively affected human health. One of the most efficient solutions is to breed cotton varieties that naturally contain colored fibers (CCFs), which are environmentally innocuous.

One of the most important factors that differentiate CCFs from white cotton fiber (WCF) during fiber maturation is pigmentation. Many factors are involved in pigmentation, including the type of pigment, the activity of phenylalanine ammonia lyase, the concentration of total carbohydrates, and the type of soluble saccharide (**Fig. 5**).

Better Cotton

Better Cotton was developed by the Better Cotton Initiative (BCI) of Switzerland to help farmers to grow cotton in a way that reduces stress on the local environment and improves the livelihoods and welfare of farming communities. Better Cotton exists to make global cotton production better for the people who produce it, for the environment it grows in, and for the sector's future. The Better Cotton Production Principles and Criteria lay out the global definition of Better Cotton, by upholding the following six principles in which it is produced by farmers who:

- (1) Minimize the harmful impact of crop protection practices.
- (2) Use water efficiently and care for the availability of water.
- (3) Care for the health of the soil.
- (4) Conserve natural habitats.
- (5) Care for and preserve the quality of the fiber and Promote Decent Work.

Conclusions

Cotton fiber is one of the most important raw materials in the textile industry. It is also a renewable natural resource; for this reason, cotton is widely grown in the world. The growth and development stages of cotton consist of emergence, seedling, squaring, flowering, boll-setting and boll opening stages, which totally last for 180–200 days. Cotton yield is formed through fruiting. The basic components of lint yield are the number of bolls per unit land area, weight per boll and lint percentage. Quality of cotton fiber can be mainly indicated by fiber length, fiber strength and fiber fineness. Comprehensive factors such as environment, planting system, agronomic measures and harvesting regulate every developmental process of the cotton plant, both vegetative and reproductive growth, and also affect the yield and quality of cotton fiber. Thus, to achieve maximum yield and quality of cotton fiber, appropriate combination of genotype, environmental conditions and cultural practices like light and simplified culture should be adopted.

See also: Development of Self-Adhesive Products Using Only Bamboo Fibers Extracted With a Machining Center. Jute/Coir/Banana Fiber Reinforced Bio-Composites: Critical Review of Design, Fabrication, Properties and Applications. Kenaf Fiber Based Bio-Composites: Processing, Characterization and Potential Applications. Kenaf Fiber Reinforced Composite in the Automotive Industry. Life Cycle Assessment of Sisal Fiber. Natural Fiber Composites: Review of Recent Automotive Trends. Natural Fiber Reinforced Composites in the Context of Biodegradability: A Review. Recyclability of Natural Fiber-Filled Thermoplastic Composites. Renewable Agricultural Fibers as Reinforcing Fillers in Plastics: Mechanical Properties of Kenaf Fiber-Polypropylene Composites. Reuse of Waste Corrugated With Coir Fibers as a Packaging Material

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Relevant Website

<https://bettercotton.org/>
Better Cotton Initiative.

Bamboo: The Emerging Renewable Material for Sustainable Construction

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Introduction

In recent years, green concept is being advocated extensively by environmentalists. Energy cut down and reduction of carbon dioxide (CO₂) emission are the examples of green concept which are always promoted to help the sustainability of our mother earth. According to the National Aeronautics and Space Administration (NASA), the heat trapping nature of CO₂ and other greenhouse gases has been demonstrated in the mid-19th century. Hence, to protect our earth, the use of environmental-friendly construction material has been promoted. One of the criteria being the environmental-friendly construction material is by having the potential in reduction of CO₂ emission during its production.

The term “sustainability” also refers to development that are capable to meet the current generation’s demands by not undermining the ability of the future generation to meet their own needs (def: as per agenda 21, World Climate Summit in Rio de Janeiro 1992). Therefore, in terms of this social sustainability of not undermining the future generation’s ability of using the resources, the use of renewable resources is always being enhanced. Last but not least, in terms of sustainability of economics, strategies for employing existing resources optimally to achieve long-term responsible and beneficial balance was always being encouraged to be executed. Due to the limitation supply of resources, the construction material’s price was always increasing. This subsequently has increased the burden of the developing country. As a result, there is always an urge to explore for new green construction materials to substitute the conventional materials.

In summary of the above criteria, bamboo, is considered as one of the new emerging materials which possess a great economic potential. Structural bamboo has been traditionally used in China, India, Philippine and Latin America for hundreds of years. It has been utilized as structural members in short-span footbridge, low-rise houses, long span roof and construction platforms. Besides, it is also exploited in signage erection, decoration, demolition, and civil works. One of the popular usages of bamboo in the South-East Asia, especially, in Hong Kong and Southern China is the construction’s access scaffoldings (Chung and Yu, 2002). The high productivity rate and short cycle of harvest enables bamboo to be an outstanding material compared to the other naturally growing resource. On top of that, bamboo has been proven that having its ultimate tensile strength on par with the mild steel (Baksy, 2013). Moreover, the ratio of tensile strength to the density of bamboo is 6 times higher than that of steel. Its high strength-weight ratio supports it to be used as a high resilient material against force generated by earthquakes and wind of high velocity.

Bamboo Species

Botanical Classification

Bamboo is a giant, perennial, woody grass categorized in angiosperms group of monocotyledon order (McClure, 1966; Liese, 1987). It is an evergreen flowering plant belonging to the grass family Poaceae (formerly Gramineae), subfamily Bambusoideae and tribe Bambuseae. It is the largest member in the grass family. Bamboo is characterized by joint stems called culms. The internodal parts of the stem are typically hollow and instead of in a cylindrical arrangement, the vascular bundles are scattered throughout the cross section of the stem. As it is monocotyledon, there is no dicotyledonous woody xylem. Consequently, rather than tapering, the lack of secondary growth brings up the stems of monocots to be columnar.

As characterized by the formation of upright canes and types of rhizome, there are generally two main categories of bamboo. The first category is monopodial bamboos, also known as running bamboos. They generally have long and thin rhizome extensions whose buds producing single shoots at regular intervals. They usually grow in scatter state and spread over a large distance. The second category is sympodial bamboo. It has short, thick rootstocks where axillary buds are formed which then developed into new stems. They usually grow in clumps. Owing to its unique rhizome-dependent system, bamboos are listed as one of the most rapid growing plants. It constitutes more than ten genera which are further categorized into about 1450 species.

Growth of Bamboo

The growth pattern of bamboo is a combination of leaf-bearing tree, palm and grass. Like leaf bearing trees, bamboo shed their leaves every year and by throwing out new branches that increase their crown each year. Due to the absence of secondary woody xylem, and it has its definitive circumference emerging from the soil, its diameter would not increase afterwards. On the other hand, bamboos are like grasses where they have tubular blades, and lancet-shaped cover leaves. The characteristics that differentiate bamboos from grasses are the lignification, branching and longevity of their canes (Patil and Mutkekar, 2014). Bamboos have a growth area of about 38,000 million ha, which covers approximately 3.2% of the total forest area around the world. Bamboo grows naturally in tropical and sub-tropical regions and is commonly found in Asia, with 65% of the total world bamboo

Table 1 Bamboo resources in Asia (1000 ha)

Countries	1990			2000			2005		
	Natural	Planted	Total	Natural	Planted	Total	Natural	Planted	Total
Bangladesh	80	10	90	76	10	86	73	10	83
China	2789	1067	3856	3235	1634	4869	3354	2090	5444
India	7844	2867	10,711	7996	2867	10,863	8434	2927	11,361
Indonesia	624	4527	2151	690	1414	2104	723	1358	2081
Malaysia	422		422	592		592	677		677
Myanmar	951	12	963	883	12	895	847	12	859
Philippines	124	3	127	153	3	156	168	4	172
Total	12,834	8486	18,320	13,625	5940	19,565	14,276	6401	20,677
% of Total	70	30	100	70	30	100	69	31	100

Note: Lobovikov, M., Ball, L., Guardia, M., Russo, L., 2007. World Bamboo Resources: A Thematic Study Prepared in the Framework of the Global Forest Resources Assessment 2005. Food & Agriculture Org.

resources, followed by Central and South America with 28% and Africa with 7% (Correal, 2016; Richard, 2013). Although most bamboo resources grow naturally, increasing attention has been given to planted bamboo these few decades. In Asia, approximately 30% of total bamboo resources are planted (Table 1) (Lobovikov et al., 2007). This percentage has remained stable over the reported period with only a very slight increase in 2005. It is worth noticing that all of the bamboo forest in Malaysia is reported to be naturally regenerated. No data were reported on planted bamboo in Malaysia but there is only a fine separation line between categorization of planted and naturally regenerated bamboo, and it requires further clarification.

Bamboo Species in Malaysia

Malaysian bamboos generally belong to the sympodial bamboo category. It is reckoned that in Peninsular Malaysia there are around 59 bamboo species which originates from 7 genera, i.e., *Bambusa*, *Dendrocalamus*, *Dinochloa*, *Gigantochloa*, *Racemobamboos*, *Schizostachyum* and *Thyrsostachys*. Fig. 1 illustrates the bamboo forest distribution in Peninsular Malaysia and the distribution data is also presented in Table 2.

Based on Table 2, the Kelantan state is found to have the highest density of bamboo within forest districts in Peninsular Malaysia, comprising of 31,035,850 culms. This is followed by Pahang (23,480,760 culms), and Perak (20,174,160 culms). The total number of culms in Peninsular Malaysia was 110,584,140 covering 421,722.38 ha of forest areas (Lockman et al., 1992). The most useful bamboo found in these areas is *Gigantochloa scortechinii*, which can be found in the Kedah, Kelantan, Perak, Selangor and Terengganu states.

Bamboo Species Currently Used in Construction in Asia

Only specific species of bamboos are suitable for application in construction. Below is the list of bamboo species that are recommended to be used as construction materials:

- *Bambusa oldhamii* – Or more well-known as the Giant Timber Bamboo. This tall species from China can grow up to around 65 ft high with a maximum diameter of 4 in.
- *Bambusa Lako* – Can grow up to 50 ft high and has a useful 4-in. diameter. As it able to retain its black color even after being harvested, it is widely used in furniture making.
- *Dendrocalamus Asper* – A very strong species from Southeast Asia and is known to grow as tall canes that have long straight sections of approximately 65–100 ft and diameter of around 3–8 in.
- *Dendrocalamus Brandisii* – Boasting canes that can grow tall and straight, can reach a height of approximately 60 ft and diameter of 6–8 in. It is an excellent building material and is one of the species that can be found throughout regions of Southeast Asia.
- *Dendrocalamus Yunnanicus* – This species has strong and straight canes that can grow to around 70 ft high. It is good for bamboo lumber and is a great species as construction industry materials.
- *Gigantochloa Apus* – It can grow up to around 60 ft high and 4-in. diameter. This is a species that has been traditionally used as an Indonesian building material.
- *Gigantochloa atrovioleacea* – It is a very straight growing plant, with strong black canes that will grow to a height of approximately 50 ft and a good 4-in. diameter. It is a species that is good for furniture making.
- *Gigantochloa Atter* – A species that has straight and strong canes and can reach an approximate height of around 60 ft and 4-in. diameter.
- *Gigantochloa Pseudoarundinacea* – An excellent bamboo species from Indonesia and have boasting canes that can grow up to 40 ft high and 4 in. in diameter.

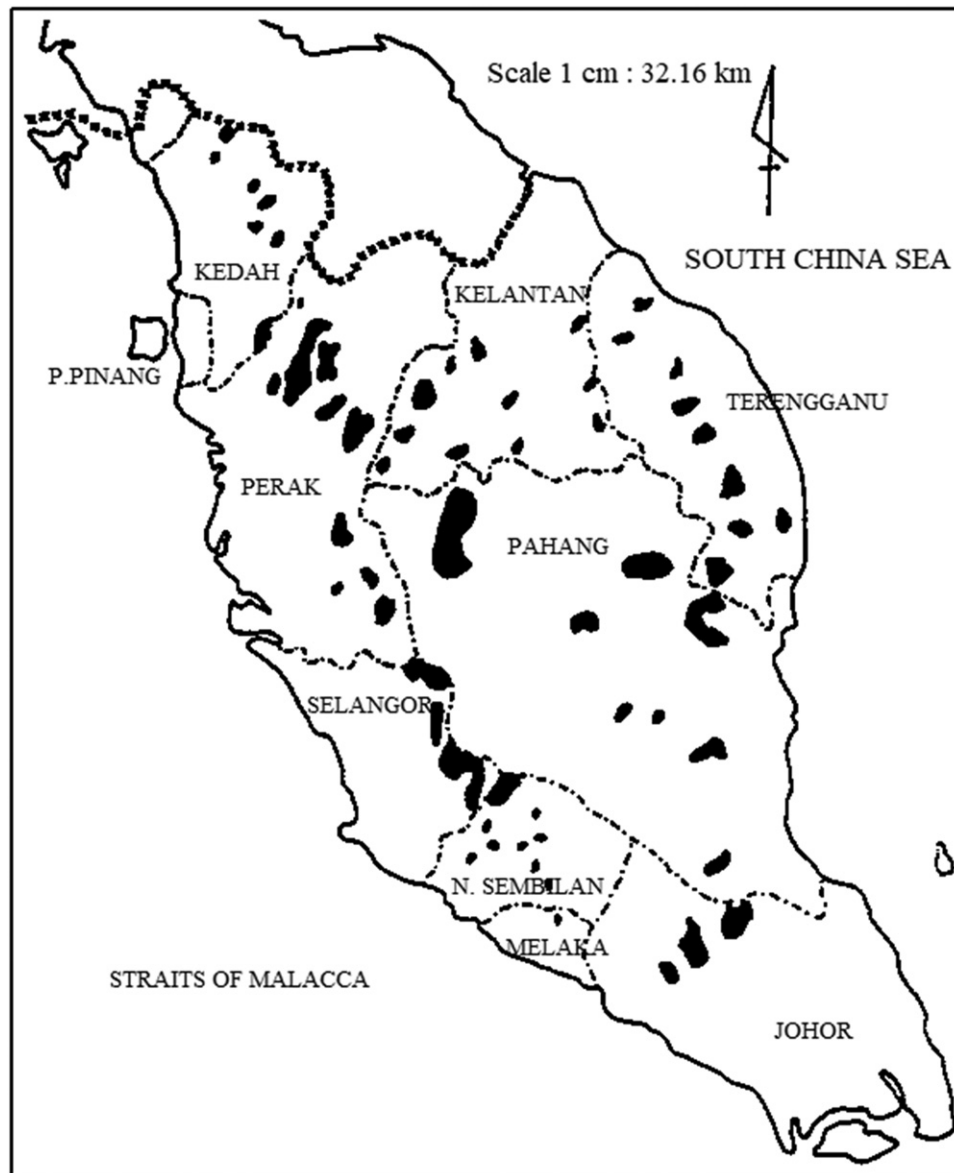


Fig. 1 Bamboo forest distribution in Peninsular Malaysia. Reproduced from Lockman, M.S., Shahwahid, H.O.M., Poh, L.Y., Saroni, J., 1992. Distribution of bamboo and the potential development of the bamboo industry. In: Proceedings of the National Bamboo Seminar I. Towards the Management, Conservation, Marketing and Utilization of Bamboos, pp. 6–19. Kepong, Kuala Lumpur, Malaysia: FRIM.

- *Gigantochloa scortechinii* – A bamboo species found in Indonesia, central and northern Peninsular Malaysia, as well as southern Thailand. Can erect up to 70 ft tall and have a diameter within the range of 5–8 in. at maturity.
- *Phyllostachys bambusoides* – This is also a giant timber bamboo originating from China that can grow up to approximately 70 ft tall and around 5 in. in diameter.

Anatomy of Bamboo

Since bamboo is a very versatile plant, all parts of the plant can be utilized fully as depicted in Fig. 2 (Correal, 2016). The two main anatomy structures of bamboo are culms and rhizomes. Culms are the parts of bamboo above ground. For construction materials purpose, culms are usually the one that are taken. Along the culm of bamboos, it is separated by solid transverse diaphragms called nodes (Fig. 3). Typically, the length of internodes increases along most of the culm height, and decreases as it reaches the top of the culm (Amada *et al.*, 1996). The cortex of the bamboo culm generally contains shorter cork, axially elongated cells, silica cells, and stomata. The cells in the internodes are composed of approximately 50% parenchyma, 40% fibers and 10% conducting tissue (Liese, 1985).

Table 2 Distribution percentage of bamboo species in Peninsular Malaysia

State	Districts	Compartment areas		Stock		Species
		Hectares	(%)	No. of culms	(%)	
Johor	North	27 615.51	86.78	4 142,340	84.86	<i>S. zollingeri</i>
	East	4205.25	13.22	739,260	15.14	<i>B. heterostachya</i>
	South	0.00	0.00	0.00	0.00	
	Center	0.00	0.00	0.00	0.00	
Kedah	South	13,585.85	64.99	2,967,150	46.32	<i>D. asper</i>
	Center	4 834.00	23.13	2,358,900	36.82	<i>G. scortechinii</i> , <i>S. grande</i>
	North	2 482.70	11.88	1,079,850	16.86	
Kelantan	South	58 489.00	64.45	20,990,850	67.64	<i>G. scortechinii</i> , <i>S. grande</i>
	East	26 470.00	29.17	6,655,200	21.44	<i>G. species</i> , <i>D. pendulus</i>
	West	5 788.00	6.38	3,389,800	10.92	
Melaka	Jasin	563.37	100.00	249,750	100.00	<i>D. asper</i>
Negeri Sembilan	West	20 930.25	86.19	5,993 910	80.83	<i>D. sinuatus</i> , <i>S. zollingeri</i>
	East	3 353.97	13.81	1,421 550	19.17	<i>D. sinuatus</i> , <i>S. zollingeri</i>
Pahang	Kuala Lipis	88,814.8	73.79	15,684,210	66.80	<i>S. brachycladum</i> , <i>S. gracile</i>
	Kuantan	9 485.00	7.88	2,456 730	10.46	
	Rampin	5 342.29	4.44	2,288 130	9.75	<i>B. vulgaris</i>
	Jerantut	12 112.12	10.06	1,986 540	8.46	<i>S. brachycladum</i> , <i>S. gracile</i>
	Temerloh	1664.72	1.38	622,860	2.65	<i>D. asper</i> , <i>B. ridleyi</i>
	Bentong	2 948.67	2.45	442,290	1.88	
	Ulu Gerik	40 045.40	59.16	12,206,550	60.50	<i>B. vulgaris</i> , <i>S. grande</i>
Perak	Kuala Kangsar	10 676.90	15.78	2,703,000	13.40	<i>B. vulgaris</i> , <i>G. wrayi</i>
	Kinta/Manjung	5 297.45	7.83	2,383,860	11.82	<i>B. vulgaris</i> , <i>S. zollingeri</i>
	Larut/Matang	5 481.00	8.10	1,492,050	7.40	<i>D. scandens</i>
	South	6 179.74	9.13	1,388,700	6.88	<i>S. grande</i> , <i>G. scortechinii</i>
Perlis		0.00	0.00	0.00	0.00	
Pulau Pinang		2 739.00	100.00	1,096,950	100.00	<i>S. zollingeri</i> , <i>B. arundinacea</i>
Selangor	Hulu Selangor	12 193.36	30.76	7,563,510	61.01	<i>G. scortechinii</i> , <i>D. asper</i>
	Center	27 448.00	69.24	4,833,900	38.99	<i>B. vulgaris</i>
	Pantai Kelang	0.00	0.00	0.00	0.00	
Terengganu	South	13 015.00	56.62	1,952,250	56.65	
	West	8 060.00	35.08	1,209,000	35.08	<i>G. scortechinii</i> , <i>D. asper</i>
	North	1 901.00	8.27	285,150	8.27	<i>D. sinuatus</i>
Wilayah Persekutuan		0.00	0.00	0.00	0.00	
Peninsular Malaysia (Total)		421,722.38	100.00	110,584,140	100.00	

Note: Lockman, M.S., Shahwahid, H.O.M., Poh, L.Y., Saroni, J., 1992. Distribution of bamboo and the potential development of the bamboo industry. In: Proceedings of the National Bamboo Seminar I. Towards the Management, Conservation, Marketing and Utilization of Bamboos, pp. 6–19. Kepong, Kuala Lumpur, Malaysia: FRIM.

Bamboo is a functionally graded material which has evolved naturally to resist the primary loading, i.e., the lateral wind loading and its own weight. This can be justified as the fibers density increases from the inside wall to the outside wall of the bamboo culm. Besides, in some species (e.g., *Bambusa blumeana*), the bamboo culm has the thickest culm wall at the base and decreases with height up along the culm. This shows the natural inherence of bamboo in gravity load reduction while maintaining the resistance for lateral wind loading (Richard, 2013). Although the fiber amount reduces from bottom to the top of bamboo culm, the bamboo fiber density does increase with height due to the tapering of bamboo culms from base to top. It was known that the ratio of fiber length to width lies between 150 and 250. This ratio varies with the species and location along the bamboo culm (Liese, 1985).

The performance of bamboo is highly related to its structure and fiber orientation. At the macro level the bamboo culm can be seen as a typical unidirectional reinforced composite with the fibers as the reinforcing phase and the supporting tissue (parenchyma) as the matrix material. On the other hand, at the meso-level, it can be seen in the cross-section of the bamboo culm wall that the fiber bundles that form a protecting sheath around the vascular bundles are distributed densely in the outer region of the wall, sparsely in the inner region, and are more concentrated in the upper part of the culm compared to the base (Osorio et al., 2018; Liese, 1998). Similar to other natural fibers, bamboo fiber is a bundle of elementary fibers bonded together by the middle lamellae (Fig. 4). Each elementary bamboo fiber wall possesses a unique multilayer configuration called polylamellate structure which contributes to the strength and modulus of the bamboo culm (Osorio et al., 2018; Liese, 1998). It is also worth noticing that the proportion of lumen tends to be higher towards the fiber bundle periphery (Fig. 4(a)). Hence, in processes involving extraction of bamboo fibers, it is desirable to remove these peripheral elementary fibers because the presence of big lumens may lead to voids in the final composite (Osorio et al., 2018).

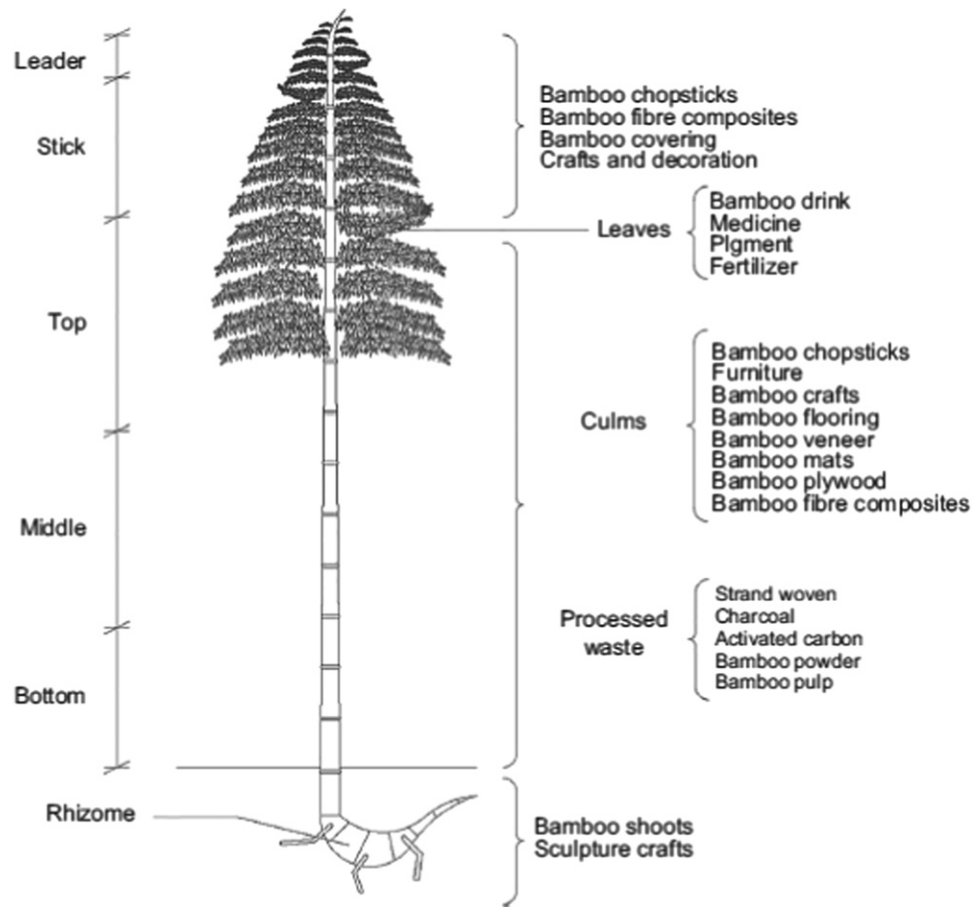


Fig. 2 Parts of bamboo and its utilization. Reproduced from Correal, J.F., 2016. Bamboo design and construction. In: Harries, K.A., Harma, B., (Eds.), Nonconventional and Vernacular Construction Materials. Woodhead Publishing.

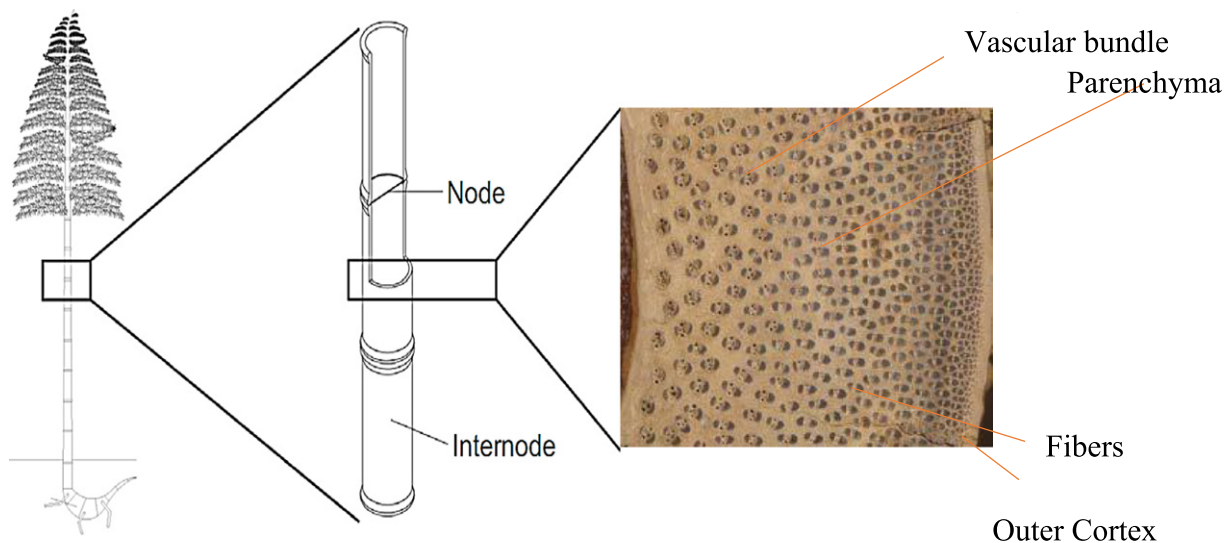


Fig. 3 Structure of the bamboo culm. Reproduced from Correal, J.F., 2016. Bamboo design and construction. In: Harries, K.A., Harma, B. (Eds.), Nonconventional and Vernacular Construction Materials. Woodhead Publishing. Richard, M.J., 2013. Assessing the Performance of Bamboo Structural Components. University of Pittsburgh.

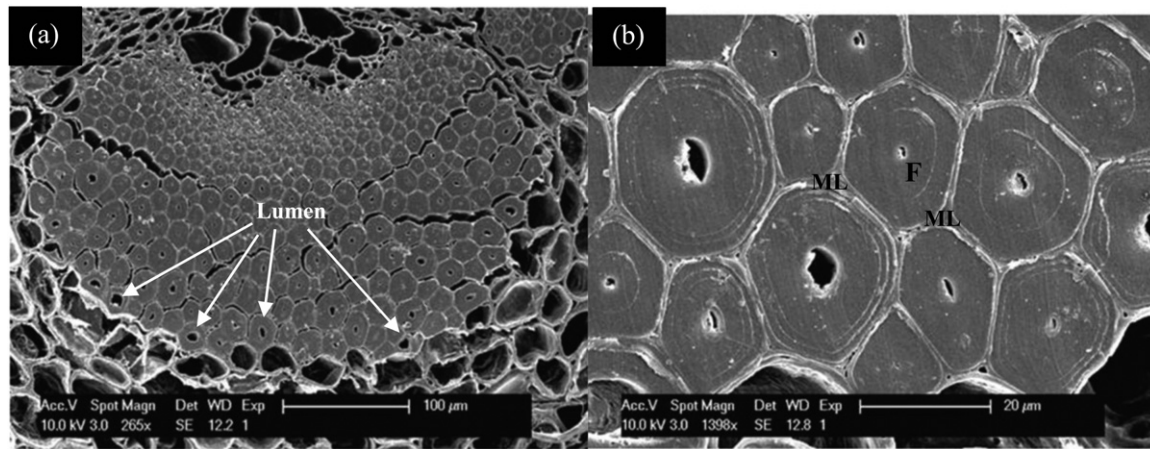


Fig. 4 (a) Bamboo fiber bundle, (b) Elementary bamboo fibers (F) bonded by middle lamellae (ML). Reproduced from Osorio, L., Trujillo, E., Lens, F., *et al.*, 2018. In-depth study of the microstructure of bamboo fibers and their relation to the mechanical properties. *Journal of Reinforced Plastics and Composites* 37, 1099–1113.

Mechanical Properties of Bamboo

It is a well-known fact that bamboo is one of the natural resources that has outstanding mechanical properties. This is attributed to the cellulose which is the main constituent in bamboo. It has also been discovered that bamboo can perform well in buckling due to the high energy absorption at the joints which created much lower stresses compared to steel. Therefore, the failure of bamboo at seismic zone is very rare.

Tensile strength

It has been experimentally proven that some species of bamboo can have an ultimate tensile strength comparable to mild steel, which falls within the range of 140–280 MPa (Patil and Mutkekar, 2014). Since the bamboo is a functionally graded material, tensile tests are usually conducted on cut-out strips at different locations along the height. From the work done by Amada *et al.* (1996,1997) on two years old *Phyllostachys edulis* Riv. (Mouso bamboo), it was found that the tensile strength obtained is within 140–230 MPa, which was much higher than that of common woods such as fir, pine, and spruce (~30–50 MPa). The strength of the inner bamboo region is found to be 80 MPa and increases parabolically with radial distance. Assuming that the mixture principle of composites can be applied to the bamboo culms, the extrapolated data shows that the tensile strength of vascular bundle can be 610 MPa which is around 12 times higher than the lignin matrix tensile strength (50 MPa) (Amada *et al.*, 1997, 1996).

As compared to the internodes of bamboo culm, bamboo nodes exhibit rather more isotropic behavior due to their entangled fibers. Nevertheless, lower tensile strength also recorded in this region (Amada *et al.*, 1997). It is also worth noticing that bamboos have rather weak tensile resistance at directions perpendicular to the fiber arrangement. When tension force is exerted in the transverse direction, the only element that acts to resist the tensile stress is the lignin matrix. This corresponds to splitting and cracking failures. According to Arce (1993), bamboo has shown to fail at a specific transverse strain of about 0.001. This value should therefore be used as a limiting criterion in the structural design. Besides, this value can also be correlated to bamboo's longitudinal direction performance since bamboo was known to have a stable Poisson's ratio of around 0.3 (Janssen, 1981).

All in all, bamboo is able to withstand more tension than compression. As the bamboo fibers run axially and its outer zone are densified with highly elastic vascular bundles, it has a relatively high tensile strength. The tensile strength of these fibers is comparable or even higher than that of steel, but it should be noted that it is rarely possible to construct connections which is able to transfer this high tensile strength (Patil and Mutkekar, 2014).

Compressive strength

The full-culm bamboo's compressive strength has been studied by many authors. Chung and Yu (2002) has studied the variation of compressive capacity against different physical properties of the bamboo culms for two species. For *Bambusa Pervariabilis* (Kao Jue), the compression capacity is found to be at its maximum of about 60 kN at the bottom of the culm, and reduced steadily to about 30 kN at the top. While for *Phyllostachys Pubescens* (Mao Jue), the compressive capacity is reduced steadily from 100 kN at the bottom to 50 kN at the top of the bamboo culm. When the bamboo is tested in wet condition or with high moisture content, it is prone to fail in the end-bearing mode (Fig. 5(a)). On the other hand, if the bamboo is tested in dried condition or with low moisture content, it will usually fail in the splitting mode as the cracks occur along the bamboo's fiber (Fig. 5(b)) (Chung and Yu, 2002). Janssen (2000) suggested that the ultimate compressive stress of air-dry bamboo can be estimated using Eq. (1).

$$f_c = 0.094\rho_{air-dry} \quad (1)$$

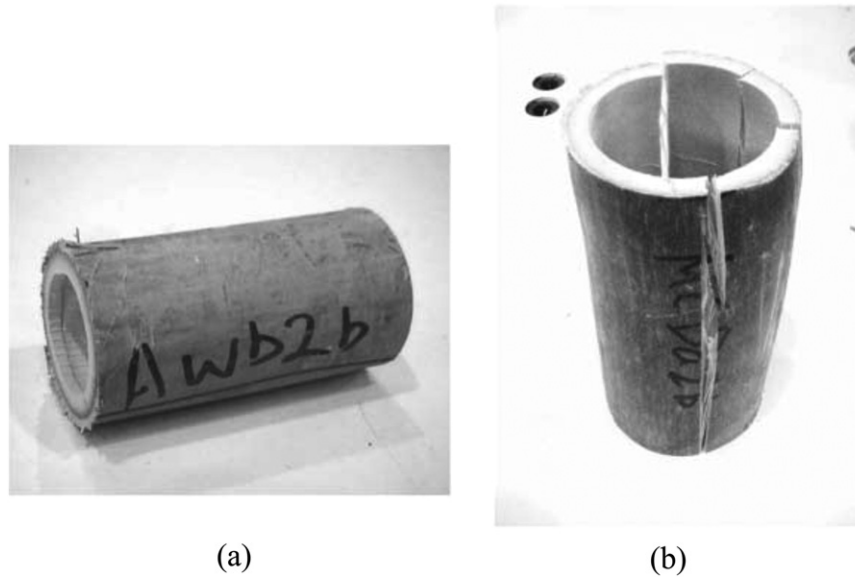


Fig. 5 Post-compression test images of bamboo with (a) end-bearing and (b) splitting failure mode. Reproduced from Chung, K.F., Yu, W.K., 2002. Mechanical properties of structural bamboo for bamboo scaffoldings. *Engineering Structures* 24, 429–442.

where f_c = ultimate compressive stress (MPa).

$\rho_{\text{air-dry}}$ = density of air-dry bamboo (kg/m^3).

Arce (1993) states that under compression test, lignin plays a significant role in bamboo failure as critical tangential strains was induced by the tangential expansive forces. For a typical compression test, the specimens are usually bulge laterally (like a wooden barrel) and develop vertical cracks. During the experiment, as the friction loading plates with the specimen together can affect the corresponding compressive strength value. For more accurate compressive strength data collection, it is suggested that friction-free loading plates should be used during the testing.

Elastic modulus

Bamboos with high elastic modulus is claimed to be of high quality. The high elasticity of bamboo is advantageous to be applied as building materials, especially in earthquake-prone areas (Patil and Mutkekar, 2014). There is a worldwide call for the use of better and sustainable building materials to rebuild safely and cost-effectively in post-disaster reconstruction programs, and one of the materials suggested is bamboo.

Generally, the Young's modulus against compression loading of bamboo is observed to vary steadily from 5 to 35 GPa from the base to the top of the culms. Research has been done on developing equations to account for the relationship between bamboo fibers number and its gradation with the bamboo elastic modulus. Janssen (2000) has reported that for the same volume of fibers, the functional gradation of bamboo fibers across the cross section has contributed to the 10% increase in stiffness. The densification of strong fibers in the outer parts of bamboo tube wall has a positive impact on the elastic modulus. Since the elastic modulus for cellulose is about 70 GPa and by assuming a bamboo fiber is of 50% cellulose, thus the apparent or effective modulus, E is approximated to 35 GPa. This value is then multiplied by the fibers percentage in the inner and outer layers of the culm (Janssen, 2000). Another way is to determine the bamboo fibers volume fraction across the wall thickness. The modulus of elasticity is then determined by the rule of mixtures (Amada *et al.*, 1996; Ghavami, 2008).

Flexural strength

For air-dry bamboo, the ultimate bending stress was estimated by Janssen (2000) using Eq. (2).

$$f_b = 0.14\rho_{\text{air-dry}} \quad (2)$$

where f_b = ultimate bending stress (MPa).

$\rho_{\text{air-dry}}$ = density of air-dry bamboo (kg/m^3).

Yet, in typical bamboo bending tests, the critical failure mode is not fiber fracture, but the longitudinal splitting of material. This was due to fracture of the weaker lignin which bonds the fibers together as shear in the section overcomes the lignin capacity. A critical transversal strain value of 0.0013 was reported to be the bamboo's bending capacity. Meanwhile, a critical value of 0.00373 for longitudinal strain and 62 MPa for ultimate bending stress are estimated based on the typical test outcome using a modulus of 17 GPa and Poisson's ratio of 0.3 (Janssen, 2000).

Shear strength

As mentioned before, the strength of the lignin matrix is always the bamboo strength restraining factor. Due to hollow cross section, bamboo culm has less cross-sectional area to resist shear compared to timber, despite the fact that bamboo lack of defects such as knots. Since bamboo fibers are unidirectional, bamboo culm has two asymmetric shear planes: one parallel to the fibers and another across the cross section. Hence, for the application of bamboo in construction, shear strength and longitudinal splitting are the important factors to be considered. A critical shear stress value of 2.2 MPa at the neutral axis was estimated by Janssen (2000) while the bamboo culm is in bending mode.

Bamboo as a Building Material

Nowadays, the adoption of bamboo as a structural material has been gaining considerable attention. The society is now emphasizing a lot on the use of green materials in each and every aspect, and the construction sector shall not be excluded as well. This is extremely important because the construction sector has been deemed as one of the prime sectors that contribute to the global carbon dioxide emission. Owing to this, green construction materials are always invented to replace the conventional building material. This is commonly achieved by the inclusion of industrial and agricultural by-products such as into the concrete production. Examples of industrial by-products include slag and fly ash; while agricultural by-products include rice husk and palm oil wastes (fiber, shells, clinker, fuel ashes). Apart from inventing new green materials, the use of natural resources has also gained the attention from the public. It is the new emerging material discussed in this article, bamboo.

In the construction industry, cost is one of the main criteria for material selection. Bamboo can be classified as an economic building material due to its high productivity rate and short cycle of harvest compared to other naturally growing resources. This was justified by researchers as that if structural bamboo plants were planted today, in about 3–4 years later mature clumps of bamboo plants will be available, and within 8 years, sufficient mature materials would be available to set up a low cost and reliable structure (Richard, 2013). Besides, the high tensile strength and excellent weight to strength ratio of bamboo are the prominent characteristic for it to be considered as potential building materials. The excellent weight to strength ratio enables it to be used as a high resilient material against dynamic forces created by earthquakes and high velocity winds. Furthermore, with these characteristic features, it is able to withstand up to 3656 kg/cm² of pressure.

When it comes to real life application of bamboo as building materials, the main concern would be the natural durability of bamboo. Bamboos generally have low natural durability (1–3 years) because they are prone to being attacked by fungi and insects. They are very difficult to be treated by normal preservative methods in dry condition since their outer and to some extent inner membranes are impermeable to liquids (Liese, 1985). However, elements made by bamboo can generally have a durable life of 30–40 years if it was properly treated and industrially processed. The treatment of bamboo will be discussed in detail in Section “Treatment of Bamboo”.

The idea of applying bamboo in construction used to be confined to the rural construction in developing countries, such as houses, school buildings, community buildings and bridges (Amada *et al.*, 1996). This kind of perception has been changed progressively as in modern construction, it has been utilized as reinforcement and shuttering for concrete (Liese, 1985). Due to its inherent superior properties, being biodegradable, regenerating, lightweight, and high tensile strength, bamboo has been used as building material since long time ago. These innumerable qualities are deemed as a treasure property that it should be enhanced and developed as a popular building material. Some main applications of bamboo in structures include:

- Foundation: Pre-treated bamboo poles are directly driven into the ground (Iyer, 2002).
- Roofing: The simplest form of bamboo roofing is bamboo tile roofing, where the culms are split into halves, the diaphragms scooped out and these run full length from eave to ridge (Fig. 6). The first layer of bamboo splits is laid concave side up and the second layer interlocks over the first with convex side up, and the resultant bamboo roof is completely waterproof (Iyer, 2002; Pande and Pandey, 2008).
- Trusses: For the spanning of larger distances such as in public utility buildings like schools, storage areas, commercial buildings, bamboo is utilized as a truss member. It was experimentally proven that bamboo’s strength is on par with timber, where the 4-meter-long span truss was tested with various jointing techniques for connections web-chord (Iyer, 2002; Patil and Mutkekar, 2014).
- Walls, Doors, Windows, Flooring and Ceiling: There are several bamboo wall building techniques developed, such as *Bajareque* wall, bamboo board wall, *Wattle* wall, mat wall, and solid wall. The higher resilience of bamboo culms made them better than conventional timber to be used as floor beams (Iyer, 2002). The use of bamboo as doors, windows and ceiling materials is particularly popular in countries with warm climate because of its low-heat transmission and high insulation properties, providing an energy saving cool interior atmosphere.

Further applications of bamboo which are relevant to construction encompass its use as scaffolding and water piping. Hong Kong is well known as the country that is widely using bamboo scaffoldings in construction, including the construction of skyscrapers (Fig. 7). It takes only about a day to put up a 1000 ft tall scaffold using bamboo and Hong Kong uses up about 5 million bamboo rods, each 7-meter-long, every year. Bamboo rods are advantageous over iron rods because they are cheaper, faster to build, and easier to transport. Despite their appearance, bamboo rods are actually safer, as they are much lighter than iron rods and cause less damage if they fall.



Fig. 6 Bamboo tile roofing. Reproduced from Iyer, S., 2002. Guidelines for Building Bamboo-Reinforced Masonry in Earthquake-Prone Areas in India. University of Southern California.



Fig. 7 Bamboo scaffolding. Reproduced from Correal, J.F., 2016. Bamboo design and construction. In: Harries, K.A., Harma, B. (Eds.), Nonconventional and Vernacular Construction Materials. Woodhead Publishing.

Advantages of Bamboo as Structural Material

It was known recently there is new wave of trend promoting the use of bamboo as structural material. It was undeniable that bamboo is a remarkable material as it possesses many prominent features which surpass the properties of the usual used materials. There are four main features that makes bamboo an advantageous structural material:

- (1) It is a sustainable material. Besides being a renewable resource, it is also the world's fastest growing woody plants. It grows 3 times faster than most other species and usually only takes 3–6 years to harvest. Therefore, it is believed that the use of bamboos can help in mitigating the pressure of ever-shrinking natural forests and conserve the global environment (Richard, 2013).
- (2) It is an environmental-friendly construction material. Bamboo is a good carbon sequestration agent as it can sequester as much as 12 tons of CO₂ per hectare. Besides, it also generates almost 35% more oxygen than equivalent stands of trees (Osorio *et al.*, 2018). With this feature, it was believed that bamboo can play a role in climate change mitigation and protecting the environment.
- (3) Bamboo is an economical material as it costs lower than most of the construction materials, such as steel. While having comparable strength, less energy is required to harvest and transport bamboos, thus manufacturing costs would be much lower compared to steel. The energy for production of bamboo compared to other building materials is shown in Table 3. It is evident from the data in Table 3 that steel has the highest production energy-to-stress ratio, followed by concrete and wood. Bamboo, on the other hand, has the lowest production energy-to-stress ratio. This shows that bamboo structures are highly energy saving compared to steel structures, with 98% energy saving in terms of production energy-to-stress ratio.
- (4) Bamboo has been proven to have high tensile strength. It is claimed that bamboo has a tensile strength of around 193 MPa, which is on par with the tensile strength of 159 MPa for mild steel (Liese, 1998). This desirable performance of bamboo has

Table 3 Energy for production of different building materials

Material	Energy for production (kg/m ³)	Service stress (N/mm ²)	Production energy-to-stress ratio
Steel	234,000	160	1500
Concrete	1920	8	240
Wood	600	7.5	80
Bamboo	300	10	30

Note: Janssen, J., 1981. Bamboo in Building Structures (PhD). Eindhoven University of Technology.

enabled it to be termed as the “green steel”. The high strength-to-weight ratio of bamboo even allows it to be applied as a high resilient material against the high-speed wind and earthquake force.

Research Development in Structural Bamboo

Bamboo has been used extensively as construction materials but little research was reported. The most significant milestone in the development of bamboo as construction material is the composing of the first bamboo testing standard in 1973 by the Bureau of Indian Standard, IS:6874. Then, the International Network for Bamboo and Rattan (INBAR) was established in 1997 and the gap in knowledge and building codes for bamboo has been filled up gradually. In year 2004, INBAR published several international building codes for bamboo (ISO 22156:2004(E), ISO 22157-1:2004(E)). However, it is presently under revision to account for advances since they were first approved.

As the construction industry is moving towards green, sustainable, and low cost materials, bamboo has gradually gain considerable experimental and literature studies over the recent years. A number of reports described bamboo as a smart natural composite material with optimized distribution of fibers and matrices, not just across cross sections but also along member lengths, in resisting environmental loads in nature (Osorio *et al.*, 2018; Amada *et al.*, 1997). There is also a large amount of data on the mechanical properties of various bamboo species (described in Section “Mechanical Properties of Bamboo”), but the data varies from species to species and in most cases, only typical ranges of values were provided.

Janssen (1981, 2000) has made a huge contribution to the compilation of knowledge on mechanical properties of bamboo in 1981 and 2000. The main conclusions drawn in his work is that the strong points of bamboo are its tension axis, compression axis (parallel to grains), bending, and form of cross section. While the weak points of bamboo are its compression axis (perpendicular to grains) and the shear axis. The recommendations to apply bamboo as construction materials is to design based on the strong points and avoid the weak ones (Janssen, 1981). Chung and Yu (2002) studied the variation of compressive strengths along the culm lengths for two bamboo species, Kao Jue and Mao Jue. Among the physical properties studies in their work, moisture content is found to be the most important factor governing the mechanical properties of bamboo. It is found that the physical and mechanical properties are generally constant along the culm lengths in Kao Jue. However, both the physical and the mechanical properties vary significantly along the culm lengths in Mao Jue, and thus, the non-uniformity should be incorporated when assessing their structural behavior. Amada and Untao (2001) studied the fracture toughness of bamboo by inserting a crack perpendicular to the fibers from the outer surface and carried out tensile tests. The fracture toughness is proportional to the volume fraction of the fibers. It is also found that the average value of fracture toughness is about 56.8 MPa m^{1/2}, which is higher than that of aluminum alloys and far higher than that of other woods (Amada and Untao, 2001).

Laroque (2007) presented a design of a low cost bamboo footbridge considering only structural weights. Examples of connections has been studied herein, which shed light on the absence of an optimum solution to transfer loads from one bamboo cane to another. The most traditional “friction-tight rope” method, appear to remain as the best solutions (Laroque, 2007). The industry calls for further researches to find a truly innovative way of connecting bamboos. In terms of design and construction with bamboo, Correal (2016) concluded that the main issues to be taken into consideration are: using bamboo at a proper mature age, the effect of moisture content on the estimation of mechanical properties, using proper treatment methods for preservation and estimating fire reaction and fire resistance of bamboo structures and assemblies.

Treatment of Bamboo

Durability is always the main concerns for the utilization of bamboo in construction. Although natural durability of bamboo usually depends on the types of species, the service life of untreated bamboo can be generally given as below (Liese, 1980):

- 1–3 years for those in direct contact with soil.
- 4–5 years for those protected from exterior exposure.
- > 15 years under very favorable conditions (e.g., internal framing or rendered).

To improve the durability of bamboo, treatment is a must. By having bamboo preservation or treatment, bamboo service life can be lengthened significantly. Generally, the aim of bamboo preservation is to eliminate the bamboo sugar content and other carbohydrate that attract fungi and insects, thus extending the life span of the bamboo structure (Correal, 2016).

In smaller scale or rural area construction projects, traditional (non-chemical) methods such as clump curing, smoking, white washing, plastering and soaking in water have been used. But in large-scale building projects, chemical methods are more suitable for bamboo preservation. However, with the absence of ray cells which form the radial transportation system that allows easy penetration of liquid through the whole wall thickness, chemical penetration into the bamboo culm tissue is rather difficult compared to wood. Still, there are inventions of safe and effective chemical preservation methods involving the use of chemicals such as boric acid, boron and borax. Open tank for cold soaking, modified Boucherie, pressure and heat treatment are the most commonly used preservation methods against biological attack. There are other preservation methods used, but these methods were scarcely reported thus not discussed in this section.

Open Tank Method

This method is also known as the “leaching bamboo” method. It is a simple soaking method and provides good protection for bamboo culms. The solution gets into the culm by diffusion through the ends and partly through the sides. Investigations carried out on the conditions for open-tank treatment indicate that immature bamboo allows much better penetration through both the outer and the inner skin compared to mature bamboo. This effect may be correlated with the amount of lignification. Both the outer and the inner skin are permeable to some extent to 169 preservatives during long soaking; however, the inner skin is a little more permeable than is the outer. Consequently, split culms can be treated more easily than round ones, and the use of split bamboo could reduce the soaking period by as much as one-half (Liese, 1980). It is also suggested that before the immersion process with or without water-soluble preservative for several days, holes should be drilled across each internode to allow better penetration of chemical solution inside the bamboo cavity. This leaching process can reduce the starch content of bamboo besides providing preservative to the bamboo culms.

Modified Boucherie Method

The Boucherie method has long proven to be effective for freshly harvested bamboo culms. The water-transporting part of the culm can be penetrated completely, and the treatment itself needs only few and cheap installations. In the classical form of the method, the preservative is forced by gravity from a container placed higher than the stem through pipes into the stem base. The higher the vessel is fixed, the faster is the penetration. It is also possible to hang the culm vertically or scratch the inner wall of the top internode so that it acts as a reservoir for treatment (Janssen, 2000).

However, the classical method was then modified or improved by the application of pneumatic pressure (air pump). At the bottom of a container, a small, metal tube is fixed from which several other tubes lead to the ends of bamboo culms. The culms are fastened to the tubes by rubber cuffs. The preservative is forced axially through the culm by an air pressure in the container. Compared to the classical Boucherie method, this modified method reduces the treatment time from several days to only 3–8 h (Liese, 1980). Even a simple hand pump or for commercial scale operation, a centrifugal pump can be used for the purpose. Also, the bamboo culm can be treated with or without branches and leaves.

The solution dripping from the top end at the beginning of the experiment will be mainly sap and subsequently the preservative. The chemical solution residue may be recycled once it is cleaned, and chemical solution is added to achieve the original concentration. The treatment is can be deemed completed as the concentration of the solution at the dripping end is about equally to that of the preservative solution.

The advantage of this treatment method is that the equipment used is low-cost, can be easily built, easy to transport and could be used directly in the forest. Moreover, it can be built in different scales, from a handy equipment to treat a few culms to a permanent plant that treats hundreds of culms per day. Furthermore, this method is one of the best in terms of penetration, distribution and retention.

Pressure Treatment

Pressure treatment is carried out in some countries, both with water-borne preservatives and with creosote. It is one of the best preservative methods for bamboo but is also expensive, and may not be economical for low cost materials like bamboo. It is suitable for bamboo treatment in commercial scale especially for high end applications such as fashionable iconic buildings. It requires specialized equipment (an autoclave) that applies pressure ranging around 0.5–1.5 N/mm². However, this treatment method may only be applied to thick-walled bamboos because culms with thin walls tend to crack under the applied pressure.

Heat Treatment

The properties and durability of bamboos were also known to be improved by heat treatment. Typically, this technique involves the immersion of bamboos in hot oil bath at a temperature range of 160–220°C for two to four hours. Vegetable oils with high boiling points such as palm oil, coconut oil and hemp oil is commonly used for this treatment process. However, some work

reported that there is reduction in strength of bamboos if the heat treatment temperature was not handled appropriately (Manalo and Acda, 2009). This could be the reason where this treatment method is less popular compared to other methods.

Future Directions in Structural Bamboo Research

The main reason that bamboo structures are yet to be accepted by the construction industry lies on the durability of bamboos. Bamboos, which is organic in nature, is highly susceptible to degradation and fungi attacks, especially in tropical countries with hot and humid weather like Malaysia. Treatment methods are available but the protection on actual sized bamboo structures have yet to be fully established. Hence, there is a need for a thorough study comparing the efficiency of treatment methods mentioned in Section "Treatment of Bamboo". Also, actual sized bamboo structures must be erected and the structural integrity must be monitored continuously for 5–20 years. The structural health monitoring data will be useful in convincing the public to accept structural bamboos. Last but not least, the final stage of the structural bamboo research is to collect sufficient data to be modeled into a comprehensive bamboo design standard, with complete guideline in terms of bamboo selection, treatment method, stress designs, connection designs, as well as durability check.

See also: A Comparative Life Cycle Assessment for Utilising Laminated Veneer Bamboo as a Primary Structural Material in High-Rise Residential Buildings. Bamboo Fiber as Fillers for Polypropylene-Nanoclay via Injection Molding. Bamboo Structural Technology. Bamboo Versus Tubular Steel Scaffolding in Construction: Pros and Cons. Constructing a PV-Integrated Permanent Bamboo Building – An Experience. Development of Epoxy Based Composites Using Bamboo and Waste Metal Chips. Development of Self-Adhesive Products Using Only Bamboo Fibers Extracted With a Machining Center. Structural Integrity Assessment of Bamboo for Construction Purposes. Study of Junctions With Bamboo: An Attempt Towards Their Classification. Sustainability and Recycling of Bamboo for Engineering Applications

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Economic Aspects of Fiber Reinforced Polymer Composite Recycling

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Glossary

Biocomposites A composite material formed by a matrix (resin) and a reinforcement of natural fibers.

Bulk molding compound (BMC) Polyester resin/glass fiber premix, for injection or transfer molding, also known as dough molding compound (DMC).

Carbon fiber Reinforcing fiber known for its light weight, high strength and high stiffness.

Composite A material made up of resin and reinforcement (usually fiber).

Fiber reinforced polymer (FRP) A general term for composite materials or parts that consist of a resin matrix that contains reinforcing fibers such as glass or fiber and have greater strength or stiffness than the resin. FRP is most often used to denote glass fiber reinforced polymer.

Fiber A unit of matter of relatively short length, characterized by a high ratio of length to thickness or diameter.

Glass fiber Reinforcing fiber made by drawing molten glass through bushings. The predominant reinforcement for polymer composites, it is known for its good strength, processability and low cost.

Impregnation Saturation of reinforcement with liquid resin.

Polymer A long-chain molecule, consisting of many repeat units.

Recyclates The raw material, collected, taken to and processed in a waste recycling plant or materials recovery

facility which will be used in the manufacturing of new materials.

Recycling The process of converting waste materials into new materials, products and objects.

Reinforcement Key element added to resin (matrix) to provide the required properties; ranges from short fibers and continuous fibers through complex textile forms.

Resin Polymer with indefinite and often high molecular weight and a softening or melting range that exhibits a tendency to flow when subjected to stress. As composite matrices, resins bind together reinforcement fibers.

Scanning electron microscope (SEM) A type of electron microscope that is used to produce enlarged images of a sample by scanning the surface with a focused beam of electrons, like reinforced CFRP samples. When the samples are placed under the microscope, the electrons mix with the constituent atoms within the composite sample. This will produce different signals that contain information about the surface topography and composition of the sample.

Sheet molding compound (SMC) A flat prepreg material, comprising thickened resin, glass fiber and fillers, covered on both sides with polyethylene or nylon film, ready for press-molding.

Thermoplastic A plastic that softens each time it is heated.

Thermoset A plastic that flows and then sets permanently on first heating, as a result of setting up a three-dimensional cross-linked molecular structure, and subsequently will not soften or dissolve.

Introduction

People have the tendency to use resources rather than to reuse or recycle these resources. Recycling has not always been treated as important until recent decades. From building and road construction materials like concrete (Khalid *et al.*, 2017; Letelier *et al.*, 2017; Liu *et al.*, 2013) to composite polymers (Ogi *et al.*, 2007; Wei *et al.*, 2018; Ignatyev *et al.*, 2014), recycling is economically viable. There is an increase in the study of recycling of composite 77 polymers (Knight *et al.*, 2012; Oliveux *et al.*, 2015; Ignatyev *et al.*, 2014), plastic waste (Jaivignesh and Sofi, 2017; Siddique *et al.*, 2008; Rebeiz and Craft, 1995), composite wastes (Halliwell, 2006; Kratz *et al.*, 2017; Meng *et al.*, 2017a,b) and nanocomposites (Hasan *et al.*, 2019). However, there are limitations and issues to recycling composites, particularly the fiber reinforced composites. Historically, the use of composite materials is dated back to about 3000 years ago in ancient Egypt. Natural fiber straws were used as reinforcements to build walls. Over the years, more durable materials were developed and today we have fiber reinforced composites that can also be produced in large scales. In the 1960s, glass fibers were used in large scale production of by mixing glass fibers and very rigid resins. However, in an attempt to save weight of the composite materials, and reduce the cost of composite materials, recycling of composites have been the trend in the past two decades (Brower, 2000; Oliveux *et al.*, 2015; Vieira *et al.*, 2017).

FRPs have great advantages that can be harnessed due to their corrosion resistance and high strength-to-weight ratio (Amaechi *et al.*, 2019a; Xu *et al.*, 2013; Yang *et al.*, 2014; Asmatulu *et al.*, 2014). These materials are applied in offshore applications, automobiles, sports, wind energy, automobiles, and wave energy converters (Zhang *et al.*, 2019; Doyle and Aggidis, 2019; Amaechi *et al.*, 2019b). The need for more sustainable materials led to development in composites. Economically, CFRP composites contribute to the decrease of greenhouse emissions by reduction in fuel consumption as they are used to manufacture



Fig. 1 Wastes from an engineering department workshop showing composite wastes. Courtesy: Lancaster University.

lighter bodies of cars and airplanes. There are also some health, safety, and design requirements during the production of composites generally (Amaechi, 2017; Ye, 2003; Murray, 2018; Job, 2015). According to Hopkins *et al.* (2014), composites are expensive, and the case study of a composite pipe is anticipated to cost approximately £10,000,000 compared with approximately £3,000,000 for the equivalent steel pipe. However, savings arise from the reduction in buoyancy tank size as well as the reduction in the lower riser assembly and upper riser termination assembly sizes. It is anticipated that the biggest cost saving would be as a result of simplifying the installation process as the reeled pipe and the smaller buoyancy tank would require less offshore installation time and smaller installation vessels. That being stated, there is no obvious argument to adopt composites based on cost alone, even with the better performance. The author concluded that the composite pipe cost is comparative to a steel option in the single leg hybrid riser configuration considered.

Currently, there are different classes of composites – Both thermosets and thermoplastics. Due to the need for better mechanical properties of these materials and the need to save some project costs, thus the use of recycled composites. These recycled composites have improved strength properties and other material properties (Wei *et al.*, 2018; Meng *et al.*, 2017a,b; Babafemi *et al.*, 2018). Some of these are due to the fiber orientations been aligned in multidirections and the methods used in manufacturing these recycled composites. The most common method for the recycling of fiber reinforced composites is by pyrolysis. GFRP is mostly considered during recycling because it uses a thermoset resin. Currently, it is not economical to recycle thermoset (CFRP using pyrolysis). Wastes can be generated in factories, workshops, schools, houses and they are collected, sorted, and then recycled. Wastes are generated from manufacturing factories, engineering workshops, scrap yards and all collected for recycling. Figs. 1 and 2 show images of wastes at an Engineering Department workshop and an automotive scrap yard, showing high composite waste materials contents that can be recycled.

Presently, FRP composite recycling has been a current debate in both the composite material industry, and the renewable and sustainable materials industry. This is as a result of the economic impact of the FRP wastes generated from both production and utilization of the FRP material. This is expected, considering the growing demand for more sustainable materials, with regards to the timeline of composite materials, as shown in Fig. 3. The application of FRP composites has risen globally in the production of materials for automobiles, households, airplanes, and in the offshore industry. There is also an increase in the researches on recycling FRP composites. Despite the availability of different types of thermoset composites, there are BMC and SMC readily available. These compounds account for the highest percentage of thermoset composite waste due to their greater applications in different forms. In the automobile industry, the use of BMCs and SMCs has increased to attain lighter cars, which will be more fuel saving.

By definition, reinforced plastics are combinations of polymer resins and reinforcing fibers, including short fibers, cut fibers, chopped fibers, and fabric reinforcement (Osmani and Asokan, 2010; Osmani and Pappu, 2010; Kamaruddin *et al.*, 2017). Generally, FRP composites are known to have increased corrosion resistance, increase strength, improved fire resistance, and are able to form complex shapes, have lighter weight, and ease design due to its functional integration. They can also be made of carbon, glass or fiber, while their matrix can be either thermoset matrix or thermoplastic matrix. Leblanc *et al.* (2015) investigated the recyclability of fiber reinforced thermoplastic composites that are randomly oriented. The authors opined that ROS that have high fiber volume fractions ($> 50\%$) have very high formability and attractive mechanical properties, when compared with long or continuous fiber composites. Thus, these properties help to increase the strength of recycled FRP composites as they have good capabilities in compression molding of complex parts of smaller sizes. Thus, this allows the ease of adjusting the parameters such as tight diameter, wall thickness, and rib. According to Lauzé (2001), the best recycling technique available today is the thermal process called conventional pyrolysis, since it generates recydate



Fig. 2 Wastes from an automotive scrap. Courtesy: Stella Job.

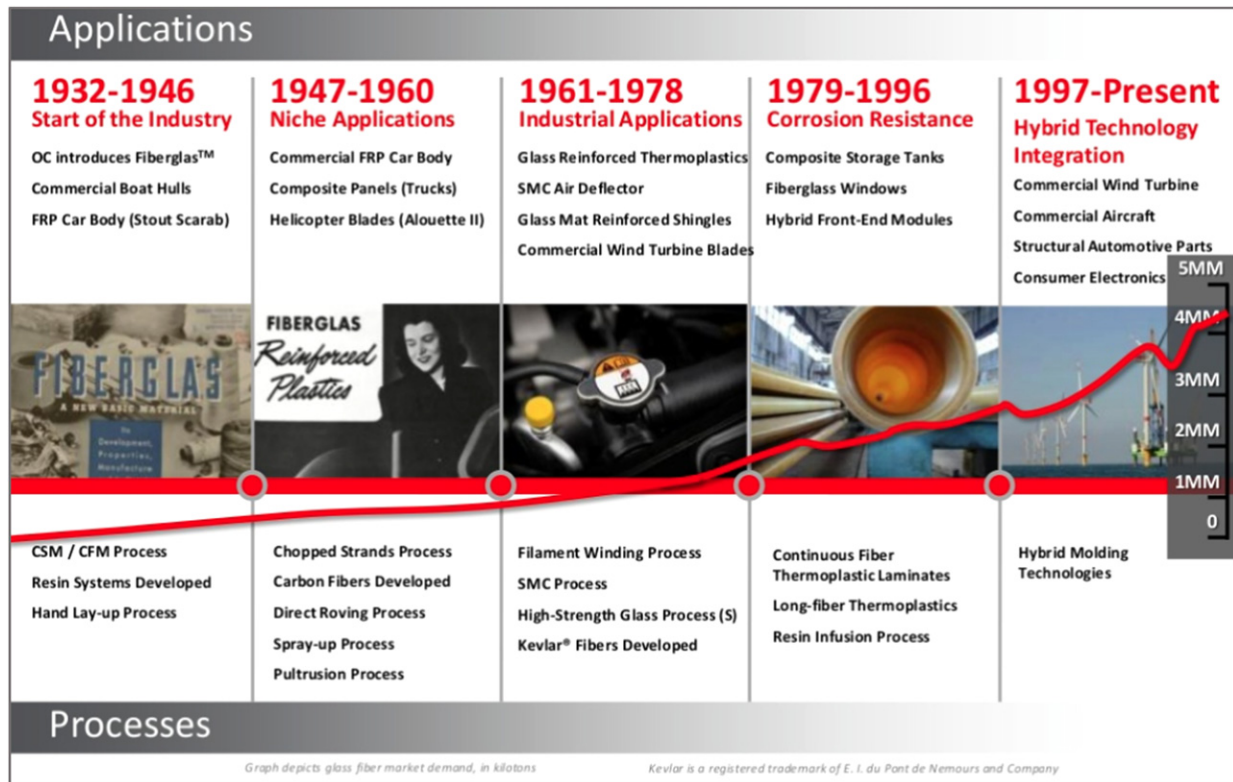


Fig. 3 Timeline on composite applications and processes. Courtesy: Hartman, D., 2014. Advances in reinforcement materials (glass fiber materials). In: Proceedings of the Composites and Advanced Materials Expo (CAMX), October 13-16, 2014, pp. 1-25. Orlando, USA: CAMX.

of excellent quality while being contamination tolerant, highly energy saving, and thus the best option economically. This is quite debatable as the thermal process takes down the fiber molecules and disorientates them. Today, there is no or a restricted deposit (or very few) of carbon fibers from aircraft, at the EOL, as aircraft that integrate such materials are only being constructed at the point and will later become waste (Prinçaud *et al.*, 2014). Connora argues that resin and fiber (e.g., carbon, glass, Kevlar) can be retrieved from epoxy composite goods produced using its Recyclamine hardeners using a “patented, low-energy recycling method.” The parts that are recovered from the epoxy and fiber can be sold, reused, redirected, or repurposed.

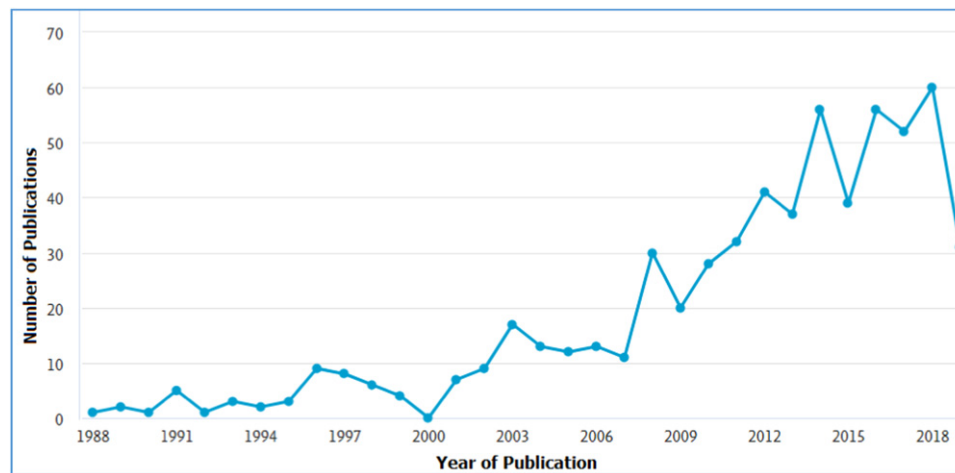


Fig. 4 Number of scientific publications on fiber reinforced polymer composite recycling. Data obtained from SCOPUS database (accessed on 12.06.19).

“X-Ray” on Recycling Fibre Reinforced Polymer Composites

From a thorough search on peer-reviewed literature on FRP composite recycling was carried out. Major article databases and search engines include Google Scholar, Science Direct, Web of Knowledge, and Scopus. The focus was on publications within the recent years with current developments. Results obtained from Scopus are presented in [Fig. 4](#). It shows that there is an increase in research on recycling of composite materials, which rose from 2000 to the current date. In the context of this encyclopedia, we will examine some issues on recycling fiber reinforced polymer (rFRP) composites based on certain popular questions on the subject. These questions will be answered within the body of this article: Can FRP composites be recycled? Why is it difficult to recycle many composite materials like FRP composites? Can epoxy composites be made 100% recyclable? What is the difference between FRP and fiberglass? How can plastics reinforced with carbon fiber be recycled? Is it more environmentally sustainable recycling than producing virgin carbon fibers? Can carbon fibers recycled from aircraft (or from aircraft and automotive waste) mechanically replace most of the carbon fibers presently used in the industrial, recreational, and sports sectors, given that recycling can be accomplished cost-effectively and that recycled fibers will not be used by the aeronautical sector? What is the role of FRP composites in sustainability? What are the economic and environmental benefits of reinforced FRP composites? What are the waste volumes of FRP composites that can be recycled? What are the best methods to collect and recycle these FRP composites? Are there safety and health concerns in saving cost during the recycling of FRP composites? What are the major applications of recycled FRP composites? What are the major issues facing the science of recycled FRP composites?

Global Market on Composite Materials

The increase in the use of composites – particularly recycled composites – has led to more developments in the application of recycled FRP composites. The market for composite products globally is anticipated to achieve an estimated \$40.2 billion by 2024 and from 2019 to 2024 it is anticipated to expand at a compound annual growth rate (CAGR) of 3.3%. It is anticipated that the worldwide market for end product composites will reach an estimated \$114.7 billion by 2024 ([Wood, 2019](#)). There is an increase in the projection for composite market globally including recycled FRP composites. According to another report, the estimated projection is from \$72.58 billion in 2016 to \$115.43 billion by 2022, at a CAGR of 8.13% from the year 2017 to the year 2022 ([Markets and Markets, 2017](#)). This implies that application of different sectors is increasing by harnessing the properties of recycled composites. These properties include increased building capacity, reduced weight, increased sustainability, and increased strength capability. This projection stated was from a survey carried out with most of the top leading composite companies: Victrex (UK), Gurit (Switzerland), SGL Group (Germany), Solvay (Belgium), Hexcel Corporation (U.S.), Owens Corning (U.S.), Toray Industries, Inc. (Japan), Teijin Limited (Japan), etc., against that of different secondary sources, such as such as Factiva, Hoovers, Manta, etc. [Fig. 5](#) shows the use of composites in the following sectors: Automobiles, aerospace, defense, renewable energy, transportation, marine (pipes, risers, and tanks); construction & infrastructure industries. In an earlier publication, the global market forecast was to grow to £75 billion by the year 2015 ([Hinton, 2017](#)).

However, there is a global challenge to bring down greenhouse gas emissions, reduce dependence on fossil fuels, and increase the use of renewable materials. To this end there is a challenge with using composites, considering that EOL management of composites, particularly the disposal and recycling pathways have not been extensively uncovered. According to the Composites Industry Market report, around 1.141 million tons of composite materials for GFRP were produced in Europe in 2018 ([Witten et al., 2018](#)). In the United States, demand for FRP was expected to increase to nearly



Fig. 5 UK market opportunity for composites. Reproduced from Hinton, M., 2017. Bristol composites institute launch and ACCIS 10th anniversary conference. In: Proceedings of the ACCIS 10th Anniversary Conference. Bristol, UK: Bristol University. Available at: [http://www.bris.ac.uk/media-library/sites/composites/documents/Bristol Composites Inst Launch 151117v4.pdf](http://www.bris.ac.uk/media-library/sites/composites/documents/Bristol%20Composites%20Inst%20Launch%20151117v4.pdf).

Table 1 US fiber reinforced polymer composites demand (million pounds)

Items	Year			% Annual growth	
	2007	2012	2017	2007–2012	2012–2017
FRP composite demand	3586	3455	4345	−0.7	4.7
Motor vehicles	864	1025	1380	3.5	6.1
Construction	1071	890	1235	−3.6	6.8
Electrical & electronic	502	550	550	1.8	−
Consumer durables	418	360	405	−2.9	2.4
Others	731	630	775	−2.9	4.2

Abbreviation: FRP, fibre reinforced polymer.

Courtesy: Freedonia, 2017. Fiber Reinforced Plastic Composites Market by Fiber, Product and Market in the US. thirteenth ed., Cleveland: The Freedonia Group. Available at: <https://www.freedoniagroup.com/Fiber-reinforced-Plastic-Composites-Market-In-The-U.S.html>.

2 million tons in 2017 as shown in **Table 1** (Holmes, 2019). In another report by Freedonia (2017), US demand for composites of FRP is projected to increase by 4.7% annually to 4.3 billion pounds in 2017, estimated at nearly \$23 billion, and will increase to 3.9 billion pounds in 2020 at an annual rate of 3.1%. Presently, the demand finally has recovered from the mild decreases encountered during the recession-impacted era 2007–2012, when possibilities were limited by a sharp decline in building activity, decreased output of motor vehicles, and decline in production of FRP boats, yachts, and recreational small ships. **Fig. 5** shows the UK market opportunity as potentially having growth. In composite part production, it potentially increased. According to a study by Lucintel LLC, there is an increase in the global market for composite products and this is expected to reach \$96 billion by the year 2020, following an increase of 40% as seen from the year 2014 as shown in **Figs. 6** and **7**. The case study of the UK Composite Market shows that there are opportunities available in UK for composites, particularly the recycled FRP composites.

In another study, it was revealed that the annual output of GFRP was approximately 55,000 t in the United Kingdom alone, with an anticipated annual manufacturing increase of 10% in 2010 (Yazdanbakhsh and Bank, 2014). Most of the production and EOL waste in the UK is landfilled, and up to 90% of the GFRP waste is landfilled (Brown *et al.*, 2018; Osmani and Asokan, 2010; Yazdanbakhsh and Bank, 2014). Different researches have been carried out using recycled composites and cement. In an attempt to improve quality of building materials, different composite and recycled debris have been introduced into concrete (Li and Kaewunruen, 2019; Ge *et al.*, 2011; Yin *et al.*, 2013).

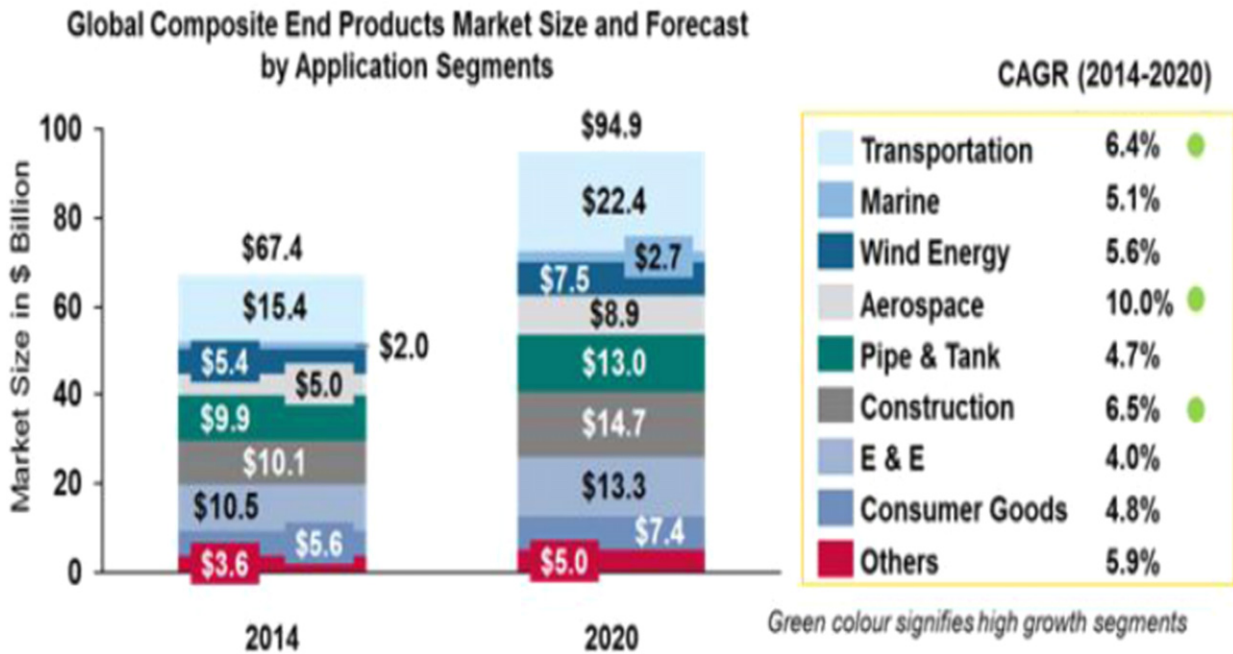


Fig. 6 Global composite end products market size and forecast by application segments. Courtesy of Lucintel LLC.

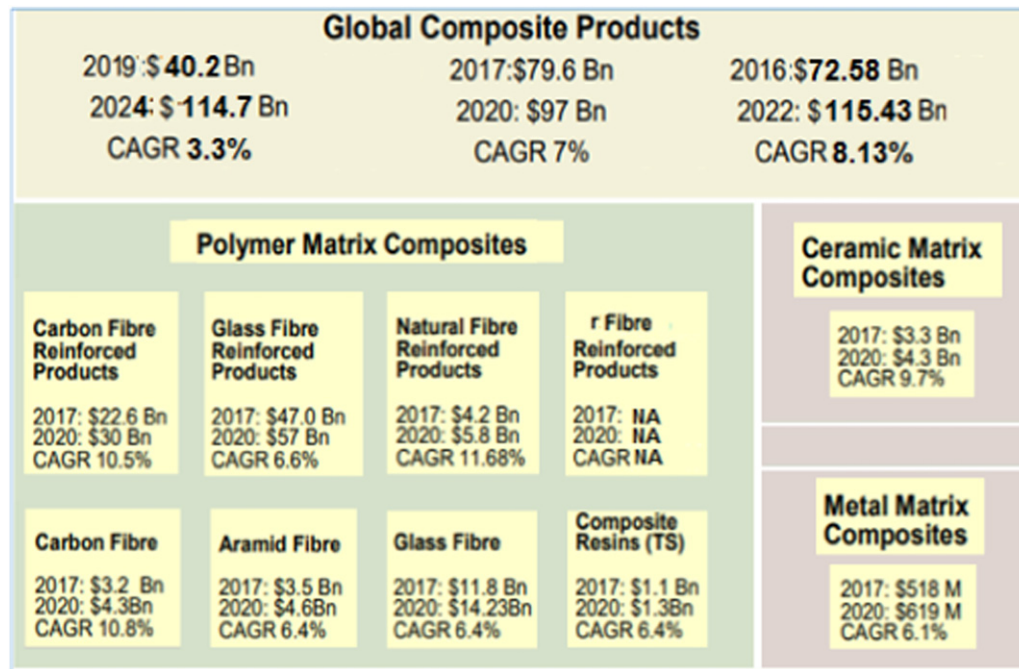


Fig. 7 Global composite products. *Source:* Markets and Markets, 2017. Composites Market by Fiber Type (Glass, Carbon), Resin Type (Thermoset, Thermoplastic), Manufacturing Process (Layup, Filament Winding, Pultrusion), Application (Transportation, Aerospace & Defense, Wind Energy), Region – Global Forecast to 2022, UK. Available at: <https://www.marketsandmarkets.com/Market-Reports/composite-market-200051282.html>.

Characteristics of Recycled Fibre Reinforced Polymer Composites

The characteristic behavior of recycled FRP composites has shown that the main properties of composites are exhibited, as in Fig. 7. Further studies on the and behavior under increasing temperature, and the wave scattering properties as carried out by Yin *et al.* (2013).

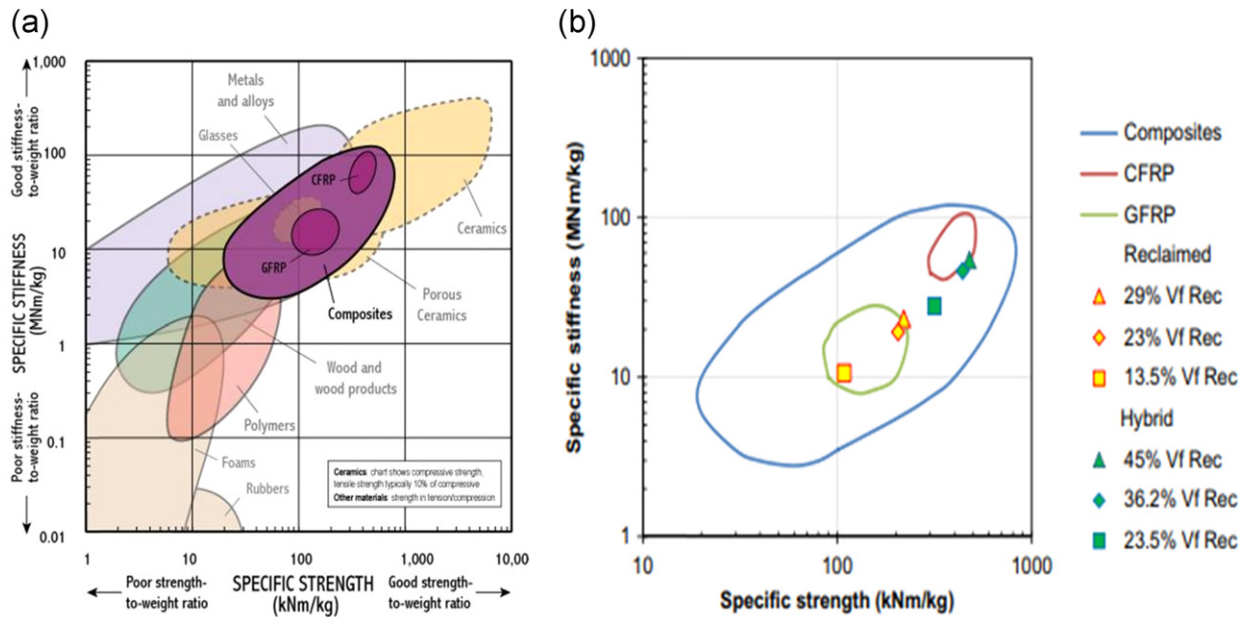


Fig. 8 Specific stiffness and specific strength of fiber reinforced polymer composites against: (a) other materials (b) reclaimed and hybrid carbon fiber laminates. Courtesy: (a) Ashby, M., Shercliff, H., Cebon, D., 2007. *Materials: Engineering, Science, Processing and Design*, first ed., Oxford: Butterworth Heinemann. (b) Kratz, J., Low, Y.S., Fox, B., 2017. Resource-friendly carbon fiber composites: Combining production waste with virgin feedstock. *Advanced Manufacturing: Polymer and Composites Science* 3 (4) 121–129. doi:10.1080/20550340.2017.1379257. University of Cambridge, 2011. Specific stiffness – Specific strength. University of Cambridge – Materials Group Interactive Charts, pp. 1–2. Available at: http://www-materials.eng.cam.ac.uk/mpsite/interactive_charts/spec-spec/basic.html (accessed 08.06.19).

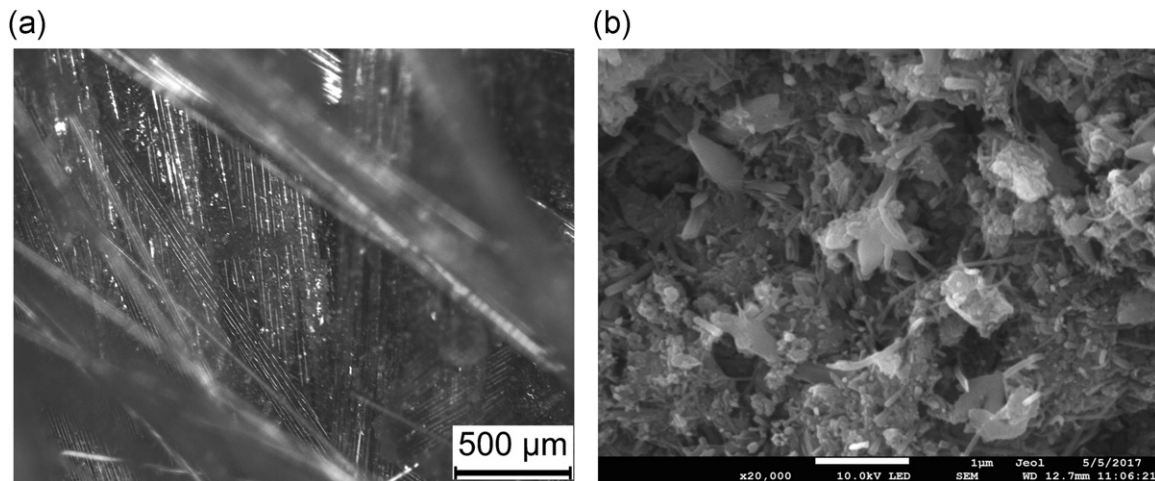


Fig. 9 Images of fibers of composites taken under scanning electron microscope, for (a) glass fiber specimen, and (b) composite using beetroot on cement.

Images of composite fibers and composite specimens with beetroot taken under the SEM show the characterization of the fibers (Hasan *et al.*, 2019) and could be used in bioengineering the recycled composites and biocomposites, as presented in Figs. 8 and 9.

Review on Recycling Pathways and Technologies

Due to the advantages of FRP recycling, it is pertinent to identify recycling pathways for recycling composites. Fig. 10 is used to show the steps that are undertaken in carbon fiber recycling. From collection to combustion with the resin all involves some energy and depends on the type of recycling process considered. A flow chart of a polymer composite waste management process is



Fig. 10 Steps (a)–(i) involved in the carbon fiber recycling process. Courtesy: ELG Carbon Fibre, 2017. Why Recycle Steel? Coseley, West Midlands, UK. Available at: <https://www.recycle-more.co.uk/why-recycle/why-recycle-steel->.

presented in **Fig. 11**. It was developed using the concept by [Rebeiz and Craft \(1995\)](#) on plastic waste management. Energy can actually be saved through recycling. Different researches on the recycling pathways have been carried out on FRP composites ([Yang et al., 2012](#); [Vo Dong et al., 2015, 2018](#)), however the crunch of it requires funding support, collaborations, and monetization of the recycling concepts.

Issues on Commercializing Recycled Fibre Reinforced Polymer

There have been different projects carried out globally on recycling FRP. Reports have also been presented on different viable options and techniques used in recycling, reclaiming, and reusing the recycled fiber reinforced carbon fibers in different products. Despite these breakthroughs, there are challenges facing these rFRP composites. Bringing both these recycling processes and the recycled products to the composite market has been difficult. **Fig. 12** shows the economic advantage of recycled composites from materials to products. During the economic recession in 2009, there was a big hit on many manufacturers, particularly in the composites industry. Due to the economic downturn that occurred, most of these manufacturers now try to keep their companies by just simply having business survival and less on sustainability. However, over these past 10 years, there has been a shift of interest to sustainability and the use of recycled materials in the composites industry and other industries. There is also an increase into the growth phase and the attention to recycling has been heated up.

To overcome these challenges, there is need to carry out more extensive tests that are economically costly but will assist in the development of standards for these products to be qualified and accepted as products with the recycled contents. To this end, there are still issues with the waste volumes generated per location, management of the waste volume to ensure there is constant supply of waste, provenance, and the amount of money that these waste will cost and the debate about companies' willingness to pay for these wastes. They are other issues with health and safety of rFRP composites, the most effective waste management system to adopt for recycled fiber reinforced composites, the requirements for waste management licenses, having a comprehensive understanding of the requirements for the health and safety of rFRP composites and the relate new processes involved in the recycling, the time for adoption of these new processes in the composites industry. Despite that all these are time consuming, it is important to get the required investment needed or the right niche company that can use the raw materials and obtain good finished products, although the recycled finished product may have low profit marginally ([Job et al., 2016](#)). There is also the issue of not having enough trained personnel on recycling of composites, as not many composites manufacturers are keen on recycled composites.

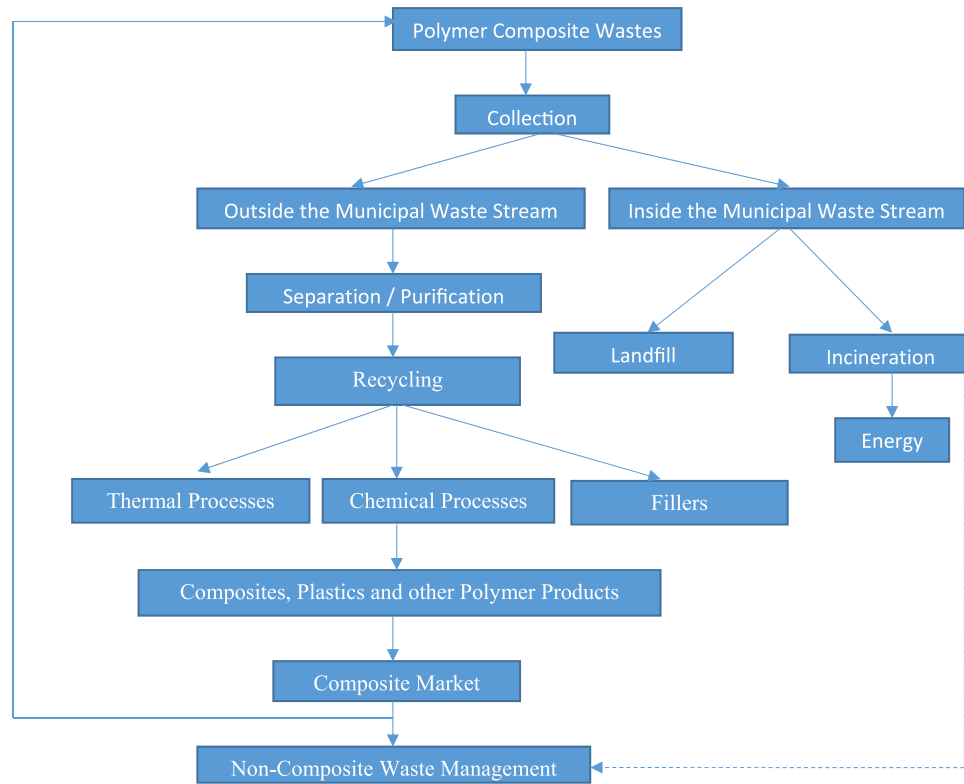


Fig. 11 Flow chart of a polymer composite waste management process.

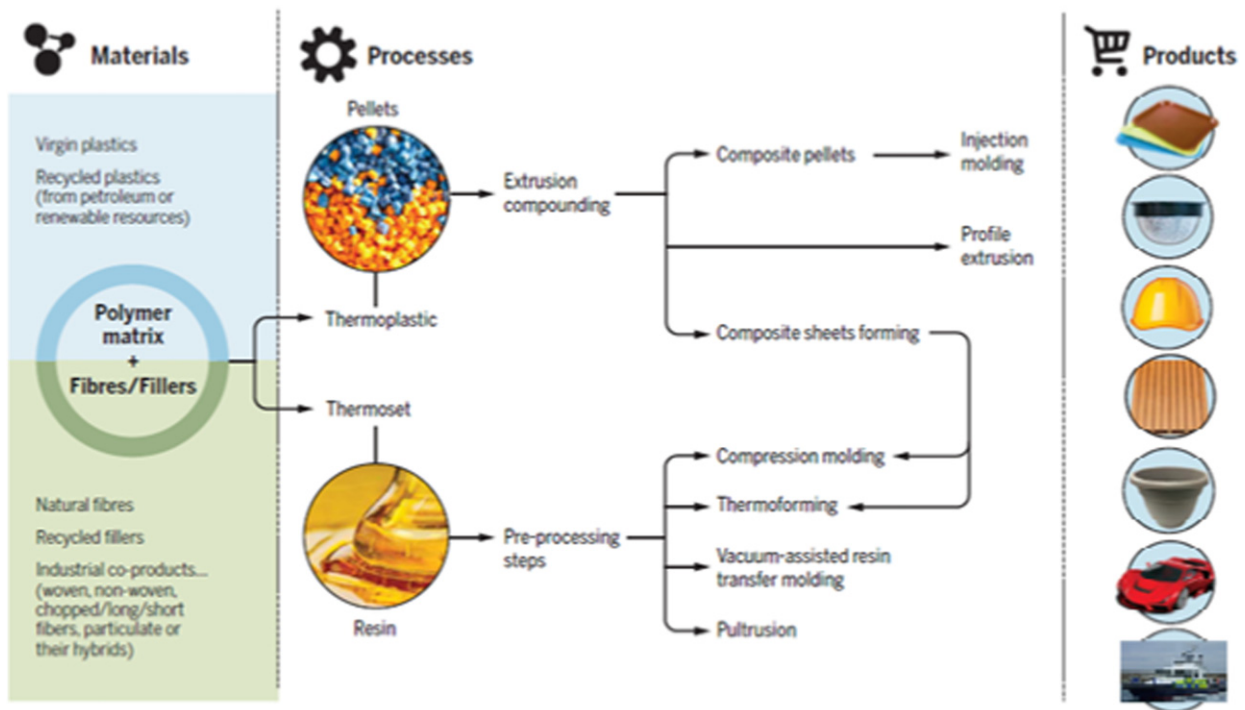


Fig. 12 Economic advantage of recycled composites from materials to products.

GFRP are seen to be recycled in cement kilns, reclaimed from landfills and mechanically recycled. The FRP wastes have economic value in energy recovery. Normally, energy is recovered from the resin, which is the mineral feedstock for cement (from the fibers and fillers). As a result of them been reinforcing fibers, they also determine the magnitude of reclamation or recycling of that will be achieved. To that note, different disposal options will have to be considered. The major disposal routes for reinforced FRP composites are landfills, mechanical recycling, cement kilns, and EfW. With respect to the EU Waste Framework Directive, it is pertinent to state that not all disposal options currently meet the requirements. The EfW incinerator bottom ash does not meet the requirements of recycling with respect to this Directive. However, both the cement kiln and the EfW are considered recycling routes that are also used in energy recovery, because the mineral content can be recycled into clinker and aggregate, respectively (Brown *et al.*, 2018). The cost of disposing the FRP wastes using landfills, cement kilns, and EfW are comparatively around the rate of £140 per t, because the waste management businesses almost have the same charge for the composites wastes, without regard to the route of disposal. In the UK, the capacity of EfW is increasing currently. With respect to this increase, the cost charged on EfW should potentially reduce as older plants have already made returns on investments and covered the capitals costs, maintenance costs, and running costs.

On the other hand, there has also been an increase in the commercialization of recycled CFRP. This increase in progression is actually in an order of magnitude been of more value than glass fiber. In addition, some large aerospace primes encourage carbon fiber recycling initiatives while an equivalent encouragement for GFRP has never been attained. In the UK, carbon fiber recycling using pyrolysis processes was first established by Milled Carbon in the West Midlands, now known as ELG Carbon Fiber since it was purchased by ELG Haniel in 2011. Currently, carbon fiber recycling based on pyrolysis is active in USA, Germany, Italy, and Japan. In the UK, recycling of glass reinforced polymer (GRP) composites is done at a very low scale, which is basically in-house activity production volume (Job *et al.*, 2016). In January 2019, ELG and Boeing formed the first material supply relationship between a carbon fiber recycler and major aircraft original equipment manufacturer. This kind of collaboration means that recycled FRP composites can be deployed in the aviation industry.

Issues on Supply Chain of Recycled Fibre Reinforced Polymer

The global demand for carbon fiber is estimated to more than double to be between 150,000 t and 180,000 t by 2020. With the manufacturing techniques used today, there is approximately 30% of the overall demand for carbon fiber becoming waste both during the conversion phase and component manufacturing phase of the recyclates. The remaining fiber is added into the finished parts, which will be disposed of later at the EOL. With the increase in the application of CFRP composites in components with shorter service lives, the EOL will range between 2 and 40 years, depending on the frequency of its usage (ELG Carbon Fibre, 2017). Fig. 13 shows a

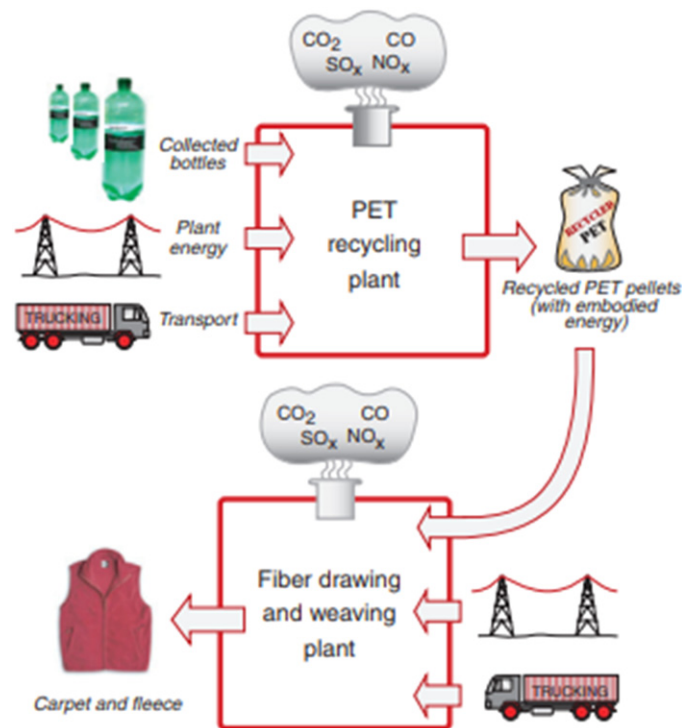


Fig. 13 Input-output sketch for the recycling process used to recover polyethylene terephthalate. Source: Ashby, M., Shercliff, H., Cebon, D., 2007. Materials: Engineering, Science, Processing and Design. first ed., Oxford: Butterworth Heinemann.

simplified supply chain diagram for recovery process for plastics and composites, with a case study of PET from plastics. The input-output sketch for the recycling process is used to recover PET, for lower-grade products such as fleece.

The market drivers that determine the best disposal solutions of wastes from FRP composites are the market forces of demand and supply, the increasing cost of landfills, the increase in awareness on circular economy thinking, the markets for recycled products, government policies, and legislations on recycled FRP composites. However, the most important driver on commercial viability of rFRP composites is the breaching of new markets (Brown *et al.*, 2018). With the increase in more composite recyclates, there is also an effect on the existing composite manufacturers, and their sources of raw materials. Currently, automobile manufacturers like BMW and VW are also researching on increasing the use of composites on their cars and also using recycled composites and biocomposites (Das *et al.*, 2016; Bharath and Basavarajappa, 2016; Mohanty *et al.*, 2018). This will also increase the economic viability of rFRP composites in the automobile industry. There is need to create more circular recycling on FRP composites, create higher value recycling routes to explore other areas of the market, and increase more economic exchanges and businesses both within the composites industry and with other industries such as the mainstream aviation industry, automobile industry and construction industry.

There are four main drivers that influence the supply chain of recycling carbon fibers. They are the affordability, security and legislative policies, and environmental responsibility. The economic conversion of both the raw wastes from manufacturing and EOL components into different recycled carbon fiber shapes, forms and component designs is very important. This material product, can then be used technically for different applications, making these lightweight carbon fiber composites less expensive. With respect to the security of the supply chain, the application of recycled carbon fibers controls any supply side capacity risk by bringing in high tonnes of carbon fiber from existing production capacity, thus buffing it up. Legislation plays a very great role, as these policies are what guide the manufacturers and the end-users about the product and its circulation in the market. The need for environmental responsibility cannot be overemphasized. In the automotive industry, EU legislation requires 85% of a vehicle to be recyclable. Carbon fiber waste can be recovered and converted to new products using less than 10% off the energy required to produce the original carbon fiber, fulfilling legislative and sustainability targets (ELG Carbon Fibre, 2017).

Issues on Environmental Aspects of Recycled Fibre Reinforced Polymer

Composite wastes could be an environmental concern too, as well as reinforced FRP composites. They could be fine ground into powder form or solid form in product or sheet material form. Composite wastes are also generated in factories, homes, schools, etc., and in different forms as shown in Fig. 14 (a)–(c). Generally, there are environmental aspects too that should be looked at in recycling of FRP composites. Just like the economic aspects of rFRP composites, the environmental aspects are also driven by same factors that affect the breaching of new markets using viable recycling routes. Environmental aspects of these reinforced FRP composites are dominated by the replaced content of the recyclates, particularly the mechanical strength from the recycling process of the virgin fiber and combusting the resin. This process contributes to energy generation and there is a transformation of energy from combustion using coal as fuel in the process.

In a study carried out in line with ISO 14040 (ISO, 2006) by Brown *et al.* (2018), three case studies were analyzed to represent the typical GFRP composite materials. They are the SMC, the continuous composite sheet, and the infused composite materials. The SMC as is often used in automobile and construction applications, assumed 30%/23%/47% resin/glass fiber/filler. The continuous sheet, as used in rooflights, or hand lay GFRP, is used for a large number of applications and is the largest process by

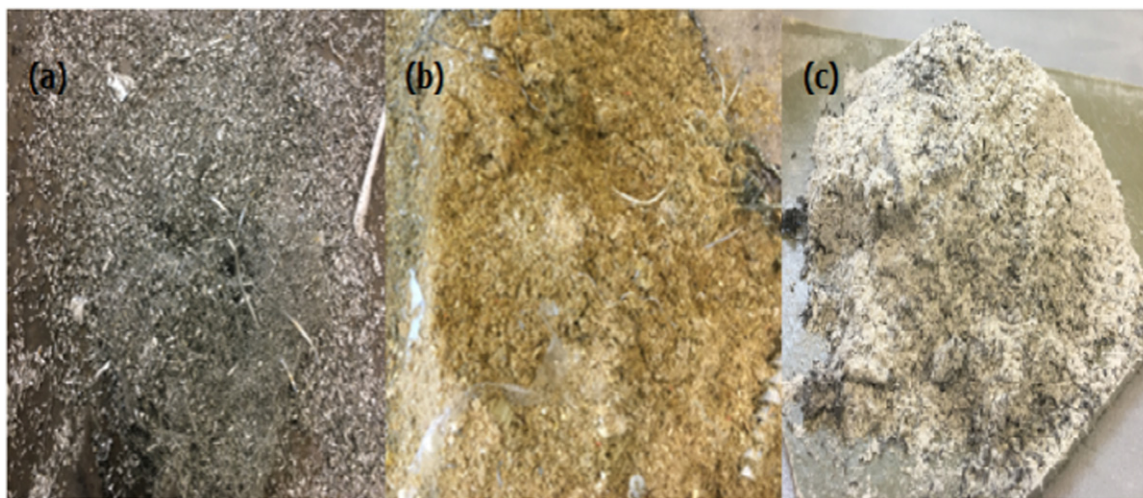


Fig. 14 Different forms of wastes for recycling (a) metal waste, (b) wood waste, (c) composite waste.

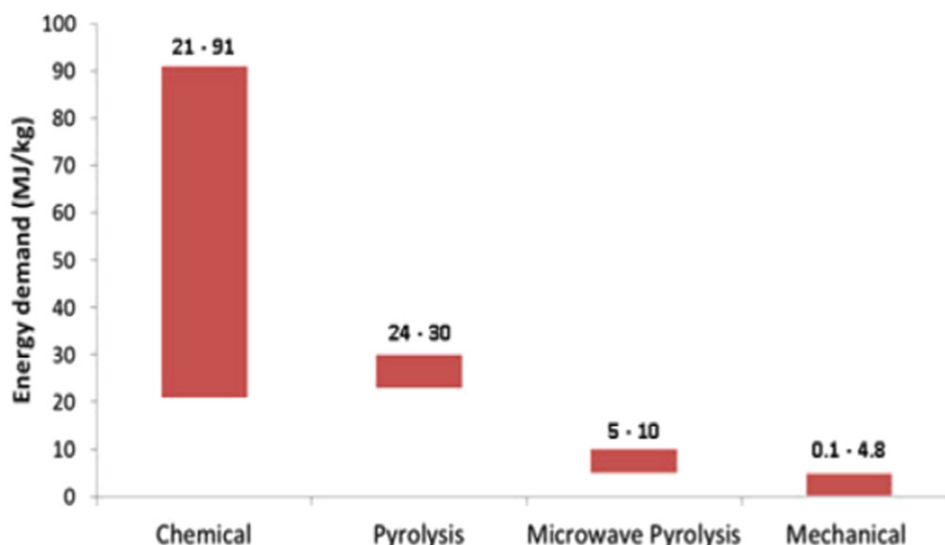


Fig. 15 Energy demand in composite recycling methods. Courtesy: Composites UK.

volume, with comparable constituents, assumed 65% resin, 35% glass fiber (CS/HL). The infused composite materials uses infusion in producing products like wind turbine blades, work boats, and leisure boats, assumed 40% resin, 60% glass fiber.

The environmental aspects of processing reinforced FRP composites are dominated by energy demand. Source of energy is the key factor considered in any manufacturing and recycling processes. In most cases, the main source of power for the energy usage is electricity. During these processes, this takes over greater percentage of the energy footprint. Reduction of energy demand is key in improving sustainability as well as the reduction of collateral damage caused by excessive energy put in by the system.

Issues on Energy Demand Aspects of Recycled Fibre Reinforced Polymer

According to [Brown et al. \(2018\)](#), the energy demand in a mechanical recycling process, for instance, is used to hammer the mill machine or to power the motor of the granulator. However, the power requirement is subject to the type of machinery. Any decrease in the energy demand will be beneficial in improving its sustainability. It can also be beneficial in decreasing the collateral damage due to excessive energy input. From [Fig. 15](#), the composite recycling processes and the corresponding specific energy demand is summarized, as carried out by Composites UK, however there is still need to clarify the issue of the nonequality between the recycling processes with respect to the energy demand. Some studies in the EXHUME project reported the energy demand to be around 0.17–0.27 MJ/kg for the Wittmann ML2201 granulator running at maximum capacity of 150 kg/h and about 0.35 MJ/kg for the Wittmann MAS1 granulator (at 30 kg/h). The Eco-Wolf grinder Model GM-2411-50 and IIT Ltd M300 machine respectively have the energy demand of 0.14 MJ/kg (800 kg/h) and 4.75 MJ/kg (around 29 kg/h). They also reported that prerecycling and postrecycling stages, for instance, shredding and sieving, are not as energy intensive as the actual recycling processes. It is noteworthy to state that the specific energy demand for each of the mechanical recycling processes is dependent on the process throughput with the most minimal lowest value when operating at its maximum machine capacity. During this stage of processing, the basic power requirement of the machine drive motors can be maximized with care thereby subsequently reducing the specific energy demand.

Today, pyrolysis and chemical processes exist commercially, as large scale recycling processes available for carbon fiber composites. From a literature review carried out by Composites UK, the average energy demand for a conventional pyrolysis process reported to be within the range of 23–30 MJ/kg but no information on processing scale is included. Microwave pyrolysis is reported as more energy efficient compared with the conventional pyrolysis due to fast and selective heating – With estimated energy demand about 5–10 MJ/kg. Also, organic by-products can be retrieved for energy or chemical feedstock from these processes. However, synthesis and refining steps may escalate the process energy demand even further. Hitachi Chemical (Japan), developed a chemical recycling process for epoxy based tennis racquet with energy demand between 63–91 MJ/kg and maximum processing capacity of 17,000 racquets per month. The solvent dissolution and water distillation steps dominated the process energy footprint. A pilot scale chemical recycling process at the University of Birmingham used a mixture of acetone and water to recycle 300 g of RTM6 CFRP plate. The process took around 3.5 h (0.085 kg/h) and had an electricity energy demand (for heating) around 21 MJ/kg. Optimization and upscaling the process will enable higher processing rate and lower specific energy demand. [Fig. 15](#) shows that the recycling energy demand is relatively lower (10 to 20 times lower) compared with embodied energy of production for virgin glass (13–32 MJ/kg) and carbon (183–286 MJ/kg) fibers. Environmental credits from avoidance of virgin material can be realized through cross sector applications of the recycle (Brown et al., 2018). An instance is using glass fiber thermoset waste in railway products

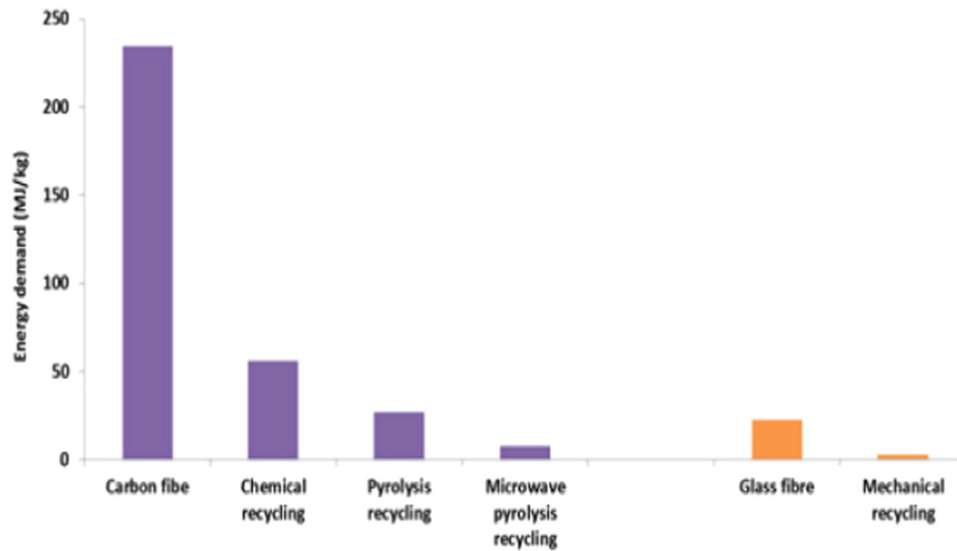


Fig. 16 Average comparison on embodied energy of fiber production and potential recycling processes. Courtesy: Composites UK.



Fig. 17 Level crossing panels including recycled glass reinforced polymer and phenolic from car parts. Courtesy: Reprocover.

can avoid production of virgin or new concrete material, by Reprocover as shown in Fig. 16. By avoiding production of high embodied energy material (such as fibers or polymer based material), major environmental benefits can be successfully achieved (Fig. 17).

End-of-Life Waste of Reinforced Fiber Reinforced Polymer

Wastes generated from the manufacturing of FRP composite and at the EOL. Currently, an estimated 1600 CFRP production waste and about 100 t of CFRP EOL. There are also an estimated 6200 t of GFRP production waste and 75,000 t of GFRP EOL waste is generated yearly in the UK. In a study by Brown *et al.* (2018), the constituent materials were broken down and it was found that at least 11,000 t of E-glass fiber waste comes from the early stages of the supply chain of FRPs.

Table 2 UK glass fibre reinforced polymer estimated typical constituents and volumes by resin and process

	<i>Total</i>	<i>UPR hand lay</i>	<i>UPR Spray up</i>	<i>UPR continuous sheet</i>	<i>UPR pultrusion</i>	<i>UPR SMC</i>	<i>UPR BMC</i>	<i>UPR infusion</i>	<i>UPR RTM</i>	<i>UPR filament winding</i>	<i>Epoxy infusion</i>	<i>Other epoxy</i>	<i>phenolic^a</i>	<i>Vinyl ester^a</i>
% resin (including combustible additives)		66	50	65	36	30	30	40	50	60	40	44	50	50
% glass fiber		34	20	35	46	23	15	60	30	40	60	56	50	50
% filler (noncombustible)		0	30	0	18	47	55	0	20	0	0	0	0	0
Resin supplied to this process (t)	59,300	24,000	7000	7000	2000 ^b	5000	2000	3000	3000	1000	3500 ^c	800	500	500
GFRP composite produced (t)	117,757	36,364	14,000	10,769	5556	16,667	6667	7500	6000	1667	8750	1818	1000	1000
Process waste (%)		6	3	12	7	4	4	3	3	3	3	10	5	5
Process waste (t)	6216	2182	420	1292	389	667	267	225	180	50	263	182	50	50
Calorific values (MJ/kg)		20	15	20	11	9	9	12	15	18	12	13	15	15
Typical fiber length (mm)		50	50	50	Long	25	25	Long	Long	Long	Long	Long	Varies	Varies
% containing halogenated FRs		5	5	80	70	1	1	5	5	0				
Factor to EOL		0.5	0.5	0.9	0.8	0.8	1.5 ^d	0.6	0.6	0.4	0.2	0.6	0.7	0.7
EOL products	75,659	18,182	7000	9692	4444	13,333	10,000	4500	3600	667	1750	1091	700	700

^aFor phenolic and vinyl ester resins, a nominal figure of 500 t resin has been assumed in each case, with 50/50 fiber and resin, as volumes are relatively small.

^bPultrusion value allows for imported pultrusions used in UK manufacturing.

^c70% of the epoxy infusion value is for offshore wind blades, much of which has recently started in manufacturing.

^dBMC EOL factor increased to allow for imported BMC parts.

Abbreviations: EOL, end of life; FRs, fibre resins; GFRP, glass fibre reinforced polymer; UPR, unsaturated polyester resin.

Note: % resin, fiber, filler are by mass. Blue rows indicated calculated values. The estimated data is anecdotal, based on interviews with experienced industry professionals.

Note: Brown, S., Forsyth, M., Job, S., *et al.*, 2018. FRP Circular Economy Study: Industry Summary – August 2018, UK. Available at: https://compositesuk.co.uk/system/files/documents/FRP_CE_Report_Final_0.pdf.

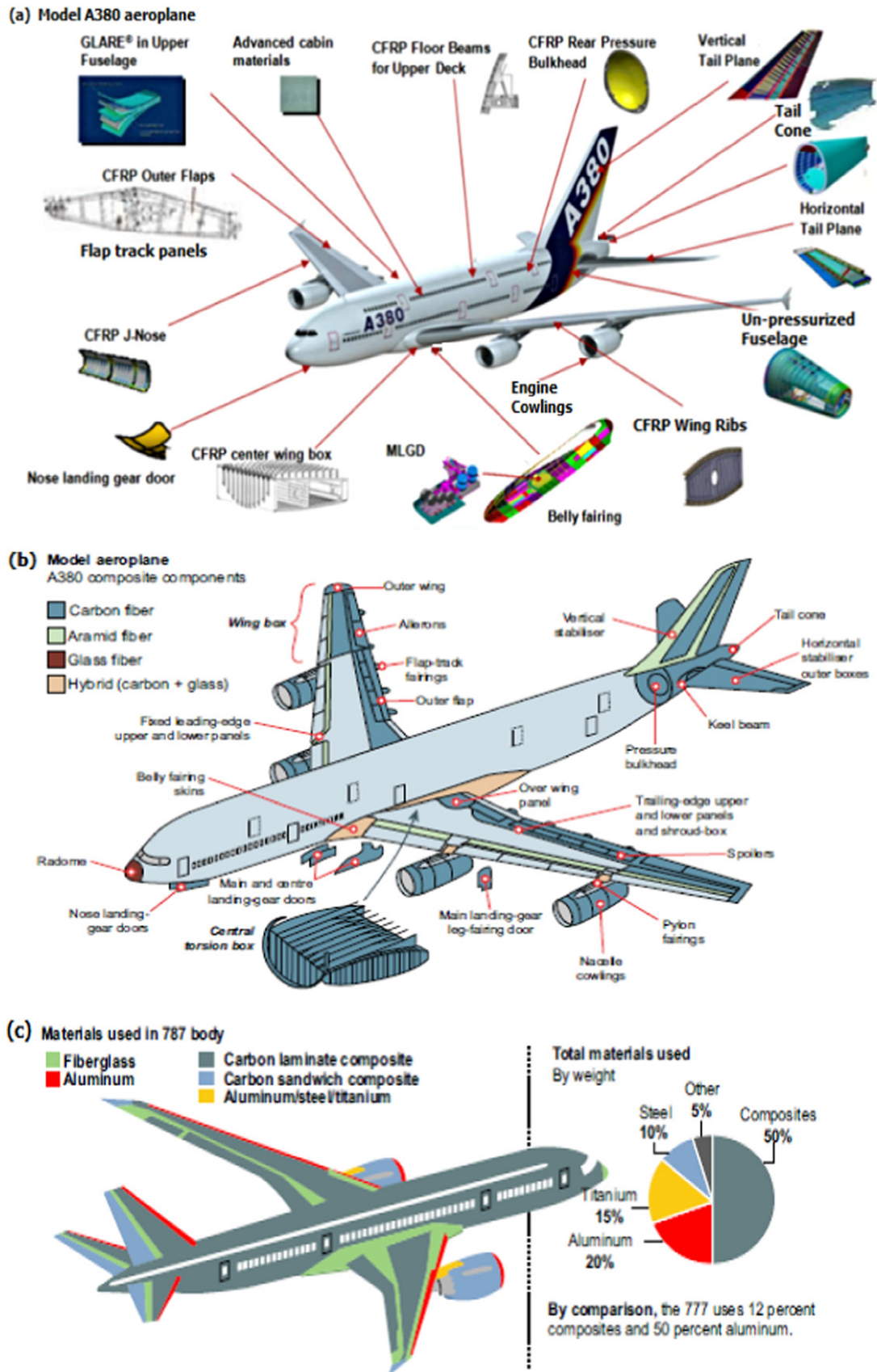


Fig. 19 Application of composites in airplane models (a)–(b) Airbus 380, (c) Boeing 787 “Dreamliner,” by Airbus Industry and Boeing Industry respectively.



2016 VW GOLF: INSIDE OUT

● RUNNING GEAR ● CONSTRUCTION
● BODY ● ELECTRONICS

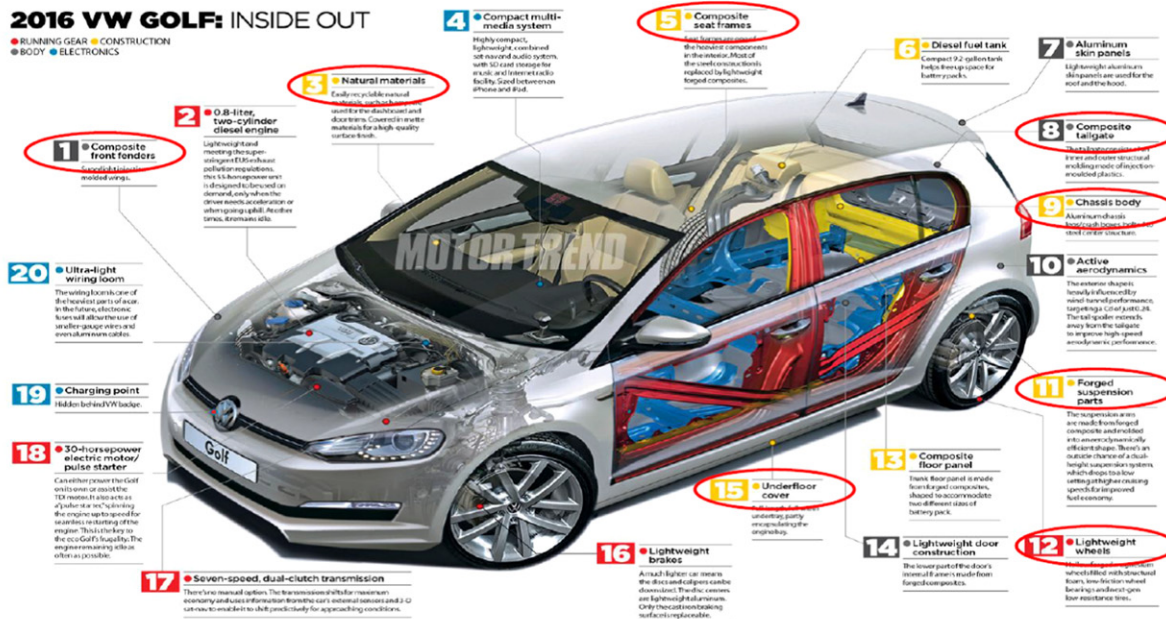


Fig. 20 Application of composites materials and other materials in VW Golf cars. Courtesy: Daimler and Motor Trend.

Fig. 18 and **Table 2** show the constituents and the estimated quantities of GFRP wastes generated in the UK, as recorded in Brown *et al.* (2018).

With the increase in the application of renewable energy, wind turbine blade waste has a high tendency to increase to over 10,000 t per year in 2030, except for challenges in the lifting, relifting, and hoisting of wind farms. In addition, there is the tendency for the value of recycled CFRP that is recycled through sylvolysis and pyrolysis to increase. An example is the simplified input–output diagram for the recycling of plastics to recover PET, for lower-grade products such as fleece. Thus, this will enable a corresponding increase in the amount of tonnes of aircraft CFRP EOL waste by the year 2030. For FRP wastes, they also have potential application to replace aggregates present in cementitious materials using fillers, but by partially replacing them (Yazdanbakhsh and Bank, 2014).

Application of Recycled Fiber Reinforced Polymer Composites

Due to the different environmental conditions for the applications of recycled FRP composites, their manufacturing and testing are slightly different. However, they make up a great number of applications in use today. The current usage of composite materials is highly driven by the aerospace, marine, and automobile industries. As can be seen in **Fig. 19**, the large proportion of the airplanes are made up of composite materials. In **Fig. 20**, composite materials are used in making automobiles. The parts of cars are made up of different materials like metals, alloys, steels, and composites. With the increase in the researches on recycled composites, recycled fiber reinforced composites are next to be seen on airplanes and on cars. There is limitation on the offshore application on large scale for recycled composites. Offshore structures like cylindrical floating production storage and offloading, paired column semisubmersibles (Odijie and Ye, 2015; Odijie, 2016; Odijie *et al.*, 2017a,b; Odijie, 2015), submarine hoses (Amaechi *et al.*, 2019b,c), composite risers (Amaechi *et al.*, 2019a; Amaechi and Ye, 2017; Gillett, 2018), and other structures require extensive design and material checks. Composites have been an enabling technology in the offshore industry, as seen in wind turbine blades and oil wells with deeper risers. However, while the standards allow small boats, leisure boats, and work boats to be built using composites, the International Maritime Organization Safety of Life at Sea regulations restrict the use of composites and greatly prohibit the structural use of composites due to reasons like combustibility (Job, 2015, 2014).

In the automobile industry, one of the objectives is to have fuel-efficient cars and also lightweight cars. Application of CFRP in car parts reduces the weight of the 30% of a standard car. In another study, it was observed that GRP waste fibers can be used to strengthen the bending in architectural cladding panels and also reduce the propagation of cracks with the cement composites, as

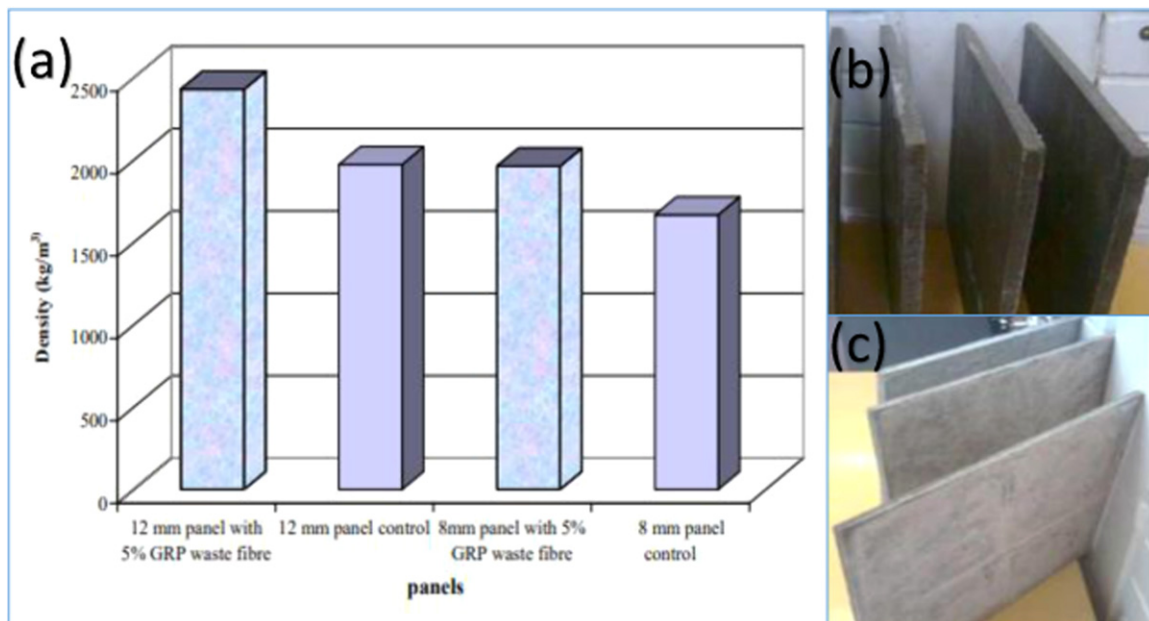


Fig. 21 Glass reinforced polymer waste fiber on architectural cladding panel showing (a) the effect on panel density, (b) 12-mm-thick panels and (c) 8-mm-thick panels. Courtesy: Osmani, M., Asokan, P., 2010. An assessment of the compressive strength of glass reinforced plastic waste filled concrete for potential applications in construction. *Concrete Research Letters* 1 (1), 1–5. Osmani, M., Pappu, A., 2010. Utilisation of glass reinforced plastic waste in concrete and cement composites. In: *Proceedings of the 2nd International Conference on Sustainable Construction Materials and Technologies*, pp. 1127–1137. Ancona, Italy. Available at: <http://www.claisse.info/2010papers/m45.pdf>.

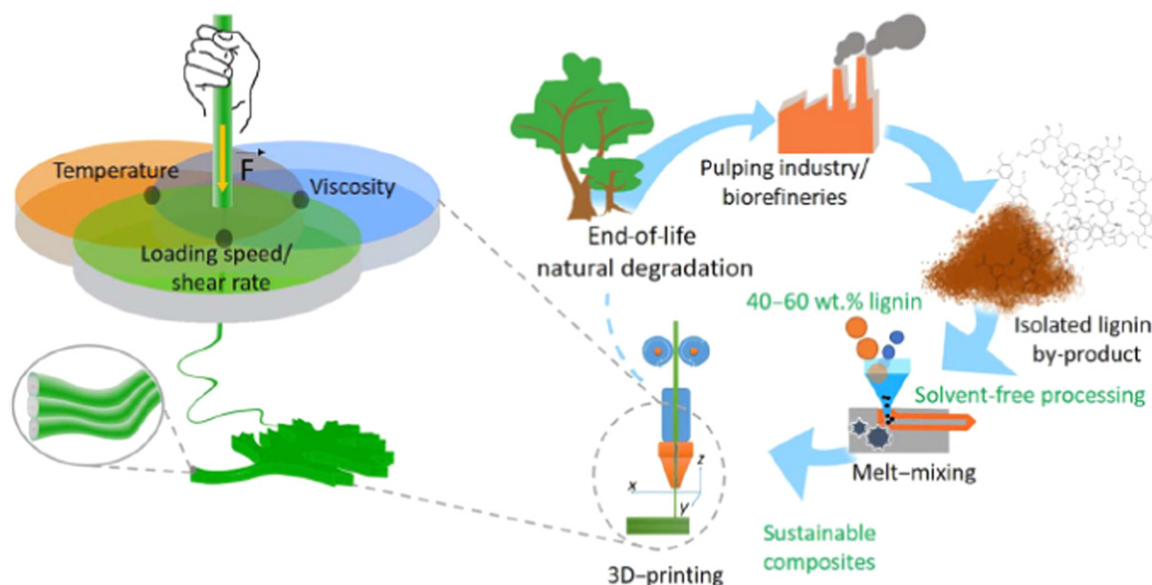


Fig. 22 Printability of renewable composites. *Source:* Nguyen, N.A., Barnes, S.H., Bowland, C.C., *et al.*, 2018. A path for lignin valorization via additive manufacturing of high-performance sustainable composites with enhanced 3D printability. *Science Advances*, 1–16. Available at: <http://advances.sciencemag.org/cgi/content/short/4/12/eaat4967>.

Table 3 Biocomposites in automotive, packaging, and other applications

Manufacturer	Resin	Filler	Applications	Reference
Ford	PP	Coir fiber	Load floor, package shelf	(Malnati, 2018)
	PP	Cellulose fibers	Console armrests	
	TPE	Powdered coconut shells, shredded tires	Structural guards	
	TPO	Powdered coconut shells, shredded battery cases, magnesium silica fibers	Rear deck lid applique brackets and side-door cladding	
Hyundai	ABS	Cork	Veneer	(Akampumuza <i>et al.</i> , 2017)
Mercedes Benz	Epoxy	Flax/Sisal fiber mats	Interior door panels	
Toyota	Bio-nylon 6,10	Short glass fiber	Radiator end tank	
Volkswagen	Polyurethane	Flax/Sisal fiber mats	Door trim panels	
Mitsubishi Motors and Fiat SpA	Bio-PBS	Bamboo fiber	Interior vehicle components	
Toyota – Lexus	Bio-PET	–	Luggage compartment liner	(Ackrill, 2018)
Club Coffee	Biodegradable polymer blend	Coffee chaff	Coffee pods	
Competitive Green Technologies	PP	BioC	Additive/coloring agent	(Bali and Tiessan, 2018)
Zespri	PLA	Kiwifruit skin	Biodegradable spoon-knife	(Graichen <i>et al.</i> , 2017)
Scion	Aliphatic polyesters	Grape pomace	Biodegradable net clip for vineyard	
Tecnaro	Natural resins	Lignin and natural fibers	Construction, electronics, furniture, headphones	(Kun and Pukánszky, 2017)

Abbreviations: ABS, acrylonitrile butadiene styrene; PBS, polybutylene succinate; PET, polyethylene terephthalate; PLA, polylactides; PP, polypropylene; TPE, thermoplastic elastomer; TPO, thermoplastic olefin.

Source: Mohanty, A.K., Vivekanandhan, S., Pin, J.-M., Misra, M., 2018. Composites from renewable and sustainable resources: Challenges and innovations. *Science* 362 (6414), 536–542.

shown in Fig. 21.

In another report by Job *et al.* (2016), the work on continuous FRTP or long FRTP is limited, but more work has been carried out using the thermoset resins. In contrast, the thermoplastic resins are reprocessed and remelted for reuse as recycled FRP composites (Pimenta and Pinho, 2011; Rebeiz and Craft, 1995; Moothoo *et al.*, 2017; Leblanc *et al.*, 2015). There are glass fiber reinforced thermoplastics that have been recycled from automobile wastes and reprocessed into new compounds. On the other hand, the glass fiber reinforced thermoset resins could be degraded thermochemically, thereby helping to recover the organic atoms with low molecular weights.

Job *et al.* (2016) stated that the properly prepared and smoothened carbon fiber reinforced PEEK molded and then injected into virgin PEEK resin and pressed up to 50 wt%, producing recycled composites with mechanical characteristics. There was also the direct recycling process without grinding was also successfully performed but has not applied to EOL composite materials. It is noteworthy that thermoset resins are highly durable, can survive high temperature and have excellent mechanical behavior. However, they can be replaced by thermoplastic resins. Some commercially available thermoset epoxy resins are easier to recycle, as developed by Connora Technologies and Adesso. These thermoset composite resins can be decomposed chemically under low temperature conditions to free up the fiber molecules, and degraded resins that can be used as recycled thermoplastics and as adhesives. Using lignin, recycled composites can also be printed using 3D printing, as shown in Fig. 21. Sustainable 3D-printed products are made from 40 to 60 wt % lignin containing polymeric materials formulated by a solvent-free process and exhibiting appropriate processability constrained by an optimum window of temperature, shear rate and/or filament feeding rate, and viscosity (Graichen *et al.*, 2017; Nguyen *et al.*, 2018) (Fig. 22; Table 3).

Conclusion

There are more economic aspects to be achieved from the recycling of FRP composites. As discussed here, state-of-the-art applications of composites in different industries show a growing demand for composites, and thus the need increases too. The trend in recycling also increases and will be beneficial in the near future based on the current recycling processes and regulations to support recycling in the composite industry. Despite challenges with the application of recycled FRP composites, due to strength issues not highly validated in large scale structures, it is still an enabling technology in some products and can be harnessed. Application of recycled FRP composites in large scale in offshore and marine applications will be one of the key challenges. Economically, it will be successful with small-scale production like remotely operated vehicle handles but will have issues with vibration requirements. Considering the different environmental conditions for oil explorations, such as those that may be harsh, benign, or squall, will also be an issue. There can be more optimization of the impacts by reclaiming fibers very well for reuse as recycled FRP composites and using the leftover resin powder in cement kilns to replace coal, with a large scale, centralized operation to reduce energy impacts. However, technical and logistical advances would be needed before a business model to support this could be proven in a circular economy.

Acknowledgment

The authors wish to acknowledge the Engineering Department, Lancaster University, and Niger Delta Development Commission, Nigeria (NNDC). We also thank the authors whose images we have used for the permissions obtained, such as Composites UK, ELF Carbon Fiber and Daimler.

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Future Eco-Efficient Cements Prepared With Kaolinite-Based Industrial Wastes

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Introduction

The greenhouse gas emissions (CO_2 , NO_x , SO_x , etc.) associated to the manufacture of commercial cements are undeniably one of the most serious problems of the cement industry, whose contribution to the global CO_2 emissions amounts to 5%–7%. The use of supplementary cementitious materials (e.g., fly ash, silica fume, blast furnace slag and natural pozzolans) as a partial replacement of Portland clinker has been improving the sustainability of the cement sector for decades and thus, presently, the carbon footprint of the process has been reduced to 800 kg of CO_2 per ton of clinker produced.

The current implementation of a Circular Economy Strategy in the European Union is encouraging the reuse of industrial waste and by-products as secondary raw materials. According to Eurostat, approximately 2500 million tons of wastes are generated in Europe per year, which represents 30% of the global waste production. Moreover, 48% of those wastes are simply being disposed of in landfills, many of which arise from the construction sector (35%) as well as the mining and quarry industry (28%). In this context, new environmental policies are to be applied, which will have a major impact on the socio-economic development of those countries. The incorporation of new recycled cementing materials into future eco-efficient cements will constitute a priority scientific and technical axis for the scientific community, which will substantially improve the sustainability of the cement sector.

The calcined natural pozzolans have been encompassed within the traditional pozzolans for years, having been included in the cement standards of the 1970s and the 1980s (designated by the letter Q). Despite this fact, the current industrial use of calcined natural pozzolans is virtually nil, probably due to the environmental impact resulting from the extraction of the raw materials (kaolinite) and the natural space protection policies. In this sense, the reuse of kaolinite-based waste for the obtaining of recycled metakaolinite, whose behavior and properties are similar to those of natural metakaolinite, can be presented as an appropriate and eco-efficient solution to mitigate the disadvantages usually related to the natural pozzolans. The studies conducted over the last years within this line of research are focused on the reuse of waste from the paper and coal mining industry as well as from the drinking water treatment plants. This kind of by-products are inert by nature and, therefore, they require a previous thermal activation process in order to convert them into highly pozzolanic materials, in which kaolinite is transformed into metakaolinite and organic matter (cellulose, plant debris, etc.) is removed.

In 2017, coal production in Europe amounted to 464 million tons ([European Association for Coal and Lignite, 2017](#)). With approximately 0.4 ton of mining waste generated per ton of produced coal, coal mining waste becomes one of the most abundant kaolinite-based industrial wastes, followed by paper sludge, a by-product of the paper industry in which recycled paper is used as raw material for the obtaining of cellulose and whose waste generation can be estimated at 14 million tons/year in Europe ([Frías et al., 2018a](#)).

The present article covers the main properties of the most widespread kaolinite-based wastes, paper sludge and coal mining waste, as well as their behavior in cement matrices. To this end, the main scientific and technical advances conducted to date are discussed in this work, based on the worldwide studies on this topic (found in the literature) as well as on the research performed by the IETcc-CSIC Material Recycling Group, which possesses a vast experience in this innovative and eco-efficient research line.

Characterization of the Raw Materials and the Activated Products

A literature review reveals that there is a partial disparity between the chemical composition of the two raw wastes under study ([Amouzadeh Omrani and Modarres, 2018](#); [Beltramini et al., 2010](#); [de Azevedo et al., 2018](#); [Frías et al., 2012, 2018b](#); [Li et al., 2016](#); [Mamat et al., 2018](#); [Modarres et al., 2018](#); [Simão et al., 2017](#); [Singh et al., 2018](#); [Vegas et al., 2009](#); [Vigil de la Villa et al., 2007](#); [Wong et al., 2015](#); [Yan and Sagoe-Crentsil, 2012](#)). Paper sludge (PS) is mainly composed of calcium, aluminum and silicon oxide, whereas coal waste (CW) displays a silico-aluminous nature. As can be seen in [Table 1](#), the chemical composition, expressed in terms of simple oxides, shows a substantial fluctuation even among wastes of the same nature, which is especially conspicuous in the case of the main oxides. Such disparity arises from a variety of factors, including the origin of the waste, the mineralogical load (carbonates/kaolinite), the proportion of recycled paper used in the paper mill or the nature of the soil in the coal mine. Attention should be drawn to the high loss on ignition (LOI) values of the raw wastes, which amount up to 75% and 48% for the PS and CW, respectively. This circumstance is attributed to the dehydroxylation processes of the minerals present in the waste (kaolinite, mica or talc), the decarbonation of carbonates and the decomposition of organic matter (plants, cellulose, etc.).

Qualitatively, a wide variety of minerals can be found in PS and CW as a consequence of the heterogeneity of the wastes, especially in the case of coal waste. The variation range of the content of the main crystalline mineralogical phases, determined by means of XRD-Rietveld methodology and obtained from the limited data available in the literature, is shown in [Fig. 1](#)

Table 1 Ranges of chemical composition of the wastes obtained from the literature (wt%)

Oxides	CaO	SiO ₂	Al ₂ O ₃	SO ₃	Fe ₂ O ₃	MgO	MnO	Na ₂ O	TiO ₂	K ₂ O	P ₂ O ₅	LOI
PS	2–79	5–22	7–16	<2	0.4–1	0.1–2.6	<0.3	<0.7	<13.2	<0.3	<1.8	46–75
APS	19–61	8–31	4–37	<9	0.5–2.6	<10.5	<0.4	<1.5	<2	0.4–3.8	<5.3	6–33
CW	<4	25–62	15–27	<1	3–8	<3.3	<0.08	<2.2	<1.1	<3.6	<0.5	9–48
ACW	2–8	52–62	20–30	<0.7	4.6–8.4	<3.5	<0.14	<2.2	<2	<4	<0.3	0.8–11.7

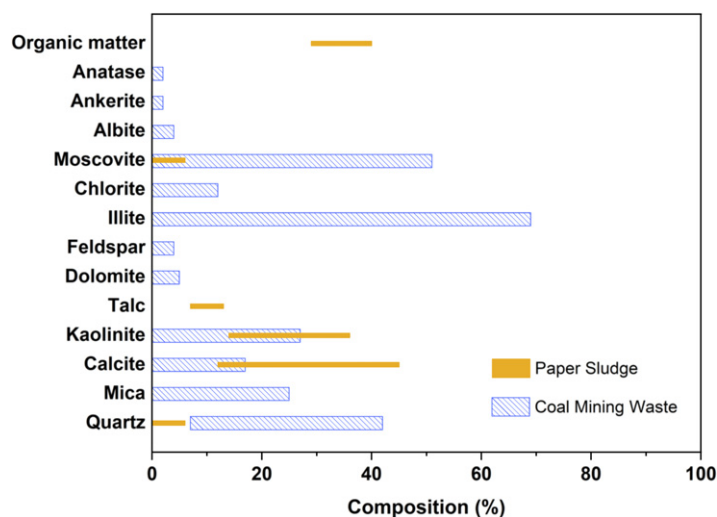


Fig. 1 Mineralogical composition of the raw wastes.

(Frías *et al.*, 2012, 2018a; Taha *et al.*, 2017; Vegas *et al.*, 2009; Vigil de la Villa *et al.*, 2007). It must be noted that the wastes exhibit a kaolinite-based nature, finding kaolinite contents between 14% and 36% in PS and up to 27% in CW. Quartz, calcite, talc and muscovite are the remaining crystalline phases found in paper sludge, whereas minerals such as quartz, calcite, mica, illite or chlorite have been detected in coal mining waste. In addition, Civeira *et al.* (2016) found substantial amounts of alunite, jarosite, gypsum and pyrite in the particular case of burning coal cleaning rejects.

The nature and crystalline mineralogy of these raw materials prevent them from reacting with the lime available in their surroundings. Therefore, in order to become supplementary cementitious materials, the wastes must undergo a thermal activation process, which mainly involves the complete transformation of kaolinite into metakaolinite (a highly reactive standardized pozzolan) and the removal of organic matter. According to Fig. 2, different activation conditions (furnace temperature and retention time) can be encountered in the literature (Amouzadeh Omrani and Modarres, 2018; Beltramini *et al.*, 2010; Dong *et al.*, 2015; Frías *et al.*, 2012; García Giménez *et al.*, 2016; Li *et al.*, 2006; Modarres *et al.*, 2018; Pera and Amrouz, 1998; Vegas *et al.*, 2009; Vigil de la Villa *et al.*, 2007). In general, there is a consensus on the fact that the optimal activation conditions are a temperature range of 600–700°C and a retention time of two hours since higher values would negatively affect the reactivity of the material due to the agglomeration of particles, which reduces their specific surface, and the recrystallization of metakaolinite.

Fig. 3 shows that the aspect of the raw wastes experiments a significant change after being subjected to the activation process. Both the activated paper sludge (APS) and the activated coal waste (ACW) exhibit lighter colors, as a consequence of the removal of residual organic matter and unburned coal. The chemical composition of the activated wastes, listed in Table 1, does not suffer from major changes, although lower LOI values can be found, as expected, since a significant proportion of the materials susceptible to dehydroxylation or decomposition are transformed during thermal activation.

Pozzolanic Activity of the Calcined Products

Different methods (direct and indirect) have been used for decades to evaluate the pozzolanic character of active additions. The IETcc-CSIC Material Recycling Group has an extensive experience in the use of an accelerated chemical methodology in pozzolan/lime systems, which allows the determination of the amount of fixed lime at different reaction times (García *et al.*, 2008).

Fig. 4 plots the fixed lime contents (expressed in percentage terms) of the activated paper sludge (APS) and the activated coal waste (ACW) after being treated at 600°C for two hours, up to 90 days of reaction. In addition, the fixed lime values determined for three supplementary cementitious materials traditionally employed in the manufacture of commercial cements have been displayed: silica fume (SF), fly ash (FA) and natural metakaolinite (MK). As can be seen from the figure, both metakaolinite-based

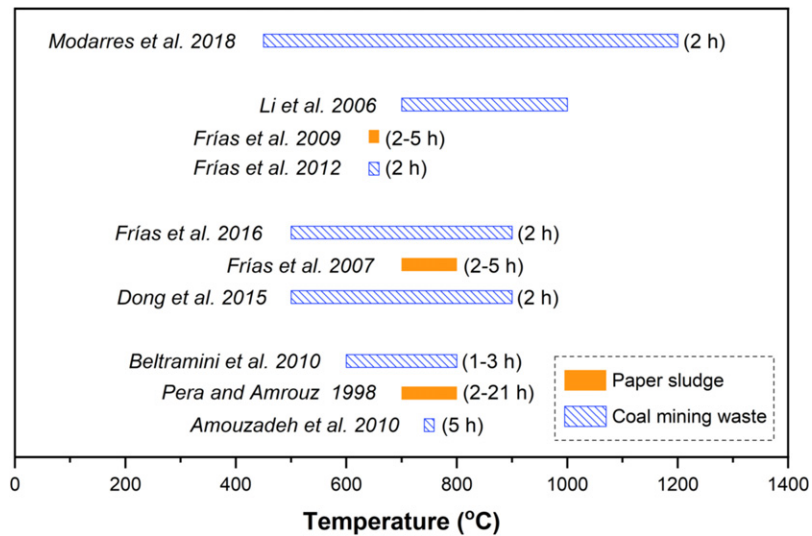


Fig. 2 Activation conditions of the wastes tested by different authors.

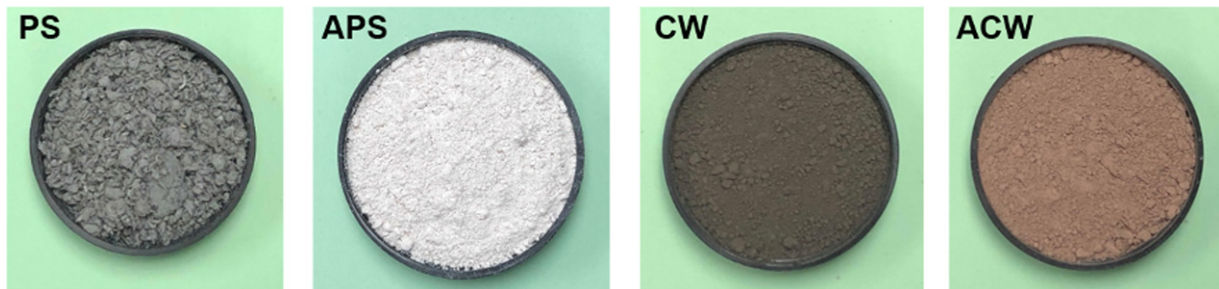


Fig. 3 Visual aspect of the raw and calcined wastes under study.

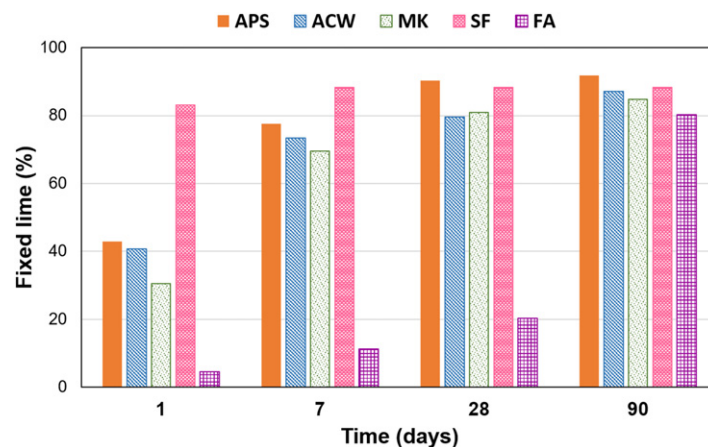


Fig. 4 Pozzolanic activity of different wastes employed as supplementary cementitious materials.

wastes show a high pozzolanic activity, fixing ~40% of the available lime at 1 day of reaction, and reaching values of approximately 90% after 90 days. It must be highlighted that the obtained results are similar to those exhibited by the 100% natural metakaolinite. With respect to the standardized pozzolans, the behavior of APS and ACW falls between that of SF and FA, displaying lower reaction rates than SF during the first 7 days of reaction and noticeably higher values than that of FA up to 28 days. Nevertheless, by the end of the experiment (90 days), the fixed lime values are very similar in all the cases under study, which amount to approximately 80%–90% of the available lime.

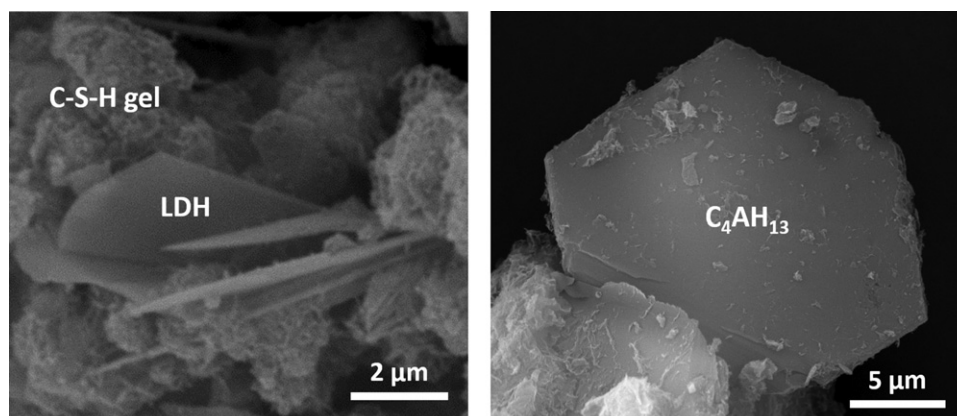


Fig. 5 Morphology of C–S–H gels and LDH compounds (left) and tetracalcium aluminate hydrate (right) found after 28 days of reaction in a ACW/lime system.

Table 2 Ranges of variation of the rheological properties of the blended cement matrices expressed in percentage terms with respect to a reference cement matrix (assigned value of 100%)

	APS content (%)					ACW content (%)				
	2.5	5	10	15	20	6	10	20	30	50
Flow	68	54–88	43–73	32–62	18–66	91	88–95	80–95	113 ^a	130 ^a
IST	–	115–156	76–242	255–297	77–359	77–97	77–103	71–116	104	85
FST	–	135–156	91–233	254–344	84–465	78–95	78–105	63–107	91	76

^aValues corresponding to the amount of water required to obtain consistencies comparable to those of the reference mortar.

Nota: Frías, M., Vigil de la Villa, R., García, R., *et al.*, 2018b. Effect of a high content in activated carbon waste on low clinker cement microstructure and properties. *Constr. Build. Mater.* 184, 11–19

According to previous research (Frías *et al.*, 2008; García *et al.*, 2015), the pozzolanic reaction studied in the pozzolan/lime system gives rise to the formation of qualitatively similar hydrated phases. Nevertheless, the concentration of those phases and their evolution with time depends on factors such as the activation conditions, the metakaolinite content or the presence of other mineralogical phases on the industrial waste (sulfates, carbonates, etc.). Overall, both APS/lime and ACW/lime systems lead to the formation of C–S–H gels, stratlingite (C_2ASH_8), tetracalcium aluminate hydrate (C_4AH_{13}) and Layered Double Hydroxides compounds (LDH). Additional hydrated phases were identified, such as monosulfoaluminate hydrate (in ACW) or thomsonite and/or chabazite-type zeolites (in APS). By way of illustration, Fig. 5 shows the morphology of some of the aforementioned compounds observed after 28 days of reaction in the ACW/lime system.

In a pozzolan/cement system, the process is more complex and the presence of other oxides as well as the pozzolan content can affect the reaction rate and the formation of the hydrated phases resulting from the pozzolanic reaction. This circumstance arises as a consequence of the existing dependency situation between the hydration rate of the anhydrous cement particles and the pozzolanic reaction, which is limited by the amount of available lime in the system.

In light of the above, the outcome of the pozzolanic reaction in a blended cement matrix varies substantially from that obtained in a pure pozzolan/lime system. The presence of ACW in a blended cement promotes the formation of C–S–H gels, tetracalcium aluminate carbonate hydrate (C_4ACH_{12}) and C_4AH_{13} , whereas the addition of APS mainly favors C–S–H gels and C_4AH_{13} as hydrated phases (Frías *et al.*, 2016; Vigil de la Villa *et al.*, 2010). It must be highlighted that the presence and amount of these phases will have a direct impact on the properties of the new eco-efficient cements.

Rheological Properties

Table 2 shows the variation ranges of some rheological properties of blended cements prepared with different amounts of APS (Ferrándiz-Mas *et al.*, 2014; Ferreira *et al.*, 2013; García *et al.*, 2008; Malaiskienne *et al.*, 2018; Yan *et al.*, 2011) and ACW (Beltramini *et al.*, 2010; Frías *et al.*, 2018b; Modarres *et al.*, 2018; Vegas *et al.*, 2015), including the slump of the standardized blended cement mortar on the flow table and the initial and final setting times (IST and FST, respectively). The values displayed in the table are expressed as relative percentages with respect to the values exhibited by a reference ordinary Portland cement matrix, which has an assigned value of 100%. Therefore, quantities over 100% imply higher slumps or setting times than those of the reference cement (mortars or pastes, respectively) and, consequently, those below 100% indicate lower values with respect to the reference.

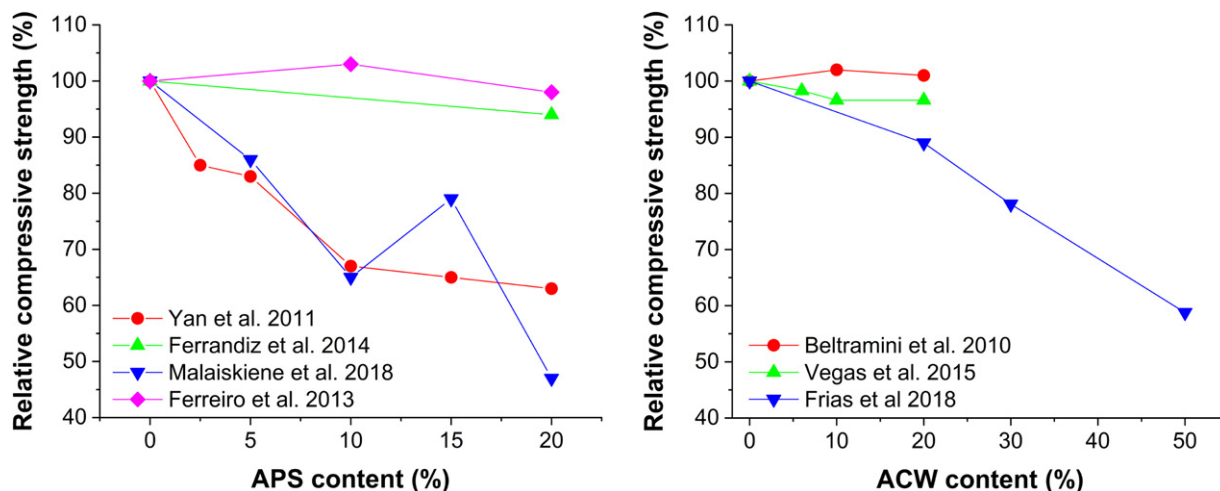


Fig. 6 Relative compressive strength at 28 days of APS blended mortars (left) and ACW blended mortars (right).

In light of the results gathered in the table, it is clear that there exists a wide variation in the rheological properties for both pozzolans, primarily due to the great chemical and mineralogical heterogeneity of the starting materials.

In general, the blended cement mortars prepared with these metakaolinite-based pozzolans at a fixed water/binder ratio present lower slump values with increasing levels of replacement, especially in the case of APS. Conversely, ACW mortars show moderate reductions in the slump test, that amounts up to 20% for a 20% level of replacement. Slump values are not available in the specific cases of 30% and 50% substitution levels and therefore, the table shows the amount of water necessary to obtain similar consistencies with respect to the reference mortar. Thus, it can be seen that water demand increases by 13% and 30% for blended mortars containing 30% and 50% of ACW, respectively.

Regarding the setting times, it can be observed that, in spite of the wide dispersion of values, there are substantial differences in the behavior of APS and ACW blended cements. A clear trend cannot be distinguished with respect to the influence of the addition of increasing amounts of APS, which can have both an accelerating and a retarding effect on the setting times with respect to the reference paste. On the other hand, ACW has a general accelerating impact on the pastes, which show values below to those of the reference paste in most of the cases.

The variation found in the literature with respect to the behavior of both the APS and ACW blended cements reveals the existence of different factors that can have a significant impact on the rheological properties of the material: the nature of the waste, the water/binder ratio employed in the preparation of the paste or mortar, the conditions of the activation process, the amount of pozzolan added to the blend, the presence of minority elements (Zn, Pb, etc.), the existence of coal remains or unburned matter, the fineness of the pozzolan, the presence of cellulose, etc. These considerations are in line with the results reported by [Modarres et al. \(2018\)](#), in which the setting of blended cements containing low substitution levels of pozzolan was accelerated due to the filler effect, whereas a retarding effect was found in those cements prepared with higher pozzolan contents as a consequence of the low cement content.

Compressive Strength

The relative compressive strength values of APS and ACW blended mortars, with respect to a reference ordinary Portland cement, measured after 28 days of hydration by different authors, are shown in [Fig. 6](#). For comparative purposes, only the results obtained after a curing time of 28 days have been plotted, as that is the age considered as a reference in the current standards for commercial cements. The literature includes several examples of compressive strength tests performed on both APS ([Ferrándiz-Mas et al., 2014](#); [Ferreiro et al., 2013](#); [Malaikiene et al., 2018](#); [Yan et al., 2011](#)) and ACW ([Beltramini et al., 2010](#); [Vegas et al., 2015](#)) blended cements with substitution levels up to 20%. Nevertheless, only one author reports the results of low-clinker cements, containing up to 50% of ACW ([Frías et al., 2018b](#)).

The evolution of compressive strength in APS blended mortars follows two different trends. Firstly, those mortars prepared with a water/binder ratio of 0.5–0.6 display mechanical properties similar to those of the reference mortar. On the other hand, the authors employing higher water/binder ratios (0.7–0.8) have reported major losses in the mechanical performance of the blended mortars, whose values exceed the replacement percentages of pozzolan.

The behavior of ACW blended mortars does not significantly differ from that of APS blended mortars when the pozzolan is added up to a 20% substitution level, showing compressive strength values comparable to those of the reference. In contrast with the previous cases, the studies performed by [Frías et al. \(2018b\)](#) and [Vegas et al. \(2015\)](#) on 20% to 50% ACW blended mortars, which include the use of a water-reducing admixture to maintain a constant water/binder ratio of 0.5, reveal an important loss in compressive strength. This circumstance relates, among others, to the excess of pozzolan with respect to the available portlandite content, the low cement content and the presence of air voids. Nevertheless, a refinement process of the microstructure was

detected in the blended mortars by the authors (Frías *et al.*, 2018b), which was attributed to the development of nucleation points for the formation of the cement hydrated phases.

Conclusions

The Circular Economy Strategy considers the reuse of industrial wastes as secondary raw materials as a priority line of action for the socio-economic development of a country.

The research conducted in the continuous search for future eco-efficient pozzolans that can be used as alternative additions to those traditionally used in the manufacture of commercial cements (silica fume, fly ash, natural pozzolans, slags, etc.) is instrumental in increasing the sustainability of the cement sector. In this context, the exploitation of kaolinite-based wastes for the production of recycled metakaolinite is becoming a subject of special interest in the scientific community.

On the basis of the findings set out in the present work, the optimal conditions for the activation of paper sludge and coal mining waste, from a scientific, technical, energy, economic and environmental standpoint, are a temperature between 600°C and 700°C and a retention time of 2 h.

Being a relatively new research line, important scientific and technical gaps can still be found regarding the properties of these kaolinite-based wastes. Consequently, the results found in the literature might appear to be inconsistent, even for the same type of waste. This circumstance is mainly motivated by a set of factors that are directly related to the nature, composition and reactivity of the waste as well as to other variables such as the activation conditions, the water/binder ratio, the substitution levels, etc. Nevertheless, the findings exposed in the present work reveal the viability of these two metakaolinite-based wastes, activated paper sludge (APS) and activated coal mining waste (ACW), as raw materials for the manufacture of future low-CO₂ cements, as they have proven to possess comparable properties to those of pure, natural metakaolinite.

In spite of this, it is still of paramount importance to enhance the scientific knowledge in this subject, particularly in those aspects related to the establishment of global action protocols for the activation process of the pozzolans, the study of the durability of the blended cements against aggressive media (CO₂, chloride and sulfate ions, seawater, freeze-thaw cycles, etc.), the assessment of the behavior of these wastes in concrete matrices and, finally, we must not forget the importance of the incorporation of these new eco-efficient pozzolans in the current standards that regulate the manufacture of sustainable cement and concrete.

Acknowledgements

The authors would like to thank the different Spanish Ministries for their financial support [refs: BIA2015-65558-C3-1,2,3-R (MINECO/FEDER); MAT2012-37005-C03-1,2,3; MAT2009-10874-C03; CTM2006-12551-C03-1,2/TECNO; MAT2003-06479-C03-1,2,3]. They are also grateful for the funding provided by the Spanish Training Program and the European Social Fund (MINECO/FSE) (Ref. Number BES-2016-078454).

See also: Utilization of Waste Expanded Glass in Cement Composites. Valorization of Marble Waste in Cement-Based Materials

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Influential Parameters on Formation of PEMs on Recycled Fibers: A Review

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Introduction

Recycled paper, as a huge source of cellulosic fibers, has been regarded as a secondary base for preparing raw material in pulp and paper industry. In some countries, accidentally, paper making industry accounts for the main consumer of recycled paper and any shortage for supplying these types of raw materials can affect production delays, and upset manufacture. Nevertheless, it is recognized that the cellulosic recycled fibers have inferior quality and strength properties compared to virgin cellulose fibers (Hubbe and Heitmann, 2007). Accordingly, most of recycled papers have been applied as fibrous raw materials for manufacturing of low-quality grade papers and paperboards. This would include newspapers, toilet roll, corrugating board and test liner, for example, in Europe and Asia. Therefore, the use of recycled fibers for making higher paper grades such as printing and writing papers is still at low level. The reasons for lower quality of recycled fibers are partly attributable to the some events took placed in the fiber structure during paper sheet forming and drying processes, including hornification phenomena (Weise *et al.*, 1998; Billosta *et al.*, 2006; Hamzeh *et al.*, 2012) and polysaccharide hardening (Atalla, 1997). Furthermore, it is generally believed that these phenomena are particularly associated with the formation of irreversible or partially reversible hydrogen jointing in pulp fibers upon drying process considered as what happened for some of the recycled fibers. Consequently, these impact will change the main characteristics of recycled fibers, including fiber strength, fiber length, fiber swelling, and jointing potential of the fibers, leading to a reduction in the strength properties of the resultant papers (Ellis and Sendlachek, 1993). Taking into consideration the fact that the quality of recycled pulp fibers depends also on how many times the secondary fibers have been experienced the cycle of fiber recycling, which intensify negative effect of recycling on the fibers characteristics and diminish suitability of these fibers for preparing market acceptability rate of paper products.

Several attempts have been made to improve the jointing ability and quality of recycled fibers for papermaking. According to the literature consulted, beating and refining, chemical additives, blending with virgin fibers, and fiber fractionation are the most frequently research and industry-led efforts to overwhelm the problems associated with the strength and quality inferiority in the recycled fibers. Refining/beating, despite of being capital- and energy-intensive operation, is the most frequently used method for improving of jointing potential in both virgin and recycled fibers (Wistara and Young, 1999). Though the inter-fiber jointing potential and strength properties of paper can be substantially improved by refining treatment of the fibers (Seth *et al.* 1979), but it also tends to generate fiber fines, decreases greatly the rate at which water can be removed from the wet web of paper sheet, finally limiting the rate production of paper (Bhardwaj *et al.*, 2004; Hubbe *et al.*, 2006, 2007). Refining action also tends to reduce the capability of the fibers to form strong inter-fiber joints when the recovered paper is consecutively made into recycled paper (Pycraft and Howarth, 1980; Weise, 1998).

Additionally, application of chemical additives such as starch derivatives which are already used in papermaking industry as dry strength agent can be considered as another alternative for modifying the jointing capability of recycled fibers (Rudi *et al.*, 2019). By this means, these bio-chemicals have attracted a lot of consideration in papermaking section since they are not only non-toxic and biodegradable but also very cost-efficient due to their low price since they are abundant and available. Practically, starch is modified to the cationic form to adsorb electrostatically onto the negatively charged cellulose fibers. The adsorbed cationic starch increases the adhesive interaction between the fibers, leading to an increase in the paper strength. In one hand, applying starch strength-enhancing agent the strength development of paper products relies heavily on the amount of absorbed cationic starch on the surface of cellulosic fibers (Wågberg *et al.*, 2002). In the other hand, the absorption rate of cationic polymers on the anionic cellulosic fibers depends remarkably on electrochemical property or surface charge, the so-called zeta potential (ζ -potential) of fibers. In other word, the higher zeta potential means larger accessibility of functional groups, imparted the surface for larger potential of absorption of strength-enhancing materials, consequently resulted in paper sheet with higher strength properties (Blomstedt, 2007; Torgnysdotter *et al.*, 2007). In case of recycled fibers, the important practical implication of this method is that it might be possible to improve the strength properties of recycled pulps samples by controlled introduction of functional groups into pulp fibers.

Based on previous published reports, polyelectrolyte multilayering (PEMs) treatment through layer-by-layer (LbL) technique, as a new way in nanotechnology, can be applied to modify the electrochemical properties of fibers (Eriksson, 2006; Ryu *et al.*, 2009). Generally, PEMs is performed by treating a charged substrate such as cellulosic fibers with oppositely charged polyelectrolytes, with intermediate rinsing step (Carosio *et al.*, 2013; Hernandez-Montelongo *et al.*, 2017). The successful charge gain after every deposition step allowed a continuous cycling of the procedure for hundreds of layers (Chin *et al.*, 2012; Dewald and Fery, 2017), which imparted a larger potential to the fibers surface for the higher absorption of target materials. Therefore, this study was intended to evaluate the formation of starch based PEMs system on the recycled fibers. It was also aimed to explore the impact of pulp pH, electrolyte (salt) content and starch degree of substitution on the variation of zeta potential of the fibers. Finally, the strength gain was investigated in the resultant papers during PEMs treatment.

Material and Methods

Fibers

The recovered papers of old corrugated container (OCC) were selected as a typical sample of recycled fibers which nowadays is widely used in papermaking industry for manufacturing different packaging grade papers. First, the contaminants and non-cellulosic parts of OCC papers were removed by hand. Then, preparation and disintegration of pulp fibers was done following SCAN-C 25:76 standard method. Accordingly, the papers were manually torn into small pieces approximately 25 mm × 25 mm in size and soaked in tap water (conductivity $\sim 217 \pm 8 \mu\text{S}/\text{cm}$) for at least 4 h. Then, the soaked sample (360 g oven dry weight of paper) was disintegrated in 23 L tap water by using laboratory L&W Valley Beater to separate the fibers of OCC papers. To complete the disintegration process, the pulp fibers were therefore screened by using laboratory flat screen Voith Sulzer. It includes a chromed plate slotted sieving mesh with size of about 0.2 mm in wide for removal of fiber bundles and oversize components. Finally, the screened pulp was fractionated according to SCAN-M 6:69 by means of Bauer McNett fiber classifier apparatus equipped by sieve frames with screens of 30, 50, 100 and 200 mesh, to prepare pulp free of fines. The fraction of pulps retained before the wire sieve No. 200 with freeness of about $345 \pm 10 \text{ ml CSF}$, which was measured by L&W CSF tester according to TAPPI T-227 om-99 method, collected and stored in lab refrigerator ($\sim 5^\circ\text{C}$) for using in subsequent experiments.

Chemicals

Cationic and anionic cassava starch was provided by Siam Modified Starch (SMS) Co., Ltd. The cationic starch had been modified with a quaternized ammonium group to a degree of substitution of 1.8, 2.7 and 4.5%. For preparation of cationic starch (CS) solution, based on the supplier instruction, it was evenly dispersed in deionized (DI) water, and heated steadily to reach the temperature of about 95°C under continuous stirring. The cooking process continued for about 30 min more under the same temperature ($\sim 95^\circ\text{C}$). In order to avoid changing of starch concentration through the water evaporation during cooking of starch solution the top of the Erlenmeyer flask containing starch solution was covered by aluminum foiling. Finally, after cooling down of the solution to room temperature, the prepared solution of cationic starch was ready and used for the tests only within 24 h.

The anionic starch (AS) has been modified by oxidation of alcohols groups into the carboxylic acid groups to a DS of about 14.5%. This type of starch was also prepared in accordance with the manufacture's recommendations. Accordingly, the anionic starch was soluble in cold water, and used after complete solubilization by homogenous agitation in cold DI water for about 30 min.

Methods

Fiber Treatment

LbL multilayering of starches was carried out by alternate adsorption of cationic and anionic starch onto the OCC pulp fibers. For each step of treatment, 500 ml fiber suspension containing 3 g dry fibers was used. Dynamic Drainage Jar (DDJ) apparatus (Electro-Craft Motomatic II, Canada) was applied to mix the fiber suspension and the starches solutions. The pulp fibers were firstly treated with cationic starch, 1% based on the OD weight of fibers. After mixing of fiber suspension and cationic starch solution for about 10 min, the sample was properly washed three times on a filter paper No. 4 in a Büchner funnel by using DI water prepared from reverse osmosis (RO) storage tank. Rinsing is quite important as it removes weakly attached, physically adsorbed components, thus preparing the fibers surface for subsequent adsorption [Lvov, 18]. At the next step of experiment, the washed pulp was consecutively treated by anionic starch with the addition of 1% based on the OD weight of fibers, and washed again by the same way as explained above. This assembles 1 bi-layer of starch polyelectrolytes on the fiber surface. The experiments were conducted to build up to 8 consecutive layers. Fig. 1 represents a schematic procedure of polyelectrolytes multilayering used

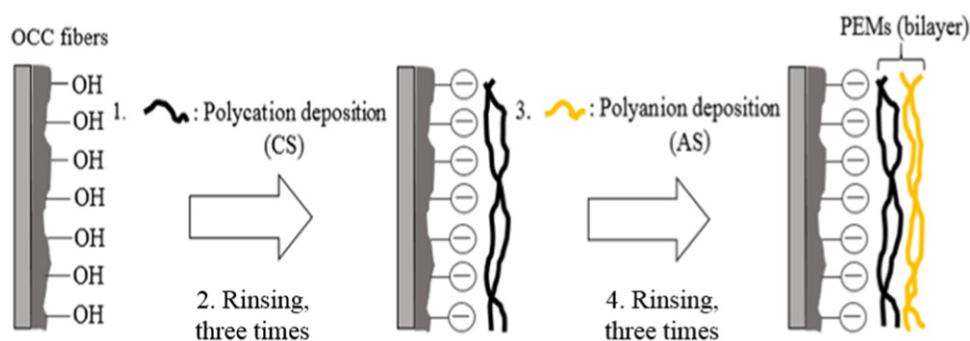
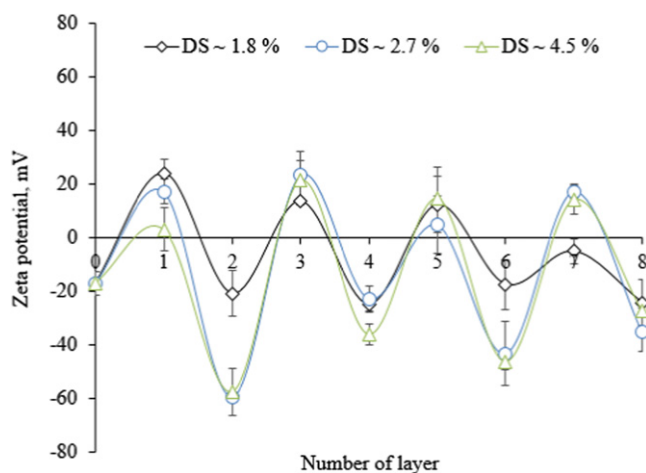


Fig. 1 A schematic illustration for layer-by-layer technique to fabricate two layers of polyelectrolyte on the negative charged OCC fibers surface (The procedure may be repeated to assemble higher number of layers on the fibers).

Table 1 Variables of current study

Parameter	Unit	Value
pH	–	5, 7 and 10
Salt concentration	M NaCl	0.001, 0.01 and 0.1
DS of cationic starch	%	1.8, 2.7 and 4.5
Number of number	–	1 to 8

**Fig. 2** Zeta potential changes of recycled fibers during forming of starch PEMs with different DS. Each value represents the mean of three replicates $\pm$ SD.

in this study. Additionally, to figure out the impact of pH, pulp electrolyte content and starch DS on the variation of zeta potential of the fibers and the tensile strength of the resultant sheets, three pH strategies for pulp suspension (~ 5 , 7, and 10) were adjusted by using 0.5 N HCl and 0.5 N NaOH. Meanwhile, the pulp salt concentration were adjusted to the values of about 0.001, 0.01 and 0.1 M NaCl, which represents pulp electrolyte content to about 140, 1160 and 10,570 $\mu\text{S}/\text{cm}$, respectively. **Table 1** represents the multilayering variables of this study.

Zeta Potential Analysis

Change on the Zeta potential of the treated fibers was measured by using a Mutek SZP-06 system after each step of LbL treatment of OCC fibers. Zeta potential (ζ -potential) of the fibers was detected to examine the charge characteristics of fibers surface and the success of cationic and anionic starch absorption. The procedure was repeated for each layer deposition until the assembly of 8 layers. The ζ -potential experiments were carried out in triplicates and the average $\pm$ standard deviation (SD) values have been represented.

Sheet Preparation and Testing

Handsheets at grammage of about $60 \pm 3 \text{ g}/\text{m}^2$ with $16.5 \text{ cm} \times 16.5 \text{ cm}$ in size were made of both untreated and treated fibers using laboratory handsheet maker. They were pressed at 400 kPa for 5 and 2 min, respectively and dried at 120°C for 2 h. Handsheets were conditioned according to SCAN-P2:75 at constant temperature of $23 \pm 1^\circ\text{C}$ and relative humidity $50 \pm 2\%$ before testing. Tensile index measurement was conducted according to SCAN P-67:93 by means of Tensile Tester, MTS Synergie 200. The system is equipped with 1 kN load cell and controlled by TestWork V.3.09 software. All the experiments were carried out in triplicate to confirm the experimental results, and the average of the values as well as standard deviation were presented, only if the percent relative standard deviation for samples was less than 5%.

Results and Discussion

Effect of Starch DS on Fibers ζ -Potential

The changes in the zeta potential after adsorption of starch layers on OCC recycled fibers as a function of starch DS are shown in **Fig. 2**. Based on the results obtained, the reversion in zeta potential showed the formation of starch PEMs successfully onto the

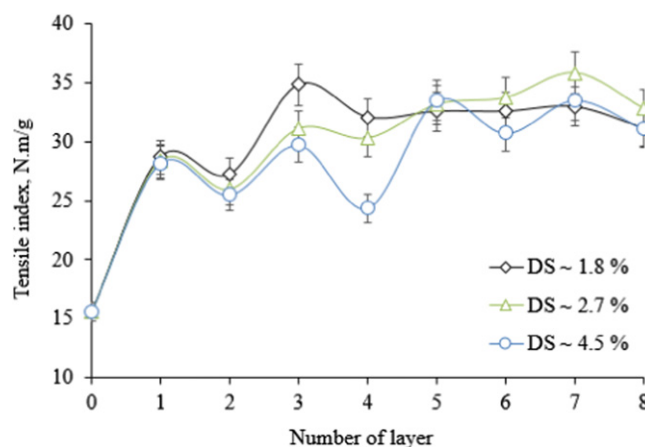


Fig. 3 Tensile index of sheets made from OCC fibers treated by PEMs with various DS of starch as a function of layer number. Each value represents the mean of three replicates $\pm$ SD.

OCC fibers surface for all starch DS combination used in this investigation. In consistent with previous results, measurement of zeta potential is a standard way to detect the achievement of polyelectrolyte multilayers construction, leading to a clear change of fiber charge after each layer assembly (Xing *et al.*, 2007; Bellanger *et al.*, 2017). Further, the starch DS shows influence on zeta potential of the fibers. The zeta potential for untreated OCC fibers, for example, due to negatively charged groups partially dissolved at the fibers surface detected a net-negative value of about -16.9 ± 4.4 mV. It was reversed to the values of about $+24 \pm 5.1$ mV and $+3.1 \pm 8.2$ mV, when starch with DS of about 1.8% and 4.5% was used, respectively. First, this verified the assembly of the first cationic layer onto the fibers surface. Secondly, by depositing of starch with low DS ($\sim 1.8\%$), the sign of the net charge was higher in the first assembled layer, which shows more effective growth of cationic layer on the fibers surface for the first layer. For the first layering, polyelectrolyte adsorption is largely influenced by the surface properties of the fibers and therefore a higher amount of lower DS starch is required to neutralize the surface charge of the fibers (Laurant and Schlenoff, 1997; Ladam *et al.*, 2000). On the contrary, by assembling of starch with high DS ($\sim 4.5\%$), the sign of the net charge was higher in larger number of layering (5th layer). This implied that higher absorption of starch took place at larger number of layer. This is attributable to the correspondence between charge property of pair polyelectrolytes, i.e., cationic and anionic starch. On other words, higher DS cationic starch accompanied by a greater charge balance with an anionic starch would lead to further adsorption, more stable ionic starch layers and higher zeta potential. This consequences higher affinity of fibers surface for higher absorption of strength-enhancing materials such as cationic starch, which remarkably affects the strength properties of the papers (Hubbe *et al.*, 2005).

The tensile index of sheets prepared from LbL-treated OCC fibers using various DS of starch as a function of layer number is shown in Fig. 3. The results shows improvement of the strength with starch PEMs formation in all DS combinations. The results also indicates that the DS of starch was influent on tensile index of the resulting papers. In accordance with the higher value measured for zeta potential, the tensile index of the sheets improved as a function of the number of adsorbed layers and depended significantly on the DS of the applied cationic starch. Correspondingly, when starch with DS of 1.8% was used, the prepared papers were stronger than those of papers made from the fibers treated with greater DS of starch, particularly in assembling lower number of layers (1st and 3rd). However, on increasing the number of layer assembled on the fibers the tensile index of the sheets increased significantly and the highest tensile index was obtained in the outmost layers (7th layer) using cationic starch with higher DS (DS $\sim 4.5\%$). As previously mentioned, greater charge balance between cationic and anionic starch would lead to more stable layers, therefore resulted in enhancing the tensile strength of the paper sheets.

Generally, recycled fibers treated by PEM deposition of ionic starches exhibited different properties from that of untreated fibers. This fact is confirmed by the different appearance of the surface and the fibers network, indicating the ability of PEM treatment for engineering the fibers surface characteristics. Based on SEM and AFM results in Fig. 4, sequential deposition of the strength-enhancing polyelectrolytes can increase the surface roughness of recycled fibers due to growing adsorption of cationic starch on the fiber surface, which resulted in generating a gel-like appearance on the surface improving inter-fiber ability between the recycled fibers.

Effect of Salt Concentration on ζ -Potential

Pulp conductivity which represents the amount of dissolved salt ions in the aqueous solution of fibers slurry is another important parameter affecting the electrochemical property of fibers and polyelectrolytes. Therefore, zeta potential values of cellulose fibers suspended in water may be profoundly affected by changes in the conductivity of the aqueous medium (Youn *et al.*, 2007) Fig. 5 shows the effect of different conductivities of pulp suspension on zeta potential during LbL treatment of OCC recycled fibers. As can be seen, the measured zeta potential is higher for the suspension free of salt ions (0 M of NaCl) in the first layering of cationic

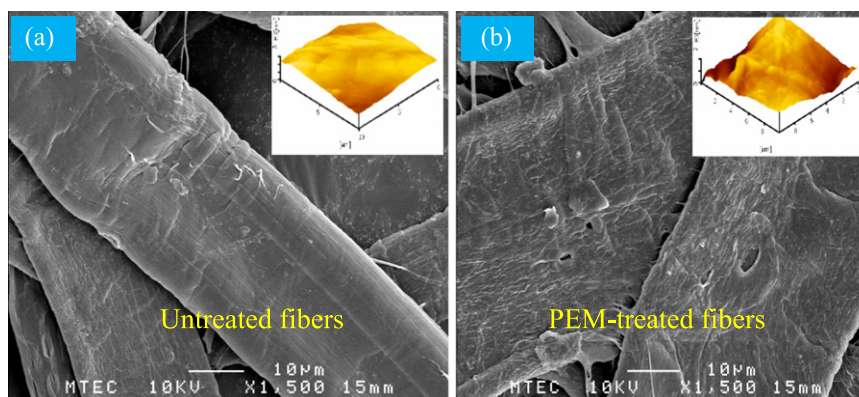


Fig. 4 SEM and AFM micrographs of the paper sheet surface (10 g m^{-2} basis weight): (a), paper made from the untreated recycled fibers; (b), papers made of the PEM-treated recycled fibers.

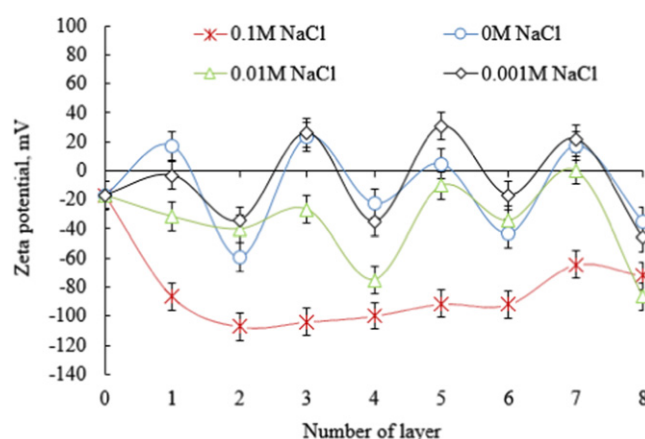


Fig. 5 Zeta potential changes of recycled fibers during forming of starch PEMs in different salt concentration. Each value represents the mean of three replicates $\pm$ SD.

starch, where there is possibility to occur both electrostatic and non-electrostatic interaction to absorb starch molecules on the fibers surface (Lundstrom-Hamala *et al.*, 2010). General suggestion is that the solution media, in this case, is the best environment for fiber surface ionization and polymer adsorption both through ionic attraction and a non-ionic interaction such as hydrogen bonding. Additionally, in the following layers, at NaCl concentration of about 0.001 M, especially when the outermost layer is cationic (odd-numbered layer, 5th and 7th layer), zeta potential is higher than those of other levels of conductivities. The output is consistent to the result from Youn *et al.* (2007). They reported that higher zeta potential was obtained when pulp fibers were multilayered at the condition of slightly salt concentration.

Meanwhile, at the electrolyte content of 0 and 0.001 M of NaCl, due to the least negative effect of salt cations, there is a regular variation in zeta potential. However, at 0.001 M of NaCl, the measured zeta potential of the fibers is higher than that of samples without any salt cations, which could be expected for the recycled fibers to absorb greater ratio of starch. In consistent with current findings, earlier reports have demonstrated that effective size or less extended conformation of the polyelectrolyte in fibrous slurry or “coiled-up” conformation of the polyelectrolytes in the aqueous solution (Youn *et al.*, 2007; Ryu *et al.*, 2009) are responsible for increasing polyelectrolytes adsorption. Fig. 6 illustrates a simplified scheme of coiled-up conformation of polyelectrolytes in the salty aqueous solution.

The effect of conductivity during LbL process on tensile index of the papers has been presented in Fig. 7. It is apparent that strength improvement in this system was connected to the number of layer assembled onto the fibers. Expectedly, the tensile value obtained for the first layering was higher when the pulp suspension has no salt ions, 0 M of NaCl. The most acceptable suggestion is that the first layer is controlled both by electrostatic and by non-ionic interactions between fibers and polyelectrolytes (Lundstrom-Hamala *et al.*, 2010). Therefore, the environment without any salt cations results in better situation for non-ionic interactions such as hydrogen bonding between cellulosic fibers and starch molecules. Simultaneously, electrostatic ionic interactions may also take place since a media without salt outcomes a reduction of Debye screening length. However, in the subsequent layering where the electrostatic attraction is only the driving force for adsorption process (Sukhorukov *et al.*, 1998), a low content of conductivity, 0.001 M of NaCl, contributes to the polyelectrolytes more efficient conformation of polyelectrolytes

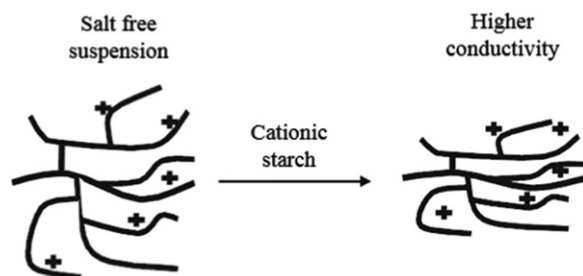


Fig. 6 The effect of increased conductivity on conformation of cationic starch molecules.

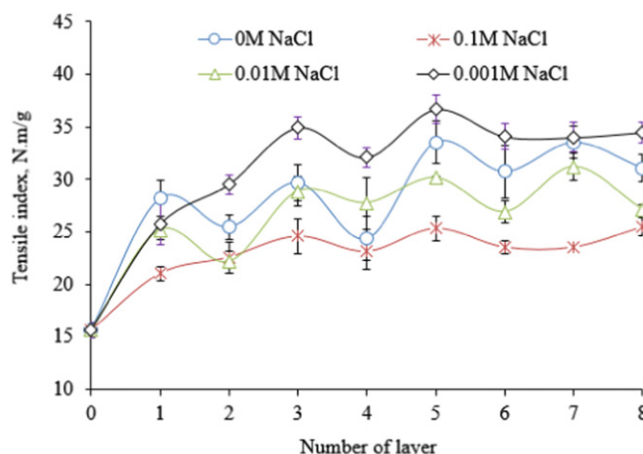


Fig. 7 Tensile index of sheets made from OCC fibers treated by starch PEMs under various conductivities as a function of layer number. Each value represents the mean of three replicates $\pm$ SD.

on the fiber surface as what explained for the variation of zeta potential. In line with current result, Larsson and Wall (1998) demonstrated that adding aluminum salts accompanying with cationic starch improves the system efficiency of starch retention. Furthermore, Ryu *et al.* (2009) reported that at low conductivity because of coiled-up conformation of polyelectrolytes in the aqueous solution, the adsorption ratio was higher. As a result, at low salt concentration of 0.001 M of NaCl, with 140 μ S/cm electrical conductivity, tensile index was remarkably increased. It was improved more than double after five layering compare to the control sample. In addition, the improvement of tensile strength was dependent on the type of outermost layer, i.e., cationic or anionic. For all electrolyte values, tensile strength improved with cationic starch, particularly when 7 layers of polyelectrolytes assembled on the fibers surface. Moreover, at higher salt concentration of about 0.1 M of NaCl, tensile strength decreases significantly. Probable explanation is that the electrostatic attraction between polymer particles and carboxyl groups on the fiber surface is screened and the adsorbed amount decreases (van de Steeg *et al.*, 1993). Another suggestion is that a high conductivity may shrink the effective size of the flocculent polymer and consequently reduces its efficiency (Wang and Hubbe, 2001).

However, in such environment added polyelectrolytes can develop the adhesion between the fibers by developing the molecular contact area and/or the number of effective fiber-to-fiber joints, which result in forming more compacted and dense paper sheets with higher tensile strength, and lower apparent thickness, as depicted in Fig. 8.

Effect of pH on ζ -Potential

Fig. 9 shows the change in zeta potential of recycled fibers during LbL treatment at different pH values. In general, an alternate fluctuation of zeta potential demonstrates the consecutive fabrication of the multilayers of cationic and anionic starch on the surface of recycled fibers in all pH values of pulp suspension. However, the results indicate less change in zeta potential were achieved at acidic pH value (pH $\sim$ 5), due more to the lower dissociation of both carboxylic acid groups on the fibers surface and polyelectrolyte molecules in the fibers suspension. On the contrary, higher zeta potential was achieved at higher pH values of fibrous slurry (pH $\sim$ 7.5 and 10), which lead to obtain more cationized fibers within the following cationic starch layering. This is in consistent with earlier reports (Youn *et al.*, 2007; Ryu *et al.*, 2009). Pulp treatment under alkaline pH conditions affects the ionic character of fibers and additives applied to absorb on fibers surface. There are some reasons with respect to the effect of pH on fibers behavior. One idea is that higher pH of pulp suspension lead to swell the fibers structure for greater accessibility of functional groups which react with additives particles effectively. Another suggestion is that it increases the degree of dissociation

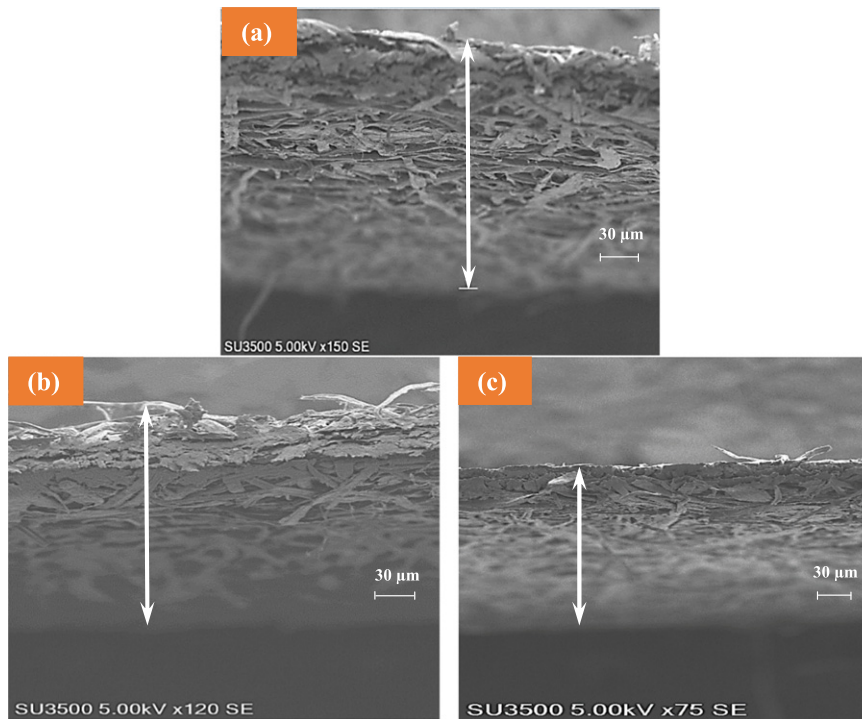


Fig. 8 SEM images of the thickness of paper sheet (60 g m^{-2} basis weight) made from (a) original CMP fibers, (b) untreated recycled CMP fibers, and (c) PEM-treated recycled CMP fibers.

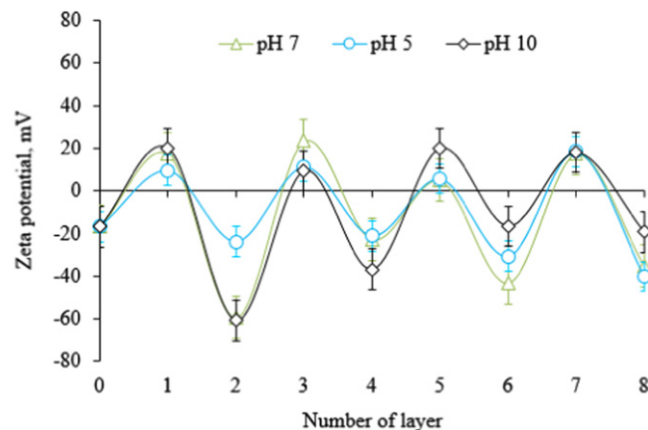


Fig. 9 Zeta potential changes of recycled fibers during forming of starch PEMs in different pH. Each value represents the mean of three replicates $\pm$ SD.

of polymers molecules and the carboxyl groups at the fiber surface, which consequently increases the joints potential between fibers and additives (Wang and Hubbe, 2001; Ryu *et al.*, 2009).

Fig. 10 shows how tensile index of the sheets made of untreated and LbL-treated fibers was changed under the investigated pH of pulp suspension. Tensile strength of paper was determined by two key factors, fiber strength and bonding strength (Page, 1969). Since polyelectrolyte multilayering does not change fiber strength, tensile strength of paper could be regarded as jointing ability between fibers (Ryu *et al.*, 2009). It has been suggested that the starch increases the specific joint strength and the molecular contact area and the number of efficient fiber-fiber joints are possibly also increased (Howard and Richard, 1992). Moreover, the increment in tensile strength with starch addition is largely due to improved specific bond strength and increased stiffness of bonded areas (Ghasemian *et al.*, 2012). However, it has been shown that the strength enhancement is dependent on the amount of starch that can be adsorbed onto the fibers (Wågberg *et al.*, 2002).

The measured tensile index for the untreated sample was about $15.6 \pm 0.7 \text{ N m/g}$. It was significantly increased with polyelectrolyte multilayering of starch at all pH values. The tensile was also depended on the layer number at all pH values. Further, the highest value of tensile strength for the first layer was revealed at pH ~ 10 ($\sim 28.3 \pm 1.5 \text{ N m/g}$). Meanwhile, when the outer layer was anionic,

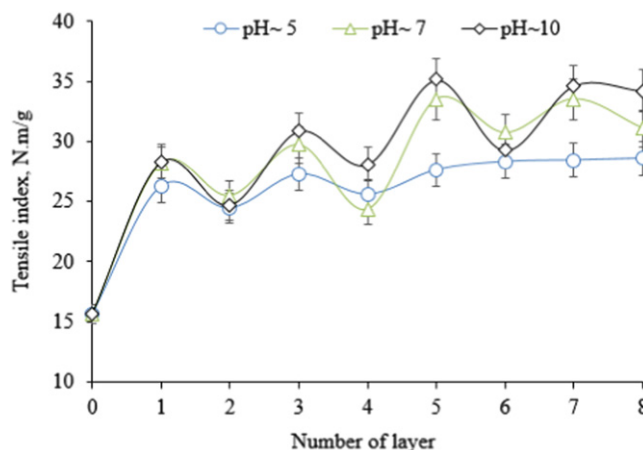


Fig. 10 Tensile index of sheets made from OCC fibers treated by starch PEMs under various pH as a function of layer number. Each value represents the mean of three replicates $\pm$ SD.

almost in all our experiments, tensile strength has been decreased relative to the previous cationic layer. A good correlation between pH during starch adsorption and the improved tensile strength was also detected. As can be seen in Fig. 8, the development of the strength was higher at pH ~7 and 10 and only minor differences were seen between the results of these two pH values. The maximum increase of tensile index to the value of about 35.1 ± 1.8 N/mg was observed when the outermost layer was cationic for the alkaline condition at pH ~10. This was obtained after constructing of five layers of starch. In other words, this showed a dramatic increase of about 125% in the tensile index compare to the paper made from untreated fibers. These findings are in agreement with previous reports (Wågberg *et al.*, 2002; Eriksson *et al.*, 2005). Generally, the pH value can affect the dissociation of various different types of carboxylic acid and other groups within cellulosic fibers (Lloyd and Horne, 1992; Youn *et al.*, 2007). In addition, it can change the conformation and degree of dissociation of polyelectrolytes in the fibrous suspension (Ryu *et al.*, 2009). It is clear that the fibers and polymers with higher active functional groups result in higher absorption of polymer particles onto the fibers surface. As a result, the resulting papers could be stronger due to the larger jointing potential of the fibers.

Conclusions

In current study, the role of the influential factors, such as starch DS, pH value and salt content of fibrous suspension, on formation of starch PEMs onto the OCC recycled fibers was examined. In PEMs formation, starch with different DS reveals significant influence on zeta potential of the fibers. For the lower number of layering, lower DS starch is more effective to neutralize the surface charge of the fibers, resulted in stronger papers. By contrast, higher DS starch would lead to more stable starch layers, higher zeta potential, and improved papers in larger number of layers. Furthermore, the electrolyte content of the pulp suspension has both positive and negative effect on the zeta potential and strength property of the papers. At lower amount of salt concentration, the zeta potential of fibers was higher, and the prepared paper was stronger than those of papers made from the pulp with higher conductivity. Greater electrolyte content screens the charge of fibers, and deteriorates the paper strength. Meanwhile, zeta potential of recycled fibers was dependent on pH value of pulp slurry during PEMs fabrication. The pH value in alkaline range is believed to further ionize functional groups in cellulosic fibers and starch particles, develops the joint affinity between them, which consequently makes stronger the papers made from recycled fibers.

See also: Development of Self-Adhesive Products Using Only Bamboo Fibers Extracted With a Machining Center. Jute/Coir/Banana Fiber Reinforced Bio-Composites: Critical Review of Design, Fabrication, Properties and Applications. Kenaf Fiber Based Bio-Composites: Processing, Characterization and Potential Applications. Kenaf Fiber Reinforced Composite in the Automotive Industry. Natural Fiber and Synthetic Fiber Composites: Comparison of Properties, Performance, Cost and Environmental Benefits. Natural Fiber Reinforced Composites in the Context of Biodegradability: A Review. Recyclability of Natural Fiber-Filled Thermoplastic Composites. Sustainable Biofuels for Automotive Applications. The Utilization of Vegetable Fibers in Cementitious Materials. Use of Bio-Fibers in Various Practical Applications

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Further Reading

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Internet of Things Platform to Encourage Recycling in a Smart City

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Introduction

The value that information has received in recent years is incalculable. Until less than a decade ago, storing data seemed far from having a benefit, implying a high cost that in many cases could not be assumed. Advances in computing have made the analysis of information one of the main interests for scientists. These scientists, applying traditional techniques of artificial intelligence in a distributed way, manage to extract in many cases a valuable knowledge that was previously unthinkable (Sanchez *et al.*, 2014; Zygiaris, 2013).

One of the main sources of data generation that can lead to great benefits is the city. The beneficiaries are their citizens. According to numerous studies (Chamoso *et al.*, 2018b), cities can generate large amounts of daily data, spread across a wide range of sectors. The sectors of energy, traffic and public transport, services or public administration are just examples of sectors that can greatly benefit from the analysis of information generated in a city.

Over the last few years, different studies have been carried out to create distributed platforms adapted to recover that information, process it, and put it to the benefit of citizens through different applications. Some well-known examples are the platforms deployed in cities such as Barcelona (Bakici *et al.*, 2013), SmartSantander (Gaur *et al.*, 2015), or Málaga (Carillo-Aparicio *et al.*, 2013). However, there is still no standard that has been taken as a model to follow when deploying a platform that turns a city into a smart city; even within these vertical platforms there are many modules that can be developed from the layer applications such as applications that encourage citizens to carry out beneficial activities for the community.

One of these activities may be to encourage the users of a city to recycle waste. And it is necessary to implement solutions to the problem of what to do with garbage. The vast majority of European countries have adopted measures to recycle this waste (Candanedo *et al.*, 2018; Rivas *et al.*, 2018b).

One of these measures was the creation of urban waste treatment plants to manage the waste generated in the cities. However, for these plants to perform their recycling function it was necessary to develop a waste collection network. In the European Union (EU) there is no common method in waste management. Some countries have deployed a series of colored containers in which the user introduces the waste according to its type; in other countries it is in supermarkets where the consumer is allowed to deliver a series of waste and packaging for recycling. The use of these measures has allowed the recovery of numerous tons of garbage that were previously completely discarded in landfills, obtaining numerous benefits for both humans and the environment.

One of the main disadvantages of these systems is that the recycling of waste is often done altruistically, so it would be interesting to develop a mechanism that encourages this recycling to turn our cities into smart cities. This mechanism can be a module of a smart city platform with those mentioned above or a platform in itself, which can obtain its own data, process it, and make decisions. That is why this article proposes a platform based on agents that take care of all the processes that an Internet of Things (IoT) platform must incorporate to be incorporated in a smart city. The platform of agents thanks to the use of a gamification algorithm performs the task of encouraging users to recycle waste and communicates with the users' mobile application for bidirectional communication processes and that the user knows the state at all times of the achievement of the challenges.

The rest of the paper is organized as follows. The section "Related Work" contains all the works related to this article. The proposed system is shown in the section "Proposed System." The section "Simulation Results" presents the main results of our model and the Conclusion shows the conclusions of our findings.

Related Work

This section reviews the three concepts on which the proposal is based (recycling methods, gamification, and IoT platforms). First, the current methods of recycling in the EU are presented, then the advantages of gamma techniques are shown, and finally the IoT platforms that allow the incorporation of gamma techniques for the encouragement of recycling and how these techniques will help us to increase citizen participation.

Recycling Methods

To prevent large quantities of waste from being deposited in landfills and being converted back into useful materials, it was necessary to develop methods that would allow this waste to be collected separately and structurally so that it could be recycled.

In the EU each country developed different methods to deal with this problem of garbage collection. Spain was the first country to install glass collection containers in 1982. It was in that same year, when a model of cooperation between Autonomous

Communities, local corporations, and manufacturers of glass containers was established for the management of the recycling of this element. In 1994, Directive 94/62/EC dictated the framework on which all the legislation of each of the countries of the European Community was to be developed.

At a general level, two predominant recycling models were developed in the EU within the European legislative framework, in which most of the countries that make up the EU are included. The first model consists of the deployment of colored containers according to the waste for which they are focused. Within this model there are small differences according to each country, such as the color of the container for each package, apart from the containers of urban waste and oil.

However, color identification is not identical in all countries that have adopted this model. For example, in Spain three containers are deployed: Blue (paper and cardboard), yellow (plastic waste), and green (glass). In France, there are three containers: Yellow (paper and cardboard), blue (plastic and aluminum), and green (glass). In Italy the colors also vary with respect to Spain and France. In addition, another variant is when the process of waste collection is carried out, which is governed by an annual planning that sets the days for throwing out the garbage (usually two days a week). The garbage must be deposited the day before the day set in the planning, and in some countries people can receive a fine if they do not recycle. There are even major differences; in Norway the system differs slightly, with one container for organic waste and another for paper and cardboard. The plastic is deposited in special bags, which are placed next to the paper and cardboard container. The glass is placed in special containers next to the supermarkets.

The second method widely adopted in Europe is the Deposit Refund System (DRS), which is being implemented in Germany, Sweden, and Denmark. In this model, in the purchase process the user pays a fee that includes this kind of waste, which is recovered once the container is deposited in perfect condition in the machines intended for collection; the user receives a ticket with which they can get this fee refunded. The DRS is complemented with the colored-container method, as in Germany.

Both methods have a good reputation and acceptance in the countries in which they are deployed, however, both methods have a number of points to review for improvement. The colored container recycling model has one disadvantage: It only allows the collection of some materials and the DRS model only serves to recover plastic or metal containers. Specifically, the DRS only allows the management of 8% of the packages, while, the model of colored containers takes care of 80% of the packages. The operation of the DRS model is linked to machines installed in supermarkets, so that citizens only deposit their packaging at the time when these establishments are open. In addition, in the DRS model the containers are engraved with a tax that the citizen has to pay when buying a product, in case the container presents a flaw or a dent and cannot be recovered.

Both models can therefore be improved, and even benefit from each other's advantages. Recycling by imposition (possibility of being fined) means that this process is carried out with reluctance and without paying attention to the correct recycling in the model of colored containers. The DRS system simply recovers the money that was paid for each container when they were purchased, and a very small percentage of containers are managed by this model.

Gamification to Encourage the Recycling of Garbage

Gambling is a technique that has been developed for incorporation into certain daily activities for their incentive through the use of the mechanisms of play. Gamification arises within the educational sphere. The games are part of a set of activities that promote learning in a playful and interactive way. These games use the typical characteristics of entertainment games to tackle learning tasks, comprehension or social impact, tackling both cognitive and affective dimensions in such a way that they are very interesting for the objectives set out in this proposal. For this purpose, dynamism and gameplay concepts are used that make participation and interaction a stimulus in the learning process.

Gamification uses the characteristics of games with a purpose beyond entertainment and clearly focused on learning. Gaming in the recycling field allows for increased citizen participation in these tasks, allowing rewards to be given to users who perform correct actions according to fixed rules and receiving penalties in the opposite case.

The use of this technique can be focused on increasing the level of participation while maintaining the citizen's commitment to the environment. This technique has recently been used in fields such as home energy efficiency with very satisfactory results ([García et al., 2017a,b](#)). However, it has been detected that it has not been used in the field of recycling so it is interesting to know if this technique produces satisfactory results in this field as well.

Internet of Things Platforms

An IoT platform is the basis for devices to be interconnected and generate their own ecosystem. In other words, a web platform integrated to the IoT is the software that connects hardware, access points, and data networks to what is usually the application the user connects to. The market for IoT platforms is booming and continually expanding; in fact, there are surveys that say that more than 80% of companies believe that the field of the Internet of Things is the most interesting for their businesses. In addition, these platforms are necessary to solve middleware problems.

There is a wide variety of IoT platforms; however, to face the problems we are facing, it is necessary that this platform has a wide capacity to communicate, coordinate, interact and cooperate to carry out different actions. A methodology that combines these characteristics in the development of platforms is the multiagent system (MAS).

These characteristics have allowed this methodology to be applied in works with objectives as varied as the management of drones for livestock monitoring or as a legal control platform for drone flights (Rivas *et al.*, 2018a; Chamoso *et al.*, 2018a), aid in the systems of currency exchange in airports (Chamoso *et al.*, 2019), classification of facial images according to gender and age (González-Briones *et al.*, 2018f), optimization of energy consumption (González-Briones *et al.*, 2018e,b,c,a,d), being in all of them a methodology that has been adapted with high precision to the needs of the problem. It is for this reason that these systems have been widely accepted by the scientific community due to their intrinsic characteristics that allow them to be used in such diverse contexts. They are widely used to model behavior, simulate situations, or solve problems that are difficult or impossible to solve for a monolithic system.

The ability to interact between them without the need for any action on the part of the users gives them their own autonomy that empowers them with the capacity to perceive changes in the environment and react to them, being, therefore, a very propitious methodology for capturing data, learning behavior patterns, and making decisions in the face of changes. The multiagent systems as a basis for the development of an IoT platform allows modeling different architectures based on the above tasks for the development of activities within the field of recycling ranging from behavior simulation, learning behaviors associated with recycling, the efficient management of waste within supply chains, or learning behavioral actions of users.

The agents that make up the platform have their own autonomy that allows them to carry out the aforementioned tasks, making it a very suitable methodology for capturing data, learning behavior patterns, and making decisions in the face of changes. Multiagent systems have been used in different proposals within the field of recycling, from simulating behavior, learning behaviors associated with recycling, the efficient management of waste within supply chains, or learning behavioral actions of users.

For this reason, this methodology has been used in works that meet some of the subobjectives set out in this proposal. One of these works is carried out by Meng *et al.* (2018) in which a platform is presented to carry out simulations of domestic solid waste recycling actions together with the carrying out of social surveys. The agents of the platform simulate different domestic scenarios and based on various decisions simulations are made but does not encourage citizen participation in recycling tasks. In another work such as the one presented by Yang *et al.* (2011) a system is presented for the evaluation of the economic sustainability of a waste recovery system by means of simulation based on agents. To assess economic sustainability, process recycling rate, and economic efficiency, sustainability metrics are used to evaluate and compare two recovery processes.

Another work based on multiagent systems is that carried out by Mishra *et al.* (2012), in which agents coordinate effectively to execute different tasks such as waste categorization, transport, waste recycling, waste management, and assignment of reusable products. The agents allow to carry out a management of all the activities that take place in the supply chain; the management of these complex tasks is carried out in an effective way thanks to the cooperation and communication of the agents that model the supply chain.

These works are a clear demonstration that the agent-based system proposed for the development of an IoT platform to enable efficient management in waste collection chains and collection decision making while encouraging citizen participation in a smart city. The use of multiagent system has shown a number of advantages to simulate this type of problems and learn from the actions taken for decision making.

The development of a platform based on an architecture based on agents that adapts to the needs raised makes it possible to manage independent environments to make more optimized decisions, being able to take these decisions by quadrants, neighborhoods, or regions within a smart city. In addition, thanks to the use of gamma techniques, the platform will reward the neighbors with the greatest participation and will penalize those who do not participate. The platform will have communication with users thanks to the mobile application used by users to measure user participation. As a model for the development of the platform is the one presented by Rodríguez *et al.* (2011), whose contribution is the ability to make dynamic and adaptive plans to distribute tasks among agents (container status, transport management, gamification process, or user management among others). Context-Aware Framework for Collaborative Learning Applications is used for the development of the gamification system as a basis for its technical and social features implementation (García *et al.*, 2015, 2017c). The system learns from the actions taken by users to adapt to them and provide new solutions to increase the recycling rate and citizen participation.

Proposed System

This section details the architecture that has enabled the technical development of the multi-agent system that implements the IoT platform that captures the data and the gamification system for the participation of users.

Infrastructure

Agents of the IoT platform communicate with the mobile application to get information from users. The mobile application captures this information from the infrastructure that needs to be deployed for the case study. This infrastructure should not mean a change in recycling model currently deployed, but a small deployment of sensors that allow data capture. The information that is required by the platform and that must be sent by the mobile application is a structure that contains data related to the quantity, type of waste, the user who performs the action, as well as the state of filling of the containers and degree of occupation of the nearest waste treatment plant.

The infrastructure installed in each container consists of the following devices: (1) a QR code reader enabling the user to be identified. (2) GPS locator, which indicates the coordinates at which the container is located. (3) Weight sensor weighs the amount of waste introduced into the container. (4) Volumetric sensor, it allows to know the state of filling of the container. (5) NarrowBand IOT (NB-IoT) communication technology, for data transmission to the system. NB-IoT technology allows data transmission over long distances. (6) Solar panel, which feeds the different sensors deployed in the container so that the system is independent at the energy level.

The process of interaction between the user, the application, and the platform begins at the moment in which the citizen deposits the waste in a container, then the data structure is generated to be received by the mobile application and then sent to the IoT platform composed of the following fields: User id, type of waste, amount of waste, container id, location of the container, filling status of the container. The data structure is sent via the MQTT protocol using the NB-IoT network to a local station. The local station will act as MQTT broker sending the data in JSON format via REST services. There is a communication line between each container and the waste treatment plant that allows a collection truck to be sent to the containers that are complete (Dijkstra's shortest path algorithm is used to trace this route).

Multiagent Architecture

The architecture is based on agents as this allows to adapt to possible changes such as the growth of the number of containers or change of the location of the containers in the region to be managed. This architecture is therefore dynamic and self-adaptable in real time to the characteristics of the context of the problem.

This process of self-adaptation is determined by the goals, desires, and tasks of each agent (amount of waste to be recycled, percentage of participation, etc.), while taking into account the objectives of the other agents, cooperating among them to achieve the common goal and specific goals. The core of the architecture is a group of deliberative agents who decide autonomously how to act and at what moment to intervene in the collective solution. The functionalities of the agents are not within their structure, but modeled as services. This methodology grants a wide capacity of adaptation to changes and in the recovery of errors. As it has been possible to extract from the review of the state of the art, a multiagent system allows us to adapt to a changing environment such as the increase or change of the location of the containers.

The architecture used is organized in four layers, with the manage layer being the layer in charge of managing the MAS and communicating with the mobile application (Figs. 1–6).

- *Manage Layer.* This layer, made up of at least one agent, is in charge of deploying the rest of the main agents in each layer. This agent also coordinates communication with users through the mobile application to update the progress of each user on the platform.
- *Smart City Layer.* The agents of this layer receive the information from the data structures that are received by manage layer. This layer checks the status of the containers to make decisions if necessary. Big data engine agents analyze the data received by complex event processing for pattern recognition. The architecture has an open data agent to acquire relevant data for analysis, such as meteorological data.
- *Data Layer.* The agents in this layer are in charge of capturing data from the infrastructure deployed in the smart city. IoT agents communicate with the agents deployed in the infrastructure layer to build the data structure that collects the data about the waste deposit in a container, which is sent in JSON format through REST services. The IoT broker performs the NGSI-to-NGSI (Next Generation Services Interface) conversion between IoT agents and the Context Broker agents, and the data is collected by data communication agents who transmit it for analysis to smart city intelligence layer.
- *Smart Government Layer.* This layer manages the results obtained by smart city layer for the collection of waste from containers or a larger deployment of containers in a certain area if the demand for waste collection or a larger shipment of trucks is not met. This layer is responsible for the process and gamification with the user, providing a bonus to or penalizing users with a decrease or increase in the rate of garbage imposed by the local government.
- *Infrastructure Layer.* The agents of this layer act as middleware between the users and the multiagent system. Each container has an associated agent that is responsible for generating a data structure (amount, type of waste deposited, user recycling, filling status of the container, occupancy rate of the nearest waste treatment plant). These agents, using LPWAN, send the information to the data layer agents.

The mobile application is a simple application developed in Android that manages the profile of users, updating the achievements of each user and showing the achievements or penalties achieved. The results shown are those that the application calculates through the smart government layer. This simple two-screen application also shows the economic benefit produced, the carbon footprint avoided by recycling, and other environmental information of general interest.

Mock-Up Simulation

To simulate the decisions taken by the architecture and by the users, a model has been developed by the BISITE Research Group. This model is designed to connect with multiagent architectures to evaluate the efficiency of IoT platforms in problems of energy optimization (demand response) or sustainability cities.

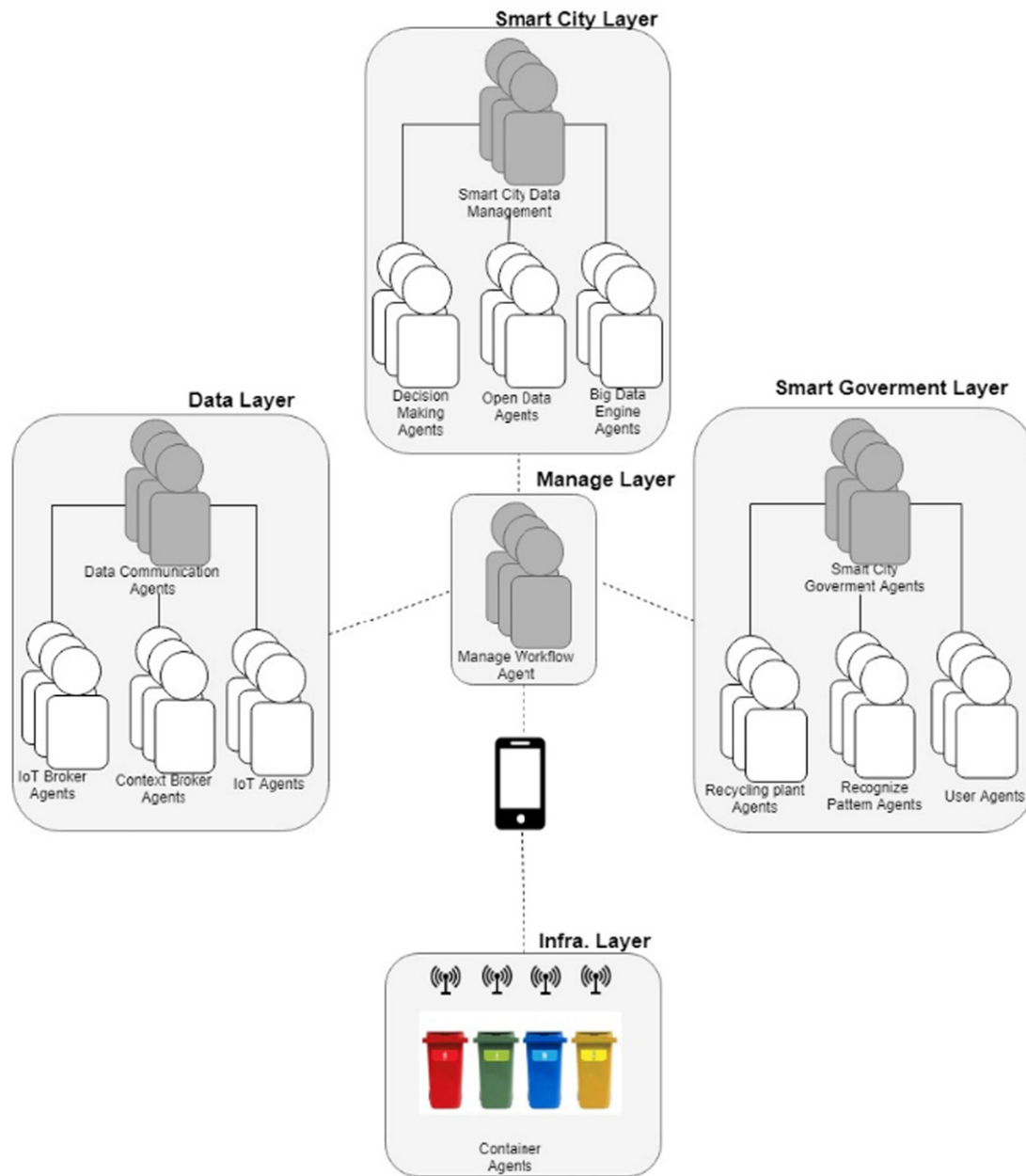


Fig. 1 Agent based Internet of Things platform.

In our case it has allowed us to simulate the results of the decisions of the algorithms of the architecture as to obtain the routes of waste collection by the shortest way using Dijkstra.

The model is designed in such a way that it can simulate from climatic conditions to electricity consumption by homes, neighborhoods, or regions defined by the user. In each of these neighborhoods is an electronic board, called cryptochip, which includes various sensors that can be referenced and integrated into different developments.

- The designed node has an accelerometer model LIS3DH with capacities to measure acceleration ranges from 0 to 16 g. This scale is dynamically adjusted according to the different needs of the moment.
- For temperature control, a TC1047A microchip sensor with ultra low power consumption of less than 35 μ A is available.
- For the positioning of the data it has a system of last generation of the manufacturer Ublox, the model MAX-M8Q able to obtain the positioning through the four global standards of positioning by triangulation: GPS, Galileo, GLONASS, and BeiDou, in this way the time is reduced to find a "fixed" of position and with it the initial consumption, the highest in this type of devices.
- The device is equipped with an HTFS 800-P power consumption sensor capable of withstanding voltages of up to 2 KV and amperage peaks of up to 800 A.

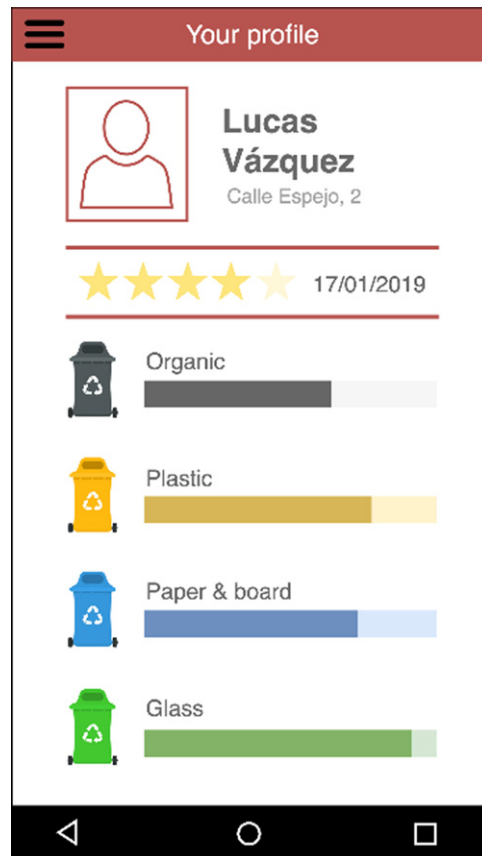


Fig. 2 Android application for the visualization of the achievements obtained by each user.



Fig. 3 BISITE Mock-up for the simulation of optimization problems, calculation of transport routes, sustainability problems in a smart city.



Fig. 4 Calculation of the route to be carried out by the garbage truck to collect the waste in a more optimal way, using the Dijkstra algorithm.

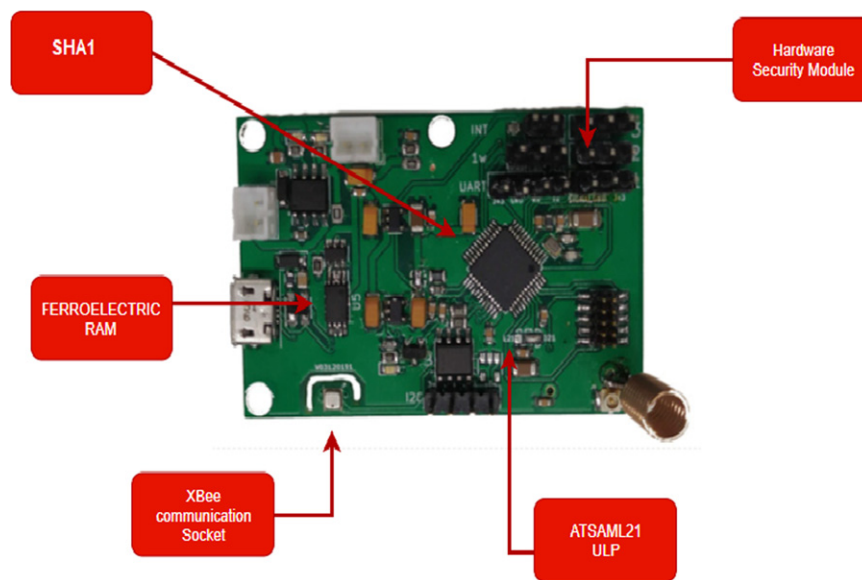


Fig. 5 Cryptochip board that manages the simulation of conditions and the sending of safe data in the model.

- It uses a LoRaWAN communication network based on LoRa modulation, due to its high noise tolerance and indoor penetration if necessary.
- ATSHA204A encryption chip with SHA1 technology.

This chip behaves like a generic gateway within the IoT paradigm. This implies that the strong points of the device are the security of the data it obtains from the environment, ensuring its reliability and in the same way transferring them safely to the upper layers of the developed architecture, being totally agnostic to them. Some of its functionalities are:

- *Data collection*, since it has the possibility of connecting multiple sensors in its pins allows to carry out a data collection depending on the type of project in which it is used.
- *Data encryption*, since it has a hardware encryption chip, it can apply an RSA signature to the data. This type of encryption algorithm is double key (public/private), therefore, the cryptochip can encrypt the information, send it, and in the destination application (or the blockchain itself) decrypt it to see the data.
- *Reading sensors*, thanks to its dedicated connectors, allows easy connection to several sensors simultaneously and have different methods of communication.
- *Reading and sending data in portable systems*, thanks to the possibility of being powered by a power bank and its low consumption, can be used in portable applications, in addition to carrying out the sending of data collected through the integrated communications modules thanks to the X-bee socket.
- *Integration in IoT systems*, thanks to the low consumption of the system, and the incorporation of wireless communication systems, allows the implementation of this board in IoT.

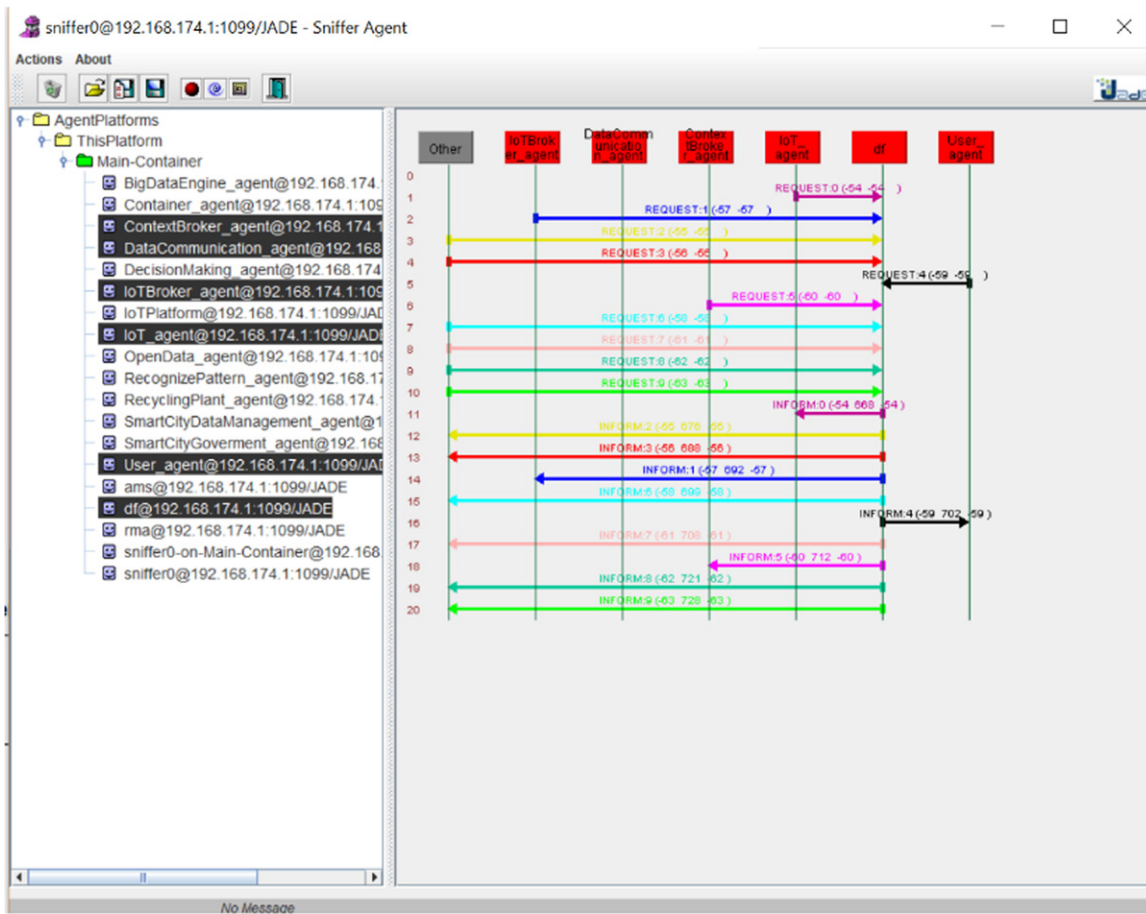


Fig. 6 Communication between agents for capturing data from the environment and the user's mobile application.

- *Traceability*, as the data collected and encrypted by the cryptochip that are sent to the blockchain have data from a GPS sensor, you can track precisely the path that has followed the cryptochip. For example, commercial transport containers, trucks, etc.
- *Internet of value*, has been built on open standards but its basis is blockchain technology. In this way we have a new tool (blockchain) to share and manage value of assets or goods without the need to depend on a trusted central entity that decentralizes the process.

Simulation Results

This section details the characteristics of the case study in which the architecture has been tested and the results obtained, to assess whether the proposed IoT platform presents an advance in citizen participation in the recycling process and in the process of optimization of waste collection routes. The system has been evaluated in the mock-up previously presented, simulating a real context. It has been simulated the characteristics of an urbanization with a population of 2200 inhabitants with 30 containers with the required infrastructure (10 blue containers for paper and cardboard, 10 yellow plastic waste containers, 10 green containers for glass), and 10 red containers of urban waste (these containers without the infrastructure).

The experiment has been divided into two phases; in the first phase the number of people who recycle and the amount of waste collected in each container has been counted, and in the second phase simulations were produced using the proposed architecture using gamma algorithms. In this second stage, the interaction of the 2200 inhabitants has been simulated, deploying agents with different behaviors based on their belief, desire, and intentions.

The process consists of each agent simulating a user who is logged by reading the QR code that identifies the container and identifies the user so as to enable the opening of the container deposit and weighing of waste. Once the waste has been introduced, the container has the quantity of waste, sends the data structure generated (quantity of waste, type of waste deposited, user that recycles, filling status of the container, occupancy rate of the nearest waste treatment plant) through the local retransmission antenna deployed using LPWAN.

The information arrives at the IoT platform and it is the agents of the different layers who are in charge of making decisions such as sending a truck to collect waste from a specific container if it is full or updating the bonus or penalty in the user's profile. Each agent allows you to visualize the achievements that your user has accumulated during the current month (each month the

Table 1 Quantity (kg) of waste collected from each container

	<i>Before system</i>	<i>After system</i>
Blue container	2214.15	2625.98
Yellow container	1731.24	2023.82
Green container	1595.07	1851.88
Total	5540.46	6501.68

profile is restarted, the achievements are not cumulative for the next month). If the user reaches the goals proposed by the municipality, the case study was proposed to increase the amount of waste by 18%. The users who obtained it obtained a reduction of 5€ on the monthly rate of rubbish (48€). At the end of the experiment, the amount of waste deposited was measured according to the simulated behavior to measure the efficiency of the system, as can be seen in [Table 1](#), in which an increase of 17.2% is observed.

Conclusion

This article presents a novel model of an agent based IoT platform that allows through gamification mechanisms to encourage citizen participation in recycling tasks. The gamification is presented as a key aspect in this type of IoT platform because the acquisition of data from the citizens of a neighborhood can propose challenges with which to increase the amount of waste to recycle.

As with any IoT platform, it is necessary to deploy an infrastructure in each container to provide information about the user's interaction with the gamification model, e.g., information about which user has recycled, amount of garbage introduced, in which container garbage has been deposited, or the occupation status of the container, among others. This information provides the necessary knowledge to the platform for the execution of the gamification model, as well as for the definition of optimal routes of waste collection according to the state of occupation of the containers and the nearest waste treatment plant, allowing an optimal and efficient management of urban waste.

The behavior of users has been recreated based on data from their real interaction in the recycling process in their city. This case study has allowed us to know the validity of the proposed platform without developing the technical deployment of the necessary sensorization. The results of evaluating the proposed platform have satisfactorily concluded the usefulness of the proposal. On the one hand, citizen participation has increased by 32.2%, the amount of waste has increased by 17.2% and, on the other hand, the number of journeys for waste collection has been reduced by 53.4%. It is clear that the use of gamification and the problem of encouraging recycling in cities allows citizens to reward their good behavior due to the savings produced by reducing the number of trips for waste collection and the increase in the garbage tax for those who do not carry out this task, apart from the other social benefits that recycling produces.

Future lines of work include the deployment of the hardware part of the platform for evaluation in a completely real scenario. This real scenario will certify the good results obtained. This platform will also allow the system to be used to carry out social measurements that will make it possible to know the behavior patterns of the users (average amount of waste it deposits, frequency with which it goes to the containers, timetable, days of the week, etc.).

Acknowledgments

This work was developed as part of "Virtual-Ledgers-Tecnologías DLT/Blockchain y Cripto-IOT sobre organizaciones virtuales de agentes ligeros y su aplicación en la eficiencia en el transporte de última milla," ID SA267P18, project cofinanced by Junta Castilla y León, Consejería de Educación, and FEDER funds.

See also: Smart Contract for Monitoring and Control of Logistics Activities: Garbage Utilities Case Study in a Smart City

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Mechanical Properties of Composites From Discarded Carpets

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Introduction

The issue of waste is a vital worldwide concern because waste is commonly discarded to landfill or incinerated, which subsequently releases greenhouse gases that contribute broadly to global climate change. In the UK alone, around 222 million tonnes of total waste was generated in 2014 (Department for Environment Food and Rural Affairs, 2018). Therefore, it is important to explore different ways in which discarded waste materials can be recycled or utilized as a resource. Furthermore, it is estimated that a tonne of waste materials being reused or recycled can save around 3 tonnes of CO₂ equivalent (Department for Environment Food and Rural Affairs, 2011).

More specifically, this article focuses on discarded carpets. Discarded carpets comprise different polymers and fillers, and can be classified as multilayered composite materials, which are expensive to reprocess and often challenging to mechanically separate at the end of their use. In the USA, about 1.5 million tonnes of carpets were discarded, and about 49 thousand tonnes were sent to landfill in 2017 (Carpet America Recovery Effort, 2018). Also, about 400,000 tonnes of discarded carpets are sent to landfill in the UK annually (Bird, 2018). Nonetheless, disposal of discarded carpets to landfill is gradually becoming difficult and impractical because of rising costs/taxation and decreased availability of landfill sites, nonbiodegradability of the synthetic fibers, and environmental impact considerations. The landfill tax associated with the disposal of discarded carpets to landfill in the UK was £24 in 2007 and has increased to £84 in 2016 reflecting a 250% increase over nine years (Gardner, 2016). The UK Government (2016) has a specific objective to reduce the amount of waste produced, whilst encouraging the increased use of alternative waste management options.

Aside from landfill, there are other processing alternatives for discarded carpets, which include energy recovery (via incineration), reuse, fiber reprocessing, plastics reprocessing, and equestrian surface applications. Energy recovery from discarded carpets via incineration involves shredding of the carpets, which are subsequently used as fuel to replace traditional sources, such as coal, for use in cement kilns or boilers. While this alternative has appeal and preferred to the landfill option, incineration of discarded carpets releases toxic greenhouse gas emissions.

Discarded carpet tiles may be reused (see Fig. 1) depending on their physical conditions, and the processing stages for reuse comprise cleaning, trimming, and possible recoloring. The reuse option is economical and leads to considerable savings in energy and raw material consumption as well as a reduction in greenhouse gas emissions. Fiber reprocessing involves the recovery of fibers from the discarded carpets by dissolving them in a chemical solvent, which enables the separation of the face fiber materials from the other carpet constituents.

Furthermore, fiber reprocessing can be used to develop textile products; for example, felt used as carpet underlay for both sound and heat insulation, as shown in Fig. 2. The use of discarded carpets for equestrian surface applications (see Fig. 3) pertains to shredding the fibers and mixing them with sand and/or waste tire rubber crumbs. Furthermore, the advantages of using discarded fibers for equestrian surface applications include better stability and dampening effect for the horses.

Plastics reprocessing of discarded carpets entails their use in engineered plastic solutions. This process involves shredding of discarded carpets at high processing temperatures, which can be extruded and injection molded into thermoplastics and/or composite materials. This is because the constituents of discarded carpets (i.e., polymers and fillers) form raw materials appropriate for the development of new composite materials and could potentially have a positive impact on the environment and yield economic benefits. The section "Processing Conditions and Mechanical Properties of Discarded Carpet Based Composites" focuses on some of the discarded carpet based composites developed and reported in the literature alongside their processing conditions and mechanical properties.

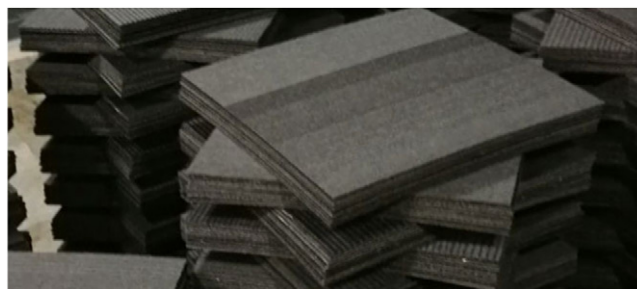


Fig. 1 Recycled carpet tiles. Reproduced from Bird, L., 2018. Carpet Recycling UK Conference 2017. Carpet Recycling UK, (accessed 06.02.18). <https://carpetrecyclinguk.com/>.



Fig. 2 Reprocessed textile felt product. Reproduced from Bird, L., 2018. Carpet Recycling UK Conference 2017. Carpet Recycling UK, (accessed 06.02.18). <https://carpetrecyclinguk.com/>.



Fig. 3 Images showing: (a) carpet fibers based equestrian surfaces and (b) close-up view.

Types and Composition of Discarded Carpets

There are different manufacturing processes for making carpets, which include tufting, weaving, and needle-punching (The Carpet and Rug Institute, 2003). Tufted carpets are the most common (representing about 76% of total carpets) and have two major style categories (i.e., level-loop and cut-pile) (see Fig. 4). The large amount of tufted carpets could be attributed to their rapid production rate and cost-effectiveness. Woven and needle-punched carpets represent 12% and 9% of total carpets, respectively (Pakravan *et al.*, 2019). Other manufacturing methods and styles contribute to the remaining 3% of all carpets. Furthermore, based on their origin and source, discarded carpets can be classified into preconsumer and postconsumer discarded carpets. Generally, preconsumer discarded carpets include off-cuts during the production or fitting stage. On the other hand, postconsumer discarded carpets include those generated at the end of their useful lives and typically consist of chemicals, dirt, and flakes that build up during usage.

There are four main layers of a carpet, which include the face fibers, primary backing, secondary backing, and adhesive. Fig. 4 shows the arrangement of the layers in a typical carpet. The top layer is the face fiber, and the primary backing is the layer that the face fibers are attached to. The adhesive [usually made of styrene butadiene rubber (SBR)] is applied to the bottom of the primary backing to attach the layers together. Calcium carbonate (CaCO_3) or barium sulfate (BaSO_4) are typically added as fillers to the adhesive. The secondary backing is attached via the adhesive to the primary backing.

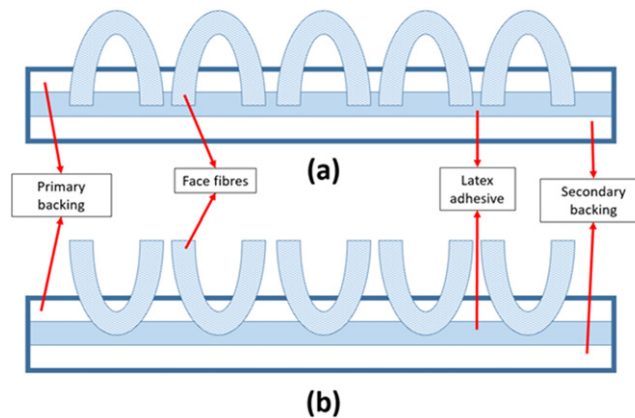


Fig. 4 Structure of carpets showing the four main layers: (a) level-loop and (b) cut-pile carpets.

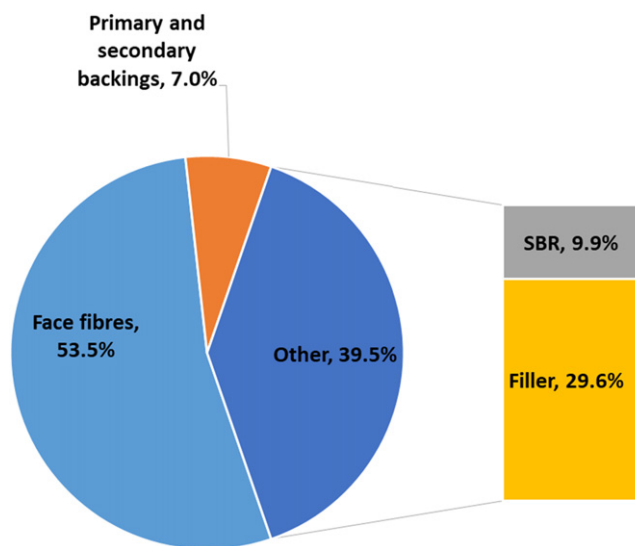


Fig. 5 Typical percentage composition of carpet components. Reproduced from Ucar, M., Wang, Y., 2011. Utilization of recycled post consumer carpet waste fibers as reinforcement in lightweight cementitious composites. *International Journal of Clothing Science and Technology* 23 (4), 242–248. doi:10.1108/09556221111136502.

Carpet has an approximate areal density of 2.4 kg/m^2 and Fig. 5 shows the approximate percentage composition of carpet components, with the face fibers constituting about half of its total weight (Ucar and Wang, 2011). Carpets consist of different materials, which include nylon, polypropylene, polyester, jute, wool, polyethylene, SBR, and polyethylene terephthalate; their mechanical properties are given in Table 1. Although both synthetic fibers and natural fibers can be used to make the face fibers, polypropylene and nylon are the most common materials used as the face fibers and primary/secondary backing because of their durability.

Processing Conditions and Mechanical Properties of Discarded Carpet Based Composites

One of the primary objectives for the development of discarded carpet based composites is to attain suitable materials, which can be used for structural applications. The conversion of discarded carpets into useful products is a sustainable alternative approach to landfilling. Examples of practical applications for discarded carpet based composites are shown in Fig. 6.

The suitcase (namely *Terracase*) was developed from discarded wool carpets with the addition of a bioresin obtained from rapeseed oil (McLaughlin, 2013). Also shown in Fig. 6 are compression molded brackets used at the bottom of a clothing rack. As discarded carpets comprise different polymers, they can potentially be used for low/medium structural applications such as decking, furniture, park benches, and fencing (Sotayo et al., 2015). As such, discarded carpet based composites can deliver a practical and cost-effective option for a variety of engineering applications, and as a result of that, utilize large quantities of discarded carpets.

When the polymers in discarded carpets are heated, they are softened or melted; this can be shaped or formed, and solidifies when cooled. Several cycles of heating and cooling can be repeated on these materials without damage, thereby allowing multiple

Table 1 Mechanical properties of different materials found in carpets

<i>Polymer</i>	<i>Young's modulus (GPa)</i>	<i>Tensile strength (MPa)</i>
Polypropylene	1.2–1.7	50–70
Nylon	2.0–3.5	60–110
Low-density polyethylene	0.15–0.24	7–17
High-density polyethylene	0.55–1.0	20–37
Polyethylene terephthalate	2.2–3.5	50–80
Wool	3.9–5.2	40–200
Styrene butadiene rubber	0.002–0.010	12–21

Note: Ashby, M.F., Jones, D.R.H., 2006. Engineering Materials 2: An Introduction to Microstructures, Processing and Design, third ed. Oxford: Butterworth-Heinemann. Callister, W.D., Rethwisch, D.G., 2007. Materials Science and Engineering: An Introduction, seventh ed. New York: Wiley. Cambridge Engineering Selector 3.1, 2000. Cambridge, UK.

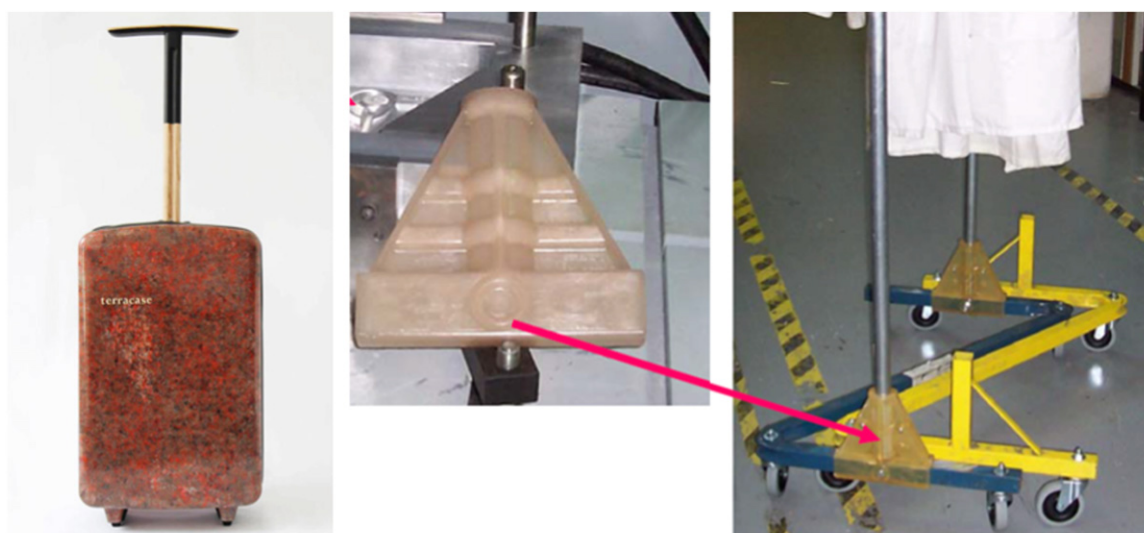


Fig. 6 Products made from discarded carpets. Reproduced from McLaughlin, D., 2013. Bio-Wool Hard Shell Luggage Made From Recycled Carpets, (accessed 31.01.13). <https://www.designboom.com/>. Muzzy, J., 2006. Recycling post-consumer carpet. In: Proceedings of the 9th Annual Conference on Recycling of Fibrous Textile and Carpet Waste, Atlanta, Georgia, 23–25 February.

reprocessing and recycling. Some of the studies from literature have demonstrated the feasibility of such composites and reported their mechanical properties. These studies also investigated the effect of utilizing other materials such as glass fibers, binding agents, and different polymeric matrices. The reported mechanical properties include flexural modulus, flexural strength, tensile modulus, and tensile strength. The modulus of elasticity of a material can be defined as the measure of the stiffness or its resistance to elastic deformation, and the strength is the maximum stress that the material can withstand before fracture. These aforementioned properties are essential for design and structural analysis.

Various manufacturing and processing conditions can be used to fabricate discarded carpet based composites, which include compression molding, intrusion molding, melt blending and hydraulic pressing, injection molding, and vacuum-assisted resin transfer molding. These different processing conditions occur at various pressures, temperatures, and processing times, which in turn could affect the mechanical properties of the discarded carpet based composites. In addition, the presence of contamination and degradation alongside pores, voids, and flaws during the manufacturing processes could significantly influence the mechanical properties of the final product.

Discarded carpets come from different sources, and many other factors can influence their mechanical properties. For example, the origin and type of discarded carpets. This is because discarded carpets are subjected to various in-service conditions and surroundings. Therefore, there are significant differences in the quantities of dirt/flake particles or chemical substances (from cleaning) embedded in discarded carpets, which subsequently leads to variations in the properties of the discarded carpet based composites. As discussed earlier, there are different types of carpets with different fractions and types of materials in it. Therefore, properties of the discarded carpet based composites can be influenced by the fraction and mechanical properties of the constituents and raw materials used in making the carpets.

The compatibility and miscibility of the polymers in discarded carpets are essential factors in influencing the properties of discarded carpet based composites. During the process of high-temperature extrusion or melt blending of the different polymers, the combination of two different polymers (for example nylon and polypropylene) can lead to a resultant composite with relatively weak mechanical properties, low quality, and poor structural integrity. Nevertheless, there are methods to improve these properties, which include the addition of polymeric binding agents (sometimes referred to as compatibilizers, compatibilizing agents, or coupling agents), matrices, additives, or fiber reinforcement.

The volume fraction or proportion and properties of the matrix and fiber reinforcement constitute to the mechanical properties of the resultant discarded carpet based composites. This is because these properties are dependent on the interfacial adhesion between the reinforcement and the matrix material (i.e., great interfacial adhesion will result in discarded carpet based composites with superior quality and good mechanical properties). Additionally, based on the rule of mixtures, the proportion or volume fraction of the fiber reinforcement or matrix material could affect the mechanical properties of the discarded carpet based composites. In general, the mechanical properties of discarded carpet based composites are significantly improved by adding fibers that have greater stiffness and strength properties in comparison to the polymers/materials present in the discarded carpets. For example, increasing the proportion of rigid reinforcement such as glass fibers will result in an improvement in the modulus of elasticity and strength properties, thus complying with the rule of mixture.

Composites With Discarded Carpet Fibers Without Matrix Addition

Table 2 gives the mechanical properties of discarded carpet based composites without matrix addition. Different types of discarded carpet based composites can be manufactured via different processes including compression molding, injection molding, and extrusion at a high temperature and pressure. They include preprocessing stages such as shredding of the discarded carpet fibers and granulation.

The production steps included shredding, granulation and extrusion of strips of discarded carpets, before being molded with no polymer addition or mechanical separation of carpet fibers (Sotayo *et al.*, 2018). The discarded carpets used included both those with natural fibers (such as wool fibers) and synthetic fibers (e.g., nylon). Experimental tests, which included tensile and flexural tests, were done on the discarded carpet based composites to determine their mechanical properties. The work showed that the flexural modulus ranged from 2.3 to 3.1 GPa, and the flexural strength from 25.9 to 31.8 MPa (see **Table 2**). The tensile modulus also ranged from 2.3–2.9 GPa, with tensile strength ranging 12.8–17.8 MPa. The study (Sotayo *et al.*, 2018) also stated that the mechanical properties of discarded carpet based composites demonstrate their potential as alternatives to common construction materials (e.g., timber and polyvinyl chloride) for fencing applications.

Compression molding was used to fabricate discarded carpet based composites, comprising nylon and polypropylene carpets (Pan *et al.*, 2016). The mechanical properties corresponding to each category of discarded carpets are given in **Table 2**. The tensile properties for the nylon and polypropylene carpet based composites are reasonably close. On the other hand, the flexural properties of the nylon carpet based composites are approximately 3–4 times greater than those from the polypropylene carpets (cf. nylon and polypropylene in **Table 1**). Also, compression molded composites from discarded nylon carpets have higher mechanical properties, which indicate their suitability for the construction and transportation sectors (Pan *et al.*, 2016).

Binding agents are typically added to enhance the miscibility and properties of the blended mixture, which also helps improve the adhesion between the different polymers. Young *et al.* (1998) produced some carpet based composites using discarded automotive carpets that comprised polyester and nylon fibers with the addition of a binding agent namely acrylic acid modified polypropylene polymer under the trademark PolyBond 1001. A combination of extrusion and injection molding was used to manufacture the discarded carpet based composites. The test results on the discarded carpet based composites showed tensile modulus and strength of 0.6 GPa and 11.8 MPa, respectively (see **Table 2**).

Table 2 Mechanical properties of discarded carpet based composites without matrix addition

Reference	Manufacturing process	Description	Tensile modulus (GPa)	Tensile strength (MPa)	Flexural modulus (GPa)	Flexural strength (MPa)
Sotayo <i>et al.</i> (2018)	Extrusion and hydraulic pressing	Polypropylene, nylon, polyethylene terephthalate, and wool carpets	2.3–2.9	12.8–17.8	2.3–3.1	25.9–31.8
Pan <i>et al.</i> (2016)	Compression molding	Nylon carpets	1.4	11.1	5.7	31.7
		Polypropylene carpets	1.8	9.9	1.4	11.8
Young <i>et al.</i> (1998)	Extrusion and injection molding	Discarded automotive carpets (nylon and polyester carpets) + 20 wt% binding agent (i.e., PolyBond 1001)	0.6	11.8	N/A	N/A
David <i>et al.</i> (1996)	Extrusion and injection molding	Nylon, polypropylene, and polyester carpets	1.7–2.7	13–31		
Murdock <i>et al.</i> (2011)	Extrusion	Polypropylene and nylon carpets + 5 wt% binding agent (i.e., Methylene Diphenyl Diisocyanate)	0.6	5		

On the other hand, discarded carpet based composites were produced with no binding agents or additives and achieved tensile modulus and tensile strength ranging from 1.7–2.7 GPa and 13–31 MPa, respectively (David *et al.*, 1996). The manufacturing process for the aforementioned composites entailed the passage of the melt blended fibers through a water bath and chopper, with the aim of producing pellets of high quality, before being injection molded.

Another method for making discarded carpet based composites entailed cutting and shredding the discarded carpets, which were subsequently mixed with Methylene Diphenyl Diisocyanate (binding agent) (5 wt%) before being extruded (Murdock *et al.*, 2011). The experimental tests on these discarded carpet based composites showed a tensile modulus and tensile strength of 0.6 GPa and 5 MPa, respectively, as shown in Table 2.

Composites With Discarded Carpet Fibers and Polyethylene Matrix

Polyethylene is a commonly used polymer used for plastic packaging (e.g., plastic bags/films), pipes, electrical insulation, and bottle containers. Polyethylene can be injection molded, blow molded, and extruded. Low-density polyethylene and high-density polyethylene are classes of polyethylene, and their mechanical properties are given in Table 1. Discarded carpet based composites have been developed using polypropylene fibers in a polyethylene matrix.

In the work by Gawayed *et al.* (1995), the composites were compression molded with the carpet fibers constituting approximately 25% fiber volume fraction. Their mechanical properties are given in Table 3. The work showed that adding the carpet fibers to low-density polyethylene led to a substantial increase in their mechanical properties in comparison to pure polyethylene. More specifically, the tensile and flexural moduli increased from 0.15 GPa and 0.086 GPa to 0.57 GPa (280% increase) and 0.137 GPa (60% increase), respectively. Similarly, the tensile and flexural strengths increased from 9 MPa and 13.8 MPa, to 38.5 MPa (330% increase) and 15.5 MPa (12% increase), respectively.

Also, a different process, namely intrusion molding (combination of injection molding and extrusion), was used to make discarded carpet based composites (Xanthos *et al.*, 2002). The discarded carpet based composites comprised 20 wt% of low-density polyethylene matrix and 80 wt% of carpet residue feedstock (containing polypropylene fibers, SBR, and calcium carbonate). The flexural modulus and strength of the discarded carpet based composites were 1.48 GPa and 15 MPa, respectively (see Table 3).

Composites With Discarded Carpet Fibers and Epoxy Matrix

Epoxy matrix is an important and commonly used thermoset material and has been widely used in reinforced composites, structural adhesives, and metal coatings because of their great mechanical properties and excellent chemical resistance. It is typically made by combining two components (i.e., hardener and resin) together. The Young's modulus of epoxy ranges from 2.1 to 5.5 GPa and the tensile strength ranges from 40 to 85 MPa (Ashby and Jones, 2006).

Vacuum-assisted resin transfer molding was used to manufacture composites from discarded carpets (Jain *et al.*, 2012). The manufacturing process encompassed the infusion of epoxy resin into the carpet layers, which were cured under pressure to form composite laminates. The flexural modulus and strength of the discarded carpet based composites ranged from 1.4 to 2.3 GPa and 24 to 35 MPa, respectively (see Table 4). Furthermore, this manufacturing technique showed that these discarded carpet based composites had excellent noise absorption properties suitable for use in infrastructure, transportation, and sound barrier walls (Mishra and Vaidyanathan, 2019).

Composites With Discarded Carpet Fibers and Phenol-Formaldehyde Matrix

Phenol-formaldehyde matrix is also a commonly used thermosetting resin and is produced via the reaction of phenol and formaldehyde. Phenol-formaldehyde matrix has good chemical and thermal resistance and has a wide range of applications, which include coatings, thermal insulation composites, molded products, and structural adhesives. The Young's modulus of phenol-formaldehyde is about 8 GPa, and the tensile strength ranges from 35 to 55 MPa (Ashby and Jones, 2006).

Table 3 Mechanical properties of discarded carpet based composites with a polyethylene matrix

Reference	Manufacturing process	Tensile modulus (GPa)	Tensile strength (MPa)	Flexural modulus (GPa)	Flexural strength (MPa)
Gawayed <i>et al.</i> (1995)	Compression molding	0.57	38.5	0.137	15.5
Xanthos <i>et al.</i> (2002)	Intrusion molding	N/A	N/A	1.48	15

Table 4 Mechanical properties of discarded carpet based composites with epoxy matrix

Reference	Manufacturing process	Flexural modulus (GPa)	Flexural strength (MPa)
Jain <i>et al.</i> (2012)	Vacuum-assisted resin transfer molding	1.4–2.3	24–35

Table 5 Mechanical properties of discarded carpet based composites with glass fibers

Reference	Manufacturing process	Description	Tensile modulus (GPa)	Tensile strength (MPa)
Zhang <i>et al.</i> (1999)	Injection molding	Pure discarded carpets without glass fibers	1.43–1.51	18–30
		Carpet composite with 40 wt% glass fibers	5.7–6.8	84–109
	Compression molding	Pure discarded carpets without glass fibers	1.72	25.5
		Carpet composite with 20 wt% glass fibers	2.12	40.7
		Carpet composite with 30 wt% glass fibers	2.76	55.2
		Carpet composite with 40 wt% glass fibers	5.90	84.1
Muzzy (2006)	Injection and compression molding	Description	Flexural modulus (GPa)	Flexural strength (MPa)
		Pure discarded carpets without glass fibers	0.86–2.7	31–70
		Carpet composite with 30 wt% glass fibers	2.0–5.7	54–147

Carpet based composites have been developed from discarded carpets enclosed in a relatively high modulus phenol-formaldehyde matrix (20 wt% volume fraction) (Kotliar, 1999). The discarded carpet based composites entailed a honeycomb sandwich structure, with the phenol-formaldehyde used to coat the fibers in the outer layers. Experimental results showed that the flexural modulus and flexural strength of the discarded carpet based composites with phenol-formaldehyde matrix were 6.9 GPa and 69 MPa. The relatively higher modulus of the discarded carpet based composites can be attributed to the high modulus of phenol-formaldehyde as well as its honeycomb sandwich structure design, which gives enhanced bending stiffness from a structural design perspective (Kotliar, 1999).

Composites With Discarded Carpet Fibers and Glass Fibers

Manufacturers use glass fibers as reinforcement materials in conventional composites (e.g., glass fiber reinforced plastic) because of their high mechanical properties. More specifically, glass fibers have tensile moduli and strengths that range from 69 to 83 GPa and 3500 to 4600 MPa, respectively (Strong, 2008).

These glass fibers can be mixed and compounded with discarded carpet fibers to obtain resultant composites with improved mechanical properties. Injection molding and compression molding processes were used to manufacture discarded carpet based composites with the inclusion of glass fibers (Zhang *et al.*, 1999; Muzzy, 2006). Table 5 gives the details and mechanical properties of these composites.

The data shows that the tensile modulus and tensile strength of the injection molded discarded carpet based composites (without glass fibers) were 1.43–1.51 GPa and 18–30 MPa, respectively (Zhang *et al.*, 1999). Similarly, the compression molded discarded carpet based composites (without glass) had a tensile modulus of 1.72 GPa and a tensile strength of 25.5 MPa. Therefore, the aforementioned mechanical properties of the discarded carpet based composites (without glass) are reasonably close. Furthermore, as shown in Table 5, an increase in the proportion of glass fibers in the discarded carpet based composites led to improvements in their mechanical properties. For example, the tensile modulus of compression molded discarded carpet based composites (with 40 wt% glass fibers) was 5.90 GPa, reflecting a 243% increase. Also, the tensile strength increased from 25.5 MPa to 84.1 MPa (230% increase).

A similar trend is shown in the flexural properties of the injection and compression molded discarded carpet based composites with 30 wt% glass fibers (Muzzy, 2006) (see Table 5). It is, therefore, demonstrated that the inclusion of glass fibers substantially increases the mechanical properties of discarded carpet based composites (Zhang *et al.*, 1999; Muzzy, 2006). This increase can be attributed to relatively greater stiffness and strength properties of glass fibers in comparison to other commonly used polymers.

Concluding Remarks

The challenges associated with waste materials are critical to the global economy and affect the issue of climate change. About 1.5 million tonnes of discarded carpets were generated in the USA in 2017, and about 400,000 tonnes of discarded carpets are sent to landfill annually in the UK. Discarded waste to landfill is a significant concern because of environmental impact considerations, decreased availability of landfill sites, nonbiodegradability of the synthetic fibers, and increasing landfill fees. Apart from the landfill option, this article also discussed some of the other processing options for discarded carpets such as energy recovery (via incineration), reuse, fiber reprocessing, plastics reprocessing, and equestrian surface applications.

Sustainability is a major objective of the global environmental agenda; therefore, it is important to explore various methods of utilizing discarded carpets as a resource or raw materials rather than being viewed as waste. The development and extensive characterization of discarded carpet based composites provide new possibilities for the efficient use of waste materials. As discarded carpets comprise different polymers and fillers, they can potentially be used to make composite materials for construction and other structural applications. Hence, this article has provided fundamental mechanical properties of discarded carpet based composites alongside their manufacturing processes (e.g., injection and compression molding). Also, recent developments

and applications of discarded carpet based composites were given. The effect of different materials (e.g., glass fibers, polyethylene, and epoxy) and additives/fillers or binding agents on the mechanical properties of discarded carpet based composites was discussed. For example, binding agents can be added to improve the compatibility and miscibility of different carpet constituents. Also, the inclusion of glass fibers in discarded carpet based composites gives a substantial improvement in their mechanical properties. Therefore, recycling of discarded carpets into useful composite materials and products offers not only a positive environmental impact but also economic benefits.

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Polymer-Recycling of Bulk Plastics

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Introduction

A life without depending on plastic cannot be imagined given the present scenario. Plastics have become hugely important in terms of human needs over the past 100 years. It is predicted that by 2050, the worldwide generation of plastics will surpass 500 million metric tonnes. Sadly, it is also predicted that there will be more plastics in the ocean than fishes due to improper mismanagement and inefficient and poor recycling techniques (Sardon and Dove, 2018). Most of the traditional plastics generated are highly persistent and less degradable due to the presence of highly packed complex carbon chains that are difficult for microorganisms to degrade, resulting in a time-consuming breakdown process (Koushal *et al.*, 2014). As a result of improper management of plastics, the next generation will be faced with toxic chemicals that will seriously affect the environment and all living organisms, causing further damage in the generations to come (Gregory, 2009). Among various countries associated with plastic leakage to the marine ecosystem China has the highest, at 1314.1–3527.9 thousand tonnes annually, and Denmark the lowest, with 0.3–0.7 thousand tonnes (Table 1). China, India, Brazil, and the USA are in the top 20 countries with the highest plastic marine debris entering the ocean. However, while China and India top the list for population, they are near the lowest gross domestic product (GDP) per capita between the eight countries. These countries represent a range of mismanaged plastic, population, and GDP. The cities themselves cover a geographical spread, varying levels of development and legal systems, appearance on the Green Cities Index (Axelsson and van Seville, 2017).

About 90% of the plastics used in automobiles, electrical gadgets, medical applications, and in other sectors are virgin in nature. The demand for plastic in various areas is exhibited in Fig. 1. About 14% of plastic is recycled and used for low-value applications. The recent decline in oil prices resulted in a reduction of virgin plastics costs, which made it harder for recyclers to compete. As a result, most of the plastic products are discarded after a single use (Carey, 2017).

On the other hand, the main hurdle is identifying suitable technologies to produce high-quality value recycled plastics that exhibit the same properties as virgin plastics. The presence of additives, fillers, and other composites in plastics and the cross-contamination of other products will make the recovery of plastics very difficult. It has been predicted by 2050, about 12,000 metric tonnes of plastic waste will accumulate in the natural environment or landfills if the prevailing improper waste management methods and uncontrolled plastic production are continued (Geyer *et al.*, 2017). These challenges can be surpassed by identifying proper assimilation methods of plastics, recovery processes, and improved separation technology (Shen and Worrell, 2014). This article focuses on discussing various recycling methods of bulk plastics. These include an overview of waste management, challenges of plastics recycling, systems for plastic recycling, properties of recycled plastics, application in various fields, environmental aspects of recycled plastics, and future directions (Fig. 2).

Table 1 Plastic leaked to the marine environment

Country	Plastic seepage from land to ocean (Thousands T/year) based on Jambeck <i>et al.</i> (2015) (2010 values)	Population in (millions) (The World Factbook – Central Intelligence Agency, n.d.)	GDP/capita (US\$) (The World Factbook – Central Intelligence Agency, n.d.)
Denmark	0.3–0.7	5.6	46,600
Singapore	1.0–2.6	5.8	87,100
Canada	1.2–3.2	35.4	46,200
Australia	2.1–5.6	23	48,800
USA	41–110.2	324	57,300
Brazil	70.2–188.6	205.8	14,800
India	89.4–239.2	1266.9	6700
China	1314.1–3527.4	1373.5	14,600

Abbreviation: GDP, gross domestic product.

Note: Axelsson, C., van Seville, E., 2017. Prevention through policy: Urban macroplastic leakages to the marine environment during extreme rainfall events. Marine Pollution Bulletin 124, 211–227. doi:10.1016/j.marpolbul.2017.07.024.

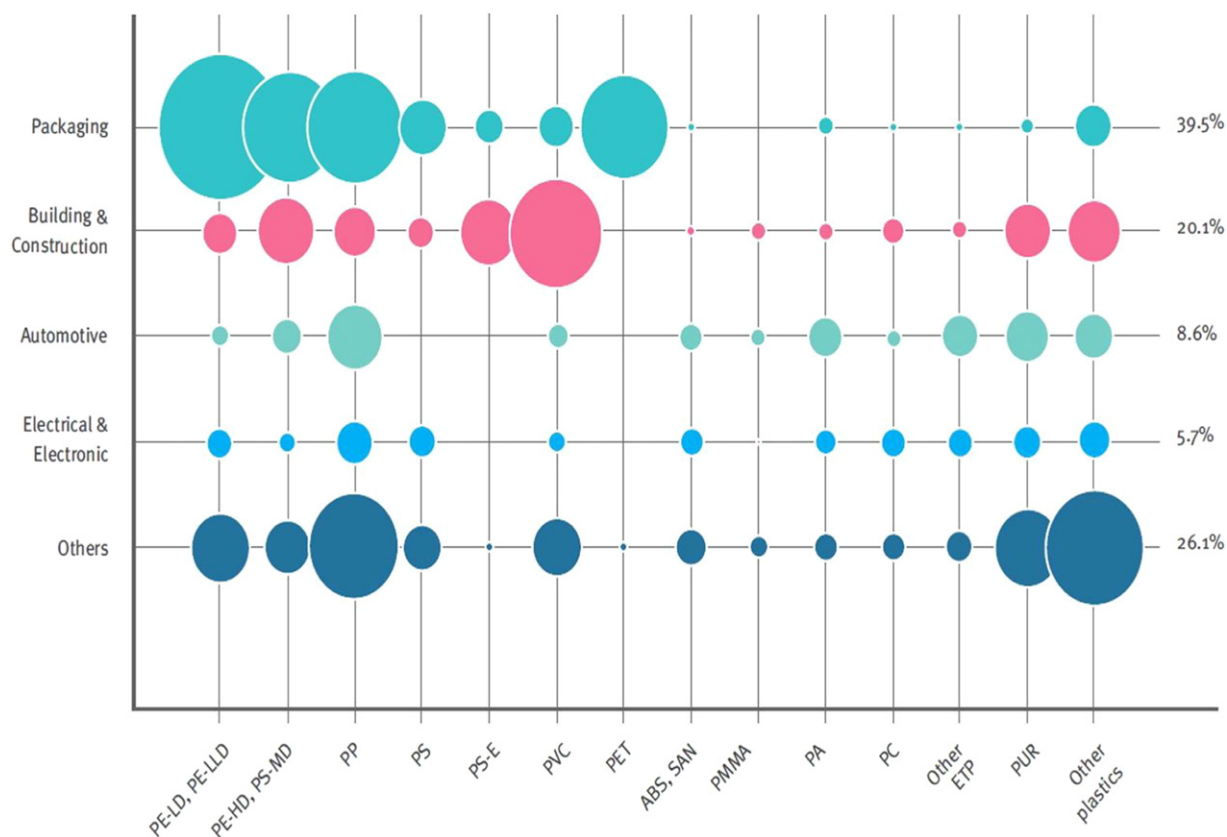


Fig. 1 Demand for plastics in various sectors. Reproduced from Ragaert, K., Delva, L., Van Geem, K., 2017. Mechanical and chemical recycling of solid plastic waste. *Waste Management* 69, 24–58. doi:10.1016/j.wasman.2017.07.044.

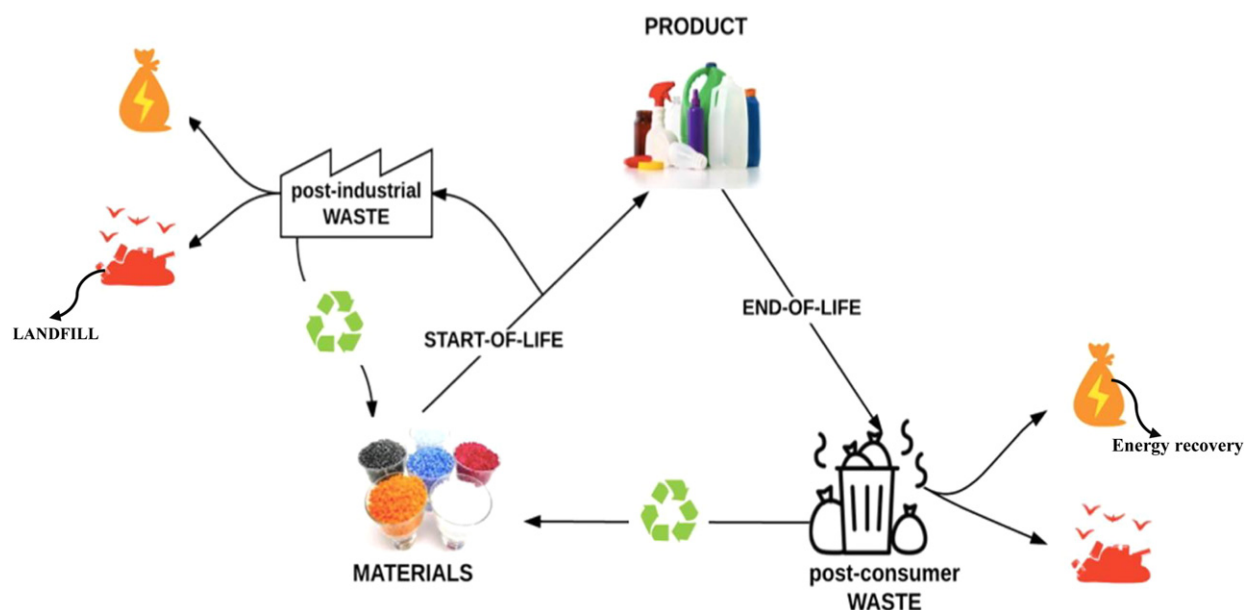


Fig. 2 Life cycle of plastic materials. Reproduced from Ragaert, K., Delva, L., Van Geem, K., 2017. Mechanical and chemical recycling of solid plastic waste. *Waste Management* 69, 24–58. doi:10.1016/j.wasman.2017.07.044.

Plastic Waste Management

Plastic waste mismanagement is a critical issue affecting different parts of the world due to the uncontrolled generation rate and improper waste management and disposal technologies. India is a significant contributor to plastic production comprising about 16% per annum and faces lots of plastic solid waste (PSW) issues ([British Plastics Federation, 2012](#)). Recently, the government of India has formulated plastic waste management (PWM) rules in 2016, which should be followed by Indian citizens ([Ministry of Environment, Forest and Climate Change, 2016](#)) ([Figs. 3, 4, 5 and 6](#)).

Some of the key aspects of these PWM rules are listed below:

- To enhance the recycling of plastics, the thickness of plastics was raised from 40 to 50 μm . By raising thickness, the cost of plastic bags increased 20%.
- Implementing PWM rules in rural areas.
- The effective arrangement of a collection of waste materials from importers, production units, and brand owners.
- Segregation of waste plastics by the institutional sectors and delivery to authorized persons for further treatment or disposal.
- Waste to energy applications should be encouraged.
- Land allocation for proper plastics disposal should be facilitated by the state government.

According to the European Commission, effective recycling of plastics comprises the following steps ([European Parliament, n.d.](#); [Interreg Europe, n.d.](#)):

- Characterization studies to analyze the strength and weakness of recycled waste plastics.
- Complete recycling of packaging plastics by 2030.
- Reduction or avoidance for single-use plastic utilization.
- Identifying mold designs for preparing suitable products in recycled plastics.
- Advancement in polymer quality utilizing the inclusion of compatibilizers or additives and evaluating the cost-effective approaches.
- The overall resource efficiency of recycling process evaluated by life cycle costing and life cycle analysis (LCA) studies and assuring the best possible way of using recycled plastics and giving awareness to the public about the importance of recycling ([Ragaert, 2016](#)).

Methods for Bulk Plastics Recycling

The most common methods used for PWM are recycling mechanisms. Recycling of bulk plastics is carried out by the closed loop and open loop recycling. In closed loop recycling, the recycled waste plastics are used to generate similar products to that of virgin plastics. The Polyethylene terephthalate (PET) polymer in packaging is a typical example of utilizing closed loop recycling. In open



Fig. 3 Schematic representation of circular economy principles. Reproduced from Ragaert, K., Delva, L., Van Geem, K., 2017. Mechanical and chemical recycling of solid plastic waste. *Waste Management* 69, 24–58. doi:[10.1016/j.wasman.2017.07.044](https://doi.org/10.1016/j.wasman.2017.07.044).

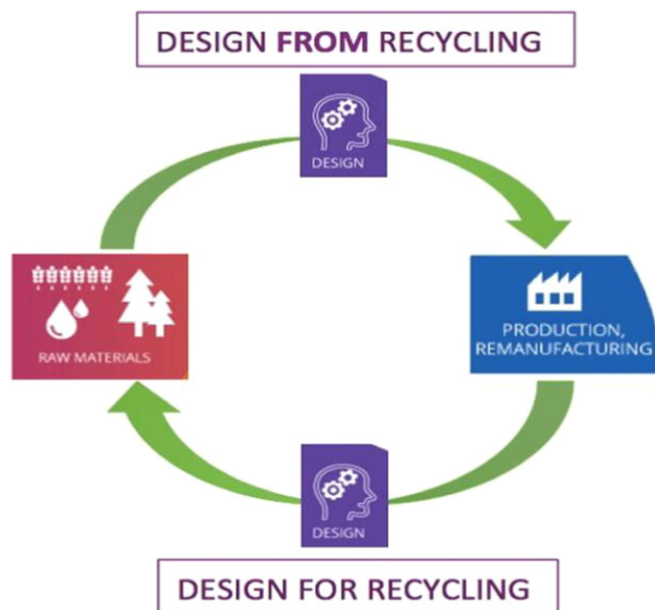


Fig. 4 Simplified representation of recycling and design in a circular economy. Reproduced from Ragaert, K., Delva, L., Van Geem, K., 2017. Mechanical and chemical recycling of solid plastic waste. *Waste Management* 69, 24–58. doi:10.1016/j.wasman.2017.07.044.

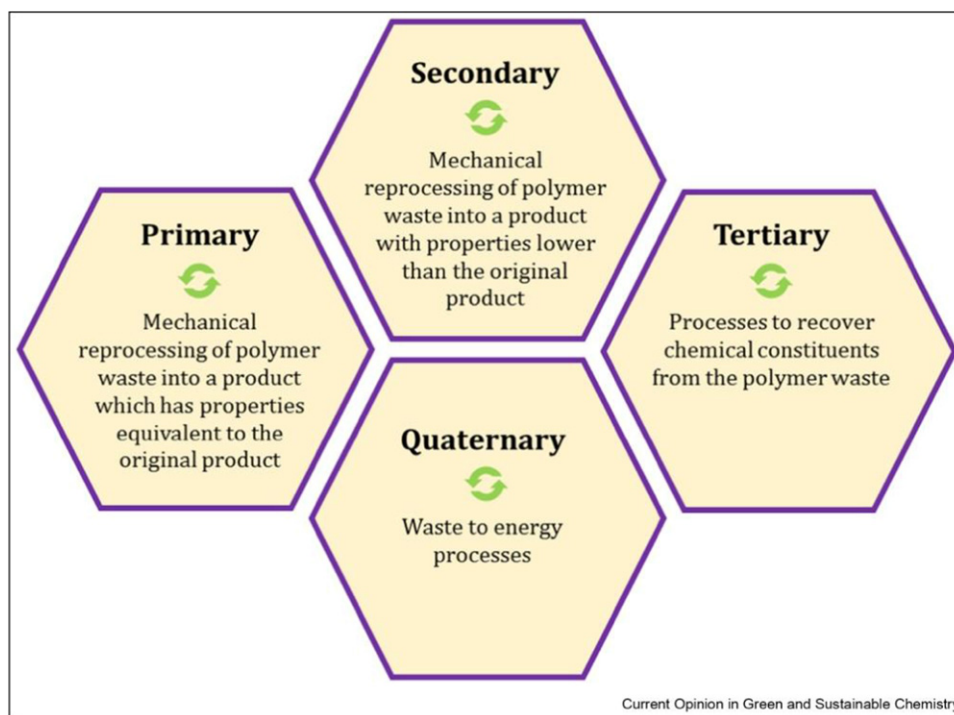


Fig. 5 Technologies for recycling bulk plastics. Reproduced from Sahajwalla, V., Gaikwad, V., 2018. The present and future of e-waste plastics recycling. *Current Opinion in Green and Sustainable Chemistry* 13, 102–107. doi:10.1016/j.cogsc.2018.06.006.

loop recycling, the recycled bulk plastics are used to generate different products compared with their original form. Examples include PET bottles and components in printers (Gort and Gerrits, 2015) (Table 2).

There are four categories of recycling mechanisms. In the primary category, mechanical reprocessing of waste plastics to a product with similar properties takes place. Physical treatment of bulk plastics is carried using pulverizing, incineration, and grinding mechanisms to minimize the size of waste plastics (Al-Salem *et al.*, 2009). Physical treatments are categorized as either thermal, UV radiation, or photooxidation processes (Orr *et al.*, n.d.). Complete disposal of bulk plastics is one of the limitations in physical treatment, which ultimately results in the generation of hazardous environmental by-products (Gilpin *et al.*, 2005).

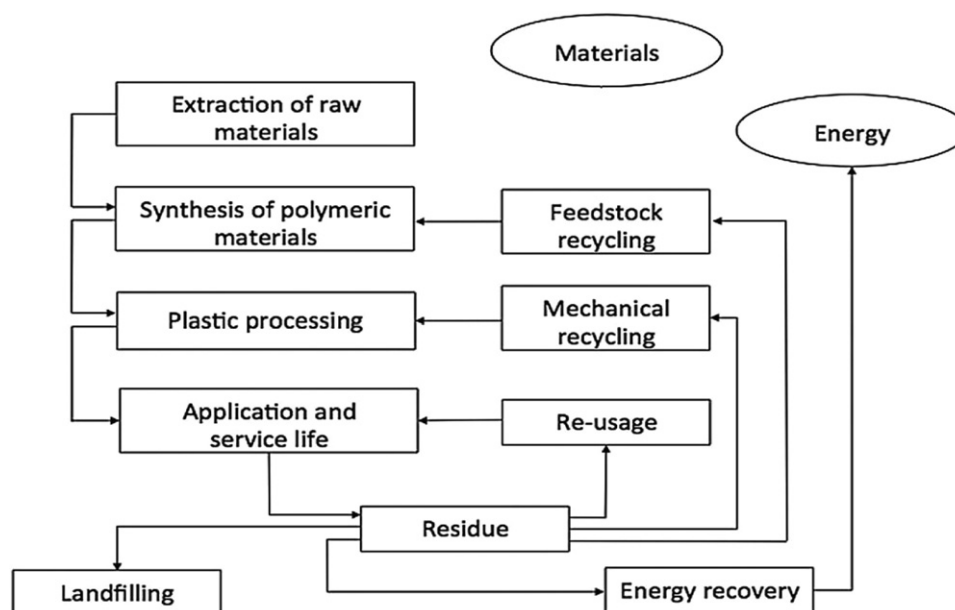


Fig. 6 Various plastic solid waste alternatives concerning polymer product lifecycle. Reproduced from Ragaert, K., Delva, L., Van Geem, K., 2017. Mechanical and chemical recycling of solid plastic waste. *Waste Management* 69, 24–58. doi:10.1016/j.wasman.2017.07.044.

Table 2 Overview of the advantages and challenges of various techniques for recycling solid plastic waste

	<i>Techniques</i>	<i>Advantages</i>	<i>Challenges</i>
Mechanical recycling and sorting	Flotation (sink-float)	Well-known technology; Cost-effective	Efficiency determined by density differences plastics Mainly limited to binary mixtures
	Melt filtration	Useful to remove nonmelting contaminants; particle size	Potential pressure fluctuations in production
	FT-NIR	Postdrying not required	Plastic should be dry; black undetectable
	Electrostatic separation	Small particle sizes allowed; Efficient for various plastics	Pretreatment
	Froth Flotation	Efficiency	Precursor step required
	Magnetic density separation	Multiple polymer fractions in a single step; Improved density-based technique	Density overlaps remain
	X-ray detection	Useful for PVC; accuracy	Cost-effectiveness
Reprocessing		High-value recycling; straightforward	Challenging for complex mixtures; thermal–mechanical degradation; miscibility of polymer blends
Chemical recycling	Chemolysis	Operational for PET; generates pure value-added products	Mainly limited to condensation polymers; requires high volumes to be cost-effective
	Pyrolysis	Suitable for highly heterogeneous mixtures of plastics	Suitable for highly heterogeneous mixtures of plastics; complexity of reactions; stable waste supply; low tolerance for PVC
	Fluid catalytic cracking	Less stringent reaction conditions lead to favorable economics; narrow product outcome	The absence of suitable reactor technology; deactivation of the catalyst; presence of inorganics
	Hydrocracking and combined	Different elements already commercialized; suitable for mixtures of plastics; quality of produced naphtha	High investment and operational costs; high cost of hydrogen; further research required
	Catalytic pressure less depolymerization	Also suitable for oxygen and halogenated compounds	Lack of technical information; chemistry still unknown
	Gasification	Syngas is a valuable intermediate	Specific drawbacks of air; presence of toxic gases

Abbreviations: PET, polyethylene terephthalate; FT-NIR, fourier transform near infrared; PVC, poly-vinyl chloride.

Note: Reproduced from Ragaert, K., Delva, L., Van Geem, K., 2017. Mechanical and chemical recycling of solid plastic waste. *Waste Management* 69, 24–58. doi:10.1016/j.wasman.2017.07.044.

The secondary level involves mechanical reprocessing of waste polymers to products that require decreased properties (Delva *et al.*, 2018b). In the tertiary level, the chemical constituent of polymers is recovered employing depolymerization which comes under chemical or feedstock recycling (Achilias *et al.*, 2012). Biological recycling is another example of tertiary recycling, which involves the degradation of plastic polymers that can be easily decomposed by microorganisms (Alaerts *et al.*, 2018).

Incineration involves the energy recovery from waste, which falls under the quaternary category of recycling. The incineration method is used for recycling packaging and medical applications (Ignatyev *et al.*, 2014). However, the incineration of mixed plastics generates furans and dioxins, which are toxic to the environment and living beings. Even though incineration limits the needs for plastics sorting, it does not conserve much energy compared with other recycling mechanisms (Rahimi and Garc  a, 2017). Hence this method in PSW is not highly encouraged (Lopes *et al.*, 2015). Landfilling of plastic waste is often inefficient and toxic to the environment because the plastic wastes are decidedly less biodegradable; therefore, more accumulated waste will contaminate groundwater and soil properties (Hidayah and Syafrudin, 2018).

Some of the emerging technologies in PSW are polymer integrated bitumen roads, plasma pyrolysis, use of plastic waste as an alternative fuel, and cement kiln coprocessing. Waste plastic polymers such as Polypropylene (PP), Polystyrene (PS), and Polyethylene (PE) are integrated with bitumen, and the mixture is used for pavement applications.

The blending of plastic wastes with bitumen enhances durability and has been found to be successful for constructing flexible pavements (Manju *et al.*, 2017). The plasma pyrolysis method was used to convert waste plastics to useful energy through catalytic and thermal methods of degradation (Sharuddin *et al.*, 2018). Thermal pyrolysis of waste bulk plastics into liquid has shown several advantages compared with other recycling mechanisms. The conversion of waste plastics to liquid fuel facilitated by a catalyst under low temperature was found to be feasible. The liquid fuel produced was found to be applicable as a blending agent with kerosene or gasoline (Garieballa, 2014). The useful liquid fuel generated was identified to be a potential energy source in various applications such as boilers, furnaces, and diesel engines (Bridgwater, 2012). The use of waste plastics in cement kilns is found to be a potential PSW mechanism. The high-temperature condition of cement kilns helps in using even some toxic plastic waste without creating many environmental impacts (Baidya *et al.*, 2016). There is no requirement for cleaning or separation of this disposal method. Hence low-value end plastics wastes act as a vital source of energy for the cement industry (Asamany *et al.*, 2017).

Systems for Plastic Recycling

Mechanical Recycling

Mechanical recycling mechanism consists of converting waste plastics into a suitable product that exhibits similar properties as compared with virgin polymers (Vanapalli *et al.*, 2019; Delva *et al.*, 2018a; Chandrasekaran and Sharma, 2019; Hahladakis *et al.*, 2018). Thermoplastics can be used for mechanical recycling because they can be easily remelted and processed again to suitable products (Ruj *et al.*, 2015). Mechanical recycling involves the following steps (Figs. 7 and 8):

- Segregation sorting is carried out based on properties such as color, density, shape, and size or chemical component of waste plastics.
- Baling: Plastic baling is used to convert any waste plastics into useful commodities and is used when the bulk plastics have not undergone processing.
- Cleaning: Organic contaminants from waste plastics are removed by washing.
- Sizing: Reduction in size of waste plastics into fragments is carried out by grinding mechanism.
- Pelletizing: This is the final step, which involves the molding or reprocessing of waste plastics into suitable pellets, which would be more accessible for use in converters.

Separation techniques and process description

The segregation of waste plastics is carried out by manual sorting and automatic sorting. Manual sorting is highly productive but labor intensive. Automated sorting of waste plastics is carried out by Fourier transform near infrared technique. However, the drawback is that this method is not well suited to distinguishing dark or black plastic products.

Since it is an optical surface based technique there are chances of the sensor showing false reading due to the presence of dirt in the waste plastics; as a result, light cannot be adequately reflected (Ruj *et al.*, 2015). The electrostatic separation technique is found useful in separating binary mixed waste plastics. Examples include PE/PP and PET/Poly-vinyl chloride (PVC) mix polymers (Reinsch *et al.*, 2014). The sorting process begins by stocking the waste plastics into a belt system from where the mixture is transferred to a shredder where size reduction of the polymer occurs (Jung *et al.*, 2018). From there the wastes undergo washing using a rotating drum in which glass, rocks, and metals are removed by force of gravity supported by water flow for washing.

Friction washers remove the organic contaminants adhering to waste plastics. Now, the larger particles undergo shredding to result in particles from 1 to 12 mm. Density-based separation of waste plastics is carried out by float-sink separation method (Qing *et al.*, 2015). X-ray technique is used for sorting PVC polymers by detecting the presence of chlorine content

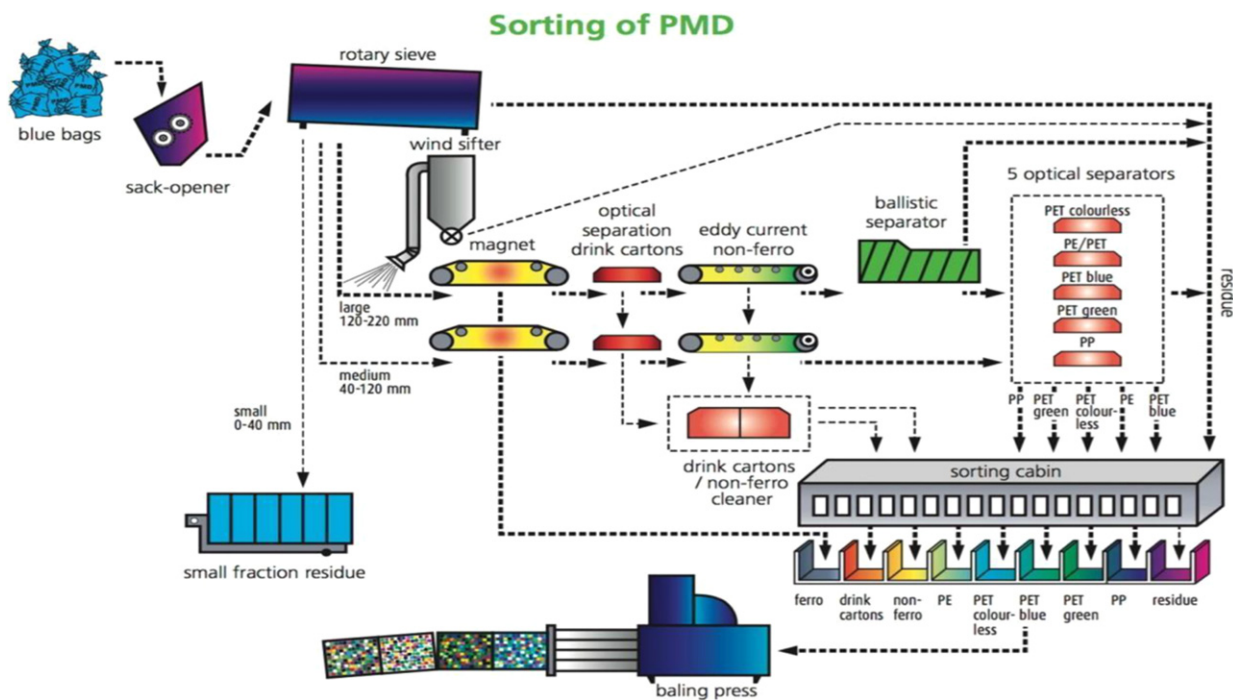


Fig. 7 Plastics, metals and drink carton sorting method for industries. Reproduced from Ragaert, K., Delva, L., Van Geem, K., 2017. Mechanical and chemical recycling of solid plastic waste. *Waste Management* 69, 24–58. doi:10.1016/j.wasman.2017.07.044.

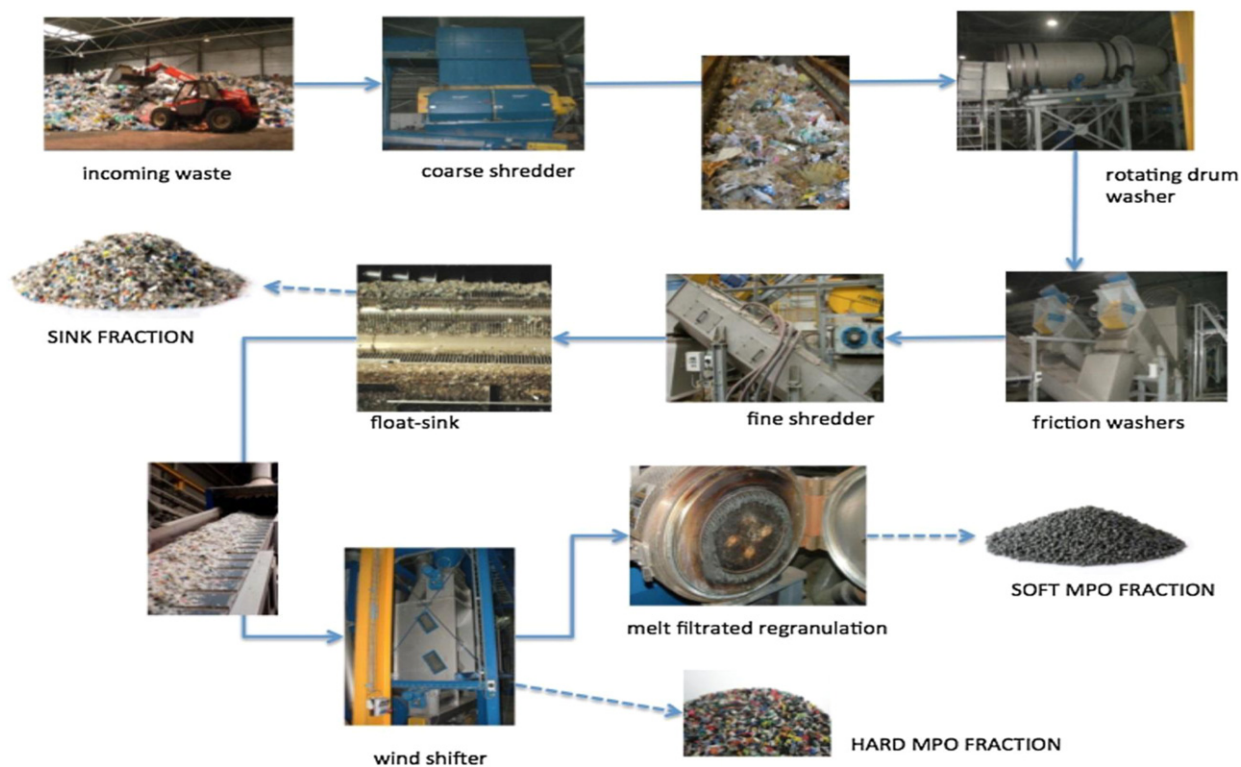


Fig. 8 Flowchart of various processes involved in mechanical recycling of polycarbonate waste polymer. Reproduced from Ragaert, K., Delva, L., Van Geem, K., 2017. Mechanical and chemical recycling of solid plastic waste. *Waste Management* 69, 24–58. doi:10.1016/j.wasman.2017.07.044.

(Arvanitoyannis and Bosnea, 2001). Froth flotation mechanism is used to sort waste polymers with uniform densities (Censori *et al.*, 2016).

Removal of ferrous components from the waste is facilitated by providing a strong magnetic field in the sink fraction and transferred to the mechanical drier. Magnetic separation using density technique is efficiently used for the segregation of waste polymers such as PE and PP from mixed polyolefins and for rubbers and PVC from constructional wastes (Serranti *et al.*, 2015; Luciani *et al.*, 2015). The float-sink fraction experiences drying and then encounters a wind sifter where mass-based separation occurs. The separation of soft plastic particles such as low-density polyethylene (LDPE) and PP occurs in upward airflow while the hard particles such as high-density polyethylene (HDPE) tumble against airflow. Since the bulk density of soft particles is too low, it is used readily by converters and finally undergoes granulation by the extrusion process (Stenvall and Boldizar, 2016). This process helps in removing nonmelting contaminants during melting and enhances the overall quality and stability of the polymer (Luijsterburg *et al.*, 2016). The hard particles are further used as a secondary resource.

Mechanical properties of plastics

Mechanical properties of bulk plastics help in the identification of elastic and strength properties of the plastic polymers and can be used for specified applications (Scott, 2000). Tensile strength specifies the hardness, firmness, and strength of plastic polymers. The tensile strength test is one of the essential factors in evaluating the mechanical properties of bulk plastics. This test helps to analyze the strength and capacity of various plastic polymers and evaluating the efficiency to combat loading in various applications (Ferreira *et al.*, 2005). Elongation is another property of plastics. The efficiency of polymer breakage at a specific elongation is studied using the polymer breakdown test. Polymer elongation is influenced by various external agents such as exposure to UV radiation, sunlight, and temperature conditions (Pedroso and Rosa, 2005).

Another essential mechanical property of plastic polymers is that of *Young's modulus*. This property is used to determine the firmness of polymers. Elastic modulus varies with fluctuations in temperature. The elastic behavior of the polymer is examined by means of the elastic modulus test calculation. The stress–strain correlation of various polymers is determined by Young's modulus (Pedroso and Rosa, 2005).

Challenges for mechanical recycling

During the mechanical recycling process, two types of polymer degradation take place, namely thermal–mechanical deterioration and life degradation (La Mantia, 2004). During melt processing, thermal–mechanical deterioration of plastic polymers through mechanical shearing and heating occurs (Beyler and Hirschler, 2002).

During the degradation process, splitting of the carbon covalent bond takes on a polymer backbone and generates free radicals. These free radicals, after going through chemical reactions, result in branching or chain scission. Chain scission diminishes the molecular weight and overall properties of plastic polymers. On other hand, the chain branching leads to cross-linking and enhancement of the molecular weight of the polymer. A typical example of chain scission occurs in PP; similarly, PE is a typical example of chain branching (Pinheiro *et al.*, 2004). To overcome the drawbacks of thermal–mechanical degradation, certain additives such as heat stabilizers, compatibilizers, pigments, and cross-linkers are added during the recycling of bulk plastics and found useful in the enhancement of plastic recycling rate (Tostar, n.d.). The mechanical properties and melt strength during recycling of PET polymer are enhanced by postcondensation method (Dimonie *et al.*, 2012).

The second type of thermal–mechanical degradation of polymers is lifetime degradation. This degradation occurs during exposure of bulk plastics to heat, light, oxidation, hydrolysis, and mechanical shearing (Ragaert *et al.*, 2017). The photooxidation process results in the generation of oxygenated groups on the surface of polymers and affects the properties of plastics. The presence of an oxygenated group is determined by mass spectroscopy techniques (Xiang *et al.*, 2002). Polyethylene and PET plastics are commonly recovered using mechanical recycling due to limitations mentioned earlier. Since each plastic differs in physical, chemical, thermal, and mechanical properties, the mechanical recycling of waste plastics seems to be challenging (García and Robertson, 2017). Since mixed polymers vary in treating temperature and melting point, recycling of bulk plastics is challenging. This results in the deterioration of polymers having a low melting point and diminishes the overall properties of recycled plastics (Ragaert *et al.*, 2017).

Chemical Recycling

The plastic waste can be utilized as feed in the production of hydrocarbon-based fuel and other valuable chemicals. The current scenario is not only limited to recovering energy or with mechanical recycling, but also focusing on recovering valuable petrochemical feedstocks and monomers. With plastic feedstocks such as nylon, polyurethane (PUR), and PET the chemical recycling options can be successfully utilized, and there is a tremendous increase in their utilization as feedstock for the recovering of high hydrocarbon content. Plastic waste entails high carbon yield and limited oxygen concentration level. In the following sections, different technologies associated with recycling and treatments of bulk plastics are discussed. The leading technologies associated with these feed streams are hydrocracking, pyrolysis, gasification, and fluid catalyzed cracking.

Chemolysis

The chemically recycled plastics are more appropriate for food applications and have expanded interest in diverse chemolysis capabilities. Chemical recycling techniques open new dimensions for new value-added products for broad commercial and industrial applications. The chemically recycled polymers are not economically feasible compared with virgin material as a result of the scale of operation, capital investment, and raw material cost (George and Kurian, 2014) (Fig. 9).

Polyethylene terephthalate: Chemically recycling

PET can be depolymerized into the following monomers: Dimethyl terephthalate, terephthalic acid (TPA), ethylene glycol (EG), and bis terephthalate. PET can also be partially depolymerized to oligomers and other substances. Various depolymerization techniques such as glycolysis, methanolysis, aminolysis, ammonolysis, hydrogenation, and hydrolysis rely upon chemical agents used for PET chain scission.

PET methanolysis depends on the treatment of PET with methanol at high-pressure levels between 20 and 40 atm and high-temperature ranges of 280°C. The degraded products of PET after aminolysis and glycolysis find potential applications as chain extenders, plasticizers, corrosion inhibitors, precursors, and cross-linking agents in the production of by-products such as textile dyes, PURs, resins, vinyl esters, epoxy resins, and antibacterial drugs.

The reaction of PET with water under basic, acidic, and neutral environmental conditions at high pressure and temperature, breaks the polymer chains down into EG and TPA; this reaction process is known as hydrolysis. The main drawbacks are the low purity of TPA and the fact that this is a comparatively slow option since it is a weak nucleophile. Glycolysis is the traditional and most straightforward technique for PET depolymerization. Glycolysis is a commercial PET recycling technique still followed by various industries to handle large quantities of PET (Ragaert et al., 2017).

The transesterification of PET with excess glycol at a temperature level of 250°C guides the development of bis(hydroxyl ethylene) terephthalate. This technique is preferred when PET feed is of high quality and not recommended for removal of low levels of copolymers. Different glycols, such as EG, diethylene glycol, propylene glycol, polyethylene glycol, 1,4-butanediol, and hexylene glycol, are used for the glycolysis of PET. Glycolysis of PET undergoes three substages: Monomers, dimers, and oligomers (George and Kurian, 2014).

Super and subcritical fluids such as alcohol and water are exceptional media for carrying out decomposition of plastics. The super and subcritical fluids could decompose the polymers more selectively and rapidly. Condensation polymers can easily be depolymerized into monomers in the absence of alcohol or water, which can act as both solvent and reactant. The thermosetting resin in flame-retardant polymers can be recycled to materials with the aid of hydrolysis using subcritical aqueous media. The by-products, fumaric acid and glycols, dissolved in the aqueous solution can be recovered and separated.

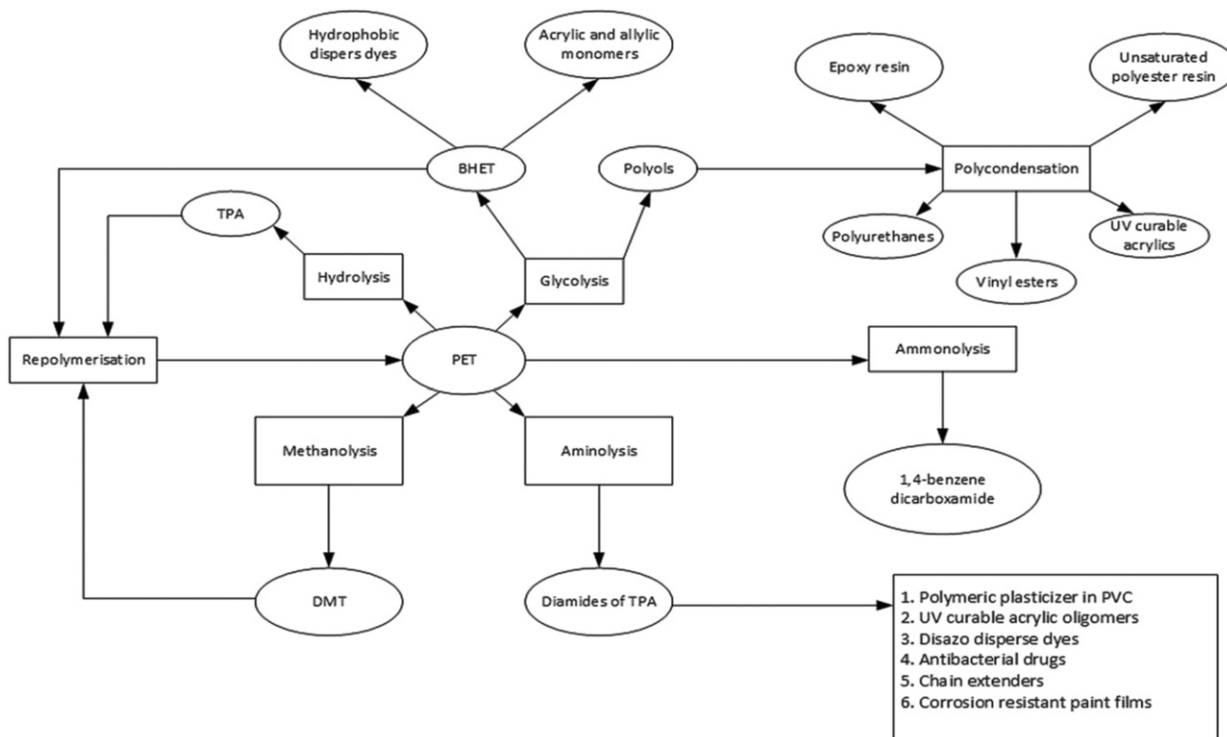


Fig. 9 Various methods for chemolysis of polyethylene terephthalate polymer and evolved value-added materials. Reproduced from Ragaert, K., Delva, L., Van Geem, K., 2017. Mechanical and chemical recycling of solid plastic waste. *Waste Management* 69, 24–58. doi:10.1016/j.wasman.2017.07.044.

Pyrolysis

Pyrolysis emerges as an exciting option for recycling of bulk plastic feeds that are difficult to recycle such as mixed PP/PE/PS, multilayer packaging, demolishing, and PUR construction wastes. These types of multilayered films seem challenging in recycling compared with other waste streams. The multilayered plastic package containers opt for PE as it is both cheap and also provides structural and bulk integrity. However, if more thickness is required, manufacturers prefer PET as it is more suitable for beverage containers.

In blocking oxygen contact with beverages, ethylene vinyl alcohol is the preferred option compared with nylon, PET, or PE. The metalized film has also been incorporated to provide an increase in thickness. The recycling of these package containers creates new challenges in mechanical recycling as it is not considered as effective; therefore, pyrolysis arises as a better option. **Fig. 10** demonstrates the typical plant design and workflow of the pyrolysis process. The pyrolysis process can handle heterogeneous mixtures, and contaminated plastic waste streams provide more flexibility in handling waste streams. However, economic viability is the main drawback of this process (Vermeulen *et al.*, 2011; Al-Salem *et al.*, 2010).

The pyrolysis process carried out at the high-temperature level of 500°C in the absence of oxygen allows for the breakdown of the macrostructure of polymers into smaller and simpler molecules. The by-products of the pyrolysis process can be decomposed into three main fractions: Solid, gas, and liquid (Al-Salem *et al.*, 2010). The most impenetrable part in pyrolysis is the occurrence of complexity when mixed waste streams are processed together. According to the nature and the composition of plastic streams, different plastics give rise to different by-products in their decomposition process. The process is sensitive; even the presence of certain impurities can affect the by-products derived or even make it lose its standard properties (Garforth *et al.*, 2004). To carry out the pyrolysis process in a cost-effective manner, it can only be achieved by through large volumes. PP, PE, PVC, and PS are more suitable and appropriate waste sources for conversion to either petrochemical fuels or monomers (Ragaert *et al.*, 2017). However, the complexity of sorting out these plastic sources from mixed waste, a distillation of obtained by-products and complex separation technologies, creates a barrier in the global acceptance of pyrolysis technology. The presence of acid, chlorine, and other toxic substances also affects the by-products quality; the pretreatment for the removal increases the expenses and operational cost. Stirred tank reactor, screw reactor, and bubbling fluidized bed reactors are most commonly utilized reactors for the pyrolysis process (Butler *et al.*, 2011). The fluidized bed reactor is the most favorable option due to its high conversion rates. However, in recent years, a new disruptive reactor design, known as the vortex reactor, has been developed.

The vortex reactor upgrades the traditional reactor's designs by improving the convective heating between phases, providing flexibility with the option of different fluidization agents, and high centrifugal acceleration (Ragaert *et al.*, 2017). A vast number of parameters influences the pyrolysis process such as temperature, composition, stable supply of water, fluidizing gas, and macrostructure of polymers (Marongiu *et al.*, 2007).

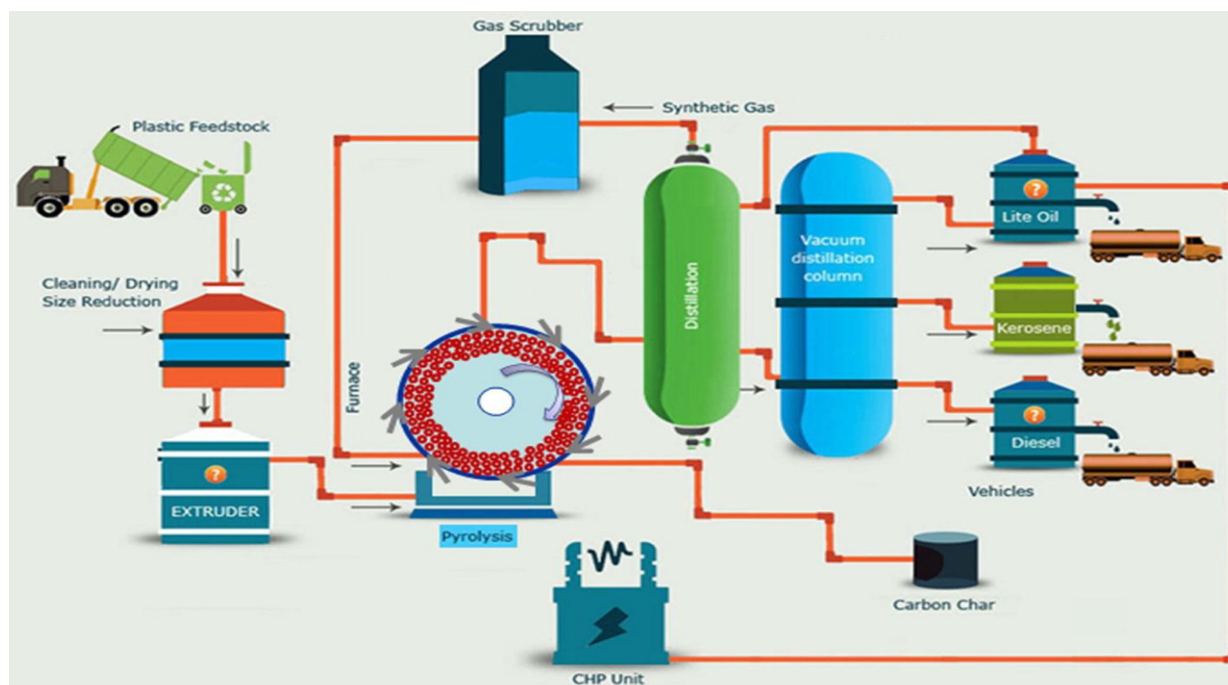


Fig. 10 Classic pyrolysis process flow diagram along with recent vortex reactor technology for treating bulk plastics. Reproduced from Ragaert, K., Delva, L., Van Geem, K., 2017. Mechanical and chemical recycling of solid plastic waste. *Waste Management* 69, 24–58. doi:10.1016/j.wasman.2017.07.044.

Fluid catalytic cracking

The use of the catalyst in thermal decomposition, allowing for the direct recovery of fuel and other by-products, depends on the process conditions. Additionally, the catalyst minimizes the energy requirements, stringent reaction conditions, and overall operational expenses in thermal decomposition plants (Thegarid *et al.*, 2014; Passamonti and Sedran, 2012). On a comparison analysis of catalytic cracking and convention thermal decomposition, it was observed that the shifting of product spectrum towards smaller carbon numbers additionally resulted in the formation of naphthenic and aromatic compounds, which were also observed in catalytic cracking.

Catalytic cracking is of two major types: Vapor phase and liquid phase. In the vapor process, the vapors derived during cracking come in contact with vapors. Similarly, in the liquid phase process, the molten polymer is in direct contact with the catalyst. The catalyst aids to carry out the pyrolysis process at a lower temperature level of 300–350°C and yields towards aromatics and iso-alkanes, suitable for gasoline products (Buekens and Huang, 1998). However, the catalytic cracking has severe downsides such as the presence of inorganic compounds can block the pores. This ultimately leads to the deactivation of catalysts, carbonaceous deposits, the requirement of pretreatment, and limitations in reactor designs.

Hydrocracking

The presence of hydrogen at temperature levels between 375°C and 400°C and at a pressure of 70 atm improves the by-product quality, that is, low aromatic content and higher C/H ratio. Catalysts such as NiMo/S or Ni/S have been employed. Hydrocracking yields better naphtha feed and mixtures of bulk plastic feed can be used. However, the hydrogen-based process involves high operational and investment costs. Integrating hydroconversion and hydropyrolysis is a catalytically based thermochemical conversion process of converting the organic materials into value-based hydrocarbon by-products. This process can handle municipal waste, cellulosic fractions, biomass residues, and plastic waste streams.

This process involves three reactions: Hydroconversion, hydropyrolysis, and reforming. In integrating hydroconversion and hydropyrolysis, the plastic waste directly converts to liquid hydrocarbons. This process does not need an external supply of hydrogen, thus making this process more economically viable. This treatment technique eliminates the pretreatment requirement of waste sources and arises as a promising technology having overall economic potential and minimizing investment risk (Shell Global, n.d.; Laxmi Narasimhan and Del Paggion, 2016).

Catalytic pressure-less depolymerization

The catalytic pressure-less depolymerization method was first introduced by the German company Alphakat GmbH, proposing the direct conversion of the plastic waste source to liquid fuels at atmospheric pressure conditions. Compared with other technologies, the catalytic pressure-less depolymerization process removes oxygen atoms and makes the final yielded liquid fuel suitable for direct utilization in combustion engines. It can handle all types of waste sources from polymer plastics and their derivatives to lignocellulose. The mild operational parameter requirements makes this process more attractive compared with other technologies such as pyrolysis (Fakhrai and Saadatfar, 2015). According to the reports from Alphakat GmbH, this technology is ready for transfer to industrial and large-scale applications after a satisfactory performance during feasibility studies.

However, the feedstock needs to undergo pretreatment to reduce particle diameter to less than 3 mm and to reduce the moisture content to less than 5 wt%. The catalyst, shredded feedstock, and lime are mixed with a carrier oil and heated to a temperature of 180°C. The catalyst employed for the process is pure crystalline alkali-doped aluminum silicate; utilization of natural origin catalyst can replicate the natural process of oil formation on accelerated form (Wongmaha, 2018). Lime is added to obtain the optimum pH of 9 to carry out the catalytic reaction. The oil mixture is supplied over to turbine reactor, and the temperature is inclined to 250°C. Solid and liquid materials are dragged by high-speed rotation of turbine blades.

Due to the centrifugal force, the hydrocarbons get separated from other residues; the frictional and mixing energy leads to the rise of temperature, resulting in the deoxygenation and depolymerization of extracted hydrocarbons. Still, further studies need to be carried out to understand the chemistry behind the process. The by-product fuel consists of high sulfur content that fails to meet environmental regulations (Labeckas and Slavinskas, 2013). Various modifications in the design model need to be adopted to improve the quality of the derived fuel (Fig. 11).

Gasification

Gasification technology is widely used to convert the bulk waste materials ranging from biomass to plastic to hydrocarbon-rich syngas (CH_4 , H_2 , CO) through partial oxidation (Heidenreich and Foscolo, 2015; Ruiz *et al.*, 2013). This process needs an oxidation agent such as air; oxygen and steam are typically used. Air is the cheapest oxidation agent option regarding operational expenses but has several downsides such as more robust in segregation and high gas flow rate (Wilhelm *et al.*, 2001). In syngas, along with the presence of rich hydrocarbons, toxic contaminants are also present; new purification technologies need to be incorporated requires additional investments. Various valuable by-products such as methanol can be extracted through the methanol-to-olefins process, whereas the paraffinic hydrocarbons can be extracted via the methanol-to-gasoline process. The gasification of bulk plastic is possible for the production of syngas rich in hydrocarbons. However, further improvement in the design of the reactor is needed before considering bulk plastic as a feed source (Brems *et al.*, 2012).

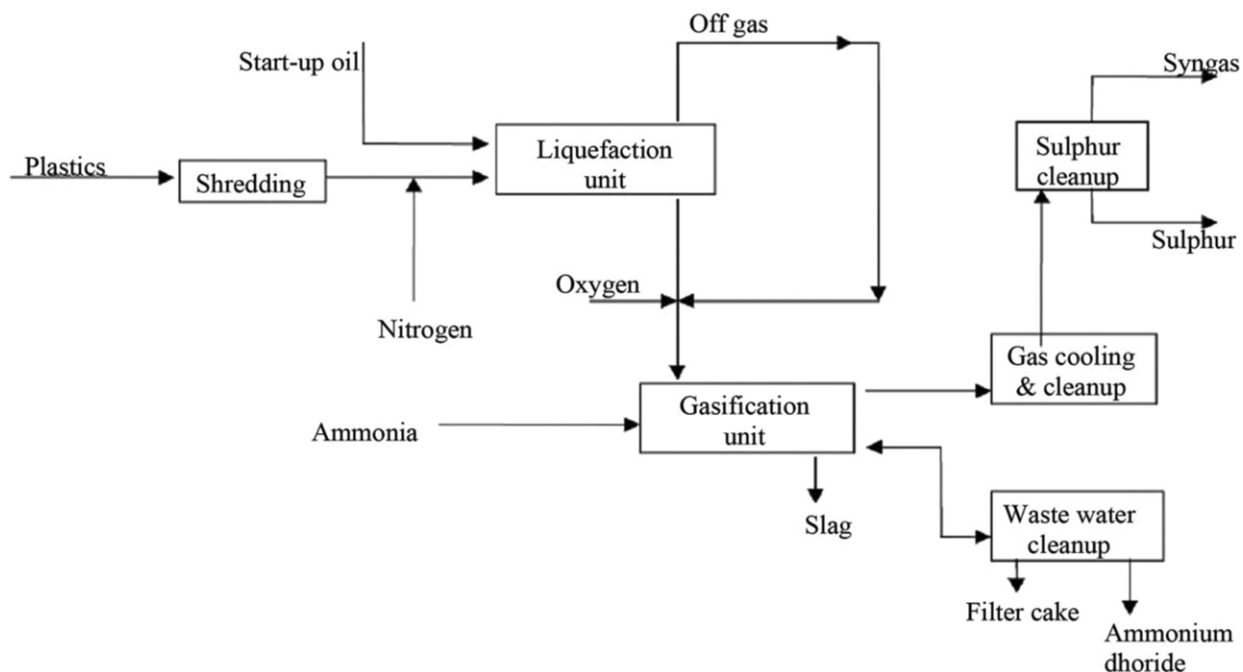


Fig. 11 Schematic diagram for Texaco gasification process. Reproduced from Ragaert, K., Delva, L., Van Geem, K., 2017. Mechanical and chemical recycling of solid plastic waste. *Waste Management* 69, 24–58. doi:10.1016/j.wasman.2017.07.044.

Hydrolysis

Hydrolysis is a chemical recycling approach utilizing alkaline, acid, or neutral environmental conditions to depolymerize plastic waste sources into monomers. The main drawback of the hydrolysis process is the requirements of high-temperature ranges from 200°C to 250°C, pressure between 1.4 and 2 MPa, and an extended time duration to complete depolymerization. In alkaline hydrolysis solution, potassium hydroxide or sodium hydroxide were employed and were followed by hydrothermal treatment.

Similarly, an acid hydrolysis treatment of sulfuric acid and other minerals acids is commonly utilized for depolymerization. Whereas in neutral hydrolysis, steam or hot water at high pressure were used for the depolymerization (Al-Sabagh *et al.*, 2016). In all these hydrolysis techniques, neutral hydrolysis gained more attention as it is considered eco-friendly.

Biodegradation Method of Recycling

Biological treatment techniques have been applied to the recycling of plastic derived from bioresources. The biodegradable plastics are comparatively advantageous due to their eco-friendly nature and can act as a replacement of traditional plastics in specific environmental applications (Kale *et al.*, 2007). Biodegradable plastics composed of starch, cellulose, and biopolymers, which are consumed by microorganisms, ascribable to the enzymatic activities the molecular weights becomes reduced (Fig. 12).

Starch is another widely utilized biopolymer in plastic production due to its availability, biodegradability, and inexpensiveness (Chattopadhyay *et al.*, 2011). Starch consists of amylase and amylopectin polymers, making it an appropriate alternative. The starch-based polymers, which are further categorized as starch-based and starch-filled polymers, are mainly used in the packaging and manufacturing industries (Jayasekara *et al.*, 2005). Various microorganisms such as fungi, algae, and bacteria are commonly employed to decompose these polymers. Most of these microorganisms are sensitive to environmental conditions under both aerobic and anaerobic conditions (Shah *et al.*, 2014).

The most commonly utilized biodegradable plastics are polylactic acid or polylactide (PLA) and poly-hydroxyalkanoates (PHA) (Alaerts *et al.*, 2018). PHAs are a biodegradable polyester derived by bacterial fermentation of lipids and sugars. PHAs polyesters have been utilized for broad applications but are prominently used in the pharmaceutical, packaging, and medical industries (Kushwah *et al.*, 2016). As stated above, the environmental conditions play a vital role in the decomposition of PHAs. Most frequently employed bacterial genres are *Cupriavidus*, *Bacillus*, *Nocardiopsis*, and *Burkholderia*.

Fungal species, such as *Micromyces* and *Mycobacterium*, are utilized in PHAs decomposition (Boyandin *et al.*, 2013). PLA is extracted from plant resources like tapioca roots, cornstarch, and sugarcane. It has been widely employed for medical applications as it is safe for consumption (Ikada and Tsuji, 2000). Studies have shown that TPA can be replaced by biologically derived 2–5 furan dicarboxylic acid for the synthesis of highly efficient and high performing bioderived PET polymer. (PLA) is the most commonly used biodegradable polymer and is composed of lactic acid in corn. PLA has less toxicity, excellent mechanical properties, and suitability in biomedical and packaging applications. However, a significant drawback of PLA polymer is its poor thermal properties. PLA polymers usually degrade within 12 months, which prevents accumulation in the environment compared

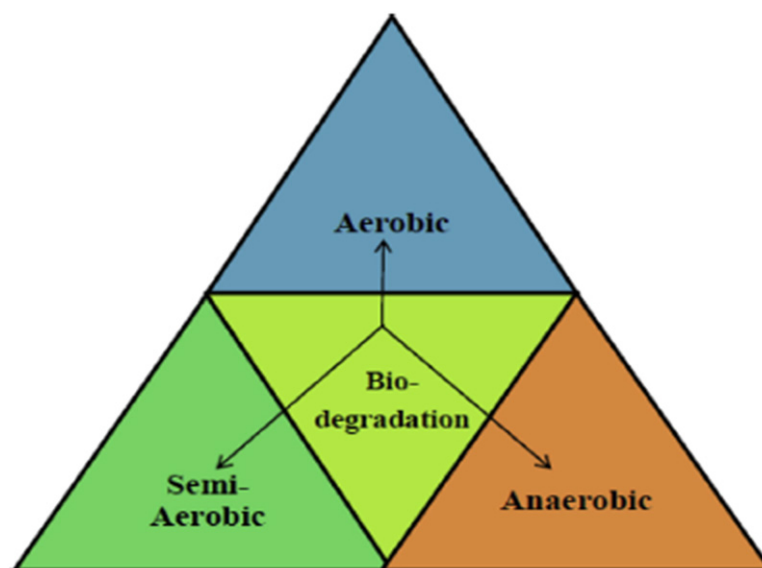


Fig. 12 Various biodegradation pathways to treat plastics. Reproduced from Moharir, R.V., Kumar, S., 2018. Challenges associated with plastic waste disposal and allied microbial routes for its effective degradation: A comprehensive review. *Journal of Cleaner Production* 208, 65–76. doi:10.1016/J.JCLEPRO.2018.10.059.

with other plastics. LCA studies have shown that PLA polymers have less greenhouse gas emissions compared with petroleum-based plastics. PLA has good mechanical, biodegradability, and availability making it a suitable option for industrial and other applications (Liu *et al.*, 2000). The by-products of hydrolytic degradation of PLA can be easily decomposed by microorganisms such as *B. licheniformis*, *Cryptococcus* sp., *Amycolatopsis* sp., etc. (Fukushima *et al.*, 2009; Anderson and Shive, 2012).

Various industry sectors, like consumer electronics and automotive industries, have incorporated bioplastics in their products. PLA blends are successfully used in the manufacturing of monitor screens and other electronics peripherals such as headsets, tablets, cell phones, game consoles, and earphones (Research and Markets, 2018). Biobased polyester has also shown its footprints in the automobile industries with its superior characteristics such as high stiffness, preferable thermal shock resistance and electrical characteristics, and improved dimensional stability. Industry giants like Toyota and Rochling automotives have included bioplastics in their automobiles (Calza *et al.*, 2017). Poly(lactic-co-glycolic acid) is another classification of biodegradable plastic widely utilized in the food and drug delivery industries (Ashter, 2016) (Table 3).

Biodegradation of plastic using microbes

The production of extracellular enzymes assists microorganisms in the degradation of biopolymers into carbon dioxide and water through enzymatic and metabolic activities (Shah *et al.*, 2014). The catalytic activity of enzymes depends on the microbial species employed and even within the strains. The efficiency of degradation varies for different species and polymer types. For example, the fungi species is more suitable for biodecomposition of lignins composed of laccases to catalyze nonaromatic and aromatic compounds through oxidation (Mayer and Staples, 2002). The preliminary mechanism in plastic biodegradation is affixing of microorganisms with polymers by surface colonization. The enzyme hydrolysis of plastics consists of two stages: The initial stage is attaching of enzymes with polymers accompanied by hydrolytic division. The by-products of degraded polymers like dimers, monomers, and oligomers, which are low in molecular weight, get converted to water and carbon dioxide through mineralization (Tokiwa *et al.*, 2009). Under aerobic environmental conditions, bacteria utilize oxygen as electron acceptor followed by synthesis of organic compounds. As a result, water and carbon dioxide are produced as the end products (Priyanka and Archana, 2011). However, in anaerobic conditions, during the absence of oxygen, the polymers are broken down by microorganisms. The anaerobic bacteria utilize iron, nitrate, manganese, carbon dioxide, and sulfate as electron acceptors. New pathways and microbial enzymes need to be studied to further optimize the degradation of biopolymers more effectively.

Factors influencing plastic biodegradation

Various factors, including environmental degradation parameters and polymer and enzyme characteristics, play an instrumental role in microorganism activities. Moisture is one of the most crucial parameters that affect the multiplication and activities of microorganisms. Sufficient moisture is adequate for microorganism survival and for carrying out the hydrolysis process. Similarly, acidic and basic parameters can influence the rate of hydrolysis reactions. From various studies, a pH of 5 is optimal for the hydrolysis reactions (Auras *et al.*, 2004; Mohanty *et al.*, 2005). Similar to pH, the softening temperature is significant for enzymatic degradation. As the softening temperature increases, the possibility of biodegradation becomes limited. Polyesters with a high melting point are less appropriate to the biodegradability option (Tokiwa and Calabia, 2004).

Table 3 Some bacterial and fungal enzymes/strains involved in biodegradation of both biodegradable and nonbiodegradable plastics

Substrates used	Various microbes used	References
Polypropylene	<i>Methylobacter</i> sp., <i>Methylocystic</i> sp., <i>Methylocella</i> sp., <i>Bacillus flexus</i> , <i>Phanerochaete chrysosporium</i> fungus, <i>Engyodontium album</i> fungus	(Muenmee <i>et al.</i> , 2016) (Arkatkar <i>et al.</i> , 2009)
Low-density polyethylene	<i>Pseudomonas Putida</i> , <i>Pseudomonas Fluorescens</i> , <i>Pseudomonas Dominate</i> , <i>Burkholderia</i> , <i>Flavobacterium</i> sp., <i>Vibrio Alginolytious</i> , <i>Pseudomonas</i> <i>aeruginosa</i> , <i>Pseudomonas Stutzeri</i> , <i>Anabena</i> sp., & <i>Pseudomonas Fluescans</i> <i>Pseudomonas aeruginosa</i> , <i>Burkholderia seminalis</i> , <i>Stenotrophomonas pavanii</i> <i>Methylobacter</i> sp., <i>Methylocystic</i> sp., <i>Methylocella</i> sp <i>S. aureus</i> and <i>E. Coli</i> bacteria <i>Bacillus subtilis</i> V8, <i>C-Paracoccus aminophilus</i> B1 4, <i>D-Pseudomonas putida</i> <i>C25</i> , <i>E-Pseudomonas</i> <i>Aeruginosa</i> V1, <i>F- Acinetobacter calcoaceticus</i> V4 <i>Bacillus pumilus</i> SAFR-032, <i>Chitinophaga</i> sp., <i>Pseudomonas putida</i> , <i>Burkholderia</i> , <i>Xanthobacter</i> , <i>autotrophicus</i> Py2, <i>Hyphomicrobium</i> sp. <i>MCI</i> , <i>Nakamurella multipatita</i> , <i>Nocardia</i> sp., <i>Rhodococcus</i> sp., <i>Nitrobacter</i> <i>winogradsky</i> Nb. 255, <i>Nitrobacter hamburgensis</i> , <i>Nitrosomonas</i> sp. AL212 <i>Nitrosomonas</i> , <i>europaea</i> , <i>Methylococcus</i> sp., <i>Methylocystis</i> sp., <i>Methylobacter</i> sp., <i>Methylocella</i> sp., <i>Methylobacterium</i> sp.	(Veethahavya <i>et al.</i> , 2016) (Mehmood <i>et al.</i> , 2016) (Muenmee <i>et al.</i> , 2016) (Manohar <i>et al.</i> , 2017) (Pathak and Kumar, 2017) (Muenmee <i>et al.</i> , 2016)
High-density polyethylene	<i>Bacillus pumilus</i> SAFR-032, <i>Chitinophaga</i> sp., <i>Pseudomonas putida</i> , <i>Burkholderia</i> , <i>Xanthobacter</i> , <i>autotrophicus</i> Py2, <i>Hyphomicrobium</i> sp. <i>MCI</i> , <i>Nakamurella multipatita</i> , <i>Nocardia</i> sp., <i>Rhodococcus</i> sp., <i>Nitrobacter</i> <i>winogradsky</i> Nb. 255, <i>Nitrobacter hamburgensis</i> , <i>Nitrosomonas</i> sp. AL212, <i>Nitrosomonas</i> , <i>Europaea</i> , <i>Methylococcus</i> sp., <i>Methylocystis</i> sp., <i>Methylobacter</i> sp., <i>Methylocella</i> sp., <i>Methylobacterium</i> sp.	(Muenmee <i>et al.</i> , 2016)
Polystyrene	<i>Methylobacter</i> sp., <i>Methylocystic</i> sp., <i>Methylocella</i> sp. <i>R. ruber</i>	(Muenmee <i>et al.</i> , 2016) (Mor and Sivan, 2008)
High impact polystyrene	<i>Pseudomonas</i> and <i>Bacillus</i> strains	(Mohan <i>et al.</i> , 2016)
Polyethylene terephthalate	<i>Arthrobacter sulfonivorans</i> , <i>Serratia plymuthica</i> , <i>Clitocybe</i> sp. fungus, <i>Laccaria</i> <i>laccata</i> fungus, <i>Thermobifida fusca</i> , <i>Humicola insolens</i> fungus	(Janczak <i>et al.</i> , 2018; Ronkvist <i>et al.</i> , 2009)
Polyurethane	<i>Comamonas acidovorans</i> TB-35, <i>Curvularia senegalensis</i> , <i>Fusarium solani</i> , <i>Aureobasidium pullulans</i> , <i>Cladosporium</i> sp., <i>Pseudomonas chlororaphis</i>	(Zheng <i>et al.</i> , 2005)
Polyester polyurethane	<i>Aspergillus tubingensis</i>	(Peixoto <i>et al.</i> , 2017)
Polyvinyl chloride	<i>Pseudomonas putida</i> AJ, <i>Ochrobactrum</i> TD, <i>Pseudomonas fluorescens</i> B-22, <i>Aspergillus niger</i> van Tieghem F-1119	(Danko <i>et al.</i> , 2004)
Polyethylene	<i>Pseudomonas species</i> (sp.), <i>Pseudomonas aeruginosa</i> , <i>Pseudomonas fluorescens</i> <i>Bacillus subtilis</i> <i>Paenibacillus macerans</i> , <i>Rahnella aquatilis</i> <i>Rhodococcus rhodochrous</i> , <i>Rhodococcus ruber</i> <i>Chaetomium</i> sp., fungus <i>Brevibacillus borstelensis</i> , <i>Rhodococcus rubber</i> , <i>Penicillium simplicissimum</i> <i>Penicillium simplicissimum</i> fungus, <i>Penicillium frequentans</i> fungus <i>Glioclodium virens</i> fungus, <i>Penicillium pinophilum</i> fungus, <i>Phanerochaete</i> <i>chrysosporium</i> fungus <i>Nocardia asteroides</i> , <i>Cladosporium cladosporioides</i> fungus, <i>Aspergillus flavus</i> fungus <i>Brevibacillus borstelensis</i>	(Rajandas <i>et al.</i> , 2012) (Vimala and Mathew, 2016) (Nowak <i>et al.</i> , 2011) (Fontanella <i>et al.</i> , 2010) (Sowmya <i>et al.</i> , 2012) (Sivan, 2011) (Leja and Lewandowicz, 2010) (Manzur <i>et al.</i> , 2004) (Koutny <i>et al.</i> , 2006; Hadad <i>et al.</i> , 2005)
Nonpretreated polyethylene	<i>Comamonas</i> , <i>Delftia</i> , <i>Stenotrophomonas</i>	(Sivan <i>et al.</i> , 2006)
Polyethylene microplastics	<i>Zalerion maritimum</i> fungus	(Paço <i>et al.</i> , 2017)
Poly-lactic acid	<i>Trichoderma viride</i> fungus	(Lipsa <i>et al.</i> , 2016)
Poly-lactic acid based composite film	<i>Phanerochaete chrysosporium</i> fungus	(Stoleru <i>et al.</i> , 2017)

Note: Moharir, R.V., Kumar, S., 2018. Challenges associated with plastic waste disposal and allied microbial routes for its effective degradation: A comprehensive review. *Journal of Cleaner Production* 208, 65–76. doi:10.1016/J.JCLEPRO.2018.10.059.

Different enzymes may have differently shaped active sites and, therefore, are more able to biodegrade certain polymers. For example, the fungal species *A. Niger* and *A. flavus* degraded straight chain polymers derived from diacid monomers quickly compared with other derived polymers (Kale *et al.*, 2007). The polymer characteristics such as shape, size, and molecular weight are also crucial parameters in biodegradability. The rate of degradation depends on molecular weight; at a high molecular weight above 4000, the rate of degradation is lower when compared with low molecular weight polymers (Kale *et al.*, 2007). Similarly, the polymer with larger surface area degrades much quicker

compared with one with a smaller surface area (Kijchavengkul and Auras, 2008). The presence of other additives such as dyes and toxic paints have an impact on the growth and overall activities of the microorganisms due to the presence of toxins (Yang *et al.*, 2005).

Challenges for Plastic Recycling

Bulk plastics usually exhibit weak mechanical properties due to inadequate interfacial adhesion. When bulk plastics are melted together, their entropy of mixing will be very low, leading to inefficient mixing and phase separation. The phase boundaries will be fragile in nature, and structural properties of the resulting compound will be very weak (Kutz, 2016). As a result, mixed plastics have minimal applications due to fewer returns. Most of the plastic recyclers focus on the single type of plastics so that their composition and properties can be identified easily and modification can be carried out to produce a recycled compound exhibiting the same properties as that of virgin plastics, ultimately bringing about great profitability (Merrington, 2017).

The presence of various additives, coatings, discoloring agents, antioxidants, and cross-contamination issues makes the recycling of plastic a tedious process (Hahladakis *et al.*, 2018). One of the significant challenges faced in the recycling of bulk plastics is that different types of plastics are not adaptable to each other at the atomic or subatomic level due to the inherent incapability of being mixed or blended (Hopewell *et al.*, 2009). For example, the presence of a PVC contaminant in the PET during the recycling process leads to the generation of HCl gas from PVC at a high-temperature condition. On the other hand, the presence of PET in a PVC recycling process generates a solid mass of undistributed crystalline PET, which will diminish the value of recycled plastic waste (Hopewell *et al.*, 2009). The recycled plastics from household waste (HW) showed higher contamination of metal concentrations such as (Cr, Zn, Ti, and Pb) compared with virgin plastics, which limits the quality and feasibility of using reprocessed plastics (Eriksen *et al.*, 2018).

The presence of chromium is identified in the recycled HW plastics at an average range of 14 and 24 mg/kg. This may be due to either the usage of additives during the postproduction phase of plastics or during the waste management process (Pivnenko *et al.*, 2015). Due to the inclusion of metal-based additives during plastics recycling and inadequacy in metal removal, there has been a build-up of metal contaminants further causing a severe threat to human life and to the environment (Pivnenko *et al.*, 2016). The exposure of waste plastics either to UV radiations or sunlight, which further undergo photooxidation process, will ultimately contaminate land and marine environments (Moharir and Kumar, 2018).

The global market for recycled plastics highly depends on the price of crude oil (Meng *et al.*, 2015). As the demand for petroleum products decreases, the demand for recycled plastics subsequently also decreases. This will automatically discourage prevailing plastic manufacturers from buying recycled plastic products (Triguero *et al.*, 2014). Recycling mixed plastics is a challenging process in PSW (García, 2016). The complexity occurs in separating residues from mixed plastics due to improper separation of blends, which will ultimately result in the generation of products with poor mechanical properties (Valavanidis, 2018). Another critical challenge is in identifying suitable plastic recycling technologies. The challenge is imposed in treating a large number of bulk plastics within minimal expenditure and fewer maintenance costs. This method has the potential of being used as a substitute for landfilling or incineration, which are known to be less eco-friendly (Jacob-Vaillancourt and Sorelli, 2018). Since plastics are a recalcitrant polymers, they will not degrade easily by natural means and they show high persistence in nature, which is usually, on average, about 100 years (Alam, 2015). Hence, proper monitoring of recycled plastics must be carried out. Additionally, the identification of efficient PWM technologies and absence of contaminations before usage should also be present.

Properties of Recycled Plastics

It is crucial to understand the characteristics of the recycled plastic for determining its suitability in various applications. After the initial life cycle or repeated usage of plastics, the used plastics can be recovered or recycled into new products. Since the recycled plastic obtained from diverse sources has been exposed to distinctive conditions, the plastic materials also exhibit distinctive degradation and performance characteristics (Merrington, 2017). The recovered plastic is categorized by its mechanical and chemical characteristics for its further application.

The plastic degradation is complex; the degradation process can primarily be categorized as either biological, mechanical, chemical, thermal, or a combination of more than one process, for example, thermomechanical, thermooxidative degradation, etc. The degradation process could exhaust inherited properties. However, in some rare cases, the properties of the recycled plastic are identical to those of virgin plastic (Najafi, 2013). There are several crucial factors that play a vital role in the recycling of plastic; such factors are discussed in the following sections.

Melting Point

The melting points of different plastic sources are listed in Table 4. Most of the plastic sources have a melting point below 200°C; however, the plastic sources containing additives and impurities have melting points above 200°C (Biron, 2017).

The melting point becomes decisive when plastic sources are composed of distinctive polymers with different melting point temperatures. In such cases, the identification of the optimal melting point is challenging. The plastic sources with lower melting point melt quickly compared with other sources having a higher melting point; as a result, the final product becomes

Table 4 List out the melting points of various commonly used plastics

<i>Plastic sources</i>	<i>Melting point (°C)</i>
Polyethylene terephthalate	245
Polystyrene	240
Polyamide 6	233
Mixed plastics	185
Polypropylene	170
Polyethylene	135
High-density polyethylene	130
Linear low-density polyethylene	123
Low-density polyethylene	115

heterogeneous. In further detail, the plastic sources consist of PP and LDPE. The melting point of LDPE is 115°C, whereas the PP has a melting point of 170°C. If the melting process has been processed to suit for the LDPE, then the unmelted PP results in defects in the final heterogeneous product (Goodship, 2007).

Furthermore, the melting of LDPE leads to impairing the mechanical characteristics of the resultant plastic. It is necessary to identify the optimum melting point of mixed plastic sources, and it can be attained by performing further experimental investigations.

Immiscibility

The segregation of recycled plastics from one another demands additional burdens. A significant burden is that of finances; therefore, it is preferable to use recycled plastics as fused. The polymer blending approach is utilized to overcome fundamental drawbacks such as low impact strength on plastics and also cut down the final production cost. The major drawback in mixing plastics is that the majority of the polymers are immiscible. The weaker physical attraction occurs at phase boundaries of immiscible blends; this could cause phase separation under stress, leading to evolving materials with poor mechanical characteristics (Chanda and Roy, 2007).

The deficiency incompatibility between polymers in blending affects the quality of the recycled plastic products. The most effective technique to enhance the compatibility between plastics is to employ the compatibilizing agents. These agents have the ability to enhance the interfacial adhesion between polymers. A compatibilizing agent dosage of 2% to 5% can be added during the reprocessing stage. However, the cost and separation processing cost raise questions as to its economic benefits.

Rheology

The melt flow index is another crucial parameter for assessing the molecular weight distribution of the plastics. The plastic sources with higher melt flow index consist of shorter chains, resulting in a lower molecular weight, which makes for easier flow. Similarly, the lower melt index indicates a high molecular weight and longer chain. The increase of molecular weight boosts impact strength. Additionally, melt viscosity also results due to lower hardness, yield strength, softening point, and stiffness (Guerreiro *et al.*, 2012). Numerous investigations have been reported on modification of plastic's rheological properties especially on the decrease of melt viscosity after repetitive injection and extrusion molding (Gere and Czigany, 2018; Li *et al.*, 2018; Wang *et al.*, 2016; Zhao *et al.*, 2018; Záleská *et al.*, 2018). During the processing of virgin plastic to other value products, the antioxidant is diminished due to excessive shearing and overheating. As a result of limited availability of antioxidants, depolymerization will occur (Najafi, 2013).

Due to the extrusion process, polymer degradation occurs due to severe stress and the thermal cycle leads to further declination in molecular weight. Antioxidants can result in slow thermomechanical degradation that results in the final product characteristics. Recycled PP tends to undergo degradation more efficiently than virgin plastics, and its recycling is followed by a reduction in melt index (Takatori, 2015). PP is more sensitive to oxidation and requires a higher concentration of antioxidants. The antioxidants aid in preserving properties of plastic at higher temperature shielding the recycled plastics from rapid degradation under direct air, oxygen, direct sunlight, pollutants, water, and other elements.

The presence of foreign matter would contaminate and ultimately decrease the impact strength of recycled plastic material (Takatori, 2015). The major drawback in using recycled PP is the reduction in mechanical strength due to the diminished number of tie molecules associated with the lamellar layer of recycled PP in contrast with virgin PP (Takatori *et al.*, 2016; Tominaga *et al.*, 2015).

Cross-Linking

The cross-linking mechanism is used to enhance the thermal properties of thermoplastics for a wide variety of applications by means irradiation with heat, UV, X-rays, or gamma radiation (Mizera *et al.*, 2012). Cross-linking helps in increasing impact strength, creep resistance by reducing crystallinity, melt flow index, and break at elongation (Najafi, 2013). Heavy cross-linking restricts the movement of molecular chains, resulting in a break in the continuity of melt flow, which ultimately changes the nature of the polymer to thermoset from thermoplastic (Maitra and Shukla, 2014).

Cross-linked polymers are used in a wide variety of application, including medical, pharmaceuticals, biomedical fields, hot pipes, solid phase extraction, paper coating, synthesizing a stronger antiviral biocide, and so on (Mane *et al.*, 2016; Hongbo *et al.*, 2016; Parhi, 2017). Recently, cross-linked polyethylene waste has been used as a modification of binder. Additionally, aggregates for asphalt mixtures were found to be useful and enhanced in the performance of road pavement applications (Costa *et al.*, 2017).

Crystallinity

The crystalline nature of thermoplastics is characterized by a thick-packed arrangement of molecular chains, hardness, resistance to heat, and rigid in structure compared with other types of polymers (Grigore, 2017). Examples of such polymers are LDPE, PP, and HDPE (Mark, 2017). An irregular arrangement of molecular chains characterizes the amorphous nature of thermoplastics. Examples include PVC, PS, and polycarbonate. The semicrystalline nature of polymers is exhibited by combined properties of crystalline and amorphous polymers and characterized by nearly ordered molecular chains (John, 2017). Examples include polyamide imide and polyester poly-butylene terephthalate.

Recycled plastics show less crystalline nature compared with virgin plastics (Yao *et al.*, 2013). PP is an economically viable thermoplastic polymer showing crystalline properties of about 40%–60%. PP is characterized by low density, high melting point, and excellent resistance to higher temperature. PP is characterized by low density, high melting point, excellent resistance to higher temperature and impacts, and better recyclability compared with other thermoplastics and applicability in electrical cable insulation, medical, and automobile sectors (Maddah, 2016).

Polarity

The formation of polar side groups makes the polymer chains stronger through strong hydrogen bonding. Thermopolymers such as PP and PE have a shallow surface free energy and polarity and are used for developing wood plastic composite (Najafi, 2013). In recycled plastics, the presence of polar groups enhances the affinity between polar lignocellulose and nonpolar plastic materials (Karumuri *et al.*, 2017). Oxidized polyolefin is used as a superior compatibilizing agent for plastics to enhance adhesiveness between nonpolar and polar matrices (Ugbolue, 2017). The compatibilizer mainly consists of maleic anhydride or carboxylic acid-functionalized ethylene copolymer (Kaiser *et al.*, 2017). During the oxidation process, a substantial amount of oxygen is assimilated into the polymer in the form of carboxyl, aldehyde, hydroxyl, ketone, and ester groups (Gewert *et al.*, 2015). It is shown that oxidized PP exhibited a better enhancement in mechanical and physical properties of wood–PP composite and was found to be more effective than maleic anhydride embedded PP (Peerbooms and Pickering, 2018).

Applications of Recycled Plastics

Recycled plastics have shown a wide variety of applications in various fields such as construction, the automobile industry, and in food packaging (Goodship, 2007). The uses of recycled plastics in various fields of applications are listed in Table 5.

Environmental Aspects of Recycled Plastics

Recycling of bulk plastics is one of the most effective methods in mitigating environmental impact and resource exhaustion (Emily and North, 2013). There are a lot of environmental benefits in using recycled plastics. Recycling of plastics aids in the preservation of petroleum resources, decreasing greenhouse gases and CO₂ emissions and limiting landfill waste contamination (Shrivastava, 2018). Waste plastic bottles can be reused and refilled, and used as storage containers (Intertek, n.d.). Recycled plastics preserve fossil usages, which are needed for synthesizing virgin plastic materials (Biron, 2017). The advantages of recycled plastics include a reduction in global warming, minimizing waste disposal in landfills, preventing air and water pollution, and conserving energy and natural resources (Richards, 2014; Soffar, 2016).

According to the Environmental Protection Agency recycling 1 pound of PET plastic waste can preserve heat energy, which aids in decreasing the damage and overload of power grids (Balakrishnan and Flora, 2017). The use of recycled plastic concrete helped in the abatement of the carbon footprint by about 15.3% and reduction of consumption of overall energy by 16.2% (Betita, 2013). However, some drawbacks include the generation of toxic volatile organic compounds gases during plastic recycling. The generation of pollutants is a drawback in assuring quality recycled products. Additionally, improper recycling procedures result in adverse environmental impacts (Hartman, 2017). For example, the recycling of PVC is quite challenging due to the presence of VCM (vinyl chloride monomer). VCM has the chemical property to break down and release chlorine components, which ultimately results in the accumulation of dioxins, a toxin, in the environment (Zhang *et al.*, 2015). Hence the quality and feasibility of using recycled plastics require better evaluation.

Table 5 Application of various recycled bulk plastics

<i>Types of plastics</i>	<i>Field of application</i>	<i>References</i>
Polyvinyl chloride	Packaging material for drinking bottle, clothes, food and medical purposes, wallpaper, coatings, construction purposes, plastic composite.	(Thakur, 2015; Petrović and Hamer, 2018; Mamoor <i>et al.</i> , 2013; Arjmandi <i>et al.</i> , 2015)
Polyethylene terephthalate	Concrete, carpet fibers, drinking and detergent bottles and polyester fiber, used as an additive in the construction of roads, water filtration, plastic cement, packaging, construction applications, 3D printing filaments.	(Gu and Ozbakkaloglu, 2016; Singh <i>et al.</i> , 2017; Zander <i>et al.</i> , 2016; Jassim, 2017; Pechyen, 2017; Bolduc <i>et al.</i> , 2018; Evans <i>et al.</i> , 2016)
High-density polyethylene	Laundry detergent bottles, mobile parts, pipes used for agricultural purposes, films, toys, and floor tiles, flat roofs, 3-D printing filaments.	(Rahimi and Garcíá, 2017; Smolka and Sobotka, 2018; Kamaruddin <i>et al.</i> , 2017; King <i>et al.</i> , 2014)
Low-density polyethylene	Agricultural plastic films, composite in rubber, composite in plastic application.	(Picuno <i>et al.</i> , 2012; Kaewduang <i>et al.</i> , 2015; Lim <i>et al.</i> , 2016)
Polyamide	Enhancement in melt flow index and elasticity modulus of waste silk, prevents greenhouse gas emissions, consumer goods, transport, industrial applications.	(Taşdemir <i>et al.</i> , 2013; Pelin <i>et al.</i> , 2017; Singh <i>et al.</i> , 2018)
Polycarbonate	CDs, audio, video, medical equipment, purification membranes, safety glasses, automobile sector, compatibilizer.	(Jones <i>et al.</i> , 2016; Antonakou and Achilias, 2013; Ramesh <i>et al.</i> , 2014)
Polypropylene	Appliances, automobile, construction of roads, enhanced properties of textile fiber, plastic bricks.	(Matei <i>et al.</i> , 2017; Appiah <i>et al.</i> , 2017; Araujo and Morales, 2018; Bredenoord, 2017)
Polystyrene	Geopolymer encapsulation, lightweight concrete for building applications, packaging, insulation, conserve natural resources.	(Makai <i>et al.</i> , 2015; Schlummer <i>et al.</i> , 2017; Castro <i>et al.</i> , 2017)
Mixed recycled plastics	Fencing, seating, bridge components, pilings, railings, military load bearing, and civil applications, a replacement for asphalt mixtures in pavement applications.	(Bajracharya <i>et al.</i> , 2014; Lee <i>et al.</i> , 2012; Zakaria <i>et al.</i> , 2018)

LCA and economic methods are used for evaluating the environmental aspects of PWM. The reports showed that the recycling mechanism showed the least environmental effects on total energy use and global warming (Bernardo *et al.*, 2016). Recently, the environmental aspect of recycling waste electrical and electronic equipment (WEEE) plastic was evaluated by LCA analysis in Brazil (Campolina *et al.*, 2017). The reports showed that the recycling of WEEE plastics resulted in the reduction of environmental effects by up to 4 times compared with incineration methods and up to 6–10 times lower when compared with the generation of virgin plastics (Wäger and Hischer, 2015). The recovery of WEEE plastics resulted in a reduction in energy needs, consumption of raw materials, and environmental impacts (Biganzoli *et al.*, 2015; Milios *et al.*, 2018).

Conclusion

Recycling of bulk plastics is the most commonly used mechanism to combat the intensifying plastic waste contamination. The ultimate aim is to implement a plastic economy where the waste plastic products are 100% recyclable, and are used for long-term applications with less environmental impact. The recycling advancements are the molecular level, the emergence of new initiatives, and support from governments and manufacturers have helped to achieve greater targets and accomplished changes in the recycling sector. Recycling of waste plastics requires high energy needs, which finally produces low-quality recycled polymers exhibiting low chemical and thermal properties. The presorting step before recycling is highly time-consuming and expensive in nature. Prevailing technologies cannot be used in recycling all plastic waste. At present, there are no effective low-energy segregation methods for mixed plastic polymers and packaging in mechanical recycling. Hence, further development is required. The presence of cross-linked polymers in elastomers and thermosets is not well adaptable to current mechanical recycling techniques. Studies have to be carried out to identify suitable polymers in which cross-linking undergoes reversal or exchange at high-temperature conditions, which further facilitates the remaking of the polymers before reusing. Recent research is focused on chemical recycling, which requires low energy, improved compatibilization of mixed plastic waste to avoid the presorting needs, and enhanced recycling apart from thermoplastics. The presence of better compatibilizing agents helps to regulate the phase behavior of polymer mixtures and reduce the contamination issues associated with mixed plastics without losing properties of recycled materials.

Another emerging area in plastic recycling is synthesizing biodegradable plastics, which can replace prevailing conventional plastics. Biodegradable polymers are more accessible to degrade by the action of microorganisms under oxygen-rich and deficient conditions, oxidation, or photodegradation. Biobased polymers have an exciting future in synthesizing highly efficient polymers. In the future, to make efficient recycling to a genuinely new recycling, approaches have yet to be identified by seeking support from the governmental, research, and industrial sectors and creating awareness of the public about the need for and benefit of recycling plastics. Developing advanced computational modeling, identifying new compatibilizing agents, and synthesizing novel polymers will help in upgrading recycling mechanisms, which will be very helpful in the future.

See also: Prospect of Recycling of Plastic Product to Minimize Environmental Pollution

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The Potential of Core-Shell Technique in the Enhancement of Different Derived Calcium Carbonate Wastes in Anticorrosive Paints

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Introduction

Waste management constitutes one of the world's main problems in our recent times due to its tremendous economic and social impact. The concern about solid wastes is increasingly growing because of the serious problems they can implement to the environment and the negative conditions to health and economic loss they can cause. Moreover, the rapid economic growth, climate change, resource depletion and the exploitation of natural resources have forefront the problem of waste management rapidly towards more studies on their reusability in different useful industries that are beneficial to daily human life services and not being a burden (Xiaoa *et al.*, 2018).

Although reusing waste materials is not a new issue particularly in the industrial sector, the appropriate waste management is one of the main requisites for sustainable development to guarantee suitable utilization of wastes according to their types, chemical structure and properties. Numbers of small and large enterprises have emerged in response, aiming at recycling and adding commercial value to the waste materials that can help to diversify production and reduce final costs, in addition to providing alternative raw materials for number of industrial sectors. Overlooking was extended to the fact that some wastes are similar in their composition to the natural raw materials used nowadays, and often contain materials that are not only compatible but also can be helpful in the fabrication of other new materials. Within this scenario, upgrading industrial wastes to alternative raw materials became interesting both technically and economically for a wide range of applications (Awasthi and Li, 2017).

Stone industry is an important one in the worldwide economy; it produces huge amounts of residues with different dimension and particle sizes (Marras *et al.*, 2010). Marble is one of the largest produced natural stone in the world and it accounts for 50% of world's natural stone production. It is crystalline metamorphic limestone, basically containing calcite (CaCO_3) and dolomite $\text{CaMg}(\text{CO}_3)_2$. The process of quarrying marble stones is performed in order to produce slabs and tiles, which are widely used in the construction industry for high quality flooring and wall cladding purposes. In the process of converting in-situ stone deposits to the final product, significant amount of waste is generated in both the mine site, and in the processing and polishing plant. These wastes are generated in the form of fragments and shapeless blocks which have no commercial value. Marble wastes produced in the quarrying and cutting processes of ornamental stones is becoming a worrying factor for both industry owners and environmentalists due to the growing amount of these rejected waste materials (Almeida *et al.*, 2007; Yeşilaya *et al.*, 2017).

Food industry also generates a lot of biological wastes which release many problems due to their disposal cost and landfill problems. However, there is an opportunity for the bio-economy society to use these residual materials in new applications, and it definitely deserves the attention of the scientific world. Eggshells are unique natural biomaterial with fascinating structures, which offers rich plethora of utilizing possibilities that can be broadened by further treatment. In recent years, great efforts are conducted for the application of eggshells as value added products (Mittal *et al.*, 2016).

Eggshells are comprised of protein fibers network, associated with crystals of calcium carbonate (96% of shell weight), magnesium carbonate (1%), calcium phosphate (1%) and also some organic materials and water. Calcium carbonate (CaCO_3) which is the major constituent of the eggshell is an amorphous crystal that occurs naturally in the form of calcite (hexagonal crystal) with low water solubility (Baláz, 2018).

Both marble and eggshells are considered as resources of calcium carbonate which have diverse uses such as employing it in the construction industry, either as a building material or limestone aggregate for road building or as an ingredient of cement or starting material for the preparation of builder's lime by burning in a kiln. Also it is widely used as an extender in paints and has traditionally been a major component of blackboard chalk, also it can be used in the production of glossy paper (Wahab, 2017).

Concerning the wastes; many attempts were made to incorporate marble wastes into raw material mixtures in order to produce different products, besides its usage as reinforcement or raw material in various areas and applications. In the construction materials sector, many researchers have studied the production of concrete with varying percentage of marble waste to replace the cement in order to enhance the concrete characteristics (Shelke *et al.*, 2012). There are also other studies investigating the reusability of marble wastes in the concrete as aggregates because of its lower water absorption compared to other natural aggregates, which can achieve improvements in the water absorption, abrasion and porosity values of the concrete whereas decreased flexural and pull-off strengths (Binici *et al.*, 2007).

Many uses have been studied also for beneficiation from the eggshells waste which is a rich source of minerals that can serve as a pharmaceutical excipient and base material for developing medicinal, dental preparations, food additive and calcium

supplement; diluent of solid dosage forms, agricultural fertilizer component, and as a component for bone implantation (Oliveira *et al.*, 2013).

New Evolving Preparation Technologies

The development of different chemical preparation techniques have become an integral research area due to the potential changes they cause in the different compounds. In planning the route of chemical synthesis, researchers usually visualize the end product, fore fronting the search toward increasingly simpler methods. Nowadays, new technologies facilitate the usage of modified plan routes for synthesizing particles with different sizes, shapes and surface morphology. The goal in developing new chemical techniques is to find how to manage the reactions of the different materials to produce new tailored materials that are capable of promoting some desired properties that can be useful in the different strategic industries. These tailored materials will lead to locomotive development of new chemical synthesis methods providing an opportunity to offer specific properties for a wide range of desired applications.

Core-shell particles have attracted considerable interest as a class of new materials with diverse applications due to their various advantages, such as low cost and ease of preparation. Core-shell technology has become an important research area since few decades, offering particles of biphasic materials with an inner core and an outer shell that are of different compositions. The core-shell materials may be of different sizes and shapes, i.e., nano shell/micronized core and vice versa or both of the same sizes. These particles contain different materials depositing on each other, and covering the cores even with thin shell of another material can bring many new properties to the formed particles including; promoted reactivity, thermal stability, or oxidative stability, etc. (Ahmed, 2009; Xiong *et al.*, 2006).

Corrosion Causes and Rehabilitation

Corrosion is a naturally occurring phenomenon and just like all natural processes, it is spontaneous and can drive the materials to its lowest possible energy states. Most of the metals and alloys have natural tendency to combine with water and oxygen present in their environment and return them to the most stable state, i.e., their native and stable oxide states (Revie and Uhlig, 2008).

Corrosion can result in dangerous and expensive damage to everything starting from home appliances, till bridges and buildings. It has many effects in our daily lives, a direct one in affecting the useful service lives of our possessions, and an indirect one that concern the producers and suppliers of goods and services which incur corrosion costs that they pass on to consumers. Corrosion can cause serious consequences on people lives, as in corrosion of steel reinforcing bar (rebar) in concrete which can proceed out of sight and suddenly result in failure of; a section of highway, collapse of electrical towers, damage to buildings, parking structures, and bridges, etc., resulting in significant repair costs and endangering public safety (Pour-Ali *et al.*, 2015).

The major cost and consequences of corrosion can be represented in three points;

- Affecting the national income because they can cause financial expensive loses.
- Waste of natural resources.
- Inconveniences and injuries to human beings and sometimes even loss of life.

Corrosion also takes place in different ways and it can be classified according to one of these three factors;

- Nature of the corroding materials; this classification is based on the condition of corrosion either “wet” or “dry”. The presence of moisture is essential for both methods which usually involves reaction with gases at high temperatures.
- Mechanism of corrosion; corrosion can occur either electrochemically or with direct chemical reactions.
- Appearance of the corroded metal; corrosion can be either uniform where the metal corrodes at the same rate over the entire surface, or localized when only small areas are affected.

Although corrosion is a natural process, it can be controlled by using effective methods and strategies including main five primary ways to control corrosion; materials selection and design, cathodic and anodic protection, inhibitors and coating.

The most generally used method for corrosion prevention is protective coatings. Their main function is providing satisfactory barrier between the metal and its environment (Mathiazhagan and Joseph, 2011).

A typical coating can offer many characteristics; aesthetic appearance, corrosion control, good adhesion, and abrasion resistance. The functioning of any protective coating is based upon three basic mechanisms;

- Barrier protection
- Chemical inhibition
- Galvanic (sacrificial) protection

In order to provide maximum protection, a protective coating should provide different functions mainly in;

- (1) Resisting the penetration of ions from salts that are in contact with the coating,
- (2) Minimize the action of osmosis,
- (3) Expanding and contracting with the underlying metal surface,
- (4) Retaining the aesthetic appearance over long period of time.

The major challenge that is facing the coatings industry during the last 40 years is the adoption of new coating materials, due to the depletion of natural resources that were used as pigments and additives. This challenge provides a great chance for reusing waste to be exploited providing new materials that are based on wastes which can be utilized in the coating industry to convert the wastes to useful materials that suit this huge industry. Therefore, appropriate and modern techniques must be utilized to produce modified waste materials with high efficiency and low cost.

Mixed Core-Shell Pigments

Pigments have very special place in the paints industry. They are the coloring elements present in paints, besides offering other main functions that lie in; hiding the substrates, providing color, modifying application properties and performance and/or reduce cost. Some of them can be classified as "functional" including specialty pigments, which can be used in broad array of coatings that can be used in a variety of applications.

Mixed pigments are novel category aiming to combine different metal oxides together in one compound with specific design and structure. The aim of developing these pigment mixtures is to enhance their efficiency and shift their characteristics to meet diverse applications to provide multifunctional roles by performing simultaneous multiple functions (Buxbaum and Pfaff, 2005).

Core-shell technology can participate in preparing new trends of mixed pigments to serve as multi-functional pigments in organic coatings. The prepared core-shell mixed pigments in this work will be based on core of different waste materials (marble and eggshells) covered with thin shell of known active pigment in anticorrosive performance. The produced particles are proposed to offer new characteristics gathering both the properties of core and shell together.

The shell will be composed of cobalt.zinc binary oxide which is considered as one of the most common multifunctional green pigments, due to its high mechanical resistance, high thermal and chemical stability, and low temperature sinterability besides offering intense green hues. They are usually synthesized at high temperature via solid-solid interaction between the two oxides, which is based on the mutual suppressing of the non-stoichiometry of the crystal lattices of ZnO and CoO, with relatively low content of CoO with respect to ZnO. Solid solution is easy to operate and does not introduce impurities (Ahmed, 2013).

CoO·ZnO binary oxide will be the shell precipitated on both marble (M) and eggshells (ES) wastes using core-shell technique to form CoO·ZnO/M and CoO·ZnO/ES core-shell pigments. The main advantage of using the core-shell technique in preparation lie in offering new enhanced properties which are different from its individuals and by choosing the suitable components the drawbacks and deficiencies of the individual components can be overcome.

For example, it is well known that cobalt is commonly used as drier, and this is a disadvantage of cobalt.zinc oxide green pigment which causes rapid curing, skinning and wrinkling of coated film, besides reduced water resistance on their use with excessive amounts in coating systems. The new pigments contain only thin shell of CoO·ZnO with low cobalt oxide content not exceeding 20%–30% of the formed compound, i.e., this low CoO content will not affect the curing time because it is now present only in very low concentration making the new core-shell pigments capable of offering better curing time without affecting the film properties or causing defects.

In this work, the new core-shell pigments will be integrated in anticorrosive coating formulations to serve in protecting steel structures exposed to marine environment and for the protection of reinforced concrete steel from corrosion damages.

Materials and Methods

Materials

- Marble waste is obtained as large pieces from working factories in Shaq El-Tho'aban area, then they were ground to fine particles using steel disk mill. After that, the ground powders were subjected to sieving process.
- Eggshells waste is collected and the organic membrane is removed, washed thoroughly with tap water, then it was dried at 80°C for 2 h. Crushing and grinding were the last steps of its preparation.
- All of the employed pigments, extenders, resins, solvents and additives are of normal chemical grades and are products of different local and international companies.
- The cement used in the preparation of concrete mix is CEM I type ordinary Portland cement.

Methods

Preparation of core-shell pigments

Three core-shell pigments were prepared; by the mixing of zinc and cobalt nitrates with eggshells and marble wastes via solid-solid interaction, i.e., grinding the solids with each other very well to be homogeneously distributed in each other, and then the mixture was calcined at 900°C.

Instrumental analysis

- X-ray fluorescence

The different concentrations of each element oxide in the different compounds were determined using Axios, sequential WD-XRF spectrometer, PANalytical 2005, USA.

- X-ray diffraction

X-ray powder diffraction patterns were obtained at room temperature using a Philips diffractometer (Model PW 1390) Japan, employing Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.5404 \text{ \AA}$). The diffraction angle (2θ) was scanned at a rate of $2^\circ/\text{min}$.

- Transmission electron microscope (TEM)

The different materials were examined using (JEOL JX 1230) technique with micro-analyzer electron probe (Japan). This technique shows a cross-section of the particles and determines the particle sizes of the different calcium carbonate sources.

- Scanning electron microscope/Energy dispersive x-ray analysis (SEM/EDAX)

Energy-dispersive X-ray analysis technique and scanning electron microscopy (JEOL JX 2840) micro-analyzer electron probe (Japan) was used in this work to estimate the particle shapes and determine the core and shell composition by showing the elements present on the surface of the formed compound.

Physical properties of the prepared pigments

The prepared pigments were evaluated according to international standard testing methods for specific gravity (ASTM D5965-02, 2013) and oil absorption (ASTM D 281-12, 2016).

Paint formulations

Epoxy resin is used in paint formulations because of many reasons that foster its use; the high adhesion related to the high polarity in its chain due to the presence of aliphatic hydroxyl and ether groups, and the strong electromagnetic attraction between the epoxy and the metal oxides found in the steel composition. Finally, the formation of chemical bonds between active hydrogen on the steel surface and epoxide groups in the coating which causes improved coating adhesion.

Also, it can participate in the anticorrosive action through the reduction of the corrosion of the metallic substrate by providing high cross-linking density, high barrier properties and also providing an effective physical barrier between the metal and the environment containing the aggressive species, such as an enhanced chloride ion concentration, O_2 or H^+ . They also serve as a reservoir for corrosion inhibitors that help the steel surface to resist attack from aggressive species.

Also, Epoxy resin represents a binder containing considerable amount of hydroxyl groups in its molecule, such groups can take part in corrosion reactions as inhibitors. Furthermore, prepared pigments are not typically evident on the surfaces, showing that they can be primarily embedded in the epoxy matrix and probably can be oriented parallel to the coating surface.

For all the previous reasons the paint formulations in this work are based on epoxy resin. Two groups containing four mixes were prepared with pigment/binder ratio P/B = 2 and pigment loadings 15 and 25 wt% of the whole solid content of the paints, these formulations are represented in Table 1.

Table 1 Paint formulations

Paint	Group I		Group II	
	CoO-ZnO/M	CoO-ZnO/ES	CoO-ZnO/M	CoO-ZnO/ES
Ingredients (gm)				
Alkyd Resin	30			
Fe ₂ O ₃	15	15	15	15
TiO ₂	5	5	5	5
Kaolin	21	21	15	15
BaSO ₄	10	10	10	10
CoO-ZnO/M	9	–	15	–
CoO-ZnO/ES	–	9	–	15
Total pigment	60			
Total	100		100	
P/B	2			

Applications in Marine Paints

Preparation of steel coupons for corrosion testing of marine paints

Carbon steel coupons 8×10 cm were used for the corrosion testing, they were first cleaned using clean lint-less cloth wet with mineral spirits, then vigorous rubbing of the panel surface was done until all soluble and loosely adhering soil were removed. After that, the steel coupons were flushed with clean solvent and dried at a temperature of $52\text{--}93^\circ\text{C}$ before use. The paints were prepared employing ball mill and then they were applied on the previously prepared mild steel panels via film applicator to give a dry paint film thickness of $120\text{--}150\text{ }\mu\text{m}$.

Corrosion tests

(1) Accelerated laboratory test

Accelerated lab test was performed by applying X scribe of 1 mm width to the coatings along the panel to expose the underlying metal to the aggressive environment. After 28 days of exposure the panels were evaluated for;

- Degree of rusting (ASTM D610-08, 2012).
- Degree of coating adhesion by means of a cross-cut test (ASTM D3359-17, 2017).
- Degree of blistering on painted steel surfaces according to ASTM D714-02 (2017).
- Filiform corrosion resistance test photographic inspection was done according to ASTM D2803-09 (2015).

(2) Electrochemical impedance measurements

The corrosion protection performance of coatings was investigated using EIS (SP-150), which is obtained from biologic science instruments, France. The reference electrode was silver/silver chloride electrode, and the auxiliary electrode was a platinum sheet. The used electrolyte was 3.5% NaCl solution, EIS measurements were carried out by applying 10 mV sinusoidal potential through a frequency domain from 35 kHz down to 100 MHz. All the experiments were carried out in an aerated solution at room temperature. Coated steel coupons of dimensions (2×1 cm) were considered as the working electrode. The measurements were taken at different interval periods against immersion time to study the corrosion protection behavior. The obtained data were analyzed and fitted according to simple circuit showed in Fig. 1.

Mechanical properties of marine paints

The physico-mechanical properties that figure out the flexibility, elasticity and strength of the paint film were tested according to following standards;

- Hardness of the paints using the pendulum apparatus was done to study the film elasticity (ASTM D4366-16, 2016).
- Impact resistance (ASTM D6905-03, 2012); the test reveals the height of the free fall of a weight (1000 gm) at which the paint film still resists impairment, the test was performed on the reverse of the panel with a coating.
- The resistance of the coating against cupping in Erichsen cupping tester (ASTM D 5638-00, 2013), the objective of this test is to identify the resistance of the paint film against distortion of a coated steel panel with a pressed-in 20 mm steel ball. The result of the test deduces cupping in mm with the first disturbance of the coating.

Applications in Concrete

Preparation of concrete specimens and mix design

(1) Reinforced bars preparation

Plain steel rebars with 6 mm diameter were prepared using emery papers to remove materials like mill scales, grease, rust, oil, and dirt. The steel rebars were then flushed with clean solvent and dried. Then, the rebars were coated by brush to reach dry film thickness about $100\text{--}150\text{ }\mu\text{m}$.

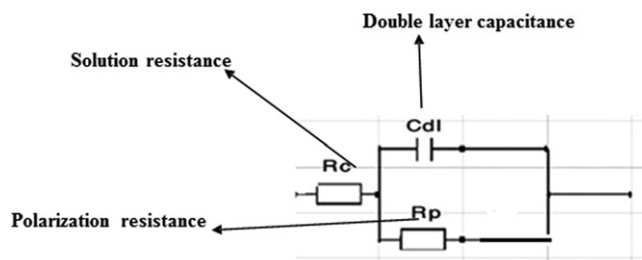


Fig. 1 Equivalent circuit for fitting EIS data.

(2) Concrete preparation and mix design

Concrete mix is prepared and cured according to [ASTM C 192/C 192M-06 \(2006\)](#) as cubes with diameter $5 \times 5 \times 5$ cm containing embedded coated rebars, the mixing proportions is given in [Table 2](#).

Corrosion test for reinforced concrete cubes

The reinforced concrete cubes were totally immersed in the artificial sea water for 28 days and each cube was placed in a separated cell for the electrochemical measurements.

Bond strength (Pull out test)

This test is performed to determine the effect of the coating materials on the adherence between the steel rebar and concrete, a concrete cylinder of 600 mm height and 150 mm diameter containing an embedded coated deformed steel bar at its center was tested by a hydrodynamic equipment in which the mounted concrete was fixed, whilst the outer part of the rebar was connected to the driving holder. This driving holder was then moved and the ultimate force required to pull the rebar off was recorded.

Results and Discussion**Characterizations of Core-Shell Pigments****X-ray fluorescence (XRF)**

X-ray fluorescence is a powerful technique that can determine the elements concentration in the whole compound. The results in [Table 3](#) showed that, with regard to loss of ignition (LOI) both marble (M) and eggshells (ES) contain calcium oxide as a major content with percentage of 95%–98%. While in the prepared core-shell pigments, there was a decrease in this percentage due to precipitating the shell on its surface, which replaced some of the calcium carbonate, beside a rise in the concentration of both cobalt and zinc oxides representing the shell. Moreover, zinc oxide appeared with higher concentration than cobalt oxide revealing that cobalt concentration is very low compared to that of zinc oxide.

Table 2 Mix design for concrete (W/C = 0.6)

Materials	Mix proportions (kg/m ³)
Ordinary Portland cement (OPC)	405
Sand	750
Aggregate	843
Water	243

Table 3 XRF of the different wastes and the core-shell pigments

Main constituents (wt%)	Marble (M)	CoO-ZnO/M	Eggshells (ES)	CoO-ZnO/ES
SiO ₂	0.78	0.95	0.22	0.27
Al ₂ O ₃	0.22	0.34	0.09	0.11
TiO ₂	0.02	–	–	–
Fe ₂ O ₃	0.22	0.20	0.02	0.05
MnO	0.02	–	–	–
CuO	0.01	–	–	0.024
ZnO	–	38.03	0.03	21.55
NiO	0.01	0.011	0.01	0.008
MgO	0.31	0.35	0.65	0.58
CaO	55.13	54.58	54.12	54.11
Na ₂ O	0.11	–	0.20	3.14
K ₂ O	0.04	0.03	–	0.06
Co ₃ O ₄	–	5.15	0.01	3.13
P ₂ O ₅	0.06	0.1	0.27	0.25
SrO	–	0.063	0.03	0.031
SO ₃	0.05	0.15	0.46	0.38
Cl	0.04	0.04	0.02	0.05
LOI	42.97	–	43.82	16.25

X-ray diffraction (XRD)

XRD results shown in Fig. 2 clarified that the dominant phase of calcium carbonate in both marble and egg shell is calcite with its main peak at 2θ 30 according to JCPDS Card No. 05-0586. On the other hand, the patterns of the prepared core-shell materials showed more crystallinity than marble and eggshells, which is clear in the appearance of extra peaks at 2θ 31.9, 34.1, 34.3, 36.2, 47.2 and 49.5 representing zinc and cobalt oxides which form the shell revealing the formation of new phases that were not present in marble or eggshells individually, confirming the formation of a new compound.

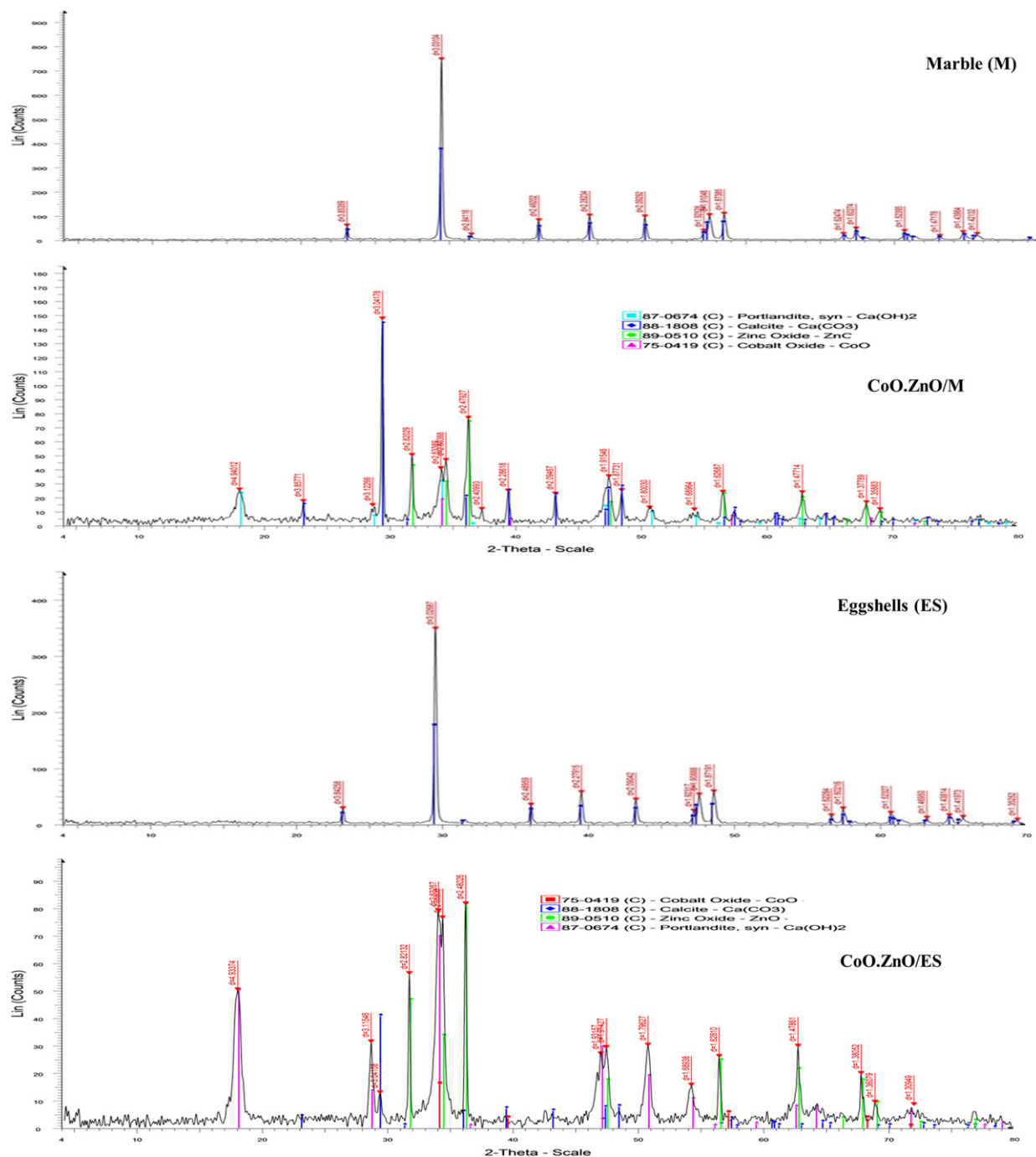
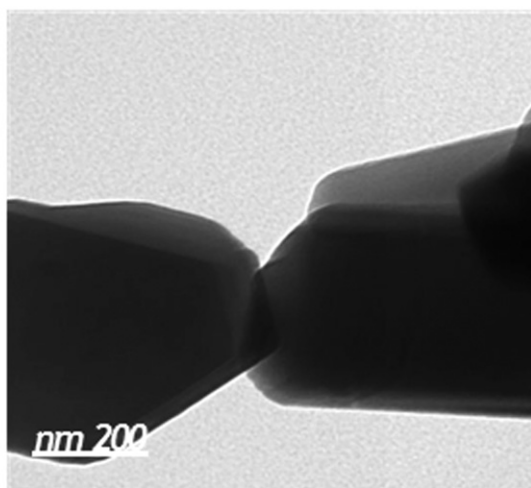
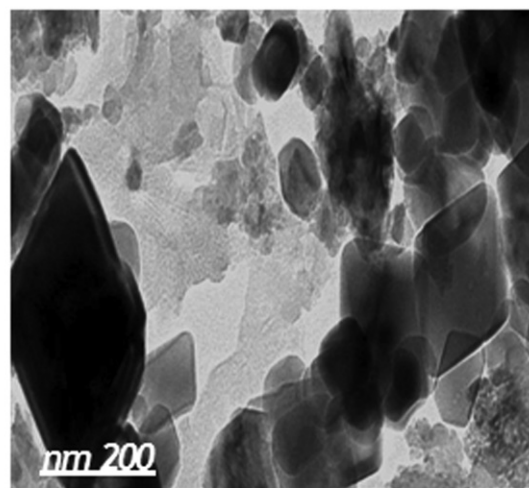


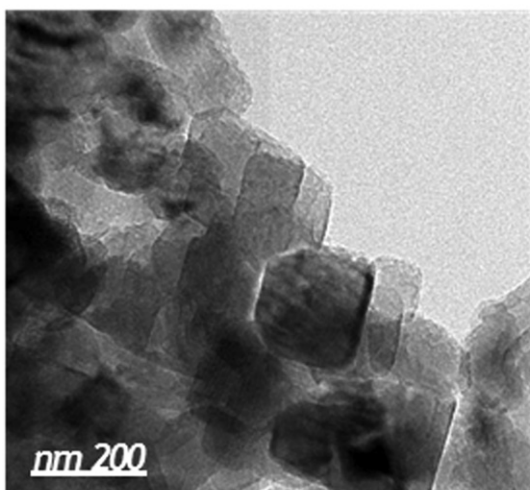
Fig. 2 XRD of the different wastes and the core-shell pigments.



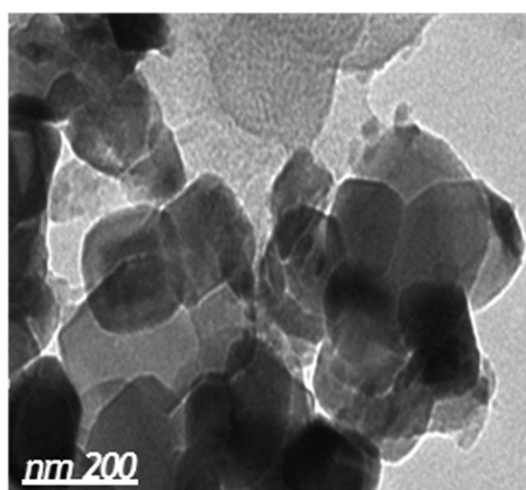
a. Marble (M)



b. CoO.ZnO/M



c. Eggshells (ES)



d. CoO.ZnO/ES

Fig. 3 TEM photos of the different wastes and the core-shell pigments.

Morphology of the particles

Figs. 3 and **4** representing the TEM and SEM photos of marble and eggshells showed the presence of the rhombohedral forms of calcium carbonate as large plate structures once as separated particles in case of marble and other as aggregates in case of egg shell.

In case of core-shell particles, these rhombohedral plates were covered with stuck particles on their surface representing the shell layer, these particles cannot be separated looking like-welded to each other in one compound.

Energy dispersive X-ray analysis (EDAX)

EDAX analysis is one of the main tools to prove the presence of the shell elements because it shows the elements on surface up to 1 μ depth. The charts in **Fig. 5** and the related tables cleared that zinc is present in higher percentage than cobalt, which is in good agreement with the XRF results in **Table 3**. Also, the presence of intense peaks for calcium revealed that its concentration is high, i.e., dominant element in the compound, while the lower concentration of cobalt and zinc oxides confirmed that the formed shell is so thin.

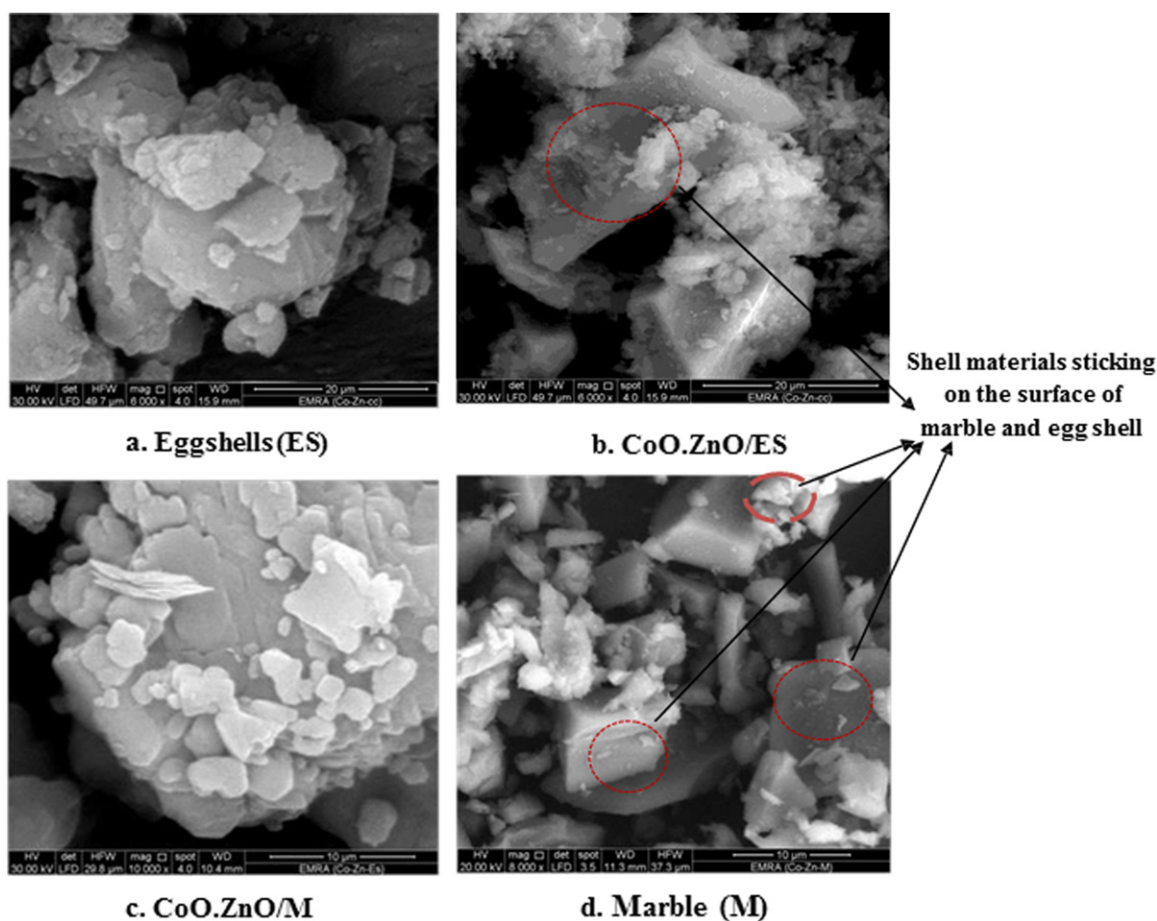


Fig. 4 SEM photos of the different wastes and the core-shell pigments.

Physical Properties of the Different Pigments

Oil absorption

Oil absorption is measured according to (ASTM D 281-12, 2016); this test gives information about the minimum amount of matrix required to wet a given weight of pigment. The results showed that both eggshells and marble possess higher oil absorption than the prepared core-shell pigments which confirms that the core-shell pigments are more economic, because less amount of oil (binder) is needed to prepare the coating film. The lower values of oil absorption can be attributed to the presence of the small plates of CoO-ZnO that overlap with the calcium carbonate rhombohedral plates or locate themselves in between them, i.e., less voids can be available for oil particles to penetrate which offers less oil absorption (Ahmed *et al.*, 2016).

Specific gravity

The specific gravity of the various materials is measured according to (ASTM D5965-02, 2013). Marble and eggshells showed high specific gravity values, while the prepared core-shell pigments offered lower values. In coatings, high specific gravity is not preferable since it can cause settling of the solid particles on storage leading to the separation of paint components. Therefore, the lower values of core-shell pigments can be considered as an advantage showing that they can be well-dispersed in the paint matrices maintaining their consistency (Table 4; Fig. 6).

Applications in Marine Paints

Corrosion studies

Corrosion protection performance of anticorrosive coatings containing CoO-ZnO/M and CoO-ZnO/ES core-shell pigments has been studied during 28 days of immersion in a chloride-containing solution (3.5% NaCl) via accelerated lab test and electrochemical impedance spectroscopy (EIS).

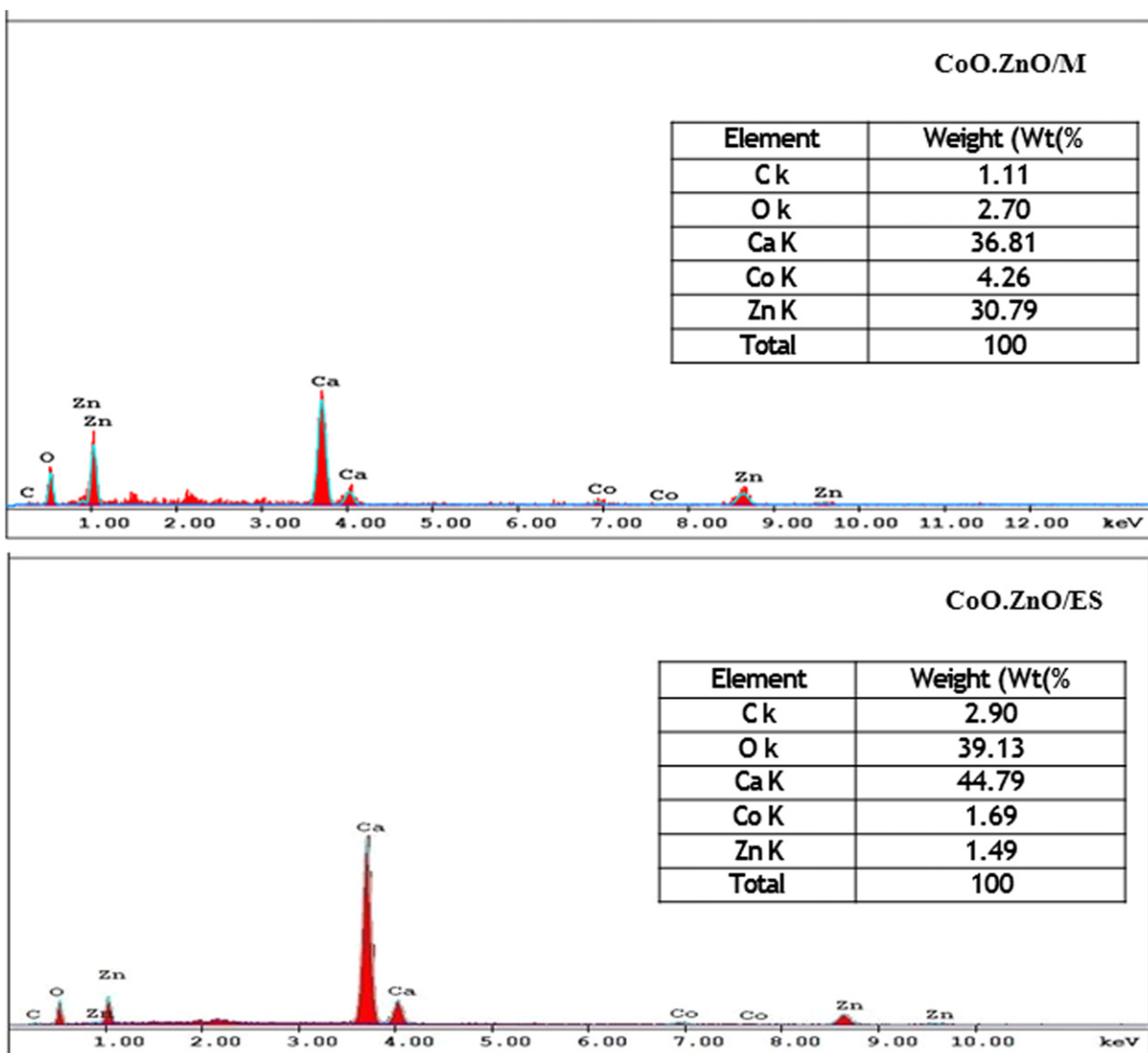


Fig. 5 EDAX analysis of the core-shell pigments.

Table 4 Physical properties of core-shell pigments

Pigment	Specific gravity	Oil absorption
Marble	2.52	101.1
Eggshells	2.31	91.9
CoO-ZnO/M	1.13	73.2
CoO-ZnO/ES	1.18	91.9

In accelerated lab test; the visual inspection of paint films containing the prepared core-shell pigments in Table 5 and Fig. 7 after 28 days showed that, there are no blisters on film surfaces.

The high adhesion caused by epoxy resin, leads to that no corrosion was detected under most films containing CoO-ZnO/M and CoO-ZnO/ES core-shell pigments after removing them from the steel substrates, but there was appearance of white zones that are located around X scribe (near the cut) which is related to the ability of CoO-ZnO to react with calcium

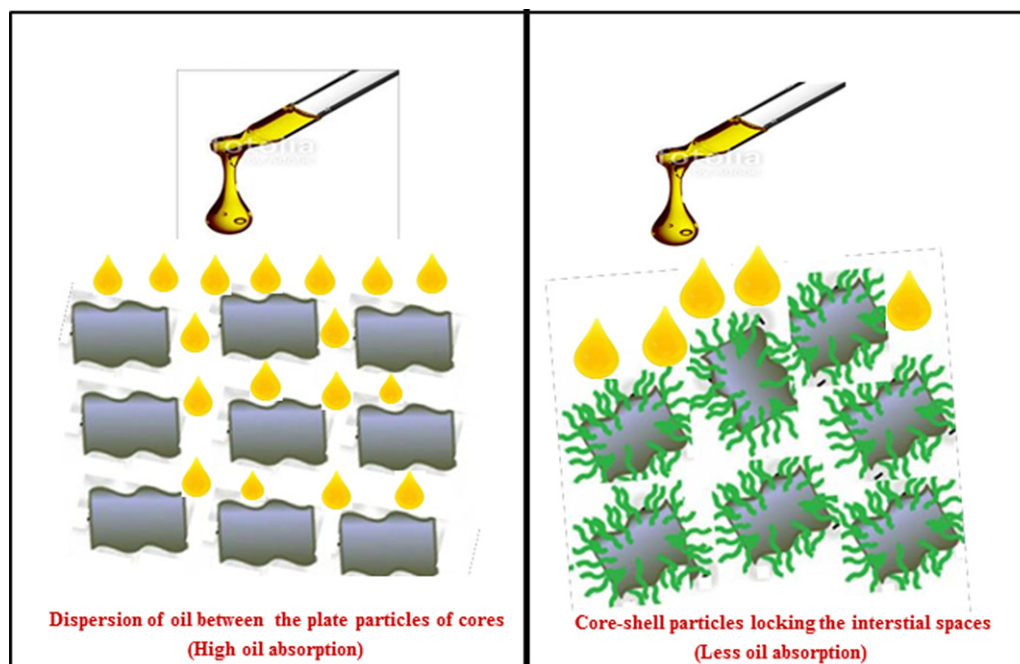


Fig. 6 Schematic diagram explaining the entrance of oil drops through core-shell pigments.

Table 5 Accelerated lab test results after 28 days in 3.5% NaCl

Formulations containing sources of calcium carbonate	Group 1		Group 2	
	CoO·ZnO/M	CoO·ZnO/ES	CoO·ZnO/M	CoO·ZnO/ES
Adhesion	GT0	GT0	GT1	GT0
Degree of blistering	10	10	10	10
Degree of rusting	10	10	10	10

carbonate in the aqueous media existing in marble and eggshells producing cobalt zinc carbonate hydroxide complex ($\text{CHCoO}_4\text{Zn}^+$). Additionally, the excess of ZnO which is predominant in the medium can react with calcium carbonate forming white zinc carbonate (ZnCO_3).

The action of $\text{CHCoO}_4\text{Zn}^+$ and ZnCO_3 as binding phases can fully cover the surface around X scribe making the coat more compact than the coating with only one phase of (ZnCO_3), hindering by that the penetration of H_2O , O_2 , and Cl^- to the substrate. Also $\text{CHCoO}_4\text{Zn}^+$ complex has an excellent corrosion resistance due to its high alkalinity, therefore adding pigments can improve the corrosion resistance via chemical bonding (Perez-Bernal *et al.*, 2009).

Also, ZnO itself is assumed to be able to polarize cathodic regions owing to its ability to precipitate virtually insoluble salts; depending on its reactivity and strong basicity that it can deactivate efficiently any acidic corrosion agents passing through the protective paint film. Moreover, ZnO offer good miscibility with other pigments, high covering power and ability to enhance the binder's oxypolymerization rate (Mosner *et al.*, 2000).

On the other hand, calcium carbonate which is the main constituent of both wastes can react with OH ions of water to form calcium hydroxide $\text{Ca}(\text{OH})_2$; depositing this hydroxide layer on the cathodic zones prevents corrosion of steel.

All the previous reasons combined together can explain the good corrosion protection performance of the prepared core-shell pigments. Even though, the waste materials by themselves showed less protection performance (Ahmed *et al.*, 2018).

After performing the accelerated laboratory Test, the two paint groups were subjected to electrochemical impedance spectroscopy to determine the corrosion resistance of the coatings and to confirm the results obtained from accelerated lab test. The Nyquist plots of coated plates are shown in Fig. 8 and the R_p values of the different coatings are presented in Table 6.

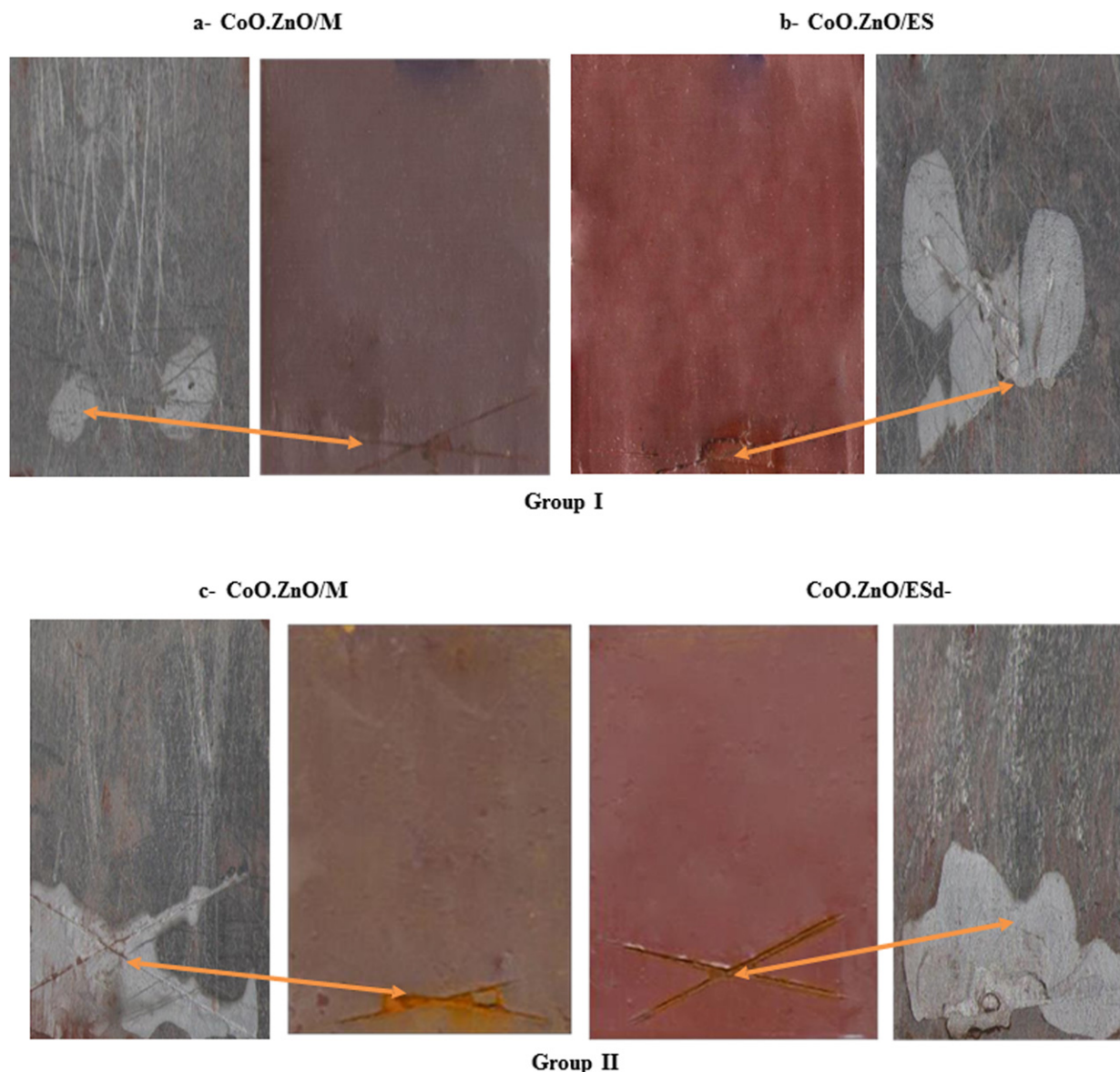


Fig. 7 Corrosion laboratory test results of Group I and II containing core-shell pigments in 3.5% NaCl after 28 days immersion.

Paint films containing core-shell pigments showed characteristic semicircles of capacitive type with high R_p values leading to the increase in the size of the semicircles. The results of R_p values after 28 days of immersion indicated that a common trend in the corrosion protection behavior is detected for both coatings containing the two core-shell pigments; step decrease in the electrical parameters during the first two weeks of immersion which can be attributed to the high chloride attack in this period at different areas on the steel surface. Then, gradual increase in the polarization resistance takes place due to the stabilization of the coating. After that blocking the active sites via different mechanisms offers high R_p values again after the second week of immersion.

It also can be concluded that, coatings containing CoO·ZnO/ES showed slightly higher corrosion resistance than coatings with CoO·ZnO/M. In addition, the group with higher pigment loadings exhibited higher R_p values, i.e., there is a direct relationship between the pigment loadings and the corrosion resistivity of paint films.

Mechanical properties of paint films containing core-shell pigments

The mechanical properties of paint films are represented in Fig. 9, it is clear that paint films containing CoO·ZnO/M showed high hardness values, less ductility and impact due to the marble massive particles which strengthen the paint films. While, films containing CoO·ZnO/ES showed better elasticity, i.e., less hardness but higher ductility and impact.

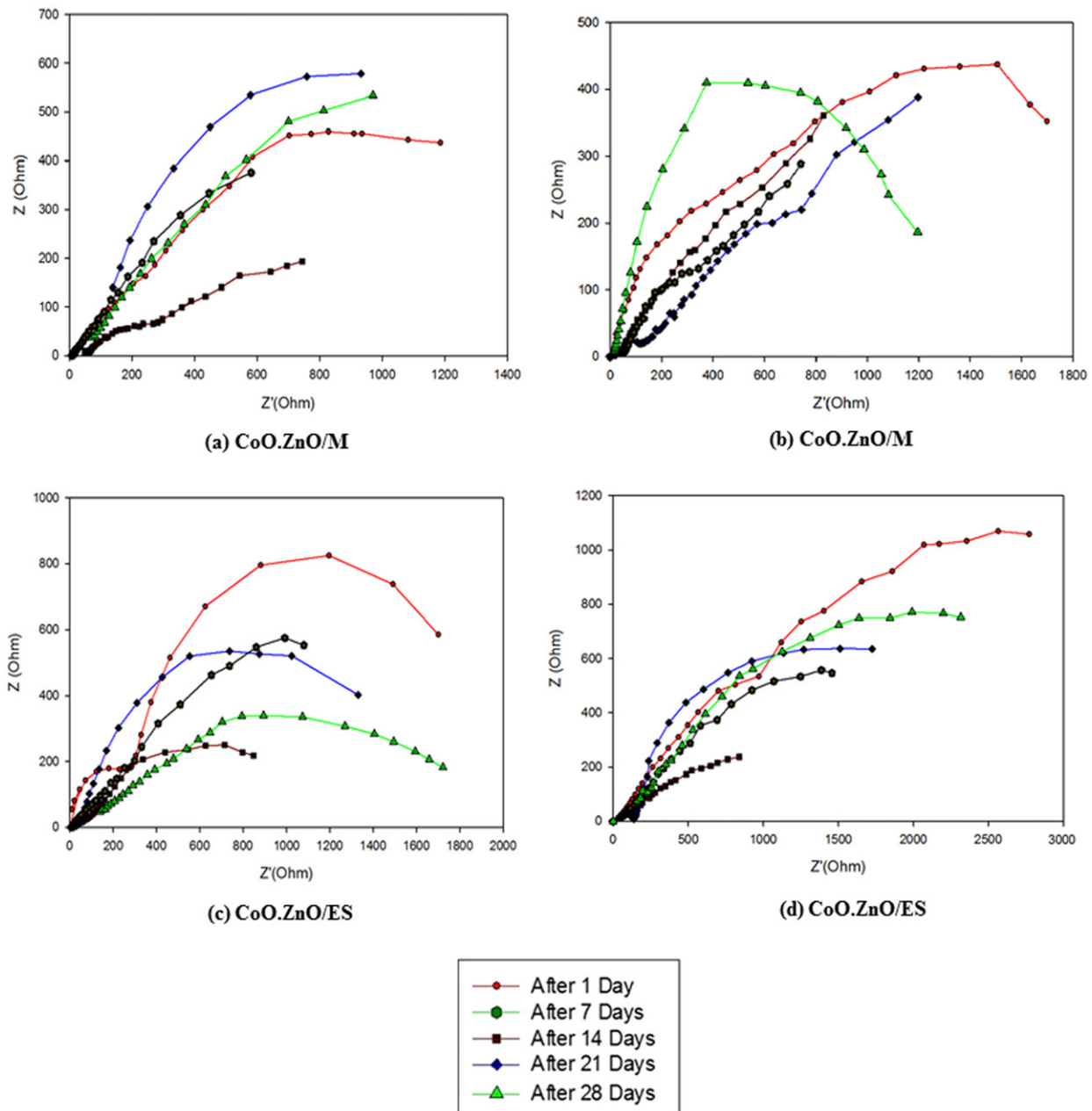


Fig. 8 EIS measurements of coated steel panels during 28 days in 3.5% NaCl.

Generally, the presence of CoO which is considered as intermetallic dispersoids can retard the rapid particle growth, causing particle refinement and hardening that results in further strengthening of the paint films (Fernandez and De Pablo, 2002).

Concrete Application

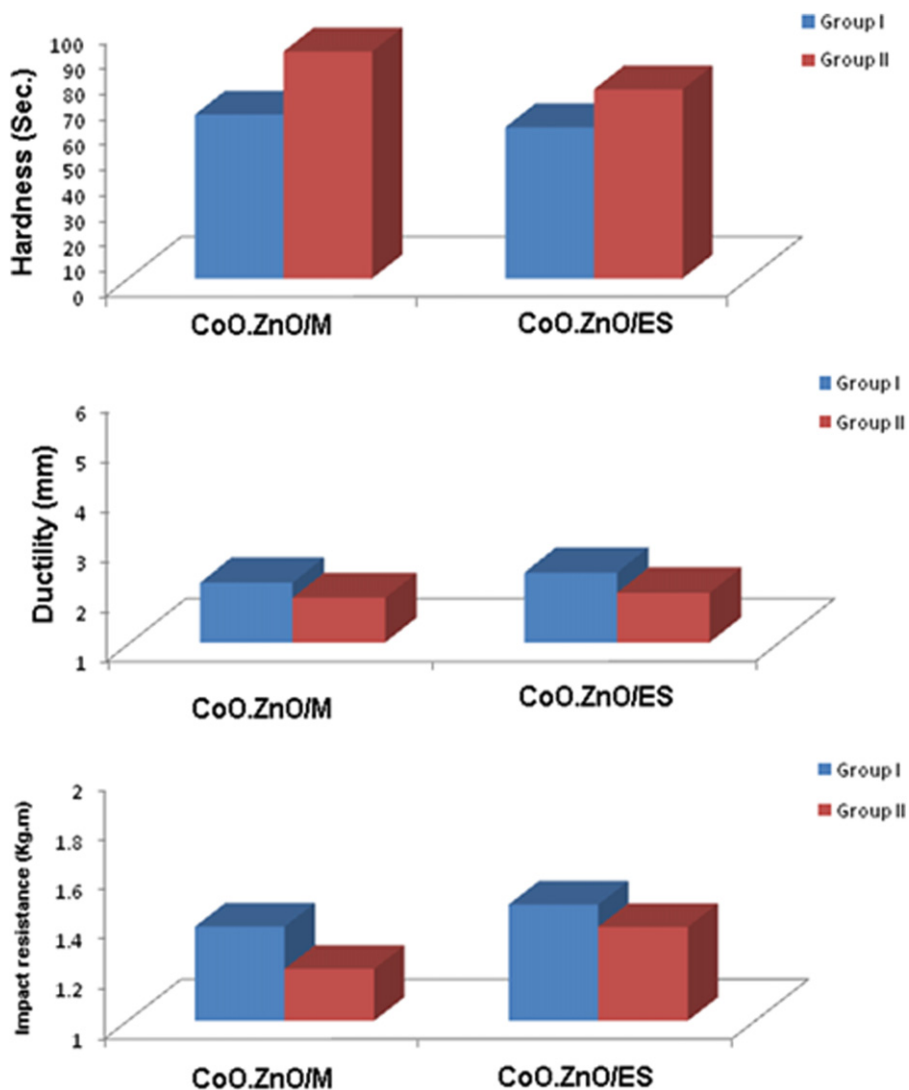
Corrosion studies

Fig. 10 showed the electrochemical impedance spectroscopy results for reinforced concrete containing both core-shell pigments and uncoated blank specimen, Table 7 showed the polarization resistance (R_p) values of all specimens during the immersion time.

Generally, the mechanism of corrosion in the concrete can be divided into two main phases; the “initiation phase” which includes the penetration of chloride ion through the concrete cover till the steel surface, resulting in the destruction of the formed

Table 6 Polarization resistance (R_p) values for coated coupons in 3.5% NaCl during 28 days in marine paints

Days	R_p ($\Omega\text{m}\cdot\text{cm}^2$)	
Coatings containing CoO-ZnO/M		
	Group I	Group II
1 day	1800	2000
7 days	1200	1500
14 days	1000	1100
21 days	1300	1680
28 days	1550	1700
Coatings containing CoO-ZnO/ES		
	Group I	Group II
1 day	2000	4000
7 days	1500	2500
14 days	1000	1750
21 days	1330	2500
28 days	1860	3000

**Fig. 9** Mechanical properties of paint films containing core-shell pigments.

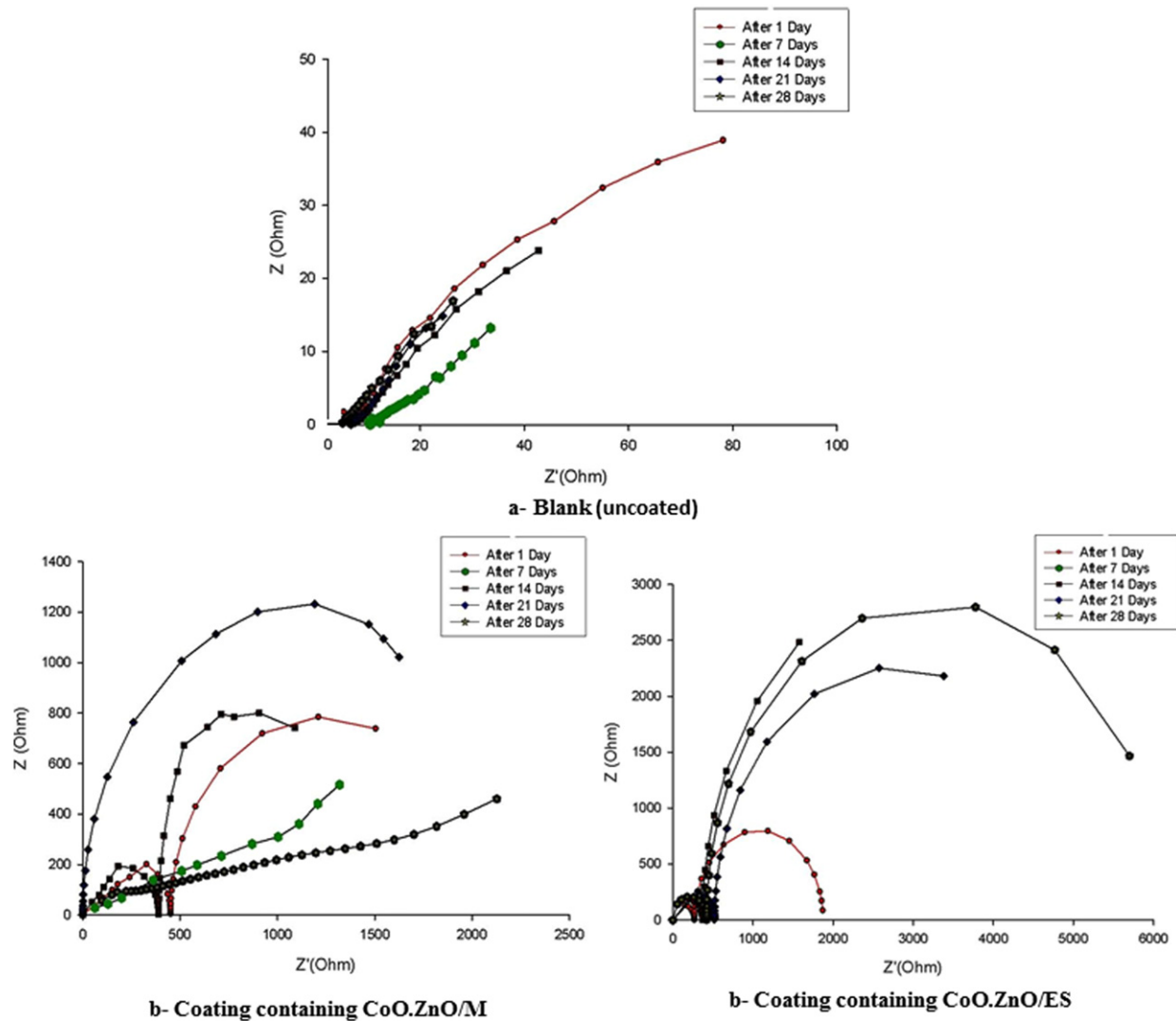


Fig. 10 EIS measurement of reinforced concrete with coated rebars.

Table 7 Polarization resistance (R_p) values for coated reinforced steel in 3.5% NaCl during 28 days

Days	R_p (Ωcm^2)
Coatings containing CoO-ZnO/M	
1 day	2210
7 days	2330
14 days	2030
21 days	2235
28 days	2829
Coatings containing CoO-ZnO/ES	
1 day	1969
7 days	2798
14 days	4300
21 days	4570
28 days	6430

passive layer due to the concrete alkalinity. This passive layer is mainly composed of thermodynamically stable compounds of iron oxides and oxyhydroxides which are formed spontaneously as thin protective oxide film due to the high alkalinity of the cement hydration and free lime formation. After that, the “propagation phase” which is related to the corrosion process that starts on the rebar surface as the passive layer is destroyed. The unique composition and properties of the core-shell pigments in paint films can strongly support the protection of the reinforced bars, because of their composition which is mainly calcium carbonate and zinc and cobalt oxides that can participate in passivating and inhibiting the corrosion reaction with different mechanisms (Bertolini *et al.*, 2004).

The results of reinforced concrete steel in 3.5% NaCl solution showed that the polarization resistance values of blank specimen (uncoated) is low against the chloride attack.

On the other hand, the coated rebars with coatings containing core-shell pigments offered higher R_p values with an increasing trend due to the presence of calcium carbonate that can provide an extra alkaline medium which supports the passive layer formation around the steel, and it is considered as the first immune line against corrosive materials, This step is the one that occurs in the first two weeks, then a stability occurred between the second and third week of immersion, after that the R_p s start to increase again in the fourth week due to the destruction of the layer due to the accumulation of high chloride ions concentration which manipulates the corrosion reaction on the rebar surface. Zinc oxide is non-water soluble, thus small parts of zinc ions (Zn^{2+}) can be separated and complete the cycle of the corrosion protection mechanisms by liberating zinc ions that can reach the anodic regions on the metal surface causing a significant decrease of metal oxidation reaction and inhibit any corrosion reaction that can occur on the metal surface (Gimeno *et al.*, 2012; Li *et al.*, 2011).

Bond strength (pull out test)

From literature, it is well known that coatings cause decrease in the bond strength between concrete and the steel rebars because of their flat surface. Also, Considering the fact that coatings have some organic constituents and the main elements of concrete are inorganic, it can be supposed that the interaction between the two materials of different natures may not be as strong as if they were of the same type (e.g., inorganic). Therefore, the presence of the inorganic pigments in the coating matrix can enhance the adhesion between the coated rebars and concrete cover especially when these pigments have the capability to interact with the concrete component (Binici *et al.*, 2012).

From Fig. 11, it can be concluded that not only there was no noticeable difference between the coated specimens and blank (uncoated), i.e., the coating layer did not work as insulator between the rebar surface and concrete cover, but also the core-shell pigments which are mainly based on calcium carbonate can provide an extra calcium oxide source which can be involved in the hydration reactions of cement found in concrete cover around the coated steel. This reaction can enhance the adhesion and the strength between the rebar and the concrete overcoming the previous known deficiencies of using epoxy coatings in the field of reinforced concrete steel.

Fig. 12 represents a schematic explanation of the role of core-shell particles against corrosion in both marine paints and concrete.

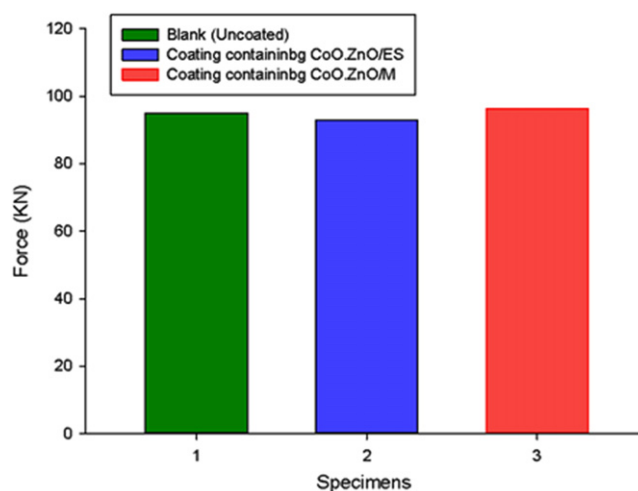


Fig. 11 Bond strength (pull out test).

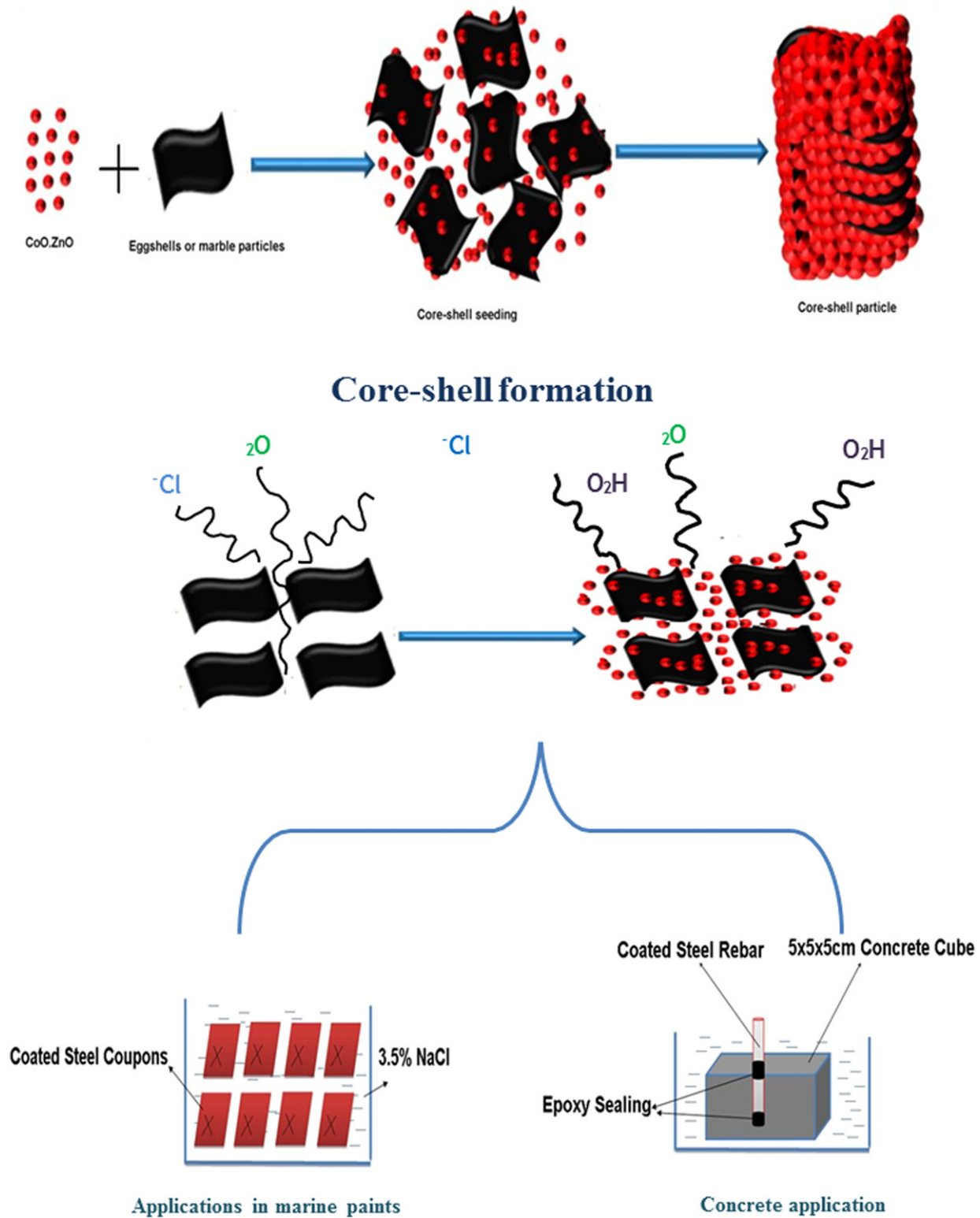


Fig. 12 Schematic diagram explaining the mechanism of corrosion protection in presence of core-shell particles.

Conclusions

Eggshells and marble wastes were reused as calcium carbonate derivatives that were mined from non-renewable sources. Core-shell preparation technique was applied to change the nature of these calcium carbonate sources by precipitating thin shell of CoO-ZnO binary oxide on their surfaces to study their role as anticorrosive paints in both marine paints and reinforced concrete steel. The prepared core-shell compounds were characterized using different instrumental analysis as XRD, XRF, SEM/EDAX and TEM to prove the formation of core-shell structure and determine their characteristics. Then the pigments were integrated in anticorrosive paint formulation based on epoxy resin to study their effect in protecting steel substrates in the different media. The results showed good corrosion protection in both marine and reinforced concrete applications. Beside that the prepared pigments contributed in the enhancement of the mechanical properties of paint films by providing cross-linking action between steel rebars and concrete which promoted the bond strength between coated rebars and concrete, solving a known disadvantage that is related since long time to the epoxy coatings in concrete.

Acknowledgment

This work was supported by Science and Technology development Fund in Egypt (STDF) under project number 25745.

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Production of High Purity α - and γ -Alumina From Aluminum Dross

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Introduction

Manufacturing a wide variety of goods and products sacrifices the natural resources and contributes towards waste generation. As a result, the public and industrial communications are progressively suffering from the critical problem of wastes. Controlling the multifariousness of the waste streams is a serious challenge for decision makers and in many cases they choose inefficient and environmentally contaminating solutions such as landfill discharge (Zaman, 2015). In addition, finding suitable landfill sites is difficult and imposes a large cost (Ngoc and Schnitzer, 2009). On the other hand, improper waste management can result in unnecessary depletion of resources and loss of energy. Furthermore, many forms of pollutions such as dust, greenhouse gases, and water contamination can be raised, as illustrated in Fig. 1 (Demirbas, 2011; Udomsri et al., 2011). Therefore, adopting appropriate strategies to reduce, reuse, and recycle (known as 3R concept) the wastes is a necessity towards a sustainable development. A sustainable material flow is affected by several factors involving society, environment, design, manufacturing, recovery technology, economics, methods and usage. In this regard, the development of recovery and recycling processes can remarkably contribute to the minimization/elimination of wastes, cleaner environment, and sustainability (Kumar et al., 2005).

The aluminum manufacturing cycle releases a diversity of wastes, each of which has its own physico-chemical characteristics. The value of each waste is assessed by the amount/type of impurities and the cost of recovery (Huang and Tolaymat, 2014; Jirang and Lifeng, 2008). Among them, aluminum dross exhibits a very toxic and hazardous nature which is the main focus of the present work.

Aluminum Dross

Aluminum dross (AD) as a hazardous solid industrial waste is generated during aluminum manufacturing process. More than one million tons of AD are annually generated by aluminum sector throughout the world. Around 95% of the AD is discarded in the landfill sites (Adeosun et al., 2014). Nevertheless, according to the 3R concept, different strategies and solutions have been suggested for the reduction, reuse, and recycling of the AD. Fig. 2 shows the hierarchy of the AD.

As clearly shown in Fig. 2, the AD can be reused in the cement and concrete production. The utilization of the AD in cement mortars can result in a 15% increase in compressive strength and a 40% improvement in flexural strength. The particle size and the weight fraction of the AD were found to be very effective parameters (Dai and Apelian, 2017). It was found that the bulk density and porosity of the AD-blended cement pastes were under the effect of the amount of the incorporated AD. The former property decreased by increase of the AD replacement level in cement, while the latter one experienced an incremental trend (Inseemmesak and Rodchanarowan, 2013). Further research proved that a 5% AD replacement level improved the 7-day compressive strength of concrete (Reddy et al., 2014). This is while, a 15% AD replacement level in concrete gave the results comparable to conventional concrete (Reddy and Neeraja, 2016). Such contradictory results may be due to the different origins and chemical composition of the AD. The reuse of the AD as a refractory material is attributed to its high alumina content (Xiao et al., 2005; Yoshimura et al., 2008). The possibility of utilization of the AD in the production of zirconia/mullite composite (Castro et al., 2009), polypropylene/aluminum dross composites (Adeosun et al., 2012), epoxy resin-aluminum dross composite (Agunsoye et al., 2014), and dense multiphase β -sialon-15R ceramics (Li et al., 2012) has been reported in the literature. In the field of adsorption applications, the AD

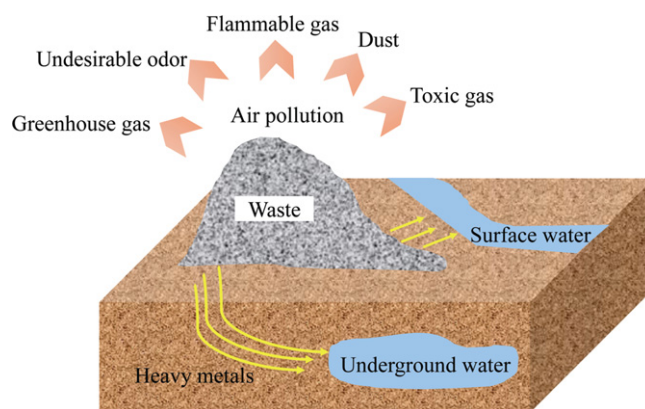


Fig. 1 Pollution of environment by waste via different pathways.

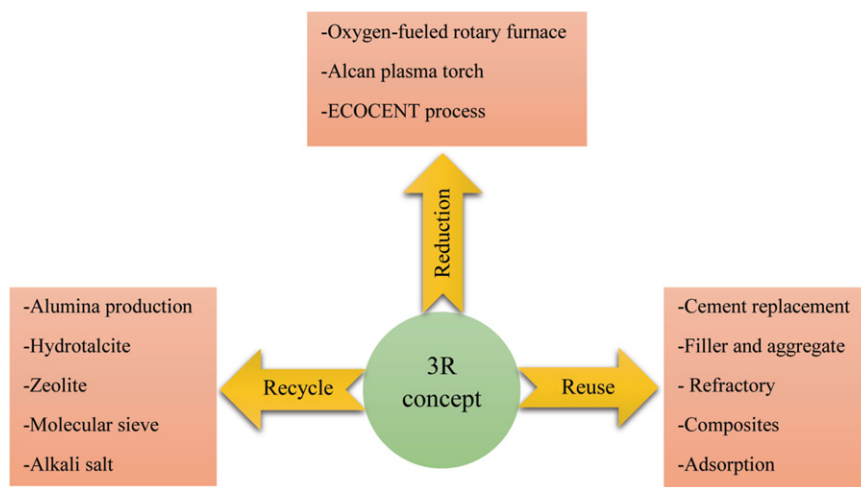


Fig. 2 Hierarchy of aluminum dross waste.

exhibited an acceptable cadmium adsorption efficiency from aqueous solution (Ahmad Zauzi *et al.*, 2016). The reuse of the AD as a filling agent was found to be positively effective on stiffness and corrosion resistance of asphalt (Dunster *et al.*, 2005).

New technologies were also developed to reduce/minimize the generation of the AD. Oxygen-fueled rotary furnace exhibited an aluminum recycling efficiency of 80%. This type of furnace requires only 5% of energy consumed by conventional rotary salt furnace (Abdulkadir *et al.*, 2015). In Alcan plasma torch process which was implemented in Canadian Hydro-Quebec Research Center, a plasma torch was employed for heating instead of gas/oil. ECOCENT technology developed by Austrian FOCON that uses hot dross centrifuge reduces the volume of flue gas emissions, lessens adverse environmental effects, and improves energy consumption efficiency (Unlu and Drouet, 2002).

The AD contains a mixture of inorganic oxides and water-soluble salts (Mahinroosta and Allahverdi, 2018a). The water-soluble salts can be recovered through rinsing and solar evaporation. It was found that such a salt recovery has an economic benefit to aluminum industry and can diminish the toxicity of the AD waste (Bruckard and Woodcock, 2009).

As a source of aluminum, the AD powder can be utilized for the synthesis of hydrotalcites (a kind of layered double hydroxide) (Gil *et al.*, 2018), $\text{AlPO}_4\text{-5}$ molecular sieve (Murayama *et al.*, 2009; Kim *et al.*, 2009), highly crystalline CrAPO-5 molecular sieve (Kim *et al.*, 2009), Zeolite-X (Hiraki *et al.*, 2009), and sodalite and analcime zeolites (Sanchez-Hernandez *et al.*, 2016) for the application in water and wastewater treatment.

The AD is an aluminum oxide-rich waste and can be considered as a secondary resource for the production of alumina. The alumina can be recovered through acidic (Dash *et al.*, 2008; Amer, 2002; Sarker *et al.*, 2015), alkali (Lucheva *et al.*, 2005; Sultana *et al.*, 2013; Park *et al.*, 2001; Tsakiridis *et al.*, 2013), and plasma radio frequency (Yang *et al.*, 2014) routes. The objective of this work is to produce α - and γ -alumina as high value-added inorganic materials from aluminum dross using a promising recovery process. The characterization of the produced alumina products and solid residue will also be discussed.

Experimental Procedure

Materials

The AD was supplied from a domestic aluminum ingot manufacturer. The chemical reagents used in this work were: ammonia (25%, Mojallali Co.), ethanol absolute (=99% purity, Riedel-de Haën), hydrochloric acid (37%, Merck), and sodium hydroxide pellets (99% purity, Merck). Deionized water was used in preparation of solutions and washing purposes.

Alumina Recycling Process

The novel hydrometallurgy-based process and experimental conditions described in previous studies (Mahinroosta and Allahverdi, 2018b,c) were utilized to leach out alumina from the AD. In these works, a comprehensive study on the effects of leaching temperature, leaching time, acid concentration, acid-to-solid ratio, and particle size was conducted. The results revealed that the temperature leaching of 85°C, the leaching time of 120 min, the acid concentration of 5 M, the acid-to-solid ratio of 20 ml/g, and the particle size fraction of 38–75 μm led to an optimized alumina recovery efficiency of more than 80%. As typically shown in Fig. 3, in the first stage, the AD was washed with deionized water at 95°C for 90 min to remove water-soluble salts. Removing salts is essential because salts may be present in the final products as impurities.

The washed AD was then leached with 5 M HCl at 85°C for 120 min. The resulting metal chlorides liquor ($\text{pH}=3.0\text{--}3.5$) was separated from acid-insoluble solid residues using a vacuum filtration system. The metal hydroxides were co-precipitated from the chloride

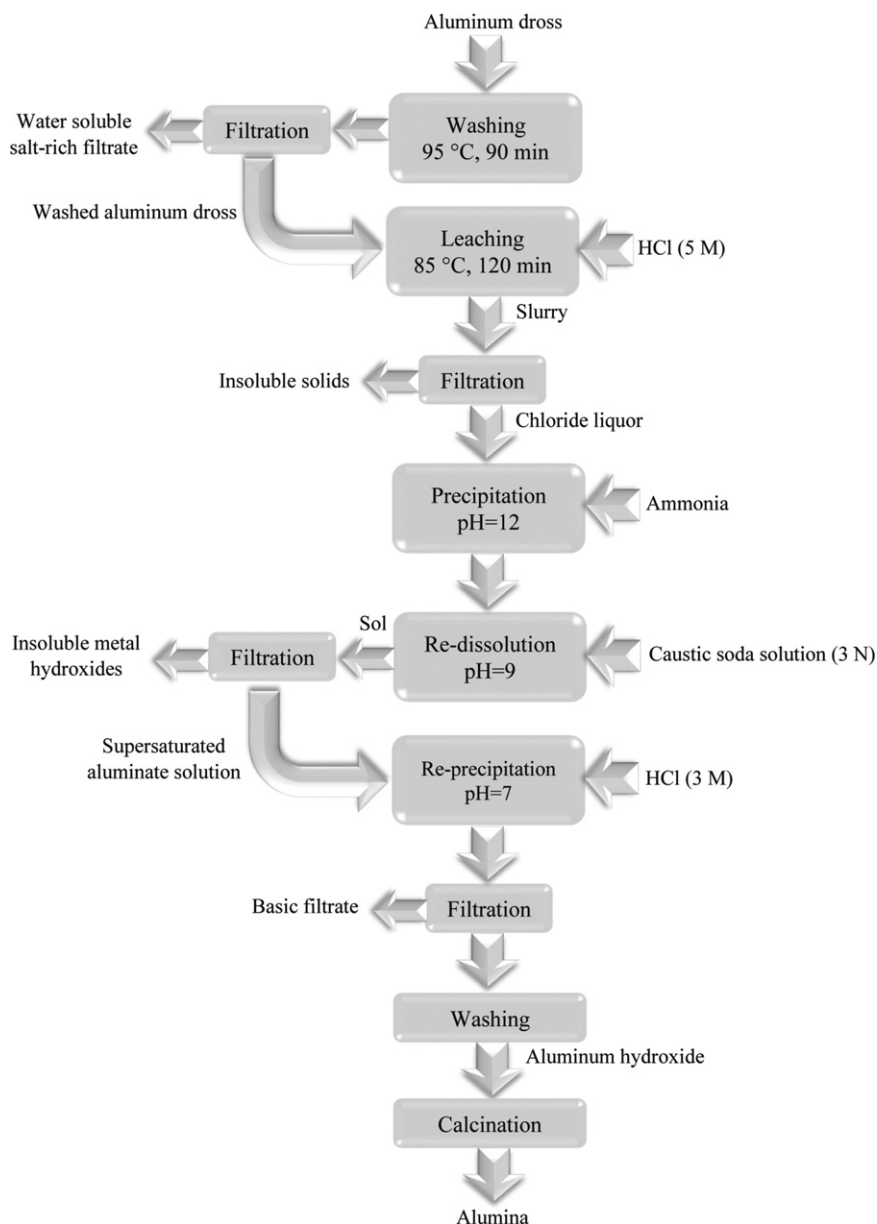


Fig. 3 Production process of γ - and α -alumina from aluminum dross waste.

liquor of the previous stage by adding ammonia until the pH value reached 11.0. To separate aluminum hydroxide from other metal hydroxides, 3 N NaOH solution was added to the co-precipitates, resulting in the formation of concentrated sodium aluminate solution and undissolved metal hydroxides. Aluminum hydroxide was re-precipitated in the form of a white gel by the addition of 3 M HCl to the concentrated sodium aluminate solution. The aluminum hydroxide gel was rinsed three times with a mixture of ethanol and deionized water. The γ - and α -alumina were eventually obtained by calcination of the aluminum hydroxide at 700 and 1200°C for 2 h, respectively.

Characterization Techniques

To determine the purities of alumina products, Zn-back titration method was applied. According to this method, the obtained alumina was dissolved in a mixture of mineral acids. Then, 0.01 M EDTA was added to the resulting solution and its pH value was adjusted at 10.0 by adding a buffer solution. The pH-adjusted solution was boiled for a few minutes to accelerate the formation of Al-EDTA complex. A few drops of Eriochrome black T indicator was then added until a blue color appeared. Excess of EDTA was titrated with 0.01 M ZnSO_4 solution. The emergence of wine red color meant the endpoint of titration. The volume of the ZnSO_4 consumed in titration was used for the determination of purity. The oxide composition of the AD was obtained employing an X-ray fluorescence device (ED2000, Oxford).

Mineralogy of the AD and also the crystalline nature of the alumina products were identified employing an X-ray diffractometer (Philips Expert System, 40 kV and 30 mA). The X-ray diffractograms were recorded at 2θ range of 10° – 90° (scanning rate = $2^\circ/\text{min}$, anti-scatter = 1° ; receiving slit 0.01 mm).

A 10 kV FESEM (TESCAN MIRA3, Czech Republic) was used to investigate the microstructure of the produced alumina products. A 30 kV scanning electron microscope (SEM) device (TESCAN VEGA II, Czech Republic) was used to observe the microstructure of the AD and solid residues. The secondary electron (SE) mode of the SEM device was selected for this purpose. A 120 kV TEM (PHILIPS CM12, Netherland) was used to evaluate the morphology of the as-prepared alumina particles. To prepare the samples for the TEM analysis, they were dispersed in 5% acetic acid solution using sonication.

The infrared spectra of the alumina products were recorded by a Fourier transform infrared (FTIR) spectrometer (SHIMADZU 8400s) to identify the nature of the chemical bonds. The spectra were recorded with a sensitivity of 4 cm^{-1} and 64 scans per spectrum taken.

The surface area and porosity analyses of the produced materials were carried out by adsorption-desorption of nitrogen at 77 K with a Microtrac Bel Corp instrument (BEISORP Mini). Before any analysis, the samples were degassed at 250°C for 5 h to remove the physically-adsorbed moisture and any impurities from the materials.

Results and Discussion

Characterization of Aluminum Dross

A sieve analysis was used to assess the particle size distribution of the as-received AD. Fig. 4 shows the results.

As can be seen, around 50% of the AD particles had a size of smaller than $214\text{ }\mu\text{m}$. The inset figure indicates that the AD has a granular form with a gray-blackish color. The X-ray fluorescence (XRF) chemical composition of the AD is presented in Table 1. The data in Table 1 reveals an aluminum oxide content of more than 61 wt%, making the AD as a secondary alumina-rich resource. The AD contains more than 16 wt% silica.

The XRD pattern of the AD is depicted in Fig. 5. The results indicate that predominant mineralogical phases such as aluminum oxide, quartz, spinel, diaoyudaoite ($\text{NaAl}_{11}\text{O}_{17}$), villiaumite (NaF), cryolite (Na_3AlF_6), silicon (Si), aluminum nitride and ferric oxide exist in the AD. In addition, defect spinel ($\text{Al}_{1.83}\text{Mg}_{0.87}\text{O}_{3.61}$) and traces amounts of halite, graphite (C), and fluorite (CaF_2) were also detected.

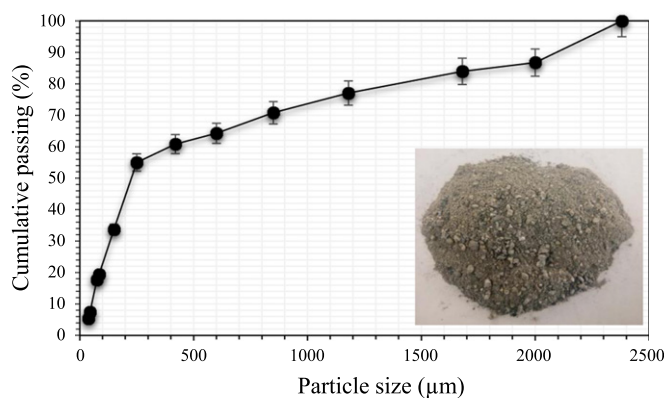


Fig. 4 Particle size distribution of the as-received AD.

Table 1 XRF chemical analysis of AD

Oxide	wt%
Al_2O_3	64.85
SiO_2	16.35
Fe_2O_3	6.74
MgO	2.96
CaO	3.82
Na_2O	2.97
K_2O	1.02
SO_3	0.28
TiO_2	0.45
MnO	0.37
CuO	0.19

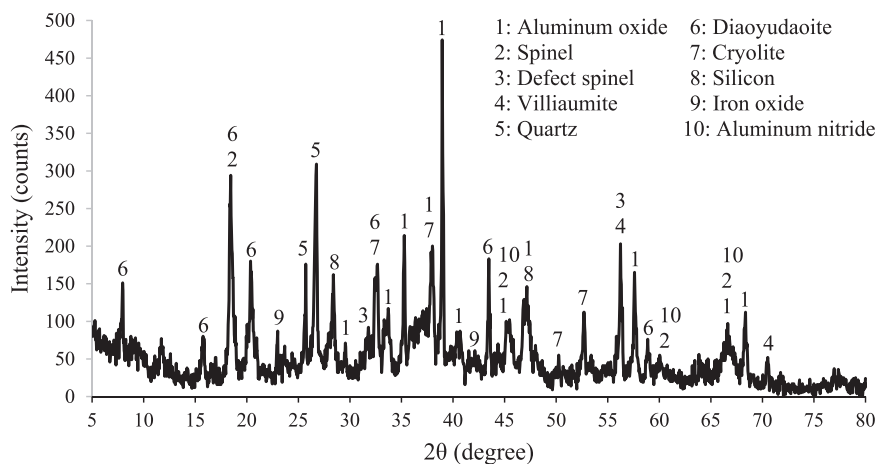


Fig. 5 XRD diffractogram of the AD.

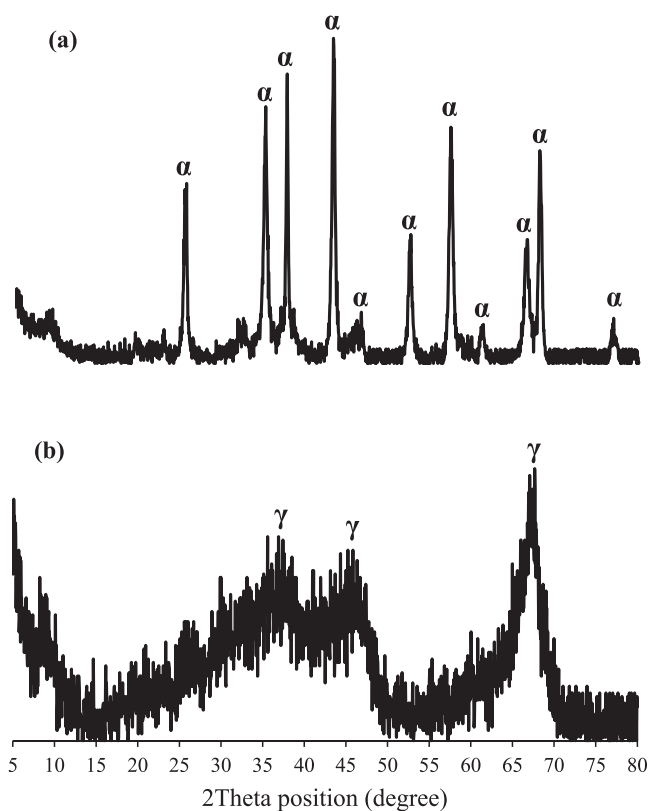


Fig. 6 XRD patterns of (a) α -alumina and (b) γ -alumina obtained from the AD.

Characterization of Products

XRD study of crystalline structure

The XRD diffraction patterns of the obtained alumina products are shown in Fig. 6. A comparison with ICDD standard cards of 00-005-0712 and 00-013-0373 confirms the formation of α - and γ -alumina, respectively. No characteristic diffraction peaks from other impurities were identified. It is very obvious from Fig. 6 that the obtained α -alumina shows a highly crystalline nature. The line broadening in Fig. 6(b) is due to the presence of very small crystallite sizes.

The chemical transformations during the formation of α - and γ -alumina occur according to the following reactions:





Based on the alumina recovery process shown in Fig. 3, the re-precipitation of aluminum hydroxide forms an initial amorphous aluminum hydroxide (aluminum trihydroxide, $\text{Al}(\text{OH})_3$) according to reaction (1). Aluminum trihydroxide is amphoteric and plays the role of a basic species against the entrance of proton. This leads to the formation of water and aluminum oxide hydroxide ($\text{AlO}(\text{OH})$) species (reaction 2). The dehydroxylation of AlOOH at 700 and 1200°C results in the emergence of transitional gamma and the most thermodynamically stable alpha phases, respectively (reactions (3) and (4)).

The mean crystal sizes (D) of α - and γ -alumina were estimated using Debye-Scherrer equation:

$$D = k\lambda / \beta \cos\theta \quad (5)$$

where $k=0.9$, λ the wavelength of incident X-rays ($1.541874 \text{ \AA}$), θ is Bragg's angle (in degree), and β is the full width at half maximum (FWHM). The mean crystal size of α -alumina calculated from the FWHM of diffraction peak at $2\theta=43.3^\circ$ is 29.7 nm. The mean crystal size of γ -alumina using the FWHM of the peak at $2\theta=67.4^\circ$ was obtained 10.8 nm.

The Zn-back titration tests disclosed a purity of more than 98 wt% for both α - and γ -alumina products. Such a purity is high enough to use the produced α - and γ -alumina in different industrial applications.

FTIR spectroscopy

Fig. 7 indicates the FTIR spectra of the produced α - and γ -alumina ranged from wavenumbers of $400\text{--}4400 \text{ cm}^{-1}$.

The absorption band at 449 cm^{-1} belongs to pseudoboehmite structure (Cui *et al.*, 2013). The lower intensity of this band in α -alumina is due to the transformation of pseudoboehmite to alumina at higher calcination temperature. The absorption bands around 574, 852, and 862 cm^{-1} are assigned to the vibrational frequencies of aluminum in octahedral (AlO_6) and tetrahedral (AlO_4) coordinates (Li *et al.*, 2006). The typical absorption band appeared at 1004 cm^{-1} is attributed to the symmetrical bending vibration of Al-O-H . The stretching vibrations of the Al-OH bond resulted in the absorption bands at 1550 and 1558 cm^{-1} . The presence of Al-OH bands may be due to the insufficient calcination time. The band observed at 1147 cm^{-1} is as a consequence of the Al-O bond (Vasquez *et al.*, 1997). The absorption bands centered at 3535 and 3562 cm^{-1} are attributed to O-H stretching vibration of water molecules adsorbed by the alumina materials. Higher intensity of absorption band around 3500 cm^{-1} in γ -alumina is due to its higher specific surface area compared to α -alumina. The appearance of weak absorption bands at 1645 and 1649 cm^{-1} are because of O-H bending mode of physically-adsorbed water (Hariharan *et al.*, 2014).

Microstructural study

Fig. 8 shows the FESEM images of the α - and γ -alumina powders obtained from the AD. As can be observed, the γ -alumina was lumps of nanosized primary particles. The α -alumina exhibited the intense agglomerates of angular rounded-corner shaped particles.

Typical TEM observations of γ - and α -alumina are shown in Fig. 9. It can be seen that the γ -alumina particles were relatively well-dispersed and exhibited a flake-like morphology. The flakes have an average size of less than 20 nm. The observation of an individual particle of the α -alumina was very difficult. As seen from Fig. 9, the α -alumina exhibited a dense overlapped aggregates of round corner-shaped particles. The aggregates appeared to be more than 50 nm.

Nitrogen sorptometry

The surface area and porosity of the produced alumina products were measured using nitrogen gas sorptometry technique. The adsorption-desorption isotherms of nitrogen for the γ - and α -alumina were presented in Fig. 10.

According to the IUPAC sorption isotherms, the produced γ - and α -alumina exhibited the typical types IV and III curves, respectively. The hysteresis loop of type H2 indicates capillary condensation phenomenon taking place in mesopores of the

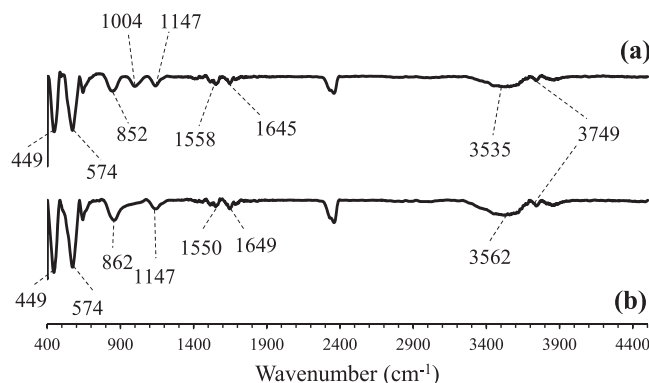


Fig. 7 FTIR spectra of (a) α -alumina and (b) γ -alumina.

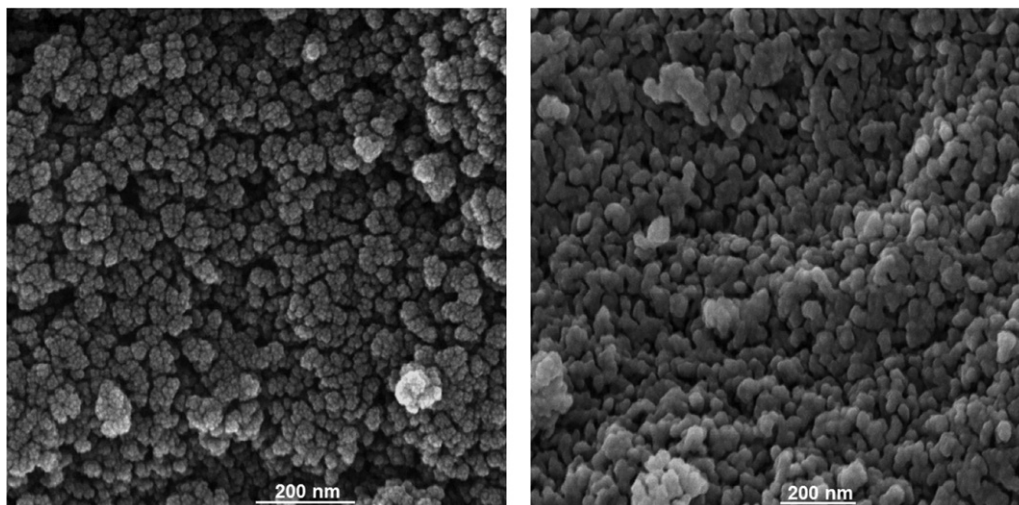


Fig. 8 FESEM images of alumina products produced from the AD. Left: γ -alumina, Right: α -alumina.

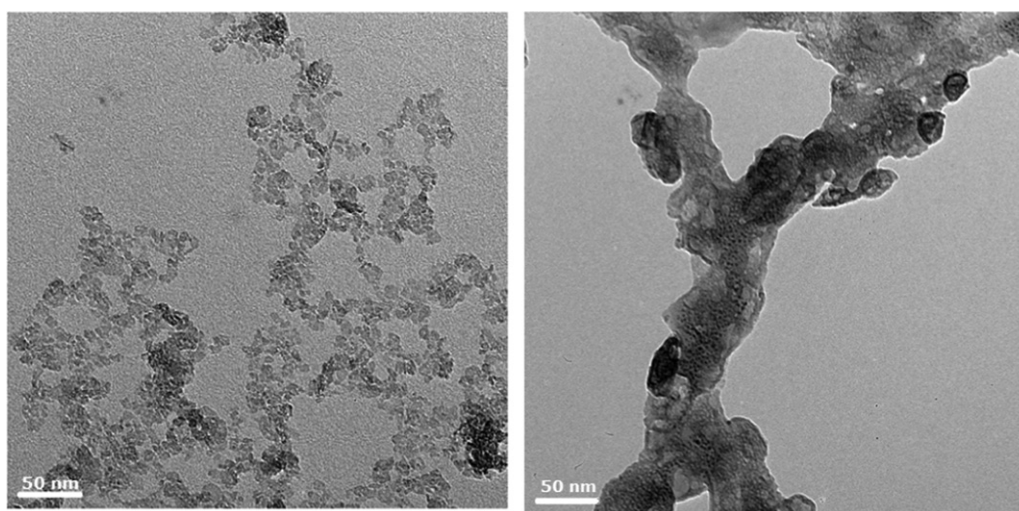


Fig. 9 TEM micrographs of alumina products produced from the AD. Left: γ -alumina, Right: α -alumina.

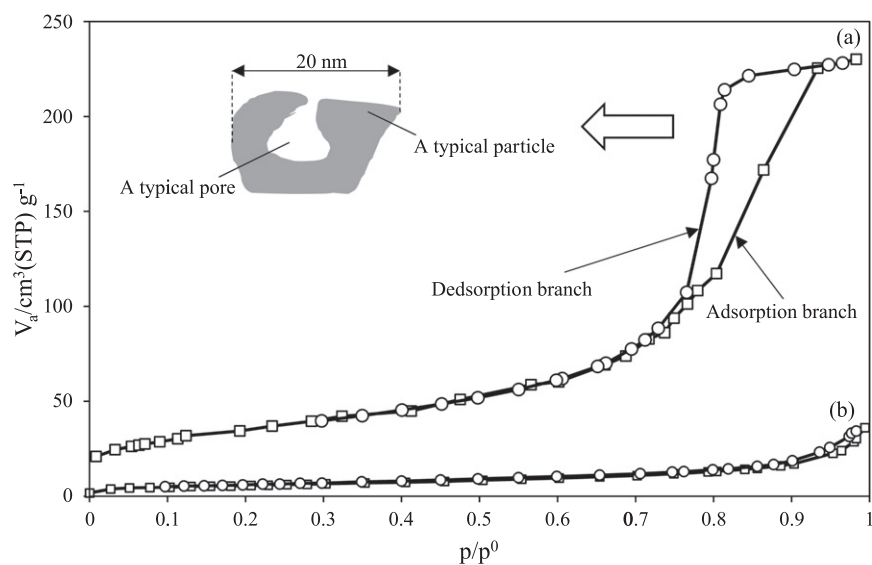


Fig. 10 Nitrogen adsorption/desorption isotherms of (a) γ -alumina and (b) α -alumina.

γ -alumina (Čejka *et al.*, 2001). Also, the emergence of this type of the hysteresis loop reminds ink bottle-shaped pores (Sing, 1982) in the flake-like particles of the produced γ -alumina, as schematically shown in the inset figure. The specific surface area and porosity characteristics of the γ - and α -alumina are presented in Table 2. As seen, the produced γ -alumina exhibited a high specific surface area and total pore volume with a mesoporosity nature. The α -alumina was expected to exhibit a lower specific surface area and total pore volume due its very high calcination temperature, which in turn resulted in a dense microstructure as previously observed by the FESEM and TEM analyses.

Characterization of Solid Residue

The SEM analyses of the as-received AD and the acid-leached residual solids after the leaching stage are shown in Fig. 11. It is clear from Fig. 11(a) that the AD is composed of irregularly shaped particles, which have formed a relatively dense microstructure. According to Fig. 11(b), after the acid leaching stage, the dense structure has been degraded and the residual solids are composed of finer particles.

Fig. 12 illustrates a simplified schema of acid leaching of a single particle. The HCl molecules attack soluble parts and enter them into the solution phase as metal cations (M^{n+}). This causes the particle to be degraded to finer particles and eventually the morphological changes take place over acid leaching time. A diffusion-controlled mechanism was found in previous study (Mahinroosta and Allahverdi, 2018c).

Fig. 13 depicts the XRD pattern of acid-leached solid residue at the end of alumina extraction process. As seen, the predominant crystalline phase is quartz. A few amounts of aluminum oxide remain undissolved during the acid leaching stage. The inset figure clearly reveals that the solid residue experienced a color change and finer particles after the acid leaching conditions. Such detected

Table 2 Specific surface area and porosity characteristics of alumina products

Sample	Specific surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
α -alumina	11	0.0487	25.16
γ -alumina	147	0.35	8.50

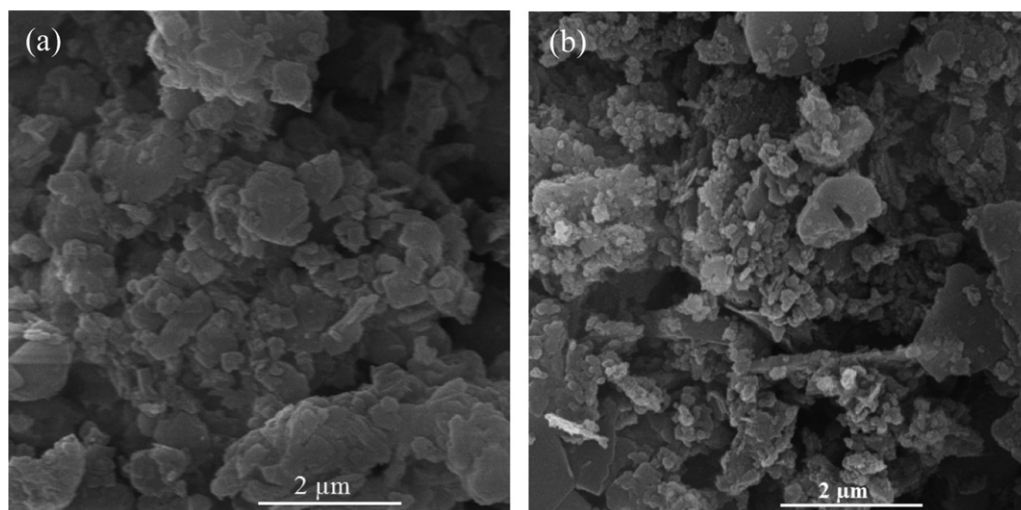


Fig. 11 SEM images of the (a) as-received AD and (b) acid-leached solid residue.

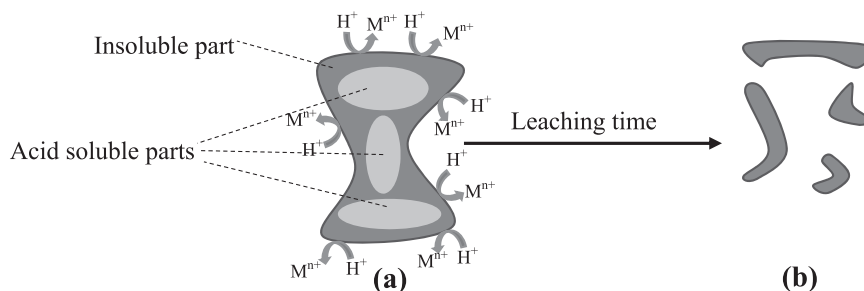


Fig. 12 (a) a single particle before acid leaching and (b) finer particles of solid residues after acid leaching.

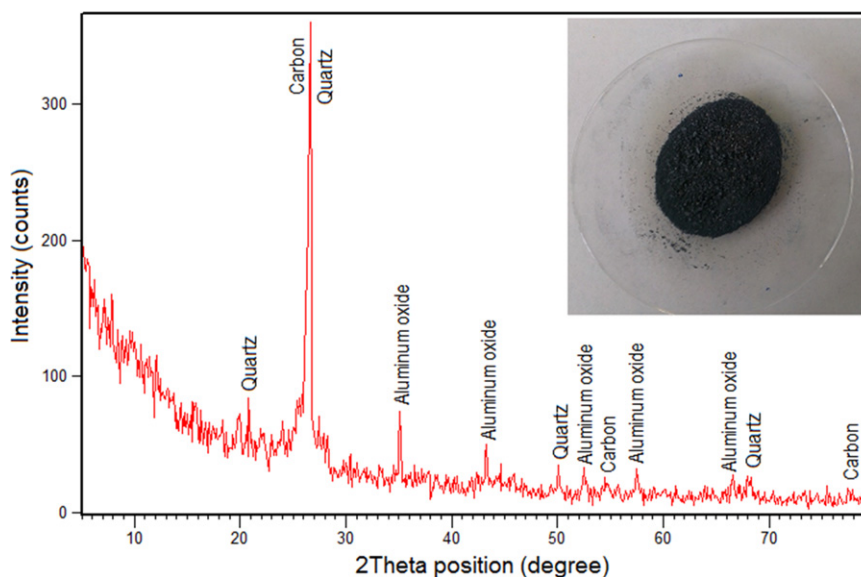


Fig. 13 XRD pattern of acid-leached solid residue.

mineralogical phases suggest that the solid residue can be reused as filler/aggregate in the preparation of building and construction materials. Or it can be accumulated somewhere without any environmental pollution.

Conclusions

This research work proposed a promising hydrometallurgical process for extracting alumina from aluminum dross waste. The proposed process involved acid leaching, co-precipitation, re-dissolution, re-precipitation, washing, and calcination stages. The leaching stage as the heart of the extraction process was performed at 85°C for 120 min using 5 M HCl. The alumina was extracted in the forms of high purity (>98.0%) γ - and α -alumina, having nanostructured natures. The γ -alumina exhibited a crystal size and a high specific surface area of 10.8 nm and 147 m²/g, respectively. The crystal size and specific surface area of the produced α -alumina were 29.7 nm and 11 m²/g, respectively. The acid-leached solid residue at the end of the process had mainly a siliceous nature with a few amounts of undissolved alumina. Such a solid residue can be suitable for application in building and construction materials. Overall, the envisaged modes of utilization of aluminum dross could substantially decline the amount of aluminum dross dump, and could contribute to the sustainability of the aluminum industries and to the decrease of environmental and public health detriments.

See also: Mining Industry. Recycling of Red Mud for Value-Added Applications: A Comprehensive Review

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Recycled Ceramics in Concrete

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Introduction

As a natural resource and energy-intensive industry that accounts for 7% of total CO₂ emissions, construction contributes significantly to humanity's environmental footprint. The construction materials industry, in particular fired clay-based product, concrete, and cement manufacturers, has adopted a number of measures to mitigate such adverse effects, including the use of industrial waste as aggregate or supplementary cementitious materials (SCMs) as well as recycling and reusing materials at the end of their life cycle.

That strategy is in keeping with the transition to a society in which the usability of products, materials, and resources is maintained for as long as possible and the generation of waste is minimized to create a circular, sustainable, low carbon, resource-efficient, and competitive economy. The transition underway affords Europe the opportunity to transform its economy, create jobs, and generate new and sustainable competitive advantages for the continent (European Commission, 2018). Attesting to the move in that direction is the growth in the EU's circular material use indicator for nonmetallic minerals (category MF3) from ~13.0% in 2010 to 15.2% in 2016.

Against that modern socioeconomic backdrop, one of the primary problems is the satisfactory management of industrial and construction and demolition waste (C&DW). In terms of volume, fired clay-based ceramic waste is of particular concern, as it accounts for a significant fraction (from 8% to 54%, Gálvez-Martos *et al.*, 2018) of the ~820 million tonnes of C&DW produced yearly in the EU. In that regard it is second only to concrete waste (40%–84%) and followed by other stony (unbound aggregate, asphalt) and nonstony (floating particles, glass) refuse (Medina *et al.*, 2015).

Manufacturing itself is a second source of ceramic waste, for 3%–7% of daily output is inevitably rejected, irrespective of technical improvements, translating in Europe into millions of tons per year (Tavakoli *et al.*, 2013). The percentage of wastage depends on the type of plant, product requirements, and other technical considerations.

Both red (brick and tile) and white (sanitary ware and electrical insulators) (Ogrodnik *et al.*, 2018) ceramic waste, present the world over, exhibit physical and chemical properties that depend on locally available raw materials and the manufacturing process (Siddique *et al.*, 2018). Despite those differences, all ceramic waste is durable, hard, and highly resistant to biological, chemical, and physical degradation. That notwithstanding, it is not recycled in any form at present (Binici, 2007).

Its use to manufacture concrete would enhance product sustainability, contributing to a greener environment. That, along with purely economic considerations, has created a pressing need for concrete made with nonconventional aggregates and binders bearing new SCMs.

This article discusses the key properties of tile, brick, sanitary ware, and electrical insulators and the mechanical performance of new cement matrices and recycled concretes bearing this type of waste as SCMs or coarse or fine aggregate. The most prominent scientific and technical advances forthcoming to date are addressed, based both on the worldwide literature and the many years of research conducted by the two institutions forming the SOSMAT (Spanish initials for "Construction Material Sustainability") associated research unit: The University of Extremadura and the Eduardo Torroja Institute for Construction Science.

Ceramic Waste Characterization

Chemical Composition

The literature on valorizing ceramic waste as an addition to cement or as aggregate for concrete manufacture reports as well on its chemical composition, summarized in Table 1. The data shows that all the products are acidic, comprising primarily SiO₂, Al₂O₃, and Fe₂O₃ (≥80.0 wt%) and containing smaller proportions of other oxides. The CaO content in tile, at 5.6%, in brick at 6.4%, and sanitary ware at 12.4% is much higher than the 0.76% in electrical insulators.

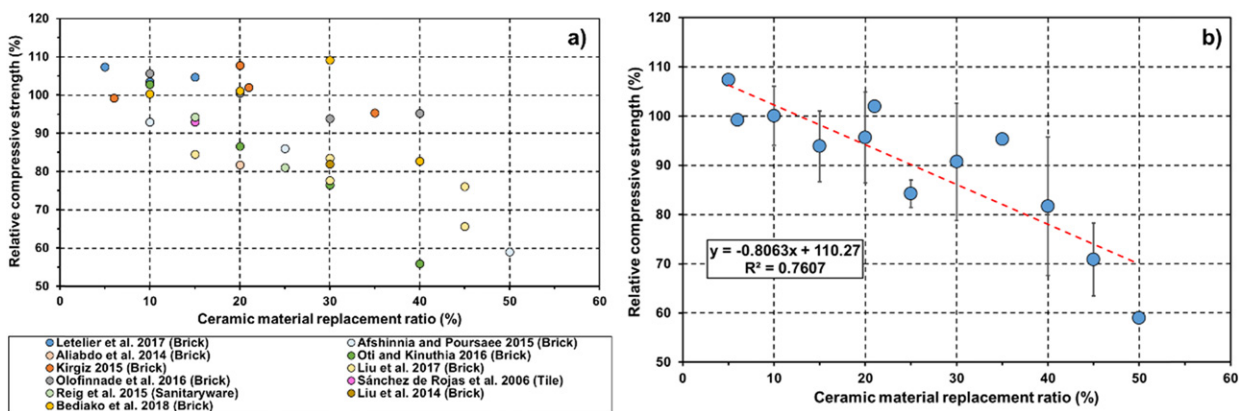
Sulfate, expressed as SO₃, is a minority component of ceramic waste, which is compliant with the 3.5% SO₃ ceiling set out in EN 197-1 (European Committee for Standardization, 2011a) for new cements bearing this refuse as an addition.

Ceramic Properties as Pozzolan Additions

Active additions or pozzolans are used worldwide for the economic, environmental, and technical benefits they afford. In European standard EN 197-1, naturally occurring fired pozzolans used to manufacture ordinary cement (CEM II/A and B-Q) are defined as materials "of volcanic origin, clays, shales or sedimentary rocks, activated by thermal treatment."

Table 1 Chemical composition (wt%) of ceramic waste

Oxide	Tile	Brick	Sanitary ware	Electrical insulators ^b
SiO ₂	71.89–64.20	88.40–50.91	68.41–28.86	70.9
Al ₂ O ₃	20.00–14.43	29.99–7.30	34.87–23.86	21.1
Fe ₂ O ₃	6.01–1.43	8.97–0.50	5.41–0.55	0.81
CaO	9.55–1.57	12.70–0.10	24.15–0.63	0.76
K ₂ O	2.68–1.63	4.83–0.24	3.00–1.45	3.57
Na ₂ O	3.44–2.01	1.43–0.83	2.36–1.25	1.47
MgO	3.35–0.72	4.06–0.10	2.86–0.19	3.57
SO ₃	0.0–0.06	2.54–0.20	0.07–0.00	–
LoI ^a	0.48–0.39	6.41–0.17	0.50–0.23	–

^aLoI: Loss on ignition.^bValues for the sole article published on the subject to date.**Fig. 1** (a) Relative compressive strength vs. ceramic replacement ratio by author; and (b) mean relative mechanical strength vs. replacement ratio and linear regression.

Although not initially pozzolanic, clays acquire that property when fired at 600–1000°C and ground to cement fineness. The loss of chemically combined water during calcination destroys the crystalline network of the clay constituents, rendering their components amorphous or vitreous. Pozzolanicity is therefore primarily an outcome of thermodynamic instability (Hea *et al.*, 1995). As activation temperature varies with the mineral composition of clay, it must be determined for each type of material and adjusted accordingly during firing (Calleja, 1968).

Activity can be assessed with the pozzolanicity test set out in standard EN 196-5 (European Committee for Standardization, 2011b) for the pozzolanic cements described in standard EN 197-1. Cements containing 20% ceramic waste in the form of tile and brick are standard-compliant at 28 days, the age established in earlier editions of the text (Sánchez de Rojas *et al.*, 2001). In that same vein, Lavat *et al.* (2009) found that 7- and 28-day cement bearing 30% tile passes the pozzolanicity test. Sanitary ware waste, when tested, is highly pozzolanic. Cements bearing just 10% of such waste pass the pozzolanicity test after 15 days and those with a 20% or 30% content are compliant after just 8 days, the earliest (=most demanding) age laid down in EN 197-1.

A pozzolanicity test alternative to the one recommended in EN 196-5 involves soaking the waste studied in a saturated lime solution. Trials run with that procedure showed that ceramic waste is more pozzolanic than fly ash and less than silica fume (Sánchez de Rojas *et al.*, 2006). Using the same method, Medina *et al.* (2016) observed the pozzolanicity of sanitary ware waste to be excellent, with results revealing values higher than tile and comparable to silica fume. Sanitary ware waste, then, exhibits activity similar to metakaolin, the best known and most active naturally occurring fired pozzolan (Frias *et al.*, 2000).

Most of the studies conducted explored pozzolanicity based on the mechanical strength of cement pastes, mortars, and concretes. The 28-day findings for cement-based materials bearing ceramic waste reported by different authors are graphed in Fig. 1.

The very visible scatter in the compressive strength values in Fig. 1 may be due to differences in the origin of the ceramic waste and/or in the fineness of the waste added to the cement (Liu *et al.*, 2017), which is a determinant for pozzolanicity. Despite that scatter, only one study (Oti and Kinuthia, 2016) observed relative compressive strength lower than the percentage of waste added. The evidence for waste pozzolanicity is therefore overwhelming, for in all but that case the reaction countered the reduction in cement content.

Table 2 Physical and mechanical properties of coarse and fine recycled ceramic aggregate

Property	Tile		Brick		Sanitary ware		Electrical insulators ^a	
	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine
Sand equivalent	–	87.9–83.4	–	88.0–80.4	–	–	–	–
Density (mg/m ³)	2.4–1.9	2.6–2.1	2.4–1.4	2.5–1.9	2.6–2.2	2.8–2.4	2.3	2.5
Water absorption (%)	11.6–1.4	17.2–2.0	18.0–1.8	18.4–0.7	2.9–0.5	2.5–0.2	0.5	0.7
LA coefficient (%)	21.8–14.7	–	49.6–30.6	–	20.0	–	–	–
Crushing value (%)	24.9–11.9	–	48.0–22.8	–	27.0–6.7	–	27.0	–

^aValues for the sole article published on the subject to date; Coarse: Particle size fraction from 4 or 5 mm to 35 mm; Fine: Particle size fraction from 0 mm to 35 mm.

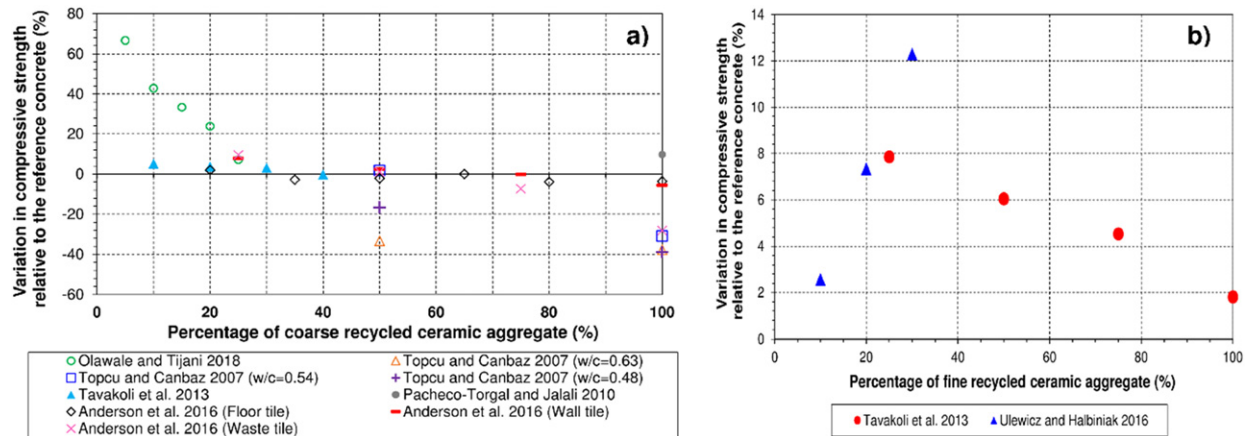


Fig. 2 Percentage variation in compressive strength of concrete vs. replacement ratio of recycled tile aggregate in (a) coarse and (b) fine aggregate.

Concrete made with cement bearing ceramic waste at small replacement ratios not only equals but improves on the mechanical strength of the reference, as observed by Kirgiz (2015) and Bediako (2018) in mortars and Letelier *et al.* (2017) and Oti and Kinuthia (2016) in concrete.

Ceramic Waste as Recycled Aggregate: Properties

The range of values found in the literature for the physical and mechanical properties of coarse and fine recycled ceramic aggregate and given in Table 2 shows that density is very similar in all four types of ceramic waste. The mean range, at 2–3 mg/m³, is lower than in natural aggregate due to the greater porosity of the waste material. The sand equivalent is similar in tile and brick and higher than 80 in both cases, an indication that as it is appropriate, the sand equivalent in clay fines has no adverse effect on the durability or mechanical strength of new concretes.

The coarse and fine aggregates made from tile and brick are much more water-absorbent than those processed from white ceramics (sanitary ware and electrical insulators). They fail to comply with the <5% recommended for conventional aggregate used in concrete manufacture due primarily to the greater porosity of red ceramics. Such high absorptivity is one of the major obstacles to their use, further to the legislation in place.

Recycled ceramic aggregate consisting of crushed brick exhibits a higher Los Angeles coefficient and crushing value than materials based on crushed tile, sanitary ware, and electrical insulators. That can be attributed primarily to the intrinsic hardness of the three latter materials afforded by the vitrification of their surface.

The Los Angeles coefficient values observed for all but the brick-based recycled ceramic aggregates lie below the 40% ceiling recommended for coarse aggregate used to manufacture concrete with characteristic strength of ≥ 25 MPa.

Performance in Recycled Ceramic Aggregate-Bearing Concrete

Compressive Strength

Further to the data in Fig. 2 that plots the percentage variation in compressive strength against the replacement ratio of recycled aggregate, the replacement of $\leq 40\%$ coarse aggregate (Fig. 2a) or 100% fine aggregate (Fig. 2b) induces no loss of compressive

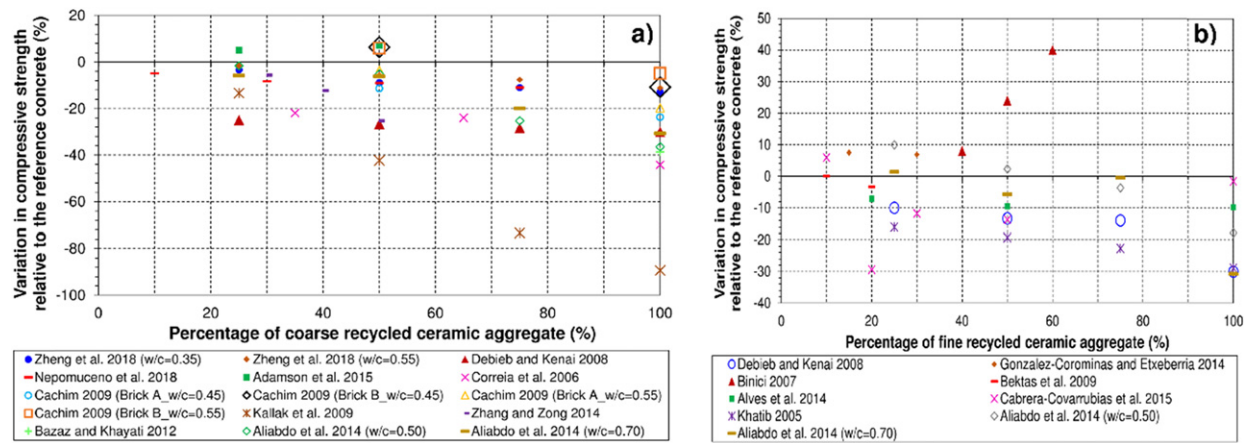


Fig. 3 Percentage variation in compressive strength of concrete vs. replacement ratio for recycled brick aggregate in (a) coarse and (b) fine aggregate.

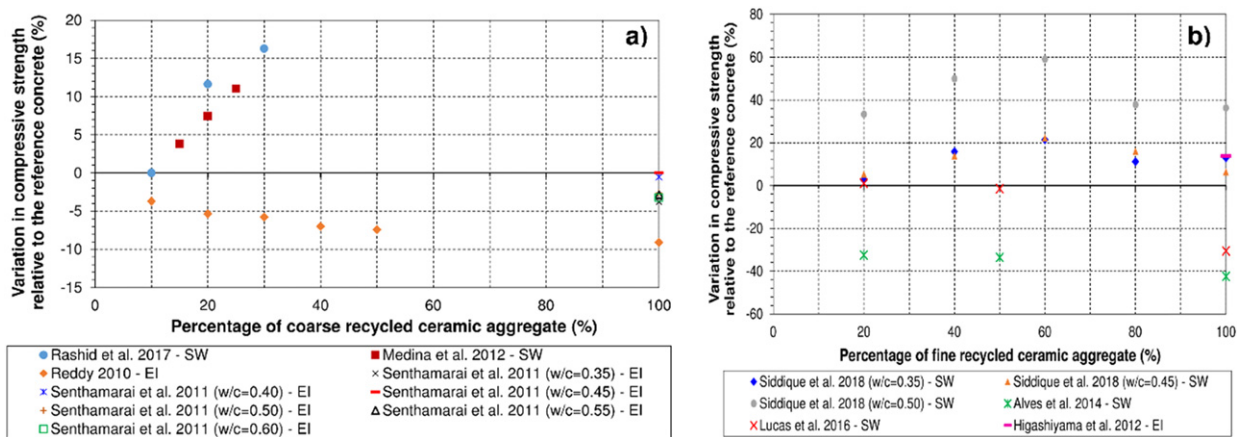


Fig. 4 Percentage variation in compressive strength of concrete vs. replacement ratio of recycled white ceramic aggregate (sanitary ware, SW; electrical insulators, EI) in (a) coarse and (b) fine aggregate.

strength. For the coarse aggregate (Fig. 2a), the variation observed at recycled waste content of 50%–100% is smaller than the replacement ratio, with values depending on the intrinsic characteristics of the tile and the water/cement ratio used in the concrete, as noted by Topcu and Canbaz (2007).

Fig. 3(a) and (b) show the effect of including different percentages of brick as coarse and fine aggregate on compressive strength relative to conventional concrete. In the former (Fig. 3a), performance declines with rising replacement ratios, except in studies conducted by Adamson *et al.* (2015) and Cachim (2009), who reported a rise in compressive strength at ratios of $\leq 50\%$. Such lower performance relative to recycled concrete containing tile or white ceramics and conventional concrete is closely related to the lower strength and higher porosity of brick-based aggregates; and their rounder shapes, that translate into weaker coarse aggregate/paste interfaces than found for aggregate with sharper edges.

Three regions can be distinguished on the graph in Fig. 3(b) for crushed brick fines. In the first, up to $\leq 15\%$, the use of the new aggregate raises compressive strength relative to the reference. In the second, for ratios of 15%–60%, no clear pattern is observed, with some authors reporting improved performance for percentages of 15%–60%, inclusive, and others decline with rising replacement ratios in the 20%–60% range. In the third, at ratios of $> 60\%$, compressive strength is observed to decline relative to the reference but by less than the replacement ratio.

Fig. 4(a) and (b) show the effect of using different percentages of white ceramics as coarse and fine aggregate on compressive strength relative to conventional concrete. Used as coarse aggregate, sanitary ware waste raises compressive strength in keeping with the replacement ratio up to 30%, due primarily to the thickness and elasticity of the new ceramic/paste interfacial transition zone (ITZ). Further to the data, electrical insulators induce a decline in performance with rising recycled aggregate content, although here also the percentage is smaller than the replacement ratio. Senthamarai *et al.* (2011), studying the effect of adding electrical insulators with different water/cement ratios, observed that at w/c of 0.40–0.45 mechanical performance was similar to that found for conventional concretes.

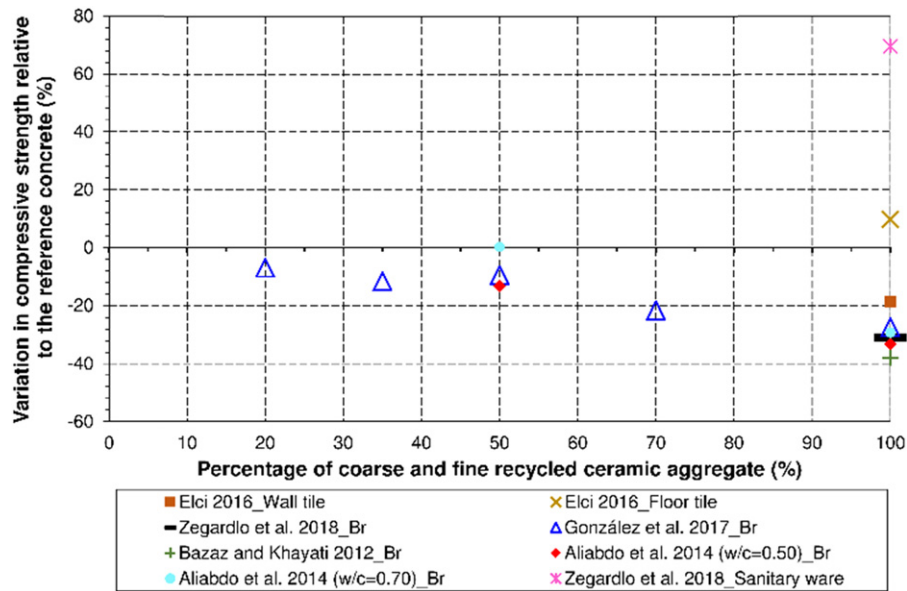


Fig. 5 Variation in concrete compressive strength with the simultaneous use of coarse and fine recycled aggregate (tile; brick, Br; and sanitary ware).

Table 3 Variation in tensile strength with replacement ratio by type of coarse and fine recycled aggregate

X (%)	Tile		Brick			White ceramics	
	Gr	Gr+f	Gr	f	Gr+f	Gr	f
5	↑15.0	—	—	—	—	—	—
10	↑60.0	—	↓6.4	—	—	↓2.1	—
15	↑70.0	—	—	↑0.2	—	↑10.8	—
20	↑20.0–↑6.5	—	—	↓1.9	↑7.5	↑19.7–↓2.7	↑25.3–↓24.7
25	↑22.6–↑10.0	—	↓6.1–↓24.6	+12.2–↓17.5	—	↑25.7	—
30	↑3.23	—	↓5.0	+2.3	—	↑11.3	—
35	—	—	↓8.6	—	↓5.0	—	—
40	—	—	—	—	—	↓12.5	↑36.7–↑6.5
50	+16.1–↓19.1	—	↑16.2–↓50.2	↓1.1–↓23.8	↓9.3–↓49.6	↓14.0	↓27.8
60	—	—	—	—	—	—	↑27.6–↑17.3
65	↑12.9	—	↓15.7	—	—	—	—
70	—	—	—	—	↓22.5	—	—
75	↑9.7	—	↓22.2	↓5.9–↓31.3	—	—	—
80	↑3.2	—	—	—	—	—	—
100	↓3.2–↓38.5	↑3.4–↓15.6	↑4.3–↓60	↓5.0–↓52.4	↓20.9–↓37.5	↓15.5	↑36.4–↓33.9

Note: X, replacement ratio; Gr, included in coarse fraction; f, included in fines fraction Gr + f, included in both coarse and fines fractions; ↑, percentage rise relative to conventional concrete; ↓, percentage decline relative to conventional concrete.

When used as fines, white ceramics, irrespective of type, were found by most studies conducted to date to have a beneficial effect, with 60% as the optimal percentage, for performance improves less at lower and higher ratios. Nonetheless, [Alves et al. \(2014\)](#) and [Lucas et al. \(2016\)](#) reported declines relative to conventional concrete.

Fig. 5, which graphs the variation in compressive strength when recycled ceramics are used in both coarse and fine aggregates, reveals a minor decline with rising replacement ratio. The decline is lower than 15% at ratios of $\leq 50\%$ and than 25% for ratios of 50%–70% recycled brick aggregate. When 100% of the aggregate is replaced with tile waste, compressive strength rises or declines depending on the type of tile. When the aggregate is crushed brick, the decline is more intense than found for the other ceramics, ranging from 27% to 38%. Replacing conventional with recycled sanitary ware aggregate raises mechanical strength significantly.

Splitting Tensile Strength

The splitting tensile strength values of recycled concrete containing ceramic waste as (coarse, fine, or coarse+fine) recycled aggregate relative to conventional concrete are given in [Table 3](#). As [Table 3](#) shows, the use of brick as a coarse aggregate induces a

steeper decline than the use of other types of ceramic aggregate, due primarily to its higher porosity and the features of the resulting ITZ, (Sáez del Bosque *et al.*, 2017). Strength is observed to rise with tile at percentages of $\leq 35\%$ and from 60% to 80%, whereas when white ceramics are used strength grows slightly or remains practically flat at replacements of $\leq 25\%$.

When crushed brick waste is used as fines, strength rises at contents of $\leq 40\%$, while the use of white ceramics raises splitting tensile strength across the board. Alves *et al.* (2014), however, reported declines irrespective of the replacement ratio studied (20%, 50%, and 100%).

The simultaneous use of white ceramic waste in the coarse and fine fractions induces rises in strength at percentages of $\leq 20\%$. The sole paper published on 100% replacement (Elçi, 2016) shows that strength rises slightly ($\sim 3\%$) with floor tile and declines ($\sim 16\%$) with wall tile waste.

Conclusions

The conclusions drawn from this review are listed below.

- $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ accounts for ≥ 80 wt% of the chemical composition of ceramic waste (tile, brick, sanitary ware, and electrical insulators).
- In terms of pozzolanicity and origin, ceramic qualifies as a naturally occurring fired pozzolan.
- A relationship is observed between compressive strength and amount of ceramic waste used. Many of the studies reviewed show that materials bearing ceramic waste exhibit compressive strength not only comparable to but higher than the reference material.
- Although recycled ceramic aggregate is less dense and has higher water absorptivity than conventional aggregate, neither fact limits its valorization in recycled concretes.
- Tile, sanitary ware, and electrical insulator waste have more suitable Los Angeles coefficient and crushing values than brick-based waste.
- Ceramic waste has a greater impact on new concrete compressive strength when used as coarse than as fine or a mix of coarse and fine aggregate.
- The beneficial effect of recycled ceramic aggregate on new concrete splitting tensile and compressive strength is approximately the same in tile and white ceramics and much smaller in brick.

Despite the research already conducted, further studies are needed for a fuller scientific/technical understanding of the effect of this type of waste on mechanical performance as well as of the resistance of new cement-based materials to aggressive environments (CO_2 , Cl^- , $\text{SO}_4^{=}$, sea water, freeze/thaw, etc.).

Acknowledgments

This study was funded by the Spanish Ministry of Science and Innovation under project BIA2016-76643-C3-1-R.

See also: Life-Cycle Impact of Concrete With Recycled Materials. Recycled Concrete. Sustainable Production of High Performance Concrete

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Recycling Aluminosilicate Industrial Wastes Into Geopolymer: A Review

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Introduction

Rapid development of infrastructures in developing countries over the past several decades has made the Portland cement (PC) as the key construction material with a world demand projected to rise 4.5% per year to 5.2 billion metric tons in 2019 (Green, 2015). PC production, however, accounts for huge amounts of greenhouse gas emission, accounting to 5%–8% of total man-made CO₂ emission (Scrivener and Kirkpatrick, 2007) both directly and indirectly. Global concerns over climate change due to excessive greenhouse gas emissions along with some superior durability properties of non-Portland cements have created increasing interest in developing environmentally-friendly cements alternatives to PC. Among non-Portland cements, geopolymer cements that can be simply produced by alkali activation or geopolymerization of appropriate aluminosilicate precursors has attracted researcher's attention.

Geopolymer cements can be considered as a sub-group of alkali-activated materials that are produced by chemical activation of suitable reactive aluminosilicate materials using highly alkaline activator solutions. Alkali-activated materials have a long history dating back to the 1940s with the introduction of alkali-activated Blast furnace slag by Purdon (1940). The work on geopolymer materials, however, started later in 1970s by the work of Davidovits (1979), who activated metakaolin (MK) with soluble alkali silicate in 1975 and named the product as the first mineral resin or mineral polymer. The term 'geopolymer' was first applied in 1978 by Davidovits (2008) to introduce a new group of alkali-activated materials characterized by a three dimensional networks of aluminosilicates.

Based on definitions given by Davidovits (1991a) and Duxson *et al.* (2007a) geopolymers or inorganic polymers are a subset of alkali- activated materials possessing a disordered aluminosilicate network of a higher degree of connectivity (overwhelmingly Q⁴). Fig. 1 represents the molecular units of the molecular structure of geopolymers proposed by Davidovits (2005).

The mechanism and chemistry of geopolymerization reactions have been the subject of much scientific discussion over the past two decades showing that the mechanism and chemistry of the binder depend on the properties of both the aluminosilicate precursor material and the alkali-activator. The presence of calcium, for example, is very determinative in the mechanism and the type of binding compound being formed. In the absence of calcium or presence of low amount of which N–A–S–(H) binding compound and geopolymer material is formed (Davidovits, 1991a; Richardson *et al.*, 1994; Wang and Scrivener, 1995; Duxson *et al.*, 2007b; Bell *et al.*, 2008; Yip *et al.*, 2008). The presence of significant amounts of calcium in the reacting media, however, results in the formation of C–(A)–S–H binding compound (Richardson *et al.*, 1994; Wang and Scrivener, 1995; Yip *et al.*, 2008).

Provis *et al.* (2005a) presented a model for the geopolymerization reactions starting with dissolution of aluminosilicate source material in alkali- activator solution with a subsequent oligomerization of silicate and aluminate monomers. The formed aluminosilicate oligomers then condense into a disordered aluminosilicate gel upon polymerization. Depending on the reacting conditions, the intermediate aluminosilicate oligomers can also result in the formation of nano-crystalline zeolite phase upon nucleation and crystallisation. Fig. 2 displays the conceptual model proposed for geopolymerization (Duxson *et al.*, 2007b).

The properties of geopolymer materials greatly depend on both the composition and properties of the starting materials and the processing conditions applied. According to Davidovits (1991b), the atomic ratio of Si:Al is very determinative so that ratios lower than 3 provide rigidity to the geopolymer and ratios higher than 15 impart ductility and polymeric character to the material. Mechanical properties (Yip *et al.*, 2008; Kaps and Buchwald, 2002; Temuujin *et al.*, 2009; Škvára, 2007) resistance to acid media (Palomo *et al.*, 1999a; Shi and Stegemann, 2000; Allahverdi and Škvára, 2001a,b, 2005; Bakharev *et al.*, 2003; Pacheco-Torgal and Said, 2011; Vafaei *et al.*, 2018), resistance to high temperatures (Pawlasova and Škvára, 2007; Krivenko *et al.*, 2013; Perera and

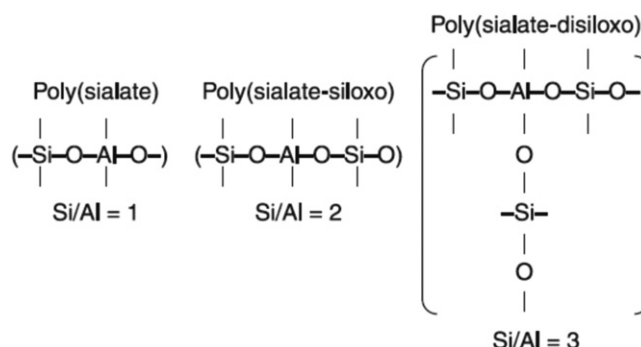


Fig. 1 Molecular units of the molecular structure of geopolymers. Reproduced from Davidovits, J., 2005. Geopolymer chemistry and sustainable development. The poly(sialate) terminology: A very useful and simple model for the promotion and understanding of green- chemistry. In: Proceedings of the 2005 Geopolymer Conference, St Quentin, 1, pp. 9–15.

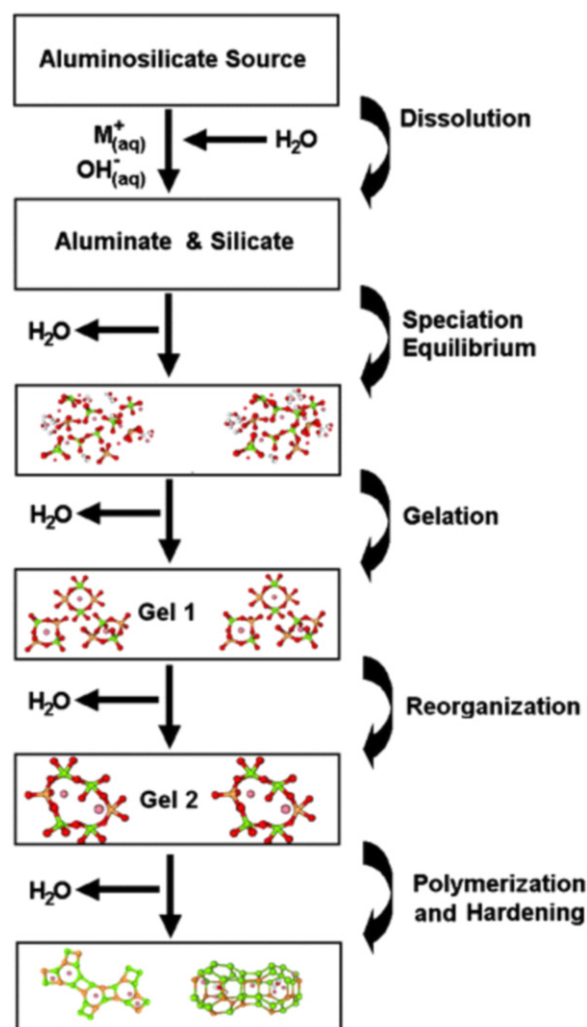


Fig. 2 Conceptual model for geopolymerization. Reproduced from Duxson, P., Fernández-Jiménez, A., Provis, J.L., *et al.*, 2007b. Geopolymer technology: The current state of the art, *Journal of Materials Science* 42, 2917–2933.

Trautman, 2006; Kong and Sanjayan, 2008; Temuujin *et al.*, 2011; Zhao and Sanjayan, 2011), resistance to cycles of freeze-thaw (Yunsheng and Wei, 2006; Dolezal *et al.*, 2007; Bortnovsky *et al.*, 2007; Slavik *et al.*, 2008; Brooks *et al.*, 2010) are among interesting properties of geopolymer materials that received increasing interest in the literature.

Geopolymer cements can be produced either by using raw/processed aluminosilicate natural source materials such as natural pozzolans (Verdolotti *et al.*, 2008; Kani and Allahverdi, 2009; Miller *et al.*, 2010; Allahverdi *et al.*, 2011; Kani *et al.*, 2012), natural zeolites (Villa *et al.*, 2010), uncalcined/calcined clays (Zhang *et al.*, 2014), etc., or aluminosilicate industrial waste materials such as fly ash (FA) (Singh *et al.*, 2015; Zhuang *et al.*, 2016; San Nicolas *et al.*, 2017; Ma *et al.*, 2018).

A survey in 2008 reported that only 43% of total annual production of FA in the United States, which amounts to about 131 million tons, is re-used with the remaining ash piles causing increased environmental threats (Johnson, 2009). Considering the significant growth in global annual production of industrial wastes, re-use of industrial waste materials for production of geopolymer cements has provided a multifold strategy for not only considering global concerns over greenhouse gas emissions, but also targeting industrial waste management, conserving natural resources that are currently being utilized in PC production and also opportunities for development of low cost cements.

The majority of the research works on alkali-activated and geopolymer materials are focused on granulated Blast furnace slag from pig iron production process and FA as a waste residue in coal combustion process due to their worldwide availability and also their high contents of reactive silica and alumina. However, many different aluminosilicate industrial waste materials can be used as a suitable precursor for synthesis of geopolymer materials. The determining key-factor for suitability of a precursor for geopolymer production is to contain enough amounts of reactive silica and alumina that are easily dissolved in alkali activator solution that provides a high pH medium. For this reason, many attempts have been devoted to the development of geopolymer materials from aluminosilicate industrial waste materials other than FA.

This paper is devoted to a systematic review on the last decade published literature on recycling non-fly ash aluminosilicate industrial waste materials such as construction and demolition wastes, waste glass, red mud, mining tailings, etc., into geopolymer material. Granulated Blast furnace slag and other calcium silicate slags are not of concern in this study, since alkali activation of these materials results in formation of calcium silicate hydrate (C-S-H) and calcium(-sodium) aluminosilicate hydrate (C,N-(A)-S-H) as the main binding compounds compared to geopolymer materials, which are mainly composed of sodium aluminosilicate hydrate (N-A-S-(H)).

Aluminosilicate Industrial Waste Materials Used as Geopolymer Precursors

Due to potential environmental and technical advantages of geopolymer binding materials over PC, conversion of aluminosilicate industrial waste materials into geopolymer material has been considered as an appropriate solution for effective management of aluminosilicate industrial waste materials. This has motivated researchers to evaluate the potential of different aluminosilicate industrial waste materials as alternative precursor for geopolymer material. Here, we briefly review and discuss the relevant literature chronologically.

Construction and Demolition Wastes (CDW)

CDW is one of the largest waste streams generated in both advanced and developing countries and its management has become an important worldwide problem. It is defined as waste materials generated from construction projects, demolition of buildings, structures and roads and land clearing activities. CDW consists of numerous materials, including concrete, bricks, ceramic and tile, gypsum boards, glass, wood, etc., many of which have potential to be recycled. In Europe, construction sector produces 820 million tons of CDW annually that is equal to about 46% of the total waste generation according to (Eurostat, 2017). The traditional tendency for CDW disposal has been discarding it in landfills or even in open dumps. But recently, due to environmental considerations reduction, recycling and reusing strategies are emphasized. Recycling of CDW into alkali activated or geopolymer binders, therefore, is an important step towards sustainable waste management.

Allahverdi and Kani (2009, 2013) used waste brick and waste concrete powders as precursor for geopolymer. They activated waste brick and combinations of waste brick with waste concrete with alkali activators of different compositions based on sodium silicate (SS) and sodium hydroxide (SH) solutions. They reported a maximum 28-day compressive strength of about 50 MPa achieved from paste specimens. Based on their results, the mechanical properties of the prepared geopolymer samples strongly depend on the composition and reactivity of the precursor materials and optimization of both dry binder and also the activator is necessary.

CDW can be used for production of quality aggregate. In the aggregate washing stage, however, a significant amount of filter cake waste mainly composed of fine silt particles is produced that has no use and is normally landfilled. Lampris *et al.* (2009) investigated the possibility of converting filter cake of aggregate washing plant into aggregate using geopolymerization technology. 100% dried and ground silt, mixtures of silt with 20% (w/w) of silt substituted by either MK or pulverized fuel ash (PFA) were activated with an alkali activator based on SH and SS solutions. Three different curing regime including room temperature curing at 25°C for 7 days (RT), heat curing at 60°C for 3 days and then continued room curing for 4 days (RT+60) and heat curing at 105°C for 1 day were applied to paste specimens. Geopolymer paste produced from 100% silt showed an average 7-day compressive strengths of 18.7 MPa and partial replacement of silt by MK or PFA increased average compressive strengths to 30.5 and 21.9 MPa, respectively. Application of heat curing at 105°C for 1 day was beneficial and resulted in a compressive strength of 39.7 MPa. Fig. 3 depicts the positive effect of curing

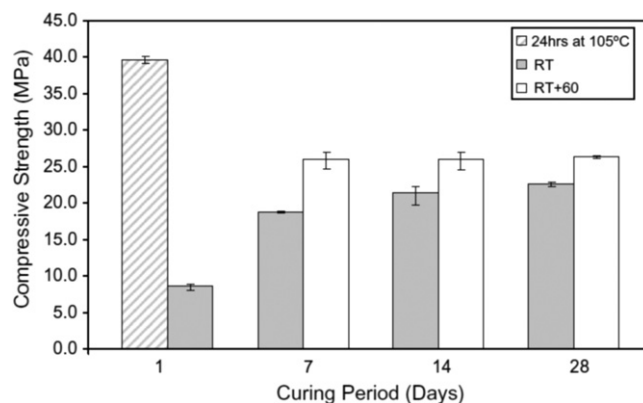


Fig. 3 Effect of curing conditions on compressive strength of silt geopolymer. RT: 7 days of curing at room temperature; RT + 60: heat curing at 60°C for 3 days and then continued room curing for 4 days; 24 h at 105°C: curing for 24 h at 105°C. Reproduced from Lampris, C., Lupo, R., Cheeseman, C.R., 2009. Geopolymerisation of silt generated from construction and demolition waste washing plants. Waste Manage 29, 368–373.

temperature on compressive strength of silt geopolymer. Based on experimental results of the research, silt generated from washing plant has potential for being reused in aggregate production.

Rapazote *et al.* (2011) used tile, brick and ceramic waste (A) and concrete and stone masonry waste (B) as precursors for geopolymer mortar preparation. A 2-h thermal treatment at 750°C was applied to material B to increase its reactivity. Calcined water treatment plant sludge (material L) was also used as an alumina rich additive material. Aggregates were also prepared from the same source materials (A and B) by crushing and classification. Plain B, combination of 0.7A + 0.3L (AL) and combination of 0.35A + 0.5B + 0.15L (ALB) were activated by a proportioned mixture of SH and SS and mortar specimens with binder-to-aggregate ratio of 0.5 were prepared and cured hydrothermally at 65°C for 48 h. Based on compressive strengths of 43.8, 42.9, and 20.6 MPa for mortar specimens based on AL, ALB, and B binders, respectively, they concluded that binder B (concrete and stone masonry waste) exhibits a low mechanical performance compared to AL and ALB. They also compared the fire resistance of geopolymer mortars using OPC mortar specimens as control. The specimens were heated inside a furnace up to 900°C, kept at 900°C for 2 h, and then left inside the furnace for 1 day to cool down. Compared to OPC control mortar that was completely disintegrated with zero residual compressive strength, geopolymer mortars retained their cohesion and exhibited significant residual compressive strengths of 18.0, 11.0, and 4.8 MPa for AL, ALB, and B, respectively.

Reig *et al.* (2013) prepared cement pastes and mortars from alkali activated red clay brick that is claimed to be a major part of CDW in Spain originating from sintered red clay ceramics. The effect of different parameters including composition and concentration of alkali activator, water-to-binder (w/b) ratio, binder-to-sand (b/s) ratio on compressive strength of mortar specimens cured at 65°C at a relative humidity (RH) of 90%–95% for 3 and 7 days were investigated. Both 3- and 7-day compressive strengths increased to peak values as the SS content of activator was increased to an optimum value. Very significant increases in compressive strength was also observed water-to-binder ratio was decreased at constant activator-to-binder and $\text{SiO}_2/\text{Na}_2\text{O}$ ratios. Compressive strengths up to 50 MPa were achieved by optimizing the w/b, b/s and $\text{SiO}_2/\text{Na}_2\text{O}$ ratios. Thermogravimetric analyses results displayed the formation of zeolitic-like phases when activators of low alkaline concentration were used.

Pathak *et al.* (2014) used concrete powder and brick powder as precursor for geopolymer paste preparation using SH and SS as activator. Based on isothermal calorimetry data, they concluded that plain concrete powder is not enough reactive for geopolymerization. The effect of milling time of brick powder and the concentration of SH and SS in activator solution on compressive strength was studied. A maximum 28-day compressive strength of 11.43 MPa was achieved from paste specimens cured at 60°C for 24 h and then kept in open-air condition at room temperature ($32 \pm 3^\circ\text{C}$).

Komnitsas *et al.* (2015) investigated the effect of synthesis parameters including precursor particle size, NaOH concentration (8–14 M), and curing temperature (60–90°C) on quality of geopolymer paste specimens produced from three different types of CDW including tile, brick and concrete and cured at room temperature for about one hour and then in an oven for 7 days. Geopolymers of each CDW-group exhibiting the highest compressive strength were then evaluated for their thermal stability by heating at 400, 600, and 800°C for 60 min, freeze-thaw resistance by subjecting to weekly freeze-thaw cycles at -10°C and 60°C for two months, and structural integrity upon immersion in distilled water for 2 months. The maximum compressive strengths of 57.8, 49.5, and 13.0 MPa achieved from tile, brick and concrete waste specimens, respectively, revealed the suitability of both tile and brick waste precursors for geopolymerization reactions compared to concrete waste. Geopolymer based on tile and concrete wastes displayed the minimum and maximum mass losses of about 6 and 15 wt%, respectively, upon heating at 800°C. The structural integrity of the all the geopolymers was significantly affected by freeze-thaw cycles and more significantly by water immersion. Specimens based on brick and tile wastes exhibited compressive strength losses by about 52 and 84% after 2 months of water immersion as shown in Fig. 4.

Rakhimova *et al.* (2015) investigated the effect of partial replacement of ground granulated blast furnace slag (GGBFS) in alkali activated slag cement by red clay brick waste (RCBW) powder of different source compositions on properties alkali-activated slag cement paste and mortar. They applied two grinding methods (separate- and inter-grinding), different fineness (from 300 to 900 m^2/kg), two alkali activators (sodium carbonate and SS) and two different curing conditions including normal curing

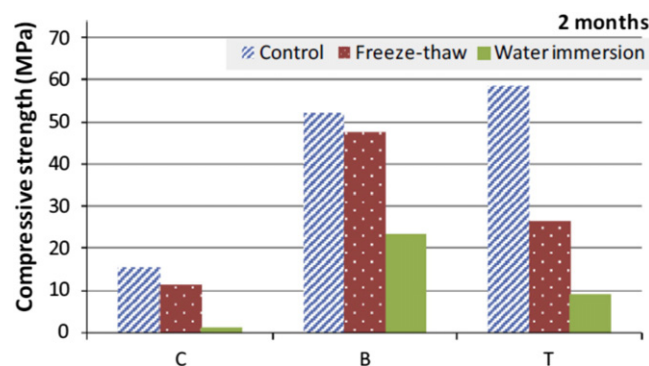


Fig. 4 Compressive strength changes of geopolymers based on concrete (C), brick (B) and tile (T) wastes subjected to freeze-thaw cycles and water immersed for two months. Reproduced from Komnitsas, K., *et al.*, 2015. Effect of synthesis parameters on the quality of construction and demolition wastes (CDW) geopolymers. *Advanced Powder Technology* 26, 368–376.

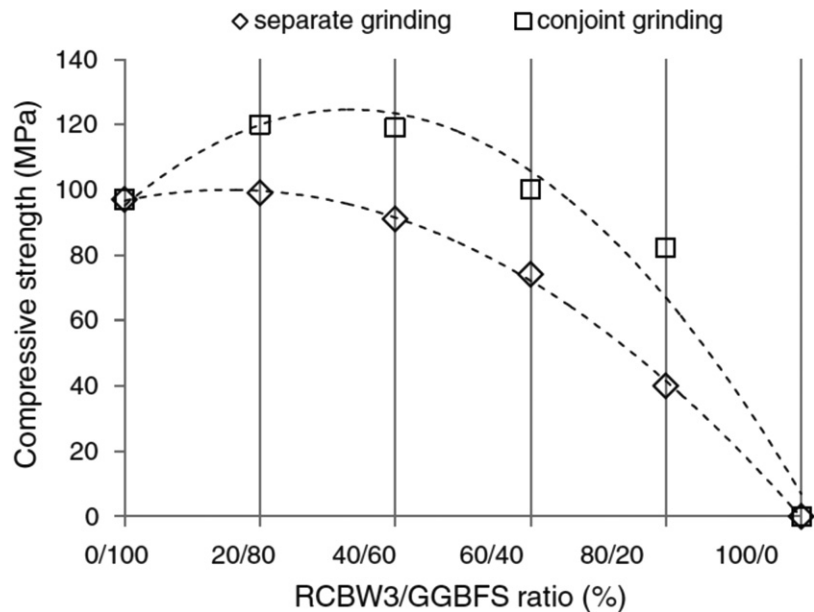


Fig. 5 The effect of RCBW/GGBFS ratio and grinding method on 28-day compressive strength of hardened AAC pastes. Reproduced from Rakhimova, N.R., *et al.*, 2015. Alkali-activated cements and mortars based on blast furnace slag and red clay brick waste. *Materials and Design* 85, 324–331.

(room temperature at RH of about 95%) and steam curing (4 h of preset, 3 h of heating, 6 h at constant temperature of 90–95°C, and finally 3 h of cooling). The results showed that 40% replacement of GGBFS with RCBW in alkali activated mortar can increase the 28-day compressive strength by about 22.6%. The replacement level can be increased up to 60% without any compressive strength loss. The effect of SS, inter-grinding, and steam curing on enhancing compressive strength was more pronounced than sodium carbonate, separate-grinding, and normal curing, respectively. Fig. 5 depicts the effect of RCBW/GGBFS ratio and grinding method on 28-day compressive strength of hardened AAC pastes.

Vásquez *et al.* (2016) activated concrete demolition waste (CDW) with SH and its combination with SS using PC and MK as corrective materials. They prepared paste specimens cured either normally at room temperature ($25 \pm 3^\circ\text{C}$) in humidity close to 90% or thermally at 70°C for 24 h at first and then continued curing in normal conditions for their experiments. Combination of SH with SS as alkali activator was more effective than using SH alone. Geopolymer based on plain CDW exhibited relatively low compressive strength up to 25 MPa and incorporation of corrective materials showed significant impacts on enhancing compressive strength. The maximum 28-day compressive strength of about 46.4 MPa was achieved from the binary precursor incorporating 10% MK activated with an activator of optimum $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 8. Microstructural studies using XRD, SEM and FTIR spectroscopy confirmed the positive effect of corrective materials in promoting the reactivity of CDW by enhancing the dissolution of its crystalline phases in alkaline activator.

Zaharaki *et al.* (2016) investigated the feasibility of using construction and demolition (C&D) wastes including tile (T), brick (B) and concrete (C) and also red mud (R), as an industrial waste, alone or in combination with ferronickel slag (S) as precursors for alkali activation. The prepared paste specimen by activating precursors of different mix proportions with a SH and SS solution of different NaOH molarity (8, 10 and 12 M) and curing them at room temperature for 4 h, then at 80°C for 24 h, followed by normal curing at room temperature up to the age of 7 days. In addition to the effect of chemical and mineralogical phase composition on compressive strength, they also investigated the structural integrity of the paste specimens after being exposed to high temperature heating ($400\text{--}800^\circ\text{C}$). As seen in Fig. 6, alkali activated tile and brick pastes exhibited significant compressive strengths compared to alkali activated slag paste. All mixed precursors exhibited compressive strengths higher than 55 MPa with maximum values up to about 76 MPa at the optimum NaOH molarity of 10.

Alkali activated pastes based on red mud alone exhibited very low compressive strengths and incorporation of red mud into alkali activated slag resulted in significant compressive strength loss. As Fig. 7 depicts, all alkali activated pastes exposed to high temperature heating exhibited relatively high compressive strength losses (about 60% at 800°C), but pastes prepared from plain slag and combination of slag with C&D wastes (25S-30T-30B-15C) possessed residual compressive strengths close to 30 MPa that is still significant.

Zawrah *et al.* (2016) investigated geopolymer production from recycled waste fired clay bricks (G) and granulated blast-furnace slag (S). In this study, plain G and binary mixtures of G and S were activated with an alkaline solution of SH and SS and paste specimens were cured normally at room temperature up to the testing age of 90 days. Geopolymer based on plain G exhibited relatively low bulk density, high porosity, high water absorption, and low compressive strength and incorporation of S up to 60% led to significant increases in bulk density and compressive strength and considerable decreases in both porosity and water

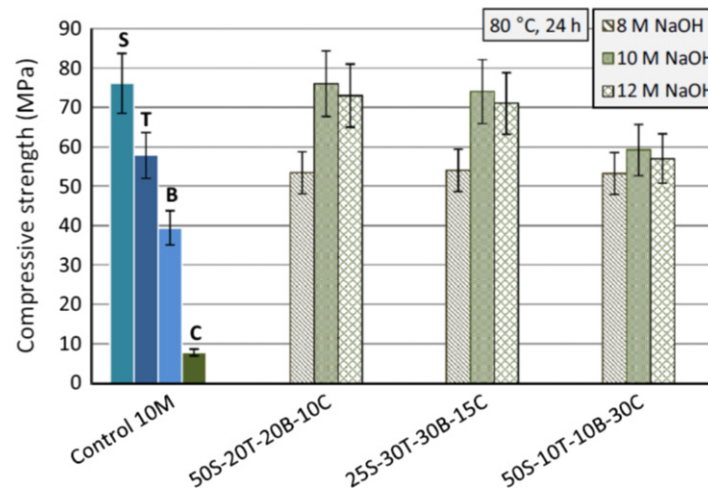


Fig. 6 Compressive strength of alkali activated pastes produced from C&D wastes alone or in combination with ferronickel slag. Reproduced from Zaharaki, D., *et al.*, 2016. Valorization of construction and demolition (C&D) and industrial wastes through alkali activation. *Construction and Building Materials* 121, 686–693.

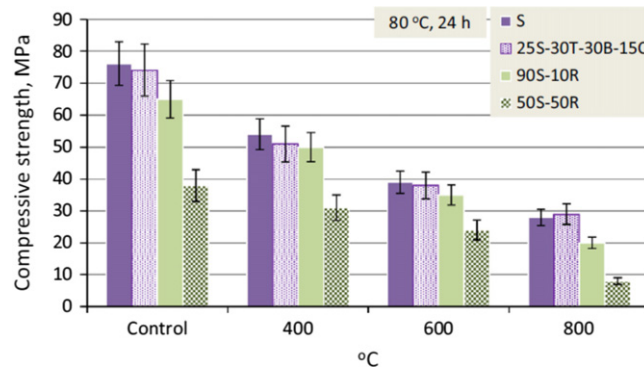


Fig. 7 Loss of compressive strength of selected alkali activated pastes exposed to high temperature heating for 1 h. Reproduced from Zaharaki, D., *et al.*, 2016. Valorization of construction and demolition (C&D) and industrial wastes through alkali activation. *Construction and Building Materials* 121, 686–693.

absorption. Higher addition of S (80%) resulted in crack formation and demonstrated negative effects on bulk density, porosity, water absorption, and compressive strength. The maximum 90-day compressive strength of 83 MPa was achieved for the geopolymer paste prepared from the binary mix of 40% G and 60% S.

Usha *et al.* (2016) studied the effect of synthesis parameters including SH concentration, SS-to-SH ratio, alkali activator-to-binder ratio and curing temperature on compressive strength of geopolymer mortar prepared from terracotta roof tile waste. They reported 7- and 28-day compressive strengths up to about 25 and 27 MPa, respectively, under optimum synthesis conditions including; SH molarity of 11, SS-to-SH ratio of 2.5, alkali activator-to-binder ratio of 0.8, and curing conditions of 24 h at 65°C.

Robayo-Salazar (2017) studied the possibility of utilizing recycled red clay brick waste (RCBW), concrete waste (CW) and glass waste (GW) into alkali activated building materials. The prepared precursors were activated with industrial grade SS and its combination with SS solution and OPC, as a CaO source, was used for partial replacement (less than 30% by weight) of RCBW and CW. The prepared paste specimens were cured either at 25°C or 70°C for 24 h and then at room temperature in a humid chamber with RH at about 90% to the testing age of 28 days. The selected optimum binders were then used in the form of mortar using river sand for RCBW- and CW-based binders and GW as fine aggregate for GW-based binder to prepare prototypes of precast building elements that were then evaluated for properties in accordance with Colombian technical standards. The results confirmed the positive effect of the presence of optimum amount of SS in alkali activator leading to significantly higher compressive strengths. Plain RCBW-based binder activated with SH and SS of optimum composition exhibited a maximum compressive strength of 66.56 MPa when cured at 70°C. Incorporation of 20% OPC into this binder enhanced the maximum compressive strength up to 102.59 MPa for normal curing at 25°C. Plain CW-based binder activated with optimum composition of SH+SS showed a maximum compressive strength of about 27 MPa with the application of thermal curing at 70°C. A 30% incorporation of OPC into this binder resulted in significantly higher compressive strength up to 33.69 MPa for normal curing conditions at 25°C. For the case of plain GW-based binder, the maximum compressive strength of about 57 MPa was obtained when activated

with optimum concentration of SH and cured thermally at 70°C. The type 2 I-shaped pavers fabricated from RCBW-based binder met the standard flexural strength, but the RCBW-based tile did not satisfy the requirement. Both manually prepared items, however, exhibited low permeability and high impact resistance. Non-structural blocks and tiles fabricated from CW- and GW-based binders, respectively, satisfied the minimum standard requirements.

Amin *et al.* (2017) prepared geopolymer bricks from fine ceramic dust waste collected in spray dryer cyclones in tile manufacturing process. After a calcination operation at 800°C for 2 h, the ceramic dust waste was activated with alkaline solutions proportioned with slaked lime (6, 8, and 10%), SH (0, 0.5, and 1%) and water (38, 40, and 42%). The prepared paste specimens were cured normally at room temperature for 28 days. In the next step, the formulation exhibiting the highest 28-day compressive strength (about 9 MPa) was identified (10% slaked lime, 1% SH, and 38% water) and used for preparation of brick sample for further investigations. Upon increasing curing temperature from 25 to 100°C, unusual results including significant decreases in bulk density and compressive strength along with considerable increases in cold and boiling water absorption and apparent porosity were observed. They attributed these unusual observations to probable reasons including the presence of feldspar and quartz in fine ceramic dust or using slaked lime together with SH or drying of brick sample upon curing at higher temperatures that could result in crack formation.

Guo *et al.* (2017) investigated the effect of adding waste brick powder (WBP), nano-silica, and nano-alumina on bulk density and pore structure (apparent, true, and closed porosities) of class C-FA (CFA) based geopolymer. Incorporation of 30% by weight WBP into CFA-based geopolymer, resulted in an increase of about 6.1% in bulk density, and decreases of 7.7%, 9.1%, and 10.4% in apparent, true, and closed porosities, respectively, after 28 days of curing depicting significant microstructural densification. A total incorporation of 3% by weight nano-silica and nano-alumina either individually or in combination, in addition to 30% WBP, enhanced the densification and pore refinements effects. Nano-silica, however, indicated a stronger effect than nano-alumina. Compared to control sample, the CFA-based geopolymer incorporating 30% WBP, 2% nano-silica, and 1% nano-alumina exhibited decreases by about 37.8%, 41.1%, and 44.3% in apparent, true, and closed porosities accompanied with an increase of 14.5% in bulk density after 28 days of curing.

In a recent study, Tuyan *et al.* (2018) characterized the morphology and the structure of waste clay brick Powder (WCBP)-based geopolymer of optimum composition. They firstly optimized the alkali activator composition based on combination of SH and SS from the compressive strength and cost viewpoints. The optimum formulation prepared with an activator having $\text{SiO}_2/\text{Na}_2\text{O}$ mass ratio of 1.6, containing 10% Na_2O by weight of binder, and exhibiting a maximum compressive strength of 36.2 MPa after curing at 90°C for 5 days was then studied using different characterization techniques. They concluded that the porosity of the geopolymer decreases when Na_2O content and $\text{SiO}_2/\text{Na}_2\text{O}$ ratio are increased to optimum levels. The alkali activation process weakened the intensity of the crystalline peaks present in WCBP and resulted in the formation of a thermally stable geopolymer structure upon heat treatment.

Waste Glass (WG)

It is a serious challenge to dispose million tons of waste glass generated all over the world annually. In 2005, USA, China and European Union produced 20 Mt, 32 Mt, and 33 Mt waste glass, respectively (IEA, 2007; Rashed, 2014). Waste glass disposal in landfills is not only expensive, but also because of being non-degradable is not a sustainable practice. In addition, mixed waste glasses of different colors and compositions cannot be recycled into new glass. This means that sustainable efforts are very necessary for an environmentally sound management of this waste.

Puertas *et al.* (2014) investigated the possibility of using glass waste in preparation of an alkali activator for activating blast furnace slag (BFS). They have prepared a number of alkali activators by dissolving different amounts of glass waste in a solution of $\text{NaOH}/\text{Na}_2\text{CO}_3$. These activators were then compared with water-glass and plain $\text{NaOH}/\text{Na}_2\text{CO}_3$ solution in activating BFS and preparing paste specimens cured in humid bath (99% RH) at $20 \pm 2^\circ\text{C}$ for 1, 2, 7 and 28 days. Based on mechanical, mineralogical (XRD, FTIR) and microstructural (porosimetry, NMR and SEM/EDX) measurements, they confirmed that dissolution of glass waste in $\text{NaOH}/\text{Na}_2\text{CO}_3$ solution at $\text{pH} = 13.6$ provides an alkali activator that activates BFS more effective than plain $\text{NaOH}/\text{Na}_2\text{CO}_3$ solution and forms C–A–S–H gels of similar composition and structure compared to those observed in conventional water-glass activated BFS.

Redden *et al.* (2014) investigated the feasibility of activating glass powder with NaOH solutions of different molarities (4, 6, or 8 M). The obtained results showed that NaOH -activated glass powder exhibits higher compressive strength compared to NaOH -activated class F-FA if cured at lower temperatures. The plain glass powder-based binder and the binder based on 50%–50% binary blend of glass powder and FA, however, suffered from very high compressive strength losses when exposed to moisture. This strength loss was attributed to the formation of sodium silicate as the main alkali activation product, which is soluble in water. They significantly improved the moisture stability of the glass powder/FA binary binder by partially replacing the FA content of which with MK and GGBFS as Al and Ca containing source materials, respectively.

Torres-Carrasco *et al.* (2015) proved that commercial water-glass can be substituted by WG for activating aluminosilicate precursors such as FA. They activated class F-FA with three different alkali activators including; 8 M NaOH solution, 10 M NaOH solution containing 15 wt% water-glass, and activators prepared by adding different amounts of finely ground WG to 10 M NaOH solution and stirring at $80 \pm 2^\circ\text{C}$ for 6 h. Based on mechanical properties and microstructural characteristics of paste specimens cured hydrothermally at 85°C for 20 h and then in a humid chamber (99% RH) until the testing date, they concluded that WG can

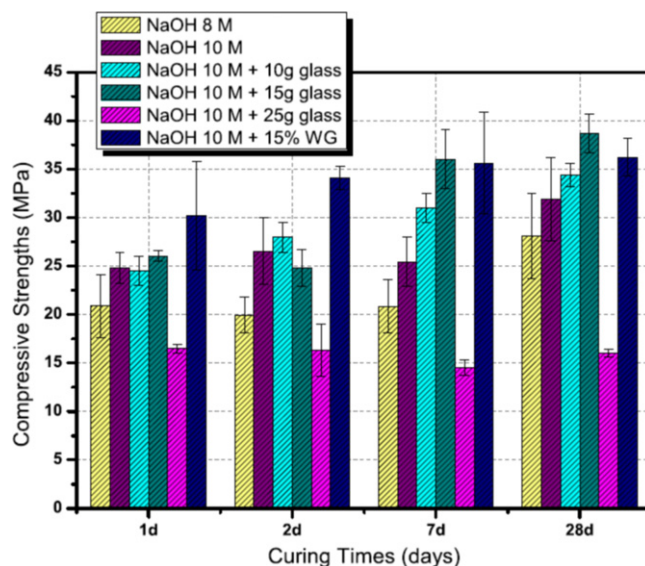


Fig. 8 Compressive strength versus curing age of FA paste specimens activated with different alkali activators. Reproduced from Torres-Carrasco, M., *et al.*, 2015. Waste glass in the geopolymer preparation. Mechanical and microstructural characterization. *Journal of Cleaner Production* 90, 397–408.

be used as an effective substitute for water-glass in preparation of geopolymer. The paste specimens activated with 10 M NaOH containing 15 wt% water-glass exhibited a 28-day compressive strength of about 37 MPa and those activated with 10 M NaOH containing WG (15 g in 100 ml) exhibited a little bit higher 28-day compressive strength with similar degree of reaction, compositional (Si/Al and Na/Al ratios) and microstructural characteristics. [Fig. 8](#) compares the effectiveness of the studied alkali activators in activating FA.

[Bobiričă *et al.* \(2015\)](#) investigated the feasibility of partially replacing FA or FA/BFS-based inorganic polymers with WG prepared from spent fluorescent lamps. Using a 30 wt% SH solution and its combination with a liquid SS ($\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio of 1.25) as alkali activators and curing paste specimens hydrothermally at 60°C for 24 h, then cooling for 24 h and continuing curing at 20°C for 26 days in sealed plastic bags, they concluded that incorporation of WG into FA or FA/BFS-based inorganic polymers decreases the polymerization degree and results in significant decreases in compressive strength. They attributed this depolymerization effect and strength loss to compositional changes, specifically increase in $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio, caused by incorporation of WG. The negative effect of WG, however, was reduced when alkali activator contained sodium silicate. This is because sodium silicate contains significant amounts of soluble silica (oligo-siloxonates) that increase the overall polymerization degree.

[Martinez-Lopez *et al.* \(2016\)](#) activated blends of urban WG (soda lime glass)/BFS using NaOH and NaOH/ Na_2CO_3 solutions as alkali activators and studied the influence of synthesis parameters including % WG, hydrothermal curing temperature, alkaline compound ratio and wt% Na_2O on 28-day compressive strength using Taguchi statistical method. Optimum compositions at the two curing ages of 28 and 180 days were 0% WG/100% BFS and 100% WG/0% BFS, respectively. Composite formulations containing 25 and 75 wt% WG, however, exhibited interesting compressive strengths. Based on statistical analysis, the compressive strength was most affected by WG, followed by curing temperature, wt% Na_2O and alkaline compound ratio. The positive effect of WG on late age compressive strengths (later than 28 days) confirmed a different hydration kinetics for WG compared to BFS. EDS analyses confirmed hydration products of different microstructure and composition depending on the WG content.

[Wang *et al.* \(2016\)](#) used waste LCD glass as fine sand in alkali activated GGBFS. Using different combinations of SS and SH as activator, they investigated the influence of different liquid–solid ratios (0.50, 0.55, 0.60), different alkaline solutions (0.5%, 0.75%, 1%) and different replacement levels (0%, 10%, 20%) of slag by waste LCD glass on workability and 3-, 7-, and 28-day compressive strengths. The workability and compressive strength of the alkali activated GGBFS increased by increasing the alkaline solution and the replacement level.

[Novais *et al.* \(2016\)](#) incorporated WG recycled from spent fluorescent lamps into MK-based geopolymer at different levels of 12.5, 25, 37.5 and 50% by weight. They used combinations of SS solution and SH solutions of 10 and 12 M and cured the specimens in different conditions including sealed in bag/open atmosphere after one-day curing at 40°C and 65% RH. They concluded that the geopolymer properties are more influenced by replacement level and curing conditions than by NaOH molarity. The lower replacement level of 12.5 wt% increased the 28-day compressive strength of the geopolymer by about 46%, while higher replacement levels resulted in lower strengths. Open atmosphere curing showed a strong effect in preventing compressive strength losses in geopolymers containing high levels of WG. The effects of WG incorporation on compressive strength and apparent density of MK-based geopolymer is displayed in [Fig. 9](#).

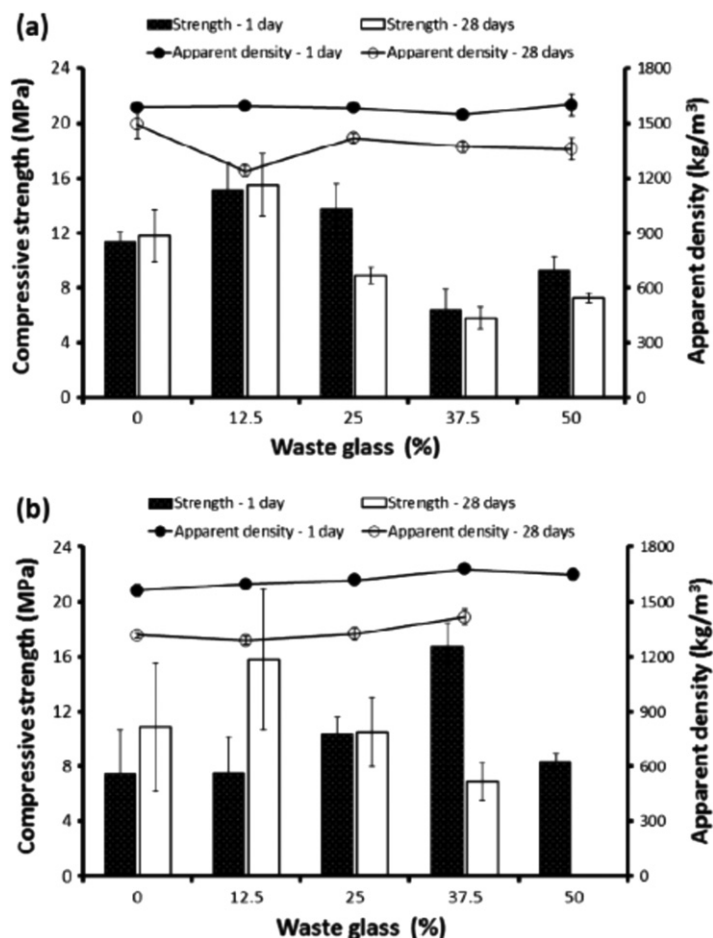


Fig. 9 The effects of WG incorporation on compressive strength and apparent density of metakaolin-based geopolymer; (a) 10 M NaOH, (b) 12 M NaOH. Reproduced from Novais, R.M., *et al.*, 2016. Waste glass from end-of-life fluorescent lamps as raw material in geopolymers. *Waste Management* 52, 245–255.

Vafaei *et al.* (2017) prepared high strength geopolymer binder using WG powder as the main source material. Since WG is poor in alumina, they used three different types of calcium aluminate cements (Fondu, Secar 71, and Secar 80) for partial replacements up to 24 wt% to improve the chemical composition of the main precursor. They activated binary blends of WG/calcium aluminate cement with solutions of SS and SH of constant $\text{Na}_2\text{O}/\text{SiO}_2$ ratio of 1.5 and different Na_2O contents (8, 10, 12% by weight of dry binder). Based on mortar specimens cured hydrothermally at 95°C for 20 h in a humid chamber (more than 95% RH) after 24 h of precuring in humid chamber at $23.0 \pm 2.0^\circ\text{C}$, they achieved compressive strengths up to 87 MPa. The results confirmed that inclusion of reactive alumina from calcium aluminate cements into silica-rich waste-glass causes more cross-linking in the molecular structure of the geopolymer and therefore greatly enhances the mechanical properties (up to 6 times) and reduces the tendency for formation of efflorescence. Among the three calcium aluminate cements used, Secar 71 was more effective in strength enhancement and efflorescence reduction due to its relatively higher reactive alumina content.

Fig. 10 depicts the influence of calcium aluminate cement incorporation on compressive strength of WG-based geopolymer mortar prepared at different Na_2O contents of activator.

Al Saadi *et al.* (2017) prepared inorganic binder exhibiting intumescent behavior (i.e., expansion upon exposure to high temperature) by activating WG powder derived from cullet of different colors with borax ($\text{Na}_2\text{B}_4\text{O}_7$) containing SH solution. They cured paste specimens in an oven at 60°C for 24 h and then in open air at 20°C for 7 days before high temperature treatment (1 h at different temperatures of 500, 600, 650, 700, 850°C). The results showed that incorporation of borax into SH solution lowers the intumescent temperature from 850°C to about 600°C . A 10% by weight replacement of WG with FA did not substantially affected the intumescent behavior of the material, but improved its moisture stability.

Torres-Carrasco *et al.* (2017) investigated the possibility of activating WG powder with different alkali activators. They activated glass powder prepared from waste soda-lime-silica glass of different colors with NaOH, KOH, water-glass, $\text{NaOH}/\text{Na}_2\text{CO}_3$ solutions and also NaOH and $\text{NaOH}/\text{Na}_2\text{CO}_3$ solutions in which a given amount of glass powder was dissolved at 85°C for 6 h. The paste specimens were then cured at 85°C for 20 h either at 99% or 6.5% controlled RH. The results showed that activators of higher concentrations resulted in the formation of less porous microstructures of higher compressive strengths. Curing at lower RH

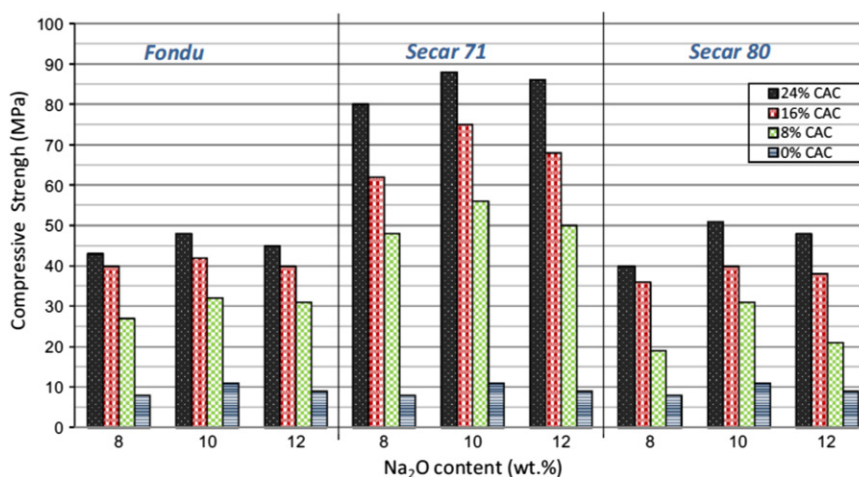


Fig. 10 Influence of calcium aluminate cement (CAC) incorporation on compressive strength of WG-based geopolymer mortar prepared at different Na₂O contents of activator. Reproduced from Vafaei, M., *et al.*, 2017. High strength geopolymer binder based on waste glass powder. *Advanced Powder Technology* 28, 215–222.

of 6.5% was also more effective in compressive strength development and 50%–75% higher compressive strengths were achieved. The activation product was a silica-rich gel irrespective of the activator type or curing condition.

Wang *et al.* (2017) incorporated waste LCD glass as sand into alkali activated GGBFS at different replacement levels (0%, 20%, and 40%) and evaluated engineering properties of the mortar at different liquid-solid ratios (0.45, 0.50, 0.55, and 0.60) considering the ratio of Na₂O equivalent to the weight of GGBFS in SH solution constant at 1%. A combination of 5 N NaOH and SS was used as alkali activator and specimens were cured for one day in the molds and then at room temperature. A 20% replacement of GGBFS with LCD glass sand resulted in higher compressive strengths, but higher replacement levels had a negative effect on compressive strength. The sulfate resistance of mortar was maximized at L/S=0.6 and replacement level of 20%. The results confirmed that engineering properties of alkali activated GGBFS can be enhanced if an optimum amount of LCD glass sand is incorporated.

El-Naggar *et al.* (2017) utilized WG in preparation of MK-based geopolymer. The WG fused with NaOH pellets at 550°C was dissolved in water to prepare an alkaline solution for activating MK. Fumed silica was also added to the alkaline solution to control SiO₂/Na₂O ratio at four different levels (1.25, 1.35, 1.45 and 1.55). An alkaline solution was also prepared from reagent grade SS and SH for comparison purposes. The undissolved portion of fused WG was also incorporated into MK to see its effect on compressive strength. The effects of MK particle size, solid/liquid ratios, undissolved WG content and particle size, alkaline silicate solutions prepared from dissolution of fused WG and fumed silica, curing temperature (25, 40, 60, and 80°C) in a 2-h precuring stage and curing time on compressive strength of geopolymer were studied. MK and undissolved WG particle size and precuring stage temperature were found to be the most influential factors on compressive strength. Enhanced 28-day compressive strength of 80.75, 82.36, 93.08 and 97.41 MPa were achieved by reducing MK particle size from less than 125 µm to less than 38 µm, incorporation of 3% undissolved WG into MK, using an alkaline silicate solution containing 7% dissolved WG at SiO₂/Na₂O of 1.55, and precuring at curing at 40°C, respectively.

Zhang *et al.* (2017) investigated the possibility of using WG powder as partial replacement (10%, 20%, and 30%) of coal FA in alkali activated FA (50%)/GGBFS (50%). A 4 M NaOH solution was used as alkali activator and paste specimens sealed with plastic foil were cured at 20°C in a humid room (≥98% RH). Based on calorimetry and TG analyses, WG is more reactive than FA and incorporation of 30% WG increased 28-day compressive strength by about 35%. This effect is attributed to the high reactive contents of SiO₂ and CaO in WG and also its finer particle size compared to FA. The main alkali activation product was found to be a C-(N)-A-S-H type gel and no N-A-S-H type gel was found.

Tho-In *et al.* (2018) recycled WG powder from fluorescent lamp and ground container into high calcium FA-based geopolymer at different replacement levels of 10%, 20%, 30%, and 40% by weight. A mixture of SS and SH (1:1) was used as alkali activator and after a 1-h precuring at 23–25°C, the plastic wrapped paste specimens were cured at 60 ± 2°C for 48 h and then held at 23 ± 2°C until the testing age of 7 days. Incorporation of WG powder from fluorescent lamp was found to have a negative effect on compressive strength, while 20% replacement of FA with WG powder from container glass resulted in a 7-day compressive strength (47.6 MPa) that was slightly higher than that of reference paste (45.7 MPa).

Zhang and Yue (2018) investigated the influence of WG powder prepared from cullet of various colors from a recycling facility on flexural and compressive strengths, drying shrinkage and sulfate resistance of alkali activated slag mortar. Using a mixture of SS and SH (SiO₂/Na₂O=1) as alkali activator and applying central composite design and response surface methodology, they optimized the alkali content (Na₂O equivalent) and the replacement level based on maximum flexural and compressive strengths. Ordinary Portland cement (OPC, CEM I 42.5R) mortar specimens were also prepared and used as reference. The effect of alkali content was found to be more significant than replacement level. The optimum alkali content and replacement level of 8.31% and

14.57%, respectively, resulted in maximum 28-day flexural and compressive strengths of 8.4 and 66.4 MPa, respectively. These optimum values reduced the amount of dry shrinkage by 15.8% and 20.3% at 1 and 120 days, respectively and the sulfate resistance of the mortar. Alkali activated slag mortar exhibited higher mechanical properties, excellent sulfate resistance, and higher drying shrinkage compared to OPC mortar.

Lu and Poon (2018) studied the effects of simultaneous incorporation of WG bottle (soda lime glass) powder and fine aggregate on workability, flexural and compressive strengths, and fire resistance of alkali activated FA-GGBFS mortar. A binary blend of FA (30%)/GGBFS (70%) was used as control and natural fine aggregate was replaced with fine WG cullet at different levels of 0, 25%, 50%, 75%, 100%. In the mortar containing 100% WG cullet as aggregate, once FA was fully replaced with WG powder (30%) and once 30% of GGBFS was replaced by WG powder. A 10 M NaOH solution was used as alkali activator and mortar specimens were cured in normal condition of $25 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ RH after 24 h in molds. Replacement of natural fine aggregate with fine WG cullet improved the mortar workability. The mortar workability, however, reduced by replacing FA with WG powder, and slightly changed when GGBFS was replaced with WG powder. WG cullet had a negative effect on compressive strength, but flexural strength was increased up to 50% replacement and then decreased at higher replacement levels. Incorporation of WG powder to replace FA and GGBFS reduced the compressive strength of mortar significantly. This negative effect of WG powder was attributed to its low reactivity compared to FA and GGBFS. Fire resistance of alkali activated cement mortars is usually reported to be better than that of OPC mortar. This property, however, was further improved by incorporation of both WG powder and WG cullet into the studied alkali activated cement mortar in this study.

Red Mud (RM)

RM is an aluminosilicate industrial waste produced in the production process of alumina from bauxite ore, the Bayer process. Disposal of RM in huge holding ponds without any treatment has led to a global environmental crisis due to its large production volume, high alkalinity and small particle size. It is estimated that each year approximately 120 Mt of RM is added to the existing stockpiles worldwide with an estimated total amount of 4 billion tons in 2015 (Zhu *et al.*, 2015). To alleviate the pressure from this worldwide crisis, many research efforts have been devoted to the development of sustainable RM recycling technologies.

Badanoiu *et al.* (2015a) prepared alkali activated binders by activating WG powder from green glass cullet and binary mixtures of WG (90%, 75%) and RM (10% and 25%) using 5 M NaOH solution as activator. Covered mortar specimens were cured at 60°C for the 1st day, then after de-molding at 60°C in 85% R.H. and then stored at $20 \pm 2^\circ\text{C}$ in the same R.H. until the testing time. The increase in pre-curing time at 60°C (from 1 to 3 days) resulted in higher compressive strengths, especially for binary mixtures containing RM of less reactivity. The plain WG binder exhibited compressive strengths between 15 and 17 MPa after 1–3 days of pre-curing and about 25 MPa if cured to the age of 7 days at 20°C in air. The increase in pre-curing time, however, decreased the stability of the material in water. Fig. 11 displays the influence of initial curing time at 60°C on compressive strength of alkali activated binders.

In a different work, the same authors (Badanoiu *et al.*, 2015b) used brown glass cullet and RM in preparation of geopolymer foam. Glass powder and a mixture of glass powder (75 wt%) and RM (25 wt%) were used as geopolymer precursor. A 5 M NaOH solution and filtrate from RM slurry processing with a pH of 12.96 were used as two different alkali activators. Geopolymer paste specimens prepared with liquid-to-solid ratio of 0.30 were cured at 60°C for the 1 day and then at 20°C in 85% R.H. for 6 days. The cured specimens were then subjected to different high temperatures (400, 600, 700, and 800°C) for 1 h at the heating rate of $10^\circ\text{C}/\text{min}$. Apparent densities lower than $0.866 \text{ g}/\text{cm}^3$ with a minimum compressive strength of 2 MPa were achieved by thermally treating waste-glass geopolymer at temperatures in the range $600\text{--}800^\circ\text{C}$. SEM studies confirmed the formation of open pores of

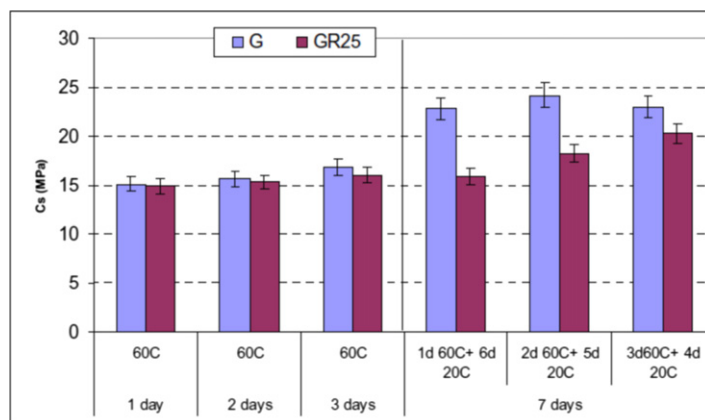


Fig. 11 Compressive strength versus initial curing time at 60°C (G: alkali activated binder from WG, GR25: alkali activated binder from 75% WG and 25% RM). Reproduced from Badanoiu, A.I., Al Saadi, T.H.A., Voicu, G., 2015a. Synthesis and properties of new materials produced by alkaline activation of glass cullet and red mud International. Journal of Mineral Processing 135, 1–10.

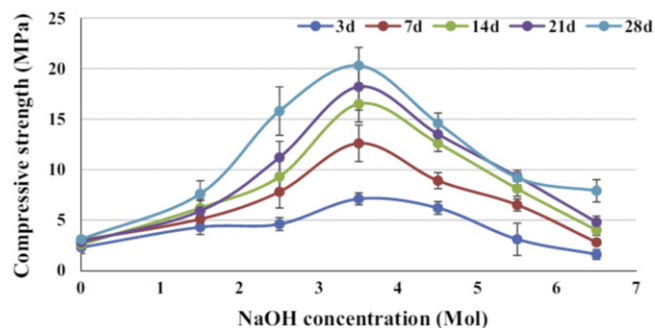


Fig. 12 Compressive strength of RM/FA geopolymer prepared from class C-FA and RM from desulfurization process. Reproduced from Nie, Q., *et al.*, 2016. Strength properties of geopolymers derived from original and desulfurized red mud cured at ambient temperature. *Construction and Building Materials* 125, 905–911.

the sizes between 1 and 100 μm due to foaming of sodium silicate (aluminate) hydrates. The presence of refractory crystalline phases in RM resulted in a higher foaming temperature (700–800°C) for the binary mixture of WG and RM. Geopolymer from binary mixture activated with filtrate from RM slurry exhibited a contraction due to partial melting when thermally treated at 700°C.

Kaya *et al.* (2016) studied the influence of RM on compressive strength and structural characteristic of MK-based geopolymer. Incorporation of RM into MK-based geopolymer at different replacement levels (10–40 wt%) resulted in dramatic loss of compressive strength and microstructural integrity. Based on XRD and FTIR spectroscopy data, this behavior from RM was attributed to iron oxide content of RM, which tends to reprecipitate as hydroxide consuming the hydroxide anions of the alkali activator in the reacting medium.

Nie *et al.* (2016) studied the possibility of using RM in binary blend of RM (50%)/FA (50%) as geopolymer precursor. Two types of FA (class C and class F) and two types of RM (original RM from Bayer process and RM used for flue-gas desulfurization in a power plant) were used and the binary blends were activated with NaOH solutions of varying concentrations. The prepared cylindrical paste specimens were cured at 20°C. The geopolymer containing RM from desulfurization process exhibited higher 28-day compressive strength (20.3 MPa) than the geopolymer derived from original RM (15.2 MPa) at optimum NaOH concentrations of 3.5 M and 2.5 M, respectively. Class C-FA with a higher CaO content (about 20%) was found to be more suitable than class F-FA for geopolymer preparation at ambient temperature. The higher 28-day compressive strength of geopolymer containing RM from desulfurization process was attributed to its Na_2SO_4 content resulted from desulfurization, which can take part in the activation process. Fig. 12 depicts the effect of SH concentration on different age compressive strength of RM/FA geopolymer prepared from class C-FA and RM from desulfurization process.

Choo *et al.* (2016) investigated the feasibility of preparing one-part FA geopolymer using RM as a solid alkali activator. They used five different FAs of relatively high unburned carbon contents ($\text{LOI} > 7.5$). RM of about 12 wt% Na_2O content was used as activator and incorporated into FA at different replacement levels ranging from 0% to 60%. For comparison purposes, a number of one-part FA geopolymers of varying NaOH pellet contents were also prepared. The paste specimens were cured at room temperature for 1 day and then at 60°C for 3 days. The alkalinity of RM at higher replacement levels promoted the geopolymerization reactions resulting in maximum unconfined compressive strengths up to 1.5 MPa. They concluded that one-part FA geopolymer prepared with RM as a solid alkali activator can be considered as a controlled low strength product. The effect of RM content on unconfined compressive strength of one-part FA geopolymers is displayed in Fig. 13.

Ye *et al.* (2016) prepared one-part RM-based geopolymer by activating RM both chemically and thermally. NaOH pellets were firstly incorporated into RM at two different levels corresponding to 10 and 15% Na_2O by the weight of RM and the mixtures were then calcined at 800°C for 1 h. Silica fume was incorporated into the mixture at different levels ranging from 0% to 30% by the weight of total solid to improve the chemical composition ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio) of the mixture and the prepared paste specimens were cured at $20 \pm 1^\circ\text{C}$ in sealed condition. The maximum 28-day compressive strength of 31.5 MPa was achieved from the mixture containing 10 wt% Na_2O and 25 wt% silica fume at the reduced water-to-solid ratio of 0.45 by adding sodium lignosulphonate (0.5 wt%) as dispersant. Based on pH measurements in leaching tests performed on one-part geopolymer binders, it is concluded that incorporation of silica fume increased the stability of geopolymerization products in water. In a later complementary work and using X-ray Photoelectron Spectroscopy (XPS) to determine the binding energies of Al-O and Si-O bonds in both the chemical-thermal activated RM and the geopolymer samples, Ye *et al.* (2017a) observed that binding energies of Al2p and Si2p in raw RM tends to decrease upon chemical-thermal activation and then to increase upon geopolymerization confirming that chemical-thermal activation of RM damages the aluminosilicate structure of raw RM and increases the reactivity of the material by decreasing the binding energies of Al-O and Si-O bonds. Based on Mössbauer spectroscopy results, they also concluded that chemical-thermal activation of RM transforms the octahedral Fe^{3+} present in raw RM mainly into tetrahedral Fe^{3+} and partially into hematite. Geopolymerization, however, transforms most of Fe^{3+} to structural octahedral Fe^{3+} again confirming that coordinated Fe^{3+} in raw RM plays a role similar to Al^{3+} and can replace it in the geopolymer molecular structure.

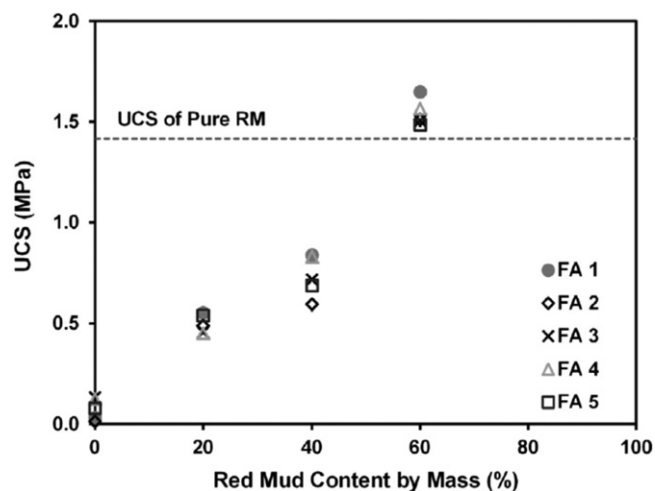


Fig. 13 The effect of RM content as solid alkali activator on unconfined compressive strength (UCS) of one-part FA geopolymers. Reproduced from Choo, H., *et al.*, 2016. Compressive strength of one-part alkali activated fly ash using red mud as alkali supplier. *Construction and Building Materials* 125, 21–28.

Krivenko *et al.* (2017) investigated the feasibility of preparing alkali activated cement and concretes containing high volumes of RM. They activated different combinations of RM (50–80 wt%), GGBFS (15–50 wt%) and OPC (5–10 wt%) using sodium carbonate, sodium metasilicate and liquid SS as different alkali activators. They also incorporated a high volume of RM (up to 38.6% by mass of dry constituents), as fine aggregate, into concrete mixes based on alkali activated GGBFS ($\approx 97\%$)/OPC (3%) activated with liquid SS. The properties of alkali activated cements and concretes were determined in accordance with Ukrainian national standards. Paste specimens of cement formulation comprising of 60% RM, 30% GGBFS, and 10% OPC activated with liquid SS and cured at $20 \pm 2^\circ\text{C}$ and $95 \pm 4\%$ R.H. exhibited compressive strengths up to 60 MPa after 28 days. They reported compressive strengths up to 70 MPa for concrete mixes. Based on XRD analyses results, the main hydration products were identified as CSH, clinoferrrosilite (FeSiO_3) and lawsonite ($\text{CaAl}_2[\text{Si}_2\text{O}_7](\text{OH})_2 \cdot \text{H}_2\text{O}$). Evaluating the radiological properties, they also confirmed the safety of the developed alkali activated concrete for road construction.

Ascensao *et al.* (2017) developed porous geopolymer of alkali diffusion and pH buffering capabilities over relatively long term for applications in biogas generation in anaerobic digestion and wastewater treatment. They activated blends of MK/RM using a combination of 10 M SH solution with a high amount of liquid SS as activator and aluminum powder as pore forming agent. The specimens sealed in plastic film were cured at 40°C and 65% R.H. for 7 days and then at normal conditions. Incorporation of high level of RM (> 35 wt%) in the presence of optimum amount of pore forming agent (< 0.025 wt%) resulted in the development of geopolymer of increased alkali content and enlarged open porosity exhibiting a prolonged high buffer capability.

Geng *et al.* (2017) investigated the feasibility of producing geopolymer from RM and coal gangue (CG) blends with RM contents ranging from 50 wt% to 90 wt%. They prepared two geopolymer series (I and II) by applying two different preparation procedures. Series I samples were prepared by firstly dry ball milling the blends followed by alkali activation and then curing thermally at 80°C for 24 h and normally at room temperature for 27 days. Series II samples were prepared by firstly calcining the blends at 800°C for 2 h followed by dry ball milling, then alkali activation and finally curing normally at room temperature. Mixtures of SH (5 M) and water glass were used as alkali activator. The results showed that the preparation procedure applied to series I samples was more effective and the optimum blend consisting of 80 wt% RM and 20 wt% CG exhibited maximum compressive strength of 30.25 MPa.

Croymans *et al.* (2017) evaluated the radiological properties of alkali activated concretes incorporating different amount of RM as fine aggregate. A composition of 87 wt% GGBFS, 5 wt% OPC, 4 wt% Na_2CO_3 and 4 wt% $\text{Na}_2\text{O} \cdot \text{SiO}_2 \cdot 5\text{H}_2\text{O}$ was used as alkali activated cement. Based on Markkanen activity concentration indexes, they concluded that the studied RM can be incorporated into concrete up to 90 wt% for road construction applications. For building construction applications and considering Radiation Protection (RP) 122 (0.3 mSv/a), they recommended incorporations less than 75 wt%.

Hu *et al.* (2018) investigated the possibility of utilizing RM along with different low-calcium (Class F) and high calcium (class C) FAs in preparation geopolymer. They activated RM/FA (50:50) blends either with SH solutions of varying concentrations or with mixtures of SS and SH. The cylindrical paste specimens were cured either at 20°C or at 60°C for 24 h and then at ambient temperature. Compared to RM/FA (class C) showing 28-day compressive strength up to about 15 MPa, combination of RM/FA (class F) exhibited almost no reactivity when activated with SH and cured under normal curing condition. The reactivity of RM/FA (class C) combination under normal curing condition was attributed to CaO content of class C-FA. Based on the results of this study, the low reactivity of RM/FA (class F), however, can be improved and compressive strengths up to about 30 MPa can be achieved by applying elevated temperature curing condition and using a relatively high concentration SH solution or mixtures of SS and SH as activators.

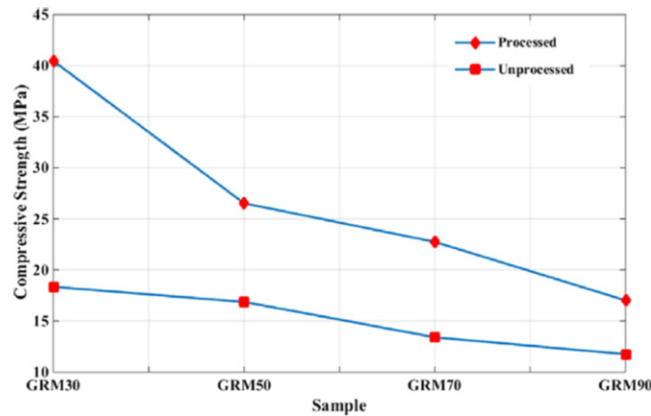


Fig. 14 7-day compressive strength of ambient cured geopolymers of different RM contents prepared from processed and unprocessed RMs. Reproduced from Singh, S., *et al.*, 2018. Effect of mechanical activation of red mud on the strength of geopolymer binder. *Construction and Building Materials* 177, 91–101.

Singh *et al.* (2018) studied the influence of RM fineness on compressive strength of RM/FA geopolymer. Binary blends of RM/FA consisting of 0%–90% by weight RM, prepared from both unprocessed and pulverized RM (GRM), were activated with combinations of SS and SH. After 2 days from casting, the paste specimens were cured either thermally at 60°C for 24 h or at ambient conditions (28–34°C and 50%–60% RH). To improve the chemical composition and the reactivity of the blends, 10 wt% microsilica was incorporated to geopolymers cured thermally and 10 wt% GGBFS to those cured at ambient. Based on results, mechanical activation of RM negatively impacts compressive strength under thermal curing conditions. They attributed this surprising observation to the reduced size and size range of nanopores in pulverized RM that in turn could result in the formation of shrinkage cracks under thermal curing conditions. Pulverization of RM, however, showed significant positive impact on compressive strength under ambient curing conditions and 7-day compressive strengths up to 40 MPa were achieved (see Fig. 14).

Chen *et al.* (2019) utilized RM/GGBFS blends in preparation of pervious concrete for adsorption of heavy metals. In this work, binary blends of RM/GGBFS with RM contents of 0, 30, and 50 wt%, limestone gravel and mixtures of SS and SH of varying concentrations were used to prepare pervious concrete. Washed RM was also used to investigate the influence of RM alkalinity on concrete strength. Concrete cubes were cured in the mold for 1 day and then in a curing chamber at $20 \pm 1^\circ\text{C}$ and 95% RH. Portland cement pervious concrete was also prepared and used for comparison purposes. The 28-day compressive strength of pervious concrete was significantly reduced with RM content. The role of alkali content of RM, however, was significant in activating the binary blend. The maximum 28-day compressive strength was 18.53 MPa from the concrete mix prepared from binary blend containing 30 wt% activated with an optimum alkali concentration of 6 wt%, which is claimed to be sufficient for light road pavement. RM, however, exhibited a strong positive impact of heavy metal adsorption capacity of geopolymer concretes and all geopolymer pervious concretes performed better than OPC pervious concrete. The binary blend containing 50 wt% RM showed maximum adsorption capacities of 84.03%, 64.16%, 63.30%, and 62.6%, for Pb^{2+} , Cd^{2+} , Cu^{2+} , and Cr^{2+} , respectively. The high adsorption capacity of geopolymer pervious concretes was attributed to both hydration products (geopolymer and CSH gels) and raw RM particles showing a high tendency for heavy metal adsorption.

Miscellaneous Aluminosilicate Industrial Wastes

Pacheco-Torgal *et al.* (2008b) studied the potential of a geopolymeric binder based on tungsten mine waste mud as a repair material for OPC-concrete. They used a mixture of thermally treated tungsten mine waste mud, hydrated lime, and coarse aggregate activated with SS and SH and exhibiting a 28-day compressive strength of about 78 MPa as repair material in slant shear test for evaluating its bond strength to OPC-concrete. Compared to reference commercial repair products, geopolymeric binder exhibited a very high bond strength even at low surface treatment roughness. In a series of studies, Pacheco-Torgal (2008a,b, 2009; Pacheco-Torgal *et al.*, 2008a) investigated the properties of similar geopolymeric mortars prepared from different aggregates. They faced difficulties in evaluating the workability of the fresh mortars due to their high stickiness to flow table. The setting time was reported to be dependent on alkali concentration, hydrated lime content and composition of alkali activator (SS/SH mass ratio). All the mortars exhibited relatively low values of unrestrained shrinkage and water absorption. A 10% hydrated lime was reported as optimum value resulting in the maximum compressive strength. All the mixes containing higher amounts of hydrated lime exhibited a strength decrease after 2 weeks of curing. Since compressive strength showed significant dependency on aggregate type and based on SEM observations, they suggested that some aggregate types (e.g., schist and granite) are chemically reactive and their partial surface dissolution in the reacting medium enhances the paste-aggregate bonding resulting in a denser and more uniform interfacial transition zone and higher compressive strengths. SEM and EDS analyses confirmed the formation of N–A–S–(H) and C–S–H gels as the hydration products. They also detected the formation of phlogopite as a new crystalline phase. Silva *et al.* (2012) studied the water-immersion behavior of alkali activated binder

prepared from calcined tungsten mine waste mud activated with a mixture of SS and SH (10 M). They reported that all specimens cured at 20°C (40% RH), especially those cured for less than 28 days, exhibited structural disintegration and loss of strength when immersed in water irrespective of the mix proportion. Specimens cured at elevated temperature 80°C (dry condition) and 130°C (dry condition), however, showed apparently higher structural stability irrespective of curing time period. Using data published on MK- and tungsten mine wastes-based geopolymer mortars (Pacheco-Torgal *et al.*, 2008a, 2011; Nazari *et al.*, 2014) developed a neuro-fuzzy interfacial systems-based model for investigating the influence of synthesis parameters on mechanical strength behavior. The study confirmed the alkali concentration as the main influencing factor, compared to curing time, hydrated lime content, alkali concentration, aluminosilicate source, H_2O/Na_2O molar ratio, and mold type. Based on the predicted results, they also reported a strength decrease after 28 days of curing.

Ahmari and Zhang (2013a) prepared geopolymer bricks from copper mine tailings and investigated the effect of cement kiln dust (CKD, 0%–10%), SH concentration (10 and 15 M) and water content (12%–20%) on brick properties and its mass and compressive strength loss after water immersion. The bricks were cured in an oven at 90°C for 7 days. Significant improvements in brick properties and durability were observed with incorporation of CKD. The improving effect of CKD was attributed to its effective contribution in geopolymerization reactions, formation of calcium carbonate, and filling effect. In a later study, the same authors (Ahmari and Zhang, 2013b) studied the durability performance and leaching behavior of geopolymer bricks in pH 4 and 7 solutions. The oven-cured (90°C) geopolymer bricks prepared by activating the mine tailings with 15 M SH solution at different moisture contents (8% to 18%) and forming pressures (0–35 MPa) exhibited substantial loss of unconfined compression strength (53% to about 78%) after 4 months of immersion. The leaching results, however, confirmed an effective immobilization of heavy metals. This strength loss was attributed to unsuitable chemical composition of mine tailings (relatively high Si/Al ratio) leading to partial geopolymerization.

Ye *et al.* (2017b) prepared geopolymer binder from binary blend of ore-dressing tailing of bauxite (70 wt%) calcined at 800°C for 1 h and slag (30 wt%) using a 20% SS solution (dry basis) as activator. They cured mortar specimens at $20 \pm 1^\circ\text{C}$ in a humid chamber (95 ± 5 R.H.) for 1-year and then in a base room with a temperature in the range 18–22°C and a R.H. between 40% and 80% and investigated their mechanical strength evolution. They reported gradual increases in both flexural and compressive strengths accompanied with gradual decrease in cumulative pore volume confirming continuous geopolymerization. The compressive strength with a 28-day value of 50.0 MPa reached to values as high as 75 after 6 years.

Kiventera *et al.* (2018) investigated the possibility of immobilizing heavy metals of gold mine tailings by alkali activation. They used paste specimens prepared from ternary blends of gold mine tailings (40–50 wt%), GGBFS (20–30 wt%) and MK (30 wt%) activated with mixtures of SH (8 and 9 M) and SS and cured in sealed plastic bags at room temperature for 24 h and then in ambient conditions (50–60 R.H.) for 7 and 28 days. The results showed high immobilization efficiencies for Cr, Cu, Ni, Zn, and Mn, which were improved with curing time. Leaching amount for As, which was high after 7 days of curing, significantly decreased with curing time. The leaching amounts for Sb, B, and V were increased with geopolymerization due to their tendency to form oxyanions with a negative oxidation state in alkaline media.

Dabbabi *et al.* (2018) investigated the possibility of converting calcined washing waste of phosphate industry into geopolymer. Phosphate washing waste (PWW) calcined at different temperatures (600, 700 and 800°C) and activated with SS and 10 M SH was used to prepare mortar specimens. They reported a maximum compressive strength of 11 MPa for geopolymer mortar prepared from PWW calcined at 700°C after 28 days of curing under laboratory ambient conditions. The geopolymer mix prepared from PWW calcined at 800°C exhibited a flash setting behavior upon mixing of ingredients.

Han *et al.* (2018) used an industrial waste called electrolytic manganese dioxide residue (EMDR) as a precursor for geopolymer preparation using phosphoric acid as activator. EMDR is mainly composed of quartz, aluminum sulfate hydrate and magnetite and therefore cannot be considered as an aluminosilicate material. They achieved compressive strength of 96.3 MPa for mortar specimens prepared from river sand and cured 80°C for 2 days. XRD results showed that quartz and aluminum sulfate hydrate remain unchanged during activation and this is the reaction between phosphoric acid and magnetite that results in the formation of an amorphous binding phase. The leaching test results showed a stabilization efficiency of 95.4% for manganese. All other elements showed leaching concentrations within the Chinese standard limits.

Moukannaa *et al.* (2018) investigated the possibility of incorporating a phosphate mine tailing called phosphate sludge (PS) into geopolymers. PS with a mineralogical phase composition of fluorapatite, quartz, calcite, dolomite, and a smectite clay mineral was incorporated into FA- and MK-based geopolymers at equal proportions (50% by weight). Using an experimental design based on response surface methodology, the effect of synthesis parameters (SH concentration, curing time and temperature) on density, water absorption and compressive strength of geopolymer paste specimens was studied. Results showed that incorporation of PS reduces the mechanical properties of the geopolymers. However, under optimum synthesis conditions (SH concentration of 12.5 M and a curing regime consisting of 24 h at 83.33°C and 13.50 days at ambient temperature) compressive strengths as high as 62 and 53 MPa were achieved for binary blends of FA/PS and MK/PS, respectively, confirming the possibility of recycling PS into geopolymers.

Sedira *et al.* (2018) prepared alkali activated binder using binary blends of tungsten mining waste mud (TMWM) with red clay brick waste (RCBW) as precursor and solution of SH and SS as alkali activator. Blends of higher RCBW content showed higher compressive strengths at all the tested ages. Paste specimens from binary blend of TMWM (50%)/RCBW (50%) cured at $60 \pm 2^\circ\text{C}$ for 24 h and then at laboratory conditions (20°C) exhibited the maximum 28-day compressive strength of 59 MPa. Studies by FT-IR spectroscopy and SEM/EDX confirmed formation of higher amounts of (N,C)–A–S–H and/or (N,K)–A–S–H gels in binary blends of higher RCBW contents.

Xia *et al.* (2019) studied the possibility of recycling hazardous lead-zinc smelting slag (LZSS) into a FA/GGBFS-based composite geopolymer for solidification and stabilization of its heavy metals (Pb, Zn, Cr and Cu). They firstly optimized the synthesis parameters of FA/GGBFS-based composite geopolymer for the highest possible compressive strength through single factor and orthogonal experiments. The optimum composition exhibiting the highest compressive strength of 47.39 MPa was used for solidification and stabilization of LZSS. Although incorporation of LZSS into composite geopolymer resulted in significant compressive strength loss, the reduced compressive strength (for example, 15 MPa for the blend incorporating 80% by weight LZSS), however, was still notable. In addition, the leaching test results were satisfactory and concentrations of leached heavy metals were far beyond the limits.

Conclusions

Recycling of aluminosilicate industrial wastes as precursor materials for geopolymer production is an important step towards sustainable waste management due to its significant environmental benefits including (1) alleviating the pressure due to land-filling expenses and environmental impacts, (2) the potential in reducing energy consumption and CO₂ emission (compared to the traditional Portland cement technology), (3) conservation of natural resources for binder production, and (4) effective immobilization of heavy metals present in aluminosilicate industrial wastes. Among different types of construction and demolition wastes and compared to concrete waste, brick, tile, and ceramic wastes show a higher potential for geopolymerization due to their higher reactive SiO₂ and Al₂O₃ contents providing suitable synthesis conditions including type, composition and dose of alkali activator and curing time and temperature. In some cases, incorporation of corrective materials such as OPC, GGBFS, metakaolin, etc., for compositional correction purposes contributes to higher degree of geopolymerization, which in turn improves the geopolymer properties significantly. Waste glass is highly deficient in its reactive alumina content and, therefore, incorporation of corrective materials rich in reactive alumina such as calcium aluminate cements, metakaolin, etc., is necessary. In contrast, red mud with its advantages of high alkalinity and ultrafine particles is highly deficient in reactive silica and, therefore, addition of corrective materials rich in reactive silica such as microsilica, GGBFS, etc., is required. Recently, tendency to recycle different aluminosilicate industrial wastes such as tungsten, gold, copper, and phosphate mine tailings into geopolymer material has increased not only for sustainable waste solidification purposes, but also for the effective stabilization of their heavy metal contents. In these cases, special consideration should be given to geopolymer soundness under water immersion condition. The published literature demonstrates the viability of recycling some of the most important aluminosilicate industrial wastes into value added products through geopolymerization technology as a sustainable and environmentally sound waste management method. Further research activities for characterizing appropriate aluminosilicate industrial wastes, improving the reactivity of the source materials by using appropriate corrective materials, optimizing synthesis and curing conditions, investigating soundness and durability performance of the geopolymer are required and will definitely contribute to the practical application of this technology.

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Recycling Approaches, Policies and Regulations on Electronic Waste With Special Focus on India

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Introduction

In a constantly evolving consumerist society, certain activities or initiatives become significant towards ensuring a sustainable development. Consequently, one of the most discussed issues in the contemporary time is the opportunities and challenges associated with 'recycling'. At the global level, there is an expanding effort on innovation and capacity building in recycling towards ensuring a closed-loop supply chain (Corder *et al.*, 2015). The recycling market could be 'considered as one of the key industries able to close the materials loop' (Cucchiella *et al.*, 2015: 264). This is imperative in an increasingly industrialized and urbanized world where quantity of waste generated observes a constant rise. With the linear economic models and the universality of the supply and demand, the aim of incessant growth is forecasted upon exhaustive use of energy and material in both the production and consumption phase (Wilson *et al.*, 2017). Resource depletion and waste generation have already been key apprehensions in several countries across the globe (Halvorsen, 2012). Managing the large volume of waste of different kinds and characteristics is particularly a major sustainability challenge today. The cities of the world are predominantly the sites of uncontrolled waste and pollution creation. For instance, in the year 2016 alone, the cities worldwide produced 2.01 billion tons of solid waste which is equivalent to a footprint of 0.74 kilograms per capita per day (World Bank, 2018).

It is essential to ensure country-specific reliable and detailed data on the generation of waste in order to confirm responsible waste management practices and policy initiatives. Several countries in the world lack such information, especially regarding toxic categories of waste such as electronic waste, biomedical waste, laboratory waste etc. As argued by Intharathirat *et al.* (2015:3), "In order to plan, manage and use municipal solid waste (MSW) in a sustainable way, accurate forecasting of MSW generation and composition plays a key role". Nevertheless, it is evident that the amount of waste generated globally, irrespective of the categories, is increasingly becoming alarmingly. As the generation of waste increases globally, the significance of recycling becomes both evident and imperative (Mueller, 2013). In order to address the global challenge of waste management towards sustainability, it is essential to initiate and ensure combined efforts from a range of public and private stakeholders (Xu *et al.*, 2018). It is because of the fact that, let alone individual researcher, no single discipline has the capacity to possess all the essential knowledge to maximize the increasingly multilayered waste management competence (Xu *et al.*, 2018).

With the rapid growth of population and urbanization, the waste generation is anticipated to upsurge by 70% from 2016's level to 3.40 billion tons in 2050 (World Bank, 2018). Accordingly, it is vital for the policymakers to decide the recycling practices to be implemented from the set of possibilities at their disposal in order to divert waste from the landfills (Mueller, 2013). Gradually, the world is acknowledging the importance of recycling towards avoiding detrimental environmental consequences. There are primarily three key benefits of recycling: environmental, economic benefits and public health and safety benefits (Kumar *et al.*, 2017). Describing the advantages of recycling of household solid waste, Nguyen *et al.* (2017:1–2) state:

"Essentially, recycling of household solid wastes is a cost-effective way of (a) efficiently utilizing landfill capacity; (b) minimizing the disposal of solid waste hence decreasing costs; (c) enhancing environmental quality; and (d) increasing socio-economic sustainability. Hence, encouraging recycling behavior is imperative, and should be prioritized especially in emerging markets, where rapid population growth, increased consumption, urbanization, and industrialization collectively cause a significant increase in solid waste generation by households. [...] the development of community recycling programs and the encouragement of participation by individuals in such programs are highly strategic, which requires comprehensive understanding of the motivations of those involved in recycling".

As there is a shift towards globalization and internationalization of knowledge creation, an increasing number of research institutes and scholars pursue their research external to their immediate surrounds (Xu *et al.*, 2018). This kind of initiatives lead to interdisciplinary, transdisciplinary and multidisciplinary research which is crucial for formulating and implementing responsible waste management policies and regulations including recycling.

In this article, we attempt to describe the regulations and policies regarding recycling, especially taking into consideration the case of electronic waste (E-waste) recycling policies in India. Electronic waste has been selected because it is one of the fastest growing waste toxic streams in the world today with immense recycling potential. First, we start with a basic description of electronic waste, followed by its potential as 'urban mines'. Understanding E-waste along with the concept of urban mines will provide the readers an idea about why E-waste recycling policies and regulations are imperative in the present-day scenario. This will act as a base for the article. We then explored the concept of circular economy where E-waste has the potential to contribute immensely. Essentially, urban mining and circular economy are two ideas on which effective recycling policies and regulations are highly focused on these days. Subsequently, we describe the current state of affairs associated with E-waste recycling policies in India. India is considered as a case because of the fact that although the country shares similar kinds of E-waste associated

challenges as that of China or many West African countries, it is yet to gain both attention and momentum in its research on E-waste (Borthakur and Singh, 2017a). Thus, our purpose is to provide a comprehensive overview on the E-waste recycling potential and evaluate how effective or ineffective the E-waste policies in India has been towards maximizing this potential.

Recycling Policies: Electronic Waste, 'Urban Mines', 'Circular Economy' etc.

A Brief Overview of Electronic Waste

Electronic waste (E-waste) is also acknowledged as Waste Electrical and Electronic Equipments (WEEE) and it has consistently been observed an increase in quantity across the globe especially during the two decades. Processing of E-waste is not only a rising concern but also a global challenge owing to an immensely huge volume generated worldwide (Dias *et al.*, 2018). Nevertheless, the exact volume of E-waste generated is a contested subject, both in the global and country-specific scale. For instance, in the context of India, it ranges from 480,000 tonnes of E-waste as estimated by a few researchers to 1.8 million tonnes as estimated by the Associated Chambers of Commerce and Industry of India (ASSOCHAM) in 2016 (Borthakur, 2017b). Such kind of disputed figures render it difficult for the researchers and policymakers to formulate effective policy responses or solutions. Yet, it is acknowledged that the quantity of E-waste generated in growing rapidly worldwide which calls for immediate interventions towards its effective management. Rapid growth in economy, progresses in information and communication technologies (ICT), advances in technological innovations, downward prices of electronic devices and increasing usefulness of most electronic equipments in the present-day context encourage a constant growth in the use of electronic and electrical equipments and generation of E-waste around the world (Borthakur and Govind, 2017c). Further, with advances in technology, automation has been accepted widely by the industries increasing the usage of electronic and electrical equipments (Kumar *et al.*, 2017).

E-waste characteristically comprises of precious and valuable materials as well as a number of hazardous constituents, which possibly could bring about environmental and economic advantages upon proper recycling (Dias *et al.*, 2018). Accordingly, recycling of E-waste is vital for numerous reasons. Firstly, the valuable and precious metal contents in E-waste has the potential to reduce the concerns and burdens associated with the natural mines. Secondly, appropriate E-waste recycling practices has the potential to minimize the environmental impacts of the hazardous constituents of E-waste. Nevertheless, E-waste disposal is inherently challenging and the involvement of the informal recycling sector without any environmental and human health considerations intensifies the challenges further. The arrival and ascendancy of the informal E-waste recycling units in countries such as India is a key concern as it includes practices (for example, acid-bathing to excerpt valued and reusable E-waste components) which are extremely perilous to the environment and human health alike (Borthakur, 2015). These informal operations involving shredding, open burning and incineration has the potential to release various toxic components present in electrical and electronic devices and create secondary pollutants such as dioxins along with lead, mercury etc. (Zeng *et al.*, 2018). There are further concerns associated with trade of E-waste (legal/illegal) where large quantities of E-waste are shipped from the developed to the developing countries. The informal E-waste recycling sector of the global south absorbs this waste sent by the global north. As argued by Davis *et al.* (2019:36):

"Over the past 20 years, informal electronic waste (e-waste) processing hubs in Asia and Africa have emerged as global sites of concern – icons of the dark side of globalization and the digital age. Drawing parallels to the outsourcing of manufacturing to overseas destinations where low labour costs and lax regulations allowed increased profits, NGO and media portrayals of e-waste hubs highlighted the poor working conditions and excessive pollution in these sites, which had become dumping grounds for the refuse of rich countries".

E-Waste as Urban Mines

Many researchers and policy experts argue that the increasing volume of E-waste in the developing world (produced both through domestic generation and illegal/legal import) could be considered as a good opportunity to industrialize the E-waste recycling sector and generate ample employment opportunities. Although there exist economic limits, complex electronics may contain up to 60 elements from the periodic table and several of these elements could be technically recoverable (see "Relevant Websites section"). The existence of precious metals such as gold (Au), platinum (Pt), silver (Ag), palladium (Pd), Gallium (Ga), tellurium (Te), tantalum (Ta), selenium (Se) and germanium (Ge) makes E-waste attractive for recycling (Khaliq *et al.*, 2014). There are other valuable metals such as copper (Cu), Aluminum (Al) and Nickel (Ni) present in E-waste. Recovering these precious/valuable metals extant in the E-waste stream as a part of what is known as 'urban mining' could be an attractive avenue for recycling (Zeng *et al.*, 2018). Describing 'urban mining' and its association with E-waste or WEEE, Cossu and Williams (2015:1, 3) state:

"Urban Mining extends landfill mining to the process of reclaiming compounds and elements from any kind of anthropogenic stocks, including buildings, infrastructure, industries, products (in and out of use), environmental media receiving anthropogenic emissions, etc. [...] The stocked materials may represent a significant source of resources, with concentrations of elements often comparable to or exceeding natural stocks. As for natural ores, extraction and processing of anthropogenic stocks is necessary and the generation of an economic benefit is essential. For these reasons, urban mining originally focused on electrical and electronic wastes (WEEE) which contain relatively high concentrations of expensive metals and rare earth elements [...] Whilst from an etymological point of view, it is clear that urban mining should refer to the exploitation of anthropogenic stocks, today the term is widely used for describing almost any sort of material recycling [...] WEEE is the backbone stream in urban mining as they concern critical raw materials of industrial interest".

An estimation by the United Nations University (UNU) suggests that the resource potential for secondary raw materials present in electronic waste is worth €55 Billion (See: *ibid*). It is, thus, indispensable to formulate and implement policies and regulations towards encouraging the idea of urban mining. Devising a comprehensive recycling policy is an essential first step here. Many countries have implemented stringent E-waste policies encouraging maximum recycling. However, these are predominantly the countries in the global North. The European Union has especially been a pioneer in this context implementing two important E-waste related directives: Restriction of Hazardous Substances (RoHS) and Waste Electrical and Electronic Equipments (WEEE) Directive. The RoHS Directive restricts the use of six substances: restrictions on the use of six hazardous substances i.e., lead, mercury, cadmium, hexavalent chromium and flame retardants such as polybrominated biphenyls (PBB) or polybrominated diphenyl ethers (PBDE). Among the developing countries, the Chinese government has actively been involved in creating an institutional and legislative framework to fulfill E-waste recycling (Yu *et al.*, 2010).

E-Waste and Circular Economy

As the concept of 'Circular Economy' began to attract attention globally against the widely dominant model of 'Linear Economy', E-waste became a major focus area. Differentiating the two concepts, Murray *et al.* (2017:371) argue:

"The term circular economy has both a linguistic and a descriptive meaning. Linguistically it is an antonym of a linear economy. A linear economy is one defined as converting natural resources into waste, via production. Such production of waste leads to the deterioration of the environment in two ways: by the removal of natural capital from the environment (through mining/unsustainable harvesting) and by the reduction of the value of natural capital caused by pollution from waste. Pollution can also occur at the resource acquisition stage. [...] By circular, an economy is envisaged as having no net effect on the environment; rather it restores any damage done in resource acquisition, while ensuring little waste is generated throughout the production process and in the life history of the product".

The concept of circular economy originated in the Europe. During the past 20 years, The EU has attempted to set the roots for the advance of a circular economy where waste is considered as resources and, consequently, utilized in a sustainable and efficient way (Cucchiella *et al.*, 2015). A flagship initiative towards resource efficiency was launched by the European Commission (EC) as the concerns associated with high commodity prices aroused and was first operationalized via the roadmap aimed at a resource efficient Europe (McDowall *et al.*, 2017). Subsequently, a wide range of policy actions recognized jointly as the 'Circular Economy Package' was announced which was later substituted by the 'Closing the Loop – An Action Plan for the Circular Economy' (McDowall *et al.*, 2017).

In the context of the developing world, China has taken commendable initiatives to ensure a circular economy. In the mid-2008, the Chinese People's Congress approved the Law for the Promotion of the Circular Economy, a national circular economy law (Mathews and Tan, 2011), which came into effect on 1 January 2009. As further described by Mathews and Tan (2011:437):

"The interest of the circular economy and its promotion in China lies in the fact that it has moved beyond an "environmental" concept to become a mainstream development goal [...] China's national leadership has clearly understood that continued development in the traditional linear manner, starting with resources taken from nature at one end and proceeding through production processes to the creation of wastes disposed in nature at the other end, is simply no longer feasible. It is destructive to the point of ruin, at both ends, and it is costly to both secure fresh resources all the time and lose resources in the form of waste: It is, in other words, both economically and ecologically inefficient [...] only in China has a circular economy been made the object of official development goals and been taken from the realm of environmental policy into the realm of development and economic policy – an extremely important step".

Recycling Policies: The Case of E-Waste Recycling Policy in India

India has a long past of recycling its waste ranging from papers, plastics, metals among many others. The E-waste recycling today constitute a major part of the country's recycling interventions. Similar to China and many other developing countries, E-waste is processed in India in small workshops or backyards using primitive processes such as open burning, strong acid digestion and manual disassembly and resulted in releasing a large amount of organic pollutants, hazardous acids and toxic metals into the immediate environment (Pradhan and Kumar, 2014). The study by Pradhan and Kumar (2014) further revealed uncontrolled informal E-waste disposal and recycling activities in the Mandoli industrial area in Delhi leading to higher levels of heavy metal contamination in groundwater, plants and surface soil. This is the story of majority of the key cities in the country. The dominance of the informal recycling activities in India, thus, calls for immediate policy attention towards averting both environmental and human health consequences. Nevertheless, addressing the concerns associated with recycling of E-waste in India is a tricky task. It is because of the fact that informal E-waste recycling activities in India is responsible for providing employment opportunities to a large number of urban poor as all the recycling associated activities like sorting, segregation, dismantling etc., are done manually in the informal recycling sites in the country (Borthakur, 2014). Further there are entrepreneurship opportunities involving low cost and other associated investments (Borthakur, 2014). The formalization of the informal sector may result in losing these employment and entrepreneurship opportunities for a section of the financially challenged mass of the country. Thus, a comprehensive E-waste management policy addressing the aspects of recycling in a local-specific way is one of the major needs in the country today.

In India, there was no regulatory framework on the management before the year 2011 which provided ample time for the unprecedented growth of E-waste in the country without appropriate management efforts. The economic liberalization policies in

India was unveiled in 1991 resulting the country emerged as one of the significant players in the global technology and outsourcing business (Sharma, 2015). The information technology and electronics sector in the country consequently observed a major boost with large volumes of consumer electronics heading to the Indian market. Although the IT revolution started in India way back in early 1990s, a proper policy related to E-waste was being introduced almost after 20 years, in 2011, in the form of the 'E-waste (management and handling) Rules, 2011' (Borthakur, 2016). This rule came into force from 1st May 2012. In the year 2016, there was an another, more exhaustive policy intervention in the form of 'E-waste (Management) Rules, 2016', enacted since October 1, 2017. While the number of registered E-waste recycling vendors has increased after the implementation of the E-waste rules in 2011 and 2016, the informal sector is still dominating the E-waste recycling businesses across the country. Moreover, the time period between formulation and implementation of policy in India is mostly much higher than that of the developed economies. The administrative delays in law enforcement are one of the major barriers in the implementation of policy measures in the country. In the year 2018, the Union Minister for Environment, Forest and Climate Change in India declared that the Government has amended the existing E-waste (Management) Rules of 2016 towards facilitating environmentally sound E-waste management in India (see "Relevant Websites section").

All the rules (2011, 2016 and 2018) associated with E-waste in India are based on the premises of Extended Producers Responsibility (EPR). The Organization for Economic Cooperation and Development (OECD) defined EPR as:

"Extended Producer Responsibility (EPR) is a policy approach under which producers are given a significant responsibility – financial and/or physical – for the treatment or disposal of post-consumer products. Assigning such responsibility could in principle provide incentives to prevent wastes at the source, promote product design for the environment and support the achievement of public recycling and materials management goals" (see "Relevant Websites section").

The first E-waste rule in the country ('E-waste (management and handling) Rules, 2011') did not set any collection target for the producers. The subsequent E-waste (Management) Rules, 2016 offered a number of rigorous alterations to the previous rules (Borthakur and Govind, 2017d). One among them is the setting up of stringent collection target. These targets were established in the rule as: (1) 30% (either by number or by weight) of the quantity of waste generation during the first two years of implementation of rules, (2) 40% during third and fourth years, (3) 50% during fifth and sixth years and (4) 70% during seventh year onwards (MoEF, 2016:22). Nevertheless, these targets proved to be too ambitious for the producers in the country and subsequently, the 'E-waste (Management) Amendment Rules, 2018' considerably lowered the existing collection targets especially for the starting year. As per this recent rules, "the phase-wise collection targets for e-waste in weight shall be 10% of the quantity of waste generation as indicated in the EPR Plan during 2017–18, with a 10% increase every year until 2023. After 2023 onwards, the target has been made 70% of the quantity of waste generation as indicated in the EPR Plan" (see "Relevant Websites section"). Overall, the constant formulation and amendment E-waste management rules in India since its inception in the year 2011 shows the complexity of the situation in the country and lack of adequate research before formulating possible management solutions. Thus, although E-waste in India has been observing a constant increase during the last two decades, the policy and regulatory measures associated with it is still at a very primitive stage (Borthakur, 2015).

On a positive note, a new economic instrument in the form of 'Deposit Refund Scheme' has been introduced in the 'E-waste (Management) Rules, 2016'. A deposit-refund system is "the surcharge on the price of potentially polluting products. When pollution is avoided by returning the products or their residuals, a refund of the surcharge is granted" (see "Relevant Websites section"). In a country where consumers expect a financial return for their recyclable waste, deposit-refund system could be a potential alternative and could aid in environmentally responsible consumer behavior. For instance, in return of some financial incentives, the local scrap dealers or kawariwalas collect most of the E-waste in the country from sources such as households, public and private sector businesses, academic institutions etc. (Borthakur and Govind, 2017c). A deposit refund system has the capability to encourage the already existent behavioral practices of the Indian citizens. It is, however, imperative to carefully ponder over how such a scheme could incorporate the actors in informal recycling sector. Nevertheless, Bhaskar and Turaga (2018) put forth that as India has no reference data on the amount of E-waste generated in the country, any quantitative evaluation of the Rules on outcomes, for instance, recycling or collection rates, is arduous. Further, the categories of E-waste are quite narrow and restricted in the country which includes only 21 varieties of electrical and electronic products as per the E-waste Management (Rules), 2016. Such restrictive definition results a confined effort of E-waste management practices and recycling initiatives in India.

Conclusions

In this article, we endeavoured to assess the regulations and policies regarding recycling taking reference to the situation of electronic waste (E-waste) in India. E-waste is selected owing to the fact that it is probably one of the most important streams of rapidly growing waste in need of immediate recycling interventions. As an emerging country and one of the largest generators of E-waste in the world, India provides an excellent case in this regard. We started with a general description of E-waste and its significance in relation to the concepts of urban mining and circular economy. Urban mining and circular economy are essentially two of the most talked about concepts in today's world towards ensuring effective resources recycling and thus, has implications in the context of E-waste. These two concepts largely decide major policy approaches in the current global scenario. Further, India's E-waste recycling policies has been discussed in detail with possible/existing challenges and opportunities.

Recycling of E-waste is vital, firstly because, the valuable, precious and rare-earth metal contents in E-waste has the potential to reduce the concerns and burdens associated with the natural mines. The concept of urban mining provides a good starting point here towards encouraging maximum resources recycling. Urban mining has the potential to encourage a circular economy involving least waste generation. Secondly, appropriate E-waste recycling practices has the potential to minimize the environmental impacts of the hazardous constituents of E-waste. The generation of E-waste is increasing rapidly and the trend is expected to continue during the near decades. Many researchers and policy experts argue that the increasing volume of E-waste in the developing world (produced both through domestic generation and illegal/legal import) could be considered as a good opportunity to industrialize the E-waste recycling sector and generate ample employment opportunities.

In India, E-waste recycling today constitute a major part of the country's recycling interventions. However, the recycling activities are dominated by the informal sector with intense detrimental repercussions to the human health and the environment. The first E-waste rule in the country is the 'E-waste (management and handling) Rules, 2011' which was followed by the 'E-waste (Management) Rules, 2016' and 'E-waste (Management) Amendment Rules, 2018'. The collection target under the 2016s rules had to be revised and reduced (at least for the initial years) in the 2018s rules. A new concept of deposit-refund system was introduced in the rules of 2016 which has the potential to aid in responsible collection and disposal facilities in the country. It is, however, imperative to carefully ponder over how such a scheme could incorporate the actors in informal recycling sector and how sustainable recycling could be ensured.

Overall, recycling associated regulations and policies are very much confined primarily in the developed countries with developing countries are yet to gain momentum in this regard. In the global south, China has taken commendable initiatives towards ensuring responsible recycling of its waste categories. India, although encounters similar E-waste problems as that of China, has a long way to go. India's E-waste recycling policies have gradually been taking shape and expected to result in positive outcomes in the near future. It is imperative that the world realizes the significance of recycling irrespective of the developed or developing countries so that sustainable development could be attained and healthy developmental activities could be ensured.

See also: A Review on Utilization of Electronic Waste Plastics for Use Within Asphaltic Concrete Materials: Development, Opportunities and Challenges for Successful Implementation

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OECD Glossary of Statistical Terms.

Recycling of Agricultural Waste for Wastewater Treatment

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Introduction

For the sustainable development, searching for novel green technologies for the pollutant abatement can be considered as an essential responsibility for the mankind to protect the environment and human health. Toxic pollutants get introduced to the aqueous effluent by means of various industrial activities viz. dyeing, mining and refining ores. Conventional methods for the removal of pollutants from contaminated aqueous solutions include physical, biological and chemical methods. The methods such as membrane separation, coagulation and chemical oxidation possess the major drawback of economic feasibility (Adegoke and Bello, 2015).

Agricultural waste materials are environmental friendly and exhibit potential biosorption capacity. Fig. 1 illustrates the overall preparation steps of agricultural waste to be utilised as an effective adsorbent for wastewater purification.

The major advantages of utilizing agricultural wastage as biosorbents as compared to the conventional methods for wastewater treatment include – (a) regeneration and recycling of biosorbents, (b) minimized sludge generation, (c) high efficiency and (d) low cost. Currently, attention has been focused towards the biological wastes collected as the by-products from large scale industrial operations and agricultural waste materials. Agro-waste contains loose and porous structure with functional groups such as the hydroxyl and carboxyl group that is responsible for their biosorption capacity (Dai *et al.*, 2018). The significant advantages of biosorption over conventional methods include: recycling of biosorbents, low cost, simultaneous waste management, high efficiency and minimization of chemical and biological sludge. Available literature reveals numerous agricultural waste materials viz. rice husk and bran, wheat husk and bran, saw dust of several plants, bark of the trees, coconut and ground-nut shells, waste tea leaves, jatropa deoiled cakes, apple, banana and orange peels, sugarcane bagasse, coffee beans, sugar beet pulp, Cassia fistula leaves, sunflower and cotton stalks, walnut shells and many more. The present article reviews the efficient and environmental friendly utilization of agricultural wastage for wastewater purification.

Mechanism of Wastewater Treatment Via Biosorption

According to the previous literatures, agricultural wastage consists of lignocellulosic materials with major structural component such as cellulose, hemicellulose and lignin. The overall mechanism of water purification via biosorption involves two phases – (1) solid phase or sorbent and (2) liquid phase or solvent. Affinity of pollutants dissolved in the solvents towards the specific sorbent acts as a driving force for an effective biosorption process. The entire process consists of several mechanisms that includes adsorption on surface and pores by physical forces or physisorption, chemisorption, complexation, ion exchange and chelation due to the driving force i.e., concentration gradient that results in effective diffusion (Sud *et al.*, 2008). Oxygen functional groups including ether along with carbonyl and hydroxyl groups bind heavy metal ions and various organic contaminants to the surface of adsorbents (Salleh *et al.*, 2011). Microorganisms are also capable of efficient absorption of water contaminants such as heavy metal in both live and dead conditions. Various microorganisms include fungi, bacteria, yeast and algae. Biosorption of metals is a complex process that depends upon various parameters such as type and state of biomass, binding capacity of the biomaterials, metal's chemical properties along with the operating conditions such as temperature, pressure and pH (Javanbakht *et al.*, 2014).

Performance of Agricultural Waste Materials as Biosorbents for Wastewater Treatment

Agroindustry residues are considered as ecologically safe and inexpensive adsorbent that requires comparably less pre-processing. Moreover, utilizing agro-waste as the substitute to conventional products possess both environmental and economical benefits.

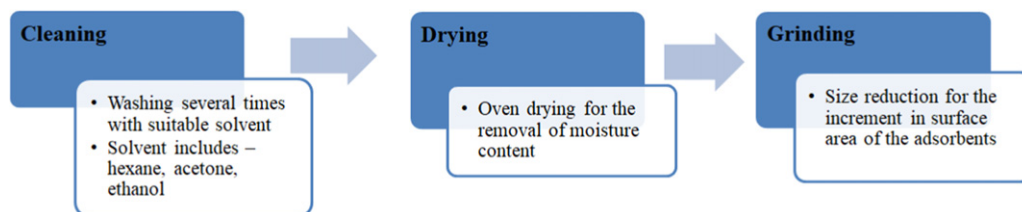


Fig. 1 Overall preparation steps of agricultural wastage to be utilised as adsorbents.

Rice Husk

Rice husk can be considered as an effective agro waste obtained from rice mills as a by-product. Rice husk ash has been mentioned in numerous literatures as an efficient adsorbent for wastewater treatment. The overall characteristics of rice husk ash depend on various factors such as – method of preparation, sources and combustion technologies (Prasara-A and Gheewala, 2016). Silica rich rice husk is an abundant waste biomass, capable to purify gas, soil and wastewater via integrated processes, adsorption and catalysis (Shen, 2017). **Table 1** summarises the research work performed for wastewater purification via effective utilization of low cost rice husk.

Saw Dust

Saw dust had been successfully studied by several researchers as a low cost adsorbent. Based on the experiments conducted, higher initial concentration and lower temperature were proved as favourable factors for the adsorption of pollutants. In addition to that, stirring speed plays an essential role in the acceleration of the overall performance of saw dust as adsorbent whereas, intraparticle diffusion hinders the adsorption rate (Dutta *et al.*, 2001). **Table 2** listed the utilization of waste saw dust for the wastewater purification.

Banana Waste

Based on the recent literatures banana wastes acts as a highly efficient adsorbent against hazardous environmental pollutants that includes organic pollutants, heavy metals and pesticides. Chemical modification is essential for the effective utilization of banana waste derived low cost adsorbent (Ahmad and Danish, 2018). **Table 3** mentioned numerous research work executed worldwide via effective application of banana peel as biosorbents.

Sugarcane Bagasse

Sugarcane bagasse prepared as an agro–agro waste can be utilised as an efficient substitute of activated carbon for the decontamination of various hazardous pollutants. Numerous pre-treatment and chemical modification methodology have been resea-

Table 1 Summary of research done by the various researchers utilizing low cost rice husk as agricultural waste material for wastewater treatment

Agricultural waste	Pollutants	Performance (%)	Reference
Rice husk (1 g at 42 mesh to 20 mL of milk)	Aflatoxins	100	Scaglioni and Badiale-Furlong (2016)
Mixture of 5, 10 and 15 % rice husk and raw sludge	Rosaniline dye, metallic cations, chlorine	100 (Rosaniline dye in 800 min.)100 (Ni(II) and Pb(II) in 600 min.)100 (chlorine in 1000 min.)	Shalaby <i>et al.</i> (2017)
Polypyrrole and rice husk ash nanocomposite	Heavy metals, anions and COD from textile wastewater	Upto 95.1 (at 5, 10, 15, 20 and 25 min.)	Ahmed and Reyad (2017)
Rice husk ash (upto 50 g/L)	Rice mill wastewater	Upto 70 (120 min)	Kumar <i>et al.</i> (2015)
Rice husk ash (10 g/L)	Rice mill wastewater	48.1 (120 min)	Kumar <i>et al.</i> (2016)
Rice Husk Ash (2 g/L)	Phosphate	89 (120 min)	Mor <i>et al.</i> (2016)

Table 2 Summary of research done by the various researchers utilizing low cost saw dust as agricultural waste material for wastewater treatment

Agricultural waste	Pollutants	Performance (%)	Reference
Saw dust blended with MgO agglomerates	Borate	760 mgB/kg (10 h)	Sasaki <i>et al.</i> (2011)
Eucalyptus wood (Eucalyptus globulus) saw dust (SD)	Congo red	Upto 95 (4 h)	Mane and Vijay Babu (2013)
Polyaniline coated on sawdust	Cd (II) ion	Upto 100 (20 min)	Mansour <i>et al.</i> (2011)
Saw dust	Zn(II) and Cd (II) ions	Upto 90 (320 min)	Naiya <i>et al.</i> (2009)
Polyacrylamide grafted rice (Oryza sativa) husk and (Tectona grandis) saw dust	Cd ²⁺ ions	Upto 85% (3 h)	Sharma <i>et al.</i> (2009)
Biochar derived from eucalyptus saw dust modified with citric, tartaric, and acetic acids	Methylene blue	178.57, 99.01, and 29.94 mg/g for citric, tartaric, and acetic acids respectively	Sun <i>et al.</i> (2015)

Table 3 Summary of research done by the various researchers utilizing low cost banana peel as agricultural waste material for wastewater treatment

Agricultural waste	Pollutants	Performance (%)	Reference
Banana corm activated charcoal	Mercury (Hg)	5 gm/l (1 ppm Hg)	Marichelvam and Azhagurajan (2018)
Banana peel powder	Rhodamine-B	Upto 81.07 % (0.4 g/30 mL, 25 mg/L Rh- B)	Singh <i>et al.</i> (2018)
Chemically modified banana peels	MB and Co(II)	1303.54 (MB) and 122.39 (Co(II)) mg/g	Yu <i>et al.</i> (2018)
Chemically modified banana peels	hexavalent chromium Cr(VI)	96 % (4 g/L, 400 mg/L- Cr in 120 min)	Ashraf <i>et al.</i> (2017)
Chemically modified banana peels	Mn(II)	94 % (4 g/250 mL)	Ali <i>et al.</i> (2016)
Banana peels powder (BPP)	Sr(II)	41.5 mg/g	Mahindrakar and Rathod (2018)
Banana peels nanosorbent	actinides (uranium and thorium)	27.1 mg/g, 34.13 mg/ g for uranium and 45.5 mg/g, 10.10 mg/ g for thorium in synthetic and real mine water	Oyewo <i>et al.</i> (2016)
Activated Surface of Banana Peels	Reactive Red Dye (RRD)	70.25% (1 g/100 mL)	Temesgen <i>et al.</i> (2018)

Table 4 Summary of research done by the various researchers utilizing low cost sugarcane bagasse as agricultural waste material for wastewater treatment

Agricultural waste	Pollutants	Performance (%)	Reference
Sugarcane bagasse cellulose mixed esters	Co ²⁺ and Ni ²⁺	0.62 and 0.53 mmol/ g for Co ²⁺ and Ni ²⁺ , respectively	Elias <i>et al.</i> (2019)
Sugarcane bagasse (SCB)	cadmium (Cd(II))	24.47 mg/g	Li <i>et al.</i> (2018)
Sugarcane bagasse	nickel (II) ions	2 mg/g	Alomá <i>et al.</i> (2012)
Maleic anhydride grafted sugarcane bagasse	methylene blue	82 mg/g (98%)	Ge <i>et al.</i> (2017)
Sugarcane Bagasse	mercury ions	35.71 mg/g	Khoramzadeh <i>et al.</i> (2013)
Wood sawdust and sugarcane bagasse modified with EDTA dianhydride (EDTAD)	Zn ²⁺	105 mg/g	Pereira <i>et al.</i> (2010)
Sugarcane bagasse	mercury ions	178 mg/g	Sun <i>et al.</i> (2018)
Immobilized sugarcane bagasse	Cr(VI) and Cr(III)	80.6% and 41.5% respectively	Ullah <i>et al.</i> (2013)
Sugarcane bagasse biochar	Malachite green dye	3000 mg/L	Vyavahare <i>et al.</i> (2018)

ched worldwide for the synthesis of low cost biosorbent (Saad *et al.*, 2010). **Table 4** summarises the application of low cost sugarcane bagasse as agro waste for wastewater purification.

Categories of Contaminants

Inorganic Pollutants

The expeditious advancement of urbanization and industrial development resulted in the contamination of inorganic pollutants such as heavy metals and non-metal including nitrogen and phosphorous. Heavy metals including arsenic, copper, lead, cadmium, nickel and many more possess detrimental effect on human as well as aquatic life.

Organic Pollutants

Organic pollutants mainly dyes, antibiotics, pesticides, aromatic compounds and oil spills have been considered as an emerging organic contaminants. Nowadays, the utilization of agro waste as adsorbents in wastewater purification has gained global attention by the researchers. As illustrated in previous sections, removal of hazardous pollutants via agricultural wastage facilitates economical and environmental friendly methodology for wastewater purification. **Fig. 2** illustrates various categories of contaminants that could be removed via agro wastage.

Adsorbent Recycling

Regeneration of adsorbent promotes solid waste management and improves the economy of wastewater purification phenomena. Numerous adsorption methods include thermal degradation of pollutant, biological methods and solvent extraction. Thermal degradation

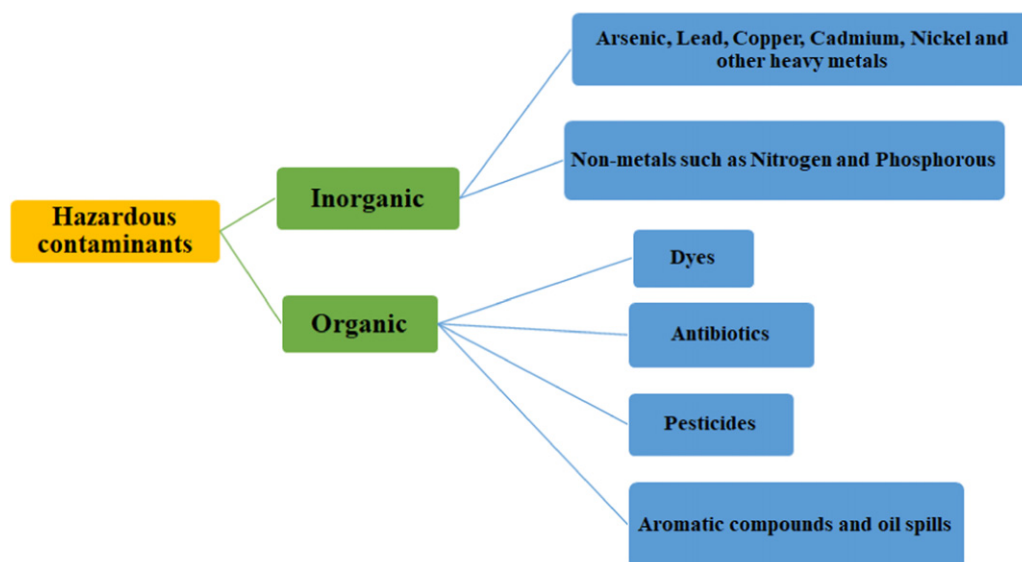


Fig. 2 List of contaminants.

method for the regeneration of the adsorbent involves calcination of the treated adsorbents with the pollutants adsorbed on the surface. During calcination at a suitable temperature for certain duration, thermal degradation of the pollutant occurs and the treated adsorbents can be reused. Before calcination, the information regarding the thermal behavior of the pollutant and adsorbent must be gathered via thermogravimetric analysis. Biological methodology utilizes certain microorganisms to desorb the treated adsorbent and considered as an environmental friendly and facile treatment. After successful desorption, regenerated adsorbent can be reused. Moreover, appropriate solvent must be selected for the efficient regeneration of the contaminated adsorbent via solvent extraction process.

Future Aspects

Utilizing or recycling of agricultural wastes for wastewater treatment exhibits dual advantages i.e., solid waste management and pollutant abatement. According to the recent analysis, China is the leading country in the production of agricultural waste (Dai *et al.*, 2018). Untreated agro-waste is majorly responsible for rural environmental pollution. Therefore, enhanced reuse of agricultural waste can efficiently reduce air pollution along with the remediation of wastewater contaminants. Based on the various literature studies, agricultural wastes can be considered as an ideal choice to deal with the persistent harmful water contaminants. For achieving enhanced efficiency, appropriate modifications to improve the adsorption capability of the agricultural waste should be conducted. Therefore, the future scope of efficient utilization and recycling of agricultural waste materials as adsorbent includes development of economically modified agro-waste and effective usage in order to deal with the wastewater treatment.

Conclusions

Agriculture based biomass exhibits the capability to replace expensive commercial adsorbents such as activated carbon for wastewater treatment. Several low cost and recyclable adsorbents derived from agricultural wastage are increasingly researched worldwide. It possess dual applicability i.e., wastewater purification and solid waste management. However, selection of the agricultural waste plays a major role in the adsorption of persistent harmful contaminants. The adsorption efficiency of porous agro based adsorbent with or without proper chemical modification gets effected by various factors such as adsorbent dosage, pH and temperature. The intention of the present article is to develop global awareness amongst the researchers to utilize the agricultural wastage for an economical wastewater purification and spontaneous solid waste management.

See also: Use of Novel Nanostructured Photocatalysts for the Environmental Sustainability of Wastewater Treatments

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Recycling of Construction and Demolition Wastes Into Renewable Construction Materials

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Background of Construction and Demolition Wastes (CDW)

Construction and demolition wastes (CDW) could be broken concrete, bricks from buildings, or broken pavements and these CDW are produced every year at huge quantities. The construction industry is a major generator of several types of CDW. Old buildings approaching the end of their lives are demolished producing millions of tons of concrete wastes, large quantity of rejected construction products for non-compliance with the required specifications, as well as marble deposits provided a large quantity of aggregates of different sizes induced by fragmentation operations, sawing of large stones, and processing plants proliferate a very large quantity of wastes consisting mainly of powders and sludge (Belachia and Hebhoub, 2018). Most of the CDW came from demolition process while minor portions (around 10%–30%) are generated during the construction process (EPA, 2018; Ning, 2017).

The total amount of CDW generated in different regions are shown in Table 1. In South East Asia countries such as Malaysia and Thailand, about 28.34% of the annually generated solid waste comes from construction and demolition waste. The Malaysian construction demolition waste generation estimation was 161.2 tons per day in 2009 and has increased to 299.69 tons per day in 2015. The waste generation is projected to reach 368.31 tons per day by 2023 (Fauziah and Agamuthu, 2003). Meanwhile, the rapid development in China also produced a massive production of CDW of 1255.6 million tons in 2013, but soon to increase by 28.5% within 4 years to 1613.3 million tons in 2016 (Ning, 2017). On the other hand, in Europe, more than 25% of total waste comes from the demolition or renovation of buildings, and half of this waste clutters landfills. It is estimated that only 30% of the materials used are currently recycled, though the practice in some European countries shows that 90% of the wastes is recyclable. According to Eurostat the total amount of waste generated in the European Union, was over 2.5 billion tons, of which almost 860 million tons belonged to construction and demolition activities (Bravo *et al.*, 2015).

Due to the massive amount of CDW generated every year and these CDW are basically non-degradable, CDW often get sent to landfills or dumped illegally, raising major concerns in terms of environmental sustainability (Yap *et al.*, 2018). CDW is often considered as a nuisance to construction industry and environmental agencies in all countries. Hence, the sustainable solution to recycled CDW including recycled concrete aggregates (RCA) and recycled marble (RM) as alternative construction materials has become a global trend nowadays with the following advantages:

- (1) To eliminate CDW by recycling and reuse, hence protecting the environment;
- (2) Help to solve some problems related to material scarcity. For example, some countries are constantly facing difficulties to source good quality aggregates such as granite;
- (3) To preserve our natural resources that are not infinite, and depleting rapidly due to the vast development of construction industry particularly in developing countries;
- (4) Reducing the landfill areas as some of the cities are suffering from land scarcities;
- (5) Giving a second life to our renewable and recyclable wastes (Fauziah and Agamuthu, 2003);
- (6) Lowering the consumption of raw coarse aggregates, which then leads to reduction in costs, energy and pollution associated with the raw material extraction and transport (Yap *et al.*, 2018).

This article will then focus on one of the sustainable solutions to handle the CDW, which is the recycling of concrete wastes into recycled concrete aggregates (RCA), as well as recycling of marble wastes into recycled marble (RM).

Table 1 Summary of construction and demolition wastes generation in 2015 according to different regions

Country	CDW (million tons)	References
Malaysia/Thailand (Region: South East Asia)	299.69	Fauziah and Agamuthu (2003)
European Nations (Region: Europe)	860.00	Yap <i>et al.</i> (2018)
United States of America (Region: North America)	547.80	EPA (2018)
China (Region: Asia)	1533	Ning (2017)
India (Region: Asia)	23.75	Arora and Singh (2018)
Algeria (Region: Africa)	15	Belachia and Hebhoub (2018)

Properties of CDW

Recycled Concrete Aggregates (RCA)

Recycled concrete aggregates (RCA) are recycled from the crushing process of demolished concrete to regain the original aggregates (Fig. 1(a)). This recycling process is essential in some of the countries where good aggregates are lacking. The most significant difference between RCA and natural coarse aggregate is the presence of mortar. The RCA normally consists of the natural coarse aggregates (NA) surrounded by a layer of adhered mortar of source concrete, as shown in Fig. 1(c). The adhered mortar being old, contains hydrated, unhydrated cement particles and sulfate. The presence of such mortar will then form a weak porous layer, influencing the strength and structural performance of the recycled coarse aggregate (Etxeberria *et al.*, 2007).

When compared to natural aggregates, the physical and mechanical properties of RCA are generally lower, as shown in Table 2. As seen from Table 2, the bulk densities of RCA and normal aggregates differ by about 7%–17%. It can be explained that the density of adhered mortar is less than the underlying aggregates when compared to normal aggregates (Arora and Singh, 2018). Also, RCA have 6 times higher porosity than normal aggregates due to the adhered mortar on the surface of RCA and their high porous nature leads to an increase in the water absorption capacity. The water absorption capacity usually ranges up to 8% for RCA (Poon *et al.*, 2004). As mentioned, the strength of concrete with RCA is directly proportional to the strength of RCA. By referring to

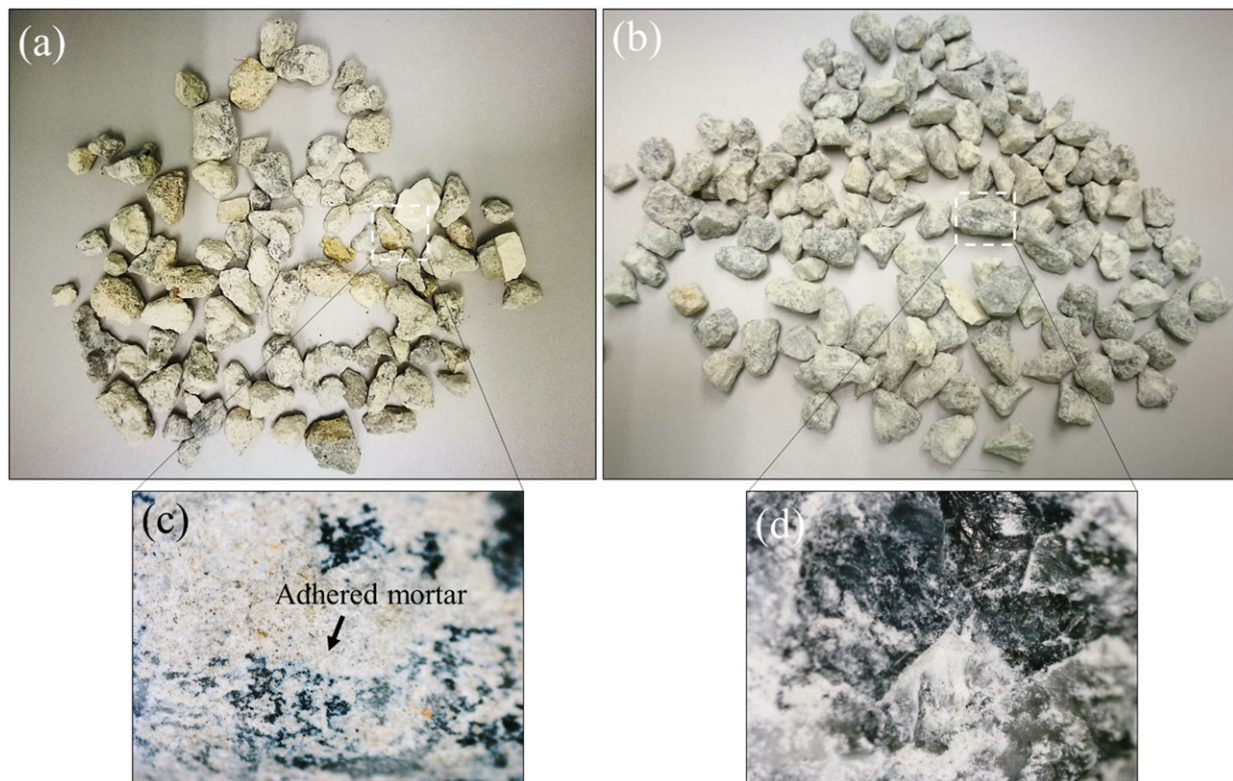


Fig. 1 (a) Recycled concrete aggregates, (b) granite aggregates, and magnified surfaces of (c) RCA and (d) natural granite aggregate. Reproduced from Yap, S.P., Chen, P.Z.C., Goh, Y., *et al.*, 2018. Characterization of pervious concrete with blended natural aggregate and recycled concrete aggregates. *Journal of Cleaner Production* 181, 155–165.

Table 2 Physical properties of recycled concrete aggregates and natural aggregates

Physical properties	Recycled concrete aggregates (RCA)	Natural aggregates	References
Bulk density (kg/m^3)	2330–2394	2620.1–2890	Katkhuda and Shatarat (2017); Yap <i>et al.</i> (2018); Arora and Singh (2018); Poon <i>et al.</i> (2004)
Porosity (%)	10.45	1.60	
Water absorption (%)	6.28–8.05	1.25–3.50	
Specific gravity	2.32	2.65–2.67	
Aggregate impact value (%)	5.28	1.67	
Aggregate crushing value (%)	24.5	15.4	
Los Angeles abrasion value (%)	10.30	10.17	

Table 2, the aggregate impact value, aggregate crushing value and Los Angeles abrasion value of RCA are much lower compared to normal aggregates. This indicates that RCA has a lower impact, crushing and abrasion resistance due the higher tendency of adhered mortar loss under different loadings. Hence, the existing mortar on RCA is always advised to be removed to reduce the discrepancy when conducting aggregate testing and concrete production.

Three common methods that are used to treat RCA is (i) Acid Treatment Method, (ii) Mechanical Treatment Method, and (iii) Thermal treatment method.

- (1) [Katkhuda and Shatarat \(2017\)](#) reported the procedures for acid treatment of RCA. The acid method involves soaking of RCA in acidic solution (range of acid concentration is 0.1–1 M) for 24 h. After 24 h of pre-soaking, the aggregates were washed in normal water to rinse off the adhered mortar and then the RCA is dried. In this treatment, the amount of mortar that remains adhered to the coarse aggregate was 2%. The water absorption recorded for untreated RCA is 4.58% and specific gravity is 2.58. The water absorption of acid treated RCA is 3.10%, which was 40% lower than that of untreated RCA and the specific gravity is 2.47, which was 5.4% higher than untreated RCA. The Los Angeles abrasion resistance of acid treated RCA concrete was found to be 29.5% of normal aggregate concrete, which was 1.5% better than the untreated RCA concrete.
- (2) [Babu et al. \(2015\)](#) reported the procedures for mechanical treatment of RCA. The RCA was treated in Los Angeles abrasion machine for 300 revolutions. Then the RCA was sieved in a 4.75 mm sieve. The amount of mortar that remains adhered to coarse aggregate after treatment is 5%. For this treatment method, the water absorption of mechanical treated RCA is 3.1%, 32.3% lower than that of untreated RCA and specific gravity is 2.54, 3.5% higher than untreated RCA. Compared to normal aggregate concrete, the bond strength of mechanically treated RCA is 11.37 MPa, which was 90% of the control sample.
- (3) [de Juan and Gutiérrez \(2009\)](#) reported the procedures for thermal treatment method. The RCA was first treated thermally at 500°C for 2 h in a furnace. After 2 h, the RCA is immediately immersed in water. The sudden change in temperature of RCA removes the mortar from the surface of aggregate. The aggregate was then given a little mechanical stress by using hammer, followed by washing, drying and crushing into required size. In this treatment, the amount of mortar that remains adhered to coarse aggregate is 11%, which is less effective compared to the other two techniques mentioned above. The water absorption of thermal treated RCA is 3.8%, 17.0% lower than that of untreated RCA and specific gravity is 2.51, 2.4% higher than untreated RCA.

From this review, the effective treatment methods of RCA are acid and mechanical treatment. However, the cost and time consumption required has rendered its use less economical. Thus, the justifications on the necessity to treat the RCA should be based on the economic benefits of applied RCA and improvement in efficiency.

Recycled Marbles

Marble is a metamorphic rock containing large amount of calcium carbonate and small amounts of silica, feldspar, iron oxide, mica and fluorine ([Topçu et al., 2009](#)). Recycled marbles (RM) is an inert material that is produced as the marble industrial by-product throughout sawing, sprucing, shaping and polishing of marble ([Fig. 2\(a\)](#)). Similar to other CDW, the common practice to handle the marble wastes is the disposal and storage in open areas, as shown in [Fig. 2\(b\)](#).

Marble wastes are available in the forms of marble dusts as well as marble fine and coarse aggregates ([Fig. 3](#)), depending on the sizes of the marble wastes. The marble dusts generally have particle size of $< 150 \mu\text{m}$, while the size of marble aggregates ranges between $150 \mu\text{m}$ and 20 mm. Marble dust is an inert powdered by-product from marble processing and these dust can make up to



Fig. 2 (a) Marble processing in factory; (b) Disposal of marble wastes in open areas. Reproduced from Li, L.G., Huang, Z.H., Tan, Y.P., Kwan, A.K.H., Chen, H.Y., 2019. Recycling of marble dust as paste replacement for improving strength, microstructure and eco-friendliness of mortar. *Journal of Cleaner Production* 210, 55–65.

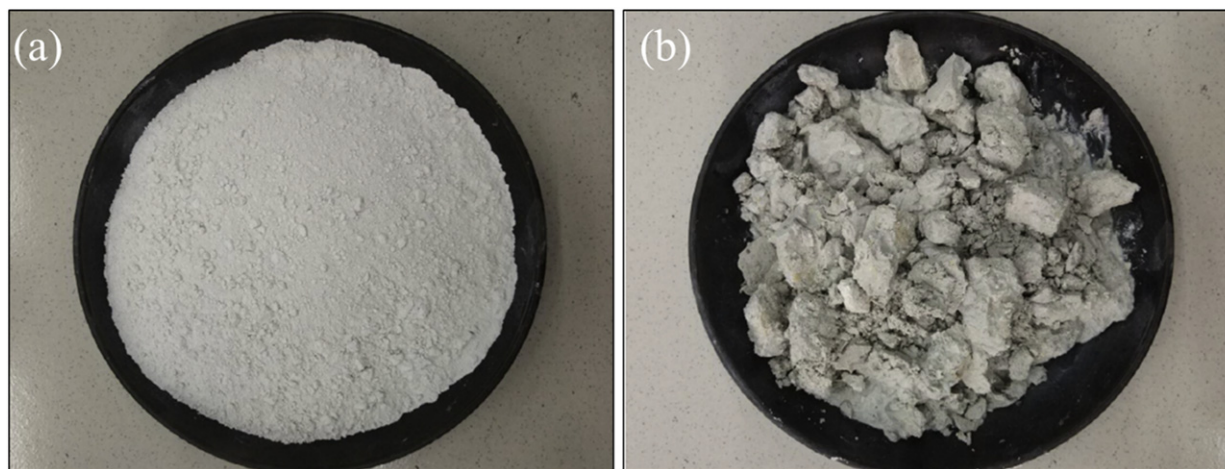


Fig. 3 (a) Marble dusts; (b) marble aggregates. Reproduced from Li, L.G., Huang, Z.H., Tan, Y.P., Kwan, A.K.H., Chen, H.Y., 2019. Recycling of marble dust as paste replacement for improving strength, microstructure and eco-friendliness of mortar. *Journal of Cleaner Production* 210, 55–65.

Table 3 Comparison of chemical compositions of marble wastes, natural aggregates and cement

Component	Marble waste (%)	Natural aggregates (%)	Cement (%)	References
SiO ₂	0.15–4.67	53.70	19.3–19.55	Kore and Vyas (2016); Topçu <i>et al.</i> (2009); Hebhouh <i>et al.</i> (2011); Belachia and Hebhouh (2018); Aruntas, <i>et al.</i> (2010)
CaCO ₃	98.67–99.05	–	–	
MgO	0.2–17.91	2.01	0.86–1.83	
CaO	33.12–54.86	4.83	61.39–63.56	
Fe ₂ O ₃	0.03–0.13	10.66	3.46–3.52	
K ₂ O	0.01	–	0.74–0.8	
Al ₂ O ₃	0.08–0.12	–	4.82–5.57	
SO ₃	0.04	–	2.76–2.91	
LOI	41.16–45.07	5.08	2.18–2.78	

2% of overall marble wastes. Marble dusts can be a reason of a heavy downside to the surroundings as these fine particles are released the atmosphere directly (Gurcharan and Madan, 2017). Among the marble wastes, marble dust (also called sludge, an agglomeration of water and very fine particles produced by cutting the stone) is the most widely studied alternative, primarily because it is quite versatile (André *et al.*, 2014). In some reports, marble fine aggregates were also considered as marble dusts, as both serve the same purpose as filler material in concrete. However, this article differentiates between the marble dust and marble fine aggregates because marble dusts are typically used as filler material to replace cement, while marble fine aggregates are substitution materials for sand. Meanwhile, there is little information on the potential use of larger marble waste as a coarse aggregate.

Table 3 shows the comparison of chemical compositions of marble wastes with natural aggregates and cement. The main components in marble wastes are calcites (CaCO₃), along with other minerals. It should be noted that there is a high amount of CaO in marble wastes (~33%–55%), which is comparable to cement. This is the reason why marble dusts are widely used as filler materials to replace cement in cement research, and this will be further discussed in Section “Concrete Properties Incorporating CDW”. Finally, the loss on ignition (LOI) in marble wastes are as high as 45% while both aggregates and cement have low LOI of > 5%. This phenomenon is due to the high carbonates content which is due to the dissociation of CaCO₃ and dolomite (CaMg(CO₃)₂) that partially transform themselves into carbon dioxide gas (CO₂) at temperatures higher than 750°C.

Meanwhile, Table 4 shows the physical properties of all forms of marble wastes. The noteworthy property is the lower abrasion resistance in recycled marble wastes compared to conventional aggregates, which will eventually result in lower mechanical properties of concrete incorporating recycled marble aggregates. However, the value remains acceptable as it is still lower than 50%, which is the maximum recommended for incorporation in structural concrete (André *et al.*, 2014).

Concrete Properties Incorporating CDW

Recycled Coarse Aggregates (RCA)

In most of the research on recycled coarse aggregates (RCA), there is a common observation obtained, which is the strength reduction in concrete with coarse aggregate replacement by RCA up to 100%. In the work done by Poon *et al.* (2004), the concrete

Table 4 Physical properties of recycled marble wastes

Marble wastes	Properties	Value	Comparison	References
Marble dust	Bulk density (kg/m ³)	2.684	–	Hebhoub <i>et al.</i> (2011)
	Porosity (%)	1.96	–	
	Water absorption (%)	0.39	–	
	Wear resistance (mm)	1.82	–	
	Impact resistance (cm)	40	–	
Marble coarse aggregate	Loose bulk density (kg/m ³)	1352	1350 (Granite aggregate)	André <i>et al.</i> (2014), Kore and Vyas (2016)
	Porosity (%)	49.7	50.1 (Granite aggregate)	
	Specific gravity	2.70	2.61 (Natural aggregate)	
	Water absorption (%)	0.05–0.66	0.54–1.08 (Natural aggregate)	
	Los Angeles abrasion value (%)	34.87–38.8	25.88 (Natural aggregate)	
Marble fine aggregates	Specific gravity	1.67	1.72 (Sea sand)	Belachia and Hebhouh (2018)

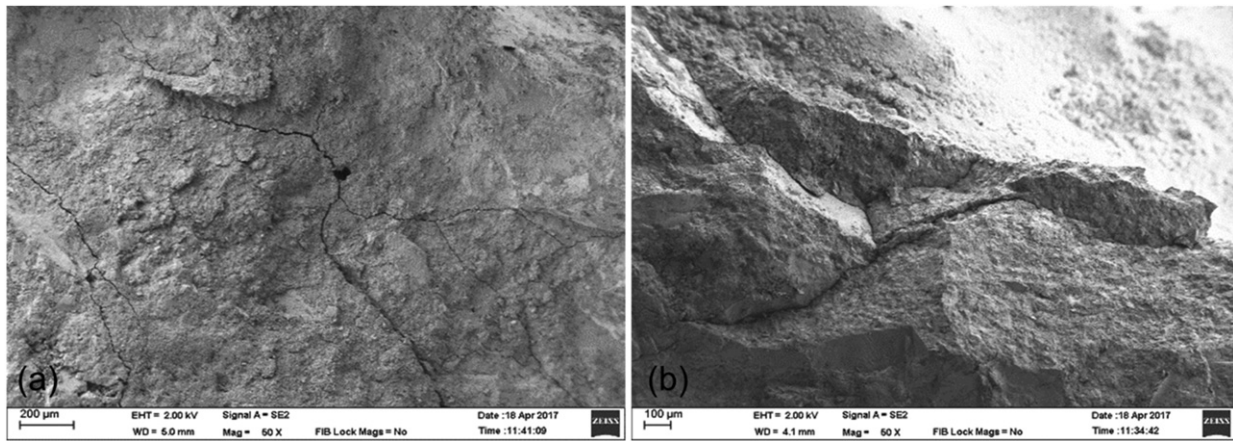


Fig. 4 Micrographs on crack propagations in (a) normal aggregate and (b) RCA fractured specimens. Reproduced from Yap, S.P., Chen, P.Z.C., Goh, Y., *et al.*, 2018. Characterization of pervious concrete with blended natural aggregate and recycled concrete aggregates. *Journal of Cleaner Production* 181, 155–165.

made with RCA shows up to 30% loss in compressive strength for 100% coarse aggregate replacement. For the strength reduction, contradict explanations had been proposed by different researchers. For instance, Barnhouse and Srubar (2016) proposed that the RCA consumed higher paste volume due to the adhered mortar which substantially reduced the strength of RCA concrete. On the other hand, Poon *et al.* (2004) explained the strength reduction was attributed to the poor bonding between aggregate and cement paste. Yap *et al.* (2018) has proven the latter was the contributor to the weaker mechanical properties in RCA concrete through microstructural characterizations. By referring to Fig. 4, both RCA and normal aggregate concretes showed different crack propagation paths. In RCA specimen (Fig. 4(b)), it was observed that the crack displays less branching, while failure plane of normal aggregate specimen showed more crack branching and direction diversion (Fig. 4(a)). A branched crack propagation often results in higher compressive strength concrete as more energy is required to cause failure.

In order to compensate the strength reduction, Etxeberria *et al.* (2007) suggested that for RCA replacement between 50%–100%, the water to cement ratio should be lowered by 4%–10% to obtain the same compressive strength as control concrete. Similar behaviors are also noticeable in tensile strengths of RCA concrete at which 10%–15% reduction in both splitting tensile and flexural strengths (Arora and Singh, 2018).

Other researches on RCA concrete can be summarized as below:

- According to the study from Yap *et al.* (2018), it was revealed that the modulus of elasticity of pervious concrete with RCA increases with higher RCA content. However, they explained that this result may not be convincing because when RCA content increases, lesser aggregate-cement paste bonding was found in RCA mixes compared to the normal aggregate mixes, and the increase in modulus of elasticity was due to the premature failure of RCA specimens under compression loading. The cause of the premature failure was suggested to be due to the preferred failure path along the adhered mortar as discussed before. On the other hand, RCA replacement showed positive impact on the concrete when mixes containing high RCA content showed lower brittleness ratios.
- In another study, Ajdukiewicz and Kliszczewicz (2002) reported that the bond strength of RCA can be more than the conventional concrete. In this study, it was found that when recycled aggregates from high strength concrete were used, the

compressive strength can be similar or even higher than for comparable normal. However, there are indication that the bond strength of natural aggregate were 9.4%–21.3% higher than RCA concrete (Pandurangan *et al.*, 2016). Such contradictions in results may have attributed to the type of bond test used. If the results are closely analyzed, it could be seen that the performance of RCA in bond tests is found to be good if pullout specimens are used for determination of bond strength. This is because the effect of adhered mortar and shape of RCA is not captured effectively in pullout tests (Pandurangan *et al.*, 2016).

- Furthermore, when 30% of natural aggregate was replaced with recycled coarse aggregate, it is found that there is no significant influence on the compressive strength. However, when the recycled coarse aggregate is used to fully replace the natural aggregate, the compressive strength for the aforementioned mix was only 30% of the 100% natural aggregate mix. As for the 28-days compressive strength of concrete replaced with 100% of recycled coarse aggregate, it has the strength of 77% conventional concrete (Pandurangan *et al.*, 2016).

Recycled Marbles

As mentioned afore, the researches on recycled marbles mainly focus on the recycling of marble dust as marble dust are more versatile as a filler material to replace cement, due to the high CaO content in marble wastes. In other hand, cement replacement is the most economical and sustainable approach to recycle the wastes materials as cement is the most expensive component in concrete, as well as the cement hydration process is the main contributor of carbon dioxide gas. Based on the literature, the optimum content of marble dust in concrete/mortar is up to 15% without showing any depreciation in concrete strength (Gurcharan and Madan, 2017). Some examples of the research on recycling marble dusts to replace cement are:

- Topçu *et al.* (2009) investigated the potential of marble dust as filler materials in self-compacting concrete and they concluded that maximum cement replacement up to 200 kg/m³ with marble dust was feasible, without affecting the fresh properties of self-compacting concrete. Also, the filling effect of the marble dust showed good potential to reduce the void content in the concrete.
- In addition, in the asphaltic concrete, the use of marble dust also showed positive effects in the design of bitumen mixes by Marshall Method (moisture susceptibility, static creep, flexural fatigue, and wheel-tracking tests) as compared to different fillers such as fly ash and granite dusts.

Meanwhile the examples of researches on the recycling marble wastes to replace concrete's coarse and fine aggregates are shown below:

- Hebhouh *et al.* (2011) reported the high potential of using wastes from marble as an alternative of natural aggregates (coarse and fine) in concrete production. Experimental research was designed on three groups of concrete mixtures: (i) fine aggregate substitution, (ii) coarse aggregate substitution and (ii) substitution of both aggregates. The outcomes showed that the mechanical properties of concrete samples were good and utilization of the marble wastes were found to adapt to the concrete production standards.
- Results from Kore and Vyas (2016) showed that, marble aggregate can be used to improve the mechanical properties of conventional concrete mixes (up to 80% replacement of coarse aggregate) with no adverse effect against acid attack. However, one of the side effects of incorporating recycled marble aggregates was a 26%–83% hike in permeability/depth of water penetration.
- In another study from André *et al.* (2014), replacement of coarse aggregates with marble aggregates produced comparable results in terms of workability, density, water absorption, carbonation depth but the incorporation of coarse marble aggregates in the mixes resulted in a significant increase of the chloride migration coefficient. The low alumina percentage of these aggregates may be the primary cause, as this compound promotes the formation of tricalcium aluminate, which favors the fixation of the chloride ions.
- Finally, on recycled marble fine aggregates, the study conducted by Belachia and Hebhouh (2018) concluded that recycled marble sand retarded the hardening at a young age. Since the sand is coarse, it does not return quickly in the hydration reaction of the cement.

Applications of CDW (Structural and Non-structural)

Based on the discussions in the Section "Concrete Properties Incorporating CDW", it was known that CDW can be converted into recycled concrete aggregates (RCA) as well as recycled marbles (RM) in the forms of marble dusts, marble coarse aggregates and marble fine aggregates. RCA can be used to fully replace conventional natural aggregates, however, the replacement may be associated to depreciation of concrete properties. Meanwhile, marble dusts had been utilized as fillers to replace cement, up to the amount of 15%. Finally, both marble fine and coarse aggregates had been proven as good substitution of conventional concrete aggregates without significant effects on strength, durability and workability. Judging from these advantages, both RCA and RM had been applied in different structural and non-structural applications, with the following examples:

- Due to the lower strength in RCA concrete, RCA mainly finds its applications in the pavement of roads, landfills and low grade concrete structures (Pandurangan *et al.*, 2016);
- Also, since the pavement blocks which requires low strengths, another famous non-structural application of RCA is as pavement blocks and pedestrian paths (Poon and Chan, 2006);

- For marble dusts, there is a way to reduce the cost and carbon emissions of cement, at which marble dust is mixed in Portland cement clinker at different ratios and the results were positive that 10% of marble dust did not affect the setting time, specific surface area but higher compressive strength. This eventually reduce the environmental problem directly related to human health and wellbeing (Aruntas, *et al.*, 2010);
- Buyuksagis *et al.* (2017) examined the accessibility of marble powder additional substance at numerous proportions instead of dolomite, which is the crude material in glue mortars of insulation board. The employment of marble powder with dolomite was also investigated economically and it had been observed that it is economical advantageous to form price calculations and in accordance with the relevant EN standards;
- Since the values obtained in the Los Angeles abrasion test are within the limits as per BIS: 2386 (part IV) – 1963, the marble aggregates can be used in concrete pavement works (Kore and Vyas, 2016).

The applications of RCA and RM are not limited to the applications described above. It is believed that with the proper design and treatment methods, the CDW can be utilized in construction industry, to produce green and sustainable concrete products, which will then reduce the carbon footprints of the concrete produced.

See also: Evaluating the Sustainability Performance of Building Systems and Technologies for Mainstreaming Sustainable Social Housing in India. Life Cycle Assessment Methods and Procedures and Their Role in Measuring the Sustainability Component of a Construction Technology. Sustainability of Advanced Materials in Construction

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Recycling of E-Waste

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Introduction

Electronic waste, commonly known as 'E-waste', is a rapidly emerging waste stream in the world today. E-waste is also known as 'Waste Electrical and Electronic Equipments' or WEEE. As the term itself suggests, E-waste primarily refers to all the end-of-life equipments that utilize electricity for functioning. With growing urbanization and modernization processes, our dependence on electrical and electronic equipments is on a constant rise which, subsequently, results in a rapidly emerging market for these equipments. Once obsolete, these electrical and electronic equipments become E-waste or WEEE, one of the major global apprehensions in the present scenario. There are a number of reasons which calls for effective management and recycling of E-waste as an immediate intervention. For instance, a considerable portion of E-waste is disposed of in uncontrolled landfills in the developing world (mostly in middle and low-income countries) and informal E-waste recycling activities are practiced extensively (Ikhlaiel, 2018). The informal E-waste recycling sites are often the areas of uncontrolled pollution of several kinds – be it air, water, soil or noise pollution (Borthakur, 2014).

In the informal recycling sites, a number of hazardous practices are prevalent without any health and safety measures towards the workers and the environment. The treatment of waste printed circuit board (WPCB) in the informal E-waste recycling sites provides for a good case here. For leaching of precious metals from WPCB, cyanide (an exceedingly toxic chemical accountable for endangering human health and the environment) is largely used owing to its advantages in the form of low cost, extremely efficient recovery and simple operation (Lu and Xu, 2016). A number of studies have recognized the human health and environmental effects of E-waste recycling in developing countries. In countries like India and Southern part of China, high level of environmental emissions from persistent organic pollutants (POPs) and heavy metals are constantly being reported (Yoshida *et al.*, 2016).

Rapid technological advances and innovations make several older electronics out-of-date way before the end of their actual useful or functional life. As the lifetime of electrical and electronic equipments (EEEs) is becoming more and more shorter during the recent decades, E-waste recycling has become a major concern worldwide (Huang *et al.*, 2016). One excellent example in this context is the intensely progressing light-emitting diode (LED), liquid crystal displays (LCDs) panels and plasma display panels (PDPs) which replaced a considerable portion of cathode ray tube (CRT) sets in the recent times (Yao *et al.*, 2018). This is responsible for the generation of millions of waste CRT units. The study by Yao *et al.* (2018) further states that the data from the E-waste collection and pretreatment market specify approximately 50,000–150,000 million tons/year of waste CRTs presently collected in Europe alone, and this quantity is not anticipated to reduce in the near future. As argued by Janse *et al.* (2010: 495):

The consumer electronics (CE) industry has high turnovers and a rapidly growing demand. Electronic devices and gadgets are becoming “must-haves” for an ever growing number of consumers. CE is a fast clockspeed sector, i.e., new products are being introduced at a high rate [...] Accompanying the frequent introduction of new products is the rise of E-waste [...] To dump perfectly good products means throwing away value, which now WEEE gives the chance to manufacturers and importers to recover. This could be the clue to competitive edge in this highly competitive industry, with short lifecycles, steep price declines, and boiling pressure on profit margins.

The material composition of E-waste is diverse and thus, requires a comprehensive recycling effort. There are a range of valuable, critical and hazardous substances present in E-wastes which necessitates intense recycling towards avoiding health and environmental concerns in one hand and environmental problems accompanying the new materials in terms of their extraction and refining processes on the other hand (Cucchiella *et al.*, 2015). E-waste consists not only of toxic substances in the form of heavy metals such as lead, mercury, cadmium, but also generates added toxins, for example, Polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) during its informal management such as inappropriate acid leaching, open burning etc., in backyard or low-technology recycling initiatives (Zeng *et al.*, 2017a,b). Particularly in countries like India, China, Pakistan, the Philippines, Vietnam, Ghana, and Nigeria, acid extraction is widely practiced to retrieve precious metals such as platinum, gold, silver and palladium from Printed Circuit Boards (PCBs) and wires are charred in open spaces in order to recover copper and remove plastic (Ikhlaiel, 2018). Such E-waste recycling and dismantling activities are intentionally or unintentionally encouraged in developing countries including China, India or Pakistan owing to their quest for economic growth and craving for raw materials (Huang *et al.*, 2016). Further, the occurrence of heavy metals in E-waste is not only a cause of soil pollution, but also creates intense water pollution. For instance, heavy metals present in soil can find its way to the nearby waterbodies through rainfall and have the potential to also contaminate groundwater by means of leaching particularly under acidic conditions (Wu *et al.*, 2015).

Although wealthy countries do not exclusively generate the E-waste, these countries are responsible for substantially contributing to the E-waste apprehensions in the middle to low income countries owing to the regulatory uncertainties that permit export of EEEs for reuse, notwithstanding the actual product functionality (Heacock *et al.*, 2016). Most of the developed countries

have well-established all-inclusive E-waste management programmes, nevertheless, in the expense of the deviation of huge quantities of E-waste to the developing world towards appropriate disposal in their own countries (Li *et al.*, 2019). Even international legislations such as the Basel Convention of 1989 (which has been ratified by 181 countries) has been struggling hard to regulate the illegal export of E-waste from the developed to the developing countries (Orlins and Guan, 2016). As argued by Dias *et al.* (2019):

In the current ever-growing population (and ever-growing consumption per capita), improving resource efficiency is crucial. In addition to consumption reduction, other actions towards waste minimization such as reuse of products and recycling have an important role in contributing towards a sustainable resource management. For instance, in Australia, the recent creation of the regulatory framework and the national recycling scheme (NTRCS) have been able to divert significant amounts of E-waste from landfill. However, due to the lack of a downstream recycling industry and the shortfall of a mechanism to promote downstream recycling, the majority of the E-waste collected through the scheme is exported for processing overseas.

Similar to Australia, several other wealthy countries such as the USA, Canada and the European Union member states divert large volumes of E-waste to the developing countries. The imported E-waste feeds the informal recycling sites in the developing world (Borthakur, 2015). Considering the ever-increasing volume of E-waste in both the global north and global south, the toxic trade of it, the possible human health/environmental repercussions and the potential of extracting valuables from the waste, it is becoming increasingly essential to ensure its appropriate management practices and recycling is a core starting point here. Accordingly, in this chapter, we attempt to analyse the recycling of E-waste in terms of its significances and possible challenges. Environmental, human health and economic reasons for E-waste recycling has been evaluated. The processes of extraction of precious, valuable and rare earth metals from E-waste have been tabulated in details. The purpose is to provide the readers a comprehensive overview of the current E-waste recycling scenario and the future perspectives towards tackling this toxic category of waste in both resource and environment friendly ways.

Significance of E-Waste Recycling

Environmental and Human Health Reasons

The current management system of E-waste, especially in the developing countries, has enormous environmental and human health repercussions (Borthakur, 2016). It is well documented that in spite of the gradual progress of the legal recycling systems in the developing world, informal recycling facilities are still largely responsible for collecting and recycling of E-waste (Yoshida *et al.*, 2016). The rudimentary recycling and disposal practices can result in high occupational and incidental exposure to a range of hazardous substances, and generate locally severe environmental contamination (Labunska *et al.*, 2015). For instance, the heavy metals present in E-waste calls for special attention among the various toxic substances omnipresent in this toxic waste category owing to their non-biodegradability, mobility and toxicity (Wu *et al.*, 2015). As argued by Zeng *et al.* (2016):

The countries most affected by informal e-recycling are China (Guiyu and Taizhou), India (Bengaluru and Delhi) and some African countries (Lagos in Nigeria, Accra in Ghana), where E-waste has been recycled or disposed with little or no regulation, using less advanced technology. Heavy metals cannot be degraded into less hazardous end products, which is different from organic pollutants with biodegradable capability. Heavy metals derived from electronic waste (E-waste), such as, lead (Pb), cadmium (Cd), chromium (Cr), manganese (Mn), nickel (Ni), mercury (Hg), arsenic (As), copper (Cu), zinc (Zn), aluminum (Al) and cobalt (Co), differ in their chemical composition, reaction properties, distribution, metabolism, excretion and biological transmission.

The persistent organic pollutants (POP) present in E-waste are of no less concern. The regularly occurring POP in electrical and electronic equipments primarily consists of: polybrominated diphenyls, brominated flame retardants (polybrominated diphenyl ethers), polychlorinated biphenyls, dibrominated diphenyl ethers, polybrominated or polychlorinated dioxins and dibenzofurans dioxins, perfluoroalkyls and hexabromocyclododecanes (Grant *et al.*, 2013). All these toxins are of immense concern from the human health and environmental protection's perspectives. For instance, polycyclic aromatic hydrocarbons (PAHs) in the form of brominated flame retardants (BFR) and polychlorinated biphenyls (PCB) have the potential to accumulate in both soils and sediments and thus become obtainable for the uptake of both aquatic and terrestrial organisms when released into the environment adjacent to an E-waste handling facility (Labunska *et al.*, 2015). As put forth by Man *et al.* (2013):

Polycyclic aromatic hydrocarbons (PAHs) are usually produced via the incomplete combustion of organic substances and comprised of a diverse group of organic compounds [...] Polycyclic aromatic hydrocarbons in the environment have drawn much attention due to their toxicity and potential carcinogenic effects on humans. Soil serves as an enormous sink for the accumulation of organic contaminants and may allow the entry of PAHs into food chains. A number of studies have focused on the variation of PAH concentrations in different soil types. In general, it has been found that PAH concentrations in soil increase with the degree of anthropogenic impact, in both industrial and domestic land use.

Luo *et al.* (2015) argue that during various E-waste recycling efforts such as the burning of E-waste, a diverse range of toxic contaminants (including PAHs) are released into the immediate environment exposing the residents (residing in the vicinity of E-waste recycling facilities) and unprotected E-waste workers to these hazardous pollutants. For instance, polychlorinated dibenzofurans, polychlorinated dibenzodioxins and dioxin-like polychlorinated biphenyls are typically the POPs which are

Table 1 Toxic substances in E-waste and their health impacts

<i>Toxic substances</i>	<i>E-waste source</i>	<i>Health impact</i>	<i>References</i>
Cadmium (Cd)	E-waste pollution site	Increased risk of adverse birth outcomes in a sex-dependent manner	Zhang <i>et al.</i> (2018)
Lead (Pb)	E-waste	Cardiovascular	Lu <i>et al.</i> (2018)
Lead and cadmium exposure	E-waste	Hearing loss in children	Liu <i>et al.</i> (2018)
Polybrominated diphenyl ethers	E waste	Adverse birth outcomes	Li <i>et al.</i> (2018)
Pb-exposed	E-waste-recycling area	Memory T cell development in preschool children	Cao <i>et al.</i> (2018)
Lead	E-waste recycling area	Decreased olfactory memory in children	Zhang <i>et al.</i> (2017a)
Lead (Pb) and cadmium (Cd)	E-waste recycling area	Effects on the immune system	Zhang <i>et al.</i> (2017b)
Cadmium exposure in preschool children	E waste	Decreased lung function	Zeng <i>et al.</i> (2017a,b)
Exposure to multiple metals and metalloids in E-waste	–	Decreased vaccine antibody titers	Lin <i>et al.</i> (2017)
Lead (Pb)	E-waste	Changes in blood morphology, hemoglobin synthesis and CR1 expression	Dai <i>et al.</i> (2017)
Lead	–	Natural killer cells in children	Zhang <i>et al.</i> (2016)
Heavy metals derived from electronic waste E-waste	Heavy metals derived from electronic waste E-waste	Ranging from minor upper respiratory irritation to chronic respiratory, cardiovascular, nervous, urinary and reproductive disease,	Zeng <i>et al.</i> (2016)
Heavy metals	E waste	Cancer risk	Huang <i>et al.</i> (2016)
Various metals and organohalogen compounds	Open burning of electronic waste E-waste	–	Fujimori <i>et al.</i> (2016)
Polychlorinated biphenyls (pcbs), polybrominated diphenyl ethers (pbdes) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs)	E-waste dismantling sites;	Thyroid hormones changes	Xu <i>et al.</i> (2014)
Mercury (Hg)	–	Hair mercury increase	Ni <i>et al.</i> (2014)
Heavy metals (Cd, Pb, Cu, Zn, and Ni)	E-waste	Potential cancer risks	Zheng <i>et al.</i> (2013)
Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs)	–	DNA damage	Alabi <i>et al.</i> (2012)

Source: Prepared by the authors (2019).

released during dismantling, incineration and smelting operations (Grant *et al.*, 2013). These contaminants have the potential to pass in to the food chain resulting in extended and unescapable exposure to people who resides in the neighborhood of an E-waste recycling area (Labunska *et al.*, 2015) (Table 1).

Economic Incentives

The limited quantity of matter, especially metals, on earth despite the population increase and yearning of humans to trail western consumption patterns will inescapably result in scarce primary resources and plentiful of urban wastes, calling for the harvest of compounds from anthropogenic waste (Billard, 2019). E-waste is known as a resource worldwide on account of the potential towards recovery of valued materials such as copper, iron, silver, gold, aluminum and several rare earth metals (Heacock *et al.*, 2016). Retrieval and recycling of these valuable metals from E-waste has, to a certain extent, the potential to lessen the overall global demand for new metal production and aid in decreasing the quantity of materials discarded in the landfills (Kumar *et al.*, 2017). For instance, the alteration of E-waste into a valued nanomaterial is considered as a sustainable and effectual method towards ensuring a circular economy (Liou and Jheng, 2018). Nevertheless, electronic and electrical equipments are usually not designed either towards their safe disposal or effectual recovery of the valuable materials (Heacock *et al.*, 2016). A number of conventional methods are regularly used to treat E-waste which comprises of repair, reuse and the reduced discarding of the residues by landfilling and incineration (Liou and Jheng, 2018). There already exist potentially wealthy reserves of secondary materials through major possession of EEEs in the industrialized nations (Pierron *et al.*, 2017). There are systematic methods in place in these countries which have the potential to ensure maximum resources recovery. Most of the E-waste in the developing world, on the other hand, is presently collected by individual collectors and recycled either by individuals or in small scaled facilities (Yoshida *et al.*, 2016).

Recycling of metals present in electrical and electronic equipments has the potential to decrease the necessity for mining of virgin materials (Heacock *et al.*, 2016). Here comes the concept of urban mining (UM) which could immensely contribute to the economy of the world today. Urban mines can acquire metals from waste products and thus, considered as an ideal alternative towards gathering raw metals which are else restricted in availability (Jo *et al.*, 2018). As Pierron *et al.* (2017) argue, “Urban mining

Table 2 Recovery of metals from E-waste

Source/type	Metal recovery/leaching	Processes	Recovery	Reference
Light-emitting diodes	Rare metals (Ga, In)	Combination of pyrolysis, physical disaggregation methods and vacuum metallurgy separation	Recovery efficiencies of 93.48% and 95.67%	Zhan <i>et al.</i> (2015)
Soil contaminated by E-waste	PBDES/Pb/Cd-contaminated electronic equipments	Elevated temperature (50 degrees c) in combination with ultrasonication (40 khz, 20 min) at 5.0 ml l ⁻¹ sunflower oil and 2.5 g l ⁻¹ carboxymethyl chitosan	Pb, and Cd were approximately 94.1, 93.4, 94.3, 99.1, 89.3, and 92.7 %	Ye <i>et al.</i> (2015)
Waste printed circuit boards (wpcbs)	Copper, nickel and iron	Cupric chloride solutions (hcl-cucl ₂ -nacl	98%) for copper, nickel and iron	Yazici and Deveci (2015)
Chloride solution of E-waste	Cadmium	Cyanex 923 impregnated amber lite xad-7hp resin	–	van Nguyen <i>et al.</i> (2015)
Gan based power device and led	Gallium	Acidic leaching	–	Swain <i>et al.</i> (2015)
ICT	Copper	Ammonia-based solution	90%	Sun <i>et al.</i> (2015)
Computer printed circuit boards	Cu-Zn-Ni	Bleaching process using ferric sulphate generated by leptospirillum ferriphilum dominated consortium	94.08% Cu, 99.80% Zn and 97.99% Ni extraction.	Shah <i>et al.</i> (2015)
Waste LCDs	Indium (in)	Sing various solid:liquid (s/l) ratios and solvents (acid mixtures)	60%	Savvilitidou <i>et al.</i> (2015)
Low-grade electric and electronic wastes	Copper	Eached in ammonia–ammonium sulphate solution	90%	Rudnik <i>et al.</i> (2015)
Coarsely ground printed circuit boards	Copper	Thermophilic bacteria using rotating-drum reactor	85%	Rodrigues <i>et al.</i> (2015)
Waste printed circuit boards	Copper	Bioleaching by acidithiobacillus ferrooxidans strain z1	81.43%	Nie <i>et al.</i> (2015)
Li-ion batteries	Mn(ii), co(ii), ni(ii) and li(i)	20% acorga m5640 in kerosene with agitation for 5 min at 30 °c a	91.2% Mn(ii), 89.3% Co(ii) and 95.6% Ni (ii)	Nayl <i>et al.</i> (2015)
Electronic scrap materials (esm)	Gold	Bioleaching	30%	Natarajan and Ting (2015)
Waste printed circuit board	In, lead, zinc and aluminum	Acid leaching–electrowinning process	98.66% for cu, 91.08% for sn, 91.25% for zn, 78.78%	Guo <i>et al.</i> (2015)
Circuit boards	Copper	Supercritical carbon dioxide	90% of the cu	Calgaro <i>et al.</i> (2015)
Discarded mobile phone	U and Ni	Acidithiobacillus ferrooxidans. Bioleaching	100% extraction of cu and ni	Arshadi and Mousavi (2015)
Cigs photovoltaic cells	Indium	Acid-resistant nanofiltration with liquid-liquid extraction	95%	Zimmermann <i>et al.</i> (2014)
Printed circuit boards	Palladium	Novel non-acid process	99.5%	Zhang and Zhang (2014)
Waste printed circuit boards (WPCBS)	Copper and other metals (i.e., Ni, Ag and Pd)	Acidic ferric sulphate solutions	(≥99% Ag/Pd)	Yazici and Deveci (2014)
Waste printed circuit boards		Acidithiobacillus ferrooxidans	Cu (96.8%), Zn (83.8%), and al (75.4%)	Yang <i>et al.</i> (2014)
Brass from waste electrical and electronic equipment	Copper and zinc	Leaching by sodium persulfate solution	–	Popescu <i>et al.</i> (2014)
Printed circuit boards	Zinc, copper, lead, nickel, cadmium and chromium	Bioleaching	48% for Zn, 93%. Cd, 48.5% and 53% for copper and nickel	Karwowska <i>et al.</i> (2014)
Recycling industry electronic waste	Cu, Zn, Ni, Cd, Al, Cr, Pb	Bioleaching by consortium of sulfobacillus thermosulfidooxidans and thermoplasma acidophilum	–	Ilyas <i>et al.</i> (2014)
Electronic waste material	Copper	Bioleaching mesophilic acidithiobacillus thiooxidans.	(60%)	Hong and Valix (2014)
Spent lithium-ion batteries	Li, mn, co, and ni	Hydrometallurgical extraction of metals	90%	Vieceli <i>et al.</i> (2018)
E-waste	Copper, iron and lead	Using citrate solutions	90%	Torres <i>et al.</i> (2018)

Table 2 Continued

Source/type	Metal recovery/leaching	Processes	Recovery	Reference
Co-fired ceramic an E-waste	Silver	Wet chemical reduction	–	Swain <i>et al.</i> (2018)
Electric and electronic equipment	Ga, Ge, In and Sn	Secondary copper smelting	–	Avarmaa <i>et al.</i> (2018)
Lcd	Indium	Non-crushing leaching method	96.80%	Zhang <i>et al.</i> (2017)
Printed circuit boards (pcbs)	Pb, Sn, Zn, Cu, Al	Bioleaching	85.23% Zn, 76.59% Cu and 70.16% Al	Xia <i>et al.</i> (2017)
Electronic waste	Gold	Moderate thermophiles	90%	Wu <i>et al.</i> (2017)
		Hydrometallurgical leaching solution through spontaneous reduction by polyaniline		
Aluminum electrolytic capacitors	Aluminum and Iron	Involving heating treatment, crushing, sieving, and magnetic separating	96.52% and 98.68% of aluminum and iron	Wang and Xu (2017)

Source: Prepared by the authors (2019).

is a construct of anthropogenic resources between landfill mining and recycling to integrate secondary material flows and stocks into the Circular Economy". The term primarily represents the methodical recycling and reuse of anthropogenic resources especially from the urban areas and thus, contains all variants of anthropogenic stocks in the form of buildings, landfills, infrastructure, emissions, products and industries (Avarmaa *et al.*, 2019). It is responsible for recovering the metal components from products that are generally thrown away as a part of people's everyday lives and subsequently refined these components into raw materials (Jo *et al.*, 2018). Owing to its utility prospects, urban mining is developing as a significant substitute towards collecting natural resources (Jo *et al.*, 2018). As put forth by Zhang *et al.*, (2019: 210):

Urban Mining (UM) concerns all the activities and processes of reclaiming compounds, energy and elements from products, buildings and waste generated from urban catabolism" [...] Among various categories of urban mines, personal electronics represent a typical, high-tech consumer device having a short lifecycle (usually less than 5 years) and containing substantial contents of valuable materials. Unused personal electronics are inclined to become idle or be discarded carelessly because of their relatively small size, making them constitute an important category of urban mines in recent years.

It is widely accepted that E-waste possibly releases polyhalogenated organic compounds and toxic metals, its landfilling and incineration methods cause environmental contamination and health menaces and thus, a feasible longstanding resolution is the exploitation of resources retrieved from this category of waste to initiate a circular economy (Liou and Jheng, 2018). Accordingly, urban mining has risen as an essential concept amongst industrialists, environmentalists, businesses and politicians (Avarmaa *et al.*, 2019). The waste printed circuit boards (WPCBs) found in all electrical and electronic equipments, which are responsible for providing the interconnection between hardware and software, are a good example here. Due to the presence of the precious metals, it is considered as the utmost valued components in E-waste (Lu and Xu, 2016). As argued by Tuncuk *et al.* (2012):

[The] WPCBs, which are resource-rich, are generally referred to as "urban mines". To illustrate, printed circuit board (PCB) of a PC can contain up to 20% Cu and 250 g/ton Au, which are significantly high i.e., 25–250-fold for gold and 20–40-fold for copper when compared with gold ores (~1–10 g/ton Au) and copper ores (~0.5%–1% Cu), respectively. Recycling turns WEEE into a secondary resource allowing the recovery and reuse of metals and non-metals contained and mitigating the environmental impact of WEEE.

Although the techniques for the recovery of the base metals from WPCBs are considered as mature, retrieval of precious metals from the same is still inappropriate in practice (Lu and Xu, 2016). As further put forth by Lu and Xu (2016), currently, the WPCBs with high concentration of expensive metals such as gold, silver, platinum, palladium etc., are the key target objects and thus, are recycled through unregulated and crude methods such as open acid washing triggering grave human health damage and environment contamination. Accordingly, it is essential to ensure recovery methods for precious and valuable metals with least repercussion to the environmental and human health. Further, it is also essential to understand consumers' E-waste disposal behavior in terms of their socio-cultural, environmental and economic considerations in order to ensure maximum E-waste recycling towards extraction of majority of the valuable and precious metal components (Borthakur and Govind, 2017).

Recovery of Metal Components From E-Waste

We have already discussed in the previous sections the significance of recovery of metals in the form of precious, valuable and rare earth metals from E-waste. There are a number of studies carried out by diverse research groups across the globe to address the recovery processes to ensure optimum response. Table 2 summarizes some of these processes and their recovery potential of metals from E-waste.

Conclusions

With growing urbanization and modernization processes, our dependence on electrical and electronic equipments is on a constant increase giving rise to a rapidly emerging market for these equipments. As these equipments become obsolete, they contribute to one of the most hazardous waste streams in the world i.e., E-waste. There are a number of reasons which calls for effective management and recycling of E-waste as an immediate intervention. For instance, the material composition of E-waste is diverse (consisting of precious, rare earth and valuable metals along with heavy metals and POPs) and thus, requires a comprehensive recycling effort. In the informal E-waste recycling sites, a number of hazardous practices are prevalent without any health and safety measures towards the workers and the environment. Thus, the current management system of E-waste, especially in the developing countries, has enormous environmental and human health repercussions. The heavy metals and POPs present in E-waste especially aggravate the environmental and human health concerns. There are further concerns about the rapid technological advances and innovations make several older electronics out-of-date way before the end of their actual useful or functional life. This is responsible for generating more and more quantity of E-waste with every passing year.

Recycling of E-waste is able to attain considerable attention during the last decade. As mentioned in the previous sections, one primary reason for this being the fact that, the quantity of E-waste generated is increasing all over the globe, while E-waste management practices are still at a very primitive stage. For instance, in most of the developing countries, the recycling efforts are still dominated by the informal sector with intense environmental and human health repercussions. Developing countries are in a better position in terms of E-waste recycling, however, they are always accused of encouraging the illegal trade of E-waste to the global south. Nevertheless, there are a number of E-waste recycling enterprises which are able to work towards responsible and sustainable disposal practices. These organizations have channelized their work efforts towards different directions and participate in different capacities towards E-waste recycling. They may participate in E-waste recycling as a non-profit organization or as a producer responsibility organization or have certain other roles. Recupel, Belgium, for instance, is a non-profit association responsible for 'organizing the collection and processing' of discarded electronic appliances and light bulbs. There are a number of such efforts in the developed world.

The processes of recovery of valuable metals from E-waste have also found significant attention in the recent past. We have tabulated a few of these efforts in our chapter. These processes are essential to ensure the maximum extraction of precious/valuable/rare earth metals from E-waste, popularly known as 'urban mines'. Nevertheless, we argue that as a waste category which gained attention only in the recent decade, it is essential to continue studying the E-waste streams across the globe and formulate policy responses to address this stream of waste accordingly.

See also: A Review on Utilization of Electronic Waste Plastics for Use Within Asphaltic Concrete Materials: Development, Opportunities and Challenges for Successful Implementation. Metallic Materials From E-Waste. Waste Printed Circuit Board (WPCB) Recovery Technology: Disassembly and Desoldering Approach

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Recycling of Flax Fiber Towards Developing Biocomposites for Automotive Application From a Life Cycle Assessment Perspective

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Introduction

Due to their high stiffness, strength, and ease of shaping, fiber reinforced polymers (FRPs) are attractive alternatives to steel and several nonferrous metals for a wide range of applications, including automobiles, shipbuilding, circuit boards, construction materials, and household equipment. However, due to the increasing severity of global environmental issues, such as climate change and fossil fuel depletion, several drawbacks of conventional FRPs are apparent because glass fiber, the major enhancement material, is produced through the material mixture input and causes intense energy demand.

To solve the sustainability challenges of the conventional glass fiber, a natural way is to shift to renewable sources for fiber production. For this purpose, plant fibers have been extensively investigated as a renewable alternative to traditional glass fiber reinforcement. Plant fibers also help circumvent the problem of glass fiber incineration. Plant fibers are combustible, and the released energy from combustion can be recovered. For application in the transport sector, the lower density of plant fibers ($\sim 1.5 \text{ g cm}^{-3}$) compared with glass fibers ($\sim 2.5 \text{ g cm}^{-3}$) is attractive: Plant fibers allow to produce lightweight structures and subsequently incur less fuel consumption in vehicle use. Thus plant fibers (such as flax, hemp, and jute fibers) are considered to be a feasible replacement for glass fibers. Currently, Plant Fiber Reinforced Polymers (PFRPs) only encompass $\sim 1.9\%$ of the total FRP market, compared with an 87% share for Glass Fiber Reinforced Polymers (GFRPs) (Shah, 2013). However, the market for PFRPs is strongly expected to grow. It is forecasted that by 2020, plant fibers together with other type of fibers derived from biobased sources will represent up to 28% of the total market of reinforcement materials (Yan *et al.*, 2014). PFRPs have already gained universal acceptance in the production of interior parts for the automotive industry (Koronis *et al.*, 2013). In fact, 95% of the commercial applications of PFRPs are currently for components in secondary/tertiary structures in the automotive industry, for example, interior components such as door panels (Shah, 2013). Therefore, PFRPs are expected to sustain some degree of loading or provide functional properties similar to those of components manufactured using traditional composites, for example, GFRP. Flax fibers are the most widely used plant fiber for composite reinforcement due to its exceptional mechanical properties (Shah, 2013). With wide availability, low cost, low density, highly specific properties, and eco-friendly image, flax fibers have been portrayed as prospective substitutes for the traditional composite reinforcements, specifically E-glass (Yan *et al.*, 2014).

To compare flax FRPs with GFRPs, the life cycle assessment (LCA) method can be applied to provide a detailed analysis in terms of environmental impacts. Current LCA studies on flax FRP are generally based on case studies with a predefined structure, and the designs of the flax FRPs are configured based on certain criteria to maintain a similar functionality with the GFRPs. For example, Boland *et al.* (2016) applied the same geometry criterion to compare the life cycle environmental impacts of various short natural fiber injection molded composites and the GFRPs for automotive component. On the other hand, the equal stiffness criterion is applied by multiple studies for the flax FRP and the reference GFRP comparison (Rajendran *et al.*, 2012; La Rosa *et al.*, 2013; Deng and Tian, 2015). Most of these studies confirmed the environmental benefits of using the flax FRP compared with the GFRP in terms of the GHG emissions and fossil depletion. However, the studies are constructed based on specific situations. The composition and mass of the flax FRPs are predefined. These case-oriented LCA results may not be able to provide guidance in the design stage since different situations require different composite structures. In this sense, a flexible LCA method is needed incorporating a material model predicting the corresponding mechanical parameters, based on which an optimized structure of the flax FRPs can be envisaged to guide subsequent product development and the environmental impact can be assessed with a specific design principle.

In this study, a parametric cradle-to-grave LCA model will be developed to assess the environmental impact of flax FRPs with different design specifications for automotive applications. Furthermore, the environmental impacts of two commonly applied flax FRPs (compression molded flax mat reinforced polymer composite and injection molded short flax fiber compound composite) are assessed and compared with conventional GFRPs.

Mechanical Properties of Flax Fiber Reinforced Polymers

Based on an extensive literature survey (Arbelaz *et al.*, 2005; Bodros *et al.*, 2007a,b; Bos *et al.*, 2006; Erasmus and Anandjiwala, 2009; Goutianos *et al.*, 2006; Li and Sain, 2003; Nystrom *et al.*, 2007; Van den Oever *et al.*, 2000; Yu *et al.*, 2009), the mechanical properties (tensile modulus and tensile strength) of different flax FRPs are summarized in Fig. 1. Applying Ashby plot (Ashby, 2005), the flax FRPs are categorized based on reinforcement formats (nonwoven mat, compound, unidirectional alignment, and woven fabric) and matrix type (thermoplastic and thermoset) focusing on conventional polymer matrices. The six

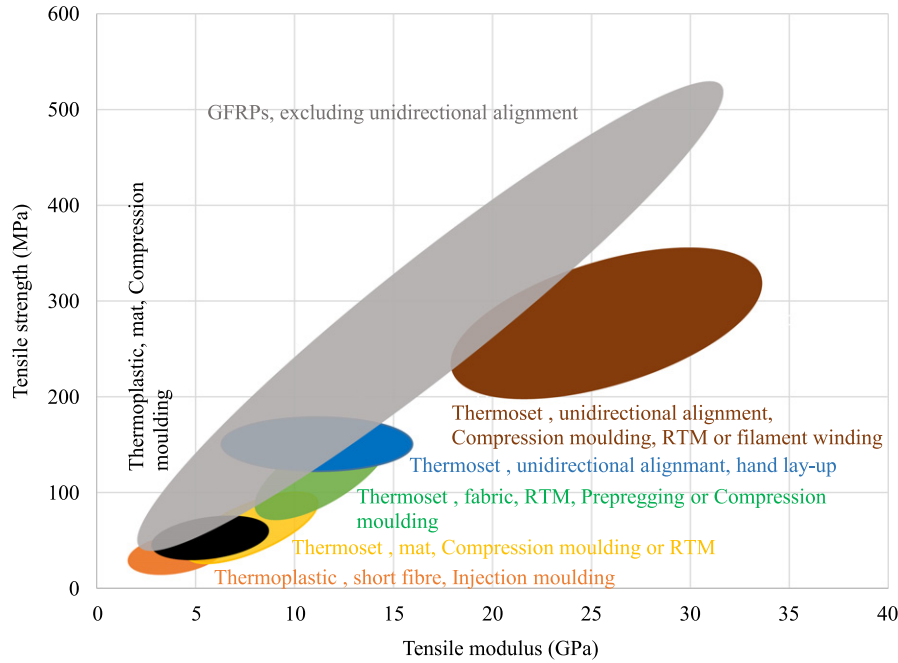


Fig. 1 Typical tensile properties for categorized flax fiber reinforced polymers.

subgroups presented in **Fig. 1** resemble an Ashby plot. The placement of these subgroups on the plot present increasing tensile properties in the following order: Injection molded composites (3D-random), nonwoven mat reinforced composites (2D-random) either via compression molding or Resin Transformation Moulding (RTM), woven fabric reinforced composites, and unidirectional fiber reinforced composites (by compression, RTM, or prepregging). The tensile strength and modulus tend to be linearly related with each other. Observing the variation in properties between the different distinguished categories, it can be concluded that the thermoset-based flax FRPs show better mechanical properties than the thermoplastic-based flax FRPs. Furthermore, the manufacturing techniques also have a noticeable effect on the composite mechanical properties, as demonstrated by the unidirectional flax FRPs when comparing the tensile properties between the hand lay-up and compression molding, RTM, or prepregging methods.

Besides several conventional polymers, for example, Polypropylene (PP), epoxy, polyester, etc., a further step, to use a biobased polymer matrix, is investigated as well (Zini and Scandola, 2011; La Mantia and Morreale, 2011; Koronis *et al.*, 2013). Typically applied biobased polymers include Polylactic Acid and Polyhydroxyalkanoates (Mukherjee and Kao, 2011; Le Duigou *et al.*, 2008; Chen *et al.*, 2011; Bodros *et al.*, 2007a,b; Roussiere *et al.*, 2012; Wrobel-Kwiatkowska *et al.*, 2007; Miller *et al.*, 2013). Other biobased polymers, for example, protein derived polymer (soy protein and wheat gluten) have also been analyzed (Lodha and Netravali, 2005; Huang and Netravali, 2007; Chabba and Netravali, 2004; Wretfors *et al.*, 2009; Hemsri *et al.*, 2012; Reddy and Yang, 2011). Comparison of the mechanical properties of flax FRPs with conventional matrix and biobased matrix reveals that, although a biobased matrix does not allow to reach the same maximum product properties as can be achieved in the case of unidirectional composite with conventional polymer matrix, both matrix types bring on comparable tensile moduli and strength values in the lower and medium levels (**Fig. 2**). Another particular phenomenon for biobased polymer matrices is that the tensile modulus and strength are not linearly related with each other. Products with low modulus and with relatively high strength are reported, as reflected in the unidirectional composites with soy protein matrix (Lodha and Netravali, 2005; Huang and Netravali, 2007). This indicates that large failure strains are present.

Mechanical Properties Modeling

To simulate the mechanical properties (tensile modulus and strength) of PFRPs, a modified generalized rule-of-mixture (ROM) model has been applied to derive the modulus and strength (Shah, 2013):

$$E_c = (\nu_f \eta_{IE} \eta_o \eta_d k E_f + \nu_m E_m) (1 - \nu_p)^2 \quad (1)$$

$$\sigma_c = (\nu_f \eta_{IS} (f \eta_o) k \sigma_f + \nu_m \sigma_m^*) (1 - \nu_p)^2 \quad (2)$$

where E_f and σ_f are the fiber modulus and fiber strength; ν_f and ν_m are the fiber and matrix volume fractions; η_{IE} and η_{IS} are the reinforcement length efficiency factors for modulus and strength modeling, respectively; η_o is the reinforcement orientation distribution factor while f accounts for the composite bear-loading efficiency to reconcile the theoretical values with the

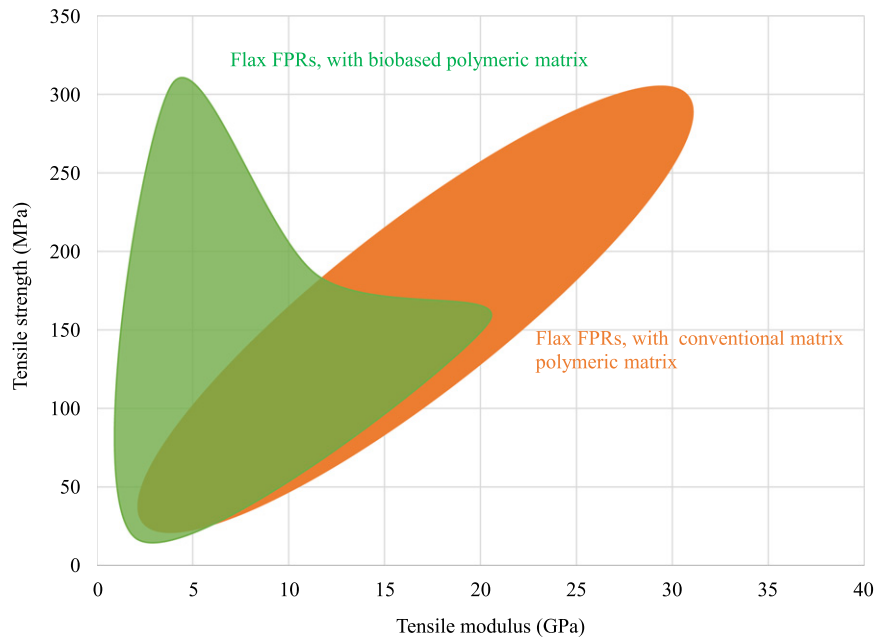


Fig. 2 Tensile properties of flax fiber reinforced polymers with biobased and conventional polymeric matrix.

experimental values in strength calculation; E_m and σ_m^* are the matrix modulus and matrix tensile stress at the fiber failure strain, respectively; the $(1-\nu_p)^2$ factor incorporates the negative influence of porosity on the tensile properties of the PFRPs; η_d incorporates a fiber diameter distribution factor reflecting the fact that the tensile modulus of PFRPs decreases quasi-linearly upon an increase in fiber diameter; and the fiber area correction factor k addresses the impact of the simplified assumption of a circular cross-sectional shape, which tends to overestimate the true cross-sectional area.

η_{IE} can be calculated according to Cox's shear lag theory (Cox, 1952) using the parameters of fiber length (l_f), fiber diameter (d_f), and for a square-packing arrangement. η_{IS} incorporates the interfacial strength of the flax fibers into the matrix and is determined by the Kelly and Tyson (1965). Both factors have a range from 0 to 1. The values of η_{IE} and η_{IS} are largely determined by l_f/l_d and l_f/l_c , respectively, where l_c is the fiber critical length defined in the Kelly–Tyson model. When the fiber length is low (<0.5 mm), both η_{IE} and η_{IS} are very sensitive to l_f . Under typical conditions, η_{IE} and η_{IS} quickly reach 0.8 when l_f increases from 0 to 0.5 mm (Shah, 2013). An enhancement in the fiber/matrix interfacial shear strength has a noticeable effect on η_{IS} when l_f is below 3 mm. It is worth noting that when the fiber length surpasses 6 mm, η_{IE} and η_{IS} both approach the unit value. Typical obtained fiber lengths are summarized according to reinforcement formats (Faruk et al., 2012; Shah, 2013). Typical values for η_{IE} and η_{IS} are collected for the compound (Bos et al., 2002; Shah, 2013) and mat structures (Bos, 2004; Shah, 2013). For reinforcement formats of woven fabric and unidirectional alignment, the long fiber length should induce unit values of η_{IE} and η_{IS} .

η_o , the orientation distribution factor, can be estimated from the Krenchel orientation distribution factor. η_o ranges between 0 (all fibers aligned transverse to the stress direction) and 1 (all fibers aligned parallel to the stress direction). The values of η_o for 3D or 2D randomly distributed fibers, as in the cases of compound and nonwoven mats, are 0.2 and 0.375, respectively. The η_o value for the woven fabric reinforcement format relies on the ply orientation, which ranges from 0.25 ($[\pm 45^\circ]$) to 0.5 ($[0^\circ, 90^\circ]$). Finally, the unidirectional fiber format should present the unit value of the orientation factor if an acceptable alignment is achieved. The bearing-load efficiency factor, f , is applied to η_o due to the fact that a large discrepancy can be observed between theoretical results from the Kelly–Tyson model and measured values in strength calculation (Garkhail et al., 2000). This factor is usually fitted from the experimental results (Garkhail et al., 2000; Bos, 2004). Based on the data for flax FRPs in (Bos, 2004; Bos et al., 2006), f is derived to be 0.22–0.42 for 2D randomly distributed flax fibers and 0.53–0.63 for 3D randomly distribution flax fibers. The fiber diameter distribution factor, η_d , has recently been proposed in (Summerscales et al., 2011), and it ranges between 0 and 1. The η_d value was determined for jute fiber, 0.46, through fiber structure analysis. In estimating the fiber area correction factor k ($k=1$ for a circular fiber cross-section), researchers show that a 2.55 correction factor is applicable to flax fiber (Thomason et al., 2011), compared with 1.42–2.08 for jute fiber and 1.99 for sisal fiber (Virk et al., 2012; d'Almeida et al., 2012).

The porosity content (ν_p) in a composite has a detrimental effect on its mechanical properties. Typically, a 5% limit is placed on a composite serving structural functions, for example, a composite used in automotive or marine applications. For PFRPs below 40 vol% fiber content, such a void limit can be satisfied. However, the porosity content can sharply increase to 25% if the fiber volume fraction exceeds 40%.

Table 1 Parameters of flax FRPs in automotive application

Reinforcement	Manufacturing	Structure	Load bearing
Flax mat	Compression molding	Panel	Bending
Short flax fiber	Injection molding	Strut	Tension

Abbreviation: FRPs: Fiber reinforced polymers.

Table 2 Material mass indices for common structures of plates and tensile bars under different loading types

Flax structure	Constraint	Variable	Objective	Load	Mass index
Short flax-PP	Length	Cross-section area	Equal stiffness	Tension	ρ_c / E_c
Short flax-PP	Length	Cross-section area	Equal strength	Tension	ρ_c / σ_c
Flax mat-PP	Length, width	Thickness	Equal stiffness	Bending	$\rho_c / E_c^{1/3}$
Flax mat-PP	Length, width	Thickness	Equal strength	Bending	$\rho_c / \sigma_c^{1/2}$

Abbreviation: PP: polypropylene.

Life Cycle Environmental Impact of Flax Fiber Reinforced Polymers

Goal and Scope

The goal of this LCA is to analyze the environmental impact of flax fiber production and cradle-to-grave environmental impact of flax FRPs compared with conventional GFRPs for automotive application, assuming a 200,000 km driving distance during the functional life span, which represents an average automotive lifespan in Europe. The flax FRPs are assumed to be used in European automotive industry since it is the strongest promoter for the application of plant FRPs. The two types of flax FRPs (**Table 1**) are widely used to produce automotive components replacing traditional GFRPs (Holbery and Houston, 2006): Injection molded short flax fiber reinforced polypropylene compound (short flax-PP), and compression molded flax mat polypropylene film (flax mat-PP) are covered in the detailed analysis. Both composite structures are included in the study to substitute glass mat-PP and short glass fiber-PP. For the glass mat-PP, a 9-kg conventional glass fiber mat reinforced with polypropylene panel (20% v/v) for the inner part of the car hatch for the Mercedes-Benz A-class (Jambor and Beyer, 1997). In the case of short glass fiber-PP, a hypothetical injection molded short glass fiber reinforced polypropylene with the same 9 kg mass is considered for comparison. Incineration with energy recovery is chosen to be end-of-life (EoL) scenario for both composites.

Design of the flax fiber reinforced polymers

To implement a systematic comparison, designs of flax FRP and GFRP must be constructed on a functional equivalence basis. Many factors, for example, physical properties, geometry, and cost, are involved in component design as the main design criteria. For composites applied in structural applications, two widely used criteria for equivalent performance are equal stiffness and strength. The material indices outlined in Ashby (2005) can be used to characterize the equivalent design under the designated objective and constraint (**Table 2**). E_c and σ_c in **Table 2** stand for tensile modulus and strength respectively, and ρ_c is composite density. Therefore, these material indices contain only the intrinsic material properties and are proportional to the mass of the panel/strut structure.

To determine the functional equivalent mass of the flax FRP, the mass index (MI_{GFRP}) of the targeted and mass (m_{GFRP}) of the GFRP are used as baseline values. Then, the mass of flax FRP is calculated according to its mass index ($MI_{\text{flax FRP}}$):

$$m_{\text{flax FRP}} = \frac{MI_{\text{flax FRP}}}{MI_{\text{GFRP}}} m_{\text{GFRP}} \quad (3)$$

The required mechanical properties can be calculated according to the generalized ROM with Eqs. (1) and (2) for modulus and strength calculation, respectively. It should be noted that for the panel structures subject to bending, the Ashby method strictly requires the flexural modulus and strength, that is, the modulus/strength measured under flexural loading, in addition to the tensile modulus/strength. Compared with the elastic modulus measured by means of a tensile test, flexural loading induces shear strains within the composite structure. Since the shear modulus value is lower than the elastic modulus ($\text{shear modulus} = \frac{\text{elastic modulus}}{1 + \text{poisson ratio}}$), the obtained strain would then be inflated leading to a reduction in the measured flexural modulus. Because no pragmatic theoretical model on flexural modulus/strength can be found, the tensile modulus is used as a proxy for the flexural properties in this analysis. This simplification was also applied in Rajendran et al. (2012) for a functionally equivalent design of a panel structure. Rodríguez et al. (2005) measured the flexural modulus and tensile modulus for various natural FRP composites. Their results show that the deviations between the respective flexural moduli and tensile moduli are within 10%.

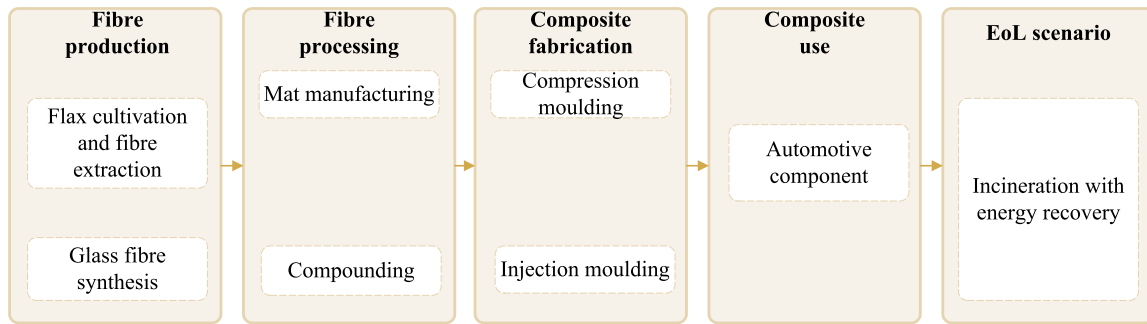


Fig. 3 Unit processes applied during the life cycle of flax fiber and glass fiber reinforced composites.

In this analysis, the functional unit of the comparison is set to use flax mat-PP or short flax fiber-PP replacing the corresponding GFRPs under equal stiffness and strength criteria. To construct formulations of flax FRP and GFRP for comparison, the 9 kg glass mat-PP and short glass fiber-PP with 20% v/v are used as baseline values. Eq. (1) is applied to calculate the E_c , which is needed to derive the mass index. Then, the corresponding mass of flax mat-PP can be determined by Eq. (3). With the references of the glass mat-PP and short glass fiber-PP composites, the masses of flax FRPs under the corresponding criteria are calculated according to Eqs. (1)–(3).

System description

Fig. 3 Depicts the system boundary for this LCA study. The geographical boundary for the LCA study is assumed to be a European setting. Specifically, France is the dominant flax fiber producer, and thus this location is selected for flax collation and fiber processing. In France, after harvesting, the green flax straw is exclusively dew-retted to decompose the pectin binder and thus facilitate the subsequent fiber extraction processes. The retted flax straw is crushed by a pair of fluted rollers and beaten by a rotating blade that forces the internal woody tissue (shive) to fall off. Multiple products, for example, long flax fibers, short flax fibers (flax tows), shives, flakes, and seeds, are obtained after the extraction (scutching). Then, the scutched long fibers are refined by the hackling process to remove woody particles. Two products are generated from hackling: Hackled long fibers (slivers) and hackled tows.

The hackled long fibers, being the most valuable product, are used to produce mat for compression molding or compound for injection molding. Afterwards, these will be used to replace the correspondent GFRP in the automotive applications. In automotive application, a change in mass typically induces a change in the fuel consumption rate. In addition to mass, durability (or service life) is another crucial factor determining the use phase. Due to lack of information on the service life of flax FRPs, initial treatment is to assume both flax FRPs and GFRPs can maintain the 200,000-km functional lifespan without need of replacement. Incineration with energy recovery is a valid scenario for composite disposal. In general, three common waste incineration technologies with energy recovery are available: Electricity as the only energy output, heat as the only energy recovery result, and coproduction of heat and electricity (CHP). CHP is the current mainstream technology and was selected during the LCA modeling of incineration as an EoL treatment scenario in this analysis.

Allocation

The upstream environmental effects may be partitioned based on the relative masses or prices when multiproducts are generated in unit processes. To account for the fact that flax hackled long fibers are the main incentive for farmers to cultivate flax, economic allocation is applied to estimate the environmental impact. The yield and yield data are sourced from literature (Le Duigou *et al.*, 2012).

Life Cycle Inventory

Fiber cultivation, processing, and composite fabrication

The inventory data for flax cultivation, fiber production, and composite fabrication have been documented in details in literature (Deng *et al.*, 2016; Duflou *et al.*, 2014). The flax cultivation and fiber extraction in France is modeled since France is the dominant producer of flax fiber (Deng *et al.*, 2016). For glass fiber, the Life Cycle Inventory (LCI) in the Ecoinvent database 2.2 for “glass fiber, at plant/kg/RER” is the primary source (Kellenberger *et al.*, 2007). The LCI data of the PP granules and PP films production, which are used as input for the injection molding and compression molding processes respectively, have been documented in the Ecoinvent report (Hischier, 2007).

Composite use

The composite use phase contains two aspects: The fuel use related to the mass of the flax FRPs and replacement ratio ($\lambda = \frac{\text{GFRP lifetime}}{\text{Flax FRP lifetime}}$) of flax FRPs if flax FRPs have a different service life as the GFRPs.

Table 3 Fitted fuel consumption among different vehicles

Type	Driving cycle	Fuel economy	R ²
Cars	0–60 mph; tacc. = 9.2–9.8 s	$FC = 0.0035M + 3.9703$	0.4177
Light trucks	0–60 mph; tacc. = 9.5–10.1 s	$FC = 0.0037M + 5.2092$	0.6084
Gasoline cars	MVEG cycle	$FC = 0.00335M + 2.8492$	0.86
Heavy trucks	Not available	$FC = 0.0034M + 7.4452$	0.9841

Note: Dufloy, J.R., De Moor, J., Verpoest, I., Dewulf, W., 2009. Environmental impact analysis of composite use in car manufacturing. CIRP Annals Manufacturing Technology 58, 9–12. Song, Y.S., Youn, J.R., Gutowski, T.G., 2009. Life cycle energy analysis of fiber-reinforced composites. Composites Part A: Applied Science and Manufacturing 40, 1257–1265. Cheah, L.W., 2010. Cars on a Diet: The Material and Energy Impacts of Passenger Vehicle Weight Reduction in the US (PhD Dissertation). Massachusetts Institute of Technology.

Table 4 Inventory data for the incineration of flax/glass-based composites

Parameter	Unit	Applied value
Flax fiber	MJ kg ⁻¹	20
Glass fiber	MJ kg ⁻¹	−1.7
PP	MJ kg ⁻¹	48.7
Electricity	%	11.3
Heat	%	31.3

Abbreviation: PP: polypropylene.

For the first aspect, the fuel–mass correlation can be presented in the following equation (Kim and Wallington, 2013):

$$FC = FRC \times M + B \quad (4)$$

where FC is the fuel consumption or fuel economy (L/100 km); FRC denotes the fuel consumption reduction coefficient (FRC) [L/(100 km*kg)] determined by rolling, gradient, and acceleration resistance; M is the vehicle mass in kg; and B is a constant representing the parasitic loss (L/100 km). The literature survey indicates that FRC s for gasoline cars show limited variation across sources: From 0.0033 to 0.0037 L/(100 km*kg) (shown in Table 3). In the automotive application, an important distinction should be made in an LCA study: Vehicle LCA and component LCA. For the component LCA in this study, the allocation of fuel use to the specific vehicle component follows the method proposed by Kim and Wallington (2013):

$$FC_c = FRC \times M_c \quad (5)$$

where FC_c stands for the fuel consumption of the specific composite component and M_c is its mass. In this research, the applied FRC is 0.0033 L/(100 km*kg), a typical value for gasoline cars. Eq. (5) essentially assumes that the fuel consumption for a vehicle component should be its mass-induced fuel consumption. The parasitic loss, represented by the constant offset B in Eq. (4), is irrelevant in a vehicle component.

For the second aspect, determining the exact value of λ is not evident. The major factor limiting the durability of flax FRPs is their high moisture absorption caused by the hydrophilic nature of biobased materials. Moisture absorption leads to fiber swelling and subsequently causes dimensional instability and, more importantly, deterioration of the composite mechanical properties (Stamboulis et al., 2000). In real practice, flax fibers can be surface treated to reduce the moisture absorption (Lincoln et al., 2008). Thus, in the study, the replacement ratio, λ , is assumed to be the unit number from a practical perspective.

Incineration with energy recovery

The net heating values, or low heating values, documented in the Ecoinvent database, were adjusted to fit the specific values of the targeted composites (Table 4). The average net energy recovery efficiencies, 31.3% (in the range of 10.5%–66.8%) for thermal and 11.3% (in the range of 3.4%–23.7%) for electricity were applied based on the average values of 44 European waste incineration plants with combined heat and power generation (see Table 4). The recovered energy (electricity and heat) was modeled to substitute for primary electricity and heat generation in Europe. (Electricity, production mix UCTE/RER U (Frischknecht et al., 2007) and Heat, natural gas, at industrial furnace > 100 kW/RER U in the Ecoinvent dataset (Zah and Hirschier, 2007). The emissions were calculated according to the coefficient emission factors of the elements, which are documented in the Ecoinvent report (Doka, 2003). The detailed procedure to construct the inventory of flax FRP and GFRP during the EoL phase is documented in (Deng et al., 2016).

Impact assessment method

The ReCiPe midpoint (H) impact assessment method (Goedkoop et al., 2009) was used in the LCA study. The evaluation was performed using Simapro® version 7.2.4. Since the LCA study covers all the life cycle stages of flax FRPs, the biogenic carbon was treated as global warming neutral. The economic allocation principle has been applied for the environmental impact assessment.

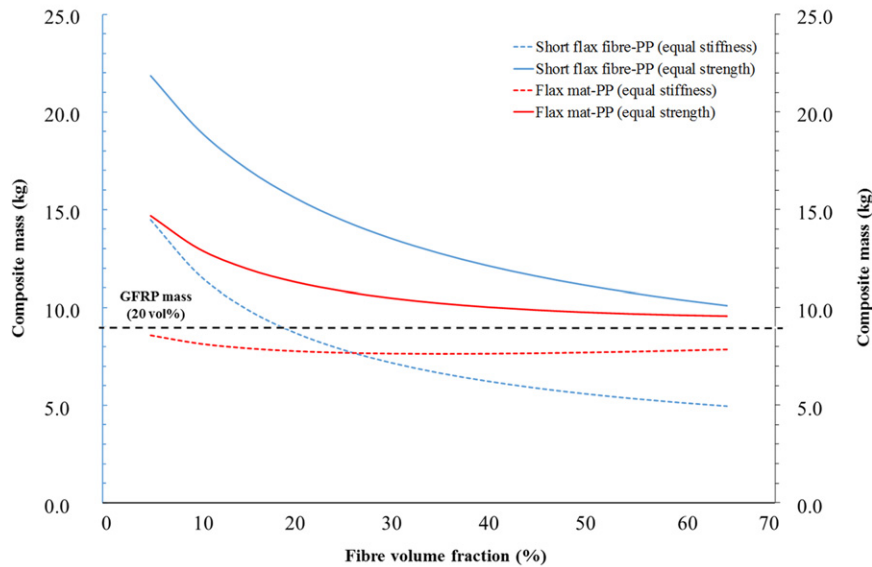


Fig. 4 Masses of flax fiber reinforced polymer relative to GFRPs under different design criteria.

Results and Discussion

Life Cycle Environmental Impact Analysis of the Design Criteria for Flax Fiber Reinforced Polymers Selection

For automotive application, the environmental impact from the use phase is generally the most significant constituent. Thus, the functionally equivalent mass is regarded as an influential parameter for the life cycle impact assessment. Fig. 4 clearly indicates only the equal stiffness criterion can result in lower mass design compared with the 9 kg GFRP references. Within the range of 5%–65% v/v, flax mat-PP presents consistent mass reductions compared with the 20% v/v glass mat-PP reference while short flax fiber-PP starts to gain mass reduction from 20% v/v onwards. On the other hand, the equal strength criterion contributes to elevated masses compared with the reference short glass fiber-PP composite.

Based on the mass analysis, we further select the 20% v/v for flax FRP as the baseline scenario to quantify the life cycle impacts under different design criteria. As shown in Fig. 5(a), lower life cycle impacts can be observed in 14 out of 17 impact categories, typically 20%–50% reductions. In particular, a 13% decrease in the climate change category and a 14% reduction in fossil depletion are achieved. Moreover, for impact categories of ozone depletion and human toxicity, up to 70% reductions can be attained. Exceptions to this observation include the categories of ionizing radiation, marine eutrophication, freshwater ecotoxicity, and agricultural land occupation. The higher burden in ionizing radiation is due to the fact that flax cultivation and fiber extraction are highly concentrated in France where a significant fraction of the electricity generated is obtained from nuclear power plants. For other impact categories, the higher environmental impact of the flax mat-PP is found to be caused by the use of fertilizers and pesticides in flax cultivation.

Compared with the mat reinforced composites, environmental impacts of short flax fiber-PP composite present virtually the same environmental impacts in multiple impact categories compared with the short glass fiber-PP composite (Fig. 5(b)). This is explained by the fact that the short flax fiber-PP leads to a virtually equal mass (9.2 kg) structure in comparison to the 9 kg conventional short glass fiber-PP combination.

When the equal strength criterion is used, in both cases shown in Fig. 5, the relative environmental benefit observed for the equal stiffness analysis is largely reverted into a burden compared with GFRP. A significant inflation from the original levels obtained under equal stiffness conditions (approximately 40% increase for flax mat-PP and 25% increase for short flax fiber-PP) was observed. The large performance gap in strength between flax FRPs and GFRPs that explains this shift is also observed by other researchers (Bos, 2004).

Analysis of the Optimal Volume Fraction of the Flax FRPs

At the baseline level, the volume fraction of the flax FRPs is set to be the same as the GFRPs for comparison. In practice, this is not necessarily the case: A designer can increase or lower the volume fraction of flax due to different concerns, such as the available manufacturing equipment, the supply of qualified flax fiber, and the cost of the flax fiber. Thus, it is beneficial to evaluate the influences of different volume fractions on the life cycle impact of the flax FRPs. The change in fiber volume fraction has dual effects on the material indices. On the one hand, since the density of the flax fiber (1.5 g cm^{-3}) is higher than the PP matrix (0.96 g cm^{-3}), higher volume fraction will create higher composite density, and thus, lift up the material indices. On the other hand, more fiber

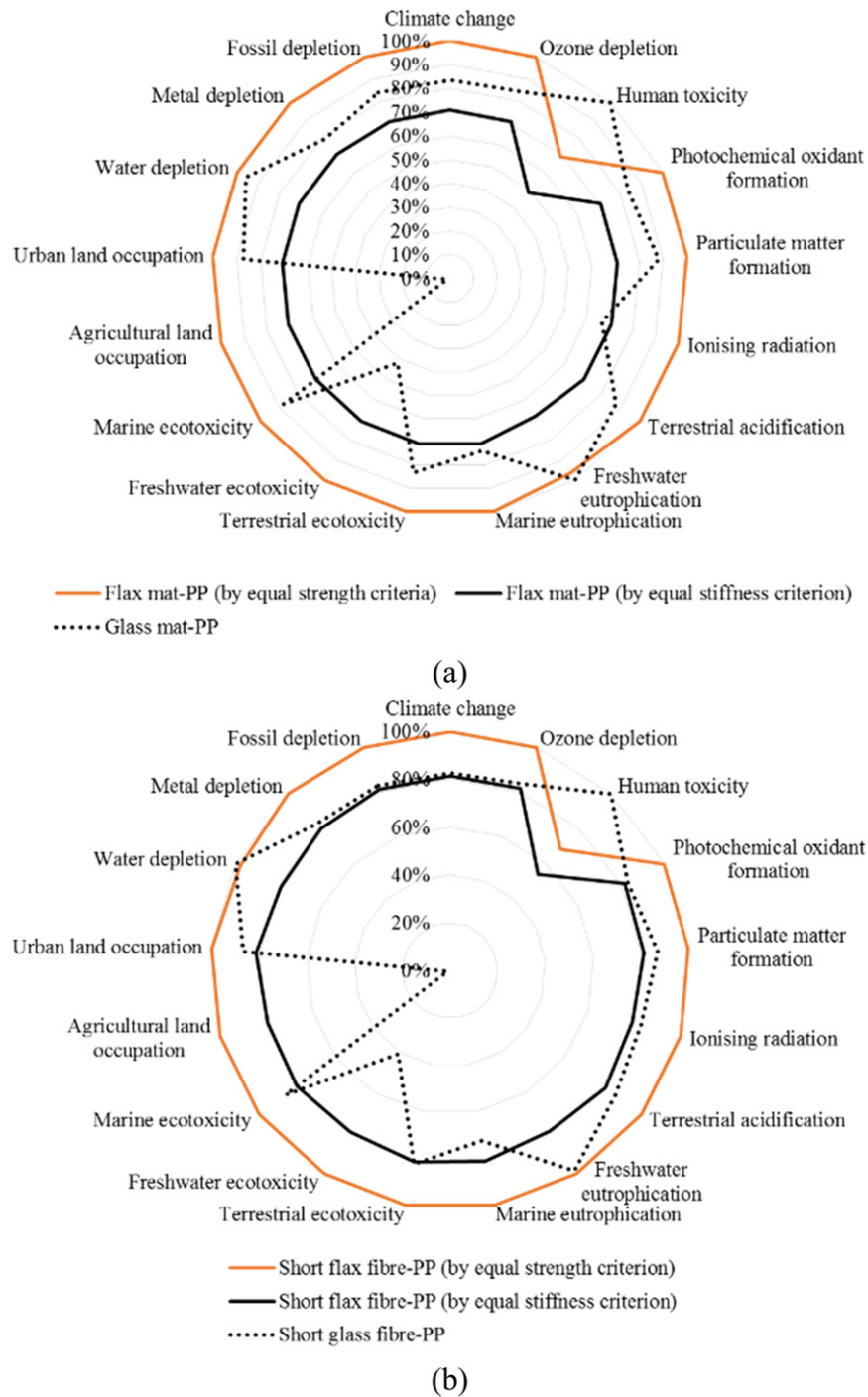
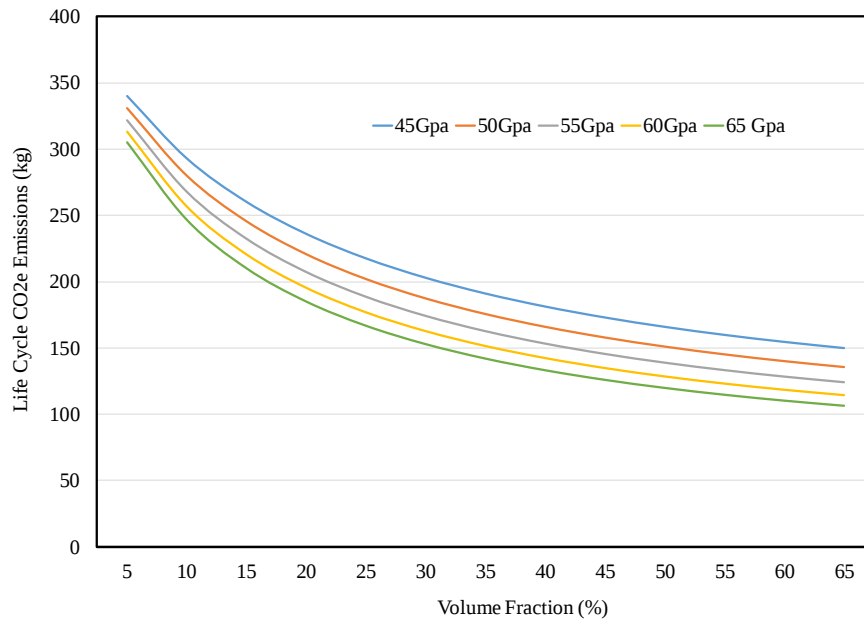


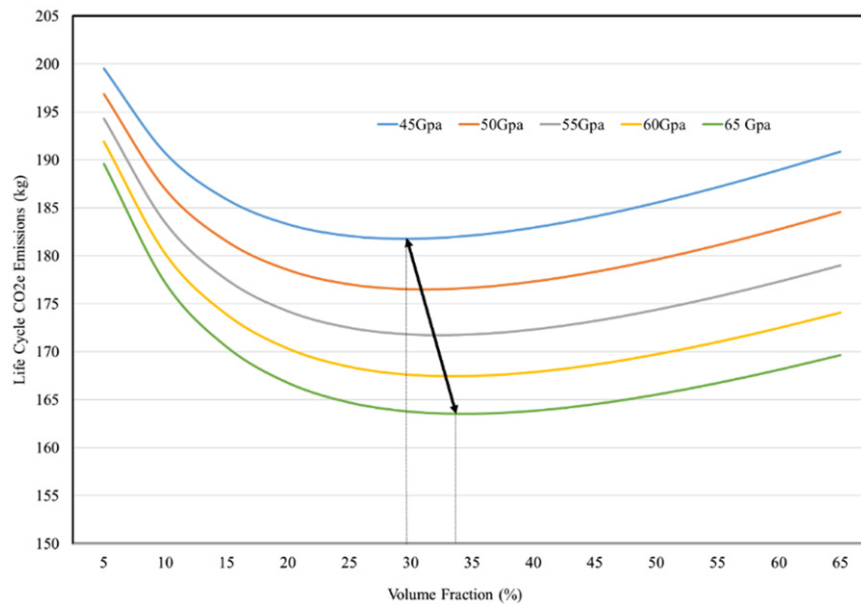
Fig. 5 Life cycle impact comparison between flax fiber reinforced polymers and GFRPs to equal stiffness and equal strength design criteria: (a) Flax mat-polypropylene (PP); (b) short flax-PP.

enhancement will improve the mechanical properties of the composite, and thus, lower the material indices. In this study, the accumulated impacts on the material indices are specifically calculated for short flax fiber-PP and flax mat-PP composites under equal stiffness criteria since it has been shown that flax FRPs are not proper candidates when strength is the main concern. The material indices of 20 vol% glass mat-PP and short glass fiber-PP composites are used as the references. The life cycle CO₂ emissions are presented in Fig. 6 due to the global concerns on global warming, and because reducing carbon emissions are the main incentive to replace glass fibers with flax fibers.

The results in Fig. 6 provide some insights on the design of the flax FRP. The first observation reveals that different types of composite exhibits different patterns when fiber volume increases. The steady decrease of the life cycle CO₂ emissions of



(a)



(b)

Fig. 6 Life cycle CO₂ emissions with changes in volume fraction: (a) Short flax fiber-polypropylene (PP); (b) flax mat-PP.

the short flax fiber-PP can be explained by the fact that the improved composite modulus (E) outpaced the increase in density (ρ_c), leading to increased material indices (ρ_c/E_c for short flax fiber-PP). Therefore, the mass of the short flax fiber-PP under the equal stiffness criterion will gradually become lower when volume fraction increases, and therefore lower the life cycle carbon emissions (Fig. 6(a)). However, the results of the flax mat-PP composite are much different. Minimal points of the life cycle CO₂ emissions present when the fiber volume fraction increases from 5% v/v to 65% v/v. Depending on the tensile modulus of the flax fiber, the optimal volume fractions of the fiber changes from 28% v/v to 32% v/v (Fig. 6(b)). Such a different pattern can be explained from the specific material index for mat structure ($\rho_c/E_c^{1/3}$). Due to the fact that increase in E_c from volume fraction enhancement is reduced by the power of $1/3$, increase in density will counterbalance the improvement of the tensile modulus, reverse the increment of the material index of the flax mat-PP composite, and finally lead to higher mass and higher life cycle CO₂ emissions.

Conclusions

This study evaluated multiple impact categories of flax FRPs compared with GFRP based on LCA for automotive application, incorporating generalized ROM and the Ashby method. Under the equal stiffness criterion, the life cycle impact of the flax mat-PP demonstrates a lower environmental impact than glass fiber-mat in most of the impact categories. Such benefits are due to a reduced fuel consumption during the use phase, which can be attributed to the lightweight structure of the flax mat-PP under equal functional stiffness condition. However, flax mat-PP composites suffer from environmental issues common to agro-products. This results in higher impacts in marine eutrophication and freshwater ecotoxicity, due to the nutrients in fertilizers and pesticide compounds respectively. Flax mat-PP composites also stress the availability of arable land area, resulting in a substantially larger agricultural land occupation impact compared with the equivalent glass mat-PP composites. The LCA study for the other analyzed flax FRPs, that is the short flax fiber-PP, leads to different conclusions. The short flax fiber-PP, applied in a strut structure produced via injection molding, requires nearly the same mass as the corresponding short glass fiber-PP composite for the equivalent functionality according to the stiffness criterion. Therefore, the total life cycle impact is very similar for the dominant impact categories when comparing the short flax fiber-PP to its short glass fiber-PP equivalent design.

This study further evaluates the influence of the fiber volume fraction, which is the critical parameter determining the mechanical properties and mass of the composite, on the life cycle environmental impact of the flax FRPs. The results yielded different patterns: The flax mat-PP composite exhibits the optimal volume fractions between 28% v/v and 32% v/v with the minimal life cycle CO₂ emissions as the main target; the short flax fiber-PP, on the other hand, shows steady decreased life cycle CO₂ emissions. Further analysis for flax FRPs from an environmental impact perspective is recommended. Another issue is the impact of surface treatment methods on flax fibers. The LCA analysis should be extended to characterize the environmental impact profiles of different chemical treatment scenarios. Furthermore, this study provides an LCA study for flax FRPs composed with conventional PP polymer. Future analysis is recommended to focus on biobased polymeric matrix solutions from both the functional and environmental impact perspectives.

See also: Influential Parameters on Formation of PEMs on Recycled Fibers: A Review. Kenaf Fiber Reinforced Composite in the Automotive Industry. Life Cycle Assessment of Sisal Fiber. Natural Fiber Composites: Review of Recent Automotive Trends. Opportunities With Renewable Jute Fiber Composites to Reduce Eco-Impact of Nonrenewable Polymers. Properties of Coconut Fiber. Renewable Agricultural Fibers as Reinforcing Fillers in Plastics: Mechanical Properties of Kenaf Fiber-Polypropylene Composites. Reuse of Waste Corrugated With Coir Fibers as a Packaging Materials. The Utilization of Vegetable Fibers in Cementitious Materials. Use of Bio-Fibers in Various Practical Applications

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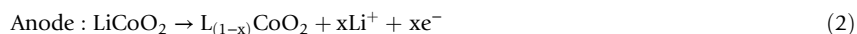
Recycling of Lithium From Li-ion Batteries

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Introduction

Batteries are used in many different applications including cars, radios, laptops, mobile phones, and watches. Batteries are classified as primary batteries and secondary batteries. The former one is known as alkaline batteries made up of zinc and manganese as primary source and mainly used for household purposes, which convert automatically chemical energy into electrical energy. The later one is usually made up of nickel (Ni), cadmium, nickel metal hydride or lithium ion and are mainly used in mobile phones, electronic items, cameras, etc. Primary batteries are not rechargeable, while the secondary batteries are rechargeable. The main concern of using batteries is the threat to the environment at the end of its usage. Among all type of batteries, Lithium ion batteries (LIBs) are gaining world-wide interest owing to use in almost all the modern life applications. Experimentation were started by Gilbert Newton Lewis in 1912 over the use of LIBs. After that disposable (primary) LIBs were developed in 1950s. Panasonic is the first company, which produced commercial primary LIBs in 1970. LIBs, a rechargeable secondary battery was first explored in 1970s by M.S. Whittingham at Exxon, which was made of titanium disulfide cathode and a lithium-aluminum anode. Since the instability of metallic lithium presented in that batteries caused safety risk, focus was primarily concentrated on the use of LiCoO_2 and carbon as the cathode and anode materials, respectively (Fey and Huang, 1999). Then, the LIBs were commercially rolled out by Sony at Japan in 1991. The significant role of electrical energy storage technologies demand for green and sustainable energy (Liu *et al.*, 2016). The chemical reactions that take place inside LIB during charging are shown in Eqs. (1–2). Further, the reverse reactions occur during discharge.



LIBs are generally used in portable electronic devices and electric vehicles (EV) due to their high energy density, low self-discharge efficiency, long storage life, light weight, non-memory effect, having wide range of application temperatures, small volume, and advantages in environmentally compatible operations (Zheng *et al.*, 2018; Li *et al.*, 2016; Guo *et al.*, 2016; Wang *et al.*, 2016; Santana *et al.*, 2017; Yao *et al.*, 2016; Xu *et al.*, 2008). The major advantage of these batteries is that they possess higher energy density (W/kg) compared to other battery chemistries being used currently. LIBs presence in the market is from the year 1990 onwards, since the demand of LIBs in electrochemical power sources such as portable electronics and electric vehicles are unavoidable, it is extremely important to come out with the proper recycling methods as it also avoids the environmental pollution due to dumping of heavy metals and toxic chemicals of spent LIBs (Zheng *et al.*, 2018). Also, it saves the energy by giving them second life until their potential is completely utilized. Nowadays, hazardous mixing is a major threat for all the living species as the exposure to pollutants are highly assured due to less care on the environment. Due to this, severe health problems are witnessed, which consequently reduces the life span of people, animals, etc. Hence, recycling of batteries is very much required to protect environment and human health. In the modern era, an efficient harvest, management and storage are three essential segments to energy consumption. Fig. 1 explains about the life history of Li in the battery applications (Winter *et al.*, 2018).

Serious environmental pollution such as the infiltration of toxic heavy metals would occur in the underground water bodies due to the disposal of spent LIBs. On the other side, considerable amount of poisonous gases, such as hydrogen fluoride (HF) will be produced to the atmosphere. This will pollute the atmosphere while burning the spent LIBs. Hence, it is required to come out with a green treatment method which should also bring economic benefits for the recycling of spent LIBs. Due to the presence of larger amount of valuable metals, spent LIBs receive greater attention on commercial aspect (Dorella and Mansur, 2007). The composition of spent LIBs generally are in the range of cobalt (Co) 5%–20%, nickel (Ni) 5%–10%, lithium (Li) 5%–7%, other metals such as copper (Cu), aluminum (Al), iron (Fe), etc., (5%–10%), and the rest are 15% organic compounds and 7% plastic (Ordoñez *et al.*, 2016). However, spent LIBs compositions vary from different sources depending on the manufacturer. The company ZSW has come out with the data of stock and new registrations of battery-electric vehicles. Data reveals that globally, USA and China are in forefront for the development of EV (Huang *et al.*, 2018; Anderson, 2011). The estimated global demand for LIBs is forecasted as per Table 1.

Structure of LIBs and Spent LIBs

LIBs are defined as greener and cleaner energy storage devices compared to other batteries due to their higher voltage, high energy density, low self-discharge efficiency, and less harmfulness to the environment. The constituents of LIBs are generally cathode and anode materials, separator, electrolyte, etc. Among these, the cathode assembly usually contains Al foil (collector), carbon black,

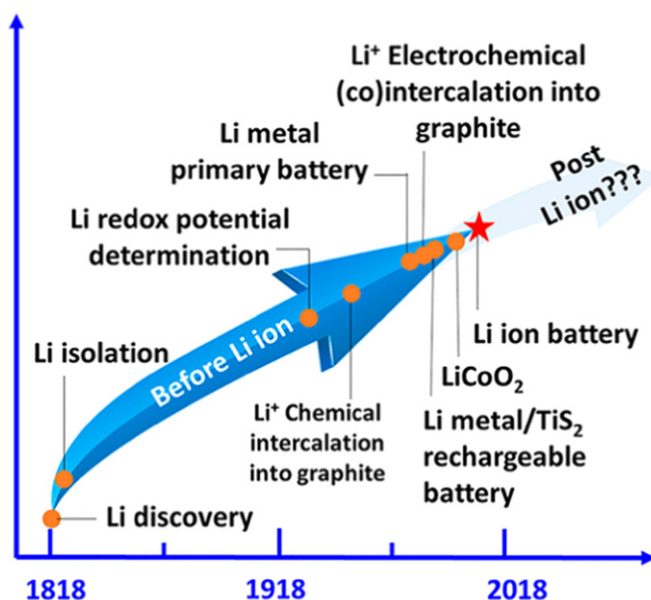


Fig. 1 Life history of Lithium in the battery applications. Reprinted with permission from Winter, M., Barnett, B., Xu, K., 2018. Before Li ion batteries. *Chemical Reviews* 118, 11433–11456.

Table 1 Estimated global forecast for requirement of LIBs

Estimated Year	Product	Estimate (t/year)	Reference
2015	Li ₂ CO ₃ with the battery grade	111,700	(Mohr <i>et al.</i> , 2012)
2050	Lithium exclusively for EV batteries	400,000	(Mohr <i>et al.</i> , 2012)
2020	Lithium ion batteries	21,000	(Anderson, 2011)
2020	Lithium carbonate	40,000–95,000	(Haber, 2008)

Polyvinylidene fluoride (PVDF) as binder, and the anode mainly contains Cu foil (collector), graphite and PVDF binder. The challenge is mainly on recovering the maximum number of valuables out of the minimum number of reagents used. Data shows that 4000 tonnes (t) of spent LIBs contain 1100 t of heavy metals and more than 200 t of toxic electrolyte (Ordoñez *et al.*, 2016). **Fig. 2** illustrates the schematic diagram of the Li intercalation–de-intercalation reaction mechanism in a rechargeable LIB containing solid electrodes and a liquid electrolyte (Roy and Srivastava, 2015).

Applications of Batteries

The LIBs are mainly used in electric cars due to their light weight nature and high energy density as battery packs, cell phone towers, and electronic gadgets like mobile phone, cameras etc.

Statistics and Legislation of LIBs

Data reveals that the production of LIBs has reached 500 million units in 2000 worldwide and in 2010, it is almost 4.6 billion units. The production of the LIBs in China has come to 5.287 billion units in 2014 (Li *et al.*, 2013; Shin *et al.*, 2005; Jha *et al.*, 2013). The greater the number of LIBs being produced; the more spent LIBs will be generated, which need to be recycled. Statistics explained that the lifetime of LIBs used in digital products will only be one to three years and the same will be five to eight years for the power vehicles (Contestabile *et al.*, 2001; Zheng *et al.*, 2018). According to these statistics, by 2020 it is expected that China will produce 2.5 billion of spent LIBs with a mass of about 500,000 t (Zeng *et al.*, 2014).

According to the available report, a directive for collection and recycling of batteries is introduced by European Union. Collection rate of 25% and 45% was targeted for all the batteries sold in 2012 and 2016, respectively. At least 50% of them needs to be recycled from the batteries collected. LIB recycling is carried out in North America, Asia and Europe only.

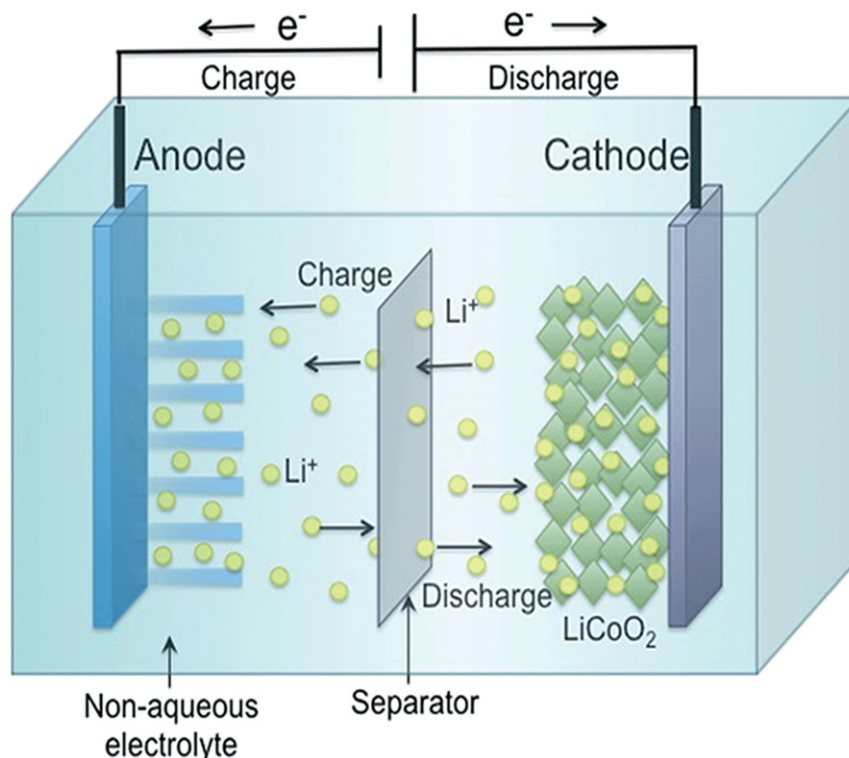


Fig. 2 Schematic diagram of the lithium intercalation–de-intercalation reaction mechanism in a rechargeable lithium-ion battery containing solid electrodes and a liquid electrolyte. Reprinted with permission from Roy, P., Srivastava, S.K., 2015. Nanostructured anode materials for lithium ion batteries. *Journal of Materials Chemistry A* 3, 2454–2484.

However, the drawback of this collective recycling facilities is capability of treating less than 30% of the world's LIB production.

Benefits of Recycling of LIBs

Environmental Protection Agency (EPA) states that, “batteries contain heavy metals such as lead, cadmium, mercury, and Ni”, which can harm the environment due to improper disposal of batteries (Sun and Qiu, 2011). The spent LIBs usually consist of large amounts of valuable metals such as Co, Mn, Fe, Li, etc. Although, the presence of metal contents is higher than natural ores in the spent LIBs, however, these are recognized as typical hazardous solid waste as these contain toxic metals as well as corrosive electrolytes. Dumping of waste LIBs in landfill sites contaminates the soil. Leakage of the organic electrolyte and the heavy metals causes serious threats to the environment. Recycling of spent LIBs is a preservation and recovery of valuable resources according to the environmental point of view. Thus, recycling of spent LIBs is highly desirable. Hence, the challenges and benefits on recycling spent LIBs highly depend on the finding green and effective way of recovering the valuable metals. There should be emerging technical resources to measure discards, find solutions and safe guard the environment. Government should enforce strict environmental rules over battery recycling to safeguard the environment from dumping of harmful metals arising from spent LIBs.

Fig. 3 illustrates the recycling of spent LIBs from different sources.

Techniques for Recovery of Li From LIBs

Li is extracted from the primary sources like mineral/clay and brines as well as from the secondary sources (LIBs). LIBs are a huge waste across the world, which will increase the health risk of humans, animals, etc. Recovering Li and other valuable metals from these waste batteries will avoid the risk of environment pollution as well as will have advantage at economic level. There are different processes to recover the heavy metals.

Apart from the highly valuable metals such as Li, Ni, and Co, but also Fe, Al, P, and other elements with low recovery values are present in the spent LIBs. Recently, many researchers have come out with the state-of-the-art processes for the metal recovery through recycling from spent LIBs which are basically divided into three types such as pretreatment processes, metal- extraction processes, and product preparation processes (Zeng et al., 2014; Ordoñez et al., 2016).

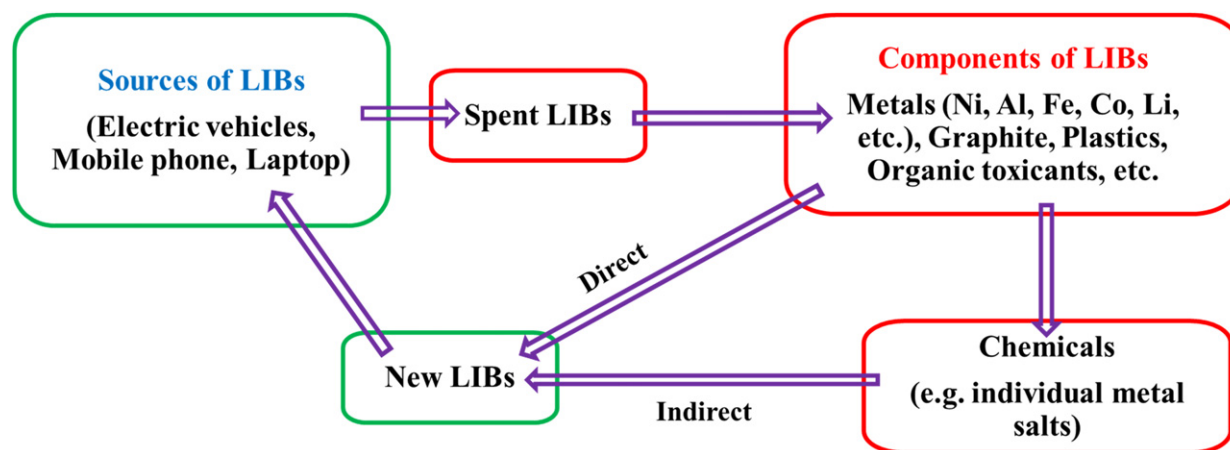


Fig. 3 Recycling of spent LIBs from different sources.

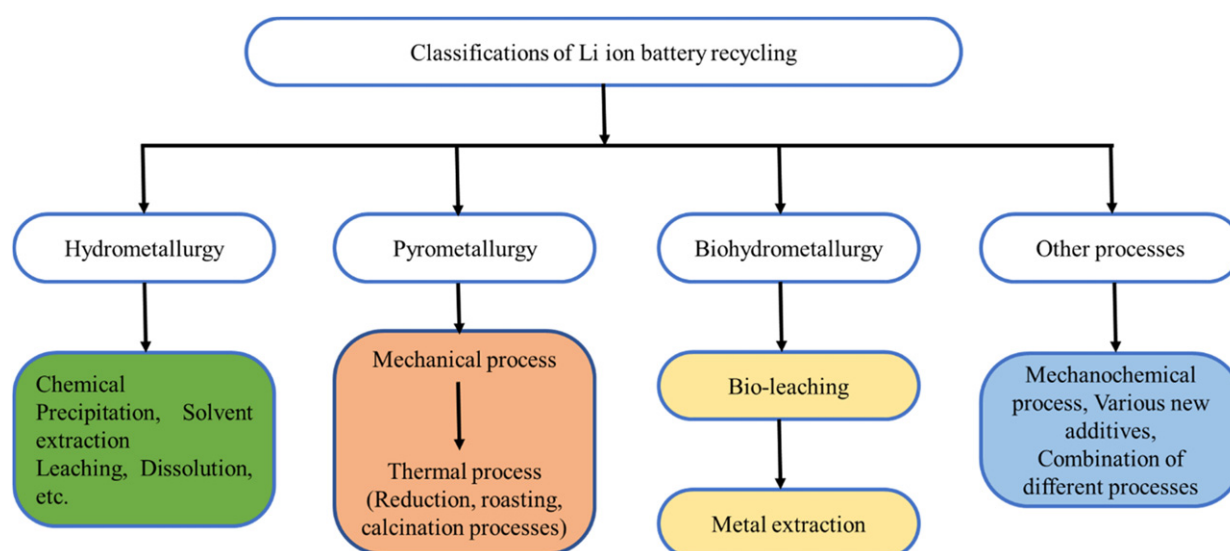


Fig. 4 Classification of Lithium-ion battery recycling process.

Pretreatment Processes

In the pretreatment process, the spent LIBs undergo manual dismantling or mechanical separation process. This helps in segregation of cathode, anode and other components (Zheng *et al.*, 2018). After that the separated constituents are taken for metal- extraction process. Since the cathode material is basically adhered to aluminum foil, separating the cathode from the foil is very difficult. In order to effectively separate the cathode material from foil, different methods such as solvent dissolution method (Yang *et al.*, 2015; Yao *et al.*, 2015; Song *et al.*, 2013), ultrasonic-assisted separation, sodium hydroxide (NaOH) dissolution method (Chen *et al.*, 2011; Ferreira *et al.*, 2009; Nan *et al.*, 2005, 2006), mechanical method (Zhang *et al.*, 2013, 2014) and thermal treatment method (Yang *et al.*, 2016; Hanisch *et al.*, 2015; Sun and Qiu, 2011) are implemented.

Metal Extraction Processes

Metal extraction processes are the most important method to recover the valuable metals (Li, Co, Mn, etc.). Most commonly procedures essentially are (i) Hydrometallurgy, (ii) Pyro-metallurgy, (iii) Biometallurgy, and (iv) Other process for the valuable metal recovery from the spent Li ion batteries (Swain, 2017). These processes have different steps to get Li from spent LIBs as shown in Fig. 4. We will now discuss various processes in detail.

Hydrometallurgy

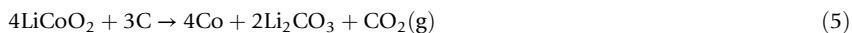
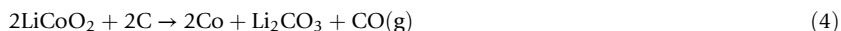
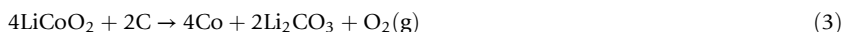
The metals were leached from the spent LIBs usually using the hydrochloric acid (Zhang *et al.*, 1998; Joulié *et al.*, 2014; Barik *et al.*, 2017; Takacova *et al.*, 2016); sulfuric acid (Joulié *et al.*, 2014; Chen *et al.*, 2015a); phosphoric acid (Pinna *et al.*, 2017; Chen *et al.*, 2017) and nitric acid (Joulié *et al.*, 2014; Lee and Rhee, 2002) etc. The metals (Co, Mn, etc.) were reduced from the high valent state (in solid phase) to easily soluble Co^{+2} , Mn^{2+} , etc., using reducing agents e.g., hydrogen peroxide, sodium carbonate, etc. The metal removal efficiency was affected by the temperature, reaction time, type of leachants, concentration of leachants and reducing agents and solid to liquid ratio.

Zhang *et al.* separated and recovered the valuable metals (e.g., Co and Li) from the spent LIBs. They also examined the effect of leachant concentration, different leachants (e.g., hydrochloric acid, hydroxylamine hydrochloride, sulfurous acid, etc.), solid to liquid ratio, temperature and reaction time for the removal of Co and Li (Zhang *et al.*, 1998). Hydrochloric acid was found to be the best leachant, which recovered 99% of Co and Li using 4 M HCl solution at 80°C for 1 h reaction (Zhang *et al.*, 1998). Co was extracted by the solvent extraction and in sequence Li was precipitate as carbonate (Zhang *et al.*, 1998). The separation and selective removal of Ni and Li was carried out from LiNiO_2 based LIBs. The PC-88A was used as a commercial extractant for the recovery of Ni and Li was recovered in form of lithium carbonate via precipitation using Na_2CO_3 (Nguyen *et al.*, 2015). Similarly, Lee *et al.* extracted Li from LiCoO_2 using oxalic acid leachant. They suggested that leachants like hydrochloric acid, sulfuric acid etc., leaches both Co and Li in the solution and add complication towards the recovery of pure Li. Oxalic acid could selectively recover/leach Li at low pH range. Li was recovered with less than 1% Co leaching as impurity. The leached Co (1%) could be precipitated in the form of Cobalt oxalate. The process was able to recover 90% Li from the LIBs at the optimum conditions. The Li ion in the solution can be transformed into Li_2CO_3 using Na_2CO_3 , after recovering of Co (Lee *et al.*, 2004).

Pyrometallurgy

A typical pyrometallurgy process is a high temperature, smelting and reduction process for the recovery of metals from the spent LIBs. The reduced valuable metals were then recovered in the form of the alloy (Zheng *et al.*, 2018, 2017). Pyrometallurgy processes are mainly focused on the recovery of the other metals (Co, Ni, etc.), while Li was lost in the slag owing to its high reactivity (Zheng *et al.*, 2017). In this process, spent LIBs were directly burned in the smelted furnace, where plastics, graphite and organic components were combusted. The metals were found in the alloy form, which were further purified using leachants and solvent extraction (Zheng *et al.*, 2018). This process results in loss of Li recovery. So, researchers have combined pyrometallurgy process with hydrometallurgy or other processes.

Li *et al.* proposed the “waste + waste → Resources” approach (Li *et al.*, 2016). The anodic materials of graphite were utilized to reduce the cathodic materials of LiCoO_2 under the oxygen free conditions. The reaction was carried out at 1000°C for 30 min under the nitrogen atmosphere separately. The residue consisted of mixture of Co, Li_2CO_3 and graphite. The following reactions might be happening during oxygen free environment (Li *et al.*, 2016).



The residue mixture was further separated by the wet magnetic separation. The recovery of Co, Li and graphite were found to be 97.52%, 98.93% and 91.05%, respectively (Li *et al.*, 2016). Similarly, Hu *et al.* presented a recovery of valuables from the cathodic materials $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$. Al was recovered via the alkaline leaching in the form of NaAlO_2 . The residue was further undergone reduction roasting followed by the carbonated water and sulfuric acid leaching. The reduction roasting was found to be optimum at 650°C for 3 h with 19 wt% carbon dosage and materials were transformed into Li_2CO_3 , Co, Ni, and MnO. The residue mixture was further treated with carbonate water leaching (20 mL min^{-1} CO_2 , solid to liquid ratio 1:10, reaction time 2 h) to recover Li and acid leaching (H_2SO_4) of concentration 3.5 mol L^{-1} at 85°C for 3 h to recover the metals (Ni, Co, Mn). The recovery of Li was found to be 84.7%, while Ni, Co, and Mn were 99% leached out by this process (Hu *et al.*, 2017). In another work, Xiao *et al.* showed the mechanical separation of mixed electrode materials from the spent LIBs containing binder, graphite and LiMn_2O_4 followed by the oxygen free roasting of the mixed metal materials. In this process, binder was decomposed into the gaseous products, while MnO and Li_2CO_3 were formed in the oxygen free roasting at 1073K for 45 min. 91.3% Li was leached in the form of Li_2CO_3 from the roasted powder. Filtered residue was burnt in the air to get Mn_3O_4 and remove graphite (Xiao *et al.*, 2017). Träger *et al.* (2015) combined the mechanical pre-treatment process with the pyrometallurgical process to recover the valuable components of batteries, while these pyrometallurgical process was carried out to recover Li at higher than 1400°C, makes it a high energy consumption process. Georgi-Maschler *et al.* proposed a process to recover all the spent batteries components using the combination of mechanical pre-treatment with pyro and hydrometallurgy. Co alloys and Li_2CO_3 were the main products after the process (Georgi-Maschler *et al.*, 2012).

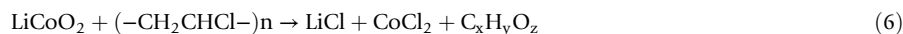
Biometallurgy

Biometallurgical processes require less equipment, environment friendly besides being a low-cost and high efficiency process. These processes can be promising alternatives than the pyrometallurgy and hydrometallurgy processes. In typical biometallurgy process, the bacteria produces organic and inorganic acids to leach the valuable metals from the spent batteries (Zeng *et al.*, 2014). Horah *et al.* used the fungal activities of *Aspergillus niger* for the bioleaching of the spent LIBs. The citric acid was found to be important for the effective leaching compared to other produced organic acids (gluconic, malic and oxalic acid). The process was conducted in three types i.e., one step (suspension containing battery powder was inoculated in sucrose medium for 30 days), two step (fungi was pre-cultured in sucrose medium for 3 days, which enters in the logarithmic phase after that battery powder was added for 27 days), and spent medium process (A. niger was first cultivated for 14 days, which enters in stationary phase and after that battery powder was added for 16 days). The spent medium process showed high recovery (100% Cu, 95% Li, 38% Ni, 65% Al, 70% Mn and 45% Co), while one step process showed leaching of 100% Li, 11% Cu and 8% Mn with negligible Ni and two-step process showed 100% Li, 61% Al, 10% Mn, 6% Cu and 1% Co leaching with negligible Ni (Horeh *et al.*, 2016). In another work, *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* were used for the removal of metals from the spent LIBs. 99.2% Li, 50.4% Co and 89.4% Ni were recovered under the optimum conditions (iron sulfate = 36.7 g L⁻¹, sulfur = 5.0 g L⁻¹, initial pH=1.5, best inoculum ratio of *Acidithiobacillus ferrooxidans*/*Acidithiobacillus thiooxidans* = 3/2) (Heydarian *et al.*, 2018). Mishra *et al.* utilized *Acidithiobacillus ferrooxidans* bacteria for the bioleaching of LIBs containing LiCoO₂, which provided the elemental sulfur and ferrous ion to produce sulfuric acid and ferric ion in the leaching medium. It has been found that Co showed faster leaching compared to Li, but slower dissolution for Li than Co (Mishra *et al.*, 2008). Xin *et al.* investigated mixed culture of sulfur-oxidizing and iron-oxidizing bacteria for the bioleaching of the spent LIBs using different systems i.e., S, FeS₂, and S+FeS₂. The bioleaching of Li was independent of energy sources, and mainly driven by acid dissolution mechanism. The bioleaching Co was favored by the collective action of acid dissolution and Fe²⁺ reduction in FeS₂ and S+FeS₂ systems, while the acid dissolution was the main mechanism for the S system (Xin *et al.*, 2009). The *Acidithiobacillus thiooxidans* and *Leptospirillum ferriphilum* were used for the bioleaching of metals (Li, Ni, Mn, Co) from the spent LIBs (LiFePO₄, LiMn₂O₄ and LiNi_xCo_yMn_{1-x-y}O₂ based batteries) and showed high recovery of metals (Xin *et al.*, 2016). Li recovery was maximum in the case of sulfur *Acidithiobacillus thiooxidans* system owing to the biogenic H₂SO₄, while other metals were recovered in the mixed energy source and mixed culture systems. The recovery of other metals (Co, Ni, Mn) was driven by the acid dissolution and Fe²⁺ reduction (Xin *et al.*, 2016). Niu *et al.* investigated the bioleaching behavior utilizing *alicyclobacillus* sp. (sulfur-oxidizing) and *Sulfobacillus* sp. (iron-oxidizing) bacteria's. The bioleaching efficiency was affected by the pulp density. 2% pulp density showed the maximum removal efficiency of 89% and 72% for Li and Co, respectively (Niu *et al.*, 2014). The bioleaching efficiency was decreased from 52% to 10% and 80%–37% for Co and Li, respectively with increasing pulp density from 1% to 4% (Niu *et al.*, 2014).

Other Processes

Pyrometallurgy and hydrometallurgy are the main processes to recover the valuable metals from the spent LIBs. Pyrometallurgy is high energy consumption and high metal loss process, and environments hazards are produced in the form of gases and dust. The hydrometallurgy process requires high quantity of chemicals. In the recent years, researcher have started new processes for the recovery of valuable metals (Zheng *et al.*, 2018).

Wang *et al.* achieved Co and Li recovery via mechanochemically. LiCoO₂ materials were first ball-milled with some additives, followed by water leaching procedure and subsequently recovery of Li and Co in the form of Li₂CO₃ and Co₃O₄ by chemical precipitation process. The ethylenediaminetetraacetic acid (EDTA) was found to be the best additive for the extraction of valuable metals. After ball milling, Li-EDTA and Co-EDTA were formed by solid-solid reaction owing to lone pair electrons (two nitrogen atoms and four hydroxyl oxygen atoms) of EDTA, which can enter the empty orbitals of Co and Li. Li-EDTA and Co-EDTA were easily recovered via water leaching. 98% Co and 99% Li could be recovered under the optimum conditions (LiCoO₂/EDTA mass ratio = 1:4, ball milling time = 4 h, rotary speed of ball mill 600 rpm, and ball/powder mass ratio = 80:1) (Wang *et al.*, 2016). Saeki *et al.* investigated Li and Co recovery via grinding with polyvinylchloride (PVC) using planetary ball mill. Li and Co were transformed into the respective chlorides, which were leached out using water to recover Li and Co. The Co and Li yields were increased to 90% after 30 h of grinding. The following reaction takes place during the mechanochemical process (Saeki *et al.*, 2004).



Wang *et al.* used PVC and other additives (Fe, Fe₂O₃, KOH, and many more) for the grinding of LiCoO₂. The ground mixture consisted of Li in the form of LiCl, Co in the form of magnetically separable CoFe_xO_y. Li was 100% converted into LiCl with the zero-valent Fe additive (Wang *et al.*, 2017). Liu *et al.* treated LiCoO₂ (spent from LIBs) and PVC by the subcritical water oxidation, where PVC acts as hydrochloric acid for the metal leaching. 95% Co and 98% Li were extracted from the spent LIBs under the optimum conditions (reaction temperature = 350°C, time = 30 min, PVC/LiCoO₂ ratio = 3:1, solid/liquid ratio = 16:1 in g L⁻¹) (Liu and Zhang 2016). Yang *et al.* targeted Li and Fe extraction from the spent LiFePO₄ batteries through the combination of mechanochemical process and H₃PO₄ leaching. 97.67% Fe and 94.29% Li were recovered from the spent LIBs at the end of the process. The leached metals were further extracted by selective precipitation and overall 93.05% Fe and 82.55% Li were recovered in the form of FePO₄·2H₂O and Li₃PO₄ (Yang *et al.*, 2017).

Table 2 contains consolidated data on the materials recovered from the spent LIBs.

Table 2 Consolidated data over the materials recovered from spent LIBs

S. No.	Recovery Conditions	Materials Recycled	Recovery	References
Hydrometallurgy				
1	Hydrochloric acid	Co and Li	99% of Co and Li	(Zhang <i>et al.</i> , 1998)
	PC-88A	Ni and Li	–	(Nguyen <i>et al.</i> , 2015)
	Oxalic acid	Co	–	(Lee <i>et al.</i> , 2004)
Pyrometallurgy				
2	High temperature, smelting and reduction process	Li	–	(Zheng <i>et al.</i> , 2018)
		Co, Li and graphite	97.52% of Co, 98.93% of Li and 91.05% of graphite	(Li <i>et al.</i> , 2016)
		Li, Ni, Co, and Mn	84.7% of Li and 99% of Ni, Co, and Mn	(Hu <i>et al.</i> , 2017)
		Li	91.3% of Li	(Xiao <i>et al.</i> , 2017)
		Li		(Träger <i>et al.</i> , 2015)
		Co alloys and Li ₂ CO ₃		(Georgi-Maschler <i>et al.</i> , 2012)
Biometallurgy				
3	Aspergillus niger	Cu, Li, Ni, Al, Mn and Co	100% of Cu, 95% of Li, 38% of Ni, 65% of Al, 70% of Mn and 45% of Co	(Horeh <i>et al.</i> , 2016)
	Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans	Li, Co and Ni	99.2% of Li, 50.4% of Co and 89.4% of Ni	(Heydarian <i>et al.</i> , 2018)
	Acidithiobacillus ferrooxidans	Li and Co		(Mishra <i>et al.</i> , 2008)
	sulfur-oxidizing and iron-oxidizing bacteria	Li and Co		(Xin <i>et al.</i> , 2009)
	Acidithiobacillus thiooxidans and Leptospirillum ferriphilum	Li, Ni, Mn, and Co		(Xin <i>et al.</i> , 2016)
	Alicyclobacillus sp. (sulfur-oxidizing) and Sulfobacillus sp. (iron-oxidizing) bacteria's	Li and Co	89% of Li and 72% of Co	(Niu <i>et al.</i> , 2014)
Other processes				
4	Mechanochemical	Co and Li	98% of Co and 99% of Li	(Wang <i>et al.</i> , 2016)
		Co and Li	90% of Co and Li	(Saeki <i>et al.</i> , 2004)
		Co and Li	100% of Li	(Wang <i>et al.</i> , 2017)
		Co and Li	95% of Co and 98% of Li	(Liu and Zhang, 2016)
		Fe and Li	93.05% of Fe and 82.55% of Li	(Yang <i>et al.</i> , 2017)

Post Treatment (Product Preparation)

The Products can be prepared via many ways. The valuable metal salts have been recovered by the biometallurgy, hydrometallurgy, pyrometallurgy etc., which usually consist of different metal salts/ions. The metal salts can be separated by different processes such as solvent extraction, floatation, chemical precipitation, etc., to get the individual metal salts. In other methods, the cathode material precursor can also be directly prepared through proper solution composition.

Different metal ions were collected in leachate form at the end of metal extraction process. These are separated by different processes such as solvent extraction, floatation, crystallization, etc. Many authors have implemented several techniques to recover CoSO₄ (Ferreira *et al.*, 2009); Cu, Co, Mn, Ni, and Li from spent LIB leachate (Chen *et al.*, 2015b); Li, Fe, and Mn from mixed cathode materials (combined LiMn₂O₄ and LiFePO₄) (Huang *et al.*, 2016). However, it is reported that due to the involvement of large amounts of chemical reagents used in the recovery process, the recovered product is not pure enough. In the case of preparation of precursors for cathode materials, direct preparation methods are followed to avoid complicated separation processes through fine tuning the composition of the leaching solution (Zheng *et al.*, 2018). Further, as obtained cathode material was processed further through co-precipitation (Sa *et al.*, 2015; Krüger *et al.*, 2014) and sol–gel (Yao *et al.*, 2015, 2016) to regenerate the same.

Conclusion

In this article, we have reviewed about the recycling of LIBs. We have discussed in-detail about the type of components present in the spent LIBs and their recycling processes to recover valuable metals. Statistics and legislation of LIBs are discussed as well and benefits of recycling of LIBs are brought out briefly. Green and affordable recycling process is essential to safeguard the environment from heavy metal contamination present in the spent LIBs. Further, effective recycling of spent LIBs will bring down the cost of the raw materials and will help in improving economics at the industrial scale.

Acknowledgments

BB acknowledges Department of Science and Technology (DST) support for providing the women scientist project award (Grant No: SR/WOS-A/CS-17/2017).

See also: Metallic Materials From E-Waste

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Recycling of Plastics for Low Cost Construction

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Introduction

It is estimated that about 8.3 billion metric tons (Mt) of virgin plastics have been produced to date (Geyer *et al.*, 2017), and 348 Million Mt of these were produced in 2017 (Plastics Europe, 2018). Therefore, it is clear that plastics are one of the most produced manmade materials. Since the discovery of polystyrene in 1839, there has been an exponential increase in research, development, production, and utilization of plastics. Recent advances in plastic production has increased versatility, and they are thus extensively used in a wide range of sectors, from food packaging to automotive, pharmacy, and medicine. Plastics are no doubt an indispensable material of the 21st century and have several benefits to which few alternatives exist. For example applications such as packaging, electronics, building and construction as well as agriculture have considerably benefited from plastics and in turn supported human development and growth by preserving produce, shaping global communications, and enhancing economic growth.

Although plastics can be reused, recycled, upcycled, or incinerated for energy recovery, a significant proportion of plastics still pose an environmental challenge because of poor disposal rates. Statistics tracking the destination of plastics reveal that only 9% of all global production has ever been recycled; 12% was incinerated, with the majority, 79%, accumulated in landfills or the natural environment (Geyer *et al.*, 2017). Plastics need several hundred years to biodegrade, which means the landfill sites are going to be a considerable environmental challenge for generations. Though the data suggests that with increased awareness of the dangers of leaving plastics in landfill, recycling and upcycling are becoming mainstream activities in many parts of the world, as recycling rates have increased over the last few decades.

Similarly, the improper disposal of plastics has had an adverse effect on marine life; this is becoming a key part of the environmental discourse, leading to significant action from environmental groups and increasing activity from nongovernment actors protecting marine life and raising awareness about the dangers of plastic waste.

These environmental challenges of sustainably disposing plastic waste are exacerbated in Low and Middle Income Countries (LMICs), particularly those in areas with poor infrastructure and weak institutions, which have inadequate waste management systems. A fairly common sight in these communities is plastic litter around the community, as illustrated in Fig. 1. The need for improved plastic waste management in LMICs becomes even more important when it is recognized that over 60% of the plastic production and consumption occurs in LMIC predominated regions: Asia, Africa, and Latin America (Plastics Europe, 2018).

In informal ecosystems, waste pickers typically drive the recovery of postconsumer waste; plastics are collected, sorted, pre-processed, and sold to plastic recyclers. This informal waste economy is quite vibrant in many LMICs and relies on the lack of coordinated waste management systems. Reusing plastic waste is also common in LMICs, for example, using plastic bottles, for storing cooking oils, portable water, and kerosene. However, these informal methods of plastic waste management are restricted to certain types of plastics and driven by demand.

An interesting development in upcycling plastic waste is the relation between low cost building construction materials and the huge demand for adequate housing in LMICs. Rapid urbanization taking place in LMICs has led to a shortage of housing in major cities, and consequently resulted in formation of informal settlements by the urban poor. The urgent need to provide homes for this population is a challenge because often resources are limited. It has been suggested that affordable and sustainable homes should employ suitable, locally sourced material and resources (Oyinlola *et al.*, 2018). Since plastic waste is often in abundance



Fig. 1 Plastic waste in low income community in Paipe.

and versatile, there is a strong case for it to be the candidate material for constructing affordable sustainable homes. Utilizing waste plastics in this form could be a driver for the development of the informal circular economy as it could place a higher premium on these waste streams. This has implications for reshaping the circular economy and incentivizing community members to partake in sustainable waste management practices.

This article explores the use of plastic waste in building construction, especially for low income homes, it reviews the different types and ways plastics have been used in construction, as well as presents some performance data. It further highlights the benefits and concerns of using plastics in low cost construction.

Plastics in Construction

Several researchers and professionals have explored the possibility of using waste plastics in constructions. This section highlights most of the common ways plastics have been used for construction.

PET Bottles as Building Bricks

Polyethylene terephthalate (PET) bottles make up a significant proportion of the plastic waste stream due to their increased use in the food and beverage sector. The opportunity to fill them up with other materials has made them an attractive option for use in low cost construction globally. There have been reports on this concept in various countries such as Nigeria, South Africa, Philippines, Norway, and India. Common names for this concept include bottle house, bottle bricks, and eco bricks.

The methods adopted for using PET bottles in construction vary from project to project. For example, plastic bottles can be filled with one or more materials such as sand, soil, and/or plastic bags. The filled bottles could be used directly as a brick or embedded inside blocks made from cement or clay. However, it is worth noting that the mortar used to hold the bottles in place varies across projects and plays an important role in the loading capacity of the wall.

Many reports of using plastic bottles have been made on websites and social media, however, few researchers have scientifically studied the suitability of plastic bottles as a candidate material for constructing low cost, environmentally-friendly homes. These studies usually focused on characterizing the mechanical, structural, and thermal properties of these materials.

In Bangladesh, [Muyen et al. \(2016\)](#) studied the structural and thermal behavior of plastic bottles filled with dry sand, saturated sand, or air. They examined the effect of bottle size (250, 500, 1250, 1500, and 2000 ml) in three types of cement mortar based samples: Cubes, bricks, and cylinders. They found that plastic bottles filled with sand have the highest compressive strength of up to 35 MPa. They also noted that the compressive strength increased with the size of the bottle. Although the strength of the plastic bottle wall was considerably less than conventional bricks, they suggested that they could still be used as a suitable building material. They noted that air filled bottles showed better thermal insulation than traditional blocks.

In India, [Rawat and Kansal \(2014\)](#) performed a series of compression tests on 600 ml soil filled bottles and found them to have an average strength of 8.99 MPa. They further stated that compared with local bricks, PET bottles have an added advantage of improved ductility and inhibition of crack propagation after its initial formation. They also found PET bottles to be more cost effective, energy efficient, and feasible compared with using standard bricks. [Mokhtar et al. \(2015\)](#) also studied the compressive strength and obtained better results. Their tests using 250 ml and 1.5 l bottles, filled with partially wet sands gave a value of 38.34 MPa and 27.39 MPa respectively.

[Oyinlola et al. \(2018\)](#) measured the compressive strength of two types of mortar mixes used when constructing the bottle house shown in [Fig. 2](#). The mortar of the first sample was made of 1:4:5 ratio of cement, clay soil, and river sand respectively. Water was used to mix for good workability. The mortar for the second sample was a 1:9 mixture of cement and sand with water. Experimental testing showed that the sample with clay had a compressive strength of 0.6 MPa while a compressive strength of 1.2 MPa



Fig. 2 Bottle house in Paipé, Abuja, Nigeria. Reproduced from Oyinlola, M.A., Whitehead, T., Abuzeinab, A., et al., 2018. Bottle house: A case study of transdisciplinary research for tackling global challenges. *Habitat International* 79, 18–29. doi:[10.1016/j.habitatint.2018.07.007](https://doi.org/10.1016/j.habitatint.2018.07.007).

was observed in the mortar mix without clay. They also gave a detailed description of how the bottles were used in construction. The bottles were laid horizontally on the ground with a spacing of about 4 cm. PET bottles were then knitted into a matrix using a rope; the rope went over a bottle and linked to the adjacent bottle in a repeated fashion. The ropes helped to hold the bottles in place before the mortar was applied and acted as a fiber reinforcement for the mortar, thus increasing the structural integrity and stability.

The examples discussed above highlight the variability in characterizing the strength of plastic bottles, which is affected by various parameters, such as size of bottles, material used for filling, and mortar. However, there is unanimity on the suitability of PET bottles as a suitable material for construction.

PET Aggregates in Concrete

Waste plastics have also been used as an aggregate in construction mortar. The manner in which this is used varies; the plastics could either be ground into smaller particles or cut into strips before being mixed into the mortar. This method of using waste plastic as aggregate is not exclusive to low cost construction and several scholars have reported on utilizing plastic waste as mortar aggregate. PET seems to be a popular candidate for this method.

Aggregates from some types of plastics, especially PET, have been found to mix well with concrete. For example, [Ochi et al. \(2007\)](#) developed concrete-reinforcing PET fiber from used PET bottles; the project team reported good mixing between the fibers and concrete at up to 3% fiber content.

Another advantage of using plastic waste aggregate is that it could enhance the properties of the mortar. For example, [Kim et al. \(2010\)](#) studied the effect of using short fibers made from recycled PET within structural concrete. This study found a significant improvement in the ultimate strength and relative ductility of the PET reinforced beams, compared with those without. Similarly, [Fraternali et al., 2013](#) produced PET strips by simply hand cutting used PET and studied the effect of using this in cement mortar. Similarly this research found that at 1% fiber volume, the reinforcing strips markedly improved the toughness of the cement mortar while [Bui et al. \(2018\)](#) found that up to 9% increase in compressive strength can be achieved when using recycled PET fibers in recycled aggregate concrete.

The properties of plastics have been exploited when used as aggregates. For example, they have been used to produce lightweight concrete ([Alqahtani et al., 2017](#)). Plastics generally have low thermal conductivity, which make them an attractive option for improving the thermal performance of building envelopes ([Poonyakan et al., 2018](#)). Using waste plastics as aggregates has been studied extensively and well documented in the literature. A review of this can be found in [Gu and Ozbakkaloglu \(2016\)](#).

Low Value Plastics

One of the most problematic types of plastic waste is used carrier bags made from polyethylene. These are especially challenging in low income communities because they have little or no value in the informal waste economy. These low value plastic wastes have been used in construction, either unprocessed or processed to make new composite materials. This section highlights some ways low value plastic wastes have been used in construction.

Unprocessed

A few studies have reported using plastic bags as key construction materials. [Taaffe et al. \(2014\)](#) conducted experiments to determine the compression, acoustic, and light transmission properties of plastic bags packed in plastic bottles, which they referred to as eco bricks. The study concluded that eco brick was a viable resource for construction purposes with a number of possible applications. The low thermal conductivity of plastics implies that they provide much better thermal insulation although at a lower strength, they found an average strength of 2.72 MPa. Using low value plastics as a filling material is advantageous for low income communities because this requires little or no specialized skill.

Another innovative use of unprocessed plastic waste was developed by a US-based start-up called Byfusion (see “Relevant Websites section”). The technology developed – Byfusion Blocker – can convert 100% of plastic waste into ByBlocks. This is achieved by superheating shredded plastics and then fusing them into building blocks. The byblocker can use any category of unsorted and unwashed plastic waste. The ByBlocks, though not load bearing, are said to have superior thermal and sound insulation properties when compared with cement based blocks. This method does not require any specialized skills, however, it requires specialized equipment and is suited for large scale recycling in municipalities.

Processed

Another way of using low value plastics is by melting them and mixing the molten plastic with other material such as soil and cement. There have been few reports about using plastics in this way. For example, in Mexico, EcoDom (see “Relevant Websites section”), based in Puebla, has produced building materials such as walls and thermic roof by recycling various types of plastic waste including PET, high-density polyethylene (HDPE), polypropylene, and acrylonitrile butadiene styrene (ABS). Their process includes sorting, grinding into flakes, and pressing at high pressure to form the raw material for their products. The company claims the products have much higher strengths when compared with traditional building materials.

Similarly, *Conceptos Plásticos* (see “Relevant Websites section”), Colombia has built several low cost homes using LEGO-style bricks made from recycled plastics. The plastics are melted and poured into a mold to form the bricks. The molds are designed to

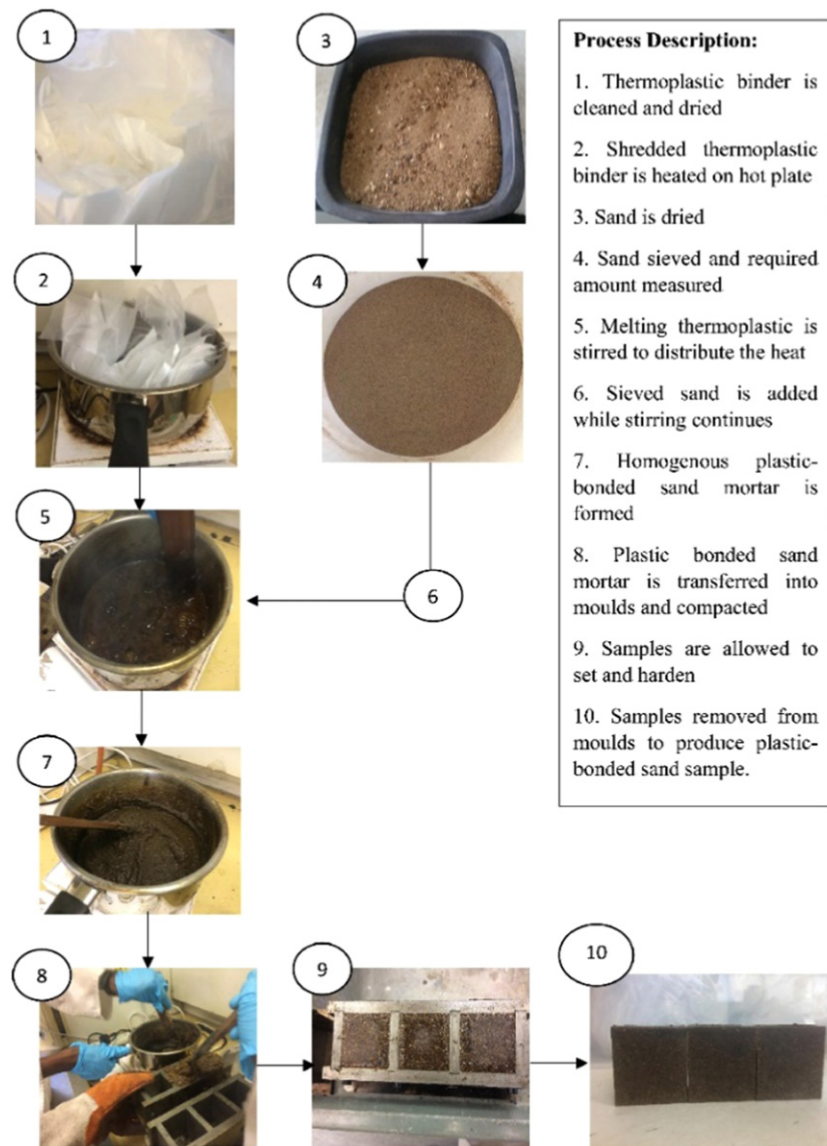


Fig. 3 Process flow diagram showing the method used to produce low-density polyethylene-sand composite materials. Reproduced from Kumi-Larbi, A., Yunana, D., Kamsouloum, P., *et al.*, 2018. Recycling waste plastics in developing countries: Use of low-density polyethylene water sachets to form plastic bonded sand blocks. *Waste Management* 80, 112–118. doi:10.1016/J.WASMAN.2018.09.003.

produce bricks that are simple in structure and can easily slot together. This eliminates the need for using mortar as well as accelerates the construction process, which requires little skill. They report a construction time of 20 man-days for a simple house, and a 30% reduction in cost compared with the traditional construction process.

Kumi-Larbi *et al.* (2018) studied the effect of sand particle size and sand to plastic ratio on density, compressive strength, water adsorption, flexural strength, and thermal conductivity. Their sand block samples were produced using a simple technology that involved mixing sand with melted low-density polyethylene (LDPE) water sachets (which is a cheaper form for packaging purified water) and forming in mold. Fig. 3 shows a process flow diagram of their process. They reported strengths of up to 27 MPa and observed an inverse relationship between the particle size and compressive strength/density.

Benefits of Plastics in Construction

Many studies have reported several benefits of utilizing plastic waste in construction. The most obvious environmental benefit is reducing the amount of plastics that go to landfill. This is very significant as recent studies have shown the negative effects waste plastics are having on life on land and underwater. Utilizing plastics in this way contributes to achieving the United Nations

Sustainable Development Goals, (SDGs) goal 14: life below water and goal 15: life on land. Furthermore since most low income communities in LMICs have weak infrastructure for waste management, utilizing waste plastics for low cost construction places a higher premium on these wastes and can further expand and strengthen the informal waste economy.

Another benefit is the potential to lower construction cost by replacing traditional materials. Most scholars have reported a lower cost, for example [Muyen et al. \(2016\)](#) reported that plastic bottle walls cost approximately 75% less than concrete block walls while [Oyinlola et al. \(2018\)](#) reported a 30% reduction on the total construction costs compared with using traditional cement blocks. It is important to note that the cost of labor in low income communities is relatively cheap, hence, materials make up the bulk of the costs for construction. Furthermore, transport costs are significantly reduced when using available building materials; even the cost of transporting waste plastics to building is relatively cheap, since they are lightweight. Therefore, using locally engineered waste materials can significantly reduce the cost.

Since plastics do not biodegrade for centuries and are impermeable, they can be considered as durable materials for construction. They have improved ductility and can inhibit crack propagation after its initial formation ([Rawat and Kansal, 2014](#)). Also, using plastics can significantly reduce construction waste since they are nonbrittle, compared with using conventional blocks. This also implies they can be reused if a wall is destroyed. The insulating properties of plastic make them an excellent material for improving thermal comfort in home. Claims have been made that walls made from sand filled bottles are bulletproof, fireproof, and earthquake resistant, however, there has been no scientific study to prove this.

Concerns About Plastics in Construction

Despite the numerous benefits of using waste plastics in low cost construction, there are also genuine concerns about their use. This section highlights some of the main concerns that have been raised about using plastics in low cost construction.

User Acceptance

Most of the studies published on using waste plastics in construction have focused on characterizing the mechanical, structural, and/or thermal properties. A glaring gap in the literature is in terms of the user acceptance of this concept in low income communities. [Oyinlola et al. \(2018\)](#) conducted a study to evaluate the user acceptance of a bottle house in Abuja, Nigeria. They noted a generally positive response to the bottle house concept from high and middle income visitors. However, members of the low income community, who could be potential occupants, were not willing to live in the bottle house. Firstly, living in a home built from waste materials would have a negative impact on their social status. Secondly, most of the sustainable measures proposed, such as the roof, would make the house different from contemporary homes in the city, thus less desirable and esthetically unacceptable. The study highlighted how sociocultural and political considerations may trump economic ones; regardless of the benefits of a material, it was important for it to look esthetically contemporary for the concept to be acceptable. This concern can be overcome by using conventional cladding materials or embedding plastics fibers into conventional building materials. However, more studies are needed to understand the barriers and drivers for user acceptability of waste plastics in construction in low income communities.

Social Viability

The informal waste economy is usually strong in low income communities, especially for PET. Plastic waste is usually collected, sorted, preprocessed (washing and grinding into flakes), and sold to plastic recyclers for further processing. Similarly, plastic containers are often reused in these communities for storing things like cooking oil, kerosene, portable water, etc. These realities mean that firstly, since there is a market for some types of plastic waste, utilizing higher value plastics in low cost construction may be challenging and/or counter sustainable, since they are already associated with a particular segment of the circular economy. In-depth lifecycle analyses to compare the environmental and economic value of utilizing waste plastics in construction as against current circular economy uses are needed.

Another concern is the practicality of deploying mechanisms for collecting and sorting plastic waste for constructing several homes. Most reports on low cost construction have been on a small scale, for example, [Oyinlola et al. \(2018\)](#) collected 10,000 PET bottles for a 2-bedroom house. This might be challenging to achieve on a large scale. The peculiarities of deploying them at a large scale need to be further studied. Furthermore, some of the methods of utilizing plastic waste require some level of skills, which might require the need to build local capacity. This can be challenging and time consuming, hence a cost-benefit analysis is essential to determine the long term viability.

The potential health hazards of using plastics in construction are another major concern. Firstly, methods that require melting of plastics are thought to produce fumes that can have a long term negative impact on health. This is especially worrying because of the absence of adequate health and safety mechanisms in LMICs. Another cause for concern is that plastics may be outgassing toxic gases at ambient temperature, which may pose a significant risk to inhabitants of homes built with plastics. This concern needs to be investigated as well as the long term performance of plastic when it is mixed with other building materials or subjected to ambient conditions over extended periods.

Conclusion

Sustainably tackling waste plastics is one of the global challenges of the 21st century and the absence of essential waste management infrastructure in LMICs exacerbates this challenge. However, there is a real opportunity to utilize this resource and help provide adequate housing for low income users, which plays a crucial role in sustainable development.

This article provided an insight into innovative ways waste plastics have been used for providing low cost housing. The properties of plastics make them an attractive material, especially when mixed with other conventional building materials. They have potential to increase strength, improve thermal performance, and provide greater flexibility in construction. Some of the methods commonly employed include using PET bottles as blocks, using them as mortar aggregates, and melting them to produce new building components. Various scholars have characterized the mechanical, structural, and/or thermal performance of plastics in low cost construction, however, there is still a wide gap in the literature in terms of understanding user acceptance, social viability, as well as understanding the long term health implications of using plastics for building homes.

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Relevant Websites

<https://www.byfusion.com>
ByFusion.

www.conceptosplasticos.com
Conceptos Plásticos.

www.en.ecodom.mx
Ecodom.

Recycling of Red Mud for Value-Added Applications: A Comprehensive Review

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Introduction

The development of the mineral industries led to the generation of large quantities of waste materials and byproducts which in turn caused various environmental problems. Over the years, the exploitation of mines/quarries has gradually decreased the quality of ores due to the extraction of rich reserves, and as a result, the amount of waste increased. The accumulation of waste, in particular waste from different stages of processing, is one of the major sources of environmental problems. Most of these mineral deposits are hazardous and, directly or indirectly affect the environment. If the waste materials are not properly controlled, their harmful substances enter the surface and underground water and pollute the vast area. Meanwhile, bauxite residue, (known as red mud (RM), red clay, alkaline clay, and cajunite) (World's Leading Producers of Aluminum Oxide, 2017), is considered as one of the environmental concerns (Power *et al.*, 2011). The RM is produced during the Bayer process, the production of alumina from bauxite ore. Due to its small particle size, high alkalinity, and huge volume of production, the RM leads to the environmental crisis (Rao *et al.*, 2016a). The annual production of the global RM is estimated at 120–150 million tons. According to 2007 statistics, more than 2.7 billion tons of RM have been accumulated in different parts of the planet, and this accumulation is still expanding, as today's accumulation is estimated at around 4 billion tons (Marin *et al.*, 2018). An average of about 1–2 tons of RM is produced per ton of alumina production in the Bayer process. The quality of the RM depends on the process conditions and bauxite quality. The main factor in bauxite quality is the nature of alumina hydroxide compounds (gibbsite, boehmite or diasporite) and its silica content. Regarding the dangerous nature of the RM, especially considering its pH value, many discussions have taken place in the European Union. Based on a number of standard criteria, any waste with a pH value higher than 11.5 is often regarded as a hazardous substance (Evans, 2016).

The International Aluminum Institute (2016) proclaimed that just in 2016, China was responsible for 55% of global alumina production, followed for Australia and Brazil with 17% and 9%, respectively. While in 2017, Australia ranked first. It is estimated that more than 85 plants are located around 32 countries, responsible for the alumina production (The International Aluminum Institute, 2016; Tsakiridis *et al.*, 2004). Fig. 1 shows the world's leading producers of aluminum oxide. Rationally, these countries are the largest origins of the RM throughout the world.

Safe disposal of RM as an initial practice is a costly and challenging approach for the alumina manufacturers. On the other hand, adopting an improper disposal method can adversely affect the ecosystem and surface and underground water. If appropriate solutions can be found for the utilization of RM, they will provide multilateral advantages both for environment and industries. First, the amount of the waste and its corresponding disposal cost will decrease. Second, the environmental pollution originated from the waste disposal will remarkably be diminished. And third, the production and development of cost-effective advanced materials from such wastes can result in the conservation of natural resources and also economic benefits. All these together facilitate a sustainable environment and development.

The global tendency for the more efficient exploitation of resources led to many endeavors for the utilization of RM in the past few years. The increase of industry enthusiasm, academic research, and funding by organizations such as the European Union considerably improved the collaboration between academic and industrial communications. In 2015, under the 2020 perspective,

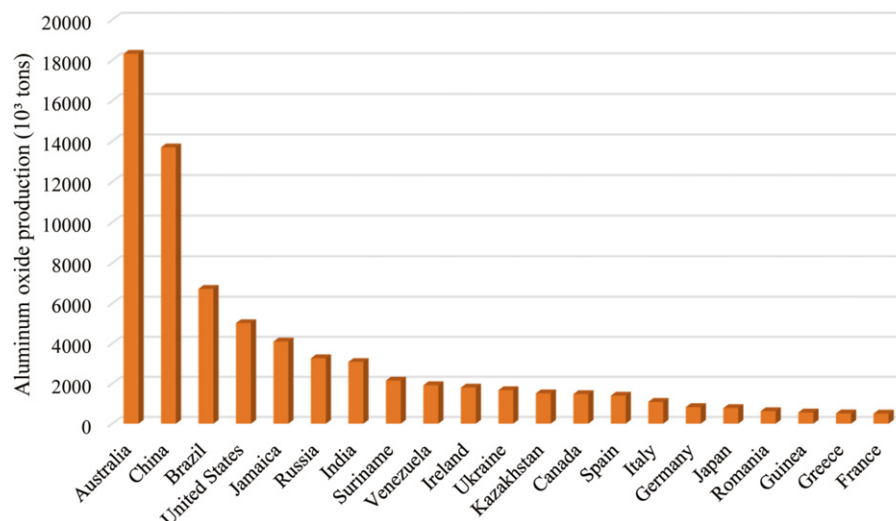


Fig. 1 World's leading producers of aluminum oxide (based on data on 26 Sep. 2017).

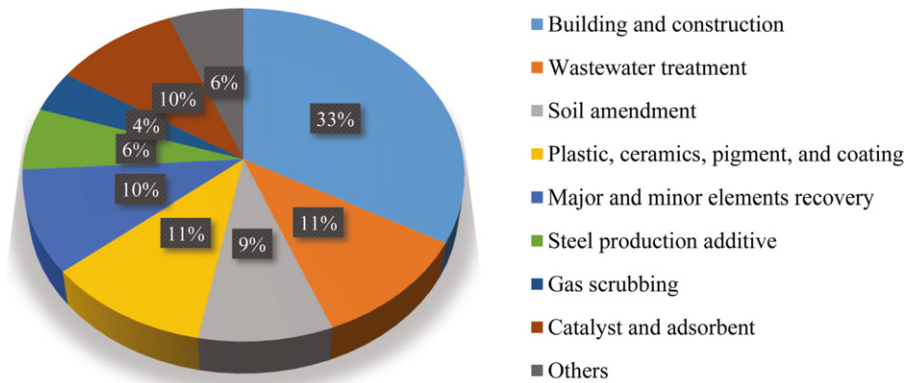


Fig. 2 Registered patents between 1964 and 2008 for the applications of red mud.

the European Union agreed to fund 15 PhD graduate for research on the recycle and utilization of RM. Approximately 3.7 million euros were funded for this purpose. The main focus of the research was on the extraction of iron, titanium, aluminum and rare earth elements (such as scandium), and the production of new construction and building materials from RM (Evans, 2016). Despite the acceptable results of utilizing RM in the construction sector, there is still no large scale application to reuse RM, because the studied options did not completely justify the requirements and economic-environmental feasibility of the research plan. Between 1964 and 2008, over 734 patents were registered on the application of the RM (Klauber *et al.*, 2009). As seen in Fig. 2, 34% of the registered patents are assigned to the civil and building construction application of the RM, followed by wastewater treatment, ceramics, and so on. Considering the huge amount of generation and also resulting ecological and safety aspects of the RM, the need for further research on this solid industrial waste is quite evident (Gräfe and Klauber, 2011).

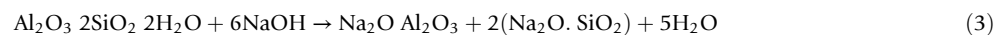
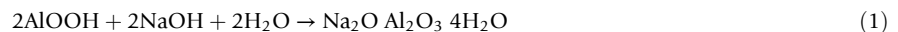
In recent years, public awareness and concerns on the quality of environment forced the legislators to pass strict regulations on environmental contamination due to the industrial wastes. Today, the need to develop economic methods for the utilization of wastes is a necessity, resulting in the great importance of recycling of the remaining valuable materials in the composition of industrial wastes (Klauber *et al.*, 2011).

This review work tries to highlight the various aspects of the RM including its chemical and mineralogical compositions, production process, environmental impacts, with an emphasis on different utilization and recycling methods.

Red Mud Production Process

The RM as the bulky waste of the Bayer alumina production process, is formed as the result of the reaction between sodium hydroxide and bauxite ore. The bauxite ore is usually a combination of minerals rich in aluminum oxide and hydroxide. However, bauxite also contains minerals of iron, silicon, titanium and rare earth elements. For each ton of alumina produced, about 1–2 tons (dry mass) of RM are produced (Wang *et al.*, 2008). Fig. 3 shows a schema of the traditional Bayer alumina manufacturing process.

This process involves the separation of alumina from unwanted components such as iron, titanium, silica, calcium, vanadium, manganese, etc., in bauxite. In this process, bauxite is heated along with the caustic soda at high pressure (~30 atm), resulting in the formation of sodium aluminate (reactions (1)–(4)) (Gil, 2005; Ma *et al.*, 2009).



Aluminate is hydrolyzed and converted to aluminum hydroxide (reaction (5)), followed by the production of aluminum oxide or alumina after calcining the produced aluminum hydroxide at high temperature ($\geq 1200^\circ\text{C}$) (reaction (6)) (Gil, 2005). After extraction, the insoluble residue is known as red mud or bauxite residue. Its color and name are due to its high iron oxide content. For each tone of alumina produced, 2–3 tons of bauxite ore should be used. Depending on the quality of bauxite ore, 1–2 tons of RM waste are also produced as a byproduct (Rai *et al.*, 2017).



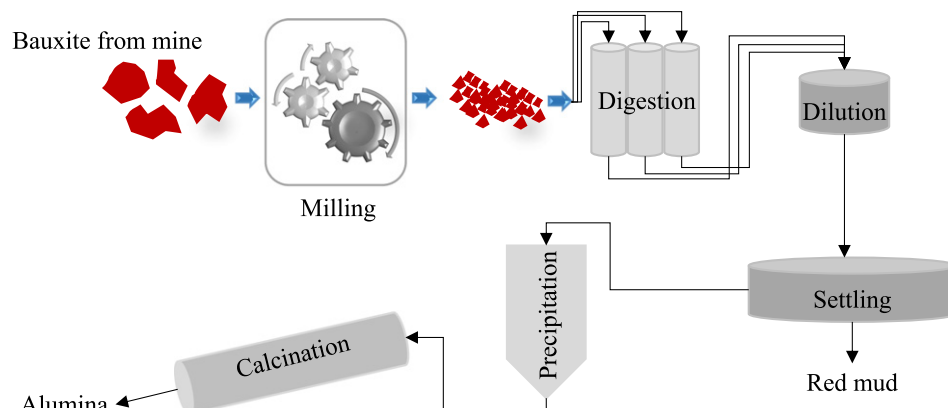


Fig. 3 A typical alumina production process (Bayer process).

Table 1 Typical chemical composition of red mud

Major element	Conc. (wt%)	Minor element	Conc. (mg/kg)	Minor element	Conc. (mg/kg)
Fe	4.53–50.10	U	50–60	Mn	86
Al	4.42–16.06	Ga	60–80	Y	60–150
Si	2.16–14.86	V	730	Ni	31
Na	0.98–7.79	Zr	1230	Zn	20
Ca	0.39–16.72	Sc	60–120	Lanthanides	0.1–1
Ti	0.98–5.34	Cr	497	Th	20–30

Note: Rao, C., Bart, B., Yiannis, P., Koen, B., Gerven, T.V., 2016a. Recovery of rare earths and major metals from bauxite residue (red mud) by alkali roasting, smelting, and leaching. *J. Sustain. Metall.* 3 (2), 393–404. Liu, Y., Naidu, R., 2014. Hidden values in bauxite residue (red mud): Recovery of metals. *Waste Manag.* 34 (12), 2662–2673.

Characterization of Red Mud

The RM has a specific gravity of 3.0–3.6 g/cm³ (World's Leading Producers of Aluminum Oxide, 2017). A typical chemical composition of the RM, including the major and minor elements, is shown in Table 1. As can be seen, the highest proportion pertains to iron. The amount of iron in various types of RM, depending on the structure of the initial bauxite ore, can range from 4% to 50%. It is possible to achieve an iron recovery efficiency of around 51% in some samples, comparable with iron ore. It is necessary to note that a wide range of other components can be present in trace amounts in bauxite, in particular oxides of As, Be, Cd, Cr, Cu, Ga, Pb, Mn, Hg, Ni, K, Th, V, Zn, Sc, and lanthanide. Some of these elements remain undissolved during the Bayer process, as they are eliminated with the RM, while some are soluble and present in the Bayer leachate or the aluminum hydroxide precipitate. The concentration of these elements in the RM depends on the temperature used in the extraction process. These valuable elements may be recovered using appropriate techniques (Rao et al., 2016a; Marin et al., 2018; Liu and Naidu, 2014; European Aluminium, 2015). A wide variety of organic compounds can also be present in the chemical composition of the RM, originating from organic matter and vegetables in the RM. These are carbohydrates, alcohols, phenols, and sodium salts of polybasic and hydroxyacids such as fulvic, humic, acetic, oxalic or succinic acids. In addition, small quantities of some sodium compounds derived from the sodium hydroxide used in the digestion process, depending on the conditions of the dewatering and the washing system, may remain (European Aluminium, 2015). The bauxite contains very few radioactive elements such as uranium (²³⁸U), thorium (²³²Th and ²³⁴Th), bismuth (²¹⁴Bi and ²¹²Bi), and polonium (²¹⁰Po). The amounts of these elements in the bauxite are naturally in the range of mg/kg and cause very low levels of radioactivity. During the Bayer process, a great part of these elements remain undissolved. Therefore, the concentration of these radioactive species in the RM is higher than that in the initial ore (European Aluminium, 2015; Miller and Miller, 2016; Hegedűs et al., 2018; Gu et al., 2017b).

To find out how the RM can be converted into valuable products, one can look at it from two different standpoints. In the first view, the RM is considered as a mixture of metal oxides and other compounds that exist or can be formed by heating over 1000°C. These components can be utilized to produce different metals such as iron, aluminum, silicon, calcium, titanium and sodium. Such an analysis is performed by X-ray fluorescence (XRF) technique (Klauber et al., 2011). An example of XRF analysis, which is performed on the RM generated in Iran Alumina Company, is presented in Table 2 (Karimi et al., 2018):

In the second view, which is a mineralogical standpoint, X-ray diffractometry (XRD) is employed to characterize the RM as a combination of various minerals (Klauber et al., 2011). As presented in Table 3, the RM has a complex mineralogical composition with a large number of different compounds such as iron-rich phases (hematite, goethite), aluminum (gibbsite, diasporite, bayerite), calcium (calcite, calcium silicate and calcium aluminosilicate) sodium (sodalite, cancrinite, dawsonite), silicon (quartz,

Table 2 XRF chemical composition of red mud waste of Iran Alumina Company

Constituent	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	Sc	Zr	Ce
Conc.	16%–18%	13%–16%	20%–25%	4%–8%	20%	1.5%	3.5%	32–60 ^a	400 ^a	70 ^a

^aIn ppm.

Note: Karimi, Z., Allahverdi, A., Mahinroosta, M., 2018. Recovery of metals from red mud using mineral acids. In: Proceedings of Iran International Aluminium Conference (IIAC2018), 24–25 April 2018. Tehran, Iran.

Table 3 Typical mineralogical composition ranges for red mud

Mineral name	Chemical formula	Typical mass percentage (%)
Sodalite	$Na_8Al_6Si_6O_{24}Cl_2$	4–40
Goethite	$FeOOH$	10–30
Hematite	Fe_2O_3	10–30
Magnetite	Fe_3O_4	0–8
Silica ^a	SiO_2	3–20
Calcium aluminate	$3CaO \cdot Al_2O_3 \cdot 6H_2O$	2–20
Boehmite	$AlOOH$	0–20
Anatase and rutile	TiO_2	2–15
Muscovite	$2KF \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot H_2O$	0–15
Calcite	$CaCO_3$	2–20
Kaolinite	$Al_2Si_2O_5(OH)_4$	0–5
Gibbsite	$Al(OH)_3$	0–5
Perovskite	$CaTiO_3$	0–12
Cancrinite	$Na_6Ca_2[(CO_3)_2Al_6Si_6O_{24}] \cdot 2H_2O$	0–50
Diaspore	$AlOOH$	0–5

^aCrystalline and amorphous.

Note: European Aluminium, 2015. Bauxite residue management: Best practice. World Aluminium. July 2015. Available at: <http://www.worldaluminium.org/publications/tagged/bauxite%20residue/>. Karimi, Z., Allahverdi, A., Mahinroosta, M., 2018. Recovery of metals from red mud using mineral acids. In: Proceedings of Iran International Aluminium Conference (IIAC2018), 24–25 April 2018. Tehran, Iran.

cancrinite, sodalite) and titanium (rutile, anatase) (Marin *et al.*, 2018; Klauber *et al.*, 2011). Also, in the composition of RM, one percent of the original goethite (α -FeOOH) may turn into hematite (α -Fe₂O₃), depending on the process conditions. Titanium minerals can react with calcium to form perovskite. Sodalite, cancrinite, dawsonite and most of calcium-containing phases are formed as a result of the Bayer process. Boehmite, gibbsite, anatase and rutile, ilmenite, perovskite and quartz are other minerals commonly found in the RM matrix (Gräfe and Klauber, 2011).

For instance, the XRD pattern of an RM sample taken from Iran Alumina Company, is depicted in Fig. 4. As clearly seen, hematite (Fe₂O₃), calcite (CaCO₃), katoite (Ca₃Al₂(SiO₄)(OH)₈), cancrinite (Na₆Ca₂Al₆Si₆O₂₄(CO₃)₂·2H₂O), spurrite (Ca₅(SiO₄)₂CO₃), and rutile (TiO₂) phases have been identified.

The chemical composition estimation based on quantitative calculations of the XRD data can be accomplished through Rietveld analysis. Fig. 5 shows the estimated chemical composition of RM of Iran Alumina Company using the XRD data. As can be seen, the calculated percentages of Al₂O₃, SiO₂, Fe₂O₃, TiO₂, CaO, MgO, and Na₂O are very close to the XRF values listed in Table 2.

Fig. 6 shows field emission scanning electron microscopy (FESEM) images of the RM sample of Iran Alumina Company. As seen, the RM comprises of various particles with different size and shape. In addition, the RM exhibits a relatively porous structure.

The RM is mainly composed of fine particles, but it may also contain small amount of coarse grains. The fine portion typically is 90% by volume below the size of 75 μ m (Singh *et al.*, 1997a; Smirnov and Molchanova, 1997), and a high surface area of between 30 and 50 m²/g (Li and Rutherford, 1996). As an instance, Fig. 7 shows particle size distribution of the RM waste of Iran Alumina Company. As seen, the coarse portion has a size between 1 and 8 μ m. The particle size distribution curve indicates that 50% of the fine portion is below 2.94 μ m, whereas 100% of the portion has a size of less than 24 μ m.

Atun and Hisarli (2000) measured the surface charge of the RM and reported an intense uptake of protons. The zero point of charge (pH_{zpc}) of the RM was obtained about 8.3 in low concentration of sodium, cesium, and strontium chlorides, which very close to the pH_{zpc} values of Al₂O₃, Fe₂O₃, and TiO₂.

Environmental Impacts

The accumulation of hazardous industrial wastes has become a global concern which imposes potentially serious ecological problems (Chaban, 2001). The major strategies currently applied to manage the RM are marine disposal, lagooning, dry stacking,

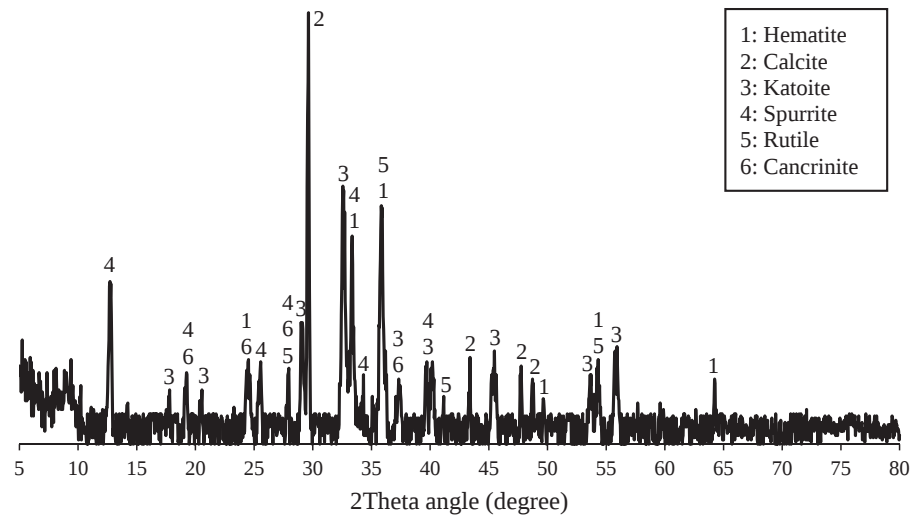


Fig. 4 XRD pattern of red mud waste of Iran Alumina Company.

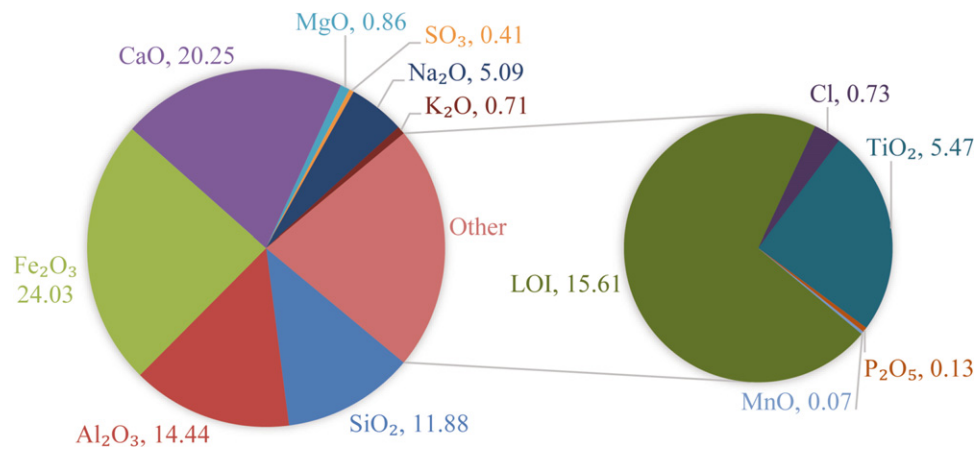


Fig. 5 Chemical composition of red mud waste of Iran Alumina Company based on XRD calculation.

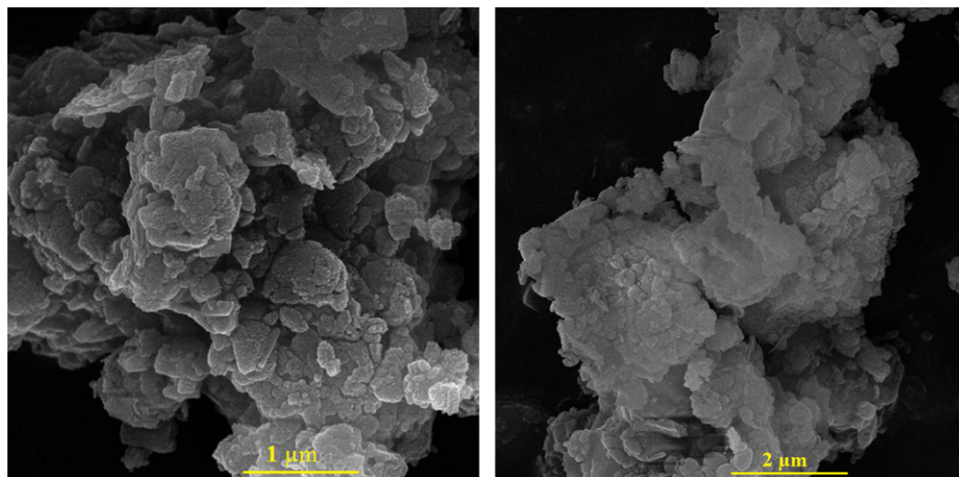


Fig. 6 FESEM images of red mud waste of Iran Alumina Company.

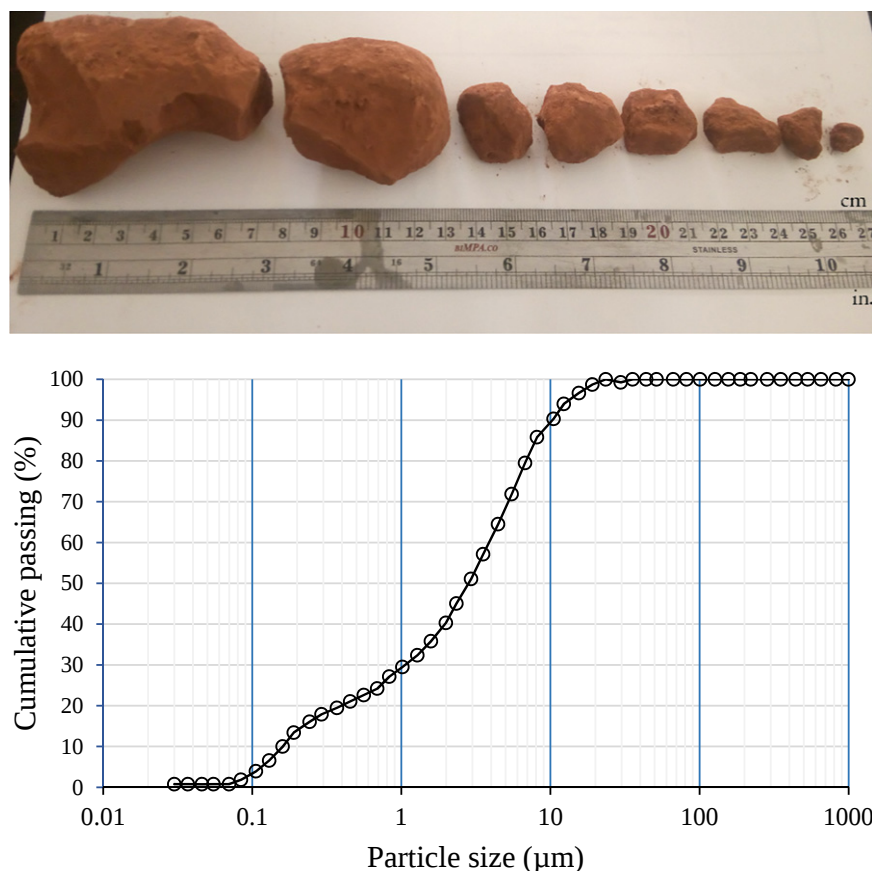


Fig. 7 Top: coarse red mud particles, Bottom: particle size distribution curve of fine portion.

and dry cake disposal (Power *et al.*, 2011). The disposal of the RM in open space is challenging for alumina production plants (Rai *et al.*, 2012). The challenge originates from two main drawbacks: (1) due to highly alkaline nature and chemical composition, the RM has an undeniable effect on the environment; and (2) disposal of the RM imposes a large expenditure and needs for vast landfill sites for alumina production industry (Díaz *et al.*, 2015). The disposal cost is about 2%–5% of alumina price (Liu and Zhang, 2011). Fig. 8 shows the latest Google Earth spatial photo of an alumina production plant in Jajarm, Iran, with RM disposal landfill sites in the vicinity of the plant.

The RM is disposed as dry, semi-dry or as slurry in ponds. The slurry contains a high solid concentration of 30%–60% and high ionic strength. Untreated RM has a high pH value ranging from 11 to 13, which makes plant growth impossible and causes serious environmental problems. As illustrated in Fig. 9, the environmental problems caused by the discharge of RM are related to its high pH, leakage of alkali, heavy metals and radionuclides to surface and underground water, safe storage, alkaline dust emissions, and need to vast landfill sites for discharge (Rai *et al.*, 2012).

Due to its high alkalinity, the presence of toxic trace elements (such as Cr, As, Cd, Hg, Ni, etc.) and radionuclides (such as ^{226}Ra , ^{230}Th), the RM can be regarded a hazardous industrial waste (Klauber *et al.*, 2011; Milacic *et al.*, 2012; Kolencsik-Tóth *et al.*, 2014; Sas *et al.*, 2015; Mora *et al.*, 2015). In most cases, alumina companies discard the RM into open-air reservoirs keeping it in a solution of caustic soda (wet storage) and stockpiling large amount of it over decades (Klauber *et al.*, 2011). The wet storage method may bring about a high risk of dam failures (Mora *et al.*, 2015; Grenczky and Wegmüller, 2011; Wen *et al.*, 2016) which can result in severe environmental disasters as it previously taken place in Brazil (Segura *et al.*, 2016) and earlier in Hungary (Szépvölgyi, 2011; Rédey *et al.*, 2013). In 2010 in Hungary, a lagoon containing RM slurry flooded, and about 700,000 m³ of the slurry waste was flowed in the region of Ajka. As a result, 10 people were died, about 350 houses were destructed and significant regions were contaminated (Szépvölgyi, 2011; Rédey *et al.*, 2013).

Regarding its nature, the RM in wet storage mode can be regarded as a complex blend of pollutants. Its broad impacts on soil ecosystem are only partially recognized. The fine particle size (preponderantly less than 20 μm) of the RM can fill the soil pores and perpetually change soil texture. This threatens the life of most of the soil biota groups (Anton *et al.*, 2012; Gruiz *et al.*, 2012; Kovács *et al.*, 2013). Also, the high sodium concentration and strong alkalinity of the RM usually have strong adverse influences on both the below- and the above-ground communities of soil biota (Rékási *et al.*, 2013; Winkler, 2014; Stenchly *et al.*, 2017). In addition, invertebrate soil organisms are also often negatively influenced by the increasing levels of trace metal contamination; however, different groups or species can react distinctively (Hodson, 2013). Despite the threats and potential hazards of an RM



Fig. 8 Google Earth image of red mud storage area in Iran Alumina Company.



Fig. 9 Environmental pollution by red mud via different pathways.

exposure, it has to be noticed that the RM can also decline mobility of such trace elements as Cd, Ni, As, Cu, and Pb in the soil, due to its high alkalinity characteristic and high Al and Fe content (Anton *et al.*, 2012; Garau *et al.*, 2007; Ujaczki *et al.*, 2016b).

Utilization of Red Mud

Over the past several decades a lot of efforts have been made to find environmentally-friendly and cost-effective techniques to utilize the RM. The recycle and reuse of very massive quantities of generated RM have been a significant challenge for the alumina industry all over the world. Moreover, the transportation costs from the alumina refinery to the processing plant is another problem (Klauber *et al.*, 2011; Liu and Naidu, 2014; Samal *et al.*, 2013). To decrease the stockpile of annual produced RM, the utilization should be not only technically applicable and effective but also economically practicable. The future management of this residue and moving it towards zero waste are two tremendous environmental concerns. According to the most important classification shown in Fig. 10, a wide range of research fields have been conducted to develop some methods for effective utilization of RM, including: metal recovery

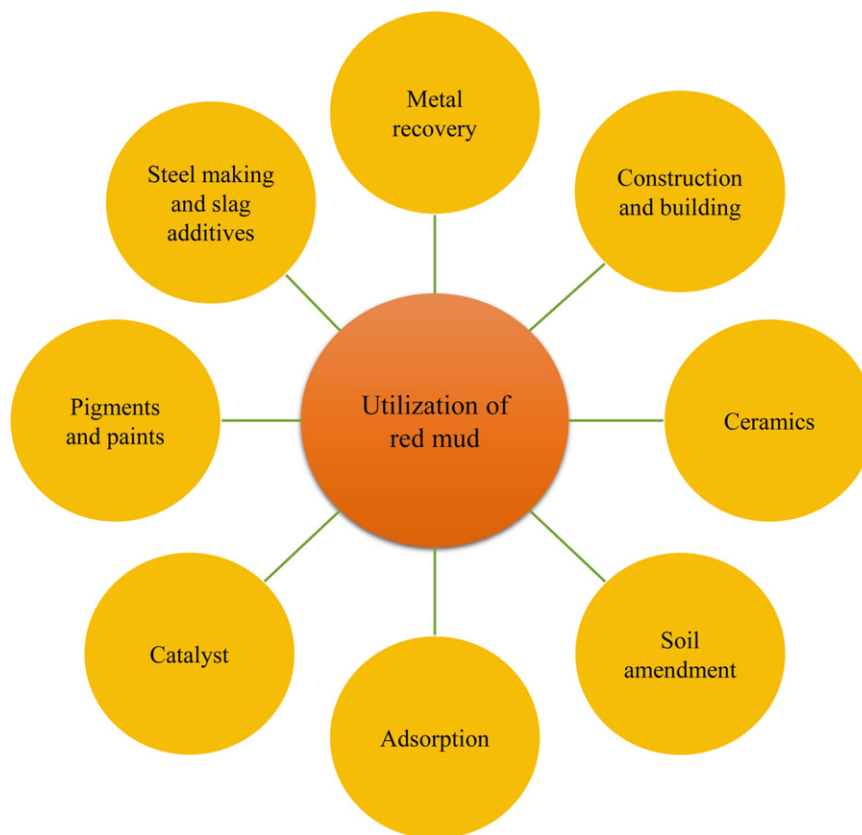


Fig. 10 The most important methods for utilization of red mud.

(Pepper *et al.*, 2016; Gu *et al.*, 2017a; Yu *et al.*, 2012; Yang *et al.*, 2015; Alkan *et al.*, 2018; Narayanan *et al.*, 2018; Ujaczki *et al.*, 2017a; Borra *et al.*, 2016; Wang *et al.*, 2018b), construction and building materials (Tsakiridis *et al.*, 2004; Liu *et al.*, 2018; Lima *et al.*, 2017; Li *et al.*, 2018; Nikbin *et al.*, 2018; Alam *et al.*, 2017; Scribot *et al.*, 2018; Zhang *et al.*, 2018; Krivenko *et al.*, 2017), low-cost adsorbents for pollutant removal (Li *et al.*, 2006; Huang *et al.*, 2008; Lopez *et al.*, 1998; Gupta *et al.*, 2001; Sahu *et al.*, 2013; Cusack *et al.*, 2018; Deihimi *et al.*, 2018a), catalysts (Wang *et al.*, 2008; Jahromi and Agblevor, 2018; Ordóñez *et al.*, 2001; do Prado *et al.*, 2017; Paredes *et al.*, 2004; Yanik *et al.*, 2001; Bento *et al.*, 2016), soil amendment (Evans, 2016; Klauber *et al.*, 2011; Liu *et al.*, 2011), ceramic production, pigments and paints, steel making and slag additive.

Metal Recovery

Recovery of metals from RM has attracted many research interests due to increasing demand and value for aluminum, iron, titanium and rare earth elements such as vanadium, gallium, scandium, zirconium and lanthanides. Iron oxide is the major oxide in the RM followed by alumina, silica, titanium dioxide and rare earth elements. Therefore, diverse topics concerning extraction of valuable metals from RM have been put forward in a large number of researches (Liu and Naidu, 2014). Treatment of the RM has different metallurgical ways consisting of pyro-metallurgy, hydrometallurgy and bioleaching. Pyro-metallurgical and hydro-metallurgical treatments are the two most commonly used methods to recover valuable metals from RM (Binnemans *et al.*, 2015). Despite the researches accomplished in recovery of metals from RM, pyro-metallurgical processes have many obstacles such as high energy consumption and generation of worthless residues. In contrast, hydrometallurgical processes are more promising for the future. However, metals can be recovered from RM either by direct metallurgical methods or by combining hydrometallurgical method with a pyro-metallurgy or bioleaching. The combined bio-hydrometallurgical method is called as a green process for recovery of valuable metals from RM (Liu and Li, 2015). Among the hydrometallurgical methods of extraction, acid leaching of metals from RM is an effective way due to its potential to allow selective recovery through extraction (Pepper *et al.*, 2016). Development of convenient metallurgical processes for metal recovery from RM plays a significant role to achieving zero waste and a thorough recovery of valuable minerals inside the RM. A brief overview on basic techniques applied for valuable metals recovery including aluminum, iron, titanium and rare earth elements (REEs) from RM are propounded in the following subsections:

Iron recovery

Iron oxide in RM is typically the major constituent. The RM is considered as a low-grade iron ore containing 30%–50% iron (Jayasankar *et al.*, 2012). As the high iron content of the Bayer RM, many attempts have been carried out on iron recovery including

direct magnetic separation (Li *et al.*, 2011; Jamieson, 2006), roasting and reduction smelting processes (Liu and Li, 2015), reduction roasting by adding sodium salt (Roasting *et al.*, 2012), reductive roasting followed by magnetic separation (Li *et al.*, 2014), reduction in hydrogen atmosphere followed by magnetic separation (Samouhos *et al.*, 2017), magnetic separation after co-roasting with pyrite (Liu *et al.*, 2014), thermal plasma technology (Jayasankar *et al.*, 2012), microwave reductive roasting (Samouhos *et al.*, 2013), mineral acid leaching (Pepper *et al.*, 2016), and selective leaching of iron with oxalic acid (Yu *et al.*, 2012; Yang *et al.*, 2015, 2016). Below is a detailed investigation of the recovery of iron from RM:

Due to lower energy costs, iron recovery by direct magnetic separation from RM is more attractive than pyro-metallurgical methods. The RM was directly separated by high gradient superconducting magnetic separation system into the high and very low iron content fractions, about 56% as Fe_2O_3 and less than 4% Fe_2O_3 , respectively (Jamieson, 2006).

The iron recovery efficiency can be increased by pyro-metallurgical method or direct reduction. Pyro-metallurgy which consists thermal treatment is one of the most widely applied method to recovery of iron from RM. The amount of RM is either diminished by using a magnetic separation technique to recover iron, or declined by smelting to produce pig iron (Kumar, 1998). The pig iron was also produced by thermal plasma technology from RM. The smelting reduction of RM was performed in a 35 kW DC extended arc thermal plasma reactor. Maximum recovery of iron was reported about 71% (Jayasankar *et al.*, 2012).

Another significant iron recovery technique from RM is direct reduction roasting process. The reductants in gaseous or solid phases are essential for direct reduction. The most common reductants are carbon powder (Liu *et al.*, 2009), coal (Roasting *et al.*, 2012), low-ash coal char (Liu *et al.*, 2012), carbon (Liu *et al.*, 2009; Raspopov *et al.*, 2013) and coke (Rath *et al.*, 2013). Carbon source, the carbon-to-RM ratio, temperature, and magnetic conditions are main parameters involved in the roasting process. In this process, the RM is first mixed with carbon and then the resulting mixture is roasted at 1300°C for 110 min before quenching with water. Afterwards, the product is milled and exposed to the magnetic separation. Total content of iron in concentrated materials can reach more than 88% (Liu *et al.*, 2009).

The reduction of iron in the RM is accompanied by various chemical reactions, as illustrated by reactions (7)–(13) (Rath *et al.*, 2013):



Pyro-metallurgical processes require high energy consumption for the sintering and roasting stages and generate valueless residues (Oustadakis *et al.*, 2008). Therefore, apart from pyro-metallurgical iron recovery processes from RM, hydrometallurgical methods have widely been investigated. Various acids such as sulfuric, hydrochloric and oxalic acids have been examined for iron recovery from RM. An iron recovery efficiency of around 47% was obtained by using 8 N H_2SO_4 and a solid-to-liquid ratio of 0.05 g/ml at the leaching temperature of 100 °C for 24 h (Debadatta and Pramanik, 2013). Another study showed that a high iron recovery of more than 97% can be obtained by using 6 M H_2SO_4 and calcination at 600°C (Liu and Li, 2015). Furthermore, it was found that the 6 M H_2SO_4 solution could leach more than 97% of the iron and 64% of the aluminum in the calcined RM at 600°C (Uzun and Gülfen, 2007).

Oxalic acid leaching of RM led to the recovery of iron in the form of Fe_2O_3 with a purity of more than 98%. Experiments demonstrated that the iron was first leached out in the form of $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ complex in the liquor obtained by oxalic acid leaching of RM and then purified by co-precipitation, selective dissolution and re-precipitation (Yang *et al.*, 2016). In order to reduce the cost of iron recovery, Yang *et al.* (2015) first washed the RM with diluted hydrochloric acid and subsequently treated the RM using oxalic acid. As a result, an iron recovery efficiency of more than 94% was obtained. Another study evinced that the iron content of the RM could be reduced from 17.6% to less than 1% after treating it by 1 M oxalic acid solution at 75°C for 2 h. Then the solution was exposed to UV light irradiation to appear Fe(II) precipitate (Yu *et al.*, 2012).

Aluminum recovery

The remaining aluminum in the RM composition ranges from 14% to 17% (Liu and Naidu, 2014). Among the metallurgical processes of aluminum recovery, the most notable ones are sintering process (Qiu-sheng *et al.*, 2008), reduction sintering process (Li *et al.*, 2009), hydrothermal process (Zhang *et al.*, 2011), combined pyro- and hydro-metallurgical process (Piga *et al.*, 1993), reduction sintering and magnetic separation, acid leaching, and bioleaching (Wang *et al.*, 2018b; Liu and Li, 2015). Variety of organic or inorganic acids, comprising of sulfuric, citric, hydrochloric and oxalic acids, individually or as a mixture, were extensively employed to extract alumina from the RM (Pepper *et al.*, 2016; Liu and Li, 2015; Liu *et al.*, 2007). The recovery of Al from the RM depends upon the type of acid for the extraction and the origin of the waste. Among four examined inorganic acids, the highest recovery efficiencies were achieved by phosphoric acid followed by sulfuric, hydrochloric and nitric acids with similar recovery efficiency. Moreover, the dissolution of Al phases such as boehmite, gibbsite, sodalite and kaolinite played different roles in the recovery of Al from RM (Pepper *et al.*, 2016). The

rate and extent of dissolution of alumina and soda increased when calcium carbonate mixed with RM. The dried RM, with a CaO/SiO_2 ratio of approximately 2, was smelted at 1400°C and the resulting slag was leached with water at 60°C . The dissolution efficiency of Al and Na was 55% and 90%, respectively (Bruckard *et al.*, 2010). The use of a mixture of organic acids for the recovery of Al from RM has been studied. The experimental results revealed that a high Al recovery of 96% could be attained using citric acid-to-oxalic acid ratio of 2:1 at $\text{pH} = 1.5$. Furthermore, biological leaching was performed using sewage sludge bacteria and pure strains of fungi including: *Aspergillus niger*, *Penicillium notatum*, *Penicillium simplicissimum*, and *Trichoderma viride*. Acids generated by *Penicillium simplicissimum* led to a high Al recovery of 75% (Vachon *et al.*, 1994).

Alumina and ferric oxide also can be recovered from iron rich-RM by reduction sintering process. Under the favorable sintering conditions, alumina and iron oxide recovery reached 89.71% and 60.67%, respectively (Li *et al.*, 2009). Another report focused on combination of pyro- and hydrometallurgical processes to recover aluminum, iron, and titanium from RM. The RM was initially blended with coal, lime, and sodium carbonate. Then, the well-mixed materials were subjected to reduction sintering at $800\text{--}1000^\circ\text{C}$. Finally, an Al recovery of around 89% was obtained by water-leaching of the resulting fine sintered product at 65°C for 1 h (Piga *et al.*, 1993). A majority of researchers have concentrated on the recovery of aluminum under alkaline conditions. As a result of their research, three distinct processes comprising of direct second caustic leaching, smelting of RM followed by iron removal and slag leaching, and leaching of RM after a sintering stage with sodium carbonate, lime and coke have been developed. These methods ascertained that it is possible to extract aluminum up to 90% from RM by applying optional alkaline processes (Kaußen and Friedrich, 2018).

Titanium and rare earth elements (REEs) recovery

The annual enhancement in the stockpile of RM provides a noteworthy secondary resource of valuable metals and REEs. Titanium metal (Ti) is extraordinarily strong, lightweight, bio-inert and resistant to corrosion. Although Ti is expensive and has a complex processing, the advantages of using titanium outweigh its cost. Titanium dioxide or titania (TiO_2) in RM can exist in the form of anatase and rutile polymorphs or with other minerals (Oustadakis *et al.*, 2008). Pyrometallurgy- and hydrometallurgy-based methods are mainly employed for titanium retrieval from RM. Pyro-metallurgical processes typically include extracting pig iron, a soda and alumina-rich stream and a slag containing titanium, silica, lime, residual alumina and magnesium (Oustadakis *et al.*, 2008). Besides the pyro-metallurgical processes, a lot of research work has been carried out on the recovery of titanium dioxide from RM using sulfuric, phosphoric, nitric and hydrochloric acids (Pepper *et al.*, 2016). It has been found that hydrochloric acid leaching of the RM followed by sodium carbonate roasting of the leached residue significantly increases TiO_2 recovery from 36% to 76%. To achieve such an increased recovery, the leaching temperature, roasting temperature and time should be 90°C , 1150°C and 115 min, respectively (Kasliwal and Sai, 1999).

Solvent extraction is another possible technique for the recovery of titanium from RM. In this process, the use of hydrochloric acid containing bis-(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302) and bis-(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex 301) led to favorable results. One important point is that the recovery of titanium does not require an exact control of pH, and titanium is easily separated from the co-recovered iron by selective stripping (Taylor, 2007).

A great number of studies have focused upon the titanium (Ti) and scandium (Sc) recovery, with a small portion on other REEs, because titanium and scandium have some unique properties for light weight alloys. These two elements are classified as critical materials due to increasingly demand. The recovery of scandium and titanium were mostly investigated by direct acid leaching method.

It was demonstrated that the combination of sulfuric acid with hydrogen peroxide (H_2O_2) could be resulted in the enhanced retrieval of scandium and titanium from RM. Various parameters including acid concentration, leaching time, leaching temperature, and solid-to-liquid ratio were shown to be effective on the scandium and titanium recovery efficiencies. Leaching with 2.5 M H_2O_2 :2.5 M H_2SO_4 mixture at 90°C for 30 min was detected to reach the highest Sc and Ti recovery efficiencies of 68% and 91%, respectively (Alkan *et al.*, 2018).

It has been proposed that the combination of sulfation, roasting and leaching can lead to the desired REEs recovery from RM. The roasting temperature, roasting time and amount of acid play a crucial role on the recovery efficiency, as the roasting temperature of 700°C , roasting time of 1 h, and 2-day sulfuric acid leaching at room temperature give rise to the scandium recovery of 60%. Under the same conditions, more than 80% of other REEs might be extracted (Rao *et al.*, 2016b).

The recovery of other REEs such as lanthanum (La), vanadium (V), zirconium (Zr), gallium (Ga), cerium (Ce), yttrium (Y) and thorium (Th) has been investigated in several researches (Marin *et al.*, 2018; Alkan *et al.*, 2018; Rao *et al.*, 2016b, 2015; Xie *et al.*, 2014; Ujaczki *et al.*, 2017b; Lyberopulu and Paris, 1994; Mukherjee *et al.*, 1990; Zhao *et al.*, 2012). A high vanadium oxide recovery of more than 99% from RM was achieved through adsorption onto activated carbon. The process included the solubilization of vanadium, adsorption onto activated charcoal, desorption, precipitation and finally calcination (Mukherjee *et al.*, 1990). Due to increasing trends of the gallium demand in electronics industry, recovery of gallium from Bayer liquor was reviewed by Zhao *et al.* (2012). By using Kelex 100 solvent extraction system, about 80% of the gallium in Bayer liquor was extracted (Zhao *et al.*, 2012). Given the current trends for REEs demand in high-technology applications and the rapid increase in their price, it is expected that research in REEs recovery from RM will continue to grow.

Cement Binders

Cement industry is confronted with serious ecological concerns. The manufacturing Portland cement not only consumes natural resources and lots of energy, but also as one of the major industrial origin of carbon dioxide (CO_2) emission, contributes to the

global warming and the formation of acid rain. In fact, this industry emits greenhouse gases (GHGs) from two main origins: clinker production process and the consumption of energy (Dongxu *et al.*, 2000; Kumar *et al.*, 2006; Hekal *et al.*, 2013; Palaniappan *et al.*, 2013). On the other hand, the growing number of strict environmental regulations has coerced the industrial communities to decrease their polluting emissions and effluents (Palaniappan *et al.*, 2013). One of the promising methods for declining environmental issues and also achieving technological and economic benefits is the increasing utilization of industrial wastes and byproducts (Dongxu *et al.*, 2000; Kumar *et al.*, 2006; Hekal *et al.*, 2013; Palaniappan *et al.*, 2013; Kumar *et al.*, 2008; Zhu *et al.*, 2012).

The reuse of RM as an inorganic additive to Portland cement has been the subject of a number of research works since 1936 (Thakur and Sant, 1983). Various positive and negative effects have been reported on the addition of RM to cement, which means that further research in this field is needed to reach a reliable and sustainable conclusion. In the case of large-scale incorporation of RM into cement, it was reported that 2.5 million tons of RM was consumed by the cement industry between 1998 and 1999 in India (Pera *et al.*, 1997).

Researchers found that the hydration reaction of Portland cement is promoted by the addition of RM as a highly alkaline medium (Pera *et al.*, 1997). The appropriate iron oxide and alumina contents of the RM can be advantageous to the strength and setting characteristics of the cement, but the sodium is detrimental. Substitution of the sodium with calcium improves the performance of the RM as an additive.

Singh *et al.* (1996, 1997b) prepared blended cements containing gypsum, bauxite and RM. The RM was opted as a source of iron and alumina in preference to other industrial wastes owing to its low silica content, and it was realized to perform better than fly ash. By optimizing the sintering temperature and the composition of the blend it was possible to prepare cements with superior setting strengths to ordinary Portland cement, with RM replacement levels of 20%–50% by dry mass. Also, the titanium content of RM was found to be advantageous to concrete strength.

Pera *et al.* (1997) thermally treated RM at an optimized temperature of 700°C to induce appropriate pozzolanic properties to RM. They indicated that Portland cement can be substituted by as high as 25% of thermally-cured RM.

Tsakiridis *et al.* (2004) evaluated the addition of RM by 1% in the raw mix for the production of Portland cement and found that the RM can be utilized as a raw material in cement production.

Senff *et al.* (2011) utilized the RM as high as 50% cement substitution in mortar and indicated that enhancement of the RM content reduced compressive and tensile strengths. In another study, Yao *et al.* (2013) scrutinized the possibility of blending RM and by-products of coal plant. Their results proved that this blend satisfies the physico-mechanical requirements of concrete. Manfroio *et al.* (2014) investigated the characteristics of cement paste containing over 15% dry or calcined RM at temperatures of 600–900°C. They concluded that the RM can be utilized as cement substitution with proper mechanical properties for construction applications. Ribeiro *et al.* (2011) corroborated that the filling effect of RM can decline the chloride penetration in concrete. Chemical activation allows to significantly improve the RM replacement level both in cements and in concretes without a decline of their physico-mechanical properties (Pan *et al.*, 2003, 2002). The restricted replacement levels of RM can be elucidated by the fact that some crucial factors such as the structure and chemical composition of constituents, and the kind of alkali activator have not been optimized. According to Glukhovskiy (1992) and Krivenko (1985), these factors are important with respect to the formation of alkaline and alkaline-alkali earth phases which consequently induce the characteristics of the resulting cement binder.

Krivenko *et al.* (2017) prepared alkali activated cements containing high volume of RM. They used RM, blast-furnace slag, and Portland cement for the preparation of blended cements. The prepared mortar cements exhibited 28-day compressive strengths of 30–60 MPa. Furthermore, they proposed an RM replacement level of 90% by mass in concrete road application.

Kang and Kwon (2017) evaluated the efflorescence properties of RM-incorporated alkali activated slag cement. They used a varying substitution ratios of RM (0%–30%). The investigations disclosed an accelerated efflorescence owing to the enhancement of nanometer-sized capillary pores originated from the incorporation of RM in the cement matrix.

Liu *et al.* (2009) firstly recovered iron from RM using direct reduction roasting process and then prepared brick specimens with aluminosilicate residue and hydrated lime. The specimens exhibited a compressive strength of about 24 MPa.

Tang *et al.* (2018) suggested to utilize RM in partial replacement of fly ash in self-compacting concrete (SCC). They examined the effect of RM on the fresh and hardened characteristics of SCC blends. Their experiments showed that the mechanical strength of concrete promoted with the enhancement of RM content. The SCC specimens containing 50% RM exhibited the best compressive strength and elastic modulus. Their microstructural analyses revealed a slight improvement in the interfacial transition zone between aggregate and cement paste for RM-based concrete.

The utilization of RM in producing cement composite mortar blocks for applications in pavement construction has been reported by Dodoo-Arhin *et al.* (2017). They observed that an RM replacement level of 5% resulted in superior or equal performance to Portland cement as the reference mortar. The increase of RM mass fraction diminished the workability of mortar, while both the initial and final setting times were accelerated. They also proposed that the addition of appropriate super plasticizers such as melamine sulfonate and polycarboxylate ether may improve the workability of the RM-based mortars.

Hu *et al.* (2018) investigated the potential utilization of RM as a raw material for geopolymer production. They used RM and three types of fly ash to prepare geopolymers. The raw materials were activated using appropriate activators (different concentrations of sodium hydroxide) and cured at both ambient and elevated temperatures. The geopolymers prepared from the contribution of RM and class C fly ash exhibited a compressive strength of around 15 MPa under ambient temperature curing at a low alkali activator concentration. As an overall conclusion, it was found that the high alkalinity of RM contributed to geopolymerization.

In another research, [Li et al. \(2019\)](#) utilized RM to prepared RM-based geopolymer. They suggested a novel activation method for the RM. Their results indicated that mechanical activation can effectively improve the reactivity of the RM. The addition of 14% sodium silicate to the prepared binder, the 28-day unconfined compressive strength reached 12.75 MPa.

[Ye et al. \(2016\)](#) revealed that alkaline heat treatment could be used to tailor the mechanical strength of RM-based geopolymer. However, this type of treatment method is expensive, making the industrialization very challenging ([Pacheco-Torgal et al., 2012](#)).

Adsorption

Since removal of organics and inorganics pollutants from aqueous media is necessary for health and environmental protection, conventional methods such as reduction, precipitation, adsorption, oxidation, membrane filtration and ion exchange are commonly used. However, among them the adsorption process is the most suitable method because of high efficiency, flexibility in design and operation, and low operational cost ([Burakov et al., 2018](#); [Li et al., 2017a](#)). Industrial solid wastes have been applied as effective adsorbents due to the easy availability and economic feasibility. Among them, RM presents an adsorption capacity for removing heavy metals from wastewater ([Burakov et al., 2018](#)). Moreover, the RM has been found to remove fluoride, arsenate, phosphate, nitrate, hexavalent chromium, copper, cadmium, lead and dyes from aqueous solution ([Li et al., 2006](#); [Bhatnagar et al., 2011](#)). Also, the RM adsorption efficiency has been compared with other low-cost adsorbents in the literature ([Liu et al., 2011](#); [Narayanan and Vetha, 2017](#); [Hu et al., 2018](#); [De Gisi et al., 2016](#)). Several activation methods have been suggested to increase the adsorption properties of RM such as acid treatment, heat treatments and mixing the RM with other materials ([Pinto et al., 2018](#)). The resulting activated RM as an inexpensive adsorbent was found to efficiently remove polluting species from aqueous solutions ([Deihimi et al., 2018b](#)). **Table 4** provides a summary of adsorption experiments and their corresponding results using the RM as adsorbent. As it can be seen, the RM, modified RM, and the adsorbents synthesized from the RM exhibit good adsorption capacities for a wide range of aqueous pollutants.

Soil Amendment

In spite of the fact that RM is often contaminated with heavy metals, its application in environmental remediation has extensively been investigated. However, the RM could be an efficient soil amendment due to its fixation of heavy metals. The leaching of metals, especially heavy metals, into the environment leads to soil pollution and contamination. The heavy metals are invariable and they are not as degradable as organic pollutants in the soil. The RM can easily adsorb different metal ions and it has a significant effect in removing heavy metals from contaminated soil ([Klauber et al., 2011](#); [Liu et al., 2011](#); [Ciccu et al., 2003](#); [Hua et al., 2017](#)).

According to [Hua et al. \(2017\)](#), a preliminary decision tree scheme (see **Fig. 11**) can be suggested to evaluate the suitability of RM as soil amendment agent. According to **Fig. 11**, the suitability of the RM for soil amendment depends on soil pH, soil electrical conductivity, and total potentially toxic elements (PTEs) of RM.

The chemical and biological effects of in-situ fixation of metals in soil using the RM were investigated by [Lombi et al. \(2002a,b\)](#). They examined efficiency of RM to stabilize heavy metals in two types of soils, soils polluted by industrial activities and sewage sludge. In both soils, using red mud resulted in low concentrations of metals in metal fluxes and the soil pore water. Due to increasing soil pH, the RM amendment not only shifted metals from the exchangeable to the Fe-oxide fraction, but also reduced acid extractability of metals ([Lombi et al., 2002a](#)). Moreover, three soil amendments (RM, beringite and lime) examined to two soils contaminated by heavy metals. All three soil amendments reduced phytotoxicity of heavy metals and the metal concentrations in plants as well as increased plant yields and soil microbial biomass ([Tor and Cengeloglu, 2006](#)). The neutralized RM (pH < 8) has the capability to decrease phosphate leaching into ground and surface waters due to the high concentration of iron and aluminum oxides ([Summers et al., 1996](#)).

In another study, the RM mixed with the sandy soil ranged between 0 and 50%. The results demonstrated that the RM applied at 5% had positive effects on the degraded acidic sandy soil, remarkably by increasing soil pH, improving water holding capacity and soil texture ([Ujaczki et al., 2016a](#)).

Since the mobility of metals is closely related to pH, the RM amendment of contaminated soil can enhance metal release from the amended soil. Moreover, the RM-amended soil can result in benefits for ecosystems in decreasing the mobility of potentially toxic elements to transfer to the environment ([Hua et al., 2017](#)). The use of RM for soil amendment would be an effective way to decrease the current storage.

Catalysis

The utilization of industrial solid wastes containing catalytically-active metals such as Ni, Fe, V etc., as an alternative to commercial catalysts can assist decrease the cost related to the use of catalyst. The RM which is majorly a combination of inorganic oxides of Fe, Al, Ti and a few amounts of Si, Na and Ca is a potential alternative catalyst at the commercial scale ([Pirkanniemi and Sillanpa, 2002](#)).

The simultaneous presence of various metal oxides in the RM composition makes it less susceptible to catalyst poisons like sulfur, and hence it is able to retain its catalytic activity over a relatively long period of time ([Sushil and Batra, 2008](#)). In addition,

Table 4 Summary of the different methods and techniques utilized to red mud as an adsorbent

Adsorbate	Methods and techniques	Maximum adsorption capacity	Ref.
Fluoride	Granular RM in batch adsorption systems	0.851 mg/g	(Tor <i>et al.</i> , 2009)
Fluoride	1 – Untreated RM	1 – 13.46 mg/g	(Wei <i>et al.</i> , 2009)
	2 – AlCl ₃ -modified RM	2 – 68.07 mg/g	
	3 – Thermally-treated RM at 200°C	3 – 91.28 mg/g	
Fluoride	Fe-Al-La trimetal hydroxide adsorbent from RM	74.07 mg/g	(Li <i>et al.</i> , 2017c)
Fluoride	HCl-activated RM	Maximum removal of 82% at pH 5.5	(Cengeloglu, 2002)
Phosphate	HCl-treated RM at pH 5.5 and 40°C	0.58 mg/g	(Huang <i>et al.</i> , 2008)
Phosphate	1 – Heat-activated RM (700 °C for 2 h)	1 – 155.2 mg/g	(Chang-jun <i>et al.</i> , 2007)
	2 – Acid-modified RM (80°C with 0.25 M HCl for 2 h)	2 – 202.9 mg/g	
Phosphate	Acid/heat-treated RM (0.25 M HCl for 2 h, 700°C for 2 h)	155 mg/l (99% phosphate removal)	(Li <i>et al.</i> , 2006)
Phosphate	Acid-activated RM (1 M HCl for 2 h)	205.13 mg/g	(Prajapati <i>et al.</i> , 2016)
Phosphate	Gypsum and seawater-treated RM	0.345–2.73 mg/g	(Cusack <i>et al.</i> , 2018)
Nitrate	1 – RM	1 – 1.859 mmol/g	(Cengeloglu <i>et al.</i> , 2006)
	2 – HCl-activated RM	2 – 5.858 mmol/g	
Arsenic	RM-modified rice straw biochar	5923 µg/g	(Wu <i>et al.</i> , 2017)
Arsenic: As(III) and As(V)	Heat/acid-treated RM:		(Altundog <i>et al.</i> , 2002)
	Heat treatment at 200, 400, 600 and 800°C for 4 h	As(III): 11.80 µmol/g	
	Acid-treatment with 0.25–2.0 M HCl at 25, 40, 55 and 70°C for 2 h	As(V): 12.57 µmol/g	
Arsenic (V)	1 – Chemically-modified RM (Bauxsol)	1 – 1.64–3.32 mg/g	(Genç-Fuhrman, 2005)
	2 – Activated Bauxsol (AB)-coated sand	2 – 2.14 mg/g	
Arsenic (III)	RM coated with Fe ₂ O ₃	21.85 mg/g	(Venkatesan and Narayanan, 2018)
Cadmium	Granular RM at 20, 30, and 40°C in batch experiments	38.2 mg/g at 20°C 43.4 mg/g at 30°C and 52.1 mg/g at 40°C	(Zhu <i>et al.</i> , 2007)
Cadmium	RM	1.16 × 10 ⁻⁴ mol/g	(Gupta and Sharma, 2002)
Cadmium	RM in the presence of 0.01 M NaNO ₃	68 mg/g	(Vaclavikova <i>et al.</i> , 2005)
Chromium and lead	Hydrogen peroxide-treated RM	Chromium: 35.66 mg/g Lead: 64.79 mg/g	(Gupta <i>et al.</i> , 2001)
Lead	RM	18.87 mg/g	(Mobasherpour <i>et al.</i> , 2014)
Lead(II)	0.5 M HCl-treated RM coated with iron oxide	27.02 mg/g	(Narayanan and Vetha, 2017)
Nickel(II)	Calcined and ground RM (63–125 µm)	13.69 mg/g	(Taylor and Hannachi, 2010)
Zinc	RM	2.22 × 10 ⁴ mol/g	(Gupta and Sharma, 2002)
Zinc	RM in the presence of 0.01 M NaNO ₃	133 mg/g	(Vaclavikova <i>et al.</i> , 2005)
Methylene Blue	6 M HCl-activated RM at 90 °C for 2 h	274 mg/g	(Hu <i>et al.</i> , 2018)
Methylene Blue	hydrogen peroxide-treated RM at room temperature for 24 h	(4.35–5.23) × 10 ⁻⁵ mol/g	(Gupta <i>et al.</i> , 2004)
Fast Green		(7.25–9.35) × 10 ⁻⁶ mol/g	
Rhodamine B		(1.01–1.16) × 10 ⁻⁵ mol/g	
Congo Red	RM boiled in 20 wt% HCl for 20 min	7.08 mg/g	(Tor and Cengeloglu, 2006)

the coexistence of these metal oxides might ameliorate the synergistic catalytic influence between transition metals (Guimaraes *et al.*, 2009; Xu and Wang, 2012).

According to Fig. 12, the RM has successfully applied as catalyst in various reaction areas including hydrodechlorination and dechlorination, hydrogenation, oxidation, exhaust gas clean-up, and miscellaneous reactions.

Oxidation reactions

It has been extensively accepted that catalytic oxidation is a very interesting method for removal of volatile organic compounds (VOCs), which induce intense environmental detriments. In this field of research, the noble and transition metals have been widely employed to eliminate VOCs, but with various restrictions (Hua *et al.*, 2017; Shim and Kim, 2010; Kamal *et al.*, 2016; Zhang *et al.*, 2016). The co-presence of metal oxides in RM sparks the idea of using the RM as an alternative catalyst for replacing the commercial noble metal and transition metal oxides in catalytic-related applications. Proper treatments can be applied to prepare RM-based catalysts. For instance, loading of Pt on the air-thermally treated RM was very efficient for the removal of VOCs (Kim *et al.*, 2015).

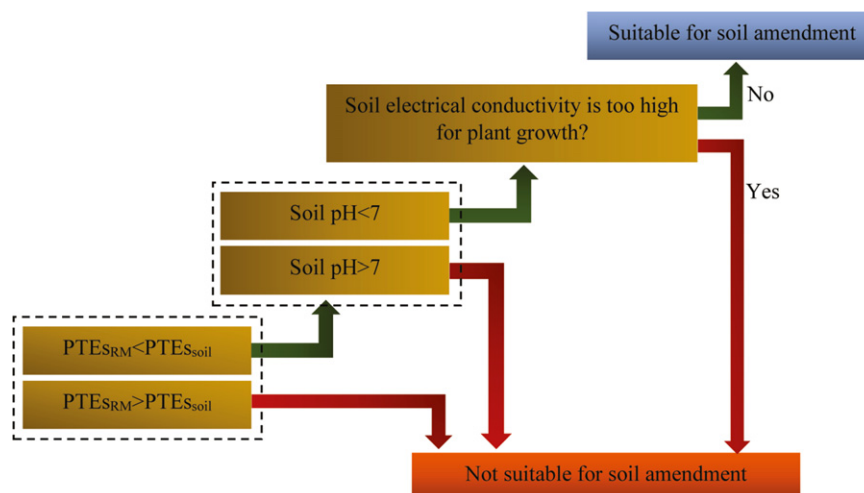


Fig. 11 The proposed decision tree scheme for evaluating the utilization of red mud as soil amendment agent.

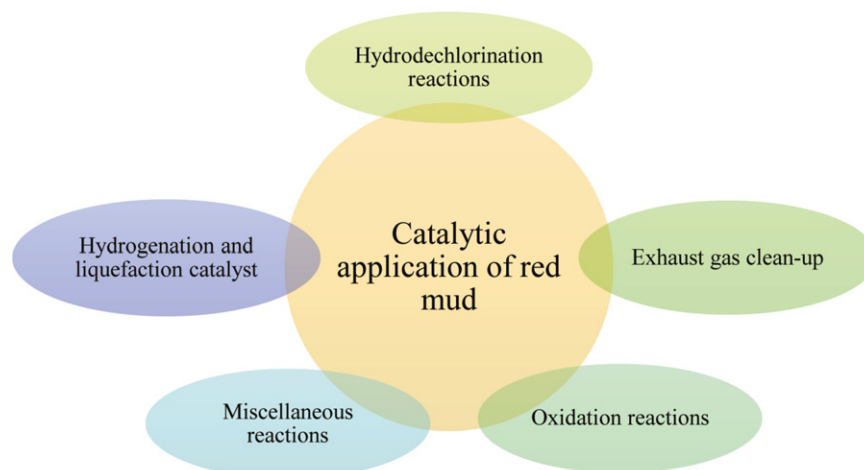


Fig. 12 Catalytic application of red mud in different reaction areas.

As the RM contains significant amounts of Fe_2O_3 and Al_2O_3 , it can exhibit a CO_2 selective behavior in the toluene oxidation reaction. The RM activity can be associated directly with the amount of iron. It has been observed that the chemical reaction specific rate (in terms of gram of Fe_2O_3) in the presence of RM is similar to that monitored in the presence of analytical grade Fe_2O_3 (Lamonier *et al.*, 2005).

Methane oxidation is another conducted experimental research. Paredes *et al.* (2004) prepared iron-based catalysts from RM by dissolution–precipitation techniques, followed by calcination in air. The RM was treated using a combination of hydrochloric and ortho-phosphoric acids. The activity and stability of the prepared catalysts for the catalytic combustion of methane was found to be comparable to that of hematite and a Cu–Cr–Ti commercial catalyst.

Oliveira *et al.* (2014) proved that biphasic oxidation reactions of organic pollutants with H_2O_2 were improved by amphiphilic catalysts from RM and carbon nanostructures.

Shim *et al.* (2018) evaluated the RM as a potential catalyst support for the complete oxidation of toxic organic compounds. They pretreated the RM using calcination and HCl. Then, the acid-treated RM was loaded with various amounts of Pd. The HCl-treated RM exhibited a better catalytic activity for complete oxidation of benzene.

Huab *et al.* (2016) prepared CuO/activated-RM with high specific surface area and suitable porosity by a series of dissolution-precipitation techniques. The resultant catalyst showed a high catalytic CO oxidation.

Hydrogenation reactions

The catalytic utilization of RM was first reported by Pratt and Christoverson (1982) for hydrogenation of naphthalene. They proposed acid dissolution and re-precipitation method for the activation of the RM. According to this method, the RM was

dissolved in HCl to obtain a metal chloride leachate. The re-precipitation was then performed by the addition of ammonia. It was found that untreated RM exhibited a naphthalene conversion efficiency of 3.55% while the treated RM possessed a conversion efficiency of 58%. Eamsiri *et al.* (1992) activated the RM by the Pratt and Christoverson method and used the activated RM for hydrogenation of phenanthrene, naphthalene, and pyrene. They observed a considerable promotion in the hydrogenation of the tested compounds. However, activation did not result in notable enhancements in overall yields of liquids and the activated RM was considerably less active than a commercial Ni–Mo–S catalyst.

In another research, Llano *et al.* (1994) used RM and activated RM for the hydrogenation of an anthracene oil. They applied the Pratt and Christoverson method to activate the RM. The RM exhibited a remarkable catalytic activity, which was meliorated by the activation. However, both RM and activated RM showed less catalytic activity than a commercial Ni–Mo/ γ -alumina hydro-treating catalyst.

Alvarez *et al.* (1995) showed that sulfided RM exhibited activity for the hydrogenation of a light fraction of an anthracene oil. They found that catalytic activity of the catalyst decreased with reaction time, due to the decline in surface area and superficial iron. In another research work (Alvarez *et al.*, 1998), they activated the sulfided RM by Pratt and Christoverson and divulged that the catalytic activity loss of the catalyst was slower than that of untreated sulfide RM. In a later study, the same authors (Alvarez *et al.*, 1999) improved the catalytic hydrogenation performance of RM by proposing a different activation method. They dissolved the RM in a mixture of aqueous HCl and H_3PO_4 and then obtained a precipitate by the addition of aqueous ammonia until pH value of 8. The precipitate was rinsed, dried, and calcined to obtain catalyst. After sulfidation, the activity and life of the prepared catalyst was examined for the hydrogenation of a light anthracene oil. The results confirmed a slightly better activity and a noticeably active life.

Hydrodechlorination and dechlorination reactions

Catalytic dechlorination and hydrodechlorination reactions are efficacious and ecofriendly methods for the decomposition of chlorinated organic compounds. A typical hydrodechlorination reaction includes the reaction between organic molecule containing C–Cl bond and hydrogen:



Several studies have been reported on the catalytic application of RM in hydrodechlorination and dechlorination reactions. Ordoñez *et al.* (1999, 2001a) comprehensively investigated the utilization of RM as a catalyst for hydrodechlorination of tetrachloroethylene. They evaluated the catalytic activity of sulfided RM and RM based-sulfided catalysts and found that the sulfided RM presented a better activity. But the catalyst suffered from a low stability at reaction conditions, because of poisoning by HCl (Ordoñez *et al.*, 1999).

The same authors continued their investigations to overcome low stability drawback. They treated the RM using dissolution-precipitation-calcination method. In this method, the RM was first dissolved in a binary acid mixture ($HCl + H_3PO_4$). The resulting solution was then precipitated by adding ammonia. Finally, the precipitate was calcined at 500°C to obtain the catalyst. The prepared catalyst exhibited a better catalytic activity and resistance to deactivation compared to untreated RM (Ordoñez *et al.*, 2001b). Then, they measured the conversion in terms of reaction time in the presence/absence of carbon sulfide in the feed and discovered a notorious enhancement in the catalyst life in the presence of carbon sulfide (Ordoñez *et al.*, 2001b).

Halasz *et al.* (2005) first calcined the RM and then used it for catalytic hydrodechlorination of 1,2-dichloroethane, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethene and tetrachloroethene. They compared the catalytic activity of the calcined RM with other iron-based catalysts, such as Fe_2O_3 , mixed Fe_2O_3/Al_2O_3 , and modified zeolite (Fe-ZSM5). The catalytic conversion of the mentioned compounds over calcined RM is comparable to that obtained for synthetic catalysts. Furthermore, the reactions occurring over RM caused a decline in alkalinity of RM making it more appropriate for disposal.

Yanik *et al.* (2001a,b) employed RM as a dechlorination catalyst for the disintegration of waste plastics and poly (vinyl chloride) (PVC) containing PVC/PP, PVC/PE, and PVC/PS into fuel oil. They found that the RM was showed a positive effect on the fixation of formed HCl gas. The RM exhibited a very efficient sorption of both inorganic and organic chlorine compounds.

Exhaust gas purification

The RM has already been studied for the catalytic removal or destruction of certain air pollutants. Among these studies are the following: recovery of sulfur from sulfurous waste gases (Khalafalla and Haas, 1972), catalytic combustion of methane (Khalafalla and Haas, 1972), selective catalytic reduction of NO_x (Lamonier *et al.*, 1995; Hosoda *et al.*, 1995), elimination of VOCs, removal of HCl from exhaust gases, dioxins and CO (Junji *et al.*, 2002), hot gas clean-up of coke oven gases and gasification products (Furimsky and Yumura, 1986).

The RMs from different sources have been employed as catalysts for reduction of SO_2 in the presence of CO. It was found that the RM wastes having high Al and Fe content exhibited good catalytic activity (Khalafalla and Haas, 1972).

Lamonier *et al.* (1995) investigated RM and Cu-impregnated RM for the selective catalytic reduction of NO_x . Paredes *et al.* (2004) studied catalytic activity and stability of RM and activated RM in the catalytic combustion of methane. Their experimental results signified that the RM exhibited the least activity, while activated RM presented the best performance for the catalytic combustion of methane both in terms of activity and resistance to deactivation. The inferior activity of RM was ascribed to the presence of catalytically inert constituents in the chemical structure of RM such as rutile, gibbsite, and goethite.

Li *et al.* (2017b) in their research found that the RM could exhibit an excellent activity in the selective catalytic reduction of NO_x . They proposed grinding/acid-alkali neutralization technique to utilize the RM waste as iron-based catalyst. The resulting catalyst presented a NO conversion of more than 90% above 400°C in the presence of SO_2 and H_2O . The result is even better than that of a commercial V-W-Ti catalyst. In another study in the same year, Wu *et al.* (2018) prepared low-cost RM-based catalyst and tested it in the ammonia-selective catalytic reduction of NO_x . They concluded that the RM was a potential material for denitration catalyst. Their results demonstrated that the doping of Ce significantly increased the NO_x conversion as much as 88%.

Miscellaneous reactions

The possibility of using the RM as a catalyst in other reactions has also been reported in the literature. Despite previously reported results, this sub-section deals with recent research.

Feng *et al.* (2016) used RM powders as catalysts for persulfate activation with sulfadiazine as the target pollutant. Their results indicated that the RM powder had a scavenger impact on the rate of sulfadiazine decomposition. They found that under the conditions of 2 g/L RM powder and 1.75 mM persulfate, the sulfadiazine could be completely decomposed.

Senthil *et al.* (2016) examined the catalytic performance of activated RM in biodiesel production from Mahua oil. From their findings, it was obvious that the use of RM as a catalyst not only enhances fuel quality, but also decreases adverse impacts on the environment.

Lee *et al.* (2016) developed ZrO_2 -impregnated RM catalysts for catalytic steam cracking of vacuum residue. They observed that the impregnation of RM with 3 wt% ZrO_2 resulted in the best catalytic performance, provided that the reaction was carried out at 470°C for 2 h under superheated steam atmosphere.

Yang *et al.* (2018) studied the catalytic mechanism of the RM on the sewage sludge pyrolysis. The RM could diminish the average activation energy of sewage sludge pyrolysis by around 20.1 kJ/mol. The char produced from RM-catalyzed pyrolysis of sewage sludge featured magnetic characteristic, which has different applications. The overall results revealed desirable catalytic activity of the RM in the pyrolysis of sewage sludge.

Jahromi and Agblevor (2018) in their research work, prepared RM supported nickel (Ni) catalysts at various concentrations of Ni. They used these catalysts to hydrodeoxygenate pinyon-juniper catalytic pyrolysis oil. According to their results, increasing the Ni concentration promoted the performance of the catalyst.

Noble metals (Pt, Pd, Ru)-supported RM catalysts were investigated for alkane synthesis from carboxylic acids and furans by Castille *et al.* (2019). They reported a maximum alkane selectivity of 100%, 87%, and 56% over Pt-, Pd-, and Ru-RM, respectively.

Other Applications

In addition to the main uses mentioned above, the RM has also been studied in other applications. Some of the RM-related patents are attributed to the application of RM in steel making and slag additives. The RM is considered as one of possible supplements utilized as a source of Al, Si, and Ca to improve the setting, separation, and quality characteristics of the slag (Klauber *et al.*, 2009).

Generation of ceramic products such as double-layer glass-ceramic tile (Yang *et al.*, 2009), glass ceramic foam materials (Guo *et al.*, 2014), roof tile/brick (Scribot *et al.*, 2018; Liu *et al.*, 2017), and lightweight ceramic floor (Wang *et al.*, 2018a) are from other areas of RM application. The microstructural and mechanical characteristics disclosed that the production of double-layer glass-ceramic tiles from the RM may be an attractive approach for converting the RM into building materials (Yang *et al.*, 2009). The low bulk density glass ceramic foams can be produced by blending RM, fly ash, and CaCO_3 as foaming agent at low sintering temperature (Guo *et al.*, 2014). By replacing natural clay with 30 wt% of low sodium hydroxide-containing RM and applying calcination temperatures of above 950°C, ceramic tiles with acceptable properties can be allowed (Scribot *et al.*, 2018). The ceramic bricks with excellent water permeability and much decreased pH and conductivity could be fabricated by mixing appropriate proportions of RM, water, and silicon dioxide. After homogenization, a 5 MPa press was exerted on the obtained blend. Thereafter, sintering was performed at temperatures higher than 1100°C (Liu *et al.*, 2017). The RM in combination with kaolin through a $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ -catalyzed pathway can result in the preparation of low-cost ceramic floor tiles. It was found that the catalytic route promoted the growth of mullite crystals. This promotion is due to the unique properties of mullite such as its low thermal conductivity and low thermal expansion as well as its excellent fracture toughness (Wang *et al.*, 2018a).

The high iron content in RM made it an appropriate component in pigments and paints. A variety of brown-red shades produced by the RM (Klauber *et al.*, 2011; Rai *et al.*, 2012; Mishra and Gostu, 2017). Sintering the RM at 1300°C makes it suitable alternative for the hematite pigment (Carneiro *et al.*, 2018b). Combining the RM with electroplating sludge in different proportions, following by calcination at 1200°C could result in black and brown pigments with appropriate coloring strength and thermal stability (Carneiro *et al.*, 2018a).

The use of RM in the preparation of composite RM/polyaluminum chloride coagulant is expected to be cost-effective for the efficient removal of phosphate from aqua medium (Ni *et al.*, 2015). The RM can also be used as Al source for the fabrication of magnetic zeolite. In a recent study (Belviso *et al.*, 2018), wool ball-shaped zeolite was synthesized using the RM and colloidal silica. The prepared zeolite can be considered for wastewater treatment. The RM can even be used for neutron shielding application. For this purpose, the RM was first treated with boric acid and then mixed with polyester resin (Guru *et al.*, 2019).



Fig. 13 Current barriers in the way of the use of red mud.

Challenges and Future Perspective

The worldwide stockpiles of RM on the planet are estimated at more than 2.7 billion tons. Annually, 120–150 million tons are added to this amount. The RM has not been distributed uncontrollably in the world, but is prevalently distributed in discrete locations almost controlled or under strict rules. In spite of the long-standing knowledge of the disadvantages of RM accumulation as well as the suggestion of a wide variety of solutions for the utilization of RM, the controlled waste disposal is still preferable to other methods, considering social, environmental, and economic conditions. The best way to solve RM disposal problems is to develop economic exploitation technologies that can process a huge amount of RM. The current barriers that need to be overcome are presented in Fig. 13.

An impressive impact on the amount of stored RM requires the development of technologies and recycling/recovery/reuse methods that can process large amounts of RM. The performance of the waste in each particular application must be able to compete with the existing options in terms of quality and cost. Also, metals and metal oxides extracted (as micro/nano form), composite products, adsorbents, catalysts, and other products should have physical, chemical, mechanical, and thermal properties comparable to existing alternatives. Economic feasibility and life cycle assessment should be performed for any process in order to provide an appropriate economic vision for industries and investors. In these assessments, the energy consumption and the downstream processing economy should also be taken into account. As far as possible, processes may be designed in such a way that their byproducts are reusable to make the process economy more desirable. For each specific application and utilization method, it should be explained that related risks are less than those dealt with controlled storage. These risks comprise environmental, public health, safety, and economic issues. Specifically, soda removal, alkalinity reduction, stabilization of heavy metals and rare earth metals should be considered further.

Conclusions

Different aspects of red mud including the production process, characterization, environmental effects, utilization methods, and challenges are elucidated in the current review study. The characterization section comprehensively explains chemical and mineralogical compositions, radioactivity, particle size distribution, and morphology of the red mud by giving an example from Iran Alumina Company waste. The main focus of this study is on the various methods of utilizing the red mud. The major applications of the red mud are presented in areas of metal recovery (iron, aluminum, titanium, and rare earth elements), cement binders, adsorption, soil amendment, and catalysis. Also, the other applications of the red mud are briefly mentioned. The valuable metals recovery from the red mud is mainly based on hydrometallurgical methods and techniques. Almost all recovery methods remain on a laboratory scale without any appropriate analysis to execute lab-scale into pilot or industrial scale. The physico-mechanical and durability characteristics of red mud indicate that it can be utilized in the production of construction and building materials, but in small proportions. In addition, red mud in some origins contains trace radioactive elements, necessitating further research to study radiation conditions. In adsorption application, the red mud appears to need to be activated to exhibit suitable adsorption capacities for a wide range of aqua pollutants. The application of red mud as soil amendment agent can be a promising option for the large volume utilization of red mud. However, this application depends on soil pH and the level of toxic elements both in soil and in red mud. The catalytic performance of red mud can be comparable with available commercial catalysts, if some appropriate modification/activation techniques are applied to improve the specific surface area and synergistic effect. The utilization of red mud in other fields such as ceramic products, pigment, coagulant, etc., requires additional research work.

See also: Mining Industry. Production of High Purity α - and γ -Alumina From Aluminum Dross

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Recycling of Renewable Composite Materials in the Offshore Industry

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Glossary

Biocomposites They are a composite material formed by a matrix (resin) and a reinforcement of natural fibers.

Bulk molding compound (BMC) Polyester resin/glass fiber premix, for injection or transfer molding, also known as dough molding compound (DMC).

Carbon fiber Reinforcing fiber known for its light weight, high strength, and high stiffness.

Composite A material made up of resin and reinforcement (usually fiber).

Fiber-reinforced polymer (FRP) A general term for composite materials or parts that consist of a resin matrix that contains reinforcing fibers such as glass or fiber and have greater strength or stiffness than the resin. FRP is most often used to denote glass fiber-reinforced polymer.

Fiber A unit of matter of relatively short length, characterized by a high ratio of length to thickness or diameter.

Glass fiber Reinforcing fiber made by drawing molten glass through bushings. The predominant reinforcement for polymer composites, it is known for its good strength, processability, and low cost.

Impregnation Saturation of reinforcement with liquid resin.

Polymer A long-chain molecule, consisting of many repeat units.

Recyclates The raw material collected, taken to, and processed in a waste recycling plant or materials recovery

facility that will be used in the manufacturing of new materials.

Recycling The process of converting waste materials into new materials, products and objects.

Reinforcement Key element added to resin (matrix) to provide the required properties; ranges from short fibers and continuous fibers through complex textile forms.

Resin Polymer with indefinite and often high molecular weight and a softening or melting range that exhibits a tendency to flow when subjected to stress. As composite matrices, resins bind together reinforcement fibers.

Scanning electron microscope (SEM) A type of electron microscope that is used to produce enlarged images of a sample by scanning the surface with a focused beam of electrons, like reinforced CFRP samples. When the samples are placed under the microscope, the electrons mix with the constituent atoms within the composite sample. This will produce different signals that contain information about the surface topography and composition of the sample.

Sheet molding compound (SMC) A flat prepreg material, comprising thickened resin, glass fiber, and fillers, covered on both sides with polyethylene or nylon film, ready for press-molding.

Thermoplastic A plastic that softens each time it is heated.

Thermoset A plastic that flows and then sets permanently on first heating, as a result of setting up a three-dimensional cross-linked molecular structure, and subsequently will not soften or dissolve.

Introduction and Background

Current trends in the use of composites have developed into more applications in various sectors. In the offshore industry, there are some challenges with the standards on the use of offshore composites, particularly as structural members. However, composites are lightweight and can be used on other areas of the offshore sector. Some research into the use of recycled composites, like other composites, show that they are good reinforcement materials, depending on the purpose of application (Gibson, 2003; Wei *et al.*, 2018; Hornsby and Bream, 2001). Boats and some leisure ships made of composites can also be recycled (Sponberg, 1999). Studies have also been carried out on the life cycle for both FRP and glass reinforced polymer (GRP) composites (ISO, 2006; Song *et al.*, 2009; Bachmann *et al.*, 2017). Fig. 1 shows the offshore developments with different offshore structures showing the need for composites. As the offshore explorations go deeper into deep waters, more lengths of risers are required which also adds on the weight of the offshore platforms. Composites can be harnessed to reduce the weight as well as enable the technologies in these offshore operations. Composites have also been used to lighten the weight of automobiles and building products commercially, such as by ELG Carbon Fiber (ELG Carbon Fibre, 2016, 2017; Gehr, 2018) and Filon (Job *et al.*, 2016). Carbon fiber can be recovered, as shown in Fig. 2, by ELG Carbon Fiber. Recycled composites have also been used in fences from recycled carpets as structurally stable and fit for use (Sotayo *et al.*, 2015, 2016, 2018, 2019). These can also be deployed on offshore applications for hand rails, guard rails and safety fences in structures where the use of composites are permitted.

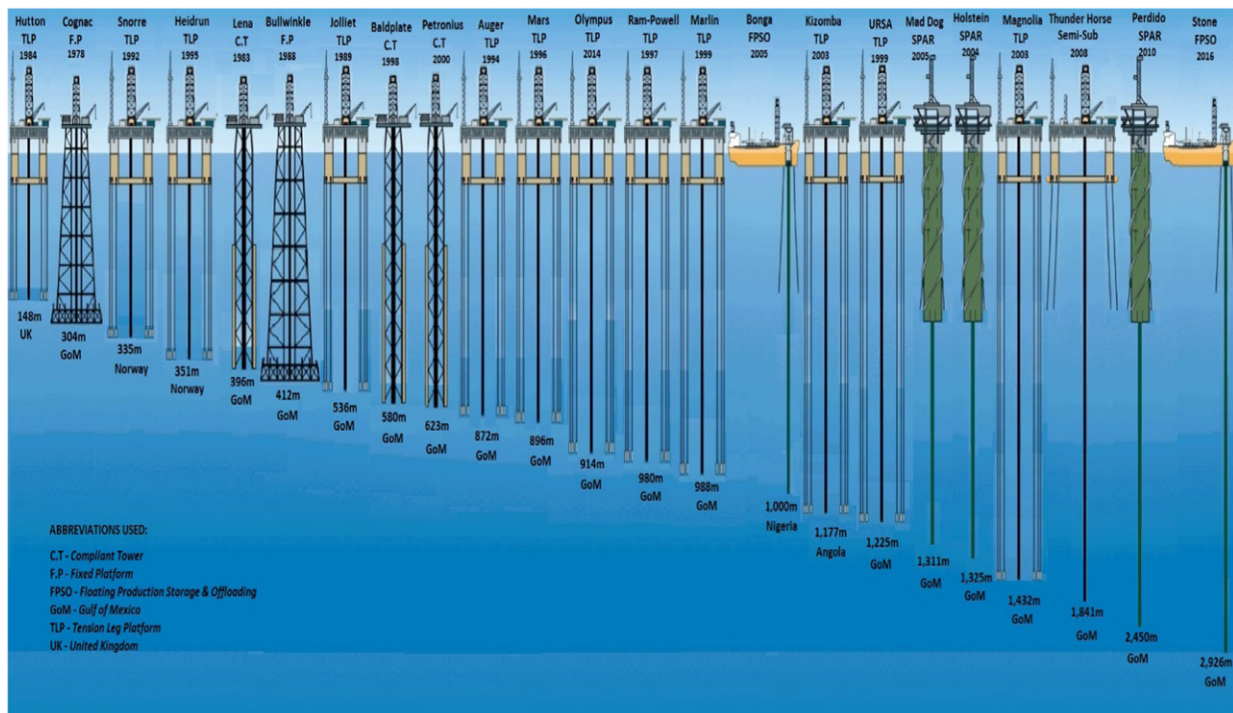


Fig. 1 History of offshore deep waters, showing the offshore structures and their water depths.

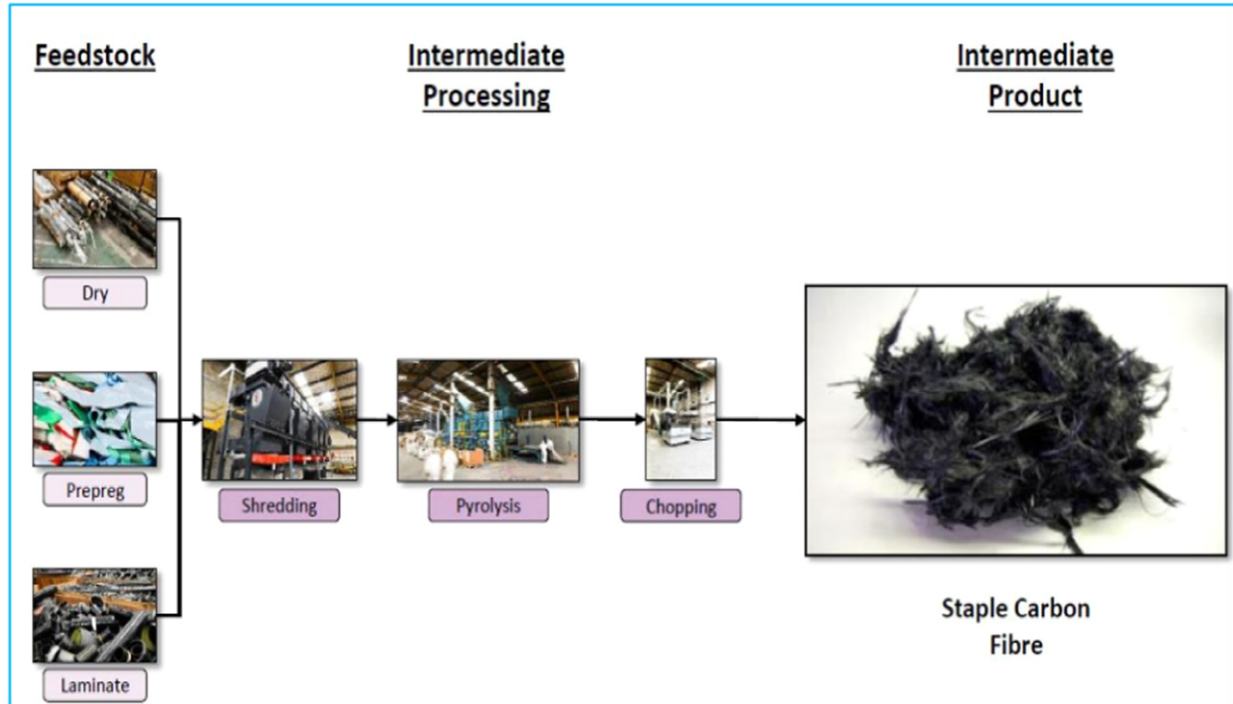


Fig. 2 Carbon fiber reclamation. *Source:* ELG Carbon Fiber, 2016. Reproduced from: ELG Carbon Fibre Recycled carbon fiber as an enabler for cost effective lightweight structures, Global Automotive Lightweight Materials (GALM), Detroit, 2016 ELG Carbon Fiber Ltd. Detroit Available at: http://www.elgcf.com/assets/documents/GALM_US_2016.pdf.

Due to the growing demand for more sustainable materials, there has been a global increase in the application of composites in the offshore industry. This includes composites for composite risers (Amaechi *et al.*, 2019a; Amaechi and Ye, 2017; Wang *et al.*, 2011a,b), composite tubes (Sparks *et al.*, 1992; Bhudolia *et al.*, 2015; Wang *et al.*, 2011a,b), submarine hoses (Amaechi *et al.*, 2019b), floating hoses, underwater vehicles, remotely operated vehicles, naval ships and submarines (Mouritz *et al.*, 2001), submersibles (Odijie, 2015; Odijie *et al.*, 2017a,b), SPARS (Amaechi *et al.*, 2019d) and floating production storage and offloadings (FPSOs). This trend for the demand of carbon material composites has also been observed in other industries. This includes the automobile industry, and the renewable energy (Doyle and Aggidis, 2019; Zhang *et al.*, 2019) and aerospace industry (Shi, 1996; Yang *et al.*, 2012).

ELG Carbon Fiber was the world's first commercial carbon fiber-recycler. They can take dry fiber, prepreg, and cured laminate waste. The waste is converted into the Carbisio range of products including chopped and milled fiber, oversized tow and nonwoven mats. Other products using recycled carbon fiber, including injection molding compounds, are under development. For glass fibers, there are presently the following options: In-house recycling, cement kiln, energy recovery, and landfills. For the in-house recycling, there may be ways you can recycle some of your GRP waste in-house, particularly if you use a spray-up or casting process. Grinding to fine filler is a proven route but is difficult to achieve economically. Ecowolf (Florida, USA) provides equipment for incorporating GRP regrind in spray-up processes. Conenor (Finland) provides advice/R&D services for multilayer extrusion that can incorporate GRP regrind. For the cement kiln (recycling/recovery), it involves mixing the shredded composite parts/offcuts with other waste to feed into cement kilns. Organic resin is burnt for energy; inorganic components become feedstock for cement. Carbon fibre reinforced polymer (CFRP) can also be treated this way but recycling is preferable. Agecko in UK and Neocomp in Germany (formerly operated by Zajons) promote this process specifically for the composites industry. For energy recovery, GRP wastes are sent for energy recovery, like to Viridor in Oxford, UK. The glass and filler will go to ash, but in some cases the bottom ash from incinerators is recycled rather than landfilled. Sometimes, the incinerator bottom ash will be recycled (as aggregate or in building products) or landfilled, and the waste can be exported for incineration overseas. The most common is the use of landfills as most GRP waste still goes to landfills.

The global demand for carbon fiber is estimated to greater than double to be between 150,000 t and 180,000 t by 2020. With the manufacturing techniques used today, there is approximately 30% of the overall demand for carbon fiber becoming waste both during the conversion phase and component-manufacturing phase of the recyclates. The remaining fiber is added into the finished parts, which will be disposed of later at the end-of-life (EOL). With the increase in the application of CFRP composites in components with shorter service lives, the EOL will range between 2 and 40 years, depending on the frequency of its usage (ELG Carbon Fibre, 2017).

The market drivers that determine the best disposal solutions of wastes from FRP composites are the market forces of demand and supply, the increasing cost of landfills, the increase in awareness on circular economy thinking, the markets for recycled products, government policies and legislations on recycled FRP composites. However, the most important driver on commercial viability of recycled FRP composites is the breaching of new markets (Brown *et al.*, 2018). With the increase in more composite recyclates, there is also an effect on the existing composite manufacturers, and their sources of raw materials. Currently, automobile manufacturers like BMW and VW (Volkswagen) are also researching on increasing the use of composites on their cars and also using recycled composites and biocomposites (Das *et al.*, 2016; Bharath and Basavarajappa, 2016; Mohanty *et al.*, 2018). This will also increase the economic viability of recycled FRP composites in the automobile industry. There is need to create more circular recycling on FRP composites, create higher value recycling routes to explore other areas of the market, and increase more economic exchanges and businesses both within the composites industry and with other industries such as the mainstream aviation industry, automobile industry, and construction industry.

There are four main drivers that influence the supply chain of recycling carbon fibers. They are the affordability, security, legislative policies, and environmental responsibility. The economic conversion of both the raw wastes from manufacturing and EOL components into different recycled carbon fiber shapes, forms, and component designs is very important. This material product can then be used technically for different applications, making these lightweight carbon fiber composites less expensive. With respect to the security of the supply chain, the application of recycled carbon fibers controls any supply side capacity risk by bringing in high tonnes of carbon fiber from existing production capacity, thus buffering it up. Legislation plays a very great role, as these policies are what guides the manufacturers and the end-users about the product and its circulation in the market. The need for environmental responsibility cannot be overemphasized. In the automotive industry, EU legislation requires 85% of a vehicle to be recyclable. Carbon fiber waste can be recovered and converted to new products using less than 10% off the energy required to produce the original carbon fiber, fulfilling legislative and sustainability targets (ELG Carbon Fibre, 2017).

Carbon Fiber and Glass Fiber Composites

Carbon fiber has been of high value in the composites market and can be also applied in the offshore industry. Currently, there are more carbon fiber-recycling companies that in operation and also thriving commercially. They include ELG Carbon Fiber, Filon, etc., as shown in Tables 1–3. Carbon fibers are composed of at least 92% carbon and most commonly have a diameter in the range 5–10 μm . They are polymers with a structure that is almost completely graphitic. This graphitic form of carbon fiber is a pure form of carbon in which the atoms are arranged in big sheets of hexagonal rings. The structure provides very high levels of stiffness and strength. Technically, carbon fibers have been produced and improved for many decades because of their excellent mechanical, thermal, and electrical properties, often exploited as carbon fiber composites for highly valuable applications in sectors including

Table 1 Current commercial composites recycling services for fiber-reinforced polymers GFRP and CFRP

<i>Company/location</i>	<i>Processes/capacity</i>	<i>Materials recycled</i>	<i>Recyclate market</i>	<i>Reference website</i>
ELG Carbon Fiber, (Formerly Milled Carbon), West Midlands, UK	Pyrolysis process, 2000 t/year recovered carbon fiber output	Dry carbon fiber waste, carbon fiber prepreg waste, carbon fiber laminates	Chopped/milled/pelletized carbon fiber. Carbon fiber random mats and discontinuous fiber yarns. Also preforms.	www.elgcf.com
Competitive Green Technologies	Uses natural fibers with PP and PE based polymer matrices and bioresins	Coffee beans, and some bio materials	Biocomposites like biodegradable bins, biodegradable cases, and carbon-based products.	www.competitive-greentechnologies.com
CFK Valley Stade Recycling, Germany	Pyrolysis, > 1000 t/year, launched in 2011. Presorting, crushing, and sorting of materials according to type of fiber and state of processing: Dry carbon fiber scraps, prepreg materials, end-of-life parts. Pyrolysis using thermal treatment excluding oxygen to recover pure carbon fibers completely by means of thermal oxidation of pyrolysis gases.	CFRP waste materials of different types	Milled 80–500 μm . Fiberball/pelletized/chopped 1–100 mm (e.g., for PA, PC, PP reinforced compounds). Wet laid veil 10–30 g/m ² (e.g., for surface optimization, EMI shielding). Air laid nonwovens 200–600 g/m ² (e.g., for RTM process for structural parts, SMC & BMC process). Refined custom-made fiber surface. Cutting and processing of carbon fibers into models “chopped” and “milled” accurately cut to desired fiber length.	www.carbonxt.de , http://cfk-recycling.com , https://www.cfk-recycling.de/index.php?id=57
Materials Innovation Technologies – Reengineered Carbon Fiber (MIT-RCF), South Carolina, USA	Pyrolysis, current capacity 2000 t/year recovered carbon fiber output (room for expansion)	All kinds of CFRP waste materials	Nonwoven rolled goods. Chopped fiber for compounding and long fiber-reinforced thermoplastic (LFT) applications. Preforms (3-DEP process).	http://mitrcf.com
Reprocover, Belgium	Thermoset waste ground to max. 6 mm granules. 30% glass fiber flakes mixed with 70% thermoset granules, resin added, high pressure cold molded.	Thermosets, including GRP with or without fiber-reinforcement. Also wastes from dry glass fibers.	Utility boxes, rail infrastructure products (e.g., cable tray covers), flower boxes, bins, etc.	www.reprocover.eu
Global Composites Recycling Solutions, UK	Ground GRP and glass fiber is incorporated with other materials into Ecopolycrete. This is to be sold as a mix for polymer concrete type applications that can be precast or poured in place for railway sleepers, parking stops, and other construction products. The material has a steel-like compressive strength and very high fire resistance. Went commercial in Tennessee, USA, around September 2014, and later in Northamptonshire, UK.	Cured GRP and glass fiber	Ecopolycrete	www.ecopolycrete.com
Global Fiberglass Solutions, Bothell, WA, USA	Recycling services to industries worldwide, including the wind energy, aerospace, maritime, and manufacturing sectors. Infinitely recycles with GFS process.	Industrial carbon fiber and fiberglass waste	Wind blade recycling, ecopoly pellets, fiberglass recycling	https://www.global-fiberglass.com/

Hambleside Danelaw, UK	Have developed a process for mechanically recycling GRP to retain fiber length. These fibers have been utilized to form reinforcements both as chopped fiber and in nonwoven recycled fiber mats. The fibers have been used in both thermoset and thermoplastic composites to form products for the construction industry. Experimentation has also been carried out in using the fibers with concrete and with rubber to enhance the properties of these materials.	Cured GRP	GRP products, roof lights, cladding flashings, and the Dryseal flat roofing system.	https://www.hambleside-danelaw.co.uk/
Extreme Eco ₂ Solutions, Netherlands	Have started collecting production and end-of-life waste, working with selected partners in the transport and dismantling sector. The intention is to shred the GRP and grind to powder. This would be transported to Norway for recycling, initially as an additive for polyethylene film products in a process that is under development.	Cured GRP including whole products (e.g., boats)	–	http://extreme-ecosolutions.com
Karborek RCF, Martignano, Italy	Pyrolysis process with energy recovery, to produce chopped/milled carbon fibers and carbon fiber felt. Capacity up to 1500 t/year. The plant was completed in October 2014, and production started around January 2015.	CFRP waste	Chopped carbon, milled carbon, fibers, and carbon fiber felt.	www.karborekrf.it
Carbon Fiber-recycle Industry Co Ltd, Japan	Utilizing thermal decomposition by self-combustion process (6.7 MJ/kg-CF, 13.2 MJ/kg-CF), the company expects a recycling output of 1080 t/year.	CFRP waste	Recycled carbon fiber (and at pilot scale at time of data collection for other products).	https://cfri.co.jp/en/
Carbon Conversions (formerly MIT-RCF), South Carolina, USA	Milling and flocking, thermoplastic compounding and for SMC and BMC (high strength recycled carbon fiber-requirements, prepreg, closed & open mold infusion, thermoforming, pultrusion, compression molding, thermoforming closed mold infusion)	CFRP waste	Chopped fiber, and nonwoven mat.	https://carbonconversions.com
Viridor, Oxford, UK	It separates glass, plastics, and polymers by polymer type including PET, HDPE, and PP pots, tubs, and trays	Plastics, glass, composites and other polymer wastes	EfW (energy from waste), some polymer products.	https://www.viridor.co.uk
Eco Waste Solutions, Burlington ON, Canada and Dublin, OH, USA	Uses a starved-air (pyrolytic style) process to convert the waste into a gas. Small waste generators with 100 kg to 15 t per day are best served by the EWS batch load waste system.	General wastes including composite wastes	EfW, some polymer products.	https://ecosolutions.com
Veolia, Rostock, Germany	Collection, sorting, then shredding to obtain PET flakes and washed in hot water. A mechanical and chemical recovery process transforms the flakes into a product suitable for food use. They are then purified before being packaged for shipment to bottle manufacturers. Up to 50% of recycled PET can be used to produce new bottles.	Plastic bottle wastes	PET flakes.	https://www.veolia.de
Reciclaia Composite, Madrid, Spain	Recycling company that optimizes composite waste management and minimize your carbon footprint	Carbon fiber and glass fiber wastes	Recycled fibers.	https://reciclaiacomposite.com

Abbreviations: BMC, bulk molding compound; CFRP, carbon fiber-reinforced polymer; GFRP, glass fiber-reinforced polymer; GRP, glass reinforced polymer; HDPE, high density polyethylene; LFT, long fiber thermoplastics; PET, polyethylene terephthalate; PP, polypropylene; SMC, sheet molding compound.

Table 2 List of the main manufacturers of various composite materials and resins

Type of composite	Company	Reference website
Thermoplastic composites	Milliken Tegriss	tegriss.milliken.com
Thermoplastic composites	Polystrand, Inc.	www.polystrand.com
Nonwoven fabrics (PolyWeb) and foam	Wm. T. Burnett & Co.	www.williamtburnett.com
Thermoplastic composites	Schappe Techniques	www.schappe.com
Thermoplastic composites	TechFiber	www.fiber-tech.net
Thermoplastic composites	TenCate	www.tencate.com
Thermoplastic composites	TherCom	www.thercom.com
Thermoplastic composites	Vectorply	www.vectorply.com
Composite materials: Resins and fibers	SF Composites	www.sf-composites.com
Formulation and manufacture of epoxy-based systems	SICOMIN	www.sicomini.com
Composite materials + resin, composite laminates	Lamiflex SPA	www.lamiflex.it
Composite materials + polyester	AMP Composite	www.amp-composite.it
Infusion, pultrusion, wet layup, prepreg, filament winding	Applied Poleramic Inc.	www.appliedpoleramic.com
Epoxy and polyurethane	Endurance Technologies	www.epoxi.com
Composite materials	Gurit	www.gurit.com
Advanced thermoset resins & adhesives	Huntsman Advanced Materials	www.huntsman.com/advanced_materials/a/Home
Advanced thermoset resins	Lattice Composites	www.latticecomposites.com
Kevlar	DuPont Kevlar	www.dupont.com/products-and-services/fabrics-fibersnonwovens/fibers/brands/kevlar.html
UHMWPE ultra high molecular weight, high performance polyethylene material	DuPont Tensylon	www.dupont.com
Innegra HMPP (polypropylene), high performance fiber	Innegra Technologies	www.innegrattech.com
Spread tow fabrics	TeXTreme	www.textreme.com/b2b
Adhesives and sealants	3M	solutions.3m.com
Prepreg and resins	Axiom Materials Inc.	www.axiommaterials.com
Fabrics, resins, composite materials	Barrday Advanced Materials Solutions	www.barrday.com
Carbon prepreg	Hankuk Carbon Co., Ltd.	www.hcarbon.com/eng/product/overview.asp
Carbon fibers and prepreps	Hexcel	www.hexcel.com/Products/Industries/Carbon-Fiber
Prepreps and compounds	Pacific Coast Composites	www.pccomposites.com
Prepreps and compounds	Quantum Composites	www.quantumcomposites.com

Note: Abramovich, H., 2017. Chapter 1 – Introduction to composite materials. In: Stability and Vibrations of Thin-Walled Composite Structures. Oxford, UK: Elsevier. pp. 3–4. doi:10.1016/B978-0-08-100410-4.00001-6.

aerospace, defense, wind energy, automotive, and sport. Specific examples of applications include aircraft wings (Wong *et al.*, 2017; Smith, 2013; Shi, 1996), wind turbine blades (WindEurope, 2017; Wong *et al.*, 2017), Tension Leg Platform tethers (Engineering and Freyssinet, 2000; Johnsrud, 1999), composite risers (Pham *et al.*, 2016; Amaechi *et al.*, 2019a,b), automotive (Akampumuza *et al.*, 2017; Vo Dong *et al.*, 2015; ELG Carbon Fibre, 2019), and tennis rackets.

According to Wise and Girard (2016), there are three main factors that influence the economy of carbon fibers. The first is the continued expansion in the market, especially in sectors such as automotive. Second is the drive towards a more cost-effective, high quality fiber that can be manufactured in large volumes. Thirdly, the availability of sustainable carbon fiber sources, including renewable precursors and routes for recycling carbon fibers from composites.

However, the challenge of recycling GRP, such as these waste trims and powdered wastes from the composites, is a stumbling block in industries where the pressure to recycle is high, as shown in Figs. 2–5. In Europe, the different processes have been tabulated to show the production volume from 2008 to 2018 by Industrievereinigung Verstärkte Kunststoffe - Federation of Reinforced Plastics (AVK) market reports, as presented in Table 4 (Witten *et al.*, 2018; Sauer *et al.*, 2017; Witten *et al.*, 2016, 2015; Witten and Jahn, 2013; Jahn *et al.*, 2012; Witten and Jahn, 2011). It shows that there is an increase that is a function of the global economy, as a decreased production was recorded in 2008–2009. Some advances in the use of biocomposites show that they can have good strength for offshore applications, as shown in Table 1.

Review on Offshore Composites

It is pertinent to discuss the applications of composites in the offshore industry in general. A suitable application for a composite riser configuration like this would be marginal fields. Smaller vessels and lighter, redeployable risers would dramatically lower the cost of small pool field development and make these smaller reserves economically feasible. Composites are currently beating digital cameras on the innovation front – around a decade from inception to the first consumer product rather than 15 years. Changing attitudes toward the technology may be a driver for this and it were not be long before riser applications, in the form

Table 3 Typical properties of mostly used reinforced continuous fibers

Material	Trade name	Density, ρ (kg/m ³)	Typical finer diameter (micro μ)	Young's modulus, E (GPa)	Tensile modulus (GPa)
α -Al ₂ O ₃ (aluminum oxide)	FP (USA)	3960	20	385	1.8
Al ₂ O ₃ + SiO ₂ + B ₂ O ₃ (mullite)	Nextel 480 (USA)	3050	11	224	2.3
Al ₂ O ₃ + SiO ₂ (alumina-silica)	Altex (Japan)	3300	10–15	210	2.0
Boron (CVD ^a on tungsten)	VMC (Japan)	2600	140	410	4.0
Carbon (PAN ^b precursor)	T300 (Japan)	1800	7	230	3.5
Carbon (PAN ^b precursor)	T800 (Japan)	1800	5.5	295	5.6
Carbon (pitch ^c precursor)	Thornel P755 (USA)	2060	10	517	2.1
SiC (+ O) (silicon carbide)	Nicalon (Japan)	2600	15	190	2.5–3.3
SiC (low O) (silicon carbide)	Hi-Nicalon (Japan)	2740	14	270	2.8
SiC (+ O + Ti) (silicon carbide)	Tyranno (Japan)	2400	9	200	2.8
SiC (monofilament; silicon carbide)	Sigma	3100	100	400	3.5
E-glass (silica)		2500	10	70	1.5–2.0
E-glass (silica)		2500	10	70	1.5–2.0
Quartz (silica)		2200	3–15	80	3.5
Aromatic polyamide	Kevlar 49 (USA)	1500	12	130	3.6
Polyethylene (UHMW) ^d	Spectra 1000 (USA)	970	38	175	3.0
High-carbon steel	Piano wire, etc.	7800	250	210	2.8
Aluminum	Electrical wire	2680	1670	75	0.27
Titanium	Wire	4700	250	115	0.434

^aCVD, Chemical vapor deposition.

^bPAN, Polyacrylonitrile. About 90% of the carbon fiber produced worldwide is made from PAN.

^cPitch is a viscoelastic material that is composed of aromatic hydrocarbons. Pitch is produced by the distillation of carbon-based materials, such as plants, crude oil, and coal.

^dUHMW $\frac{1}{4}$ ultra-high-molecular-weight polyethylene (or polyethene, the most common plastic produced in the world) is a subset of the thermoplastic polyethylene.

Source: From Harris, B., 1999. Engineering Composite Materials, the Institute of Materials. London, UK, p. 193. Jones, R.M., 1999. Mechanics of Composite Materials, second ed. Philadelphia, PA: Taylor & Francis, p. 519. Abramovich, H., 2017. Chapter 1 – Introduction to composite materials. In: Stability and Vibrations of Thin-Walled Composite Structures. Oxford, UK: Elsevier. pp. 3–4. doi:10.1016/B978-0-08-100410-4.00001-6.



Fig. 3 Carbon fiber sample. Courtesy: Wise, R., Girard, P., 2016. Carbon fibres: A review of technology and current market trends. Available at: <https://www.ktn-uk.co.uk/articles/ktn-report-provides-extensive-overview-of-carbon-fibre-industry>.

discussed or otherwise, will begin cutting costs in the oil and gas industry. Composites can be classified for matrix/reinforcement and by manufacturing process, as illustrated in Figs. 6 and 7, respectively. Due to the technological developments, composites can be reused and recycled, as presented in Fig. 8. An application of the state-of-the-art on composite materials in the offshore industry, is shown in Fig. 9.

The renewable composites used in the offshore industry are mostly limited to wind turbines, and lightweight composites used in offshore structures. There are challenges with using renewable composites on ships and offshore platforms due to restrictions



Fig. 4 Glass reinforced polymer trimmed waste. *Courtesy: Filon products.*



Fig. 5 Glass fiber dust waste from Strongwell's Extren laminated glass fiber composite sheet.

with the standards. Basic structural members in most of the offshore standard recommend the use of steel members, as the main reinforcing and load-carrying member of the platform ([Tables 3](#) and [5](#)).

Historically, the Chinese were the first to create oil pipes, using bamboo trunks as conduits from local oil wells. This trend later led to development of more sustainable materials that can be used to transfer oils. Thus, steel pipes came into existence. However, with the need to lighten the weight of the structures as explorations move deeper, composite risers ([Amaechi et al., 2019a](#); [Amaechi and Ye, 2017](#); [Gillett, 2018](#)) are potentially a good option. Due to the different environmental conditions for oil explorations, such as that

Table 4 Glass reinforced polymer production volumes in Europe by processes/parts

	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018
	<i>kt (kilotonnes)</i>										
SMC	210	160	198	198	188	184	190	191	198	202	204
BMC	70	56	69	69	70	71	74	74	76	78	81
Σ SMC/BMC	280	216	267	267	258	255	264	265	274	280	285
Hand lay-up	202	123	160	160	145	142	138	139	140	140	140
Spray-up	103	74	92	98	90	90	94	96	97	98	99
Σ Open mold	305	197	252	258	235	232	232	235	237	238	239
RTM	106	94	113	120	120	126	132	137	141	146	148
Sheets	69	56	72	77	78	84	84	86	89	93	96
Pultrusion	46	39	47	51	47	47	48	49	50	53	55
Σ Continuous processing	115	95	119	128	125	131	132	135	139	146	151
Filament winding	79	69	82	86	80	78	79	80	80	78	79
Centrifugal casting	62	55	66	69	67	66	66	68	68	67	69
Σ Pipes and tanks	141	124	148	155	147	144	145	148	148	145	148
GMT/LFT	95	75	100	105	108	114	121	132	140	145	152
Others	16	14	16	16	17	18	17	17	17	18	18
Total	1058	815	1015	1015	1010	1020	1043	1069	1096	1118	1141

Abbreviations: BMC, bulk molding compound; GMT, glass mat thermoplastic; LFT, long fiber thermoplastics; RTM, resin transfer molding; SMC, sheet molding compound.

Source: AVK Composite Market Reports 2011–2018.

may be harsh, benign, or squall, there are advances in the application of offloading systems adopted recently like Chinese lantern configurations (Amaechi *et al.*, 2019b) and lazy-S configurations (Amaechi *et al.*, 2019c) on CALM buoys. These systems have hose connections that are used to transfer oil and other fluids offshore and onshore. The materials used in the making of the offshore vessels and the submarine hoses have also composite materials in them. Airborne Oil and Gas (Jak, 2018; Smits *et al.*, 2018; Spruijt, 2018) and Magma Global (Wilkins, 2016; Hatton, 2012; Mintzas *et al.*, 2013) are currently two companies that have developed these offshore structures called composite materials.

The offshore industry has seen different technological advancements in recent years, which started when oil explorations in Texas and California increased creating more opportunities in oil, rather than gold. In the Gulf of Mexico (GoM), the Stone FPSO operates in 2926 m while the Perdido SPAR platform operates in 2450 m as they are currently the deepest offshore structures as shown in Fig. 2. However, there are still more developments on different offshore structures, as shown in Fig. 3.

Despite these applications of composites in the offshore industry, the industry has not been at the forefront in leading on the advances in composite applications. Some other industries have applied composites for decades successfully to improve performance and safety, like using composite handrails on ships. The marine industry has increased in the application of composites in hull making for ships, yachts, and leisure boats. However, the aerospace industry has notably used composites double every five years since 1987 (Murray, 2018). Composites have since been applied to the oil and gas industry (offshore and marine industries included), as they have changed the landscape of the industry. This allows reduction in airframe weights, less operating costs, and fuel savings. Composite materials are lightweight, with weight reduction ranging from 20% to 50% (Murray, 2018). The main characteristics of composites that make them more suitable in the composite industry are presented in Tables 3 and 5, for reinforced composites and biocomposites, respectively.

Dressed Landing String Joints

Landing String Solutions (LSS) LLC developed the concept of applying composites in their landing string scheme, and thus were the first in the offshore industry to use composites in buoyancy for landing strings. This concept provides the option of improving safe rig operations, optimizing critical path time and significantly decreases cost by reducing the hook load while running heavy enclosures and buoyancy casings (Murray, 2018). The challenge was to get the suitable material that will not be affected by the wellbore fluid used during drilling. It is important that all composites used in all drilling operations are very suitable for use in seawater. Secondly, drilling mud has a different mix of chemical components with their varying temperatures too.

Buoyancy Modules

Trelleborg developed some of their buoyancy modules for oil drilling and offloading operations using polymer-based composites that are syntactic buoyancy materials. The raw materials used include hollow glass microspheres powders that are talcum-looking

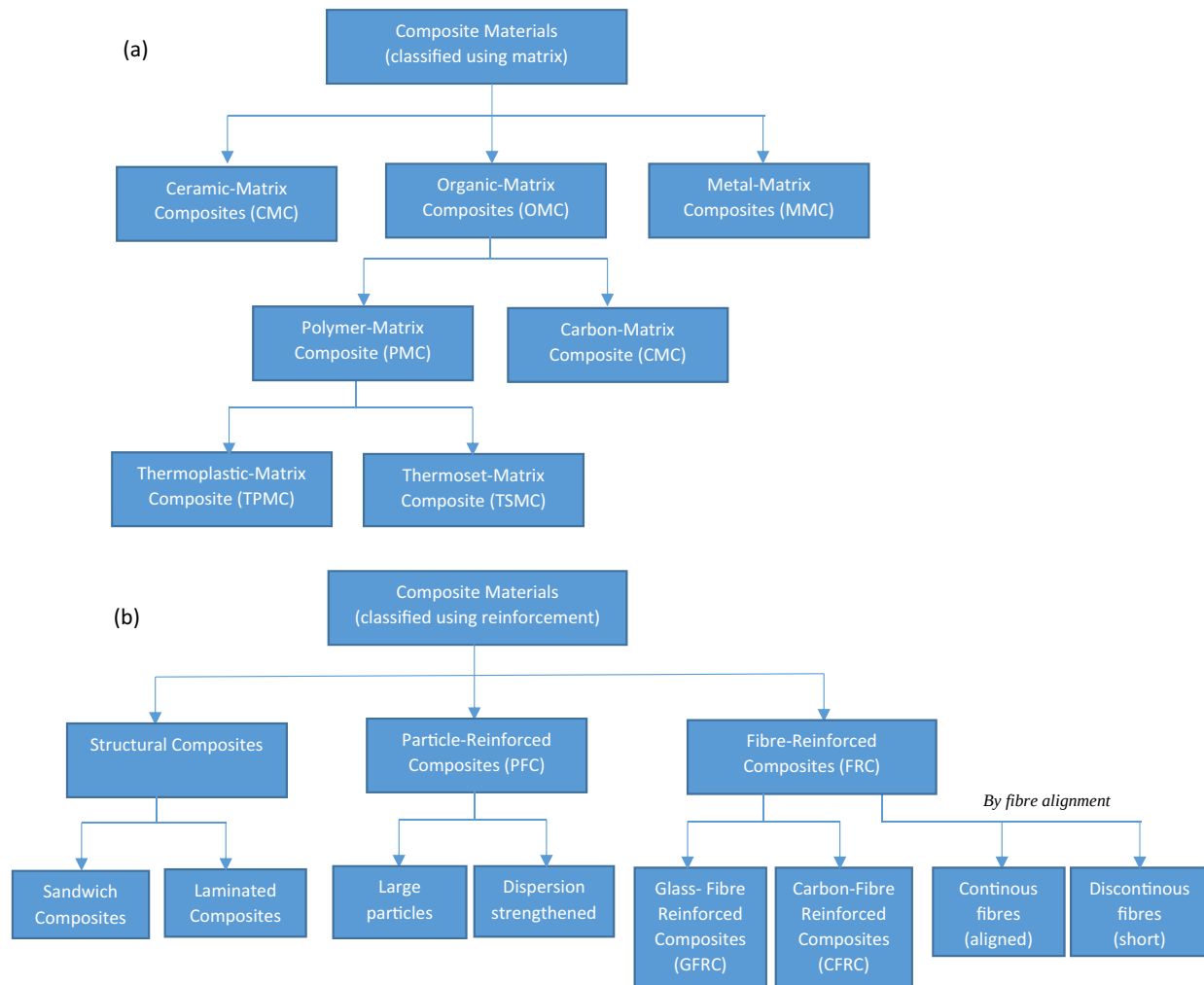


Fig. 6 Classification of composites by (a) matrix, and (b) reinforcement.

but of high strength glass bubble. The material is also used in aerospace applications because of its high strength characteristics. For the buoyancy modules, it is covered by a polyurethane skin to ensure that it provides high syntactic buoyancy service.

Composite Buoyancy System

Trelleborg and LSS developed the first composite buoyancy system that is deployed on a drillpipe landing string. According to *Offshore Magazine* (2015), the system is the first application of buoyancy in drilling riser. The application of buoyancy on the landing string enhances deployment of more number of casings, reduces the rig time and also reduces operational cost. The buoyancy was successfully tested in the a testing field located in the GoM, and has been proven to be successful up to an operational pressure of 41.36 MPa (6000 psi). By design, the new composite buoyancy system was designed to offset the landing string weight up to 80% but not in all cases. "In this particular application, this is not a better mousetrap. It's not a step change. This is a new trap altogether. This is an enabling technology. The composite-based system creates buoyancy once the casing/ landing string is in the riser, which reduces the hook load, decreasing the risk of the vessel exceeding its maximum hook load rating. This gives a smaller and cheaper rig the opportunity to do the job safely which means potentially eliminating liner tiebacks and running longer casing strings" (Murray, 2018).

Composite Risers

Development of composite risers have progressed greatly from the first time composite risers were installed successfully on Heidrun platform in 2002 (Salama and Mercier, 1988; Ochoa and Salama, 2005; Salama *et al.*, 2002). Recent developments on composite risers include the composite thermoplastic pipes, Magma M-pipe (Hatton, 2012; Mintzas *et al.*, 2013; Wilkins, 2016), and Airborne composite riser pipe (Steuten and Van Onna, 2016; Onna *et al.*, 2014; Van Onna and O'Brien, 2011), composite

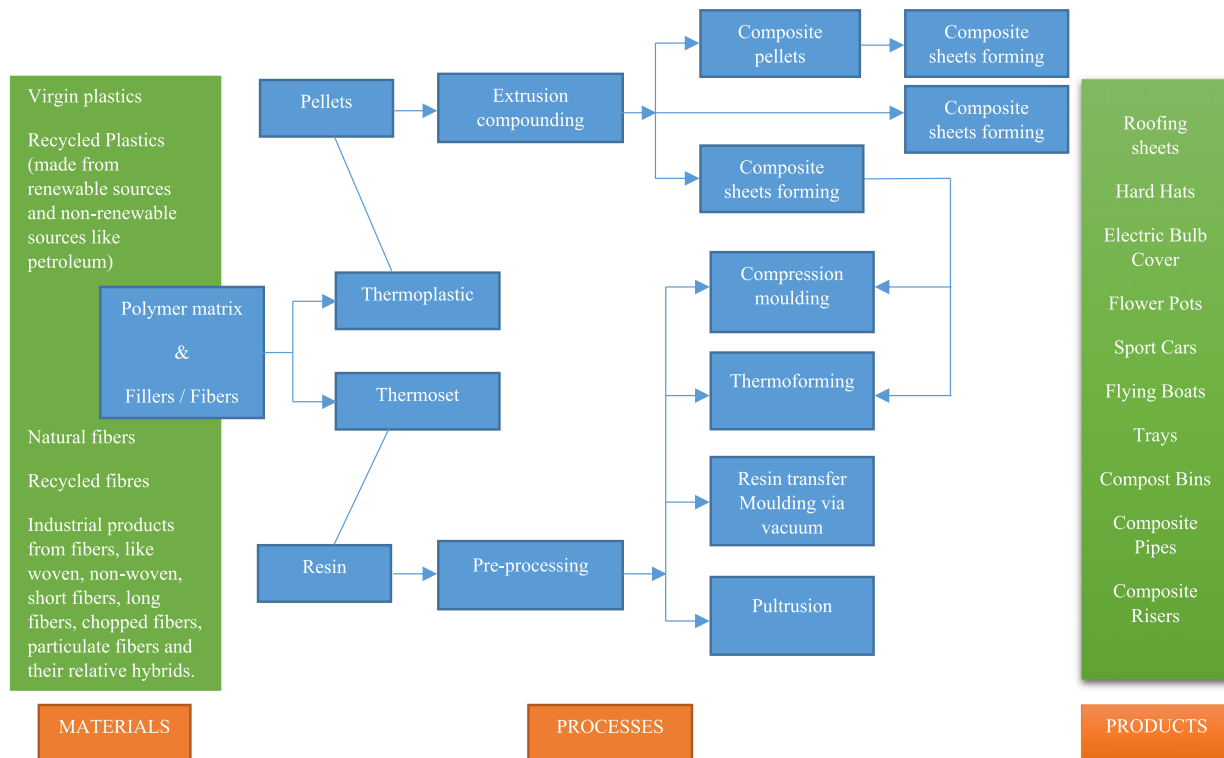


Fig. 7 From raw materials to manufacturing of composite product with some examples.

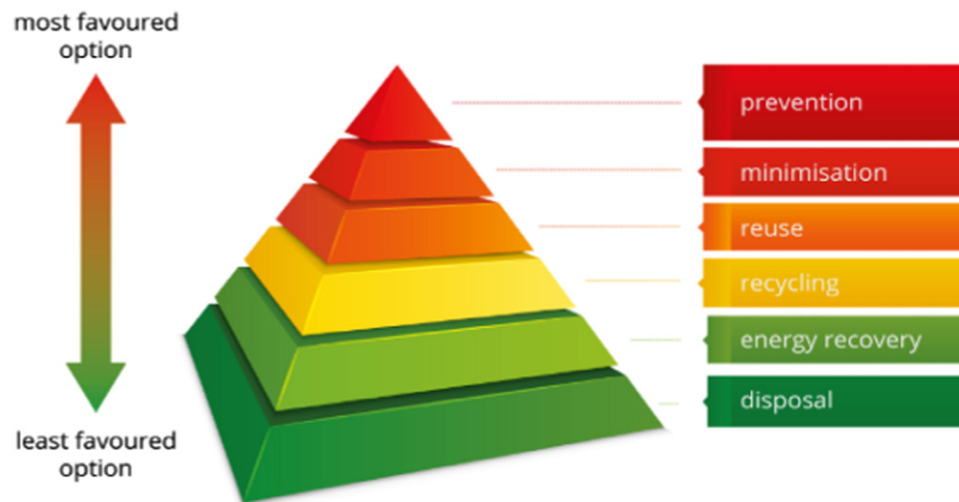


Fig. 8 Pyramid of reuse and recycling of composites.

flowline (Spruijt, 2018 and Jak *et al.*, 2018) and composite umbilicals (VisionGain, 2014; Van Onna and Lyon, 2017). Other design concepts on composite riser end-fittings (Amaechi and Ye, 2017; Amaechi *et al.*, 2019a; Hatton *et al.*, 2013) are presented in Fig. 3. The mechanical properties of composite risers can be seen in Tables 6–8.

Composite Choke and Kill Lines

Despite the various challenges, they are gain-worthy in the industry, academia, and research institutes. Developments in offshore composites kicked off trying to improve on its application in aerospace composite researches. The issue with offshore structures is the environmental loads, such as wave, excess pressure, internal pressure, manufacturing challenges, metal composite interface



Fig. 9 Reuse of offshore oil drums at Liverpool, UK as leisure furniture.

Table 5 Application of biocomposites showing mechanical strengths and sources

Resin	Fiber/filler	Impact strength	Tensile strength	Tensile modulus	Comments	References
Plastic waste (PE and PP)	Wood flour	2.9–6.2 kJ/m ² Unnotch	6–13 MPa	2.3–3.9 GPa	MAPE compatibilization and lubricant utilization	(Turku <i>et al.</i> , 2017)
PP	Wood, poultry litter biochar	8.1 kJ/m ² Notch	27 MPa	4.3 GPa	Hybrid biocomposites–MAPE compatibilization	(Das <i>et al.</i> , 2016)
PP	Flax fiber	751 J/m Unnotch	40 MPa	6.5 GPa	Needle-punch fiber mat composite	(Oksman, 2000)
Waxy maize starch	Neat and modified liquid crystalline cellulose, microcrystalline cellulose	–	505–790 MPa	22–32 GPa	Starch/cellulose hybrid biocomposites	(Rahman and Netravali, 2018)
Epoxy/acrylate	Glass fiber	237 kJ/m ² Notch	532 MPa	37 GPa	Methacrylated epoxidized sucrose soyate resin/glass fiber	(Hosseini <i>et al.</i> , 2016)
Biopolyurethane (BioPU)	Sisal fiber	–	57–119 MPa	1.2–2.2 GPa	Rubber seed oil polyurethane	(Bakare <i>et al.</i> , 2010)
PBS/PLA	Flax fiber	9.1–17.8 kJ/m ² notch	39–55 MPa	3.6–7.4 GPa	Fully biodegradable composite	(Bourmaud <i>et al.</i> , 2015)
PLA	Carbon fibers, twisted yarns of jute fibers	–	57–185 MPa	5.1–19.5 GPa	Continuous fiber-reinforcement probed by 3D printing	(Matsuzaki <i>et al.</i> , 2016)

Abbreviations: MAPE, maleic anhydride-grafted Polyethylene; PBS, polybutylene succinate; PE, polyethylene; PLA, polylactide; PP, polypropylene.

end, fittings, and weight of steel. It has been found that composites can offer some advantages on it but the thickness of the wall has to be considered because it involves high pressure high temperature, and the weight of other lines like the flow lines, choke, and kill lines (Skaugset *et al.*, 2013) all contribute to the total weight of the riser joint assembly system. Thus the need to introduce lightweight materials have been found to reduce the top tension load on the riser system (Omar *et al.*, 1999; Skaugset *et al.*, 2013; Hatton, 2012).

Table 6 Physical properties of water, steel and other composite riser materials

Property	Specific gravity	Density (kg/m ³)	Thermal conductivity (W/m/°C)	Heat capacity (J/kg/°C)	Poisson ratio V_{12}	Young's modulus (GPa)
Sea water	1.0	1030	0.6	4200	0.5	2.15
Steel	7.8	7850	50	480	0.30	200
Titanium	4.43	4430	19	540	0.342	113.8
Aluminum	2.78	2780	204.26	910	0.33	68.9
AS4-Epoxy	1.53	1530	—	—	0.32	—
AS4-PEEK	1.56	1561	—	—	0.28	66
P75/Epoxy	1.78	1776	—	—	0.29	—
P75/PEEK	1.77	1773	—	—	0.30	33
PEEK	1.32	1300	—	—	0.40	5.15
Composite riser	1.68	1680	0.5	1200	0.28	—

Abbreviation: PEEK, polyether ether ketone.

Table 7 Comparison of the key design aspects of steel risers and composite risers

Parameter	Steel	Composite	Comments
Max hang-off load (Te)	94	93	In an SLHR, the flexible jumper to the vessel acts as interface between the vessel and the vertical riser leg thus keeping the two isolated. Therefore negligible change in hang-off loads
Max hang-off bending moment (kNm)	261	282	
Max stress utilization	0.63	—	While stress is the driving criteria for steel, strain is the driving criteria for composites
MBR safety factor	—	2.76	MBR is larger than minimum acceptable
Max tension utilization	—	0.14	Tension is small in comparison to allowable
Buoyancy tank displacement (m)	247	211	Smaller drag area causes smaller buoyancy tank displacement
Buoyancy tank tension (Te)	451	258	43% less tension required
Max bending moment at base of URA (kNm)	116	62	Approximately 50% lower bending moment for both lower upper riser assemblies
Max bending moment at top of LRA (kNm)	581	270	

Abbreviations: LRA, lower riser assembly; MBR, minimum bend radius; URA, upper riser termination assembly.

Note: Hopkins, P., Saleh, H., Jewell, G., 2015. Composite riser study confirms weight, fatigue benefits compared with steel. Offshore Magazine 75 (9). Available at: <https://www.offshore-mag.com/pipelines/article/16758323/composite-riser-study-confirms-weight-fatigue-benefits-compared-with-steel>.

Table 8 TCP material selection by Airborne Oil & Gas

Glass-HDPE	Carbon-PA12	Carbon-PVDF
Fully qualified to 60–65°C	Temperature up to 80°C	High temperature up to 121°C
Used in permanent application	High pressure of 10 ksi	High pressure of 10 ksi
Medium pressure of 5 ksi	Low permeation	Lowest permeation
Low permeation	Used in an application	Highest chemical resistance
High chemical resistance	DNV qualified in 2018	DNV qualified in 2019

Abbreviations: DNV, det Norske Veritas; HDPE, high density polyethylene; PA12, polyamide 12; PVDF, polyvinylidene fluoride.

Note: Spruijt, W., 2018. Installation of the world's first subsea thermoplastic composite flowline for hydrocarbon service. In: Proceedings of the Offshore Technology Conference, OTC-28540, pp. 1–9. Kuala Lumpur, Malaysia: OnePetro/OTC.

Benefits of Composites in Offshore Industry

Composite materials give a variety of advantages that could enhance risk technology. Composites are lightweight and provide decent levels of strength. They can be easily formed into complex shapes due to their flexibility and can provide elevated levels of fatigue resistance and corrosion resistance. Maintenance needs are relatively low, and they can be installed via reel lay. Composite materials also a low axial and bending stiffness when compared to steel. However, composite materials have high material cost with limited track record offshore unlike steel, despite widespread applications in other industries. Currently, there are few codes and standards with direct applicability to composite risers.

Some of the benefits that composites may bring to the riser industry include cheaper installation costs (due to lessened weight), lower maintenance requirements in the offshore industry, lower roughness on internal bore (offering increased flow rates), and

Table 9 Benefits of composites for some offshore applications: Composite risers, composite propellers, composite choke and kill lines, and wind turbine blades

<i>Composite risers</i>	<i>Composite propellers</i>	<i>Composite choke and kill lines</i>	<i>Wind turbine blades</i>
Offer reduced weight of buoyancy and reduced size; lightweight (m-pipe is 1/10th of steel in air, and 1/5th in water); have excellent fatigue performance; reduce the variable deck load; ease of transport and deployment, like towing on site; enable drilling operations in ultradeep water and high reservoir pressures; have smooth bore for higher flow rate; reduced subsea project risk; require no upper riser assembly for deployment; have high pressure capability; offer lower life cost and lower system cost; have improved corrosion resistance	Enhance some weight saving on the ships; enhance fatigue performance of the structure; enhance the inception speeds with the use of thick flexible blades; enhance vibration-damping characteristics; enhance easier fabrication into more complex shapes; reduction of cost for fabricating the blades; reduction of the through-life maintenance costs; reduction of corrosion issues; reduction of noise signatures; reduction of electrical signatures; reduction of magnetic signatures; reduction of corrosion issues; reduction of wear on the shaft and gearbox; reduction of steel parts used in the propeller connections	Can have increased ID of choke and kill lines with same weight; extend operational envelope of an existing drilling rigs; have excellent fatigue performance; reduce the variable deckload; store more riser joints on the deck; have increased mud flow rate and better well control	Reduction of cost for fabricating the blades; reduction of the through-life maintenance costs; enhance some weight saving on the turbine; increase energy efficiency; ease installation of wind turbine; easier to form into complex shapes; low field life; less maintenance cost; resistance to corrosion; resistance to conductivity; resistance to fatigue damage; long field life; high-impact resistance; thermal stability; tolerance to damage

reduction in vessel hang-off loads (Hopkins *et al.*, 2015, 2014; Saleh, 2015). Despite these benefits, replacing steel with composite materials is unlikely to reduce the costs for existing designs. The real advantage composites offer is as an enabling technology for new concepts and operations in challenging locations and environments. Further concerns relate to damage to the sublaminar, which is hard to inspect on a manufactured pipe, and to the challenges of making up connections and end fitting design. A comprehensive review on the benefits of composites on some offshore applications is presented in Table 9.

Recycling Process of Renewable Composite Materials

There are different processes that are considered in the recycling of renewable composite materials in the composites industries that are beneficial for the offshore industry. There range from mechanical to thermal processes, as discussed in this section. Different literature present development of pyrolysis-based carbon fiber-recycling processes and these are now commercially available in several places since the launch of Milled Carbon (presently known as ELG Carbon Fiber) located in the West Midlands, UK (ELG Carbon Fibre, 2017; Job *et al.*, 2016; Job, 2013). However, the economic value of carbon fiber is about 10 times that of glass fiber. This inadvertently affects the commercialization of these recycling processes, making it quite challenging. It is noteworthy to state that although commercializing it has been a bit difficult, it has been “easier” than finding recycling routes for GRP, despite the much smaller volumes. According to AVK 2018 market report, in 2018, the carbon fiber-reinforced polymers (CRP) were estimated at 128,000 tonnes while the total European GRP market had an estimated total of 1.141 million tonnes with predicted growth rate of 2.1 % (Witten *et al.*, 2018). This was higher than that of the AVK 2012 market report, which presented 76,000 t of CRP compared to about 1 million tonnes GRP parts produced in Europe in 2012 (LinseT, 2013; Job, 2013; Sauer *et al.*, 2017).

The recycling process supported by European Composites Industry Association (EuCIA), and available in Germany, involves the addition of GRP waste to cement kilns. This gains value from all parts of the composite and is commercially active in Germany through the route known as Compocycle, operated by Zajons and feeding Holcim’s cement kilns. However there is still a significant gate fee for the process. In Germany regulations leave no option to landfill so the volumes of GRP waste are sufficient to justify such a process. Composite manufacturers such as Fiberline in Denmark have supported that process, being close enough to take advantage of it. But this route reduces the value of the material to that of calcium carbonate and at present is not economic compared with landfill where landfill is an option.

There are several processes that are either commercially exploited or under development whereby discontinuous fibers are converted into intermediate products. Several companies produce nonwovens using short carbon fibers. In many cases these are still virgin fibers and come from offcuts, weaving selvedge, etc. The nonwoven textiles can be made by the air laying, carding, or wet-laid processes. The other approach being employed is to chop the fibers to a fairly short length (a few millimeters) and then mix these with either a thermosetting resin to make a sheet or bulk molding compound or with a thermoplastic melt to produce a compound for injection molding. Care has to be taken during mixing to avoid fiber breakage. Recovery of the fibers from parts already impregnated with resin is more complex, but can be done by pyrolysis or solvolysis. The advantage of these recycling solutions is that it will lower the cost of carbon fiber (Holmes, 2017; Boucherat, 2016). According to an ELG Carbon Fiber report, 30% of the carbon fiber manufactured worldwide each year becomes waste, which is equal to about 18,000 tonnes per year. The carbon fiber industry has moved away from being a niche industry only producing 100 tonnes per year; as such the issue of waste needs to be tackled.

Recycling, which is a means of returning the material back to the composite market, will create the possibility for stability, longevity, and extra source of supply to the industry.

Mechanical Recycling Process

The composite waste is first sorted then it is milled or ground using a hammer mill or related tools to obtain the required sizes. Researches on mechanical recycling show that energy is used in this process (Howarth *et al.*, 2014). The reduction of sizes is used to convert the grades of the wastes into different fractions and then it is sieved into powders. Different fractions of the fillers and ground resins as well as other fibers of varying lengths are all embedded into the resin. Also contained in the recyclates are flakes of the materials, which are seen in SMC, BMC as seen in GRP composite wastes. One drawback here is that this method has very limited applications on CFRP composites. The ground composite materials are used for either fillers or as reinforcements. The fillers are not considered to be commercially profitable because of the low cost of the virgin fillers, for instance, silica and calcium carbonate. These fillers, which are the recovered powders from the mechanical process after sorting, can be incorporated into new materials. However, it must not be more than 10% in weight due to the breaking down of the molecules as a result of deterioration of the mechanical properties as well as more problems associated with processing higher filler contents due to higher viscosity of the compound. To this end, they have been applied as alternative energy sources due to the high organic compositions of the resins used. Fig. 14 shows the steps carried out during mechanical recycling.

Recycling of GRP by mechanical grinding has been ongoing for some decades. As far back as in the 1970s, the late Wolfgang Unger was developing his proprietary Seawolf technology in Florida in the United States, to grind fiberglass scrap and use it for replacing rotten boat transoms or incorporate it using spray-up equipment for making bathtubs and other products (LinseT, 2013). Unger's company is now called Eco-Wolf (Unger, 2011) managed by his daughter Sabine Corinna Unger. Eco-Wolf in 2011 partnered with Global Fiberglass Solutions, which is seeking to build and manage facilities to collect and recycle fiberglass across the United States, having developed applications such as railroad ties (railway sleepers), just like Reprocover and 3B fibers did.

Another commercial outfit was ERCOM Composite Recycling GmbH established in Germany in 1990 to recycle automotive production and postuse waste by shredding and grinding graded parts into powder, to be used in new sheet molding compound (SMC) in proportions up to 20% (Marsh, 2001). ERCOM terminated in 2004. This approach of grinding GRP to fine powder for use as filler is well established in several industries, but as with the cement kiln route, it reduces the value of the material to that of calcium carbonate, which can be purchased at very low cost (around £200/t). In addition, it requires a significant amount of energy input to grind the material finely. Thus apart from some in-house recycling (see below), attempts to commercialize this as a recycling route have failed.

Thermal Recycling Process by Pyrolysis

Pyrolysis, according to Sponberg (1999), is the process of chemically decomposing or transforming a material into one or more recoverable substances by heating it to very high temperatures in an oxygen-depleted environment. This process differs from incineration, which is carried out in an open atmosphere. Pyrolysis is a thermal process that is carried out at a temperature range of 450–600°C, subject to the environmental conditions and the resin used. In other words, pyrolysis is the decomposition of the resin using heat. This can be achieved by applying a batch process with the use of an inert atmosphere or vacuum. This decomposes the resin to a mixture of chemicals, which tend to volatilize from the resin and then condense in the outlet as pyrolysis oil, which can be burnt as a fuel or distilled to recover chemicals. Although, the process also generates a char which is a hard glassy (noncrystalline) carbon and this can be well adhered to the fibers and bond fibers together. The higher temperatures are used for the epoxies and thermoplastics of high performance like PEEK composites, while the lower temperatures are used for the polyester resins. Thermal degradation of the resin matrix produces oil, gases and solid products made up of fibers, char and possibly fillers. To reduce the amount of char produced, it is oxidized using small quantity of oxygen. Char can only be removed here by oxidation. With this method, the recovery of fibers, fillers as inserts are possible (Job *et al.*, 2016; Castro *et al.*, 2013; Thakur *et al.*, 2007). The breakdown of the resin into molecules of low-weight, lower-weight, and much lower-weight produces the gases and oil fraction, which can be recovered chemically into other chemicals, and sometimes burnt to generate energy such as EfW energy recovery processes. Pyrolysis has been successfully applied on plastic wastes as well as composite wastes (Sekula and Leszczynski, 2009; Kennerley *et al.*, 1995) as well as in the offshore industry (Demirbas and Taylan, 2015).

As stated earlier, the product from pyrolysis depends on the conditions, and thus affects the resulting mechanical properties of the fibers. For glass fibers, the tensile strength can be varied between 52% and 64% while the tensile strength of carbon fibers can be varied between 4% and 85%. This shows the influence of temperature on the resulting fiber properties. A pyrolysis temperature of 450°C is usually the lower limit while the temperature range between 500°C and 550°C appears to be the upper limit of the thermal process of pyrolysis. As this temperature range, an acceptable fiber strength that is typically viable commercially for carbon fiber is achieved.

Any thermal or chemical process strips the sizing off the fibers. In the case of glass fiber, this results in dramatic loss of strength and handling/processability. Thus, thermal and chemical treatments are not suitable for GRP unless the fibers are posttreated. A

Table 10 Comparisons between different recycling technologies

<i>Recycling technologies</i>	<i>Strengths</i>	<i>Weaknesses</i>	<i>Points of attention</i>
Mechanical recycling	Efficient waste management process (high throughput rates)	High decrease of (mechanical) properties Material undergoes downcycling Recyclate with a high content of other material (including polymers, contaminants, paint, coatings) Small, unstructured, coarse, and nonconsistent fibers High operational costs and capital investment (running costs, installations) Has up to 40% material waste	It requires full use of PPEs. Fine dust released into the surrounding atmosphere. Potential of fibers to stick into human skin or mucous membranes causing irritation.
Pyrolysis	Pyrolysis gas and oil can be used as energy source making it a self-sustained process Wax recyclate can be used as fuel or intermediate for chemicals production Easily scaled-up to multitonne capacity Microwave pyrolysis involves heating the material at its core with microwave radiation It creates room for easier control of the heating process leading to decreased induced damage to the fiber material	Fiber product may retain oxidation residue or char Sizing degradation of glass fibers leads to changes in the composition (chemical structure)	Potential combustible gases leakage from waste treatment chambers
Cement kiln (coprocessing)	Highly efficient and fast process: Residence time of 4–5 s in cement kilns Large quantities can be processed Up to 75% substitution of cement raw materials which significantly reduces CO ₂ that is emitted by the cement industry No ash left over, minerals are trapped in the matrix of the clinker	Complete loss of material characteristics (fiber form) High processing temperatures	Emissions from pollutants and particulate matter
Solvolytic	Recovery of clean fibers in their full length Recovery of resin (like polymers or oligomers) that can be reused	Insufficient efficiency (throughput) of the technology High energy consumption due to the high-temperature and high-pressure Use of large amounts of solvents	Gas emissions (depending on catalysts potentially toxic, e.g., from alkali catalysts) Human health impact and ecotoxicity High water consumption (although reuse options could be explored)
High voltage pulse fragmentation	Able to treat industrial quantities, which produces sufficient scalability of the process to treat larger capacities Low investments required to reach the next level	Only laboratory- and pilot-scale machines are available Heavily decreased modulus of glass fibers	Working near high voltage
Gasification (fluidized bed)	Highly flexible (in terms of different process capabilities) and simple process High efficiency of heat transfer	Low fiber qualities for glass fibers (significantly reduced fiber tensile strength) Will only be economically viable if it reaches capacities of more than 10,000 t per year (Yang <i>et al.</i>) Defluidization is problematic: Fluidized bed can locally collapse	Emissions (e.g., CO ₂) related to the process Quite stable and efficient performance in case of reactor operability and safety concerns

Abbreviations: CO₂, carbon dioxide; PPE, personal protective equipment.



Fig. 10 Offshore wind turbine as composites application in offshore renewable energy.



Fig. 11 Image of space rocket module in NASA facility, USA.

posttreatment to recover glass fiber properties after thermal treatment has been proposed in literature (Thomason *et al.*, 2016; Bashir *et al.*, 2017; Tajeddin, 2017) as well as other methods to recover the strength of the glass fibers. According to Job *et al.* (2016), an increase in the scale upwards to produce glass fibers that can compete with virgin glass fibers would require the substantial application for chopped glass fibers, for instance, automotive thermoplastic composites. However, it is difficult to achieve this without economic loss, because glass fiber has comparatively low value. There are three novel methods in pyrolysis, namely continuous pyrolysis, chain conveyor pyrolysis, and fluidized bed pyrolysis.

Continuous Pyrolysis

To achieve the continuous pyrolysis, the process has to have steady supply of high temperature. Carbon fibers are comparatively oxidation-resistant up to about 500°C, thus it is possible to burn off the resin and with careful control of the conditions inside the furnace still avoid a significant loss in strength. This is the method employed at ELG carbon fibre company (ECF) in a patented furnace process called continuous pyrolysis. Combustion of the resin depletes the oxygen levels in the furnace so the oxidation of

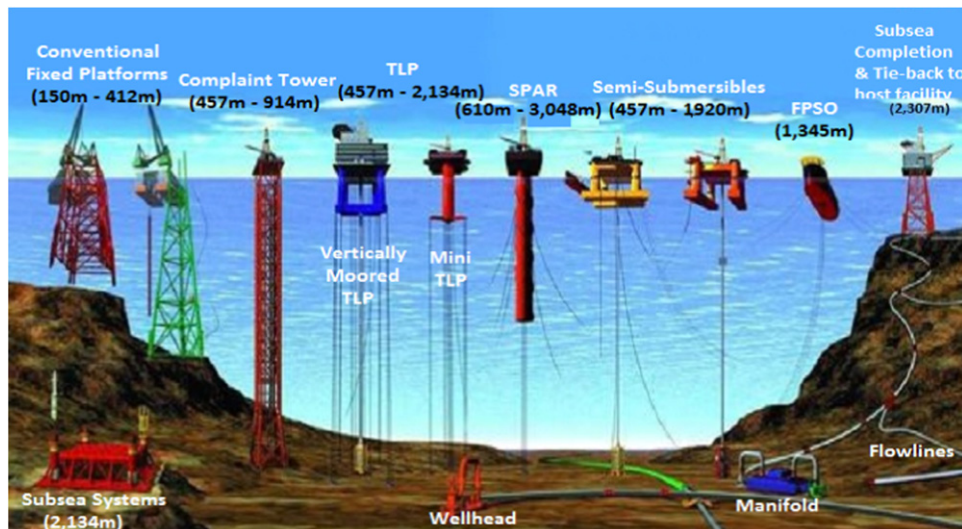


Fig. 12 Offshore deep water systems showing the platforms and riser types. Modified with permission, NOAA.

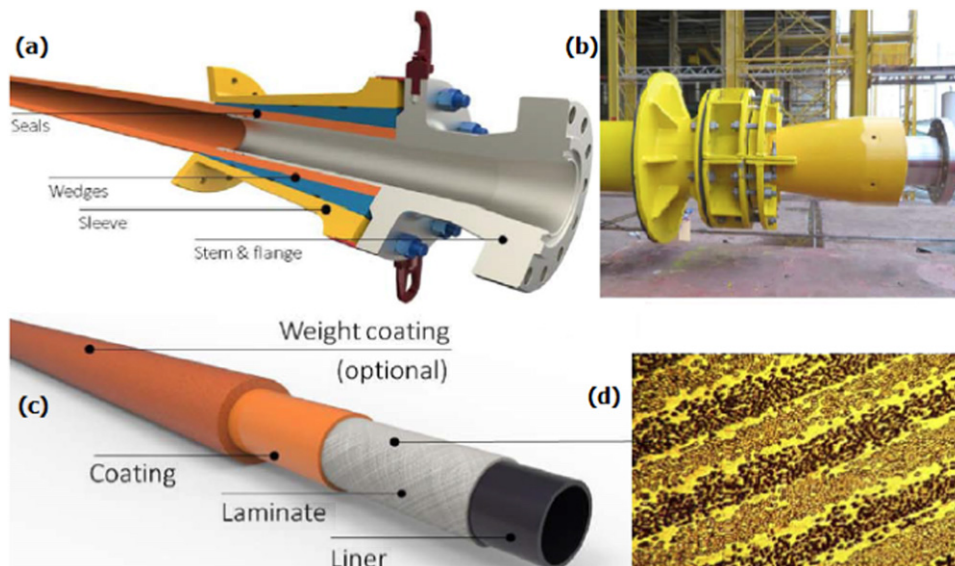


Fig. 13 Thermoplastic composite pipe (TCP) with (a) end-fitting concept, (b) installed 6-in. ID end-fittings installed on an I-tube, (c) TCP pipe concept, and (d) laminate microscopy. Courtesy: Spruijt, W., 2018. Installation of the world's first subsea thermoplastic composite flowline for hydrocarbon service. In: Proceedings of the Offshore Technology Conference, OTC-28540, pp.1–9. Kuala Lumpur, Malaysia: OnePetro/OTC.

the fiber is minimized. The presence of oxygen minimizes char formation because entropy considerations do not favor char formation over combustion and any char that is formed oxidizes faster than the fibers. Regardless of how the fibers are won from the waste, they are liberated as discontinuous, poorly aligned fibers. Subsequent processing is necessary to take this low bulk density material to convert it to products that the industry wants to buy (Harris, 2017; SNW, 2019).

Thermal Recycling Process by Solvolysis

Solvolysis has also been applied to recycle composites and plastic polymers as a chemical process (Prinçaud *et al.*, 2014; Oliveux *et al.*, 2017; Yang *et al.*, 2014). In solvolysis the resin matrix is decomposed or dissolved by a solvent. As composite resins are generally engineered to be durable in typical service conditions, they tend to have excellent resistance to chemicals. Dissolving the resin therefore requires aggressive chemicals and/or elevated temperatures and pressures. For example, it is known that carbon

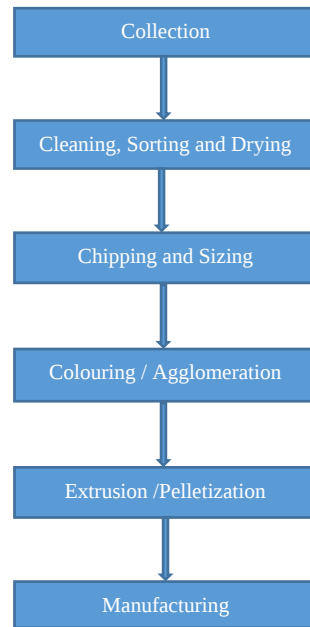


Fig. 14 The steps for mechanical recycling.

Technology	Inputs	Outputs
Pyrolysis		
Gasification (Fluidised bed)		
Solvolysis		
HV Pulse Fragmentation		
Mechanical Grinding		
Cement kiln		

GFRP
 CFRP
 Electricity
 Gas
 Coal
 Water
 Clay, limestone
 Fibres
 Fibrous powder
 Chemicals
 Emissions
 Waste
 Clinker

Fig. 15 Inputs and outputs for recycling technologies for wind turbines. *Source:* Reproduced from Ierides, M., Reiland, J., Dierckx, A., 2019. Wind turbine blade circularity: Technologies and practices around the value chain. In: Proceedings of the WindEurope Conference & Exhibition, 2-4 April 2019, pp. 1–38, Workshop on Blade Disposal. Bilbao: Bax & Company.

fibers can be liberated from an epoxy laminate by boiling it in concentrated nitric acid for several hours (ISO 14127). It has also been proven that a supercritical acetone/water mix (320°C, 170 bar) also dissolves the resin. Neither method has been scaled up to tonnage quantities and there are still significant challenges to be addressed before this technology becomes commercially viable.

Thermal Recycling Process using Cement Kiln

The application of cement kiln in recycling glass fiber composites is one of the recommendations of EuCIA (2011). According to the European Composites Industry Association (EuCIA), GRP is “recyclable and compliant with EU legislation.” The process of incineration of the GRP wastes is impractical because relatively 50%–70% of the GRP material is composed of minerals and ends up as ash, which ends up in landfills. To coprocess these using the cement kilns, the sizes of the GRP composite parts are reduced and then mixed together with other composite wastes to introduce into the cement kilns. Typical GRP composite is made up of E-glass, which is mostly aluminoborosilicate, organic resin, and some calcium carbonate filler. Once the mix is sent into the cement kiln, the organic resin burns providing energy (about 12 MJ/kg of waste) while the mineral constituents provide feedstock used as the cement clinker (LinseT, 2013; Job, 2013). Usually, the clinker is ground to form cement paste or powdered cement, and the calcium carbonate calcines (which releases

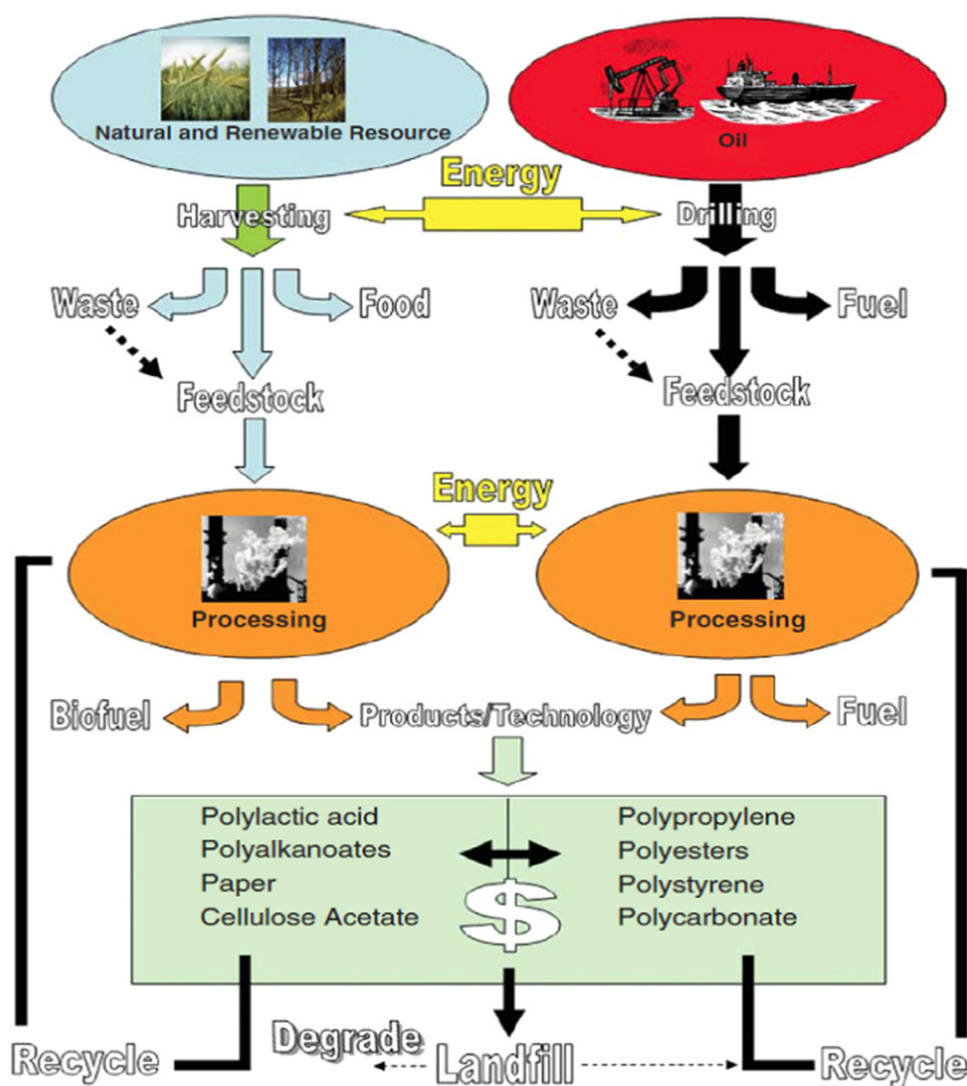


Fig. 16 Summary of renewable materials vs. oil production indicating stages of energy input. Reproduced from Eichhorn, S.J., Gandini, A., 2010. Materials from renewable resources. *MRS Bulletin*, 35(3), 187–193.

carbon dioxide) to calcium oxide, which is the primary component of Portland cement. Alumina and silica also have cementitious properties in an alkaline environment and are typically present in Portland cement at about 25%, and in much higher proportions in cement alternatives from fly ash and slag. Boron, which is found in most E-glass, can cause a reduction in early strength during the setting of cement, but as long as proportions are kept low it is not considered a problem (Pickering, 1993, 2006).

Comparisons Between the Recycling Options

Considering the different recycling options discussed, we can use a diagram to compare the different recycling options, as presented in Fig. 15 and Table 10. Different researches have been reviewed to attain the results on the comparisons between the recycling options. Details can be found in literature (Liu *et al.*, 2017; Pickering, 2006; Oliveux *et al.*, 2015) (Tables 7, 8 and 10).

Case Study of Energy for Waste

Waste minimization, reuse, and recycling are essential to achieve more sustainable waste management. There are, however, technical and commercial reasons why all waste cannot be recycled. There will always be some residual waste. It is important that local authorities and businesses have a way to manage residual waste and recover maximum value. There is a view that EfW is competing with recycling. Experience across Europe shows that best practice can involve high levels of recycling combined with EfW for the remaining waste that cannot be reused or recycled. Switzerland, the Netherlands, Sweden, and Denmark, for example, all have high levels of EfW as an integral part of their waste management strategies. These countries also have high waste recycling rates. Fig. 10 is an application of offshore wind turbine which can be used in the description of the EfW process (Eichhorn and Gandini, 2010) (Figs. 11 and 12).

Case Study of Building Recycled Boats

One of the earliest reports made of building recycled boats was first noted in Sweden (Sponberg, 1999). According to the author, Ryds Battindustri AB, the Swedish largest boatbuilder as of 1999, was producing about 3600 small powerboats yearly in 36 models ranging in size from 3.3 m (11 in.) to 5.95 m (20 in.) using a lot of fiberglass composites. Ryds partnered with the Swedish Institute of Composites to develop on manufacturing boats using closed loop recycled scrap, which accounted for about 10% of its layup production. The result was a 4.75 m (15.5 in.) concept boat, containing about



Fig. 17 Mechanical recycling of wind turbine blades after demolition, in pretreatment stage. Courtesy: Source: Estevez, D.G., 2019. Demonstration of wind turbine rotor blade recycling into the coal clough windfarm decommissioning opportunity. In: Proceedings of the Wind Europe Conference & Exhibition, 2-4 April 2019, pp. 1-16, Workshop On Blade Disposal. Bilbao: LIFE + Brio.

20% recycled fiberglass by weight. The original single-skin laminates of sprayed-polyester fiberglass in the hull and deck were cut back by 50% and replaced with a sprayable polyester mixture containing 33%–40% ground scrap. Scrap mixture was used to replace the core materials, such as Coremat, plywood, and Divinycell. The boat's laminates had equal or better strength in all respects and, where the recycled compound replaced plywood, screw-holding power improved significantly. Other applications of composites can be seen on offshore ind turbines, NASA's space craft modules, offshore composite risers and leisure boats (Figs. 10–13).

The equipment for processing the scrap mix includes a grinder, a high/low shear mixer, and eight specially designed spray equipment (see photos above), all developed by and licensed from Seawolf Industries, which is owned by Wolfgang Unger. The grinder can quickly grind scrap to predetermined fiber lengths and keep fibers intact, which is important to the strength of boat laminates. In addition, compound additives developed by Seawolf resolved problems of premature catalyzation, viscosity, and fibers settling to the bottom of the mix. Seawolf now sells its machinery to any fiberglass manufacturer who wants to start recycling. Ryds anticipated its concept boat would go into production at about 50 boats per year. Unfortunately, recycled production boats did not go on as they planned at that time (Sponberg, 1999). Over time, other boat makers started to try fiberglass recycling.

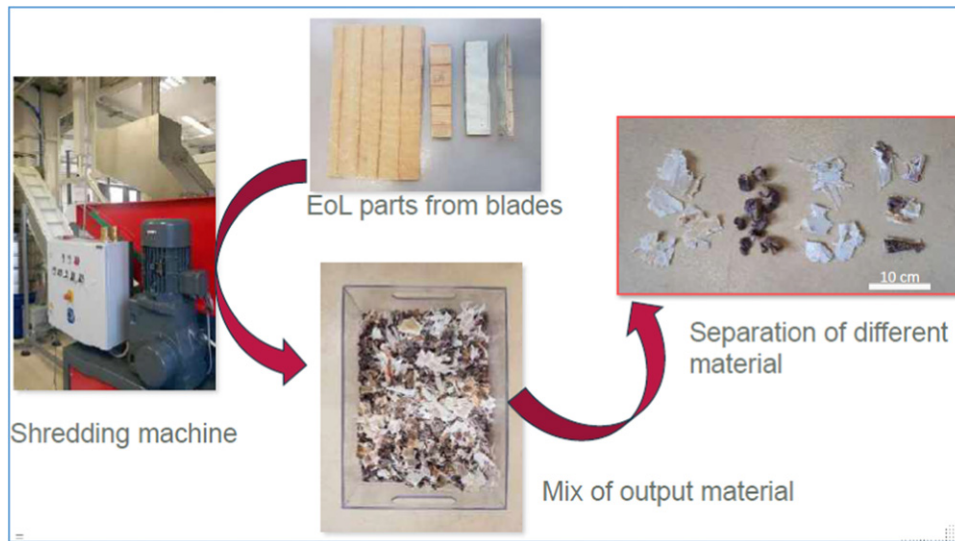


Fig. 18 Mechanical recycling. Courtesy: FiberEUse. *Source:* Garcia, S., Arcarazo, A., 2019. Large scale demonstration of new circular economy value-chains based on the reuse of end-of-life fiber reinforced composites. In the proceeding WindEurope Conference & Exhibition, pp. 1–12. 2–4 April 2019, Workshop on blade disposal. Bilbao: FiberEUse.



Fig. 19 Thermal recycling for wind turbine blades. Courtesy: FiberEUse. *Source:* Garcia, S., Arcarazo, A., 2019. Large scale demonstration of new circular economy value-chains based on the reuse of end-of-life fiber reinforced composites. In the proceeding WindEurope Conference & Exhibition, pp. 1–12. 2–4 April 2019, Workshop on blade disposal. Bilbao: FiberEUse.



Fig. 20 Thermal recycling of aeronautic waste. Courtesy: FiberEUse. *Source:* Garcia, S., Arcarazo, A., 2019. Large scale demonstration of new circular economy value-chains based on the reuse of end-of-life fiber reinforced composites. In the proceeding WindEurope Conference & Exhibition, pp. 1–12. 2–4 April 2019, Workshop on blade disposal. Bilbao: FiberEUse.



Fig. 21 Thermal recycling of construction wastes. Courtesy: FiberEUse. *Source:* Garcia, S., Arcarazo, A., 2019. Large scale demonstration of new circular economy value-chains based on the reuse of end-of-life fiber reinforced composites. In the proceeding WindEurope Conference & Exhibition, pp. 1–12. 2–4 April 2019, Workshop on blade disposal. Bilbao: FiberEUse.

Offshore Wind Turbine Blade Recycling

The recycling of wind turbine blades involves the integration of innovative remanufacturing technologies addressed to develop profitable reuse options for mechanically or thermally recycled EoL GFRP and CFRP composites. Different steps are involved in mechanical recycling process of composites, as illustrated in Figs. 14 and 15. Each process has its limitation and process capacity, as presented in Tables 1 and 10, depending on the source of raw materials and the recycling company's capacity.

Challenges of Recycling Renewable Composites

The renewable composites used in the offshore industry are not limited to lightweight composite pipes and offshore wind turbine blades, as illustrated in Figs. 13 and 15, respectively. Despite the application, there are challenges that are faced in composite applications in the offshore industry. According to ECF, the main challenges in recycling carbon fiber composites have included dealing with the complex nature of the waste streams. Even relatively clean waste streams from composites manufacturing still contain resins of varying chemical composition and unwanted materials such as paper or plastic backing films, and the recycling process has had to be optimized to ensure the complete removal of these unwanted materials without damaging the fibers. The second challenge is classification of the fibers. The composites industry has grown up with a wide variety of carbon fiber grades available from different manufacturers. Although the recycling process has only a small effect on the properties of the fiber, it is not desirable to retain the original fiber designation after fiber recovery. ECF has addressed this by introducing a generic classification system based on the Young's modulus and tensile strength range of the recovered fibers. Wind turbine blade recycling and reuse is a current practice in the industry. In addition, other natural renewable materials can also be sourced and recycled such as basalt and flax. An example is presented in Fig. 16, depicting the stages of energy input and recycling from agro industry and the oil



Fig. 22 Wind turbine blade waste disposal. *Courtesy: Ageeko.*



Fig. 23 The result from recycling a wind blade made of glass fiber. *Courtesy: Reciclaia.*

and gas industry. More wind turbine wastes generated are also disposed to recycling plant, as shown in [Figs. 17–23](#). According to [Liu and Barlow \(2017\)](#) the expected blade material usage in the future will continue to increase, as shown in [Fig. 24](#).

Qualification

First is the issue of qualification of the offshore composite structures ([Skaugset et al., 2013](#); [Wilkins, 2016](#); [Johnson et al., 1998](#)). Based on the qualification process that is applied in the development of composite structures and the failure mechanism that can occur after testing, these may be as a result of the design load not in line with predictions, failure predictions as a result of coupon strength, the type of loading (collapse, burst, bending, or long term loading). This can also be seen in the cycles depicted in mechanical recycling of composites by [Estevez \(2019\)](#) and [Garcia and Arcarazo \(2019\)](#), as depicted in [Figs. 18–21](#). An example of the product of recycling wind turbine blades is presented in [Fig. 23](#). Other applications of recycled composites is on the railway track as shown in [Fig. 25](#). With the increase in the researches on recycled composites, more qualification is expected on application of recycled composites on ship decks and cars, as presented in [Figs. 26 and 27](#).

Standardization

Another issue is standardization; however, newer standards are under development ([Van Onna and Lyon, 2017](#); [Gibson et al., 2002](#); [Echtermeyer and Steuten, 2013](#)). In boats, FRP composites have been in use about 70 years as boat making materials. Thus, most boats and motorsports are made from composites and even half of the structural airframes of modern aircrafts, like the Boeing 787 Dreamliner and the Airbus A380. They have also been used in the automobile industry as seen in [Table 2](#). FRP bridges also have been in existence for over a decade. Composites have been an enabling technology in the offshore industry, as seen in wind turbines blades and oil wells with deeper risers. However, while the standards allow

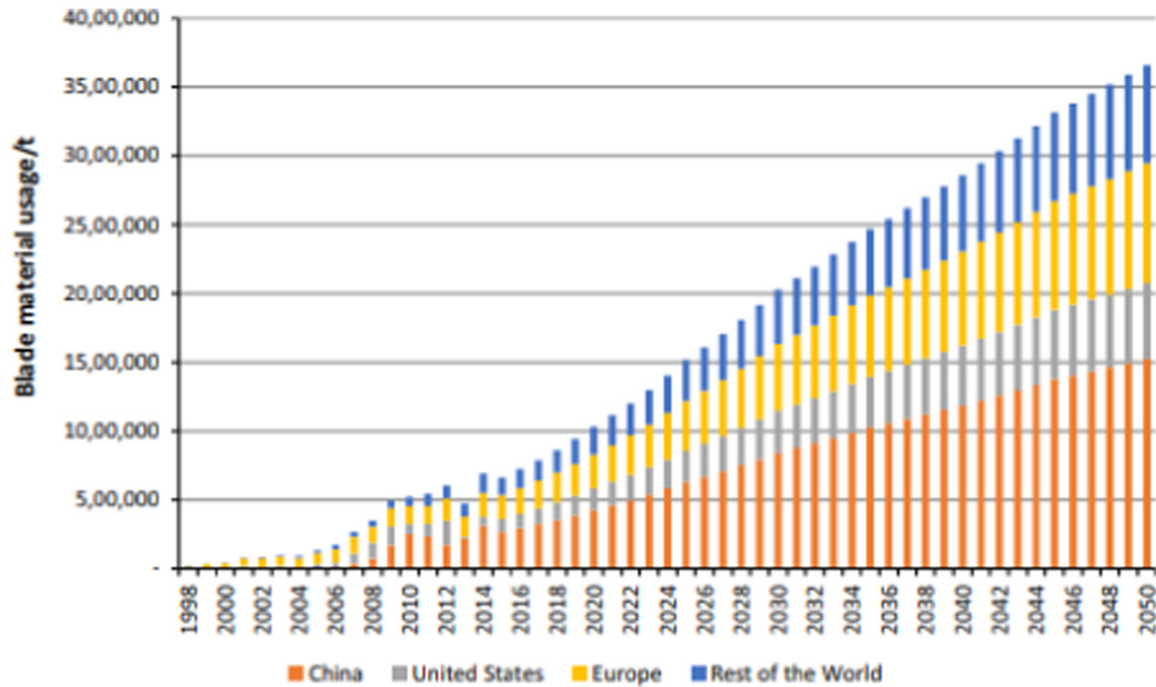


Fig. 24 Predicted blade waste in Europe until 2050. Reproduced from Liu, P., Barlow, C.Y., 2017. Wind turbine blade waste in 2050. *Waste Management* 62, 229–240. doi:10.1016/j.wasman.2017.02.007.



Fig. 25 Level crossing panels including recycled Glass Reinforced Polymer and phenolics from car parts. *Courtesy: Reprocover.*

small boats, leisure boats, and work boats to be built using composites, the IMO and SOLAS regulations restrict the use of composites and greatly prohibits the structural use of composites due to reasons like combustibility (Job, 2015, 2014). Currently, some recycled wind turbine blades are used in making pedestrian bridges, to show that they are structural of high strength, although the service life is not high.



Fig. 26 The 1000-t deckhouse of destroyer USS Zumwalt (DDG 1000) is craned toward the deck of the ship at General Dynamics Bath Iron Works. The deckhouse is primarily made from balsa-cored carbon fiber using vacuum assisted resin transfer molding. Reproduced from Job, S., 2015. Why not composites in ships? *Reinforced Plastics* 59 (2), 90–93. doi:10.1016/j.repl.2014.12.047.



Fig. 27 Application of composites on automobiles. Courtesy: Malnati, P., 2018. Recycled waste products get new life as lightweight, cost-effective auto parts. *Plastics Engineering*, 74(6), 18–25. Available at: http://read.nxtbook.com/wiley/plastics_engineering/june_2018/recycled_waste_products_get_n.html.

Conclusion

Carbon fibers and glass fibers are high performance materials widely used in many fields thanks to their specific properties. As a result, research and development in this field is very active and one major driver is cost reduction. However both FRP and GRP do not have equal amount of usage as renewable offshore composites. This study has looked at major offshore applications of renewable composites in the industry, and a brief history of their usage and recycling technologies. Some comparative studies were

also presented on the technologies and their options for a circular economy. For easier reference, this study also present some current commercial recycling facilities as well as some composite facilities, but not a fully comprehensive list due to the scope of the work.

Acknowledgment

The authors gratefully acknowledge the funding support of Lancaster University Engineering Department, Lancaster, UK, and Niger Delta Development Commission (NDDC), Nigeria. The research reported in this paper is part of the Project 51879143 supported by the National Natural Science Foundation of China (NSFC). The financial support is highly appreciated. We also acknowledge all the support from Dr. Marco Longana from Bristol Composites Institute for some reference materials and Peggy Malnati for the original images of automotives reproduced in Fig. 27 with help with obtaining the permission from SPE Automotive Division, Ford Motor Co. and Hyundai Motor Group, General Motors Co. We also thank all those who granted us permission to use their images in this project and also appreciate all who worked on the market reports on composites which were used in this study. Lastly, the authors acknowledge Stephen Hatton of Magma Global and Martin Van Onna of Airborne Oil & Gas for technical supports on composite risers.

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Smart Contract for Monitoring and Control of Logistics Activities: Garbage Utilities Case Study in a Smart City

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Introduction

Nowadays logistics is a core area for companies which is concerned with transporting products between parties. However, the problem of this sector is that its scale may lead to delays and defaults in the delivery of goods as well as other issues. In addition, large distributors need a large volume of workers to meet all the demands of stores. All this may contribute to big delays in order processing and increases the possibility of losing orders (Li, 2016). In an attempt to solve this problem, companies have automated all their processes, contributing to a significant increase in the number of businesses and distributors in the logistics sector. However, an increase in the amount of digitized data and the expansion of Internet companies means that the risk of attacks on their databases is also greater. Hackers may intend to modify, steal or delete data (Chamoso, 2017; Lima, 2015).

We suggest an alternative way of solving this problem. In our case study (i.e., Garbage Utilities), we are going to consider a hybrid scenario (Li, 2014a,b). Firstly, we provide security to the data of the companies involved in the garbage logistics sector with the inclusion of blockchain. Secondly, MAS will be used for the organization's problem (Li, 2014a,b, pp. 1–8). It has been proven that MAS (MAS) provide efficient solutions to a huge variety of problems (Wooldridge, 1995). These include, but are not limited to, the use of agents for image classification (Coria, 2014), decentralized network control (Najafi, 2018), real-time problems (Carrascosa, 2008) and Internet of Things applications (Gazafroudi, 2017).

In this paper we propose a new hybrid model that uses blockchain, smart contract and a MAS to protect the data of the garbage utilities sector (Tapia, 2013) and improve logistic activities (i.e., our model allows to remove intermediaries and speed up logistics activities). In addition, multi-agents are capable of coordinating all the logistic services (i.e., our model improves organization, security and distribution times). This model is designed to improve the efficiency of the garbage utilities sector. For this purpose, data is protected and smart contracts are used to remove intermediaries (Costa, 2011) (Rodríguez, 2010). On the other hand, the MAS validates all transactions and the miners' system is responsible for creating the blockchain with the transactions made by the agent system through smart contracts (Dhuric, 2017). Although there is a lot of discussion on the use of blockchain in logistical services, there have not been any systems that would implement and evaluate it. Our approach is a functional prototype which has been evaluated empirically. Furthermore, it has been proven that it resists third-party attacks, in the case study context, more efficient than a traditional logistic model. In the methodology section, the model is proposed and in the discussion section, its advantages and disadvantages are evaluated in line with the conventional logistic model. The main contribution of this paper can be summarized as follows:

- A novel system of smart contracts to optimize the operations of the garbage logistics sector.
- A new MAS to coordinate the tasks that monitor and control the garbage logistics sector.
- A hybrid system that integrates the contributions described above to optimize the efficiency of the garbage logistics sector.

The rest of the paper is organized as follows. Section "Introduction" provides the introduction to the topic. Section "Related Work" have all the related works to this paper. The proposed system is show in Section "Proposed System". Section "Simulation Results" present the main results of our model and Section "Conclusion" show the conclusions of our findings.

Related Work

A blockchain is a distributed data structure that is replicated and shared among the members of a network (Bremer, 2017). It was introduced with Bitcoin (Nakamoto, 2008) to solve the double-spending problem. As a result of how the nodes in Bitcoin (the so-called miners) mutually validate the agreed transactions, Bitcoin blockchain establishes the owners and states what they own. A blockchain is built using cryptography. Each block is identified by its own cryptographic hash and each block refers to the hash of the previous block. This establishes a link between the blocks, forming a blockchain (Antonopoulos, 2014; Cardoso, 2017). For this reason, users can interact with a blockchain by using a pair of public and private keys. Miners in a blockchain need to agree on the transactions and the order in which they have occurred. Otherwise the individual copies of this blockchain can diverge producing a fork; miners then have a different view of how the transactions have occurred, and it will not be possible to keep a single blockchain until the fork is not solved (Santos, 2016).

To achieve this a distributed consensus mechanism is required in every blockchain network (Casado-Vara, 2018a,c,d). Blockchain's way to solve the fork problem is that each blockchain node can link next block. Just a correct random number with SHA-256 has to be found (Casado-Vara, 2018c,d), so you have number of zeros that the blockchain expects. Any node that can solve this puzzle has generated the so-called proof-of-work (pow) and gets to shape the chain's next block. Since a one-way

cryptographic hash function is involved, any other node can easily verify that the given answer satisfies the requirement. Notice that a fork may still occur in the network, when two competing nodes mine blocks almost simultaneously. Such forks are usually resolved automatically by the next block (Marín, 2015; Becerra-Bonache, 2014).

With the implementation of blockchain, smart contracts are included to make transactions between different users faster and more effective (Casado-Vara, 2018b). Nick Szabo introduced this concept in 1994 and defined a smart contract as “a computerized transaction protocol that executes the terms of a contract” (Szabo, 1994). Szabo suggested that the clauses of contracts could be transferred to code, thus reducing the need for intermediaries in transactions between parties. In the blockchain context a smart contract is a script that is stored on a blockchain (Szabo, 1997). Smart contracts have a unique address in a blockchain (i. e., they are in a block with a hash that identifies it). We can trigger a smart contract in a transaction by indicating the address on the blockchain. It is executed independently and automatically in a prescribed manner on every node in the network, according to the data contained in the triggered transaction.

A MAS is a computerized system composed of multiple intelligent agents that interact with each other. MAS are used to solve complex problems with very good results. MAS are used in a wide range of applications. Gazafroudi (2017) presents a MAS for the intelligent use of electricity in a Smart home and thus, an increase in its energy efficiency. Another problem that MAS have solved effectively is the monitoring of sound in a variety of situations. The application of a MAS to logistics is not a new problem, in Li (2018) a MAS is proposed to provide a solution to the logistical problem. In addition, another successful application of MAS is the problem of distributed computing (Banerjee, 2017). Therefore, some of the proposals that we find in the literature combine the advantages of blockchain and MAS. From a range of systems that integrate blockchain and MAS the work of Aitzhan (2018) is worthy of mention. The frame of JADE has been chosen for the development of the MAS for this project. This framework Java provides mechanisms to incorporate agents who manage safety aspects in order to measure in order that the quiet information is really the one that is transmitted and analyzes (González-Briones, 2018a,b). The architecture has been developed for the incorporation of multiple heterogeneous sensors, so that the functionality could grow in the future for the incorporation of new services (González-Briones, 2018a,b). The system is designed specifically to analyze the behavior of the user, the information of the sensors, the information of third parties and the capture of decisions.

This work proposes to use both technologies to increase security and privacy in decentralized energy networks. In Yuan (2016) authors propose a model that employs agents and blockchain for a ride-sharing system. In addition, there are other applications of blockchain and MAS. In Daza (2017) the authors propose an innovative blockchain model for IoT. However, after looking at the state of the art, we believe that the current blockchain and MAS models have some shortcomings. We propose a new model that leverages smart contracts and MAS, it is aimed at increasing efficiency in the logistics system management. This paper describes a case study which verified the proposed model, it focused specifically on logistics transport in the pharmaceutical sector.

Proposed System

This section presents the model that has been designed to optimize garbage collection with blockchain technology.

Business Model

This paper presents a new model which consists of the following elements: a blockchain in which all transactions are stored. Smart contracts that manage transactions between the different parties in the garbage utilities sector. And a that MAS coordinates all these operations. In this section we describe the how our model works. The members of each logistic operation have smart devices which monitor the status of each one. The case study was conducted in the garbage management sector, Fig. 1 shows process members. One of the parties involved in garbage logistics is the production of garbage. People buy all kinds of things and use them. In this way they produce a lot of garbage in their homes or workplaces. This garbage is placed in bins and in some cases in recycle bins to recycle the garbage. On the other hand, the waste management companies are responsible for the maintenance of the waste bins and the collection of the waste.

Once the garbage is collected, the garbage management company processes it by recycling what it can and storing or destroying the rest. In order to optimize this process, we have developed a smart contracts system based on blockchain. Performance of this platform is as follows: (1) Recycling bin. The waste that is produced is deposited in the recycling bin. When these bins are full the weight sensors detect it and the smart contract recycling bin creates a contract with the waste management utility to empty it. In this way, the recycling bin is intelligent and can be self-managed. One of the main advantages of this system managed by smart contracts is that the recycling bin will only be emptied when are needed. (2) Waste management utility. The waste management company has to collect the garbage from the recycling bin when the smart contract recycling bin runs because it has detected that it is full. Once the garbage has been collected, the smart contract waste management utility runs so that the waste management utility takes it to the recycling plant. In this way, the garbage stores are never filled and do not produce collapses in the storage and recycling of the garbage. (3) Recycling station. This is where the waste that can be recycled is recycled. At this stage of the logistic process the smart contract validates the amount of material that is introduced into the recycling plant. In the same way, the smart contract counts the amount of material that has been recycled. Therefore, the result of this smart contract will be the amount of waste that has been recycled and the amount of waste that has to be stored or destroyed.

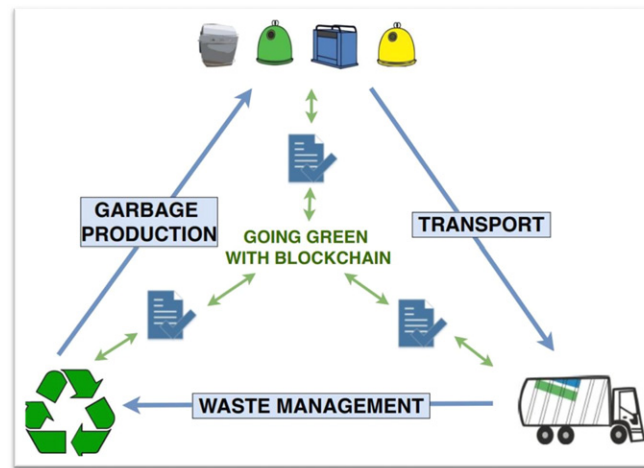


Fig. 1 Graph based on smart contract for garbage management utilities.

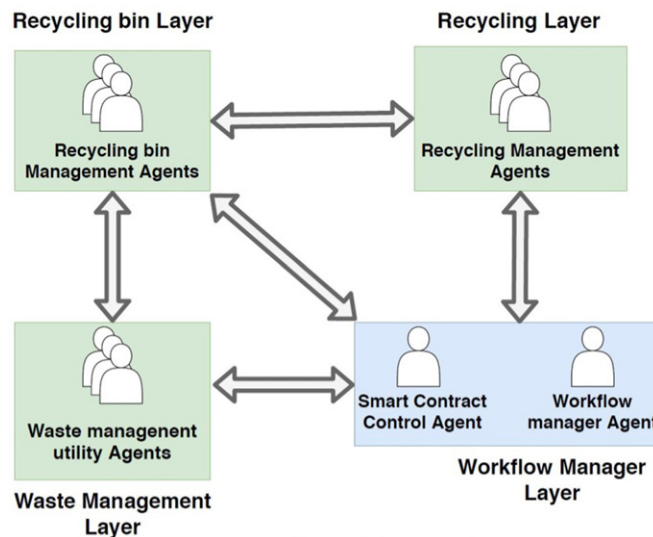


Fig. 2 Multi-agent architecture. The logistic control agents are shown in green while coordinator agent is shown in blue.

Multi-Agent Model

A MAS coordinates the whole process (see Fig. 2). The architecture of the MAS is built in JADE and consists of the following layers:

- (1) Recycling bin layer. In this layer are the recycling bin. In each of them there is a BISITE PCB v.2 with a built-in weight sensor shown in Fig. 3. Thus, when the sensor detects that the recycling bin has a pre-set weight, the smart contract runs and puts that bin in a priority queue for the garbage collection trucks to include it in their path. Therefore, these agents coordinate the task of incorporating the bin into a priority list so that the bin is emptied.
- (2) Recycling Layer. In this layer the agents that coordinate it have the task of monitoring the entrance of garbage, and the exit of recycled and non-recycled garbage. That is to say, they are creating an inventory of the garbage processed to be stored and of the recycled garbage.
- (3) Waste management utility Agents. The agents of this layer coordinate that the trucks collect the garbage containers in an effective way. To do this, they create a graph with the streets and the position of the full bin, and execute an optimal route algorithm for the trucks ~cite{goldberg2005computing}.
- (4) Workflow Management layer. In this layer the agents have the task of coordinating all the other agents so that they work correctly and the smart contracts are executed when necessary.

Hardware

In this manuscript we will proceed to show the most relevant features of the BISITE PCB v.2 development board for implementation in order to cite the features in order to analyze the feasibility of its use in the case study of waste management



Fig. 3 Simulation of vehicles through a path to find full bins.

within an intelligent city. Some of the most relevant features are the sensors and electronic components included in the board, it integrates accelerometer, temperature controller, energy consumption sensor, positioning data through GPS, Galileo, GLONASS and BeiDou and also an ATSHA204A encryption chip with SHA-256 technology. The LoRaWAN network based on LoRa modulation is used as communication mode, due to its high noise tolerance and indoor penetration if necessary. The board has certain expansion ports to add sensors and/or actuators to extend the functionality of the device. These ports are specifically designed for various sensors in our case we will use the I2C input as a plug/&play. In the case study is used as load sensor Load Sensor Sparkfun also called extensometer that can measure up to 500 kg. This second version of the device has been developed with a view to reducing its size so that it can be used in a wide range of applications as an IoT device for the collection of safe data. Between the observable differences, besides the specialization of the sensors in the developed field, there is the addition of an advanced system of load management with network monitoring and the addition of an energy source such as a battery or solar.

Simulation Results

For the simulation of the model we are designing, a model of a smart city with several streets and buildings has been used. The vehicles are simulated with autonomous programmable robots that are connected with a MAS that coordinates the movements coded with JADE. In **Fig. 3** we can find several captures made on the tests that have been made in the simulations. In them the development plate presented in **Fig. 3(C)** and **(D)** (the black box) send the simulated signals to the MORE that the containers are full. In this way, the MAS creates a graph with the streets of the smart city and the bin, executes the algorithm for the calculation of the optimal routes and proceeds to their collection.

To take it to the recycling plant and garbage storage. In this way, we have seen that the routes are optimized, because instead of making a route throughout the city collecting the bin are full or not, you only go through the bin that are full. Therefore, the efficiency of garbage collection is improved. In addition, it calculates the optimal route through the city to collect only the containers that are full, therefore, also optimizes the route. That is to say, it supposes a quite remarkable improvement in the method that there is at the moment to collect the garbage in the city of Salamanca in Spain.

Conclusion

This paper presents a new Smart contract approach to improving logistics garbage services. The novelty of this paper lies in a blockchain to store all transaction information in the logistical process of the proposed case study. In addition, the multi-agent system uses smart contracts to manage the entire logistics process more efficiently, this is because smart contracts remove intermediaries. Our model can be used to improve any logistics system. The case study conducted in this proposal focuses on the garbage sector. Our model has improved security and efficiency as it is automated by the agent system. By incorporating blockchain we provide the logistics system with solid security features. Shipments can be tracked, origin and destinations authenticated, and proof of all transactions can be stored. Future lines of research include improving the multi-agent system by introducing new agents for the monitoring of procedures. In addition, our model could be enhanced by integrating a case-based reasoning system (CBR).

Acknowledgements

This work was supported by the Spanish Ministry of Economy and Competitiveness (MINECO) and FEDER funds. Project: "SURE, Intelligent System for integrated and sustainable management of urban fleets" with ID: TIN2015-65515-C4-3-R.

See also: Internet of Things Platform to Encourage Recycling in a Smart City

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Sustainable Geo-Materials in Construction Towards Climate Change Adaptation

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Introduction

Global statistics on waste tires reveal that, about 1 billion waste tires are generated every year in different parts of the world. Most of those waste tires are either burnt to produce energy or landfilled. Thermal recycling, however, is harmful to the environment because it releases more CO₂ compared to the other efforts of recycling, such as material recycling and cascaded recycling (Hazarika *et al.*, 2018). In order to encourage the recycling of waste tires that minimizes the CO₂ release, utilization of such industrial by-product in cascaded form (returning on different product) is gaining attention in recent years. It is, therefore, necessary to shift the share of recycling from thermal to cascaded recycling. When recycled in cascaded form they can be called tire derived geo-materials (TDGM). TDGM (Fig. 1) are not only low cost and low carbon (LC²) materials, but they also possess many advantageous properties such as vibration and sound absorption, good permeability, high durability and good thermal conductivity. In addition, these materials are non-dilatant in nature unlike other granular geomaterials (Hazarika, 2013). Owing to these characteristics, they can replace other conventional materials (such as gravel), in applications such as drainage, leachate, reinforcement, and so on.

For the past one decade, research related to the utilization of tires in construction projects has been gaining momentum. Due to their advantageous physical and mechanical characteristics, TDGM either in the form of shreds, chips or crumbs have been used as fill material for embankments (Humphrey, 2008), as fill material behind retaining walls and abutments (Garcia *et al.*, 2012; Hartman *et al.*, 2013), as base isolation for buildings (Tsang, 2008), and as liquefaction prevention material (Yasuhara *et al.*, 2010). The environmental aspects of such materials were thoroughly reviewed by Edil (2008).

The Japanese research covers a wide range of waste tire utilization. Few examples of those include: use of whole tires or in conjunction with other granular materials (Fukutake and Horiuchi, 2006) or use of tire chips and tire shreds (Hazarika *et al.*, 2012b; Karmokar *et al.*, 2006) and tire chips as lining in tunnel construction (Kim and Konagai, 2001). Also, tire chips mixed with cement-treated clay was used as a sealing material at a waste disposal sites in Tokyo bay (Mitarai *et al.*, 2006). Use of tire chips as a material to prevent liquefaction in soil also was experimented by Yasuhara *et al.* (2010) and Uchimura *et al.* (2008).

On the other hand, in recent years, the world has seen large scale earthquake induced hazards or climate change related hazards. Especially, in Japan, such natural hazards are too frequent in recent years. Also, in most of the developing countries, where the infrastructure development is still in infancy, adequate and cost-effective disaster mitigation efforts are urgently needed. The key issues in most of the developing countries are the balance between the cost and the increased burden to environment while undertaking any infrastructural projects. In this paper, recycling of waste tires and disaster mitigation in the context of Japanese experiences were focused, and few geo-disaster reduction techniques developed in Japan using TDGM are described.

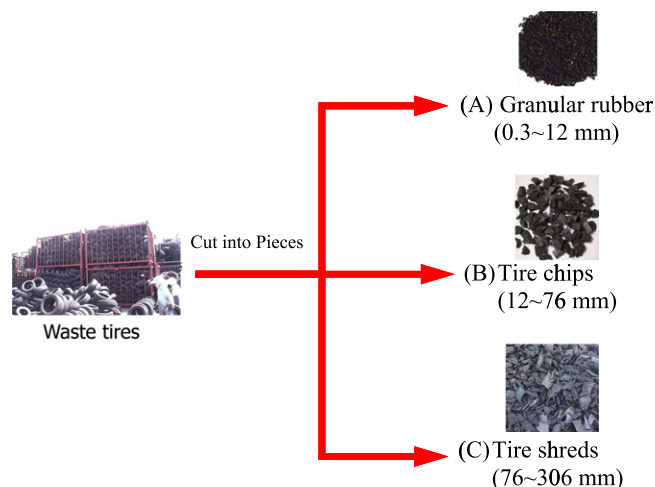


Fig. 1 Tire derived geo materials.

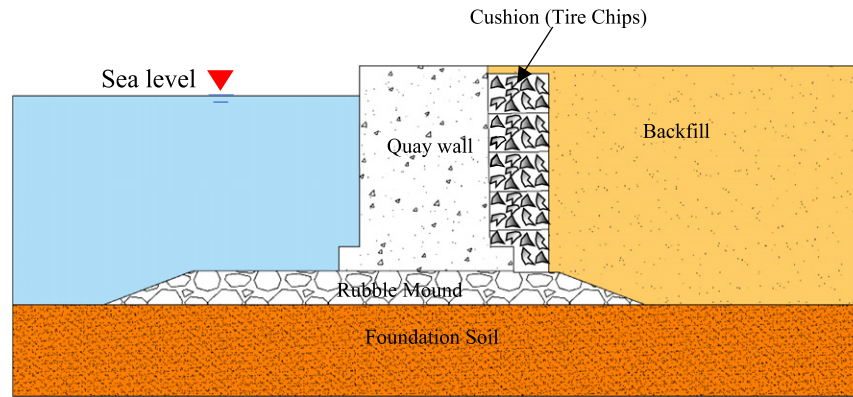


Fig. 2 Quay wall with tire chips cushion as backfill. Modified from Hazarika, H., Kohama, E., Sugano, T., 2008. Underwater shake table tests on waterfront structures protected with tire chips cushion. *Geotechnical and Geoenvironmental Engineering* 134, 1706–1719.

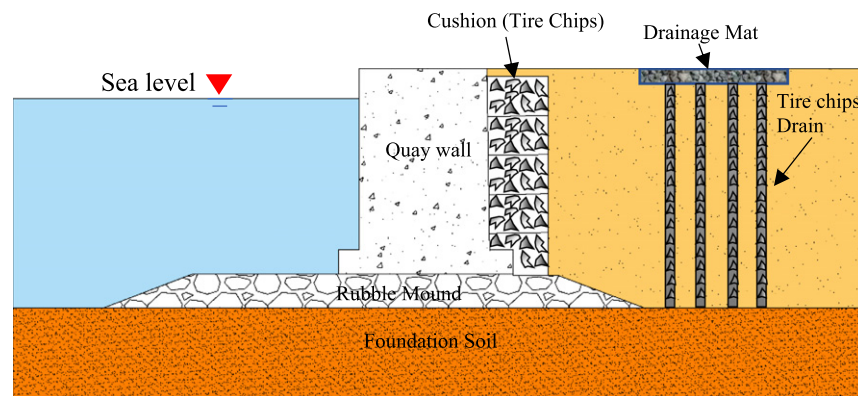


Fig. 3 Vertical inclusion technique. Modified from Hazarika, H., 2012. Earthquake resistant reinforcement of coastal structure using recycle material from waste tires. *Expected Materials for the Future* 12, 34–41. (in Japanese).

Geo Construction Techniques for Hazards Mitigations Using TDGM

Quay Wall Protection During Earthquake Using Vertical Inclusion

During the 1995 Hyogo-ken Nanbu Earthquake, Japan many waterfront retaining walls were reported to be tilted in the seaward direction, while soil liquefaction was also observed in the backfill soil (Inagaki *et al.*, 1996). A technique to protect retaining wall from such damage was developed and validated through experimental investigations, which were reported in Hazarika *et al.* (2008) and Hazarika *et al.* (2010).

Description of the technique

The technique, named SAFETY (Structural Stability and Flexibility during Earthquakes using Tires), consists of a compressible inclusion made of tire chips, which was placed as a cushion behind the retaining wall as can be seen in Fig. 2. The purpose of the installation of such cushion behind the quay wall was to absorb the impact due to an earthquake, and at the same time restricting the displacement of structures.

However, in order to optimize the amount of tire chips to be used in making the cushion, some percentage of sand or gravel can be mixed with tire chips by enclosing the mixture inside geotextile bags, and then placing those behind the structure. This kind of mixing and confining technique saves the amount of tire chips/tire shreds to be used in a project. At the same time, it also reduces any unwanted vertical settlement due to vertical load coming from the structure on the backfill, since tire derived materials have high compressibility. In addition, mixing and confining of the materials before placing makes the execution easier and faster.

In the backfills of waterfront retaining structures, which are susceptible to liquefaction, vertical drain installation in the backfill was proposed (Hazarika, 2012). Vertical reinforcing inclusion, thus, refers to the cushion and vertical drains which are made of highly permeable tire chips, and are placed vertically as part of backfill material. The vertical drains can quickly dissipate the generated excess pore water pressure during earthquake. The schematic diagram of SAFETY technique is shown in Fig. 3. The drains

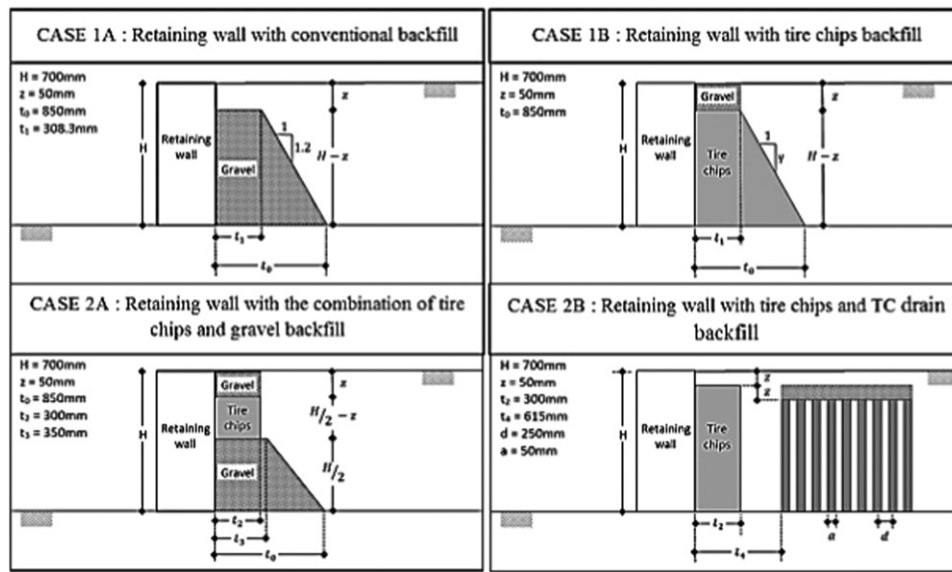


Fig. 4 Models used in the shaking table experiment.

can also be made of mixtures of tire chips and gravel in an optimum mixing percentage, as both the materials possess almost similar permeability.

Test cases and test procedures

Experimental verification of the technique described above, was made by conducting 1 g shaking table test using the large three-dimensional underwater shaking table assembly belonging to the Port and Airport Research Institute (PARI), Japan. The circular shaking table of diameter 5.65 m is mounted on a 15 m long, 15 m wide and 2 m deep water pool. Details of the shaking table assembly and the model construction procedures used in this study can be found in Hazarika *et al.* (2008) and Sugano *et al.* (1996).

A caisson type quay wall was used in this testing, which were placed in a soil box of 4 m long, 1.25 m wide and 1.5 m deep. Four different models were constructed in which each of the models differs on the selection of backfill material as shown in Fig. 4. In Case 1A, a conventional caisson with gravel as part of the backfill was used. In Case 1B, the entire gravel backfill was substituted by tire chips. A layer of gravel was placed on top of the tire chips to prevent any uplifting of tire chips during earthquake due to their low weight. Case 2A is the case in which the top half of the gravel in Case 1A was replaced by tire chips. In Case 2B, a compressible inclusion and a series of vertical drains made of tire chips were installed as part of the backfill as explained in Fig. 3 in the section above. A total of 23 vertical drains of diameter 50 mm were installed with a spacing of 210–250 mm in triangular pattern. To ensure proper water drainage during earthquake loading, on top of the entire drains a 50 mm thick gravel layer underlying a 50 mm thick soil cover was laid. This later also could prevent any uplifting of the tire chips drain. A cross sectional view of this case and the instrumentations of the testing program are shown in Fig. 5.

The test models consist of 0.1 m thick bedrock layer, 0.45 m thick dense seabed layer (relative density of 78.59%), 0.1 m thick foundation rubble and 0.85 m thick backfill soil (relative density of 45.95%). Saturation of the backfill was achieved by elevating the water level up to 1.3 m at a slow rate, after constructing and instrumenting the models.

Scaling law for model to prototype ratio of 1/10 was selected in this study. The similitude of various parameters in 1 g gravitational field were calculated based on the soil-structure-fluid system proposed by lai (1989). The test models shown in Fig. 4 were subjected to an actual earthquake loading (the N-S component of the strong motion acceleration record at the Port Island, Kobe, Japan during the 1995 Hyogo-ken Nanbu Earthquake).

Test results

Fig. 6 shows the time histories of horizontal displacement experienced by the caisson during the test duration at the top (D2) and bottom (D1) of the caisson. Negative signs of the horizontal displacement indicate that the displacement was towards the sea. It can be seen that the residual displacement of the retaining wall with conventional backfill (Case 1A) was 9.1 mm and 7.8 mm at the top and the toe respectively. Replacing the rubble backfill with tire chips (Case 1B) helps reducing the amount of residual displacement by almost 50% where the displacements recorded were 4 mm and 3.3 mm at the same points. The combination of tire chips and rubble as backfill material (Case 2A) also shows some reduction in the residual horizontal displacement compared to the conventional case. The vertical inclusion technique (Case 2B), yields similar residual horizontal displacement as in the case of Case 1B.

Fig. 7 shows the dissipation capabilities of the excess pore water pressures (EPWP) generated during earthquake, due to the installed drains. Sustained and non-dissipative excess pore water pressures lead to the liquefaction of loose sandy soils. As can be

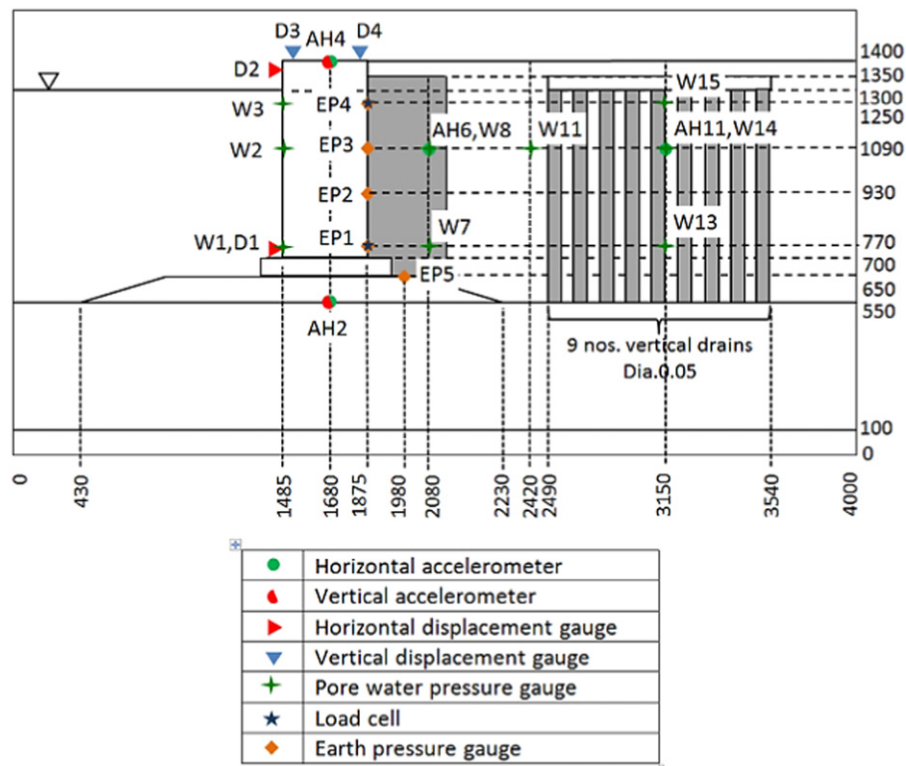


Fig. 5 Cross section and instrumentations of the models used in the experiment. All dimensions are in mm.

seen in this figure, In Case 1A (conventional backfill), the EPWP is continuously increasing and sustaining in that state for a longer duration, indicating the backfill liquefied. Case 1B also shows the same trend. However, Case 1C and 1D in which tire chips and gravel tire chips were used as drainage enhancing materials, the dissipation is faster, thus could prevent any liquefaction in the backfill.

Tsunami Protection of Sea Wall Using Whole Tires

Many sea walls were damaged during the 2011 off the Pacific Coast of Tohoku Earthquake and resulting tsunami. Examples of failures of many seawalls and breakwaters during that disaster are reported in [Hazarika et al. \(2012a\)](#). Any countermeasures, to protect seawalls from future damage during tsunami, require the knowledge of damage mechanism of seawalls due to tsunami. When incoming tsunami overflows the seawall, it collides with the seawall foundation, and due to rapid overflow, seawall embankment is scoured due to the impact of water resulting in outflow of the concrete panel covering of embankment. On the other hand, when the tsunami returns to sea (backrush), the force of backrush hits the sea wall with a huge impact force, and as a result seawall collapses completely due to reduced strength of the foundation and the structure. Therefore, to protect seawall from damage due to tsunami, we need to adopt two countermeasures simultaneously: (a) protection of soils behind the seawall due to tsunami impact force and (b) protection of concrete cover behind the seawall due to force of backrush. A countermeasure, taking into the account the above two factors, is described below.

Description of the technique

To protect seawall from impact force of tsunami, a new concept of using waste tire (a resilient material) structures behind seawall was developed ([Hazarika and Fukumoto, 2016](#)), which is shown in [Fig. 8](#). Considering the esthetic, suitable plants can be planted within the tires to preserve the greenery ([Hazarika et al., 2016](#)).

To evaluate the tsunami impact force absorption and the load dispersion effect of the protective tire structures explained in [Fig. 8](#), Tsunami Overflow Tests (TOT) were conducted by placing model tires behind the seawall in various configurations and different filling conditions of tires.

Test model and test conditions

A new apparatus for TOT was developed by the research group of adaptation to global geo-disaster and environment at Kyushu University. In this apparatus, a model soil box made of acryl (1200 mm in length, 300 mm in width and 1000 mm in height) was used to reproduce the overflow phenomenon of tsunami. The schematic diagram of the apparatus developed in this research is

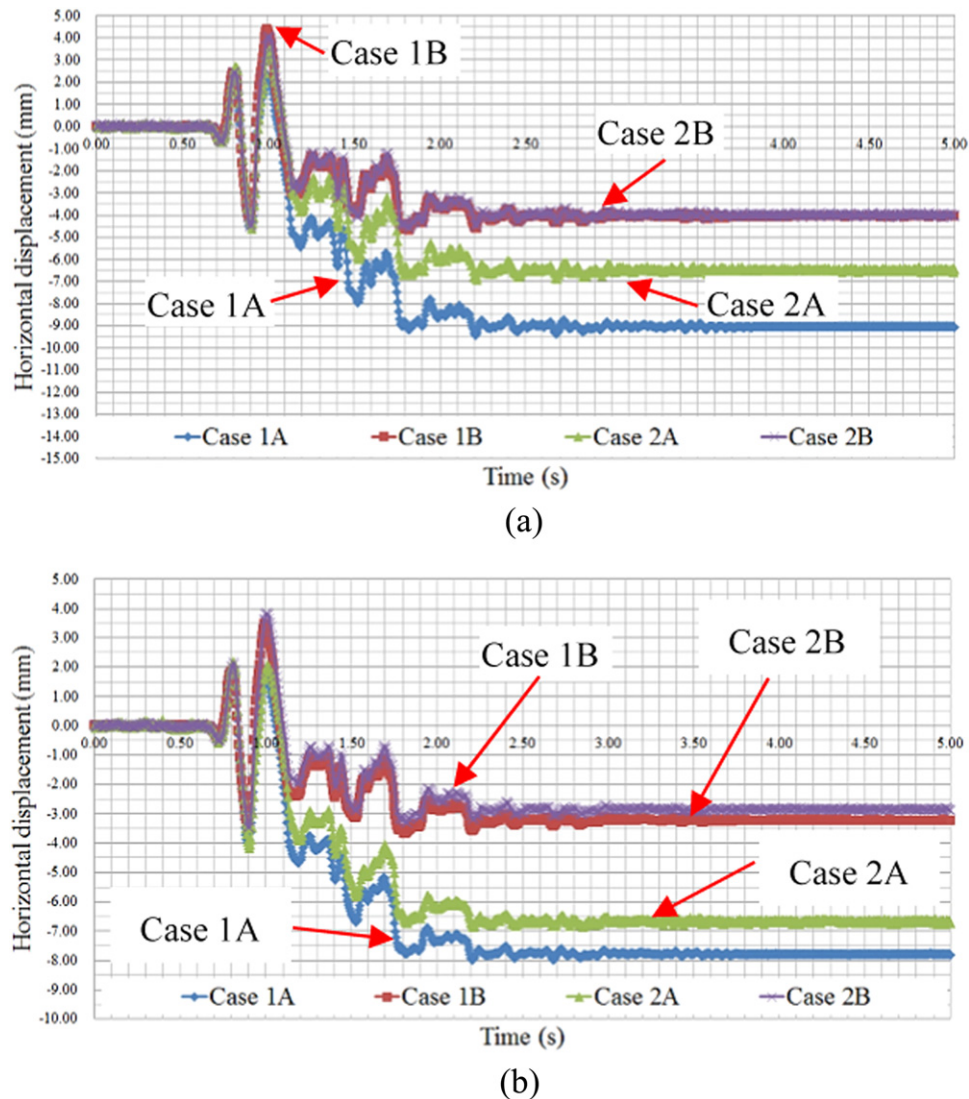


Fig. 6 Comparison of the horizontal displacements of the caissons (a) At the top of the caisson (D2 of Fig. 5) (b) At the bottom of the caisson (D1 of Fig. 5).

shown in Fig. 9. The model seawall (height 60 cm and crown width 12 cm) is placed inside the soil box. There is a hinge gate above the model seawall that stores water and can reproduce the overflow phenomenon of tsunami.

It was expected that the ability of tires to reduce the impact force of tsunami, will be different according to the number of tire layers, types of filling material and style of tire placing (configurations). Therefore, the following test cases were examined as explained in Fig. 10. Vertically laying cases (Case 2: two layers, Case 3: three layers) and alternately laying case (Case 5: slopped three layers). Three different filling conditions of tire were examined: (1) Hollow tire (without any filling) (2) Tire filled with Masado (decomposed granite soils abundant in Kyushu area, Japan) and (3) Tire filled with tire chips (TC) of maximum grain size 2 mm.

In the tests, model tires with outer diameter 85 mm, inner diameter 45 mm and thickness 21 mm were used instead of actual tires. There are five load tables (Table 1–5) in the landside of the apparatus shown in Fig. 9. Each load tables are supported with two load cells as shown in the figure. In the data analysis of this test, average value of the two load cells (in each table) was taken, and then the maximum of those average values was determined.

Test results

Fig. 11 shows the calculated values of the water impact force against the time of overflow. Two typical cases are shown in the figure. One with no tire placed on the back of sea wall and the other is the case of sea wall reinforced by slopped 3 layers of tires (Case 5 of Fig. 10). Comparison of the results shows that there is a considerable reduction (more than one third) of the impact force due to tire placement.

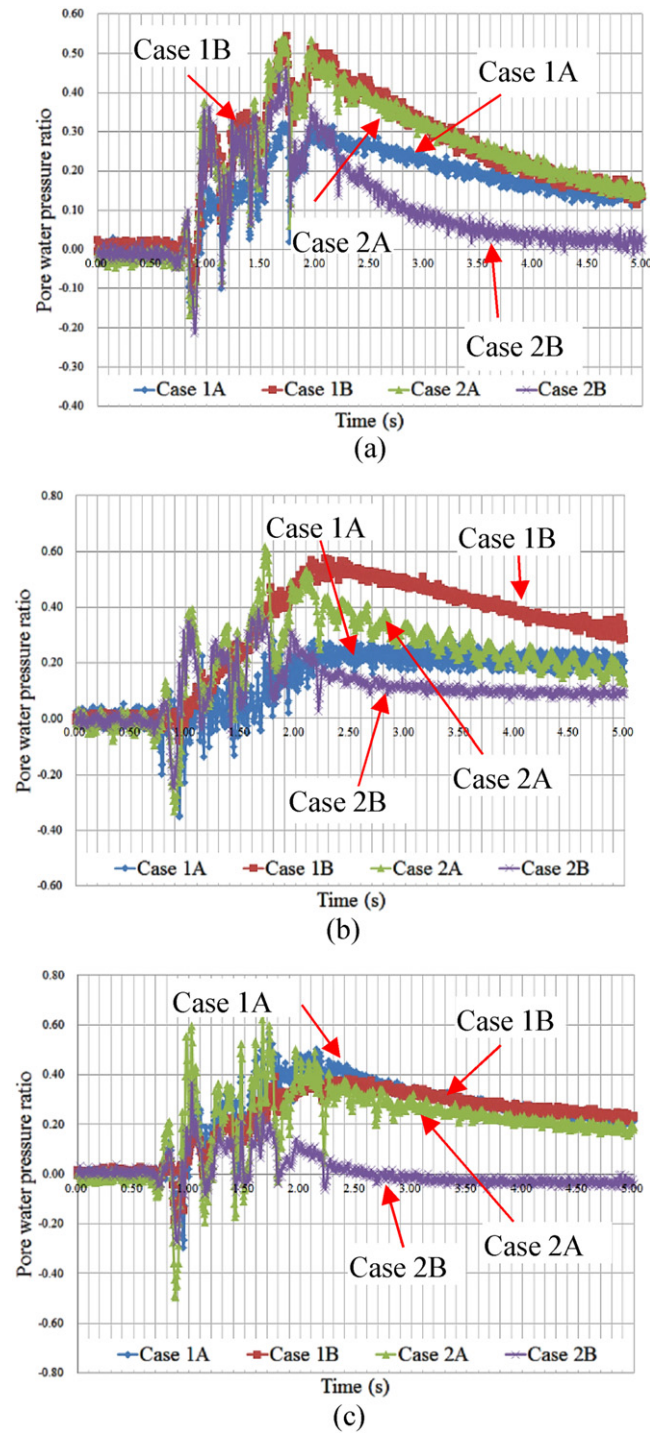


Fig. 7 State of the pore pressure dissipation with time in the four cases (a) W13 (Backfill bottom) (b) W14 (Mid-height of the backfill) (c) W15 (Top of the backfill).

Comparisons were also made for the magnitude of impact force for different filling conditions of tires, as indicated in Fig. 12. This figure shows the variation of impact loads due to Case 5 (three layered slope arrangement) for the different filling conditions. It can be observed that, the impact force is reduced when the model tires are introduced behind the seawall in all the filling conditions of tires. This figure indicates that the impact force is reduced to some extent when hollow tires (without any filling materials) are placed behind the seawall. The impact force is further reduced when the tire chips-filled or the soil-filled model tires are used. In addition, the reduction is faster (time taken to reach the steady state is smaller) in these two cases (filled tires). The

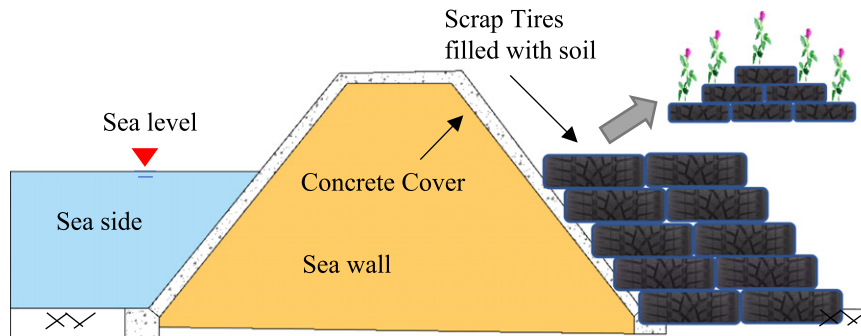


Fig. 8 Protection of sea wall by using whole tires. Modified from Hazarika, H., Fukumoto, Y., 2016. Sustainable solution for seawall protection against tsunami-induced damage. *International Journal of Geomechanics* 16, C4016005.

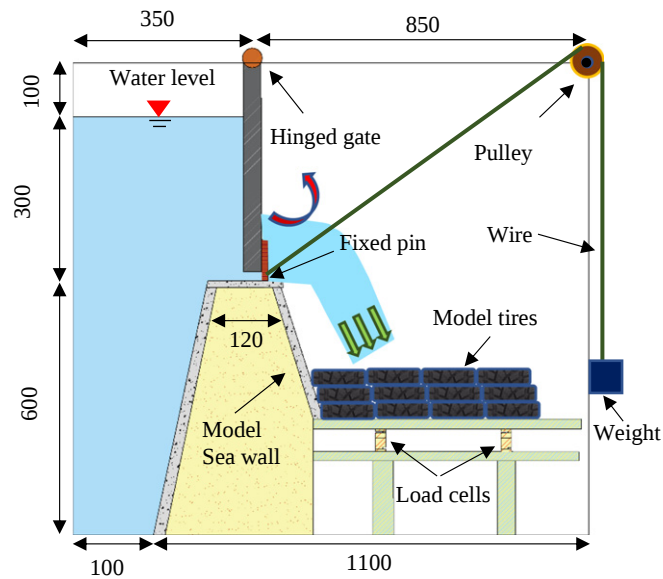


Fig. 9 Tsunami overflow testing (TOT) apparatus. Modified from Hazarika, H., Fukumoto, Y., 2016. Sustainable solution for seawall protection against tsunami-induced damage. *International Journal of Geomechanics* 16, C4016005.

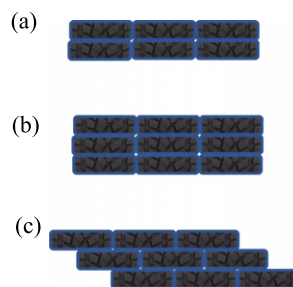


Fig. 10 Test Cases (a) Case 2 (Vertically placed two layers) (b) Case 3 (Vertically placed three layers) (c) Case 5 (Slopped three layers).

reduction percentage is found to be different depending on the filling materials of the tires. Tires filled with soils lead to the significant decrease of the impact load as compared to tires filled with pure tire chips. Therefore, it can be said that, instead of using pure tire chips, mixing tire chips with soils can be a viable alternative when applying the technique in actual field conditions.

From esthetic point of view, filled tires on the back of a seawall is not appealing. Therefore, cultivation of suitable plants inside actual tires (used passenger car tire) was done in field using a yard inside the Ito campus of Kyushu University. Field test shows that the greening effect could be maintained in all the seasons in a year by appropriate selection and plantation inside the tires. The details of those field tests can be found in [Hazarika et al. \(2016\)](#).

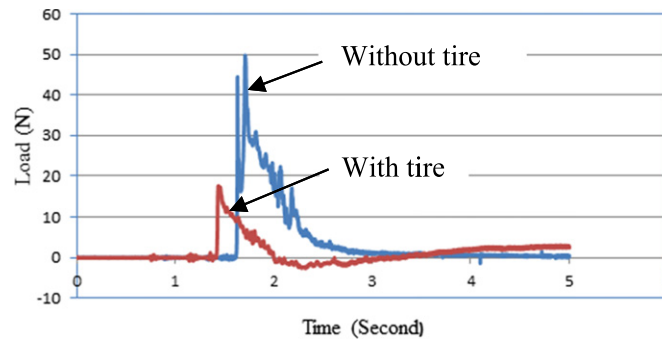


Fig. 11 Comparison of impact force of Tsunami with and without tires.

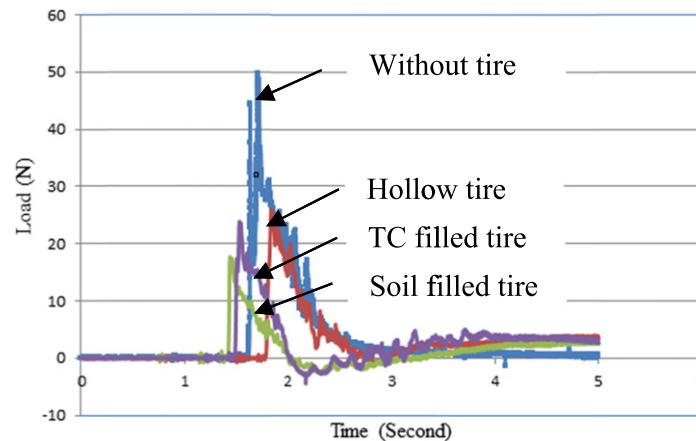


Fig. 12 Comparison of impact force of Tsunami for different filling conditions of tires.

Protection of Residential Building During Earthquake Using Horizontal Inclusion

According to the Ministry of Land, Infrastructure, Transport and Tourism, Japan (MILT, 2015), nearly 27,000 houses were damaged owing to liquefaction due the 2011 Off the Pacific Coast of Tohoku earthquake, about half of which were located in the Tokyo Bay area. Liquefaction occurred widely along the Tokyo Bay area, owing to high underground water levels and reclaimed land filled with loose sandy soils (Yasuda *et al.*, 2012). Similarly, a large number of residential buildings in Kumamoto prefecture suffered from liquefaction induced damage by the 2016 Kumamoto earthquake (Hazarika *et al.*, 2017). Severe damage to buildings resulting from liquefaction due to past earthquakes has demonstrated the importance of prevention measures to protect buildings and infrastructure by minimizing ground settlement and lateral spreading.

Description of the technique

To prevent vibration-induced as well as liquefaction-induced damage of residential buildings during earthquakes, it is important to adopt low cost ground improvement technique, since house owners cannot afford to go for the expensive ground improvement techniques applied in conventional infrastructural projects (Hazarika and Nakazawa, 2018). One such low cost technique was developed by Hazarika *et al.* (2009), and later modified as shown in Fig. 13. The modified technique utilizes tire chips mixed gravel under the foundation of residential housing.

Horizontal inclusion, thus, refers to a layer made of tire chips and gravel which are placed horizontally as shown. Mixture of gravel and tire chips layers along with geogrid reinforcement (if necessary) provide sufficient bearing capacity to the foundation that otherwise has to rest on highly compressible tire chips layer.

1 g shaking table test

A series of 1 g model shaking table tests were performed, using the shaking table assembly of Kyushu University, to evaluate the technique described in Fig. 13. The test model (prototype to model ratio of 20) is shown in Fig. 14. Model test box was 600 mm in length, 300 mm in width and 500 mm in height. Toyoura sand was used as foundation soils of a model house. Pure tire chips (2 mm in size) or tire chips mixed gravel (grain size identical to tire chips) were used as the horizontal inclusion. Adjusting the height of the ground in the soil box up to 300 mm, the relative density of base layer and the layer containing horizontal inclusion

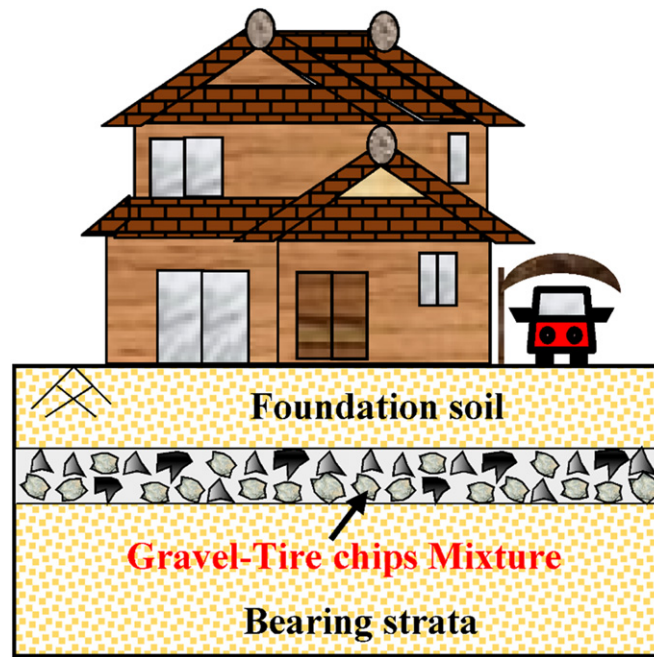


Fig. 13 Protection of residential building using horizontal inclusion.

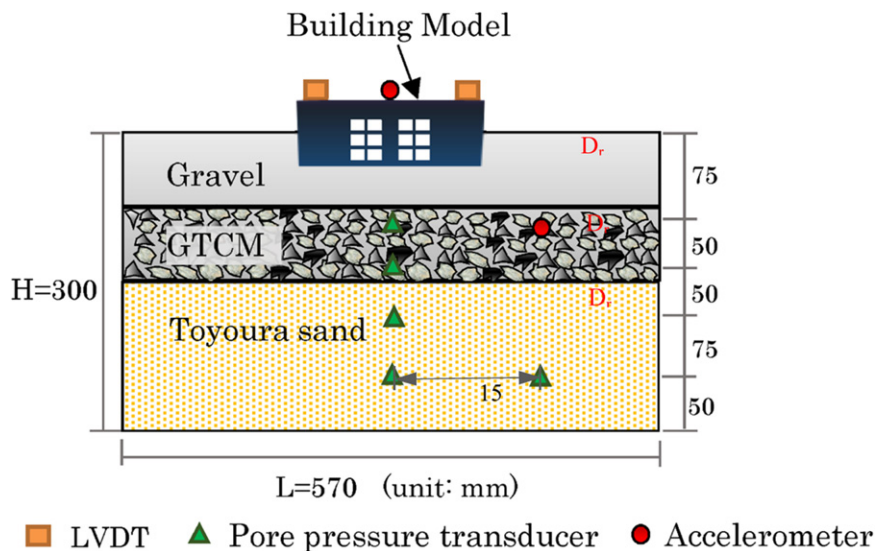


Fig. 14 Model for 1 g shaking table test.

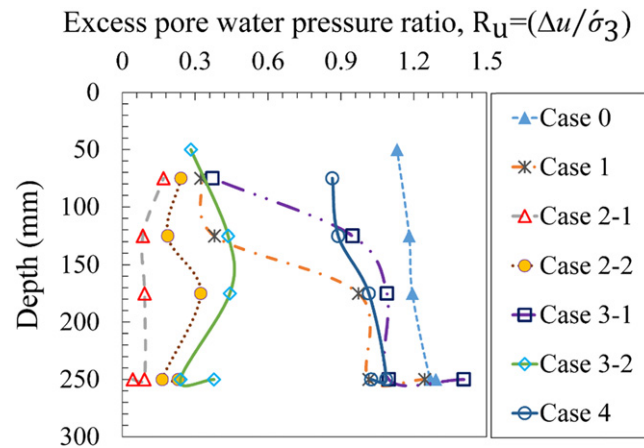
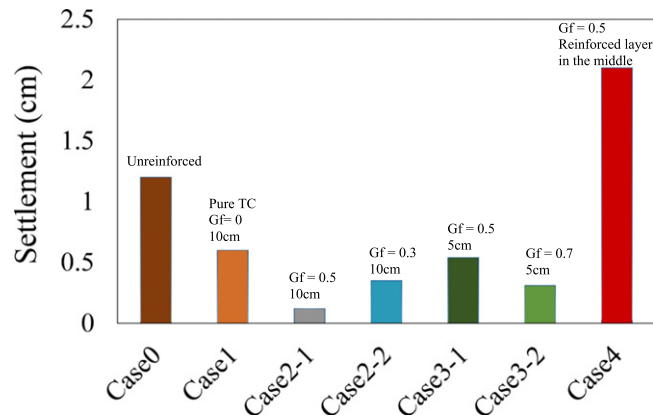
was adjusted to be around 50%. The layer immediately below the foundation was made of gravel, which represents the top layer of foundation with some sort of soil improvement.

A total of 7 test cases were examined under three different conditions of the horizontal inclusion, which are shown in [Table 1](#). In the Table, Case 0 represents the conventional foundation soil. Case 1, Case 2-1 and Case 2-2 represent the cases in which the thickness of horizontal inclusion was 10 cm. Case 3-1 and Case 3-2 represent the conditions in which the thickness of horizontal inclusion was reduced to 5 cm. Finally, in Case 4, the reinforced layer was located between the upper and lower sand layers. In the table TC refers to tire chips and gf (gravel fraction) refers to the percentage of gravel in the mixture by volume. 30%, 50% and 70% gravel fractions (gf) were used in the tests.

A sinusoidal acceleration of 300 Gal with 3 Hz frequency was imparted into the model for 45 s, and the responses were measured using the LVDT, accelerometers and pore water transducers, which were installed at various locations within the foundation soils shown in [Fig. 14](#).

Table 1 Different configurations of the model test

Depth (mm)	Case 0	Case 1	Case 2-1	Case 2-2	Case 3-1	Case 3-2	Case 4
50	Gravel	Gravel	Gravel	Gravel	Gravel	Gravel	Gravel
100	Sand	Pure TC	TC + gravel (Gf = 50%)	TC + gravel (Gf = 30%)	TC + gravel (Gf = 50%)	TC + gravel (Gf = 70%)	Pure sand
150							
200		Sand	Sand	Sand	Sand	Sand	TC + gravel
250							Sand
300							

**Fig. 15** Liquefaction potentials of the foundation in each case.**Fig. 16** Comparisons of the settlement of model house in each case.

Test results

The maximum of excess pore water pressure ratios at various depths within the foundation soils are shown in Fig. 15. In the unreinforced foundation (Case 0) the excess pore water pressure exceeds 1.0 at all the depths indicating liquefaction in the foundation soils. Except for Case 4, in all the other cases the liquefaction was restrained in the reinforced layer. While Case 2-1 is the most effective in restraining liquefaction, Case 2-2 and Case 3-2 also display no liquefaction in all throughout the depth. These results imply that when the thickness of reinforced layer is 10 cm, liquefaction can be prevented using the proposed horizontal inclusion technique. However, when the layer thickness is reduced to 5 cm, the gravel fraction has to be over 70% to ensure its function. This may be attributed to the light weight nature of tire chips, which may not be able to exert sufficient overburden pressure on the layers underneath.

The average final settlements of the model house due to the cyclic loading for each case are shown in Fig. 16. From this figure it is clear that the settlement of the house reinforced by pure tire chips (10 cm thick inclusion) can be reduced to half that of the

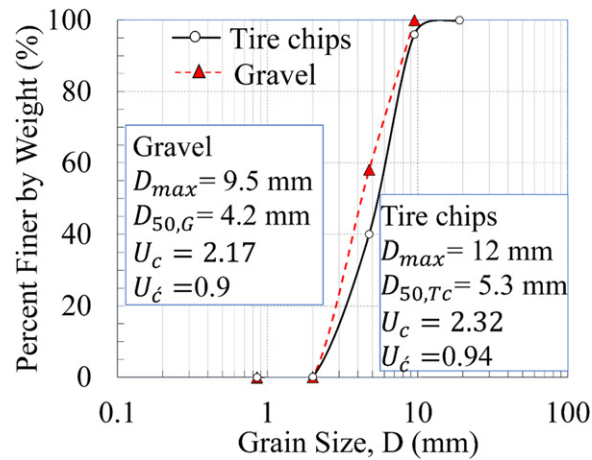


Fig. 17 Grain size distribution of gravel and tire chips.

non-reinforced foundation. However, when comparing with the gravel mixed tire chips reinforced foundation (10 cm thick inclusion), it can be observed that the settlement of the house was reduced further to half as compared to the foundation reinforced with pure tire chips. This implies that mixing gravel to tire chips can decrease the differential settlement due to enhanced bearing capacity.

In addition, the settlement decreases with the increase in the thickness of reinforced layer and the amount of gravel fraction. Furthermore, Case 2-1, in which the reinforced layer thickness was 10 cm and gravel fraction was 50%, the settlement is significantly less. In Case 4, the settlement was found to be even larger than the unreinforced foundation. This implies that this particular pattern of reinforcement is not appropriate for the model considered in this study. In other words, the location and thickness of the horizontal inclusion are also important design consideration in this technique.

Dynamic Properties of Gravel and Tire Chips Mixtures

Evaluation of dynamic behavior of gravel-tire chips mixture (GTCM) is necessary to firmly establish the techniques described above. Therefore, to investigate the influence of gravel fraction on dynamic properties as well as liquefaction resistance of GTCM, a series of stress controlled consolidated undrained cyclic triaxial tests were conducted on GTCM with different gravel fractions.

Test Materials and Procedures

Fig. 17 demonstrates the particle size distribution of gravel and tire chips (TC) used in this study. Other physical characteristics of materials such as maximum diameter of gravel and tire chips particles (D_{max}), coefficient of curvature (U_c), coefficient of uniformity ($U_{\dot{c}}$) are also displayed in **Fig. 17**. The maximum grains size of TC and gravel were limited to less than 1/6 of specimen diameter to avoid the effect of sample size on the results of experiments. According to the Japanese Geotechnical Society Standard (JGS 0131), this type of gravel is classified as poorly graded (SP). The specific gravities (G_s) of gravel and TC were determined as per the Japanese Geotechnical Society (JGS 0111) recommendations, and they were found to be 2.81 and 1.17 for gravel and TC respectively.

In order to have homogenous samples, the under-compaction method was used for the preparation of specimens (Ladd, 1978; Pasha *et al.*, 2019). Mixtures of desired relative densities were obtained by mixing manually and carefully, placed into the mold and compacted in 10 layers. Samples were saturated by allowing de-aired water to flow through from bottom of the sample. The back-pressure technique was adopted to enhance the degree of saturation of samples. Full saturation was assumed to be achieved when Skempton's B parameter ($\Delta u / \Delta \sigma_3$) was greater than 0.95. An isotropic consolidation pressure was applied to samples, while maintaining constant initial backpressure (200 kN/m²). Samples were consolidated to the effective confining pressure of 50 kN/m² and 100 kN/m². Stress-controlled undrained cyclic triaxial tests were conducted at a constant frequency of 0.1 Hz, relative density of 50% and different cyclic stress ratios ($\sigma_d / 2\dot{\sigma}_{3c}$).

Test Results

Typical results (stress paths) on cyclic behavior of GTCM at stress ratio ($\sigma_d / 2\dot{\sigma}_{3c}$) of 0.3 with different gravel fractions for relative density of $Dr = 50\%$ and confining pressure of $\dot{\sigma}_{3c} = 100$ kPa are shown in **Fig. 18**. As is evident, the effective mean stress ($\dot{p}$) decreases with cyclic deviator stress (q), however, none of the GTCM samples did reach the state of zero mean effective stress at the conclusion of cyclic loading. The decrease in the effective mean stress ($\dot{p}$) occurs due to the rapid generation of excess pore water pressure during cyclic loading. Furthermore, mechanism of the failure for GTCM with $Gf = 100\%$ and $Gf = 87\%$ is similar to that

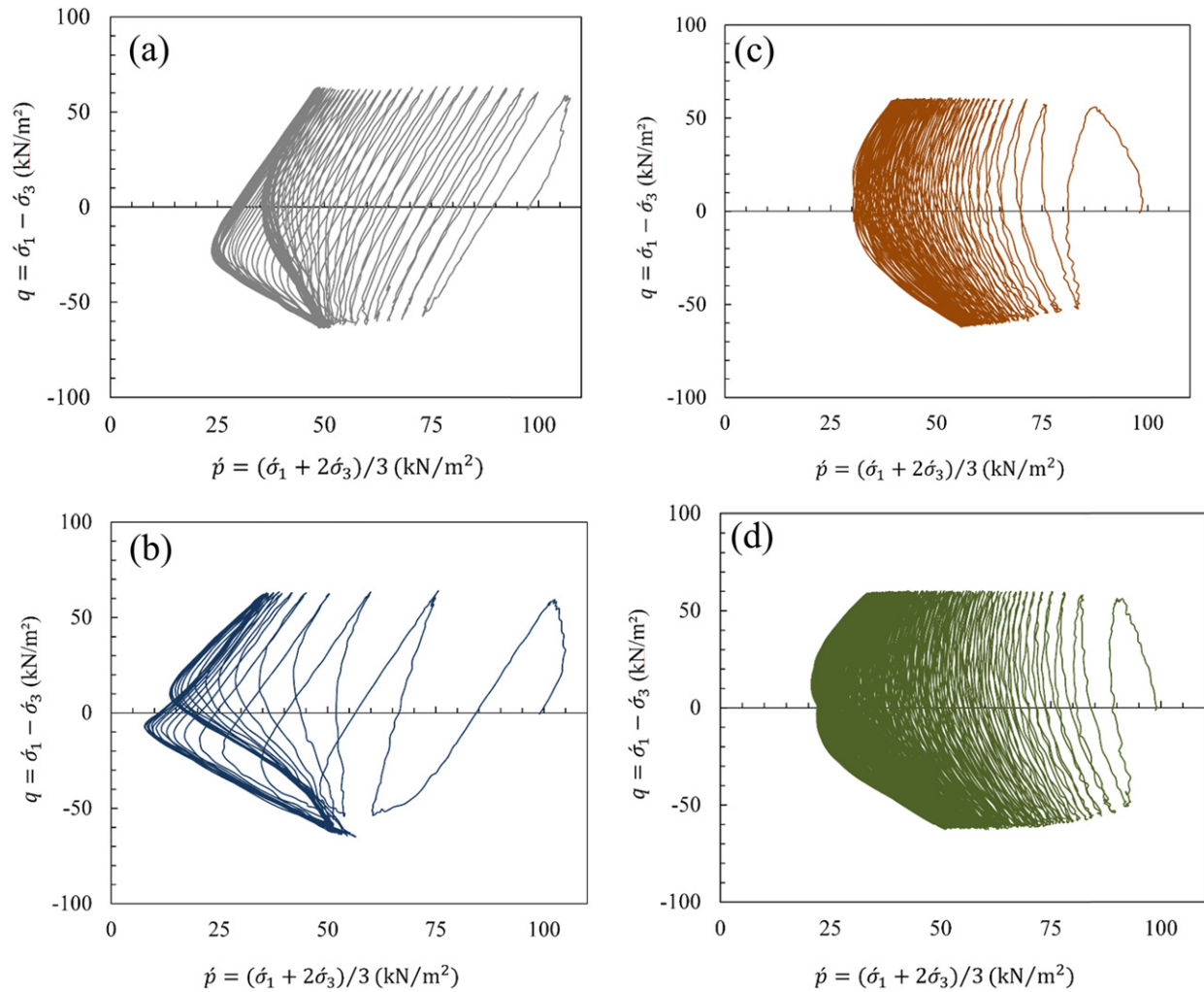


Fig. 18 Cyclic effective stress paths of GTCM at $\sigma_d/2\sigma_{3c} = 0.3$, $D_r = 50\%$ and $\sigma_{3c} = 100$ kN/m²: (a) $G_f = 100\%$; (b) $G_f = 87\%$; (c) $G_f = 44\%$; (d) $G_f = 30\%$.

of flow type failure in which the samples exhibit combination of contractive and dilative behavior. The samples underwent excessive deformation leading to complete loss of shear strength due to the rapid building up of excessive pore water pressure during the cyclic loadings. For the GTCM samples with $G_f = 44\%$ and $G_f = 30\%$ similar mechanism to that of cyclic mobility type of failure is observed.

The effect of confining pressure on the pore water generation of GTCM with $G_f = 30\%$ and $D_r = 50\%$ at $(\sigma_d/2\sigma_{3c})$ of 0.35 is shown [Fig. 19](#). The GTCM samples exhibit higher liquefaction resistance even at low confining pressure. This behavior is similar to that of denser sand samples at higher confining pressure. The reduction in effective confining pressure remarkably enhances liquefaction resistance of representative GTCM samples with $G_f = 30\%$. This might be caused due to the reduction in the hydraulic conductivity of mixture with the effective confining pressure ([Edil and Bosscher, 1994](#)).

In [Fig. 20](#), for a given number of cycles ($N_l = 20$), the maximum of excess pore water ratio ($R_u = u/\sigma_{3c}$) of GTCM samples with relative density of $D_r = 50\%$ is plotted at stress ratio $(\sigma_d/2\sigma_{3c}) = 0.3$ and confining pressure of $\sigma_{3c} = 100$ kN/m² for different G_f . It can be seen that liquefaction resistance decreases with decreasing gravel fraction from 100% to 87% and then increases with further decrease in gravel fraction. Possibly, in GTCM with $G_f = 100\%$ (pure gravel) the soil sample is in medium dense state and exhibits relatively high dilative behavior resulting in high liquefaction resistance. When small amount of tire chips is added to the mixture, GTCM matrix is still formed by gravel particles. However, some of the solid gravel particles are replaced by soft tire chips particles with relatively low stiffness. Presence of those soft tire chips inclusions in the voids of the mixture, GTCM sample with $G_f = 87\%$ shows gravel like behavior in relatively loose state, which results in relatively low liquefaction resistance in comparison to that of $G_f = 100\%$. Optimum value of gravel fraction in which GTCM sample shows remarkable improvement in liquefaction resistance of mixture was around 50%.

The shear modulus variations of GTCM samples with different $G_f(\%)$ are shown in [Fig. 21](#). For the GTCM specimens with $G_f = 100\%$ and $G_f = 87\%$ shear modulus decreased drastically with the shear strain within the few cycles of loading. This

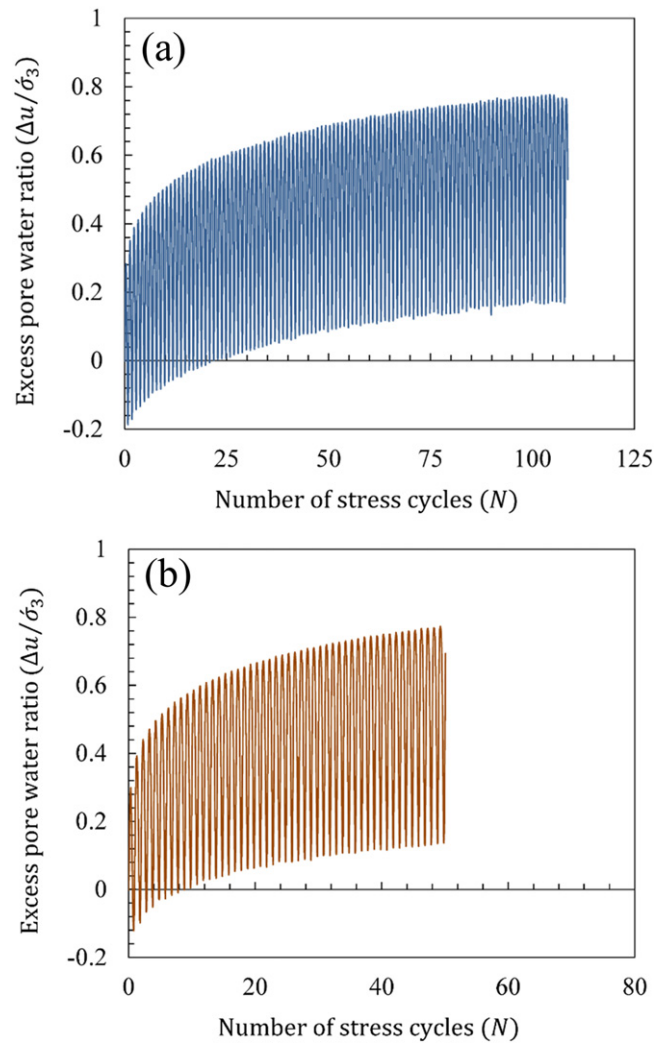


Fig. 19 The effect of effective confining pressure on the evolution of excess pore water ratio of GTCM against number of stress cycles (N) at $G_f = 30\%$ and $\sigma_d / 2\dot{\sigma}_{3c} = 0.35$ (a) $\dot{\sigma}_{3c} = 50 \text{ kN/m}^2$ $\dot{\sigma}_3 = 100 \text{ kN/m}^2$; (b) $\dot{\sigma}_{3c} = 100 \text{ kN/m}^2$.

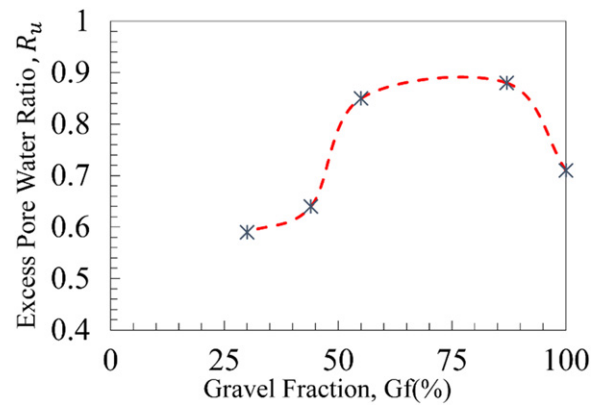


Fig. 20 Maximum excess pore water ratio of GTCM with different $G_f(\%)$ at Cyclic Stress ratio $\sigma_d / 2\dot{\sigma}_{3c} = 0.3$, $\dot{\sigma}_{3c} = 100 \text{ kN/m}^2$ and number of cycles ($N = 20$).

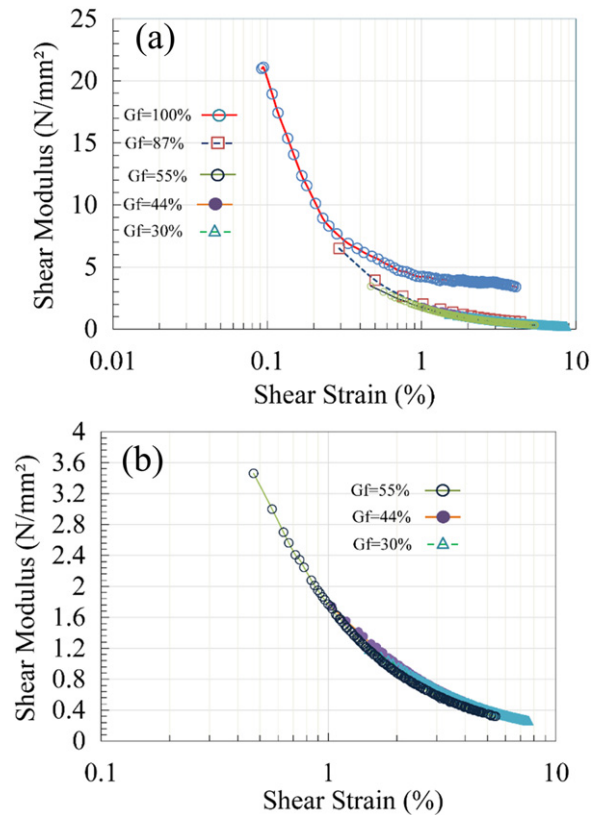


Fig. 21 Effect of gravel fraction on shear modulus of GTCM: (a) $30\% \leq G_f \leq 100\%$ (b) $30\% \leq G_f \leq 55\%$.

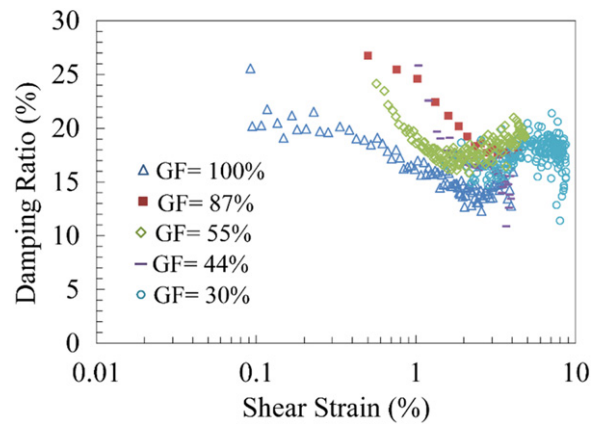


Fig. 22 Evolution of damping ratio with shear strain for GTCM specimens.

reduction in shear modulus with an increase in shear strain can be attributed to the decrease in the gravel inter-particle contact after rapid development of pore water pressure during the cyclic loading. Tire chips content did not significantly affect the shear modulus of specimen for $G_f = 55\%$, 44% and 30% and shear modulus of specimens at higher shear strains are almost identical. This is probably because gravel inter-particle contacts are minimal (especially at very high shear strains $> 1\%$) where GTCM matrix is mainly formed by tire chips particle with relatively low stiffness in comparison to that of gravel particles.

Evolution of damping ratio of GTCM mixtures with shear strain is shown in Fig. 22. Damping ratio slightly increases with decreasing gravel fraction in mixture. The reduction in damping ratio value with shear strain may occur due to the rapid development of pore water pressure during cyclic loadings. Inter-particle contacts significantly decrease with pore water pressure, which results in a reduction of frictional energy loss in soil skeleton with the number of cycles.

Conclusions

The following are the some of the main conclusions of this research.

- (1) The use of pure tire chips or in combination with gravel as part of the backfill of retaining structure improves the performance of the structure during an earthquake.
- (2) Significant lowering of the pore water pressure build up within the backfill could be achieved in the case of backfill improved by vertical inclusion technique.
- (3) The tsunami impact force behind sea walls can be reduced considerably by placing filled whole tires (with a suitable filling material) to protect the damage of such structures from impact force and resulting scouring and erosion.
- (4) Tires must be filled with soils (or with other materials) to provide certain stiffness, so that they should be able to absorb the impact force of tsunami.
- (5) In the case of horizontal inclusion technique, tire chips was found to be an excellent liquefaction mitigating material, However, due to its' light weight nature, it may also cause unexpected settlement of the structure. When the reinforced layer is mixed with gravel, the shear stiffness in reinforced layer will be increased, and thus the settlement will be reduced.
- (6) When the thickness of reinforced layer is 10 cm (2 m in prototype) and gravel fraction is 50%, the technique yields the best performance, as the rise of excess pore water pressure could be significantly restrained. This ultimately leads to the reduction of earthquake induced settlement of the structure.
- (7) When the thickness of horizontal inclusion is 10 cm (2 m in prototype) and gravel fraction is 50%, the liquefaction mitigation technique yields the best performance, as the rise of excess pore water pressure could be significantly restrained. This ultimately leads to the reduction of earthquake induced settlement of the structure.
- (8) Two behavioral zone (gravel like and gravel-tire chips like behavior) of GTCM can be used to explain the liquefaction potential as well as dynamic behavior of GTCM specimens.
- (9) Liquefaction resistance of GTCM specimens are remarkably influenced by gravel fraction in mixture. For the higher gravel fractions ($G_f > 87\%$), soil matrix are mainly formed by gravel, and thus, adding small amount of tire chips decreases the liquefaction resistance due to reduction in gravel inter-particle contacts during loading. However, for $G_f < 87\%$, liquefaction resistance increases with a decrease of gravel fraction in the mixture. This is because the mixture tends to exhibits gravel-tire chips like behavior or tire chips like behavior (non-liquefiable materials).
- (10) Gravel fraction plays an important role in the dynamic behavior and liquefaction resistance of the GTCM. 50%–60% is the best mixing percentage, in which the rise of excess pore water pressure could be significantly restrained without compromising the stiffness of the reinforcing inclusion.

Application of the geo-disaster mitigation techniques discussed here, is expected to contribute towards reducing the global warming by cutting down the release of greenhouse gas through recycling of waste tires, and thus, could be an effective adaptation measure against climate change. The techniques also possess tremendous potentials for adopting in developing and emerging economies, where alarming rate of car usage as the mode of commuting are already creating problems of stockpiling and illegal dumping, which in turn are placing a huge burden on our environment. Through a judicious decision during design process, if the cost reduction can be additionally achieved through use of such materials in geotechnical constructions, establishment of groundbreaking adaptive technology will not be a distant dream.

To implement the technique, prototype testing using centrifuge model test, and numerical simulation using the material behavior described in this paper will be essential. Mapping of constitutive relationship of the material using Artificial Intelligence (Pasha *et al.*, 2018) could be a useful tool in that direction.

Acknowledgment

The authors gratefully acknowledge the financial support provided by Kyushu University under the research grant of Progress 100 (2018–2020).

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Synthesis of Multiwalled Carbon Nanotubes (MWCNTs) From Waste Cooking Oil Catalyzed by Mill-Scale Waste for Development of Microstrip Patch Antenna (MPA)

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Introduction

Carbon nanotubes (CNTs) are made of hexagonal carbon rings in the form of cylindrical carbon molecules with nanometer-sized diameter and micrometer-sized length (where the length to diameter ratio exceeds 1000). The structure is made of enrolled cylindrical graphitic sheet (called graphene) rolled up into a seamless cylinder with diameter of the order of a nanometer. This one-dimensional material having different chirality is dependent on the position of the carbon atoms. There are two types of CNTs: Single wall carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs).

Currently, many studies have used waste materials for various potential applications. As for MWCNTs, there is a number of carbon sources from waste materials such as waste vegetable/animal oil, industrial waste, and waste plastics (Deng *et al.*, 2016). Cooking palm oil, which belongs to the vegetable waste group, is widely used in the consumer food chain and has escalated due to small to medium enterprise ventures in the food and beverages manufacturing industry recently. The dumping of cooking palm oil waste has triggered a major concern over its effect on the environment in terms of the stability of ecosystem, biodiversity, and pollution of Earth. In this article, we look at the beneficial use of waste cooking oil as the starting material for the synthesis of CNTs. It will be synthesized via modified chemical vapor deposition (CVD) method by using the injection of waste cooking oil as the carbon source and mill-scale waste (Fe_3O_4) as the catalyst. This interesting method is even more convenient compared with other previous CVD method as reported in MWCNTs synthesis studies (Ahmad *et al.*, 2013; Baddour *et al.*, 2008; Bhatia and Prasad, 2010; Kumar and Ando, 2010; Tripathi *et al.*, 2017). CNTs exhibit a great range of remarkable properties, including unique mechanical and electrical characteristics. These remarkable properties have led to the use of CNTs as microstrip patch antenna (MPA) in the past few years.

Recycling of Waste Materials Into Carbon Nanostructures

A key part in the production of CNTs is the carbon source and catalyst. The types of carbon source would greatly influence the morphological structure of the end product due to not only providing the carbon atoms, but also affecting the growth of the CNTs. Meanwhile the catalyst also plays the role of affecting the morphological structure and yield of CNTs synthesized. Conventional carbon sources such as ethylene, benzene, acetylene, and methane are widely used. These carbon sources however are also required by many other industries for other applications. It is of great importance to develop new abundant cost-saving carbon sources for the synthesis of CNTs. Other carbon sources from waste materials are tabulated in Table 1.

Many types of catalyst were used in the synthesis process of CNTs (Table 1), however recycling of waste materials as catalyst is not widely reported. This article describes a method on using mill-scale waste as a catalyst for synthesis of CNTs via CVD method. Mill-scale waste is a porous, hard, and brittle coating of several distinct layers of iron oxides (predominantly Fe_3O_4) formed during the fabrication of steel structures from steel mills. It is magnetic in nature with iron content up to as high as 93%. Most of the steel mill-scale waste (almost 80%) end ups in a landfill; a small fraction of it is also used to make reinforced concrete.

Application of Carbon Nanotube in Microstrip Patch Antenna

MPA consists of a thin metallic patch kept on dielectric substrate, and below the dielectric substrate there is a conducting ground plane as shown in Fig. 1. Previous studies have embarked on the usage of carbon fiber composites such as CNTs, which has caught the interest of many researchers in the attempt to replace metals in antenna. This article intends to present the application of CNTs made of waste cooking oil as a patch antenna and discuss the design and fabrication of these structures and the properties of the acquired antenna.

The theory of fundamental transmitting properties of SWCNTs as dipole antennas has been explored by Hanson (2005), with a 10- μm -long CNT serving as a dipole antenna. However, it is still considered a short dipole antenna compared with free-space wavelength, and in reality it is still very difficult to obtain a few centimeter lengths of CNTs. Therefore, recently the focus has been switched to producing CNT-based patch antenna, which can be fabricated using multiple methods, as well as possibility of utilizing the antenna in flexible environment. Keller and Zaghoul (2011) demonstrated a simulation of meshed CNT threads for patch antenna, of which conducting CNT threads and semiconducting CNT threads were interwoven to serve both as conductive

Table 1 Hydrocarbon sources from waste materials for synthesis of CNT

Hydrocarbon source	Catalyst	Method	Synthesis temperature (°C)	Morphology of carbon nanostructures	Raman ID/IG ratio	Refs.
Tube plastic waste made of polypropylene	Stainless steel 316 (SS 316) metal tube (acted as both reactor vessel and catalyst)	Two-stage self-catalytic chemical vapor deposition (CVD) reactor	900	Multiwalled carbon nanotubes	0.48	(Tripathi <i>et al.</i> , 2017)
Waste polyethylene bags	Not mentioned	CVD technique	800	Carbon nano beads and a mix of carbon nanotubes and carbon nano beads	0.86	(Khan <i>et al.</i> , 2018)
Waste cooking oil	Ni ₃ La ₇ O _y /Al ₂ O ₃	Fixed bed reactor	500–800	Multiwalled carbon nanotubes	1.46	(Xue <i>et al.</i> , 2018)
Low density polyethylene	Fe(NO ₃) ₃ ·9H ₂ O and gamma Al ₂ O ₃	Two-stage pyrolysis reactor	700–900	Multiwalled carbon nanotubes	1.66–1.93	(Acomb <i>et al.</i> , 2015)
Waste plastic made of PP and PE	Ni/Al ₂ O ₃	Fluidized bed reaction system	700	Multiwalled carbon nanotubes	0.86	(Yang <i>et al.</i> , 2018)
Waste high density polyethylene plastics	Ni/AAO and Ni/Al ₂ O ₃ catalysts	Two-stage reactor	700	Multiwalled carbon nanotubes	–	(Liu <i>et al.</i> , 2017)
Waste engine oil	Ferrocene	CVD technique	750	Quasi-aligned single- and multiwalled CNTs	0.90	(Suriani <i>et al.</i> , 2015)
Waste cooking palm oil	Ferrocene	Thermal chemical vapor deposition	800	Multiwalled carbon nanotubes	0.47	(Suriani <i>et al.</i> , 2016)
Oil sludge and hydrophobic soot	Nickel	CVD technique	650–800	Multiwalled carbon nanotubes	1.03– 0.69	(Nazhipkyzy <i>et al.</i> , 2017)
Waste chicken fat	Ferrocene	Thermal chemical vapor deposition furnace	750	Vertically aligned carbon nanotubes	0.63	(Suriani <i>et al.</i> , 2013)

Abbreviation: CNTs, carbon nanotubes.

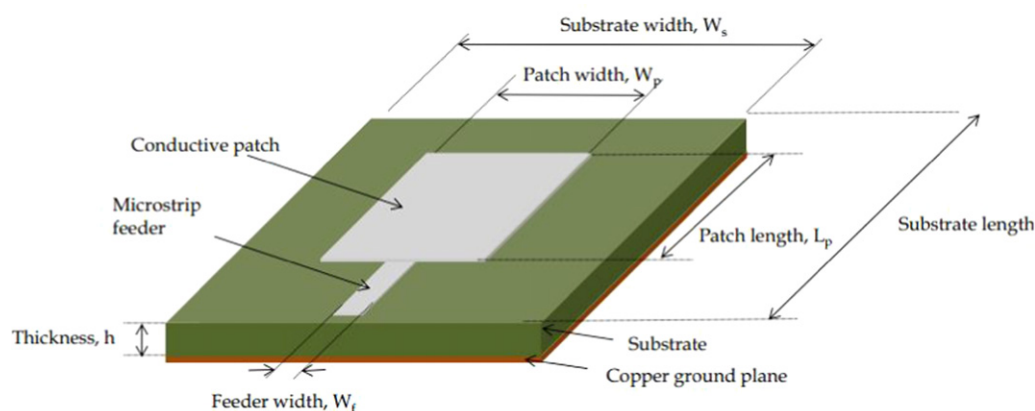


Fig. 1 Microstrip patch antenna.

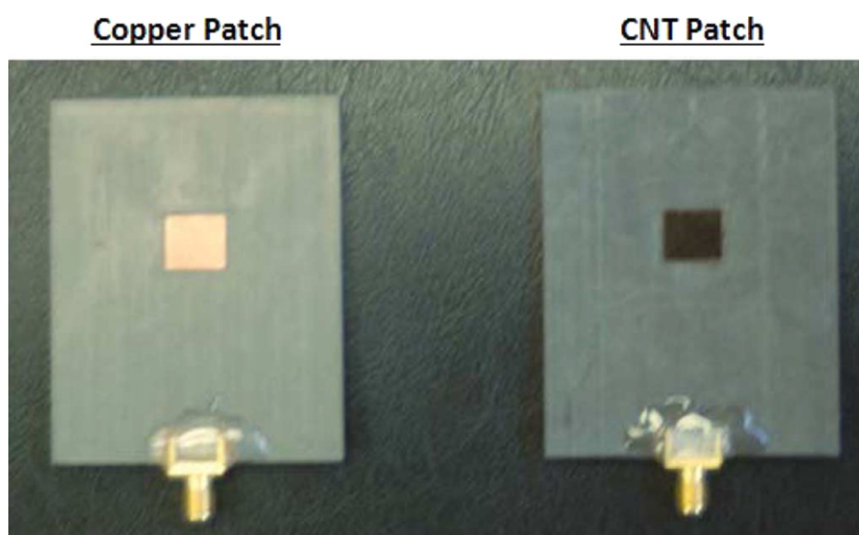


Fig. 2 Copper- and carbon nanotube (CNT)-sheet-based microstrip patch antenna. Reproduced from Keller, S.D., Zaghloul, A.I., Shanov, V., *et al.*, 2014. Radiation performance of polarization selective carbon nanotube sheet patch antennas. *IEEE Transactions on Antennas and Propagation* 62 (1), 48–55.

patch for antenna, and also as the dielectric resonator for gas sensing. Later, Keller *et al.* (2014) successfully fabricated a CNT sheet antenna with different sheet thickness giving impact to the radiation performance of the MPA itself (Fig. 2). The CNT sheet was sandwiched between Kapton tape, which served as adhesive tape on one side and protection film on the other side. CNT sheet with higher thickness value exhibited better reflection coefficient and gain as compared with lower ones, however the thickness is still below the skin depth of the material as compared with the copper patch, which is around 17 μm , which leads to performance reduction overall.

Meanwhile, Elwi *et al.* (2010) demonstrated a MWCNT-based patch antenna using inkjet printing method, of which the CNTs were added to a sodium cholate solution to produce a MWCNT ink with concentration of 5 mg/l and then was filled into inkjet cartridge for printing purpose (Fig. 3). The results exhibited improved bandwidth for MWCNT-based MPA as compared with MPA using copper patch; however the gain is lower than copper-based MPA due to low conductivity of the MWCNT ink. It is noted that the radiation patterns remained unchanged.

Another approach to incorporating CNTs to MPA structure (Fig. 4) is by mixing or doping CNTs with conductive polymer, such as polyaniline (PANI), as demonstrated by Hamouda *et al.* (2014). The PANI/CNT composite was fabricated onto Rogers RT/Duroid 5870 substrate, with the composite having three different thickness of 50, 70, and 110 μm to study the effect on the performance of MPA. The results showed improvements in terms of bandwidth, but reduction in the return loss. Further improvement can be realized in the conductivity of the PANI/CNT composite can be further increased.

In summary, the use of CNTs as conductive materials for fabrication of MPA has proven to give good results, although the conductivity of the composite can be further increased, hence can be compared with copper-based MPA. The method in CNT

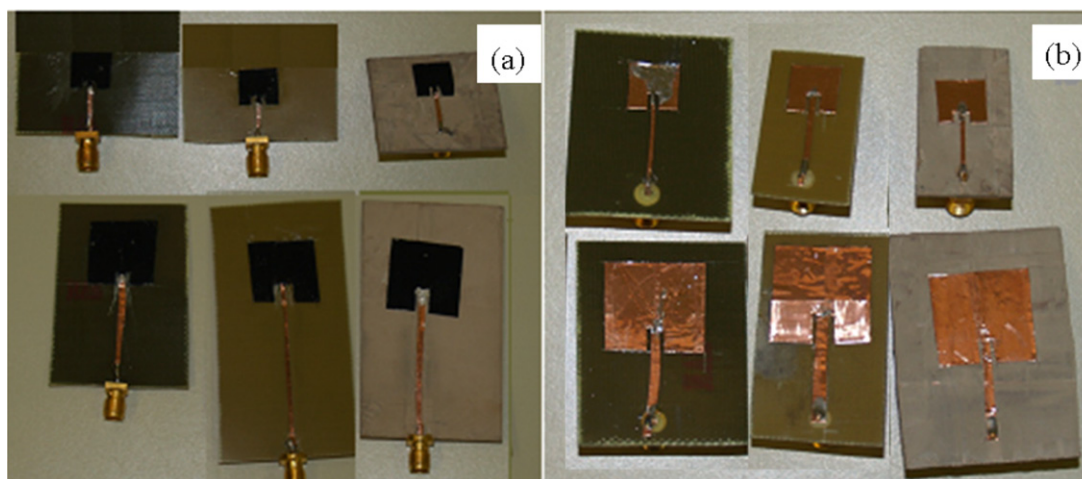


Fig. 3 Fabricated microstrip patch antennas on various substrates. (a) Carbon nanotube-based MPA, (b) copper-based MPA. Reproduced from Elwi, T.A., Al-Rizzo, H.M., Rucker, D.G., *et al.*, 2010. Multiwalled carbon nanotube-based RF antennas. *Nanotechnology* 21 (4), 045301.

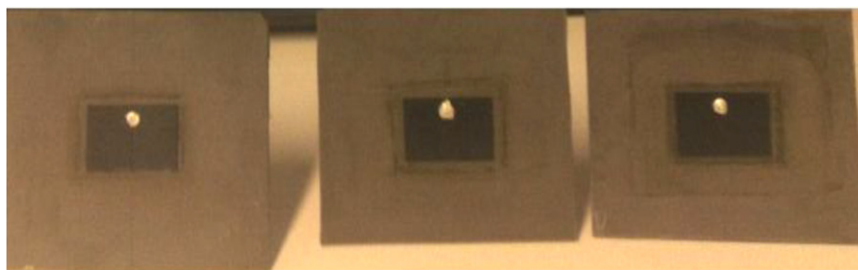


Fig. 4 Polyaniline/carbon nanotube composite as conductive patch of microstrip patch antenna. Reproduced from Hamouda, Z., Wojkiewicz, J., Pud, A.A., *et al.*, 2014. Polyaniline-carbon nanotubes composites-based patch antenna. In: *Proceedings of the 8th European Conference on Antennas and Propagation (EuCAP 2014)*, pp. 2635–2638.

patch antenna can also be studied, of which this work aims to study the method of producing CNT patch antenna using thick film technology that utilizes a screen printing process. The CNT paste can be mixed with an organic vehicle with suitable ratio, therefore the CNTs volume can be increased and subsequently increase the conductivity of the CNT patch when it is fabricated.

Experimental Synthesis of Carbon Nanotubes From Waste Cooking Oil for Microstrip Patch Antenna

The methodology of the research work is divided into three stages: (1) synthesis of MWCNTs, (2) CNT thick film paste preparation, and (3) MPA fabrication. Some results from the above research work are also discussed.

Synthesis of Multiwalled Carbon Nanotubes

The starting raw powder materials of millscale (Fe_3O_4) waste were milled using a Spex8000D milling machine with a ball to powder ratio of 10:1 for 6 h to obtain nanosized particles. The milled mill-scale powder or iron oxide nanoparticles were used and acted as a catalyst to synthesize MWCNTs via CVD method. An alumina boat containing approximately 0.5 g milled powder was placed at the center of the furnace and was flushed with argon at 100 sccm. Then, the furnace was heated at different synthesis temperature (ST) of 650°C, 750°C, and 850°C. Once the furnace reached the targeted ST, the filtered waste cooking oil was injected with constant flow of 10 ml/H with a syringe pump into the alumina ceramic tube containing the catalyst under an argon gas flow. The furnace was cooled down to room temperature before the sample was extracted for analysis. The setup of the CVD method is shown in Fig. 5. The extracted CNTs were then characterized by using field emission scanning electron microscope (FESEM) (FEI Nova NanoSEM 230), energy dispersive X-ray (EDX), high resolution transmission electron microscope (HRTEM), X-ray diffraction (XRD), thermal gravimetric analysis/differential thermal analysis (TGA/DTA) (Mettler Toledo TGA/DSC 1 HT) and Raman spectroscopy (Witec Alpha 300R).

Carbon Nanotube Thick Film Paste Preparation

An organic vehicle or binder was used in the paste preparation process. It was prepared by mixing 85 wt% linseed oil (CAS no. 67746-08-1, Daler Rowney) with 12.5 wt% m-xylene (CAS no. 108-38-3, Sigma-Aldrich USA, ReagentPlus grade, 99% assay) using magnetic stirrer at 250 rpm for 3 h, and later 2.5 wt% α -terpineol (CAS no. 10482-56-1, Sigma-Aldrich USA, natural, $\geq 96\%$ assay) was added to the mixture. Next, the mixture was continually stirred for another 2 h with temperature kept at 40°C (Abadi, 2010). Then, the prepared organic vehicle was added to CNTs with powder to organic vehicle weight ratios of (50:50), and mixed thoroughly using magnetic stirrer for 3 h to obtain a homogenous paste.

Microstrip Patch Antenna Fabrication

Fabrication of MPA was carried out by printing CNT paste onto kapton substrate via screen printing method. Next, the prepared samples were annealed at temperature of 300°C for 30 min in a box furnace. Then, a SubMiniature version A connector was attached by soldering it to the patch antenna. A copper tape was attached behind the patch of kapton substrate as a ground plane. Finally, after fabrication of antenna is completed, the return loss (S_{11}) and resonant frequency of all samples were measured using Vector Network Analyzer (Keysight, PNA 5227A) in the frequency range of 1–8 GHz.

Results and Discussion of Synthesis of Carbon Nanotubes From Waste Cooking Oil for Microstrip Patch Antenna

Fig. 6 shows the micrograph of powder sample milled for 6 h, which has been carried out using scanning electron microscopy. The particle size was found to have an average around ~ 140 nm as can be seen in the particle size distribution (Fig. 7). The agglomerations of the particles, as can be observed, occurred due to magnetic forces of nanoparticles. The particle size distribution

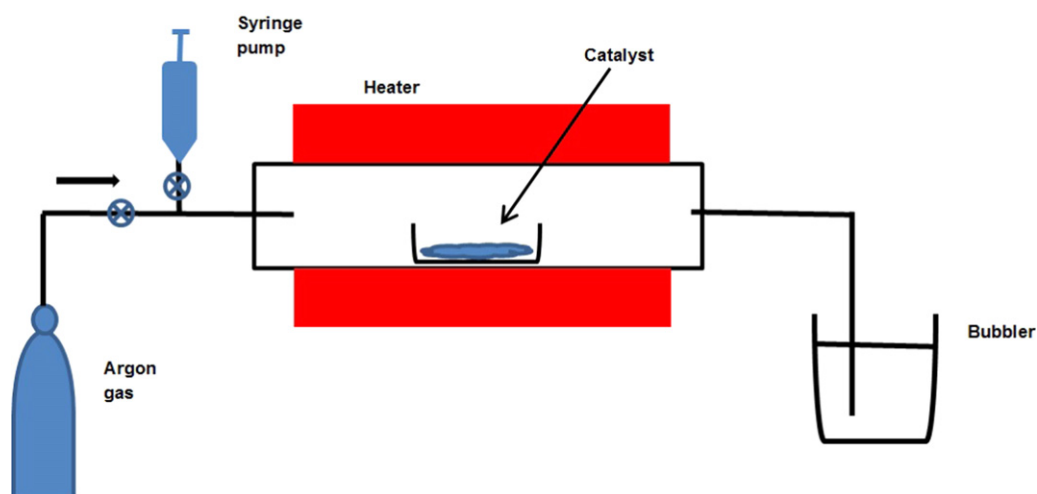


Fig. 5 Experimental setup of chemical vapor deposition method for carbon nanotubes synthesis using mill-scale waste as catalyst.

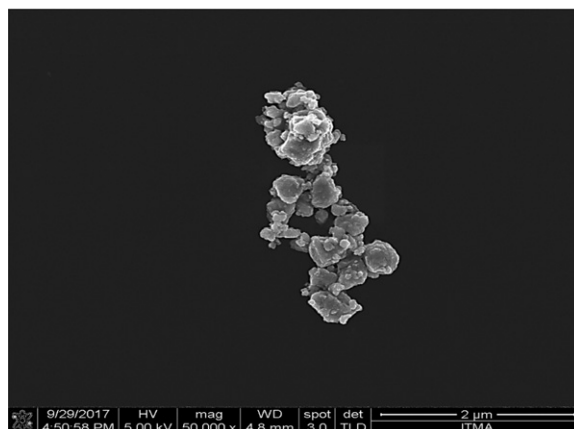


Fig. 6 Scanning electron microscopy micrograph of resulting particles after 6 h of milling time.

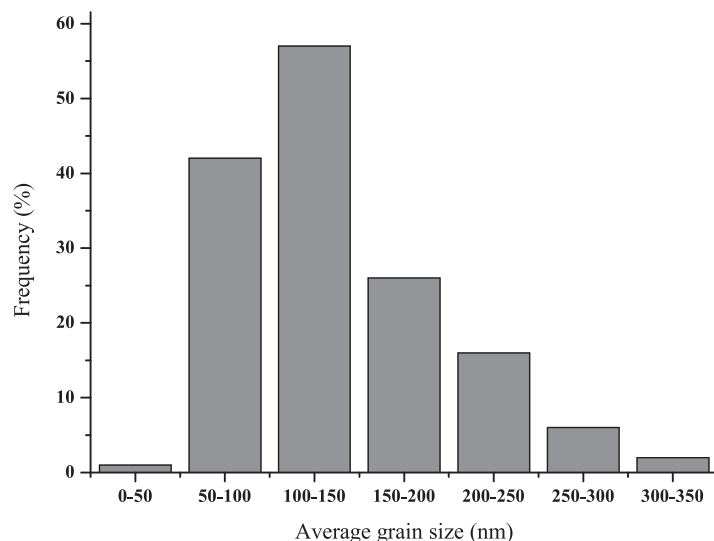


Fig. 7 Particle size distribution of milled mill-scale powders.

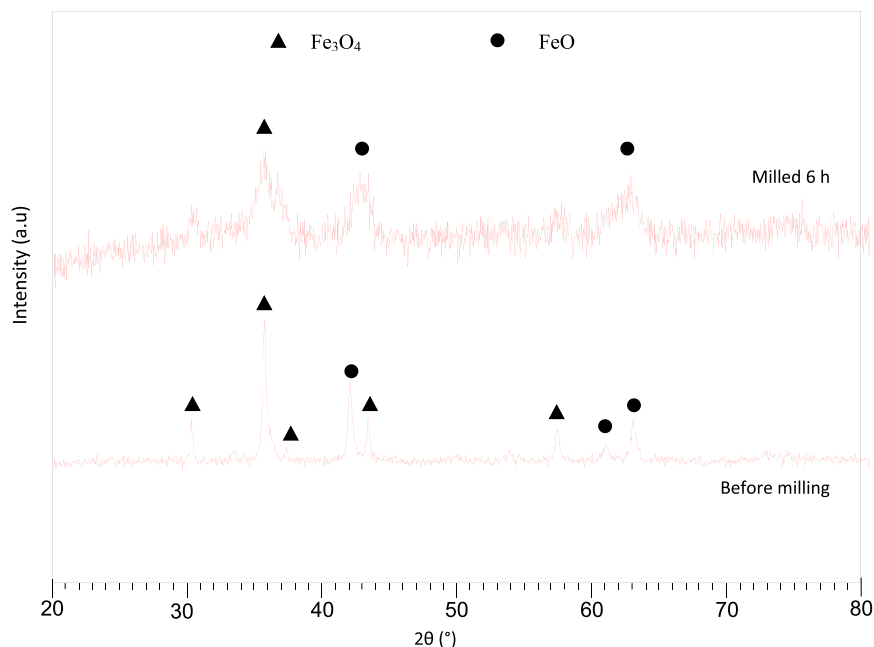


Fig. 8 X-ray diffraction pattern of mill-scale milled using high energy ball milling for 6 h.

obtained from FESEM micrograph shows that the size distribution is broad as various particle sizes were obtained during mechanical alloying process. Nanosized particles have high reactivity due to larger surface area and it is one of the most important parameter to be considered for the growth mechanism of CNTs on the surface of millscale (Nershev *et al.*, 2003; Kukovitsky *et al.*, 2002; Helveg *et al.*, 2004; Cheung *et al.*, 2002).

The XRD spectra of mill-scale before and after milling using high energy ball milling at 6 h is shown in **Fig. 8**. The result exhibits the occurrence of magnetite (Fe_3O_4) and wustite (FeO) phases only. This can be obtained by comparing the peaks with the standard reference code data for Fe_3O_4 (01-089-3854) and FeO (01-074-1886). The presence of magnetite can be seen in the plane (113) at $2\theta = 36.33^\circ$ and the presence of wustite (002) and (022) were detected at $2\theta = 42.09^\circ$ and 61.04° respectively.

FESEM images of MWCNTs grown by CVD method at 650°C , 750°C , and 850°C are shown in **Fig. 9(a–c)** respectively. The web-like structure consists of nanotube bundles. The bundling structure results from the attractive van der Waals forces between nanotubes. A group of CNTs can form a randomly oriented CNT mat or super aligned CNT arrays, depending on the density of catalyst and their activities at different synthesis conditions (Devi *et al.*, 2017). External diameters of each sample are 146.3, 133.1, and 99.7 nm for different ST and their size distributions are shown in **Fig. 10**. The growth of MWCNTs were also seen to be tangled

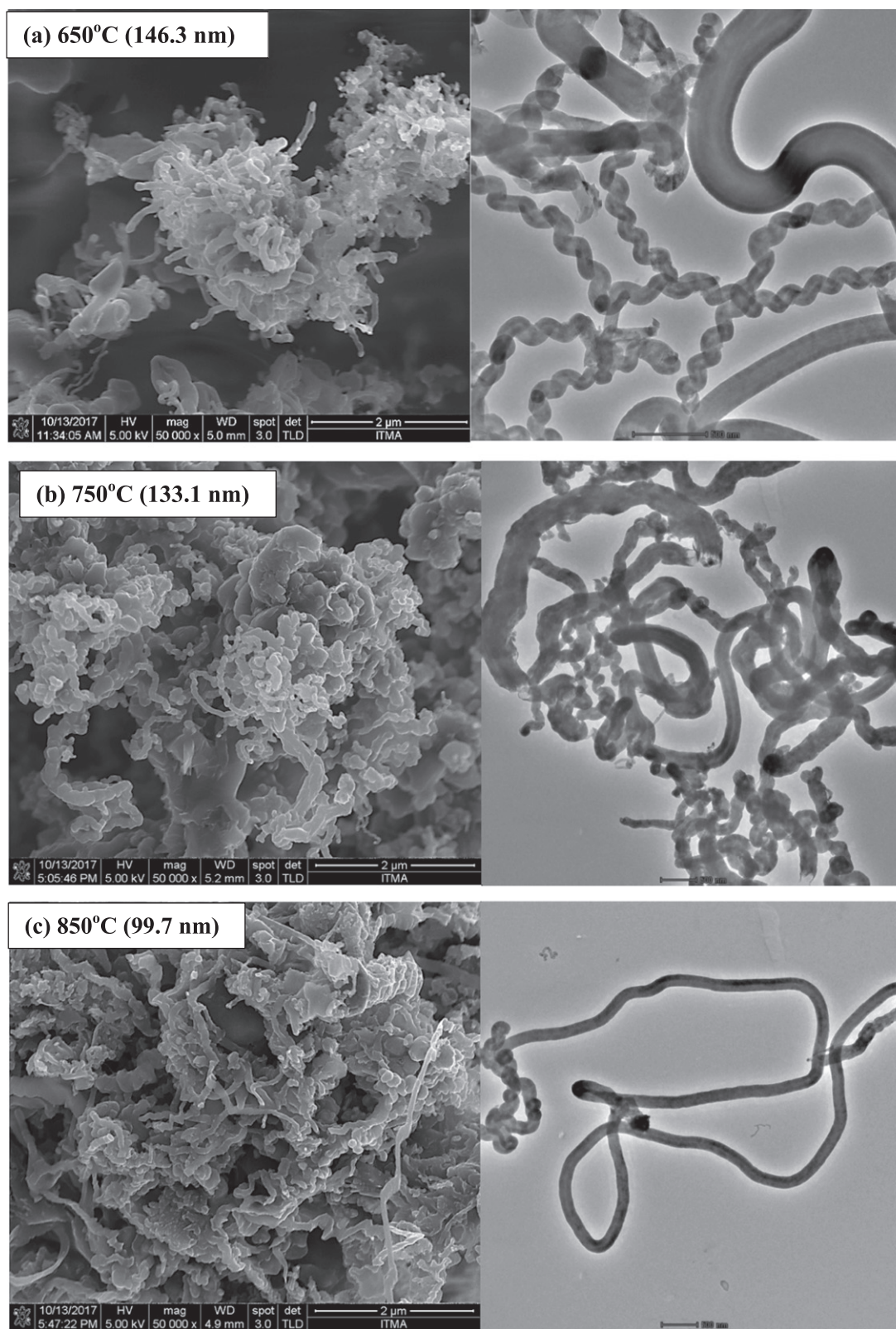


Fig. 9 Field emission scanning electron microscope and high resolution transmission electron microscope micrographs of multiwalled carbon nanotubes catalyzed by mill-scale nanoparticles at temperature of: (a) 650°C, (b) 750°C, and (c) 850°C.

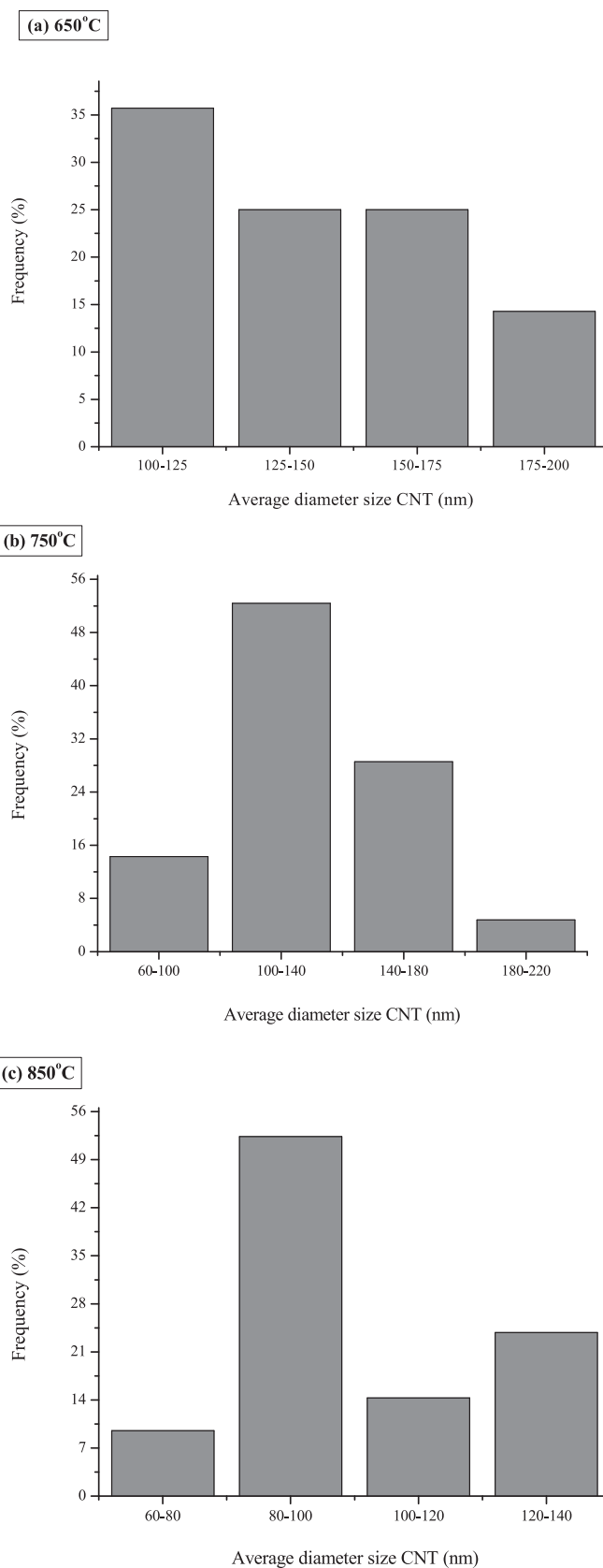


Fig. 10 Diameter size distribution of multiwalled carbon nanotubes synthesized at (a) 650°C, (b) 750°C, and (c) 850°C.

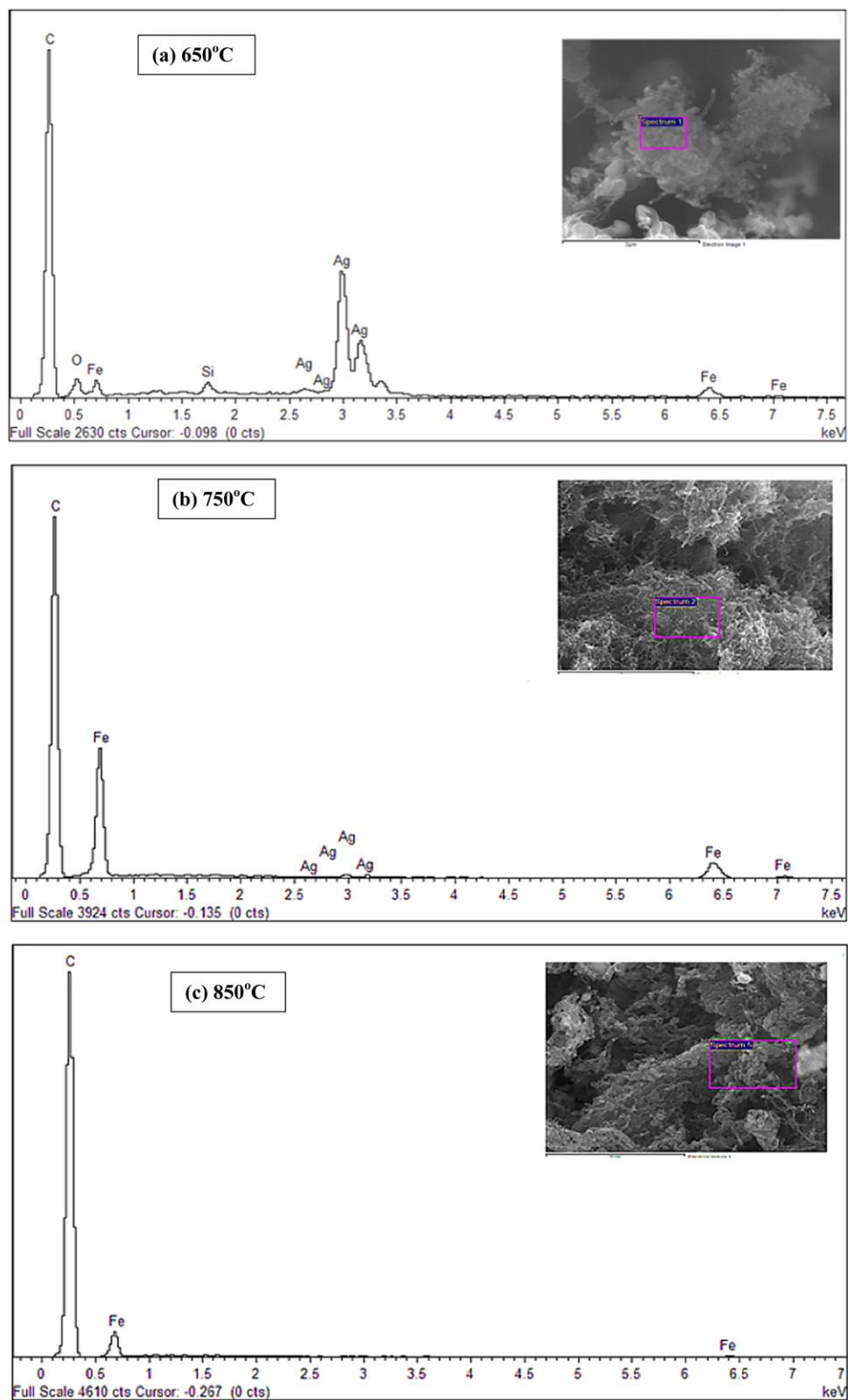


Fig. 11 Energy dispersive X-ray spectrum of multiwalled carbon nanotubes at different synthesis temperature.

Table 2 Fractions of weight percent of MWCNTs at 650°C, 750°C, and 850°C

ST (°C)	Element	Weight (%)
(a) 650	Carbon	53.79
	Oxygen	10.01
	Silicon	0.75
	Iron	3.66
(b) 750	Argentum	31.78
	Carbon	87.87
	Iron	10.67
(c) 850	Argentum	1.46
	Carbon	98.51
	Iron	1.49

Abbreviation: MWCNTs, multiwalled carbon nanotubes.

and in a disorderly arrangement. According to the results obtained by Qi *et al.* (2007), CNT-Fe and CNT-Co present a nonlinear growth. It is also common to find the catalyst encapsulated inside the CNTs, as a result of the growing process and the little chemical interaction between catalysts. In this sense, the equilibrium state of iron oxide phases (millscale magnetite) promotes the agglomeration of the catalyst nanoparticles and decreases the encapsulation. The EDX spectrum reveals the presence of iron (Fe), carbon (C), and argentum (Ag) peaks in FESEM view without any other impurities (Fig. 11). The peak of Ag was present in the EDX spectra due to the use of silver paste during sample preparation for putting MWCNT samples on aluminum stub. The fractions of weight percent of CNTs at different ST are listed in Table 2. It was observed that the percentage of carbon content in CNTs was slightly increased as the ST increased as confirmed by EDX analysis.

The FESEM and HRTEM images of as-synthesized MWCNTs in Fig. 9(a–c) reveal the presence of bundles and entanglements with structures mostly straight, spiral, and twisted. However, there is also existence of netlike fibers that were formed by the aggregation of very fine fibers and particle-like carbon [Fig. 9(a)]. One of the reasons for the formation of coiled like structure is due to the regular insertion of pentagon–heptagon pairs at the junction (Dunlap, 1992, 1994).

TGA/DTA can be used to evaluate the thermal stability of a material and characterize the graphitic nature of MWCNTs. Fig. 12 presents TGA/DTA profiles of the as-prepared MWCNTs at a heating rate of 20°C min^{−1} to 1000°C in an atmosphere of air flowing at 50 ml/min^{−1}. For all ST samples, the TGA curves show that the weight loss with thermal degradation at about 481–544°C and decomposed completely at about 716–783°C. It can be found that weight was lost slowly corresponding to the loss of low water content and a few amorphous carbons (Chen *et al.*, 2002). At the temperature range from 480°C to 790°C, the weight decreased sharply indicating that the decomposition of the MWCNTs (Elwi *et al.*, 2010). Also a thing to note is that the curve slope maintained almost the same value from 480°C to 790°C. It is illustrated that the MWCNTs were decomposed at a constant speed, signifying that the CNTs reached to a high purity at 480°C. After 790°C, the weight of the sample remains unchanged. The remainders may be assigned to the metal catalyst used to catalyze the nanotubes, as well as the oxidation products of this catalyst (Chen *et al.*, 2002; Lehman *et al.*, 2011). The figure demonstrates the purity of measured MWCNTs reaching 74.9%, 71.1%, and 77.3% for each respective sample. The primary oxidation temperature for each material is defined as the temperature at the highest peak for the material on the derivative weight curve and can represent the thermal stability of the material (Lehman *et al.*, 2011; Cheng *et al.*, 2011). There is an obviously exothermic peak at 636–650°C for all ST samples, which is attributed to the peak of CNTs.

Raman spectroscopy of MWCNTs yields information about the purity, defects, and graphitic structure and contributes in the distinction presence of MWCNTs relative to other carbonaceous materials. The two dominating peaks present in Raman spectra of MWCNT bundles for all ST samples (Fig. 13) are namely as carbon G (graphite) and D (disorder) band. The D-bands have been attributed to the presence of amorphous carbon due to surface defects of CNTs (Saito *et al.*, 2001) while the G-bands are due to the presence of ordered graphitic CNTs in the prepared samples. The G- and D-band explicitly appears in range ~1575 cm^{−1} and ~1347–1352 cm^{−1} for each sample. The intensity ratio of the two peaks (I_D/I_G), considered a parameter in characterizing the quality of CNTs. The ratio of I_D/I_G was observed to decrease with increase of ST from 650°C to 850°C as shown in Table 3. The lower I_D/I_G value close to zero corresponds to a better degree of graphitization (Wepasnick *et al.*, 2010). The higher I_D/I_G values are influenced by two factors, which are the presence of structural, lattice defect and other carbon materials such as nonuniform nanotubes (Adnan *et al.*, 2015).

Microstrip patch antenna measurement

A rectangular MPA has been designed using transmission line model according to targeted parameter on kapton substrate. The detailed design parameters used are listed in Table 4.

The proposed antenna was examined using a vector network analyzer to determine the S_{11} value of the antenna fabricated using MWCNTs on the kapton substrate. In Fig. 14, the minimum reflection loss (RL) of sample synthesized at 650°C was 12.42 dB at 5.46 GHz. Moreover, for the sample synthesized at 750°C, the minimum RL was 15.97 dB at 3.75 GHz. As for the sample prepared at 850°C, it shows the lowest RL is around 27.82 dB at 3.03 GHz. These results revealed that the

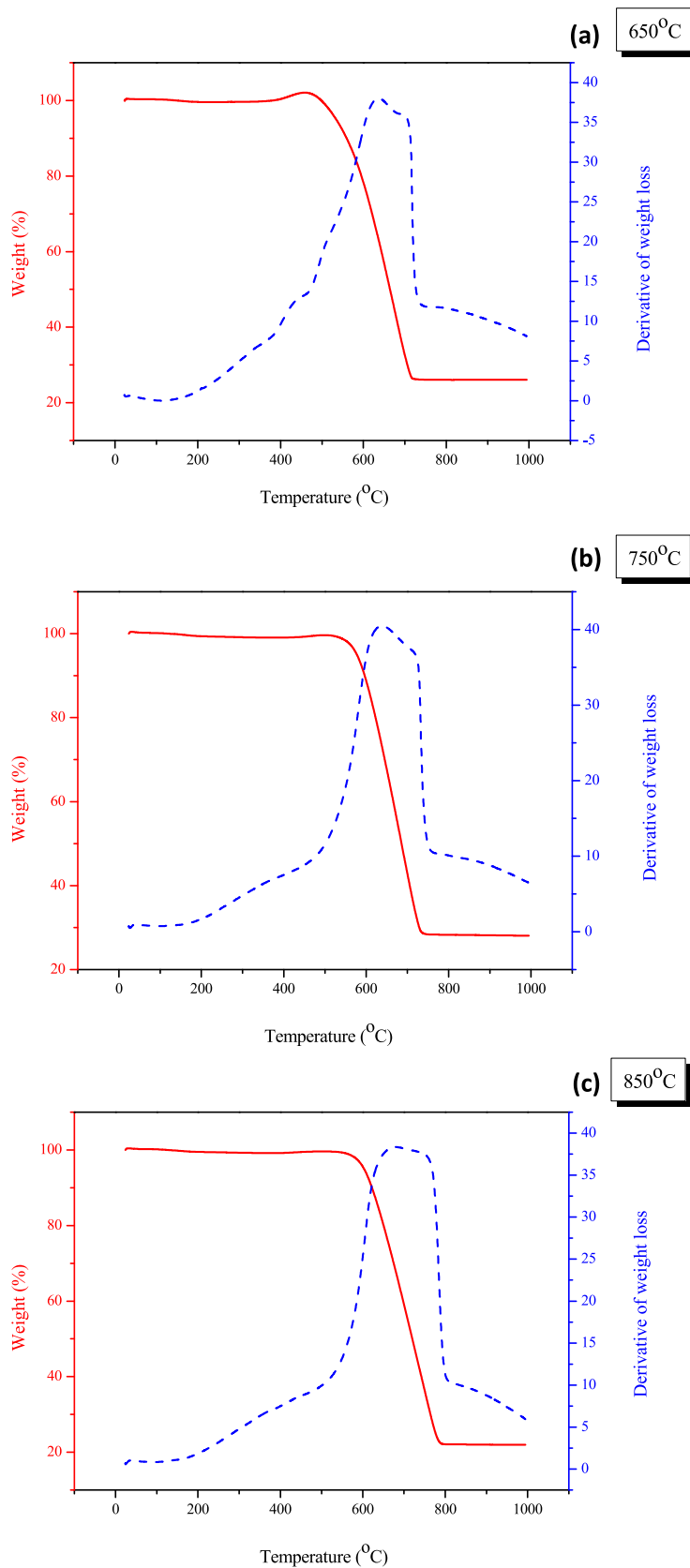


Fig. 12 Thermal gravimetric/differential thermal analysis of multiwalled carbon nanotubes synthesized at: (a) 650°C, (b) 750°C, and (c) 850°C.

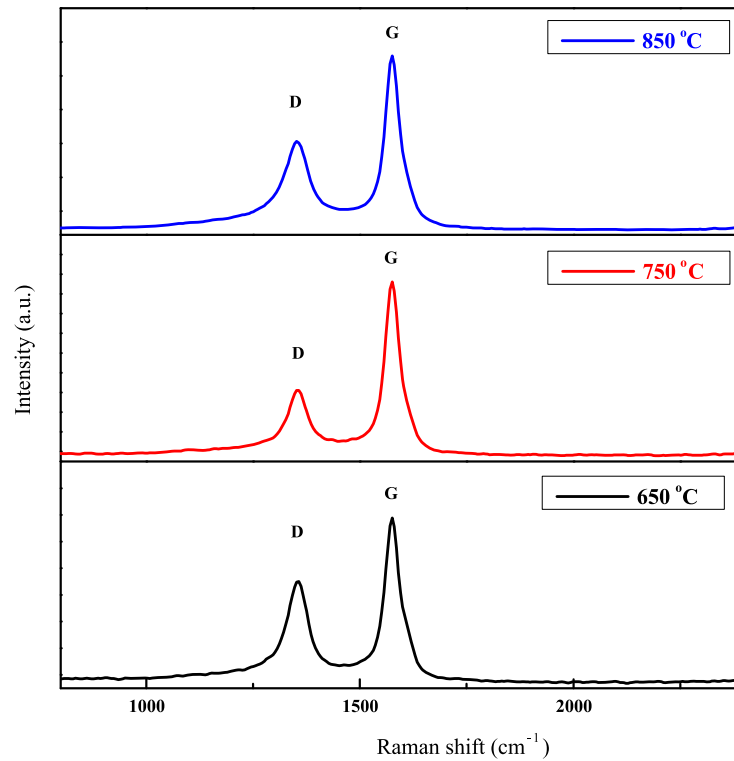


Fig. 13 Raman spectrum of carbon nanotubes at different synthesis temperature.

Table 3 Table of *D*- and *G*-band peak height and intensity and ratio of *D*- and *G*-bands (I_D/I_G) obtained from Raman spectra of MWCNTs

<i>ST</i> (°C)	<i>D</i> -band		<i>G</i> -band		I_D/I_G
	Peak, cm^{-1}	Intensity, a.u.	Peak, cm^{-1}	Intensity, a.u.	
650	1352.19	1023.95	1575.91	1144.05	0.89
750	1352.19	1005.38	1575.91	1280.99	0.78
850	1347.16	1499.37	1575.91	2146.73	0.70

Abbreviation: MWCNTs, multiwalled carbon nanotubes.

Table 4 Dimensions value of substrate and patch of MPA

Item	Value
Relative permittivity, ϵ_r	3.5
Thickness, h (mm)	0.1
Length of patch, L_p (mm)	13.0
Width of patch, W_p (mm)	17.0
Length of substrate, L_s (mm)	15.0
Width of substrate, W_s (mm)	20.0

Abbreviation: MPA, microstrip patch antenna.

existence of MWCNTs enhanced its electromagnetic (EM)-wave absorption performance. MWCNTs can form conductivity net, and enhance the dielectric loss capability. In addition, the interfacial between magnetite nanoparticles and CNTs enhanced the interfacial polarization capability. The *RL* values reveal that the effect of carbon content in magnetic nanoparticles did play a role to give better absorption properties. Without MWCNTs, only magnetic loss and very weak dielectric

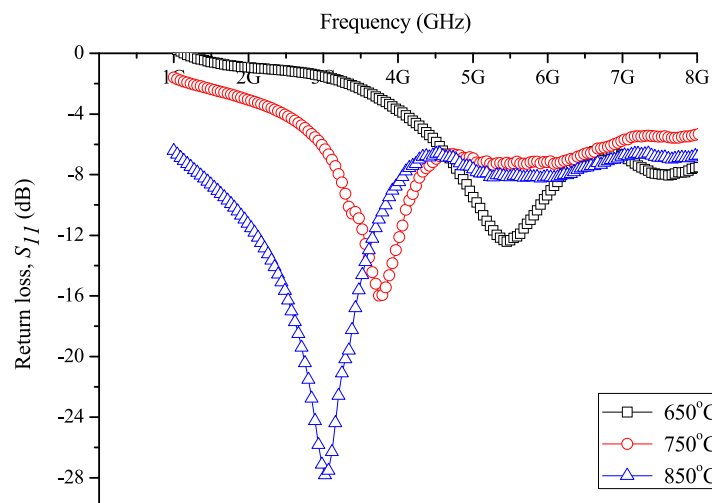


Fig. 14 Reflection loss, S_{11} of microstrip patch antenna at different synthesis temperature.

Table 5 Electromagnetic wave absorption properties of MPA at different ST

ST ($^{\circ}$ C)	Resonant frequency, f_r (GHz)	Return loss, S_{11} (dB)	Bandwidth (GHz) (RL < -10 dB)
650	5.46	12.42	0.76
750	3.75	15.97	0.77
850	3.03	27.82	2.03

Abbreviations: MPA, microstrip patch antenna; ST, synthesis temperature.

loss work in magnetite nanoparticles to attenuate the EM wave that enters the absorber inside. Raman results revealed that higher ST produced fewer defects and highly graphitic MWCNTs, which in turn improved the conductivity. The increased conductivity due to higher carbon content allows the interfacial polarization and dielectric loss to attenuate the EM wave, which results in the enhanced EM-wave absorption capability of the samples. The microwave energy is conducted by the CNT structures through electron motion, which then generates mobile charges when exposed to EM wave (Elwi *et al.*, 2010). The bandwidth was observed to increase with increasing temperature from 0.76 to 2.03 GHz (Table 5). The MWCNTs are highly current carrying conductive materials where each of the nanotubes in the patch acts as a primary resonator and resonate with electromagnetic waves. Subsequently, current flowing along the edges of the patch induces additional resonances, which enhance the fundamental resonance of the radiating element. Thereby, it will enhance the impedance bandwidth. As explained in Hanson (2006), CNT is usually modeled as an infinite and thin tube-like cylinder formed by a graphene sheet. The impedance of CNTs, z , can be expressed by:

$$z = \frac{1}{2\pi a \sigma d} \quad (1)$$

where a is cross section of CNT radius, σ is material conductivity, and d is CNT wall thickness. Therefore it can be concluded that the role of bulk conductivity and wall thickness of CNTs with thin but finite-thickness tube shape is equal to that of CNT conductance as a whole. Higher conductivity will then lead to lower impedance, thus enhancing current flow of the CNTs.

As a conclusion, MWCNTs were successfully synthesized by using waste cooking oil as a hydrocarbon source via modified CVD. Different characterization techniques were used to investigate the formation of MWCNTs. Raman spectra revealed that I_D/I_G values were decreased as the sintering temperature increased. The decrease of I_D/I_G indicated that the MWCNTs have better graphitization with increasing temperature. Changing the ST can result in better properties of CNTs that would affect the properties of the electron transport in CNTs hence giving better absorption in microwave patch antenna.

This experimental work demonstrated that waste cooking oil, a low-cost and readily available resource, can be used as an inexpensive carbon source for the production of CNTs. Mill-scale waste from the steel factory can also be utilized as catalyst in the CVD process. This article not only describes a new application of waste cooking oil in the field of microwave application, but also offers a solution to the environmental pollution of ecosystems caused by improper cooking oil disposal.

Acknowledgment

The authors thank the students and staff from the Functional Devices Laboratory (FDL) and Materials Synthesis and Characterization Laboratory (MSCL), Institute of Advanced Technology, Universiti Putra Malaysia (UPM) for the support, help, and facilities given throughout the duration of this research. We also would like to acknowledge Putra Muda Research Grant (Vot: 9545400) provided by UPM.

See also: Removal of Chromium With CNT Coated Activated Carbon for Waste Water Treatment

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The Utilization of Vegetable Fibers in Cementitious Materials

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Nomenclature

FRC Fiber reinforced concrete

FSP Fiber saturation point

LDPM Large date palm fibers

M Moisture content

PS Preparation process

SDPM Small date palm fibers

VF Vegetable fibers

W_0 Anhydrous weight of specimen

W_h Humid weight of specimen

Introduction

The use of vegetable fibers (VF) as a raw material is a return to old civilizations from centuries ago. For instance, 3000 years ago in Egypt, walls were built by reinforcing clay with straw. Recently, a new social awareness has pushed the scientific community to look for suitable solutions for the environment and to reduce the depletion of petroleum resources. Thus, since the second half of the twentieth century, VFs have been extensively used as a suitable reinforcement in many fields of industry (Campilho, 2015). During the last few years, a significant effort has been made by scientists and engineers to provide a technical database for the various types of VF. The reinforcement of polymeric materials with VF as an alternative to conventional synthetic reinforcement can thus become a reality, and also contribute to the increase of the economic value of VF wastes. Furthermore, the production of low cost and eco-friendly composite materials that have some advantages for particular applications such as thermal and acoustic insulation is a very possible concept (Bledzki *et al.*, 2002). The reinvention of natural fibers and the combination of them with polymers has given rise to a new class of materials that can compete with or replace synthetic materials for some structural, but mostly for nonstructural and semi-structural applications.

The introduction of VFs in cementitious matrices began in the 1980s. More recently, housing construction has seen an increase in the application of VF in various non-structural and some structural building components in both exterior and interior applications such as walls, floors, roofing, siding, external cladding, internal lining, building boards, bricks, bracing and fencing. VF composites are also found in the construction of decks and dams, as well as in the building of roads and bridges (Campilho, 2015).

The mechanical behavior of VF reinforced cementitious composites vary according to the origin of the fibers and the type of cementitious matrix. Generally, the utilization of VF in lightweight cementitious composites has shown interesting results due to the compatibility between the fiber and the matrix. Lightweight cementitious materials have mechanical properties close to that of VFs, meaning that they can stop the matrix from breaking the fibers, guarantee a good adhesion and reduce the pullout phenomena of fibers inside the matrix. Furthermore, VF could support the matrix by exhibiting more tensile strength to the lightweight cementitious matrix, which is basically a brittle material, therefore improving the cracking resistance of cementitious materials.

The article reviews the recent research papers which focused on the utilization of VF in the reinforcement of cementitious materials. Firstly, it represents a general overview on the availability of VFs and their properties. Thereafter, the selected mechanical behavior of various types of cementitious materials is summarized.

Short Introduction to Vegetable Fibers

Generality

Natural fibers can be classified according to their origin into animal, mineral and vegetable fibers (VF). The latter one, which are also known as lignocellulosic fibers due to their main components being cellulose, hemicellulose, and lignin (Hakeem *et al.*, 2014) are classified according to their chemical composition as wood and non-wood fibers. Wood fibers have a higher amount of lignin when compared with non-wood fibers, and can be divided into either softwood or hardwood fibers. Softwood fibers can be found in pines, firs, etc., and hardwood fibers are found in birch, eucalyptus, beech, etc. Non-wood fibers cover four major categories according to which part of the plant the fibers are located (e.g., bast, seed, leaf, stalk and reed fibers) (Ardanuy *et al.*, 2015). Fig. 1 shows examples of natural fibers and their classification (based on Jawaid and Abdul Khalil (2011)).

The actual trend of the waste generation process from abundant in nature ago-based materials such as VF has found a wide application in multiple fields of industry, as shown in Table 1 (based on Al-Oqla and Salit (2017)). The annual worldwide production of VF derived from wood and non-wood fibers is presented in Fig. 2, based on the studies of Stokke *et al.* (2013), Väisänen *et al.* (2016) and Al-Oqla and Salit (2017).

The price of VF when compared with the price of synthetic fibers is very low, for example, the price of glass fibers varies between 1200 and 1800 \$/ton, whereas VF costs between 200 and 1000 \$/ton (Satyanarayana *et al.*, 2009; Ardanuy *et al.*, 2015). Moreover,

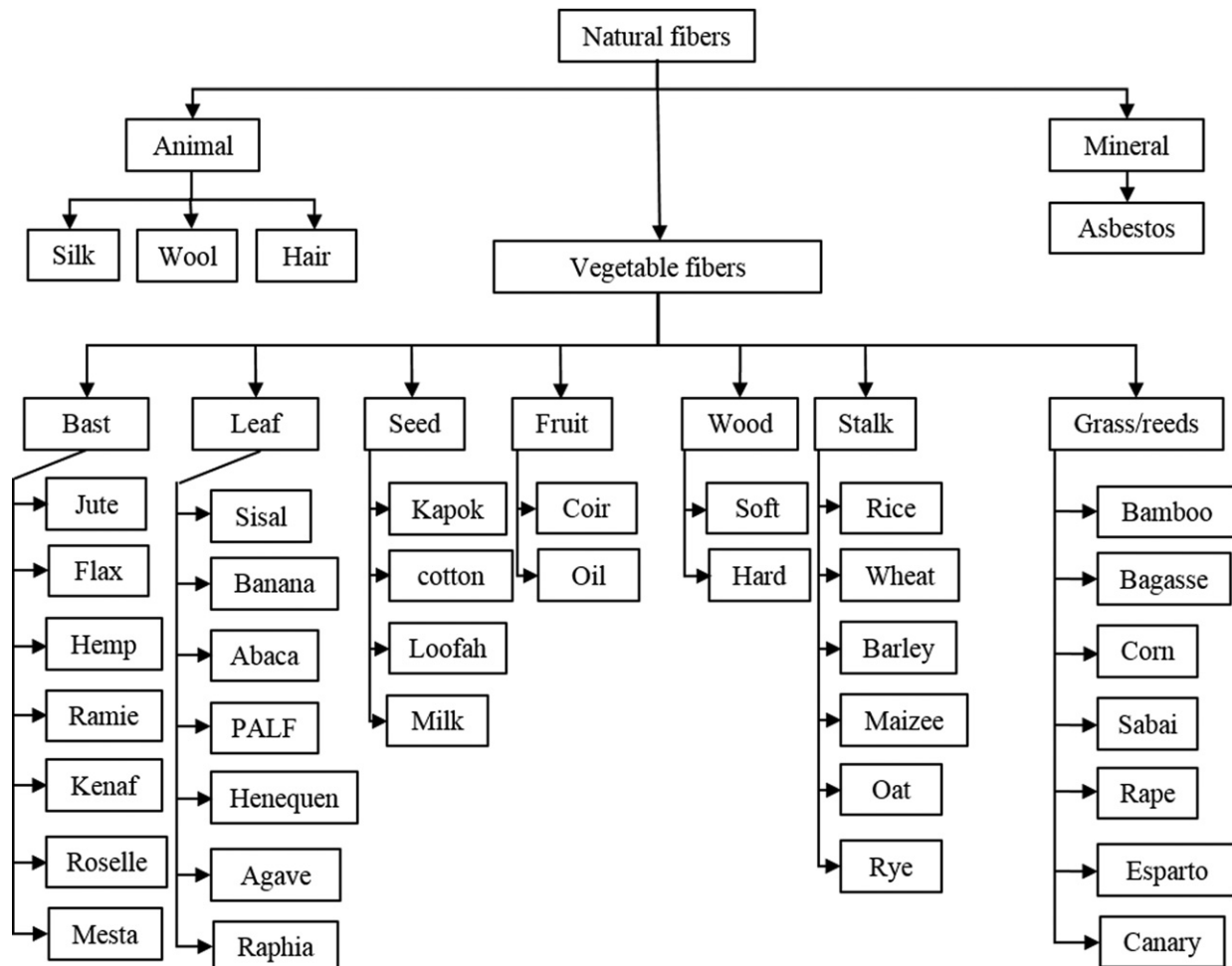


Fig. 1 Classification of natural fibers.

Table 1 Fields of application and the market of natural fiber composites

<i>Application field</i>	<i>Part in market</i>
Construction and building	15%
Electrical and electronic	4%
Agriculture	3%
Functional	2%
Automotive and transports	16%
Textiles	18%
Consumer goods	18%
Packaging-flexible	9%
Packaging-rigid (incl. food service-ware)	15%
Other	1%

the price of VF varies depending on the available amount and the market demands of these fibers. For instance, the yearly product of date palm and hemp fibers is 4,200,000 tons and 214,000 tons, respectively. This difference in the production ratio makes the date palm fibers 60 times cheaper than hemp fibers, with a price value of about 20\$/ton (Al-Oqla and Salit, 2017). More details concerning the price of some VFs are shown in Fig. 3.

The structure of plant fiber is comparable to a stack of composite folds, whose structure is detailed in Fig. 4 (based on Baley (2005)).

The fiber consists of a primary and a secondary wall, with the secondary wall consisting of the 3 layers S1, S2, and S3. The S2 layer is the thickest one and sets the behavior of the whole fiber. This multilayer structure imparts anisotropy to the material. In a

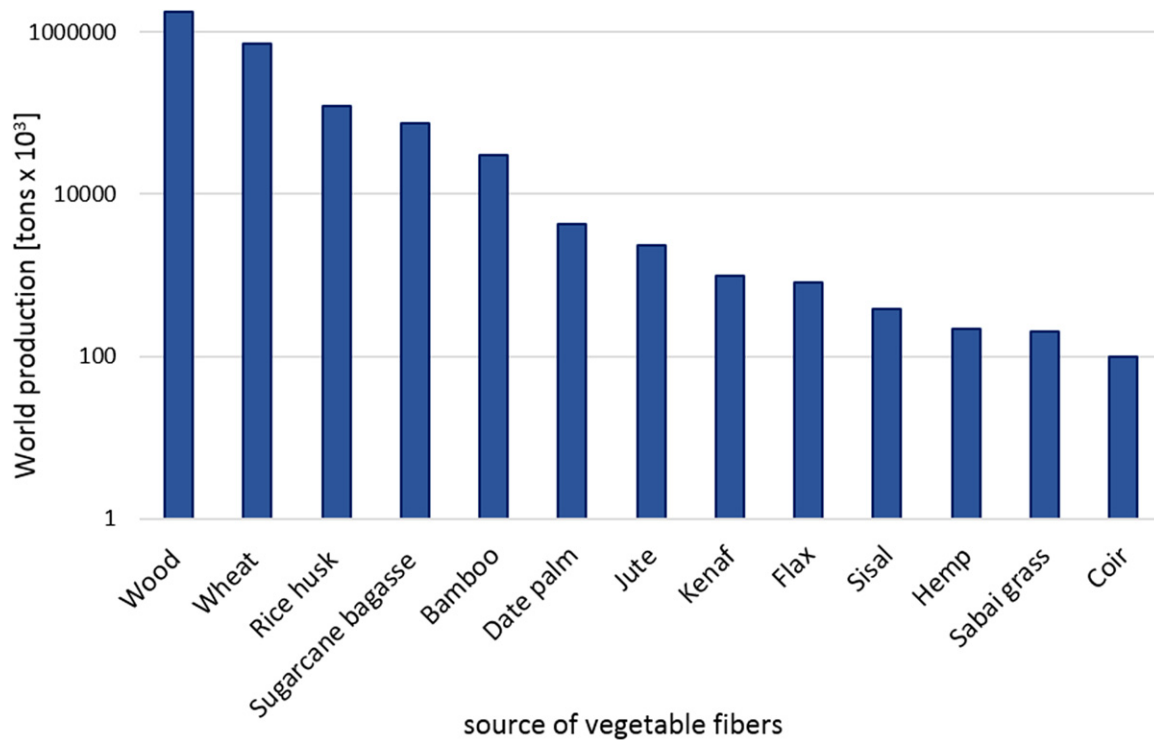


Fig. 2 Annual production of VF.

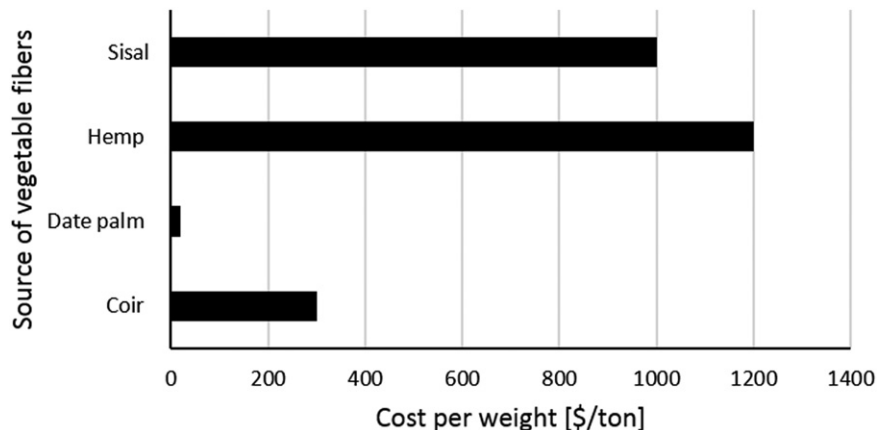


Fig. 3 Price of selected VF products.

plant, the fibers are usually assembled in the form of a bundle, which in turn forms their polygonal shapes. The primary and secondary walls contain a frame formed of cellulose microfibrils that is surrounded by a matrix containing hemicellulose and lignin.

The cellulose

Cellulose is a natural polymer and is the most available biopolymer on earth. It can be found in many fields of industry, such as packaging, textiles and paper, as well as being used as a food additive. Cellulose consists of long chains of glucose anhydride unit molecules of up to 15,000 molecules. The glucose anhydride particles are linked together by beta bonds [$\beta(1,4)$]. The cellulose molecule has a linear formation due to this bonding configuration (see Fig. 5). The degree of polymerization (d.p) determined by scientists, which is based on counting the glucan residues, is about 10,000 for wood cellulose (Stokke *et al.*, 2013).

The cell unit form of cellulose is known in literature by different names, such as microfibrils, elementary fibrils, and protofibrils. Such a configuration of different cellulose components is shown in Fig. 6 (based on Al-Oqla and Salit (2017)).

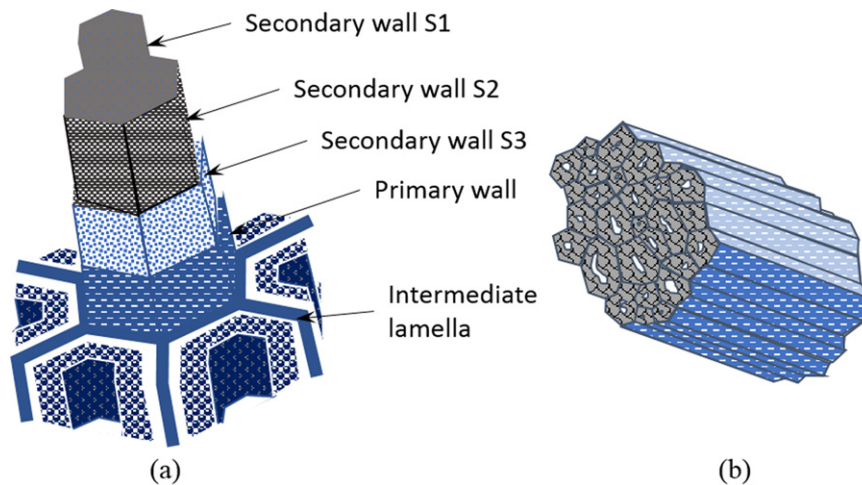


Fig. 4 (a) Complete structure of hemp fiber in a bundle. (b) Fibrillar structure of hemp fiber.

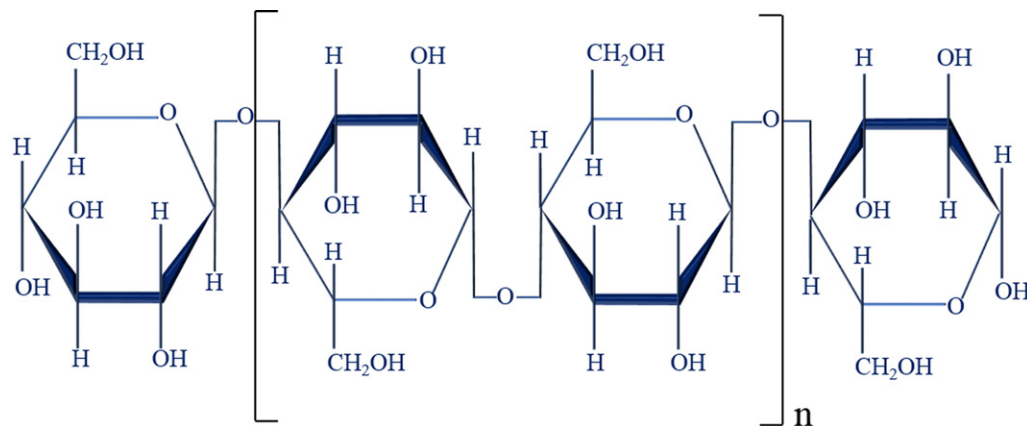


Fig. 5 Cellulose molecule.

The hemicellulose

Hemicellulose is a natural polymer like cellulose, consisting of carbohydrate monomers. However, hemicellulose consists of a variety of carbohydrate monomers, unlike homopolysaccharide cellulose. Thus, the monomers that hemicellulose consists of are arabinose, mannose, galactose, glucose, and xylose. Since hemicellulose has considerable side-branch groups, its structure is more open and non-crystalline. Hemicellulose is more hygroscopic than cellulose and attracts more water molecules due to its open structure. The degree of polymerization of hemicellulose in wood is about 100–200, which is very low when compared to that of cellulose, which is 10,000. The difference between wood and non-wood fibers does not appear in the content of cellulose, however, it does appear in the contents of hemicellulose and lignin. Non-wood fibers such as grasses (wheat, corn, rice) contain up to 40% of the major hemicellulose found in grasses, whereas wood fibers are composed of 25%–35% of hemicellulose by dry weight. **Fig. 7** illustrates a typical hemicellulose molecule found in a type of wood fiber named Arabinoglucuronoxylan (xylan) (Stokke *et al.*, 2013).

The lignin

Lignin is an extremely heterogeneous macromolecule that represents about 30% of the organic carbon in the biosphere. Lignin is totally amorphous, and unlike the other carbohydrate-based cellulose and hemicellulose, it contributes to the protection of the cell walls by working as the glue that holds the cells. Lignin has an aromatic structure represented by three precursors: p-coumaryl, sinapyl, and coniferyl alcohol (see **Fig. 8** (based on Stokke *et al.* (2013))). The contents of lignin in a vegetable fiber vary from 2% to up to 45% (Stokke *et al.*, 2013; Al-Oqla and Salit, 2017).

Mechanical Properties of Vegetable Fibers

Vegetable fibers (cotton, jute, hemp, flax, sisal, kenaf, coconut, abaca, wood,...) have biological structures mainly composed of cellulose, hemicelluloses and lignin. Cellulose is a polymer that, unlike the other components of the fiber that have an amorphous

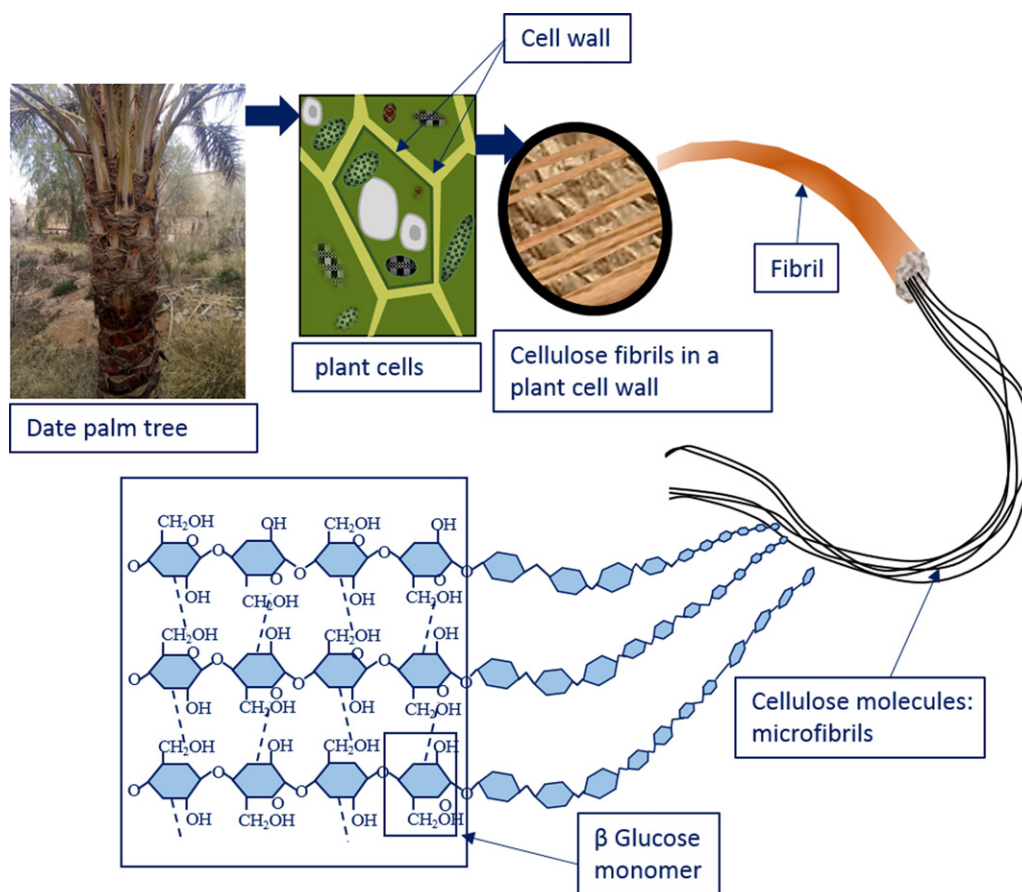


Fig. 6 Organization of cellulose components in the cell wall of a typical plant fiber.

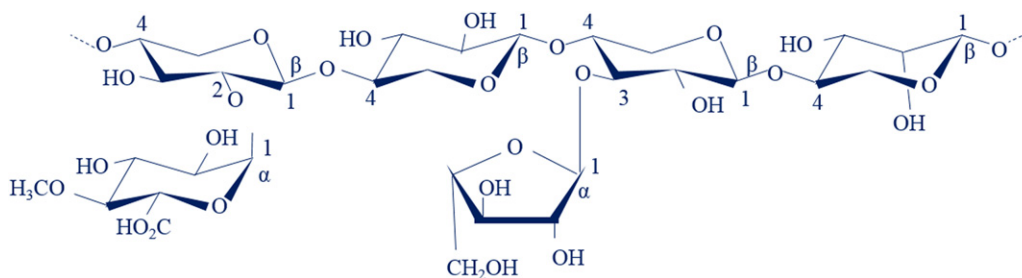


Fig. 7 Structure of hemicellulose (xylan) consisting of a xylopyranose backbone, with glucuronic acid (1→2) and arabinofuranose (1→3) side branches.

structure, has a largely crystalline structure that gives a modulus of elasticity of about 136 GPa compared to that of 75 GPa for glass fibers. Vegetable fiber is comparable to a composite material reinforced with fibrils of cellulose. The matrix is mainly composed of hemicellulose and lignin. The cellulose fibrils are helically oriented at an angle called the “microfibrillar angle”. This angle is located between the fibrils and the axis of the fiber. The degree value of the microfibrillar angle influences the stiffness of the fiber.

The properties of natural fibers are often subject to discussion due to the fact the techniques used to cultivate, extract or separate the fibers vary significantly, which may modify their behavior. For instance, the factors that can affect the properties of VF could be attributed to the variety, the conditions of cultivation (soil, treatment, climate), maturity, degree of preparation (retting, scutching, combing...), moisture content, crystalline structure (degree of crystallinity, degree of polymerization, cellulose type...), and morphology (cell diameter, microfibrillar angle, lumen size), etc. Usually, the amount of reinforcement and the orientation of fibers in a composite material set the elastic and rupture characteristics. Similarly, in a plant fiber, the physical properties of natural fibers are mainly determined by the chemical and physical composition, structure, the percentage of cellulose, the microfibrillar angle, the aspect ratio L/d (length/diameter: which is an important parameter allowing the transfer of charge between the fibers and matrix), the transversal section, and the degree of polymerization. To simplify, for a given percentage of cellulose, the

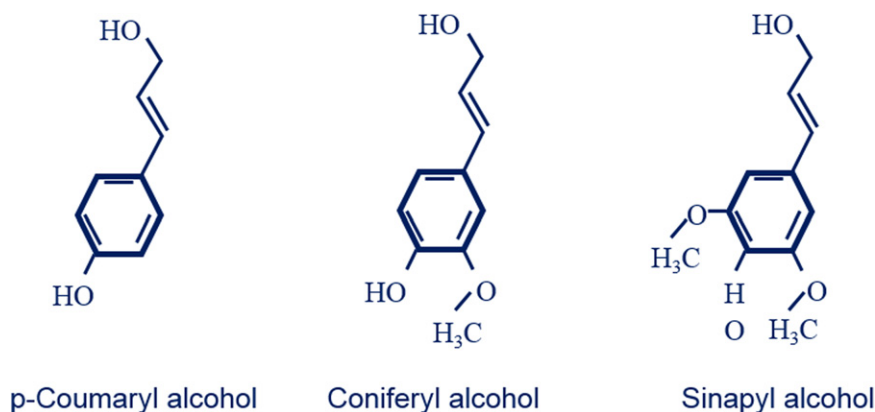


Fig. 8 Structure of lignin precursors.

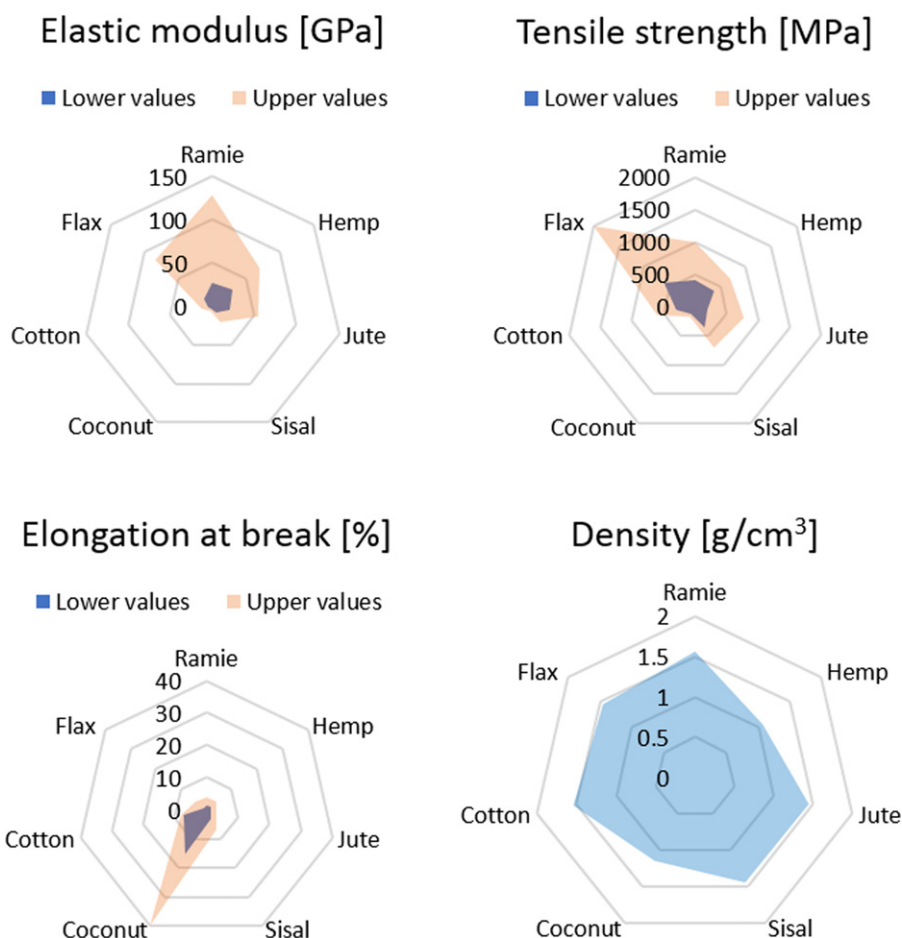


Fig. 9 The average mechanical properties of different types of VF.

microfibrillar angle will be weak and the strength of the fiber will be higher; moreover, the microfibrillar angle will be significant and the elongation at breakage will be important. Strong dispersions of physical, mechanical or thermal property measurements make the characterization of VF more delicate. These dispersions follow the structural differences observed in the fibers. For example, the size of cells not only depends on the variety of the fiber to which they belong, but also on their maturation stage, their “meteorological history” and their location in the plant. The mechanical properties of different fibers from different origins of plants used for the reinforcement of common composite materials are shown in [Fig. 9](#) (based on [Chabert \(1988\)](#) and [Väisänen et al. \(2016\)](#)). By taking into account the natural behavior of these fibers, some dispersions can be noticed.

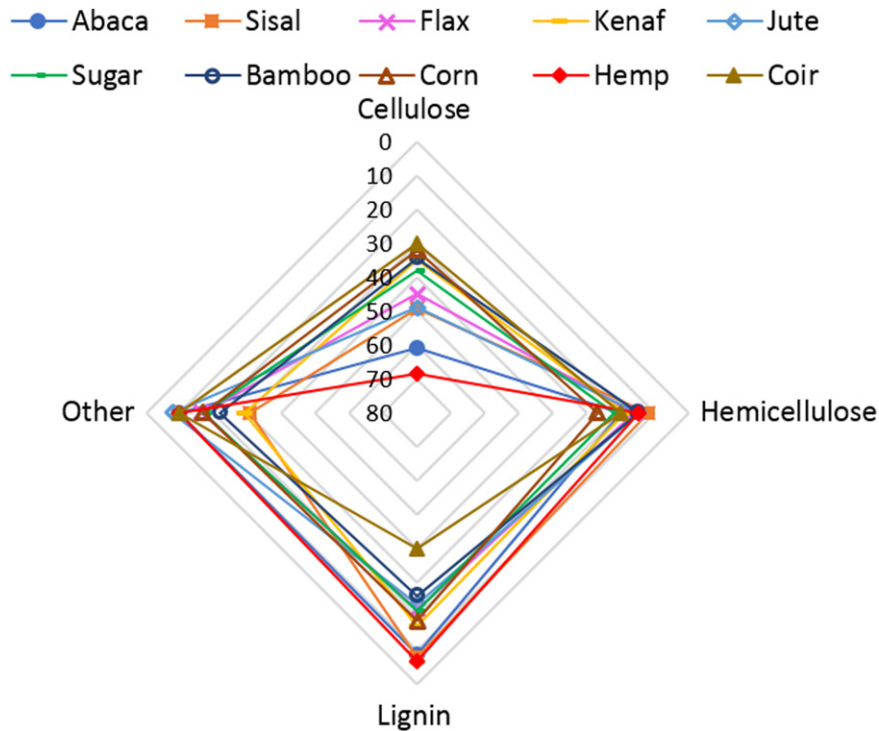


Fig. 10 Chemical analysis of some VFs.

Chemical Properties of Vegetable Fibers

The main constituents of VF are cellulose, hemicelluloses and lignin. Other products like proteins, pectin, starch, and inorganic salts are present in smaller amounts (Rowell, 1995). The chemical composition of VF depends on its origin, but in general, cellulose is always predominant with percentages by weight ranging from 22% for Sabai fibers to 85% for linters of cotton (see Fig. 10 (based on Sbiai (2011) and Väisänen *et al.* (2016))). Lignin concentrations vary from 7% to 24% by weight, and those of hemicelluloses from 12% to 27% by weight. These compounds are heteropolymers, which exhibit great variability in chemical composition according to their origin. The inorganic compounds, characterized by their ash content, also vary depending on the nature of the fiber. Thus, this content is about 1% by weight for wood lignocellulosic fibers and of the order of 14% for fibers from rice.

Physical Properties of Vegetable Fibers

Hygroscopic properties of vegetable fibers

The dimensional instability with respect to moisture is the main property of wood, which makes its use more delicate. When a tree is alive, it contains water that flows through its cells. The wood material, therefore, contains a certain rate of humidity, depending on the weather conditions. Water plays the role of plasticizer for the polymer chains constituting the cell walls, which is the reason behind the fact that the moisture content and diffusion phenomena govern all the characteristics of the wood. If not for constituent water, represented by the atoms of hydrogen and oxygen that compose the molecules of the polymer's structure, water is found in two forms:

- Free water: it fills the cells and the vessels, is held by capillary forces and is not involved in dimensional variations.
- Bound water: it is fixed on the polymers structure by physisorption or chemisorption. The forces involved are electrostatic or of the type of hydrogen bonds with hydroxyl groups.

The dimensional variation of hygroscopic material is mainly due to the water content, with the amount of water (bound water and free water) contained in the wood being characterized by a parameter called "moisture content of wood", which is defined as the ratio:

$$M(\%) = \frac{(W_h - W_0)}{W_0} \times 100 \quad (1)$$

where:

W_h : the humid weight of the specimen

W_0 : the anhydrous weight of the specimen

During the wood drying process, it is the free water that evaporates first. The fiber saturation point of the wood is reached when the moisture content is about $M = 30\%$. By continuing the drying process, it is the bound water which begins to evaporate. Dry wood in the air has a moisture content of 13%–17% according to the seasons. It can have a drier state when artificially dried; in particular, it reaches an anhydrous state after being dried for several hours in an oven at a temperature of 100–105°C. Therefore, it is conceivable that there is a moisture content threshold for which the adsorption sites are saturated (cell walls have the maximum amount of bond water). When there is no free water, the fiber saturation point (FSP) is reached. The moisture content at the FSP is very variable depending on the species, but is between 25% and 35% of moisture content for most types of fibers. Generally, it is more suitable to give a value of 30%, which corresponds to the behavior of the majority of species.

The moisture content of some types of VF is significantly different, as shown in Fig. 11 (based on the study of Ahmad *et al.* (2015) and Kocak and Mistik (2015)). This difference is related to the hydrogen bonding of cellulose and the amount of hemicellulose.

By submerging VF in water, the moisture content, in this case, will be beyond the FSP, including both the bond and the free water. In this context, as mentioned in the research study of Benmansour *et al.* (2014), the properties of moisture also depend on the aspect ratio of fibers. In this study, the authors evaluated the water absorption of date palm fibers as a function of immersion time. They found that the fibers with a small surface absorb more water compared to those with a larger surface (see Fig. 12).

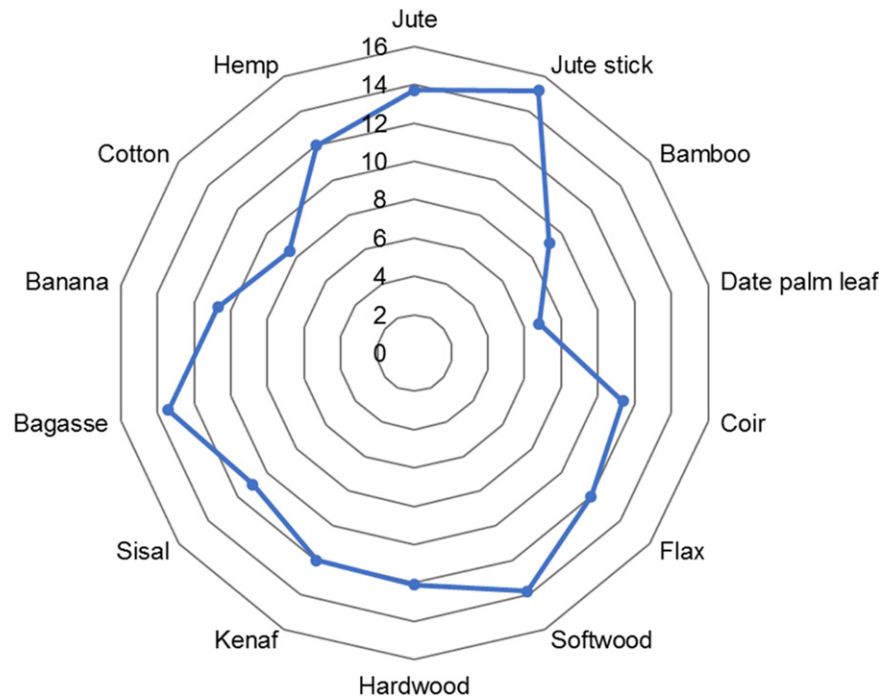


Fig. 11 Moisture content of some selected VFs.

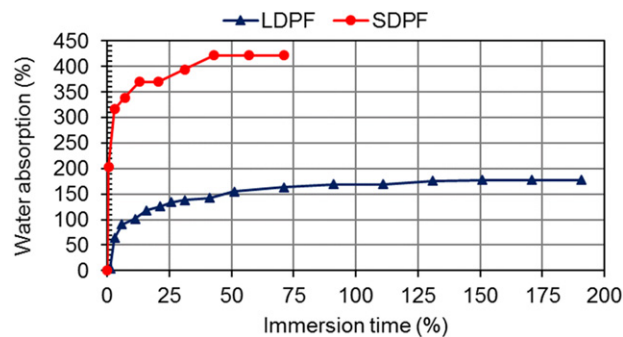


Fig. 12 Water absorption ratio of date palm fibers as a function of immersion time.

Fresh Properties of Cementitious Materials Modified With Vegetable Fibers

The incorporation of VF leads to a significant decrease in workability. This is due to the water absorbed by the VF. However, the mixture needs to have sufficient flowability for the casting process. A mixture that is too dry could lead to a final product that is insufficiently compacted, which would probably contain more voids. Conversely, a mixture that is too wet will lead to a decrease in mechanical strength.

The other important aspect of workability is the formation of fiber pellets, which is also known as the agglomeration of the fibers together during the mixing process. The degree of agglomeration depends on the type and length of fibers used, the volume fraction of fibers, and the size of aggregates in the cementitious composite (Bentur and Mindess, 2014). Fiber agglomeration should be avoided as it has a detrimental effect on mechanical strength. Some arrangements can be made during mixing to minimize the agglomeration effect. Normally, the progressive addition of fibers at the end of the mixing operation, when the other components are completely mixed, reduces this agglomeration effect. The use of a water-reducing plasticizer also makes it possible to substantially increase the workability without harming the mechanical performance of the composite (Sawsen *et al.*, 2015). Moreover, according to Aziz *et al.* (1981), the reduction of the granular dosage also makes it possible to limit the formation of pellets (Aziz *et al.*, 1981).

The flow ability of reinforced fresh mortar was negatively affected by the presence of fibers in the study of Çomak *et al.* (2018). This reduction (see Fig. 13) was attributed to the increase of water absorption by the increase of the fiber content. Nevertheless, the length of fibers has no effect on the flowability of cementitious materials (Çomak *et al.*, 2018).

Another aspect has a significant influence on the workability of fresh mortar, namely, the methodologies adopted to mix the VF homogeneously in the mortar matrix.

In this context, Chakraborty *et al.* (2013) tested three different processes of preparing the cement mortar composite by including 5 different fractions of jute fibers (0.5%, 1%, 2%, 3% and 4%). The first mixing process, which is termed as PS1, was conducted as follows: the slurry was made with 50% of the total quantity of cement and water, the fraction of chopped jute fibers was then added continuously during 10 min of mixing time, the remaining part of cement was mixed with the required quantity of sand separately for 5 min, the dry mix (sand and cement) was then added to the slurry (jute fibers, water, and cement) and mixed for 5 min, and finally, the remaining quantity of water (50%) was added into the slurry (Sand, cement and jute fibers). The second type of mixing, which is termed as PS2, was similar to PS1. The difference in this process was in the phase in which the fibers were incorporated. The jute fibers were first submerged in 50% of the total quantity of water, then 50% of the total quantity of cement was added and the slurry was mixed for 10 min. The remaining part of cement was dry mixed with sand and the dry mix was added to the slurry. Finally, the remaining part of water was added to the slurry. The third mixing process, which was termed as PS3, was performed as follows: the chopped jute fibers were immersed in water for 24 h until reaching full saturation, the saturated fibers were mixed with 50% of the total quantity of cement and water, and then the required amount of sand and remaining quantities of cement and water were added to the slurry.

The highlight of the results obtained (see Fig. 13 (based on Chakraborty *et al.* (2013) and Çomak *et al.* (2018))), showed that the workability decreased by using process PS1 and PS2 in the preparation of mortar due to the hydrophilic nature of the jute fiber. Nevertheless, the third type of mixing process, PS3, showed flowability values similar to that of the control mortar specimen. The reasons behind this difference can be explained by the fact that in preparation processes PS1 and PS2, the jute fibers were added

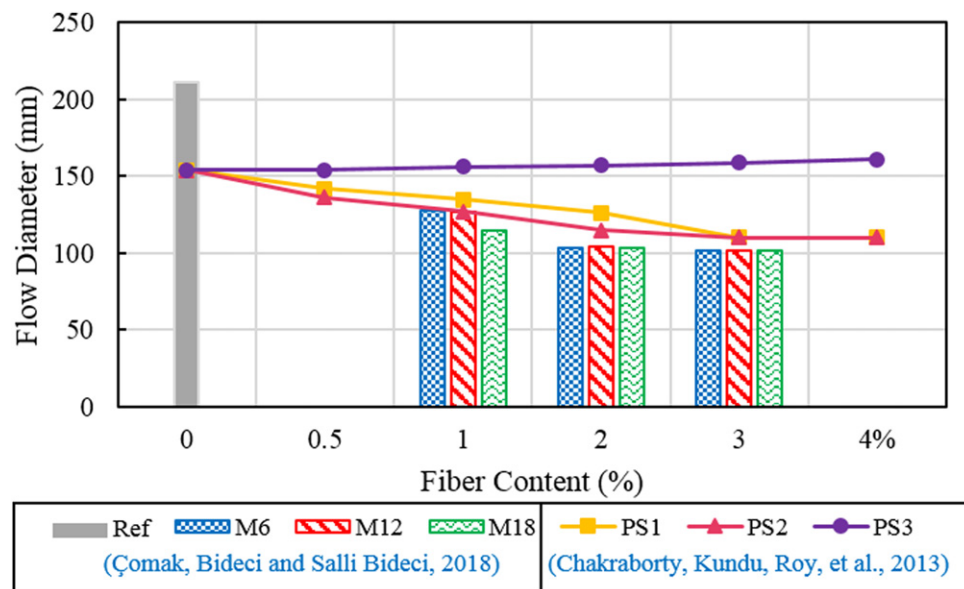


Fig. 13 Workability of cement mortar reinforced with: (i). Jute fibers (0%, 0.5%, 1%, 2%, 3% and 4%) using three different mixing process (PS1, PS2 and PS3), (ii). Hemp fibers (0%, 1%, 2% and 3%) with different lengths (Ref:0 mm, M6:6 mm, M12:12 mm and M18:18 mm).

dry into either the cement slurry (PS1) or into the water (PS2). In both cases, (PS1) and (PS2), the amount of water required for hydration of the cement was reduced by the presence of the jute fibers, which, as mentioned earlier, have a hydrophilic nature. Therefore, the significant reduction of workability by using preparation processes PS1 and PS2 is due to the incomplete hydration process of the cement mortar. In process PS3, however, the jute fibers were already saturated. The required amount of water for cement hydration was not affected by the presence of fibers since they are wet. Therefore, the workability of the mortar mixture prepared using process PS3 showed similar workability as that measured for the control mortar specimen.

The key factors that affect the reduction of the workability in cement mortars are the aspect ratio and the volume fraction of the fibers. The reduction of the workability could be remedied by the pre-treatment of fibers to reduce the chemical components that absorb the water. The VF could be pre-wetted before inclusion in the mixture. Otherwise, the absorption rate of fibers could be considered when preparing fiber reinforced mortar mixtures by adding a determined extra amount of water (Onuaguluchi and Banthia, 2016).

Mechanical Properties of Cementitious Materials Modified With Vegetable Fibers

The mechanical properties of VF reinforced cementitious materials, as with other fiber-reinforced concrete (FRC), are affected by a large number of factors (American Concrete Institute (ACI), 2009). The main ones are:

- Type of fibers: sisal, hemp, jute, coir, date palm, etc.
- Morphology of fibers: length, diameter, transversal section.
- Type of fiber's inclusion: single fibers, bundle, strand.
- Fiber surface: smooth, rough, coating agent.
- Matrix properties: type of cement, size of aggregates, admixtures.
- Proportions of the different constituents: W/C ratio, fiber content, proportion of aggregates.
- Mixing process: type of mixer, sequence of constituent's addition, method of fiber incorporation, period and speed of mixing. Implementation method: vibration standard, extrusion.
- Curing condition: air, water.

In this section, the mechanical behavior of cementitious composites reinforced with VF will be discussed based on the previous studies available in the literature. More precisely, the mechanical behavior will be analyzed in terms of compressive and flexural strength.

Compressive Strength

According to many researchers (Kriker *et al.*, 2005; Ozerkan *et al.*, 2013; Hamzaoui *et al.*, 2014; Lima *et al.*, 2014; Al-Rifaie and Al-Niami, 2016; Tian *et al.*, 2016; Tioua *et al.*, 2017; Belakroum *et al.*, 2018), the compressive strength of cementitious materials is negatively affected by the inclusion of VF. For instance, Kriker *et al.* (2005) mentioned in their study that the compressive strength decreased by increasing both the content of fibers and their length. The compressive strength of the concrete specimen reinforced with 2% by volume of date palm fibers in which the fiber length is 15 mm represents 90% of the compressive strength when compared to the unreinforced concrete specimen. However, the specimen reinforced with 3% of fibers of 60 mm length represents 55% of the compressive strength of plain concrete. The authors attributed this decrease to the increase in the number of defects and the non-uniformity of fiber distribution.

In a similar study, Tioua *et al.* (2017) investigated the compressive strength of a self-compacting concrete reinforced with two volume fractions of date palm fibers (0.1% and 0.2% by volume) of two different lengths (1 and 2 cm). In this study, two different curing conditions were utilized (laboratory and hot-dry climate). The authors concluded that specimens cured in a hot-dry climate had a higher strength when compared to those cured in the laboratory after 1 day of being cured. This was due to the accelerating effect of the temperature on the hydration rate. Moreover, the specimens cured in the laboratory had a larger compressive strength after 7 and 28 days of being cured. However, in both curing conditions, the specimens containing date palm fibers had a lower compressive strength compared to the control specimen. The authors attributed this decrease to the increase of the porosity introduced by the date palm fibers.

Other parameters, such as the saturation degree of the fibers, could influence the compressive strength of cementitious composites reinforced with VF, which was indicated by Hamzaoui *et al.* (2014) in a study on the mechanical behavior of modified mortar using dry and wet hemp fibers. In this study, the compressive strength decreased in both cases when using dry or wet hemp fibers. Moreover, the dry hemp fibers caused a significant decrease when compared to wet hemp fibers.

A new green composite material containing a high amount of fly ash (fixed to cement at a rate of 1.6) and reinforced with three different volumes of bagasse fibers (3%, 8%, and 12% by volume) was mechanically investigated by Tian *et al.* (2016). By increasing the content of bagasse fibers, a significant reduction of the compressive strength in early age could be noticed. For instance, at the age of 7 days, the composite reinforced with 3% of bagasse fibers showed a compressive strength value of 24.24 MPa. This value dropped by 51.7% and by 43.52% for composites reinforced with 8% and 12% of bagasse fibers, respectively. The authors indicated that this high reduction in early age is related to the unsaturated hydration of cementitious composites, which is influenced by the uneven

Table 2 Various compressive strength results of different cementitious materials blended with different VF reinforcements

References	Type of fibers	Type of cementitious matrix	Dosage [%] (Length of fibers [cm])	Compressive strength [MPa]
(Al-Rifaie and Al-Niami, 2016)	Date palm	Plaster	2, 4, 6, 8 and 10	A gradual decrease with the increase of fibers
(Belakroum <i>et al.</i> , 2018)	Date palm	Lime	20, 35 and 50	A gradual decrease with the increase of fibers
(Kriker <i>et al.</i> , 2005)	Date palm	Concrete	0, 2, and 3 (15 and 60)	A gradual decrease with the increase of both dosage and length of fibers
(Ozerkan <i>et al.</i> , 2013)	Date palm	Cement mortar	0, 0.5, 1 and 2	Appropriate with 0.5% of fibers addition, a decrease beyond 0.5% of fibers addition
(Tian <i>et al.</i> , 2015)	Bagasse	green composite	3, 8 and 12	A gradual decrease with the increase of fibers
(Tioua <i>et al.</i> , 2017)	Date palm	SCC	0.1 and 0.2 (1 and 2)	A gradual decrease with the increase of fibers
(Hamzaoui <i>et al.</i> , 2014)	Dry and wet hemp	Cement mortar	1.1, 2.1 and 3.1	Reduced
(Çomak <i>et al.</i> , 2018)	Hemp	Cement mortar	1, 2, and 3 (6, 12 and 18)	improved
(Andiç-Çakir <i>et al.</i> , 2014)	Coir	Cement mortar	0.4, 0.6 and 0.75	A gradual improvement with the increase of fibers

distribution of water due to the hydrophilic nature of bagasse fibers. Nevertheless, the change in compressive strength of the composites at the age of 28 days became more stable.

Some studies mentioned that the addition of low quantities of VF could lead to beneficial results in compressive strength (Ozerkan *et al.*, 2013; Andiç-Çakir *et al.*, 2014; Çomak *et al.*, 2018).

Ozerkan *et al.*, (2013) noticed in a study related to the mechanical performance of cement mortar reinforced with date palm fibers that inclusion of 0.5% of date palm fibers has the desired effect on the compressive strength of cement mortar. This result was found due to the high compaction between the mortar matrix and the fibers, which led to a good homogeneity of this mix.

Andiç-Çakir *et al.* (2014) tested cement mortar composites prepared with the use of fine aggregates and coir fibers with an addition ratio of 0.4%, 0.6% and 0.75% by weight of the total mixtures. The authors indicated that the increase of coir fibers led to an increase in compressive strength, and this increase varied between 3.64% and 14.25% for the reinforced specimens with untreated coir fibers. Moreover, an increase varying between 9% and 17.94% was achieved for specimens containing alkali-treated coir fibers.

A similar result was obtained in the experimental study performed by Çomak *et al.* (2018), in which the authors mentioned that VF could have a good effect on the compressive strength of cementitious materials. In this study, cement-based mortar incorporating hemp fibers with a fiber content ratio of 1%, 2%, and 3% with different lengths of 6, 12 and 18 mm was investigated. The authors recorded an increase in the compressive strength of up to 30%. The authors considered that the long fibers' orientation to sample length was found to be better and contributed to a much bigger increase in compressive strength.

The results obtained from different studies concerning the effect of VF reinforcement on the compressive strength of cementitious materials are summarized in Table 2.

Flexural Strength

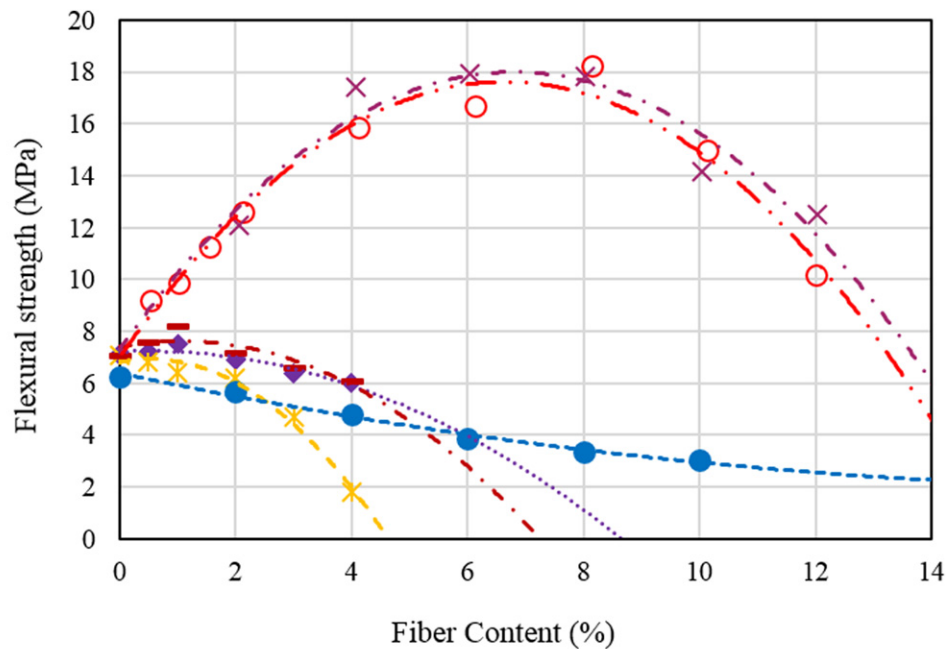
The studies carried out on the flexural behavior of the VF reinforced cementitious composites were highlighted. The plain matrix of cementitious composite presented a brittle linear behavior in flexural strength. The bio-composite samples, on the other hand, presented non-brittle behavior and continued to support a significant load after the maximum load. Sedan (2007) compared the mechanical properties of cement paste and cement matrix incorporating hemp fibers (16% by volume). For this purpose, three-point bending tests were carried out on these two materials after 28 days of being cured in water.

The author distinguishes that the bending behavior of the cementitious composite has three phases:

- Phase I: Quasi-linear behavior close to that of the cement paste specimen. In this phase, the efforts are mainly supported by the matrix.
- Phase II: Appearance of the first crack in the matrix just before reaching the peak load. Then, the forces are transformed to the fibers that support the load and in turn limit the propagation of the crack by their bridging effect.
- Phase III: Beyond the peak load (post-peak phase), the load decreases in a controlled manner, unlike the cement paste which breaks suddenly. The author associates this phase with a progressive rupture of the fiber/matrix interfaces, followed by the fibers pull-out.

The transition from a brittle matrix to a ductile composite material exhibiting controlled post-peak behavior is noted by all authors. However, this behavior transformation is not always accompanied by an improvement in flexural strength (Kriker *et al.*, 2005).

By analyzing the research studies carried out on the flexural behavior of cementitious materials reinforced with VF, it was noticed that the flexural behavior of these composites is related to the nature and the dimensions (aspect ratio) of fibers, the type of cementitious matrices, the dispersion of fibers in the matrix, and also to the preparation process that was adjusted to prepare the



(Chakraborty, Kundu, Roy, *et al.*, 2013)

Jute fibers with
Three Preparation processes PS1 PS2 PS3

(Coutts and Warden, 1992)

Pulped sisal fibers Soda pulping Kraft pulping

(Benaimeche, Carpinteri, Mellas, *et al.*, 2018)

Raw date palm mesh fibers

Fig. 14 Various flexural strength results of different cementitious materials containing different VF.

VF (raw, wet, treated). Some of the results obtained by different researchers are shown in **Fig. 14** (based on Chakraborty *et al.* (2013), Coutts and Warden (1992) and Benaimeche *et al.* (2018)).

Chakraborty *et al.* (2013) studied the mechanical influence of jute fibers with 4 volume fractions (0.5%, 1%, 2%, 3% and 4%) by using three different processes (PS1, PS2 and PS3) of preparing the fibers, which was described in Section “Fresh Properties of Cementitious Materials Modified with Vegetable Fibers”.

The authors concluded that using processes PS1 and PS3 contributed to an increase of the flexural strength with a corresponding increase of the amounts of jute fiber up to 1%. However, using more than 1% leads to a gradual decrease in flexural strength (see **Fig. 14**).

Regarding process PS2, the flexural strength was gradually decreased with the increase of fiber inclusion. The authors attributed this decrease to the agglomeration phenomena of fibers when using this process in the preparation (PS2). Among all the processes used, the PS3 process exhibited the best fiber dispersion. Therefore, the mortar specimens prepared according to PS3 showed the highest value of flexural strength, in which it was improved by 16% for 1% of jute fiber reinforcement when compared to the control specimen.

In the recent study performed by Benaimeche *et al.* (2018), the mechanical behavior of cement mortar reinforced with date palm mesh fibers as a raw material was investigated. The authors indicated that a reinforced mortar specimen with 10% of DPMF leads to a decrease of about 50% in flexural strength. Therefore, it can be concluded that the addition of date palm fibers as a raw material does not have a beneficial effect on flexural strength.

In the research studies performed by Coutts and Warden (1992), flexural strength was found to be improved when using up to 8% of fibers (see **Fig. 14**). This may be explained by the specific processes of the fiber’s preparation, such as the Kraft and pulping process, as well as due to the casting process of the specimen by using a dewatering method to remove the extra amount of water.

Although the fiber’s dosage had a significant influence on the flexural performance of the cementitious composites, the length of the fibers was also a parameter of influence. Tung *et al.* (2012) studied cement mortars reinforced with flax fibers (see **Fig. 15**). The authors mentioned that the flexural performances of the composite are directly related to the length of the flax fibers. Initially,

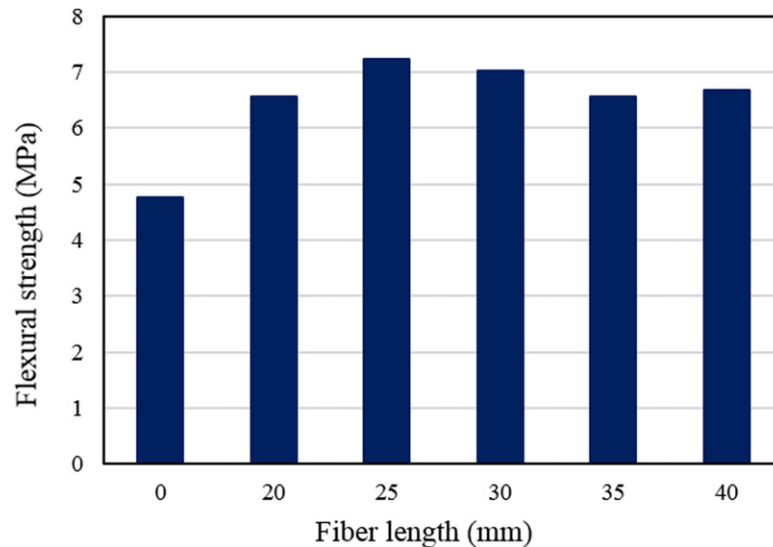


Fig. 15 Influence of the fiber's length on the flexural strength of cement mortars reinforced with flax fibers.

the increase in fiber length resulted in an increase in flexural strength. However, from a length value of 30 mm, which is considered as a critical value, the strength no longer increases and instead begins to decrease. Nonetheless, it is still higher than that of the control cement mortar.

Conclusion

Based on the reviewed papers, the general conclusion can be summarized as follows:

- The mechanical behavior of VF showed a big margin between the lower and the upper values due to the variety in their chemical components.
- The cellulose molecule governs the total behavior of the fiber. This is due to the crystalline structure it has when compared with the amorphous structure of hemicellulose and lignin.
- The moisture content of VF in nature rises by up to 17% according to the weather. When submerging VF in water, the moisture content can reach a value of 400%.
- The addition of VF negatively affects the fresh and hardened properties of cementitious materials, in which the flowability of reinforced fresh mortar decreases with the corresponding increase of fibers. This can be attributed to the hydrophilic nature of VF. Nevertheless, it gives better results when adopting such a mixing process in which the fibers are added wet to the mixture.
- The compressive strength of cementitious materials decreases due to the low density of applied fibers.
- In terms of flexural strength, the use of VF as a raw material showed a decrease in flexural strength. However, as shown in the literature, such a chemical treatment adopted for the fibers, and such preparation methods of the composites, could bring a significant improvement.

This article showed the ability to use vegetable fibers in cementitious materials. These fibers can be used in construction practice for, among others, non-structural building elements.

See also: Future Eco-Efficient Cements Prepared With Kaolinite-Based Industrial Wastes. Utilization of Waste Expanded Glass in Cement Composites. Valorization of Marble Waste in Cement-Based Materials

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Utilization of Waste Expanded Glass in Cement Composites

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Introduction

One of the existing civilization problem is the problem of energy consumption. According to the statistics published by [European Commission \(2018\)](#) recently buildings in the European Union (EU) are responsible for approximately 40% of the energy consumption in that region. As a consequence, environmental and economic restrictions are still increasing. One of the efforts for construction industry is to obtain more energy efficient construction materials. It can be done by improving their thermal insulation properties. According to the [European Commission \(2018\)](#) the EU has set a target for all new buildings to be nearly zero-energy by 2020. Therefore, it is very likely that the production of heat-insulating materials with improved thermal insulation properties will continue to grow.

Another existing civilization problem is a generation of huge amount of different kind of wastes. The utilization of these wastes each year is getting to be more expensive. Thus, companies must compete not only for the best price, quality and widest variety, but also in the area of environmental protection. For example the construction industry is improving sustainability by increasing the use of recycled aggregates in production of cement composites. Usually 60%–75% of concrete volume can be occupied by an aggregate. Therefore, even partial substitution of the natural aggregate with recycled material can give obvious environmental benefits. It results in reduction of production costs and because of the re-use of waste materials there is no need to pay environmental taxes and put them into landfill.

The remedy for the existing civilization problems can be the application of lightweight aggregate made from different kind of wastes. Lightweight aggregate is characterized by good thermal properties and is made from recycled products. Lightweight aggregate can be used for the production of lightweight concrete. It has been used since early days of Roman Empire. For example the Colosseum and the Pantheon were partly constructed with lightweight aggregate from crushed brick together with crushed lava and pumice ([Kralj, 2009](#)). Recently, the most frequently used lightweight aggregate are based on expanded clay, shale, vermiculite, perlite, polystyrene, different kinds of pelleted or sintered waste, including waste glass, silica sludge, sewage sludge ash and residue from the polishing process of different types of stone (see, e.g., [Ducman et al., 2002](#); [Ducman and Mirtiĉ, 2009](#)). They can be sourced from inorganic artificial products (e.g., expanded/foam glass made of recycled glass) and inorganic natural products (e.g., expanded clay, shale, perlite, etc.).

Glass has been used for decades in various applications. As a result of it a large amount of glass waste is being generated. Glass has very good properties. It is non-flammable, has high compressive strength and it is not permeable for water (or even air). In addition, it is considered as long living material. Unfortunately, this last advantage of glass is simultaneously its drawback while it creates serious utilization problem.

The first attempts to use glass as an aggregate in concrete has been undertaken almost 60 years ago. However, no success was then achieved due to problems caused by the alkali-silica reaction (ASR). ASR is caused by reaction between the reactive silica in glass and highly alkaline solution of the cement paste. It results in excessive expansion and microstructure degradation of cement composite. In the last few decades many studies were conducted to investigate the influence of the particle size and type of the used glass on the ASR. It was shown, that ASR can be reduced, or even eliminated, when ground waste glass with particle size up to 100 μm is used. According to [Shayan \(2002\)](#), ASR can be also reduced by using a suitable pozzolanic material such as metakaolin, silica fume, fly ash or ground blast furnace slag. As a result, grounded waste glass can be successfully used as an additive in cement composites. Nevertheless, the use of grounded waste glass help to solve only the pollution and utilization problems since its addition to cement composites do not improve their thermal properties. Therefore, it is better to use the waste glass in concrete as lightweight aggregate.

Highly porous glass in the form of expanded (foam) glass can be used as lightweight aggregate. It can be also used in the form of blocks, gravel (foam glass gravel) and expanded glass granules ([Manevich and Subbotin, 2008](#)). As pointed out by [Manevich and Subbotin \(2008\)](#), expanded glass in different forms can be used for insulating industrial refrigerators, marine oil terminals, ships, as foundations in permafrost conditions or in atomic energy, where the fire safety requirements are highly rigorous. Since expanded glass itself has poor mechanical properties, it is widely used as a one of the constituent of cement composites to create both, heat-insulating and construction material, utilizing wastes at the same time. However, as each material, expanded glass granules have their practical limitations when using them as one of the constituent of cement composites. Therefore, this work presents the possibilities of the expanded glass granules use in cement-based mixes in order to look at the latest developments and point out the future perspectives.

A Look on the Materials and Methods

Preparation of Expanded Glass Granules

Expanded glass granules are produced by mixing fine ground waste glass with a proper expanding agent and firing the mixture at a high temperature above the softening point of glass. It is of the primary importance to use an agent that degasses at a temperature higher than the glass softening point but still within the range where the viscosity of the glass is high enough to trap the gas inside

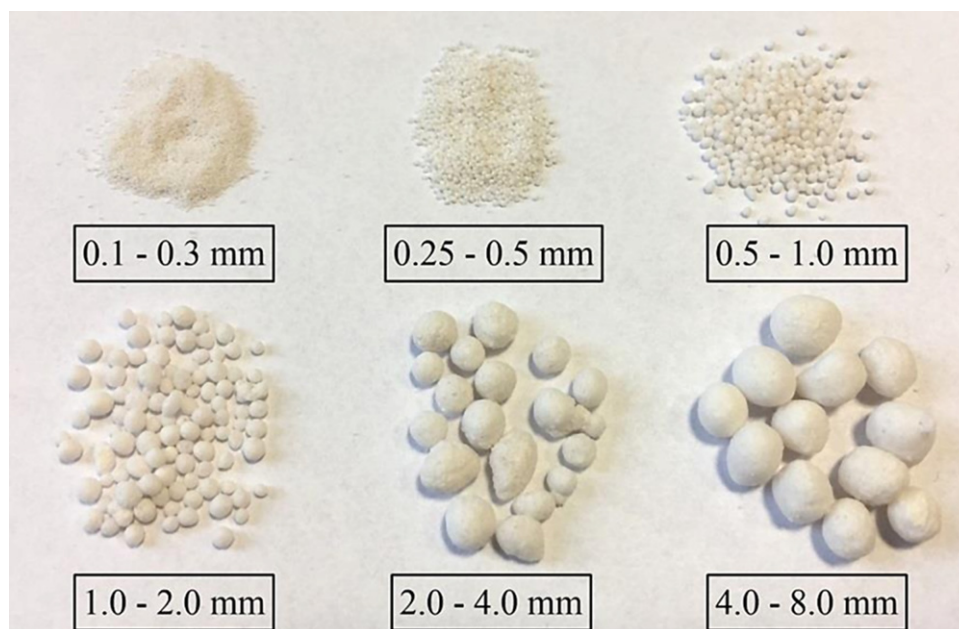


Fig. 1 Most commonly used fractions of expanded glass granules as lightweight aggregate.

(see, e.g., [Ducman et al., 2002](#)). According to [Limbachiya et al. \(2012\)](#), the most common temperature used is in the range from 700 to 900°C. As pointed out by [Ducman and Mirtiĉ \(2009\)](#) foaming agents are usually chosen from carbonates, sulphides, water-glass, SiC, Fe₂O₃ and MnO₂. To achieve a granulated structure of expanded glass, usually the glass-expansive agent mixture is granulated in drum and plate granulators, fluid or fluidized bed reactors, without or with a binder (see, e.g., [Ducman et al., 2002](#)).

For the production of expanded glass granules usually waste glass crushed and grinded to a particles size less than 100 µm are used. For this purpose mainly flat glass, vertically dawn sheet glass, colorless bottle, half-white, green glass or rolled glass can be especially used. As pointed out by [Manevich and Subbotin \(2008\)](#) after additional processing also brown containers, lead crystals, electric-lamp and kinescope glass can be suitable.

Evaluation of the Properties of the Expanded Glass Granules

In most studies the properties of expanded glass granules, such as bulk/apparent density, porosity, water absorption and thermal conductivity, were reported. The porosity of expanded glass granules can be evaluated using mercury porosimetry, helium pycnometry and graphical analysis of the scanning electron microscope images. In addition, some other properties such as alkali-silica reactivity, compressive strength, crushing resistance, sound absorption coefficient and pore diameter were reported. Most properties were evaluated using standard procedures. In [Ducman et al. \(2002\)](#) alkali-silica reactivity was determined by the ASTM chemical test ([ASTM C 289, 1994](#)). Structure investigation like pore diameter evaluation was mainly conducted using scanning electron microscope or optical microscope.

The properties of expanded glass granules highly depend on the granule size. Therefore, it is important to measure each property separately for each granule size. Also the knowledge on the particle size distribution is crucial. Usually, the following granule sizes are used: 0.1–0.3, 0.25–0.5, 0.5–1.0, 1.0–2.0, 2.0–4.0 and 4.0–8.0 [mm] (see [Fig. 1](#)).

Amount of Substitution of Natural Aggregate With Expanded Glass Granules in Mortar and Concrete Mixes

Because of different sizes of expanded glass granules they can replace both, fine and coarse natural aggregate. Therefore, expanded glass granules, as the lightweight aggregate, are used in the production of mortar and concrete, depending on the size of granules. Full and partial substitution of natural aggregates by expanded glass granules were reported in various references. Applied ratio between the mass of the cement and the mass of expanded glass granules (c/EGG ratio), used size of the expanded glass granules (particles diameter, ϕ) as well as produced type of cement composite (mortar or concrete) reported in the literature are summarized in [Table 1](#). In addition, [Table 1](#) is supplemented with the value of the mass of expanded glass granules per 1 m³ of the cement composite to show the utilization amount of the waste glass in mortar/concrete.

Preparation and Curing of Mortar and Concrete With Expanded Glass Granules

The design, preparation and casting of cement-based mixes containing expanded glass granules are similar to the normal cement composites. However, higher water absorption of lightweight aggregate in comparison with natural aggregate can have a negative

Table 1 Produced composite type, diameter (ϕ) of expanded glass granules, c/EGG ratio and expanded glass granules content reported in the literature

Reference	Type of composite	ϕ [mm]	c/EGG ratio [dimensionless]	Content of expanded glass granules [kg m ⁻³]
Ducman <i>et al.</i> (2002)	Mortar	1.00–3.00	4.50	–
Kralj (2009)	Concrete	1.00–8.00	1.05	–
Liu <i>et al.</i> (2010)	Concrete	1.18–4.75	3.96–4.46	112–150
Limbachiya <i>et al.</i> (2012)	Mortar and concrete	0.10–20.0	0.12–0.30	9–875
Bumanis <i>et al.</i> (2013)	Concrete	0.25–5.60	1.23	220
Yu <i>et al.</i> (2013)	Concrete	0.10–4.00	2.11–3.10	135–202
Yu <i>et al.</i> (2015)	Concrete	0.25–8.00	1.53–2.12	205–212
Yu <i>et al.</i> (2016)	Concrete	0.10–8.00	1.17	299

Table 2 The cement type, w/c ratio and additives used in mortar and concrete mixes reported in the literature

Reference	w/c ratio	Cement type	Additives
Ducman <i>et al.</i> (2002)	0.39	–	–
Kralj (2009)	0.70	CEM II/A-S 42.5R	Air-entraining agent
Liu <i>et al.</i> (2010)	0.30–0.50	CEM I	Superplasticizer, silica fume, expanded clay
Limbachiya <i>et al.</i> (2012)	0.40–0.76	CEM I 42.5N	Fine and coarse natural aggregate
Bumanis <i>et al.</i> (2013)	0.92	^a	Limestone powder, chemical admixtures
Yu <i>et al.</i> (2013)	0.38–0.59	CEM I 52.5N	Natural aggregate, limestone powder, superplasticizer
Yu <i>et al.</i> (2015)	0.50–0.72	^b	Limestone powder, nano silica, superplasticizer, air-entraining agent
Yu <i>et al.</i> (2016)	0.40	CEM I 52.5R	Polypropylene fibers, ether-based superplasticizer

^aCEM I 42.5R, CEM I 42.5N, CEM II/A-LL 42.5R, CEM II/A-LL 42.5N, CEM II/A-M (S,L,L) 42.5N, CEM I 52.5R, CEM I 52.5N.

^bCEM I 52.5N, CEM II/B-V 42.5N, CEM III/A 52.5N, CEM V/A (S-V) 42.5N.

influence on the workability of the fresh mix since it can absorb a certain amount of water from the mixture. To overcome this problem, two methods are widely used, i.e., pre-soaking the lightweight aggregate in water or using higher water to cement (w/c) ratio to compensate for the absorption of aggregate. In most cases of mortar and concrete with expanded glass granules production, the latter method is applied (see, e.g., Bumanis *et al.*, 2013) or no extra water is added when lightweight aggregate with low absorption is used (Yu *et al.*, 2013).

Because of the possible ASR reaction, low-alkali cement contacting low amount of Na₂O-equivalent is sometimes chosen when using waste glass as an additive. Nevertheless, in general, the use of different cement types can be found in various studies with no special reason or explanation. A comprehensive comparison of the cement type on the properties of lightweight concrete containing expanded glass granules was made in Bumanis *et al.* (2013) where eight different cement types were used.

Different additives are added into the mortar and concrete mixes, e.g., air-entraining agent, limestone powder, superplasticizer, nanosilica, etc. The cement type, w/c ratio and additives used in mortar and concrete mixes with expanded glass granules are shown in Table 2.

Mixing conditions are usually not given in details, but to prepare cement composites with expanded glass granules, standard procedures are usually used. For example, in Bumanis *et al.* (2013) all dry materials were mixed with hand mixer for 1.5 min, then 70% of water was added and all was mixed for another 1.5 min; finally, the rest of the water was added and mixing was continued for 2 min. In some cases also vibration was performed (see, e.g., Yu *et al.*, 2013).

Unfortunately, in most cases the proportions of the mixtures are not justified or designed with a proper care. Nevertheless, in few studies a particle packing model (the modified Andreasen and Andersen model) was applied in order to maximize the packing density of the granular solid materials (e.g., Yu *et al.*, 2013). It was shown, that optimized packing approach results in more compacted, homogeneous and characterized by lower porosity composite containing expanded glass granules.

Evaluation of Macroscopic Properties of Mortar and Concrete With Expanded Glass Granules

The properties evaluation of mortar and concrete with expanded glass granules are usually made by standard procedures adopted for conventional mortar and concrete specimens. The properties are usually evaluated for the fresh mixes and hardened samples after 28 days.

The following properties of fresh lightweight aggregate can be found in literature: air content, slump workability, consistence of fresh mortar by flow table method, density or compacting factor. In turn, the following properties are most commonly evaluated for hardened samples: density, water absorption, compressive strength, flexural strength, modulus of elasticity (static or dynamic) and thermal conductivity. As mentioned before, because of high content of SiO₂ in expanded glass it is possible that it may react expansively with alkalis in the cement. Therefore, alkali-silica reactivity have to be also measured. ASR is usually determined by testing mortar bars immersed in a 1 M sodium hydroxide solution for 14 days at the temperature of 80°C according to ASTM C1260-01 (2003).

Evaluation of Microscopic Properties of Mortar and Concrete With Expanded Glass Granules

Macroscopic properties depend on the properties of the cement paste, aggregates and the interfacial transition zone. Therefore, the properties of the interfacial transition zone should also be investigated in the case of cement composites. Physical as well as chemical characteristics of expanded glass granules can strongly affect the properties of the interfacial transition zone. Physical process is caused by the water absorption. In turn, as pointed out by Yu *et al.* (2013), chemical process can be caused either by pozzolanic reaction (between expanded glass granules and the alkaline solution) or an impregnation process (deposit of hydroxide in the pores of lightweight aggregate). The physical process occurs mostly in early age while chemical process occurs at later age.

Microstructure of mortar containing expanded glass granules (including interfacial transition zone) was usually investigated by the scanning electron microscope. However, some more sophisticated method was also used, i.e., X-ray micro-computed tomography (Lanzón *et al.*, 2012).

A Look on the Recent Results

Properties of Waste Expanded Glass Granules

The pores of expanded glass granules to some extent are interconnected, but most of them are separated and closed in the form of a honeycomb. It was shown in Yu *et al.* (2013) that expanded glass granules are not homogeneous because their pore sizes decrease closer to the outer surface and outer surface is mostly closed. Usually, the porosity of expanded glass granules can vary from 77% to 89%. However, in Limbachiya *et al.* (2012) expanded glass granules with much lower porosity (45%–48%) were used. The most commonly reported properties of expanded glass granules are presented in Table 3. The parameters were evaluated by authors themselves or the data was taken from the manufacturer. Note that, the measurement of very fine particles of expanded glass granules are subject to larger measurement error, e.g., water absorption evaluation (for more details see Liu *et al.*, 2010) in comparison with coarse expanded glass granules particles.

It can be seen in Table 3, that expanded glass granules are characterized by very low density (bulk density in the range 0.14–0.56 [g cm⁻³]), low thermal conductivity (0.069–0.071 [W m⁻¹ K⁻¹]) and high strength (crushing resistance up to 3.5 MPa). Despite the high discrepancies in water absorption results, in most cases the water absorption of expanded glass granules after 1 h is between 0.6% and 12%. In addition, expanded glass is a fire-resistant material with a very long lifetime in comparison with other heat-insulating materials. Temperature of use of expanded glass granules can reach 600°C.

Most properties of expanded glass granules depend on their density and granule size. In general, with increasing granule size of expanded glass granules their bulk density, thermal conductivity, compressive strength and water absorption decrease according to one of the manufacturer data (JSC Stikloporas, 2018, M. K. Čiurlionio g. 111, LT 66161 Druskininkai, Lithuania) (see Fig. 2).

Despite the many advantages of expanded glass granules, the alkali-silica reactivity tests of expanded glass granules according to ASTM C 289 (1994) showed that they are highly reactive and are the additional source of alkalis (Ducman *et al.*, 2002). Therefore, some precautions have to be taken when using expanded glass granules as lightweight aggregate in cement composites.

Properties of Fresh Mortar and Concrete Mixes With Expanded Glass Granules

Various mixes can be found in the literature characterized by fresh densities in the range 0.73 g cm⁻³ (Bumanis *et al.*, 2013) to 2.39 g cm⁻³ (Limbachiya *et al.*, 2012), slump workability from 30 mm (Limbachiya *et al.*, 2012) to 460 mm (Yu *et al.*, 2015) and flow table from 168 mm (Bumanis *et al.*, 2013) to 348 mm (Yu *et al.*, 2016). It was shown, that, in general, the use of lightweight aggregate made of waste glass has negligible effect on concrete workability (initial slump) but the compacting factor can decrease over time when lightweight aggregate content increases due to its higher water absorption capacity in comparison with standard aggregate (Limbachiya *et al.*, 2012).

Table 3 The diameter (ϕ), apparent and bulk density, water absorption, thermal conductivity as well as compressive strength of expanded glass granules reported in the literature

Reference	ϕ [mm]	Apparent density [g cm ⁻³]	Bulk density [g cm ⁻³]	Water absorption after 1 h (by mass) [%]	Thermal conductivity [W m ⁻¹ K ⁻¹]	Compressive strength [MPa]
Ducman <i>et al.</i> (2002)	1.00–3.00	0.15–0.22	–	11	–	–
Kralj (2009)	0.25–16.0	0.27–0.59	0.14–0.34	–	0.070	0.80–2.60
Liu <i>et al.</i> (2010)	< 4.75	–	0.35–0.56	3–12 (28–52) ^a	–	–
Limbachiya <i>et al.</i> (2012)	0.10–20.0	0.95–1.85	0.45–0.55	3.7–6.5 (mass?)	–	–
Bumanis <i>et al.</i> (2013)	0.25–5.60	–	0.19–0.23	up to 50	0.069–0.071	0.75–0.80
Yu <i>et al.</i> (2013)	0.10–4.00	0.31–0.81	–	0.6–1.7 (2.8–8.5) ^a	–	–
Yu <i>et al.</i> (2015)	0.25–8.00	0.30–0.54	0.17–0.30	–	–	2.00–2.90 ^b
Yu <i>et al.</i> (2016)	0.10–8.00	0.30–0.81	0.17–0.45	0.6–1.7 (2.8–9.1) ^a	–	2.00–3.50 ^b

^aAfter 24 h.

^bCrushing resistance.

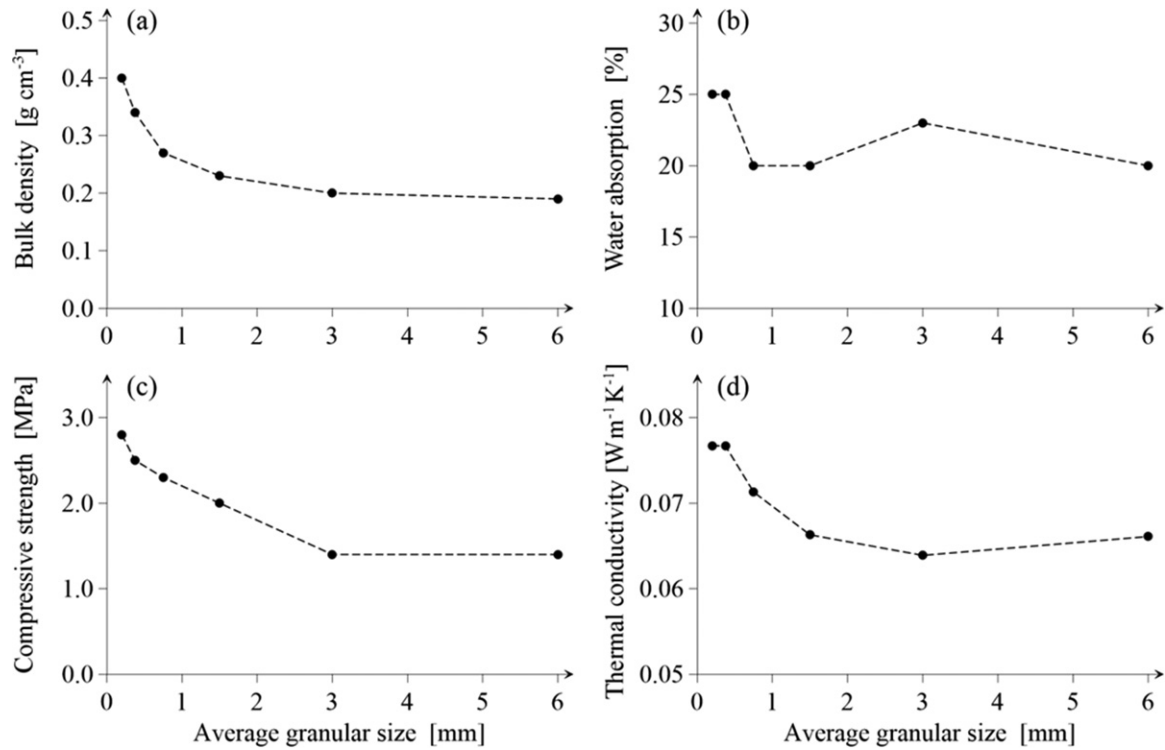


Fig. 2 The size of expanded glass granules and their corresponding parameters, i.e., (a) bulk density, (b) water absorption after 24 h, (c) compressive strength and (d) thermal conductivity.

Table 4 Dry density, water absorption, thermal conductivity, compressive/flexural strength at 28 days and ASR linear strain for hardened mortar/concrete with expanded glass granules reported in the literature

Reference	Dry density [g cm ⁻³]	Water absorption [%]	Thermal conductivity [W m ⁻¹ K ⁻¹]	Compressive strength at 28 days [MPa]	Flexural strength at 28 days [MPa]	ASR linear strain [%]
Ducman <i>et al.</i> (2002)	–	–	–	–	–	[–] 0.036–0.082
Kralj (2009)	0.58	–	0.180	4.5	–	–
Liu <i>et al.</i> (2010)	1.31–1.39	13.6–17.1	–	21.0–24.0	–	–
Limbachiya <i>et al.</i> (2012)	–	–	–	5.0–48.5	2.9–6.1	[+] 0.055–0.100
Bumanis <i>et al.</i> (2013)	0.49–0.56	–	–	2.8–4.0	1.0–1.5	[+] 0.160–0.205
Yu <i>et al.</i> (2013)	1.28–1.49	–	0.485–0.847	23.3–30.2	6.4–8.0	–
Yu <i>et al.</i> (2015)	0.65–0.70	–	0.120–0.130	10.0–12.2	–	–0
Yu <i>et al.</i> (2016)	0.72–0.75	30.6–35.0	0.160–0.171	11.8–14.5	3.0–4.5	–

Macroscopic Properties of Hardened Mortar and Concrete With Expanded Glass Granules

The properties of hardened cement composites with expanded glass granules reported in the literature are summarized in [Table 4](#). In specific, the properties such as dry density, water absorption, thermal conductivity, compressive/flexural strength at 28 days and ASR linear strain are presented.

As it can be seen, cement composites with expanded glass granules differ from regular concrete in a number of aspects such as improved thermal conductivity and lowered density. However, it is characterized by lower compressive and flexural strength as well as decreased modulus of elasticity.

The upper limit of the density of lightweight concrete is equal to 2 g cm⁻³ ([EN 13055-1, 2002](#)). Lightweight concrete is categorized to 3 grades: low density concrete (also referred as ultra-lightweight, super-lightweight or infra-lightweight concrete) with a dry density <0.8 g cm⁻³, moderate strength concrete with a dry density in the range 0.8–1.4 [g cm⁻³] and structural concrete with a density between 1.4 and 2.0 [g cm⁻³]. Therefore, it can be seen that in many cases expanded glass granules was used to produce ultra-lightweight concrete (see [Table 4](#)). Ultra-lightweight concrete is mainly used for insulation purposes because

of its low compressive strength. However, nowadays, when properly designed, ultra-lightweight concrete with moderate compressive strength (10.0–12.2 [MPa]) can be found in the literature (Yu *et al.*, 2015).

In general, three main approaches are used when utilizing expanded glass granules in cement composites. The first approach is to utilize waste glass while still remaining high properties of mortar/concrete. In this case high compressive strength was obtained (more than 20 MPa) while having much lower thermal conductivity (usually from 0.485 to 0.847 [$\text{W m}^{-1} \text{K}^{-1}$]) than ordinary concrete and lower density by about 25%–45%.

The second approach is to create the composite characterized with as low thermal conductivity as possible. In these cases the compressive strength is not the most important parameter. For example, ultra-lightweight concrete with expanded glass granules characterized by thermal conductivity equal to 0.12 $\text{W m}^{-1} \text{K}^{-1}$ and 28-day compressive strength of 10 MPa was obtained in Yu *et al.* (2015).

The last main approach is to produce the cement composite characterized with the highest ratio between mechanical and thermal properties. The modified Andreasen and Andersen packing density model seems to be very useful for this purpose. One of the best example is ultra-lightweight concrete reinforced by polypropylene fibers characterized by the compressive strength equal to 14.5 MPa and thermal conductivity equal to 0.165 $\text{W m}^{-1} \text{K}^{-1}$ (Yu *et al.*, 2016). Based on the literature data, Fig. 3 presents relationship between compressive strength and thermal conductivity of lightweight concrete containing expanded glass granules in comparison with other types of lightweight concrete.

According to Limbachiya *et al.* (2012) the lightweight aggregate made of waste glass do not affect the carbonation depth in comparison with standard aggregate. In addition, expanded glass granules can have positive effect when used as an additive in lightweight concrete production, e.g., faster increase of strength at early ages (Limbachiya *et al.*, 2012). In addition, lightweight concrete with expanded glass granules have lower open porosity and capillary water absorption in comparison with lightweight concrete with expanded perlite (Lanzón *et al.*, 2012) as well as higher resistance to water and chloride-ion penetration compared with lightweight concrete with expanded clay of even higher unit weights and regular concrete (Liu *et al.*, 2010).

Although the expanded glass granules are highly reactive, in many cases they do not cause significant expansion (ASR linear strain, see Table 4) and cracks in the mortar. Cement mortar tested in Ducman *et al.* (2002) achieved -0.047% of linear strain after 6 months of exposure (shrinkage instead of expansion). It was explained in Ducman *et al.* (2002) by the high porous structure of the glass aggregate that can accommodate the high amount of gel produced. The same conclusion can be found in Limbachiya *et al.* (2012) where authors showed that the silica gel formed can dissipate through the porous structure of expanded glass when using up to 50% of it instead of standard aggregate. On the contrary, in the paper (Bumanis *et al.*, 2013) it was shown that due to high expansion of lightweight concrete and strength loss, lightweight concrete with foam glass cannot be used in building industry even with low alkali (low Na_2O equivalent) cement (e.g., CEM I 52.5R) without additional operations to prevent deleterious reactions. However, a proper composition of concrete mix can lead to ultra-lightweight concrete with expanded glass granules without the risk of the alkali-silica reaction (see, e.g., Yu *et al.*, 2015). Laboratory results show that the use of air-entraining agent is an effective method to reduce or eliminate the ASR expansion since the expansive reaction products can permeate into additional pores.

Microscopic Properties of Hardened Mortar and Concrete With Expanded Glass Granules

The microstructure investigation using scanning electron microscope in Liu *et al.* (2010) shown improved interfacial transition zone between expanded glass granules and cement paste compared with conventional concrete containing natural aggregate. Micro-computed tomography investigation performed by Lanzón *et al.* (2012) confirmed good adhesion (no cracks or discontinuities in the interfacial transition zone) of expanded glass granules to the cement paste. Good quality of the interfacial transition zone can be caused by the fact, that expanded glass granules absorb a certain amount of water (higher than natural aggregate) and as a result in the surrounding cement paste there is reduced w/c ratio.

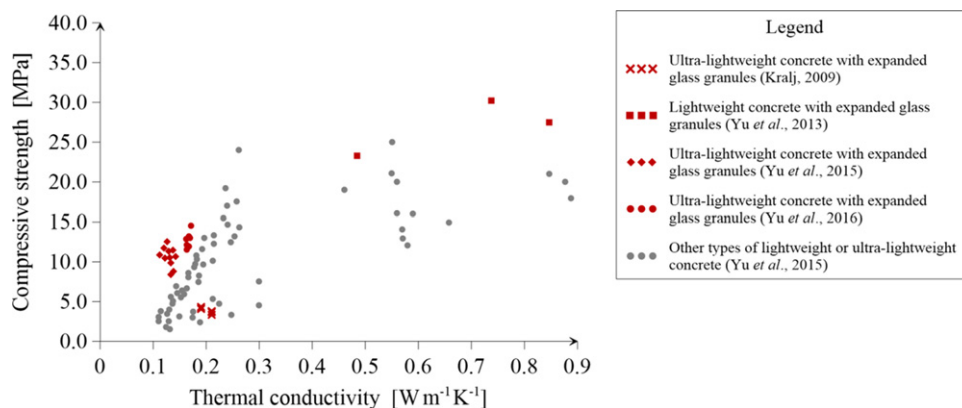


Fig. 3 Relationship between the compressive strength and the thermal conductivity of lightweight concrete containing expanded glass granules (in comparison with other types of lightweight concrete).

Nevertheless, in most studies the interfacial transition zone investigation was only qualitative in nature, based mostly on visual observation. Therefore, more quantitative analysis should be made, using scanning electron microscope, micro-computed tomography or nanoindentation, to better understand the physical and chemical processes that take place in interfacial transition zone in cement composites with expanded glass granules.

Conclusions and Perspectives

Waste glass in the form of expanded glass granules can be successfully considered as the lightweight aggregate in cement composites. Main three approaches seems to be the most suitable for waste glass utilization in cement composites:

- Utilize waste glass while still remaining high properties of cement composite (usually small amount of waste glass can be utilized),
- Produce the cement composite characterized with the highest ratio between mechanical and thermal properties (moderate amount of waste glass utilization),
- Create the cement composite characterized with as low thermal conductivity as possible (highest value of waste glass utilization).

Such composites differ from regular concrete in a number of aspects. Their main advantage is that they show a low thermal conductivity while still retaining good mechanical strength. In addition, crushed lightweight concrete with expanded glass granules may be used for further production of concrete what is proven in [Kralj \(2009\)](#). However, when producing this type of composite, the alkali-silica reaction should be always taken into account and a proper precautions should be considered.

Lightweight concrete with expanded glass granules can be used in high-rise buildings, long span bridges, buildings where soil conditions are poor, or specialized structures as offshore platforms, floating and marine structures (see, e.g., [Liu et al., 2010](#); [Yu et al., 2016](#)).

Based on the literature it can be seen that the following research should be undertaken for better understanding of the lightweight concrete with expanded glass granules:

- Parameters of hardened mixes should be investigated at early ages and after a longer times (usually the parameters of hardened mixes are evaluated only after 28 days of curing),
- More quantitative analysis of microstructure should be done to better understand the physical and chemical processes that take place in the interfacial transition zone,
- More research except [Huiskes et al. \(2016\)](#) using geopolymer as the binder instead of cement should be done in order to improve thermal properties of composite containing expanded glass granules. In addition it can create another possibility to overcome the problem of ASR,
- An attempt to correlate the micro- and macro-properties should be undertaken to more efficiently design the composition of composite with expanded glass granules.

See also: Future Eco-Efficient Cements Prepared With Kaolinite-Based Industrial Wastes. Valorization of Marble Waste in Cement-Based Materials

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Valorization of Marble Waste in Cement-Based Materials

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Nomenclature

f_{cd} Compressive strength
MGR Marble granite residue
MP Marble powder
MS Marble sludge
MSD Marble stone dust
OPC Ordinary Portland cement

PCC Portland composite cement
RH Relative humidity
SCC Self-compacting concrete
WMD Waste marble dust
WMP Waste marble powder
WMS Waste marble slurry
 γ_{ad} Apparent density

Introduction

The cement production typically requires about 3.2–6.3 GJ of energy and 1.7 tons of raw materials (chiefly limestone) per ton (t) of clinker produced (Oss and Padovani, 2003). Moreover, it is followed by a significant emission of carbon dioxide (CO₂), and also nitrogen oxides, sulfur oxides and particulates. The average intensity of carbon dioxide emissions from total global cement production is 222 kg of C/t of cement (Worrell *et al.*, 2001). For these reasons, the worldwide cement production has known recently high interest toward the mineral addition in attempts to reduce the clinker manufacture activity.

In order to minimize the polluting and the expensive industrial process, the mineral additions could be found abundant in the nature. In particular, it could be found as the natural pozzolana from (a deposit of pumice ash or tuff, the explosive volcanic eruption, and opaline shales, rice husk ash and metakaolin) (Ciuperca, 2018). In addition, it could be manufactured as a fly ash which is a by-product that is obtained during the combustion of pulverized coal in the electric generation process. Moreover, another type of addition could be cited that is created during the quarrying operations of the aggregate materials and the ornamentals stone. Large quantities of fine by-products wastes generated such as quarry dust and marble sludge, which cause serious environmental problems. This fine by-product waste is basically a limestone material which is extensively used recently as cement replacement material or as fine aggregates (Galetakis and Soutana, 2016). The waste generated from the marble industry can represent as much as 80%–90% of the total extracted soil and stone (Sardinha *et al.*, 2016).

The present article reviews the recent contributions which deal with the valorization of marble powder in the cement-based materials. In particular, it focuses on the historical overview of the marble production and the marble wastes generated in some valorization domains as well as its physical, chemical and mineralogical composition. Finally, it summarizes the effect of the use of marble powder as cement substitution on the properties of fresh and hardened cement-based materials.

Historic Overview

The Romans discovered marble stone (Fig. 1). At first, they were used for religious architectural achievements like statues of deities, temples, tombs, and after a while, they developed its industry from the manufacture of floors, cladding, sculptures, statues, and others as a building material. Its manufacture passes through several operations, shaping, sawing and polishing, during these operations, waste including marble powder are produced. This powder can be stolen in the air by wind effect; this can pollute the environment considerably and can threaten even agriculture and public health. These problems have stimulated researchers for recycled it; at the same time, in the construction branch, there are many problems, the cost of cement materials, gas emissions during cement production, the aggressive environment, so the first idea that came to researchers, which is the incorporation of the marble powder in the production of the cement-based materials. Bartoli and Bartoli (1965) incorporated the powder into the mortar composition as a partial substitution of OPC with a proportion of 1% to improve its properties. The researchers do not stop here, Burnett (1977) tries to prepare a mortar based on this powder by increasing its incorporation percentage up to 25%, this mortar is used for the repair of tiles ceramic (fill the joints between the porous edges). Research continued until 1982 when it came Sadler (1982) who proposed a mixture of mortar contains 6.7%–20% of marble powder to make this mixture more economical without noticeable degradation of its physical characteristics. Until now, researchers still want to develop building materials and minimize its cost by recycling this waste. The marble powder generally used by researchers Egyptians, Turks and Indians because the rate of marble waste is higher in their countries.

Marble stone

Since antiquity, marble has been widely used as a material for sculpture and architecture. Marble is a metamorphic rock derived from recrystallized limestone or dolomite sedimentary, composed mainly of calcium carbonate (CaCO₃) and magnesium

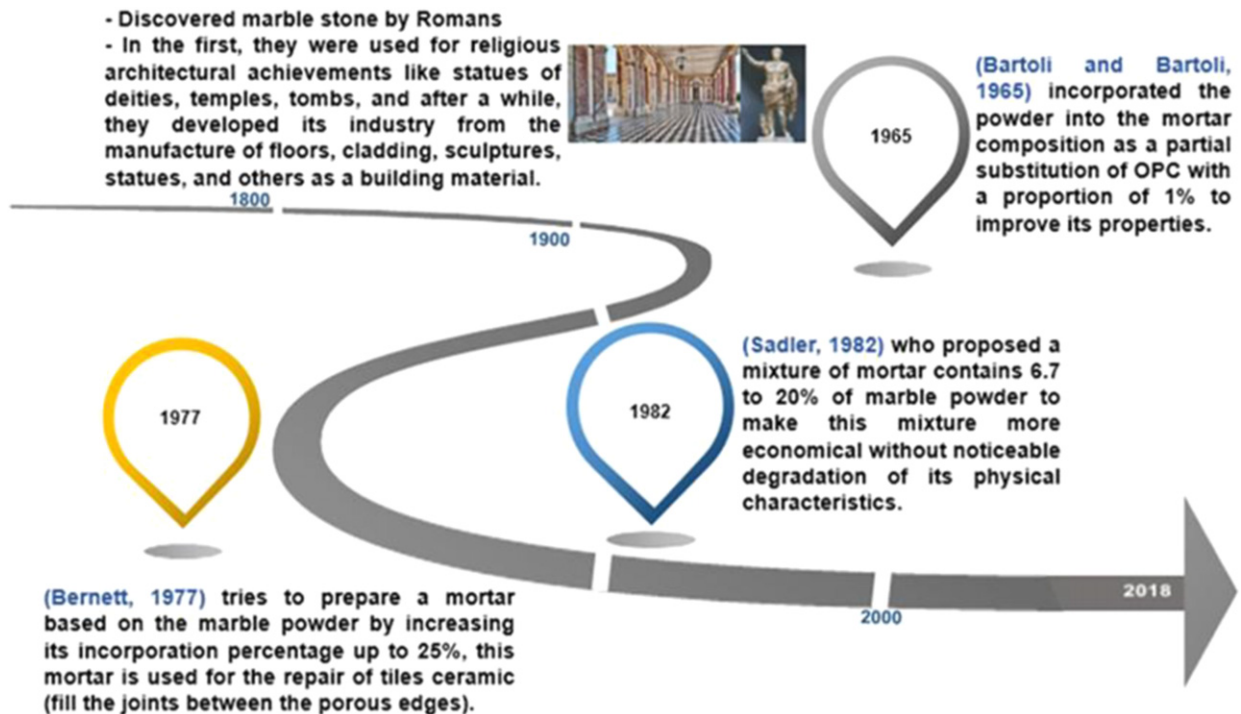


Fig. 1 Historic overview.

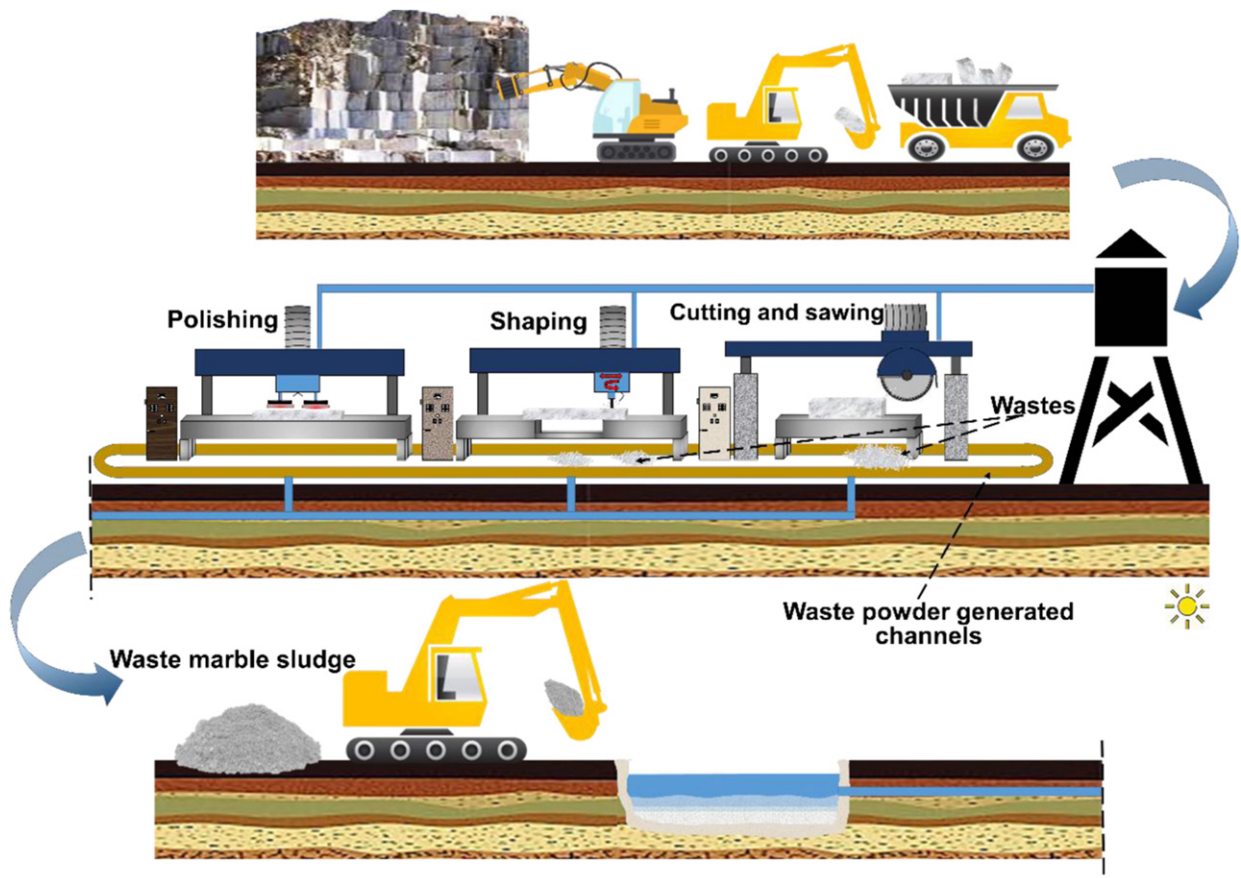


Fig. 2 Marble manufacture and waste generating process.

carbonate (MgCO_3). It is generated by the influence of the pressure, the temperature and the action of vapors that come from the deep parts of the globe.

Marble characterized by various colors, which are usually due to various mineral impurities such as clay, silt, sand, iron oxides, or chert that are originally present as grains or layers in the limestone (Ghosh *et al.*, 2008) but the white is the most common.

Application of marble stone

Because of its strength, durability, formability, architectural adaptability and aesthetic satisfaction, the marble has utilized throughout historic time as an important building material. Marble industry comprises two major branches; the first produces the carved marble, it is blocks or slabs that meet size and shape specifications. The application areas of carved marble include building stone, monumental stone, ashlar, wainscoting, veneer paneling, tiling, statuary and others. The second produces the crushed and ground marble, which ranges in size from large blocks to fine granular.

Marble powder

Marble powder is an inert material of pure limestone produced during the extraction and treatment of marble stones (Fig. 2). Since antiquity, it was used as a coating material due to its perfect impermeability and served as pigments.

Application of marble powder

The manufacture of marble pass through several stages: extraction, sawing, shaping and polishing that generate waste including marble powder.

The marble powder can be used in many branches, are as follows:

- Coating, decorative plaster, paint.
- Ceramic industry.
- Glass industry (used as mineral powders).
- Manufacture of paper (stone paper).
- Manufacture of plastic materials.

Advantages of marble powder

The marble powder has many advantages it can be mentioned:

- An economic and environmental interest by recycling that allows to reduce the pollution.
- Marble powder can be used as a coating material.
- Marble powder can be used as an additive in concrete and mortar to improve its mechanical properties.
- Marble powder can be used in the manufacture of limestone-cement.
- Possibility of mixing with many materials.

Disadvantages of marble powder

During the manufacturing processes of the marble stone, only 20%–25% of the final product (waste) is obtained. In addition, the marble stone is not available in all places.

The application, advantage and disadvantage of marble stone and marble powder are briefly shown in Table 1.

Table 1 Application, advantage and disadvantage of marble stone and marble powder

	<i>Application</i>	<i>Advantage</i>	<i>Disadvantage</i>
Marble stone	● Building stone, monumental stone and ashlar ● Wainscoting ● Veneer paneling ● Tiling ● Statues	● Strength ● Durability ● Formability ● Architectural adaptability ● Aesthetic satisfaction	● Expensive ● Not available in all places
Marble powder	● Coating, decorative plaster and paint ● Ceramic industry ● Glass industry (used as mineral powders) ● Manufacture of paper (stone paper) ● Manufacture of plastic materials	● Reduce the pollution. ● Used as a coating material ● Used as an additive in concrete and mortar ● Used in the manufacture of limestone-cement. ● Possibility of mixing with many materials.	● The waste obtained is ¼ of marble ● Not available in all places.

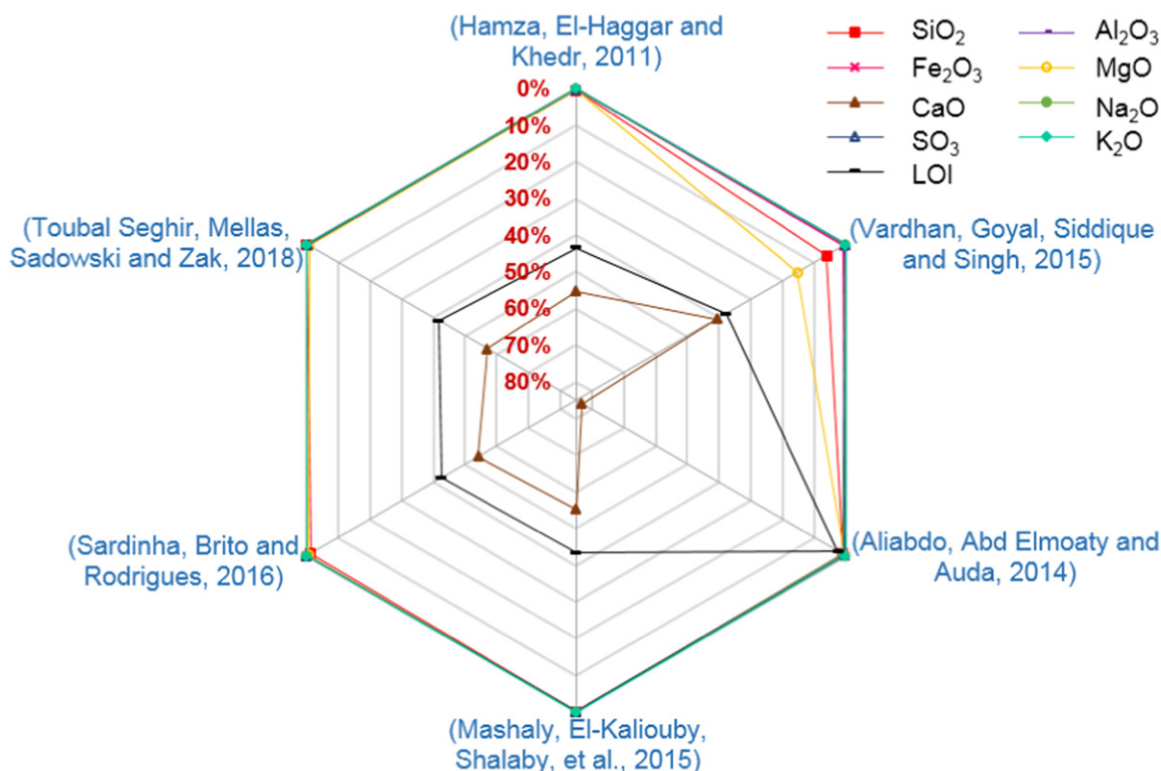


Fig. 3 Chemical analysis of marble powder used in the existing literature research.

Marble waste rate in some countries

Several researchers have estimated the amount of waste after the operations mentioned previously.

- In Turkey and exactly in the Afyon region about 340,000 tons of marble waste resulting from 409 marble processing plants that produce 19% of the total slab in Turkey (Celik and Sabah, 2008).
- In Brazil, the amount of waste left after the process of mining and the manufacture of ornamental stone can reach up to 40% of the total volume extracted, while the amount of waste after cutting and sawing operations can easily reach 20%–25% of the total block volume (Saboya *et al.*, 2007).
- In India, from the marble industries about 6 million tons/year of waste is released through cutting, polishing, processing and grinding operations (Pappu *et al.*, 2007).
- In Egypt, the industrial area of marble and granite processing “Shaq Al-Thoaban” produces about 800.000 tons/year of waste (Hamza *et al.*, 2011).

Chemical and Mineralogical Compositions of Marble Powder

Several studies have carried out on marble powder to know its chemical and mineralogical compositions for incorporating in the mixture of concrete and mortar as partial replacement of cement or sand in order to obtain a cement-based material having good properties and intended for construction.

Chemical compositions

The X-ray Fluorescence (XRF) diffraction is generally used for the chemical analysis quantitative. The chemical compositions of the MP used in some different studies are presented in Fig. 3. By examining the results indicated in this figure it can be seen that the main chemical component of the marble powder is Calcium oxide (CaO). In addition, it also indicated the presence of small amounts of Silicon dioxide (SiO₂), Magnesium oxide (MgO), Iron and Aluminum oxide (Fe₂O₃ and Al₂O₃), with a loss on ignition around 40%. The results shown in the figure reflect the typical composition of a marble which is mainly composed of the calcite (CaCO₃) and the dolomite (CaMg (CO₃)₂). The chemical analysis results of marble powder are briefly shown in Fig. 3.

The ternary diagram CaO–SiO₂–Al₂O₃ showing position of marble powder and other cementitious materials is shown in Fig. 4.

As can be seen from this figure, the main components of cement are CaO and SiO₂ and it has a small amount of Al₂O₃.

By comparison to the cement, the fly ash has a higher placement in the diagram. In this case, it can be mentioned that its main components are SiO₂ and Al₂O₃. The main components of blast furnace slag are identical as cement but with higher amounts.

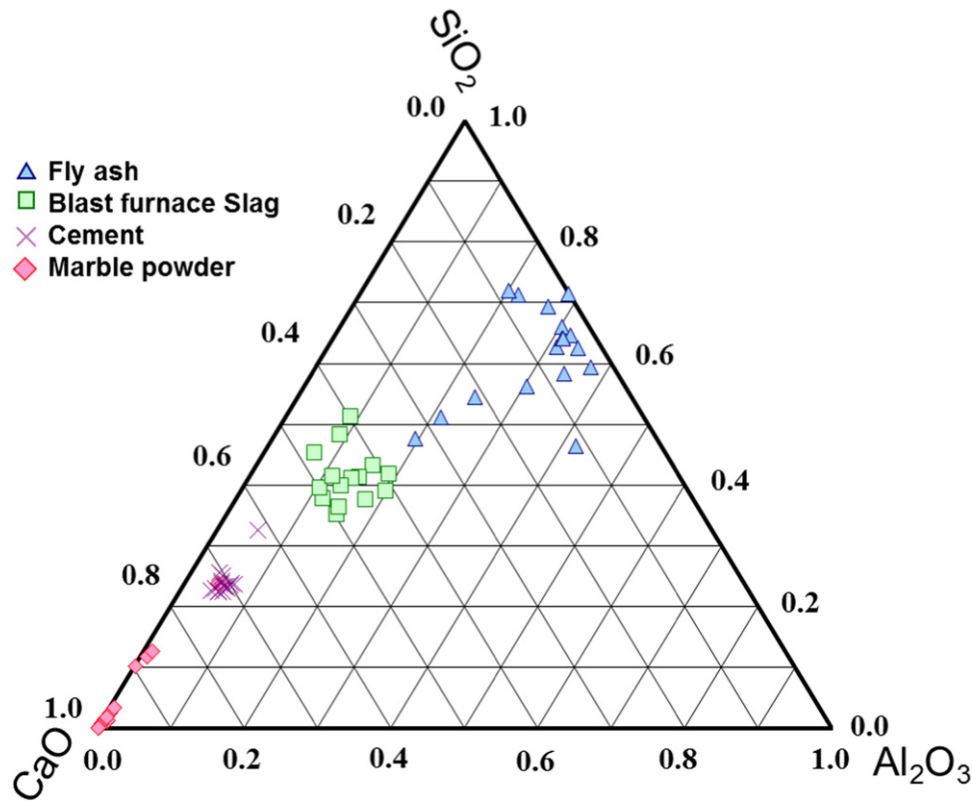


Fig. 4 Ternary diagram $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ showing typical position of marble powder and other cementitious materials.

By comparison to the other cement-based materials, the MP is located at the bottom of the diagram and its main component is CaO . Furthermore, it has minor amounts of SiO_2 and traces of Al_2O_3 . Thus, its utilization as a partial replacement of cement leads to an increase of CH content and a decrease of C-S-H, this is attributed to the excess of CaO provided by MP (Toubal Seghir *et al.*, 2018).

Mineralogical compositions

X-ray diffraction analysis (XRD) is usually used for the determination of the mineralogical composition of mineral powder as shown in the Fig. 5 (Toubal Seghir *et al.*, 2018). The majority of the recent studies indicated that the most dominant crystalline mineral of marble powder is mainly calcite (calcium carbonate CaCO_3) (Chaid *et al.*, 2011; Ergün, 2011; Mashaly *et al.*, 2015; Vardhan *et al.*, 2015; Toubal Seghir *et al.*, 2018).

Utilization of Marble Powder in the Manufacturing of Cement-Based Materials

The choice of a suitable formulation of a cement-based material requires a compromise between three objectives: facility of implementation defined by its workability, strength referred to different stages of maturation and durability with respect to physicochemical attack from the environment.

Marble powder (MP) can be used as a partial substitution of OPC in the concrete and mortar, its effect is expressed by the following:

Effect of Using Marble Powder on the Properties of Fresh Cement-Based Materials

Normal consistency and setting times

According to research performed by Aliabdo *et al.* (2014), which is presented in Fig. 6. The amount of water needed by each mixture is not so much varied from each other by using MP with a specific area about $3996 \text{ cm}^2/\text{g}$ as cement substitution up to 15%. In addition, the initial and final setting times of OPC pastes are not also affected, as shown in Fig. 4. The results are almost similar to that obtained by (Toubal Seghir *et al.*, 2018) which used the MP with a specific area about $3869.46 \text{ cm}^2/\text{g}$.

The increase of the MP fineness up to $6700 \text{ cm}^2/\text{g}$ increases the water requirement of all samples containing MP. However, as visible from the results published in the literature, there is a sudden reduction in the initial and final setting times as shown in Fig. 7. Nevertheless, the setting times of all OPC pastes are complying with the limits of ASTM C 150 (Mashaly *et al.*, 2015).

The results of the effect of cement substitution on the consistency and setting times are briefly shown in Table 2.

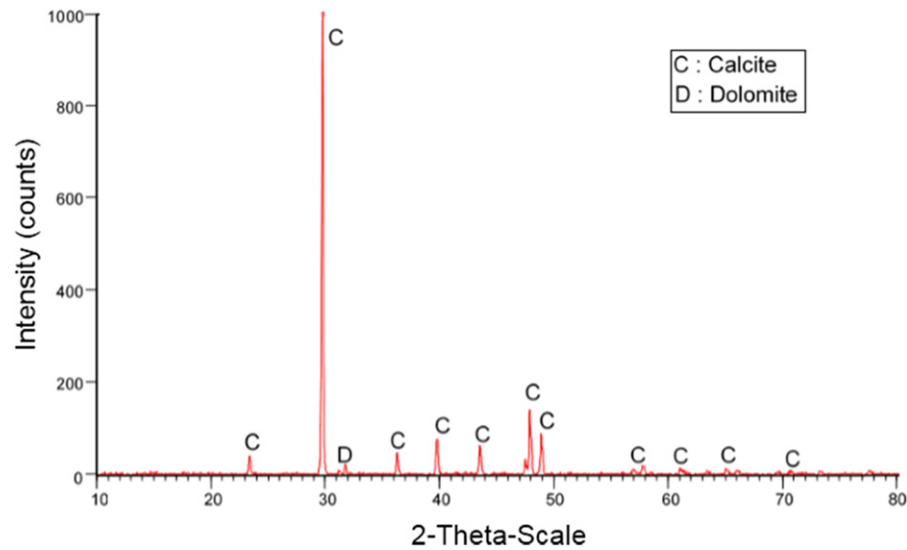


Fig. 5 Typical XRD pattern of marble powder.

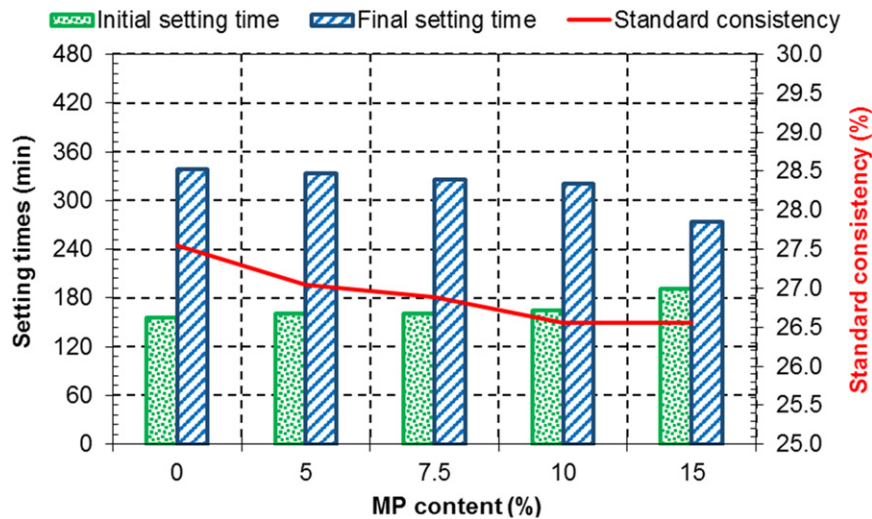


Fig. 6 Normal consistency and setting times.

Workability

The fluidity of the OPC pastes made by partially substituting cement with MP up to 50% at w/b ratios of 0.48, 0.50 and 0.52 was evaluated by marsh cone test; it is taken as the inverse of flow time. The literature results illustrated in Fig. 8 show that the maximum benefit of improved workability is achieved up to 10% of the added marble powder at w/b ratios of 0.50 and 0.52 where the flow time is almost identical (Vardhan *et al.*, 2015).

This ratio of substitution (10% MP) was used in the manufacturing of concrete by Ashish *et al.* (2016). The authors concluded that the use of MP with higher specific area leads to an increase of friction and a decrease of workability. Similarly, Rana *et al.* (2015) conducted a study on concrete mixes prepared with marble sludge (MS) at 0.38 w/c. On the other hand, Sardinha *et al.* (2016) indicated that the decrease of cement content using MS with lower specific area does not affect the workability.

The results of the effect of cement substitution on the workability are briefly shown in Table 3.

The density of the fresh cement-based material

In the research published in the literature it is visible, that the density of fresh concrete made with 0%, 5%, 10% and 20% of MP as cement substitution measured right after the mixes production slightly decreases as the substitution ratio increases (Fig. 9). This may be due to the fact that the MP has a lower bulk density than the cement (Sardinha *et al.*, 2016). On the contrary, Singh *et al.* (2017) concluded that the incorporation of WMS does not significantly affect the density of concrete.

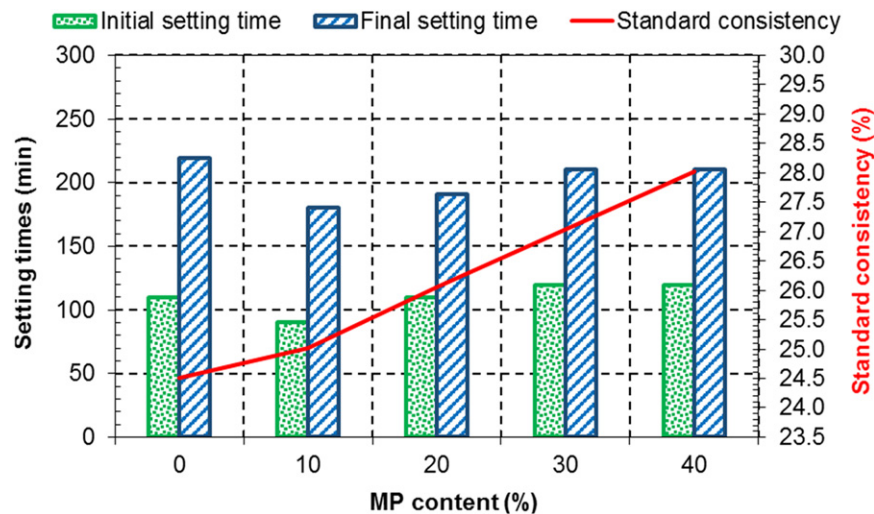


Fig. 7 Normal consistency and setting times of OPC pastes.

Table 2 Effect of cement substitution on water requirement and setting times

Researchers	Marble type	Fineness (cm ² /g)	Optimum (%)	Consistency	Setting times
Aliabdo <i>et al.</i> (2014)	WMD	3996	10	Slightly reduction	Ignored reduction
Mashaly <i>et al.</i> (2015)	MS	6700	20	Increase	Sudden reduction
Toubal Seghir <i>et al.</i> (2018)	MP	3869.46	10	Ignored increase	Ignored reduction

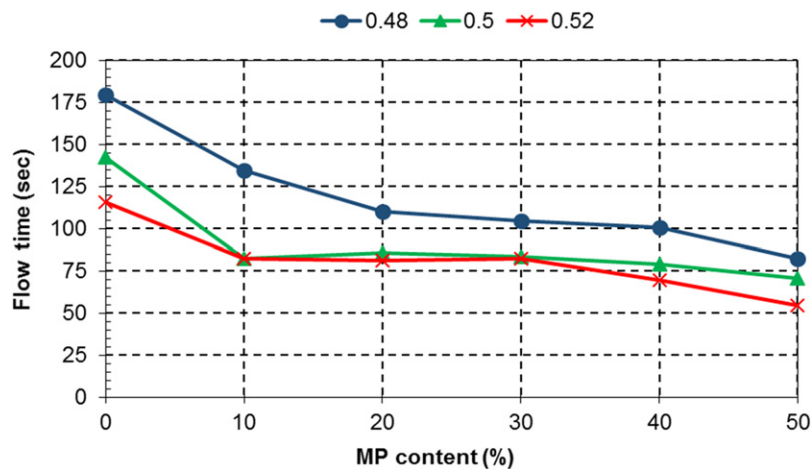


Fig. 8 Workability of OPC pastes at various replacement levels of MP.

Effect of Using Marble Powder on the Hardened Properties of Cement-Based Materials

Physical properties

The physical behavior of cement-based materials represented in terms of density, water absorption, permeability, and porosity.

The density of the hardened cement-based material

Mashaly *et al.* (2015) determined the dry bulk density of water-cured concrete containing 10%, 20%, 30% and 40% of MS as cement substitution. They concluded that the incorporation of 10% and 20% of MS slightly increases the density by 0.5% and 1.4% respectively, due to the filler effect of fine MS particles that filling of voids among aggregate particles. While the substitution by 30% and 40% showed a reduction in bulk density by 2.3% and 2.8% respectively, due to the lower specific gravity of MS

Table 3 Effect of cement substitution on cement-based material's workability

Researchers	Marble type	Cement-based material	Optimum (%)	w/b	Workability
Vardhan <i>et al.</i> (2015)	MP	Cement paste	10	0.5–0.52	Improved
Rana <i>et al.</i> (2015)	MS	Concrete	10	0.38	Reduce
Ashish <i>et al.</i> (2016)	WMP	Concrete	–	0.42	Lower
Sardinha <i>et al.</i> (2016)	MS	Structural concrete	–	0.54–0.55	Ignored reduction

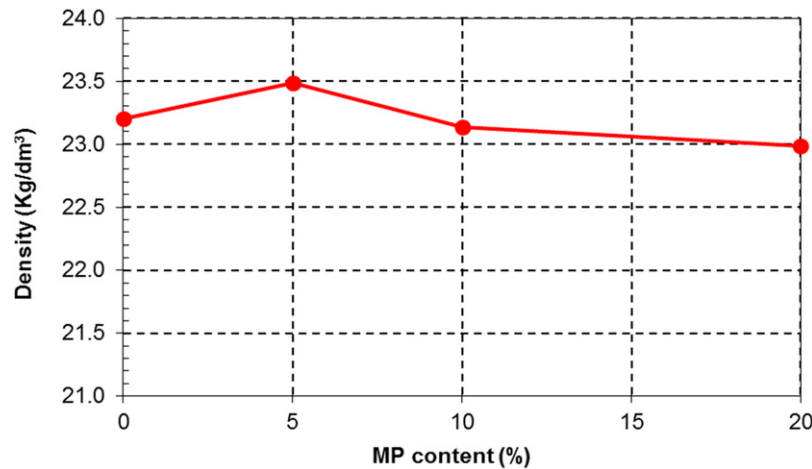


Fig. 9 The density of fresh concrete at various replacement ratio.

Table 4 Effect of cement substitution on fresh cement-based material's density

Researchers	Marble type	Cement-based material	Optimum (%)	Density
Mashaly <i>et al.</i> (2015)	MS	Concrete	20	Slightly increases
Toubal Seghir <i>et al.</i> (2018)	MP	Cement paste	–	Decrease almost imperceptible

when compared to the OPC. On the contrary, Toubal Seghir *et al.* (2018) observed that the incorporation of MP by 5, 10 and 15% as cement substitution in the manufacturing of air-cured cement paste slightly decreases the apparent density due to the presence of ultrafine particles provided by MP, and the specific gravity of the MP is lower than the specific gravity of the cement. However, the change in the apparent density was almost imperceptible.

The results of the effect of cement substitution on the density of fresh cement-based material are briefly shown in Table 4.

Water absorption

The incorporation of MP with the high surface area ($6700 \text{ cm}^2/\text{g}$) as cement substitution led to an increase of apparent porosity thus increases the water absorption, as presented typically in Fig. 10. However, the progression in curing time leads to decrease of these properties due to the filling of some pores by the hydrate product that represents twice of anhydrous OPC (Mashaly *et al.*, 2015). In fact, as mentioned in the literature, the tricalcium aluminate (C_3A) reacted with calcite (CaCO_3) which led to the forming of calcium carbo-aluminates (CCA) (Ergün, 2011; Arel, 2016; Toubal Seghir *et al.*, 2018). In addition, the CaCO_3 can be reacted with tetracalcium-aluminoferrite to form calcium carbo- aluminoferrites (CCAF) (Toubal Seghir *et al.*, 2018) that may increase the total volume of the hydration products and decrease the apparent porosity and water absorption of the hardened OPC paste (Mashaly *et al.*, 2015).

In the experimental study (Chaid *et al.*, 2011), it can be concluded that the increase of the surface area of MP decreases the capillary absorption coefficient, the authors incorporate the MP as cement substitution with fineness of about $12,000 \text{ cm}^2/\text{g}$, the typical results shown in Fig. 11 indicate that its incorporation in concrete samples can help to get concrete with low water absorption capacity. This is may be due to the filler effect of MP associated with porosity reduction (Mashaly *et al.*, 2015).

The results of the effect of cement substitution on the water absorption are briefly shown in Table 5.

Permeability

Rana *et al.* (2015) reported that the concrete containing 5%–15% MS showed better resistance to water permeation than the control mix. The impermeability of concrete was credited to lower capillary pores (pore size and pore distribution) and their

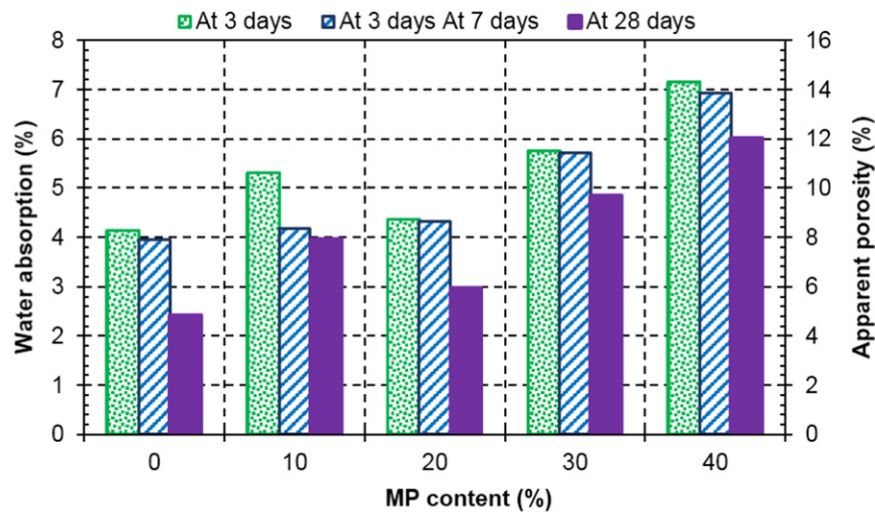


Fig. 10 Water absorption and apparent porosity of OPC pastes.

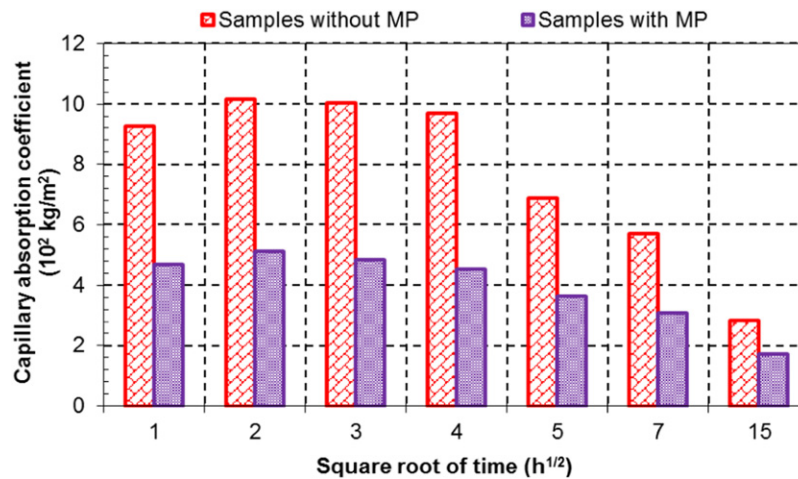


Fig. 11 Evolution of the capillary absorption coefficient versus time.

Table 5 Effect of cement substitution on cement-based material's water absorption

Researchers	Marble type	Fineness (cm ² /g)	Cement-based material	Optimum (%)	Water absorption
Mashaly <i>et al.</i> (2015)	MS	6700	Cement paste	20	Slightly increase
Toubal Seghir <i>et al.</i> (2018)	MP	12,000	concrete	–	Decrease

discontinuity. However, further addition of MS (more than 15%) could not compensate for the poor microstructure thus increased the permeability of concrete. Fig. 12 shows typical reduction in concrete permeability.

Porosity

Rana *et al.* (2015) measured the porosity of water-cured concrete made with MS by MIP (Mercury Intrusion Porosimetry) technique. They concluded that the porosity of concrete containing 5 and 10% of MS was found lower than that of the control concrete whereas the pores within the concrete mixture were identified as fewer and discontinuous. However, the increase of MS more than 10% led to an increase in the concrete porosity. Some other studies found that the substitution of cement more than 10% by MP reduces the porosity. As Aliabdo *et al.* (2014) which concluded that the substitution of cement by 15% of MD reduced the concrete porosity due to the filler effect of MD. Moreover, intersected substitution percentage was up to 20% of MS determined by (Mashaly *et al.*, 2015) which observed that cement paste and concrete mixes containing 20% of MS displayed lower porosity

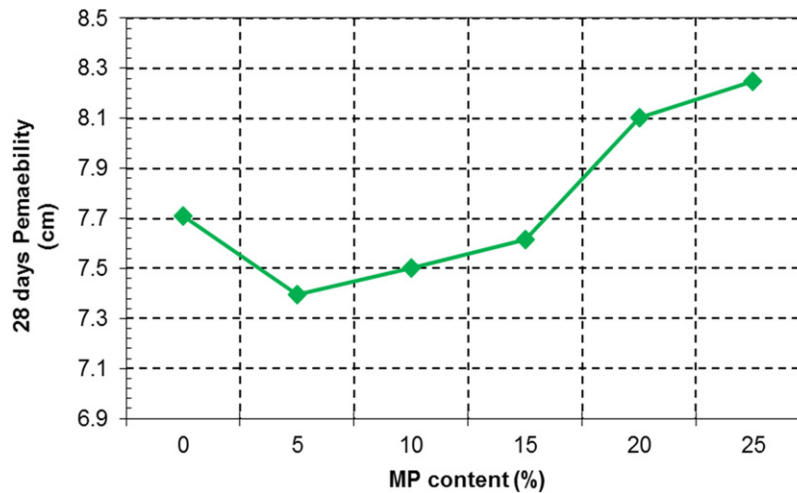


Fig. 12 Concrete permeability versus MS content.

Table 6 Effect of cement substitution on cement-based material's porosity

Researchers	Marble type	Cement-based material	Curing condition	Optimum (%)	Porosity
Aliabdo <i>et al.</i> (2014)	MD	Concrete	Water	15	Reduce
Rana <i>et al.</i> (2015)	MS	Concrete	Water	10	Lower
Mashaly <i>et al.</i> (2015)	MS	Cement paste and concrete	Water	20	Lower
Toubal Seghir <i>et al.</i> (2018)	MP	Cement paste	Air	–	Increase

than the corresponding cement paste and concrete mixes prepared without MS at the different water-to-binder ratio. They explained the reduction of porosity by both physical and chemical effect of MS that fill some of the pores.

On the contrary, Toubal Seghir *et al.* (2018) observed that the incorporation of MP by 5, 10 and 15% in the manufacturing of air-cured cement paste led to an increase of the porosity which measured by methanol exchange method due to the decrease in the volume of hydrate products by the reduction of C_3S and C_2S in the cement paste, also due to an incomplete hydration process which resulted by water evaporation under lower relative humidity.

The results of the effect of cement substitution on the porosity are briefly shown in Table 6.

Mechanical properties

Compressive strength

The compressive strength (f_{cd}) of hardened cement-based materials is evaluated by testing of specimens prepared and cured according to a national or international standard.

Aruntaş *et al.* (2010) investigated the usability of waste marble dust (WMD) as cement substitution in cement production. Two types of cement were studied. In type I mixes, the mortar were prepared with Portland composite cement (PCC) which was substituted by WMD at levels 0%, 2.5%, 5%, 7.5%, and 10%. Type II mixes, the ordinary Portland cement (OPC) was used with same substitution ratio. The authors concluded that the f_{cd} of mortar containing WMD at a cement-substitution ratio of 10% was higher than those of mortar based on PCC by 10% and lower than those of mortar based on OPC by 14% at 28 days. However, Mashaly *et al.* (2015) concluded that the increasing percentage of marble sludge (MS) from 10% to 40% resulted in a decrease of f_{cd} by 17%, 9%, 21%, and 30%, respectively at 28 days.

Toubal Seghir *et al.* (2018) investigated the effect of using MP as a partial substitution of OPC (0, 5, 10 and 15 % by weight). The MP incorporated in the mixture was grinded in order to obtain its fineness in the OPC fineness range, they reported that the use of MP in air-cured cement paste decreases the compressive strength at all curing age (3, 7, 28 and 65 days).

Singh *et al.* (2017) investigated the hardened properties of mortar and concrete containing 10% WMS as a substitution of cement after 7, 28 and 56 days. They concluded that the f_{cd} was improved by using 10% of WMS in a mortar and less than 10% in concrete, this is attributed to micro filler effect of WMS. The use of WMS more than 10% lead to decrease the f_{cd} . In a similar investigation, Boukhelkhal *et al.* (2016) evaluated the f_{cd} of SCC prepared with partial substitution of cement by MP. A continuous decrease in compressive strength was observed with increasing substitution ratios, the reduction in compressive strength was attributed to the use of an inert mineral unlike to the pozzolanic admixture. Contrarily, Aliabdo *et al.* (2014) concluded that the substitution of cement by WMD (10%) improved the f_{cd} of concrete at 0.40 w/c. However, the increase of w/c up to 0.5 lead to decrease the f_{cd} . Similar lines, (Ashish *et al.*, 2016) reported a decrease of f_{cd} with the incorporation of 10% MD in concrete at 0.42 w/c.

Table 7 Effect of cement substitution on cement-base material's compressive strength

Researchers	Marble type	Cement-based material	Optimum (%)	Compressive strength (f_{cd})
Aruntaş <i>et al.</i> (2010)	WMD	Mortar	10	Satisfactory
Corinaldesi <i>et al.</i> (2010)	MP	Mortar	–	Reduced
Ergün (2011)	WMP	Concrete	5	Improved
Gesoğlu <i>et al.</i> (2012)	MP	SCC	–	Systematic reduction
Aliabdo <i>et al.</i> (2014)	WMD	Cement paste and concrete	10	Improved
Mashaly <i>et al.</i> (2015)	MS	Cement paste and concrete	20	Appropriate
Ashish <i>et al.</i> (2016)	WMP	Concrete	–	Reduced
Boukhelkhal <i>et al.</i> (2016)	MP	SCC	–	Reduced
Singh <i>et al.</i> (2017)	WMS	Concrete	10	Improved
Toubal Seghir <i>et al.</i> (2018)	MP	Cement paste	5	Acceptable

Ergün (2011) examined the mechanical properties of concrete using WMP as cement substitution, the superplasticizer was used to decrease water demand in the production of concrete and to keep it constant in all mixes. The substitution of 5% cement by WMP affect positively the f_{cd} . The increase in f_{cd} was attributed to the filler properties of WMP and low water demand caused by using a superplasticizer admixture.

According to Arel (2016), in Turkey the concrete production costs US\$40/m³ and the use of MD substitution of 5% increases the f_{cd} by 12% thus reduced the cost by US\$4/m³, while the use of 10% MD reduced the cost by US\$7/m³ correspondingly, decreases the global annual carbon dioxide (CO₂) releases also by 12%. Worldwide, both cement production and the CO₂ emissions will decrease by 10%.

Generally, the use of 5%–10% MP as cement substitution was beneficial and more than 10% decreases the f_{cd} , this decrease was attributed to the significant reduction of C₃S and C₂S in the cement-based material, which is mainly responsible for the development of compressive strength. It is commonly known as the dilution of pozzolanic reactions (Ergün, 2011; Aliabdo *et al.*, 2014; Mashaly *et al.*, 2015; Toubal Seghir *et al.*, 2018).

The results of the effect of cement substitution on the compressive strength are briefly shown in Table 7.

Chemical properties of hardened cement-based materials

Carbonation

Rana *et al.* (2015) measured the carbonation resistance of concrete prepared with MS in the accelerated carbonation chamber of $5 \pm 0.2\%$ carbon dioxide concentration at 50–65%RH and $27 \pm 2^\circ\text{C}$ temperature. Concrete prepared with MS showed poor resistance to carbonation than the control concrete. At all substitution ratios, the carbonation depths gradually increased. This increase due to the lower bicarbonate alkalinity of MS (89 mg/l) compared to that of Portland cement (113 mg/l).

Chloride ion migration

Rana *et al.* (2015) reported that the chloride diffusion coefficient of the concrete containing 5%–10% MS as cement substitution was found lower in comparison to the control mix. The fine particles of MS help to fill the capillary pores this phenomenon explains the lower apparent chloride diffusion coefficient obtained.

Corrosion resistance

Rana *et al.* (2015) measured the corrosion activity of concrete containing MS using the half-cell potential with CSE (Copper-Copper sulfate electrode). The use of 5%–10% MS as cement substitution enhances the corrosive resistance of concrete. This indicates that the fine particles of MS occupy voids and densify the concrete microstructure. However, the incorporation of 15%–25% MS deteriorated the corrosive resistance of the concrete mix.

Chemical effect of marble powder on the hardened cement-based materials

Prassianakis and Prassianakis (2004) defined that the marble is a metamorphic product of pure limestone, resulting from its transformation under the heat and/or pressure effect. During its extraction and treatment operation, the WMP produced. Several studies pointed out that this waste is an inert by-product. However, as mentioned by Ergün (2011), Arel (2016) and Toubal Seghir *et al.* (2018) the calcium carbonate (CaCO₃) provided by WMP can be reacted with tricalcium aluminate C₃S presented in cement which formed calcium carbo-aluminates (CCA). Toubal Seghir *et al.* (2018) pointed out that the CaCO₃ also reacts with Tetra-calcium-aluminoferriite to form calcium carbo-aluminoferriites (CCAF).

Toubal Seghir *et al.* (2018) analysis the specimen of cement paste containing MP using SEM-EDX. They mentioned that the use of MP as cement substitution, lead to an increase of calcium hydroxide (CH) and a decrease of silicate hydrate thus decreases the C–S–H content, this decrease allowed for a decrease of compressive strength and an increase of porosity.

Vardhan *et al.* (2015) were studied the mortar specimen by XRD diffraction technique for identification of phases present in the hardened mortar containing marble stone dust (MSD). The results indicate that MP is an inert material and there is no change in the phase composition qualitatively of the cement-based materials.

Conclusions

The present article reviews the recent peer-reviewed paper available online on the utilization of marble powder in the cement-based materials as cement substitution. The main conclusion could be summarized in the following points:

- (1) The consistency and setting times of cement pastes are not affected when using the MP as a cement substitution with almost similar fineness to that of cement. Whereas, the increase in fineness of MP showed an increase of the water requirement and a sudden reduction in the setting times.
- (2) The marble powder influence positively on the workability of the fresh cement-based material by an inclusion ratio up to 10%.
- (3) The fresh concrete density showed contradictory results in the literature. Some researchers have mentioned that the density of fresh concrete decreases with an increasing percentage of MP. Others have pointed out that the density affected slightly by using MP as cement substitution.
- (4) The incorporation of MP as cement substitution led to an increase of apparent porosity thus increases the water absorption of cement paste, contrary, the use of MP in the production of concrete decreases the capillary absorption coefficient thus reduced the porosity.
- (5) The dry bulk density of cement-based materials slightly increases by using up to 20% MS due to its fine particles that filling voids among aggregate particles. Some other authors found that the use of MP up to 15% slightly decreases the apparent density due to the lower specific gravity of MP compared to that of cement.
- (6) The porosity of water-cured cement-based materials showed a decrease by using MP as cement substitution due to the effect of MP that filling some pores.
- (7) The porosity of air-cured cement-based materials showed an increase by using MP as cement substitution due to the reduction of C_3S and C_2S . In addition, due to an incomplete hydration process which resulted by the water evaporation.
- (8) The incorporation of MP up to 10% as cement substitution give acceptable results in term of compressive strength.
- (9) The use of 10% MP decreases the cement production and the global annual CO_2 emissions by 10%. Thus, reduced the cost by US\$7/m³.
- (10) The marble powder is an inert material; however, the $CaCO_3$ of MP can be reacted with C_3A of cement and Tetracalcium-aluminoferrite.
- (11) The SEM-EDX of cement-based materials indicates that the addition of MP resulted in an increase of CH and a decrease of silicate hydrate thus decreases the C–S–H content, this decrease allowed for a decrease of compressive strength and an increase of porosity.
- (12) XRD diffraction technique appears that marble powder does not lead to much change in the phase composition of the mixture.

The general conclusion of this review is that the incorporation of marble powder as cement substitution was beneficial. The properties of cement-based materials with more than 10%MP will be inappropriate. While replacing cement with 5%–10% marble powder yielded the favorable results. The substitution at appropriate ratios, marble powder has no adverse effects on cement-based materials quality.

The existing research showed the possibility to utilize the marble waste in cement-based materials. The future research in the field of the utilization of marble waste may be related to the applications in structural concrete. These applications may also include non-structural parts of the buildings such as for example the concrete floor screeds.

See also: Future Eco-Efficient Cements Prepared With Kaolinite-Based Industrial Wastes. The Utilization of Vegetable Fibers in Cementitious Materials. Utilization of Waste Expanded Glass in Cement Composites

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Bio-Based Materials in Sportswear Applications

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Main Principles of Biomimetics

Through millions of years of evolution, biological structures have relied on their ability to adapt to their changing environments to survive (Ngo, 2015). The overarching principle of biomimicry is that of taking inspiration from these biological structures and mechanisms and transferring the concepts to the man-made world. Whilst some of the biological key properties can be considered as self-assembly, reproduction, self-repair, and redistribution of vital resources, man-made structures are usually designed with one aim, which remains unchanged during the useful life of the product (Kapsali and Dunamore, 2008).

To adapt biological principles to a man-made world, design principles must be adopted to ensure an effective solution is found. “Bottom up” and “top down” are two such methods that are used.

The premise of the bottom up approach is that of the discovery of a process or structure existing in the natural world. The phenomenon is studied to gain an understanding of its biological principles. Once fully explored, potential uses of these findings are identified in the man-made world. Conversely, the top down approach originates with the identification of a gap in the market for which a biological principle is researched as a solution.

Whilst these approaches are useful, they are considered basic methodologies and do not allow for creative approaches to problem solving. The lack of creative approach is considered by some researchers as the main reason why biomimetics has not been adopted more rapidly into mainstream use.

Natures Inspiration for Sportswear

In the field of performance sportswear, functionality is a key driver of the product's success. Major players in the field, such as Nike and Adidas, are constantly in pursuit of the latest innovation that will elevate their products in both the professional performance and mass market.

Biomimetics is a relatively new field of research and as such, many developments and practical implementations are still in their infancy, but, used effectively, could give a competitive advantage to a manufacturer. As previously discussed, the natural world has been used for inspiration for several years, yet the science itself is still unfolding. Phenomena such as spider silk, crab shells, and bird beaks provide new insights into impact protection, whilst sharkskin, bird feathers, and humidity sensitive bacteria have allowed great design leaps in performance sportswear. The following sections aim to discuss some of these phenomena in more detail, alongside specific applications.

Biomimetics in Sports Apparel

Biomimetic textiles can be thought of as “a platform to transfer properties and functionalities identified in biological systems into fibrous structures” (Kapsali, 2015, p. 77). One of the first examples of this was the development and subsequent patenting of Velcro®. This technology is universally recognized and has numerous applications, yet it all began with the investigation of the sticking of burdock plant burrs to animal fur in 1941. The discovery that each burr is covered in needle-like hooks led to the development of a textile that has applications well beyond the scope of apparel.

Whilst the natural environment offers a rich supply of inspiration from which to develop cutting edge textiles, the field has been slow to develop and translation into useable garments still remains a largely untapped resource. Leading academics in the field, such as Veronika Kapsali, suggest this is due to the disconnect between design and technology disciplines in the field of textiles and apparel design (Kapsali, 2016).

However, there have been some developments in sportswear that may prove to pave the way for a wider uptake in biomimicry in apparel.

Swimming/Water Sports

In the field of competitive swimming, there has been much attention focused on drag and the streamlining of the swimmer's body to reduce this.

Many underwater animals are covered in scales and secrete a mucus that contribute to a reduction in drag friction and protect against abrasion. Sharkskin was first studied in relation to the reduction of drag in aircraft shells (Vincent, 2009). However, sharkskin differs in that the “scales” are more akin to ribbed skin (dermal denticles), and channel the water over the body, reducing pools of slower water currents and thus improving the aqua dynamics of the creature (Kapsali, 2016).

In 2000, Speedo (a swimwear company and part of the Pentland group) launched Fastskin™. This full body swimsuit is made from fabric that is designed to mimic sharkskin. However, this was not the only special design feature. This development also focused on the shape of the swimmer's body in the water and how the flow of water around it impacted movement and speed. Thus, the suit was designed to be extremely tight fitting, effectively changing the wearer's body shape and improving aqua dynamic flow. It was suggested that this was the feature giving the most impact on performance and further suits were developed with the focus shifted to the change in body shape and how to achieve this. Ultimately, this was so successful that it was deemed to give an unfair competitive advantage to those athletes who could afford the suit, leading to a ban by FINA in 2010.

However, the concept of sharkskin was not completely abandoned. Today it is used in the coatings of boat and ship bodies to reduce algae build up, water friction, and ultimately improve fuel consumption (Garty, 2015).

Keeping warm in the water has long been a puzzle for sportswear developers. Many animals live in the water and it is commonly understood that animal survival in colder water temperatures is reliant on a thick layer of subcutaneous blubber. However, not all animals possess this thick fat layer. Researchers at the Sheico group in Taiwan (a sporting goods manufacturer) wanted to find ways in which surfers could keep warm in the water, without an increase in wetsuit weight. Current neoprene wetsuits rely on the trapping of air within the foam like structure for insulation – however, improved insulation is only achieved by increasing the thickness of the neoprene and therefore the weight of the suit.

This led to the study of semiaquatic mammals (such as beavers), who keep warm when diving by trapping air within their fur. Working with a research team from Massachusetts Institute of Technology (MIT), a series of models were created with rubber “hairs” on the surface of varying lengths and densities. By submerging these in liquids at various speeds, these prototypes could be evaluated in terms of surface drag, hair movement, and subsequent air bubble entrapment. From this work, a mathematical model was developed that can be used to quantify the air entrapment of a given textile material with a hair like surface, enabling further development in this field to take place (Coxworth, 2016).

In contrast to this, a penguin ensures insulation in arctic waters via a different mechanism. Muscles at the base of the animal's feathers, alongside the feather construction, are capable of creating an adaptable coat to allow the animal to survive a variety of environmental conditions. This allows a waterproof barrier to be created for diving, which can then adapt to an insulating, windproof barrier once out of the water.

This ability to essentially change the configuration of the feathers is considered a “variable geometry” principle, which has been used in clothing to impart similar insulating effects. Using two layers of fabric at right angles to each other “skews” the fabric. It is the degree of skewing between the fabrics that determines the amount of air trapped between them. The wearer can inflate or deflate the garment as required, thus adapting the product to the environmental conditions. W.L. Gore in collaboration with Nike used this principle in their Airvantage range, suggesting the products were a “personally adjustable insulation system” (Drier, 2002).

Extreme Climate Protection/Athletics

One of the problems faced by sportswear designers is that of moisture management. This plays an important role in wearer comfort and keeping the body dry and cool (or warm where necessary) is a constant challenge.

The ability of the clothing to allow perspiration to flow away from the body and evaporate is key in sportswear clothing design – breathability is critical to the comfort of the wearer. There have been many adaptations in garment engineering to accommodate this, such as zipped vents in the torso of hill walking jackets and meshed areas incorporated into gym wear. However, biomimicry is allowing the textiles themselves to be engineered to address this issue.

Fabric manufacturers such as Schoeller® textiles and MMT textiles have used nature as inspiration for moisture control – namely the pinecone. The pinecone is highly sensitive to temperature and humidity, with its scales opening in dry, warm weather to allow the seeds to escape and spread, and closing in wetter, cooler conditions to protect the seeds. Schoeller® has adapted this principle to a fabric structure, marketed as c_change™ technology, whilst MMT textiles have created the Inotek® fiber – both solutions imparting moisture management properties to the textile (MMT, 2018; Schoeller, 2018).

Another approach to moisture management has taken inspiration from plant respiration (Stegmaier et al., 2008). The pores on leaves, known as stomata, open and close to allow gaseous exchange with the environment. This process of transpiration allows moisture to be lost from the leaf. Stomatex® is a neoprene-based textile, with small dome shaped indentations on the surface (Fig. 1), each with a small pore at its center (Stomatex, 2018). Perspiration and heat from the body accumulate in these chambers and are allowed to escape as the pores open during flexing of the textile with the body's movement. Equally, cooler, drier air is allowed in from the outside, maintaining a comfortable microclimate within the clothing (Kapsali, 2016). Stomatex® is used in a variety of sporting applications, including heat acclimatization suites for the England rugby Union squad and British Olympic team (Stomatex, 2018).

Whilst not strictly considered biomimicry, microbiology has been used by researchers at MIT to address the issues of moisture control in sports garments. Rather than taking the principles of the bacterial mechanisms and copying these in a man-made setting, it is the bacteria themselves that have been used to impart the required properties. The bioLogic project is a collaboration between MIT, The Royal College of Art, and New Balance. A bio printer is used to deposit a hybrid film containing specific bacteria (*Bacillus subtilis natto*) onto fabric. This bacterium is known for its sensitivity to humidity and therefore the printed fabric is able to “sense” when the body is becoming warmer through increased perspiration production. The bacteria can expand or contract depending on the moisture levels and this action is used in garment design. Ventilation zones are created in the garment in the form of fabric

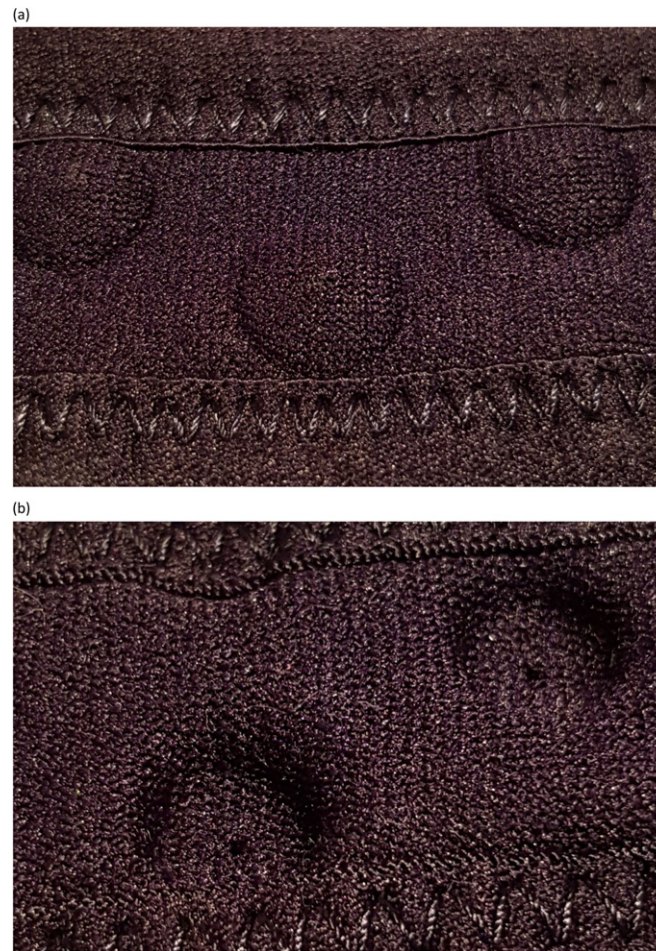


Fig. 1 Stomatex[®] neoprene fabric showing domes with tiny pores at apex on (a) fabric face, (b) fabric reverse.

flaps. These zones are engineered at points on the body to be most effective at perspiration evaporation. As the body heats up, the bacteria react to the increased moisture and the flaps open to allow perspiration to evaporate; as the body cools and perspiration levels drop, the bacteria react again and the flaps in the fabric close. This is using the bacterial world at its best to create a truly responsive garment.

Biomimetics in Sports Equipment

Rackets

Dunlop Sports has been an innovator in the field of tennis rackets for many years. In 2011 they launched a range of rackets, named the Biomimetic range, based on three principles inspired by nature – Sharkskin, gecko feet, and a beehive.

The main body of the frame's structure is carbon based, which has long been established in racket manufacture. However, HM6 carbon has a honeycomb molecular arrangement. It is well documented that the honeycomb in a beehive, whilst made of wax, has improved strength due to the hexagonal formation of the structure. Arranging carbon atoms in this way not only improves the structural strength of the racket, vibrations through the frame after the ball is struck are also reduced.

The outer skin of the racket frame is covered in dimples, marketed as Aeroskin. It is suggested that this mimics the skin of a shark, using the same principles of enhanced hydrodynamics to improve the movement of the racket through the air. This effect is also believed to reduce air friction and therefore less energy is expended with each strike of the tennis ball.

Finally, the grip of the racket has been inspired by feet of the gecko. The ability of the gecko to scale walls has been studied at length, revealing this ability to be down to microscopic hairs that protrude from the pads of the animal's toes. It is the combined action of the hundreds of thousands of each of these hairs and the force they impart that exerts the huge gripping force observed by researchers. This principle is applied to the grip of the racket, marketed as "Gecko-Tac." Dunlop claims that "Gecko-Tac technology provides up to 50%* more grip and tack than previous Dunlop technology, giving greater control, feel and precision" (Dunlop, 2018).

Protective Helmets

Nature provides us with many opportunities to study the field of impact protection. It comes as no surprise that the natural world has evolved a variety of solutions to this problem. Several of these principles have been investigated as a means to protect the human body from impact.

An obvious place to start with biomimicry for impact control is to look at creatures with hard exoskeletons. Crustaceans have been studied for many years, but a recent development is the research by MIT looking at the structure of the scaly-foot snail. This snail's shell has the ability to withstand prolonged, high pressure from crab claws and the MIT team have found the shell comprises three layers: Two more rigid layers with a thicker, more flexible, "padding" layer sandwiched between these. The innermost layer sitting beside the body is made of aragonite (calcium carbonate), common in many mollusks. The outermost is pyrite and greigite (iron sulfides) – this snail is the only animal in which these minerals are found. The presence of iron sulfides acts as a shock absorber, dissipating energy from impact by creating thousands of microcracks in the shell, preventing one large crack and ultimately the complete rupture of the exoskeleton. This composite material is of great interest as it is so novel in the animal kingdom and researchers are looking at how these properties can be transferred and developed for applications such as body armor, bicycle, and motorcycle helmets (Kapsali, 2016).

Hedgehogs are able to protect themselves from falls or blows to the body by rolling into tight balls, causing their spines to protrude. The spines take the full force of the impact, bending under the force, but rarely breaking. This dissipates and absorbs the kinetic energy of the collision, preventing serious damage to the soft torso underneath. This principle has led researchers to investigate how this concept can be incorporated into protective helmets, particularly in the field of American football (Hedegemon, 2018). Whilst this could be an interesting development, current work shows that spines do break on occasion. Whilst these are regrown in nature, they would not be replaced in a man-made structure, reducing the efficacy of the helmet protection over time if this issue is not sufficiently addressed.

Animal paw pads have also been identified as "natural" shock absorbers. Studies of the members of the feline family show that when falling from height, the animals have the propensity to fall on their feet. However, for the heavier animals, such as lions, the stress on the legs is far greater than, for example, the domestic cat. The lion's paw pads have evolved over time to absorb impact energy, which serves not only to protect the skeletal structure, but to "silence" the animal's movements, critical whilst hunting in the wild (Hubbard *et al.*, 2009; Ninomiya *et al.*, 2011). Studies conducted on other animals such as foxes, dogs, and beavers have all revealed shock absorbing properties. It is thought that there is a honeycomb type structure of collagen fibers found in paw pads that contributes to the shock absorbing properties. It is this principle that has been harnessed in the development of horse riding helmets.

Impacts to the head, whilst causing crushing trauma to the skull, can also cause torsion damage to the neck leading to severe injury. This has led to further developments in protective headwear – and further investigation into how nature can lead the way.

Rams take repeated blows to the head as part of the battle against other males in the flock. Constant hitting of this magnitude would cause severe damage to the human skull. Whilst a ram's skull is extra strong, any damage to the neck by the kinetic forces of the repeated blows is minimized by a thin lining of fluid around the ram's skull. This goes some way to dissipating the energy of the striking force, therefore reducing the chance of neck damage. Some high-end motorcycle helmets use this principle. The helmets are made of a tough outer layer covering a viscous gel (allowing some movement), which in turn covers the inner shock absorbing material. If the rider hits their head at high speed on the ground, the skull is protected from the shock and impact whilst the neck is protected from violent whipping injury.

Other motorcycle helmet designs take their inspiration from bird beaks. The inner part of a toucan's beak is almost honeycomb like in texture, made from a scaffold of keratin and calcium, whilst the outer part is covered with keratin in a scale formation. This makes for a lightweight, but extremely tough shock absorbing structure. Researchers at the University of California believe that whilst this structure is useful for protective helmets, there could also be an application in car body design (Rovner, 2005).

Other birds have also been used for inspiration in garments for impact protection. Many studies have been conducted around the woodpecker beak and the bird's ability to withstand the repeated impacts of drumming on trees with no damage to its brain. It has been found that the bird's porous bone structure dissipates low frequency vibrations, whilst the outer case of the beak is extremely strong to resist fracture. Coupled with a unique support structure for the tongue, a woodpecker can drum at speeds of 22 beats per second with decelerations of 1200 g, with no damage to soft or nervous tissue. At decelerations of 80–100 g, humans are often left concussed. Using these principles, researchers have designed shock absorbers using glass beads, rubber, and aluminum to mimic the bird's skull and beak structure. However, these concepts could easily be transferred to either protective helmets or protective wear in sports such as Formula One racing in which drivers are often subjected to dramatic decelerations during the course of a circuit (Yoon and Park, 2011; Marks, 2011).

Shoes

Silk has always been of interest to the textile industry due to its high strength, heat and moisture management properties, and lustrous appearance. Spider silk is of particularly high strength and it is the molecular arrangement of the proteins within the spider silk structure that imparts these properties (Holland and Vollrath, 2008). It is therefore imperative that this structure is mimicked as closely as possible if one is to replicate these high-performance properties through artificial spinning techniques. Through several years of product development, a German company, AM Silk, claims to have developed a fiber that mimics spider

silk in terms of strength, elasticity, moisture management, odor management, and feel against the skin. The fiber, named Biosteel[®] is also claimed to be 100% biodegradable (Biosteel, 2018).

Adidas have long been trailblazers in innovative technologies and it comes as no surprise that as a company they are keen to explore the benefits of biomimicry. In collaboration with the AM Silk team, they have developed a product based on the Biosteel[®] fiber and incorporated this into a high-performance shoe, unveiled at the Biofabricate conference in New York in 2016 (Biofabricate, 2018). The shoe, part of the Adidas Futurecraft range, is an additional development in the Adidas quest for sustainable product innovation. James Carnes, Vice President of Strategy Creation at Adidas, states: "In a year of ground-breaking innovations from Adidas, the announcement of our partnership with AMSilk – and the unveiling of the Adidas Futurecraft Biofabric shoe – is another step in our commitment to redefining the sports industry. This concept represents premium innovation. By using Biosteel[®] fiber in our products, we have achieved an unrivaled level of sustainability. We are moving beyond closed loop and into an infinite loop – or even no loop at all. This is a pioneering stride forward beyond sustainability into a new territory of bionic innovation" (Adidas, 2018).

Summary

Biomimicry has a potential for a huge impact in sportswear and sporting goods development. However, uptake has been slow within the sports industry and many developments have not progressed beyond the concept stage.

Nevertheless, using creative design principles, it is possible to envisage a time when much of the product development in this field takes its inspiration from nature in one form or another. It can be considered that the botanical world is much more efficient at evolving to meet the ever-changing demands of its environment and as developers relatively new to the field, we would be foolish to not take nature's lead. For example, the natural shock absorbing ability of bird beaks and animal paw pads has the potential to lead to innovative solutions for protective equipment for humans, and bacteria may hold the key to moisture management control in sports apparel.

In the future, using nature as inspiration, it may be possible to solve some of those issues that human engineers still have not solved, even after hundreds of years of study.

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Biodegradable Packaging Materials

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Introduction

Packaging is a necessity in today's world as nearly all the consumer goods in the market usually appear with some kind of packaging materials that not only provide protection from external abuses but also fulfill customers' desires, as well as industry requirements for product information, convenience, and safety. Traditionally, several kinds of materials, such as glass, metal, wood, plastic, paper, or combination of materials, are widely employed for varying categories of packaging like primary, secondary, or tertiary packaging. The primary packaging materials that are in contact with the consumer goods are often brought home by the customers and are diffused at the household level, and get contaminated or damaged when coming in contact with other materials. On the other hand, secondary packaging materials are employed to pack the many units of primary packaged items, while tertiary packaging materials facilitate the transportation of manufactured goods in wooden pellets, cardboard boxes, or plastic wrap. Thus these secondary and tertiary packaging materials are seen by retailers, wholesalers, and manufacturers and are thus comparatively simpler to gather and categorize for reuse or recycling. However, the primary packaging materials often cause reuse or recycling issues because they cannot be easily sorted (Davis and Song, 2006). This leads to the complication of waste disposal contributing to the concern on environment pollution.

Recently, great efforts are being taken to develop such packaging materials that not only improve performance but are also easy to recycle and reuse. A new class of packaging materials following these properties is the biodegradable packaging materials derived from the renewable biological sources known as biopolymers, which offer excellent protection to the product and are easier to degrade after use, exhibiting the potential as an eco-friendly alternative to traditional petroleum derived materials like metal, glass, paper, plastic, etc., which are not biodegradable (Khan *et al.*, 2016). The biodegradable packaging materials are highly beneficial in one time use or short-duration packaging requirements like disposable cups and plate, garbage bags, diapers, medical devices, food and beverage package, etc.

Biodegradables mean anything that must be degenerated and compostable under the suitable conditions of temperature, moisture, and oxygen leaving behind no toxic or harmful residues. Thus the biodegradable packaging materials are those that undergo the process of degradation by naturally occurring organisms, such as bacteria, yeast, or fungi (Sorrentino *et al.*, 2007), and can be used as humus or fertilizer when composted (Siracusa *et al.*, 2008). Currently, various kinds of biodegradable and compostable polymers, such as starch, cellulose, chitosan, and lignin, are commercially available. Even some synthetic polymers are mixed with minute amounts of biopolymers for making them biodegradable.

The best biodegradable materials are derived from the renewable and bio-based sources called biopolymers. The main function of biodegradables like any other packaging material is to protect the contents from surrounding and maintain its quality throughout the storage life. Therefore, other characteristics like mechanical (tensile strength, tear and burst strength, etc.) and barrier properties, such as permeability of vapors, gases, light, etc., are equally important. The biopolymers are effective barriers against vapors and gases. But their mechanical and barrier properties can be improved by blending two or more biopolymers. Several active components or additives like antimicrobials, color, nutrients, antioxidants, etc. can be incorporated for increasing their performance (Clarival and Halleux, 2005). Thus, the biopolymers serve as an eco-friendly alternative for the use of nonrenewable and nonbiodegradable plastic based packaging materials. The study of recyclable and biodegradable polymers is an interesting and growing area in packaging science but immense research is required for improving their performance, thermal, mechanical, and physical characteristics, and commercial use, which might be possible in a few years.

The few developments of biodegradable polymers are mentioned as follows:

1. LDPE-starch blend were commercialized under the trade name Ecostar® in 1993 (Siracusa *et al.*, 2008).
2. Alexandre and Dubois (2000) manufactured the biopolymer-layered silicate nanocomposites that have remarkably enhanced the physical characteristics including higher gas barrier attributes, tensile strength, and thermal stability.
3. Li *et al.* (2003) revealed that the lignin would accelerate the thermal degradation of poly(L-lactic acid) (PLLA) when the content of lignin was more than 20%.
4. Al-ltry *et al.* (2012) improved the thermal stability, mechanical and rheological characteristics of polylactides (polylactic acid – PLA), polybutylene adipate-co-terephthalate and their blends using the reactive extrusion with functionalized epoxy in July 2012.
5. Khankrua *et al.* (2013) employed the silica nanoparticles to increase the onset and inflection temperature of thermal degradation in PLA, polybutylene succinate (PBS) as well as poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) nanocomposites. However, the mechanical properties were slightly improved at low concentration of silica and worsen at the higher levels of silica due to the agglomeration of silica in the polymer matrix.
6. Nevalainen (2013) developed a heat-sealable biodegradable packaging material, a package or a container produced thereof, and used the resin in the extrusion coating.

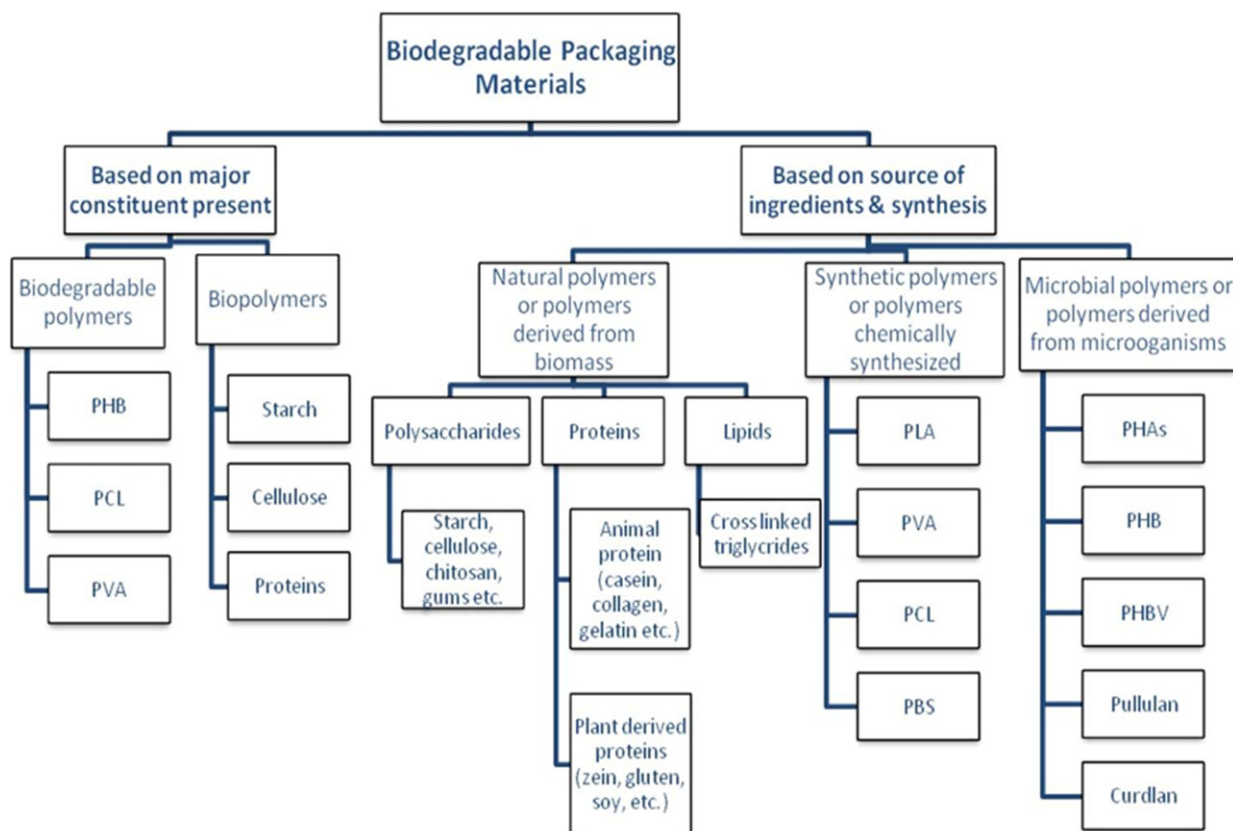


Fig. 1 Classification of biodegradable packaging materials based on the major constituents present and the origin of ingredients and their synthesis. PBS, polybutylene succinate; PCL, polylactic acid; PHA, polyhydroxyalkanoate; PHB, polyhydroxy butyrate; PLA, polylactic acid; PVA, polyvinyl alcohol. Reproduced from Clause, J.W., 2000. Bio-based packaging material for food Industry. European Concerted Action Project, pp. 13–50. ISBN: 87-90504-07-0.

Types of Biodegradable Packaging Materials

The biodegradable packaging materials can be classified into several categories as shown in [Fig. 1](#) based on different criteria. Broadly, on the basis of major constituent present, they can be of two types:

1. Biodegradable polymers: these possess certain degree of intrinsic biodegradability. These are basically synthetic oil derived polymers. For example, polyhydroxy butyrate (PHB), polycaprolactone (PCL), and polyvinyl alcohol (PVA).
2. Biopolymers: as the name suggests, these are biologically derived polymers or long chain biomolecules like starch, cellulose, proteins, etc., which are naturally decomposed into eco-friendly metabolic products.

However, the most common criterion considered for classification of biodegradables is the source or origin of raw materials and their synthesis. According to this, biodegradable materials are classified into three types:

1. Natural polymers or polymers derived from biomass.
 2. Synthetic polymers or polymers chemically synthesized from renewable sources.
 3. Microbial polymers or polymers derived from microorganisms.
1. Natural polymers: the commonly available natural polymers are derived from animal, marine, and agricultural sources, which include the polysaccharides, such as starch, cellulose, chitosan, gums etc., proteins like animal extracted protein (casein, collagen, gelatin, etc.), and plant derived proteins (zein, gluten, soy, etc.) and lipids including cross linked triglycerides ([Garcia et al., 2000](#); [Bertan et al., 2005](#); [Karnnet et al., 2005](#); [Perez-Gago and Krochta, 2001](#)). Most of these polymers are hydrophilic and crystalline in nature, which might cause several issues in moist food packaging, but these polymers are effective barrier against gas transmission.

Among these polymers, starch is the most widely used as packaging material, and is mainly derived from corn, potato, or rice. The starch alone cannot produce films having sufficient mechanical strength, and therefore are often blended with other materials or chemically or genetically modified because starch when exposed to moisture may swell and undergo deformation. The major



Fig. 2 Cellophane film for packaging of confectionery products and tea. Reproduced from Molenveld, K., van den Oever, M., Bos, H., 2015. Biobased packaging catalogue. Wageningen: Wageningen UR Food & Biobased Research.

disadvantage of starch-based polymers is their brittleness, which can be minimized by the incorporation of biodegradable plasticizers, such as glycerol, urea, polyhydroxy compounds, etc., by reducing the water activity. Several starch-based polymers include PHB, polylactide, and polyhydroxyalkanoate (PHA).

Cellulose, the most abundant natural polymer, is commonly used as paper or cardboard due to the presence of hydroxyl groups and regular structure leading to the formation of crystalline microfibrils and fibers containing strong hydrogen bonds. Cellulose in its raw form is very difficult to use as it is hydrophilic and crystalline in nature possessing poor mechanical properties. Therefore, it must be treated with chemicals like NaOH, H_2SO_4 , CS_2 , etc. to produce cellophane having excellent mechanical characteristics. Cellophane (Fig. 2) has been extensively used in commercial food packaging for products with long shelf-life. Likewise, several cellulose derivatives, such as carboxy-methyl cellulose, methyl cellulose, ethyl cellulose, cellulose acetate, hydroxyethyl cellulose, etc., are widely used.

Chitosan or chitin, the second abundant polysaccharides after cellulose is employed for the production of films or specifically edible coatings with high gas barrier properties and sometimes used with another films lacking gas barrier features. Moreover, the chitosan and chitin absorbs the heavy metals' ions, and they also possess antimicrobial properties, which reduces the oxidation process and is beneficial for increasing the shelf life and quality of food products particularly (Gemili *et al.*, 2009).

Proteins, made up of amino acids, are highly desirable to modify the required characteristics of packaging materials due to the presence of unique side chain in their structure. There are typically two kinds of proteins employed for synthesis of packaging materials: (1) protein derived from animal sources (casein, collagen, whey, etc.) (2) protein derived from plants (gluten, zein, soy, etc.). Protein based packaging materials have excellent gas barrier properties but they (except keratin) are adversely affected by their hydrophilic nature like starch-based polymers. Therefore, they also need to be blended with other polymers or must be chemically or microbiologically modified.

Casein, the milk-based protein, when processed with suitable plasticizers, turns from brittle and stiff to flexible materials perfect for film blowing. Irrespective of its comparatively high cost, it is still widely employed for bottle labeling due to its outstanding adhesive properties. Gluten based polymers are highly glossy, provide ambient moisture resistance, and do not dissolve in water. But they may absorb some water on immersion. Gluten carries immense scope as biopolymer packaging material due to its low price and abundance. Soy protein possesses similar performance characteristics like gluten due to the presence of disulfide linkages in both cases. The cheapest protein, keratin, is extremely difficult to process due to the high amount of cysteine. The material derived from keratin is water insoluble and completely biodegradable in nature. Collagen, the structural protein in animal tissues, is highly insoluble and difficult to process due to its fibrous nature. On the other hand, whey proteins, byproducts from the cheese industry, are widely employed as edible films and coatings.

Several lipid components like fatty acids, natural waxes, resins, and vegetable oils are generally incorporated in the films to provide hydrophobicity so that moisture barrier properties can be improved.

2. Synthetic polymers: this category usually includes PLA, PCL, PVA, polyglycolic acid (PGA), PBS, etc. Among these, PLA, the polymer of lactic acid, was the first biopolymer employed over industrial scale because lactic acid is simply produced from the carbohydrate based feedstock, such as agricultural crops (wheat, rice, maize, etc.) and waste or byproducts derived from the agriculture and food industry. The PLA properties may alter significantly from the semicrystalline to amorphous materials based on the proportion of D-PLA/L-PLA. The high content of L-PLA leads to the lower degradation of polymer because of higher crystallinity (Kale *et al.*, 2006). Therefore, the right ratio must be selected to produce PLA films that can be easily processed and have improved performance characteristics. The PLA based films possess higher molecular weight, good gas and moisture transmission properties and water solubility resistance, and are compostable as well as recyclable. They are used to pack food products (Fig. 3) with low shelf-life. PLA is commercialized in industry under different names by several companies, such as Natureworks PLA developed by the Natureworks LLC, United States (Siracusa *et al.*, 2008).

PCL is a thermoplastic as well as completely biodegradable polymer obtained from the nonrenewable sources, such as crude oil. It is a linear semicrystalline polymer that is soluble in several kinds of solvents. It is typically not employed to pack food products but when blended with starch, it produces a fairly biodegradable material that is mainly used for trash bags. This polymer



Fig. 3 Disposable cup and trays made from polylactic acid (PLA). Reproduced from Molenveld, K., van den Oever, M., Bos, H., 2015. Biobased packaging catalogue. Wageningen: Wageningen UR Food & Biobased Research.

offers good chemical resistance to oil, water, chlorine, and solvent with very low viscosity and melting time too. Due to its low glass transition temperature (around -60°C), it is employed as compatibilizer, while formulating the polyurethane. Commercially, PCL is observed under different trade names, such as Tone[®] from Union Carbide (Texas), CAPA[®] from Solvay (Belgium), Celgreen from Daicel (Japan), etc. (Pawar and Purwar, 2013).

PVA is derived from the partial or complete hydrolysis of polyvinyl acetate, offers good water solubility, and is fully biodegradable under aerobic or anaerobic conditions. It is employed for several applications in the nutraceutical, medical, and food industries. PVA is also considered a useful polymer matrix to entrap enzymes.

Glycolic acid on polymerization leads to the synthesis of PGA that is linear aliphatic, semicrystalline (46%–52% crystallinity), and fully biodegradable polyester. It offers excellent mechanical properties. It is generally insoluble in majority of nonpolar solvents (except hexafluoroisopropanol) due to its crystallinity. It shows the glass transition temperature of $35\text{--}40^{\circ}\text{C}$ and possesses high melting point, nearly $220\text{--}225^{\circ}\text{C}$ (Nair and Laurencin, 2007).

PBS and its other copolymers are derived from the condensation reactions of glycols like ethylene glycol and 1,4-butanediol with the aliphatic dicarboxylic acids like succinic and adipic acid. Bionolle is the first commercial biodegradable polyester resin developed by Showa High Polymer (Japan). In addition to PBS, several polymers have been synthesized from these condensation reactions, such as polyethylene succinate (PES) and PBS-co-adipate (PBSA). PBSA, a copolymer, is obtained when adipic acid is added. PBS, a white crystalline thermoplastic, has moderate melting point varying from 90 to 120°C and very low glass transition temperature (-45 to -10°C), which falls in between the glass transition temperature of polyethylene (PE) and polypropylene (PP) thus resulting in the similarity of PBS mechanical properties with PE and PP. PBS shows a better processability than that of PGA and PLA. On the incorporation of adipates, the tensile strength of polyester reduces in PBSA while other physical attributes remain unaffected. PBS has the highest tensile strength among the polyesters but the copolymers PBSA (60/40) and PBSA (80/20) exhibit modified elongation features.

3. Microbial polymers: this class includes the polymers that are synthesized from the microbial fermentation of polysaccharides. It is a quite recent and innovative field that has immense potential in industry. This category typically includes the polymers, such as polyhydroxy alkanates (PHA), PHB, PHBV, etc., and microbial polysaccharides like pullulan and curdlan. The polyalkanoates have a more hydrophobic nature than the polysaccharide derived materials leading to the production of a material with good moisture barrier properties but poor gas barriers. The PHA family is widely employed, and is synthesized from the sugars or lipids using bacterial fermentation. The polymer is usually synthesized from the fermentation process in microbial cells and is extracted using solvents like methylene chloride, chloroform, or propylene chloride. Being thermoplastic in nature, it has a wide range of melting points varying from 40 to 180°C based upon the monomer employed in production. PHB is the most common type of PHA among more than 100 PHA composites and is synthesized from the 3-hydroxybutyrate monomer. It carries similar properties like PP but is more brittle and stiffer, while PHBV is less tough and stiff. It degrades under both aerobic and anaerobic conditions forming CO_2 and H_2O in the former case and methane in the latter.

Several kinds of waste from the food and agriculture industry may be used as C-source to synthesize a range of PHA polymers. The PHA/PHB based films exhibit better performance than the conventional films like PE, PP, etc. and may be used to replace those. However, the major drawback in their commercial use is the high cost of manufacturing route. The film properties may be altered by changing the proportions of hydroxybutyrate (HB) and hydroxyvalerate (HV) by controlling the growth media. The high amount of PHB provides a stiff and strong film, while polyhydroxyvalerate (PHV) modifies the toughness and flexibility.

The utilization of microbial polysaccharides, such as xanthan, pullulan, curdlan, etc., as a packaging film is a novel concept and needs biotechnological techniques. Pullulan is synthesized using *Aureobasidium pullulans* from substrates containing sugars and is fairly water soluble, linear, and exopolysaccharide. It is employed for packing in several industries like food, medicine, and cosmetics. It is tasteless, odorless, nontoxic, and biodegradable in nature. Pullulan based films are generally transparent, homogeneous, heat sealable, printable, flexible, edible, and are a good barrier to oxygen but have poor mechanical properties (Freitas et al., 2014). These are employed to inhibit the fungal growth thus making them suitable for food applications particularly. Curdlan, the bacterial polysaccharide, is produced from *Agrobacterium biovar* and *Agrobacterium tumefaciens* and is a linear

Table 1 Commercially available biopolymers and their manufactures

Type of polymers	Manufacturers	Brand	Applications
Starch	Biotec Dupont Novamont	Bioplast Biomax Mater-Bi	Bags, loose fill, films, wrap film, trays
Cellulosics	Eastman Chemical FKuR Innovia films Sateri	Tenite Biograde Nature flex Sateri	Flexible film
PLA	BASF Cargill Dow NatureWorks Synbra	Ecovio EcoPLA Ingeo Biofoam	Rigid containers, films, barrier coating
PHA/PHB	Biomer Monsano	Biomer Biopol	Films, barrier coating, trays
PCL	Daicel Union Carbide Solvay	Celgreen Tone CAPA	Wrap films, trash bags

Abbreviations: PCL, polylactic acid; PHA, polyhydroxyalkanoate; PHB, polyhydroxy butyrate; PLA, polylactic acid.

Source: Hu, B., 2014. Biopolymer-based lightweight materials for packaging applications. In: *Lightweight Materials from Biopolymers and Biofibers*, ACS Symposium Series, Washington, DC.

β -(1,3)-glucan consisting of glucose units. It is mainly used as a gelling agent in the food industry but has enormous potential in the development of packaging films, which is yet to be discovered.

On the other hand, xanthan is produced by the aerobic fermentation of *Xanthomonas campestris* using sucrose or glucose as its major carbon source. It is a heteropolymer consisting of repeated glucose, mannose, and glucuronic acid in 2:2:1 ratio and also pyruvate and acetyl substituent groups. It is highly viscous, water soluble and nontoxic in nature. Not much data is available about the potential of xanthan in the packaging sector. This may be due to the high cost of production. However, acerola when wrapped with xanthan coating exhibited reduced weight loss, respiration thus maintaining the color and enhancing the shelf life (Quoc *et al.*, 2015).

Currently, several kinds of biopolymers are used commercially, as described in Table 1, that are synthesized from the starch (Fig. 4(a) and (b)), cellulose (Fig. 4(c) and (d)), PLA, PCL, or other kind of biodegradable packaging materials. However, extensive research is required in future to modify the properties of biodegradable packaging materials and to reduce their cost of production too.

Properties of Biodegradable Packaging Materials

The knowledge about properties of packaging materials is essential as they predict the shelf life of product and package. Generally, the small molecules of vapors, gases, water, and other liquids can be moved in and out of the package wall thus adversely affecting the product quality and shelf life. Sometimes the light penetrates the packaging materials and speeds up the oxidation reactions thus reducing the shelf life. Therefore, the properties of any biopolymer are described in detail as:

1. Gas and oxygen barrier properties: specific environment is needed to maintain the quality and freshness of many food products during storage. For that purpose, a certain gas mixture mainly consisting of carbon dioxide (CO₂), oxygen, and nitrogen or their combinations is incorporated in packages to ensure the optimum quality and safety. Therefore, the packaging materials must possess the definite gas barriers to sustain the established gas concentration in the package (Clause, 2000). Scientists have compared the gas barrier properties of biodegradable polymers with the traditional mineral oil derived packaging materials as shown in Fig. 5. It can be observed that biopolymers exhibit quite good resistance to the oxygen transmission and currently, many efforts are being carried out to modify the barrier properties of biopolymers. However, the oxygen transmission rate (OTR) is higher in bio-based packages than the traditionally used polymers, which may increase the oxidation reactions and reduce the shelf-life of product (Auras *et al.*, 2003). Likewise, the CO₂ barrier property of polymers is also important mainly in the case of fresh produce packing.

Traditional high barrier films include the combination of many layers to produce a film with the required attributes. The most commonly used laminate is made up of ethylene vinyl alcohol (EVOH) or polyamide-6 (PA6) layer along with low density polyethylene film (LDPE) film, which fuses the gas barrier features of EVOH or PA6 with the excellent sealing, mechanical strength, and moderate water vapor barrier properties of LDPE. Likewise, two or more bio-based polymers can be combined together to develop the polymer film carrying the necessary attributes. As seen in Fig. 2, the starch-based polymer along with plasticized chitosan may become a cheaper alternative to the currently used materials, such as EVOH or PA6.

2. Water vapor barrier properties: the water barrier properties of packaging material depend on the kind of product to be packaged. For powder, the equilibrium moisture content of products is important to maintain its shelf-life and the moisture



Fig. 4 Mater-Bi (a) and (b) and Nature Flex (c) and (d) flexible films made from starch and cellulose. Reproduced from SlideShare. Available at: www.slideshare.net/cwataya/pptofbiodegradablepackaging-120816064437phpapp02-1.

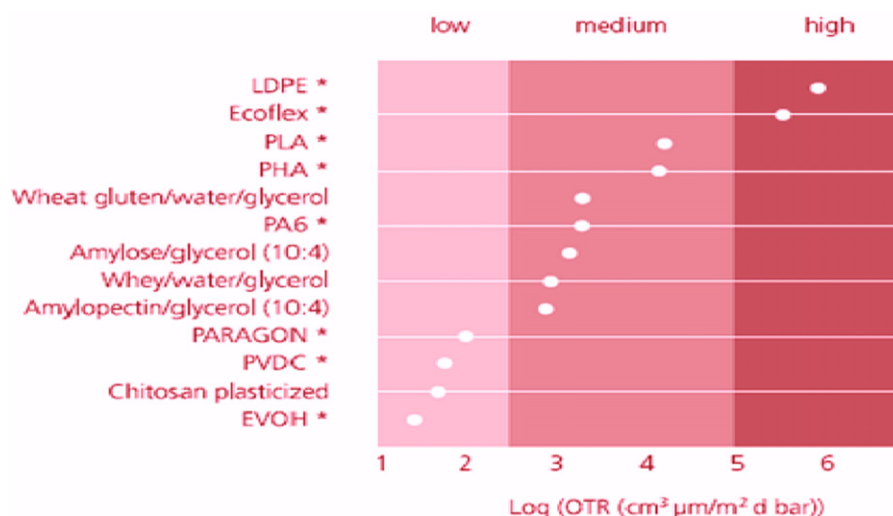


Fig. 5 Comparing the oxygen transmission rate (OTR) of biodegradable materials with traditional materials. Transmission rate of “*” marked materials was measured by ATO, Wageningen, NL (23°C, 50% RH). ATO, Agrotechnological Research Institute; LDPE, low density polyethylene film; PA6, polyamide-6; PARAGON, the trade name of the starch-based biopolymer with ester linkage manufactured by Avebe, Netherlands; PBS, polybutylene succinate; PCL, polylactic acid; PHA, polyhydroxyalkanoate; PHB, polyhydroxy butyrate; PLA, polylactic acid; PVA, polyvinyl alcohol; PVDC, polyvinylidene chloride. Reproduced from Pawar, P.A., Purwar, A.H., 2013. Biodegradable polymers in food packaging. American Journal of Engineering Research 2, 151–164.

must be restricted inside the package. The water vapor must be transmitted inside of packaging materials for fresh produce to avoid dehydration, while bakery products need packages that should inhibit the permeability of water vapor.

The major limitation of bio-based packaging materials is their hydrophilic behavior because many products (some discussed above) require moisture-free conditions. When water vapor barrier properties of biopolymers are compared with the mineral oil-based materials as shown in Fig. 6, a composite biopolymer can be developed whose transmittance rates are somewhat near to the traditional plastics. The biodegradable packaging materials are a good choice in case of products that require high water vapor

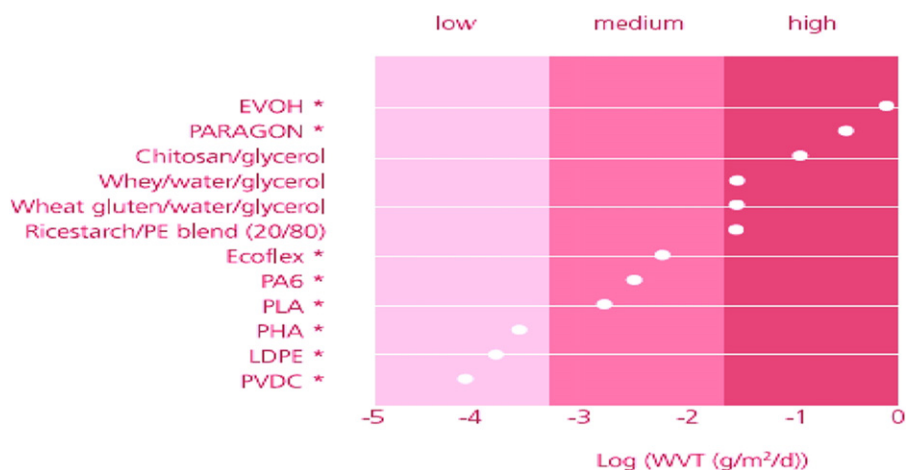


Fig. 6 Comparing the water vapor transmission rate of biodegradable materials with the traditional materials. Transmission rate of “*” marked materials was measured by ATO, Wageningen, NL (23°C, 50% RH). LDPE, low density polyethylene film; PA6, polyamide-6; PBS, polybutylene succinate; PCL, polylactic acid; PHA, polyhydroxyalkanoate; PHB, polyhydroxy butyrate; PLA, polylactic acid; PVA, polyvinyl alcohol. Reproduced from Pawar, P.A., Purwar, A.H., 2013. Biodegradable polymers in food packaging. *American Journal of Engineering Research* 2, 151–164.

transmission. Intense research has been carried out to improve the water barrier properties of bio-based materials either by combining several layers or using nanotechnological or biotechnological techniques.

3. Light barrier properties: the radiation energy derived from sunlight either in the form of visible or UV light speeds up the deterioration reactions that adversely affect photosensitive products. Light also acts as a catalyst to increase the rancidity of lipid based foods. Further, light can also induce the oxidative degradation in the polymers resulting in the weakening and discoloration of the polymers including both traditional and bio-based packaging materials. In order to avoid the photodegradation of polymers and products, UV stabilizers/absorbers can be incorporated in the packaging materials (Borghetti and Coltro, 2007).
4. Thermal and mechanical properties: in addition to barrier properties, the thermal and mechanical properties of biopolymers are equally important not only for processing but also in the case of product modeling (like sheet extrusion, injection molding, blow molding, thermoforming, film forming, etc.) derived from these materials. Commercially, several containers are employed to pack or store the product below room temperature; therefore, the mechanical properties under such conditions must be known. The thermal properties of bio-based polymers are nearly similar to the traditional polymers. For mechanical properties, a wide range of tests, such as tensile strength (MPa), percent elongation at break and yield (%), and elastic modulus (GPa) must be carried out and obtained values can be compared with the commercial conventional polymers. Standard tests should be performed to determine the impact and compressive resistance of biopolymers. However, the modulus and stiffness of biopolymers are almost similar to the traditional mineral oil-based polymers. And also the modulus of bio-based polymers can be improved by cross-linking, blending with other polymers, or plasticizing. For instance, the bacterial cellulose can be incorporated where special mechanical properties are required.
5. Compostability: it is the most critical requirement of bio-based polymers as it differentiates the biodegradable materials from recyclable materials because the composting process must change the biodegradable waste into beneficial soil products. Compostability of polymers strongly relies on characteristics of the materials. For instance, the initial step of composting is mostly the hydrolysis of polymer and hydrolysis rate depends on the water resistance and water vapor transmittance of the material. Further, the duration during which the polymer has undergone the accepted disintegration degree is called composting time. However, the complete biodegradation duration is not represented by the composting time. The composting time required for full disintegration is greatly affected by the technology used in composting. A low technology based composting, for example, passive windrow composting, usually takes more duration to acquire mature compost when compared to high technology derived tunnel composting. Moreover, particle size of polymer also influences the complete disintegration thus affecting the composting time. For instance, wood sawdust or small chips are quickly composted, while wooden logs usually disintegrate fully in a year or more (Clause, 2000).

Mechanism of Biodegradation

Biodegradation means disintegration, degradation, or loss of mechanical attributes of packaging materials using microorganisms and is progressed by hydrolysis followed by oxidation. The biodegradation rate is greatly based on the temperature (varying from 50 to 70°C), kind and amount of microorganisms, and humidity. Fast degradation is possible only if all these parameters (mentioned above) are present. Biodegradation exists quickly in the composting process where biopolymers are degraded to water, CO₂, and biomass during average 6–12 weeks (Siracusa *et al.*, 2008). The degradation can be anaerobic or aerobic in nature resulting in the formation of methane and hydrogen (biogas) in the former case and compost or sludge in the latter. Generally, the products derived from polymers biodegrade under a regulated manner. Natural biopolymers like starch, cellulose, etc. are

hydrophilic and swellable in nature in contrast to the polyolefins that are used in central packaging material and are hydrophobic in nature, exhibiting high resistance toward hydrolysis, peroxidation, and biodegradability. Prooxidants must be incorporated in polyolefins to initiate the oxobiodegradation in them. Technically, natural polymers are not suitable for food packaging due to their poor performance, which must be modified. On the other hand, the aliphatic polyesters like PLA, PHA, etc. are in between the two extremes of polyolefins and natural polymers in terms of performance, as well as biodegradability.

The oxo-biodegradation mechanism is followed in the biodegradation of natural and synthetic polymers; however, standard biodegradation needs the instant mineralization measure. Further, oxobiodegradation at room temperature is a very slow mechanism as compared to hydrobiodegradation (Scott and Wiles, 2001). According to Scott and Wiles (2001), the oxobiodegradation of carboxylic acid ($-\text{COOH}$) results in alcohol, aldehyde, and ketone molecules, which are degradable using low molar mass generated during the peroxidation that is commenced either by light or heat. This is the main reason why the hydrocarbon polymers lose their mechanical properties. After this, bioassimilation initiates by the enzymes, bacteria, or fungi resulting in the CO_2 and biomass hence producing humus. The antioxidants or stabilizers present in the synthetic polymer adversely affect the biodegradation process by inhibiting the oxidation of polymers. But these compounds are necessary to incorporate in polymer to increase the shelf-life of materials and to improve the performance also. Likewise, hydrobiodegradation is mainly employed for starch, cellulose, polyesters, etc. The aliphatic polyesters like PHBV are disintegrated and bioassimilated quickly, like cellulose and starch in an aqueous atmosphere.

Modifying the Properties of Biodegradable Packaging Materials

The biodegradable materials are associated with several major drawbacks limiting their use in the industry. Functionality of these polymers is a big issue in addition to their higher cost and availability concerns. Thermal instability, brittleness, low melt strength, high water vapor and oxygen permeability, and poor heat sealability hinder the commercial use of PLA as food packaging (Jamshidian *et al.*, 2010). Due to the hydrophilic nature of cellulose and starch materials, the water vapor transmission resistance is very low resulting in poor mechanical properties as well as stability. Other limitations include the brittleness, poor processability, and susceptibility to the degradation (Müller *et al.*, 2011). PHA/PHB films also exhibit stiffness, brittleness, poor thermal stability, and impact resistance. Therefore, great efforts are being taken to improve the functionality of biopolymers, such as:

1. Coating: it means the covering of biopolymer using a further thin film of another material. Several bio-based and non-bio-based materials can be employed as coating. For example, PLA can be layered using PCL-Si/SiO_x, PEO-Si/SiO_x (polyethylene oxide), or PLA-Si/SiO_x, which improves the barrier properties of PLA (Iotti *et al.*, 2009). Chitosan can be employed as a bio-based coating for polymers that possess poor gas barrier properties. It can be an efficient and economic technique to improve the performance of polymer. The application of coating typically improves the barrier properties, such as water vapor and oxygen permeability, grease or oil resistance, and to a little extent, the mechanical properties (elasticity).
2. Nano-based blends: nanotechnology deals with the generation and development of nanoscale (10–9 m) structures with modified and novel properties due to the high surface-to-volume ratio. In order to modify the biopolymer, there must be a healthy interaction between the nanofiller (discontinuous phase) and polymer (continuous phase), which can be achieved through polymerization, melt intercalation, and solvent intercalation. Nanoparticles, mainly nanoclays (montmorillonite and kaolinite), are preferred to improve the properties of bio-based polymers. However, it was reported that they negatively influenced the elongation at break in case of PLA films (Peelman *et al.*, 2013). On the incorporation of nanoparticles, the barrier properties are improved by the “confinement effect,” which means that the biopolymer molecules are confined between the gas molecules and dispersed nanoparticles thus presenting a tortuous way to force the water molecules. Further, the volatile compounds are slowly diffused on the degradation of nanocomposite, improving the thermal stability (Silvestre *et al.*, 2011).
3. Physical/chemical modification: physical or chemical modification of the biopolymers is another technique used for improving the polymer performance. Such kinds of modification provide a healthy effect on the barrier and mechanical properties in addition to improving the compatibility among polymers. Generally starch is modified to enhance the hydrophobicity so that they can be better compatible with other hydrophobic materials. The addition of citric acid to starch films reduces their water vapor transmission rate because carboxyl ($-\text{COOH}$) groups react with the hydroxyl ($-\text{OH}$) groups present in starch and thus decrease the free OH groups. Also, recrystallization and retrogradation are also inhibited due to the formation of strong hydrogen bonds. Further, the addition of citric acid, a cross-linking agent improves the mechanical properties of starch (Ghanbarzadeh *et al.*, 2011; Shi *et al.*, 2008). Gelatinized starch, when heated with lithium chloride (LiCl) in the presence of some organic solvent, becomes water resistant and flexible also (Fang *et al.*, 2005). Likewise, the incorporation of acetic anhydride in microfibrillar cellulose improves the hydrophobicity as well as oxygen permeability. The limited substitution of gluten with keratin (hydrolyzed) improves the barrier properties of gluten based films, which may be due to the formation of linkages between two proteins. Further, gluten film on exposure to UV irradiation formed cross-linkages within the film, enhancing the tensile strength (Peelman *et al.*, 2013).
4. Blending of other materials: the blend of two or more biopolymers seems to be of great significance provided that the polymers must be compatible with each other's features. The compatibility can be increased by adding a reactive functional group, chemical modification, or esterification. However, positive effects of blending immiscible polymers were also observed. Biopolymer cellulose can be incorporated to the bio-based polymer mainly to decrease the water vapor transmission rate and to improve the Young's modulus and tensile strength. Incorporation of starch, glycerol, or other degradable polyester into the PLA

Table 2 Applications of biodegradable packaging materials

Packaging applications	Biopolymer	Company	References
Starch-based Milk chocolates	Cornstarch trays	Cadbury Schweppes, food group, Marks & Spencer	IBAW (2017)
Organic tomatoes	Corn-based packaging	Iper supermarkets (Italy), Coop Italia	IBAW (2017)
Cellulose Kiwi	Bio-based trays wrapped with cellulose film	Wal-Mart	Blakistone and Sand (2007)
Potato chips	Metalized cellulose film	Boulder Canyon	IBAW (2017)
Organic pasta	Cellulose-based packaging	Birkel	IBAW (2017)
Sweets	Metalized cellulose film	Qualitystreet, Thornton	IBAW (2017)
Poly(lactic acid) (PLA) Coffee and tea	Cardboard cups coated with PLA	KLM	Jager (2010)
Beverages	PLA cups	Mosburger (Japan)	Sudesh and Iwata (2008)
Fresh salads	PLA bowls	McDonald's	Haugaard <i>et al.</i> (2003)
Carbonated water, fresh juices, dairy drinks	PLA bottles	Biota, noble	Sudesh and Iwata (2008)
Freshly cut fruits, whole fruits, vegetables, bakery goods, salads	Rigid PLA trays and packs	Asda (retailer)	Koide and Shi (2007); Jager (2010)
Yoghurt	PLA jars	Stonyfield (Danone)	Haugaard <i>et al.</i> (2001); Jager (2010)
Organic fruit and vegetables	PLA packaging	Mont Blanc Primeurs	IBAW (2017)
Pasta	PLA packaging	Biorigin	IBAW (2017)
Herbs	PLA packaging	Asda (retailer)	IBAW (2017)

Source: Reproduced from Peelman, N., Ragaert, P., De Meulenaer, B., *et al.*, 2013, Application of bioplastics for food packaging. Trends in Food Science & Technology 32, 128–141.

would be beneficial in reducing the film brittleness. Chitosan film on the addition of PLA exhibited a positive effect on the barrier properties with slight reduction in the elasticity modulus and tensile strength (Cabedo *et al.*, 2006; Suyatma *et al.*, 2004).

Applications of Biodegradable Packaging Materials

The bio-based materials are mainly used to pack fresh agriculture produce, such as fruits and vegetables, fresh juices, meat, and fat rich foods. It has been observed that biopolymers have a positive effect on these mentioned products compared with traditional packages. Currently, bio-based packages are being utilized to pack products that have short shelf-life requiring low barrier properties. Commercially, PLA is widely used among several biopolymers. The bio-based packaging materials have several applications and some of them are given in Table 2.

Conclusions

Biodegradable materials are like a spell, as they can satisfy the package requirements and also do not harm the environment by breaking down into the organic matter. The biopolymers exhibit few constraints about the performance, such as mechanical and barrier properties and also cost, which can be improved by novel strategies, such as chemical or physical modifications, blending, or using nanotechniques. Biopolymers have already been used in pharmaceutical applications where functionality is more important than cost. In the food industry, these are used as biowaste bags cups, carry bags, plates and cutlery, film to pack short shelf-life food products, loose film in transport, etc. However, they are still at the beginning of commercialization. These polymers require in-depth research to improve the barrier properties and to maintain the food integrity. Further, research and development in the biodegradable polymers is the need of the hour because of humans' responsibility toward environment. That is the main driving force establishing the enormous potential of biopolymers in future.

See also: Biodegradable Packaging. Bio-Polymeric Packaging Material for Packaging of Raw Food. Food Waste for Sustainable Packaging Materials. Recyclability of Packaging Materials for Domestic Applications. Reuse of Waste Corrugated With Coir Fibers as a Packaging Materials. Role of Green Polymers in Food Packaging. Tailor-Made Bioplastics for Environmentally Friendly Food Packaging: A Methodological Approach to a Challenging Problem

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Relevant Website

<https://www.slideshare.net/cwataya/pptofbiodegradablepackaging-120816064437phpapp02-1>
SlideShare.

Bioresorbable Polymers for Surgical Suture Applications

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Glossary

Bioresorbable “Bioresorbable” is used interchangeably with the term “biodegradable” for polymers in the

literature. These polymers are broken down in the body into smaller moieties through hydrolytic and enzymatic degradation. They are then metabolized and finally excreted.

Introduction

A surgical suture is a biomaterial device, used for closing wounds. Sutures play a critical role in bringing and holding tissues together after injury or surgery. They promote wound healing through increasing the proximation between tissues, maintaining tension and strength across the wound until the tissue regenerates. Sutures can either be natural or synthetic. The choice for sutures is determined by the biocompatibility, the risk of infection and the mechanical requirements for the anatomical site of application. An undesirable biological response may get triggered when sutures are placed in contact with tissues which cause a severe and prolonged inflammatory reaction which delays the normal healing process. In this regard the ideal suture should have a negligible toxic or allergic reaction and ensure the environment is conducive to wound healing. Thus, a surgical suture is perfect for medical applications if it has the following characteristics (Pillai and Sharma, 2010; Balaji, 2013):

- Should be easy to handle
- Must cause minimal tissue reaction and no allergic response
- Maintain sterile conditions at the wound site by not supporting bacterial growth
- Exhibit high tensile strength and withstand tension within sutured tissues
- Must be easy to sterilize without changing the properties, such as strength and the rate of degradation
- Should have no carcinogenic or toxic effect systemically or at the site of application
- In the case of resorbable sutures, it must be absorbed after serving its function

Therefore, to promote wound healing without unprecedented failure, a suture must have adequate tensile properties and exhibit gradual degradation and resorption in body fluids, maintaining the rate of strength loss to match the rate of tissue growth. In this regard, intensive research has been undertaken in the past two decades to improve the properties and performance of surgical sutures. Additionally, sutures are the most popular mode of wound closure compared to other techniques like staples, tapes, and adhesives. This has resulted in tremendous growth in the need and use for sutures with expected market share for sutures to be USD 5.02 billion by 2023 (see “Relevant Website section”).

History of Sutures

Suturing techniques have been prevalent for more than 4000 years. They have been used since ancient times for wound closure and healing. Sutures originated and evolved in ancient Egypt and India, where linen, animal tissue, flax, hair, grass, cotton, and silk were used for closing wounds. The practice of suturing with several of these materials was cited in detail in the original Samihita, the prehistoric Indian medical literature by Sushruta, which was written in 500 BCE. Following this, other newer materials were reported by ancient physicians in Egypt, Babylon, and Greece. Advancements in suturing technology using catgut were first reported around 175 CE by Galan a physician to Roman gladiators. This resulted in the use of catgut, cotton, and silk as common suture materials until the early 20th century (Pillai and Sharma, 2010; Muffy et al., 2011). In 1869, it was a Lord Joseph Lister who developed the concept of sterilizing catgut sutures by impregnating them with chromic acid (Pillai and Sharma, 2010; Balaji, 2013). In the 1900s scientists attempted to improve the infection resistance of sutures. In this context, iodine sterilization of sutures by Claudius in 1902 became the standard sterilization method for sutures for nearly half a century (Balaji, 2013; Lupi, 2003). Until the 1930s and before the advent of synthetic materials, silk and catgut remained the most acceptable suture materials. Nylon, polypropylene, and polyethylene terephthalate (PET) in the 1940s became the predominant permanent or non-resorbable sutures, followed by the appearance of resorbable sutures in the 1960s with the discovery of polyglycolic acid (PGA). With a wide spectrum of available synthetic materials for both permanent and resorbable applications, the use of bovine catgut as a suture material has been phased out mainly because of the diseases linked to it, such as “mad cow” disease or Creutzfeldt–Jakob Disease (CJD) (Lupi, 2003; Kim et al., 2013; Devi and Vasudevan, 1985).

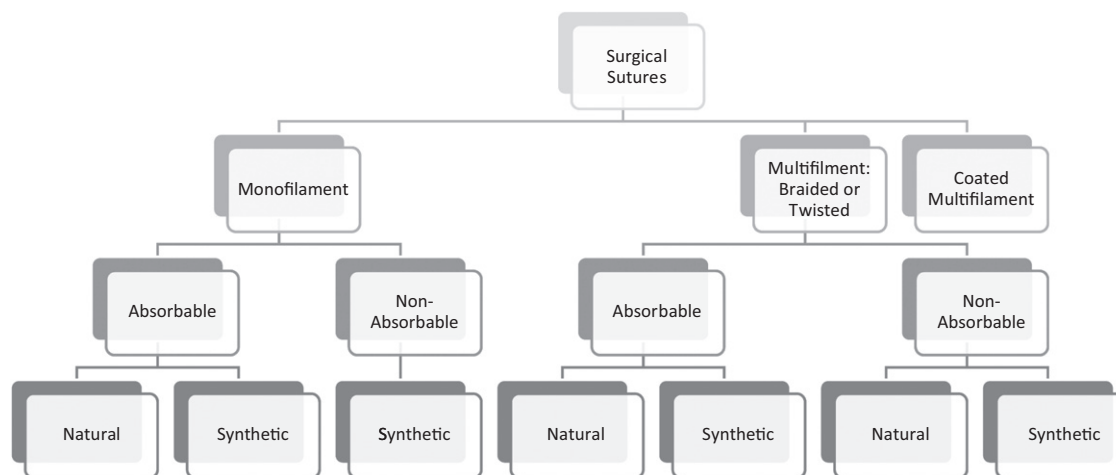


Fig. 1 Classification of sutures.

Classification of Sutures

Sutures are classified generally based on their source (synthetic or natural), the degradation profile and the expected lifetime in the patient's body (resorbable or permanent), and the method of construction (monofilament, twisted or braided). Since sutures are classified as a medical device, the approval for new suture materials and their manufacture comes under the regulatory control of the Food and Drug Administration (FDA). The guidelines for the suture industry and their manufacturers is set by a comprehensive collection of authoritative documents in different regions like the US Pharmacopoeia (USP), the European Pharmacopoeia (EP) and the British Pharmacopoeia (BP). The basic classification of sutures is based on their origin, i.e., collagen, synthetic resorbable, and synthetic non-resorbable. Non-resorbable or permanent sutures are further classified into three classes as follows (Pillai and Sharma, 2010; Chellamani *et al.*, 2013; King *et al.*, 2013):

- Class I – Silk or synthetic fibers of monofilament, twisted, or braided construction; where coating, if any, does not contribute to the thickness
- Class II – Cotton or linen fibers or coated natural or synthetic fibers, where coating significantly changes the thickness but does not contribute to the strength
- Class III – Monofilament or multifilament metal wire

Classification based on construction

As mentioned in Fig. 1 the construction of sutures is classified as either monofilament or multifilament. Monofilament sutures are single threads manufactured by polymer extrusion and monofilament spinning. Monofilament sutures exhibit a smooth low friction surface that provides the advantage of minimal tissue reaction and limited tissue trauma during suturing, and a reduced risk of bacterial growth compared to multifilament sutures. Owing to the single filament, it is comparatively easy to make a knot during a surgical procedure. However, there are drawbacks with monofilament sutures, such as low knot security and less flexibility, which makes the handling and formation of a small secure knot difficult. In addition, because of their filament thickness, monofilament sutures have a memory that retains the figure of 8 shape in the package, which contributes to the knotting problems. Currently monofilament sutures are made from: polyethylene terephthalate (PET or polyester), polyglycolic acid (PGA), polylactic acid (PLA), poly-4-hydroxybutyrate (P4HB), polyamide (PA or nylon), polypropylene (PP), polydioxanone (PDO) and stainless steel. Fig. 2 illustrates difference between the monofilament and multifilament sutures (Chellamani *et al.*, 2013; King *et al.*, 2013).

In contrast to a monofilament suture, multifilament sutures consist of several filaments being braided or twisted together. Polyesters, polyamides and silks are commonly used for manufacturing braided sutures, while catgut (reconstituted collagen), cotton and stainless steel are available in twisted multifilament form. Unlike monofilament sutures, multifilament sutures provide ease of handling and better knot security, since the threads exhibit high strength and high flexibility. To reduce their surface friction, a minimal amount of foreign coating material is added to the surface of the sutures while processing. Even so, their rough and uneven surface results in tissue drag, trauma and damage to surrounding tissue during suturing. This can result in the surrounding tissue experiencing injury, which is unlikely to happen with monofilament sutures.

Furthermore, the presence of microvoids within the structure of braided and twisted multifilament sutures results in the formation of microcapillaries that assist in the wicking of fluid into these void spaces. The accumulation of fluid around wounds is likely to cause the harboring of infectious microorganisms in multifilament sutures. As cited by Chu (King *et al.*, 2013), once filled with tissue exudate it is difficult for bactericidal inflammatory cells to reach these small hidden locations within the microvoids. This results in multifilament sutures being associated with infections and severe inflammatory tissue reactions, which compromise



Fig. 2 (a) Monofilament suture, (b) Braided multifilament suture (Courtesy of Ethicon Inc.), and (c) Coated multifilament suture (https://moskva.all.biz/poliefir-pletenyj-pb70140b0-m4-s-igloj-kolyushchej-g2019557#.Wi_9jt-nFPZ).

the tissues ability to defend against bacteria (Chellamani *et al.*, 2013; King *et al.*, 2013; Zhukovskii *et al.*, 2015). There has been research to address these negative issues associated with monofilament sutures. In this regard, the development of pseudo-monofilaments by Chellamani *et al.* (2013), and the coating of multifilament sutures with a thin polymer layer, as illustrated in Fig. 2. The ideal coating should be capable of eliminating the capillary action and imbibition of fluid, which fosters the bacterial growth (King *et al.*, 2013; Zhukovskii *et al.*, 2015). In addition, as can be observed in Fig. 2, sutures are manufactured in different colors by adding pigments, dyes or coatings, to facilitate their identification and improve their handling properties, particularly by making knotting easier and reducing tissue drag (King *et al.*, 2013).

Classification based on size

The USP (United States Pharmacopeia) and EP (European Pharmacopeia) are currently two standards used to classify sutures according to their size. To define the size and strength requirements of sutures, the USP standard involves a series of Arabic numbers that are either above (thicker than) or below (thinner than) zero as shown in Table 1 (Pillai and Sharma, 2010; King *et al.*, 2013; Benicewicz and Hopper, 1990; Bernhardt, 2016). So for sutures above size 0, they are denoted by a single digit such as 1, 2, 3, etc., where the greater the number, the larger the suture diameter. For sutures finer than size 0, the USP previously referred to sizes as 00 and 000. This designation has now been replaced by using a two-digit code where the first number refers to the number of 0's. As a result, a 4/0 suture is finer than 3/0 suture, and so on. On the other hand, the EP standard suture sizes are coded from 0.1 to 10 in the order of increasing diameter and decreasing fineness. The corresponding minimum diameter (mm) can be easily calculated. The EP standard provides ease of converting the code to the diameter in mm by simply dividing by 10. At the same time it should be remembered that the tensile strength of sutures is reduced by a decrease in suture diameter or an increase in fineness (Benicewicz and Hopper, 1990).

Classification based on degradation behavior inside the body

Surgical sutures are classified as (i) resorbable and (ii) permanent or non-resorbable, based on the strength loss in the stipulated time inside the human body. Resorbable sutures are reported to undergo enzymatic or hydrolytic degradation and subsequent tensile strength loss within the first 2–3 months inside the body. This is different from permanent or non-resorbable sutures, that retain their tensile strength near to the original value not only for several months, but usually for many years in vivo. These suture materials include stainless steel, polyester (polyethylene terephthalate), polytetrafluoroethylene (PTFE), nylon and polypropylene. However, silk and linen sutures are also considered “permanent” or “non-resorbable”, since they take more than 60–90 days to start their degradation process. Resorbable and non-resorbable sutures are further classified based on their polymer origin (i.e., natural and synthetic), as illustrated in Fig. 1. Details about the different polymers in these categories are given in the following section.

Non-Resorbable or Permanent Surgical Sutures

Silk is the oldest known and effective surgical suture material produced from the moth larvae of *Bombyx mori*. However, an associated protein called sericin, generates a negative biological response when placed in the human body, which raises concerns about the biocompatibility of silk. The literature reports that the reason for the incompatibility of silk in vivo have been attributed to this sericin coating. Successful removal of the sericin through a degumming process has resulted in no negative inflammatory response when the silk is used as a suture or as a scaffold for tissue engineering or other biomedical applications (Nakamura *et al.*, 1993; Das *et al.*, 2014). The major use of silk sutures is in ophthalmology, oral, dental and bladder surgery (King *et al.*, 2013; Naskar *et al.*, 2014; Koh *et al.*, 2015; Das *et al.*, 2014). In order to increase the rate of biodegradability and improve its anti-bacterial properties, research has been conducted on silk by applying a 4-hexylresorcinol (4HR) and silver coating to the sutures (De Simone *et al.*, 2014; Jo *et al.*, 2017). To provide a substitute for silk sutures, nylon monofilaments and braided nylon sutures have been developed. Both nylon 6 and nylon 66 are fabricated and used as suture materials in the United States, whereas, in view of its stiffer mechanical properties, only nylon 6 is used in Europe. Nylon sutures find applications in cataract surgery and for

Table 1 Suture classification based on size

USP size codes		EP size codes	Average suture diameter (mm)	Potential surgical applications
Naturally available resorbable materials	Nonresorbable and synthetic resorbable materials	Resorbable and nonresorbable materials	Min. Max.	
	12/0	0.01 and 0.05	0.001–0.009	Ophthalmology, microsurgery
	11/0	0.1	0.01–0.019	
	10/0	0.1	0.02–0.029	
	9/0	0.3	0.03–0.039	
9/0	8/0	0.4	0.04–0.049	Face, blood vessels
8/0	7/0	0.5	0.05–0.069	
7/0	6/0	0.7	0.07–0.099	
6/0	5/0	1	0.10–0.14	
5/0	4/0	1.5	0.15–0.19	Face, neck, blood vessels
4/0	3/0	2	0.20–0.24	Mucosa, neck, hands, limbs, tendons, blood vessels
3/0	2/0	2.5	0.25–0.29	Limbs, trunk, gut, blood vessels
2/0	0	3	0.30–0.39	Trunk, fascia, viscera, blood vessels
0	1	4	0.40–0.49	Abdominal wall closure, fascia, drainage sites, arterial suture lines, orthopedic surgery
1	2	5	0.50–0.59	
2	3	6	0.60–0.69	
3	4	7	0.70–0.79	
4	5	8	0.80–0.89	
5	6	9	0.90–0.99	
6	7	10	1.00–1.09	

Note: Pillai, C.K.S., Sharma, C.P., 2010. Review paper: Resorbable polymeric surgical sutures: Chemistry, production, properties, biodegradability, and performance. *Journal of Biomaterials Applications* 25 (4), 291–366. King, M.W., Gupta B.S., Guidoin, R., 2013. *Biotextiles as Medical Implants*. Cambridge: Woodhead Publishing. Benicewicz, B.C., Hopper, P.K., 1990. Review: Polymers for resorbable surgical Sutures – Part I. *Journal of Bioactive and Compatible Polymers* 5 (4), 453–472. Bernhardt, M., 2016. Suture materials. *Skinmed* 14 (2), 1–125.

suturing nerves and blood vessels. Due to their inertness and ease of handling, nylon sutures are used for cosmetic surgery. Like silk, they degrade slowly over longer periods through hydrolytic degradation, which causes a slow loss in strength over time. On the other hand, polyester (polyethylene terephthalate) (PET), (polybutylene terephthalate) (PBT) and polytetrafluoroethylene (PTFE) are used for long-term applications where high tensile strength is required for the lifetime of the patient, in procedures such as the installation of a prosthetic heart valve, hernia mesh repair, and fascia and sternum closure.

Likewise, stainless steel sutures are also used for load bearing high strength applications. Next to steel and polyester, polypropylene (PP) sutures are often used, but they are difficult to handle and knot due to their high stiffness. Recently polyvinylidene fluoride (PVDF) has been developed in order to provide a long-term solution for vascular surgery, since PVDF sutures exhibit low thrombogenicity. They have similar handling characteristics to PP sutures and long-term biostability matching that of polyester (PET) (Pillai and Sharma, 2010; Chellamani *et al.*, 2013; King *et al.*, 2013).

Advantages of Resorbable Polymers for Surgical Sutures

A permanent or non-resorbable suture is resistant to biodegradation, because it becomes encapsulated in fibrous tissue, and remains encapsulated as a foreign body unless it is surgically removed or extruded. On the other hand, biodegradable polymers from both natural and synthetic origin have recently been developed with good biodegradability and biocompatibility. However, they have inherent problems that need to be discussed, and scientific and technological solutions need to be found. To address this issue, there are a number of synthetic biodegradable polymers and copolymers made from renewable resources, such as lactic acid. Currently, polylactic acid (PLA)/polyglycolic acid (PGA) co-polymers are the most widely used synthetic biodegradable materials in biomedical applications. However, there are certain limitations to PLA, such as its low hydrophilicity and slow rate of degradation, poor soft tissue compatibility, inferior physical properties, lack of processability and high cost of production. Despite PLA's increased use in medicine, it is necessary to search and develop new materials that exhibit unique properties for specific medical applications.

By using a resorbable polymer, this eliminates the need to remove the sutures after the wound has healed. Using sutures made from a resorbable polymer has the additional benefit of promoting tissue integration in the organ or body cavity following the surgical procedure. Nevertheless, the main basic reason for using a degradable polymer as an implantable device begins with the simple desire to implant a device that once it is no longer needed will not necessitate a second surgical procedure for its removal (Gomes and Reis, 2004; Papazoglou *et al.*, 2010; Sajid *et al.*, 2014; Luckachan and Pillai, 2011; Suzuki and Ikaka, 2012).

In addition to not requiring a second operation, biodegradation offers other advantages. For example, a fractured bone, fixed with a rigid, nonbiodegradable stainless steel plate, may not heal completely, and can lead to a repeated fracture upon removal of the bone plate. This happens because the load is carried by the rigid stainless-steel plate and the bone does not carry sufficient load during the healing process. This phenomenon is known as 'stress shielding'. However, a less rigid implant prepared from a biodegradable polymer can be engineered to degrade at a rate that will slowly transfer the load to the healing bone (Gomes and Reis, 2004; Papazoglou *et al.*, 2010; Sajid *et al.*, 2014; Luckachan and Pillai, 2011; Suzuki and Ikaka, 2012).

Resorbable Surgical Sutures

Catgut and Collagen Sutures

Catgut or reconstituted collagen is the most well-known natural material used for making sutures and the strings of musical instruments. It is biochemically similar to Type 1 collagen. Interestingly the term 'catgut' is completely unrelated to the feline species. Back in 1599 J.A. Murray described a 'violin, stringed instrument' as a 'cat' and hence the name 'catgut'. Collagen is the major protein component of the human body and is present in ligaments, cartilage, tendons, skin, and bone. In most cases catgut has been extracted from a bovine or porcine source, and the monofilament is referred to as either a plain and chromic type, based on the treatment that is used for its preservation. In chromic sutures, brown chrome salts are used to cross-link the collagen, which slows down their rate of absorption in the body. Catgut sutures exhibit high elasticity and tensile strength. The degradation times for losing half their strength are 7 days and 14 days for the plain and chromic sutures respectively. As a result, catgut sutures are usually used to close skin or renal incisions and wounds, where tissue regeneration occurs rapidly (Pillai and Sharma, 2010; Devi and Vasudevan, 1985; King *et al.*, 2013; Benicewicz and Hopper, 1990).

Catgut sutures are easy to handle, but their knot security is poor and their abrasive surface causes trauma to the neighboring tissues while suturing. The sutures are packaged in an alcohol solution so as to retain flexibility, and they are usually sterilized in ethylene oxide or by gamma irradiation. There have been attempts to improve the handling properties by adding a glycerine coating and avoiding the use of alcohol for packaging. The coating increases the suture thickness which raises other concerns. In addition, newer and less injurious crosslinking methods have been introduced to improve the handling and tensile properties of catgut sutures (King *et al.*, 2013; Gajjar and King, 2014).

Since catgut sutures are made from 98% collagen, they easily degrade in the body through proteolysis. In addition, collagen is thrombogenic and acts as a hemostatic agent. Therefore, catgut is generally used for closing wounds where the tissue growth is fastest. However, there are some disadvantages for catgut sutures, like an inflammatory foreign body reaction and the need for a protocol to prevent the risk of infectious disease transmission to patients. Unfortunately, regardless of these measures, some diseases, like Creutzfeldt–Jakob disease, otherwise known as 'mad cow disease', and bovine spongiform encephalopathy (BSE) have been reported to be transferred from catgut sutures to patients (Benicewicz and Hopper, 1990; Araújo and Suassuna, 2016; Barrows, 1986; Adams, 2001).

To overcome these concerns, synthetic resorbable polymers are preferable to natural polymers. In addition, synthetic polymers provide greater control over the uniformity and desired mechanical properties. Also, it is easier to predict and control the rate of degradation and loss in mechanical properties of synthetic polymers compared to those of natural origin. We will now discuss synthetic polymers used for suture applications.

Poly(Glycolic Acid) (PGA)

PGA as illustrated in Fig. 3, sometimes referred as polyglycolide, has been one of the oldest synthetic bioresorbable polymers investigated for biomedical applications. Being 45%–55% crystalline it exhibits a high tensile modulus and a low solubility in organic solvents. The glass transition temperature (T_g) of PGA ranges from 35 to 40°C and the melting point (T_m) is around 230°C. Although it has low solubility, a variety of forms and structures can be fabricated for biomedical applications. This can be done mainly through extrusion, injection and compression molding as well as by particulate leaching and solvent casting. In view of its excellent fiber forming capability, PGA have been investigated for fabricating resorbable sutures. The first PGA-based bioresorbable synthetic suture called Dexon was approved in 1969 by the United States Food and Drug Administration (FDA). In addition, non-woven PGA fabrics have been extensively used as scaffolds for tissue regeneration owing to their predictable rate of degradation, tunable mechanical properties and cell viability. PGA implants degrade by bulk erosion as a result of scission of the

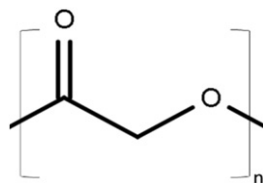


Fig. 3 Repeat unit of poly(glycolic acid).

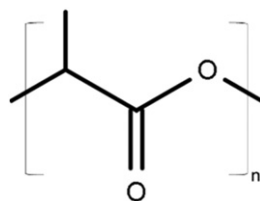


Fig. 4 Repeat unit of poly(lactic acid).

ester bonds in the polymer backbone. The suture when hydrolyzed inside the body is known to lose its strength in 1–2 months and lose its mass within 6–12 months. The main degradation products of PGA are glycine and glycolic acid, which can be metabolized by the body and excreted in urine or converted into carbon dioxide and water via the citric acid cycle. Thus, no immune or toxic response takes place. However, PGA has limited solubility, and during bulk degradation or when the rate of degradation is high, the acidic degradation products pose constraints to its use in biomedical applications. To overcome these limitations, the glycolide units are often used to synthesize copolymers (Benicewicz and Hopper, 1990, 1991; Araújo and Suassuna, 2016; Barrows, 1986; Adams, 2001; Abhari *et al.*, 2017; Bernhardt, 2016; Nair and Laurencin, 2007; Gajjar and King, 2014; Vroman and Tighzert, 2009; Ulery *et al.*, 2011; Middleton and Tipton, 2000).

Poly(Lactic Acid) (PLA)

In contrast to glycolic acid, lactic acid being a chiral molecule has two optically active forms: L-lactic acid and D-lactic acid. Poly-L-lactic acid or poly-D-lactic acid are formed after polymerization of the individual monomers and the polymers are semi-crystalline in nature (Fig. 4). L-lactide is a naturally occurring isomer and is more readily available compared to its D-lactide counterpart. However commercial polylactic acid polymer obtained from a natural source, such as Natureworks' Ingeo polymer derived from corn oil, contains both isomers with about 98% PLLA and about 2% PDLA. PLLA generally has around 37% crystallinity which is dependent on the molecular weight and processing parameters. It has a higher Tg than PGA, i.e., around 60–65°C, and its Tm is approximately 175°C. In addition, PLLA exhibits high tensile strength (~59 MPa) and high modulus (~4 GPa). PLLA is a slower degrading polymer compared to PGA. This is attributed to the presence of the voluminous methyl group present on the backbone chain that is responsible for its initial hydrophobic surface, which hinders aqueous attack. Further it has good tensile strength, low extension and a high modulus. Thus it forms a suitable candidate for implants especially in load bearing applications, such as surgical sutures and orthopedic fixtures. Some of the commercially available PLLA based orthopedic products are Phantom Suture Anchors (DePuy), Full Thread Bio Interference Screws (Arthrex) and Meniscal Stingers (Linvatec). Superior mechanical properties result in the use of PLLA in textile scaffolds for ligament replacement and augmentation devices to replace permanent fibers, such as Dacron polyester. Biomedical research continues on the use of PLA as the base material for blood vessel conduits and lipoatrophy (Araújo and Suassuna, 2016; Barrows, 1986; Adams, 2001; Abhari *et al.*, 2017; Bernhardt, 2016; Benicewicz and Hopper, 1991; Nair and Laurencin, 2007; Gajjar and King, 2014; Vroman and Tighzert, 2009; Ulery *et al.*, 2011; Middleton and Tipton, 2000; Lehtonen *et al.*, 2013).

Additionally, being more hydrophobic than PGA due to the presence of its methyl groups, PLA has a slower rate of degradation. In fact it has been observed that for high molecular weight PLA implants, they can remain from 2 to over 5 years *in vivo* before they are totally resorbed. Like PGA, the mechanism of PLA bioresorption also takes place through bulk erosion. Nevertheless, the rate of degradation depends to a large degree on the level of crystallinity as well as the porosity and thickness of the implant. Although the polymer is known to lose some of its strength and elastic modulus in the first 6 months due to the plasticizing action of water, no significant changes will occur in the mass until much later. Therefore, currently co-polymers of L-lactides or D-lactides with glycolides are being studied with the objective of developing polymers with a wider range of properties and hence increasing their scope of applications.

Polyglactin 910 or Poly(Lactide-co-Glycolide) (PLGA)

Poly(lactide-co-glycolide) (PLGA) is among the most common co-polyesters that have been investigated extensively for a multitude of applications (Fig. 5). Different ratios of poly(lactide-co-glycolides) have been researched and commercially developed to be used as resorbable fibers for biomedical applications. Panacryl is a suture on the market melt spun from a co-polymer with a higher lactide/glycolide ratio to slow down the rate of degradation. With further research, several alternative block co-polymers have subsequently been developed for the fabrication of monofilament sutures, such as poly(glycolide-co-trimethylene carbonate) and poly(glycolide-co-caprolactone) containing hard and soft segments along the polymer backbone to achieve the desired properties. Other applications include the development of tissue engineered scaffolds for skin called Dermagraft (Nair and Laurencin, 2007; Gajjar and King, 2014).

Analogous to PLA and PGA, PLGA also undergoes bulk erosion through hydrolysis of the ester bonds. In this case, besides molecular weight, shape and porosity, the degradation rate also depends on a lactide/glycolide ratio. So in the case of PLGA the ability to control the degradation rate compared to the previously mentioned homopolymers is an advantage. In addition, its

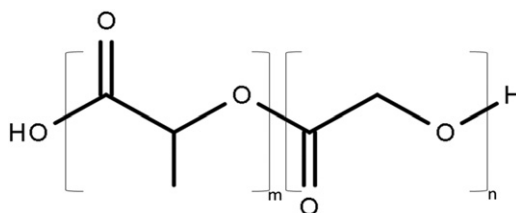


Fig. 5 Repeat unit of poly(lactide-co-glycolide).

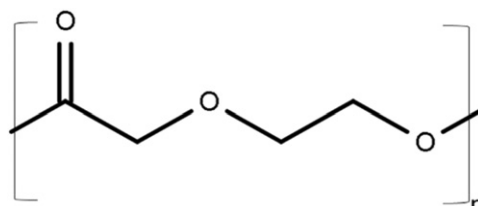


Fig. 6 Repeat unit of polydioxanone.

biocompatibility and processability have made it a popular polymer for biomedical applications. PLGA has become a potential candidate for sutures and tissue engineering scaffolds as it promotes cell adhesion and proliferation in the process of developing healthy tissue. Several drug and protein delivery vehicles are also made from PLGA in the form of microspheres, microcapsules, nanospheres and nanofibers which are able to control their rate of release. However, due to bulk erosion of PLGA being dependent on the thickness of the material, gradual release from such drug delivery systems has been found to be problematic. Further, when used for protein release, protein denaturation occurs due to the acidic degradation products released during bulk degradation. This limitation has been overcome by using surface eroding polymers in order to achieve zero release kinetics (Benicewicz and Hopper, 1990, 1991; Araújo and Suassuna, 2016; Barrows, 1986; Adams, 2001; Abhari *et al.*, 2017; Bernhardt, 2016; Nair and Laurencin, 2007; Gajjar and King, 2014; Vroman and Tighzert, 2009; Ulery *et al.*, 2011; Middleton and Tipton, 2000).

Polydioxanone (PDO)

Bioresorbable polymers like PLA, PGA and PLGA have been successfully used to develop multifilament sutures. Recently extensive research has been undertaken to develop polymers for resorbable monofilament sutures that will replace multifilament braided sutures, reduce the potential risk of infection and lower the surface friction that causes tissue trauma when pulling the suture through soft tissue. Polydioxanone (PDO) was the material used for developing the first monofilament suture in 1980 under the trade name of PDS (Fig. 6). It has also been studied for orthopedic applications, such as the suturing of small bone and osteochondral grafts. PDO is synthesized by a ring opening polymerization of p-dioxanone. It is a colorless, semi-crystalline polymer with a low Tg ranging from -10 to 0°C , and a Tm at 106 – 115°C . PDO fibers have a low tensile modulus (1.5 GPa), and good flexibility, which can be attributed to its low Tg (Benicewicz and Hopper, 1990, 1991; Araújo and Suassuna, 2016; Barrows, 1986; Adams, 2001; Abhari *et al.*, 2017; Bernhardt, 2016; Nair and Laurencin, 2007; Gajjar and King, 2014; Vroman and Tighzert, 2009; Ulery *et al.*, 2011; Middleton and Tipton, 2000).

Degradation takes place due to non-specific scission of the ester backbone. But due to its high crystallinity ($\sim 55\%$) and hydrophobicity, PDO exhibits only a moderate rate of resorption. When implanted in the body PDO breaks into glyoxylate moieties, and is either excreted in the urine or may react with enzymes and be converted into glycine. Glycine is subsequently converted into carbon dioxide and water as in the case of PGA. Due to the slow absorption of fluid and partial degradation, the polymer is known to lose its strength within 1–2 months. Thereafter, with increased hydrolytic degradation, complete mass loss takes place within 6–12 months.

Poly(Caprolactone) (PCL)

Polycaprolactone (PCL) is a semicrystalline polymer synthesized by ring opening polymerization using a relatively cheap monomer ‘ε-caprolactone’, which makes it an attractive raw material for spinning resorbable fibers and sutures (Fig. 7). Its low Tm of 55 – 60°C and Tg of -60°C enables PCL to be easily processed. It is readily soluble in a wide range of organic solvents and forms miscible blends with a wide range of polymers. Being a polyester, it also undergoes hydrolytic degradation initiated at the water susceptible ester bond, but at a slow rate, with complete resorption taking 2–3 years. Due to its slower rate of degradation, its high permeability to many drugs and its non-toxicity, PCL is promoted as a long-term drug/vaccine delivery agent.

PCL exhibits low tensile strength (~ 23 MPa), but a high elongation at breakage, with values sometimes reaching 500% – 700% . It has also been used as a suture, but in copolymer form, because of the low strength of the homopolymer. Monocryl is a

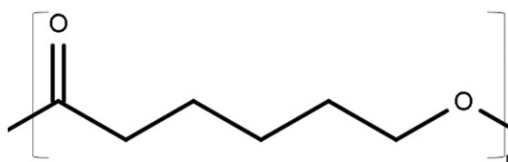


Fig. 7 Repeat unit of polycaprolactone.

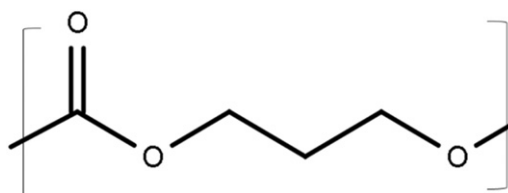


Fig. 8 Repeat unit of poly(trimethylene carbonate).

commercially available monofilament suture spun from a caprolactone and glycolide copolymer. This has resulted in less stiff and more extensible sutures compared to those made from the polyglycolide homopolymer (Benicewicz and Hopper, 1990, 1991; Araújo and Suassuna, 2016; Barrows, 1986; Adams, 2001; Abhari *et al.*, 2017; Bernhardt, 2016; Nair and Laurencin, 2007; Gajjar and King, 2014; Vroman and Tighzert, 2009; Ulery *et al.*, 2011; Middleton and Tipton, 2000).

Poly(Trimethylene Carbonate) (PTMC)

PTMC is an elastomeric aliphatic polyester with a T_g of -17°C and poor mechanical strength. However, when it is polymerized to a high molecular weight through a ring opening reaction, it has excellent flexibility (Fig. 8). In order to take advantage of these properties PTMC scaffolds have been investigated for soft tissue regeneration. At the same time low molecular weight PTMC has been investigated as a drug delivery agent. Unlike the previously described aliphatic polyesters, PTMC undergoes surface degradation and erosion, which makes it a suitable candidate as a drug delivery vehicle. The rate of degradation in the case of PTMC has been found to be higher in vivo than in vitro attributed to enzymatic degradation being experienced in vivo. Several copolymers with other cyclic lactones have been developed for PTMC. The objective of this approach is to overcome the disadvantage of its inferior mechanical properties, as this has limited its potential applications. Block co-polymers of trimethylene carbonate and glycolides have been developed and are used as a flexible suture material, namely Maxon®, and an orthopedic fixture, such as Acufex®. Additionally, a terpolymer with glycolide, dioxanone and trimethylene carbonate is commercially available and is marketed as a suture material called BioSyn® (Benicewicz and Hopper, 1990, 1991; Araújo and Suassuna, 2016; Barrows, 1986; Adams, 2001; Abhari *et al.*, 2017; Bernhardt, 2016; Nair and Laurencin, 2007; Gajjar and King, 2014; Vroman and Tighzert, 2009; Ulery *et al.*, 2011; Middleton and Tipton, 2000).

Polyhydroxyalkanoates

Polyhydroxyalkanoates, also referred to as bacterial polyesters, are naturally available bioresorbable polyesters produced from bacteria which generate the polymer as a means of storing energy. The most common bacterial polyester is poly(3-hydroxybutyrate) (P3HB) illustrated in Fig. 9(a). It was discovered in 1920, produced from the bacteria "*Bacillus megaterium*". Since then, other strains of bacteria have been found to produce other types of polyhydroxyalkanoates (Fig. 9). These polymers once extracted from their bacteria, yield a pure, semi-crystalline and isotactic structure. Like other polyesters they also undergo hydrolytic degradation at the ester bond. The mechanism involves surface erosion and follows zero order kinetics, losing the total mass in 24–30 months. The degradation products of the polyhydroxybutyrates (PHBs) are usually the monomer species, i.e., D-(-)-3-hydroxy-butyric acid, which is a normal constituent of blood. Furthermore, it melts in the range of $160\text{--}180^\circ\text{C}$, which facilitates polymer processing. In addition to bacterial synthesis, chemical synthesis routes have also been explored for PHB production. Ring opening polymerization of optically active β -butyrolactone has been used for synthesizing PHBs, which are identical to their bacterial counterpart. Copolymers of PHB and 3-hydroxyvalerate (P(HB-HV)), as illustrated in Fig. 9(c), have also been investigated. They are semi-crystalline, although they have a lower T_m , which is mainly dependent on the HV content. In addition, this copolymer features a T_g in the range of -5 to 20°C . Both PHB and P(HB-HV) have been reported to be soluble in a variety of solvents, which allows them to be processed and fabricated into various shapes, such as films, sheets, spheres and fibers.

Copolymers are comparatively less brittle and tougher than PHB homopolymers, which broadens their potential use in biomedical applications. Additionally, P(HB-HV) has a unique piezoelectric property, making it attractive for orthopedic applications, as electrical stimulation helps in bone healing. Due to its high crystallinity the degradation rate of PHB homopolymers is

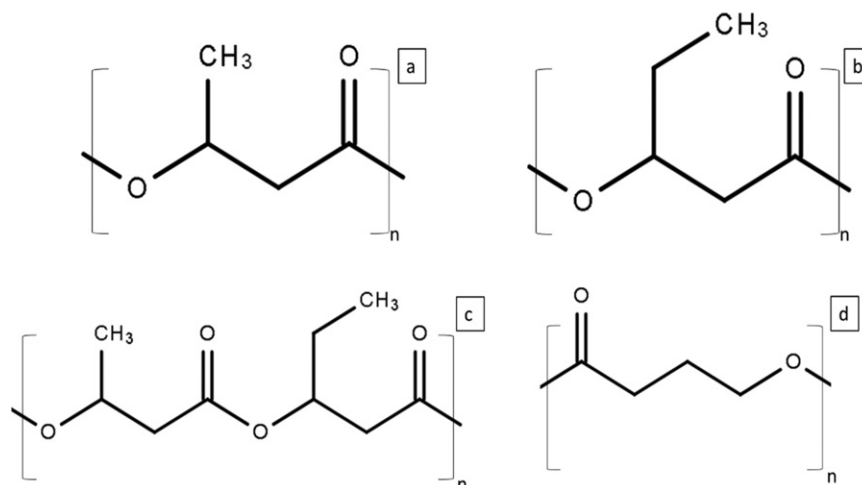


Fig. 9 Repeat units of (a) poly(3-hydroxybutyrate), (b) poly(3-hydroxyvalerate), (c) poly(3-hydroxybutyrate-co-3-hydroxyvalerate), and (d) poly(4-hydroxybutyrate).

Table 2 Comparison of properties of P4HB with other aliphatic polyesters

Polymer	T_m ($^{\circ}\text{C}$)	T_g ($^{\circ}\text{C}$)	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Resorption time
PGA	225	35	70	6900	<3	6 weeks
PLLA	175	65	28–50	1200–2700	6	1.5–5 years
DL-PLA	Amorphous	50–53	29–35	1900–2400	6	3 months
PDO	110–115	–10 to 0	–	1.5	–	6–12 months
P3HB	180	1	36	2500	3	2 years
PCL	57	–62	23	400	700	2 years
P4HB	60	–51	50	70	1000	8–52 weeks

Note: Gajjar, C.R., King, M.W., 2014. Resorbable Fiber-Forming Polymers for Biotextile Applications, first ed. Cambridge, Heidelberg, New York, Dordrecht, London: Springer. Martin, D.P., Williams, S.F., 2003. Medical applications of poly-4-hydroxybutyrate: A strong flexible resorbable biomaterial. *Biochemical Engineering Journal* 16 (2), 97–105. Williams, S.F., Rizk, S., Martin, D.P., 2013. Poly-4-hydroxybutyrate (P4HB): A new generation of resorbable medical devices for tissue repair and regeneration. *Biomedical Engineering* 58 (5), 1–13.

slower than that of synthetic polyesters, and complete mass loss takes around two years. However, copolymerization increases the degradation rate owing to the decrease in crystallinity. Although the relationship between the degradation profile and the HV monomer content has yet to be established, considerable research effort is focused in this direction. By increasing the rate of degradation, P(HB-HV) becomes a more attractive copolymer for use in vivo as a tissue engineering scaffold (Nair and Laurencin, 2007; Gajjar and King, 2014; Wang *et al.*, 2011; Anjum *et al.*, 2016; Bugnicourt *et al.*, 2014; Chen and Wu, 2005; Kehail *et al.*, 2017; Langer *et al.*, 2002).

In 2007 the FDA approved the use of another bacterial polyester, poly-4-hydroxybutyrate (P4HB), for the manufacture and use as a resorbable suture (Fig. 9(d)). The suture is now produced and marketed under the tradename Tephaflex® by melt-spinning the P4HB polymer. An article by Martin and Williams (2003) was the first report dedicated to presenting P4HB and its properties. However, the article focused on the commercialization and patent owned by Tephaflex Inc., and instead of describing a detailed experimental study, the paper compared the physical properties of P4HB with other polymers as illustrated in Table 2 (Suzuki and Ikaka, 2012).

Since P4HB is naturally produced from bacteria it does not contain any manufacturing additives, like catalysts and residual monomer, which can lead to post-implantation tissue inflammation. Although it is produced by bacteria, its structure is very simple and similar to that of PGA and PCL, with differences in the number of carbons in the repeat unit as illustrated in Fig. 9. The P4HB monofilament is a strong and malleable thermoplastic with similar ultimate mechanical properties, such as breaking load, to polypropylene and PDO sutures. In addition, P4HB exhibits elongation at break of 100%, resulting in a highly elastic performance. As with other PHBs, copolymerization of P4HB with other butyrates has been undertaken to enhance its mechanical or absorption properties. In addition, there have been efforts to modify the structure by functionalizing the P4HB polymer so as to produce nonacidic degradation products and improved control over the rate of degradation (Williams *et al.*, 2013; Odermatt *et al.*, 2012; Zhang *et al.*, 2013).

Preliminary studies have reported that P4HB sutures degrade more slowly than PGA and PDO sutures. However, in the study conducted by Odermatt *et al.* (2012) to assess the toxicity of the degradation byproducts of Monomax® (P4HB) sutures, it was

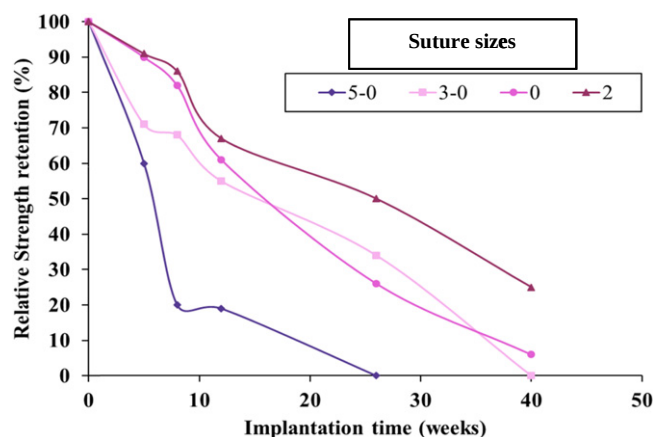


Fig. 10 P4HB monofilament strength retention. Adapted from reference Odermatt, E.K., Funk, L., Bargon, R., *et al.*, 2012. MonoMax suture: A new long-term resorbable monofilament suture made from poly-4-hydroxybutyrate. *International Journal of Polymer Science* 2012, 1–12.

found that they degraded more slowly in the body compared to PDS II® (PDO) sutures. On the other hand, the rate of degradation for P4HB is known to be faster than for PLLA, PCL and other PHA's *in vivo*. Recently, Williams and Odermatt have published other papers describing the suture's degradation performance in the human body and its use in other applications such as in tissue engineering scaffolds. The effect of P4HB suture size on its degradation profile is illustrated in Fig. 10.

In the last 10 years there has been an increasing number of patents related to P4HB and its applications, but few of them have discussed the fundamental concepts and mechanisms of biodegradation and bioresorption in the body. As mentioned above this biopolymer has a unique set of properties that have resulted in its introduction as a distinct new class of innovative, fiber-based commercial products for soft tissue repair. Current studies in the authors laboratory is generating information about the degradation mechanism of P4HB under various pH and enzymatic conditions. This work will help in generating the fundamental understanding that will be used for developing new biomedical applications (Williams *et al.*, 2013; Odermatt *et al.*, 2012; Williams *et al.*, 2016; Buell *et al.*, 2017).

Surgical Suture Properties

The selection of a suture by a surgeon is dependent on the required knot performance, in terms of knot strength and knot security, as well as on the anatomical environment and type of tissue it is approximating. The physical, mechanical and surface properties of the suture material will affect the suture's function, which in turn will determine the inflammatory response and the rate of wound healing.

Mechanical Properties

The mechanical properties of sutures are dependent on the polymer used and its processing conditions. It is critical to understand these properties for all polymer materials, and select only those which closely match the clinical need, the mechanical loading environment and the desired rate of wound healing. The initial and subsequent mechanical behavior of a suture comprises its strength, stiffness (resistance to stretching), viscoelasticity, coefficient of surface friction and flexural rigidity (or ease of bending), which are dependent on its thickness or diameter and its degradation profile. The mechanical properties of sutures are measured in terms of their tensile strength, modulus of elasticity, elongation at break and toughness. In addition to these general tensile properties, the knot strength and security are critical for defining the suture's functionality and *in vivo* performance. The knot strength, besides being dependent of the suture material and its processing history, is also affected by the sutures ease of bending and handling, as well as the knotting procedure, the suture size and the number of throws in the knot (Chellamani *et al.*, 2013; King *et al.*, 2013).

The tensile breaking strength of a suture is used to compare the strength of different suture materials having different sizes since it is obtained by normalizing the ultimate tensile force with respect to the suture's cross-sectional area. However, since the linear density can be measured in denier or tex more precisely for a twisted or braided multifilament suture than its cross-sectional area, it is more common in textile engineering circles to refer to the "tenacity" of a suture or yarn, rather than its tensile strength. The tenacity is calculated from the ultimate breaking force divided by the linear density measured in denier or tex, which is the mass in grams of 9000 m or 1000 m of yarn or suture respectively. The American Society for Testing & Materials (ASTM) describes the test method and test conditions for measuring, reporting and comparing the tensile properties of yarns and sutures under both dry and wet conditions.

However, one needs to refer to the U.S. Pharmacopeia in order to find the test method for measuring the tensile properties of a knotted suture. It is critical to use a suture with a tensile strength that can withstand the tension during clinical use. But equally important is the tying of a knot that will remain secure and will not fail in the patient's body during the healing period. This means that the suture needs to have high static friction on its surface so as to promote knot security. At the same time, the surface of the suture should not be rough and cause injury or trauma to the tissue it passes through. This points to the need for the suture surface to have high static friction and low dynamic friction. This apparent conflict of requirements is normally resolved with the application of suitable surface lubricants or finishes. Thus, optimal physical, tensile and surface properties are critical for sutures with respect to the anatomical location and the type of tissue they are being used to approximate (Pillai and Sharma, 2010; Chellamani *et al.*, 2013; King *et al.*, 2013; Suzuki and Ikaka, 2012).

Bending stiffness is another important mechanical attribute for a suture, which is dependent on its bending modulus. This regulates the handling characteristics of the suture in terms of ease of knotting and knot security. Suture diameter, its construction (monofilament or braided), and any treatment, like a surface coating, are the main factors determining the suture's stiffness. An increase in the bending stiffness due to increased diameter or a coating will restrict the suture's ability to bend, its pliability and ease of handling. In addition to stiffness, stretch and recovery are important properties. The amount of stretch is the ease with which the suture deforms under applied tensile stress, and the recovery is the extent to which the original form and shape is regained after the applied stress has been removed. Both these properties are significant for *in vivo* applications. Stretch and recovery play important roles when edema and swelling of the wound occurs after injury or surgery (Pillai and Sharma, 2010; Chellamani *et al.*, 2013; King *et al.*, 2013).

Handling Properties

Handling properties are those subjective attributes that the surgeon feels and experiences during the suturing process, making them difficult to quantify. However, to understand the handling of sutures, they are categorized into pliability (or stiffness), ease of knotting, knot security, package memory, surface friction, viscoelasticity and tissue drag. They are either directly or indirectly related to the physical, mechanical and surface properties as explained above. For example, the bending stiffness relates to the suture's pliability. Furthermore, the ease of handling is dependent on the coefficient of surface friction of the suturing material. This is the measure of slipperiness (i.e., low dynamic friction) which, as mentioned previously, is affected by the suture's construction and surface finish. Controlling the coefficient of friction to an optimum value is critical, because it will affect the extent of drag on the surrounding tissues and the ease with which knots can be tied in terms of the "knot tie-down" force. Drag is high when the coefficient of dynamic friction is high, resulting in trauma to the surrounding tissue. So finishes are applied to produce a more slippery surface with a lower dynamic coefficient of friction.

However, as explained earlier, making the suture smooth or reducing the static coefficient of friction will compromise the knot security. And knot security needs to be high as it is the force required to cause a knot to slip, either partially or completely, and come undone. In addition, package memory is another factor related to the flexibility and recovery of the suture. In the case where sutures exhibit package memory and remember their figure of 8 shape, handling them becomes difficult for the surgeon, as the knots tend to untie due to this memory effect. In general, monofilament sutures exhibit more package memory than braided ones. Package memory is evaluated by hanging the suture in air under a nominal load and determining the time required for the suture to straighten out (King *et al.*, 2013; Suzuki and Ikaka, 2012).

Biocompatibility

Since sutures are foreign materials in the human body, they automatically trigger an inflammatory response. The severity and duration of this response is dependent on the material, construction and size of the suture, as well as its stiffness and tension *in situ*. The anatomical environment where it is placed in the human body also has an important role to play, since it will define the pH and enzymatic activity. This biological response generated by the human body to the introduction of the suture is referred to as its "biocompatibility" (King *et al.*, 2013).

Firstly, the type of polymer from which the suture is made has a role in the tissue response. Eventually, resorbable sutures will cause less scar tissue formation due to their bioresorption over time, which is not the case for permanent or nonresorbable sutures. However, the degradation products formed in the case of bioresorbable sutures are an important factor to be considered. The degradation products like lactic acid and glycolic acid are easily metabolized by the body, although in the case of acid build up there may be a temporary negative cytotoxic tissue response. This is further governed by the environmental conditions. For example, the pH varies in different parts of the body. It is around pH 5 on the skin, while blood has a pH of 7.4. The pH reaches extreme values in the stomach and gastro-intestinal tract before and after digestion, reaching pH 3 and pH 8 respectively. Secondly, the physical properties like stiffness and hardness have significant roles to play in the tissue response. In the case of open incisions that need to be closed or when tissues are under tension, a more severe inflammatory response is generated in the surrounding tissue. In addition, the construction of a suture, i.e., whether it is monofilament or multifilament, affects the extent of wicking due to capillary action. For multifilament twisted and braided sutures the size distribution of the pores within the braid can lead to an increased risk of infection, a more severe inflammatory response, subsequent increased tissue activity and an increased risk of forming adhesions (Suzuki and Ikaka, 2012).

Design and Fabrication of Surgical Sutures

Advancements in synthetic fiber technology with the availability of an extensive range of synthetic bioresorbable polymers discussed above have opened up opportunities to harness these new polymers in the development of new suture designs. Bioresorbable polymer-based sutures exhibit a number of advantages over the non-resorbable or permanent materials. The resorption process usually provokes a healthy inflammatory response, which promotes the infiltration of cells, the formation of new blood vessels (*vasa vasorum*), the laying down of collagen and extra cellular matrix, and the generation of new tissue. This increases the rate of healing and improves the anchoring of the suture to the surrounding tissue capsule. The rate of healing occurs more slowly when permanent or non-resorbable sutures are used. In addition, the suture tension plays a critical role in this healing response, as cells behave differently when exposed to different conditions of applied stress.

Of all the bioresorbable polymers only a few can be spun into fibers and filaments for suture applications. These polymers need to have fiber forming characteristics so that they can be spun by existing melt or solution spinning technologies. The most important prerequisites for forming fibers from resorbable polymers is that they should have adequate viscosity in the melt or solution, so that they can withstand the high shear and elongational stresses in the spinline without tensile failure. In addition, the developed fibers or filaments should have an oriented and semi-crystalline structure, so they can have the desired mechanical properties and tensile performance. As stated before, not all polymers have an ability to be spun into fibers and this is primarily governed by the chemical structure of the monomer, the linear nature of the polymer chain, a high enough degree of polymerization and average molecular weight, and the ease of forming crystalline regions from the polymer melt or solution. Besides, polymers should not degrade. They should remain stable at processing temperatures and at the ambient temperature of use. The chemical structure and crystallization profile (including the rate, type and shape of the crystals) controls the extent of orientation within the fibers in the spinline during the drawing or stretching process. The degree of crystallinity and orientation have a strong influence on the mechanical properties, the absorption behavior and, most importantly, the degradation profile of the resorbable fibers. For example, interchain interactions and cross-links improve the order of the polymer structure. This leads to improved orientation and crystallinity, thus increasing the overall tensile performance and reducing the rates of hydrolytic degradation and reabsorption. By this means, bioresorbable polymers have the ability to be spun into fibers and filaments and fabricated into thin, lightweight porous textile structures that are required as tissue engineering scaffolds, drug delivery vehicles and implantable organs for the treatment of injury and disease (Gajjar and King, 2014).

Most resorbable polymers are thermoplastic. This means that they can be synthesized in the form of resin pellets and then meltspun, as illustrated in Fig. 11. Melt spinning is the most common method due to the speed of production, cost efficiency and reduced environmental impact. Here the polymer is melted in an extruder and then pumped through a filter pack and spinneret to

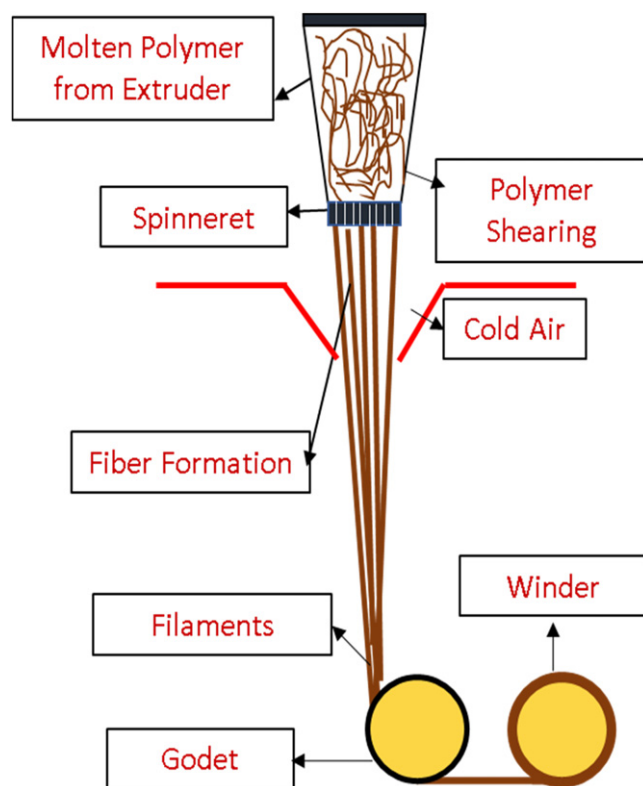


Fig. 11 Melt spinning process for suture manufacture.

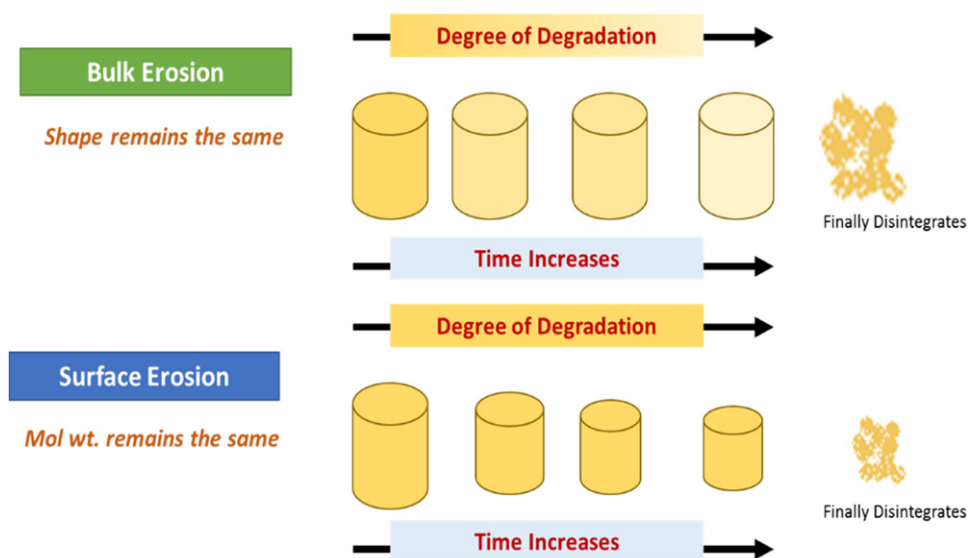


Fig. 12 Degradation mechanisms – Bulk erosion and surface erosion.

form continuous filaments (Fig. 11). One advantage of this process is that one can spin filaments with various cross-sectional shapes, like trilobal, multilobal or hollow fibers depending on the desired application. However, in the case of sutures the shape is usually round. Additionally, bicomponent or multicomponent continuous filaments with enhanced fiber properties can also be obtained from this spinning method.

Subsequent drawing and heat setting operations are then required so as to achieve improved mechanical properties. Other modes of spinning, like solution spinning and gel spinning, are also available for spinning polymers that are not thermoplastic, or when thermally sensitive drugs need to be added to the polymer for spinning drug delivery fibers. Depending on the suture application, the filaments are spun as either monofilaments or multifilament yarns that have to be braided or twisted in a subsequent process. There are a number of processing parameters that effect the final suture properties, and hence its clinical performance. Higher processing temperatures during melt spinning which cause mechanical shear stresses may lead to premature polymer degradation. If the polymer resin is not completely dry prior to melt spinning, the rate of degradation may increase several fold due to the presence of moisture which will initiate the hydrolysis of such resorbable polymers. In addition, there may be the formation of process-induced monomer that serves as an autocatalytic initiator of the degradation process, thus increasing the rate of degradation and further impairing the mechanical properties. Also, high temperature sterilization techniques can have a significant impact on the suture degradation profile by weakening and breaking inter-molecular bonds and causing inferior mechanical product performance (Gowariker *et al.*, 1986; Gupta and Kothari, 1997).

Most importantly, controlling the rate of spinning, including the linear flow rate and the shear stresses in the spinneret is essential so as to obtain adequate crystallinity in the spun and drawn fibers. The level of crystallinity not only controls the mechanical properties, but also the rate of resorption and the degradation profile of the fibers (Ali *et al.*, 1993). Following spinning and drawing, the fabrication of suture materials involves additional processing, such as twisting and/or braiding as well as the application of finishes and coatings. In addition, commercial surgical sutures are exposed to an extensive sterilization process, which involves minimal handling. Sterilization is achieved either by a low temperature ethylene oxide treatment followed by aeration or by gamma irradiation. These procedures have been developed to prevent premature degradation or changes in the performance of the resorbable sutures while being sterilized.

Degradation Mechanism for Bioresorbable Sutures

The bioresorption time, in terms of its half-life, is an important factor used to measure the rate of degradation of a polymer inside the body. The first half-life is defined as the time required for the tensile strength to fall to half its original value. Furthermore, there is a second half-life related to the loss of mass of the suture material. This half-life is defined as the time required for the mass to reach half its original value. It is important to remember that both these half-life factors are influenced by the suture's thickness, its diffusion properties and the anatomical environment in which it is located.

Process of Bioresorption

Bioresorbable fibers are hydrolytically degradable. These fibers are made up of polymers that have chemical bonds in their backbone chain that are susceptible to aqueous attack or hydrolysis. These bonds include esters, orthoesters, anhydrides, carbonates, amides, urethanes and ureas. Bioresorption generally involves four steps in the following sequence: water absorption, loss of

Table 3 Characteristics of different resorbable sutures

<i>Class (Chemical name)</i>	<i>Commercial name</i>	<i>Manufacturer</i>	<i>Break strength straight pull (MPa)</i>	<i>Break strength knot pull (MPa)</i>	<i>Elongation to break (%)</i>	<i>Young's modulus (GPa)</i>	<i>Degradation</i>	<i>Strength loss time</i>
Catgut/collagen	Suruchrom, Surucor Plain or mild chromic, chromic gut, Surgical gut – plain or chromic, Softcat plain or chromic, PDS	Surgical Specialties Corp, Dynek Sutures, SURU International, PVT, Medtronic, Ethicon, Aesculap, Inc., B. Braun, Astra, D/G, SSC, Kollsut, DemeTech	310–380	110–210	15–35	2.4	Enzymatic collagenases and metalloproteinases	7–14 days
Poly(glycolic acid) (PGA)	Dexon-braided multi-filament, Dexon Plus, Dexon II, Safil, B. Braun, DemeTech, Serafit	Medtronic, Surgical Specialties Corp, Deknatel, SURU International PVT, B. Braun, Aesculap Inc.	–	–	<3	–	Hydrolytic	~1 month
Poly(glycolide/L-lactide), Poly(glycolide co-TMC), Poly(glycolide/trimethylene carbonate) copolymer	Polyglactin 910 (Vicryl _L), Polysorb, RadikTM, Maxon, Monosyn, Vicryl Plus, Panacryl	Ethicon, US Surgical, Specialities Inc., B. Braun, Medtronic	570–910, 654–882, 760–920	280–480, 300–400, 310–590	18–25, 67–96, 18–25	3–3.4, 7–14	Hydrolytic	–
Poly(lactic acid) (PLA)	Orthodek	TephaFlex Medical	–	–	–	–	Hydrolytic	1.5–5 years
Polydioxanone (PDO)	PDS II, MonoPlus	B. Braun	450–560	240–340	26–38	1.2–1.7	Hydrolytic	1–2 months
Poly-4-hydroxybutyrate (P4HB)	TephaFlex (MonoMax)	Tepha, Inc., B. Braun	–	~400	1000	0.485	Hydrolytic	8–52 weeks

Note: Pillai, C.K.S., Sharma, C.P., 2010. Review paper: Resorbable polymeric surgical sutures: Chemistry, production, properties, biodegradability, and performance. *Journal of Biomaterials Applications* 25 (4), 291–366. King, M.W., Gupta B.S., Guidoin, R., 2013. *Biotextiles as Medical Implants*. Cambridge: Woodhead Publishing.

molecular weight, reduction in mechanical properties, and finally the complete loss of weight or mass. The process of bioresorption starts with physicochemical hydrolysis or degradation of the polymer at pH 7.4, the normal pH for healthy whole blood. This is without any enzymes, and so it results in degradation into smaller moieties such as monomer units that are bioresorbed. When placed in the body, water and aqueous biological fluids diffuse into the material initiating the process of hydrolytic degradation. This results in a loss in mechanical performance over time. Initial hydrolysis starts in the amorphous regions of the polymer where the water and aqueous fluids can enter easily owing to a lack of interchain bonding and an amorphous structure with greater space in between the molecular chains. The entry of fluid into the polymer matrix results in an initial loss in strength and modulus since the fluid acts as a plasticizer. Thereafter, the hydrolytic degradation and breaking of bonds causes a reduction in molecular weight followed by a change in shape and disintegration. The disintegrated fragments are metabolized into oligomers, which are either absorbed or excreted by the body. Bioresorption of fibers and polymers can take place by one or more of the following mechanisms:

- (1) Solubilization (e.g., dextran, polyvinyl alcohol, and polyethylene oxide);
- (2) Ionization followed by solubilization (e.g., polyacrylic acid and polyvinyl acetate);
- (3) Enzymatically catalyzed hydrolysis (e.g., polysaccharides and polyamides); and
- (4) Simple hydrolysis (e.g., aliphatic polyesters).

Out of these four, the main mechanisms for bioresorption of implantable fibers and polymers are simple hydrolysis and enzymatically induced hydrolysis. Basically, both these mechanisms involve hydrolytic bond cleavage along the polymer backbone chain that result in fragmentation of the polymer and produces low molecular weight oligomers that are metabolized by the body (Li, 1999; Ali *et al.*, 1993).

The bioresorption process basically takes place by two alternative degradation mechanisms: (i) bulk erosion or (ii) surface erosion, as illustrated in Fig. 12. In bulk erosion, the rate of diffusion of water into the polymer structure is much faster than the rate of hydrolysis of the polymer. Due to this the hydrolysis starts from the inside and moves outwards. Thus, the shape of the polymer stays intact until there is a sudden and rapid loss in structural integrity as the polymer sample breaks open and rapidly releases its degraded material and acidic monomers into the surrounding tissue. In contrast, in surface erosion the rate of hydrolysis is faster than the rate of diffusion. As a result, the mass loss occurs at the external polymer/water interface and takes place from the outside in. As the shape diminishes over time the erosion is responsible for device thinning. The bulk integrity of the polymer is maintained throughout the degradation process. So the continuous surface erosion makes this type of polymer a suitable candidate for developing a drug delivery device.

In addition to the rate of resorption being controlled by the rate of hydrolysis of the functional groups in the backbone chain and the rate of diffusion of water inside the matrix, the polymer resorption is also governed by the thickness of the suture or polymer material. If the thickness of the material is more than the critical dimension, which is calculated for each particular polymer, then surface erosion will inevitably take place, because aqueous fluids are not able to diffuse into the polymer sample. However, if it is smaller than the critical dimension, then bulk erosion takes place. Additionally, the resorption process is made more complicated if the polymer undergoes autocatalytic degradation as is the case with PLA and PLGA scaffolds. Autocatalysis results in the generation of acidic oligomeric products like carboxylic acid, that cause a localized fall in pH and hence accelerate the degradation process. This self-catalyzed hydrolysis results in the formation of hollow structures inside fibers and polymer materials leading to a rapid deterioration in mechanical properties and a sudden loss of structural integrity. It is critical to understand this phenomenon, especially for those polymers that are used as scaffolds for tissue engineering as acidic conditions are likely to have a cytotoxic effect of cell adhesion, proliferation and growth (Gorman *et al.*, 2011; Gopferich, 1996; Tsuji, 2002; Ndazi and Karlsson, 2011; Lee *et al.*, 2014; Lee and Song, 2011) (Table 3).

Summary

Surgical sutures have been in use for more than 3000 years, witnessing during this time a multitude of research and development. From catgut to the development of synthetic bioresorbable sutures, their use and handling have been made easier for surgeons while leading to lesser traumatic conditions for patients. With new polymers being synthesized and investigated, it is important to understand both their functional properties when used as sutures as well as their ease of processing during manufacture. In order to promote the process of wound healing and make it less traumatic and pain free, further research and development is needed in the field of biomaterials for surgical sutures. This review lists the current clinical options as well as the functional properties that are expected in the future.

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Bio-Waste Based Nanofiber Materials

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Introduction

In the wake of climate change, Paris Climate Accord was signed in 2015 to reduce the greenhouse gas in order to limit the global warming. Bio-waste remediation is one of the biggest challenges in reducing greenhouse gases as they tend to emit greenhouse gases (GHG), namely – CO₂, CH₄, NO_x (Schott *et al.*, 2016). In order to reduce the emission, the early open dump approach of 1960s to get rid of bio-waste changed to the current practice of integrated waste management (Hettiaratchi, 2007). One of the key aspect and undoubtedly the most prevalent and popular method of bio-waste remediation is to dump them in a landfill. However, in a landfill, the waste often undergoes anaerobic oxidation resulting in release of GHG (Chiemchaisri *et al.*, 2007; Sadasivam and Reddy, 2014). Among these GHG, it was found that CH₄, NO_x are more potent GHG in comparison to CO₂. As an example, the lifetime of CH₄ in the atmosphere is 12 years, whereas CO₂ has a lifetime of 172.9 years. However, the radiative efficiency of methane is much higher with a value of $3.7 \times 10^{-4} \text{ W m}^{-2} \text{ ppb}^{-1}$ in comparison to that of CO₂, which is $1.4 \times 10^{-5} \text{ W m}^{-2} \text{ ppb}^{-1}$ (Solomon *et al.*, 2007). Higher the radiative efficiency, higher is its warming potential per unit time. As a result of which, CH₄ warms up the atmosphere faster in comparison to CO₂. As per recent report from European commission (EU Commission, 2016), the production of methane from bio-waste decomposing in landfills, accounted for some 3% of total greenhouse gas emissions in the EU-15 in 1995. The Landfill Directive (1999/31/EC) from European Union, obliges Member States to reduce the amount of biodegradable municipal waste that they landfill to 35% by 2020.

Two of the other aspects of integrated waste management (Hettiaratchi, 2007) are recovery of energy from waste and residual waste management via recycling. However, the residual waste management via recycling seems to be energy intensive and the resulting recycled products are mostly commodity product, which makes recycling of bio-waste materials least lucrative. In fact it can be seen that while global waste management market is expected to reach \$285.0 billion by 2023 (Allied Market Research, 2018), the global biodegradable plastics, a recycled product developed from bio-waste, market is accounted for only \$2.25 billion in 2017 and is expected to reach a meager \$6.98 billion by 2026 (Report Buyer, 2018). One of the key possibilities can be development of high value nanomaterials from bio-waste materials.

While the bio-waste materials are significantly large and diverse in number, they can be broadly classified into two categories – protein and polysaccharides (Wicklein and Salazar-Alvarez, 2013). In this article, the focus will be only on three bio-waste families – cellulose and chitin/chitosan (polysaccharide); collagen (protein). While discussing about these materials, their sources, production methodologies and applications will be discussed. For all these materials two widely used nanofiber manufacturing methods, electrospinning and solution blowing will be discussed in detail. It needs to be mentioned that nanofibrillated materials obtained from the bio-wastes are also called nanofibers in literature. In order to avoid confusion, nanofibrillated materials obtained from bio-wastes will be called nanofibrils and the polymer nanofibers produced by electrospinning and solution blowing will be called nanofibers throughout the rest of the text unless mentioned otherwise.

Nanofibrillated Bio-Waste Materials

Cellulose

Cellulose is one of the world's most abundant, renewable, biodegradable and nontoxic material on earth. According to some estimates, yearly production rate of cellulose $\sim 10^{11}$ – 10^{12} tons/year (French *et al.*, 2004). This polysaccharide is the product of photosynthesis. Cellulose can be widely found in wood, hemp, bamboo, cotton, flax, algae etc. (García *et al.*, 2016). The first wide scale use of cellulose dates back 2nd century BCE China, where cellulose pulp was used to make paper. Cellulose was first discovered in mid-1800 by French chemist Anselme Payen. By late 1800s, cellulose was widely used in large scale manufacturing of high value materials celluloid, rayon etc. The most interesting part of cellulose is the hierarchy. For an example- while a tree can be as tall as ~ 100 m, the basic cellulosic structure is ~ 3 – 30 nm in diameter and 100 – 800 nm in length (Wicklein and Salazar-Alvarez, 2013). A hierarchical breakdown of cellulose is shown in Fig. 1 (Kaushik *et al.*, 2015; Thomas *et al.*, 2018). Cellulose is a linear polysaccharide composed of repeated nanometric β -1,4-linked anhydro-glucose units (AGU). These AGUs bind together via hydroxyl bonds to form larger units called microfibrils. These microfibrils then form fibrils and united fibrils form a fiber (Rol *et al.*, 2019). It needs to be mentioned that not all cellulose structures are same owing to the variety and nature of hydroxyl groups present on each AGU.

As it was mentioned in the previous paragraph, individual cellulose nanofibrils attach with each other through hydroxyl group. As a result of which, in order to produce nanostructures, be it nanofiber or nanofibrils, special emphasis is given to break the hydroxyl groups. Depending on the size and synthesis method of nanofibrils obtained from cellulose, they are broadly divided into three

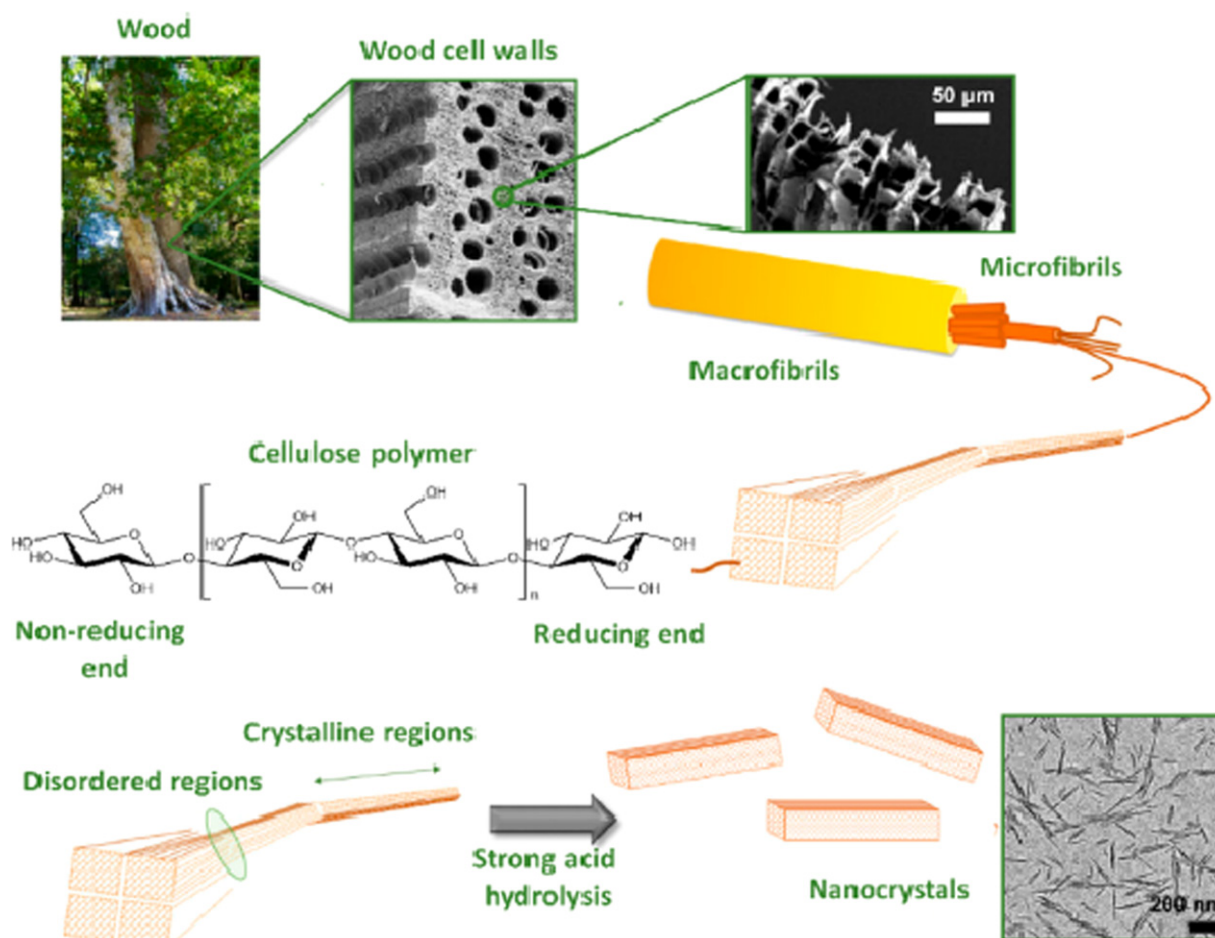


Fig. 1 Hierarchical structure of cellulose from macro to nano-scale is shown here in the top. The schematic shows how using strong acid cellulose can be broken into nanocrystals. While the top corner shows SEM image of the cellulose microfibrils, the bottom corner showed the TEM images of the cellulose nanocrystals. Reproduced from Thomas, B., Raj, M.C., Athira, K.B., *et al.*, 2018. Nanocellulose, a versatile green platform: From biosources to materials and their applications. *Chemical Review* 118, 11575.

categories (Rol *et al.*, 2019) – (a) nanocrystalline cellulose (NCC) or cellulose nanocrystal (CNC) (length ~ 100 – 250 nm and diameter ~ 5 – 70 nm), (b) nanofibrillated cellulose (NFC) or microfibrillated cellulose (MFC) (length ~ 1 – 10 μm and diameter ~ 5 – 60 nm) and (c) bacterial nanocellulose (BNC) or bacterial cellulose (diameter ~ 20 – 100 nm) (Mishra *et al.*, 2019; Xue *et al.*, 2017a,b). It needs to be mentioned that throughout literature the nanofibrillated cellulose structures are called by different names, which is why at least two examples of the same material names are mentioned here. A representative SEM image of all three types of nanofibrillated cellulose is shown in Fig. 2, where Fig. 2(a–c) shows SEM images of CNC (Fortunati *et al.*, 2016), MFC (Leszczyńska *et al.*, 2018) and BC (Pötzinger *et al.*, 2019) respectively. A detailed description on the relative difference of all three types of cellulose nanofibrils are described in detail in Thomas *et al.* (2018) and Mishra *et al.* (2019). Interested reader are strongly encouraged to read these articles. However, in the following paragraphs a concise description of cellulose nanofibrils along with the cellulose based nanofibers will be provided.

Nanocrystalline cellulose (CNC)

CNCs are the smallest of the cellulose nanofibrils. As shown in Fig. 2(a), it can be seen that they have rod like structures. It needs to be mentioned that during production of CNCs, the amorphous regions are removed, which results in highly rigid and very high crystalline nanomaterial (John and Thomas, 2008). The production methods are extremely energy and/or chemical intensive. A detailed description of CNC manufacturing can be found in (Mishra *et al.*, 2019). However, one of the most wellknown method of making CNC is TEMPO-oxidation (Lorenz *et al.*, 2017). However, another very popular and high yield method is strong acid hydrolysis (Islam *et al.*, 2017; Kian *et al.*, 2018). Primarily sulfuric acid is used for acid hydrolysis. Apart from acid hydrolysis, solution plasma processing was also used (Surov *et al.*, 2018). Multiple efforts were put forward to reduce the dependence on strong acid and/or harsh chemical (Chowdhury and Abd Hamid, 2016; Cui *et al.*, 2016). However, still there hasn't been significant improvement in order to create a true "green" process, which is scalable industrially.

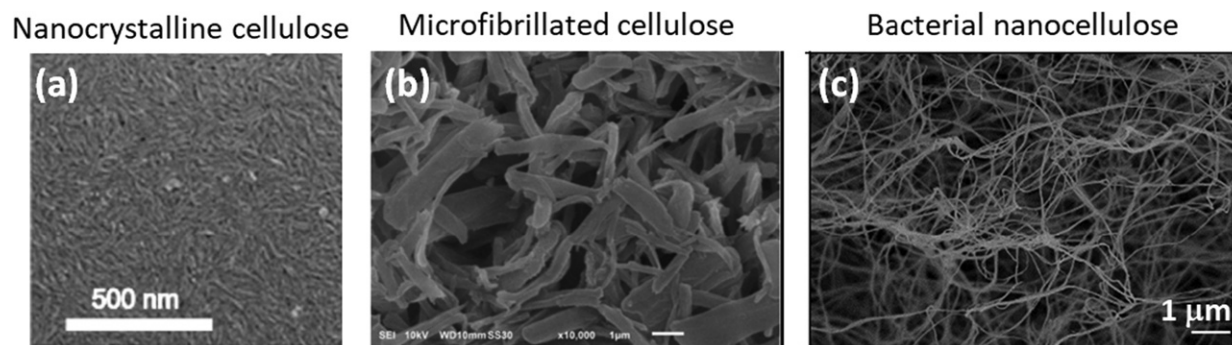


Fig. 2 SEM images of (a) CNC (b) MFC and (c) BC are shown. Reproduced from (a) Fortunati, E., Luzi, F., Jiménez, A., *et al.*, 2016. Revalorization of sunflower stalks as novel sources of cellulose nanofibrils and nanocrystals and their effect on wheat gluten bionanocomposite properties. *Carbohydrate Polymers* 149, 357. (b) Leszczyńska, A., Stafin, K., Pagacz, J., *et al.*, 2018. The effect of surface modification of microfibrillated cellulose (MFC) by acid chlorides on the structural and thermomechanical properties of biopolyamide 4.10 nanocomposites. *Industrial Crops and Products* 116, 97. (c) Pöttinger, Y., Rahnfeld, L., Kralisch, D., *et al.*, 2019. Immobilization of plasmids in bacterial nanocellulose as gene activated matrix. *Carbohydrate Polymers* 209, 62.

Owing to the size and chemical properties, CNCs have wide range of applications. CNCs have been used for heavy metal removal (Khoo *et al.*, 2018). CNC was used as an excellent templating material to create nanostructured material to create extremely active catalytic material (Xue *et al.*, 2017a,b; Chen *et al.*, 2017). CNC was also shown to create extremely transparent film in conjunction with guar gum with excellent oxygen barrier properties (Cheng *et al.*, 2015). Owing to the strong hydrogen bonds of CNC, it was shown to act as a potent reinforcing material to create extremely strong materials with excellent barrier properties (Cha *et al.*, 2014; Xu *et al.*, 2013; Wang *et al.*, 2015). CNC was also used antibacterial material, aerogel materials and other high value composites (Tavakolian *et al.*, 2018; De France *et al.*, 2017; Shi *et al.*, 2013; Kaushik and Moores, 2016).

Microfibrillated cellulose (MFC)

Microfibrillated cellulose or MFC is intrinsically long cellulose nanofiber. They are much longer than CNCs. In fact unlike CNCs, MFC has amorphous region attached to it resulting in longer structure with various shapes starting from cylindrical to flat ribbon like structure as seen in Fig. 2(b) (Li *et al.*, 2017). The production method of MFCs are less chemical intensive than that of CNCs. However, MFC production requires lot of mechanical energy. MFCs can be prepared via a plethora of processes. A detailed yet concise description can be found in Rol *et al.* (2019). Irrespective of the processes and specifics, the basic mechanism of producing MFC is the following. The pulp or the stock solution is subjected to very high shear force and impact force, resulting in cellulose nanofibrillation. This results in MFC. This process of nanofibrillation can be achieved via homogenizer, extruder, grinder, ultrasonicator, microfluidizer, ball mill, cryocrusher and other methods (Dinand *et al.*, 1999; Zimmermann *et al.*, 2004; Nair *et al.*, 2014; Ho *et al.*, 2014; Deng *et al.*, 2016; Dufresne *et al.*, 1997; Boufi and Chaker, 2016). Although in comparison to CNC manufacturing, these processes are relatively “greener”, they require lot of energy and the yield is pretty low. However, presently there had been commercially available process, where the pulp is mixed with abrasive and inexpensive inorganic particles. Upon grinding these particles accentuate shear and impact force resulting in MFC at a lower energy (Fiberlean, 2018). However, the process results in MFC with many unwanted inorganic particles.

MFC were used in creating silver nanowire based transparent conductive film, where the MFC was used to improve film adhesion, homogeneity and ageing (Hoeng *et al.*, 2016). MFC are widely studied in wound healing and biomedical purposes (Dumanli, 2017; Xue *et al.*, 2017a,b). MFC on being functionalized by nanoparticles and other starting from noble metals to inorganic and organic chemicals shows significant promise as antibacterial material, which in turn can be used for drug carrier, wound dressing and packaging material (Li *et al.*, 2018). Owing to high number of hydrogen bond sites, MFC is used to make functional nanocomposites, paper manufacturing and barrier material, which holds the potential for large scale manufacturing (Lavoine *et al.*, 2012; Siró and Plackett, 2010; Boufi *et al.*, 2016; Liu *et al.*, 2011; Morits *et al.*, 2017).

Bacterial nanocellulose (BC)

BC is the cellulose created by some species of bacteria. BC was first discovered in 1886 (Brown, 1886), where it was found that BC was synthesized by *Acetobacter xylinum*, an acetic acid bacteria, under aerobic condition. In this work, the author found that the bacteria synthesize cellulose using glucose as carbon source. As the field progressed, it was found that BC can be synthesized by different bacteria species, namely – *Gluconoacetobacter xylinus*, *Agrobacterium*, *Pseudomonas*, *Rhizobium*, and *Sarcina* using culture media containing glucose, phosphate, carbon, and nitrogen sources (Klemm *et al.*, 2011; Bodin *et al.*, 2007; El-Saied *et al.*, 2004). As BC is a byproduct of biosynthesis, the morphology, size etc can be controlled via varying incubation conditions, namely – oxygen ratio, bacterial strain, nutrient type, carbon source and incubation time. BC is very pure and mainly composed of α -cellulose. BC has a characteristic ribbon-like nanofibril structure (cf. Fig. 2(c)) with high degree of crystallinity (Czaja *et al.*, 2004) and requires no mechanical energy and harsh chemicals unlike other cellulose nanofibrils. However, it needs to be mentioned that the output of BC is

significantly low in comparison to CNC and MFC making it extremely expensive and thus limiting its uses. However, there has been some commercial applications, where BC is used as commercially available wound dressing material for periodontal diseases reconstruction (Farah, 1990).

BC is an excellent nanomaterials as the fibrils are straight and have very little polydispersity from the viewpoint of their dimension. Additionally, the BC fibrils have higher percentage of crystallinity resulting in very high elastic modulus ~ 78 GPa (Thomas *et al.*, 2018). It was also found out that BC is hydrophilic in nature with the capability holding large amount of water and interpenetrating structure with pore size comparable with that of cell (Klemm *et al.*, 2006; Thomas *et al.*, 2018). However, as it was mentioned, BC output is extremely low resulting in higher cost of making BC en masse. As a result of which, in spite of superior properties, BC application is limited to biomedical application. A detailed description of application of BC as biomedical nanomaterial can be found in Barud *et al.* (2016). In a nutshell, BC was used as wound dressing material for burnt victims (Fontana *et al.*, 1990). Following the work of Fontana significant effort was put forward to use BC as wound healing material, where it was found that BC reduces healing time (Czaja *et al.*, 2007). In this work, the authors hypothesized that the healing results for capture of ions via hydrogen bond resulting in efficient execution of healing pathway like skin. BC based system was also used controlled drug delivery (Alkhatib *et al.*, 2017; Wang *et al.*, 2011). Owing to the repeating structure, controlled porosity and ability to soak large amount of water BC is widely used as main constituent in scaffolding material (Bäkdahl *et al.*, 2008). In order to produce ideal scaffolding material several techniques were used, e.g., sacrificial matrix, freeze drying etc (Bäkdahl *et al.*, 2006; Gao *et al.*, 2011). Owing to its superior hydrogen bond, BC based ultrafilters are also used for ultrafiltration (Xu *et al.*, 2018).

Chitin

Chitin is the second most abundant biopolymer in the world with a production rate $\sim 10^{10}$ – 10^{11} ton/year (Gopalan and Dufresne, 2003). It also one of the most wasted biopolymers. Chitin is mainly found in the exoskeletons and cell walls of crustaceans (e.g., shrimp, crab, lobsters etc), insects, arthropods, mushroom, certain variant of fungi to name a few. It is polysaccharide in chemical nature. Chemically it is almost similar to cellulose. It is known to be cellulose analogues with a (1,4)- β -N-acetyl glycosaminoglycan-repeating structure (Fig. 3). In order to solubilize in water, chitin is deacetylated to produce Chitosan, whose chemical structure is also similar to cellulose and chitin as shown in Fig. 3. Chitin is a semicrystalline biopolymer. It mainly consists of nanofiber, which are ~ 10 – 50 nm in diameter and 300 nm in length being embedded in protein matrix. Owing to its linear structure with two hydroxyl groups and an acetamide group, antiparallel chitin nanofibrils are arranged in a highly crystalline fashion with strong hydrogen bonding having high binding energy (Raabe *et al.*, 2006; Chen *et al.*, 2008; Giraud-guille, 1984; Raabe *et al.*, 2005). High crystallinity coupled with high aspect ratio and excellent material properties position chitin nanofibril as a potent nanomaterial. It needs to be mentioned that as chitin nanofibril can be obtained from variety of sources, depending on the source, chitin nanofibril dimensions can be drastically different (from tens of nanometer to micron range). However, in spite of excellent properties, most chitin is thrown away as industrial waste, which provides us a significant opportunity to create a high value nanomaterial.

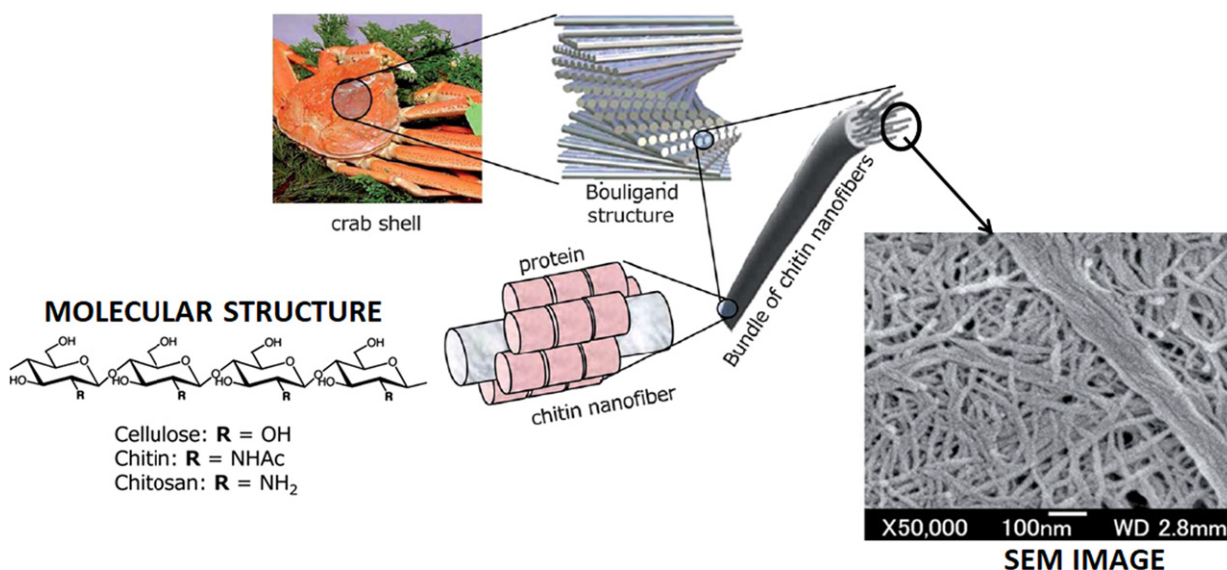


Fig. 3 Schematic of hierarchical organization of Chitin from crab shell to nanofibril structure is shown. On the left hand side the generic molecular structure of chitin, chitosan and cellulose is shown emphasizing the basic similarity in structure. On the right hand side SEM image of chitin nanofibril is shown. Reproduced from Ifuku, S., Saimoto, H., 2012. Chitin nanofibers: Preparations, modifications, and applications. Nanoscale 4, 3308.

Owing to the similarity in structure between chitin and cellulose, the extraction of chitin nanofibril are quite similar and follow almost similar protocol as described for CNC and MFC (Lin *et al.*, 2012). The basic method of extraction varies from mechanical shearing and impact to grinding to enzymatic-mediated production to ionic liquid preparation to combine mechanical shearing or grinding with chemical processes (Lin *et al.*, 2012). In Ifuku and Saimoto (2012) authors produced chitin nanofibers from crabs, prawns and mushroom by a simple mechanical treatment (a grinder, a Star Burst atomization system, and a high speed blender) after the removal of proteins and minerals. They subsequently washed the raw materials by HCl and NaOH successively. They found that mechanical treatment under acidic conditions facilitate fibrillation of Chitin. In Kadokawa *et al.* (2011) the authors soaked crab shell in ionic liquid, 1-allyl-3-methylimidazolium bromide (AMIMBr). This results in swelling of chitin. Then they heated the swollen structure at 100°C, which resulted in a gel. Then the gel was soaked in methanol and sonicated to a chitin nanofibrils were obtained.

Chitin nanofibril has excess positive charge on its surface (Feng *et al.*, 2018). This intrinsically makes nanofibrillated chitin an ideal candidate for creating nanocomposites. Cellulose nanofibril on the other hand are intrinsically negatively charged on the surface. This results in successful creation of transparent film composed of chitin and cellulose nanofibrils (Feng *et al.*, 2018). Owing to surface charge and strong mechanical properties, nanofibrillated chitin was mixed as a reinforcing agent with negatively charged PEO to create polymer electrolyte film, which can be used in Li-ion battery (Azizi Samir *et al.*, 2004, 2005). Chitin nanofibril grafted with PCL have also been directly thermoformed and injection molded to create strong and sustainable polymer composite (Xu *et al.*, 2008). In another work (Fadaie and Mirzaei, 2018), the authors showed polymer film created with PCL and chitin nanofibril showed better mechanical strength along with improved cell viability making such composite a suitable candidate for making scaffold. Chitin nanofibril was freeze dried to create highly porous aerogel with abundant acetyl amino groups ($-\text{NHCOCH}_3$) on the surface followed by surface grafting of Ag_2O , which showed high iodine capture efficiency (Gao *et al.*, 2017). Lin *et al.* (2011) developed a pH-sensitive microsphere based controlled release system for drug delivery using CNC, chitin nanofibrils and platelet-like starch nanocrystals integrated in a, alginate-based microspheres. These microspheres, containing interpenetrating structure of polysaccharides, loaded with drug were able to inhibit burst release of drugs.

Collagen

Collagen is the most abundant protein in most mammals. It is the basic building block of mammals particularly in tendons, bones, skin, corneas, and cartilage. The name collagen stems from Greek, which means “glue forming” compound. In fact in earlier days, it was used to produce glue. Collagen serves multiple function in mammal’s bodies ranging from scaffolding, morphogenesis and repair. It is the basic building block of bones, which acts as load bearing unit. It creates linkage between different parts of the body to smoothly transfer the load and also store excess energy. In a nutshell, collagen provides strength, fracture resistance capability along with flexibility. Such versatility of collagen can be attributed to its complex hierarchical structure. From its polypeptide sequence, multiple (>28) distinct collagens are identified (Pauxkandle *et al.*, 2002) and can be broadly classified into: (i) fibril forming collagen; (ii) fibril-associated collagens with interrupted triple helices (FACITs); (iii) network-forming collagens; (iv) transmembrane collagens; (v) endostatin-producing collagens; (vi) anchoring fibrils; and (vii) beaded-filament-forming collagens (Kadler *et al.*, 2007; Neel *et al.*, 2013). However, the major collagen is the fibril forming collagen, termed as collagen I and this type of collagen is of interest in this chapter.

Collagen I are generally made up from combinations of 10 polypeptide chains, denoted by $\alpha 1(\text{I})$, $\alpha 2(\text{I})$, $\alpha 1(\text{II})$, $\alpha 1(\text{III})$, $\alpha 1(\text{V})$, $\alpha 1(\text{V})$, $\alpha 3(\text{V})$, $\alpha 1(\text{XI})$, $\alpha 2(\text{XI})$ and $\alpha 3(\text{XI})$ (Neel *et al.*, 2013). Irrespective of the polypeptide chains, these chain consists of amino acid triplets- glycine-proline- hydroxyproline (termed as Gly-X-Y). Although this primary structure is well studied, there can be variation owing to post-translational modification. The collagen fibrils diameter ~ 100 nm and length ~ 1 μm (Fig. 4). Collagen

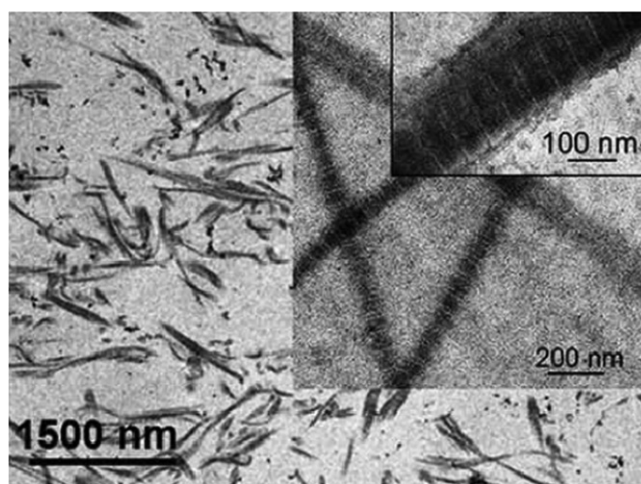


Fig. 4 TEM images of collagen I. Reproduced from Wicklein, B., Salazar-Alvarez, G.J., 2013 A functional hybrids based on biogenic nanofibrils and inorganic nanomaterials. *Materials Chemistry* 1, 5469.

nanofibrils are obtained from variety of natural sources namely- chicken, kangaroo tail, rat tail tendons, duck feet, equine tendon, alligators bon/skin, bird's feet, sheepskin etc. (Rodriguez *et al.*, 2018). Apart from natural sources, collagen is also manufactured synthetically by using 36 amino acids that self-assemble into triple-helix nanofibril structure (Kumar *et al.*, 2014). This synthetic collagen nanofibril is called KOD and it eliminates the variability that stem from collagen nanofibril and results in higher yield.

Owing to its price point and difficulty in manufacturing collagen nanofibril is primarily limited to biological and cosmetics application. It is used as a bio-active filler in dental fillers (Breschia *et al.*, 2018). It is used to create membranes for guided tissue regeneration as the matrix helps to organise the cells in space and provides attachment (Khan *et al.*, 2011). Collagen scaffolds formed by various methods (Neel *et al.*, 2013) were used for various medical purposes ranging from neural to bladder repair to skin substitute to ligament and tendon repair. A detailed discussion about how collagen based medical solution improved patient healing can be found in Neel *et al.* (2013). Collagen was also used to make nanocomposite to create artificial bone, where Collagen was mixed with different inorganic material, namely-hydroxyapatite, calcium phosphate etc. to engineer bone tissue (Kuttappan *et al.*, 2016). Based on this ideology, commercial products are already available in market, e.g., Bio-Oss Collagen®, GingivAid®, CopiOs Sponge and Paste, Puros® DBM Putty, INFUSE® Bone Graft, Vitoss® etc. Owing to high biocompatibility and ability to retain water collagen nanofibril based cosmetic products are widely used and promoted (Rodriguez *et al.*, 2018).

Continuous Nanofiber Manufacturing Techniques

As it can be seen, nanofibril obtained from bio-waste materials require significant amount of harsh chemical and/or energy treatment. Additionally it requires, lot of post processing in order to use the bio-waste based nanofibril. Another big challenge is that the yield in almost all the cases is extremely low making the nanofibril production methods economically expensive. This poses the question if it is possible to create bio-waste based nanofiber structures en masse. Electrospinning and solution blowing are two processes that allow us to create bio-waste based nanofiber system en masse. In this section basics of electrospinning and solution blowing will be provided. Following that some of the key examples of making nanofibers from bio-waste material will be provided along with some applications

Electrospinning

Electrospinning is the process of making nanofibers via electrohydrodynamic process. During electrospinning process, polymer solution of sufficient viscoelasticity is supplied through a nozzle, which is then subjected to electric field ($\sim 1\text{--}2\text{ kV/cm}$) and the final product is collected at the ground electrode, which is situated at 10–15 cm distance from the nozzle. Schematic of electrospinning is shown in Fig. 1. Electrospinning is capable of producing nanofibers with diameter $\sim 100\text{--}500\text{ nm}$ (Doshi and Reneker, 1995; Reneker *et al.*, 2000; Reneker and Yarin, 2008). Apart from needle based electrospinning, there have also been for needle less electrospinning (Yarin and Zussman, 2004; Elmarco, 2019). However, the principle of manufacturing nanofibers remain the same. Although electrospinning is a matured technology today, the first record of electricity mediated hydrodynamic process dates back to 16th Century, observed by William Gilbert and later in 1750 by French physicist Jean-Antoine Nollet. Later, the theoretical background of electrohydrodynamic process describing electrospinning was described by Rayleigh (1882) and in 1960s by Taylor (1964, 1966, 1969). Although significant focus generated around electrospinning in 1990s following research work by Doshi and Reneker (1995), according to Filatov *et al.* (2007), former Soviet Union secretly made significant progress in electrospinning in 1950s with primary focus towards interception of fragments generated by nuclear bomb (Sinha-Ray, 2018).

In the seminal work, by Dr. Reneker and Dr. Yarin's group in 2000s (Reneker *et al.*, 2000; Reneker and Yarin, 2008), theoretical models describing in electrospinning in detail was developed supplemented by experimental observation. The readers interested in the theoretical description of electrospinning are highly encouraged to read these works. For the sake of brevity, in this work, only the underlying mechanism will be described. During electrospinning (cf. Fig. 5), the polymer solution is subjected high electric field. Owing to this electric field near the nozzle a conical shaped meniscus of polymer solution is formed. This is called "Taylor cone". In this zone the characteristic time of charge relaxation (τ_c) is way smaller than characteristic time of hydrodynamic residence (τ_H). As a result of which in the Taylor cone polymer solution behaves as conductor and the charge remains on the surface and the polymer jet initiates. In the polymer jet domain τ_c/τ_H increases significantly. As a result of in this domain charged polymer jet behaves as dielectric and the charge resides inside the jet. In this way, during both of these two electrohydrodynamic processes, polymer solution behaves as leaky dielectric. In this jet mode, small perturbation increases exponentially owing repulsion caused neighbouring charge as shown in Fig. 5(b). This results in vigorous bending and flapping of polymer jet. If the polymer jet has required viscoelasticity, it stretches and solvent evaporates during the vigorous bending and flapping and within a distance $\sim 10\text{ cm}$ from the needle exit, liquid polymer jet of diameter $\sim 1\text{ mm}$ turns into solid polymer nanofiber of diameter $\sim 100\text{--}500\text{ nm}$. The beauty of electrospinning is that polymer nanofiber is being created at room temperature. As a result of which bio-waste materials, which in most of the cases are temperature sensitive, can be turned into nanomaterials. In addition to that such nanofiber making doesn't require "clean room" type condition, which is typically required for production of nanomaterials, which makes this process cost-effective.

Brief introduction to solution blowing

Unlike electrospinning, solution blowing is relatively new process to make nanofibers. The process was reported around the same time by two independent groups (Medeiros *et al.*, 2009; Sinha-Ray *et al.*, 2010). Since then, significant work has been done to create monolithic and core-shell soy-protein containing nanofibrous nonwovens (Yarin *et al.*, 2014; Sinha-Ray *et al.*, 2015, 2011; Khansari *et al.*, 2012; Sinha-Ray *et al.*, 2012; Zhang *et al.*, 2013; Khansari *et al.*, 2013b) as shown in Fig. 6(a), where the solution

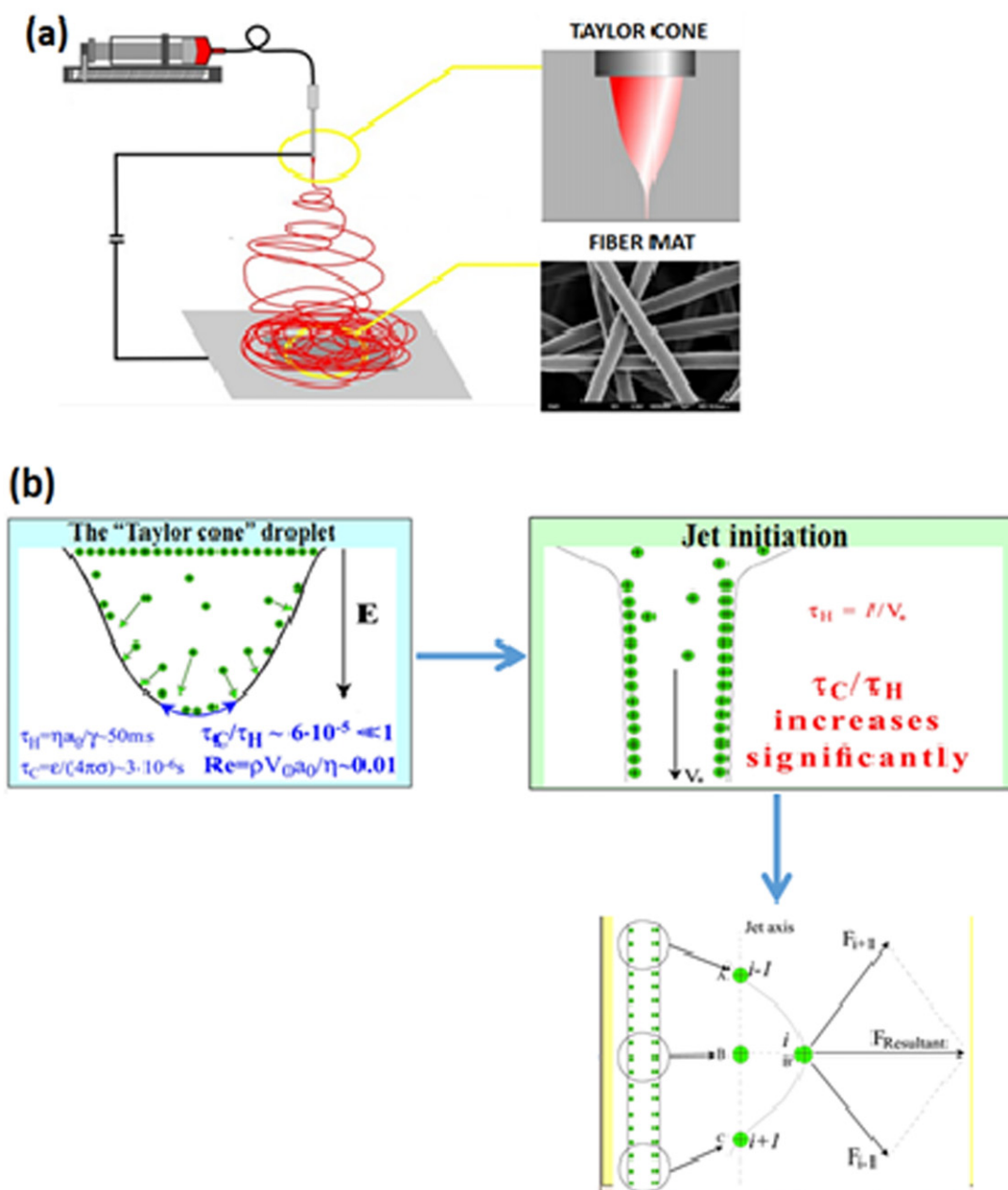


Fig. 5 Schematic for electrospinning. In panel (a) in the inset representative image of the electrospun nanofiber. Panel (b) shows the schematic for the jet initiation and bending resulting in nanofibers and nanoparticles. Reproduced from (a) Zupancic, S., Sinha-Ray, S., Sinha-Ray, S., *et al.*, 2016. Controlled release of ciprofloxacin from core-shell nanofibers with monolithic or blended core. *Molecular Pharmaceutics* 13, 1393.

blowing die and the lab-scale process is shown. The basic working principle of solution blowing is also shown in the inset of Fig. 6(a) (Kolbasov *et al.*, 2016). In a typical solution blowing process the polymer solution is delivered from a syringe pump at a rate $\sim 5 \text{ mL/h}$ to a reservoir attached to the core nozzle. Air is supplied through the concentric nozzle at the pressure of 3–5 bar from a high pressure line. Polymer solution from the reservoir is issued into the surrounding high-speed air jet flow (the gas jet has velocity in the 150–200 m/s range). The gas jet accelerates and stretches the core polymer jet. The latter possesses a short ($\sim 1 \text{ mm}$) straight part followed by a large-scale part which undergoes not only stretching but also a substantial bending instability, i.e., flapping. Stretching and bending instability result in significant thinning of the polymer solution jet, while solvent is gradually evaporating. At a certain stage, polymer precipitates, nanofibers solidify, and are collected on a solid grid-like collector, or on a wide rotating wheel. SEM images of solution blown monolithic PAN nanofibers are shown in Fig. 6(b) and (c). It can be seen that the nanofiber diameter range is within 150–250 nm and the individual nanofibers are quite uniform in the longitudinal direction (Sinha-Ray *et al.*, 2010).

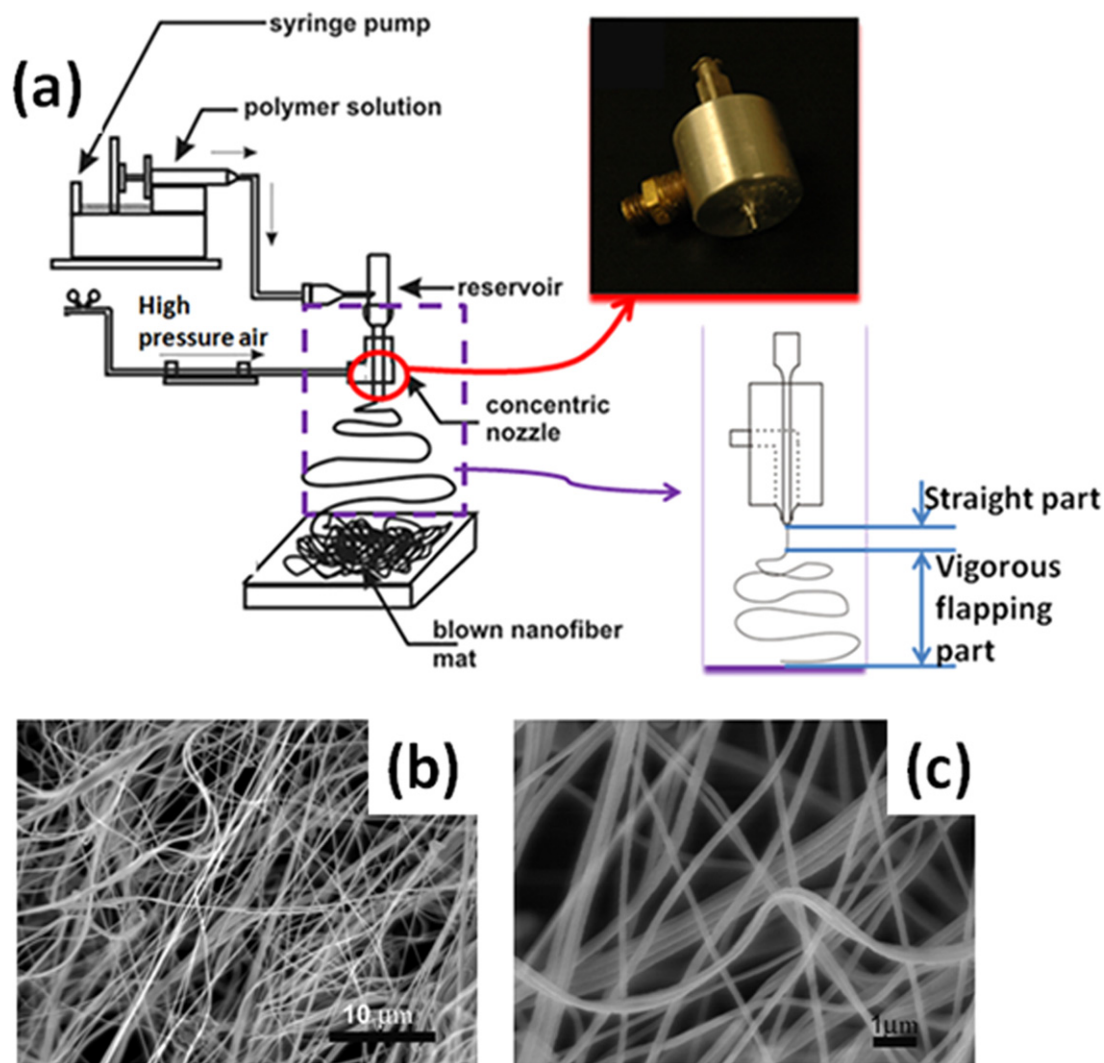


Fig. 6 (a) Schematic of a single-needle setup for solution blowing of monolithic nanofiber mats. In the inset in panel (a), an actual single-needle die and schematic of the solution blowing process are shown. SEM image of solution blown nanofiber is shown in panel (b) and (c). Reproduced from (a) Kolbasov, A., Sinha-Ray, S., Joojode, A., *et al.*, 2016. Industrial-scale solution blowing of soy protein nanofibers. *Industrial & Engineering Chemistry Research* 55, 323. (b, c) Sinha-Ray, S., Yarin, A.L., Pourdeyhyimi, B., 2010. The production of 100/400 nm inner/outer diameter carbon tubes by solution blowing and carbonization of core-shell nanofibers. *Carbon* 48, 3575.

Following the same principle and design criteria developed for a single-needle die described in the previous paragraph, an industrial scale up process is described in Kolbasov *et al.* (2016), which uses concentric air nozzles. The schematic of the experimental setup used in the industrial-scale solution blowing is shown in Fig. 7(a). Polymer solution was poured into the hopper and by gravity fed into a positive-displacement gear pump. The flow rate was controlled by adjusting the angular speed of the gear pump with 1 RPM corresponding to 10 mL/min. The pump speeds in the range 0.5–3 RPM were used in the experiment. From the pump, solution was supplied into a redistribution chamber and then to the spinneret. The spinneret consisted of an array of concentric annular nozzles with 41 nozzles per row and 8 rows (Fig. 7(b)). The solution was discharged through the inner nozzles into a high temperature, high-speed air jet issued from the outer nozzles. The air temperature was controlled by the output of an electrical heater. A representative solution blown mat using Biax die is shown in Fig. 7(c), whereas Fig. 7(d) shows the SEM images of the fiber mat showing that significant amount of fibers are submicron in diameter. This work clearly demonstrates the ability of solution blowing process to produce nanofibers en masse.

Electrospun and solution blown nanofibers and their applications

Electrospinning and solution blowing provides the avenue for producing bio-waste based nanofiber mat with a high yield, where solution blowing holds the potential to produce nanofiber mats at industrial scale. This provides significant opportunity for turning bio-waste materials into a high value nanomaterial. Irrespective of the process, the basic idea is the following. Most of the bio-waste materials can't be spun by itself owing to their low viscoelasticity. To add additional viscoelasticity the materials are

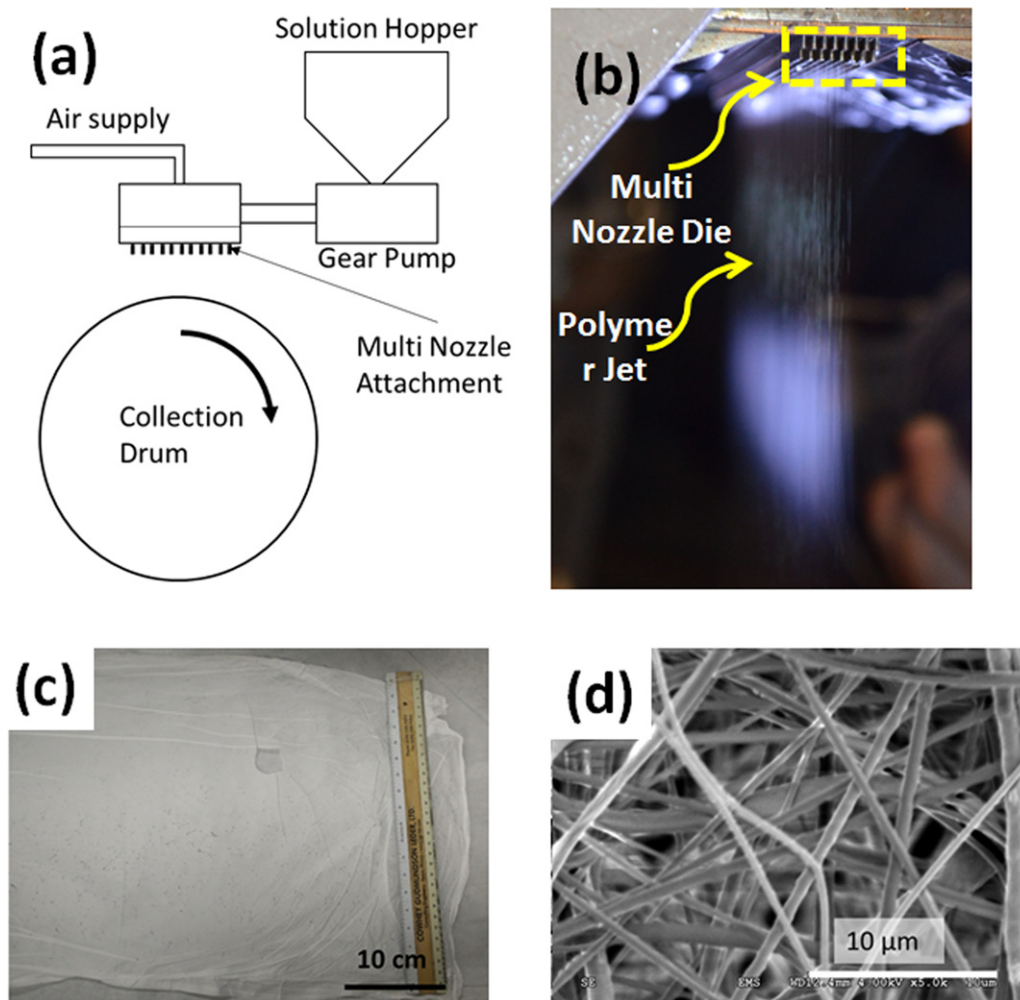


Fig. 7 (a) Schematic of the industrial-scale solution blowing setup used in the experiments. (b) An actual multi-nozzle solution blowing process using Biax die nose-piece. It consists of 41 nozzles per row and 8 rows. (c) A sample of soy protein isolate and PEO based nanofiber mat is shown, (d) SEM image of the nanofiber mat is shown here. In this work, no special measures for vapor removal were taken, since only aqueous solutions were used. Reproduced from Kolbasov, A., Sinha-Ray, S., Jiojode, A., *et al.*, 2016. Industrial-scale solution blowing of soy protein nanofibers. *Industrial & Engineering Chemistry Research* 55, 323.

dissolved in a host polymer solution, where the polymer and the bio-waste materials are dissolved in a common solvent. The resultant solution is then spun. Significant work has been done in creating electrospun nanofiber from cellulose and chitin (Min *et al.*, 2004; Ohkawa *et al.*, 2004; Subramanian *et al.*, 2004; Noh *et al.*, 2006; Khil *et al.*, 2005; Liu and Hsieh, 2002; Son *et al.*, 2004). The electrospun bio-waste based nanofiber mats were used for controlled drug delivery, cell growth, separator for Li-ion battery etc. (Zupancic *et al.*, 2016; Sheng *et al.*, 2017; Jayakumar *et al.*, 2010). However, the idea of utilizing bio-waste to make nanofiber got significant push, when it was first shown it is possible to produce soy protein based nanofiber mat with very high loading of soy protein isolate (Sinha-Ray *et al.*, 2011). This work was motivated by the fact that USA is world's one of the largest soy producer. Soy is used to produce biodiesel and the remnant material, soy protein, is dumped resulting in greenhouse gas emission. This work was the first significant progress towards developing soy based nanofiber mat that can be produced at scale at a significantly lower cost. Such produced soy based nanofiber mats were tested for their strength (Khansari *et al.*, 2012). It was found that these soy protein nanofiber mats were as strong as host polymer nanofiber mats. These soy protein based solution blown nanofiber mats were loaded with model drugs and it was shown that as soy protein leaches out over time, these nanofiber mats can be used to control burst release of drugs, which is otherwise prevalent in other nanofiber based drug delivery system (Khansari *et al.*, 2013a,b). The soy protein based nanofiber mats were decorated with silver nanoparticles, which showed significant antibacterial activity (Zhang *et al.*, 2013). Both of these two works show that the soy protein based nanofiber mats hold the potential to be antibacterial nanomaterial with the ability of controlled drug release that can promote wound healing. The idea of making solution blown nanofiber mat was extended with bio-waste based materials, namely – zein, lignin, cellulose acetate, silk protein (sericin) and bovine serum albumin (Khansari *et al.*, 2013a,b). These nanofiber mats showed that they can be physically and chemically crosslinked in order to produce strong nanofiber mat with pore size $\sim 10 \mu\text{m}$ thus opening the possibility of

making packaging material with superior barrier properties. Similarly, bio-waste based nanofiber mats were also used as a filter for heavy metal from water effectively owing to their active surface moieties (Kolbasov *et al.*, 2017).

Conclusion

Famous English poet William Wordsworth once wrote, “*Come forth into the light of things, let Nature be your teacher*”. Bio-waste based nanomaterials hold similar key to a lot of problems starting from mitigation of greenhouse gas to advanced healthcare to energy storage to packaging materials and other application. In this article, a brief overview has been provided to understanding the present status of bio-waste based nanofiber materials ranging from sources to preparation method to applications. However, as it can be seen from the nanofibrils that the biggest challenge is that their yield is low despite being extremely high power and chemical dependent. Electrospinning and solution blowing reduces the yield problem but the challenge is that most of the chemical needed to prepare the solutions are harsh and it requires sophisticated solvent capturing method for making these processes low on harsh chemical footprint. So, there is a huge potential and opportunity for researchers to make a positive impact by creating improved processes by developing “Green Solvent”, low power processing condition etc. Another challenge is to create mass awareness around the perils of wasting bio-waste materials. In this way, the future interdisciplinary research potential is huge, where chemists, process engineers, economists, social scientists and policy makers can work in tandem to create a true green process. Borrowing from famous poet, Robert Frost, “miles to go before we (researchers) sleep” to truly create ubiquitous and impactful bio-waste based nanofiber materials.

See also: Green Composites From Sustainable Cellulose Nanofibrils

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Developing Successful Biobased Product: Key Design and Manufacturing Challenges

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Introduction

The biobased products have explored potential all over the world due to green globalization regarding the environmental hazard linked to synthetic products. Now researchers are giving emphasis on the sustainability as they are giving importance to the biobased products whose raw materials are biodegradable. Clearly, biodegradable materials are disintegrated naturally and do not hamper the eco-system, hence the environmental sustainability is maintained. Sustainability means full-filling the present need without hampering the future (Shahinur and Ullah, 2017). Indeed nature is the source of all biobased materials, which are mainly collected from minerals, plants, and animals. Bio-products mean bio-fuels, organic chemicals, bioenergy, material and composites, intermediary biochemical and biomaterial, and other bioproducts. In this particular article, the biobased fiber product will be emphasized. Bio-based materials namely, fibers, can be particles, chopped as well as long form in the biobased-composites or products.

Based on the different sources, biobased-materials can be categorized. For example, jute, banana, and kenaf, are categorized as bast fiber; coir, cotton, piassava, and date palm are fruits fiber; sisal, abaca, pineapple are leaves fiber; bagasse and bamboo are grass fiber; rice, wheat, barley, and maize are stalk fiber; wood, silk, sheep wool, eggshell, and hair are animal fiber; whereas asbestos is mineral fiber. Biobased materials are collected from nature and have a positive impact on the eco-system as shown in Fig. 1.

Biobased products are made from the above-mentioned biobased sources. After use of a biobased-product in the artificial world, it is disposed in nature or recycled as shown in Fig. 1. From Fig. 1 it is clear that if biobased-material is consumed in the product, the eco-system will not be affected. That means sustainability can be maintained. One important part of the biobased product life cycle is product design and development. A product, namely, headphone has different components such as frame, speaker, rubber, connecting wire and foam. Suppose, a manufacturer will produce a product such as frame of the headphone which has specific shape, which performs a function, which is made of a material or group of materials and which is a system or part of a system (as shown in Fig. 2). To manufacture this component of the headphone, one needs to design that component having a specific shape that will perform a particular function and that will be made of cheap, good quality, and widely available materials. Furthermore, this component will be a part of headphone as shown in Fig. 2. Among these four issues as mentioned before, material selection is an important one. If the selection of material is biobased material for the frame, the headphone will be lighter (as biobased materials have low density), partially biodegradable, as well as the energy consumption due to manufacturing and transportation, will be less.

In this article, the biobased material particularly, biobased-fiber, for biobased product development has been considered due to light weight. Let us consider the case of a vehicle. In the vehicle, 75% fuel cost is paid due to heavyweight. A lightweight vehicle is possible if we go through the biobased composite for vehicle component. Biobased composites simply made of these types of biobased materials are 50% lighter compared to the glass composite as natural fibers, as well as biobased materials have low density. Despite having some limitations of the biobased products such as progressive moisture absorption, less fire resistance, microbe infection, low temperature limitations, and poor mechanical properties, most importantly, the price variations during

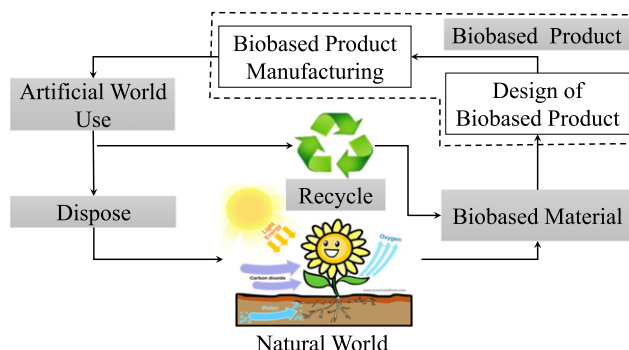


Fig. 1 Biobased product development and life cycle.

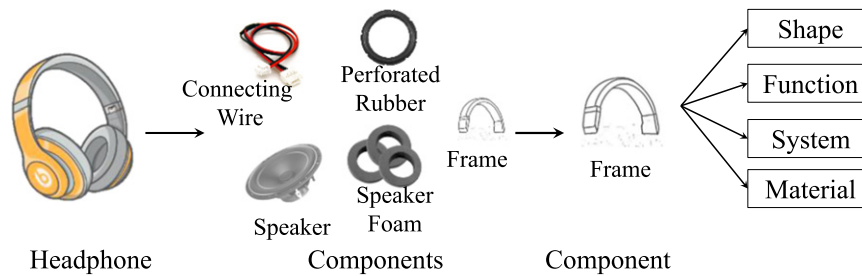


Fig. 2 Different elements of a product, headphone.

yearly harvesting compared to the metal, they will be lighter compared to any other primary material for product development (Khan *et al.*, 2018). In that sense, the biobased material has a huge potential in the product development sector.

A product, in this particular case, biobased product is a crude thing which satisfies the customer need and it is also related to the economy. There is a relation between design and manufacturing of a product. If there is no customer there will be no necessity of the product. Before designing and fabrication of a product, first material is required and according to design. After that selection, the material needs to be processed in order to reduce the fabrication complexity, cost, and improve sustainability, durability, reliability, and customer satisfaction. Moreover, the product design has a great impact on product manufacturing as well as the product life cycle. In macro, micro as well as nano biobased product development sector, the fabrication method is dependent on the design. In addition, the design of a biobased product is dependent on the performance of the product (Basha *et al.*, 2015). Thus, design and manufacturing are interdependent.

The design and manufacturing of biobased products are important issues to attain the best performance from the primary biobased material. Moreover, there are different types of challenges for successful biobased product development. In present article, an emphasis is given on these two topics for successful product development. One is key design and other is manufacturing challenge regarding biobased product development. Furthermore, there has been no such comprehensive survey on the challenges of biobased product development and design issue. And authors intend to fill this gap in present article. The approach presented in this study will make a significant contribution to develop a biobased product design and successful manufacturing. Section "Introduction" outlines the key design factor for successful product development. Under this section, the challenges of designing biobased product are also highlighted. Section "Key Design Factors for Biobased Product Development" defines the manufacturing challenges regarding biobased product development. Furthermore, Section "Manufacturing Challenges for Biobased Product Development" and Section "Limitation of Biobased Products" deal with the problem and related solution regarding biobased product designing as well as manufacturing. Finally, concluding remarks are delivered in Section "Conclusion".

Key Design Factors for Biobased Product Development

This section describes the key design factors for biobased product development. Design should be appropriate to fulfill a successful product service. Furthermore, achieving the desired product dimensions is a complicated task. For reducing the number of trials and errors, a finite element method is highly useful (Soury *et al.*, 2009). There is a tendency that the final structure is overdesigned (Awad *et al.*, 2012). Thus, it is important to design a product properly for successful development. Furthermore, synthetic fibers are easy to manufacture with accurate criteria, whereas biobased fiber criteria are uncertain. Synthetic fibers are the competitors of the natural fiber thus, appropriate design of the biobased product is important to sustain in this artificial world. The design is qualitative as well as quantitative. The final cost of the product, aesthetic view and risk tradeoff in the product development mainly depends on the design of the product. To obtain the desired output, biobased material particularly, fibers are chemically treated which leads to better bonding between biobased material and other reinforcing material, as well as additional treatments, increase the acetylation, biobased material's surface heterogeneity, p^H level, orientation in case of fiber (Khan *et al.*, 2018). If the design is appropriate, there will be a negligible amount of problem during the product fabrication, assembling, quality control, and operational performance. During design of a product, the following items need to be considered on the subject of successful biobased product development.

- (1) Appropriate material selection
- (2) Shape of the product (Aesthetic) optimization
- (3) Fabrication and assembling fixation
- (4) Tolerance of product consideration
- (5) Environmental sustainability consideration

Despite the broad scope, in this article, the discussions will be limited to the topics in the above five categories. Different scholars provide an excellent review of the engineering design literature, while a number of survey papers have been published

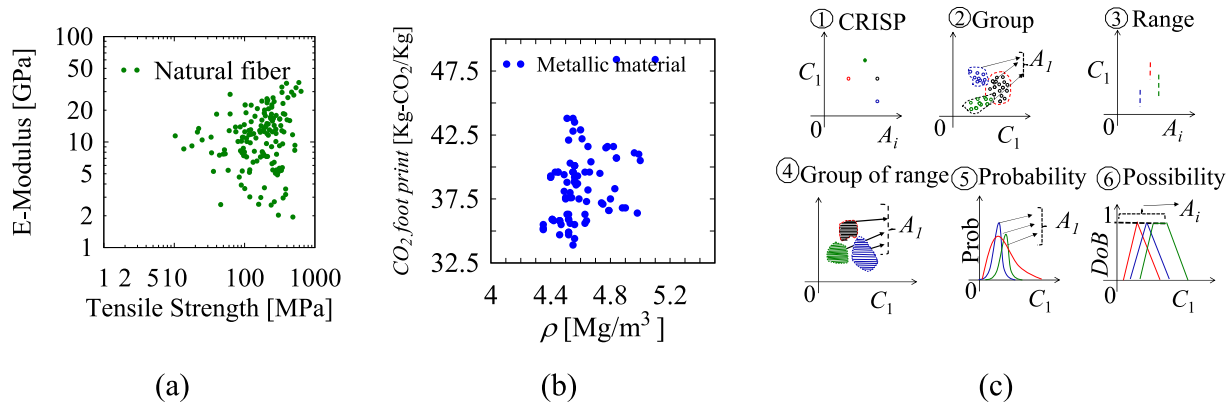


Fig. 3 Uncertainty of natural material regarding (a) tensile strength- E-modulus, (b) CO₂ emission- density and (c) Data storage system. Reproduced from (a) Ullah, A.M.M., Shahinur, S., Haniu, H., 2017. On the mechanical properties and uncertainties of jute yarns. *Materials* 10 (5), p. 450.

reviewing the metallic product (Krishnan and Ulrich, 2001) and biobased product. Important design factors are going into detail in the following subsection.

Appropriate Material Selection

Typically, most of the production cost is occurred due to the processing of material (Banerjee, 2014). Moreover, cost due to transportation and fabrication process is dependent on the material selection for a product. In addition, other parameters (such as sustainability, durability, quality along with reliability) for a component of the product also depend on the material selection. A similar story is true for biobased products. Before designing a biobased product or a component selecting an appropriate biobased material is required for durable, reliable, efficient, and sustainable biobased product development. However, in the case of biobased product, there is uncertainty in the criteria (C) of biobased material (A) (Shahinur and Ullah, 2017) which can be represented by Fig. 3(a).

From Fig. 3(a) and (b), it is clear that there is a variation in mechanical properties as well as sustainable properties in case of metallic as well as the natural material. Other materials have similar types of uncertainty in their criteria. However, these types of uncertainties are more prominent in the case of biobased material as they grow naturally. Thus, based on the different proposed data base of biobased materials (see Fig. 3(c)), a designer cannot select the design parameters for further biobased product development. Therefore, based on this database material selection is critical. To develop a biobased product, it needs technical information or data of related materials criteria that are logically arranged and organized through following a reliable method. There are different types of databases available regarding the major families of materials such as metals, ceramics, polymers, and composites (Ashby, 2007; Granta Design, 2017), however, it is disorganized in case of primary biobased material particularly natural fiber or any other form of natural material such as yarn, fabrics, and nanoparticle. Different authors suggest different types of natural fiber databases where data are represented as CRISP (Fig. 3(c)①), Group of crisp (Fig. 3(c)②), range (Fig. 3(c)③), group of range (Fig. 3(c)④), distribution, and possibility distribution (Biswas *et al.*, 2013; Ganguli, 2013; Bongarde and Shinde, 2014; Hossain *et al.*, 2014; Pickering *et al.*, 2016; Ullah *et al.*, 2017). When data of a criterion for a bio-material is represented as a range (see Fig. 3(c)③ and Fig. 3(c)④), has wide variation from one researcher to another and unclear the method for data representation, is unreliable for designing a biobased product. Researchers also suggest the database depending on the condition (in case of fiber, gauge length is one of the conditions for testing a specimen) as well as the assumption consideration (normal distribution, Weibull distribution as shown in Fig. 3(c)⑤). Both of these databases have variation from one researcher to another for a single criterion of a biobased material and they are unreliable to select the design a parameter of the biobased product. Based on the above contemplation, data needs to be quantified and stored as database using a single transparent method like possibility distribution as shown in Fig. 3(c)⑥ (see Shahinur and Ullah, 2017 and Sharif Ullah and Shamsuzzaman, 2013 for detail). This can be an open research topic. After quantification of the data for a particular criterion, selection of a material for a product is needed. In addition, there are many methods (such as Technique for Order of Preference by Similarity to Ideal Solution (TOPIS), Fuzzy simulation, Analytic Hierarchy Process (AHP), Ashby method, VIKOR, Preference Ranking Organization Method for Enrichment of Evaluations (PROMETHEE), ELimination and Choice Expressing Reality (ELECTRE), Genetic algorithm (AL-Oqla and Salit, 2017; Gul *et al.*, 2017; Babanli *et al.*, 2018) available to select material for a component of a product. Under uncertainty, the method of material selection would be different. Thus, material selection method development for biobased product where biobased material is in the form of fiber or any other (for example, particle, chopped, long) is an open research topic.

Besides, the data of a criterion for a natural material are big as well as uncertain due to variation in the experimental methods (Ashby, 2007), surrounding conditions and non-homogeneity in their material structure. Thus, the dealing of these types of data is different from as usual man made material data. Therefore, this is another research area for developing the method to deal with

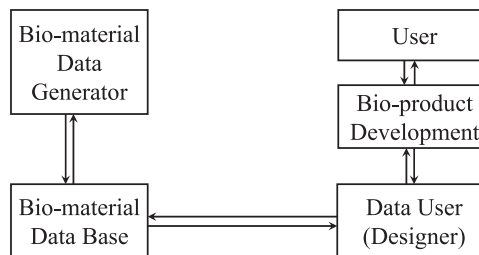


Fig. 4 Data flow from generator to end user.

such big data. As a result, the data should be analyzed efficiently. Furthermore, natural fibers data are heterogeneous. For this reason, a storage system (as shown in [Fig. 4](#)) needs to be developed for further use of the data.

This is another new research topic for biobased-product development. From the developed data base engineer, designer, as well as the manufacturer will be systematically benefited as shown in [Fig. 4](#). After the generation of the database, the designer will use this data for product development, particularly physical shape considering manufacturing method, assembling of the components, environmental issue, finishing, and tolerance of the product.

Shapes of Product Optimization

Optimization of physical design for manufacturability is essential, to ensure the success of manufacturing for a biobased product ([Lin et al., 2007](#)). However, the biobased material are moderately comparable to other materials, the shape of biobased products need to be adopted compared to the traditional product. Performance has been enhanced using variation in the shape of the product. For example, weaving design of fabric makes them bulletproof ([Milne, 2014](#)). In addition, low strength paper material is used in the construction material by changing the shape of the primary as well as secondary material. Furthermore, the shape of a constituent part in the final product also has an influence on its performance. For example, a plain paper is easily torn whereas diamond shape inside the paperboard makes them high strength construction material. Biobased material is also used in the construction material in Japan floor top (see [Ban, 2000](#) for detail). Furthermore, biobased material dimensional stability is poor compared to metal. Whereas biobased material has multi-directional properties due to non-homogeneity in its structure. In order to develop a biobased product, the shape should be modified to take advantage of its directional properties, which will have a positive impact on the cost, weight, and performance. For example, a rooftop can be designed honey-comb shape when biobased material is used for product development because this design enhances the performance of the roof ([Ban, 2000](#)).

Various types of modified window panel designs are now available for houses and offices. Due to this modified design of the window panel, the strength, efficiency, and durability are increased however, the weight and fuel cost are decreased. In addition, a moderate design of a table ([Sciarra et al., 2010](#)) made of biobased-material is now also available. For better service, the shape of the products needs modification. For example, in the medical sector, the patient beds now have six different types of movement whereas only four types of movement were available in the early version of the design ([Portillo-Velez et al., 2016](#)). Such types of upgrading of specific shape or design of the product are important for better service in daily life activities. Sometimes the shape is changed due to the fabrication process of the product. Last but not least, the physical, mechanical and other properties of the biobased materials are not like metallic material. Due to this, when biobased material will be selected for construction material, shape of the product should be selected properly which make them easy to fabricate and assemble.

Fabrication and Assembling Fixation

After the creation of a database (through the research) for a criterion of a biobased material, designer selects a biobased material for a components, and finally fabricats (using an appropriate manufacturing method) and assembles the components for the end product. Thus, one of the important design factors of the biobased product is the fabrication method, which has an effect on the performance of the product. The shape of the product cannot be optimized through a single manufacturing method. In the case of biobased composite fabrication, drying, electro-spinning, gelling, precipitation, hot press, injection molding, and hand layup methods are available. For example, Col-nHA (Collagen Hydroxyapatite) composite can be fabricated through drying, electro-spinning, gelling, precipitation, and hot pressing. However, manufacturing method had the effect on the performance (such as mechanical, physical as well as chemical) of the biobased product in macro, micro as well as nano levels (see [Basha et al., 2015](#) for detail). Thus, it is important to select an appropriate method during the design of a biobased product. One of the biobased materials is biobased fiber which can be used as a raw or composite form in the biobased product. In the case of a composite, biobased materials need to be modified by chemical, mechanical as well as physical treatment. Mixing is also not uniform all around the composite during the composite fabrication. To increase the material surface area of the product the raw biobased material is converted into micro or nano dimensional form. Different types of researches regarding the biobased based nano product are being carried out and better performance was realized from the products in medical ([Basha et al., 2015](#)), and aerospace industries ([Khan et al., 2018](#)).

Table 1 Transformation of polypropylene (PP) matrix and biobased material

Material	Modified	Material	Modified
Virgin	Virgin Polypropylene	Jute Fiber	Composite
Grafted	MAgPP (Shahinur <i>et al.</i> , 2017a,b)	Grafted jute fiber	Grafted fiber composite
Electrical coating	Electrical conductive PP (Kalaizidou <i>et al.</i> , 2008)	Coated jute fiber (Shahinur <i>et al.</i> , 2017a,b)	Electrically coated fiber composite (Anwer <i>et al.</i> , 2018)
Chemically treated	Flame retardant PP (Alibaba.com, 2018)	Treated jute fiber (Shahinur <i>et al.</i> , 2013)	Chemically treated fiber composite (Suppakarn and Jarukumjorn, 2009)

In addition, to obtain desired criteria of biobased material they are blended or mixed with other man-made or natural biobased materials. In this regards hybrid fiber composites take place to tailor for better performance. Correspondingly, to tailor the performance of the composite the matrix material also comes in hybrid form. Sometimes they are chemically treated or radiated using a different method as shown in Table 1.

In addition, at the start of the design, it must be determined which fabrication method, as well as the assembling method, will be used otherwise the performance of the product will be affected. Besides, different adhesive performs differently during the composite assembling. Regarding this issue, the performance is changed due to assembling and machining of the composite material. Last but not least, 3D-printer using CAD (Computer Aided Design) is also used for prototype development regarding the issue of high accuracy and cheap price for large scale production.

Tolerance of Biobased Product Consideration

Tolerance of biobased product is related to the design, manufacturing method and raw material selection. Tolerance of a biobased product is also dependent on the product consumption condition. When the biobased product is used in critical applications (for example, space, civil, aircraft, medical) the tolerance of product development becomes important. As biobased materials are easily degraded in contact with moisture and soil, their performance will change (Katogi and Takemura, 2015). Therefore, the biobased product life time is limited under certain weather condition and after that time limit they are recycled or disposed. However, in the case of controlled weathering condition, their performance can be improved (Shahinur *et al.*, 2017a,b). In the medical sector, the biobased products are categorized into micro, macro, as well as nano dimensions. Moreover, the immune system of the living body in changing day by day, thus, the adoption of biobased composite for particular diseases is changing. Thus, modification of biobased composite (Basha *et al.*, 2015) is needed with the update of diseases. Thus, the tolerance level of the product is important which can be developed during the design time. To increase the tolerance level of the biobased product in different sectors, different scientists are working on biobased composites. Based on the above contemplation it can be concluded that tolerance level of a biobased product can be improved if it is considered during the design.

Environmental Sustainability Consideration

During product design, the environmental impact of the product needs to be considered along with the customer aspiration. A product itself has an environmental effect whereas product development or manufacturing process has a wide range of effect on the environment as shown in Fig. 5.

From Fig. 5 it is clearly observed that in the case of ecological pollution, the factory emits different types of hazardous gases during the product life cycle from biobased material to end product (Office, 2018). If the number of exposure is reduced, the CO₂ footprint of a product will be less. The biobased material, particularly plants fiber, CO₂ absorption, and O₂ emission (enrich the environment) during fiber production are higher whereas they emit less CO₂ during primary material production as they are lightweight and less dense compared to metallic and other materials. Thus, research is needed to reduce the CO₂ emission during secondary material production for a sustainable product development. Furthermore, during the processing of the primary material they emit different types of health hazardous gases including CO₂, CFC, formic acid, formaldehyde, benzene, and different types of toxic material (for example, Mercury, Lead, Cadmium, Tin, and Arsenic) are released into the environment (Aikpokpodion *et al.*, 2013). Thus, it is important to design product based on customer need, which meets environmental sustainability as much as possible.

Weight and transportation cost are related to each other, so it is required to design lightweight product in order to reduce fuel consumption which has a great impact on the environment. Processing cost of a product needs to be optimized to make the product cheaper and keep the environment healthy. As biobased fiber and material have hydroxyl (-OH) group and they absorb moisture from the environment as well as their moisture regain varies to a large extent, which will affect the dimensional stability of the product. Hence, for sustainable product development, one needs to select an appropriate biobased material and fabrication method which do not emit lots of CO₂ in the environment.

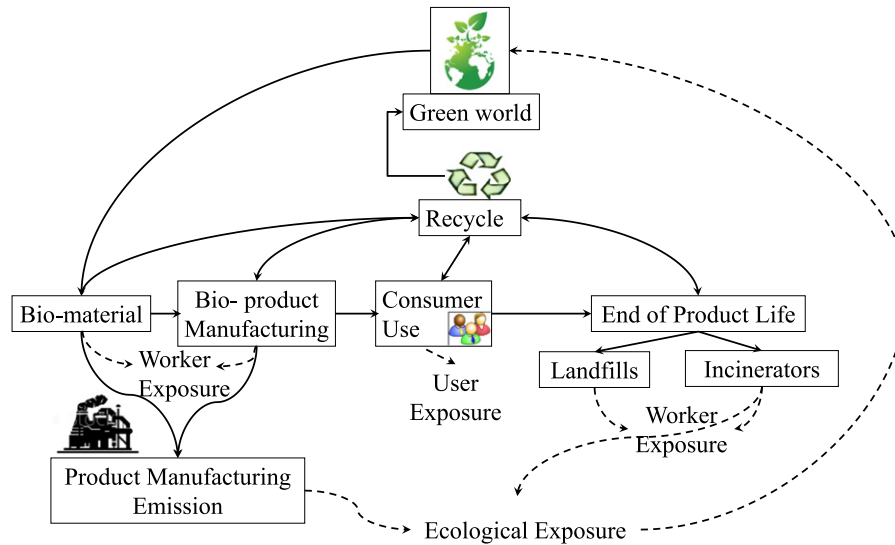


Fig. 5 Effect of biobased product development in the environment.

Manufacturing Challenges for Biobased Product Development

During the manufacturing of a product, the producer faces numerous types of challenges, which will be briefly discussed in this section. Different types of biobased macro, micro, nano or above nano scale) composites (for example, collagen, gelatin, and chitosan biobased composite) have shown different mechanical and physical properties due to the variation of the manufacturing process (Basha *et al.*, 2015). As a result, their performance is hampered in a specific area. Thus, manufacturing method optimization is important. However, during the design, it is optimized while the product performs differently in the application field. As a result, the manufacturing method is modified to obtain the desired performance. During the manufacturing of a product, there are few disadvantages of using experimental investigation such as high cost and longer time consumption. This types of challenges need to be managed for better product development. In addition, product manufacturing cost has an important effect on the developing countries where resources are limited. That means, when resources are limited design development is an important issue. In addition, there is some limitation of nano product development due to technology deficiency. Additionally, the manufacturers use a method which is easy, less time-consuming as well as cheap to supply the product in time. To attain these types of quality of the fabrication method they face some types of challenges which are listed below. Besides, in this section attention is devoted to the manufacturing challenges based on very limited literature available regarding this field.

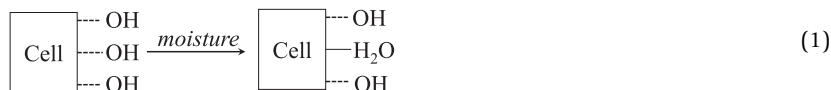
Manufacture handling and safety, skilled labor shortage, Internet of things (IoT), manufacturing the right inventory level, robotics and automation change, system usability, customer self-service application, intelligence from a machine, project management, wastage management (Boggess, 1994), environmental consideration, lack of supply chain transparency, product inconsistency are considered as some of the important challenges for sustainable biobased product development. Furthermore, for biobased product manufacturing by 3-D printing with high accuracy is a big challenge. To obtain better performance using 3-D printer design needs to be improved.

Huge data is one of the major challenges for manufacturing as well as design while the biobased-materials data are uncertain. Secondly, the supply chain issue is another important factor for biobased product development as the production of a particular region is fully dependent on climate, disaster, and farmers' wish. Furthermore, biobased material, particularly plant production is changed from year to year. Business downtime is another factor of the manufacturing challenges of the biobased product because new materials having improved properties are being developed day by day which is the competitor of the biobased-material. On the other hand, unplanned maintenance, development, and innovation of the new technology, health care cost, are also the challenges in the biobased product development (Anon, 2017). In a factory or farm, the working condition should be fair and protect human rights. As biobased material have OH, low mechanical, thermal, physical performance, manufacturer faces following types of challenges during industrial production.

Moisture Absorption

In the case of biobased product, moisture is one of the important issues for industrial manufacturing. As biobased-material particularly natural fibers are hydrophobic and they have free hydroxyl ($-OH$) group, they absorb moisture and the dimensional stability hamper by Eq. (1). Thus, water retardant treatment required for long term sustainable biobased-product development. Fuqua and Ulven (2012) has shown improved water retardant quality in the biobased product due to the addition of compatibilizers in the composite. Therefore, these types of pre or post treatment may improve product quality as well as reliability.

During manufacturing, different types of product such as raincoat, umbrella they are using a coating to retain the dimensional stability from moisture, dew, fog, as well as rainwater. Furthermore, by improving this property bamboo fiber is used in sanitary and baby napkin regarding the environmental sustainability issue (Dutta, 2017).



Bio-based products have wide variety of applications including textiles and home furnishings. Biobased materials get shrunk after treatment (sizing, de-sizing, scouring, and bleaching) during dyeing method, and become faded due to sunlight which requires improvement through use of chemicals (during industrial production), which are not bio-degradable. Different categories of researches are going on dyeing and printing of biobased product using bio-material. Bio-based dyes (such as lichi leaves, indigo, merigold onion peel) and printing materials have some limitations (such as expensive, limited shade of color is achievable, unsustainable). That is why, they need to be improved for sustainable printing and dyeing industries. Vankar *et al.* (2008) and Miah *et al.* (2016) have been working on bio-based dyeing from biobased material which would be eco-friendly.

Moderate Mechanical Properties

Biobased materials are environmentally sustainable. The alertness of the biobased product is growing due to the adverse side effect of the artificial material. Mechanical performance is poor in case of biobased-material compared to the metallic material. Different researchers have obtained a wide range of mechanical properties using different modifications (for example, chemical, physical, and mechanical) in the biobased material. Furthermore, biobased-material is incorporated in the polymer and their properties are enhanced in the final product (Shahinur *et al.*, 2017a,b; Dos Santos *et al.*, 2018). Depending on the application, biobased material is incorporated in different types of matrix material for biobased composite manufacturing. Thus, these types of modification of the biobased material are important for quality biobased product development. Furthermore, biobased fabric shrinks due to detergent wash, which needs to be improved. Thus, it is an open research topic.

Thermal Performance

In mass production, thermal performance is an important issue for cutting or, machining. Due to cellulose content natural fibers become highly flammable which can be improved by chemical treatment (Khan *et al.*, 2018). Due to cellulose, hemicellulose, and lignin, natural materials start to burn at 200–800°C (Shahinur and Hasan, 2019) whereas some metallic materials melt at above 2000°C. Thus, thermal tolerance needs to be improved for machining of the biobased product. Thermal performance can be improved through different modifications in spray, and solid phase of biobased product (Soury *et al.*, 2009; Shahinur *et al.*, 2013). Phosphorus salt is used in solid phase for improvement of thermal properties whereas halogens with phosphorus act in the vapor phase (Ulsamer *et al.*, 1980). Due to the modifications, biobased-materials become less biodegradable whereas their performance is enhanced. Thermal degradation also affects mechanical performance. Due to heat, the structure of bio based material is changed and mechanical properties are hampered. For example, Shahinur *et al.* (2013) have revealed that when thermal properties are increased, mechanical properties are decreased due to fire retardant treatment on the biobased material. However, Huang *et al.* (2003) found an improvement of mechanical properties with thermal properties due to chemical modification.

Poor Bonding Mechanism

Poor interfacial strength of the biobased composite is another challenge for manufacturing. Due to surface roughness and hydrophobicity, the poor bonding occurs in the biobased composite particularly, fiber and the matrix. Furthermore, the biobased-materials are chemically treated which are toxic or not environmentally friendly. Though in the developing country the biobased product development will generate employment opportunities, the percentage of chemical incorporation is small, which needs to be overcome through modern technology to ensure environmental safety.

Non-Homogeneity

When biobased products are manufactured the quality standard of the products is not consistent due to the non-homogeneous material characteristics. In addition, due to this criterion the mechanical, thermal, structural, physical as well as the aesthetic performances of the biobased material may vary significantly. As they grow naturally there is non-homogeneity in the structure of a biobased material. The percentages of bio-elements are not homogeneous all over a particular bio-material. For example, biobased fibrous plants' lignin content varies from one portion to another. Moreover, in case of biobased fiber the percentages of bio elements vary with the age of fiber. Furthermore, biobased composite is produced to control this non-homogeneity. In the case of biobased composite one material is mixed with other material or biobased material. By changing the genome sequence of a biobased material, this non-homogeneity might be improved. Thus, it is a new area of research for further improvement in biobased material non-homogeneity.

Limitation of Biobased Products

Though biobased products are attractive due to their low weight, cost, CO₂ emission, and O₂ absorption, they also have some limitations. Among the limitations, biobased products face a critical problem of performance degradation when they expose to an outdoor environment which needs to be minimized. In addition, the limitations of biobased materials cause machining, milling, and drilling problem during the manufacturing of a biobased component and need to overcome for a sustainable biobased product development. Abrate and Walton (1992) and Mohamed *et al.* (2016), informed the machining technique of product which could be suitable for biobased product. Thus, this sector needs to be improved for biobased product machining. Despite having the machining issues, the researchers are giving more importance to the opportunity of environmental sustainability with the biobased products.

Conclusion

During the design of a biobased-product considerations should be made on the uncertainty in biobased material properties, shape optimization in micro, macro as well as nano field, manufacturing and assembling fixation, and finally tolerance of the biobased-based product. Thereafter, designing a product when it goes for manufacturing faces different problem which needs to be solved for sustainable development. Biobased products are being developed in huge varieties due to customer need, which need enabler during the product design and manufacturing for mass customization (AlGeddawy and ElMaraghy, 2011). In addition, in case of product design economic growth of a country, national and individual prosperity are the controlling factors. Furthermore, biobased-materials have a wide range of performance parameters from the highest and lowest. Thus, one needs to balance them in term of customer need and satisfaction compared to the other existing products. If value added product is developed through appropriate design, with other supporting factor and step of the marketing, biobased products will be sustainable in the market. There are different areas for further developments in the product design and the challenges to overcome regarding the manufacturing of biobased products. As a result, farmers, suppliers, and users will be benefited and the earth will stay green for a longer time for the next generation.

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The Effect of CaCO_3 Nanoparticles and Chitosan on the Properties of PLA Based Biomaterials for Biomedical Applications

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Introduction

Blending of chitosan (CS) with suitable polymer matrix is an often used and effective method to improve the physical and mechanical properties of blend composites. Polylactic acid (PLA), chitosan (CS) and nanoparticles based biocomposites/biomaterials as natural polymers have proven its high potential in biomedical applications, such as tissue engineering, wound dressing, drug delivery system, orthopedic devices, surgical sutures, enzyme immobilization, catalysis, antibacterial coatings and so on. These biocomposites are non-toxic, antibacterial, biodegradable and biocompatible biopolymers (Zhang and Cui, 2012; Jayakumar *et al.*, 2010).

Poly(lactic acid) (PLA) is bioactive and biodegradable thermoplastic aliphatic polyester derived from various renewable resources, such as corn starch, sugarcane, tapioca roots and so on. Generally, PLA is produced from lactic acid and the cyclic diester, lactide monomer. The most frequently used procedure of PLA production is the ring-opening polymerization of lactide with different metal catalysts in solution, in the melt or as a suspension. The metal-catalyzed reaction overlook to cause racemization of the PLA, decreasing its stereo regularity compared to the starting material (Grande and Carvalho, 2011).

There have various different types of polylactic acid to include Regular PLLA (Poly-L-Lactic Acid), Racemic PLLA (Poly-D,L-Lactic Acid), PDLA (Poly-D-Lactic Acid) and PDLLA (Poly-DL-Lactic Acid). Each of them have slightly different individual characteristics but are similar in that both of them are produced from a renewable resource (like lactic acid: $\text{C}_3\text{H}_6\text{O}_3$). The production procedure of PLA is very cost efficient. When exposed to the environment PLA degrades naturally which makes its versatile applications. There has a high potential for PLA to use in short lifespan applications where biodegradation is highly required. PLA has a crystallinity of around 37%, melting temperature 173–178°C, glass transition temperature 60–65°C and the tensile modulus 2.7–16 GPa (Södergård and Stolt, 2002; Middleton and Tipton, 2000). PLA is generally soluble in chlorinated solvents, hot benzene, tetrahydrofuran and dioxane (Garlotta, 2001). The biodegradation of PDLA is milder than for PLA due to having higher crystallinity of PDLA. PLA is fairly unsuitable for high temperature applications due to its relatively low glass transition temperature (generally 44°C to 63°C) and it is slightly more brittle than ABS for 3D prototyping.

The applications of natural polymers which are biodegradable and biocompatible has become increasingly important nowadays because of their outstanding properties, such as natural abundance, low costs, non-toxic and wide range of applications (Mathew *et al.*, 2005; Jonoobi *et al.*, 2010). Recently biodegradable polymers have been focused for the preparation of food packaging films from the concern about the environment. These types of food packaging films are usually highly loaded with antimicrobial agents to inhibit growth of food-born microorganism when come contact with foodstuffs (Jayakumar *et al.*, 2010). PLA has many other applications such as barriers for sanitary products, diapers, milk and water bottles and also used in retail markets for fruits, salads and vegetables (Pei *et al.*, 2010). PLA is being used because it functions very well and provides excellent properties at a competitive price.

Chitosan (CS) (poly-1,4-D-glucosamine) is a biodegradable natural polymer obtained from renewable sources such as from the shell of shellfish and the wastes of the seafood industry. It may also be produced by alkaline deacetylation of chitin. It has some novel properties including biodegradability, biocompatibility, antibacterial, natural abundance, wound-healing activity and so on. Chitosan biopolymer has a wide range of commercial and possible biomedical applications including wound dressing, tissue engineering scaffolds, drug delivery system, bandages to reduce bleeding and other hemostatic agents, as an antibacterial agent and so on. Hemostatic properties of chitosan help to reduce pain by blocking nerve endings (Kumar *et al.*, 2014). Chitosan is frequently used in the field of bandages because of its antioxidising, antiseptic, antiviral, antibacterial and hypoallergenic properties. Chitosan-based plastic wrap doubles the shelf life of some foods. It is frequently used in food processing industries as edible coatings or films to extend foodstuff's shelf life, such as fruits, meat, fish and seafood because of its non-toxic and edible properties. CS is reported to be an active polymer with antimicrobial and antifungal activities because of its biodegradability and biocompatibility. Among the biodegradable polymers, it is one of the most abundant in nature. Moreover, with the increasing attention about the environment, the newly developed biodegradable packaging materials, such as CS films, could be an interesting alternative to petroleum-based synthetic polymers. In order to fulfill the aforementioned applications, various investigations and researches have been devoted to produce new polymer systems incorporating Chitosan as a bioactive material.

PLA has few drawbacks that limit its use such as poor thermal stability, low water vapor and gas barrier properties and embrittlement (Petersson *et al.*, 2007; Qu *et al.*, 2010). These negative properties of PLA may be overcome by blending it with suitable synthetic or natural polymers. Blending is a more effective and easier way to attain desired properties of multiphase polymeric materials (Sanadi *et al.*, 1994).

Therefore, PLA may be an effective and suitable option to blend with chitosan. However, the problem is that PLA is not miscible with chitosan due to their differences in polarities. Therefore, it is essential to mix up a third polymer in order to reduce

Table 1 The properties of PLA and chitosan

	PLA	Chitosan
Chemical and physical properties	Thermoplastic Nucleating agent Crystallinity of around 37% Glass transition temperature 60–65°C Aliphatic polyester Tensile modulus 2.7–16 GPa	Complexing and chelating properties Soluble in dilute aqueous acidic solutions High viscosity Ionic conductivity High crystallinity and hydrophilicity Strong nucleophile
Biological properties	Biodegradable Bioactive Renewable resource Antibacterial Biocompatible Biopolymers	Adsorbable Biocompatible Bioactive Nontoxic Bioadhesive Antimicrobial Hypolipidemic

Table 2 Applications of PLA and chitosan

	PLA	Chitosan
Applications	Tissue engineering, wound dressing, drug delivery system, orthopedic devices, surgical sutures, enzyme immobilization, catalysis, antibacterial coatings	Food packaging, sanitary products, diapers, milk and water bottles, wound dressing, tissue engineering scaffolds, drug delivery system, bandages to reduce bleeding and other hemostatic agents, as an antibacterial agent

the interfacial tension among the polymers to improve the attractive forces between the discrete phases in order to attain the compatible blend. **Table 1** shows various properties whereas **Table 2** shows different important applications of PLA and chitosan.

Calcium carbonate is a chemical compound with the formula CaCO₃ is an important incorporating agent with the PLA/CS blend biocomposite. It is a common substance found in rocks limestone and minerals calcite. It is generally found in pearls and the shells of marine organisms, snails and eggs. Calcium carbonate has medicinal applications as a calcium supplement or as an antacid. Stimulated body fluid with excellent apatite-forming ability of ceramic-polymer biomaterial was prepared by hot pressing a mixture of poly-L-lactic acid (PLLA) and calcium carbonate. The modulus of elasticity of the biocomposite was effectively improved by 3.5–6 GPa, when 30 wt% calcium carbonate was introduced. The composite showed no brittle fracture behavior and a comparably high bending strength of approximately 50 MPa (Kasuga *et al.*, 2003).

By melt extrusion process, precipitated calcium carbonate (PCC) and halloysite natural nanotubes (HNT) of PLA nanocomposites were prepared. Xuetao Shi described the thermal, mechanical, crystallization and morphological properties of HNT/PLA, HNT/PCC/PLA and PCC/PLA composites (Shi *et al.*, 2015). Young's modulus is increased, but tensile strength is decreased with the addition of inorganic nanofillers in PLA composites. The elongation at break properties is increased with the incorporation precipitated calcium carbonate (PCC) (Shi *et al.*, 2015).

Various commercial PLA products are already available in the market. These include long life consumer goods such as compact disc (CD), computer keys, casing of walkman, blanket, and different packaging products such as envelope with transparent window, transparent paper bag for bread, trays, and bowls for fast food and some agriculture and horticulture products.

Modifications of PLA

As discussed early, PLA has poor chemical modifiability, mechanical ductility and poor hydrophilicity. Therefore, chemical and physical modifications such as incorporation of functional monomers with different compositions are very much helpful to improve its applicability.

Chemical modification of PLA

Cross-linking and copolymerization are two major techniques for chemical modification of PLA.

Cross-linking

Cross-linked PLA can be obtained by various chemical reactions or by irradiation. Quynh attained stereocomplexes by cross-linking blends of PLLA and low molecular weight PDLA (Quynh *et al.*, 2009). By radiation cross-linking, alkaline hydrolysis and enzymatic degradation can be controlled. Without irradiation, only by chemical reactions between linking agents and the polymer chain with various gel fractions and cross-linking densities, PLA can be modified (Agrawal *et al.*, 2010).

Table 3 Mechanical properties of pure PLA and its composites (mean values; all the specimens were tested at 0°C)

Types of samples	Young's modulus, (N/mm ²)	Tensile strength, (N/mm ²)	Charpy impact strength, (KJ/mm ²)	Elongation at break, (%)
Pure PLA	3820.2	30.1	24.4	0.83
Hemp-PLA	8064.2	57.5	9.5	1.24
Cotton-PLA	4242.3	41.2	28.7	3.07
Kenaf-PLA	7138.6	52.9	9.0	1.05
Hemp/Kenaf-PLA	7763.8	61.0	11.8	1.22
Hemp/Lyocell-PLA	7034.9	71.5	24.7	1.65
Lyocell-PLA	6783.8	81.8	39.7	4.09

Copolymerization

Polycondensation of PLA with lactone-type monomers generally obtain low molecular weight copolymers. This type of polycondensation is possible for the hydroxyl group and carboxyl groups of lactic acid. The crystallinity of this type of copolymers is increased. Biocompatibility, hydrophilicity and antibacterial activity are increased by obtaining copolymerized products of PLA with poly(ethylene glycol)(PEG) and poly(ethylene oxide)(PEO) (Metters *et al.*, 2000).

Physical modifications of PLA

PLA can be modified to increase various applicable properties by different physical methods such as plasticization, composition variations and blending method.

Plasticization

Normally, PLA has poor elongation properties as glassy polymer. The ductility and softness of PLA can be increased and the glass transition temperature, T_g can be lowered by modifying the PLA with various biodegradable plasticizers with low molecular weight and high boiling point. Ljungberg have blended PLA with five various plasticizers (triethyl citrate, tributyl citrate, acetyl tributyl citrate, acetyl triethyl citrate and tri acetone) and observed that tributyl citrate and triacetone were more effective as plasticizers which decrease T_g of PLA (Ljungberg and Wesslén, 2002).

Composition variations

Graupner *et al.* (2009) made composites from various types of natural fibers (such as hemp, cotton, kenaf, etc.,) and some modified cellulosic fibers by compression molding. A few types of surface modifiers can enhance adhesion between the fibers and the PLA matrix. Wang made a composite from PLA and microcrystalline cellulose modified by L-lactic acid (Wang *et al.*, 2002). The tensile strength of the composite was higher than pure PLA. The mechanical properties of these fiber composites are summarized in Table 3

Blending

Jamshidian performed extensive reviews in "Food Science and Food Safety" and found that huge investigations have been done on the blending of various polymers with PLA such as poly(ethylene glycol), poly(vinyl acetate), poly(ethylene oxide), cellulose acetate and poly(hexa-methylene succinate) (Jamshidian *et al.*, 2010). Polymer blending is very effective technique to develop new properties. Various expected properties can be attained by blending with PLA. Xu *et al.* (2009) have blended PLA with a new degradable thermoplastic derived from konjac glucomannan (TKGM) in order to promote the mechanical and processing properties of PLA without sacrificing its biodegradable and biocompatible properties (Table 4).

Materials and Method

Preparation of Nano-Sized CaCO₃ and Characterization

The micron-sized eggshell powders were first prepared according to the method of previous study on almost similar reports which was using cockle shell (Islam *et al.*, 2011). First of all, approximate 250 g of eggshells were scrubbed to remove dirt and washed with distilled water. It is then being boiled for 10 min and cooled at room temperature. The eggshells then washed again with acetone and leave for a day so that it will dry completely and ready for grinding. The outer and inner membranes under eggshells were removed and only the shells were grinded manually using mortar and pestle. The powders obtained were sieved with aperture size of 90 µm to obtain micron sized less than 90 µm in diameter powders. The powders were ready to make into nano-sized calcium carbonate.

For the synthesis of calcium carbonate nano-sized particles, 10 g of prepared micron-sized eggshells were used. 100 mL distilled water was added to form slurry. The mixture was then stirred vigorously for 120 min at room temperature using a magnetic bar and a mechanical hot plate stirrer at the rate of 1000 rpm. The samples were then separated using a filter paper. The product was then dried at 70°C for a day and packed in polyethylene plastic bag for further use. The brownish white sample obtained was then

Table 4 PLA modifications for various applications

<i>Types of modification</i>	<i>Treatments/Materials added</i>	<i>Observed effects</i>
Physical modifications	Annealing	Toughness is increased
	Aging	Glass transition temperature is increased
	Orientation	Tensile and impact properties are improved
	Drawing	Tensile and fracture properties are improved
Copolymerization of PLA	Polyvinyl chloride	Toughness and strength are improved
	ϵ -Caprolactone	Decomposition temperature and crystallinity are increased
	Acrylonitrile-butadiene-styrene	Elongation at break with a slight loss in modulus and impact strength and tensile strength are increased
	D,L-mandelic acid	Mechanical properties and glass transition temperature, T _g are improved
Blending with	Poly ethylene glycol (PEG)	Enhance the crystallinity of PLA and biodegradability
	Poly ethylene oxide (PEO)	Elongation at break is improved.
	Poly ϵ -caprolactone (PCL)	Mechanical properties are highly improved
	Polyvinyl acetate	Percent elongation and tensile strength are increased
	Polycarbonate	Mechanical properties and biodegradation rate are increased.
	Starch with various plasticizers	The price is lowered, crystallinity is increased, T _g and biodegradability are decreased
Modifiers	Poly(1,3-butylene adipate)	Glass transition temperature is decreased but elongation at Break is increased

sent for XRD and FTIR analysis to ensure that pure calcium carbonate was obtained. The powders were then stored to be used to prepare composites.

The structural properties of the formed nano-sized CaCO₃ particles were investigated by the X-ray diffraction (XRD) using Shimadzu 6000 X-Ray machine with nickel filtered Cu K α ($\lambda=1.542$ Å) radiation. The average crystallite size of the CaCO₃ nanoparticles has been calculated from the line broadening using the Scherrer's relation as following:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where D is the crystallite size (in nm), λ the wavelength of X-ray ($\lambda=1.542$ Å),

β the full width at half maximum (FWHM—in radian) intensity and

θ the Bragg diffraction angle (°).

The scanning angle of the XRD analysis was 20–70°C in 2θ at the rate of 10°C min⁻¹.

Fourier transforms infrared spectroscopy (FT-IR) was performed using a Perkin Elmer 1725 X Spectrometer. The CaCO₃ nanoparticles were dispersed and mixed with the KBr particles together and pressed into pellets. The spectrum of CaCO₃ nanoparticles were recorded in the range of 4000–280 cm⁻¹. The transmission electron microscopy (TEM) studies were performed with Hitachi H-7100 TEM. The sample was prepared by dispersing the drop of colloid on the copper grid, covered with the carbon film and the solvent was evaporated. Micrographs were taken to study the morphological and crystallinity of CaCO₃ nanoparticles.

Preparation of Biomaterials and Characterization

Materials

Poly(lactide (Nature WorkTM PLA 300ID) in pellet form having a specific gravity of 1.24 g/cm³ and a melt flow index (MFI) of 15 g/10 min (190°C/2.16 kg) was used for this study. Commercially available chitosan (practical grade 75% DD) from sigma Aldrich was used as the reinforcing filler. Nanoparticles of 2% CaCO₃ nanoparticles was used as a compatibilizer. Chloroform was used as solvent secured from Merck, Malaysia.

Preparation of PLA/CS/CaCO₃ nanoparticle composites

Different weight percentage (wt%) of CaCO₃ nanoparticles (0.5, 1 and 2 wt%) was mixed into chloroform respectively together with 10 wt% PLA pellets and 5 wt% CS. The solution was stirred in a water bath at 60°C until all the pellets were fully dissolved. The PLA/CS/CaCO₃ NPs solution was then casted on Petri dish and left at ambient temperature for 24 h for solvent to evaporate. The thickness of the cast solution was about 100 μ m. The resultant films were then peeled off from the casting surface.

Preparation of PLA/CS composites

10 wt% of PLA pellets was mixed together with 5 wt% of CS in chloroform solution. The solution was stirred in a water bath at 60°C until all the pellets were fully dissolved. The PLA/CS solution was then evenly casted on Petri dish and left at ambient temperature for 24 h for solvent to evaporate. The thickness of the casted solution was about 100 μ m. The resultant film was then peeled off from the casting surface.

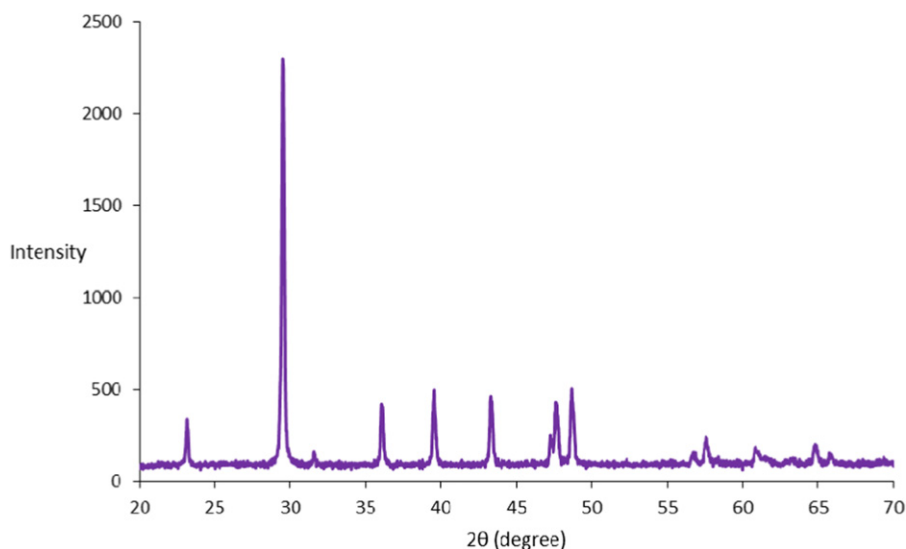


Fig. 1 XRD pattern of CaCO₃ nanoparticles prepared at room temperature.

Preparation of pure PLA film

A 10 wt% solution of PLA pellets in chloroform was prepared by stirring the solution in a water bath at 60°C until all the pellets were fully dissolved. The PLA solution was then evenly casted on Petri dish and left at ambient temperature for 24 h for solvent to evaporate. The resultant film was then peeled off from the casting surface. The developed composites were then tested for characterized various properties.

Structural and surface morphology of developed composites were analyzed through Fourier transforms infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). FTIR was performed using a Perkin Elmer 1600 Infrared spectrometer. The significant transmittance peak at a particular wave numbers was measured by using the “find peak tool” provided by Nicolet OMNIC 5.01 software. SEM analysis was carried out using a SEM-EDX Oxford INCA 400 model at an acceleration voltage 10 kV. The samples were sputter-coated with gold to prevent charging. Mechanical test was carried out using the Instron 4400 Universal Tester to measure the tensile strength at the point of breakage for each sample. Tensile tests were carried out at room temperature, according to the ASTM D882 type V. A fixed crosshead rate of 10 mm/min was utilized in all cases and the results were taken as an average of five tests.

Results and Discussions

Characterization of Nano-Sized CaCO₃

X-ray diffraction (XRD)

Fig. 1 showed XRD pattern of CaCO₃ nanoparticles as prepared from eggshells at room temperature. It was carried out under 20–70°C. The XRD pattern matched to standard aragonite CaCO₃ powder sample (JCPDS file No. 00-041-1475) and also calcite CaCO₃ powder sample (JCPDS file No. 00-047-1743). The XRD curve showed diffraction plane corresponded to 2θ values and tabulated in the [Table 5](#).

These values of diffraction shown a orthorhombic CaCO₃ with lattice parameter of $a = 4.9623 \text{ \AA}$, $b = 7.9680 \text{ \AA}$ and $c = 5.7439 \text{ \AA}$. CaCO₃ nanoparticles was in a mixture of both aragonite and calcite form. Aragonite form 6 diffraction peaks as shown as **Fig. 1** above. $\lambda = 1.542 \text{ \AA}$. The remaining peaks showed value of diffraction matched to calcite form CaCO₃ nanoparticles. Based on Debye Scherrer equation, which relating the width of powder diffraction peak to average dimensions of crystallites in a polycrystalline powder by volume.

$$\beta_s(2\theta)_{hkl} = \frac{K\lambda}{T \cos \theta_{hkl}}$$

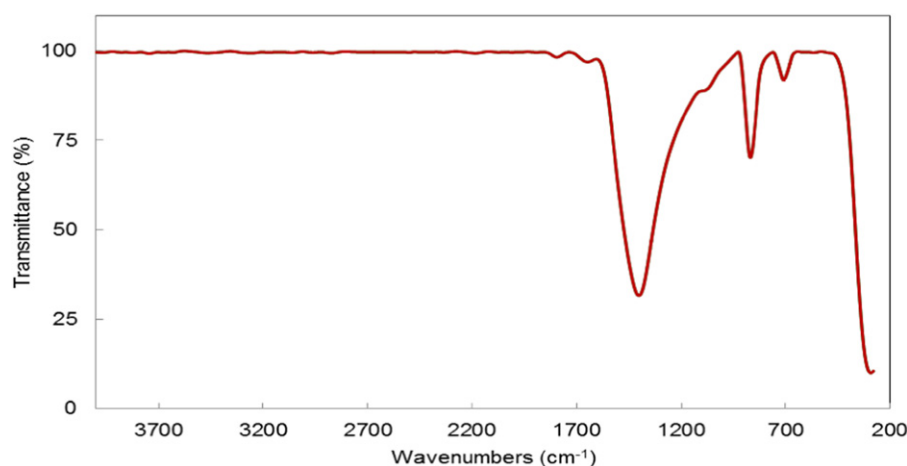
Where β_s is the crystallite size contribution to the peak width (FWHM) in radian, K is a constant near unity (0.9), and T is the average thickness of the crystal in a direction normal to the direction to the diffracting plane hkl . The value of K may have slight change depending to the FWHM or integral width chosen to be characterizing the peak breath. It was crucial to understand precisely dimensions that were used on the equation and how the crystallite size broadening was estimated accurately.

As the diffraction peaks shown were sharp, it can be concluded that CaCO₃ nanoparticles were highly crystalline. The diffraction peak with 2θ value of 29.529° having the plane (1 0 4) was used to calculate the crystallite size contribution. It was the prominent peak and found that the size contributed was 8.104 nm.

Table 5 XRD reflection of CaCO₃ nanoparticles

Angle 2θ (deg)	D-spacing ($\text{\AA}$)	Miller indices
23.1492	3.84232	(0 1 2)
29.529	3.0251	(1 0 4)
31.5796	2.83319	(0 0 6)
^a 36.0608 ^a	2.49074	(2 0 0)
39.5563	2.27832	(1 1 $\bar{3}$)
43.2779	2.09064	(2 0 2)
47.2335	1.92437	(0 2 4)
47.6601	1.90814	(0 1 8)
^a 48.6103 ^a	1.87304	(2 0 2)
^a 56.6804 ^a	1.62403	(3 1 0)
57.5554	1.60141	(1 2 2)
60.8156	1.52314	(1 2 $\bar{4}$)
^a 63.1829 ^a	1.47165	(3 2 1)
^a 64.7584 ^a	1.4396	(0 0 4)
^a 65.8285 ^a	1.4176	(2 2 3)

^aIndicated the aragonite formed CaCO₃ reflection.

**Fig. 2** FTIR peaks of CaCO₃ nanoparticles.

Fourier transform infrared spectra (FTIR)

Fig. 2 shows the FTIR spectrum of the synthesized CaCO₃ nanoparticles, which was acquired in the range of 4000–400 cm⁻¹. The most prominent peak of carbonates with 1402.52 cm⁻¹ was appeared as asymmetrical stretching vibration C–O bond. This peak was attributing to alkyl group which was present in the aragonite polymorphs. The characteristic peaks, represent CO₃²⁻ of aragonite, were observed at 869.45 cm⁻¹ and 709.93 cm⁻¹. The CO₃²⁻ peaks observed were in OCO bending mode vibration (Andersen and Brecevic, 1991). The weak peaks beside the prominent peaks appeared to be 1795.06 cm⁻¹ was due to C=O bonding of CO₃²⁻ (Chen *et al.*, 2011).

Transmission electron microscope (TEM) for CaCO₃ nanoparticles

TEM analysis was carried out to determine the morphology, size and crystalline nature of the synthesized eggshells based CaCO₃ nanoparticles. **Fig. 3** shows TEM analysis of the CaCO₃ nanoparticles. The TEM images show spherical and rod-shaped CaCO₃ nanoparticles with the average size of 21.3 nm and 548.7 nm respectively (Hassan *et al.*, 2014). Although, the mixture of CaCO₃ polymorphs were synthesized, the crystal size of both spherical and rod-shaped produced were smaller in size than the previous researches. The mixture of CaCO₃ polymorphs were most probably due to absence of catalyst that was used in previous research (Islam *et al.*, 2013). This was due to the catalyst was not suitable for biological purposes. The agglomeration of CaCO₃ crystal was due to their high specific surface areas and the strong tendency to form aggregates (Lam *et al.*, 2009; Wang *et al.*, 2002).

If the particle sizes were to compare between the results of TEM and XRD which was calculated previously, there was a net difference of 62%. The reason behind the variation may be due to nano-sized particles having high specific surface areas and therefore having strong tendency to form aggregates. As the aggregation nature of nanoparticles precise determination of primary particle size were unavoidable with significant error. These also thus explain the necessity of different analysis approach including TEM (Lam *et al.*, 2009).

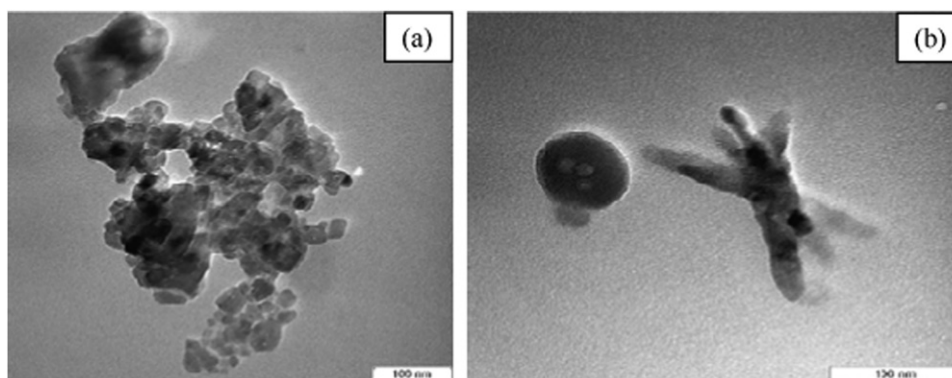


Fig. 3 TEM of (a) spherical and (b) both spherical and rod-shaped CaCO_3 nanoparticles.

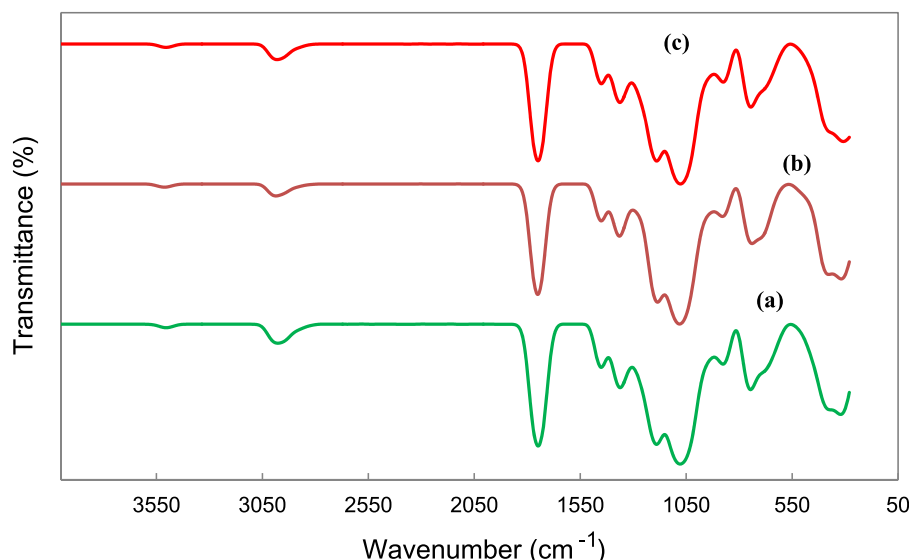


Fig. 4 FT-IR results of (a) PLA, (b) PLA/CS and (c) PLA/CS/ CaCO_3 .

Characterization of Biomaterials

Fourier transform infrared spectroscopy (FT-IR)

The interaction between PLA, CS and CaCO_3 was investigated by FT-IR spectroscopy and is shown in **Fig. 4**. The FTIR spectrum of the neat PLA (**Fig. 4(a)**) clearly showed the characteristic absorption band in the region of $3500\text{--}3600\text{ cm}^{-1}$, $2946\text{--}2999\text{ cm}^{-1}$ and 1757 cm^{-1} due to O–H stretching, C–H asymmetric stretching and C=O stretching vibration respectively (Jeevitha and Amamath, 2013). On the contrary, it can be seen from **Fig. 4(b)** that the characteristic absorption band of PLA at 3418 cm^{-1} and 2918 cm^{-1} has shifted towards lower wave numbers with narrowband intensity upon incorporation of CS. Therefore, it can be implied that CS adequately dispersed in the PLA matrix and formed PLA/CS composites.

Fig. 4 represented the FT-IR spectra of PLA/CS/ CaCO_3 composites respectively. It was found that the characteristic absorption band of PLA/CS has shifted towards lower wave numbers when CaCO_3 was added into PLA/CS matrix. This indicated some level of interaction and the formation of PLA/CS/ CaCO_3 composites. All these results pointed towards good dispersion and interaction between PLA, CS and CaCO_3 which significantly changed the morphological properties of the composites.

Scanning electron microscopic (SEM)

SEM micrographs of fractured composite samples shown in **Fig. 5(a)** and **(b)** indicated that the PLA/CS fractured surfaces were covered with uneven fibrils layers and a number of micro-voids throughout the surface. This indicates that the two polymers (PLA and CS) were not properly miscible (Balakrishnan *et al.*, 2012).

Conversely, the tensile test fractured surfaces of PLA/CS/ CaCO_3 samples (**Fig. 5(b)**) showed smooth and homogeneous surface upon incorporation of CaCO_3 in the matrix. It can also be seen that the fibrils and micro-holes significantly reduced after addition of CaCO_3 into the PLA/CS matrix. This result indicates that the PLA, CS and CaCO_3 were well blended in the matrix and the

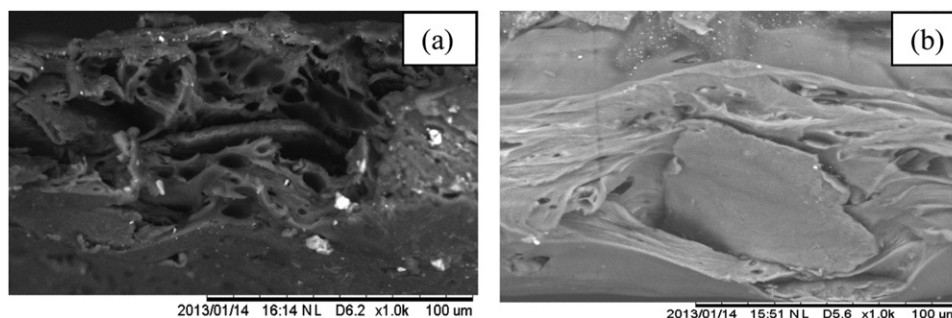


Fig. 5 Typical SEM of (a) PLA/CS (10% CS) and (b) PLA/CS/ CaCO₃ (10% CS).

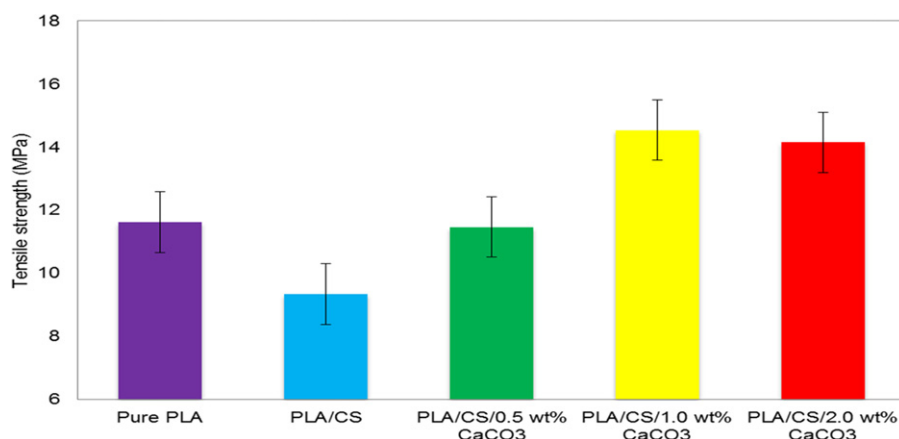


Fig. 6 Tensile strength of various composites.

interaction between PLA and CS was strong. Thus this result confirms that CaCO₃ significantly improved the adhesion and interaction between PLA and CS (Zakaria *et al.*, 2013; Julkapli *et al.*, 2011). Therefore, the mechanical strength of PLA/CS/CaCO₃ composites should be higher as compared to the pure PLA/CS.

Tensile strength

The tensile strength of the composites was displayed in Fig. 6. Generally, it can be seen that the tensile strength and tensile modulus of the pure PLA composite decreased upon the incorporation of CS. Both the tensile strength and tensile modulus of the PLA/CS composite showed improvements as CaCO₃ nanoparticles being incorporated into the composites up to 1.0 wt% CaCO₃ nanoparticles loading. This same goes to the elongation at break of the composites which showed steady increment up to 1.0 wt% CaCO₃ nanoparticles loading of PLA/CS/CaCO₃ nanoparticles composite.

The effectiveness of the reinforcement to facilitate effective stress transfer in ultimate tensile strength of the composites was the interface of the matrix and filler. Fig. 6 showed that PLA/CS exhibited weaker tensile strength compared to the pure PLA composite. Both the CS and PLA formed intermolecular hydrogen bonds between the N-H of chitosan and C=O of PLA, leading to the tensile strength of the PLA/CS composite. However, the tensile strength of PLA/CS decreased with further increase in the PLA:CS ratio, which may be due to the formation of intramolecular hydrogen bonds rather than intermolecular hydrogen bond, resulting in phase separation between the two main components (Eichhorn *et al.*, 2010). As CaCO₃ nanoparticles being incorporated into the PLA/CS composite, tensile strength of the composite was improved by 34.2% at 1.0 wt% CaCO₃ nanoparticles loading. However, the tensile strength of the composite declined with the increment of CaCO₃ nanoparticles loading until 2.0 wt%. The tensile strength increased with the increase in CS loading up to 5 wt% and then decreased gradually up to 15 wt%. This implies that 5 wt% is the optimum concentration beyond which agglomeration of CS particles occur causing stress concentration within the matrix which consequently lowers the tensile strength. However, PLA/CS/CaCO₃ exhibited a higher tensile strength than the PLA/CS at all CS loading. This may be due to the incorporation of CaCO₃ into the PLA/CS matrix, which increased the compatibility and adhesion between PLA, CS and CaCO₃, thereby resulting in higher tensile strength for composites (Yew *et al.*, 2005).

TGA of nanocomposites

Based on Fig. 7, it was observed that thermal stability of PLA/CS decreased when CaCO₃ nanoparticles was added. This indicated that thermal stability decreased with addition of CaCO₃ nanoparticles. Thermal decomposition of all five composites showed almost same

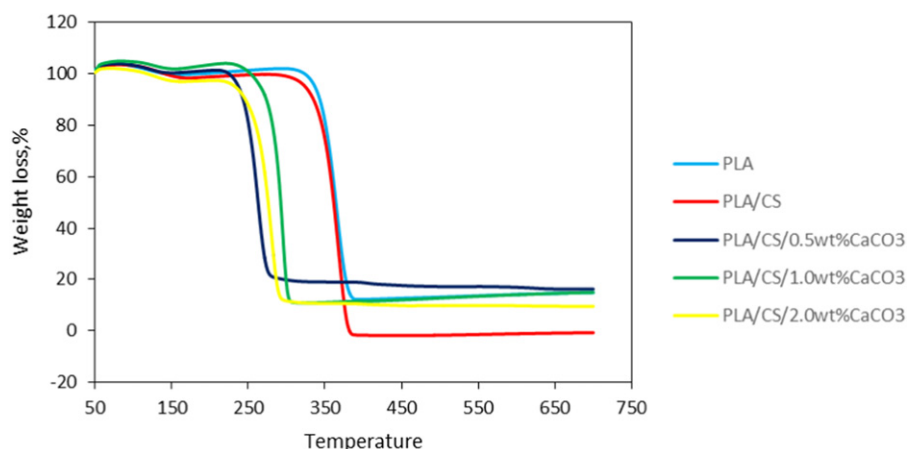


Fig. 7 TGA thermo grams of various composites.

curve. Pure PLA film showed a better thermal stability than PLA/CS composite which suffered greatest loss by 89.7% as seen from [Fig. 7](#). Thermal stability seems improved as CaCO₃ nanoparticles were incorporated into the composites to offset the effect of addition CS. On the other hand, thermal stability of blended CaCO₃ nanocomposites showed that 1.0 wt% CaCO₃ nanoparticles had highest thermal stability with similar wt% loss with 0.5 wt% CaCO₃ nanoparticles. PLA/CS/2.0 wt% CaCO₃ had same thermal decomposition temperature but had greater loss than that of other blended CaCO₃ nanocomposite.

Antibacterial Activity of Chitosan-Based Materials

Dongwei carried out a research work on synthesis of chitosan-based silver nanoparticles and their antibacterial activity ([Wei et al., 2009](#)). In his work, Chitosan-based silver nanoparticles were synthesized by reducing silver nitrate salts with nontoxic and biodegradable chitosan. The silver nanoparticles thus obtained showed highly potent antibacterial activity toward both Gram-positive and Gram-negative bacteria, comparable with the highly active precursor silver salts. Compared with pure chitosan films, chitosan films with silver showed both fast and long-lasting antibacterial effectiveness against *Escherichia coli*. The silver antibacterial materials prepared in the system are promising candidates for a wide range of biomedical and general applications.

Chitosan/ZnO nanoparticle composite membranes was synthesized and characterized by [Li et al. \(2010\)](#). In their works, novel chitosan/ZnO nanoparticle (CS/nano-ZnO) composite membranes were prepared via the method of sol-cast transformation. The antibacterial activities of composite membranes were measured by the diameter of bacterial colonies, compared to a positive control and the pure CS membrane. The antibacterial activities of CS membranes for *Bacillus subtilis*, *Escherichia coli*, and *Staphylococcus aureus* were found to be enhanced by the incorporation of ZnO. CS/nano-ZnO composite membranes with 6–10 wt% ZnO exhibited high antibacterial activities by their research.

Conclusions

The current study showed that CaCO₃ nanoparticles was successfully prepared and fabricated novel biomaterials using newly synthesized CaCO₃ nanoparticles via solution mixing and film casting method. The CaCO₃ nanoparticles had been successfully incorporated into the PLA/CS matrix as the FTIR spectrum showed improved interaction between the PLA, CS and CaCO₃ nanoparticles in the composites. The fabricated composites also showed improvement in mechanical strength and 1.0 wt% CaCO₃ nanoparticles were the most optimum amount to be incorporated into PLA/CS matrix. These improvements were attributed to good attractive interaction between the composites components. Meanwhile, addition of CaCO₃ nanoparticles into the PLA-CS matrix helped to offset the effect of CS in the matrix and reduce the weight loss. However, the thermal stability seems to be also reduced as the CaCO₃ nanoparticles were introduced into the matrix. Research has demonstrated that silver (Ag) and Zinc oxide (ZnO) nanoparticles based chitosan biomaterials exhibited high antibacterial activities.

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Injected Mold HDPE/Nanoclay Composite Products: Mechanical Properties and Quality

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Introduction

In current advances of material sciences and technology, polymer nano composites have become the trending amongst researchers. Furthermore, with the latest invention of nano-materials, numerous blends of polymeric matrix materials with appropriate and accurate ratio of nanofiller have been reported, with improved filler/matrix interaction, and innovative procedures in polymer nanocomposites preparation. More potential applications have also been identified such as building and constructions, medical, packaging, aerospace and automotive appliances (Saba *et al.*, 2014).

During the preparation of this material, the most important factors that need to be monitored are the quality of dispersion of the nano-reinforcement particles and the interfacial interaction between the matrix and the reinforcement phase. These two factors need to be optimized through several methods and treatments. Failures might be occurred due to poor dispersion and interfacial interaction, resulting some of the findings had become not significant in the end of process. Nevertheless, many improvement have been achieved in term of the processability of material and the improved quality and properties of end results. For instance, polymer nanocomposites have been rectified as the material with improved tensile strength, heat distortion temperatures, thermal and electrical conductivities, and enhanced gas barrier properties (Utracki, 2004). To obtain in-depth knowledge of the processing and applications of polymer nanocomposites, the requirements to comprehend these properties are vital before performing further research. Besides, portions of micron sized fillers also could provide changes in certain properties. These changes were attained within the range of 3–5 wt% of nanofillers. This range was attained based on a review, stated that with just a small quantity, the addition of nano-sized layered silicates in plastics has been found to offer improvements to the above-mentioned properties. More research could be carried out to increase the usage quantity of nanofiller without compromising the good properties of the polymer matrix, since polymer nanocomposites have gained tremendous interest in both the academic and industrial research due to their advantageous and exclusive structure (Gupta and Bhattacharya, 2008).

One of the prime polymer that was typically used in plastic manufacturing process is high density polyethylene (HDPE). This material was favored due to its abundance, low price and ability to be recycled. HDPE provides good mechanical and thermal properties with fair modulus and yield strength in conjunction with high-impact strength. Hence, an improvement was needed by reinforcing this material with inorganic minerals such as clay, wollastonite, glass bead, and calcium carbonate. Based on previous research, the growth in crystalline can be attributed to the nucleating effect of nanoclay, while the motive for crystallization temperature of HDPE/nanoclay nanocomposites continue to be unchanged. In this case, the key factor was the particle–matrix interaction, which critically affects the free energy of cluster formation and the rate of nucleation, whereby the weak interaction lowers the rate of nucleation (Thabet *et al.*, 2011).

HDPE-Nanoclay Composites Preparation

High density polyethylene is one of the common commodity plastics available commercially in market. Researchers have performed several attempt to develop new composite by using this material as the matrix (Akdoğan and Bektaş, 2018). In order to prepare the polymer nanocomposites made from HDPE and nanofillers, there are three methods that can be utilized, which are solvent intercalation, in situ polymerization and melt intercalated, as presented in Fig. 1 (Ray and Okamoto, 2003).

Based on a review, a research about HDPE/nanoclay preparation through solvent intercalation had been carried out. The mixture was prepared through solution blending with sodium montmorillonite cation exchanged with protonated dodecylamine. Unfortunately, poor dispersion was obtained due to the existence of large stacks in the composites system. At that moment, the exfoliated morphology could only be obtained by applying the in-situ polymerization. Later, the idea was succeeded by using the modified oligomer. This method could facilitate the polarity between silicate layers and polymer, thus improving the dispersion of clay. By using this preparation method, a research had been carried out about the flammable

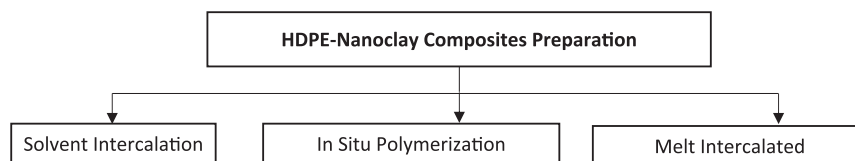


Fig. 1 HDPE-nanoclay composites method of preparation. Reproduced from Ray, S.S., Okamoto, M., 2003. Polymer/layered silicate nanocomposites: A review from preparation to processing. *Progress in Polymer science* 28 (11), 1539–1641.

properties of this material. By adding not less than 1 wt% clay, the exfoliated nanocomposites burning rate had decreased 10%–15%, due to the formation of a high performance carbonaceous-silicate char that builds up on the surface. Hence, the underlying clay had insulated the composite when the diffusion of oxygen reduced. The mass loss rate of the product also become slow (Gupta and Bhattacharya, 2008).

To quote an example for the third preparation method, which is melt intercalation, a research has been carried out about the ability to prepare nonpolar nanocomposites. This research was performed by adding cation surfactant as reactive compatibilizer. Trials towards combustion had been carried out, resulting a deduction of heat release rate by 32%. Hence, it was proven that HDPE/nanoclay was the suitable material that can be chosen for high temperature environment, such as component for automotive section (Wang *et al.*, 2001).

One of the research related to multiple preparation process had been conducted by using three cationic surfactants. These surfactants were used to alter the clay (montmorillonite) and polyethylene (PE)/maleic anhydride grafted polyethylene (PE-g-MAH)/organic-montmorillonite (Org-MMT). These nanocomposites were prepared by direct-melt blending and solution blending. Based on the intercalation behavior and microstructure analysis, the intercalation effect of nanocomposites had improved. The degree of crystallinity of composites and the crystalline thickness perpendicular to the crystalline plane was decreased with increasing amounts of PE-g-MAH. It was also found that the crystalline thickness of the sample made by the solution method was much smaller than that made by direct-melt blending. Therefore, based on the heterogeneous nucleation effect, it showed that the nanocomposite made by the solution-blending method is better than that made by the direct-melt intercalation process (Liang *et al.*, 2004).

As mentioned before, the dispersion and interaction of layers were very important to determine the performances of polymer nanocomposites. Even though previous research had concluded that the solution-blending method is better than that made by the direct-melt intercalation process, a full exfoliated clay dispersion could be achieved by adding the maleated HDPE through melt blending process, enhanced by the incorporation of mixing and shearing elements and high residence times, in the twin-screw extruder (Mehrabzadeh and Kamal, 2004). Another research also had found the same findings. Through long residence time obtained by using twin screw extruder, the effects of clay content and state of clay dispersion on the rheological, tensile properties, and flame retardancy of nanocomposites containing very small amounts of clay, in the range of 0.05–1.0 wt%, were analyzed. According to wide-angle X-ray diffraction and transmission electron microscopy, a higher degree of exfoliation for nano sized clay particles is key to enhancing the rheological, mechanical, and flame retarding properties even when small amounts of clay (less than 1%) are used (Lee *et al.*, 2007).

Hence, it can be concluded that melt compounding is a preferred technique used in HDPE/nanoclay preparation, due to the readiness of twin screw compounders and friendly towards environment because the exclusion of solvent usage. This breakthrough had stimulate the event of having more and more research to be performed. Based on several reviews, majority of research had been concentrate on material variables, such as compatibilizer, filler types/content and types of polymer. Therefore more studies were needed to rectify the influence of processing conditions, such as extruders design and configurations, internal mixers settings, temperature and pressure control as well as the processing condition optimization (Ujianto *et al.*, 2015).

Effect of Nanoclay Content

Most of electric and electronic devices were made from plastic. However, the advancement of this application oblige multi-functionality in a single material. Pristine plastic could not provide certain function needed for manufacturing requirement. To solve this problem, a multi-functional composite could be fabricated by mixing the plastics with additives, fillers, and reinforcements. Conventionally in plastic manufacturing process, additives, fillers, and reinforcements were manipulated to alter and expand certain physical and mechanical properties of matrix in composites. Fillers were used to improve modulus while reinforcement was utilized to modify the mechanical properties. Typical fillers have unfavorable geometrical features, surface area or surface chemical composition. However, this features could amend certain matrix moderately. Most of fillers were used to reduce cost by decreasing the quantity of polymer matrix, especially for those special and costly material. More than that, it could enhance the production by promoting faster molding cycles through the increment of thermal conductivity. Type of fillers also could influenced certain properties of polymer, like fibrous material could experience higher melt viscosity with the addition of fillers (Thabet *et al.*, 2011). Furthermore, shrinkage, warpage and thermal expansion also could be improved through the incorporating fillers with several types of polymer, as well as by adopting a systematic statistical optimization method (Ibrahim *et al.*, 2014).

Choosing the type of clay is very important, since a clay modifier could improve the exfoliation of clay layers in HDPE/nanoclay system. This clay modifier could become a nucleation agent, increases marginally the crystallization temperatures, and reduces the crystallite size and act as a compatibilizer (Mehrabzadeh and Kamal, 2004). More evidence had proved that different type of clay also influenced the final outcome. For instance, a local montmorillonite clay obtained from Kutch region in western part of India was blended with HDPE. Before that the clay was modified by Hexadecyl trimethyl ammonium bromide, a quaternary ammonium compound to make it organophilic. Evaluation had been made towards mechanical, electrical and thermal properties. It was found that the tensile readings was value-added, and the electrical properties also improved considerably, through the treatment of silane and titanate compounds towards the organoclay (Shah *et al.*, 2009). As for another example, a comparison of surface energy had been made between the pristine and the thermally stable phosphonium-modified montmorillonite usage on polymer/clay nanocomposites. Values of the Hamaker constant and thermodynamic work of adhesion for HDPE/nanoclay nanocomposites were the factors that need to be monitor since it was correlated with the dispersion behavior and mechanical properties (Kamal *et al.*, 2009).

Besides type of clay, the amount of clay loading also could affect the properties of HDPE/nanoclay. According to a research, the elastic modulus and tensile strength shows certain improvement by adding the nanoclays in HDPE foam, as compare with pristine HDPE foams. The best clay loading recommended was 0.5 wt% (Jo and Naguib, 2007). More research had been conducted to examine the effect of clay loading towards HDPE/nanoclay nanocomposite. The difference in this research was the existence of pine flour in the nanocomposite system. The compound was prepared through melt intercalation. Then, the compound was injected mold to prepare test specimens. Based on the results, there were an increment of flexural and tensile strength. The optimum clay loading is 1 wt%. However there was a negative effect towards impact strength, but the condition remain even though more clay was loaded (Lei *et al.*, 2007). Furthermore, some findings have been summarized, regarding the properties that should be obtained by testing the HDPE/nanoclay nanocomposites, with numerous clay loading within the range from 0 wt% (pristine HDPE) to 4 wt% nanoclay MMT. The summary stated that (Venkatesan *et al.*, 2014):

- The increment of the clay loading shall produce the increment of tensile strength as well.
- 3 wt% of MMT clay is the optimum clay loading for the impact strength and shore hardness.
- The highest the flexural strength can be attained with 3 wt% and 4 wt% of clay loading, even with the increment of cycle loading number.
- The flexural strength also increase slightly and then sustains nearly constant there off for all clay loadings during the introduction of cyclic loading.
- Mechanical properties of HDPE/nanoclay could be control by selecting the suitable amount of clay loading.

Effects of Compatibilizer and Reinforcement

In composite preparation, the usage of compatibilizer and reinforcement is very important to ensure the desired properties will be achievable.

Further cutting-edge polymer nanocomposites could be attained by extending the formulation of HDPE/nanoclay with the usage of various compatibilizer and reinforcement. The additional of natural fiber for reinforcement, such as bamboo or kenaf could bring more benefits in term of mechanical properties. To quote one example, a research had been completed towards HDPE/nanoclay/bamboo fiber, with different fraction of maleated polyethylene (MAPE) and clay loading. Based on the findings, the addition of nanoclay had reduced the resistance towards impact. However, the tensile strength, bending modulus and strength can be upgraded with the use of compatibilizer (MAPE). Since the dispersion of nanoclay had compromising the properties of HDPE/nanoclay/bamboo fiber, therefore a different technique such as pre-coating fibers might be useful to recover the properties of these polymer nanocomposites (Han *et al.*, 2008).

More research had been conducted since the usage of compatibilizer had become major interest among researcher. By manipulating the various type of modified clay and the amount of maleic anhydride (compatibilizer), the effects toward intercalation condition and mechanical properties were analyzed. According to the findings, the clay type I.30TC was preferred, and the grafted maleic anhydride HDPE had added a higher degree of intercalation in clay particles. The compatibilizer also had increased the tensile modulus, but need to be sustained at specific amount to recover the range of intercalation (Mehrabzadeh *et al.*, 2009). Another research had examine the effect of various amount of maleic anhydride grafted high density polyethylene (MA-g-HDPE) to determine the morphology of HDPE/nanoclay nanocomposites. Through spray electrostatic powder technique, an extruded composite powders were applied on treated steel surfaces, followed by curing process with specific temperature and time. Based on the scanning electron microscopy, the surface uniformity of produced coating films was analyzed and the findings indicate that by using 15 wt% MA-g-HDPE, the highest adhesion and bending strength and more surface uniformity could be achieved (Mardani *et al.*, 2014).

Applications and Recycling of HDPE/Nanoclay

The idea of using nanoclay as a filler for HDPE was made due to improve several properties and at the same time to obtain an effective cost savings solution by reducing the amount of polymer used in various type of product, such as food packaging, automotive components and so on. The improved barrier properties gained from the intercalated organic layered structure also one of the benefits that can be achieved (Cabello *et al.*, 2010). To quote one example, a research had found that the usage of nanoclay could enhanced the oxygen and water vapor transmission rates for HDPE/nanoclay nanocomposites. These properties were very suitable for packaging films and containers for food or other perishables. Moreover the use of nanoclay could provide a higher specific gravity HDPE, which is good for barrier properties even if it meant the article or film was more brittle as a result (Qian *et al.*, 2009). Besides that, HDPE/nanoclay also can be used for pipes and fittings, since the existence of nanoclay could improve the slow crack growth resistance of the nanocomposites, even if it was made from the recycled HDPE (Na *et al.*, 2017). The summary of application for this material is displayed as Fig. 2.

The addition of nanoclay also could affect the HDPE/nanoclay composites in terms of flammability and the sensitivity toward temperature. Several experiments have been performed for this material characterization, by using X-ray diffraction, transmission electron microscopy, thermogravimetric analysis, crystallinity (differential scanning calorimetry and wide angle X-ray scattering techniques), and cone calorimetry technique as well for flammability study (Szustakiewicz *et al.*, 2013). Hence, product such as

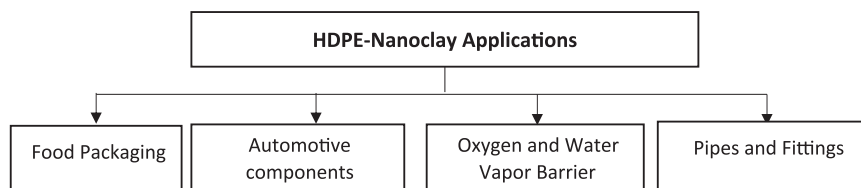


Fig. 2 HDPE-nanoclay applications. Reproduced from Cabello, J.M.L., Torres, e.g., Mas, L.C., 2010. U.S. Patent Application No. 12/159,532. Qian, G., Jarus, D., Zabrocki, V., 2009. U.S. Patent No. 7,629,406. Washington, DC: U.S. Patent and Trademark Office. Na, S., Nguyen, L., Spatari, S., Hsuan, Y.G., 2017. Effects of Recycled HDPE and Nanoclay on Stress Cracking of HDPE by Correlating Jc With Slow Crack Growth. US Department of Energy Publications, 368.

engine casing or covers should be suitable for applications. However, several factors need to be monitored, such as properties of interior plastic structures that are noticeably changed after being exposed repeatedly to sun light and rains. Such defects like loose fasteners and clips could happen if the thermal behavior was not analyzed properly (Kim *et al.*, 2011).

As for HDPE/nanoclay potential to be recycled, a research had been carried out towards the waste of HDPE/nanoclay-unmodified and organo-modified. Several findings have been clarified, such as XRD and FESEM results show a considerable effect of exfoliation and interaction organo-modified nanoclay layers in HDPE matrix. The melting temperature of HDPE/nanoclay also maintained at same level with no major shifts, according to the differential scanning calorimetry, or DSC analysis. The best behavior for the enthalpy of fusion was offered at 3 wt% clay loading for the waste HDPE/nanoclay compound. This waste nanocomposites also produced highest elastic modulus with the increment of 7.4%. However, several properties were compromised, such as tensile stress at maximum load, strain at break and tensile stress at yield were found slightly decreased in the low OMMT clay content. As for the conclusion, a better reinforcement of the waste HDPE in melt interaction method could be obtained, based on the revision of waste polymer recycling through dissolution/re-precipitation method (Hadi *et al.*, 2018).

Conclusion

This article provides a review of the injected mold HDPE/nanoclay polymer nanocomposite, in terms of preparation, effect of nanoclay, compatibilizer and reinforcement of this material. The applications and recycling issues also have been discussed. Several reviews and summaries were made from previous findings so that this article could become a good reference for future researches and manufacturing guidelines.

See also: Bamboo Fiber as Fillers for Polypropylene-Nanoclay via Injection Molding

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Jute/Coir/Banana Fiber Reinforced Bio-Composites: Critical Review of Design, Fabrication, Properties and Applications

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Introduction

Recent research on the interesting environment friendly issue has motivated the researchers to investigate biodegradable as well as economically viable bio-based composite. In bio-composite either reinforcing material or matrix material is bio-degradable (Nam *et al.*, 2011) or both are bio-degradable. These bio-degradable materials mainly grow naturally and they are directly or indirectly collected from nature. Bio-based material, in this particular case natural fiber, is mainly collected from plant's stem, leaf, seed, stalk, bast and fruit. Jute, coir, bamboo, banana, cotton, hemp, kenaf, pineapple leaf, okra, mesta, sisal and dhaincha fiber are in this categories. As they are natural, heterogeneity exists in the fiber characteristics. This heterogeneity of the fibers is controlled in the characteristics of end product, particularly mechanical and thermal properties. Many studies found that in bio-composites, fiber property is reinforced and the composite showed different mechanical and thermal criteria compared to the fiber and matrix. Therefore, each type of composite has the specific application due to their specific criteria. Moreover, bio-material has low density, high strain, high modulus of elasticity, and above all they contain OH group. Due to this OH group, they can easily absorb water and are attracted by bacteria and subsequently they become bio-degradable (Haque *et al.*, 2009, 2010). Furthermore, bio-material gives a lot of oxygen in the air during their production and emits a negligible amount of CO₂ as compared to synthetic fiber production. Therefore, bio-composite has a great impact on the life cycle, which is fully decomposed in nature or environment at a certain condition. Moreover, the use of bio-based composites is also economical as they grow naturally. Therefore, the bio-based composite can be used for several applications in small as well as large industries including household, building, vehicle, construction material, medical appliance, sports accessories and aerospace industry (Mohammed *et al.*, 2015). However, according to bio-based news jute fiber production (3300 MT) is in the 2nd position after cotton, whereas coir 1022 MT which is 4th position after wool among the natural fiber production in 2016 (Dommermuth, 2016). These types of natural fiber's properties are comparable with synthetic fiber except deviation of criteria, and less thermal stability. Thus, value added production from this natural fiber is important.

In composite, there are two parts, reinforcing material and matrix material, whereas filler is sometimes added for improved performance. Reinforcing material particularly fiber is discussed in the previous paragraph, which can be natural and manmade (not biodegradable). On the other hand, matrix material can be metallic, ceramics and polymer. In addition, there are two types of polymer matrices namely, thermoplastic (polypropylene, polyethylene, and polyvinyl chloride) and thermoset (such as polyester, acetal, phenolic, polystyrene, polycaprolactone, polylactic acid, polyhydroxybutyrate, vinyl ester and epoxy). Biodegradable matrix is also available. Based on the reinforced fiber present in the material, the composite materials can be categorized in two classes. When there is no reinforcement, it is termed as monolithic. On the other, hand when there is a reinforcement material or fiber present in a matrix material it is termed as composites such as jute-PP (polypropylene), jute-polyester and jute-epoxy. However, with more than one reinforcing material or fiber involvement is termed as hybrid composite. For example, jute-coir-PP, coir-bamboo-polyester and banana-jute-starch. The amount of fiber incorporation in the matrix depends on the fabrication method. Enormous research activities involve regarding bio-composite fabrication, characterization, comparison. There is heterogeneity in the research, the fiber has diversity in their criteria and there are different characteristics of matrices. Based on this contemplation, it is not possible to get clear idea about the design, fabrication and the final use of bio-composite. In the present article, a critical review has been made on design, fabrication, properties and application of three bio-based composites.

Design

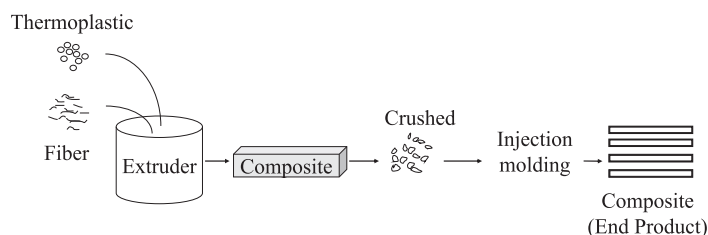
Monolithic, composite and hybrid composite designs are used to tailor the criteria of composites. The design of the fabrication of composite depends on the criteria of fiber and matrix, fabrication method, the desire of criteria, as well as required final products characteristics. Mostly used fabrication designs based on the fiber loading are listed in Table 1. Different percentages of fiber are used for composite fabrication because criteria of the composite are dependent on the percentage of the fiber loading in the composite. In case of injection molding, fiber incorporation can be increased as compared to hand lay-up technique. In composite, reinforcement can be in the form of a particle short fiber as well as long fiber. Based on the form of fiber in the composite, the required criteria of the end product of composite are changed. Similarly, the concept of the hybrid composite is developed and showed better performance.

Fabrication

This section describes common fabrication techniques of the bio-based composite. Different methods have been used by researchers and industries for composite fabrication. Such as hand-lay-up, wet-lay-up, vacuum bag, mandrel wrapping, filament

Table 1 Design of composite based on fiber loading

Types	Design	Fiber	Matrix	References
Monolithic	PP		100%	Shahinur <i>et al.</i> (2017)
	Polyester		100%	
Composite	Jute matrix Treated jute matrix	15%, 20%, 25%, 30%, 35%, 40%, 50%		Rahman <i>et al.</i> (2008), Rahman <i>et al.</i> (2009), Shahinur <i>et al.</i> (2017)
	Coir matrix Treated coir matrix	15%, 20%, 25%, 30%, 35%		Haque <i>et al.</i> (2010), Haque <i>et al.</i> (2009)
	Banana matrix Treated banana matrix	2%–10%, 20%, 30%, 40%, 50%		Ramesh <i>et al.</i> (2014), Amir <i>et al.</i> (2017), Ogunsile and Oladeji (2016), Nagendra <i>et al.</i> (2017)

**Fig. 1** Flowchart of thermoplastic composite fabrication by injection molding.

winding, pultrusion, injection molding, hot press, compressing molding, extrusion and bladder molding. In the present article injection molding and hot press methods are discussed in detail. These two are the most commonly used methods so far throughout the industry and research sectors.

Injection Molding

In case of injection molding method first reinforcing material or bio-based fiber was first cleaned and chopped into an approximate length of 3 mm. Thereafter, dried fiber was randomly mixed with thermoplastic granules in order to prepare the composites as shown in **Fig. 1**. Both raw and treated fibers were mixed with desire matrix at different weight percentage separately. Composites were prepared by passing the mixtures through a single screw extruder machine at a constant temperature of $135^{\circ}\text{C} \pm 5^{\circ}\text{C}$. The extruded composites were cut into 15–20 cm long small pieces. All the pieces were then crushed into smaller granules using a grinding machine. The granules were dried in a vacuum oven at 65°C for 1 h and fed into an injection molding for making specimens. The dried granulates were molded according to ASTM standard for characterization (Nahar *et al.*, 2013; Shahinur *et al.*, 2017).

Hot Press

Another important composite fabrication technique is hot press method. During hot pressing, according to the design, the fiber was cleaned and chopped into certain specified length (< 5 mm or greater) or in the form of a particle. After that dried fibers were randomly mixed with thermoplastic granules (**Fig. 2(a)**) or sheet (fibers are evenly distributed in the layers of sheet) (Sayeed *et al.*, 2014) at different wt% as shown in **Fig. 2(b)**. Thereafter, the mixture was heated and pressed at melting temperature of matrix to fabricate the desired composite.

According to published literature, thermoplastic material such as acrylics, polyethylene (Sultana *et al.*, 2013), polyvinyl chloride (Saheb and Jog, 1999), polypropylene (Sayeed *et al.*, 2014; Haque *et al.*, 2009; Haque *et al.*, 2010) and polystyrene (Plackett *et al.*, 2005) matrix are used in different areas according to their individual characteristics (Nirmal *et al.*, 2015). The properties of jute, coir and banana fibers are listed in **Table 2**.

From **Table 2** it is clear that jute fiber has higher percentage of cellulose, whereas coir has higher percentage of lignin content. These raw fibers are incorporated in the composite to reinforce the specific criteria. However, for better result, sometimes natural fibers are chemically treated and physically modified. Important used chemicals are benzene diazonium salt, Cu salt, ammonium salt (Shahinur *et al.*, 2017), uric acid, potassium di chromate, sodium hydro-oxide (Sayeed *et al.*, 2014), sodium peroxide and permanganate (Jordan and Chester, 2017). Bio-fibers are also radiated or grafted for better performance of the bio-composite. Furthermore, the hydroxyl group in the bio-based fiber is responsible for high water absorption and the weak interfacial bond between the fiber and matrix. There are actually three hydroxyl groups present in a cellulose anhydrous-glucose unit of fiber as shown in **Fig. 3**.

One is a primary hydroxyl group at C_6 and the other two are secondary hydroxyl groups at C_2 and C_3 . Although the primary hydroxyl group is more reactive than the secondary groups, the salt breaks the OH group of C_6 and C_2 during the reaction. This

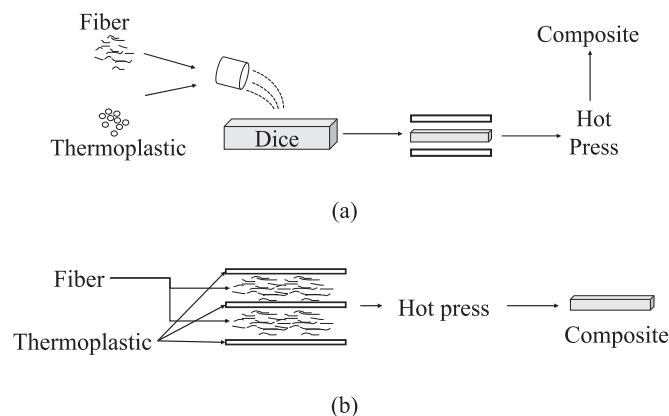


Fig. 2 Flowchart of thermoplastic composite fabrication using (a) granule and (b) using sheet through hot press process.

Table 2 Chemical constituent and mechanical properties of three bio-based materials/fibers

Chemical constituent	Jute	Coir	Banana
Cellulose (%)	59–61	43.44	53.45
Hemi cellulose (%)	22.1	0.25	28.56
Lignin (%)	15.9	45.84	15.42
Ash (%)	1	2.22	1
Density (gm/cc)	1.3–1.5	1.2–1.3	1.3–1.5
Fiber length mm	1.2–1.5	20–150	–
Fiber tensile strength (MPa)	400–800	220	355
Fiber modulus of elasticity (GPa)	70	6	33.8
References	Mohammed <i>et al.</i> (2015)	Haque <i>et al.</i> (2009), Haque <i>et al.</i> (2010)	Jordan and Chester (2017), Saheb and Jog (1999)

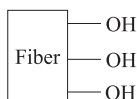


Fig. 3 Reaction group of bio-based fiber.

converts the two hydroxyl groups into related compound. The FT-IR spectroscopic analysis of the raw fiber, namely, jute (Shahinur *et al.*, 2015), coir (Haque *et al.*, 2010), and banana (Merlini *et al.*, 2011) confirms this phenomenon.

Properties

A good number of researches have been carried out on the characterization of bio-based polymer composite. In this study, mechanical, physical and thermal properties of bio-based composites are highlighted in the following sections.

Mechanical Properties

Under the mechanical properties there are tensile, flexural, toughness, hardness, ductility, fatigue strength and elasticity. In this particular study tensile, impact and hardness of the three bio-based composite are described as follows.

Tensile properties

The tensile strength of raw and treated fiber reinforced bio-composites for three different fibers is shown in Table 3. Tensile fracture behavior of composites is ductile. For the raw fiber reinforced composites, the tensile strength decreased with fiber loading, which is supported with the findings of Haque *et al.* (2010) and vice versa (Nam *et al.*, 2011). When fiber load is increased, the weak interfacial area between the fiber and matrix increased, as a result, tensile strength decreased. After chemical treatment, the reaction took place deep down in the specimen, which improved the mechanical properties of the related composites. From Table 3 it is

Table 3 Mechanical properties of bio-based polymer composite

Bio-composite	Tensile strength (MPa)	Young's Modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	References
Coir-PP	22–27	1.25–3.5	46–50	1.5–3.5	Haque <i>et al.</i> (2010)
Treated coir-PP	27–30	1.5–4.5	53–60	1.5–4.2	Siddika <i>et al.</i> (2014), Nam <i>et al.</i> (2011)
Jute-PP	17–34	2–4.5	20–32	1–1.6	Rahman <i>et al.</i> (2008), Nahar <i>et al.</i> (2012)
Treated jute-PP	15–51	1.0–3.5	15–58	0.7–5.0	Shahinur <i>et al.</i> (2017)
Banana-PP	11.45–24.16	0.44–0.87	38–42	1–5	Mishra <i>et al.</i> (2000), Chattopadhyay <i>et al.</i> (2011)
Treated banana-PP	23–24	0.5–0.8	36–39	1.5–2.3	Mishra <i>et al.</i> (2000)
Jute- polyester	50–95	6–7	80–135	4–6	Sever <i>et al.</i> (2012)
Coir- polyester	18–47	2.24	5–69.27	2.14	Rout <i>et al.</i> (2001)
Banana-polyester	12–23.04		76–124.92		Dhakal and Keerthi Gowda (2017)

Table 4 Impact, hardness, and water absorbance of jute, coir, and banana bio based polymer bio-composites

	Impact Kg/m ²	Hardness Rockwell L	Water absorbance %	References
Polypropylene	19/22.34	66.4	0.09	
Jute	25–85 (Ranganathan <i>et al.</i> , 2015)	78–97 (Sultana <i>et al.</i> , 2013)	0.7–1.26	Khan <i>et al.</i> (2010), Rahman <i>et al.</i> (2008)
Treated jute	18–24	77–87	0.73–1.22	
Coir	35–60	80–90	0.3–1.7	Haque <i>et al.</i> (2010), Haque <i>et al.</i> (2009)
Treated coir	40–60	90–105	0.3–0.7	
Banana	1.2–1.8	60–66	15–30	Mishra <i>et al.</i> (2000)
Treated banana	0.9–1.5	66–72	10–25	
Polyester				
Treated jute	40–160		6.13	Deb <i>et al.</i> (2017)
Treated coir	40–55	85–95		Haque <i>et al.</i> (2010)
Treated banana	32–147		1.5–4.74	Muktha and Keerthi Gowda (2017)

cleared that, due to chemical treatment the related composites improve the tensile strength as well as Young's modulus. The stronger fiber shows more fiber pull out compared to the weaker fiber composites.

Flexural properties

Flexural strength and flexural modulus of raw and treated bio-based fiber composites for different fiber are listed in **Table 4**. The data are collected from different research articles and that data are represented as range based on obtained flexural properties. As the flexural fracture behavior of the composites is also ductile, the flexural strength increased with fiber loading for some fiber composite (Haque *et al.*, 2009). However, there was a decrement for certain fiber loaded composites (Shahinur *et al.*, 2017; Nahar *et al.*, 2013). Furthermore, from **Table 3** it can be concluded that after chemical treatment the flexural properties of the related composites are improved compared to untreated fiber composite for PP as well as polyester matrix composites. In case of high flexural strength there is high fiber pull out and vice versa.

Impact properties

Variation of the Charpy impact strength for both raw and chemically treated three different bio-based fiber composites are listed in **Table 4**. Impact strength increased with fiber loading (Haque *et al.*, 2010; Rahman *et al.*, 2008). However, there was a decrement in the impact property for some specific fiber loaded (Chattopadhyay *et al.*, 2011).

Hardness and water absorption characteristics

Table 4 shows the hardness of various manufactured composites for three different bio-based fiber, namely jute, coir and banana. Average hardness increased with chemical treatment of fiber (**Table 4**) and fiber loading (Haque *et al.*, 2010). This is due to the increase of stiffness of the respective composites. The hardness of jute-PP composite is about 66.4, which is increased in chemically treated fiber composite. Similar trend is found for coir as well as banana polymer composite as shown in **Table 4**.

Water absorption characteristics of manufactured composites are shown in **Table 4**. Water absorption (%) generally increases with an increase in fiber loading (Haque *et al.*, 2010). As mentioned earlier, the hydroxyl groups in bio-fiber, namely, jute, coir and banana, are responsible for high water absorption. With the increase in fiber loading, the number of hydroxyl groups in the composites increased, which in turn increased the water absorption. Chemically treated bio-fiber reinforced composites had lower

Table 5 Thermal properties of jute, coir and banana bio-based polymer composites

Item	Thermal stability	References
Jute matrix	250–365°C	Kabir <i>et al.</i> (2012), Kabir <i>et al.</i> (2013), Rahman <i>et al.</i> (2008)
Treated jute matrix	250–400°C	Singh and Palsule (2014)
Coir matrix	25–250°C	Haque <i>et al.</i> (2009)
Treated coir matrix	250–400°C	Haque <i>et al.</i> (2010)
Banana matrix	25–250°C	Indira <i>et al.</i> (2012)
Treated banana matrix	250–300°C	

Table 6 Application of jute, coir and banana fiber reinforced composites

Jute based composite	Coir based composite	Banana based composite
Building panels, roofing sheets, door frames, door shutters, transport, packaging, geotextiles, and chipboards, absorbent cotton, storage device, furniture, transportation, house hold accessories, Bio-degradable shopping bag.	Building panels, flush door shutters, roofing sheets, storage tank, packing material, helmets and postboxes, mirror casing, paperweights, projector cover, voltage stabilizer cover, a filling material for the seat upholstery, brushes and brooms, ropes and yarns for nets, bags, and mats, as well as padding for mattresses, seat cushions	Biodegradable sanitary napkin and diaper (Barman <i>et al.</i> , 2017).

water content compared to the raw ones, as the treatment decreased the number of hydroxyl groups in the resultant composites. Water absorption (%) decreased over the raw fiber polymer composites.

Thermal Properties

Thermal stability of the composite depends on the matrix as well as fibers (jute, coir and banana) that we use as reinforcing material. For example, HDPE, MAGPP, epoxy, polyester, and starch matrix sustain at 525°C, 450°C, 400°C (Bansal and Agarwal, 1984), 245–289°C (Bora *et al.*, 2013) and 250°C respectively. Whereas jute, coir and banana fiber are thermally stable at 25–250°C. The related thermal stability of the selected bio-based composites is listed in Table 5. Thermal stability of jute composite is 25–265°C whereas it is increased after chemically treated jute composite. The similar phenomenon is observed in the case of raw and treated coir as well as banana fiber as shown in Table 5. It is clear that the range of thermal stability for treated composite, is increased due to specific chemical modification of natural fiber. The upper range of thermal stability depends on the matrix material as well as chemical concentration.

Applications

According to Mohammed *et al.* (2015) bio-fiber is used in the house hold industry and car interior. Due to the advantages of bio-composites such as biodegradability, high stiffness, cheap and lightweight give them appropriateness in the various application in engineering application such as building industries, structural concrete elements as reinforcement, while coir fiber composites have been used in roofing components in order to replace asbestos. In addition, bio-fiber composite products in building applications like bar, sheets (plain, corrugated) and boards are light in weight and are appropriate for use in roofing, ceiling, and walling for the construction of low-cost houses. Due to good sound absorption properties, bio-fiber composites are used in theater and conference hall. Due to good thermal property the bio-based composites are used in agriculture sector in cold region. Table 6 shows the various applications of cellulose fiber in industry, construction, and other industries.

Conclusion

Natural fiber-based composites are eco-friendly compared to fully synthetic composite. However, design, fabrication, properties and applications of different categories of bio-based composites are explained in this article, sustainability of these types of bio-based composite is also an important issue for the next generation regarding green globalization. Sustainable properties such as CO₂ emission, recycle fraction, safety and water usage of these bio-based composites are needed to analyze regarding the sustainability of bio-based composite. Nevertheless, these sustainable properties particularly CO₂ emission is related to the electricity consumption for final product development. Natural materials absorb CO₂ and emit O₂ during the primary material, namely, fiber production, which has a positive impact on the total CO₂ emission of the bio-based composite production. If the composite becomes sustainable the bio-based product will be sustainable indeed. Based on the above contemplation sustainable properties are the important issues for the green revolution. Thus, this is an open research topic for future research.

See also: Properties of Coconut Fiber. Reuse of Waste Corrugated With Coir Fibers as a Packaging Materials

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Kenaf Fiber Based Bio-Composites: Processing, Characterization and Potential Applications

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Introduction

Recently, natural fibers have received a great interest due to their possible use in manufacturing environmental friendly composites materials along with many intrinsic properties such as strength, thermal, water barrier and biodegradability (Kumar *et al.*, 2013). The worldwide availability of natural fibers is accountable for the new polymer materials and industrial research, and the exploration for a maintainable technology. Natural fibers were presented with the intention of yielding lighter composites, together with lower costs lower density as compared to the glass fiber, which confirms the production of lighter composites (Abdul Khalil *et al.*, 2008). Various conventional petroleum based polymers are used widely with natural fibers such as jute, bamboo, banana, hemp, sisal, coir, wood, kenaf etc., (Akil *et al.*, 2011). Recently, the rapidly expanding use of composite components in automotive, construction, sports and leisure, and other mass production industries, has been focused on sustainable and renewable reinforced composites (Azwa and Yousif, 2013). Among all natural fibers, kenaf fibers have received much attention in the composite industry due to its potential as polymer reinforcements. Kenaf fibers are becoming increasingly popular in Malaysia as one of the natural materials that may contribute to the development of environmental friendly resources for the automotive, food packaging, furniture and sports industries. In recent times, it has been used as an alternative to wood in pulp and paper industries in order to help preserve forests, and as non-woven mats, it has been applied in industries such as automotive, textiles, and fiberboards. In the composite industry, mature kenaf fiber have been employed as fiber reinforcements to various matrices. Studies have shown that the addition of kenaf fibers have improved the mechanical properties of neat polymers (Azwa and Yousif, 2013). Kenaf fiber is extracted from the bast of the annual fast growing plant named *Hibiscus cannabinus*. The main constituents of kenaf are cellulose (45–57 wt%), hemicelluloses (21.5 wt%), lignin (8–13 wt%), and pectin (3–5 wt%). Kenaf fibers having good mechanical properties and thermal properties compare to the other types of natural fibers when it's Blend with PP (Jeyanthi and Janci Rani, 2012). Kenaf is one of the natural (plant) fibers used as reinforcement in Polymer Matrix Composites (PMCs). Kenaf has been found to be an important source of fiber for composites, and in other industrial applications (Karnani *et al.*, 1997). It is well known as a cellulosic source with both economic and ecological advantages; in 3 month (after sowing the seeds), it is able to grow under a wide range of weather conditions, to a height of more than 3 m and a base diameter of 3–5 cm (Aziz *et al.*, 2005). Kenaf filaments consist of discrete individual fibers, of generally 2–6 mm. Each layer is composed of cellulose embedded in a matrix of hemicellulose and lignin; a structure that is analogous of artificial fiber reinforced composites. Scientists state that the overall properties of kenaf fiber depend on the individual properties of each of its components (Rouison *et al.*, 2004). The strength and stiffness of the fibers are provided by cellulose components via hydrogen bonds and other linkages. Hemicellulose is responsible for biodegradation, moisture absorption, and thermal degradation of the fibers. On the other hand, lignin (pectin) is thermally stable, but responsible for the UV degradation of the fibers. To make kenaf a successful alternative crop, it must be incorporated into value-added products. People have skillfully made use of kenaf from ancient times, traditionally as ropes, canvas, sacking, and more recently, kenaf has been used as an alternative raw material in place of wood used in pulp and paper industries to avoid the destruction of forests. It has also been used to make non-woven mats in the automotive industry and textiles. About 35% of kenaf is bast fiber, which is suitable for paper, textiles, and rope; and about 65% is core (Lee and Mark, 2001). Kenaf is presently being used in paper production on a very limited basis. Various uses of the bast fibers have been explored, such as in the making of industrial socks to absorb oil spills, as well as making woven and non-woven textiles. The kenaf bast fiber is known to have the potential as a reinforcing fiber in thermoplastic composites, because of its superior toughness and high aspect ratio in comparison to other fibers. A single fiber of kenaf can have a tensile strength and modulus as high as 11.9 GPa and 60 GPa, respectively (Karnani *et al.*, 1997). Rowell *et al.* (1999) studied the potential of kenaf as a reinforcing fiber in a polypropylene matrix and compared the mechanical properties with other commonly used composite systems. Kenaf core fibers are also used in product applications such as animal bedding, summer forage, and potting media (Ramaswamy *et al.*, 2003). Kenaf fiber has potential as reinforcement filler in polymer matrix composite (PMC). The purpose of producing PMC is to create a new material that has better properties compared to their individual material. Kenaf fiber can generally be classified into two types. The first type is the outermost layer known as bast while the second type is the inner part, known as core. The core is very soft, hollow and suitable for application as organic filler in plastic, while bast fiber has hard properties and is suitable for blending with plastic, textile industry and also fiberglass technology applications. Kenaf fiber is also used as reinforcement for plastic and synthetic product, cosmetic product, organic filler and medicine. Besides that kenaf fiber is also environmental friendly (Salleh *et al.*, 2014).

Due to environmental concern, kenaf fiber is widely used as filler in composites materials. However, kenaf fiber based composites suffer from lower physico-mechanical properties compared to synthetic fiber reinforced composites. In an attempt to solve these problems, kenaf fibers is chemically treated with suitable chemicals or combined with a stronger synthetic or natural

fiber to form a hybrid formulation which is then incorporated in the polymer matrix. This will produce chemically modified or hybrid composites that take full advantages of the best properties of the constituent fibers and thereby an optimized, superior and economical composite can be obtained. Hybrid or modified natural fiber polymer composites thus provide designers freedom of tailoring composites formulations and achieving properties in a more cost-effective way that is less likely to be attained in binary systems containing one type of fiber dispersed in the matrix (Thakur *et al.*, 2014). Using a hybrid composite that contains two or more types of different fibers, the advantages of one type of fiber could complement what are lacking in the other. As a consequence, a balance in performance and cost could be achieved through proper material design. In this respect, kenaf, wood and coir fiber have the highest potential as hybrid polymer reinforcements (Akil *et al.*, 2011).

Kenaf Fiber as Reinforcement in Polymer Bio-Based Composites

The main disadvantage encountered during the addition of natural fibers, including kenaf fiber into a polymer matrix, is the lack of good interfacial adhesion between the two components, which results in poor properties in the final product (Tserki *et al.*, 2006). Polar hydroxyl groups, on the surface of the kenaf fiber, have difficulty forming a well bonded interphase with a relative nonpolar matrix; as the hydrogen bonds of the fiber surface tend to prevent the wetting of the filler surface. Furthermore, the incorporation of kenaf fiber as filler in a polymer matrix is often associated with agglomeration, as a result of insufficient dispersion caused by the tendency of fibers to form hydrogen bonds with each other (Liu *et al.*, 2004). Fiber-matrix interfacial adhesion can be improved with many chemical modifications of the fiber and one of the familiar and effective modifications applied to kenaf fiber, is an alkaline treatment based on sodium hydroxide (NaOH) (Edeerozey *et al.*, 2007). Humidity aging is widely recognized as one of the main causes of long-term failure of an organic matrix exposed to the atmosphere; or in contact with an aqueous media. There are several recognized modes of humidity aging, namely plasticization of the matrix; differential swelling related to concentration gradients, embrittlement linked the degradation of the macromolecular.

Kenaf Fiber as Reinforcement in Hybrid Bio-Based Composites

The incorporation of several different types of fibers into a single matrix has led to the development of hybrid bio-based composites. The behavior of hybrid composites is a weighed sum of the individual components in which there is a more favorable balance between the inherent advantages and disadvantages. Also, using a hybrid composite that contains two or more types of fiber, the advantages of one type of fiber could complement with what are lacking in the other. As a consequence, a balance in cost and performance can be achieved through proper material design. The properties of a hybrid composite mainly depend upon the fiber content, length of individual fibers, orientation, extent of intermingling of fibers, fiber to matrix bonding and arrangement of both the fibers. The strength of the hybrid composite is also dependent on the failure strain of individual fibers (George *et al.*, 2001). Maximum hybrid results are obtained when the fibers are highly strain compatible. The term hybrid effect has been used to describe the phenomenon of an apparent synergistic improvement in the properties of a composite containing two or more types of fiber. The selection of the components that make up the hybrid composite is determined by the purpose of hybridization, requirements imposed on the material or the construction being designed. The problem of selecting the type of compatible fibers and the level of their properties is of prime importance when designing and producing hybrid composites. The successful use of hybrid composites is determined by the chemical, mechanical and physical stability of the fiber/ matrix system.

Processing of Kenaf Fiber

In order to increase the interfacial interaction between kenaf fiber and polymer matrix of a kenaf/polymer biocomposites, the fiber is generally chemically modified with various chemical regents. The chemical modifications have been reported in earlier studies, which include alkaline treatment, silane treatment, isocyanate treatment, and acetylation (George *et al.*, 2001). Some other chemical treatments may also be effective to kenaf fiber, which is often used to treatment of many natural fibers. These treatments are- benzoylation, acrylation and acrylonitrile grafting, maleated coupling agents, permanganate and peroxide treatment. Most of the chemical treatment remove hydroxyl group from the natural fiber or to form bond with hydroxyl group.

Alkaline Treatment

Alkaline treatment is one of the most widely used chemical treatments for natural fibers, especially the kenaf fiber when reinforcing thermoplastics and thermosets (Edeerozey *et al.*, 2007; Li *et al.*, 2007). This modification is carried out by immersing the fibers in a NaOH solution for a period of time (Li *et al.*, 2007; Bogoeva-Gaceva *et al.*, 2007). The important modification that is done by alkaline treatment is the disruption of hydrogen bonding in the network structure, thereby increasing surface roughness. This treatment removes certain hemicelluloses, lignin, wax and oils covering the external surface of the fiber cell wall;

depolymerizes cellulose, and exposes the short length crystallites. Alkaline treatment leads to fibrillation of the fiber bundles into small fibers.



It is reported that alkaline treatment has two effects on the fiber: (1) It increases surface roughness, resulting in better mechanical interlocking; and (2) it increases the amount of cellulose exposed on the fiber surface, thus increasing the number of possible reaction sites.

Silane Treatment

Silane is used as coupling agents to allow natural fiber to adhere to a polymer matrix, thus stabilizing the composite material. Silane coupling agents may reduce the number of cellulose hydroxyl groups in the fiber-matrix interface. In the presence of moisture, the hydrolysable alkoxy group leads to the formation of silanols. The silanol then reacts with the hydroxyl group of the fiber, forming stable covalent bonds to the cell wall that are chemisorbed onto the fiber surface. The reaction schemes are given as:



Silane treatment has been introduced to kenaf fiber by previous researchers over the past few years (Huda *et al.*, 2008). Magnificent results were recorded for treated composites, in terms of interfacial adhesion between kenaf filler and the polymer matrix.

Acetylation

The acetylation of plants is a well-known esterification method of introducing plasticization to cellulosic fibers. Acetylation has been extensively applied to wood cellulose to stabilize the cell wall, improving dimensional stability and environmental degradation. Acetylation is based on the reaction of the cell wall hydroxyl groups of lignocellulosic materials, with acetic or propionic anhydride at an elevated temperature (usually without a catalyst) (Dhakal *et al.*, 2007). The reaction scheme is given as follows:



Acetic acid (a by-product from the reaction) must be removed before the fibers are used. The hydroxyl groups that react with the reagent are those of lignin and hemicelluloses (amorphous material), while the hydroxyl groups of cellulose (crystalline material), being closely packed with hydrogen bonds, prevent the diffusion of the reagent and thus result in very low extents of reaction. It has been shown that etherification improves the dispersion of fibers in a polymer matrix, as well as the dimensional stability and interface of the final composites (Edeerozey *et al.*, 2007; Li *et al.*, 2007).

Manufacturing of Kenaf Composites

Kenaf and EFB fiber with ranges of 2–3 mm was purchased from National Kenaf and Tobacco Board, Kubang Kerian Kelantan and Poly Region (M) Sdn. Bhd respectively. TT Biotechnologies Sdn. Bhd, Penang, Malaysia supplied polylactic acid (PLA). Both fibers were cut in Institute of Tropical Forestry and Forest Products (INTROP), UPM Serdang into an around length of 2 mm by using a ring knife flaker. To obtain uniform size of fiber, these jute fibers that been cut were then sieved manually using a very small size sieve (0.6 mm). Fibers were dried at open-air under direct sunlight for few days. The fibers were mixed with polylactic acid (PLA) granules using Brabender mixer machine thoroughly and homogeneously. The ratio used for fiber to PLA was 60:40 with 1:1 ratio between kenaf and EFB fibers. According to ASTM 638 and 790 standards design of mold fabrication and desire composite thickness were made. The composites were fabricated using a hot press machine. Manual hydraulic press was used to press the mold until the pressure reached 1000 psi. Temperature was set was at 160°C for both upper and lower heater and the mold was heated for 5 min. The mold was cooled to room temperature in order to prevent shrinkage during extraction of the composite.

Characterization of Kenaf Composites

The machinery Industrial Co. Ltd. cutter was used to cut samples biocomposite into ASTM standard dumb bell shape from the flat sheet samples for tensile test. The test was conducted using ASTM D 638-03 method and INSTRON 8821S (INSTRON, USA) universal testing machine. According to ASTM D790-03, flexural test was performed using the same machine mentioned above. For impact test, notched biocomposite specimen was attached horizontally and supported unclamped at both ends. The hammer was released and allowed to strike through the specimen. The impact energy in Joules (J) was obtained from the machine. Impact strength was then calculated by dividing the impact energy with length of the notch. The water absorption test of prepared biocomposites was carried out according to ASTM D 570-99. Structural and thermal properties of composites were characterized using a Perkin-Elmer 1600 Fourier transform infrared spectrometer, JSM-5510 JEOL scanning electron microscope, thermogravimetric analyzer, differential scanning calorimeter and PAN analytical X-Ray diffractometer.

Structural Analysis of Kenaf Composites

Fourier Transform Infrared Spectrometric (FTIR) Analysis

Fig. 1 shows the FTIR spectra of kenaf and EFB fiber. The broad peaks at the region of $3600\text{--}3070\text{ cm}^{-1}$ for all spectra were corresponding to the presence of free -OH groups, while the peak at 2946 cm^{-1} attributed to C-H stretching. The absorption peak at 1740 cm^{-1} and 1622 cm^{-1} due C=O and C=C stretching band (Islam *et al.*, 2017). On the other hand, the peaks at 1250 cm^{-1} and 1030 cm^{-1} represent C-O stretching. All characteristic absorption peaks as mentioned earlier confirmed the presence of polymeric constituent such as lignin, cellulose and hemicelluloses in the fiber.

Scanning Electron Microscopy (SEM)

Fig. 2 shows SEM micrographs of the tensile fractured surfaces of EFB/PLA, kenaf/PLA and EFB/kenaf/PLA composites. Surface interaction and adhesion between fiber and polymer matrix increased after fiber hybridization (Yousif *et al.*, 2012). No significant changes were observed on the micrographs of hybrid fiber composite. However, smooth fractured surface was produced after the hybridization of two fibers, which illustrate good adhesion of fibers to polymer matrix.

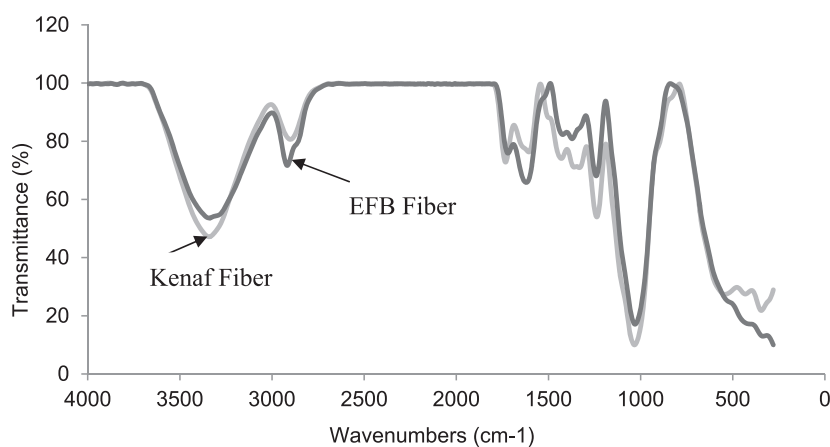


Fig. 1 FTIR spectra of kenaf and EFB fiber.

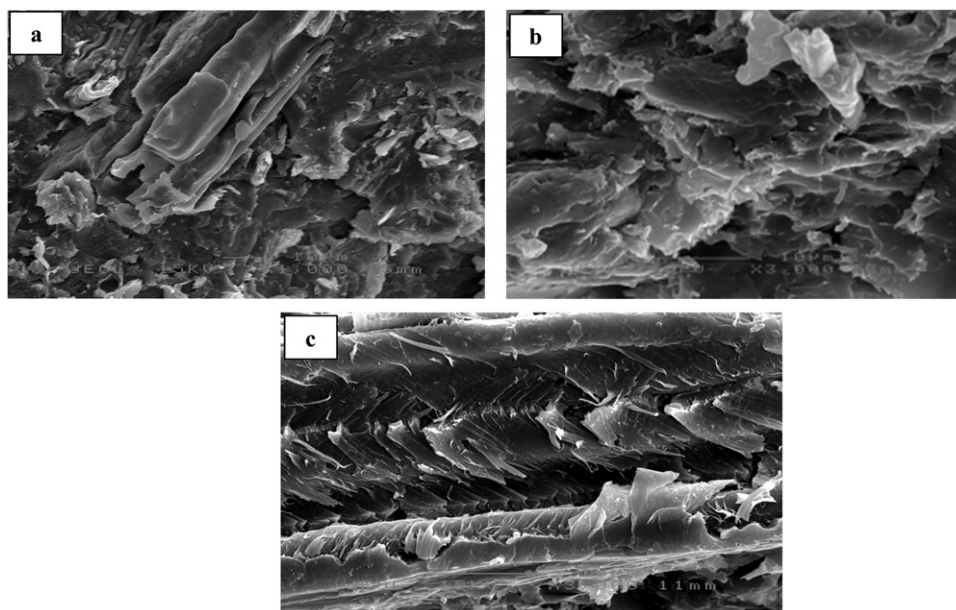


Fig. 2 SEM micrographs of (a) EFB/PLA bio-based composite, (b) kenaf/PLA bio-based composite and (c) EFB/kenaf/PLA hybrid bio-based composite.

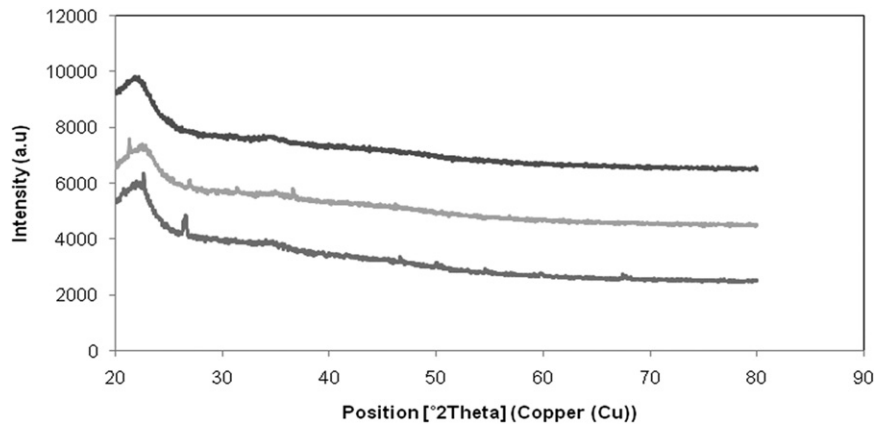


Fig. 3 XRD patterns of (a) EFB/PLA bio-based composite, (b) EFB/kenaf/PLA hybrid bio-based composite and (c) kenaf/PLA bio-based composite.

Good adhesion of polymer matrix and fiber plays a key role in enhancing the mechanical properties of composites. This result reflected the improvement of mechanical strength upon fiber hybridization. Therefore, it can be concluded that incorporation of two fibers proposed good wettability properties, which decreased the formation of voids at the fibers-polymer interface and formed composites with high stiffness and strength leading to high storage modulus (Kruk *et al.*, 1997).

X-ray Diffraction Analysis

Fig. 3 shows the XRD patterns of EFB/PLA, kenaf/PLA and hybrid EFB/kenaf/PLA bio-based composites. The crystallinity values of EFB/PLA, kenaf/PLA and EFB/kenaf/PLA bio-based composites were 73.14%, 71.71%, and 74.27% correspondingly. As compared to single fiber/PLA composites, the crystallinity of hybrid EFB/kenaf/PLA composites was higher. Other than that, a new peak (2θ) at 35.0° was detected for the hybrid composites. This indicates that the crystallinity and stiffness of composites were increased slightly after fiber hybridization which led to improved mechanical strength.

Mechanical Properties of Kenaf Composites

The quality of material is classified in terms of mechanical characteristics, such as tensile strength, strain properties, impact properties and compression properties. These properties are important to determine material ability under extreme and critical conditions. Recently several studies have been performed on kenaf fiber composite, in order to fully understand its mechanical behavior in engineering applications. Some of the mechanical properties of kenaf fiber reinforced composites that important to determine such as ultimate tensile strength, fracture strain, flexural modulus and impact strength. Generally, the tensile and flexural properties of kenaf reinforced composites vary depending on the type of fiber, its orientation, content, and the type of plasticizer used. Statically, the tensile strength of kenaf reinforced composites were approximately 223 MPa in samples with a fiber fraction of 70.

Figs. 4 and **5** represent the tensile modulus and tensile strength of EFB/PLA, kenaf/PLA and EFB/kenaf/PLA composites respectively. **Fig. 4** shows that the tensile strength dramatically decreased when fiber was changed from EFB to kenaf. After hybridization of fiber, the strength of hybrid biocomposite was found to be higher as compared to that of single kenaf fiber biocomposites. However, it was still lower than single EFB fiber biocomposite. The same result was also found for the tensile modulus of the biocomposites as shown in **Fig. 5**. The modulus was found to be decreased from 431 to 321 MPa and the modulus was increased to 345 MPa after hybridization. Both tensile strength and modulus values indicate that the hybridization of fiber was capable to produce biocomposite with optimum tensile properties. This in turn proved that the great mechanical possessions of EFB fiber were able to support the low mechanical properties of kenaf fiber. The strong bonding between the matrix and fiber will lead to improve interfacial adhesion between them and therefore a higher transfer of stress from the matrix to the fibers during tensile testing (Kruk *et al.*, 1997; Pickering *et al.*, 2016).

Figs. 6 and **7** represent the flexural modulus and flexural strength of EFB/PLA bio-based composite, kenaf/PLA bio-based composite and EFB/kenaf/PLA hybrid bio-based composite. **Fig. 6** shows that the flexural strength was radically increased when fiber changed from EFB to kenaf. However, after hybridization of fiber, the strength of the hybrid biocomposite was found to be higher as compared to that of single BFB fiber biocomposite. However, it was still lower than single kenaf fiber biocomposite. The same result was found for the flexural modulus of the composites as shown in **Fig. 7**. The modulus was found to be increased from 3.9 to 4.8 GPa and decreased to 3.6 GPa after hybridization. This rise may be described by a better fibers-matrix interaction under the compressive stresses during bending, developed in the transverse section of the flexural specimens (Joshi, 1983). In general, the

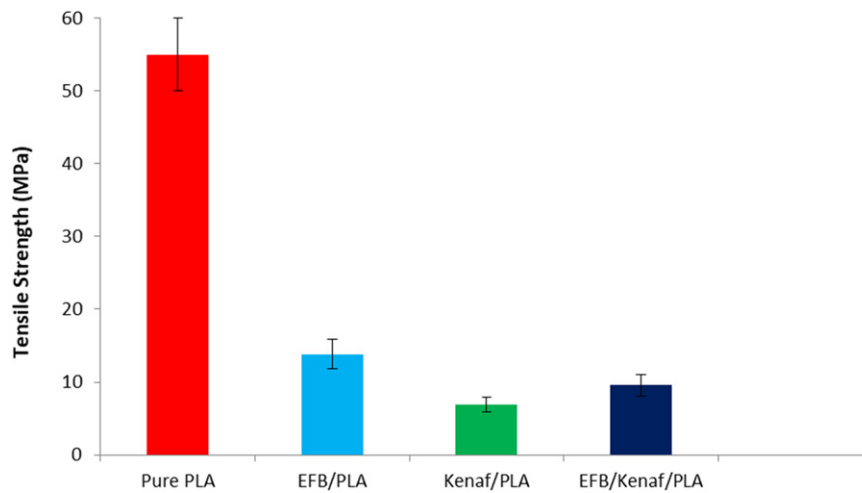


Fig. 4 Tensile strength of pure PLA, EFB/PLA bio-based composite, kenaf/PLA bio-based composite and EFB/kenaf/PLA hybrid bio-based composite.

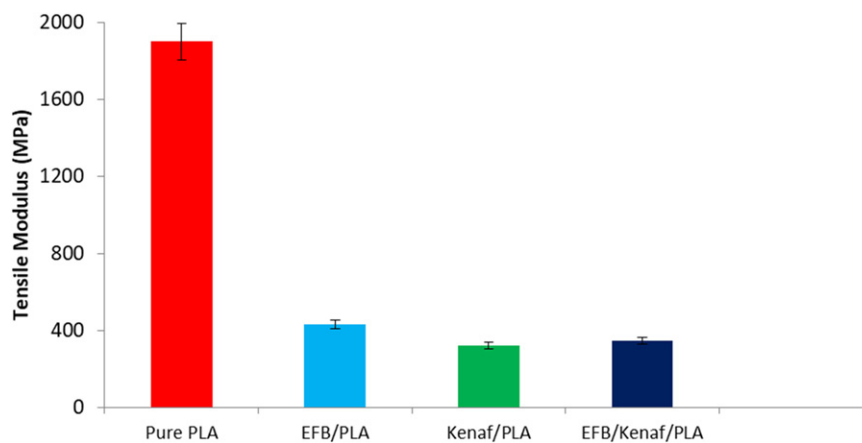


Fig. 5 Tensile modulus of pure PLA, EFB/PLA bio-based composite, kenaf/PLA bio-based composite and EFB/kenaf/PLA hybrid bio-based composite.

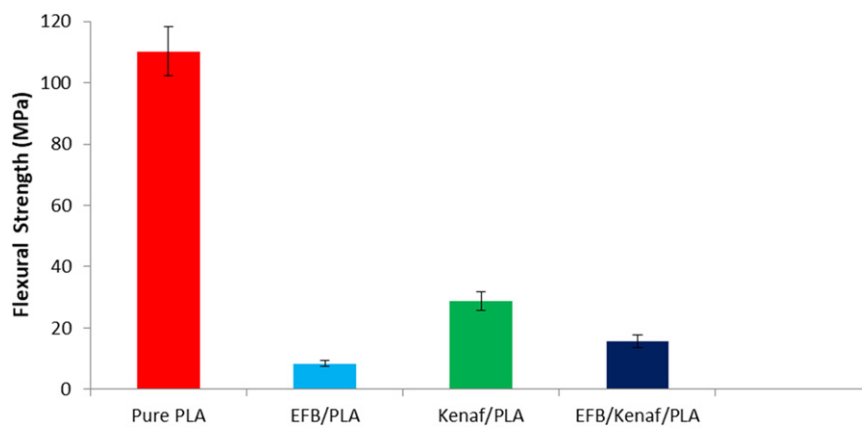


Fig. 6 Flexural strength of pure PLA, EFB/PLA bio-based composite, kenaf/PLA bio-based composite and EFB/kenaf/PLA hybrid bio-based composite.

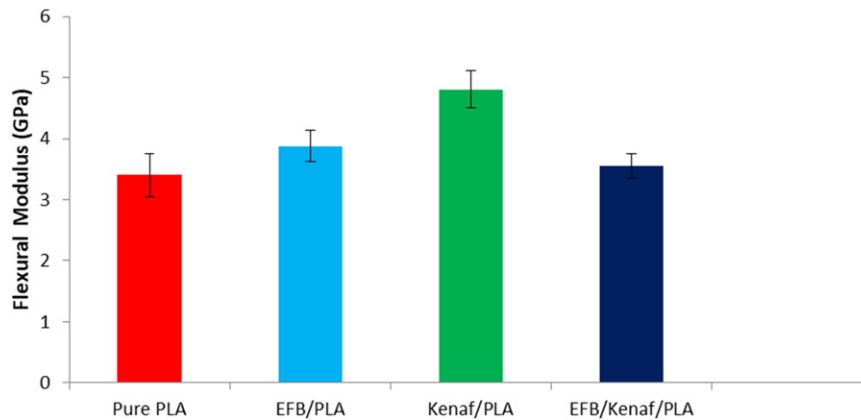


Fig. 7 Flexural modulus of pure PLA, EFB/PLA bio-based composite, kenaf/PLA bio-based composite and EFB/kenaf/PLA hybrid bio-based composite.

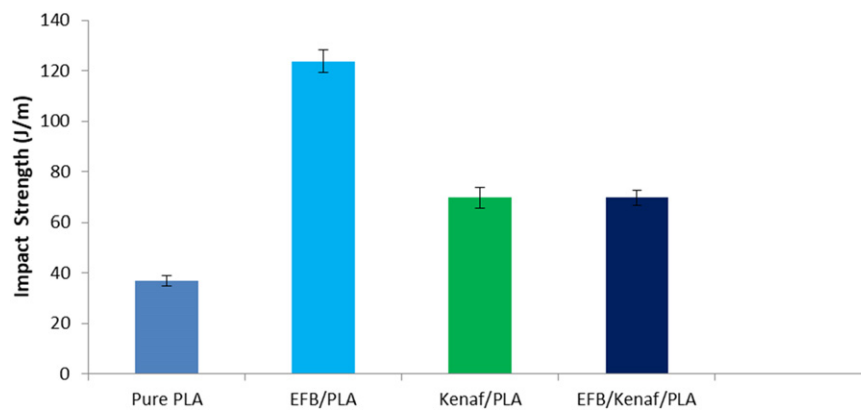


Fig. 8 Impact strength of pure PLA, EFB/PLA bio-based composite, kenaf/PLA bio-based composite and EFB/kenaf/PLA hybrid bio-based composite.

best fiber content depends with the nature of fiber matrix interfacial, fiber aspect ratio, processing techniques, fiber and matrix adhesion, fiber agglomeration, and so on (Hassan *et al.*, 2017).

Fig. 8 represents the impact strength of EFB/PLA bio-based composite, kenaf/PLA bio-based composite and EFB/kenaf/PLA hybrid bio-based composite. Impact strength sharply decreased when EFB fiber changed to kenaf. However, after hybridization of fiber, the impact strength of biocomposite was almost similar as single kenaf fiber biocomposite. This proves that hybridization of fiber was not capable to support the low impact properties of kenaf fiber.

Water Absorption Behavior

Water absorption test was carried out for EFB/PLA, kenaf/PLA and EFB/kenaf/PLA hybrid bio-based composites and the results were shown in **Fig. 9**. It was observed that water absorption of biocomposites was increased for the first 8 days, after that it almost became constant. Hybrid fiber biocomposites had the highest percentage of water absorption as compared to single fiber biocomposite. This might be due to the hydrophilic properties of fiber which increased upon mixed up of two different fibers. So, hybrid fiber composite absorbed more water compared to single fiber biocomposite (Pickering *et al.*, 2016).

Thermal Properties of Kenaf Composites

Thermogravimetric Analysis (TGA)

Thermal stability of EFB/PLA, kenaf/PLA and EFB/kenaf/PLA bio-based composites were measured through TGA test analysis and are shown in **Fig. 10**. It can be seen from TGA thermogram that the weight of all biocomposites slight decreased in the range 55–135°C. This could be explained by the existence of residual water in the composites that was gradually released at above 100°C (Joshi, 1983). It was also observed that the onset temperature of thermal degradation of EFB/PLA and EFB/kenaf/PLA bio-based composites was around 240°C, however this temperature for kenaf/PLA biocomposite was at 270°C. This is due to better interaction and dispersion of kenaf

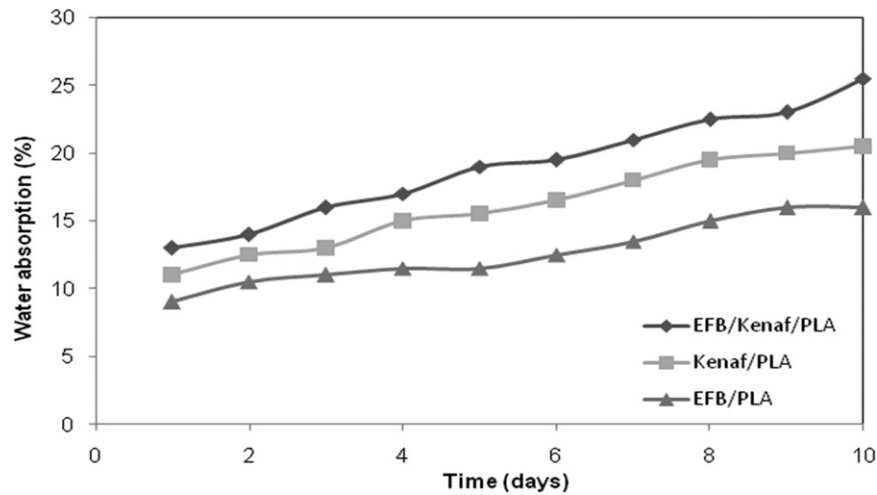


Fig. 9 Water absorption of EFB/PLA bio-based composite, kenaf/PLA bio-based composite and EFB/kenaf/PLA hybrid bio-based composite.

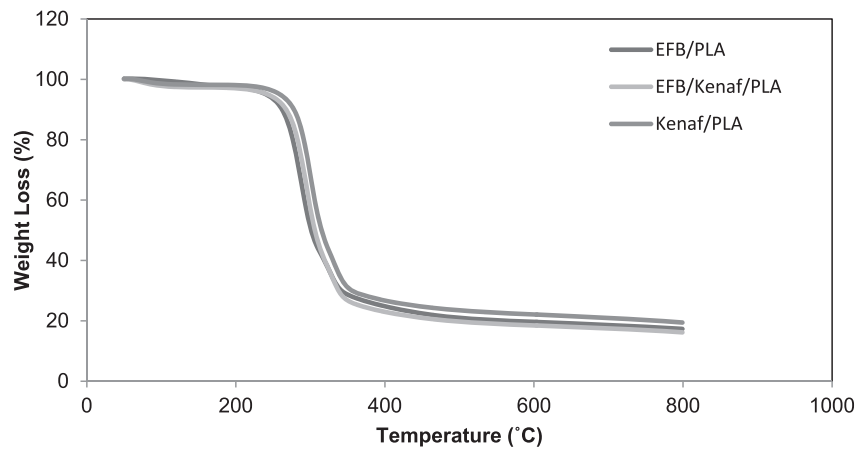


Fig. 10 TGA plots of (a) EFB/PLA bio-based composite, (b) kenaf/PLA bio-based composite and (c) EFB/kenaf/PLA hybrid bio-based composite.

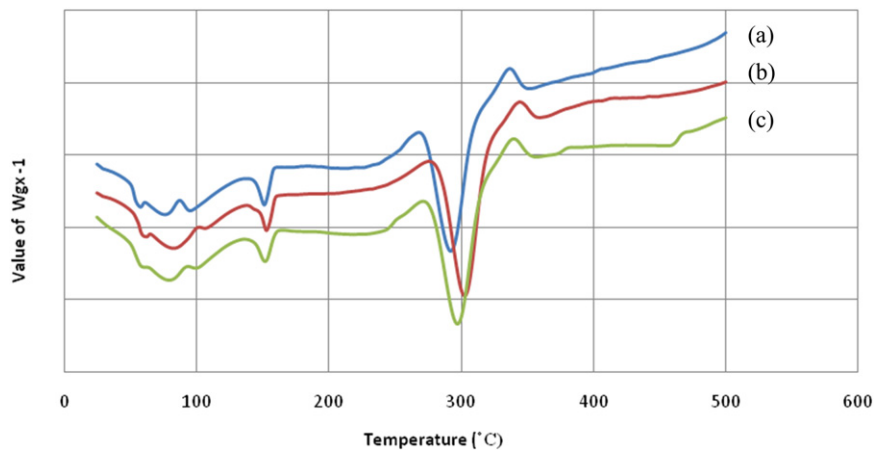


Fig. 11 DSC plots of (a) EFB/PLA bio-based composite, (b) kenaf/PLA bio-based composite and (c) EFB/kenaf/PLA hybrid bio-based composite.

Table 1 Some potential application of natural fiber biocomposites

<i>Types of fiber</i>	<i>Application</i>
Kenaf	Package shelves
Kenaf and flax mixture	Door panel and Package trays inserts
Coconut fiber	Back cushions, seat bottoms and head restraints
Cotton	Sound proofing
Abaca	Under floor body panel
Wood fiber	Seatback cushion and sliding
Corn	Mounts tire

Note: Holbery, J., Dan, H., 2006. Natural-fiber-reinforced polymer composites in automotive applications. JOM 58 (11), 80–86.

was found that standard PLA resins are suitable for the manufacture of kenaf fiber bio-composites with useful engineering properties (Hassan *et al.*, 2017). Some of the specific application of kenaf composite as follows:

- Aerospace industry.
- Sporting Goods Industry.
- Automotive Industry (panels, frames, dashboards, body repairs).
- Home Appliance Industry.
- Sinks, bathtubs, hot tubes, swimming pools.
- Boat hulls.
- Golf clubs, fishing poles, hockey sticks &
- Electrical boxes, circuit breakers, contacts etc. (Fig. 12, Table 1).

Conclusion and Future Perspective

Kenaf based biocomposite is creating a great opportunity for engineering applications because of its exceptional properties and environmental friendly credibility. Present discussion reveals that a biocomposite with good properties could be useful and successfully improved using kenaf and EFB fibers as the filler for the PLA matrix via melt blending method. Mechanical test results indicated that high mechanical properties of one fiber were capable to support low mechanical properties of another fiber. X-ray diffraction pattern shows that the percent crystallinity of biocomposites significantly increased after hybridization. On the other hand, hybridization of fibers had no significantly influence on the thermal properties of the biocomposites. The percentage of water absorption of hybridized biocomposites was higher than the single fiber biocomposite. The morphology of biocomposites was also not much effected for fiber hybridization. The presence of two different fibers proposed good wettability properties, which decreased the development of voids at the fibers-polymer interface and created composites with high stiffness and strength. Kenaf fiber found to be an alternative source to substitute conventional or any other synthetic fiber composites. Chemical modification and processing techniques are one of the most important steps for producing better biocomposites. The application of kenaf based biocomposite as an alternative composite material, especially in automotive, aerospace, home appliance, building and construction industry. The manufacturing of kenaf composites can be open the door of new jobs in the urban and countryside. In order to fulfill market demands, more critical research work are required on appropriate manufacturing process and commercialization of biocomposites.

See also: Kenaf Fiber Reinforced Composite in the Automotive Industry. Properties of Coconut Fiber

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Materials Selection Charts for Designing Products With Biocomposites

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Introduction

Despite the tremendous interest and vivid research in natural fiber composites for over two decades, to date, they have been successfully established only in the automotive industry for nonstructural interior panels, and the construction market for mainly house deckings (Shah, 2013; Carus *et al.*, 2014). While it is clear that there is great scope for plant fibers to be exploited as composite reinforcements, it is often suggested (Shah, 2013; Wambua *et al.*, 2003; Pickering, 2008) that the critical aspects limiting the wide industrial applications of biocomposites relate to:

- The variable and often inferior mechanical properties of plant fibers in comparison to synthetic fibers like E-glass, aramid and carbon,
- The lack of – or at least limited – empirical data on critical atypical loading conditions such as off-axis, multiaxial, high-strain rate, fatigue and creep loading,
- The inadequate – or unknown – performance effects of environmental conditions such as humidity/moisture and temperature/fire,
- The limited availability of natural fiber preforms in specific architectures (e.g., unidirectional or multiaxial fabrics),
- The limited options for biobased matrices with reasonable properties and processing characteristics.

Arguably, another key and long-overlooked aspect is the lack of comprehensive materials selection databases on natural fiber composites. The consequence is that biocomposites may not be on the radar of engineers and product designers in all relevant industries as viable alternative materials.

Materials Selection Processes

Materials selection is an integral part of the product design and development process (Fig. 1). To manufacture *products* that perform their *function* in specified *operating conditions* over their *design life*, appropriate materials need to be employed. Typically, the selection criteria for materials choice are defined by the component function, objective, and constraint. Invariably, the material processability and part manufacturability, dictated by the shape, reproducibility, and assembly of the final component, may also affect the materials choice. Due to the large variety of materials and associated manufacturing processes available, the selection of materials for a given component may be a challenging task. Indeed, if the selection process is not rigorous, the designer may opt for an inappropriate material or more possibly, overlook an attractive alternative material. Utilizing systematic materials selection processes is therefore essential.

Numerous materials selection techniques have been developed over the years (Ashby, 1992; Kutz, 2002; Jahan *et al.*, 2010), all of which rely on a large data bank of materials and their properties. The two key steps in materials selection are *screening* and *ranking*, which are part of the conceptual design stage of the design process (Fig. 1) (Ashby, 1992; Kutz, 2002; Jahan *et al.*, 2010). Screening enables to quickly narrow the field of possible materials to a manageable few while ranking narrows the choices further and then evaluates and ranks the choices to identify the optimal materials.

Ashby's materials selection chart method

One of the most popular techniques for initial screening of materials is the materials selection chart method, pioneered and popularized by Prof Mike Ashby. Ashby (1992) compares the relative performance of a variety of materials for a specific constructive function by using performance indices as design criteria. Materials screening, on the basis of these performance indices, is best achieved by plotting the performance indices that are typically a mathematical combination of material properties on each axis of a materials selection chart, also known as an Ashby plot. Individual materials or material subclasses appear as balloons that define the range of their properties. Ashby plots, such as the one presented in Fig. 2, are very useful for four key reasons (Ashby, 1992, 2008):

- (1) They allow quick retrieval of the typical properties of a particular material,
- (2) They allow quick comparison of the properties of different materials, revealing their comparative efficiencies,
- (3) They facilitate the selection of the materials/manufacturing processes during the product design stage, and
- (4) They enable substitution studies exploring the potential of one material to replace another.

A list of useful materials performance indices can be found in Ashby (1992). Generally, minimizing material weight (density ρ), cost $C_m\rho$, and/or eco-impact $I_e\rho$ are key objectives for industrial products. The key mechanical parameters, defined by the component function and constraint, are typically stiffness E and strength σ . Following Ashby (1992), the critical material performance indices that need to be maximized for a lightweight beam/plate loaded in pure tension are specific tensile stiffness

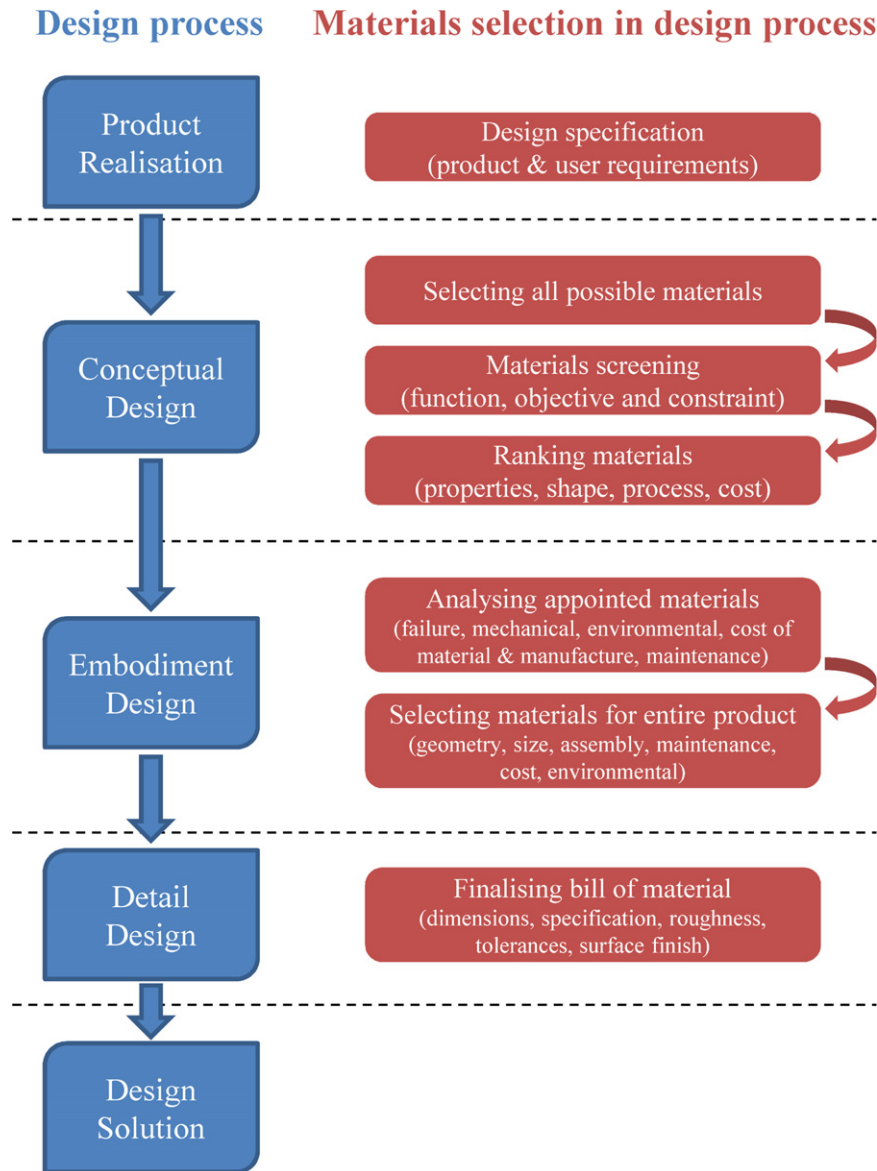


Fig. 1 Key steps in materials selection through various stages of product design.

E/ρ and specific tensile strength σ/ρ . For a lightweight beam/plate loaded in bending mode, specific flexural stiffness $E^{1/3}/\rho$ and strength $\sigma^{1/2}/\rho$ need to be maximized. Similarly, materials performance indices can be determined for vibration-limited design, fatigue-limited design, damage-tolerant design, thermal, thermomechanical, electrical, electromechanical design, to name a few.

Literature on Materials Selection Methods for Plant Fiber Composites

A survey of current (industrial and academic) applications of natural fiber composites has been presented in [Shah \(2013\)](#), [Madsen and Gamstedt \(2013\)](#), [Dicker et al. \(2014\)](#) and [Pil et al. \(2016\)](#). An increasing number of scientific studies have looked at various technical applications of biocomposites, from musical instruments ([Phillips and Lessard, 2012](#)) to structural wind turbine blades ([Shah et al., 2013a](#)). Although these studies often articulate the general design specifications the component and material need to satisfy, they seldom demonstrate through a systematic materials selection process that the natural fiber composite materials selected or developed in the study are better than conventional materials and offer specific mechanical, technical, economical, environmental, or ergonomical advantages. While the concept of materials selection is not new, there are only limited studies that have focused on applying materials selection techniques to natural fiber composites or even presenting useful and comprehensive data sets on biocomposites which may be applied during the conceptual design stage.

Conducting a materials selection exercise solely on plant fiber composites (i.e., excluding other materials and polymer composites subgroups), [Sapuan et al. \(2011\)](#) and [Mansor et al. \(2013\)](#) have demonstrated the use of the analytical hierarchy process, a multicriteria

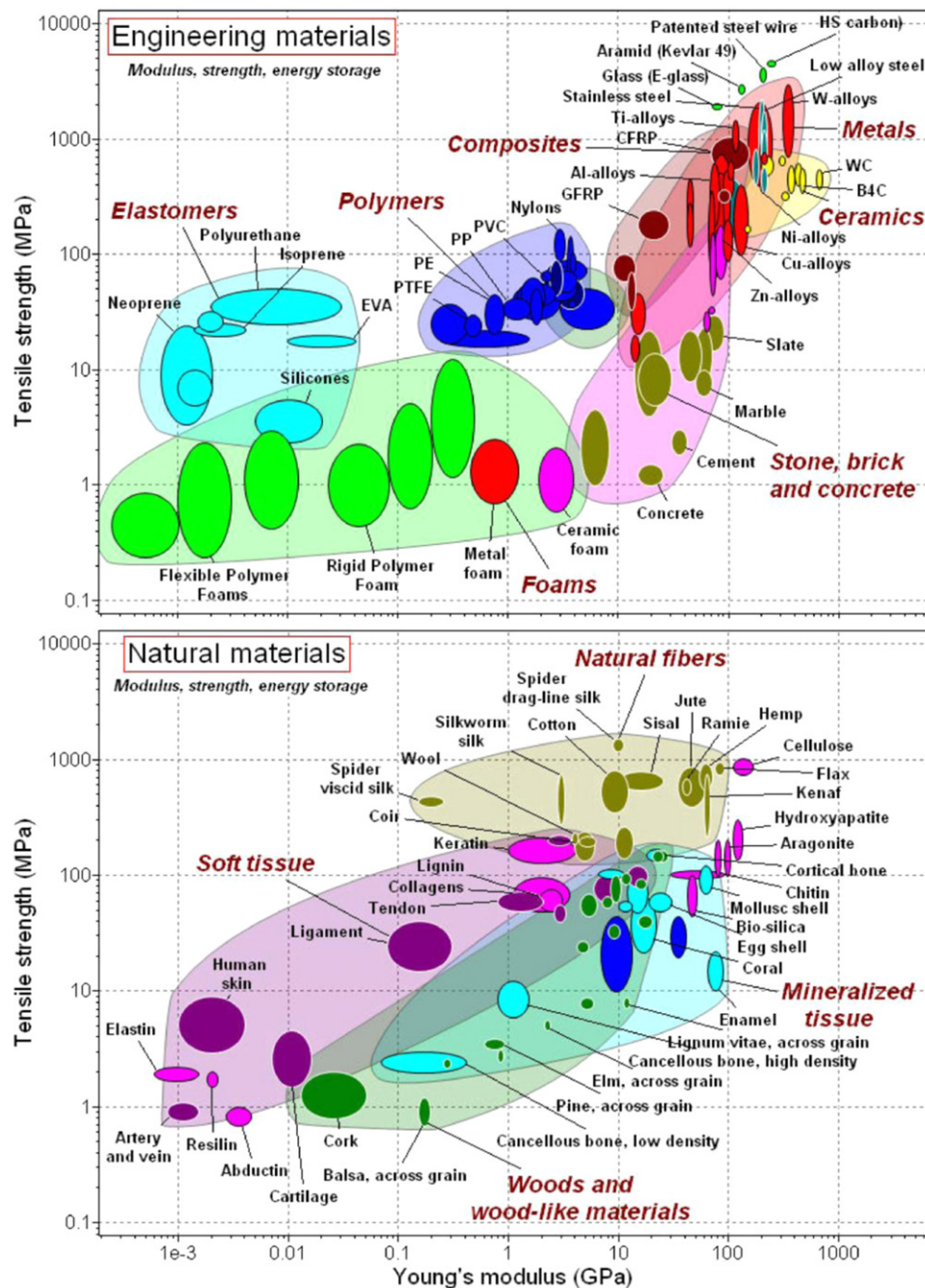


Fig. 2 Ashby plot from illustrating the Young's modulus and tensile strength of traditional engineering materials (top) and natural materials (bottom) on the same axis. Reproduced from Ashby, M., 2008. The CES EduPack Database of Natural and Man-Made Materials (MFA, 20/12/2007). Cambridge: Cambridge University and Granta Design.

decision making method for analyzing and ranking candidate plant fiber composites on the basis of key mechanical and physical properties. They carried out case studies on selecting the optimum plant fiber composites for automotive dashboard panels and brake levers. The same research group has also employed technique for order of preference by similarity to ideal solution, another multicriteria decision making method, to design a concept car bumper beam with hybrid biocomposites material (Davoodi *et al.*, 2011), however the study focuses on optimizing the bumper design for a preselected biocomposite material.

Koronis *et al.* (2013) reviewed green composites (i.e., natural fibers reinforcing a biobased matrix) as adequate materials for automotive applications, and proposed the use of ternary diagrams as materials screening tools. The ternary diagrams consider three weighted bidimensional material properties such as specific stiffness, specific strength and cost per weight, and different materials show up as balloons in different regions of the triangle's area.

Other researchers (Shah, 2013; Ashby, 2008; Dicker *et al.*, 2014; Schuh, 1999; Dittenber and Gangarao, 2012; Sobczak *et al.*, 2012; Carus and Gahle, 2008; Miao and Finn, 2008; Steger, 2010) have looked to produce Ashby-type charts to compare the general mechanical properties of various subclasses of plant fiber composites, against both each other and conventional composites. In particular, the articles by Fortea-Verdejo *et al.* (2017), Sobczak *et al.* (2012), Dicker *et al.* (2014), and Shah (2013, 2014) have been more comprehensive than the others. Fortea-Verdejo *et al.* (2017) illustrate a comparison of the tensile properties of plant fiber composites with glass fiber composites. Sobczak *et al.* (2012) produce detailed mechanical property profiles considering absolute and specific tensile strength and stiffness and Charpy impact strength, for a subgroup of plant fiber composites: Polypropylene composites reinforced with plant and wood fibers. In summarizing major material attributes of plant fiber composites and identifying potential areas of applications, Dicker *et al.* (2014) provide Ashby plots with data on plant fibers (not their composites) amongst other classes of materials such as metals and ceramics. Shah has also compared the performance of silk fiber composites with plant fiber and glass fiber composites in materials selection charts (Shah *et al.*, 2014).

The main objective of this book article is to present Ashby-type materials screening charts on biocomposites to facilitate the product design and development process and consequently aid design engineers in closing the existing gap between current scientific knowledge and actual market applications. Comprehensive mechanical property profiles are presented for both plant fibers and their composites, although focusing on the latter. The Ashby charts will portray (1) absolute tensile properties, (2) tensile properties per unit density, (3) tensile properties per unit cost, and (4) tensile properties per unit eco-impact. The tensile properties of various bast fiber composites are also compared with other classes of engineering materials, and specifically similar glass fiber composites. In addition, other mechanical parameters, specifically fatigue endurance strength, are also employed to produce materials property charts for plant bast fiber composites.

The materials property charts for the plant fiber composites are derived from a large database, which can be found in the appendix of the published articles (Shah, 2013, 2014), to illustrate the effects of different (1) reinforcements forms (short fibers: Pellets and nonwovens; long fibers: Multiaxials and unidirectionals), (2) polymer matrices (thermoplastic and thermosetting), and (3) manufacturing techniques (injection molding, compression molding, hand lay-up, vacuum infusion, resin transfer molding and prepregging). Note that the plant fiber composites included in the database only consider plant bast fibers (e.g., flax, jute, hemp) as reinforcements and nonbiodegradable, petrochemical-derived matrices (e.g., polypropylene, epoxy, polyester). I have previously shown (Shah, 2013) that short-fiber biocomposites show similar mechanical properties for plant fibers from all categories (i.e., bast, leaf, seed, or grass/reed). In addition, only bast fibers [with the exception of cotton (seed) and sisal (leaf)] are commercially available in the form of continuous yarns and textile fabrics that can be used to manufacture aligned composites with significantly improved properties. In addition, the only nonplant based natural fiber with a reasonably wide circulation yarn and fabric form is silkworm silk (ca 250 ktonnes per annum) (Shah *et al.*, 2014). Therefore, bast fibers are ideal to show the typical range in properties of various biocomposites.

With regards to the matrix, most studies and current applications on and of natural fiber composites employ a non-biodegradable or nonbiobased matrix and consequently more data is available for them in literature. Notably, not all biobased matrices are biodegradable and therefore natural fiber composites with biobased matrices may not necessarily be biodegradable. The use of natural fibers as reinforcements in a nonbiodegradable or nonbiobased matrix has been attractive as at least one element (namely, the fiber) is replaced by a renewably sourced material, and such natural fiber composites can be incinerated for energy recovery. While fully green composites are certainly an interesting subset of biocomposites, as biobased thermosets (like furfuryl alcohol and furan resin, and soybean oil based epoxies) typically have inferior mechanical properties to synthetic thermosets, and biobased thermoplastics have comparable mechanical properties to synthetic thermoplastics, the charts produced here can be used for indicative purposes.

Ashby Plots for Plant Fibers

Plant fibers can be categorized according to either the region of the plant they are extracted from, or their utilization upon extraction (Fig. 3). In the former case, plant fibers are classified as bast or stem fibers, leaf fibers, seed fibers, and other fibers (including grasses, reeds, roots, and wood fibers). In the latter case, plant fibers are grouped as primary fibers that are cultivated specifically for their fiber content, and secondary fibers that are waste- or by-products from some other primary utilization. Invariably, fibers from the same category tend to bunch together even in materials property charts (Fig. 4).

In terms of absolute tensile properties [Fig. 4(a)], bast fibers exhibit high strength (up to 700 MPa) and stiffness (up to 70 GPa). Amongst bast fibers, ramie, flax, and hemp have higher properties than jute and kenaf. Leaf fibers tend to have moderate to high strength (300–700 MPa), but much lower stiffness (10–30 GPa) in comparison to bast fibers. Seed fibers, on the other hand, have low to moderate strength (100–500 MPa) and very low stiffness (up to 15 GPa).

Note that the clustering of fibers amongst their respective groups is expected and is due to the distinct chemical composition and structural morphology of fibers from a given group (Shah, 2013), which in turn is a result of evolutionary incentive based on the function of the fiber in the plant. For instance, seed fibers have no structural role in a plant. Consequently, they have low cellulose crystallinity (20%–50%) and high microfibril angles (30–50°) (Shah, 2013) leading to inferior mechanical properties. Bast fibers, on the other hand, exhibit high cellulose crystallinity (50%–90%) and low microfibril angles (2–10°) (Shah, 2013) giving them the structural integrity required to support the plant stem.

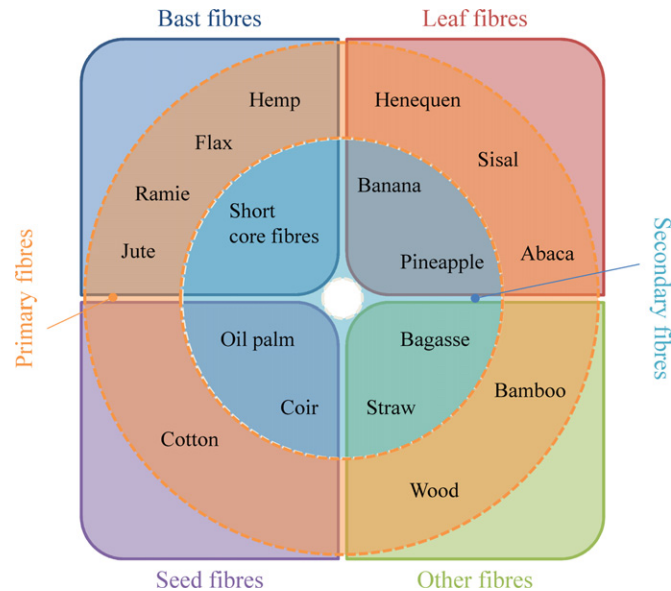


Fig. 3 Venn diagram illustrating how plant fibers can be classified based on the part of the plant they are extracted from (i.e., bast, leaf, seed, and other), or their utilization upon extraction (primary, i.e., commercially useful, or secondary, i.e., waste/by-product).

When specific tensile properties of plant fibers are considered [Fig. 4(b)], clustering in their groups of origin is still observed as the density of plant fibers is in the same general range of $1.3\text{--}1.6\text{ g cm}^{-3}$. However, seed fibers, which have a lower density (in the range of $0.7\text{--}1.6\text{ g cm}^{-3}$) due to their low cellulose crystallinity and high luminal porosity (Shah, 2013; Mwaikambo and Ansell, 2001) become slightly more comparable to the leaf fibers. It is interesting to note that while E-glass is not even on the chart (i.e., “in another league”) for absolute tensile properties [Fig. 4(a)], plant fibers appear to be more comparable to E-glass in terms of specific properties [Fig. 4(b)] due to the latter’s higher density of $\sim 2.6\text{ g cm}^{-3}$.

To be viable replacements to synthetic fibers like E-glass, plant fibers not only need to offer better if not comparable specific properties, but also need to do this at a lower if not comparable cost. Considering the tensile properties per unit cost [Fig. 4(c)], it is observed that most of the fibers overlap a strength per unit cost of $650\text{ MPa}/(\text{£kg}^{-1}\text{ g cm}^{-3})$ or a stiffness per unit cost of $32\text{ MPa}/(\text{£kg}^{-1}\text{ g cm}^{-3})$. While some seed and leaf fibers offer high tensile strength per unit cost, bast fibers offer high tensile stiffness per unit cost. Notably, alongside E-glass, pineapple fibers offer a strong combination of strength and stiffness per unit cost. Jute fibers and wood pulp supersede the performance of all the other fibers in terms of property per unit cost. Cotton, on the other hand, is a clear underperformer. It is interesting that despite its low tensile properties per unit cost, cotton fibers were the second largest reinforcing natural fiber in plastics in the European Union in 2010 (Shah, 2013); while 170,000 t of plastics were wood fiber reinforced and 100,000 t of plastics were cotton fiber reinforced, only 45,000 t of plastics were reinforced with other plant fibers with flax, jute, and hemp accounting for 64%, 11%, and 10% of the share (Shah, 2013). It is possible that the availability of the fiber plays an important role in their usage as reinforcements: While the global production of all bast fibers was under 5 million tonnes in 2010, more than 20 million tonnes of cotton was produced in the same year (Shah, 2013).

As plant fibers are from a renewable source, they have acquired an image of being green and requiring low production energies. This is true for most raw plant fibers save cotton due to its high demand of pesticides and fertilizers. As observed in Fig. 4(d), most plant fibers outperform E-glass in terms of tensile properties per unit eco-impact, where embodied energy is taken as the measure for eco-impact. The property chart reveals that the plant fibers group themselves in terms of utilization [Fig. 4(d)]. Primary fibers like flax, jute, and hemp are specifically produced for their fiber content and hence the fibers take up most, if not all, of the environmental burden of growing the plant. Secondary fibers that are waste or by-products from some other primary utilization and therefore do not carry the environmental burden of the primary utilization of the plant. It is expected therefore that primary fibers are heavily penalized in terms of property per unit eco-impact, while secondary fibers receive a boost.

The results in Fig. 4 are generally interesting and show the position of different plant fibers in comparison to one another in terms of mechanical properties that are absolute, specific, per unit cost, and per unit eco-impact. While it could be said that bast fibers offer high absolute and specific properties, and that secondary fibers offer high properties per unit eco-impact, there are underlying complexities that need to be acknowledged. For instance, there are processing limitations with secondary fibers: As these fibers are typically short and there is no established textile industry to produce yarns/rovings and fabrics from them, the manufacture of aligned textile composites for high-performance applications is difficult. Therefore, while raw coir and pineapple fibers may be eco-friendly alternatives to even raw flax and cotton fibers for nonwoven composites for applications in non-structural components such as automotive interior components, the former are not practical options for structural applications. Moreover, the cost and eco-impact of raw plant fibers is considerably different to that of plant fiber rovings/yarns and fabrics (Shah, 2013; Shah et al., 2013a). These need to be incorporated appropriately in the comparison. In essence, in the process of

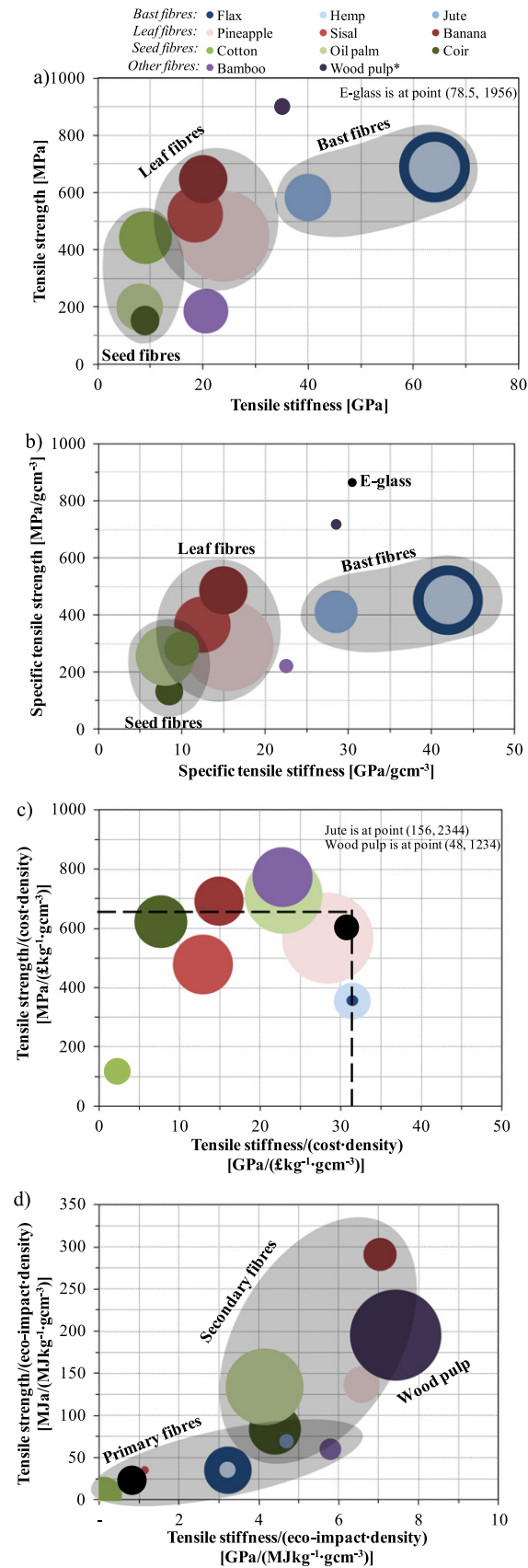


Fig. 4 Ashby charts comparing the (a) absolute tensile properties, (b) tensile properties per unit density, (c) tensile properties per unit cost, and (d) tensile properties per unit eco-impact, for various categories of plant fibers. Bast fibers are a shade of blue, seed fibers are a shade of green, leaf fibers are a shade of red. Adapted from Shah, D., 2014. Natural fiber composites: Comprehensive Ashby-type materials selection charts. Materials and Design 62, 21–31.

materials selection, property data should be on the actual material form being used (e.g., raw fiber, processed yarn, or textile fabric) and the interpretation of the Ashby charts should be done in combination with information on component processing and fabrication and possibly multiple product specifications.

For comparative purposes, [Fig. 2](#) maps the tensile properties of natural fibers against other natural materials, as well as traditional engineering materials.

Ashby Plots for Plant Fiber Composites

For the construction of materials property charts on natural fiber composites that capture the range of their typical properties, an extensive literature survey was conducted ([Shah, 2013, 2014](#)). While the literature survey focused on biocomposites employing plant bast fibers as reinforcements, properties for a range of (1) reinforcements forms (short fibers: Pellets and nonwovens; long fibers: Multiaxials and unidirectionals), (2) polymer matrices (thermoplastic and thermosetting), and (3) manufacturing techniques (injection molding, compression molding, hand lay-up, vacuum infusion, resin transfer molding (RTM), and prepregging) were incorporated.

[Fig. 5\(a\)](#) presents an Ashby plot for various biocomposites illustrating the range in tensile strength and stiffness. It is noted that that tensile strength and stiffness tend to increase linearly, at an approximate rate of 10 MPa strength to 1 GPa stiffness. More interestingly, it is evident that biocomposites can be categorized into four distinct subgroups with increasing tensile properties in the following order:

- (1) Injection-molded plant fiber composites based on short-fiber pellets whose mechanical properties are low and comparable to the matrix material,
- (2) Plant fiber composites based on nonwoven reinforcements (randomly oriented short fibers),
- (3) Plant fiber composites based on multiaxial textile reinforcements (woven and stitched biaxials, for instance), and
- (4) Unidirectional plant fiber composites.

Therefore, the reinforcement form, in terms of fiber length and orientation, has a governing effect on the properties of the resulting biocomposite due to the substantial difference in length and orientation efficiency factors between the reinforcement forms ([Shah, 2013](#)). The effects of matrix type and manufacturing technique on the properties are comparably smaller but not insignificant as they shift the material properties within that subgroup. In particular, it is found (expectedly) that thermoset-based biocomposites have better mechanical properties than thermoplastic-based biocomposites. The manufacturing technique has a larger effect in the case of unidirectional biocomposites than multiaxial and nonwoven materials. The achievable fiber volume fractions increase and porosity content decrease in the following order: Hand lay-up, vacuum infusion, RTM, compression molding, and prepregging ([Shah, 2013; Harris, 1999](#)). Consequently, the tensile properties of the biocomposites are also observed to increase in the same order.

Despite some dissimilarity in the fiber volume fractions of the plant fiber composite subgroups in [Fig. 5\(a\)](#), in terms of specific properties [[Fig. 5\(b\)](#)] no drastic shifts are observed in their relative positions. This indicates that increasing the fiber volume fraction increases not only absolute but also specific properties. The specific tensile strength and specific stiffness increase fairly linearly, at an approximate rate of 10 MPa/g cm⁻³ specific strength to 1 GPa/g cm⁻³ specific stiffness. Notably, the better absolute and specific properties of aligned and long fiber biocomposites (i.e., multiaxial and unidirectional) indicate that they are more suitable for applications where structural integrity and possibly light weight are the only objectives. [Shah et al. \(2013a\)](#) have previously demonstrated that aligned flax composites are suitable for structural wind turbine blade applications; their flax blade was 10% lighter than a similar construction E-glass blade, with no compromise on mechanical strength.

The Ashby plots in [Fig. 5\(a\)](#) and [\(b\)](#) suggest that unidirectional plant fiber composites, for instance provide 2–20 times better (absolute and specific) tensile properties than nonwoven plant fiber composites and up to 5 times better tensile properties than multiaxial plant fiber composites. However, this does not necessarily imply that unidirectional plant fiber composites would be preferred over the other materials for all applications. Indeed, while reducing cost has long been a critical objective for composites in industrial applications including automotive parts, reducing eco-impact is also becoming an increasingly common target. Subsequently, performance indices incorporating cost and eco-impact may be used to produce a more appropriate materials selection chart for these cases. For simplicity, only the cost and eco-impact (in terms of embodied energy) of the constituent materials, namely the reinforcement and the matrix, have been included in this study. The cost and eco-impact of employing a particular manufacturing process have not been included as these are dependent on various factors such as the part size, production volume, cure process, and labor and direct costs (which are different for different countries). In fact, it is not uncommon for design engineers to use separate selection charts for materials and processes/tools. However, it is notable that with composite materials often the final product (including reinforcement form and matrix type) and the manufacturing process are strongly interdependent.

[Fig. 5\(c\)](#) presents the typical tensile properties per unit cost for the various plant fiber composites. It is worth commenting that in comparison to absolute and specific tensile properties, the spread is much larger for properties per unit cost. Typical thermoplastic matrices such as polypropylene and polyethylene tend to be of lower cost (0.5–2 £/kg) in comparison to thermosetting matrices such as unsaturated polyester, and particularly epoxies and phenolics (1–5 £/kg). Consequently, thermoplastic-based

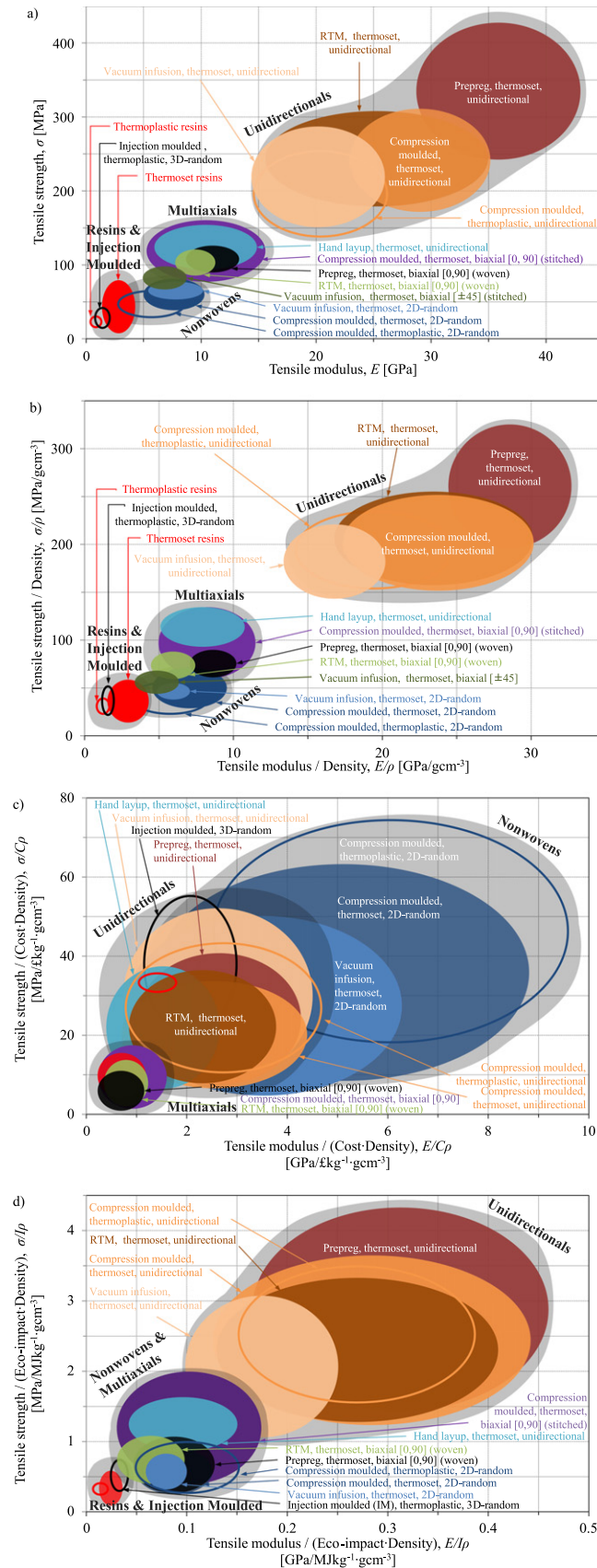


Fig. 5 Materials selection chart for plant fiber reinforced plastics manufactured with thermoplastic (unfilled balloons) or thermoset (filled balloons) resins, short-random or long-aligned fiber reinforcements, and various manufacturing routes. Charts show (a) absolute properties, (b) specific properties, (c) properties per unit cost, and (d) properties per unit eco-impact. Adapted from Shah, D., 2014. Natural fiber composites: Comprehensive Ashby-type materials selection charts. *Materials and Design* 62, 21–31.

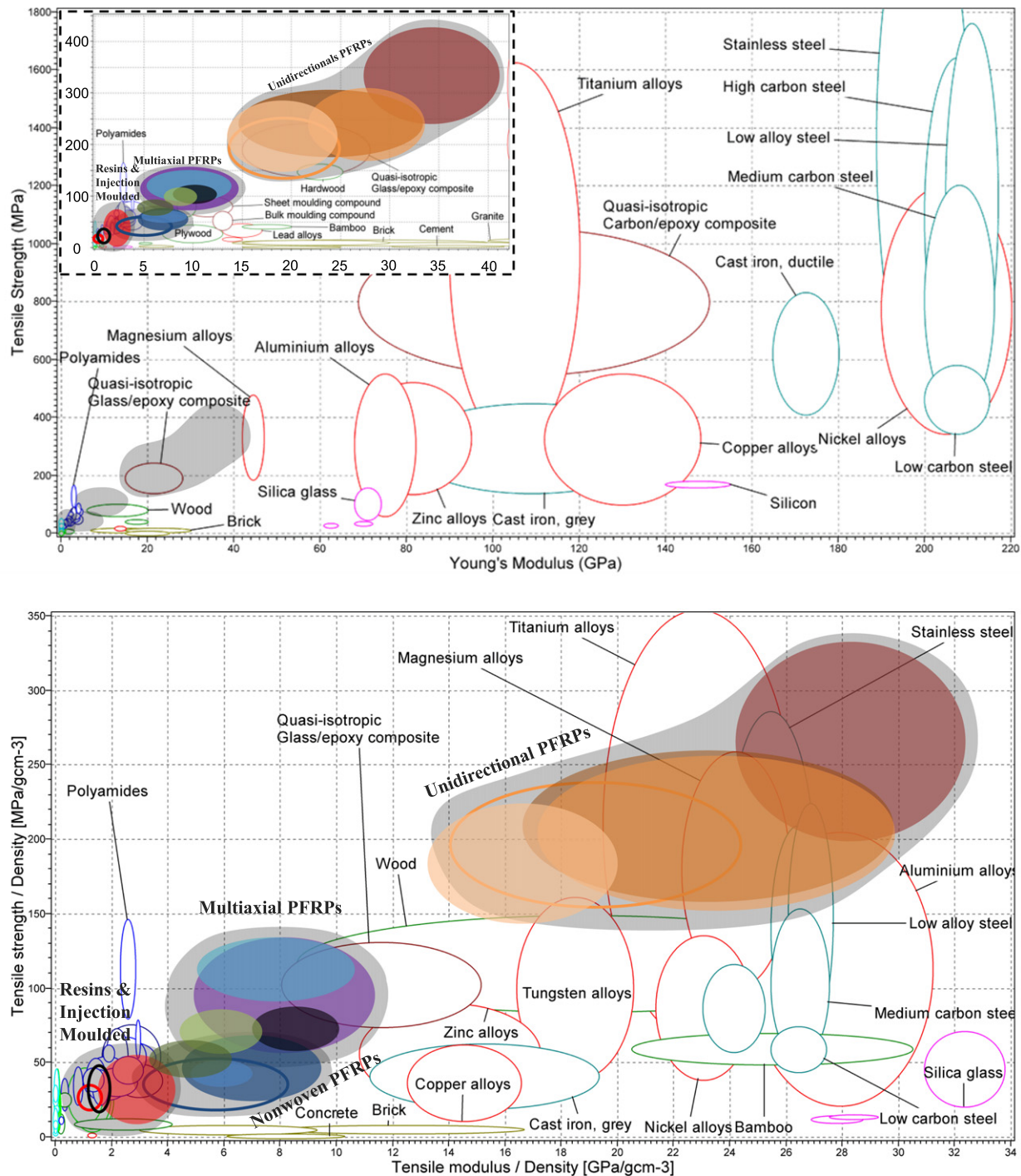


Fig. 6 Ashby plots comparing the (a) absolute and (b) specific Young's modulus and tensile strength of plant fiber composites (filled balloons) with various other engineering materials (unfilled balloons). The inset zoom image in (a) shows materials with properties in a similar range to plant fiber composites. Adapted from Shah, D., 2014. Natural fiber composites: Comprehensive Ashby-type materials selection charts. Materials and Design 62, 21–31, with data on engineering materials from Ashby, M., 2012. CES EduPack. Cambridge: Granta Design Limited.

plant fiber composites perform better in comparison to similar reinforcement thermoset-based plant fiber composites. However, the greater effect (again) is from the reinforcement form, and a trade-off between processing (vis. cost) and fiber orientation (vis. mechanical properties). Nonwoven plant fiber composites outperform unidirectional and multiaxial plant fiber composites in terms of property per unit cost, while injection-molded plant fiber composites are comparable to unidirectional plant fiber composites. Aligned plant fiber reinforcements have additional processing steps and incur substantial costs in converting naturally discontinuous plant fibers, which are readily useable for pellets for injection-molding and nonwoven mats, into yarns/rovings

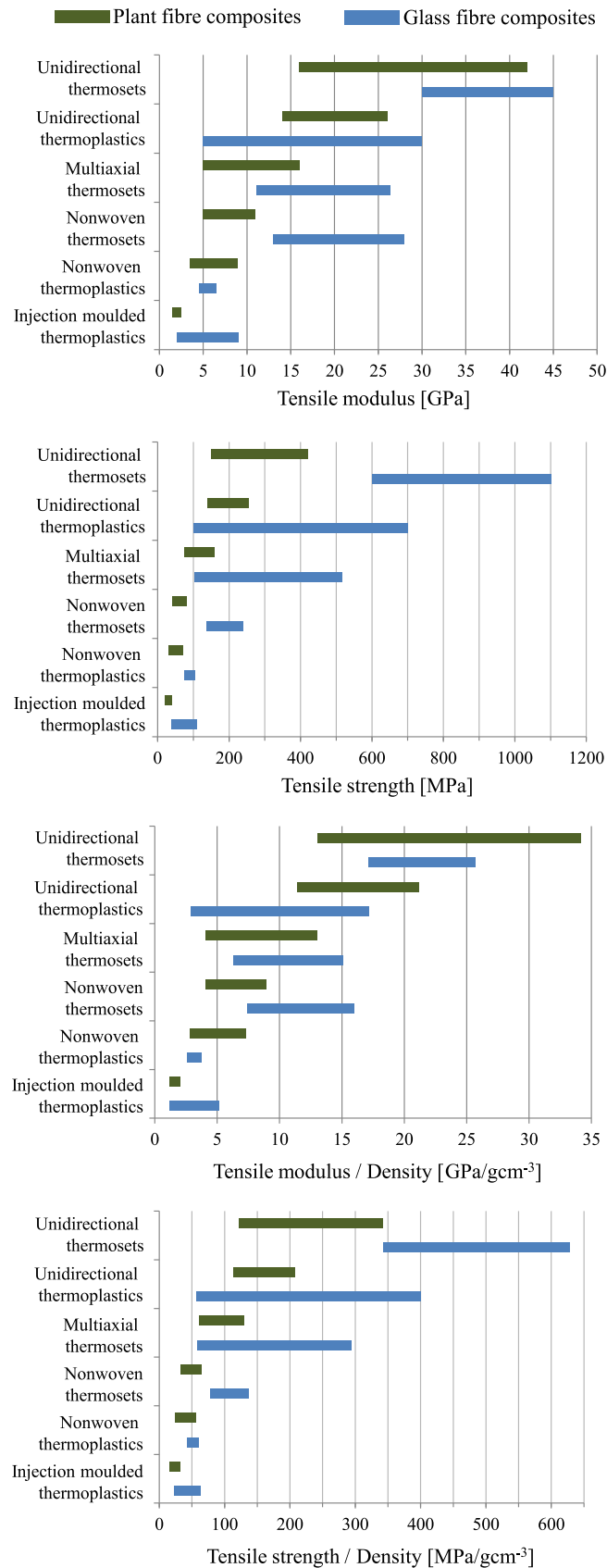


Fig. 7 Comparison of the absolute and specific tensile properties of plant fiber reinforced plastics with E-glass reinforced plastics. Adapted from Shah, D., 2014. Natural fiber composites: Comprehensive Ashby-type materials selection charts. *Materials and Design* 62, 21–31, with data for glass fiber composites from Ashby, M., 2012. CES EduPack. Cambridge: Granta Design Limited. Sims, G., 2000. 2.05 – Glass fiber reinforced plastics – Properties. In: Kelly, A., Zweben, C., (Eds.) *Comprehensive Composite Materials*. Elsevier, 151–197.

followed by stitched/woven fabrics (Shah *et al.*, 2013a). It is interesting to note that the superior position of nonwoven plant fiber composites justifies their widespread application for nonstructural applications in the cost-driven automotive industry.

When considering properties per unit eco-impact [Fig. 5(d)], the materials selection chart once again reorganizes to a similar form as in Fig. 5(a) and (b) for absolute and specific tensile properties. Unidirectional plant fiber composites offer the highest properties, followed by nonwovens and multiaxial plant fiber composites in a similar range, and then injection-molded plant fiber composites. However, unlike in absolute and specific properties, when considering properties per unit eco-impact, the range of properties for nonwoven plant fiber composites is in the same range as multiaxial plant fiber composites, while the properties of multiaxial plant fiber composites overlaps with unidirectional plant fiber composites. This is due to the lower eco-impact of nonwoven mats in comparison to unidirectional mats and multiaxial fabrics. However, the difference in eco-impact of the reinforcement forms is not as large as observed with cost.

Comparing Plant Fiber Composites With Other Engineering Materials

The materials selection charts generated in Fig. 5 only compare the properties of various plant fiber composites. The database can be used to compare biocomposites with other traditional engineering materials such as wood and other building materials, metals and alloys, ceramics and glasses, and polymers and composites. Fig. 6(a) and b show the relative position of the various PFRPs to some traditional engineering materials, in terms of absolute and specific tensile properties.

It is found that the biocomposites tend to have much lower stiffness and strength than steels and carbon composites [Fig. 6(a)]. Metal alloys of zinc, copper, and aluminum have much higher stiffness, but comparable strength to the biocomposites. The inset zoom image in Fig. 6(a) shows traditional materials with properties in a similar range to biocomposites; these include woods (ply, hard, soft), unreinforced plastics (like poly-amides, epoxies, styrene, urethanes), glass fiber reinforced composites (sheet and bulk molding compounds, and textile composites laminates), and building materials (like brick and concrete).

As plant fiber composites, and polymer composites in general, have low densities, their specific properties are more interesting for comparison [Fig. 6(b)]. In fact, plant fiber composites show comparable specific properties to some metals and their alloys due to the much higher densities of the latter.

Comparing plant fiber composites with glass fiber composites

As E-glass composites dominate the fiber reinforced plastics market, plant fiber composites have often been targeted to replace glass fiber composites (Shah, 2013). Consequently, it would be useful to compare the properties of the various plant fiber composites with similar glass fiber composites.

Fig. 7 presents another format of materials property chart comparing the absolute and specific tensile properties of plant fiber composites with glass fiber composites. Various composite types have been considered based on the matrix type (thermoplastic or thermosetting) and reinforcement form (pellets for injection molding, nonwovens, multiaxials, and unidirectionals). It is revealed that plant fiber composites, particularly unidirectional thermosets and thermoplastics, and nonwoven thermoplastics, perform exceptionally well against similar glass fiber composites in terms of both absolute and specific stiffness. However, both the

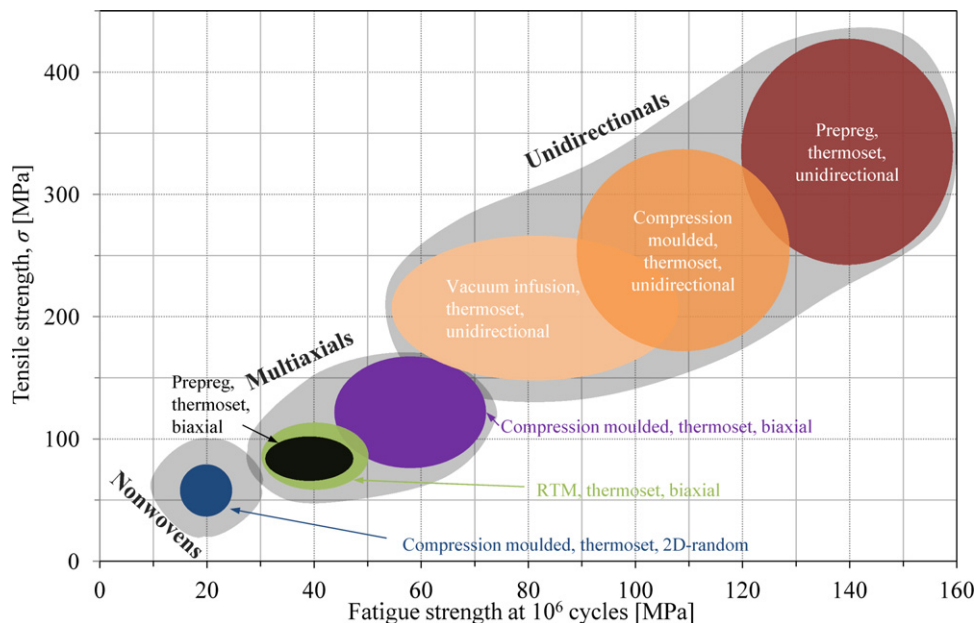


Fig. 8 Materials selection chart for plant fiber reinforced plastics based on tensile strength against fatigue strength at 10^6 cycles. Adapted from Shah, D., 2014. Natural fiber composites: Comprehensive Ashby-type materials selection charts. *Materials and Design* 62, 21–31.

absolute and specific tensile strength of plant fiber composites tends to be lower than that of glass fiber composites. Consequently, in terms of tensile properties, it can be said that plant fiber composites may be potential alternatives to glass fiber composites in stiffness-critical applications, but not in strength-critical applications.

Considering Other Mechanical Properties

While tensile properties are commonly used as mechanical parameters for performance indices in material selection charts, depending on the component function and objective other mechanical parameters such as flexural stiffness and strength, impact strength, and fatigue strength may be employed.

As an example, an Ashby plot of ultimate (single-cycle) tensile strength against fatigue strength at 10^6 cycles for plant fiber composites is presented in Fig. 8. The fatigue strength at 10^6 cycles is often used as an endurance limit to design for infinite fatigue life. Note the fewer data points on this chart as fatigue characterization of plant fiber composites is a relatively new area of research. Fig. 8 demonstrates that the fatigue endurance strength of biocomposites is proportional to their tensile strength; this has been suggested by some researchers previously (Shah *et al.*, 2013b; Liang *et al.*, 2014).

Conclusions

As the wide variety of plant fibers offer a range of useful properties, and the versatile nature of composites implies that properties can be tailored by intelligent selection of various composite parameters, plant fiber composites will obviously cover a wide array of properties. Here, comprehensive Ashby-type materials selection charts for plant fiber composites have been produced to facilitate product design and development. The charts are derived from a large database which includes properties for various plant fiber composites based on different (1) reinforcements forms (short fibers: Pellets and nonwovens; long fibers: Multiaxials and unidirectionals), (2) polymer matrices (thermoplastic and thermosetting), and (3) manufacturing techniques (injection molding, compression molding, hand lay-up, vacuum infusion, resin transfer molding and prepregging). The general tensile mechanical property profiles presented will enable the design for (1) optimal stiffness and strength, (2) minimal weight (i.e., optimal specific properties), (3) minimal cost, and (4) minimal eco-impact.

As plant fiber composites are often viewed as alternatives to glass fiber composites, for demonstrative purposes the tensile properties of the various plant fiber composites were compared with similar glass fiber composites. It is foreseen that readers would be able to similarly compare the performance of plant fiber composites with various other materials, particularly natural composites like wood and other conventional polymer composites like aramid and carbon fiber composites.

Highlighting that other mechanical parameters may be critical performance indices for specific products and applications, a materials property chart for a fatigue-limited design was also produced for demonstrative purposes. Similar charts for impact-critical structures, and flexural- or compressive-stress dominated structures, vibration- and damage-tolerant structures would be highly useful.

Acknowledgment

This book article is an adapted version of 'Shah, DU, Natural fiber composites: Comprehensive Ashby-type materials selection charts. *Materials and Design*, 2014. 62: p. 21–31.' with permission from Elsevier (License # 4552940803678).

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Nanomaterial Based Sustainable Thermal Management

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Introduction

In the year 2005, World Summit on Social Development laid out the key markers for sustainable development goals – economic development, social development and environmental protection (United Nations, 2005). In this key definition, in distinction with earlier viewpoints in economics of development, the most important parameter is to attain them altogether and not neglecting the other. In this regard, sustainable use of resources to drive overall growth of the society without impacting the environment was key to sustainable development. In order to achieve that one of the key drivers of growth is energy. In 2018 the total energy demand of the world amounted to 14046 Mtoe ('Mtoe' means million tons of oil equivalent) with a year over year growth of 2.3%, resulting in 1.7% increase in CO₂ production (Global Energy Statistical Yearbook, 2018). On a broader look this energy demand stems from various sources, starting from HVAC in a building to increase in energy consumption by the microelectronics devices.

According to EIA, in USA 39% of total energy is used by residential and commercial building sector. With regard to building sector, the basic premise of energy efficiency is to decrease energy consumptions, without compromising thermal comfort and indoor air quality in buildings (Asadi et al., 2012). As a result of which, there has been significant amount of research activity in order to improve energy conservation in a building. One of the biggest challenges in this industry is to strike the balance between cost versus performance versus ease of application. Additionally, construction industry also has significant building code restriction, which makes the problem scientifically more challenging.

In the case of microelectronics, the problem with thermal management is even severe. In the year 1965, Gordon E. Moore had predicted that the number of transistors in a dense integrated circuit to be used for computing will double up almost every two years and that prediction is still holding true to keep up with the pace of computing, automation and boom in datacom industry. This has been fueled by change in consumer behavior and scientific advancement. This resulted in an exponential increase in the number of computations per input power (MegaFlops per watt), as high as from 20 MFlops/watt in the year of 2004 to 600 MFlops/watt in 2010 (Garimella et al., 2012). Miniaturization of transistors posed an acute problem in heat dissipation and effective heat removal from microelectronic equipment became one of the biggest challenges as this results in drop in performance, which in turn makes the systems work harder and set the vicious cycle of poor management of resources resulting in ever increasing energy. In order to put things in perspective, according to a recent research report (Shehabi et al., 2016), the total electricity demand for data centers in USA was 4% of national electricity demand. In order to improve the efficiency one of the key aspect is to manage the thermal load properly in order to balance the energy demand sustainably.

All of these clearly show that in order to keep up with the energy demand, the energy production needs to go up. The low hanging fruit is to develop more fossil fuel powered electricity plants but that results in environmental pollution. In order to reduce the environmental impact and to keep up with the energy demand significant amount of energy needs to come from the renewable resources. According to a recent study by British Petroleum, by 2050, one third of world energy needs to come from renewable resources (Mearns, 2014). That is why there has been significant focus on utilizing solar energy to generate power, which can range over different solar collector technologies: (i) photo-voltaic (PV) collector, (ii) solar thermal collector and (iii) photo-voltaic/thermal (PV/T) collector (Ahmed et al., 2017; Khartchenko and Kharchenko, 2014). Whereas a photovoltaic cell's performance decrease with increased temperature, a solar thermal collector requires to store the energy over long period of time to have sustainable supply of heat.

All of these clearly show that there is a definitive need for sustainable thermal management. Nanomaterials provide an interesting approach towards thermal management problem. In this article, we will discuss about three basic nanomaterials for thermal management: (a) thermal interface materials (TIMs), (b) phase change materials (PCMs) and (c) nanofibers for liquid-vapor phase-change heat transfer. These materials broadly classify and describe the overall efforts in the field of nanofiber based sustainable thermal management.

Thermal Interface Materials (TIMs)

As electronic devices with thinner and higher power densities have been developed, thermal load on the device gets higher. The most popular method of managing the heat load is to attach a sink material to the heat producing part, which in most of the cases are the heat producing chipsets. The intent is that the sink draws heat from the chipsets and releases it into another medium (e.g., ambient air, heat transfer fluid etc.). In order to transfer the heat efficiently, the interface between the heat source and the heat sink is extremely critical. The schematic of the heat transfer from the heat source to the heat sink is shown in Fig. 1 (Akbulut and Scholar, 2018). As it is shown in Fig. 1, without TIM, there is always contact resistance between heat source and heat sink owing to

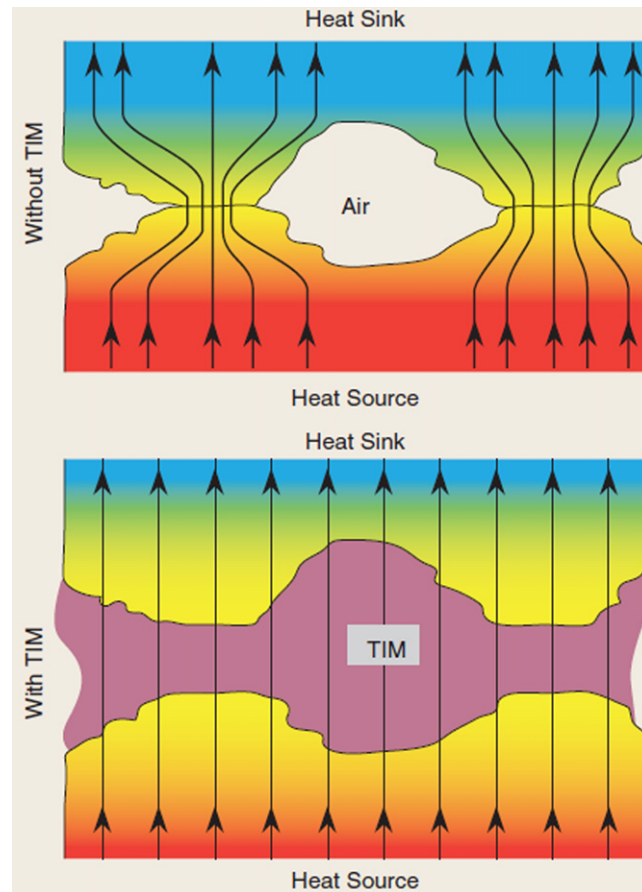


Fig. 1 Schematic of the heat transfer from the heat source to the heat sink, with and without TIM. Reproduced from Akbulut, M., Scholar, E.A., 2018. IEEE Nanotechnol. 12, 19.

the innate surface undulations. Additionally, owing to the phonon or electron scattering process at the interface, the heat transfer across the contact junctions is further reduced (Swartz and Pohl, 1989). To add to that if the contact size is of the order of mean free path of the energy carriers their transport is even further hindered through the quantum confinement effect and changes in phonon/electron dispersion (Pernot *et al.*, 2010). As a result of which, a soft and compliant interface material, called as Thermal Interface Material (TIM), is needed to be applied between heat source and sink, which in essence fills up the undulating structures between heat source and heat sink and thereby reduces the contact resistance. Some of the traditional TIMs are thermal adhesive, thermal grease, thermal filler, phase change materials etc.

The biggest challenge with traditional TIMs are that they lack mechanical strength resulting in additional fixation and/or lack desired thermal conductive properties. As a result of which nanomaterial based TIMs are presently an active area of research. It needs to be mentioned that nanomaterials owing to their smaller size, results in faster response time (t) as $t \sim L^2/\alpha$, where L is the characteristic length of the materials and α is thermal diffusivity. This simple calculation clearly shows that owing to smaller size the characteristic time of response can reduce drastically for nanomaterial based TIMs. As a result of which there has been significant research undertaking of research in the field of TIMs. In development of nanomaterial based TIMs the strategy is to add thermally conductive filler material in a compliant and thermally stable polymeric matrix and use it to capture heat from source and effectively transfer it to heat sink. Along with higher thermal conductivity, another important parameter is co-efficient of thermal expansion (CTE). A high value of CTE can result in poor performance at elevated temperature. It needs to be mentioned that in order to effectively use the nanomaterials to create a material of high thermal conductivity without sacrificing the strength and toughness, nanocomposites with aligned structures are considered to be promising starting materials (Liang *et al.*, 2011; Xie *et al.*, 2005; Chen *et al.*, 2017). In order to achieve that, nanocomposites comprising of aligned 1D CNTs were prepared, which showed efficient heat dissipation and reduced interfacial thermal resistance, yielding excellent through-plane TCs ($KL = 0.46\text{--}4.87 \text{ W/m K}$) (Marconnet *et al.*, 2011; Borca-Tasciuc *et al.*, 2007; Huang *et al.*, 2005). Similar to CNTs, boron nitride nanotubes (BNNTs) were also used to make high thermal conductivity composite materials. It needs to be mentioned that BNNTs has similar structure like CNTs resulting in high thermal conductivity but very low electrical conductivity making it one of the ideal candidates as TIMs. It was shown that it is possible to obtain 20-fold thermal conductivity improvement in BNNT-PMMA polymeric composite, while holding excellent electrical insulating properties (Zhi *et al.*, 2009). However, the challenge with

tubular filler to produce TIMs with high thermal conductivity is that it is extremely difficult to mix higher amount of filler owing to high aspect ratio of the filler. Additionally, the method of producing these tubular structure is extremely expensive. As a result of which significant focus has been provided to produce TIMs with 2D nanofillers, namely-graphene, hexagonal boron nitride (hBN), transition metal dichalcogenides (TMDCs), and black phosphorous etc. (Akbulut and Scholar, 2018; Renteria *et al.*, 2014; Saadah *et al.*, 2017; Shtein *et al.*, 2015; Weng *et al.*, 2016; Bao *et al.*, 2016; Jo *et al.*, 2013; Liu *et al.*, 2017; Zhang *et al.*, 2017; Zha *et al.*, 2016; Lee *et al.*, 2015). In the following two paragraphs, we will talk in detail about graphene and hBN nanosheets based TIM.

Pristine graphene is a zero-bandgap material, whereas hBN has a bandgap of 5.9 eV, which means that while graphene is electrically conductive, hBN is electrically insulating. Additionally, hBN is thermally more stable in comparison to graphene as graphene in presence of oxygen oxidizes to graphene oxide (GO) at 450°C hBN shows no sign of oxidation temperatures below 850°C (Akbulut and Scholar, 2018). Individual graphene nanosheets is $\sim 1500\text{--}2500$ W/m K (Faugeras *et al.*, 2010) whereas its out-of-plane thermal conductivity ~ 6 W/m K (Balandin, 2011). However, thermal conductivity increases with the logarithm of graphene length, L , plateauing around a length of 8–9 μm (Akbulut and Scholar, 2018). hBN nanosheets have very high in-plane thermal conductivity ($\sim 600\text{--}1000$ W/m K) but very poor out-of-plane thermal conductivity (~ 2 W/m K) (Ma and Sun, 2017). However, as the thickness increases the overall thermal conductivity of hBN nanosheets reaches its bulk value. Another important thing is that the CTE of graphene and hBN are $8 \times 10^{-6} \text{ K}^{-1}$ and $7.2 \times 10^{-6} \text{ K}^{-1}$, which almost as the same order as silicon, gallium arsenide, copper and aluminum making both of these two materials very attractive material for electronics application (White, 1973).

Significant work has been done to produce graphene and hBN based TIMs. Some of the most popular methods are vacuum-assisted filtration (Liang *et al.*, 2011; Li *et al.*, 2014), layer-by-layer (LBL) assembly (Song *et al.*, 2017), magnetic and electrical fields (Lim *et al.*, 2013); freeze casting (Yang *et al.*, 2017; Zhao *et al.*, 2017), solvent evaporation techniques (Kumar *et al.*, 2016). Zeng *et al.* (2018) in their work created large-area bulk oxidized cellulose nanocrystal (OCNC)/graphene nanocomposites with highly oriented structures using a large scale evaporation induced self-assembly process followed by thermal curing. They showed that this process resulted in well aligned nano-sized graphene layers. This resulted in highly interconnected and continuous thermal transport parallel to the alignment resulting in excellent in-plane thermal conductivity of 25.66 W/m K and a thermal conductivity enhancement (η) of 7235% with only a 4.1 vol% graphene loading. They also showed how their well aligned graphene layer resulted in extremely well dissipation heat in comparison to randomly oriented graphene layers (Fig. 2(a)). Chen *et al.* (2019) produced PVDF and hBN based nanofiber mat by electrospinning, which showed significant flexibility without even at a very high loading of hBN nanosheets. The resulting structure had an in-plane thermal conductivity of 16.3 W/m K at a thickness of 18 μm . They have also used it with MOFSET as a TIM and showed its efficacy (Fig. 2(b)).

Phase Change Materials (PCMs)

PCMs are one of the most ubiquitous families of materials used in our daily lives. PCMs are used as thermal energy storage (TES) materials. As the name suggests, these materials use the phase change process of the material to store energy, in the latent form. During the phase change process of turning from solid to liquid, their temperature remains constant, while the material consumes energy. Below and above the temperature range at which the phase change occurs, heat is stored as sensible heat but the temperature of the material increases. In the case of PCMs, these materials change from solid to liquid when heated, thus absorbing energy in the endothermic process. When the ambient temperature drops, the liquid PCMs will turn into solid state materials again while releasing the earlier absorbed heat in an exothermic process. The use of PCMs date back to almost 500 BCE, when Greeks and Romans used mutton fat (tallow) to make candles. In China during Qin dynasty (almost 200 BCE), whale fat was used to make candles. These candles are perfect example of PCMs. Owing to the innate capability of PCMs to store energy, they are considered to be one of the key components of TES medium. Their applications range from construction practice to renewable energy storage to maintaining thermal equilibrium of electronics chipset (Amaral *et al.*, 2017; Raam Dheep and Sreekumar, 2014; Wan *et al.*, 2016). PCMs can be broadly classified into three categories – inorganic, organic and eutectic mixtures (Amaral *et al.*, 2017). Some of the advantages and disadvantages of these PCMs are shown in Table 1 (Amaral *et al.*, 2017; Ahmed *et al.*, 2017). However, although the inorganic PCMs are quite attractive from the viewpoint of price but their high temperature of operation, corrosive nature, toxicity etc., limits their applications to some specific uses, e.g., thermal energy storage for solar applications (Ahmed *et al.*, 2017). Whereas, organic PCMs, namely-paraffin wax, has been used over a wide range of applications (Amaral *et al.*, 2017; Raam Dheep and Sreekumar, 2014; Wan *et al.*, 2016). However, irrespective of the PCMs, the biggest drawback for PCMs are that their thermal diffusivities are intrinsically low. This results in poor thermal response. In order to avoid that two possible techniques can be employed: (a) addition of high thermally conductive filler to increase effective thermal diffusivity, (b) encapsulate PCMs in nanotubular structures and thereby reducing the characteristic time of response. In the next two paragraphs a brief overview of both of these two methods will be described.

PCMs Incorporated With Conductive Nano-Filler

In order to achieve higher thermal conductivity aka effective higher thermal diffusivity, one of the most intuitive and well researched area is the incorporation of highly conductive nano-filler (e.g., CNTs, graphene, metal and ceramic nanoparticles etc.).

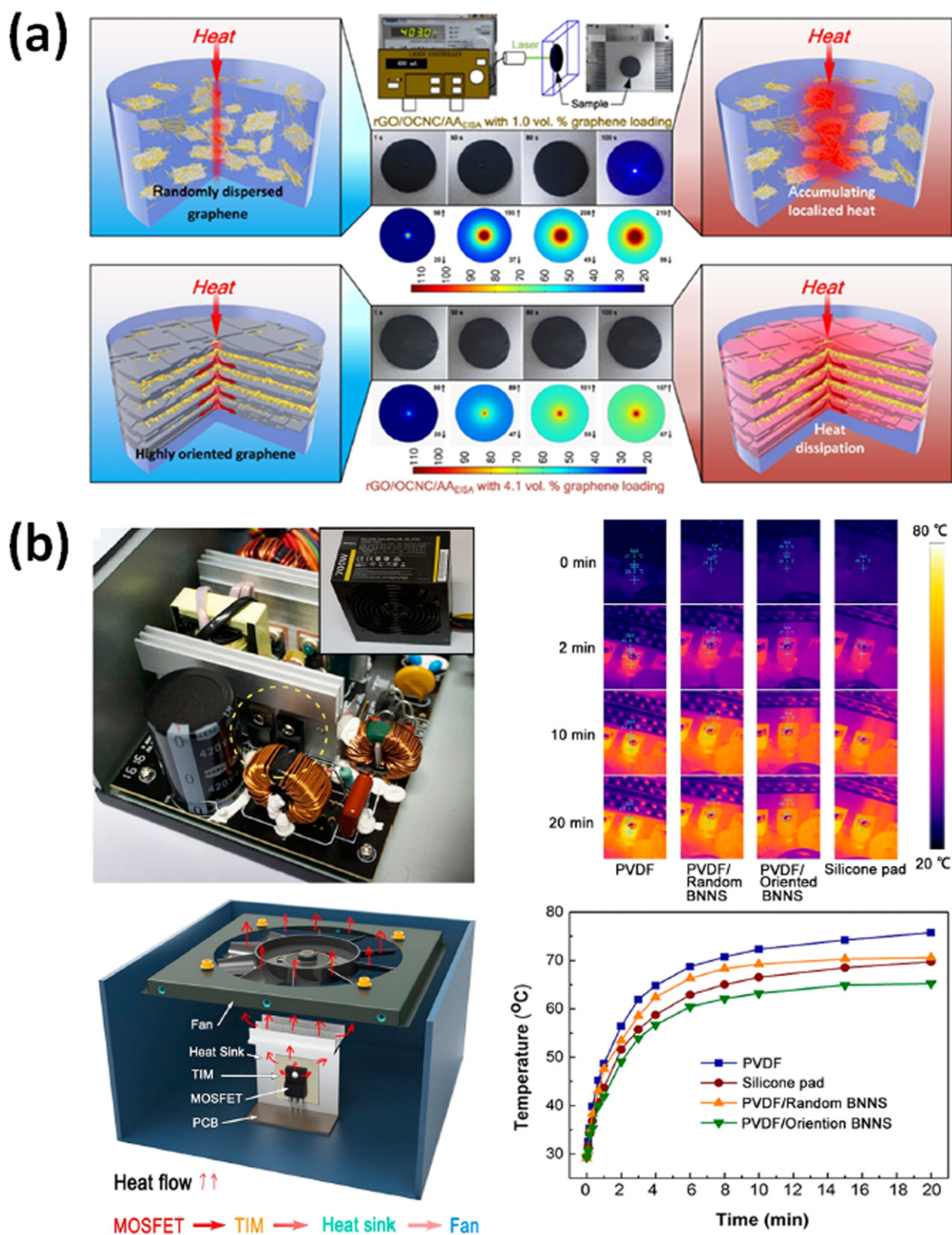


Fig. 2 (a) Schematic of the thermal test setup, finite-element analysis of surface temperature variations with time and demonstration of thermal transport properties of oxidized cellulose nanocrystal (OCNC)/graphene nanocomposites with randomly dispersed graphene sheets and highly oriented graphene sheets are shown. (b) Upper left corner of the panel shows the optical photograph of the MOSFETs integrated with thermal interface materials prepared from electrospun PVDF and hBN nanosheets, whereas lower left corner shows schematic diagram of a MOSFET integrated with a thermal interface material. Upper right hand corner shows the infrared thermal images of MOSFETs integrated with different thermal interface materials and lower right hand corner shows the surface temperature variations of MOSFETs versus time. Reproduced from (a) Zeng, H., Wu, J., Ma, Y., *et al.*, 2018. *ACS Appl. Mater. Interfaces* 10, 41690. (b) Chen, J., Huang, X., Sun, B., Jiang, P., 2019. *ACS Nano* 13, 337.

Table 1 Different types of PCMs and their relative advantages and disadvantages

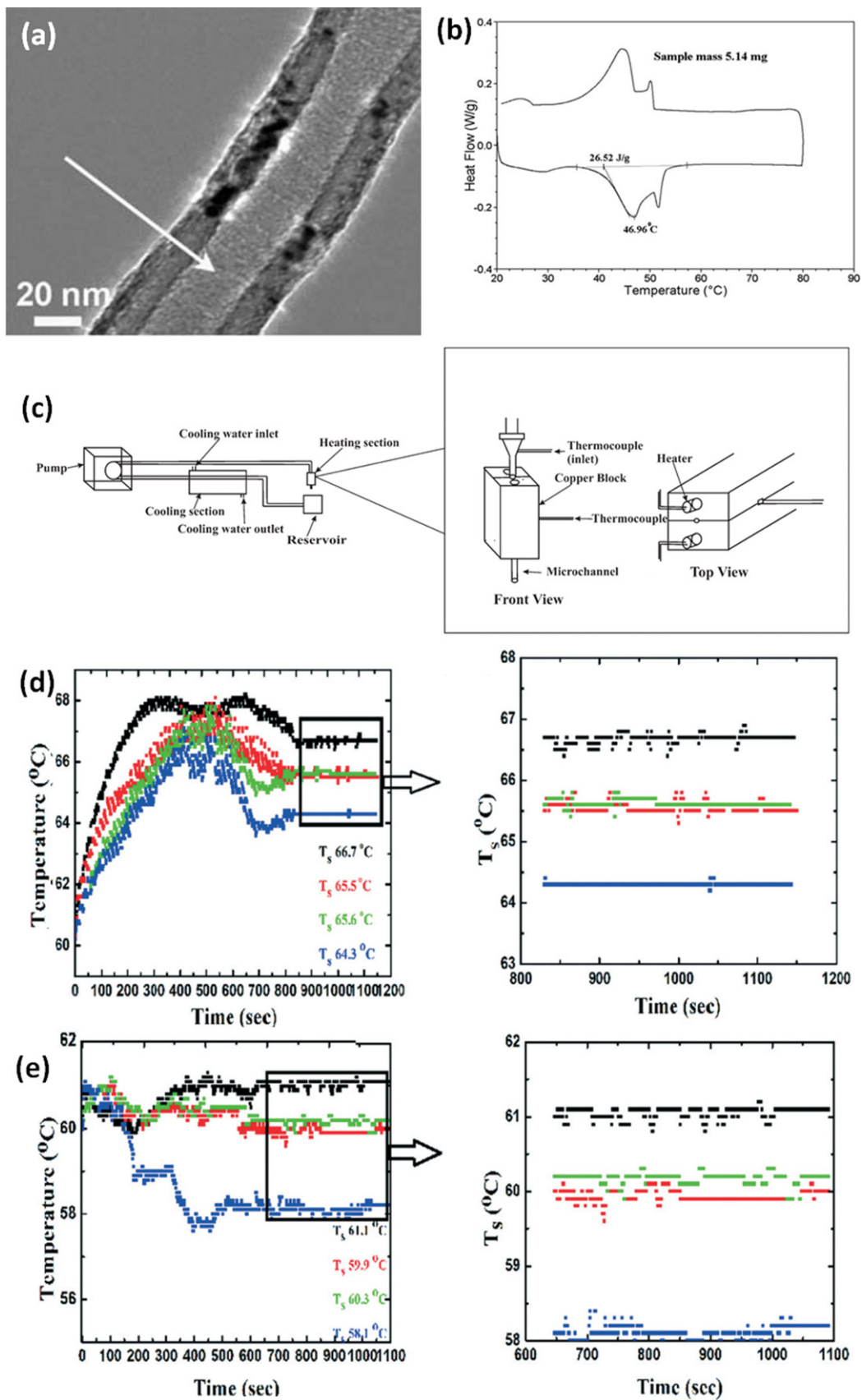
Type of material	Advantages	Disadvantages
Organic (e.g., Paraffin wax)	● Non corrosive ● Low or no supercooling effects ● Chemical and thermal stability ● Good thermal behavior ● Adjustable transition zone ● Availability in a large temperature range ● No segregation ● Good nucleation rate ● No dangerous (chemically) ● Recyclable ● Compatible with wide range of materials	● Low phase change enthalpy ● Low thermal conductivity, density and melting point ● Flammability ● Highly volatile ● Volume change during phase change ● Expensive
Inorganic (e.g., Hydrated salts)	● Great phase change enthalpy ● High energy storage density and thermal conductivity ● Not flammable ● Less expensive (Low cost) comparative to the organic ● Low volume change ● Sharp phase-change	● Supercooling effect ● Corrosive ● Decomposition and phase separation ● Phase segregation and lack of thermal stability ● Lower compatibility with other materials ● Slightly toxic ● Incongruent melting and dehydration in the process of thermal cycling ● Poor nucleating properties
Eutectic mixtures (e.g., Mixture of different PCMs)	● Sharp melting temperature ● Volumetric thermal storage density slightly above organic compounds ● No segregation and congruent phase-change	● Limited data are available on their thermophysical properties ● Quite strong odor

Note: Amaral, C., Vicente, R., Marques, P.A.A.P., Barros-Timmons, A., 2017. *Renew. Sustain. Energy Rev.* 79, 1212. Ahmed, S.F., Khalid, M., Rashmi, W., Chan, A., Shahbaz, K., 2017. *Renew. Sustain. Energy Rev.* 67, 450.

The reasons for addition of nanofiller are that: (a) the mixing is relatively straight forward, (ii) with relatively lower loading, it is possible to get higher thermal conductivity owing to improved percolation of nano-fillers. Parameshwaran *et al.* (2013) incorporated silver nanoparticles to organic ester. investigated the performance of organic ester by incorporating silver nanoparticles, where they were able to reduce latent heat capacities by 7.88% in freezing and 8.91% in melting whereas thermal conductivity of composite PCMs increased by 10%–67% more compared to base PCM and thereby increasing effective thermal diffusivity. Wang *et al.* (2010) showed that by adding copper nanoparticle to paraffin wax they were able to change thermal properties significantly. In this work they added various amount of copper nanoparticle (0.1, 0.5, 1.2 wt%). It was found that the latent heat changed significantly. Li *et al.* (2013) prepared MWCNT based nanocomposite with stearic acid as the PCM and found that addition of MWCNT improves the thermal conductivity and also increases the discharging rate to about 91% and lowers the charging rate to 50% of stearic acid, when the volume fraction of the additive is 5%. Sari and Karaipekli (2007) investigated the effect of addition of expanded graphite in paraffin and found that by increasing amount of expanded graphite the thermal conductivity can be increased by almost 4 times. Several studies were performed for the focus work of EU DISTOR (Energy Storage for Direct Steam), where the intent was to build better steam accumulator for solar thermal power plant, where both lab-scale and industrial application of graphite- $\text{NaNO}_3/\text{KNO}_3$ were studied in detail (Tamme *et al.*, 2008; Steinmann and Tamme, 2008; Pincemin *et al.*, 2008; Acem and Lopez, 2010). They found that they were able to increase the thermal conductivity between 10 and 31 times depending on the graphite particle size, working temperature and elaboration time (dispersion, infiltration and cold compression). Liu *et al.* (2018) created graphene aerogel embedded with alkane, alcohol and carboxylic acid PCMs using hydrothermal synthesis. They found that resultant composite structure comprising of rGO/PCM has a significantly enhanced thermal conductivity of $3.21 \text{ Wm}^{-1} \text{ K}^{-1}$ with the rGO loading of 10 wt%. They also replaces part of graphene with silver nanoparticles and found that the thermal conductivity of rGO/PCM/Ag could be as high as $5.89 \text{ Wm}^{-1} \text{ K}^{-1}$.

Nanoencapsulated Phase Change Materials

Nanoencapsulation or nanoconfinement of PCMs allow us to reduce the length scale drastically and thereby improve the characteristic time of response. Apart from improving thermo-physical properties, confinement also improves upon other drawbacks of PCMs. As an example- for inorganic PCMs one of the biggest challenges is the loss of crystallization water during phase transition and supercooling. Encapsulation at nanoscale help prevent such issues. There has been significant amount of work in literature regarding nanoencapsulation of PCMs. A very good review of the techniques of nanoencapsulation can be found in Aftab *et al.* (2018). One of the popular method is to encapsulate PCM in polymer capsule in situ, which can be achieved via emulsion polymerization (Huang *et al.*, 2017; Shirin-Abadi *et al.*, 2011), in-situ polymerization (Fang *et al.*, 2013, 2008). Similar to nanoencapsulation in a polymer



shell via polymerization, sol-gel methods were also used to encapsulate PCMs in inorganic shell (Zhu *et al.*, 2015). Apart from in situ encapsulation, PCMs were also encapsulated in the core of electrospun nanofiber (Sirohi *et al.*, 2015; Semnani Rahbar *et al.*, 2016). PCMs were also encapsulated in mesoporous silica particles (Mitran *et al.*, 2018; Zhang *et al.*, 2010; Lai *et al.*, 2016).

One of the most interesting and easily scalable process was proposed by Sinha-Ray *et al.* (2011a). In this work, the wax was encapsulated inside CNTs via self-sustained diffusion (Bazilevsky *et al.*, 2007, 2008). CNTs were added to solution of wax and sonicated for 30 min resulting in homogeneous suspensions. After that the vial cap was kept open in a chemical hood until complete evaporation of benzene. During this process the self-sustained diffusion of solutes into CNTs took place. Then, benzene was added to the deposit and sonicated for 3–4 min to rinse any solute which possibly could have been deposited outside the CNTs. A representative TEM image is shown in Fig. 3(a). It was also found that owing to nanoencapsulation, apart from reduction of characteristic time of response, the temperature range of operation widened (as shown in Fig. 3(b)). Following this work, CNTs intercalated with erythritol and wax was prepared (Sinha-Ray *et al.*, 2014a), which was used to create coolant suspension to cool microchannels, where for intercalated wax sample aqueous and intercalated erythritol oil based suspension was prepared (Fig. 3(c)). Special care was taken to create surfactant stabilized aqueous suspensions of 1 wt% CNTs, which did not clog a 603 μm channel, whereas in a 1803 μm channel flows of suspensions of up to 3 wt% wax-intercalated CNTs were found to be possible. The flow rates of such suspensions were in the range 5–55 ml min^{-1} . It was found that the presence of the surfactant NaDDBS in water led to an apparent slip at the channel walls, which enhanced the convective heat removal from a hot copper block, in which the microchannels with flowing aqueous coolant were embedded. The presence of wax inside CNTs additionally facilitated heat removal through the latent heat of wax fusion. Wax melted in the range 45–47°C and this effect alone was responsible for the maximum temperature reduction of 1.9°C (Fig. 3(d)). The erythritol melted in the range 118–120°C and this effect alone was responsible for the maximum temperature reduction of 3.2°C in flows of the oil-based 1.5 wt% suspension of erythritol-intercalated CNTs (Fig. 3(e)). The present approach showed possibility in the case of mixtures of different PCMs, e.g., wax and erythritol (separately in different CNTs, or together in the same CNTs) to widen the temperature range in some applications.

Nanofibers for Liquid-Vapor Phase-Change Heat Transfer

As the energy and cooling demand for microelectronics increases, there has been significant emphasis on cooling technique with enhanced heat removal capacity. Liquid-vapor phase-change processes, such as boiling, evaporation, and condensation, is the most efficient and widely exploited for thermal management of high-power systems to maintain adequate performance and to ensure system reliability and safety (Wen *et al.*, 2018a,b; Amir, 2012; Boreyko and Chen, 2013). There has been significant amount of work that has been done by nanotexturing the surface (Wen *et al.*, 2018a,b). The basic premise of all these works has been to increase the hydrophilicity of the surface. However, most of these processes are extremely expensive and thereby lacks the practical or large scale application that can be employed from device level to large scale applications. However, recent progress in polymer nanofibers via electrospinning, solution blowing and electricity assisted solution seems to have the answer to this problem. For readers unfamiliar with these processes are highly encouraged to read the following references to get a brief overview of the process (Sinha-Ray, 2018). In this section, we will limit our discussions to nanofiber mediated heat transfer via liquid-vapor phase change process. Two different modes of heat transfer methods will be discussed: (a) drop impact method and (b) pool boiling method.

Drop Impact Method

Drop impact method (spray on demand) of cooling a hot surface is extremely well known. Applications can range from UAVs, space shuttles, data centers to autonomous vehicles etc. However, the challenge is that as the temperature of the hot surface nears the boiling point of the coolant, the coolant bounces off the surface because as the drop touches the surface, immediately a vapor pillow forms underneath the drop resulting in levitation of the drop. This effect is called “Leidenfrost Effect” (Fig. 4(a)). As a result of the Leidenfrost effect the water droplet bounces around the surface without getting fully utilized. In fact, we all have seen this effect in our everyday life. In kitchen, if we put drop of water on a hot skillet, the water bounces around. In order to quickly cool the skillet, we hold hot skillet under running faucet and inherently use a lot more coolant (water). For a kitchen type application, such usage is OK but when we think about mission critical and space crunched situations like UAVs, space shuttles, autonomous vehicles etc., neither we have the luxury nor we have the resources to use such a huge amount of coolant. So, the most important way to improve the efficiency of cooling under drop impact is to do away with the Leidenfrost effect and electrospun fibers seem to have the capability to do so efficiently.

Fig. 3 (a) TEM image of a wax intercalated CNT is shown. (b) DSC thermogram of wax intercalated CNT is shown. (c) Schematic of the experimental setup employed to study heat removal using microchannel flows of wax-intercalated CNTs is shown. (d) and (e) show the temperature evolution in a microchannel flow for wax and erythritol suspension respectively. Black symbols correspond to pure water, red symbols to the aqueous surfactant solution, green symbols to the aqueous suspension of the empty CNTs, and blue symbols to the suspension of the PCM-intercalated CNTs. Reproduced from (a–b) Sinha-Ray, S., Sahu, R.P., Yarin, A.L., 2011a. *Soft Matter* 7, 8823. Sinha-Ray, S., Zhang, Y., Yarin, A.L., 2011b. *Langmuir* 27, 215. (c–e) Sinha-Ray, S., Sinha-Ray, S., Yarin, A.L., *et al.*, 2014a. *Int. J. Heat Mass Transf.* 70, 1107. Sinha-Ray, S., Sriram, S., Sinha-Ray, S., Yarin, A.L., 2014b. *Lab Chip* 14, 494.

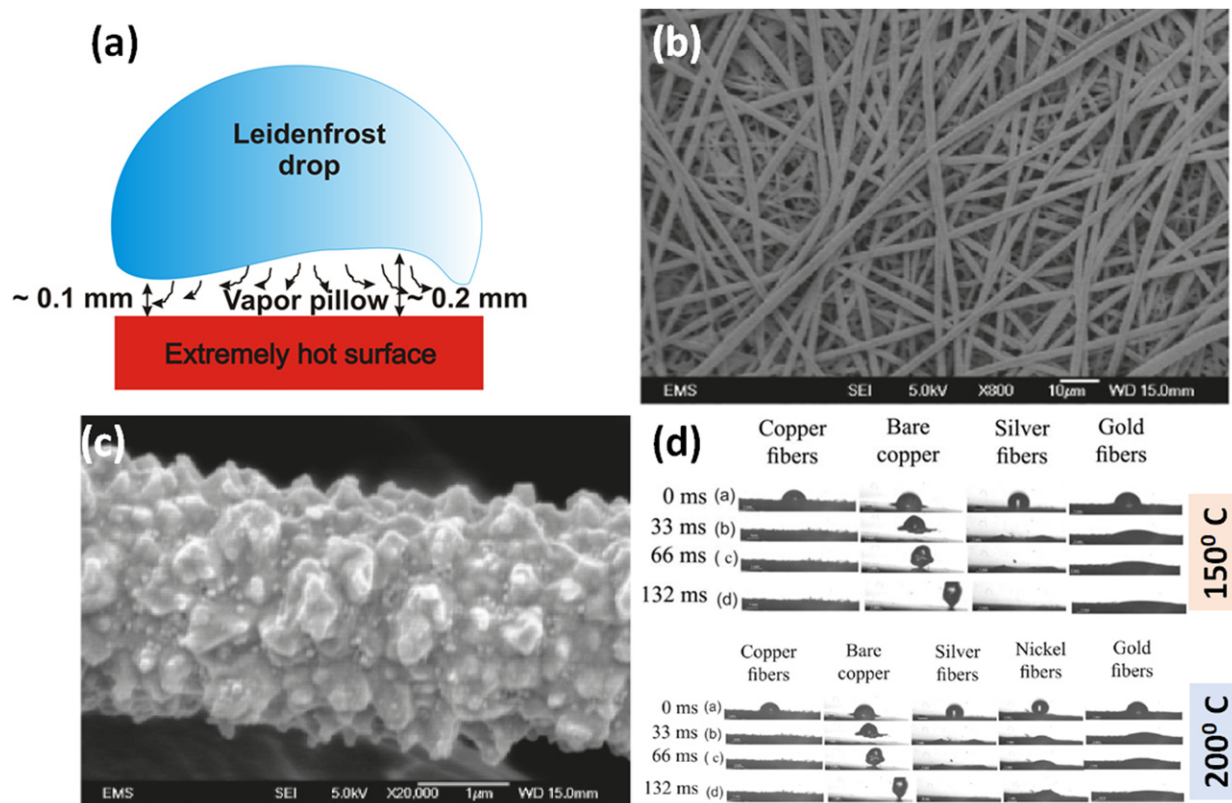


Fig. 4 (a) Schematic of the Leidenfrost effect is shown. (b) and (c) SEM image of copper nanofiber mat is shown. (d) Evolution of water droplet impacting metallized nanofiber coated copper surface and bare copper surface at 150 and 200°C are shown. Reproduced from (b–d) Sinha-Ray, S., Sahu, R.P., Yarin, A.L., 2011a. *Soft Matter* 7, 8823. Sinha-Ray, S., Zhang, Y., Yarin, A.L., 2011b. *Langmuir* 27, 215.

Lembach *et al.* (2010) came up with an elegant yet powerful solution to eliminating Leidenfrost effect. They first theoretically showed that if a coolant droplet of diameter a hits a porous surface with pore diameter $\sim D$ at a velocity of U , the velocity of penetration inside the porous surface (V) $\sim Ua/D$. This shows that by increasing a/D ratio, we can increase V . Electrospun nanofiber mat has a pore size $\sim 10\text{--}40\text{ }\mu\text{m}$. If the coolant droplet has a diameter $\sim 1\text{ mm}$, with $U \sim 1\text{ m/s}$, V can be extremely large. Additionally, the pores in electrospun fibers are interconnected. As a result of which, once the coolant enters the electrospun mat, it gets pinned. Based on this theoretical knowledge, it was shown that surface coated with polymer nanofiber mat can do away with Leidenfrost effect (Lembach *et al.*, 2010; Weickgenannt *et al.*, 2011). However, one of the biggest challenges with polymer nanofibers in thermal management application is that owing to the low thermal diffusivity of the polymer nanofibers, the heat transfer capability of hot surface coated with polymer nanofiber under drop impact can suffer. As a result of which, it is extremely important to have a high thermal diffusivity nanofiber mat coating. In order to alleviate the problem, a simple yet powerful method of preparing metallized nanofiber mats were shown (Sinha-Ray *et al.*, 2011b). First of all the nanofiber mat deposited on the copper surface was sputter coated. Then the sputter coated nanofiber mats were electroplated using simple electroplating bath. Metallized nanofiber mats with different metals (copper, nickel, silver and gold) were prepared. SEM image of electroplated copper nanofiber is shown in Fig. 4(b) and (c). First of all it was found that all the metallized nanofiber mats were able to do away with Leidenfrost effect as shown in Fig. 4(d), where it can be seen that water droplet keeps bouncing around with evolution of time, whereas the water droplet gets pinned on the metallized nanofiber mat coated copper substrate. It was shown that out of all the metallized nanofiber mats, copper nanofiber performed the best from the viewpoint of structural integrity and heat transfer efficiency. It was found that the copper nanofiber is capable of removing almost 1 kW/cm^2 of heat flux. This work was extended to find the efficiency of the copper nanofiber mat under continuous drop impact using a drop-on-demand generator under different gravity condition (0 g, 1 g and 1.8 g) and it was found that in all of these cases the coating was able to remove high heat flux in comparison to the bare surface and do away with Leidenfrost effect (Sinha-Ray *et al.*, 2014a,b).

Pool Boiling Method

Pool boiling is known as a very effective mechanism of liquid vapor phase change heat transfer due to its high heat flux values. The regimes of pool boiling can be divided on the boiling curve as free convection boiling, nucleate boiling, transition boiling, and film boiling (Nukiyama, 1966). Among them nucleate boiling is considered to be the most desirable heat transfer regime, since it is

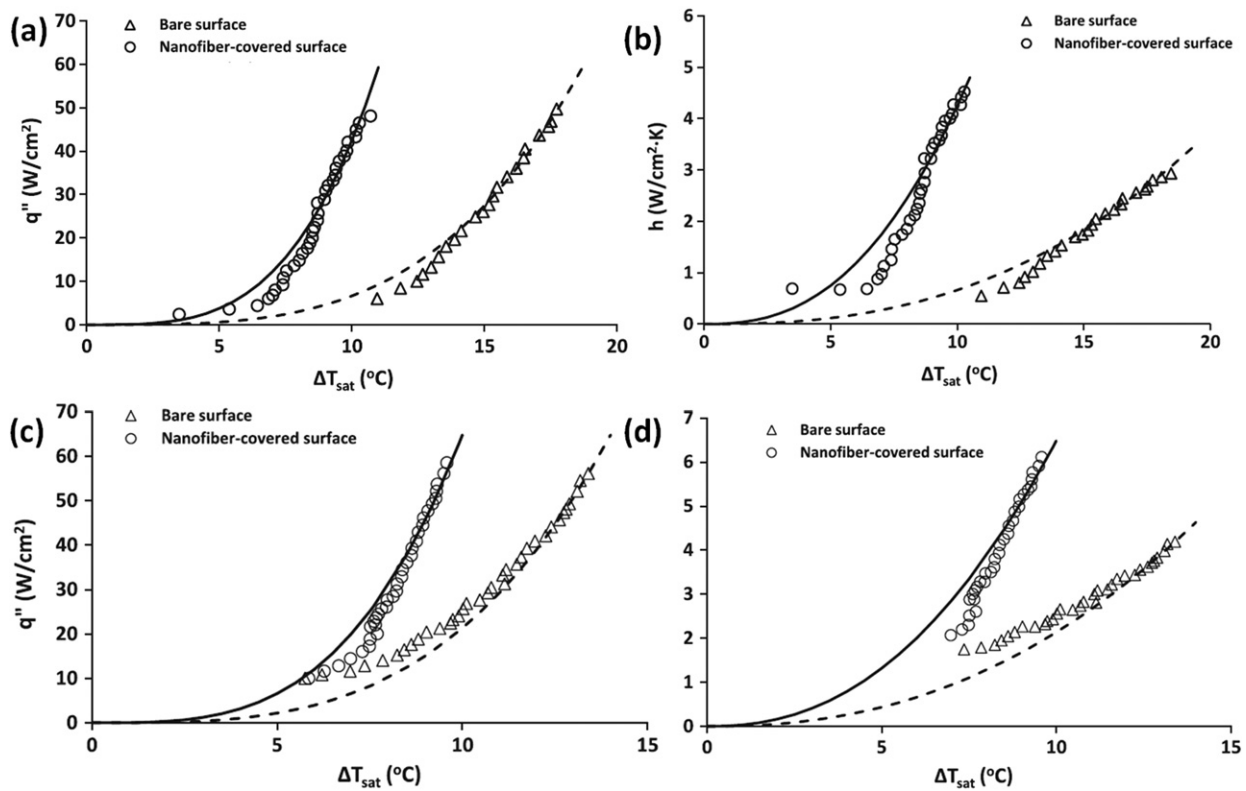


Fig. 5 Comparison of pool boiling data for bare copper and metallized nanofiber coated surface is shown. Panel (a) and (b) shows evolution of heat flux and BHT vs. wall superheat for ethanol as boiling medium respectively. Panel (c) and (d) shows evolution of heat flux and BHT vs. wall superheat for water as boiling medium respectively. Reproduced from Jun, S., Sinha-Ray, S., Yarin, A.L., 2013. *Int. J. Heat Mass Transf.* 62, 99.

associated with high heat fluxes at low superheat surface temperature, which is attractive for such practical applications as cooling of electronics, boilers, nuclear and chemical reactors and refrigeration systems. However, there exists a critical value of heat flux called critical heat flux (CHF) at which nucleate boiling transforms into film boiling. The latter involves heat transfer through coolant vapor rather than through liquid coolant itself, which is a weak heat transfer mechanism. There were multiple efforts to increase CHF and boiling heat transfer coefficient (BHT), which is by definition the heat flux divided by the corresponding superheat temperature. In particular, boiling on roughened surfaces was investigated (Webb and Kim, 2005). It was found that roughened surfaces increase BHT coefficient, which stems from an increased area density of nucleation sites. Microporous coatings to enhance pool boiling were studied in Song *et al.* (2018), Li and Peterson (2010), Rainey and You, (2000). In particular, the authors of Li and Peterson (2010) sintered microporous surfaces and found that CHF on them strongly depends on the coating thickness, volumetric porosity and pore size. They attributed the improvement of heat transfer in their experiments to an increased effective heat transfer area. It was also found in Li and Peterson (2010) that when the coating thickness reaches approximately 2 mm, CHF reaches maximum, which was twice that corresponding to bare surface. Volumetric porosity does not affect much CHF value. On the other hand, CHF increases with increasing the pore size upto 250 μm (Li and Peterson, 2010). The effect of nanoparticles suspended in liquid on pool boiling was studied in Jothi Prakash and Prasanth (2018), You *et al.* (2003), Kim *et al.* (2007), Kim and Kim (2009). The authors (You *et al.*, 2003) reported that CHF can be doubled due to the presence of nanoparticles. An enhancement of CHF in nucleate boiling in presence of nanoparticles is commonly attributed to an increase surface in wettability and surface roughness and some other factors (Kim *et al.*, 2007; Kim and Kim, 2009). However, in Kim *et al.* (2007) the BHT coefficient decreased due to (i) a build up of nanoparticle layer, which reduces heat transfer from the metal surfaces in pool boiling and (ii) a reduction of nucleation site density caused by a decrease in the contact angle. Pool boiling on a surface coated by nanofiber mat seems to do away with the problems and improve heat transfer efficiency BHT coefficient and enhance CHF.

One of the first work in this direction was done by Jun *et al.* (2013). In this work, the authors used metallized nanofiber mat coated mat based on the techniques developed earlier (Sinha-Ray *et al.*, 2011a,b). In this work, it was shown that nanotextured copper surfaces coated with copper nanofiber mats possess a 6–8-times higher heat flux and heat transfer coefficient in nucleate boiling of ethanol in comparison with those of the corresponding bare copper surface (Fig. 5(a–b)). For the nucleate boiling of water, the heat flux and heat transfer coefficient of nanotextured surfaces is 3–5 times higher than those of the bare copper surface (Fig. 5(c–d)). The reason was also explained theoretically. The theory attributed the superiority of nanotextured surfaces in comparison to the corresponding bare surfaces to the fact that the effective liquid temperature in liquid in the vicinity of such fluffy surfaces is higher than near the smooth surfaces. In the theoretical work, it was shown that because of the fluffiness, the average

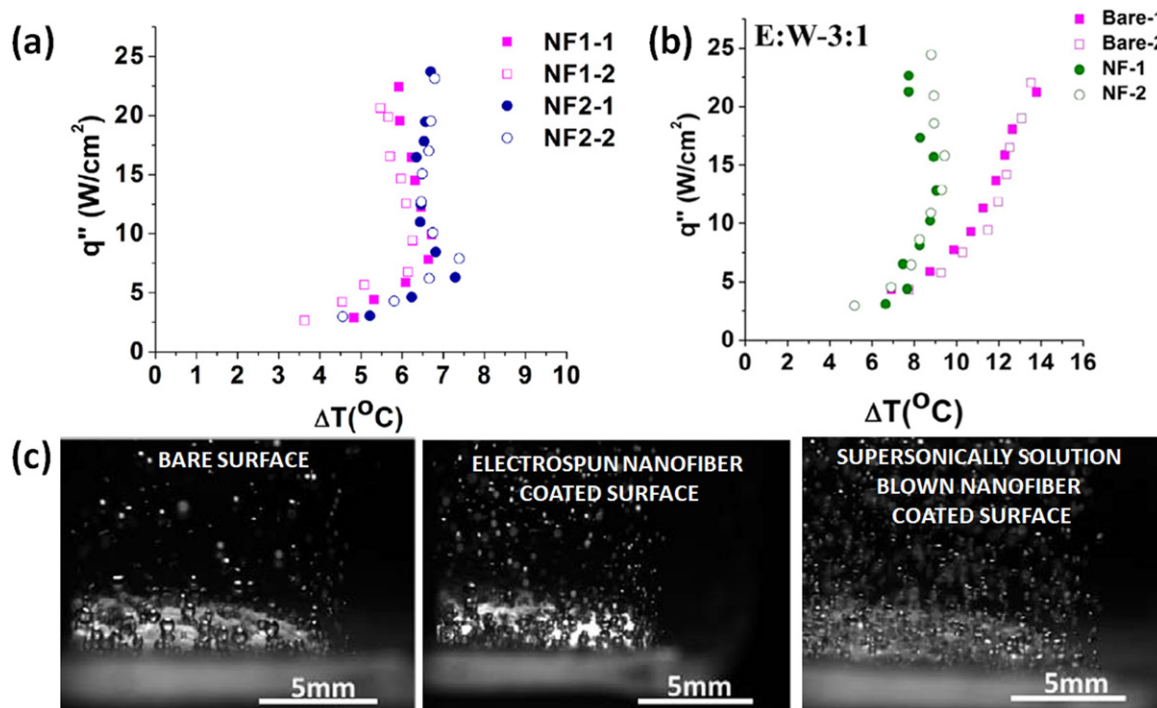


Fig. 6 (a) Pool boiling of ethanol on metallized supersonically solution blown nanofiber is shown for two different experiments. (b) Comparison of pool boiling of ethanol water mixture (3:1) on bare surface with metallized supersonically solution blown nanofiber is shown, where the same surface was used twice to do the experiments and the filled and open structure shows pool boiling done on same surface at two different times. (c) High speed images of pool boiling of Novec 7300 on bare surface, electrospun nanofiber coated surface and supersonically solution blown nanofiber coated surface are shown. It can be visibly seen that supersonically nanofiber coated surface creates the smallest sized bubble. Reproduced from (a–b) Sahu, R.P., Sinha-Ray, S., Sinha-Ray, S., Yarin, A.L., 2015. *Int. J. Heat Mass Transf.* 87, 521. (c) Sinha-Ray, S., Zhang, W., Sahu, R.P., Sinha-Ray, S., Yarin, A.L., 2017. *Int. J. Heat Mass Transf.* 106, 482.

temperature the boiling fluids feel near the surface is significantly higher than that of bare surface resulting in higher heat flux removal rate.

However, one of the big challenges of this work was that the electrospun nanofiber mats were delaminating making them difficult to use for long term application. To mitigate that supersonically solution blown nanofiber followed by copper plating was used (Sahu *et al.*, 2015, 2016). Firstly pool boiling of ethanol, water and their binary mixtures were studied for bare copper and nano-textured surfaces formed by supersonically solution-blown, copper-plated nanofibers (Sahu *et al.*, 2015). It was found that boiling curves measured on nanotextured surfaces revealed heat fluxes 2–7 times higher than those on the bare surfaces with the same surface superheat within the range of the heat flux supplied in the present work. Moreover, in several cases, such as pure ethanol and ethanol–water mixture (3:1), a hysteresis of the boiling curve was observed in pool boiling on nano-textured surfaces. Namely, as the heat flux at the surface was increasing, the surface superheat reached a maximum of 7.2°C and then started to decrease resulting in a backward turn of the boiling curve (Fig. 6(a–b)). The long pool boiling experiments of duration of 5–6 h, also repeated twice on the same nano-textured surface, showed that the surfaces did not delaminate from the underlying copper substrate or deteriorate, in distinction from the Jun *et al.* (2013). The surface was also used to study pool boiling of Novec FC 7300 fluid, pure water and self rewetting water–heptanol mixture (Sahu *et al.*, 2016). The heat flux (the heat removal rate) and the corresponding heat transfer coefficient were found to be higher on the copper-plated nanofiber surface. The pool boiling data for the self-rewetting fluid revealed a higher heat removal rate from the nano-textured surfaces than even the one for pure water. In all these works, copper plating was used, which may not be possible for lot of practical applications. As supersonically blown nanofibers are intrinsically extremely small in diameter in comparison to electrospun nanofiber, the characteristic time of response is fast and adheres strongly with the surface. Based on this logic, Sinha-Ray *et al.* (2017), used supersonically blown nanofiber to nanotexture the surface and studied the pool boiling characteristic of Novec 7300 and water. It was found that the supersonically-blown polymer nanofibers significantly enhanced the heat removal rate from the heater surface, especially in the case of Novec 7300 fluid where the maximum surface superheat was reduced by at least 7°C versus 5°C for the electrospun surface. The supersonically blown polymer nanofibers (diameter ~100 nm) facilitated bubble nucleation serving as active nucleation sites. Such nanofiber mats also possess a larger number of small pores than electrospun nanofibers, which cut and release the growing bubbles. Supersonically-blown nanofibers revealed the best adhesion to the copper substrate and retained their architecture after prolonged 7.5 h of boiling. The experiments conducted with DI water did not show as strong enhancement of the heat removal rate, as the experiments with Novec 7300 fluid did, even though compared to the bare copper surface, the surface superheat was

reduced on supersonically blown nanofibers by 1.7°C at the maximum heat flux after 8 h of boiling. Novec 7300 is a low surface tension fluid and the onset of heterogeneous nucleate boiling takes place at a lower surface temperature compared to DI water. Accordingly, in Novec 7300 fluid the size of vapor bubbles is smaller and thus affected by the nanotexture of the heater surface (Fig. 6(c)). DI water, on the other hand, possesses a high surface tension, and thus the onset of boiling takes place at a higher surface temperature. The larger bubbles in DI water are insignificantly affected by the surface nano-texture, and accordingly, the enhancement of heat removal is diminished in DI water compared to Novec 7300 fluid. It was also found that after boiling in DI water, electrospun nanofibers were completely delaminated from the copper substrate, unlike the supersonically-blown nanofibers which retained their adhesion and architecture.

Conclusion

Development in a society can be described almost like a double-edged sword. On one hand without growth, development is difficult to attain, whereas on the other hand the resources required to sustain growth results in depletion faster than the rate of replenishment resulting in unsustainable development. In this regard, ecological economist Herman Daly once asked, “what use is a sawmill without a forest?” Power is the key to our society’s development. In order to develop sustainably, there are dire needs for efficient utilization of available energy, which necessitates efficient thermal management across different applications. Nanomaterials for thermal management is an exciting area of research. While the development continues, the biggest challenge for efficient utilization of nanomaterials for thermal management is the price competitiveness. While microelectronics can afford the cost of nanomaterial based thermal management system, it can be hard for mass market application (e.g., construction industry, solar cell etc.) to handle the cost. In that regard, the researchers need to develop systems that are more cost effective. At the same time, as nanomaterial based thermal management system hold key to a lot of issues with efficient thermal management system. So, the policymakers also need to think of policies (e.g., incentives) to bring the technologies to fruition.

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Further Reading

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Natural Fiber and Synthetic Fiber Composites: Comparison of Properties, Performance, Cost and Environmental Benefits

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Introduction

Due to the limited natural resources, scientists are seeking new material that can replace heavy and expensive materials needed in product manufacturing. Based on this concept composite idea was originated and now composites have become a major research topic due to their versatile properties, applications as well as economic utilization of resources. The metallic materials have their own properties, whereas the composite properties are customizable according to the desire of customers through a specific fiber, fiber orientation, fiber volume and fiber modification. Due to this tailoring property, the interest on composite is highly increasing in automobile, aerospace, underwater and household accessories from small component to large component.

In composite, there are two components, namely fiber (reinforcing material) and matrix. The matrix material can be polymer, ceramics and metal. Depending on the end use, matrix materials are selected during composite fabrication. Depending on the available fiber form, reinforced materials are used in the composite. In the composite fiber can be in the form of particles, fiber as well as sheet or fabric. There are several methods to fabricate the polymer matrix composites. Compared to other popular methods, extrusion compounding and injection molding processes are commonly employed to fabricate polymer composites (Maity *et al.*, 2007). Thereafter, prepared composite are tested and the results are analyzed. If the obtained results are according to the desired expectation, the technology is transferred to the industries for manufacturing otherwise; again fiber modification is done so that they can be more widely used as shown in Fig. 1.

On the other hand, fiber can be natural and synthetic or man-made. However, in bio-composite, biodegradable natural fiber is used as reinforcing material and synthetic fiber is used as reinforcing material in case of the synthetic fiber composite. Matrix can be polymer (polyester, polypropylene, epoxy, polyethylene, polyvinyl chloride and so on), metal and ceramics. As natural fiber grows naturally, there is non-homogeneity in their property, whereas synthetic fibers are man-made whose properties are not varied widely. Important physico-mechanical properties of selected synthetic and natural fibers are listed in Table 1.

From Table 1, it is clear that the range of tensile properties for synthetic fibers is higher compared to natural fibers. Synthetic fiber such as glass, Kevlar also has different categories. These categories such as kevlar (29, 49, 100, 119, 129, 149, 981), carbon (type I and type II) and glass (A, C, D, E, R, S, ECR) are based on their properties. The tensile strength of glass fiber varies between 2900 and 3620 MPa. The maximum and the minimum value of tensile strength for glass fiber are listed as a range in Table 1. Similarly, in this article, the range for a criterion of an alternative presents the maximum and minimum value of respected criteria for a respected alternative. From Table 1, it is perceived that boron fibers are denser as compared to other fibers, however natural fibers are lighter indeed as well as perishable. Usually stronger and stiffer fiber is used in the composite to improve the performance. To obtain better performance for a particular application appropriate fiber and matrix selection is required.

In case of fiber selection for a composite, researcher or any industry first seeks for local fiber. For example, a scientist or entrepreneur of industry in Bangladesh will first try through jute, rice husk, banana, bamboo, and coir as they are easily available regarding bio-composite. On the other hand, sisal and abaca fibers are not available in this region. Thus, they try to will ignore these types of fibers during composite design. Furthermore, the matrix selection also depends on the matrix availability in the local market as well as price. However, matrix selection mainly depends on the final use that is composite properties, available fabrication methods, cost of labor and environmental consciousness. Some of the important criteria of commonly used selected polymer matrix material (for example thermosetting, thermoplastic and bio-degradable) are listed in Table 2. The polymer matrix material can be in the form of granule, palate, along with the liquid. Thermoplastic matrix polypropylenes (PP), low density polyethylene (LDPE) are available as granule and sheet whereas bio-degradable polylactic acid (PLA) is available as liquid and thin

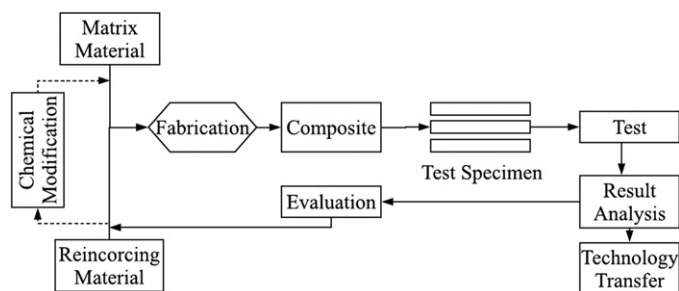


Fig. 1 Flow diagram of fiber reinforced composite development.

Table 1 Physico-mechanical properties of natural and synthetic fiber

	Fiber	Density (gm/cc)	Tensile strength (MPa)	Young's modulus (GPa)	References
Synthetic fiber	Aramid	1.40	300	124	(Pandita <i>et al.</i> , 2013)
	Kevlar (29)	1.30–1.44	2900–3620	70–83	(Yan <i>et al.</i> , 2014)
	Nylon	1.14	54	0.94–3	(Yan <i>et al.</i> , 2014)
	Glass (E)	2.50	2000–3000	70	(Célino <i>et al.</i> , 2014)
	Carbon	1.40	4000	230–240	(Célino <i>et al.</i> , 2014)
	Boron	2800	385	2.5–2.6	(Yan <i>et al.</i> , 2014)
Natural fiber	Jute	1.30–1.45	393–773	13–27	(Célino <i>et al.</i> , 2014)
	Coir	0.67–1.15	220	6	(Célino <i>et al.</i> , 2014)
	Banana	1.35	335	33.8	(Célino <i>et al.</i> , 2014)
	Bamboo	1.32	140–230	11–17	(Célino <i>et al.</i> , 2014)
	Sisal	1.45–1.50	67	3.7	(Célino <i>et al.</i> , 2014)
	Flax	1.54	28–85	0.3–2	(Célino <i>et al.</i> , 2014)

Note: Data were collected from Pandita, S.D., Yuan, X., Manan, M.A., *et al.*, 2013. Evaluation of jute/glass hybrid composite sandwich: Water resistance, impact properties and life cycle assessment. *Journal of Reinforced Plastics and Composites* 33 (1), 14–25. Yan, L., Chouw, N., Jayaraman, K., 2014. Flax fibre and its composites – A review. *Composites Part B: Engineering* 56, 297–317. Céline, A., Freour, S., Jacquemin, F., Casari, P., 2014. The hygroscopic behavior of plant fibers: A review. *Frontiers in Chemistry* 1, 43.

Table 2 Physico-mechanical properties of the thermoplastic, thermosetting and biodegradable polymer matrix

	Matrix	Density (gm/cc)	Tensile strength (MPa)	Young's modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	References
Thermoplastic	PP	0.89–0.92	32	0.9	35	1.0	(Yan <i>et al.</i> , 2014; Abraham and George, 2009)
	LDPE	0.89–0.92	29	0.20	0.09	0.1	
Thermoset	Polyester	1.20–1.50	20–40	3.3–3.9	45	3.3	–
	Epoxy	1.10–1.40	73	5	60	–	
Bio-degradable	PLA	0.90–1.27	25–66	2.3	48–110	0.3–3.6	

Note: Data were collected from Yan, L., Chouw, N., Jayaraman, K., 2014. Flax fibre and its composites – A review. *Composites Part B: Engineering* 56, 297–317. Abraham, T. N., George, K. E., 2009. Studies on recyclable nylon-reinforced PP composites: Effect of fiber diameter. *Journal of Thermoplastic Composite Materials* 22 (1), 5–20.

sheet. In addition, a thermosetting polymer such as polyester is available as fiber and liquid whereas epoxy is available as liquid only. From [Table 2](#), it is clear that the Young's modulus is lower for a thermoplastic matrix, whereas it is higher in case of thermosetting matrix materials.

Thermoset polymers are good for long fiber composite fabrication and from [Table 2](#), it can be concluded that thermoset polymers have high density (1.1–1.5 gm/cc), high tensile strength (20–73 MPa) and Young's modulus (3.3–5.0 GPa) as compared to thermoplastic and bio-degradable matrix materials. However, they need long curing time and difficult to recycle. On the other hand, thermoplastic polymers need short production time, are able to recycle and can be reused as well as good for short and discontinuous fiber composite fabrication. Nevertheless, thermoplastic resin has a high melting temperature and low strength. In addition, bio-degradable resins (such as PLA) are eco-friendly while have low strength, stiffness as well as required high production cost due to complexities in extraction ([Senthilkumar *et al.*, 2018](#)).

There are enormous researches regarding synthetic and natural fiber composites that put us in a precarious position regarding fiber selection of the composites based on the fabrication process, mechanical properties, cost, environmental effect as well as sustainability. In this article, a review is made on the natural and synthetic fiber composite, where matrix materials are polymer particularly, thermoplastic, thermosetting and bio-degradable. A review based on the properties, performance, cost, the environmental effect has been done. Section "Comparison of Properties" describes comparison among the properties of natural as well as synthetic fiber composites, Section "Performance of Natural and Synthetic Fiber Reinforced Polymer Composites" outlines the performance of natural and synthetic composite, cost of the composite is stated in Section "Cost of Composites" and finally, the environmental effect is deliberated in Section "Environmental Effect".

Comparison of Properties

Mechanical properties of natural fibers (such as jute, coir, bamboo, banana, sisal, flax fiber) and synthetic fibers (for example, nylon, glass, kevlar and carbon) are described in the previous Section. These fiber properties are modified when they are incorporated in the matrix to obtain the desired criteria of the composite. Sometimes the related fibers are chemically treated for better performance. Thermoplastic material needs to be heated at their melting temperature whereas curing material need to add for

Table 3 Mechanical properties of synthetic fiber polymer composites

Polymer	Fiber	Strength		Modulus		References
		Tensile (MPa)	Flexural (GPa)	Young's (MPa)	Flexural (GPa)	
PP	Kevlar	20–47	–	0.7–2.3	–	(Fu <i>et al.</i> , 2018)
	Nylon	30–35	37–45	1.3–1.5	1–1.3	(Abraham and George, 2009)
	Glass	40–90	85	2–7.5	13	(Sathishkumar <i>et al.</i> , 2014)
	Carbon	32–37	–	1–1.2	–	(Brandl <i>et al.</i> , 2004)
Polyester	Kevlar	159	95	8.7	2.2	(Yeung and Kamineni, 2014)
	Nylon	–	–	–	–	
	Glass	60–85	16–444	72	18.2	(Bindal <i>et al.</i> , 2013; Sathishkumar <i>et al.</i> , 2014)
	Carbon	–	–	–	–	
Epoxy	Kevlar	300–375	160–250	16–22	3–6	(Taraghi <i>et al.</i> , 2014)
	Nylon	7–18	42–48	0.7	–	(Narendar <i>et al.</i> , 2014; Meshram <i>et al.</i> , 2018)
	Glass	179–784	297	6.7–43	–	(Sathishkumar <i>et al.</i> , 2014)
	Carbon	20–100	550–850	6–70	4–72	(Hossein <i>et al.</i> , 2014)
LDPE	Kevlar	1500–1600	70–99	85–92	1.5–2.3	(Yeung and Rao, 2012)
	Nylon	–	–	–	–	
	Glass	45–90	15–27	1.5–2.5	–	(Jahan <i>et al.</i> , 2012)
	Carbon	12–30	–	0.22–0.41	–	(Khan <i>et al.</i> , 2008)
PLA	Kevlar	–	–	–	–	–
	Nylon	30–55	–	2–4	–	(Thongpin <i>et al.</i> , 2015)
	Glass	–	–	–	–	–
	Carbon	80–250	59–275	20	13	(Tian <i>et al.</i> , 2016; Li <i>et al.</i> , 2016)
Nylon	Glass	156–212	196–165	3–5	3.8–4	(Dickson <i>et al.</i> , 2017)
	Carbon	198	250	8.5	13.0	(Dickson <i>et al.</i> , 2017)
	Kevlar	110–161	106–125	4.2–4.8	4.5–6.6	(Dickson <i>et al.</i> , 2017)

Note: Data were collected from Fu, S., Yu, B., Tang, W., *et al.*, 2018. Mechanical properties of polypropylene composites reinforced by hydrolyzed and microfibrillated Kevlar fibers. *Composites Science and Technology* 163, 141–150. Abraham, T.N., George, K.E., 2009. Studies on recyclable nylon-reinforced PP composites: Effect of fiber diameter. *Journal of Thermoplastic Composite Materials* 22 (1), 5–20. Sathishkumar, P.S., Satheshkumar, T., Naveen, J., 2014. Glass fiber-reinforced polymer composites – A review. *Journal of Reinforced Plastics and Composites* 33 (13), 1258–1275. Brandl, W., Marginean, G., Chirila, V., Warschewski, W., 2004. Production and characterisation of vapour grown carbon fiber/polypropylene composites. *Carbon* 42 (1), 5–9. Yeung, K.K.H., Kamineni, P.R., 2014. Mechanical properties of boron and kevlar-49 reinforced thermosetting composites and economic implications. *Journal of Engineering Science* 10 (2014), 19. Bindal, A., Singh, S., Batra, N.K., Khanna, R., 2013. Development of glass/jute fibers reinforced polyester composite. *Indian Journal of Materials Science* 2013, 6, Article ID 675264. Taraghi, I., Fereidoon, A., Mohyeddin, A., 2014. The effect of MWCNTs on the mechanical properties of woven Kevlar/epoxy composites. *Steel and Composite Structures* 17 (6), 825–834. Narendar, R., Priya Dasan, K., Nair, M., 2014. Development of coir pith/nylon fabric/epoxy hybrid composites: Mechanical and ageing studies. *Materials and Design* 54, 644–651. Meshram, P., Sahu, S., Zahid Ansari, M., Mukherjee, S., 2018. Study on mechanical properties of epoxy and nylon/epoxy composite. *Materials Today: Proceedings* 5 (2), 5925–5932. Hossein, R., Heydar, S., Mahmoudi, N., Shohreh, S., 2014. Mechanical properties of carbon fiber/epoxy composites: Effects of number of plies, fiber contents, and angle-ply layers. *Polymer Engineering and Science* 54 (11). Yeung, K., Rao, K., 2012. Mechanical properties of Kevlar-49 fibre reinforced thermoplastic composites. *Polymers and Polymer Composites* 20 (5), 411. Jahan, A., Rahman, M.M., Kabir, H., *et al.*, 2012. Comparative study of physical and elastic properties of jute and glass fiber reinforced LDPE composites. *International Journal of Scientific and Technology Research* 1 (10), 68–72. Khan, M.R., Mahfuz, H., Kyriacou, A., 2008. Synthesis and characterization of low density polyethylene (LDPE) reinforced with functionalized CNTs. *Mechanics of Solids, Structures and Fluids* 12. Thongpin, C., Chaemprasith, K., Teeralertpanich, J., Saensuk, P., 2015. In situ reinforcement of PLA using Nylon 6 in PLA/Nylon 6 extrudate blend via twin-screw extrusion. *Key Engineering Materials* 659, 428–435. Tian, X., Liu, T., Qingrui, W., Ziegmann, G., 2016. Recycling and remanufacturing of 3D printed continuous carbon fiber reinforced PLA composites. *Journal of Cleaner Production* 142, 10. Li, N., Li, Y., Liu, S., 2016. Rapid prototyping of continuous carbon fiber reinforced polylactic acid composites by 3D printing. *Journal of Materials Processing Technology* 238, 218–225. Dickson, A. N., Barry, J. N., McDonnell, K. A., Dowling, D. P., 2017. Fabrication of continuous carbon, glass and Kevlar fibre reinforced polymer composites using additive manufacturing. *Additive Manufacturing* 16, 146–152.

thermosetting matrix material. The respected data for synthetic polymer composites are collected from different sources and represented them as a range in **Table 3**. Mechanical properties particularly tensile strength, flexural strength, Young's modulus as well as flexural modulus of synthetic fiber polymer composites are listed in **Table 3**.

From **Table 3**, it is observed that tensile as well as flexural properties have ranges. This is because to obtain better performance different researcher modified the fiber through different treatments. In addition, the researchers also modified the matrix (for example, PP is modified by maleic anhydride by grafting process), fabricate the composite using modified materials and obtained the modified results. Sometimes the advanced process (such as an advanced manufacturing process, 3D printing) was used for fabrication to attain better performance (Dickson *et al.*, 2017). In this article, mechanical properties of raw and modified synthetic fiber polymer matrix composites are listed as a range. The ranges of tensile strength, flexural strength, Young's modulus and flexural modulus for synthetic fiber polymer composites are 0.7–1600 MPa, 15–850 MPa, 0.7–92 GPa, and 1–18 GPa respectively.

Mechanical properties of natural fiber polymer composites are listed in **Table 4**. Usually, mechanical properties of the composites change with the volume fraction of the fiber. However, in this article, only maximum value and the minimum value of a particular criterion have been considered ignoring the volume fraction of the fiber and represented them as a range. Moreover, different authors use different standard methods (ASTM) to measure the mechanical properties which are not highlighted in this article. Sometimes synthetic fibers are chemically modified to attain desirable properties.

Table 4 Mechanical properties of natural fiber reinforced polymer composites

Properties		Strength		Modulus		References
Matrix	Natural fiber	Tensile (MPa)	Flexural (MPa)	Young's (GPa)	Flexural (GPa)	
PP	Jute	15–51	15–58	1.5–4.5	0.8–5	(Rahman <i>et al.</i> , 2008; Nahar <i>et al.</i> , 2012)
	Coir	22–30	46–60	1–4.5	1.5–4.2	(Haque <i>et al.</i> , 2010; Siddika <i>et al.</i> , 2014)
	Banana	11–24	36–42	0.4–0.9	1–2.3	(Mishra <i>et al.</i> , 2000)
	Bamboo	24–63	38–80	0.5–1.77	1.6–6.3	(Chattopadhyay <i>et al.</i> , 2010; Nahar <i>et al.</i> , 2012)
	Sisal	20–30	30–60	–	–	(Jayaraman, 2003)
Polyester	Jute	50–95	80–135	6–7	4–6	(Sever <i>et al.</i> , 2012)
	Coir	18–47	5–69	2.24	2.14	(Rout <i>et al.</i> , 2001)
	Banana	12–23	76–125	–	–	(Dhakal and Keerthi Gowda, 2017)
	Bamboo	20–126	128	1–3	3.7	(Wong <i>et al.</i> , 2010; Prasad and Rao, 2011)
	Sisal	20–60	50–100	0.5–2	1.5–3	(Prasad and Rao, 2011)
LDPE	Flax	85–277	135–239	8.7–23.4	–	(Pozo Morales <i>et al.</i> , 2017)
	Jute	31–55	31.8	0.3–1.75	1.4	(Jahan <i>et al.</i> , 2012)
	Coir	12	18	0.7	0.8	(Prasad <i>et al.</i> , 2018)
	banana	11–14	15–2	0.4–0.9	0.2–5.4	(Jordan and Chester, 2017; Prasad <i>et al.</i> , 2018)
	Bamboo	74–126	119–128	2.4	3.7	(Abdul Khalil <i>et al.</i> , 2012)
Epoxy	Sisal	6–13	–	0.07–0.1	–	(Ahmad and Luyt, 2012)
	Flax	13–41	–	3000–4000	–	(Joseph <i>et al.</i> , 1999)
	Jute	30–105	10–55	30–32	17–19	(Biswas <i>et al.</i> , 2015)
	Coir	3.2–13	25–35	1.3–2.6	–	(Zhang <i>et al.</i> , 2018)
	Banana	45	75	1.9	1.85	(Arthanarieswaran <i>et al.</i> , 2014)
PLA	Bamboo	86–99	99–127	4.2–6.7	1.1–8.0	(Kushwaha and Kumar, 2009)
	Sisal (mat)	250–400	150–325	5–10	8–30	(Rong <i>et al.</i> , 2001; Gupta and Srivastava, 2014)
	Flax	115–383	130–300	16–35	–	(Pozo Morales <i>et al.</i> , 2017)
	Jute	50–60	35–100	0.4–1.6	2.5–3.7	(Ma and Joo, 2010)
	Coir	53–73	20–58	1.4–1.7	1.4	(Sun <i>et al.</i> , 2017)
	Banana	46–78	50–300	0.9–4.7 (nano)	3–7.8	(Shih and Huang, 2011)
	Bamboo	230	250	38	–	(Pozo Morales <i>et al.</i> , 2017)
	Sisal	53–58	50–80	–	3–6	(Li <i>et al.</i> , 2011)
	Flax	44–107	–	6.3–8	–	(Pozo Morales <i>et al.</i> , 2017)

Note: Data were collected from Rahman, M.R., Huque, M.M., Islam, M.N., Hasan, M., 2008. Improvement of physico-mechanical properties of jute fiber reinforced polypropylene composites by post-treatment. *Composites Part A: Applied Science and Manufacturing* 39 (11), 1739–1747. Nahar, S., Khan, R.A., Dey, K., *et al.*, 2012. Comparative studies of mechanical and interfacial properties between jute and bamboo fiber-reinforced polypropylene-based composites. *Journal of Thermoplastic Composite Materials* 25 (1), 15–32. Haque, M., Islam, M.N., Haque, M., *et al.*, 2010. Coir fiber reinforced polypropylene composites: Physical and mechanical properties. *Advanced Composite Materials* 19 (1), 91–106. Siddika, S., Mansura, F., Hasan, M., Hassan, A., 2014. Effect of reinforcement and chemical treatment of fiber on the properties of jute-coir fiber reinforced hybrid polypropylene composites. *Fibers Polymer* 15, 1023. Mishra, S., Naik, J., Patil, Y., 2000. 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From different studies, it is found that tensile strength of the composites increases when the reinforcing materials are mat, fabrics, nano form or due to new additive fabrication method. From [Table 4](#), it is observed that flexural strength and modulus of natural fiber polymer composite is higher as compared to tensile strength and Young's modulus respectively. Mechanical properties of the composites vary according to the matrix material as well as fiber reinforcing material. Natural fiber PP composite showed better tensile strength as compared to natural fiber polyester composites. In addition, natural fiber low density polyethylene composites show less mechanical properties compared to natural fiber polypropylene composites. However, natural fiber polylactic acid composites perform satisfactorily regarding mechanical properties, as shown in [Table 4](#).

According to [Tables 3](#) and [4](#), mechanical properties of synthetic and natural fiber polymer composites are different. In the case of natural fiber, diameter is different in different regions, thus the cellulose and other contents are also different. As a result, fiber properties are also varied and hence composite properties is varied. In the case of synthetic fiber, this variation is less compared to the natural fiber. Though mechanical properties of natural fiber polymer composites are lower they are partially or fully biodegradable compared to synthetic fiber polymer composites except for natural fiber biodegradable polymer composites. From [Tables 3](#) and [4](#) it is observed that, mechanical properties of synthetic fiber polymer composite are higher for a specific matrix material. For example, the range of tensile strength for synthetic fiber polypropylene composite is 20–1600 MPa, whereas that of natural fiber polypropylene composite is 3.2–277 MPa. That means synthetic fiber polymer composites have wide range of tensile strength. Similar phenomenon is also found for other properties.

Performance of Natural and Synthetic Fiber Reinforced Polymer Composites

In this Section, performance of natural as well as synthetic fiber polymer composites is highlighted. The adhesion between the interface of the fiber and matrix leads the performance of the composites. Natural fibers are cheap, eco-friendly, lightweight, as well as competitive with synthetic material regarding material properties. To increase the performance of the bio-based fiber composite the raw material such as fiber and matrix material are chemically or physically modified. The performance of the natural and synthetic fiber polymer composite is shown in [Table 5](#) at different artificial damage conditions (such as a hole, indentation, thermal aging, moisture and weathering).

From [Table 5](#), it can be stated that the performance of natural fiber composite is better as compared to synthetic fiber composites. The loss of tensile strength is less in case of natural fiber polymer composites as compared to synthetic fiber polymer composites. However, due to gamma radiation the performance of natural fiber polymer composite has enhanced. The Young's modulus of synthetic fiber polymer composite shows a higher range as compared to natural fiber polymer composites. Due to time-bound other polymer and fiber matrix performance is not collected. Usually, Due to different treatments on the fiber as well as matrix increase the interfacial adhesion. As a result, the performance of the composite is increased. High-performance fiber leads the high performance polymer composite industries. That means in the case of natural fiber the adhesion may be better compared to synthetic fiber polymer composites. Some of the polymer matrix composites perform satisfactorily in the aerospace and navy where performance of the polymer composite properties (strength, stiffness, and resistance to the hostile environment) are controlling factor. In addition, some application composite needs to sustain at high temperature where bio-based polymer composites will not perform satisfactorily. Thus, it is desirable to improve the performance of the composite regarding the reinforcing properties. To improve the performance it is needed to align the molecule of fiber along the fiber axis compared to randomly oriented fiber. A good number of scientists are involved in improving the performance of the composite by different treatments. Performance (strength and Young's modulus) of natural fiber polymer composite in an outdoor environment is influenced by different factors such as moisture, temperature, ultraviolet radiation and microorganism activities. The natural fibers have

Table 5 Mechanical performance of natural and synthetic fiber polymer composites

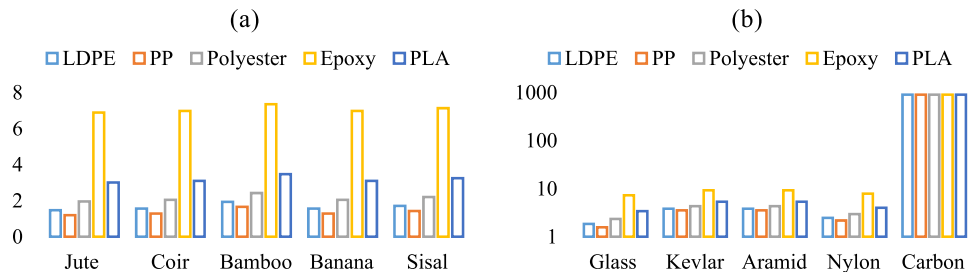
Matrix	Fiber	Tensile strength performance (%)	Young's modulus performance (%)	Condition	References
PP		27–35↓	11–20↓	Artificial damage	(Rawal and Sayeed, 2013)
PP	Jute	14–46↓	6–62↓	Artificial damage	(Rawal and Sayeed, 2013)
PP	Silk	1–10↑	5.55–16.66↑	Gamma radiation	(Shubhra <i>et al.</i> , 2010)
	Silk	4–10↓		Thermal aging	(Shubhra <i>et al.</i> , 2010)
	Silk	1.81–12.72↓		Soil condition	(Shubhra <i>et al.</i> , 2010)
	Silk	15–28↓		Weathering	(Shubhra <i>et al.</i> , 2010)
	Viscose	21–84↓		Artificial damage	(Rawal <i>et al.</i> , 2013)
PP	Viscose	28–66↓		Artificial damage	(Rawal <i>et al.</i> , 2013)
Epoxy	Jute			Artificial damage	(Pandita <i>et al.</i> , 2013)
	Glass			Artificial damage	(Pandita <i>et al.</i> , 2013)

Note: Data were collected from Rawal, A., Sayeed, M., 2013. Mechanical properties and damage analysis of jute/polypropylene hybrid nonwoven geotextiles. *Geotextiles and Geomembranes* 37 (2013), 54–60. Shubhra, Q.T.H., Alam, A.K.M.M., Khan, M.A., Saha, M., 2010. Study on the mechanical properties, environmental effect, degradation characteristics and ionizing radiation effect on silk reinforced polypropylene/natural rubber composites. *Composites Part A: Applied Science and Manufacturing* 41 (11), 1587–1596. Rawal, A., Patel, S.K., Kumar, V., Saraswat, H., Alamgir Sayeed, M.M., 2013. Damage analysis and notch sensitivity of hybrid needlepunched nonwoven materials. *Textile Research Journal* 83 (11), 1103–1112. Pandita, S.D., Yuan, X., Manan, M.A., *et al.*, 2013. Evaluation of jute/glass hybrid composite sandwich: Water resistance, impact properties and life cycle assessment. *Journal of Reinforced Plastics and Composites* 33 (1), 14–25.

Table 6 Cost of synthetic and natural fiber in the context of Bangladesh

Categories	Description	Market price BDT(USD)	Categories	Description	Market price BDT (USD)	References
Synthetic fiber	Glass mat	165/kg (\$1.97)	Matrix material	LDPE	150.76/kg (\$1.8)	(Alibaba.com, 2018)
	Kevlar	711/kg (\$8.5)		PP fiber PP granule	159.00/kg (\$1.9) 117.26/kg (\$1.4)	
	Aramid	3350/kg (\$0)		Polyester	209/kg(\$2.5)	
	Nylon	335/kg (\$4)		Epoxy	800/kg(\$9.55)	
	Carbon	251,280/kg (\$3000)		PLA	335/kg (\$4)	
Natural fiber	Jute fiber	58/kg (\$0.7)	Matrix material	Banana fiber	83.76/kg (\$1.0)	
	Coir fiber	83.76/kg (\$1.0)		Sisal fiber	125/kg (\$1.5)	
	Bamboo fiber	188/kg (\$2.25)				

Note: Data were collected from Alibaba.com, 2018. www.alibaba.com. (Online) Available at: https://www.alibaba.com/trade/search?fsb=y&IndexArea=product_en&CatId=&SearchText=pp+granule&viewtype= (accessed 09.11.18).


Fig. 2 Cost of (a) natural and (b) synthetic fiber composite (30/70) in dollar (US\$).

better performance compared to synthetic fibers as well as their composites. Moreover, natural fibers emit oxygen and absorb CO₂ in the air while synthetic fibers emit CO₂ only. Synthetic fibers have a severe environmental impact as they need fossil fuels for primary production whereas natural fibers have better environmental performance because they consume solar energy and few fossils. Last but not least, high performance synthetic fiber composites are used in high speed and precision machinery, robotics and structural material.

Cost of Composites

One of the important reasons for increased use of natural fiber is its cheap price as compared to synthetic fiber. The price list of the bio-based fiber as well as the synthetic fiber is given in Table 6. From Table 6, it is clear that the synthetic fibers are 4–3000 times more expensive than the natural fiber. The elongation properties of polyester and epoxy gradually increased and due to this incremental property, their price is also gradually increased as shown in Table 6.

As natural fibers are of low density, the transportation cost of the natural fiber is less as compared to synthetic fiber. In addition, due to the cheap price of the natural fiber when they are incorporated in the matrix, the price of the composite will be cheaper compared to synthetic fiber polymer composites. A comparison between the fabrication cost of natural fiber (jute, coir, bamboo and banana) polypropylene composites as well as synthetic fiber (glass, kevlar, nylon, and carbon) polypropylene composite sis shown in Fig. 2. For cost estimation, the prices of PP, natural fibers as well as synthetic fibers are considered according to Table 6.

From Fig. 2, it is clear that the raw material price to fabricate a 30/70 natural fiber polymer composite is lower as compared to synthetic fiber polymer composite. For natural fiber, the price lies between \$1.5 and \$7.8, whereas it lies between \$1.5 and \$906 for synthetic fiber polymer composite. In this article, five types of natural fiber, synthetic fiber as well as polymer matrix are considered for cost estimation. The cost of the bio-fiber polymer composite is reduced compared to synthetic fiber composite by a certain percentage which cannot be ignored as shown below.

Case I: Cost analysis for 1:3 fiber ratio of Glass PP composite in the contest of Bangladesh

Cost of glass fiber = \$1.3

Cost of PP = \$0.42

When 30% glass incorporated in the PP the cost of raw material is = \$1.799.

Case II: Cost analysis for 1:3 fiber ratio of Jute PP composite in the contest of Bangladesh

Cost of Jute fiber = \$0.21

Cost of PP = \$0.42

When 30% jute fiber is incorporated in the PP, the total cost of raw materials is = \$0.63

Thus, the reduction of cost (\$) due to bio-fiber incorporation in the composite is = 64.98%.

Based on the above contemplation it can be concluded that 30% incorporation of natural fiber, jute fiber, in the PP matrix, total 64.98% cost will be reduced. In addition, the total price of the composite will be reduced depending on the percentage of bio fiber loading. Similarly, the price will be reduced when any bio-based fiber incorporates in any other natural or manmade polymer matrix. No other cost rather than the cost of raw materials is considered during composite cost estimation.

Environmental Effect

Natural fiber has a great impact on the environment. Natural bio-based fibers emit oxygen and absorb CO₂ during the primary fiber production. Thus, CO₂ foot print of the natural fiber is lower and they have a good impact on the composite life cycle as shown in Fig. 3. The primary material namely, fiber, is used in the composite that will be further used in the manufacturing of products. After the consumption of that product, they are recycled. When no longer recyclable it will be used as a land filled for disposal. This disposed material will be consumed by the green plant to maintain the eco-system. If there is only synthetic fiber in the composite material this life cycle will be hampered.

On the contrary, synthetic fibers emit huge CO₂ during primary material production as well as product manufacturing, which have bad impact on the green globalization. CO₂ foot prints of natural as well as synthetic material are listed in Table 7. From Table 7, it is detected that CO₂ foot print of natural fiber is lower as compared to the synthetic fiber. Though natural fibers have

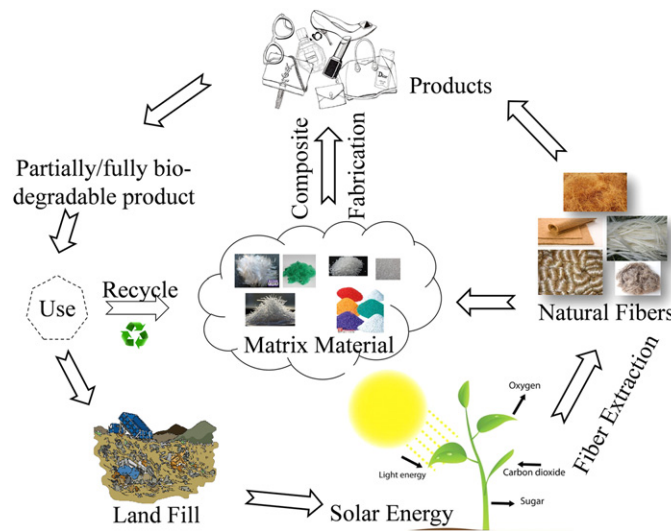


Fig. 3 Natural fiber composite life cycle.

Table 7 CO₂ foot prints of natural fiber, synthetic fiber and polymer matrix material

	Fiber	CO ₂ foot print (kg-CO ₂ /kg)	References
Natural fiber	Jute	0.566	(Singh <i>et al.</i> , 2018)
	Coir	0.367	(Grasselly <i>et al.</i> , 2009)
	Flax	0.520	(Singh <i>et al.</i> , 2018)
Synthetic fiber	Glass	0.85	(Patty and Anne, 2004)
	Glass fiber	1.45	(Anon, 2012)
	Glass composite	8.1	
Polymer materials	Polyester	0.00952	(Patty and Anne, 2004)
	PP	1.4	(Narita <i>et al.</i> , 2002)
	PE	1.3	(Narita <i>et al.</i> , 2002)
	Epoxy	5.7	(Anon, 2012)
	PLA	4.7 ± 1.5	(Patty and Anne, 2004)

Note: Data were collected from Singh, A., Mukesh, K., Mitra, S., 2018. Carbon footprint and energy use in jute and allied fibre production. Indian Journal of Agricultural Sciences 88, 1305–1316. Grasselly, D., Hamm, F., Quaranta, G., Vitrou, J., 2009. Carbon footprint of coconut fibre (coir) substrates. Infos-Ctiifl 249, 55–59. Patty and Anne, L., 2004. O Ecotextiles. (Online) Available at: <https://oecotextiles.wordpress.com/category/fibers/pla-or-polylactic-acid/> (accessed 13.11.18). Anon, 2012. Carbon Footprint Assessment Alternative Sites Assessment and Route Selection Report (Phase 2), Dublin: Greater Dublin Drainage. Available at: http://www.greaterdublindrainage.com/wpcontent/uploads/2012/05/ASA_Phase2_Main_Report.pdf?fbclid=IwAR06gdOLxmuf_0Cc5GUUTv7A4U5DbtHzDG_9YK_W4h04kd8x23tFb0ZW3k. Narita, N., Sagisaka, M., Atsushi, I., 2002. Life cycle inventory analysis of CO emissions manufacturing commodity plastics in Japan. The International Journal of Life Cycle Assessment 7 (5), 277–282.

CO₂ foot print, they absorb CO₂ as well as emit oxygen that has a good impact on the green globalization. Furthermore, bio-based materials are naturally bio-degradable while synthetic materials are not bio-degradable except bio-degradable man-made fiber and matrix material. In addition, health hazard condition occurs during the production of the synthetic composite. However, natural fibers have OH group which leads them to biodegrade and due to this property, they show dimensional instability, anisotropic behavior as well as low thermal behavior (Célino *et al.*, 2014).

Furthermore, when the reinforcing materials are incorporated in the matrix, in case of natural fiber OH group reacts with the matrix material and the related compound is formed. Due to this OH group, the bio-based composites are hydrophobic and they absorb moisture from the air and the interfacial bond between the fiber and matrix degrade after a certain time. Moreover, as synthetic fibers require fossil, their cost is higher compared to natural fiber. Last but not least; natural fibers will increase manpower in the developing country as well as the climate without hampering the green globalization.

Conclusion

A review of properties, performance, cost and environmental benefits for natural and synthetic fiber reinforced composites is conducted in present article. Both natural and synthetic fiber composites have a wide range of mechanical, thermal and other properties. In comparison, synthetic fiber composites generally have better properties. However, natural fiber reinforced composites showed better performance and the cost of producing natural fiber composites is much lower as compared to that of synthetic fiber reinforced composites. Natural fiber reinforced composites also have better impact on environment as compared to the synthetic fiber reinforced composites.

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Natural Indigo for Textiles: Past, Present, and Future

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Introduction

Colorants including both dyes (which are water-soluble) and pigments (which are water-insoluble) from natural sources, particularly from the plants, have a long tradition throughout world history until the invention of synthetic dyes in 1856 in England. They can be extracted from the whole plant (e.g., weld), the leaves (e.g., woad, indigo species), the roots (e.g., madder), the flowers (e.g., saffron), the fruits (e.g., common buckthorn), the shell (e.g., Persian nut), the bark (e.g., oaks), or the skin (e.g., onions) (Cardon and du Chatenet, 1990). Tyrian purple, one of the most exquisite shades of purple, which had dominated the luxurious works of artists and served as a status symbol for the Royals throughout the history, used to come from the Phoenician city of Tyre (presently a part of Lebanon) and was obtained from sea snails of the Murex family. Chemically it was a complex mixture of indigoid colorants and was rare and exclusive, therefore, it was used to imitate the Tyrian purple to achieve similar shades using other colorants (Cardon, 2009). Examples of these imitations were described in the Babylonian and Egyptian texts, such as the dyeing of wool in two steps, first with woad or indigo, then with madder and extracts of certain insects (Cardon, 2007). Interestingly, Tyrian purple and indigo have very similar chemical and physical properties and both of them belong to the same class of colorants known as vat dye (Clark *et al.*, 1993).

Indigo is a fascinating blue colorant that has always been adored throughout the whole world due to its brilliance and stability of the hue it produces when applied on textiles. The best source of color-fast blue dyes is indigo plants (see Fig. 1), scattered in many different botanical families found in many diverse natural environments (Balfour-Paul, 1998). It is obtained as an insoluble pigment from the leaves of indigo plant and has to be chemically converted into water-soluble dye for use in textile coloration (John *et al.*, 2019). The predominant sources of natural blue dyes are included in Table 1. Indigo (*Indigofera tinctoria*) is a plant of tropical climate. However, in Europe blue colorant was obtained from another plant of a related family, locally available woad (*Isatis tinctoria*), to imitate the most prestigious antique color of purple (Cardon, 2009). The variety of indigo plants provides different shades of blue due to the presence of different side components in its chemical structures; therefore, a distinction between different sources is easily possible. Today the synthetic indigo is the most predominant dyestuff in use with approximately thousands of tons produced annually due to the popularity of denim industry (Roessler *et al.*, 2002; Głowacki *et al.*, 2012; Buscio *et al.*, 2014; Chavan, 2015). However, this article will focus on natural indigo only.

Historical Background

Archeological evidence shows that indigo had been used for more than 4000 years in India, Egypt, and China. Wherever the indigo bearing plants were available, the ancient inhabitants found a way to extract colorant from the plants for use in coloration of

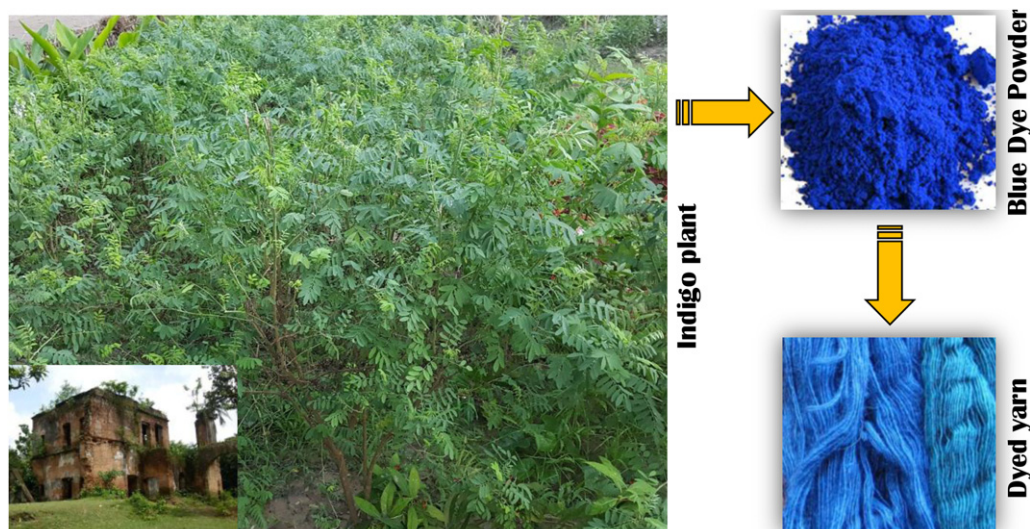


Fig. 1 Indigo plant for natural colorant extraction. Pictures taken from a ruined Indigo factory (inset) in Bhatpara, Gangni, and Meherpur, Bangladesh; built in 1778 during British rule of India.

Table 1 Sources of major natural blue colorants from plant species

Plant species: Botanical name	Plant species: Common name	Origin	Reference
<i>Isatis tinctoria</i> L.	Woad	Europe	(Biertmpfel and Wurl, 2009)
<i>Periscaria tinctoria</i> (old name <i>Polygonum tinctorium</i>)	Polygonum or Japanese indigo	Northern/Central Italy, Germany, Japan, China, Korea	(Biertmpfel and Wurl, 2009; John and Angelini, 2009; Maier <i>et al.</i> , 1990)
<i>Indigofera tinctoria</i>	Indigo, <i>Nila</i>	Tropical countries in Asia such as Indian subcontinent, China, Thailand, Malaysia, Cambodia, Laos, Philippines, Myanmar, Indonesia, India, Pakistan, Sri Lanka, America, and Africa	(Linh, 2009)
<i>Indigofera argentea</i>	–	Egypt (e.g., Nubia, Kordofan, Sennar), Abyssinia	(Melo, 2009)

different objects including textiles. Although there are different plants other than indigo that provide blue colorant, it is interesting that indigo gained the most popularity, even in ancient times, despite the complex way of extracting and developing this color on textiles that needed to be followed (Clark *et al.*, 1993).

Indigo has been used for various purposes other than textile dyeing, for example, as a medicinal substance in the Middle East, as ingredients of cosmetics including hair dye and skin ointment, and as religious symbolism in Judaism (Scholem and Margulies, 1980). It was used in India in the protohistoric city of Mohenjodaro in the Middle to Bronze Ages of the second millennium BCE. In fact, the word *indigo* derived from the Greek word *indikou* or Latinized *indicum*, which refers to a substance from India. The cultivation of blue dye bearing plants from local sources had been established in various parts of the world, and a network of trade had been established to import of those blue dyes in the West to meet the growing demand in terms of both quantity and quality. Natural indigo pigment was a very rare commodity in Europe until 14th century in oppose to the available blue color from indigenous woad, which was inferior in quality compared with that of Indian indigo. Anti-indigo sentiment was very powerful among the woad growers in Europe, which led to describe it as “devil’s food or devil’s dye” with restriction of use in several European countries (Clark *et al.*, 1993).

The history of indigo has direct relation with the colonization by the European settlers throughout Asia and Africa, and in particular with the emergence of commercial plantation in the colonies from the 17th century. Large-scale cultivation started in the Caribbean and Central and South America under direct supervision of the European planters with the use of cheap labor in the form of slavery (Kumar, 2012). Although India was famous for tropical indigo plants (Gittinger, 1982) and central to the early history of indigo (Balfour-Paul, 1998), it was nowhere in the international map until the British imperial rule resurrected the plantation due to the shortage of indigo supply sourced from other parts of the world. The plantation in Bengal (presently divided into Bangladesh and West Bengal of India) was a no-brainer due to the then British rule and rich climate suitable for indigo plant; however, it took a relatively long time to start due to priority trials in various parts of India, such as Madras and Bombay, where it was not successful. In fact, from the beginning of the 19th century Bengal emerged as the leading supplier of indigo to the world (Kumar, 2012) and remained as the last frontier of natural indigo cultivation before the advent of synthetic dyes. Over time indigo manufacturing geographically pivoted into lower Bengal in the subcontinent (see Fig. 2), and attracted 20.26 million rupees of capital with a direct and indirect employment of 1.36 million in the 19th century (Ray, 2004). The fate of natural indigo is directly linked with the fate of Bengal peasants, who were forced to plant indigo. Although indigo cultivation was native to the Bengal, the commercial scale plantation was more of a colonial enterprise to meet the extensive demand in Europe. As a result, a movement by the peasants against the planters took place between 1859 and 1862, which is known as the “indigo rebellion” or “blue mutiny” and wiped out the entire indigo industry from lower Bengal to North Bihar (Kumar, 2012).

Indigo Production

Blue colorants come from different indigenous varieties of plants. In India, this comes from the *indigofera tinctoria*, while in Europe it comes from *Isatis tinctoria* (see in Fig. 3). There are about 250–300 species of *Indigofera* across the world but not all species yield dye. *Indigofera tinctoria* produces superior quality dye to any other species (Clarke, 2004) and it is, therefore, also referred to as “true indigo” (Teanglum *et al.*, 2012). Good quality indigo colorant from the Bengal contains as high as 60% indigo pigment (Clark *et al.*, 1993).

Indigofera tinctoria L. species have straight branches approximately 1 m in height and grow in a bush. The leaves are long, egg-shaped, and arranged in double alternate within the branch. The branches are 1.5 to 2.5 cm long, thin, and narrow at the stem. The flowers grow in cluster and are white and purple in color. The *indigofera* seeds are planted from February to May and harvested from August to October (Reid, 1887). After harvesting, if the roots are left, new plant will continue to grow. *Indigofera* sp. is a leguminous plant, whose roots are rich in nitrogen. Thus it can be used as a rotational crop that enriches the soil for paddy production (Balaram, 2011). Extraction of indigo involves dipping the leaves at the right temperature with fermentation and reduction process to allow the indigo precursors to leach out of the leaves. To give an estimation, from 100 kg of plant leaves, 3 kg of indigo powder can be produced, which contains 300–400 g of indigo pigment (Linh, 2009). The amount of dye that can be obtained from woad is much less than that from *Indigofera* species (Clark *et al.*, 1993). According to Perkin (1900), a good sample of indigo contains 61.4% indigo blue, 7.2% indigo red, 4.6% indigo brown, 1.5% indigo gluten, 19.6% mineral, and 5.7% water.

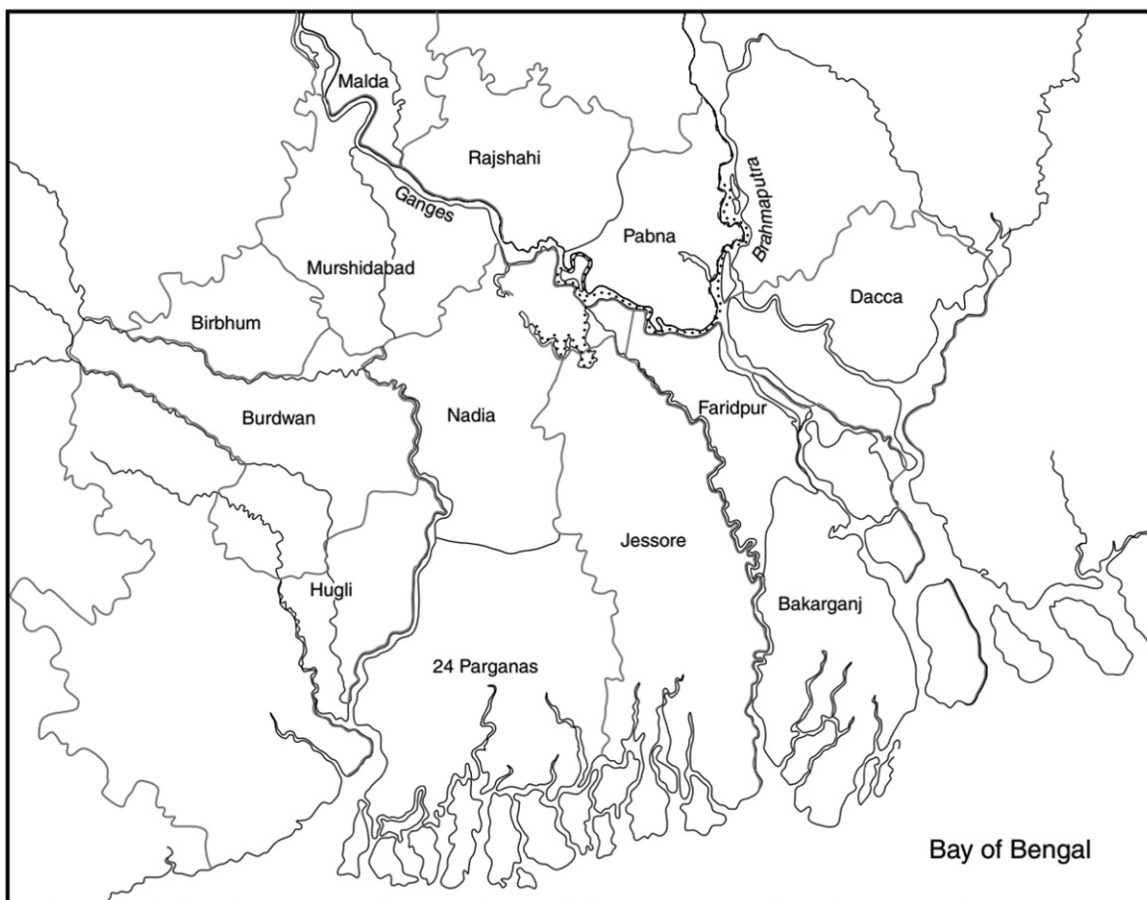


Fig. 2 Indigo manufacturing districts in Bengal in the undivided Indian subcontinent during the early 19th century. Reproduced from Kumar, P., 2012. The odyssey of indigo. Indigo Plantations and Science in Colonial India. New York: Cambridge University Press, 1–24. doi:[10.1017/CBO9781139150910.002](https://doi.org/10.1017/CBO9781139150910.002).

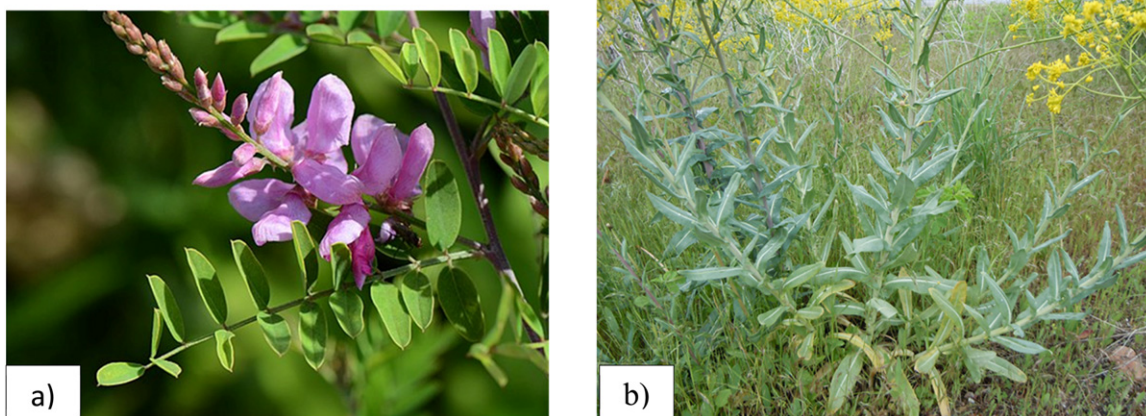


Fig. 3 The species of indigo (a) *Indigofera tinctoria* (b) *Isatis tinctoria*. Source: Wikimedia with creative common license.

Indigo Chemistry and Traditional Coloration Process

Indigo, like any other natural dyes, does not come in a ready to use state from the plant. It belongs to a class of vat dyes, which are insoluble in their natural state. It is one of the most light-stable organic dyes, which explains its wide use throughout the history (Sousa *et al.*, 2008; Melo, 2009). The structure of indigo can be reduced to form leuco-indigo, which is almost colorless (see Fig. 4; Cardon and du Chatenet, 1990; Clark *et al.*, 1993). Indigo is also known as indigo blue and indigotin (C.I. Vat Blue 1, C I 7300,

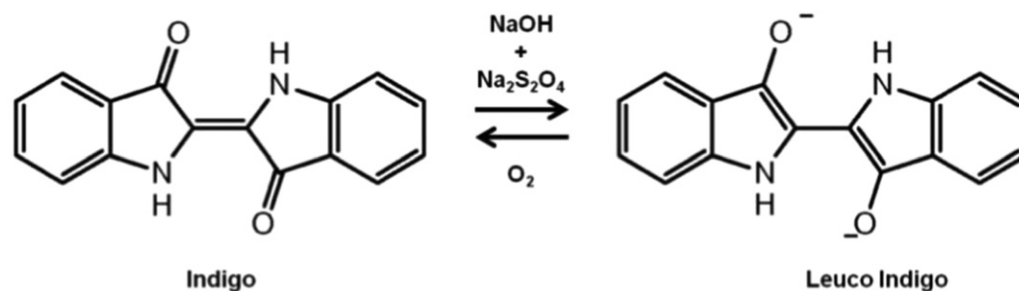


Fig. 4 Insoluble indigo (=indigotin) and leuco-indigo. Reproduced from Cardon, D., 2009. Colors in civilizations of the world and natural colorants: History under tension. In: Bechtold, T., Mussak, R. (Eds.), Handbook of Natural Colorants. first ed. Chichester: John Wiley & Sons, Ltd., 21–26. doi:10.1002/9780470744970.ch2.

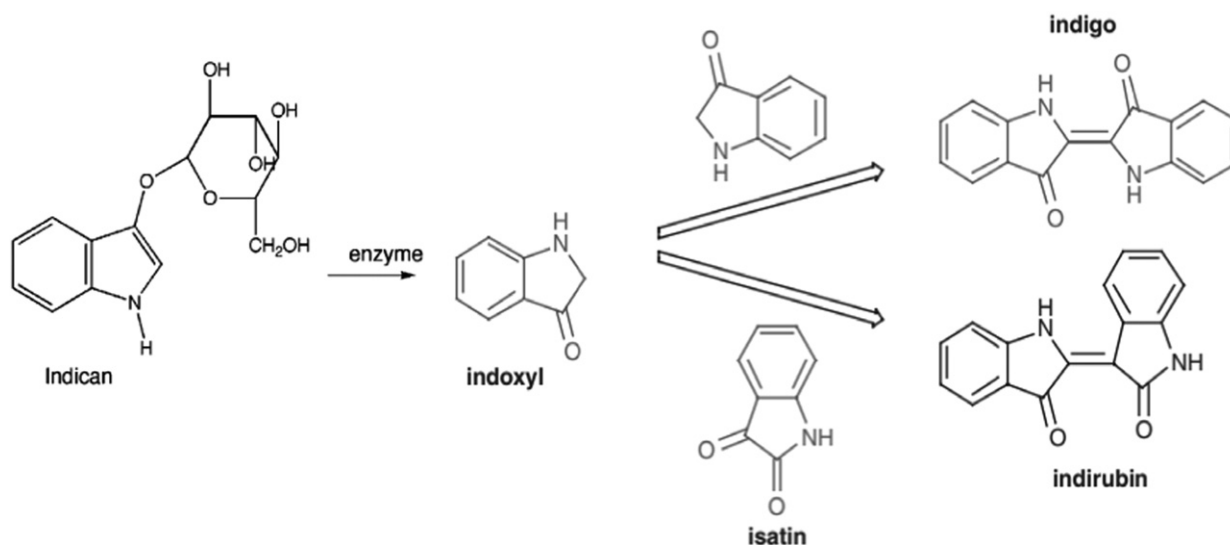


Fig. 5 Indigo transformation in dye-bath. Reproduced from Cardon, D., 2007. Natural Dyes: Sources, Tradition, Technology and Science. London: Archetype. Available at: <https://www.worldcat.org/title/natural-dyes-sources-tradition-technology-and-science/oclc/751145775> (accessed 17.03.19). Melo, M., 2009. History of natural dyes in the ancient mediterranean world. In: Bechtold, T., Mussak, R. (Eds.), Handbook of Natural Colorants. first ed. Chichester: John Wiley & Sons, Ltd., 1–20. doi:10.1002/9780470744970.ch1. Glowacki, E.D., Voss, G., Leonat, L., *et al.*, 2012. Indigo and tyrian purple – From ancient natural dyes to modern organic semiconductors, Israel Journal of Chemistry 52 (6), 540–551. doi:10.1002/ijch.201100130.

CAS number: 482/582-89-3, IUPAC name 3H-indol-3-yl, 2-(1,3-dihydro-3-oxo-2H-indol-2-ylidene)-1,2-dihydro-, chemical formula $C_{16}H_{10}N_2O_2$) (Chavan, 2015).

Indigotin is a precursor of indigo and can be extracted from the plants, as a solution of indican, a water soluble indoxyl glucoside, which is fermented by an enzyme called glucosidase to produce indoxyl via hydrolysis. Indoxyl reacts further with another indoxyl molecule to produce indigo or reacts with isatin to produce indirubin, known as a red shade of indigo Balfour-Paul (2006), often found in different ratio in indigo leaves. Fig. 5 shows transformation of indoxyl in two different shades (Cardon, 2007). Traditionally many substances were introduced in a dye-bath to create and accelerate the fermentation process, such as madder roots, wheat bran, honey, dates, raisins, plant seeds, and glucose (Meksi and Mhenni, 2015). Today, other than natural fermentation, there are other procedures to reduce indigo such as chemical reduction, electrochemical reduction, catalytic hydrogenation, and electrocatalytic hydrogenation (Chavan, 2015).

Since indigo dye extraction was not a straightforward process, the British planters in Bengal developed an expansive manufacturing process, which involved systematic processing of leaves in large “factories” to turn indigo into a dye, with mechanization, steam power, and use of chemical substances (Kumar, 2012).

The traditional recipe of dyeing fabrics with indigo involves the following ingredients and process (Chavan, 2015).

- 250 g of locally available lime in lump form, mixed with 2 l water to make a smooth slurry
- 500 g wood ash mixed with 2 l water
- 500 g of casetora seeds (methi), boil with 2 l water for 1 h
- 500 g of indigo paste

The indigo paste is thoroughly mixed with 15 l of water and the other ingredients mentioned above in a vat, a mud pot. The vat is closed with a lid or piece of fabric and allowed to ferment for 7 to 10 days, until the appearance of a yellowish green color is seen, which indicates a complete reduction of indigo. The fabric to be dyed is then wetted and dipped into the solution, squeezed thoroughly and exposed to air for the formation of indigo color through oxidation. Depending on the depth of the blue shade required, the process of dipping and exposure to air continues for 6 to 10 times. The same vat is used continuously for several months with the fresh addition of indigo and other ingredients. The indigenous knowledge of indigo dyeing is still practiced in Bangladesh, India, Japan, and some parts of Africa and America, however, is rapidly disappearing due to the competition with synthetic dyes in the global market.

Natural Versus Synthetic Indigo

The history and subsequent demise of natural indigo are linked to the birth of chemical industry also. A significant milestone for the chemical industry was achieved when William Henry Perkin, an 18-year-old chemist from England, developed the first synthetic dye “Mauvine” in 1856 (OpenLearn, 2007). Since then a relentless competition had developed between the British and the German scientists to imitate the naturally available dyes such as alizarine, indigo, etc. Perhaps this could be considered as the beginning of the end of natural indigo production, including Bengal (Balfour-Paul, 1998; Cardon, 2009). At that time the big synthetic dye manufacturers were also suppliers (Geigy) or merchant (Hoechst, Baeyer, or Badische Anilin- und Soda-Fabrik (BASF)) of natural dyes, with production and distribution of natural extracts, preparations, and synthetic dyes (coal tar dyes) were often all carried out as a single business entity (Engel, 2007).

German chemist Adolf von Baeyers (Nobel Laureate of 1905) first discovered the chemical structure of indigo in 1883 (Głowacki *et al.*, 2012). For the first time in 1897, German synthetic dye company BASF launched its version of synthetic indigo, “pure indigo from BASF,” in the market, with a commercially successful route (Clark *et al.*, 1993). The use of the relatively cheap aniline as the raw material, and subsequent discovery of sodamide as the condensation agent, which lowered the overall reaction temperature from 300°C to 200°C, were the two key factors in the economic success of the BASF–Hoechst indigo synthesis (Chavan, 2015). This development of synthetic indigo cost BASF 900,000 euro, 30 years of research, and 152 German patents by 1900 (Brunck, 1901; Głowacki *et al.*, 2012), however in 1899, indigo sales earned enough to pay for the amortization and dividends on the capital for BASF (Abelshauser *et al.*, 2004). Soon other German companies followed and started to manufacture synthetic indigo (Kumar, 2012). Synthetic indigo become the symbol of dominance of the German chemical industry over its British rivals.

The arrival of synthetic indigo further provoked the adversaries between imperial and colonial or between colonial and native interests, and interrupted the social hegemony of the world (Kumar, 2012). The marketing of synthetic indigo created tension within imperial Britain with colonial interest, and threatened the investments of British expatriate planters in India. In fact, by 1900, the production of synthetic indigo reached to a point that was equivalent to a quarter million acres in India. In 1914, the export of natural indigo from the undivided India including Bengal fell to 1000 t, which was 19,000 t and 8000 t in 1897 and 1901 respectively (Clark *et al.*, 1993). By 1914, BASF was producing 80% of the world’s synthetic indigo (Freeman, 1997). Since Germans were outside the control of imperial Britain, it could do little to stop the tide of this global trend. As a result the demise of natural indigo of Bengal was not only linked to the protest by the native Bengal peasants but also the coincidental development of the synthetic chemical industry (Travis, 1993; Kumar, 2012).

Future Trends

With the increasing concerns on health and environment and the effect of global climate change, consistent efforts have been taken to reduce the adverse impact of the production process of synthetic indigo. As a result, the focus turned to natural dyes as they are from renewable sources and involve little chemical reaction and sometimes have a curative effect on health (Patel, 2011). During the end of the 19th century, the successful replacement of natural indigo was possible because synthetic was cheap and consistently pure, greater than 90%, with no presence of indigo red, indigo brown, or indigo gluten, which imparts certain shades on indigo blue (Perkin, 1900). Whereas the purity of extracted indigo from tropical *Indigofera tinctoria* varies from 20% to 90% (Perkin, 1900) while purity of indigo extracted from *P. tinctorium* ranges from 2% to 12.3% (John *et al.*, 2019). In addition, extraction of natural indigo is also inefficient as at least 40% indoxyl is lost during transformation to indigo (Garcia-Macias and John, 2004). Therefore, to become an alternative to synthetic indigo, the purity of the natural indigo remained an important consideration. A European Commission-funded project Sustainable Production of Plant-derived Indigo (see “Relevant Website section”) was launched in 2000 with an aim to reintroduce indigo-yielding crops to European agriculture and to provide a means for European farmers to produce natural indigo with high purity. The project worked with nine partners in Spain, Finland, Germany, Italy, and the UK and examined woad (*Isatis tinctoria*) and *Polygonum tinctorium*, resulting in purity up to 60% (John *et al.*, 2019).

Although it seems the battle for dominance of natural indigo versus synthetic indigo will continue, both will keep their respective places. The growing interest of natural indigo may also continue to rise, but given the market size and requirements, it will always be a niche market among the enthusiasts. The companies which are active on the market in selling natural dyes in ready powder form include De la Robbia of Milan, Allegro Natural Dyes from USA, Livos Pflanzenchemie Forschungs und Entwicklungs



Fig. 6 Indigo dyed saree made by Aranya crafts in Dhaka, Bangladesh.

GmbH from Germany, Bleu de Pastel from France, or Fibrecraft from UK (Hill, 1997) and Aranya crafts from Bangladesh. Fig. 6 shows a Saree dyed from natural indigo made by the Aranya crafts, Bangladesh.

Similarly synthetic indigo, with market monopoly, is also trying to reduce its environmental footprint through green chemistry such as replacing reducing agent sodium dithionite with reducing sugar (Saikhao *et al.*, 2018), microbial production/synthesis of indigo (Ma *et al.*, 2012; Chavan, 2015), and alternate environment friendly technology of indigo dyeing. In addition, an entirely new concept of blue denim production has emerged without indigo, which may drastically change the landscape (Chavan, 2015). However, the indigo colorant with all possibilities of sources, such as natural, synthetic (including recycled), and microbial will be in the market side by side, with different volumes over time (Hill, 1997; Cardon, 2009).

Conclusion

After thousands of years, natural indigo still continues to be cultivated, produced, and used throughout the world, but in a remarkably low quantity in comparison to its historical use before the advent of synthetic dyes. Provided the big volume of synthetic dyes being industrially produced and used at present, it is very unlikely that the natural indigo will be able to regain its fame and dominance anywhere in the near future. However, it will certainly continue to be adored by nature-loving consumers and enthusiasts. Certainly more investment and effort in research to enhance the productivity, purity, and processing of natural indigo will strengthen its chance of healthy coexistence with synthetic indigo.

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Relevant Website

www.spindigo.net
Spindigo – Indigo Fitness.

Opportunities With Renewable Jute Fiber Composites to Reduce Eco-Impact of Nonrenewable Polymers

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Introduction

Fiber reinforced polymer composite (FRPC) materials consist of polymer matrices imbedded with textile fibers as fillers (Groover, 2004). The common thermoplastic polymers that are used as matrices are polypropylene (PP), polyethylene (PE), and polyvinyl chloride (PVC). On the other hand, phenolic, epoxy, and polyester resins are the most common thermosetting matrices used in composite fabrication (Malkapuram *et al.*, 2008). The use of FRPCs is increasing significantly due to their low weight, high specific modulus, low cost, appropriate strength, biodegradability, and eco-friendliness. As reinforcements, the synthetic fibers, such as glass and carbon, traditionally dominate in composite manufacturing. However, the natural fibers have emerged as attractive alternatives for use as fillers and reinforcements in polymer composites that do not require very high mechanical performance (Nabisaheb and Jog, 1999). The natural fibers are biodegradable, renewable, cost-effective, and eco-friendly materials and they can solve the disposal problems associated to polymeric composites.

Natural fibers can come from both plant and animal origins. Fibers that come from plants can be classified into three categories: (1) Bast fibers (produced in plant stems, such as jute, kenaf, flax, hemp, ramie, *etc.*), (2) leaf fibers (produced in the leaves of the plants, such as pineapple, sisal, abaca, banana *etc.*), and (3) seed-hair fibers (grown around the seeds, or fruits of the plants such as cotton, coir, kapok *etc.*). Table 1 presents a list of common natural fibers and their producing countries.

Bast fibers exhibit good mechanical properties and therefore, they are preferred for structural application in composites (Gay *et al.*, 2003). The common properties that are considered for the selection of reinforcements in composite fabrication are tensile strength, elastic modulus, specific elastic modulus, density, compatibility with matrix material and moisture regain. The mechanical properties of key natural fibers, in comparison to glass fiber are presented in the Table 2 and the chemical composition of some selected natural fibers are shown in Table 3. This article introduces green composites and gives an overview of partly biodegradable jute-FRPCs that can reduce the environmental impact of nonrenewable polymers.

Green Composites

Green composites include at least one biodegradable component, either matrices or fillers, or both (La Mantia, and Morreale, 2011). They can be divided into two groups, namely, (1) partially biodegradable or partially green, and (2) fully biodegradable or fully green composites. In partially green composites, either matrix material or reinforcement is derived from the natural resources. The combination may include natural fibers such as jute, flax, *etc.* As for example reinforcements or fillers, and synthetic polymers such as PP, or PE as the matrix material; or synthetic fibers such as glass, or carbon fibers as reinforcement and polylactic acid (PLA) as the matrix. On the other hand, fully green and biodegradable composites are those that include both filler and matrix materials derived from natural resources. For example, a green composite would include a natural fiber is used as a filler and a natural polymer such as PLA and polyvinyl alcohol *etc.* as a matrix. If a composite material is completely biodegradable, that is, both filler and matrix are from natural origin, it is also identified as a biocomposite (Cheung *et al.*, 2009).

Table 1 Common natural fibers and their producers

Fibers	Plant origin	Major producers
Cotton	<i>Gossypium sp.</i>	China, India, USA
Jute	<i>Corchorus sp.</i>	Bangladesh, India, China
Flax	<i>Linum usitatissimum</i>	Canada, France, Belgium
Hemp	<i>Cannabis sativa</i>	China, France, Philippines
Kenaf	<i>Hibiscus cannabinus</i>	Bangladesh, India, USA
Ramie	<i>Boehmeria nivea</i>	China, Brazil, Philippines, India
Sisal	<i>Agave sisilana</i>	Tanzania, Brazil
Coir	<i>Cocos nucifera</i>	Bangladesh, India, Sri Lanka

Note: Adekomaya, O., Jamiru, T., Sadiku, R., Huan, Z., 2016. A review on the sustainability of natural fibre in matrix reinforcement – A practical perspective. *Journal of Reinforced Plastics and Composites* 35 (1), 3–7. Sayem, A.S.M., Haider, J., 2019. An overview on the development of natural renewable materials for textile applications. In: *Reference Module in Materials Science and Materials Engineering*. Elsevier. Available at: <https://www.sciencedirect.com/science/article/pii/B978012803581810983X>.

Table 2 Mechanical properties of selected plant-based natural and glass fibers

Fibers	Density (g/cm ³)	Tensile strength (MPa)	Elastic modulus (GPa)	Specific modulus	Elongation at failure (%)	Moisture regain (%)	Price (US\$/kg)*
Cotton	1.5	400	12	8	7–8	8.5	1.56–2.0
Jute	1.3	393–773	10–30	8–23	1.5–1.8	13.75–17	0.8–0.9
Flax	1.4	800–1500	25–80	18–57	2.7–3.2	9.24–12	0.6–0.8
Hemp	1.47	690	38–70	26–48	1.6–4	8–12	0.7–0.8
Kenaf	1.50	350–930	40–53	27–35	1.6	10–12	0.7–0.8
Ramie	1.5	400–938	61.4–128	41–85	1.2–3.8	8.5–17.5	1.52
Sisal	1.33	511–635	9.4–38	7–29	2.0–3.0	14.0	0.7–0.8
Coir	1.25	593	4–6	3–5	15–25	13.0	0.5–0.84
E-glass	2.55	2000–3500	70–73	27–29	2.5–3.7	–	2.0

Note: Data presented in the last column [Price (US\$/kg)]* were collected from Dunne, R., Desai, D., Sadiku, R., Jayaramudu, J., 2016. A review of natural fibres, their sustainability and automotive applications. *Journal of Reinforced Plastics and Composites* 35 (13), 1041–1050. Malkapuram, R., Kumar, V., Yuvraj, S.N., 2008. Recent development in natural fibrereinforced polypropylene composites. *Journal of Reinforced Plastics and Composites* 8, 1169–1189.

Table 3 Chemical composition of selected plant-based natural fibers

Fibers	Composition (%)			
	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)	Extract (wt%)
Cotton	82.7	5.7	–	0.6
Jute	71	14	13	2
Flax	71	21	2	6
Hemp	70	22	6	2
Kenaf	36	21	18	2
Ramie	76	17	1	6
Sisal	73	14	11	2
Coir	32–43	10–20	43–49	4

Note: Khalil, H.A., Bhat, A.H., Yusra, A.I., 2012. Green composites from sustainable cellulose nanofibrils: A review. *Carbohydrate polymers* 87 (2), 963–979.

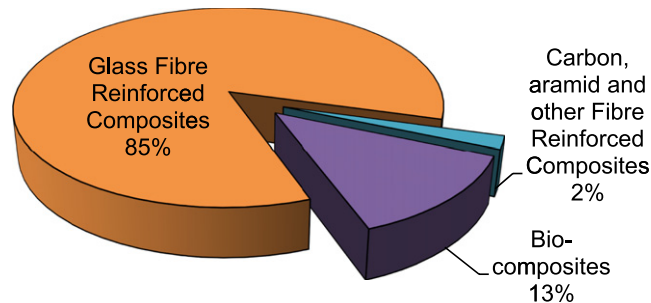


Fig. 1 EU market share of fiber reinforced composites in 2010. Reproduced from Shah, D.U., 2013. Developing plant fibre composites for structural applications by optimising composite parameters: A critical review. *Journal of Materials Science* 48 (18), 6083–6107.

Green composites are finding notable applications in the areas like food packaging, agriculture, composting bags, furniture, etc. **Fig. 1** presents the EU market shares of different FRPCs in the year 2010.

Choices of Matrix for Green Composites

PP, PE, epoxies, and biopolymers such as PLA, polyhydroxybutyrate (PHB) are the most commonly used polymer matrices for fabrication of FRPCs. The common biopolymers used as matrices are PLA, PHB, soy-based plastics, cellulose polyesters, starch-based bioplastics, vegetable-oil derived bioplastics, poly (trimethylene terephthalate), biopolyethylene etc. The global consumption of bioplastics increased significantly from 15,000 tons in 1996 to 225,000 tons in 2008 (Pilla, 2009). Mechanical properties and prices of few biopolymers with reference to PP are listed in the **Table 4**.

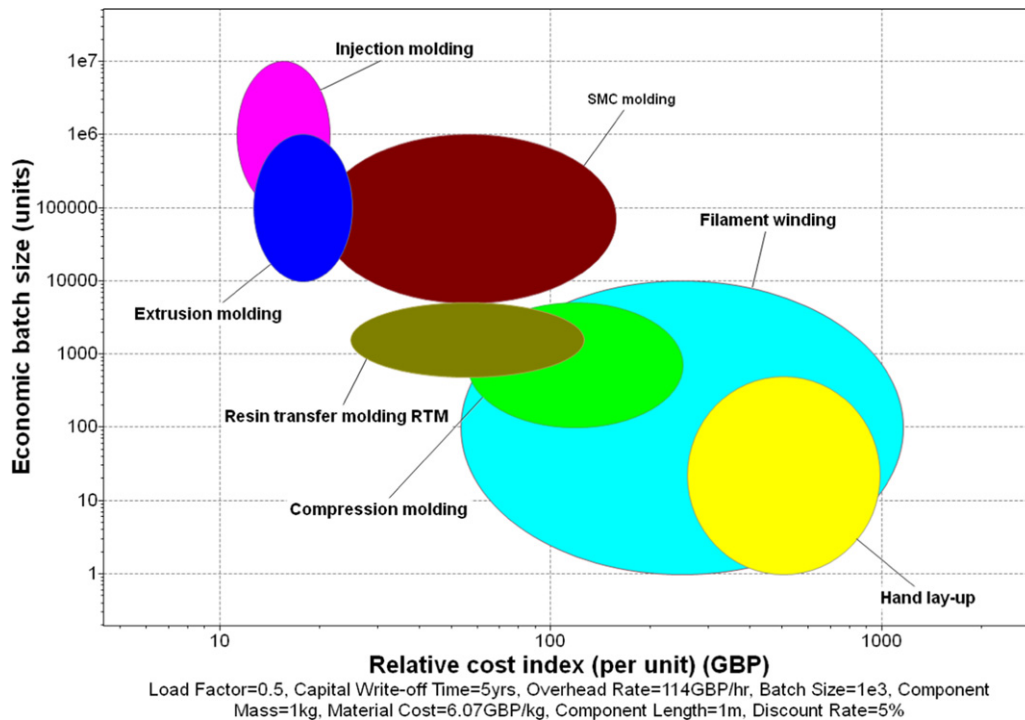
Different surface treatments of natural fibers, namely silane, acetone and alkali treatment, etc. and coupling agents (maleic anhydride, potassium permanganate, etc.) are normally used to enhance the interfacial adhesion between fiber and matrix. The

Table 4 Properties of natural polymers in relation with polypropylene

Polymer	Density (g/cm ³)	Melting point (°C)	Tensile strength (MPa)	Young modulus (GPa)	Elongation at break (%)	Price (US\$/kg)
Thermoplastic starch	1–1.39	110–115	5–6	0.125–0.85	31–44	5.5
PLA	1.21–1.25	150–162	21–60	0.35–3.5	2.5–6	2.42
PLLA	1.25–1.29	170–190	15.5–65.5	0.83–2.7	3–4	4.5
PHB	1.18–1.26	168–182	24–40	3.5–4	5–8	4.0
PHBV	1.23–1.25	144–172	20–25	0.5–1.5	17.5–25	3.5
PP	0.9–1.16	161–170	30–40	1.1–1.6	20–400	1.65

Abbreviations: PHB=Polyhydroxy butyrate; PHBV: Poly(3-hydroxybutyrate-co-3-hydroxyvalerate); PLA: Poly(lactic acid); PLLA: Poly-L-lactide acid; PP: Polypropylene.

Note: Koronis, G., Silva, A., Fontul, M., 2013. Green composites: A review of adequate materials for automotive applications. Composites Part B: Engineering 44 (1), 120–127.

**Fig. 2** Comparison of different composite forming techniques in terms of cost and batch size. Graph drawn by CES EduPack software.

desirable mechanical properties of a composite are obtained when the applied load is effectively transferred from the matrix to the reinforcing fibers through the interface.

Manufacturing Techniques of Biocomposites

The existing manufacturing techniques for biocomposites are hand lay-up, filament winding, pultrusion, extrusion, injection molding, compression molding, resin transfer molding (RTM), and sheet molding compounding (SMC). A comparison of different techniques is presented in Fig. 2. Compression molding (including hot and cold pressing) is a popular method for fabricating FRPCs because of its simplicity (Shah, 2013). However, this is a slow process and not appropriate for mass production. Again hand lay-up and filament winding are also low volume processes with higher relative cost index per unit. The ideal manufacturing technique for mass production is injection molding due to its high processability; although the degradation of reinforcing fiber may happen during processing (Arao et al., 2015). SMC and extrusion molding are also suitable for mass manufacturing and this can bring down the relative cost index per unit. In terms of both manufacturing tolerance and labor intensity, extrusion and injection molding are best as shown in Fig. 3. SMC and RTM require medium to high labor intensity but hand lay-up and filament winding show the weakness of producing products with higher manufacturing tolerance. The key manufacturing techniques used for plant fiber reinforced composites with corresponding percentages used are shown in Table 5.

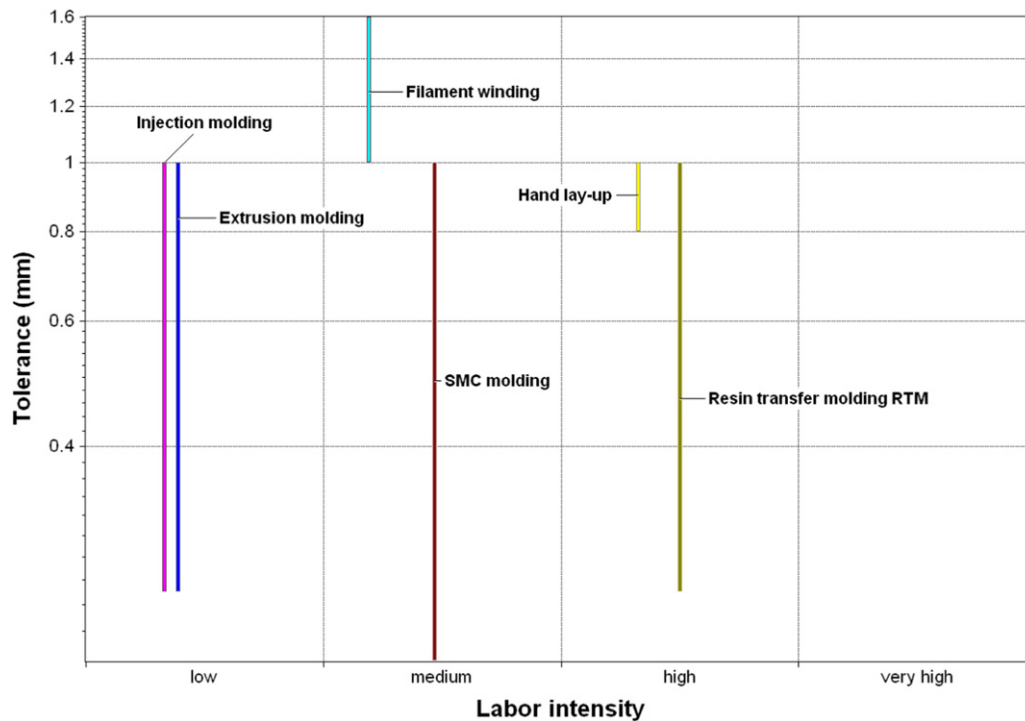


Fig. 3 Comparison of different composite forming techniques in terms of manufacturing tolerance and labor intensity. Graph drawn by CES EduPack software.

Table 5 Manufacturing techniques used for plant fiber based composites

Composite type/matrix type	Manufacturing technique	Percentage used (%)
Plant fiber reinforced composite/thermoset	Compression molding	30
Plant fiber reinforced composite/thermoplastic	Compression molding	60
Plant fiber reinforced composite/thermoplastic	Injection/extrusion molding	10

Note: Shah, D.U., 2013. Developing plant fibre composites for structural applications by optimising composite parameters: A critical review. *Journal of Materials Science* 48 (18), 6083–6107.

Challenges for Natural Fiber Reinforced Polymer Composites

The main limitations identified in the natural FRPCs are moisture absorption, decreased durability, weak interfacial adhesion between the fiber and matrix, and relatively poor mechanical properties (Gassan and Gutowski, 2000; Haq *et al.*, 2018). Degradation causing exposure to outdoor environment is another vital issue of natural FRPCs. The moisture absorption properties of plant based natural fibers confines the outdoor applications of natural FRPCs. Several methods, namely surface treatment and addition of coupling agents, are employed with the purpose of decreasing moisture absorption and enhancing interfacial bonding and mechanical properties of the FRPCs (Ahmad *et al.*, 2006; NabiSaheb and Jog, 1999). Percentages of moisture absorption by some selected natural fibers are given in Table 2. It is revealed that the lower the moisture content in fiber, the higher the mechanical properties of the fiber as well as FRPCs. Moreover, lack of innovation in appropriate commercial manufacturing techniques and composites having higher mechanical properties with natural fibers as reinforcement are also limitations in the field of natural fiber based polymer composites. Another disadvantage of using natural fibers as reinforcements is the low processing temperature required for the fabrication of composites. The maximum acceptable processing temperature is 200°C, beyond this limit, plant based natural fibers were found to degrade and shrink that consequently cause lower mechanical performance of the green composites.

Composite Architecture and Fiber Parameters

Factors like fiber geometry and orientation, packing arrangement, and volume fraction generally govern the mechanical performance of FRPCs. Among them, fiber volume fraction (V_f) is the most important factor that influences the properties of FRPC directly. It is found that the mechanical performance of FRPCs increases with an increase in V_f up to a certain limit.

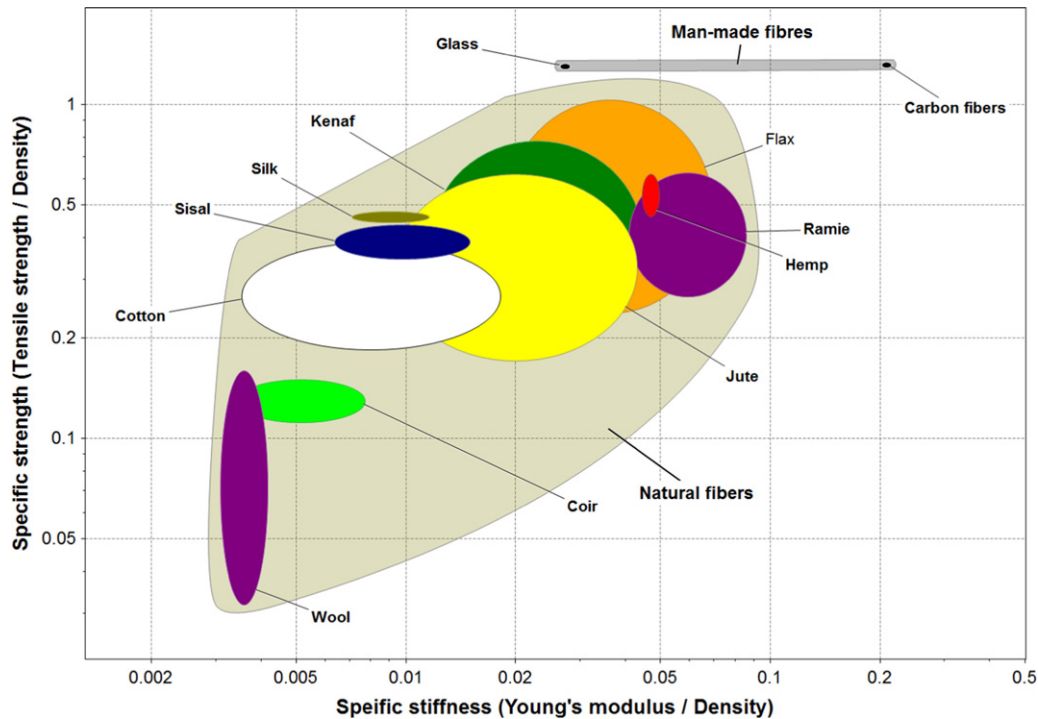


Fig. 4 A comparison of specific strength vs. specific stiffness between natural and some selected man-made fibers. Graph drawn by CES EduPack software.

High fiber volume fraction is necessary for better composite performance. However, for better mechanical performance, distribution of both fiber and matrix should be uniform along with the component. The longitudinal modulus of FRPC is determined by the simple rule of mixtures approach, which is represented by Eq. (1);

$$E_L = E_f V_f + E_m (1 - V_f) \quad (1)$$

where E_L is the longitudinal modulus of elasticity, (i.e., the direction of parallel fibers oriented in the longitudinal direction), V_f is the fiber volume fraction of the composite, E_f is the modulus of the fiber, and E_m is the modulus of the matrix.

The Fiber–Matrix Interface

The interfacial behavior and adhesion between fiber and matrix is a very important factor that determines the performance of FRPCs. The interface acts as a medium for transferring any externally applied tensile force to the reinforcing fibers through shear stresses over itself. The interaction between fiber and matrix in a FRPC can be enhanced through surface modification (chemically or physically) of natural fibers and textile substrates made of natural fibers. The plant based natural fibers are strongly hydrophilic in nature as they contain many hydroxyl (–OH) groups in their cellulosic polymer chains. This hydrophilicity of natural fibers is a possible reason for incompatibility, poor interfacial adhesion, and dispersion problems with hydrophobic polymer matrices. Different experimental works show that the surface modification of plant based natural fibers such as acetylation, silylation, and other chemical treatments decrease their hydrophilicity and moisture absorption capacity (Fowler *et al.*, 2006).

Jute Fiber

Jute is one of the plant fibers found abundantly in nature and can be easily used as a reinforcing fillers for the fabrication of FRPCs. Cellulose is the major chemical composition for all the plant based natural fibers, even though the amount of different chemical composition (such as cellulose, hemicellulose, lignin, and other extracts) varies from fiber to fiber (Table 3). Among the natural fibers, jute, flax, and hemp are suitable for fabrication of structural, automotive composites and many other value-added applications mainly because of their tensile properties. The different mechanical properties of the major natural and manmade fibers are shown in Fig. 4. Comparing the specific strength (tensile strength/density) and specific modulus (elastic modulus/density) of natural fibers and manmade fibers, it is evident that specific strengths of carbon and E-glass fiber are higher than that of all natural fibers. However, the specific modulus of E-glass fiber is comparable to the specific moduli of jute, hemp, flax and kenaf fibers. This data proves that the properties of the lignocellulosic bast fibers such as jute, kenaf, and flax fibers are comparable to that of glass fibers.

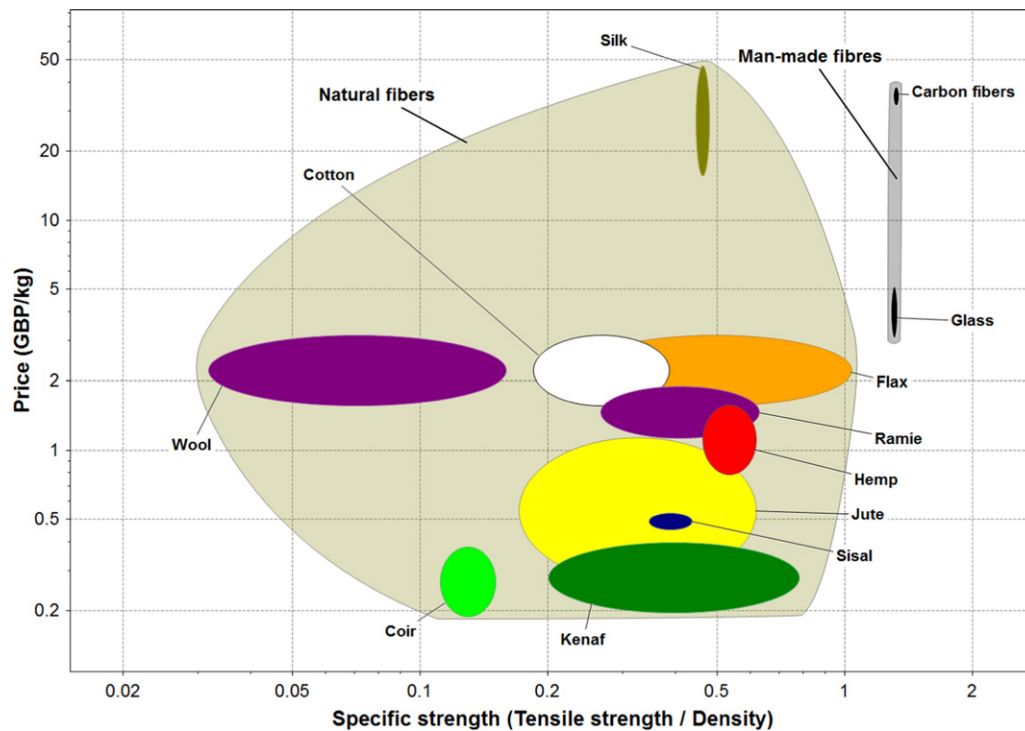


Fig. 5 A comparison of price and specific strength of fibers used in composite manufacturing. Graph drawn by CES EduPack software.

Like other plants of natural fibers, jute plants have a capacity for absorbing a large amount of carbon dioxide (CO_2) from environment and consequently clean the air by reducing the carbon content in air (Holbery and Houston, 2006). Jute fiber is called as bast fibers since it is produced from the plant stem. The most commonly cultivated varieties of jute in Bangladesh and India are *Corchorus capsularis* (also known as white jute) and *Corchorus olitorius* (known as Tossa jute) (see Table 1). The moisture regain (%) and tensile modulus of jute fiber is very high, nevertheless the breaking elongation is very low. However, considering the low density of jute fiber, the specific modulus and strength of jute fiber are comparable to those of glass fiber (see Table 2). Besides, jute possesses very good technical properties, for a specific strength it is also one of the cheapest fibers compared with the other natural and manmade fibers as shown in Fig. 5.

The outer stems of jute plants are used to make the fiber but other parts of the plant are equally useful such as green leaves are used as vegetable, dry leaves are used as a drink, and jute stick is used as firewood, charcoal, light construction material, etc.

Jute Fiber Reinforced Composites

Several natural fibers such as jute, flax, hemp, sisal, coir, etc. have already been applied as fillers in FRPCs, however jute fiber based FRPCs have been found with moderate tensile and flexural properties (Khan et al., 2013; Mohanty et al., 2000). Jute fibers can be used as fillers for FRPCs in various forms such as chopped fibers, yarns, and fabrics (woven, knitted or nonwoven) (Sayeed et al., 2014). Fig. 6 presents a schematic diagram of different types of fiber/fabric orientations in jute FRPCs.

Based on the types of reinforcements used for the fabrication of composites, FRPCs are divided as (1) unidirectional, (2) bidirectional continuous fiber composites, or (3) discontinuous reinforcement composites (aligned or randomly oriented in the form of particulates, short fibers, and whiskers). A large number of research works have been conducted on fully biodegradable and partially biodegradable jute-FRPCs. Table 6 reviews some of the reported works on the mechanical properties of jute-reinforced composites. Here, fiber weight fraction, fabrication technique, matrices used, tensile strength, and tensile modulus are reported to compare the mechanical properties of jute fiber reinforced composites with that of glass fiber reinforced composites.

Chemical Modification of Jute Fiber

As mentioned already the natural hydrophilic fibers can be chemically treated for the enhancement of interfacial adhesion with the hydrophobic matrices. In case of jute, the interfacial adhesion can be improved by alkali treatment (Li et al., 2007), acetylation (Hill et al., 1998) and silanization (John et al., 2008) methods. Alkali treatment is the most commonly used chemical process applied for the surface modification of jute fibers and jute-based textile substrates used in FRPC fabrication. Valadez-Gonzalez et al. (1999) demonstrated that alkali treatment of fiber increases surface roughness leading to better mechanical bonding and

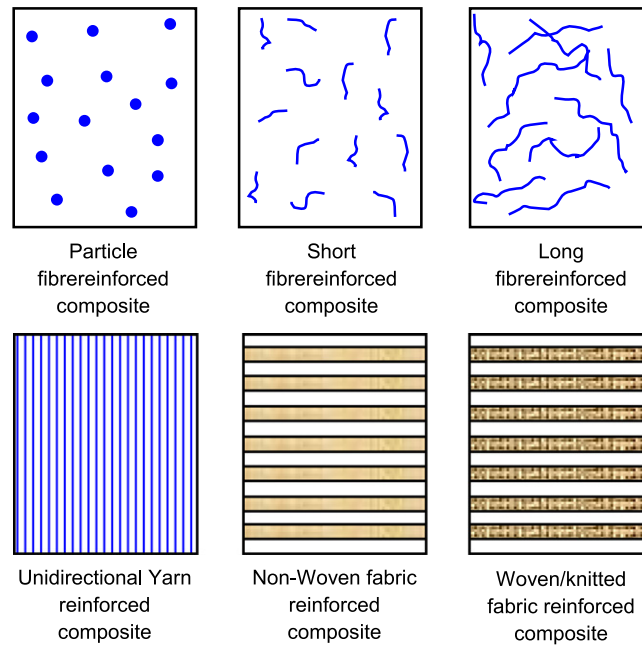


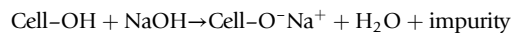
Fig. 6 Jute fiber/fabric orientations in jute fiber reinforced composites.

Table 6 The mechanical properties of jute fiber reinforced composites fabricated by various processes compared with the traditional glass fiber reinforced composites

Fiber/Matrix	Fiber content (wt%)	Fabrication technique	Tensile strength (MPa)	Tensile modulus (GPa)	Source
Jute mat/PP	40	CM	30	4.0	Wambua <i>et al.</i> (2003)
Jute mat/PLA	40	CM	100.5	9.4	Plackett <i>et al.</i> (2003)
Jute/PLA	35–39	IM	49	10.5	Yang <i>et al.</i> (2012)
Jute/PLA	50	IM	82.2	–	Gunning <i>et al.</i> (2014)
Woven Jute/PP	45 (by volume)	Hand lay-up	60 L 35 T	7 L 3.5 T	Gowda <i>et al.</i> (1999)
Jute/PLA	30	IM	81.9	9.6	Bledzki and Jaszkiwicz (2010)
Jute/PP	30	IM	47.9	5.8	Bledzki and Jaszkiwicz (2010)
Jute/PHBV	30	IM	35.2	7.0	Bledzki and Jaszkiwicz (2010)
Jute/PP	20	IM	26.5	1.5	Rahman <i>et al.</i> (2009)
Jute/PP (MAPP)	20	IM	30.0	1.7	Rahman <i>et al.</i> (2009)
Jute mat (alkali treated)/PP	33	CM	28	2.8	Sayeed <i>et al.</i> (2014)
Jute fabric/HDPE	18.5	CM	36.37	–	Sayem <i>et al.</i> (2018)
Jute fabric/PP	30	CM	32	0.74	Khan <i>et al.</i> (2010a)
Jute fabric/PP	45	CM	52	1.03	Khan <i>et al.</i> (2013)
Jute/PP	30	IM	40	4.8	Bledzki <i>et al.</i> (2007)
Nonwoven Jute/soy resin	60	CM	37.1	1.04	Behera <i>et al.</i> (2012)
Woven jute/soy resin	60	CM	35.6	0.972	Behera <i>et al.</i> (2012)
Jute/PLA	50	CM	155	5.28	Goriparthi <i>et al.</i> (2012)
Jute (silane treated)/PLA	50	CM	210	7.30	Goriparthi <i>et al.</i> (2012)
Jute/PP	15	IM	35	2.20	Hong <i>et al.</i> (2008)
Jute/PP without coupling	50	IM	29.82	7.48	Karmaker and Youngquist (1996)
Jute/PP (MAPP)	50	IM	59.13	7.56	Karmaker and Youngquist (1996)
Jute yarn (uncoated Yarn)/PP	50	CM	107 UD	6.0	Khondker <i>et al.</i> (2005)
Jute yarn (coated yarn)/PP	50	CM	122 UD	6.6	Khondker <i>et al.</i> (2005)
Jute fabric/PP	50	CM	48	2.5	Khan <i>et al.</i> (2010b)
Starch-based biopolymer/Jute strand	30 (Alkali Treated Fiber)	IM	26.3	2.5	Vilaseca <i>et al.</i> (2007)
Jute Fabric/BAK 1095	32 (Alkali Treated)	CM	35.8	–	Mohanty <i>et al.</i> (2000)
E-Glass Fabric/PP	50	CM	85	7.0	Khan <i>et al.</i> (2010b)

Abbreviations: BAK 1095: Biodegradable polyester amide; CM: Compression molding; HDPE: High-density polyethylene; IM: Injection molding; L: Longitudinal; PP: Polypropylene; PHBV: Poly(3-hydroxybutyrate-co-3-hydroxyvalerate); PLA: Polylactic acid; T: Transverse; UD: Unidirectional.

simultaneously, it also increased the exposure of cellulose polymer on the fiber surface, which enhances the number of possible reaction sites. It is reported that alkali treatment can eliminate the hydroxyl ($-OH$) groups from jute polymer system and can improve the compatibility with hydrophobic thermoplastic matrix by decreasing the hydrophilic nature of the jute (Liu and Dai, 2007). The typical reaction that takes place when alkali ($NaOH$) is applied on jute surface is presented below.



Sodium hydroxide treatment removes lignin and hemicellulose and makes the interfibrillar regions in jute polymers less dense and less rigid (Bledzki and Gassan, 1999). As a result, these fibrils can perform better in tensile load sharing through rearranging themselves easily when any tensile load is applied.

Different Forms of Jute Substrates as Composite Reinforcement

Experimental trials with all different structural forms of jute based textile substrates, such as fiber (Bisaria *et al.*, 2015; Gopinath *et al.*, 2014), sliver (Das and Bhowmick, 2015), yarn (Memon and Nakaib, 2013; Pujari *et al.*, 2015), woven (Sudha and Thilagavathi, 2015; Sayem *et al.*, 2018; Arju *et al.*, 2015), knitted fabrics (Arju *et al.*, 2015), and nonwoven sheets (Karaduman *et al.*, 2014; Sayeed *et al.*, 2014) have already done in fabrication of FRPCs using both thermoplastic (Sayeed *et al.*, 2014) and thermoset polymeric matrices (Bisaria *et al.*, 2015; Das and Bhowmick, 2015; Pujari *et al.*, 2015) individually.

Haydaruzzaman *et al.* (2010a) treated bleached fabric of tossa jute with a solution of 50%–90% oligomer urethane acrylate, 2% photoinitiator in methanol, and irradiated under UV light for 24 h before heat pressing five layers of treated fabrics to form composite laminate. They identified the best mechanical properties from the composite that was made from jute fabrics treated with 70% of oligomer, 28% methanol and 2% photoinitiator followed by UV radiation. Kafi *et al.* (2011) prepared multilayered jute-polyester composite after atmospheric plasma treatment of jute fabrics and found improvements in flexural strength and modulus and interlaminar shear stress. Khan *et al.* (2012) prepared composite by compression molding of four layers of hessian fabrics within five layers of PVC and found the composite containing 40% fiber showed the best performance. An increase in tensile, flexural, and interlaminar shearing strength was observed by Seki *et al.* (2012) in composite made from alkali and oligomer siloxane treated single layer of jute fabric compression molded into two layers of high-density polyethylene (HDPE). Zaman *et al.* (2012) varied the concentration of urethane acrylate oligomer including photoinitiator for pretreating bleached hessian fabric and UV radiated for 24 h for preparing thermoset laminate from five layers of treated jute fabrics through compression molding. They found best results from 70% oligomer treated fabrics. Khan *et al.* (2013) discussed an ecofriendly biocomposite made by compression molding of single layer of jute fabrics sandwiched between poly (ϵ -lactic acid) (PLLA) films. Berhanu *et al.* (2014) sandwiched two layers of jute fabrics between three layers of PP sheets and made thermoplastic composites by hot pressing. They reported significant enhancement of mechanical properties of jute-reinforced composites with the increase of fiber content up to 40% (in weight). Sudha and Thilagavathi (2015) reported a jute-vinylester composite material by compression molding of four layers of alkali treated jute fabrics (16 EPI & 13 PPI; 430 GSM) impregnated with a solution of vinylester resin, catalyst and accelerator. Arju *et al.* (2015) prepared jute reinforced PP composites from single layer of plain (1/1, EPI 10–12 & PPI 10–12) and twill (2/1, EPI 18–20 and PPI 9–10) fabric structures separately sandwiched between two layers of PP sheets and found that the composites having twill structured fabric displayed higher tensile strength than the composites with the plain fabrics. Table 7 shows some examples for manufacturing processes of jute fabric reinforced composite materials.

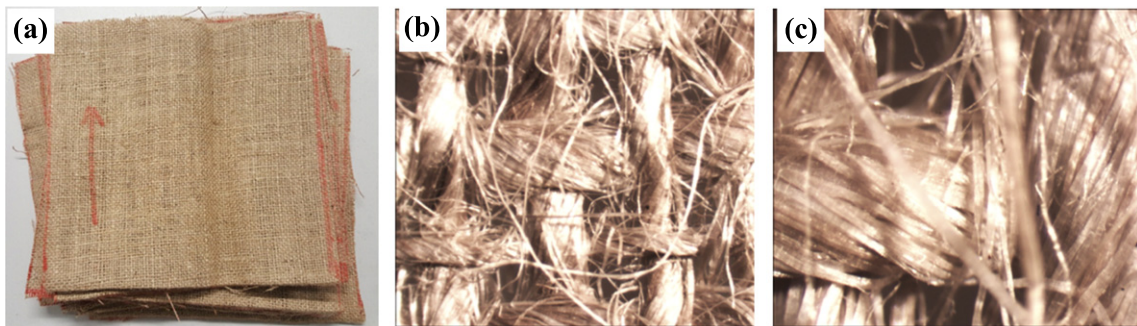
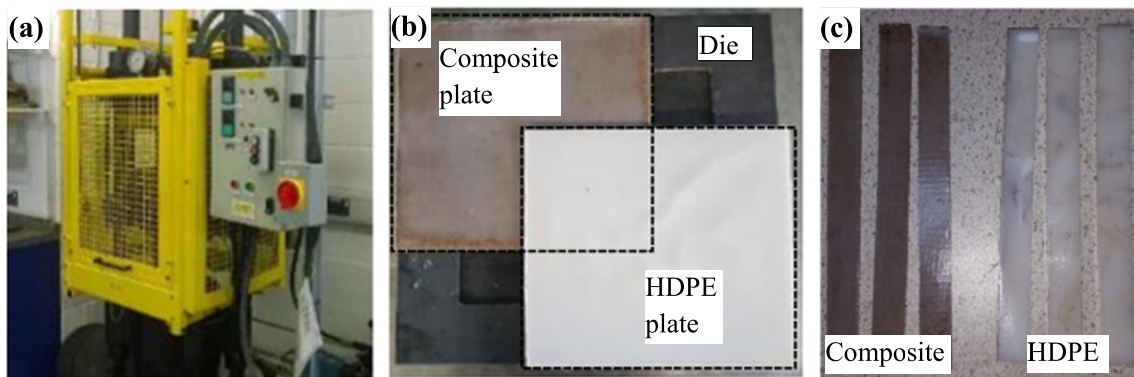
A work done by Sayem *et al.* (2018) demonstrated the manufacture and analysis of mechanical performance of multilayered jute fabric reinforced thermoplastic composite material. In that work, different layers of jute hessian fabrics having 1/1 plain weave, weight 209 g/m², ends/in. (EPI) 10, and picks/in. (PPI) 9 (Fig. 7), were sandwiched in 0° orientation into several layers of HDPE polymeric sheets and pressed at high temperature and pressure to form composite laminates (Fig. 8). Microscopic findings showed that the placement and orientation of fiber and yarns within the fabric structure remained unchanged in the jute-FRPC. There has been no visible void in the structure. Mechanical performance of the jute-FRPC having a small percentage of fiber content had been found to have improved remarkably when compared with the pure HDPE laminates. The tensile and flexural strength of the laminate composite with optimum number of layers (6-layer makes a weight fraction of 18.50%) were improved by more than 50% (Sayem *et al.*, 2018). The fracture morphology of the jute-FRPC investigated by a scanning electron microscope showed close adhesion of the jute fabrics with the polymer matrices.

Eco-Impact of Nonrenewable Polymer

Nowadays, the biggest end user of plastics worldwide is the packaging sector. It is anticipated that annual production of plastics will be more than 380 million metric tons by 2015 (Geyer *et al.*, 2017). This huge amount of plastics will exhaust approximately 4% petrochemicals as a feedstock; and another 3%–4% is used as energy for manufacturing process. Average per capita consumption of plastics in developed countries is in the range of 80–100 kg/year. In China, annual creation of plastic waste is around 4 million tons of which only 10% are recovered and recycled, 20%–30% are incinerated or landfilled, and the remaining 60%–70% are dumped, discarded, and washed away (Ren, 2003). These plastics are not biodegradable, renewable, and recyclable, thus creating a huge amount of waste, becoming a burden for the environment and as they are dumped in landfills. Therefore, the present usage of plastics is not sustainable and renewable. Biodegradable plastics may work as a promising solution to the

Table 7 Examples for manufacturing processes of jute fabric reinforced composite materials

<i>Jute fabric</i>	<i>Pretreatment</i>	<i>Matrix</i>	<i>Fabric layer</i>	<i>Type</i>	<i>Method</i>	<i>Reference</i>
Bleached tossa jute fabric	Methyl-methacrylate	Urethane acrylate oligomer (2% photoinitiator in methanol)	5	Thermoset	UV curing + heat press	Haydaruzzaman <i>et al.</i> (2010a)
Bleached tossa jute fabric	2-hydroxyethyl methacrylate and starch	Polypropylene (PP)	4	Thermoplastic	Heat press	Haydaruzzaman <i>et al.</i> (2010b)
Unbleached woven jute fabric	Atmospheric plasma (He/Ac/N)	Polyester resin	12	Thermoset	Vacuum bagging	Kafi <i>et al.</i> (2011)
Hessian fabrics	n/a	Polyvinyl chloride	4	Thermoplastic	Heat press	Khan <i>et al.</i> (2012)
Jute fabric	Alkali and oligomer Siloxane	High-density polyethylene	1	Thermoplastic	Heat press	Seki <i>et al.</i> (2012)
Hessian fabric	n/a	Hexanedioldiacrylate	5	Thermoset	UV curing + heat press	Zaman <i>et al.</i> (2012)
Jute fabrics (plain weave)	n/a	Poly (L-lactic acid)	1	Thermoplastic	Heat press	Khan <i>et al.</i> (2013)
Woven jute fabrics	n/a	PP	2	Thermoplastic	Heat press	Berhanu <i>et al.</i> (2014)
Jute fabric (plain weave)	Alkali	Vinylester resin, catalyst and accelerator	4	Thermoset	Compression molding + Curing @ RT	Sudha and Thilagavathi (2015)
Jute fabric (plain, twill weave)	n/a	PP	1	Thermoplastic	Heat press	Arju <i>et al.</i> (2015)

**Fig. 7** Hessian jute fabric: (a) Normal view; (b, c) magnified views.**Fig. 8** (a) Compression molding machine, (b) prepared composite and HDPE plates with die and (c) specimens for mechanical testing.

overloaded landfills by decomposing, recycling these natural fiber based plastic materials. **Table 8** shows that packaging is the major source of waste plastics in the UK (Waste Watch, 2003). Other sources such as building and construction, electrical, and electronics are also contributing towards significant portions of waste plastics. Since the majority portion of the packaging materials are fabricated from nonrenewable and nondegradable synthetic plastics, therefore, the top position in landfills is

Table 8 Consumption of plastics and waste generation by sector in the UK in 2000

Application area	Usage		Waste arising	
	ktons	(%)	ktons	(%)
Packaging	1640	37	1640	58
Building and construction	1050	23.5	284	10
Electrical and electronics	355	8	200	7
Furniture and housewares	335	8	200 ^a	7
Automotive and transport	335	8	150	5
Agriculture and horticulture	310	7	93	3
Other	425	9.5	255 ^a	9
Total	4450	100	2820	100

^aEstimate. Note: Waste Watch, 2003. Plastics in the UK Economy. London: Waste Watch & Recoup.


Fig. 9 Biodegradable and environment-friendly jute-based polymer bag.

engaged by the packaging waste. Moreover, there have been several health hazards, particularly in the food division, owing to using synthetic polymers for packaging. This has worked as a driving force to identify and apply biobased and biodegradable alternatives for the packaging sector (Pilla, 2009).

Recently, Bangladesh Jute Mills Corporation (BJMC) has developed a biodegradable and environment friendly jute-polymer based bioplastic bag branded as the Sonali bag (Fig. 9), as an alternative to polythene bag. BJMC is working closely with Futamura Chemical Ltd., a UK-based company, for commercial production of the Sonali bag. This jute-based polymer sheet may work as polymer matrix for making fully biodegradable jute-FRPC.

Conclusions

Jute-FRPCs have many potential applications in automobiles as door panels, seat backs, headliners, dashboards, trunk liners, and parts in railway coaches; in building infrastructure as ceiling, floor, window, wall partition, *etc.*; and as furniture, for example, table, chair, kitchen cabinet, *etc.* The specific modulus of jute fiber is comparable to that of glass fibers (see Table 2), which indicates jute can be used as a substitute of glass fiber in composite manufacturing for certain applications. In 1996, Mercedes used jute to make door panels in its E-class vehicles (John and Thomas, 2008). Alves *et al.* (2010) demonstrated the fabrication of a structural frontal bonnet of off-road vehicles (buggy) with jute/polyester composite as a replacement of glass fibers. It is reported that all major car manufacturers in Germany, namely Daimler Chrysler, Mercedes, Volkswagen, Audi, BMW, Ford, and Opel, are using biocomposites for different applications in cars (John and Thomas, 2008). Jute stands as a potential candidate for all these applications.

See also: Jute Pulping: Opportunities and Challenges. Renewable and Sustainable Materials in Automotive Industry

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An Overview on the Development of Natural Renewable Materials for Textile Applications

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Introduction

Theology establishes the fact that the mankind had attempted to cover itself using flexible natural materials since the day of its existence on earth. Archaeological discovery of ancient needles dated back to 26,000–20,000 BCE indicates the craft of sewing was in practice even in the pre-historic time. Further evidences, such as the three-ply cordage dated from 18,000–15,000 BCE found in France and two-ply willow bast net dated to late 8000 BCE found in Finland (Schoeser, 2003), establish that bast fibres, which are collected from the stem of different dicotyledonous plants (Cook, 2001), were among the early natural textile materials used on the earth. Among all bast fibres, flax is known to be first processed industrially to make wearable textiles. According to biblical writings, the spinning and weaving of flax were well advanced even thousands of years ago. The Egyptian mummy cloths aged more than 4500 years old are identified as Linen, the fabric made of flax (Cook, 2001). Following flax, all different natural fibrous materials are used as the only textile materials on the earth until early 1900 when viscose started to appear on the market (Chen, 2015) and then 1940 and 1941 when Nylon and Polyester were introduced to the market respectively (Deopura and Padaki, 2015) and subsequently many other synthetic fibres.

Classification of Textile Materials and Their Applications

According to their geometrical structure and physical appearance, textile materials can be categorised as one of the following types: fibres (including filaments), yarns and threads, fabrics, assembled products (both clothing and non-clothing materials). The basic and starting unit of a textile material is known as a fibre, a hair-like pliable material usually having a length at least hundred times of its diameter. When a fibre comes with an indefinite or endless length, it is termed as a filament. Fibres with limited length, usually short length, are known as “staple fibres” or “short staple fibre” in the textile industry.

Yarn is an intermediate product between fibre and fabric. The International Organisation for Standardization (ISO) considers it as a general term that covers the specific types and structures of single yarn, multiple wound yarn, folded yarn and cabled yarn (ISO 1139, 1973). A single yarn can be made from either discontinuous staple fibres or continuous filaments. For the former case, staple fibres are mechanically twisted together to produce a linear strand capitalising the physical cohesion acts between the fibres to hold each other together. For the latter case, either a monofilament or multifilament yarn is formed from one or more continuous filaments with or without any twist. When two or more single yarns wound together without any twist, they form a multiple wound yarn. However, a folded yarn is formed by twisting together two or more single yarns. Subsequently, if two or more folded yarns (or alternatively folded and single yarns) are twisted together by one or more folding operations, they produce a cabled yarn.

Traditionally fabrics are made from yarns by following two techniques – (1) interlacement of two sets of yarns, or (2) interlocking of loops formed by one set of yarn. The former process is known as weaving and the latter one is as knitting, from which the resultant materials got their names as woven and knitted fabrics respectively. However, fabric like flat assemblies can also be made directly from fibres using bonding technologies like chemical, mechanical and thermal bonding technology etc. As they are neither woven nor knitted, they could be termed as either non-woven or non-knitted, however, the term “non-woven” has become popular and industrially established to refer to those kind of fibrous assemblies. Clothing materials made for our use or sometimes for animal use are assembled products out of mostly fabrics combined with threads and minor non-textiles materials known as fashion accessories. However, assemblies of textile materials with higher percentage of non-textile materials are also made sometimes for industrial applications. Textiles reinforced composite materials are the biggest examples of this type of non-clothing materials.

Fibre Classification

Based on their origin and sources, fibres can be broadly classified as either natural or manufactured (or manmade) fibres (see Fig. 1). Natural fibres comes broadly from three sources: animal, plant and mineral. Synthetic fibres dominate within the group of man-made fibre. A subgroup within the manufactured fibres is natural polymers, which are regenerated from natural resources. They can be considered as “semi-natural” fibres. For example, viscose is manufactured from wood cellulose. In the years 2016 and 2017, the shares of natural fibres in the world production of fibres were 27% and 28% respectively, and regenerated cellulosic fibres belonged to around 6% of the global fibre production in both of the years (see Fig. 2). In the global production of natural fibres, cotton alone takes the share of more than 90% (ToI, 2018).

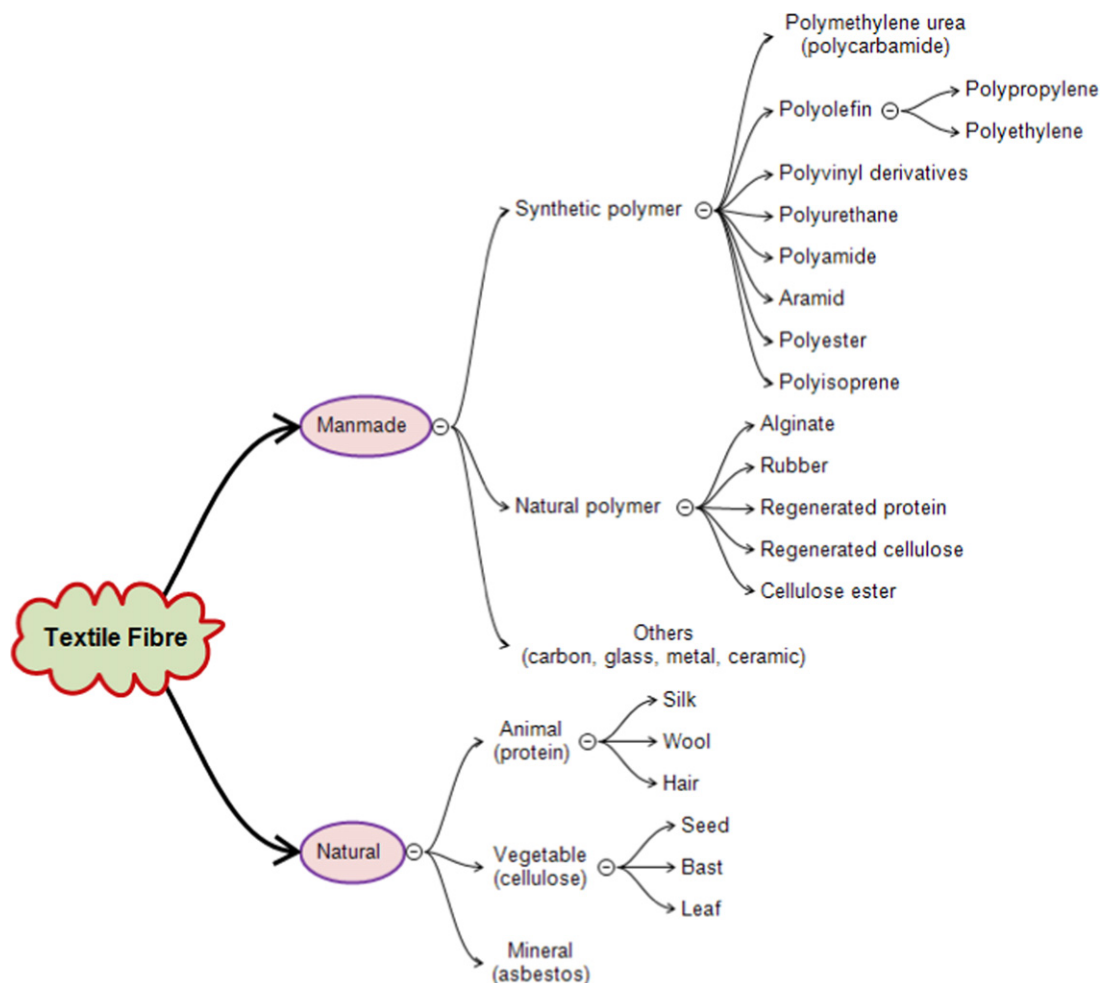


Fig. 1 Fibre classification by the Textile Institute. Reproduced from Textile Institute, 1994. Textile Terms and Definitions, tenth ed. Textile Institute: Manchester.

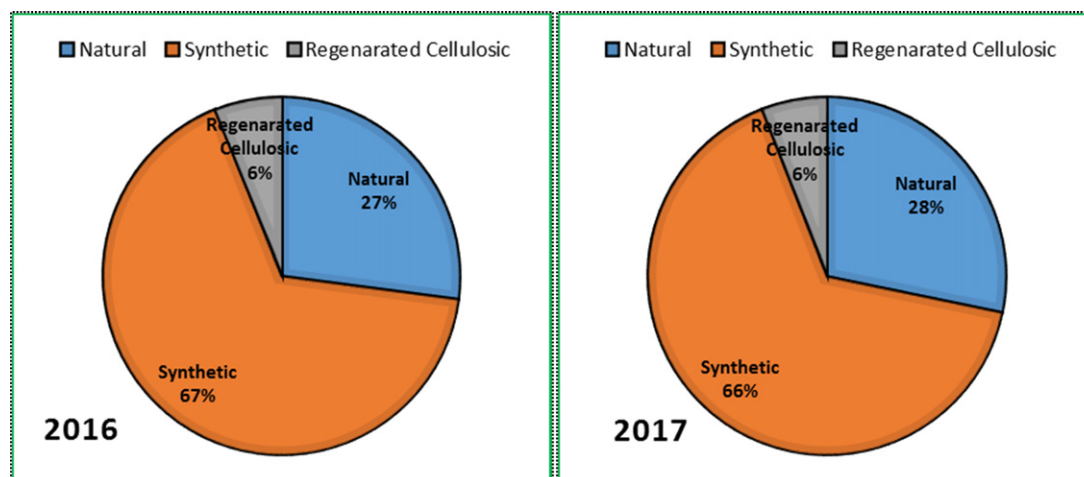


Fig. 2 Shares of natural fibres in world fibre production in 2016 and 2017. Reproduced from Tol, 2018. Textile Outlook International, Business and Market Analysis for the Global Textile and Apparel Industries, No 191. Textiles Intelligence Limited: United Kingdom.

Table 1 Characteristics of common spinning techniques

<i>Spinning techniques</i>	<i>Twist insertion per minute</i>	<i>Delivery speed (m/min)</i>
Ring	15,000–25,000	20–30
Rotor	80,000–150,000	100–300
Air-jet	150,000–250,000	150–450
Friction	200,000–300,000	150–400

Note: Adapted from Elhawary, I.A., 2015. Fibre to yarn- staple yarn spinning. In: Sinclair, R. (Ed.), Textiles and Fashion, Materials, Design and Technology. United Kingdom: Wood head Publishing, Elsevier, pp. 159–212.

Table 2 Classification of yarns

#	<i>Classes</i>	<i>Examples</i>
1	Staple spun yarns	Carded ring spun, Combed ring spun, Worsted, Semi-worsted, Woollen, Rotor spun, Compact ring-spun, Air-jet spun, Friction spun, Hollow-spindle wrap spun
2	Continuous Filament yarns	Twisted, False twisted, Stuffer-box crimped, Bi-component, Air-jet
2	Composite yarns	Core-spun (filament or staple fibres forming the core and staple as sheath)
4	Novelty yarns	Fancy (Marl, spiral, gimp, diamond, boucle, loop, snarl, knop, slub, fascinated, tape, chainette, chenille, ribbon yarns etc.), Metallic
5	Plied yarns	Two or more yarns twisted together

Note: Adapted from Lawrence, C.A., 2003. Fundamentals of Spun Yarn Technology. Florida: CRC Press. Alagirussamy, R., Das, A., 2015. Conversion of fibre to yarn: An overview. In: Sinclair, R. (Ed.), Textiles and Fashion, Materials, Design and Technology. United Kingdom: Wood head Publishing, Elsevier, pp. 159–212.

All of the natural fibres, except silk, come with limited lengths and they are usually referred as short-staple fibres. Exceptionally, silk is the only natural filament. Man-made fibres are produced as endless filaments, however, they can be cut into staple lengths based on requirement, especially, when they are blended with natural fibres to spin into blended yarns.

Yarn Classification

A yarn is made by inserting twist into a group of fibres that imparts cohesive forces among fibres to make them stick together while forming a linear structure. **Table 1** shows the rate of twist insertion by different spinning techniques used for yarn manufacturing. There are various types of yarns, and they can be grouped into five general classes, such as *staple spun yarns*, *continuous filament yarns*, *composite yarns*, *novelty yarns* and *plied yarns* (see **Table 2**). The common spinning methods used for making staple spun yarns are: Ring, Rotor, Compact, Air-jet, Friction and Wrap spinning. Yarns produced by them are commonly named after them, such as carded ring spun yarn, combed ring spun yarn etc. Worsted and woollen yarns are made from wool using mule-spinning techniques and the steps involved in the processes making them differ from each other. Continuous filaments are mechanically twisted together to produce filament yarns. Silk is an example of natural filament, which is twisted together in different numbers to make yarns depending of the desired thickness and drape of the fabrics to be made out of them. Composite yarns are engineered from more than one component yarns. An example of composite yarn is core-spun yarn, in which filaments or staple fibres form the core and staple fibres surround them as sheath. Novelty yarns are the name of a group that includes fancy and decorative yarns made with regular or irregular design elements and effects, for example slub, flake, spiral ratinè yarns etc. The plied yarns are secondary yarns made from two or more single yarns twisted together.

Fabric Classification

As mentioned earlier, fabrics can be grouped into three categories: woven, knitted and non-woven. The machine used for weaving is commonly known as loom and there are varieties of looms available such as shuttle looms, that include tappet, dobby and jacquard looms, and shuttle-less looms, which include projectile, rapier, water-jet, air jet etc., (Ormerod and Sondhelm, 1995). In weaving technique, two sets of yarns, namely warp and weft, are interlaced in different pattern patterns to produce a two-dimensional surface structure. According to weave design, woven fabrics are commonly classified as *plain*, *twill* and *satin* fabrics as presented in **Fig. 3**. Several derivatives are possible within each of the classes. Even if made with same types of yarns, the fabrics of these three classes will have different textures and different properties, e.g., tensile strength.

Knitted fabrics are broadly categorised as weft or warp knitted fabrics considering the technologies involved in them (see **Fig. 4**). A weft-knitting machine can produce three basic knit designs such as plain, rib and purl (Brackenbury, 1992) and fabrics

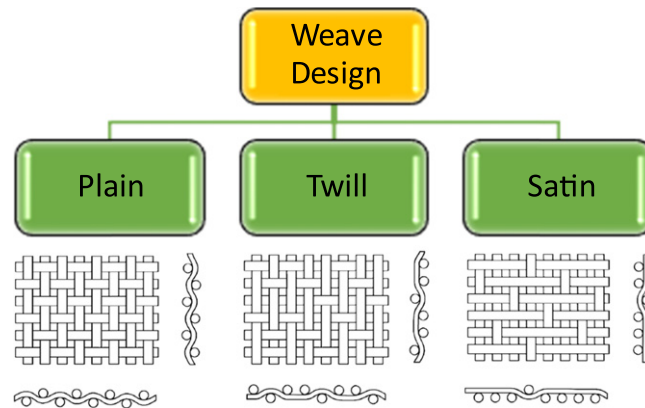


Fig. 3 Classification of weave designs.

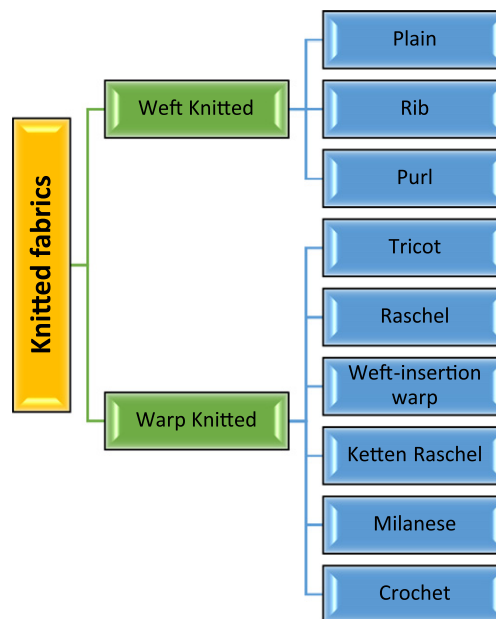


Fig. 4 Classification of knitted fabrics.

produced are named after the design they contain. Many derivatives are possible within each design type. Warp knitting technique can produce seven different types of fabrics, namely tricot, raschel, ketten raschel, milanese, simplex, crochet and weft-insertion warp (Corbman, 1983).

Non-woven materials are mainly classified into three groups based on the techniques used to lay the fibres together, such as *drylaid*, *wetlaid* and *polymer-laid* (or spunmelt) (Wilson, 2007). Manmade fibres dominate in nonwoven industry by holding over 90% of the share of fibre use. Among the natural fibres, wool can be used alone to make felt which belongs to the category of drylaid non-woven. Other natural fibres such as cotton, jute, kenaf, flex, hemp, coir, sisal, and milkweed etc., have found little nonwoven applications (Mukhopadhyay, 2014; Ma *et al.*, 2011; Ganesan and Karthik, 2016).

Assembled Products and Textile Applications

Application of textile materials can be seen from two major point of views. One is wearable textiles for on-body applications, which include the classic and fashion items that we put on every day or on special occasions. The other one is non-wearable application, which includes home textiles and technical textiles (Fig. 5). Wearable textiles, mostly in the form of a garment, come on to the market in different sizes and styles and in the categories of intimate-wear, outerwear, sportswear, protective gears etc. They are usually made targeting the age and gender of consumers. Home textiles are used for household purposes and they may have functional and/or aesthetic features. Examples of home textiles are bed sheets, pillowcases, blankets, terry towels, tablecloths, carpets, rugs and upholstery.

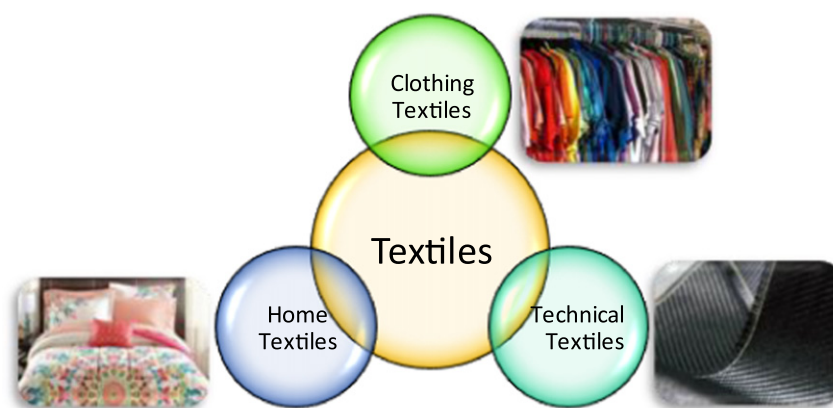


Fig. 5 The major branches of textiles.

Table 3 Subgroups of technical textiles

#	Subgroup of technical textiles	Areas of application
1	Agrotech	Agriculture, aquaculture, horticulture and forestry
2	Buildtech	Building and construction
3	Clothtech	Technical component of footwear and clothing
4	Geotech	Geotextiles and civil engineering
5	Homotech	Technical component of furniture, household textiles and floorcoverings
6	Indutech	Filtration, conveying, cleaning and other industrial uses
7	Medtech	Hygiene and medical
8	Mobiltech (Transport tech)	Automobiles, shipping, railways and aerospace
9	OekoTech (Ecotech)	Environmental protection
10	Packtech	Packaging
11	Protech	Personal and property protection
12	Sporttech	Sports and leisure

Note: Byrne, C., 2000. Technical textiles market – An overview. In: Harrocks, A.R., Anand, S.C. (Ed.), *Handbook of Technical Textiles*. Cambridge: Woodhead.

Technical textiles use the materials, which are made primarily to capitalise their technical and performance properties rather than their aesthetic or decorative properties (Textile Institute, 1994). Table 3 presents a classification and application areas of technical textiles. Market of technical textiles is rapidly growing as the industrial and academic research activities on the non-traditional application of textiles soared up in the last few decades. In the areas of Buildtech, Homotech and Mobiltech (see Table 3), textile reinforced composite materials have attracted significant attention. However, textile structures from man-made high performance fibres, such as carbon, dominates in the application areas where very high mechanical performance is required, such as aeroplane and car bodies. Natural textile reinforced composite materials are finding their applications in the areas that do not require very high mechanical resistance such as window and doorframes, indoor furniture panels, automotive panels and upholstery, parcel shelves and noise insulating panels etc., (La Mantia and Morreale, 2011).

Natural Renewable Textiles

Textile Materials From Plants

The common polymeric constituent of all plant or vegetable fibres is cellulose, which is a which a polysaccharide consisting of a linear chain of several hundreds to many thousands of $\beta(1 \rightarrow 4)$ linked D-glucose units. However, unlike the glucose in simple sugar, fibre-forming cellulose is not soluble in water due to its huge polymeric size. At elemental level, it is made of carbon (44.4%), hydrogen (6.2%) and oxygen (49.4%), therefore, it is also classified as a carbohydrate. Other than cellulose, vegetable fibres also contain different percentages of hemicellulose, lignin, pectin and wax (see Table 4). Cellulose-rich natural fibres for textile applications can be found from different parts of plants, such as seed, stem and leaf, which are further discussed in the following subsections.

Seed fibres

Table 5 provides a list of common seed fibres, their origins and different applications. Cotton is the most popular and adorable one among all vegetable fibres accounting the lion share of all natural fibres produced worldwide. It is a single cell fibre that

Table 4 Chemical composition of selected natural fibres

Natural fibres	Cellulose (wt%)	Lignin (wt%)	Hemicellulose (wt%)	Pectin (wt%)	Wax (wt%)	Micro-fibrillar/spiral angle (°)	Moisture content (wt%)
Cotton	82.7	0.7–1.6	5.7	–	0.6	14.0	6–8
Jute	61%–71.5%	12%–13%	13.6–20.4	0.2	0.5	8.0	12.6
Flax	71	2.2	18.6–20.6	2.3	1.7	10.0	10.0
Hemp	70.2–74.4	3.7–5.7	17.9–22.4	0.9	0.8	6.2	10.8
Ramie	68.6–76.2	0.6–0.7	13.1–16.7	1.9	0.3	7.5	8.0
Sisal	67–78	8.0–11.0	10.0–14.2	10.0	2.0	20.0	11.0

Note: Fakirov, S., Bhattacharyya, D., 2007. Engineering Biopolymers: Homopolymers, Blends and Composites. Munich: Hanser Publishers. (ISBN: 978-1-56990-405-3). Mohanty, AK., Misra, M., Hinrichsen, G., 2000. Biofibres, biodegradable polymers and biocomposites: An overview. Macromolecular Materials and Engineering 266–277 (1), pp. 1–24.

Table 5 Seed fibres and origin and applications

Fibre type	Fibre name	Plant origin (Common species)	Applications
Seed fibres	Cotton	<i>Gossypium hirsutum</i> , <i>Gossypium barbadense</i> , <i>Gossypium arboreum</i> , <i>Gossypium herbaceum</i>	Different types of garments (shirts, blouses, trousers, jeans etc.), home textiles (sheets, towels, table cloth etc.) and industrial textiles (tarpaulins, bookbinding threads, zipper tapes etc.).
	Java Kapok	<i>Ceiba pentandra</i>	Padding and stuffing for upholstery, lifebelts and other sea-safety equipment.
	Indian Kapok	<i>Bombax malabaricum</i>	
	Coir	<i>Cocos nucifera</i>	Cordage, matting, brushes.
	Milkweed	<i>Asclepias incarnate</i> , <i>Asclepias syriaca</i>	Padding of upholstery, substitute for kapok in lifebuoys
	Balsa	<i>Ochroma pyramidale</i>	Stuffing of mattresses and cushions
	Kumbi	<i>Cochlospermum gossypium</i>	Stuffing of cushion and upholstery
	Silk floss	<i>Chorisia speciosa</i>	Fine fabrics, stuffing for pillow and mattress
	Nepal Trumpet	<i>Beaumontia grandiflora</i>	Coarse rope and stuffing for upholstery
	Calotropis Floss ^a	<i>Calotropis gigantea</i>	Ropes, stuffing for upholstery and pillow
	Cattail fibre	<i>Typha latifolia</i> , <i>Typha augustifolia</i>	Substitute for kapok in life jackets, heat and sound insulation

^aN.B.: Poisonous plant, needs safety precaution while handling.

Note: Cook, J.G., 2001. Handbook of Textile Fibres, vol. I – Natural Fibres. London: Woodhead Publishing Ltd.

evolves from the epidermis or outer skin of a cotton-seed, which may host as many as 20,000 fibres around it. It is an annual crop and grows in the countries, which offer long frost-free time, warm weather, sunshine and adequate moisture. The top cotton producing countries in the world are China, India, United States, Pakistan, Brazil, Uzbekistan, Australia, Turkey, Turkmenistan and Greece (Cotton Australia, n.d). Fibre can be harvested after 5–7 months of planting the seeds, when the ripen seedpods burst to yield a fleecy white cotton boll. These bolls are picked from the plants either manually or mechanically and then passed through a process called “Ginning”, which separates the fibres from seeds and makes them ready for spinning into yarns and threads.

Cotton spinning involves several sub-processes in it, such as blending, opening, cleaning, carding, drawing (stretching), combing, roving and spinning. The earliest and most widely used technique to make cotton yarn is the Ring spinning technique, which can produce both fine and course yarns (Corbman, 1983). Other two techniques, which are relatively new, are Rotor and Friction spinning techniques. These two techniques used to make coarse and bulky yarns. The slub yarns, which are known for their fancy and decorative effects, are usually made by Friction spinning technique (Elhawary, 2015).

Cotton yarns are converted into fabrics by using both weaving and knitting techniques. Cotton fabrics are made using all of basic weaves (plain, twill and satin) and their numerous derivatives. The construction of a woven fabric is usually expressed by the density of warp and weft yarns (industry expressed as Ends per inch (EPI) or Picks per inch (PPI) respectively), the count (i.e., the thickness) of these two types of yarns and weave design that was used for weaving it. A list of few common commercially produced woven cotton fabrics is presented the Table 6.

In case of knitting, weft knitting technique is commonly used to knit cotton yarns into fabric. Industrially cotton knitted fabrics are made by using both circular weft knitting machines and flat knitting machines. Thus, the fabric got its names as circular and flat knitted fabric. The fabrics used for making t-shirts, polo-shirt and similar items are traditionally knitted as circular tubular form. The parts of jumpers and cardigans are usually knitted as flat fabrics.

No other fibre listed in the Table 5 is processed industrially like cotton to produce yarns and fabrics out of them. They are usually processed manually in small scale and home scale facilities.

Bast fibres

Bast fibres grow underneath the bark of dicotyledonous plants. Table 7 presents the list of bast fibres grown and processed for textile applications around the world. Jute is the second most important natural fibre after cotton and mostly produced in Bangladesh, India and China (Quarshie and Carruthers, 2014). Like cotton, the chemical constitution of jute polymer is dominated by cellulose (over

Table 6 List of few common commercially produced woven cotton fabrics

Fabric name	Construction (Warp count x Weft count – EPI x PPI)	Weave Design
20's Sheeting	20's/1 × 20's/1–60 × 60	1/1 Plain
30's Sheeting	30's/1 × 30's/1–68 × 68	1/1 Plain
40's Poplin	40's/1 × 40's/1–132 × 72	1/1 Plain
80's Voile	80's/1 × 80's/1–92 × 88	1/1 Plain
30's Twill	30's/1 × 30's/1–124 × 64	3/1 or 2/1 Twill
8 oz Drill	16's/1 × 12's/1–96 × 56	3/1 Twill
12 oz Bull Denim	7's/1 × 7's/1–68 × 36	3/1 Twill

Table 7 List of bast fibres, their origins and applications

Fibre type	Fibre name	Plant origin (Common species)	Applications
Bast Fibres	Jute	<i>Corchorus capsularis</i> , <i>Corchorus olitorius</i>	Sacks and packing cloths, bags, bailing and bundle cloth, bedding foundation, bonded fabrics, boot and shoe linings, mine brattice cloths and vent tubing, camp bed, cattle beddings, concrete cleavage fabrics, tarpaulins, damp course, cables, plastic reinforcement, filter cloths, fire curtains, furnishings, handbags, mail bags, motor car body linings, concrete reinforcement, roofing felt and upholstery foundation, etc.
	Flax	<i>Linum usitatissimum</i>	Clothing, linen sheets, sail and tent canvas, fishing lines and book-binders' thread.
	Hemp	<i>Cannabis sativa</i>	Sacking and canvas fabrics, ropes and twines
	Sunn/ Sann Hemp	<i>Crotalaria juncea</i>	Cordage, sacking, carpet, rug and fishing nets.
	Kenaf	<i>Hibiscus cannabinus</i>	Ropes, twines, canvas and sacking fabrics and carpets.
	Urena	<i>Urena lobata</i>	Sacking and yarn and fabric as jute alternative.
	Rammie	<i>Boehmeria nivea</i> , <i>Boehmeria tenacissemata</i>	Heavy canvas and packing materials, upholstery and furnishing fabrics, clothing, fishing nets and sewing threads.
	Nettle	<i>Urtica dioica</i> , <i>Urtica pilulifera</i>	Twine and rope, canvas and sail cloth, clothing and furnishing fabrics.

Note: Cook, J.G., 2001. Handbook of Textile Fibres, vol. I – Natural Fibres. London: Woodhead Publishing Ltd. Sayem, A.S.M., Haider, J., Sayeed, M.M.A., 2018. Engineered Material from Natural Fibre for Interior Design Applications, Textile Institute World Conference. United Kingdom: University of Leeds, 23–25 July 2018.

61%–71.5%) (Kabir *et al.*, 2012). However, its chemical composition is specially characterised by the presence of Hemicellulose (13.6%–20.4%) and exceptionally high content of lignin (12%–13%), see Table 4, and therefore, is identified as a lignocellulosic fibre. Unlike cotton, the bast fibres cannot be picked from the plants for use as raw material for making yarns and fabrics. They need to be separated from the bark through a process called “retting”. In traditional retting process, fibre producing plants are immersed in water to allow micro-organisms to act on the bark to dissolve or rot away the surrounding tissues to separate the bundle of fibres from the stem. Nowadays chemical process has also been developed and are being used for retting bast fibres within shorter period of time. Retting process is used for all bast fibres listed in the Table 7 except Ramie, which undergoes different processes called decortication (peeling and beating the bark and bast material) and “degumming” with caustic soda, bleaching powder and dilute acid (Cook, 2001).

Almost, all of the bast fibres are industrially processed to make yarns and fabrics. Based on the physical characteristics of the fibres, their spinning processes differ from each other's. However, these include the basic steps like carding, drawing and twisting. Yarns from these fibres are usually much coarser than cotton yarns. Therefore, the fabrics out of them are also coarser. Usually weaving technique is used to make fabric out of them, except flax, which can also be knitted. Fabric from flax is known as linen and only linen, which has found some uses as clothing material. The fabrics from the rest of the bast fibres mention the Table 7 are used for non-clothing and technical applications.

Bast fibres including jute, flax, hemp, kenaf have been experimented in the last few decades for potential applications as reinforcement in engineered composite materials and have been found very promising. These fibres have good strength and stiffness, whilst being significantly lighter in weight than conventional reinforcements such as glass fibres. Although the tensile strength of these fibres are lower than that of glass fibre, their density is approximately the half, therefore the specific moduli is higher, and tensile moduli is more or less similar, as it can be seen in the Table 8 (Quarshie and Carruthers, 2014; Kabir *et al.*, 2012). On top of that, the environmental drivers like their ability of absorbing atmospheric CO₂ for photosynthesis during production in contrary to synthetic materials and their non-toxic nature, have made them ideal candidates for incorporation into composites for industrial and technical applications that do not require very high mechanical resistance such as window and doorframes, indoor furniture panels, automotive panels and upholstery, parcel shelves and noise insulating panels etc., (La Mantia and Morreale, 2011). The most notable example of industrial use of natural fibre reinforced polymeric composite material is the jute-based thermoplastic door panels produced and commercialised by German automaker Mercedes-Benz in the 90s (La Mantia and Morreale, 2011; Summerscales *et al.*, 2010). Jute has been applied in all possible different forms, such as fibre (Bisaria *et al.*, 2015; Gopinath *et al.*, 2014), sliver (Das and Bhowmick, 2015), yarn (Memon and Nakaib, 2013; Pujari *et al.*, 2015), woven (Sudha and Thilagavathi, 2015; Arju *et al.*, 2015) and knitted (Arju *et al.*, 2015) fabrics as well as non-woven sheets (Karadumana *et al.*, 2014; Sayeed *et al.*, 2014) in composite manufacturing using either thermoplastic (Sayeed *et al.*, 2014) or thermoset

Table 8 Mechanical properties of natural fibres vs. glass fibres

Fibre	Density (g/cm ³)	Tensile modulus (GPa)	Specific modulus (GPa/g/cm ³)	Tensile strength (MPa)	Elongation to failure (%)	Moisture absorption (%)
Flax	1.4	60–80	43–57	500–900	1.2–1.6	7
Hemp	1.48	30–70	20–47	300–800	1.6	8
Jute	1.46	20–55	14–38	200–800	1.8	12
Ramie	1.5	44	29	500	2	12–17
Coir	1.25	6	5	220	15–25	10
Sisal	1.33	9–38	7–29	100–800	2–3	11
Cotton	1.51	6–12	4–8	300–600	3–10	8–25
Glass	2.55	73	29	2400	3	–

Note: Quarshie, R., Carruthers, J., 2014. Biocomposites – Technology Overview. Materials KTN and NetComposites Ltd. Available from: <https://netcomposites.com/media/1211/biocomposites-guide.pdf> (accessed 24.08.17).

Table 9 List of common leaf fibres and their origins and applications

Fibre type	Fibre name	Plant origin (Common species)	Applications
Leaf Fibres	Sisal	<i>Agave sisalana</i>	Cordage, twine, sacks, paper filter, matting, rugs, floor covering, hat.
	Pineapple/Pina	<i>Ananas comosus</i>	Fine cloth, ropes, twines
	Abaca	<i>Musa textilis</i>	Tea-bags, stencil tissue, meat casing, ropes, cordage, hawsers and ships' cable, fishing nets and lines, fabrics for clothing, carpet, table mats etc.
	Henequen	<i>Agave fourcroydes</i>	Agricultural twine, coarse fabrics.
	Canton	<i>Musa species</i>	Cordage
	Pacol		
	Cantala	<i>Agave cantana</i>	Native fabrics
	Letona	<i>Agave letonae</i>	Coffee bag, canvas, hammock cloth
	Mauritus Fibre	<i>Furcraea gigantea</i>	Bagging and coarse fabrics
	Phormium	<i>Phormium tenax</i>	Ropes, twines, coarse bagging materials
	Sansevieria	Various species of genus <i>Sansevieria</i>	Ropes, twines, coarse bagging fabrics
	Caroa	<i>Neolazovia variegata</i>	Ropes, twines, clothing fabrics
	Pita Floja	<i>Aechme magdalenae</i>	Ropes, twines, coarse fabrics
	Bromelia	<i>Species of Bromelia</i>	Canvas-type fabrics, ropes and twines
	Palma	<i>Samuela carnerosana</i>	Ropes, twines, bagging fabrics, brushes
	Fique	<i>Furcraea macrophylla</i>	Bagging fabrics, canvas for hammocks etc.
	Piassava	<i>Bahia piassava</i> , <i>Para piassava</i>	Brooms and brushes
	Raffia	–	Horticulture uses, hats etc.

Note: Cook, J.G., 2001. Handbook of Textile Fibres, vol. I – Natural Fibres. London: Woodhead Publishing Ltd; Corbman, P.B., 1983. Textiles–Fiber to Fabric, sixth ed. Singapore: McGraw-Hill.

(Bisaria *et al.*, 2015; Das and Bhowmick, 2015; Pujari *et al.*, 2015) polymeric matrices. Similarly, flax has also got notable applications in composite industry (Quarshie and Carruthers, 2014; Sayem *et al.*, 2018).

Leaf fibres

The leaves of monocotyledonous plants grows fibres in them. Table 9 shows the list of fibres that can be extracted from plant leaves, their origin and applications. Among them, only Sisal and pineapple have got some significant commercial importance and rest of them are produced and processed locally and natively in limited places.

To extract fibre from the leaves, fresh leaves are processed by decorticating machine and then washed with water or sometimes kept for retting to make them ready for spinning (Yu, 2005; Yu and Frank, 2005). Like Jute, Sisal fibres need to be oiled to make them softer and smoother to process to the subsequent stages of yarn manufacturing. Ring spinning technique is used from making sisal yarn (Yu, 2005). The weaving of sisal is similar to that of jute and kenaf. For making rope and twine, pineapple fibre is processed on the jute spinning system. However, for making fine yarns that suitable for fabrics targeting garment manufacturing, pineapple fibres are passed through an enzymatic or chemical degumming process and then spun into yarns using cotton or worsted spinning system (Yu and Frank, 2005).

Textile Materials From Animals

Fibres that come from animal kingdom are based on naturally occurring protein; therefore, they are also known as protein fibres. Fibre forming proteins are composed of different amino acids and can be of very complex to simple structures. Common animal

fibres are silk from different insects, wool from sheep and hairs from different camel and goat like animals. Silk is the strongest among all natural fibres (Corbman, 1983; Cook, 2001).

Silk fibre

The larvae of the caterpillar of the species *Bombyx mori*, known as silkworm, produces liquid protein which solidifies in contact with air when excreted through natural spinneret (caterpillar's jaw). At a certain stage of its life cycle, a silkworm produces a cocoon by wrapping itself with its own protein fibres. If left undisturbed a cocoon develops into a moth within two week. However, in sericulture industry silk worms are reared just to produce the cocoons from which silk fibres are collected. Silkworm larvae are fed on mulberry leaves and hatched for around 35 days before they become ready for reeling, the process of unwinding of silk filaments from cocoons. It requires the cocoons to be immersed within hot and cold water step by step to soften the natural gummy substance, *sericin*, that holds together the filament strands. Reeled silk is then transformed into filament yarns by a process called throwing (an alternative term of twisting used in the silk industry). Fabrics from silk yarn are usually made by following weaving technique. Silk fabrics are usually soft, lighter in weight than fabrics from any other natural fibres and have a luxurious appearance, and they are popular for clothing applications.

Wool fibre

Wool fibre is formed by a complex protein called "keratin" that grows from the follicle in the skin of sheep. Including all breeds and cross-breeds of sheep found around the world, there over 200 distinct grades of sheep from which wool can be collected (Corbman, 1983). The best quality wool are known as merino wool. It comes from a breed of sheep known as merino which includes the varieties of Ohio Merino, Australian Silesian and French Rambouillet. Sheep are normally shorn of their fleece every year. Raw wool contains a lot of dust and dirt, natural grease and dried perspiration "suint". Therefore, it needs to be scoured with warm water containing detergent before spinning into yarns. Woollen and worsted are two different types of yarns produced from wool. Woollen yarns are thicker, fuller and looser than the worsted yarn. The fibre preparation and spinning processes also vary for these two type of yarns. Both weaving and knitting technology are used to make fabrics out of woollen and worsted yarns. Wool fabric provides warmth to the users; therefore, varieties of winter clothing are made from it.

Other hair fibres and feather

Different species of camels and goats are sources of protein fibres that can be used as textile materials. However they are not usually nurtured in large scale like sheep to produce fibres. Two-humped Bactrian camel is known for its fine hair fibres. Other camel like animals from which hair fibres are collected are Llama, Alpaca, Vicuna and Guanaco. Cashmere wool and mohair fibres come from Cashmere and Angora goats respectively. Hairs from Angora rabbit and Qiviut ox are also known for their textile uses. Fillers for cushions, pillows quilted outerwear are also made from cow hair, horse hair, down and feathers from ducks and geese.

Textile Materials From Minerals

The natural fibrous materials come from minerals formed in varieties of rock found in Italy, South America and Canada are known as asbestos. Chemically it is a form of silicate of magnesium and calcium containing iron, aluminium and other minerals. Asbestos can be spun into yarn, and in the past, it found applications in the firefighting suits and different fire resistant materials like theatre curtains, draperies etc., due to its fireproof property. However, the use of asbestos is banned in many countries today as it was found hazardous to health.

Comparison of Properties among the Natural Fibres

This section compares density, stiffness, strength and energy storage properties of the bio-based natural fibres both from plant and animal origin using Ashby charts (see Figs. 6–8) derived from CES EduPack Software (Ashby, 2007). Other than direct natural fibres, three other natural materials (wood, bamboo and palm) are also considered in the chart for reference purpose. The only mineral fibre, asbestos, is presented in the graphs but not considered in the discussions as it is currently not being used for technical application. It should be noted that their property values are given for bulk material as their corresponding fibre property values are not available in the database. Some popular man-made fibres such as Kevlar, glass, steel, carbon, polyethylene were also plotted to compare their properties with the natural fibres. Additional man-made materials in the bulk form such as polyester, nylon and rubber were also plotted.

Stiffness and density

Higher stiffness and lower density are important properties of fibres needed for textile applications. Fig. 6 presents the relationship between stiffness defined by Young's modulus and density of different natural and man-made fibres. Each bubble represents an individual material with its ranges of Young's modulus and density. The large envelopes enclose a group of materials for a particular class such as natural fibre, natural material, elastomer, plastic and man-made fibres. The chart reveals that natural materials can cover a wide range of density and Young's moduli similar to the engineering materials currently being used (Shah, 2014). The specific values of densities and Young's moduli for individual materials are listed in Tables 10 and 11. In

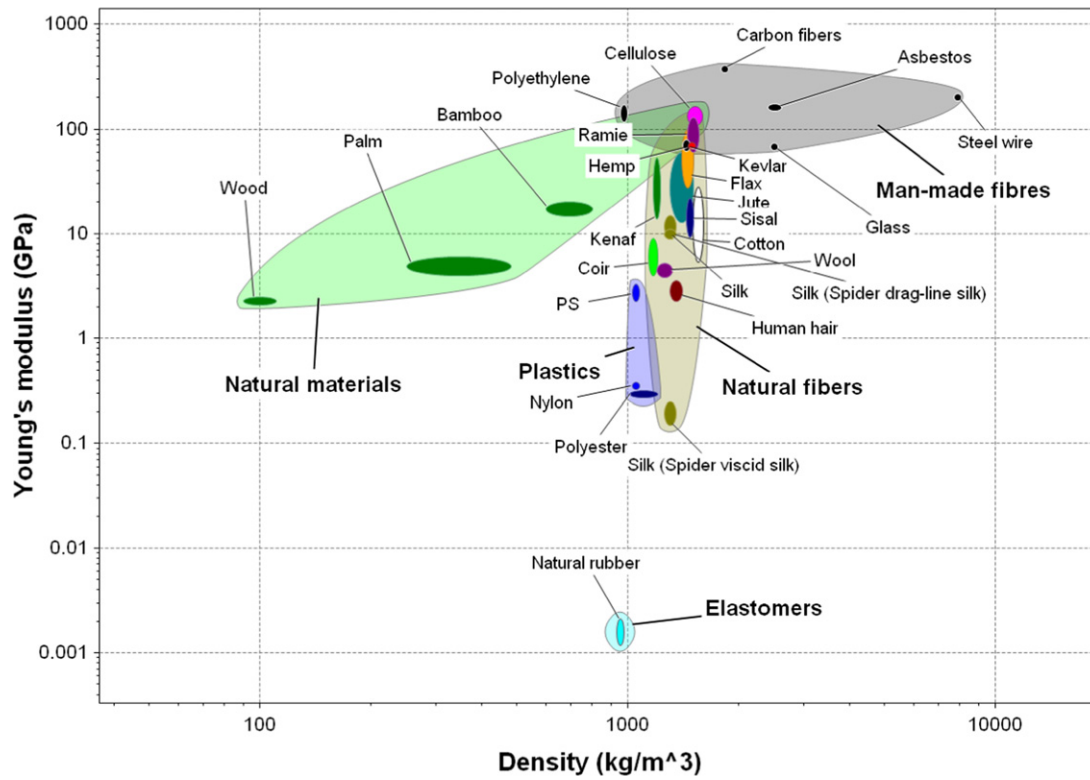


Fig. 6 A comparison of stiffness vs density between natural and some selected man-made fibres.

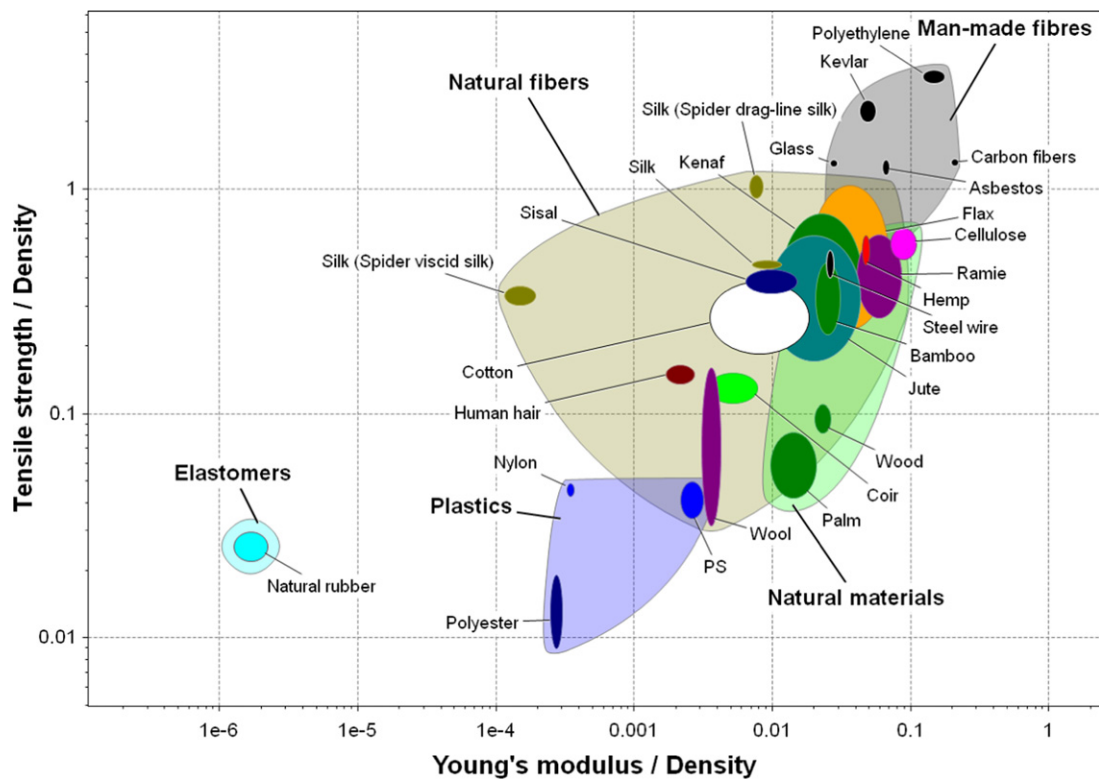


Fig. 7 A comparison of specific strength vs specific stiffness between natural and some selected man-made fibres.

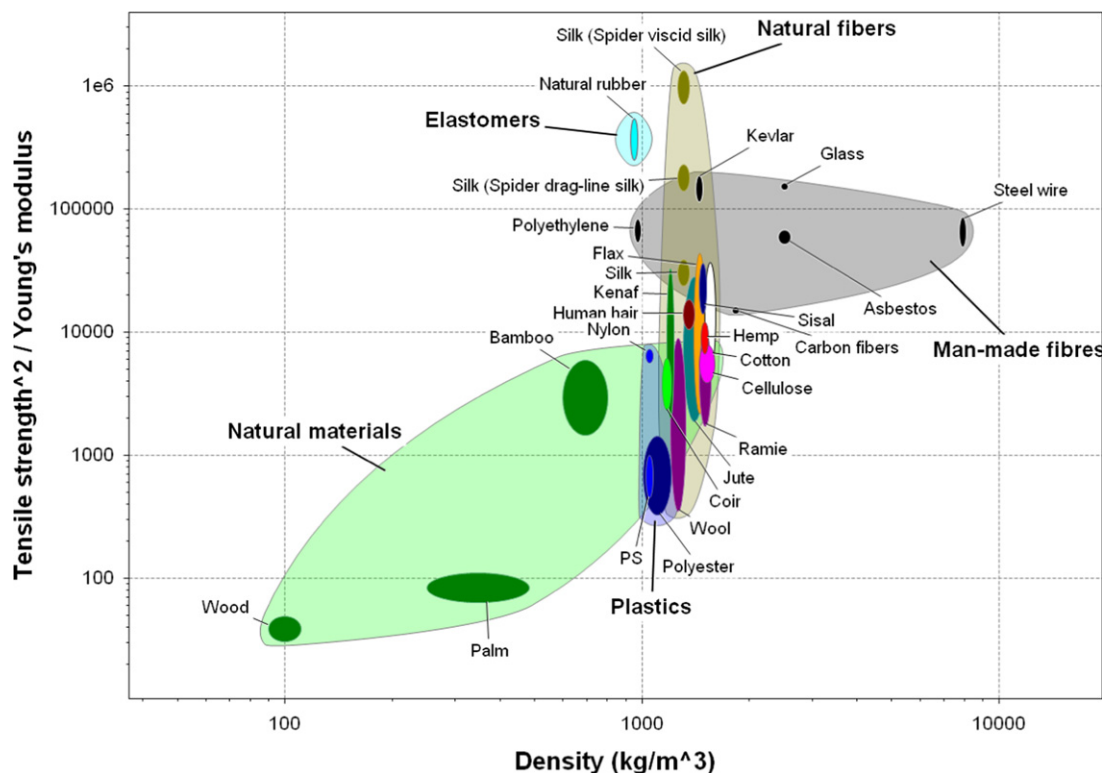


Fig. 8 The maximum capacity of elastic energy storage with density for the natural fibres and some selected man-made fibres.

general, the densities of bio-based fibres are clustered in a narrow range from 1.14 kg/m^3 (coir) to 1.60 kg/m^3 (cotton). Among the man-made fibres, only Kevlar and polyethylene fibres have densities falling within the same range for the natural fibres. Due to low density and weight of natural fibres is also very low and this makes them attractive for the textile applications. In general, animal-based fibres are lighter than the plant based fibres.

On the other hand, the Young's modulus of bio-based fibres varies over a long range from 0.15 GPa (Silk-Spider viscid silk) to 73.5 GPa (hemp). Ramie has even better strength than some of the strongest man-made fibres such as Kevlar and glass fibres. Other bast fibres such as kenaf, jute, flax and hemp have similar strength compared to that of Kevlar. It is interesting to note that fibres from animal sources display lower strength than the plant based fibres.

Strength and stiffness

In general, the textile fibres should have both high axial stiffness and strength that determines their performance in application. In many cases, nature has already accommodated those properties in the bio-based fibres. Specific tensile strength (strength/density) and specific stiffness (stiffness/density) of different fibres are plotted and presented in Fig. 7. In terms of both specific strength and stiffness, some of the bast fibres such as ramie, flax, hemp, kenaf and jute can perform equal or better than steel. However, few man-made fibres such as Kevlar, carbon, glass and polyethylene perform far better than the bio-based fibres. Among the plant-based fibres, flax displays the best performance under tensile loading condition. However, the performance of animal-based fibres are not quite as good as the bast fibres.

Elastic energy and density

Fibres, like a rubber band, can store energy when stretched. Elastic energy storage is a measure of the energy required to stretch a fibre. The maximum energy storage is measured by the quantity $\sigma_{ts}^2/2E$ per unit volume or $\sigma_{ts}^2/2\rho E$ per unit weight, where σ_{ts} is tensile strength, E is Young's modulus and ρ is density. A higher energy storage value for a material indicates that the material has the ability to act like a spring, which can help in absorbing an impact load. Fig. 8 presents a chart of energy storage and density (Ashby, 2007). Among the natural materials, silk has the capacity of storing highest elastic energy even better than rubber or steel. A number of other plant-based natural fibres such as flax, cotton, sisal, hemp, jute and ramie also have either equal or better ability to store elastic energy than some of the polymeric materials such as nylon and polyester.

Semi-Natural Renewable Textiles

As presented in the Fig. 1 in the Section "Fibre Classification", a portion of man-made fibres comes from natural polymers extracted from pure natural sources existing in different physical forms other than in fibre form. These include alginate, rubber,

Table 10 Range of densities for different natural fibres and materials with their man-made counterparts

Material type	Name	Density (kg/m ³)
Polymer and elastomer	Polyethylene fibre	965–975
Seed fibre	Coir	1.14e3–1.2e3
Bast fibre	Kenaf	1.19e3–1.2e3
Animal fibre	Wool	1.2e3–1.32e3
	Silk (Spider drag-line silk)	1.26e3–1.35e3
	Silk (Spider viscid silk)	1.26e3–1.35e3
	Silk	1.26e3–1.35e3
	Human hair	1.3e3–1.4e3
Bast fibre	Jute	1.3e3–1.5e3
Bast fibre	Flax	1.4e3–1.5e3
Man-made fibre	Kevlar 29	1.43e3–1.45e3
Leaf fibre	Sisal	1.45e3–1.5e3
Bast fibre	Ramie	1.45e3–1.55e3
Bast fibre	Hemp	1.48e3–1.5e3
Seed fibre	Cotton	1.5e3–1.6e3
Man-made fibre	Carbon fibre	1.8e3–1.85e3
	Glass, C grade	2.49e3–2.5e3
	Steel wire	7.85e3–7.9e3

Table 11 Range of Young's modulli for different natural fibres and materials with their man-made counterparts

Material type	Name	Young's modulus (GPa)
Animal fibre	Silk (Spider viscid silk)	0.15–0.25
	Human hair	2.3–3.6
	Wool	3.9–5.2
Seed fibre	Coir	4.0–9.0
	Cotton	5.5–28
Animal fibre	Silk (Spider drag-line silk)	9.0–11.0
	Silk	9.3–15
Leaf fibre	Sisal	9.4–22
Bast fibre	Jute	13–60
	Kenaf	14–53
	Flax	27.6–100
	Ramie	61.4–128
	Kevlar 29	62–80
Man-made fibre	Glass, C grade	66–70
	Hemp	66.5–73.5
Bast fibre	Polyethylene fibre	120–170
Man-made fibre	Steel wire	200–210
	Carbon fibre	370–390

regenerated protein, regenerated cellulose and cellulose ester. The regenerated cellulosic filament viscose, also known as rayon, is the leading semi-natural fibre that has got commercial importance. Lyocell is another regenerated cellulosic fibre, which follows an eco-friendly production process and possesses improved fibre properties compared to viscose.

Sustainability Analysis of Bio-Based Fibres

Product Life Cycle (PLC) of Natural Fibres

A product life cycle of natural fibres for textile application is presented in Fig. 9. Most of the bio-based fibres come from plants, which absorb environmentally harmful carbon dioxide (CO₂) and releases lifesaving oxygen (O₂) during plant life cycle. Thus, CO₂ footprint from the plant-based natural fibres would be much less at the source compared to the man-made fibres. After fibres are extracted from natural sources, few additives are often added to them to improve their performance in subsequent processes to convert them into value-added intermediates like yarns and fabrics. Finally, commercial products are made from them through design, manufacturing, assembly and packaging operations. After consumer use, a number of options available for the natural textiles materials that make them attractive from sustainability point of view. The old clothes in good condition can be donated or sold to the consumers in developing countries to

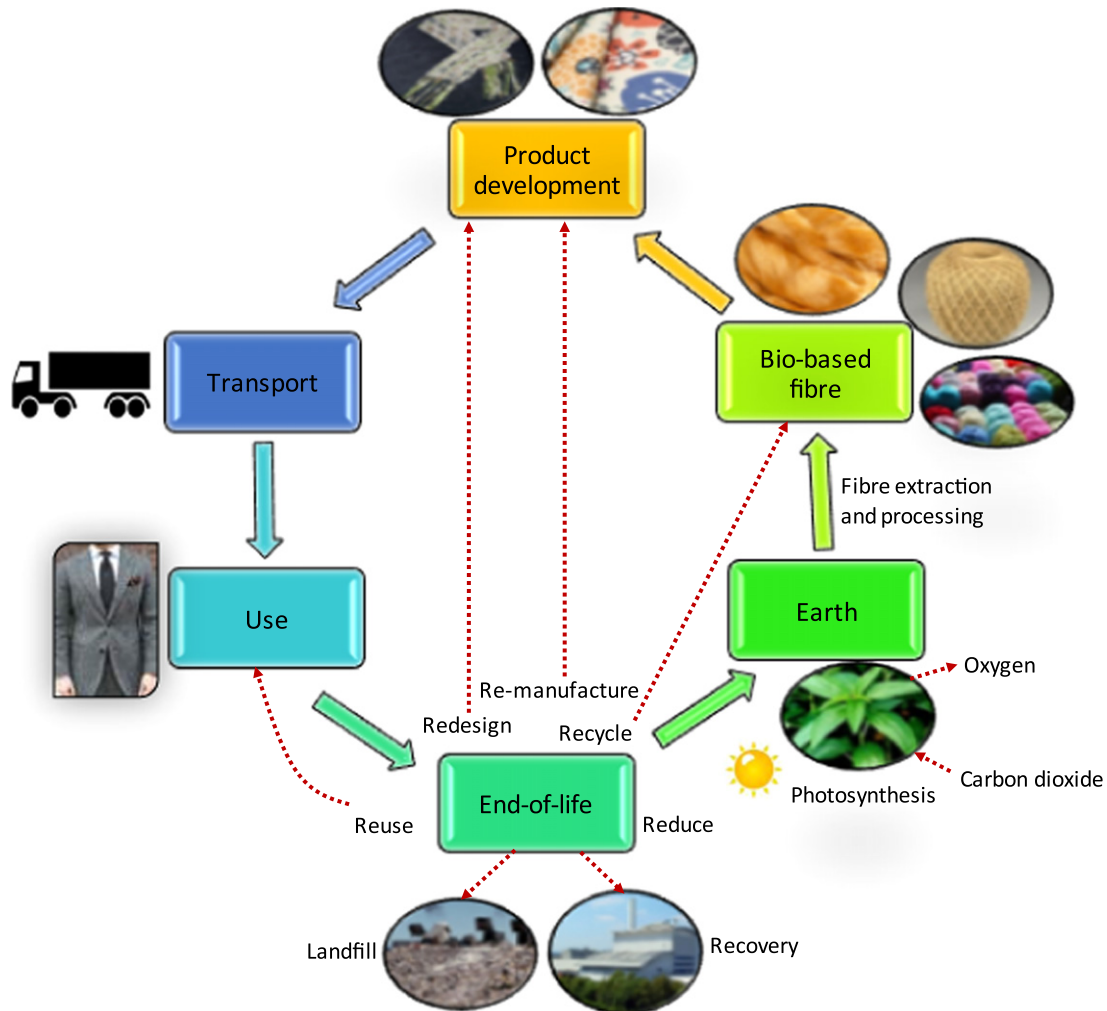


Fig. 9 Product life cycle of natural fibres.

expand their life cycle. The used textiles can be recycled by extracting the fibres out of them to feed them back in the product life cycle. The used products in good condition can be also be used for making other products through disassembly, redesigning and remanufacturing. The materials that are not suitable for further recycling, can be disposed to the landfills. Through natural degradation in course of time, the disposed materials get mixed with soil and become integral part of mother earth.

CO₂ Footprint and Embodied Energy for Natural Fibres

During primary material production, CO₂ footprint and embodied energy are the two indicators most frequently used to measure the environmental impact. CO₂ footprints of natural fibres and some synthetic fibres are presented in Fig. 10. It is very clear that CO₂ footprint of natural fibres during primary production is lower than that of the manmade fibres such as glass, carbon, Kevlar and polymeric fibres. Lower CO₂ footprint from the natural fibres is not the only benefit but the fibre-producing plants also absorb CO₂ from the nature and release oxygen. This creates a positive impact from sustainability point of view. In addition, the bio-based fibres are naturally biodegradable and benign to eco-system. Unlike synthetic fibre, plant-based fibres do not produce any toxic emission during production, although, raising animals for fibre collection can some emit greenhouse gases. In general, the price of the bio-based fibres are much less than the price of their synthetic counterparts. In general, the man-made fibres are more expensive than the natural fibres but steel and glass fibre prices are somewhat closer to the prices of the natural fibres. Jute and kenaf are the cheapest among the bast fibres. An almost identical chart can also be obtained for embodied energy versus price as shown in Fig. 11.

Research and Innovation

Research is being carried out to explore non-traditional natural resources as a source of textile materials. Few examples are presented in this section.

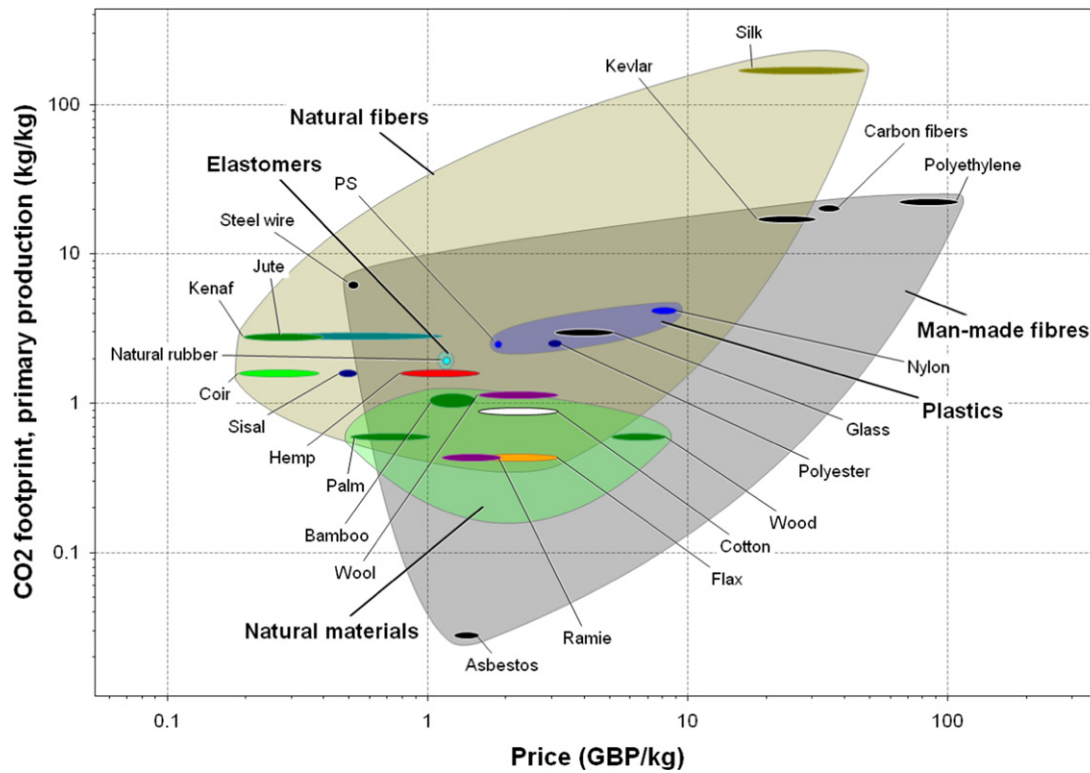


Fig. 10 CO₂ footprint for different fibres with prices.

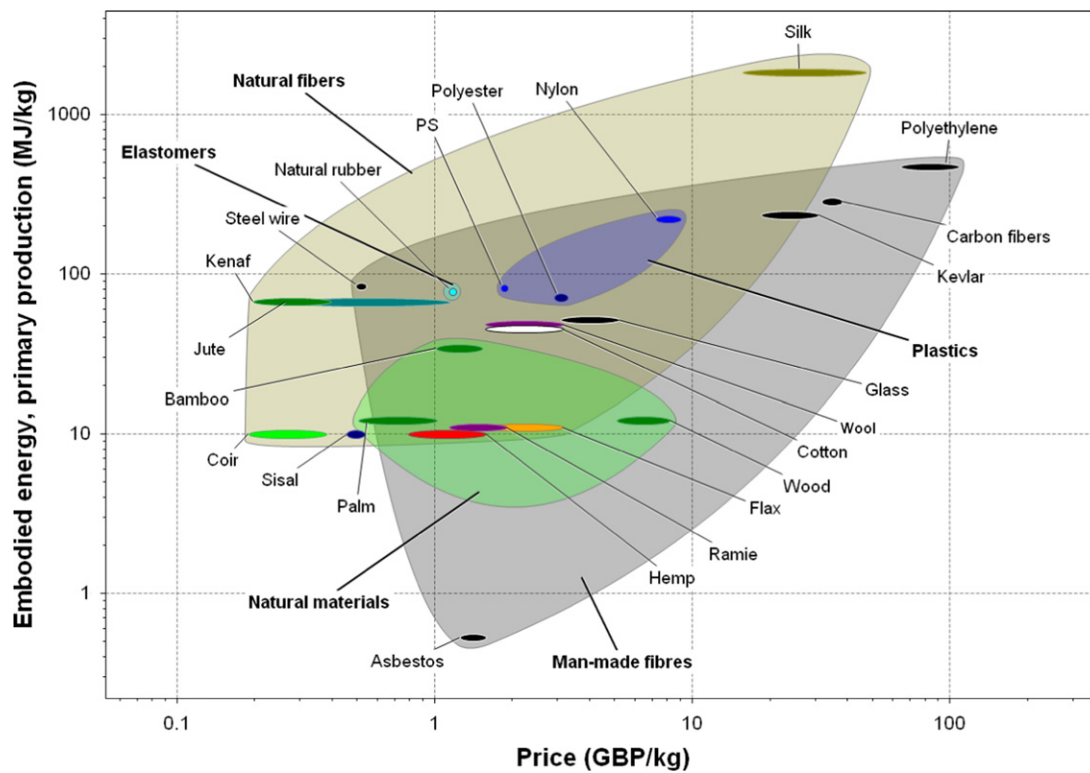


Fig. 11 CO₂ footprint for different fibres with prices.

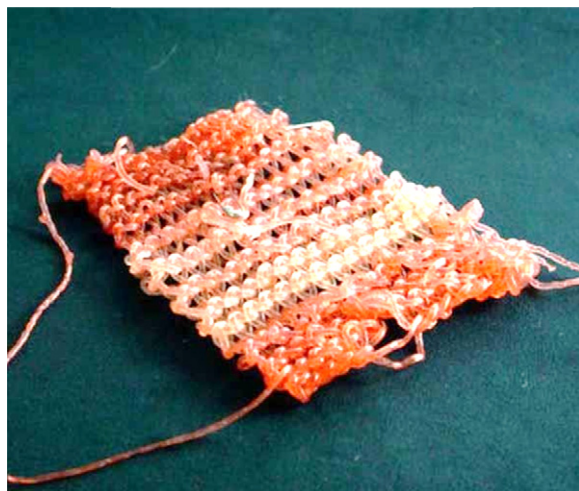


Fig. 12 Knitted swatch from alginate yarns. Reproduced from Preuss, S., 2018. Sustainable textile innovations: Bio yarn made from kelp fibres. Available at: <https://fashionunited.uk/news/business/sustainable-textile-innovations-bio-yarn-made-from-kelp-fibres/2018032628811> (accessed 11.12.18).

Protein Fibre From Yeast

Recent developments in genetic engineering have enabled researchers to impregnate protein producing DNA into yeast to produce protein in laboratory (Vendrely and Scheibel, 2007). A company called “Bolt Threads” (see “Relevant Websites section”) has reported the production of fibre and yarn for textile uses from protein achieved through fermentation of genetically modified yeast in the presence of sugar and water (Bolt, n.d.). They extract the liquid protein from yeast and extrude it through spinneret to get filaments in the same way acrylic and viscose filaments are extruded.

Alginate Fibre From Algae

Some species of seaweeds from the orders Laminariales and Fucales, commonly known as kelps and fucoids, respectively, are a great source of alginate (Peteiro, 2018). This can be chemically extracted as sodium alginate solution to convert to fibres (FAO, n.d.; Quin, 2008). A biomaterials research company AlgiKnit (see “Relevant Websites section”) has reported a compostable yarn from kelp that can be formed into wearable textiles. It extracts alginate from kelp and combines it with other renewable biopolymers to produce yarn, which is strong enough and stretchable enough to be knitted by hand or by machine to be used in textile manufacturing (see Fig. 12). The fabric from this type yarn can also be dyed with natural pigments.

Lotus Fibre

A Cambodian company Samalota Lotus Textiles (See Relevant Websites Section) is promoting the extraction of natural fibre from lotus stems to make woven fabric out of this (Preuss, 2017). Lotus plants grow in abundance in many Asian wetlands. The lotus flower, according to Buddhist teaching, is a symbol of inner-determination and spirituality. Lotus clothes were worn by Buddhist monks centuries ago for this spiritual value. After years of oblivion, this lost handicraft has now been brought back to life by this Cambodian company. The extraction of fibre from lotus stem is quite time-consuming but the fibres produce luxurious fabrics that feel like a combination of silk and raw linen. After harvesting the lotus stems from lakes, the artisans slice the end of the stems and pull out the long, thin fibres from the centre. The long strand of fibre are then washed and hung to dry and finally handwoven on looms into fabric.

Conclusion and Future Trend

As an industry, textile is one of the largest industries globally and one of the most polluting ones (European Commission, 2013). At the same time, production and processing of textile materials is very energy consuming and resource hungry. Although at the production stage, most pollution may occur from the production of manmade fibres, natural fibres are also not free from the guilt. Growing cottons require a high level of water and pesticide consumptions. Examples of serious impact of toxic chemical used cotton farming include the reports of death of a US cotton farmer from a brain tumour and serious birth defects in Indian cotton farmers’ children (Parry, 2018). The evolve of pest-resistant genetically modified cotton varieties also may lead to problems further down the line, such as the emergence of “superweeds” which are resistant to standard pesticides and will require more toxic

pesticides to control them, which will be eventually more harmful to surrounding livestock and humans (Parry, 2018). Although research and initiatives are being undertaken to develop new sources of renewable textiles, it is also important to undertake more and more research on fixing the hundreds of years old pollution-prone techniques of producing and processing textiles materials.

In order to reduce the ecological impact of textile industry, it is important to make use of more and more bio-based renewable and biodegradable fibres as a building block of textile products. However, the key challenge is to first find out natural fibres, which have critical performance properties same as the man-made fibres as it is not just enough for the natural fibres having only low CO₂ footprint. The bio-based additives are equally important to introduce in the processing of the natural fibres to further lowering the eco-impact. Consumers usually feel good about their clothing made of bio-based fabrics and are even ready to pay more to help create a sustainable world. However, building awareness among consumers is still an important issue to encourage the increased use of bio-based textiles avoiding synthetic textiles.

See also: Natural Fiber Composites: Review of Recent Automotive Trends

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<https://boltthreads.com>

Bolt Threads.

<https://samatoa.lotus-flower-fabric.com/>

Samatoa Lotus Textiles the Most Spiritual Fabric in the World.

An Overview on the Opportunities for 3D Printing With Biobased Materials

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Introduction

The blanket term *biomaterials* is usually used to mean biological, biomedical, and bioderived materials (Ashby and Pereira-Medrano, 2015). Natural materials that are produced directly by biological systems (such as skin, bone, wood, shell, hair, etc.) are biological materials. Materials like paper, plywood, twine, and rope, which are synthesized from natural biological materials, are classified as bioderived materials. In this paper, the term *biobased materials* is used to cover both biological and bioderived materials. This article does not cover biomedical materials, which are biocompatible, but nonbiomaterials like bioglass, alumina biceramics, titanium, silver amalgam etc., and bioinspired materials and structures that mimic nature and biological materials.

Three-dimensional (3D) printing is a technique of physical prototyping from virtual CAD models through layer-by-layer deposition of materials. It is also known as additive manufacturing, solid freeform fabrication, and layered manufacturing (Bose *et al.*, 2018). Until recently, 3D printing was mainly limited to model making and one-off product manufacturing for specialized applications such as body part replacement in biomedical field. One of the key reasons for the limited application can be attributed to the lack of available materials in the form suitable for 3D printing. Polymers have been widely used as the primary material for many years. However, more recently materials all major families are becoming popular in 3D printing industry due to a number of reasons such as advancement in 3D printing technologies, advancement in materials processing in suitable form, worldwide push towards digital manufacturing, etc. Fig. 1 presents some of the popular materials used in 3D printing. The technology has become very popular nowadays and both home-scale and industrial scale 3D-printers are now available on the market for a variety of application areas (Fig. 2). There has also been a great interest of 3D printing using biobased raw materials from industry and academia in the recent years. This article provides an overview of the development of biobased materials for 3D printing and its research and future application prospects.

Biobased Materials

A General Overview

Proteins, polysaccharides, and minerals are the basic structural building blocks of nature. Proteins are fundamental components of all living cells and they are complex organic macromolecules made from the basic elements hydrogen, oxygen, nitrogen, and sulfur. Polysaccharides are polymers of monosaccharides such as glucose, fructose, and galactose. Polysaccharides that serve as energy storage in plants and animals are starch and glycogen. Common examples of structural polysaccharides are cellulose and chitin. Cellulose is abundantly found in plants and is said to be the most abundant organic molecule on Earth. Chitin has a similar

Polymers	Composites	Natural/ biobased	Ceramics	Metals and Alloys
•Acrylonitrile Butadiene Styrene (ABS) •Polycarbonate •Polystyrene •Polypropylene •Epoxies •Polyetherether keytone (PEEK) •Polyurethane (Elastomer)	•PLA+natural fibres (e.g., hemp) •Polyamide (Nylon) 11 and 12-Glass /carbon/metal (Al) filled •Concrete	•Polylactic Acid (PLA) •Paper •Chocolate •Sand •Tissue	•Alumina •Silicon carbide •Silicon nitride •Zirconia	•Aluminum alloys/Co–Cr alloys/Ti–6Al–4V/Nickel-based superalloys (Inconel) •Stainless steel/Tool steel •Gold/Silver/Titanium

Fig. 1 Examples of materials used in 3D printing from different groups. Reproduced from Bourell, D., Kruth, J.P., Leu, M., *et al.*, 2017. Materials for additive manufacturing. CIRP Annals 66 (2), 659–681. Ngo, T.D., Kashani, A., Imbalzano, G., Nguyen, K.T.Q., Hui, D., 2018. Additive manufacturing (3D printing): A review of materials, methods, applications and challenges. Composites Part B: Engineering 143, 172–196. Gardan, J., 2019. Smart materials in additive manufacturing: State of the art and trends. Virtual and Physical Prototyping 14 (1), 1–18. Tappa, K., Jammalamadaka, U., 2018. Novel biomaterials used in medical 3D printing techniques. Journal of Functional Biomaterials 9 (1), 17.

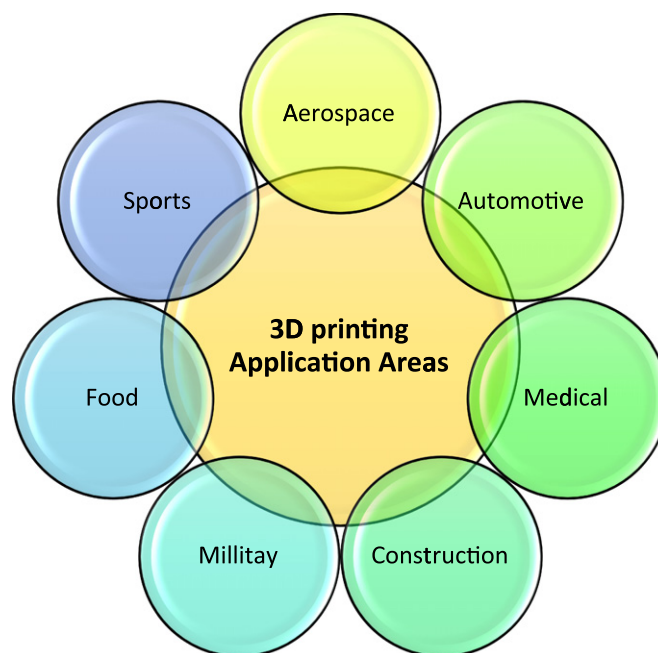


Fig. 2 Major application areas for 3D printing. Reproduced from Tofail, S.A., Koumoulos, E.P., Bandyopadhyay, A., *et al.*, 2018. Additive manufacturing: Scientific and technological challenges, market uptake and opportunities. *Materials Today* 21 (1), 22–37.

structure to cellulose, but differentiated by its nitrogen-containing side branches. It is found in arthropod exoskeletons and in the cell walls of some fungi.

Complex of covalently linked protein and polysaccharides, such as glycoproteins and proteoglycans, are also found in biological systems. Collagen is a glycoprotein that serves as natural structural molecule and antibodies. Other important natural materials that are part of biological systems are minerals in form of ceramics such as calcite, aragonite, hydroxyapatite (HA), and biosilica. Living tissues incorporated with these minerals are known as mineralized tissues.

Biobased materials exist in a variety of forms in nature such as soft tissues, mineralized hard tissues, wood and wood-like materials, and natural fibers (Ashby and Pereira-Medrano, 2015). There are two broad groups of soft tissues found in animals – active (muscle) and passive (connective tissues). Muscles are predominantly protein based and connective tissues such as ligament, tendon, and cartilage are predominantly acellular composite materials made of proteins, polysaccharides, and glycoproteins. Although included in this group, the keratinized tissues such as hair, horn, hoof, and the shells of turtles and tortoises are much stiffer and stronger than other tissues.

The mineralized hard tissues include dentine and enamel (of teeth and tusk), bone, antler, shell (of exoskeleton), and corals. These are living tissues combined with minerals. All wood and wood-like materials are made of cellulose and their examples include tree-wood, palm wood, bamboo, cork, and nutshells. Other forms of biobased materials are natural fibers that are also abundantly found both in the plant and animal kingdoms. Further details of natural fibers can be found in Sayem and Haider (2019).

Bioplastics

The organization called European Bioplastics defines bioplastics as the plastic materials that either biobased or biodegradable, or both. According to this definition, the term covers the following three groups: Biodegradable biobased, biodegradable fossil-based, and nonbiodegradable biobased bioplastics (Norwegian Environment Agency, 2018), as can be seen in Table 1.

Hydrogel

Another very promising and well-researched biopolymer is hydrogel. Hydrogels are 3D polymer gel networks capable of holding nutrition within the water and extruding them in a controlled and precise manner (Skardal and Atala, 2015). They have been used in regeneration medicine such as drug delivery and tissue engineering because of the ability to produce them with a tunable elastic modulus that can mimic soft tissue (Seliktar, 2012). Basically, hydrogel can be made of natural polymer, synthetic polymer, or a combination of the natural and the synthetic polymer (Kirchmayer *et al.*, 2015). In contrast to the hydrogel made of natural polymer, hydrogel from synthetic polymer suffers from nonbiocompatibility, poor cellular adhesion, and limited or no biodegradability (Murphy and Atala, 2014; Skardal and Atala, 2015). However, they have advantages of tunable molecular weight, high mechanical property, and other limitations can be avoided with proper programming in processing and material selection

Table 1 Three groups of bioplastics

#	Groups of bioplastics	Examples
1	Biodegradable biobased	Poly(lactic Acid), Poly(hydroxyalkanoates), starch blends (including Mater-Bi), Poly(butylene Succinate (Adipate) [PBS(A)]
2	Biodegradable fossil-based	Poly(butylene adipate terephthalate, [PBS(A)], Polycaprolactone, Poly(vinyl Alcohol)
3	Nonbiodegradable biobased	Biopoly(ethylene Terephthalate), Biopoly(ethylene), Poly(ethylene furanoate), BioPoly(propylene), Biopoly(amide (Nylons/bioPA), Poly(trimethylene terephthalate)

Note: Norwegian Environment Agency, 2018. BioBased and biodegradable plastics. An assessment of the value chain for biobased and biodegradable plastics in Norway. Available at: <https://www.miljodirektoratet.no/Documents/publikasjoner/M1206/M1206.pdf> (accessed 26.02.19).

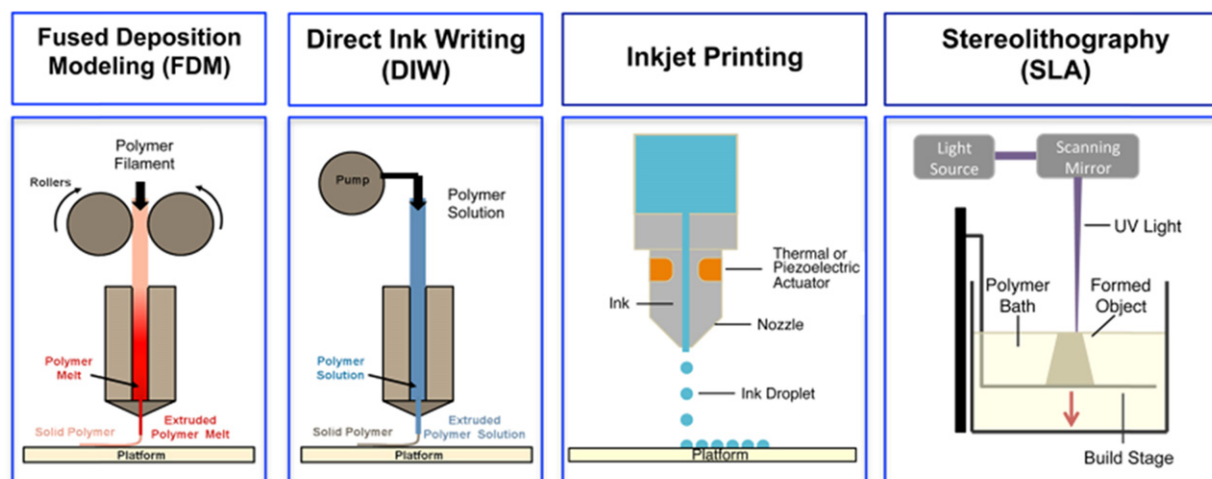


Fig. 3 Schematic depiction of 3D bioprinting methods: Extrusion-based methods such as fused deposition modeling and direct ink writing, inkjet printing, stereolithography. Reprinted with permission from Guvendiren, M., Molde, J., Soares, R.M.D., Kohn, J., 2016. Designing biomaterials for 3D printing. *ACS Biomaterials Science and Engineering* 2 (10), 1679–1693. doi:10.1021/acsbiomaterials.6b00121. Copyright (2016) American Chemical Society.

(Murphy and Atala, 2014; Kirchmayer *et al.*, 2015). Poly(ethylene glycol) (PEG) is ethylene oxide with ether functional group and is most commonly used in 3D bioprinting (Kirchmayer *et al.*, 2015). An acrylate chemical modification of PEG is poly(ethylene glycol) diacrylate (PEGDA), which facilitates cell encapsulation more efficiently than raw PEG (Skardal and Atala, 2015). The monomer covalently bonds to create the polymer, which is not biodegradable, but biocompatible (Kirchmayer *et al.*, 2015).

3D Printing Technology

The basic components of 3D printing technology are (1) hardware, the physical constituents of the machine itself; (2) software to develop and process 3D design and to convert it into machine-readable instructions; and (3) the raw materials used as ink for producing 3D objects. The physical properties of 3D printed objects depend on the material selection, printing principles, and printing process parameters (Guvendiren *et al.*, 2016). The 3D printing process is very robust and it can be tuned to utilize numerous functional materials including biobased materials in the form of ink for printing complicated 3D structure like scaffold for cell growth, implantable tissues, etc. (Skardal and Atala, 2015). A number of 3D printing methods are shown in Fig. 3, which include extrusion-based 3D printing methods, inkjet printing, stereolithography (SLA), and laser-induced forward transfer method (Skardal and Atala, 2015; Guvendiren *et al.*, 2016; Jammalamadaka and Tappa, 2018). Selection of a printing method from any of these depends on the fluid (ink) flow properties and the desired structural resolution of the printing object.

Extrusion-based methods such as fused deposition modeling (FDM) is based on the simple idea that a filamentary thermoplastic material is forced through a heated nozzle that simultaneously melts the material and follows a predefined path determined by a computer model to build up a 3D object layer-by-layer in the vertical direction. The extruded material solidifies with time that can be detached from the printing bed when the printing process is fully executed (Guvendiren *et al.*, 2016). The FDM process is feasible for printing with biomaterials that are thermoplastic in nature, but not suitable for other types of temperature sensitive biomaterials.

On the other hand, direct ink writing (DIW) method uses a thixotropic fluid (as ink), which is formulated with the proper mixture of a fluid loaded with filler particles and the polymeric binder (Guo *et al.*, 2013). The ink material is extruded through a nozzle that can travel in X, Y, and Z directions similar to FDM method. The printed material can be solidified via thermal or light energy.

The popular inkjet printing process can also be tuned to use functional ink and develop high-resolution 3D object by layer-by-layer deposition of droplets on demand (Skardal *et al.*, 2012). Unlike, FDM, DIW, and inkjet, SLA can print 3D objects from the bottom up by shining UV light pattern in the resin bath. The light can solidify the resin during its travel (Soman *et al.*, 2013). However, this process is restricted for all the other types of functional materials, which are not photocurable. Further details about the advancement in 3D printing technologies can be found in the recent literature (Wijk and Wijk, 2015; Ngo *et al.*, 2018; Liu *et al.*, 2019; Tofail *et al.*, 2018).

Carbon Neutral Manufacturing With 3D Printing of Biobased Materials

Petroleum based polymer materials are being used in a wide variety of applications. However, from the sustainability point of view, they are not the most attractive options due to a number of reasons such as CO₂ generation during production, gradual depletion of limited feedstocks, landfill with nonbiodegradable polymers, and CO₂ generation during combustion. Therefore, biobased polymers from plant cellulose open up the opportunity to overcome those barriers and to create a sustainable planet. Traditional manufacturing techniques such as machining work on the subtractive principle where material is removed to create a shape, meaning a lot of waste. On the other hand, 3D printing works on additive principle and is considered as a waste-free process. Therefore, the combination of biobased materials and 3D printing can create the opportunity to realize carbon neutral manufacturing in the near future. In this concept, the products made out of the biobased polymers can be recycled to manufacture new products or be fully degradable upon landfilling (Fig. 4).

A group of Russian researchers developed biomass-derived poly(ethylene-2,5-furandicarboxylate) and made objects via 3D printing, which showed better performance than commonly available materials such as acrylonitrile butadiene styrene (Kuchero *et al.*, 2017). Several successive recycling of the material in 3D printing did not show any significant degradation of performance.

The bases of electric lamps were manufactured by 3D printing from electrically conductive biobased plastic partially from renewable resources and graphite (Villanueva *et al.*, 2018). Filament was made by extrusion technique and used as a raw material for manufacturing the lamp base by FDM. Sustainability analysis shows that 3D printed biobased lamps can reduce environmental impact such as CO₂ footprint when compared with the lamps made of glass and metallic materials and opens up the opportunity to replace these high carbon traditional materials. The biobased materials also can reduce the weight of the lamp by 55%, which has other environmental benefits during transportation such as lower fuel consumption and emission.

It is a big challenge to protect complex, sensitive, or fragile parts during transportation using standard packaging as in most of the cases their designs are not suitable to match the shape of the part. This demands adaptive packaging design and manufacturing, which could be very costly and time consuming. 3D printing of adapted packaging using renewable biobased waste materials such as wood flour, rice husk, or miscanthus fiber has been trialed to overcome the challenges in packaging (Zeidler *et al.*, 2018). The

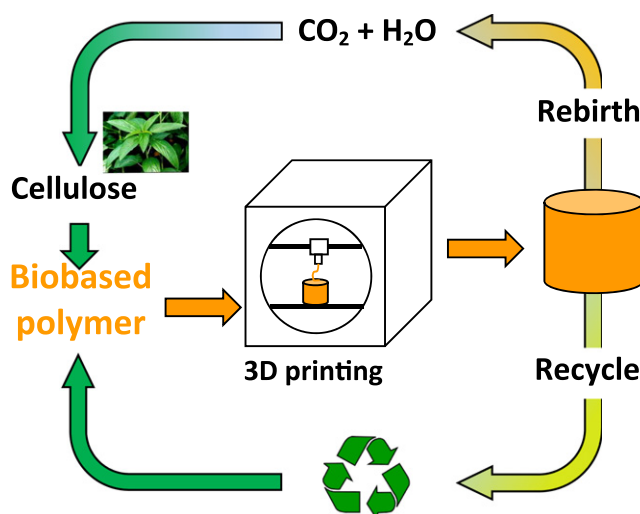


Fig. 4 Carbon neutral cycle from 3D printed biobased product. Modified from Wiley Newsroom, 2017. From cellulose to 3D objects: 3D printing with a biobased polymer for CO₂-neutral manufacturing. Available at: <https://newsroom.wiley.com/press-release/angewandte-chemie-international-edition/cellulose-3d-objects-3d-printing-biobased-poly>.

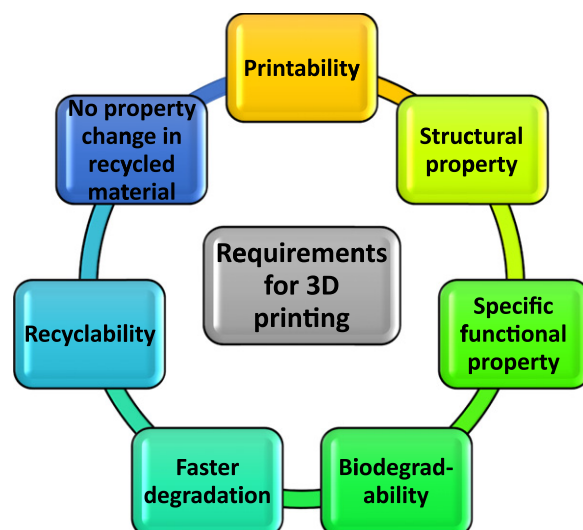


Fig. 5 General requirements for 3D printing with biobased materials. Modified from Liu, J., Sun, L., Xu, W., *et al.*, 2019. Current advances and future perspectives of 3D printing natural-derived biopolymers. *Carbohydrate Polymers* 207 (1), 297–316.

combination of biobased material and 3D printing creates an attractive scenario for carbon neutral manufacturing of sustainable and biodegradable packaging through re or upcycling of biobased waste materials. 3D printing can also conform to the ability of making complex adaptive packaging just-in-time.

Biobased Materials Requirements for 3D Printing

To make commercially viable sustainable products by 3D printing using biobased raw materials, certain criteria must be complied with both from the materials and processing point of views as shown in [Fig. 5](#). [Liu *et al.* \(2019\)](#) discussed key characteristics that the biobased materials should have to be used as raw materials in 3D printing for few specific applications such as biomedical, food, and textile products. The following subsections highlight the requirements from biobased materials for specific application areas relevant to 3D printing.

Medical and Pharmaceutical Applications

The ample use of biobased polymers in 3D printing technology opens up many windows and extends the existing possibilities in biomedical engineering as it is easy and simple to process them and the cost involved is low ([Skardal and Atala, 2015](#); [Guvendiren *et al.*, 2016](#); [Jammalamadaka and Tappa, 2018](#)). The areas of biomedical and pharmaceutical research where 3D printing is being applied are (1) fabrication of tissue and organ including customization of prostheses, implants and anatomical models; and (2) personalized drug dosage delivery system and drug screening ([Derby, 2012](#); [Melchels *et al.*, 2012](#); [Murphy and Atala, 2014](#); [Ventola, 2014](#); [Zhang *et al.*, 2015](#)). The 3D printing techniques, which are found suitable for medical and pharmaceutical applications, are extrusion-based printing technique, inkjet-based technique, fused particle based technique, and light-assisted 3D technique. These techniques will demand different mechanical and chemical properties from raw materials related to processing and printing performances. However, the biobased materials should meet the strict requirements in terms of printability, biocompatibility, degradability (degradation into safe by-products) and good degradation kinetics, ability of tissue biomimicry and appropriate mechanical properties in general for medical, and pharmaceutical applications ([An *et al.*, 2015](#); [Derby, 2012](#); [Murphy and Atala, 2014](#)).

Food Production

The 3D printing techniques that have found application in food fabrication are extrusion-based technique, selective sintering technique with laser or hot air, binder jetting, and inkjet printing technique. These different techniques will demand different physical, chemical, rheological, structural, and mechanical features from the raw materials they use. However, the biobased materials for use in 3D printing of food should be primarily edible, nontoxic, rigid, and stiff enough to support their own weight and resistant to post-processing such as baking, cooking, and frying. The biobased materials that have been used in 3D food printing so far are cellulose, hemicellulose, pectin, starch, alginate, agarose, and chitosan due to their favorable features like nontoxicity, edibility, high abundancy, bioactivity, and compatibility with foods ([Alec, 2016](#); [Godoi *et al.*, 2016](#); [Lille *et al.*, 2018](#)).

Textile Application

3D printing technique has yet to reach sufficient efficiency to reproduce true textile structures with appropriate fineness, flexibility, and drape characteristics. However, 3D printing has been found effective to build different small components on textile surfaces. FDM and SLS (selective laser sintering) techniques have been applied for 3D printing associated to textile applications (Beecroft, 2016; Tenhunen *et al.*, 2018). Among the biobased materials, PLA shows potential for this field. Among the key requirements from biobased raw materials, the most notable ones are flexibility, drapability, and washability, when it comes to any textile application.

Current Research and Challenges

3D printing With Bioplastics

Poly(lactic acid) (PLA) is a widely used biopolymer to print different tissues, including liver, kidney, and cardiac tissues, which forms the organs that are transplanted most (Serra *et al.*, 2013). Transformation of PLA into filament is very easy and can be printed in extrusion printing methods. However, the long-term biodegradability and the formation of acetic acid during degradation lead to tissue death and make this polymer unsuitable. To solve this problem, PLA is combined with ceramics and forms a composite, which improves the mechanical properties and reduce the formation of the localized acidic environment (Serra *et al.*, 2013). PLA bioplastics are mainly printed by FDM printing methods to fabricate packaging devices (Serra *et al.*, 2013; An *et al.*, 2015). Some other polymers such as poly(propylene fumarate), poly(D, L-lactide) are successfully used in SLA method as biodegradable and photocrosslinkable polymer (Guvendiren *et al.*, 2016).

Often biobased materials are mixed with nonbiobased materials to improve the performance of 3D printed parts/products. For example, ceramics materials are largely used in 3D bioprinting of bone and tissue engineering. Due to their osteoconductive and osteoinductive nature, metal and inorganic salt of calcium and phosphates are potentially used to print scaffolds for bone and dental tissue engineering. In this case, pressure extrusion 3D printing method is a potential candidate since this process does not require high temperature melting process during printing. β -tricalcium phosphate (β -TCP), α -tricalcium phosphate, HA, bi-phasic calcium phosphate (BCP a mixture of β -TCP and HA), calcium sulfate, calcium phosphate cement, and titanium are potentially used as biomaterial for 3D printing (Tarafer and Bose, 2014; Chia and Wu, 2015; Sa *et al.*, 2018). However, the scaffolds produced using the ceramic materials are brittle in nature. To improve cytocompatibility, vascularization, and mechanical properties, some polymeric biomaterials such as chitosan, polycaprolactone, PLA, poly L-lactide-glycolic acid, and PEGDA are added to the salts of calcium and phosphates (Chia and Wu, 2015). Some examples of 3D printing in the biomedical field are presented in Fig. 6.

3D Printing With Hydrogel

Hydrogel made of the natural polymer has the disadvantage of carrying pathogens from its sourcing body and inconsistency in structure and molecular weight as they are extracted from the various living body (Collier and Segura, 2011). However, they show the most excellent biocompatibility and degradability as they have a natural attachment to interact with cell (Kirchmayer *et al.*, 2015). The hydrogels made of a natural polymer such as alginate, collagen, fibrin, hyaluronic acid retain their innate biological activity. As a result, they do not require any biological preprogramming (Murphy and Atala, 2014). Inkjet printing, photopolymerization, and extrusion are some efficient methods of hydrogel printing (Skardal and Atala, 2015). The printed polymer ink or solution is stabilized by either physical bonding or chemical bonding (Guvendiren *et al.*, 2016). Physical bonding such as electrostatic bonding, photocuring, and curing avoid the potentiality of toxic chemicals, whereas chemical bonding evolves the polymer to be resistant to mechanical stress (Guvendiren *et al.*, 2016).

Collagen is a proteinaceous biopolymer that acts as reinforcement in scaffolds in gel form under neutral pH and crosslinking agent, which is dissolved in acetic solution. This pH-sensitive property is used for 3D printing where gelation occurs by physical bonding and crosslinking as well (Wang *et al.*, 2015). However, this acidic requirement creates a deadly environment for the survival of cells. Glutaraldehyde is a potential crosslinker for the gel state formation (Rajaram and Chu, 1990).

Alginate is a polysaccharide used for cell encapsulation in microsphere. It is also more inexpensive than collagen because it is derived from seaweed and algae (Skardal and Atala, 2015; Kirchmayer *et al.*, 2015). This hydrogel is formed by electrostatic interaction between negatively charged carboxylate group of alginate and calcium ion, which is called ionotropic hydrogel (Chitkara *et al.*, 2006). Owing to the high interaction, gelation occurs within seconds, which leads to poor control over geometrical shape (Chitkara *et al.*, 2006).

Hyaluronic acid contains repeating units of disaccharide and is chemically modified for 3D bioprinting, such as photocrosslinkable methacrylate hyaluronic acid with or without gelatin, thiolated carboxy-methyl hyaluronic acid with or without gelatin and gold nanoparticle to obtain soft and robust hydrogel (Kirker *et al.*, 2004; Liu *et al.*, 2007; Skardal *et al.*, 2010). These modified hydrogels have applications in regenerative medicine, such as wound healing, tumor modeling, bioprinting, cell encapsulation, etc. (Skardal and Atala, 2015).

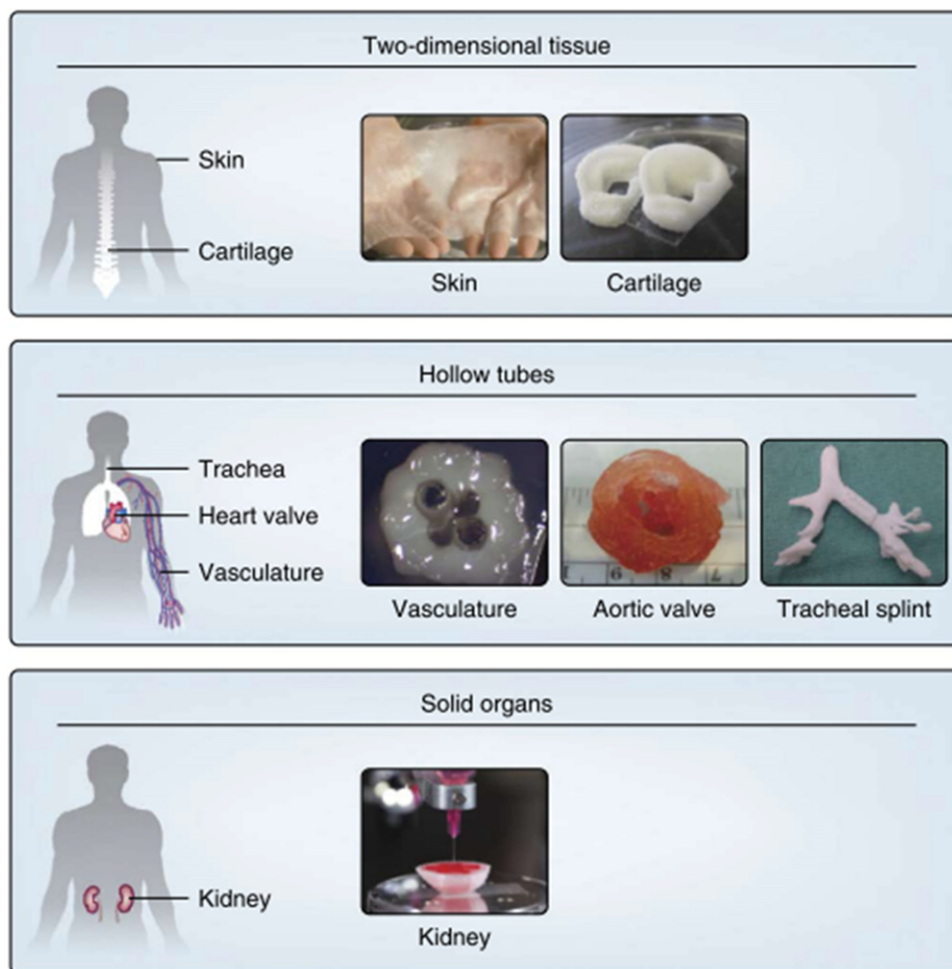


Fig. 6 3D printed tissue and human organs. Skin (top left: Unpublished; Wake Forest Institute of Regenerative Medicine), cartilage (top right): poly (ethylene glycol) dimethacrylate with human chondrocytes inkjet printed via photopolymerization vascular rod (middle left): multicellular aggregates microextrusion bioprinted aortic valve (middle): alginate/gelatin hydrogel microextrusion bioprinted airway splint (middle right): polycaprolactone laser bioprinted and kidney (bottom): microextruded (unpublished: Wake Forest Institute of Regenerative Medicine). Reprinted with permission from Murphy, S.V., Atala, A., 2014. 3D bioprinting of tissues and organs. *Nature Biotechnology* 32 (8), 773–785. doi:10.1038/nbt.2958. Copyright (2014) Nature Biotechnology.

Ink from the cellulose nanofibril (CNF) hydrogel has been found biocompatible and therefore has attracted much attention in biomedical research (Liu *et al.*, 2016a,b). Native cellulose has also found application in 3D printing of food as it serves as dietary fiber and acts as bulk filling agent, rheological modifying ingredients, and reinforcing agents with good indigestibility, excellent mechanical performance, and high viscosity (Liu *et al.*, 2019). CNF gel has been mixed with other food ingredients to develop customized 3D printed healthy foods, and shows improved shape stability but decreased hardness after drying (Lille *et al.*, 2018).

Challenges

Price and speed are the most-noted limitations with 3D printing. Biobased materials have been found suitable for use in 3D printing of different structures for biomedical, food, and textile applications. For the biomedical field, 3D bioprinting shows potential for manufacturing functional organs. However, living organs are not just solid structures; they include vascular structures of different sizes to ensure fluid transfer. Ensuring this vascularization is a big challenge in 3D printing of bioorgans or tissues (Pantra and Young, 2016). In addition to vascularization, mimicking the unique and complex cellular combinations and organizations of living tissues is another challenge for 3D bioprinting. For example, a reproduction of kidney will require at least one million glomeruli and nephrons to be made (Pantra and Young, 2016), which is not only a massive undertaking but also challenge in terms of scalability.

The challenges in 3D printing of textile structures are to achieve the weave and knit structures in miniature forms as well as to ensure the flexibility and drapability, which is still not close to reality.

Summary

Since its advent in the 1980s, 3D printing technology has made notable progress in terms of direct transformation of CAD into products, making complex and intricate parts with mass customization capability, reducing overall product development time and time to market, combining several manufacturing steps into one, and manufacturing from a wide variety of materials with minimum waste and maximum material utilization. However, a number of challenges still need to be overcome such as poor dimensional accuracy and surface finish, anisotropic properties, internal defects (porosities), etc. Recent innovations in 3D printing of biobased materials opens up numerous application opportunities in aerospace, automotive, textiles, food and biomedical industries and it is believed to be the future of sustainable manufacturing (Zeidler *et al.*, 2018). The big advantage is that any product made by 3D printing of biobased materials can be completely recycled at the end of its lifecycle to create a new part, or can be disposed as biodegradable waste without causing any harm to nature.

See also: A Comprehensive Study for 3D Printing of Rapid Tooling From Reinforced Waste Thermoplastics. Renewable and Sustainable Materials in Automotive Industry

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Palm Oil Fuel Ash: Innovative Potential Applications as Sustainable Materials in Concrete

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Introduction

Concrete is a most frequently consumed materials in the construction industry and this has led to the depletion of natural resources and caused significant environment issue. According to [Celik et al. \(2014\)](#), the global cement production is approximately 3.3 million tonnes per annum and it is also expected to increase to 4 billion tonnes by the year of 2020. It was estimated that about 1 tonne of carbon dioxide (CO₂) was liberated for the production of one tonne cement ([Karim et al., 2013](#)). The industry for cement production contributes to approximately 5%–10% of the GHGs emissions in the world ([Scrivener and Kirkpatrick, 2008](#)), and 12%–15% energy used in the entire industry ([Madlool et al., 2011](#)). These greenhouse gases have severe adverse effect on the climate change. Due to increasing in suitability concern, researchers are looking for alternative materials, which could improve the sustainability in construction industry. The Supplementary cementitious materials (SCM) have been used extensively over the last few decades in the production of concrete. SCM such as granulated blast furnace slag (GBFS), fly ash (FA) and silica fume (SF) are commonly used to blend with cement to form more reactive cementitious materials. According to [Aprianti et al. \(2015\)](#), some agro-waste materials such as bagasse, rice husk ash, palm oil fuel ash (POFA) and wood waste ash, could also be incorporated in cementitious composite materials to replace normal cement.

The data provided by the United States Department of Agriculture showed that there were 64.5 million tons of palm oil being produced globally in the years of 2016 and 2017. ([Hamada et al., 2018](#)). Malaysia is the major palm oil producer and supplier worldwide. It was estimated that Malaysia will maintain the position to lead over in palm oil industry for the coming half decades and its production was projected to be 18 million tons which would be approximate 40% of the global palm oil in 2020 ([Basiron, 2015](#)). POFA is one of the significant by-product of palm oil industry. There are several chemical components present in the POFA, which mainly include SiO₂, Al₂O₃, Fe₂O₃, CaO, and MgO. It is generated from the combustion of solid waste generated from palm oil extraction including palm oil fiber, husk, kernel, empty fruit bunches and shell. These components are burnt in the power plants for producing energy. POFA is traditionally disposed through landfilling; while the yearly increasing amount of these deposits has brought burden to the authority. ([Chindaprasirt et al., 2007](#)). The widespread improper handling of the solid wastes especially the agricultural as well as industrial products has resulted in the consequence of environmental issue. [Tay and Show \(1995\)](#) highlighted that the disposal of untreated POFA can cause various diseases and hazard issue to human health. Due to the increasing demand for supplying palm oil products, the amount of respective wastes produced also escalates. Without having appropriate disposing procedures, these wastes could potentially be harmful to human as it will cause environmental issues which eventually lead to health problems and financial losses. Thus, researcher initiated to study the incorporation of POFA as materials in producing concrete. Many recent research proved that treated POFA can be used as SCM in concrete production ([Tangchirapat et al., 2009](#)). [Tangchirapat et al. \(2009\)](#) demonstrated that POFA is capable of making concrete that is having high strength of more than 60 MPa. [Fig. 1](#) shows untreated and treated POFA.

Due to the availability in large quantity while possessing proper characteristics as pozzolans, POFA has been recognized by many researchers that it is highly potential to be used as SCM in concrete production. The practice of using waste from agriculture in construction industry can be regarded as a break-through that promotes sustainability. The following sections present the physical and chemical properties of POFA, its effects on fresh properties as well as the properties in hardened state. It will be shown that POFA has high potential to be incorporated in concrete as SCM.

Properties of POFA

Physical Property

POFA can be visually inspected as greyish in colour, but the colour becomes darker when it contains more unburned carbon. [Zeyad et al. \(2016\)](#) stated that the colour of POFA is highly dependent on the process of heat treatment, which can reduce the carbon content. Lower carbon content can lead to lighter colour for POFA. It consists of irregular particles although the shape of POFA is relatively spherical ([Awal and Shehu, 2013](#)). Grinding of POFA can reduce the particle size of POFA and increase its fineness. The particle of ungrounded POFA usually has spherical shape while the grounded POFA particle exhibits angular and irregular shape. Varying size of POFA has been used and the desired size can be obtained by the grinding process. Besides, the POFA has generally specific gravity in the range of 1.86–2.6, which is much lesser when compared to cement ([Hamada et al., 2018](#)).

The pozzolanic characteristics and hydration rate of POFA are greatly influenced by its fineness. Improvement in compressive strength of concrete can be achieved when finer particle size of POFA is used ([Khalid et al., 2016](#)). The porous structure of POFA can be minimized by reducing the particle size. It is demonstrated by [Paya et al. \(1996\)](#) that the grinding process can reduce the



Fig. 1 (a) Raw POFA, (b) Treated POFA.

Table 1 Chemical compositions of POFA

Compositions	G-POFA (Johari et al., 2012)	U-POFA (Johari et al., 2012)	G-POFA (Awal and Shehu, 2013)
SiO ₂	51.18	65.01	59.62
Al ₂ O ₃	4.61	5.72	2.54
Fe ₂ O ₃	3.42	4.41	5.02
CaO	6.93	8.19	4.92
MgO	4.02	4.58	4.52
K ₂ O	5.52	6.48	7.52
SO ₃	0.36	0.33	1.28
LOI	21.6	2.53	8.25
SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃	59.21	75.14	67.18

particle size of POFA and resulted in improved porosity. The fineness and specific gravity are increased when POFA experience the grinding process to obtain finer particle size. However, Jaturapitakkul et al. (2007) discovered that although the finer particle size of POFA can improve the resistance against sulphate attack, it can decrease the concrete compressive strength.

Chemical Composition of POFA

The chemical composition of ground POFA (G-POFA) and ultrafine POFA (U-POFA) are presented in Table 1. A number of researchers reported a notable variation of POFA chemical composition. These variations could be due to the grinding process, treatment process, burning conditions, the source of materials and different practice of handling in factories (Zeyad et al., 2013; Tangchirapat and Jaturapitakkul, 2010). Compared to OPC, POFA is moderately rich in silica content. POFA has a significant amount of silicon dioxide and it can react with calcium hydroxide (Ca(OH)₂) to form calcium silicate hydrate (CSH), the strength contributing gel. Hydration of cement will release secondary product of Ca(OH)₂ which will not provide any strength to the cementitious mixture. The additional CSH gel can strengthen the bonding of mixture of concrete. Thus, theoretically, the performances of concrete in term of strength and durability will improve proportionally to the reactive silica quantity present in the POFA. The POFA having higher silica content is obtainable through combustion of palm kernel and tree (Tangchirapat and Jaturapitakkul, 2010).

Advantages of Using POFA

POFA is deemed ideal because it can be easily obtained since oil palm plantation is extensive where its supply is constant and stable. The costs associated to its pre-treatment are found to be relatively lower. Construction costs can be reduced significantly with the use of alternative waste materials while providing comparable performance. In terms of structural performance, when appropriate treatment processes are applied, POFA become highly efficient pozzolan and thus improving the concrete fresh state

property including workability as well as its hardened state properties such as strengths under tension and compression, structural porosity and resistance to the intrusion of chloride, water and gas (Johari *et al.*, 2012). In terms of environmental aspect, the use of POFA satisfies the green construction requirements as it is being recycled and reused materials. The utilization of POFA in concrete production brings about many advantages to the environment, which may include the reduction of cost for landfilling of POFA waste, reduction of carbon footprint due to cement production as well as the conservation of raw resources.

Effect of POFA on the Workability of Concrete

Workability of concrete is the ability of concrete to ease and maintain its homogeneity in fresh state under the process of mixing, placement and consolidation without any segregation. Degradation of workability was observed for concrete with high level POFA replacement due to the unburn carbon in POFA. Ahmad *et al.* (2008) reported that the slump values decreased from 190 mm to 110 mm for 15% replacement of POFA. This might be due to the size and shape of the POFA as it was not ground to make a fine particle.

Johari *et al.* (2012) removed the carbon from raw POFA through heat treatment and then grinded it into ultrafine in size. Subsequently, the treated POFA was used to replace normal cement with level of 0%–60% in making concrete. It was found that the slump value, the time for the first setting and final setting of concrete to take place became longer when the ultrafine POFA contents increased. It was explained that the ultrafine POFA provided more volume of binder paste in concrete, which lubricated the concrete and allowed smoother movement of aggregates that eventually increased the workability. Alternatively, the dosage of super plasticizer could be reduced to maintain the same slump value and hence, it will reduce total concrete production cost. With the initial setting time and the final setting time increased significantly with the increasing of ultrafine POFA, this could be again fully utilized in the hot weather concreting.

Lim *et al.* (2013) performed experimental tests to investigate the use of POFA in affecting the fresh properties of lightweight foamed concrete (LFC). From the inverted slump cone test, it was shown that the fluidity of LFC relied more on the water content of the mixes. The slump spread value increased for every increment of w/c ratio. Meanwhile, the slump values reduced slightly with the increment of POFA replacement level. It was implied in the literature that the POFA possessed characteristic of high water absorption, which decreased the fluidity of the concrete. Besides, POFA used was unprocessed and its particles were angular and porous which reduced the flowability of the LFC. The author proposed that optimum w/c ratio for 0%, 10% and 20% of POFA replacement level were 0.56, 0.54 and 0.56, respectively.

Mohammadhosseini *et al.* (2015) studied the addition of POFA in self-compacting concrete (SCC) at the replacement level of 60% and 100%. The water to binder (w/b) ratios of 0.4, 0.45 and 0.5 were used for each replacement level. The authors found that the increase in POFA content could result in the increase of superplasticizer required to achieve workability. Meanwhile, Nagaratnam *et al.* (2016) studied the workability of binary and ternary blends by using cement, fly ash and POFA in SCC at the replacement level of 10%–40%. All the mixes satisfied the requirement of SCC in terms of passing ability, filling ability and segregation resistance. The authors noticed that the implementation of POFA in SCC at high level replacement required more superplasticizer to obtain self-compacting ability which agreed with the findings of Mohammadhosseini *et al.* (2015). It was explained that POFA possessed high water absorption and its nature of hygroscopic reduced the water available for hydration to take place in the concrete. The author concluded that ternary blend of cement, fly ash and POFA had the optimum workability when compared to binary mix.

Zeyad *et al.* (2018) studied the impact of carbon-laden POFA (GPOFA) and ultrafine carbon-free POFA (UPOFA) on workability at the replacement level of 0, 20, 40 and 60%. The authors observed that the increase in UPOFA content can improve the slump flow value when compared to control mix. Meanwhile, GPOFA had negative effect on the workability of concrete. The authors explained that UPOFA can enhance workability by increasing the paste volume of the cementitious mixture.

Effect of POFA on the Hardened Properties of Concrete

Compressive Strength

The compressive strength of concrete is regarded as one of the utmost important mechanical behaviors whereby it can significantly affect the outcomes of any structural designs. Thus, aiming to bring forward the POFA concrete to the current construction industry, it is necessary to discern the effect of POFA on the concrete compressive strength. In general, the POFA is having the characteristics of improving the compressive strength of concrete (Tangchirapat *et al.*, 2012; Ranjbar *et al.*, 2016; Sata *et al.*, 2007). Yet, the present researches have shown that the strength improvement by the POFA is limited to certain proportion of its substitution. However, the concrete compressive strength may reduce should the POFA replacement level is outside of the range (Ahmad *et al.*, 2008; Sata *et al.*, 2004; Muthusamy *et al.*, 2015). The dosage ranges of the POFA in providing the improvement of compressive strength varies with the sources and properties of the POFA. These properties could include chemical composition, particle size, pozzolanic reactivity, etc. (Hussin *et al.*, 2010; Jaturapitakkul *et al.*, 2011). Hence, the optimum dosage for POFA in concrete will also change if a different type of POFA is used, and several literatures showed that it will generally be at lower replacement level of 10%–30% by cement weight (Islam *et al.*, 2016; Ismail *et al.*, 2011).

Tangchirapat *et al.* (2012) used grounded palm oil fuel ash (G-POFA) which possessed higher fineness with intention to strengthen the concrete mechanical properties made up of recycled concrete aggregates. The quantity of G-POFA incorporated was in the range of 0%–50% by weight of the total binder content. It was observed that the concrete compressive strength increased

when 20% of G-POFA was used to replace cement. [Ahmad et al. \(2008\)](#) found that concrete mixture having 15% of POFA can give the concrete an optimum compressive strength. However, the concrete compressive strengths of 5% and 10% of POFA were less than the anticipated strength. Moreover, POFA was also used to replace cement in producing lightweight concrete ([Islam et al., 2016](#)). In the study, the incorporation of POFA in the concrete up to 25% obtained comparable compressive strength as the normal concrete. The replacement level of 10%–15% of POFA improved the compressive strength of concrete. In the investigation, the compressive strengths of POFA obtained were more consistent than the conventional OPC concrete. This is because the POFA was less sensitive to poor curing since the POFA was finer than OPC, which provided filler effect to the concrete.

Furthermore, [Awal and Hussin \(2011\)](#) discovered that the compressive strength of POFA based concrete at the ages of 1 day, 7 days and 28 days are lower than control concrete. They also observed that during the early age, the strength gaining rate of the POFA concrete was relatively slow when compared to cement based concrete but in later ages it was faster. From this study, it can be deduced that the rate of strength gaining in pozzolanic concrete is slower compared to the cement based concrete. Besides, [Ranjbar et al. \(2016\)](#) examined the effect of ground POFA on the compressive strength of self-compacting concrete (SCC). The study included three replacement levels which were 10%, 15% and 20% of cement by weight. For the early compressive strength (7 days), POFA concrete achieved lower strength than the normal concrete for every level of cement replacement. Nevertheless, the POFA concretes achieved comparable long-term compressive strength, especially the strength after 180 days. The author implied the observation as the effect of pozzolanic activity of ground POFA whereby longer duration is required to build up calcium silicate hydrate (C-S-H) gel. High contents of SiO_2 in POFA react with calcium hydroxide ($\text{Ca}(\text{OH})_2$) from the cement hydration to generate C-S-H gel. $\text{Ca}(\text{OH})_2$ is a secondary product from cement hydration which will not provide any bonding strength to the concrete. The C-S-H gel is the key agent that binds the aggregates together and gives strength to concrete. On top of that, [Sata et al. \(2007\)](#) also investigated the compressive strength behavior of G-POFA on high strength concrete (HSC) up to the age of 180 days. They found that (1) the HSC containing 10% G-POFA achieved higher compressive strength than the concrete made up of 0%, 20% and 30% POFA at the 7 days. (2) For the later strengths, the 20% G-POFA concrete yielded higher strength than those of 0% G-POFA, 10% G-POFA and 30% G-POFA concretes.

[Hussin et al. \(2010\)](#) made a study related to the effects of various factors on the compressive strength of aerated concrete incorporated with and without POFA. These factors included the sand size and its distribution, the quantity of gas foaming agent, as well as the dosage of superplasticizer. The investigation showed that the aerated concrete containing POFA acquired higher strength than the concrete made up of ordinary Portland cement. [Jaturapitakkul et al. \(2011\)](#) used three different sizes of ground POFA in mortar to investigate the compressive strength. The mean particle size of small particle (SPA), medium particle (MPA) and large particle (LPA) are 12.3 μm , 13 μm and 30.8 μm respectively. They found that (1) the compressive strength of control mortar is higher than POFA base mortar up to the age of 7 days, (2) mortars mixed with SPA yielded higher compressive strength than the control mortar from 28 days and onwards, and (3) mortars mixed with MPA and LPA yielded lower compressive strength than the control mortar strength at all ages. This had shown that the finer POFA exhibited better pozzolanic property, of which the voids in the mortar can be filled, and hence giving a higher compressive strength.

Tensile Strength

The structural members, particularly the beam and column, require ample tensile strength to resist tensile stress such as the bending stress in beam and buckling of unrestrained column. It is known that the concrete is weak in tension, and yet, it is still widely used provided that the concrete is adequately reinforced with steel reinforcement and its cracking strength is higher the minimum requirement. Therefore, when considering the mechanical property of POFA concrete, the influence of POFA on the concrete tensile strength should not be neglected. Several literatures had reported the positive influence of POFA on the tensile strength ([Lim et al., 2013](#); [Aldahdooh et al., 2014](#)). Nevertheless, its negative effect on the tensile strength was also discovered by the researchers ([Altair et al., 2012](#); [Islam et al., 2016](#); [Ranjbar et al., 2016](#)). In this connection, studies were made to improve the performance by modifying the POFA as well as incorporating additive ([Alsubari et al., 2018](#); [Mohammadhosseini et al., 2018](#)). The tensile strength of concrete can generally be determined experimentally through conducting flexural strength test or splitting tensile test.

In the study of [Lim et al. \(2013\)](#), light foam concretes (LFC) were incorporated with POFA and their tensile strengths were determined. The concretes containing 10%–20% possessed greater splitting tensile strength than the control concrete at all curing ages. As additional C-S-H was formed by the incorporation of POFA, bonding property of the LFCs was enhanced and higher imposed load was required to split the cylindrical specimens. Besides, it was also noted that the trend of tensile strength development was similar to the compressive strength and their relationship was found to be linear. Furthermore, [Aldahdooh et al. \(2014\)](#) studied the influence of POFA on the flexural and tensile strengths of fiber reinforced cementitious composites. The aim of the study was to obtain cementitious composites, which are ultra-high performance and at the same time are environmentally green. In the investigation, the authors found that the U-POFA could improve the flexural and uniaxial tensile capacity of the cementitious composite.

Nevertheless, some literatures had shown that the incorporation of POFA can reduce the tensile strength of concrete. [Ranjbar et al. \(2016\)](#) partially replaced the ordinary Portland cement with POFA in producing self-compacting concrete (SCC). The replacement level was in the range of 10%–20% and from the tests, the early-age and long term flexural strengths of POFA concrete in this range of replacement level were slightly reduced. The authors explained that, with the support of permeability test, the decrement might be due to porous structure of SCC having POFA, which caused stress concentration that weakened the bonding of aggregate and paste. Moreover, [Islam et al. \(2016\)](#) investigated the effect of curing conditions on the tensile strength of POFA

concrete through tensile splitting test and flexural test. The curing conditions included air curing (AC), full water curing (WC) and partial water curing (PWC). In the tests, the POFA replacement levels varied from 0% to 25%. Based on the tensile splitting test, the strengths of POFA concrete were all less than the conventional concrete, except for the case of concrete having 5% POFA under PWC condition. The splitting tensile strength increased by approximately 10% when POFA content increased from 0% to 5%, but the strength dropped for further POFA content increment. The concrete specimens cured under WC condition acquired higher strength than that cured under AC and PWC conditions. In the study, similar increment of tensile strength as the compressive strength was not observed. This had shown that POFA was not effective in providing improvement to the bond between aggregate and cement matrix.

Altwaier *et al.* (2012) assessed the flexural strength green-engineered cementitious composite (ECC) incorporated with POFA at the ages of 3, 28 and 90 days by conducting four-point bending tests. They demonstrated that by increasing w/b ratio, strengths at first cracking point as well as flexural strengths of all ECCs were reduced. This was primarily due to the increase in the pore volume in the matrix. Besides, the dilution effect occurs when the POFA content became higher and this had contributed to the declining of initial cracking strength. As the POFA to cement ratio increased, the cracking strength at the initial point of the ECC decreased. At low w/b ratio, the flexural strengths of POFA–ECC mixtures were higher than that of the control mixture. Meanwhile, when w/b ratio is higher, the flexural strengths of all mixtures containing POFA were higher than that of the control mixture. The increase in fiber–matrix interfacial bond concurrently reduced the flexural deflection capacity.

As a consequence of possible reduction in the mechanical property of POFA concrete, Alsubari *et al.* (2018) used modified treated POFA (MT-POFA) in making self-compacting concrete (SCC). The volumes of POFA used were 0%, 30%, 50% and 70%. Based on the experimental study, the concrete splitting tensile strength improved when POFA content increased from 0% to 30%, but it reduced for the further increment of POFA content up to 70%. The highest tensile strength obtained from the test was for the concrete containing 30% of POFA. In addition, the investigation regarding the incorporation of waste carpet fibers into POFA concrete was performed by Mohammadhosseini *et al.* (2018) as an impact from the increasing waste produced by textile and carpet industries. The waste carpets were then modified and incorporated into the concrete production with the purpose of improving its mechanical property, particularly the tensile strength. The POFA content was kept constant which was 20% of the cement content while the fiber contents included were 0%, 0.25%, 0.5%, 0.75%, 1% and 1.25%. The POFA concretes were found to have higher tensile strengths than the control concrete where the improvement was in the range of 15%–26%. The results also indicated that the incorporation of POFA into concrete could enhance the splitting tensile strength. However, the increment was more obvious for long-term strength and this was due to slow pozzolanic reaction provided by POFA. It was concluded in the study that the addition of both POFA and waste carpet fibers was capable of improving the interfacial transition zone, the region between the aggregate and cementitious paste of the concrete, thus increasing the tensile strength.

Modulus of Elasticity

Elastic modulus of concrete is also a significant mechanical property that is used to determine the concrete hardness and its abrasion resistance. In general, the concrete elastic modulus is closely related to its compressive strength. The elastic modulus of concrete will increase when its compressive strength increases. Yet, most of the literatures show negative effect of POFA on the concrete elastic modulus although the compressive strength has been improved (Awal and Hussin, 2011; Sata *et al.*, 2004; Islam *et al.*, 2016). On the other hand, there are some researches proved that POFA possesses positive effect on improving the elastic modulus of concrete (Tangchirapat and Jaturapitakkul, 2010; Hussin *et al.*, 2010; Alsubari *et al.*, 2018). In fact, the aggregate will be mainly contributing to the concrete elastic modulus while the incorporation of POFA may change the bonding behavior of the aggregate and the cementitious paste.

Research carried out by Sata *et al.* (2004) indicated that the G-POFA content up to 30% had contributed insignificant effect on concrete modulus of elasticity. It was also proposed that the decrease in the coarse aggregate of concrete as a result of the incorporation of G-POFA had caused slight reduction in the elastic modulus. Besides, the static elasticity of concrete containing 30% POFA and concrete without POFA were measured by Awal and Hussin (2011). The results showed that the POFA concrete has lower modulus of elasticity than the normal concrete. The pozzolanic exhibit of 30% POFA exhibited lower strength than the hydration of OPC. Furthermore, the elastic moduli of concrete made up of varying POFA contents and cured under air (AC) and full water (WC) conditions were determined by Islam *et al.* (2016). From the investigation, concrete elastic modulus decreased gradually with the increment of POFA content (0% to 25% POFA). This was explained in the literature that the POFA had limited effect on improving the interfacial zone of concrete. Nevertheless, the reduction in the elastic modulus was minimal, for instance, the elastic modulus decreased by 15% when POFA contents increased from 0% to 25%. Meanwhile, the elastic modulus of water-cured concrete was approximately 10%–23% higher than the corresponding air-cured concrete.

Hussin *et al.* (2010) carried out study on plain aerated concrete specimens and found that the POFA aerated concrete possessed higher stiffness value and thus having greater elastic modulus than the control concrete. The partial replacement of cement by POFA enabled pozzolanic reaction to take place, which produced additional C-S-H gel, and hence resulted in densification of lightweight concrete internal structure, making it stiffer. Besides, Tangchirapat and Jaturapitakkul (2010) deduced that use of coarse POFA (CP) and fine POFA (FP) has insignificant effect on altering the concrete elastic modulus as compared to OPC concrete. In fact, the strength provided by the coarse aggregates has more effect in determining the concrete elastic modulus rather than the strength from cementitious paste.

Moreover, [Alsubari et al. \(2018\)](#) incorporated modified treated POFA (MT-POFA) in making SCC. It was shown that the elastic moduli increased slightly when MT-POFA content increased from 0% to 30% for the concretes at age of 28 days and 56 days. This was due to the pozzolanic property of MT-POFA which improved the bonding between cement paste and aggregate. Yet, the elastic moduli decreased significantly for the subsequent increment of 50% and 70% POFA. The concrete elastic modulus is primarily affected by the coarse aggregate content. Therefore, the reduction of elastic moduli for concretes of 50% and 70% was due to the decrease in aggregate-to-paste ratio, where the aggregate content reduced. In addition, [Lau et al. \(2018\)](#) incorporated POFA and lime-treated sewage sludge in making lightweight aggregate and was termed as Posslite LWA. In the study, the Posslite LWA was used to produce concrete. It was found that the concrete elastic modulus made with Posslite LWA was slightly lower than the control concrete, but, it was still comparable to the control concrete. Similarly, the reduction of elastic modulus was attributed to the weaker interfacial transition zone of concrete containing Posslite LWA.

Resistance to Chlorine Penetration

Throughout the service lifespan of any concrete structure, there is possibility for the chloride to penetrate and travel through the pores in concrete, whereby the corrosion of the steel reinforcement may be initiated. This is particularly true for the application of concrete in the marine environment where the source of chlorine will be abundant. Therefore, the ability of a concrete to resist and prevent the penetration of chloride ion is essential to be investigated. The chlorine penetration resistance can generally be evaluated by conducting the rapid chloride penetration test (RCPT) or rapid migration test (RMT). Several works made by past researchers showed that the POFA can reduce the chloride penetration of concrete ([Ofuyatan and Edeki, 2018](#); [Ranjbar et al., 2016](#)). Besides, current researches focused on the modification of POFA by incorporating some industrial wastes to improve the durability of concrete ([Chindaprasirt et al., 2008](#); [Alsubari et al., 2018](#); [Lau et al., 2018](#)).

[Ofuyatan and Edeki \(2018\)](#) conducted RCPT for self-compacting concrete incorporated with 0%–30% of POFA. It was found that the surface resistivity to chloride diffusion of the concrete increased when the POFA content increased. Also, it was shown that the rate of surface resistivity increment reduced gradually when the POFA replacement level is high. The POFA added is able to refine the concrete pore structure by densifying the structure and thus reduce the void content. Furthermore, [Ranjbar et al. \(2016\)](#) determined the effect of 0% to 20% of POFA in concrete on the hydrochloric acid resistance. The concrete samples were immersed in the solution containing 3% of HCl acid for 75 days, and afterwards, the mass loss and compressive strength of the samples were determined. The mass loss of the concrete specimens reduced when the POFA content increased, indicating improvement of resistance to the acid. Similarly, the loss of compressive strength after the acid attack reduced with the increment of POFA content from 0%–20%. The improvement in the resistance was mainly due to the pozzolanic property of POFA in providing additional CSH gel by converting the weaker product of $\text{Ca}(\text{OH})_2$. Also, the author explained that better finishing surface of POFA concrete had provided fewer voids on the surface of concrete, resulting in minimum entrance to acid.

[Chindaprasirt et al. \(2008\)](#) presented a study regarding the uses of POFA, rice husk ash (RHA) and fly ash (FA) in improving chlorine penetration resistance of concrete. At 20% and 40% replacement levels, POFA was shown to effectively reduce the passing charge from 1900 C to 1050 C respectively. Coulomb charges for blended pozzolans of POFA and FA were very low which were 1250°C and 850°C for mortars made up of 20% and 40% of the blended cementitious materials respectively. These values were much lesser than the mortars made with single pozzolan at the equal replacement levels. Meanwhile, incorporations of 20% and 40% POFA showed the reductions of depths for the conducted rapid migration test (RMT). Accelerated chloride penetration depths of 20% and 40% of POFA-FA blended pozzolans were also improved to 5.5 mm and 4.0 mm respectively. The results above had also been verified by actual chloride penetration test in which the mortar was immersed in the solution containing 3% of sodium chloride for 30 days. The outcomes were similar to the test results obtained from RMT. As for the RCPT, although minor magnitude differences were observed but similar trends were demonstrated. All these indicated that POFA as well as FA and RHA (all are pozzolans) increased nucleation sites for hydration products precipitation, reducing $\text{Ca}(\text{OH})_2$ and ameliorated the mortar permeability. This had contributed to the significant improvement in chloride penetration resistance.

Besides, the modified treated POFA (MT-POFA) was incorporated in the concrete in the study performed by [Alsubari et al. \(2018\)](#). The concretes were made by 0%, 30%, 50% and 70% of POFA content. The results indicated that the chloride penetration resistance reduced significantly where the improvement of 40% in resistance was observed, when 30% POFA was incorporated. The resistance decreased for 50% and 70% POFA content concretes, but they are still higher than the control concrete. The improvement of chloride penetration resistance in POFA concrete was mainly due to the CSH components acquired from pozzolanic reaction of POFA which reduced the concrete porosity and permeability. On top of that, the Posslite lightweight aggregate (LWA) made up of POFA and lime-treated sewage sludge was used by [Lau et al. \(2018\)](#) in producing lightweight concrete. The chloride penetration test conducted in the study showed that the Posslite LWA concrete possessed similar resistance to chloride penetration as the control concrete for the short-term and long-term cases. The author implied that the Posslite LWA possessed dense and hard shell, which prevented the intrusion of chloride ion into the concrete. In addition, [Mohammadhosseini et al. \(2017\)](#) used POFA and waste carpet fibers in producing green concrete. The RCPT was performed for the concrete containing POFA volumes of 0% and 20% while the waste carpet fibers content varied from 0.25% to 1.25%. The results showed that POFA increased the chloride penetration resistance of concrete at any content of waste carpet fibers added. Also, the increment of waste carpet fiber content showed positive effect on the resistance but the increment reached maximum at 1% of waste carpet fiber. By conducting the scanning electron micrograph (SEM) analysis, the author explained that the POFA had converted $\text{Ca}(\text{OH})_2$ into CSH gel which breakdown the bigger pores of concrete, densifying the concrete structure in a microscopic level.

Drying Shrinkage

The drying shrinkage occurs in the concrete when the process of drying out takes place after the concrete is hardened. The concrete drying shrinkage is primarily because of the loss of water component in the concrete through the micro-pores. This can result in the occurrence and subsequently growth of microcracks at the surface of the concrete. Harmful substances can travel into the concrete easily which eventually can undesirably affect the concrete durability. Therefore, it is particularly essential to assess the drying shrinkage of POFA concrete.

Tangchirapat and Jaturapitakkul (2010) studied shrinkage of concrete incorporating ground coarse POFA (CP) and ground fine POFA (FP). The higher water-to-binder (w/b) ratio of CP incorporated concrete than the OPC concrete has caused it for not having a reduced drying shrinkage. The CP concrete exhibited almost the same shrinkage as that of OPC concrete in the long term. Concretes with 10%–30% of FP replacement however exhibited 10%–17% lesser drying shrinkage than the normal concrete. Since the FP exhibited better pozzolanic property, its incorporation in concrete could reduce the pore size by filling the large pores. The refinement of the pore is vital in reducing water loss, and thus the drying shrinkage. Besides, no shrinkage was observed by Hussin *et al.* (2010) for water cured aerated concrete specimen as it was continuously immersed in water for 1 year. However, swelling took place for the concrete because it was fully saturated. Meanwhile, shrinkage was however detected for the air-cured samples, indicating the specimens that are in contact with drier atmosphere are more subjected to drying shrinkage. It was proven that the POFA is able to minimize the drying shrinkage in concrete. Furthermore, Ranjbar *et al.* (2016) investigated the effect of POFA content of 0%–20% on the shrinkage of SCC. The results showed that the drying shrinkage strain of POFA concrete reduced at any replacement level up to 20%. When compared to the reference concrete, the maximum reduction of shrinkage was observed in the 10% POFA concrete. Meanwhile, the lowest reduction of shrinkage was found in 20% POFA concrete. The author explained that although the POFA content had increased the volume of pore in concrete, however, the pozzolanic property exhibited by the POFA transformed the larger pores into smaller one, providing a higher packing effect on the microstructure of the concrete.

Nevertheless, some researches indicated that the POFA content can have negative effect on shrinkage of concrete. Shrinkage values of POFA concrete were measured by Awal and Hussin (2011) and they found that the POFA concrete exhibited greater shrinkage strain than that of 100% OPC concrete. At 28 days, OPC concrete showed a shrinkage magnitude of 275.2×10^{-6} . Meanwhile, with 30% POFA replacement, shrinkage of 328.8×10^{-6} was achieved and it was 18% more than that of OPC concrete. This may be due to the different nature of the paste, which absorbed more water and thus led to the development of strain by shrinkage. On top of that, Mohammadhosseini *et al.* (2017) incorporated POFA an polypropylene (PP) carpet fibers in producing green concrete. The POFA concretes of 0% and 20% replacement level were casted while the PP carpet fibers content varied from 0% to 1.25%. The drying shrinkages of concretes reduced with the incorporation of PP carpet fiber in any volume used. In the test, concrete containing 0.75% carpet fibers acquired the minimum shrinkage strain. The carpet fibers were capable of improving the concrete tensile strength and thus reduced the possibility to crack. Also, when comparing POFA concrete and the OPC concrete, the shrinkage experienced by the POFA concrete was lower than the OPC concrete. Besides, the POFA and the waste metalized plastic (WMP) fibers were used by Mohammadhosseini and Tahir (2018) to make concrete. The POFA of 20% replacement level as well as 0%–1.25% of WMP fibers were incorporated in the concrete and their effects on drying shrinkage were studied. In the concrete without POFA, the highest shrinkage strain was observed in 0% WMP fibers while for the remaining replacement level of fibers, the shrinkage strain reduced. The maximum reduction in shrinkage was found in concrete incorporated with 0.75% of WMP fibers. The bridging effect provided by the fiber along the cracks reduced the shrinkage strain of the concrete. However, it was found that POFA concrete experienced higher shrinkage than the reference concrete for all volumes of WMP fibers. This could most probably be due to the lower rate of pozzolanic reaction attributed by the POFA. In short, POFA might not be helpful in reducing the concrete shrinkage at early age.

Water Permeability

The water permeability of a concrete is also a critical aspect in examining the durability of the concrete. The concrete water permeability can be examined by the water absorption of concrete. It refers to the ability of the concrete in preventing the water penetration into the concrete through the pores presented. Hence, water permeability is strictly related to the concrete porosity. The neglect of water permeability in concrete can result in various failure mechanisms of concrete due especially harmful agents are presented adjacently. Thus, the influence of POFA addition on the concrete water permeability is noteworthy to be studied.

Tangchirapat and Jaturapitakkul (2010) revealed that by utilizing of 10%–30% of ground coarse POFA (CP) and ground fine POFA (FP) as a cement replacement in concrete, promising results in water permeability were obtained. It was proven that FP concretes were having lower water permeability values than those of CP concrete as well as the reference concrete. Besides, water permeability of ground POFA concrete declined when its strength under compression increased. This had shown that water permeability of concrete is closely related to the compressive strength. It was implied that ground POFA possessed high pozzolanic properties that could densify the concrete morphology. Thus, higher volume of paste and less aggregate could be used and this combination provided concrete with lower water permeability. Furthermore, Ofuyatan and Edeki (2018) conducted water absorption rate test to study the concrete permeability by water that contained 0%–30% of POFA. The tests were carried out for the concrete at the age of 14, 28, 56 and 90 days. The experimental results indicated that the water permeability of concrete at all ages reduced when the POFA content increased. The maximum water permeability reduction was 24% and it was observed in the concrete incorporated with 30% POFA. The POFA can act as filler to seal the pores of the concrete, thereby reducing the permeability of water.

The surface absorption test was performed by [Ranjbar et al. \(2016\)](#) on the self-compacting concrete containing 0%–20% POFA after 28 and 56 days of curing. The results proved that the water permeability decreased when the POFA volume increased. The minimum water permeability was found at 20% of POFA content. Even though the concrete containing 20% POFA possessed lower compressive strength than any other replacement level, it had the lowest water permeability among the concretes. The reduction of water permeability was most probably due to the densely packed microstructure of POFA contained matrix, which had finer pores. Additionally, the water permeability of MT-POFA incorporated self-compacting concrete was also investigated by [Alsubari et al. \(2018\)](#). The levels for cement to be replaced MT-POFA were 0%, 30%, 50% and 70%. It was observed in the water absorption test that water permeability of 30% and 50% MT-POFA concrete decreased significantly by approximately 35% and 27% at 56 days of curing. The water permeability of 70% MT-POFA was higher than the concrete made by control mix. The author implied that the increase in water permeability was because of the slow pozzolanic reaction exhibited by the MT-POFA which resulted in incomplete filling of voids in the concrete. However, although the water permeability 70% MT-POFA concrete was greater than other concretes, it was still rated as good concrete according to the CEB-FIP requirement. Moreover, [Mohammadhosseini and Tahir \(2018\)](#) used POFA and waste metalized plastic (WMP) fibers in producing concretes and studied their water permeability. The results showed that the concrete water permeability reduced when the fiber volume increased from 0% to 0.5%, but it increased for further increment of fiber content up to 1.25%. It was explained in the literature that the fibers in high amount could cause balling effect where it affected and disturbed the compaction of concrete which eventually led to the forming of cavitation in the concrete. Nevertheless, the POFA had improved the durability of concrete whereby the water permeability reduced for all fiber volumes added. This was attributed to the finer and smaller pores due to the hydration product from pozzolanic reaction of POFA.

Sulphate Resistance

When concrete is externally exposed to sulphate, the transportation of sulphate ions into concrete core through the micro-pores can result in severe deterioration of concrete properties. The cementitious matrix of the concrete will be attacked by the sulphate as a result of complex reaction between inter-action of aggressive solution and the cement paste compound took place ([Ofuyatan and Edeki, 2018](#)). An expansive compound, which usually referred to as gypsum will form which cause the concrete to crack, lose strength and soften. Hence, the potential of POFA content in providing improvement to concrete sulphate resistance should be investigated thoroughly.

The effect of 0%–30% of POFA contents on the concrete sulphate resistance was investigated by [Ofuyatan and Edeki \(2018\)](#). The sulphate resistance was measured based on the mass loss of concrete as well as the loss in concrete compressive strength. From test of weight loss, it was observed that the concrete weight loss reduced when the POFA content increased from 5% to 30%, indicating improvement of the concrete to sulphate attack. For the loss of compressive strength, the loss decreased for the POFA content of 5%–20%; while for the POFA volume up to 30%, the loss of compressive strength increased. This could potentially be due to the incomplete pozzolanic reaction of the POFA, especially for the inner portion of the concrete. The outer part of the concrete exhibited a more completed pozzolanic reaction and thus preventing intrusion of sulphate ion. Besides, [Jaturapitakkul et al. \(2007\)](#) performed study to examine the effects of POFA on improving concrete sulphate resistance. By exposing concretes to solution containing 5% of MgSO_4 solution for 2 years, the concrete expansion and loss of concrete compressive strength were determined. The authors stated that the grounded POFA possessed high pozzolanic properties, but it was not for the ungrounded POFA. In this investigation, it was proven that the POFA fineness played an important role improving concrete resistance to sulphate attack. The experimental works showed that the concrete made with finer POFA experienced lesser the expansion and also compressive strength loss reduced.

[Tangchirapat et al. \(2009\)](#) investigated the use of highly fine ground POFA (GPA) in replacing cement to make high strength concrete (HSC). The authors found that the HSC having incorporated with GPA possessed better sulphate attack resistance. Furthermore, [Ranjbar et al. \(2016\)](#) studied the effect of 0%, 10%, 15% and 20% of POFA content in self-compacting concrete on its sulphate resistance. The tests were carried out by immersing the concrete samples in 5% magnesium sulphate solution and the concrete compressive strengths were measured afterwards. The losses of compressive strengths for 0%, 10%, 15% and 20% POFA concrete were approximately 9.5%, 8.2%, 7.8% and 7.3% respectively. It was clearly observed that the concrete resistance to sulphate attack enhanced when the sulphate content increased. Similarly, the pozzolanic reaction of POFA converted free $\text{Ca}(\text{OH})_2$ into CSH gel which provided the concrete with a more densely packed pore structure. On top of that, [Mohammadhosseini et al. \(2018\)](#) used both POFA and waste carpet fibers in producing green concrete. The POFA content used was 20% while the waste carpet fibers content varied from 0.25% to 1.25%. The concrete sulphate resistance was determined by calculating the strength loss of the concrete specimen after immersing in magnesium sulphate solution for 365 days. All concretes containing POFA exhibited lower strength loss than the OPC concretes, indicating improvement in concrete sulphate resistance. Meanwhile, the concrete containing 0.25% of waste carpet fibers showing the lowest reduction in compressive strength. The bridging effect provided by the waste carpet fibers prevented the formation of crack of concrete.

Future Applications and Research

Recently, palm oil fuel ash (POFA) has become a significant research interest, especially in Malaysia due to its abundance as a result of solid wastes generated from agricultural industry. Based on the present literatures, researches concerning the incorporation of POFA as supplementary cementitious material in concrete, particularly its effects on the concrete workability,

mechanical properties and durability, has been carried out and reported extensively. Hence, the following statements are some recommendations for future applications and research with regard to POFA in concrete industry.

- Past researches have shown the incorporation of POFA is notable in enhancing the durability of concrete by providing a more densely packed microstructure. Therefore, POFA is potential to be used to produce high performance concrete (HPC) and the research regarding this is yet still limited.
- It is reported in the literatures that POFA contains as much as 60% silica and significant portion other hard particles. Therefore, due to the existence of rich siliceous material, POFA could be a potential material for possible inclusion in metal matrix composite (MMC) composites for improved properties. Few researches are made on the utilization of POFA in MMC.
- Researches of POFA are found in producing self-compacting concrete (SCC) and lightweight concrete (LWC) due to its ability in improving concrete workability. However, there is no approach found to bring forward their application to construction industry. It will be beneficial if standardized approaches are developed to use SCC and LWC as this can greatly reduce the construction time, materials and energy.

Conclusions

The literature review summarizes the current researches that have been carried out on using POFA in concrete industry. POFA is a green agriculture waste material, which can be obtained with relatively low cost. The review encapsulates the various usage of POFA as construction materials, highlights of some important findings and results with regard to concrete hardened state properties, analysis of POFA in current applications and some recommendations for further research. Based on the review, conclusions are drawn and listed below:

- POFA can be easily obtained from the oil palm plantations in Malaysia, Indonesia and Thailand. It can be constantly and extensively supplied by the plantations.
- The pre-treatment costs are found to be relatively lower. When appropriate treatment processes are applied, POFA become highly pozzolanic and the concrete fresh state property and the concrete hardened state properties will be improved.
- The slump value, the initial setting time and ultimate setting time generally increase when fine POFA contents increase. Addition of POFA is capable of improving the concrete workability and thus it has high potential to be incorporated in self-compacting concrete (SCC).
- The improvement on concrete compressive strength containing POFA relies on the POFA fineness as well as its pozzolanic reactivity. Most literatures show that the optimum POFA content for strength is limited to low content with maximum volume substitution of approximately 30% due to slow strength gaining rate provided by POFA pozzolanic reaction.
- The durability of the concrete improve with the addition of POFA. The incorporation of POFA in concrete fills the voids of concrete, provides a more densely packed microstructure and thus minimizes the concrete porosity.

See also: Valorization of Olive Biomass Fly Ash for Production Eco-Friendly Ceramic Bricks

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Polysaccharide-Based Flocculants for Industrial Effluents

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Introduction

Oil and natural gas industries consume a large quantity of water for preparing water-based drilling fluids. Water-based drilling fluids are pumped through the downhole tubing during the drilling process and are circulated back to the surface through the casing annulus and collected in the return pit. At the end of recycling of the drilling fluids, large quantities of drill cuttings or solid materials are generated from the drilling fluid waste. In the drilling process of oil and gas wells generally, two types of wastes are generated: liquid drilling fluids waste and drill cuttings (Onwukwe and Nwakaudu, 2012). The oilfield drilling fluids waste produces the second largest volume of total waste (Haut *et al.*, 2007). The disposal of the drilling fluid wastes has proven to be one of the most difficult environmental problems in the world as the above wastes are made of various minerals, clays, organic materials, and other solids (Zou *et al.*, 2011). The most common toxic substances present in drilling fluid wastes contain a high concentration of chromium (a heavy metals), inorganic salts, biocides, hydrocarbon and solid cuttings. These toxic substances resulting from the chemical additives used for the preparation of the drilling fluids (Ayotamuno *et al.*, 2007). These oilfield waste materials have the ability to cause cancer and its toxicity affects mankind and the eco-system (Ismail *et al.*, 2017). The physical and chemical properties of the drilling fluid wastes are given below Table 1. Typical elemental composition of common constituents of drilling fluid waste is given in Table 2.

Discharge of drilling fluid waste containing drill cuttings into seabed is the most significant effect on the environment during offshore drilling operations. A case study had shown the impact of toxicity to the marine population due to presence of additives in the drilling fluid waste (Gbadebo *et al.*, 2010). The study conducted by Soegianto *et al.* (2008) was also showed that the effect of toxicity due to drilling fluid waste. Oil-based drilling fluid wastes are the most toxic drilling fluid compared to water or synthetic based drilling fluids (Ismail *et al.*, 2017). The removal of such toxic contaminants from the drilling waste and drilling wastewater is most desirable before their final disposal. The common methods to dispose the drilling fluid waste and drilling wastewater are: gravity separation, baffle and vacuum separation. In deep drilling well, when the components of drilling fluid waste are more complex, the density of drilling fluid waste becomes higher. To minimize the environmental impact of drilling fluid waste is one of the most important challenges in the petroleum industry (Shon *et al.*, 2016).

Table 1 Basic characteristics of drilling fluid waste

Parameters	Numerical value
Density (g ml ⁻¹)	1.62
Apparent viscosity (mPa s)	36.50
Plastic viscosity (mPa s)	26.70
Dynamic cutting (Pa)	9.80
Solid content (%)	54.40
Oil content (%)	5.00
pH	11.64

Note: Zou, J., Zhu, H., Wang, F., *et al.*, 2011. Preparation of a new inorganic–organic composite flocculant used in solid–liquid separation for waste drilling fluid. Chemical Engineering Journal, 171 (1), 350–356.

Table 2 Pollutants containing of drilling fluid waste

Sl. No.	Pollutants	Concentration (mg l ⁻¹)
1.	Cr	1.55
2.	Hg	0.0004
3.	Cd	0.22
4.	As	0.024
5.	Pb	1.2
6.	Zn	0.12
7.	Cu	< 0.1
8.	Fluoride	5.24
9.	Content of solid	344

Note: Zou, J., Zhu, H., Wang, F., *et al.*, 2011. Preparation of a new inorganic–organic composite flocculant used in solid–liquid separation for waste drilling fluid. Chemical Engineering Journal, 171 (1), 350–356.

The solid-liquid separation by the coagulation and flocculation plays an important role in waste management technique. The effective waste management techniques are waste minimization, recycling, solids control, treatment, and disposal (Onwukwe and Nwakaodu, 2012). The term flocculation and coagulation are often used interchangeably although the two processes are quite different. Coagulation is the process by which components of a stable suspension in solution are destabilized by the addition of an inorganic chemical. On the other hand, the process of forming larger agglomerates of particles in suspension or of small agglomerates already formed as a result of coagulation by high molecular weight polymeric material is called flocculation (Bratby, 1980; Karmakar, 1994).

Generally, flocculating agents in the waste water treatment can be classified broadly into two categories: inorganic and organic. The inorganic flocculants are mostly the salts of multivalent metals like aluminium and iron. Aluminium compounds (alum) with a chemical formula $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ are most often used in waste water treatments. The organic flocculating materials are further classified into natural and synthetic polymeric materials (Zou *et al.*, 2011). The synthetic polymers are based on various monomers but natural polymers are mostly polysaccharides (Kolya *et al.*, 2017). Natural polymers, as well as synthetic anionic, cationic and non-ionic polymers are widely used in flocculation studies. Natural polysaccharides have been used extensively as flocculants but their performances are not good. Natural polymers are mainly polysaccharides which are easily available from reproducible farm or forest resources. They are inexpensive and fairly shear stable and biodegradable but less efficient as flocculants. On the other hand, the polyacrylamide-based synthetic polymers are efficient flocculating agents, but they are shear degradable. Hence both the synthetic and natural organic flocculants have their own advantages and disadvantages (Singh *et al.*, 2003, 2009, 2014; Kolya *et al.*, 2017). A new class of polymeric flocculants i.e., the graft copolymers have been developed which are synthesized using natural and synthetic polymers. Graft copolymerization is a useful technique for modifying the chemical and physical properties of natural and synthetic polymers. Grafting of the synthetic polymer is a convenient method to add new properties to a natural polymer with minimum loss of the initial properties of the substrate. Many researchers have carried out grafting reactions of acrylamide onto the natural polysaccharides like starch, amylose, amylopectin, guar gum/hydroxypropyl guar gum, xanthan gum, sodium alginate and carboxymethyl cellulose (CMC) (Rath and Singh, 1997; Karmakar and Singh, 1998; Tripathy *et al.*, 1999, 2000, 2001; Nayak and Singh, 2001; Pal *et al.*, 2005, 2006, 2008, 2011).

Keeping the above perspective in mind, the present investigation was undertaken to evaluate the flocculation characteristics of the graft copolymers. The graft copolymers based flocculants have been prepared by using potassium persulphate (KPS) initiator solution methods of graft copolymerization of polyacrylamide onto polysaccharide backbones (starch, guar gum and amylose) in our laboratory. The synthesized graft copolymers have been characterized using various instrumental methods of analysis. The effects of various synthetic flocculants and their concentrations in combination with the coagulants on coagulation/flocculation of bentonite based drilling fluid waste have been studied. The effects of coagulant/flocculant dosage, salts concentration and pH on the degree of flocculation of bentonite based drilling fluid waste have been investigated.

Materials and Methods

Materials

Starch, amylose, guar gum, hydroquinone, potassium persulphate ($\text{K}_2\text{O}_2\text{S}_8$) were procured from Loba Chemie, Mumbai, India. Acetone, hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium chloride (NaCl), aluminium sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$), acrylamide were procured from Merck Life Science Private Limited Mumbai, India. Polyacrylamide (PAM) was obtained from Merck, Germany. Drilling fluid waste sample was collected from oilfield Kadi, Oil & Natural Gas Corporation Limited (ONGC) Ahmedabad Gujarat, India (Fig. 1). The zeta potential of the drilling fluid waste sample was found to be -23.1 mV at pH 4.

Synthesis of Graft Copolymers

The graft copolymers of starch, amylose and guar gum has been synthesized in inert atmospheric of nitrogen using potassium persulphate (KPS) as initiator. During synthesis 1 gm of starch/amylose/guar gum were slowly dissolved into 80 ml double distilled water in a three necked round bottom flask. The flask was fitted with an electrically operated magnetic stirrer (REMI, Model-2 MLH Magnetic Stirrer) and kept in water bath maintained at a temperature of $75 \pm 1^\circ\text{C}$ with constant stirring speed of 250 rpm. The reaction set up for graft copolymerization is shown in Fig. 2. Then nitrogen gas was purged for 15 min: afterwards, 0.1 gm of KPS was dissolved in 10 ml double distilled water and added to the solution. Then after 15 min the desired quantity of acrylamide (Table 3) dissolved in 50 ml double distilled water was poured slowly to the homogenous solution. The reaction was continued for another one hour under at $75 \pm 1^\circ\text{C}$ with stirring speed of 250 rpm. The reaction was terminated by addition of hydroquinone solution. The reaction was continued under continuous nitrogen gas purging from its initial reaction to final reaction. The reaction mixture was cooled to room temperature and the product was precipitated with acetone. Afterwards, it was dried in a hot oven at 55°C for 24 h, pulverized by mortar pestle and sieved through 100 mesh screens. The synthesis parameters are reported in Table 3. Synthetic details of graft copolymers are given below:

- St-g-PAM-I: Starch grafted polyacrylamide (8 gm of acrylamide, 1 gm of starch)
- St-g-PAM-II: Starch grafted polyacrylamide (15 gm of acrylamide, 1 gm of starch)
- Am-g-PAM-I: Amylose grafted polyacrylamide (8 gm of acrylamide, 1 gm of amylose)
- Am-g-PAM-II: Amylose grafted polyacrylamide (15 gm of acrylamide, 1 gm of amylose)
- Gr-g-PAM-I: Guar gum grafted polyacrylamide (8 gm of acrylamide, 1 gm of guar gum)



Fig. 1 Oilfield drilling fluid wastes.

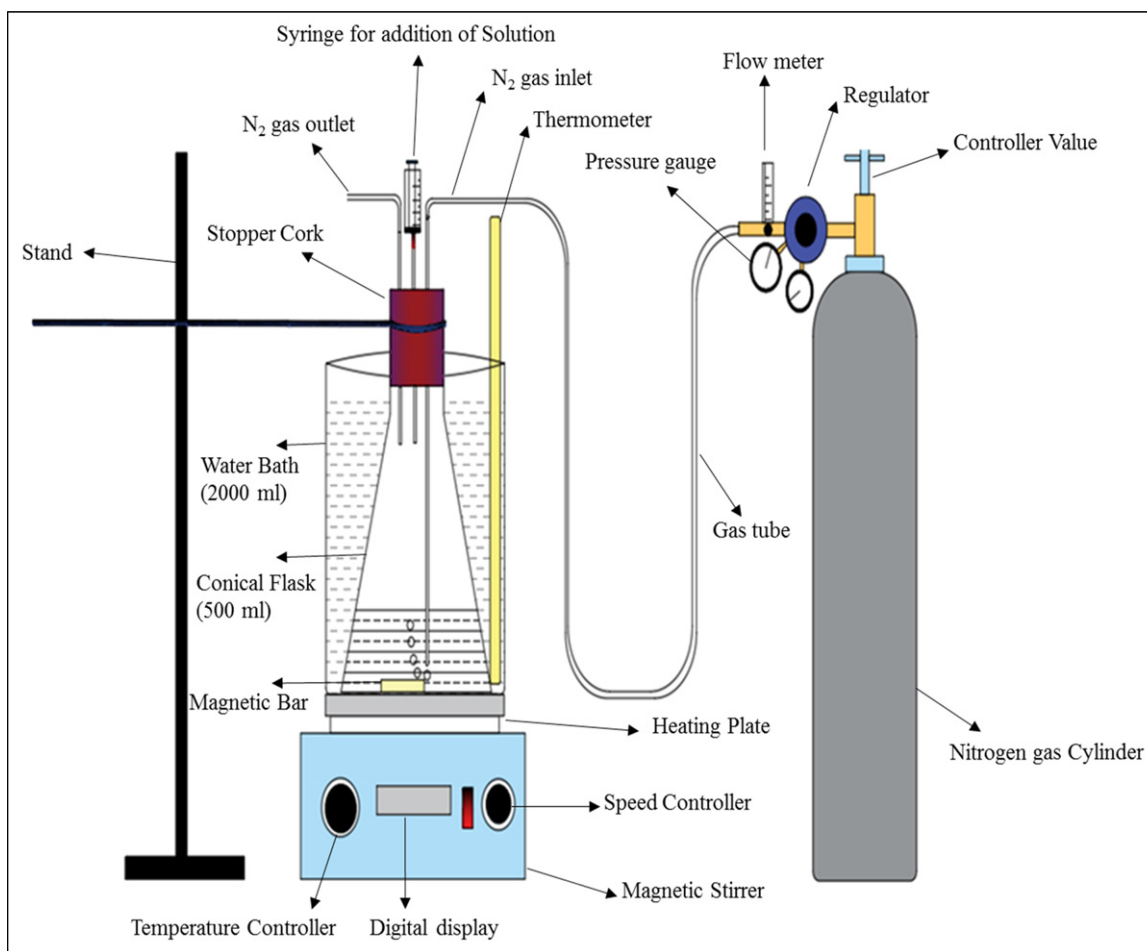


Fig. 2 Reaction set up for graft copolymerization.

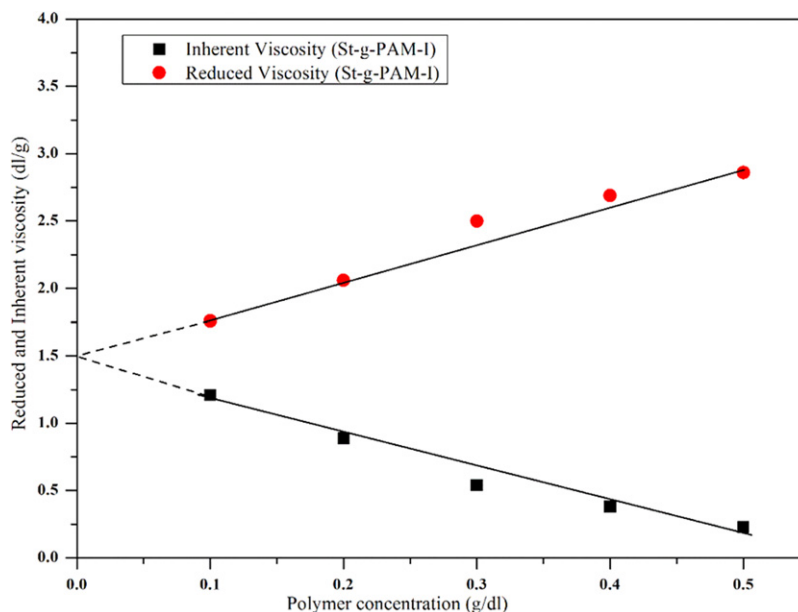
Characterization of Graft Copolymers

Intrinsic Viscosity Measurement

Viscosity measurement of polymer solutions was carried out with the help of Ubbelohde viscometer (Constant: 0.003867) at 25°C. The viscosities were measured in dilute aqueous solution. The pH of the aqueous solution was neutral. The time of flow for solutions was measured at five different concentrations. From the time of flow of polymer solution (t) and that of the solution (t_0 , distilled water), relative viscosity ($\eta_{rel} = t/t_0$) was obtained. Specific viscosity was calculated from the relation, $\eta_{sp} = \eta_{rel} - 1$.

Table 3 Synthetic details of graft copolymers

Graft copolymer	Polysaccharides (gm)	Acrylamide (gm)	Amount of KPS (gm)	% Conversion	Intrinsic viscosity $[\eta](\text{dl g}^{-1})$	$M_n \times 10^6$	$M_w \times 10^6$
St-g-PAM-I	1	8	0.1	93	1.48	0.118	0.290
St-g-PAM-II	1	15	0.1	97	1.42	0.112	0.275
Am-g-PAM-I	1	8	0.1	92.8	1.07	0.072	0.193
Am-g-PAM-II	1	15	0.1	99.63	1.35	0.107	0.258
Gr-g-PAM-I	1	8	0.1	94	1.88	0.332	0.391

**Fig. 3** Reduced and inherent viscosity vs concentration curve for measurement of intrinsic viscosity of St-g-PAM-I.

Then, the reduced viscosity (η_{sp}/C), and the inherent viscosity ($\ln \eta_{rel}/C$) were calculated, Where, C is the polymer concentration in g/dl. The intrinsic viscosity was obtained from the point of intersection after extrapolation of two plots (Collins *et al.*, 1973; Tripathy *et al.*, 2000; Pal *et al.*, 2006), i.e., η_{sp}/C versus C and $\ln \eta_{rel}/C$ versus C , to zero concentration (as shown in Fig. 3). The intrinsic viscosity values of various polysaccharides grafted copolymers are listed in Table 3.

XRD Analysis

The synthesized graft copolymers were characterized X-ray diffraction (XRD) analysis to determine the qualitative mineral contents in the samples. XRD analyses were carried out using Philips PW 1040 Model diffractometer with Cu target at voltage 30 kV, current of 10 mA. The scattering angle (2θ) was varied from 0 to 80° .

FTIR Spectroscopy

FTIR spectra of various polymer samples were recorded using Perkin Elmer model Spectrum Two (USA) and range of the above measurements was $500\text{--}4000\text{ cm}^{-1}$. 1 mg of sample was mixed with a very small amount of KBr and KBr pellets were prepared using a hydraulic press by applying a pressure of 100 psi for the 60 s. The IR spectrums of the KBr pellets were recorded and 100 scans were collected.

Scanning Electron Microscopy (SEM) Analysis

The morphologies of the various polymer samples used in this study were analysed using ZESIS Model EVO 60 (Curl ZESIS SMT, Germany) with Air Lock chamber to examine the morphology of different polymers samples. The samples were charged with platinum coating to get clearer images. The elemental analyses of graft copolymers were carried out using Energy dispersive X-ray spectroscopy (EDX analyzer). The Scanning Electron Microscope (SEM) couple with Energy Dispersive X-ray Spectroscopy (EDX

Table 4 Elemental analysis results of starch, amylose, acrylamide, polyacrylamide and graft copolymers

Polymer	Carbon (wt%)	Oxygen (wt%)	Nitrogen (wt%)
Starch	53.49	6.71	39.80
Amylose	33.19	52.03	14.78
Acrylamide	18.40	56.20	25.40
Polyacrylamide	32.65	47.61	18.76
St-g-PAM-I	59.81	37.67	2.52
St-g-PAM-II	53.69	37.72	8.59
Am-g-PAM-I	61.23	35.29	3.48
Am-g-PAM-II	56.45	28.81	7.04
Gr-g-PAM-I	51.00	33.86	15.14

analyzer) was used to determine the elemental composition of the above samples. The estimation of carbon, oxygen and nitrogen, was undertaken. The results are shown in [Table 4](#).

Flocculation Studies of Drilling Fluid Waste

The flocculation studies of various polymers were carried out using standard jar test methods ([Bratby, 1980](#); [Singh et al., 2000](#)). The apparatus contained six spindles with the blades (length 46 mm, width 17 mm, and thickness 3 mm) and variable speed ranging from 0 to 200 rpm with digital display. Each spindle is connected simultaneously by a series of stirrers connected with an electric motor through gears. The drilling fluid waste was diluted using distilled water (50% v/v). The adjustment of pH ranging from 4 to 10 was made by adding hydrochloric acid or sodium hydroxide (0.1 M HCl or 0.1 M NaOH concentration). The pH values of the samples were measured using a digital pH meter (Model 802, Systronics Ahmedabad, India). Afterwards, the diluted samples were put into 500 ml glass beakers. Required quantities of coagulant/flocculants/NaCl (0.001–0.1 M) were added from the top of the jar, and stirring speed was controlled by speed selector switch. The solution was mixed rapidly by increasing the speed (75 rpm) of stirrer for 1–2 min. After this rapid mixing, the solution was subjected to slow mixing (20–25 rpm) for 10 min. Finally, the flocs formed were allowed to settle for a period of 25 min.

Turbidity Measurements

After the settling of the flocs, supernatant liquid was carefully withdrawn from the top of the jar for the turbidity measurements using a syringe. The turbidity values were recorded in Nephelometric Turbidity Units (NTU) using a digital turbidity meter (Model 331E, Electronics Kolkata, India). Determination of total solid (TS), total dissolved solid (TDS) and total suspended solid (TSS) in the drilling fluid wastes were carried out gravimetrically ([Greenberg, 1999](#)).

Colour Removal Study

The colour removal study was carried out of oilfield drilling fluid waste by using synthesized graft copolymers. The detail experimental procedure was as follows; 100 ml of diluted drilling fluid waste was taken in 250 ml beaker and stirred by a magnetic stirrer (REMI, Model-2 MLH Magnetic Stirrer) at 300 rpm with 10 ppm polymer solution and varying NaCl concentration or pH for 30 min at room temperature. The solution was allowed to settle for 25 min and the supernatant liquid was collected from the top layer by syringe ([Kolya et al., 2017](#)). The colour measurement of the treated and untreated drilling fluid waste samples has been determined and represented graphically (absorbance versus wavelength) using UV-Visible Spectrophotometer (Thermo Scientific, Model: EVOLUTION 201).

Results and Discussions

Synthesis

The graft copolymers were synthesized using potassium persulfate (KPS) as a free radical initiator in nitrogen atmospheric, maintaining the reaction temperature at $75 \pm 1^\circ\text{C}$. Monomer (acrylamide), initiator, and 2.5 g of polysaccharides Starch/Amylose/Guar gum were used to synthesize the graft copolymers. Initially, the amount of monomer and polysaccharide were taken as 20.0 g and 2.5 g respectively, and were dissolved in 80 ml and 50 ml double distilled water respectively. But, due to high viscosity of the solution, the graft copolymerization could not be performed properly when the initiator was added to the solution. It was also observed the reaction product broke up while washing with acetone. The probable reasons were that the higher concentration of monomer resulted in the formation of undesirable homopolymers and higher concentration of polysaccharides resulted in higher viscosity of the solution. The above phenomenon caused hindrance in normal graft copolymerization by restricting the movement

of free radicals resulting in a less efficient initiation process and grafting efficiency (Ogbeifun and Okieimen, 2004; Pandey and Mishra, 2011; Maia *et al.*, 2012). Finally, the amount of monomer and polysaccharides were reduced to optimum concentrations (1.0 g of polysaccharides and 8.0/15.0 of monomer) considering its suitability for high grafting efficiency. The probable mechanism in the synthesis of graft copolymer was based on the generation of free radical sides on the backbone of biopolymer by KPS, which in turn reacted with the monomer (acrylamide) to form graft copolymer through initiation, propagation and termination (Jain *et al.*, 2014, 2017).

Calculation of the Approximate Molecular Weight

Molecular weight of the polymer samples can be estimated from the intrinsic viscosity $[\eta]$ values. The Mark- Houwink equation, $[\eta] = KM^\alpha$ is generally employed for the estimation of molecular weight of linear polymers, where K and α are constant. For a given polymer/solvent/temperature system. For polyacrylamide the value of K and α are given below (Mendelson, 1969; Erciyes *et al.*, 1992; Karmakar and Singh, 1998; Tripathy *et al.*, 2000; Biswal and Singh, 2004).

$$[\eta] = 6.8 \times 10^{-4} (M_n)^{0.66} \quad (1)$$

$$[\eta] = 6.31 \times 10^{-5} (M_w)^{0.80} \quad (2)$$

Where, M_n is the number-average molecular weight and M_w is the weight-average molecular weight. Several workers (Erciyes *et al.*, 1992; Karmakar and Singh, 1998; Tripathy *et al.*, 2000; Biswal and Singh, 2004) have been used the Mark- Houwink equation to estimate approximate molecular weight, which is applicable for linear polymers. The same has been done in the present case. The estimate approximate molecular weight of the graft copolymers are given in Table 3.

$$\% \text{ Conversion} = \left(\frac{\text{Wt. of graft copolymer} - \text{Wt. of polysaccharide}}{\text{Wt. of acrylamide monomer}} \right) * 100 \quad (3)$$

X-ray Diffraction Analysis

X-ray diffraction pattern of all the polysaccharides grafted copolymers (St-g-PAM-I to Am-g-PAM-II) are shown in Fig. 4. In this pattern of XRD analysis, all graft copolymers do not show single peak indicating crystallinity in between a range of 2θ (21–45°). The X-ray diffraction patterns also do not show a sharp peak. However, the grafted products do not indicate any crystallinity or any

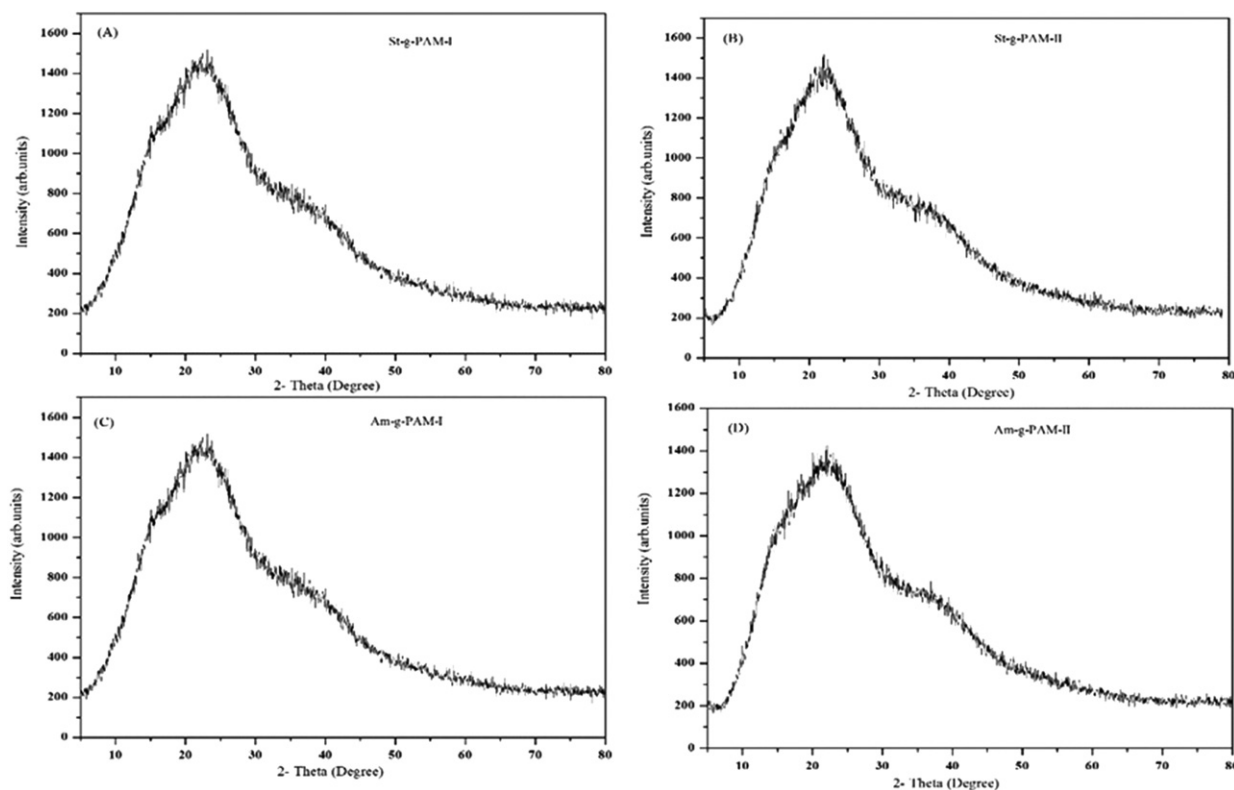


Fig. 4 X-ray diffraction pattern of graft copolymer (A) St-g-PAM-I, (B) St-g-PAM-II, (C) Am-g-PAM-I, (D) Am-g-PAM-II.

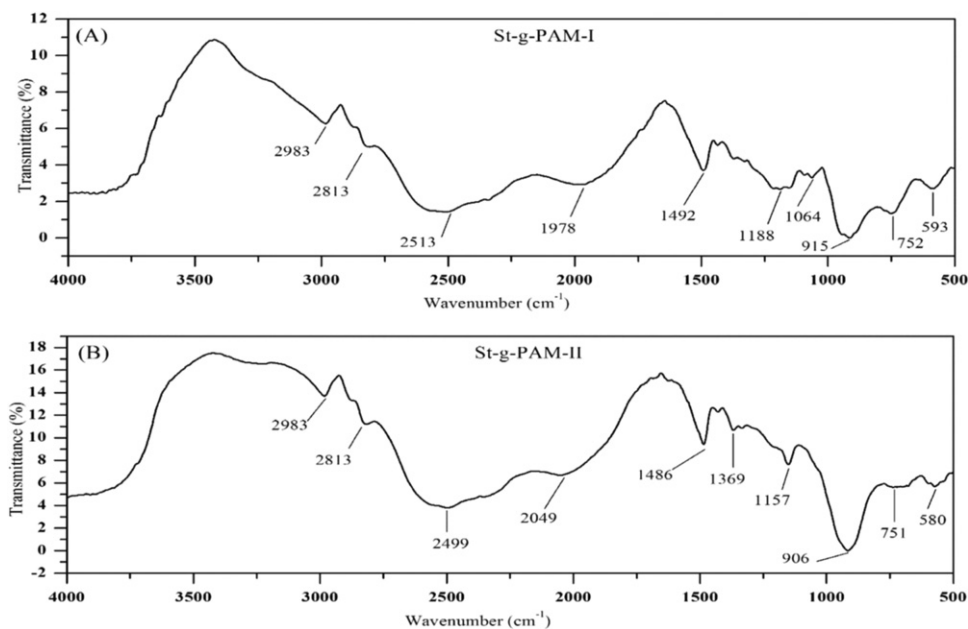


Fig. 5 FTIR spectra of graft copolymer (A) St-g-PAM-I, (B) St-g-PAM-II.

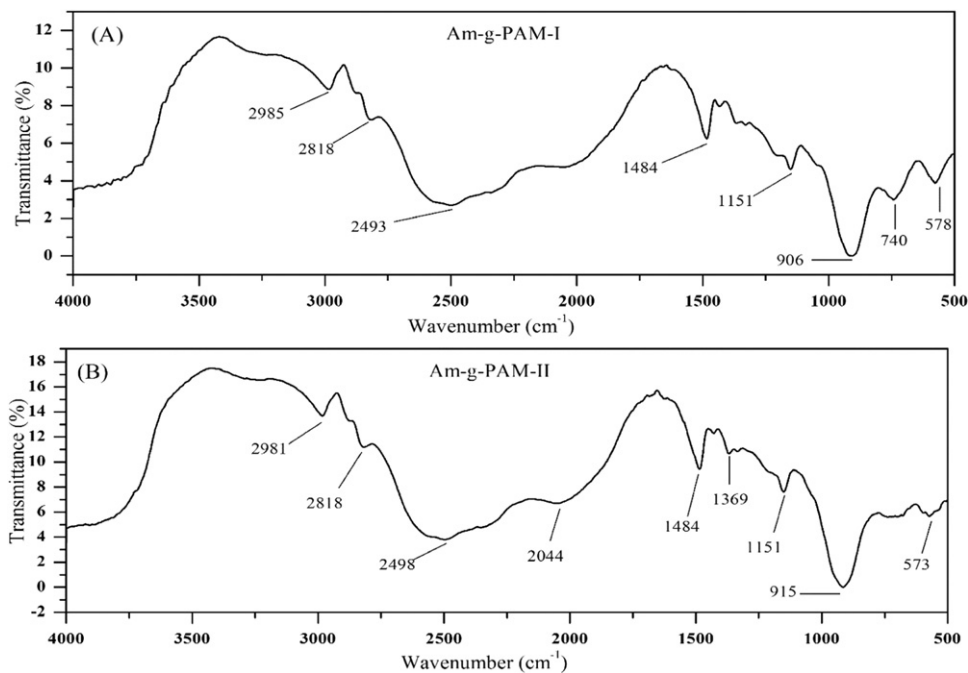


Fig. 6 FTIR spectra of graft copolymer (A) Am-g-PAM-I, (B) Am-g-PAM-II.

sharp peak due to acrylamide monomer. Similar results have also been obtained from the analysis of grafted products synthesized by earlier workers using the same method (Tripathy *et al.*, 1999; Biswal and Singh, 2006).

FTIR Analysis

The FTIR spectra of polysaccharides grafted copolymers (St-g-PAM-I, St-g-PAM-II, Am-g-PAM-I and Gr-g-PAM-I) are shown in Figs. 5(A) and 6(B). The spectrum of St-g-PAM-I (Fig. 5(A)) displays a broad absorption band at 2983 cm^{-1} , 2813 cm^{-1} , and 2513 cm^{-1} are due to N-H, C-H and O-H groups stretching vibration. The bands at 1975 cm^{-1} and 1492 cm^{-1} belong to

C=C and N-O groups stretching vibration. The bands at 1188 cm^{-1} and 1064 cm^{-1} belong to C-O group stretching vibration, but the bands at 915 cm^{-1} and 752 cm^{-1} belong to C=C and O-H group bending vibration. In case of St-g-PAM-II (Fig. 5(B)), the stretching vibration are due to C-H group at 2983 cm^{-1} and 2819 cm^{-1} respectively. The bands at 2499 cm^{-1} and 2049 cm^{-1} belong to S-H and N=C=S groups stretching vibration. But, the medium absorption bands at 1486 cm^{-1} and 1369 cm^{-1} belong to C-H or O-H groups are due to bending vibration. Again, the strong absorption bands at 1157 cm^{-1} , 906 cm^{-1} and 751 cm^{-1} are the stretching or bending vibration in the presence of C-O, C=C and C-H groups.

Fig. 6(A) shows the FTIR spectrum of Am-g-PAM-I. The medium absorption bands at 2985 cm^{-1} and 2818 cm^{-1} are due to C-H stretching vibrations. The presence of a weak and strong band absorption at 2493 cm^{-1} and 2036 cm^{-1} confirms the presence of S-H and N=C=S groups respectively. But, the bands at 1484 cm^{-1} , 906 cm^{-1} and 740 cm^{-1} are assigned to C-H, C=C and C-H groups bending vibration. The strong band absorptions at 1151 cm^{-1} and 578 cm^{-1} are due to C-O and C-I groups stretching vibrations. Finally, in the spectrum of Am-g-PAM-II (Fig. 6(B)) a broad medium absorption bands at 2985 cm^{-1} and 2818 cm^{-1} are stretch for C-H group. The bands at 2498 cm^{-1} and 2044 cm^{-1} are represents stretching vibration of S-H and N=C=S groups respectively. The bands around at 1484 cm^{-1} , 1369 cm^{-1} are assigned to C-H group and at 915 cm^{-1} is confirms due to C=C group bending vibration. But, the bands at 1151 cm^{-1} and 573 cm^{-1} are a typical stretch of C-O and C-I groups.

Scanning Electron Microscopy (SEM) Analysis

The scanning electron microscopy (SEM) was used to investigate the surface morphological feature of starch, amylose and synthesized graft copolymers (St-g-PAM-I and Am-g-PAM-I) with acrylamide. The morphological feature of starch shows cohesive and dense structure (Fig. 7(A)). The morphological feature of amylose is a smooth and continuous surface and granular structure with no distinct perturbations (Fig. 7(B)). After grafting the granular appearance of starch and amylose were distorted and changed to fibrillar. The morphology of acrylamide has also found to be changed after grafting with starch and amylose (Fig. 8). The SEM micrograph of graft copolymer St-g-PAM-I and Am-g-PAM-I showed that the graft copolymerization of starch and amylose with acrylamide dramatically changed the conformation of polysaccharides polymer (starch and amylose) chain. The similar morphological structure changes were also observed by earlier workers while performing the graft copolymerization using chitosan and polyacrylamide (Soliman *et al.*, 2014). This observation suggests that the grafting of acrylamide affects the morphological arrangement of polymers. The micrograph of graft copolymers showed a number of long chain of acrylamide which got agglomerated and changed in fibrillar structure (Fig. 9(A) and (B)) (Jain *et al.*, 2017).

Flocculation Characteristics

The drilling fluid waste sample collected from Kadi, ONGC Ahmedabad, Gujarat was treated for coagulation and flocculation studies. The initial pH of the waste was 8.25, the turbidity value was 1589 NTU. While treating the waste, it was observed that it was very difficult to treat the waste with either alum or polymer alone by coagulation or flocculation. The concentrated solutions (90% volume of drilling fluid waste along with 10% volume of distilled water) could not be treated effectively. This was due to the fact that the oilfield drilling waste mainly contained lignosulfonates, lignin, solid drill cuttings, and high molecular weight polymeric compounds. The plastic and the apparent viscosity of the drilling fluid wastes were also high. It was difficult to

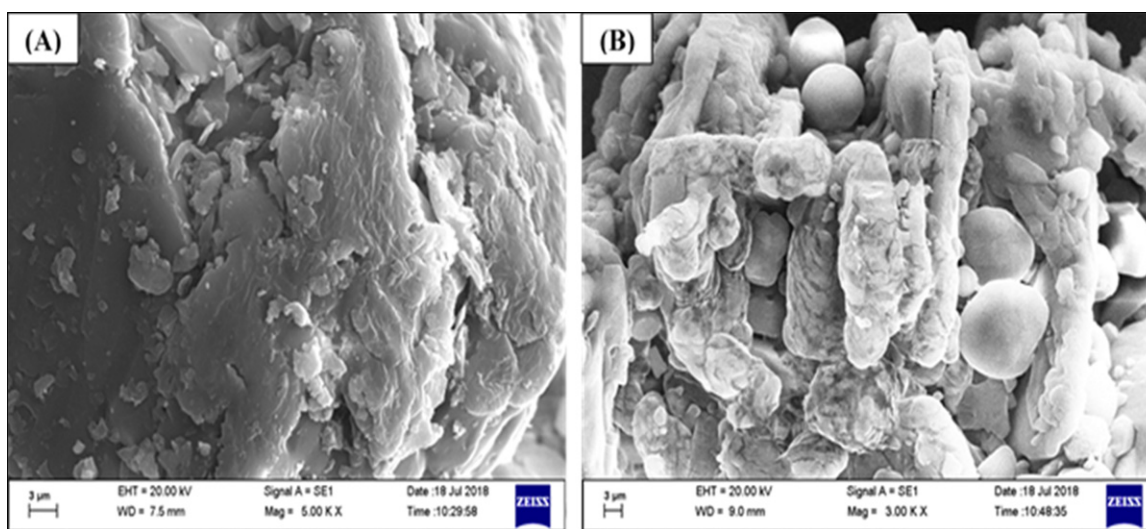


Fig. 7 Scanning electron micrograph of (A) starch, (B) amylose.

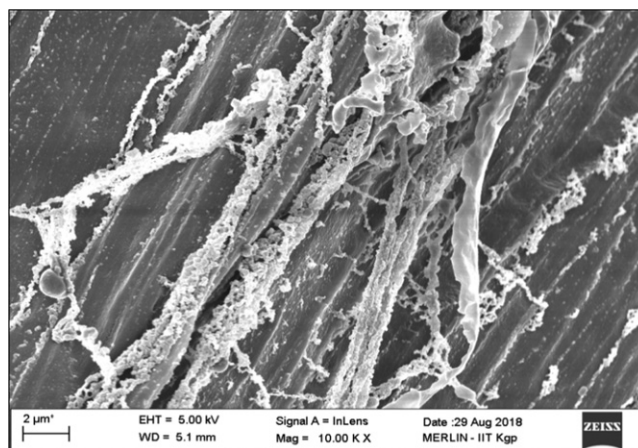


Fig. 8 Scanning electron micrograph of acrylamide.

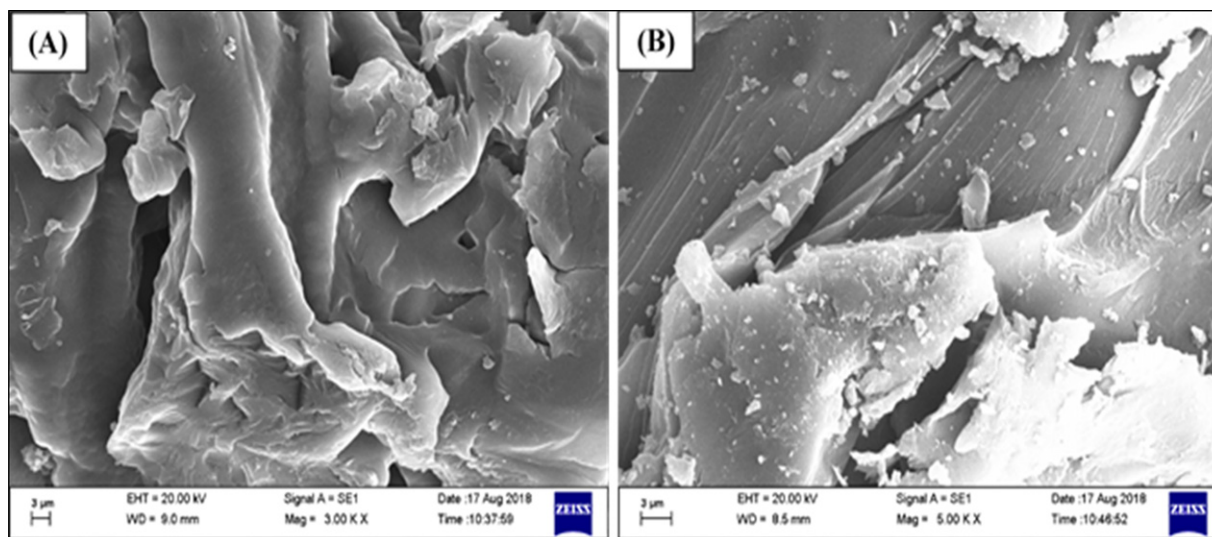


Fig. 9 Scanning electron micrograph of graft copolymer (A) St-g-PAM-I, (B) Am-g-PAM-I.

flocculate the particles with polymeric flocculants alone. Therefore, the original waste was diluted with the addition of equivalent amount of distilled water. Afterwards, it was coagulated with coagulant $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ and then flocculated with grafted copolymers. Standard jar test method was followed for flocculation and the supernatant turbidity values in NTU were measured after specific settling period after flocculation. **Fig. 10** showed that untreated drilling fluid waste sample before flocculation test and after flocculation test.

Effect of flocculants

The diluted drilling fluid waste was first coagulated with $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ by fast mixing at 75 rpm for one minute. Then flocculants (graft copolymers) were added and stirrer for one more minute. Subsequently, it was subjected to slow mixing at 20 rpm for 10 min and settling for 25 min. Initially, the 10 ppm concentration of polyacrylamide/graft copolymer was fixed while varying the alum concentration from 10 ppm to 80 ppm. Increasing the alum concentration resulted in decreasing the turbidity of the waste up to a certain concentration of the alum. Further increase in alum concentration resulted in increasing the turbidity value. The turbidity value of the supernatant liquid was recorded 320 NTU at 40 ppm and then further increase in alum concentration resulted in restabilization of the particles showing the turbidity value of 546 NTU at 80 ppm. Hence, 40 ppm of alum concentration was fixed while varying the graft copolymer concentrations from 10 ppm to 50 ppm for the next set of experiments. It was observed that when the polymer concentration increased from 10 ppm to 30 ppm the turbidity value of supernatant liquid decreased from 224 NTU to 201 NTU. Further increase in the concentration of graft copolymer up to 50 ppm, the turbidity value of supernatant liquid increased from 304 NTU to 384 NTU (St-g-PAM-I). The turbidity value was found to be lowest 201 NTU when 30 ppm of the Am-g-PAM-II polymer was used. The results of flocculation performance above grafted

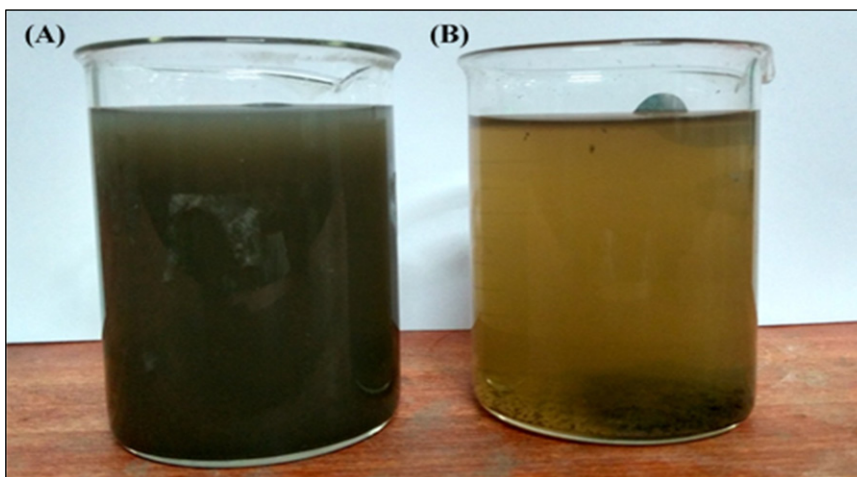


Fig. 10 (A) Untreated drilling fluid waste, (B) Treated drilling fluid waste.

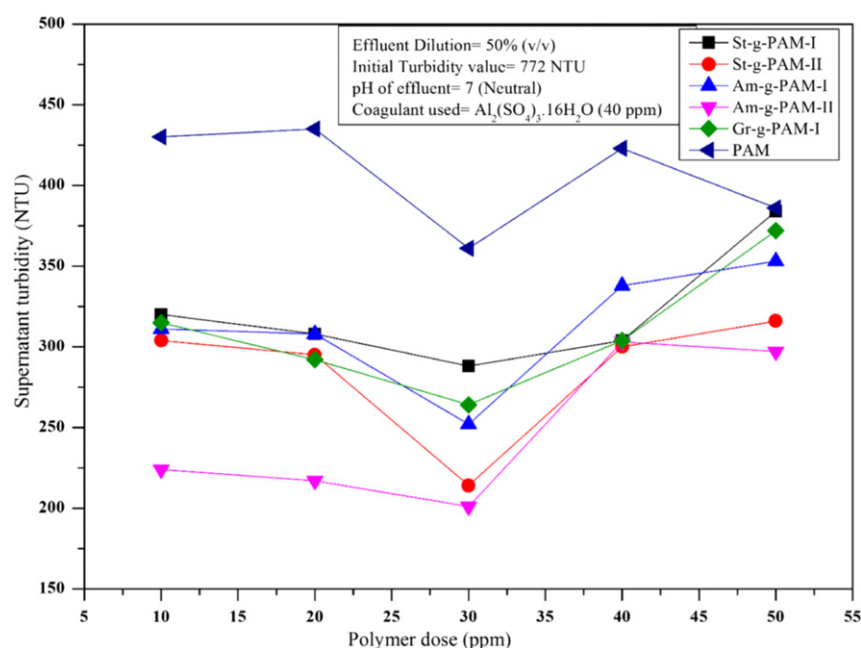


Fig. 11 Comparison of flocculation performance of grafted copolymers in oilfield drilling fluid waste.

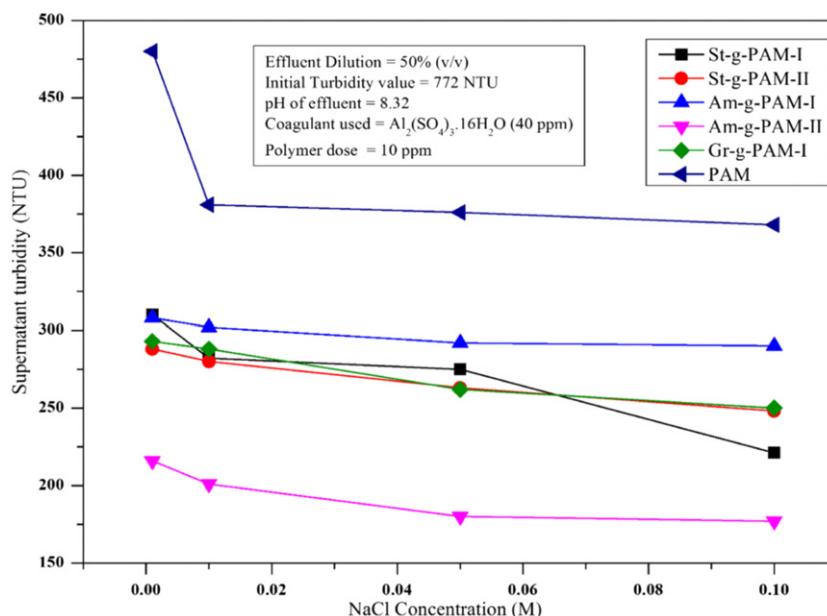
copolymers are given in Fig. 11. It is clearly indicated that the Am-g-PAM-II had shown better flocculation performance (Table 5) in comparison with other graft copolymers and commercial (PAM) flocculants.

Effect of NaCl concentration

A series of coagulation-flocculation tests were carried out with varying NaCl concentration (0.001 M, 0.01 M, 0.05 M and 0.1 M) while fixing the concentration of alum at 40 ppm and the concentration of graft copolymers at 10 ppm. The supernatant turbidity values in NTU were recorded as a function of NaCl concentration of the system. The results are given in Fig. 12. It was found that the supernatant turbidity values decreased when the NaCl concentration of the system was more than 0.05 M. The drilling fluid waste was highly flocculated in the interval of 0.05–0.1 M of NaCl concentration. The flocculation of the waste with NaCl concentration < 0.001 M resulted in deflocculation which showed high values of supernatant turbidity. Using 10 ppm of Am-g-PAM-II graft copolymer it was observed that when the NaCl concentration of the system was increased from 0.001 M to 0.1 M the supernatant turbidity value was decreased from 216 NTU to 177 NTU. It was clear that the supernatant turbidity value was decreased to about 47.75% with 0.1 M NaCl concentration at 10 ppm of the graft copolymer (Am-g-PAM-II). This was the higher percentage of turbidity reduction compared to other graft copolymers. The results are plotted in Fig. 12. It was observed that the polysaccharide grafted copolymers (Am-g-PAM-II) had shown better flocculation performance in presence of NaCl solution.

Table 5 Flocculation performance of the graft copolymers in oilfield drilling fluid waste

Polymer	Turbidity value (NTU)	TS (ppm)	TDS (ppm)	TSS (ppm)
Without polymer	772	126	81	45
PAM	430	40.82	37.08	3.74
St-g-PAM-I	320	33.00	28.32	4.68
St-g-PAM-II	304	29.70	26.56	3.14
Am-g-PAM-I	311	37.22	39.97	4.25
Am-g-PAM-II	224	17.22	14.00	3.22
Gr-g-PAM-I	315	22.28	19.07	3.21

**Fig. 12** Effect of NaCl concentration (M) on supernatant turbidity value.

Effect of pH suspension

As discussed earlier, for effective flocculation the drilling fluid waste was diluted with addition of equivalent amount of distilled water. The pH of the system was adjusted by adding hydrochloric acid or sodium hydroxide (0.1 M HCl/0.1 M NaOH concentration). The coagulation-flocculation studies were carried out using 40 ppm of alum and 10 ppm of graft copolymer/polyacrylamide using standard jar test method. After flocculation, the turbidity values of the supernatant liquids were determined under various pH conditions. The supernatant turbidity values in NTU were recorded as a function of pH of the system. The results are presented in Fig. 13. It was observed that as the pH value of the system increased the supernatant turbidity value decreased. This was due to increase in the +ve charge density of the ions present in alkaline media (at pH 9). The attraction between the positively charged ions and negatively charged hydroxyl groups of the alkali enhanced the aggregation of the particles. The turbidity value of the supernatant liquid was recorded highest at 420 NTU using 10 ppm of PAM at pH 4 of the system. It also was found that the turbidity value was lowest at 204 NTU using 10 ppm of Am-g-PAM-II at pH 10 of the system. Finally, it was observed that at pH 10, Am-g-PAM-II was the most effective flocculant for the above system.

Colour Removal Study

The colour removal study of the oilfield drilling fluid waste effluent by the five polysaccharides grafted copolymers were carried out in a UV-Visible Spectrophotometer under optimum condition (polymer dose 10 ppm varying pH or NaCl concentration, time 30 min and room temperature). The UV-Visible results were shown in Figs. 14–16. The comparison was carried out among polysaccharides grafted copolymers (St-g-PAM-I, St-g-PAM-II, Am-g-PAM-I, Am-g-PAM-II and Gr-g-PAM-I). It was obvious from Fig. 14 that polysaccharides grafted copolymer (St-g-PAM-I) showed a better colour removal performance

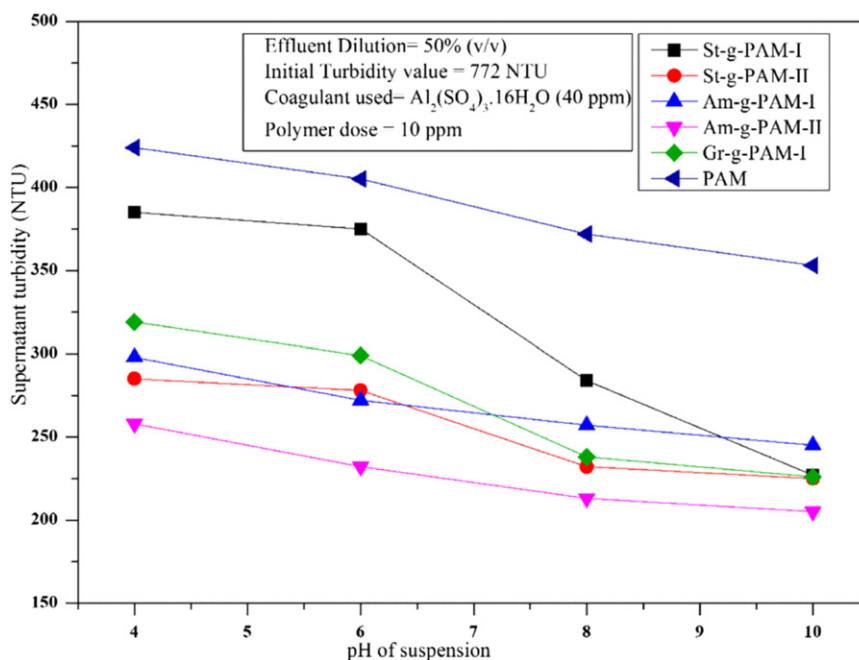


Fig. 13 Effect of pH on supernatant turbidity value.

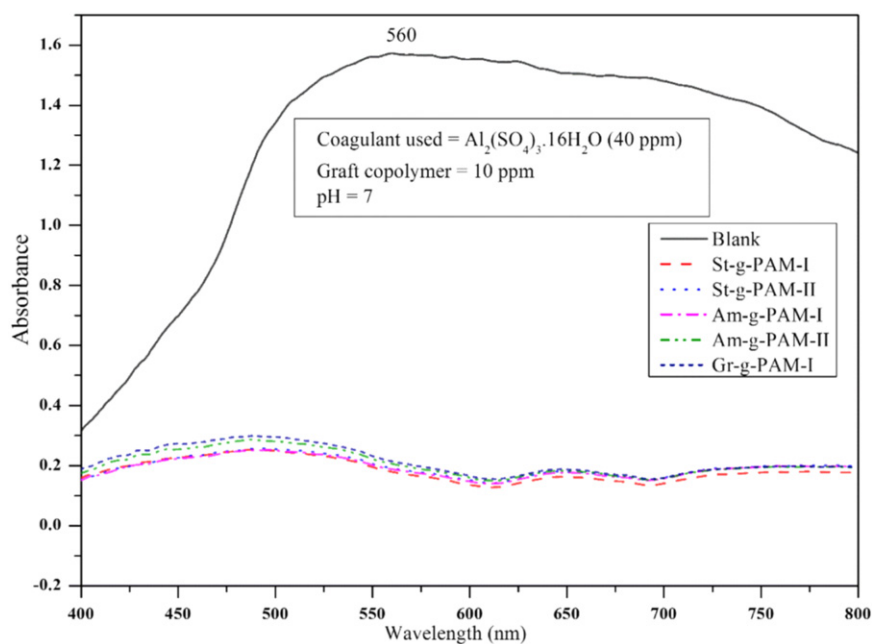


Fig. 14 Colour removal characteristics of polysaccharide grafted copolymers in drilling fluid waste.

compared to other grafted copolymers. In this case, the colour removal efficiency was compared by the absorbance value at $\lambda_{\max}$ 560 nm. The absorbance values were lower, showing that higher will be the colour removal efficient. The performance of grafted polysaccharides copolymer (St-g-PAM-I) was also explanted at varying NaCl concentration and pH of suspension. It was found to be the performance of St-g-PAM-I at pH 4 was better compared to the other pH of suspension for colour removal efficiency. The result was shown in Fig. 15. It was also obvious from in Fig. 16 that at NaCl concentration 0.01 M the polysaccharides grafted copolymer (St-g-PAM-I) had a better performing for colour removal than compared to other concentration of NaCl.

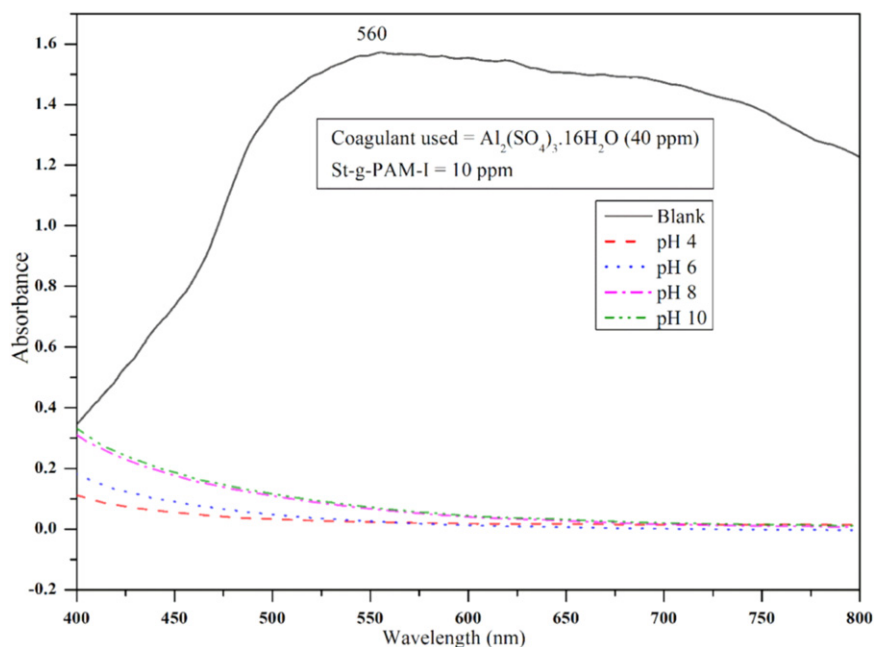


Fig. 15 Colour removal characteristics of St-g-PAM-I at varying pH in drilling fluid waste.

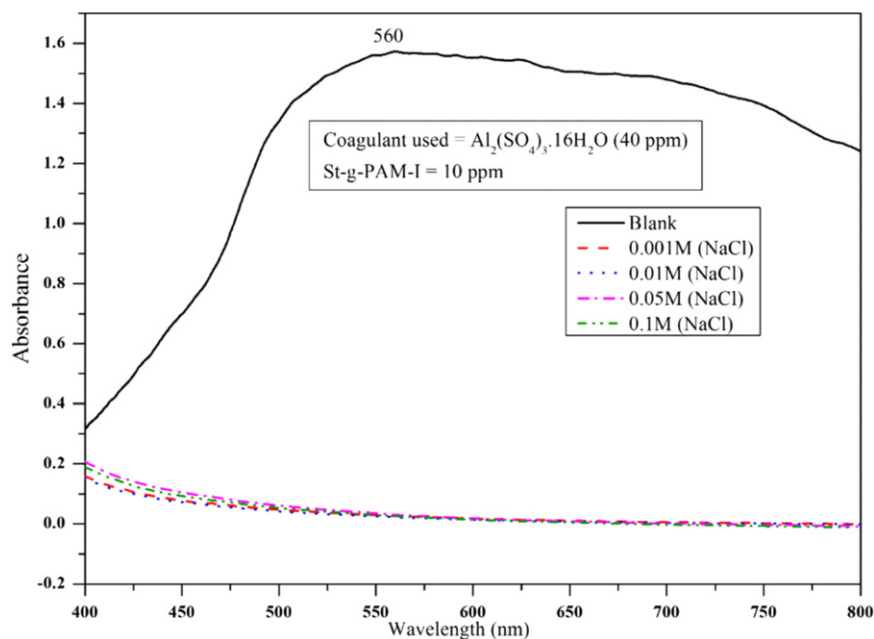


Fig. 16 Colour removal characteristics of St-g-PAM-I at varying NaCl concentration in drilling fluid waste.

Conclusions

- (1) Grafting of acrylamide monomer on starch, amylose and guar gum polysaccharide backbones were successfully carried out using potassium persulphate (KPS) as an initiator.
- (2) The synthesis of the above graft copolymers were confirmed by the instrumental analyses of their products.
- (3) The Am-g-PAM-II had shown better flocculation performance in comparison with other graft copolymers and commercial flocculants (PAM) for the bentonite suspension.

- (4) While treating the drilling fluid waste, it was observed that neither a coagulant nor a flocculant alone could completely flocculate such complex systems. After destabilizing such wastes with a suitable coagulant, polysaccharide grafted polymers could be used as flocculant aids for the complete flocculation of the contaminants present in the systems.
- (5) Polysaccharide based grafted copolymers were found to be efficient flocculants aids for treatment of the drilling fluid wastes in presence of NaCl and at higher pH conditions.
- (6) The polysaccharide based grafted copolymer (St-g-PAM-I) have a better performing for colour removal efficiency than compared to other grafted copolymers.

Acknowledgements

We are thankful for Oil and Natural Gas Corporation Limited (ONGC), Ahmedabad Gujarat, India for providing oilfield drilling fluid waste sample. We also thank Prof. K. Pathak, Department Mining Engineering IIT Kharagpur for providing the laboratory for personal help, which has been helpful for my research work.

See also: Eco Friendly Flocculants: Synthesis, Characterization and Applications

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Potentials of Natural Dyes for Textile Applications

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Introduction

The history of natural colorants or dyes goes back many hundreds of years. For example, indigo (Fig. 1) has been known for more than 5000 years and catechu has been in use as a brown colorant in India for over 2000 years (Wickens, 1983). Different natural sources of colorants such as flowering plants, fungi, lichens, insects, shellfish, and various earth minerals are available around us. They have found applications in the areas of food, pharmaceutical, dye sensitized solar cells, tanning, pH indicator, agriculture, textiles, cosmetics, and fragrance (Adeel *et al.*, 2017). This article gives an overview of the natural colorants for textile applications. Cannon and Cannon (2002) presented a list of 47 flowering plants that have been historically used in textile dyeing in their book *Dye Plants and Dyeing*. Different parts of these plants including leaves, flowers, fruits, seeds, barks, and roots contain coloring materials that can produce different shades on textiles. Natural colorants were used solely for textile coloration until 1856, when an 18-year-old British man named William Henry Perkin accidentally synthesized a purple colorant from aniline, one of the simplest chemical components of coal tar, while experimenting to synthesize the antimalarial drug quinine, and found that his colorant could readily dye silk material (Openlearn, 2007).

Classification of Natural Colorants

The colorants that come from nature can be classified in a number of ways, such as, based on their origins, chemistry, application methods, and the main hues they produce (see Fig. 2).

Natural colorants can be derived from plants, insects/animals, and minerals (Patel, 2011) as shown in Fig. 3. Extract from various parts of plants and herbs including the stem, wood, roots, bark, leaves, flowers, and fruits can produce distinct pale to dark shades on both natural or synthetic fibers; for example, logwood, turmeric, pine wood, catechu, madder, etc. From the animal kingdom, the exudation of dried bodies of a few insects and mollusks can act as coloring substances. For example, the colorants carminic acid, kermesic acid, and accaic acid come from the dried bodies of cochineal, kermes, and lac respectively (Yusuf *et al.*, 2017). Some natural colorants are obtained from mineral sources. For example, red ocher and yellow ocher are two clay earth pigments that occur naturally as minerals.

Plant-based natural colorants, which are known for their medicinal and herbal applications, are mainly phenolic compounds (Alihosseni and Sun, 2011). Flavonoids are one of the most abundant colorants found in flowers, leaves, fruits, and seeds and they make up almost 50% of all the natural colorants used for textiles and listed in the color index (Alihosseni and Sun, 2011). The major dye classes within the family of flavonoids are flavones and flavonols, and the predominant flavonols in nature are



Fig. 1 Indigo plant for natural colorant extraction. Pictures taken from a ruined indigo factory (inset) built in 1778 during British rule of India; Bhatpara, Gangni, Meherpur, Bangladesh.

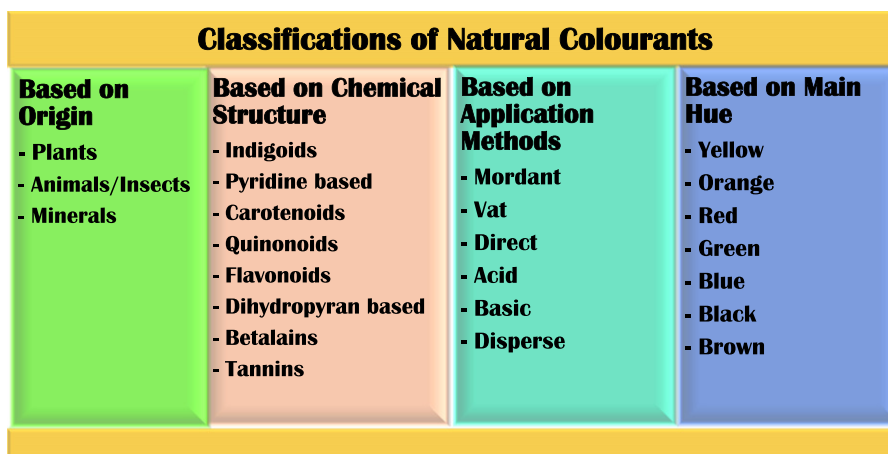


Fig. 2 Different classifications of natural colorants. Modified from Yusuf, M., Shabbir, M., Mohammad, F., 2017. Natural colorants: Historical, processing and sustainable prospects. *Natural Products and Bioprospecting* 7, 123–145, doi:10.1007/s13659-017-0119-9.

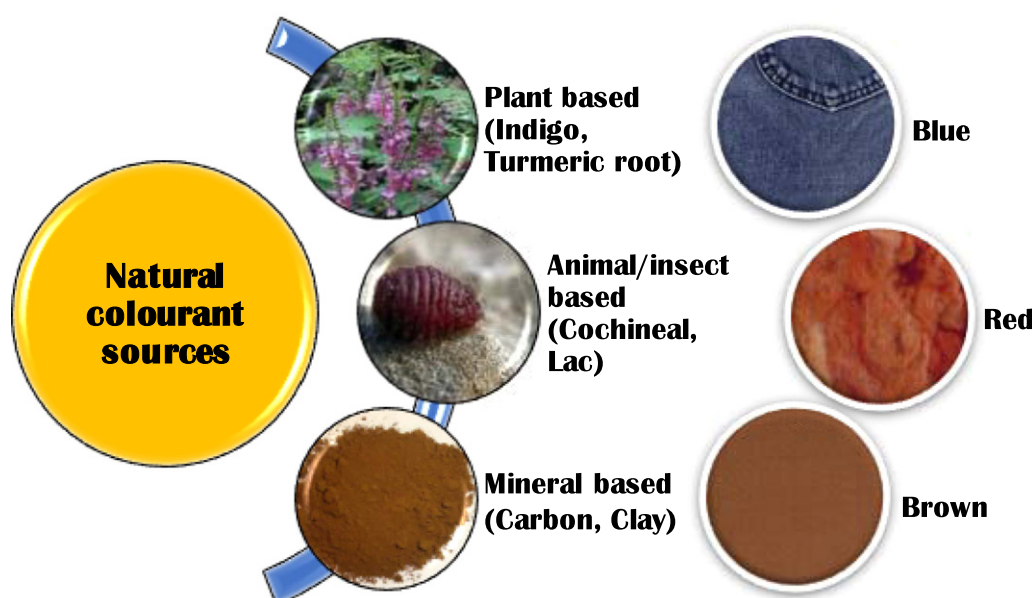


Fig. 3 Main sources of natural colorants.

quercetin (Fig. 4) and kaemferol (Alihosseni and Sun, 2011). Flavonoids have been identified as having antioxidant, anti-inflammatory, antiallergic, anticarcinogenic, and antimicrobial functions (Sarkar and Dhandapani, 2009).

Natural colorants from different sources impart different colors on textile substrates. Tables 1 and 2 present a list of common natural colorants from various sources together with their hues and chemical classes (Table 3).

Coloration Techniques

Although a few natural dyes are substantive (or direct or nonmordant) dyes, for example walnuts and onion skins, a majority of them require helping chemicals to promote their absorption into and fixation with textile fibers. They are collectively known as adjective or mordant dyes and the helping chemicals are known as mordants, which work by forming chemical bonds between the dye molecules and fiber polymer. Some mordants can be natural substances, for example, urine, wood ash, plants galls, tannins, and crabapple juice, whereas some are pure chemical compounds with metallic ions. These chemical compounds are commonly salts of aluminum (potash alum – potassium aluminum sulfate, ammonia alum – ammonium aluminum sulfate), chromium (potassium dichromate), iron (ferrous sulfate), tin (stannous chloride), and copper (copper sulfate). In textile dyeing, mordant

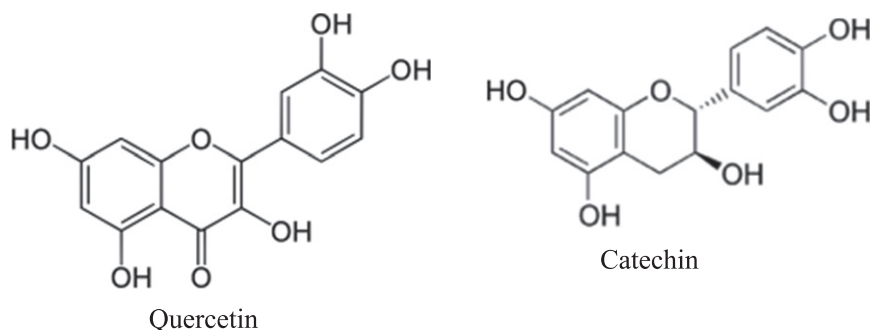


Fig. 4 Examples of flavonoids. Reproduced from Vankar, P.S., 2017. *Natural Dyes for Textiles*. Woodhead Publishing, pp. 45–88.

Table 1 Examples of natural colorants from plant origin

Name of colorant	Plant's scientific name	Colorant extracted from	Hue	Chemical class	References
Catechu	<i>Acacia catechu</i>	Wood	Brown	Flavonoid	Samanta and Konar (2011), Hong <i>et al.</i> (2015)
Jackfruit	<i>Artocarpus heterophyllus</i>	Wood	Yellow/light yellow	Flavonoid	Patel (2011)
French marigold	<i>Tagetes patula</i> , <i>Tagetes erecta</i>	Flower petal	Yellow, golden	Flavonoid and carotenoid	Patel (2011), Guinot <i>et al.</i> (2008)
Annatto	<i>Bixa orellana</i>	Seed	Orange	Carotenoid	Vankar (2000)
Onion	<i>Allium cepa</i>	Skin	Yellow orange	Flavonoid	Patel (2011)
English madder	<i>Rubia tinctorium</i>	Wood	Red	Anthraquinonoid	Patel (2011)
Indigo	<i>Indigofera tinctoria</i>	Leaf	Blue	Indigoid	Vankar (2000), Patel (2011)
Woad	<i>Isatis tinctoria</i>	Leaf	Blue	Indigoid	Patel (2011), Vankar (2000), Yusuf <i>et al.</i> (2017)
Henna	<i>Lawsia inermis</i>	Leaf	Yellow-orange	Quinonoid	Patel (2011)
Tulsi	<i>Ocimum sanctum</i>	Leaf	Green	Flavonoid	Kumar (2014)
Neem	<i>Azadirachta indica</i>	Leaf	Greenish	Flavonoid	Govindachari <i>et al.</i> (1998), Subapriya and Nagini (2005)

Table 2 Examples of natural colorants from animal origin

Name of colorant	Scientific name	Colorant extracted from	Hue	Chemical class	References
Cochineal	<i>Coccus cacti</i>	Dried body	Crimson, scarlet and pink	Quinonoid	Patel (2011), Yusuf <i>et al.</i> (2017)
Lac	<i>Laccifer lacca</i>	Dried body	Red, scarlet, brown	Quinonoid	Patel (2011), Vankar (2000), Yusuf <i>et al.</i> (2017)
Kermes	<i>Kermes vermilio</i>	Dried body	Red, purple	Quinonoid	Patel (2011), Yusuf <i>et al.</i> (2017)

can be used before, during, or after the dyeing process, therefore the techniques are known as premordanting, simultaneous mordanting, or postmordanting respectively.

Printing with natural dyes varies according to the use of mordant and thickener combination in print paste. For printing, extracted dye liquor is made concentrated by boiling and combining with thickener, and applied mostly on premordanted fabric. Print paste may also be prepared by combining mordant with natural dyes and thickener and applied on scoured or bleached fabric. Printing is usually done by flat screen print or batik printing methods.

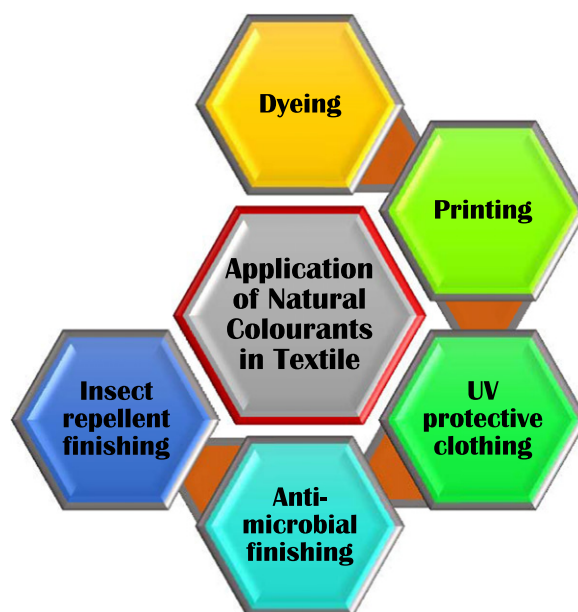
Research and Innovations

The advent of synthetic dyes has hindered the use of natural colorants over centuries as the synthetic dyes have become widely available and they exhibit better fastness properties with good reproducibility. However, there is a growing interest in research surrounding the use of natural dyes for textiles because of the environmental impact of the production and use of synthetic colorants. Fig. 5 represents the potential applications of natural dyes in textiles.

Table 3 Examples of natural colorants from mineral origin

Name of colorant	Colorant extracted from	Hue	Chemical class
Cinnabar or sulfide of mercury	Dust	Scarlet, brick red	Mercury sulfide
Red Ocherochre	Dust	Yellow to deep orange, brown	Anhydrous and hydrated iron oxide ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$)
Red lead	Dust	Bright red	Lead oxide
Yellow Ocherochre	Dust	Yellow	Limonite/hydrated ferric oxide ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$)
Sienna	Dust	Yellow	Iron oxide and manganese oxide
Orpiment	Dust	Lemon yellow	Arsenic sulfide
Litharge	Dust	Pale yellow	Lead oxide
Green earth	Dust	Yellow green to greenish gray	Mixture of hydrosilicates of Fe, Mg, Al, and K (glauconite and celadonite)
Malachite	Dust	Green	Copper carbonate hydroxide
Verdigris	Dust	Bright and deep green	Acetate of copper
Ultramarine blue (lapis lazuli)	Stone dust	Deep blue	Lazurite
Azurite	Dust	Blue	Copper carbonate hydroxide
White lime	Dust	White	Calcium carbonate
White lead	Dust	White	Carbonate and hydroxide of lead
Zinc white	Dust	White	Zinc oxide
Charcoal black	Powdered after burning in a close pot	Black	Lightweight black carbon and ash residue hydrocarbon
Graphite	Dust	Dull gray	Allotrope of carbon
Black clay	Dust	Black	Carbonate of calcium, iron, and manganese with clay
Black earth	Dust	Black	Carbonate of calcium, iron, and manganese with clay

Note: Produced based on and adapted from Yusuf, M., Shabbir, M., Mohammad, F., 2017. Natural colorants: Historical, processing and sustainable prospects. *Natural Products and Bioprospecting* 7, 123–145, doi:10.1007/s13659-017-0119-9.

**Fig. 5** Various applications of natural colorants in textiles.

Currently research activities are being undertaken around the world on a number of topics including chemistry of natural dyes, extraction of colorant from new sources, interaction of mordants, natural dyes and textiles, optimization of dye extraction, mordanting, and dyeing methods (Samanta *et al.*, 2018). An overview of the recent research and innovations related to the renewable natural colorants is provided in the following subsections.

Extraction and Traditional Dyeing With Natural Dyes

Efficiency of extraction of natural dyes largely depends on the type of sources and various processing variables such as pH, temperature, time, liquor ratio, and particle size. The methods of extraction of natural dyes can be classified based on the media

used in extraction, such as aqueous, nonaqueous, organic, and mixture of aqueous–organic extraction. This may be performed in varying pH, temperature, and duration. Extraction of colorant from aqueous solution of the flower petals of the “flame of forests” (*Butea monosperma*) has been performed at varying process conditions and the optimum condition was reported as around 74°C temperature and 154 min of duration (Sinha *et al.*, 2012). The efficiency of extraction was found to be 8813.67 mg/L. Dayal and Dobhal (2001) successfully extracted aqueous solution from the leaves of eucalyptus hybrid and seeds of *Cassia tora* and *Grewia optiva*. There are also reports on potential use of natural dyes extracted by aqueous medium from different plant sources, for example coffee seed (*Coffea*), tea (*Camellia sinensis*), onions (*Allium cepa*), tamarind (*Tamarindus indica*), henna (*Lawsonia inermis*), lemongrass (*Cymbopogon citratus*), cardamom (*Elettaria cardamomum*), beetroot (*Beta vulgaris*), sandalwood (*Santalum*), saffron (*Crocus sativus*), biomass precursors like cutch (*Senegalia catechu*), ratanjot (*Alkanna tinctoria*), and madder (*Rubia tinctorum*) (Teli and Paul, 2006; Tsatsaroni and Eleftheriadis, 2008; Khan *et al.*, 2006). Vankar *et al.* (2001) utilized supercritical CO₂ for the extraction and purification of colorant from eucalyptus bark. Ticha *et al.* (2017) isolated anthocyanins dyes using ultrasonic energy from the aqueous extract of fruits of *Parthenocissus quinquefolia*.

Natural dye isolated from cumin seeds (*Cuminum cyminum*) in different buffer mediums as acidic, neutral, and alkaline was applied successfully on premordanted and nonmordanted cotton fabric and compared with the commercial reactive dyes (Tayade and Adivarekar, 2013). Their report presented good potentiality of the natural dyes in terms of color yield, fastness quality, and economical for industrial application as compared with the regular synthetic dyes. Bleached and double premordanted jute fabric can be successfully dyed with single and binary mixtures of different aqueous isolation of red sandalwood (*Pterocarpus santalinus*), manjistha (*R. cordifolia*), jackfruit wood (*Artocarpus heterophyllus*), marigold (*Tagetes*), sappan wood (*Biancaea sappan*), and babool (*Vachellia nilotica*) (Samanta *et al.*, 2009).

Räisänen *et al.* (2001) dyed polyester and polyamide successfully with natural anthraquinones, isolated from fungus *Dermocybe sanguinea* as natural disperse dyes, at high temperature method and compared with an equivalent disperse dye. Natural anthraquinones are found to be useful alternatives to the existing synthetic disperse dyes offering bright hues with excellent colorfastness. Wool is found to be dyeable with yellow and red dyes extracted from the fungi *Penicillium murcianum* and *Talaromyces australis* respectively, which show great potential for commercialization (Hernández *et al.*, 2019).

Pretreatments, Modification, and Nontraditional Dyeing

Different technical pretreatments can be applied on textiles to improve the uptake of natural dyes into textiles during coloration processes. Maulik *et al.* (2011) modified cotton fabrics using acrylamide in presence of potassium peroxodisulfate (K₂S₂O₈) by graft copolymerization in pad-dry-cure technique to enhance dye uptake, tensile strength, wrinkle recovery angle, and overall fastness quality with tea (*C. sinensis*) and pomegranate (*Punica granatum*) dye extracts. They found that premordanting with ferrous sulfate following a presalt application of the modified cotton resulted in improved depth and all-round colorfastness.

Haji (2017) treated cotton fabric with low-pressure oxygen plasma and applied chitosan coating before dyeing with the extraction of pomegranate rinds. Plasma treatment was found to be effective in enhancing the color strength of dyed textile. At the same time, the fabric coated with chitosan and dyed with pomegranate extraction was also found to be functional against bacteria. Dayioglu *et al.* (2015) dyed silk with the fruit extraction of dwarf elder (*Sambucus ebulus* L) by conventional and microwave-assisted dyeing methods. They treated silk fabric with oxygen plasma prior to dyeing and found that the plasma treatment time and microwave energy contributed towards the increased dye diffusion into the silk polymer. Similar effect of plasma treatment on premordanted wool fabric prior to dyeing with Acacia plant extraction was reported by Ratnapandian *et al.* (2011).

An interesting procedure of gamma ray radiation on natural dye and cotton fabric prior to dyeing was reported by Khan *et al.* (2014). They exposed powder of red calico (*Alternanthera bitzickiana*) leaves to different doses of gamma radiation before extraction in aqueous, alcoholic, and alkaline media, and cotton fabric before mordanting and dyeing. According to them, cotton fabric after exposure to gamma radiation can be dyed with red calico extract using reduced the amount of mordants yielding high colorfastness properties.

Sonicator dyeing method has been successfully applied to improve dyeing performance of cationized cotton textile with red cabbage (*Brassica oleracea*) isolation (Ticha *et al.*, 2016). Several explorations on ultrasonic assisted dyeing that have been reported by far are cotton dyeing with neem (*Azadirachta indica*) leaf extraction (Senthilkumar *et al.*, 2002) and sappan wood (*Biancaea sappan*) extraction (Ghorpade *et al.*, 2000); dyeing of enzyme pretreated cotton with isolation from *Acacia catechu* and *Tectona grandis* (Vankar and Shanker, 2008); and wool dyeing with lac (Kamel *et al.*, 2005).

Functionalization and Value Addition by Dyeing With Natural Colorants

Selective natural colorants exhibit functional characteristics. Wool fabric dyed with the extraction from walnut hull (*Juglans regia*) and henna (*L. inermis*) was found to be effectively mothproof (Nazari, 2017). Silk fabric dyed with chemically modified water-soluble curcumin extracted from the root of *Curcuma longa* L was found to be UV protective in addition to having antibacterial functionality (Zhou and Tang, 2016).

Tannins extracted from *Dioscorea cirrhosa* tuber produce stunning shades on silk and the dyed fabric exhibits a number of functionalities like antibacterial and antioxidant activities (Yang *et al.*, 2018). Particularly condensed tannin coating including

postmordanting with iron salt enables the silk fabric to be flame retardant and waterproof. The findings from recent studies show that multifunctional textiles can be developed by using natural dyes in different methods on different substrates. For example, a multifunctional wool fabric developed from the extraction of *Lycium ruthenicum* Murray (Dong *et al.*, 2018), and antibacterial silk fabric dyed with isolation from red prickly pear fruit (*Opuntia ficus-indica*) (Ganesan and Karthik, 2017).

Printing With Natural Dyes

Several studies on printing of different textile fabrics with natural dyes have been reported in different literature (Salem *et al.*, 2013; Maamoun *et al.*, 2014; Rekaby *et al.*, 2009; Chattopadhyay and Pan, 2018). Polyester fabric can be printed with the extracts from different plants like turmeric (*Curcuma longa*), alkanet (*A. tinctoria*), and rhubarb (*Rheum rhabarbarum*) using natural and synthetic thickeners at various processing conditions of transfer printing, and satisfactory fastness properties can be achieved (Salem *et al.*, 2013). Cotton/wool blended fabric printed with nanoparticles of turmeric, madder, and rhubarb was found to have excellent wash, rubbing, and perspiration fastness (Maamoun *et al.*, 2014). Rekaby *et al.* (2009) applied different fixation techniques for cotton, wool, silk, and flax substrates printed with extracts of alkanet and rhubarb colorants. They found steam fixation provided better color strength (K/S) as compared with the thermofixation. Very good fastness with varying color yields were obtained with different mordants. Chattopadhyay and Pan (2018) attempted screen printing with the extracts from annatto (*Bixa Orellana*), roots of manjistha (*Rubia cordifolia*), and bark of ratanjot (*A. tinctoria*) of bioscoured, bleached, and premordanted jute fabrics and achieved very good wash and rubbing fastness properties.

Natural Versus Synthetic Colorants

Nowadays the use of natural dyes has attracted a lot of attention in the textile industry due to their eco-friendliness and renewable characteristics, and these colorants are gradually making their way into the global market. A number of other benefits of using natural dyes are highlighted in the literature (Samanta and Konar, 2011; Arora *et al.*, 2017). Natural dyes:

- Are biodegradable, nontoxic, and nonallergic.
- Have color shades usually soft, lustrous, and esthetically appealing to the human eye.
- Are widely available from natural sources such as plant (leaves, bark, flower, etc.), insect/animal, and mineral.
- Exhibit medicinal effects such as reduced chances of melanoma through absorption of UV, antiallergens, and antibacterial properties.

The use of natural dye can also bring some positive impacts to the environment and society in general such as:

- Earning carbon credit through reduction of petroleum based synthetic colorants.
- Creating job opportunities in cultivation, extraction, and application.
- Utilizing wasteland to cultivate the dye plants in a large scale.
- Disposing of natural dye waste in a simple and inexpensive way as biofertilizer for agriculture or the biomass for energy generation.
- Creating an overall sustainable system for the textile industry.

On the other hand, the synthetic colorants are nonrenewable, nonbiodegradable, sometimes carcinogenic, and cause water pollution, and produce toxic waste and present a huge challenge in disposing the byproduct waste in a cost effective way. However, some key benefits of synthetic colorants in terms of producing in large scale at economical price with consistent color quality and numerous color variation outweigh the benefits of natural dyes (Fig. 6). Therefore, the synthetic dye still remains as the prime choice for textile industry.

Challenges for Natural Dye in Commercial Use

The market for synthetic colorants is valued at around \$23 billion for a total production volume of approximately 1.3 million tonnes (Sengupta and Singh, 2003). It is estimated that only 1% of total world textiles are dyed with the natural colorants. This indicates that the natural colorant has to overcome a number of technical, logistical, and commercial challenges to enter into the mainstream textile processing. Fig. 7 summarizes some of the key challenges and potential solutions, which will also be elaborated briefly in the following subsections. Further details about the natural colorants and their future prospects can be found in the recent literature (Adeel *et al.*, 2019; Gürses, 2019; Arora *et al.*, 2017; Gürses *et al.*, 2016; Saxena and Raja, 2014; Shahid *et al.*, 2013; Samanta and Konar, 2011).

Technical Challenge: High Quality Dye Production

Plants, the major source of natural colorants, may vary from one season to another, one cultivating region to another, one soil quality to another, one agroclimate to another, high maturity to low, and one species to another, which causes variation in color

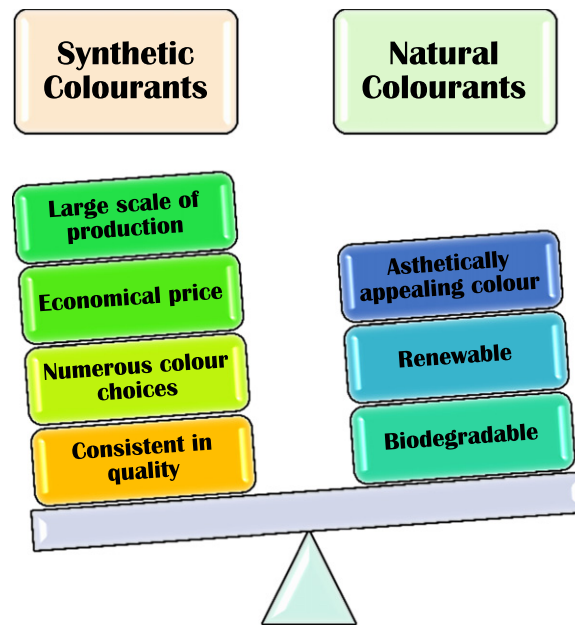


Fig. 6 Balance between natural and synthetic colorants.

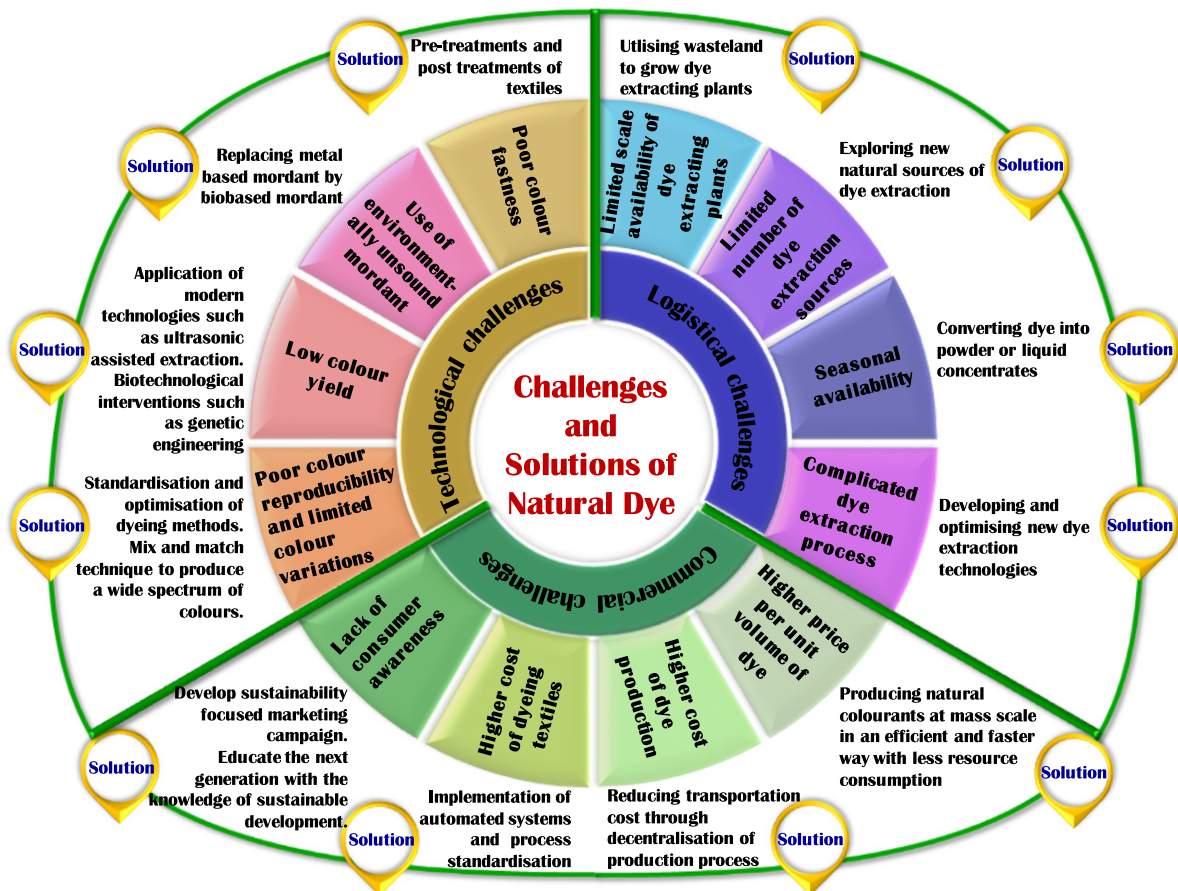


Fig. 7 Challenges of natural colorants and possible solutions.

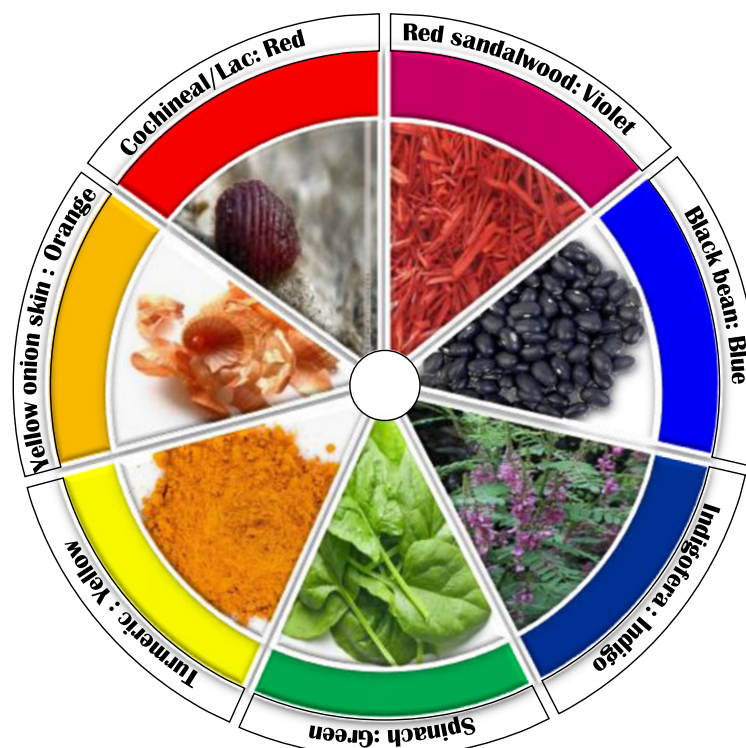


Fig. 8 Rainbow of textile dye colors from a variety of natural sources. Inspired from Arora, J., Agarwal, P., Gupta, G., 2017. Rainbow of natural dyes on textiles using plants extracts: Sustainable and eco-friendly processes. *Green and Sustainable Chemistry* 7, 35–47. Sims, A., 2018. 4 Steps to Naturally Dyeing Any Fabric Using Foods. Available at: <https://www.architecturaldigest.com/story/how-to-naturally-dye-using-foods> (downloaded April 8, 2019).

reproducibility of natural dye (Saxena and Raja, 2014). Poor color reproducibility could also result due to variations in conditions of dye extraction and dyeing. Therefore, dye extraction and dyeing methods must be optimized for specific dye–fiber–mordant combinations through scientific studies (Samanta *et al.*, 2018) to get the maximum color intensity with reproducible shades.

The traditional challenges of lack of color variations can be overcome by processing the dye from the same plant extract with different mordants, extraction mediums, and dyeing techniques (Arora *et al.*, 2017) as a mix and match system. An entire rainbow of colors could be created from different plant and biological sources as shown in Fig. 8. Again mixing of different compatible natural colorants in different quantities could produce a wide spectrum of color shades (Samanta *et al.*, 2018).

In general, low color yield of source plant materials restricts the availability of natural colorants in a large scale and thus more dyestuffs, longer dyeing time, and mordanting are required. Application of modern technologies such as ultrasonic, microwave, and enzyme assisted dye extraction can be adopted to improve dye yield (Samanta *et al.*, 2018). In future, dye yield can be significantly improved by biotechnological interventions such as genetic engineering (Saxena and Raja, 2014).

In the majority of the cases, environmentally unsound metal-based mordant or mordant assistant is required to fix the natural dye onto the fabric. During the dyeing process, a part of the mordant is left unexhausted in the residual dye bath and this may cause serious effluent disposal problems (Saxena and Raja, 2014). Metal-based mordants can be replaced by suitable biobased mordants to reduce the environmental impact.

Colorfastness on exposure to lighting, washing, contact with human perspiration, and rubbing of natural dye is relatively poor compared with synthetic dye. Pretreatments and posttreatments have been successfully applied to improve the color fastness properties of synthetic dyed textiles. However, treatments for natural dyed textiles are limited (Khan *et al.*, 2014) and therefore new fastness improved from natural materials needs to be explored (Samanta *et al.*, 2018). Standardization and optimization of mordanting and dyeing procedures can improve the poor colorfastness issue (Saxena and Raja, 2014). New sources of dye extracting plants with improved colorfastness properties also need to be explored.

Logistical Challenge: Availability in Large Quantity

As a rule of thumb, 1 kg of dye plant is required to dye 1 kg of textile. The plants contain natural dye in small quantity. Therefore, to meet the current dye demand of massive quantity, it would require a huge amount of plants, which nature simply cannot provide and thus necessitates cultivation of dye extracting plants. Again, land for growing food crops cannot be used for this purpose as meeting the continuously growing demand of food crops for the increasing world population is far

more important than cultivation of dye extracting plants. However, the plants can be grown in wastelands to increase their availability. Some of the colorants are obtained from tree bark, roots, and stems, which again cannot be obtained without damaging the tree. Although agricultural by-products such as pomegranate rind, onion skin, or fruits and leaves of trees are available at the farm or point of use, no logistics for making them available for dye production are in place. Therefore, a large supply chain network for agrobased byproducts needs to be established to enhance the availability of dye containing raw materials (Saxena and Raja, 2014). Extracting dye as a byproduct from the timber industry is sustainable but cutting trees only for dye extraction would lead to a serious problem of deforestation, which needs careful consideration. However, cultivating plants that can grow quickly and using part of a tree for dye extraction without destroying the whole tree wherever possible could solve part of the problem.

So far many dye containing sources have been identified but they are simply not enough for large-scale dye production and to meet unlimited variation of color choices. Further research is required to identify new sources of dye extraction and their health and safety risks during dye production and use must be evaluated before the commercial application.

Most of the natural colorants come from plants, whose availability may depend on a particular season. This issue of seasonal availability can be addressed by converting the colorants into ready-to-use soluble powders or liquid concentrates with a long shelf life.

Again, the natural dye extraction process is complicated, time consuming, and not backed up by scientific studies. New scientific research in developing new technologies for dye extraction and application on textile materials is required to increase the productivity.

Commercial Challenge: Availability at a Comparable Price and Forms

Higher price of natural dye compared with synthetic dye is the key commercial challenge that the dye and textile industries need to address. Like any other mass-consumed products, the commercial success of the natural dye depends on cheap production at a very large scale. The current production techniques are not sustainable and must be upgraded to make them more efficient, faster, less resource intensive, and less waste generative.

The general practice in the textile industry is to produce colorants at a central facility and transport them to the dyeing facility for textile manufacturing through dyeing and printing. This centralized system presents a complex logistical challenge and can add significant production cost. Transportation cost can be reduced by a decentralized production system. The transportation cost is only a part of the total production cost. Therefore, every other cost associated with the whole production cycle such as raw material, labor, energy consumption, water consumption, etc. also needs to be significantly reduced to make natural dye a commercially viable option.

Similar to dye production, the textile dyeing process is also expensive owing to the requirement of skilled labor, and time-consuming and labor-intensive, complex dyeing process, where many industrial dyeing machines are not compatible with the natural dye.

The application of eco-friendly natural colorants in the textile industry is urgently needed in response to the growing consciousness of harmful environmental effects of synthetic dye on the earth. Environment conscious manufacturers of colorants and textile producers should come forward in investing heavily in research, development, and manufacturing of natural dyed textile. Furthermore, government regulations should be in place to discourage the use of synthetic dye. A global consensus between the world leaders should be made to reduce the consumption of synthetic dye as a part of the sustainable development summit. More importantly, consumer awareness initiatives on the health and environmental benefits of using natural dyed products should be undertaken via sustainability focused marketing campaigns. Results of a customer survey found that the majority (81.58%) of respondents will not buy natural dyed products due to relatively higher cost, poor color repeatability, difficult maintenance, and lack of color choices in the textile products (Kamboj and Mahajan, 2017). However, the consumer willingness to buy can be improved through increased awareness of benefits of natural dyed products. Most of the respondents strongly agreed to wear natural dyed products as it enhances their personality and brings them a “green,” conscious status. In addition, the new generation should be educated about sustainable development so that they can be informed decision makers, entrepreneurs, or consumers for maintaining future sustainability of the earth by promoting the use of natural dye.

Conclusion

Although natural colorants suffer from the limitations of higher price, low colorfastness properties, and low color reproducibility, avenues of improving them have already been identified through different research activities, as it has been mentioned in the previous sections. However, those innovations are yet to reach to the hands of commercial dyers and printers. Natural colorants are not abundantly available on the market in ready-to-use format although they are abundantly present in nature. Considering the environmental impact of producing and using synthetic colorants, natural colorants can be promoted as the safer alternatives capitalizing on their long history and heritage. Nevertheless, it should be emphasized that as it stands the natural colorants are only suitable for small-scale application and they can be only a complimentary option to synthetic dye rather than a replacement. In the long term, the natural colorants can be a competitor when they are produced at large scale in a cost effective way by solving technological, logistical, and commercial challenges through adoption of new technologies for dye extraction and dyeing, process

optimization and standardization, exploration of new natural sources, large scale cultivation of dye extracting plants, creation of a well-connected supply chain network, and improvement of consumer awareness.

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3D Printing of Carbon-Based Conductive Materials for Electrochemical Energy Storage (EES) Application

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Introduction

Electrochemical energy storage (EES) such as supercapacitor, batteries have become the key devices for electricity storing and transportation in recent years since they exhibit high performance, adaptability, and versatility. Recent developments in electronics and portable devices push the researchers and industries to develop more efficient EES devices with flexibility, high power and energy density, fast charge/discharge rate, and long life. Researchers are introducing new and advanced materials, and focusing on process engineering to put these building materials into devices to improve their performance. The performance of the EES devices fundamentally depends on the electrolyte ion and electron diffusion rate, high surface area, and architect of the engineered porous structure of the electrode materials. Supercapacitors and batteries are composed of electrodes, electrolyte, current collectors and separator in most of the cases. Common carbon-based conductive materials such as graphene, graphene oxide (GO), reduced graphene oxides (rGO) activated carbon (AC) are the widely used carbonaceous materials in EES devices due to some intrinsic properties such as high surface area, surface porosity, electron mobilization. Addition of some other polymers or metal oxides with common carbon-based materials significantly increases the device performance (Zhu *et al.*, 2011; Ervin *et al.*, 2014; Hyun *et al.*, 2017; Chua *et al.*, 2014; Borenstein *et al.*, 2017; Kim *et al.*, 2017; Khair *et al.*, 2019). Here in this article, we discuss the carbon-based conductive materials used in fabricating EES devices and their additive manufacturing 3D printing technology. 3D fabrication techniques in EES are significantly different from conventional fabrication methods. 3D printable colloidal ink require extra care to be produced and processed for fabrication. In industry, the conventional fabrication technique used for EES devices experience a few steps such as chemicals deposition, electrode rolling, roll cutting, cell assembly with a separator, electrolyte filling, and finally packaging with re-cutting. All of these steps are restricted in further scaling up fabrication methods other than making production line longer. On the other hand, 3D printing diminishes all of these steps. This novel technique allows fabrication of electrode, electrolyte separator chronologically using the command of computer aided software. Thus, this method is more scalable and sophisticated in energy storage device fabrication.

Supercapacitor and Active Material

Capacitance is the ability to store charge in the electrodes and the interface of electrode and electrolyte. Electrical double layer capacitor (EDLC) and pseudocapacitor are two supercapacitors that allow fastest charge discharge cycle as they avoid the kinetics of chemical reaction of batteries (Zhu *et al.*, 2011; Khair *et al.*, 2019; Jost *et al.*, 2014; Lu *et al.*, 2015). However, they suffer from low power and energy density.

$$C = \frac{A\epsilon}{4\pi d} \quad (1)$$

$$C_s = \frac{C}{m} \quad (2)$$

$$ESR = \frac{V_{iR}}{i} \quad (3)$$

$$E = \frac{CV^2}{2} = \frac{QV}{2} \quad (4)$$

$$P = \frac{V^2}{4R_s} \quad (5)$$

According to Eq. (1) accessible surface area A of electrodes and d path of ion diffusion are two critical parameters of these supercapacitors (Lu *et al.*, 2015, 2011; El-Kady *et al.*, 2016). Accessible surface area increases with the increment of pores, therefore capacitance depends on number of pores (Lu *et al.*, 2015). On the contrary, too high and too low pore size have negative impact on the capacitance (Lu *et al.*, 2015). The pore size must be equal to the size of ions of electrolyte. Because, larger the pore size higher the distance between pore wall and center of ion thus increasing the overall distance d which is inversely proportional to the capacitance (Lu *et al.*, 2015). This equation predicts that thickness of electrode is very critical parameter to obtain the highest capacitance. Researchers are printing electrodes with lower thickness so that ions can properly diffuse and current collector achieve high adhesion (Areir *et al.*, 2017b).

Specific capacitance is the intrinsic capacitance of electrodes which generates because of the material ability to hold charge, surface area and porosity, and it is calculated by dividing the capacitance (C) of electrode by its mass (m) or sometimes surface area Eq. (2). Specific capacitance does not determine the capacitance of the whole capacitor as it depends on other parameter such as electrolyte, ion diffusion

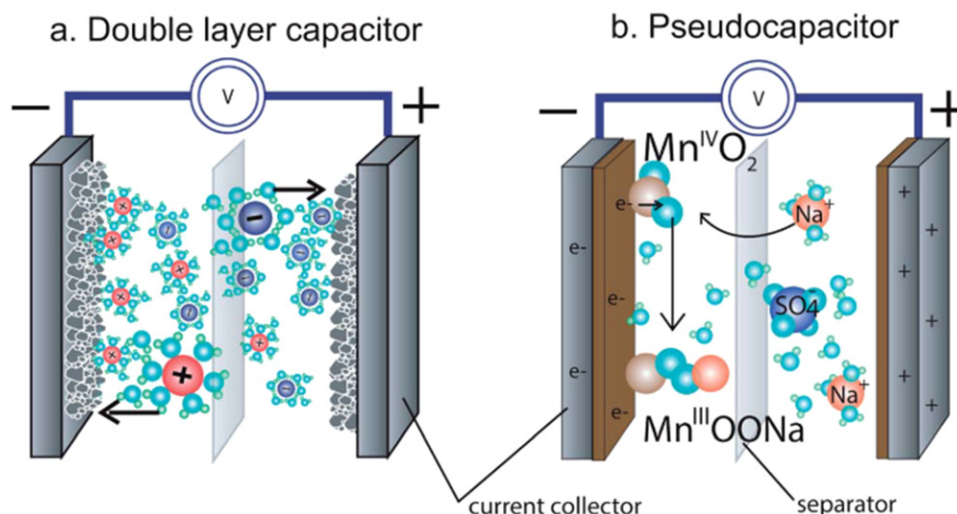


Fig. 1 Illustration of Electrical Double Layer Capacitor (EDLC) and Pseudocapacitor mechanism. (a) EDLC adsorb charge on its electrode surface and diffuse ion through the separator (b) Pseudocapacitor electrode surface facilitate fast surface redox reaction. Reproduced with permission from Jost, K., Dion, G., Gogotsi, Y., *et al.*, 2014. Textile energy storage in perspective. *J. Mater. Chem. A* 2 (28), 10776–10787, with permission from the Royal Society of Chemistry.

path, ion accessibility and capacitor assembly (Lu *et al.*, 2015). Electrical sheet resistance (ESR) determines the internal resistance of capacitor which depends on resistivity of electrode and contact junction of electrode and electrolyte (Areir *et al.*, 2017b). Lower the resistance, higher the electron conductivity and higher the capacitance. Because of the high conductivity material such as graphene and Carbon nanotube (CNT) are popular choices for selecting the electrode material. ESR of an electrode is determined electrochemically in a capacitor in the presence of electrolyte from the voltage drop (v) and electrical current (i) at charge discharge cycle Eq. (3).

Energy density (E) and power density (P) are the outcomes of all architecture used in building the energy device. Some researchers also prefer to use current density to evaluate the efficiency of an energy device. Eqs. (4) and (5) determine that energy E and power P is directly proportional to voltage (v) of the overall capacitor, which critically depends on electrode material and electrolyte used in the capacitor. Ionic liquid, organic, and solid state- three types of electrolytes are being explored because of their unbalanced properties. Ionic electrolyte has higher concentration of ion and smaller ionic radii such as 1 M H_2SO_4 (Lu *et al.*, 2015). Smaller ionic radius facilitates ion diffusion through the pores of electrode and separator. However, they generate as low as 1.2 V in the electrode electrolyte interface of capacitor which reduce the energy density (Lu *et al.*, 2015). On the other hand, organic electrolyte such as polyaniline, acetonitrile, propylene carbonate generates 3–5 V in the capacitor. However, these organic electrolytes are sometime toxic and always requires as low as 3–5 ppm of water contents (Lu *et al.*, 2015). In order to implement the advantages of both electrolytes, scientists have been using a combination of organic and ionic electrolytes. 1 M H_2SO_4 and Polyvinyl alcohol (PVA) solid state gel electrolyte is the most common type of electrolyte being used commonly in supercapacitors (Zhu *et al.*, 2011; Khair *et al.*, 2019; Jost *et al.*, 2014; Lu *et al.*, 2015; Ambrosi and Pumera, 2016). This electrolyte gives the balanced electrochemical performance with sufficient mechanical stability by avoiding leakage problem of ionic electrolytes (Fu *et al.*, 2016).

In Electrical Double Layer Capacitor (EDLC) ions are adsorbed physiologically in the accessible surface of electrodes and in pseudocapacitor fast surface redox reactions takes place with the presence of additional capacitance material such MnO_2 and RuO_2 in the electrodes Fig. 1 (Zhu *et al.*, 2011; Ambrosi and Pumera, 2016; Zhang *et al.*, 2017). In theory, single layer graphene 2D sheet has the capacitance of $21 \mu F cm^{-2}$ and energy density of $169 Wh kg^{-1}$. However, practically graphene capacitors showed much lower energy density of $15\text{--}35 Wh kg^{-1}$ (El-Kady *et al.*, 2016). This discrepancy with the calculated energy density is attributed to the defective structure of graphene, its intrinsic nature of aggregation, intersheet junction contact resistance of printed electrodes (El-Kady *et al.*, 2016). Moreover, the pristine graphene has hardly any pores and limited accessible surface area. 3D printing technologies has recently been introduced in printing electrochemical energy storage devices in order to challenge these issue (Borenstein *et al.*, 2017; El-Kady *et al.*, 2016). Freestanding energy device such as hydrogel, aerogel, sponges, foams are the outcomes of 3D printing (Zhang *et al.*, 2017; Chi *et al.*, 2014; Foster *et al.*, 2017). Graphene-based electrodes are being printed in addition with bioplastics using direct 3D printing (Xu *et al.*, 2014). Electrochemical performance of energy device depends on the thickness of electrode to allow ion diffusion through them (Fu *et al.*, 2017). In comparison to 2D graphene 0D graphene nanosphere such as quantum dot avoids the restacking tendency with higher capacitance and faster response time because of their dimension (El-Kady *et al.*, 2016).

Nonporous Graphene

2D sheet of nanoporous graphene has superior electron mobility of $200,000 cm^2 V^{-1} s^{-1}$, high surface area of $2630 m^2 g^{-1}$, high intrinsic specific capacitance $550 F g^{-1}$, low thermal expansion with excellent thermal conductivity, flexibility, optical

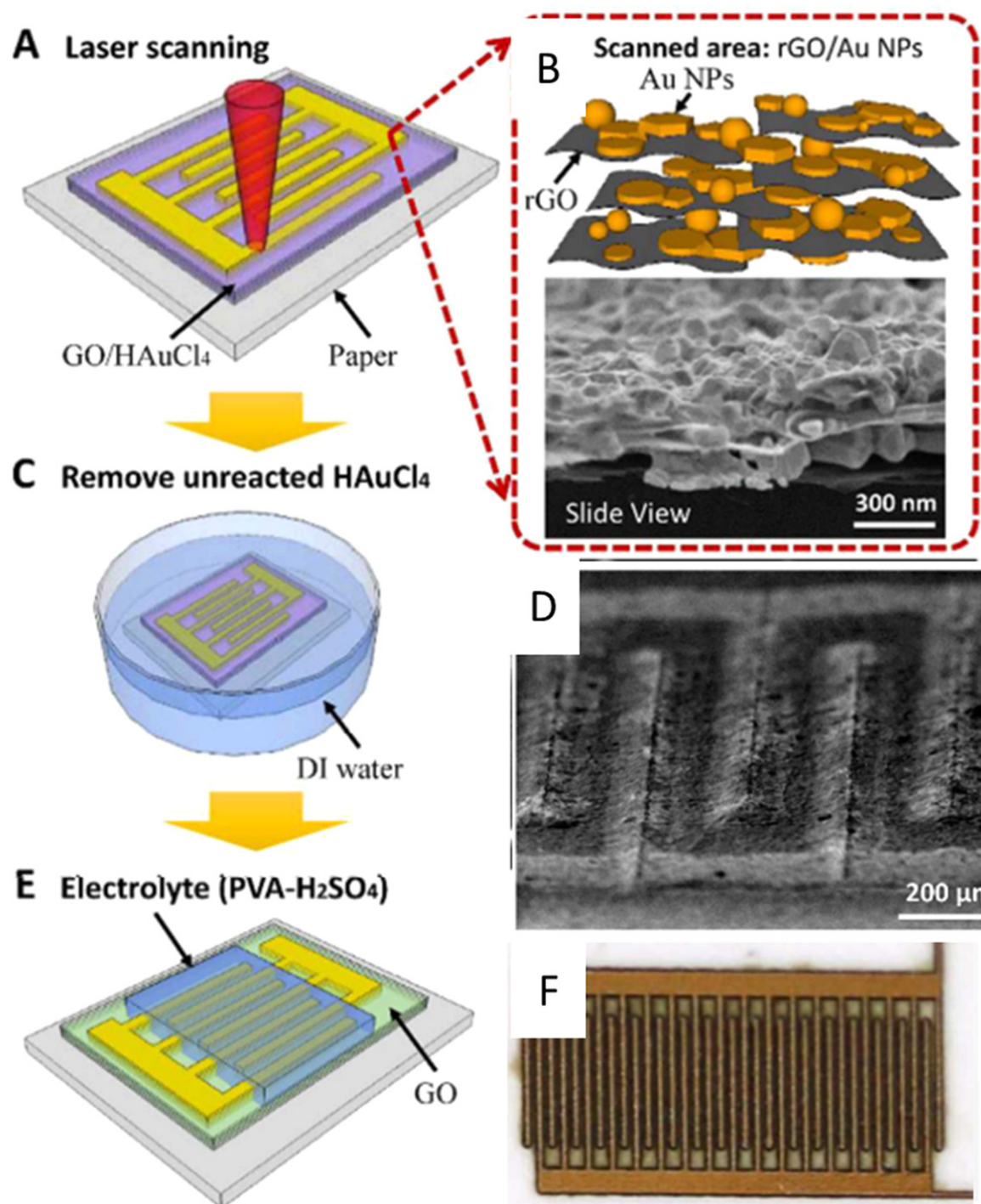


Fig. 2 Schematic, optical and SEM images of rGO and gold nanoparticle 3D printed supercapacitor (A) direct femto laser writing of gold nanoparticle/rGO electrode (B) SEM image of the surface of gold nanoparticle/rGO top and side view (C) Illustration of removing unreacted HAuCl₄ from electrode surface using distilled water (D) SEM image of interdigitated 3D gold nano particle/rGO electrode (E) Drop casting of PVA/H₂SO₄ electrolyte on supercapacitor (F) Optical image of gold nano particle/rGO 3D supercapacitor. Reproduced from Li, R.Z., Peng, R., Kihm, K.D., *et al.*, 2016. High-rate in-plane micro-supercapacitors scribed onto photo paper using: In situ femtolaser-reduced graphene oxide/Au nanoparticle microelectrodes. *Energy Environ. Sci.* 9 (4), 1458–1467, with permission from the Royal Society of Chemistry.

transparency with exceptional mechanical strength (El-Kady *et al.*, 2016; Foster *et al.*, 2017; Yang *et al.*, 2015). High surface area and high conductivity make them suitable for energy devices, and its other properties such as flexibility and transparency replaced other traditional energy storing materials used in supercapacitors and batteries (Hyun *et al.*, 2017; Foster *et al.*, 2017).

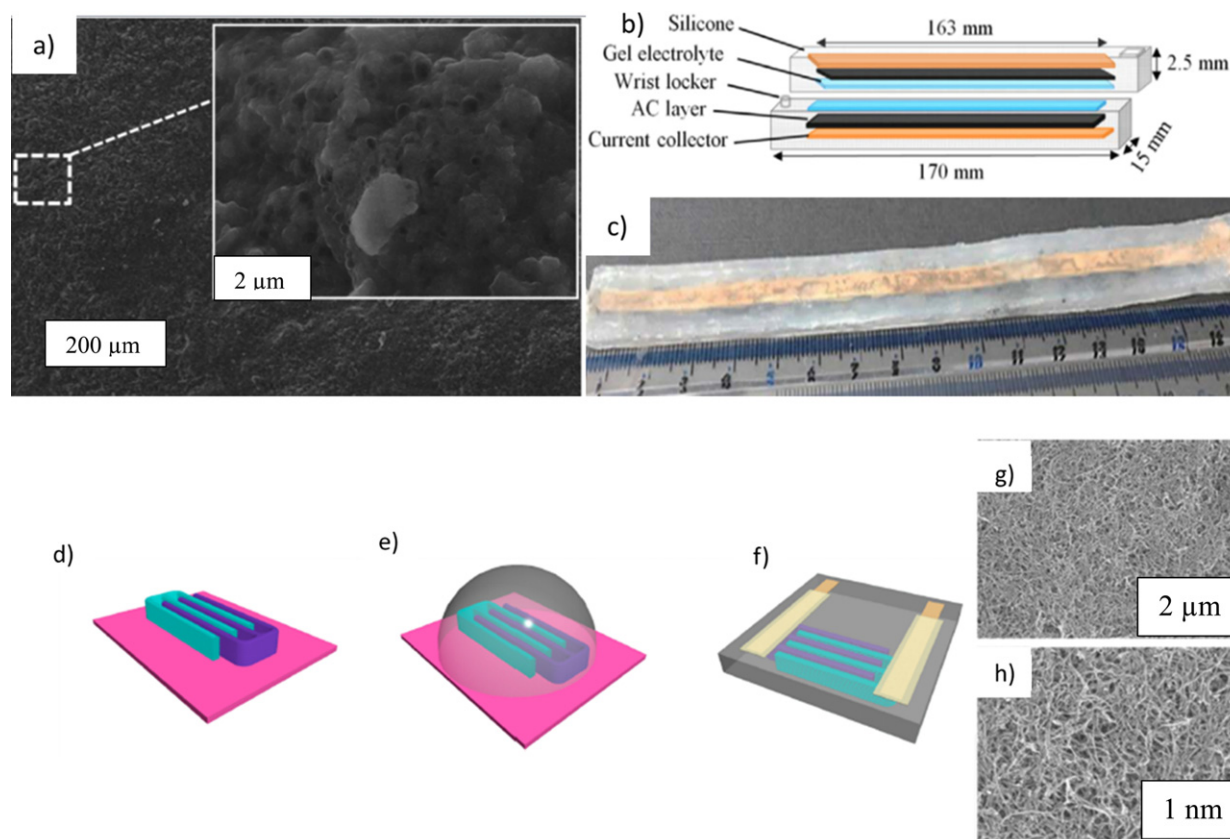


Fig. 3 (a) SEM image of 3D printed activated carbon electrode (b) illustration of the structure of EDLC (c) optical image of the EDLC. (d) illustration of 3D printed CNT electrodes (e) illustration of drop casting PVA/H₂SO₄ gel electrolyte (f) supercapacitor (g) SEM image of the CNT electrode (h) enlarge SEM of the electrode. Reprinted from (c) Areir, M., Xu, Y., Harrison, D., *et al.*, 2017. 3D printing of highly flexible supercapacitor designed for wearable energy storage. *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.* 226 (August), 29–38, with permission from 2017 Elsevier B.V. (h) Areir, M., Xu, Y., Harrison, D., *et al.*, 2017. 3D printing of highly flexible supercapacitor designed for wearable energy storage. *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.* 226 (August), 29–38, with permission Copyright 2017 American Chemical Society.

Graphene Oxide

Graphene oxide, (GO) has been architected for direct 3D printing technology instead of pristine 2D graphene because of their ability to suspend and easy synthesis process (Le *et al.*, 2011; El-Kady *et al.*, 2016; Yang *et al.*, 2015). GO has attached functional groups such as OH⁻, COOH⁻, O⁻ etc. which provide electrostatic repulsion and the basal plane provide the Van der Waals attraction between the layers of GO (El-Kady *et al.*, 2016). Therefore, GO is suspended in common solvents very rapidly. On the other hand, 3D direct printable gel is prepared when the Van der Waals attraction outdo the electrostatic repulsion (El-Kady *et al.*, 2016). Preparation of GO suspension for electrochemical application requires some architecture and state of the art research. Traditionally, GO suspension is stabilized by using surfactant that is adsorbed in the surface of GO (Khair *et al.*, 2019). However, in order to fabricate electrochemical energy device GO ink must be prepared without the use of surfactant (Xu *et al.*, 2014) since surfactant adsorbed active material resists the penetration of electrolyte ion on its surface (see Fig. 2). Moreover, it increases the inter layer junction resistance and particle resistance which reduce conductivity (Ervin *et al.*, 2014; Le *et al.*, 2011). The GO suspensions of tuned rheology using additional polymer allow researcher to develop 3D printed architecture which is later reduced to evolve electrically conductive reduced graphene oxide (rGO). GO is a good electrical insulator; however, it is a very good proton conductor when moisture is adsorbed on the layers of GO sheet, Fig. 2 refer. This interesting property allows researcher to produce only rGO-GO-rGO supercapacitor without the presence of electrolyte and separator, where GO acts as an ion conductor (El-Kady *et al.*, 2016; Yang *et al.*, 2015). This capacitor has as high specific capacitance as 0.86 mF cm⁻².

Similar to aerogel, sponge etc., graphene 3D porous structure, GO is also 3D printed to produce aerogel (Zhu *et al.*, 2016) by treating the GO suspension with fumed silica powder to tune the ink rheology and produce porous graphene oxide (Fu *et al.*, 2017). Printed electrodes are also exfoliated to produce porous and rough surface in electrochemical device to increase ion adsorption on their surface. Researchers have explored many techniques to induce porosity in GO sheets such as annealing of KOH treated GO electrodes which induce nanoscale porosity, annealing of 1-butyle-3-methylimidazolium tetrafluoroborate treated GO control pore size of the GO sheets (Ervin *et al.*, 2014). Recently Das *et al.* (2016) have converted 2D rGO electrodes printed over cellulose paper into petal-like topological 3D rGO electrode using UV-laser pulsed light of wavelength 355 nm and energy 70 mJ cm⁻². 2D electrodes had 20 MΩ because of

presence of binder, unjointed graphene flakes, defected edge and residual oxygen group. Photon of laser light induces interconnected corrugated structure where graphene flakes are connected thus removing edge defect and creating continuous graphene sheet. Because the loosely packed carbon atoms of the flake expand horizontally which fills the inter flakes gaps by the energy induced by photon (Das *et al.*, 2016). Therefore, this connected graphene sheet has much lower resistance of $700\ \Omega$. Moreover, the stakes of graphene shrink laterally which induce the nano and micro scale petal like 3D structure which is responsible for high electrochemical performance of the energy device (Das *et al.*, 2016). Corrugated or wrinkled sheet of graphene where graphene flakes are jointed and for a 2D layer can also be obtained by high temperature thermal treatment of GO at 400°C because thermal treatment expands loosely packed carbon atoms of graphene flakes (Nathan-Walleiser *et al.*, 2014). Moreover, these high temperature thermal treatments decomposes the functional groups of GO which results in gaseous pressure in between the graphene flakes. As a result, GO of porous surface with surface area $593\ \text{m}^2\ \text{g}^{-1}$ is obtained which was later 3D printed to build electrodes of supercapacitor (Nathan-Walleiser *et al.*, 2014). A further improvement of this 3D fabrication method was conducted by bridging the rGO sheets using gold nanoparticles (Li *et al.*, 2016). In this process GO and HAuCl_4 ink was direct 3D laser written to fabricate micro electrodes of thickness $13.7\ \mu\text{m}$ and reduced to Au NPs an rGO by femtolaser beam irradiation of wavelength $1030\ \text{nm}$ and $80\ \text{mW}$ power (Li *et al.*, 2016). Gold nanoparticles largely improved conductivity of rGO because it acts as nanospace creator between the rGO sheets (Li *et al.*, 2016). Capacitance of this electrodes was also improved by photothermal evaporation of functional groups as gas from GO through superimposed 3D printed layers which leads to micro cavities in the electrodes (Li *et al.*, 2016). A supercapacitor was assembled using PVA/ H_2SO_4 gel electrolyte which showed 100 times much higher capacitance than that of bare rGO electrode supercapacitor even in lower scan rate. This high capacitance is clearly attributed to improved conductivity imparted by gold NPs which reduces ESR of the electrode (Li *et al.*, 2016) (Fig. 2).

Activated Carbon (AC)

AC is another porous structure of carbon which is built by chemical, thermal or combination activation of carbonaceous materials. KOH , H_2SO_4 , H_2O_2 , ZnCl_2 , H_3PO_4 are some common chemical treatment of activating carbon followed by high temperature ($\sim 1000^\circ\text{C}$) annealing using N_2 gas (Khair *et al.*, 2019; Islam *et al.*, 2019). Porosity and pore size largely depend on the rate of activation which creates pore in the surface of carbon. Generally, AC has been being used in 2D and 3D energy devices because of its surface area of $1700\text{--}1800\ \text{m}^2\ \text{g}^{-1}$ and moderate intrinsic specific capacitance of $92\ \text{F}\ \text{g}^{-1}$ (Areir *et al.*, 2017b; Brunet *et al.*, 2009). In 3D printed supercapacitor, AC is next to graphene and its oxide-based supercapacitor in terms of capacitance and energy density. In 2016 and 2017 Areir *et al.* (2017a,b) 3D printed AC slurry (AC and PVA) with a thickness of $2\ \text{mm}$ and $0.6\ \text{mm}$ respectively on a fabric surface to construct electrodes of supercapacitor. AC electrodes require additional current collector such as silver paint (Areir *et al.*, 2017b), gold, silver-zinc/polyvinylidene fluoride (Areir *et al.*, 2017a) because the electrode does not possess sufficient conductivity similar to graphene or carbon nanotubes. The two capacitor with different thickness used PVA/ H_2SO_4 (Areir *et al.*, 2017b) and PVA/ H_3PO_4 (Areir *et al.*, 2017a) solid state gel electrolyte in order to avoid leakage and mechanical distortion Fig. 3 (a-c). AC electrodes houses electro ionic charge in its high surface area which facilitates adsorption and diffusion of ions and electrodes during reduction and oxidation stages (Areir *et al.*, 2017b). The capacitors showed $68.7\ \text{mF}$ (Areir *et al.*, 2017b) and $1.4\ \text{F}$ (Areir *et al.*, 2017a) capacitance at $20\ \text{mV}\ \text{s}^{-1}$ scan rate. Such low capacitance (Areir *et al.*, 2017b) is attributed to the high thickness of electrode which hindered the current collector to channelized the electrons through the electrodes (Areir *et al.*, 2017b). Reduction of thickness lowered the kinetic movements of ion which finally resulted high capacitance (Areir *et al.*, 2017a).

Carbon Nanotube

CNT is a novel carbonaceous nano material which has superior conductivity, mechanical strength, aspect ratio, high surface area $1300\ \text{m}^2\ \text{g}^{-1}$, and resiliency. However, because of its extremely high cost of production and low accessible surface area CNT has not being used popularly on energy related application as electrode (Lota *et al.*, 2011). Moreover, pure CNT has capacitance as low as $5\text{--}40\ \text{F}\ \text{g}^{-1}$. Scientists have conducted many states of the art research to gain capacitance from CNT as it has very high conductivity. Interestingly, it has shown that, presence of nitrogen (N) as heteroatoms on outer wall of CNT provides high capacitance as N increase the electron wettability, and surface redox reaction (Lota *et al.*, 2011). Moreover, other pseudocapacitance material such MnO_2 , RuO_2 were also applied on CNT to obtain capacitance. Very recently, CNT based micro supercapacitor was 3D printed using a CNT ink which was prepared by ball milling process in the presence of a dispersion agent, ethylene glycol and isopropyl alcohol as solvent (Yu *et al.*, 2017). The 3D printed electrodes were assembled in the supercapacitor using PVA- H_3PO_4 solid state gel electrolyte Fig. 3 (d-h). Interestingly, post printing removal of dispersion agent improved the capacitance because of improved contact between CNT and electrolyte (Yu *et al.*, 2017). Both solvents add ink rheological property to facilitate 3D printing, where, isopropyl alcohol evaporates before the droplet touches the basal glass plate allowing partial solidification, and ethylene glycol evaporates post printing annealing (Yu *et al.*, 2017).

3D Printing Technology

Additive manufacturing also known as 3D printing has been widely used to rapid prototyping both in industry and academia over the last few years. It has emerged as a promising method for the fabrication of complex 3D structures by using advanced materials and

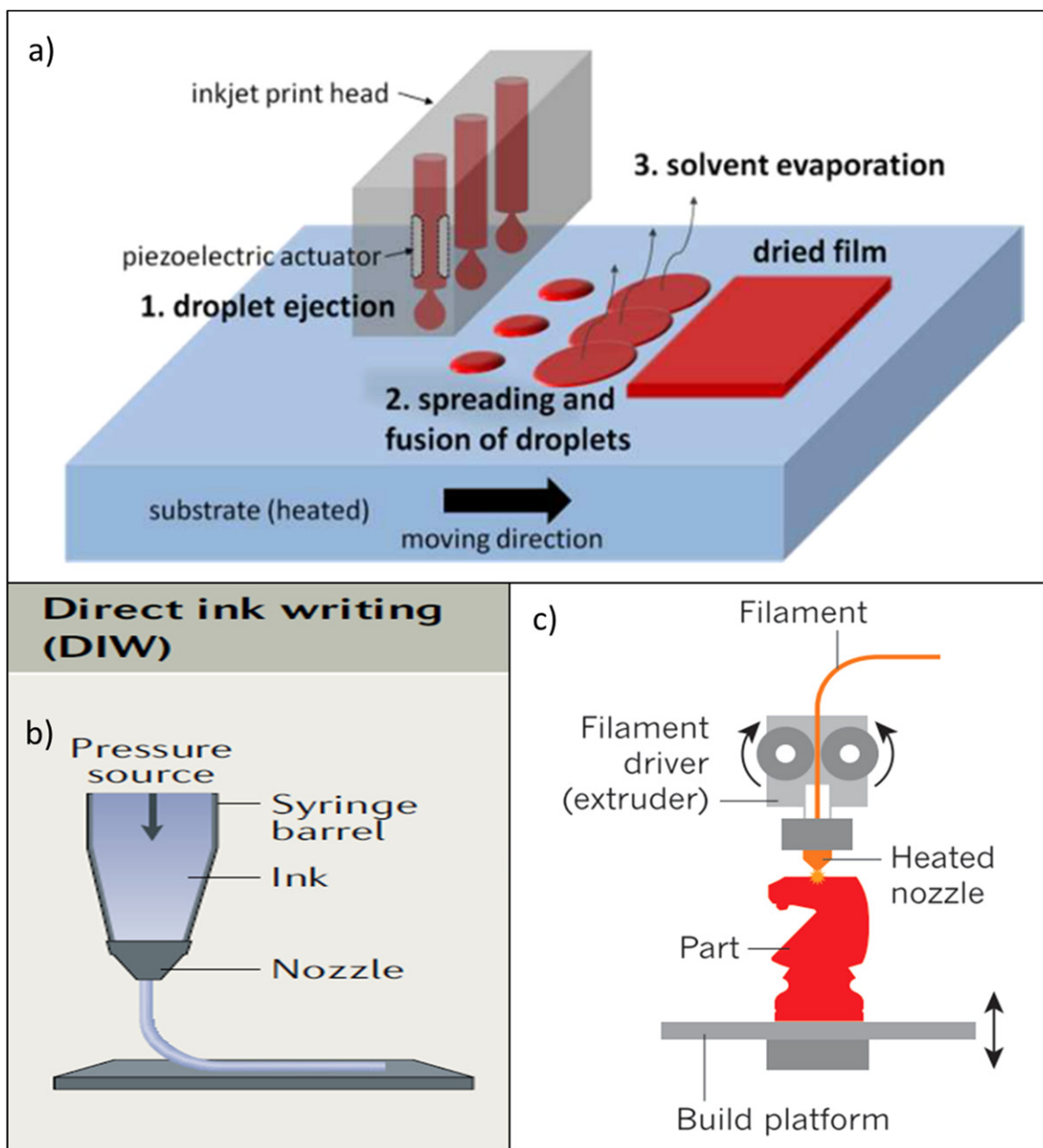


Fig. 4 Schematic representation of (a) 3D IJP technology, (b) DIW printing technology, and (c) FDM printing technology. Reproduced from (a) Vinet, L., Zhedanov, A., 2011. Towards industrialization of polymer solar cells: Material processing for upscaling. *J. Phys. A Math. Theor.* 44 (8), 085201, with permission from The Royal Society of Chemistry. (b) Wallin, T.J., Pikul, J., Shepherd, R.F., *et al.*, 2018. 3D printing of soft robotic systems. *Nat. Rev. Mater.* 3 (6), 84–100, with permission from Copyright 2018 Springer Nature. (c) Truby, R.L., Lewis, J.A., 2016. Printing soft matter in three dimensions. *Nature* 540 (7633), 371–378, with permission from Copyright 2016 Springer Nature.

recently has shown the potentiality to replace the conventional techniques. 3D printing technology encompasses with a wide range of solid and ink-based methods, which make possible to fabricate 3D objects and patterns. This process starts with the creation of a 3D virtual model of an object using computer-aided design followed by layer by layer printing of the object. In EES device fabrication, the use of 3D printing has been increasing due to the control of electrode thickness, architecture, and geometrical shape. 3D printing technology exhibits the process flexibility, geometry controllability. 3D printed particle space architectures and pores enable the fast ion transport in EES devices which commensurate for fast charging/discharging. This technology ensures high active materials loading which promotes high energy storage. Precise layer by layer deposition of materials can control the thickness of the electrodes. High electrode thickness with uniform surface improves the energy density in unit area. Moreover, very low thickness electrode can also be fabricated for flexible EES devices. Wide range of materials such as polymers, composites, metal oxides, carbon-based materials, and ceramics can

also be printed by using various 3D printing processes for EES device fabrication. Here in this section, we will discuss about efficient printing methods of carbon-based conductive materials or composites.

Inkjet Printing (IJP)

3D IJP is an extrusion-based material conserving deposition technique that can print high-resolution 3D objects, patterns, and shapes of uniform thickness. The control of thickness, fineness and pattern geometry of the architect of carbon-based EES is well defined by this technology. The process involves the ejection of a fixed quantity of ink from a chamber, through a nozzle as a response of sudden, quasi-adiabatic reduction of the chamber volume via piezoelectric action. The chamber filled with liquid contracts in response to application of piezoelectric mechanical change under applied voltage. This sudden volume reduction sets up a shockwave in the liquid, which causes a liquid drop to eject from the nozzle (Singh *et al.*, 2010). The small ink droplet dries during the flight from the nozzle to the substrate because of their size. The droplets interact with the substrate and solidifies upon the subsequent annealing process (see Fig. 2a). Thus, high-resolution objects are created without spreading the ink droplets. Solidification of the ink and the pattern geometry of the EES depend on the volatility of the solvent and the ink rheological properties such as viscosity, viscoelastic behavior, and surface tension. The ink for IJP must be well formulated and free from agglomeration in order to avoid possible nozzle clogging during printing. IJP uses low viscous ink. The typical ink should be a dispersion or solution of active materials with a dynamic viscosity of less than 20 $\mu\text{Pa s}$ (de Gans *et al.*, 2004a) surface tension value below 80 $\mu\text{N m}^{-1}$ (de Gans *et al.*, 2004b). In general, the ink characteristics such as viscosity μ , surface tension σ , and density ρ , must be within certain ranges and satisfy certain rules for a fixed nozzle diameter d to allow the inkjet process to work properly. The inverse Ohnesorge number Z is commonly used to predict if a stable inkjet drop will be formed: $Z = \frac{1}{Oh} = \frac{\sqrt{\rho d \sigma}}{\mu}$, whereas ρ , d , σ , μ are denoted as ink density, nozzle diameter, ink surface tension, and viscosity, respectively. Only if $1 < Z < 10$, can the ink be expected to produce stable droplets (Zhang *et al.*, 2017).

Direct Ink Writing (DIW)

DIW is another extrusion-based material deposition technique that is typically carried out in room temperature. It's a versatile printing technique that can print carbon ink, hydrogel, melt polymer and ceramics for various purposes (Zhu *et al.*, 2017). The printing ink must have high yield stress and storing modulus to allow shape retention. DIW printing technique relies on the fluid flow-based printing of viscoelastic ink with shear thinning behavior. Fig. 4b shows that a pressure source (i.e., plunger) forces a liquid ink of active carbon-based materials with or without additives above the yield stress, allowing it to be selectively deposited through a nozzle. Once extruded, a sudden stress reduction, phase change, solvent evaporation, or combination of them restrains the deposited material into a specific shape. The solidification process competes with the gravitational fluid flow, 'wetting-out' and self-leveling tendencies of the ink and must be properly balanced to ensure shape retention and interlayer adherence (Wallin *et al.*, 2018). Post-extrusion heating can thermally evaporate the volatile solvent from the printed pattern and ensure porous structure electrode. Since DIW uses the high viscous liquid ink, the risk of nozzle clogging is very low. High mass loading of active materials in DIW printing technology ensures the significant amount of increase in the areal capacitance and energy density. Although DIW is the flexible printing technology, the resolution of the printed pattern and the pattern geometry largely depend on the diameter of the nozzle. DIW has been used for 3D printing of carbon-based materials such as graphene, GO, rGO, CNTs, and activated carbon for supercapacitor and battery (Borenstein *et al.*, 2017).

Fused Deposition Modeling (FDM)

In additive manufacturing, FDM is one of the popular and affordable 3D printing methods that create the 3D objects layer by layer by using melt cure polymers which are heated to melt the polymers at their glass transition state. In the FDM method, the preheated extrusion nozzle melts the filaments or wires and deposits the molten ink on a substrate. Later the molten materials are converted into solid state because of the cooling process. Biobased Poly (lactic acid) (PLA) and acrylonitrile-butadiene-styrene (ABS) are the widely used melt polymer in the FDM method (Zhang *et al.*, 2017). The resolution of the printed objects and pattern geometry are restricted by the diameter of the nozzle. In addition, the molten polymer can introduce heterogeneities, defects or voids. Melting temperature of polymer must be controlled to confirm that polymer filaments melt in the nozzle without creating voids. FDM method has been successfully used in 3D printing of carbon-based conductive materials for electrochemical energy storage devices (EES). Researchers have been using carbon-based materials as conductive fillers to fabricate conductive electrode. In order to use FDM printed 3D objects as an electrode for EES, conductive carbonaceous material such as graphene, GO, CNTs and AC must be incorporated in the molten ABS and PLA (Fu *et al.*, 2017; Podsiadly *et al.*, 2019). Fig. 5 shows the step by step process of producing GO-ABS composite for FDM in order to make a 3D printed electrode for EES applications. In this process, G/ABS composites, GO-NMP (5 mg/ml) and ABS-NMP (15 mg/ml) were homogenized (Wei *et al.*, 2015). The obtained composited was then extruded through a 1.75 mm diameter filament at 210°C. Then this filament was used in FDM to print 3D electrode. Graphene/PLA composite was also produced using the same way. Compared to other melt cure polymers, PLA is more environmentally friendly and biodegradable. CNTs and AC can also be promising candidate used as conductive fillers in the melt cure polymer composite for FDM. The incorporation of melt cure polymer improves the mechanical property in terms of bending and

stretching of FDM printed electrodes. However, the incorporation of melt cure polymer reduces the conductivity of the electrode. Nowadays, increase in the percentage of the conductive fillers and the removal of ABS and PLA via post-processing such as etching and calcination are carried out in order to solve this problem (Zhang *et al.*, 2017; Wallin *et al.*, 2018).

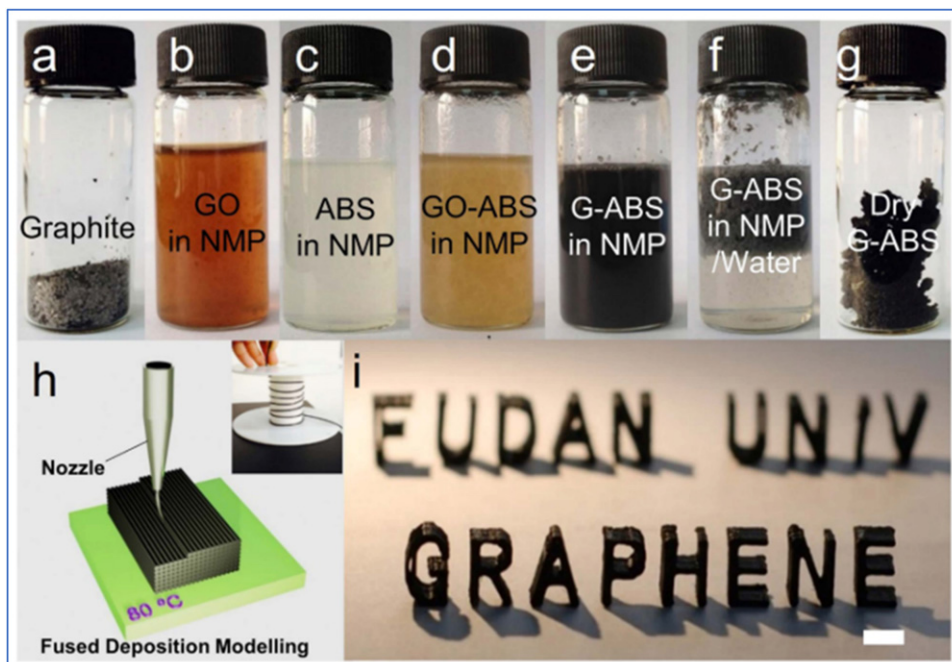


Fig. 5 (a–g) steps of producing liquid ink for fused deposition modeling (h) Schematic representation of FDM technique (i) FDM 3D printed structures. Reproduced from Wei, X., Li, D., Jiang, W., *et al.*, 2015. 3D printable graphene composite. *Sci. Rep.* 1–7. with permission from Nature 2015.

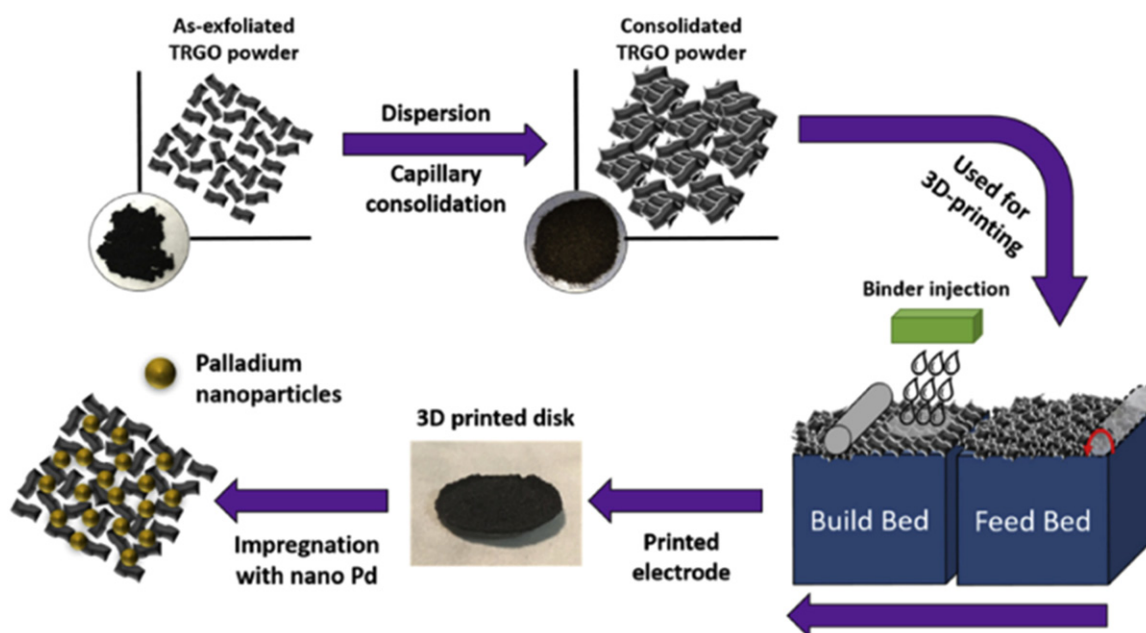


Fig. 6 Step by step process of binder jetting fabrication technology for EES device fabrication. Reprinted from Azhari, A., Marzbanrad, E., Yilman, D., *et al.*, 2017. Binder-jet powder-bed additive manufacturing (3D printing) of thick graphene-based electrodes. *Carbon* 119, 257–266, with permission from 2017 Elsevier.

Table 1 Different 3D printed methods, ink formulation recipe for EES device fabrication and the performance of EES devices

3D printing	Active materials	Additives	EES type	Specific capacitance	Energy density	Power density	Refs.
IJP	2 mg/ml GO	Distilled water	SC	48–132 F/g	6.74 Wh kg ⁻¹	2.19 kW kg ⁻¹	(Le <i>et al.</i> , 2011)
	AC	EG, Triton X100, PTFE	SC	–	–	–	(Conédéra <i>et al.</i> , 2009)
	2 mg/ml GO	Distilled water	SC	192 F/g	5.5 Wh kg ⁻¹	19 kW kg ⁻¹	(Ervin <i>et al.</i> , 2014)
	GO	Distilled water	SC	51 F/g	54.2 Wh kg ⁻¹	16.2 kW kg ⁻¹	(Jung <i>et al.</i> , 2014)
	NGP powder (200 mg), PANI (200 mg)	SDBS (200 mg) and H ₂ O (100 mL)	SC	82 F/g	2.4 Wh kg ⁻¹	124 kW kg ⁻¹	(Xu <i>et al.</i> , 2014)
	LiCoO ₂ , CB	Lomar D, monoethanolamine, binder-CMC sodium	Li-ion battery				(Huang <i>et al.</i> , 2008)
	CB, LFP	CMC, Triton X-100	Li-ion battery				(Delannoy <i>et al.</i> , 2015)
	Sulfur infused SWNT-MET	CHP	Li-ion battery				(Milroy <i>et al.</i> , 2017)
	100 mg of graphene	5 mL phenol or camphene	SC	305 F/g	26.74 Wh kg ⁻¹		(Lin <i>et al.</i> , 2016)
	6, 7, and 8 wt% CNTs	IPA, 30 wt% dispersion agent, and EG	SC	2.44 F/cm ²	0.12 mWh cm ⁻³	3.72 W cm ⁻³	(Yu <i>et al.</i> , 2017)
DIW	20 mg/ml GO			41.8 F/cm ³	7.6 mWh cm ⁻²	29.2 mW cm ⁻³	(Chua <i>et al.</i> , 2014)
	Highly concentrated TRGO (thermally reduced GO)	Isopropanol (15 g/L)	SC	3.55–1.76 mF/cm ²	4.43 mWh cm ⁻³	42.74 kW cm ⁻³	(Nathan-Wallester <i>et al.</i> , 2014)
	80% of AC	10% of additive carbon, 10% CMC, IPA and distilled water	SC		4.43 mWh cm ⁻³	42.74 kW cm ⁻³	(Nathan-Wallester <i>et al.</i> , 2014)
	3.6 g 40 mg/cm ³ GO suspensions	2 g R-F solution, 0.3 g GNP, and 0.9 g fumed silica			0.43 Wh kg ⁻¹	76 W kg ⁻¹	(Zhu <i>et al.</i> , 2016)
	80 wt% LFP	10 wt% CB, 10 wt% PVDF, NMP	Li-ion battery				(Ying, 2016)
BJ	80 wt% graphite	10 wt% CB, 10 wt% PVDF, NMP	Li-ion battery				(Ying, 2016)
	Thermally reduced graphene oxide	Binder (>90% water, 8% glycerol and 2% other humectants)	SC	260 F g ⁻¹			(Azhari <i>et al.</i> , 2017)

Binder Jetting (BJ) 3D Printing

Binder jetting 3D printing is a powder bed additive manufacturing process which is inspired by the technology of inkjet printers. In this process, a liquid binder is selectively deposited on a powder bed with the print head. It's a growing process that allows the production of parts for the manufacturing medical and dental industries. This technique enables the production of metallic and ceramic parts as well as sand molds for casting (Azhari *et al.*, 2017). Nowadays this process is successfully used in EES device fabrication. To start this process, a 3D drawing is imported into the printer software (refer to Fig. 6). The powder to be used is placed in a dispenser which ensures a constant supply during printing. First, a powder layer of a specific thickness is poured thereafter the printing head moving on two axes projects binder where it is necessary. Before moving on to the next layer of the solvent contained in the binder is evaporated by an incandescent lamp. The powder bed is lowered and the new powder bed is deposited therefore the production takes place in a series of steps that build the part layer by layer. When the cycle is completed the binder is cured to remove from the printed objects by placing the container in a furnace. The temperature and time depend on the type of binder used in the printing process. After these steps, unbound particles are removed to reveal the part. According to materials used in this process, post-treatment is performed. In EES device fabrication, carbon-based conductive materials are used as the powder bed and then suitable binder for the materials are injected from the printer head (Zhang *et al.*, 2017). Recent literature reported on the fabrication of supercapacitor by using binder jet printing process. Thermally reduced GO particles were used as the powder bed, then the aqueous based binder was (>90% water, 8% glycerol and 2% another humectant) was injected through printing head. The printed electrodes were further impregnated with palladium nanoparticles in order to increase the specific capacitance and energy density (Azhari *et al.*, 2017). In this process, it is possible to build complex 3D structures with interconnected pores. Such interconnected pores resulting from the voids formed between powder agglomerates would also allow for rapid ion transport inside the electrodes of batteries and supercapacitors. The specific capacitance of printed graphene electrode is 265 F/g. This printing technique removes the process of formulating ink where no chemical solvents are used. Additionally, binder jetting printing reduces the microcracking from the supercapacitor electrodes because no subsequent evaporation of solvents requires like other 3D printing processes. However, this process is not still scalable for bulk manufacturing of EES devices and requires extensive study for all carbon-based materials (Ambrosi and Pumera, 2016).

Table 1 shows the compares the specific capacitance, energy density and power density of electrochemical energy storage devices varying different 3D printing processes, and selection of active materials.

Conclusion

3D printing technology has advantages over 2D printing methods because it eliminates different intermediate steps of fabricating energy devices by printing of electrode, electrolyte in a precise and predesigned fashion. 3D printing has made it possible to fabricate highly sophisticated micro structured energy devices for self-powered microelectronics. The thickness of electrodes can be critically controlled in the 3D printing process to optimize capacitance which is a key parameter of energy devices. In short, the ability to process renewable carbonaceous materials through 3D printing helps to create impact of functional materials for commercially viable energy storage applications.

See also: A Comprehensive Study for 3D Printing of Rapid Tooling From Reinforced Waste Thermoplastics

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Processing, Properties and Prospects of Nano-Biocomposites

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Introduction

In the field of polymer science, nano-biocomposites research had become recent interest and provide much opportunities, for both academician and manufacturing players. Since some of the pristine polymer's amount supplied from fossil fuel had decreased, efforts to reduce and replace the content of polymer in composites by using biomaterials have become the priority in research, development and commercialization. Nano-biocomposites have been manipulated in terms of mechanical, electrical, thermal and other properties to achieve possible encounters to understand, make prediction, and manage the potential application and prospect. Therefore, future industries could obtained the profits of these new material properties and in the same time reducing the impact towards the environment (Lau *et al.*, 2009).

Producing nano-biocomposites is heavily depending on the method of producing the nanocomposites itself, and the type/content of nanofillers. Before analyzing the nano-biocomposites, understanding their morphologies is essential, whereby different morphologies can be achieved for this advanced material. The early group of nanocomposites that was found were microcomposite (Alexandre and Dubois, 2000), intercalated nanocomposites (Ray and Okamoto, 2003) and exfoliated nanocomposites (Vaia and Giannelis, 1997a,b). The condition of microcomposite occurred when the aggregation of clay particles were achieved without the penetration of the polymer chains into the inter-layer spacing. As for the second group, the intercalated structures was obtained through the diffusion of the polymer chains in between the platelets. The third group is the exfoliated state, whereby delamination of clay layers were stacked individually, and dispersed homogeneously in the polymer matrix. The thing to be observed was the intermediate dispersion, where intercalated–exfoliated structures could happened. However, this division of groups was not consider the dispersion multi-scale structure, such as percolation phenomenon, preferential orientation of the clay layers, etc., (Ray and Okamoto, 2003). Thus, any discussion about how to prepare and defining the suitable method to process, as well as the gain properties and the potential prospect of nano-biocomposites material shall heavily reliant on these group.

Besides morphologies, the percentage of nanofillers content also plays important roles in improving the properties. Even small amounts of nano-sized fillers, with less than 10 wt%, could affect the outcomes. The outcomes could be in terms of extensive/strong interaction and well dispersed particles (Bordes *et al.*, 2009).

Nano-biocomposites research also depends heavily on the type of matrix used in the production of this material. Biopolymers matrix, or biodegradable polymers, produced through synthesized chemical or biosynthesized during the growth cycles of organisms. Table 1 proposes categories, example and family of bio polymers (Averous and Boquillon, 2004). According to categories, the last type of bio polymer which is synthesized from fossil resources was not obtained from resources which could be renewable (Bordes *et al.*, 2009).

Processing of Nano-Biocomposites

As stated in introduction, usual preparation of nano-biocomposites was subjected to the nanofillers condition bio-polymer's morphology. From this time, three major processing of nano bio-composites have been recognized. The processing techniques are (Ray and Okamoto, 2003):

- (1) In situ polymerization.
- (2) Solvent intercalation process.
- (3) Melt intercalation process.

In Situ Polymerization Process

Based on this approach, the monomer solution (liquid monomer) was utilized to swell the nano layer silicates. The existence of polymer formation will took place in between the intercalated sheets. Then, the initiation and propagation of monomer polymerization is materialized. During this process, the increment of macromolecules molecular weight and the condition of almost fully exfoliated morphology could be achieved for several studied systems. Some researchers have successfully perform this approach to produce nanocomposites (Messersmith and Giannelis, 1993; Alexandre and Dubois, 2000; Ray and Okamoto, 2003). According to some research, the polymerization process also can be commenced through (Ojijo and Ray, 2014):

- (1) Heat or radiation,
- (2) Diffusion of a suitable initiator.
- (3) An organic initiator.
- (4) Catalyst fixed through cationic exchange inside the interlayer before the swelling step by the monomer.

Table 1 Categories of bio polymers

No	Category	Examples	Family
1	Biomass polymers (agro polymers from agro resources)	Starch, lignin, xylan, chitosan, gluten cellulose	Agro polymer
2	Microbial polymers	Polyhydroxyalkanoates	Bio polyesters
3	Polymers of monomers, chemically synthesized (agro resources)	Poly (lactic acid)	Bio polyesters
4	Polymers of monomers, chemically synthesized (fossil resources)	Polycaprolactones, polyesteramides, polybutylene succinate/adipate	Bio polyesters

Source: Bordes, P., Pollet, E., Avérous, L., 2009. Nano-biocomposites: Biodegradable polyester/nanoclay systems. *Progress in Polymer Science* 34 (2), 125–155.

Most of the nano-biocomposites could be prepared through this approach, accept polysaccharides because the chains of this biomaterial were synthesized during the plant growth and then extracted from the vegetal (Chivrac *et al.*, 2009).

To quote more example, Hwang *et al.* (2009), have used this approach to prepare poly (butylene succinate)/montmorillonite nanocomposites through direct esterification and polycondensation. The objective of their research was to apprehend the function of urethane group, 1, 6-diisocyanatohexane, on the organoclay. The outcome of this research were the effects of preparation to the structure and properties of the poly (butylene succinate)/montmorillonite nanocomposites. They revealed that different extents of delaminated structures could be produced based on the modification of clay surface. This research was further expand to explore the effects of the same urethane modification on the poly (butylene succinate)/montmorillonite crystallization behavior, by applying the same nanocomposites preparation method (Hwang *et al.*, 2010).

Based on the review made by Ojijo and Ray, not many research that used this method have been published. Maybe the in situ polymerization process was quite intricate and costly. Henceforth, lots of research is focused on the beneficial of melt intercalation process (Ojijo and Ray, 2014).

Solvent Intercalation Process

As for the second method, this solvent intercalation process was expanded by utilizing the solvent system. The polymer used for this process was soluble with the swellable silicate layers. Firstly the polymer was dissolved in suitable solvent. The example of solvents that were used to swell the silicate layers are water, chloroform, or toluene. During the same time, to obtain a miscible solution, the swollen clay will dispersed into the same solvent. The weak forces that stack the layers together causing the layered silicates dispersed easily. As soon as the swelling is completed, the mixture of polymer solution with the layered silicate solution had been achieved. The polymer chains intercalation will occurred when both systems were pooled together. When the polymer chains intercalate, it will displaced the solvent within the interlayer of the silicate, and adsorb onto the silicate surface. The solvent evaporation process shall be the next sequence in order to get the final material in nanocomposites form. To quote one example, poly (butylene succinate)/clay or poly [(butylene succinate)-co-adipate] nanocomposites might be prepared by using this method. Once the solvent used in this method evaporates, the intercalated structure shall stay in the form of poly (butylene succinate)/clay nanocomposites or poly [(butylene succinate)-co-adipate]/clay nanocomposites (Ojijo and Ray, 2014).

According to the review made by Ojijo and Ray, more research was desired to be explored for this method. However there are few good references to be mentioned as the guidelines in processing, properties and prospects of nano-biocomposites intercalation (Ojijo and Ray, 2014). For instance, a research had reported about the preparation of poly (butylene succinate)/clay nanocomposites through solvent intercalation process (Shih *et al.*, 2007, 2008; Shih and Wu, 2009). However, based on the analysis of these researches, still there are lacking of details in procedures during solvent intercalation implementation. As for another example, a research had been performed about how to elucidate the solution intercalation procedure during the preparation of poly (butylene succinate)/clay nanocomposites. They used biodegradable aliphatic polyester (biodegradable aliphatic polyester)/montmorillonite nanocomposites, to characterize and perform analysis towards the material thermal and rheological properties. According to the results they managed to form a large intercalated structures of nanocomposites.

Nevertheless, they also found certain difficulties, whereby some of solvents are toxic (not environmentally friendly and only fewer attempts could be made). This method was less effective as compared to melt intercalation method (Lim *et al.*, 2002).

So it can be a caution to say that the drawbacks of this method are the consumption of abundant solvents, particularly for non-water-soluble polymers in solvent intercalation this process was not friendly to environment and causing cost expansion as well. Furthermore, lower interfacial interaction between the polymer and the clay surfaces could happened when there was still a slight amount of solvent remaining in the final outcome (Jin *et al.*, 2002). As for an example, for polysaccharides such as chitosan or pectin, due to high thermal or thermo-mechanical degradations, these biomaterials cannot be melt processed. Then, to yield polysaccharide/clay hybrid materials, massive used of solvent could took place (Chivrac *et al.*, 2009).

Melt Intercalation Process

The third method that can be used to prepare nano-biocomposites is melt intercalation. By using this method, the mixing of the polymer and the layered silicate was occurred during molten condition. The melt temperature during mixing was set above the

polymer's softening point. The thermodynamic interaction between the particles of host silicate and the polymer matrix will be the important key to achieve good formation of biopolymer nanoclay nano-biocomposites. This factor also shall influence the transportation of polymer chains, originally from the bulk melt into the silicate galleries. A sufficient compatibility between polymer and the surface of layer silicate will be the priority during this process. If this process is a success, then a range of nano-biocomposites with intercalated to exfoliate structure could be obtain. However degree of penetration of the polymer chains into the silicate galleries need to be monitored closely. As been mentioned before, this method was preferred not only due to no chemical solvent involved, but melt intercalation also near to extrusion and injection molding process. These processes are very well known as a massive industrial manufacturing method (Vaia *et al.*, 1996; Vaia and Giannelis, 1997a,b).

Based on the success of this method, most of the nano-biocomposites such as poly (butylene succinate)/clay nanocomposites or poly [(butylene succinate)-*co*-adipate]/clay have been prepared through this method (Ojijo and Ray, 2014). More details and advancement of research related to nano-biocomposites have been achieved through this method. To quote one example, besides the study of polymer/nanofiller affinity, the effects of the residence time and the shearing towards the nano-dispersion of the nanoclay have been studied. In order to induce the platelets delamination from the clay tactoids, shearing will be the key parameter that need to be control. As for the extended residence time, it will affect the polymer chains to diffuse into the inter-layer gallery. This diffusion is important to get an exfoliated morphology. The type of bio-materials used for this research comprehensively was polysaccharide. However, there are several drawbacks such as partial chains degradation could happened due to the thermal or thermo-mechanical inputs. Additionally, matrix degradation also becomes a problem due to long residence times, since a high residence times were needed to improve the clay exfoliation process. Thus, the balancing and optimizing parameter or processing condition during melt intercalation were necessary in order to reduce the degradation of chains and to get a fine exfoliated morphology (Chivrac *et al.*, 2009).

To quote another example of research related to melt intercalation process, the mixture of poly (butylene succinate)/C18-montmorillonites have been studied in term of preparation, structure, and mechanical properties. The first step in preparation was mixing the poly (butylene succinate) pellets and C18- montmorillonites organoclay in a bag. Then the mixture was melt extruding, with the temperature of 150°C to yield gray strands. After extrusion, the compound was pelletized and dried under vacuum for seven hour at 75°C. The drying process was perform because any moisture in the compound need to be eliminated. The pellets of poly (butylene succinate)/C18- montmorillonites nanocomposites were then transformed into sheets. These sheets were pressed in a mold at 1.5 MPa for three minutes at 135°C temperature to produce a sample with thickness range from 0.7 to 2mm. A rapid quenching process was performed towards these sheet, between glass plates. The next step was annealing for 1.5 h at 60°C temperature. The annealing process was performed to ensure the sheet was completely crystallize before measurement took place. In relation to the nanocomposites character/morphology analysis, it was found that the formation of stacked and intercalated layers of organoclay was successfully achieved (Ray *et al.*, 2002).

One more research that adopting the melt intercalation process involved with produce poly [(butylene succinate)-*co*-adipate]/C25A nanocomposites. Specifically in this research, the C25A nanoclay was twice-functionalised. The researchers used two types of silane coupling agents, which are (glycidyloxypropyl) trimethoxy silane and (methacryloyloxypropyl) trimethoxy silane. Firstly the organoclays need to be dispersed in methanol (10 g/ml) and sonicated for 10 min. The second step is to scatter the solution over the pellets of poly [(butylene succinate)-*co*-adipate]. Then this mixture was dried under vacuum. Melt intercalation process was performed for six minutes at 160°C temperature. Stacks of clay layers in the poly [(butylene succinate)-*co*-adipate] matrix was found well dispersed with multiple ordered platelets. There are several factors that could affect the degree of silicate layers exfoliation, which were the reaction between the end-groups of poly [(butylene succinate)-*co*-adipate] and the epoxy groups on the coupling agents, and the polar interaction between the ester groups in the coupling agents and poly [(butylene succinate)-*co*-adipate] (Chen and Yoon, 2005).

Properties of Nano-Biocomposites

In term of properties, the advancement of nano-biocomposites material with specific nano-structures have provide exceptional mechanical/thermal, conductivity and permeability properties. These materials have increasingly widespread and significant in terms of engineering applications through initiatives involving relevant research and development activities (Avérous, 2010).

Table 2 shows a summary of several nano-bio composite material properties obtained from previous research.

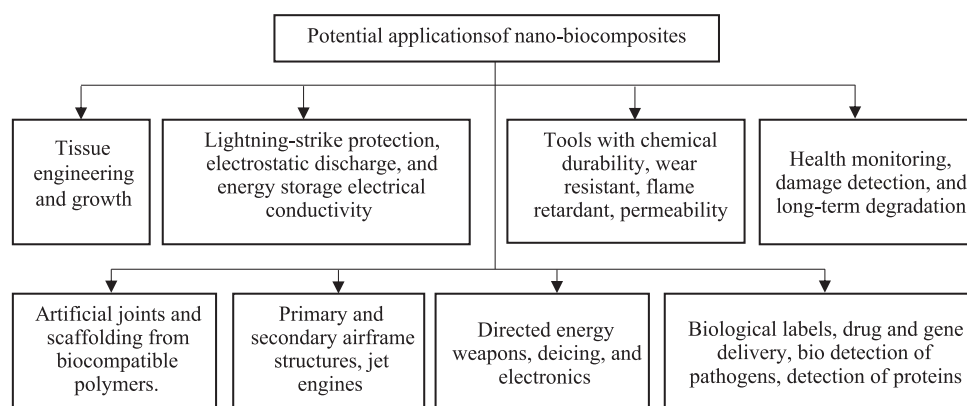
Application and Prospects of Nano-Biocomposites

There are specific reasons why researchers are fond of exploring more about nano-biocomposites. Obviously, the application of this new material could cater wide selection of engineering benefits towards many types of merchandises (prototypes or commercialized) by utilizing the special characteristic of this advanced composites. Besides, awareness and solutions have been taken towards the disadvantages of this material, especially any potential defects that could harm the users and environment (Avérous, 2010).

Challenges in understanding, predicting, and managing potential adverse effects should start from understanding the structure of nano-biocomposites, which compressed from biopolymer matrix with the additional of nanofillers that could improve

Table 2 Nano-biocomposites materials properties summary

No	Authors	Nano-biocomposites materials	Properties findings
1.	Fortunati <i>et al.</i> (2012)	Cellulose nanocrystals/poly(lactic acid)	● Good oxygen barrier properties ● Decreases of water permeability
2.	Oksman <i>et al.</i> (2006a,b)	Cellulose whiskers/poly(lactic acid)	● Good mechanical properties ● Increased of elongation to break
3.	Park <i>et al.</i> (2002)	Thermoplastic starch/clay	● Higher tensile strength ● Better barrier properties to water vapor
4.	Zaidi <i>et al.</i> (2010a,b)	Starch/clay	● Decrease of the weight-average molecular weight ● Faster thermal degradation of the poly (lactide) ● Slight increase of modulus and hardness
5.	Pirani <i>et al.</i> (2014)	Poly(lactic acid) and nanoclay (Cloisite 30B)	● Greater mechanical strength ● More ductile fractures
6.	Olivato <i>et al.</i> (2015)	Starch/poly (butylene adipate-co-terephthalate)	● Thermal degradation affected ● Increase in mechanical properties
7.	Corrêa <i>et al.</i> (2012)	Poly (hydroxybutyrate-co-hydroxyvalerate), montmorillonite clay and acetyl tributyl citrate	● Decrease in thermo-mechanical degradation ● Good mechanical and barrier properties ● Appropriated biodegradation kinetic ● Enhanced the crystallization ● Improving the thermal stability ● Increase the processing temperature range (lower melting temperature)
8.	Salaberria <i>et al.</i> (2014)	Starch, chitin nanocrystals and chitin nanofibers	● Better thermal stability, mechanical properties, and storage modulus
9.	Carli <i>et al.</i> (2011)	Cloisite® 30B,/halloysite, and poly(hydroxybutyrate-co-hydroxyvalerate)	● Increase in the Young's modulus
10.	Han <i>et al.</i> (2012)	Poly(lactic acid) with Graphite nanoplatelets (xGnP) and kenaf	● Enhanced the flexural modulus ● Positive effect on the heat distortion temperature
11.	Zaidi <i>et al.</i> (2010a,b)	Poly(lactide) layered silicate	● Increase mechanical properties, thermal and linear mechanical properties
12.	Furtos <i>et al.</i> (2016)	Nano forsterite biocomposites	● Good compressive, modulus and diametric tensile strength ● Improved flexural strength, modulus
13.	Chung <i>et al.</i> (2010)	Starch-clay	● Improved modulus and strength without a decrease in elongation at break

**Fig. 1** Potential application of nano-biocomposites.

properties with preservation of the material biodegradability, without eco-toxicity. Hence, the field that can utilize these benefits are bio medics and short period applications, such as hygiene devices, packaging, agriculture etc., (Bordes *et al.*, 2009). Some of the potential applications explored by researchers are displayed in Fig. 1 (Lau *et al.*, 2009; Salata, 2004).

Based on the trend of exploration with regard to nano-biocomposites application, more research have been steered either in in-vitro and in-vivo environments extensively. Research about the biocompatibility of natural polymer to assist bone repair, teeth filling, scaffolding, wound healing, artificial joint fabrication etc., have been carried out as the results of tissue engineering applications. Nano fillers such as nano-apatite, lamellar nanoclays (montmorillonites), and nanofibers (carbon nanotubes) have been utilized to improve the structure as the reinforcement. The addition of these materials could

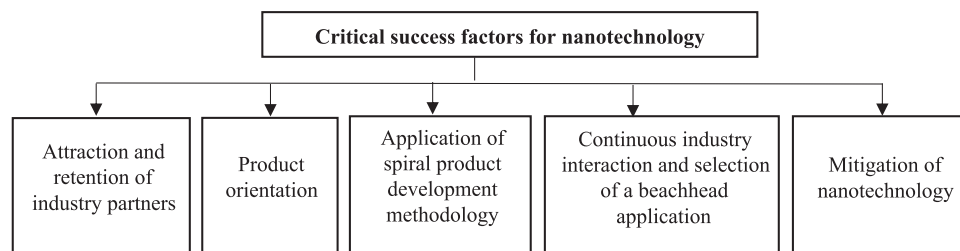


Fig. 2 Critical success factors for nanotechnology. Reproduced from Sun, Y., Xia, Y., 2002. Shape-controlled synthesis of gold and silver nanoparticles. *Science* 298 (5601), 2176–2179

improve the mechanical and thermal stability (Avérous, 2010). To provide more examples about the applications and prospect of nano-biocomposites, several test had been conducted by previous researchers, in terms of drug delivery, organic dyes and controlling nano probes. More than that, further development had been steered to make these materials multi-functional and controllable by external signals or by local environment. Then, nano-biocomposites could be manufactured as nano-devices with wider engineering applications (Salata, 2004). In terms of bio-nanocomposites prospect as the packaging material, it is critical to justify the use of biomaterial in contact with food. Research needs to be done if the new food packaging product need to be produced from this material. Even though such advantages like better mechanical and barrier properties with the antioxidant and antimicrobial benefits, the potential hazards need to be monitored as well. The safety and risk associated with nanomaterials, migration properties, possible ingestion considering mechanisms for nanoparticles to interact with the human body and legal regulations need to be considered earlier before executing the applications (Jiménez and Ruseckaite, 2012).

Yet, until now, most nano-biocomposites are expensive, as compared to the conventional thermoplastic. Some of this material also too weak for practical use. Hence, the needs of improvement are vital to make them viable in the market. To extend their applications, more investigation about the formulation, optimization and blending of nano-sized fillers, could bring a more variety of improved properties such as stiffness, permeability, crystallinity and thermal stability (Bordes *et al.*, 2009). There are several issues related to bio-nanocomposites, such as nano reinforcement and polymer's compatibility and how much shear forces are needed to break the agglomerates apart. Certain areas need to be monitored such as isolation/separation of reinforcement material, degradation, suspension feeding problem, agglomeration of biopolymer, compatibility of matrix and biomaterial and extruder screw configuration (Oksman *et al.*, 2006a,b). Therefore, the success factors of these material's growth need to be summarized. There are five critical success factors for nanotechnology growth and development, as displayed in Fig. 2 (Sun and Xia, 2002).

In terms of the attraction and retention of industry partners, investors and corporate partners could be the success factor by commencing the effective sharing of context-rich technology knowledge. This action could increase the value for the nano-technology with minimal risk in achieving the necessary milestones in product development. As for product orientation, this factor should satisfy the focus on the single application, which is the most viable and attainable, and starting to make a list of prospects. Application of spiral product development methodology could engage the researcher with lead potential users. This engagement shall enhancing product development, by increasing the probability of product that could meet the customer's demand (Sun and Xia, 2002).

The next success factor is a continuous industry interaction and selection of a beachhead application. This factor could help the researchers in term of focusing on the development of the single most viable and attainable product opportunity once known, until it is successfully scaled-up or it fails. As for mitigation of nanotechnology, this factor provide the risk of the technology applied to this material, as the technical risk may occurred in the sense of costing, the control of quality and how much acceptance of this technology in manufacturing, as well as any treats towards the occupational and environmental health and safety considerations (Sun and Xia, 2002).

Conclusion

To conclude the findings of this article, the processing, properties and prospect of nano-biocomposites have been deliberated with appropriate explanations and examples. Usually there are four categories of nano-biocomposites, which were biomass polymers, microbial polymers, polymers of monomers chemically synthesized (agro resources) and polymers of monomers chemically synthesized (fossil resources).

Based on previous findings, montmorillonite were often selected for nanofillers. Hence, the processing methods were related to blend montmorillonite into the nano-biocomposites system. The methods are in situ polymerization, solvent intercalation process and melt intercalation process. Since the first and second method involves with the usage of chemical, which is not environmentally friendly, therefore, the third method which is melt intercalation was chosen. Moreover this method was eased for industrial mass production process. By using this method, the mixing of the polymer and the layered silicate was occurred during

molten condition, whereby the thermodynamic interaction between the particles of host silicate and the polymer matrix will be the important key to achieve good formation of biopolymer nanoclay nano-biocomposites.

In terms of properties of nano-biocomposites, a summary of material properties had been delivered, such as higher tensile strength, increment of storage modulus, improved barrier properties for gas /liquid, as well as faster degradation and thermal stability. To quote one example, a cellulose nanocrystals / poly(lactic acid) was found to possess good oxygen barrier properties and decreases of water permeability. Another example is a mixture of poly (hydroxybutyrate-co-hydroxyvalerate), montmorillonite clay and acetyl tributyl citrate. This blend could provide exceptional mechanical and barrier properties, decrease in thermo-mechanical degradation and provide appropriated biodegradation kinetic. This nano-biocomposite also could also enhanced the crystallization, improving the thermal stability and increase the processing temperature range with lower melting temperature.

Nano-biocomposites have many potential applications, such as tissue engineering growth, artificial joints and scaffolding from biocompatible polymers. This material also can be used as a primary and secondary airframe structures, jet engines and health monitoring, damage detection, and long-term degradation. However, to gain the benefit extensively, the critical factors to attain success in nano-biocomposites research need to be monitored, such as the attraction and retention of industry partners, product orientation, application of spiral product development methodology, continuous industry interaction and selection of a beach-head application and mitigation of nanotechnology. Yet, until now, most nano-biocomposites are expensive and too weak for practical use. Hereafter, more development and upgrading were needed to make nano-biocomposites viable in the market. To extend their applications, more investigation need to be executed, in terms of the formulation, optimization and blending of other types of nano-sized fillers. These recommendations were made to improve the properties such as stiffness, permeability, crystallinity and thermal stability of nano-biocomposites, so that these material have more demand in future.

Finally, this article could provide better understanding about nano-biocomposites, in terms of the processing, properties and applications of these materials. Since these materials are technically and financially competitive as compared with traditional composites, therefore it will open a new dimension of plastic manufacturing process, and in the same time encouraging more efforts in term of future research and applications, based on the established directions and recommendations summarized from this article.

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Renewable Energy Production From Environmental Hazardous Palm Oil Mill Waste Materials: A Review

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Nomenclature

C/N Carbon-to-nitrogen

CH₄ Methane

CO₂ Carbon dioxide

COD Chemical oxygen demand

CPO Crude Palm Oil

GHG Greenhouse gas

HRT Hydraulic retention time

OLR Organic loading rate

pH Potential of hydrogen

POME Palm oil mill effluent

SRT Sludge retention time

WtE Waste to Energy

Introduction

The palm oil industry in Malaysia and Indonesia are growing rapidly to become one of the key agro-industries of the world. The total production of crude palm oil in Malaysia was reported at 19,919,331 and 19,516,141 tons in the year 2017 and 2018 respectively (MPOB, 2016;2018b); which are about 21% of the Fresh Fruit Branch (FFB) of palm oil plant; and other 79% of FFB appeared as wastes. The estimated waste biomass materials are about 90 million tons, which regarded as palm oil mill waste and hazardous elements. These wastes are available in two forms as solid and effluent. However, it has been stated that palm oil mill waste is a bioenergy source (Shahidul *et al.*, 2018c). In the Malaysian case, over the last 30 years, the Malaysian palm oil industry has grown and at present, it is one of the largest agro-based industries (Wah *et al.*, 2002). The country's palm oil accounted for about 39% of the world palm oil production where the industry has contributed to the export earning of the country in the tune of about US\$3.2 billion. In the Indonesian perspective, this industry is stronger than Malaysia. It has been reported that in 2016 the total country's export was about 36.0 million tons which account for about 60% of the global palm oil production; and estimated waste biomass materials is about 170.0 million waste biomass materials (Khatiwada and Silveira, 2017).

The interest in renewable and clean energy sources is growing each day; due to the effect of fossil fuels on the environment relating to the reduction of global warming. Biomass-based energy would be an alternative to the conventional fossil fuels in providing cleaner and sustainable energy supply in the near future, as biomass is renewable. The current status of waste biomass material is the fourth largest energy source behind coal, oil and natural gas (Ladanai and Vinterbäck, 2009) by contributing about 9% of the total renewable energy sector. It is anticipated that the optimal use of biomass will contribute to reduce the formation of greenhouse gases and climate change effects. It is therefore argued that the optimization of the waste biomass used for energy production serves as a crucial means of mitigating the problem of fossil fuel scarcity while promoting sustainable development in the environment. However, the countries involved with Crude Palm Oil (CPO) production need technology and skills to convert hazardous palm oil mill wastes to produce energy for achieving sustainable energy supply. In this aspect, the waste biomass of palm oil mill would be providing us with three major benefits. Firstly, it will provide renewable energy supply which is known as Waste to Energy (WtE). Secondly, it saves the environment from the hazardous effect of wastes. And Finally, it reduces the working load on wastes materials management (Shahidul and Lamoh, 2017). In order to address these two issues, saving the environment and to produce renewable energy from waste biomass the current study has been carried out. Fig. 1 shows the stages of palm oil waste biomass production.

Fossil Fuel and Climate Change

The Fossil Fuel in Energy Landscape

Undoubtedly, fossil fuel resources, especially oil, coals, and gas will continue to dominate the global energy mix. Oil is the major hydrocarbon resource that poses an ultimate constraint to sustaining long-term economic growth and human progress. This is because there is no immediate viable substitute for oil as a dominant energy source in terms of its intrinsic qualities of extractability, transportability, versatility and cost (Singhania *et al.*, 2009). Close to 40% of the global energy consumption is based on



Fig. 1 Palm oil mill waste generation from the milling of palm oil fruit. Reproduced from Shahidul, M.I., Lamoh, M.M., 2017. Advanced Eco-Farming Technology to Achieve Sustainable Agriculture Growth in Sarawak, UNIMAS.

oil and no other fuel source holds as much energy as the oil is offering. Indeed, the petroleum oil holds 1.3–2.45 times more economic value per kilocalorie than coal (Hanson, 1999). Hence, it is an essential input in many of the production chains or economic activities but its long-run supply capacity is fixed and finite. Thus, continued exploitation of such limited resources would lead to depletion once it reaches its peak production level. EIA (2007) stated that the many of the global oil fields have reached their peak oil production levels and this scenario overserved in many counties include the Lower 48 States and East Texas oil fields in the United States, and the major North Sea oil fields in the United Kingdom and Norway (EIA, 2007; Euan, 2006; Kitani *et al.*, 2013; Zittel, 2001). Therefore, sourcing new sources of renewable energy and the use of it needs to continue as a substitute of depleting hydrocarbon based energy sources in order to reduce the greenhouse effect and to create sustainable energy supply (Shahidul *et al.*, 2018a).

Climate Change With the Fossil Fuel Energy Consumption

After hardworking of the last two decades to reduce fossil fuel consumption, there is no effective global deal to manage the risks of climate change. In this perspective, an obvious question to relevant stakeholders is, what is the next plan to achieve the goal of reducing climate change effect? Twenty years of hard work put into setup conferences, writing reports, intergovernmental meetings, placing public debate to reduce greenhouse gas (GHG) emission for mitigating climate change, but all efforts are nearly have failed. It seems essential to go back to the Paris climate change agreement for reviewing the status of carbon emission from the using of fossil fuel (Butler, 2019).

The reality is hydrocarbons continue to supply about 80% of global energy needs, just as they did two decades before. Indeed, the only difference is that the absolute amounts behind this percentage have grown. As a result, the amount of carbon emission continues to rise, and the estimated CO_{2eq} emissions become more than 40% higher than they were in 2000 (IPCC, 2017; Shahidul *et al.*, 2018a). The current global carbon emission situation is getting worse compare to the previous years. At this juncture, there is no viable collaborative mechanism active for tackling the global carbon emission problem. At this moment, the world is on an inexorable track to the point at which atmospheric carbon concentrations exceed the levels judged likely to raise temperatures by 1.5°C (IEA, 2015; International Energy Agency, 2017; Shahidul *et al.*, 2018a). As the climate change is connected to science, the answer to climate change problem should come first from science, and as well technology and engineering. To get the solution to this problem, the scientists should gather to get a solution rather than politicians who regularly meet to formulate solutions to the challenge (Shahidul, 2016). However, Lord Rees, former president of the UK's Royal Society, a scientific academy, has suggested for a few practical strategies to countering climate change in his most recent book entitled 'On the Future'.

They are improved electricity storage; increased low-carbon power generation; greater efficiency of consumption; and more reduction of emissions from methane, black carbon and CFCs all of which would contribute to mitigating global warming. However, the overall aim should be to identify, create and disseminate technologies that can give everyone the chance to use low-cost, low-carbon energy as soon as possible (Montford, 2012; Nurse, 2011).

The purpose of international events on energy and climate to mark progress on the ambitions expressed in the Paris agreement should be to confirm such choices, to share knowledge on the work being done in different parts of the world and to identify the areas where more effort and resources are needed. The exercise should not repeat the mistakes of the political debate over the past 20 years by always waiting for the slowest to catch up (IPCC, 2014; Sterner, 2015).

The other question relating to energy use and climate change is *how the science should be funded to address this issue*. The best answer is to pool available renewable resources for energy production. Why not the world communities establish an investment fund open to subscriptions from both the public and the private sector? Maybe the answer to this question is very difficult, because most world business giants are looking for profit. The technologies that meet the challenge of renewable energy from waste materials are likely to do well, and those who have invested deserve a reward. If some people generate income through the development of renewable products that serve the general public and community, good luck to them. The UN-backed conference

of the inter-government should start by accepting this reality that a part of their GDP may spend for research in developing renewable energy sources for mitigating the climate change. However, further work is needed to meet the goals of achieving a targeted carbon emission rate (Frankel, 2011; Nurse, 2011).

Palm Oil Mill Wastes Biomass

Palm Oil Mill Waste Biomass Materials in the Renewable Energy Landscape

Various studies on the energy potential of biomass waste offer a critical mitigating solution to fossil fuel resource constraints. The waste biomass materials also serve as an environmentally benign energy option to reduce waste disposal problems which at the same time reduces greenhouse gas emission. In the Southeast Asian perspective, the optimum use of the unutilized biomass materials would offer to reduce dependence on the fossil fuel-induced socio-economic development (Agamuthu, 2015). Particularly, optimizing the use of about 250 million tons of palm oil mill waste biomass would be a fossil fuel-saving approach (Shahidul and Lamoh, 2017); and at the same time, the use of waste materials would undoubtedly contribute to reducing the severe environmental problems (BE Sustainable, 2015).

The Economic development solely based on finite and depletable fossil fuel resources would bring serious effect on climate change; rather adopting the environmentally benign “waste to energy [WtE]” strategy would offer an inexorable solution to mitigate the entropic hydrocarbon resource depletion problem. Optimizing the use of biomass waste would also serve to protect the sink capacity of our biosphere from the cumulative environmental impacts of the ever-increasing volume of waste disposal (Shahidul *et al.*, 2018d). The Southeast Asian nations along with Thailand and other palm oil producer nations are shifting the geopolitics of global energy due to their insatiable appetite for energy demand amidst robust economic growth. However, the biomass waste materials would be a renewable energy resource as an alternative to the depletable fossil fuel reserves such as coal, oil and natural gas. Conceivably, the finitude fossil fuels coupled with increasing carbon footprint and anthropogenic climate change have led to growing regional interest in exploring alternative energy sources. One potential solution is to re-model the energy mix away from fossil fuel resources to waste biomass energy (Choy, 2016).

Palm Oil Mills Waste Biomass in Global Landscape

The palm oil industry in the global economic landscape is growing rapidly, and becoming one of the key agro industries of the world. In 2016, the estimated production of palm oil was about 58.000 tons with waste biomass about 170.0 million tons (Khatiwada and Silveira, 2017; MPOB, 2016). But, the waste biomass is negatively associated with the GWP and environmental hazard.

The palm oil mills generate a large number of organic waste materials, often these wastes mismanaged and dispose of the environment. These waste materials are two types such as solid and liquid. The liquid waste produces during the crude palm oil (CPO) process. The palm oil extraction process involves the use of water; it is estimated that for 1 ton of CPO produced, 5–7.5 tons of water is required, and more than 50% of the water will end up as palm oil mill effluent (POME) with biomass materials (Ahmad *et al.*, 2003). This waste biomass with POME is source of methane gas which is emitted to the atmosphere as greenhouse gas (Choi *et al.*, 2013; Shahidul *et al.*, 2018a). On the other hand, the optimal use of solid waste biomass is also expected to contribute to energy security, a significant reduction in greenhouse gas and mitigation of waste accumulation problems (McPhail *et al.*, 2012).

The palm oil mills generate a large quantity of organic wastes materials, and mostly in the Southeast emerging economies; these biomass waste materials remain basically unused or underutilized. This not only poses major disposal problems but also raises crucial environmental concerns. It is thus argued that optimizing the use of waste biomass materials for energy production serves as a crucial means of mitigating fossil fuel scarcity problem while also promoting environmentally sustainable development. This issue should be systematically analyses and demonstrated by scientist and policy maker for achieving sustainable energy supply to mitigate climate change effects (Shahidul and Lamoh, 2017; Kaewmai *et al.*, 2013).

Only in the Malaysian case, the palm oil plantation has expanded rapidly from about 54,790 hectares (ha) to about 1.26 million ha in 2014 and is expected to cover two million ha by 2020 (MPOB, 2014). The rapid expansion of the palm oil industry indicates the availability of waste materials, which would create an opportunity for producing renewable energy to reduce the dependence on fossil fuel for power generation. If the country comes forwards with funding for research to produce energy from waste materials of palm oil mill (MPOB, 2012; Rana *et al.*, 2017).

Carbon Emission From Palm Oil Waste Biomass Materials

Increasing palm oil demands in the global market is positively associated with global warming potential (GWP) due to its carbon emission intensity from waste biomass (Kaewmai *et al.*, 2013; Oosterveer, 2014). Indeed, biomass waste increases with the demand for palm oil. However, nowadays, this industry becomes a point of discussion of global carbon emission issue (Sridhar and Adeoluwa, 2009a,b). It was reported that CH₄, CO₂, and N₂O have a large share in the total global warming potential (GWP) (Wicke *et al.*, 2008). It has been also reported that the palm oil industry emits GHG in three ways (Shahidul *et al.*, 2018d). The first route of carbon emission is fuel burning in palm oil harvesting machinery. The second route is emission from electric production

Table 1 Solid and liquid waste produced per tonne of Fresh Fruit Bunch (FFB) processed

Biomass waste	Kg of waste from 1000 kg FFB
Empty Fruit Bunches	220
Palm Nut Shell	55
Mesocarp Fibre	130
Palm Oil Mill Effluent (POME)	650

to operate the process. And the third route is emission from the wastewater treatment process called POME (Zah *et al.*, 2007; Shahidul *et al.*, 2018d). Damen and Faaij (2006) and reported that the total GHG emissions from three routes are up to about 30 tCO₂eq (t CPO)⁻¹; and among this CH₄ emission is significantly harmful (Renewable Fuel Agency, 2008; Ng *et al.*, 2011). Reported that CH₄ emission potential of POME is about 9 kg (t FFB)⁻¹. The EIA (2007) stated that the total emission of POME would about 18.3 m³ CH₄ (t POME)⁻¹ including CO₂ and N₂O. Ng *et al.* (2011) reported that emission from FFB is about 190 kgCO₂-eq(tFFB)⁻¹. The Statistics Portal (2018) reported that CH₄ emission could be reduced from 9.0 m³ (t POME)⁻¹ to 5.5 m³ (t POME)⁻¹ by using efficient methane capturing technology (Chynoweth *et al.*, 2000). However, Sridhar and Adeoluwa (2009a,b), and Ng *et al.* (2011) reported that biogas (CH₄, CO₂, and H₂S) yield from POME would be up to 28 m³ (t POME)⁻¹. Based on the estimate made by Wicke *et al.* (2008) and Zah *et al.* (2007), the average emission from palm oil industries is about 30tCO₂eq (tCPO)⁻¹ and a similar report has been made by Damen and Faaij (2006). It was also reported that the contribution of palm industry to global emission was 1569.6tCO₂eq in 2013, 1680tCO₂eq in 2014, 1779tCO₂eq in 2015, 1824tCO₂eq in 2016 and 1854tCO₂eq in 2017 (Wicke *et al.*, 2008). This report concludes that palm oil mill waste materials is a potential source of methane gas emission and this gas should be captured and converted to energy to give a sustainable renewable energy supply (Shahidul *et al.*, 2018b).

Properties of Palm Oil Mill Wastes Biomass

It has been stated that palm oil biomass materials comprise (i) empty fruit bunches (EFB), (ii) palm kernel shells and (iii) mesocarp fibers, which are derived from the palm oil production process. The palm oil industry also generates substantial amounts of liquid waste in the form of palm oil mill effluent (POME) (Klimowicz, 2014).

In the aspect of waste biomass materials, a more serious observation is that only about a five percent of the total waste biomass potential is being collected and if all the usable biomass wastes are to be optimized for its energy potential, it would create 1.2 billion tons of coal equivalents (tce) or 0.84 billion tons of oil equivalent (toe) (Klimowicz, 2014). Other than Palm oil mill waste; Southeast Asia also has a huge biomass potential from various biological sources including 30 million cubic meters of woody biomass annually. This untapped biomass may be used for power and heat generation as a fossil fuel substitution. In this regards; Ohimain and Izah (2014) stated that the conversion process of FFB would produce 10%–30% CPO with the by-product of 30%–70% solid waste and 60%–70% palm oil mill effluents (POME). According to Nasution *et al.* (2014), the composition of solid wastes generated by the palm oil mills in Indonesia consists of fibers (12%–15%), shells (5%–7%) and empty fruit bunches (20%–23%), depending on the technology process applied; total accounts for about 165 million tons waste biomass materials. However, the palm oil mill waste in terms of unit weight of FFB and waste constituents are listed in Table 1.

Table 1 indicates that the waste biomass constitutes about 65% of total FFB. Considering 58,000 million tons of CPO production worldwide, the estimated waste biomass is about 275,000 million ton of waste biomass (Khatiwada and Silveira, 2017).

Renewable Energy Production From Palm Oil Mill Wastes and Environmental Sustainability

There are four types of waste biomass to energy conversion technology being used: a. *Thermal conversion*: Direct combustion, Pelletization, and Pyrolysis. b. *Thermochemical conversion*: Gasification, Liquefaction, and Torrefaction c. *Biochemical conversion*: Help of enzymes, bacteria and other organisms. d. *Chemical conversion*: Involves the use of chemical agents (Fauzianto, 2014).

By using all these technologies in waste biomass conversion, the societies would be benefited from harnessing renewable energy from palm oil mill wastes materials in two ways. Firstly, reducing the environmental burden due to reducing GHGs emission. Secondly, getting a sustainable energy source as a substitute for depleting and harmful fossil fuel (Shahidul *et al.*, 2018c; Kaewmai *et al.*, 2013). It has been also stated that the available palm oil mill waste would be used for bioenergy production, and this energy can be a crucial means of mitigating the pressure on hydrocarbon resource, reduce waste disposal management and the GHGs emission effect (Yoshizaki *et al.*, 2013; Yusoff, 2006).

The ensuing discussion highlights the fact that the search for alternative renewable energy sources in a finite natural world poses one of the biggest challenges humanity has ever faced. Biomass in general and palm oil biomass, in particular, can be a sustainable energy source to rely on. The palm oil waste biomass that available in the emerging Asian economies including Indonesia, Thailand and Malaysia would be a dependable renewable energy source (Kitani *et al.*, 2013).

Renewable Energy statement no 21 that made in 2013, stated that biomass accounted for about 19% of global final energy consumption, and biomass for energy (bioenergy) remained the major contributor to renewable energy worldwide at nine percent of all

Table 2 High heating value and proximate analysis of oil palm biomass residues in comparison with coal (mass fraction in % dry basis except for moisture content)

Sample	Gross calorific value (MJ kg ⁻¹)	Moisture content (wt%)	Ash content (wt%)	Volatile matter content (wt%)
Empty fruit bunch	18.88	67.00	4.60	87.04
Mesocarp fibre	19.06	37.09	6.10	84.91
Palm kernel shell	20.09	12.00	3.00	83.45
Oil palm fronds	15.72	70.60	3.37	85.10
Oil palm trunks	17.47	75.60	3.35	86.70
Bituminous coal	28.3	11.00	8.7	46
Lignite coal	2.8	39.00	10.7	29

Note: Choy, Y.K., 2016. Can palm oil waste be a solution to fossil fuel scarcity and environmental sustainability? A Malaysian case study provides the answer. *Waste Management and The Environment* VIII, 1, WIT Press, 97–108. doi:10.2495/wm160101.

renewables in the same year (REN21, 2015; Teske *et al.*, 2015). It was also stated that biomass is the fourth largest energy source after coal, oil and natural gas. It is also considered to be the most important renewable energy option (Ladanai and Vinterbäck, 2009).

Kramanandita *et al.* (2014) were working with palm oil mill solid and liquid wastes with the aim to evaluate its energy potential. The solid waste biomass in palm oil mill has divided into four components namely: waste biomass in fruit bunches is 53.63%, waste biomass in empty fruit bunches is 26.97%, Waste fiber 17.67%, and biomass in shells 6.46%. The composition of POME was mud (18.38%), biomass (30%) and water (42.05%). In this study, they concluded that the solid wastes are a potential source of biohydrogen, biogas, and bioethanol, while the liquid wastes (POME) is a source of biogas and biohydrogen.

It has been reported by Booneimsri *et al.* (2018) that bio-waste of palm oil mills (POMs) is an eco-friendly renewable energy source, which is economically and environmentally sustainable to produce steam and electricity, as what has been done in Thailand for decades. The author found the POMs is energy-efficient when used in the cogeneration power plant including recovery of waste heat emitted by sterilization steam venting and the biogas engine in the power generation system. The outputs of the palm oil mill biomass waste had been incorporated with the power plant, contributing to achieving sustainable electricity supply in Thailand.

It has been reported that Indonesia to be one of the major contributors of renewable energy sources in the world with its palm oil biomass potential (Fauzianto, 2014). The author reaffirmed his argument with research findings and other published data that palm mill waste contains 14%–15% fibre, 6%–7% palm kernel, 6%–7% shell, and 23% EFB which is biomass and a potential source of energy. However, the Government of Malaysia has set up renewable energy Policy and Action Plan to produce 2080 MW and 4000 MW electricity by 2020 and 2030 respectively; and the palm oil mill biomass waste will be used to achieve this target. In Peninsular Malaysia, the agricultural residue has been estimated at 17.0 Mt. out of which 77% of the total residues are from oil palm. Based on the energy potential of palm oil mill biomass waste that is listed in Table 2, the Malaysian government has been made target to produce renewable energy (Choy, 2016; Loh, 2017).

Table 2 demonstrates that the energy properties of palm oil mills biomass waste are higher than coals; in this aspect, palm oil mills biomass waste is a potential renewable energy source. It is glaring from Table 2 that optimizing the use of biomass from the palm oil industries has great potential to contribute towards greening energy-mix system, making it a sustainable substitute of fossil fuels towards increasing security in the power generation sector (Suruhanjaya Tenaga, 2014).

Energy Potentials of Palm Oil Mill Solid Waste Biomass

The Renewable Energy potential of palm oil mill solid biomass waste had evaluated by Harsono *et al.* (2012); in this study, the sample has been taken from for Malaysia and Indonesia. The estimated energy potential for each case is listed in Tables 3 and 4 respectively.

Table 3 demonstrates that waste biomass materials of Malaysian Palm oil mills are a good energy substitution of 323,731 tons of petroleum oil; which would contribute to reducing a significant amount of GHGs emission. Similar evaluations have made by Embrandiri *et al.* (2013) and Husain *et al.* (2003).

Table 4 demonstrates that waste biomass materials of Indonesian palm oil mills are a good energy substitution of 624,658 tons of petroleum oil; which would contribute to reducing a significant amount of GHGs emission. A similar study conducted by Embrandiri *et al.* (2013) and Husain *et al.* (2003). As demonstrated clearly in Tables 3 and 4, the total renewable energy potential of Palm oil mill waste biomass materials in Indonesia and Malaysia is about 10.0 billion kWh which may be a substitute of about 1.0 million tons petroleum oil; and this amount of energy recovery from palm oil waste could mitigate about 420 million tons of CO₂ equivalents (Langerak, 2018; Choy, 2016).

The Energy Potential at Solid and Liquid State of Palm Oil Mill Waste Materials

Choy (2016) has reported that the energy potential of palm oil mill waste materials in Malaysia and Indonesia are significant, and this amount of waste materials would be a suitable substitute for conventional fossil fuel. The estimated energy potential of these two countries is listed in Table 5.

Table 3 Energy potential of the palm oil industry in Sarawak, Malaysia (Malaysian case)

<i>Basic information</i>		<i>Residual materials produced per tonne of fresh fruit bunch (FFB)</i>		<i>Total amount of residue materials produced in 2014 (tonne)</i>	<i>Electricity/ tonne FFB (kWh)</i>	<i>Energy potential</i>	<i>Fossil-fuel saving potential (tonne of oil equivalent, toe)</i>
		<i>Waste category</i>	<i>Tonne</i>				
Total planted are (2014)	5,392,235 ha	Empty fruit bunches (EFB)	0.22	20,522,847	59	1,210,847,945	104,114
FFB yield per tonne per ha per year (2014)	17.3 per tonne/ha/yr	Palm nut shell	0.055	5,130,712	70	359,149,814	30,881
Total FFB yield (2014) (tonne)	93,285,666	Mesocarp fibre	0.13	12,127,137	51	618,483,966	53,180
		Palm oil mill effluent (POME)	0.65	60,635,683	26	1,576,527,755	135,556
Grand total				98,416,378		3,765,009,480	323,731

Note: Harsono, S.S., Prochnow, A., Grundmann, P., Hansen, A., Hallmann, C., 2012. Energy balances and greenhouse gas emissions of palm oil biodiesel in Indonesia. GCB Bioenergy, 4 (2), 213–228. doi:10.1111/j.1757-1707.2011.01118.x.

Table 4 Energy potential of the palm oil industry in Indonesian case

<i>Basic information</i>		<i>Residual materials produced per tonne of fresh fruit bunch (FFB)</i>		<i>Total amount of residue materials produced in 2014 (tonne)</i>	<i>Electricity/ tonne FFB (kWh)</i>	<i>Energy potential</i>	<i>Fossil-fuel saving potential (tonne of oil equivalent, toe)</i>
		<i>Waste category</i>	<i>Tonne</i>				
Total planted are (2014)	8,000,000 ha	Empty fruit bunches (EFB)	0.22	39,600,000	59	2,336,400,000	200,894
FFB yield per tonne per ha per year (2014)	22.5 per tonne/ha/yr	Palm nut shell	0.055	9,900,000	70	693,000,000	59,587
Total FFB yield (2014) (tonne)	180,000,000	Mesocarp fibre	0.13	23,400,000	51	1,193,400,000	102,613
		Palm oil mill effluent (POME)	0.65	117,000,000	26	3,042,000,000	261,564
Grand total				189,900,000		7,264,800,000	624,658

Note: Harsono, S.S., Prochnow, A., Grundmann, P., Hansen, A., Hallmann, C., 2012. Energy balances and greenhouse gas emissions of palm oil biodiesel in Indonesia. GCB Bioenergy, 4 (2), 213–228. doi:10.1111/j.1757-1707.2011.01118.x.

Table 5 Environmental and energetic benefits of palm oil waste in Malaysia and Indonesia

	Malaysia	Indonesia	Total	Remarks
Energy potential (kWh)	3,765,009,480	7,264,800,000	11,029,809,480	Promoting energy security
Fossil-fuel saving potential (tonne of oil equivalent, toe)	323,731	624,658	948,389	Mitigating fossil fuel depletion problem
Palm oil mill effluent (POME) (tonnes)	60,635,683	117,000,000	177,635,683	Mitigating waste disposal problem
Major solid waste (tonnes)	37,780,695	72,900,000	110,680,695	Mitigating waste disposal problem
Methane emission (tonnes)	333,496	643,500	976,996	Mitigating greenhouse gas emission problem
Methane emission (CO ₂ equivalent) (tonnes)	8,337,406	16,087,500	24,424,906	Mitigating greenhouse gas emission problem

Note: Choy, Y.K., 2016. Can palm oil waste be a solution to fossil fuel scarcity and environmental sustainability? A Malaysian case study provides the answer. *Waste Management and The Environment* VIII, 1, WIT Press, 97–108. doi:10.2495/wm160101.

As demonstrated in **Table 5**, the amount of renewable energy potential Indonesia and Malaysia in palm oil waste would contribute to mitigating greenhouse gas emission including CO₂ significantly; and as well as the substitution of fossil fuel (Embrandiri *et al.*, 2013; Husain *et al.*, 2003). It was reported that Malaysia and Indonesia may adopt zero-emission measures in the palm oil industries by optimizing the full use of available in palm oil waste materials (Shahidul and Lamoh, 2017) with the aim to achieve fossil fuel scarcity and environmental sustainability.

It is also demonstrated in **Table 5**, the amount of energy Indonesia may recover from palm oil waste is approximately 7.3 million kWh or 624,000 toe, and the amount of greenhouse gas aversion is about 643,000 tons of methane or 16 million tons of CO₂ equivalents. In the Malaysian case, it can be also seen from **Table 5** that the amount of energy may recover from palm oil waste is approximately 3.7 million kWh or 323,731 toe, and the amount of greenhouse gas aversion is about 333,496 tons of methane or 8.3 million tons of CO₂ equivalents (Choy, 2016).

In a study report, Kramanandita *et al.* (2014) stated that to meet the energy requirements of the palm oil mills, the solid wastes can be converted into biohydrogen, biogas, and bioethanol, while the liquid wastes can be converted into biogas and biohydrogen and water sources. The author further stated that the work station with the highest value of energy input and output is the sterilizer station by 385,008 MJ/h. The total energy produced by the by-product of palm oil mills was equal to 42,865 MJ/h consisting of the three largest components, namely condensate water (16,063 MJ/h), fibers (2722 MJ/h) and shells (8104 MJ/h). In this report, the author also added that to tap the energy potential of palm oil mills waste needs appropriate technology (Kramanandita *et al.*, 2014).

The potential of solid biomass wastes from palm oil mills as an energy source has been widely studied by Husain *et al.* (2003), Nasution *et al.* (2014) and Ohimain and Izah (2014). The energy potential of POME also studied by Gobi and Vadivelu (2013). The summary of all studies postulates that palm oil mills waste is a potential renewable energy source and an energy substitute for fossil fuel.

Renewable Energy Production From Palm Mill Effluent

This section of review demonstrates the research findings on methane potentials of POME. Historically, POME has always been regarded as highly polluting wastewater generated from palm oil mills (Begum *et al.*, 2013; Shahidul *et al.*, 2018d; Sterner, 2015) during CPO production (Ahmad *et al.*, 2003). POME is a brownish liquid composed of biomass, BOD and COD. POME is also recognized as a source of CO₂ and CH₄ emission responsible for GWP (Irvan *et al.*, 2012; Sarwani *et al.*, 2014). However, various research findings demonstrated that methane potential of POME could be a dependable renewable energy source instead of carbon emission (Chin *et al.*, 2013; MPOB, 2018a). It has been reported that about 28 m³ of biogas could be produced from 1.0 m³ of POME (Azri *et al.*, 2017), which has the methane potentials of about 15 m³. The POME is the most extreme wastewater compared to other wastewaters. The high organic value of POME can be converted into biogas production. Recently, the biogas system from POME has been utilized in several palm oil mills in Indonesia, Malaysia, and Thailand (Ichsan *et al.*, 2014).

The POME is also a potent source of methane emission when it undergoes an anaerobic process. By using methane capturing technology, this gas would be the most promising sources of renewable energy (Chin *et al.*, 2013). However, the composition of biogas produced from POME is listed in **Table 6**.

The biogas properties demonstrated that methane gas is the major component in biogas produced from POME (Rahayu *et al.*, 2015). The review of this section concludes that methane gas potential in POME is significantly high, which shall capture to achieve sustainability in energy supply.

Technology for Energy Production From Palm Oil Mill Waste

This section presents the review findings on the successful use of various technologies in biogas production from POME. A few anaerobic reactors have been listed in the scientific journals; though the operating variables and machinery are not much different from each other.

The COD balance and energy efficiency of the two-stage thermophilic reactor for biomethane production from POME were studied by Kongjan *et al.* (2013) with the aim to evaluate the energy yield. The estimated energy was 12.9 J/mL-H₂ (Kongjan *et al.*, 2011) for

Table 6 Composition of biogas

Element	Formula	Composition (Vol%)
Methane	CH ₄	50–75
Carbon dioxide	CO ₂	25–45
Water	H ₂ O	2–7
Oxygen	O ₂	<2
Nitrogen	N ₂	<2
Hydrogen sulphide	H ₂ S	<2
Ammonia	NH ₃	<1
Hydrogen	H ₂	<1

Note: Shahidul, M.I., Malcolm, M.L., Eugene, J.J., Mamunur, R., 2018b. Optimization of factors affecting biogas production from POME. Science International 30 (6), 851–859, (Retrieved from: <https://ir.unimas.my/22601/>).

hydrogen and 40.1 J/mLCH₄ for methane (Kongjan *et al.*, 2013). The energy yield of 0.95 kJ/g-COD was obtained from the hydrogen fermentation stage. The methane produced from POME by using the UASB reactor with an energy yield of 13.73 kJ/g-COD. The overall energy recovery from the was 14.68 kJ/g-COD. A similar result obtained from a laboratory scale two-stage anaerobic (Chu *et al.*, 2008; Mamimin *et al.*, 2015; Nathao *et al.*, 2013; O-Thong *et al.*, 2016). Khanal (2009) stated that the COD removal in the first stage was 15% and in the second stage was 73% and the total COD removal was 90% (Khanal, 2009). It was concluded that the two-stage anaerobic fermentation could increase COD degradation efficiency, increase net energy production with increasing of CH₄ production rates.

Methane Production From Combined Anaerobic Hybrid Reactor and Anaerobic Baffled Filter

Jeong *et al.* (2014) conducted an experiment with an Anaerobic Hybrid Reactor (AHR) and Anaerobic Baffled Filter (ABF) for methane production from POME. The specific objective of this study was to evaluate the effect of operating temperature on methane production. Both mesophilic and thermophilic temperatures were used in this study. The range of organic loading rate (OLR) to the combined reactors was from 2.0 to 15.0 kg COD m⁻³ d⁻¹ with Hydraulic retention time (HRT) of 5 days for AHR and 6 days for ABF. The methane production data demonstrated that the COD removal efficiency and methane production performance at thermophilic environment was about 93% at AHR and about 95% at ABF which is higher than that produced at mesophilic operations at about 35°C.

The research concluded that the combination of AHR and ABF in methane production from POME at thermophilic environment was higher than the mesophilic condition. The findings of this study also demonstrated that thermophilic environment at a temperature between 55 and 70°C would be the good option for producing methane by using combined AHR and ABF reactor (Jeong *et al.*, 2014; Shahidul *et al.*, 2018c).

Methane Production by Expanded Granular Sludge Bed Reactor From POME

By increasing COD removal performance from POME, methane gas production performance was tested by Wang *et al.* (2015) by using an Expanded Granular Sludge Bed Reactor (EGSB). The experiment was conducted at OLR 6.45 kg COD m⁻³ d⁻¹ and reactor were operated at 35°C temperature. In order to reduce a load of suspended solid from POME, a dissolved air flotation (DAF) equipment and Cationic polymer (PAM) was used. The VSS and effluent were circulated in the system to increase methane gas production performance of EGSB.

The experiment demonstrated that the COD removal efficiency was 94.89% with the biogas production about 27.65 m³ (m³ POME)⁻¹, which contains over 65% methane. The study concluded that the application of DAF and PAM in POME process for methane gas production was effective. It was also concluded that due to the reduction of suspended solids and recycling of the effluent, the organic materials conversion to methane had increased to a significant level (Wang *et al.*, 2015). A similar finding was reported by Shahidul *et al.* (2018c) while working on COD reduction from POME.

Methane Production From POME by Up-Flow Anaerobic Sludge Blanket-Expanded Granular Sludge Bed Reactors

Up-flow Anaerobic Sludge Blanket-Expanded Granular Sludge Bed Reactors (UASB-EGSB) used by Fang *et al.* (2011) with the target to improve biogas production performance from the bio-fluid POME. His interested was to evaluate the effect of palm oil free POME on biogas production. The UASB-EGSB reactor was operated with thermophilic conditions at 55°C with the adjusted pH 7.0. The reactor was operated at HRT of 10 days with the OLR range from 1.3 to 10.4 gVSS L⁻¹ d. Aged granulated POME sludge was used as the substrate to accelerate the digestion process.

The study demonstrated that the maximum methane yield achieved was about 503 mL-CH₄ gVSS⁻¹. When de-oiled POME was used in the same reactor, the maximum methane yield was 610 mL-CH₄ gVS⁻¹.

The study concluded that a combination of UASB-EGSB with de-oiled POME has higher methane potential, and thermophilic conditions have also contributed to increase biogas production performance.

Methane Production From POME by Anaerobic Sludge Blanket-Continuous Stirrer Tank Reactor

Krishnan *et al.* (2016) were working with POME for producing biogas as renewable energy. The research was evaluated the effects of various OLRs on H_2 and CH_4 production at the Anaerobic Sludge Blanket-Continuous Stirrer Tank Reactor (UASB-CSTR). The study was conducted in the two-stage digestion process. At the first stage, the UASB reactor was used to produce H_2 while the CSTR reactor was used in the second stage to produce CH_4 . Both cases, the study was conducted at the thermophilic conditions (55°C). The OLR was the manipulated variable, which varied at 25, 50, 75, 100, and $125 \text{ kg COD m}^{-3} \text{ d}^{-1}$ for UASB reactor. The OLR for CSTR were 4, 8, 12, 16, $20 \text{ kg COD m}^{-3} \text{ d}^{-1}$. The HRT was 6 days for both the digestion process. The CSTR was rotated at a constant 120 rpm. At UASB unit, the biogas production rate was 4.5 L d^{-1} with COD removal rate of 40% at OLR of $75 \text{ kg COD m}^{-3} \text{ d}^{-1}$. The performance of UASB started to reduce at OLR beyond $75 \text{ kg COD m}^{-3} \text{ d}^{-1}$. In the CSTR unit, the highest COD removal was 85% at OLR of 12 kg COD m^{-3} . The highest values for CH_4 content in biogas was 68%.

This research concluded that the two-stage digestion process contributed to an increase in methane gas yield. The microbial activities in hydrolysis and abiogenesis contributed to produce the substrate for the methanogens process, which enhance methane production (Krishnan *et al.*, 2016). A similar report has been produced by Shahidul *et al.* (2018a,b,c,d) when working on the optimization of COD reduction from POME.

Methane Production From POME by Two-Stage Thermophilic Fermentation and Mesophilic Methanogenic Process

Mamimin *et al.* (2015) studied with POME for evaluating the effects of two-stage thermophilic fermentation and mesophilic methanogenic process on digestion stability for methane production. At first stage he used Anaerobic Sludge Bed Reactor (ASBR) and operated at 55°C , the ASBR reactor was tested for hydrogen production at pH 5.5 and 2 days of HRT. Subsequently, the UASB reactor was tested for methane production at mesophilic temperatures between 28 and 34°C , at pH 7.5 and HRT of 20, 15, and 10 days.

While the ASBR was operated at OLR of $60 \text{ g COD L}^{-1} \text{ d}^{-1}$ and HRT of 2 days, the maximum hydrogen production rate was $1.84 \text{ L H}_2 \text{ L}^{-1} \text{ d}^{-1}$ with an average of $1.8 \text{ L H}_2 \text{ L}^{-1} \text{ d}^{-1}$. And at this operating condition, the COD removal rate was 38%. The maximum methane production rate was recorded of $2.6 \text{ L CH}_4 \text{ L}^{-1} \text{ d}^{-1}$ at HRT of 15 days and OLR of $6 \text{ g COD L}^{-1} \text{ d}^{-1}$.

In the UASB unit, maximum hydrogen production rate was $1.84 \text{ L H}_2 \text{ L}^{-1} \text{ d}^{-1}$ at the temperature of 55°C , HRT of 2 days and OLR of $60 \text{ gCOD L}^{-1} \text{ d}^{-1}$. The optimum HRT in the UASB was 15 days in which the maximum methane production rate was of $2.6 \text{ L CH}_4 \text{ L}^{-1} \text{ d}^{-1}$.

The study concluded that the two stages digestion process has contributed to increasing energy production yield from POME; though at UASB the HRT is higher compared to the CSTR system.

Engineering Efforts for Energy Production and Carbon Emission Reduction From Palm Oil Mill Waste

A few engineering activities are reported in published science journals for reducing CO_2 and CH_4 emission from palm oil mill waste (Ng *et al.*, 2011; The Statistics Portal, 2018). The total carbon emission was estimated from three levels: palm plantation; oil refinery at mills for CPO production and POME processing in open ponding system. The estimated carbon emission was $30\text{tCO}_2\text{eq}(\text{tCPO})^{-1}$ (Damen and Faaij, 2006), which was reduced to about 40% by the aid various engineering inputs (IPCC, 2007) such as installing carbon capturing machinery and advance technology in CPO production.

Yacob *et al.* (2006) and Sridhar and Adeoluwa (2009a,b) reported that the use of advanced technology in the palm oil industry for reducing energy consumption from $90 \text{ kWh}(\text{tCPO})^{-1}$ to $50 \text{ kWh}(\text{tCPO})^{-1}$ which contributed to reducing carbon emission. It was also reported that various engineering efforts have contributed to reducing GHGs emission to a significant level (Sridhar and Adeoluwa, 2009a,b; Ma *et al.*, 2010). Developing an anaerobic reactor for digestion of biomass-based palm mill waste to produce CH_4 is a significant contribution of engineering to the environment (IPCC, 2007; Kaewmai *et al.*, 2013). However, the most efficient anaerobic reactor development for harnessing energy from biomass waste materials was an important contribution which includes the expanded granular sludge bed (Oosterveer, 2014), up-flow anaerobic sludge-fixed film reactor (IPCC, 2007), and anaerobic fluidized bed single stage reactor (Zhang *et al.*, 2008).

The anaerobic reactor has been reported to be an efficient technology for biomass digestion to produce methane and to use in electricity production (Shahidul *et al.*, 2018d). Yacob *et al.* (2006) and Sridhar and Adeoluwa (2009a,b) reported that CH_4 emission reduced successfully from $9.0 \text{ m}^3\text{CH}_4(\text{tPOME})^{-1}$ to $5.5 \text{ m}^3\text{CH}_4(\text{tPOME})^{-1}$ by using efficient carbon capturing technology. However, Sridhar and Adeoluwa (2009a,b) and Ng *et al.* (2011) reported that CH_4 and CO_2 capturing capacity of an Anaerobic reactor is up to $28 \text{ m}^3 (\text{t POME})^{-1}$, which is high value-added innovation in engineering domain (IAI, 2016; Sridhar and Adeoluwa, 2009a,b).

Conclusion

Sustainable economic growth would be difficult to achieve with the use of current level backstop technology, lack of energy substitution, and continuing to exploration the finite fossil fuel. Given the finiteness of resources as well as the limited

capacity of our terrestrial biosphere to absorb GHGs, the current study demonstrates the harnessing the energy potential of the palm oil mill waste biomass which would enhance energy security and mitigating the climate change effects. With this view, the current review is conducted on palm oil waste biomasses with the aim to collect information on the energy potentials of this waste to support in mitigating the imminent threat of hydrocarbon resource depletion and renewable energy production (Choy, 2016; Shahidul *et al.*, 2018d). However, this review article aims to identify the various options of producing methane gas as renewable energy from palm oil mill waste biomass, and the various research findings have been formatted in line with WtE model (IAI, 2016; International Energy Agency, 2017).

Special emphasis has been given to collect information on methane production process and effectiveness of anaerobic reactors in optimizing CH₄ gas capture. The models used to estimate CH₄ potential in POME have been discussed in this article from the published scientific journals. This review also discussed the optimal operating condition of the anaerobic reactor for maximum biogas production. This study has revealed that global renewable energy potential as methane gas in POME is about 600 million m³ per year; which is mostly emitted to air as GHGs, having 25 times higher GWP potential compared to carbon dioxide (Abdullah and Sulaim, 2013; Shahidul *et al.*, 2018c). By using WtE model, this waste methane could be captured and used as renewable energy for producing heat and electricity (Langerak, 2018); and thus this paper could contribute to achieving sustainability in energy supply and environment.

Exploiting organic wastes as a source of renewable energy seems a promising alternative to energy sources; indeed, palm oil mill wastes in South-East Asia would be a good source for generating bioenergy due to its high organic contents (Choy, 2016; Shahidul and Lamoh, 2017). The abundant amount of palm oil mill waste biomass would provide the most reliable renewable and sustainable energy source if appropriate technology could be put in place. Thus, with the aid of technology and good governance, the palm oil industry would be able to contribute continuously to economic growth, and in supplying renewable energy (Aziz and Hanafiah, 2017).

However, this review could be a potential source of information for researchers involved in the field of renewable energy production from hazardous palm oil mill waste biomass including POME. This paper would be also a guideline in selecting a model to produce energy from palm oil mill wastes. Aside from this, the information published here would be utilized for renewable energy production to contribute to reducing about 37,251 million tons of CO₂-eq (Langerak, 2018) emission per year.

The summary of this study is about 270.0 million tons palm oil mill waste biomass available globally in a year would be an energy substitute of 189 million tons of coals which could reduce about 420.0 million tons carbon emission (Langerak, 2018; Choy, 2016). The study concluded that palm oil biomass waste materials are potential renewable energy sources for fossil fuel substitution to reduce climate change effects.

Acknowledgement

Authors would like to acknowledge the financial supports from Ministry of Agriculture, State of Sarawak Malaysia under grant GL/F02/ORSSG/2016. Authors are pleased to offer special thanks to management and academic staff of Engineering Faculty and RIMC, Universiti Malaysia Sarawak.

See also: Traditional Biomass: A Replacement for Petro-Fuels

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Wound Care: A Material Solution

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Introduction

Wound care materials are mainly fiber based products that include fibers, yarns, fabrics, and fibrous composites made from natural and synthetic sources. These fibrous substances have some outstanding characteristics in strength, elasticity, flexibility, length, fineness, cross-sectional shape and geometry, three-dimensional structures, air and moisture permeability, and liquid absorbency (Qin, 2016). Moreover, many fibrous substances have some unique inherent qualities such as biodegradability, biocompatibility, antimicrobial activity, hemostasis property, etc. Besides, the structural properties of fibrous materials and incorporation of functional additives provide additional functionalities of dressing products to treat specific wounds. Due to these structural and material characteristics they can show very effective performance in wound healing and management. Dressing materials act as a protective barrier permeable to moisture and oxygen, however, they can keep the wounds free from microbial infection and external contamination and shocks. Numerous dressing products, approximately 3000 types of wound dressings, in different forms are found in the current market used for caring for both acute and chronic wounds. According to their functions and uses most of the dressing materials are categorized as primary wound dressing or skin contact layer, absorbent pad, protective layer and bandage, etc. (Qin, 2016).

Wounds: Classification, Effects, and Healing Mechanisms

The term *wound* refers to an injury, damage, or break in the skin and surrounding tissues, or even any body part due to external actions such as physical, chemical, mechanical, thermal, or surgical actions. The Wound Healing Society states that a wound is the result of “disruption of normal anatomic structure and function” (Lazarus *et al.*, 1994). Damage or disorder of the skin by any means breaks the body’s protection system, and then pathogens can easily penetrate into the body to attack the normal biological systems, which primarily causes inflammation and infection locally or septicemia (septicemia is a systemic disease caused by pathogenic microorganisms, especially bacteria or their toxins in the blood. Usually it’s called “blood poisoning”) (Percival, 2002). This interrupts the physiological functions of injured body part. The disorder or injury of the skin or body part may happen due to disease, internal shocks, or penetration of any external objects into the body.

Classification of Wounds

Based on the nature and the duration of the healing process, wounds are classified into two major categories: Acute and chronic wounds (Boateng *et al.*, 2008). Usually, frictional contact, abrasions, or tears between skin and hard surface causes acute wound, for instance, tearing of the skin due to penetration of sharp objects (e.g., knives, bullet, surgical incision, etc.) into the body, burns, chemical injuries, etc. Sussman and Bates-Jensen (2007) define the acute wound as “a disruption in the integrity of the skin and underlying tissues that progress through the healing process in a timely and uncomplicated manner.” Although the healing time depends on the severity and nature of the wound, these types of mechanical injuries heal completely within a short time, usually 8–12 weeks (Percival, 2002; Boateng *et al.*, 2008).

However, the chronic wounds take longer time to heal, beyond 12 weeks, or even fail to do so because of repeated tissue insults or underlying physiological conditions such as diabetes, malignancies, persistent infections, poor primary treatment, and other patient related factors, for example, food habits and lifestyle, etc. (Moore *et al.*, 2006; Boateng *et al.*, 2008). Chronic wounds cannot proceed through the normal healing process in an orderly and timely manner, or even fail to restore normal anatomic and functional integrity (Lazarus *et al.* 1994). Sussman and Bates-Jensen (2007) define a chronic wound as “one that deviates from expected sequence of repair in terms of time, appearance, and response to aggressive and appropriate treatment.”

The chronic wounds fail to progress through the healing process according to the expected pattern and they do not provide restoration of structural or functional integrity of the wound tissues (Ovington, 2007). Examples of chronic wounds include decubitus ulcers such as bedsores or pressure sores and leg ulcers such as venous, ischemic, or of traumatic origin (Boateng *et al.*, 2008). In general, chronic wounds include pressure ulcers, diabetic ulcers, venous leg ulcers, vascular ulcers, arterial ulcers, pressure ulcers, etc.

Wounds can also be classified as superficial, partial-thickness, and full-thickness wounds. Superficial wounds affect only the surface of the epidermis layer of the skin, whereas the partial-thickness wounds affect both the epidermis and dermis layer, and full-thickness wounds affect epidermis, dermis, and the deep of subcutaneous layer (Boateng *et al.*, 2008).

Complications of Wounds

Infection

Microbial acquisition by wounds includes three distinct phases: Contamination, colonization, and infection (Copper, 2005). At the initial stage of injury microorganism contamination may occur but these microorganisms cannot multiply or persist due to the

action of inflammation of the wound. Inflammation is responsible for removing the microorganism contamination. However, when the decontamination process does not work properly and contamination exists in the wound, a prolonged inflammation occurs that ultimately leads to colonization and invasive infection (Guo and DiPietro, 2010). This happens when the self-resistance of the body's immune system fails against microorganisms. As a result, localized wound infection occurs and uncontrolled colonization of microorganisms exists in the wound (Baranoski and Ayello, 2012).

The term "contamination" refers to the presence of nonreplicating microorganisms in a wound, while the term "colonization" represents the presence of replicating microorganisms in the wound without tissue damage (Guo and DiPietro, 2010). When a microorganism colonization exists in the wound, the normal healing process is hindered seriously and the wound becomes infectious or complex, which is seen in most chronic wounds. Hence, the wound infection can be defined as "the invasion and multiplication of microorganisms in wound tissue resulting in pathophysiologic effects or tissue injury" (Altemeier, 1976). In the infection stage, the microorganisms grow, divide freely, and cause invasion into host tissues that leads to cellular injury and explicit host immunological reactions (Copper, 2005). The wound infection causes serious problems that can lead to delays in recovery as well as adverse patient complications such as sepsis, amputation, and even death (Harding and Renyi, 2009). Experts (Dowsett and Newton, 2005; Cutting and White, 2004a; Stotts and Hunt, 1997; Collier, 2004) have identified the following common signs and symptoms of infection that are observed in both acute and chronic wounds:

- Pain
- Erythema (redness of the skin)
- Edema (swelling or fluid retention in the skin)
- Purulent discharge and (drainage of pus)
- Higher body temperature

However, chronic wounds include the following additional signs along with the above symptoms:

- Delayed healing
- Increased exudates
- Bright red discoloration of granulation tissues
- Generating friable tissues
- Spread of the infection into surrounded area
- Malodour

Exudates

Although the discharge of exudates is a part of the normal healing process it may be a sign of an infectious or chronic wound. In this case the volume of exudates increases rapidly, and the exudates become viscous and malodorous. If the overflowed exudates are not managed properly they may spread over the surrounding area of the wound and may attack the fresh tissues to cause maceration (the softening and weakening condition of skin due to prolonged contact of liquid or exudates, which may cause the breaking down of the skin) (Bishop *et al.*, 2003). Due to maceration the surrounded tissues become fragile and unfasten, which may lead to breakdown of the tissues from a minor shock (Fletcher, 2002). This situation deteriorates the clinical status of the wound and seriously affects the patient's well-being. Moreover, the exudates may bring on allergic irritation and discomfort in the surrounding skin.

Necrotic tissues

Sometimes the wounded tissues may die due to insufficient supply of blood and nutrients, which lead to dehydration of the tissues. These tissues then form a black leathery bead or layer on the surface of the wound. When the bead becomes dry it shrinks and causes localized pain and discomfort. Moreover, the necrotic tissues are also responsible for causing a bad smell.

Malodor

Wound malodor is a side effect of infectious and sloughy wounds. The malodorous wounds create enormous psychological pressure on the patient and the quality of life of the patient is seriously affected. Several factors are associated with this situation: Bacterial infection, tissue necrosis, and exudates. In general, the infectious chronic wounds such as ulcers, fungating lesions, and malignant wounds produce an extreme foul odor.

Wound Exudates

The fluids produced as the result of vasodilation (widening of blood vessels) during the early inflammatory stage of healing and discharged from a wound are called exudates. Due to the disruption of dermis a variation of tissue fluid pressure occurs between the unwounded (high fluid pressure) and wounded (low fluid pressure) area, which leads to the spillout of fluid from the wound (Vowden and Vowden, 2004). This fluid is generated due to the influence of inflammatory mediators such as histamine and bradykinin. Microbial colonization of wounds, especially in the chronic wounds, causes vasopermeability that increases the loss of wound fluid (Hampton, 2004). Exudates are a part of normal healing process and maintain the "moist-wound" environment, which ultimately helps the healing process (Thompson and Stephen-Haynes, 2007; Winter, 1962). Moreover, the wound fluid supplies essential nutrients and growth factors to the wound, which assist the reformation of the epithelium. However, excessive

fluid secretion from the wound causes maceration (softening) and other complications in the surrounded area. Exudates are composed of different molecules and cells like white blood cells, red blood cells, platelets, enzymes, glucose, fibrin, plasma proteins, growth and immune factors, microorganisms, electrolytes and inflammatory mediators, etc. (Adderley, 2010; White and Cutting, 2006).

The acute wound exudates contain high protein contents, molecules, and cells that assist the healing process whilst the chronic wound exudates contains proteolytic enzymes that degrade the growth factors, which ultimately hampers the healing process (White and Cutting, 2006). Chronic wounds contain more dead white cells, bacteria, high levels of inflammatory mediators, and protein digesting enzymes that disrupt the healing process and create an irritating environment in the surrounding area of the wound (Adderley, 2010). The exudates of chronic wounds can slow down or even hinder the migration and proliferation of the cells, which ultimately affects the wound healing and repair (Schultz *et al.*, 2003). Overall, the excessive discharge of wound exudates may cause several problems such as maceration or propagation of wound to the surrounded skin, pain, malodor, protein and electrolyte loss, dehydration, delayed healing, sustained infection, soiled clothing and bedding, etc.

Wound Malodor

Unpleasant odor from a wound causes tremendous distress and embarrassment for both the patient and the carers. The quality of life of a patient with a malodorous malignant wound is seriously affected due to the physical obstruction and mental pressure. A patient with malodorous wounds suffers from some physical and psychological disorders, which include pain, bleeding or exuding, itching, alteration of body image, depression, denial, shame, guilt, fear, disgust, lack of self-respect and confidence, problems with sexual expression, and social isolation (Naylor, 2002). Most of the infectious chronic wounds such as venous leg ulcers, diabetic foot ulcers, pressure ulcers, and fungating lesions or malignant wounds are responsible for producing bad smells (Thomas *et al.*, 1998).

Exudates do not create any unpleasant odor at the initial stage of a wound but they may spread a bad smell when the wound becomes sour and increased bacterial growth or infection occurs. Due to the loss of vascularity in the malignant wounds aerobic and anaerobic bacteria proliferate rapidly and cause malodor with abundant exudates (Morris, 2008). At this stage the malodor is generated due to bacterial decomposition of serum proteins present in the wound fluids (Lipman and van Bavel, 2007). The mixture of volatile agents, which include short chain organic acids such as n-butyric, n-valeric, n-caproic, n-haptanoic, and n-caprylic acid, that are produced by the action of anaerobic bacteria, together with a mixture of amines and diamines such as cadaverine and putrescine created by the metabolic processes of other proteolytic bacteria produces the bad smell (Moss *et al.*, 1980; Thomas *et al.*, 1998). Anaerobic bacteria such as *Bacteroides* and *Clostridium* and aerobic bacteria such as *Staphylococcus aureus* and *Pseudomonas aeruginosa* are mainly responsible for producing offensive wound odors (Fletcher, 2008). Moreover, the necrotic or sloughy tissues of the wounds with excessive exudates also produce wound malodor (Lee *et al.*, 2006).

Wound Healing Mechanism

Wound healing is a complex biological process, which is largely related to physiological parameters of growth and regeneration of damaged cells. It can be defined as the physiological processes by which the body replaces and restores the functions to damaged tissues (Lee *et al.*, 2006). The body regenerates the dermal and epidermal tissues through a natural healing process. The natural healing process begins when the wound occurs and ends with complete wound closure. There are some distinct but overlapping biological and physiological phases of the wound healing process, which include hemostasis, inflammation, migration, proliferation/repair (regeneration of cell), and remodeling (maturation) (Zahedi *et al.*, 2010).

Hemostasis refers to stoppage of bleeding, which is considered as the first stage of the wound healing process. In the inflammatory phase, the neutrophils (first type of white blood cell) and the monocytes (second type of white blood cell) enter into the wound and begin the critical task of phagocytosis to remove unwanted or foreign materials, microorganisms, and damaged tissues from the wound (Diegelmann and Evans, 2004). During the migration phase the epidermal cells and fibroblasts are relocated into the wound and replace the injured and damaged cells (Boateng *et al.*, 2008). In many references this phase is merged with the proliferation phase and it was not shown as a separate phase. The proliferation phase begins with growing and depositing extracellular matrix (ECM) in the wound. At this stage, the wound is fully covered with epithelium and new granulation tissues are formed in the wound (Zahedi *et al.*, 2010; Baranoski and Ayello, 2012). At the end of this stage the epidermal cells reach to the normal level of the skin that restores the skin structure. Thus, this phase is considered as the repair stage of wound. The regenerated ECM becomes cross-linked and organized during the final remodeling phase (Diegelmann and Evans, 2004). At this stage the wound is completely recovered and refilled with new cells, and no surface flaws are left in the skin.

Wound Treatment and Management

Treatment and management of wounds are extremely difficult when they become complex with sustained infections. A number of potential factors such as the size, shape, depth and position of the wound, the status of infection, the status of exudates, the presence of necrotic tissues, and the presence of malodor need to be considered for choosing the treatment and the management

technique of wounds. Krasner (1995) identified some key tasks that can manage the chronic wounds effectively: Preventing wound infection, optimizing exudates control, removing foreign bodies, and preventing premature wound closure or contracture, especially in the case of infected or undermining wounds. In general, wounds, whether acute or chronic, partial or full-thickness, need either medication or dressing, or both. This section focuses on the formats of different dressings and their functions, advantages, and disadvantages.

Medication for Wound Treatment

Although acute wounds may heal without any medication, infectious wounds need medications, mainly antimicrobial therapy. Antimicrobial therapy comprises antiseptics and antibiotics, which act directly to eradicate microorganisms involved in the infections. Antibiotics such as gentamicin, ofloxacin, minocycline, tetracycline, and metronidazole are used as selective agents and administered systematically to kill microorganisms. However, antiseptics are normally used as nonselective cleaning agents, which reduce the microbial growth in the wound. Antiseptics containing silver and iodine are also effective for killing microorganisms. The most common antiseptics that are used in wound treatment include acetic acid, chlorhexidine, silver, iodine, honey, hydrogen peroxide, sodium hypochlorite, potassium permanganate, polyhexamethylbiguanide, triclosan, etc. (Qin, 2009). These antimicrobials can be applied to the wounds in the form of liquid, lotion, ointment, soaked with dressing, or incorporated with the dressing materials to achieve the optimum results. However, antiseptics have toxic effects on human cells and the emergence of bacterial resistance to antibiotics are the two potential drawbacks of using these agents in wound treatment.

Furthermore, several growth factors such as epithelial growth factor (EGF), platelet derived growth factor, fibroblast growth factor (FGF), transforming growth factor (TGF), insulin-like growth factor, and human growth hormone are used to facilitate wound healing (Steenfos, 1994). Besides, vitamins A, C, E and the minerals copper and zinc can also be used to promote wound healing (Wallace, 1993).

Silver as Antimicrobial for Wound Treatment

Silver has a long history in the treatment of burns and chronic wounds even in cases of venereal diseases, fistula from salivary glands, bone, perianal abscesses, postoperative cares, and in different medical devices to sterilize them (Lansdown, 2002). In the health care sector, the bioactive silver ion (Ag^+) has widely been used in wound dressings, catheters, bone cements, dental devices, hygiene textiles, and other associated products to achieve antibacterial or antifungal properties (Lansdown, 2002). Also the other forms of silver such as silver nitrate, silver sulfadiazine, silver oxide, silver phosphate, silver chloride, silver zirconium, organic complexes of silver, and silver nanoparticles can be used as antimicrobial agents (Qin, 2009; Lok et al., 2006).

Although silver has some toxicity to mammalian cells, clinicians still prefer using silver to treat and manage infectious wounds because of the emergence of antibiotic-resistant bacteria and potential side effects of using antibiotics (Chopra, 2007; Parsons et al., 2005). Silver is an effective antimicrobial against a large number of microbes with minimal toxicity to mammals at low concentrations (Jones et al., 2004; Lansdown, 2002). It is an effective killing agent against a broad spectrum of bacteria: Gram-negative such as *acinetobacter*, *escherichia*, *pseudomonas*, *salmonella*, and *vibrio*, etc. and Gram-positive bacteria such as *bacillus*, *clostridium*, *enterococcus*, *listeria*, *staphylococcus*, and *streptococcus*, etc. (Burrell et al., 1999). Silver is also effective against antibiotic-resistant strains such as methicillin-resistant and vancomycin-resistant *S. aureus* and *Enterococcus faecium* (Percival et al., 2007).

Chemically, metallic silver is an inert substance but when it comes in contact with moisture of skin or wound fluids it produces active silver ion (Ag^+), which acts as a biocidal agent. The Ag^+ is the functional site of a silver compound, which can react with negatively charged components of proteins and nucleic acids of bacteria, thereby causing structural deformation and reformation in the bacterial cell wall and membrane. The Ag^+ then enters into the cell to damage the DNA and bacterial proteins involved in key metabolic processes of bacteria, impeding bacterial replication and, ultimately, leading to cell death (Dallas et al., 2011; Chaloupka et al., 2010). Ag^+ has a high affinity towards sulfur and phosphorous containing cell membrane and reacts with sulfur containing proteins inside or outside the cell membrane, which destroys the cell viability of the bacteria (Morones et al., 2005). It is believed that ionic silver strongly interacts with phosphorous moieties in DNA that results in the inactivation of DNA replication (Matsumura et al., 2003).

Silver not only shows antimicrobial activity but also stimulates the epithelialization of a wound by increasing the concentration of calcium ions in the wound surface. In the last century, silver nitrate was used to remove granulation tissues to promote epithelialization and promote skin formation on the surface of wounds (Rai et al., 2009). Moyer et al. (1965) reported that silver nitrate of 0.5% solution possesses effective antibacterial property against *S. aureus*, *P. aeruginosa*, and *Escherichia coli* without affecting the epidermal proliferation. Moreover, silver decreases surface inflammation, surface metalloprotease activity, and exudates matrix metalloprotease activity for assisting wound healing (Lakshman et al., 2010).

Wound Dressings

Wound dressings are the materials that can produce a physical barrier against microorganisms and soiling but allow moisture and oxygen. These materials are most effective in wound care, which keeps the wound free from contamination, infection, or other external shocks. It is a clinical device, used for cleaning, covering, and shielding the wounds to facilitate healing

(Mao and Russell, 2004). A good dressing provides a positive environment to the wounds by maintaining the moisture balance that ultimately accelerates the wound healing process and increases the rate of epithelialization (Gates and Holloway, 1992; Percival, 2002). However, modern dressings, especially the active dressings, also encourage the production of granulating tissues in the wounds, keep the wound safe from environmental and bacterial contamination, and provide painless autolytic debridement (Hurd *et al.*, 2009) with minimal interference with the patient's life. Wound dressing materials promote the healing process through regeneration and repairing of dermal and epidermal tissues.

Wound dressings for treatment and management of infection

Dressings containing antimicrobial agents are a good option to prevent and eradicate wound infection. Silver is the most common antimicrobial that is used in wound dressings. Silver in elemental or compound form can be incorporated into the dressing materials by physical attachment or chemical treatment. A number of dressings based on ionic silver such as Silvercel, Actisorb Silver 220, Aquacel Ag, and Acticoat, etc. and silver compounds such as Urgotul SSD and Biostep Ag, etc. are available in the market. Most of the silver dressings are made of alginate, CMC, polyurethane foam, hydrogel, and hydrocolloid materials (Lindsay, 2011). However, iodine based dressings are also effective to reduce the bacterial load and infection from the wounds. Iodine is used in wound dressings as povidone-iodine (PVP-I) such as in Inadine (Systagenix) or cadexomer iodine such as in Iodosorb (Smith & Nephew). All of these dressings are found effective against wound infections. Hence, dressings containing antimicrobials along with antiseptics for cleansing of the wound are the most effective solution to manage infected wounds.

Wound dressings for treatment and management of exudates

Dressing is the most popular and effective tool to manage most wounds, both acute and chronic. A number of dressings are available in the market but the use of the right dressing for a selective wound is crucial. A low exuding or dry wound needs a dressing that can provide moisture to maintain the wound healing moisture balance. For example, hydrogel dressings can provide a moist-wound microenvironment to promote wound healing. However, chronic and infectious wounds with heavy exudates need a dressing with high absorption capabilities, for instance, alginate, hydrofiber, or foam dressings.

Management of exuding wounds is extremely difficult because of a number of factors that are associated with exuding wounds: The size and depth of the wound, the presence of infection, and the status of exudates. The status of the exudates includes type, amount, and viscosity, which are the key factors in choosing appropriate exudate management tools. Sustained release of poorly managed or unmanaged exudates may lead to serious problems. Thompson and Stephen-Haynes (2007) stated that "failure to manage exudate can lead to tissue saturation and leakage onto the surrounding skin with the potential to damage and prolong wound healing time." Using an appropriate absorbent dressing is the best option to handle the wound exudates.

The first recognized absorbent dressing, Gamgee, invented by Joseph Sampson Gamgee in 1880 (Gamgee, 1884), was made from bleached cotton and wool fibers to absorb high volume of exudates. However, cotton fibers may stick to the wounds, which leads to difficulty, discomfort, pain, or even further injury to the wound during removal of the dressing. These gauze based dressings had limited fluid retention ability and were not effective in providing a moist-wound environment. However, modern absorptive dressings such as alginate, hydrofiber, hydrocolloid, polysaccharide, and foam have overcome these limitations.

Wound dressings for treatment and management of malodor

There is no specific method to handle malodorous wounds but the use of appropriate antibiotics (usually metronidazole) or antimicrobial agents can prevent or decrease the wound infections that are mainly responsible for malodor in many cases (Houghton and Young, 1995; Thomas *et al.*, 1998; Paul and Pieper, 2008; Poteete, 1993). Poteete (1993) found that the use of 0.75% topical metronidazole gel to the wound surface is effective to reduce the wound malodor. Alternatively sugar paste and honey are also effective against bacteria especially the antibiotic resistant bacteria. Products with high sugar content have the ability to produce a hyperosmotic wound environment that restrains bacterial growth and assists in wound debridement (Molan, 1999; Naylor, 2002). Some wounds with the presence of large amounts of liquefying or sloughy tissues may cause a bad smell that can be absorbed and removed using a suitable absorptive dressing. Cleansing of the necrotic or sloughy tissues is an effective way to reduce the malodor from the wounds (Fletcher, 2008).

However, identifying the actual cause and taking appropriate action to diminish the cause are the key steps for successful management of wound malodor. In some cases, several factors are responsible for the bad smell and it is not possible to apply any specific strategy; simple actions such as good hygiene, cleansing and debridement, use of antimicrobials, use of specialist odor-absorbing dressing would be more appropriate and realistic to handle these wounds (Lee *et al.*, 2006; Fletcher, 2008; Lipman and van Bavel, 2007). However, in many cases the use of suitable odor absorbing dressings can give immediate results to minimize the wound malodor. These odor absorbing dressings are mainly based on activated charcoal cloth such as CarboFlex (ConvaTec), Lyofoam (SSL International), Actisorb Silver 220 (Johnson & Johnson Healthcare, Ascot), or cyclodextrins such as Exuderm OdorShield (Medline Industries, Inc).

Desirable Properties of a Wound Dressing

Selection of an ideal wound dressing is mostly dependent on the nature and depth of the wound. No single dressing developed yet is suitable for all kinds of wounds. The functions and efficiency of the dressings are mainly dependent on the materials being used

and the structure of the dressing. Moreover, structural features such as porosity in desirable size and shape, and appropriate mechanical strength suitable for supporting cell growth and proliferation should be considered in tissue regeneration technology from synthetic polymeric materials (Gunatillake and Adhikari, 2003). However, the ultimate objective of the dressings is to quicken wound healing with maximum comfort. The following properties are commonly expected from an ideal wound dressing product (Zahedi *et al.*, 2010; Ahamed *et al.*, 2010; Winter, 1975; Jones and Miguel, 2006):

- Nontoxic, nonallergic, nonsensitizing, nonscarring, and sterilized
- Ability to absorb and retain excessive wound exudates
- Providing moist microenvironment in the interface of wound surface and dressing
- Facilitating autolytic debridement to remove unexpected necrotic tissue and eschar, foreign objects, and contaminations from the wound
- Ability to protect from environmental contamination
- Ability to withstand normal mechanical shock/trauma/pressure
- Allowing gaseous and fluid exchange between wound and dressing
- Making a strong barrier for bacterial protection
- Easy removal of wound dressing fully without any pain or trauma
- Ability to absorb wound malodor
- Assisting regeneration of damaged tissue
- Providing thermal insulation
- Comfortable and conformable
- Long service life
- Available in different sizes and shapes
- Cost effective

However, it is expected that advanced dressings would perform not only the aforementioned functions but also interact with the wound to encourage healing. The dressings containing functional additives such as antimicrobials, growth factors, and inbuilt biosensory mechanisms can be more effective to enhance wound healing and repair (Sweeney *et al.*, 2012). In recent years, tissue-engineered fibrous substrates or scaffolds constructed from biomaterials have been focused as a key research area to develop smart wound dressing devices. Tissue-engineered dermal substitute and artificial ECM are such types of devices that are successful for repairing and regenerating the damaged tissue cells in unrepairable burns or chronic wounds.

Selection of a Wound Dressing

Selection of the right dressing at the right time is the key to success of wound healing. Before choosing a particular dressing for a particular wound one must have a clear understanding about the function of the dressing materials and how they work, and what factors influence the wound healing process. Baranoski and Ayello (2012) proposed the following wound care decision algorithm, which is effective for choosing the right dressing for a particular wound (Fig. 1).

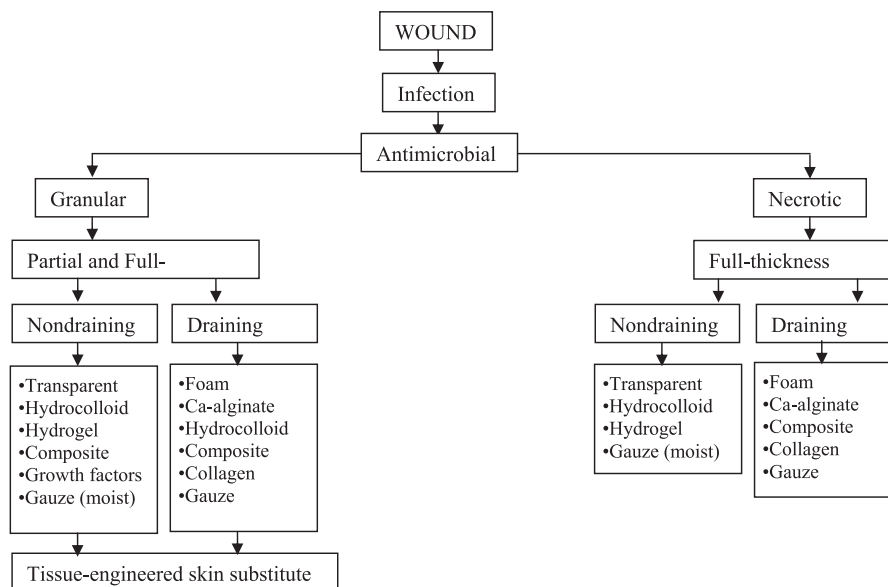


Fig. 1 Wound care decision algorithm. Reproduced from Baranoski, S., Ayello, E.A., 2012. Wound Care Essentials: Practice Principles, third ed. Philadelphia, PA; London: Lippincott Williams & Wilkins.

Dressing Formats

Wound dressings can be in a variety of formats that include film, rope, ribbon, fiber, yarn, or fabric. The fabric forms woven, knitted, braided, and nonwoven are the most common. The structure of the wound dressing is important because the physical and mechanical properties of the dressing are mostly dependent on its structure. In many cases the functional properties of the wound dressing are dependent on its structure. The different formats of wound care dressings are briefly discussed below.

Fibers

Fibers are the fundamental materials extensively used in wound dressing in different forms. Fiber pads can be used to clean and cover wounds. Other formats of dressings are also produced from fibers. The diameter of the fibers can be from a few microns to a few millimeters. Practically, many fibers, categorized as below, are used in producing wound dressing products.

Degradable fibers: Cotton, viscose rayon, lyocell, wool, silk, bamboo, alginate, carboxymethylcellulose, chitin, chitosan, collagen, gelatin, etc.

Nondegradable fibers: Polyester, polyamide, polyethylene, polypropylene, polyurethane, polytetrafluoroethylene, etc.

Resorbable fibers: Poly(lactic acid) (PLA), polyglycolic acid (PGA), poly(lactic acid-co-glycolic acid), etc.

Specialty medical fibers: Super absorbent fibers, activated charcoal fibers, catgut, brananferulate, etc.

Yarns

The continuous form of twisted fibers or filaments is known as yarn. Usually, yarns are made from staple fibers or continuous filament, or combining both staple fibers and filament. Yarns are used to produce woven, knitted, and braided fabrics for dressings. However, the forms of thick yarn, rope, roving, and sliver can be used as wound dressing for specific wounds.

Woven fabrics

Woven fabrics for wound dressing are produced in sheet form using two sets of yarns, warp and weft. The woven structure is comparatively inexpensive and dimensionally stable, and easy to handle. This structure is commonly seen in gauze fabric. The woven structure of fabric can also be used as a base or support structure of other formats of dressing ([Fig. 2](#)).

Knitted fabrics

Knitted fabrics are comparatively soft, flexible, and more drapable than woven fabrics. However, the higher porosity and dimensional instability are the major limitations of knitted fabrics as wound dressings.

Braided fabrics

Braided fabrics are used when a dressing with small diameter is necessary. These fabrics are mechanically stable like woven fabric, but more flexible and conformable than woven fabrics ([Gupta and Edwards, 2009](#)).

Nonwoven fabrics

Nonwoven fabrics are the most common in wound dressing products. These fabrics are soft, woolly, and more resilient than woven or knitted fabrics. Importantly, the production method of nonwoven fabrics is simple and inexpensive because these fabrics are made directly from fibers. These fabrics are suitable for producing absorptive dressings that are effective in absorbing large amounts of wound fluids.

Nanomaterials

Nanofibers from biocompatible natural and synthetic polymers are used to produce dermal substitute, tissue engineered skin, scaffold, and implantable devices. A number of studies ([Chong et al., 2007](#); [Venugopal and Ramakrishna, 2005](#); [Li et al., 2002](#)) have reported that nanofibrous matrixes from biocompatible materials promote cell attachment, adhesion, growth, spreading, and proliferation. Electrospinning is the most simple and effective method to produce such kinds of nanofibrous matrixes that mimic the ECM of natural tissue. Moreover, some nanomaterials such as silver, carbon, copper, zinc, etc. can be incorporated into the fibers, yarns, or fabrics to make more efficient and multifunctional wound dressings ([Mao and Russell, 2004](#)).

Classification and Structures of Wound Care Dressings

Depending on the functions, wound dressings can be classified as inert/passive, interactive, and bioactive dressing. However, according to their uses wound dressings can be classified as primary dressing, which is placed in contact with skin, and secondary dressing, which is used as a supportive layer or cover over primary dressings. A summary and the functions of these dressings in wound applications are presented below ([Zahedi et al., 2010](#); [Jones and Miguel, 2006](#); [Miraftab, 2006](#); [Mao and Russell, 2004](#); [Hoekstra et al., 2002](#)).

Inert/passive dressings

The inert wound dressing encompasses gauze, lint, and tulle, which are usually used to cover the wounds. These materials are mainly used on lightly exuding wounds to keep them safe and free from contamination and infections. These types of

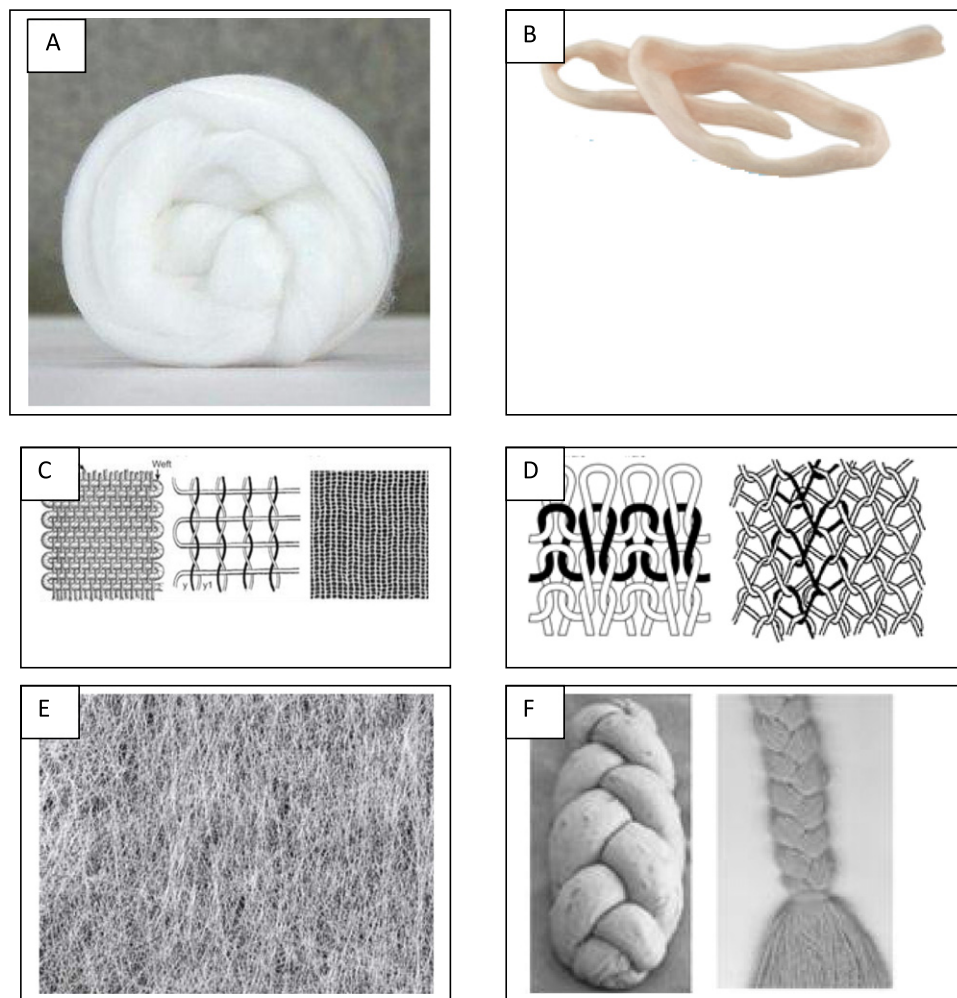


Fig. 2 Different dressing formats: Fibers web (A), roving or sliver (B), woven structure (B), knitted structure (D), nonwoven structure (E), and rope or braid structure (F).

dressings help to rehabilitate the wounds beneath the dressing materials, but are not usually used as a primary dressing. The modified inert dressings, for example, EXU-DRY (Smith & Nephew) dressing, can be used as secondary dressing over moderate to highly exuding wounds over primary dressings (Weller and Sussman, 2006). When an inert dressing, for instance, cotton, is used as primary wound dressing this may adhere to the wound and cause trauma on removal. However, modern synthetic fiber meshes, for instance, Adaptic, Cuticerin, or Atrauman (Cutting and White, 2004b) can be good alternatives to conventional inert dressings. They can maintain moisture balance in the wound and reduce the distortion of the wound and tissues.

Gauze

These are mainly lightweight normal woven fabrics with loose plain weave or sponge suitable for covering different wounds including minor injuries, burns, and surgical wounds. They are usually inert sterile substances such as gauze pads, gauze rolls, gauze sponges, gauze dressing made from cotton, viscose rayon, polyester, or combination of these fibers. Since these gauzes can easily stick to the wounded skin they are mainly used as secondary dressing. However, they can also be used as primary dressings especially for exuding wounds. The gauze dressings are categorized as impregnated dressings, wrapping gauzes, and sponges. Impregnated gauze dressings are usually saturated with petroleum jelly, oil, paraffin, hydrogel, antiseptics, or antimicrobials. The gauze impregnated with petroleum and hydrogel maintain a wet healing wound environment that promotes the healing process. The gauze is impregnated with white or yellow colored liquid paraffin to provide nonadherence and semiocclusive characteristics. These gauze dressings can also be medicated or impregnated with antiseptics such as povidone iodine, chlorhexidine, and sodium fusidate for providing resistance to microbial contamination. Wrapping gauzes are usually made from cotton, elastic, and nylon, and mainly used for securement, padding, and protection of wounds from external shocks and contamination. Sponges are mainly gauze pads folded into a square.

Tulle

Gauzes with grease or petroleum that do not stick to the wound surface are suitable for flat or shallow wounds. Functional materials such as honey and iodine solution can be added with the tulle to incorporate functional properties. Jelonet, Bactiqras, and Activon Tulle are such examples available in the market.

Transparent film dressing

Transparent film dressings are actually transparent sheets supported by an adhesive backing, made of polyurethane. Although they allow moisture, air, and oxygen to pass, they prevent penetration of liquids and microorganisms. They are usually used on partial-thickness or minor wounds including intravenous sites, lacerations, abrasions, wounds with minimal exudates, and second-degree burns (Gupta and Edwards, 2009). Due to their transparent characteristics they are suitable for following-up and inspection of covered wounds without removing the dressing.

Interactive dressings

The interactive dressings are mainly polymeric films, and/or foams that maintain the moist-wound healing environment and positively interact with the wound surface. These dressings facilitate wound healing by exchanging vapor and atmospheric oxygen with the wound. These polymeric dressings not only assist the wound healing but also protect the wound from bacterial attack and contamination. A large spectrum of wounds from minor injury to complex wounds can be handled by using these dressings.

Semipermeable films

Semipermeable films are made from polyurethane, and they are suitable for superficial, low exuding wounds. These thin and transparent films allow moisture and oxygen but protect against bacterial contamination. They can be attached to the dry or slightly exuding wound surface with acrylic adhesive. They are suitable as a primary dressing but can also be used as a secondary dressing over alginate or hydrogel dressings. For example, Tegaderm (3M, Bracknell), OpSiteFlexigrid (S&N, Hull), Mefilm (Molnlycke Health Care), etc. are some common commercial semipermeable film dressings available in the market.

Semipermeable foams

These are polyurethane or silicone based soft foam, adhesive or nonadhesive, absorbent, flexible, conforming, moisture retentive dressings suitable for moderate to highly exuding wounds. They allow oxygen and provide thermal insulation to the wounds. They are usually used as a primary dressing. For example, Allevyn (S&N), Versiva XC (ConvaTec), Lyofoam (Seton Healthcare), etc. are some commercial semipermeable foam dressings available in the market.

Hydrogel dressing

These dressings consist of an insoluble polymer matrix that contains water and other ingredients to maintain wound healing moisture balance. They provide comfort and rehydration to the dry wounds, and facilitate removal of dead tissues from the wounds. They are usually used as a primary dressing, and are easily removable from the wound bed. For example, Aquaform gel (Unomedical), Intrasite gel (S&N), Nu-gel (Systagenix), etc. are some commercial hydrogel dressings available in the market.

Hydrocolloid dressing

These polyurethane based wafers contain hydrocolloid particles such as Na-CMC, gelatin, and pectin that absorb exudates and are converted into gel. They are suitable for lightly to heavily exuding, sloughing, or granulating wounds. They are usually used as a primary dressing. For example, DuoDerm (ConvaTec), Tegaserb (3M Company), Comfeel Plus (Coloplast), etc. are some commercial hydrocolloid dressings available in the market.

Bioactive dressings

Bioactive wound dressings are multifunctional and made from functional bioactive materials such as alginates, hydrofibers, collagens, hyaluronic acid, chitosan, etc. These dressings contain functional ingredients such as silver antimicrobial, growth factor, and ECM components to achieve advance functionalities. They can meet almost all the requirements to be an ideal wound dressing. They promote the healing process and provide internal cell regenerating environment for wound closure. They are remarkably effective for treating acute and chronic wounds compared with other dressings. They can even administer antibiotics.

Alginates dressing

These highly absorbent (absorbency is about 15–20 times of their dry weight) biocompatible dressings maintain a physiologically moist microenvironment that promotes wound healing and the formation of granulation tissues in the wound. When the calcium alginate fibers of wound dressing come in contact with exuding wounds they absorb the exudates and form sodium alginate gel by ion exchange reaction between the calcium ions of alginate fibers and sodium ions of sodium salt of wound fluids. The gel provides a moist wound environment that is desirable for wound healing and reepithelialization.

Moreover, it is believed that the calcium ions stimulate platelet aggregation and coagulation to assist blood clotting, that is, hemostasis (Mao and Russell, 2004; Blaine, 1947), which reduces blood loss and shortens the healing time (Barnett and Varley, 1987). Thus, the alginate dressing is suitable for hemostasis, exudate absorption, and providing moist-wound environment to the wound. For example, Kaltostat (ConvaTec, UK) is a calcium sodium alginate (80% Ca: 20% Na) nonwoven dressing derived from

the brown kelp *Laminaria hyperborean* (Vanstraelen, 1992). It is capable of absorbing large amount of fluid when it comes in contact with wounds; the fibers gradually convert into a viscous, nonadherent gel-like product that maintains wound healing moist environment and allows trauma-free removal of the dressing from the wound.

Incorporation of functional ingredients such as silver antimicrobial with alginate dressing would provide additional benefits. Alginate dressings are suitable for moderate to high exuding wounds and they help in the debridement of necrotic tissues. They are usually used as primary dressing. Kaltostat (Convatec), Sorbsan (Unomedical), Algisite Ag (Smith & Nephew), etc. are some examples of alginate based commercial dressings available in the market.

However, alginate dressings have some drawbacks. First, they may dehydrate the wounds, which can negatively affect the healing process. Second, they have structural instability after gel formation, which may lead to difficulty in removing the dressing from the wound. Third, they have limited fluid retention capacity. The alginate dressings are not suitable for dry or low exuding wounds as they make the wound more dehydrated. Moreover, when alginates convert into gel after absorbing the exudates they attain a loose form that is difficult to handle. Besides, alginate fiber has limited retention ability compared with Na-CMC fiber, which may cause maceration in the fresh skin around the wound.

Hydrofiber dressing

These are nonwoven soft pads or ribbons made from sodium carboxymethyl cellulose fibers. When these fibers come in contact with wound fluids they absorb large amount of fluids and convert into soft gel. These high absorbent dressings are suitable for a wide range of acute and chronic deep wounds. They can maintain wound healing moisture balance and absorb harmful components from the wound to accelerate the healing process. For example, Aquacel (Convatec), Aquacel Ag (Convatec), Versiva (Convatec), etc. are some commercial hydrofiber dressings available in the market.

Collagen dressing

These are gels, pads, particles, pastes, powders, sheets, or solutions derived from bovine, porcine, or avian sources. They are suitable for exuding wounds like ulcers, burns, surgical wounds, etc. They not only promote wound healing but also assist regeneration of new tissues because the collagen acts as a structural scaffold for tissues. They can be used as primary and secondary wound dressings. For example, Biostep Ag is a collagen based commercial dressing.

Chitosan dressing

Chitosan is a biocompatible material that is used as solution, gel, sponge, film, or nonwoven material in wound care products. It has natural antibacterial and hemostasis effects. Due to limited spinnability the chitosan fibers can be blended with other fibers such as polypropylene and viscose to form dressing structures. For example, Chitopack C (Eisai Co), Tegaderm (3M Company), Chito-Seal (Abbot), etc. are some chitosan based commercial dressings available in the market.

Composite dressing

Composite wound dressings are the combination of different dressings that provide several functions depending on the constituent materials and structure. Usually, composite wound dressings consist of multiple layers, commonly three layers, including a semi- or nonadherent skin contact layer that adheres to the wounds with help of an adhesive border. The outermost layer protects the wound from bacterial invasion and allows air to circulate. However, an absorptive layer, in between the skin contact layer and outermost layer, is composed with absorptive materials such as CMC, alginate, polyacrylate, etc., which maintain the moisture balance of wounds. These dressings can be used as a primary and/or secondary dressing for both acute and chronic wounds. They are versatile and suitable for a wide range of wounds that includes minor injuries, low to heavy exuding wounds, ulcers, and surgical wounds.

Foam dressing

Foam dressings are usually made of semipermeable polyurethane foam with small, open cells that can absorb and hold liquids into air-filled spaces by capillary action. Silicone based foam dressing is also used as an adhesive wound contact layer. This foam can be applied as a layer to another structure for obtaining better features. Due to their porous structure they can absorb and retain a huge amount of liquid from their surroundings. They can protect the wounds from external shocks and discomfort. These dressings are very effective in managing heavily exuding and odorous wounds but are not appropriate for dry wounds. However, these dressings are suitable for managing both acute and chronic wounds of both partial- and full-thickness wounds. Foam dressings are produced with a variety of thickness and shapes containing adherent or nonadherent and nonlinting skin contact surface. These dressings are usually soft and flexible supported by a silicone adhesive, which helps the dressings to stay on the wounded place. They are very easy to use and easy to remove and fulfill most of the criteria of an ideal dressing used in moist wound healing. They can be easily cut in appropriate size to fit irregular wounds and curve areas. The hydrophobic and waterproof outer surface of foam dressings keeps them safe from bacterial and external contamination. Sometimes, the foam dressings are functionalized incorporating therapeutic elements such as silver, Manuka honey, cadexomer iodine, antibiotics, etc. Production, storage, and application and removal from the wound are very easy and simple.

Table 1 Silver-loaded commercial dressings

Dressing	Antimicrobial ingredient	Dressing construct	Manufacturer
Acticoat absorbent	Ionic silver	Calcium alginate	Smith & Nephew, Inc.
Actisorb Silver 220	Ionic silver and charcoal cloth	Silver impregnated charcoal cloth	Johnson & Johnson Medical Ltd
Aquacel Ag	Ionic silver	Hydrofiber	ConvaTec Ltd
Contreet H	Ionic silver	Hydrocolloid	Coloplast Corp
Silvasorb	Ionic silver	Hydrogel sheet or amorphous gel	Medline Industries, Inc.
Silvercel	Ionic silver	Alginate and CMC based nonwoven pad	Systagenix
Optifoam Ag	Ionic silver	Absorbent foam	Medline Industries, Inc.
Biostep Ag	Silver chloride	Collagen matrix	Smith & Nephew, Inc.
Urgotul SSD	Silver sulfadiazine	Polyester mesh	Laboratories Urgo

Note: Ovington, L.G., 2007. Advances in wound dressings. *Clinics in Dermatology* 25 (1), 33–38. Lindsay, S., 2011. Silver White Paper. Available at: <http://www.systagenix.com.br/media/originals/20120412-101643-8910.pdf> (accessed 03.02.19).

Silver-Loaded Dressings

Silver-loaded dressings are effective and widely used to control a large spectrum of microbial wound infections. Depending on the demand of a wound condition the silver content in the dressing may vary as high, medium, or low. Qin (2009) stated that high silver content dressings provide rapid release of silver that is necessary for the wounds with high infection and bacterial colonization. The dressings with medium content of silver provide sustained release of silver over several days and are effective for treating wounds with moderate to high infection and bacterial colonization. Dressings with low silver content are useful to treat wounds with minimal infection in chronic wounds as well as to prevent infection in acute wounds, burns, and surgical injuries. The silver ions can be incorporated into the wound dressings by the following three general methods (Qin, 2009):

- Physical treatment. In this method the fiber or fabric of the dressing are coated with metallic silver.
- Chemical treatment. The dressing materials are treated with silver solution; an ion exchange reaction occurs. As a result, the silver ions are attached to the fiber or fabric of the dressing.
- Blending. In this method fine particles of silver compounds are blended with the dressing materials.

A number of silver dressings based on alginate, CMC, films, hydrogel, hydrocolloids, polyurethane foams, and charcoal cloth, etc. are available in the market (Karlsmark *et al.*, 2003; Ovington, 2007; Lindsay, 2011). Table 1 includes some prominent silver-loaded wound dressings available in the market.

Malodor Absorbing Dressings

Dressings with the ability to resolve the causes (e.g., infection) of wound malodor are the most effective way to handle wound malodor. However, the dressings containing odor absorbing ingredients such as charcoal and cyclodextrins are effective for capturing and controlling the volatile malodorous molecules from the wounds. Activated charcoal as charcoal cloth has been used successfully in wound dressing to adsorb and bind the molecules responsible for malodor. However, charcoal cannot function when it is saturated with wound exudates. Hence, charcoal based dressings are not suitable for an exuding environment, which is common in most malodorous wounds.

During the last few decades a number of charcoal-based odor absorbing dressings have been introduced in the market. Since wound malodor is correlated with microbial infection and the presence of sloughy tissues or exudates, the absorptive dressings containing antimicrobials and odor absorbing components would be more effective than a single odor absorbing dressing. In some commercial dressings, for instance, Actisorb, which is the first charcoal-based dressing, introduced by Johnson & Johnson Medical Ltd, the charcoal bed is used to achieve additional benefits with exudates absorbability. The improved version of Actisorb is Actisorb Silver 220, which is a sterile multifunctional wound dressing formed from a composite structure that includes an activated charcoal cloth in a spun bonded nylon envelope. The charcoal cloth is impregnated with 0.22% w/w elemental silver (Lindsay, 2011).

Besides charcoal, cyclodextrins have the ability to entrap the volatile molecules responsible for wound malodor. Cyclodextrins have a cavity (host) in their structure and the targeted molecules (guests) are enclosed into the cavity. The effectiveness of this inclusion depends on the size of host cavity and guest molecules. Thus, the mixture of common cyclodextrins with different cavity sizes, α CD, β CD, and γ CD, incorporated with dressing material are capable of capturing the optimum number of malodorous molecules present in wounds (Lipman and vanBavel, 2007). Hence, cyclodextrins based dressings, for instance, ExudermOdor-Shield (Medline Industries, Inc.), have been introduced into the market. They are effective in capturing the malodorous molecules from the exuding wound environment (Medline, 2007). Table 2 shows some odor absorbing commercial dressings.

Nanofibrous Dressings and Skin Substitute

Due to their high specific surface area and microporous structure, electrospun nanofibrous mats can be used as an interactive wound dressing that is able to quickly start signaling pathways and attract fibroblasts to repair damaged tissues in the wound

Table 2 Odor absorbing commercial dressings

<i>Dressing</i>	<i>Odor absorbing ingredients</i>	<i>Dressing construct</i>	<i>Manufacturer</i>
Actisorb Plus	Charcoal cloth (CC)	Consists of a CC of 95%–98% carbon, produced from knitted viscose rayon fabric. The rayon fabric is enclosed in an envelope of spun-bonded nonwoven nylon.	Johnson & Johnson Medical Ltd
Actisorb silver 220	Charcoal cloth (CC)	Consists of silver impregnated CC. This dressing contains 220 mg silver per 100 g activated charcoal cloth.	Johnson & Johnson Medical Ltd
CarboFlex	Charcoal cloth (CC)	Multilayered dressing consists of alginate and CMC fibers wound contact layer. A plastic film beneath the CC is placed between the wound contact layer and an absorptive layer on top.	ConvaTec Ltd
Lyfoam C	Charcoal granules (CG)	A nonwoven fabric along with CG is enclosed with two pieces of polyurethane foam, bonded together around the perimeter.	Seton Healthcare
Carbonet	Charcoal cloth (CC)	Multicomponent dressing consists of knitted viscose wound contact layer backed with a cellulosic absorbent layer and a charcoal cloth layer. This assembly is sandwiched between two layers of polyethylene net.	Smith & Nephew Medical
Sorbsan plus carbon	Charcoal cloth (CC)	Multilayered absorptive dressing consists of CC cloth and an alginate fibrous wound contact layer.	Pharma-plast Ltd
Exuderm OdorShield	Cyclodextrins (CDs)	Hydrocolloid substance with the mixture of α -, β -, γ -CDs	Medline Industries, Inc.

Note: Thomas, S., Fisher, B., Fram, P., Waring, M., 1998. Odour Absorbing Dressings: A comparative laboratory study. *World Wide Wounds*. Lee, G., Anand, S.C., Rajendran, S., Walker, I., 2007. Efficacy of commercial dressings in managing malodorous wounds. *British Journal of Nursing*, 16 (6), S14–S20. McQueen, R.H., 2011. Chapter 17 – Odor control of medical textiles. In: Bartels, V.T. (Ed.), *Handbook of Medical Textiles*. Woodhead Publishing.

(Chen *et al.*, 2008; Chung *et al.*, 1994). These materials provide the necessary mechanical strength and stability in three dimensions to allow cells and tissues to colonize and regenerate the damaged or missing skin/organs, which ultimately enhances wound healing and repair (Mirafteb, 2006). Nanofibrous scaffolds have been successfully used to repair and restore the damaged skin especially burn injured skin. Numerous studies (Zahedi *et al.*, 2010; Chen *et al.*, 2008; Chung *et al.*, 1994; Khil *et al.*, 2003; Chong *et al.*, 2007) have reported about the effectiveness, functions, and advantages of nanofibrous wound dressings. The functions and advantages of nanofibrous dressings are presented below.

Hemostasis

The nanofibrous dressing material closely adheres with the wound surface and blocks the spilling of blood more successfully compared with other conventional wound dressing materials. In the wound healing process, they act as a hemostatic agent to promote bleeding off.

Absorbability

As the nanofibrous materials are fluffy and porous they can absorb wound liquids effectively. Due to high surface area-to-volume ratio they show 17.9%–213% water absorption, which is significantly higher than conventional film dressings (Dabney, 2002). Thus, the nanofibrous dressing materials can manage heavy exudates more effectively compared with their counterparts.

Semipermeability

The nanofibrous mesh acts as a semipermeable membrane that allows the atmospheric oxygen into the wound but prevents access of harmful substances, bacteria, and viruses. This can also maintain the moisture balance of the wound, which promotes wound healing.

Effective wound coverage

The maximum coverage and contact of the wound surface with dressing material are influenced by the fineness of constituent fibers. As the fibers of nanofibrous dressing are very fine and flexible, they can easily conform to the contour of a wound. Thus, a nanofibrous mesh can easily fit and conform to any complicated outlines of wounds.

Functional ability

In recent years, multifunction wound dressings are constructed to achieve high quality wound management for both patients and clinicians. Incorporation of functional ingredients with bioactive nanofibrous material can provide advanced functional properties in wound dressing. Depending on the necessity, functional drugs such as antibiotics; active pharmaceutical components such as antimicrobial, vasodilators (e.g., minoxidil for promoting wound epithelialization and neovascularization); growth factors (e.g., FGF, EGF, and TGF); and cells (e.g., keratinocytes) can be incorporated into the nanofibrous substrates.

Table 3 Nanofibrous based commercial dressings

Dressing	Dressing construct	Manufacturer
Tegaderm	Poly(ϵ -caprolactone) (PCL)/gelatin nanofibrous scaffold is directly electrospun onto a polyurethane dressing to form dressing construct	3M Company
Biobrane	Highly purified peptides derived from porcine dermal collagen is bonded to the nanofibrous nylon/silicone membrane	Smith & Nephew
ChitoFlex	It is fabricated from chitosan nanofibers, which are effective to stop bleeding	HemCon Med. Tech. Inc
Permacol	Dermal collagen matrix of porcine nanofibers	Covidien
DermaFuse	It is composed of borate glass nanofibers	Mo-Sci Corporation
Apligraf	It consists of bovine collagen nanofibrous sponge with living cells (fibroblasts) and structural proteins (keratinocytes)	Noveris
Integra	It is a biodegradable porous matrix made from collagen-glycosaminogly as main component	Integra Life Sciences
TransCyte	Composed of human newborn fibroblasts, which are then cultured on the nylon nanofibrous mesh	Advanced Tissue Science

Note: Varma, A., 2012. Medical textiles: Nanofiber-based 'smart' dressings for burn wounds. [Online] Available at: <http://www.nanowerk.com/spotlight/spotid=25577.php#ixzz35-BafFgXT> (accessed 02.02.19).

Scar-free

Although it is difficult to achieve wound healing without leaving any scar, the nanofibrous wound dressing can heal the wounds with minimal scar. Electrospun bioactive fibrous mesh allows the regeneration of epithelial cell in its structure, which facilitates the forming of natural ECM from the inside of the wound to replace the dead or damaged tissues. Incorporation of antibacterial agents with these substances provides double action: Bactericidal effect and reformation of wound tissues that ensure quick wound healing without producing large amounts of scarring. Table 3 shows some commercially available nanofibrous wound dressings.

Conclusions

Wound dressings are the primary choice for wound care and management. A large number of wound care dressings are available in the market both for acute and chronic, full or partial-thickness wounds. The dressings are made of different polymeric and fibrous substances originated from natural or synthetic sources. Some of the fibrous substances are inert in function and some of them have intrinsic functional properties. The fibrous materials such as alginate, carboxymethylcellulose, collagen, chitosan, PLA, PGA, etc. have additional functional characteristics that make them suitable for producing advanced wound care dressings. Moreover, the specific therapeutic or medicinal agents such as antimicrobials, growth factors, vitamins and mineral supplements, etc. can be incorporated to these dressings to promote the healing process. At present, wound care professionals have a wide range of options to choose the right dressing from simple cotton gauzes to high-tech multifunctional dressings, and even skin substitutes. However, an ideal dressing to treat and manage large number of wounds specifically chronic wounds has not been developed yet.

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Library of Congress Cataloging-in-Publication Data

A catalog record for this book is available from the Library of Congress

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library

ISBN 978-0-12-813195-4

For information on all publications visit our
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PREFACE

The *Encyclopedia of Renewable and Sustainable Materials* is a novel initiative, launched to cater for researchers, industrial practitioners and environmental conservationists to bring to the fore the issues of renewability, regeneration, recyclability and sustainability of natural material resources for the greater good of the environment, society and renewable resources. With these objectives the project was constituted of 11 sections, led by one Section Editor each. There are about 4,000 printed pages, accommodated in five volumes ranging from 600 to 1000 pages each.

This encyclopedia is the primary reference source for researchers at different levels and stages in their career in academia and industry and those with an interest in environmental protection and sustainability, including re-use and recycling of natural and synthetic materials and regeneration of natural materials. The work encompasses the knowledge and understanding of many experts into a single, comprehensive work of about 370 articles comprising a combination of review articles, case studies and research findings resulting from research and development activities in both industrial and academic domains. The encyclopedia, focuses on how some of these topics bring advantages for a broad range of technologies and environmental protectionists. These include harnessing existing materials both natural and synthetic, their re-usability and regeneration possibilities for the greater good of society and the environment. The aspects of feasibility, conservational objectives and practicability of implementation have been addressed through a number of relevant articles.

As Editors in Chief of this five-volume comprehensive publication, a truly collaborative work, we are greatly indebted to the 11 Section Editors who are internationally renowned experts in their fields, for guiding and selecting the topics for their respective sections which constitute the five volumes, commissioning authors and reviewing the contents so meticulously. Their true dedication to the scientific community and society is reflected in the time and energy they have given to this project. My sincerest thanks are due to all the authors – researchers, environmental protectionists and practitioners who have contributed extensive coverage of literature review as well as recent works of research to this substantial five volume encyclopedia. The excellent insight and specialist knowledge in their respective fields is reflected in the high quality content of this unique work.

Both of us and all the section editors are greatly appreciative of all the hard work undertaken by all concerned to turn this concept of the *Encyclopedia of Renewable and Sustainable Materials* into a publishable work. Our special thanks go to Ruth Rhodes and Michael Nicholls, the Project Manager, along with Kshitija Iyer and the rest of the team at Elsevier who served successively to keep the project on track through friendly nudges in order to ensure timely completion. We are also hugely grateful to other colleagues at Elsevier production unit for the coordination of the proofs.

The extensive research treatment of core ethos of renewability, recyclability and regeneration, supplemented by applied case studies has drawn together many areas of research and we sincerely hope that this work will prove to be of great help to both the young and experienced members of the international research community, academics and industrial practitioners associated with sensible utilization of natural and synthetic materials for many years to come.

Saleem Hashmi and Imtiaz Ahmed Choudhury
Editors in Chief – *Encyclopedia of Renewable and Sustainable Materials*

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Application of Nanofluids for Radiator Cooling

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Nomenclature

A_s Surface area of solid particle
 EG Ethylene glycol
 C_p Specific heat
 DW Distilled water
 d Diameter of nanoparticles
 Nu Nusselt number
 Pr Prandtl number

g Acceleration due to gravity
 Ra Rayleigh number
 h Heat transfer coefficient
 Re Reynolds number
 Q Volume flow rate
 T Temperature
 k Thermal conductivity
 X Mole fraction

Greek Symbols

Φ Particle concentration
 η_0 Base fluid viscosity

ρ Density
 η Dynamic viscosity

Subscripts

nf Nanofluid
 max Maximum

$avg.$ Average
 np Nanoparticles
 bf Base fluid

Introduction

Vehicle engine thermal management is important to make the vehicle system more efficient and sustainable. Going into the brief history of the evolution of car and truck radiator cooling, it was found that a number of generation has been evolved in order to improve and maximize the efficiency of engine cooling. To improve the efficiency, air cooling was shifted to water because of its availability and ability to absorb and carry heat efficiently. However, Water has its limit of operating temperature range and inability to provide corrosion resistance. In order to improve its properties additives and other fluid like ethylene glycol has been added. In order to improve thermal properties more, the researcher focused on the addition of solid particles which have higher thermal properties into the conventional coolant called as nanofluids (Saunders, 1936). Nanoparticles can be dispersed in any of the liquid in that way it should fulfil requirement of thermal properties like viscosity, specific heat, density, thermal conductivity, surface tension, stability in the operative environment. However, the choice of base fluid in engine cooling system for enhancing heat transfer needs capabilities like high boiling and low freezing point, high thermal conductivity, high heat capacity etc. Base fluids such as water, ethylene glycol, mixture of water and ethylene, oil etc. are preferred in the cooling system. Some additives added into the conventional coolants to enhance the heat transfer characteristics. The additives were used to prevent corrosion on the engine wall and overheating and freezing of the coolants. The properties of conventional coolant water, Ethylene glycol (EG) and mixture of water and EG measured experimentally by Conrad *et al.* (1940), Tsierkezos and Molinou (1998) and Sun and Teja (2003) are given in Tables 1 and 2.

Lately, Micali *et al.* (2018) used the CuO nanoparticles into the engine coolant (pure water) and found that at 2.5 vol% of nanoparticles the reduction of temperature is 13.6% compared to water in the exhaust valve seat at 100% full load. Moghaieb *et al.* (2017)

Table 1 Thermal properties of water, ethylene glycol and mixture of water and ethylene glycol

Properties/ EG + Water	$X=0$ (Water)	$X=0.25$	$X=0.50$	$X=0.75$	$X=1$ (EG only)
Density (kg/m ³)	998	1068	1094	1106	1120
Viscosity (mPa s)	1.001	3.69	7.61	12.3	19.1
Thermal conductivity (W/m K)	0.614	0.391	0.316	0.269	0.258

Table 2 Freezing and boiling points of water, ethylene glycol and mixture of water and ethylene glycol

Properties/% by weight of EG in Water	0	20	40	60	80	100
Freezing point (°C)	0	− 8.3	− 22.6	− 49.3	− 46.8	− 13.5
Boiling point (°C)	100	102.2	104.4	111.1	127	197

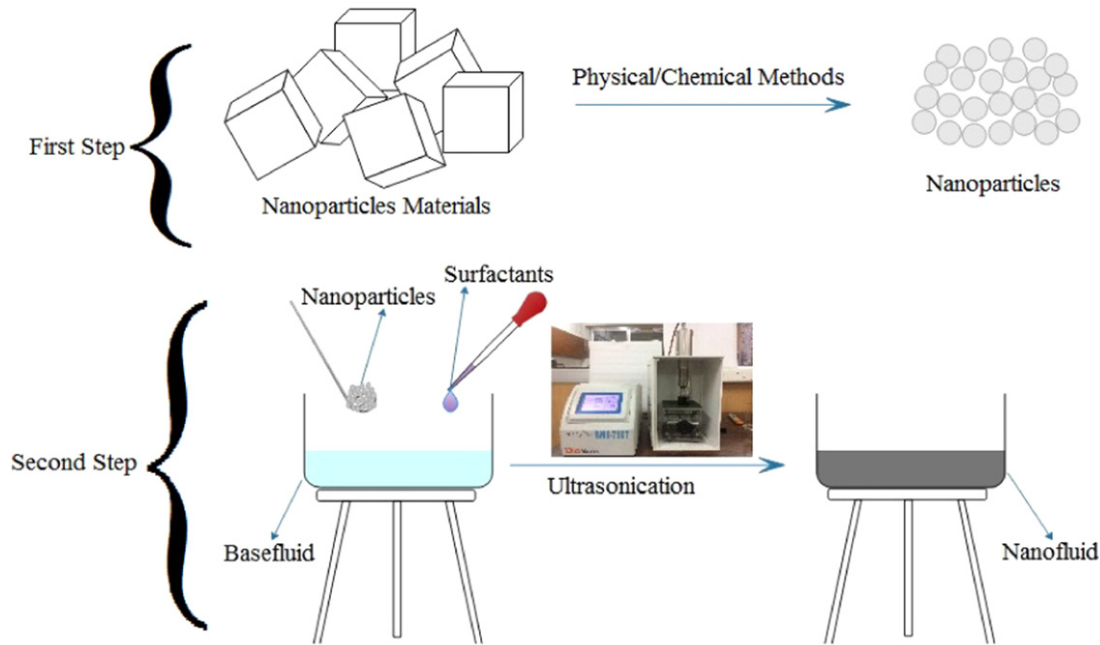


Fig. 1 Two step method to prepare Nanofluid.

investigated the characteristics of heat transfer for alumina water nanofluid and found that maximum enhancement in the heat transfer is 78.67% with 1 vol% concentration of nanoparticles into the water. The heat transfer analysis on the nanofluids comprised of different material nanoparticles in water and ethylene glycol are widely investigated (Darabi *et al.*, 2015). Sahin *et al.* (2013) investigated the turbulent convective heat transfer inside a circular tube and found that increasing heat volume concentration of nanoparticles into the base fluid enhanced the heat transfer. Furthermore, the viscosity also increased with the concentration which leads to increment of the friction factor. Raveshi *et al.* (2013) taken alumina nanoparticles dispersed in water and mixture of water and and ethylene glycol and stated that the optimum volume concentration of nanoparticles is 0.75% with a 64% maximum boiling heat transfer.

In this article, a comprehensive review of nanofluid focusing on engine cooling is compiled thoroughly for the researchers working in this field. The paper provides the recent developments in this field and facilitates researchers to find a latent research gap to develop new techniques for enhancing the overall efficiency of the heat transfer system. The article begins with the first section which explains existing synthesis techniques of nanofluids the next section contains the effect on the thermal properties of the various parameter of nanofluids followed by last section concluding the convective heat transfer analysis on the vehicle radiators or cooling system with nanofluids.

Preparation of Nanofluids

Nanofluids are generally consist suspension form of solid nanoparticles. Solid nanoparticles typically made out from the materials having higher thermal conductivity like metals. Thermophysical properties like thermal conductivity, viscosity, specific heat and density plays a vital role to enhance the heat transfer capability of the base fluids (Khurana *et al.*, 2016a,b). Metals, metal oxides, non-metals, carbon based materials and some organic materials having high thermal conductivity are used to synthesis nanofluids. Number of ways are there to synthesis nanofluids broadly categorised into two approaches which are one step method and two step method. The two step method include two steps to prepare nanofluids, first step to prepare dry nanopowder from the available physical or chemical techniques the second step consist dispersion of previously prepared nanopowder into the base fluid with the help of magnetic stirrer and ultrasonic sonicator, shown in Fig. 1. One step method includes simultaneous making and dispersion of nanoparticles into the basefluids. The Submerged arc nanoparticle synthesis system (SANSS) is one step method to prepare nanofluids shown and explained in Fig. 2 (Lo *et al.*, 2007). The one step method sidesteps the drying, storage and transportation of nanoparticles. However, one step has advantages over two step method but researchers prefer two step because it is easy and simple. Table 3 shows the summary of methods used to prepare nanofluids.

Nanofluid Thermophysical Properties

The nanoparticles colloidal suspension into conventional base fluid can modify the thermophysical property according to the desired requirement (Kumar and Subudhi, 2018). The idea behind using a colloidal suspension is to enhance the thermal conductivity of the

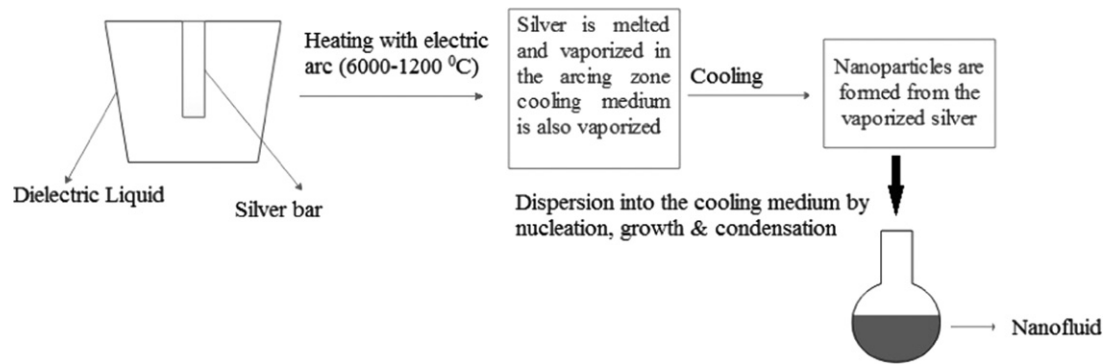


Fig. 2 Submerged arc nanoparticle synthesis system (SANSS) flow diagram (one step method) to prepare Nanofluid. Reproduced from Lo, C.-H., Tsung, T.-T., Lin, H.-M., 2007. Preparation of silver nanofluid by the submerged arc nanoparticle synthesis system (SANSS). *Journal of Alloys and Compounds* 434–435, 659–662.

Table 3 The reported synthesis of nanofluids

Author	Material of nanoparticles	Base fluid	Concentration	Method
Tseng and Lin (2003)	TiO ₂	Water	0.05–0.12 vol. fraction	Two Step
Liu <i>et al.</i> (2005)	MWCNT	EG and engine oil	0.2 to 2 vol%	Two Step
Yang <i>et al.</i> (2005)	Graphite	Commercial automatic transmission fluid and Mixture of two synthetic base oil	2 and 2.5 wt%	Two Step
Ding <i>et al.</i> (2006)	MWCNT	Water	0–1 wt%	Two Step
Chopkar <i>et al.</i> (2006)	Al ₇₀ Cu ₃₀	EG	0.2–2.0 vol%	Two Step
Lo <i>et al.</i> (2007)	Ag	EG and Deionized Water	–	One step
Chen <i>et al.</i> (2007)	TiO ₂	EG	0.5–8 wt%	Two step
Phuoc <i>et al.</i> (2007)	Ag	Deionized Water	0.01 vol%	One step
Beck <i>et al.</i> (2007)	Al ₂ O ₃	EG	1–4 vol%	Two step
Lee <i>et al.</i> (2008)	Al ₂ O ₃	Water	0.01–0.3 vol%	Two step
Choi <i>et al.</i> (2008)	Al ₂ O ₃ and AlN	Transformer oil	0.5 and 4 vol%	Two step
Nguyen <i>et al.</i> (2008)	Al ₂ O ₃	Water	1–13 vol%	Two step
Phuoc and Massoudi (2009)	Fe ₂ O ₃	Water	1–4 vol%	Two step
Duangthongsuk and Wongwises (2010)	TiO ₂	Water	0.2–2 vol%	Two step
Chandrasekar <i>et al.</i> (2010)	Al ₂ O ₃	Water	0.33–5 vol%	Two step
Yu <i>et al.</i> (2010)	Fe ₃ O ₄	Kerosene	1 vol%	Two step
Lee <i>et al.</i> (2011)	SiC	Deionized Water	0.001–3 vol%	Two step
Paul <i>et al.</i> (2011)	Al ₉₅ Zn ₀₅	EG	0.01–1 vol%	Two step
De Robertis <i>et al.</i> (2012)	Cu	EG	–	One step
Paul <i>et al.</i> (2012)	Ag	Water	–	One step
Singh <i>et al.</i> (2012)	Al ₂ O ₃	EG and water	0.25–1 vol%	Two step
Fazeli <i>et al.</i> (2012)	SiO ₂	Water	3.5–5 vol%	Two step
Kumaresan and Velraj (2012)	CNT	Water + EG	0.15–0.45 vol%	Two step
Pang <i>et al.</i> (2012)	Al ₂ O ₃ and SiO ₂	Methanol	0.005–0.5 vol%	Two step
Syam Sundar <i>et al.</i> (2012)	Fe ₃ O ₄	Water + EG	0–1 vol%	Two step
(Hung <i>et al.</i> , 2013)	Al ₂ O ₃	Water	0.5–3 vol%	Two step
Selvakumar and Suresh (2012)	CuO	Water	0.1 and 0.2 vol%	Two step
Esmailzadeh <i>et al.</i> (2013)	γ-Al ₂ O ₃	Water	0.5 and 0.1 vol%	Two step
Choudhary and Subudhi (2016)	Al ₂ O ₃	Water	0.1–2 vol%	Two step
Irani (2019)	Graphene Oxide	Water + MDEA	0.1 and 0.2 wt%	Two step
Dalkılıç <i>et al.</i> (2018)	CNT-SiO ₂	Water	0.1–2 vol%	Two step
Ahmed <i>et al.</i> (2018)	TiO ₂	Water	0.1–0.3 vol%	Two step
Anamalai <i>et al.</i> (2018)	Cellulose nanocrystal (CNC)	Water + EG	0.1–1.5 vol%	Two step
Moldoveanu <i>et al.</i> (2018)	Al ₂ O ₃ -SiO ₂	Water	1–3 vol%	Two step

conventional heat transfer fluids to enhance the heat transfer (Das *et al.*, 2008). Investigations using higher thermal conductivity material nanoparticles such as Al₂O₃, CuO, MWCNT, TiO₂, Ag, etc. in conventional heat transfer fluids were ruled. Other thermo-physical properties like viscosity, density, specific heat etc., also plays a vital role to define nanofluid as a heat exchanging fluid. In the area of engine cooling the thermal conductivity and viscosity of nanofluids are very imperative properties to enhance the heat transfer.

Thermal Conductivity

A plethora of literature shows that the thermal conductivity of nanofluids is higher than the base fluid. Researchers focused the use of nanofluids as a cooling fluids in the engine cooling of car radiator. Mohammadi *et al.* (2009) compared the thermal conductivity of γ - Al_2O_3 -engine oil and CuO-engine oil nanofluids and marked that the thermal conductivity increase with the concentration. Compared to base fluid the thermal conductivity of both the nanofluid is enhanced and at 2 vol% concentration γ - Al_2O_3 shown 5% enhancement and CuO shown 8% enhancement. Kole and Dey (2010) reported the enhancement 10.41% at 3.5 vol% concentration of alumina nanoparticles in car engine coolant (HP KOOLGARD). Investigation also reported that the enhancement in thermal conductivity is proportional with concentration and temperature and maximum enhancement reaches 11.25% with 3.5 vol% at 80°C. Vasheghani (2012) dispersed α - Al_2O_3 , γ - Al_2O_3 and AlN nanoparticles at different concentrations separately in engine oil and investigated the thermal conductivity of the prepared nanofluids samples. Increasing tendency of thermal conductivity with concentration for all the cases and at 3 wt% the maximum enhancement recorded 31.47%, 37.49% and 75.23% for engine oil based α - Al_2O_3 , γ - Al_2O_3 and AlN nanofluids respectively. Etefaghi *et al.* (2013) researched with MWCNTs in different concentration in engine oil and stated that it affect the thermal properties of nanofluids. The thermal conductivity of the of nanofluid increased by 13.2% with 0.1 wt% concentration. Elias *et al.* (2014) researched on the thermophysical properties of alumina nanoparticles dispersed in water and EG based car coolant. The thermal conductivity increased with concentration of nanoparticles and temperature, the maximum increment in thermal conductivity was 8.30% for 1 vol% at 50°C. Micali *et al.* (2018) researched on 4-strokes biodiesel engine cooling system based on CuO-water nanofluid. The maximum enhancement in the thermal conductivity was 18% at 4 vol% nanoparticles concentration.

Viscosity

The heat transfer in any fluid flow critically depends upon the viscosity, a minor change in the viscosity affects the convective heat transfer. Furthermore, the nanofluids viscosity depends upon so many factors, the most important factors are nanoparticles concentration and temperature. Einstein Eq. (1) only based upon volume fraction is the theoretical or mathematical expression to find out the viscosity of nanofluid valid only for low concentration (Einstein, 1956). For higher concentration upto 50%, (Kuntiz, 1926) given a correlation Eq. (2).

$$\eta_{nf} = \eta_0(1 + 2.5\phi) \quad (1)$$

$$\eta_{nf} = \eta_0(1 + 0.5\phi)/(1 - \phi)^4 \quad (2)$$

Kole and Dey (2010) dispersed the Al_2O_3 nanoparticles into the car engine coolant (EG based) and found that the nanoparticles concentration enhanced the viscosity. Elias *et al.* (2014) shows the similar trend with Al_2O_3 dispersed in car radiator coolant (EG + Water) and found maximum enhancement was 150% for 1 vol% at 10°C. Mahbubul *et al.* (2013a), Mahbubul *et al.* (2012) and Mahbubul *et al.* (2013b) investigated on the Al_2O_3 -R141b refrigerant and found the similar trend of enhancement in viscosity with the concentration.

Heat Transfer Analysis

As discussed above the conventional fluids have their limitation for convective heat transfer because of their constrained poor thermal properties and for that reason, highly effective sustainable compact technology is necessary to accomplish high heat transfer. The car radiator consists of tubes and fins to circulate fluid and air respectively. Many researcher setups the experimental test rig like shown in Fig. 3 to explore the experimental research. The test rig provides the similar condition of actual vehicle engine.

Experimentally, Kulkarni *et al.* (2008) investigated with aluminum oxide nanofluids as jacket water coolant in diesel electric generator and found that high convective heat transfer coefficient of nanofluids increases the heat exchanger efficiency and the heat transfer coefficient increased with the particle volume concentration. Peyghambarzadeh *et al.* (2011a,b, 2013) focused the research on automobile radiator with Al_2O_3 -water nanofluids and used different variations in concentration. The application of alumina nanofluids enhanced the convective heat transfer upto 45% with low concentration comparison to water. Naraki *et al.* (2013) reported the 8% increment with the CuO-water nanofluid used to investigate overall heat transfer coefficient in laminar flow regime with Reynolds number in between 100 and 1000. Chavan and Pise (2013) used the Al_2O_3 -water nanofluids with low concentration to study the convective heat transfer coefficient. The results show the enhancement of 40%–45% in convective heat transfer efficiency compared to pure water and enhancement increases with flow rate and particles concentrations. Ali *et al.* (2014) researched the on the effects of nanoparticles concentration on the vehicle radiator. The Al_2O_3 -water nanofluid with different concentrations is used and the different parameters are taken into consideration. Results show that the particles concentration upto an optimum level enhanced the heat transfer beyond that heat transfer start deteriorate. The gradual enhancement in heat transfer is upto 1 vol% and after that at 1.5 and 2 vol% the heat transfer deteriorates. Chougule and Sahu (2014) researched on different nanofluids with different concentrations in automobile radiator cooling. Al_2O_3 -water and CNT-water in the range 0.15–1 vol% were prepared and used for cooling performance. The nanofluids exhibit high heat transfer compared to pure water, the maximum enhancement occurred at 1 vol% of 90.76% and 52.03% for CNT-water and Al_2O_3 -water respectively compared to water. Hussein *et al.* (2014a,b) used TiO_2 -water and SiO_2 -water in radiator to augment heat transfer in radiator cooling system. Significant heat transfer enhancement proportional with nanoparticles concentration

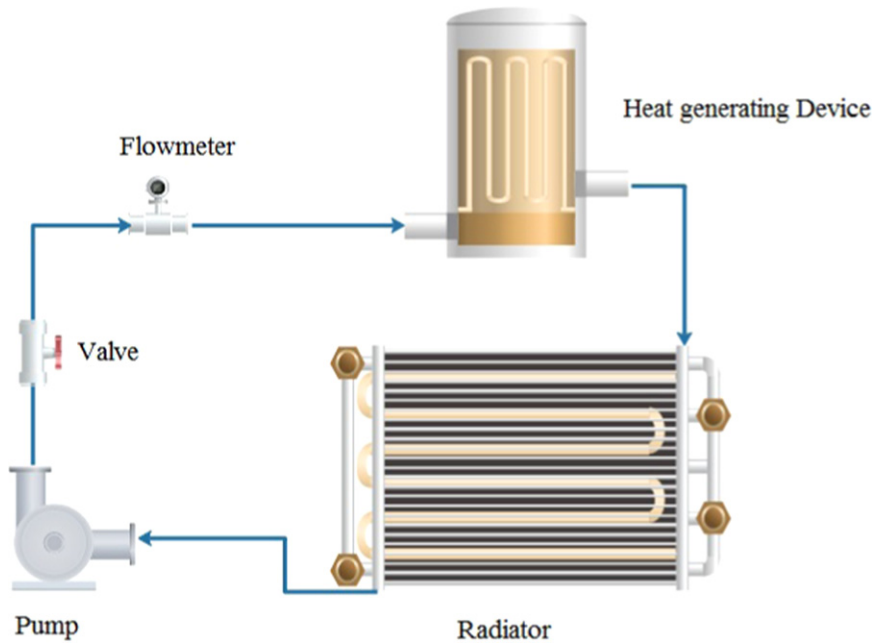


Fig. 3 Experimental setup test rig providing similar condition of actual engine.

was observed. Maximum Nusselt number increased 11% and 22.5% for TiO_2 -water and SiO_2 -water nanofluids respectively. To predict Nusselt number the authors developed a mathematical model given in Eqs. (3)–(5) for water, TiO_2 -water and SiO_2 -water nanofluids with 2–4 deviation. Sasank and Naik (2014) used Al_2O_3 -water to investigate effects on the performance of automotive radiator cooling and found maximum heat transfer of 12.4% at 0.1 vol% of nanofluid.

$$\text{Nu} = 1.69414 + 0.325529 \text{ } Q + 0.0058446 \text{ } T \quad (3)$$

$$\text{Nu} = 6.38776 + 0.06018 \text{ } Q - 0.0610291 \text{ } T - 285.668 \text{ } \phi + 0.0176852 \text{ } Q \text{ } T + 51.2556 \text{ } Q \text{ } \phi \quad (4)$$

$$\text{Nu} = -3.0125 - 1.31736 \text{ } Q + 0.083777 \text{ } T - 1071.89 \text{ } \phi \quad (5)$$

Heris *et al.* (2014) used base fluid water + EG (40/60) to suspend CuO nanoparticles in order to study performance of radiator and the maximum enhancement of heat transfer apprehended about 55% compared to base fluid. Hussein *et al.* (2014a,b) investigated with SiO_2 -water nanofluids in the range 1–2.5 vol% concentration and reported that the maximum enhancement in convective heat transfer was about 50%, the friction factor also increased upto 22% compared to water. Satyamkumar *et al.* (2015) used Al_2O_3 -water nanofluids in radiator and found a 26% maximum enhancement at 8 vol% of nanofluid. Sandhya *et al.* (2016) used water + EG (60/40) basefluid with TiO_2 nanoparticles, the experiment conducted in the range between 4000 and 15,000 of Reynolds number. The enhancement upto 37% is apprehended at low concentration of nanofluids. Fig. 4 (a) and (b) shows the results of different researchers between Reynolds and Nusselt number. Higher the Nusselt number higher will be the convective heat transfer. Almost all the researchers find an enhancement proportional with nanoparticles concentrations. M'hamed *et al.* (2016) used MWCNT- water + EG (50/50) nanofluid in car engine system (Proton Kelisa 1000cc) radiator to study heat transfer performance. The heat transfer enhancement was proportional to volume concentration of nanoparticles and for 0.5 vol% almost 200% enhancement is reported. Goudarzi and Jamali (2017) used inserts in the tube of radiator with EG based Al_2O_3 nanofluids and reported the heat transfer enhancement and stated that the thermal performance of the system with inserts is more than 1 which means that this technique can be used into the radiator for research in order to enhance the heat transfer. Selvam *et al.* (2017) studied the performance of radiator with graphene- water + EG nanofluid, the convective heat transfer apprehended start from 20% and upto 51%. However, the pressure drop also increased while increasing concentration. Lately, Subhedar *et al.* (2018) reported the reduction in frontal area if base fluid replaced by nanofluid. The research was focused on the heat transfer in car radiator by Al_2O_3 -water + Mono EG (50/50) nanofluid as a coolant. The Nusselt number changes from 3.89% to 28.47% as the particle concentration change from 0.2% to 0.8%. Almost 30% rise noted with the low vol% concentration of nanoparticles compared to base fluids. Ahmed *et al.* (2018) researched on the radiator performance with TiO_2 -water nanofluid with 0.1, 0.2, and 0.3 vol% in laminar range between 560 and 1650 of Reynolds number. The significant enhancement with 0.2 vol% is captured almost 47% compared to water.

Numerically, Tijani and Sudirman (2018) studied the performance of Al_2O_3 and CuO – water + EG (50/50) nanofluid as a coolant of car radiator with heat transfer models simulated using ANSYS fluent solver. The CuO based nanofluid at higher concentration apprehended more heat transfer compared Al_2O_3 and base fluid. Mutuku (2016) studied the heat transfer performance of nanofluids as a coolant in radiator, CuO , Al_2O_3 and TiO_2 nanoparticles dispersed into EG. The similarity approach

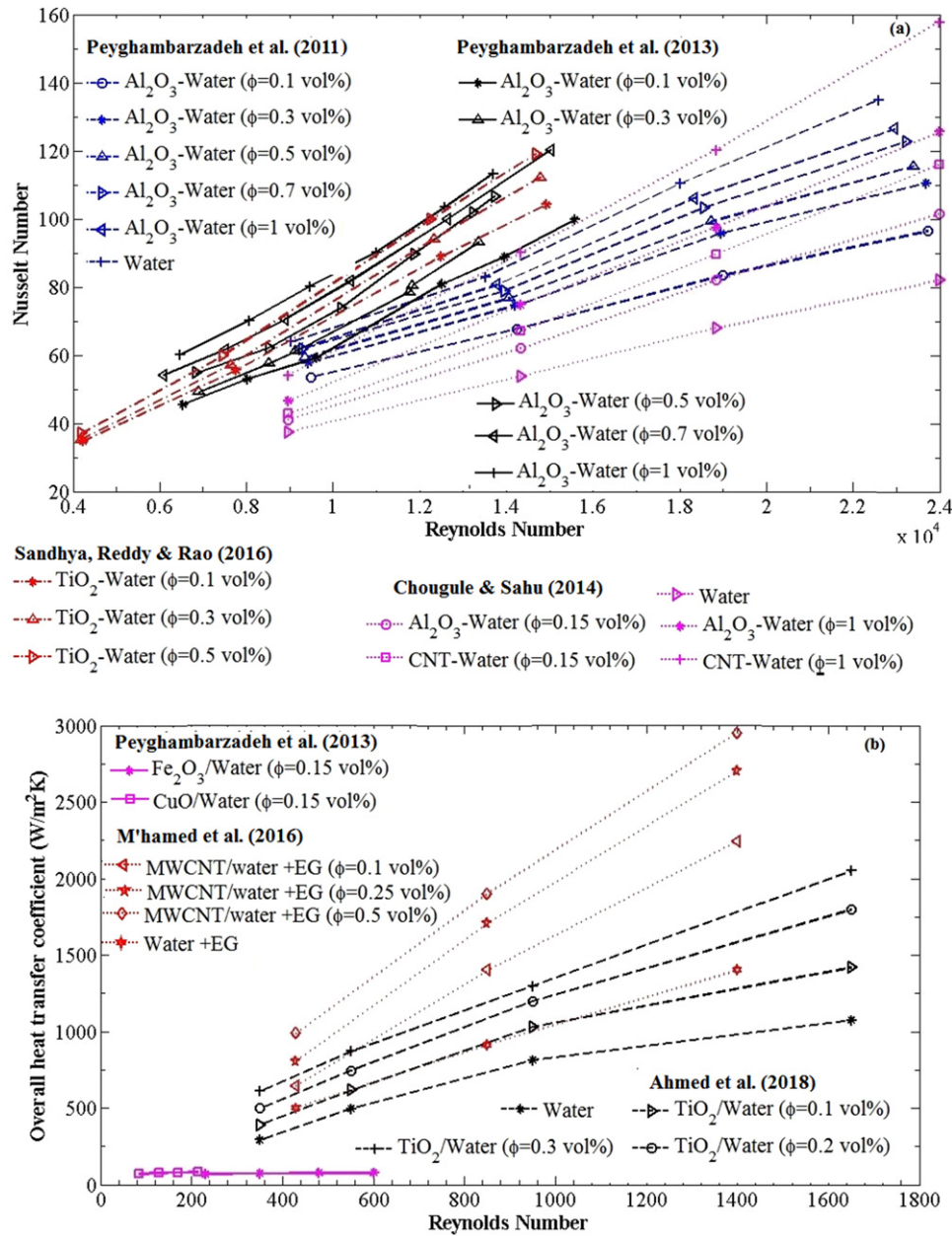


Fig. 4 Experimental heat transfer analysis of (a) at higher Reynolds number (b) at low Reynolds number.

using Runge–Kutta–Fehlberg method used. [Leong et al. \(2010\)](#) studied the performance of automobile radiator with nanofluid as a coolant. Different data and empirical correlation are used to investigate heat transfer performance mathematically and reported that heat transfer rate enhance with concentration. Reduction in frontal area about 19% with optimum parameters.

Challenges, Application and Future of Nanofluids

Recent researches on the nanofluids as an engine coolant are summarized in this article. The challenges that are facing by nanofluid industrial application are reviewed from the literature. Firstly, both the techniques used to prepare nanofluids are facing problems and that should be addressed for large scale cost effective production. More experimental and simulation work needs to be done to know the mechanism for stable nanofluids. Though two step method of preparation of nanofluids is mostly used and it is cost effective and can be used for large scale production but researchers still facing the stability problems with this technique. The main disadvantage with one step method of preparation is the high cost of synthesis. The other important factor needs to be addressed is the no chemical and corrosion effects on the heat transfer system. Better and longer stability of nanofluids will be the

indispensable milestone in the evolution of nanofluids as a coolant. The mechanism behind the enhancement of thermal conductivity is still indistinct, also the precise reliable theoretical model to predict thermal conductivity is unavailable. More experimental work is required to know the phenomena behind the enhancement in thermal conductivity and to develop a reliable general theoretical model to predict thermal conductivity. Moreover, the results of researchers are not consistent for different thermophysical properties. Another significant factor is increment in the viscosity which leads to requirement of additional power to pump high viscous nanofluids. Selection of optimum parameter such as shape, size, concentration of nanoparticles could be used to produce a coherent nanofluid with high thermal conductivity and less viscosity. The other vital opinion to increase the potential application of nanofluids is that no major changes only minor changes have to be in the cooling system.

Apart from application in car radiator cooling, the nanofluids can be applicable to engine lubrication. The application field of nanofluid is very wide like electronics cooling, medicine, space, nuclear, defence, biomedical, solar etc. Kim *et al.* (2007a,b) studied the feasibility of nanofluids in nuclear applications (Buongiorno *et al.*, 2009). In medical field the nanofluids are used with significant results in so many cancers related diseases (Scherer and Neto, 2005; Raj and Moskowitz, 1990). There are so many fields in which nanofluids can directly be applicable, researchers are working to make the nanofluids more consistent to make it commercial (Wong and Leon, 2010).

Moreover, nanofluids can be inevitably applicable to almost every field of heat energy exchanging system in the future. The industrial large scale cost effective production with better and longer stability of nanofluids will bring the revolution in the heat exchanging system field.

Outlook

The automobile engine cooling system and the coolants are summarized in this article. The different methods to synthesize nanofluids are discussed thoroughly. Thermal conductivity and viscosity are the key parameters of nanofluids potential in car radiator cooling. Effect of fundamental parameters on these key properties is discussed and compared. The performance of automobile car radiator experimentally and numerically studied by researchers are compared. The convective heat transfer in the radiator is compared of different researchers for different nanofluids. The Nusselt number and Reynolds number at various concentration for different material nanofluids car radiator are summarized. The challenges for the nanofluids in the radiator or car engine cooling is reported along with different application field and future scope of the nanofluid.

See also: Mechanical and Transmissibility Effect on Recyclable Suspension System for Different Loading of Carbon Black. Renewable and Sustainable Materials in Automotive Industry. Renewable Biofuels and Their By-Products for Automotive Applications

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An Assessment of Hydrogen Energy Utilization for Sustainable Development

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Introduction

Production and conversion technologies for hydrogen have been developed and well documented. It is proven that the utilization of hydrogen as a fuel has superior advantages over that of the other forms of fuels. Despite of all these advantages, hydrogen has not been extensively used in an industrial scale except in the outer space for space programs. Technical, social, economic and political aspects all contribute to the limited use of the hydrogen in a large scale. On the other hand, there is a growing awareness on the environmental damage and health consequences in using the fossil fuels. Thus, it has become inevitable to replace the conventional fossil fuel-based technologies with cleaner alternatives. Hydrogen based economy is a promising alternative.

When considering the environmental impact such as harmful emissions and waste of resources the energy efficiency is found to be the most important aspect. Therefore, it is desirable to improve the energy efficiency and the performance of any process to reduce the environmental consequences. Once the energy efficiency is improved, the harmful emissions and waste of resources will be reduced. The economic aspects of such processes will also improve.

Commercial use of hydrogen includes variety of processes such as ammonia production, hydrogenation of oils and fats, production of methanol, production of hydrochloric acid, and reduction of metallic ore. Hydrogen is also used in its liquid form as a cryogenic substance and for superconductivity. A major portion of the commercial hydrogen (nearly two-thirds) is used for ammonia production. Other uses of hydrogen include chemical processes such as hydrocracking, hydrodealkylation, and hydrodesulphurization. Hydrogen is also used as a fuel to a lesser extend for power and electricity production, and for heating purposes in buildings.

Since hydrogen is a clean source of energy without any harmful products during its use as a fuel it can help in preserving the healthy environment by reducing and/or eliminating the hazardous emissions that occur during the conventional fossil fuel consumption.

As the awareness on the environmental consequences of using non-renewable fossil fuels is increased, hydrogen-based economy has become one of the attractive options. However, hydrogen is not freely available in the earth in large quantities and therefore it is not a source of energy. Currently, it is produced through burning the fossil fuels such as natural gas, coal and oil. Thus, the production of hydrogen through these conventional methods lead to serious environmental problems. The clean option for producing the hydrogen remains to be its production through the renewable energy sources. As the renewable energy sources such as solar and wind are intermittent in nature, the hydrogen produced by the renewable energy sources is considered to be an energy carrier. This means that, the long term and wide spectrum of hydrogen-based economy and electricity production must be based on the hydrogen that is originated from the renewable energy sources.

Hydrogen-based economy is a very attractive option especially for the developing countries that do not have large amount of fossil fuel reserves and the required infrastructure but possess considerable amount of renewable energy. Stand-alone applications of the renewable energy sources make it more attractive for the under-developed countries and the remote localities where the national electrical grid is not available. The hydrogen generated through the renewable energy systems, then, may be converted to power through the fuel-cell power systems. Although the initial cost of such fuel-cell systems may be high, in the long run, they will be profitable from the economic and environmental point of view (Veziroglu and Barbir, 1992).

When hydrogen-based economy is considered, the entire system needs to be evaluated through the technologies used for the production, storage, transportation, distribution, and utilization of hydrogen.

Why Hydrogen Energy?

Depletion of Fossil Fuels

Currently two-thirds of the world energy demand is met by the fluid fossil fuels such as oil and natural gas. This is because these fuels provide convenience and are readily available as they can be easily transported and stored. Coal also have a significant share in world energy supply. However, these non-renewable energy reserves of are expected to become non-feasible as they are being depleted. The production of fossil fuels is estimated to decrease after a peak is reached. On the other hand, the world energy demand is expected to increase in a continuous manner, as a result of increase in the population and the need for improving the living standards that would require more energy consumption per capita.

The total world population was estimated to be 7.7 billion in 2018 and is expected to reach about ten to twelve billion by the end of the 21st century. The energy demand is estimated to double by the end of the century. Therefore, there will be a growing gap between the demand and the production of fossil-fuels that are not renewable. This will lead to increase in the prices of fossil fuels during the coming several decades. This motivates the development of technologies for the non-fossil and renewable energy alternatives such as solar, wind, geothermal, biomass, and the development of hydrogen-based economy that is based on such renewable alternatives.

Damage to the Environment

It is well known that the technologies used for extraction, storage, transportation, processing and utilization (i.e., combustion) of fossil fuels lead to serious environmental damage and result in negative impact on the economy and the society (Barbir *et al.*, 1990).

The harmful emission through the combustion of fossil fuels cause air pollution that is a source of damage for the human health, animals, plants, and buildings. In turn, the air pollution leads to global warming and reduced visibility. The pollutants that are emitted to the atmosphere form acid rain in the form of sulfuric and nitric acids after chemically reacting with water and other atmospheric compounds with the aid of the sunlight. These acids that are produced may also appear in the form acid dew, acid fog, and acid snow. The harmful pollutants may turn into secondary pollutants too such as ozone, aerosols, and peroxyacyl nitrates.

Carbonic acid is produced by carbon dioxide in equilibrium with water. Deposition of this carbonic acid in wet or dry from causes damage for the terrestrial ecosystem. It causes soil and water acidification which affect the life on the earth through adverse consequences in humans, animals, plants and buildings. Carbon dioxide and other combustion (greenhouse) gases such as methane, nitrogen oxides and chloro-fluorocarbons lead to warming of the atmosphere. This occurs as a result of increased absorption of the infrared radiation emitted by the earth into the atmosphere and the solar irradiation causing global warming. As the atmospheric temperature rises the ice cap around the poles melt causing serious climate changes and rise of the sea level. This in turn, results in natural disasters such as floods and storms in some areas and droughts, heat waves and wildfires in the other.

Properties of Hydrogen

Hydrogen is the smallest element. Its molecular mass is 2.016. It has no color and odor. The density of hydrogen is 0.08376 kg/m^3 that is roughly 14 times less than the air at the standard atmospheric temperature and pressure. The heating value of the hydrogen is two to three times higher than that of other fuels. Combustion of hydrogen is possible over a wide range of gas concentrations. As the hydrogen is burned it produces only water causing no harm to the environment. Therefore, hydrogen is a clean and harmless fuel if it is produced using the renewable energy sources. It can be produced by breaking apart the water molecule and separating the hydrogen in a so-called electrolysis process using electricity. When it is re-combined with oxygen in the air electricity or heat can be produced. As the hydrogen is burned, the combustion products contain only water and no polluting agents such as particulate, carbon dioxide, or carbon monoxide are produced.

Challenges in Using Hydrogen

Despite of all the above-mentioned superior properties of hydrogen, it is not yet widely used in a large scale for industrial applications. Various unresolved political, economic and social issues hinder the development of hydrogen economy. Lack of consensus on the energy priorities, the public perception in relation to the safety of hydrogen energy and the economic aspects of hydrogen energy production, storage and transportation all contribute in restricting the widespread use of hydrogen energy. On the other hand, there are other supporting aspects for the hydrogen economy development. Dependence on the foreign energy supply is a primary concern for national security. The environmental degradation in using fossil fuels and the increasing demand for the energy are some of the supporting aspects in the development of the hydrogen-based economy.

Apart from the political, economic and social issues there are yet significant challenges in relation the scientific and technical aspects in promoting the hydrogen economy. These challenges refer to the production, storage, transportation and use of hydrogen. Once the scientific and technical challenges on the production, storage, transportation and use are resolved the required infrastructure need to be built or part of the existing energy infrastructure may be modified and used for the smooth transition to hydrogen economy. The infrastructure needed should accommodate all the technical steps from the production to the consumption of hydrogen. For the hydrogen economy to become a reality, it should also be demonstrated that hydrogen as the energy carrier is competitive in terms of unit cost of energy.

Hydrogen Production Technologies

Hydrogen From Fossil Fuels

Currently, most of the industrial hydrogen is produced from the natural gas through the steam reforming process. Coal and biomass are also used for hydrogen production, but these resources produce larger amounts of CO_2 . Steam reforming of these resources is also complicated because they contain water, sulfur, nitrogen and nonvolatile minerals.

Hydrogen that is produced from the fossil fuels is mostly used in the agricultural (to produce fertilizer), petroleum and chemical industries. It is also used for transportation and food industries. Therefore, it is important to establish safe and cost-effective methods for treating and storing the generated CO_2 in reforming the fossil fuels. In relation to safe storage of the produced carbon dioxide various technologies are proposed. These include injection into deep ocean, depleted oil wells and saline reservoirs (Kim and Edmonds, 2000). The non-purity of hydrogen produced by the steam reforming of fossil fuels poses another

challenge and drawback in direct utilization of hydrogen for the fuel cells and for the transportation sector. The purification process requires costly purification systems.

Hydrogen From Solar Energy

Solar energy is the most promising source of clean energy for producing hydrogen. Hydrogen can be produced using solar energy through electrolysis of water with solar cells, photocatalytic and photobiological processes in which water is split into hydrogen and oxygen, and through solar thermal process. The advantages of producing hydrogen through these processes using solar energy include its purity and suitability for use in low temperature fuel cell applications and for automobiles. There are many applications of solar hydrogen. However, the main drawback for the wide-spread use of solar hydrogen is the cost of solar cells and their efficiency. The current efficiency of solar photovoltaic cells varies between 3% and 25%. For the solar hydrogen to be a widespread and feasible option, the cost of solar cells and particularly their efficiencies need to be improved. Then, the solar hydrogen with its high purity will promote the wide-spread implementation of fuel cells by eliminating the expensive purification systems.

Hydrogen From Biological Systems

Hydrogen is the most common element in biological systems. Most commonly used method of hydrogen production from the biological systems is the anaerobic fermentation (Etiope and Klusman, 2002). Renewable and clean hydrogen can be produced by gasification, anaerobic digestion and cellulosic ethanol processes. The biomass gasifier produces carbon monoxide, carbon dioxide, methane and hydrogen. The anaerobic digesters primarily produce methane by which hydrogen is produced using steam reforming process. During the cellulosic ethanol production hydrogen can also be produced through a thermochemical process. There are significant efforts directed to understanding the type of organisms and the biochemical processes that are responsible for efficient production of biological hydrogen (Reysenbach and Shock, 2002). These processes can be improved considerably and optimized for large scale cost-effective hydrogen production.

Hydrogen production from the biological systems occurs naturally in a substantial amount. However, this process takes place in highly distributed fashion and in low density. Large quantities and concentrated form of biological hydrogen production would be needed for the industrial applications of such resources. Yet the efficiency of biological hydrogen production through living microorganisms is relatively low as compared with that of solar photovoltaic electrolysis process. Cost competitive biomass-based hydrogen can be produced as a result of maturing of the biomass gasification technology and reduction in the feedstock costs.

Hydrogen Production by Thermal Energy

Thermal energy can also be used directly to split water into hydrogen and oxygen without a need for the electrical energy and electrolysis process. In this case, the process is named thermo-chemical water-splitting for which the thermal energy or heat required is obtained through concentrated solar energy, burning fossil fuels or nuclear reactions. The temperature needed for such process is in the order of 500°C which can easily be obtained by concentrated solar power. There are several proposed thermo-chemical cycles available in the literature for producing hydrogen from the thermal energy using high temperature reactors (Brown *et al.*, 2002). Among these cycles; the calcium bromide-iron oxide cycle, the Westinghouse cycle, and the sulfuric acid-hydrogen iodine cycle are the most promising ones. In such cycles, corrosion and high temperature failure of materials are the challenges to overcome. Finding suitable materials for enduring such aggressive chemical environment is the main barrier for the development of this technology.

Safety Hazards in Hydrogen Use

For the public reception of the hydrogen economy there are two main issues. These relate to the safety and the environmental concerns. Safety is perhaps the most important concern when it comes to adopting the fuel in an industrial scale. Safety hazards of hydrogen exposure for the human health needs to be assessed in a detail manner. Long term exposure in particular may be harmful for the health. Safety and environmental concerns are directly associated with the social and technical challenges that need to be considered and resolved for the viability and success of hydrogen economy. The safety hazards in relation to use of hydrogen can be classified into three main types; they are either *physiological* (frostbite, respiratory ailment, and asphyxiation), *physical* (phase changes, component failures, and embrittlement), or *chemical* (ignition and burning) (NASA, 1997).

Physiological Hazards

Due to the small size of hydrogen molecule, it has higher tendency and ability for leakage as compared with other gases. On the other hand it can be ignited in a wide range of concentrations. Therefore, hazards in relation leakages, fires, explosions may occur. These will lead to injury of the people and toxicity of the surrounding. Leakage of hydrogen gas in the air may lead to dilution of the oxygen which in turn may cause asphyxiation especially in closed spaces. Explosion of hydrogen gas may also cause injury for

the people around as it may result in pressure waves. As the flame originating from the hydrogen burning is invisible it may affect people by radiant heat from the hydrogen flame. The level of the injury in this case depends on many factors such as the time of exposure, rate of burning, heat of combustion, size of burning area, and the humidity of air in the surrounding. Contact with the cryogenic liquid hydrogen may cause cryogenic burning. Exposure with the large amount of cryogenic liquid hydrogen could result in hypothermia unless proper precautions are taken.

Physical Hazards

Due to its smaller size, hydrogen's ability to leak through holes and joints at low pressure is 1.26–2.8 times faster than that of natural gas (Larminie and Dicks, 2003). Therefore it requires more careful sealing when stored in vessels and transported through the fuel lines. Another serious aspect of the hydrogen use is that long term exposure of hydrogen gas causes hydrogen embrittlement for the metallic and non-metallic materials in contact with it. This will degrade the mechanical properties of the storage containers, pipe lines and the seals.

The range of flammability (ignition range) of hydrogen and air mixture varies from 4% to 75% on volume basis as shown in Fig. 1. This range is considerably larger than that of methane and gasoline. The ranges of flammability for natural gas, propane, and gasoline are 5.3%–15%, 2.1%–10%, and 1%–7.8%, respectively. Lower limit of ignition of hydrogen is slightly less than that of methane but higher than gasoline and propane (Larminie and Dicks, 2003; Ogden, 2002).

The energy required for the ignition for hydrogen as well as methane and gasoline is shown in Fig. 2. It needs very low energy (0.02 mJ) for igniting hydrogen. The other two fuels, namely methane and gasoline, require about ten times higher energy for the ignition. This shows how easy it is for the hydrogen to catch fire. The flame speed of hydrogen is roughly 7 times larger than that of the natural gas or gasoline. Therefore, detonation and deflagration may occur much easier during the hydrogen combustion. On the other hand, the detonation in case of hydrogen combustion may start at 13%–18% hydrogen/air mixture which is 2 and 12 times higher than that of natural gas and gasoline, respectively. In addition, the explosive energy during the explosion of hydrogen

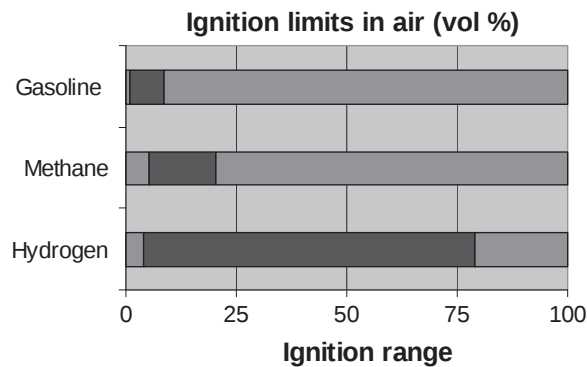


Fig. 1 Flammability ranges of three gaseous fuels in air.

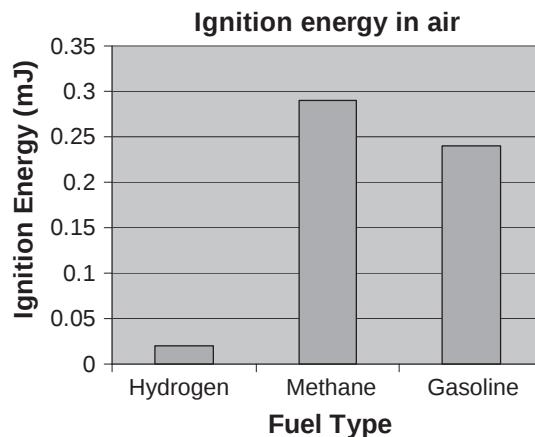


Fig. 2 Comparison of ignition energies of three gaseous fuels in air.

gas is 22 times less than that of gasoline vapor for the same volume of fuel. However, dangerous explosion may occur when hydrogen leaks through a relief valve. As the flame of hydrogen is invisible, people may not be aware of the flame and the existence of fire when it occurs.

Chemical Hazards

Oxygen depletion is one of the serious consequences in burning hydrogen. As the combustion process takes place oxygen is permanently removed from the atmosphere (Santilli, 2000). This happens when the hydrogen that is generated using fossil fuels reacts with oxygen in the air. The solution for this problem would be to use renewable energy such as solar power for producing the hydrogen fuel via electrolysis process. However, this process is costly and has low efficiency.

Density of hydrogen is very low. Therefore, it does not have sufficient energy density and is not suitable in its compressed form for use in vehicles. Therefore, it needs to be carried in the liquid form. This causes additional cost and complication during the transportation, storage, distribution and use.

Hydrogen in its gas form must be kept confined in storage tanks and transportation lines so that no leak occurs. It is essential to study the consequences of leak in large quantities in case it occurs especially in closed spaces.

Hydrogen gas has its own characteristic features different from the conventional fuels. Its ability to embrittle the materials that it is in contact with for long duration, its very low density and therefore its high buoyancy, its easily leaking and fast diffusion behavior, and its combustion characteristics are all very different from the other common fuels. As the hydrogen economy is promoted further research needs to be carried out to explore the hazards in dealing with hydrogen. At the same time, considerable efforts are needed for educating people on the consequences of hydrogen use and required training should be provided to the personnel that will handle hydrogen in various fields of hydrogen economy.

Storage of Hydrogen

Hydrogen is stored either in gaseous form, or liquid form, or in metal hydrides. There are challenges in each of this type of storage technologies. Due to its low density and low boiling point, a reasonable amount of hydrogen fuel for driving a vehicle will require a very large size of tank. In automotive industry, hydrogen tanks containing gaseous hydrogen at a pressure of up to 800 bar are being used. The advantage of storing hydrogen in gaseous form under high pressure is that it does not require additional energy to extract the hydrogen from the storage medium. However, filling the fuel tank with high pressure is rather costly since this requires powerful compressors. Other methods of storing large quantities of hydrogen gas include underground caverns, salt domes, and depleted oil/gas fields.

Cryogenic hydrogen in the liquid form provides high energy density. Liquid hydrogen is usually stored in metal storage tanks. It can also be stored in organic liquids. The main advantage of storing hydrogen in the liquid form is that it provides high energy density without requiring high pressures. However, the main disadvantage of liquid hydrogen storage is that it is a very costly process to liquefy hydrogen. In addition is required to provide good insulation. Otherwise, the evaporated liquid hydrogen as a result of heat leak to the cryogenic hydrogen needs to be vented in order to prevent over-pressurization of the storage tank. This constitutes significant losses of hydrogen.

Hydrogen can also be conveniently stored in certain materials by adsorption, absorption, and chemical reaction. For the case of adsorption, hydrogen in its molecular form is attached to the surface of solid materials that are kept at low temperatures and high pressures. Hydrogen is extracted by reducing the pressure and increasing the temperature. This method requires highly porous materials with high surface area. In this respect, zeolites, metal oxides, carbon nanotubes and graphene are some of the popular choices as adsorption materials. Since high pressure is not needed, this method is a relatively safe method of hydrogen storage. For the case of absorption, hydrogen is absorbed in the bulk of material that is named metal hydrides. Metal hydrides can provide large storing capacity of hydrogen and are resistant to damage. The main disadvantage in using metal hydrides is that refueling of hydrogen may take longer. In this regards, light weight metals such as Li, Mg, Al and Na are being investigated in order to reduce the weight of the metal hydride storage system. In chemical hydrogen storage method, chemical reactions are used to generate and use hydrogen. In this regard, chemical hydrides are reacted with water and alcohol to produce hydrogen.

Transportation of Hydrogen

Transportation of hydrogen is done currently in three major methods; pipelines, high-pressure trailers, and liquified hydrogen tankers. Transportation of hydrogen through pipeline requires expensive infrastructure, however, the operation cost will be low. Hydrogen embrittlement is an important issue and therefore the current pipeline can not be used for this purpose. High pressure trailers are more convenient for transporting pressurized hydrogen gas, however, the cost is higher. This mode of transportation is especially suitable for small market needs because the capacity of the trailer is limited. Liquified hydrogen tankers are more convenient for transporting hydrogen in longer distances using trucks, railway, and ship. The major problem in this kind of transportation is the insulation to minimize the heat transfer and therefore the

evaporation losses. This mode of transportation is the most common and preferred method and offers the cheapest among all the options of transportation.

Hydrogen Energy Conversion Methods

There are mainly two methods of energy conversion using hydrogen. As a fuel, hydrogen can be used in internal combustion engines and in fuel cells. Hydrogen can be used in the existing internal combustion engines with small modification. The required modifications are due to the different properties of hydrogen as compared with those in other fossil fuels. These properties are the required low ignition energy, the flammability range, flame speed, autoignition temperature, diffusivity rate and the density. The most important advantage of hydrogen over the other common fuels is that hydrogen combustion does not produce any environmental pollution. On the other hand, hydrogen is directly converted to electricity in fuel cells through electrochemical process. The most fuel cells are proton exchange membrane and solid oxide fuel cells.

Conclusions

Use of hydrogen as an energy carrier in a wide spread hydrogen economy was discussed. The challenges and the safety issues that need to be addressed were presented. The socio-economic aspects of hydrogen energy use were analyzed. It is shown that hydrogen economy has superior advantages over the current fossil-based economy in terms of environmental impact and sustainability. However, there are still important scientific and technical challenges to overcome before the hydrogen economy to become a reality. Many of these challenges can be overcome through the recent advances in renewable energy with the help of materials science, physics, biology, chemistry, and nano-science. The superior properties of hydrogen over the conventional fossil fuels offer motivation and promise for implementation of the hydrogen economy. The concerns related to the safety hazards for the people, equipment and the environment have been presented by considering the phases of production, storage, transportation, and end usage.

Acknowledgement

The author acknowledges the support provided by the Deanship of Scientific Research at King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia for this work under Research Grant IN161064.

See also: CO₂ Capture, Storage, and Enhanced Oil Recovery Applications. Utilization of Bio-Hydrogen in HCCI Engines as a Most Renewable Fuel for Sustainable Transportation – A Thermodynamic Analysis

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Bacterial Cellulose Based Nanocomposites for Electronic and Energy Applications

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Cellulose is a naturally occurring biopolymer produced by both plants and certain types of bacteria. Cellulose has a highly developed hierarchical structure made of the basic block or monomer $[C_6H_{12}O_6]$ which is nothing but a simple sugar molecule. This saccharide molecule undergoes polymerization to a long chain polysaccharide which forms the backbone of the macroscopic cellulose fiber. The number of monomers in this long chain polymer vary depending on the source, plant or bacteria, and also on the synthesis technique, up to $\sim 15,000$ units. The alternate chains are rotated by 180° in order to overcome the steric hindrances so as to achieve a dense packing of chains. These bundles of chains are known as microfibrils with a typical diameter of about 3–4 nm and the crystallographic unit in these microfibrils has typical unit cell size of $0.8 \text{ nm} \times 0.8 \text{ nm} \times 1.0 \text{ nm}$. This means the microfibril has a width of 3–4 unit cells. It should be noted here that cellulose exists in many polymorphic forms – Cellulose I to IV depending on the treatment given to the natural cellulose which is Cellulose I. The microfibrils in turn are aligned and bundled into aggregates known as macrofibrils which can range in diameter/width from 10 to 30 nm and can extend in length up to several microns. The essential differences between plant and bacterial cellulose are:

- Average degree of polymerization in plant cellulose is typically lower compared to bacterial cellulose and as a result, the microfibril length is reduced.
- Plant cellulose invariably exists together with hemicellulose and lignin which are amorphous polysaccharides with short chain length. Bacterial cellulose, on the other hand, is pure form and hence has better mechanical strength compared to plant cellulose.
- The extent of crystallinity in the microfibrils is far higher compared to that of plant derived cellulose.

Bacterial cellulose (BC) with its high purity, crystallinity and hence mechanical strength is considered to be an excellent choice to be functionalized for a variety of applications ranging from simple speaker diaphragm to active electronics. The added advantage of this material is that it is biocompatible together with being biodegradable. Hence some of the most recent applications of BC for the electronics and energy sector are discussed below. These applications are by no means exhaustive in collection and are only intended to highlight the role of BC. Before discussing these applications, the biochemical synthesis mechanism and commercial production methodologies are discussed in brief as it is non-trivial to synthesize large quantities of good quality BC.

Biochemical Synthesis Mechanism

Microbial cellulose is produced naturally by a variety of microorganisms such as bacteria, and algae. Gram-negative bacteria such as *Acetobacter*, *Agrobacterium*, *Azotobacter*, *Rhizobium*, *Pseudomonas*, *Salmonella*, *Alcaligenes*, and Gram-positive bacteria such as *Sarcina ventriculi* are capable of producing cellulose. However, the most widely studied bacterial genera belong to three major groups namely, *Acetobacter xylinum*, *Acetobacter hanseii*, and *Acetobacter pasteurianus*. Amongst these, *Gluconacetobacter xylinum* (now renamed as *Komagataeibacter xylinus*) has been extensively used for the synthesis of cellulose at a laboratory scale as the cellulose yield obtained is quite high in terms of quantity and quality, which also justifies the growing commercial interest. The exact biological function of cellulose, synthesized extracellularly by different prokaryotes such as bacteria and algae is still not completely known. It is widely believed that these microbes, especially the bacteria, produce cellulose in order to protect themselves from extreme conditions in the environment (heat, UV radiation, etc.). It is also speculated that the low density of cellulose allows the bacteria to remain anchored to them at the interface of the culture medium and air (in static reactor models), thereby providing ambient conditions for optimal growth through cell division (Vitta and Thiruvengadam, 2012).

Nevertheless, the biochemical processes that lead to the formation of cellulose and the synthesis pathway are very well understood in the bacterium *Gluconacetobacter xylinum*. The synthesis proceeds via two main steps:

- The first step consists of the formation of uridine diphosphoglucose (UDPG) from carbon precursors by phosphorylation reaction (which maybe sugars such as glucose or fructose, or other compounds such as pyruvates, di-carboxylic acids, etc).
- The second step involves the polymerization of glucose into long and unbranched chains of cellulose through β -1,4-glycosidic linkages.

In the first step, glucose and fructose (which are present together in the culture medium) get converted to Glucose-6-phosphate through some enzyme-mediated reaction steps involving glucokinase, phosphoglucumutase, etc as biocatalysts. The Glucose-6-Phosphate thus obtained, forms the basis for the production of uridine diphosphoglucose (UDPG) in the presence of UDP-glucose pyrophosphorylase. Phosphorylation of glucose is the most important step in this process as the UDPG serves as the substrate for the enzyme cellulose synthase, in the second step. The complex enzymatic machinery with one end bound to UDPG in the cytoplasm and the other end extending outward from the phospholipid bilayer outer membrane performs the essential task

of synthesizing cellulose by polymerizing approximately 200,000 glucose units per second (Ross *et al.*, 1991). Cellulose synthase is assisted by accessory proteins present in the cytoplasmic membrane and the cellulose produced, extends outwards through pores present on the cell surface, each orifice measuring ~ 10 nm in diameter. Through the pores, sub-elementary fibrils of 1.5 nm of cellulose emerge and aggregate together to form a microfibril. Several bundles of microfibrils extend three-dimensionally to create the highly porous network of microbial cellulose. The packets of microfibrils are highly directional in their orientation, and these are associated with high crystallinity which is observed in BC.

In addition to the high degree of crystallinity (about 71%), BC is exceptionally pure (99% water and 1% cellulose in hydrogel form) and possesses good tensile strength (Young's Modulus of 33.3 GPa). Moreover, it is chemically inert, highly flexible, biocompatible and biodegradable. Due to its superior properties, efforts have been made to scale up the production of microbial cellulose, and some pilot plants have been set up.

Production of Bacterial Cellulose

Bacterial cellulose utilization on a commercial scale requires the production of BC in large quantities, and the prospects in this regard are quite challenging. This section aims to provide a brief overview of the various traditional and industrial methods of BC cultivation and the latest developments in this field.

The most common method of laboratory synthesis of microbial cellulose involves acetic acid bacteria of the genus *Gluconacetobacter*. Static and dynamic culturing methods have been used for growing cellulose. In the static mode, the bacterial culture is kept undisturbed in a shallow tray for several days till a smooth, continuous pellicle growth of cellulose is observed. The dynamic method includes airlift reactors, shaker flasks, rotary reactors, and agitated cultures. While the static reactors yield thin sheets of bacterial cellulose of homogenous thickness, those obtained by dynamic methods are in the form of lumps and globules (Wu and Li, 2015).

Production of BC in the static reactor method depends on the surface area and the availability of air for the cellulose growth. The bacteria responsible for the production of cellulose are often found anchored to the growing cellulose sheet, and the growth of cellulose ceases as soon as oxygen supply gets interrupted at the interface of culture medium. However, at present, BC is cultivated for commercial applications from Nata De Coco by the fermentation process and is often termed as 'biocellulose' (National Research Council (U.S.), 1992). Biocellulose is produced in large quantities in the form of 'bacterial cellulose fleece' which are obtained from large plastic containers under static conditions. Biocellulose thus obtained is suitable for food and cosmetic industries but cannot be used for other applications in medical, pharmaceutical, electronic and energy devices as it requires BC grown under uniform culture and growth conditions with exceptional purity and material stability. Furthermore, BC production using conventional static reactors cannot be scaled up for commercial applications due to the slow growth rate of microbes and the limitation in oxygen supply at the interface of the cellulose. Therefore, taking economic factors into consideration, horizontal lift reactors, rotating disc reactors and bubble columns are preferred for the growth of cellulose in bulk quantities for industrial applications (Krystynowicz *et al.*, 2002).

In a rotating disc reactor, the bacteria responsible for the growth of cellulose are attached to the rotating disc such that they alternate in contact with the culture media and oxygen during the course of rotation. The production of BC in these reactors is influenced by factors such as the ratio of surface area to volume of the media and rotational speed. The advantages of this process are ample supply of oxygen and lack of shear stresses in the solution which serves to promote the growth of bacteria thereby increasing the output of cellulose. Optimal production of BC was achieved by Krystynowicz *et al.* (2002) with a rotational speed of 4 rpm and a surface area to medium volume ratio of 0.71 cm^{-1} .

Jung *et al.* (2005) developed and investigated a novel system equipped with a turbine impeller and a spin filter for the production of BC. The entire system comprising of the impeller with six blades and a spin filter, is encased in a stainless steel cylinder, attached to an agitator shaft. The maximum yield of BC was 4.57 g/L after 140 h of culture using *Gluconacetobacter Hanseii*, maintained at an acidic pH of 5.0 at ambient temperature. This reactor is a static reactor where BC pellicles form on both the surface of an oxygen-permeable synthetic membrane and on a liquid surface. Also, thin sheets of bacterial cellulose have been obtained by the use of support structures such as silicone rubber, porous membranes, polymer composite materials and agar (Islam *et al.*, 2017). However, the yield is still considered quite low for pilot-scale production of BC.

The latest addition to the list of bioreactors for the production of BC is the Horizontal Lift Reactor or HoLiR which is a novel bioreactor that combines the benefits of both static and agitated cellulose growth methods. The approach was first demonstrated by Kralisch *et al.* (2009) by using a 180 L bioreactor. HoLiR allows for steady-state yet semi-continuous cultivation and harvesting of BC fleeces in planar form. The method has been adopted and successfully scaled up by JeNaCell, the German company that leads the production of high-quality BC-based products for cosmetics and dermatological applications. Other pioneers in the field include BOWIL Biotech in Poland, S2Medical in Sweden, fzmb in Germany and DePuy Synthes in Pennsylvania, USA, who are engaged in the development of therapeutic and cosmetic products based on BC (Klemm *et al.*, 2018).

The up-scaling of HoLiR by JeNaCell has paved the way for mass production of high-quality BC which could open up new avenues for sophisticated applications in the electronics and energy sectors apart from the medical industry. However, it is believed that detailed studies on the biochemical pathways, media used for cultivation of BC and its control variables, as well as the design parameters for bioreactors could improve the production efficiency of BC even further.

Electronic Devices

Electronic appliances, in general, are posing a serious threat to environment, specifically with respect to mounting quantities of waste. Among the several items that comprise electronic appliances, computers and mobile phones contribute the maximum to mounting waste because of their relatively short life span compared to appliances such as washing machines, air conditioners and so on. This electronic waste contains both metals and polymers which can cause significant environmental damage and thus detrimental effects to human health, if not properly handled and recycled. Hence it becomes imperative to develop highly efficient handling and recycling technologies to mitigate environmental damage. A better alternative, however, would be to develop new environmentally compatible and sustainable materials that will deliver the same functionalities. In this context, cellulose becomes a highly attractive material due to its environmental suitability and sustainable nature coupled with its mechanical strength. Functionalizing this material for various applications ranging from imparting simple electrical conductivity to different actuators can lead to better environmentally friendly devices. A few of such most recent efforts in developing BC based nanocomposites are discussed below.

Bacterial cellulose with its fibrous structure exhibits extremely good mechanical strength and a dielectric behavior due to the polar arrangement of saccharide molecular chains. Apart from these two inherent properties, cellulose does not have any other property which can result in functionality to cellulose. Hence in order to induce other functionalities, suitable secondary phase materials have to be incorporated. To induce dual functionalities of electrical conduction and magnetic response, Thiruvengadam and Vitta incorporated nanoparticles of Ni in one case and permalloy in the other into freeze dried BC by aqueous state reduction of precursors (Thiruvengadam and Vitta, 2017a,b). The conductivity of Ni particles incorporated in the BC was found to increase by 7 orders of magnitude for a loading of 20 vol% of nanoparticles. This composite paper had a magnetic energy product of $\sim 60 \text{ J m}^{-3}$, Fig. 1(a) and (b). The permalloy incorporated bacterial cellulose xerogel also exhibits soft magnetic behavior as well as electrical conductivity, Fig. 2(a) and (b). The presence of electrical conductivity as well as magnetic sensitivity even in the hydrated state of the nanoparticle composite clearly shows that the nanoparticles are firmly attached to the cellulose fiber surfaces and not loosely held in its porous structure. This work clearly demonstrates that multiple functionalities can indeed be induced in bacterial cellulose. The main limitations of this approach however are:

- (1) The cellulose loses its transparency as well as becomes black in color, and
- (2) Changes in conductivity and magnetization with repeated cycles of bending to demonstrate flexibility have not been reported.

These studies would be very relevant for practical application of these nanocomposite sheets.

The loss of optical transparency and color of bacterial cellulose due to functionalization can be a limitation in certain applications. In order to overcome the loss of color, Sriplai *et al.* (2018) have developed a 'sandwich' strategy to overcome the blackening and synthesized a white, magnetic, xerogel paper. The black magnetic paper consisting of CoFe_2O_4 nanoparticles dispersed in the cellulose reticulate structure was sandwiched between two white cellulose sheets consisting of ZnO nanoparticles. The ZnO nanoparticles in cellulose provide 'whiteness' while the CoFe_2O_4 nanoparticles induce magnetic response, Fig. 3(a). The magnetic nanoparticles loading was $\sim 43 \text{ wt\%}$ and the whitening ZnO nanoparticles was either 24 wt% or 39 wt%. The whitening index of the resulting sandwich xerogel paper increased from $\sim 27\%$ to $\sim 85\%$ due to the addition of two 39 wt% ZnO

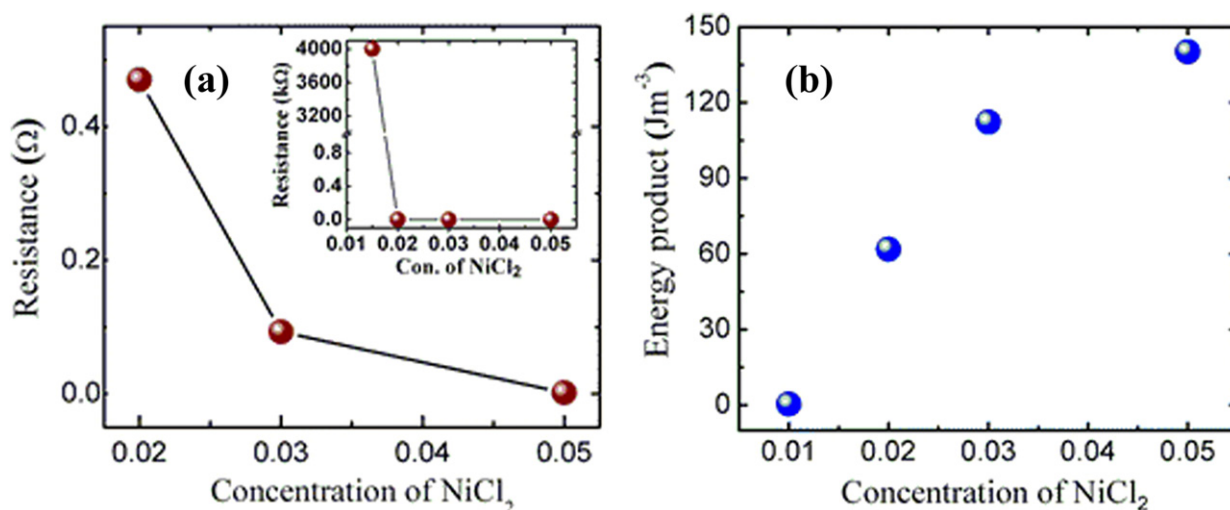


Fig. 1 (a) Variation in electrical resistance of Ni nanoparticle embedded BC nanocomposite with increase in the concentration of NiCl_2 in the precursor solution from 0.02 to 0.05. Inset: Sharp drop in electrical resistance by several orders of magnitude as a function of precursor concentration shows the onset of conductivity. (b) Increase in magnetic energy product (BH_{max}) of NiBC nanocomposite with increasing concentration of NiCl_2 precursor solution.

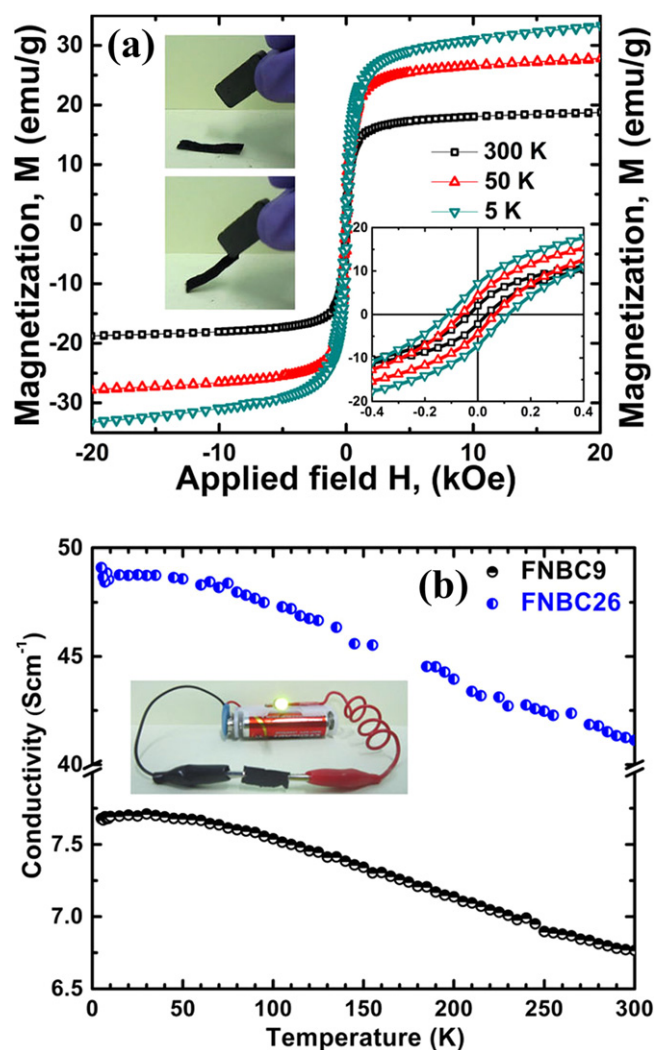


Fig. 2 (a) Field dependent isothermal magnetization, M of FeNi_3/BC nanocomposite xerogel hot pressed at 60° at 9 MPa (FNBC9) at temperatures of 5, 50 and 300 K. Inset: Hysteresis loops at low fields for FNBC9 at 5, 50 and 300 K show coercivity and hence ferromagnetic behavior. Photograph illustrates the magnetic actuator response of the xerogel sheet. (b) Comparison of temperature dependent d.c. electrical conductivity of FNBC9 and FNBC26 xerogels indicating metallic conduction behavior. Photograph demonstrates electrical conductivity at room temperature.

nanoparticles containing hydrogel sheets on either side of the magnetic hydrogel. The specific magnetization of the resulting xerogel paper is about 20 emu g^{-1} , $\sim 1/4$ the specific magnetization of bulk CoFe_2O_4 . This work clearly shows that a white magnetic paper can indeed be synthesized albeit by the addition of two ZnO-nanoparticle containing papers. This work, like the earlier work wherein metal/alloy nanoparticles were introduced into bacterial cellulose, does not clearly demonstrate flexibility of the paper except for a tensile test. The tensile test only proves that the ductility and strength of the white, sandwich paper, and decreases compared to that of bacterial cellulose, [Fig. 3\(b\)](#).

One physical property, which is of extreme importance for any material to be used in electronic devices is its electrical conductivity. Bacterial cellulose lacks electrical conductivity due to the nature of bonding that exists between the different elements in it, although it is predominantly composed of carbon. Hence in order to induce a conducting behavior to this cellulose, various strategies such as incorporation of different types of conducting secondary phase materials varying from metals to carbon nanotubes and polymers have been explored. Most recently, Thiruvengadam and Vitta demonstrated that introduction of metal and alloy nanoparticles such as Ni and permalloy achieves the dual purpose of imparting electrical conductivity together with magnetic sensitivity ([Thiruvengadam and Vitta, 2017a,b](#)). These nanoparticles, however, are not completely biocompatible and if used in electronic implants or devices in the human body, tend to display cellular toxicity. Hence for bioelectronic device applications, secondary phase materials which are non-toxic to the human body environment need to be selected.

Recently, feasibility of making electrically conducting bacterial cellulose films consisting of noble, bio-inert elements such as Ag and Au has been demonstrated. [Lv et al. \(2018\)](#) synthesized bacterial cellulose film and Ag nanowires of size 196 nm width and 150 μm long separately. These nanowires were then spread onto BC film by suction filtering method, which consists of filtering the

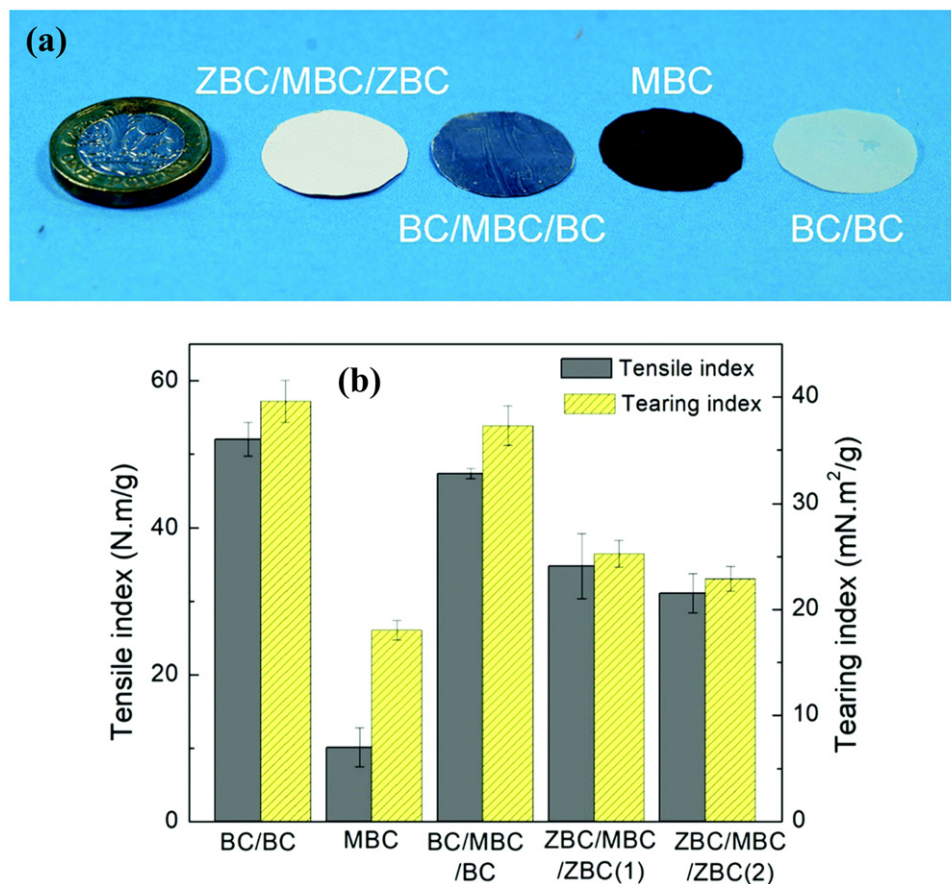


Fig. 3 (a) The photograph shows clearly the formation of white magnetic paper due to sandwich strategy. MBC and ZNC represent magnetic BC and ZnO containing BC respectively, (b) The mechanical behavior, strength and tearing index of the different xerogel sheets is shown here.

homogeneously dispersed solution of nanowires through the BC film acting as the filtering medium. This resulted in the formation of Ag nanowire-containing film on BC and imparted electrical conductivity. It is however, not very clear if the 150 μm long Ag wires are retained on the top of BC or if they indeed penetrate into the BC film to provide bulk conductivity. This appears to be a major limitation of this approach to impart electrical conductivity to BC. Moreover, it is not clear whether the Ag nanowires undergo rupture after cyclic loading and the subsequent effects on electrical conductivity have not been demonstrated in this work. Khan et. al. followed a similar approach of synthesizing the two components, BC film and Au nanoparticles separately and subsequently introduced the Au nanoparticles into the BC film by soaking the BC pellicle in a solution containing these particles (Khan et al., 2018). In order to ensure complete electrical conductivity, a conducting polymer, PEDOT:PSS was also incorporated extrinsically by immersing the BC-Au nanoparticle film into the PEDOT:PSS solution. The Au nanoparticles varied in size from ~ 5 to 20 nm and were attached to the surface while the amorphous conducting polymer coated these fibers as well as filled the pores of the BC fiber structure. Incorporation of two electrical conductors i.e., Au nanoparticles and PEDOT:PSS polymer resulted in increasing the conductivity of Au filled BC from $2.95 \times 10^{-2} \text{ S cm}^{-1}$ to 16.65 S cm^{-1} , an increase in two orders of magnitude. Exposure of these films to osteoblast cells, commonly found in the extracellular matrix of bones, showed that these cells continued to grow even after 3 days with no cytotoxicity change compared to pure BC, Fig. 4(a) and (b). These studies clearly indicate the potential of developing biocompatible, non-toxic BC based electrically conducting films which can be used in implantable devices.

One of the biggest requirements of modern technology is sensors i.e., devices that can convert an external stimulus into change in magnitude of the intrinsic property of the material. Among several parameters that define the quality of a sensor, one of them is its sensitivity which is a measure of the maximum magnitude of intrinsic property change that can be created in the shortest possible time in response to an external stimulus. Hosseini et al. (2018) synthesized a BC composite with multiwalled carbon nanotubes incorporated into the cellulose matrix during the growth stage of cellulose itself. Various amounts of MWCNTs were introduced into the culture medium and it was found that the resulting BC has MWCNT incorporated into it. The composite exhibits enhanced electrical conductivity of $\sim 10^{-2} \text{ S m}^{-1}$ for a volume concentration of 0.0041 corresponding to percolation attainment. The strain sensitivity of this composite was investigated at two different strains of 2% and 8% for up to 10 cycles by measuring the change in resistivity of the composite. The strain sensitivity was reversible up to 10 cycles for low values of strain i.e., 2%, while for the higher strain, irreversible changes in the composite lead to deteriorating performance, Fig. 5(a)–(c). The gauge factor which is a measure of strain sensitivity was 21, a high value compared to typical strain sensors based on resistive metallic bridges. The strain sensitivity was

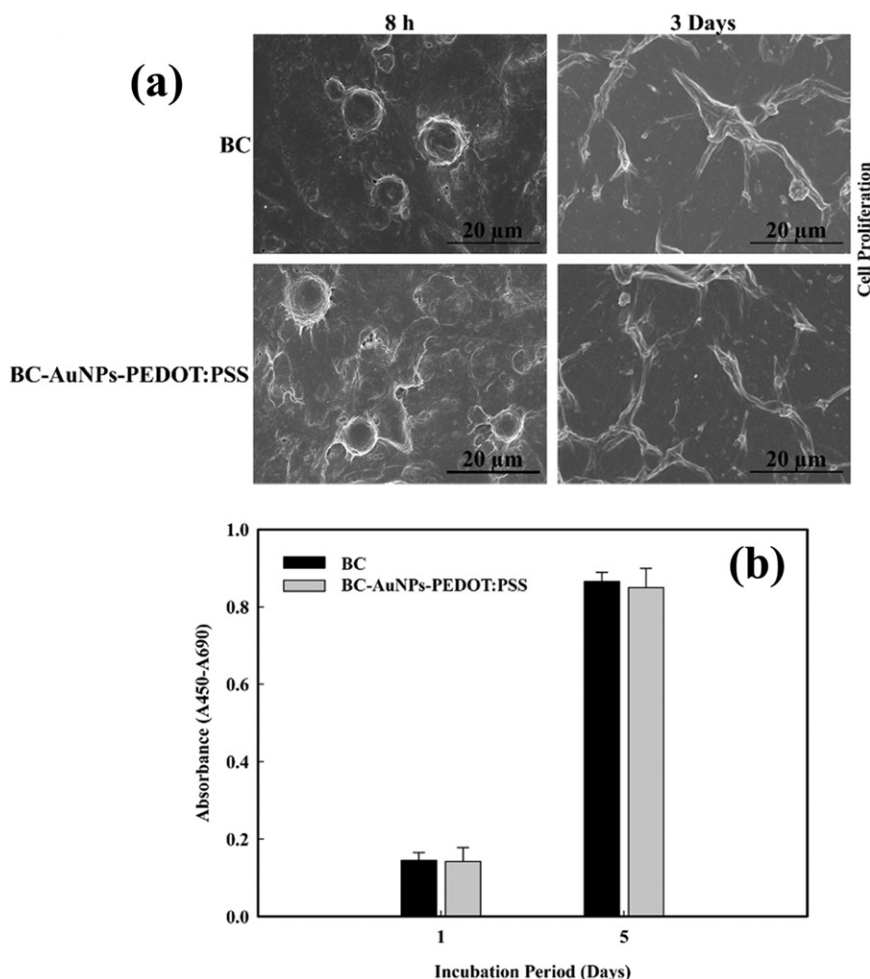


Fig. 4 (a) Morphology of animal osteoblast cells attached to BC and BC/AuNPs-PEDOT:PSS composites as observed under a Field-Emission Scanning Electron Microscope (FE-SEM). The images were obtained after an 8-h incubation period and after a prolonged 3-day incubation period for both samples. (b) Comparison of cell viability on BC and BC/AuNPs-PEDOT:PSS using 3-dimethylthiazol-2,5- diphenyltetrazolium bromide (MTT) assay. No significant difference in cell viability was observed after incubation for 1 day and 5 days.

found to be retained after 100 twisting cycles and 100 cycles of 180° bending, **Fig. 6(a)** and **(b)**. These results clearly demonstrate the potential of this strain sensor for practical application under different conditions.

Energy Devices

Another physical property of a material which is of importance for sensors and also energy conversion is 'piezoelectric' nature which facilitates interconversion of electric field and mechanical stress or strain. These materials respond to external stress by generating an electric field due to the displacement of ions from their equilibrium positions resulting in polarized structure formation. Such materials are extremely important for conversion of mechanical stress into electrical power. For e.g., when incorporated in to shoes, they can convert human mechanical working energy into electrical power. Bacterial cellulose being made of polar molecules i.e., saccharides, can indeed exhibit piezoelectric behavior. Their random spatial arrangement, however, results in very low conversion efficiencies which prevent them from being used in the native state for this application. In order to enhance the polarizability of this material, cellulose nanocrystals have been extracted and made into thin films containing highly aligned layers of these nanocrystals. An alternative approach is to incorporate a piezoelectric secondary phase into the bacterial cellulose reticulate structure. Zhang *et al.* (2018) used this alternate approach and incorporated Vanadium doped ZnO nanoparticles to make nanogenerators. The Vanadium doped ZnO nanoparticles were in situ synthesized in the BC structure and it resulted in the formation of 5 μm particles which in turn were made of ~100 nm thick ZnO plates. The exact amount of ZnO particles loading, however, was not determined. To determine the amount of power that can be generated by bending action, the composite film was mounted onto Kapton substrate with the top and bottom faces acting as two electrodes, **Fig. 7(a)**. The maximum output current density and voltage reached 80 nA cm⁻² and 1.5 V corresponding to a power density of 60 nW cm⁻² for a matching external load

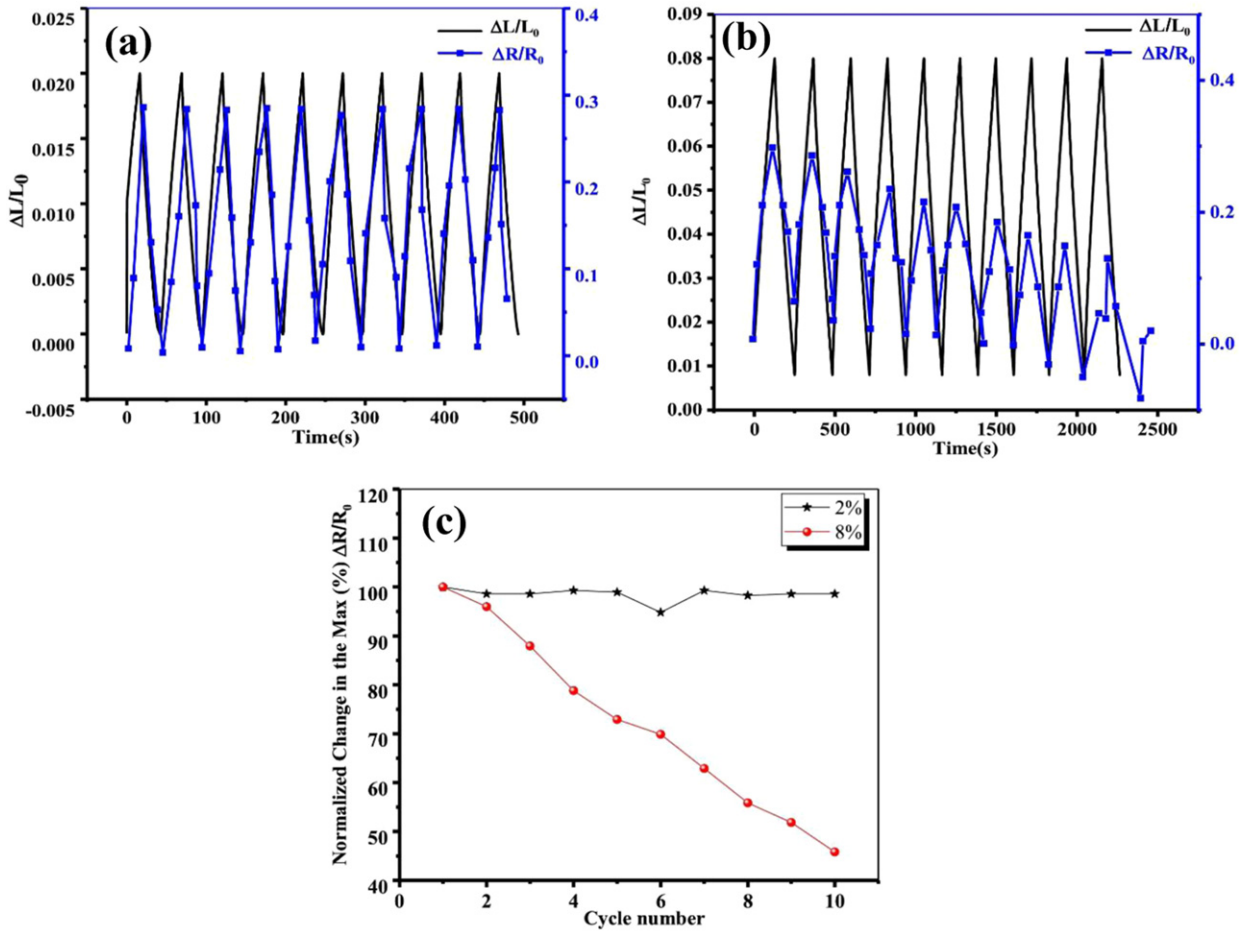


Fig. 5 Variation in relative resistance of BC/MWCNT nanocomposite aerogel for ten loading-unloading cycles at strain rate of (a) 2% and (b) 8%. (c) Variation in maximum normalized strain rate with cycle number for the aerogel based strain sensor over 10 cycles. It is seen that the strain sensing performance decreases at higher strain values.

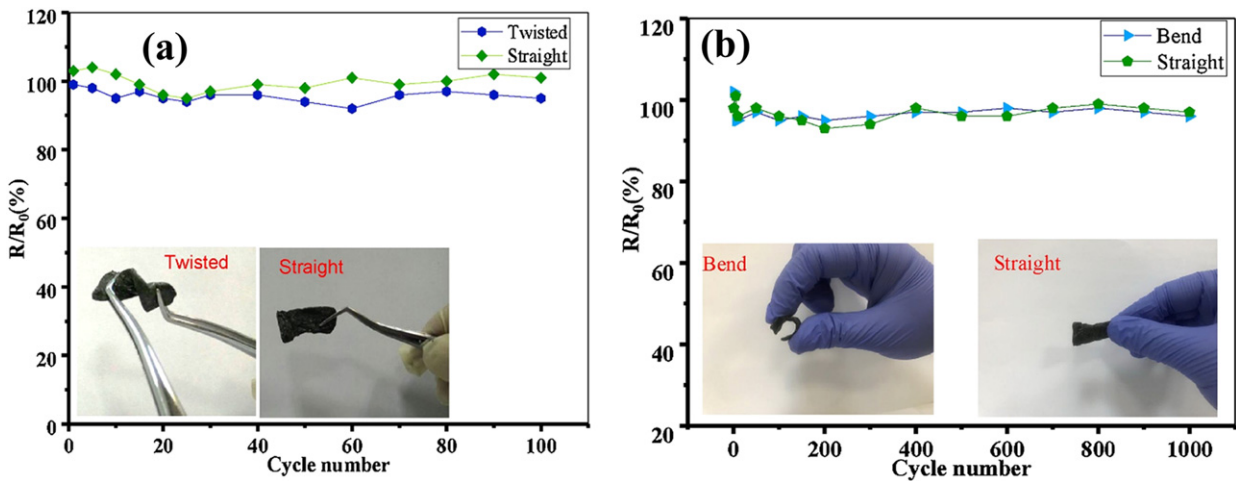


Fig. 6 Change in resistivity on (a) twisting and (b) bending of BC/MWCNT nanocomposite. Figure shows very little change over 100 cycles demonstrating its flexibility.

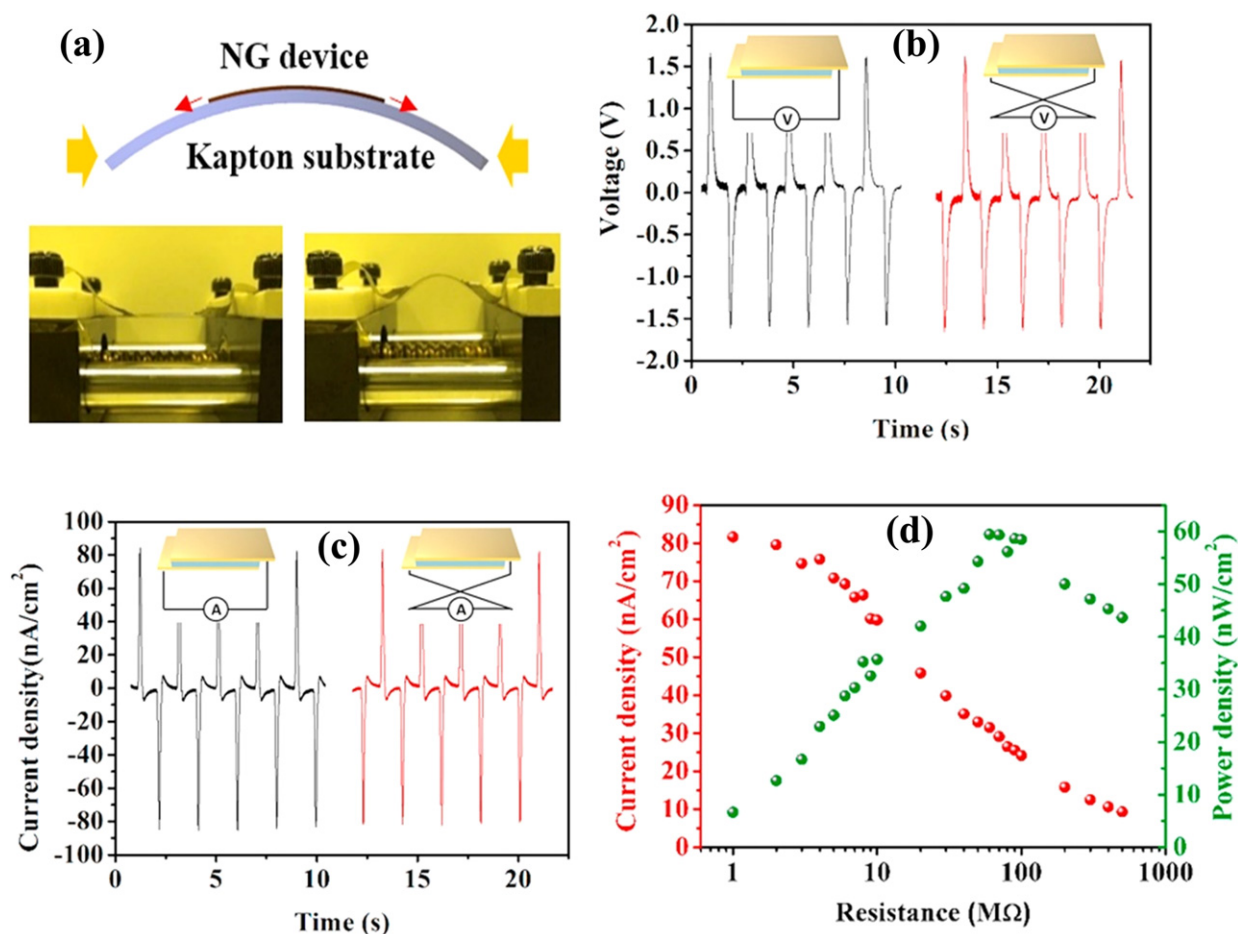


Fig. 7 (a) Schematic and photographs show bending stage that consists of nanogenerator (NG) device attached to Kapton substrate (b) Output voltage in forward and reverse mode and (c) Current density under forward and reverse mode of operation for V-doped ZnO/BC based Piezoelectric Nanogenerator (PENG) film. (d) Variation in the output current and output power density of the nanocomposite film with load resistance.

resistance of 70 MΩ, Fig. 7(b)–(d). The current density and voltage are an order of magnitude higher compared to those of either pure BC or undoped ZnO, clearly indicating the role of Vanadium doping. The current density generated by the nanocomposite film increased linearly with increasing bending angle, an effect of increased strain in the film. The composite film retains its output performance even after being subjected to 10,000 bending and releasing cycles. This work demonstrates the potential of the concept of mechanical to electrical energy conversion. Use of materials with higher piezoelectric response can result in significantly higher energy conversion efficiencies.

The internet of things (IOT) has resulted in a paradigm shift in the use of communication devices such as hand held telephones or mobiles which are becoming powerful with several functionalities. Since these devices require wireless electrical power, batteries have gained significant importance. The size, power density, discharge/charge time scales and longevity of these batteries is being continuously improved due to the discovery of new materials and designs. The three basic components of a battery are the two electrodes and the separator. The separator in the battery plays a crucial role in maintaining the two electrodes physically apart as well as storing the electrolyte. It facilitates ion exchange across its thickness and hence should possess sufficient porosity together with robustness. The decreasing size of mobiles requires the batteries to be compact without compromising its power delivering capacity. These requirements have resulted in the development of thinner separators with sufficient strength and porosity. In this context, Xu *et al.* (2017) have developed a BC/Al₂O₃ composite film for lithium ion battery separator. The composite membrane was made by in situ synthesis of Al₂O₃. This results in uniformly coating the BC fibers with an amorphous Al₂O₃ layer and thus retains the porous nature of BC. The retention of porous structure leads to an enhanced electrolyte uptake capacity of ~4.5 mg cm⁻², which is twice that of a conventional polymer separator, PP-PE-PP, Fig. 8(a). The enhanced electrolyte uptake also results in increasing the ionic conductivity from 3.39 mS cm⁻¹ for the polymer separator to 4.91 mS cm⁻¹, Fig. 8(b). The enhanced Li-ion transport capability leads to better battery performance, Fig. 8(c). Although, the incorporation of Al₂O₃ improves the electrochemical performance, it results in decreasing the elasticity of the membrane. This could possibly limit application of this BC/Al₂O₃ composite membrane from being used in batteries for flexible electronic applications.

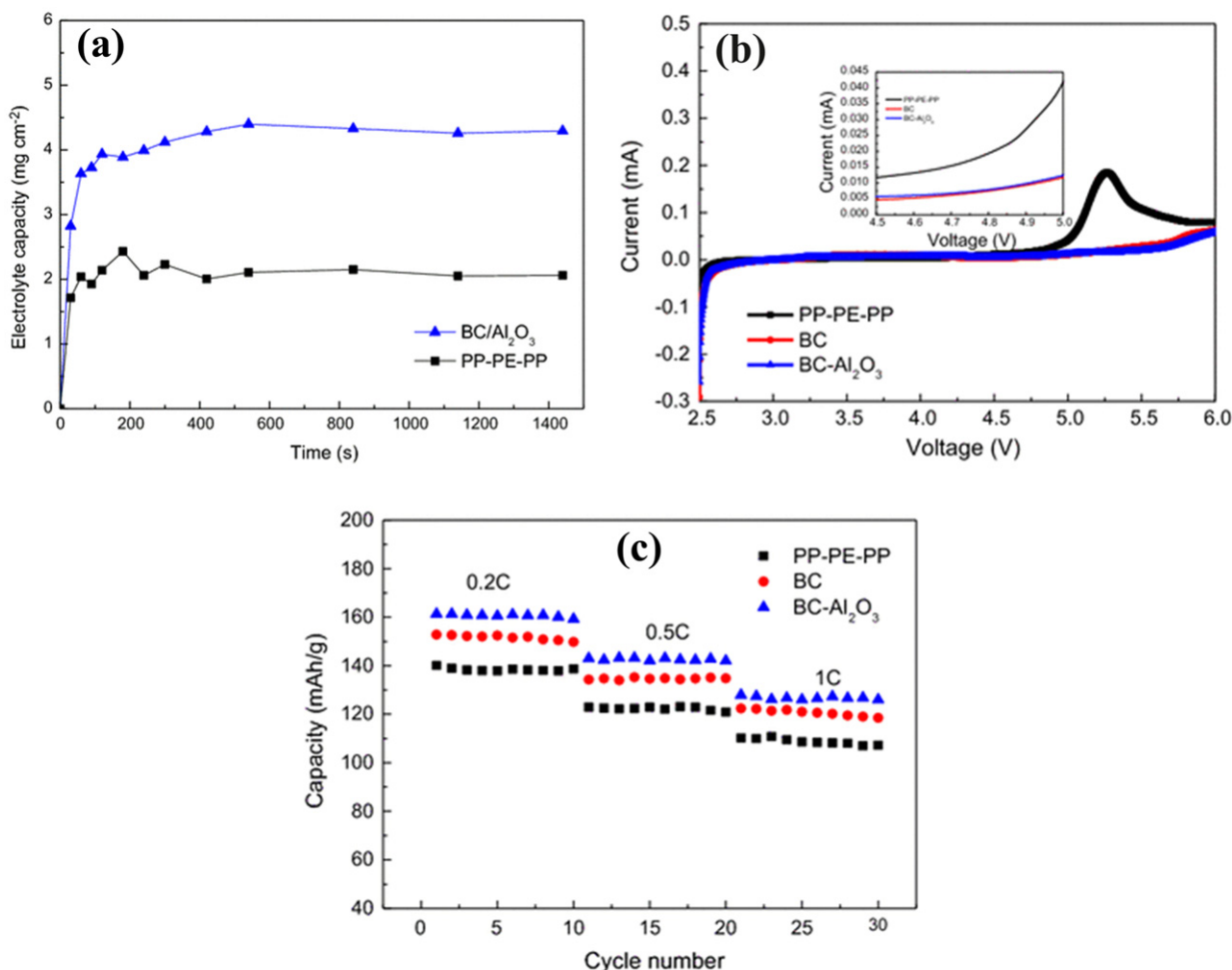


Fig. 8 (a) Comparison of electrolyte uptake capacity of BC/Al₂O₃ separator film with that of commercial separator PP-PE-PP, as a function of time, (b) Linear sweep cyclic voltammograms of commercial separator PE-PP-PE and BC/Al₂O₃ separator film at scan rate of 1.0 mV s⁻¹. (c) Comparison of rate capacity of the cells using PE-PP-PE and BC/Al₂O₃ separators at different C-rates.

Capacitor is a device which stores electrical energy in the form of separated charges and delivers it on demand. Capacitors are used in a variety of applications and range in capacity by several orders of magnitude from pico Farads to several Farads. The advent of modern electronic devices varying from hand held communication devices to personal computers have imposed a demand for the development of capacitors with highest possible specific capacitance. This has driven the demand for ultra-capacitors or supercapacitors with specific capacitance values of the order of 10³ F g⁻¹. These specific capacitance values coupled with flexibility for the capacitor leads to using BC as a highly suitable medium. Peng *et al.* (2017) used flexible, biodegradable BC to make supercapacitors with polypyrrole and CuO incorporated in it. The CuO nanoparticles were incorporated into the BC by in situ synthesis and subsequently the polypyrrole was infiltrated by dipping the BC/CuO membrane into an aqueous solution containing the polymer. Various tests were performed in order to study the capacitor characteristics. It was found that the specific capacitance decreased with increasing voltage scan rate as well as the cycling. The highest specific capacitance was found to be 897 F g⁻¹ which decreased with charging rate as well as cycling indicating that the cycling stability is not high. The thermal stability of the composites was low due to the incorporation of CuO nanoparticles. These studies show the feasibility of making flexible supercapacitors using BC membrane as a template.

In summary, BC is a naturally sustainable, biodegradable and biocompatible polymer which can be used for a variety of applications. The hierarchical fibrous structure together with high degree of crystallinity compared to plant cellulose imparts high mechanical strength and flexibility. The reticulate structure with different sized pores, ranging from few nanometers to microns, facilitates the incorporation of a wide variety of materials. This versatility allows BC to be used as a template to insert metals, alloys, oxides and polymers and thus impart a range of functionalities from electrical conductivity to piezoelectricity and magnetism to optical transparency. With an increasing demand to develop environmentally benign materials which are sustainable and at the same time deliver a wide range of functionalities, BC will find increasing demand. This will also lead to a growth in large scale production of BC using different and novel methodologies.

See also: An Assessment of Hydrogen Energy Utilization for Sustainable Development

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Biodegradable Packaging

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Introduction

Packaging plays a vital role in containing and protecting food as it moves through the supply chain to extend its shelf life. It is estimated that 37% of the packaging products are made from plastics, which makes plastic the most used packaging material (Rexam, 2011). Plastic packaging represents 26% of the overall plastic market (Plastics Europe, 2015). The domination of plastic packaging in food packaging market is due to their low production cost, mechanical resistance, heat sealability, water & gas barrier properties, and shape flexibility. By 2023, it is expected that global plastic films sheets market will witness a significant growth of USD 146,813.87 million (Market Future Research, 2019). Asia Pacific is the largest market of plastic films, where China, Japan and India are being the main players (Market Future Research, 2019). In Europe, packaging applications represent about 40% of the total plastics demand (European bioplastics, 2014). In USA, approximately 380 billion plastic bags are used every year that is more than 1200 bags/US resident/year. In India, packaging materials account for 25% of the total production of plastics, but it accounts for 52% in terms of consumption. However, only 3% of the plastic waste is being recycled worldwide. The accumulation of these plastic packaging on earth is a major threat to environment due to its non-biodegradability and its impact on health of terrestrial and aquatic animals (Thompson *et al.*, 2009). Recent studies estimate that 31% of the plastic debris in marine environments originates from food and beverage packages. Plastic pollution of the global marine environment is a persistent and pervasive problem, about 8 million tons of plastics has been leaked into the ocean annually, which is equivalent to dumping one garbage truck into the ocean every minute. If no action has been taken, this is expected to increase to two per minute by 2030 and four per minute by 2050 (Jambeck *et al.*, 2015). Considering that 31% of a garbage truck is filled with plastics originating from plastic food and beverage packaging, it becomes clear that food and beverage packaging is an important contributor to the pollution of the marine environment. Thus even a small reduction in the amount of plastic materials used for each package would result in a significant reduction in air and water pollution, improve solid waste disposal and conservation of non-renewable resources (fossil-based plastics). Recently, due to growing concerns about health and environmental protection, there has been a growing interest in developing natural and biodegradable packaging to maintain the postharvest quality of fruits and vegetables (Arnon *et al.*, 2014; Fagundes *et al.*, 2015). Presently, the global biodegradable plastic market represents less than 1% of the overall plastic market but it is expected to grow at a fast pace in the coming years (Markowicz *et al.*, 2019). The development of new biodegradable packaging is a very interesting alternative to reduce the volume of waste from plastic packaging materials. However, large price difference between biodegradable packaging and conventional plastic packaging is the major limitation that will affect the market growth (Future Market Research, 2016). The growth of biodegradable packaging industry depends upon the consumer preference towards environmental friendly products, government policies towards green procurement and use of renewable and bio-based raw products. The research and developments in the area of biodegradable packaging is a key and unique field of exploration within food packaging which possesses enormous commercial and environmental potential.

Biodegradable and Compostable: Definitions and Standards

The term 'biodegradation', 'biodegradable material' and 'composting' are very common but they are frequently misused and misunderstood. The solubility in water is frequently considered as a synonym of biodegradability, and biodegradability as a synonym of compostability. According to the American Society for Testing of Materials (ASTM) and the International Standards Organization (ISO), the degradable plastics undergo a significant change in chemical structure under specific environmental conditions. These changes result in loss of physical and mechanical properties which can be measured by standard methods. The biodegradation of polymers is a very complex process and can occur in a number of ways. Biodegradable polymers undergo degradation due to the action of naturally occurring microorganisms such as bacteria, fungi and algae. "Biodegradable" is defined by ASTM as "Capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds, or biomass in which the predominant mechanism is the enzymatic action of microorganisms, that can be measured by standard tests, in a specified period of time, reflecting available disposal condition (ASTM, 2005)." In the European Union (EU), there are no standards for biodegradation of materials, in contrast to composting. It is a general acknowledgment that in nature there is at least one enzyme which is responsible for speeding the breakdown process of chemical bonds of a polymer chain. However, degradation will not occur in an unfavorable environment or the biodegradable material will not degrade within in a short time. Notably, the term "biodegradable" does not imply a fast process. It is, therefore, important to couple the term biodegradable with the specification of the particular environment where the biodegradation is expected to happen, and of the time scale of the process (CEN, 2014).

The EU Directive 94/62/EC has specified that composting of packaging waste is a form of recycling, in which original package is transformed into a new product – 'the compost'. The biological treatment may have a very important role to reach the recovery targets fixed by the Directive. The biological treatment can be aerobic (compositing) or anaerobic (biomethanization). Composting leads to the transformation of waste into carbon dioxide, water and compost, usable for agricultural purposes.

Biomethanization leads to formation of biogas (methane and carbon dioxide) and sludge. The anaerobic sludge is then usually transformed into compost by a subsequent composting step. For this reason, the term 'composting' is used as a synonym of biological treatment of solid waste, covering both aerobic and anaerobic processes. The European Committee of Standardization (CEN) has been appointed by the European Commission with the Mandate M200 to prepare the technical norms to support the EU Directive 94/62/EC. In particular, the group denominated CEN TC261 SC4 WG2 (within the Technical Committee 261, 'Packaging') and prepared the norm EN13432 "Requirements for packaging recoverable through composting and biodegradation – Test scheme and evaluation for the final acceptance of packaging". This standard defines how quickly and to what extent a biodegradable plastic must degrade under industrial composting conditions (Oever *et al.*, 2017). According to the EN13432 standard, compostable material must have following characteristics:

- The packaging material and its relevant organic components are naturally biodegradable (The ability to convert compostable materials into carbon dioxide under the action of microorganisms). This property is measured according to EN 14046 (also published as ISO 14855: biodegradability under controlled composting conditions). To demonstrate complete biodegradability, the level of biodegradation of at least 90% must be achieved in less than 6 months.
- Disintegration (physical fragmentation) and loss of visibility of the packaging material takes place in the final compost, composting measured by testing in laboratory conditions (EN 14045).
- The packaging material has no negative effect on the composting process.
- The packaging material does not negatively influence the quality of the final compost and have low levels of heavy metals.

According to ASTM D6400/D6868 (for compostable plastics) a product or material must meet three key criteria to be certified as compostable:

- Material or product must disintegrate into small fragments but should not be screened out.
- Material or product must convert into CO₂, water and organic matter at an satisfactory rate.
- Finished product must support plant growth and must not leave behind any toxic residue.

There are still no European standards for 'home compostable' and 'soil degradable' packaging. The most common private institutes providing certificates for composting and biodegradation of materials are the European company 'Vincotte' and the U.S. Company 'BPI'. According to various international standards such as EN13432, ASTM D6400 and Green Pla, biodegradable and compostable materials are marked. In an attempt to articulate the conditions under which products will biodegrade, Vincotte offers certifications for the different kinds of environments where products are likely to end up: water and soil. Thus, these products are labeled as 'OK biodegradable SOIL', especially beneficial in agricultural uses, 'OK biodegradable WATER', reducing waste streams in natural fresh water and 'OK biodegradable MARINE' reducing waste in marine water.

Factors Responsible for Biodegradation

Several factors are known to affect biodegradation. The chemical structure of the polymer is most important factor responsible for biodegradation. Polymer characteristics such as nature of the chemical bond, functional group stability, reactivity, hydrophobicity and swelling behavior, flexibility of the chains, crystallinity, hydrophobicity, molecular size, and environmental factors such as temperature, pH of the medium, presence of oxygen, moisture, microorganisms such as bacteria, fungi etc., and enzymes affect biodegradation in its various stages. Therefore, both the biodegradability and the degradation rate of a biodegradable polymer product may be different on the soil, in the soil, in humid climate, in dry climate, in marine water, in surface water, in home composting, in industrial composting or anaerobic digestion (Van Der Zee, 1997; OWS, 2013). Some linkages (amide, ester, urethane, anhydride, orthoesters etc.) of polymers are more susceptible to hydrolysis by hydrolytic enzymes and microorganisms because of flexibility of these polymers to fit into active sites of enzymes. It was observed that the polymer having both hydrophobic and hydrophilic properties have more biodegradability than the polymer having either hydrophobic or hydrophilic properties (Nair and Laurencin, 2007). Two factors affecting the enzymatic degradation of synthetic polymers are the steric configuration of the polymer itself and the nature of the substituents adjacent to the susceptible bond. For example, biodegradation is inhibited by branching of the molecular chain and it was observed that chain branching in polymers like polystyrene and polypropylene cause difficulty in biodegradation. The copolymer composition and morphology play a significant role in biodegradation. The processing conditions such as annealing, sterilization process, storage history, etc., also play significant roles in biodegradation (Joshi and Patel, 2012). Other factors that affect degradation rates are water diffusion, hydration, disruption of van der Waals forces and hydrogen bonds, monomer solubility and diffusion, device geometry and size, erosion mechanism, etc., (Adeosun *et al.*, 2012; Nampoothiri *et al.*, 2010).

Chemistry of Biodegradation

The biodegrading of polymeric material is a complex process and generally take place in two stages (Pillai, 2014). In the first stage, there is depolymerization of the larger molecules of polymeric into the shorter chains while in second stage there is mineralization. Depolymerization of the macromolecules normally occurs outside the organism due to the size of the polymer chain and the

insoluble nature of many polymers. During this step, presence of microorganisms, heat (degradation rate depends on temperature), and humidity are responsible for breaking the carbon bonds of polymer chain. During second step i.e., mineralization, small size oligomeric fragments are transported into cells where they are bio-assimilated by the microorganisms and then mineralized. Second step of biodegradation process begins when shorter chains become energy sources of microorganisms (bacteria, fungi or algae). This process is confirmed as biodegradation in full sense only when carbon compounds become food and microorganisms are transformed into water, biomass or carbon dioxide (Barone and Arikian, 2007). These changes result in a loss of physical and mechanical properties, as measured by standard methods. Polymers may also be nominated as photodegradable, oxidatively degradable, hydrolytically degradable, or those that may be composted, or thermally and mechanically degradable (Jakobek, 2014).

The Mechanism of Biodegradation of Polymers

- Photodegradable polymers: These polymers breaks down (i.e., braking of chemical bonds) under the influence of natural light (photooxidation).
- Oxidatively degradable polymers: These polymers breaks down by oxidation.
- Hydrolytically degradable polymers: These polymers breaks down by hydrolysis.
- Thermally degradable polymers: These polymers breaks down by thermal process.
- Degradable polymers: The polymer whose chemical structure is changed under the influence of moisture and oxygen.
- Biodegradable polymers: These polymers are broken down under the influence of naturally occurring microorganisms.

Biodegradable Polymers and its Classification

Biodegradable polymers are very large molecules having long chain-like structure with high molecule weight, produced by living organisms. They are very common in nature and form the building blocks of plant and animal tissue. Biodegradable polymers are materials that can be broken down by microorganisms (bacteria, fungi, algae) into water, naturally occurring gases like carbon dioxide and methane and biomass.

Biodegradable polymers can be broadly divided into different categories based on the origin of the raw materials (renewable or non-renewable) and the processes used in their manufacture (Fig. 1). Polymers derived from renewable resources (biopolymers) are broadly classified according to method of production, as follows:

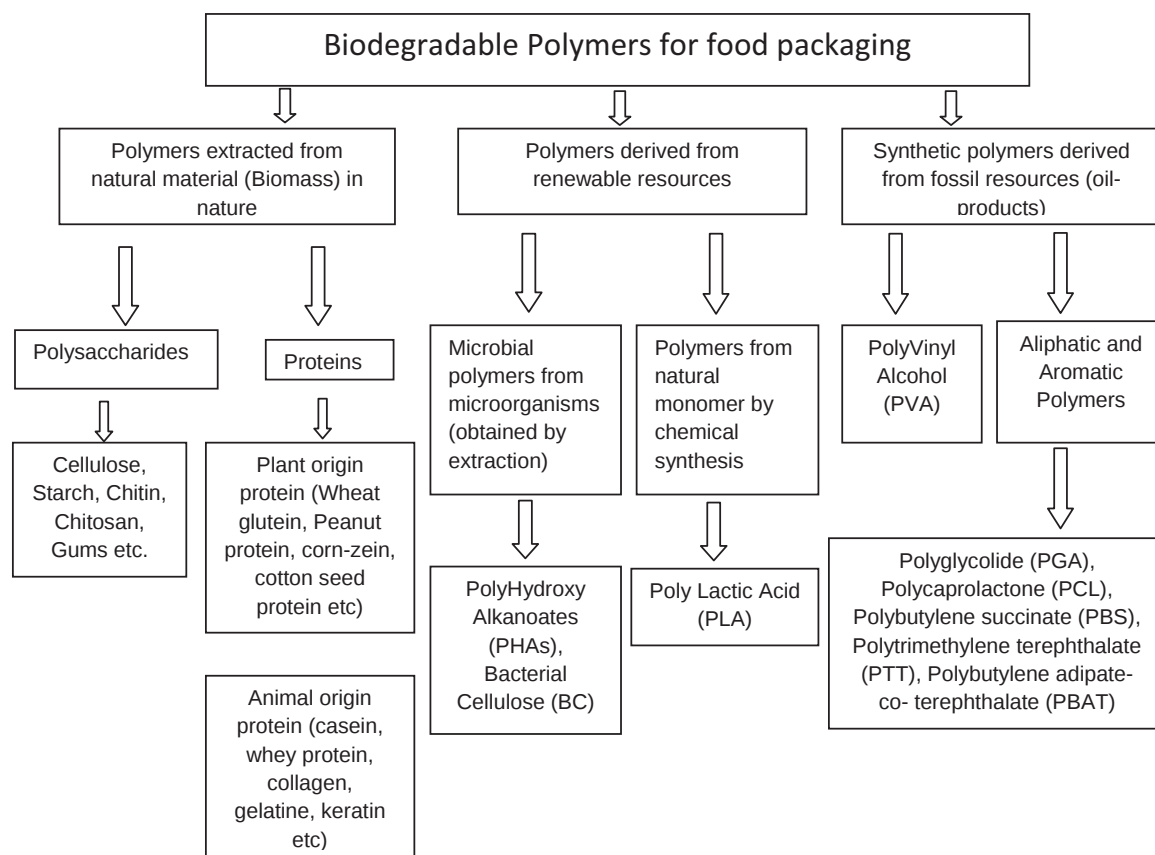


Fig. 1 Classification of biodegradable polymers for packaging.

- (1) Polymers directly extracted/removed from natural materials (plants, marine and domestic animals). Examples are polysaccharides (starch, cellulose, chitin, chitosan), protein (whey protein, casein, collagen, soy protein, myofibrillar proteins of animal muscle, etc.).
- (2) Polymers produced by microorganisms or genetically transformed bacteria. The best known bio-polymer types are the polyhydroxyalkanoates (PHAs), mainly polyhydroxy butyrate (PHB) and copolymers of hydroxy-butyrate (HB) and hydroxyvalerate (HV) (Petersen *et al.*, 1999).
- (3) Polymers produced by “classical” chemical synthesis from renewable bio-derived monomers. A good example is polylactic acid, a biopolyester polymerized from lactic acid monomers. The monomer itself is produced via fermentation of carbohydrate feedstock.

In addition to the natural polymers and polymers from renewable resources, man-made synthetic biodegradable polymers developed from non-renewable resources (oil products) have been developed, mostly for biomedical and agricultural applications, but they also have applications in packaging industry (Mitrus *et al.*, 2009). They offer more advantages over natural polymers because they can be tailored to give a wider range of properties and can be made into a degradable material for specific applications. Generalizing, they are biologically inert, readily available and have more predictable properties (Rydz *et al.*, 2015).

According to the European Bioplastics (2015), biopolymers made from renewable resources have to be biodegradable and especially compostable, so they can act as fertilizers and soil conditioners. Whereas plastics based on renewable resources must not necessarily be biodegradable or compostable, the bioplastic materials do not necessarily have to be based on renewable materials, because the biodegradability is directly correlated to the chemical structure of the materials rather than the origin. In particular, the type of chemical bond defines whether and in what time the microbes can biodegrade the material.

The problems associated with renewable biopolymers are threefold: performance, processing and cost. Although these factors are somewhat interrelated, problems due to “performance and processing” are more pronounced with polymers extracted directly from biomass (cellulose, starch, proteins). Conversely, polymers belonging to categories 2 and 3 above, generally perform very well and are easily processed into films using standard plastic techniques, but tend to be expensive compared with synthetic analogs (Petersen *et al.*, 1999).

Polymers Extracted/Isolated Directly From Natural Material (Biomass)

Natural products and natural product derived compounds play an important role in the food packaging industry. The outstanding aspect of natural biopolymers is their wide variety, which gives innumerable opportunities for structural modifications and utilization. Polymers of this category are obtained from plants, marine and domestic animals. Examples are polysaccharides (starch, cellulose, chitin, chitosan), protein (whey protein, casein, collagen, soy protein, myofibrillar proteins of animal muscle, etc.). Nature has a plethora of natural enzymes for degrading natural polymers. Due to their natural origin, all natural polymers are biodegradable because for each action of a polymerase, there is depolymerase that can catalyze the degradation in order to maintain the balance of nature (Khemani and Scholz, 2012; Rydz *et al.*, 2015). The advantageous properties of these polymers are their biodegradability, supplementary nutritional food value, incorporated antimicrobial and antioxidant properties, renewable origin, relatively low cost, prevalence, and the fact that they have no negative impact on the environment like a traditional plastic material (Sam *et al.*, 2015).

(1) Starch

Starch is a promising raw material because of its annual availability from many plants parts such as tubers, seeds, stems and leaves (Chen and Evans, 2005). Starch is a polymeric carbohydrate produced by many plants, such as corn, potato, wheat, rice, barley, oat and soybean. In addition to being staple food, starch has recently gained interest as a renewable and biodegradable plastic (Wang *et al.*, 2009) because of the worldwide environment and resources problems resulted from petroleum-derived plastics (Averous *et al.*, 2000). Starch contains two types of D-glucopyranose polymers: amylose (20%–30%) and amylopectin (70%–80%). Depending on the source, starch has different proportions of amylose and amylopectin. Amylose is a linear polymer of α -D-glucopyranosyl units linked (1–4). These molecules can be comprised of 100 to over 1000 glucose units. Amylopectin is a branched polymer of α -D-glucopyranosyl units containing (1–4) linear linkages and (1–6) linkages at the branch points. Amylopectin is three or more times larger than amylose. Most naturally occurring starches contain approximately 30% amylose; however, specific starches and their properties are determined by the size and amount of each type of polymer molecule present in the material.

Starch is one of the promising biopolymer materials due to biodegradability, non-toxicity, availability, and renewability. It is oil resistance, flexible in nature, oxygen impermeable, heat stable, and water soluble (Krogars *et al.*, 2003). Amylose has the film-forming property of starch (Claudia *et al.*, 2005). Starch can be used to form edible or biodegradable films. Different sources of starch, high amylose starch, modified starch (Mali and Grossmann, 2003; Mali *et al.*, 2006; Roth and Mehlretter, 1967; Wolff *et al.*, 1951) have been used to form self-supporting films by casting from aqueous solution. The starch-based films are tasteless, colorless, odorless, translucent (not transparent), non-toxic, biologically absorbable, semi-permeable to CO₂, and impermeable to release of O₂ (The *et al.*, 2009). They are used in applications where transparency is not required. Starch based films are frequently used in cellophane based barrier laminates to allow heat sealing. These types of laminates are used in pouches for products like cereals and cookies. Starch based trays (rigid or foamed) can be used to pack fruits and vegetables.

Starch based trays are not transparent. A specific type of foamed starch tray is Paperfoam™ and it is mainly used for packaging where product protection is important, e.g., egg boxes, electronic devices. The starch based edible film reduces the microbial growth, control, enzymatic reaction and lowering water activity of packed food products (Wong *et al.*, 1994).

There are many hydrogen bonds between the starch macromolecules, which reduce the movement of these molecules, so the native starch has poor processing ability. Due to the fact that starch film is brittle in food packaging materials, thermoplastic starch can be obtained by the destruction of the granules in the presence of plasticisers under specific conditions. Polyols are the most widely used plasticisers, such as glycerol (Fishman *et al.*, 2000), glycol (Smits *et al.*, 2001; Yu *et al.*, 1996), sorbitol (Wang *et al.*, 2000), xylitol, and sugars; of these, glycerol is the most commonly used plasticiser. Thermoplastic starch (TPS) is a mixture of starch and plasticiser after the gelatinization process. It is hygroscopic; therefore this material is not suitable as packaging for high-moisture and liquid food products. However, it has good oxygen-barrier properties. Blending of starch with polyesters is necessary to improve water resistance, processing properties and mechanical properties. Commonly the starch content of starch based plastics is lower than 50% and the overall bio-based content of these materials depends on the nature of the other components. Glycerol-plasticised thermoplastic starch can recrystallize (retrograde) on storage. In order to prevent retrogradation, some plasticisers containing amide groups were used, such as formamide and acetamide (Ma and Yu, 2004a), urea (Ma and Yu, 2004b) and the formamide/urea mixture (Ma *et al.*, 2004). However, these amide group-containing plasticisers are toxic and would not be allowed in many applications, such as fast food service-ware, food packaging, pharmaceutical and biomedical application. To solve this problem, a nontoxic plasticiser is required. DL-Lactic acid is rated as nutritionally harmless compared to other substances used for derivatisation. DL-Lactic acid will act as a plasticiser. DL-Lactic acid that reacts with starch can be considered as an internal plasticiser. Starch can also be plasticized by genetic and chemical modification or blending with materials like poly vinyl alcohol (PVA), poly(ϵ -caprolactone) (PCL), and others. Thermal and mechanical properties of thermoplastic starch depend on the content of these polymers in the blended plastic (Lu *et al.*, 2009). Starch/PCL blends with glycerol and citric acid as compatibilizers have better properties than plain starch film and show that even small amounts of PCL (10 wt%) allow lowering the glass transition temperature and increasing the water vapor barrier properties (Ortega-Toro *et al.*, 2016a). Serier and Aoufi (2017) reported that the glycerol and DL-lactic acid blended films have better film properties (water vapor permeability, mechanical strength). López *et al.* (2015) prepared packaging bags from thermo-compressed films based on thermoplastic starch modified with talc nano-particles. The strength properties of the film were the best but it did not show better film properties, such as mechanical properties or water vapor barrier as compared to plain starch films (Ortega-Toro *et al.*, 2016b). The acetylated or oxidized arracacha native starch may be used to manufacture biodegradable films. The films produced with acetylated starch present high transparency, moreover, the physicochemical and microbiological tests show that acetylated starch could be used in films for food packaging (Medina *et al.*, 2012). The sugar palm starch, combined with different plasticizer types (such as a glycerol, sorbitol, and glycerol/sorbitol combination) may be used for preparation of biodegradable packaging films. Regardless of plasticizer types, the films demonstrate increased water vapor permeability (WVP) (Sanyang *et al.*, 2015). Starch converted into a foamed material by water steam can be used as packaging material for trays or disposable dishes (Siracusa *et al.*, 2008).

The advantage of these TPS based products is that these products can be composted together with the organic waste. Starch blends are generally compostable and various materials (depending on the other blend components) are also biodegradable in soil, anaerobic digestion installations, fresh water or marine environment. Not all starch blends are allowed for food contact applications and this depends on the presence of blend components that can potentially migrate out of the starch blend. Starch-based thermoplastic materials were used for food wrappings and cups, plates, expanded trays, and other food containers (Rejak *et al.*, 2014). Novamont is one of the leading companies in processing starch-based products using their own starch-based blend (Babu *et al.*, 2013).

(2) Cellulose and derivatives

Cellulose, which is essentially linear polymer of anhydroglucose, is the most abundant natural polymer on earth. In recent times, cellulose has attracted considerable attention as one of the most well-known renewable and ecological raw materials for obtaining environmentally friendly and biocompatible technological products. Biomass produced by photosynthetic organisms such as plants, algae, and some bacteria is made up of cellulose and for that reason it is the most abundant biopolymer on earth (Klemm *et al.*, 2005). As a result, the use of cellulose-based materials in composites has increased over the last few years because of their relative low price compared to conventional materials, their recyclability, and their mechanical properties. Wood pulp remains the most important raw material for the processing of cellulose (Klemm *et al.*, 2005). Wood contains 40%–50% cellulose by weight. Cellulose is unsuitable for film production because it is highly crystalline, fibrous, and insoluble in water. Therefore, cellulose is dissolved in a mixture of sodium hydroxide and carbon disulfide and recast into sulfuric acid to make a cellophane film. Cellophane has good mechanical properties, but it is sensitive to moisture. It is often coated with nitrocellulose wax or polyvinylidene chloride to improve its moisture barrier properties. Coated cellophane is used for baked goods, fresh produce, processed meat, cheese, and candy. Cellophane has good gas barrier properties at low relative humidity. However, its barrier properties are reduced at intermediate and high relative humidities. Cellophane is not heat sealable owing to its non-thermoplastic nature (Petersen *et al.*, 1999). Hemicellulose, the second most abundant plant polymer in the world, is in its infancy as a biomaterial research for food packaging (Grondahl *et al.*, 2006). Cellulose nanocrystals (CNC) are a novel class of nanomaterials with many promising applications. Cellulose nanoparticles have a strong tendency for self-association due to the interaction between surface hydroxyl groups. CNC are obtained in aqueous suspension from strong acid hydrolysis of cellulosic fibers.

(3) Chitin and chitosan

Chitosan is a chitin derivative, and second most abundant polysaccharide found in nature after cellulose. Commercially it is prepared by chemical N-deacetylation of chitin, which is a component of shells from marine crustaceans (shrimp, oysters, crabs, lobsters, and Antarctic krill), fungal cell walls and other biological materials (Andrady and Xu, 1997). The degree of deacetylation and the molar mass of the polymer is one of its most important chemical characteristics, which is the base of the biological properties of chitosan (Rabea *et al.*, 2003). It is structurally almost identical to cellulose. Chitosan is classified as a dietary fiber. It's also a good source of minerals and increases the gastric emptying (Zhao *et al.*, 2011).

As a packaging material, chitosan has many valuable features. The chitosan polysaccharide is non-toxic, biofunctional and biodegradable (Wang, 1992; Shahidi *et al.*, 1999; Jayakumar *et al.*, 2007, 2005, 2006; Jongrattiporn *et al.*, 2001). The chitosan-based film is generally adhesive and cohesive with a smooth surface (Coma *et al.*, 2002) and it has poor solubility with neutral water. Chitosan produces highly viscous products (Peniston and Johnson, 1980) and has the ability to form films without the use of other additives, and it is resistant to heat. Chitosan has good permeability to oxygen and carbon dioxide and excellent mechanical properties (Yam, 2009). Chitosan biopolymer has hypoglycemic and hypolipidemic anti-oxidant activity (Kim and Thomas, 2007; Yao *et al.*, 2008). Furthermore, it also has antimicrobial activity and can therefore be used to extend the shelf life of food and as a component of biodegradable edible films for food. One of the mechanisms of microbial inhibitory effects of chitosan is that it can induce the synthesis of chitinase in plant tissues, degrading microbial cell walls (Lin and Zhao, 2007). The type of solvent used for the formulation of the coating solution of chitosan can also present an antimicrobial effect due to the acid environment created such as the case of acetic acid (Ochoa-Velasco and Guerrero-Beltran, 2014). Chitosan has antifungal properties to various fungi. Some studies have shown that chitosan coatings can effectively reduce the growth of fungi extending the life of strawberries and blueberries (Duan *et al.*, 2011). Chitosan can also act as an excellent carrier of other functional substances. The addition of cranberry leaf extract in the chitosan coating formulation can improve its antimicrobial features. The addition of nisin, garlic extract, potassium sorbate, lysozyme, and many other compounds as antioxidants and preservatives allow for longer storage of products without the development of bacteria and fungi (Youwei and Yinzhe, 2013).

Chitosan membrane is used for coating fresh fruits, in particular, strawberries, berries, and grapes (Ribeiro *et al.*, 2007; Duan *et al.*, 2011; Petriccione *et al.*, 2015). It forms semi-permeable films and when applied as a coating on fruit modifies the internal gas atmosphere of the fruit as well as barrier to water vapor to reduce moisture loss, delays the dehydration of fruits and reduces decaying. De Oliveira *et al.* (2014) studied the effect of chitosan coating on table grapes and observed that the physicochemical and sensory characteristics of fruits were not affected during storage. Han *et al.* (2014) studied the effect of chitosan coating on sponge gourd and observed that the chitosan coating effectively reduce the respiration rate and the weight loss, preserves the strength and visual appearance, retains the ascorbic acid content and total phenolic compounds, and delays the polyphenol oxidase (PPO) activity.

Chitosan is used as food additives in dairy products, cereals, meat and seafood, juice, and eggs (Kerch *et al.*, 2010; Friedman and Juneja, 2010). Chitosan can be blended with different polymers. Joseph *et al.* (2011) reported that the chitosan/PCL blend films had lower water vapor transmission than plain chitosan films. It is expected that fruits and vegetables packaged in this film will have potentially extended shelf life. Massouda *et al.* (2012) reported that the extrusion films with chitosan and DuPont ionomer of ethylene acid copolymer with poly(vinyl alcohol-co-ethylene) may be used for antimicrobial package. Tan *et al.* (2015) produced novel composite film based on chitosan with grapefruit seed extract to pack bread samples and observed that the shelf life of bread samples is two times longer than those packaged using synthetic packaging films. The film also prevents the growth of fungi and bacteria and has mechanical strength and flexibility almost like synthetic polyethylene film (National University of Singapore, 2016).

Proteins

In their native states, proteins can be divided into 2 groups i.e., fibrous proteins and globular proteins. Fibrous proteins are water insoluble and obtained from animal tissues (e.g., casein, whey protein, collagen, gelatin, keratin) whereas globular proteins are soluble in water or aqueous solutions of acids, bases or salts and obtained from plant origin (e.g., wheat gluten, soy protein, peanut protein, corn-zein, cotton seed protein) (Gennadios *et al.*, 1996). The two most common vegetable (globular) proteins used in the production of biodegradable packaging are chickpeas and isolated soy protein. Other vegetable proteins used for packaging are extracted from wheat, pistachios, peas and sunflower (Dean and Yu, 2005). The animal proteins used for the production of biodegradable packaging are albumin, casein, fibrinogen, silk and elastin but these are used on limited scale because of difficulty in processing as these proteins do not melt without decompression, and face difficult to mix with other polymers due to incompatibility (Battacharya *et al.*, 2005).

(1) Whey protein (WP)

Whey protein (WP) is a by-product from the cheese production and is particularly rich in β -lactoglobulin. Whey proteins (20% of total milk proteins) when appropriately processed produce flexible but brittle films (Kaya and Kaya, 2000). WP is capable of forming flexible films, and due to moderate moisture permeability, good oxygen barriers, and good biodegradability they are used as raw material for producing edible films, biodegradable films, or materials for biodegradable packaging (Ramos *et al.*, 2012; Wang *et al.*, 2013). WP is one of the most common and least expensive raw materials used in the preparation of edible films. Plastic films formulated with the use of WP are biodegradable and have a high barrier to oxygen

(Bugnicourt *et al.*, 2010). It can be used as a coating on paper and also on plastic substrates with polymers such as polypropylene (PP), polyvinyl chloride (PVC), and low-density polyethylene (LDPE). The coatings showed good mechanical properties and visual properties, such as excellent gloss and transparency (Ozdemir and Floros, 2008). WP based coatings blended with plasticizers have high barrier properties and moderate moisture permeability (Popovic' *et al.*, 2012; Verbeek and Van den Berg, 2010). The blending of WP with Bio-Flex improves oxygen barrier properties but does not affect the rate of its biodegradation (Cinelli *et al.*, 2014). The nanocomposite films consisting of whey protein isolate (WPI) with zein nanoparticles (ZNP) coated with sodium caseinate can be used as biodegradable food packaging materials (Oymaci and Altinkaya, 2016).

(2) *Corn zein*

Corn zein is the most important protein in corn that has both hydrophobic and hydrophilic properties. It is a prolamine protein found in corn endosperm and therefore dissolves in 70%–80% ethanol (Dickey and Parris, 2002). It has poor mechanical properties, however, can potentially be used for food packing, especially as a protective, impermeable coating, due to its good gas barrier, biodegradation, and biocompatibility properties (Ozcalik and Tihminlioglu, 2013). Films prepared from this protein are used for separating layers of food, such as slices of cheese, and the coating of many products including fruits and vegetables, nuts, meat, and cooked sweets. Furthermore, corn zein films are used to cover food fried in deep fat (for the reduction of fat absorption by the product) (Cutter, 2006). The application of plasticized corn zein coatings on the polypropylene film with a plasticizer such as PEG and glycerol reduced the oxygen and water vapor permeability (Tihminlioglu *et al.*, 2010). Ozcalik and Tihminlioglu (2013) observed that PP film coated with a corn zein nanocomposite successfully improve the barrier and mechanical properties of final packaging material. Corn zein films have also shown an ability to reduce moisture and firmness loss and delay color change (reduce oxygen and carbon dioxide transmission) in fresh tomatoes (Park *et al.*, 1994). Corn zein based films with oleic acid, nanocarbonate and glycerol as a plasticizer show the possibilities of using the material with nanocarbonate to pack food products (Ribeiro *et al.*, 2015).

(3) *Wheat gluten (WG)*

Wheat gluten (WG) is a general term for water-insoluble proteins of wheat flour which is composed of a mixture of polypeptide molecules, considered to be globular proteins. Cohesiveness and elasticity of gluten give integrity to wheat dough and facilitate film formation. WG contains the prolamine and gluten fractions of wheat flour proteins, typically referred to as gliadin and glutenin, respectively. While gliadin is soluble in 70% ethanol, glutenin is not. Edible films can be formed by drying aqueous ethanol solution of WG. Addition of plasticizer such as glycerin in WG films is necessary to improve film flexibility (Gennadios *et al.*, 1996). However, increasing film flexibility by increasing sorbitol content reduces film strength, elasticity and water vapor barrier properties. Tensile strength of gluten films can be improved by using a cross-linking agent such as glutaraldehyde, or heat curing at 80°C (Gennadios and Weller, 1990; Koelsch and Labuza, 1992). El-Wakila *et al.* (2015) produced nanocomposites consisting of WG, cellulose nanocrystals (CNC), and TiO₂ nanoparticles, and observed that the suspension blend has excellent antimicrobial activity and good mechanical properties and can be used to coat commercial packaging, such as unbleached Kraft paper. Ferreira *et al.* (2012) observed that the biopolymers obtained by mixtures of WG and glycerol (plasticizer) could be used for producing barrier materials. Rafieian *et al.* (2014) showed that carboxylated cellulose nanocrystals (CCNC) can be used as reinforcing fillers for WG composite packaging films. Cho *et al.* (2010) prepared a laminated film with WG, plasticizer (glycerol) and polylactide (PLA) and observed that the resulting laminated film has very good oxygen barrier properties and low water vapor transmission rate. Türe *et al.* (2012) reported that the antimicrobial film consisting of glycerol-plasticized wheat gluten and potassium sorbate has antimicrobial activity against *Aspergillus niger* and *Fusarium incarnatum*.

(4) *Soy protein*

Soy protein is the protein that is found in soybeans. Soy protein isolate (SPI) is a highly purified form of soy protein made up of 90% protein on a moisture-free basis. The protein content of soybeans (38%–44%) is much higher than the protein content of cereal grain (8%–15%). Most of the protein in soybeans is insoluble in water but soluble in dilute neutral salt solutions (Kinsella and Phillips, 1979). Soy protein consists of two major protein fractions referred to as the 7S (conglycinin, 35%) and 11S (glycinin, 52%) fraction. Both 7S and 11S contain cysteine residues leading to disulfide bridge formation and processing is, therefore, similar to wheat gluten with similar mechanical properties. SPI may be used to prepare edible and biodegradable packaging films. The films obtained from SPI exhibit excessive friability, therefore, plasticizer such as glycerol are added to improve its performance (Kokoszka *et al.*, 2010). Carpiné *et al.* (2015) concluded that the emulsion-based edible films made of SPI, virgin coconut oil, soy lecithin, and glycerol (plasticizer) can be used for food packaging applications. González and Igarzabal (2013) prepared biodegradable bilayer films from SPI and polylactide (PLA), and observed that the resulting film has high transparency and strong adhesion between layers. Moreover the PLA layer considerably increases the mechanical properties of the films relative to those of pure SPI films. The bilayer film can be used as a biodegradable material for active food coatings.

(5) *Collagen*

Collagen is a flexible polymer but due of its complex helical and fibrous structure, it is very insoluble and difficult to process. It is a major constituent of skin, tendon and connective tissues and is most prevalent and widely distributed fibrous protein in the animals. Collagen is the basic raw material for gelatine production. The characteristic features of gelatin are high content of the amino acids- glycine, proline and hydroxyproline. Gelatin also has a mixture of single and double unfolded chains of hydrophilic character (Ross, 1987). Gelatine is produced via either partial acid or alkaline hydrolysis of

collagen. Such treatments disrupt the tight, helical structure of collagen and produce water-soluble fragments that may form stiff gels, films or light foams. Gelatine is a very processable material, but it is extremely moisture sensitive. Therefore, for prolonged use in packaging, research is needed for the chemical modification of gelatine to improve moisture sensitivity (Claus, 2000).

(6) *Casein*

Casein is a milk-derived protein which do not dissolve directly in water, but show approximately 50% weight gain after 24 h of immersion. It is easily processable due to its random coil structure. Upon processing with suitable plasticizers at temperatures of 80–100°C, materials can be made with mechanical performance varying from stiff and brittle to flexible and tough. Casein is highly stretchable making them suitable for film blowing. In general, casein films have an opaque appearance.

(7) *Keratin*

Keratin is the cheapest protein which is non-sensitive to relative humidity. It can be extracted from waste material such as hair, nails and feathers. Due to its structure and a high content of cysteine groups, keratin is also the most difficult protein to process. After processing, a fully biodegradable, water-insoluble-plastic is obtained. However, mechanical properties are still poor compared to the other proteins.

Microbial Polymers Produced by Microorganisms or Genetically Transformed Bacteria

Many bacteria accumulate these polymers as a source of energy and as a carbon source. Genetic transformation of bacteria offers unique opportunities to create non-natural analogs of biopolymers and gives the possibility for further polymer modification (Kim *et al.*, 2015). Different composition units depend not only on the carbon source and type of microorganisms, but also on the dilution rate, the carbon to nitrogen ratio, time, and temperature (Hartmann *et al.*, 2004; Kim *et al.*, 2007). This group includes Polyhydroxyalkanoates (PHAs) and bacterial cellulose (BC).

Polyhydroxyalkanoates (PHAs)

Polyhydroxyalkanoates (PHAs) belong to the polyesters, naturally produced by microorganisms as a carbon storage source. More than 300 different microorganisms are known to synthesize and accumulate PHAs (Lee *et al.*, 1999). A wide variety of mechanical properties, from hard crystalline to elastic, are some of the main advantages of PHAs and the properties depend on the compositions of monomers (Bugnicourt *et al.*, 2014; Rudnik, 2013). PHAs also exhibit printability, flavor and odor barrier, heat sealability, grease and oil resistance, temperature stability, and are easy to dye, which improve its applications in the food industry (Tripathi *et al.*, 2015). Plackett and Siro (2011) described 150 different monomer types of this polymer group. PHAs are biodegradable and as such they can be used for food packaging. To expand the range of materials with food packaging applications, some modification of PHAs has been developed. These strategies include inter alia, chemical or enzymatic modification, preparation of blends and composites, and obtaining functional multilayer films (Koller, 2014). Medium-chain length PHAs can be applied as biodegradable cheese coatings, disposable diapers, fast food service wares, and single-use medical devices (Katiyar *et al.*, 2015a). Poly(3-hydroxybutyrate) (PHB) is the main and the best known representative of the PHA family. PHB is 100% biodegradable and it has similar physical properties with polypropylene (PP). PHB is a polymer of 3-hydroxybutyrate and are intracellular granules produced by prokaryotic organisms as energy and carbon storage during starvation. Bucci *et al.* (2005) compared the properties of PHB and Polypropylene (PP) jars and observed that PHB has 50% lower deformation value than PP but during refrigeration PHB exhibit poor performance than PP. This does not restrict the use of PHB in food packaging and results proved that PP could be substituted by PHB for packaging of fat rich products during refrigeration. The low moisture vapor permeability feature of PHA is very useful in packaging (Katiyar *et al.*, 2015b) and it was observed that the water vapor permeability coefficient of PHA is similar to poly(ethylene terephthalate) (PET) (Koller, 2014). Another important representative of PHAs are PHB copolymers: poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV), poly(hydroxybutyrate-co-hydroxyhexanoate) (PHBHx), poly(hydroxybutyrate-co-hydroxyoctanoate) (PHBO), poly(hydroxybutyrate-co-hydroxyoctadecanoate) (PHBOD), and poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P3HB4HB). A certain amount of those copolyesters have attracted industrial interest and were commercialized. PHBs are highly crystalline, brittle and have a high melting point, while PHBVs are more flexible, tougher, and degrade easier when discarded into the natural environment (Katiyar *et al.*, 2015a). Copolymer P3HB4HB has better processing properties than PHB and its mechanical properties are adjustable i.e., it has gained interest in biodegradable food packaging.

The blending of synthetic and natural polymers can have a significant impact on the physical properties and biodegradability of PHAs. Josta and Kopitzky (2015) observed that the blending of PBHV (20%–35% concentration) with Polylactic acid (PLA) improves the mechanical and barrier properties of the obtained material. Boufarguine *et al.* (2013) reported that the blending of PLA with small amount of PHBV (10%) improves the barrier properties and increase elongation at the break point. PLA/PHB blends were used as a matrix in nanocomposite films with synthesized cellulose nanocrystals (CNCs) or surfactant modified cellulose nanocrystals (s-CNCs). s-CNCs as bio-based reinforcements contribute to enhancing the interfacial adhesion between PLA and PHB. Low cost, suitable mechanical properties, high stiffness, low density, and biodegradability show that this material is ideal for food packaging applications (Arrieta *et al.*, 2014). Cunha *et al.* (2016) used two different biodegradable commercial polyesters poly(butylene adipate-co-terephthalate) (PBAT) and poly(butylene sebacate-co-terephthalate) (PBSeT) in the preparation of blends with PHBV and observed that the resulting film has good properties for food packaging, namely tear resistance,

water vapor permeability (WVP), and sealability. Kwiecień *et al.* (2016) observed that the blending of oxidized short-chain polyethylene (OXPE) with PHB improves the mechanical properties of the prepared polymeric material.

The high cost of PHA restricts its commercial use but blending of polymer material with cheap fillers and other additives not only reduces the cost but also improves its properties (e.g., viscoelasticity). Cunha *et al.* (2014) transformed brewers' spent grain (BSG) into brewers' spent grain fibers (BSGF), which were then used as fillers in bio-based composites. BSG is a brewing industry by-product, representing around 85% of the total by-products generated. BSG contain about 17% cellulose, 28% noncellulosic polysaccharides, chiefly arabinoxylans, and 28% lignin. Use of BSGF as a natural filler into the PHA matrix can reduce the cost and improve the viscoelastic properties of the final material. The addition of jute fibers to the biodegradable polymer composites has attracted attention in regards to lowering the cost, renewable nature, and reduction of energy requirements for processing. Commercially available PLA/P3HB4HB blends were used as a matrix in bio-based composites with jute fibers (Musiał *et al.*, 2015). Distiller's dried grains with solubles (DDGS) are a low-cost co-product of the corn-ethanol fuel industry. Use of DDGS as a filler to the PHA matrix seems to be a good solution in the reduction of the composites' cost, but also in the utilization of waste products (Hong, 2014). Kovalcik *et al.* (2015) concluded that the blending of PBHV with lignin decreases diffusion of oxygen and carbon dioxide and resulted stable viscoelastic properties of composed film.

Fabra *et al.* (2013) observed that the use of corn zein as nanostructured interlayers in multilayer PHBV-based films significantly decrease the oxygen permeability values of composed film. Inorganic or organic nanofillers in the nanocomposites based on PHAs may efficiently modify their crystallization behavior, morphology, stability, rate of biodegradation, mechanical, barriers, and thermal properties of the composed film (Khosravi-Darani and Bucci, 2015).

Bacterial cellulose

Bacterial cellulose (BC) is obtained by microbial fermentation in static or agitated cultures (Stoica-Guzun *et al.*, 2013). The use of antibacterial packaging can significantly reduce the use of preservatives in food products. BC based materials has attracted great attention due to its antibacterial properties and low cost (Gao *et al.*, 2014). BC produced by *Acetobacter xylinum* is widely used in food processing as it possess better properties than cellulose from plants (higher water holding capacity, higher tensile strength, distinctly soft texture, and high fiber content).

BC fibers can be used in combination with PVA and the prepared product can be used as packaging materials as it possesses better mechanical strength and biodegradability but unfortunately have high moisture sensitivity (Stoica-Guzun *et al.*, 2011). Due to its high moisture sensitivity, only few reports of applications of BC/PVA in the food packaging industry were observed. Jipa *et al.* (2012) reported that the multilayer films (two external defrost BC membranes and an inner layer containing sorbic acid) can be used as active packaging material with controlled release of an antimicrobial agent. BC can also be used for the preparation of nanocomposite materials with PCL and the obtained film showed good thermal stability and better mechanical properties than PCL (Figueiredo *et al.*, 2015).

Polymers Produced by Classical Chemical Synthesis From Renewable Bio-Based Monomers

It is possible to get a large range biopolyesters by chemical synthesis. The previous packaging materials can be replaced by new types derived from renewable monomers, provided it is economically viable (Berezina and Maria Martelli, 2014). The most famous of this group biopolymer is polylactic acid (PLA).

Poly(lactic acid) (PLA)

PLA is biodegradable thermoplastic linear polyester having similar properties as of polystyrene. Lactic acid, the monomer of PLA, may easily be produced by fermentation of carbohydrate feedstock. The carbohydrate feedstock may be agricultural products such as maize, wheat or alternatively may consist of waste products from agriculture or the food industry, such as molasses, whey, green juice etc., (Garde *et al.*, 2000; Sodergard, 2000). PLA derived from renewable resources, for example, corn, wood residues, or other biomass, is of current interest not only because of the need to ultimately replace many petroleum-based polymers but also because of their useful physical and mechanical characteristics (Haugaard *et al.*, 2003; Frederiksen *et al.*, 2003). Specific benefits of PLA in packaging applications are its transparency, gloss, stiffness, printability, biodegradability, GRAS status, processability and excellent aroma barrier. An antimicrobial packaging system based on PLA would be superior to other antimicrobial system due to its comparable cost, effective antimicrobial activity, few regulatory concerns, and environmental friendliness. The properties of the PLA material are highly related to the ratio between the two monomers (L or D) of the lactic acid. PLA is approved for direct contact with food (NatureWorks, 2016a) and is applied in a range of packaging products (NatureWorks, 2016b). Zhou *et al.* (2016) proposed a method to fabricate super-robust PLA barrier films, which has properties of high efficiency gas barriers, high strength and toughness. PLA is mainly processed into thermoformed pads and containers for packing and serving food, films, transparencies and bottles and other packaging blown, but also mixed with other bio-based and or biodegradable polymers to improve stiffness and strength and to reduce costs. The addition of nanoclay particles to PLA (PLA 3051D) enhances the degradation rate of composite materials (Rapacz-Kmita *et al.*, 2013). A fabric produced from PLA provides a silky feel, durability and moisture management properties. There have been developments in Europe and North America that have involved the use of PLA-based packaging for supermarket products. A few major companies like Nature works LLC, Purac (the Netherlands), Galatic (belgium), Cargil (USA) and several Chinese companies are successfully producing PLA with specification from biomedical applications. The company KHS is using SiOx

technology (multi barrier layer) to produce PLA bottles with excellent barrier properties (reduces moisture vapor transmission rate by 60%), otherwise, it is not possible to use PLA for packaging of soda (Klages, 2013). PLA containers have been used for packaging foods such as Biota™ PLA bottled water, Noble™ PLA bottled juices, and Dannon™ yogurts. The containers meet German and EU food grade requirements.

Synthetic Polymers Produced From Fossil Resources

Synthetic polymers have more predictable properties and the source of raw materials used to obtain such polymers is more readily available (Rydz *et al.*, 2015). The methods commonly used to manufacture synthetic biodegradable polymers are ring-opening polymerization (ROP) for synthesis of polyesters such as PCL, traditional polycondensation reactions for aromatic or aliphatic-aromatic (co)polyesters, or alkaline hydrolysis of poly(vinyl acetate) to PVA. Postpolymerization modification (physical or chemical) leads to synthetic derivatives of common polymers.

Polyvinyl alcohol (PVA)

PVA is a water-soluble and biocompatible polymer that is obtained from poly(vinyl acetate) through alkaline hydrolysis. PVC was one of the first polymers to be used in food packaging applications, and it replaced many traditional materials (glass, paper, cardboard). PVC's toughness combined with good clarity and resistance to oils and other substances makes it suitable for making blow-molded bottles. Flexible PVC film has found wide acceptance for food preservation. These materials have both 'stretch' and 'cling' properties; therefore, they are suitable for the hand wrapping of fresh produce. These materials can also be heat sealed (Leadbitter, 2003). The very low permeability of this polymer to gases (O₂ and CO₂) makes its wide application in food packaging, such as water-soluble packaging films. However, the tendency to absorb moisture limits its use under high moisture conditions. To improve its properties, PVA could be blended with other polymers, for example, food additives such as citric acid, succinic acid, and tartaric acid (Birck *et al.*, 2014). PVA blended with Poly(3-hydroxybutyrate) (PHB) can be used in the packaging industry (Olkhov *et al.*, 2003). Bonilla *et al.* (2014) studied the mechanical, water vapor barrier, and antimicrobial properties of PVA/Chitosan films for its use in food packaging. Musetti *et al.* (2014) investigated active packaging with grapefruit seed extract (GSE) and PVA for food packaging applications. Gaikwad *et al.* (2016) investigated active films from apple pomace and PVA for antimicrobial activities during food packaging.

Poly glycolic acid (PGA)

Polyglycolide (PGA) is another polymer that can be produced not only from petrochemicals, but also from renewable derived monomers. PGA is rigid simplest linear hydrolyzable aliphatic polyester with high crystallinity and barrier properties against carbon dioxide and oxygen. It has a high melting point (220–225°C) and excellent mechanical properties due to its high crystallinity (Vroman and Tighzert, 2009; Daniela and Ovidiu, 2012). PGA has vital advantage of degradability as it loses its strength within 1–2 months when hydrolyzed and loses mass within 6–12 months (Daniela and Ovidiu, 2012). Therefore, in packaging applications, PGA is used as protective layer in multilayer packaging systems, such as PET bottles for carbonated soft drinks and beer (Coles and Kirwan, 2011). The Kureha Corporation owns patents that protect the production process of multi-layer films and sheets for cups, daily dishes, or pizza trays (Kureha Corporation, 2010, 2011). According to the Kureha Corporation website, the biodegradation of PGA resin Kuredex occurs in compost over one month and is considered safe for composting because its degradation product is a natural metabolite – glycolic acid (Kureha Corporation, 2016).

Polycaprolactone (PCL)

Polycaprolactone (PCL) is synthetic biodegradable polyester which is produced from crude oil and biodegradable thermoplastic polymer. It has a good resistance to water, oil, solvent and chlorine (Alp *et al.*, 2011; Nafisa *et al.*, 2015). PCL crystallinity indirectly depends on the molecular weight i.e., increase in molecular weight tends to decrease its crystallinity (Alp *et al.*, 2011). At room temperature, PCL is a semi-rigid material has a modulus in the range of low-density polyethylene (LDPE) and high density polyethylene (HDPE). Enzymes and fungi easily biodegrade PCL. To improve the degradation rate, several copolymers with lactide or glycolide have been developed (Vroman and Tighzert, 2009). Co-polymers of caprolactone with DL-lactide have yielded materials having high rate of degradation (Daniela and Ovidiu, 2012). PCL has a wide range of application area, such as packaging, medical implant, and controlled drug delivery system.

Forms of Biodegradable Packaging

Biodegradable packaging is produced in several different forms to adapt to the requirements for packaging and storage of various products currently the most biodegradable gels, films, bags, boxes with lids and trays.

Biodegradable Gel

The gels are commonly used to prevent microbial contamination, such as a hydrogel, the hydrogel chemical and polymeric network (IPN) (Farrisa *et al.*, 2009). There is no visible positive effects of using impregnating gel on quality of lettuce, while, use of protective gel on fruits of pepino has positive effect on maintaining its beta-carotene content (Schreiner *et al.*, 2003). It was observed that the hydrogels prepared from combination of various polymeric materials reduced the shelf life of certain fruits, probably due to migration of water from the surrounding area (Garcia and Barrett, 2002). White extruded ginseng extract has good potential to maintain the concentration of antioxidants if used together with biodegradable stretch film (Rico *et al.*, 2007).

Biodegradable Films

Biodegradable films are designed with the intention of replacing the polyethylene (PE) film used for different purposes. Biodegradable films have better properties than traditional non-degradable plastics. They are resistant to moisture, warm organic materials for a period of several weeks or even months without changes in physical properties. This allows greater flexibility composting program. The permeability of biodegradable film for oxygen and carbon dioxide showed that the films with low permeability negatively affect the quality of the packed fruits. However, when the permeability of the biodegradable films is in-line with the respiration rate of the fruit, then it results into prevention of contamination by microorganisms and insects, which ultimately have positive effect on the durability and quality of the produce (Muratore *et al.*, 2005).

Biodegradable Bags

The biomaterial used for production of biodegradable bags is polyester. These bags are 100% biodegradable, safe to use for storage and have largest application in food industry. The use of natural raw materials improves the physical properties of this product. Biodegradable bags are strong, flexible, resistant to breakage and damage, and resistant to moisture and temperature changes because of its composition. After use, these bags are decomposed within soil or in the compost to carbon dioxide and water, over a period of several weeks, and also do not reduce the value of the resulting compost, which makes these bags substantially different from previously known polyethylene (Nampoothiri *et al.*, 2010).

Biodegradable Boxes With Lids

Box with a cover made of bi-oriented polystyrene, produced from corn. Such packaging is biodegradable after 47 days, depending on the conditions, and the process and it does not release harmful substances into the environment. It is crystal clear, allowing better visibility of contents, and is resistant to grease and withstands temperatures from -60°C to $+80^{\circ}\text{C}$.

Trays for Fruits and Vegetables

It was found that salad, and sliced broccoli, tomatoes, sweet corn and blueberries can be successfully kept in biodegradable trays of pulp wrapped in foil packaging of poured caprolactone. Such patches are resistant to moisture but brittle. Correspond to the products during freezing them does not change their structural properties well (Makino and Hirata, 1996).

Nanotechnology Functionality

The problems associated with biodegradable polymers are threefold: performance, processing and cost, although these factors are somewhat interrelated. The problems due to performance and processing are common to all biodegradable polymers in spite of their origin (Scott, 2000). In particular, brittleness, high gas and vapor permeability, poor resistance to prolonged processing operations have strongly limited their application. The application of nanotechnology to these polymers may open new possibilities for improving not only the properties but also the same time the cost-price-efficiency (Sorrentino *et al.*, 2007). Nanotechnology is generally defined as the creation and utilization of structures with at least one dimension in the nanometer length scale (109 m). These structures are called nanocomposites and could exhibit modifications in the properties of the materials or create novel properties and phenomena to the materials. To achieve these modifications, a good interaction between the polymer matrix (continuous phase) and the nanofiller (discontinuous phase) is desired (Peelman *et al.*, 2013).

There is growing interest in the incorporation of nanotechnology to enhance the functionality of food packaging for fresh fruit and vegetables. The packaging with antimicrobial compounds such as nano-titanium dioxide and nano-argentum inhibited fruit respiration and decay in Chinese bayberry (Wang *et al.*, 2010). Nano-zinc oxide inhibited ethylene production in fresh-cut apples (Li *et al.*, 2011), while chitosan coatings containing a nanoemulsion of mandarin essential oil aided in the preservation of green beans when combined with both high pressure and pulsed light processing treatments (Donsi *et al.*, 2015). The nanocomposite films consisting of whey protein isolate (WPI) with zein nanoparticles (ZNP) coated with sodium caseinate can be used as biodegradable food packaging materials (Oymaci and Altinkaya, 2016). Corn zein based films with oleic acid, nanocarbonate and glycerol as a plasticizer show the possibilities of using the material with nanocarbonate to pack food products (Ribeiro *et al.*, 2015). De Moura *et al.* (2012) reported that

the thin film created by hydroxypropyl methyl cellulose (HPMC) and silver nanoparticles' (AgNPs) matrix has antibacterial properties with respect to *Escherichia coli* and *Staphylococcus aureus* and can be used for applications in food packaging. Rodríguez *et al.* (2014) showed that nanocomposites with antimicrobial activity based on cellulose acetate, modified montmorillonite (Cloisite30B), thymol as a natural antimicrobial component, and triethyl citrate as a plasticizer are really promising for use in manufacturing food-packaging materials.

When bioplastics are mixed with nanoclay particles, the resulting nanocomposites exhibit improved barrier properties compared with the pure bioplastics, and after their use can be composted and returned to the soil. Nanoclay-composites have been developed for potential use in a variety of food packaging applications and some products are already available for the consumer. Other nanomaterials can be utilized including nanoparticles, nanofibers and nanowhiskers (Sorrentino *et al.*, 2007; Robinson and Salejova, 2010). Introduction of the dispersed clay layers into the polymer matrix structure greatly improves the overall mechanical strength and barrier properties of the material, making the use of nanocomposites films more practical for industry (Sorrentino *et al.*, 2007).

Consumers have shown major concerns with use of nanotechnology in food packaging, including the potential contamination of foods from the release of harmful substances such as silver via migration from packaging (Su *et al.*, 2015). Unless addressed, these concerns may restrict the widespread adoption of this technology.

Potential Applications of Biodegradable Packaging

Research and developments in the biodegradable packaging have been increased in the last decade due to environment pollution issues but these packaging are still rarely seen in the market. Packaging industry and food manufacturers are currently testing biodegradable packaging materials for food. In this section, potential bio-based and biodegradable packaging materials are discussed for packaging of fruits and vegetables only. These suggested materials should not be used directly but these need further optimization.

Fruits and vegetables remain as living tissue until they are consumed fresh, cooked or processed. As soon as the fruit or vegetable is harvested, there is increase in the respiration rate of these living tissues, resulting in metabolic loss which ultimately takes the fruit or vegetable to a gradual maturation and eventual senescence. In fresh-cut fruits and vegetables, the wounding of tissues leads to texture breakdown, development of off-flavor and brown discolouration on the cut surface. In the packed fruits and vegetables, there is continuous change in concentration of carbon dioxide, oxygen, water and ethylene. Controlled respiration of these living tissues would improve storability and extend the shelf life of fresh and fresh-cut fruits and vegetables. Several packing material like LDPE, HDPE, PP, LDPE with thin perforation, expanded (foamed) Polystyrene, shrink films, cling films, netted bags, PET, molded pulp trays, CFB boxes, kraft paper etc are presently used for packaging of fruits and vegetables. The net stocking carriers can be made from biobased material for packaging of fruits and vegetables. The properties of PLA based material matches with the requirement for packaging of mushroom (High water vapor permeability, low gas permeability) (Haugaard and Festersen, 2000). The other possible biobased material used for packaging of fruits and vegetables are perforated PFA, cellulose acetate, cellophane films (for wrapping), starch based trays. Edible coatings may contribute to extend the shelf-life of fresh and fresh-cut produce by regulating the transfer of moisture, oxygen and carbon dioxide; by retaining the aroma and taste compounds in a food system, and by improving the mechanical handling property of foodstuff (Baldwin *et al.*, 1996; Park, 1999). Edible coatings may also be used to improve structural integrity of frozen fruits and vegetables and preventing moisture absorption and oxidation of freeze-dried fruits or vegetables (Baker *et al.*, 1994; Baldwin and Baker, 2002; Olivas and Barbosa-Cánovas, 2005; Park *et al.*, 2005). In addition, edible coatings can carry active ingredients such as antibrowning agents, colorants, antioxidants, antimicrobials, nutrients, flavors and spices to further enhance food stability, quality, functionality and safety (Krochta *et al.*, 1994; Krochta and De Mulder-Johnston, 1997; Debeaufort *et al.*, 2000; Min and Krochta, 2005). Besides this, edible coatings may replace, plastic packaging to some extent by natural and biodegradable substances and their use could lead to reduction in overall packaging requirements and waste disposal problems.

Commercial Application of Biodegradable Packaging

The markets for biodegradable polymers are expanding because of significant developments in terms of novel design strategies and engineering. Presently, there are many research institutions and private companies that are manufacturing polymers based on natural reproducible resources, which including: Bioplast™ (Biotec GmbH, Germany), BAK-1095 and BAK-2195 (BASF and Bayer AG, Germany), Ecoplast™ (Groen Granulaat, Canada), Eco™ (National Starch and Chemical Company, USA), Celgreen™ CA-BNE (Daicel Chemical Industries, Japan), EverCorn Resin™ (Japan Corn Starch, Japan), Mater-Bi™ (Novamont S.P.A., Italy), Novon (Warner-Lambert Co., USA), Solanyl™ (Rodenburg Biopolymers B.V., the Netherlands), Biopac™ (Biologische Verpackungssysteme, Germany), Bioceta™ (Tubize Plastics, France). The many other companies which are manufacturing biodegradable polymers include some names like, Biocell (France), Plantic Technologies Ltd (Switzerland), NatureFlex Innovia Films (United Kingdom), New Greensack (Convex Plastics, Italy), Corbion N.V. (Netherlands), NatureWorks LLC (U.S.), Biome Technology PLC (U.K.), Bio-on (Italy), Kaneka (Singapore), Meredian (USA), Mitsubishi Gas Chemicals (Japan), PHB Industrial S/A (Brazil), Shenzhen O'Boer (China), Tephra (USA), Tianan Biological Materials (China), Tianjin Green Biosciences (China), Yikeman Shandong (China) and others.

BASF, a world leader in the chemical and plastic industry, is working on further development of biodegradable plastics based upon polyester and starch. 'Eco-flex' is a fully biodegradable plastic material that was introduced to consumers by BASF in 2001. The material is resistant to water, grease, hygienic for disposable wrapping, decompose in normal composting systems. Consequently, Eco-flex has found a number of suitable applications as a packaging wrap. Environmental polymers (Woolston, Warrington, UK) has also developed a biodegradable plastic material, known as 'Depart', the polyvinyl alcohol (PVA) product is designed for extrusion, injection molding and blow molding. 'Depart' features user-controlled solubility in water that is determined by the formulation employed. Examples include hospital laundry bags which are washed away, allowing sanitary laundering, wrap for disposable food service items, agricultural products and catheter bags. Biotec (Emmerich, Germany) has three product lines of thermoplastic starch (TPS) which include Bioplast® granules for injection molding, Bioflex® film, and Biopur® foamed starch (Mohanty *et al.*, 2000).

Twenty-four companies are known to be involved in PHA production and applications globally. The most famous company that produces PHA and has received many awards for environmental protection efforts is Metabolix Inc. (USA). The P3HB4HB based copolymers produced by Metabolix Inc, USA is known as Biopol™. Manufacture of blow-molded bottles using Biopol for packaging shampoo was started by Wella AG (Darmstadt, Germany) (Mohanty *et al.*, 2000). Biomer (Germany) is producing PHB using *Alcaligenes latus*, in which accumulation of PHB can receive over 90% of the cell dry mass. PHB obtained that way is used for manufacturing bullets, pens, combs, and so on. The Tsinghua University in Beijing, China, uses *Aeromonas hydrophila* in the production of PHBHx in collaboration with the Guangdong Jiangmen Center for Biotech Development, China; KAIST, Korea, and Procter & Gamble, USA. Recently, Procter & Gamble, USA have begun to develop a large range of polyhydroxybutyrate co-hydroxyalkanoates, which are trademarked as 'Nodax'. Jiangmen Center for Biotech Development, China produces films, flexible packaging, thermoformed articles, coated paper, and other items using Nodax. Tianjin Green Bioscience, China and Metabolix, USA used *Ralstonia eutropha* and recombinant *E. coli* to produce P3HB4HB. *Ralstonia eutropha*, which accumulates 80% PHBV in the cells was used to the model process of PHBV production with high efficiency. Ningbo Tianan, China, developed this process in collaboration with the Institute of Microbiology, affiliated with the Chinese Academy of Sciences (Chen, 2010). Mater-Bi ZI01U/C (biodegradable and compostable bio-based plastic produced by Novamont) was used as a matrix to blend with PHA and bacterial biomass (Scaffaro *et al.*, 2012). Eco Cortec is manufacturing different biodegradable polymers for their application in packaging industry (Table 1).

Polyglycolide and PLA are manufactured under different trade names for various applications by a number of firms. The containers meet German and EU food grade requirements. Some of the important firms that manufacture PLA are Cargill Dow Polymers, the largest producer of PLA resins (NatureWorks PLA), Mitsui Chemical Inc. (Lacea), Schimadzu Corporation (Lacty), Hygai (PLA), Chronopol (Heplon, industrial developmental), Alkermes (Medisorb), Birmingham polymers [poly(L-lactide), poly(DL-lactide) PLAGA], Neste [poly(L-lactide), industrial developmental], Purasorb (PLA, Purasorb, PD, Purasorb, PDL, PURAC), Boehringer

Table 1 Commercial biodegradable packaging material by Eco Cortec

Trade name	Properties
Eco Film®	Certified compostable per ASTM D 6400; 300% stronger than LDPE; High and low temperature stable; heat-sealable, convertible, laminations; Biodegrades rapidly in soil (within 45 days); Elastic and visually attractive material; Accepts printing for marketing and identification
Eco Film® Cryogenic film	Certified by BPI, Din Certco per ASTM D 6400; Specific Eco Film® formula for frozen goods; does not become brittle at extremely low temperatures; all the benefits of Eco Film®; ideal for frozen packaging
Eco Works® Premium films & bags	Certified compostable per ASTM D 6400 and DIN CERTCO; Meet proposed USDA definition of Biobased; New formula Eco Works® 70 has been tested for biobased content at Iowa State University and has a completed BEES environmental profile for "Durable Films"; Certified and approved for Food Contact (Faculty of Food Technology and Biotechnology Zagreb, Croatia); 300% stronger than LDPE; more rigid than Eco Film® (allows handle bags)
Eco Wrap® Compostable stretch film	Up to 60% better yield per roll; Wraps 60% more pallets than standard stretch film; perfect for frozen food & medical; does not become brittle; applied with the same stretch equipment; withstand 400% pre-stretch; accepts printing
Eco-Corr® VpCI biodegradable/compostable films and bags	100% Biodegradable per Din V 54900; BPS Certified; offers superior strength compared to LDPE; heat and water stable; Once exposed to a compost environment Eco-Corr® will biodegrade rapidly with no harmful effects to the environment
Eco-Corr® ESD Compostable Films and bags	Meets requirements for compostability; combines all the benefits of Eco-Corr®, Eco Film®, Eco Works®; Multi-metal corrosion protection (VpCI); electro-static discharge; designed specifically for electronics; leaves no residue after unwrapping
CorrTainer™ brand of corrugated boxes	Fully recyclable and repulpable; moisture resistant; eliminates the need for secondary packaging in some applications; cost effective, environmentally friendly, corrosion protection; easy to use, with no need for desiccants or poly-coated wraps
EcoShield® Paper and Linerboard	Environmentally friendly barrier coating; Offers the same if not better barrier protection than wax or poly-coated paper; fully recyclable and repulpable; complies with FDA and USDA regulations for direct and indirect food contact; offers protection to both ferrous & nonferrous metals

Ingelheim (Resomer L, Resomer R, Resomer, LR, poly(l-lactide-co-D,l-lactide)) etc., (Nampoothiri *et al.*, 2010). PLA containers have been used for packaging foods such as Biota™ PLA bottled water, Noble™ PLA bottled juices, and Dannon™ yogurts.

Nowadays, many commercial edible coatings are used on fresh and fresh-cut fruits and vegetables. Several commercial products available in the market for postharvest use, such as Biosave (*Pseudomonas syringae*) registered in the USA and “Shemer” (*Metschnikowia fructicola*) registered in Israel (Droby *et al.*, 2009). Pro-long, TAL-Prolong (Courtaulds Group, London), Semperfresh (AgriCoat Industries Ltd., Berkshire, UK), and Natural Shine 9000 (Pace International, Seattle, USA) are commercially available composite coating formulations based on CMC (Nisperos-Carriedo *et al.*, 1992). Nature-Seal (Ecoscience Product System Division, Orlando, FL), is another cellulose-based edible coating formulation used for delayed ripening of tomatoes and mangoes. A commercial fruit coating, Nutri-Save (Nova Chem, Halifax, Canada), was developed to serve as both film former and natural preservative and to create a modified atmosphere around fruits to reduce respiration rate and desiccation of these commodities. The some of the commercial applications of edible coatings on fresh fruits and vegetables have already been discussed (Dhall, 2013). The commercial application of new generation of edible coatings on fresh-cut fruits and vegetables has been discussed (Dhall, 2016).

Conclusion

To date, the majority of the packaging used today is synthetic in nature and has been derived from fossil fuels. However, there are now global concerns about the depletion of non-renewable raw materials for manufacturing plastics. The production of microbial biodegradable polymers from agro-food waste residues seems a promising route to create an innovative, more resilient, and productive waste-based food packaging economy by decoupling the food packaging industry from fossil feed stocks and permitting nutrients to return to the soil (Guillard *et al.*, 2018). Presently, the production of biodegradable packaging is mostly at research level and has limited commercial use. However, growing consumer awareness towards these packages may lead to grow this industry in near future (Rydz *et al.*, 2018). Despite the advantages of biodegradable materials which have been presented by scientists, a number of obstacles in their development potential have to be overcome, such as cost effectiveness, food safety, food quality, improved water vapor permeability barrier and technological application methods. Full commercial production and application of biodegradable packaging is still some way off, but its potential has now being realized.

See also: Recyclability of Packaging Materials for Domestic Applications

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Bio-Polymeric Packaging Material for Packaging of Raw Food

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Introduction

Food quality preservation and shelf-life extension of packaged foods make packaging a crucial part of food safety (Appendini and Hotchkiss, 2002). Packaging is integral among all food manufacturing processes, since it maintains food quality during processing, storage, transportation, and distribution (Han, 2014; Marsh and Bugusu, 2007a). These processes are responsible for influencing food quality, and consumer health, hence, are related economics of food industry (Han *et al.*, 2018). Petrochemical-based plastics such as polyethylene terephthalate (PET), polystyrene (PS), polyethylene (PE), polyvinylchloride (PVC), polyamide (PA) and polypropylene (PP) have been widely used as packaging materials in food industry for decades because of their large availability, easy processability at relatively low cost, and desirable mechanical (tensile and tear strength), barrier (air and moisture) and thermal insulation (heat sealability) properties (Siracusa *et al.*, 2008; Hu, 2014). However, most of the plastic disposal wastes get accumulated in landfills owing to their slow decomposition and/or resistance to microbial degradation, thus, generating serious problems in the ecosystem (Kirwan *et al.*, 2003). As per a Eurostat report, during 2006–2015, plastic packaging waste amounts to 15.9 million tonnes in Europe, which constitutes nearly 19% of total packaging waste generated by packaging material (EU, 2018). This urges the need for the packaging industry to switch to biodegradable, renewable, as well as cost-effective materials, to reduce burden on the environmental pollution and climate change to certain extent (Siracusa *et al.*, 2008; Petersen *et al.*, 1999).

Development of eco-friendly products using biodegradable materials such as renewable raw materials derived from plant and animal sources have suitable attributes to address these persisting environmental issues (Davis and Song, 2006; Gontard and Guilbert, 1994; Bastioli, 2001). For sustainable growth of food packaging industry, manufacturers are moving towards a “greener packaging” era to address the ecological concerns and consumer demands. To this end, recycled and recyclable packaging materials are emerging as key food packaging trend being an alternate to plastics and other environmentally-unfriendly materials (Del Nobile *et al.*, 2009; Schmid *et al.*, 2012). Biodegradable packaging materials offer advantages over synthetic plastics such as biodegradability and/or compostability, and renewable raw materials (Tharanathan, 2003; Licciardello, 2017; Peelman *et al.*, 2013; Narayanan *et al.*, 2017). Now-a-days both of these properties are of commercial interest in food packaging industry to satisfy market and consumer needs. Biodegradable and recyclable packaging materials include biopolymers and paper-based products (Tang *et al.*, 2012; Kirwan, 2003). These materials can be degraded into simpler substances (water and carbon dioxide) or small molecules upon exposure to open environment (having optimum temperature, moisture, oxygen content and microorganisms) (Siracusa *et al.*, 2008; Davis and Song, 2006). Biodegradable polymers, based on types of raw materials (which could be renewable) have much faster biodegradation rates (varying from weeks to months) compared to petroleum based plastics (extending up to years). Based on the constituents of polymers and available conditions for degradation process, bio-degradation of polymers vary (Siracusa *et al.*, 2008; Gross and Kalra, 2002). Eventually, it minimizes the environmental problems associated with the packaging disposal wastes by reducing the amount of solid-waste in landfills.

Food packaging also includes preservation and protection of food quality during processing, storage, handling and marketing (Coles *et al.*, 2003; Smith *et al.*, 1990). The food packaging industry has developed ways to maintain the food quality (organoleptic properties of food), shelf-life, food safety, and reduce chances of food-borne diseases by reducing effects of oxidation and microbial action on foods (Robertson, 1998). Packaging protects food from environmental impacts such as moisture, gases (O₂, CO₂), heat, light, aroma, pressure, dirt, insects, microorganisms, also provides antimicrobial and antioxidant properties and minimizes any mechanical damage (Brody *et al.*, 2008). Therefore, active food packaging has emerged as a new technology in satisfying consumer and market demands. These are designed to extend food shelf-life by promoting desirable interaction with food by incorporating active substances into packaging aimed to be released/absorbed into food or absorbed/released from the packaged food to the surrounding environment of food (Rooney, 1995; Ozdemir and Floros, 2004). This article discusses biodegradable packaging materials focusing towards its sustainability in accordance to food stability, consumer health and environmental impact.

Properties of Packaging Materials

The protection that needs to be provided by the packaging materials is summarized in Fig. 1.

Properties of the packaging film, including permeability of gases (oxygen and CO₂), water vapor permeability, tensile strength, elasticity, thermal stability, etc., need to be determined for packaging applications. These properties can be modified using different additives such as: cross-linking agents, plasticizers, texture agents, antioxidants, and antimicrobial agents (da Rocha *et al.*, 2018). Standardized protocols are utilized to define barrier properties of different materials used for food packaging.

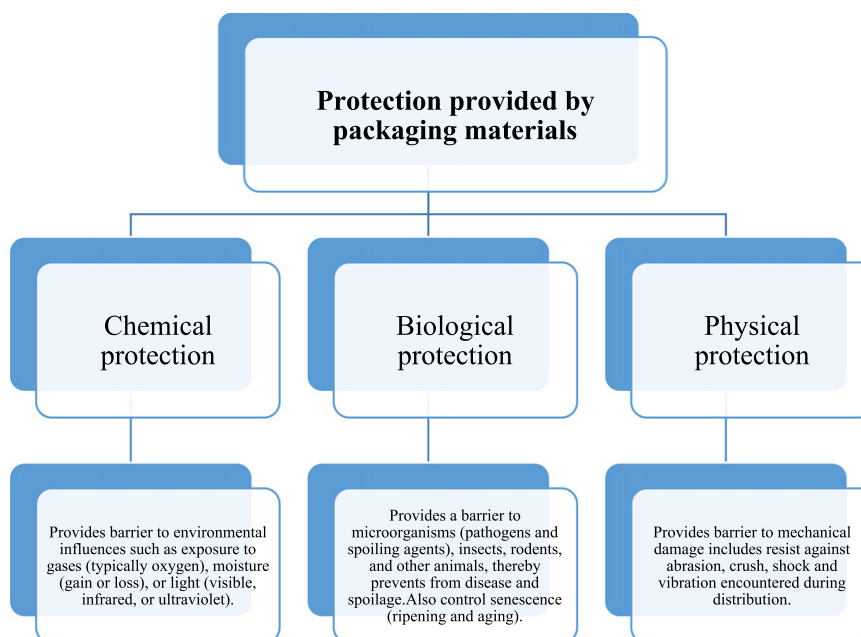


Fig. 1 Summary of protection provided by packaging materials.

Barrier Properties

Oxygen permeability is quantified by the oxygen transmission rate (OTR), defined as the amount of oxygen that permeates per unit area and unit time in packaging materials, measured at different relative humidity following methods recorded in ASTM F1927-07 or ASTM D3985-05. Oxygen barrier property for fresh food packaging (e.g., ready-to-eat meals, fruits, and salads) plays crucial role in its preservation since transfer of oxygen to and from the surroundings through packaging can change food quality and shelf-life.

The water vapor transmission rate (WVTR), defined as the amount of water vapor transmitted per unit area and unit time through packaging materials, measured using different standards such as ASTM E96 (ASTM E96/E96M-16, 2016), ISO 2528 (ISO 2528:2017), TAPPI T 448, and TAPPI T 464. Moisture transfer from the internal or external environment through packaging materials can affect food quality, especially flavor, aroma, color and so on. Thus, OTR and WVTR of packaging films are strongly influenced by nature and composition of the film as well as by the environmental factors (temperature and relative humidity).

Similarly, amount of water absorption by packaging material can be measured by Cobb test (ISO 535), defined as mass of water absorbed on test area over specified time (usually 60s). Grease or oil resistance methods can be determined from stain on paper from greasy substance (TAPPI T 454, and TAPPI T 507).

Mechanical Properties

Mechanical properties of packaging materials are important since they provides protection to the packaged foods by maintaining their integrity during handling and storage.

Mechanical properties of bio-based packaging films include tensile strength, tear propagation resistance, penetration resistance, and seal strength.

Tensile properties

Composition (polymer synthesis, additives, blends, chemical modifications or combinations of above, and also their processing) and storage (temperature condition and relative humidity) conditions of packaging materials can affect their tensile properties. Tensile properties under specified conditions can be measured using standard test method ISO 527-3:1995 (ISO 527-3, 2018) or ASTM D882-12 (ASTM, D882-12, 2012).

Tear propagation resistance

This test ensures packaging is protected against any kind of accidental damages. This evaluates tearing behaviour of film (tear initiation followed by tear propagation) following any localized failure (e.g., initial puncture, rupture due to accidental penetration or impact etc.). Tear propagation of films were evaluated using standard test methods: ISO 6383-2:1983 (ISO 6383-2, 1983) or ASTM D1922-15 (Elmendorf tear method) (ASTM D1922-15, 2015) and ISO 6383-1:2015 (ISO 6383-2, 1983) or ASTM D1938-14 (Trouser tear method) (ASTM D1938-14, 2014).

Penetration resistance

Package integrity might loss due to puncture leading to penetration of contaminants (gases or odors) which can further affect the packaged food quality. This property is usually expressed as load puncture or energy (area under load deformation curve) and can be measured using standard methods: ASTM F1306-90(2008) (ASTM F1306-902008e1, 2008) or EN 14477:2004.

Seal strength

To facilitate sealing and opening of any packaging, a minimum level and an upper limit of seal strength is set. Seal strength is measured according to ASTM F88/F88M-15 (ASTM F88/F88M-09, 2009).

Antimicrobial Activity

Antimicrobial properties of food packaging can delay or inhibit microbial growth responsible for deterioration of food quality leading to off-flavor, discoloration, nutrient loss, and reduced shelf-life, which further enhances chances of food-borne illness (Biji *et al.*, 2015; Malhotra *et al.*, 2015; Cooksey, 2005). Antimicrobial food packaging materials can be developed in two ways: one type packaging is making direct contact with the food and the other type is without making direct contact with the food surface (Sofi *et al.*, 2017; Realini and Marcos, 2014; Kerry *et al.*, 2006). In case of direct contact, antimicrobial agents can be evaporated or migrated (volatile substances) into food products, mostly used for vacuum-packed or wrapped products (Sung *et al.*, 2013). In non-contact antimicrobial packaging, include MAP (modified atmosphere packaging) technologies (Realini and Marcos, 2014), various bioactive compounds, such as: spices, and essential oils, enzymes, polysaccharides, bacteriocins, and other bioactive phytochemicals (Malhotra *et al.*, 2015; Suppakul *et al.*, 2003; Irkin and Esmer, 2015; Raveendran *et al.*, 2018; Hanušová *et al.*, 2013), can be incorporated to produce antimicrobial packaging systems. Incorporation of antimicrobial agents depends on processing techniques (extrusion, compression, or molding) used for preparation of an antimicrobial film as well as on the properties of film material and antimicrobials (heat stability and compatibility) (Lucera *et al.*, 2012).

Antioxidant Activity

Presence of oxygen in food packages facilitate microbial growth, oxidation of nutrients, lipids, and pigments, leading to deterioration of food quality (change in flavor, color, nutritive value, texture). It can form toxic compounds due to degradation of fatty acids, and can also alter the respiration rate and ethylene production of fruits and vegetables leading to their early quality degradation (Gómez-Estaca *et al.*, 2014). So it is necessary to remove oxygen from head space of food packages to maintain food quality and ensure food safety. Though vacuum packaging/MAP in combination with good oxygen barrier in the packaging film can effectively remove oxygen inside packages, residual oxygen during packaging or oxygen permeation due to poor sealing can have effect on the food inside (Coma, 2008; Ahmed *et al.*, 2017).

Oxygen scavengers, containing antioxidant agents, can be added to food packages in different forms (pads, sachets or labels). Oxygen scavengers can be metallic (fine powders of iron and ferrous oxide) and non-metallic (catechol, ascorbate salts, ascorbic acid, sulfites, and enzymes (ethanol oxidase/glucose oxidase)) (Yildirim *et al.*, 2018). Other ways of developing antioxidant packaging is incorporation of antioxidant agents into packaging film itself, where antioxidant compounds are released into food products or head space (Yildirim *et al.*, 2018; Park *et al.*, 2012; De Dicastillo *et al.*, 2011; Shahidi and Zhong, 2005; Torres-Arreola *et al.*, 2007). Release rate of active compounds should be optimized from/into the food packaging. Thus, manufacturing of antioxidant packaging material depends on properties of packaging material and antioxidant compounds. Furthermore, choice of active compound depends on compatibility of food product and active compound. Few examples of synthetic antioxidants include: butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), propyl gallate (PG), tertiary butyl hydroquinone (TBHQ) (Sanches-Silva *et al.*, 2014). To examine antioxidant activity various tests are available, like: radical scavenging assay, ferric-reducing antioxidant power (FRAP), 2,20-azinobis (3-ethylbenzothiazoline-6-sulfonate) (ABTS) assay, 2,2-diphenyl-1-picrylhydrazyl radical (DPPH), N-diethyl-p-phenylenediamine (DPD), and total phenolic content (Abramovič *et al.*, 2017; de Dicastillo *et al.*, 2015).

Bio-Based Raw Materials for Food Packaging Film

The above mentioned properties can be modified using composites, polymers blends, coatings, multilayer systems, chemical treatments, nano-additives or combinations of above technologies to maintain quality and shelf-life of packaged food (Shalini and Singh, 2009; Pawar and Purwar, 2013; Wróblewska-Krepsztul *et al.*, 2018; Johansson *et al.*, 2012). Bio-based packaging materials, along with their composites, developed to meet the needs of sustainable packaging are discussed below.

Biopolymers

Biopolymers based on starch and derivatives

Starch is a polysaccharide produced by plants and is comprised of repeating units of glucose, which includes two types of molecules: amylose (linear and crystalline) and amylopectin (branched and amorphous) (Kaseem *et al.*, 2012). It is mostly extracted from potatoes, corn, wheat, rice, seeds, legumes, cereals, and fruits. Starch-based packaging can be metabolized by microorganisms making them biodegradable.

However, high sensitivity of starch polymers towards water vapor permeability and poor mechanical strength have limited their food packaging application (Rejak *et al.*, 2014; Mali *et al.*, 2005). To overcome these limitations, it is usually plasticized in presence of plasticizers that include glycerol, sorbitol, xylitol or binary polyol mixtures and is extruded or casted to form polymer films (Farahnaky *et al.*, 2013; Sanyang *et al.*, 2015; Talja *et al.*, 2007). Starch is mostly used as a thermoplastic in food industry called thermoplastic starch (TPS) and the type and amount of plasticizer added to them influences their physical, mechanical, thermal and barrier properties (Zuo *et al.*, 2015). For instance, the transition temperature (T_g) decreased slightly with the addition of increased amounts of different plasticizers while the plasticizers increased the water vapor permeability (WVP) of sugar palm starch (SPS) films (Sanyang *et al.*, 2015). Change in WVP values is attributed to plasticizers causing structural modifications in starch network which makes the film matrix less dense but more mobile and flexible (Rodríguez *et al.*, 2006).

TPS still faces multiple issues such as high water susceptibility, poor mechanical properties and low degradation temperatures. To overcome these issues, TPS have been blended with different polymers such as PE, PP, PS, and ABS (Kaseem *et al.*, 2012). PE and PP blends showed improved mechanical properties and thermal stability, PS blends show improved thermal stability but poor mechanical properties, while ABS proved to be incompatible with TPS. Other ingredients have also been blended to starch-polymer matrix to improve their mechanical properties, such as nano-clays, carbon nanotubes (CNT), carboxymethyl cellulose (CMC), microcrystalline cellulose (MC) (Taghizadeh and Favis, 2013; Tongdeesontorn *et al.*, 2011; Chowdhury and Das, 2014).

Biopolymers based on cellulose and derivatives

Cellulose is a linear polymer of repeating glucose units usually found in plant cell walls. A number of cellulose derivatives have been synthesized commercially to extend their applications from food packaging films to water-soluble edible films, since derived celluloses are quite resistant to enzymatic cleavage, microbial attack, moisture and gas permeability, at the same time providing structural and mechanical support (Park *et al.*, 1993; Hefft, 2017). Few of the cellulose derivatives used for food packaging applications are: cellulose ethers (methylcellulose, ethylcellulose, hydroxyethyl methylcellulose, hydroxypropyl methylcellulose, hydroxymethylcellulose, carboxymethylcellulose) and cellulose esters (cellulose acetate, cellulose triacetate, cellulose acetate butyrate) (Siracusa *et al.*, 2008; Turhan and Şahbaz, 2004; Gemili *et al.*, 2009; Sata *et al.*, 2004). Amongst all, Cellulose acetate (CA) is commonly used for food packaging use because of its good barrier properties. CA along with cellulose diacetate (CDA) and cellulose triacetate (CTA) forms rigid wrapping film that is widely used in food packaging application (Paunonen, 2013). Triacetyl glycerol is used as a plasticizer during film molding. Casting composition, wet casting thickness, and drying temperature alter film porosity which further have an impact on the properties of the films (Wu *et al.*, 2014; Suderman *et al.*, 2016). Antimicrobial CA films can be prepared by crystallization of antimicrobial agents like, potassium sorbate, lysozyme, and sodium propionate, within the cellulose films (Gemili *et al.*, 2009; Sayanjali *et al.*, 2011). Therefore, the degree of porosity during drying affects crystallization of these antimicrobial agents. Incorporation of antimicrobial agents in CA films enhances shelf life of packaged food products. Further, keratin filled CA forms compostable films (Paunonen, 2013).

Biopolymers based on proteins

Protein films can prevent food from biological deterioration, microbial growth, control moisture migration and oxidation of nutrients as they offer barrier to vapors, gasses and oils (Yada, 2017). They also functions as carriers of antimicrobials, antioxidants, flavors and colors, which consequently helps to improve shelf-life and safety of packaged products. Few proteins that have been used as edible films include collagen, gelatin, corn zein, wheat gluten, whey protein, soy protein, mung bean protein (Wittaya, 2012).

Collagen is structural protein of connective tissue of bone, tendons, cartilage, and ligaments, in mammals. Collagen films being non-toxic and biocompatible has been successfully used as edible films (Khan and Khan, 2013). Different cross-linking agents such as glutaraldehyde, transglutaminase, and carboxamide, have been used to improve mechanical, and thermal properties of collagen films (Grover *et al.*, 2012). Upon increase in relative humidity collagen films fail to serve as a good oxygen barrier (Aguirre-Loredo *et al.*, 2016). However, this low resistance of collagen hydrosylates to moisture can be improved by enhancing the cross-linking density with polysaccharide derivatives (Lin and Gu, 2015; Tierney *et al.*, 2009). Collagen and synthetic polymers (PVA, PVP, and PEG) have been blended and casted to form films that possess high tensile strength (Vesely *et al.*, 2015; Sionkowska, 2012).

Gelatin is a natural water soluble protein obtained from the partial hydrolysis of collagen. Active packaging to preserve and improve food shelf-life includes films and coatings having natural additives that comprise essential oils or extracts obtained from plants and spices which exhibit antimicrobial and antioxidant properties (Clarke *et al.*, 2016). Few examples of such active additives are cinnamon essential oil, tea polyphenols, peppermint essential oil, orange leaf essential oil, bacteriocins, beet root residue powder, and thyme essential oil (Ramos *et al.*, 2016). These natural additives are able to reduce food deterioration by preventing food oxidation or microbiological effects on them. Also to enhance structural features of gelatin based films, different substances such as plasticizers, cross-linkers, and strengthening agents were added to reduce hygroscopic nature of gelatin by modifying their hydrophilic character or forming strong covalent bonds in the

protein-film network (Grover *et al.*, 2012; Suderman *et al.*, 2018; Catalina *et al.*, 2011; Rawdkuen *et al.*, 2012). Different biopolymers have been blended with gelatin to improve their mechanical and water resistant properties such as starch, chitosan, pectin, whey protein, lignin, or isolates of fish protein etc. (Al-Hassan and Norziah, 2012; Mohammed Manshor *et al.*, 2018; Bai *et al.*, 2013; Jiang *et al.*, 2010). Biodegradable gelatin based films have also been produced using water soluble synthetic polymer like: PVA (Dafader *et al.*, 2016).

Plant proteins, namely zein (protein found in corn), are relatively hydrophobic due to high amount of non-polar amino acids. Zein shows good film-forming ability and solubility in ethanol; forms mostly hydrophobic and hydrogen bonds within chains of film-matrix (Yamada *et al.*, 1995). Zein film exhibits good water vapor permeability (Wang and Padua, 2004) and addition of suitable plasticizers enhances their flexibility (Paramawati *et al.*, 2001). Flexible antimicrobial and antioxidant food packaging have been developed using zein/polymer or fatty-acid blends viz. PP/zein and zein/wax incorporating suitable antimicrobials and/or antioxidants (Arcan and Yemenicioğlu, 2013; Yemenicioğlu, 2016).

Wheat gluten, another commonly used plant protein, has good film-forming properties because of its integral cohesive and elastic nature (Gueguen and Popineau, 1998). Wheat gluten is insoluble in water, but shows solubility in aqueous solutions having varying pH (Tanada-Palmu and Grosso, 2003). It contains glutenins (offers stronger films and better barrier properties) and gliadins (offers good optical properties) (Kuktaite *et al.*, 2011). Gluten films have low oxygen permeability but high water vapor permeability because of hydrophilic nature of its protein. Addition of film plasticizers such as, glycerol can improve flexibility, tensile strength, oxygen and water vapor permeability (Gontard *et al.*, 1993).

Poly(lactic acid)(PLA)

PLA is a biodegradable bioplastic, that has been extensively used as suitable replacement of non-degradable petrochemical-based plastics (Muller *et al.*, 2017). Due to its wide availability, desirable mechanical properties, easy processability, and low comparative cost, PLA and PLA/starch blend products have the largest market share in biodegradable plastic market. PLA-based films are brittle in nature, therefore, different plasticizers (Tanrattanakul and Bunkaew, 2014; Jamshidian *et al.*, 2013; Mekonnen *et al.*, 2013) such as: glycerol, tributyl acetyl citrate (TBAC), glycerol triacetate (GTA), tributyl citrate (TBC), triethyl-2-acetyl citrate (TEAC), PEG of different MWs, and epoxidized soybean oil are added to alter their mechanical properties by decreasing the glass-transition temperature (T_g) and increasing strain at break (Arias *et al.*, 2013). Turalija *et al.* modified surfaces of PLA films with silver by simultaneous plasma polymerization/sputtering to achieve antimicrobial PLA films (Turalija *et al.*, 2016). Oxygen permeability of PLA films can be improved by addition of chitosan and montmorillonite (MMT) clay (Muller *et al.*, 2017). PLA can, possibly, be a good carrier for antioxidants like butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), tert-butylhydroquinone (TBHQ) and ascorbyl palmitate, and control food oxidation reactions (Jamshidian *et al.*, 2012; Byun *et al.*, 2010). Factors affecting antioxidant release from PLA include simulant polarity, film thickness, temperature, antioxidant solubility in simulant, polymer degradation, and antioxidant molecular weight (Jamshidian *et al.*, 2013). PLA/chitosan blend films have showed significant antimicrobial activity (against aerobic mesophilic and coliform microorganisms) with less rigid and stretchable films (Bonilla *et al.*, 2013). Corona treated (CT) PLA films have showed improved gas (O_2 , CO_2 , He,) barrier properties (Rocca-Smith *et al.*, 2016). Despite these advances, PLA and PLA-blended film properties still need to be improved, especially their barrier properties (moisture and gas), mechanical properties, and thermal stability.

Polyhydroxyalkanoates (PHAs)

PHAs are biodegradable natural plastics produced by microbial fermentation of carbon-based feedstocks such as: corn starch-based glucose, cane sucrose (Koller, 2014) or sugar beet sucrose under nutrient-limited conditions. PHAs can act as substitute to polystyrene (PS), polyethyleneterephthalate (PET), low-density polyethylene (LDPE) and high-density polyethylene (HDPE). PHA films are processed using injection molding (Peelman *et al.*, 2013), melt-extrusion techniques (Thellen *et al.*, 2008), and thermoforming. Thermal stability and mechanical properties of PLA films can be improved upon incorporation of kaolinite nanofillers (Peelman *et al.*, 2013). Oxygen permeability of PLA was reduced up to 90% after addition of 5 wt% cellulose nanowhiskers (CNW) (Peelman *et al.*, 2013). Addition of montmorillonite-layered silicate, coating of PLA-Si/SiO_x, or thin AlO_x-coating, to PLA improved the barrier properties (water vapor and oxygen) of PLA films making it applicable for food packaging especially for medium shelf-life products (vegetables, processed and/or fresh meat, cheese) (Peelman *et al.*, 2013). Hany *et al.* demonstrated anti-biofouling properties of medium chain length PHA (mcl-PHA) by conjugation of zosteric acid (Koller, 2014). PHA-based composites have improved film barrier properties, thermal stability, and mechanical properties, making them good candidates to be used as food packaging material.

Paper and Paper-Board

Paper and paperboard are made of an interlaced network of cellulose fibers, obtained from trees and/or recycled from recovered papers. Additives are added to pulp, during processing or after processing, to attain different technical functionalities of paper and board required for food packaging purpose (see "Relevant Websites section") (Kirwan, 2003; Delphine *et al.*, 2004). Application of paper and board in packaging have been enhanced in last 50 years because of their many advantages such as: recyclability (as prepared from renewable raw materials, recovered paper), biodegradability, robustness and adaptability, low cost of production, and ease of being molded, coated and printed (Delphine *et al.*, 2004). Global paper packaging market was valued USD 64.4 billion in 2017 and is expected to reach USD 82.4 billion by 2023 (see "Relevant Websites section") Types of papers used for food packaging are as follows (Kirwan, 2003): Kraft paper, used for paper bags in grocery store, wrapping, cushioning and other

uses; Sulfite paper, used as bags and wrappers for bread rolls, cakes, savory products and biscuits; Greaseproof paper, used to wrap fresh fish/meat, oily foods, also used as liner for biscuits, butter/cheese, snack foods; Glassine, used as liner for fast foods, baked foods, biscuits; Parchment paper, used for butter, cheese, margarine packaging; Laminated paper (paper laminated with aluminum/plastic to improve its properties) used for packaging of dried products (herbs, and spices, soups).

Paperboards are mainly used to make containers (cartons, boxes, trays) for shipping (Marsh and Bugusu, 2007b). Types of paperboards include: White board (typically used as the inner layer of a carton for direct contact with food); Solid board (used as baking trays, pizza boxes, trays for fruits and vegetables, clamshell packaging, also used as liquid cartons after lamination with PE); Chipboard (used as outer layers of cartons for foods like: cereals and tea); Fiberboard (used for shipping bulk food and retail food products).

In spite of their wide usage, there remains a need to improve the strength of paper material, enhance their barrier properties to maintain functionalities, make them resistant to moisture, and reduce quantity of raw materials used for manufacturing paper and board based packaging material. Ways of improving the barrier properties of paper based packaging is being widely studied. A few bio-materials have been investigated as barrier coatings (focusing mainly on oxygen, water vapor, and aroma permeability) for paper such as starch, corn, chitosan, alginate, cellulose derivatives, whey proteins, soy proteins, caseinates, wheat gluten, and zein (Khwaldia *et al.*, 2010; Lin *et al.*, 2017; Wang and Jing, 2016; Vikele *et al.*, 2017; Kopacic *et al.*, 2018; Jiang *et al.*, 2014; Elyas *et al.*, 2016; Xu *et al.*, 2016; Mazhari Mousavi *et al.*, 2018; Han and Krochta, 2001; Khwaldia *et al.*, 2014; Guillaume *et al.*, 2013, 2010; Trezza and Vergano, 1994; Parris *et al.*, 2002). High amount ($> 10 \text{ g/m}^2$) of whey protein coating on paper reduces water vapor permeability of paper and also acts as a grease barrier (Han and Krochta, 2001). Further, addition of sucrose to less concentrated whey protein coatings imparted good grease resistance to paper. A composite coating of sodium caseinate/wax on paper improved water vapor barrier property of paper (Khwaldia, 2010; Rastogi and Samyn, 2015). Wheat gluten-coated paper showed an decrease of nearly 56% in WVTR and 400-fold reduction in oil wettability in comparison to uncoated paper (Guillaume *et al.*, 2010; Cho *et al.*, 2012). Soy protein-coated paper also showed improvements in the oil barrier properties (Park *et al.*, 2000). Adequate weight of zein coatings on paper was found to decreased WVTR and improve grease resistance (Khwaldia *et al.*, 2010). Chitosan coating to paper decreased WVTR by up to 62.5% when compared to normal paper (Bordenave *et al.*, 2007). Paper impregnated with starch acetate showed improvement in water vapor permeability due to reduction in diffusivity (starch impregnation reduces pores available for water vapor exchange) and solubility (starch less hygroscopic than paper) (Larotonda *et al.*, 2005; Fringant *et al.*, 1998; Ni *et al.*, 2018). Alginate in combination with chitosan coating enhanced fat barrier properties paper (Khwaldia *et al.*, 2010; Ham-Pichavant *et al.*, 2005). Paper coated with carboxymethylated nano-fibrillated cellulose showed 6-fold decrease in air permeability and increase in grease resistance (Xu *et al.*, 2016; Syverud and Stenius, 2009; Aulin *et al.*, 2010).

Concluding Remarks

The current trend of sustainable food packaging is based on use of renewable and recyclable materials, reduction in consumption of raw materials (reducing demand on fossil fuels), and reduction of waste, which have increased the interest in biodegradable food packaging. Improved properties, functionality, and lower cost options will undoubtedly enhance acceptance of bio-degradable packaging in current market. Still few short-comings need to be addressed before we observe a major shift of food packaging to bio-based materials that satisfy consumer demands and environmental safety. Researchers and scientists are working towards this aspect trying to expand bio-based food packaging industry in most sustainable way using biopolymers and their composites.

See also: Recyclability of Packaging Materials for Domestic Applications

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CO₂ Capture, Storage, and Enhanced Oil Recovery Applications

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Introduction

Geological formations or reservoirs of oil and gas where CO₂ can be injected and stored for a long time include deep saline formations, depleted oil and gas fields, and unmineable coal seams. Each of these formations has a distinct capacity for holding and trapping CO₂, and each method of geologic storage has different cost components and projections. The storage of CO₂ can occur in a variety of geologic formations chosen for their ability to efficiently trap CO₂, the capacity of the formation to accept the intended volume of CO₂, and the formation's ability to limit the extent to which it migrates throughout the structure [1]. Oil and gas field reservoirs are the porous rock matrix that once held oil/gas. Injected CO₂ may trap into this porous and impermeable rock matrix. Moreover, during the long-term storage, CO₂ injected into these oil/gas reservoirs helps in recovering trapped oil reserves that are difficult to reach [2,3]. The deep saline aquifer consists of porous rock saturated with brine with a cap of impermeable rock formations to serve as the trapping mechanism for the CO₂ once it is injected. These types of formations have higher storage capacity and are more widespread regarding their location in comparison to oil and gas reservoirs and coal seams [4].

Once the fossil fuels from depleted reservoirs have been removed, CO₂ can be injected into the layer of porous rock where the clay particles and sediment grains packed the cap rock too densely for the CO₂ gas to move through it. Thus the injected CO₂ is permanently trapped in these fields.

For the existing reservoirs, CO₂ is widely used in oil recovery utilizing an enhanced oil recovery approach. Primary production of oil by its natural pressure could only produce about 5%–20%, and after this approach comes the secondary recovery stage in which water is incorporated to extricate the immobile and trapped oil [1,5,6]. Still, after secondary recovery completion, at least 50% of the original oil in place (OOIP) remains captive in the oil reservoir [7–11]. A CO₂ injection can dislodge more oil by displacing and dissolving trapped oil [12,13]. A number of CO₂ flooding projects are in practice or have been accomplished worldwide, which recover thousands of barrels of oil every day. In addition to oil recovery by means of CO₂, the process is equally useful for CO₂ long-term storage in oil reservoirs. The CO₂ as greenhouse gas emission is well thought out as the most crucial factor in global climate change. CO₂ flooding potential would be much more if at low cost and a substantial volume of the CO₂ gas is available.

EOR using CO₂ as an injected material offers a pathway to store large volumes of CO₂ and oil production boosting process to offset capture facility capital costs. Furthermore, after the EOR operations accomplishment, the sequestration activities may linger to maximize storage of CO₂ in the depleted reservoir [14].

Here we discussed the potential of CO₂ to use as EOR injection phase to boost the crude oil production while at the same time storing CO₂ gas permanently under the subsurface.

CO₂ EOR Potential

Approximately 1 kg of injected CO₂ can recover one-quarter extra oil. The produced carbon dioxide when oil is burnt, in most of the projects, is disposed of and wasted to the environment. At high pressure, CO₂ mixes with the oil and can recover up to 40% of the remaining oil (after water flooding). From the literature and case studies in the USA, approximately half of the country's water flooded oil fields could be exploited beneficially by CO₂ flooding. Light crude oil fields are considered as the preeminent option for CO₂ flooding process, as the larger North Sea fields are an attractive prospect of CO₂ injection compared to American fields [15].

Yanchang Petroleum Group in China is implementing CO₂ capture coupled with EOR in Ordos Basin, which is considered as one of the leading areas of CO₂ emission in China. Extensive R&D was done to check geological conditions suitable for the CO₂-EOR process. It was found that more than 87% of Yanchang oil reservoirs in Ordos Basin, China are good for the CO₂-EOR approach with tremendous CO₂ gas storage capacity [16].

Nicholas *et al.* analyzed the database of more than 30 CO₂-EOR projects to better understand the process of CO₂ retention in the reservoir, its oil recovery performance, and the CO₂ utilization in net for EOR process. At three of the selected sites, they calculated the cumulative CO₂ retention and found 23.1%, 48.3%, and 61.8% were retained. The incremental oil recoveries for these sites were 5.3%, 12.2%, and 21.5% of the OOIP (original oil in place) of the reservoir, and the net CO₂ utilization was calculated to be 4.8, 8.7, and 10.5 Mscf/STB (stock-tank barrel). The work provides useful information to estimate the potential range of expected performance of CO₂ injection, and CO₂ storage potential in the candidate fields [16].

CO₂ Storage and EOR Working Mechanism

Literature indicated that around 40%–50% volume of the injected CO₂ gas is stored enduringly in the porous medium. Primarily, it is the residual and solubility trappings' mechanisms that govern the CO₂ storage process. A CO₂ gas injection at immiscible

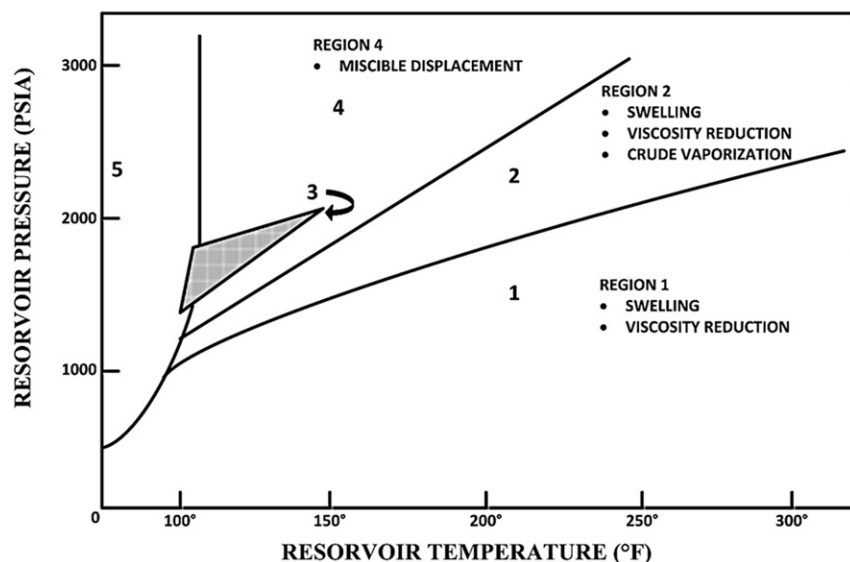


Fig. 1 Temperature and pressure effect on CO₂ flooding.

settings (i.e., $Pop < MMP$) favors higher volume of CO₂ loading in the porous medium. CO₂ storage is optimal near operating pressures at close to the minimum miscibility pressure (MMP) of the system and beyond that operating pressure; the storage capacity of CO₂ is not significantly improved. On the other hand, conferring to the EOR point of view, recovery factor is considerably boosted by increasing pressure and attain maximum value at the miscible operating pressure condition (i.e., $Pop \geq MMP$) [17].

The CO₂-EOR oil recovery performance depends on the oil reservoir temperature, pressure, and the crude oil composition. On the basis of mode of action of CO₂ used in EOR under the particular set of reservoir conditions, the basic mechanism of the CO₂ performance can be broadly divided into five different regions as shown in Fig. 1 [18].

In region I, the CO₂ solubility in the crude oil is the controlling parameter of CO₂ oil recovery performance. Under these reservoir conditions, shown in region I of Fig. 1, the CO₂ gets dissolved when it contacts with the reservoir crude oil. The dissolved CO₂ swells the oil; due to this swelling of oil, it forced the oil-water to come out of the pores of the rock. This process leads to the saturation of the crude oil in pores and increases its relative permeability, which favors flow conditions of the oil trapped in the pores. The viscosity of the crude oil in the reservoir is drastically decreased by the CO₂ saturation in the crude oil, which ultimately accelerates the oil drive towards the production wells.

In region II at an intermediate pressure and high temperature conditions, (in addition to the oil swelling and its viscosity reduction as in region 1 occurs typically), the process of CO₂-EOR is dependent on the oil droplet swollen; the light hydrocarbon of the crude oil vaporization takes place.

In region III, CO₂ action mechanism is similar to region II. It involves the swelling of oil and reduction in viscosity factors as in region II as the driving forces to recover the trapped oil at the same pressure conditions as in region II but at lower temperature settings. The CO₂-rich phase formed by the CO₂-rich liquid front formation due to the lighter crude oil components extraction process, it further contacts the oil and even lighter components are extracted. This process ultimately leads this fluid to develop the miscible conditions with the oil. This process is termed the multiple contact miscibility.

In region IV, a high-pressure mechanism exists. Oil swells in this set of conditions, which reduces its viscosity as in the other regions. However, the process of vaporization and its miscibility by multiple contacts happens in a very quick manner. Therefore, the process is considered as "first contact" miscible with crude oil of the reservoir. The CO₂ rich oil phase and oil-rich CO₂ phase become indistinguishable as they are present in one phase.

These mechanisms are the mode of actions of CO₂ in a reservoir for the productive and effective uses of CO₂ for oil recovery applications.

The CO₂-EOR oil recovery process can be classified as miscible and immiscible processes for the oil displacement [17]. The CO₂ miscible and immiscible processes take place under specific conditions of pressure, temperature, and the oil composition. As discussed earlier, the CO₂ is immiscible with oil on its first contact with oil. However, as it makes contact with crude oil of the reservoir, it is enriched with light components present in the crude oil. This composition modification develops a miscible zone between the oil and CO₂. The process works more efficiently above MMP. Fig. 2 shows the mode of action of CO₂-EOR process [19].

In contrast to miscible process, the immiscible process of oil displacement is in action where the pressure of reservoir is less than the MMP or in case the composition of the crude oil is not favoring miscibility with the CO₂. In these circumstances, the oil swelling, oil viscosity reduction, and also lowering of the surface tension are the dominant and primary modes of action of CO₂ oil recovery process.

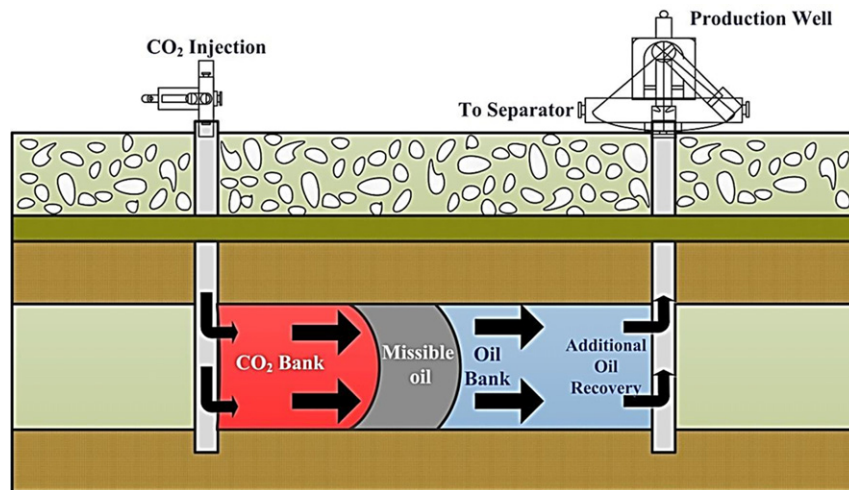


Fig. 2 A schematic of the water-CO₂ EOR operation.

Both miscible and immiscible injection approaches are contributed to the oil recovery by two different mechanisms, that is, oil swelling and interfacial tension reduction process. However, extraction of light components in the miscible injection scenario is considered as the core mechanism of the oil recovery process [17].

Problems of CO₂-EOR

Theoretically as well as practically at the small scale in core lab tests, nearly all of the trapped quantity of the oil can be recovered by using the CO₂-EOR strategy, mainly when the CO₂ injection occurs above the MMP. However, some properties of CO₂ such as the low viscosity and density, and the high CO₂ mobility, affect the overall performance severely and results in a poor oil sweep efficiency of the process [20,21]. Schematics of the CO₂ viscous fingering and gravity overriding processes are shown in Figs. 3 and 4, respectively [7,19].

High mobility and low viscosity result in CO₂ viscous fingering and early breakthrough, hence CO₂ passes ahead of the native reservoir fluids [22–24]. The low density of CO₂ compared to the oil triggered gravity override and inhibits the CO₂ contact with oil in the lower regions of the reservoirs. CO₂–oil is segregated from each other and CO₂ occupies the attic and oil remains at the reservoir cellar [25,26]. Figs. 3 and 4 explain the CO₂ problems that commonly occur in a reservoir.

Solutions to Overcome CO₂ Problems

The increase in CO₂ density is not feasible in practical terms. Conversely, substantial control of the CO₂ mobility is possible via different tactics such as water alternating gas (WAG) method. This technique is the easiest (but not very effective) way to overcome the mobility issues of the injected gas. In this practice, the CO₂ saturation is reduced by alternate slugs and as a result, reduces the relative permeability as well as the CO₂ mobility. However, this exercise of using alternate water and gas slugs may obstruct the CO₂ and oil mixing. The process also delays the injection of the specific amount of CO₂. Additionally, facilities for water flooding are also required. The WAG practice deepens the problems of oil and water separation related to the postproduction, and the production of water is also increased. Hence, the scientific community's attention has been focused towards other techniques as well to minimize the CO₂ mobility issues. The use of CO₂ thickener in a small amount to increase the CO₂ viscosity is another attractive and effective option to control the CO₂ mobility. Though direct thickeners used as CO₂ viscofiers similar fluorothickeners formed at the University of Pittsburgh have been developed, these are only available at lab scale, and their commercial availability is uncertain [27–29].

Foam to Overcome CO₂ Mobility Issues

CO₂ mobility reduction using foam flooding is another approach to resolve the CO₂ gas mobility concerns. The scheme involves the injection of alternate CO₂ and the surfactant slugs. In this process, the foam generated inside the porous media exhibits an incredible CO₂ mobility reduction [30–33]. Fig. 5 explains the foaming action in a reservoir [34].

Fig. 5 illustrates that the CO₂ gas alone cannot sweep the oil reservoir adequately. The WAG practice is comparatively better, but unswept zones are still present. In this situation, foam alternate WAG may exhibit the improved sweep performance. Foam slows down the CO₂ breakthrough as well as it also reduces gas cap gas production. CO₂ gas mobility reduction is a key

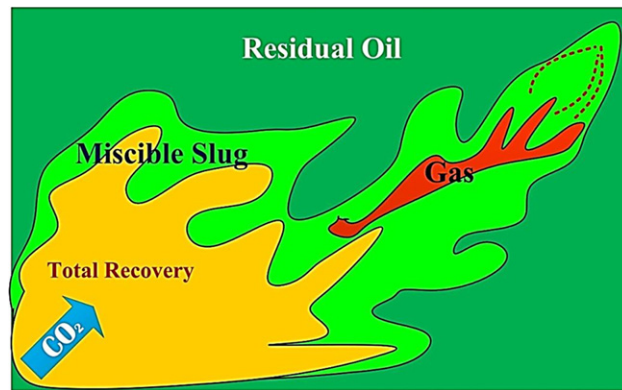


Fig. 3 Schematic of the CO₂ viscous fingering.

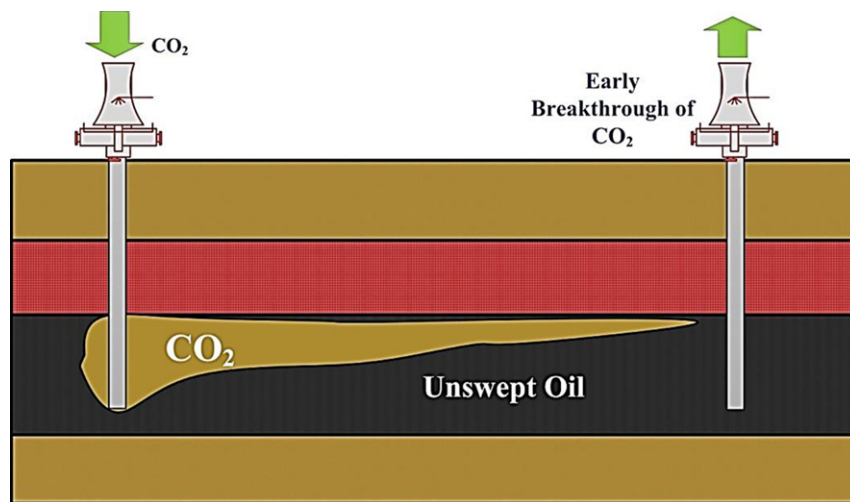


Fig. 4 CO₂ gravity override and early breakthrough (schematic).

advantage of the foam usage. Of course, the stability of the foam will influence the efficacy of the injection of foam in the reservoir [35–37]. Fig. 6 shows the process and explains how foam helps to overcome CO₂ fingering and slows down early breakthrough [38,39].

CO₂ Sequestration in Existing EOR Sites: Potential and Benefits

The innovation and improvement in carbon capture technology pooled with CO₂-EOR hold the potential to reduce the carbon footprint released from coal-fired power plants as well as from the other sources. At the same time, the approach is equally good and contributing significantly to crude oil recovery. Historically, injection of CO₂ in a reservoir or deep formations is very old. CO₂-EOR started in the 1970s at SACROC field in West Texas to recover oil. The properties of crude oil changed as the CO₂ mixes with it, which results in producing additional trapped oil flowing towards the production wells.

CO₂ EOR approach is much mature in the world, especially in the United States. However, many of the target reservoirs still have not been flooded with CO₂. As oil is more viscous than CO₂, first its viscosity is reduced, and a mixture of oil and carbon dioxide (CO₂) is brought to the surface. Currently, around 22 companies are working on about 99 different projects using EOR-CO₂ approach for oil production.

Many of the reservoirs running at EOR stage may be ideally good for CO₂ sequestration as these sites:

- (1) Provide traps which hold oil over geologic time,
- (2) Have CO₂ gas injection and transportation infrastructure,
- (3) May offer potential for additional stacked storage,

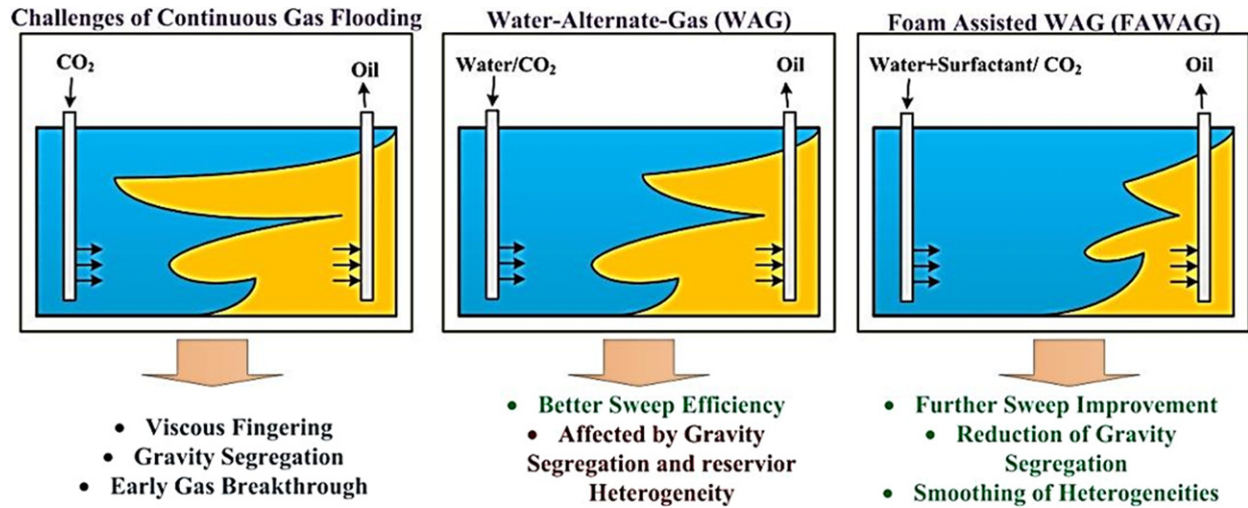


Fig. 5 Explanation of foaming action in reservoir.

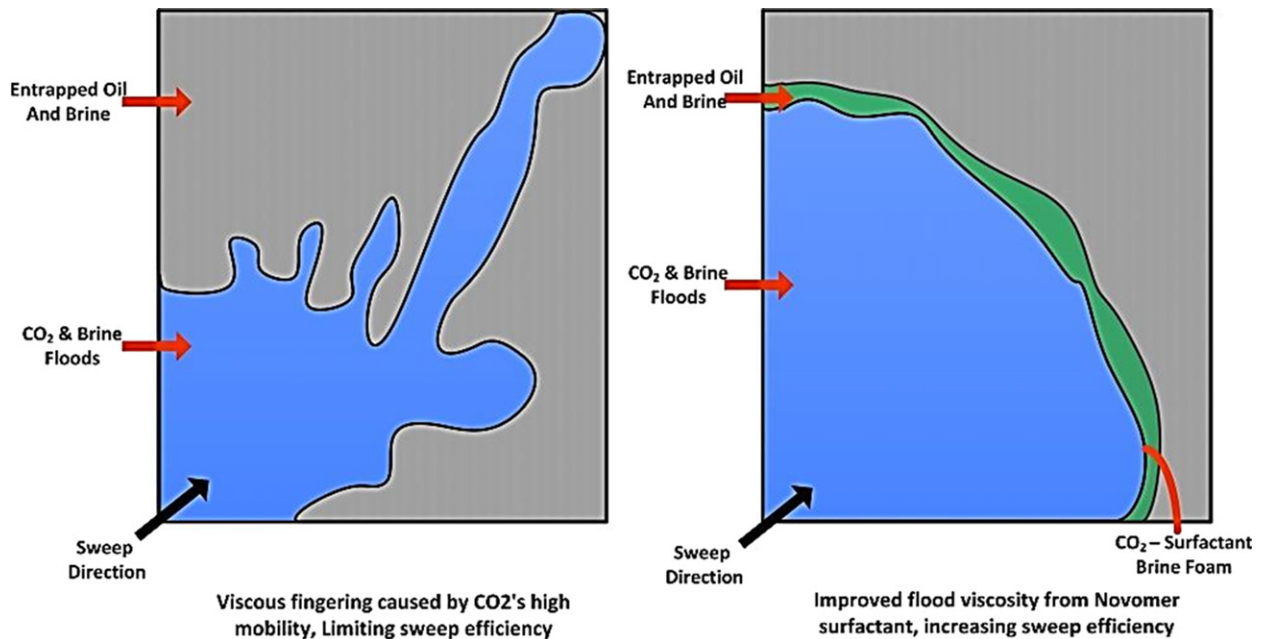


Fig. 6 Foam action to overcome CO₂ fingering and slow down early breakthrough.

- (4) Offer commercial benefits for CO₂ capturing companies,
- (5) Have already proven the injectivity of the reservoir,
- (6) Facilitate underground CO₂ gas management,
- (7) Present where the general public accepts these injection projects, and
- (8) These sites also have advantages of monitoring, already available infrastructure, experienced service providing company is in contract, and lastly, have preinjection data, etc. [14–17]. Even with these advantages, for long-term CO₂ containment for atmospheric purposes as well as for reduction in CO₂ quantities, these practices may ensure better prospects for CO₂ capture and its sequestration. Long-term storage of CO₂ can be improved by validating the reservoir and the suitability of its existing wells. Secondly, the storage capacity may be enhanced by evaluating the compatibility of well construction with long-term exposure to low pH fluids. At the third step, calculating CO₂ volume that can be stored permanently. Finally, by calculating the longevity of the CO₂ in the reservoir, this may be performed by flood monitoring or by monitoring and site closure [14–17].

Conclusions

Enhanced oil recovery using CO₂ offers a channel to store vast volumes of CO₂ permanently under the subsurface in depleted crude oil reservoirs. This CO₂-EOR strategy can be a reliable approach to recover trapped oil from the reservoirs as well as to permanently store the excess of CO₂ to make the environment clean. Almost 40%–50% of injected CO₂ quantity can be stored forever in the porous medium. It is also concluded that the foam can be effectively used to overcome the problems associated with CO₂ gas injection, which include but are not limited to the low viscosity and density of CO₂, and the high CO₂ mobility, which normally result in a poor oil sweep efficiency of the enhanced oil recovery process. Utilizing CO₂ for enhanced oil recovery is a well-understood technique, and it is also being practiced commercially. CO₂, on the other hand, in the context of greenhouse gases, needs to be sequestered and stored deep in the earth to reduce its adverse impacts to the environment. It is evident that using CO₂ for EOR not only can help to produce trapped oil to meet energy demands, but also can assist in permanent storage of CO₂ gas in deep reservoirs. It is also concluded that using novel ways of conducting CO₂-EOR process could help a lot to achieve an all-win solution both for the oil business and help to achieve climate change mitigation goals. In nutshell, it is concluded that moving from a simple EOR technology to “EOR + ” technology, represents a huge potential, attractive, and economically favorable technology. CO₂-EOR strategy can be modified such as by use of foam, CO₂ philic surfactant to play a much significant role in oil recovery and to improve the capacity for CO₂ storage. Overall this CO₂-EOR + technology can be used both for CO₂ long-term storage in addition to oil recovery in such a manner that is economically remarkable for industry.

See also: An Assessment of Hydrogen Energy Utilization for Sustainable Development

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Further Reading

National Energy Technology Laboratory, Presented at WEF/A&WMA 10th annual industrial wastes technical and regulatory conference.

Development of Self-Adhesive Products Using Only Bamboo Fibers Extracted With a Machining Center

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Introduction

Applications to environmentally friendly natural materials for industrial products has attracted attention in the industrial fields along with the recent rise in environmental consciousness. As an example, natural fiber reinforced plastics using natural fibers as reinforcing materials are used as interior materials for automobiles (Holbery and Houston, 2006). On the other hand, natural fiber reinforced biodegradable resin matrix composite materials, which is called green-composites, are beginning to be used for enclosures of electronic devices and spare tire covers of automobiles (Netravali and Chabba, 2003; Sujito and Takagi, 2011; Takagi and Takeichi, 2012). Therefore, it can be said that the application of these natural fibers to industrial products is entering the practical stage. From a different viewpoint, in the musical instrument industry, there is a demand of manufacturers to recycle waste materials generated after manufacturing the instruments, as well as user needs to use sustainable renewable instruments using natural materials even if their cost is high. However, among woods used as materials for musical instruments, there are many things that have become rare resources now. For example, rosewood used for marimba, silophone, etc., is said to take over 200 years to grow sufficiently as a material. Moreover, it is said that strict growth control is required. Therefore, substitute materials using glass fiber reinforced plastics etc., are currently being developed (Abe, 1999; Miyakosi *et al.*, 2000). However, a substitute material of 100% natural material has not been developed yet. Therefore, in this research, we aim to develop sustainable materials, which is important not only to environmentally friendly but also to resource-recycling rare timber (the soundboard wood has a higher Young's modulus and a lower attenuation rate than other woods) (Ono, 1996). In previous research, we focused on bamboo growing more rapidly, requiring only about 30 days to grow sufficiently, and widely in Japan as unused forest resources and we proposed a method to extract high quality bamboo fibers using a machining center to improve the shape accuracy of fibers extracted (Ogawa *et al.*, 2008). Next, we proposed a sustainable manufacturing system focusing on the natural growth of bamboo and evaluated environmental impact by LCA (Ogawa *et al.*, 2010). Moreover, we fabricated self-adhesive molded bodies of 100% bamboo fiber, which is an isotropic and homogeneous material were produced by a hot press method. As molding conditions, first, only the molding temperature was changed to evaluate the properties of the molded specimen, and it was revealed that an appropriate temperature exists (Ogawa *et al.*, 2010). However, the influence of other molding conditions including the shape of the fiber has not been evaluated. Therefore, in the present study, we aimed to clarify the influence of molding condition factors on the properties of molded bodies by preparing molded bodies under various molding conditions other than molding temperature and evaluating their mechanical properties.

Experimental Methods

Extraction of Bamboo Fiber and Hot Press Forming of Products

Natural bamboo with density of 0.7-g/cm^3 was air dried and used as a test material. We cut the straight culm (bamboo straight and branch free) of bamboo with an outer diameter of about 50-mm into a cylindrical shape and fixed it in the machine table of a 3-axis vertical machining center. Bamboo fiber was extracted by processing with a spiral tool path shown in Fig. 1. In order to extract bamboo fiber with straightness, a ϕ 6-mm straight end mill with straight two flutes, which is made of high-speed steel, was used as a cutting tool. Cutting conditions were fixed at a tool rotation speed of $10,000\text{-min}^{-1}$, a feed speed of 1000-mm/min , and a radial depth of cut of 0.05-mm . Bamboo fibers of different lengths were extracted by changing the axial depth of cut ($\approx$ fiber length), but base value was 10-mm .

A self-adhesive bamboo fiber board was produced by performing hot press molding only with the bamboo fiber obtained in this way. The shape of the bamboo fiber board was a rectangular parallelepiped of $25\text{-mm} \times 125\text{-mm} \times$ various thickness, and bamboo fibers were randomly oriented and formed. The hot press forming conditions were as follows: standard weight of 7.0-g , molding pressure of 20-MPa , molding time of 10-min , molding temperature of 190°C (Ogawa *et al.*, 2010) as standard conditions shown in Table 1. In the present study, the influence of these on the bamboo fiber board properties was evaluated with the bamboo fiber amount M , the mixing ratio ϕ of the bamboo powder, the fiber length L , and the molding pressure P as molding condition factors.

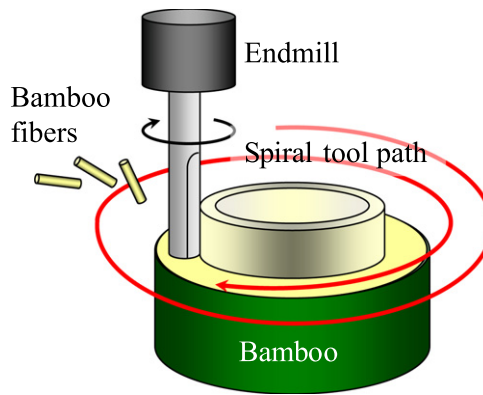


Fig. 1 Bamboo fiber extraction with a machining center.

Table 1 Standard condition of hot press forming for fabrication of self-adhesive bamboo fiber board

Hot press forming temperature T ($^{\circ}\text{C}$)	190
Hot press forming pressure P (MPa)	20
Hot press forming time T_h (min)	10
Cooling time T_c (min)	30
Weight of bamboo fiber M (g)	7
Length of bamboo fiber L (mm)	10
Rate of bamboo powder ϕ (%)	0

Evaluation of Performance of Product Made From Bamboo Fibers

Static characteristics such as bulk density, bending strength and Young's modulus were evaluated on the assumption of application to automotive interior materials and spare tire covers. We also evaluated dynamic characteristics such as natural frequency and logarithmic damping factor, assuming application to musical instrument materials.

For the density, the bulk density before molding was determined from the volume and mass of the container, and the bulk density after molding was obtained from the size and mass of the molding. The bending strength and Young's modulus were measured by a three-point bending test (loading speed 5-mm/min, distance between gauge points 80-mm) using a universal tensile testing machine.

The natural frequency and the logarithmic damping rate were obtained by fixing one end in the longitudinal direction so that the bamboo fiber board becomes a cantilever beam. We applied an external force near the free end of the other end to vibrate so that the time history of the displacement was measured with an eddy current type displacement sensor. At this time, a conductor sheet with a thickness of 20- μm was attached to the surface of the bamboo fiber board. The primary natural frequency and the logarithmic damping factor were determined the measured value. Hereinafter, the natural frequency means the primary natural frequency.

Experimental Results and Discussion

Influence of Board Thickness

Since self-adhesion between bamboo fibers was considered to be due to thermal fusion of components contained in bamboo fiber, in the previous study (Oawa *et al.*, 2010). Therefore, as molding conditions, firstly only the molding temperature was changed to evaluate various properties of the bamboo fiber board. As a result, it was revealed that an appropriate temperature exists. If the properties of the bamboo fiber board are attributable to thermal fusion of the fibers, it is considered that the thermal conductivity to the inside of the bamboo fiber board changes. That is, the characteristics of the bamboo fiber board also can change when the thickness t changes. Therefore, by changing only the fiber weight M used for the bamboo fiber board, molded bodies having different thicknesses were produced, and the influence of the plate thickness on the bamboo fiber board characteristics was investigated.

The appearance of the bamboo fiber board is shown in Fig. 2. As the plate thickness increases, the area of the brown part (black part) on the surface of the molded article tends to decrease. This browning phenomenon is called a Maillard reaction. It is a phenomenon accompanying heat softening of hemicellulose which is one kind of sugar contained in bamboo fiber. Since the area of the brown part due to this reaction tends to decrease as the plate thickness increases. There is a concern that when the plate thickness is large, the interior is not sufficiently heated. Changes in the bulk density of the bamboo fiber board with plate thickness

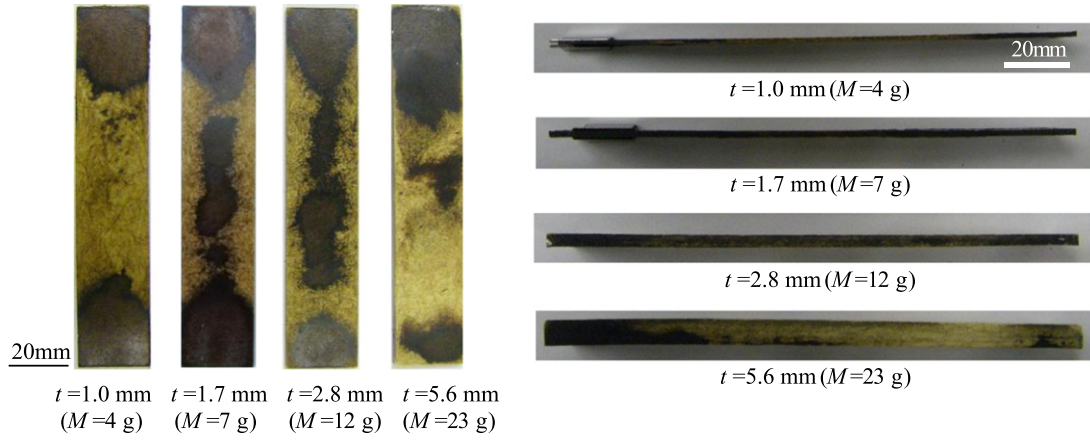


Fig. 2 Appearance images of self-adhesive bamboo fiberboard by changing board thickness ($\phi=0\%$, $L=10$ mm, $P=20$ MPa).

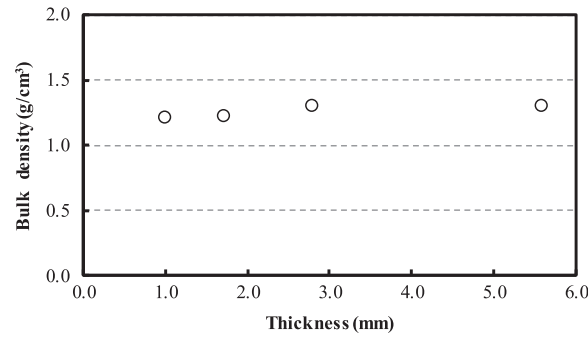


Fig. 3 Effect of board thickness on bulk density of self-adhesive bamboo fiberboard ($\phi=0\%$, $L=10$ mm, $P=20$ MPa).

are shown in **Fig. 3**. It is found that the bulk density of the bamboo fiber board gradually increases as the plate thickness increases. This is presumably because the heat conduction to the inside of the bamboo fiber board became insufficient as the plate thickness became larger, and moisture contained in the bamboo fiber remained unvaporized.

Changes in Young's modulus and bending strength of the bamboo fiber board with plate thickness are shown in **Fig. 4**. It is found that when the plate thickness is increased, the Young's modulus of the bamboo fiber board gradually decreases, and the bending strength becomes maximum when the plate thickness is about 2-mm. **Fig. 5** shows SEM images of the fracture surface of the bamboo fiber board when the thickness is 1.7-mm. Many cavities (voids) are generated inside the bamboo fiber board, and this cavity is thought to reduce thermal conductivity to the inside of the bamboo fiber board. Under the same molding condition, the volume ratio of this cavity to the bamboo fiber board is considered to be proportional to the plate thickness. Therefore, as the thickness increases, the thermal conductivity of the cavity is further lowered due to the cavity. From this fact, it is considered that the reason why the bending strength decreases when the plate thickness is as large as 5.6-mm is due to insufficient thermal fusion bonding between the fibers due to insufficient heat conduction to the inside of the bamboo fiber board during molding. On the other hand, the reason why the bending strength became small even when the plate thickness is 1.0-mm is believed to be because the bamboo fiber undergoes thermal damage due to overheating and the strength of the fiber itself is reduced. Even in the previous report, when the molding temperature was 220°C, which was formed at a high temperature, embrittlement of the fiber due to carbonization occurred and the strength of the bamboo fiber board was lowered.

Measurement results of natural frequency and logarithmic decay rate with plate thickness are shown in **Fig. 6**. As the plate thickness increases, the natural frequency increases and the logarithmic attenuation factor also increases. Here, the natural frequency f_n of the bending vibration of the cantilever and the logarithmic attenuation factor $\tan\delta$ are expressed by Eqs. (1) and (2), respectively. The result of calculating the natural frequency and the logarithmic decay rate using the values obtained in the experiment is also shown in **Fig. 6**.

$$f_n = \frac{\lambda^2}{2\pi l^2} \sqrt{\frac{EI}{\rho A}} = \frac{\lambda^2}{2\pi l^2} \sqrt{\frac{Et^2}{12\rho}} \quad (1)$$

$$\tan\delta = \frac{4.4\pi}{T_{60}\lambda^2} \sqrt{\frac{12\rho}{Et^2}} = \frac{4.4\pi}{T_{60}\lambda^2} \sqrt{\frac{12Ml^3}{Ebt^3}} \quad (2)$$

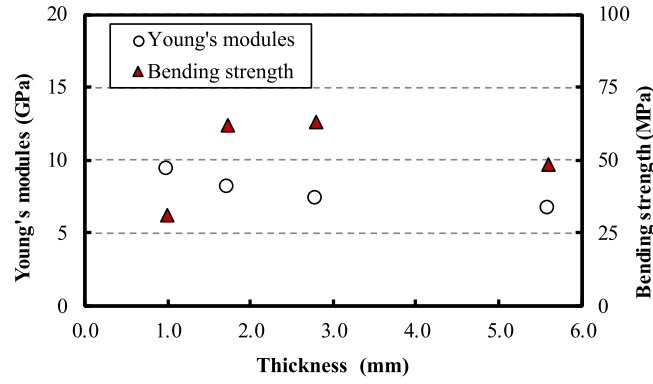


Fig. 4 Effect of board thickness on Young's modulus and bending stress of self-adhesive bamboo fiberboard ($\phi=0\%$, $L=10$ mm, $P=20$ MPa).

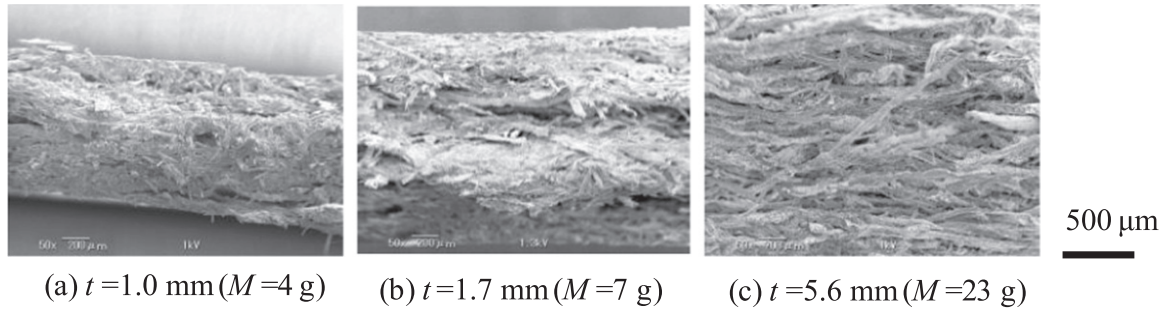


Fig. 5 Fracture surface images of self-adhesive bamboo fiberboard after bending test ($\phi=0\%$, $L=10$ mm, $P=20$ MPa).

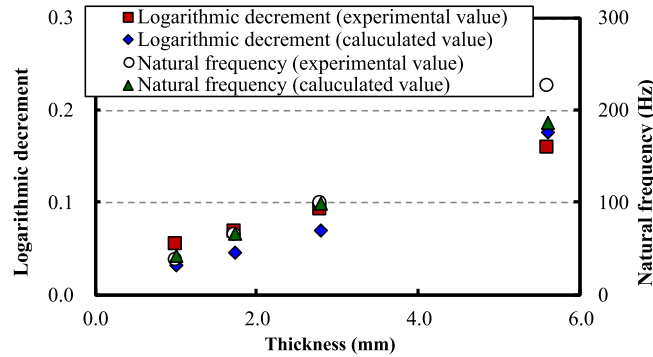


Fig. 6 Effect of hot board thickness on logarithmic decrement and natural frequency of self-adhesive bamboo fiberboard ($\phi=0\%$, $L=10$ mm, $P=20$ MPa).

Here, λ is an eigenvalue, E is a Young's modulus (GPa), I is a geometrical moment of inertia, l is a plate length (m), ρ is a bulk density (kg/m^3), A is a cross sectional area of (m^2), t is a plate thickness (m), b is width (m), T_{60} is a reverberation time (s).

It is found that the difference between the measured value of the natural frequency and the calculated value increases as the plate thickness increases. It is considered that the difference between the measured value and the calculated value occurred because the inside of the bamboo fiber board was not filled with uniform particles but an anisotropic material in which fibrous objects were solidified. Comparing the relationship between Young's modulus and natural frequency in Eq. (1), it can be seen that the natural frequency of this bamboo fiber board is higher than other objects having the same Young's modulus and having Eq. (1). That is, high sound is likely to occur. In addition, at the logarithmic decay rate, since the restraining force between the fibers due to thermal fusion is weak inside the bamboo fiber board, the fibers rub against each other at the time of excitation. It is considered that the internal friction was promoted, and the logarithmic decay rate was influenced by increasing the mass of the molding, that is, increasing the fiber amount.

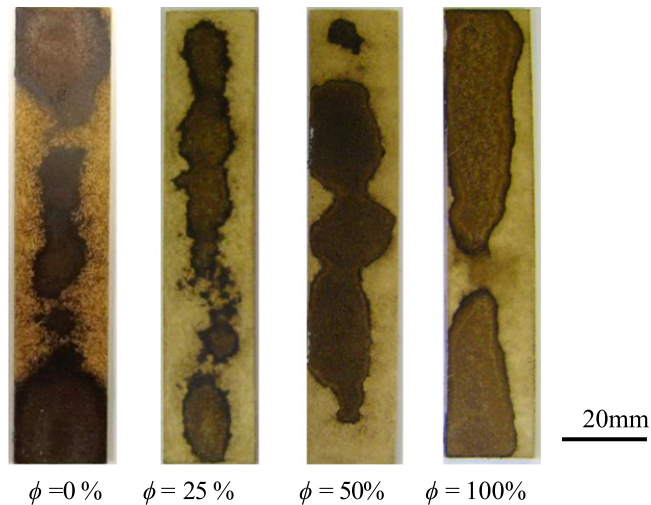


Fig. 7 Appearance images of self-adhesive bamboo fiberboard by combination ratio of the bamboo powder ($M=7.0$ g, $L=10$ mm, $P=20$ MPa).

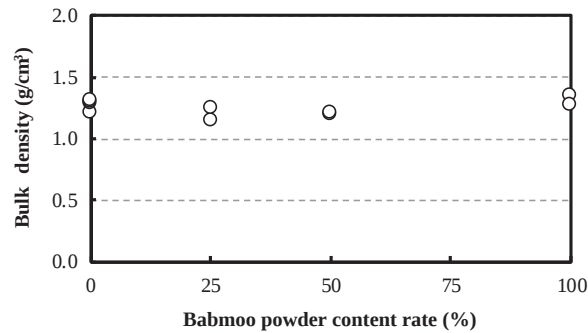


Fig. 8 Effect of board thickness on bulk density of self-adhesive bamboo fiberboard ($M=7.0$ g, $L=10$ mm, $P=20$ MPa).

Influence of Combination Ratio of Bamboo Powder

In the previous section, the Young's modulus decreased as the plate thickness increased, and the bending strength also decreased in the region exceeding the plate thickness of 3-mm. This phenomena was considered to be due to suppression of heat conduction to the interior of the bamboo fiber board due to the cavity inside the bamboo fiber board and insufficient thermal fusion of bamboo fibers to each other, so that bamboo powder is mixed with bamboo fiber at the time of hot press forming. We try to fill the cavity between the fibers with bamboo powder to improve the thermal conductivity to the interior of the bamboo fiber board and promote thermal fusion between the bamboo fibers. For the bamboo powder to be mixed, those which were discharged at the time of extracting the bamboo fiber at the machining center were classified with a sieve having an opening of 212- μ m and used. Further, in order to unify with the mass of the whole bamboo fiber board to 7.0-g, the ratio of bamboo powder, which was the compounding ratio, was changed.

Fig. 7 shows the appearance of bamboo powder mixed bamboo fiber board. It can be seen that there is no major difference in the brown area although there is a difference in the portion of the bamboo fiber board. That is, it can be seen that there was no significant change in the thermal conductivity of the bamboo fiber board. Changes in the bulk density of the bamboo fiber board according to the mixing ratio of the bamboo powder are shown in **Fig. 8**. It can be seen that the bulk density slightly increases even if the mixing ratio of bamboo powder changes. From this result, it can be seen that bamboo powder is filled in the cavity between the fibers.

Changes in the Young's modulus and bending strength of the molded body with the mixing ratio of bamboo powder are shown in **Fig. 9**. It is found that the Young's modulus and the bending strength tend to decrease as the mixing ratio of bamboo powder increases within the range where the bamboo fiber board having bamboo fiber. It is thought that the bamboo powder entered between the fibers and weakened the bonds between the fibers as much as possible to reduce the Young's modulus and the bending strength. The SEM images of the fracture surface of the bamboo fiber board is shown in **Fig. 10**. When the mixing ratio becomes high, that is, when the amount of bamboo fiber decreases, the fracture surface tends to be flat, and it is understood that the bonding of the fibers is easy to loosen. Although the molded body strength is lowered by increasing the mixing ratio, the quality of the surface is improved, and the arithmetic average roughness R_a

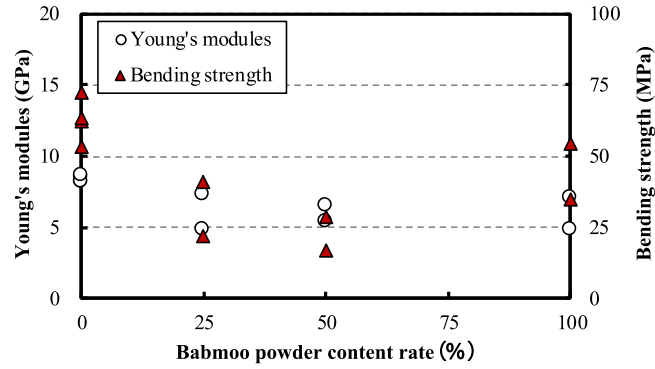


Fig. 9 Effect of combination ratio of the bamboo powder on Tensile stress of self-adhesive bamboo fiberboard ($M=7.0$ g, $L=10$ mm, $P=20$ MPa).

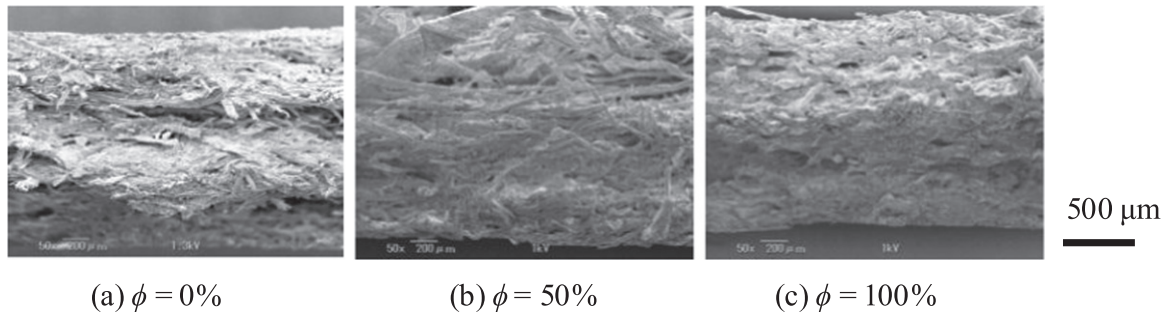


Fig. 10 Fracture surface images of self-adhesive bamboo fiberboard after bending test ($M=7.0$ g, $L=10$ mm, $P=20$ MPa).

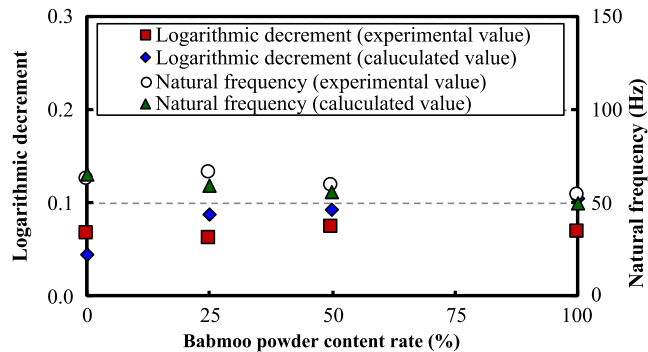


Fig. 11 Effect of hot board thickness on logarithmic decrement and natural frequency of self-adhesive bamboo fiberboard ($M=7.0$ g, $L=10$ mm, $P=20$ MPa).

when the mixing ratio is 100% is about 1- μ m, which is almost the same as the surface roughness of the mold used for fabrication of the bamboo fiber board.

Measurement results of natural frequency and logarithmic decay rate in each bamboo fiber board and the Eq. (1) are shown in Fig. 11. As the mixing ratio of bamboo powder increases, the natural frequency is gentle but decreasing and the log decay rate tends to increase. It is easy to understand that the above tendency will become more pronounced as density increases from Eq. (1). However, using the physical property values obtained from the experimental values, it is understood that when the natural frequency is obtained, the measured value of the natural frequency is larger than the calculated value. The same thing as in the previous article can be mentioned, but since this area contains bamboo powders, since the area of the interface increases, it is thought that the natural frequency also increased with the same plate thickness. It is considered that the logarithmic decay rate was caused by an increase in density.

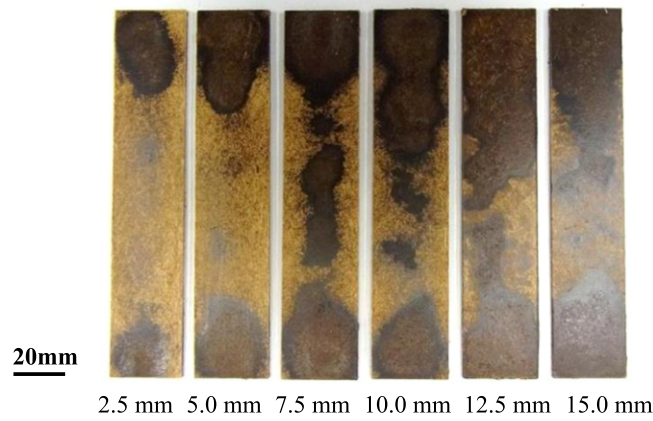


Fig. 12 Appearance images of self-adhesive bamboo fiberboard by combination ratio of the bamboo powder ($M=7.0$ g, $\phi=100\%$, $P=20$ MPa).

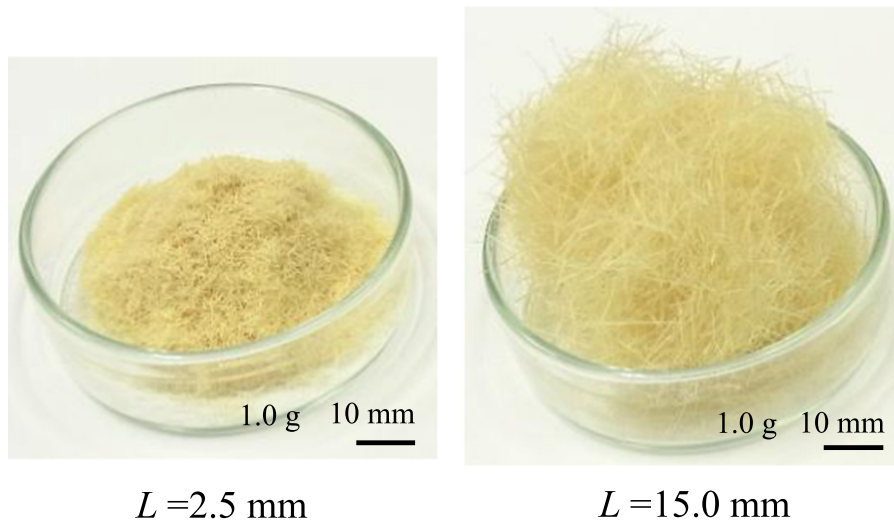


Fig. 13 Appearance images of bamboo fiber by bamboo fiber length.

Influence of Bamboo Fiber Length

From the previous section, it was found that although bamboo powder is mixed with bamboo fiber, the quality of the molded body improves but the strength decreases. Then, by reducing the fiber length of the bamboo fiber, we will make the fibers dense and study the effect. Fibers having a length of 2.5–15.0 mm were obtained by changing the axial depth of cut during bamboo fiber extraction to 2.5–15.0 mm.

Changes in the appearance of the bamboo fiber board are shown in Fig. 12, and changes in the appearance of the bamboo fiber used are shown in Fig. 13. The plate thickness with the fiber length, and changes in the bulk density before and after the molded body are shown in Figs. 14 and 15, respectively. As the weight of the bamboo fiber boards is the same, the plate thickness increases as the fiber length becomes longer and the bulk density decreases, so in this case as well, it is considered that a cavity is formed inside the bamboo fiber board. It can be considered that the reduction of the brown part area is due to the reduced thermal conductivity of the bamboo fiber board due to the cavity inside bamboo fiber board. It is also found that the bulk density after hot press forming gradually decreases as the fiber length increases. This is due to the bulk density of the fiber before hot press forming, and the bulk density before hot press forming is sharply reduced from the fiber length of 7.5-mm or more. It is thought that the aspect ratio, which is a value of fiber length per fiber diameter, increases as the fiber becomes longer, and the bulk density becomes larger by the frictional force between the fibers. It is considered that the bulk density difference became smaller by being compressed by applying pressure of 20-MPa at the time of hot press forming to this fiber. Although the bulk density decreased despite the application of pressure, this tendency was due to the fact that the bulk density before hot pressing was large and the cavity was formed inside the bamboo fiber board even after pressurization, it was said that it affected the decrease in the bulk density.

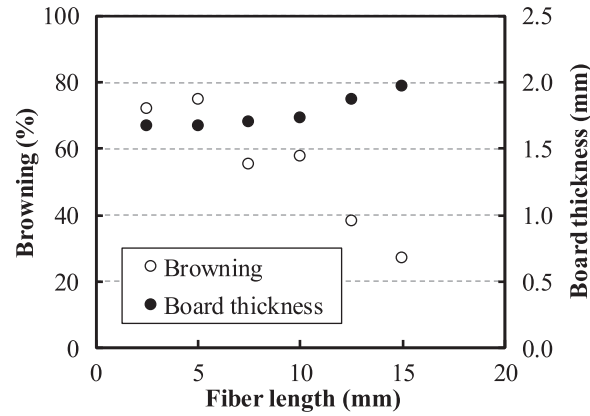


Fig. 14 Effect of bamboo fiber length on browning and thickness of self-adhesive bamboo fiberboard ($M=7.0$ g, $\phi=100\%$, $P=20$ MPa).

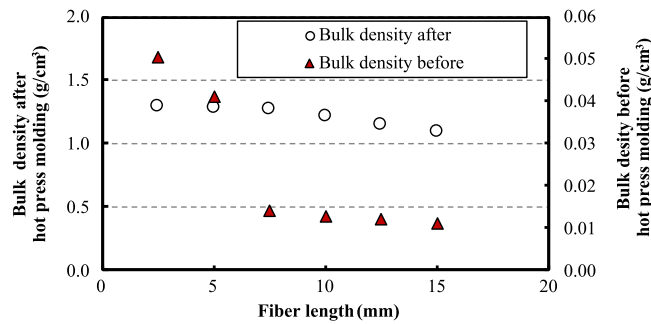


Fig. 15 Effect of bamboo fiber length on bulk density of self-adhesive bamboo fiberboard ($M=7.0$ g, $\phi=100\%$, $P=20$ MPa).

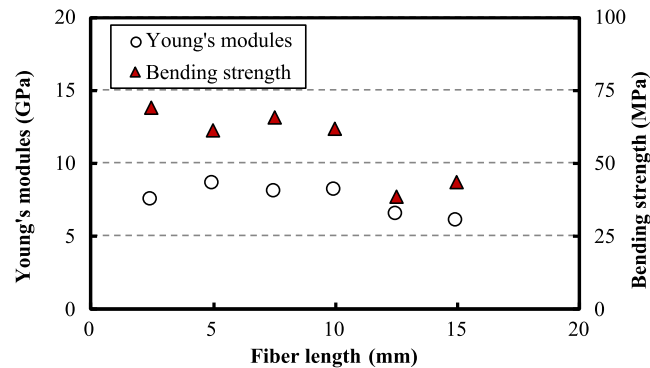


Fig. 16 Effect of bamboo fiber length on Young's modulus and bending stress of self-adhesive bamboo fiberboard ($M=7.0$ g, $\phi=100\%$, $P=20$ MPa).

Changes in Young's modulus and bending strength of a bamboo fiber board with bamboo fiber length are shown in [Fig. 16](#). SEM images of the fractured surface of the bamboo fiber board is shown in [Fig. 17](#). As the fiber length becomes longer, the Young's modulus and the bending strength of the bamboo fiber board are reduced. In addition, fragments of fibers on the fracture surface cannot be confirmed from the SEM images in case of bamboo fiber board using short fibers such as 2.5 mm in length. It is considered that the fibers were sufficiently bonded by thermal fusion. On the other hand, it can be confirmed that many fibers are pulled out on the fracture surface of the bamboo fiber board using long fibers such as 15-mm in length. Furthermore, many cavities can be confirmed, so that it is understood that the fibers are not adhered sufficiently. Therefore, as shown in the result of [Fig. 16](#), it is considered that the bending strength decreased due to the increase of the fiber length. Similarly, it can be seen from [Fig. 16](#) that the Young's modulus decreases as the fiber length becomes longer.

Measurement results of natural frequency and logarithmic decay rate in each bamboo fiber board and calculated values using Eq. (1) are shown in [Fig. 18](#). It can be seen that as the fiber length becomes longer, the natural frequency of the compact increases

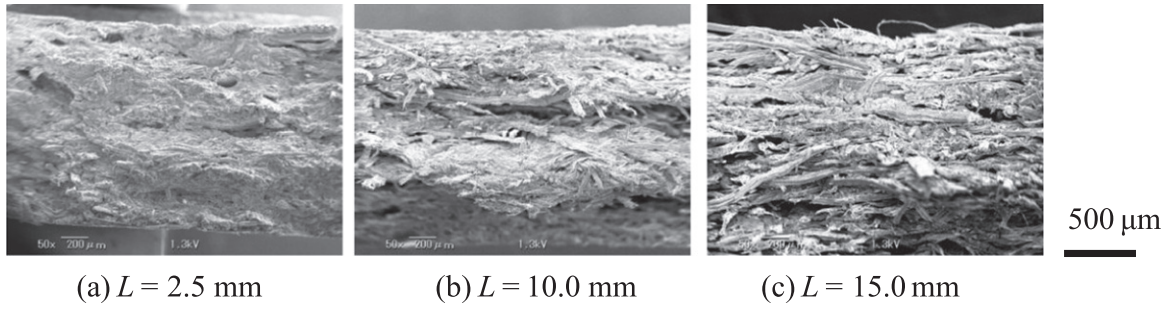


Fig. 17 Fracture surface images of self-adhesive bamboo fiberboard after bending test ($M=7.0$ g, $\phi=100\%$, $P=20$ MPa).

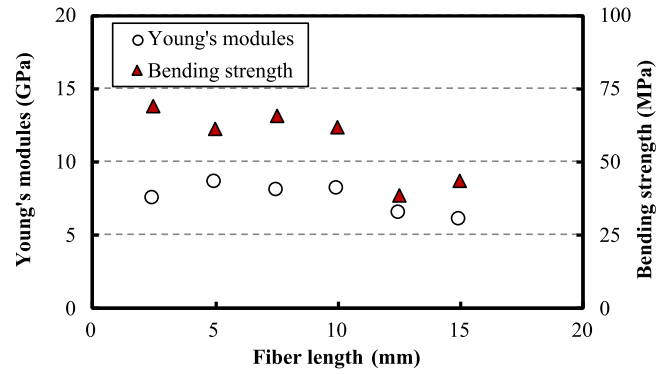


Fig. 18 Effect of bamboo fiber length on logarithmic decrement and natural frequency of self-adhesive bamboo fiberboard ($M=7.0$ g, $\phi=100\%$, $P=20$ MPa).

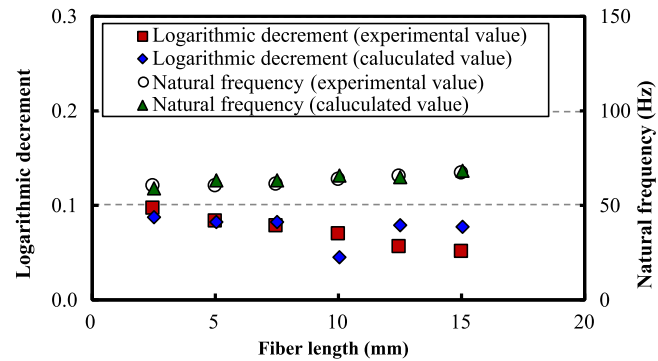


Fig. 19 Effect of bamboo fiber length on logarithmic decrement and natural frequency of self-adhesive bamboo fiberboard ($M=7.0$ g, $\phi=100\%$, $P=20$ MPa).

moderately and the logarithmic attenuation factor decreases. As the fiber length becomes longer, the number of fibers used in the bamboo fiber board becomes smaller, the abrasion area generated between the fibers decreases and the logarithmic decay rate also decreases.

Influence of Pressure During Hot Press Forming

In the previous section, the strength of the bamboo fiber board was improved by changing the fiber length to increase the bulk density between the fibers. Therefore, if the molding pressure is increased, the adhesion between the fibers is improved and the strength is considered to be high. Here, the effect of molding pressure is investigated.

The appearance images of the bamboo fiber board are shown in Fig. 19. When the hot press forming pressure was low, such as 0, 10 MPa, the brown part was very slight, and almost no thermal fusion of the fibers occurred. Changes in the bulk density of the

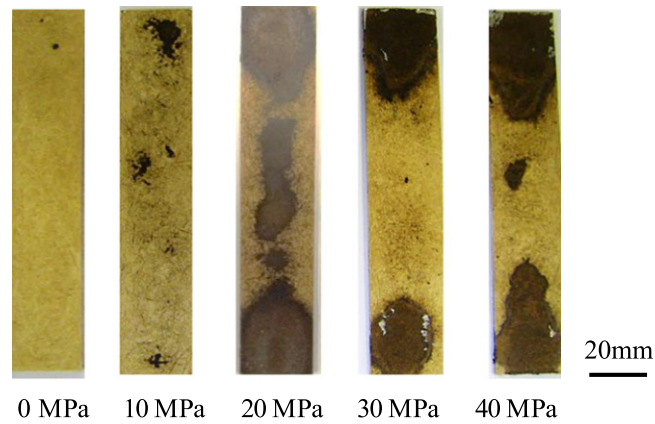


Fig. 20 Appearance images of self-adhesive bamboo fiberboard by changing pressure ($M=7.0$ g, $\phi=100\%$, $L=10.0$ mm).

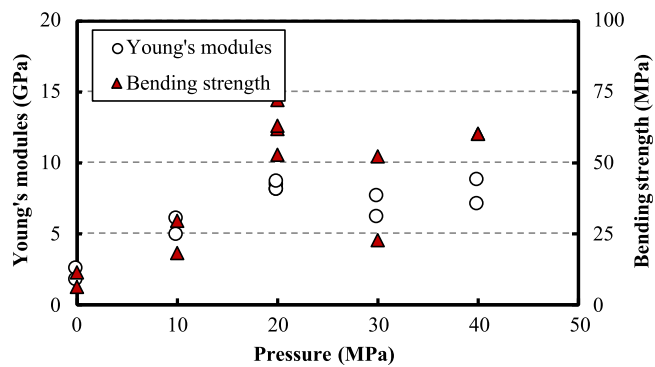


Fig. 21 Effect of hot press forming pressure on bulk density of self-adhesive bamboo fiberboard ($M=7.0$ g, $\phi=100\%$, $L=10.0$ mm).

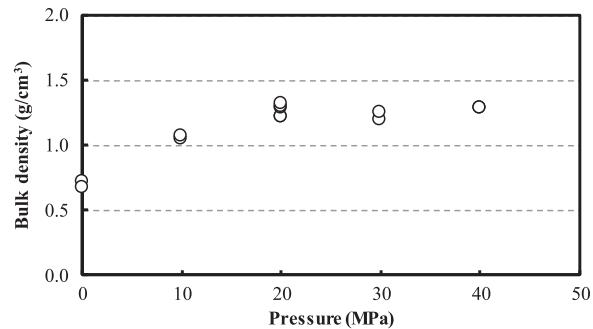


Fig. 22 Effect of hot press forming pressure on bulk density of self-adhesive bamboo fiberboard ($M=7.0$ g, $\phi=100\%$, $L=10.0$ mm).

compact are shown in Fig. 20. It can be seen that the bulk density decreases with pressure of 20-MPa but decreases with decreasing the pressure. Although a further effect can be expected, the pressure of 40-MPa is the limit in view of the performance of the hot press machine used in this study. Based on the above tendency, the bulk density of the bamboo fiber board with a fiber length of 10-mm in this experimental facility is considered to be the upper limit of 1.3-g/cm³, which seems to be about 2 times the original bamboo material density of 0.7-g/cm³. The fact that the brown part of the bamboo fiber board did not become large was also believed to be because the bulk density decreased at the pressure of 20 MPa or more.

Fig. 21 shows changes in Young's modulus and flexural strength of the bamboo fiber board with hot press forming pressure. It can be seen that the pressure is also similar to the bulk density trend, though the rate of change decreases with pressure of 20-MPa but increases with the pressure. The bending strength and Young's modulus of the bamboo fiber board are considered to be correlated with the density. When the bulk density is low, many cavities are formed, and it is considered that this cavity lowers the thermal conductivity during hot press forming and the strength at which thermal fusion between fibers occurs decreases.

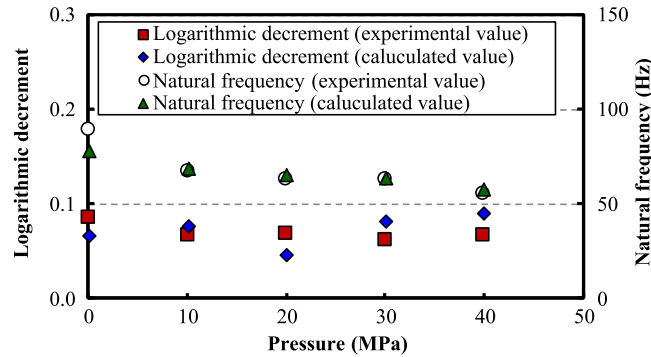


Fig. 23 Effect of hot press forming pressure on logarithmic decrement and natural frequency of self-adhesive bamboo fiberboard ($M=7.0$ g, $\phi=100\%$, $L=10.0$ mm).

The measurement results of the natural frequency and the logarithmic decay rate in each bamboo fiber board and the calculated values using Eq. (1) are shown in Fig. 22. It can be seen that the natural frequency and the logarithmic decay rate decrease as the hot press forming pressure increases. However, the tendency is gentle at the pressure of 20-MPa. This trend is similar to other physical property values, and it can be seen that the situation inside the bamboo fiber board changes at 20-MPa. In low-pressure bamboo fiber board, the distance between the fibers is wide and thermal fusion does not occur, so it can be said that the bonding between the fibers is loose. Therefore, it seems that natural frequency and logarithmic attenuation rate become large. Therefore, it seems that they showed the same tendency as bulk density and Young's modulus (Fig. 23).

Summary

From the above results, it has been reported that the strength of the bamboo fiber board is improved as the strength of the natural fiber-reinforced biodegradable resin-based composite material, which is generally called green composite, increases as the length of the fiber used is longer. Strength prediction by fiber reinforcement theory etc., has been shown (Goda *et al.*, 2004). However, in this study, since a biodegradable resin is not used as a matrix and a heat fusible substance contained in bamboo fiber is used, the closer the distance between fibers is, the more effectively the effect of thermal fusion is exerted. Therefore, it is considered that the strength of the short fiber having a higher bulk density is increased. In the hot press forming pressure as well, the high pressure at which the bulk density is increased likewise resulted in increasing the strength. In addition, as the thickness of the bamboo fiber board became larger, the brown portion decreased, sufficient thermal fusion was not performed, and the strength decreased. Since the strength of the main forming is due to heat, in order to obtain optimum strength, it is necessary to change the amount of heat to be charged according to the volume of the molded body, and the hot press forming time (heating time) not mentioned here is future work to do. We think that it is also necessary to make a formulation for drawing a proper hot press forming condition according to the product shape, size, and number of productions.

On the other hand, it was found that the logarithmic attenuation factor of the bamboo fiber board is largely due to the friction between the fibers. In particular, the change when changing the fiber length was large, it was found that the logarithmic attenuation factor can be changed by changing the fiber length, and it is found that the logarithmic decay rate can be easily manipulated. Even in other natural fiber reinforced composite materials, it can be expected to greatly change the performance and properties of molded bodies by changing the properties of reinforcing fibers. Calculating the natural frequency using the equation to calculate the natural frequency using the bending vibration of the cantilever as a model and the physical property values obtained from the experimental values resulted in irregularities in the measured value and the calculated value. This bamboo fiber board is not filled with uniform particles inside but is an anisotropic material in which fibrous objects are solidified. It was found that the natural frequency of this compact was higher than other objects having the same Young's modulus and satisfying Eq. (1), and it was found that this compact was likely to produce high sound.

Conclusions

In the production of a self-adhesive products using only high-quality bamboo fiber extracted with a machining center, various hot press forming conditions were evaluated on the performance of bamboo fiber board. The conclusions obtained are as follows.

- (1) It was found that the mechanical properties of molded bodies are largely due to the adhesiveness between fibers due to thermal fusibility and are closely related to the distance between the fibers.
- (2) Since the logarithmic attenuation factor is caused by friction occurring between fibers, it is possible to control the logarithmic attenuation factor of the products by controlling the plate thickness. The logarithmic attenuation factor can also be controlled by the fiber length and pressure during hot press forming.

- (3) Within the range of molding conditions in this study, the bulk density is about 1.3-g/cm^3 , which is the limit, which is about 1.9 times the limit of the original bamboo material. From this result, it was found that optimum values exist for the pressure and the fiber length.
- (4) Optimum hot press forming conditions for product when focusing on the static characteristics are to use only fibers having a fiber length of 7.5-mm or less, with a bamboo fiber board having a thickness of 2–3 mm and a molding pressure of 20 MPa or more is there.
- (5) When paying attention to the logarithmic decay rate, it was found that a thin plate with long fibers was suitable as a substitute material for rare wood used for musical instruments.

See also: Toward Reclamation of Fibrous Waste Stream Materials

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Effect on Compounding Process in Natural Rubber for Sustainable Suspension Materials

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Introduction

Materials can be classified into several groups depending on their different structure and properties. One of them is the polymers. Polymers have been widely used in various applications including the bulletproof vest, home appliances, compact disk, ropes, toys, and fabrics. In comparison to other types of materials, the polymers have several advantaged characteristics such as low density, good electrical insulator, good resistance to corrosion and some chemicals and economical. However, polymers are known to have low strength as compared to the other materials and not suitable for high temperature applications.

Polymers can be divided into three main categories which are thermoplastics, thermosets, and elastomers. Thermoplastic behaves like plastic, which possesses ductile attribute and can be heated repeatedly, thus can be recycled. Thermoset is more brittle than thermoplastic and cannot be heated repeatedly and decomposes due to crosslinking that occurs with the presence of heat. Thus, thermoset is difficult to recycle.

Meanwhile, elastomer exhibits a unique behavior since it can present as thermoplastics or thermosets, depending on compounding ingredients and processing method. The elastomer can also undergo irreversible crosslinking in polymer chains. As a result, it is found that elastomer is also hard to be recycled. There are several studies that have been done to overcome problems relate to the rubber product waste disposal. For instance, there are several studies discuss about the mixing of recycled elastomers with other materials such as fibre and cement (Thomas *et al.*, 2015; Mazzotta *et al.*, 2017; Medina *et al.*, 2017). In addition, the elastomer also possesses both viscosity and elasticity properties or viscoelasticity and exhibits low Young's modulus value and high elastic deformation that is usually larger than 200% of strain (Askeland *et al.*, 2011). Elastomer is also used interchangeably with the word rubbers.

The natural rubbers are available in two types, which are synthetic and natural. The synthetic rubber is an artificial rubber that is produced through polymerization process of petroleum by-product. The synthetic rubber was invented to reduce the dependencies on the natural rubber during the War World 2. As for today, there are more than 20 types of synthetic rubber that are available for various applications. On the other hand, natural rubber is naturally extracted from the rubber trees through the tapping process. This tapping process is a process of latex secretion by shearing a thin layer of rubber tree's bark by using a special tapping knife. There are more than 2500 known species of plants that can produce latex. In spite of that, only latex produced from *Hevea Brasiliensis* tree is mostly used for rubbery products due to its quality.

Although synthetic rubbers are well known to offer plenty of advantages in terms of mechanical and chemical properties, the natural rubber also possesses advantages over synthetic rubbers. The natural rubber can be considered as green material since it can be continuously supplied by nature as compared to the synthetic rubber, which is derived from the non-renewable sources (Boonkerd, 2017). The price of raw natural rubber is more economical than the synthetic rubber. The price of synthetic rubber is normally fluctuated depending on the current crude oil prices. Other than that, the properties of natural rubber compound can be derived from better formulation and processing. Instead, the natural rubber also allows low heat build-up in dynamic force to make it able to withstand large deformations and grants the natural rubber with the ability to instantly recover when distorted at room temperature (Chandrasekaran, 2010). The application of the natural rubber as main material does not require an extensive maintenance due to its capability of maintaining itself for a long period of time. Additionally, the natural rubber also exhibits inherent damping and spring-like performance in order to reduce the resonant effect. The natural rubber can be bonded with other materials such as metal in order to increase its strength (Lindley *et al.*, 1984).

As one of the largest natural rubber manufactures and exporters, Malaysia has taken an initiative to promote local natural rubber in various fields like construction, automotive and sports. For example, local rubber product is used to produce rubber glove for medical purpose. Malaysian government has established the Malaysian Rubber Board (MRB) and Tun Abdul Razak Research Center (TARRC) to provide the best infrastructure for research and development (R&D) of local NR. The quality and competitiveness of Malaysian natural rubber products, especially in vibration isolation and also for sustainable suspension materials, have been proven to be the best in the world.

One of the example of Malaysian natural rubber application in vibration isolation can be found in the great structure of the Sultan Abdul Halim Muadzam Shah Bridge, Penang. Besides that, most of the Malaysian ports also use the Malaysian-made dock fenders as a bumper to absorb impact from the collision between the boat and the jetty. There are a lot of other examples that prove the natural rubber is an ideal material for the vibration isolation applications in building and also in automotive suspension system (Yu *et al.*, 2001; Kim *et al.*, 2004).

Table 1 Application of the NR due to its properties

<i>Application</i>	<i>Properties</i>
Surgical gloves	Tear resistance, strain induce crystallization
Blow-out preventers, hoses, connectors, inner tubes, and bladders.	Oil-resistance, gas impermeability
Tires	Tear strength, wet-grip, rolling resistance/abrasion
Bearings	Elasticity, low dissipation factor, wear resistance
Shoes	Damping
Suspension system	Damping, stiffness

Table 2 Energy storing values for different materials

<i>Material</i>	<i>Energy store (j/kg)</i>
Grey cast iron	1.11
Soft steel	9.18
Rolled aluminum	22.6
Hardened steel	284
Vulcanized rubber	44,800

Natural Rubber as the Sustainable Green Materials for Suspension Materials

The natural rubber has been extensively used in various applications due to its distinctiveness over other materials like excellent physical properties, renewable sources origins, and economical. The elasticity and flexibility of the natural rubber are the main reasons for this material to be applied in various fields especially in the engineering area. In addition, the ability of the natural rubber to withstand exceptional large stress without permanent deformation or fracture has ensured the survival of the materials itself and makes it suitable to be used in various environments, except for the environment that exposed to the ozone and chemicals. Some application of the natural rubber according to its typical properties has been listed in [Table 1](#).

The basic strength of the natural rubber is actually depending on its basic chemical structure. Like any other natural products such as cellulose and silk, the natural rubber can be categorized as high polymer material. The natural rubber is classified in the hydrocarbon group with 99% of its builds up is from poly-isoprene arranged of high cis-1,4 configuration. The presence of such chemical configuration gives the natural rubber a glass transition temperature of approximately -75°C , which makes the natural rubber to become extremely elastic and works very well at room temperature ([Chandrasekaran, 2010](#)). It also manifests the natural rubber ability to undergo strain-induced crystallization that leads to excellent tensile strength and great resistance towards tearing and abrasion. In addition, the natural rubber also has high bulk modulus due to relatively strong intermolecular forces in the compound with the value around 10,000 MPa and Poisson's ratio value of 0.499 ([Tabor, 1994](#)). Due to the high bulk modulus value, the natural rubber can be assumed to be nearly incompressible when compressed in the solid state.

Carter and Paul in 1991 described the mechanical properties of the natural rubber in terms of stress and strain curve. Based on the open literature, the curve exhibits two different phases; the large elongation at low-stress phase and the small elongation at large phase. During the first phase, low stress is needed to stretch the coiled polymer network and causes the curve to exhibit small Young's Modulus reading. Besides that, in this state, the natural rubber is able to return to its original shape or length. Meanwhile in the second phase, as the strain is continuously applied, the natural rubber networks start to uncoil and stretch to its maximum. Thus, higher stress is needed to stretch the natural rubber, which resulting in higher Young's Modulus reading. In response to the applied stress, some of the natural rubber networks have become fully extended and unable to withstand the applied stress.

Then, the natural rubber is also known for its superior ability to store energy as compared to other materials as shown in [Table 2](#). A curve of complete load-unload cycle for rubber compound. The retraction curve is produced under the extension curve, which indicates the rubbers behavior during the unloading process. The differences between the extension and the retraction stress values under similar strain value represent the hysteresis in rubber. This hysteresis behavior is occurred due to internal friction between the rubber particles, which reacts towards extension and retraction. During the extension of rubber, work increases as the area under the curve increases and high energy is required to perform work. Meanwhile, during the retraction, less energy is needed to perform work. Thus, the excessive energy that equivalent to the area in the curve loop is converted into heat. The larger loop indicates that higher energy is released. Thus, it indicates low elasticity of the natural rubber. The hysteresis can be observed in both natural and synthetic rubbers. In the case of the natural rubber, hysteresis is highly affected by the types of reinforcing filler, fillers amount and the test strain rate. The genuine natural rubber exhibits less hysteresis than the filled the natural rubber since it is more elastic.

Other than that, the natural rubber is also known to exhibit stress softening behavior under repeated loadings. The softening in rubbers, also named as Mullins effect, was extensively investigated by Mullins and his colleagues. Mullins in 1948 reported that the

softening effect was only found in filled rubber and directly proportional to the stiffening ability of the NR. However, an extended study by Harwood *et al.* (1965) reported the occurrence of softening in the filled the natural rubber as well as in unfilled natural rubber compounds. The softening in rubber, which is often observed after the first cycle, has shown the reduction of stress at the continuous repeated loading with similar maximum strain as showed in a study conducted by Diani *et al.* (2009). The researchers also found that the softening effect increased with the increasing strain in the carbon filled the natural rubber compound. The researcher also observed that Mullins softening was highly depended on the filler loading. The natural rubber compound with higher filler loading experienced the softening effect at lower strain as compared to the compound with less filler content.

In contrast to the softening effect caused by stress-induced, the crystallization happens with the application of strain at room temperature by changing the amorphous state into semi-crystalline state. The ability of the natural rubber to crystallize is often related to its high regularity of chemical structure. In order to crystalize, the natural rubber chains stretch up to align towards the direction of applied strain and causing the entropy to decrease. The crystallite regions in the natural rubber act as self-reinforcement. It is similar as nanoscopic fillers or crosslinks that help to improve the mechanical properties of the natural rubber, such as the ultimate strength and tear resistance (Spratte *et al.*, 2017). Besides that, the formation of the crystallization is also found in both filled and unfilled vulcanized natural rubber (Mullins and Tobin, 1957; Trabelsi *et al.*, 2003).

There are several factors that influence the strain-induced crystallization in the natural rubber: crosslink density, temperature, strain rate, fatigue, crack tip and the addition of fillers. A research conducted by Rault *et al.* (2006) proved that the fillers, especially the carbon black could act as the strain amplifier as proposed by Mullins and Tobin (1965). Spratte *et al.* (2017) studied the influence of strain-induced crystallization in the natural rubber composites reinforced with carbon black and silica to the mechanical and temperature measurements. The researchers verified that the natural rubber with carbon black compound exhibited the highest degree of crystallization, followed by the natural rubber with silica/silane system compound and the natural rubber reinforced with silica without silane system compound. In addition, Poompradub *et al.* (2005) as cited in Huneau (2011) has investigated the stress-strain behavior and the strain-induced crystallization of the natural rubber at different carbon loadings (0, 20, and 40 phr). Throughout the studies, the researchers found that SIC appeared at lower strain in the natural rubber with carbon black and the crystallites size was slightly difference in the natural rubber with different carbon black loadings. In addition, the researcher also agreed about the existence of higher disorientation in carbon black filled N natural rubber compound rather than the unfilled natural rubber compound. Huneau (2011) concluded that the addition of carbon black reduced the global stretch ratio to the crystallization onset in the stretched natural rubber compound.

Modified Natural Rubber

The natural rubber alone is inconvenient for the customer's usage, especially in its raw state. In fact, the natural rubber is well known to have low resistance towards weather instead of having poor wet grip properties, which are essential in vehicles tires application and high solvent solubility (Gelling, 1991; Wan *et al.*, 2010). Thus, modification of rubber compound is the best solution for researchers to enhance the natural rubber properties depending on its application, which can be conducted by altering the compound either physically or chemically. The physical modification can be divided into three methods; by removing protein contents in the natural rubber through deproteinization, adding processing aid or blowing agents in the natural rubber compound (Merabet *et al.*, 2012), turning the natural rubber into a thermoplastic elastomer by adding up the polypropylene, and mixing the vulcanized and non-vulcanized rubbers as a compound. Meanwhile, the chemical modification is done by rearranging the molecular chain of the natural rubber in various ways such as depolymerizing and adding a new functional group into NR molecular chain. The epoxidized natural rubber (ENR) and constant viscosity rubber (SMR CV) are the examples of chemical modified the natural rubber that have been extensively used in rubber industries. Since this study focusing on ENR and SMR CV rubbers, only these types of the natural rubber will be explained later.

Epoxidized Natural Rubber

The epoxidation method has become a major option as it exhibits a simple reaction procedure and effective compounding cost. The epoxidation process involves the addition of oxygen atom into a proportion of carbon-carbon double bonds through the addition or substitution reaction to produce the epoxide ring. This process becomes more effective when it is conducted at the latex stage by using several chemicals such as performic acid, hydrogen peroxide and formic acid. Performic acid is a soluble liquid with strong oxidizing properties. The natural rubber can be epoxidized up to 75 mol% under a controlled condition to produce the natural rubber compound with superior properties such as better resistance towards the hydrocarbon oil and high mechanical properties. However, the epoxidation of the natural rubber up to 100 mol% produces hard thermoplastic materials (Baker *et al.*, 1970).

The advantages of ENR over other modified the natural rubbers are the outstanding damping properties, high resistance to hydrocarbon oils, good strength properties, high wet grip and lower air permeability. For these reasons, ENR has been used in various applications such as automotive tire tread, adhesive, bladders, vibration mount, and shoe soles. Besides that, epoxidation process supplies ENR with high glass transition temperature and high polarity. High polarity in ENR makes it suitable to be used with vulcanized the natural rubber of different polarities and bonded with metals (Baker *et al.*, 1970). Currently, only two types of ENR are commercially used, which are ENR 25 and ENR 50. In Malaysia, ENR is commercialized by Malaysian Rubber Board (MRB) under the name of Ekoprena 25 and Ekoprena 50.

Table 3 Grades chart for ENR 25

Parameter	ENR 25	ENR 50
Epoxidation level, %	25 ± 2	50 ± 2
Ash (max wt%)	0.50	0.50
Density (Mg/m ³)	0.97	1.02
Solubility parameter (Jm ⁻³) ^{0.5}	17.4	18.2
Lovibond color	4.5	3.5
Mooney viscosity ML(1' + 4'') 100°C	70–100	70–100

Table 4 Physical properties of ENR 25 and ENR 50 at 60 phr of carbon loading

Property	ENR 25	ENR 50
Tensile strength (MPa)	22.4	21.0
Elongation at break (%)	497	465
Rebound resilience, at 23°C (%)	39.7	25.9
Compression set (72 h, RT) (%)	16.5	20.5
Tear strength (N/mm)	94.0	57.0

Table 3 presents the grades chart of ENR 25 and ENR 50 according to their parameters. The difference between ENR 25 and ENR 50 is the epoxidation level: 25 mol% epoxide and 50 mol% epoxide. The low epoxidation level causes ENR 25 to have low glass transition temperature at $-45 \pm 2^\circ\text{C}$ as compared to ENR 50 at $-20 \pm 2^\circ\text{C}$. Higher epoxidation level causes the glass transition temperature and damping to increase, thus reducing the resilience of the rubber compound (Pire *et al.*, 2010). It is very suitable using for sustainable suspension systems.

In a comparison study of vulcanized ENR filled with 60 phr of carbon black, and (Wan *et al.*, 2010) found that the ENR 25 exhibited better tear strength and good resilience at room temperature as compared to ENR 50. Besides that, it was also found that the tensile strength of ENR 25 was slightly higher than ENR 50. Davies *et al.* (1983) also found that the degree of SIC also reduced when the level of epoxidation was more than 50%. The physical properties of ENR 25 and ENR 50 are summarized and presented in **Table 4**.

Standard Malaysian Rubber Constant Viscosity

Variety grades of coagulated the natural rubber compound are available and all of them have been technically specified according to the American Society for Testing Materials (ASTM). All coagulated compounds are measured based on their physical properties such as the dirt content and the method of production. However, the detailed description of the natural rubber can also be obtained through the respective rubber producing countries. As in Malaysia, the basic grades of coagulated natural rubber compound are promoted as Standard Malaysian Rubber (SMR). The SMR 5, SMR 10, SMR 20, SMR GP and SMR L are the examples of the natural rubber compounds under the SMR scheme. In order to obtain the consistence viscosity of the natural rubber latex, a specialized grade with a constant viscosity (SMR CV) is introduced. The constant viscosity properties are also available for the SMR grade and the products are labelled as SMR 10CV and SMR 20CV.

The SMR CV grade contains about 0.15% of hydroxylamine hydrochloride or hydroxylamine neutral sulphate. The main purpose of the chemicals addition is to maintain the viscosity of the raw rubber liquids in order to prevent hardening during storage period. Rubber hardening occurs due to the reaction of particle crosslinking process with the low humidity of storage surrounding. SMR CV-50 and SMR CV-60 are the examples of SMR CV grade that are commercially available. The only difference between both types of constant viscosity the natural rubber is their Mooney viscosity values, which are 50 and 60 Mooney unit. The technical specifications of SMR CV-60 are tabulated in **Table 5**.

The SMR CV is more expensive as compared to other grades of the natural rubber. However, the usage of SMR CV helps to reduce the energy consumption during processing. The constant viscosity properties enhance the processing step of dry the natural rubber by allowing direct mixing without premastication step. Thus, it reduces the required mixing energy as well as the production cost (Lindsay, 2012). Other than that, the texture of SMR CV rubbers is softer than any other technically specified rubber and makes it easier for other ingredients to disperse uniformly during the mixing process. Thus, it reduces scraps and the compound probability to be rejected. SMR CV rubbers also exhibit good green strength and better resistance to chipping and chunking, which are important for tires application (Rodgers, 2015).

Rejab *et al.* (2013) studied the effects of increasing carbon filler percentages (0%, 20%, and 45%) in four types of rubbers, which were the SMR CV-60, ekoprena, pureprena, and synthetic rubber. The authors observed that all rubbers with the highest

Table 5 Grades chart for SMR CV-60 according to Tenaga Gemas Sdn Bhd (2017)

Parameter	SMR CV60
Dirt (max wt%)	0.02
Ash (max wt%)	0.50
Nitrogen (max wt%)	0.55
Volatile matter (max wt%)	0.50
Wallace rapid plasticity (P_n) (min)	N/A
Plastic retention index (PRI) (min)	60
Lovibond color	N/A
Mooney viscosity ML(1' + 4") 100°C	60(±5)

Table 6 Tensile properties of the SMR CV-60 and ENR 50 at various blending ratios

Property	Blend ratio, MPa (SMR CV-60 to ENR 50)				
	0/100	25/75	50/50	75/25	100/0
Tensile strength (MPa)	10.70	9.50	12.50	14.00	13.20
Elongation at break (%)	700	700	700	700	700
Tensile modulus at 300% of elongation (MPa)	1.65	1.60	1.60	1.70	2.60

percentage of carbon yielded the best results for tensile, compression, hardness and static stiffness. Meanwhile, in another study conducted by Sasitaran *et al.* (2016) on the preparation and characterization of cross-linked SMR CV-60 and ENR 50 blend, the authors found the change in the properties of cross-linked pure and blends rubber. A tensile test was conducted on the blend of SMR CV-60 and ENR 50 with the blending ratios of 0%/100%, 25%/75%, 50%/50%, 75%/25% and 100%/0%. The authors found that the cross-linked rubber presented better tensile properties as compared to the non-cross-linked rubber in terms of tensile modulus at 300% elongation, tensile strength, and elongation at break. It occurs due to the formation of three-dimensional network that limits the molecular chain movement and resulting to stiffer and stronger rubber chains. The tensile properties of the rubber blend are presented in Table 6.

Compounding and Processing Pure and Modified Natural Rubber for Sustainable Suspension Materials

The natural rubber is known to be weak in its raw state and can only be improved through compounding. Compounding can be defined as a process of adding other ingredients into raw elastomers and may include several compounding processes. Instead of enhancing the properties of the natural rubber compound, the added ingredients also affect the processing behavior such as the number of mixing cycle, mixing time and rate of extrusion. These processes highly influence the properties of the rubber compound in terms of its static and dynamic properties. For example, Payne (1965) found that the increased in mixing time reduced the dynamic modulus and viscosity as well as the phase angle value at a moderate amplitude of oscillation for vulcanized rubber reinforced with the carbon black. This finding proved that the dynamic properties of vulcanized rubber could be affected by the mixing time and it was associated with the dispersion of the carbon black in the compound. Thus, this sub-article will elaborate more on the compounding ingredients and their effects on the NR and also the processes to produce the rubbers compound (Salim *et al.*, 2016).

Compounding Ingredients

The rubber compound is a combination of rubber with different ingredients at specific composition and manufacturing process. The main purpose of rubber compounding is to enhance the properties of the raw rubber to match with customer's requirement and application. Usually, the compounding formulation is designed to meet the physical and chemical requirements of the product. As a reference in material selection of rubber compound, the compounding ingredients can be divided into five categories as follow: elastomer types, vulcanizing system, anti-degradant system, reinforcing system, and special materials. Each of the ingredients plays an important role in changing the properties of the rubber compound. The "phr" or "pphr" unit stands for unit per hundreds of rubber and it is used as the measurement unit in a rubber formulation.

Elastomer exists in two types: natural or synthetic rubber. Each of the elastomer possesses specific characteristic and requires different parameters of compounding process such as the vulcanizing mixing period. NR offers a wide range of grades, which can be divided into three basic types: technically specified rubber, visually inspected rubber, and specialty rubber. Besides that, the

natural rubber is also available in various forms such as sheets, block rubbers, and preserved latex concentrations. The selection of elastomer type and form is made depending on the rubber product application and processing method as well as suitability with the required environmental service.

Vulcanization is a process of improving the properties of rubber compounds by creating a new polymer network through crosslinking between the polymer chains (Coran, 2013). The main function of the vulcanization system is to convert the physical properties of raw rubber from tacky into non-tacky and elastic rubber. The vulcanizing system needs three important ingredients for the system to function efficiently, which are the vulcanizing agents, accelerator, and activator.

Vulcanizing agent is the most important ingredient in this system as it is used to strengthen the rubber compound properties through the vulcanization process. Normally, this process is conducted by heating the mixture of raw rubber with vulcanizing agents at specific vulcanization time in a pressurized mold. Three types of the vulcanizing agent are extensively used; the sulphur, insoluble sulphur, and peroxides. After all, sulphur is the most generic vulcanization agent as it is easily available, inexpensive and effectively enhanced the rubber compound (Chandrasekaran, 2007). It helps to increase the crosslink density of rubber compound, which resulting in the increase of rubber properties such as tensile strength, tear strength, static and dynamic modulus, hardness, and fatigue life.

The accelerator is added into the rubber compound to boost up the efficiency of sulphur in the vulcanization process. The main purpose of accelerator addition in the rubber compound is to increase the rate of crosslinking between the sulphur molecules and the rubber chains. The accelerators are classified into two, which are organic and inorganic. The examples of accelerators are n-cyclohexylbenzothiazole-2-sulphenamide (CBS), t-butyl benzothiazolyl sulphenamide (TBBS), morpholino thio benzothiazole (NOBS), n-oxydiethylenbenzothiazole-2-sulphenamide (MBS), tetrabutylthiuram disulphide (TBTB), tetramethylthiuram disulphide (TMTD), sodium diethyl dithiocarbamate (DETC), hexamine, and many more (Chandrasekaran, 2007; Kothandaraman, 2009). The organic accelerators are often consumed in the rubber industry since they can reduce the amount of sulphur and less curing time. Some of the accelerators especially the sulphonamides classes (CBS, TBBS, and NOBS), help to speed up the curing time without reducing the scorch safety, even at the higher parts per hundreds rubber (Salim *et al.*, 2014).

The activator, such as zinc oxide and stearic acid, acts as a catalyst to boost up the sulphur and accelerator performance during the crosslinking process. Besides that, the activator also helps in dispersing the sulphur evenly in order to prevent the agglutination and the blooming phenomena, which can occur due to excessive sulphur content in the natural rubber compound. Occasionally, the selection of vulcanizing systems such as the accelerator and activator composition and the rate of the vulcanization are likely depended on the types of elastomer used: where it was known that the natural rubber could be vulcanized faster than some other elastomers such as SBR (Rodgers and Waddell, 2013).

Some of the rubber products are used in the applications that expose to elevated temperatures, hazardous gases, and weather changes. The exposure to this kind of conditions for several periods can affect the mechanical properties of the rubbers and resulting to the fatal failure when repeated load is applied. Besides that, in thermosetting elastomer especially for the natural rubber, the formation of carbon-carbon double bond increases the probability of the natural rubber to be subjected to oxygen and ozone attack. Prior to that condition, the anti-degrading system is included in the rubber compounding formulation as a protection against the degradation causes by those conditions and it is followed the regulation of the suspension system, basically.

The anti-degrading can be divided into two; the anti-oxidant and the antiozonant. The effective amount of anti-oxidant in rubber compound is around 1–2 phr (Institute, 2000). The anti-oxidant is available in two types, which are the non-staining antioxidant and staining anti-oxidant. The staining anti-oxidant is extensively used as general anti-oxidant due to its efficiency to evade the oxidation against heavy metals such as nickel and copper ions. The low volatility of staining anti-oxidant enhances the durability and the temperature stability in the rubber compound. Besides that, it also improves fatigue resistance properties and gradually reduces the color of the compound. The non-staining antioxidant is used to solve the discolouring problem but eventually, provides less effective anti-aging action.

On the other hand, rubber compound requires 0.5–5 phr of antiozonant ingredients to work effectively against the reaction with the ozone. There are various types of antiozonant; however, the wax type is known to be the most efficient. In a static state, the wax usually blooms into the rubber product surface, to form a protective layer to prevent the rubber from reacting with ozone. The ozone outbreak usually happens in the strained state, where the protective layer breaks due to applied force. However, for saturated rubber such as EPDM, SBR, and NR, it contains polymeric antiozonant, which makes it prone to ozone.

The addition of vulcanizing agent and anti-degrading alone are not sufficient to acquire the desired properties in producing viable rubbery products. Thus, the reinforcement of fillers becomes the solution. Reinforcing can be defined as the influence of fillers on the physical properties of the natural rubber. The fillers, which are cheaper than the main materials, are added to reduce the manufacturing cost, improving the processing step, and enhancing the mechanical and thermal properties of materials.

The fillers can be divided into three classes: reinforcing, semi-reinforcing, and non-reinforcing. The reinforcing filler is able to improve the mechanical properties of rubber compound such as tensile, tear, and abrasion. The semi-reinforcing fillers also work well as the other reinforcing fillers except for abrasion resistance properties. Meanwhile, the non-reinforcing fillers only function as a diluent as they do not affect the properties of the natural rubber compound. The reinforcing filler is also available in two types, which are the black and non-black filler. The carbon black is the example of black fillers, while zinc oxide, magnesium carbonate, silica, and clays are the example of non-black fillers. Since carbon black is extensively used as filler for the sustainable suspension systems, its influences in the natural rubber compound will be explained further in the other subsection.

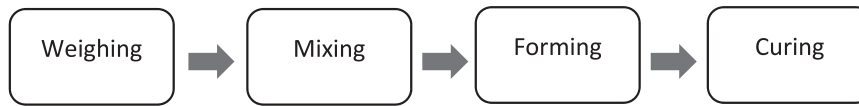


Fig. 1 Flow of rubber compounding process.

Table 7 General properties of rubber mixers according to ASTM 3182

Parameter	Types of mills		
	Standard mills	Standard internal mixer	Standard miniature internal mixture
Roller diameter, mm	150–155	N/A	N/A
Chamber volume, cm ³	N/A ^a	1575 ± 50	N/A
Mixer head volume, cm ³	N/A	N/A	120
Loading capacity, cm ³	N/A	1170 ± 40	64
Rotor speed, rpm	24 ± 0.50	77	60 + 3,–0

^aN/A = Not available.

Specials materials can be defined as inclusion of other special purpose materials such as the processing aid, softeners, and plasticizers, fire retardants, blowing agents, resins, pigments, and dyes. Those special materials are used to improve the efficiency of rubber compound processing. Besides that, it also helps to reduce the viscosity of rubber compound, which is important to provide better extrusion characteristic during processing.

Normally, those materials are added in small parts per hundred grams of rubber to avoid any effect neither in physical or chemical properties of the rubber compounds. It also helps to disperse filler evenly in order to maintain the physical strength of the compound. Examples of processing aid that have been used extensively in rubber compounding industry are paraffin, fatty acid, low viscosity naphthenic oil, factice and homogenized resins.

Instead of the compounding ingredients, it is found that the compounding process also affects the properties of the rubber compound. Mostly, the compounding process is conducted following the guidelines describe in ASTM 3182. The standard provides a complete reference of preparing a rubber compound including the procedures, precautions, and general equipment features for the involved process. **Fig. 1** shows the flow of the compounding process for rubber compound, which starts by weighing the ingredients to the correct amount according to the specified recipe for rubber.

The next process includes the mixing of all ingredients at a specific period. There are three types of general mixing equipment, which are the standard mill, the standard internal mill, and the standard miniature internal mixer. All these mixers have different properties in terms of their roller diameter, speed, and mill rolls temperature and mixing procedure as shown in **Table 7**. In the standard mill, all compounds and rubber are mixed on the slow roll at a constant temperature. Meanwhile, for the internal mill, the compound is prepared in two stages; firstly, in the internal mixer and secondly in the standard mill. Rubber is cut into smaller pieces to allow fast feeding at required discharged temperature. Then, the compound is sat on the flat metal surface to cool down before proceeding to the second stage by using the standard mill. As for the miniature internal mill, the mixer head is preheated 5 min before compounding process starts. The ingredient is mixed together at three different roll separations 0.5 mm, 3 mm, and 0.8 mm. All batch of rubber compound needs to be tested on viscosity and process ability by referring to ASTM D1646 and D6204. Then, the test sample is taken from the master batch to determine the vulcanization characteristic based on ASTM D2084 and D5289.

The next process is the forming process, where the rubber compound is shaped in the form of sheets or pallets, depending on the application or the test that will be conducted. The general relative humidity for sheeted rubber compound must not more than 55% from 1 to 24 h at 23 ± 3°C during the process, unless it is set to a certain value. After that, the process is proceeded with the curing process at the specific temperature and period. The sheeted compound is cut a bit smaller than the size of the mold cavity and placed on the flat, clean and dry metal surface with the mark of milling direction. The mold is preheated in the closed press for 20 min to the curing temperature before inserting the rubber pieces. After the mold achieves the required curing temperature, the rubber pieces are quickly inserted to avoid heat loss. The mold is placed in the closed press with a minimum pressure of 3.5 MPa at the specified curing time. The curing time is calculated from the moment the pressure is completely applied until the moment of the pressure is completely released.

Conclusion

This article has discussed in details of the effects of compounding ingredients toward properties and the process ability of sustainable suspension materials. The compounding ingredients can be categorized into five: elastomer types, vulcanizing system, anti-degradant system, reinforcing system, and special materials. All these ingredients gave specific effects on the compound. In addition, this sub-article also explains all the related processes in rubber compounding.

See also: Mechanical and Transmissibility Effect on Recyclable Suspension System for Different Loading of Carbon Black

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Experimental Investigations for Friction Stir Welded 3D Printed Dissimilar Thermoplastics With Consumable Tool

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Introduction

Friction stir welding (FSW) is one of the advancements in the solid-state welding techniques, which offers the joining of similar as well dissimilar metals, alloys, and thermoplastics. FSW has attracted the attention of today's researcher/scientists due to its lower thermal degradation on the joint. The rotating pin in the rotor generates heat due to friction between rubbing surfaces and mechanical mixing also ensures good bonding at the joint (Vijendra and Sharma, 2015). The input process variables of FSW such as rotational speed, indentation depth, longitudinal speed or feed, axial load, and tilt angle affect the mechanical, thermal, and morphological properties. It has been observed that porous/blow holes are generated at low rotational speed due to improper bonding at the interface of the joints (Jaiganesh *et al.*, 2014). The mechanical properties of the friction welded parts are largely influenced by the rotational as well as longitudinal speed. From visual inspection it has been studied that more defects take place at the retarding side of the sample joint than the advancing side (Eslami *et al.*, 2015). Some studies have reported that the vertical coordination of glass fiber in the nylon66 parts does not affect the mechanical properties of the FSW joint with the vibrating tool. The properties of the joined matrix define the properties of the joint (Węglowska and Pietras, 2012). Some researchers have reported investigations of mechanical, thermal, and metallurgical properties for frictionally welded joints (Taylor *et al.*, 1989; Yilbas *et al.*, 1995; Kostka *et al.*, 2009). The deformation and microstructure at the welded joints were investigated using scanning electron microscope and optical microscope to check influences of input process parameters (Gao *et al.*, 2015; Sluzalec, 1990). Welding of acrylonitrile butadiene styrene (ABS) or Nylon 6 to itself or welding of ABS to high density polyethylene has been reported as a success. The influences of using a threaded pin for FSW of nylon 6 sheets have enhanced mechanical mixing at the joint interface (Stokes and Hobbs, 1993). Friction inertia welding is widely accepted in aerospace applications (Stokes, 1993; Yilmaz *et al.*, 2002). The reinforcement of nanocomposite (carbon nanotube, graphene, and nanosized metal powder) with polymers is responsible for the improved mechanical and metallurgical properties (Rotundo *et al.*, 2010; Panneerselvam and Lenin, 2014; Attallah, 2012; Raab *et al.*, 2015; D'Alvise *et al.*, 2002). For transferring such development technologies from lab scale to production house, it is mandatory to justify the controlled physical characteristics of the obtained part each time. For such justifications, process capability indices can be of immense help in prevention of the manufacturing of defective items and can also be used for the improvement of the process (Healy *et al.*, 1976). Further, statistical quality control and the capability methods are effective for identifying quality problems and thereby eliminating them from the process (Hoseinlaghab *et al.*, 2015).

The reported literature reveals that welding of similar and dissimilar metals, alloys, and thermoplastics is possible by varying process parameters or reinforcement. Some of the studies have reported process capability analysis of different manufacturing processes. However very little has been reported on use of statistical quality control for FSW of dissimilar thermoplastic materials. In this study the FSW process was controlled by varying the rotational speed (rpm), transverse speed (mm/min), and plunge depth (mm) for melt flow compatible dissimilar thermoplastic composites. Further, the welded joints were subjected to tensile, flexural, and hardness tests. Based upon the optimized input setting, repetitive experiments were performed and tensile, flexural, and hardness testing was carried out. The results are plotted as X-chart, process capability histogram, and normal probability curves for investigating the process capability.

Experimentation

The approach of FSW by using consumable pin is shown in Fig. 1. ABS and polyamide (PA)6 in granular form (size: 1–1.5 mm) have been selected and blended with Al metal powder (size: 50 μ m). The blends of Al metal powder and thermoplastic were poured into a melt flow indexer for investigating the variations of Al content on the melt flow index (MFI). The results of MFI suggested that ABS with 15% Al content and PA6 with 50% Al content were observed 11.57 g/10 min and 11.97 g/10 min, respectively. So, upon similarity in MFI, ABS-15%Al and PA6-50%Al have been considered as the final composition for further experimentation. The feedstock filaments of ABS-15%Al were extruded by twin screw extruder setup under 220°C barrel temperature, 30 rpm screw speed with 20 kg load and PA6-50 Al under 245°C barrel temperature, 20 rpm screw speed with 15 kg load. Further 3D printing (cylindrical surface: 50-mm diameter and 50-mm length) by using fused deposition modeling has been performed for both thermoplastic composites under 30 mm/s printing speed, covering by 6 perimeters at 250°C temperature.

The pilot experimentation involves examining weldability of Al reinforced substrate using melt flow compatible consumable tool under rotational speed range of 1000–1500 rpm, traverse speed of 30–50 mm/min, and consumable pin depth up to 4 mm.

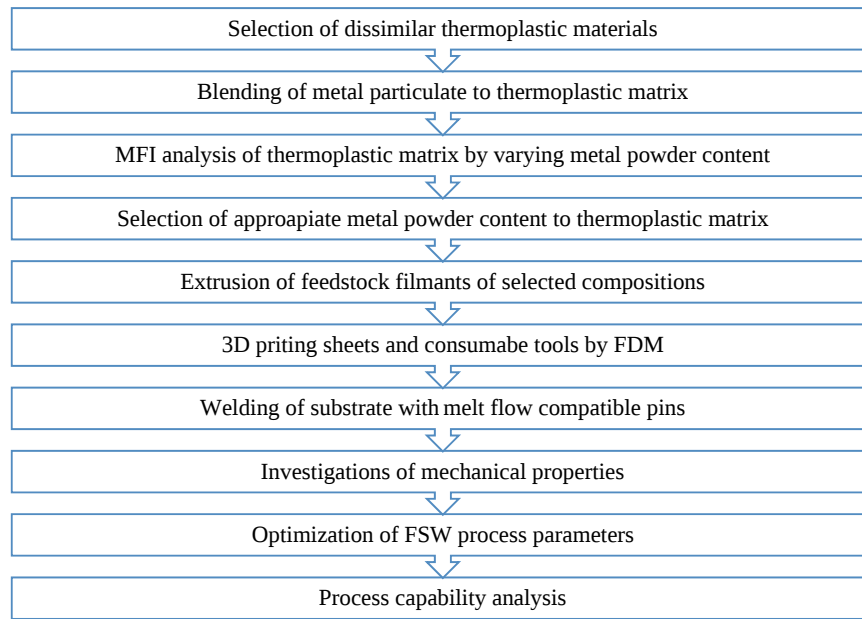


Fig. 1 Methodology for friction stir welding by using consumable pin.

Table 1 Tensile, flexural, and shore D hardness of joints

<i>Trial</i>	<i>Peak tensile strength (MPa)</i>	<i>Peak flexural strength (MPa)</i>	<i>Shore D hardness</i>
1	100.1	225.5	83.0
2	100.6	224.1	82.5
3	101.1	225.4	82.5
4	100.4	225.8	83.0
5	100.5	224.9	83.5
6	100.7	225.6	83.0
7	100.6	224.9	82.5
8	100.7	225.1	83.0

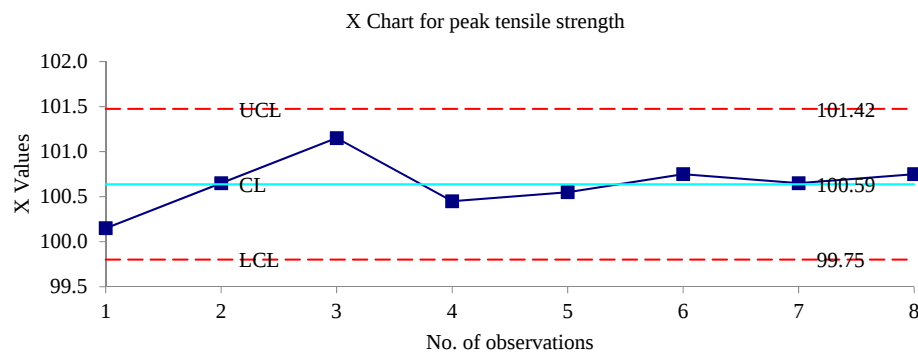


Fig. 2 X-chart for peak tensile strength.

Further three levels of rotational speed (1000, 1200, and 1400 rpm), traverse speed (30, 40, and 50 mm/min) and consumable pin depth (2, 3, and 4 mm) have been selected for deciding the optimum set of input process parameters. It has been observed that maximum value of tensile strength, flexural strength, and shore D hardness were obtained at 1400 rpm, 50 mm/min feed rate, and 3 mm consumable pin depth. Under the suggested input process parameter setting, 8 repetitions of FSW have been performed for investigations of process capability analysis (see [Table 1](#)).

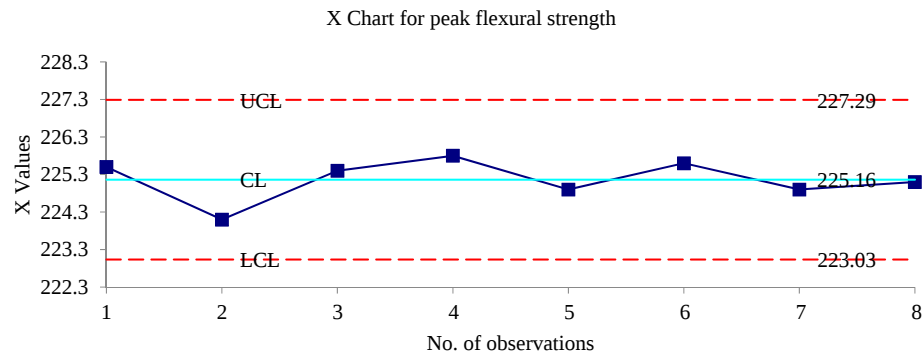


Fig. 3 X-chart for peak flexural strength.

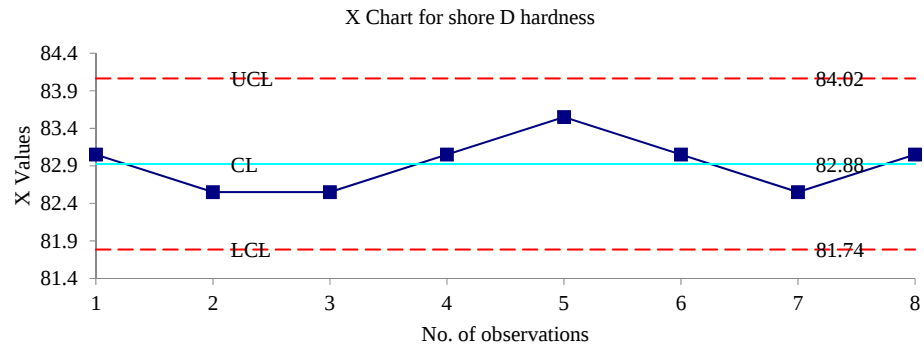


Fig. 4 X-chart for shore D hardness.

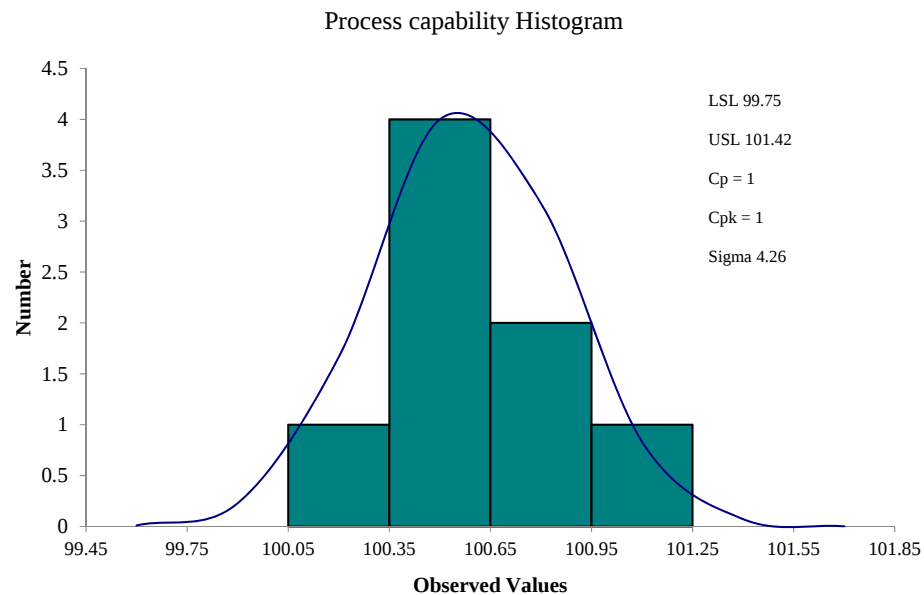


Fig. 5 Process capability histogram for peak tensile strength.

Results and Discussion

Based upon observations in Table 1, Figs. 2–4 respectively show the X-chart for peak tensile strength, peak flexural strength, and shore D hardness. As observed from Figs. 2–4 for peak tensile, peak flexural, and shore D hardness as output the plotted data lies well within the upper control limit and lower control limit, which have been judiciously selected based upon industrial applications.

Further for process capability analysis the peak tensile strength data (Table 1) has been used to plot process capability histogram for eight repeated set of observations (see Fig. 5) and process capability indices Cp and Cpk were calculated.

As observed from Fig. 5 for peak tensile strength data Cp and Cpk values near to 1 ascertain that the process is under statistical control. Similar observations were made for peak flexural and shore D hardness.

Summary

In the present study statistical analysis on a novel route for joining the dissimilar thermoplastic based composite materials by FSW with consumable tool for batch production has been reported. The X-chart, Cp and Cpk values near to 1 ascertain that the proposed settings for this novel route are under statistical control and may be fixed as industrial standard for future reference.

Acknowledgment

The authors are highly thankful to Board of Research in Nuclear Science (BRNS) No: 34/14/10/2016-BRNS/34036 and Center for Manufacturing Research, GNDEC, Ludhiana for providing financial/technical assistance.

See also: Joining of 3D Printed Dissimilar Thermoplastics With Friction Welding: A Case Study. Joining of 3D Printed Dissimilar Thermoplastics With Nonconsumable Tool Through Friction Stir Welding: A Case Study.

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Impact Behaviors of Acrylonitrile Butadiene Styrene and Polylactic Acid Materials for Topological Industries

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Introduction

Geospatial technology is an advanced technology that provides geographical mapping and analysis about the earth and human societies. This technology has been widely used in daily life and it is evolving over time. It has been applied in a variety of uses for the purpose of facilitating human activities. The daily application of geospatial technology such as the Global Positioning System (GPS), Geographic Information System (GIS), and remote sensing have been significantly increasing especially in the field of monitoring systems (Albert, 2012).

Geospatial technology consists of two important components, which are computer hardware and software. These two components are used to collect, manipulate, store, analyze, and display geospatial data that has been gathered. This technology is evolving and being adapted with other technologies for the usage of the human particularly in visual positioning such as GPS, GIS, remote sensing, and other visualization systems. They have become available to nearly everyone through a variety of devices. Consumer demand has been increasing for these devices as a way to manipulate and display geospatial information, which can be seen over the past decade. For example, the implementation of GPS data with digital maps has been used in vehicle navigation devices and is used every day for navigation and directional purposes by many people worldwide. The application of Google Earth launched in 2005 has enabled everyone to manipulate digital maps and geospatial data (Folger, 2010).

GIS can be described as a computerized information storage, processing, and retrieval system that is equipped with hardware and software. It is specially designed to cooperate with geographical referenced data and corresponding attribute information. It is also an organized collection of computer hardware, software, and geographical data, which is designed to efficiently capture, store, update, manipulate, analyze, and display all forms of geographical referenced information. There are three steps in GIS spatial analysis, which are preparation of an appropriate model, proper visualization, and analysis of data from a simple map to statistical models. The modern GIS uses detailed digital maps, satellite images, and computer models as its data sources in locating the position that is necessary to provide appropriate reaction, so that all the data that have been collected can be interpreted in a simple way.

According to DeMers (2008), there are two basic concepts of GIS. The first one is that the features have attributes associated with them. A GIS tells us “where” and “what” it is. Geographical location replies to “where” something is and “what” it is. Thus, GIS can clearly distinguish itself from nongeographical spatial data management system like Computer Assisted Cartography (CAC) or Computer Aided Design (CAD), which do not use georeferenced data. CAC is excellent for visualization and can be used specifically for mapping purposes while CAD is excellent for producing architectural drawings and simplifying editing process. It can also perform map analysis.

The second basic concept of GIS is that the collected information must be separated into layers. GIS features like rivers, roads, or forests are usually stored in different layers so that they can be added or taken off during GIS projects as needed. Layers are usually called coverage or databases and in most cases they consist of several computer files that have the same name but with different extensions. Layers represent the information of particular classes and can be combined to create new layers, which contain specific selected information to a particular query on the GIS. Basically, there are three fundamental features by which any layer can be presented.

Nowadays, GIS has been widely used in various applications and fields such as scientific investigations, resource management, asset management, environmental impact assessment, urban planning, cartography, criminology, history, sales, marketing, and logistics. Topographic and mapping (cartography) visualization is one of the components that can be accessed using GIS. GIS can display the Earth in realistic, three-dimensional perspective views and animations that convey information more effectively to the audiences as compared with conventional two-dimensional of static maps.

The application of GIS mapping in mine suspected areas can provide effective management of suspected mines. It can also enhance mine security, offer interactive access, and manage the database. In addition, it also enables the management to have statistical information analysis and visualization of digital maps by multimedia data. The implementation of GIS mapping resulting two-thirds of 1230 km² of area have been identified covered by flood from 26,960 km² of contaminated mine areas. The implementation of GIS also manages to determine active landslides that occurs, which nearly above 2000 locations or points. The Mine Action Center (BiH) has stated that there are more than 100,000 mines. In this situation, dangerous areas can be labeled as floods triggered mine. In some recorded cases, the explosion of mines that are shifted by floods have occurred in the area of Brcko District in the north of the country. All of these identification processes can be implemented by using GIS mapping.

In terms of urban planning, there are three classifications of urban planning functions that use GIS as a tool, which are general administration, development control, and plan making. The use of GIS is according to functions, scales, sectors, and stages of urban planning. The statistical data shows that the use of the data management, visualization, spatial analysis, and modeling components of GIS vary according to different functions of urban planning (Nyerges *et al.*, 2011). Data management, mapping,

and spatial analysis are generally important in urban planning process and spatial modeling is used as strategic planning tools. General administration employs mainly data management and mapping. Finally, development control mostly uses the visualization and spatial analysis functions of GIS.

Materials and Parameters Selection

Commonly, 3D models have been used by various planning sectors such as city or urban planning, natural resource management, and transportation planning. With higher demand on application of GIS in industry and the need of proper visualization of 3D model, 3D modeling has evolved in producing more realistic models such as city landscapes with buildings, street furniture, and topographic variation. The 3D modeling for GIS data requires more analytical process in creating 3D model or 3D topology (Ellul *et al.*, 2013).

Traditionally, 3D physical models of landscape or mapping are generated or produced manually or by semimanual methods. The implication of this method is it consumes more time and manual effort to make a model that has high quality of visualization and precision according to the GIS data. It involves the use of cardboard sheet as material to build the 3D model. The cardboard sheets need to be cut and pasted on top of each other to produce a three-dimensional representation of topography. The geographical element can significantly be marked by using suitable common tools such as pushpins (point), colored string (lines), and paint (area). The advanced technology of 3D printing with the help from GIS data enables the 3D model to be rapidly built and can avoid delay to the business or operation due to 3D model production. Thus, it can speed up the process of negotiations especially during conflict resolution.

The GIS 3D model development is not to replace the paper maps or VR technique. It solves the visualization problem of current mapping method (2D) such as depth prediction, which can be resolved by a minor movement of the head or body. Other than that, the distance and height estimation become more effective and precise with 3D printing model due to lifelong experience with 3D views (Buchroithner, 2012).

The variation of printing parameters that involves printer setting parameters may influence the material properties, which will affect the reliability of the 3D part. The variation may alter the material properties, either making the material more durable or vice versa. There are several printing parameters that have been identified that may influence the material properties of printing material, which are the layer thickness, printing speed, printing and build orientation, and build infill of material.

The built layer of thickness can affect the material properties of tensile and flexural strength. It summarizes that, the 3D printing part, which made with thicker layer than each individual layer is capable to have high resistance against failure as compared with 3D printing part which is made with thinner layer. The “stepped effect” is suspected to affect the flexural and tensile strength, but it decreases with respect to the increase of layer thickness. Smaller layer height interlayer has strong bond strength. By decreasing layer height, more layers are needed to be printed for any given object. It yields benefits due to the layer can be reheated on the underlying bond lines. It promotes polymer diffusion and entanglement, which are caused by the increase of layer printing number (Abbott *et al.*, 2018).

The strength of 3D printing segment varies with the process parameter layer thickness. The smallest layer of thickness will have higher impact strength of the segment as compared with high layer thickness. This is because the small layer thickness provides the material with higher absorption of impact energy as compared with the part made with high layer thickness (Othman *et al.*, 2018).

Different built orientation of 3D printing can influence the quality of the printed product. Built material can react dissimilarly due to the relative position and the internal channel of the axial load, which depends on building orientation. The bond between layers is discovered to have only 74% to 79% of strength due to weaker bond between the layers. Built part that is constructed according to the X-direction (flat) has high strength and elongation before it achieves failure, and followed by the part that is built in the Y-direction and Z-direction (Raney *et al.*, 2017).

Polylactic acid (PLA) is a biodegradable 3D printing polymer material produced from renewable raw materials such as starch. Stereolithography and digital light processing 3D printing use PLA material in the form of resin while fused deposition method (FDM) 3D printing uses material in the form of filament. PLA material has lower performance of material properties as compared with acrylonitrile butadiene styrene (ABS), but it is available in several colors and is user friendly and to easy to handle in 3D printing. The extrusion temperature, which is also known as melting point of PLA, is around 180–230°C and the printing bed temperature is required to be controlled around 50–60°C. This range of parameters is beneficial in producing a high quality printed object or part. The PLA material is preferred to be used for printing of large parts because it has thermally less contractive properties. At high temperature process, PLA material does not emit toxic fumes and the installation of a fume hood becomes optional. Similar to ABS material, PLA material also has the characteristic to absorb moisture from ambient air and it affects the material properties and causes difficulties during the printing process.

Then, ABS is a commonly used 3D printing polymer material in varieties of application especially for FDM 3D printing. This because it is an inexpensive material and can be easily used by heating up the nozzle to a temperature to 250°C. The melting point of ABS materials is 230°C and the standard printing temperature is 230°C and above. ABS has excellent material properties such as strong, durable, partially flexible, and heat resistant, which makes it suitable for varieties of application. ABS material used for FDM 3D printing is usually in the filament form, which is available in various colors. Temperature of the printing bed needs to be controlled around 110°C for ABS material 3D printing. However, this type of polymer is not a biodegradable polymer but it can be recycled. Safety precautions are needed because ABS will produce harmful fumes when it undergoes high temperature processing. ABS also requires proper handling and storage because its performance can be degraded when it is exposed to sunlight for a long time. The printer performance can also be affected when it uses moisture ABS due to its properties to attract moisture from the air.

Research Methodology

There are two available standards in conducting Izod Impact Test, which are ASTM 256 and ISO 180. These standards focus on impact testing of notch specimen. The Izod impact test specimen sizes for ASTM 256 and ISO 180 are shown at Figs. 1 and 2, respectively.

Impact test is a mechanical test that is used to study the ability of material to resist impact loading by striking the tested material at high relative speed. There are two types of impact testing methods, which are pendulum and drop method. The pendulum method of impact test involves striking the specimen using an accelerated swinging pendulum. There are two types of pendulum method of impact test that are commonly used for plastic material testing, which are Charpy and Izod pendulum impact test. For Charpy impact test, the specimen is supported by a horizontal beam and it is broken at the line of impact between the supports by a single swing of a pendulum. The Izod impact test is similar to the Charpy impact test and the only difference is the position of the specimen, which is vertical against the striking pendulum. Another method of impact test is the drop method, which consists of two types: The falling dart and falling testing specimen method. The falling dart method involves striking the specimen with falling impact dart by gravity to determine its failure against falling impact, while the falling specimen method involves dropping the specimen at certain height to determine the material behavior when the impact is applied to the material.

By doing an impact test, the impact strength of a material can be determined. Impact strength is the material ability to sustain mechanical energy due to deformation and fracture under impact loading. It is also related to evaluating the material toughness, which is the ability of material to absorb energy by striking the specimen with pendulum. Theoretically, the material with high toughness has the ability to absorb higher amount of impact energy. Meanwhile, the low toughness material tends to absorb lower energy prior to fracture.

ASTM 256 standard is used to test plastic material in determining the resistance of plastic to standardized pendulum type hammers. The standard specimen is mounted in a standardized machine and breaks with one pendulum swing. This standard requires the specimen to be prepared accordingly. There are several types of test method that are stated in the standard. One of the methods requires the specimen to be held as a vertical cantilever beam and broken by single swing of pendulum. For the

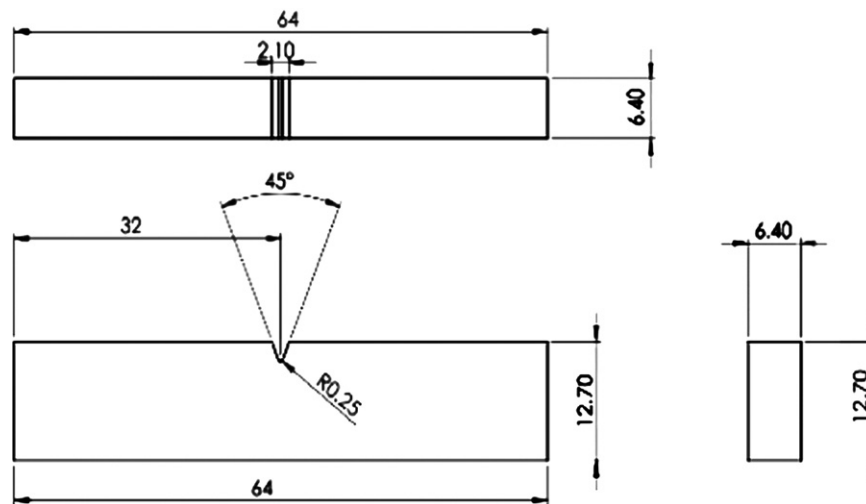


Fig. 1 Schematic diagram of the specimen for Izod impact test ASTM 256.

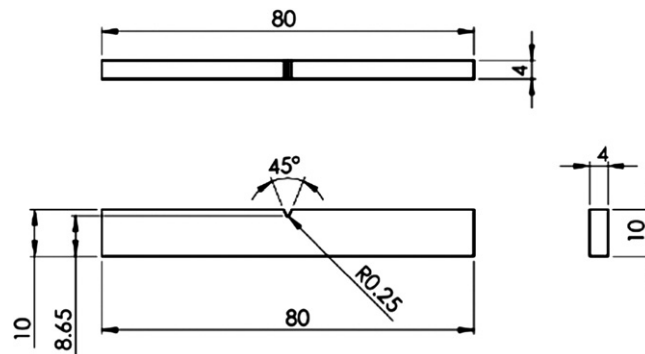


Fig. 2 Schematic diagram of the specimen for Izod impact test ISO 180.

placement of the specimen on testing jig, the specimen line of initial contact is at fixed distance from the specimen clamp and from center line of the notch. The notch of the specimen will be facing the striker pendulum as shown in Fig. 3.

The striker of the pendulum is made from hardened steel type with cylindrical surface and can deliver 2.7 J. If the material requires more energy to break, additional load of the pendulum can be added. The testing procedure begins by placing the specimen at testing jig and the pendulum is pulled until it reaches 120°, which is measured by taking the location of specimen at zero location. The test needs to be conducted at standard temperature and condition, which are at 23°C and 50% relative humidity. The pendulum is released from its initial position when all parameters of the testing have been set up and the impact energy is recorded.

Results and Discussion

Impact test involves the study of material behavior against the impact loading, which in this case is focusing on dynamic loading effect on ABS and PLA material. Izod impact test is conducted to study the impact toughness, which is also known as impact strength of material. This approach has been used regularly for plastic material. Fifteen v-notch specimens of each material are prepared and tested to compare the impact strength between ABS and PLA materials. The impact specimens are fabricated according to ASTM 256 specimen size by using 3D printing method as shown in Fig. 4 for ABS and Fig. 5 for PLA. Even though the specimen notch is printed, an additional milling process is applied to make a notch of the specimen to have the desired notch

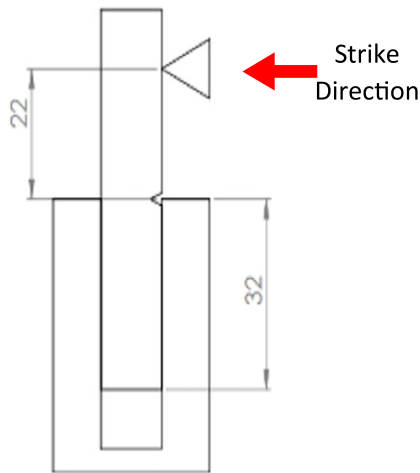


Fig. 3 Schematic of the Izod impact test.



Fig. 4 Impact test specimen for acrylonitrile butadiene styrene materials.



Fig. 5 Impact test specimen for polylactic acid materials.

Table 1 Data and results for impact test

Material	Specimen	Cross sectional area (m ²)	Type of failure	Energy of impact (J)	Impact strength (kJ/m ²)
ABS	1	0.00006848	Hinge break	0.78	11.39
	2	0.00006848	Hinge break	0.84	12.27
	3	0.00006848	Complete break	0.81	11.83
	4	0.00006848	Hinge break	0.78	11.39
	5	0.00006848	Complete break	0.81	11.83
	6	0.00006848	Hinge break	0.76	11.10
	7	0.00006848	Hinge break	0.83	12.12
	8	0.00006848	Hinge break	0.87	12.70
	9	0.00006848	Complete break	0.69	10.06
	10	0.00006848	Hinge break	0.71	10.37
	11	0.00006848	Hinge break	0.76	11.10
	12	0.00006848	Hinge break	0.74	10.81
	13	0.00006848	Hinge break	0.86	12.56
	14	0.00006848	Hinge break	0.95	13.87
	15	0.00006848	Hinge break	0.76	11.10
	Average	–	–	0.80	11.63
	Std.Dev	–	–	0.80	0.98
	R-Squared			0.997	
PLA	1	0.00006848	Complete break	0.20	2.92
	2	0.00006848	Complete break	0.28	4.09
	3	0.00006848	Complete break	0.30	4.38
	4	0.00006848	Complete break	0.20	2.92
	5	0.00006848	Complete break	0.17	2.48
	6	0.00006848	Complete break	0.23	3.36
	7	0.00006848	Complete break	0.29	4.23
	8	0.00006848	Complete break	0.19	2.77
	9	0.00006848	Complete break	0.16	2.34
	10	0.00006848	Complete break	0.20	2.92
	11	0.00006848	Complete break	0.30	4.38
	12	0.00006848	Complete break	0.21	3.07
	13	0.00006848	Complete break	0.20	2.92
	14	0.00006848	Complete break	0.27	3.94
	15	0.00006848	Complete break	0.22	3.21
	Average	–	–	0.23	3.33
	Std.Dev	–	–	0.05	0.69
	R-Squared			0.991	

Abbreviations: ABS: acrylonitrile butadiene styrene; PLA: polylactic acid.

according to the standard. **Table 1** shows the impact test results for ABS and PLA materials and **Figs. 6** and **7** show the condition of specimens after the testing procedure.

In material behavior studies, method that is used to evaluate material toughness is the impact test. The theory of material toughness is related to the ductility and brittleness of a material. It can be explained by using stress–strain diagram to compare the differences between the ductile and brittle materials. The measurement of ductility and brittleness of material depends on the degree of plastic deformation that leads to material fracture, which is also known as the work done by material to fracture. Brittle material has small region of plastic deformation as compared with ductile material. The impact energy of material is the area under the stress–strain curve. Theoretically, material that has greater impact energy, which is ductile material, will have greater area under the stress–strain curve as compared with brittle material.

In impact test, there are four types of material fracture category, which are complete break, hinge break, partial break, and nonbreak fracture. The types of fracture must be recorded for the purpose of microstructure study regarding the material behavior. The notch specimen is used to enhance the sensitivity and reproducibility of the measurement, which serves as a stress concentration zone.

By doing impact testing on a material, the absorbed energy for the material to break or fracture can be determined to find the impact strength of the material. The absorbed energy that causes the material to break can be determined by hitting the material with high velocity impact pendulum. Absorbed energy is the amount of energy that can be absorbed by the specimen during the entire impact test procedure. It represents the energy to withstand maximum load when the specimen experiences failure at the maximum load point. In other words, it is the total impact energy that involves energy from initial and after impact. At the end of the impact test, the toughness of the material can be determined or compared by referring it to the impact strength of the material.

By making comparison between the impact test results of ABS and PLA materials, the correlation between both materials impact test results can be found. **Fig. 8** shows the values of impact strength for ABS and PLA materials. From the test, ABS material



Fig. 6 Acrylonitrile butadiene styrene specimens after impact test.



Fig. 7 Polylactic acid specimens after impact test.

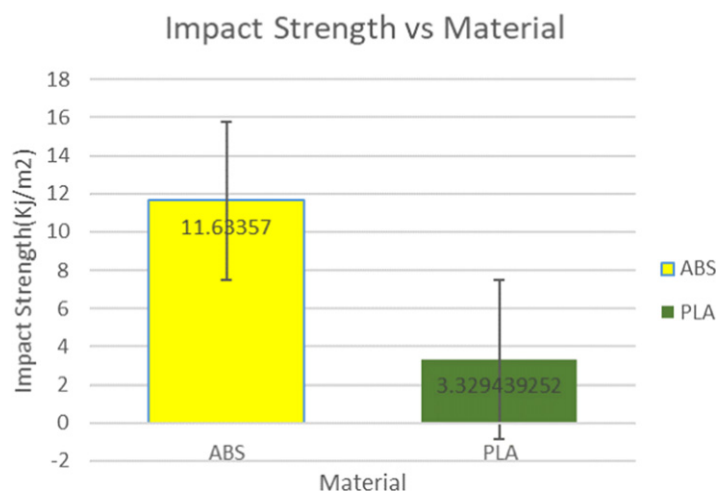


Fig. 8 Comparison of impact test result between acrylonitrile butadiene styrene and polylactic acid material.

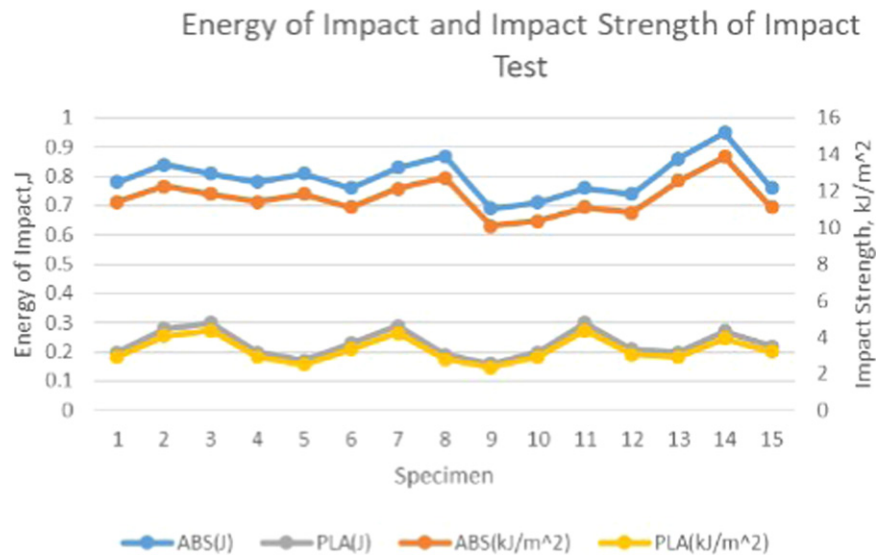


Fig. 9 Specimen vs. energy of impact and impact strength.

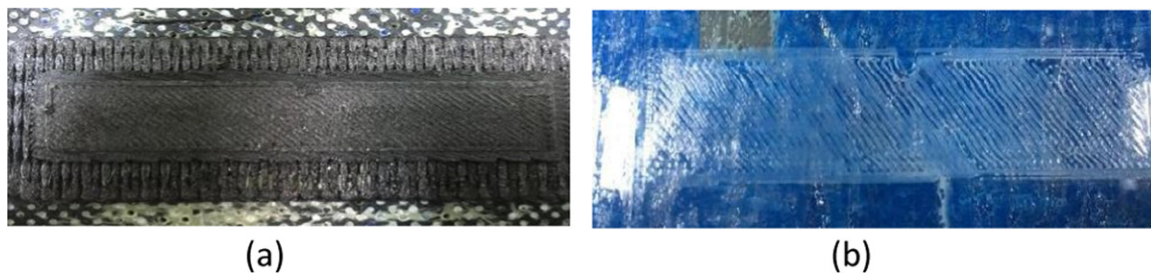


Fig. 10 Comparison first layer of build between acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA) material (a) ABS and (b) PLA.



Fig. 11 Polylactic acid material after impact test.

has higher value of impact strength with 11.63 kJ/m^2 as compared with PLA material with the value of 3.329 kJ/m^2 . This shows that ABS can resist higher impact than PLA material with 71.36% differences.

As seen in **Fig. 9**, all the ABS specimens show higher value of impact energy and impact strength than PLA material. Both materials can be categorized as polymer, which are classified as brittle material. From the theory of toughness, PLA material is more brittle than ABS material. This is because PLA material has a lower degree of plastic deformation as compared with ABS. The smaller region of plastic deformation for PLA material yields the effect of work done to the material until fracture. PLA material has lower work done to fracture, which is also known as modulus of toughness than ABS material. This because PLA material has lower

area under the stress–strain curve than ABS material. With this, PLA material only requires low absorbed energy for the material to fracture.

The other reason why PLA has lower impact strength as compared with ABS material is due to inconsistency or poor formation of first built layer of printing. As shown in [Fig. 10](#), PLA material shows poor formation of first layer of build as compared with ABS material. From the observation, PLA built filament, which is deposited as the first layer of build, does not consistently deposit, which causes the poor first layer of build. This affects the next layer of build if it is not deposited perfectly with other build layers. The poor deposited build material causes the formation of high intensity of air gaps and voids. The presence of air gaps and voids affect the strength of material against impact. Other than that, the higher intensity of voids and air gap has poor filling degree of built material and causes air inclusion between the printed strand. PLA material is suspected to have this kind of problem, which leads to very low impact strength. This is because the presence of high intensity of air gaps in the printed parts is responsible for weaker bonding between the built layer and printed filament, which causes the specimen to absorb low amount of energy required for complete fracture ([Santhakumar *et al.*, 2016](#)).

As shown in [Fig. 11](#), there are strands of filament that dissociate from the fractured specimen that can be observed after the test. It shows that the weak bonding between the built filament caused by the presence of voids and air gaps can affect the toughness of material.

Conclusion

Geospatial technology has been widely used nowadays due to its ability to provide geographical information and analysis effectively. It reaches the audience of the general public especially with the use of GPS in vehicle navigation devices. The use of geospatial technology in GIS has rapidly evolved especially with the introduction of 3D imaging. It provides the opportunity for topographical data to be visualized in mimicking the real conditions. 3D printing has been used to replace the manual method of using cardboard in producing these 3D images. One of the most-used approaches of 3D printing technique in topographical analysis is FDM. This article discusses the use of two types of FDM material that are commonly utilized, which are ABS and PLA. The impact behaviors of both materials are discussed in detail especially regarding the testing procedure and factor that contributing to the material's failure mode. From the experimental result, it shows that ABS material has greater impact performance than PLA and it is the preferred choice to be used in making 3D images of topographical data.

See also: Oil Palm Kernel Shell – A Potential Sustainable Construction Material

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Joining of 3D Printed Dissimilar Thermoplastics With Consumable Tool Through Friction Stir Spot Welding: A Case Study

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Introduction

In commercial applications TSE is one of the established processes for uniform blending of reinforcements in thermoplastic matrix resulting into improved morphology and mechanical properties of the composite prepared (Giles *et al.*, 2004). The reported studies based upon the destructive and non-destructive testing of thermoplastic composites with TSE have suggested significant improvement of polymeric composite properties (Agassant *et al.*, 2017). It has been observed that while using TSE for the feedstock filaments developments of fused deposition modeling (FDM) requires relatively high holding time for the heating and uniform mixing (Singh *et al.*, 2018a). But at the same time, overheating of materials in barrels should be minimized otherwise it may burn or degrade the mixture and can lead to losses of mechanical and morphological properties (Olahanmi *et al.*, 2016; Ray and Easteal, 2007; Chaitanya and Singh, 2017).

The FDM is one of the key processes for 3D printing of functional/nonfunctional prototypes, as it is capable of developing complex geometries in the short time. The rapid tools prepared by FDM have been applied in some studies for friction/friction stir welding and can be used for repair/maintenance purposes (Singh *et al.*, 2018b,c, 2016; Kumar *et al.*, 2018a,b,c). Conventionally friction stir welding (FSW) and friction stir processing (FSP) are the similar process but differentiated by the nature of application. FSW is techniques where a non-consumable tool of rotating type is inserted in between the interfaces of two sheets to create the diffusion of their edges for joining of materials, whereas FSP is considered as advancement for refinement of micro structural properties. For repair/maintenance of pipelines welding/joining of two similar material is quite common and various studies have been reported for joining of ABS-ABS, PA-PA, low density polyethylene (LDPE)-LDPE, high density polyethylene (HDPE)-HDPE etc. (Squeo *et al.*, 2009; Gonçalves *et al.*, 2015; Paoletti *et al.*, 2015). But when joining/welding of two dissimilar thermoplastic material was performed, it was not as simple to join/weld because both polymer exhibit different properties (e.g., melt flow index (MFI), melting point, molecular weight etc.) (Simões and Rodrigues, 2014; Oliveira *et al.*, 2010; Buffa *et al.*, 2016). After maintaining the MFI of two different polymers (ABS and PA6) by metal powder reinforcement in the close range, joining of dissimilar polymers was feasible (Kumar *et al.*, 2018d; Singh *et al.*, 2017a,b; Singh and Kumar, 2017; Kumar and Singh, 2018; Singh *et al.*, 2017c).

The literature survey reveals that in last two decades most of studies reported the approaches of FSSW by varying its input process parameters. But hitherto very little has been reported on the use of consumable tool for joining of thermoplastic composites sheets. In this study a framework of FSSW with the use of consumable pin as rapid tooling has been explored to be potentially applied it in maintenance and repair applications. The study demonstrates detailed methodology for use of TSE, FDM for melt flow compatible thermoplastic composite preparations and vertical milling setup for joining of Al reinforced ABS sheets with pin of Al reinforced PA6 as a case study.

Materials, Methods and Equipments Required

Fig. 1 shows the detailed methodology of TSE, FDM and FSSW processes for preparations of thermoplastic composites and joining with use of consumable pin profile. To conduct the experimentations, ABS (Grade - EX58) and PA6 (Grade - PX99848) thermoplastics of 1 mm granular size has been procured from the Batra polymers Pvt Ltd, India. Al powder as the reinforcement of 50 μ m size has been procured from Shiva chemical Pvt Ltd, Ludhiana, India.

The study is focused on the composite preparations and joining of substrates by using consumable tools. Following equipments have been used: MFI, TSE, FDM and vertical milling machine for FSSW process.

MFI

MFI of any thermoplastic composites is defined as the flow of materials from the nozzle of the MFI tester at standard temperature and loading conditions. For the present study the ASTM D 1238 standard has been used (Company: Shanta engineering, Pune, India, Model: 2013). The proportions of Al metal powder in the ABS and PA6 thermoplastic materials were varied from 0% to 50%.

TSE

For the extrusion of Al reinforced ABS and PA6 materials a TSE of co-rotating screws has been used (Company: Thermo scientific, Model: HAAKE MiniCTW). The TSE processing results into uniform mixing of the Al metal powder with ABS and PA6

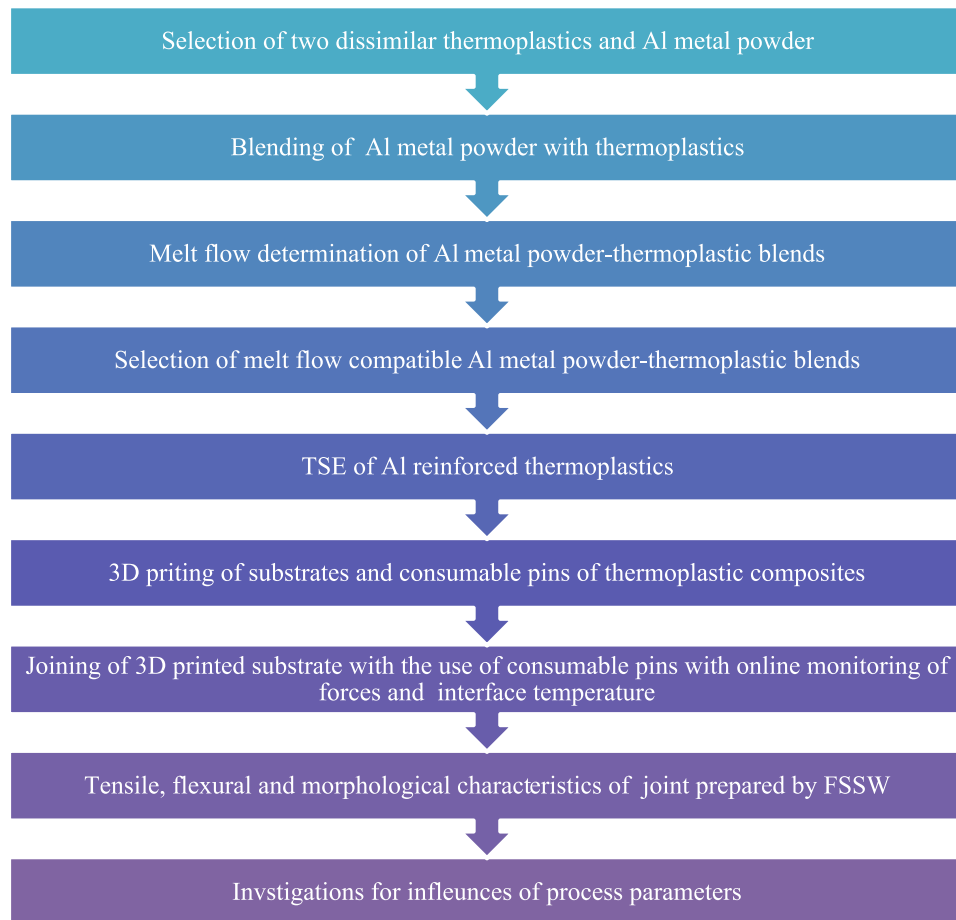


Fig. 1 Detailed methodology for FSSW using consumable pin profile.

thermoplastic for preparation of feedstock filament with good control of dimensions. In the present case study, the feedstock filaments of 1.75 ± 0.05 mm size were prepared.

FDM

FDM is one of the low cost 3D printing techniques which is based upon the additive manufacturing concept. In this study, a commercial FDM printer (Company: Divide by Zero, India, Model: Accura 250Di) has been used for preparations of substrate and consumable pins of Al reinforced ABS and PA6 thermoplastic composites. FDM setup requires a .STL file format (stereo lithography) of 3D geometrical shape prepared on software. These geometrical .STL files are further mathematically oriented and sliced for desire prototype fabrication. The rectangular substrates of Al reinforced ABS and consumable pins of Al reinforced have been prepared under suggested processing conditions.

Vertical Milling Machine for FSSW Process

Fig. 2 shows the experimental setup for FSSW of Al reinforced ABS substrate by using consumable pins of Al reinforced PA6. The FDM printed samples were fixed on vertical milling setup with dynamometer arrangement (Make: Industrial engineering instrument, India, Model: Multi component digital force indicator, Model: 652) for FSSW. The thermal imaging camera was maintained at 500 mm distance with projectile angle of 60° . The measurement of axial and transverse forces has been taken to correlate it with the outcomes of the mechanical and morphological properties.

Experimentations

The rheological analysis reveals that ABS with 15% Al content and PA6 with 50% Al content results into MFI 11.57 g/10 min and 11.97 g/10 min respectively. Based upon these observations, ABS-15%Al and PA6-50%Al have been considered as the final

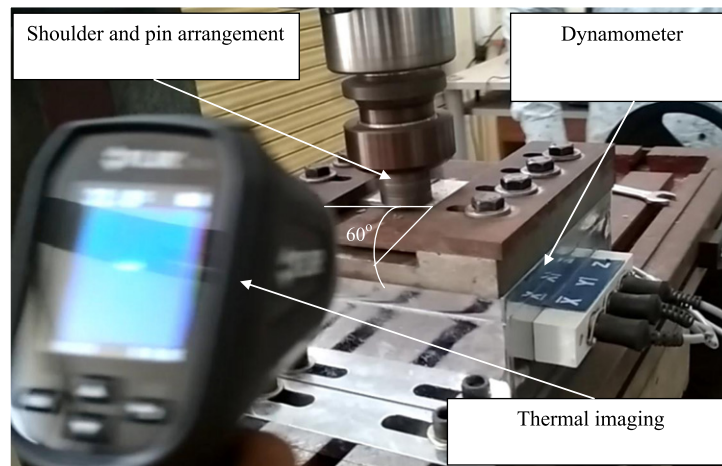


Fig. 2 Vertical milling setup equipped with thermal imaging and dynamometer for FSSW.

Table 1 Experimental condition for FSSW

Experiment no.	Rotational speed (rpm)	Plunge depth (mm)	Stirring time (s)
1	1200	2	15
2	1200	3	20
3	1200	4	10

composition for further experimentations. ABS-15%Al and PA6-50%Al were processed by TSE (Company: Thermo scientific, Model: HAAKE MiniCTW) for preparations of feedstock filaments. ABS-15%Al filaments was prepared at 220°C temperature, 30 rpm screw speed with 20 kg external load whereas feedstock filaments of PA6-50%Al was prepared at 245°C, 20 rpm screw speed with 15 kg external load. The levels of process variables were selected on the basis of pilot experimentations and it has been observed that uniform feedstock filaments were obtained only under these processing conditions.

3D printing of 60 × 60 × 4 mm sheets and 4 mm diameter pin by FDM was processed under infill percentage of 80%, filament diameter of 1.75 ± 0.05 mm, 6 perimeters, rectilinear filling, perimeter speed of 30 mm/s, printing speed 60 mm/s, extruder temperature of 250°C and printing bed at 55°C. Further FSSW was performed at 1200 rpm rotational speed of shoulder by varying the plunge depth (2–4 mm) and stirring time (10–20 s) for investigating the influences of process parameters (see [Table 1](#)). The range of selected levels of input process variables is dependent upon the feasibility of the FSSW process.

The mechanical (on universal tensile tester, Company: Shanta Engineering, Model: SE-500 kgf), thermal and morphological (by optical microscope, Model: XJL-17) properties FSSW welded parts were observed to investigate the influences of process parameters. ASTM D638 type IV (speed: 20/min) was followed for tensile properties evaluation and ASTM D 790 for flexural properties. ASTM E2015-04(2014) was followed for morphological analysis.

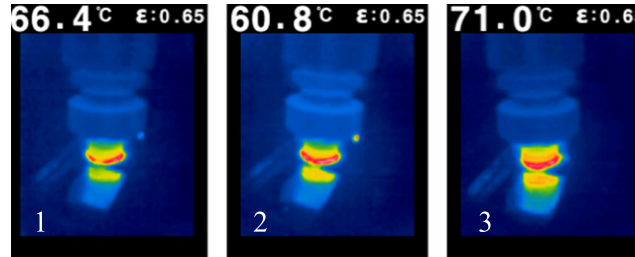
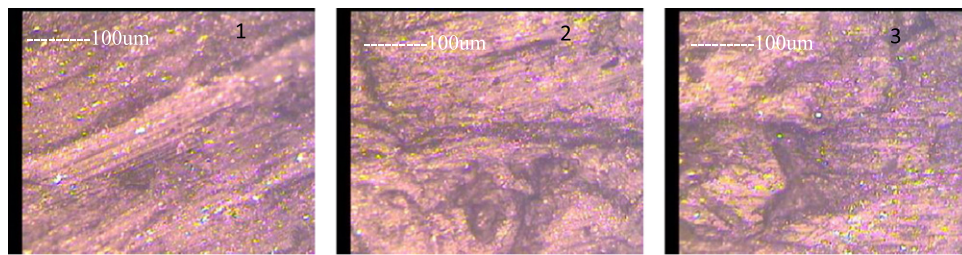
Results and Discussion

The joints were subjected to tensile, flexural, hardness and morphological testing, which shows that there is a significant variation of mechanical and morphological properties by varying the process parameters. The results are also supported by maximum interface temperature, maximum axial and transverse force which was observed during FSSW (see [Table 2](#)). It has been observed that maximum tensile strength at peak (91.1 MPa), maximum flexural strength at peak (66.90 MPa), maximum Shore D hardness (81.5 Shore D) and minimum percentage porosity at joints (13.09%) were obtained in experiment no. 3 (experimental conditions: 1200 rpm, plunge depth 4 mm and stirring time 10 mm) ([Table 2](#)). This may be due to the fact that maximum plunge depth and minimum stirring time contributed to more heat generations (71.0°C) and minimum force requirement (transverse force: 57 N and axial force: 120 N). In other words maximum plunge depth may have contributed for maximum heat generation so the joints prepared are uniformly stirred and free from porosity.

[Fig. 3](#) shows the thermal images of joints which were captured during FSSW process. It should be noted that maximum interfaced temperature was observed for sample 3 (671.0°C) and minimum for sample 2 (60.8°C). The sample 3 was processed

Table 2 Mechanical, morphological and online measured data for joining of ABS-15%Al substrate with consumable pin of PA6-50%Al

Experiment no.	Tensile strength at peak (MPa)	Flexural strength at peak (MPa)	Shore D hardness	Maximum interface temperature ($^{\circ}$ C)	Maximum axial force (N)	Maximum transverse force (N)	Percentage porosity at joints
1	89.2	66.90	79.0	66.4	145	60	14.58
2	72.4	61.0	78.0	60.8	170	55	13.58
3	91.1	66.90	81.5	71.0	120	57	13.09

**Fig. 3** Thermal images captured at different experimental conditions.**Fig. 4** Photomicrographs of FSSW joints at different experimental conditions.

with 4 mm depth of consumable pin which covers full thickness of ABS-15%Al substrate. The full length depth of pin profile resulted in the maximum heat generation which further contributed to maximizing mechanical strength.

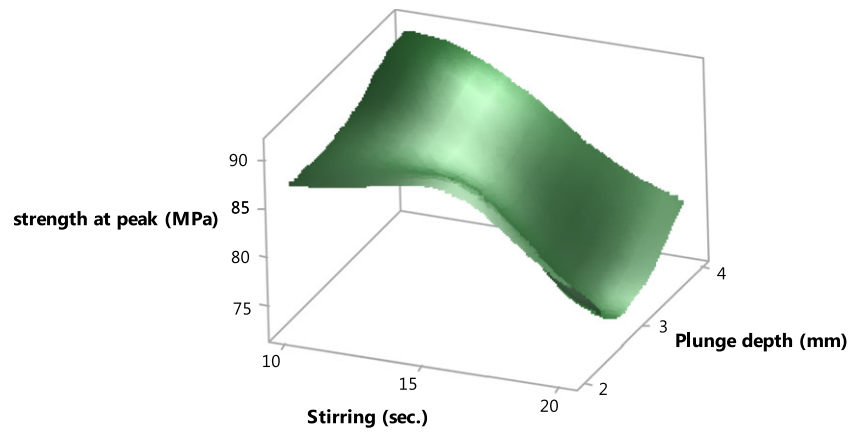
Fig. 4 shows the photomicrographs of FSSW joints at different experimental conditions observed at 100 $\times$ magnifications. It should be noted that photomicrograph of sample 2 was obtained very rough and un-uniform with significance of un-mixed layers whereas photomicrograph of sample 3 has obtained with more stirred region and uniformly mixed surfaces.

Selecting the Optimum Process Parameters for Mechanical Properties

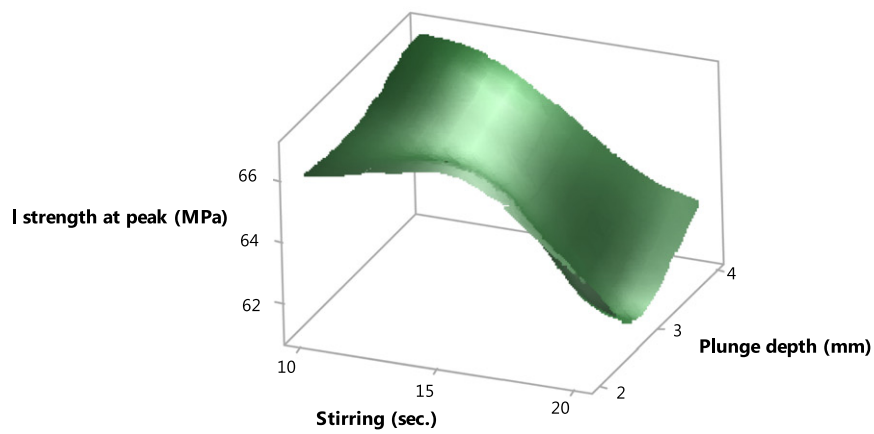
A surface plot for each mechanical property has been plotted to select the best set of process parameters. It should be noted from **Fig. 5(a–c)** that surface plot of tensile strength at peak, flexural strength at peak and Shore D hardness was elevated at 4 mm plunge depth and 10 s stirring time. So it is recommended that FSSW should be performed at 1200 rpm, under 10 s welding time with 4 mm depth of consumable pin.

Summary

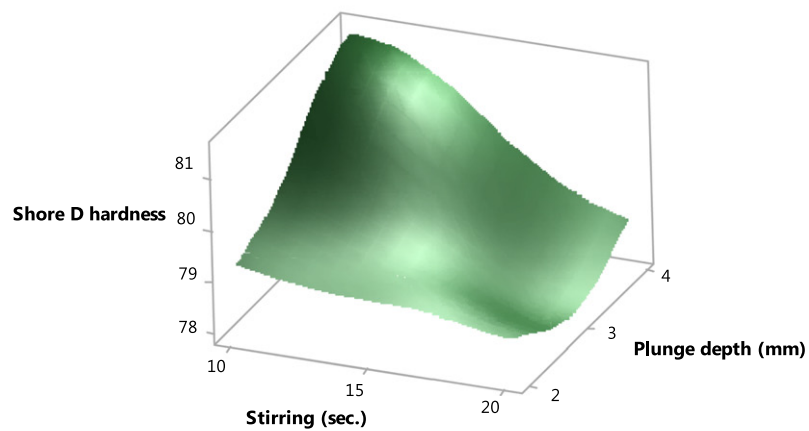
The proposed route of FSSW for joining of 3D printed substrate by using consumable tools is recommended for use in repair and maintenance of cracked pipelines, and from mechanical strength view point, it has been observed that maximum tensile strength at peak (91.1 MPa), maximum flexural strength at peak (66.90 MPa), maximum Shore D hardness (81.5 Shore D) and minimum percentage porosity at joints (13.09%) were obtained in experiment no. 3 (experimental conditions: 1200 rpm, plunge depth 4 mm and stirring time 10 mm). It should be noted that maximum interfaced temperature was observed for sample 3 (71.0 $^{\circ}$ C) and minimum for sample 2 (60.8 $^{\circ}$ C). The sample 3 was processed with 4 mm depth of consumable pin which covers full thickness of ABS-15%Al substrate. The full length depth of pin profile resulted in the maximum heat generation which further contributed to maximizing mechanical strength. Based upon the analysis made for selecting the optimum set of process parameters, it is recommended that FSSW should be performed at 1200 rpm, under 10 s welding time with 4 mm depth of consumable pin.



(a)



(b)



(c)

Fig. 5 (a) Surface plot for tensile strength vs. plunge depth and stirring time. (b) Surface plot for flexural vs. plunge depth and stirring time. (c) Surface plot for Shore D hardness vs. plunge depth and stirring time.

Acknowledgment

The authors are highly thankful to Board of Research in Nuclear Science (BRNS) No: 34/14/10/2016-BRNS/34036 and center for manufacturing research, GNDEC, Ludhiana for providing financial/technical

See also: Joining of 3D Printed Dissimilar Thermoplastics With Friction Welding: A Case Study. Joining of 3D Printed Dissimilar Thermoplastics With Nonconsumable Tool Through Friction Stir Welding: A Case Study

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Joining of 3D Printed Dissimilar Thermoplastics With Friction Welding: A Case Study

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Introduction

Conventionally, friction welding is a metalworking or forming process which is developed about 6 decades ago, is applied now in wide engineering fields such as: automobile, aviation, marine and oil industries (Kumar *et al.*, 2018a,b). Friction welding comes under solid state welding process which is basically performed under temperature below the melting points of parent materials (Kumar *et al.*, 2018c,d). The friction welding of metals, metallic alloys and composites, similar kind thermoplastic is quite common and it is adopted in real field applications due to sustainable joints formations (Abibe *et al.*, 2016; Oliveira *et al.*, 2010; Kumar *et al.*, 2018e; Singh *et al.*, 2019). But the friction welding of dissimilar thermoplastic or thermoplastic composite materials is still a challenging task because of difference in MFI, molecular weight, melting point, specific heat capacity, glass transition temperature etc. (Singh *et al.*, 2018a,b,c; Singh *et al.*, 2016). One of the reported alternatives for performing the friction welding of dissimilar thermoplastic (ABS and PA6) material is by maintaining similar MFI of those thermoplastics by reinforcement of metallic/nonmetallic particles in their matrix (Kumar *et al.*, 2017). Performance of friction based welding is dependent upon varying the input process variables and reinforcements (Kumar *et al.*, 2019). It has been reported that mechanical, thermal and metallurgical properties of solid state welded ABS joints were affected by level of vibration (Stokes and Hobbs, 1993). Study reported that interface properties like; fusion, deformation mechanisms and microstructure characteristics of friction welded interface are varied accordingly by rotational speed (Yilbas *et al.*, 1995; Yilmaz *et al.*, 2002). ABS and Nylon6 are commonly used thermoplastics with excellent mechanical properties and are used generally for friction welding application (Gao *et al.*, 2015). The joining of ABS or Nylon 6 to itself or welding of ABS to HDPE is feasible (Panneerselvam and Lenin, 2014). But, there is a limitation of joint strength (for friction welded joints) of these thermoplastics that hinders its use in different engineering applications. Friction stir welding (FSW) is one of the variants of solid-state joining/friction welding technique that uses a non-consumable tool to join two facing work pieces without melting the work piece material (Pabandi *et al.*, 2017).

Some studies suggested that reinforcement of metallic/nonmetallic particulates in thermoplastic matrix enhance basic material properties (thermal conductivity, MFI, specific heat capacities, melting points etc.) so the joints can be easily formed. But the gap has been found in ascertaining the role of heat generation on the mechanical strength of the welded joints. In the present study, 3D printed ABS and PA6 thermoplastic has been joined by friction welding on lathe setup under online interface temperature measuring by thermal imaging camera. Further analysis has been conducted to investigate the role of heat generation on mechanical properties of joints.

Materials and Methods

First of all pilot experimentation were conducted to check the feasibility for joining of ABS and PA6 on lathe setup by varying rotational speed from 5000–1500, feed rate of 0.045–0.18 mm/rev and actuating time of 2–20 s. It has been observed that joint obtained from friction welding of ABS and PA6 was weak and easily broken with small loading. The reason for weak joint may be related with wide difference in melt flow properties of ABS (MFI=8.76 g/10 min) and PA6 (MFI=23.27 g/10 min). So based upon these observations, a process chart has been developed to make feasible joints of ABS and PA6 by modifying their melt flow properties (see Fig. 1). Al metal particle (size: 50 μ m) were mechanically mixed into granules of ABS and PA6 matrix to investigate the MFI by varying its proportion from 0% to 50%.

It has been observed that MFI of ABS and PA6 thermoplastics resulted into similar MFI by incorporating 15% Al in ABS (MFI: 11.57 g/10 min for ABS-15Al) and 50% Al in PA6 (MFI: 11.97 g/10 min for PA6-50 Al). The feedstock filaments of ABS-15 Al were extruded by TSE setup under 220°C barrel temperature, 30 rpm screw speed with 20 kg load and PA6-50 Al under 245°C barrel temperature, 20 rpm Screw speed with 15 kg load (levels of parameters were selected as per pilot results). Further 3D printing (cylindrical surface: 50 mm diameter and 50 mm length) by using FDM has been performed for both thermoplastic composites under 30 mm/s printing speed, covering by 6 perimeters at 250°C temperature (see Fig. 2).

Further the mechanical, thermal and rheological properties of ABS-15 Al and PA6-50 Al have been checked as per ASTM standards (see Table 1).

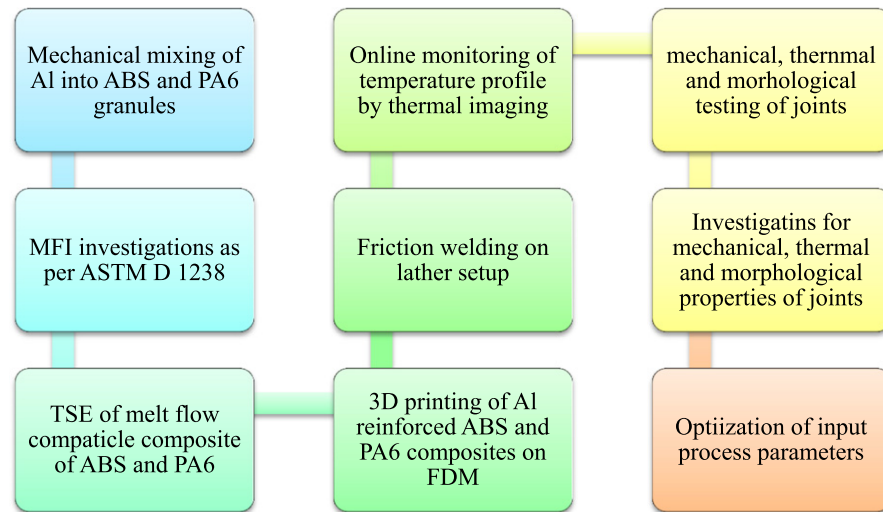


Fig. 1 Methodology for joining of dissimilar thermoplastic based materials.



Fig. 2 Specimen (ABS-15 Al and PA6-50 Al) prepared by 3D printing for friction welding.

Table 1 Basic property of ABS-15 Al and PA6-50 Al

Materials	MFI (g/10 min)	Melting point (°C)	Break strength (MPa)	Peak strength (MPa)	Percentage elongation at break (%)	Percentage elongation at peak (%)
ABS-15 Al	11.57	203.20–223.59	202.07	224.30	12	11
PA6-50 Al	11.97	221.06	198.19	220.20	14	14

Experimentation

Based upon feasibility of joints formation, 3 different levels of rotational speed (500, 750 and 1200 rpm), welding actuation rate (0.045, 0.09 and 0.18 mm/s) and welding actuation time (4, 6 and 8 s) have been selected for final experimentation on lathe setup. The Taguchi L9 orthogonal array (O.A) approach has been employed for experimentation (see Table 2).

Fig. 3 shows photographs of joints obtained by friction welding.

Table 2 Design of experiment as per Taguchi L9 O.A

Experiment no.	Rotational speed (RPM)	Actuation rate (mm/rev)	Actuation time (s)
1	500	0.045	4
2	500	0.09	6
3	500	0.18	8
4	775	0.045	6
5	775	0.09	8
6	775	0.18	4
7	1200	0.045	8
8	1200	0.09	4
9	1200	0.18	6

**Fig. 3** Joint of ABS-15 Al and PA6-50 Al by friction welding.

Results and Discussion

Friction welding conducted by controlling rotational speed, actuation time and actuation rate with monitoring interface temperature. The joints were subjected to mechanical, morphological and thermal testing for investigating effects of process parameters.

Mechanical and Morphological Properties

It has been observed that maximum tensile and flexural strength (break and peak) and Shore D hardness were obtained at experiment no. 7 (parametric combination: 1200 rpm, 0.045 mm/min and 8 s) and minimum at experiment no. 3 (parametric combination: 500 rpm, 0.18 mm/min and 8 s) (see Table 3). The percentage porosity on joint surface may have contributed to weaker strength as largest porosity obtained for experiment no. 2. The porosity was lesser for sample of experiment no. 7 (exhibited maximum mechanical properties). The porosity on the joint surface may occurred due to improper mixing by insignificant heat generations.

Fig. 4 shows stress vs. strain curves of tensile properties. The maximum strength obtained for sample of experiment no. 7 whereas maximum elongation was observed for sample of experiment 8.

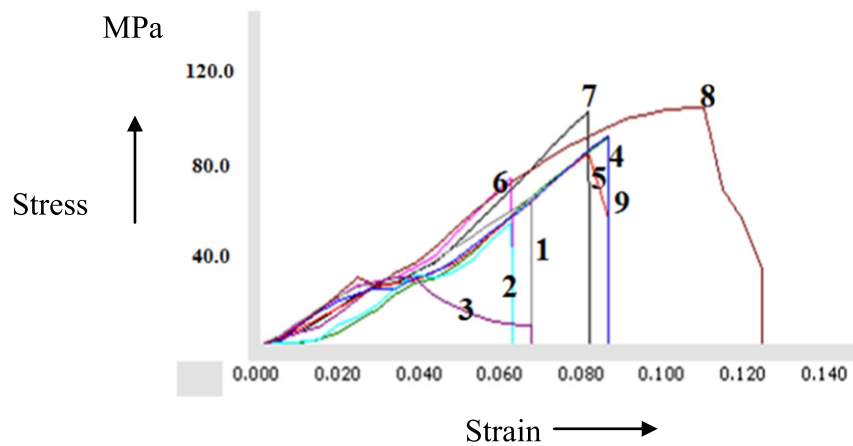
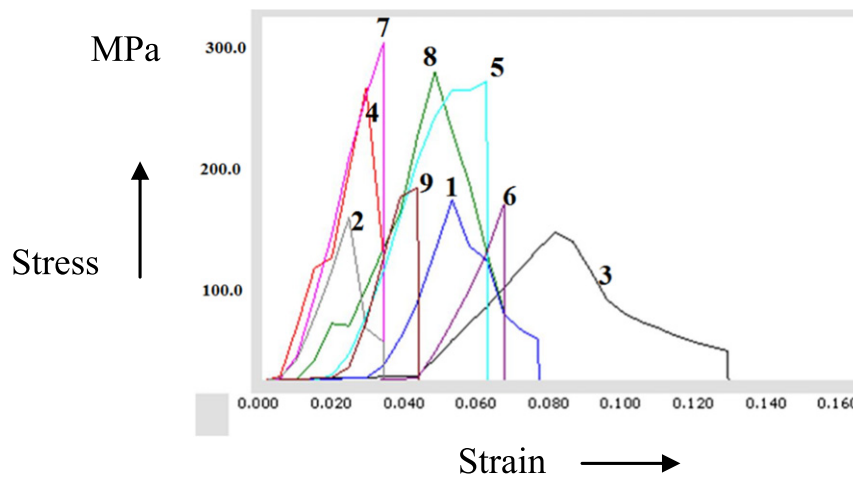
Fig. 5 shows stress vs. strain curves of flexural properties. The maximum strength obtained for sample of experiment no. 7 whereas maximum elongation was observed for sample of experiment 3.

Thermal Imaging

The interface temperature during friction welding is a measure of heat generation which promotes material flow. The material flow is an important aspect of welding process which ensures the soundness of the joints. In this study, the maximum temperature was measured for sample of experiment no. 7 (237.0°C) and minimum for experiment no. 3 (166.4°C) (see Fig. 6). It may occur due to a fact that higher rotational speed (1200 rpm) with lower actuation rate (0.045 mm/min) have contributed for better heat

Table 3 Mechanical and morphological properties of friction welded joints

Exp. no.	Tensile properties				Flexural properties				Shore D hardness	Porosity at joints (%)
	Strength at peak (MPa)	Strength at break (MPa)	% Elongation at peak	% Elongation at break	Strength at peak (kg/Sq mm)	Strength at break (kg/Sq mm)	% Deflection at peak	% Deflection at break		
1	63.3	57.0	7	7	159.7	143.7	5	8	79.0	17.25
2	56.0	50.4	6	6	150.0	135.0	2	3	78.5	22.24
3	30.7	27.6	4	7	123.2	110.9	8	13	77.0	25.47
4	91.6	82.5	9	9	270.1	243.1	3	3	80.5	15.45
5	83.1	74.8	8	9	247.4	222.6	6	6	80.0	16.05
6	71.9	64.7	6	6	160.9	144.8	7	7	79.5	16.67
7	102.5	92.2	8	8	300.4	270.3	3	3	82.5	12.57
8	100.5	90.5	10	12	255.7	230.1	5	7	81.5	13.05
9	90.7	81.6	8	9	197.4	177.7	4	4	81.0	14.57

**Fig. 4** Stress vs. strain curves for tensile properties.**Fig. 5** Stress vs. strain curves for flexural properties.

generation. Due to better heat generation material flow occurred better in case of sample of experiment no. 7 which promoted better material mixing (also minimized percentage porosity at joints). Similarly maximum porosity for sample of experiment no. 3 may occurred because improper material mixing promoted by insufficient heat generation.

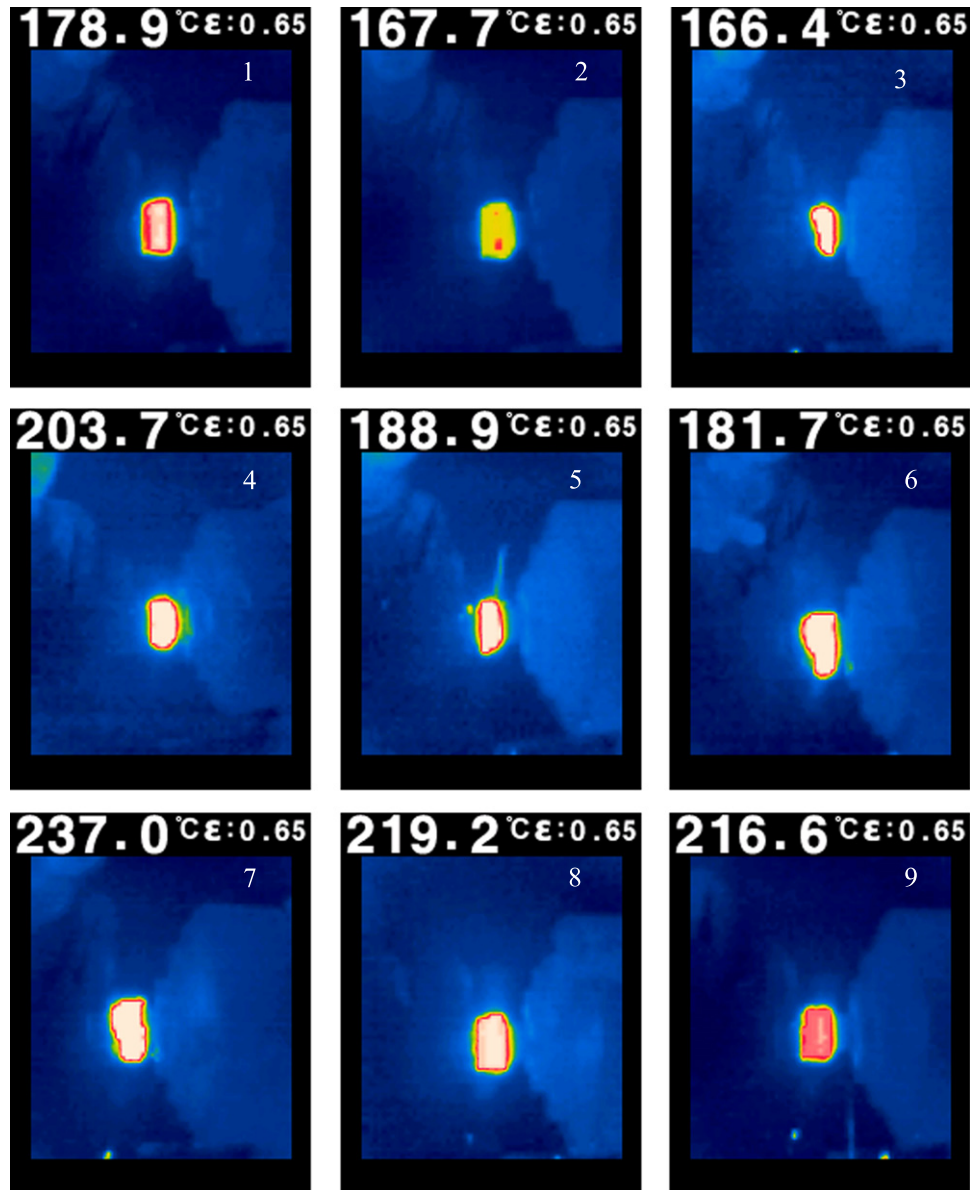


Fig. 6 Thermal images of friction welding at different experimental conditions.

Photo-Micrographic Observations

The photomicrographs obtained at X30 magnification to investigate the joint morphology affected by varying process parameters (see Fig. 7). The joints of experiment no. 3 has obtained porous because of improper material mixing during joining. The porous structure was appeared as defect in the present study which minimizes the joints strength and joint hardness. On the other hand, the micrograph of experiment no. 7 has appeared more uniform and layer are uniformly mixed (it may occurred due to significant heat generation).

DSC

Samples of experiment no. 3 and 7 have been thermally tested by DSC equipment to investigate the role of input process variables. It should be noted that melting peak for sample of experiment no. 3 was obtained 218.85°C and for experiment no. 7 219.35°C (see Fig. 8). The more melting peak in case of sample of experiment no. 7 has paped due to fact that high rotational speed may



Fig. 7 Photomicrograph of joints interface at X30 magnification.

provided better material flow which made those material thermally more stable. This information can also be interpreted by normalized heat capacity rate as 26.21 J/g energy was required to melt the samples of experiment no. 3 whereas 58.50 J/g energy was required to melt the sample of experiment no. 7. The more heat required for melting indicates that more thermally stable is the materials.

Optimization of Process Parameters for Mechanical Properties

The signal to noise (SN) ratio of each property has been calculated to optimize the input process parameters. The mechanical properties (tensile, flexural and Shore D harness) were taken as 'larger is better' for calculating SN ratios (see [Table 4](#)).

[Fig. 9](#) shows main effect plot of SN ratio for mechanical and morphological properties. The mechanical properties were considered under 'larger is better' type case. The best setting obtained for each properties were also shown in [Table 7](#).

For optimization of each input process parameters as per variations over mechanical properties, a mathematical approach has been utilized as per results of SN ratio. [Table 5](#) shows analysis of variance (ANOVA) for SN ratios of peak strength (tensile). The rotational speed was contributed maximum whereas actuation time contributed least. Residual error was observed lesser than 5% shows acceptance of present model.

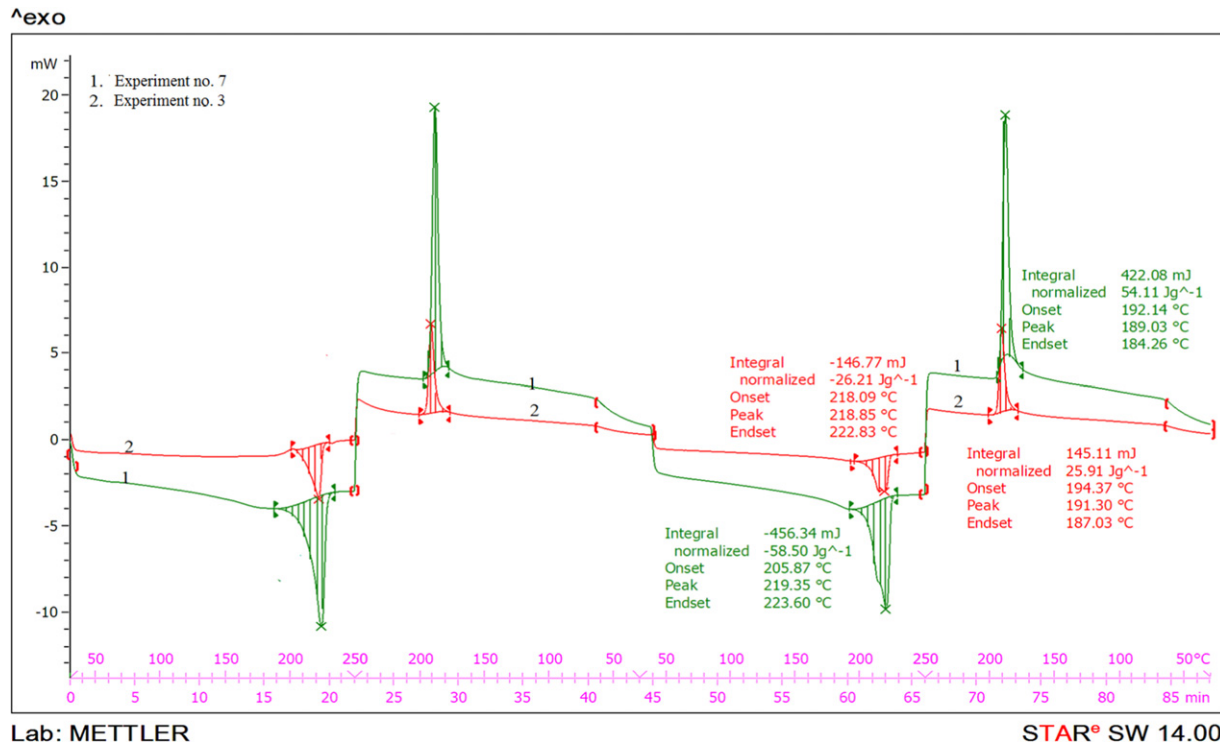


Fig. 8 DSC interpretation of sample of exp. 3 and exp. 7.

Table 4 SN ratio of mechanical and morphological properties

Exp no.	Tensile properties				Flexural properties				Shore D hardness
	Strength at peak	Strength at break	% Elongation at peak	% Elongation at break	Strength at peak	Strength at break	% Deflection at peak	% Deflection at break	
1	36.02	35.11	16.90	16.90	44.06	43.14	13.97	18.06	37.95
2	34.96	34.04	15.56	15.56	43.52	42.60	6.02	9.54	37.89
3	29.74	28.81	12.04	16.90	41.81	40.89	18.06	22.27	37.72
4	39.23	38.32	19.08	19.08	48.63	47.71	9.54	9.54	38.11
5	38.39	37.47	18.06	19.08	47.86	46.95	15.56	15.56	38.06
6	37.13	36.21	15.56	15.56	44.13	43.21	16.90	16.90	38.00
7	40.21	39.29	18.06	18.06	49.55	48.63	9.54	9.54	38.32
8	40.04	39.13	20.00	21.58	48.15	47.23	13.97	16.90	38.22
9	39.15	38.23	18.06	19.08	45.90	44.99	12.04	12.04	38.16

Table 6 shows response table SN ration for of peak strength. Rotational speed ranked 1, actuation rate ranked 2 and actuation time was ranked 3.

The optimum value of peak strength in tensile testing can be predicted by using following equation:

$$\eta_{opt} = m + (m_{A3} - m) + (m_{B1} - m) + (m_{C2} - m) \quad (1)$$

Where 'm' is the overall mean of SN ratio, m_{A3} is the mean of SN ratio for rotational speed at level 3, m_{B1} is the mean of SN ratio for actuation rate at level 1, and m_{C2} is the mean of SN data for actuation time at level 2.

Now for lesser is better by type case

$$y_{opt}^2 = (1/10)^{\eta_{opt}/10} \quad (2)$$

For properties, Larger is better type case

$$y_{opt}^2 = (10)^{\eta_{opt}/10} \quad (3)$$

Calculation:

Overall mean of SN ratio (m) was taken from Minitab software.

$m = 37.21$ dB (see Table 5)

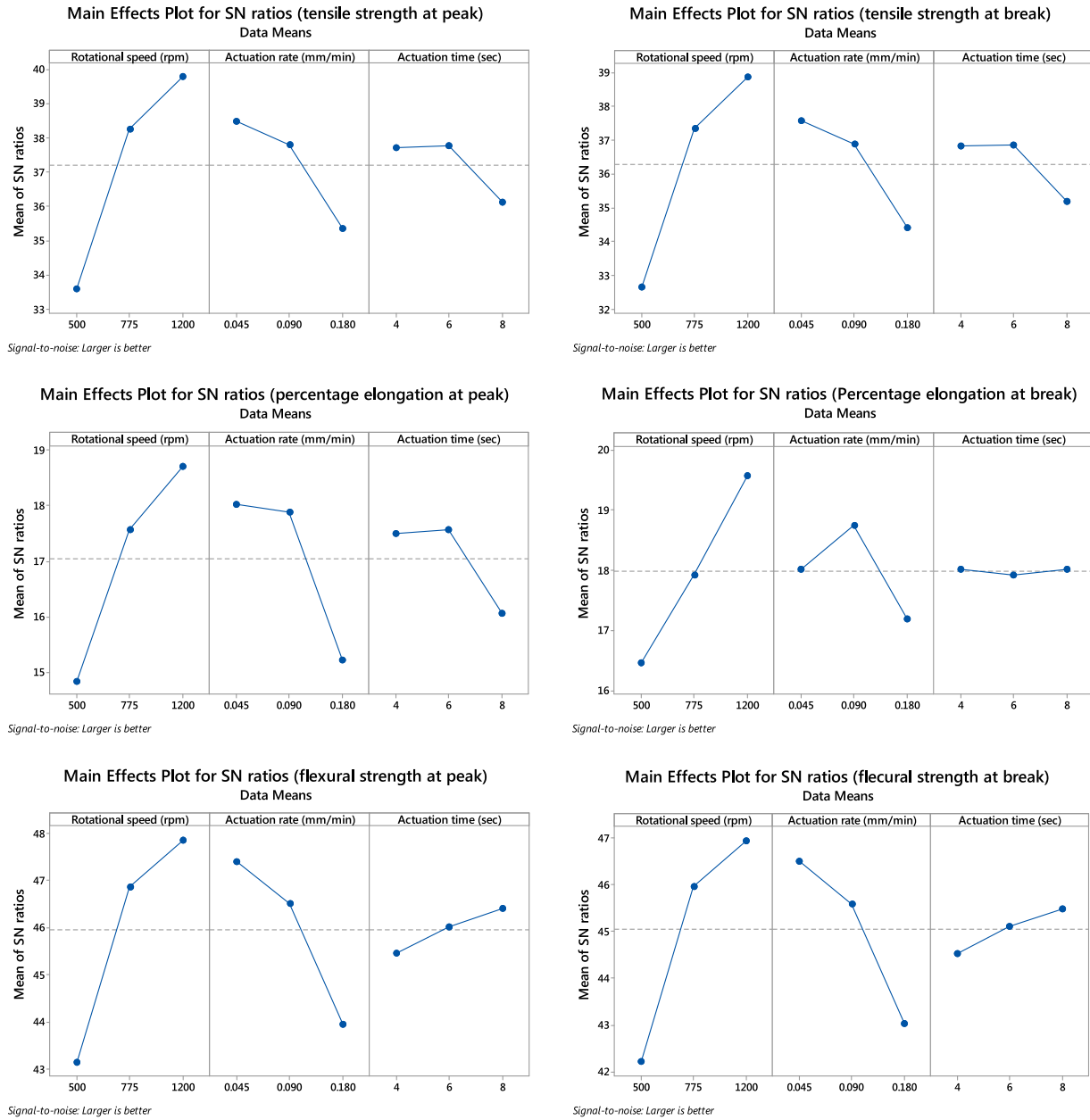


Fig. 9 Linear model of SN ratios for different properties.

Now from response table of signal to noise ratio, $m_{A2} = 39.80$, $m_{B2} = 38.49$, $m_{C2} = 37.78$, (From [Table 6](#))

Now taking [Eq. \(1\)](#), putting the values

$$\eta_{\text{opt}} = 37.21 + (39.80 - 37.21) + (38.49 - 37.21) + (37.78 - 37.21)$$

$$\eta_{\text{opt}} = 41.65$$

Now, from [Eq. \(3\)](#) $y_{\text{opt}}^2 = (10)^{\eta_{\text{opt}}/10}$

$$y_{\text{opt}}^2 = (10)^{41.65/10}$$

$$y_{\text{opt}} = 120.92 \text{ MPa}$$

The predicted optimum value for peak strength in tensile testing = 120.92 MPa

Similarly this approach has been used to predict the optimum setting of each output parameters. [Table 7](#) shows predicted setting, predicted value and observed values of each output process parameters as per calculation made by [Tables 4–6](#).

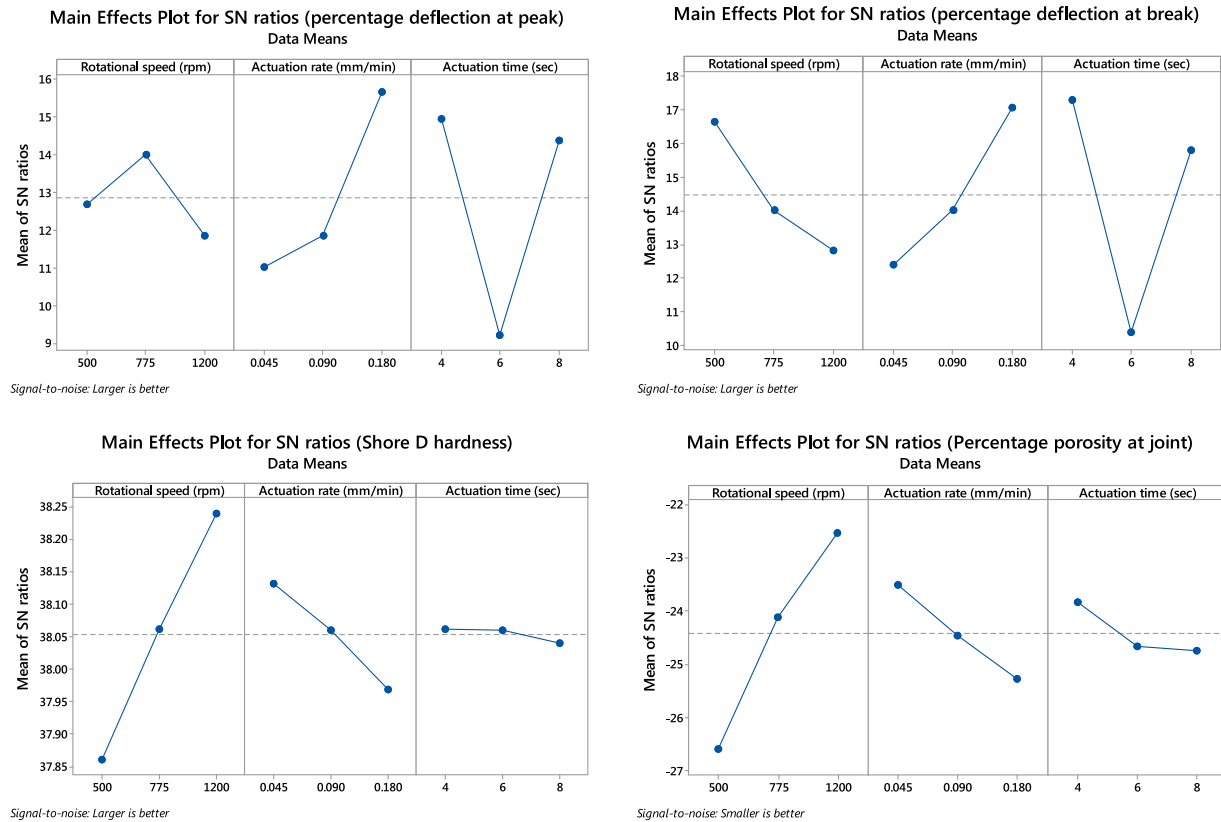


Fig. 9 (Continued)

Table 5 ANOVA for SN ratios of peak strength (tensile)

Source	DF	Seq SS	Adj SS	Adj MS	F	P	Percentage contribution
Rotational speed (rpm)	2	63.021	63.021	31.510	17.14	0.050	71.17%
Actuation rate (mm/min)	2	16.440	16.440	8.220	4.47	0.183	18.56
Actuation time (s)	2	5.406	5.406	2.703	1.47	0.405	6.10
Residual error	2	3.677	3.677	1.838			4.15
Total	8	88.544					

Table 6 Response table for SN ratios for peak strength (tensile) (Larger is better)

Level	Rotational speed (rpm)	Actuation rate (mm/min)	Actuation time (s)
1	33.58	38.49	37.74
2	38.25	37.80	37.78
3	39.80	35.34	36.12
Delta	6.23	3.15	1.67
Rank	1	2	3

Following Table 4, SN ratios of all properties were further optimized by considering 'larger is better' type case. Fig. 10 shows main effect plot of combined properties. It should be noted that optimum setting for mass production is 775 rpm, 0.18 mm/min and 4 s.

Table 7 Predicted and observed values at optimum setting

	<i>Tensile properties</i>				<i>Flexural properties</i>				<i>Shore D hardness</i>	<i>Percentage porosity at joint (%)</i>
	<i>Strength at peak (MPa)</i>	<i>Strength at break (MPa)</i>	<i>% Elongation at peak</i>	<i>% Elongation at break</i>	<i>Strength at peak (kg/Sq mm)</i>	<i>Strength at break (kg/Sq mm)</i>	<i>% Deflection at peak</i>	<i>% Deflection at break</i>		
Predicted setting	1200 rpm, 0.045 mm/min and 6 s	1200 rpm, 0.045 mm/min and 6 s	1200 rpm, 0.045 mm/min and 6 s	1200 rpm, 0.09 mm/min and 8 s	1200 rpm, 0.045 mm/min and 8 s	1200 rpm, 0.045 mm/min and 8 s	775 rpm, 0.18 mm/min and 4 s	1200 rpm, 0.18 mm/min and 4 s	1200 rpm, 0.045 mm/min and 4 s	1200 rpm, 0.045 mm/min and 4 s
Predicted value	120.92	109.14	10.31	10.44	308.31	277.97	8.88	12.63	82.50	3.16
Observed value	120.20	108.88	10.0	11.0	307.20	277.54	9.0	13.0	82.50	3.25

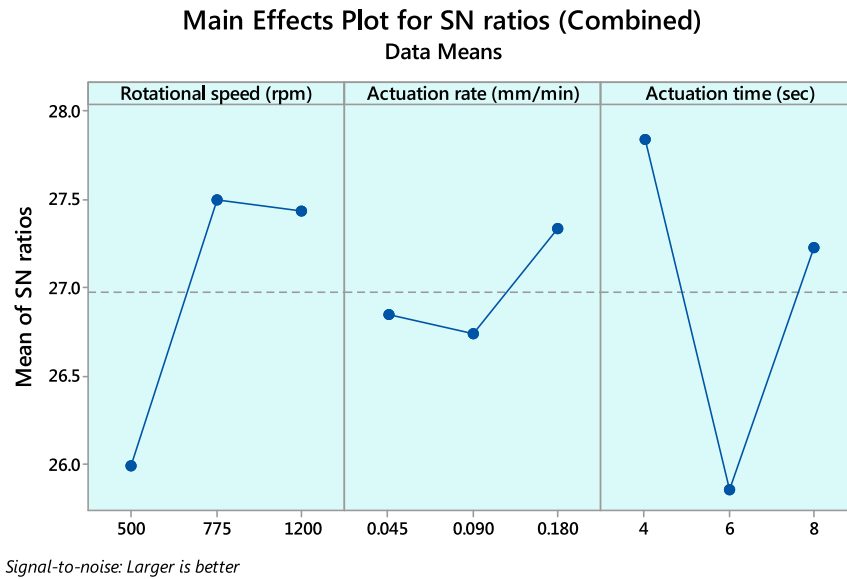


Fig. 10 Main effect plot for SN ratios of combined properties.

Conclusions

Following conclusions can be made from present study:

- The maximum tensile and flexural strength (break and peak) and Shore D hardness were obtained at experiment no. 7 (parametric combination: 1200 rpm, 0.045 mm/min and 8 s) and minimum at experiment no. 3 (parametric combination: 500 rpm, 0.18 mm/min and 8 s).
- Due to better heat generation material flow occurred better in case of sample of experiment no. 7 which promoted better material mixing (also minimized percentage porosity at joints).
- The joints of experiment no. 3 has obtained porous because of improper material mixing during joining. The porous structure was appeared as defect in the present study which minimizes the joints strength and joint hardness. On the other hand, the micrograph of experiment no. 7 has appeared more uniform and layer are uniformly mixed (it may occurred due to significant heat generation).
- This information can also be interpreted by normalized heat capacity rate as 26.21 J/g energy was required to melt the samples of experiment no. 3 whereas 58.50 J/g energy was required to melt the sample of experiment no. 7. The more heat required for melting indicates that more thermally stable is the materials.

Acknowledgement

The authors are highly thankful to Board of research in nuclear science (BRNS) No: 34/14/10/2016-BRNS/34036 and center for manufacturing research, GNDEC, Ludhiana for providing financial/technical assistance to carry out the research work.

See also: Experimental Investigations for Friction Stir Welded 3D Printed Dissimilar Thermoplastics With Consumable Tool. Joining of 3D Printed Dissimilar Thermoplastics With Consumable Tool Through Friction Stir Spot Welding: A Case Study. Joining of 3D Printed Dissimilar Thermoplastics With Nonconsumable Tool Through Friction Stir Welding: A Case Study.

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Joining of 3D Printed Dissimilar Thermoplastics With Nonconsumable Tool Through Friction Stir Welding: A Case Study

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Introduction

Friction welding (FW) was initially developed for similar metal/alloys welding, and later on it was also used for welding of thermoplastic composites (Taylor *et al.*, 1989; Yilbas *et al.*, 1995; Kostka *et al.*, 2009). The previous studies have reported for investigating the mechanical, thermal and metallurgical properties of friction welded surfaces (Gao *et al.*, 2015; Sluzalec, 1990; Stokes and Hobbs, 1993; Stokes, 1993). The interface properties at joints were examined to check the fusion, deformation and microstructure of friction welded surfaces by some researchers (Kostka *et al.*, 2009; Yilmaz *et al.*, 2002; Rotundo *et al.*, 2010). The acrylonitrile butadiene styrene (ABS) and nylon6 are commonly used thermoplastics having good range of mechanical, thermal, chemical, and morphological properties and are used in commercial FW application (Gao *et al.*, 2015). As per reported literature, joining of ABS with nylon 6 or joining of ABS to high-density polyethylene is possible with some iteration in rheological properties (like melt flow index (MFI)) for good mechanical strength (Panneerselvam and Lenin, 2014). However, joining of dissimilar material is limited because joint strength (for friction welded joints) is not up to the mark, which hinders its use in different engineering applications. Some of the studies have highlighted the use of a tool in the form of a ring that is rotated in between the interface of two pipes. This becomes heat deformed by friction created due to rotation of the ring, so welding of the pipeline is possible (Faes *et al.*, 2009). Friction inertia welding is widely accepted in aerospace applications (Attallah, 2012; Raab *et al.*, 2015). Reinforcement of polymer with nanocomposite can make the FW process feasible. The studies also highlight that friction spot welding of polymethyl-methacrylate and polymethyl-methacrylate-SiO₂ is feasible (Junior *et al.*, 2014a,b). The reinforcement of nanocomposite with polymers is responsible for the improved mechanical and metallurgical properties (D'Alvise *et al.*, 2002). The friction stir welding (FSW) process overcomes problem of void formation caused during FW. FSW requires a shoulder that is protruded with a pin called a probe. The shoulder arrangement creates the frictional heating and the pin probe facilitates stirring to the joint interface (Mohanty *et al.*, 2013). The FSW tool is one of the most important parts for success of the process. The tool consists of a rotary round shoulder and a threaded type of cylindrical pin (Thomas *et al.*, 1995; Dawes and Thomas, 1996; Nicholas and Thomas, 1998; Thomas *et al.*, 1999, 2003). Although prominent efforts have been made in previous years to develop economic and reusable tools, most of the attempts have been empirical in nature and further work is needed for refinement in tool geometry to modify the practice of FSW to hard metals and alloys (Rai *et al.*, 2011).

The reported studies for welding of dissimilar thermoplastic materials are limited with the use of different process variables and material variations. Some studies have reported the use of nanoparticulate for enhancing the joining compatibility of two different thermoplastic materials. Some authors have also reported the feasible joint formation after maintaining the MFI. The joints were subjected to tensile, flexural, and morphological analysis to investigate the influences of process parameters (Kumar *et al.*, 2019). However, no work has yet been reported on statistical analysis of the joints prepared by FSW process for batch production activities. The present work is an extension of work reported by Kumar *et al.* (2019) in which the FSW process has been employed for joining of ABS-15%Al with nylon6-50%Al from a statistical quality control (SQC) viewpoint.

Experimentation

Based upon the suggested methodology the ABS (Grade- EX58) and nylon6 (Grade- PX99848) thermoplastics along with Al metal powder have been selected for experimentation purposes (Kumar *et al.*, 2019). The mechanical mixing of thermoplastic with metal powder has been performed for uniform dispersion of metals into thermoplastic matrix. Further MFI of ABS with 15% Al content and nylon6 with 50% Al content were observed as 11.57 g/10 min and 11.97 g/10 min, respectively. So based upon similarity in MFI, ABS-15%Al and nylon6-50%Al have been considered as the final composition for further experiments. Twin screw extrusion and fused deposition modeling, as suggested in previous studies, were used for preparations of 60 × 60 × 4 mm sheets of ABS-15%Al and nylon6-50%Al (Kumar *et al.*, 2019). Fig. 1 shows the detailed procedure for the present experimental study.

Further the FSW of dissimilar sheets has been performed by using a nonconsumable pin profile of mild steel (see Fig. 2).

It has been reported that maximum joint strength in welding of ABS-15Al and PA6-50%Al was achieved at 1400 rpm rotational speed, 3 mm plunge depth, and 50 mm/min transverse speed (Kumar *et al.*, 2019). For establishing the proposed settings as industrial standards, the experiments were repeated at the proposed settings followed by SQC analysis (see Table 1).

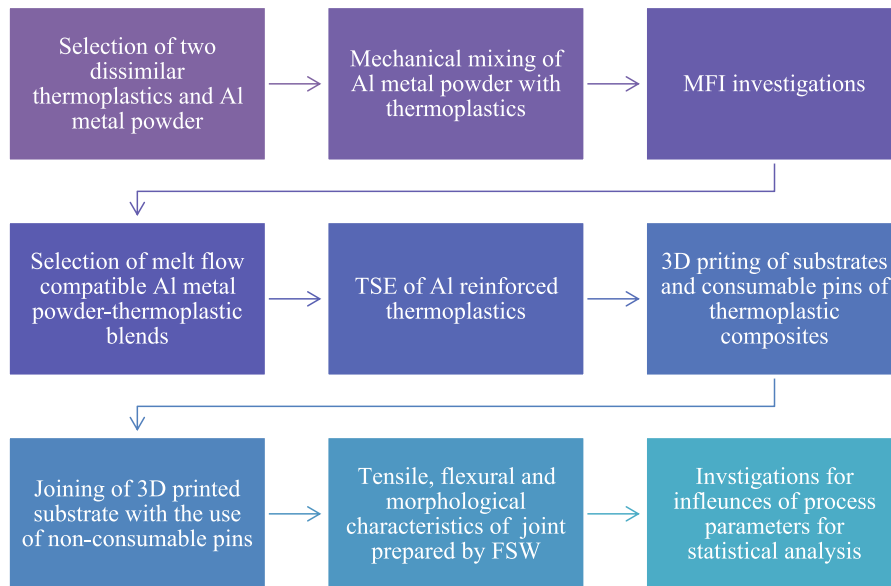


Fig. 1 Steps involved for joining of dissimilar thermoplastic materials.

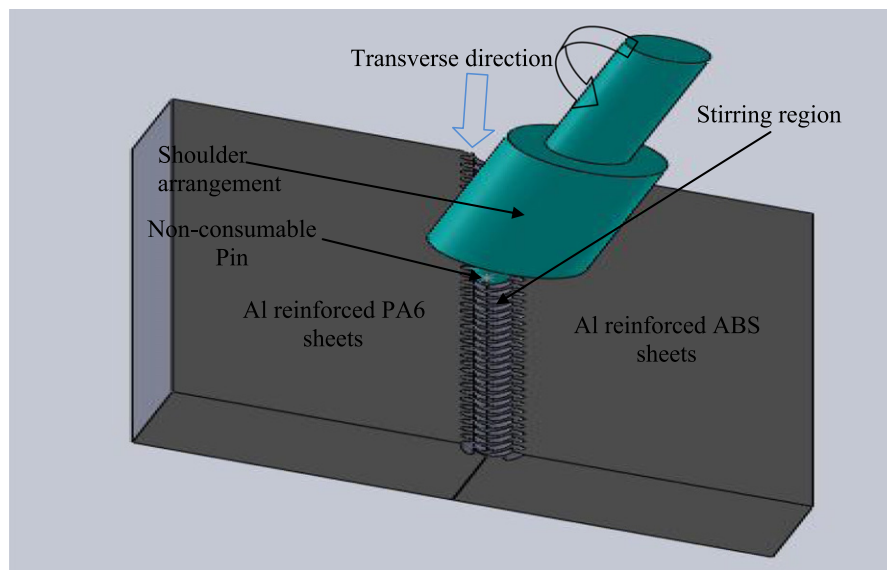


Fig. 2 Friction stir welding process for dissimilar thermoplastic joining. Reproduced from Kumar, R., Singh, R., Ahuja, I.P.S., 2019. Friction stir welding of ABS-15Al sheets by introducing compatible semi-consumable shoulder-less pin of PA6-50Al. Measurement 131, 461–472.

Table 1 Observed value of mechanical properties at 1400 rpm, 3 mm plunge depth, and 50 mm/min transverse speed

Experiment no.	Peak tensile load (N)	Peak flexural load (N)	Shore D hardness
1	529.1	360.4	81.0
2	528.9	360.1	81.0
3	528.8	360.7	81.5
4	529.4	359.9	81.3
5	528.5	360.9	81.2
6	528.8	360.4	81.5

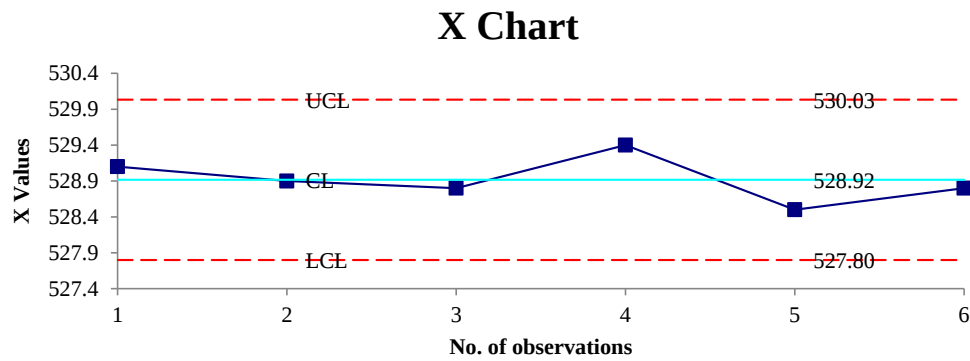


Fig. 3 X chart for peak tensile load.

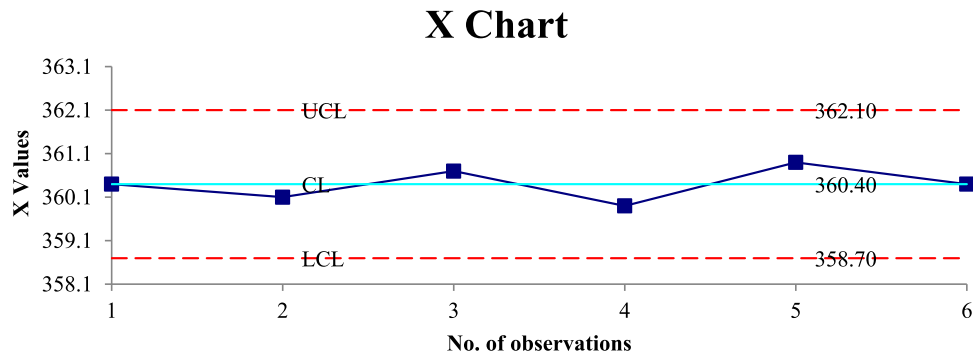


Fig. 4 X chart for peak flexural load.

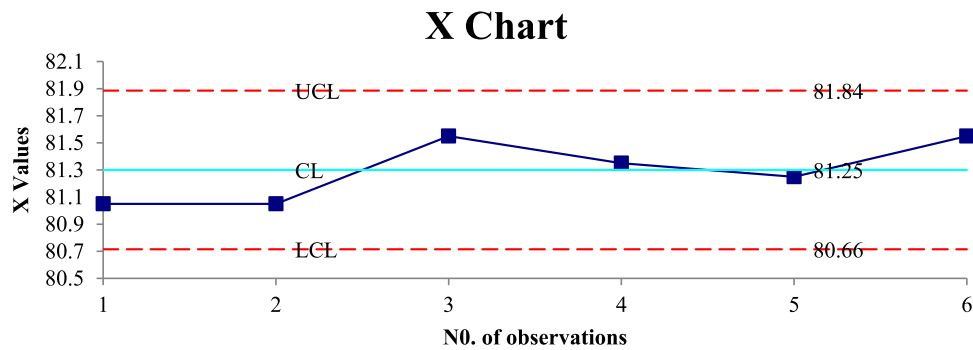


Fig. 5 X chart for shore D hardness.

Discussion

Based upon observations in [Table 1](#), X chart for peak tensile load, peak flexural load, and shore D hardness were plotted ([Figs. 3–5](#)).

As observed from [Figs. 3–5](#) the output parameters (tensile load, flexural load at peak, and shore hardness) are within the upper control limit and lower control limit, which have been judiciously selected based upon industrial applications. Since in the previous reported studies these output parameters have been maximized based upon analysis of variance data ([Kumar et al., 2019](#)), the 06 repetitions were made for SQC analysis. Further based upon [Table 1](#), process capability histogram and normal probability plot were drawn ([Figs. 6 and 7](#)) and Cp and Cpk values were computed ([Table 2](#)).

As shown in [Figs. 6 and 7](#) a well-defined bell-shaped curve with controlled deviation from mean value was observed. Further as shown in [Table 2](#), Cp and Cpk values are quite close to 1, thus ascertaining this process to be statistically controlled.

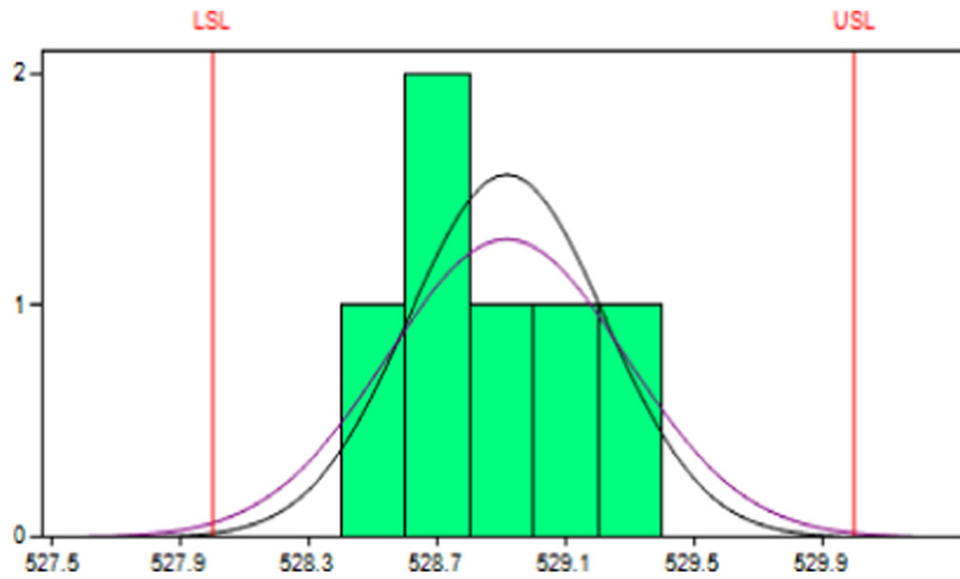


Fig. 6 Process capability histogram.

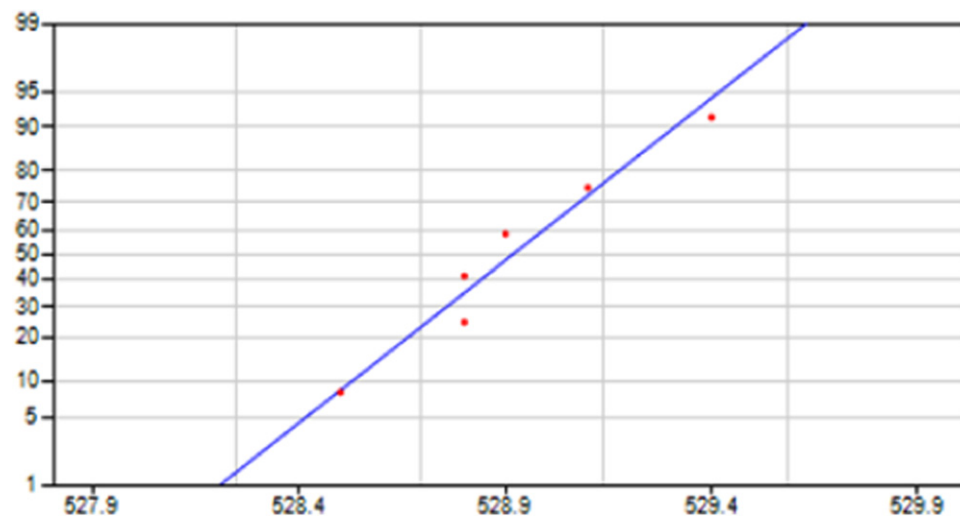


Fig. 7 Normal probability plot.

Table 2 Statistical quality control analysis

Readings	6	Subgroup size	1
Tolerance range		Data range	
USL	530	Maximum	529.4
Target	NA	Average (X-Bar)	528.917
LSL	528	Minimum	528.5
Tolerance	2	Data range	0.9
p value	0.6354	Kurtosis	0.629
Potential Capability		Overall capability	
Std. deviation	0.372340	Std. deviation	0.306050
Cp	0.895	Pp	1.089
Cpk	0.821	Ppk	0.998

Abbreviations: LSL: lower specification limit; USL: upper specification limit.

Summary

In the present study SQC analysis on a novel route for joining the dissimilar thermoplastic based composite materials by FSW for batch production has been reported. The X chart, Cp and Cpk values near to 1 ascertain that the proposed settings for this novel route are under statistical control and may be fixed as industrial standard for future references.

Acknowledgment

The authors are highly thankful to Board of Research in Nuclear Science (BRNS) No: 34/14/10/2016-BRNS/34036 and Center for Manufacturing Research, GNDEC, Ludhiana for providing financial/technical assistance.

See also: Experimental Investigations for Friction Stir Welded 3D Printed Dissimilar Thermoplastics With Consumable Tool. Joining of 3D Printed Dissimilar Thermoplastics With Consumable Tool Through Friction Stir Spot Welding: A Case Study. Joining of 3D Printed Dissimilar Thermoplastics With Friction Welding: A Case Study

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Mechanical and Transmissibility Effect on Recyclable Suspension System for Different Loading of Carbon Black

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Introduction

Recently, the invention of synthetic rubbers is initiated to overcome the dependencies on the natural rubber due to the high demands of the rubber supplies. Consequently, it affects the demands of the natural rubber since the synthetic rubber offers better resistance to oils, temperature, and chemicals. Nevertheless, with specific compounding formulation, fillers additions and accurate manufacturing process enable the natural rubber to be continuously used in various applications such as vibration isolator and suspension system. The addition of fillers in the natural rubber compound can highly affect the properties and strength of the compounds, depending on the fillers types, sizes, and loading. Aside from that, it is also found that most of the projects in Malaysia prefer to use the imported rubber instead of the locally manufactured rubber, although it possesses comparable qualities.

On the other hand, based on previous research, it was found that the development of the suspension system for automotive mounting application is currently in trend (Salim *et al.*, 2013, 2014). Therefore, in this article, the application of Malaysian natural rubber, which is the vulcanized standard Malaysian rubber constant viscosity 60 (SMR CV-60) reinforced with carbon black (CB) as the potential main material is combined with the metal plate for the development of recyclable suspension system for different loading has become the interest. This article focuses on the investigation of the vulcanized SMR CV-60 mechanical properties through the transmissibility effect.

The development of recyclable suspension system for high-frequency protection application becomes the current research interest. Therefore, many agencies have taken an initiative to optimize the usage of local grade natural rubber instead of imported rubbers in the development of the suspension system by introducing SMR CV-60 as the main substance. Thus, in this article, the theories and the advantages of SMR CV-60 and ENR 25 are described. The importance of compounding ingredients and processing method in rubber compound are also explained. Besides that, the influence of carbon black in the natural rubber compound properties is also presented. The theories of transmissibility also literally presented in this article. Last but not least, the basic concept of the vibration isolation system, history and recent studies on the suspension system are also included to prove the effectiveness of natural rubber as the main substance of recyclable suspension system.

Carbon Black in Natural Rubbers

Nowadays, most of the rubber products used by customers especially in the anti-vibrating applications are reinforced with fillers. Different kind of fillers are available, however, only two types of fillers are known to reinforce rubber effectively, which are the CB and silica (Zhang *et al.*, 2001; Gent, 2012). Being easily available and inexpensive, both fillers are known to excellently improve the mechanical properties of the natural rubber in terms of tensile strength, elastic modulus, hardness, and hysteresis (Donnet, 2003). However, carbon black is frequently used as a filler in industrial applications as it is available in various sizes and easier to be produced. The effectiveness of carbon black over the other type of fillers as the reinforcing filler in the natural rubber compound has been proved through several studies (Ismail and Suryadiansyah, 2004; Ahmad *et al.*, 2016; Brum *et al.*, 2018).

In practical, the natural rubber is reinforced with carbon black for the purpose of providing extra strength for both raw and vulcanized rubbers at low manufacturing cost and at the same time to improve the rubber manufacturing process. The effect of carbon black in the natural rubber compound is highly depended on the chemical and physical interactions between the rubber matrix and fillers molecules. There are several factors that influence the interaction between the rubbers and carbon black molecules; the specific surface area, surface structure, particle size, and lastly the number of fillers loading.

The specific surface area and surface structure of carbon black influence the determination of rubber matrix chains and fillers entanglement level (Fröhlich *et al.*, 2005). The specific surface area of the carbon black is determined through its ability to absorb the cetyltrimethyl ammonium bromide (CTAB) in aqueous solution, as described in ASTM 3765. The CTAB unit is m^2/g . Filler with higher surface area, N472 for example, usually gives better reinforcement performance by having more available contact area to be bonded with rubber particles. On the other hand, the surface structure of carbon black is measured through the bulkiness of the carbon black aggregates and characterized by using its dibutylphthalate absorption number (DBPA) with the unit of $\text{cm}^3/100 \text{ g}$. Further explanation of the surface structure test method has been described in ASTM 2414. The bigger the carbon black aggregates, then the higher the carbon black structure. High carbon black structure increases the opportunity for carbon black to reinforce with rubber particle.

An investigation on the influence of carbon black structure towards the properties of the natural rubber compound by using FTIR and H-NMR has been conducted by Salaeh and Nakason (2012). Two types of carbon black with different

Table 1 List of N-type CB particle size

<i>N-type CB</i>	<i>Particle size, nm (according to ASTM)</i>
N100–N199	11–19
N200–N299	20–25
N300–N399	26–30
N400–N499	31–39
N500–N599	40–48
N600–N699	49–60
N700–N799	61–100
N800–N899	101–200
N900–N999	201–500

structure and surface are used: the high-abrasion furnace (HAF) and extra conductive furnace (ECF). Throughout the FTIR and H-NMR results, it is found that natural rubber with ECF-type CB exhibits good cure characteristics and mechanical properties which are Young's Modulus and hardness, respectively. Wide surface area and large surface structure in ECF encourage the entanglement between the rubber chain and carbon black molecule, increase the resistance of natural rubber compound towards the applied load. Meanwhile, in a study of material properties and fatigue life of natural rubber reinforced with different size of N-type of carbon black (N330, N990, N650), [Kim and Jeong \(2005\)](#) had found that natural rubber with N330 carbon black exhibited the highest hysteresis, small-scale roughness, and fatigue life cycle. The enhancement of natural rubber properties and fatigue life cycle is because of N330 has the largest specific surface area and surface structure as compared to N990 and N650. It causes the friction between rubber and carbon black particle to increase during the application of load, resulting the high hysteresis.

The next factor is the carbon particle size, which also influences the properties of the natural rubber compound. Particle with planar size (clay for example) has more contact probability with the rubber chain rather than the spherical size particle at similar average particle sizes such as carbon black and calcium carbonate. However, the smaller size of spherical size particle also gives better reinforcement performance as it appears as anisometric aggregates in per unit weight, which is small enough to make contact with the rubber chain. In contrast to the specific surface area factor, the reinforcing effects become more efficient as the particle size decreases; which the effective carbon particle sizes range from 20 nm to 50 nm ([Fröhlich et al., 2005](#)). Large particle size may contribute to the failure of rubber compound under the large stress such as stretching and flexing, especially when the particle size surpasses the inter-chain distance in the polymer itself. Smaller carbon particle also disperses evenly in rubber and agglomerates at moderate size, which is an additional factor for great rubber performance. [Rattanasom and Prasertsri \(2009\)](#) observed the effect of partial replacement of clay with three different grades of CB (N330, N550, and N774) on the vulcanized the natural rubber at similar hardness level. The authors found that the vulcanized natural rubber with N330 exhibited the highest edge-cut tensile strength, highest tensile and tear strength, and possessed the lowest resilient compared to the others. Notably, this occurrence is due to the great interaction between filler and rubber matrix, which resulting from good filler dispersion. The rubber chain is strongly linked on the carbon black surface, providing a good orientation of natural rubber chain along the applied force, thus gives more strength to the vulcanized natural rubber. The particle size of N-type carbon black (N is referring to the normal curing) ranges from semi reinforced to the highly reinforced is presented in [Table 1](#).

The last factor that influences the reinforcement of carbon black in natural rubber compound is the carbon loading. The high-performance polymer composite usually contains 50%–80% reinforcement particle by volume. The increase of carbon loading causes the inter-aggregate gap to become smaller, thus allowing the probability of rubber matrix filler network formation. [Ismail and Suryadiansyah \(2004\)](#) in their study on the effect of the carbon black loading (range from 0 to 30 wt%) in the polypropylene-natural rubber-recycle rubber composites had discovered the increase of stabilization torque value, tensile strength, and Young's Modulus in the composites with the increase of the carbon black loading. In addition, [Sangwichien et al. \(2008\)](#) in their study regarding the effect of various carbon black loading (ranged from 0 to 50 phr) on natural rubber or polypropylene composites also proved that the tensile strength increased as the carbon black loading was increased.

The carbon black used in this study was N330 carbon black, which was known to have good surface activity and chemical properties, which influenced the good interface interaction between the rubber chain and carbon black particle. However, the tensile strength value of the composites was found to slightly decrease for the compound with 50 phr of the carbon black. The excessive fillers content affected the processing characteristics and also the rubber compound crosslinking properties. As the carbon content was extended to a significant amount, the mechanical properties started to drop, which was attributed to the increase of viscosity in the matrix and in turn the increase in porosity and decrease in the wettability of the composites. The study also proved that the addition of the carbon black loading increased the hardness and reduced the tear strength, cure time and resilience values as well. In other research, [Fairuz et al. \(2016\)](#) also agreed that the increasing amount of filler loading will increase the tensile and flexural properties of the pultruded composites in terms of strength and stiffness. A study on the effect of clay loading on the natural rubber composite, conducted by [Mohd Nor and Othman \(2016\)](#) also agreed that the increase in filler loading will increase the curing characteristic and tensile properties in natural rubber composites.

Mechanical Testing for Rubbery Materials

Elastomer test is conducted to yield engineering design and quality control data for rubber compound. In mechanical testing for rubber compound, there are three classes of rate test procedure, which are the static test, dynamic test and quasi-static test methods. Besides, there are three types of testing within the three classes of rate test procedure, which are the tensile, compression and bending tests. Since this studies is only focusing on tensile and compression tests, only these two tests will be further discussed. The loading parameters to describe the elastomer behavior under mechanical loading are normally explained in term of stress and strain. Stress is defined as the force that acting on per unit area. The stress unit is often written in Pascal (Pa). The strain can be defined as the change in the dimension per unit length. The strain has no dimension. However, it can be written in cm/cm or mm/mm or in any equivalent dimension to measure the specimen length.

Tensile Test of Natural Rubber

Tensile test is considered as the fundamental test in mechanical testing. Even though it is hard to find the natural rubber application that involves the extension, but tensile properties are the most seek properties of the natural rubber compound after the hardness. The purpose of conducting this test is to ensure the quality of rubber compound for each production, in which occurs due to problems related to ingredients dispersion and insufficient vulcanization in compounds especially when reinforced with carbon black fillers (Dick, 2003). Besides that, the tensile properties are also used as the general measure to prove the rubber compound quality as the main substance in multiple applications (Sommer and Yeoh, 2012). Another advantage of the tensile test is several parameters can be obtained from a single test which is the stress, strain and modulus at specific elongation (normally at 100%, 300% and elongation at break).

Tensile test and properties are conducted and measured based on the guideline as stated in ASTM D412, which is the tensile test method for vulcanized thermosets rubbers and thermoplastic elastomers. This standard is referred for two different test methods: method A is for dumbbell and straight specimen and method B is for cut ring specimens. The specific shapes and sizes are also provided and can be chosen based on materials application.

Through the tensile test, there are several patterns of stress-strain curves that can be observed depending on the types of materials and the reinforcing fillers; as presented in Fig. 1. The curve in (a) exhibits a linear behavior starting from initial loading until rupture. It normally represents for brittle materials. Examples of brittle materials are ceramic, glass, and cast iron. Meanwhile, the nonlinear curves in b, c, & d represent the ductile materials with yield points (b & c) and without yield point (d). Examples of ductile materials are aluminum alloys, copper, mild steel and other metals. Unlike the other typical stress-strain curve, the elastomeric stress-strain curve as in (e) exhibits for a nonlinear "S" line with low stress and modulus at very high strains.

Several findings on the tensile test that had been conducted by previous researchers to determine the mechanical properties of rubbers at different types of fillers and loading were summarized in Table 2.

Compression Test on Natural Rubber

Compression test is used to determine the stress-strain behavior of materials under compressive loads. As compared to other tests of determining mechanical properties under axial loadings such as tensile and hardness tests, the compression test does not attain

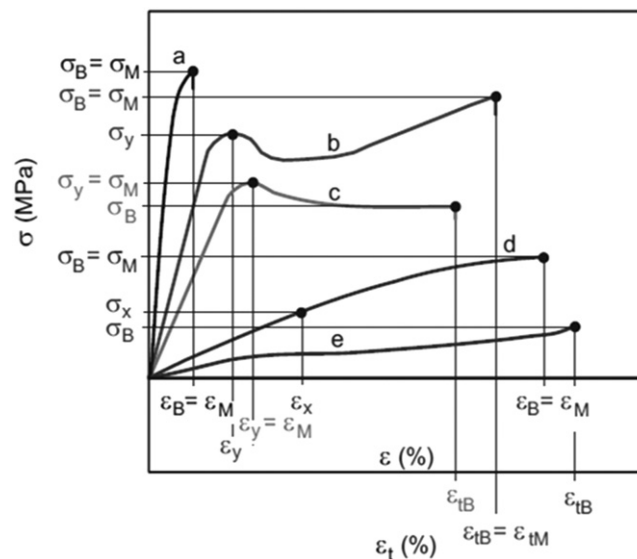


Fig. 1 Stress-strain diagrams for different materials parameters.

Table 2 The current findings from the other researchers for the tensile test

Matrix	Blend ratio	Fillers	Loading (phr)	Tensile properties			Authors
				Tensile strength (MPa)	Elongation at break (%)	Tensile modulus, at 300% (MPa)	
NR (RSS5)	–	Semi efficient PBT-H modified kaolin	6	22.8	710	2.4	Sreelekshmi <i>et al.</i> (2017)
SMR L/NBRr	95/5	CB (N330)	30	19.00	610	6.40	Ahmad <i>et al.</i> (2016)
ENR 50/NBRr	95/5	CB (N330)	30	21.00	650	7.50	
SMR 20	–	Clay	4	21.45	938.33	2.31	Mohd Nor and Othman (2016)
NR Latex	–	Kenaf powder	1	0.43	0.60	–	Karim <i>et al.</i> (2016)
PVC/ENR50	70/30	Kenaf powder	10	4.9	170	8.00	Majid <i>et al.</i> (2014)
PP/ENR50	90/10	Mah-PP	15	31.00	415	–	Mohamad <i>et al.</i> (2013)
ENR 25	–	HAF (N330)	50	25.52	530	6.03	Salaeh and Nakason (2012)
ENR 50	–			25.43	494	7.56	
MNR	–			14.34	325	5.86	
PCL/SMR CV-60	90/10	–	–	30.00	360	10.00	Wan <i>et al.</i> (2010)
SMR CV-60	–	CB (N220)	20	29.20	–	–	Azura <i>et al.</i> (2008)

the equivalence signification due to the relative irrelevance between the testing data and actual application measurement of the materials. Thus, the compression test is limited to the following applications; building construction, vibration isolation, fluid seal, suspension system and packaging.

In polymer, there are three ways that are usually considered in determining the compressibility in rubber compounds. Horgan and Murphy, 2009 classified compression test into three; which were the simple compression, volumetric, and hydrostatic compression tests. Simple compression was conducted by placing the cylindrical rubber between the compression platens unbounded, under compressive load. Meanwhile, the volumetric compression was conducted as the simple compression, somehow with rigid annulus. The rigid annulus was referred to the contact surface diameter of the rubber specimen with the unchanged platens while compressed. The hydrostatic compression test, which was also called as pure dilatation test involved a hydrostatic compression of the rubber samples.

As the compression test discloses the dependency of the materials under pressure, there are several things that might affect the compression test results. First is the ratio of the height to diameter of the specimen. High ratio value causes the buckling effect while low ratio value increases the friction rate between the specimen and compression plates. The ideal ratio is between 2 and 2.5 (Tscharnuter *et al.*, 2012). Secondly is the presence of friction between the sample and metal platen surface when the axial force is applied. The presence of friction restrains the rubber from expanding in a lateral direction under compressive force. Horgan and Murphy (2009) stated that the friction was unavoidable and could not be eliminated with the application of the lubrication. The authors also mentioned that even the smallest friction could significantly affect the measured stiffness and compression results either at low or high strain. Due to these factors, all compression results are measured by assuming zero friction and the compression data needs to be conducted with high precaution in order to minimize the friction effect.

According to the ASTM testing standard, there are two types of test method to measure the properties of NR under compression. First is the ASTM 395, which is the test method for the rubber that is subjected to the compressive stress in air or liquid. The significance of this test method is to measure the ability of the rubber to retain its elastics properties in response to the compressive stress. This test is also called as compression set test, which is frequently conducted under the influence of elevated temperature. This standard offers two options of the testing method, either by conducting the compression test under constant force or constant deflection. Secondly is the ASTM D575, which is the standard test method to measure the properties of rubber compound. This test method also offers two options of test method, which are the compression test of specified deflection or specified force. Both methods can be used to determine the compression-deflection and comparing the stiffness in the rubber compound.

A typical simple compression force-deflection curve that exhibits the loading and unloading phase is showed in Fig. 2. In compression properties measurement, the modulus of deformation can be derived from the compressive stress-strain curve (Auvray *et al.*, 2017). All findings that were related to the simple compression test that had been conducted by the previous researchers are presented in the Table 3.

Recyclable Suspension System Theory

Suspension system is installed in most of mega-structures such as high-rise buildings, nuclear reactor plants, bridges, and offshore jacket platform. The main purpose is to reduce the excessive vibration transmission from the sources of excitation from the base to the bodies or vice versa. A simple suspension system concept can be presented in a form of lumped element system, as shown in Fig. 3. The system consists of the mass, M , the isolation system (a spring, k and a damper, C) and the foundation. Basically, the

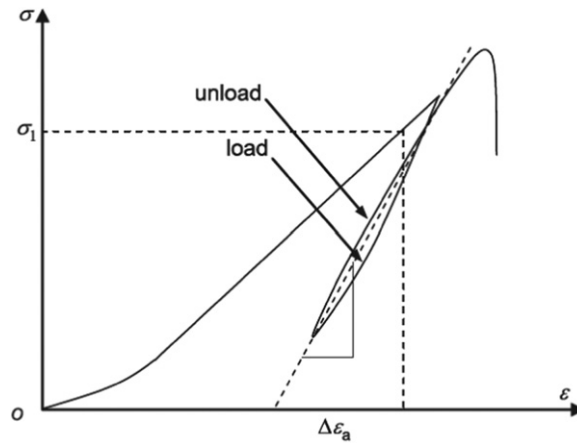


Fig. 2 The typical simple compression stress-strain curve.

Table 3 The current findings from the other researchers for the simple compression

Matrix	Blend ratio	Fillers	Loading (phr)	Compression properties			Authors
				Compression strength (MPa)	Deflection (%)	Compressive modulus (MPa)	
Toarcian claystone	–	–	–	–	–	35,000	Auvray <i>et al.</i> (2017)
Polyurea	–	–	–	27.5	80	270	Bai <i>et al.</i> (2016)
NR/BR	10/90	Black smoke	20	0.26	–	–	Arguello and Santos (2016)
NR/SBR	10/90			0.34	–	–	
NR/EPDM	10/90			0.39	–	–	
Pultruded kenaf	–	CaCO ₃	40	85	–	–	Fairuz <i>et al.</i> (2016)
PDMS/curing agent	5/1	–	–	–	–	3.7	Wang <i>et al.</i> (2014)
NR	–	N330	18	–	–	5.34	Omnès <i>et al.</i> (2008)
		N650	18	–	–	4.59	
SRM 385	–	Dicumyl peroxide	5	–	–	3.66	McKenna and Zapas (1983)

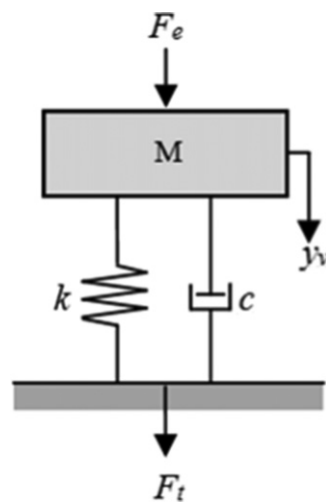


Fig. 3 Lumped parameter model for suspension system.

suspension system that consists of a spring and a damper act as an absorber to stop the oscillation in the system. It is located in between the source of excitation force, F_e , and the protected body. This system acts by weakening the transmitted vibration that larger than the excitation frequency, thus reducing the transmitted force, F_t to the protected body.

The lumped parameter model as shown above can be mathematically explained by using the equation of motion for a single degree of freedom system. There are several assumptions that is taken into consideration while deriving the equation: the mass of the block is negligible, only the vertical force is considered in the derivation and the force is assumed to be applied at a constant speed. Thus the general form of the equation of motion for the suspension system is derived in Eq. (1) as follows;

$$F_e(t) = M\ddot{y} + c\dot{y} + ky \quad (1)$$

where F , M , c , and k are the force, mass, viscous damping and stiffness matrices.

Meanwhile, the equation of the harmonic motion is written as Eq. (2) and derived into Eqs. (3), and (4), respectively.

$$y = Y_e^{j\omega t} \quad (2)$$

$$\dot{y} = j\omega Y_e^{j\omega t} \quad (3)$$

$$\ddot{y} = -\omega^2 Y_e^{j\omega t} \quad (4)$$

where Y is the amplitude and ω is the frequency.

Since the motion of the suspension system is assumed to be harmonic, the harmonic motion in Eqs. (2), (3) and (4) can be substituted into the equation of motion in Eq. (1). In general form, the equation is written as in Eq. (5) and simplified into Eq. (6).

$$F_e^{j\omega t} = M(-\omega^2 Y_e^{j\omega t}) + c(j\omega Y_e^{j\omega t}) + k(Y_e^{j\omega t}) \quad (5)$$

$$Y = \frac{F_e}{-\omega^2 M + \omega jc + k} \quad (6)$$

Thus, the excitation force equation is written by rearranging the Eq. (6) into Eq. (7).

$$F_e = Y(-\omega^2 M + \omega jc + k) \quad (7)$$

On the other hand, the equation of motion and the harmonic motion equation for the transmitted force to the foundation are derived as in Eqs. (8) and (9), which are

$$F_t(t) = c\dot{y} + ky \quad (8)$$

$$F_t = Y(\omega jc + k) \quad (9)$$

The performance of the vibration isolator is highly influenced by its characteristics and evaluated through the ratio of the transmitted force to the excitation force (F_t / F_e) that is known as transmissibility, TR . Measured in decibels units (dB) and assumed to be in the single degree of freedom, the transmissibility can be expressed in term of the differential equation of motion as in Eq. (10), which is

$$TR = \frac{F_t}{F_e} = \sqrt{\frac{1 + (2\xi r)^2}{(1-r^2)^2 + 2(\xi r)^2}} \quad (10)$$

where ξ is the damping ratio and r is the frequency ratio. The damping ratio and the frequency ratio are written as Eq. in (11) and (12), respectively.

$$\xi = \frac{c}{C_c} = \frac{c}{2M\omega_n} \quad (11)$$

$$r = \frac{\omega}{\omega_n} \quad (12)$$

where ω_n is the natural frequency of the suspension system and C_c is the critical damping. The natural frequency of the system can be calculated by using the Eq. (13) below.

$$\omega_n = \sqrt{\frac{k}{M}} \quad (13)$$

Fig. 4 shows the transmissibility curve in a system with different damping values. Based on the figure, it shows that the suspension system is acquired when frequency ratio is larger than 1.4 and the transmissibility increases with the increase of damping value. It is also found that the transmissibility peak reduces as the damping value is increased. In overall, it exposes of poor isolation at high frequency. Under those circumstances, it can be concluded that an ideal suspension system must possess:

- (1) Low natural frequency than the excitation frequency for effective suspension system due to isolation.
- (2) Low transmissibility in the amplification phase.
- (3) Rapid decrease of transmissibility at the frequency higher than natural frequency.

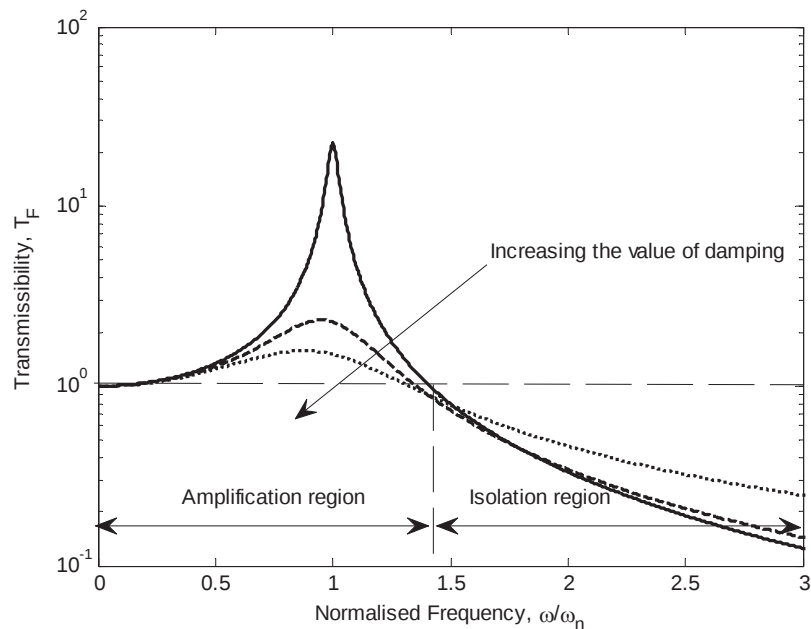


Fig. 4 The curve of transmissibility with different damping values.

Conclusion

This article elaborated mechanical and transmissibility effect on recyclable suspension system for different loading of carbon black. Some conclusion can be made which are the effectiveness of suspension system is based on the low natural frequency due to the isolation performance. Secondly, low transmissibility effect is only happening at amplification phase compare to the isolation region, and finally the transmissibility will drop when the frequency is increased.

See also: Application of Nanofluids for Radiator Cooling

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Natural Oils as Green Lubricants in Forming Processes

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Introduction

Animal and plant based oils have been used as a lubrication a long time ago. The petroleum discovery and following improvements in the technologies of refining replaced the oil based lubricant to the mineral oil based ones which is considered as an environmental pollutant. The total world energy consumption is estimated to be increased by about 33% during the period of 2010–2030, [Saidur et al. \(2011\)](#). The increasing global awareness of the health and environmental burdens connected using metal cutting fluids (mineral-based) in machining operations is forcing scientists and industrialists to seek for the development of new alternative, sustainable and environmentally friendly options such as nanoparticle suspended in vegetable oil. The characteristics of vegetable oils on respect of biodegradable, renewable and non-toxic make it the primary alternative for environmentally aspects. In addition to the wide range of its lubricant applications ranging from grease to hydraulic oils. The low thermal conductivity of cutting fluids necessitates that nanoparticles of carbide, oxide, non-metals, metal nitrides and Carbon Nano Tubes (CNT) are introduced into cutting fluids which increases the thermal conductivity of cutting fluids.

The employment of lubricants in metal forming processes provides desirable tribological conditions at the interface between tool and workpiece. Furthermore, it is important to increase the formability of material, increasing the tool life and reducing the energy consumption. The hazardous effects of mineral based lubricants led to more awareness and concerns towards the substantial a step forward replacing them with environmental friendly lubricant. The heat transfer coefficient subjected to lubricant is affected by various parameters, such as heat flux, mass flux, oil concentration, vapor quality, saturation temperature geometric configuration, transport properties and thermodynamic. The heat transfer performance could be increased or decreased by using lubricant depending on the oil concentration, surface tension and geometry. In general, the presence of lubricant in metal forming processes will decrease the heat transfer performance as a results of oil film deposition, [Wang et al. \(2012\)](#). Biodiesel industries is expected to rapidly grow worldwide in the coming years and information on biodiesel production, feedstock, and characteristics will be crucial than ever, [Issariyakul and Dalai \(2014\)](#).

The vegetable oils have performed satisfactorily in metal working applications and have shown promising performance as engine oils and greases. From survey, the selection of lubricant to be used in such application is based on price, performance, and then the environmental consideration. The selection would change either by reducing the cost of the biodiesel or with the legislative pressure to restrict using of petroleum based products, [Mannekote et al. \(2018\)](#). **Fig. 1.** shows the different lubricant state and their working temperature ranges, [Syahir et al. \(2017\)](#).

Forming Processes

Manufacturing processes consist of many types such as forming, machining, casting and non-conventional methods. Forming is a process that uses suitable stresses causing material plastic deformation to produce certain shapes. Metal is the main material used in forming processes. However, plastic can be formed too as a request for plastic based products market. The main forming processes methods are, Forging, Rolling Extrusion, Sheet metal working, Thread rolling Rotary swaging, Electromagnetic forming and Explosive forming. **Fig. 2** shows some examples of forming processes, [Hashmi \(2014\)](#).

Palm pressed fiber (PPF) is the biomass waste produced at the palm oil production. PPF oil is a promising source of lubricant. Researcher investigated PPF using pyrolysis experiments and estimate the functional and yield properties of the produced oil. The obtained PPF oil through pyrolysis process need to be tested as a lubricant by comparison with palm olein (PO). The test of lubricate used one of the metal forming processes which is the cold work drawing. During the metal forming process test, the utilize of PPF perform effectively as lubricants PO, [Hafis et al. \(2013\)](#). **Fig. 2** shows the decrees of tool die angle with the decrees of the forming load as a results die geometry and opening ratio of die-to-die. **Fig. 3** shows the different products yield (gaseous, oil and char) from exposing PPF at temperature of 450°C. The results show that the PPF oil product yields are relatively high values with the right temperature set during pyrolysis process, [Hafis et al. \(2013\)](#).

Friction Coefficient Estimation

A tribometer is a measurement instrument of tribological parameters, such as friction force, coefficient of friction and wear volume, between two contacting surfaces as in **Fig. 4**. The tribometer was used to measure the wear and friction at ambient conditions to study the utilize of phosphonium and imidazolium-based Lubricants. The ITeE-PIB Polish method for testing lubricants under deterioration conditions was setup with a four-ball tribotester to evaluate the deterioration load and capacity of load-carrying (poz) at extreme pressures (EP). The technique has confirmed to be sensitive to extreme-pressure additives. The

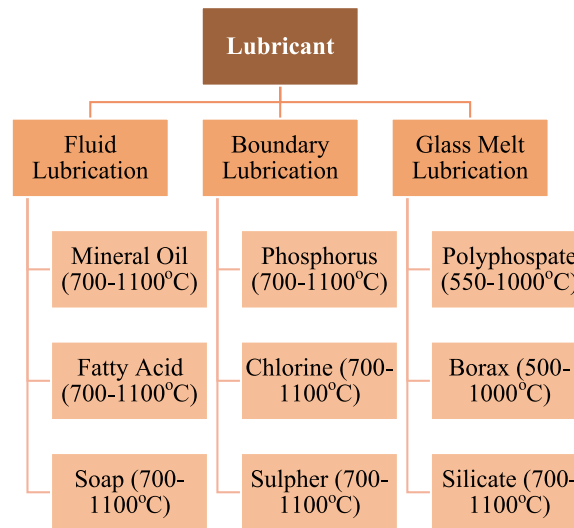


Fig. 1 Different lubricant state and theirs working temperature ranges. Reproduced from Wan, S., Tieu, A.K., Xia, Y., *et al.*, 2016. An overview of inorganic polymer as potential lubricant additive for high temperature tribology. *Tribol. Int.* 102, 620–635.

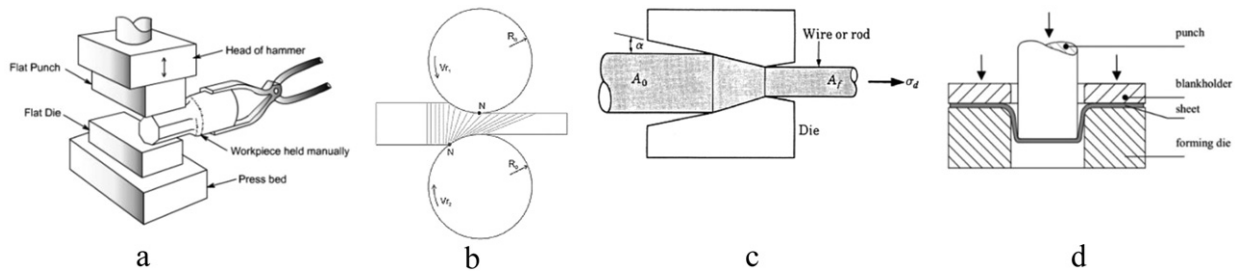


Fig. 2 Examples of forming processes, (a) Forging, (b) Rolling, (c) Rolling and (d) Sheet-metal Forming. Reproduced from Hashmi, S., 2014. *Comprehensive Materials Processing*. Newnes.

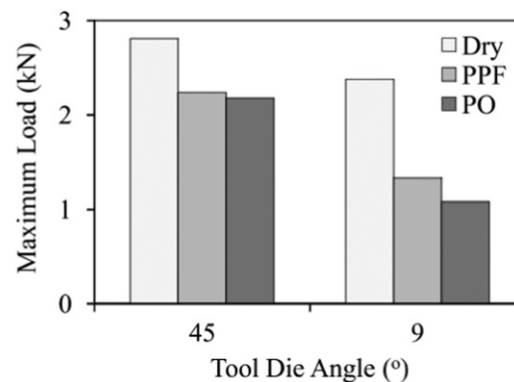


Fig. 3 Maximum load verses tool die angles of 45° and 90° for the contact surfaces of dry, palm pressed fiber PPF lubricated oil and palm olein PO. Reproduced from Hafis, S.M., Ridzuan, M.J.M., Mohamed, A.R., *et al.*, 2013. Properties of palm pressed fibre for metal forming lubricant applications. *Proced. Eng.* 68, 130–137.

optical 3D-surface measurement system has been used to characterize the surface roughness of worn materials. The geometric parameters shown in Fig. 5 are used to estimate the friction coefficient through the compression tests.

The surface contact mechanics is the most influence on the viscosity level of lubricant. The higher viscosity leads to carry a higher load of the lubricant to enhance the anti-wear and antifricition ability of the interacting surfaces. Fig. 6 shows the formation of the type of Bowden-Tabor of a boundary film.

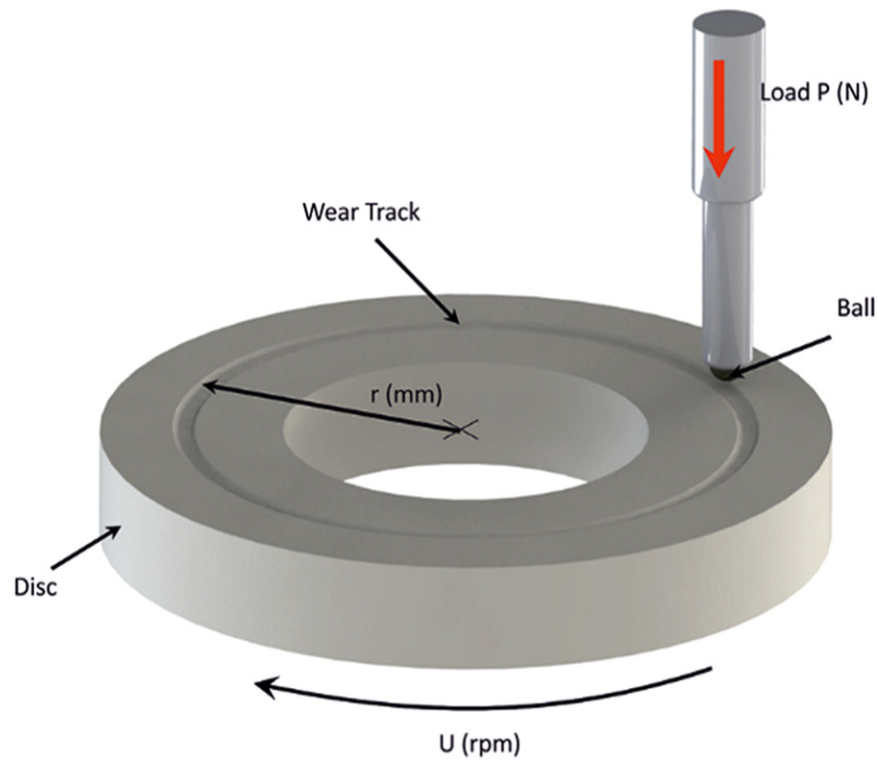


Fig. 4 Schematic of Schematically Pin-on-Disk test to ASTM G 99. Reproduced from ASTM G99-95a, 2000. Standard Test Method for Wear Testing With a Pin-on-Disk Apparatus, pp. 1–5.

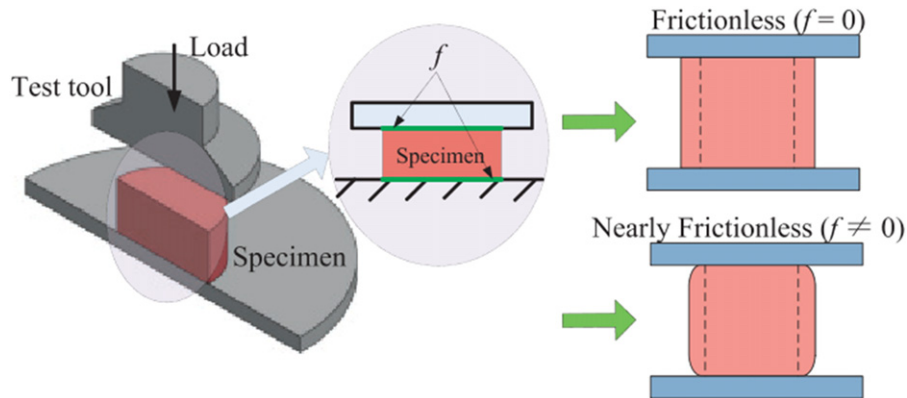


Fig. 5 Friction estimation apparatus and geometric parameters. Reproduced from Yang, J., Yu, L., Wang, L., Wang, W., Cui, J., 2018. The estimation method of friction in unconfined compression tests of liver tissue. *Proceed. Inst. Mech. Eng., Part H: J. Eng. Med.* 232 (6), 573–587.

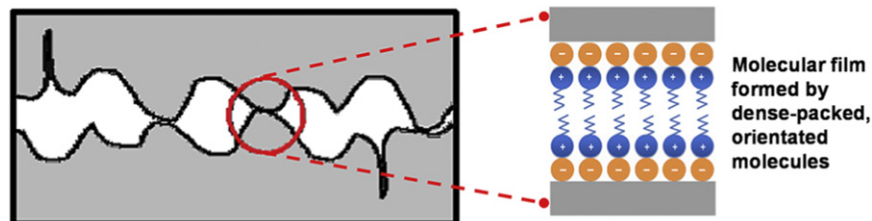


Fig. 6 The Bowden-Tabor type boundary film model. Reproduced from Amiril, S.A.S., Rahim, E.A., Syahrullail, S., 2017. A review on ionic liquids as sustainable lubricants in manufacturing and engineering: Recent research, performance, and applications *J. Clean. Prod.* 168, 1571–1589.

The multiphase lubricants and surface texture (additives in base oil) effect the wear and friction performance throughout sliding. To study the effect of multiphase lubricants which environmental friendly at the transfer layer creation throughout sliding against different surface textures. The grinding angle is influenced the coefficient of friction (COF) in addition to the transfer layer formation (TLF). The grinding angle can be minimized by utilizing an optimum concentration of additive such as graphene, [Siddaiah et al. \(2019\)](#).

One of the promising green lubricant additives are Halloysite clay nanotubes (HNTs). They are non-toxic, low-cost and naturally-occurring nanoparticles. Experimental results exhibited that 0.05 wt% HNTs delayed of deterioration initiation. Moreover, they increased the load-carrying and scuffing load endurance by $\sim 72\%$ and 50% respectively. Wear volume loss and coefficient of friction were both lowered by $\sim 70\%$, and surface roughness was decrease as result of the formation of a tribofilm. The enhanced lubrication provided by HNT lubricant additives may reduce the cost by reducing the energy consumption and increasing tool life, [Peña-Parás et al. \(2017\)](#).

Prominent Natural Oils

The degradable vegetable oil has good biodegradability, high viscosity index, non-toxicity, smaller relative change in viscosity with temperature, abundant resources and high yield. It would decrease lubricant pollution to the environment and handling cost. It has a higher molecule weight, boiling or flash point which relatedly decreases loss during gasifying and atomizing and liable to hydrolyze, [Steigerwald \(2005\)](#). The conventional metal working fluid provide fluid like "flood" in the work area then filtered and recirculated in the system.

Some studies show that a significant exudation phenomenon at 80°C for all oils tested using the bi-layers rheology technique and exudation analysis. The problem could overcome by using vegetable tung oil with specific highly reactive characteristic. The oil polymerisation by thermal activation without utilizing catalysts permitted it to avoid the exudation phenomenon by increasing oil viscosity. In contrast, the degree of exudation was greatly decreased when using pure tung oil from 8% to 1% .

In high-strength applications, there is an increasing attention to epoxidized vegetable oils (EVOs) because of their high epoxy equivalent weight (EEW). Perilla oil extracted from *Perilla frutescens* seeds (Non-edible), was used to produce sustainable green epoxy using Prilezhaev epoxidation reaction. Thermodynamic characteristics such as activation entropy, activation enthalpy and Gibbs' free energy of activation were evaluated for both oxirane ring cleavage reactions and epoxidation. All the thermodynamic characteristics were perceived to be higher for post-oxirane cleavage reaction compared to epoxidation reaction, [Bétron et al. \(2016\)](#). Fish wastes are a prominent resource of bio-lubricant. The fish waste potential for biofuel od bio-lubricant is a function of the size and location of the processing plant, characteristics of the fish waste and type of lubricant requirements, [Jayasinghe and Hawboldt \(2012\)](#).

Addition of Nanoparticles

Nanoparticles as lubricant additives afford a reduction in wear and friction of nanoparticle-containing lubricant formulations in addition to improve tribological performance of metal-forming tools. The small and effective lubricant additives in the preparation of the base stock leads to significant enhancements to the lubricants characteristics. The lubricant attributes such as tribological characteristics, anti-oxidation capability and thermal properties could be improved through selected additive, [Shahnazar et al. \(2016\)](#).

Researchers utilized different test to evaluate the coefficient of friction such as standard ring compression test. The test was utilized to estimate the efficiency of measured lubricants. Friction coefficient and deformation load was used to compare the performance of lubricants. The test shows that the enriched nano-lubricants with nanoparticles have more capability of the friction reduction than the conventional lubricants ([Zareh-Desari and Davoodi, 2016](#)).

The room temperature ionic liquids (RTILs) is one of new family that environmentally friendly and sustainable. It has been utilized as green sustainable fluids additives and as in plant-based avocado oil to enhanced the tribological characteristics. The coefficient of friction could be decreased by 68.88% and the wear volume could be decrease by 73.37% by adding a certain percentage mix of RTIL with avocado oil, [Reeves et al. \(2018\)](#).

Detonation nanodiamond (DND) particles are green carbon additive to motor oils. Researchers studied DND impact on the performance of lubricant and found a positive compositions and fuel economy in engine tests. DND-based nanolubricants must be carefully produced due to the abrasive nature of diamond to avoid increased wear of the friction surfaces. Furthermore, to obtain an advantages from the friction reduction of polished surfaces, [Ivanov and Shenderova \(2017\)](#).

The SiO_2 and CuO nanoparticles were distributed in rape seed and soybean oils in diverse concentrations and their lubrication attribute were compared with two conventional metal forming lubricants, solid lubricant of zinc phosphate plus sodium soap and CM202A press drawing oil.

Chemical Processing Lubricant Without Additive

Chemical modification of lubricant is required for certain applications to overcome its disadvantages such as substandard low temperature characteristics and oxidative stability., The bio-based lubricants can perform better than the conventional lubricants

with suitable base oil and additive packages preparation, Syahir *et al.* (2017). Mineral based lubricants are categorized as hazardous wastes because they contain high levels of toxic organic particles. The used lubricants had been reused to supplement the conventional energy sources. However, the process has low cost but it also has the high environmental risk (Jafari and Hassanpour, 2014).

Triazolidione (TAD) is a straightforward, additive-free, crosslinking and functionalization chemistry strategy used to enhance many plant oils. The TAD equimolar functionalization reactions monitored by Nuclear Magnetic Resonance (NMR) and Mass Spectrometry (MS) analysis. Researchers used a sequence of synthesized bifunctional TAD molecules which used for the chemical crosslinking of plant oils. The obtained plant oil-based foils polymer networks showing a better thermal property, Türlüç *et al.* (2015).

The application of vegetable oils as potential metal working fluids due to the high performance of these oils for wide range of materials and working conditions. Amongst the vegetable oils are sunflower, soybean and rapeseed which possess the relevant properties as a potential lubricant fluid, Shashidhara and Jayaram (2010). The full hydrogenation reaction of polyunsaturated FAMES into methyl stearate (MS) is an industrial feedstock for the metalworking or machining such as emulsifiers, surfactants, etc., Bouriazos *et al.* (2015). The epoxidation of oleic FAMES or methyl oleate high from vegetable oils was carried out in a one-pot reaction utilizing copper catalysts throughout cumene as oxygen carrier, Scotti *et al.* (2015).

The bio-lubricant Tri-esters of fatty acids with polyols can be prepared through direct esterification of different acids with the polyol in the existence of amorphous solid acid catalysts, Zaccheria *et al.* (2016).

Heat Transfer Parameters

The heat removing capacity into the cutting fluids enhanced due to higher thermal conductivity, increased surface area of the nanoparticles, streamline motion and lower Reynolds number, Aurich *et al.* (2014). The thermal conductivity of the suspension increased by almost 20%–30% with small addition of nanoparticles (1–5 vol%), Wang and Fan (2011).

Hot forging, rolling and stamping processes can permit sufficient plastic flow of workpiece for final products in its essential intricate form. One of the problem facing the hot rolling process is that the roll surface temperature has to remain below 600°C, while the workpiece must be heated to 800–1200°C. The temperature distribution of hot strip rolling shown in Fig. 7. The consequently abrasive wear and the severe surface oxidation occurs at the tool surface, potentially can embed into the end-products to produce a low surface quality with erroneous dimensions, Wan *et al.* (2016). Hot metalworking process comprises high temperature tribology. Using of inorganic polymers lubricants in such application need to be adjusted to satisfy high temperature in hot manufacturing operations. Borax-, polyphosphate- and silicate- additives are deliver the appropriate friction and wear properties, will help to minimize materials loss of the high temperature metalworking process, and increase surface quality from the standpoint of tribology. Polyphosphate salt additives is a lubricant can adapt to a high temperatures metalworking application. It is also a cost effective and very stable friction at the mating surfaces, Wan *et al.* (2016).

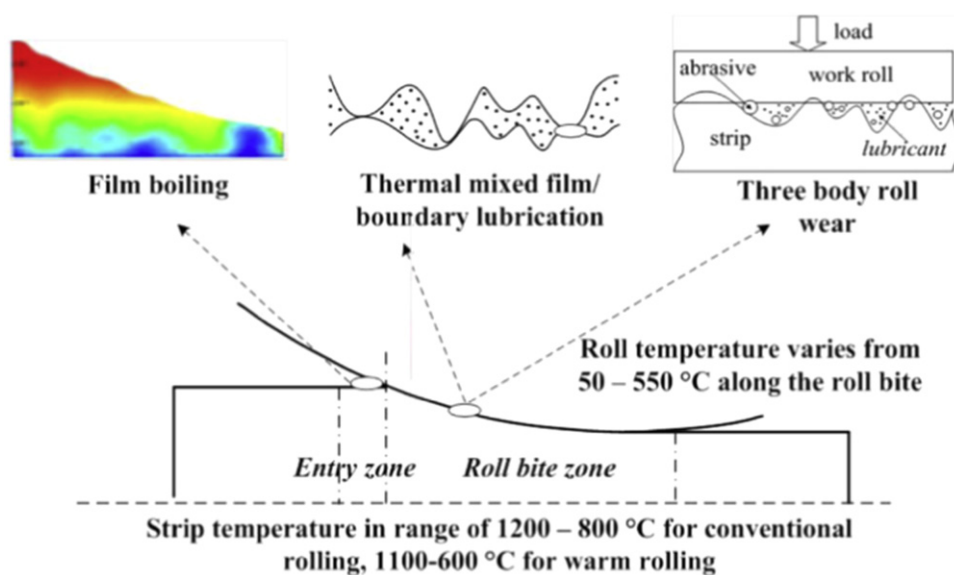


Fig. 7 The interface in hot metal rolling processes. Reproduced from Wan, S., Tieu, A.K., Xia, Y., *et al.*, 2016. An overview of inorganic polymer as potential lubricant additive for high temperature tribology. Tribol. Int. 102, 620–635.

Limitation of Bio-Lubricant

The increase use of plant oils, has to compete with the increasing demand for bioenergy, that could lead to unbalanced supply and demand and the increasing demand for food in the world, [Salimon et al. \(2012\)](#). The conventional lubricants are not environmental friendly resulting of accidental spillage, mishandling and leakage etc., attitude threat and serious concern. These vegetable oils and their respective derivatives are environmentally friendly and therefore can be chosen as an alternative to the harmful oils currently used as lubricant, [Suhane et al. \(2018\)](#).

Researchers found that the vegetable oils have limited range of viscosities. Low viscosity constrains utilizing such biolubricants in several industrial applications. Thus, nanoparticle additive must be added to the lubricant to enhance its performance. Among of the additive are ethylene-vinyl acetate copolymer (EVA) and ethyl cellulose (EC), [Quinchia et al. \(2014\)](#).

One of vegetable oils disadvantage is their limited oxidative stability. The study has been made to carry out the effect of oxidation on the tribological performance of few vegetable oils. Under controlled conditions inducing the oxidation method, the oil samples were subjected to accelerated ageing in a dark oven at different temperatures. The samples were analyzed for the variation of viscosity, peroxide number and percentage of free fatty acid, then compared with fresh oils samples. The results showed that, the ageing temperature has effect on the oxidation of oil samples as the increased free fatty acids. The low coefficient of friction observed using four ball test for oxidized oil samples was a results of soft iron soap formation having low resistance to shear, [Mannekote and Kailas \(2012\)](#).

The recent developments in the area of biodegradable synthetic is the ester base stocks for formulation of lubricants. The developed products applicable in metal working fluids, automotive transmission fluids, fire resistant hydraulic fluids, neat cutting oils, industrial gear oils and automotive gear lubricants, [Nagendramma and Kaul \(2012\)](#). The lesquerella field pennycress, meadowfoam and cuphea PSR-23 crop were compared with commodity vegetable oils for their fatty acid (FA) profiles, low temperature, lubricating (viscosity and wear), and oxidative stability properties. The crop oils with an antioxidant additive (1%–3%) were as oxidatively stable as current conventional petroleum oil by utilizing the rotating pressurized vessel oxidation test with times > 200 min using the 4-ball anti-wear test. The test showed best results for cuphea and pennycress, [Cermak et al. \(2013\)](#).

The amino acid surfactants are less toxic than traditional surfactants and had excellent interfacial properties, [Liu et al. \(2018\)](#). Tailor-made ionic liquids (IL) investigated for application as lubricants. The physical and chemical characteristics of IL, have shown more promising. The ionic liquids are applicable as neat lubricants or additives on dissimilar sliding pairs. It is an excellence potential replacement to the conventional lubricants in industrial applications in regards of environmental hazards, biodegradability issues and future prospects.

The solid-state lubricant graphene-zinc oxide is composite film was studied as a friction and wear reduction. The graphene-zinc oxide film is able to maintain its lubricating effects under extreme operating conditions including 450 m sliding distance and 15 N normal load. The optical and spectroscopic analysis followed by tribological testing of the formed wear scars reveal a persistent protective film. The tribological performance of this graphene-rich composite was excellent that because of the zinc oxide adhesion effect, [Fraccascia et al. \(2018\)](#). The green products should have close proximity with high Relative Comparative Advantage (RCA). The maximum proximity green products with high RCA will have the highest growth ([Fraccascia et al., 2018](#)).

The commercial vegetable-based fluid LB 2000 (not edible) was studied to quantify their lubri-cooling capacity in addition to the chemical and physical properties. canola and Cottonseed oils showed decent results, considering that they are non-polluting and non-toxic. Attrition or adhesion was the main wear mechanism met, regardless of the oil tested, [Araújo Junior et al. \(2017\)](#).

Conclusion

In conclusion, the natural oil lubricant was raised as an alternative to mineral based lubricant. The environmental, economic and technical sides are the most parameters that led to adopting such kind of lubricant. Technical deficiency of natural oil such as thermal parameters and durability could be resolve by adding some particulate additive.

See also: Natural Oils as Green Lubricants in Machining Processes

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Natural Oils as Green Lubricants in Machining Processes

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Introduction

Conventional machining processes are always associated with heat generation, tool wear, energy consumption, surface and subsurface defects of the workpiece including surface roughness, residual stresses etc. All these problems can be reduced/eliminated by providing proper lubrication to the machining zone during the machining process. The cutting fluid reduces coefficient of friction at the chip-tool interface as well as at the tool-workpiece interface. This in-turn diminishes frictional forces at the two interfaces resulting in reduction of resultant force. At the same time, it also helps in removal of chips during machining and cooling down the cutting zone effectively. The most common and conventional method of the use of lubricant during machining is flooded lubrication technique in which the lubricant is allowed to impinge on the cutting zone in abundance. Flooded lubrication technique is associated with various economic and environmental issues. Abundant usage of lubricant increases manufacturing cost and causes dermatological and respiratory syndromes to the machinists. A large amount of fluid used in this technique is generally mixed with biocides to make it reusable. Biocides are detrimental to the environment. Disposing of cutting fluid is also a great ecological concern if it is non-biodegradable. That is why governmental rules are becoming stricter towards the use and disposal of cutting fluids. The best and ideal alternative is to perform dry machining where no harmful cutting fluid is used. However, dry machining is not feasible in most of the cases. Another alternative is to use natural vegetable oils. The most important property of these oils is that they are biodegradable. However, the problem is that they can be used only after mixing with various additives. The additives are mixed in the vegetable oils to make them suitable for the use as cutting fluids. Several blends of such cutting fluids are available in the market. Initially, the share of such lubricants was very low in the worldwide lubricant market, but now, the growth is anticipated at a very high rate annually.

Natural Oils as Metal Cutting Fluids

Conventional lubricants can be effectively replaced by natural oils in machining processes. In the recent years, the demand for green lubricants is increasing day by day because they are non-toxic, environment-friendly and readily biodegradable in nature along with having good lubricating properties. In some cases, vegetable oils, having high affinity to the mating surfaces, show better lubricating properties than that of the petroleum-based oils. These oils can be used as base oils in lubricants because they generally remain liquid at room temperature as well as they contain at least one ester as a functional group. Chemical properties of a natural oil affect its successful application in machining process. Adsorption property of a natural oil that makes it able to adsorb onto frictional surface and prevent their contact during machining process depends on interaction of functional groups of the oil with the surfaces. Properties which allow a lubricant to act as metal cutting fluid include its non-toxicity, biodegradability, high viscosity index, good lubricity (Mahadi *et al.*, 2017) and its ability to form a boundary lubricant through penetration into the mating surfaces during machining. By adding suitable additives, properties of a natural oil acting as base oil can be altered to make it suitable for acting as a lubricant in machining processes. There are three important factors on which performance of a lubricant depends namely, base oil, additives and formulation methodology as shown in Fig. 1. Vegetable oils, though costly, performed better than synthetic or mineral oils.

Low thermo-oxidative stability is a major issue encountered during the use of natural oils in metal cutting applications. Their stability can be improved either through esterification/transesterification process for modification of the carboxyl group or through the methods like selective hydrogenation, dimerization/oligomerization, formation of C–C and C–O bonds, metathesis or oxidation used for modifications of the fatty acid chain (Shashidhara and Jayaram, 2010).

Additives

Natural oil alone (without additives) cannot be used as a metal cutting fluid because it lacks various lubricating features. Lubricant's performance is improved with the addition of proper additives. Additives affect significantly the properties of tribofilms or boundary lubrication film. This surface protection film is developed between the mating surfaces by chemical changes on the surfaces which are influenced by these additives. Most commonly used additives are sulphur based, zinc based or phosphorus based.

Commonly used additives can be subdivided into following groups on the basis of their function:

1. Anti-wear additives (AW)
2. Extreme pressure additives (EP)
3. Anti-oxidants (AO)
4. Emulsifying agents (EA)
5. Biocides

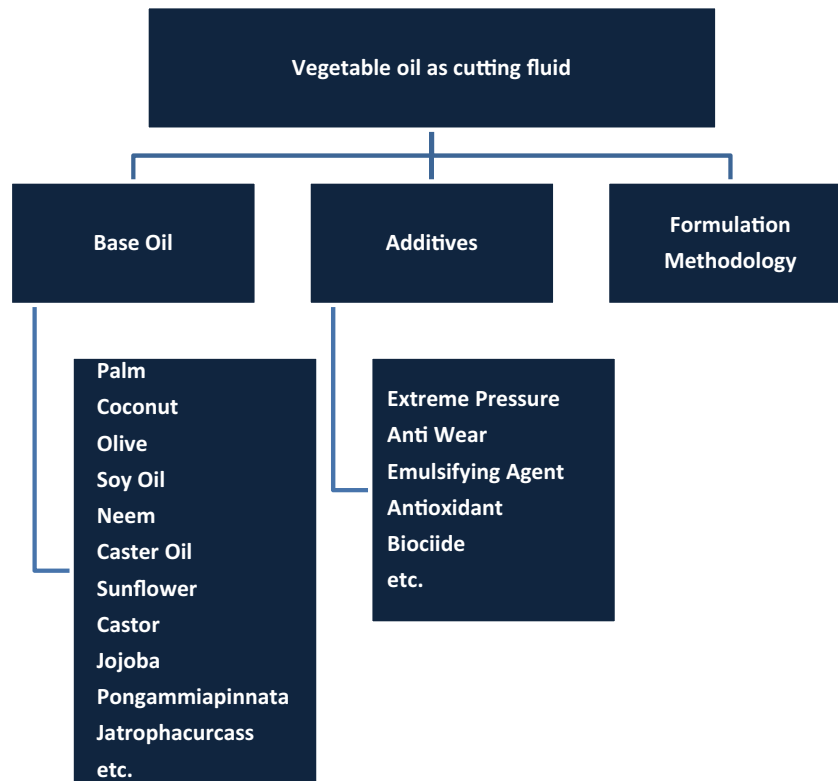


Fig. 1 Natural oils as lubricants.

A protective molecular film is produced by the AW additives that adheres to the contacting friction surfaces. This adsorption may be chemical or physical. Some of the examples of AW additives are zinc dialkyl dithiophosphates (ZDDP), S-[2-(acetamido) thiazol-1-yl] dialkyl dithiocarbamates, Palm oil methyl ester (POME) and Dibutyl 3.5-di-t-butyl-hydroxy benzyl phosphate (DBP). The additives form polar head of the molecular layers, which are closely packed and arranged in a proper order to form the lubricating film. Extreme Pressure (EP) additives form layers of sulphides, chlorides or phosphates of iron through tribochemical reactions and protect the mating surfaces in EP conditions. Zinc-Dialkyl-Dithio-Phosphate (ZDDP) acts as EP additive. Butylated hydroxyl anisole (BHA), Butylated hydroxyl toluene (BHT), Mon-tert-butyl-hydroquinone (TBHQ), propyl gallate (PG) etc. are those additives that act as chain-breaking antioxidants. Zinc dithiophosphates (DTP) and Dithiocarbamates (DTC) are the examples of peroxide decomposer antioxidants.

In addition to these additives, emulsifying agents (EA) are also to be mixed to develop stable natural oil-in-water emulsion. Polyoxyethylene (20) sorbitan monopalmitate, polyoxyethylene (40) sorbitan tetraoleate, polyoxyethylene (20) sorbitan mono-stearate, Ethoxylated oleic acid ester are some common non-ionic EA.

Biocides and anti-corrosive agents are to be added as additives according to the requirement. Ethanolamine is a good example of anti-corrosive agent as it helps in stabilizing the emulsion too. Biocides generally belong to family of triazine derivative (triclosan). They restrict the growth of bacteria and fungus in the vegetable oil. Selection of the additives should be made intelligently and only those additives should be added, which are necessary for a particular application.

Properties of Natural Oils

Natural oils demonstrated similar or in some cases better machining performance than that of the conventional mineral oils. In some basic properties, natural oils are superior to mineral oils. As far as their application in machining is concerned, the most important property is the lubricity of the natural oil. Boundary lubrication is the dominant lubrication mechanism in the vegetable oils because of high polarity of the base oil due to which strong interaction occurs between the fluid and the mating surfaces during machining. They show good lubricating behavior during machining because of the development of a relatively tight and sticky oily layer due to the following two reasons:

1. Polar charge present in fatty acids of the oil draws the molecules of oil towards the metallic surface. These molecules do not flow out easily from the interacting surfaces.
2. Oxygen-containing functional groups are present in these oils. These groups also have an affinity towards metallic surfaces.

Table 1 Properties of vegetable oils as lubricants

<i>Advantages (required qualities of metal working fluids)</i>	<i>Disadvantages</i>
High biodegradability	Low thermal stability
Low pollution of the environment	Oxidative stability
Compatibility with additive	High freezing point
Low production cost	Poor corrosion protection
Wide production possibilities	
High flash point	
Low volatility	
High viscosity indices	
Low toxicity	

Note: Shashidhara, Y.M., Jayaram, S.R., 2010. 'Vegetable oils as a potential cutting fluid – An evolution'. Tribology International 43 (5–6), 1073–1081. doi:10.1016/j.triboint.2009.12.065.

The most basic component of a vegetable oil is a glycerol molecule. Triacylglycerides (triglycerides) are glycerol molecules consisting of three long-chain fatty acids. Hydroxyl groups are attached to the fatty acids through ester linkages. Long chains of fatty acids are polar in nature, which make them able to provide lubricant films of high strength. This film interacts strongly with metallic surfaces and reduces both friction and wear.

Viscosity of natural oils is substantially higher than that of the mineral oils. Therefore, natural oils generally provide stable boundary lubrications during machining when they are applied through flooded lubrication technique. Some researchers found that during application of Minimum Quantity Lubrication (MQL), fluids with low viscosity and high coefficient of friction are required to get good machining performance. The fluid provides lubrication and the compressed air provides cooling during MQL. Therefore, in order to use these fluids during MQL, natural oils having comparatively lower viscosity should be used so that the fluid can easily penetrate the cutting zone even in the mist condition. In view of that, water-based emulsion of the natural oil is a good remedy for MQL applications because an emulsion has low viscosity than that of the straight oils. Furthermore, an emulsion of the natural oil has good thermal conductivity and high specific heat.

Another important characteristic of the natural oils, which make them favorable to the metal cutting applications is their high flash point. During machining operations, high temperature occurs in the machining zone. An oil with high flash point reduces the risk of fire and smoke.

In addition, natural oils are environmentally safe, neither posing any harm to the environment nor hazardous to life. Non-toxicity, biodegradability, and environmentally sound characteristics make natural oils green lubricants. Some favorable and unfavorable properties of natural oils to act as machining lubricants are listed in [Table 1](#).

Application of Natural Oils in Machining Processes

Performance of natural oils developed for metal cutting operations was evaluated for different conventional machining processes. The works reported by various researchers working in the area of application of natural oils during machining processes are described in the following sections to showcase the broad knowledge of the available literature on the subject.

Turning

Turning is the most basic and conventional machining process in which workpiece rotates during machining. The turning performance can be improved through proper lubrication. Natural oils showed satisfactory performance when applied during turning of different materials. Generally, researchers developed few cutting fluids based on different natural oils and their performance characteristics were investigated in terms of different performance indices like tool wear, surface roughness, forces etc. When the effect of different cutting fluids during turning of hardened steel were looked into, it was concluded that emulsion without mineral oil performed better than dry cutting or cutting with emulsion containing mineral oil. This was attributed to the improved lubricating action of fluid without mineral oil due to the presence of grease in it. Generally, groundnut oil proved to be the best cutting fluid when compared with other vegetable oils like palm kernel, coconut oil and shear butter oil during turning of aluminum and Al-alloys. Using groundnut oil, lowest forces were observed for machining aluminum at all feeds and for copper at high feed. Palm kernel oil provided lowest forces for copper at low feeds only. Performance of coconut oil was found to be superior as compared to water-soluble mineral oil and straight cutting oil. Even during turning of stainless steel, coconut oil provides lower values of workpiece surface roughness and tool flank wear at low speeds as compared to water-soluble mineral oil and straight cutting oil. This was attributed to the viscosity of the coconut oil which lies in between the viscosities of the other two fluids. Coconut oil penetrated the interfaces easily during cutting and provided proper lubrication as well as cooling. High heat dissipating ability made the coconut oil advantageous for metal cutting applications. The effect of food-grade vegetable oil applied through MQL technique during turning of AISI 9310 steel, as shown in [Fig. 2](#) below, was investigated by [Khan et al. \(2009\)](#) and compared with the dry and flooded lubrication. The MQL with natural oil reduced the temperature in the machining zone, eliminated built-up edge, reduced flank wear and improved the MRR and workpiece surface finish.

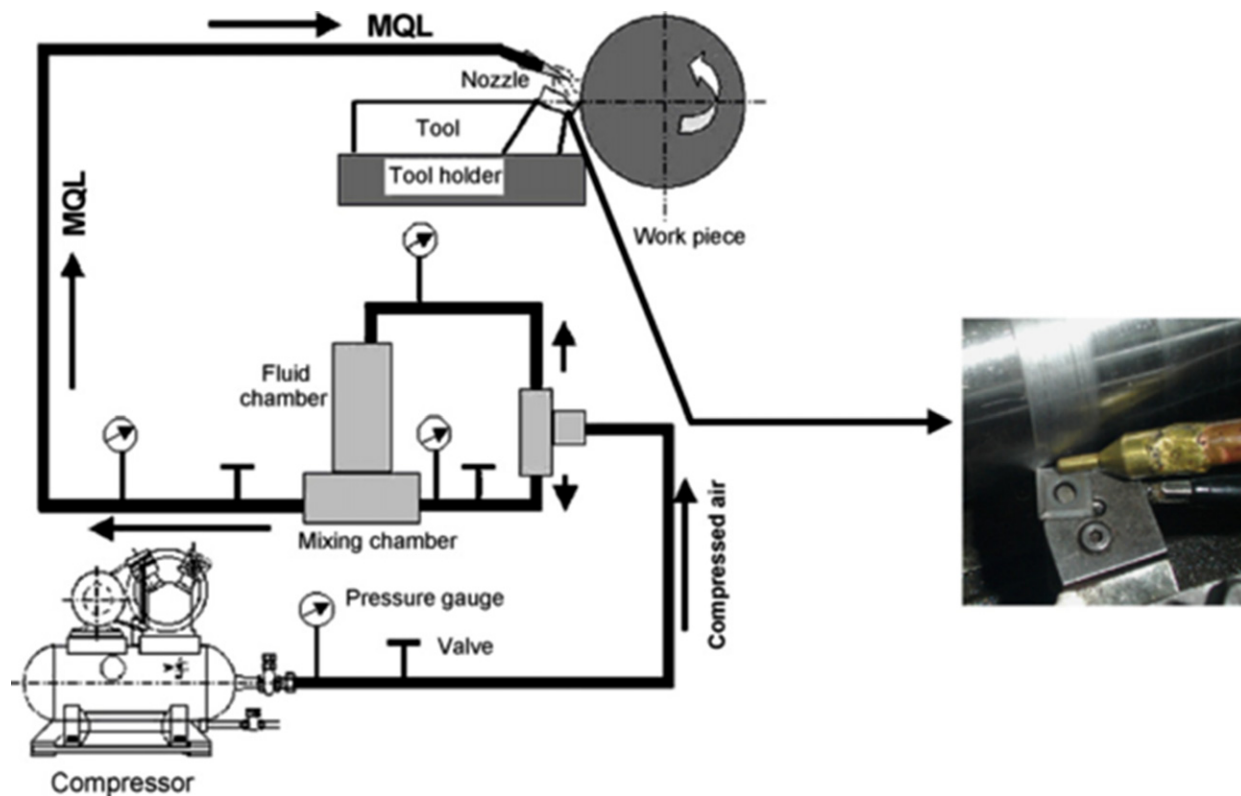


Fig. 2 Schematic view of MQL unit. Reproduced from Khan, M.M.A.A., Mithu, M.A.H.H., Dhar, N.R., 2009. 'Effects of minimum quantity lubrication on turning AISI 9310 alloy steel using vegetable oil-based cutting fluid'. *Journal of Materials Processing Technology* 209 (15–16), 5573–5583. doi:10.1016/j.jmatprotec.2009.05.014.

Natural oils mixed with nano-fluids also outperformed conventional metal cutting fluids containing nano lubricants during turning of steels. MoS_2 , Al_2O_3 , graphite and boric acid powders are well known solid lubricants. Lower values of cutting temperatures, tool flank wear and surface roughness were obtained when coconut oil-based nanofluids were used as compared to SAE-40-based nanofluids. Suspension of very small amount of nanoboric acid into the natural oil was found to be the best alternative. Neem oil provided better cooling capacity than that of the Karanja oil during turning of mild steel. Better surface finish was obtained when neem oil was used. Canola-based cutting fluid consisting of extreme pressure (EP) additive showed best performance when compared with other fluids. However, the amount of the additives should be judiciously selected. According to Ozelik *et al.* (2011a), canola-based cutting fluid, consisting of 8% of EP, showed best performance when canola-based and sunflower-based cutting fluids were developed with the addition of 8% and 12% sulphur-based extreme pressure (EP) additive, respectively (Polartech XP 9018). Therefore, petroleum-based cutting fluids can be replaced with natural oils effectively. Application of natural oils containing nano-particles of solid lubricants through MQL technique is an effective method to improve the machinability of super alloys. A commercial natural oil (Coolube 2210^{EP}) containing Al_2O_3 in suspended form applied through MQL technique during turning of Inconel 600 alloy performed satisfactorily. Significant reduction was observed in surface roughness, cutting force and tool wear when 6 vol% nano-particles of Al_2O_3 mixed with the cutting fluid was applied through MQL as compared to dry and MQL without nano-particles (Vasu and Reddy, 2011). Non-edible vegetable oils like Pongam (*Pongamia pinnata*) and Jatropa (*Jatropha curcas*) can also be applied as natural oils after some modifications. When two thermoxidatively modified non-edible vegetable oils, Pongam (*Pongamia pinnata*) and Jatropa (*Jatropha curcas*) were applied through MQL technique during turning of AA 6061 steel, both of the natural oils offered better performance than the mineral oil but Jatropa-based fluids provided minimum cutting power followed by Pongam-based fluids and then mineral oil (Shashidhara and Jayaram, 2013). Lawal *et al.* (2014) developed oil-in-water emulsions using palm kernel and cottonseed oils as shown in Fig. 3 below for turning AISI 4340 steel. Both the fluids performed satisfactorily for reducing cutting forces and surface roughness.

Milling

Like turning, natural oils performed well when applied during milling of various ferrous and non-ferrous materials. Sunflower oil and canola oil with 8% extreme pressure additives gave better results as compared to commercial semi-synthetic cutting fluid as far

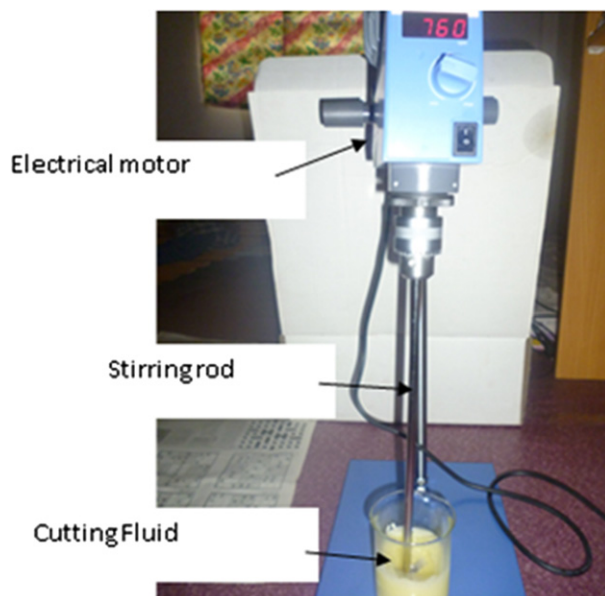


Fig. 3 Mixing with mechanical overhead stirrer. Reproduced from Lawal, S.A., Choudhury, I.A., Nukman, Y., 2014. 'Evaluation of vegetable and mineral oil-in-water emulsion cutting fluids in turning AISI 4340 steel with coated carbide tools'. *Journal of Cleaner Production* 66, 610–618. doi:10.1016/j.jclepro.2013.11.066.

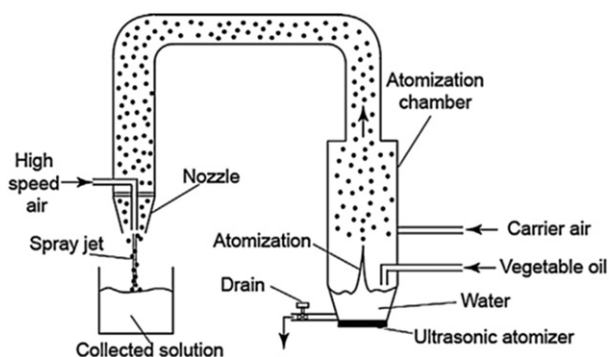


Fig. 4 A schematic of the experimental setup to test emulsification of vegetable oil in water. Reproduced from Burton, G., Goo, C.S., Zhang, Y., Jun, M.B.G., 2014. 'Use of vegetable oil in water emulsion achieved through ultrasonic atomization as cutting fluids in micro-milling'. *Journal of Manufacturing Processes* 16 (3), 405–413. doi:10.1016/j.jmapro.2014.04.005.

as surface roughness and forces were concerned during milling of stainless steels. High viscosity of palm oil having a large amount of unsaturated fatty acid lead to the formation of high strength lubricating film acting as a boundary lubricant during flooded lubrication. Palm oil can be applied through flooded lubrication technique during milling of Al-matrix composite to get minimum forces as compared to coconut oil, sunflower oil, and soyabean oil. Natural oils applied through MQL technique is a good alternative in milling process too. When palm oil was applied through MQL technique during flat end milling of stainless steel by uncoated solid carbide tools, surface roughness was reduced even when the tool had worn out. Palm oil provided highest tool life as compared to fatty alcohol and dry cutting. Commercially available vegetable oil applied through MQL during milling of steel using solid carbide cutting tool provided higher tool life through proper selection of cutting parameters. Excessive use of emulsifying agents cannot be justified due to their negative financial and environmental effects. In a one-of-its-kind attempt, water-based emulsion of canola oil through ultrasonic atomization was developed by Burton *et al.* (2014) as shown in Fig. 4, which completely circumvents the use of additives and emulsifying agents. The cutting fluid showed similar or better machining performance than conventional fluid in terms of reduction in chip thickness, burr formation and peak-to-valley values of forces during micro-milling of Al and steel (Burton *et al.*, 2014).

Natural oils containing no antioxidant performed better than the oils mixed with antioxidants during MQL-assisted milling of non-ferrous alloys like Inconel. High oleic sunflower oil (with no antioxidant) is a better option when compared with sunflower oil, castor oil and commercially recycled oil investigated in terms of their tribo-rheological behavior and environmental

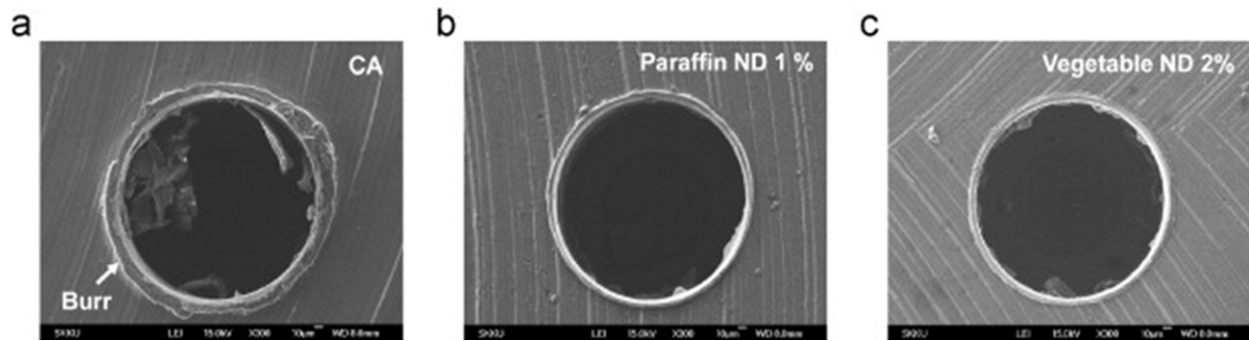


Fig. 5 SEM micrographs of the drilled holes: (a) Run 1 – Compressed air lubrication. (b) Run 4 – Nanofluid MQL with paraffin oil and 1 vol% of nano-diamond. (c) Run 7 – Nanofluid MQL with vegetable oil and 2 vol% of nanodiamond. Reproduced from Nam, J.S., Lee, P.H., Lee, S.W., 2011. 'Experimental characterization of micro-drilling process using nanofluid minimum quantity lubrication'. *International Journal of Machine Tools and Manufacture* 51 (7–8), 649–652. doi:10.1016/j.ijmachtools.2011.04.005.

soundness. High oleic sunflower oil (with no antioxidant) was recommended because of the improvement in the tool life and providing similar environmental impact as compared to commercially available canola oil. The improvement in the tool life was attributed to the combined effect of high friction coefficient and low viscosity of the cutting fluids (Pereira *et al.*, 2017).

Drilling

Vegetable-based cutting fluids reduced thrust force and increased tool life significantly during drilling of steels. Emulsions of natural oils developed by mixing additives along with one or two surfactants to the base oil showed good drilling performance. Examples of such fluids containing surfactants are crude sunflower oil containing Tween 80 as a surfactant, refined sunflower oil containing Tween 80 as a surfactant, and sunflower oil containing a mixture of Tween 80 and Peg 400 as surfactants. Natural oils containing nanoparticles of solid lubricants also showed superior performance when applied through MQL. Micro-drilling process was characterized by Nam *et al.* (2011) using pure MQL and nanofluid (containing diamond particles of diameter 30 nm) MQL formed through vegetable oil and paraffin oil and compared with compressed air (CA) lubrication. Drilling torque, thrust force and quality of the drilled holes shown in Fig. 5 below suggested improvement in the process when MQL nanofluid containing 2 vol% of nanoparticles were added in the vegetable oil or 1 vol% of nanoparticles were added in the paraffin oil (Nam *et al.*, 2011).

Palm oil is also a better alternative for high-speed drilling of non-ferrous alloys. It showed the ability to provide low wear rate when applied through MQL technique in high-speed drilling of Ti-alloy. Low wear rate was attributed to the lubricant layer formed on the sliding interfaces. Two reasons for the formation of this thick lubricant layer were the high viscosity of the palm oil and the fatty acids present in the palm oil having a long chain of carbon which reacted with metallic oxides. Sometimes, vegetable oil-based lubricant developed by mixing more than one surfactant outperformed the one that contains only one surfactant. It was found that canola oil containing two surfactants performed better than the one that contains only one surfactant. Similarly, water-based emulsion of refined sunflower-based cutting fluids are also a good alternative. Based on statistical analysis it was concluded that it gave better surface finish as compared to mineral and semi-synthetic cutting fluids. The emulsion formed with refined crude oil mixed with Tween 85 (20%) and Peg 400 (3%) as surfactants outperformed other fluids due to its better lubricating capabilities (Ozcelik *et al.*, 2011b). Mathematical models based on fuzzy logic and regression analysis were developed for thrust force and surface roughness during drilling of steel using natural oils. Canola oil based lubricant developed by mixing two surfactants outperformed the one that contains only one surfactant (Kuram and Ozcelik, 2013). Canola-based cutting fluid showed better lubricating properties when compared with different natural oils containing crude or refined sunflower oil. Therefore, when evaluated in terms of different drilling responses like wear of the drill bit, thrust force and workpiece surface roughness during drilling of steel with HSSE tool, canola-based cutting fluid demonstrated best performance. In order to get high material removal rate values during drilling of steel, Jatropha-based oil is a better option than Pongam and mineral oil.

Grinding

Various new environment-friendly cutting fluids were developed by researchers to get high lubrication ability and good performance during grinding process in terms of radial wheel wear, grinding forces, workpiece surface quality etc. The base oil used in the new cutting fluids was a natural oil. Natural oil was generally mixed with water, derivative of triasine as bactericide, composition of synthetic ester as anticorrosive agent and polyglycol of synthetic ester as an emulsifying agent to make it suitable for the proper grinding operation. This type of eco-friendly cutting fluid fulfilled all environmental requirements and showed reduced wheel wear, grinding forces, and surface roughness. This type of fluid performed satisfactorily during CBN grinding of hardened steels too. Utilization of used cooking oil lubricant for grinding application is also a cheap and comparable alternative. When

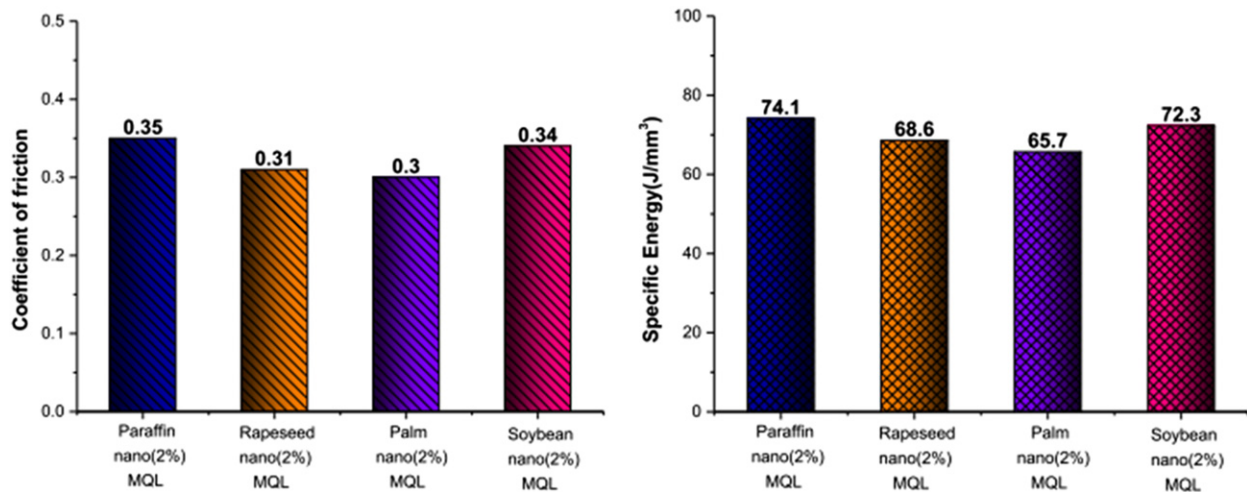


Fig. 6 Coefficient of friction and specific grinding energy for the nanoparticle jet MQL grinding experiment with four types of base oil. Reproduced from Zhang, Y., Li, C., Jia, D., Zhang, D., Zhang, X., 2015. 'Experimental evaluation of MoS₂ nanoparticles in jet MQL grinding with different types of vegetable oil as base oil'. *Journal of Cleaner Production* 87 (C), 930–940. doi:10.1016/j.jclepro.2014.10.027.

these fluids were applied during grinding of hardened materials (hardness > 60 HRC) with vitrified bonded CBN grinding wheel, such lubricants did not show any negative effect on quality of workpiece surface and performed well for reducing wheel wear as compared to commercially available vegetable-based and mineral-based lubricants. Nano-particles like MoS₂ provided optimum performance when mixed with different natural oils and applied to the grinding of different types of steels. Lubricating properties of the natural oils containing MoS₂ in sequence were soybean oil followed by rapeseed oil and palm oil when these three oils were compared. Performance of soybean oil mixed with MoS₂ nanoparticles applied with different lubricating conditions (like flooded lubrication, MQL etc.) during surface grinding of steel and ductile cast iron was superior. Both frictional losses and energy consumption were reduced due to the addition of nanoparticles in the natural oil applied through MQL technique. Zhang *et al.* (2015) prepared three different types of cutting fluids based on soybean oil, rapeseed oil and palm oil containing MoS₂ nanoparticles and applied with MQL technique during grinding of 45 steel. As compared to liquid paraffin, the natural oils performed well in terms of coefficient of friction and specific grinding energy value as shown in Fig. 6.

Research and Development Challenges in the Application of Natural Fluids in Machining

Most of the researchers claimed better machining performance of various natural fluids as compared to conventional cutting fluids. They stated the observed results without discussing the mechanism or the reasons for those observations. Deep-seated investigation must be performed to find the actual mechanism of the working of natural oils during machining of different materials with different fluids.

In order to use natural oils as metal working fluids, various additives are to be mixed. Toxic and hazardous additives must be avoided. Harmless additives must be identified and developed so that the industries producing cutting oils use these additives enhancing the usage of the natural oils in the market.

Emulsifying agents are not recommended to be used in the fluids because these elements are hazardous to human health and detrimental to the environment. A very little work has been reported on the development of water-based emulsion of natural oils without mixing emulsifying agents. The methods developed so far must be explored further for different natural oils.

Most of the research was performed on ferrous metals and Aluminum alloys. Application of natural oils during machining of super alloys must be examined extensively.

Optimization of the parameters of the natural oil working as metal working fluids must be performed through multi-objective optimization techniques for different machining processes. It will make the implementation of the best suited natural fluids to a particular machining process on the shop floor easy and effective.

Conclusion

Natural oils have shown great potential to act as green lubricants for machining processes. Conventional lubricants that have been used in metal cutting industries must be replaced by the natural oils. This task is unavoidable as far as environmental issues are concerned. Although natural oils in their crude form are not suitable for metal cutting industries, they perform well after proper modifications. Application of the natural oil-based cutting fluids through MQL is also a promising technique. The performance can further be improved by mixing nano-particles into the fluid. Intelligent usage of the techniques developed so far is based on the optimization of the parameters governing the properties of the fluid along with the machining parameters.

See also: Natural Oils as Green Lubricants in Forming Processes

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Oil Palm Kernel Shell – A Potential Sustainable Construction Material

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Introduction

Oil palm shell (OPS) is a key waste product generated after the extraction of oil from oil palm tree (Okpala, 1990; Okafor, 1988). Oil palm nut produces two types of oil, namely palm oil and kernel oil. These are extracted from outer and inner cores of the oil palm nut, respectively. After oil extraction, the inner core of the nut, known as palm kernel, has the potential to be used as concrete coarse aggregate. Covered by a hard endocarp, palm kernel shell is also known as oil palm shell (Pantzaris and Jaaffar, 2002). Malaysia has abundant cultivation of palm oil trees. According to Tripathi *et al.* (2015), 52% of the total palm oil in the world has been produced in Malaysia. In Malaysia, there are about 3.8 million hectares of oil palm tree being planted and the coverage area is expected to increase to 5 million hectares in the year 2020 (Alengaram *et al.*, 2013a; Gungat *et al.*, 2013). OPS is produced in large quantities by oil palm mills. Over 4 million tonnes of solid wastes are produced annually (Alengaram *et al.*, 2013a; Aslam *et al.*, 2016; Nagaratnam *et al.*, 2016). Since the demand for palm oil is increasing, the production of solid wastes by oil palm industry is expected to increase too. These waste materials, a component of which is OPS, are traditionally disposed of either through incineration by conventional process or in landfill (Rahman Sobuz *et al.*, 2014). These disposal methods are not only expensive but also have created many environmental issues. To minimize environmental impacts of handling and disposing these agricultural wastes, many researchers have been studying the potential of using OPS as replacement material in construction industry.

In the last three decades, extensive research has been carried out on using waste (OPS) as alternative aggregates for the production of lightweight concrete in South East Asia (Alengaram *et al.*, 2013a). OPS is generally a porous material with porosity of 37% (Okpala, 1990). The porous structure of OPS greatly reduces the density and also improves the thermal conductivity. As a result, cellular structure of OPS reduces the weight of concrete and provides better thermal insulation. The reduction in density of OPS concrete is about 20%–25% when compared to normal concrete (Shafigh *et al.*, 2010). Earlier, poor workability (with low slump value) of concrete using OPS was reported by several researchers (Okpala, 1990; Okafor, 1988; Mannan and Ganapathy, 2001) even though high water to cement ratio was used. This is due to the irregular flaky shaped shape of OPS which makes cement difficult to lubricate aggregates to achieve appropriate workability. However, desirable workability was observed with the incorporation of small amounts superplasticizer (Neville, 1995). Superplasticizer has been used in developing OPS concrete by subsequent researchers (Shafigh *et al.*, 2012; Mo *et al.*, 2016b; Serri *et al.*, 2015). Additionally, several researchers demonstrated that properly proportioned OPS concrete can achieve compressive strength above 30 MPa (Shafigh *et al.*, 2011, 2012; Farahani *et al.*, 2017).

The incorporation of OPS in concrete provides an opportunity for this solid waste material to be implemented in construction industry. It is environmentally friendly and sustainable in the long run. The following sections present the physical properties of OPS, its effects on fresh properties of concrete as well as the properties in the hardened state. It is observed that OPS has a high potential to be incorporated in concrete as alternative coarse aggregates.

Physical Properties of OPS

In general, the mechanical properties of OPS concrete are significantly dependent on the physical properties of OPS itself. The specific gravity of OPS reported by several researchers is in the range of 1.17–1.62. The specific gravity of OPS is obviously lower than that of normal weight aggregates and the typical particle size distribution of OPS is shown in Table 1. It is noted that the particle size distribution of OPS is in the range of 3–14 mm. The loose bulk density of OPS is the range of 500–600 kg/m³ while compacted bulk density is in the range of 600–740 kg/m³. The bulk density of OPS is generally influenced by its shape and size.

As for the shape of OPS aggregate, it could take the form of irregular flaky shape, angular, circular or polygonal, depending on the extraction method. Typical OPS aggregate is shown in Fig. 1. The surface texture of OPS remains fairly smooth on both sides. Rough and spiky attire can be observed at the broken part. The thickness of OPS varies from 0.15 to 8 mm.

OPS aggregate is composed of porous structure and hence it tends to have high water absorption. Depending on the oil palm tree species and OPS maturity age, the 24-h water absorption can vary from 14% to 33%. Table 1 shows the water absorption of OPS reported by several researchers.

Since OPS has lower specific gravity and bulk density, the density of OPS concrete commonly falls in the range of 1600–1900 kg/m³. However, smooth texture and irregular shape of OPS can cause poor bonding between aggregates and cement paste. The water absorption of normal weight aggregate is commonly reported as 0.5%–1%, which is extremely low when compared to OPS.

Table 1 Physical properties of OPS

Researcher	Specific gravity	Loose bulk density (kg/m ³)	Compacted bulk density (kg/m ³)	Water absorption (%)
Okpala (1990)	1.37	512	589	27.3
Jumaat <i>et al.</i> (2009)	1.37	566	620	23.8
Shafigh <i>et al.</i> (2016)	1.21	–	–	20
Gibigaye <i>et al.</i> (2017)	1.31	530	–	19.93
Farahani <i>et al.</i> (2017)	1.19	–	674	20.6

**Fig. 1** Oil palm shell aggregate.

Workability of OPS Concrete

Several researchers (Okpala, 1990; Okafor, 1988; Mannan and Ganapathy, 2001) reported poor workability (low slump value) of OPS concrete even though high water to cement ratio was used at the earlier age. The irregular flaky shaped shape and high water absorption of OPS caused poor workability. By incorporating small amount of superplasticizer, reasonable workability can be achieved (Neville, 1995). As such, superplasticizer is used in developing OPS concrete by subsequence researchers (Shafigh *et al.*, 2012; Mo *et al.*, 2016b; Serri *et al.*, 2015). Similar to normal concrete, the workability of normally vibrated OPS concrete improves with increasing of water to cement ratio. However, several researchers stated low slump value does not necessarily assure its compressive strength. Yew *et al.* (2014a) studied OPS concrete with different age of OPS ranging from 3 to 15 years and the influence of OPS aggregate size on workability and observed that the workability of OPS improved when older age OPS was used. However, the workability was degraded when maximum aggregate size decreased from 12.5 to 9.5mm and the explanation was attributed to the crushing processes which increases the shape irregularity of OPS which can prevent the concrete to achieve full compaction. Moreover, Farahani *et al.* (2017) reported that the inclusion of supplementary cementitious material (SCM) such as fly ash and silica fume can improve the workability of OPS concrete significantly.

Hardened Properties of OPS Concrete

Compressive Strength

Extensive research has been carried out on using waste (OPS) as alternative aggregates for the production of lightweight concrete in South East Asia (Alengaram *et al.*, 2013a). Much effort has been made to improve compressive strength of OPS concrete through research. It is noted that the mix proportion and curing condition have influence on compressive strength of OPS concrete. At earlier years, Abdullah (1984) designed OPS concrete with w/c ratio of 0.4 in accordance to ACI. The designated OPS concrete achieved cube compressive strength of 20 MPa. Okafor (1988) concluded that concrete with compressive strength above 30 MPa cannot be produced by using OPS as aggregates.

Several researchers studied the method to improve the compressive strength such as chemical treatment of OPS (Chai *et al.*, 2014) and curing condition (Mannan *et al.*, 2002; Shafigh *et al.*, 2012). Mannan *et al.* (2006) carried out pre-treatment to OPS aggregates by using concentrated borate, sodium dichromate, ferrous sulphate, cupric sulphate pentahydrate, acetic acid, slaked lime and polyvinyl alcohol (PVA) solutions. The authors noticed that the concrete with OPS pre-treated with PVA solution was able to improve the compressive strength by almost 40%, which was from 23.6 to 32.84 MPa. The authors explained that OPS pre-treated with PVA solution

was able to improve the adhesion bond between OPS and cement paste. However, it will not be economical to carry out pre-treatment to OPS aggregates for industrial use. Shafigh *et al.* (2012) studied the effect of curing conditions including continuous dry and moist skin conditions curing, no curing regime and initial water curing regimes of 2, 4 and 6 days on compressive strength. The sensitivity due to poor curing can be minimized by reducing the w/c ratio of OPS concrete. The authors explained that the water content in the pore of OPS can provide internal curing which gives rise to improved hydration and strength development. It can also minimize autogenous shrinkage and cracking and hence enhance strength.

Also, several researchers demonstrated that properly proportioned OPS concrete can achieve compressive strength above 30 MPa. Shafigh *et al.* (2011) successfully produced high strength OPS concrete with 28-day compressive strength of 42–48 MPa. Shafigh *et al.* (2012) also reported the compressive strength of 34–53 MPa in their studies. A more recent research by Farahani *et al.* (2017) showed that OPS concrete with compressive strength 28–40 MPa can be produced with binary and ternary blended cement.

Okpala (1990) stated that the compressive strength of OPS concrete is greatly dependent on the interface bonding aggregates and cement paste. Mannan and Ganapathy (2004) reported that the individual characteristics of OPS aggregate including strength, thickness and density are lower than those of granite aggregate. The authors stated that OPKS shape irregularity leads to poor bonding and hence lowers concrete compressive strength. The authors further explained that compressive strength relies on both the strength of the aggregate and cement paste and also depends on which one of these two fails first. Alengaram *et al.* (2011) observed that compressive strength of OPS concrete specimens that contained supplementary cementitious material was higher than those without supplementary cementitious material. The authors stated that the infilling of pores by the finer particle generally strengthens the bond between the OPS and the cement matrix in the interfacial transition zone (ITZ). The authors demonstrated that the mortar has filled in the empty pores in SEM analysis. It can be concluded that the compressive strength of OPS concrete is highly dependent on the bonding between binder and aggregates in ITZ.

Splitting Tensile Strength

One of the most important properties of OPS concrete is its tensile strength. It is particularly true in the application of flexural structural member, to resist the tensile stress so as to prevent severe buckling. Several researchers (Shafigh *et al.*, 2012; Farahani *et al.*, 2017; Shafigh *et al.*, 2016) reported that the splitting tensile strength is 6%–10% of its compressive strength. Alengaram *et al.* (2010) stated that weaker bond between aggregate matrix contributes to the lower tensile strength in OPS concrete when compared to normal aggregates concrete. Shafigh *et al.* (2012) compared the splitting tensile strength of normal concrete and OPS concrete. The authors reported that the ratio of tensile splitting to compressive strength of OPS concrete is generally lower than normal aggregate concrete by 28%. Shafigh *et al.* (2013) studied the effect of high volume fly ash on splitting tensile strength of OPS concrete and reported that although 10% of fly ash replacement can increase the compressive strength of OPS concrete by 3.6%, the splitting tensile strength decreased by 19.7%. The authors explained that the material quality of interfacial transition zone (ITZ) that is responsible for tensile strength is poor. In the later study of Shafigh *et al.* (2016), the authors reported that a high volume of fly ash replacement can significantly reduce its splitting tensile strength. Yew *et al.* (2015) studied different type of polypropylene fiber on the splitting tensile strength of OPS concrete. It was noticed that addition of polypropylene fiber has positive effect on splitting tensile strength of OPS concrete and it significantly improves when the replacement volume increases. Several researchers derived the equation relating splitting tensile strength of OPS concrete to its compressive strength as shown in Table 2. Some equations have the similar value of coefficient. These equations are derived in the form of

$$f_t = k f_{cu}^a$$

where k and a is the coefficient derived from experimental data.

Modulus of Elasticity

Elastic modulus is another key property that determines the deformation of structural element under flexure. The compressive strength of concrete is closely related to its compressive strength. However, research shows that OPS has negative effect on the elastic modulus since it contributes lower compressive strength in concrete. Yew *et al.* (2014b) studied the effect of heat treatment on the elastic modulus of OPS concrete. The authors reported that heat treatment has positive effect on elastic modulus and increases it by 8.4%. The use of suitable heat treatment technique brings about a significant improvement to the compressive

Table 2 Equations for splitting tensile strength

Researchers	Equation
Shafigh <i>et al.</i> (2012)	$f_t = 0.358 f_{cu}^{0.675}$
Shafigh <i>et al.</i> (2014b)	$f_t = 0.27 f_{cu}^{0.63}$
Farahani <i>et al.</i> (2017)	$f_t = 0.146 f_{cu}^{0.835}$
Shafigh <i>et al.</i> (2018)	$f_t = 0.14 f_{cu}^{0.85}$

strength as well as elastic modulus, due to the enhanced adhesion between OPS and the cement matrix. [Yew et al. \(2015\)](#) also studied the effect of polypropylene fiber on elastic modulus of OPS concrete. The authors reported all the elastic modulus is the range of 12–15.4 GPa. Improvements of elastic modulus by incorporating fiber are observed in their studies. Due to higher aspect ratio and geometry of fibers, the shrinkage cracks in the concrete have been arrested and therefore the strain induced under compression loading has been reduced. Subsequently, the elastic modulus is improved. [Shafigh et al. \(2018\)](#) studied effect of combination two different aggregates, which are OPS and expanded clay, on the elastic modulus. The authors noticed that when aggregate was substituted with OPS by 25% and 50%, the elastic modulus was reduced by 4.4 and 12.7%. The reduction of elastic modulus was attributed to the weaker interfacial transition zone of concrete containing OPS.

Permeability and Void Content

The concrete permeation property determines the durability of the concrete in service since the concrete with high penetrability is more vulnerable to the ingress of harmful substances. Hence, it is essential to study the permeability of OPS concrete. The concrete permeability is closely related to the pore or air void present in the concrete where the deleterious objects can travel through the pore to damage the concrete ([Basheer et al., 2001](#)). According to [Mo et al. \(2015\)](#), OPS concrete was found to possess lower permeability than normal concrete, after performing water absorption and sorptivity tests. SEM analysis showed that there were fewer micro-cracks present and formed in the interfacial transition zone of concrete due to the softer properties of OPS aggregates which eventually reduced the permeability of concrete. In addition, [Shafigh et al. \(2011\)](#) designed several mix proportions of OPS concrete and conducted water absorption test for each mix design. The water absorption of OPS concrete was found in the range of 3%–6% which was below 10% and was graded as good concrete.

The majority of the research showed that the use of OPS as coarse aggregate in concrete could increase the permeability of concrete to water. The initial surface absorption of OPS concrete was determined to be 12%–40% more than the normal concrete, indicating higher concrete permeability ([Mannan and Ganapathy, 2002](#)). It was explained in the literature that the OPS aggregates contained large amount of pore and possessed high capacity of absorption which caused the OPS concrete to absorb more water. Furthermore, the flaky irregular shapes of OPS aggregates affected negatively the OPS concrete in achieving full compaction, resulting in the formation of void in the concrete ([Mannan and Ganapathy, 2004](#)). Besides, [Khankhaje et al. \(2016\)](#) showed that the high permeable property of OPS is appropriately to be used in producing pervious concrete where water can travel through easily. This type of concrete could be used for flatwork application as the permeable concrete allowed rainwater to pass through. The results show that the concrete permeability increases as the amount of OPS included increases.

The increment of concrete permeability as a result of using OPS could be minimized by adding supplementary cementitious materials. For instance, [Mo et al. \(2016a\)](#) incorporated ground granulated blast furnace slag (GGBS) in OPS concrete. It was found the water absorption rate of OPS concrete with GGBS reduced at replacement level of 20%–60%. The GGBS enhanced the interfacial transition zone of the cement matrix and aggregate in the concrete by densifying the pore structure.

Shrinkage

Shrinkage of concrete occurs when there is change in volume of the concrete. The volume change is mainly attributed to the movement of water in concrete where the water may be lost as a result of evaporation from wet concrete (plastic shrinkage), drying of hardened concrete (drying shrinkage) or hydration process (autogenous shrinkage) in concrete ([Silva et al., 2015](#)). Cracks will form on the surface of hardened concrete due to shrinkage and this may ease the entrance of harmful objects. Drying shrinkage of OPS concrete was studied by [Shafigh et al. \(2014a\)](#). In the investigation, drying shrinkages of OPS concrete and expanded clay (EC) concrete were compared. It was found that the initial drying shrinkage value of OPS concrete was twice more than the EC concrete. The difference between the shrinkage of two concretes slightly decreased with time. The reason could be due to the OPS concrete possessed lower elastic modulus which exhibited higher drying shrinkage than the EC concrete.

[Mannan and Ganapathy \(2002\)](#) found the drying shrinkage of OPS concrete was 6% and 14% higher than the control concrete at the 28th and 90th day respectively. According to the authors, concrete made with lightweight aggregates generally exhibited approximately 50% more shrinkage than the normal weight concrete. Also, lightweight aggregate such as OPS have open textured and irregular surface which gives the concrete a higher shrinkage value. Another study showed that OPS concrete exhibited more shrinkage than conventional concrete ([Mo et al., 2016a](#)). The lower rigidity of OPS aggregates offered lesser restraint to the deformation caused by the shrinkage of concrete. The smooth curved surface of OPS aggregates also provided less resistance to shrinkage movement in the concrete. In the study, GGBS was introduced to improve concrete performance. However, the results showed that the incorporation of GGBS increased the concrete shrinkage. It was implied in the literature that GGBS slowed down the hydration process which allowed more time for free water to escape from the pores.

[Traore et al. \(2018\)](#) found that the average shrinkage deformation of OPS concrete was two times higher than the control concrete. This was mainly due to the lower elasticity of OPS aggregates which could not resist distortion of cement paste caused by shrinkage. In their study, the effect of OPS aggregates treatment on the concrete shrinkage was investigated, namely treatment with lime (CH), sodium silicate (SS), polyvinyl alcohol (PVA), heat (TH) and OPS saturation (SAT). The OPS concrete treated with SAT method was found to have the lowest shrinkage deformation. The authors implied that there was free water available in the treated OPS aggregates which maintained the internal humidity of concrete, thus reducing concrete shrinkage.

Thermal Conductivity

Thermal conductivity of concrete is essential to be examined because it determines the insulation ability of a building. Concrete thermal conductivity refers to the capability of the concrete to transfer heat through the material. Due to the popularity of using various waste materials such as OPS in concrete, thermal conductivity of concrete has become an attentive study by recent researchers (Misri *et al.*, 2018). Based on the experimental study conducted by Okpala (1990), thermal conductivity of OPS concrete was less than normal concrete and categorized as poor conductor. This was attributed to the high porosity of the OPS concrete where the air voids minimized the propagation of heat.

Alengaram *et al.* (2013b) used OPS aggregates to make foamed concretes and determined their thermal conductivity. It was shown that the OPS foamed concrete possessed approximately 56% lower thermal conductivity than the conventional brick. OPS aggregate was porous which contained large amount pores that could entrap air. Apart from that, the thermal conductivity of concrete depended on its density whereby thermal conductivity would decrease with the density. Another investigation made by Liu *et al.* (2014) showed that both foamed and non-foamed OPS concretes were having lower thermal conductivity than block and bricks. It was explained that the OPS foamed concrete had cellular microstructure which prevented the loss of heat. Also, as the air was poor in conducting heat, this had contributed to the lower heat conductivity in porous OPS concrete.

Furthermore, Serri *et al.* (2014) studied the influence of cement content on the thermal conductivity of OPS concrete. It was shown that the heat conductivity of OPS concrete increased when the cement content increased. When more cement was added, more C-S-H gels were formed as a result of hydration which filled up the concrete pores, thus providing more solid medium for heat transfer. In another study, it was found that the thermal conductivity of OPS concrete were approximately 50% lower than conventional concrete (Traore *et al.*, 2018). The low value could be attributed to the better insulating properties of OPS aggregates. The authors also discovered that the OPS aggregates treated with saturation method exhibited the lowest thermal conductivity. This was due to the extra porosity created as a result of OPS pre-wetting which increased the air contents that insulated the heat.

Future Applications and Challenge

In the past decades, significant research interest concentrated on oil palm shell (OPS), particularly in South East Asia, as it was abundantly generated as solid wastes from agricultural industry. The present study provides framework for further investigation of OPS concrete, in terms fresh properties, hardened properties and long term durability. The following statements are some recommendations for future application regarding OPS in concrete industry.

- Past research has shown that OPS is suitable to be used as coarse aggregates both in crushed and uncrushed states. However, no research has been done to crushed OPS to be used as fine aggregates for concrete production.
- Currently, all the mix designs of OPS concrete are based on ACI and trial and error method. The target slump value and compressive strength cannot be achieved by following ACI method. As such, the development of simple performance based guideline for proportioning OPS concrete mix design is required.
- It has been reported in literature that the production of high strength OPS concrete requires relatively large amount of cement. It will be more beneficial to develop OPS concrete as self-compacting concrete which eliminate the requirement of concrete vibration to compensate the cost of extra cement requirement.

Conclusions

OPS is easily available from oil palm plantations, particularly in Malaysia and Indonesia, and therefore can be extensively supplied. It has attracted interest in research field. Based on the literature review above, the following conclusions can be drawn:

- OPS has significant potential to be used as lightweight coarse aggregates in concrete production.
- The workability of OPS is relatively poor when it is fully replaced with coarse aggregates. Addition of superplasticizer is capable of improving the concrete workability. The inclusion of optimum supplementary cementitious material such as silica fume and fly ash can slightly improve the OPS concrete workability.
- The compressive strength of OPS is highly dependent on individual strength of OPS, and the bond between the OPS and the matrix in the interfacial transition zone. The pre-treatment of OPS by using can polyvinyl alcohol (PVA) solution can improve the compressive strength of concrete by 40%.
- The concrete made by OPS aggregates is highly permeable to water since the concrete contains more air void. However, incorporation of supplementary cementitious material such as GGBS is capable of reducing the concrete permeability as it can densify the concrete pore structure.
- Since the OPS aggregates are soft and having lower modulus of elasticity, the OPS concrete experiences higher deformation due to shrinkage. Yet, the treatment of OPS through saturation (SAT) method can reduce the shrinkage.
- The thermal conductivity of OPS concrete is lower than the conventional concrete. This is due to high porosity of OPS aggregates that can entrap air to insulate heat energy.

Acknowledgement

The authors would like to acknowledge the research funding from Curtin Malaysia Research Institute (CMRI).

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Further Reading

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Recyclability of Packaging Materials for Domestic Applications

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Introduction

The polymer waste is a form of solid waste with has high impacts on the environment (Takoungsakdakun and Pongstabodee, 2007). The reported studies highlights that annual consumption of polymers have increased up to 20 times in present time from few million tons in 1950–2004 and it is still increasing. There is no authentic estimation available on the total amount of plastic waste generated, however, it is estimated that 70% of total plastic consumption is discarded as a waste, thus approximately 5.6 million tons per annum (TPA) of plastic waste is generated in developing country like India, which is about 15,342 tons per day (TPD). A survey has been conducted to analyse demand break up of plastic by types (see Table 1).

As observed from Table 1, PVC/PP/HDPE/LDPE contributed more toward the consumption of plastic. Due to highly versatile in nature, lighter than competing materials and customized abilities, are the major reasons for their usage as a packaging material. Further the increase in polymeric waste, creating a pressure to limit its usage (Mølgaard, 1995).

Presently, the scenario has changed and polymer packaging material waste can be recycled by different processes/methods (i.e., primary, secondary, tertiary and quaternary) along with the various identification/separation techniques. Most of the polymer waste originated from post-consumer based plastic materials. The literature reported that, recycling of post consumed plastic materials; find new possibilities in the area of product development (Lei et al., 2007; Marzouk et al., 2007; James et al., 2007). Among these HDPE and LDPE are most commonly used plastic packaging materials in commodities. Recycling of these materials is the only possibility to manage polymeric waste.

The recycling consists of four tasks namely collection, separation, reprocessing and marketing (Mølgaard, 1995; Shen et al., 1999). Recycling of polymer requires less energy in comparison to production of same polymer from virgin material (Curlee and Das, 1991). Studies showed that, some recycled polymers has established a great market value in the field of composites (Muzzy, 2006), auto parts (Scheirs, 1998), soil reinforcement (Murray et al., 2000), artificial implants, healthcare applications, medical delivery systems, removal of bacteria and water desalination (Subramanian, 2000). Therefore recycling is a rising issue in recent years due to great use of plastic (Gondal and Siddiqui, 2007). The main reasons of this growth are strength, user-friendly design, fabrication capabilities and low density. Researchers have also reported various recycling techniques for the preparation of products like plastic lumber (Breslin et al., 1998), composites by reinforcing metallic/ceramic materials etc., (Singh and Singh, 2016). However, reinforcements in polymer material can be performed economically by the mechanical recycling (primary and secondary).

Polymeric Packaging Materials

Various polymers/plastic based materials are used in daily life and may be considered as a waste after use. Two basic categories of plastic are designated as thermosetting (long strands) and thermoplastic (short link) materials. The 6 main families of thermoplastics used as packaging material are: LDPE, HDPE, polypropylenes (PP), polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PVC). A part from above acrylonitrile butadiene styrene (ABS) is a strong material for making plastic bodies such as water purifier body, laptop body etc. Table 2 shows some of the applications of recycled/virgin thermoplastics.

Although, virgin plastics are easily available in the market and can be processed with conventional methods, but in terms of energy requirement these plastics are on the verge of elimination of fossil fuels. First, plastics can be regarded as a form of stored potential energy as each year, producing virgin plastics requires 4% of the world's oil production equivalent to 1.3 billion barrels a year (Kreiger et al., 2014). So, it is always advisable to reuse and recycle the plastic waste.

Table 1 Demand breakup of plastic

Sl. No.	Polymeric material	TPD
1	Other polymeric materials	2
2	PS	3
3	LDPE	5
4	LLDPE	18
5	HDPE	20
6	PP	24
7	PVC	28

Source: Chemicals & Petrochemical Statistics, Analysis by Tata Strategic.

Table 2 Thermoplastic commercial applications

<i>Sl. No.</i>	<i>Thermoplastic</i>	<i>Application</i>
1	PVC	Clothing Automobile Construction Medical appliances Electrical fittings Packaging
2	PLA	Feminine hygiene products Decomposable packaging stuff Bags/cups Upholstery Garments (Disposable) Awnings Diapers (Disposable)
3	ABS	Automotive components Vent pipes Musical instruments Recorders and piano movements Golf club head
4	PS	Plastic cutlery Dinnerware CD cases Plate frames Smoke detector housings
5	PC	Telecommunications/electrical hardware
6	PET	Packaging film PET Bottle Carpet yarn Engineering plastic Filaments Non-woven Packaging stripes Staple fibre
7	PA	Tire Cords Rope Thread Brushes Bearings Gears Cams
8	PP	Clear bags Carpets Rugs and mats
9	LDPE	Packaging for hard drives/screen cards/optical disc drives Trays General purpose containers
10	HDPE	Toys Utensils Bottles Pipe and processing equipment Cable insulations

Note: Bakker, E.J., Rem, P.C., Fraunholz, N., 2009. Upgrading mixed polyolefin waste with magnetic density separation. *Waste Management* 29 (5), 1712–1717.

PVC is a universal polymer which can be processed into a wide variety of short-life or long-life products (Sadat-Shojai and Bakhshandeh, 2011). Among these major types of plastics, the consumption of PVC contributes to 12% of total demand. Global plastics production capacity of PVC was about 61 million tons in 2013 (Kou *et al.*, 2009). Rigid plasticized PVC is commonly used in pipes, window framing, floor coverings, roofing sheets, and cables; thereby it is discarded at a high rate (Janajreh *et al.*, 2015). HDPE is a better material than the LDPE; it is most widely used material. It takes 1.75 kg of petroleum to make 1 kg of HDPE. It is commonly recycled material. Earlier, there was a major recycling of LDPE (low density polyethylene) but it takes high energy requirement of making LDPE as

compare to HDPE (Hamad *et al.*, 2013). Another form of HDPE is available, called rHDPE (recycled HDPE), HDPEi completely came from industrial waste (Lu and Oza, 2013) and is easily available from post-consumer based products (bags, glass, cups, bottles) (Achilias *et al.*, 2009). It is basically composed of carbon and hydrogen atoms joined to form a high molecular weight product (Hamad *et al.*, 2013). Being linear chain material it has higher strength than LDPE. HDPE is used for various industrial applications (because of good mechanical properties) and emerging as a potential structural matrix (Jaggi *et al.*, 2014). Most of researchers dealt with the HDPE as it is easy to recycle and contribution of HDPE in home products or commodities is highest amongst others. So post-consumer based waste plastic is HDPE based. LDPE is very less used polymer in these days because of its manufacturing requirement and other properties constraint. LDPE requires extremely high pressures. This high-pressure polymerization creates polyethylene with many branches; the branches are created due to intermolecular and intra molecular chain transfer during polymerization. The utility of low-density polyethylene is limited due to the high number of branches leading to poor strength properties and requirement of extreme pressure condition for its production (Kumar *et al.*, 2011). The structure of this LDPE is less crystalline as compare to HDPE with little or no branching (Hamad *et al.*, 2013). Plastic bottles are usually made up of PET (Welle, 2011). Use of plastics as bottles is increasing throughout the world (Kalantar *et al.*, 2012). But recycling of materials based on PET is often very complex and it requires heavy machinery and high investment, so most of the recycler is not interested in recycling of plastic materials based on PET.

Recycled Polymeric Packaging Materials for Additive Manufacturing Applications

Extrusion techniques are commonly used for the processing of polymeric based composites, which accommodates agricultural raw materials, food, waste, meat, and leather, as well as other raw materials (Mikulionok and Radchenko, 2012). Presently, both single and twin screw extruder are available for the recycling of polymeric materials.

Case Study

Among various additive manufacturing technologies, Fused Deposition modeling (FDM) is one of extensively used process for modeling and prototyping applications (Boparai *et al.*, 2016). Singh *et al.* (2016a) reported use of commercial FDM setup (U-Print model, Stratsys, USA) for using recycled thermoplastics. The work mainly focused on the developing alternate feed stock filament (having reinforcement in various combinations/proportions of particle sizes of Al_2O_3 in waste Nylon-6). The effect of particle size on mechanical properties of developed filament has been recorded. The single particle size (SPS), which have particle size of 100 μm , double particle size (DPS) represents particle sizes 100 μm and 120 μm , in equal proportion (by weight) and triple particle size (TPS) consists of three particle sizes (100 μm , 120 μm and 150 μm) in equal proportion (by weight) were explored. Here, the main focus was on the enhancement of FDM domain by developing alternative feedstock filament, with tailor made properties. The recyclability of waste Nylon 6 was carried out for additive manufacturing applications. The selected proportions of Al_2O_3 and waste Nylon 6 along with melt flow index (MFI) values are tabulated in Table 3. The average of three experimental runs for MFI and mechanical properties were carried out. It should be noted that MFI is required to estimate the processing conditions of alternative feedstock filament in FDM. The standard/commercial material for FDM is ABS (P-430 grade). Therefore it is necessary that MFI value of alternative material should be equal to standard material, so that FDM can process the alternative material without making any change in its software and hardware. The feedstock filaments of selected compositions/proportions were fabricated on single screw extruder. The mechanical properties such as percentage elongation, Young's Modulus, yield stress etc. were determined according to ASTM D 638 standard on universal testing machine.

In another study, Singh *et al.* (2016b) collected waste of HDPE and LDPE from local market. The process started with the washing of polymer waste in order to remove the contaminants and dirt particles. After washing of polymer different samples of HDPE and LDPE were taken for the MFI testing. Further separate case studies for HDPE 100%, HDPE90%+10%Fe, LDPE 100% and LDPE 94%+6% Fe powder reinforcement have been reported. From this study it has been concluded that polymer waste mainly HDPE and LDPE can be successfully used for structural engineering applications by preparing filament wire with screw extrusion route along with the metal powder reinforcement. The mechanical properties like (peak elongation, break strength and shore D hardness) and metallurgical property like porosity can be controlled based upon specific application. In case of reinforced HDPE i.e., 90% HDPE and 10% Fe powder, the mechanical properties obtained were better.

Subsequently, Boparai and Singh (2017) investigated the wear properties of rapid tooling (RT) with nano scale fillers for grinding applications. The RT has been prepared by using bio compatible composite material (BCCM) feed stock filament (consisting of waste Nylon6 as a binder, reinforced with biocompatible nano scale Al_2O_3 particles) on fused deposition modeling (FDM) for the development of grinding wheel having customized wear resistant properties. A comparative study has been conducted under dry sliding conditions in order to realize the tribological characteristics of FDM printed RT of BCCM and commercially used acrylonitrile butadiene styrene (ABS) material. Finally, it was concluded that, the FDM printed RT of proposed BCCM feedstock filament are more suitable for grinding applications especially in clinical dentistry.

Boparai and Singh (2018) also highlighted the thermal characterization of ABS-Graphene blended three dimensional (3D) printed functional prototypes by fused deposition modeling (FDM) process. These functional prototypes have some applications as an electro-chemical energy storage device (EESD). Initially, the suitability of ABS-Graphene composite material for FDM applications has been examined by melt flow index (MFI) test. After establishing MFI, the feedstock filament for FDM has been prepared by an extrusion process. The fabricated filament has been used for printing 3D functional prototypes for printing of in-

Table 3 MFI and mechanical properties of Al_2O_3 and waste Nylon 6 proportions

	<i>Nylon 6 (in wt%)</i>	<i>Al_2O_3 100 grade (in wt%)</i>	<i>Al_2O_3 120 grade (in wt%)</i>	<i>Al_2O_3 150 grade (in wt%)</i>	<i>MFI (g/10 min)</i>	<i>Percentage elongation</i>	<i>Tensile strength (kg/sq mm)</i>	<i>Yield strength (kg/sq mm)</i>	<i>Young's modulus (kg/sq mm)</i>
SPS	50	0	50	0	5.23	16.63	2.68	0.33	69.82
	60	0	40	0	6.61	10.9	3.99	0.96	55.10
DPS	50	25	25	0	4.29	6.88	3.25	0.74	88.90
	60	20	20	0	4.72	5.45	3.38	0.31	70.22
	50	25	0	25	2.82	5.35	2.63	1.65	47.12
	60	20	0	20	4.15	3.55	3.71	0.99	36.70
	50	0	25	25	3.25	15.6	4.54	1.14	28.10
	60	0	20	20	5.82	7.2	4.51	3.18	21.68
TPS	50	16.66	16.67	16.67	4.12	8.83	3.12	1.82	55.71
	60	13.34	13.33	13.33	4.80	4.7	2.35	1.78	43.14
Virgin (Nylon-6)	—	—	—	—	10.3	2–150	4–33	—	112–1630
Virgin ABS (P-430)	—	—	—	—	2.41	3	3.77	—	232

house EESD. The differential scanning calorimeter (DSC) analysis was conducted to understand the effect on glass transition temperature with the inclusion of Graphene (Gr) particles. It has been observed that the reinforced Gr particles act as a thermal reservoir (sink) and enhances its thermal/electrical conductivity.

Summary and Outlook

Plastics have been one of the materials which entered every production sector of our lives such as automotive, packaging, aerospace, building, furniture, toys, clothing, medical etc. This is mainly attributed due to its versatility and relatively low cost. The serviceability of plastic products is limited and the use of plastic packaging materials in daily life makes a vast plastics waste stream that causes a serious environmental problem. Therefore, suitable waste management strategy is one of the important aspects for sustainable development. The reinforcement of fillers (metal, ceramics, fibers etc.) in recyclable polymeric packaging materials such as HDPE, LDPE, Nylon etc. not only minimize plastic waste but also makes the product economical. The reported case studies highlighted some of the fields for active research in additive manufacturing with recycled packaging material along with gaps that requires further attention.

See also: Bio-Polymeric Packaging Material for Packaging of Raw Food

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Recycled Polypropylene-Nanoclay Composites – Mechanical Properties

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Introduction

Engineering materials were typically divided into several classification, such as polymer, metal, ceramics and composites. Polymer was chosen in many types of applications as a result of this material outstanding properties such as cost effective material, low density, and better at certain mechanical properties. Moreover this material is easy to be processed and recycled as well. After the polymer had been used, most of the waste shall be dumped in landfills. Microbes need long time to decomposition this material because most of the polymer is non-biodegradable. Since 1960, a dramatic growth has been informed, that polymer waste had increased not less than 13% of community solid waste stream. Hence, polymer recycling had triggered the researchers to study the effect and method of polymer recycling towards the economy and environment (Zare, 2013). To quote one example, a research had been carried out by mixing the recycled polypropylene with the virgin material and using Taguchi method as the technique for improve the quality of part that created (Mehat and Kamaruddin, 2011). Another approach of recycling also had been discovered, whereby the waste polymer can be recycled to valuable chemical feedstock through chemical recycling process. These feedstock can be used in refineries and petrochemical industries (Salmiaton and Garforth, 2011).

It is easy to recycle a pure polymer hence the properties and handling can be predicted easily. But currently, the growing consumption of polymer products creates the urge to combine polymer with fillers. Nanotechnology is expected to become the imperative technology in the current century. Hence, many researchers tried to develop the application of nanofillers in the polymers such as polypropylene nanoclay nanocomposites, whereby substantial enhancements of mechanical, thermal, optical and barrier properties were gained by using the nanofillers. More than that, the addition of the nanofiller could proliferate the interphase surface of the molecules in matrix, and apparent area to volume ratio as well (Zare, 2013).

Another main issue regarding the high interest towards nanocomposites is the difference between nanofillers and micro fillers. It was found that outstanding advances could be attained with low content of nanoclay, deprived of additional charge, increment of density or decreasing the light transmission properties of matrix. Nonetheless, recycling of these nanocomposites materials is not that easy. Further research had been studied and required, to determine the current status of polymer recycling in nanotechnology, specifically for polypropylene nanoclay, to lead more research to cover the manufacturing industry need and interest (Zare, 2013).

Therefore, this article was made specifically to deliberate details about the recycling of polypropylene nanoclay composites. After a brief introduction, explaining the effect of clay loading, preparation and the application of this material, a review of mechanical properties for this material and its recycled compound shall be elucidated. The final conclusion and the future trend will be also delivered at the end of this article.

Polypropylene-Nanoclay Composites: Clay Loading, Preparation, and Application

Typical nanocomposites materials strengthened their matrix with one or more nanomaterials with the purpose to improve mechanical, tribological, physical, and thermal properties. PPNC or polypropylene nanoclay nanocomposites usually promotes improvement in properties such as high modulus, increased strength and heat resistance, decrease gas permeability and flammability, and it gets a lot of attention because of it (Othman *et al.*, 2013).

Generally PPNC has better materials properties among the other virgin polymer, such as the increase of modulus, strength and heat resistance, even with smaller fraction of clay content could change the properties with various processing condition. According to a review, a PPCN containing 1 wt%, 3 wt%, 5 wt% and 7 wt% of nanoclay have been studied before, and it was found that the tensile strength of PPCN had expanded proportional to the expanding in nanoclay content from 0 to 5 % of weight. As for composite with content more than 5 % weight, there is no significant improvement. The findings continued with dynamic mechanical analysis, with the results show that higher progression of modulus was obtained within the research's temperature range. Most nanocomposites which contained nanoclay also reducing the flammability behavior of the material, and the heat release rate as well. The main issue before utilizing this material in manufacturing industry is the preparation method to blend the polymer and nanoclay. The in situ intercalative polymerization and polymer solution intercalation will utilized the solvent, and melt intercalation was used by using twin screw extruder. Each method has its advantages and disadvantages to produce PPNC with good quality. However, melt intercalation was preferred as the standard in producing PPNC (Othman *et al.*, 2014). Moreover, higher melt strength and viscosity could be attained by using twin screw compounder during this preparation method, but certain provision need to be scrutinized in term of discrepancy of material dimension after leaving the die. This problem is critical in producing sheets or profiles shapes (Hamzehlou and Katbab, 2007).

In melt intercalation, there are several processes involve in this technique, such as annealing, and heat the mixtures of polypropylene and nanoclay to the melt point. In annealing the polymer chains of bulk polymer melt is mixed into the galleries between the silicate layers in annealing process. The polymer chain penetration rate into silicate galleries influence the various

nanocomposites with structures from intercalated to exfoliated that can be obtained. The experimental results show that polymer intercalation results are highly depend on the function of silicates and their constituent interactions. This technique has big advantages over in situ intercalative polymerization and polymer solution intercalation as this method is nonthreatening to the environment due to the absence of organic solvents. Moreover, injection molding method is very useful in the business, this method can create extensive amount of plastic products and furthermore can spare the time and the cost to make the product, and now more of plastic industries use injection molding method (Othman *et al.*, 2014).

During preparation of these nanocomposites, the amount of clay also plays a major role in affecting the properties of PPNC. For example, increasing the clay content in with a well-dispersed two-component system, can cause the impact strength to decrease while the crystallization kinetics and the spherulite size remained almost the same. On the other hand, an intercalated three-component system containing some dispersed clay as well as the clay tactoid, showed a much smaller size of spherulites and a slight increase in impact strength with increasing the clay content (Svoboda *et al.*, 2002).

Generally the main advantage of PPNC is this material is a lightweight material and more economical when compare with other material. It also very competitive with other commodity plastics that already exist in some applications. This material can be used in many part of automotive and food packaging industries. Henceforth, with the good mechanical properties improvement, ease in preparation the material and simple processes, the recycling process for this material could open the gate of a new era for plastic and composites (Sinha Ray and Okamoto, 2003).

Recycling of Polypropylene-Nanoclay

Until today, waste polymer treatment still working hard to increase their efficiency. Combustion and land fill are the last choice, because it is not environmental friendly. Hence, recycling will be the preferred option. Many method of recycling can be considered such as primary, mechanical, chemical or feedstock recycling and energy recovery as well (Sadat-Shojai and Bakhshandeh, 2010). According to a data, in year 2015, it is not more than 9.1 % of recycling rate achieved for the recycled plastic, which is relatively insignificant (see “Relevant Websites section”). The main reason of plastic’s low recycling rate is the separation process (Burat *et al.*, 2009). Plastics can be separated by the numerical coding system according to The ASTM International Resin Identification Coding System (ASTM D7611/D7611M-18, 2018). Other than separation process, another reason is the degradation of polymer structure, which can caused the decrease of properties (Goto *et al.*, 2006). To overcome these limitations, it seems that the easiest way to recycle the waste plastics is by utilizing the development of blends and composites from recycle materials.

Most of polymer especially polyolefins could be recycled. However, the most important factor of recycling process is cost and difficulty, whereby these factors needs to be reduced for economical reason. The recycling has several process such as sorting, collecting, cleaning and reprocessing. Recycling process for polypropylene begin by separating polypropylene with other plastic polymers to allow for recycling. Separation is obtained from the sink-float method, it works by distinguishing polypropylene density with other polymers, polypropylene will float and not with other material. Polypropylene has specific density of 0.93–0.95 g/cm³, polypropylene must also be separated by color before processing. If polypropylene is uniform, it will be shredded or chopped into pieces that can be sold again into recycled feedstock. Polypropylene can be further processed, mixed with other materials to produce a solid plastic pellet with an extruder (Thomas, 2012).

However, when the polypropylene matrix was been mixed with certain filler, the recycling process will be slightly different, as well as the outcomes. For instance, a research had been carried out regarding the preparation and characterization of recycled polypropylene that had been used as the matrix for nanocomposites. Based on the findings, it was found that the nanocomposite of recycled polypropylene and Cloisite 15A nanoclay had provided the highest improvement in mechanical properties, compared with other prepared samples. This research also designates the important of clay loading, compatibilizer and the processing parameter as well (Cengiz, 2008).

More research had been performed about the recycling process of polypropylene and the mechanical properties of recycled polypropylene/organoclay nanocomposites. Based on the researcher’s findings, some of the researcher suggest using a high temperature profile could increase the viscosity and modified the viscoelastic properties, but causing a reduction of mechanical properties. As for the differential scanning calorimetry analysis, it was found that the crystallization temperature and crystallization time decrease as a function of the number of extrusion cycles. Even though such drawbacks happened during recycling, there is a room to improve the properties of this recycled material. The improvement can be attained, by using the organophilic layered silicates and maleic anhydride grafted polypropylene compatibilizer. This step can improves significantly the mechanical properties of the recycled polypropylene (Tri Phuong *et al.*, 2008).

A method that could be considered to recycle polypropylene nanoclay is the reprocessing extrusion. Few researchers have tried to determine the influence of reprocessing or multiple extrusion steps on the properties of recycled polypropylene nanoclay. For an example, a research revealed that after four cycles, the thermal and mechanical properties of this material were decreasing as been expected. The more important fact is during recycling, the structure of this material was severely affected, which made the recycling process far more complex than traditional polymer (Touati *et al.*, 2011). However, the efforts of exploration the potential of this material to be recycled had been continued, even with limited number of cycles, lack of nanocomposites microscopic behavior analysis (Oikonomidou *et al.*, 2012), no comparison between the pristine, polypropylene/compatibilizer and complete polypropylene nanoclay, virgin PP and PP/compatibilizer mixtures, also short of findings in terms of mechanical and morphological characteristics (Silvano *et al.*, 2013). Then, the research continues with a study about polypropylene nanoclay, which was subjected to repeating 15 extrusion

cycles. Based on the results, the increment of processing cycles had reduced the resistance towards impact and Young's modulus. The properties decrease, due to poor filler-matrix interaction that was originated from the degradation of clay (Delva *et al.*, 2014).

Therefore, the most important notes about the reprocessing process is the degradation of thermal, thermal oxidation and thermal mechanical properties, due to aggressive shear and modification of the filler morphology. Hence, this process was influenced by several factors such as the composition and nature of raw materials, shear level, temperature, polluting agents and number of cycles (Dorigato and Pegoretti, 2013). These factors need to be taken care off, before proceeding the recycling process of polypropylene nanoclay nanocomposites.

Mechanical Properties of Recycled Polypropylene Nanoclay

The fundamental that comprise the reactions to any applied load is called the mechanical properties. The usefulness of a material and their range of service life can be predicted by these properties. Material identification and classification also can be determined. Typical properties that are commonly analyzed are strength, ductility, hardness, impact resistance, and fracture toughness. Mechanical properties are generally specific to product form such as sheet, plate, extrusion, casting, forging, and etc. Additionally, it is common to see mechanical property listed by the directional grain structure of the material (see "Relevant Websites section").

A research had been conducted specifically to study the effects of reprocessing cycle of polypropylene-nanoclay nanocomposites (PPNC) towards its mechanical properties. Research started from performing injection molding process towards PPNC. The flow of mechanical test was displayed in Fig. 1 (Othman *et al.*, 2017).

In this experiment, the average tensile strength value was obtained for 0%, 25%, 50%, 75%, and 100% recycled polypropylene nanoclay. The result of average tensile strength is illustrated in Table 1 (Othman *et al.*, 2017).

Table 1 showed that the sample of 0% PPNC, trial no. 4 produces the highest tensile strength with value 29.556 MPa. As for the sample of 25% PPNC, the highest value is trial no. 4 with value of 29.118 MPa. The highest value of 28.742 MPa at trial no. 4 was obtained from 50% PPNC, and the same trial number produced the highest value of 28.954 MPa for 75% of PPNC. Finally the highest value obtained for 100% PPNC was 28.831 MPa (Othman *et al.*, 2017).

For further research, samples of polypropylene nanoclay were produced and then measured using Shore hardness test and Charpy impact strength test method. Then, the product was crushed back into pellets for reprocessing cycles. The reprocessing process was repeated for four times. For comparative purpose, neat polypropylene (PP) also underwent the same reprocessing process as PPNC. Table 2 shows the results of hardness and impact strength obtained from the experiment (Othman *et al.*, 2016).

The highest hardness number obtained was 62 shore which was the result for the first reprocessing cycle of neat PP while the lowest hardness number obtained from the experiment was 57 shore which was the result for the fourth reprocessing cycle of PPNC. The highest impact strength result obtained was 0.40 J/m² which was the result for the first reprocessing cycle of neat PP

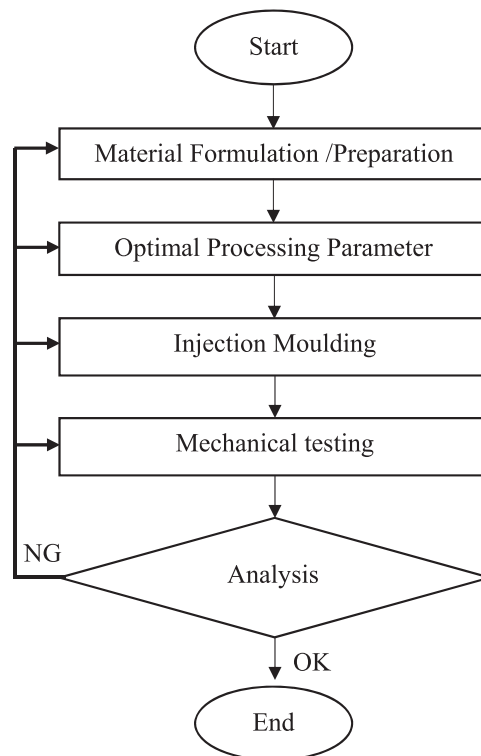


Fig. 1 The flow of mechanical test for recycled PPNC.

Table 1 Tensile strength value for 0%, 25%, 50%, 75% and 100% recycled polypropylene-nanoclay composites

Trial no.	MT (°C)	PP (%)	SS (%)	FT (s)	Tensile strength (MPa)				
					0% PPNC	25% PPNC	50% PPNC	75% PPNC	100% PPNC
1	160	60	50	1	29.457	28.858	27.730	28.615	28.320
2	160	70	60	2	29.328	29.096	27.620	28.193	28.246
3	160	80	70	3	28.842	28.791	28.045	28.828	27.763
4	165	60	50	3	29.556	29.118	28.742	28.954	28.187
5	165	70	60	1	28.808	28.621	28.558	28.367	28.107
6	165	80	70	2	29.315	28.438	28.454	28.420	27.765
7	170	60	50	2	29.386	27.456	28.611	28.831	26.726
8	170	70	60	3	26.384	28.694	28.485	28.696	28.217
9	170	80	70	1	27.604	28.449	28.090	27.960	28.036

Note: Othman, M.H., Aisha, M.M, Khamis, S.Z., 2017. Injection moulding reprocessing cycles effects towards mechanical properties of polypropylene nanoclay, International Journal of Advances in Mechanical and Automobile Engineering 4 (1), 89–95.

Table 2 Average hardness number and impact strength of PPNC and PP after each cycle

Material	Hardness number (Shore)				Impact strength (J/m ²)			
	1st Cycle	2nd Cycle	3rd Cycle	4th Cycle	1st Cycle	2nd Cycle	3rd Cycle	4th Cycle
PP	62	61	61	59	0.40	0.32	0.29	0.28
PPNC	61	60	58	57	0.19	0.21	0.20	0.18

Note: Othman, M.H., Hasan, S., Ibrahim, M.H.I., Mat Sedik, N.A.N., 2016. Compounding of recycled clothes with polypropylene-nanoclay for injection molding feedstock, In: Proceedings of the Putrajaya International Built Environment, Technology and Engineering Conference (PIBEC2016), 24–25 September 2016. Hotel Bangi-Putrajaya, Bangi, Malaysia.

while the lowest impact strength result was 0.18 J/m² which was the result for fourth reprocessing cycle of PPNC. The findings of this research had been concluded that when the reprocessing cycle of PPNC increase, the hardness number and impact strength of PPNC decrease. The hardness number of PPNC decreased in a total of 6.56% from the first reprocessing cycle to fourth reprocessing cycle. Meanwhile, for impact strength of PPNC, the declination happened starting from second reprocessing cycle to fourth reprocessing cycle. The total declination was 14.29%. The impact strength of the first reprocessing was lower than the second reprocessing cycle by 10% due to some errors. It can be concluded, reprocessing cycle has affected the impact strength of PPNC more than it has affected the hardness of PPNC. However, when compared to neat PP, neat PP has higher hardness number and impact strength than PPNC (Othman *et al.*, 2016).

Conclusion and Future Trends

As for conclusion, this article had outline the important information related to the recycling of polypropylene nanoclay composites. The first part of this article is a brief introduction about polymer recycling. After that, an explanation was made about the effect of clay loading, preparation and the application of this material. The information was important because it will affect the recycling process and performance. Then, a review of mechanical properties for this material and its recycled compound have been elucidated.

In term of future trends, more studies were needed to gain more success in term of attaining good properties for recycled polypropylene, as well as improving the cost efficiency to make the process competitive. The good properties could be achieved, by focusing more towards the interaction and interfacial adhesion of polypropylene nanoclay. The use of compatibilizer, functionalizer and surface modifier could assist the process. More research was also needed to improve the filler through modification and combination of other material as well. Other advanced preparation method and optimization through statistical approach also the key points that should be considered for future development (Zare, 2013). More than that, efforts were also needed, in term of providing the correct tools for recycling such as using the sustainable material management, waste reduction model and reuse and recycling opportunities and demolition, so that the recycle process of polymer nanocomposite could be utilized more productively over their entire life cycles (see “Relevant Websites section”).

See also: Impact Behaviors of Acrylonitrile Butadiene Styrene and Polylactic Acid Materials for Topological Industries

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Recycling and Downstream Processing of Aluminium Alloys for Automotive Applications

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Introduction

Energy Consideration and Sustainability of Aluminium Alloys

The aluminium industry is making continuous improvements in the environmental efficiency of producing aluminium through primary and secondary processes. According to Miller *et al.* (2000), A large difference in energy requirements for production of primary aluminium (113 GJ/t) vis-à-vis secondary aluminium (13.6 GJ/t) has prompted recycling of aluminium alloys. The benefit of recycling to the aluminium industry has recently been addressed numerically by Choate and Green in which they showed that production of primary aluminium requires ~45 kWh of energy and emits ~12 kg of CO₂ for each kilogram, whereas the studies of Miller *et al.* (2000) show that secondary aluminium produced from scrap requires only ~2.8 kWh of energy and emits ~0.6 kg of CO₂ for each kilogram of aluminium recovered. A 10% increase in aluminium end of life recycling rates decreases industry greenhouse gas emissions by 15%. Primary aluminium melt contains a higher level of sodium, aluminium carbide and non-metallic inclusions; whereas Das (2006) says recycled aluminium tends to have increased levels of hydrogen, calcium and large oxide inclusions due to high temperatures used for melting secondary aluminium. The use of aluminium to make industrial products inherently brings sustainable results. As an example, structures built with aluminium exteriors naturally reflect light and remain cooler.

Existing Technologies for Recycling of Aluminium Alloy Scraps

In the current recycling infrastructure, mixed aluminium scrap composed of castings and wrought pieces are sold by automotive shredders to the secondary aluminium industry for recycling into foundry alloys as per Das (2006). Recycled aluminium may involve a mixture of alloys from a fairly wide variety of sources, including a selection of castings containing rather high percentages of Si. While most of this metal may be used in new castings, there is a significant challenge in its use as sheet, plate, forgings, and extrusions.

It is estimated that, by 2020, worldwide consumption of aluminium products is expected to double, driven by growth and industrialization in China, India, Russia, and Brazil. Modern automotive recyclers use a number of efficient processes to recover valuable materials from end-of-life vehicles. Mechanical or physical recycling of vehicles includes magnetic separation, eddy current separation and density-based separation. Some of the new technologies in aluminium scrap processing includes colour sorting and Laser induced breakdown spectroscopy (LIBS). Apart from conventional re-melting process to recycle aluminium alloys, solid state recycling process utilizing compression and extrusion at room or moderate temperature has been developed for significant energy savings. Solid state recycling is limited to turning and chips and is a challenge for automotive aluminium scrap due to inhomogeneous property of the scrap, iron contamination and organic coating. In one of the work, Das (2006) have emphasised on developing and evaluating recycle-friendly aluminium alloys. Such an approach requires compositions with (a) relatively broad specification limits on major alloying elements such as Cu and Mg and (b) more tolerant (i.e., higher) limits on Fe, Si, and other impurities, without significant restriction on performance characteristics for many applications.

Recycling of Automotive Aluminium Alloy Scraps

Aluminium Alloys Used in Automotive Sectors

The automotive sector has provided the maximum impetus for recycling of aluminium alloys being one of the highest consumers. Most of the reclaimed aluminium today goes back into low value automotive castings, which comprises ~75% of the aluminium in cars rather than higher-value wrought products. It was reported that each year more than 50 million vehicles reach the end of their life worldwide. As per Miller *et al.* (2000) the average total aluminium content per car for European cars was 140 kg in 2012 which can be divided as follows – Power-train (69 kg), Chassis and suspension (37 kg) and car body (26 kg).

Typical aluminium alloys used in automobiles include, (a) cast alloys - A359, A356, A361, A413, A332 – which account for 78% and (b) wrought alloys – AA6060, AA6082, A3003, AA5182, AA5754, AA6016, AA7020 – which account for 22%. Apart from conventional alloys, new and lighter aluminium alloys for automotive applications are being developed to meet the need for super light cars that cannot be met by the present aluminium alloys. Few examples being, high Mg containing 5xxx alloy for warm forming and new 6xxx alloys for structural applications and fast paint bake response to withstand thermally

induced plastic deformation. All of the aluminium alloys above need to follow four basic design criteria to be considered for automobile applications: maximum property-to-weight ratio, minimum number of alloys in any one part, choosing standard alloy families based on IADS standard and avoiding expensive/exotic alloying elements. The difficulty in recycling wrought aluminium alloys is its low tolerance, the ability of an alloy to absorb impurities, which is not normally present in its composition.

Alloy Design and Application Challenge in Recycling of Automotive Aluminium Alloy Scraps

Currently the automotive industry uses 5000 series formable alloys for the outer panel applications and the heat treatable 6000 series alloys for the inner panel applications. The current challenge is to make an alloy that can be used for both the inner and outer panel applications. Such an alloy will result in improved recycling efficiency. Hoogovens rolled products Duffel, has developed 6xxx alloy within the EN6016 specification (HANV6016) for outer panels and a highly formable 5xxx alloy, (HANV5182) registered as inner-lite, for inner panels within the EN5182 specification. The mechanical properties of these alloys were comparable to that of the traditional alloys. Attempts are being made to design a common alloy for the entire automobile.

Current Projected Trends in Recycling of Aluminium Alloys

The usual method of recycling is re-melting of the scrap and subsequent processing it in numerous ways. One of the recently developed techniques is the hot press technique which is a melt less recycling technique. A6061 aluminium chips were recycled using by this technique under various operating temperatures and holding times. Yusuf *et al.* (2017), showed that the mechanical properties of the recycled samples showed similar properties to that of A6061 T4 tempered sheets.

One of the issues with recycling by re-melting route is the build-up of oxides. The oxides formed during the service of a material get agglomerated during the re-melting and unless these are removed or broken and uniformly distributed in the melt, recycling will not be effective. This problem is addressed using the melt conditioning treatment. This not only solves the problem of oxide build up but also eliminates the need for the addition of grain refiners. Melt treatment before casting is called melt conditioning. The currently used melt conditioning techniques utilize the principle of shear to disperse the particles. Techniques have been developed to shear the melt at different speed and accordingly are classified into high shear and low shear melt conditioning techniques. The high shear melt conditioning process is done using two techniques – (a) twin screw mechanism which uses high speed rotating twin blades to shear the melt and, (b) rotor stator mechanism which uses a rotor to do the same. Both are limited to batch processing of melts. But for a continuous process involving larger quantities of melt, low shear processes would be much suitable. One such process is the slope casting technique. This equipment can be subjected to vibrations to increase the effective of particle dispersion using the low shear process.

Fundamentals of Recycling Automotive Aluminium Alloy Scraps

Automotive aluminium alloy scraps contain particles of various size, nature and morphology. A fraction of the particles with favourable lattice registry will act as potent nucleation sites.

The traditional heterogeneous nucleation theory considers the balance between the interfacial energy changes during the creation of the spherical cap on the substrate and uses contact angle as a measure of the substrate potency. The energy barrier for the nucleation is determined by the energy fluctuation in the melt and a steady state nucleation rate can be derived as a function of temperature by statistical analysis. However this classical theory will be invalid for the potent nucleating substrates where the contact angle is so small (effectively zero) that the creation of a spherical cap becomes unphysical. Heterogeneous nucleation involving potent substrates is better treated as an thermal and deterministic process where the number of nuclei depends on the driving force only and is independent of time. This lead to the development of the free growth model for grain initiation on a potent surface. As per the free growth model by Fan (2013) suggests that a new phase could start to grow freely without any delay due to the very small dimensions of the substrate which facilitates fast under cooling.

At the atomic level, the process of heterogeneous nucleation on a potent substrate can be considered to be atom-by-atom building of the initial solid phase on a template. Therefore, the lattice matching across the solid/substrate interface should play an important role in this process. Relevant to this process is epitaxial growth of a thin layer of one material on the surface of another material (substrate). Scientific basis for the epitaxial growth of strained layers on a substrate originates from the theory of Frank and Vander Merve. Fan (2013) theory predicts that a coherent layer of a crystal can grow on a substrate with a slight lattice misfit provided the thickness of the layer is less than a crystal thickness (h_c) (Figs. 1 and 2).

In the schematic (a) sketch shows the L/N interface before the growth of the PS layer ($h = 0$); (b) sketch shows the initial formation of the pseudomorphic solid (PS) with a coherent PS/N interface; and (c) sketch shows the completion of the epitaxial nucleation at a critical thickness (h_c) by creation of misfit dislocations at the S/N interface to change the PS layer into the solid and to convert the coherent PS/N interface to a semicoherent S/N interface.

The lattice misfit of aluminium with commonly found oxides like MgO, Al_2O_3 and $MgAl_2O_4$ in the recycled scrap is 3.2%, 8.36% and 12.93% which is comparable with the traditionally used grain refiner TiB_2 which has a lattice misfit of 4.22%. Hence the

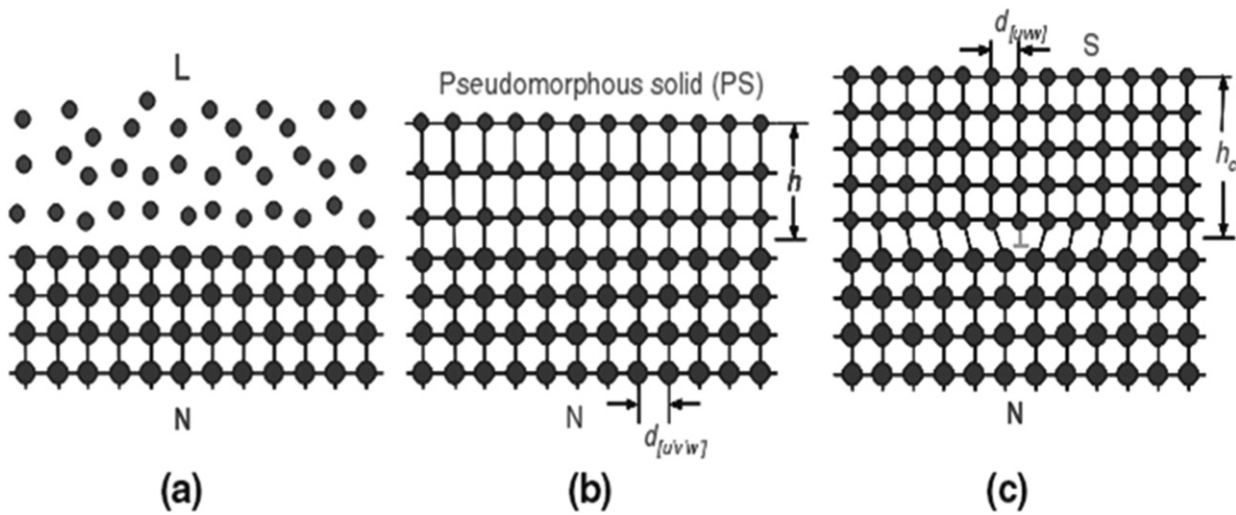


Fig. 1 Schematic of the epitaxial model for heterogeneous nucleation.

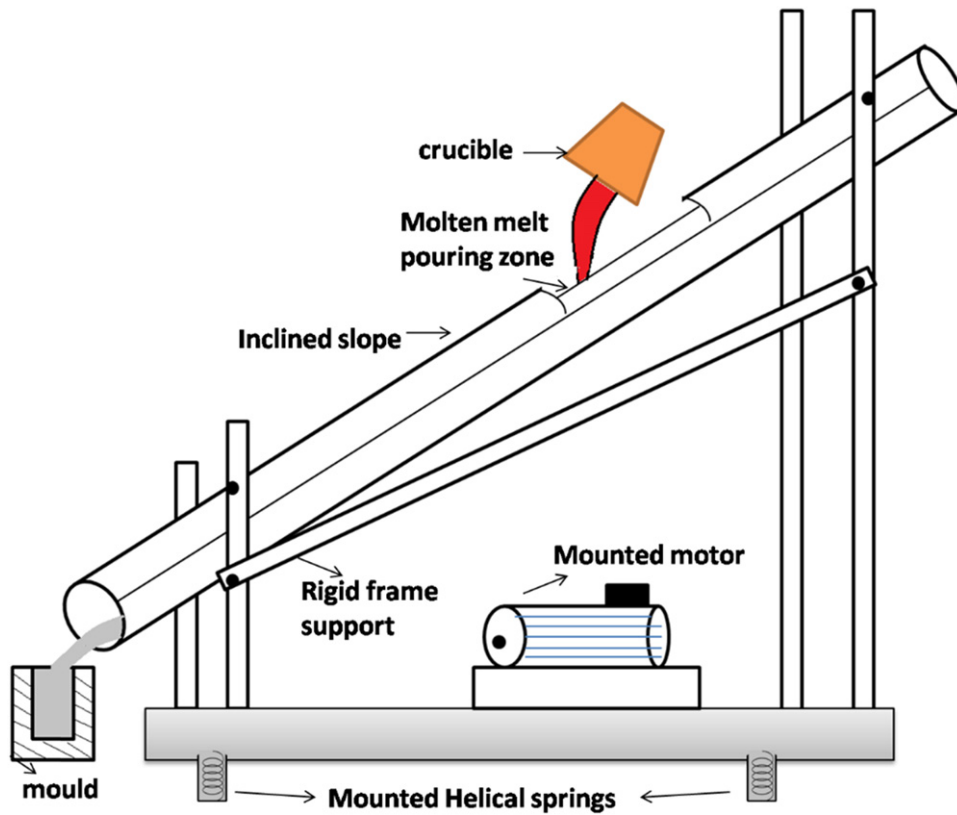


Fig. 2 Schematic illustration of an inclined slope vibrating setup.

oxides can act as the potent nucleants for grain refining. The grain refining increases the number of grains per unit area which in turn increases the number of grain boundaries to obstruct the motion of the dislocations. The pile up of the dislocations causes an increase the strength of the material. This entire phenomenon is explained by the Hall Petch relation which gives the effect of grain size on the yield stress (σ_y) of the material.

$$\sigma_y = \sigma_i + kd^{-1/2}$$

Where σ_i is the yield stress of the material when there are no grain boundaries present in the material. K is a constant and d is the average grain diameter. Hence the yield strength increases with decreasing grain diameter.

Microstructure-Property Relationship in Aluminium Alloys Produced by Slope Casting

The evolution of microstructure in aluminium alloys produced using slope casting is discussed. The patented (Patent application no.:201831030977) low shear vibration melt conditioning setup was developed in the authors' laboratory that includes a stainless-steel vibrating slope. This setup is suitable for batch wise casting and continuous casting system as well.

The effectiveness of slope casting was demonstrated using two cast alloys, A356 and Al-7Si in one of the work by Jha *et al.* (2018), which is summarized in this section. The macrostructure of vertical cross-section of A356 alloy cast under three different conditions, i.e., as cast condition, cast after flowing through the slope and cast after flowing through the slope subjected to vibration is shown in Fig. 3. The macrostructure consists of columnar grains at the periphery and equiaxed grains at the casting interior (Fig. 3(a)). When the alloy was passed along the slope, fine equiaxed grains are observed throughout the macrostructure (Fig. 3(b)) as compared to Fig. 3(a). However, in Fig. 3(b) the grain size at the casting interior is fine and relatively coarser at the edges. In the case where the alloy is cast after flowing through the slope subjected to vibration, the presence of fine grains are seen uniformly throughout the macrostructure (Fig. 3(c)). The grain size as per Jha *et al.* (2018) in this case was found to be finer (118 μm) as compared to the alloy cast without any vibration (155 μm).

Subjecting the melt to low shear during the flow through the slope helps in fragmentation of oxide films (Al_2O_3 , MgO and AlMg_2O_4) and consequently increasing the number of nuclei. The problem with agglomerated particles is that when one oxide particle would nucleate α -Al, due to local recalescence other oxide particles would not be able to nucleate α -Al grains. Thus, shearing increases number of individual oxide particles by breaking the oxide films. A combined action of shearing and vibrations come into play to form a homogeneous refined microstructure. Similar melt conditioning experiments were carried out for Al-7 wt% Si alloy and the microstructures (Fig. 4). The eutectic silicon is partially refined when the melt is cast along the slope subjected to vibration, and the grain

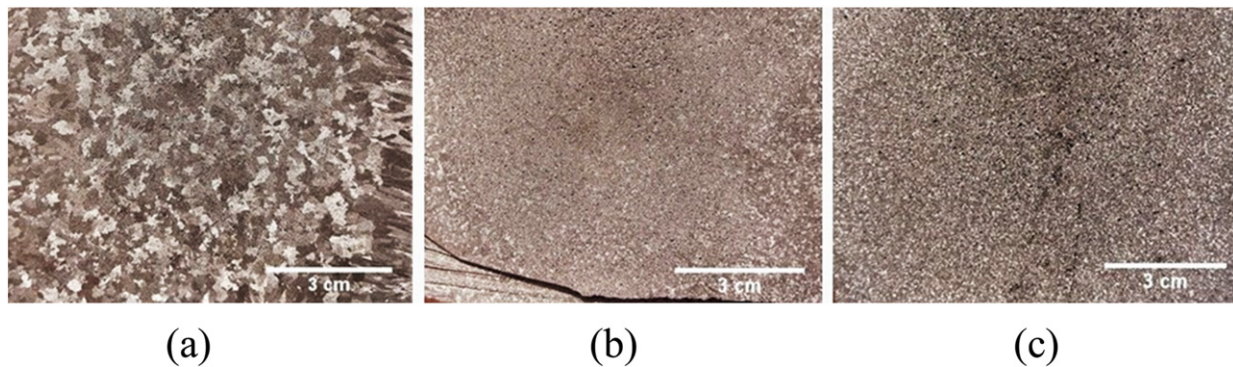


Fig. 3 Macrostructure of A356 alloy cast under different conditions (a) as cast condition, (b) cast after flowing through the slope and (c) cast after flowing through the slope subjected to vibration. Reproduced from Jha, S., Aditya, G.S.L., Mandal, A., Dhindaw, B.K., 2018. Microstructural changes in hypoeutectic Al-Si alloys by low shear and vibration induced melt conditioning setup. Transactions of the Indian Institute of Metals 71 (11), 2783–2787.

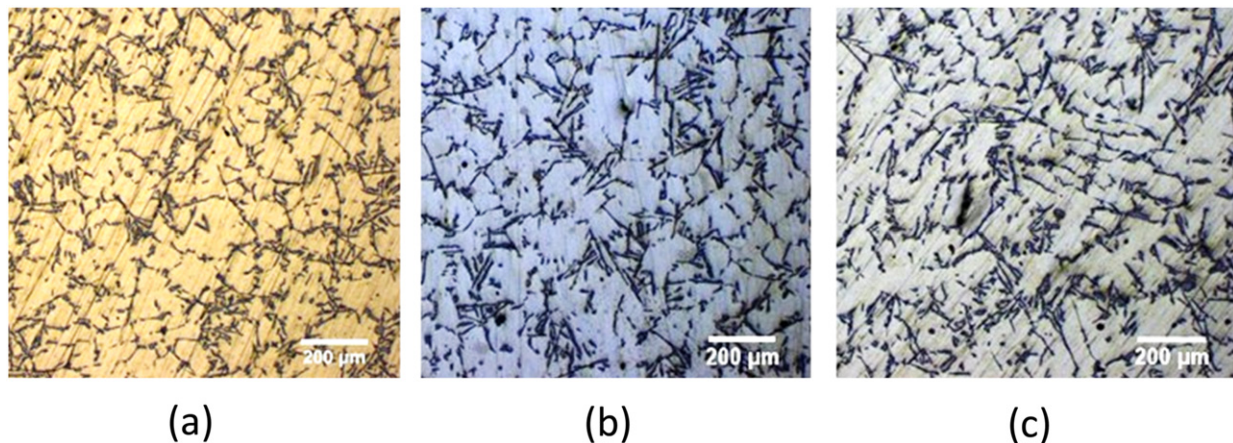


Fig. 4 Microstructure of Al-7Si alloy cast under different conditions (a) as cast condition, (b) cast after flowing through the slope and (c) cast after flowing through the slope subjected to vibration. Reproduced from Jha, S., Aditya, G.S.L., Mandal, A., Dhindaw, B.K., 2018. Microstructural changes in hypoeutectic Al-Si alloys by low shear and vibration induced melt conditioning setup. Transactions of the Indian Institute of Metals 71 (11), 2783–2787.

Table 1 Grain size of alloys (in microns) cast under different conditions

	<i>As cast condition</i>	<i>Without vibration of slope</i>	<i>With vibration of slope</i>
Al-7Si alloy	210 ± 10	145 ± 14	122 ± 27
A356 alloy	184 ± 49	155 ± 23	118 ± 19

size of the alloy subjected to vibration ($122 \pm 27 \mu\text{m}$) showing refinement compared to that of without vibration ($145 \pm 14 \mu\text{m}$). The summary of grain size of both alloys under different conditions is given in [Table 1](#).

It must be mentioned that the effect of vibrating the slope is prominent in A356 alloy possibly due to the presence of additional Mg which form bi-oxides and promote heterogeneous nucleation.

Thus, melt conditioning can be obtained by applying high shearing action and low shearing action in aluminium alloys to effectively obtain a refined microstructure. The presence of oxide forming elements like Mg helps the cause by acting as effective nucleating sites. It can be concluded that low shear melt conditioning with vibrations can be used as an effective technique to refine the recycled aluminium alloys which inherently have oxides present in them.

Downstream Processing of Aluminium Alloys

Direct Chill (DC) Casting and Other Sustainable Processes

Production of aluminium sheets by continuous casting route offers an opportunity to substantially reduce the cost as compared to conventional DC casting and hot mill method.

DC casting is a vertical semi-continuous casting process used for fabrication of cylindrical billets or rectangular ingots/blooms for Al, Cu and Mg alloys. The mould used in DC casting process is usually very short (75–150 mm). The casting rate is normally 50–150 mm/min. In the process the molten melt is poured onto a starter block which immediately solidifies the melt due to the difference in temperatures (direct chill). This starter block is moved downward to increase the mushy zone (semi solid zone) which will facilitate the formation of the final product, usually a billet. The mould walls are cooled continuously with a water film. Most of heat (~80%) is extracted by the direct chill and only 20% is removed by heat transfer through the mould wall. The main benefit of DC casting is that the solidification (and the formation of structure and defects) occurs in relatively narrow layer of a billet and can be well controlled.

Hot milling is another predominant downstream process where the metal is rolled between rolls above the recrystallization temperature of the metal. The number of rolls used depends on dimensions of the final product. The surface defects are eliminated to a maximum extent but rolling defects like alligatoring, buckling and others are commonly seen in the final products due to the differences of the speed of the rolls, roll loads and geometry of the rolls.

Twin-roll casting (TRC) process, a technique for producing aluminium sheets directly from liquid metal, has gained popularity due to lower greenhouse emissions, low capital investment and possibilities of easy diversification. [Barekar et al. \(2014a\)](#) tells that it consists of a pair of robust rolls capable of withstanding the high roll torques and roll separation forces. Based on the method in which the molten melt is allowed to pass through the rolls, the TRC processes are classified into two types: (i) horizontal twin roll caster [Fig. 5\(a\)](#) (ii) vertical twin roll caster [Fig. 5\(b\)](#).

The various regions which determine the quality of the strip after the completion of TRC process are indicated in [Fig. 6](#) as described by [Barekar and Dhindaw, \(2014b\)](#). These regions are prominently controlled by roll speed, pouring temperature or superheat of the melt, thickness of the sheet and alloy composition.

Few studies carried out on TRC and slope casting of aluminium alloys by our group are highlighted in the subsequent section. [Barekar et al. \(2014a\)](#) work, TRC and melt conditioned TRC (MCTRC) sheets of Al-5 wt% Mg alloy were produced using laboratory scale horizontal twin roll casting process. Al-5 wt% alloy was chosen as there is projected demand to accommodate long freezing range alloys for TRC. Another arrangement involved melt conditioning of Al-5 wt% Mg alloy, wherein rotor-stator type of high shear device rotating at 5000 rpm was employed to disperse naturally occurring oxides in the melt causing grain refinement. The sheets so obtained are referred to as MCTRC sheets. Both TRC and MCTRC sheets were deformed by cold rolling (10% reduction) and homogenized at 550°C for 1 h. The sheets were further cold rolled to a final thickness of $1.7 \pm 0.1 \text{ mm}$ (66% reduction) followed by homogenization at 300°C for 1 h.

[Fig. 7](#) shows that as cast TRC sheets have non-uniform microstructure with coarse α -Al grains of average size of $380 \pm 17 \mu\text{m}$, while MCTRC sheets have relatively fine equiaxed grains of average size of $245 \pm 87 \mu\text{m}$. Channel segregates comprising of low melting point regions are seen at the centre of sheets. They appear as thick black features in TRC strip ([Fig. 7\(a\)](#)) and much finer and uniformly distributed in MCTRC sheet ([Fig. 7\(b\)](#)).

The microstructure across the thickness in the transverse section of cold rolled and homogenized sheets prepared by TRC and MCTRC show α -Al grains of $96.5 \pm 9 \mu\text{m}$ and $69.2 \pm 6 \mu\text{m}$ respectively. [Fig. 8](#) below shows hardness contours across the transverse

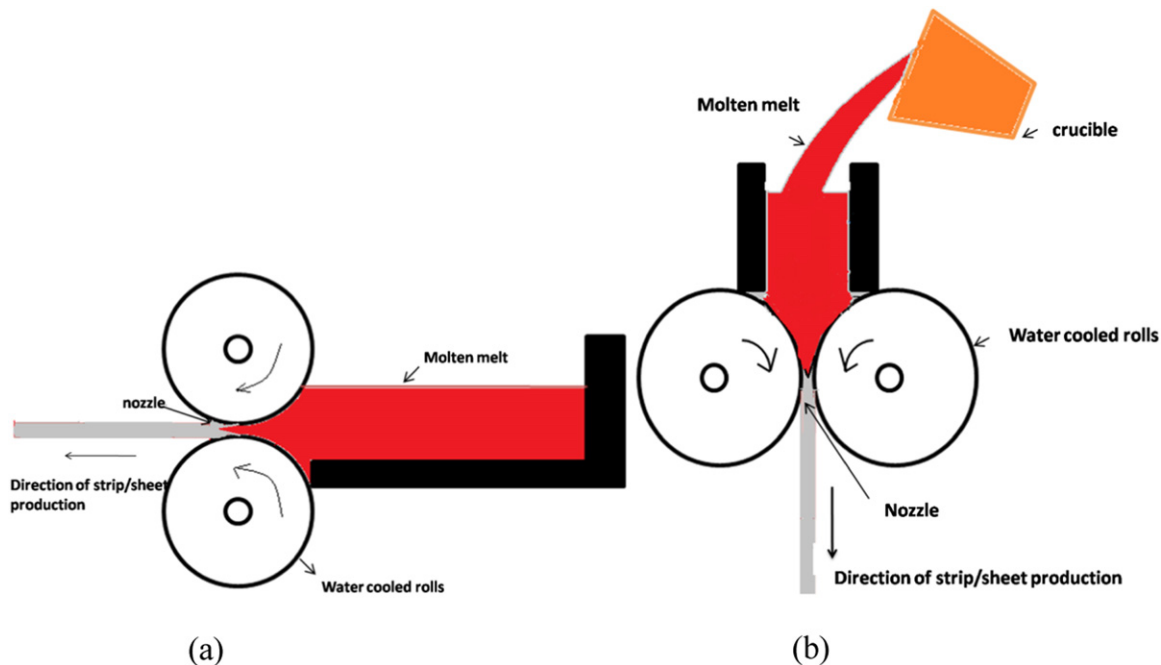


Fig. 5 Schematic of (a) horizontal twin roll caster and (b) vertical twin roll caster.

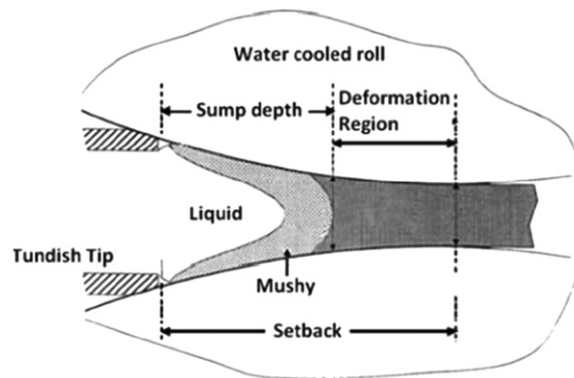


Fig. 6 Schematic diagram of various regions from molten metal to formation of solidified sheet in a TRC process. Reproduced from Barekar, D., 2014b. Twin-roll casting of aluminum alloys – An overview. *Materials and Manufacturing Processes* 29 (6), 651–661.

section of cold rolled and homogenized TRC and MCTRC sheets. The hardness contours in MCTRC Al-5 wt% Mg sheet appears to be more uniform compared to TRC sheets. This suggests uniform distribution of Mg aided by faster homogenization in fine grained MCTRC sheets. The calculated values of time required for homogenization of as cast TRC and MCTRC samples of Al-5 wt% Mg alloys was found to be 9.5 and 3.9 h respectively.

The tensile plots for TRC and MCTRC cold rolled (66%) and homogenized at 300°C for 1 h is shown in Fig. 9. The higher tensile properties in MCTRC sheet as compared to TRC sheet is due to the following: (a) elimination of severe centre line segregation, (b) finer grain size and uniform microstructure.

Future Perspectives

Recycling is synonymous with reduction of energy as it consumes only a fraction of energy to produce a component with comparable properties with a primary alloy. The ever-increasing demand for aluminium alloy scraps by various countries is indicative of the importance of recycling and its downstream processing. This stems from the fact that lightweight aluminium is infinitely recyclable and is fast expanding. The recycled alloy components have a great potential to meet today's demanding

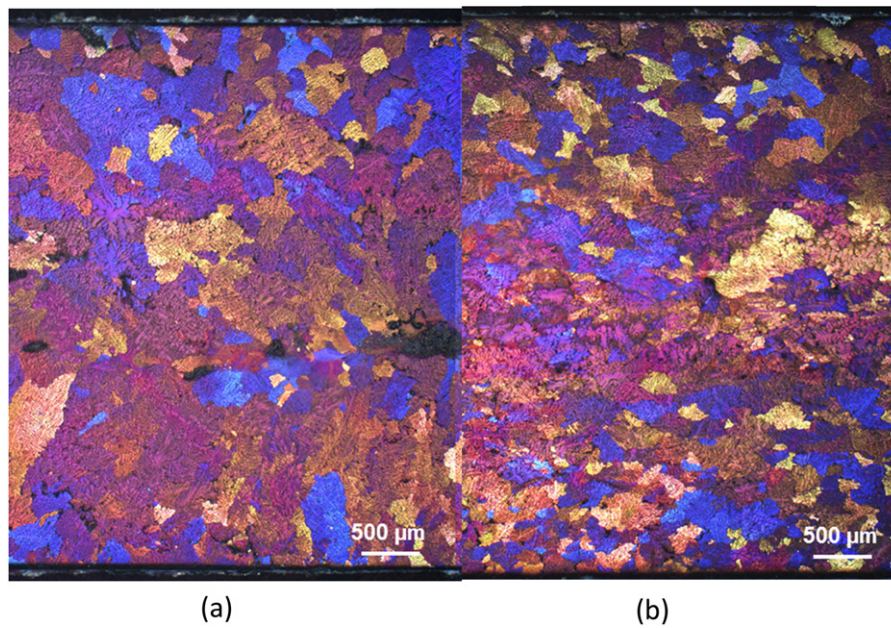


Fig. 7 Microstructures across transverse cross-sections (thickness) in as-cast Al-5 wt% Mg sheets prepared by (a) TRC and (b) MCTRC.

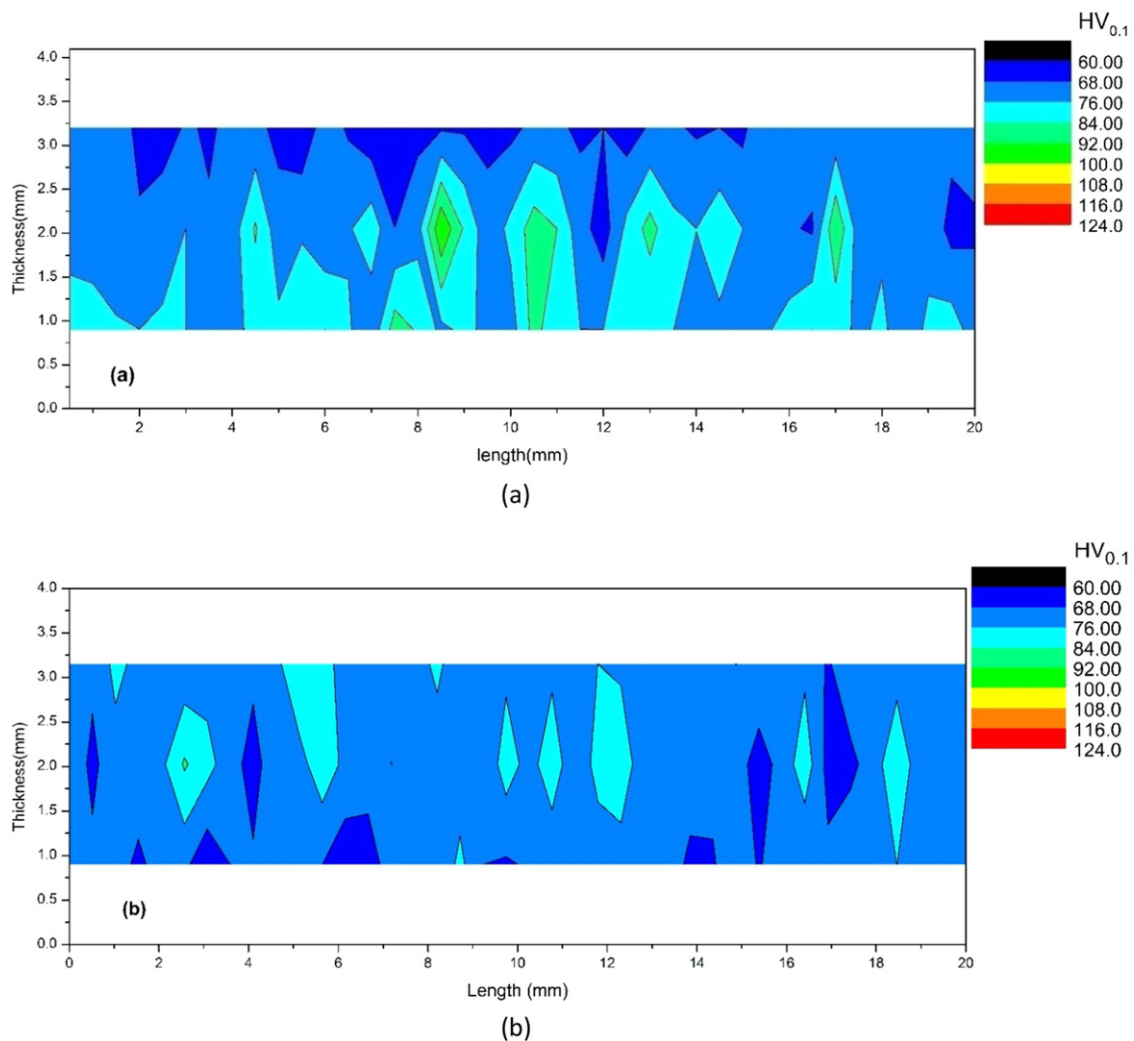


Fig. 8 Microhardness contours of transverse section of Al-5 wt% Mg alloy after cold rolling and homogenization at 550°C (a) TRC and (b) MCTRC sheets.

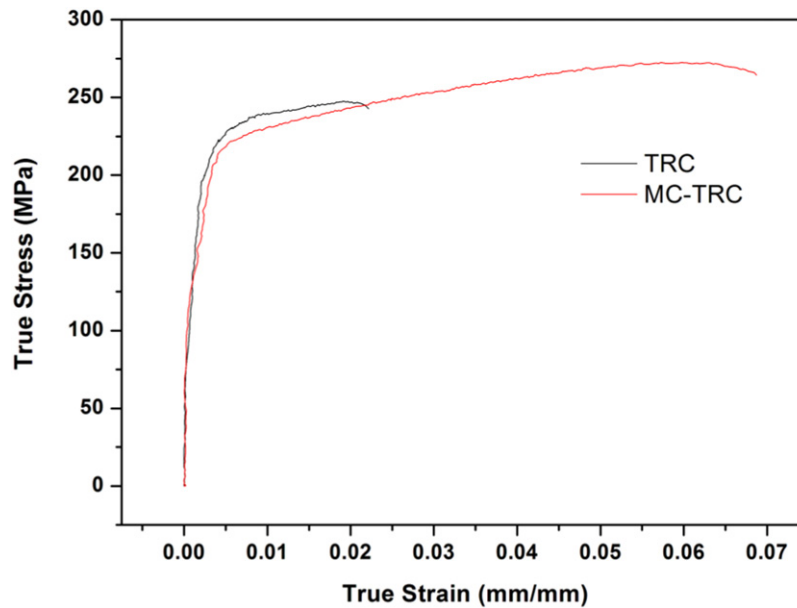


Fig. 9 Tensile properties of cold rolled and homogenised Al-5 wt% Mg TRC and MC-TRC sheets in transverse section.

performance standards. To keep in pace with stringent demands of automotive sector, new technologies need to be developed which can be scaled up easily.

Acknowledgement

The authors would like to thank Dr. Nilam Barekar, BCAST, UK for conducting the tensile testing of the samples. Apart of the work was completed under the Uchchar Aviskar Yojana (Phase 1) program of MHRD. The authors would like to thank MHRD (Govt. of India) and NALCO, India for funding part of the research presented.

See also: Recycled Polypropylene-Nanoclay Composites – Mechanical Properties

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Renewable and Sustainable Materials in Automotive Industry

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Introduction

Motivation for increased levels of renewability normally include: (a) having high electricity load responsible for considerable CO₂ emissions which, combined with rising market prices for electricity, results in significant economic and environmental burden (b) operating mostly in a carbon-intensive industry, as a result of which, emissions have higher than allowed carbon footprint levels. The automotive industry requires a huge bulk of raw materials, mostly metals. Depending on fresh resources at the initiation of every manufacturing process would impose a high demand on the available resources and cause their rapid depletion. It is thus, a natural consequence that renewable materials be used.

Renewable, recycled or innovative lightweight materials are not a new feature of automotive design. However, with an increased emphasis on the overall life cycle impact of a car, there has been a recent surge in research and development in this area of material science. A comprehensive account of such developments has been provided here, in order to identify and provide plausible solutions to the problem of increasing carbon footprint faced by the automotive industry presently.

Apart from measures taken to infuse renewability in the automobile industry, sustainability is another aspect that must be focussed on. The negative impacts of high carbon footprint, hazardous waste dumping, and poor landfill waste management have led to sustainable initiatives becoming more prevalent in many industries including the automotive industry. Environmentally-friendly and sustainable mobility is, therefore, a goal for most, if not all automakers, and not just an aspiration. However, it is clear that a perfect model of sustainable mobility cannot emerge from technology alone, but rather a lot of other relevant inputs. There have been multiple surveys looking into the current scenario of sustainability in the automotive industry. One of such reports, SMMT's 19th Sustainability Report, reviews data from 2017. It witnessed a healthy increase in the number of signatories and for the first time includes a materiality assessment, examining current, emerging and future priorities of vehicle manufacturers and suppliers, as well as other stakeholders, including government advisors, academics, charities, environmental NGOs and trade unions.

Present day car manufacturers have implemented methods like effective waste management, using more and more renewable energy sources and developing materials which improve the fuel efficiency of the vehicle.

The following parts suggest how the problems of increasing renewability and sustainability can be addressed in a systematic manner, thereby also enumerating the developments being made in terms of the materials selection, or the tailoring of materials to be used in the body of the car or the designs chosen. These measures would eventually go all the way in providing plausible solutions to the current problems.

Need for Renewable and Sustainable Materials

So far as the current scenario of automobile industry is concerned, it is going through a challenging situation considering so many aspects like its environmental, social, economic impact etc. If the basic problems are considered, they can be categorized into four major issues, which are (i) durability, (ii) huge and heavy material usage, (iii) higher fuel consumption and (iv) environmental pollution. To overcome the above-mentioned issues, concept of 'Sustainable and Renewable Development' is introduced. Some of the points are discussed below about how the sustainable and renewable approaches in automobile sector can resolve or restrict each of these problems.

Overcoming the Durability Challenge: Life Cycle Assessment (LCA)

Life cycle assessment is a process which is used to measure the environmental impacts due to a product from its constitution to end-of-life i.e., cradle-to-grave. According to Sundin (2004) the life of an industrial outcome can be classified into five parts, namely:-

(a) its extraction from raw materials, (b) manufacturing, (c) distribution, (d) use and finally (e) its end of life stage. According to Ashby (2009) while assessing the life cycle, environmental impact of the vehicle, energy consumption during its use stage is an indicator of its environmental burden. However, LCA measurement methods in association with the international standards ISO 14040, 14041, 14042, 14043 are important, especially at the inception and design stage. According to Pennington *et al.* (2004) and Govetto (2008) the ISO 14000 series can be classified into four different phases; which are: the goal and scope phase, the inventory analysis, the impact assessment, and interpretation phase. The first phase 'goal and scope' indicates the purpose, boundary, metrics and the input and output units that will be assessed and the second phase 'inventory analysis' mainly deals with the information collection on different aspects. The third phase was introduced to measure impact on environment due to first two phases. Finally, the last phase 'interpretation' is to talk about the conclusion and to give a brief model of first three phases.

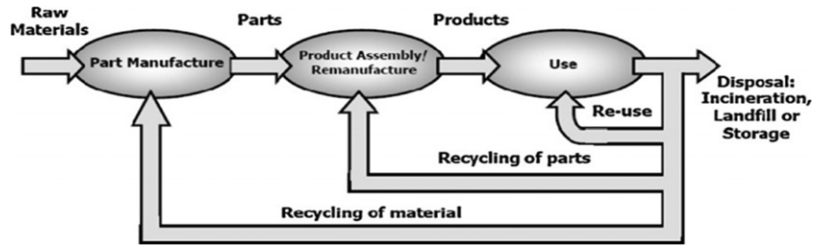


Fig. 1 Physical product life cycle. Reproduced from Sundin, E., 2004. Product and Process Design for Successful Remanufacturing. Linköping: Linköping University Electronic Press.

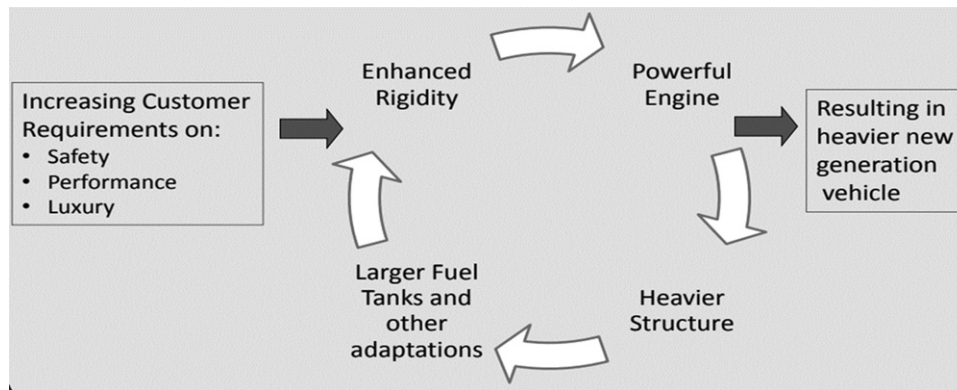


Fig. 2 Vicious cycle of weight. Reproduced from Marathe, S.R., 2013. Light weighting in automotive industry, In: Proceedings of the Automotive Manufacturing Solutions India Conference 2013, ARAI, Pune.

The LCA of an automobile inspects the vehicle from primary i.e., raw material state to its end-of-life state. Refer to the diagram below (Fig. 1), which is basically a schematic diagram, better to say a flow chart representing the LCA of a vehicle.

By the life cycle assessment, we get to know about the suitable materials for the vehicles to be used in different purposes and for different time spans. The main criterion is to satisfy maximum durability. Thus, concept of sustainability comes into the picture. While assessing the end-of-life part, it is better if the materials of a car could be reused after a complete life cycle. Thus, the idea of recyclability and hence renewability is introduced.

Huge and Heavy Material Usage Related Problems: Introduction to Advanced Materials

Usage of heavy materials is currently a burden to the leading automobile producers due to its adverse effects on both environment and economy. Though the heavyweight materials provide significantly high strength, their high production cost and comparatively low cost-effectiveness compel producers to seek for advanced materials. These advanced materials are lightweight and have high strength as well. They can be high strength steels, aluminium, magnesium, reinforced plastics, metallic foams generated by various processing methods.

The need for light weighting can be well described by the cycle (Fig. 2):

The benefits of using lightweight materials can be categorized into economic and environmental benefits.

- *Economic advantages* – The first and foremost advantage of using lightweight materials is lower production and parts-assembling cost. When the overall body weight of a vehicle is reduced then smaller mechanical parts including engine, brakes, gear box are used and hence further weight reduction and cost minimization take place. The weight saving in the structural part can also be substituted by some luxury accessories or safety kits. Light weight vehicles also minimize the fuel consumption and are efficient for road handling.
- *Environmental advantages* – Vehicle weight directly impacts the fuel consumption therefore light-weighting lowers the CO₂ emission to a considerable extent. This is an example of direct weight saving. Indirect weight saving may also happen through downsizing of some components, lowering energy demand, shortening braking distance keeping the brake power same etc., 100 kg mass reduction achieved on a car saves 8 g of CO₂ per km at the exhaust pipe. (Reducing Mass Is Necessary to Reduce CO₂ Emissions, 2007).

Sustainable approaches are necessary to introduce lightweight high strength materials in place of conventional heavy materials and to get maximum benefits from the materials. On the other hand, renewable materials restrict the problem of huge material usage as these materials can again be used in other vehicles by recycling after end-of-life of a particular vehicle.

Restricting Higher Fuel Consumption: Mileage Enhancement

At its most fundamental, fuel-efficiency refers to the ability of a vehicle to extract energy from fuel. The more energy a vehicle can extract from fuel, the greater fuel-efficiency the vehicle is said to have. Similarly, the less energy a vehicle extracts, the less fuel-efficient the vehicle is. A vehicle is described as fuel-efficient if it is listed as having less than 6-L per 100 km (or greater than 16.5 km per litre). This standard prevents car manufacturers from listing their vehicles as “fuel-efficient” in cases when they quite palpably are not. It means that a vehicle needs 6-L of fuel, or less, to travel a distance of 100 km. It depends on the type of engine, too. In general, diesel engines are more fuel-efficient than petrol engines. They use compression ignition, which extracts more energy than spark plugs.

When it comes to improving fuel economy, engines, powertrains, fuels and batteries seem to get all the attention. To replace a car's traditional steel side panel or rooftop, usage of advanced lightweight materials at even the most basic car equipment can improve overall fuel efficiency. Reducing a vehicle's weight by 10% can improve fuel economy by 6%–8% (see “Relevant Websites section”). Steel is currently used as almost 60% of a vehicle's total weight. But in order to meet consumer demands and increasingly stringent federal fuel economy standards, automakers are looking to alternatives, including advanced high-strength steel, aluminium, magnesium and carbon fibre. Lightweight materials are a cost-effective way to boost fuel efficiency on conventional combustion engine vehicles and advanced automobiles like hybrids, electric vehicles and hydrogen fuel-cell vehicles.

Resolving Pollution Problems and Green Development

Only around 15%–20% of the energy in fuels is used to drive a car. The rest is rejected unused into the car's surroundings as waste heat or other losses. Thanks to advanced technologies, these losses are being reduced, step by step. Many already existing technologies, along with technologies that are not yet in mass production, are available to further improve the efficiency of cars.

The average CO₂ emissions level of new cars in the EU (as reported by car manufacturers) decreased from 170 grams per kilometre (g CO₂/km) in 2001–136 g/km in 2011 – a 20% reduction in 10 years (Fig. 3). As CO₂ emissions and fuel consumption are directly related to each other, this CO₂ emissions reduction can be expressed as a reduction in fuel consumption from roughly 7.0 litres per 100 kilometres (71/100 km) to 5.6 l/100 km.

The manufacturing of cars has been one aspect of the auto industry where green business practices have been lacking for years now. However, in the last five years, car manufacturing has made a significant transition into the green initiative by incorporating far more recyclable materials into car production, choosing fuel alternatives that allow companies to reduce their fossil fuel intakes, and making car parts that are overall more reliable and eco-friendlier (see “Relevant Websites section”).

When it comes to more recyclable materials that save fuel economy, Al comes into the picture because Al is much lightweight and malleable, this means that it can be used to manufacture any car, reduces the fuel intake of said cars, and also is easily recyclable likewise. Although cars cannot be completely comprised of aluminium for safety concerns, it is estimated that, by 2025, cars will be comprised of roughly 550 pounds of aluminium. This will ultimately lead to a far more efficient, cheaper, and more environmentally friendly mode of transportation that can be quickly recycled and redistributed likewise.

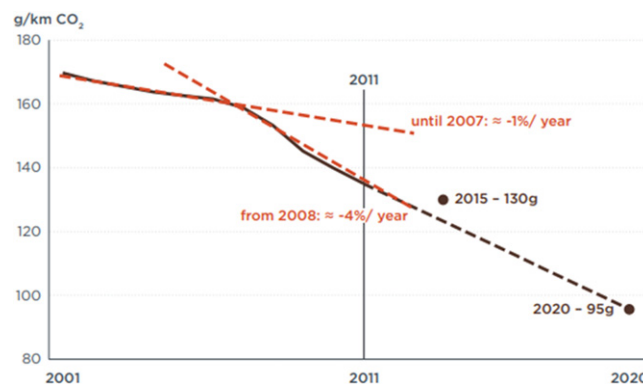


Fig. 3 Average CO₂ emission levels for new passenger cars in the EU. Reproduced from Anon, 2013. Reducing CO₂ and Fuel Consumption From New Cars: Assessing the Near-Term Technology Potential in the EU, ICCT. Available at: www.theicct.org/sites/default/files/publications/Briefing%20Technology%20Potential%20Long%20EN%20v3.pdf.

Methods to Incorporate Sustainability

Materials Selection

The automobile industry uses a tremendous number of materials to build various parts of the automobile (Hovorun *et al.*, 2017). For e.g., iron, aluminium, steel, glass, rubber, petroleum products, copper, steel and others. These materials have evolved greatly over the decades, becoming more sophisticated and safer. They have changed as new automotive manufacturing technologies have emerged over the years, and they are used in increasingly innovative ways. Based on both domestic and foreign sources of information, it follows that car manufacturers are constantly pushing to create the lightest cars possible to increase speed and power. Research and development into lightweight materials is essential for lowering their cost, increasing their recyclability, and maximising their fuel economy benefits. Light weighting without compromising on strength and speed properties is the present, and the future too, of the automotive manufacturing industry. It brings innovative materials to the frontline of design.

The categories into which the current raw materials, considering both interior and exterior, may be divided are: metals and their alloys (ferrous and non-ferrous), polymers, glass, textiles, coatings, fluids and lubricants etc.

From Fig. 4, one can conclude and in fact assume, for even a greater scenario (than the American industry), that steel and its various variants leads the percentage of materials usage, in the body of the car, while considering both interior and the exterior.

From here on, the ways to improvise upon the existing slew of materials shall be listed, so as to introduce the aspect of sustainability into the automotive industry, concentrating more on those materials which have relatively greater usage in the body of the car.

Fig. 5 represents a pictorial analysis of the various types of steel used for the different parts of the present car. In addition to that other variants have also been shown which can be used instead of steel in order to increase the strength to weight ratio of the car.

The following subparts separately highlight the various materials that can be used and up to what extent to guarantee a sustainable future of the automotive industry, keeping in mind these 3 criteria upon which selection (Jasinski *et al.*, 2016) has to be made: increased strength to weight ratio, durability, cost efficiency.

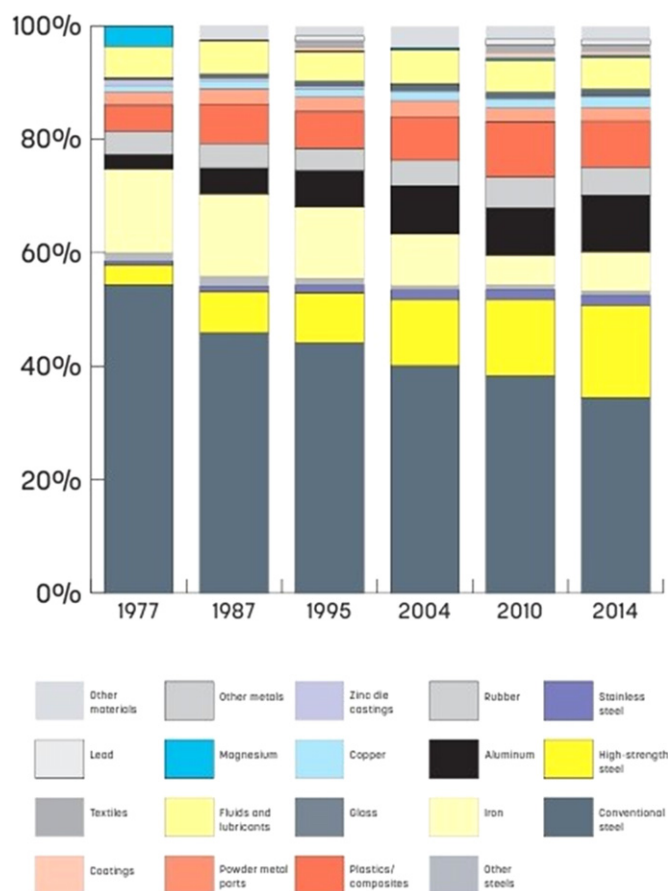


Fig. 4 Material distribution (in %) of an average American car by year. Reproduced from Henriksson, F., 2017. *Introducing New Materials in the Automotive Industry*. Linköping: Linköping University Electronic Press.

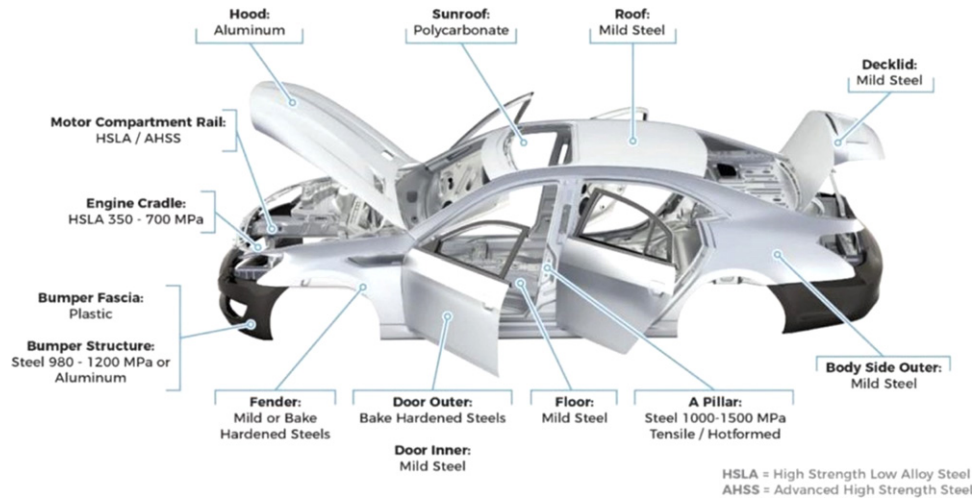


Fig. 5 Materials used most commonly for major vehicular structural components in the current fleet (www.cargroup.org/publication/).

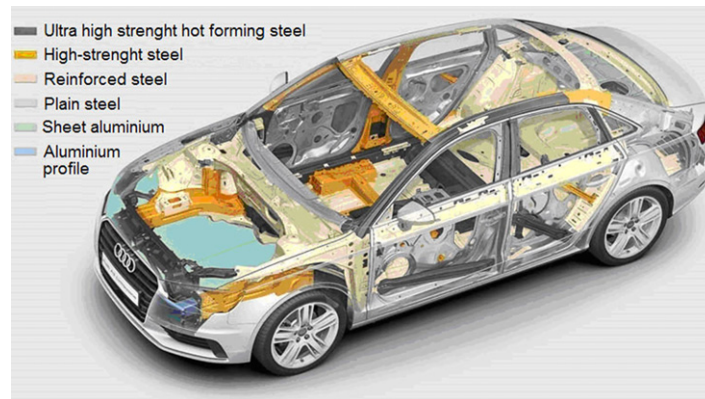


Fig. 6 Parts made of metals, especially ferrous alloys (forums/forums/showthread.php?t=7278).

Steels

The automobile industry is imposing very high demands on steel because, first of all, it must meet two diametrically opposite criteria. On the one hand, the requirement to reduce the mass of products involves the use of high-strength materials, on the other – the growth requirements for the production of technology involve the use of high-plastic materials (see “Relevant Websites section”). **Fig. 6** indicates the different varieties of steels used in a typical car body.

The goal in making a car lighter is to increase performance and efficiency while maintaining safety and comfort. Roughly speaking, when a car’s weight is decreased by 10%, the efficiency of the vehicle can increase anywhere from 5% to 8%. This may not seem like a lot, but in the competitive automotive industry, it can make a world of difference (see “Relevant Websites section”).

Introducing increased strength to weight ratio:

An interesting variant in this aspect is the AHSS – Advanced High Strength Steel, whose microstructure has both ferritic and martensitic grains (Khedkar *et al.*, 2016). Such Dual Phase Steels (DPS) have the advantages like low yield strength, low yield to tensile strength ratio, roughly equal to 0.4–0.5, high initial strain hardening rates, good uniform elongation, good fatigue resistance, high Strength i.e., high energy absorbing capacity before failure.

New grades of AHSS enable carmakers to reduce vehicle weight by 25%–39% compared to conventional steel. When applied to a typical five-passenger family car, the overall weight of the vehicle is reduced by 170–270 kg, which corresponds to a lifetime saving of 3–4.5 tonnes of greenhouse gases over the vehicle’s total life cycle. This saving in emissions represents more than the total amount of CO₂ emitted during the production of all the steel in the vehicle (see “Relevant Websites section”).

There exist different varieties of AHSS based on their microstructural differences – TRIP (Transformation induced plasticity), DP (Dual Phase) – (refer **Fig. 7**), CP (Complex Phase), MS (Mild Steel).

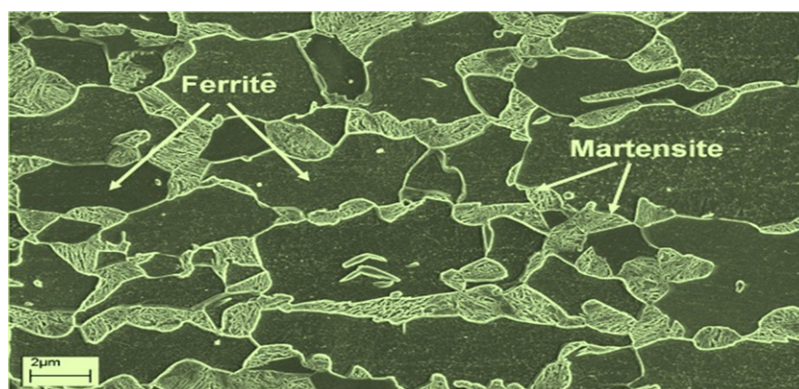


Fig. 7 Microstructure of DPS.

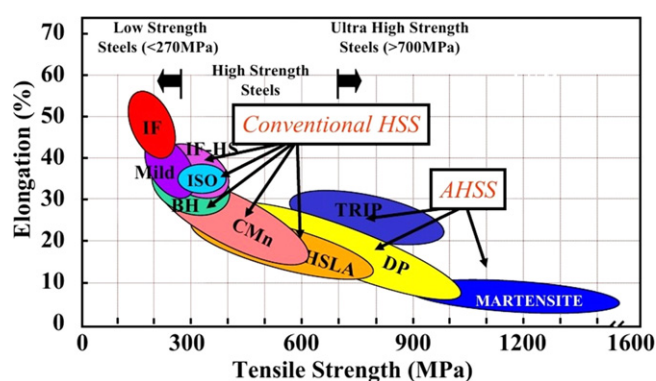


Fig. 8 Ashby plot correlating elongation to tensile strengths of conventional steels and AHSSs (wenku.baidu.com/view/2e4419e4b9d528ea81c77975.html?re=view).

First generation

The 1990s saw the development of modern multiphase AHSS having tensile strength more than 450 MPa. Consequently, variants like DP, TRIP and CP steels having tensile strengths more than 1000 MPa were developed due to new processing lines, designed for integrated steel plants. Nowadays, by an adjustment of different constituents in their complex composite microstructure, a large range of mechanical properties can be offered by this steel family to the automotive industry. This excellent combination of mechanical properties and formability performance makes such steels the perfect choice for interior safety related panels (see "Relevant Websites section").

The stellar combination of strength and drawability as a result of the combination of strength and ductility, as well as the high strain hardenability gives DP Steels good strain redistribution capacity. For some applications it is important that the initial yield strength of steels is further increased by work hardening and the Bake Hardening (BH) process.

Steels having ferrite-martensite structure cover tensile strength ranging from 490 to 1180 MPa enabling them to be used in numerous car parts requiring resistance to denting, fatigue, intrusion, impact, and so on (Rana and Singh, 2017).

High tensile strength results in high fatigue properties. The high strength and strain hardening capacity of these steels combined with a strong BH effect give them excellent potential for reducing the weight of structural and closure parts. As shown, based on their high energy absorption capacity and fatigue strength, cold rolled dual-phase steels are particularly well suited for automotive structural and safety parts such as longitudinal beams, cross members and reinforcements. Fig. 8 depicts a comparative study by showing the Ashby plots of Elongation vs Tensile Strength for different types of High Strength Steels.

Second generation

For obtaining superior combinations of strength and ductility, so as to allow automobile parts, where integration of parts is possible, TWIP and Duplex/Triplex steels were developed, having Mn (12–35 wt%). Constituting of an fcc crystal structure, TWIP Steels have low Stacking Fault Energy (15–50 mJ/m²) at room temperature. Consequently, the plastic deformation is characterized by the pronounced dislocation glide and the dissociation of perfect dislocation to Shockley partial dislocations and formation of wide stacking faults.

With lowering stability of the austenite, the austenitic microstructure may transform to strain-induced ϵ -martensite and/or α' -martensite phase during plastic deformation, which is however undesirable. By twinning induced plasticity, these steels achieve outstanding combination of mechanical properties which makes them very attractive for automotive applications, especially where high strength and high ductility is required. Perfectly suited to manufacturing complex automotive parts e.g., side members the superior formability of these steels is ideally adapted to manufacturing components allowing only one or limited number of required forming operations. TWIP (Twinning-Induced Plasticity) steels boast of tensile strength ranging from 800 MPa to ~ 1200 MPa with a product tensile strength – total elongation up to $\sim 70,000$ MPa (Bracke *et al.*, 2009).

Triplex Steels, a low-density steel family, has considerably huge amounts of Carbon (up to 1.3%) and Mn (up to 30%). However, the added Mn should be less than 35% in order to avoid formation of brittle β -Mn. Aluminium was also introduced as an alloying element to increase the resistance to corrosion and oxidation. The utility of Triplex steels in the automotive industry has recently piqued interest owing to their strength-elongation compromise coupled with a low density. From the three phases that could be present in its microstructure – austenitic matrix, ferrite, and intra-granular χ -phases – the precipitation of the nanosized χ -phase inside austenite could lead to important precipitation hardening.

Third generation

These advanced high strength steels often have microstructures containing retained austenite, which undergo the TRIP and/or TWIP effect during straining or shear-band induced plasticity. Identified by a lean TRIP composition, such as TRIP bainitic ferrite (TBF) steels and Quench-and-Partitioning (Q&P) steels or medium Mn content lower than the above mentioned TWIP and Triplex steels – these steels are thereby called medium Mn TRIP steels.

Apart from medium Mn TRIP steels, all the other steel grades have the soft polygonal ferritic matrix generally replaced by a harder one consisting of either bainite (TBF steels) or tempered martensite (Q&P steels), respectively. The difference of hardness of the matrix and the inclusions is considerably lower using such a technique. More the homogeneous microstructure lowers the local micro-strains between matrix and inclusions, which, in turn, improves the bending and hole-expansion properties by a large margin. In addition to that, strained induced transformation of retained austenite to martensite during straining provides a much higher deep drawability. Consequently, these steels are suited for both bending and deep drawing operations rendering them especially suitable for manufacturing complex components like seat parts. The tensile strength of TBF and Q&P steels is > 1000 MPa with total elongations $> 10\%$ by superior bendability and hole expansion properties. Medium Mn TRIP steels are comprised of 4–7 wt% Mn having microstructures of ultrafine-grained ferritic matrix with a grain size typically less than $1 \mu\text{m}$ and a high-volume fraction of retained austenite usually up to 30 vol%. Tensile strength of these steels is usually > 1000 MPa along with total elongations in a range of 25%–40%.

Due to their higher ferrite potential compared to high Mn twinning-induced plasticity (TWIP) steels, medium Mn steels, exhibiting austenitic-ferritic microstructures, are hence suitable for third-generation advanced high-strength steel applications. Since the strain hardening characteristics of medium Mn steels are inferior to those of fully austenitic high Mn steels alloy design strategies to obtain fully austenitic medium Mn steels capable of the TWIP effect have been developed.

In order to achieve a fully austenitic microstructure, the martensite start temperature is lowered by raising the C concentration to > 1 mass%, thereby facilitating the formation of cementite. The cementite formed during cooling from austenitization temperature is counteracted by alloying with Al. The high affinity of Al for oxygen favors the formation of an oxide layer on the surface of steels. This oxide layer can in turn protect the bulk alloy from further oxidation and act as a barrier against the outward diffusion of C during high temperature solution annealing of high C steels. Furthermore, Al addition reduces the specific weight and can provide an additional tool to adjust the stability of austenite.

Fig. 9 illustrates the Ashby Plot for different generations of AHSSs correlating elongation to tensile strength.

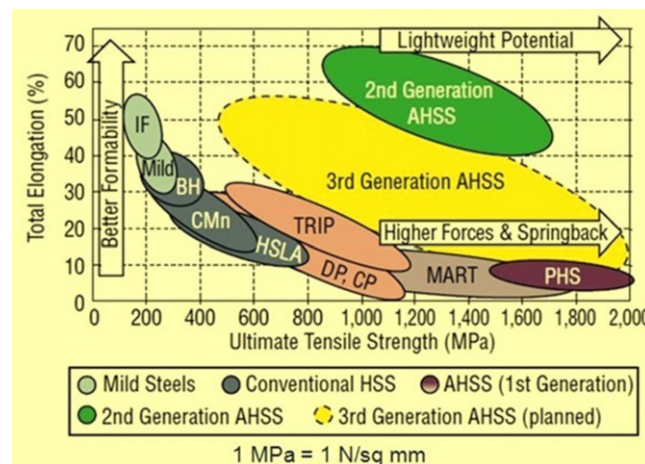


Fig. 9 Ashby plot representing the correlating elongation to tensile strengths of the different generations of AHSSs.

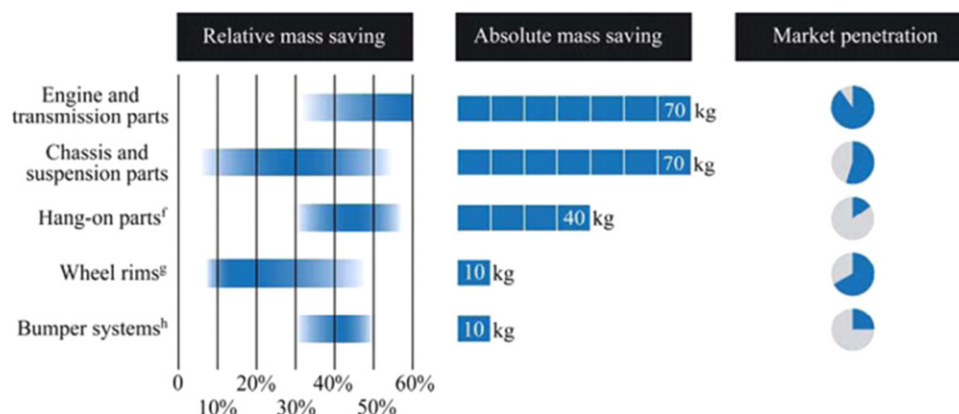


Fig. 10 Aluminium's direct mass savings and market penetration. Reproduced from Anon, 2012. EAA Brochure "Aluminium in Cars". Ducker Report. Available at: www.scribd.com/document/157245456/EAA-Aluminium-in-Cars-Unlocking-the-Light-Weighting-Potential.

Aluminium (Al)

Aluminium is the material of interest to many automotive producers for making vehicle parts such as chassis, body due to its low density, good formability, and corrosion resistance (see "Relevant Websites section"). Aluminium alloys customized by appropriate variations in chemical composition and processing perfectly support many requirements, like the non-heat treatable Al-Mg alloys used in chassis optimized for superb resistance against intercrystalline corrosion and concurrent high strength or the heat treatable Al-Mg-Si alloys for extrusions and autobody sheet modified for improved age-hardening response during the automotive paint bake cycle (Hirsch, 2014).

The average total aluminium content per car for European cars was 140 kg in 2012. Its distribution has been analysed systematically as: (i) Power-train (engine, fuel system, liquid lines): 69 kg (25 components analysed) in engine block and cylinder head, transmission housings and radiators. (ii) Chassis and suspension (cradle, axle): 37 kg (17 components analysed) in wheels, suspension arms and steering systems. (iii) Car body (body-in-white (BIW), hoods, doors, wings, bumpers and interiors): 26 kg (20 components analysed) in bonnets and doors, front structure and bumper beams. Fig. 10 shows mass saving level due to use of aluminium in automobile and hence its market-penetration.

Aluminium is incorporated in vehicle body parts by three forms, like age-hardening Al-Mg-Si alloys (mainly 6xxx series alloys are used), preparing non heat-treatable Al-Mg-Mn alloys (5xxx alloys are important here), aluminium extrusions and casting.

By far, the biggest advantage offered by using aluminium in automobiles, including both engine and structural components, is the significant reduction in weight it provides. In fact, Al components weigh about half of equivalent steel components. This weight difference translates to much better fuel economy for drivers.

In addition, using Al doesn't require a compromise in the strength of vehicle components. It provides the same structural integrity as steel, so its weight-reducing advantages and increased fuel economy can really shine. The most important advantage of using Al over other materials in car industries is Al provides high strength-to-weight ratio, high corrosion resistance and advanced crash protection simultaneously.

In fact, Al components weigh about half of equivalent steel components. This weight difference translates in too much better fuel economy for drivers. In addition, using Al does not require a compromise in the strength of the vehicle components. It provides the same structural integrity as steel, so its weight-reducing advantages and increased fuel economy can really shine. Al and its alloys show very high corrosion resistance. So, from the durability perspective it is very beneficial to use Al in vehicle especially in the body parts. Al makes alloy with almost every metal to produce stronger and more qualified materials. Its 3xxx, 5xxx, 6xxx alloys are good examples of that. Al is much more efficient in crash protection than other metals currently in use. In the event of an accident, Al can absorb a lot more of the kinetic energy that would otherwise be transferred to human occupants of vehicles. Injury likelihoods are lessened as drivers and passengers are both kept safer. The scope of Aluminium usage in various car-parts is given in the Fig. 11.

Polymers

Plastics industry is very important in supporting the automotive industry. Automobile engineers are working together closely to optimize other systems, integrating injection and blow moulded parts offering a better product without expensive assembly work. Plastics are also finding their way into the structural design of the cars. There are four areas in automobile, interior, body and exterior, powertrain and chassis and light weighting which need highest-priority research and development with plastics (see "Relevant Websites section"). According to the European automobile researchers, it is possible to incorporate 350 kg engineering plastics to an average car. The Fig. 12 indicates the areas in which plastic can be useful in which form.

The following table shows the scope of use of some polymers in various parts of a car, their sources and key characteristics Table 1.



Fig. 11 Use of Al in various parts of a car. Reproduced from Mayyas, A., Qattawi, A., Omara, M., Shana, D., 2012. Design for sustainability in automotive industry: A comprehensive review. *Renewable and Sustainable Energy Reviews* 16, 1845–1862.

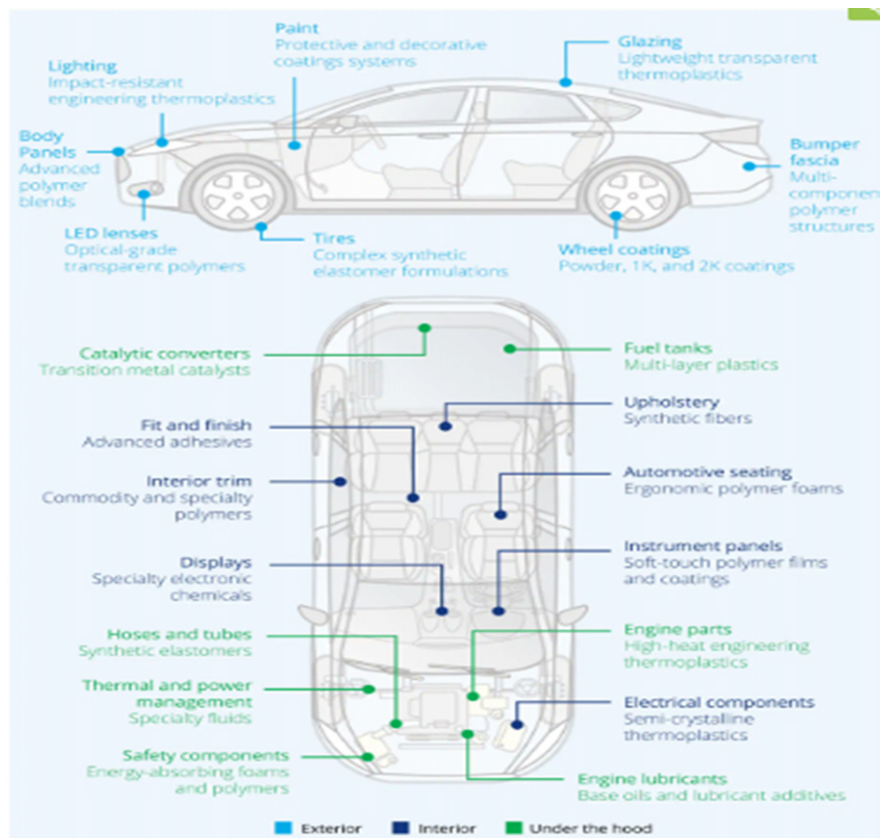


Fig. 12 Applicability of plastics in various car parts (www.deloitte.com/insights).

Other than advanced steels, Al alloys and polymers there are so many engineering materials which can enhance sustainability to automobile industry. A recently introduced technique is freeze casting of metals and ceramics to introduce lightweight foams. Titanium is very much responsive in this technique. NASA has already applied freeze casting technology to build advanced

Table 1 Polymers and their chief usage

Name of polymer	Source	Key advantages	Best applications
Polypropylene (PP)	Propylene monomer	It is rugged and unusually resistant to many chemical solvents, bases and acids.	Automotive bumpers, chemical tanks, cable insulation, gas cans, carpet fibers.
Polyurethane (PUR)	Organic units joined by carbamate links	Solid Polyurethane is an elastomeric material of exceptional physical properties including toughness, flexibility, and resistance to abrasion and temperature. Polyurethane has a broad hardness range, from eraser soft to bowling ball hard. Other polyurethane characteristics include extremely high flex-life, high load-bearing capacity and outstanding resistance to weather, ozone, radiation, oil, gasoline and most solvents.	Flexible foam seating, foam insulation panels, elastomeric wheels and tires, automotive suspension bushings, cushions, electrical potting compounds, hard plastic parts.
Poly-Vinyl-Chloride (PVC)	Vinyl-Chloride monomer	PVC has good flexibility, is flame retardant, and has good thermal stability, a high gloss, and low (to no) lead content. Polyvinyl chloride moulding compounds can be extruded, injection moulded, compression moulded, calendared, and blow moulded to form a huge variety of products, either rigid or flexible depending on the amount and type of plasticizers used.	Automobile instruments panels, sheathing of electrical cables, pipes, doors.
Acrylonitrile Butadiene Styrene (ABS)	ABS is a copolymer made by polymerizing styrene and acrylonitrile in the presence of polybutadiene.	The styrene gives the plastic a shiny, impervious surface. The butadiene, a rubbery substance, provides resilience even at low temperatures. A variety of modifications can be made to improve impact resistance, toughness, and heat resistance.	Automotive body parts, dashboards, wheel covers.

lightweight spacecraft materials. It will be of great pleasure to material scientists when freeze casted foams will be introduced to automobile sector.

Sustainable Designing

The present automobile industry is still primarily focused on using metals, instead of newer, more efficient materials. The need for product sustainability, however, is ultimately driving automobile design toward new materials technologies such as plastics and composites, which can be up to 10 times lighter than ferrous metals.

The motivation for going for a much lighter and streamlined design is driven by the observations from the following calculations:

$$\text{Drag force}(F_D) : F_D = \rho/2 \times v^2 \times c_d \times A \quad (1)$$

$$\text{Roll resistance}(F_R) : F_R = c_{ar} \times m \times g \times \cos\alpha \quad (2)$$

$$\text{Gradient resistance}(F_G) : F_G = m \times g \times \sin\alpha \quad (3)$$

$$\text{Acceleration resistance}(F_A) : F_A = m \times a \quad (4)$$

In Fig. 13, ρ = Air density, c_d = Drag coefficient, m = Mass of car, A = Cross-sectional area, c_r = Coefficient of rolling friction – CRF, g = Acceleration due to gravity, a = Acceleration of car, α = Angle of inclination.

Upon analysis of Eqs. (1)–(4), it can be observed that if ρ , c_d , c_r , g , a and α are treated as constants while considering the design of the car, then each of the resistances can be reduced by bringing down the mass (m) of the car. Moreover, the Drag Force can be reduced by decreasing the cross-sectional area (A). This forms the motivation for striving towards designs offering streamlined automobiles, thereby presenting lesser cross-sectional areas to air-drag.

Another aspect which comes into the scene, when considering the sustainability of the automotive industry is the economic viability of the overall car, ensuring that the quality of the car is not compromised in order to economize its material selection and manufacturing process (Mayyas et al., 2012).

Designing manufacturing processes based on the model of sustainability

In a search for flexibility, at the production level as well as in redefining the concept of cars, as friendly as possible, the automakers have been looking forward to extend its market that was restricted to only 20% of the planet by the end of the 20th century.



Fig. 13 Various forces acting on a moving car.

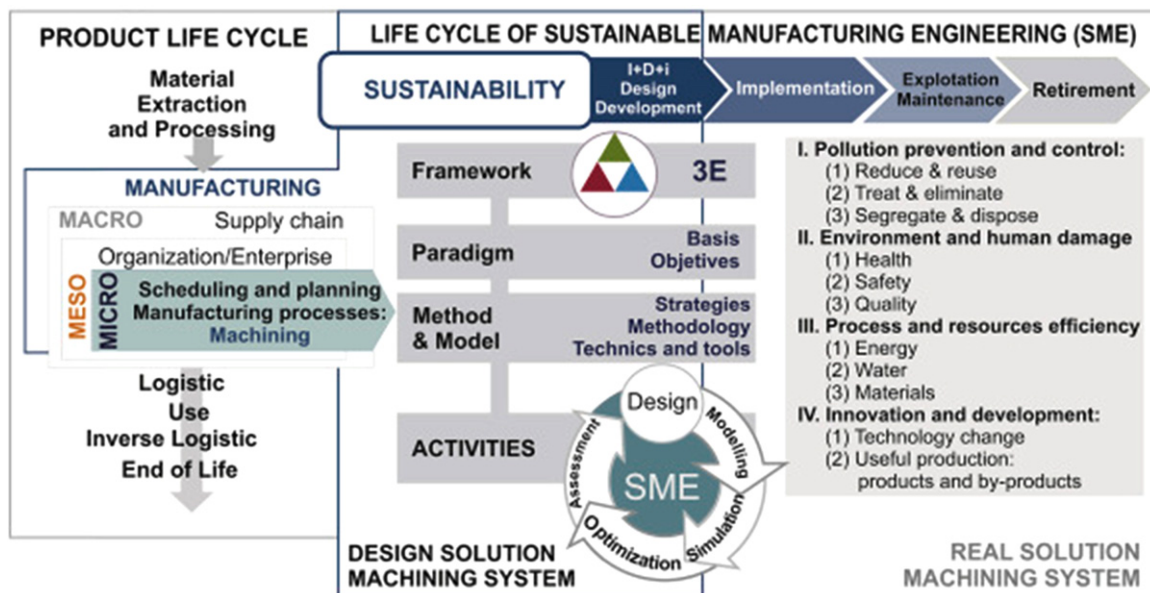


Fig. 14 Design based upon product life cycle. Reproduced from Peralta, M.E., Bárcena, M.M., González, F.A., 2017. On the sustainability of machining processes. Proposal for unified framework through the triple bottom line from an understanding review. *Journal of Cleaner Production* 142, 3890–3904.

Thereby, the primary step to assure this concept of “eco-car” or “green-car” is to reimagine and reengineer the way that cars are designed, incorporating environmental parameters from the very initial stages – manufacturing. LCA and eco-design have very important roles to play in this developing scenario as the methodological framework and a systematic and integrated approach towards the development of novel productive models, which can provide a sustainable basis for the automotive industry in the 21st century. Fig. 14 shows how product life cycle may affect design of an automobile.

In this sense, the future efforts on R&D at Renault, besides the short term ones such as the development of more efficient catalytic converters and particulate filters, are aiming for low or free emissions vehicles by using: (i) LPG (liquid petrol gas) (ii) Natural gas (iii) Electric vehicles (iv) Hybrid vehicles (combining electric and internal combustion engines) (v) Fuel Cells (hydrogen that emits nothing but water vapour) (Medina and Naveiro, 2003).

Apart from the design of the car itself, focus must also be shifted to the huge range of activities that the automotive industry spans, such as casting, machining, metal pressing, body assembly, surface treatment, painting and final assembly. Although these facilities do not represent a “high risk for the environment” (as set out in the 1996 European so-called Soveso directive), they nevertheless cause a series of environmental impacts that must be controlled.

These measures, which have already been adopted by leading car manufacturers around the world, include (i) reducing emissions per vehicle of Volatile Organic Compounds (VOCs), produced by paint solvents, (ii) using advanced technology

equipment (plasma torch) and developing control systems, to significantly reduce foundry dust emissions (iii) lowering of water consumption per car produced by a factor of 2.5 (iv) recovery of production waste.

Designing for recyclability

The rapid pace of automotive technology development has shown a significant growth in end-of-life vehicles (ELVs) waste streams globally. The number of ELVs is projected to increase continuously. ELV recycling plays an important role in maximising recovery of high-quality materials that can eventually be reused in a closed-loop vehicle manufacturing system. It is crucial to choose the proper combination of materials and joining techniques to achieve the optimal recycling. Most of the current recycling facilities are only capable of recovering metals cost-effectively, and the trend of new car designs is showing an increasing usage of light metals, plastics and composites that are not traditionally recovered. The flow diagram given under Fig. 15 shows the processes involved in recycling an automobile.

Design for recycling targets the same features as design for disassembly. It addresses more specifically the selection of materials and sets their recycling rate. It further points out the need to form recycled materials into new products. Particularly, fewer dissimilar materials in assemblies, or in subassemblies of products designed for disassembly, will improve the possibilities of material life extension. At present, there is a high recyclability rate for metallic vehicle components but a low recycling rate for the non-metallic materials.

The process of ELV recycling comprises of the following steps:

- Dismantling:** The recycling value of the components is highly increased in the dismantling process and allows the reusability of the product. The dismantling industry has a great potential. However, the full implementation of the EU directive for ELV dismantling is highly limited at present because it is labour intensive and uneconomical. Only a few high-value components are removed from the vehicle before sending to the shredding process. Dismantling companies can be branded into two types of businesses, the first comprises high-value parts businesses that remove and inventory the useful and high-value parts for resale. The other comprises scrap yard businesses that store the ELVs while the parts are gradually removed and then sold to local repair shops as well as Do It Yourself (DIY) owners.
- De-pollution processes:** De-pollution processes are seen as the removal of hazardous substances, battery, fluids, tires etc. It is good to note that high-value components are removed via manual disassembly. Several small facilities separate pure stream plastic for direct selling to recyclers and re-processors. The rest of the vehicle body is subjected to shredding operations for post-fragmentation recovery. Once the ferrous content has been recovered, the non-ferrous scraps are removed through dense media separation processes. The remaining components are sent to landfills.

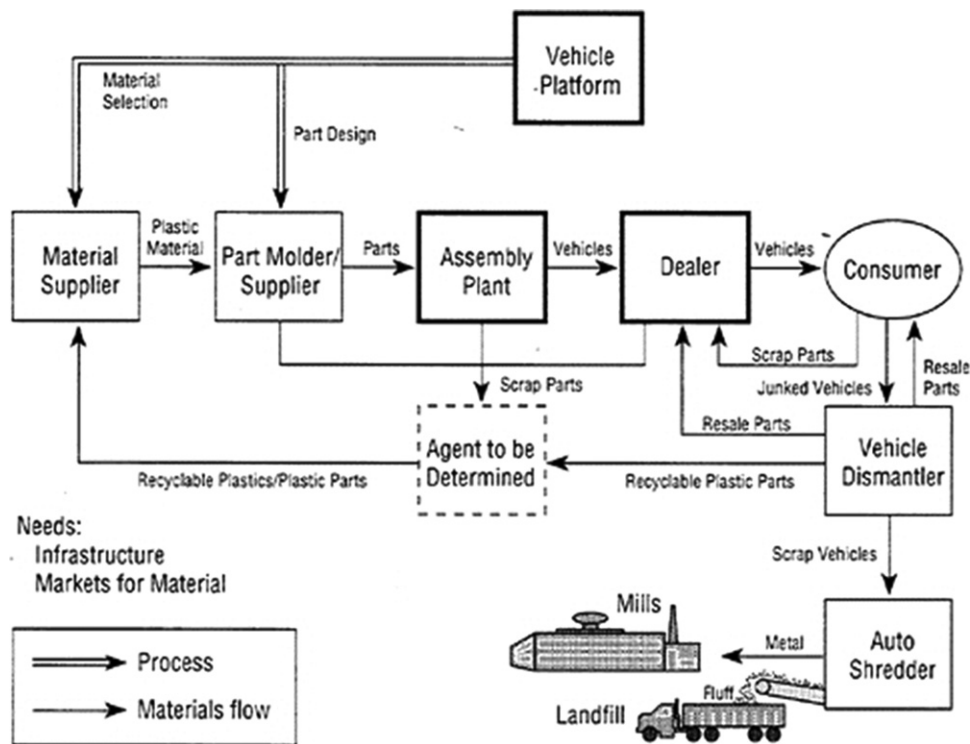


Fig. 15 Recycling a vehicle. Reproduced from Klimisch, R.L., 1994. Designing the modern automobile for recycling. The Greening of Industrial Ecosystems. Washington, DC: National Academy Press, 165–170.

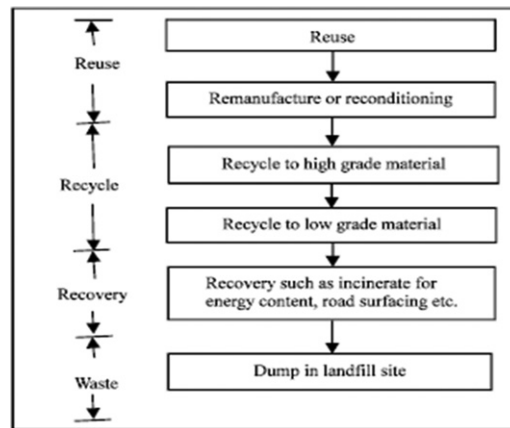


Fig. 16 Steps of recycling.

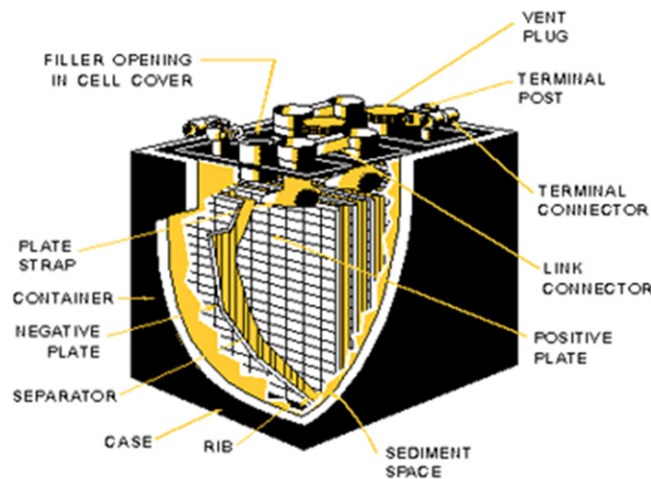


Fig. 17 Structure of a lead-acid battery, inside out.

- (c) Shredding process: This is another process of ELV disposal. Shredding industries can process large quantities of ELVs at capital-intensive sites. The main output from this process is ferrous metal, which is sent to steel industries for recycling. In the shredding process, rotating hammers rip parts of the compressed ELV, dropping it easily from the output grid where the light materials are separated from the heavy materials (such as plastic from steel). However, the process efficiency depends on the characteristics of the applied design. Therefore, recycling success can be increased by considering the hierarchies of the recycling process in the early design stages, which are listed out in [Fig. 16](#).

Recycling car batteries

Lithium-ion batteries ([Fig. 17](#)) are starting to be used in significant quantities for automotive propulsion. Because these batteries are expected to last the life of the vehicle, they will not be ending their useful lives in large numbers for about 10 years. They may subsequently be used for utility energy storage, but eventually their useful lives will end. The question is, what steps can be taken to ensure that these spent Li-ion batteries are recycled. In an ideal system, these batteries would be sent for responsible recycling and not be exported to developing countries with less stringent environmental, health, and safety regulations.

The lead-acid battery components are recycled by a simple process. First, the battery case is broken open, and the sulphuric acid electrolyte is drained out and collected. The plates and connectors can be removed from the case at this point and recovered whole. Alternatively, the drained battery can be sent to a hammer-mill for size reduction, and the plastic and lead can be separated by a simple sink-float device. The recovered lead (a low-melting metal) is re-melted and purified to make new battery components. Lead and sulphur emissions from secondary smelting is tightly regulated by the Environmental Protection Agency. The plastic is melted and moulded into new cases. The acid can be neutralized or processed to sulfate salts for various uses, such as the manufacture of soap. [Fig. 18](#) depicts the life cycle of a typical lead acid battery.

The recycling operation is profitable because recycled lead (taken back to its elemental form and purified) is known to be of high quality, so there is little incentive to export to places with less-stringent regulations. Some battery manufacturers prefer new

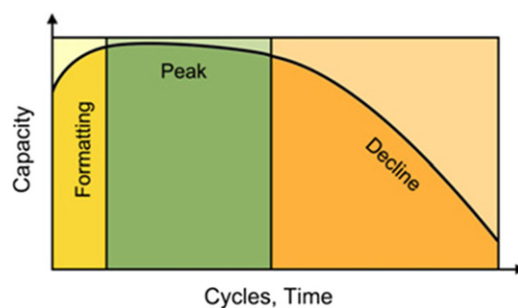


Fig. 18 Life-cycle of a battery (https://batteryuniversity.com/learn/article/how_to_restore_and_prolong_lead_acid_batteries).



Fig. 19 CLEVER – Compact low emission vehicle for urban transport (wired.com).

over the recycled lead. A key reason for the success of lead-acid battery recycling is that essentially all of the manufacturers use the same raw materials: lead, lead oxide, and sulphuric acid in a polypropylene case. As the battery design is similar for the manufacturers; automated technology can be used for battery disassembly. In summary, lead-acid recycling works well because it is profitable, it is illegal to dispose of the batteries without recycling, the battery disassembly is simple because of the standard design used, the battery chemistry does not require segregation, and the recycling process is simple.

Designing green cars – The cars of tomorrow

New designs have been suggested and are being developed even as you read this sentence. These designs would allow for greater fuel efficiency, reduced emissions per vehicle and high-cost efficiency among other benefits. A few of such designs have been listed below:

(1) CLEVER – (Fig. 19)

The CLEVER was originally conceived as a project at the Technical University of Berlin, as engineers aimed to design the lightest, cleanest city car possible. While still in prototyping stages under BMW, the final form of the CLEVER is expected to weigh less than 400 kg, and emit less than 60 g/km of carbon dioxide from its compressed natural gas engine. Perhaps the boldest design innovation by the team was giving the meter-wide vehicle the ability to lean like a motorcycle in corners, using kinetic energy in a far more efficient fashion. Power comes from a 230-cc single-cylinder engine that produces 12.4 kW (16.7 hp). BMW claims Clever can do zero to 60 km/h (37.2 mph) in around 7 s and tops out at approximately 100 km/h (62 mph). Clever is safer than it might look. It has special seat belts and a specially developed driver airbag that allowed Clever to comply with the Euro NCAP crash test requirements. The passengers, who sit tandem, are ensconced in a survival cell.

(2) SIMPLE – (Fig. 20)

“Sustainable and Innovative Mobility Product for Low Energy consumption” (SIMPLE) combines the best features of cars and motorbikes in one package, apparently, with the protected cabin of a car suited to the size and dynamics of a two-wheeler. The Simple does much of the work with hydraulics in place to prevent any accidents, stepping in during very slow traffic when the vehicle is the most unstable. Simple tips the scales at only 450 kg (920 pounds), so the internal combustion engine motivating it is commensurately small, putting out only 36 kW (48.2 hp). BMW says the three-wheeler will do zero to 62 mph in less than ten seconds and has a super-slippery drag coefficient of 0.18. The car’s most notable feature is it leans like a motorcycle in turns.



Fig. 20 SIMPLE by BMW (<https://www.evo.co.uk/bmw/10617/bmw-simple-concept/>).

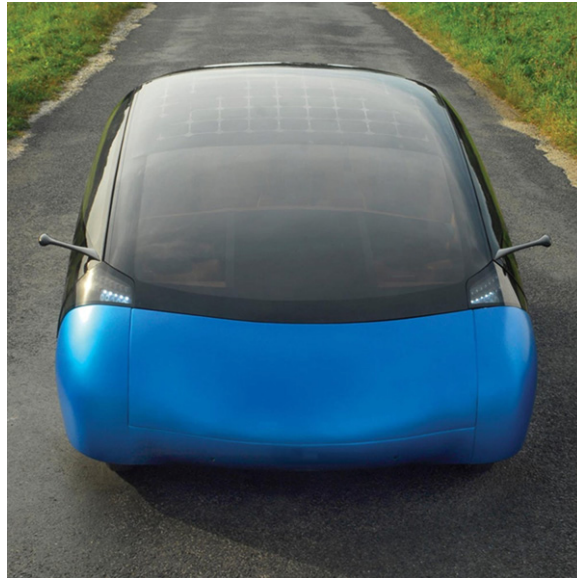


Fig. 21 Antro SOLO (<https://hungarian-success-stories.com/2013/03/13/futuristic-hybrid-car-solo-duo-and-porto/>).

(3) Antro SOLO – A human-electric-hybrid (Fig. 21)

Antro's prototype has been built using a light magnesium alloy/carbon fibre frame and body construction and features electric assist for when the occupants tire or the driver is alone. Photovoltaic cells incorporated in the roof provide the power for the electric hub motors at each wheel and although the current model doesn't have one yet, the designers are aiming to install a fuel engine to give a longer range than the 12 miles or so that the electric motors currently provide. It is intended that the fuel engine will achieve fuel efficiency in the region of 150 miles to the gallon and reach speeds of around 87 mph.

Renewability in Automobile Industry – Vision of Developers

The term 'renewability' in automobile industry is the combination of two approaches that can be incorporated by the car developers- firstly, the use of recyclable materials and arrange for the ease of their recyclability and secondly, use of renewable energy sources in vehicles bypassing the huge usage of conventional energy sources. Renewability is the most important significant step towards green development, i.e., to deal with the pollution worries. The renewability measurements in automobile can be use of eco-friendly and bio-degradable products such as polymers, composites, advanced plastics in internal and external body parts, use of highly efficient batteries and thermoelectric materials etc. Various approaches to enhance renewability in automotive sector are discussed below.



Fig. 22 Local motors has 3D printed a fully working crowd-sourced car called the Strati (newatlas.com/local-motors-strati-imts/33846/).

Incorporating 3-D Printed Plastics and Thin Air Technology

Some automakers foresee the potential to use 3-D printing to create cars in widely distributed, smaller manufacturing facilities, using far fewer parts and some point to a future of rapid customization and personalization of cars: going from unique design, computer modeling, to building (printing) in days, not years. This new manufacturing model may also lead to further improvements in sustainability. While mainstream automakers already use 3-D printing for rapid prototyping to help bring cars to market faster, the race is on to build 3-D printed cars that meet both government safety standards and consumer performance expectations (Anon, 2017). Two major initiatives to introduce 3-D printing in automobile industry are: (i) The Divergent Manufacturing Platform enables manufacturers to quickly design and build new cars at a fraction of the cost and environmental effect of those produced in traditional factories. Using 3D printing as part of its unique NODE (see “Relevant Websites section”) system, Divergent 3D claims it can produce vehicle structures that are over 50% lighter with lower automotive production costs and fuel consumption. The NODE system is a new approach to manufacturing that incorporates 3D printed joints, which can connect carbon fibre structures to build an industrial strength chassis in just minutes. And (ii) Local motors designed first 3-D printed electric car “Strati”, which is made of carbon-fibre-reinforced plastic. The process of 3-D printing the Strati is quite efficient – it takes only a couple days to print the body of the vehicle, which is manufactured as one large piece (Fig. 22).

Another outstanding approach towards renewability by Ford is to produce car parts from thin air. They are aiming to make auto parts using plastics made in part from captured carbon dioxide waste streams. According to Ford researchers, they were inspired by plants that take in carbon dioxide and create complex sugars. In a similar manner, Ford is taking excess carbon dioxide and making durable plastics to use in vehicles. It will reduce the carbon-footprint of the producer as well.

These are the most advanced initiatives on waste management and undoubtedly these are having the power to incorporate recyclability in a sustainable manner.

Using Engineering Plastics (Polymers)

High performance polymers often known as engineering plastics can play an important role in vehicle production. Of course, they produce lightweight vehicles than metallic vehicles, which lead to increase fuel efficiency of the vehicle. But their advantages are not limited to lightweight production only, other chief advantages are like minimal corrosion, ease in recyclability, flexibility in integrating components, safety, comfort and economy etc. From the renewability point of view, first two advantages are mostly important. Corrosion minimization yields longer vehicle life and more importantly it lowers the amount of waste after end-of-life which allows most of the vehicle parts to undergo recycling. The recycling process of some polymers is much easier too than the metals which are used in automobile like Steel, Aluminium etc. The five most usable plastics in automotive industries are Polypropylene (PP), Polyurethane (PUR), Poly-vinyl-chloride (PVC) and Acrylonitrile Butadiene Styrene (ABS).

Plastics are in use in automobiles since the 1950s, but the latest innovations are really changing the industry for the better. Engineered plastics are on the way to replace aluminium and other metals in automobiles, with the average car interior now being made up of over 50% plastics (see “Relevant Websites Section”). Tough, lightweight plastics can help improve automotive fuel efficiency and when used plastics are recycled, it helps to keep valuable materials out of landfills so they can live another life as car parts or other products. Below some statistics are given for plastic usage by leading automobile producers (Anon, 2014):

Chrysler

Uses recycled polyurethane foam plastic in the seat cushions of its Jeep Grand Cherokee, and the wheel liners on the Jeep Wrangler and Chrysler 200 are made with 64% recycled plastics. In 2013, nearly 40% of the thermoplastics (the most widely used types of plastics in autos) in Chrysler’s European vehicles were recycled plastics.

Ford

Uses recycled plastics to create upholstery for passenger seat cushions in numerous models. For example, the seat fabric for each Focus is made with approximately 22 plastic water bottles. The company used more than 50 million pounds of post-consumer recycled plastics on the exterior of Ford vehicles made in North America – that equals nearly 18 pounds per vehicle on average. In the U.K., Ford also collects damaged bumpers to make plastic materials for replacement bumpers.

Honda

Recycles scrap bumpers generated during the manufacturing process. Plastics from bumpers produced at five Honda plants in the U.S. and Canada are reformulated and reused in Honda's supply chain to make mud and splash guards.

General motors

Uses air deflectors (used to direct air flow) for its Volt made from plastic caps, bottles, and other recycled materials. The company also uses plastic caps and shipping aids from its Fort Wayne facility to make radiator shrouds (used to protect the radiator) for the Chevrolet Silverado and GMC Sierra pickups built at that facility.

Renewable Energy Sources in Automotive Industry

The main aim of automobile producers these days is to restrict fuel using and reducing the usage of conventional energy sources, i.e., to control the carbon footprint of automotive industry considering the environmental issues. The major outcome of this concept is the recent bulk use of electric vehicles worldwide. Apparently, it seems that electric vehicles save conventional energy by not taking the fuel, but the real scenario is quite different.

Fig. 23 describes that electric cars need charging for their battery, charging stations need electricity to provide battery charging and finally these stations create additional pressure to thermal power stations and again conventional energy sources like coal, diesel is burnt. So, they are saving energy in a little amount which is not significant to restrict the hazardous impacts of automobile on environment.

It will be more fascinating if thermoelectric materials can be introduced in electric vehicle. In 2011 researchers introduced the idea of putting thermoelectric materials at exhaust pipes, which can generate significant amount of electricity and enhance the fuel efficiency of vehicle ([Matheson, 2014](#)). As there is no heat outcome in electric cars so, thermoelectric materials can be used in rooftop of the vehicle which will work only with solar energy and that transformed electricity can be used in small appliances like interior lights, music system, wipers, central locking system and in some tiny sensors. These materials should also be lightweight to be sustainable. Another energy saving technique that can save the battery, i.e., will aid the driver by increasing interval between two charging is regenerative braking system. The main function of this system is to store the lost kinetic energy due to braking and the stored energy can be utilised later. No doubt the use of thermoelectric materials and regenerative braking system will further enhance the energy efficiency of electric cars and maximum energy efficient vehicles can be obtained.

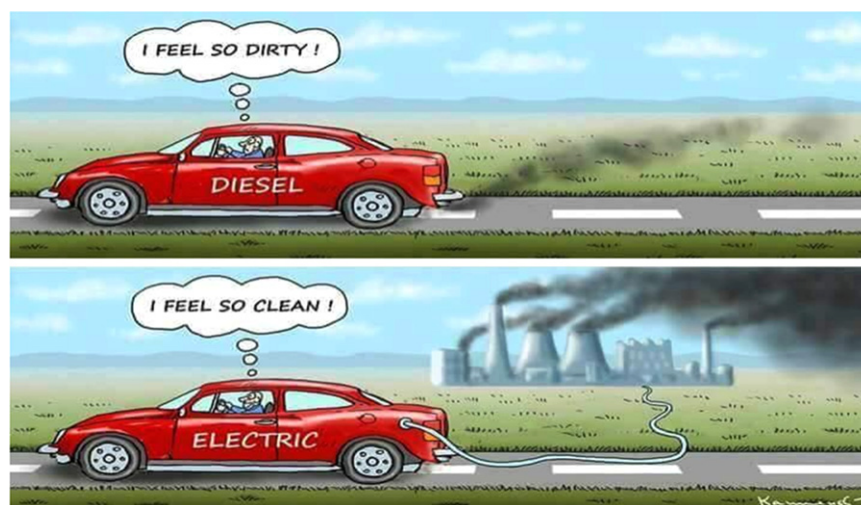


Fig. 23 Apparent energy saving vs real scenario for electric cars. Reproduced from Schneider, R., 2018. Materials Selection for a More Sustainable Automotive Future. Western Norway University of Applied Sciences.

Summary

This article briefly highlights the present challenges associated with a typical automobile industry and their possible solutions – which are incomplete without the concepts of renewability along with sustainability. It is discussed how sustainable approaches can be beneficial to achieve the most advanced state without creating an adverse impact as well as how renewability serves as the key for green development. Various methods and ongoing applications are given to incorporate renewability and sustainability. A comparative study between conventional and recently developed advanced materials has also been included. Finally, the article shows recent technologies, like electric cars, can be made more commercially efficient and environment friendly.

See also: Application of Nanofluids for Radiator Cooling

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Renewable Biofuels and Their By-Products for Automotive Applications

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Introduction

The rate of economic development and urbanization has created a huge burden on the fossil fuel reserves of the world because they are the main source of primary energy. Due to the limited reserves of crude oil, the cost of petroleum based products is increasing continuously. In addition, these crude oil based products are also responsible for generation of greenhouse gasses which leads to catastrophic climate change. Automobile sector is the main consumer of petroleum based products, especially petrol and diesel, and hence also responsible for greenhouse gas emissions. Another reason is the fact that a large percentage of crude oil is imported from other countries oil fields. India meets over 82% of its crude requirement through imports and has been facing the onslaught of rising crude rates and Rupee depreciation which have been adding pressure on the Current Account Deficit (CAD), fiscal deficit and inflation. The use of conventional fuels leads to various problems such as environmental damage and health problems. The increasing industrialization and modernization of the world is leading to a sharp increase in demand for petroleum products. The current situation has sparked research interest in less polluting, non-petrochemical and renewable fuels for automobile application. Therefore, it is urgent to find fuel that can replace the conventional fuel. Reducing dependency on crude oil and minimizing the emissions from automotive sector is an important area in which researchers are working.

The development and use of alternate fuels, especially biofuels for automotive application, has attracted the researcher's attention. Biofuels offer several benefits, like reduced emissions, less dependency on conventional fuels and can be harvested on fallow lands which could provide jobs in rural areas, over conventional forms of fuels (Bluhm *et al.*, 2012; Dale *et al.*, 2010; Eriksson and Gustavsson, 2008; Ramos *et al.*, 2016). Biofuel can be produced from carbon rich sources such as plant biomass by fermentation and photosynthesis process. Since it can be produced from plant waste biomass, thus biofuels production is economical too. When bio-fuels are burnt, they emit low carbon and simultaneously control the production of poisonous substances, due to which air pollution levels are also low in the atmosphere. Technologically biofuel's properties suit all the existing automotive engine quality in most of the conditions. In addition, the engine running with biofuels needs less maintenance, low cost, no pollution and hence the long life of the vehicle as well as the environment.

Based on the types, biofuel can be found in all three forms, liquid, solid and gas such as wood charcoal, bioethanol, biobutanol, biodiesel, biohydrogen and biogas. First generation biofuels are produced directly from food crops to be used as biodiesel or bioethanol through fermentation. However, first generation biofuels have a number of associated problems. Most importantly, there is a contention of fuel versus food when it comes to these and in effect first generation biofuels have not found many takers across the world. This gave rise to the second and third generation biofuels. Second generation (2G) biofuels are produced from non-food crops such as wood, organic waste, food crop waste and specific biomass crops, therefore eliminating the main problem with first generation biofuels. Third generation biofuels (3G) on the other hand, mostly refers to those derived from algae. These biofuels come with their fair share of problems, including commercial, non-viability in some cases, the requirement for large areas of land/water as the case may be, contention on the actual carbon footprint across the entire value chain and many more.

Thus, as with most emerging opportunities, next generation biofuels present a promising future, but with challenges on the way. Hence, a balanced understanding of the opportunities the sector promises along with its inherent challenges is needed before investment decisions can be made. Now, in order to establish the biofuels as a potential alternate fuel for automotive applications the economic aspect must be studied by using life cycle cost analysis. Since, to proliferate in the market the final cost of the biofuels must be competitive with current petroleum products. The final cost of the biofuels is commonly assessed in terms of life cycle perspective (Singh *et al.*, 2010; Wang *et al.*, 2013), starting from the cultivation of the grains till the biofuel distribution in the market. The production of biofuels varies from place to place which affects its production cost. Therefore, life cycle cost of biofuels is an important aspect to determine the optimized cost and performance of the biofuel. In order to mitigate various consequences, alternative oilseeds are being investigated as biodiesel feedstocks.

Madhuca commonly known as the butter-nut tree is a large sized deciduous trees growing up to a height of 20 m is one of the promising tree species suitable for providing oil for biodiesel production, which conforms to international standards. It is commonly known as Mahua in Hindi. Madhuca is a widely adaptable tree, which can be grown on a wide variety of soils. For better growth and productivity, well drained deep loam or sandy loam soils are ideal but it also occurs on shallow stony, clayey and calcareous soils. A large variability exists in its fruits and oil percentage and there are no varieties available for block plantation. Mahua is indigenous to India; it is a frost resistant species that can grow in marginal areas of dry tropical and subtropical forests up. It can be found scattered in pastures, in crop fields in central India, and on river banks in semi-evergreen forests. It grows well where annual rainfall is between 500–1500 mm, and where temperatures are in the range of 2–46°C.

In this article the life cycle cost analysis of Mahua used for the production of biodiesel in India has been done. In the life cycle assessment, every stage like land purchasing, land preparation, nursery and plantation, irrigation, wedding, harvesting, drying and decertification, decortications, oil-extraction, filtering and finally trans-esterification is included.

Methodology

The tree has a potential of enhancing rural income. Being an evergreen variety and is a well adapted to varied weather condition. With its wide spreading branches and circular crown the tree presents a visually appealing structure. Seed yield ranges from 20 to 200 kg per tree every year, depending on its growth and development. The drying and decertification yield 70% kernel on the weight of seed. The kernel of seed contains about 50% oil.

For preparation of biodiesel, raw mahua (Seed) has been collected from the local area and filtered. The biodiesel from the vegetable oils has been prepared by the trans-esterification process. In this process, the vegetable oil has been heated to a temperature of about 60–65°C and methanol (30% of vegetable oil). Then, sodium hydroxide (NaOH) (1% of raw oil) has been added as a catalyst. Then, the mixture has been stirred for proper mixing and kept undisturbed for next 48 h. After completion of the reaction, the total mixture gets separated into two layers. The upper layer is methyl ester or biodiesel and the lower layer is glycerol. The upper layer (methyl ester) is separated and warm water of around 10% of the ester is added to remove any impurities like excess catalyst and methanol and suspended soap present in the ester and settled down for another 48 h. This process is called washing. Then the upper layer (around 85%) is decanted gently to another flask to rule out the presence of any impurity and the decanted oil is again heated to a temperature of around 60–65°C in order to evaporate the excess water. The biodiesel obtained are used for analysis purpose. **Fig. 1** shows step-by-step process of production of biodiesel from mahua.

Life Cycle Assessment and Discussion

In life cycle assessment the every stage like land purchasing, land preparation, nursery and plantation, irrigation, wedding, harvesting, drying and decertification, decortications, oil-extraction, filtering and finally trans-esterification should be included. Mahua trees are vegetatively propagated. Scions from the mother plant are grafted on year-old seedlings in July and are planted. Mahua responds positively to N, P, K fertilizers. Seeds are sown at a depth of 1.5–2.5 cm on raised beds. The seeds germinate in about ten days. One-month-old seedlings are transplanted in plastic containers of 15 × 25 cm. Six to twelve months old-seedlings are used for planting in the main field (5). The trees start bearing fruit in 10 years after planting and can yield fruits for up to 60 years. Older trees are more productive than young trees. Irrigation may be useful during fruit development, but should be avoided during flowering and leaf shedding. Man work 8 h/day (7). Before plantation, the field should be ready for plantation (Site preparation, alignment and stacking, digging of pits). The cost of FYM is 2.5 Rs./kg and the cost of fertilizer [Nitrogen(20 kg), Phosphate (10 kg), Potassium (15 kg)] are 108 Rs./ha, 90 Rs./ha, 960 Rs./ha (8). FYM, Fertilizer, irrigation, weeding and carriage charge are included up to 10 years. As per calculation ten yeas old Madhuca plantation has a sequestration capacity of 12 t/ha/year and 20 year old plantation has a sequestration capacity of about 27 t/ha/year.

Harvesting

In India, the fruits are harvested in May, June and July. Mahua trees are also harvested for their flowers and yield 100–150 kg of flower DM/tree/year. During 1st year seed yield 60 kg, 2nd year it will grow by 5% of its weight and 3rd year it will grow by 8% of its previous weight and 4th year up to 10th years it will grow by 10% by its previous weight. According to this, the labors also increase. Labor capacity of harvesting is 50 kg/day and for this they are paid 300 Rs./day. **Table 1** shows the amount of seeds/ha harvested for 10 years.

- Mahua seed.
- Mahua flower.

The growth rate of flower is 1% per year. Manpower increases accordingly. Open sun drying charge (900 Rs.) is also included every year in harvesting. The current price of the mahua flower is 20 Rs./kg. Hence total cost is found by quantity flowers and current price. In the first year this cost is Rs. 400,000.00/-. **Table 2** shows amount of profit from flowers/ha.

Total cost – Total investment = positive (profit). Here total cost is greater than total investment.

Decortication

Decortication is the process for separation of hull from seed yield. The decorticator is available in IIT (BHU), Varanasi of 1.5 kW with 150 kg/h capacity. **Table 3** shows the total cost in decortications. The extraction of oil from seed by screw press expeller of [5.5 kW with capacity 50 kg/h]10 kW with capacity 100 kg/h. Filtering of oil after oil extraction carried out with filter press of 1.5 kW with a capacity of 600 kg/h. oil and oil cake are available after crushing the seeds.

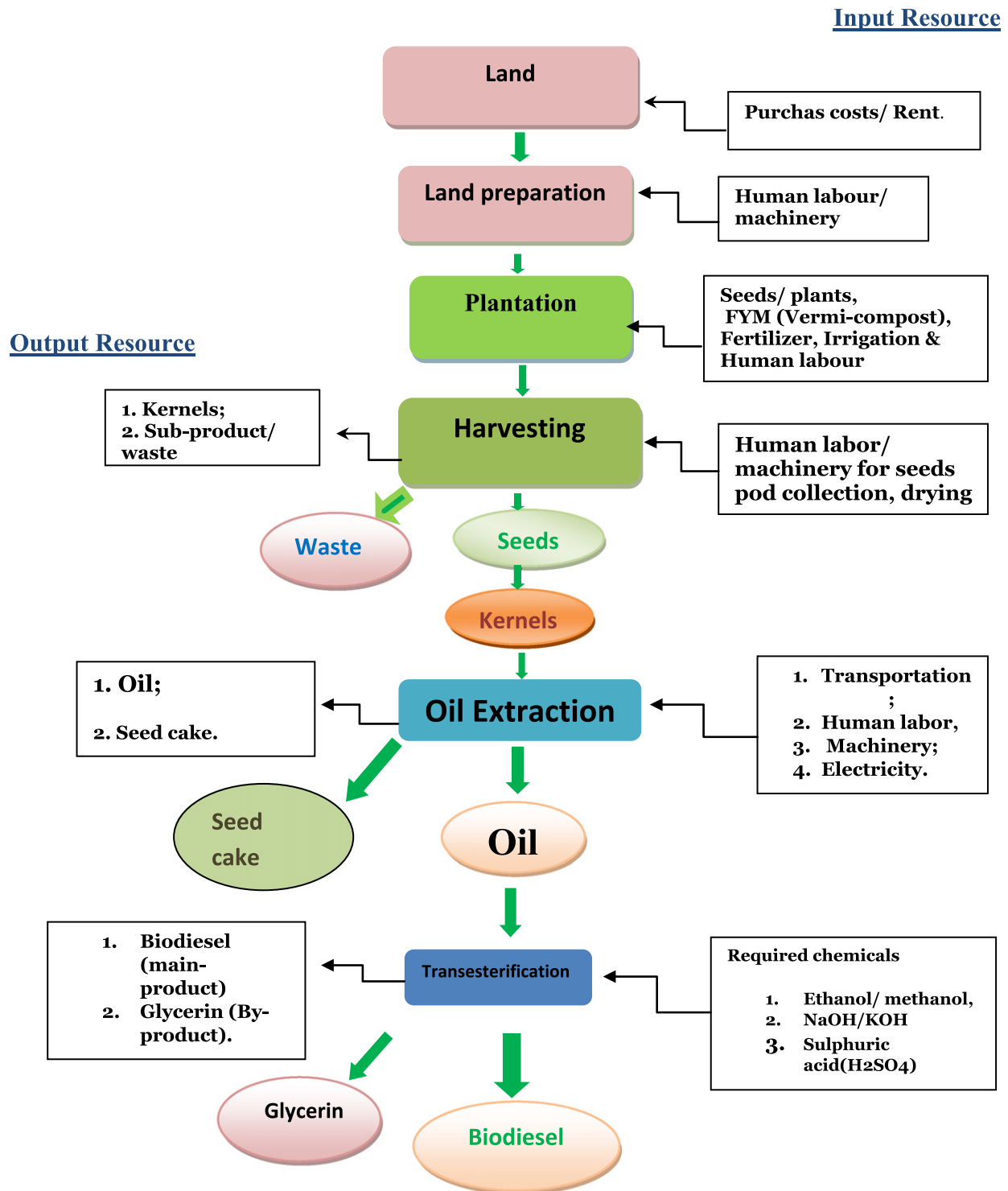


Fig. 1 Process of biodiesel production from Mahua.

Men work = amount (kg)/capacity of the decorticator (kg/h).

Man work hour = 8 h/day.

Hence, Men power cost = days × 561/-Rs. (9) [the minimum wage rate in rupee per month 16,858/-(skilled employees) hence 561/- per day].

Electricity consumed = capacity of decorticator (kW) × time period (h).

Commercial rate of electricity- 10 Rs./unit.

Transportation charge- according to amount.

Table 1 Seeds harvested per hectare

	MD/day	Seed kg per tree	kg/day	Harvesting cost per MD 300 Rs./day	Seed kg/ha	Amount of seed (harvesting charge)/ha
1 yr	24	60	1200	7200.00	12,000	72,000.00
2 yr	25	63	1260	7560.00	12,600	75,600.00
3 yr	27	68	1361	8164.80	13,608	81,648.00
4 yr	30	75	1497	8981.28	14,969	89,812.80
5 yr	33	82	1647	9879.41	16,466	98,794.08
6 yr	36	91	1811	10,867.35	18,112	108,673.49
7 yr	40	100	1992	11,954.08	19,923	119,540.84
8 yr	44	110	2192	13,149.49	21,916	131,494.92
9 yr	48	121	2411	14,464.44	24,107	144,644.41
10 yr	53	133	2652	15,910.89	26,518	159,108.85
11 yr	58	146	2917	17,501.97	29,170	175,019.74

Table 2 Amount of profit from flowers/ha

Flower per tree(kg)	Flower per ha (kg)	m/d	kg/day	Charge/d	10 days harvesting and open sun drying (Total investment)	Market price (20 Rs./kg) total cost	Profit
100	20,000	40	2000	12,000.00	120,900.00	400,000.00	279,100.00
101	20,200	40	2020	12,120.00	122,100.00	404,000.00	281,900.00
102	20,402	41	2040	12,241.20	123,312.00	408,040.00	284,728.00
103	20,606	41	2061	12,363.61	124,536.12	12,120.40	287,584.28
104	20,812	42	2081	12,487.25	125,772.48	416,241.60	290,469.12
105	21,020	42	2102	12,612.12	127,021.21	420,404.02	293,382.81
106	21,230	42	2123	12,738.24	128,282.42	424,608.06	296,325.64
107	21,443	43	2144	12,865.62	129,556.24	428,854.14	299,297.90
108	21,657	43	2166	12,994.28	130,842.80	433,142.68	302,299.88
109	21,874	44	2187	13,124.22	132,142.23	437,474.11	305,331.88
110	22,092	44	2209	13,255.47	133,454.66	441,848.85	308,394.20

Table 3 Cost incurred in decortications

	Amount(kg)	Time period			Cost chart			Total cost
		Men work days(8 h/day)	Total work (h)	Electricity (kWh)	Men work	Electricity	Transportation charge of seed	
1st yr	8400	7	56	84	3927.00	840.00	2500.00	7267.00
2nd yr	8820	7	59	88	4123.35	882.00	2750.00	7755.35
3rd yr	9526	8	64	95	4453.22	952.56	3162.50	8568.28
4th yr	10,478	9	70	105	4898.54	1047.82	3636.88	9583.23
5th yr	11,526	10	77	115	5388.39	1152.60	4182.41	10,723.40
6th yr	12,679	11	85	127	5927.23	1267.86	4809.77	12,004.86
7th yr	13,946	12	93	139	6519.96	1394.64	5531.23	13,445.83
8th yr	15,341	13	102	153	7171.95	1534.11	6360.92	15,066.98
9th yr	16,875	14	113	169	7889.15	1687.52	7315.05	16,891.72
10th yr	18,563	15	124	186	8678.06	1856.27	8412.31	18,946.64
11th yr	20,419	17	136	204	9545.87	2041.90	9674.16	21,261.93

Oil Extraction

After decortication, we get 70% seed by the weight of fruit. [Table 4](#) shows amount, time required and cost of oil extraction. Mahua oil is obtained from the kernel of the Mahua seed (*Madhuca Indica*) and contains 50%–55% oil.

Filtering

After filtering oil 2% impurities removed from the oil from the previous amount. [Table 5](#) shows the total cost of oil after filtration

Table 4 Amount, time and cost of oil extraction

<i>Oil extraction</i>								
	<i>Amount</i>		<i>Time period</i>			<i>Cost chart</i>		
	<i>Oil (kg)</i>	<i>Seed cake(kg)</i>	<i>Men work (h)</i>	<i>Work day (8h/day)</i>	<i>Electricity (kWh)</i>	<i>Men work</i>	<i>Electricity</i>	<i>Seed cake(Rs.)</i>
1 yr	5880	2520	59	7	588	4123.35	5880.00	35,280.00
2 yr	6174	2646	62	8	617	4329.52	6174.00	37,044.00
3 yr	6668	2858	67	8	667	4675.88	6667.92	40,007.52
4 yr	7335	3143	73	9	733	5143.47	7334.71	44,008.27
5 yr	8068	3458	81	10	807	5657.81	8068.18	48,409.10
6 yr	8875	3804	89	11	888	6223.59	8875.00	53,250.01
7 yr	9763	4184	98	12	976	6845.95	9762.50	58,575.01
8 yr	10,739	4602	107	13	1074	7530.55	10,738.75	64,432.51
9 yr	11,813	5063	118	15	1181	8283.60	11,812.63	70,875.76
10 yr	12,994	5569	130	16	1299	9111.97	12,993.89	77,963.34
11 yr	14,293	6126	143	18	1429	10,023.16	14,293.28	85,759.67

Table 5 Total cost after filtration

<i>Filtering</i>			<i>Total cost oil extraction + filtering</i>
<i>Amount (liter)</i>	<i>Time filtering (h)</i>	<i>Cost filtering cost</i>	
2940	5	73.50	10,076.85
3087	5	77.18	10,580.69
3334	6	83.35	11,427.15
3667	6	91.68	12,569.86
4034	7	100.85	13,826.85
4438	7	110.94	15,209.53
4881	8	122.03	16,730.49
5369	9	134.23	18,403.54
5906	10	147.66	20,243.89
6497	11	162.42	22,268.28
7147	12	178.67	24,495.11

Table 6 Total cost of trans-esterification

<i>Trans-esterification</i>										
	<i>Amount</i>			<i>Time period</i>			<i>Cost charge</i>			<i>Total cost</i>
	<i>Oil (liter)</i>	<i>Methanol (30%)</i>	<i>NaOH (1%)</i>	<i>Men work (hr)</i>	<i>Day of man work</i>	<i>Electricity (kWh)</i>	<i>Men work</i>	<i>Electricity</i>	<i>Chemical</i>	
									<i>Methanol NaOH</i>	
1 yr	2881	864	29	58	7	430	4040.88	4298.75	24,202.08 1123.67	33,665.4
2 yr	3025	908	30	61	8	451	4242.93	4513.69	25,412.18 1179.85	35,348.7
3 yr	3267	980	33	65	8	487	4582.36	4874.78	27,445.16 1274.24	38,176.5
4 yr	3594	1078	36	72	9	536	5040.60	5362.26	30,189.67 1401.66	41,994.2
5 yr	3953	1186	40	79	10	590	5544.66	5898.49	33,208.64 1541.83	46,193.6
6 yr	4349	1305	43	87	11	649	6099.12	6488.34	36,529.51 1696.01	50,813
7 yr	4784	1435	48	96	12	714	6709.04	7137.17	40,182.46 1865.61	55,894.3
8 yr	5262	1579	53	105	13	785	7379.94	7850.89	44,200.70 2052.18	61,483.7
9 yr	5788	1736	58	116	14	864	8117.93	8635.98	48,620.77 2257.39	67,632.1
10 yr	6367	1910	64	127	16	950	8929.73	9499.57	53,482.85 2483.13	74,395.3
11 yr	7004	2101	70	140	18	1045	9822.70	10,449.53	58,831.14 2731.45	81,834.8

Table 7 Total cost on the investment

Years	Land charge (1,200,000) Rs.	Cost of plantation (87,669 Rs.)	Harvesting cost (Rs.)	Decortication cost (Rs.)	Oil extraction and filtering (Rs.)	Trans-esterification cost (Rs.)	Total cost (Rs.) or total investment
1 yr	60,000	8766.90	72,000.00	7267.00	10,076.85	33,665.38	191,776.13
2 yr	60,000	8766.90	75,600.00	7755.35	10,580.69	35,348.65	198,051.59
3 yr	60,000	8766.90	81,648.00	8568.28	11,427.15	38,176.54	208,586.87
4 yr	60,000	8766.90	89,812.80	9583.23	12,569.86	41,994.20	222,726.99
5 yr	60,000	8766.90	98,794.08	10,723.40	13,826.85	46,193.62	238,304.84
6 yr	60,000	8766.90	108,673.49	12,004.86	15,209.53	50,812.98	255,467.76
7 yr	60,000	8766.90	119,540.84	13,445.83	16,730.49	55,894.28	274,378.33
8 yr	60,000	8766.90	131,494.92	15,066.98	18,403.54	61,483.70	295,216.04
9 yr	60,000	8766.90	144,644.41	16,891.72	20,243.89	67,632.07	318,179.00
10 yr	60,000	8766.90	159,108.85	18,946.64	22,268.28	74,395.28	343,485.96

Price of seed cake is 14 Rs./kg and glycerol is 50 Rs./liter.

Biodiesel per liter cost = total cost of biodiesel/total amount of biodiesel.

Table 8 Per liter cost of biodiesel

Amount of biodiesel (liter) 85% of oil	Reduction cost		Total cost of biodiesel (Rs.)	Cost per liter (Rs.)
	Seed cake cost (Rs.)	Glycerol cost (Rs.)		
2449	35,280	21,609.00	134,887.13	55.08
2571	37,044	22,689.45	138,318.14	53.79
2777	40,007.52	24,504.61	144,074.74	51.88
3055	44,008.27	26,955.07	151,763.65	49.68
3360	48,409.10	29,650.57	160,245.17	47.69
3696	53,250.01	32,615.63	169,602.12	45.88
4066	58,575.01	35,877.19	179,926.13	44.25
4473	64,432.51	39,464.91	191,318.61	42.77
4920	70,875.76	43,411.40	203,891.83	41.44
5412	77,963.34	47,752.54	217,770.08	40.24

Trans-Esterification

The main reaction for converting oil to biodiesel is called trans-esterification. The trans-esterification process reacts an alcohol (like methanol) with the triglyceride oils contained in vegetable oil, animal fats or recycled greases, forming fatty acid alkyl esters (biodiesel) and glycerin. The reaction requires heat and a strong base catalyst, such as sodium hydroxide or potassium hydroxide.

Table 6 shows the total cost of trans-esterification process.

Biodiesel plant capacity:

Feature: capacity – 50 kg/h onwards.

Fuel-electricity power required – 10 hp onwards.

Hence, 10 hp = 7460 W = 7.460 kW.

Pure oil amount is 2881.2–2881 liter, hence time taken by plant will be 57.62 h (near about 7 days).

Men power:- days × 561/- Rs.

Electricity:- capacity of plant (kW) × time period (h) = unit (kWh)

Commercial rate of electricity – 10 Rs./unit

First year:

7.460 kW × 57.62 h = 429.875 kWh – 10 × 429.875 kWh = 4298.75 Rs.

Chemicals used:-

Generally 30% methanol by volume of oil is used and liquid methanol price 28 Rs./liter from Bharat Biodiesel.

NaOH: –1% NaOH, generally by volume of oil. Price of NaOH is 39 Rs./kg.

Cost Analysis

The total cost of biodiesel production = [(land charge + cost of plantation + harvesting cost + decortication cost + oil extraction cost and filtering cost + trans-esterification cost) – cost of glycerol – cost of seed cake]

Till the 11th year Land charge and cost of plantation became fixed cost so it is separated into 10 years. The cost of seed cake and the cost of the glycerol are taken as reduction cost for increasing cost efficiency. **Tables 7** and **8** show total investment and per liter cost of biodiesel production respectively.

Conclusion

Life cycle cost benefit analysis presents following results:

- Total output is greater than total input and per liter biodiesel cost is decreases accordingly as production of biodiesel increases.
- Profit of mahua flower (279,100 Rs. 1st year) is greater than total cost of biodiesel (134,887.13 Rs. 1st year) hence *biodiesel is free of cost*.

There are another methods to increase the efficiency and reduce the cost. “Hielscher ultrasonic” devices are tested and proven in multiple plants to increase biodiesel yield and lower operational cost.

See also: Application of Nanofluids for Radiator Cooling. Renewable and Sustainable Materials in Automotive Industry

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A Review of the Value-Added Chemicals and Materials From Bio-Based Lignin Feedstocks

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Introduction

The presence of a polymerized structure and polyelectrolyte properties are the foundation of all existing commercial applications of lignin except for combustion and synthetic vanillin production from lignin. Around 75% of commercial lignin is converted to dispersants, binders, emulsifiers, and sequestrants (Holladay *et al.*, 2007). These applications have low value and limited growth. Lignin's commercial application as polymeric and polyelectrolytic materials, however, can generate higher value products (Holladay *et al.*, 2007). The production of carbon fiber, adhesives, polymer modifiers, and resins benefits from the macromolecular structure of lignin. Lignin polymerization needs technological improvement with respect to catalyst development, fractionation, and purification (Strassberger *et al.*, 2014).

Carbon Fiber (CF)

Carbon fiber (CF) composites are lightweight but strong and substitute 40%–50% of the mass of steel in vehicles (Ragauskas *et al.*, 2014; Strassberger *et al.*, 2014). Currently, the commercial process for the production of carbon-fiber precursors that use polyacrylonitrile (PAN) is costly (Ragauskas *et al.*, 2014). Lignin is a low-cost source of carbon and is the ideal substitute for precursors and synthetic polymers such as PAN (Holladay *et al.*, 2007; Ragauskas *et al.*, 2014). Lignin-based carbon fiber, like other CF composites, is lightweight and strong and hence can considerably reduce vehicle weight and, accordingly, fuel use and economy (Holladay *et al.*, 2007; Strassberger *et al.*, 2014). However, inadequate understanding of the basic chemistry of carbon fiber production has retarded its progress (Ragauskas *et al.*, 2014). Carbon fiber production requires high purity lignin; all impurities must be removed (Strassberger *et al.*, 2014). Producing high-quality carbon fiber from lignin is challenging since purifying heterogenous complex lignin is not easy (Baker and Rials, 2013).

To produce lignin-based carbon fiber, lignin is first turned into fibers by extruding filaments from a melt (Ragauskas *et al.*, 2014). Electrospinning is the most straightforward and dominant approach for generating continuous micron and sub-micron diameter fibers from polymer solutions (Wang *et al.*, 2013; Dallmeyer *et al.*, 2010; García-Mateos *et al.*, 2017a). Lignin fibers are stabilized through oxidation and in the presence of air at 100–250°C to prevent fiber fusion during the following carbonization step (Holladay *et al.*, 2007; Ragauskas *et al.*, 2014; Ruiz-Rosas *et al.*, 2010). Stabilization can be done using oxygen in the presence of air or thermally using only heat.

The oxidized fibers then undergo carbonization at 600–1000°C or pyrolysis in an inert or nitrogen environment at 800–2400°C. Under these conditions, fibers are carbonized through the loss of CO₂, CO, H₂O, volatiles, and the oxidized components (Ragauskas *et al.*, 2014; Ruiz-Rosas *et al.*, 2010).

Lignin can be thermally pretreated before the extrusion of filaments. This pretreatment not only removes volatiles that disturb the integrity of fiber during thermal spinning but also reduces the hydroxyl content and hence decreases the intermolecular interactions (i.e., condenses lignin into macromolecules) and produces a well-structured microporous fiber (Kadla *et al.*, 2002; Ruiz-Rosas *et al.*, 2010). Thermal pretreatment under a vacuum results in a fusible lignin with excellent spinnability (Kadla *et al.*, 2002). Thermal fiber spinning and the stabilization that follows convert the thermoplastic nature of the lignins to thermosetting (Kadla *et al.*, 2002).

Norberg *et al.* (2013) were the first to thermally stabilize kraft lignin in the absence of oxygen. They found that softwoods stabilized quicker than hardwoods, and stabilization in the presence of air occurred in a shorter time. Stabilization and carbonization were completed in one step, only with different temperatures and times. These findings, if applied, can remarkably decrease the processing time and costs for the commercialization of CF production from lignin.

Ruiz-Rosas *et al.* (2010) produced CF through the one-step stabilization and carbonization method described above by Norberg *et al.* with and without platinum in the ethanol solution. Ethanol is a delignifying agent that dissolves lignin. The resulting CFs had a microporous structure, high oxidation resistance due to the defectless surface, and high structural order. However, the presence of Pt decreased the oxidation resistance of CF. Increasing the carbonization temperature produced CFs with a highly porous structure.

The incorporation of phosphorus in lignin carbon fibers loaded with Pt increased the fiber surface area and resulted in lower size and better distribution of Pt particles (García-Mateos *et al.*, 2017a). Phosphorus enhances fiber's resistance to oxidation and electro-oxidation. The produced carbon fibers can be used as electrodes without the need for a binder or conductivity promoter. The loaded Pt lignin fibers exhibited remarkable catalytic effects on methanol and ethanol electro-oxidation. The presence of phosphorus increased the higher heating rate by 10°C min^{−1} and reduced the isothermal stabilization step from 100 h to 1 h, thereby preventing the fibers from melting.

Acetic acid lignin (lignin from acetic acid pulping) from softwood can undergo faster heating rates than acetic acid lignin from hardwood (Uraki *et al.*, 2001). Moreover, ACFs from softwood acetic acid lignin exhibited higher specific surface areas than ACFs from hardwood acetic acid lignin. The former also offered greater adsorption capacity and satisfactory strength in the range of high-performance commercial ACFs.

Dallmeyer *et al.* (2010) investigated the electrospinning of seven different technical lignins and the effect of lignin structure on fiber formation. The results showed that only when poly(ethylene oxide) (1–5 wt%) was added could lignins be electrospun into continuous uniform fibers. The authors found a linear relation between fiber diameter and lignin concentration for all lignins. Electrospinning behavior and solution properties were greatly affected by lignin structure, intermolecular interactions, and viscosity.

Kubo and Kadla (2005) studied the effect of blending hardwood kraft lignin with synthetic polymer on the final fiber properties. Lignin was thermally blended with poly(ethylene terephthalate) (PET) and polypropylene (PP) and spun to obtain fibers, thermostabilized, and finally carbonized. PET-blend fibers could be stabilized at higher heating rates and had better thermal stability than corresponding homofibers. Carbon fiber yield decreased with decreasing proportions of lignin in the blend. Heterogeneous blend (PP-lignin) fibers exhibited a hollow and/or porous fiber, while homogeneous blend (PET-lignin) fibers displayed a smooth surface. The tensile and mechanical properties of blend fibers were comparable to those of commercially activated carbon fibers. The authors and their colleagues showed in another study that lignin polymer blends facilitated spinning, but the blends were thermally unstable and showed inter-fiber fusing during carbonization (Kadla *et al.*, 2002).

Tensile strength and modulus increased with decreasing fiber diameter, and the mechanical properties of carbon fibers from kraft lignin were found to be the same or better than non-commercially produced lignins. The overall carbon fiber yield was 40% for Alcell and 45% for kraft lignin (Kadla *et al.*, 2002). However, compared to petroleum-based carbon fibers, lignin-derived ones exhibited lower mechanical strength and were not graphitic structure-oriented. The latter is hard to reach in lignin-based carbon fibers (Ragauskas *et al.*, 2014). Also, there is not enough knowledge of the basic chemistry of the process or other sources of lignin used for the same application (Ragauskas *et al.*, 2014).

Kayocarbon fiber, the only commercial-scale carbon fiber lignin, was produced by Nippon Kayaku Co. in Japan, starting in 1967. The company folded in 1973. The lignin source was lignosulfonate, which was plasticized by poly(vinyl alcohol) (Johnson *et al.*, 1975).

Activated Carbon (AC)

Activated carbon (AC) is a highly porous carbonaceous material used to adsorb pollution from gaseous and aqueous solutions (Hayashi *et al.*, 2000). Lignin can be used as a precursor for the production of AC via chemical or physical activation to produce low-cost activated carbon.

In Hayashi *et al.*'s chemical activation study, lignin was mixed with an activating reagent (i.e., K_2CO_3 , Na_2CO_3 , KOH, NaOH, $ZnCl_2$, H_3PO_4) and water, kneaded, and then dried at 110°C. It was then carbonized at various temperatures in a nitrogen environment at the rate of 10°C min⁻¹ for 1 h. Finally, the sample was cooled, washed, and dried again (Hayashi *et al.*, 2000). Carbonization at 600°C in $ZnCl_2$ and H_3PO_4 activating reagents led to the highest surface areas for lignin-activated carbons, in the range of commercially activated carbons. The highest surface areas in the presence of alkali metal were obtained at 800°C and were much larger than commercially activated carbons except for Na_2CO_3 . $ZnCl_2$ limited tar formation and acted like a dehydration reagent; it encouraged char formation when the carbonization temperature was below 600°C. K_2CO_3 performed as a dehydrogenation reagent when the activation was below 500°C.

Fu *et al.* (2013) in their studies on physical activation, carbonized lignin in the absence of oxygen and at a heating rate of 15°C min⁻¹. They then activated the lignin using steam at a rate of 100 cm³ min⁻¹ and a pressure of 0.5 MPa. A carbonization temperature of 450°C for 60 min and an activation temperature of 725°C for 40 min resulted in the optimized activated carbon.

In one study, eucalyptus kraft lignin was partially gasified using CO_2 to produce AC (Rodríguez-Mirasol *et al.*, 1993). Temperature did not affect the porosity within the studied thermal range (750–900°C), but burn-off affected it substantially.

Proper use of AC as an adsorbent is defined based on its physical and chemical characteristics such as pore volumes, size, and surface areas (Cotoruelo *et al.*, 2012). Fu *et al.* (2013) found that lignin-activated carbon adsorbs methylene blue (MB) from wastewater better than other adsorbents made of industrial and agricultural wastes. Activated lignin-chitosan extruded (ALiCE) pellets exhibiting maximum adsorption capacity of 36.25 mg g⁻¹ also adsorbed MB and can absorb cationic organic pollutants from streams (Albadarin *et al.*, 2017).

AC adsorbent, prepared from the carbonization (350–800°C) of kraft lignin in N_2 atmosphere followed by CO_2 partial gasification (750–850°C) was able to remove p-nitrophenol (PNP) from an aqueous solution (Cotoruelo *et al.*, 2012).

Gonzalez-Serrano *et al.* (2004) produced ACs with a high surface area and well-structured micro- and mesoporosity from chemical activation via the pyrolysis of H_3PO_4 -impregnated kraft black liquor lignin. Best operating conditions were an impregnation ratio of 2 g H_3PO_4 per g lignin and an activation temperature of around 427°C, although other operating condition values also led to activated carbons with good adsorption capacities. The adsorption capacities of the produced activated carbons were comparable or even better than those of the other activated carbons for three main water toxic pollutants (phenol, Cr[VI] and 2,4,5-trichlorophenol).

Activated Carbon Fiber (ACF)

Unlike powder, fibers are flexible, and fibrous catalysts offer immobility, strong interaction of particles and support, short diffusion distance, and low resistance to flow through fiber bundles. As a novel porous material, activated carbon fiber (ACF) offers massive surface area and thus great adsorption capacity and many surface functional groups and with that strong reactivity and reduction properties, which is promising for catalyst preparation. ACFs were employed as support in Pt nanoparticle electrocatalysts (Pt/ACF) for direct alcohol fuel cells (alcohol oxidation) and exhibited double the anodic densities of alcohol oxidation as well as higher electrochemical stability and catalyst activity in alcohol oxidation than commercial Pt/C catalysts (Huang and Chen, 2008). Homogeneous Pt particles were uniformly dispersed on ACF. Fibers were carbonized at 850°C under N₂ flow before being activated using steam at the same temperature for 1 h to prepare Pt/ACF (Huang and Chen, 2008).

In a study by Shen *et al.* (2011) lignin-phenol-formaldehyde (LPF) was melt-spun and thermally treated to produce ACFs. When guaiacyl units in lignin were reacted with formaldehyde, lignin was found to be the dominant component affecting LPF thermal properties and AC pore size and related properties. Lignin's three-dimensional structure does not allow phenolic resin to be easily decomposed. It also inhibited the formation of large pores. 14% lignin incorporation into resin led to ACFs with great pore structure and adsorption characteristics.

Carbon Catalyst

Bedia *et al.* (2009) produced a carbon-based acid catalyst by a single-step chemical activation of H₃PO₄⁻ impregnated Alcell lignin under constant nitrogen flow (150 cm³ min⁻¹) and 2 h carbonization at a temperature of 500°C and a heating rate of 10°C min⁻¹. Incorporating acid surface groups by the chemical oxidation of the carbon surface was not required. Although there was a washing step, a large amount of phosphorus was left on the surface, which led the carbon surface to exhibit a particular chemistry with high amounts of surface acid groups that were thermally stable. The resulting catalyst converted 2-propanol to propylene via dehydration over the Brönsted acid sites that formed during the activation.

García-Mateos *et al.* (2017b) produced a basic activated carbon catalyst for the decomposition of alcohol that has various textural and surface properties resulting from the carbonization of kraft lignin. Kraft lignin has a high sodium compound content. Kraft lignin carbonization generated chars with a high oxygen group content on the surface of mainly carbonyl, quinone, and carbonate (sodium carbonate). These oxygen groups were the result of carbon oxidation and sulfur salt's reduction to sulfide. Washing and partially gasifying this char with CO₂ led to carbons with a basic surface of carbonyl and quinone groups and carbon basal planes that can act as electron donor sites. Carbonization occurred at temperatures of 500–900°C under a constant flow of nitrogen (150 cm³ min⁻¹). Using the basic activated carbon catalyst, 2-propanol, methanol, and ethanol transformed to acetone, formaldehyde, and acetaldehyde, respectively, at atmospheric pressures. Lignin catalyst conversions were not as great as expected but selectivities were higher than 80%.

Ruiz-Rosas *et al.* (2014) and Valero-Romero *et al.* (2014) studied lignin/zeolite mixture carbonization followed by inorganic template basic etching. Lignin-derived templated carbons exhibited an oxygen-rich surface as well as pyridine and pyridinic groups, which improved capacitance considerably compared to petroleum-based carbons. Hierarchical porous carbon can be used in carbon electrodes to produce electrochemical capacitors, in catalysis, energy storage, and adsorption, and can be prepared in a straightforward and environmentally friendly process using lignin as the carbon precursor and through the liquid phase impregnation method.

Fuel Cell

A fuel cell converts the chemical energy of a fuel directly into electricity without the need for prior processes such as gasification or structural changes. The direct carbon fuel cell (DCFC) has attracted increasing attention because of its superior efficiency (80% of the assumed value of a practical fuel cell) and low pollution (Lima *et al.*, 2013).

Lima *et al.* (2013) were the first to use a mixture of lignin or lignin and active carbon and electrolytes (50% mass ratio) as a fuel cell anode in which lignin was both fuel and electrode. Hydrophilicity and/or wettability are critical parameters for direct lignin fuel cell performance. Hence the pH of the lignins was changed by alkalinizing them to pH 10 by dissolving them in 0.1 M NaOH solution. Alkalified lignins exhibited higher maximum current density than the original lignins with 0.68–0.69 V open circuit voltage and 74–79 mA cm⁻² maximum current density. In addition, blending pure carbon with lignins (lignosulfonate ([LS], kraft [KL])) enhanced electrical conductivity because of carbon's high surface area, and KL + AC and LS + AC offered power densities of 12 and 24 mW cm⁻². Activated carbon has similar wettability to lignosulfonate and better than kraft lignin.

This application has not reached commercialization (Strassberger *et al.*, 2014), and because Lima *et al.*'s study was the first application of lignin in fuel cells, further study is required for adjustments and improvements of the DCFC using lignin. For example, the effect of lignin impurities should be tested on the key parameters (Lima *et al.*, 2013).

Electrode in Batteries

Increasing demand for energy storage has brought to the fore high-performance, inexpensive, renewable, and environmentally friendly materials like lignin (Kim *et al.*, 2014).

Rechargeable lithium-ion batteries are the most efficient storage devices and the most widely applied in portable electronic devices, emerging smart grids, and hybrid electric vehicles (Wang *et al.*, 2013). Because of their low cost, processability, and easy accessibility, carbonaceous materials have been found to be the most suitable for commercialization as electrodes in lithium-ion batteries. However, there are problems associated with the graphite, the current commercialized anode, such as poor energy density (Wang *et al.*, 2013). Also, new nanocarbon materials, though they benefit from remarkably better performance such as conductivity and accessible surface area, suffer from the high cost of the carbon precursors, nonrenewability, and the complex manufacturing processes, all of which are a barrier to commercial-scale production (Wang *et al.*, 2013; Milczarek and Inganäs, 2012). With respect to low-cost sodium-ion batteries, although they are promising for grid electricity storage, anode development is critical for their commercialization. Amorphous carbonaceous materials were found to be the most promising materials for this purpose. The problem with these carbonaceous materials is their high cost, a result of expensive precursors, and low carbon yield (Li *et al.*, 2016). Electrodes from renewable biopolymers offer low cost, better safety, and nontoxicity, and can be operated in water. The only problem associated with these electrodes may be self discharge (Milczarek and Inganäs, 2012). The high carbon content (> 60%) of lignin makes it the most attractive sustainable candidate as a precursor for carbonaceous materials (Nelson and Northey, 2004).

Popova *et al.* (2008) studied the feasibility of using graphite produced from hydrolysis lignin as an artificial graphite in electrodes. Graphite produced through the thermal modification of lignin exhibits high efficiency compared to other graphite materials, is a superior matrix for lithium intercalation, and can produce high specific energy content graphite electrodes.

Lignin nanocrystals confined on reduced graphene oxides have shown highly reversible and fast pseudocapacitive behavior (Kim *et al.*, 2014). Hybrid electrodes owe their outstanding capacitive characteristics to synergizing the fast and reversible redox charge transfer of quinone and the favorable interplay of hybrids. The resulting pseudocapacitors exhibited excellent cyclic performances of around 96% retention after 3000 cycles and a maximum capacitance of 432 F g⁻¹ (close to theoretical numbers), which was six times more than reduced graphene oxides.

Milczarek and Inganäs (2012) used lignin, an electronic insulator, as an additive in polypyrrole/lignin composite electrodes with low weight ratio (50 >) to prepare cathodes. Phenolic groups in lignin can be converted to quinones via oxidation processes. The quinone group in lignin can be used for proton and electron exchange and storage. The capacitance and charge density of the resulting composite were higher than most of the polypyrrole/carbon composites. Only polypyrrole/nanostructured carbons are reported to have values close to polypyrrole/lignin.

Li *et al.* (2016) also fabricated amorphous carbonaceous materials from a mixture of lignin and pitch. The emulsification interaction between pitch and lignin prevented the graphitization of pitch during carbonization and resulted in low-cost amorphous carbon material with a high carbon yield of 57%. AC was obtained by optimizing conditions that presented an appropriate morphology and microstructure along with a promising high reversible capacity of 254 mAh g⁻¹ and superb cycling stability and performance rate.

Supercapacitors

A supercapacitor is an energy storage device that is made of high-surface area carbon in aqueous electrolytes. Fuel cells show the highest specific energy, followed by batteries, but suffer from low specific power. Capacitors are exactly opposite; they have the highest specific power and the lowest specific energy. Supercapacitors have high specific power and medium specific energy systems and fill the gap between batteries and capacitors (Winter and Brodd, 2004). Lignin can be considered as a low-cost substitute for the production of porous carbons in large volumes. Different lignin types produce different porous carbons (Jeon *et al.*, 2015).

Jeon *et al.* (2015) were the first to carbonize lignin directly in a study in which a high surface area porous carbon was produced without any required activation steps or templating agents. Carbonization increased lignin porosity remarkably. This one-step process eliminated the chemical and physical activation steps and so reduced the complexity of the process and the production cost. Lower molecular weight lignins produce porous carbons with a higher surface area that are less defective than other carbons. The highest surface area (1092 m² g⁻¹) was found in porous carbon from kraft lignin. The carbonized lignin offered good capacity retention and high specific capacitance, energy density, and power.

Electrodes for supercapacitors can be obtained from the electrospinning of lignin/ethanol solutions followed by thermal conversion into interconnected and porous carbon fibers (CFs) with submicron diameters (Berenguer *et al.*, 2016). The CFs exhibited excellent storage performance including ultrafast charge-discharge and outstanding energy density and cyclability. Power and energy densities up to 61 kW kg⁻¹ and 10 Wh kg⁻¹, respectively, of the supercapacitor were in the range of or greater than top available structures. Also, it was found that more than 90% of the energy densities and 100% of the initial power of the supercapacitor was still available after 100,000 charge-discharge cycles at 5 A g⁻¹.

Hu *et al.* (2014) fabricated KOH-activated highly porous submicron-activated carbon fibers (ACFs) from low sulfonate alkali lignin into supercapacitors. Alkaline hydroxide activation caused hydrophobic CFs to be converted to hydrophilic ACFs with structures dissimilar to CFs. This different carbonaceous structure is the reason for the ACF supercapacitor's superb electrochemical properties. The KOH-activated ACF supercapacitor exhibited a notable 344 F g⁻¹ specific capacitance. Also, KOH-activated ACFs

generated a supercapacitor with superior electrochemical properties compared to the one prepared by NaOH-activated ACFs. However, both supercapacitors exhibited low equivalent series resistance and excellent cycling stability. After 5000 charge/discharge cycles, over 96% capacitance retention rates were reached. These outstanding performances proved lignin to have great potential for electrical energy storage.

Nanoparticles

Lignin nanoparticles (LNPs) have a wide range of applications, for example as coatings, composites, nanoglue drug delivery, Pickering emulsions, glue, microfluidic devices, antimicrobial materials, and wound healing (Lievonen *et al.*, 2016).

Lievonen *et al.* (2016) proposed a simple, straightforward technique to produce LNPs with an average diameter of 200–500 nm using tetrahydrofuran as the solvent. They conducted experiments in which the process occurred at room temperature in pure water and with no need for lignin chemical modification. Softwood kraft lignin was dissolved in tetrahydrofuran (THF), then water was added through dialysis. The dialysis bag solvent exchange offers great control over the concentration of nanoparticle dispersion. The process presented promising results for any kind of lignin soluble in THF. LNP dispersion was stable for more than two months in pure water and at atmospheric temperature; however, high salt concentration (>500 mM) or very low pH (<4) provoked accumulation. LNPs prepared using tetrahydrofuran had a uniform round shape and were more symmetric than the ones prepared using ethylene glycol. Pre-dialysis concentration of lignin affects the nanoparticle's final size. The surface charge of LNPs can be reversed, and when the polyelectrolytes that carry opposite charges (like poly[diallyldimethylammonium chloride]) were adsorbed, stable cationic LNPs were produced. THF could be recycled through evaporation and reused in the process. So this process requires a high amount of organic solvents and produces LNPs as an environmentally friendly dispersion.

Qian *et al.* (2014a) used alkali lignin from black liquor to make uniform nanometric colloidal spheres obtained through self-assembly. To form lignin colloidal spheres, lignin was acetylated followed by the gradual hydrophobic aggregation of acetylated lignin molecules while water was steadily added to the acetylated lignin-THF solutions. Acetylated lignin colloidal spheres are water-dispersive, while acetylated lignin itself is insoluble in water. Acetylated lignin colloids were found to have similar average density but a much larger average aggregated number than colloids from conventional polymers. The colloids from conventional polymers are prepared from block copolymers and their cores and shells are comprised of hydrophobic and hydrophilic blocks, respectively, but acetylated lignin colloids have cores and shells with stronger hydrophobicity and hydrophilicity abilities. Uniform colloidal spheres are prepared using this acetylation, followed by hydrophobic aggregation, although lignin-based aggregates are basically irregular. This method also provides a solution for lignin insolubility in water, which is one of the most important limitations for its industrial applications.

Through a simple, inexpensive, and novel method, Frangville *et al.* (2012) produced biodegradable, highly porous LNPs from lignin. They precipitated stable LNPs over wide ranges of pHs using diluted acid solutions from an ethylene glycol solution. Another method of producing LNPs is acidic precipitation of lignin from a basic solution. LNPs produced in their study by this method were found to be stable only at low pH. The resulting LNPs are non-toxic for microalgae and yeast and have great potential for substituting current non-biodegradable and possibly toxic nanoparticles.

Gonugunta *et al.* (2012) synthesized LNPs using thermal stabilization and carbonization following a freeze-drying process. Lignin with a foamy and porous microstructure was formed after freeze-drying. Thermal stabilization of the product during the first step prevented agglomerated nanoparticles from forming during the following carbonization process. The addition of KOH affected the size of the LNPs remarkably; the smallest LNPs, 25 nm, were obtained at 15% KOH.

Silver-infused LNPs coated with a cationic polyelectrolyte layer are a green biodegradable substitute to the silver nanoparticles that linger in the environment (Richter *et al.*, 2015). LNPs with biodegradable cores have greater antimicrobial activity and a less negative environmental impact than silver nanoparticles. They can easily neutralize common gram-positive and gram-negative human pathogens, as well as quaternary amine-resistant bacteria, while consuming at least 10 times less silver than conventional silver solutions.

LNPs can also be obtained via physical methods such as ultrasonic/acoustic irradiation, which modifies lignin to obtain LNPs (Gilca *et al.*, 2015). Ultrasound could lead to the development of a range of chemical reactions.

Foams

Del Saz-Orozco *et al.* (2012) found that introducing LNPs to phenolic foams produced LNP-reinforced phenolic foams (LRPFs) with 128% and 174% more compressive modulus and compressive strength, respectively, than unreinforced foams. Interestingly, with the same density, up to 31% of the blowing agent used was saved when producing reinforced foam compared to unreinforced foam. LNP incorporation into foam makes LRPFs competitive with synthetic fiber-reinforced phenolic foam in terms of mechanical strength and, moreover, produces more environmentally friendly foam.

Emulsifiers

Lignin is insoluble in acidic conditions and this is the basic principle of forming lignin particles that can be used as an efficient emulsifier for novel pH-responsive Pickering emulsions (Wei *et al.*, 2012). Chemical emulsifiers or surfactants are essential parts of conventional

emulsion polymerization. They can contaminate the final product and contribute to environmental pollution. The emulsifier prepared through this method provides a cheap, green, and recyclable method for the polymerization of industrial emulsions.

Atom transfer radical polymerization grafting of 2-(diethylamino)ethyl methacrylate of lignin makes it water soluble (Qian *et al.*, 2014b). CO₂ bubbling of the resulting samples that contains lignin disperses lignin in water, but N₂ bubbling precipitates lignin. These features make this lignin a potential green candidate for many applications including as a surfactant for Pickering emulsion. The emulsification/demulsification is repeatable and reversible.

Resins

Da Silva *et al.* (2013) used organosolv lignin to prepare resins (following a classical procedure) that can be used as matrices in composites. The authors found that replacing phenol with organosolv lignin in phenolic-type resins led to a greater resistance to deformation and a higher impact strength composite compared to composites prepared from phenol-formaldehyde resin.

The phenol-substituted organosolv lignin resin can be used in thermosets as phenolic-type resins. Thielemans and Wool (2005) esterified lignin with anhydrides to make it soluble in nonpolar solvents like styrene, which is used in the preparation of thermoset resins. Styrene-soluble lignin can be incorporated in unsaturated thermoset composites.

Ramires *et al.* (2010) produced phenolic-type resins using lignin from organosolv acid hydrolysis without extra purification. Lignin replaced phenol in a lignin-formaldehyde pre-polymer. The resulting composite showed good adhesion in a fiber/matrix interface and good impact strength. For pre-polymer synthesis, lignin was spread in the formaldehyde solution and stirred for 15 min at room temperature. Potassium hydroxide was then added, and, after being stirred for 2 h, the mixture temperature increased to 97°C.

Adhesives

Phenol-formaldehyde (PF) adhesive is applied for high bonding strength and water resistance of bonded plywood. All the components of this adhesive are petrochemical-derived materials (Zhang *et al.*, 2013).

Wood adhesives can be produced from lignin-phenol-formaldehyde (LPF) resin (Khan and Ashraf, 2007). Incorporating up to 50% of lignin in a phenol-formaldehyde adhesive improves adhesive and shear strength, but lignin addition of up to 25% leads to a resin with the same thermal stability as phenol formaldehyde.

Moubarik *et al.* (2013) found that alkaline lignin from bagasse exhibited high reactivity, due to the high activated free ring position content, high molecular weight, and good thermal stability (high thermal decomposition temperature). These characteristics mean this lignin is a great candidate for replacing up to 30% of the phenol in PF resins used in plywood without affecting bond properties. Plywood prepared with this resin has the requirements of interior-grade panels, according to international standard specifications.

Yang *et al.* (2015) prepared LPF resin adhesives using a new formulation build based on accurate investigation of various lignins' functional groups. LPF resin adhesives prepared this way had a similar structure and curing behavior to commercial phenolic resin adhesives. Plywood with high performance and low formaldehyde emissions was produced from LPF resin adhesives (Yang *et al.*, 2015; Moubarik *et al.*, 2013).

Zhang *et al.* (2013) studied the incorporation of lignin from lignocellulosic ethanol production into phenolic resins to prepare LPF adhesives. They found that lignin can substitute phenol by up to 50% in the resulting adhesive and that LPF had a similar structure and higher thermal stability in the initial thermal degradation than PF. The study confirmed that plywood bonded by this adhesive has acceptable performance and preparing LPF is industrially feasible.

Qiao *et al.* (2015) substituted phenol with enzymatic hydrolysis lignin to produce adhesives. Even with the incorporation of up to 50% lignin in PF resin, the adhesive strength did not decrease. However, 60% lignin incorporation lowered adhesive strength, though it was still above the requirements of Chinese first grade plywood. LPF resin exhibited a similar structure but a lower thermal resistance than PF resin.

El Mansouri and Salvadó (2006) studied the characteristics of various types of lignin including kraft, soda-anthraquinone, organosolv, lignosulfonate, and ethanol process lignins for adhesive production. They found that kraft and soda-anthraquinone lignins are more reactive and so more suited to modification than the others and are better raw material candidates for the incorporation into resins, adhesives, and, particularly, phenol-formaldehyde resins. The highest amounts of phenolic hydroxyl are in kraft and soda-anthraquinone; organosolv has a moderate amount. Also, the highest aliphatic hydroxyl content is found in kraft lignin. Better lignins for adhesive production contain more phenolic hydroxyl and aliphatic hydroxyl groups and have a structure with the possibility of forming quinone methide intermediates, unsubstituted 3- or 5-positions on phenolic C9 units, and lower apparent molecular weight. All of these features signal kraft lignin as the best choice for adhesive production.

Nanocomposites

Ma *et al.* (2017) prepared lignin-based poly(acrylic acid) (LBPA)/organo-montmorillonite (OrgMMT) nanocomposites through the copolymerization of lignin-grafted N, N'-methylene-bisacrylamide with acrylic acid. Water absorbency, swelling and

de-swelling rate constants, and absorption capacity of Pb^{2+} of LBPAA were higher than in poly(acrylic acid). LBPAA/OrgMMT has potential applications, including as a fast and feasible way to remove Pb^{2+} ions from polluted wastewater and as a water retention agent with good salt tolerance and low cost.

Plastics and Composites

While the petrochemical-derived plastic market is about 260 million tonnes, around 350,000 tonnes of biodegradable plastic is produced globally; this figure is less than 0.2% of the worldwide plastics market (Song *et al.*, 2009). A short supply of crude oil and its unsustainability as a source for plastic synthesis applications have triggered bioplastics use (Howard, 2002). Rapidly filling landfills, along with water and land pollution issues resulting from excessive use of non-biodegradable petrochemical-based plastics, have also brought increased attention to bioplastics (Song *et al.*, 2009; Howard, 2002; Zheng *et al.*, 2005). Plastics' long-lasting life and degradation period are a concerning environmental burden (Amaral *et al.*, 2012). Plastics' biodegrading depends on the nature of the polyol used (Amaral *et al.*, 2012). Biodegradable polymers from renewable resources have gained considerable attention recently because of their independence on petroleum as well as the negative environmental impacts of nondegraded polymers (Thielemans *et al.*, 2002). Lignin is biodegraded by fungi through oxidation (Yamamoto *et al.*, 1999).

A major problem with the incorporation of lignin into unsaturated polyester and resin is that unmodified lignin is polar and so it is incompatible with styrene. Styrene is used largely in unsaturated polyester resin materials and is nonpolar. However, Thielemans *et al.* (2002) found that a modification with epoxidized soybean oil maleic anhydride remarkably enhanced lignin solubility in liquid resin containing styrene.

One of the most multipurpose three-dimensional polymers is polyurethane (Amaral *et al.*, 2012). It has various applications including as elastomer, foam, adhesive, and paints whose properties can be easily controlled. Its great insulation and mechanical properties make it an excellent candidate in construction, the automotive industry, nautical applications, and equipment manufacturing.

Kubo and Kadla (2004) found that blending up to 25% lignin to poly(ethylene oxide) (PEO) increased the PEO crystalline domain size. Compared to organosolv, Alcell lignin exhibited superior behavior and the associated blends held excellent properties. Moreover, Alcell lignin blends had stronger intermolecular interactions and higher tendency to establish these interactions compared to other lignins (Kubo and Kadla, 2004). Kraft lignin copolymerization with N-isopropylacrylamide (NIPAM) through atom transfer radical polymerization (ATRP) altered the thermal decomposition temperature or thermostability and water solubility of the resulting copolymers (Kim and Kadla, 2010). Lignin can be directly incorporated into other polymers. Blending lignin with natural and synthetic rubber (Kramarova *et al.*, 2007), poly(vinyl alcohol) (PVA) (Fernandes *et al.*, 2006), polyolefins (Cazacu *et al.*, 2004), poly(methyl methacrylate) (PMMA) (Ciemniecki and Glasser, 1988), polyesters (poly(hydroxybutyrate) with up to 40 wt% lignin) (Mousavioun *et al.*, 2010), and poly(ethylene adipate) urethanes (PU) (with up to 10% lignin) (Ignat *et al.*, 2011) improved tensile strength, macromolecular organization, and overall thermal and photochemical stability, as well as anti-oxidant, dynamic mechanical, and bulk and surface properties. However, the initial decomposition temperature of the blend may decrease (Mousavioun *et al.*, 2010). These blends offered enhanced properties at low cost.

Lignin contains both aromatic and aliphatic hydroxyl groups that form urethane linkage effectively by providing reactive sites for isocyanates (da Silva *et al.*, 2009). The downside of urethane production from lignin is that the polyurethanes produced are mostly rigid and brittle because of their highly branched three-dimensional structure. This is the result of lignin structure. Incorporating a linear polyol such as polyethylene glycol (PEG), which is the current practice, can overcome this limitation. Lignin type, content, molecular weight, and polyol type can significantly affect the efficiency of this method. However, lignin's highly branched, variable, and multidimensional structure and composition pose some technical challenges and limitations for composite and plastics applications. A practical and encouraging approach to overcome these challenges is oxypropylation. Oxypropylation releases hydroxyl groups and, particularly, phenolic groups with difficult accessibility and also converts solid lignin to a liquid polyol with an optimal hydroxyl index for polyurethane production (da Silva *et al.*, 2009). Oxypropylation improves the OH functionality of lignin by moving these groups to the ends of the chain of the inserted polyether fragments. It also enhances viscosity and the hydroxyl index and other properties of the polyol (Aniceto *et al.*, 2012). Operational variables such as time, catalyst and propylene oxide amounts, pressure, and temperature should be optimized based on the raw material used and the intended application for the polyol (Aniceto *et al.*, 2012). Compared to non-catalytic pathways, catalytic polymerization was found to produce lignin polyurethane films with consistent properties (Ni and Thring, 2003). However, the ultimate strength, Young's modulus, and crosslink densities of the catalyzed PU films were lower than the ones for the noncatalyzed films. As the NCO/OH molar ratio and lignin content increased, the ultimate strength and Young's modulus improved, but the ultimate strain reduced for both films.

Because of oxypropylation, higher levels of lignin could be incorporated into the PU, and polyol properties were controlled better than when solid lignin was reacted directly with any of diisocyanate, PEG and diisocyanate, or polyether triol and diisocyanate (Li and Ragauskas, 2012).

Lignin from chemical pulping is the major source of lignin-derived plastics (Ragauskas *et al.*, 2014). Lignin structure changes considerably during the pulping process, making it inappropriate for most high-value applications such as material production. However, this lignin would be well suited to plastic production. Different molecular weight, process-

Table 1 Various materials from lignin and their associated production processes

Application	Process	Lignin form/source	Remarks	Refs.
Anode in direct carbon fuel cells (DCFC)	• Anode preparation using a mixture of lignin and electrolytes with a mass ratio of 1 • Dry powder-pressing: loading a mold with the anode powders before pressing at 19.6 MPa for 10 s	Lignosulfonate and kraft lignin	• Direct lignin fuel cell is viable • Hydrophilicity of raw material lignin is critical for fuel cell performance • The Energy conversion of all lignins was the same when pH was adjusted to 10 to alter the lignin structure or add active carbon	(Lima <i>et al.</i> , 2013)
Carbon fibrous mats as anode in lithium ion batteries	• Dispersing lignin and polyethylene oxide into dimethylformamide under magnetic stirring • Heating the suspension • Cooling to room temperature naturally under continuous stirring • Electrospinning • Drying nanofibers • Thermostabilizing in a tube furnace in \atmosphere • Carbonization • Thermal annealing of lignin-derived fused carbon fibrous mats in the presence of urea	Alcell lignin	• The Incorporation of specific proportions of low melting point polymer additives resulted in carbon fibers with good electrochemical performance and lower electrical resistance, comparable to PAN-derived carbon fibers • Doping with nitrogen further improves specific capacity and electrochemical conductivity • Fabrication was both straightforward and economical	(Wang <i>et al.</i> , 2013)
Cathodes	• Dissolving lignin in HClO₄ • Adding same amount of pyrrole to the mixture • Galvanostatic polarization of the substrate electrode • transferring film-covered electrode to pure HClO₄ and • developing quinone functions by cyclic voltammetry	Lignosulfonates from brown liquor	• Polypyrrole /lignin can be used for energy storage and charge transport • Use of the renewable biopolymer should lower the electrode cost and improve safety and nontoxicity • Further developments are needed to enhance capacitance and charge density	(Milczarek and Inganäs, 2012)
Pseudocapacitor used in hybrid electrodes	• Exfoliating graphite oxide in water • Addition of lignin • Addition of hydrazine solution • Placing the resulting stable suspension in an oil bath at 60°C for 12 h to yield a homogeneous dispersion	Softwood sodium lignosulfonate	Hybrid electrodes had: • Good rate and cyclic performances • A maximum capacitance close to the theoretical capacitance	(Kim <i>et al.</i> , 2014)
Nanoporous carbon in supercapacitors	• Immediately transferring lignin extracts placed on alumina crucible to furnace • Purging furnace with argon gas • Increasing temperature step wise to carbonize lignin	Purified kraft lignin, ethanol extracted lignin, and diluted alkali lignin	• Additional activation agents are not required • Lower molecular weight lignins produce porous carbons with higher surface area and fewer defects • Amount of oxygen consumed during carbonization considerably affects porosity	(Jeon <i>et al.</i> , 2015)
Submicron porous carbon fibers for electrode in supercapacitors	• Electrospinning of lignin-ethanol solutions by a co-axial configuration • Thermostabilization under air • Carbonization under inert (N₂) or 1 vol% O₂ under a N₂ atmosphere	Alcell lignin	Power and energy densities comparable or even better than top engineered structures till now	(Berenguer <i>et al.</i> , 2016)
Submicron activated carbon fibers in supercapacitors	• Electrospinning lignin/polyethylene oxide mixture with or without alkaline hydroxides; NaOH/lignin and KOH/lignin • Rolling and placing electrospun precursor fiber mats in an electric furnace • Carbonization under flowing N₂	Alkali lignin with low sulfonate	Supercapacitors from lignin ACFs showed somewhat low equivalent series resistance and exceptional cycling stability, ACFs from alkali Lignin with low sulfonate is superior carbonaceous electrodes for supercapacitors in aqueous electrolytes	(Hu <i>et al.</i> , 2014)

Carbon fiber	● Electrospinning of lignin/ethanol/platinum acetyl acetate and lignin/ethanol (for fibers doped with platinum [ALFPt]) solutions ● Fiber stabilization in air ● Carbonization with a flow of N₂	Alcell lignin	● Diameter and length of fibers are controlled by viscosity, flow, concentration of electrospun solution, or applied voltage (Ruiz-Rosas <i>et al.</i>, 2010) ● Increasing carbonization temperature increases carbon and decreases oxygen content
Activated carbon	● Mixing lignin with the activating reagent and water and kneading ● Drying at 110°C to prepare the impregnated sample ● Carbonization under N₂ flow	Lignin precipitated to form kraft black liquor	● Increasing carbonization temperature increased mesopore volumes (Hayashi <i>et al.</i>, 2000)
Activated carbon for pollution adsorption	● Carbonization in a muffle furnace in N₂ ● Activation carbonized chars under a constant flow of steam	Dewatered black liquor lignin	● Black Liquor lignin can be converted to low-cost activated carbon by physical activation with steam (Fu <i>et al.</i>, 2013) ● Activation Time and temperature and carbonization temperature greatly influenced pore structures of lignin
Activated lignin-chitosan extruded (ALiCE) in dye absorption	● Preparation of lignin-chitosan blend granulating mixture with 20 cm³ of aqueous acetic acid (10% v v⁻¹) extruding the resulting wet mass spherionising to produce pellets ● Drying wet pellets	Alkali low sulfonate content	● Basic Characteristic of ALiCE is lower than its basic characteristic (Albadarin <i>et al.</i>, 2017) ● Dye Removal Efficiency rises slightly with pH increase from 2 to 4, and then the efficiency increases with pH increase from 4 to 7
Acid carbon catalyst for alcohol dehydration	● Impregnation of lignin with aqueous H₃PO₄ at room temperature ● Drying in a vacuum dryer ● Activation under continuous N₂ flow	Alcell lignin	● Increasing the strength and amount of acid sites increased the catalytic activity but did not have a remarkable effect on the value of the dehydration reaction activation energy (Bedia <i>et al.</i>, 2009)
Base carbon catalyst for alcohol dehydrogenation	● Carbonization under a continuous N₂ flow	Sodium-lignosulfonate powder	● 2-propanol, methanol, and ethanol transformed to acetone, formaldehyde, and acetaldehyde, respectively, at atmospheric pressures (García-Mateos <i>et al.</i>, 2017b) ● Conversions were low but selectivities were higher than 80%
Pt-supported submicron carbon fiber electro-catalysts for alcohol electro-oxidation	● Electrospinning in a co-axial configuration and solvent ethanol ● Addition of platinum acetylacetone concentrations to obtain lignin fibers with platinum nanoparticles in one step ● Thermostabilization in air ● Isothermal treatment in furnace under air ● Carbonization with a continuous flow of N₂	Alcell lignin	● The best electrospinning behavior was obtained with a lignin-to-ethanol ratio of 1 (García-Mateos <i>et al.</i>, 2017a) ● Carbon fibers with phosphorus exhibited superior oxidation and electro-oxidation resistance ● Pt-containing carbon fibers can be used as electrodes directly without any binder or promoter
Nanoparticle	● Dissolving lignin in tetrahydrofuran ● Filtering the solution and introducing it into a dialysis bag ● Slow stirring	Kraft process-extracted lignin (LignoBoost)	● Unlike previous method proposed, hazardous chemicals such as acetyl bromide are not needed in this method (Lievonon <i>et al.</i>, 2016) ● Pre-dialysis concentration of lignin is effective on nanoparticles final size

(Continued)

Table 1 Continued

<i>Application</i>	<i>Process</i>	<i>Lignin form/source</i>	<i>Remarks</i>	<i>Refs.</i>
Nanoparticle	● Dissolving lignin in deionised water with KOH ● Solidifying using liquid nitrogen ● Freeze-drying ● Thermal stabilization ● Carbonization under N₂ atmosphere	Protobind 2400 lignin (a by-product of the paper industries)	● Increasing the KOH decreases thermal stabilization yield but increases carbonization yield and decreases overall yield	(Gonugunta <i>et al.</i> , 2012)
Nanoparticle	● Sonicating lignin suspensions for 60 min	Alkali lignins from wheat straw and Sarkanda grass	● Sonication did not result in any significant changes in lignin composition or structure at the intensity applied but depends on the nature of the lignin ● Dominant reactions were cleavage/depolymerization rather than oxidative coupling/polymerization	(Gilca <i>et al.</i> , 2015)
Phenol substituent in phenolic resins for thermosets	● Reacting lignins, potassium hydroxide, glutaraldehyde (a dialdehyde obtained from natural sources) and water ● Stirring ● Acidifying to pH 6 with HCl ● Addition of toluene ● Filtering resins	Organosolv sugar-cane bagasse lignin	● Lignin-glutaraldehyde composites had superior or similar properties to phenol-formaldehyde resin composite	(Da Silva <i>et al.</i> , 2013)
Phenol substituent phenolic-type resins in composites	● Dispersing lignin in the aqueous formaldehyde solution under mechanical stirring ● Addition of potassium hydroxide and mixing ● Heating and stirring ● Neutralizing with concentrated hydrochloric acid	Lignin from organosolv acid hydrolysis of sugarcane bagasse	● Replacing lignin remarkably improved adhesion at the fiber-matrix interface ● Lignocellulosic fiber-reinforced composites exhibited great mechanical properties	(Ramires <i>et al.</i> , 2010)
Phenol substituent in phenol formaldehyde resin	● Transferring lignin cake in a beaker ● Addition of phenol ● Stirring to obtain a homogenous paste ● Addition of formaldehyde solution and methanol ● Addition of sodium hydroxide	Bagasse lignin	● Thermal stability depends on the lignin source ● Incorporation of up to 50% lignin enhances adhesive and shear strength of phenol formaldehyde resins	(Khan and Ashraf, 2007)
Phenol substituent in phenol formaldehyde resin	● Mixing phenol, lignin, and sodium hydroxide aqueous solution ● Cooling ● Resinification	Enzymatic hydrolysis lignin	● Lignin can replace up to 50% phenol in phenol formaldehyde resin without worsening the adhesive strength	(Qiao <i>et al.</i> , 2015)
Incorporation in phenol-formaldehyde (LPF) resin adhesive	● Mixing phenol and lignin ● Addition of NaOH solution ● Heating ● Cooling ● Addition of formaldehyde and NaOH solution in two steps ● Addition of NaOH and urea solution ● Rapid cooling	Corn cob lignin, two kinds of poplar wood lignin, and wheat straw lignin	● Plywood offering high-performance and low-formaldehyde-emission can be prepared with these LPF resin adhesives synthesized based on the new formulation designed following accurate analysis of the active sites in lignin ● The formulation can be adapted to other lignins	(Yang <i>et al.</i> , 2015)

Polyurethane foam	● Mixing lignin, polyol, water (blowing agent), surfactant and catalyst (Kosmos 29) ● Addition of MDI and stirring vigorously	Hardwood organo-solv lignin (HOL) or hardwood kraftlignin (<i>HKL</i>)	● Lignins were not just trapped in the foam-like filler; they were chemically crosslinked (Pan and Saddler, 2013) ● The addition of up to 25%–30% HOL ● Or 19%–23% <i>HKL</i> resulted in foams with acceptable structure and strength ● PUs from HOL offered better strength at the same lignin amount because HEL had a better miscibility with the polyol than <i>HKL</i>
Polyurethane foam	● Drying in a vacuum oven ● Mixing lignin, propylene oxide, and KOH ● Heating, increasing pressure suddenly, and releasing it to produce lignin polyols via oxypropylation ● Mixing polyol with silicone (surfactant) and catalysts (dimethylcyclohexylamine and Mannich base catalyst) ● Addition of pentane (blowing agent) and comonomer methylene diphenyl diisocyanate (MDI) ● Strong stirring till foams are formed	Softwood kraft pine lignin	● Solid lignin modified successfully to liquid polyol with proper hydroxyl index (Li and Ragauskas, 2012) ● Lignin polyol can be used solely for preparation of rigid PU foam without the need to add other polyols or chain extenders ● Rigid PU foam made of lignin polyol offered better mechanical properties than its commercial counterpart
Polyurethane	● Mixing lignin with PEG and THF (solvent) ● Reacting with tolylene 2,4-diisocyanate TDI in the presence of stannous octoate (catalyst) at room temperature	Black liquor lignin	● Poly(ethylene glycol) of molecular weight 200 and a lignin concentration of 50% resulted in polyurethane offering optimum thermomechanical properties (Chahar et al., 2004) ● Shear strength of lignin polyurethane adhesive joints was higher than the commonly used phenol formaldehyde resin prepared using phenolated lignin
Polyurethane film	● Solubilizing lignin and MDI in THF ● Stirring at room temperature till dissolved ● Addition of dibutyltin dilaurate (catalyst) and PEG and stirring under nitrogen	Solvolytic lignin (organosolv)	● Crosslink density of PUs improved with increasing amount of lignin and chain length of PEG (Thring et al., 2004) ● Ultimate strength and Young's modulus of Pus increased with increasing lignin amount till 30 wt% lignin content ● PEG 400 exhibited best results for synthesizing lignin polyurethanes
Polyurethane foam	● Lignin oxypropylation (chain extension) in propylene oxide and in the presence of KOH (oxypropylation catalyst) ● Mixing polyol, surfactant (silicone-based compound for cell stabilization), and catalyst ● (Combination of dimethylcyclohexylamine and Niax A-1) and water (a small amount), stirring vigorously ● Addition of blowing agent (such as pentane for foam formation) and stirring ● Addition of polyisocyanate (MDI) and stirring vigorously	● Soda lignin from Alfa (Stipa tenacissima), organosolv lignin from hardwoods, kraft lignin from softwood, and oxidized organosolv lignin	● Straightforward process (Hamid et al., 2005) ● Polyols have similar characteristics to the conventional materials used in PU preparation ● PUs exhibited good dimensional stability and thermal properties
Slow-release nitrogenous fertilizers	● Oxidative ammoniation (ammonoxidation)	Organosolv kraft, soda, and ASAM (alkaline sulfite anthraquinone-methanol), fermented lignosulfonate from a sodium sulfite process	● Kraft and organosolv lignin resulted in the highest nitrogen contents followed by lignosulfonate (Meier et al., 1994) ● Most influential parameters on ammonoxidation were temperature and oxygen pressure ● 14% nitrogen was fixed in lignins at 150°C and 15 bar

related impurities, and poor ability to be used for further processing retard lignin use for composite applications (Ragauskas *et al.*, 2014).

Lignin offers natural mechanical interlocking within the composite matrix because of its irregular shape, so it connects to the surface and can be used as a surface treatment agent (Thielemans *et al.*, 2002). This interlocking enhances composite properties by improving fiber-matrix strength. Lignin can be incorporated into petroleum-derived composites by/as a toughening agent, network connectivity enhancer, providing extra stiffening units to the matrix, sizing agent between fibers and the matrix, comonomer, toughness enhancer (by prompting plasticity), behaving as a free radical trap to decrease the effects of radical scission during fracture, enhancing flame resistance, increasing biodegradability, improving photo resistance and thermal stability, expanding fatigue lifetime, and green material precursor (Thielemans and Wool, 2005).

Yi *et al.* (2015) synthesized spherical multilayer composite microcapsules, loaded with a healing agent (isophorone diisocyanate), through the polymerization of lignin nanoparticle-stabilized oil-in-water Pickering emulsion templates. The microcapsule showed superb resistance to damage from high temperature, moisture, and solutions. The microcapsule's self-healing coating exhibited a significant anticorrosive and protected the steel plate even after 120 h of immersion in 10 wt% NaCl solution (no corrosion), whereas the control sample was rigorously corroded. Self-healing coating occurs when active agents transferred out of the microcapsules then polymerize, fill the cracks, and prevent corrosive attack. Automatic repairing and promising self-healing properties make these microcapsules strong candidates for industrial and environmental applications.

Concrete

Volume-based lignosulfonates are the dominant admixture used in the construction sector (Plank, 2004). Lignosulfonate is added to concrete with two main aims: as a plasticizer to firm concrete and enhance its pourability, uniformity, flowability, and workability; and to reduce the amount of water required to produce a good workable concrete with a low water-to-cement ratio and high compressive strength. Lignosulfonate reduces the water content by up to only 15%, but synthetic superplasticizers can reduce it by up to 40%. Therefore, for better effects, blending lignosulfonates with synthetic superplasticizers is required. The main reason to use lignosulfonate is its cost competitiveness.

Ammoxidized lignosulfonate prepared via oxidative ammonolysis or ammoxidation (Gargulak *et al.*, 2001) can be used as dispersant in cement or mortar as well as in many other applications including as carbon black, clays, mineral, slurries, and pigments (Syahbirin *et al.*, 2012). Ammoxidized lignosulfonate was found to exhibit remarkably lower entrapped air and retardation than its corresponding lignosulfonate before ammoxidation.

Other Applications

Lignin has other potential applications that need further investigation, for instance as vegetation proxies in lake sediment cores and natural waters (Heidke *et al.*, 2018), molecular marker of plant carbon turnover (Panettieri *et al.*, 2017), etc. Meier *et al.* (1993) found that mixtures of lignosulfonate with fertilizer improved nitrogen recovery and fertilizer efficiency. Acar *et al.* (1991) found that calcium lignosulfonate used as a binder in animal feed pellets offered better pellet quality, excessive dietary energy level, and helped in fat deposition. Chemical pulping lignin dominates the commercial market as an additive in cement, drilling fluid in oil recovery, and dust suppression (Ragauskas *et al.*, 2014; Strassberger *et al.*, 2014).

Table 1 shows various macromolecule products from lignin and the associated process characteristics.

Conclusion

This article reviewed different possible approaches to lignin-based higher value chemical and material production. Considering increased lignin production resulting from developments in cellulosic biorefineries and ethanol production plants, it is not reasonable to just burn lignin as a waste fuel while making use of lignin brings about profit. Benefiting from its polymerized multi-dimensional structure, lignin can be converted to various polymeric and high performance materials. There are many potential applications of lignin to value-added use through the processes and to the materials described in this article. However, to achieve the best results, all of the following need to be efficient and optimized: lignin isolation from biomass, lignin degradation, value-added production pathways, and the purification of final products.

Acknowledgements

As a part of the University of Alberta's Future Energy Systems research initiative, this research was made possible in part thanks to funding from the Canada First Research Excellence Fund. The authors are grateful to the NSERC/Cenovus/Alberta Innovates Associate Industrial Research Chair Program in Energy and Environmental Systems Engineering and the Cenovus Energy Endowed Chair in Environmental Engineering at the University of Alberta for financial support for this research. Astrid Blodgett is thanked for editorial assistance.

See also: Development of Self-Adhesive Products Using Only Bamboo Fibers Extracted With a Machining Center

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Sustainable Air-Conditioning

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Introduction

Improved economy, technological advancement and their easy accessibility, rapid growth in world population and increase in standards of living have led to a substantial rise in energy demand. Number of buildings and their energy consumption is rapidly increasing. There are approximately 1.6 billion installed air conditioning equipment all over the world, which collectively account almost 20% of the total energy consumption (IEA, 2018). The main objectives of air conditioner are to provide human thermal comfort and desirable hygienic indoor air quality. Indoor environmental conditions significantly affect human health and work efficiency. It is controlled by the regulation of temperature, humidity and purity of air within prescribed limits. In conventional air conditioners, thermal comfort is attained by cooling the outside air below its dew point value and subsequently, air is reheated to desired supply condition. Enormous amount of energy is expended in overcooling and reheating of air which escalates the overall running cost of the system. Wet surfaces created by condensation of air act as a breeding ground for fungi and bacteria, which severely influences human health. Moreover, the harmful gases (CFC, HCFC and HC) released from the air conditioner causes environmental threats like ozone layer depletion and/or global warming. Although vapor compression is the most sophisticated and well developed technology, it does not handle moisture reduction process in an energy efficient way. Therefore, worldwide there is a need to developed proficient air conditioning devices which can handle sensible and latent load efficiently. Use and development of sustainable and eco-friendly HVAC (heating ventilation and air conditioning) systems such as solar air conditioning, geothermal heat pump, absorption and adsorption based desiccant cooling systems can considerably normalize the limitations of conventional air conditioners.

Need for Sustainable and Renewable Energy Based Air Conditioning

Despite the fact that we have made significant progress in all fields of science but still our primary energy demand is met through fossil fuels. The energy production through fossil fuels has created many environmental concerns such as oil spills, acid rain, acid rain, climate change, global warming etc. Fig. 1 shows the primary energy consumption in different sectors. Major portion of the electricity consumed in building (residential and commercial) is required for heating and cooling. The energy consumed in HVAC is approximately 50% of the total building energy in developed countries (Pérez-Lombard *et al.*, 2008). It is estimated that worldwide energy intake for cooling buildings will increase to 4000 TWh (Terawatt-hour) in the year 2050 (Mucke *et al.*, 2016). Therefore, to alleviate the consumption of non-renewable sources of energy in HVAC – the development of efficient heating and cooling systems running primarily through renewable and sustainable energy is the need of the hour. Renewable energy is generated through sources that naturally replenished themselves and never get exhausted. The most common sources are hydroelectricity, solar energy, wind energy, wave power, geothermal energy, and tidal power. As depicted from the Fig. 2 – the interest in renewable energy is growing rapidly. Renewable has many advantages; it can help in combatting energy security and climate change issues together. Hydro, tidal and solar create zero air pollution, while the emission from biomass and geothermal is minimum. Downside of renewable energy – it is difficult to generate large-scale power from renewable sources same as fossil fuels. Building dams and wind farms can disrupt wildlife and ecological balance. The generation of solar energy is intermittent in nature as it is available during sunshine. Sustainable and renewable sources of energy offer a promising alternative to greenhouse gas emission from fossil fuels. As the technology advances; renewable energy will become more accessible, affordable and efficient.

Conventional Air-Conditioning System

The modern air conditioning system based on vapor compression (VC) technology is the most versatile and extensively used system to achieve comfortable indoor air quality. The basic elements of vapor compression system are compressor, condenser, evaporator, and throttling valve. These systems work in a closed cycle, where a fixed amount of working fluid (refrigerant) continuously flows in a closed loop of components. The Fig. 3 shows the simple vapor compression system. The compressor works between the evaporator and condenser pressure. Compressor converts the low pressure and low temperature saturated vapor refrigerant into high temperature superheated refrigerant. This superheated refrigerant at high pressure and temperature enters the condenser, rejecting the heat of condensation to ambient air/cooling water (produced through cooling tower) and subsequently it is converted in to liquid form. The liquid refrigerant at high pressure is transformed to a low pressure liquid-vapor refrigerant by the throttling valve. Then, the low temperature refrigerant at the inlet of evaporator undergoes a phase change by absorbing heat

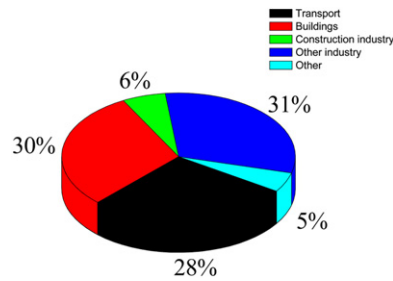


Fig. 1 Primary energy consumption in different sectors (<https://www.iea.org/buildings>).

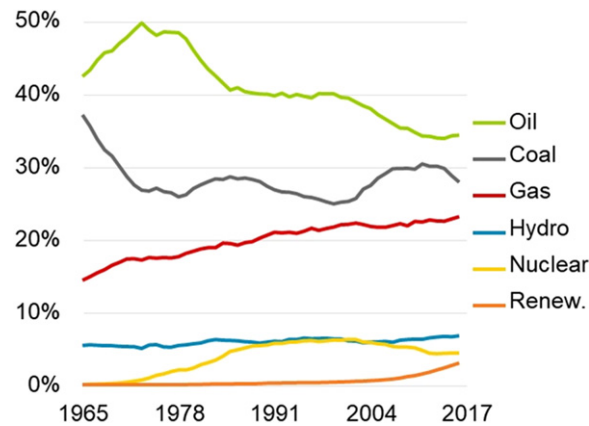


Fig. 2 Share of global electricity generation by fuel (<http://www.bp.com/globalcorporateenergy-economic-statistical-review-of-world-energy>).

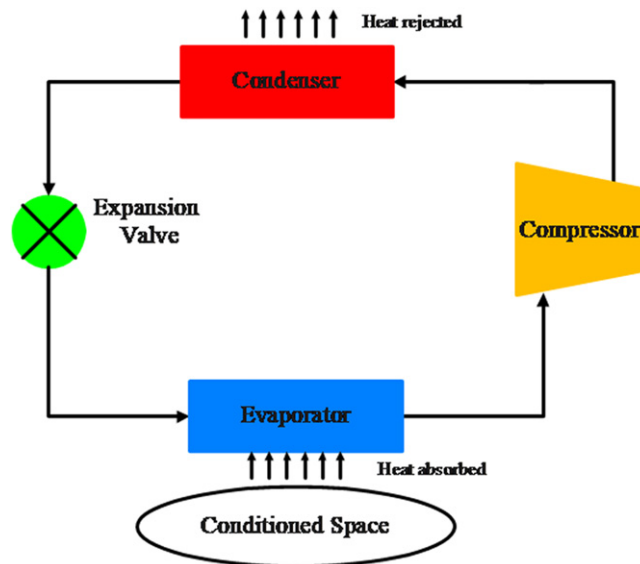


Fig. 3 Vapor compression system.

from the conditioned space. The vapor refrigerant then enters the compressor to complete the thermodynamic cycle. The vapor compression system can be used for both heating and cooling the conditioned space. Fig. 4 shows the typical room air conditioner. The cooling capacity and energy requirement of the air conditioning system depends on the room latent and sensible load. The cooling and heating effect is produced in a cyclic manner through evaporation and condensation of refrigerant in evaporator and condenser. Compressor is the only work consuming element in the VC system. The heat rejected from condenser represents the heating load while the heat absorbed by evaporator represents cooling load.

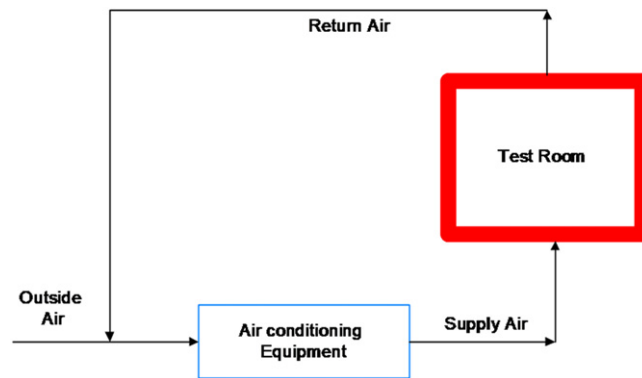


Fig. 4 Typical room air conditioner.

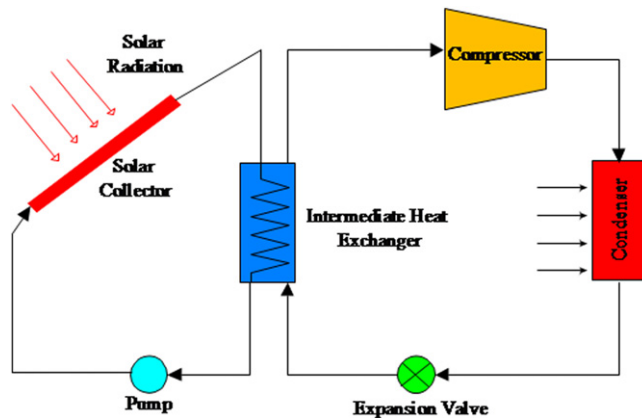


Fig. 5 Solar heat pump.

Sustainable Air Conditioning

The thermal and economic performance of compression heat pump can be elevated by using solar thermal collector (Mohanraj *et al.*, 2018). The combination of solar system with heat pump is an emerging alternative for building space heating.

Solar Heat Pump

Solar heat pump is the integration of vapor compression heat pump and solar thermal collectors (Fig. 5). The heat pump includes basic elements such as condenser, expansion valve, evaporator (intermediate heat exchanger). The heat pump includes basic elements such as condenser, expansion valve, evaporator (intermediate heat exchanger). The fundamental function of solar thermal collector is to absorb the solar radiation (heat) and transfer it to the working fluid flowing inside the pipes attached to the absorber plate. The heat energy absorbed by the working fluid is transferred to the heat pump fluid via indirect intermediate heat exchanger. The heat pump uses the condenser heat of the system to maintain the temperature of the space in warm state. The commonly used working fluid in solar system is either water or glycol and heat pump uses any HCFC/HFC refrigerant such as R-134a. Advantage of combining solar system with heat pump is to improve the performance of sub system which eventually increases the performance of solar heat pump as a whole. The system works in the presence of solar radiation; hence during night hours some additional in absence of it, some auxiliary heat exchanger auxiliary heating medium (electrical heating or condenser heat) is used. Emam Hassanien *et al.* (2018) investigated the viability of solar heat pump for greenhouse heating in China. They showed that system can provide more than 35% of the heating requirement for heating greenhouse. Bellos and Tzivanidis (2017) compared the thermo-economic performance of conventional heat pump with solar heat pump. They concluded that electricity saving between 30% and 40% is possible through solar heat pump.

Direct-Expansion Solar Heat Pump

Sporn and Ambrose in 1955 introduced the concept direct expansion solar heat pump (DXSHP). With high potentials for cooling, heating, drying, and air conditioning application; the investigation on DXSHP has progressed in the past decade. Direct expansion

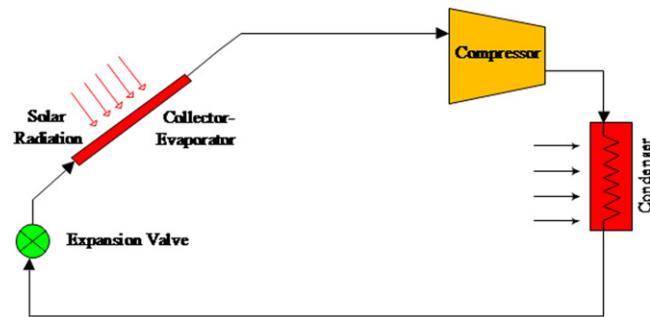


Fig. 6 Direct expansion solar heat pump.

heat pump if adapted for cold climatic conditions allows sustainable space heating and hot water production simultaneously. In this type of configuration, usage of high and low intensity insolation for heating requirement is made viable via direct heating and expansion of refrigerant in the solar collector-evaporator. **Fig. 6** shows the schematic diagram of DXSHP. The solar module can be a simple solar thermal collector or a photovoltaic-thermal (PVT) module. The system performance is affected by intensity of insolation, ambient temperature, compressor speed and type of refrigerant (Kong *et al.*, 2018). DXSHP is largely investigated for water heating application followed by space heating and very few investigations is reported for space cooling (Omojaro and Breitkopf, 2013). The advantages of DXSHP over conventional heat pump are as follows: (1) Superior thermodynamic performance. (2) Reduction in corrosion problem of solar collector. (3) Longer life of solar collector. (4) Lower system cost.

Solar Photovoltaic-Thermal Heat Pump

The concept of solar photovoltaic-thermal heat pump was initiated by Kern and Russell in 1978. Many research studies had investigated photovoltaic thermal hybrid solar collectors (Charalambous *et al.*, 2007; Emmi *et al.*, 2017; Noro and Lazzarin, 2018). The solar photovoltaic thermal collectors are devices, which simultaneously convert solar radiation into thermal energy and electrical energy. The collector comprises a photovoltaic module with absorber plate affixed to the back of PV module. The absorber plate maintains temperature of photovoltaic module by absorbing thermal energy as well as heat released during conversion of solar energy into electrical energy. The two different system i.e., solar heat pump and photovoltaic thermal hybrid solar collector are integrated to form solar photovoltaic thermal heat pump. In this technology evaporator of heat pump and solar photovoltaic thermal collector are combined in a single unit. **Fig. 7** shows the schematic diagram of solar photovoltaic thermal heat pump. The PV thermal collector simultaneously provides heat source and electricity to evaporator and compressor. The efficiency of photovoltaic thermal collector increases due to absorption of heat from photovoltaic module. Huide *et al.* (2017) mathematically and experimentally compared the performance of photovoltaic system, solar thermal collector and hybrid photovoltaic thermal collector for different location in China. The findings indicated that hybrid system has the greatest energy saving potential for urban areas as compared to other solar systems and for rural areas depending on the area of installation the hybrid or photovoltaic system can be the most optimal option.

Solar-Geothermal Hybrid Heat Pump

Solar and geothermal energy both are widely used renewable source of energy. Both are cleaner and sustainable energy that can be used to avoid adverse environmental impacts caused by burning fossil fuels. When the solar radiation is sufficient the heating system absorbs heat only from the solar collector otherwise some auxiliary heating source such as geothermal energy can be used. Solar geothermal heat pump technology integrates solar collector and geothermal heat exchanger with a heat pump system. The solar collector and geothermal heat exchanger can be connected either in series or parallel configuration. The sources of energy for heating are solar and geothermal. **Fig. 8** illustrates the line diagram of solar geothermal hybrid heat pump. When the temperature rise of water in the solar collector is not sufficient, it is sent to geothermal heat exchanger to absorb the extra heat. The refrigerant exchanges energy with the hot water through the intermediate heat exchanger. The series combination is more efficient as compared to parallel configuration (Mohanraj *et al.*, 2018). The combination of geothermal heat exchanger with solar collector reduces the overall size of geothermal heat exchanger. The amount of solar radiation and temperature of ground have significant impact on the compressor work. A performance simulation study on solar-geothermal heat pump for residential heating application under different operating conditions was carried out by Kim *et al.* (2013). The result showed that with increase in ground temperature from 11°C to 19°C, the pressure ratio of compressor decreases from 3 to 2.5 and maximum COP reaches to 2.81.

Solar Thermoelectric Air Conditioning System

The thermoelectric cooling technology was invented by Peltier in 1834. The principle of thermoelectric cooling is based on Peltier effect which is also known as reverse of Seebeck effect. In a circuit consisting of two different metals, an emf (Electromotive force)

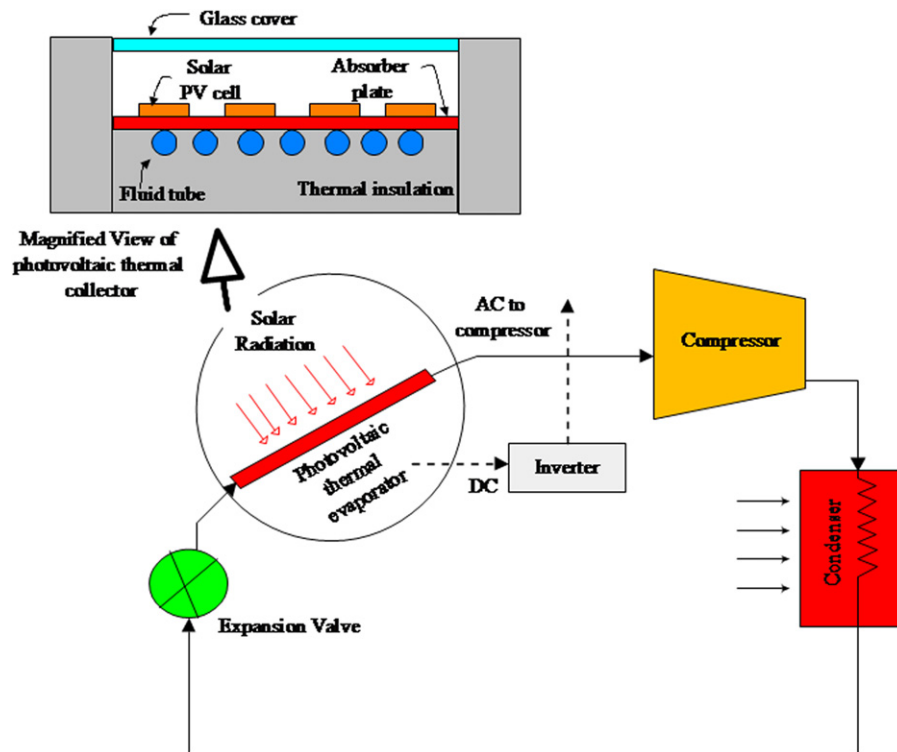


Fig. 7 Solar photovoltaic thermal collector heat pump.

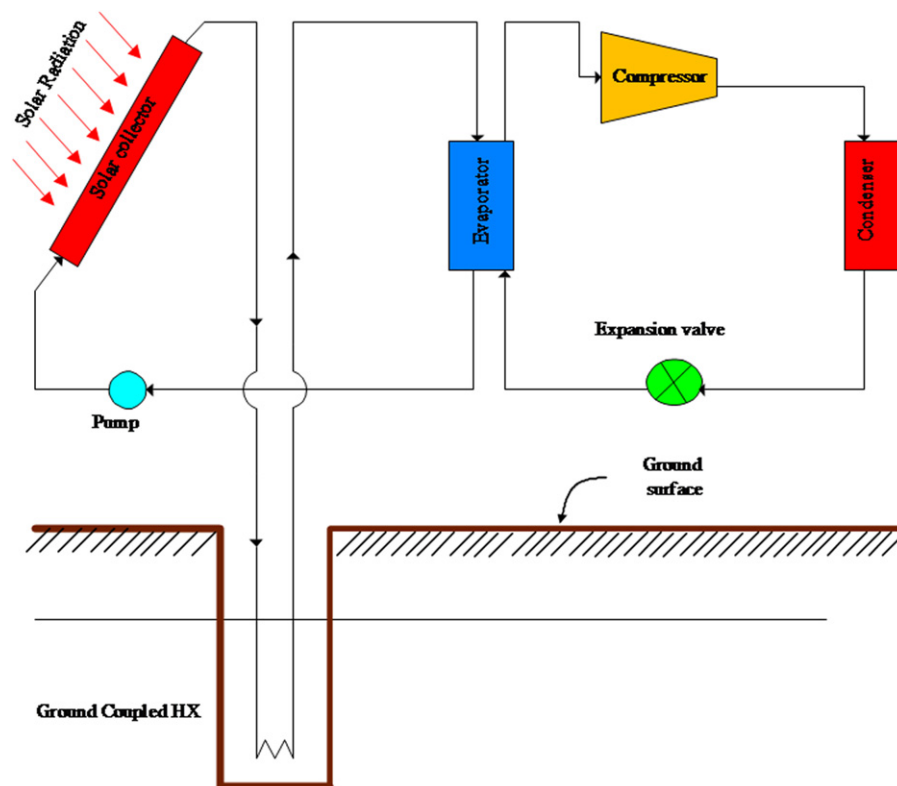


Fig. 8 Solar geothermal heat pump.

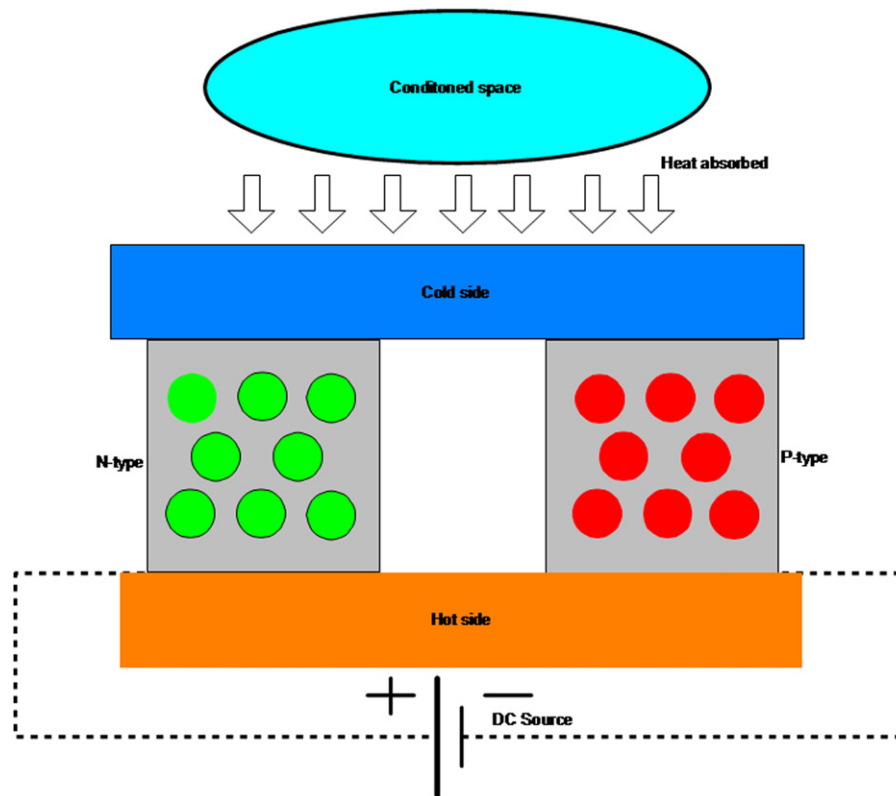


Fig. 9 Thermoelectric air conditioning system.

is generated, when two junctions are maintained at different temperatures. This effect is known as thermoelectric effect or Seebeck effect. The magnitude of emf generated depends on the type of material and the temperature maintained at two different junctions. The two junctions can act as a source of absorption and rejection of energy. Although the thermal efficiency of solar thermoelectric air conditioning system is low, the system is quite popular because of simple design, low space requirement, and low cost (Liu *et al.*, 2015b). Moreover, as the system is not having any mechanical parts; it is free from wear, tear and noise problems. A typical thermoelectric module comprises of a stack of P-type and N-type semiconductor pellets sandwiched between ceramic substrates. The P-N pellets are usually designed to connect electrically in series and thermally in parallel. When current is supplied to module, charge carrier (positive and negative) in the pellet stack absorbs thermal energy from one side of substrate surface and releases it to opposite side. Fig. 9 shows the schematic of thermoelectric air conditioning. One surface becomes cold, where heat energy is absorbed and the opposite surface becomes hot, where heat energy is released. The photovoltaic (PV) collector can be used directly to power the thermoelectric module, which can largely reduce the cost of the overall system. In the daytime, the solar panel supplies energy to thermoelectric air conditioner through conversion of thermal energy into electrical energy by photovoltaic module. If the power supplied exceeds, it can be stored in a battery in addition to driving the solar thermoelectric module. During night or cloudy day the electrical energy from the battery can be used to power the thermoelectric module.

Vapor Absorption System

Vapor compression system (VCS) is electrical energy driven system. It is not feasible to use VCS, where there is shortage of electricity. In such conditions, an alternative to VCS Vapor absorption systems (VAS) can be used. VAS are heat driven systems, they require major energy as heat. They are gradually becoming more popular as heat can be supplied through various sources including the renewable as well as waste heat available from the industry.

Vapor Absorption Air Conditioning System

The working components of VAS are similar to VCS. The compressor in VAS is replaced by absorber, pump and regenerator. Fig. 10 shows the working of VAS system. Low temperature and low pressure refrigerant in gaseous form is driven towards the absorber due to negative pressure gradient. The absorber vessel is filled absorbent solution, which has high affinity to absorb the refrigerant. The absorbent absorbs the refrigerant vapor and heat of vaporization is liberated. The liquid solution is then pumped to the regenerator. The solution rich in refrigerant is heated in the regenerator for separation of the absorbed refrigerant in gaseous form

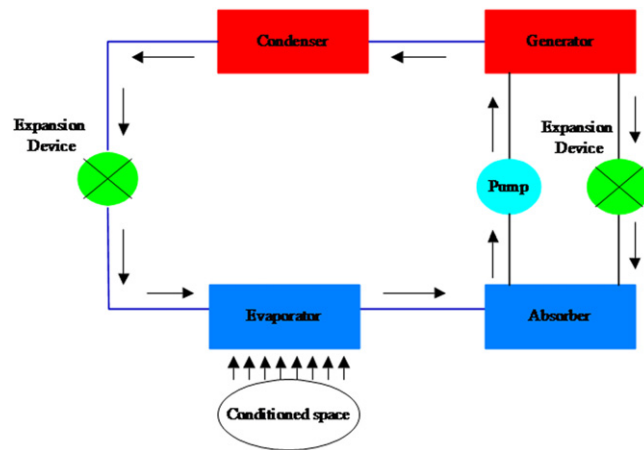


Fig. 10 Vapor absorption system.

out of rich solution. Then, the gaseous refrigerant is condensed in the condenser to liquid form by rejecting heat to the environment (external sink). Finally, the refrigerant is throttled from condenser pressure to evaporator pressure inside the expansion valve. In regenerator, hot and strong absorbent solution is throttled back to the absorber side. Same pressure is maintained in the condenser and regenerator and in evaporator and absorber. Energy consuming devices in VAS are regenerator and liquid pump. The mechanical work required for running the liquid pump is almost negligible in comparison to compressor of VCS system. Although VAS system is promising alternative to VCS, yet on account of poor COP and bulky size – the technology could not enjoy the commercial success similar to VCS. The thermal efficiency of VABS can be improved by employing efficient solar collector to drive regenerator of VABS (Kojok *et al.*, 2016).

Solar Vapor Absorption System

Vapor absorption system driven by solar energy had attracted the interested of many researchers (Siddiqui and Said, 2015; Sarbu and Dorca, 2018; Shirazi *et al.*, 2018). The pioneering work in solar absorption system was started by Farber at the University of Florida. Fig. 11 illustrates the vapor absorption cycle powered by solar energy. Heat generated in the solar collector elevates the temperature of weak solution (inside regenerator) large enough to lead the separation of refrigerant vapor. The superheated refrigerant gas at high temperature and pressure is condensed in the condenser. High pressure condensate temperature is reduced through throttling process and subsequently it produces cooling effect through evaporation of liquid portion of the refrigerant in to evaporator. Vapor generated in the evaporator is absorbed inside the absorber due to presence of low pressure absorbent solution. Additional devices such as rectifier may be required for effective separation of pure refrigerant inside the regenerator in case the boiling temperatures of refrigerant and absorbent solution are close. Lithium bromide–water (LiBr–H₂O) and water–ammonia (H₂O–NH₃) are the two most-commonly used refrigerant–absorbent pair in the vapor absorption system. In Lithium bromide–water (LiBr–H₂O) pair; water is a refrigerant and Lithium bromide solution is an absorbent, whereas in case of water–ammonia (H₂O–NH₃) pair; water is an absorbent and ammonia act as a refrigerant. The H₂O–NH₃ generally used for large scale cold storage, whereas LiBr–H₂O is used for air conditioning application – otherwise LiBr salt will crystallize. Regeneration temperature required for water–ammonia (H₂O–NH₃) is higher and its COP is lower as compared to Lithium bromide–water (LiBr–H₂O) working fluid pair (Li and Sumathy, 2000).

Geothermal Vapor Absorption System

In vapor absorption system, the desired cooling effect is obtained by coupling two separate working fluids, these fluids are separated inside the regenerator using high thermal energy. The energy needed for their separation can be supplied through different sources i.e., electric heater, solar collector, and geothermal system. Geothermal energy in stand-alone mode can be used for both cooling and heating applications but is more economical in case used for heating application. The temperature required for regeneration in single stage vapor absorption cooling system is rated around 115°C (Yilmaz, 2017). Therefore, the prospect of combining heat driven vapor absorption cooling system with geothermal application is enormous. Using geothermal energy in place of some fossil fuel burning or even solar energy for regeneration purpose helps in reducing greenhouse gas emission as geothermal energy is available for 24 h on continuous basis. In the evaporator the liquid-vapor refrigerant absorbs the heat from the conditioned space and converts into vapor form, these refrigerant vapors are sent to absorber where it is mixed with cold absorbent, causing the refrigerant to liquefy. The solution rich in refrigerant and absorbent is pumped to the regenerator. In regenerator the solution is heated through geothermal fluid, which helps the refrigerant to evaporate and separate itself from absorbent solution. The vapors are passed through rectifier which only allows vapor to pass to the condenser, in condenser the

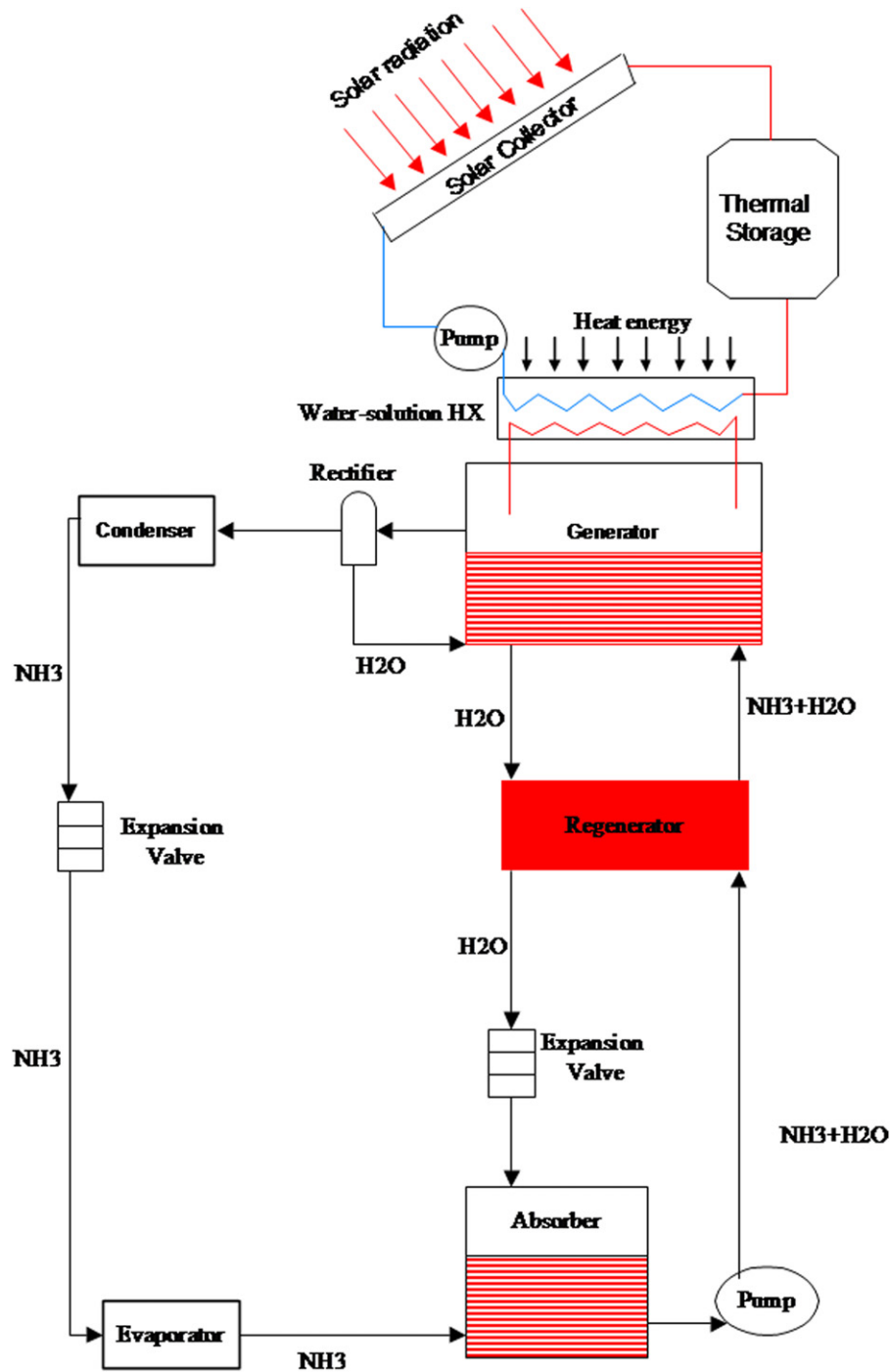


Fig. 11 Solar vapor absorption system.

solution is again condensed and sent to expansion device. From the regenerator, the weak solution is expanded and sent to absorber again. The low temperature refrigerant in the evaporator produces the cooling effect by absorbing heat from the conditioned space. Fig. 12 shows the geothermal vapor absorption system.

Desiccant System

The desiccant cooling technology is another promising alternative to conventional air conditioners. Desiccant cooling system is an air conditioning method, which operates with ecofriendly working fluid. They are also known as open absorption system thus they

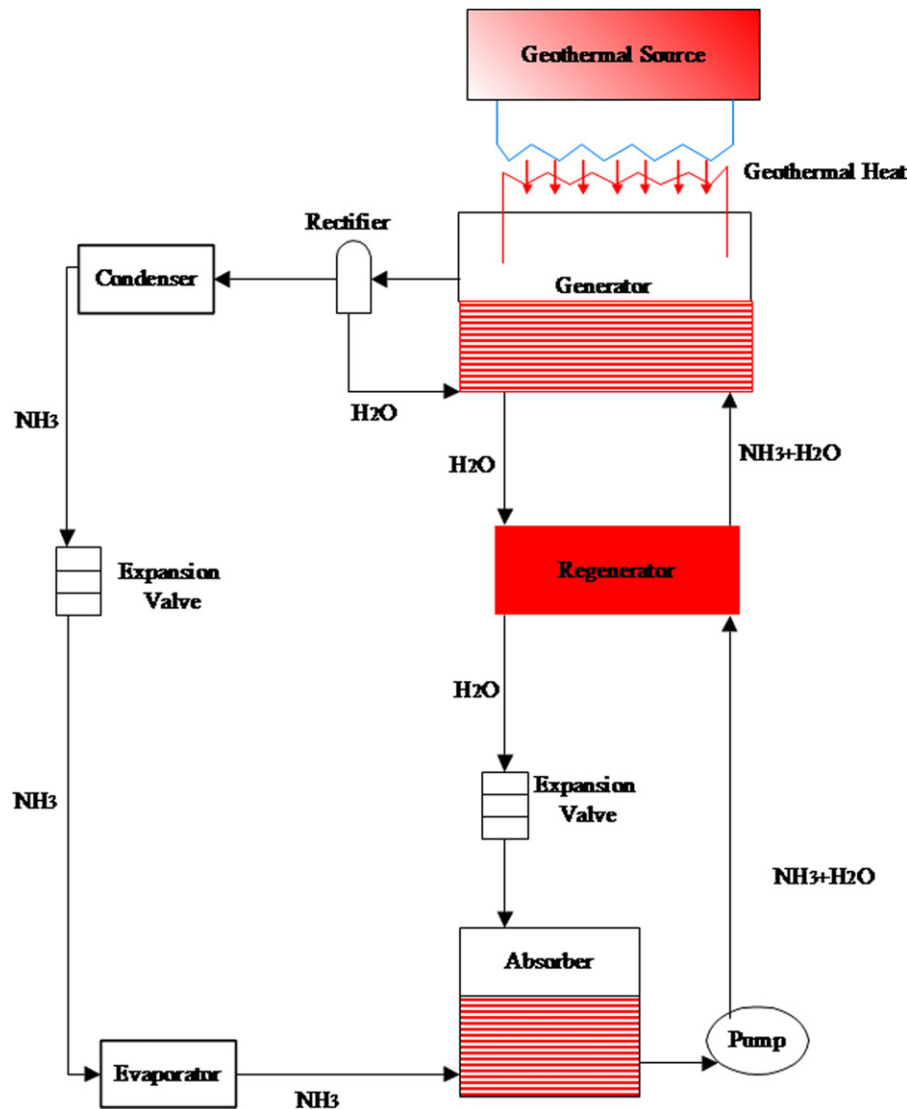


Fig. 12 Geothermal vapor absorption system.

permits the use of water as the refrigerant. They can help in solving technical limitations of both vapor compression and vapor absorption system. They cannot suffice sensible heat demand of the air conditioning system thus needs to be coupled with either with VCS, VAS, geothermal or evaporative cooling system. Low thermal energy sources such as waste energy at low temperature, flat plate solar thermal collectors can be used to regenerate the desiccant material. Desiccants are hygroscopic materials, which have natural affinity to absorb moisture from the air. They are classified as solid desiccant or liquid desiccant on the basis of physical state. The physical process governing the moisture removal is different for both the desiccants. In the case of a solid desiccant system, moisture reduction is obtained by physical entrapment of water vapor in the micro porous structure of the desiccant (adsorption). On the contrary, the moisture is absorbed at interface of the liquid solution (absorption) in the liquid desiccant system.

Solid Desiccant Air Conditioning System

The concept of solid desiccant dehumidification was proposed in 1935 by Hausen. Solid desiccant materials are impregnated, embedded or coated over a lightweight honeycomb shaped matrix called a desiccant wheel. This honeycomb structure has a very large surface area, which is coated with adsorbent material. The adsorbent material is full of tiny holes that further enhance the surface area. The most vital component of the solid desiccant system is the desiccant wheel which continuously rotates at low speed. **Fig. 13** shows a typical solid desiccant wheel. The desiccant wheel consists of two section adsorption side and regeneration side. The most commonly used solid desiccant materials are silica gels, zeolites, synthetic zeolites, activated alumina, carbons, and synthetic polymers (Giampieri *et al.*, 2018). The desiccant wheel creates a low vapor pressure on the adsorption side leading to

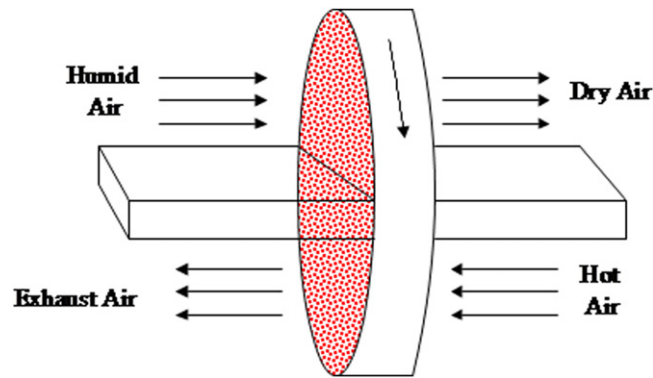


Fig. 13 Solid desiccant wheel.

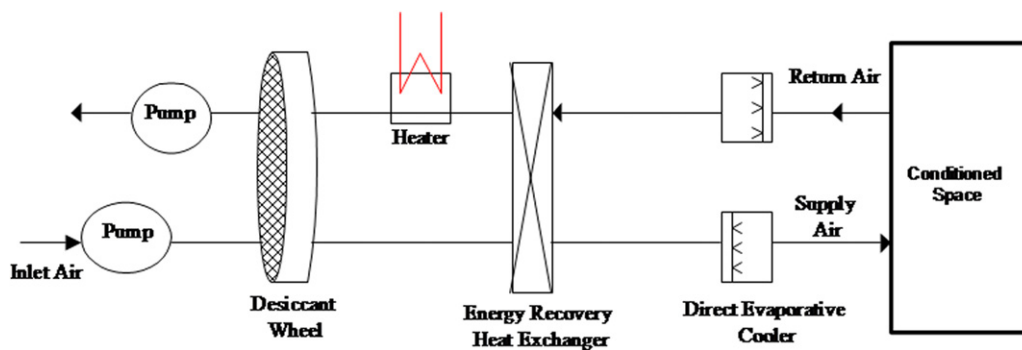


Fig. 14 Solid desiccant system.

dehumidification of process air and on the regeneration side hot air is used for reactivation of solid desiccant matrix. **Fig. 14** represents the working of commonly used solid desiccant dehumidification system. The desiccant wheel initially lowers the moisture content of the inlet air. Air temperature increases during the dehumidification process. The warm and dry air is cooled with help of energy recovery wheel transferring heat from hot air side to exhaust air side and subsequent cooling in evaporative cooling system. The conditioned air is then supplied to the space requiring air-conditioning. The return air from the conditioned space on the exhaust side passes through energy recovery wheel to exchange a part of heat with the supply air. The exhaust air still needs more thermal energy (shown through electrical heating) before supplied to the regeneration side. The temperature of regeneration air depends on the demand of cooling. Liquid desiccant systems have following advantages over solid desiccant system: (1) It is quite simple to obtain isothermal dehumidification and regeneration. (2) The liquid desiccant solutions have strong thermal storage capability. (3) The liquid desiccant can sterilize many organic impurities present in air apart of reducing dust particles. (4) Liquid desiccant system requires lower regeneration temperature. On commercial front solid desiccant system has emerged as successful commodity but liquid desiccant systems are still struggling with technical limitations of corrosion and carryover problems.

Solar Solid Desiccant Cooling System

The solar solid desiccant cooling system is the integration of solar hot water system with solid desiccant dehumidification system. The hot water generated through the solar system transfer heats up return air through some air-liquid heat exchanger such as fin-tube heat exchanger. Coupling of solar heat certainly helps in reducing the external thermal energy demand but the requirement of alternate heating source cannot be entirely exterminated considering intermittent availability of solar energy and large variation in solar irradiance. **Fig. 15** shows the typical solar solid desiccant system. Depending on the requirement of regeneration temperature advance concentrated solar thermal panels such as parabolic trough and linear fresnel systems can be used. The regeneration air heated from flat plate solar collector ([Merabti et al., 2017](#)) vaporizes the water molecules absorbed in the pores of the desiccant material.

Liquid Desiccant System

Fig. 16 shows the schematic diagram of a simple liquid desiccant system (LDS). In absorber cooled and concentrated desiccant enters from the top of tower while air may flow from cross, counter or same direction. The process air is dehumidified due to

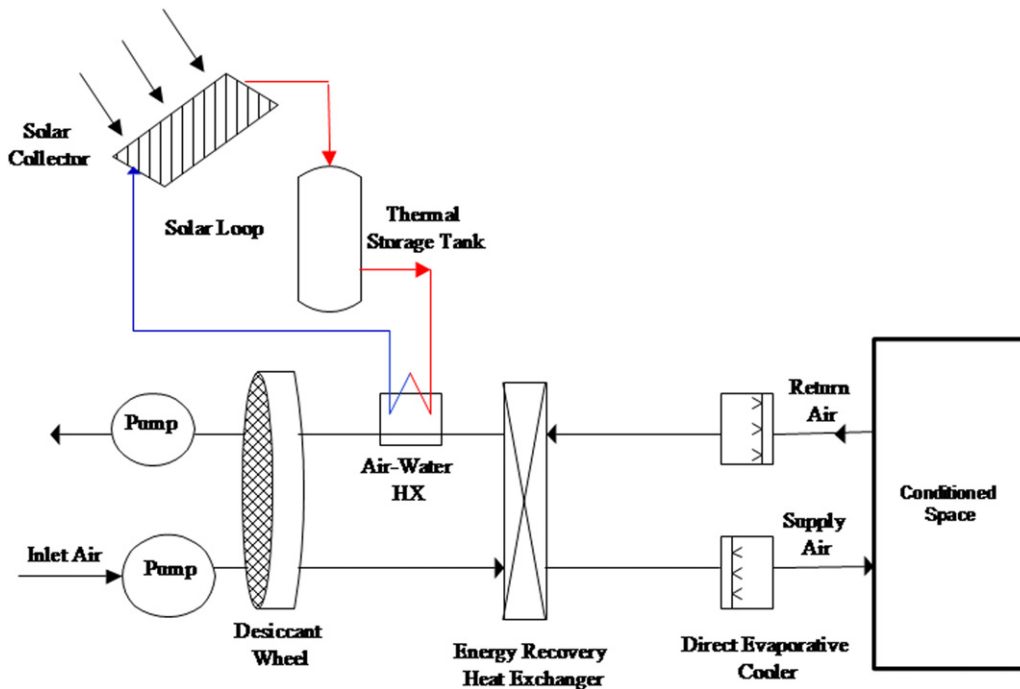


Fig. 15 Solar solid desiccant system.

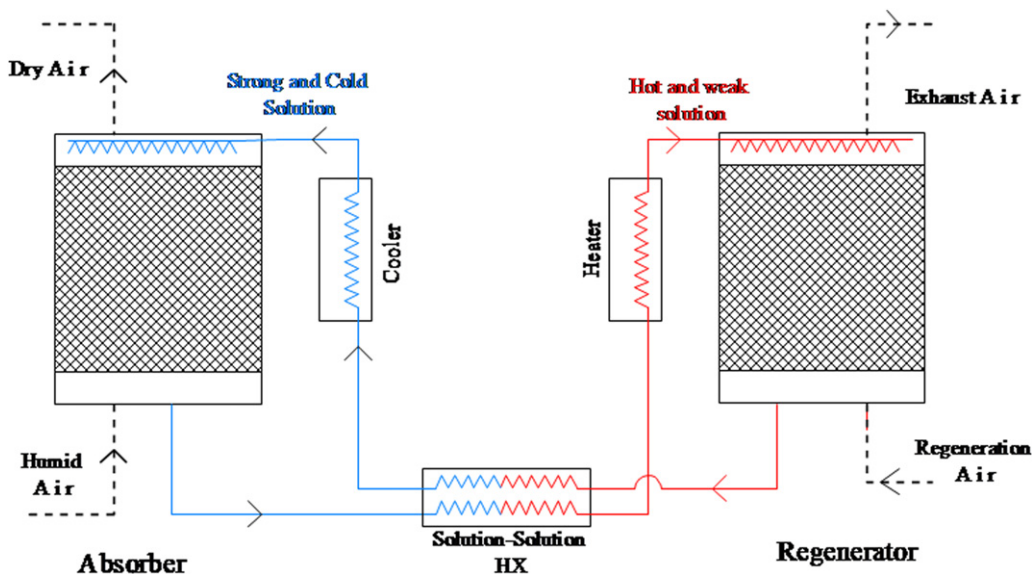


Fig. 16 Liquid desiccant system.

difference of vapor pressure between moist air and the surface of desiccant solution. Heat is released during moisture transfer process, which increases the temperature of air as well as liquid desiccant both. The solution becomes diluted due to absorption of moisture from the process air. Before entering the regenerator, the weak solution is first passed through a solution-solution heat exchanger so that its temperature can be increased using hot solution coming out of the regenerator unit. The solution is further heated by a heating coil to the required regeneration temperature. The heating of desiccant solution increases its vapor pressure. The solution strips excess moisture to another stream of air passed inside the regenerator. The concentrated solution is reverted back towards the absorber side for completion of the cycle. It is cooled first inside the solution to solution heat exchanger through the diluted solution and then passed through the cooler before being sent to the absorber. Cooling of concentrated solution helps in reducing the vapor pressure of it, which ensures effective dehumidification of process air inside the absorber. The physics of the

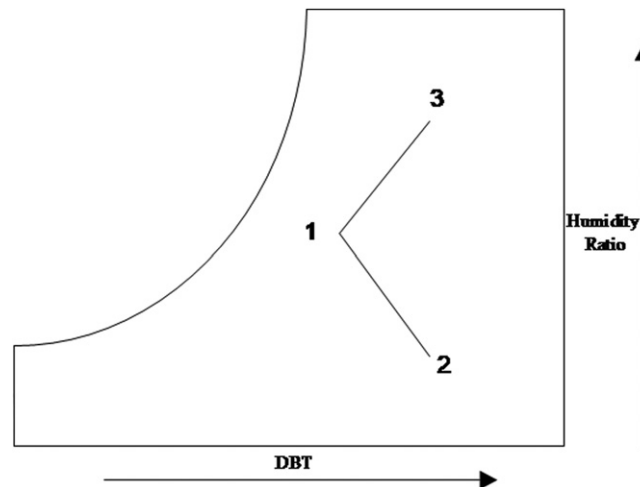


Fig. 17 Psychrometry of air in LDS.

both absorption and regeneration process is same except the purpose. **Fig. 17** shows the psychrometric chart of air as it flows through the absorber and regenerator. Process 1–2 represent the air state transformation inside the absorber; similarly process 1–3 represent the air state transformation inside the regenerator. The temperature of air increases as the result of heat liberated during dehumidification process, whereas the air temperature during regeneration process increases due to sensible heating of air through hot liquid desiccant solution. The absorber and regenerator are chemical reactors – conventional designs of chemical towers are: packed, spray and falling film reactors. Packed bed design is suitable for large capacity systems whereas falling film is suitable for small capacity residential systems. In general metallic surfaces are used as packings or solid surface in case of packed tower or falling film tower respectively. Recently, interest in plastics has increased (Liu *et al.*, 2015a; Patil *et al.*, 2016) to avoid corrosion problem of metallic surface. The use of plastic can offer promising future for the development of long life liquid desiccant air conditioning system.

Solar Liquid Desiccant Systems

The temperature required for regeneration is comparatively low in liquid desiccant systems compared to closed vapor absorption system or solid desiccant system. Solar energy can be most effectively utilized in desiccant solution. Liquid desiccant can be heated either directly or indirectly through solar energy. **Fig. 18** shows the basic indirect solar liquid desiccant system. Different types of solar collectors: the flat plate solar collector, evacuated tube, and parabolic collector can be used for that purpose. A 16 kW prototype of solar desiccant system was developed and tested by Gommed and Grossman (2007). The system consisted of packed bed absorber (dehumidifier), regenerator (desorber), heat exchangers, and a flat plate solar collector. The system had a thermal COP of 0.8, and solar collector was utilized for providing the thermal energy for heating the solution. Audah *et al.* (2011) tested the feasibility of liquid desiccant powered by solar energy to produce fresh water and thermal comfort together for the city of Beirut. Direct solar regenerator is the simplest method of removing water vapor from the liquid desiccant solution. The desiccant solution is directly heated in the solar collector, releasing water vapor from the weak solution. The scavenging air then eliminates the water vapor by absorbing it along the collector plate. Kabeel (2005) experimentally compared the performance of cross forced air flow solar regeneration collector with free convection regenerator. They concluded that performance of free convection solar regenerator is low as compared to cross forced convection regenerator. The direct regeneration method is economical as it eliminates the need of separate regeneration tower; further electric heater can be used after solar collector to increase the system performance. The greatest setback is the heavy dependence of system on weather conditions.

Liquid Desiccant-Based Evaporative Cooling

Evaporative cooling based liquid desiccant system is suitable for comfort applications. The evaporative cooling is simple and passive cooling technology, where cooling is provided through evaporation of water. In this system, liquid desiccant and evaporative cooler are combined together to supply cool and dehumidified air at desired level. These systems offer promising application for achieving thermal comfort especially in hot and humid region. The desiccant system handles the latent load, whereas evaporative cooler facilitates in achieving desired sensible cooling. Energy is mainly consumed to drive the fans, water pump and to regenerate the liquid desiccant. Renewable sources like solar collector, geothermal heat exchanger, biomass etc. can provide the required energy for regeneration purpose. Evaporative cooling systems are classified as direct (swamp) evaporative systems, indirect evaporative systems and regenerative evaporative cooling systems. In the direct evaporative cooling system cooling produced through evaporation of air is directly transferred to the process air, whereas in the indirect system the cooling is

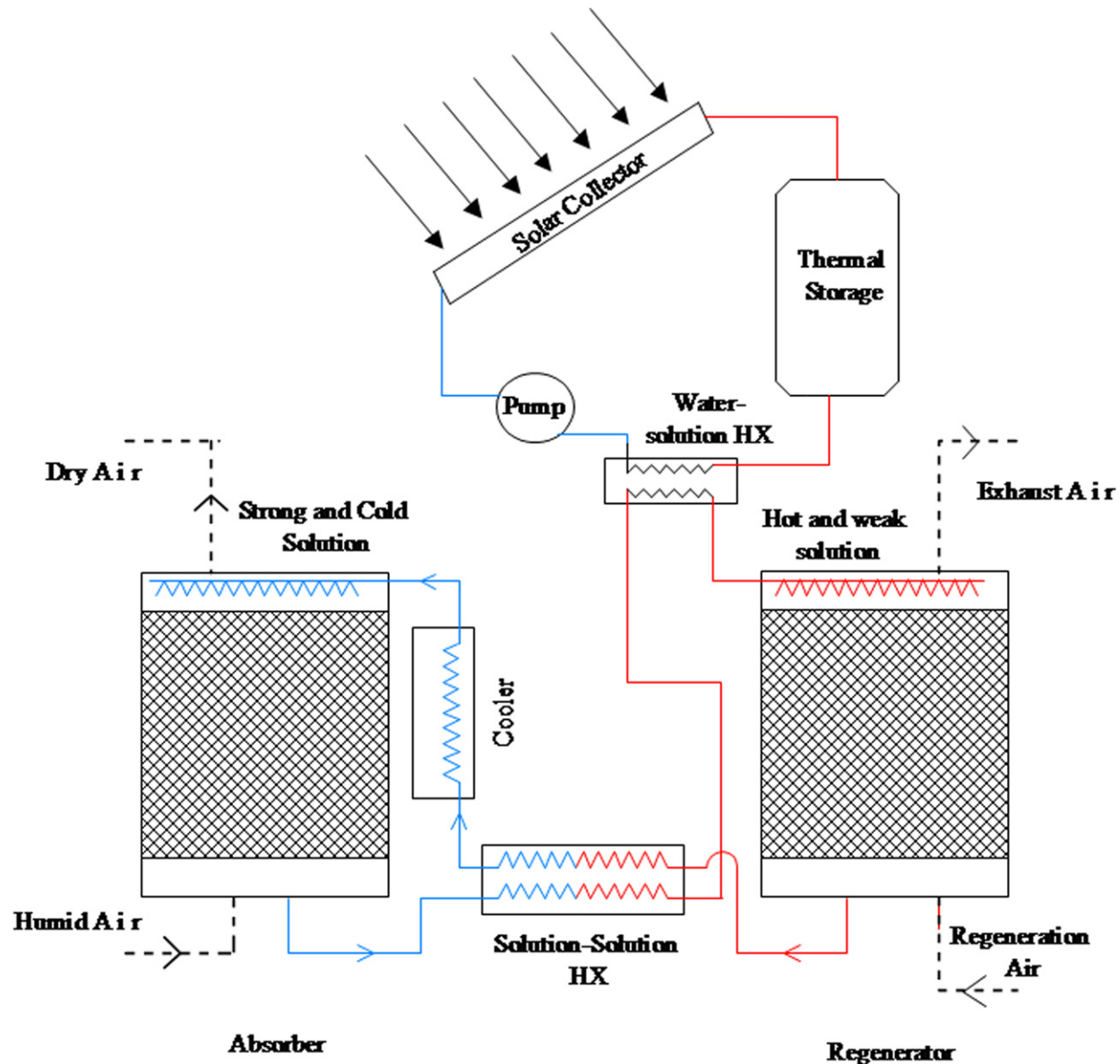


Fig. 18 Solar liquid desiccant system.

transferred to the process air indirectly thus humidity content of process air remains constant unlike direct evaporative cooling system. Regenerative evaporative cooler consists of series of multiple pairs of wet and dry channels separated by a heat transfer medium in a compact heat and mass exchanger. The air in the dry channel is cooled close to its dew point value as water evaporates in the multiple wet channels. [Fig. 19](#) illustrates the typical evaporative cooling coupled liquid desiccant system. The potential combination evaporative cooling principle with desiccant system had been investigated by many researchers ([Jain et al., 1994](#); [Kumar et al., 2009](#); [Buker et al., 2015](#)).

Affordable and Promising-Liquid Desiccant Based Cooling System

Desiccant based evaporative cooling system capable of providing sensible cooling but at the cost of over dried air than required humidity level. Absorber needs to dehumidify the process air than desired levels that lowers the efficiency of overall system. The vapor compression systems are best option to handle the sensible cooling requirement. The combination of vapor compression system and liquid desiccant system is usually known as hybrid liquid desiccant systems. The [Fig. 20](#) shows the working of simple hybrid liquid desiccant system. The sensible cooling of the air can be carried out before of the dehumidification process inside the absorber or after of that utilizing evaporation of refrigerant vapor inside the evaporator of VCS. In the past, integration of liquid desiccant with VCS has been largely studied by [Dai et al. \(2001\)](#), [Mucke et al. \(2016\)](#) and [Su and Zhang \(2017\)](#). The hybrid cycle

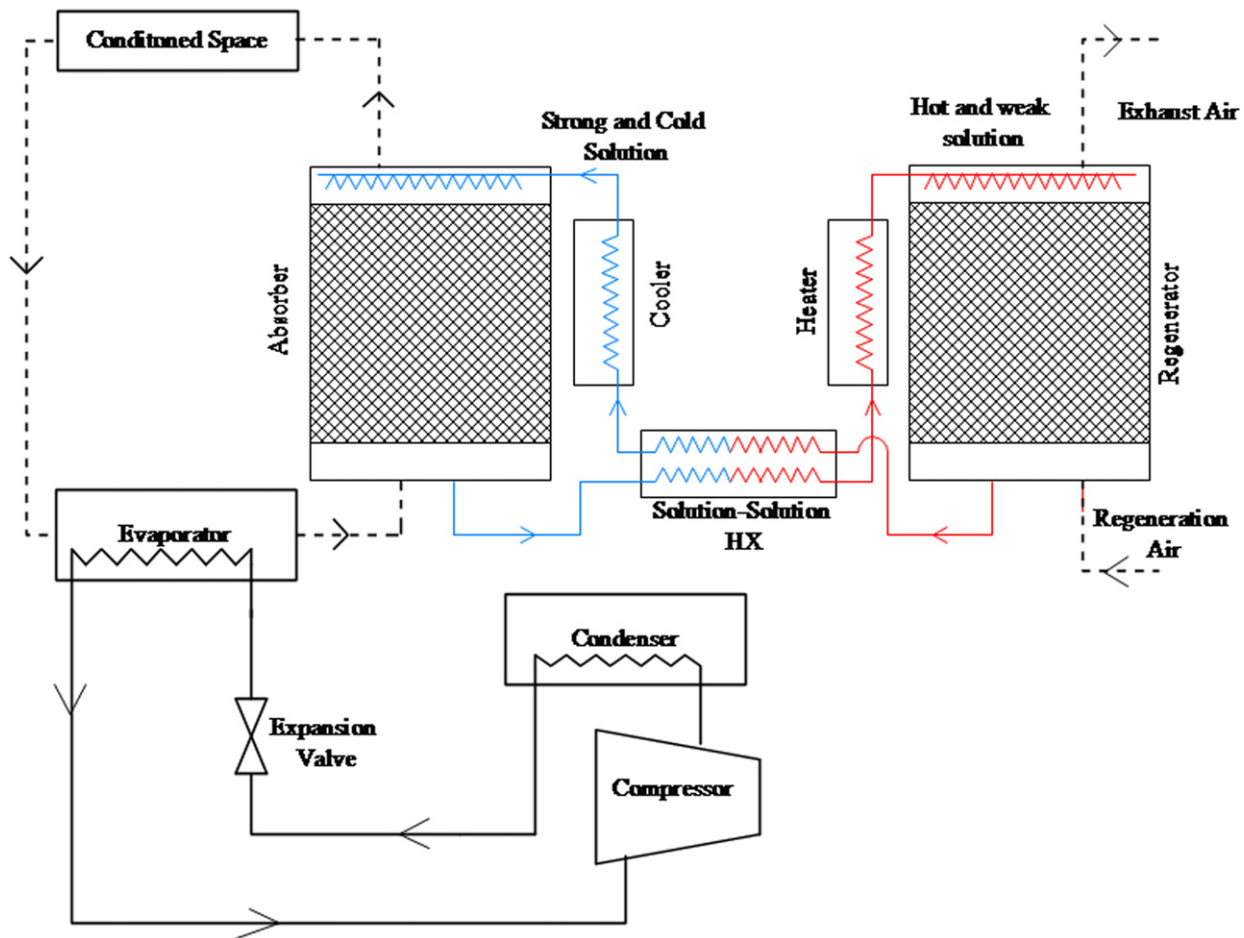


Fig. 20 Hybrid liquid desiccant system.

Solar energy has a promising application in hybrid liquid desiccant system. In the past decade, the notion of solar hybrid liquid desiccant system is getting more and more attention. The use of solar energy is economical as it obliterates the use of auxiliary thermal heater in hybrid liquid desiccant system. The performance of hybrid solar system consisting of conventional vapor compression heat pump and liquid desiccant air conditioning system was analyzed by [Sick et al. \(1988\)](#). Simulation study using TRNSYS was carried out on different operation mode of the hybrid system including regeneration through solar energy. The author concluded that system operated with solar flat plate collectors for regeneration had the lowest operating cost. [Khalid Ahmed et al. \(1997\)](#) simulated open vapor absorption cycle integrated with liquid desiccant with partly close-open solar collector for regenerating the solution. Maximum COP of 1.25 was obtained under hot and humid conditions with this system.

Advantages of HLDAC System

(1) HLDAC system offers more energy saving and enhancement in COP as compared to standalone VCS (2) Moreover, renewable energy like solar and geothermal can be used effectively in HLDAC system (3) The condenser heat eliminates the need of auxiliary thermal heater when it is used for heating the solution (4) Hybrid liquid desiccant air conditioning reduces the power intake by achieving thermal comfort by a smaller VCS (5) This system is economical where humidity and cost of electricity is high.

Other Emerging Technologies

Application of Phase Change Material (PCM) in Air Conditioning

PCMs are group of material which have inherent capability to store and release large amount of thermal energy during phase change. There are varieties of PCMs of different materials (organic, inorganic and eutectic mixture) meant for different applications. The endothermic and exothermic phase change process can be utilized effectively to provide heating and cooling effect. In PCM thermal energy storage approach, during night cold (low temperature) energy is stored by solidifying the PCM and in the next daytime the

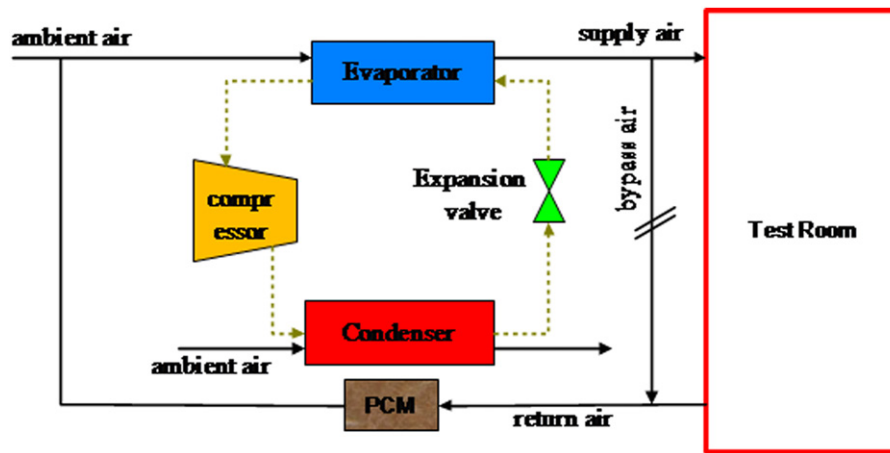


Fig. 21 PCM assisted air conditioning system.

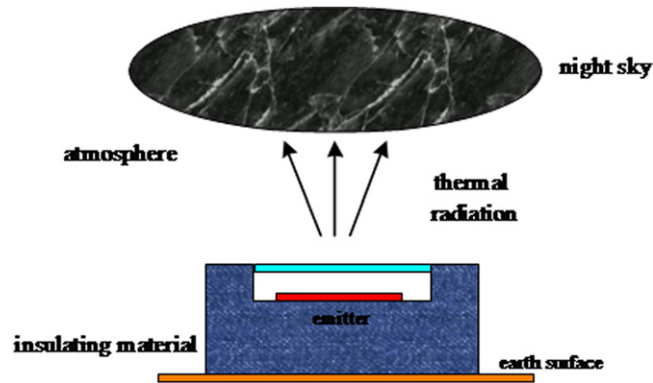


Fig. 22 Radiative cooling system.

stored energy is utilized for cooling purpose. [Fig. 21](#) shows the application of PCM to air conditioning system. Various researches investigated the concept of PCM to improve the cooling efficiencies of air conditioner. [Stritih and Butala \(2010\)](#) demonstrated an experimental study using paraffin to cool air at daytime and to store cold energy at night time. [Said and Hassan \(2019\)](#) experimentally investigated the integration of PCM plates with the condenser of AC unit. The result indicated that the performance of AC unit with PCM plates is superior as compared to AC unit without PCM plates. They reported that power reduction of 11.2% was achieved with PCM plates. Energy and economic analysis of air conditioning with PCM was carried out with by [Chaiyat \(2015\)](#). They concluded that electric consumption of air conditioner could be reduced to 3.09 (kilowatt-hour/day), with a cost saving of 170 USD/y.

Radiative Cooling

With increase in cooling demand; the greenhouse gas emissions accredited to HVAC industry will increase. Especially the cooling demand is expected to increase rapidly overlooking the wide visualized influence of global warming. There exit an amazing opportunity to augment the efficiency of cooling system by 10%–20%, which could have enormous impact on our greenhouse gas emission both today and later this century. The concept of radiative cooling is not new, it had been used centuries ago for production of ice in desert climate. [Fig. 22](#) shows the commonly used radiative cooling technology. All matter on earth emits thermal radiation, a part of which is absorbed by the earth atmosphere and the rest is reflected back. At certain wavelength in particular between eight to thirteen microns; the earth atmosphere acts as transparent window. Through this window, body is cooled by emitting heat in the outer cold space which is considered as infinite thermal reservoir at atmospheric temperature. For instances, frost and dew drops in morning are direct consequences of radiative cooling. Radiative cooling is a free and passive cooling technology to dissipate heat to the outer cold space which is a natural heat sink. Nighttime radiative cooling been widely investigated since 1918 with both organic and inorganic materials of different infrared-emissivity. Recently, [Zhao et al. \(2017\)](#) proposed a combined photovoltaic-radiative cooling system for buildings that can produce electricity during daytime through photovoltaic conversion and provide cooling effect in night via radiative cooling. [Hu et al. \(2018\)](#) designed a practical scale hybrid

system consisting of photovoltaic-photothermal-radiative cooling collector. The integrated system was capable of providing heat and electricity during day time and cooling energy at nighttime. The overall cooling energy obtained at typical clear night was 2.90 MJ with electrical/thermal efficiency in the range of 40.4% and 56.9%. Daytime radiative cooling has not been investigated widely because of Sun's heating. In the year 2014, Raman *et al.* (2014) designed a rooftop nanophotonic radiative cooler. The difference between the atmospheric temperature and nanophotonic cooler was 5°C right at the peak sunlight of 900 W/m². The authors designed a novel nano structure that reflected almost all the daytime sunlight while emitting maximum radiation in the range of 8–13 µm. The potential application of radiative cooling technology is promising for improving the energy efficiency of existing systems.

Conclusion

The chapter gives a brief description of renewable energy application in air conditioning system with few references to the current and past study. It is urgent need to increase the use of renewable energy in all sorts of air conditioning systems (both conventional and non-conventional). The main motivation of using renewable energy technologies is to cut down greenhouse gas emission and emission of other harmful refrigerant in to our environment. Many research findings have indicated that the combination of solar and geothermal energy decreases the energy intake and size of the geothermal heat exchanger. The solar assisted heat pumps have a promising future as it alleviates the energy load on heat pumps. The low-grade energy from the solar collector provides an effective source to match the heating load of the regenerator in liquid desiccant system. The solar assisted hybrid desiccant system has a much wider scope to provide comfortable indoor air quality at optimum energy requirements. Emerging technologies such as passive radiative cooling and phase change material are promising for achieving thermal comfort. Sustainable uses of renewable energy will not only curb down the CO₂ emissions but will also safeguard the high-grade source energy for future need. The use of renewable energy is very much essential for developed and developing country to sustain their energy demands.

See also: Application of Nanofluids for Radiator Cooling

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Toward Reclamation of Fibrous Waste Stream Materials

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Introduction

Indirect materials (those not in final product, *i.e.*, waste) may have properties to function as direct materials for other applications. Companies pay millions to produce a more efficient method of production by minimizing cost and waste. Decreasing waste and minimizing cost has numerous benefits like increased savings for consumer/producer as well as environmental benefits. Fibrous materials are sent to landfills, taking up space and leading to potential hazards, particularly in residential areas (Al-Yaqout and Hamoda, 2002). Problems with waste sites arise many years after they have been filled, covered, and built upon (Emberton and Parker, 1987). Much of the United States' waste is transported across oceans to third world countries where land costs less and the people living nearby have little to no ability to voice their opinion based on education, income, or social standing.

Researchers have been investigating numerous waste products to replace high cost insulation. Thousands of different waste materials have unknown insulating properties that go silently into landfills. One research project measures thermal properties of bio-based waste from Tetra Pak® panels and wool fibers (Hassanin *et al.*, 2018). Increased testing of waste product can lead to numerous benefits.

A simple test of insulating properties is to subject the material to a heat source and measure the temperature gradient as a function of time (Sparavigna, 2012). This method was developed for conducting materials. The R -value can be determined from

$$R = \frac{\Delta T}{\Phi_q} \quad (1)$$

$$\Delta T = R\Phi_q = -\kappa R|\vec{\nabla} T| \quad (2)$$

$$\kappa = \alpha\rho c_p \quad (3)$$

$$\Delta T = R\Phi_q = -\alpha\rho c_p R|\vec{\nabla} T| \quad (4)$$

$$\frac{1}{R} = -\frac{\alpha\rho c_p}{\Delta T}|\vec{\nabla} T| \quad (5)$$

$$\frac{1}{R} = -\frac{\alpha\rho c_p}{\Delta T} \sqrt{\left(\frac{\partial T}{\partial x}\right)^2 + \left(\frac{\partial T}{\partial y}\right)^2 + \left(\frac{\partial T}{\partial z}\right)^2} \quad (6)$$

The ΔT is the difference between the temperatures across the insulating barrier, α is the thermal diffusivity, ρc_p is the volumetric heat capacity and ∇T is the temperature gradient across the thermal barrier. The thermal diffusivity α can be measured experimentally using the heat equation

$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T \quad (7)$$

$$\frac{\partial T}{\partial t} = \alpha \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) \quad (8)$$

which then reduces to

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial z^2} \quad (9)$$

for tall, narrow sample shapes where the x and y dimensions are small compared to the z dimension. This means that the R -value can also experimentally reduce to

$$\frac{1}{R} = \pm \frac{\alpha\rho c_p}{\Delta T} \left(\frac{\partial T}{\partial z} \right) \quad (10)$$

for the same reasons.

The theoretical temperature field provides a usable value for $\frac{\partial T}{\partial z}$ from Eq. (10). Based upon a solution to the heat equation of the form

$$T(z, t) = T_0 \sin(\omega z) e^{-\alpha\omega^2 t} \quad (11)$$

where T_0 is the initial temperature of the sample. Then the heat Eq. (9) becomes

$$\frac{\partial^2 T}{\partial z^2} = \frac{1}{\alpha} \frac{\partial T}{\partial t} = \frac{T_0}{\alpha} \sin(\omega z) (-\alpha\omega^2) e^{-\alpha\omega^2 t}$$

and

$$\begin{aligned}
 \frac{\partial T}{\partial z} &= \frac{1}{\alpha} \int \frac{\partial T}{\partial t} dz \\
 &= \frac{1}{\alpha} \int T_0 \sin(\omega z) (-\alpha \omega^2) e^{-\alpha \omega^2 t} dz \\
 &= -\omega^2 T_0 e^{-\alpha \omega^2 t} \int_0^L \sin(\omega z) dz \\
 &= \omega^2 T_0 e^{-\alpha \omega^2 t} \cos(\omega z) \Big|_0^L \\
 &= \omega^2 T_0 e^{-\alpha \omega^2 t} [\cos(\omega L) - 1]
 \end{aligned}$$

where L is the height in the z -dimension of the sample. The boundary conditions on the sample chamber ($\frac{\partial T}{\partial t} = 0$) provide values for ω .

$$\omega L = (2n + 1) \frac{\pi}{2} \quad (12)$$

Take $n = 0$ so that $\omega = \frac{\pi}{2L}$ and use the steady state limit so that

$$\frac{\partial T}{\partial z} = -\frac{\pi^2 T_0}{4L^2} \quad (13)$$

Finally,

$$\frac{1}{R} = \mp \alpha \frac{\pi^2}{4} \frac{\rho c_p}{L^2} \frac{T_0}{\Delta T} \quad (14)$$

Now, find ΔT from

$$\frac{\partial T}{\partial z} = \omega^2 T_0 e^{-\alpha \omega^2 t} \cos(\omega z)$$

where

$$\begin{aligned}
 T(z, t) &= \omega^2 T_0 e^{-\alpha \omega^2 t} \int \cos(\omega z) dz \\
 &= \omega^2 T_0 e^{-\alpha \omega^2 t} \sin(\omega z)
 \end{aligned}$$

In the steady state,

$$T(z, t) = \omega^2 T_0 \sin(\omega z)$$

Using the same values for ω as in Eq. (12) and evaluating $\Delta T = T(L, t) - T(0, t)$ gives

$$\Delta T = \omega^2 T_0 \sin(\omega z) \quad (15)$$

$$= \frac{\pi^2 T_0}{4 L^2} \quad (16)$$

Now, Eq. (14) becomes

$$\frac{1}{R} = \alpha \rho c_p \quad (17)$$

consistent with the definition of the R value for insulation.

Eq. (17) now provides a basis for the procedures used to establish the thermal properties of waste stream materials. They are:

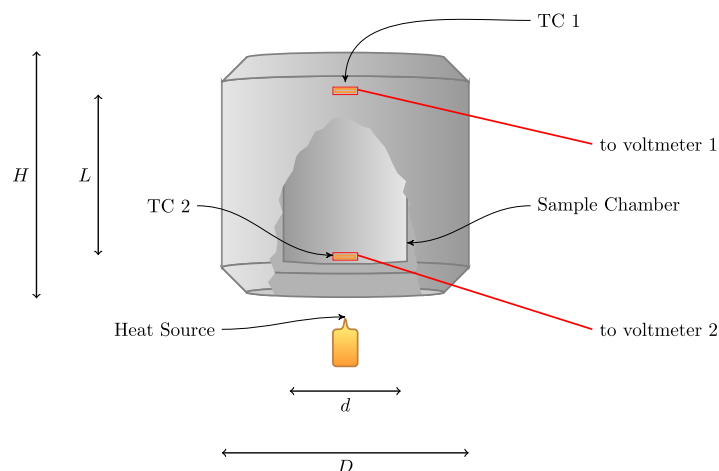
- (1) Determine the thermal diffusivity (α) from experimental measurements of the sample temperatures as a function of time, according to Sparavigna (2012).
- (2) Compute the volumetric heat capacity (ρc_p) from experimental measurements of sample mass, volume, and an estimate of its specific heat capacity.
 - (a) The specific heat capacity (c_p) can be estimated at 1200 J Kg⁻¹ K⁻¹ from the values for wood and air (Table 1).
 - (b) The volumetric heat capacity (ρc_p) is then either

$$\rho c_p \approx \begin{cases} 31,200 \\ 58,800 \end{cases} \quad (18)$$

for 8 g and 15 g samples, respectively, in units of (J m⁻³ K⁻¹).

Table 1 Specific heat capacities (c_p) in common building materials

Substance	Phase	$c_p \left(\frac{\text{J}}{\text{kg}\cdot\text{K}} \right)$
Gypsum	Solid	1090
Asphalt	Solid	920
Pyrex	Solid	753
Soil	Solid	800
Wood	Solid	1200–2900
Air	Gas	1000

**Fig. 1** Schematic of apparatus used to characterize thermal properties of indirect materials. $L = 8$ cm is the same variable used starting with Eq. (12). $H = 12.5$ cm, $d = 7$ cm and $D = 10$ cm. The container portion of the apparatus had a mass of 164 g.

Methods

There are multiple methods for testing the thermal insulation properties of materials (Sparavigna, 2012; Sparavigna *et al.*, 1992). A straight-forward measurement is an apparatus consisting of thermocouples, voltmeters and an insulating sample chamber (Fig. 2). The samples for this article were donated by a large fibrous material manufacturer. Five different material types were used (deemed “a” through “e”). Each had a different ratio of typical fibrous material components: cotton, polyester, rayon, tencel, viscose, polyethylene terephthalate, *etc.* The specific composition and weave of the materials is proprietary (Fig. 1).

The thermal diffusivity of paper-like material samples can be measured experimentally to estimate the R -value of the material. The sample chamber in the apparatus is made up of two separated metal containers (Fig. 2). One thermocouple (TC 1) is placed at the top. Another thermocouple (TC 2) can be mounted at the entrance of the chamber, at the bottom in the figure. TC 2 measures the temperature near the heat source while TC 1 measures the temperature on the other side of the sample material.

The thermocouple sensors create measurable voltages proportional to the temperature at the site of the thermocouple. The sensing principle of the thermocouple relies upon what is sometimes called the Peltier-Seebeck effect and is schematically depicted in Fig. 2. Small temperature variations across a thermoelectric material result in a measurable voltage difference across the device. The voltages generated by the thermocouple sensors can then be recorded at regular time intervals to experimentally determine R -values of indirect wastestream materials.

The samples were parsed into bundles of either 15 g or 8 g loosely-packed, as-donated material. They were placed as evenly as possible into the sample chamber.

While heating the samples continuously, the thermocouple measurements were recorded at sixty second intervals. The samples were heated until the temperatures stabilized.

Results

All materials provided significantly better insulation than air alone. Thermocouple sensors read between 2.0 and 8.0 relative temperature units with just air in the sample chamber. All materials tested had relative temperature units much lower than that,

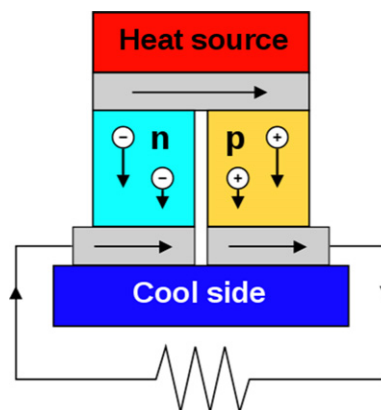


Fig. 2 A thermoelectric circuit composed of materials of different Seebeck coefficients (p-doped and n-doped semiconductors), configured as a thermoelectric generator. If the load resistor at the bottom is replaced with a voltmeter, the circuit then functions as a temperature-sensing thermocouple.

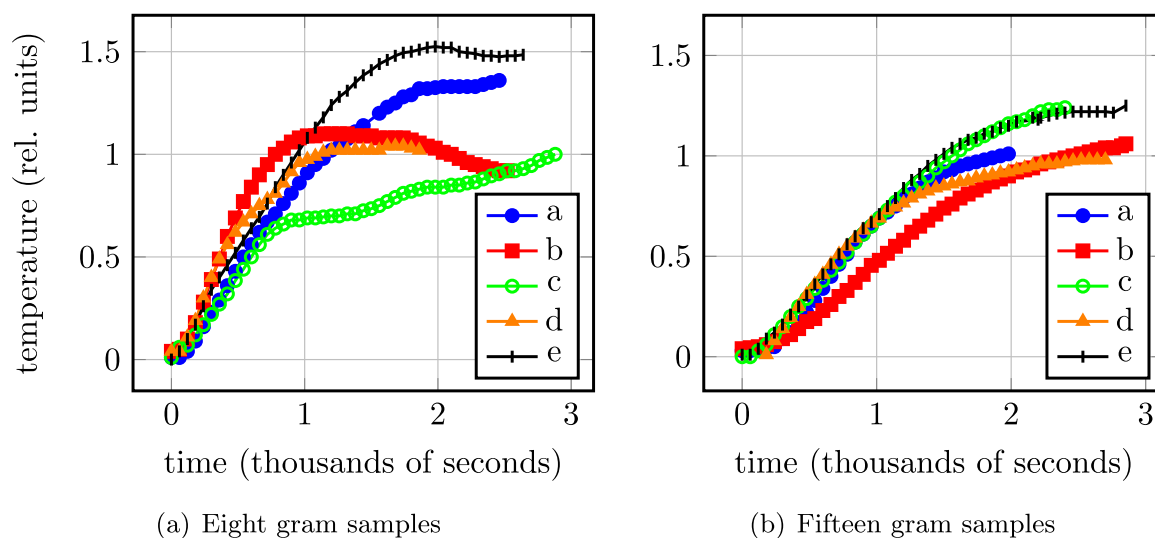


Fig. 3 Comparison of samples with temperatures measured at the chamber's top at TC 1. The other thermocouple, TC 2, consistently registered between 2.0 and 8.0 relative units. Five different material types (a–e) were tested in both 8 g and 15 g sample masses.

indicating they prevented the sample chamber temperature from rising to the air sample control temperature. The curves shown in the graphs indicate that the heat source would increase the temperature at the top of the sample chamber over time. After the heat source was removed, the temperatures began to drop again to room temperature (Fig. 3).

TC 2 results showed a consistent temperature of approximately the control sample temperature profile (heated room air). This remained between 2.0 and 8.0 relative units during measurements. The largest variation in insulating properties resulted from the amount of material tested. This indicates that more data would be helpful with larger amounts of material bundles. It raises the question, of whether the main benefit of the fibrous material is to block thermal convection and mixing. Another question is raised about the space-filling properties of the fibrous material and how that would impact the insulating properties.

Computation of the thermal diffusivity followed (Sparavigna, 2012). A minimization curve allowed determination of the value at approximately $4.5 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$. This is comparable with fibrous material. For reference, yellow pine wood has a diffusivity of $8.2 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ and air a value of $1.9 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ (Fig. 4).

Discussion

The data suggests that the amount of material used is extremely important and suggests that each material has a maximum performance density. Testing lateral heat flow (conductive) in addition to the upward (convective) heat flow tests would be

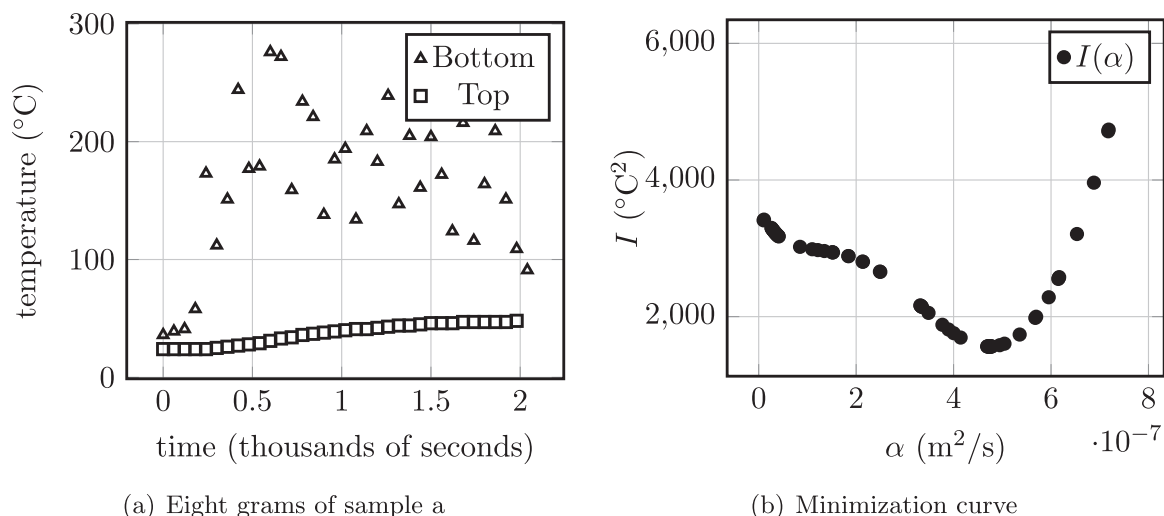


Fig. 4 Sample “a” heated for about an hour. A minimization curve ($I(\alpha)$) allowed determination of the value of the thermal diffusivity of $\approx 4.5 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$. For reference, yellow pine wood has a diffusivity of $8.2 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ and air a value of $1.9 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$.

interesting. The sample materials should also be tested for flammability to give an indication of safety measures that would need to be considered in the event that the materials may become wall insulation.

The determination of the R value for one of the samples is a proof of concept; fibrous waste stream materials can be characterized according to their thermal insulative properties with relatively inexpensive equipment and in a reasonable amount of time. This method could be deployed “in the field” by automating the computation for faster analysis.

Conclusion

The “ R ” value for this waste stream material was determined to be $\approx 72 \text{ m}^2 \text{ K W}^{-1}$ or roughly R-10. This is typical for standard insulation materials such as silica aerogels and standard construction insulation panels. The experiment is an example of how research can lead to alternate uses of waste stream materials. The results show that waste stream materials have valuable properties that can be utilized in re-manufacturing.

Acknowledgments

The experimental data collection for this paper was done by Mr. Devon Manuele, an undergraduate majoring in Applied Science at the University of Wisconsin – Stout. Dr. Todd A. Zimmerman helped compute the minimization function values with a Python script. UW-Stout's Department of Chemistry and Physics provided the infrastructure and lab equipment. The samples were donated *via* UW-Stout's Discovery Center.

See also: Development of Self-Adhesive Products Using Only Bamboo Fibers Extracted With a Machining Center

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Utilization of Bio-Hydrogen in HCCI Engines as a Most Renewable Fuel for Sustainable Transportation – A Thermodynamic Analysis

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Nomenclature

$\dot{Q}$ Rate of heat transfer (kW)

$\dot{I}$ Rate of lost available work (kW)

$\bar{R}$ Universal gas constant (kJ/kmol-K)

$\dot{m}$ Mass flow rate (kg/s)

C_p Specific heat at constant pressure (kJ/kg-K)

E Exergy, Energy (kJ)

e Specific exergy of fuel (kJ/kg)

g Acceleration due to gravity (m/s²)

H Hydrogen

h Specific enthalpy (kJ/kg)

LHV Lower heating value (kJ/kg)

N Nitrogen

n Polytropic index (dimensionless)

O Oxygen

p Pressure (bar)

S Entropy (kJ/K)

s Specific entropy (kJ/kg-K)

T Temperature (K)

t Time (s)

v Specific volume (m³/kg)

V Velocity (m/s)

W.D. Work done (kJ)

y_i Mole fraction of a species 'i'

z Elevation (m)

Greek Letters

η Efficiency (%)

ϕ Ratio between the actual air flow rate and the theoretical flow rate

γ Ratio of specific heats (C_p/C_v)

$\alpha, \beta, \gamma, \delta, \epsilon$ Constants

Subscripts

α Air

0 Ambient conditions

BT Brake thermal

cv Control volume

Cw Cooling water

ex Exergy

FM Fuel air mixer

gen Generation

Hw Hot water

i Inlet, species of the mixture

Mix Mixture

Introduction

Climate change and energy security concern increases the demand improving the internal combustion engine efficiency and emissions which may be met through the use of alternative fuels and clean combustion process. One of such alternatives is to use bio-hydrogen as an energy carrier and to extract energy using a modified internal combustion engines on account of its renewability, clean burning characteristics, high calorific value etc., (Verhelst and Wallner, 2009). It is also shown that compared to hydrocarbon fuels, hydrogen has very high flame speed and higher exergetic efficiency of combustion indicating greater effectiveness of transformation of the chemical exergy of the fuel into useful work (Rakopolous *et al.*, 2008). Due to its carbon free nature and high flame hydrogen combustion produces almost zero emissions of oxides of carbon and unburned hydrocarbon but produces considerably higher emissions of NO_x than gasoline fueled engine due to high adiabatic flame temperature (Ji and Wang, 2009). Many researchers have investigated the thermodynamic and emissions level performance of hydrogen fueled engines. Kahraman *et al.* (2007) carried out some investigations which show that thermal efficiency of the hydrogen engine was higher than that of a gasoline engine. Al-Baghdadi (2004) found that increased compression ratio is beneficial for enhancing the power output and thermal efficiency of the hydrogen engine. However, due to the engine operation in spark ignition mode NO_x emissions rose to higher level. Ganesh *et al.* (2008) claimed that thermal efficiency of the hydrogen engine was about 2% higher than that of the gasoline engine. A study conducted by Ji and Wang (2013) show that fuel energy flow rate was reduced with the increase of excess air ratio for the pure hydrogen fueled engine at idle and lean conditions.

These studies clearly show that use of pure hydrogen in SI engines only reduces the emissions of oxides of carbon and unburned hydrocarbons (UHC). The non-trivial exhaust gas emissions of nitrogen oxides and the particulate matter (PM) remain formed during combustion. Therefore in order to reduce the NO_x and PM along with the oxides of carbon and UHC, a modified combustion strategy is needed to utilize hydrogen in engines in a most eco-friendly manner. In this context, homogeneous charge compression ignition (HCCI) engine has been emerged due to its potential to reduce engine NO_x and

PM whilst still maintaining a higher thermal efficiency (Antunes *et al.*, 2008; Khaliq *et al.*, 2011). Therefore, pure hydrogen fueled internal combustion engine in HCCI mode is found to be one of the possible alternative for achieving zero – emission engine operation while maintaining higher efficiency and hence it could be a promising technology for sustainable surface transportation.

The purpose of the current study is to conduct a thermodynamic analysis of the pure hydrogen fueled internal combustion engine in HCCI mode using simultaneously the first and second law of thermodynamics. The latter through the concept of exergy, quantifies exergy losses and hence identifies the thermodynamic imperfections due to which a deviation is observed between the ideal and observed performance of engines. Results obtained through current research is a big source of data for the engine manufacturers to design an efficient and reduced emissions engine for transportation.

Engine Cycle Description

To facilitate the first and second law analyzes of a pure hydrogen fueled HCCI engine, its schematic diagram is shown in Fig. 1.

The ambient air enters the compressor which delivers air at high pressure and temperature followed by the heat exchanger which uses water as a cooling medium, reduces the compressed air temperature to the desired level (93°C). Next hydrogen which is stored at a high pressure of 200 bar in the cylinder is injected into the fuel vaporizer at a pressure of 6 bar and at an ambient temperature of 20°C. The pressure of hydrogen is reduced from 200 bar to 6 bar through a pressure reduction valve. The hydrogen at a pressure of 6 bar and temperature of 20°C mixes with the compressed air which enters fuel vaporizer at 93°C. The mixing process in the fuel vaporizer produced a homogeneous mixture of hydrogen and air, which then enters HCCI engine. An engine compression ratio of 17:1 is assumed to ensure auto-ignition of the hydrogen air charge where a chemical reaction in the freshly burned zone occurs under constant volume conditions, resulting in a pressure rise in the combustion products which are in a state of chemical equilibrium. The freshly burned products expand to equilibrate the cylinder pressure and hence develop power, and thereafter mix with the previously burned gases to form a homogeneous charge.

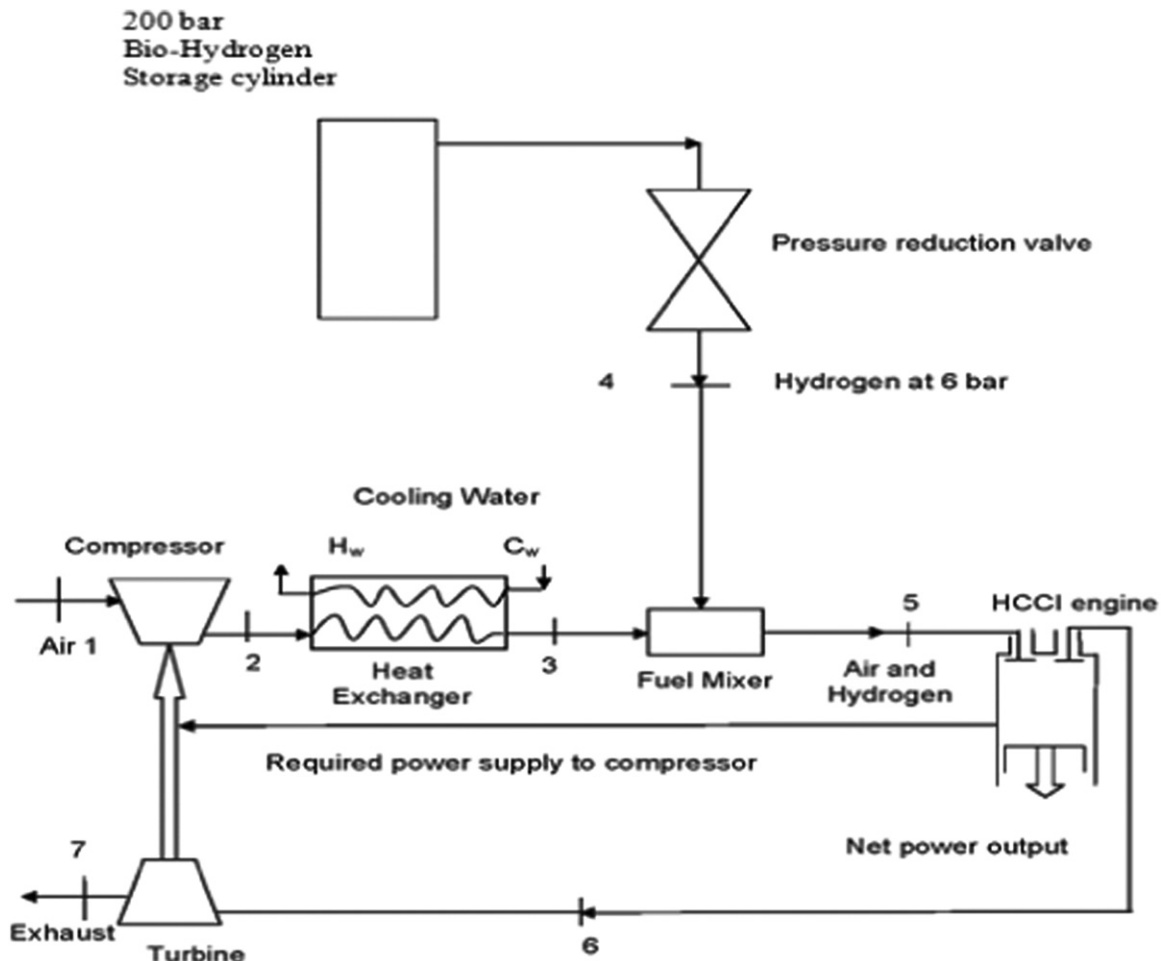


Fig. 1 Schematic diagram of a Bio-hydrogen-fueled HCCI engine.

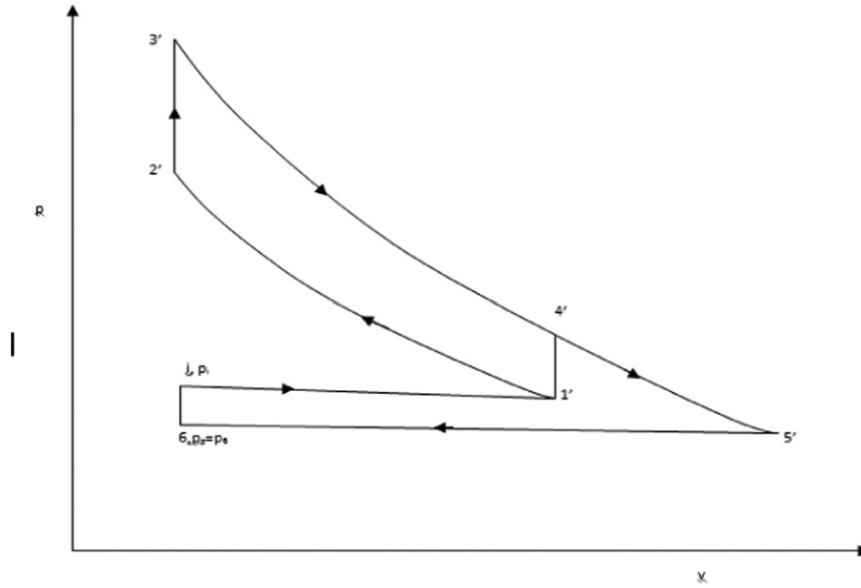


Fig. 2 p-v representation of HCCI engine combustion.

The cylinder exhaust gases enter the turbine to generate power for the turbocharger. The power consumed by turbocharger compressor is more than the power developed by the turbine, therefore some power is extracted from the engine cylinder to meet out the power requirement of turbocharger.

The following assumptions are made for the proposed analysis of a pure hydrogen fueled HCCI engine (Antunes *et al.*, 2008).

- The HCCI combustion process is represented by a time dependent, variable volume well mixed reactor.
- The overall burn rates of HCCI combustion are typically fast and if correctly phased in the cycle could approximate ideal Otto cycle. Fig. 2 illustrates the PV diagram of an ideal HCCI operating condition.
- Fuel and air are premixed in the fuel vaporizer prior to entering the engine combustion chamber.
- The volumetric efficiency of the engine is 100% meaning the volume of air and fuel inducted into the engine cylinder is equal to the displacement of the cylinder.
- Thermal losses in ducts are negligible.
- Pressure drop in heat exchanger and duct is negligible.
- Turbocharger mechanical losses are neglected.
- Engine is assumed to operate at a constant speed of 2200 rpm and non-varying load.
- The residual gas fraction is considered as ($f = 0.03$), its value is not much effected at high compression ratio as assumed in the present analysis.

The engine details are given in Table 1.

Energy and Exergy Analyzes

For the transient operation of a HCCI engine configuration (engine cylinder, exhaust manifold, turbocharger etc.) experiencing mass exchange with the surroundings, the following equations holds for the energy and entropy balance of the component or system

$$\frac{dE_{cv}}{dt} = \dot{Q}_{cv} - \dot{W}_{cv} + \sum_i \dot{m}_i \left(h_i + \frac{V_i^2}{2} + gz_i \right) - \sum_e \dot{m}_e \left(h_e + \frac{V_e^2}{2} + gz_e \right) \quad (1)$$

The fundamental equation for combustion of hydrogen-air mixture in the HCCI engine may be written as

$$\frac{dS_{cv}}{dt} = \sum_i \frac{\dot{Q}_i}{T_i} + \sum_i \dot{m}_i s_i - \sum_e \dot{m}_e s_e + \dot{S}_{gen} \quad (2)$$

where, ϕ is greater-than-one number representing the ratio between the actual air flow rate and the theoretical flow rate.

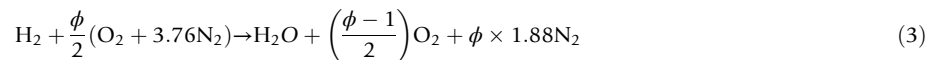


Table 1 HCCI engine specifications

Displacement	1.9 L
Compression ratio	17:1
Bore	100 mm
Stroke	105 mm
Engine speed	2200 rpm
Ratio between actual and theoretical air (ϕ)	ϕ is greater than 1 number
Type of loading	Non varying load
Fuel	Hydrogen
Nature of combustion in HCCI engine	Bulk autoignition process controlled by chemical kinetics
Intake air cooling by water	Necessary to bring air at 93°C before fuel-air mixer
Mass flow rate of hydrogen	1.5×10^{-4} kg/s
Hydrogen injection pressure and temperature	6 bar and 20°C
Air inlet temperature	93°C
Cooling water inlet and exit temperatures	25°C and 35°C

Source: Khaliq, A., Trivedi, S.K., Dincer, I., 2011. Investigation of a wet ethanol operated HCCI engine based on first and second law analyses. Applied Thermal Engineering 31, 1621–1629. Antunes, J.M.G., Mikalsen, R., Roskilly, A.P., 2008. An investigation of hydrogen fuelled HCCI engine performance and operation. International Journal of Hydrogen Energy 33, 5823–5828.

Assuming, that, the system under consideration (fuel – air mixture) is an ideal gas, consisting of species that behave individually as ideal gases, the absolute entropy of the species ‘i’ at a given temperature and pressure (T, p) is given by Djermouni and Oudha (2014).

$$\bar{s}_i(T, p) = \bar{s}_i^0(p_o, T_o) + \int_{T_o}^T \frac{\bar{C}_{p_i}(T)}{T} dT - \bar{R} \ln \left(\frac{y_i p}{p_o} \right) \quad (4)$$

The superscript 0 and subscript 0 denotes the properties of species i, at ambient pressure and ambient temperature. The absolute entropy of a mixture at a given (T, P) is given by

$$\bar{s}_{mix}(T, p) = \sum_{i=1}^{i=n} y_i \bar{s}_i(T, p) \quad (5)$$

where, $\bar{s}_i(T_o, p_o)$ is the absolute entropy of a species i in kJ/kmol-K at an ambient pressure and temperature (restricted dead state), $\bar{C}_{p_i}$ is the specific heat of a species ‘i’ at a given temperature ‘T’ in kJ/kmol-K, $\bar{R}$ is the universal gas constant in kJ/kmol-K, y_i is the mole fraction of species i in the mixture and p is the absolute pressure of mixture and T is its temperature in K.

The specific heat of a particular species in the mixture $\bar{C}_{p_i}(T)$ at a given temperature is calculated by the relation

$$\frac{\bar{C}_{p_i}(T)}{\bar{R}} = \alpha + \beta T + \gamma T^2 + \delta T^3 + \epsilon T^4 \quad (6)$$

The values of constants, α , β , γ , δ and ϵ for a given species, are directly obtained from Rakopolous *et al.* (2008).

The absolute entropy of a mixture (fluid stream) at a given state is calculated after using Eqs. (3) and (4), and then the generation of entropy in any process of the engine cycle is evaluated after using Eq. (2).

The rate of lost available work $\dot{I}$ in a process is characterized by entropy generation $\dot{S}_{gen}$ in the process. For continuous process performed by a system, it can be written as

$$\dot{I} = T_o \dot{S}_{gen} \quad (7)$$

where $\dot{I}$ is the rate of lost available work during the process.

Performance Parameters

The overall performance of hydrogen fueled HCCI engine can be estimated based on first and second laws of thermodynamics.

Energy Efficiency (η)

The first law (energy) efficiency is the fuel utilization efficiency which is defined as ratio of specific brake thermal power output to the specific energy input and is given by

$$\eta_I = \frac{\dot{W}_{BT}}{\dot{m}_f LHV} \quad (8)$$

where LHV is its lower heating value of fuel in kJ/kg and WBT is the brake thermal power which may be evaluated as.....

$$\dot{W}_{BT} = 0.8W \cdot D.$$

where

$$\dot{W} \cdot D = \dot{m} \left[\frac{(p'_3 v'_3 - p'_4 v'_4)}{n-1} - \frac{(p'_2 v'_2 - p'_1 v'_1)}{n-1} \right]$$

Exergy Efficiency (η_{II})

The second law (exergy) efficiency is a more accurate measure of thermodynamic performance of the engine and is defined as the ratio of amount of exergy supplied in the product to the amount of exergy associated with the fuel. By definition, it is then given by the following expression (Nieminen and Dincer, 2010)

$$\eta_{II} = \frac{W_{BT}}{E_{fuel,in}} \quad (9)$$

where, $E_{fuel,in}$ is exergy of fuel in kJ/kg.

Results and Discussion

The effect of variation of excess air ratio and the effect of change in ambient temperature have been observed on the energy efficiency and exergy efficiency of the hydrogen fueled HCCI engine.

Effect of Excess Air

Fig. 3 shows the effect of variation of excess air in a fuel-air mixture on the energy and exergy efficiency of hydrogen fueled HCCI engine. It is observed that the energy efficiency based on first – law performance is initially increasing with the increase in excess air. This is due to the fact that lower value of excess air results in the increase of the temperature of air at the cylinder inlet which reduces the engine power output and hence results in a lower value of its energy efficiency. As the excess air increases temperature of the inlet air at the cylinder decreases which increases the engine power output and hence its efficiency. It is observed that further increase in excess air results in the decrease of energy efficiency. This is due to the reason higher excess air, increases its much lean burn operation characteristics which results in lowering the combustion temperature or mean temperature of heat addition and hence results in lowering the energy efficiency of the engine. It is found that between the excess air of 20% and 40% respectively, the energy efficiency ranged from 42% to 40% and a maximum efficiency of 45% is observed at the excess air of 25%. The higher value of energy efficiency even for lean operation of engine is obtained due to its high compression ratio (17:1) which is permitted in HCCI mode not in SI mode.

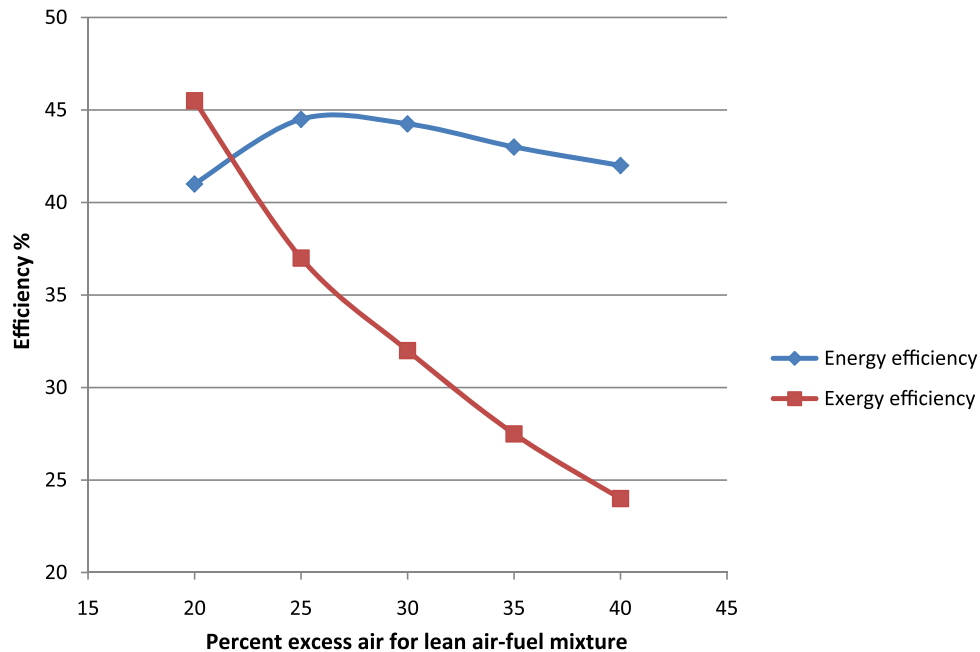


Fig. 3 Effect of variation of percent excess air on hydrogen operated HCCI engine efficiencies.

The variation of exergy efficiency of the HCCI engine with the increase in excess air is also shown in Fig. 3. A significant reduction in exergy efficiency is observed at the lower values of excess air and it becomes gradual at higher values of excess air. This is due to the reason that chemical exergy losses are high at lower values of excess air due to the presence of combustible product species, which results in the significant reduction of the exergy efficiency of the engine. As the excess air in the fuel-air mixture increases the combustion temperature decreases which results in the higher combustion irreversibility and lower exergy loss due to heat transfer between the combustion zone and the cylinder wall. The increase in exergy destruction during combustion dominates over the reduction of exergy loss via heat transfer. Therefore, a gradual reduction in the exergy efficiency is observed at a higher percent of excess air. A wide range of exergy efficiency of 25%–45% is obtained between the excess air of 20% and 40%, respectively.

Effect of Ambient Temperature

There have been prior attempts for evaluating the effect of ambient temperature on the energy and exergy efficiency of an alternate fueled HCCI engine. A recent analytical investigation by Khaliq *et al.* (2011) on wet ethanol fueled HCCI engine is a significant effort in this area.

In the present study, the effect of ambient temperature on energy and exergy efficiency of hydrogen fueled HCCI engine is shown in Fig. 4. It is found that energy efficiency decreases with the increase in ambient temperature while the exergy efficiency increases with the same. The reason for this kind of trends obtained may be noted as; increase in ambient temperature increases the fuel-air mixture intake temperature which results in reduced power output due to a reduction in volumetric efficiency and hence the lower energy efficiency of the engine. Another reason for this kind of trend is, hydrogen has high energy content in the reactant system (represented by the product of the fuel moles and the heating value) and consequently loses more heat from combustion zone to cylinder wall which further reduces the energy efficiency. Therefore, the decrease in energy efficiency with the increase in ambient temperature is the combined effect of increase in fuel-air intake temperature and type of fuel (hydrogen) used for the analysis.

The reason for increase in exergy efficiency with the increase in ambient temperature may be highlighted as; first increase in ambient temperature results in a decrease of excess air ratio in a fuel-air mixture which results in the higher combustion temperature and hence the lower combustion irreversibility. Second, the fuel used hydrogen has the simplest (lighter) molecular structure which results in a lower entropy generation during combustion due to the formation of chemically complicated molecule from the less chemically structured molecule. Therefore, an increase in exergy efficiency of hydrogen fueled HCCI engine with the increase in ambient temperature shown in Fig. 4 is the combined effect of above two discussed reasons. The exergy efficiency in the range of 32%–36% is obtained between the ambient temperature of 13°C and 41°C respectively while the energy efficiency is obtained in the range of 48%–44% between the same range of ambient temperatures.

Fig. 5 shows the percentage of fuel (hydrogen) exergy destroyed during various processes of the HCCI engine at mean operating conditions ($T_o = 300\text{K}$ and excess air = 30%). A study based on comprehensive second law analysis reveals that the majority of exergy is destroyed in HCCI engine (compression, combustion, expansion) which is around 37.83% of the fuel exergy supplied, rest of the fuel exergy destruction occurs in turbocharger, heat exchanger and turbine; which are of the values of 5.43%, 4.36%, and 4.14% respectively. A 40.34% of fuel exergy is obtained as the work output of the engine, and around 7.83% of fuel exergy is lost via engine exhaust. The distribution of 100% fuel (hydrogen) exergy supplied to the combustion engine in HCCI mode may be represented as, around 52% of fuel exergy is destroyed due to irreversible processes in various components of the HCCI engine 40.34% is produced as work output, and 7.83% is lost via exhaust.

The results obtained in the analysis for hydrogen fueled HCCI engine especially the variation of energy and exergy efficiency in Fig. 4, have been compared with the results obtained for another promising renewable fuel (wet-ethanol) driven HCCI engine under same operating conditions (Khaliq *et al.*, 2011) in order to clarify the theoretical efficiency benefits obtained in the current study. These comparative results are graphed in Fig. 6. Comparison of the results clearly shows that hydrogen fueled HCCI engine

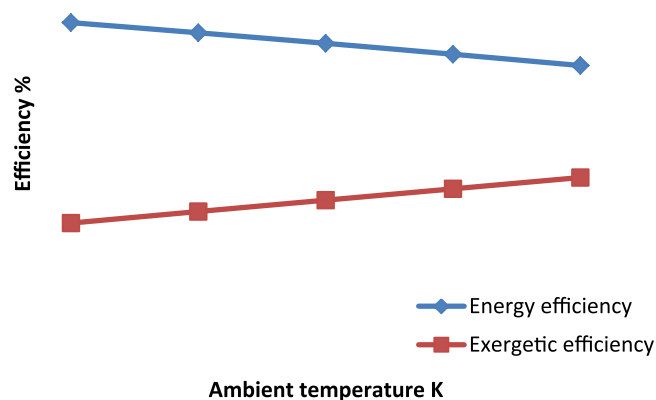


Fig. 4 Effect of variation of ambient temperature on Hydrogen operated HCCI engine efficiencies.

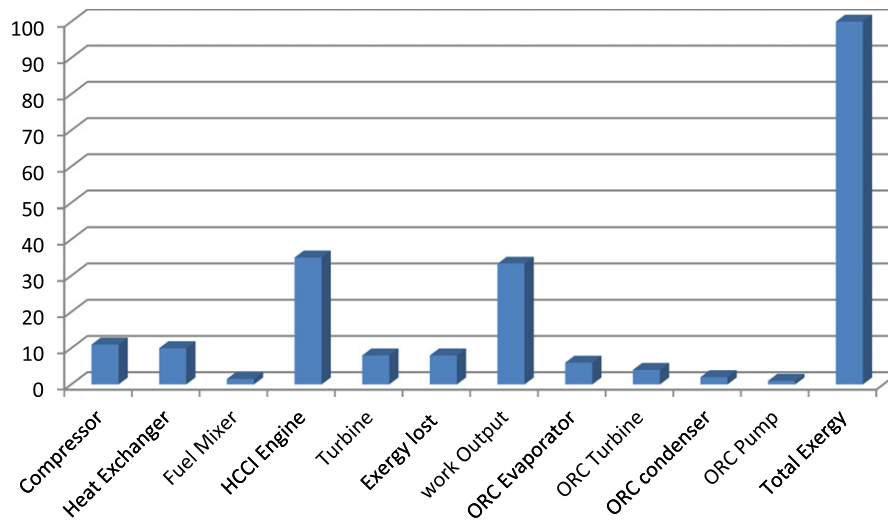


Fig. 5 Percentage of exergy destruction in each component of hydrogen operated HCCI engine.

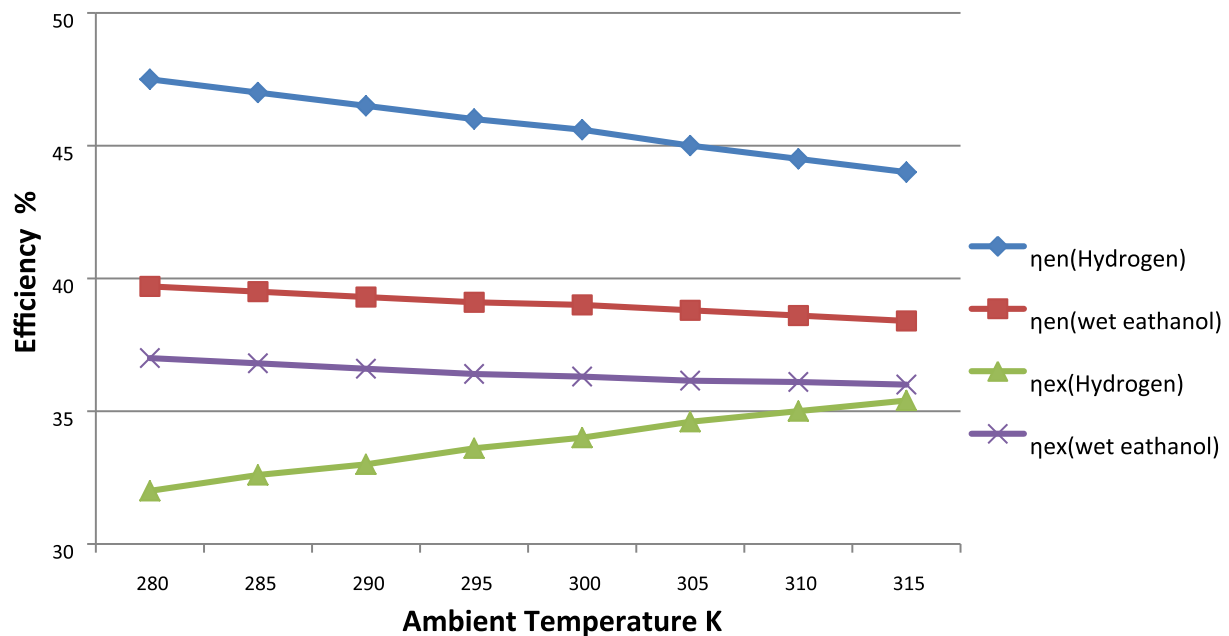


Fig. 6 Comparison of ambient temperature effect results of hydrogen and wet-ethanol for energy and exergy efficiency of HCCI engine.

provides a higher energy and exergy efficiency than wet-ethanol fueled HCCI engine for the same operating conditions. The energy efficiency for both the fuels shows the same trend of decreasing with the increase in ambient temperature but the exergy efficiency in case of hydrogen increases with the increase in ambient temperature and decreases in case of wet-ethanol with the same. This opposite trend for variation of exergy efficiency between the two fuels is observed due to the fact that hydrogen has much simpler molecular structure than wet-ethanol. Combustion of hydrogen results in less entropy generation than ethanol during combustion and hence provides a higher exergy efficiency of the engine.

Conclusions

The thermodynamic analysis clearly reveals the parts of the operating cycle where the capability of the working medium to do useful mechanical work is destroyed due to thermodynamic irreversibilities (such as combustion) and losses through undesirable exergy transfers (such as heat transfers to the cylinder walls and loss of thermal exergy to the exhaust). The results obtained based on first and second law analyzes may be summarized as follows:

- (1) A maximum energy efficiency of 45% and an exergy efficiency of 37% were obtained at an excess air of 25% and an ambient temperature of 300K.
- (2) Exergy analysis reveals that maximum exergy destroyed in HCCI engine which is 37.83%. Exergy destruction in the turbo-charger, heat exchanger, and turbine are of the values of 5.43%, 4.36%, and 4.14% respectively. Exergy destruction in fuel-air mixer was found to be negligible.
- (3) Around 52% of the fuel (hydrogen) exergy is destroyed in various components of HCCI engine due to their irreversible operation, 40.34% is produced as available work output, and 7.83% is lost via engine exhaust.

The results, obtained in the present study is a source of data for researchers and engineers to obtain a better design of hydrogen fueled HCCI engine for nearly zero emission operation.

See also: An Assessment of Hydrogen Energy Utilization for Sustainable Development

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Advanced Vehicle Systems and Technologies: Economic and Environmental Implications

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Introduction

As per current scenario, the steadily growing transportation sector is responsible for nearly 60% of total world oil demand. It is believed that in between 2006 and 2030, the oil demand from transportation will reach around three quarters of the projected increase in oil demand ([U.S. Energy Information Administration, 2010](#); [An, 2010](#)).

Not only the energy crisis, environment is a big concern. The conventional internal combustion Engine Vehicles (ICEVs) run by fossil fuels (i.e., gasoline or diesel) emits the major greenhouse gases (GHG) like Carbon-di-Oxide (CO₂), Methane (CH₄) and Nitrous Oxides (N₂O). Besides, Hydro-Fluorocarbon (HFCs) leaked out from air conditioning also contribute to GHG emissions. Not only that, transportation sector also emits harmful criteria pollutants like Carbon Monoxide (CO), Ozone (O₃), and Aerosol ([Atabani et al., 2011](#)).

To improve the fuel economy and reduce carbon dioxide emission in the transportation sector different types of initiatives can be opted like; (i) Fuel economy and greenhouse gas emission standards, (ii) Consumer information and labeling, (iii) Research and innovation for vehicle technology, (iv) De-emphasize increases in vehicle acceleration and horsepower performance, (v) Use of alternative fuels such as advanced bio-fuels, hydrogen fuel cells and natural gas as alternatives to oil and alternative power plants such as hybrid vehicles (HEV) and fuel cell vehicles (FCV), (vi) Vehicle taxation and charges linked to emissions performance, (vii) Eco-driving, (viii) Reducing the distances travelled per vehicle, (ix) Consumer behavior and congestion avoidance, (x) Investing in rail for freight and also passengers, (xi) Establishing green zones and green parking places for clean and fuel efficient cars such as in big cities, (xii) Offering incentives for low emission vehicles to encourage investment in appropriate emission reduction technologies ([Wagner et al., 2009](#); [Sierra club, 2010](#); [Cheah and Heywood, 2011](#); [Van West, 2006](#); [Pundir, 2010a,b](#); [IEA, 2010](#)).

Key Fuel Economy Reports

Considering huge potential of energy saving, fuel economy standards, labeling of vehicles and technologies advancement have been promoted in the transportation sector.

Fuel Economy and Greenhouse Gas Emission Standards

Fuel economy and greenhouse gas emission standards have proven to be one of the most effective tools in controlling oil demand and greenhouse gas (GHG) emissions. Globally, major regions around the world have implemented or proposed various fuel economy and greenhouse gas (GHG) emission standards. Among them Japan and European Union (EU) led the world with the most stringent passenger vehicle fuel economy standards. The Environmental Protection Agency (EPA) enacted the Clean Air Act (CAA) and National Highway Traffic Safety Administration (NHTSA) implemented the Energy Policy and Conservation Act to maintain tailpipe carbon emission and fuel economy for both passenger cars and light-duty trucks ([Atabani et al., 2011](#)).

Labeling

Labeling of vehicles plays an important role in consumers' vehicle purchasing decisions between similar vehicles that have different fuel efficiency ratings. Labeling provides the information regarding passenger car model, year of application of the label, absolute fuel consumption [l/100 km, km/l], CO₂ emission, comparison of relative fuel economy [%], fuel costs for 50,000 km. Labeling accompanied by standards of an appropriate type and level of stringency may yield synergistic results and different regions like USA, United Kingdom, Canada, China and Australia already reviewed several fuel economy levels ([Atabani et al., 2011](#)).

The Technological Advancement

The technological advancement plays an important role to improve fuel efficiency of motor vehicles. Throughout the history of automobiles the technology and design improvements have been always directed towards improvement of engine, transmission, vehicle body and accessories for obtaining higher fuel economy.

Case studies

The first generation Toyota Prius introduced in 1998 with 1.5 l, 43 kW gasoline engines and upgraded to 53 kW in 2001. The second generation Toyota Prius produced in 2004, adjudged as best engineered vehicle of the year by the Automotive Engineering

International. It uses a 4-cylinder gasoline engine with DOHC, 4-valve/cylinder and VVTi. The 2001 model gave 48 mpg (20.4 km/l) on CAFÉ (Corporate Average Fuel Economy Program) test cycle. The second generation Toyota Prius weighs 1250 kg and gives 55 mpg (23.4 km/l) on combined US city and highway fuel economy test cycle compared to the CAFE standard of 27.5 mpg.

A number of manufacturers like Toyota, Honda, Ford and Mercedes have introduced hybrid SUVs. These SUVs are for the customers who normally preferred high power SUVs using V-6 and V-8 engines. A 2004, hybrid SUV using gasoline engine gave 27.6 mpg and a diesel engine powered hybrid SUV gave 33 mpg on CAFE test cycle (*Automotive Engineering International, 2004*). Chevrolet Tahoe, GM hybrid SUV with 8 passenger capacity, 2810 kg curb weight achieves 50% better city cycle and 30% better combined cycle fuel economy compared to its gasoline engine counterpart (*Automotive Engineering International, 2008*).

Advancement of Vehicle System and Technology

Vehicles are broadly classified into Internal Combustion Engines (ICEVs) and Electric Vehicles (EVs). Based on hybridization ratio with ICEVs, EVs are commonly categorized into hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs) and battery electric vehicles (BEVs).

Internal Combustion Engine Vehicle (ICEV)

ICEV is a heat engine where fuels ignited with an oxidizer (usually air) in a combustion chamber. Then the chemical energy is transformed to heat energy and kinetic energy to propel a vehicle.

Conventional ICEV is mostly dependent on petroleum based fossil like gasoline, diesel oil, liquefied petroleum gas (LPG) and compressed natural gas (CNG) (*Balat and Balat, 2009*). It has no Electric Motor (EM) to support the fuel economy.

Micro-hybrid electric vehicles (micro-HEV) take the assistance of EM to restart the ICEV from off state without contributing any power to propel the vehicle. Currently, the Citroën C3 is being sold in Europe, is a micro-HEV (*Tie and Tan, 2013*).

Electric Vehicle (EV)

Robert Anderson first invented Electric-powered vehicle in between 1832 and 1839 powered by non-rechargeable primary cells (*Guarnieri, 2011*). The technology advancement of DC electric motor and rechargeable battery introduced EV commercially into the market first time in 1897. In just three years, EVs took up 28% of the road vehicles and was the favored vehicle of choice (*International Energy Agency Internet, 2014*). In 20th century, after invention of gasoline powered vehicles such as Ford Model T, Electric Vehicle faded out of popularity due to availability of cheap petrol and distance travelling limitation of EVs. But recently the global warming issue and depletion of fossil fuel brought the EV back and it was reborn due to rapid development of power electronics. Governments had implemented regulatory actions to reduce air emissions and promote electric and hybrid vehicles development. Toyota introduced the world's first commercial hybrid electric vehicle (HEV), Prius in Japan and 18,000 units were sold in the first production year (*Bellis, 2014*). As the oil price kept increasing, more automakers were committed to vehicle electrification. From year 2010 onwards, battery electric vehicles (BEVs) and plug-in hybrid electric vehicles (PHEVs), such as Nissan Leaf, Mitsubishi i-MiEV, Chevrolet Volt and Tesla Model S have started to enter into automotive industry (*Yong et al., 2015*).

Battery Electric Vehicles (BEVs) operate purely on the battery power, whereas the hybrid Electric Vehicles HEVs and PHEVs usually propel through a combination of two energy sources: internal combustion engine and electric motor. HEVs cannot accept charge from external energy sources, such as power grid. The battery is charged by the built-in internal combustion engine or through an energy recovery mechanism called regenerative braking which converts the kinetic energy into chemical energy and stores in battery for later use. PHEVs are similar to HEVs but with extra features, such as larger battery packs and can be recharged from the distribution grid.

A few power train configurations are developed for HEVs and PHEVs in order to achieve different objectives, such as improve fuel economy, increase power and minimize cost. The most common power train configurations of HEVs and PHEVs are series, parallel and series-parallel configuration, as depicted in *Fig. 1* (*Yong et al., 2015*).

As shown in *Fig. 1(a)*, a series HEV or an extended range electric vehicle uses power from electric motor as the only propulsion source. Other than recharging the battery by regenerative braking, an internal combustion engine and a generator are included to recharge the battery whenever the state of charge (SOC) of the battery is low. The electric motor is mechanically attached to the transmission and wheels. Meanwhile, the internal combustion engine is mechanically decoupled from the transmission and not connected to the wheels. The series HEV is suitable for city driving as it can deal with frequent stop-and-run driving pattern. This type of HEV can improve the overall vehicle efficiency to around 25% and is simpler to design, control and implement (*Tie and Tan, 2013*).

A HEV with typical parallel power train configuration is depicted in *Fig. 1(b)*. In a parallel HEV, both the electric motor and internal combustion engine are mechanically coupled to transmission and simultaneously transmit power to turn the wheels for vehicle propulsion. Due to two propulsion sources in a parallel HEV, the overall vehicle efficiency improvement of this HEV type is more than series HEV, approximately 40% more efficient than conventional car (*Tie and Tan, 2013*). A parallel HEV is suitable for city driving pattern and also highway driving pattern because electric motor and internal combustion engine can complement each other during different driving conditions. Some available parallel HEVs in market now are Honda Insight and Ford Escape.

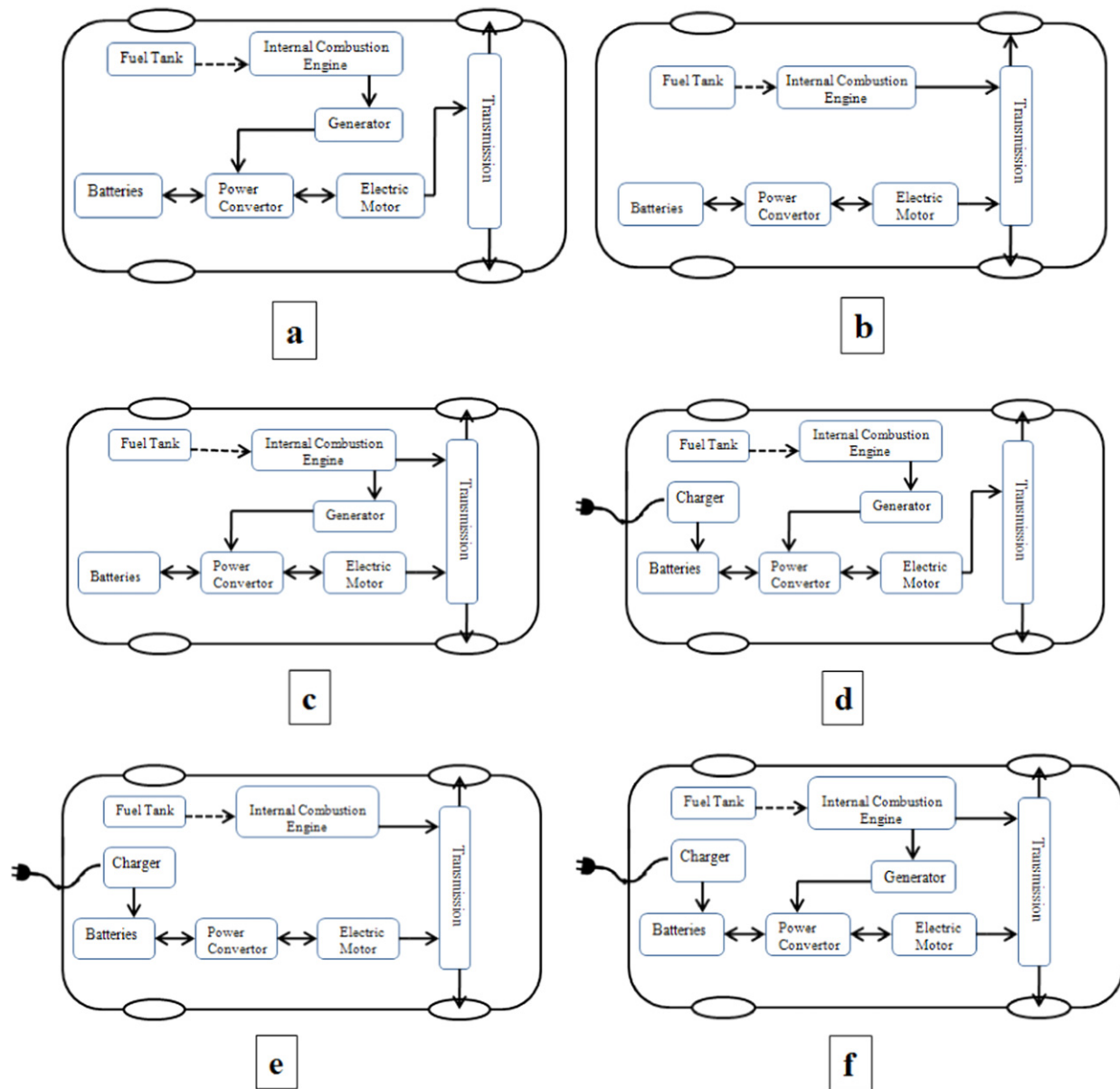


Fig. 1 Power train configurations: (a) Series HEV, (b) Parallel HEV, (c) Series-parallel HEV, (d) Series PHEV, (e) Parallel PHEV, (f) Series-parallel PHEV. Reproduced from Yong, J.Y., Ramachandaramurthy, V.K., Tan, K.M., Mithulananthan, N., 2015. A review on the state-of-the-art technologies of electric vehicle, its impacts and prospects. *Renew. Sustain. Energy Rev.* 49, 365–385. Available at: www.elsevier.com/locate/rser.

The series-parallel HEV, as shown in **Fig. 1(c)**, combines the features of series HEV and parallel HEV. Both the electric motor and internal combustion engine are mechanically coupled to transmission and wheels. The series-parallel HEV can run in either series or parallel mode. Despite having the benefits of both series HEV and parallel HEV, the design of a series-parallel HEV is much more complicated and costly. Toyota Prius is an example of a commercial series-parallel HEV.

Similar to HEV, PHEV can have series, parallel and series-parallel power train configuration with additional on-board battery charger, as depicted in **Fig. 1(d–f)**. However, PHEV can be plugged-in to power grid and externally charged. PHEV has larger battery pack and can propel in all-electric drive mode for longer period compared to HEV. There are two operating modes for PHEV, which are charge depleting mode and charge-sustaining mode (Emadi, 2011). PHEV usually operates in charge-depleting mode at vehicle start up, where the vehicle propulsion power comes from battery power. When the battery state of charge reaches a predefined threshold, charge-depleting mode is switched to charge-sustaining mode, where the internal combustion engine turns on. Hence, vehicle is powered by two sources and the battery state of charge is maintained at the predefined threshold in charge-sustaining mode.

Fig. 2 shows a typical power train configuration of BEV. BEV uses electric motor as the sole propulsion source. Therefore, BEV has all electric propulsion system and always operates in charge-depleting mode. The large battery packs can be recharged through

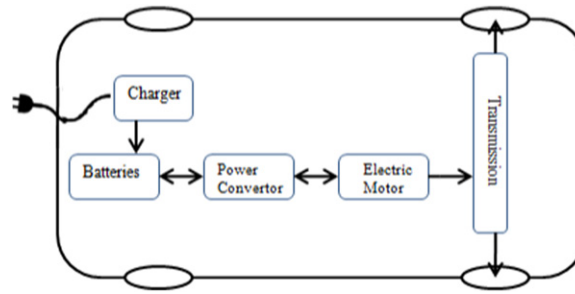


Fig. 2 Typical power train configuration of BEV. Reproduced from Yong, J.Y., Ramachandaramurthy, V.K., Tan, K.M., Mithulananthan, N., 2015. A review on the state-of-the-art technologies of electric vehicle, its impacts and prospects. *Renew. Sustain. Energy Rev.* 49, 365–385. Available at: www.elsevier.com/locate/rser.

regenerative braking on drive and externally charged when the vehicle stops. Since BEV has all-electric propulsion system, the distance it can travel is based on the battery capacity. For instance, Nissan Leaf has a 24 kWh lithium-ion battery packs installed and can travel up to 160 km in a single full charge. Generally, BEV is suitable for city drive as it has limited all-electric drive range. However, BEV has decent benefits, such as zero tailpipe emissions and better vehicle performance (Yong *et al.*, 2015).

Battery

Battery is major storage device which consists of one or more electrochemical cells that can convert the stored chemical energy into electrical energy. It has been a major focus of research since batteries cost as much as one-third of the total EV cost.

The Lead-acid battery is most commonly used being the cheapest one. But it was replaced soon by Nickel based battery as there were few apparent drawbacks of Lead-acid battery, like low energy density, heavy; require inspection of electrolyte level and is not environment friendly. Afterwards lots of developments were done in battery technology with nickel–cadmium (Ni–Cd), nickel–metal hydride (Ni–MH), ZEBRA battery or Sodium-nickel chloride (Na–NiCl₂).

Introduction of the Lithium based battery shifted EV into a new era and dominated the most recent groups of EVs. Such Lithium-ion battery packs are used in Nissan Leaf, Mitsubishi i-MiEV, Tesla Models and Chevrolet Volt, which are the top EV choices at the present time.

But none of the battery technologies is free from drawbacks. So developments are still ongoing with different promising technologies like lithium–sulfur (Li–S), zinc-air (Zn-air) and lithium-air (Li-air). The theoretical high energy density of more than 1700 Wh/kg allows Li-air battery to compete with conventional ICEVs (Rahman *et al.*, 2014). But the Li-air battery is still in the prototype stage and has not been commercialized yet.

Table 1 shows the comparison of available battery technologies for EV application. The characteristics of the batteries, such as nominal voltage, energy density, and specific power, and lifecycle, percentage of self discharge per month, memory effect, operating temperature and production cost per kWh have been numerically revealed in details.

Economic Aspect

At a first glance, the economic impact of EV deployment is not positive. Although EV has low operating cost due to the use of efficient electric motor and inexpensive electricity (Windecker and Ruder, 2013), but has higher initial purchase cost for the expensive battery component. Many actions have been implemented to ease the high initial purchase cost of EV, such as mass-producing EVs (Gass *et al.*, 2014), implement energy trading policy (Lunz *et al.*, 2012) and adopt appropriate charging strategies (Karabasoglu and Michalek, 2013). One hand the EV requires high initial purchase cost than ICEV and on the other hand the power grid must have more generation capacity for the additional EV load demand.

The power demand can be optimized by implementation of the smart grid. The smart grid is a modernized electrical power grid that utilizes the computer-based remote control and automation to improve the reliability, efficiency and sustainability of the power supply (Bhatt *et al.*, 2014). As it is the two-way communication between utility and customer, customers can help to balance the energy supply and demand by changing their electricity uses pattern (Smart Grid Information Clearing house Internet, 2014). Additionally, due to intelligent monitoring control, the self healing smart grid takes immediate corrective measures to restore itself from disruption, and provides better reliability and reduces risk against attacks and natural disaster (Reddy *et al.*, 2014).

The proper management of Vehicle-to-grid (V2G) technology in smart grid brings active power regulation. Unidirectional V2G technology is inexpensive and does not degrade the EV battery from discharging since it only controls energy flow from the power grid to EV (Sortomme and El-Sharkawi, 2011). The main driver for unidirectional V2G deployment is introduction of an energy scheduling or incentive system for the EV owners for charging their EVs during off-peak periods (Fasugba and Krein, 2011; O'Connell *et al.*, 2012). The controlled EV charging will disperse the EV loads over the off-peak periods and level the load profile for cost saving and power losses reduction (Sortomme and El-Sharkawi, 2012, 2011) and mutual benefits for EV owners and power grid attained.

Table 1 Comparison of EV battery types

Battery type	Normal voltage (V)	Energy density (Wh/kg)	Volumetric energy density (Wh/L)	Specific power (W/kg)	Life cycle	Self discharge (% per month)	Memory effect	Operating temperature (°C)	Production cost (\$/kWh)
Lead acid (Pb-acid)	2.0	35	100	180	1000	<5	No	− 15 to +50	60
Nickel-cadmium (Ni-Cd)	1.2	50–80	300	200	2000	10	Yes	− 20 to +50	250–300
Nickel-metal hydride (Ni-MH)	1.2	70–95	180–220	200–300	> 3000	20	Rarely	− 20 to +60	200–250
ZEBRA	2.6	90–120	160	155	> 1200	<5	No	+ 245 to + 350	230–345
Lithium-ion (Li-ion)	3.6	118–250	200–400	200–430	2000	<5	No	− 20 to +60	150
Lithium-ion polymer (LiPo)	3.7	130–225	200–250	260–450	> 1200	<5	No	− 20 to +60	150
Lithium-iron phosphate (LiFePO ₄)	3.2	120	220	2000–4500	> 2000	<5	No	− 45 to +70	350
Zinc-air (Zn-air)	1.65	460	1400	80–140	200	<5	No	− 10 to +55	90–120
Lithium-sulfur (Li-S)	2.5	350–650	350	–	300	8–15	No	− 60 to +60	100–150
Lithium-air (Li-air)	2.9	1300–2000	1520–2000	–	100	<5	No	− 10 to +70	–

Note: Tie, S.F., Tan, C.W. 2013. A review of energy sources and energy management system in electric vehicles. *Renew. Sustain. Energy Rev.* 20, 82–102. Rahman, M.A., Wang, X., Wen, C. 2014. A review of high energy density lithium–air battery technology. *J. Appl. Electrochem.* 44 (1), 5–22. Powarider [Internet], 2014. EV battery comparison. [cited 1 February 2014]. Available from: http://www.powarider.com/pdfs/EV_Battery_Comparison.pdf. Kolosnitsyn, V.S., Karaseva, E.V., 2008. Lithium-sulfur batteries: Problems and solutions. *Russ. J. Electrochem.* 44 (5), 506–509. Johnson, L., 2010. Research [Internet]. The viability of high specific energy lithium air batteries. [updated 7 October 2010; cited 5 February 2014]. Available from: <http://www.research.com/johnsonliarbaty/Session4-350-Johnson.pdf>. Christensen, J., Albertus, P., Sanchez-Carrera, R.S., et al., 2012. A critical review of Li/air batteries. *J. Electrochem. Soc.* 159 (2), 1–30.

Implementation of bi-directional V2G technology can bring different benefits to EV deployment like peak saving, load leveling and voltage regulation. Based on scale of EV fleet V2G technologies categorized as vehicle-to-home (V2H), vehicle-to-vehicle (V2V) and Vehicle-to-grid (V2G) (Berthold *et al.*, 2011; Liu *et al.*, 2013; Ghosh *et al.*, 2013).

V2H is used within home automation network and hence it has the smallest scope among all the categories. In a home automation network, the excessive power generation from the home solar photovoltaic unit can be stored by the EV. This power can be discharged towards the other smart appliances in case of low renewable generation. V2H technology in combination to the renewable distributed generation is able to create a safe, energy efficient and eco-friendly living environment (Berthold *et al.*, 2011). Wherever there is a larger EV fleet context like EV parking lots present at commercial buildings, they are significant and the energy exchange of all EVs can contribute towards certain objectives. V2V technology allows energy sharing among EVs (Liu *et al.*, 2013). The V2G technology can be used effectively to transfer energy from the power grid to charge the EVs. It can also be used to discharge the EVs batteries into power grid for grid support (Ghosh *et al.*, 2013; Yilmaz and Krein, 2012).

But utilizing EV battery in the V2G technology increases the EV charging and discharging cycles, which accelerates the battery degradation. So, more research is yet to be conducted to improve the technical and economical performances of EV battery.

Environmental Implications

Life Cycle Assessment (LCA)

LCA is a systematic tool for environmental impact related to any goods and services. The total life cycle stages start from material acquisition and manufacturing to use and end-of-life sometimes referred to as “cradle-to-grave” (Baptista *et al.*, 2011; Messagie *et al.*, 2010; Van Mierlo *et al.*, 2003) or as “vehicle cycle” (Gao and Winfield, 2012; Jaramillo *et al.*, 2009; Lane, 2006). In the ISO standard, the terminology is used as “equipment life cycle” (ISO, 2006).

The wells-to-wheel (WTW) study is one type of LCA of vehicles, which focuses on the life cycle of the energy carrier used to propel the vehicle, such as liquid fuel or electricity (Fig. 3). The WTW life cycle can be subdivided into the well-to-tank (WTT) stage, which focuses on the delivery of energy from its source to the storage equipment in the vehicle, and the tank-to-wheel (TTW) stage, where the energy carrier is used to propel the vehicle during operation. The WTT stage involves all processes from harnessing a primary energy flow or stock to different forms of conversion, distribution, and storage of energy carriers. The environmental impact of the WTT stage differs a lot, depending on how the energy carrier is produced. For example, there is a large difference between electricity produced from hydro-power and coal-fired plants.

The present transportation sector is mostly dependent on gasoline or petrol for propulsion and there was no interconnection between the transportation and power grid before Electric Vehicles came into the market.

EV was widely adopted in the market as it can be plugged-into power grid to receive energy. Although EVs have zero tailpipe emission, but the EVs use energy from power grid to charge their batteries and the carbon intensive power generation process is mostly dependent on fossil fuels and emits greenhouse gases as well.

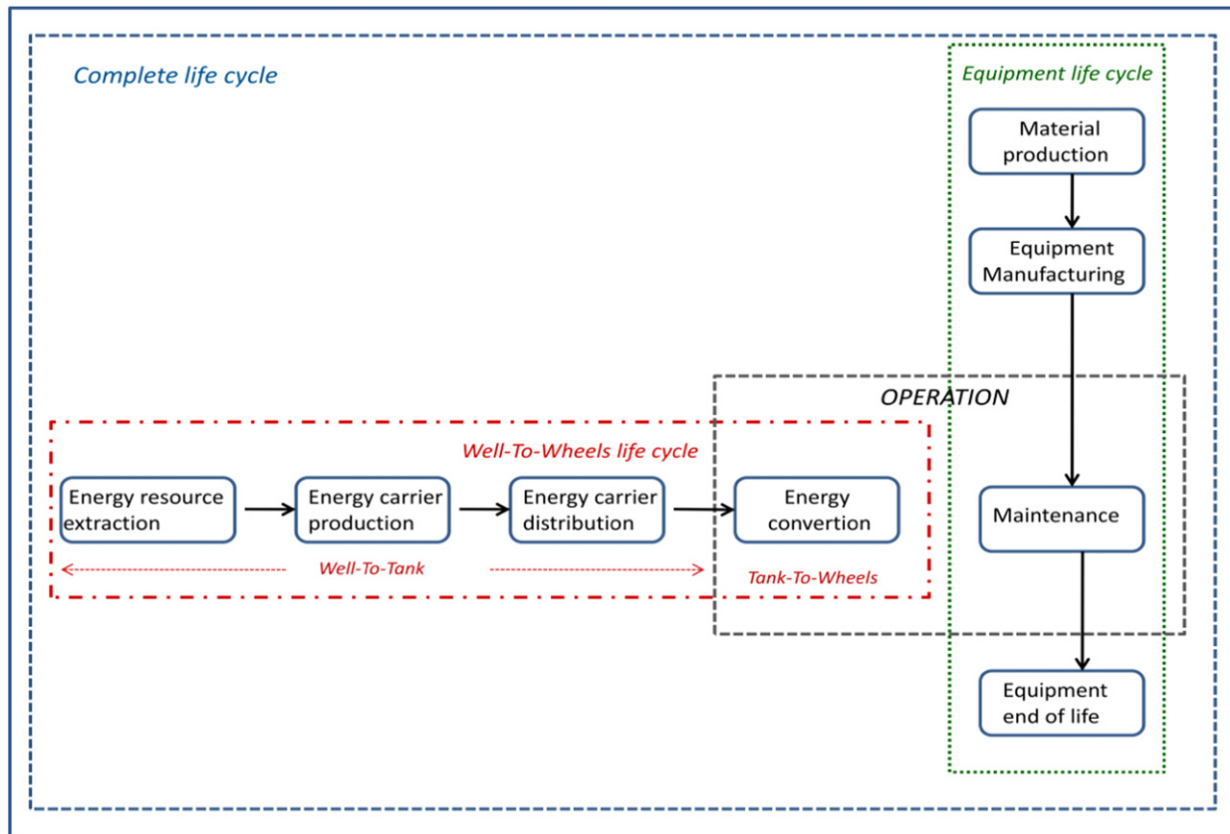


Fig. 3 Simplified view of the Well-to-wheel and equipments flows (a more detailed view include, for example, recycle option). Reproduced from Nordelöf, A., Messagie, M., Tillman, A.M., Söderman, M.L., Van Mierlo, J., 2014. Environmental impacts of hybrid, plug-in hybrid, and battery electric vehicles – What can we learn from life cycle assessment? *Int. J. Life Cycle Assess.* 19, 1866–1890.

So the point of arguments is that the electric powertrains are more energy efficient for propelling vehicles than conventional internal combustion engines fuelled by petrol or diesel or not. The full electric propulsion does not emit tailpipe emissions (IAE, 2011; Sadek, 2012). In addition, electric powertrains can assist in decoupling the transport sector from its heavy reliance on fossil fuels. On the other hand, electric vehicles may require additional electricity production (Tran et al., 2012) and this can be done using several different energy sources with diverse environmental impacts. Furthermore, electric powertrains require new advanced components (Chan, 2007), causing additional, or at least different, environmental impacts compared to conventional vehicles.

To solve the argument LCA studies come in many shapes and cause diverging arguments about environmental implication. WTW approach used to guide government promotion policies toward different types of powertrains and alternative fuel options (Ou et al., 2010).

In the most thorough review of LCA of electric vehicles, Hawkins et al. (2012) benchmarked 55 studies and also surveyed their own recommended practice and definition of a state-of-the-art complete LCA of electrified vehicles. It was argued that such studies have limited utility for informing policy makers as they only cover limited subsets of the complete system (Hawkins et al., 2012).

Helmerts and Marx (2012) compiled a broad description of technical characteristics and environmental impacts of electric and hybrid vehicles and concluded that electric vehicles have many benefits over conventional ones, but that the LCA literature on the subject “is complex.”

Nanaki and Koroneos (2013), Windecker and Ruder (2013) and Lorf et al. (2013) concluded that EVs have the lowest wells-to wheels emission.

But few cases have shown the reverse result. For instance, the Texas power grid, which has a mix of coal-and natural gas-fired generation, has been shown to yield higher emissions from EVs than ICEVs (Sioshansi et al., 2011). Similarly, the Ohio power grid with coal-fired generation yields higher SO_2 and NO_x emissions with use of EVs, although a CO_2 emissions reduced upto 24% from EVs than ICEVs (Weiller, 2011). These results conclude that EVs could not be environmental-friendly if EVs are charged from a dirty powergrid.

Althaus (2012) observes that results come out as diverging and that there is “a rather weak consensus” on the environmental performance of electric vehicles. Also, Frischknecht and Flury (2011) argue that results are diverging and, as an example, mention that emissions for electric vehicles vary between 95 and 240 g $\text{CO}_2\text{-eq./km}$.

Environmental Impact Assessment

For the environmental impact assessment a LCA needs to be extensive, complete and must cover impacts on three important areas of protection: natural environment, natural resources, and human health (ISO, 2006).

Natural environment

The airborne pollutants are mainly caused by combustion in the vehicle or at a power plant. The typical impact of airborne pollutants includes global warming potential (GWP), reporting all GHGs as CO₂-equivalents; photo-oxidant creation potential (POCP), which indicates how local air pollutants (NO_x and unburned hydrocarbons) build up smog under the influence of sunlight and harm both health and growing crops; Eutrophication potential (EP) which covers the effect of macronutrients in soil and water (including NO_x). Additionally, the acidification potential (AP) indicates the potential environmental impact of acidifying substances such as NO_x and sulfur oxides (SO_x) (Nordelöf *et al.*, 2014).

Natural resources

Abiotic resource depletion potential (ADP) aggregates the abiotic resource uses of metals and oil and often expressed in terms of antimony equivalents (kg Sb-eq.). Notter *et al.* (2010) compared ADP for two different versions of a vehicle in the compact class: an ICEV and a BEV and the results obtained from the study were around 260 kg Sb-eq./vehicle life (26% equipment cycle and 74% WTW cycle) for the ICEV and 190 kg Sb-eq./vehicle life (41% equipment cycle and 59% WTW cycle) for the BEV.

In previous ADP characterization the fossil energy depletion used to get more weightage, but recently, the frequently used Life Cycle Impact Assessment (LCIA) indicators, for example ReCiPe2008, placing more weightage on copper and nickel (Goedkoop *et al.*, 2012). Also, materials which currently play a key role in vehicle electrification, such as lithium and rare earth metals, are not covered by any of the easily available LCIA methods (Goedkoop *et al.*, 2012; Goedkoop and Spriensma, 2001; Joliet *et al.*, 2003).

Human toxicity potential (HTP)

Toxic emission at manufacturing stage specially connected with battery production of Electric vehicle was highlighted by Hawkins *et al.* (2013). The Human toxicity potential (HTP) analyzed in units of 1, 4-dichlorobenzene(DCB) equivalents, a well-known pesticide (Messagie, 2013).

Not only manufacturing, mining processes also have significant role in HTP as excavation is required for metal production as well as nuclear and fossil electricity. Material processing is especially energy intensive, and leakage from the waste disposal of mining spoils of nuclear and hard coal energy contributes to toxicity (Dones *et al.*, 2007). High use of copper and nickel, in batteries and electric motors, and copper and gold, in power electronics, increase disposal of mine tailings containing sulfides (Classen *et al.*, 2009). Consequently, improved waste handling in the mining industry and a less coal dependent energy mix could dramatically change these results and decrease the environmental load of BEVs.

But human toxicity and various types of ecological toxicity are complicated and uncertain as it relates different substances, their inherent toxicity, persistency and accumulation in the food chain (Finnveden *et al.*, 2009). The human health damage is caused not only by human toxicity, but also contributed by global warming, particulate matter formation, photochemical oxidant formation, ozone depletion, and ionizing radiation. As for example ReCiPe2008, climate change as a consequence of global warming contributes most to human health damage caused by vehicles (Goedkoop *et al.*, 2012). Calculated by this way, the petrol and diesel vehicles thus have a larger impact on human health than the BEV (Nordelöf *et al.*, 2014).

Key Remedies

Recycling

Recycling is a key factor for the environmental impact and battery is the main focus to recover the virgin material. The potential for recycling of lithium-ion batteries, which is both energy efficient and has high recovery rate, has been investigated in several papers (Dunn *et al.*, 2012; Gaines *et al.*, 2011; Li *et al.*, 2013; Sullivan *et al.*, 2011). However, highly efficient recycling processes are currently in practice only in the case of lead acid batteries.

This means that for newer technologies, an entirely new and large-scale recycling industry must be put in place if these results are to be realized (National Research Council, 2013). Additionally, battery technology is progressing very rapidly and data for environmental performance outdates quickly. Today it is often argued that the battery will last as long as the vehicle (Zackrisson *et al.*, 2010).

Interaction of renewable energy sources (RES) with V2G in smart grid

Initiatives have been taken to make the power grid greener with the wide employment of green renewable energy sources (RES) to reduce the wells-to-wheels emissions of EVs.

The adoption of Renewable energy sources primarily solar photovoltaic and wind energy, into power grid can create a greener and more sustainable electric power system. But these energy sources are not continuous and dependent on weather condition. The power generation fluctuates due to the variation of wind speed and solar irradiance. This intermittency issue of RES is the main barrier for the RES deployment. This issue can be resolved by using stationary energy storage system which can absorb excessive RES generation and supply in case of low RES generation (Mwasilu *et al.*, 2014). But it requires high investment. The issue has been

resolved by integration of bi-directional Vehicle-to-grid (V2G) technology and RES in smart grid system. EV charging can be utilized to stabilize the inconsistent generation of RES and EVs with RES can achieve mutual benefit enabling the power grid towards sustainability.

Interaction of EVs with solar photovoltaic and wind turbine

The literature study concluded that the interaction of EV with solar photovoltaic is beneficial from all respect of environmental, economic and technical viewpoint. It significantly reduces carbon emissions and fossil fuel usage. The appropriate energy management of EV and photovoltaic can increase the revenues for both photovoltaic suppliers and EV owners. Solar photovoltaic generates high power during daytime and can be used to supply the daytime charging demand of EVs. EVs can be utilized to absorb the excessive solar power generation and supply power to other loads during low solar power generation. Thus, the co-existence between RES and EVs bring about a positive impact and several studies have been conducted which are summarized in **Table 2**.

Wind energy harnessing has been developed due to their green nature and economic advantages. Many experiments have been carried out in different countries like Germany and Northeastern Brazil to assess the future wind energy utilization for EV charging (Hennings *et al.*, 2013; Borba *et al.*, 2012). Hennings *et al.* (2003) show that there are about 15% of excessive wind power generation by the year 2030 in Germany which can be utilized for EV charging purpose. Borba *et al.* concluded that the short-term interaction between EVs and wind energy generation is able to boost up the penetration of EVs into the market. Meanwhile, EVs can assist the regulation of wind generation intermittency in the long run (Borba *et al.*, 2012) (summarized in **Table 2**).

A number of investigations also have been conducted to examine the potential integration of EVs with solar photovoltaic and wind turbine altogether in the power grid and achieved 20% saving in the total energy cost (Berthold *et al.*, 2011). Fazelpour *et al.* (2014)

Table 2 Interaction of RES with EV in various power systems

Interaction of RES with EV	Application scopes	Contributions	References
Solar photovoltaic and EV	(a) Smart home	(a) Implication of EV and photovoltaic deployment in smart home system for emission reduction.	(Ida <i>et al.</i> , 2014)
		(b) Development of standalone solar-based home EV charger for home-to-vehicle application.	(Becherif <i>et al.</i> , 2011)
		(c) Development of uninterruptible future home by utilizing the interaction of solar photovoltaic with V2G technology.	(Cvetkovic <i>et al.</i> , 2009)
	(b) Parking lot	(a) Impact analysis of EV charging using solar energy at workplace parking lot.	(Birmie, 2009; Tulpule <i>et al.</i> , 2013)
		(b) Stochastic charging and discharging scheduling for EV intelligent parking lot consisting of solar photovoltaic	(Honarmand <i>et al.</i> , 2014a,b)
	(c) Grid distribution network	(a) Impact assessment on the power system performance with the integration of grid-connected EVs and photovoltaic	(ElNozahy and Salama, 2014; Denholm <i>et al.</i> , 2013; Iwai <i>et al.</i> , 2014)
		(b) Design of EV charging control strategy for a grid-connected solar-based charging station	(Goli and Shireen, 2014; Traube <i>et al.</i> , 2012)
	(d) Micro-grid	(c) Development of optimization algorithm for coordination of V2G service and solar photovoltaic.	(Marra <i>et al.</i> , 2013; Ghofrani <i>et al.</i> , 2014)
Wind turbine and EV	(a) Grid distribution network	(a) Generation scheduling formulation for industrial micro-grid consisted of solar photovoltaic generation and EVs	(Derakhshandeh <i>et al.</i> , 2013)
		(a) Research on the potentials of EV interaction with wind energy generation in the power system.	(Hennings <i>et al.</i> , 2013; Borba <i>et al.</i> , 2012)
	(b) Micro-grid	(b) Development of V2G optimization scheme to solve wind intermittency issue.	(Luo <i>et al.</i> , 2014; Liu <i>et al.</i> , 2012)
Solar photovoltaic, wind turbine and EV	(a) Smart home	(a) Coordinated energy dispatching of V2G technology and wind generation via optimization algorithm.	(Wu <i>et al.</i> , 2013)
		(a) Design of control strategy for a smart home consisting of renewable energy sources and grid-interactive EV	(Berthold <i>et al.</i> , 2011)
	(b) Parking lot	(a) Development of intelligent optimization framework for the integration of EVs and renewable energy resources	(Fazelpour <i>et al.</i> , 2014)
		(a) Potential assessment of grid-connected EVs in balancing the intermittent generation of renewable energy sources	(Dallinger <i>et al.</i> , 2013)
	(c) Grid distribution network	(b) Analysis of EV emissions associated with the renewable energy source generation	(Querini <i>et al.</i> , 2012)
		(c) Optimized algorithm to integrate grid-connected EVs and renewable energy resources.	(Jin <i>et al.</i> , 2013; Jin <i>et al.</i> , 2014)
	(d) Micro-grid	(a) Propose of V2G control to maximize renewable energy sources integration in micro-grid	(Peas Lopes <i>et al.</i> , 2009; Su <i>et al.</i> , 2014)

Note: Reproduced from Yong, J.Y., Ramachandramurthy, V.K., Tan, K.M., Mithulanathan, N., 2015. A review on the state-of-the-art technologies of electric vehicle, its impacts and prospects. *Renew. Sustain. Energy Rev.* 49, 365–385. Available at: www.elsevier.com/locate/rser.

developed an intelligent optimization framework using Genetic Algorithms for design step of a practical grid-friendly parking lot. [Peas Lopes et al. \(2009\)](#) designed V2G controller in MATLAB software and can be utilized to maximize the RES integration in micro-grid (summarized in [Table 2](#)).

Automated Vehicles

Automated Vehicles are the most recent evolution in the transportation sector. Rapid development in communication, robotics and the need of catering the aging population in developed countries have potentially made AVs a necessity and a vital business paradigm ([Hong et al., 2008](#)). Uber is the current example which brought struggle for taxi companies to retain in business and remain competitive.

The first attempt towards driverless vehicles started in the early 1920s ([Weber, 2014](#)) and got momentum in the 1980s ([Fenton and Mayhan, 1991](#); [Ioannou, 2013](#)). Afterwards AVs were largely made in Germany and the U.S. during 1980–2000 ([Anderson et al., 2014](#); [Lantos, 2010](#)) and Google car brought AVs to the spotlight ([Guizzo, 2011](#); [Markoff, 2010](#)). Moreover, the automotive industry spends around €77 billion worldwide on R&D in order to nurture innovation and to stay competitive ([ACEA, 2015](#); [Nieuwenhuijsen, 2015](#)). Competition started between the giant car makers: BMW, Mercedes-Benz, Nissan, Google, General Motors ([Knight, 2013](#)).

For the developing countries, adoption of AVs may spare them the costs associated with expanding capital-intensive infrastructure, in similar way the mobile phone technology exempted them from expensive landline infrastructure ([Anderson et al., 2014](#); [Sridhar and Sridhar, 2007](#)).

In general, AVs operate on a three-phase design known as “sense-plan-act” which is the premise of many robotic systems ([Behere and Törngren, 2015](#); [DiClemente et al., 2014](#); [Siciliano and Khatib, 2008](#)).

The Society of Automotive Engineers (SAE) International ([SAE International, 2016](#)) taxonomy defines five levels of vehicle automation. In level 1 (driver assistance) and level 2 (partial driving automation), the human driver monitors the driving environment and is assisted by a driving automation system for execution of either the lateral or longitudinal motion control (level 1) or both motion controls (level 2). In level 3 (conditional driving automation), an automated driving system performs all dynamic tasks of driving (monitoring of the environment and motion control), but the human driver is expected to be available for occasional control of the vehicle. In level 4 (high driving automation) and level 5 (full driving automation) an automated driving system performs all dynamic tasks of driving, without any human intervention at any time. In level 4, the automated driving system controls the vehicle within a prescribed operational domain (e.g., high-speed freeway cruising, closed campus shuttle). In level 5, the automated driving system can operate the vehicle under all on-road conditions with no design-based restrictions.

The AV enhances fuel economy by 4%–10% because of its advance design and engine efficiency ([NRC, 2010](#)). Its implementation associated with a variety of positive societal impacts such as a safer transport system, a lower cost of transport as well as enabling a modicum of mobility to the non-ambulatory and disabled as well as to those in lower income households. It is estimated that the direct societal value that will be created will be between 0.2 and 1.9 trillion dollars annually by 2025 ([Manyika et al., 2013](#)). Such positive impacts are the driving forces behind the emergence of AV technology, making it a viable, economic model in the near future and beyond.

AVs also provide an opportunity for vehicles to communicate their maneuvers and actions with each other which may reduce idle time, improving both traffic and drive-cycle efficiencies ([Anderson et al., 2014](#)). The concept of “connected vehicles” (United States) or “cooperative ITS” (Europe) was known to the Intelligent Transport Studies (ITS) industry to resolve the communication and data sharing among vehicle-to-vehicle (V2V) and between Vehicle-to-infrastructure (V2I/I2V) and to improve the performance and safety of the automation system.

Implication of Travel Cost, Road Capacity and Travel Choices

The fixed costs of automated vehicles will very likely be higher than for conventional vehicles due to the advanced hardware and software technology involved. The increased fixed cost could influence the penetration rate and subsequently the magnitude of the effects of the automated vehicles. The Generalized transport cost (GTC), on the other hand, is expected to decrease because of lower effort, time, and money needed to travel. First, more travel comfort, enhanced travel safety, higher travel time reliability, and the possibility to perform activities other than driving (like working, meeting, eating, or sleeping) while on the move will likely lead to lower values of time. Second, less congestion delays because of increased road capacity and reduced (or even eliminated) search time for parking owing to self-parking capability, but also increased use of shared vehicles, would possibly require less travel time. Third, enhanced efficiency of traffic flow along with more fuel-efficient vehicles because of their lighter design (owing to less risk of having an accident) could also reduce the monetary cost of travel. Due to shorter headways, air resistance will possibly decrease; further reducing fuel use and costs. However, potential increase of vehicle travel demand because of enhanced road capacity, reduced GTC, and/or proliferation of vehicle sharing systems and urban expansion in the longer term, could compromise travel time and cost savings. The counter effects of increased vehicle demand could include increased congestion delays, longer trips, and more fuel costs ([Milakis et al., 2017](#)).

Implication Based on Ownership and Sharing, Location Choices, Land Use and Transport Infrastructure

Literature results suggest that shared automated vehicles could replace a significant number of conventional vehicles (from about 67% up to over 90%). The overall reduction of the conventional vehicle fleet could vary according to the automated mode

(vehicle-sharing, ridesharing, shared electric vehicle), the penetration rate of shared automated vehicles and the presence or absence of public transport. Few studies have explored the impact of automated vehicles on location choices and land use. According to their results, automated vehicles could enhance accessibility citywide, especially in remote rural areas, triggering further urban expansion. Automated vehicles could also have a positive impact on the density of economic activity at the center of the cities. Parking demand for automated vehicles could be shifted to peripheral zones, but could also remain high in city centers, if empty cruising of shared automated vehicles is not allowed. Moreover, several studies showed that shared automated vehicles can significantly reduce parking space requirements up to over 90%. Finally, because of automated vehicles the pavement-rutting damage could be accelerated. Still, the increase in speed of automated vehicles could compensate for such negative effect by decreasing rut depth (Milakis *et al.*, 2017).

Implication Comprises Energy Consumption and Air Pollution, Safety, Social Equity, the Economy, and Public Health

Literature results suggest that the use of automated vehicles can result in fuel savings and lower emissions in the short term. The net effect of vehicle automation on energy consumption and GHG emissions in the long term remains uncertain.

Various longitudinal, lateral and intersection control algorithms and optimization systems can offer significant fuel savings and lower emissions of NO_x, CO, and CO₂. Studies reviewed in this paper reported fuel savings upto 31% for longitudinal and lateral movement controllers and up to 45% for intersection controllers. Both fuel economy and emission reductions are reported higher as the penetration rate of vehicle automation systems increases. Furthermore, shared use of automated vehicles is associated with reduced emissions (VOC and CO in particular) because of the lower number of times a vehicle starts. One study (Greenblatt and Saxena, 2015) associated the long-term impacts of battery electric shared automated vehicles with up to 94% less GHG and nearly 100% less oil consumption per mile, compared to conventional internal combustion vehicles. Yet, several factors could lead to increased energy use e.g., longer travel distances and increased travel by underserved populations such as youth, disabled, and elderly. Thus, the net effect of vehicle automation on energy consumption and GHG emissions remains uncertain.

Many social factors are also uncertain like what could be the scale of job losses (or gains) due to full vehicle automation? Which sectors and which countries and/or regions would be most affected? And what could be the strategies to mitigate the economic impacts of expected job losses? (Milakis *et al.*, 2017).

Conclusion

In view of greenhouse gas emission reduction potential, advanced Vehicle systems, generally EVs are cleaner than the conventional Internal Combustion Engine vehicles (ICEV) as EVs have zero tailpipe emission. The RES integration with V2G technology facilitates to reduce the dependency on carbon intensive power generation and carbon footprint as well. Additionally, the smart grid provides economic advantages by numerous service and regulation to power grid.

On the other side the Advanced Vehicle Systems technology is not fully-matured, battery requires lots of research as it has restricted energy density, limited life cycle and high initial cost. Moreover, bi-directional V2G technology increases the EV charging and discharging cycles and accelerates the battery degradation. Battery life is a major concern for EV owners which may be a huge social barrier for V2G technology and EV deployment as well. Appropriate incentive-based policy can resolve this issue.

Charger technology and infrastructure are also point of concerns for EV deployment. Most of the EV chargers adopted in the market are uni-directional charger type. Bi-directional charger for V2G technology is under experimental stage. The EV deployment needs proper planning and huge investment cost to install complex infrastructure.

With the most recent advancement in Autonomous Vehicle (AV), a natural and organic synergy can be brought between shared AV fleets and EV technology to resolve the practical limitations of EVs including travel range anxiety, access to charging infrastructure and charging time management. Accordingly, the transportation sector can be more eco-friendly and economic. But AVs are also in stage of infancy. EVs and AVs need more maturity, further research and development to bring positive impact of vehicle advancement in economic and environmental aspect. Bottom line: Every citizen is responsible to reduce greenhouse gas emission; it also has impact while choosing transport system options. So, leave your car at home and hire cycle, walk or catch public transport. Also, don't forget about electricity.

Acknowledgement

Special thanks to Mr. Palash Dutta, Senior Project Manager, Cognizant Technology solutions, Kolkata; Dr. Anurup Datta, Purdue University, USA and Mr. Anirban Basu Roy Chowdhury, Chemistry Department, JIS College of Engineering, Kalyani for their valuable support.

See also: Selected Issues in Economics of Greenhouse Gas Emission Mitigation

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Further Reading

Automotive Engineering International, 2004. High performance hybrids.

Advances in Surface Engineering for Improved Energy Storage

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Introduction

With the increase in greenhouse gases in the environment, the unpredictability along with fatal damages of the environment has significantly increased since the last two decades. The major production of greenhouse gases are through the combustion of fossil fuels. The major consumption sectors of fossil fuels are through Industries, Residential (electric power produced from fossils) and Automobiles. The air quality needs to be ameliorated which can be achieved by mitigation of content of Carbon products in the atmosphere. This can be achieved by using renewable and clean sources of energy. These include production of energy from Solar, Tidal, Geothermal and many more sources. However the use of Hydrogen as a clean fuel has been proposed as a very good alternative. Hydrogen as a clean fuel cell has been used in Proton Exchange Membrane Fuel Cells. However this approach is very uneconomic with cost of Hydrogen Fuel Cells in Engines exceeding almost 7 times the IC engines run by fossils and the reliability is a major concern in this field as well ([Chalk and Miller, 2006](#)). Hence this topic is under continuous research with advances in different sectors for tackling this situation.

So with advances in various fields for developing various techniques in order to enhance the use of renewable resources, advances were made in improving the storage capacities of energy obtained from renewable sources. These were done with the aid of Surface modification techniques using nano-materials, phase change materials, polymers, composites and paper based devices etc. Surface modifications of electrodes in Lithium ion based batteries and supercapacitors with the help of graphene, CNTs and other materials is under rigorous research as it has offered good alternatives to reduce the carbon content in the atmosphere.

With the advances in renewable energy is considered as one of the proposed viable solution to this predicament the renewable sources vary independently from the demand of the situation. Though their conversion techniques are becoming advanced and affordable. Nevertheless their contribution to sustainable energy will be decisive only when the storage methods are properly developed.

Microencapsulated Phase Change Materials (MPCM)

Phase Change Materials (PCM) are latent heat storage materials. They absorb or reject heat energy and instead of rise in temperature of the body the phase (gas, liquid or solid) of the body changes ([Hawladar et al., 2003](#)). They are used for storage of thermal energy. They are most suited in applications or regions where the energy storage is periodic or inconsistent. For instance their application was showed in the concrete walls to save thermal energy in an experimental setup in Spain ([Cabeza et al., 2007](#)). They offer many advantages in such a system. The Phase change temperature is almost equivalent to what is required in the system. The density of such materials is also very high. The Low density variation of these materials allows its efficient use. Thermal Conductivity is almost same in all phases. There is no undercooling. In addition to all these advantages the material is non-toxic, non-polluting and non-flammable. It is available at a cheap price ([Zalba et al., 2003](#)).

The Solid-liquid phase change PCM contained organic and inorganic materials. The organic materials provides chemical and thermal stability, good anti-corrosion properties and no undercooling takes place. However for inorganic materials the phase change enthalpy is very high. With the PCM offering so much advantages both from scientific and economy point of view, their uses are very high. However their use has been limited due to the lower thermal conductivity from several phases particularly when solidifying on the heat transfer surface ([Zalba et al., 2003](#)). This limits the heat power which can be extracted from this system. This reduces the efficiency of the system. Hence application of highly conductive metal fins were used in order to increase its efficient working. This increased the overall cost and weight of the system. Hence, a solution to such a problem was Phase Change Slurry. This Slurry contained PCM in the nano or micro phase. This slurry acts as a thermal energy carrier and thermal storage media. It provides the function of low temperature applications. These MPCM is composed of core PCM with polymer or inorganic shell to prevent the leakage and spilling of PCM during phase change ([Huang et al., 2011](#)). Good alternatives in microencapsulation are developed with much better performances. These include microencapsulate Paraffin, polystyrene, polymethyl methacrylate, polyvinylacetate, poly ethyl methacrylate, fatty acids, silica gel polymer, n-octadecane, polymethyl methacrylate and many more ([Hawladar et al., 2000](#); [Alkan et al., 2009](#); [Sari et al., 2010](#); [Ji et al., 2015](#); [Hariharan et al., 2018](#)).

So this is one of forms of engineering where the surface of materials is modified to improve the stability and the thermal energy storage.

Advances in Lithium Ion Batteries

In order to decrease the Carbon footprints from our atmosphere we need to limit the use of fossil fuels in our day to day life. A major consumption of these fossil fuels is in the automobile sector. This can be done by using vehicles which runs on electric

batteries or hydrogen. The vehicles running on batteries have been proved more efficient compared to hydrogen fuel cells vehicles in terms of cost and the net output work.

Lithium Ion batteries has found a lot of real life applications due to the rechargeable nature of its battery. It offers an advantage of a much lower discharging rate over other rechargeable batteries.

The Li ion battery contains a Carbon electrode, a positively charged metal oxide electrode with a lithium salt immersed in an organic solvent as an electrolyte. In order to achieve better performance of this battery many researches have been carried on in the field of materials science and surface engineering. The nanoscale materials and structures containing Carbon particles in the nano-dispersed phase possess higher charge storage capacity compared to normal carbon electrodes (Stephenson *et al.*, 2014). Hence researchers aim to efficiently produce such nano-materials at a rate which eventually reduces the overall cost of the rechargeable battery.

The cathodes contain an intercalation material which acts as a hold the Lithium ion. The lithium ion acts as a guest ion which can enter and leave the intercalation materials. The metal chalcogenides have acted as good materials which serve this purpose. These included TiS_3 and NbSe_3 . However LiTiS_2 offered high gravimetric energy as well as high life cycles compared to other intercalation compounds (Whiteley *et al.*, 2017). Transition metal oxides like LiCoO_2 is commercially used in many Lithium ion batteries. It is a very used transition cathode material because of low discharge voltage. It also possess high volumetric capacity, high specific capacity and has good cycling performance (Du Pasquier *et al.*, 2003; Graetz *et al.*, 2003). The main disadvantages of using this material is its uneconomic nature in the commercial market. The high price of this material is due to the presence of Cobalt in its compound. Not only it has low thermal stability but also its fast capacity fade at high current rates. The lower thermal instability of the material may have reduced its application in commercial sectors. Even deep cycles (extraction of more than 50% Lithium from the electrolyte) caused the distortion of the lattice of the material. Hence in order to overcome these difficulties surface engineering techniques were implied on these materials. Materials like Manganese, Aluminium, Iron and Chromium (Ceder *et al.*, 1998; Alcantara *et al.*, 1999; Madhavi *et al.*, 2002; Stoyanova *et al.*, 1994) were used instead of Cobalt or were doped with them. The problem was resolved on a limited basis. Nevertheless Coatings (a higher surface engineering technique) of metal oxides like Aluminium Oxide, Titanium Oxide and Zirconium Dioxide were used (Scott and Nicholls, 1980; Cho *et al.*, 2001). These metals ameliorated the mechanical and chemical stability of the battery as the chemically stable compound were formed which increased not only the structural stability of the material but also the side reaction with the electrolytes. This caused improved performance of the material even in deep cycling.

The surface engineering technique was best used when NMO ($\text{Li}(\text{N}_{0.5}\text{Mn}_{0.5})\text{O}_2$) electrode was developed with the help of using cheap Nickel replacing the costly Cobalt. The presence of Ni^{2+} ion in the cathode produce high pathways and very low strain (Kang *et al.*, 2006). Further application of this technique was used to involve Cobalt in the NMO electrode which improved the specific capacity of the electrode. The pure NMO electrode cannot be used as the Ni^{2+} ion substitutes the Li^{2+} ion. Further improvements were carried on in the field of intercalation materials by finding better materials and using improved surface engineering techniques and by using polyanion compounds.

With the use of materials such as Carbon Nano Tubes (CNT), graphenes and its components were used effectively as thin film current collectors (Zhang *et al.*, 2006). The thickness was less than 300 μm but it possessed high mechanical flexibility as well as high energy densities. However occasional electrolyte leakage took place which caused short circuiting of the device. Hence PVdF (polyvinylidene difluoride) was applied onto it (Lee *et al.*, 2013) because it is a highly non-reactive thermoplastic and has low thermal conductivity.

Conversion Cathode Materials are those materials which undergo solid state redox reaction while lithiation or delithiation. Lithiation is the incorporation of Lithium to an electrolyte in a battery. Metal salts of chlorides and fluorides can act as good conversion cathode material due to intermediate operation voltage and high specific and volumetric capacities. They suffer from poor conductivity, unwanted side reactions, large voltage hysteresis. Hence surface engineered materials were used where synthesis of nanoparticles of these materials were done. These materials were wrapped in conductive matrix to overcome the low conductivity. For instance FeF_3/CNT , $\text{FeF}_3/\text{grapheme}$, $\text{BiF}_3/\text{MoS}_2/\text{CNT}$ are some of the most efficiently used materials.

A hybrid sandwiched phosphorus-graphene(phosphorene) was synthesised by some researchers which showed remarkable specific and volumetric capacities (Sun *et al.*, 2015).

Anode material of these batteries include Carbon. The main reason behind it is that it is commercially usable even after 20 years of running. Carbon possess higher cycle life, more power density, moderate energy density and a relatively low cost. However the volumetric capacity of these electrodes are on a lower side.

Lithium Titanium Oxide is one of the most promising material for anode as it allows the superior combination of thermal stability, cycle life and high volumetric and specific capacities (Amine *et al.*, 2010) though it has high cost. These properties generate due to zero strain conditions during lithiation and delithiation cycles. This is because there is a maximum of 0.2% change in volume (Schamer *et al.*, 1999; Colin *et al.*, 2010). But the surface reactions are completely unavoidable. It undergoes gassing. This is due to the reaction between the active metal in the Lithium Titanium Oxide anode and the organic electrolyte (Belharouak *et al.*, 2012; Bernhard *et al.*, 2014; He *et al.*, 2015). This can be overcome by using proper surface engineering technique of coating the material with Carbon (Song *et al.*, 2014; He *et al.*, 2013). However coating with Carbon will cause the electrolyte to dissociate and form Solid-electrolyte interphase.

In order to overcome this Carbon composites were prepared by alloying it with different materials. It is so adopted because the alloying material have very satisfactory size for providing higher mechanical stability, transportation of electron and Lithium ions. Since the solid-electrolyte interphase expands in volume and needs to be stabilized, it is generally encapsulated within a carbon

shell with space inside it to provide volumetric expansion. Silicon and Tin has been used as an effective alloying component but a different approach was taken by some researchers to stabilize the solid-electrolyte interphase by adding some additives to the electrolyte. However Tin suffers from fracturing under moderate conditions (Qin *et al.*, 2014). But researchers showed that in-situ grapheme engineered Sn encapsulation is possible which provided very splendid results (Zhou *et al.*, 2015). The size of Sn varied between 5 and 30 nm. This was possible because of the high elasticity of grapheme material which caused the structural and interfacial stabilization of tin nanoparticles while subsiding the stress developed due to the volume change of the nanoparticles. This in-situ procedure was done by Chemical Vapour Deposition technique. This surface engineering technique of Chemical Vapour Deposition can be used for several materials like Nickel, Germanium, Gallium and even Silicon. Silicon has low delithiation energy, very high gravimetric energy, and chemical stability, low cost and also is non-toxic. A very unique material MoS_2 was used as a material to engineer the porous surface of the Carbon on order to render better working of the anodes (Luo and Zhi, 2015; Chang and Chen, 2011; David *et al.*, 2014). Their application was not only limited to batteries but also to supercapacitors due to their high retention power (Cao *et al.*, 2013; Tang *et al.*, 2015).

Supercapacitors

A supercapacitor is a capacitor which serves the purpose of high energy storage compared to normal capacitors. The use of supercapacitor is analogous to the use of flywheels in IC engines. Supercapacitors are amidst a battery and a capacitor in terms of energy storage i.e., more than a capacitor but less than that of a battery. However its quick charging capability and its ability to turn on quickly helps it to find its application in Hybrid vehicles, energy harvesting and smartphones. Supercapacitors use two layers of solid dielectrics to store energy. These are called electrochemical double layer capacitors. The supercapacitors use two mechanisms to store energy namely electrical double layer capacitance and pseudocapacitance (Conway, 2013). The electrochemical double layer capacitors uses carbon materials with high surface area where charge gets accumulated from the electrolyte/electrode interface. Pseudocapacitors use metal oxides or conducting polymers as the materials for electrodes for fast and reversible redox reactions (Zhang *et al.*, 2010). A high pseudocapacitance is not required because it makes the response time high capacitance decay rate (Liu *et al.*, 2010). Graphene based supercapacitors have been reported to have best serve the purpose of supercapacitors. This is because of the intrinsic capacitance of graphene is $21 \mu\text{F}/\text{cm}^2$. However its doping with different materials has improved supercapacitor properties. These include CNTs/graphene, metal oxides/graphene, etc. The formation of single walled carbon nanotubes as an electrode through zipping technique has allowed the electrode to have the property of individual single walled carbon nanotubes (Futaba *et al.*, 2006).

The use of conducting polymer based electrodes offer several advantages like its flexibility and its high conductivity. These material can be engineered to make very thin films which allows rapid energy release rate. The major disadvantage of such a capacitor is its cycle life. In order to increase the cycle life of these supercapacitors a surface engineered technique of formation of composites is used. The composite is made of the conducting polymer with the carbon nanotubes. This increases the volume, the porosity and the area for the swelling of the conducting polymer. This is done by co-deposition of several different conducting polymers in an ionic liquid (Snook *et al.*, 2011; Zhang and Zhao, 2009). Metallic Organic Framework composites with the incorporation of CNTs and graphene oxide has shown very exciting results for the researchers. The reason for their advanced results is the pseudocapacitance offered by the graphene oxide sheets (Ramachandran *et al.*, 2018; Rahmanifar *et al.*, 2018). Coleman *et al* found that the capacitance can be increased by increasing the thickness of the electrode. However this system fails to perform in a high rate capacitance. This failure was overcome with the surface engineering technique of introducing Carbon Nanotubes in the electrode. These carbon nanotubes not only removed such failure but also imparted mechanical stability to the electrodes. The incorporation of these nanotubes also improved the charge distribution in the electrode. This improves the intrinsic capacitance of the electrodes (Ling *et al.*, 2018; Nguyen and Gomes, 2019).

Conclusion

There is a dire need to reduce the percentage of greenhouse gases and the carbon percentage from the atmosphere. This can be done by limiting the use of fossil fuels in various sectors of our daily work. The use of fossil fuels needs to be limited because of the increasing global warming effects. However this cannot be done at the cost of sacrificing one's personal standard of living. Hence better, newer and efficient techniques needs to be formed or invented to form a stabilized environment. This article covered some aspects of how it can be achieved through the application of surface engineering techniques. There are many surface engineering techniques that are developed each day and implemented to give superior results compared to what has been found in the past. This article covered some of those techniques. The use of micro-encapsulating materials for their phase change is one of the ways to preserve the solar energy. This can limit the use of fossil fuels if the usage of these renewable energies increases. Another extensive but efficient way to decrease the carbon footprint is by using Hybrid vehicles or electric vehicles. These vehicles runs on batteries which can be surface engineered to increase the performance of the vehicles. The cathode and anode were doped and coated using materials which improved its cycle life and decreasing its commercial cost. The Supercapacitors were the next close thing to batteries which can also be used as their alternate. The use of graphene oxides and CNTs as thin films and dopants on the electrodes enabled them to

superimpose their own pseudocapacitance to the capacitance of the electrode materials. There are various other techniques of Surface Engineering which contributes to net reduction of the greenhouse gases and Carbon footprints in our environment.

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Alternate Photovoltaic Material: Its Environmental Consequences

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Introduction

The alarming rates at which the fossil fuel reserves are decreasing and the steady rise in the energy requirement for the growing population attribute to the main driving force for finding alternative solutions to the prevalent conventional sources of energy. A shift towards the hydrogen economy from the carbon-based economy is a primary priority to counter the challenges of global warming. Combustion of all fossil fuels generates large amounts of CO₂, CO, SO₂, NO₂, CH₄ and all other greenhouse gases which is heating up the surface of the earth in an unprecedented rate resulting in temperature change and rapid ecological disbalance. One of the main concerns of the scientists since the past century has been the replacement of the conventional energy sources by renewable and environment-friendly sources of energy more commonly known as “Green Energy”.

Solar energy sector predominates the renewable energy economy. Concentrated research beginning from the early nineteenth century to date has established solar energy as an almost-conventional form of energy. Research reveals that the surface of the earth receives about 10²⁴ Joules of solar power annually (Chapin *et al.*, 1954) with the spectral range varying from 250 nm to 2500 nm in wavelength. The two commercially prevalent methods for converting solar energy are the use of photovoltaic cells and concentrating solar power with the aid of reflectors. The various ways by which solar energy can be used consolidate into the solar economy. PV (photovoltaic) technology used for the conversion of light to electricity directly, solar collectors, artificial photosynthesis for producing carbohydrates and hydrogen by the water-splitting method, biomass technology for generating complex carbohydrates to generate biofuels, etc., are the comprising units of the present solar economy (Bailey, 1972).

The relentless effort to establish solar energy as a sustainable form of energy resource has been alleviated with the inculcation of nanotechnology in the fabrication of the solar cells. The main reasons for embracing nanotechnology in the solar economy are the increased efficiency at a reduced manufacturing cost and ease of installation as well as fabrication. Moreover, nanotechnology also serves as the key to low-cost systems for generating, storing and transporting energy. Nanoscale level synthesis and designs combined with thin films offer economical solutions to the otherwise sophisticated methods of not only solar thermal systems but also for the other forms of renewable energy.

The present silicon solar cell-based technology, also known as the first-generation photovoltaic cell, dominates the economy with more than 86% of the global solar cell market. The second-generation of photovoltaic materials is comprised of thin film layers (1–2 nm) of semiconducting materials. Nanoparticles made of direct bandgap semiconductors are more commonly known as nanocrystal quantum dots. These serve as the basis to thin film solar cells on silicon or other substitutive conductive transparent oxide (CTO), such as indium-tin-oxide (ITO) substrate with nanocrystal coating. The prevalent researchers are extremely interested to explore the photo-catalyzed decomposition of pollutants at various Titania surfaces as well.

One of the basic pillars for establishing any technology as a sustainable one is the impact of that technology on the biotic as well as the abiotic environment. In spite of the huge promises that nanotechnology offers with respect to the solar energy sector, one of the most important underlying concerns remains largely neglected. Though advocated as green technology, the justification of it by exploring the various adversities that the nanoparticles offer is discussed in the literature review as follows.

Solar Cells

Evolution of Solar Cell Technology

First generation solar cells

The onset of developing solar energy as a potential substitute for fossil fuel began when Alexandre-Edmond Becquerel first observed the photovoltaic (PV) effect in 1839 (Yadav and Kumar, 2015). Since then a significant population of scientists has had devoted their studies for innovating the solar energy sector. Nevertheless, the first modern solar cell made of silicon was invented by Russell Ohl in the year 1946 (Yadav and Kumar, 2015; Castellano, 2010).

The initial photovoltaic solar cells were comprised of thin silicon wafers which function by transforming solar energy into electrical power. On the other hand, the working principle of the modern photovoltaic technology is solely based on the creation of an electron-hole in each cell composed of two different layers (p-type and n-type materials) of semiconductor material. In this type arrangement, when the p-type and n-type junction of the semiconducting material is struck by a photon carrying sufficient amount of energy, an electron is ejected with the aid of the energy gained from the impinging photon. The emitted electron then moves from one layer to another, thus creating an electron and a hole in the process and as a consequence of this movement, electrical power is generated (Srinivas *et al.*, 2015). The different types of materials used in fabricating photovoltaic solar cells are predominantly in the form of silicon (single as well as multi-crystalline, amorphous), cadmium-telluride, copper-indium-gallium-selenide (Srinivas *et al.*, 2015).

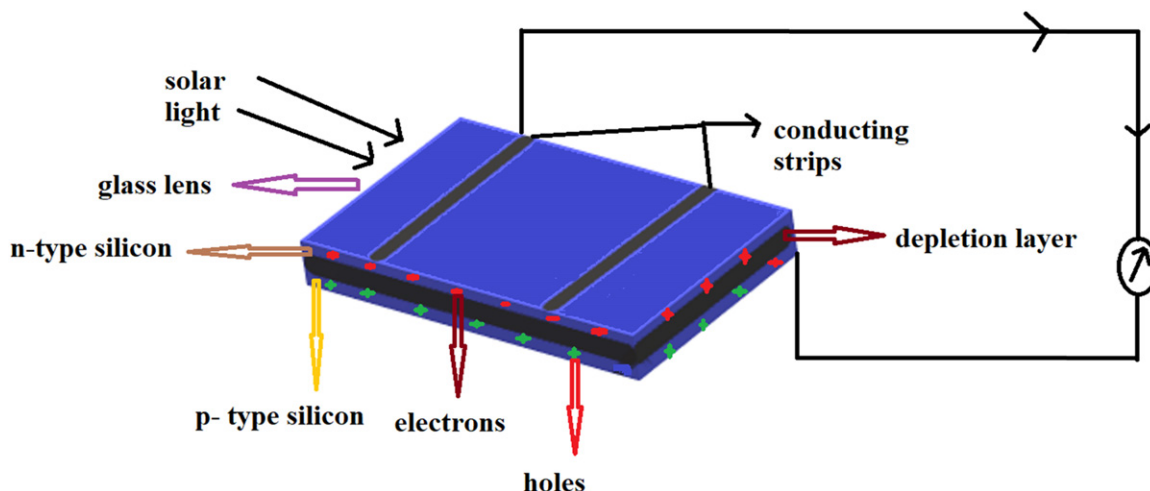


Fig. 1 Schematic diagram of crystalline Silicon solar cell.

The first-generation solar cells gained popularity for their significant high efficiency. The silicon wafer-based technology had been further classified on the basis of the number of crystals. The single or monocrystalline silicon solar cells were mainly synthesized by the Czochralski process (Srinivas *et al.*, 2015; Wurfel and Wurfel, 2009; Dmitrijev, 2006). Though the efficiency reached 17%–18%, yet the process of “recrystallizing” was expensive. The second classified category: polycrystalline silicon solar cells were composed of a wide variety of crystals generally coupled to one another in a single cell. The efficiency of this type of solar cells varied in the range of 12%–14%. Though lower efficient, the manufacturing costs for this variety being significantly lesser than the former one, the polycrystalline solar cells were considered economically feasible. Hence, they occupied almost 48% of the global solar cell production in 2008 (Saga, 2010) (Fig. 1).

Second generation solar cells

The primary motive for the invention of the second-generation solar cells was to diminish the huge disparity between cost and efficiency in the prevalent solar cells as much as possible. The chief constituents of the second-generation solar cells were the thin film and the amorphous silicon solar cells.

Amorphous silicon solar cells

The amorphous silicon thin film solar cells were the first solar cells that were manufactured on an industrial level. The thickness of the light absorbing layers of silicon wafer-based solar was approximately 350 μm thick, whereas the thin-film solar cells enjoy the advantage of very thin light-absorbing layers in comparison to the former, generally of the order of 1 μm thickness (Chopra *et al.*, 2004). The major advantage of using amorphous (a-Si) solar cells was the low manufacturing cost. Due to a considerable low processing temperature, various polymers and other suitable substrates suited the manufacturing criteria instead of using pure silicon which is way more expensive and thus the energy required for processing was vastly reduced (Imamzai *et al.*, 2012).

The low manufacturing cost made the a-Si solar cells widely available and popular. The word “amorphous” in regard to solar cell corresponds to the fact that the silicon constituents of the cell do not have a uniform alignment of atoms in the lattice that is they are non-crystalline in structure. The fabrication was done by coating the doped silicon material to the rear side of the substrate. While the conducting side had a silver hue, the reflecting side was in general dark brown in color (Sharma *et al.*, 2015). Though the efficiency and the cost of manufacture were compatible, the major problem was the lack of stability in case of efficiency. At PV module level, the efficiency dropped considerably. The efficiency of the prevalent PV solar cells ranges between 4%–8% at almost all conditions, including elevated temperatures or at conditions where the sunlight is available for a meager few hours (Maehlum, 2015).

CdTe solar cells

One of the leading candidates for the development of cheaper, economically viable photovoltaic (PV) devices is Cadmium Telluride. As a matter of fact, it also regarded as the first PV technology at a low cost (Yogi Goswami and Kreith, 2007; Luque and Hegedus, 2003). Possessing a band gap of ~ 1.5 eV combined with high optical absorption coefficient and chemical stability, Cadmium Telluride was a lucrative option for solar cell designing. Since CdTe is an excellent direct band gap crystalline compound semiconductor, the absorption of light is easier and thus making the efficiency higher. CdTe has a direct optimum band gap (~ 1.45 eV) and a high absorption coefficient of around $5 \times 10^{15}/\text{cm}$ (Elsabawy *et al.*, 2012). The efficiency of CdTe PV solar cells varies in between 9%–11% (Badawy, 2015). Though CdTe solar cells can be fabricated on polymer substrates and are flexible in nature, there are some serious environmental concerns. Cadmium which is regarded as heavy metal has been found to be

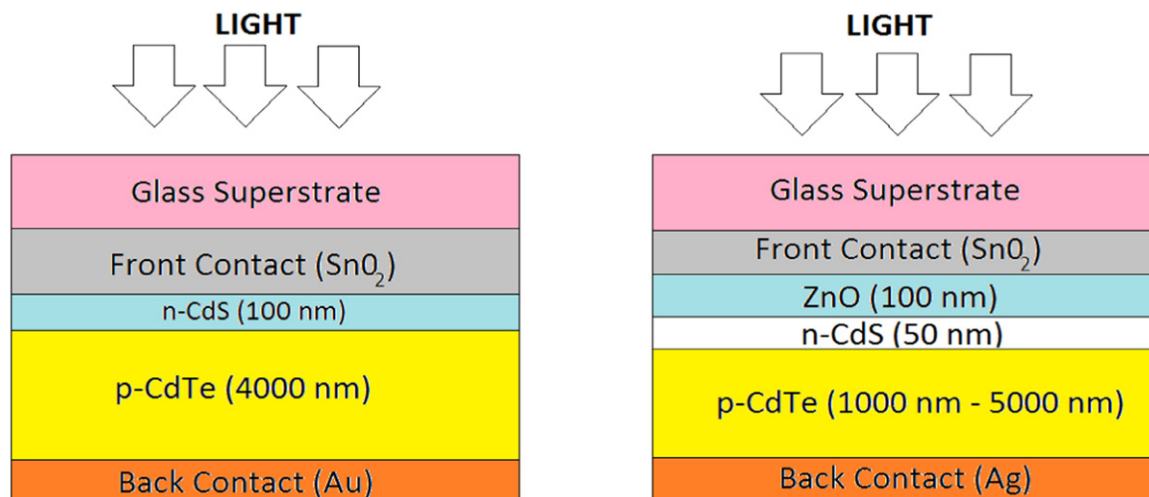


Fig. 2 Gold and silver cadmium telluride solar cell.

potentially toxic which can accumulate and cause serious harm to not only human beings but also animals and plants. Moreover, the disposal of Cd-based materials and their recycling is regarded as a highly sophisticated and expensive process as it poses serious threats to the environment and ecology (Maehlum, 2015). Therefore, the primary reasons to put CdTe solar cell technology to a halt were the serious disposal problems and the hazardous effects on the environment (Luque and Hegedus, 2003; Elsabay et al., 2012; Badawy, 2015; Sethi et al., 2011) (Fig. 2).

Copper indium gallium selenide (CIGS) solar cells

Copper, Indium, Gallium, and Selenium are the chief constituting elements of the quaternary compound semiconductor better known as CIGS (Andorka, 2014). CIGS falls into the category of important direct band gap type semiconductors. The efficiency of CIGS thin-film solar cell ranges about ~10%–12% which is higher in comparison to the CdTe solar cell efficiency. The higher efficiency range combined with more or less an environment-friendly nature are the two major reasons for favoring CIGS solar cell technology over the CdTe modules. Sputtering, evaporation, electrochemical coating technique, printing and electron beam deposition, etc., are the most widely used methods to fabricate CIGS PV solar cells (Razykov et al., 2011). The prolonged life-span without a much significant degradation is the specialty of the CIGS type solar cell (Badawy, 2015) (Fig. 3).

Third generation solar cells

Quantum dot solar cells

The solar cell design that utilizes quantum dots as the absorbing photovoltaic material are known as quantum dot solar cells. The primary motive behind this kind of solar cell is to replace bulk materials such as silicon, CIGS or CdTe. In bulk materials, the bandgap remains fixed. On the other hand, by changing the size of the dots, the bandgaps of the quantum dots can be tuned across a wide range of energy levels. In multi-junction solar cells, harvesting multiple parts of the solar spectrum is the primary principle. Thus, a wide variety of materials are used to enhance the efficiency of solar cells. Hence for this purpose, quantum dots perfectly fulfill all the required criteria.

Quantum dots are semiconducting particles which have radius lower than that of the Exciton Bohr radius. Similar to the energies of an atom, because of quantum mechanical considerations, the electron energies that can exist within them become finite. As a result of this, the Quantum dots are also referred to as “artificial atoms”. The sizes being the primary cause of the alteration of band gaps make quantum dots suitable for tuning the energy levels. A variety of bandgaps can be expressed with the aid of quantum dots which can be suitably grown over a wide range of particle sizes keeping the underlying material or construction techniques unchanged (Baskoutas and Terzis, 2006). In typical wet chemistry preparations, the synthesis duration or temperature are usually varied to achieve tuning of the quantum dots.

Colloidal Quantum dots (CQDs) synthesized by single junction methods using Lead Sulphide (PbS) are capable of being tuned into the far infrared and frequencies which are usually difficult to achieve with the prevalent traditional form of solar cells. A significant portion of the solar energy reaching the Earth is in the infrared spectrum while most of the radiation lies in the near infrared region. Infrared energy is made accessible as easily as any other spectral region with the help of colloidal quantum dots (Sargent, 2005). Moreover, the synthesis and preparation of CQDs are comparatively easier and faster. Though CQDs are usually synthesized in small batches, they can be mass-produced as well.

Distribution of the dots on a substrate is done majorly by spin coating, either by hand or by an automated process. Large-scale production generally uses spray-on or roll-printing systems which reduce the cost to a great extent. Expensive molecular beam epitaxy processes were used initially but later economically profitable fabrication methods like wet chemistry, solution processing

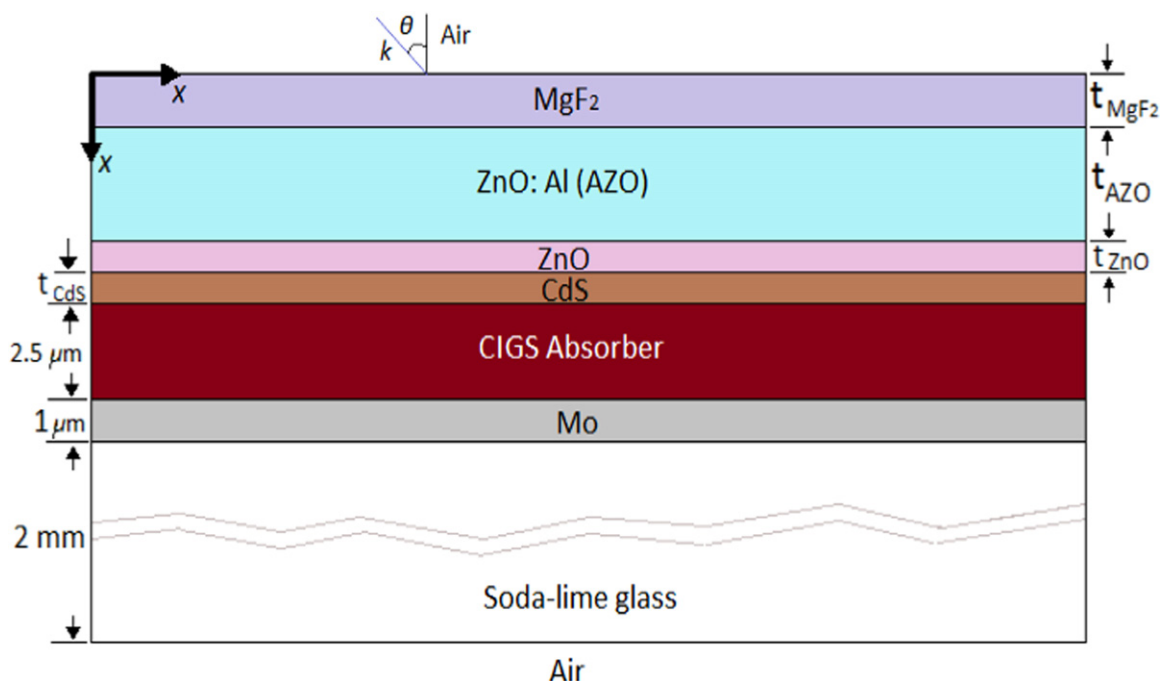


Fig. 3 Conventional CIGS solar cell model.

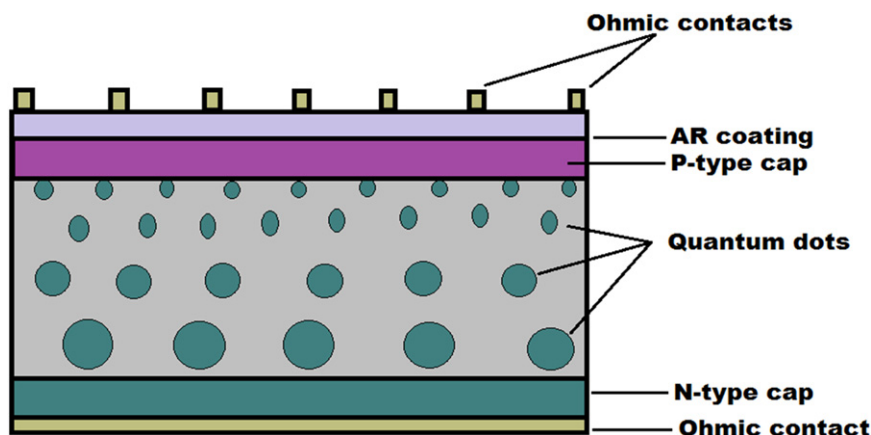


Fig. 4 Schematic representation of quantum dot solar cell.

methods, etc., were developed. Long hydrocarbon ligands help in stabilizing the concentrated nanoparticle solutions which help in keeping the nanocrystals suspended in solution. Since carrier recombination deteriorates the device performance due to the trap states present, engineering the nanocrystal surface chemically can better passivate the nanocrystals. An efficiency of 7.0% is achieved by following this process (Ip *et al.*, 2012). The use of iodide as a ligand that does not bond to oxygen was introduced in 2014 which was shown to maintain stability between the n- and p-type layers. As a result, the absorption efficiency got boosted, which thus generated a power conversion efficiency up to 8% (Shruti *et al.*, 2015) (Fig. 4).

Dye sensitized solar cells (DSSC)

Since the late twentieth century, the research has been primarily focused on increasing solar efficiency by not only manipulating molecular orientation but also use nanotechnology for harvesting light energy extensively (Li *et al.*, 2006; Zhan *et al.*, 2006; Graetzel *et al.*, 2012; Nozik, 2010; Suhaimi *et al.*, 2015; Liang *et al.*, 2007; Bertolli, 2008; Bagher *et al.*, 2015; see "Relevant Websites section"). The pioneer in the field of dye sensitized solar cell (DSSC) was Michel Gratzel from the Swiss Federal Institute of Technology (Bagher *et al.*, 2015; see "Relevant Websites section"). The DSSCs works on the principle of employing dye molecules between the various electrodes. The chief four components comprising the DSSCs are semiconductor electrodes in the form of

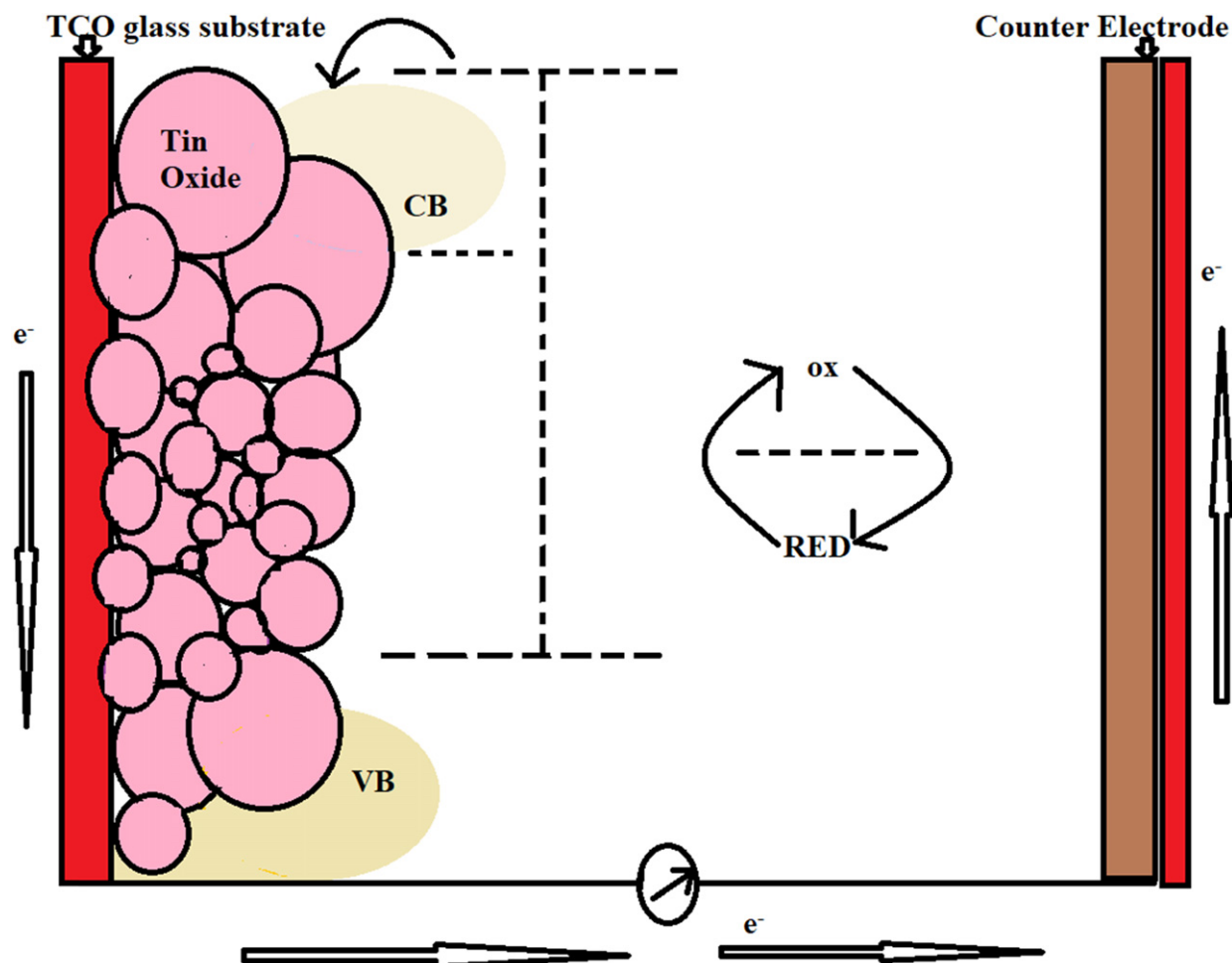


Fig. 5 Dye-sensitized solar cell.

n-type TiO_2 and p-type NiO , a dye sensitizer, redox mediator, and a counter electrode which can be either carbon or Platinum (Nozik, 2010). Simple conventional processing methods like printing technique are the primary method used to fabricate DSSCs.

The high flexibility, transparency and the low cost of production are the factors that make DSSCs a lucrative alternative to the solar cells of the previous generations (Bagher *et al.*, 2015). The photosensitization of nano grained TiO_2 coatings combined with the visible optically active dyes help to increase the efficiency of the DSSCs greater than 10%, thus making it suitable to be considered a novelty (Li *et al.*, 2006; Zhan *et al.*, 2006; Graetzel *et al.*, 2012; Nozik, 2010; Suhaimi *et al.*, 2015; Liang *et al.*, 2007). However, like all new technologies, it comes with the question of degradation of the dye molecules and hence issues concerning with stability are raised (Bagher *et al.*, 2015) (Fig. 5).

The poor optical absorption of sensitizers attributes to the questioned poor conversion efficiency. Unlike the quantum dot solar cells, the dye particles in DSSCs when exposed to the ultraviolet and the infrared radiations degrade which makes DSSCs unsuitable for use beyond a particular spectrum. Though coating with a barrier layer acts as a buffer and help reduce the degradation of the particles in the UV or IR region, it adds to the extra cost of the fabrication, thus making it economically unfeasible (Bertolli, 2008).

Perovskite solar cells

The class of compounds defined by the formula ABX_3 where X represents a halogen such as I^- , Br^- , Cl^- whereas A and B represent cations of different size are commonly known as Perovskites. The most recent discovery in the solar cell research community is the Perovskites and researchers are excited with this, in particular. Varied advantages over conventional silicon and thin film based solar cells helped the Perovskites gain huge popularity despite being a very new idea. The conventional Si-based solar cells are synthesized by high-temperature processes ($>1000^\circ\text{C}$) which are usually multi-step and are way more expensive than the methods employed for Perovskites and on top of that, fail to deliver efficiency at par with the manufacturing cost (Ahn *et al.*, 2015; Casey, 2015). The efficiency of the Perovskites solar cells reaches almost up to 31% (Shi *et al.*, 2015). According to an interesting investigation recently performed by Volkswagen, Perovskites have emerged as a potential candidate in the next generation electric-automobile batteries (Casey, 2015; Shi *et al.*, 2015). The stability and durability of the perovskite solar cells are the main

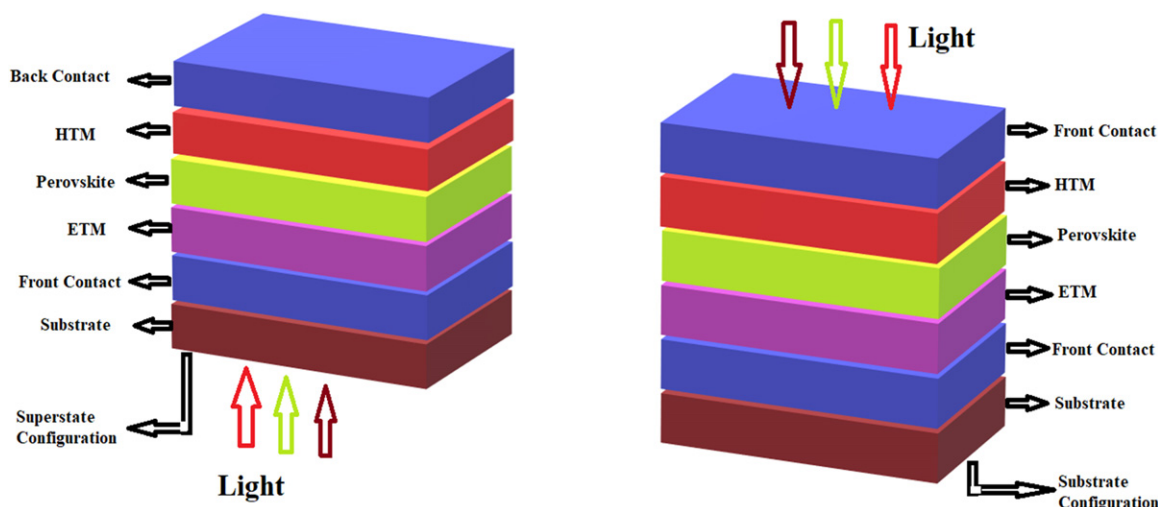


Fig. 6 Superstrate and Substrate configuration of perovskite solar cell.

drawbacks of the technology. Because of the degradation of the materials over time, the efficiency drops notably, hence questioning the durability of the solar cells. Moreover, the environmental impacts of Perovskites discussed later also contribute to the hindrance of commercialization (Fig. 6).

Environmental Impact of Alternative Photovoltaic Cell Technology

Effect of amorphous silicon solar cells

The Eco-indicator methods are the tools to assess the environmental impact of all the stages of the solar power generation process. The impact of a process on three specific fields: the effect to Human Health, the impact to the quality of Ecosystem, and the adversities upon Resource depletion are measured with the aid of this method (Goedkoop and Spriensma, 2000). Disability Adjusted Life Years abbreviated as DALYs are used to measure human health damages. Losing one life year by an individual is indicated by damage of 1, whereas a weight of 0.25 indicates four years of disability suffered by an individual. The study of DALYs comprises of mainly carcinogenic and respiratory effects on humans caused by organic as well as inorganic substances. Issues relating to climate change, ionizing radiation, and ozone layer depletion are also included in the studies of this method (Wasin et al., 2017).

Ecosystem Quality damages are measured in terms of PDF*m²*yr. PDF stands for "Potentially Disappeared Fraction of Species". It measures the extinction rate or the declination of the population of species in an area of land over a period of time. For the disappearance of all species within an area of one m² for one year, the rating is unity.

The measurement of ecosystem quality consists of detailed studies on ecotoxic emissions, the cumulative effect of acidification and eutrophication and reports on the land occupation as well as land conversion. The extraction of minerals and fossil fuels is quantified by "Resource Depletion". MJ surplus energy is the unit to measure the damage and represent the surplus energy required for future extractions of fossil fuels, compressed gases, and mineral resources (Wasin et al., 2017). To properly compare the categories of damage, an aggregation of various units into a single environmental impact function, known as an eco-indicator was implemented. By using a set of dimensionless weighting factors, the final result is being measured in terms of eco-points (Pt) (Henryk, 2011).

Tables 1 and 2 analyses the data used in the process of production of thin film amorphous silicon solar cell modules, for 1 kWh power generated. The input and output data related to the transportation stage were similarly obtained from solar cell power plant surveys and published literature concerning the production statistics (Chamsilpa et al., 2010). The consumption of fuel and emissions to the environment because of conveying the modules is discussed in Table 3.

Since, multi-crystalline photovoltaic solar cells require an electrical input, the consequence of this input results in the emission of nitrogen, oxygen, water vapor, nitric oxide, nitrogen dioxide, and NO_x. Whereas, in amorphous silicon solar cells, none of these gases are produced. This is because thin film amorphous cells do not require any electrical input. Table 4(a) and 4(b) quantifies the data used for analyzing the cumulative input and output for 1 kWh of power generation from solar energy.

Table 5(a) and 5(b) show that by recycling and reusing the material of old photovoltaic cells, there is a significant decrease in both energy consumption and material consumption. By constructing solar panels from old cells there is an energy saving of around a 1/3 when compared to using new materials (Richard, 2008). Furthermore, approximately 90% of the glass in an old cell can be recycled and used in new glass products (Monier and Hestin, 2011). Of the other recyclable materials, it was possible to reuse approximately 86.5% of them (Ancil, 2012).

Table 1 Input associated with the production of thin film amorphous silicon solar cell module per kWh power generated from solar energy

<i>Description</i>	<i>Process</i>	<i>Unit</i>	<i>Quantity</i>
Silicon	Silicon production	kg	Low
Glass	Module assembling	kg	1.01E-01
Aluminium	Module assembling	kg	6.55E-03
EVA	Module assembling	kg	1.82E-03
Copper	Module assembling	Kg	7.90E-04
Electricity	Silicon production	kWh	3.43E-01

Note: Chamsilpa, M., Vorayos, N., Katsiriroat, K., 2010. Environmental impact analysis of solar cell power plant compared with fossil fuel power plants in Thailand. *Asian Journal on Energy and Environment*, 103–117. Stoppato, A., 2008. Life cycle assessment of photovoltaic electricity generation. *Energy* 33, 224–232. Wasin, K., Somchai, M., Chantana, P., 2017. A comparison of the environmental impact of solar power generation using multi-crystalline silicon and thin film of amorphous silicon solar cells: Case study in Thailand. *Journal of Ecological Engineering* 18 (4), 1–14.

Table 2 Output associated with the production of thin film amorphous silicon solar cell module per kWh power generated from solar energy

<i>Emission to air</i>	<i>Process</i>	<i>Unit</i>	<i>Quantity</i>
CO ₂	Silicon production	kg	9.58E-02
CH ₄	Module assembling	kg	1.97E-04
SO ₂	Module assembling	kg	3.27E-05
NO _x	Module assembling	kg	4.72E-05
PM	Module assembling	kg	3.00E-06

Note: Chamsilpa, M., Vorayos, N., Katsiriroat, K., 2010. Environmental impact analysis of solar cell power plant compared with fossil fuel power plants in Thailand. *Asian Journal on Energy and Environment*, 103–117. Stoppato, A., 2008. Life cycle assessment of photovoltaic electricity generation. *Energy* 33, 224–232. Wasin, K., Somchai, M., Chantana, P., 2017. A comparison of the environmental impact of solar power generation using multi-crystalline silicon and thin film of amorphous silicon solar cells: Case study in Thailand. *Journal of Ecological Engineering* 18 (4), 1–14.

Table 3 Fuel consumption and environmental emissions from conveyed modules per kWh of power generation

<i>Description</i>	<i>Unit</i>	<i>Quantity</i>
Fuel consumption		
Diesel	Litres	1.59E-04
Emission		
CO ₂	kg	5.08E-04
CO	kg	4.86E-06
CH ₄	kg	3.48E-08
NO _x	kg	5.79E-06
N ₂ O	kg	1.73E-08
NM VOC	kg	1.10E-06

Note: Chamsilpa, M., Vorayos, N., Katsiriroat, K., 2010. Environmental impact analysis of solar cell power plant compared with fossil fuel power plants in Thailand. *Asian Journal on Energy and Environment*, 103–117. Stoppato, A., 2008. Life cycle assessment of photovoltaic electricity generation. *Energy* 33, 224–232. Wasin, K., Somchai, M., Chantana, P., 2017. A comparison of the environmental impact of solar power generation using multi-crystalline silicon and thin film of amorphous silicon solar cells: Case study in Thailand. *Journal of Ecological Engineering* 18 (4), 1–14. Goedkoop, M., Spriensma, R., 2000. *The Eco – Indicator 99 – A Damage-Oriented Method for Life Cycle Impact Assessment*, second ed. PRÉ Consultants b.v.: Amersfoort. Henryk, M.S., 2011. Environmental impact of rail and road transport. *Economic and Environmental Studies* 11, 405–421.

Table 6 characterizes the summarised results for 1 kWh of power generation from solar energy. The impact of transportation and installation remained comparable to that of the generation of multi-crystalline PV solar cells. On the other hand, because of the recycling process, the environmental effects on a few impactful categories decreased. For example; the effects relating to change in climate, acidification or eutrophication, the respiration of inorganic as well as organic substances, and the extraction of minerals decreased by 53.33%, 50.57%, 46.68%, 25.09%, and 0.02% respectively solely because of recycling (Richard, 2008; Monier and Hestin, 2011; Anctil, 2012).

Table 4(a) Input associated with installation of solar cell modules per kWh power generated from solar cell power plant

<i>a-Si solar cell plant input</i>	<i>Unit</i>	<i>Solar cell array</i>	<i>Inverter stations</i>	<i>Transformer stations</i>	<i>Control center</i>	<i>Substations</i>
Solar energy	kWh	9.46E+00	0	0	0	0
Electricity	kWh	0	1.67E-03	1.14E-03	0.83E-03	1.32E-03
Water	cm ³	4.74E+01	0	0	2.88E+00	0
Arable land	M ²	1.67E-02	2.81E-05	1.41E-05	4.21E-05	5.61E-05

Note: Chamsilpa, M., Vorayos, N., Katsiriroat, K., 2010. Environmental impact analysis of solar cell power plant compared with fossil fuel power plants in Thailand. *Asian Journal on Energy and Environment*, 103–117. Stoppato, A., 2008. Life cycle assessment of photovoltaic electricity generation. *Energy* 33, 224–232. Wasin, K., Somchai, M., Chantana, P., 2017. A comparison of the environmental impact of solar power generation using multi-crystalline silicon and thin film of amorphous silicon solar cells: Case study in Thailand. *Journal of Ecological Engineering* 18 (4), 1–14. Goedkoop, M., Spriensma, R., 2000. The Eco – Indicator 99 – A Damage-Oriented Method for Life Cycle Impact Assessment, second ed. PRé Consultants b.v.: Amersfoort. Henryk, M.S., 2011. Environmental impact of rail and road transport. *Economic and Environmental Studies* 11, 405–421.

Table 4(b) Output associated with installation of solar cell modules per kWh power generated from solar cell power plant

<i>Output</i>	<i>Unit</i>	<i>Solar Cell Array</i>	<i>Inverter stations</i>	<i>Transformer stations</i>	<i>Control center</i>	<i>Substations</i>
CO ₂	kg	0.16E-04	12.1E-04	8.29E-04	6.06E-04	9.56E-04
CH ₄	kg	0.06E-05	4.84E-05	3.31E-05	2.43E-05	3.82E-05
N ₂	kg	0	1.40E-02	0.96E-02	0.70E-02	1.10E-02
O ₂	kg	0	2.52E-03	1.72E-03	1.26E-03	1.99E-03
Water Vapor	kg	0	0.96E-03	0.65E-03	0.48E-03	0.75E-03
NO	kg	0	1.69E-07	1.16E-07	0.84E-07	1.33E-07
NO ₂	kg	0	0.14E-07	0.09E-07	0.07E-07	0.11E-07
NO _x	kg	0	2.72E-07	1.86E-07	1.36E-07	2.15E-07

Note: Chamsilpa, M., Vorayos, N., Katsiriroat, K., 2010. Environmental impact analysis of solar cell power plant compared with fossil fuel power plants in Thailand. *Asian Journal on Energy and Environment*, 103–117. Stoppato, A., 2008. Life cycle assessment of photovoltaic electricity generation. *Energy* 33, 224–232. Wasin, K., Somchai, M., Chantana, P., 2017. A comparison of the environmental impact of solar power generation using multi-crystalline silicon and thin film of amorphous silicon solar cells: Case study in Thailand. *Journal of Ecological Engineering* 18 (4), 1–14. Goedkoop, M., Spriensma, R., 2000. The Eco – Indicator 99 – A Damage-Oriented Method for Life Cycle Impact Assessment, second ed. PRé Consultants b.v.: Amersfoort. Henryk, M.S., 2011. Environmental impact of rail and road transport. *Economic and Environmental Studies* 11, 405–421.

In spite of having lower waste generated and lesser harm done to the environment in comparison to the traditional crystalline silicon photovoltaic technology, the thin film amorphous silicon solar cells were unable to create a significant impact. The main reasons behind this were first, their low efficiencies given the higher requirement of land area for production and installation, and the second being, almost comparable consumption of resources with respect to multi-crystalline solar cells without much difference in results (Alsema *et al.*, 2006).

Effect of CdTe solar cells

The only thin film technology with costs lower than the conventional solar cells made of crystalline silicon in multi-kilowatt systems is the Cadmium Telluride photovoltaic solar cell (Gessert *et al.*, 2014; Zweibel *et al.*, 2008; David, 2008). Taking one lifecycle as the basis of calculation, CdTe PV potentially has the smallest carbon footprint, least water usage and shortest energy payback time of all prevalent solar technologies (Peng *et al.*, 2013; Fthenakis and Kim, 2010; de Wild-Scholten, 2013). The energy payback time of CdTe being less than a year accounts for the faster reduction in carbon emissions without short-term deficits of energy.

The toxicity of cadmium is a serious environmental concern which can be mitigated to a certain extent by the recycling of CdTe modules at the end of their lifetime (Fthenakis Vasilis, 2004). There are still uncertainties about proper recycling (Werner, 2011; Allen *et al.*, 2011) and the opinion, in general, is quite skeptical towards this technology (Trabish, 2012; Mullins, 2008). Cadmium being a rare earth material may also become a limiting factor to the scalability of CdTe technology at an industrial level in the near future.

The acute scarcity of tellurium – of which Telluride is the anionic form – is almost equivalent to that of platinum on the earth's crust thus, contributing significantly to the cost of the module (Woodhouse *et al.*, 2013). Despite the high manufacturing cost and the difficulty in availability of the raw materials required for production, CdTe technology is accounted for more than half of the thin film market in 2013 comprising of almost 5.1% of the global economy (Bagher *et al.*, 2015).

Cadmium is widely considered as one of the deadliest and toxic materials present on the surface of the earth. However, in terms of direct exposure, CdTe is apparently less toxic than cadmium in elemental form. This cannot be inferred to be harmless though. If ingested, Cadmium telluride is toxic in nature. It can cause serious respiratory and skin ailments if the dust is inhaled accidentally or if it is mal-handled (i.e., without wearing appropriate gloves and taking other necessary safety precautions). It has been recently

Table 5(a) Input associated with recycling of solar cell modules per kWh power generated from solar cell power plant

Description	Unit	Quantity
Glass	kg	-9.07E-02
Silicon	kg	Low
Aluminium	kg	-2.62E-06
Electricity	kWh	-1.97E-01

Note: Wasin, K., Somchai, M., Chantana, P., 2017. A comparison of the environmental impact of solar power generation using multi-crystalline silicon and thin film of amorphous silicon solar cells: Case study in Thailand. *Journal of Ecological Engineering* 18 (4), 1–14. Richard, M.G., 2008. Solar Industry Creates Scheme to Recycle Solar panels in Europe. Available at: <http://www.treehugger.com/files/2008/05/solar-panelsrecycling-recycled-europe.php>. Monier, V., Hestin, M., 2011. Study on photovoltaic panels supplementing the impact assessment for a recast of the WEEE directive. Available at: <http://ec.europa.eu/environment/waste/weee/pdf/Study%20on%20PVs%20Bio%20final.pdf>. Ancil, A., Fthenakis, 2012. Recyclability challenges in "abundant" material-based technologies. In: *Proceedings of the 27th European Photovoltaic Solar Energy Conference and Exhibition*. Alsema, E.A., Wild-Scholten, M.J., Fthenakis, V.M., 2006. Environmental impacts of PV electricity generation – A critical comparison of energy supply options. In: *Proceedings of the 21st European Photovoltaic Solar Energy Conference and Exhibition*.

Table 5(b) Output associated with recycling of solar cell modules per kWh power generated from solar cell power plant

EMISSION TO AIR	UNIT	QUANTITY
CO ₂	Kg	-5.49E-02
CH ₄	Kg	-1.13E-04
SO ₂	Kg	-1.87E-05
NO _x	Kg	-2.71E-05
PM	Kg	-1.72E-06

Note: Wasin, K., Somchai, M., Chantana, P., 2017. A comparison of the environmental impact of solar power generation using multi-crystalline silicon and thin film of amorphous silicon solar cells: Case study in Thailand. *Journal of Ecological Engineering* 18 (4), 1–14. Richard, M.G., 2008. Solar Industry Creates Scheme to Recycle Solar panels in Europe. Available at: <http://www.treehugger.com/files/2008/05/solar-panelsrecycling-recycled-europe.php>. Monier, V., Hestin, M., 2011. Study on photovoltaic panels supplementing the impact assessment for a recast of the WEEE directive. Available at: <http://ec.europa.eu/environment/waste/weee/pdf/Study%20on%20PVs%20Bio%20final.pdf>. Ancil, A., Fthenakis, 2012. Recyclability challenges in "abundant" material-based technologies. In: *Proceedings of the 27th European Photovoltaic Solar Energy Conference and Exhibition*. Alsema, E.A., Wild-Scholten, M.J., Fthenakis, V.M., 2006. Environmental impacts of PV electricity generation – A critical comparison of energy supply options. In: *Proceedings of the 21st European Photovoltaic Solar Energy Conference and Exhibition*.

Table 6 Characterised results for 1 kWh of power generation from solar energy

Category impact	Unit	Module manufacturing	Transportation	Installation	Recycling	Total
Carcinogenic	DALYs	0	0	0	0	0
Resp. organic	DALYs	2.52E-12	1.41E-12	1.85E-12	-1.45E-12	4.33E-12
Resp. inorganic	DALYs	8.08E-09	5.14E-10	1.44E-10	-4.08E-09	4.66E-09
Climate change	DALYs	2.10E-08	1.10E-10	1.40E-09	-1.20E-08	1.05E-08
Radiation	DALYs	0	0	0	0	0
Ozone depletion	DALYs	0	0	0	0	0
Ecotoxicity	PDF*m ² *yr	1.15E-02	0	0	0	1.15E-02
Eutrophication	PDF*m ² *yr	3.04E-04	3.31E-05	9.27E-06	-1.75E-04	1.71E-04
Land use	PDF*m ² *yr	0	0	1.41E-02	0	1.41E-02
Mineral	MJ surplus	4.46E-02	0	0	-6.24E-06	4.46E-02
Fossil fuel	MJ surplus	0	7.97E-04	0	0	7.97E-04

Note: Goedkoop, M., Spriensma, R., 2000. *The Eco – Indicator 99 – A Damage-Oriented Method for Life Cycle Impact Assessment*, second ed. PRé Consultants b.v.: Amersfoort. Richard, M.G., 2008. Solar Industry Creates Scheme to Recycle Solar panels in Europe. Available at: <http://www.treehugger.com/files/2008/05/solar-panelsrecycling-recycled-europe.php>. Monier, V., Hestin, M., 2011. Study on photovoltaic panels supplementing the impact assessment for a recast of the WEEE directive. Available at: <http://ec.europa.eu/environment/waste/weee/pdf/Study%20on%20PVs%20Bio%20final.pdf>. Ancil, A., Fthenakis, 2012. Recyclability challenges in "abundant" material-based technologies. In: *Proceedings of the 27th European Photovoltaic Solar Energy Conference and Exhibition*. Alsema, E.A., Wild-Scholten, M.J., Fthenakis, V.M., 2006. Environmental impacts of PV electricity generation – A critical comparison of energy supply options. In: *Proceedings of the 21st European Photovoltaic Solar Energy Conference and Exhibition*.

studied that the highly reactive surface of cadmium telluride quantum dots aggravates extensive reaction with oxygen thus causing potential damage to the cell membrane, mitochondria, and cell nucleus (Marco *et al.*, 2007). Thus, it cannot be concluded that the resulting toxicity is solely attributed to the cadmium content.

In addition to this, the recrystallization of cadmium telluride is typically done with the toxic compound of cadmium chloride. In the large-scale commercialization of cadmium telluride solar panels, the disposal and degradability are the major concerns. It has been recently suggested by scientists from the U.S. Department of Energy, Brookhaven National Laboratory, that large-scale use of CdTe PV modules does not present any significant risk to human health and the environment. Moreover, recycling the modules at the end of their useful life resolves a large portion of the environmental concerns. It has also been found that during their operation, these modules do not produce any pollutants, unlike fossil fuels, thus becoming an eligible candidate for green technology. Among all the present uses of cadmium, CdTe PV modules are apparently more environmentally friendly than the rest.

However, the approach of safety with respect to the use of CdTe in the European countries and China is, much more skeptical and cautious. In the European Union, cadmium and its compounds are identified as toxic carcinogens. Likewise, regulations in China allow all Cd products for export only. The issue of regulating the use of Cadmium Telluride is currently being discussed in Europe (see "Relevant Websites section").

Effect of quantum dots

The diversity involved in the synthesis of QD makes the topic of QD toxicity somewhat ambiguous. Hence, to avoid confusion, the first thing that should be considered is the difference in the physical and chemical properties of QDs with varying synthesis methods. The lack of studies based on toxicology, the varied concentrations of exposure or dosage of QD accounted in the scientific literature, combined with the widely varying physicochemical properties of individual QDs are the basic reasons why the studies of QD toxicity is anomalous.

Concentrates specifically intended for toxicologic appraisal (e.g., portion, term, recurrence of introduction, systems of activity) are not many. A large number of the investigations from which QD poisonous quality data is inferred and that have been referred to in reference to QD harmfulness were performed by nanotechnology specialists as opposed to toxicologists or well-being researchers. The greater part of the present investigations inspected here was intended to make inquiries concerning the physicochemical properties of novel QD items, for example, fluorescence, perceptibility, steadiness, and cell naming efficacy, not QD poisonous quality as such. Critically, and a potential wellspring of perplexity in surveying QD lethality, QD poisonous quality relies upon various components got from both individual QD physicochemical properties and natural conditions: QD estimate, charge, focus, external covering bioactivity (topping material, useful gatherings), and oxidative, photolytic, and mechanical dependability have each been appeared to decide factors in QD harmfulness.

For instance, some QDs have been observed to be cytotoxic simply after oxidative and additionally photolytic corruption of their center coatings. Last, in light of the fact that QD dose/introduction varies greatly in their units of estimation (e.g., milligrams per milliliter, molarity, milligrams per kilogram body weight, number of QDs per cell), associating measurement crosswise over current investigations is difficult. Despite the fact that the potential unfavorable impacts of nanomaterials on nature and human well-being have as of late been tended to by research activities sorted out under the National Science Foundation and the U.S. Ecological Protection Agency, no real data is presently accessible with respect to courses of QD introduction, QD security, aerosolization, half-lives, and how they parcel into natural media are right now ineffectively comprehended. Be that as it may, thought of introduction courses might be extrapolated based on what is known with respect to materials of comparative size and physicochemical properties.

Potential courses of QD introduction are hugely dependent on ecology, work environment, and helpful or demonstrative organization. Working environment exposures (e.g., engineers, analysts, clinicians) may result from inward breathing, dermal contact, or ingestion. For inward breath highways, a broad assemblage of toxicologic research exists on other nanoscale particles (e.g., asbestos, ultrafine particles) that may give an establishment from which approach to QD inward breath is considered. QDs differ in size, extending from around 2.5 nm up to 100 nm, contingent upon covering thickness and shift in their destinations of testimony in pneumatic tissues once aerosolized. For example, QDs < 2.5 nm may affect the lung and connect with the alveolar epithelium, while bigger aerosolized QDs get accumulated in bronchial spaces. Be that as it may, under what conditions QDs aerosolize and whether they structure totals in encompassing air are not known (Oberdörster *et al.*, 2005). Inward breath exposures may present potential dangers given that QDs have been appeared to be joined by means of endocytosis by an assortment of cell types and may live in cells for a considerable length of time extending up to months. The dangers due to exposures through dermal assimilation and unintentional ingestion may present is right now obscure.

The probable cause for significant concern through the course of introduction, given the social and monetary estimation of helpful/analytic QD items, are exposures coming about because of QD organization to people for restorative purposes. These sorts of exposures are at present hypothetical, as QD items are not right now endorsed for remedial/analytic purposes only. In any case, the potential for undesired/unforeseen impacts coming about because of the therapeutic/symptomatic organization of these materials likely will figure conspicuously in the improvement of medicinally based QD items. Their potential lethality by means of managerial courses of presentation is the very subject to a suite of variable and ineffectively gotten elements: QD toxico-and pharmacokinetics, toxico-and pharmacodynamics, and in vivo strength. It can be assumed that when QD energy and elements are quantified and proper kinetic analysis is made, the dangers presented by these exposures might be alleviated through quality control instruments (e.g., consistency and unwavering quality in volume creation), as they right now are with pharmaceuticals.

Exposures through ecological media (pollution) are a potential course of concern fundamentally as a result of QD metalloid center synthesis, and to some degree on account of QD center coatings. Numerous QD center metals (e.g., Cd, Pb, Se) are known to be dangerous to vertebrate frameworks at moderately low focuses (parts per million). Understanding the dangers presented by QDs in the earth is complex in nature, as poisonous quality differs broadly with the concoction condition of the metals, and natural change/debasement and parceling; which in turn will decide the dimension of the human wellbeing risk. As of now, nothing is known with respect to the soundness of QDs in the earth, item lifetimes, or how these materials segment into natural media. Presentation of QDs into natural media may happen by means of waste streams from enterprises that incorporate or use QDs and by means of clinical and research settings. Thus, transfer of QD materials and the dangers of spillage and spilling amid assembling and transport are potential wellsprings of concern. Ecological exposures are a significant hotspot for a few reasons: (a) the natural centralization of anthropogenic substances increments in direct extent to their utilization in the public eye, and given their wide scope of uses, QDs may see considerable change in generation volumes; (b) the half-existence of these materials might be very long (months to perhaps years); and (c) natural presentation will rely upon where these materials degrade (e.g., air, water or soil). As a result of the decent variety of physicochemical properties among the diverse sorts of QDs, almost certainly, illustrating ecological dividing will be troublesome. These are vital contemplations given that corruption of these materials in natural media, in the occasion they achieve ecological compartments, will without a doubt happen, and their rates of rot are probably going to be exceedingly factor, contingent upon both QD physicochemical qualities and the ecological media in which they segment.

Albeit little data right now exists with respect to courses of QD introduction, all courses depicted are of potential concern given QDs have been appeared to be fused into an assortment of cell types through endocytic components. Ebb and flow explore likewise recommends that there might be a danger of bioaccumulation of these materials (e.g., metals) in organs and tissues, as QDs have been appeared to live in cells for a considerable length of time to months and conceivably may give issues body troubles. Basic to all courses of introduction is the issue of QD soundness. For all intents and purposes, nothing is thought about QD digestion invertebrate creatures or their courses of discharge. In spite of the fact that QDs have been appeared to corrupt under photolytic and oxidative conditions, debasement items have not been identified/defined in vivo apart from the arrival of part center metals, for example, Cd and Se. It can be inferred, in regards to the courses of presentation, it is critical to recollect that not all QDs are similar; every individual QD type has its very own one-of-a-kind physicochemical properties that will direct its presumable course of introduction.

In vitro examinations recommend certain QD types might be cytotoxic. It was found that CdTe QDs covered with mercaptopropionic corrosive (MPA) and cysteamine was cytotoxic to rodent pheochromocytoma cell (PC12) societies at concentrations of 10 µg/mL (Lovric *et al.*, 2005). Uncoated CdTe QDs were cytotoxic at 1 µg/mL. Cell demise was the consequence of chromatin build-up and membrane blebbing, symptomatic of apoptosis. Cytotoxicity was increasingly articulated with lesser decidedly charged QDs (2.2 ± 0.1 nm) than with bigger similarly charged QDs (5.2 ± 0.1 nm) at equivalent concentrations (cytotoxicity controlled by MTT [3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide] examination).

QD estimate was likewise seen to influence subcellular appropriation, with smaller cationic QDs confining to the atomic compartment and bigger cationic QDs limiting to the cytosol. The instruments engaged with cell passing were not known but rather were viewed as because of the nearness of free Cd (QD center debasement), free extreme development, or communication of QDs with intracellular segments prompting the loss of capacity. The impact of QD-instigated responsive oxygen species on cell demise was evaluated with N-acetylcysteine (NAC; a known inhibitor of Cd poisonous quality), cow-like serum egg whites (BSA), and Trolox (a water-solvent nutrient E). Both NAC and BSA yet not Trolox significantly diminished CdTe QD harmfulness, proposing that QD-actuated lethality might be in part initiated by Cd. Researches show that treatment with the QD topping material mercaptoundecanoic corrosive (MUA) alone (without QD) for 12 h caused extreme cytotoxicity in murine T-cell lymphoma (EL-4) cells at 100 µg/mL (Hoshino *et al.*, 2004a). A 12 h Treatment with cysteamine alone demonstrated weak genotoxic nature at 100 µg/mL. Henceforth, cytotoxicity was credited to QD topping material instead of the center metalloid complex itself (Hoshino *et al.*, 2004b). It is, notwithstanding, impossible that the danger seen can be exclusively ascribed to the QD coatings (MPA and cysteamine), as both size and charge and the impacts of NAC and BSA recommend something else (Lovric *et al.*, 2005). CdTe QD- instigated cytotoxicity appeared to be somewhat subject to QD estimate and might be expected to be a consequence of QD covering intracellular responses of the surface coatings, or intracellular debasement of QDs to metalloid particles. QD-actuated toxicity was observed in the MUA-covered CdSe/ZnS QDs which were seen to be cytotoxic to HeLa cells and essential human hepatocytes at centralizations of 100 µg/mL (MTT measure) (Shiohara *et al.*, 2004).

A few in vitro and in vivo investigations have been referred to in the writing as showing an absence of proof for QD-instigated cytotoxicity (Hoshino *et al.*, 2004a; Ballou *et al.*, 2004; Dubertret *et al.*, 2002; Jaiswal *et al.*, 2003; Larson *et al.*, 2003; Voura *et al.*, 2004). But a couple of the above examinations do propose that QDs can influence cell development and suitability. QD micelles, CdSe/ZnS QDs in a hydrophobic center of n-polyethyleneglycol phosphatidylethanolamine (PEG-PE) and phosphatidylcholine, brought about cell variations from the norm (feasibility, motility) when infused into *Xenopus* blastomeres at convergences of 5×10^9 QDs/cell (~ 0.23 pmol/cell), though cells infused with 2×10^9 QDs/cell displayed a typical phenotype and were said to be factually like un-injected developing lives (Dubertret *et al.*, 2002). Henceforth, QD cytotoxicity was additionally observed to be portion subordinate (Hoshino *et al.*, 2004a). EL-4 cells brooded (10^6 cells/well) with concentrations varying in the order of 0.1, 0.2, and 0.4 mg/mL of CdSe/ZnS- SSA QDs displayed a dose- reaction relationship on a 24 h basis. Cell reasonability diminished at QD fixations above 0.1 mg/mL, and practically all phones brooded with 0.4 mg/mL were nonviable past 6 hr period. Curiously, roughly 10% of EL-4 cells held QDs following 10 days of culture. The fluorescence force (QDs) of cells slowly diminished and was exceptionally amassed in

endosomes, proposing intracellular corruption of QDs. Despite the fact that cytotoxicity was seen at 0.1 mg/mL in vitro, EL-4 cells brooded in 0.1 mg/mL SSA-conjugated QDs, and in this way infused into naked mice, were not identified to be dangerous in vivo. Another resulting study (Lovric *et al.*, 2005) watched reversible DNA harm in WTK1 cells (comet measure). DNA harm was noted after 2 h of treatment with 2 μ M QD- COOH (carboxylic corrosive), yet after 12 h, QD-actuated DNA harm was effectively fixed.

Thus, it can be proposed that QD poisonous quality relies upon different variables derived from both the intrinsic physicochemical properties of QDs and ecological conditions. QD measure, charge, fixation, external covering bioactivity (topping material and practical gatherings), and oxidative, photolytic, and mechanical solidness are each factor that, all things considered, and independently, can decide QD harmfulness. Of these physicochemical attributes, practical covering and QD stability of the core unmistakably and likely are the significant factors in evaluating the danger of QD poisonous quality in certifiable presentation situations.

Effect of perovskites

The life cycle assessment (LCA) approach is implemented in the following studies on one agent i.e., tin-based PSC, which has been accounted for to reach up to 6.4% of intensity change efficiency (Noel *et al.*, 2014) along with two lead-based perovskites cells (Espinosa *et al.*, 2015). The three structures investigated are (a) Glass-ITO/PEDOT:PSS/lead-perovskite/PCBM/Al (You *et al.*, 2014), (b) Glass-FTO/TiO₂/lead-perovskite/Spiro-OMeTAD/Ag (Liu *et al.*, 2013) and (c) front terminal (FTO) Glass/minimal TiO₂/tin-perovskite+ mesoporous-TiO₂/Spiro-OMeTAD/Gold (Hao *et al.*, 2014). The areas of investigation primarily incorporate the extraction of fossil fuels for the production and installation of the PSC modules. The other primary areas of investigation in the arena of PSC modules include (1) landfill and (2) incineration succeeded by incomplete recuperation of metals. The practical unit for this survey is taken to be a supply of 1 kWh of energy, being required by 114.89 cm² of light harvesting area (yearly insolation of 1700 kWh m⁻² and 80% of execution proportion or performance ratio).

The Life Cycle Data System (ILCD)26 strategy was chosen to evaluate other natural effects of tin-based PSCs and contrasted it with the effects of two toxic PSCs. Results demonstrate that the creation of a practical unit of tin-based PSCs devours more energy than lead PSCs and it presents bigger ecological effects, for the most part, brought about by its low efficiency. The evaluation of the energy and lifecycle discharges of the tin-based PSC reveal that the epitomized energy per useful unit is 124.1 MJ kWh⁻¹ and the identical measure of CO₂ is 9.4 kg kWh⁻¹; the two qualities practically two fold than those for the lead-based PSCs. The tin-based PSC has bigger ecological effects than both toxic PSCs in almost all classifications. Specifically, tin-based PSCs score multiple times higher in resource consumption than the other PSCs where the FTO is in charge of $\approx$ 40% of this effect (mostly from tin production) and the back-anode represents $\approx$ 60% (due to the expensive means for extraction of gold, where the related mining process has a high ecological effect, particularly for open-pit mining).

To match the production of one functional unit, tin PSC requires twice the land area than that of the other lead-based PSCs, due to their lower efficiency. The only mean by which this difference between the two categories can be reduced is a noticeable improvement in the power conversion efficiency of tin-based PSC. In case of environmental change, the ascent in efficiency ought to be 12.4%, for human lethality 28% and 109%– malignancy and noncancer impacts, respectively– and an increase in 55% in efficiency for having comparative resource exhaustion scores. If hypothetically, silver is considered as the back anode for tin-PSC, rather than gold, the expected proficiency to rival lead-PSC would be 12% in all shown classes, aside from resource depletion which would be 24%. Despite stability being the main drawback, the lead-based PSCs do offer promising results in low cost compared to the existing technologies (Hwang *et al.*, 2015).

With respect to the impacts of lead on human toxicity, effects of tin are negligible in the sphere of both malignant and benign effects of this impact category. The major concern with lead lies in the stage where the life cycle of the lead-based PSCs end. The European restriction on hazardous substances (RoHS) (Bagher *et al.*, 2015) is the amount of lead which is limited by weight in any homogeneous material. If the mixture of TiO₂with perovskite and spiroOMeTAD as a homogeneous layer is considered, the lead content is 0.55% for the tin-based PSC (Green *et al.*, 2014). In this case, the percentage slightly exceeds the already established RoHS limit. Due to the fact that the finish of-life for the perovskite solar cell is as yet an unexplored field, and can bargain the security of this new innovation, diverse courses are yet to be analyzed before concluding straight away.

In the first transfer situation, the cells are landfilled, while in the second situation the cells are burned including the recuperation of lead from the cinders. At the point when the cells are landfilled, the lead is produced to the earth through draining impacts also known as leaching (Spalvins *et al.*, 2008). In the most pessimistic scenario, it is viewed as that up to 70% of lead will be extracted in the first year (Hailegnaw *et al.*, 2015). The second situation is the point at which the combustion of cells takes place and the lead is recouped from the debris (Nagib and Inoue, 2000), where 98% of lead is recuperated by treating it in a basic solution.

To account for recycling benefits, the most common approach is that of calculating “environmental credits”. This method employs substitution of the newly produced materials along with the recycled materials which are coined as “environmental” credits. It has been assumed that the inherent properties of the recycled materials are unchanged and have the same properties that they possessed before combustion. Thus, the recycled products are safe enough to suitably replace the original materials (ISO, 2006) The recovered energy from materials from the incineration processes is regarded as an “environmental” credit which acts as a suitable alternative to the energy produced from conventional sources of energy.

The human health (cancer and noncancer effects) and fresh water, and resource depletion are the most affected categories due to both manufacturing as well as recycling of the PSCs. The impact of perovskite layers is 36.8% on malignancy and human toxicity, followed by the waste treatment of polyethylene terephthalate which holds for about 28.4%, the front electrode comprising of 15.9% and 12.8% in case of back electrode. Because of the small amount of lead that the solar cells are comprised of, lead recovery is not very feasible. An innovative approach suggests that these lead PSCs after use can be utilized as lead-storage devices,

thus averting pertinent problems like lead disposal and/or extraction at the end of the life cycle, etc. According to a section of the scientific community, these devices can be transformed into long-term storage cells for lead especially the ones that have been recycled from car batteries (Li *et al.*, 2015; Chen *et al.*, 2015).

In spite of the pressing concern of higher toxicity of lead over tin as individual elements, the latter suffers from drawbacks too many to be considered as the ultimate photovoltaic technology. Though Tin is almost 6.3 times more expensive than lead, (LME) yet it is the third most critical metal in strategic energy technologies. Tin production is fairly concentrated, taking place mainly in countries with high political risks, such as China, Indonesia, and Peru, which together make up about 82% of the world in supply thus questioning the availability of the metal throughout the world (Moss *et al.*, 2011). It is apprehended that the terrestrial ecotoxicity and global warming contribution due to the tin can be ten times more than that of lead (Voet *et al.*, 2013). Thus it can be said that though PSC is a very promising candidate to replace all the existing solar-based technology, yet needs a significant scientific breakthrough to stay true to its promise.

Conclusion

The biggest drawbacks that hindered the growth of traditional silicon-based photovoltaic cell generation were the total cost involved throughout the manufacturing, transporting, installing processes and the adversities that the technology burdened the environment with. These very reasons gave the scientists and technologists a drive to develop cleaner technologies as suitable alternatives to the existing PV cell sector. Along the course of this article, various limitations of these inventions have been identified.

Just after a few decades of analyzing the derogatory side of crystalline Si PV cells, thin film amorphous silicon cell technology came into being. The apparently cost-friendly amorphous cell technology suffered its major setback when the efficiency of the cell in question failed to be compatible with the area of land it required for manufacturing and the number of natural resources it consumed for production as well as recycling.

Similarly, the other second-generation solar cell technology viz Cadmium Telluride cells or CIGS cells could not mark a significant impact. On analyzing the environmental perspective, Cadmium which is identified as one of the most toxic elements on earth poses danger not only from the degradability point of view but also is considered a notorious carcinogen. Moreover, the scarcity of the element also made this technology an economically unfeasible one. Stringent laws in regards to the manufacture and regulatory duties dealing with Cadmium make the mentioned technologies almost skeptical for commercialization.

Perhaps the most promising alternative to the traditional PV cell technology is the Quantum Dot Cell. One of the chief concerns regarding the eco-friendly nature of QDs is the usage of Cadmium and selenium, two of the most widely used constituent metals in QD core metalloid complexes. These two metals are widely known to be the cause of acute and chronic toxicities in not only vertebrates but are also capable of considerable human health and environmental derogation. Since QDs are comprised of highly engineered nanomaterials, the toxicity of each type varies with both inherent physicochemical properties and environmental conditions. The size, charge, concentration, outer coating bioactivity, oxidative, photolytic, and mechanical stability all play key roles in the variance of QD toxicity. Since generalization is not possible in the case of quantum dot cell technology, further concentrated researches are required to be conducted in details as the QDs definitely do not qualify to be environmentally absolutely harmless.

The final topic of discussion was the analysis of the much-popularised Perovskite Cell technology from a “clean technology” frame of reference. The two main types of perovskite cells discussed in this review were tin-based and lead-based cells. Though the toxicity of lead is higher than tin, the lead-based perovskite is less harmful than tin PSC. The reason being the usage of comparatively harmless lead iodide in the former one. A detailed optimization study has to be conducted with the other forms of PSCs like gold, OPV, etc to assess holistically. It has also been discussed on how incineration has advantages over landfill at the end of the PSC life cycle.

Though the most recent technology in the form of Quantum Dots and Perovskites exhibit adversities and a toxic facet, yet it is believed that troubleshooting is possible. If researchers and scientists work extensively on eradicating the small but unmistakable environmental and economic concerns, then the optimism with which these technologies rose to prominence will not go in vain.

The vision with which the renewable energy especially solar energy was developed over the years was considered almost successful with the significant lower carbon emission associated with manufacturing, installing and using the alternative solar cell technology. But what scientists termed as “hidden carbon footprint” or “Carbon debt” along with effects on the other environmental aspects are to be very cautiously scrutinized. An overview of a few highlighted environmental issues due to the usage of the alternative PV cell technology has been discussed in this article. Detailed and more in-depth research related to the mitigation of environmental hazards can surely bring about a path-breaking change in the future commercialization of alternative photovoltaic energy.

See also: Thermoelectric Materials: Improving Energy Efficiency and Decreasing CO₂ Emissions

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Application of Remote Sensing in Wind Resource Assessment

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Introduction

The high-quality wind measurement is a fundamental and pressing need in wind energy industry particularly at higher heights as well as in hilly and complex terrain. The modern wind turbines are becoming bigger and higher, reaching into the unknown turbulence and wind regimes in the atmosphere. It is essential to assess the availability of wind resource before starting the wind project in terms of atmospheric characteristics that may generate turbulence, power production and for a successful return on the project investment (Pena *et al.*, 2015).

The mast mounted cup anemometer is only accepted and calibrated sensor for both wind resource and power performance testing. However, the increase in turbine size has exposed the challenges related to cup anemometer measurement-point measurement i.e., it is important to place the cup anemometer at wind turbine hub-height, with increase in turbine's height cup anemometry measurement and instrumentation becomes expensive, cumbersome and logistically complex affair. Additionally, the present practice of measuring power performance on a single hub-height point measurement is not technically representative for large swept areas. So, to mitigate this challenges wind energy industry requires multi-height and volume measurement strategy for measuring wind distribution at the tip of the turbine blade as well as over the entire rotor of wind turbine (Courtney *et al.*, 2008). The remote sensing instruments can play a significant role in mitigating above challenges and can be used as an alternative technique for meteorological mast erection.

The most promising, accurate and quantitative remote sensing techniques for wind energy measurement includes sound and light wave propagation and backscatter detection based instrument for example SODAR, LIDAR, Scatterometry and SAR. The SODAR (Sound Detection and Ranging) and LIDAR (Light Detection and Ranging) are direct measurement and works on the principle of Doppler shift, scatterometry works on proxy-empirical calibration methods. The remote sensing instrument can serve wind energy sector for a number of purposes such as Wind resource assessments, wind park development projects, Power curve measurements, Bankability, Wind model and wind resource (wind atlas) uncertainty evaluation (Pena *et al.*, 2015). Furthermore the recent and improved developments have helped wind energy industry to integrate wind LIDAR directly into wind turbine blade, hub and spinners. These developments extended the performance of LIDAR for enhanced wind turbine yaw control, lead-time control for individual pitch control, prolonging the wind turbine longevity, protection against fatigue.

Wind lidars in the market for vertical mean and turbulence profile measurements are available based on two different measurement principles i.e., Continuous wave (CW) lidars Pulsed lidars. Several wind lidars are commercially available in the market. CW based wind lidars are manufactured by Natural Powers (ZephIR) and OPDI Technologies & DTU Fotonik (WINDAR) while Coherent Technologies Inc. (Wind tracer), Leosphere (WindCube), CatchtheWindInc (Vindicator) and Sgurr Energy (Galion) manufacture pulsed lidars. There are several sodar manufactures on the wind RS market today including for example Remtech, Atmospheric Systems Corporation (formerly Aerovironment), Metek, Scintec, Second Wind Inc. and Swedish AQ System to mention the most dominant.

This article presents the brief overview of different remote sensing technique used in wind energy sector along with the case study, measurement campaign conducted at the southern part of India.

Remote Sensing of Wind

Light Detection and Ranging (LiDAR)

It is an active ground-based optical remote sensing instrument that transmits the electromagnetic signal and then analyzes the backscattered signals that are received back to determine the information of atmospheric particle from which the electromagnetic energy or waves scatter. The light signals strike the atmospheric particle such as water droplet, dust, pollen and salt crystals that are suspended and travelling along at the speed of the wind. The speed of wind can be determined by detecting the change in backscattered wave's frequency. It measures data across ten user-defined heights up to 300 m and measures fifty data across 360-degree scan every second. The frequency of the emitted light (f_E) is reflected back to the receiver (f_R) changes due to the interaction with the moving aerosols particles available with the wind. The change in frequency - its Doppler shift (Δf) can be measured as

$$\Delta f = f_R - f_E \quad (1)$$

and the speed of the aerosols in the line-of-sight of the laser orientation (V_{LoS}) can then be calculated as

$$V_{LoS} = -\Delta f \times \lambda \quad (2)$$

where λ wavelength of laser emissions.

The Fig. 1 below shows the working principle and components of ZephIR 300 Wind LiDAR.

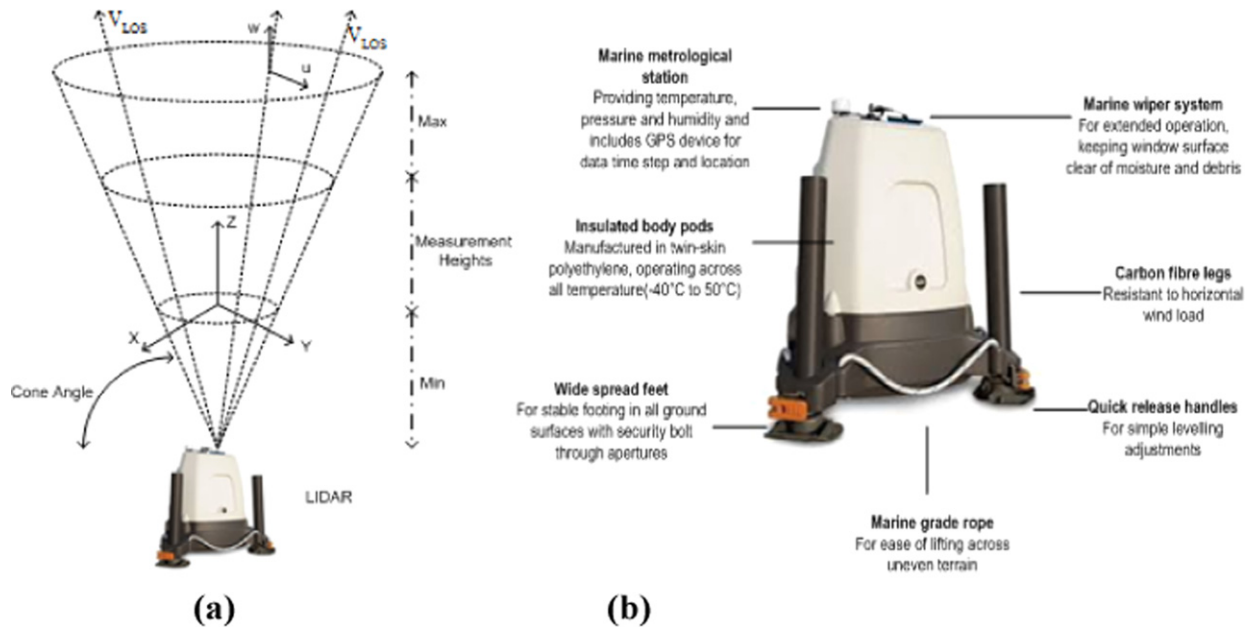


Fig. 1 (a) Working principle and (b) different components of ZephIR 300 Wind LiDAR.

Wind LiDAR for measurements are available based on two measurement principles i.e., Continuous Wave (CW) LiDARs and Pulsed LiDARs.

Continuous wave (CW) LiDAR

The CW LiDAR emits a continuous beam of laser at a measurement height and the backscatter beam is detected due to Doppler shift. The measurement range and spatial resolution is controlled by the focal properties of the telescope as well as for the multi height measurement the CW LiDAR adjusts its telescope. This LiDAR system operates in the telecommunications near-IR band around $1.55 \mu\text{m}$. Motion of the target in the beam direction causes change in the frequency of the light via Doppler shift. This shift in frequency is correctly measured by the return signal and the resulting beat is sensed by the photodetector at the different frequency. CW LiDAR is a simplest form of LiDAR which operates at a given range by beam focussing and wind profiling is done by continuously scanning the beam. The output signal is digitized by an analogue to digital converter, after that Fast Fourier Transformation (FFT) generates a Doppler spectrum and at last the value line of sight wind speed can be evaluated using velocity estimation algorithm (Pena *et al.*, 2015; Courtney *et al.*, 2008).

Pulsed wave LiDAR

In pulsed wave lidar the laser pulses are transmitted into the atmosphere and are scattered due to the presence of small dust particle. The pulsed wave lidar uses the optical heterodyne detection for the measurement of wind and aerosols entrained in the atmosphere. A pulsed LiDAR has a continuous wave laser, known as master oscillator to generate the local oscillator beam as well as to generate the powerful transmitted pulse. The master oscillator supplies the laser wavelength, the laser line width, the laser intensity noise and the state of polarization. The pulsed laser sends cyclic pulses of high energy. The pulse time period is some hundreds of nanoseconds, that determine the length of the pulse in the atmosphere and so the spatial resolution. Once the pulse leave the laser, the detector starts to detects the backscatter signal from the range gates. The pulse first crosses the telescope optics and produces a zero Doppler signal which is used as a reference for the zero distance. The collected signal from each pulse provides the total wind speed information (Pena *et al.*, 2015; Courtney *et al.*, 2008; Lang and McKeogh, 2011).

The key difference between Continuous Wave LiDAR and Pulsed LiDAR are as follows (Table 1):

Sound Detection and Ranging (SODAR)

Sodar is an acronym for Sound Detection and Ranging and has commercially been used in the wind industry since 1980 for various purposes such as micrositng, wind resource assessment, wake measurement etc. The advances in SODAR technology have enhanced the accuracy and reliability of SODAR systems. SODAR is a ground based remote sensing technique works on Doppler principle. SODAR transmits a short acoustic sinusoidal 'chirps' (a sound beam) vertically upward into atmospheric boundary,

Table 1 Key difference between CW and Pulsed Wave LiDAR

Parameters	Continuous wave LiDAR	Pulsed wave LiDAR
Velocity accuracy	Restricted by the coherence time	Restricted by the pulse duration
Range gate	Determined by focus, increases as R^2 increase	Constant around $CT/2$
Number of range gates	Less than 10	More than 100
Laser source	1000 mW laser	10 mW and 200 mW power amplifier
Linear polarization	Not necessary	Essential
Maximum range	Few hundred of meters	To some kilometers

Note: Pena, A., Hasager, C.B., Badger, M., *et al.*, 2015. Remote sensing for wind energy. DTU Wind Energy. DTU Wind Energy-E-Report-0084 (EN). Courtney, M., Wagner, R., Lindelow, P., 2008. Commercial lidar profilers for wind energy: A comparative guide. In: Proceedings of the European Wind Energy Conference, Brussels, Belgium, (April).

**Fig. 2** Second wind TRITON SODAR.

while at the same time the backscattered chirps is reflected back to the receiver. The wind speed, direction and turbulent structure depending on sonic frequency, system's power output, atmospheric stability and existing noise environment are determined by using intensity and Doppler shift of the returned signals at lower atmosphere approximately 2 km. The mono-static phase array SODAR is mostly used for wind resource assessment. The amount of backscattering results from turbulent fluctuations is about half of the wavelength of the sound pulse. This scattering is known as Bragg scattering. The power of the signal received by the receiver is a function of the emitted power and the scattering that occurs. The power received by the receiver can be mathematically written as (Pena *et al.*, 2015; Lang and McKeogh, 2011):

$$P_R = P_0 \frac{A_R}{R^2} L_v e^{(-2r\alpha)} \sigma(R)_E \quad (3)$$

Where, P_R is the received power, P_0 is the transmitted power, α is the atmospheric attenuation, A_R is the effective area of the receiver, L_v is probe length $\sigma(R)_E$ is the scattering cross-section at range r . The term $P_0 A_R L_v$ can be described as a 'system function' which is specific to each SODAR (Fig. 2).

Commercial SODAR devices are available in a various configurations:

Monostatic phased array SODAR

These SODAR systems have an array of transceivers, arranged in a rectangular framework. A phase delay between transceivers and the emitted sound chirps in a particular direction make a SODAR listen to provide a signal.

Similarly, Monostatic multiple independent antennas SODAR utilize three or more transceivers to emit sound chirps and record the backscattered sound signal. The antennas are configured such that the three components of the wind can be acquired using a multi-beam.

Bistatic phased array SODAR

Bistatic SODAR uses a separate transmitter and receiver to explore the atmosphere. Both the transmitter and receiver scan the vertical volume to provide vertical component of the wind field. In other hand the transmitter can transmit vertically and the receivers can alter their azimuth to measure at different elevations.

Scatterometry

The Synthetic Aperture Radar (SAR) is an instrument that processes the backscattered signal but only wind speed measurements can be retrieved. Radar scatterometers, operates at different sub-bands of the microwave range of electromagnetic spectrum and are used to draw near-surface wind speed and direction over the ocean from sun-synchronous satellites.

Mitigating Greenhouse Gas and Carbon Footprint

The concern to decrease greenhouse gas emission is gaining a huge attention globally. Carbon dioxide is one of the major constituent to accelerate greenhouse gas emission. The various countries have initiated several policies to minimize the carbon emissions, such as encouraging development of renewable energy and technical innovation in renewable energy sector. The renewable energy like wind power, solar and biogas may provide an alternative opportunity to reduce greenhouse gas emission and global warming issues through restricting the utilization of conventional energy resources. According to the report of Global Carbon Project, last year (2017) China produces 27% of global emissions, United States accounts for 15% of emissions, the European Union 10% and 7% is emitted by India. China's emissions are projected to go up 4.7%, United States emissions are expected to increase 2.5% and India's emissions are projected to rise 6.3% in 2018.

The greenhouse emission can be reduced by identifying the sources of emission, which can be obtained by proper measurement, monitoring and corroboration of GHG emissions. A Carbon footprint can be measured by undertaking a GHG emissions measurement or other calculative activities denoted as carbon accounting. Once the volume of a carbon footprint is acknowledged, a strategy can be devised to reduce it, e.g., by technological developments, use of green energy sources, reduction of fossil fuel consumption, appropriate waste management and recycling to save material cost and energy, carbon offsetting and others. Carbon Footprints can be reduced through the development of alternative projects, such as solar and wind energy, which are environment friendly, renewable resources, or reforestation. These examples are known as Carbon Offsetting, the counteracting of carbon dioxide emissions with an equivalent reduction of carbon dioxide in the atmosphere.

Among all the sources of green energy, wind energy has an immense potential to reduce GHG emissions. Also, wind energy has a small environmental footprint when compared to others energy supply resources. Wind energy has taken a commanding lead among other renewable energy sources. The wind energy resource assessment plays a significant role in estimating wind potential and contributes to a more secure energy supply. The advanced ground-based remote sensing techniques like SODAR and LiDAR measures wind speed at higher heights as well as at complex terrain accurately and efficiently. This advanced technique provides additional environmental benefits, management and site characteristics for wind farm project development along with reduced greenhouse gas emissions. The remote sensing technique further decreases the cost and reduces wind energy's footprint. The production of electricity using wind energy reduces considerable amount of CO₂ emission in the environment, if the same power is generated using conventional sources of energy. Application of remote sensing techniques can mitigate considerable amount of GHG emission.

A Case Study at Kayathar, India

Site Detail

The wind resource measurement was conducted at Kayathar, situated at southernmost part of India (latitude 08° 57' 44.27" N and longitude 77° 43' 10.80" E). The terrain has a gentle slope in western direction and the roughness length of the site is 0.03 m with open farm land, few trees and buildings (Ahmed, 2015) and the annual average temperature at the site is 38°C and relative humidity of the site 72% respectively. The measurement is done at two heights i.e., at 80 m and 100 m using ground based SODAR and LiDAR instrument.

The Table 2 illustrates the mean wind speed, standard deviation, kurtosis and skewness by both the techniques. The Fig. 3 shows the location of site on the map of India.

In this study, 10 min average time series wind data at a height of 80 m and 100 m from 01 September 2014 to 30 September 2014 are used for evaluation of Weibull parameter, wind characteristics, turbulence and shear factor. This case study also presents an economic comparison between remote sensing instrument and meteorological mast. The time series wind data were collected simultaneously by Cup anemometer mounted on 120 m long lattice structure meteorological mast, SecondWind Triton SODAR and Zephir 300 continuous-wave wind LIDAR profiler for the same period of time and at same height mentioned above.

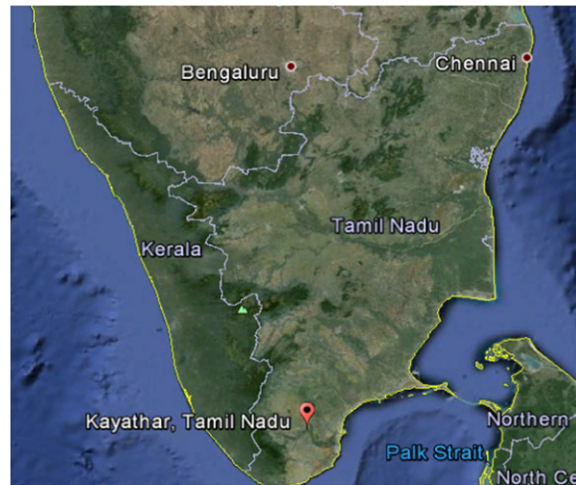
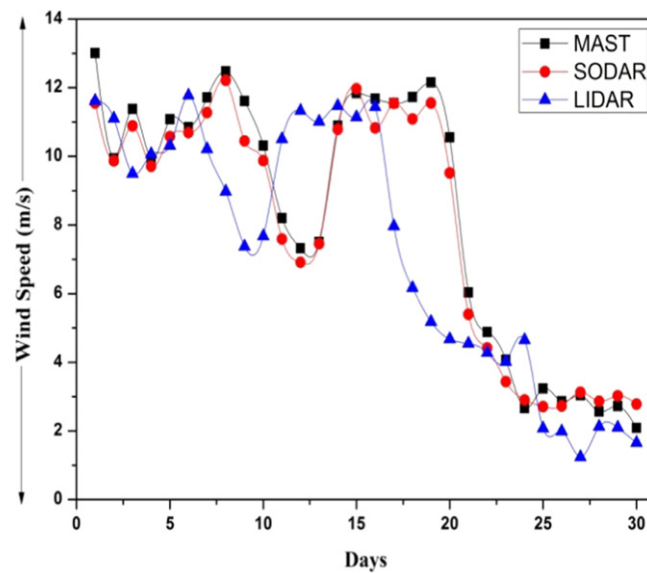
Comparison of Wind Characteristics

Wind speed

The comparative analysis of wind speed between met mast technique and remote sensing technique for the recorded data is shown in Figs. 4 and 5. The Figure shows the daily mean wind speed at 80 m and 100 m respectively. It can be seen from Figs. 4 and 5 that SODAR and LIDAR measurement follows the comparable trend as of cup anemometer. The mean wind speed measured by LIDAR

Table 2 Statistics of measured wind speed data at Kayathar

Height	Assessment technique	Mean wind speed (m/s)	Standard deviation (m/s)	Median	Skewness	Kurtosis
80 m	MAST	8.330	4.2137	9.258	−0.2686	1.8709
	SODAR	7.989	3.9734	8.971	−0.2964	1.8142
	LIDAR	8.647	3.6212	9.501	−0.3916	2.3344
100 m	MAST	8.446	4.4178	9.488	0.1014	5.1747
	SODAR	8.351	4.0388	9.340	−0.3161	1.8970
	LIDAR	9.019	3.6339	9.993	−0.5167	2.5001

**Fig. 3** Geographical location of Kayathar.**Fig. 4** Comparison of daily mean wind speed profile at 80 m.

is higher whereas SODAR measure lower wind speed as shown in Table 2 which can be due to different medium (light and sound) adopted to detect wind speed.

The Fig. 6 (a) and (b) shows probability distribution function of measured data for both the technique. It is observed that the remote sensing measurement shows discrepancy with met mast measurement at both the heights due to wind driven wave

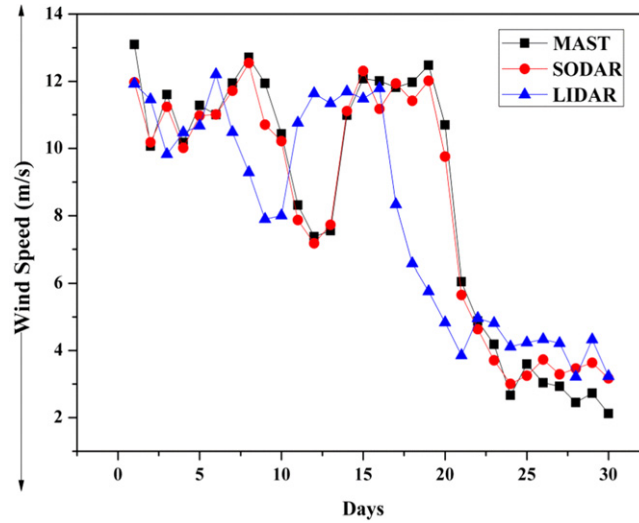


Fig. 5 Comparison of daily mean wind speed profile at 100 m.

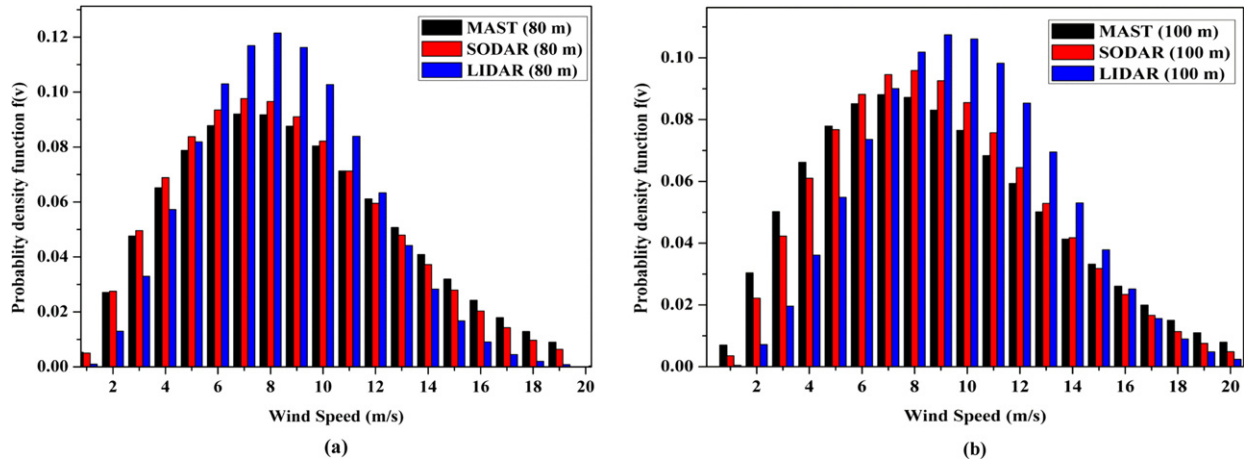


Fig. 6 (a) Comparison of remote sensing technique with met mast. (b) Comparison of remote sensing technique with met mast.

distorting the intensity of the sound beam and light beam. It is seen that SODAR measurement shows better performance at both heights.

Estimation of weibull parameter

Weibull distribution is a significant tool to estimate wind energy potential and to express the wind speed frequency distribution. The Weibull is a two parameter distribution function and is represented by a dimensionless shape parameter k and scale parameter c in units of wind speed (m/s) and it can be described by its probability density function $f(v)$ and cumulative distribution function $F(v)$ as given below (Chaurasiya et al., 2018, 2017a).

$$f(v) = \frac{k}{c} \left(\frac{v}{c}\right)^{k-1} \times \exp\left[-\left(\frac{v}{c}\right)^k\right] \quad (4)$$

$$F(v) = 1 - \exp\left[-\left(\frac{v}{c}\right)^k\right] \quad (5)$$

where v is the wind speed, k is the dimensionless shape parameter, and c is the scale parameter having the same unit as v (m/s). This case study involves the estimation of Weibull parameter from both the techniques along with the statistical analysis to prove the effectiveness of result. The Weibull parameter is estimated using nine different numerical methods for each instrument at both the heights.

The meteorological mast is used as a standard instrument in wind energy sector for monitoring wind parameter, furthermore this study indicates that remote sensing measurements follows the same trend as of meteorological mast measurement for the measurement of both scale and shape parameter. There were no major difference between the computed parameter of k and c from SODAR and meteorological mast (Figs. 7–12).

The SODAR measurement has a mean absolute percentage error of less than 10% at both heights where as LIDAR measurement has a higher error in the computed values of k and c (Table 3).

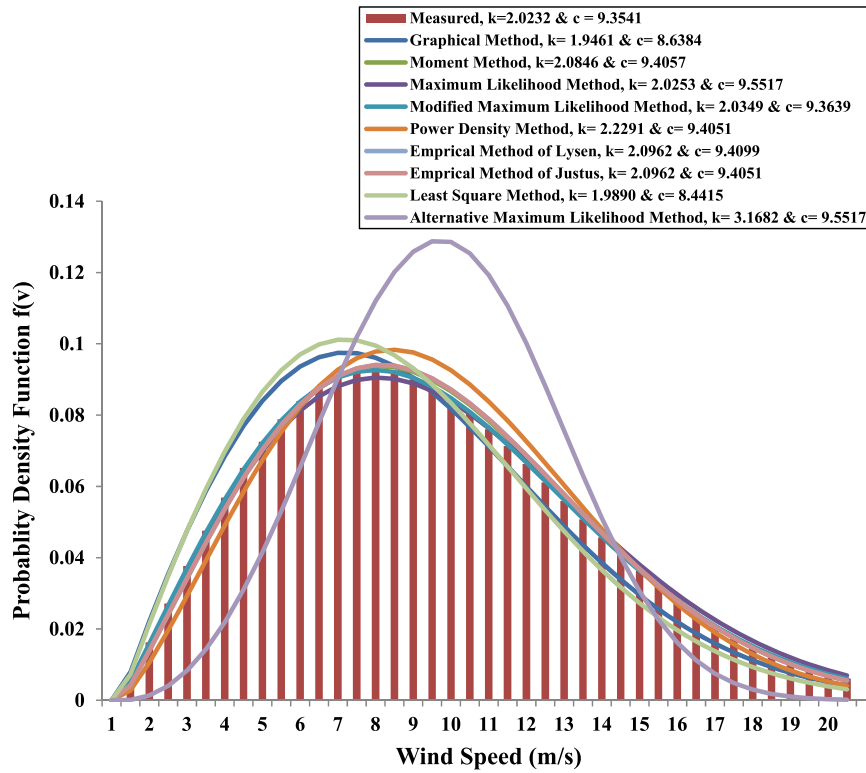


Fig. 7 Weibull distribution at 80 m measured from MAST.

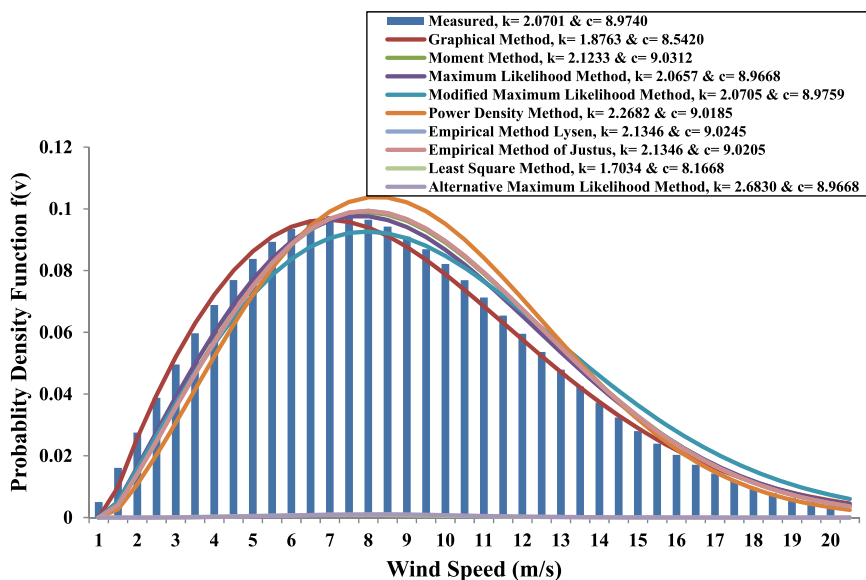


Fig. 8 Weibull distribution at 80 m measured from SODAR.

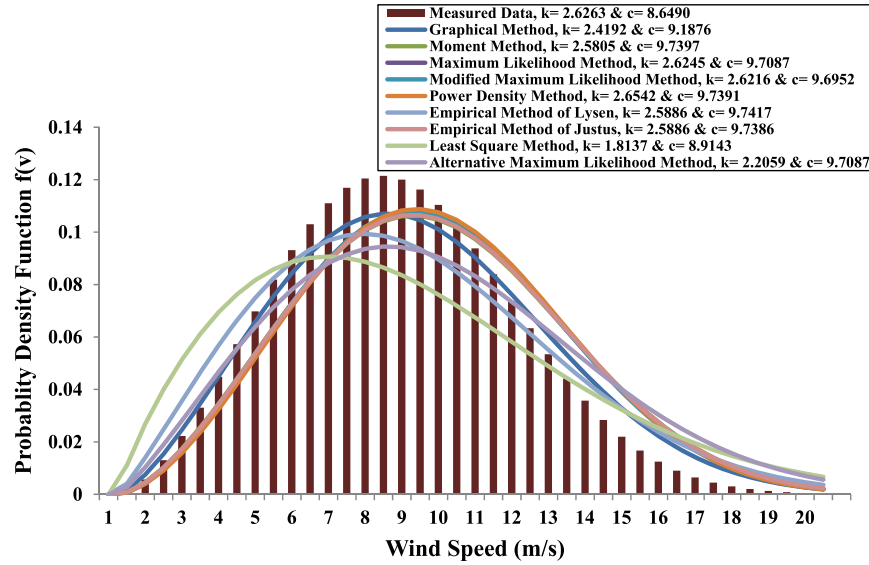


Fig. 9 Weibull distribution at 80 m measured from LIDAR.

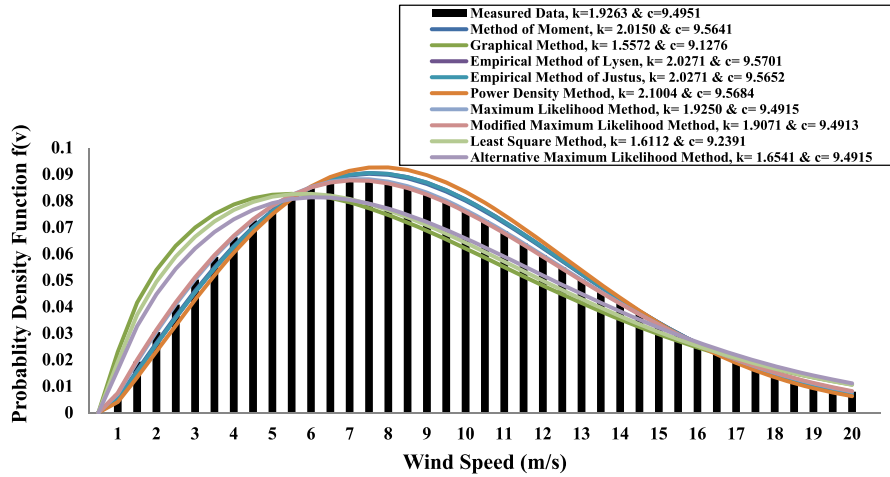


Fig. 10 Weibull distribution at 100 m measured from MAST.

Wind power density and characteristics

Wind power density shows the total available energy at the site for conversion, which can be calculated as (Ahmed, 2015):

$$\frac{P}{A} = \frac{1}{2} \rho c^3 \Gamma \left(1 + \frac{3}{k} \right) \quad (6)$$

The Table 4 below summarizes the calculated wind power densities and wind characteristics i.e., most probable wind speed (V_{mp}) and maximum energy carrying wind speed (V_{me}) by both the measuring instrument at measurement heights. At a given location the peak of wind speed probability distribution is shown by most probable wind speed, whereas the peak of wind power probability distribution is shown by maximum energy carrying wind speed. The value of V_{mp} and V_{me} can be calculated from the following equations (Ahmed, 2015)

$$V_{mp} = c \left(1 - \frac{1}{k} \right)^{\frac{1}{k}} \quad (7)$$

$$V_{me} = c \left(1 + \frac{2}{k} \right)^{\frac{1}{k}} \quad (8)$$

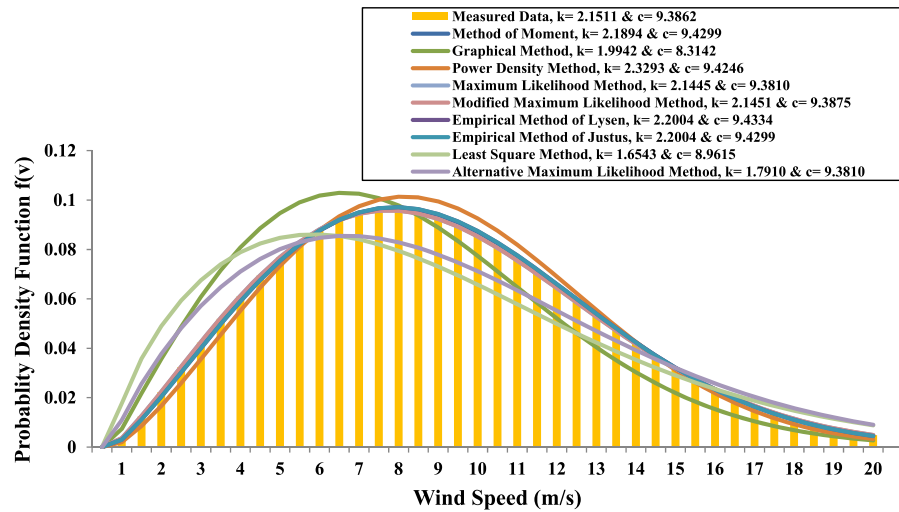


Fig. 11 Weibull distribution at 100 m measured from SODAR.

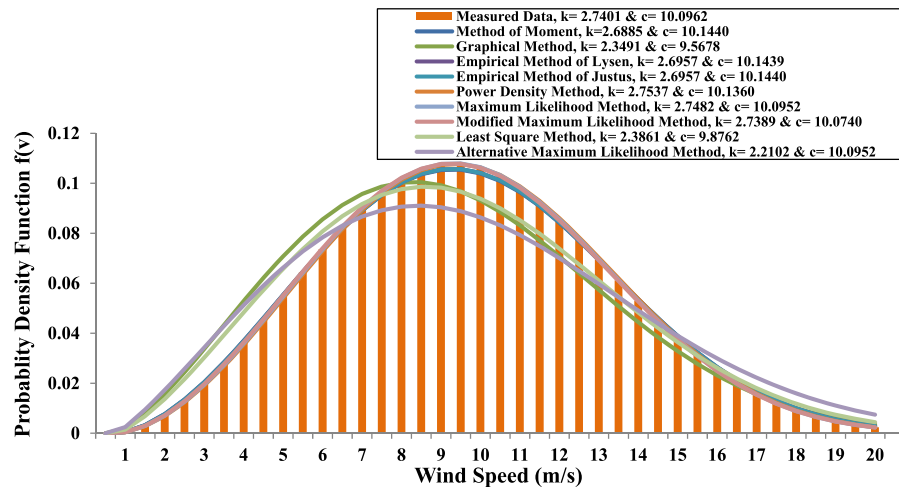


Fig. 12 Weibull distribution at 100 m measured from LIDAR.

Table 3 Comparative statistical analysis of remote sensing technique

Height (m)	SODAR				LIDAR			
	R^2	RMSE (m/s)	χ^2	MAPE (%)	R^2	RMSE (m/s)	χ^2	MAPE (%)
80	0.9878	0.0033	0.0107	6.1755	0.9291	0.0152	0.2072	12.713
100	0.9636	0.0054	0.0293	7.4799	0.8427	0.0182	0.2661	17.232

Turbulence and shear analysis

The high sensitivity and different signal processing technique, data analysis strategies of ground based remote sensing techniques has made it possible to measure shear and turbulence at different heights along rotor. The later techniques can also be used for formulate and analyze rotor equivalent wind speed which is considered to provide more accurate and representative power curves particularly for bigger machine with large rotor diameter.

In this study the vertical wind speed models are used to extrapolate wind speed at higher heights. The comparison of the vertical wind speed profile measured from SODAR is compared with power law (Verhoef *et al.*, 2009) and the log law (Verhoef *et al.*, 2009)

Table 4 Wind power density estimation using Weibull parameters

Height	Measurement technique	Experimental value	Characteristics wind speeds (m/s)	
		Wind power density (W/m^2)	V_{mp}	V_{me}
80 m	MAST	658	6.67	13.13
	SODAR	568	6.52	12.44
	LiDAR	623	6.77	13.65
100 m	MAST	702	6.63	13.49
	SODAR	622	6.99	12.70
	LiDAR	671	6.82	13.03

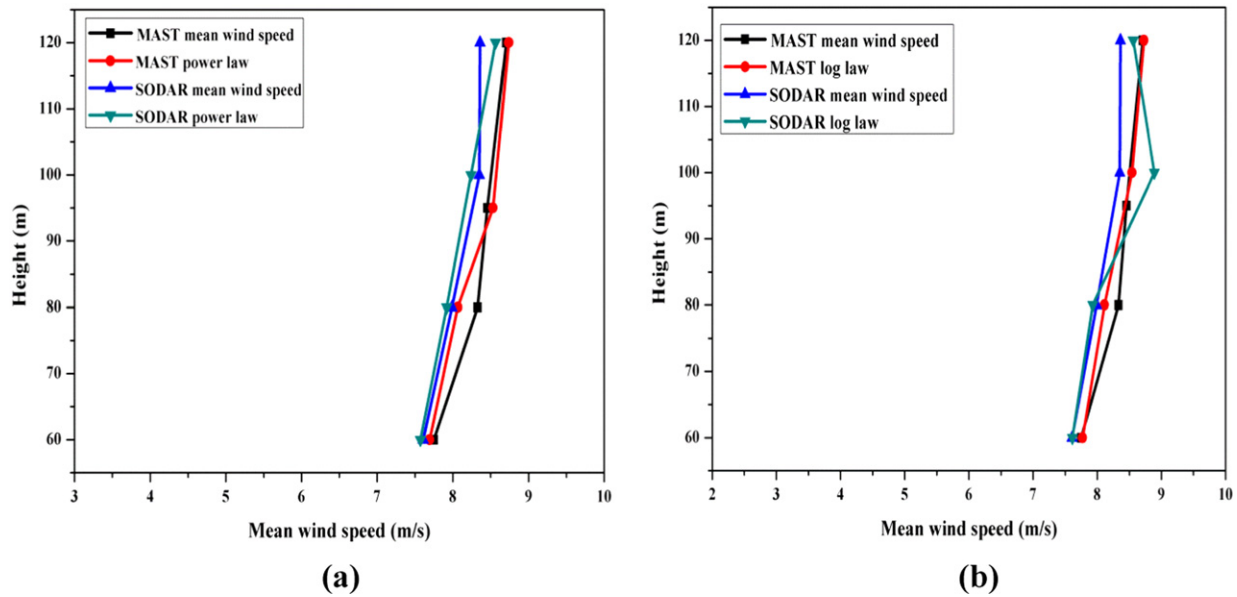
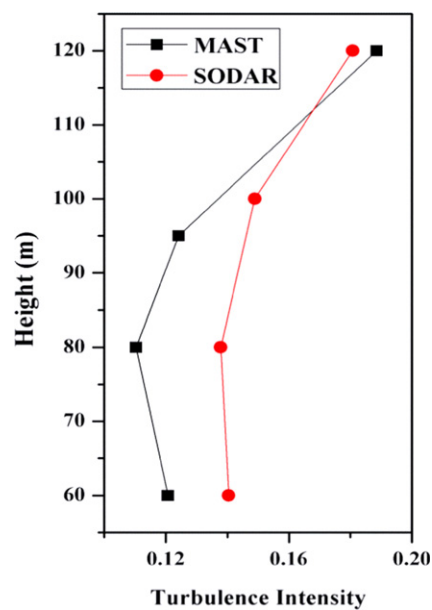
**Fig. 13** Comparison of vertical wind speed profile (a) power law (b) log law.**Fig. 14** Vertical profile of turbulence intensity.

Table 5 Comparative payback period and AEP

Parameters	Formula	Heights				Unit
		80 m		120 m		
		MAST	SODAR	MAST	SODAR	
Turbine capacity	TC	2000	2000	2300	2300	kW
Capacity factor	CF	20	20	20	20	%
Annual energy production (Y)	$Y = TC \cdot CF \cdot 8760 \text{ h/year}$	3,504,000	3,504,000	4,029,600	4,029,600	kWh/year
Total electricity generation(20 year)	$V_{\text{tog}} = Y \cdot 20$	70,080,000	70,080,000	80,592,000	80,592,000	kWh
Export fraction	F	100	100	100	100	%
Total cost (V_{tot})	$V_{\text{tot}} = (T_c + O_c + W_c + W_m)$	143,560,000	145,750,000	179,970,000	176,125,000	INR
Unit cost of electricity generation	$G_c = V_{\text{tot}}/ V_{\text{tog}}$	2.048	2.079	2.233	2.185	INR
Payback period	$P_b = V_{\text{tot}}/ A_{\text{exp}}$	12.08	12.27	13.17	12.89	Years
Total saving	S	–	–	–	3,868,416	INR

Table 6 Comparative saving in GHG emission using remote sensing technique

Parameter	Coal	Wind power using remote sensing technique	
Grams of CO ₂ equivalent per Kilowatt-hour of electric energy	955	at 80 m 21	at 100 m 21
Electric generated	3,504,000	3,504,000	4,029,600
Grams of CO ₂ equivalent generation	3,346,320,000	73,584,000	84,621,600
Saving of grams of CO ₂ equivalent per Kilowatt-hour of electric energy		3,272,736,000	3,261,698,400

along with mast measurements. The power law model is commonly used for defining vertical profile in wind energy. It is observed from the Fig. 13 that the SODAR-derived mean wind speed profile fits well with both power law and log law. The little deviation can be observed mainly due to the influence of wind-driven wave. It is also seen that the variation between the SODAR measurement and standard vertical wind profile is dependent on mean wind speed, higher mean wind speed results in higher deviations.

The mean value of turbulence intensity decreases initially at 60 m and 80 m height, above then it increases due to mechanical friction. The turbulence intensity measured by SODAR was poorly correlated with meteorological mast, the correlation were reasonable. Further study is required to facilitate accurate measurement of turbulence intensity using SODAR. The Fig. 14 suggests that there is exponential descend in the value of turbulence intensity with decrease in height.

Economic and GHG Emission Aspects

The new and recent advances in remote sensing techniques have made it possible to reduces GHG emission and economically feasible for the project. But aside from the price of instruments, accurate measurement with validation, project duration and other legal proceedings are necessary to make it bankable and attract the investors.

This case study shows the economic comparison of the approximate cost of wind resource monitoring done through traditional meteorological mast and SODAR at 80 m and 120 m height. Additionally, it also discusses the saving in GHG emissions using remote sensing techniques. This economic calculation assumes no incentive or loan, grant, discount rate and wind farm land rate. By using SOADR system the unit cost of electricity generation reduces to 2.14% and payback period to 2.12% compared to mast measurement (Chaurasiya *et al.*, 2017b). Hence, by adopting SODAR system for wind resource assessment it is possible to reduce the total cost of the wind project without degrading the superiority and performance of wind turbines and it is also possible to attain a payback period of less than 20 years (Table 5).

The Table 6 shows the saving of GHG emissions using remote sensing techniques in wind energy sector. From Table 6, it can be seen that by using remote sensing techniques a significant amount of emission is saved as compared to conventional energy source.

Conclusion

Today, remote sensing techniques are properly calibrated, accurately aligned, installed and maintained and their signal processing concepts are well interpreted as well as the volume-averaged wind measurement provides information in all the three direction at each point at discrete hub-heights, are indeed accurate and technically representative wind measuring instrument. Remote sensing

instrument are very much capable of matching the wind industry's demand and can be used as supplement to high mast tower for wind profile measurement and wind resource assessments. The application of remote sensing technique in wind energy resource assessment reduces the greenhouse gas emission and carbon footprint to higher extent and can lead to mitigate challenges in global warming.

Before, remote sensing wind measurements can become fully certified and accredited to wind industry standards, new and revised IEC standards have first to be set and come into effect. However, the measurement campaign shown in this study clearly provides the insight ability of ground based remote sensing instrument. All the parameters measured from the ground based remote sensing instrument were found to be approximate closer to the tall meteorological measurements.

See also: Wind Farm Repowering Using WAsP Software – An Approach for Reducing CO₂ Emissions in the Environment

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Biomass for CO₂ Sequestration

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Introduction

Bioenergy consisting of solids, liquids, semi liquids or gas-based fuels are usually of bio (organic origin). Liquid fuels may be exploited directly for various energy needs as transport fuels for the roads, rail lines, and as aviation fuels for the air transportation. Other uses may include applications in various types of engines, turbines, electrical power generators and several other energy conversion operations. Gaseous and solid energy fuels can be applied in the area of electrical power production for direct and indirect purpose designed power plants; in boilers and other power utilities (heavy and light current incorporated). Chemical and end products are usually elicited from several organic matter produced by solid and liquid fuels as by-products. Subsequently, more chemicals and more energies can be produced from the use of flora/organic derived materials and feedstocks, animal residues, urban/commercial by-products and wastes and agricultural residues or forestry products. Resources from biomass are mainly of primary, secondary or tertiary sources. Resources from primary biomass are directly produced through photosynthetic processes. These photosynthetic energy processes are of direct land-based uptake by short-rotation perennial woody plant/crops, herbaceous produce, oil crop seeds, energy crops, algae, and post agricultural residues of forest products, trees, crops of all kinds including leaves of plants/trees, switch grasses, wheat straws, all manner of corn residues, bark/pericarps from trees, shells and so on. Secondary biomass resources on the other hand, are products of primary biomass resources processing which may be directly derived including products like: bagasse from sugar cane, saw dust/residues from mills or chemically-derived in the case of coal tar, waxes, bio-oils, glycerols, black liquors, lignin from paper/pulping processes. They may also be biological in the production of energy for example in the case of excreta production by animals and may include cow dungs, poultry droppings and the likes. Resources from tertiary biomass are residues from post-consumer spills, for example: greases and fats from animals, waste cooking or vegetable oils, packaging wastes, domestic/kitchen wastes, grey water, debris from demolition and construction sites and others.

But several pre- and post- conversion technologies have been developed in recent years for the conversion of various biomass resources into direct energies, heat, power and fuels for several domestic and industrial application in virtually all the countries of the world. Conversion technologies of biomass may be classified under three or more processes according to several authors: direct combustion process, biochemical processes and thermo-chemical conversion processes. In all three processes, energy conversion technologies will have to be concerned with the feedstock having the potential of variability in energy and mass densities, moisture content, sizes, sustainable supplies. It is therefore imperative that modern technologies to be adopted are all encompassing to include hybridising conventional fuel/biomass technologies which may employ fossil fuels for some operations such as preheating, drying and constant fuel supply maintenance as back up in the event of interruption of biomass supply during this developmental stages. Tateishi (2016) in YANMAR Technical review presented four biomass conversion technologies to include carbonisation and biodiesel production. European Biomass Industries Association (EUBIA) in the most recent technical report highlighted instead to include direct combustion; anaerobic digestion; oil extraction for biodiesel; fermentation for alcohols; pyrolysis for biochar, oil and gas production and gasification for CO and syngas rich in hydrogen (EUBIA, 2018). These are encapsulated in Fig. 1 which also gives a general overview of modern conversion technologies with their attendant end-products.

Energy derived from biomass is presently taking over the total energy use in most countries and in the United States, it is almost one third. The contribution to the energy mix are accounted for by biomass energy production technologies. Of the predominance of the conversion technologies, biomass combustion technologies is the most dominant source of the energy production from biomass in Europe and United States. Research and development are currently harnessing biomass resources for various renewable energy technologies. Aside biomass combustion, gasification technologies and or biochemical processing, biomass carbon sequestration has been developed as another milestone potential for capturing carbon emission for storage and utilisation and for mitigation of climate change currently plaguing the world over.

Carbon sequestration and storage from combustion of conventional fossil fuels in recent years have been developed as a means of eliminating climate change, curtailing emissions and creating more renewable energies. It is a known fact that emissions of CO₂ and CO from biomass resources or fossil fuels as a consequences of combustion can be sequestered. Biomass energy from carbon sequestration as a carbon sink has net negative impact which would also deliver free form of energy for electricity, hydrogen and heat. Energy from biomass is no doubt neutral, negative or positive depending on biomass resource in juxtaposition with land availability. Therefore regeneration of the biomass by replanting or the release of carbon during/after combustion is recaptured and the energy scheme in itself becomes normally carbon (CO₂) neutral (Schlamadinger *et al.*, 2001). Also the possibility of the carbon released from biomass conversion being sequestered and stored is achievable in geological deposition which is very much analogous with carbon sequestration and storage. With this type of technology in place, the feasibility of displacing fossil fuels, removing atmospheric CO₂ and reduction of CO₂ emission on sustainable and continuous cycle has been attained.

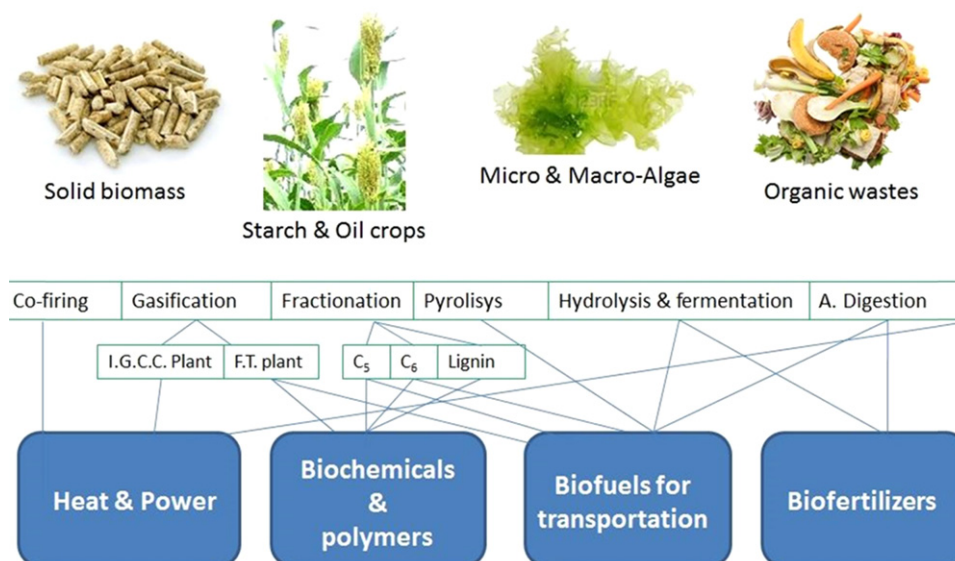


Fig. 1 Overview of Several Biomass Energy Conversion Technologies. *Source:* European Biomass Industry Association, EUBIA, 2018. Biomass Processing Technologies, EUBIA, Brussels. Tateishi, T., 2016. Development of High Efficiency BP-G 300kW-Class Biogas Co-Generation System. YANMAR Technical Review, Research and Development Management Division.

The recovery of concentrated stream of CO₂ from emissions and flue gases is simply a matter of splitting atmospheric CO₂ and N₂. Chemical adsorption is an option using amines. There are also membrane separation, cryogenic distillation and solid–solid adsorption using molecular sieves. It is also possible to eliminate air-borne nitrogen (N₂) before combustion and subsequent recycling of the flue gas into combustion in order to thermally control overheating of the system. Chemical adsorption has proven itself the most effective and promissory capturing approach. Adsorption by amines involves the use of monoethanolamine (MEA) due its high CO₂ carrying capacity. Almost 90% of the 13% concentration of air can be captured and sequestered (recovered) from flue gases. The carbonation of biomass by hydrothermal cracking process can bring about the sequestration of CO₂. The product of hydrothermal cracking as a carbonized by-product–hydro-char possesses huge potential in the sequestration of atmospheric carbon. Any biomass can be a feedstock for this process. The amount of emissions of CO₂ from biofuel combustion are estimated to be equal to the same amount sequestered in biomass which makes the whole process carbon neutral.

Biomass Carbon (CO₂) Sequestration (Bio-CCS)

Carbon sequestration can be defined as a process of long term capturing and removing of atmospheric CO₂ and its other forms to mitigate and defer global warming. This is done through biological, chemical and physical methods or mechanisms including artificial mechanisms which includes algal CO₂ sequestration; it involves producing biomasses by capturing CO₂ with some photo-synthetic mechanisms to produce energy (Eloka-Eboka and Inambao, 2017). Atkin *et al.* (2012) noted in their study that the act of sequestering is solely dependent on the nature of carbon sink achieved through several methods and forms. For example, directly by chemical reactions which are inorganic and can result into CO₂ in the various forms of salts: carbonates and bicarbonates, bonding with other dissolved minerals and salts. This chemical chain forms compounds such as Ca and Mg carbonates. Storing CO₂ and other forms of carbon can indeed assist in mitigating the varying effects of greenhouse gases. Additional income can also be generated by forest land-owners from storing carbon on their managed forestlands. There are already research and development activities in place in integrating or fusing several energy schemes into carbon capture and sequestration technologies, giving rise to energy products with net negative ambient carbon emissions. The attention of a technology development of this nature is focused primarily on the need to provide an approach that will reduce carbon emissions drastically from the mix of non-renewable energy resources. The strategic mechanism culminates from the compatibility of the existing energy infrastructures for transformation. The technology can be integrated in juxtaposition with biomass energy systems.

The application involves that ambient carbon which are in biomass during production are captured and sequestered - taken away from the atmosphere for biomass production thus there is a net carbon sink or negative net emissions if any. This technology is still evolving, but several factors accounts for its attractiveness. These include: (a) Net reduction in ambient/atmospheric CO₂ from bio-CCS systems which provides strategies for offsetting emissions from anywhere in the climate economy; (b) Limited and efficient land and water resources utilisation of the system; and, (c) Availability of current conventional systems and facilities for Bio-CSS and so there is no need for installation of new technological facilities. The process of photosynthesis combined with solar energy, air and water, forms glucose that is stored within living plant tissues. Microbes are classified as autotrophs by deriving their energy from the sun through photosynthetic chemical reactions or processes. Through microbial putrefaction of biomass, plants

and animal materials and tissues are broken down to form carbohydrate compounds, organic acids, proteins, waxes, coal oil, shale oil, natural gas and humic substances. It is the autotrophs which are responsible for fixing CO₂, to make their own food fuelled by the light energy from sun (photoautotrophic), or through oxidation of nitrogen, and sulphur (chemoautotrophic). Chemoautotrophic include: the cyanobacteria, green sulphur bacteria, purple sulphur bacteria and purple non sulphur bacteria. It is important to mention that sulphur based bacteria use sulphide of hydrogen as hydrogen donor instead of using water as in a photosynthesis and by cyanobacteria (Atkin *et al.*, 2012).

A number of motives and factors that the scientific and research communities have identified and advanced in the containment of CO₂ emissions. CO₂ is the primary contributor in the evolution and emissions of greenhouse gases, therefore its control as an emission is not insufficient in restricting the continuous global increase of temperature to below 2°C as contemplatively demanded by IPCC (Le Quéré *et al.*, 2009). Carbon emissions can be effectively controlled and minimized by sequestering them into solid biomass of micro- and macro-algae (Eloka-Eboka and Inambao, 2017). There are a number of authors who have conducted extensive research on this technological concept such as (Shabani, 2016; De Lary *et al.*, 2012; Zheng *et al.*, 2012; Ponnuswamy *et al.*, 2014). The production and growing of algae has been identified as the main process by which the sequestration of carbon can be achieved. There are a number of other studies which have been conducted to highlight the impact of CO₂, level and concentration as a source material in the production of algal biomass, nutrients, food and lipids. Among the researchers whose studies are enlisted include: (Singh and Singh, 2014; Hu *et al.*, 2014). Activities such as burning of fossil fuel, deforestation and power generation which are classified as anthropogenic being human induced contribute to the precarious growth in greenhouse emissions and gases (GHG). The USAEPA estimates that about 70% or more of greenhouse gas emissions are contributed mainly by transport, other energy consumption (domestic and industrial) and production in just 2010. It also reported that since 1990–2010, the trend was increasing at a rate of 34%–35% (Wilbanks *et al.*, 2012; Wilbanks and Fernandez, 2014). CO₂ levels have tremendously increased since the pre-industrial revolution till the present as reported by Rahaman *et al.* (2011) and Singh and Ahluwalia (2013).

Although CO₂ is essentially an indispensable gas in photosynthetic processes and industrial applications, its unending increase is threatening the entirety of the eco-system and thus increasing global warming further due to its longer atmospheric e-decay lifespan and retention of between 50 years to 200 years (Van Den Hende *et al.*, 2012; Turns, 2012). It is the principal contributor to global warming. Due to the urgency of reducing greenhouse gas emissions and to avert environmental disasters attributed to global warming. The world community of nations and leading 37 highly industrialized countries and the European community adopted the Kyoto protocol on 1997 (Kyoto Protocol, 1997) in an attempt to reduce greenhouse gases by 18% between 2013 and 2020 (Cheah *et al.*, 2015; Yoo and Al-Attayah, 2013). Besides the effort by international community and individual governments in trying to contain increase in greenhouse gases, the scientific and research communities have been looking at carbon sequestration of biomass feedstock or from micro- and macro- algae. Micro-algae have long been recognized as an alternative to biodiesel fuel production. This is intended to reduce utilisation and overdependence on fossil fuels, thus reducing significantly greenhouse gas emissions and accumulation. Micro-algae are considered to be photosynthetic efficient in the conversion of the CO₂ biochemically, produce high biomass, high lipid accumulation and valuable other non-fuel co-products as reported by Xie *et al.* (2014), Eloka-Eboka and Inambao (2017). Micro-algae have a very high potential to deal with carbon dioxide emissions. They provide almost 10%–50% times more efficiency in cleaning CO₂ as compared to terrestrial plants (Cheng *et al.*, 2013; Lam *et al.*, 2012; Anjos *et al.*, 2013; Zhao and Su, 2014; Kao *et al.*, 2014). It should be mentioned also that the contribution of terrestrial plants to reducing CO₂ emissions is 3%–6% globally (Ho *et al.*, 2011; Kao *et al.*, 2014).

During photosynthesis, CO₂ is used as a carbon source and converted into organic compounds through solar power energy. In micro-algae nutrition, carbon is the primary source of nutrition with nitrogen and phosphorous in that order (Lam and Lee, 2011; Aziz *et al.*, 2017; Choong *et al.*, 2017). Micro-algae are a very strong agent in the bio-sequestration of CO₂ where dried micro algae alone contains 50% of carbon derived from CO₂ (Lam *et al.*, 2012) and approximately 1.83 kg of CO₂ fixed for every 1 kg of micro-algae biomass produced (Jiang *et al.*, 2013; Kumar *et al.*, 2015; Clares *et al.*, 2014). According to biomass in the world energy supply of electricity, heat and transportation fuel accounts for 8%–15% and 33%–50% respectively of the current world consumption of energy by the projections of 2050. In addition to increase in demand for wood fuels (Huotari *et al.*, 2015), the demand for bioenergy is also increasing. The agricultural sector is the leading contributor of biomass wastes such as shells, pits, fruits, seeds, coir, bagasse, fodder, pulps, and cake from different plant species in the sector activities. This wastes have a potential to be used as biofuels (Barbanera *et al.*, 2016; Buratti *et al.*, 2016). Agricultural biomass is also richer in fertilizer elements such as K and P compared to wood biomass (Vassilev *et al.*, 2013a,b). It has come to be generally accepted that biomass is a renewable energy resource that does not contribute to the development of greenhouse gas due to their CO₂ conversion being neutral. Agricultural biomass is highly alkaline and enriched with alkaline earth components thus significantly contributing to the capture of CO₂. This is done through formation of carbonates due to solid gas reaction of CO₂ released during the burning or atmospheric Ca, K, Mg and Na oxyhydroxides formed during combustion of biomass (Vassilev *et al.*, 2013a).

In discussing carbon sequestration, it is imperative to remember that although it carries advantages and is receiving global attention, in environmental active carbon pools like oceans, care must be taken to avoid exchanging one environment solution to another since this can create a transferable problem to another environment (Lackner, 2003). The use of fossil fuel globally exceeds 5000 gigatonnes of carbon (GtC) (Rogner, 1997) as compared to global consumption of 6 GtC annually. However, towards the 2050 and beyond, stabilization of atmospheric CO₂ concentration and maintaining a healthy economic growth in the global economy, will require the world to adopt carbon neutral energy that will surpass current world energy consumption projections

(Hoffert *et al.*, 2002; Hernandez *et al.*, 2015). It is crucial to remember that the energy sector is vital and key in mitigating climate change and greenhouse gas emissions (Intergovernmental Panel on Climate Change, 2007). If the world community wants to achieve the aims and objectives of carbon sequestration, it has to operate on a multiterawatt scale according to (Lackner, 2003) while trying to carbon sequester. There are two factors which heavily affect and impact on carbon sequestration, storage time and storage capacity. These two factors affect biomass sequestration and CO₂ utilisation, due to the limitation for example of oceans to absorb carbonic acid relative to carbon resources (Lackner, 2003). However underground injection becomes the simplest and effective technique for carbon sequestration. It is suitable even for large scale carbon sequestration projects (Holloway, 2001; Hastik *et al.*, 2015) as an example in the USA state of Texas where this technology has been implemented and consumes about 20 million tonnes of CO₂ (Lackner, 2003). However, in the northern sea, the Norwegian energy company Statoil has sequestered CO₂ removed from natural gas using the underground injection technique (Hinzman *et al.*, 2005; Chadwick *et al.*, 2000; Arts *et al.*, 2007).

Enhancement of Carbon Removal in Biomass

It is a well understood fact that all green plants have the ability to absorb CO₂ during growth and on harvest/utilisation, release CO₂. This is termed carbon cycle and a process culminating from photosynthesis. Biomass for carbon reduction or removal (sequestration) uses the plant crops and their interaction/relationship with carbon cycle to allow the permanent sequestration of elemental carbon within the soil, air and water. It is simply achieved by selecting processes or methods which will ultimately return biomass to the soil while enhancing the conditions for plant carbon or the unstable carbon deposited in the plant/crop to be reduced, returned or restored to its original elemental form and then stored in a stable state. Typical strategies include the implantation of the use of cover crops and some legumes, weeds and grasses to temporarily shield farmlands and crops between planting seasons. Also concentrating grazing livestock in consecutively in days in lesser paddocks within a period, *t*, so the grazing is quite lightly but uniform. This type of activities opens up the soil and creates conditions where plant roots grow deeper and deeper into the soil for better carbon permeation. There are proper soil tilling and mixing due to the fact that animal stocks assist in tilling the soil with their hooves.

There are mastication and grinding of old grasses and deposition of manures into the soil according to FACTBOX (2010). Bare paddocks should be well covered with forages, hays and dead vegetations. These and similar practices will convey technical protection of the soil from the sun which also assist the soil to retain more water and be more poised, attractive and ready for carbon-capturing by microorganisms (FACTBOX, 2010). Restoration of soils of degraded/depleted lands naturally slows down the release of carbon but returns the land to good agricultural and/or other uses. Sequestration of biomass has positive impacts and effects on air, soil and the quality of water generally and there are quite a few good essence and benefits to animals, plants, wildlife, and attendant expansion of food production. It reduces the pollution or the level of contamination from the soil, air, and surface water; also emissions on the land and atmosphere. It is also possible to reverse the overall effects and contributions of soil sequestration. The scenario created can present a situation where the soil is not tilled, rather disrupted or abandonment of agricultural tillage practices, what happens to the soil is that it becomes a net source or harbinger of emissions and greenhouse gases (GHG). The natural situation is that beyond 20–30 years of this type of sequestration (without tillage practices), the soil therefore attains GHG saturation point where it ceases to absorb further carbon.

The carbon fills up soil pore spaces and nothing more. What this entails is that there is a global holding limit/capacity to this type of sequestration, the total amount of carbon that any soil can retain (Sundermeiera *et al.*, 2010), and when this limit is reached, there are consequences. Many possible factors affect the technology and economic costs of carbon sequestration. These include the quality of the soil, transactional costs implications, CO₂ leakages/slippages and probable other unforeseeable damage to the environment. Atmospheric CO₂ reduction is usually a long-term process, therefore the concern for possible immediate turn-over over a long period brings about the reluctance in terms of deployment or in adopting extra expensive techniques/approach to improve the approach. There may be need for a clear-cut techno-economic benefits in terms of breaking even before further investment is anticipated. In countries such as New Zealand and maybe Australia, considerations are rife in for farmers to sell and buy carbon credit emanating from this technologies and good practices already elucidated in sequestering carbon. This is allowed as soon as there are evidences to prove that the farmers have effectively and sufficiently enhanced soil carbon content using the mechanism of sequestration practices (FACTBOX, 2010; Smith *et al.*, 2008; Environmental Co, 2006; Lal, 2004).

Carbon sequestration from biomass or biomass sequestration have demonstrated significant and intensive potential to attain net removal of ambient CO₂ from the environment at technological reduced costs in comparison with the conventional carbon sequestration technologies. There are technical uncertainties however because the development and implementation of large scale biomass sequestration is lean due to lack or little experience and technical know-hows. Demonstration plants of biomass sequestration have not been fully developed; there are still gaps in climate policies to drive implementation. In terms of the economics of production, frameworks for accounting have not been developed. Financial instruments are still missing with vague information on acceptability and public perception on socio-economic impacts and other sustainability issues which are complex and unclear. It is necessary to make conclusion that the deployment of the technologies of biomass carbon capture and sequestration may not be possible in isolation without thoughts on impacts and effects on other inter-related sectors of

climate-energy-food-water nexus. It will no doubt require an integrated approach that will holistically address the complicated links within the nexus and then synergistically harness all together. Average daily CO₂ concentrations continues to plummet geometrically due to anthropogenic activities and industrial consumption of fuels (Sedjo and Sohngen, 2012).

The numerical concentrations are in the neighbourhood of mega and giga parts per million (ppm) of CO₂ from year to year (Hodrien, 2008). If global carbons are increasingly sequestered through expansive enlargements of various proportions of forest plantations of lands on the earth planet, it has been recommended as the most effective and combative measure to mitigate elevated atmospheric concentrations of carbon (IV) oxide, recorded in the *Energy Terms Glossary S* (2010) and in the Glossary of Climate Change. Trapping of CO₂ by forests trees, herbaceous and woody forest products are the major carbon sequestration mechanisms and these materials are natural carbon sinks. An estimation of 50.9% of woody conifers are composed mainly of carbon (Alberta Producers, 2004). Forests and forestry products are considered to proffer the most effective mitigation strategy in reducing and eliminating global warming and its effects (Strack, 2008). The forest ecosystem are carbon pools with traps and storage facilities for more carbon than other terrestrial ecosystems. These have been elaborated in other sections of this chapter. They accumulate long carbon residence time organic compounds inclusive of carbon (Lovett, 2008; McDermott, 2008). To that end, the carbon pool of the forest ecosystem with huge potential have become the focus of the current climate change researchers and scientists (Gorte, 2007).

As forests trees and plants grow, carbon is automatically removed from the atmosphere; they are trapped/stored in the leaves, trunks, branches, wood and soil. It remains stored in the forest ecosystem; but ultimately will be unleashed into the atmosphere once again when these stored materials of the forests are burnt or fully or partially combusted (McPherson *et al.*, 2013) in the form of carbon monoxides (CO) and carbon dioxide (CO₂). As the world's forests covers nearly one-third of the landed space of the earth and also covering up to 80% of the total above-ground terrestrial carbon with almost 40% of the below-ground carbon, therefore playing an extreme critical role in the economy of global carbon cycle (Velasco *et al.*, 2016). Approximations established by the Global Forest Resources Assessment (GFRA) proves that the world's forests can accommodate the storage of over 700 Gtonnes (Gt) of carbon; split into 290 Gt in the biomass which is about 45%; up to 74 Gt in dead woods and litters which is about 12% and finally, about 290 Gt in the soil accounting for almost 45% (Nelson, 1999). The planted areas of forests have presently peaked at 265 million hectares of land which contributes up to 7.5% of the total global forest areas (Poeplau and Axel, 2015). Even though most planted forest areas merely have contributed lesser portions to the total terrestrial carbon equilibrium, their ultimate potential and capacity to absorb, trap and store carbon can be less quantified as it has been acknowledged to play more significant and indispensable roles in the now and future climate change mitigation globally with massive environmental and energy impacts (Goglio *et al.*, 2015).

Processes Used for Biomass Carbon Sequestration

The process transfer and safe confinement or storage of atmospheric CO₂ into other carbon sinks or pools that would have otherwise be emitted or remains in the atmosphere is termed carbon sequestration or sequestration of carbon. The rates of emission of CO₂ from conventional fossil fuels have geometrically increased by over 40% between 1980s and 2000s (Wofsy, 2001) due to increased exploitation, demand, utilisation and expanded industrialisation. The quantities of CO₂ however which have accumulated in the ozone layers of the atmosphere within this same period have remained unaffected, constant and unchanged. The fact is that the excess CO₂ that are being released have only being trapped by other carbon sinks within the ecosystems: the oceans, soils, plants, forests and others. As consequences in this specific situation, sequestration be it naturally induced or anthropogenic, is the only solution led process to curtail this excesses. Anthropogenic carbon sequestration approach will only be aimed at balancing the global carbon account in order to present a future climate safety in addition to anticipated economic growth as a result of this carbon trading. This growth is predicated on neutral carbon strategy of zero gain in the atmospheric carbon sink. This type of approach will require a sequestration of anthropogenically induced CO₂ through safe, environmental friendly and stable techniques with assurance of limited or zero leakage risks and threats (Wofsy, 2001; Lal, 2008). There are numerous processes used for sequestration of atmospheric CO₂ into one of the other sinks also seen as pools. Fig. 2 represents a summary of various processes used for carbon sequestration with technological options for adopting and mitigating atmospheric abundance of CO₂. The choice however of one or more combination of several technologies can be strategic in optimising an acceptable approach as it will better improve the system and also direct actions in developing energy policies for economic growth and climate change mitigation.

Types of Carbon Sequestrations

Sequestration types may be structured into two distinctive categories. They are: abiotic and biotic carbon sequestrations.

Abiotic sequestration

Abiotic carbon sequestration is basically established and confined based on physical and chemical reactions in addition to other engineering techniques and applications without any actual involvement of living organisms whether plants, animals, microbes or

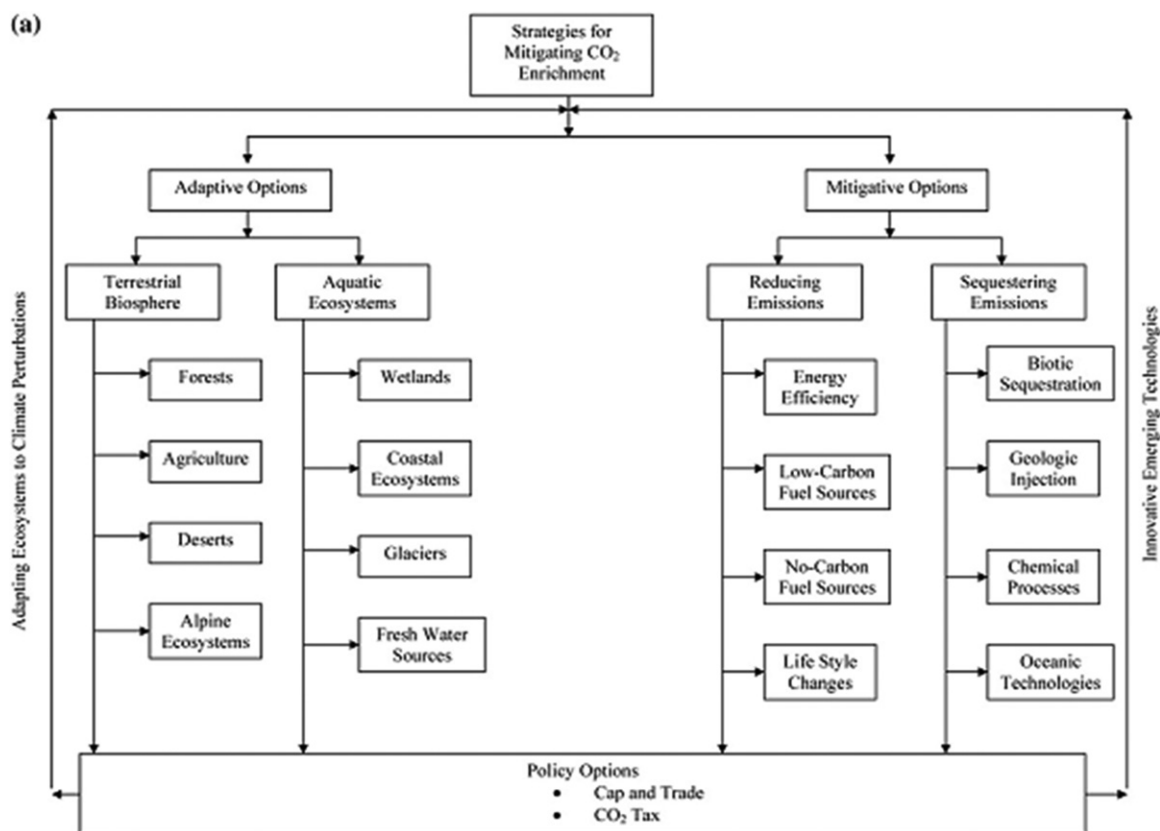


Fig. 2 Summary of various processes used for carbon sequestration with technological options. *Source:* Lal, R., 2008. Sequestration of atmospheric CO₂ in global carbon pools. *Energy and Environmental Science* 1, 86–100.

living organisms. This is according to Lal (2008). The strategy of carbon sequestration by abiotic means in the ocean and in other geological entities or structures elicited considerable research and industrial interests (Freund and Ormerod, 1997) and since then, several development have been unfolding. This is because abiotic sequestration of carbon proves to possess larger and robust sink capacity than its counterpart, the biotic carbon sequestration (Lal, 2008). More interesting and evolving progress has being made in both harnessing, developing and testing the technologies for this type of CO₂ capture; also its transportation and injection modes and processes (Kerr, 2001).

Oceanic injection

Injecting CO₂ streams subterranean into the ocean has been articulated for the last three decades. This method has substantially developed and presents many advantages. However, outgassing can be a weak point. Therefore, a need for stabilization and minimization is necessary.

With regard to stabilization and minimization of outgassing, the injection of CO₂ must be done at subterranean depths. The techniques employed in liquefying separated CO₂ from industrial sources can be achieved using the following techniques:

- injection must be lower than 1000 m from a manifold from the ocean floor and the injected CO₂ being less dense than water will rise to almost 1000 m subterranean forming droplets of fluid dynamic plumes;
- As a more dense CO₂–seawater mixture, the injection is between 500 and 1000 m depth, which sinks the mixture into the deeper ocean floor;
- Discharge can be carried out large pipes and towed behind a ship to drag
- Pumping can be done into a hollow at the bottom of the ocean floor and forma a pool of CO₂ lake.

Finally the liquefied CO₂ that was injected at a subterranean depth of equivalently 3000 m is expected to remain stable as reported by O'Connor *et al.* (2001). The sink capacity of CO₂ sequestrated ocean is approximated at between 5000 and 10,000 Pg C yr⁻¹. This no doubt exceeds the world fossil fuel reserves ever reported (Herzog *et al.*, 1997, 2002). Nonetheless, further research incursions by Auerbach *et al.* (1997), Caulfield *et al.* (1997) and Seibel and Walsh (2001) has it that there are very serious unpleasant effects on sea biota culminating from CO₂ injections. Furtherance to the economics of the technology of CO₂ injection, the question of stability of

oceanic injection should be well explored, investigated and analysed from different perspectives following the ever increasing oceanic stratification and water column in juxtaposition with its adventurous turn over through natural processes.

Geological injection

Generally, the method for geological injection of CO₂ involves the following distinctive approaches: CO₂ capture; CO₂ liquefaction; CO₂ transportation and CO₂ injection into the deep geological strata of the earth. There are also possibilities of injecting CO₂ into old and new coal seams. It is reported that there is possibility of CO₂ injection to be undertaken in coal seams or beds, abandoned oil wells (for yield intensification), saline aquifers and stable rock strata. Researchers like [Klara et al. \(2003\)](#), [Tsang et al. \(2002\)](#), [Baines and Worden \(2004\)](#) and [Gale \(2004\)](#) presented saline aquifers as underground bed layers of very porous sediments filled up with brackish water. Usually, aquifers filled with saline waters are densely positioned underneath the reservoirs of freshwater having layers that are impermeable in between. So industrially produced CO₂ on a large scale can be pumped into the aquifer and hydrodynamically sequestered. In this case, the CO₂ can form carbonates by reacting with other dissolved salts available. Also, supercritical injection mode is used to inject CO₂ having density and viscosity lower than the liquid brine, which it will displace at the spot. In situ sequestration happens when it forms in a gas-like phase and dissolves spasmodically in the aqueous phase, creating a multi-phase cum multi-component condition. It has been reported by [Lal \(2008\)](#) that the injection of CO₂ into reservoirs where oil and gas are displaced could be a potential economic strategy of enhancing oil recovery from the wells. CO₂ can therefore be injected into un-mineable coal beds. In this case, methane as, CH₄ is directly absorbed into the system as studied and presented by [Lal \(2008\)](#). The main concerns regarding geological sequestration of CO₂ are almost similar to oceanic injection earlier presented ([Kintisch, 2007](#); [Schrage, 2007](#)).

The operational and process cost in addition to CO₂ leakages are main issues of concern in geological sequestration. It requires innovative solutions and low-cost approach in order to make this strategy competitive. Low density and low viscosity of injection under supercritical conditions presents daunting challenges; the risks associated with CO₂ leakages and sometimes slippages through confined strata may be too high compared to the currently injected liquid wastes according to [Tsang et al. \(2002\)](#). Furthermore, there is the need to consider chemical interactions of CO₂ in storage with different geological formations; because overtime, this can stimulate other geochemical reactions which may be deleterious and can aid the migration of harmful substances. When articulating strategies for suitable monitoring controls, these facts in addition to impacts must be considered ([Lal, 2008](#)).

Scrubbing and mineral carbonation

Scrubbing and carbonation of mineral carbon is accomplished through the simulation of mimicking of the usual natural inorganic chemical transformation of CO₂. It is a two-way process and the process allows the conversion of industrial CO₂ emissions (from any source) into Na₂CO₃, MgCO₃, K₂CO₃, CaCO₃, and other related minerals ([Fan and Park, 2004](#)). These carbonates being the final products are known to be stable geologically and thermodynamically. This is the aspect of carbon mineralisation. With regards to scrubbing, CO₂ chemical absorption is carried out using an amine or carbonate solvent which is broadly used for carbon capture. Therefore, in this process, scrubbing purifies CO₂ by passing the stream through amine solvent absorption column. Other solvents such as lithium silicate, K₂CO₃ ceramic, absorbent clay, nickel-based compounds are also employed in scrubbing during the absorption phase process. Pure gaseous CO₂ is thereafter recovered by subjecting the CO₂-rich amine to heating and then re-precipitated through mineral carbonation. [Lal \(2008\)](#) reported the successful implementation of carbon scrubbing and mineral carbonation in CO₂ sequestration.

Biotic sequestration

Biotic sequestration focuses on the use micro-organisms and some higher plants (flora) aiming to remove and trap CO₂ from the atmosphere. This option uses the nature ability to remove CO₂ and it is totally different when compared to management options in which there are reductions of emissions or offset of emissions.

Oceanic sequestration

With more than the earth's 70% and its surface, the ocean has a vital prevailing role in the cycling and recycling of global carbon. Also, in climate and its changes, patterns of weather and others. The estimation of 93% of the earth's CO₂ being deposited and stored in vegetation, algae and coral reefs beneath the sea and cycled through the ocean is a reality. Numerous biological processes exist even though more diversified that can lead to the sequestration of carbon in the ocean through photosynthesis. Photosynthetic process by phytoplankton and other such organisms is reported by [Rivkin and Legendre \(2001\)](#) as one of such mechanisms or techniques of oceanic carbon sequestration. It is reported in the ocean floor, some of the phytoplankton's or other organismic particulate organic materials from organisms are dropped and consequently and sequestered. Some metals are necessarily significant in this oceanic processes. It is discovered that the accessibility of Fe is one of the limiting factors on the growth of these organisms, phytoplankton inclusive in the oceanic ecosystems. Hence, quite a substantial number of research have attempted to analyse the significance of fertilization of Iron (Fe) on biotic sequestration of CO₂ in the ocean ecosystem. The studies of [Martin and Fitzwater \(1988\)](#) kick-started the insights, [Falkowski \(1997\)](#), [Martin et al. \(2002\)](#) and [Boyd et al. \(2004\)](#) made several contributions with various perception and variations in results. It was therefore argued and presented that incremental carbon could be trapped and sold as credits using the developing global carbon platform as marketplace. Analogous to this deep injection, [Chisholm et al. \(2001\)](#) in a separate study presented an important fact that ocean fertilization can affect the entirety

of the ecology of the ocean. However, the present situation is that ocean fertilization remains a controversial issue and has affected the way and manner technological incursion towards ocean sequestration are generated (Johnson *et al.*, 2002).

Terrestrial carbon sequestration

The allocation and subsequent transfer of atmospheric CO₂ into biotic carbon sinks is established as terrestrial carbon sequestration. It is reported that about 40%–50% of CO₂ that are anthropogenically emitted are atmospherically stored. This is due to the fact that undetermined terrestrial pools sequester atmospherically stored CO₂ which no doubt plays significant and important roles in the entire carbon cycle globally according to Lal (2008). Our ecosystems that are terrestrial in nature are composed of a major carbon sink directly influenced by photosynthesis which brings about the storage of CO₂ from both living and dead organic matters (flora and fauna). Due to several additional beneficial factors including improved good water quality, soil, air and attendant regeneration of retrogressed ecosystems with increased agricultural yields, terrestrial carbon sequestration has been successively being categorised as a natural strategy of win–win situation by researcher like Lal (2003). Terrestrial sequestration presents numerous advantages in addition to the natural elimination of global climate change incursions and threats. Three main components of terrestrial carbon sequestration are considered in this discourse: They are soils, forest and wetlands terrestrial sequestration based ecosystems. In terms of forest ecosystems, carbons are stored lignin and cellulose. There are also other resistant polymeric carbon compounds relatively present.

It is reported by Wofsy (2001) that in the forest ecosystem, forest carbon is sequestered both in woody debris, woody products, wood leaves and branches, trunks, barks and harvestable timber; also encroaching woody plants and grasses on grasslands. Forestry practices like afforestation can be one of the sustainable options available for carbon sequestration in a terrestrial ecosystems as reported by the intergovernmental panel on climate change (IPCC) in 1999s report and also as presented by Fang *et al.* (2001) and Lamb *et al.* (2005) in their research works. Afforestation however on a commercial and industrial scale can significantly affect other sectors like water resources and environment. It is documented that with afforestation, substantial and steady losses were recorded in streams and river flows. Also, Jackson *et al.* (2005) noted that increased soil salinization and acidification as a result of afforestation. It is also reported by Gorham (1991) and Warner *et al.* (1993) that in terms of wetlands ecosystems, the associated soils or histosols create large and extensive pedologic agglomeration estimated at circa 450 Pg. Wetland soils terrestrial sequestration may constitute as much as 200 times more carbon than the associated vegetations according to Milne and Brown (1997) and Garnett *et al.* (2001).

Soil carbon sequestration suggests the process of enhancing the concentration of pools of soil organic carbon and soil inorganic carbon and sequester them as secondary carbonates or compounds through the conversion of land-use and subsequent implementation of recommended best management practices (RMPs) in the pastoral, agricultural and forestry ecosystems with the restoration of retrogressed and extremely distressed soils. Afforestation is among the most practical possibilities of carbon sequestration in all terrestrial ecosystems. The various reports and studies of IPCC (1999), Fang *et al.* (2001) and Lamb *et al.* (2005) confirm this. In practice, almost 350 Mha or more of most tropical forests have been exploited and converted to other land usages. In addition, over 500 Mha of marginal and non-marginal forests have been degraded to extreme varying scales according to successive studies of (Lal, 2005a,b,c). Consequently, the creation of productive, non-invasive but monocultures of plantations of eucalyptus, acacia, pinus, jatropha and others can bring about the enhancement of the terrestrial carbon sinks and pools in these ecosystems. The schematics in Fig. 3 gives a vivid information on biotic sequestration and the linkages with sub- sequestration options in biosphere as highlighted.

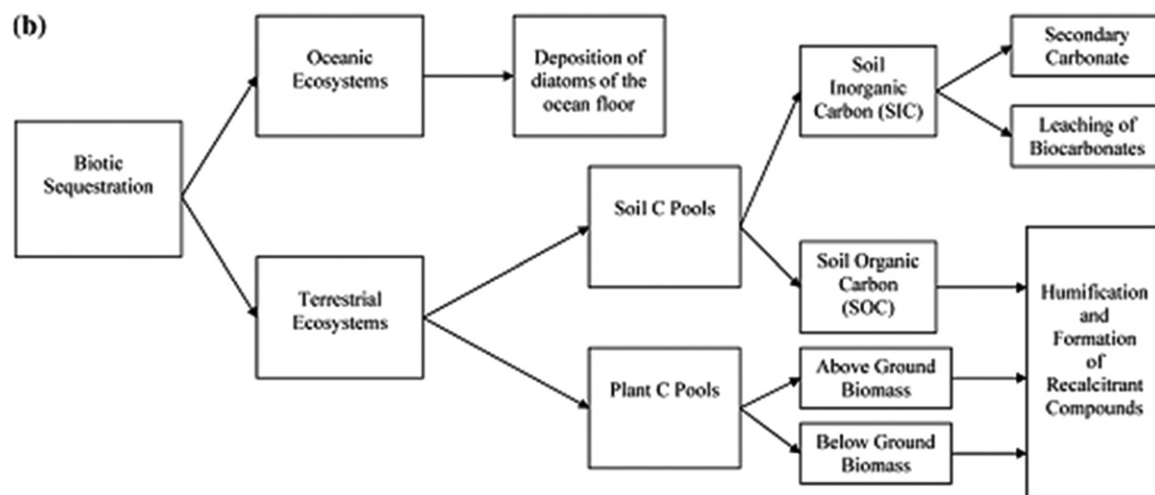


Fig. 3 Processes of carbon sequestration within the biosphere. Source: Lal, R., 2008. Sequestration of atmospheric CO₂ in global carbon pools. Energy and Environmental Science 1, 86–100.

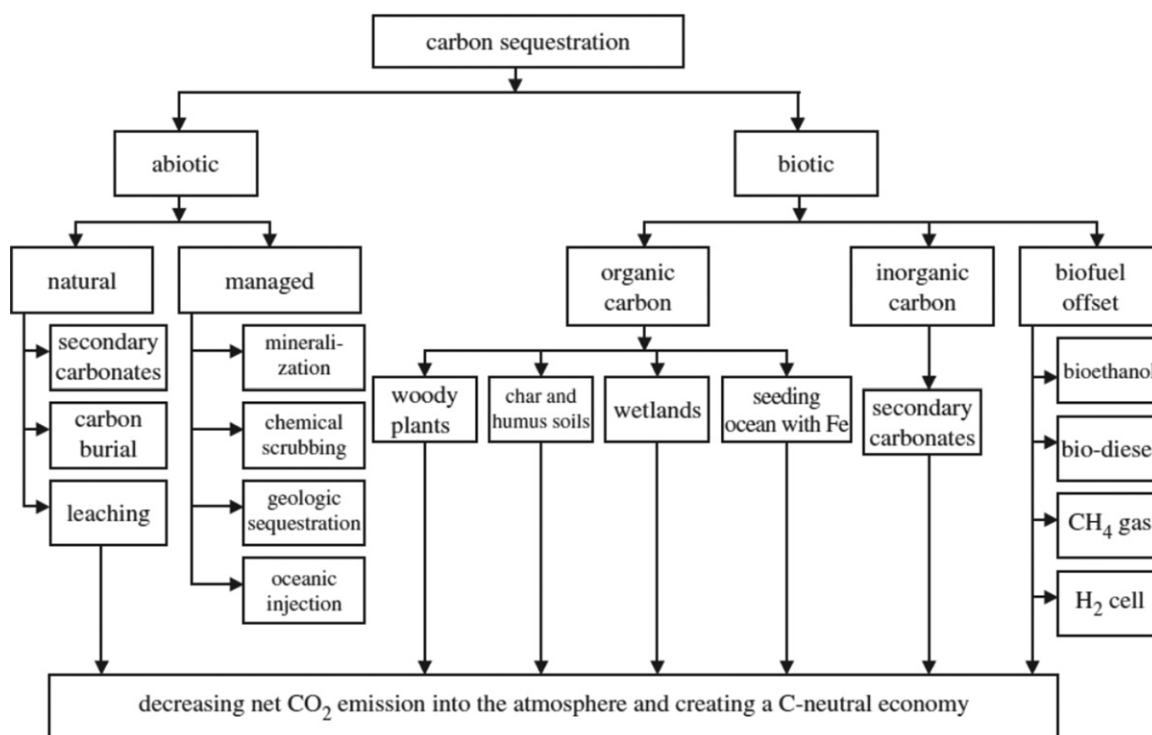


Fig. 4 Various processes used for carbon sequestration. From Lal, R., 2008. Sequestration of atmospheric CO₂ in global carbon pools. *Energy and Environmental Science* 1, 86–100.

Table 1 Comparative analysis of biotic and abiotic sequestration

Parameters	Biotic sequestration	Abiotic sequestration
Type of Process	Humidification by Photosynthesis (Natural)	Technological (capture, injection, sequestration)
Capacity of Sink	finite (between 50 and 100 Pg)	Hugely large (in terms of thousands of Pg)
Horizon Time	Immediately: next 25–50 years	Between 10 and 20 years
Cost Implication	Low, none or negative	High
Yield reduction risk of biomass and NPP	Low or insignificant	
Risk of Human health	Insignificant to low in terms of agricultural chemicals	High
Risk (Leakages)	Small or insignificant (ploughing and so on)	Expensive and complex approach/method
Risk (Environmental)	Effect: positive	High
Verification and monitoring	Routine and simple methods	Expensive and complicated methods
Regulatory approach	Pecuniary incentives may be necessary	Policy and essential legislative measures

Comparison summary between biotic and abiotic methods

The following table summarizes the differences between biotic and abiotic methods for carbon sequestration and the comparison of various parameters. This comparison is further expounded in the schematics in Fig. 4. Highlighted are the various sub-processes as presented by Lal (2008) (Table 1).

Algae Carbon Sequestration

Microalgae are known as photosynthetic microorganisms which can be deployed in the mitigation of CO₂ and concurrently produce value-added products such as fuels and pharmaceuticals. This is possible because being photosynthetic in nature attract CO₂ to themselves which are used in energy creation as green plants in the presence of chlorophyll. In this wise, algae strains or species can provide specific advantages with regard to carbon sequestration and are natural. They are known for their fastidious growth rate, their capability to use brackish, saline, ocean or waste waters rather than fresh water, emissions and effluents for production and therefore, there is no reliance or dependence on arable land resources. Their perennial growth allows for the use of important nutrients like nitrogen and phosphorus compounds and other salts. However, carbon in the form of CO₂ is very

Table 2 Species suitable for CO₂ capture of emission from power plants in literature

Genres and Species	Maximum CO ₂ concentration known	Year and citations of study
<i>Cyanidium celdanum</i>	100%	(Seckbach <i>et al.</i> , 1971)
<i>Scenedesmus sp</i>	80%	(Hanagata <i>et al.</i> , 1992)
<i>Chlorococcum littorale</i>	60%	(Kodama <i>et al.</i> , 1993)
<i>Synechococcus elongates</i>	60%	(Miyairi, 1995)
<i>Euglena gracilis</i>	45%	(Nakano <i>et al.</i> , 1996)
<i>Chlorella sp</i>	40%	(Hanagata <i>et al.</i> , 1992)
<i>Eudorine spp.</i>	20%	(Hanagata <i>et al.</i> , 1992)
<i>Dunaliella tertiolecta</i>	15%	(Nagase <i>et al.</i> , 1998)
<i>Nannochloris sp.</i>	15%	(Yoshihara <i>et al.</i> , 1996)
<i>Chlamydomonas sp.</i>	15%	(Miura <i>et al.</i> , 1993)
<i>Tetraselmis sp</i>	14%	(Matsumoto <i>et al.</i> , 1996)

Note: Huntley, M.E., Redalje, D.G., 2007. CO₂ mitigation and renewable oil from photosynthetic microbes: A new appraisal. *Mitigation Adaptation Strategies for Global Change* 12, 573–608.

important and indispensable in increasing biomass production rates and their influence on the lipids production content to certain degrees are unquantifiable. The use of algae can offer higher rates of carbon capture than any terrestrial plants and this can step up and so can avoid the inherent food vs energy competition with food crops and aimed at limited supplies of land and water. Algae can be grown in any wastewater, murky water, pools, systems and can consume carbon while producing more crude bio- oil under certain manipulation such as: after starvation and variations in the light and dark conditions (Bwapwa *et al.*, 2018a,b).

Characteristics of algae-based CO₂ capture

In describing the features or characteristics of algae based on CO₂ capture, it is emphatic to relate that most microalgal culture does not necessarily required high purity of CO₂. The possibility of direct feeding of flue gases containing between 2% and 5% of CO₂ to the photobioreactor is desired and most cases, has an optimal implication for direct capturing and sequestering. This no doubt simplifies the separation of CO₂ significantly from flue gases. In this situation, other products of combustion including Sox, NOx, VOCs can effectively be employed as nutrients for the microalgae and can simplify the scrubbing of flue gas meant for the combustion scheme or system. The culturing or growing of microalgae can yield high-value sustainable and commercial end-products which could take care of all the capital costs and operational expenses of the entire process while also producing energy for the system. Such process products may include: (1) Mineral-based carbon for steady sequestration, and (2) High commercial and sustainable value chemical compounds. Depending on the choice of algae genres and species selected, more or more of these products or their combination can be aimed and produced during the process.

Species of algae suitable for CO₂ capture from emissions

Table 2 presents a summary of various species that have CO₂ tolerance. It is important to specify that there are species of micro-algae that have the capacity to tolerate or withstand higher concentrations of CO₂ than listed the few listed and the researchers who studied them.

Cost challenges affecting algae-based CO₂ capture

It is reported that there are few or non-comprehensive and evidence-based estimates or quantification so far established on cost implications and estimates of CO₂ sequestration of various sources especially from power plants using algae as spin-off. Most operation are still at the research and development scale. Earlier initial estimates lacks integrity in terms of the economics and technology of exploring algae sequestration of CO₂ especially with current mode of cultivation technologies both at open pond level and with the use of photo-bioreactors.

The Technology of Carbon Sequestration

Carbon capture with sequestration (CCS) is a bioenergy technology that has been well reported in recent literatures (Eloka-Eboka and Inambao, 2017; Zhao and Su, 2014; Xie *et al.*, 2014; Velasco *et al.*, 2016; Poeplau and Axel, 2015; Bwapwa *et al.*, 2018a,b). Carbon sequestration can hypothetically be a compared approach adopted in the reduction of emissions of NOx, SOx, volatiles, particulates, VOCs and others. The only difference however is that CO₂ is the target and the quantity of CO₂ that is generated to be sequestered which are usually much more than those of other emissions. It is therefore possible that CO₂ can be economically sequestered, stored and transported as fuels. The pathways to capture carbon for sequestration have three potential source routes. (1) Many industrial processes and operations generate relative quantity of streams concentrated of CO₂ as derivative by-product. With inherent CO₂ capture in the process, there is relatively low cost of technology. (2) Fossil power plants account for the emission of the overall CO₂ emissions globally, the potential and attention for carbon capture is mostly prevalent. The

concentration of CO₂ in this option is low but there is significant quantity to be captured; the cost of capture is quite significant at 3.5%–5% from gas plants and up to 12%–15% from coal fired plants.

Opportunities for CO₂ sequestration are higher in terms of production of hydrogen fuels from carbon-rich feedstocks. Sources may include: coal, natural gas, biofuels and biomass. These account for relatively pure CO₂ by-products with attendant incremental costs of carbon capture being quite low. Produced hydrogen from this technology could be employed in fuel cells of low temperature. Other hydrogen fuel-based technologies are possible, but also there are issues of technological costs in contemplating and implementing research and development for the huge market and in addition to infrastructures for the new products. The large quantity of captured CO₂ have to be utilised commercially. The values are ideal for scaled projection even as large-scale applications may not be unlimited in the time being. Chemical operations and processes utilising CO₂ needs relatively minimal amounts in the neighbourhood of millions of tonnes: even as billions of tonnes are generated directly from the burning (partial and total combustion) of non-renewable fossil fuels. There is also the possibility to capture huge quantities of CO₂ which could be detained and stored in geological formations and in ocean depths and sea bed. Geological basins for CO₂ include: exhausted oil and gas reservoirs, unmined coal seams at various locations worldwide and deep saline formations. Collected together can take up thousands of mega and giga tons of carbon. The know-how and the equipment for injecting CO₂ into the ground has developed and there are an established techniques. The injection of CO₂ is used to enhance oil recovery. Sequestration in deep saline formations is possible by a combining three mechanisms: (1) In situ fluid displacement by CO₂; (2) CO₂ dissolution into the fluids; and (3) reaction of CO₂ with minerals present in the formation in order to form stable, solid compounds which includes: carbonates, sulphates, phosphates and so on.

There is initial displacement domination, later on, dissolution and reaction becomes more prominent over decades and centuries. Sometimes, abandoned coal closures and strata are prospective storage spots or sites. CO₂ will ordinarily diffuse through the outlets of pore orifice of coals and thereafter are physically adsorbed. The process is analogous to the manner by which adsorption naturally takes place using activated carbon to remove impurities from substances, air or water. CO₂ can be further employed in the enhancement of the recovery of methane in coal beds which can be quite cost-effective as the additional removal of methane from the system can eliminate the operational costs of CO₂ accumulation and storage. The ocean no doubt is the largest potential anthropogenic CO₂ sink. It encompasses an estimate of over 40,000 billion metric tonnes of carbon. While the atmosphere harbours only 750 billion metric tonnes. The terrestrial biosphere has 2200 billion metric tonnes. Extrapolating a timeline of about 1000 years; more than 80% of the current anthropogenic CO₂ emission will be conveyed into the ocean water body. But if the anthropogenic CO₂ is directly evacuated into the ocean, it would facilitate the continuing but slow natural process of sequestration and in turn, will decrease the peak concentration of atmospheric CO₂ and the rate of build-up will be eliminated.

Conclusion

Production of energy generally and subsequent utilisation are the major drivers and contributors of the overall greenhouse gas emissions globally. Biomass carbon sequestration is an interesting technology and a pertinent approach in recovering resources from greenhouse emissions and converting them to useful energy products while at the same time mitigating climate change effects and challenges. It is a strategy towards overall emission reduction and climate change mitigation in the present and future energy dynamic systems, environment and economy. Atmospheric unleashing of greenhouse gases as a result of unprecedented anthropogenic activities is a huge contributor to the ravishing effects of climate change in the global world to date. Every indication allays the fear that with continuous unabated growth in greenhouse emissions, there is a decimal certainty that the impact will lead to accelerated dramatic unimaginable consequences in the earth's planet's climatic, bio and eco-systems. The strategy for mitigation needs to change and potentially urgent too. It has therefore become the focus of many R and D activities giving rise to biomass carbon sequestration. The significance of this reduction and mitigation cannot be over-emphasised as the global world is heading towards a net neutral carbon environment free from pollution and challenging effects of climate change. With many processes being developed to deal with the challenges, effects and issues associated with global warming and overall climate change, biomass carbon sequestration is the most sustainable, significant and acceptable approach and it employs natural and engineered techniques such as biotic and abiotic options while producing more energy which are clean and environmentally acceptable. These options have exhibited huge potentials but require more improvement and development in order to establish low cost investment and sustainable route in the current world. More studies are needed in the future to diversify this technology beyond the use of biomass feedstocks to other renewable energy resources and thereby establishing sustainable methods to eradicate systematically the effect of global warming and climate change in addition to more energy production for the growing world population. Thus the development and deployment of global carbon market can be kick-started with biomass sequestration.

See also: CO₂ Sequestration Using Algal Biomass and its Application as Bio Energy

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Further Reading

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Carbon Capture and Storage (CCS) Technology: Challenges to Implementation

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Introduction

The emissions of greenhouse gas (GHG) has noticed a steadfast upsurge since the outset of industrial revolution with an annual increase over the last decade reported to be by an average of 2.7% (Cuellar-Franca and Azapagic, 2015). In order to avert catastrophic aftermath, two major global gatherings took place in Kyoto (1997) and the other one in Paris (2015). The scientific suggestion that came from the two meetings was that average global temperature increase as a result of climate change should be limited to no more than 2°C (Voll *et al.*, 2012). For this target to be achieved, worldwide GHG emissions must be reduced by at least 50% of their current values by 2050 according to IPCC (2013). Carbon dioxide (CO₂) is the most popular and well-known among various other gases that act as GHGs. It is characterized by high anthropogenic emission which acts as one of the major contribution factor to global warming, caused mainly by fossil fuel combustion (Ustadi *et al.*, 2017). The harmful nature and impact of climate change and of fossil fuels are well established (McDonagh *et al.*, 2019).

From pre-industrial level to present, concentration of CO₂ was reported to have increased from 280 parts per million by volume (ppmv) to 395 ppmv and it is estimated to reach a level of 570 ppmv by the end of this century (Goel *et al.*, 2015). The current atmospheric concentration of CO₂ is estimated to be about 750 Giga tonnes which was projected to be on the increase for the next 100 years to come (Fig. 1). This in turn caused the ocean to become acidic and more dangerously creating an imbalance in the manner by which solar ultra-violet rays are trapped in the atmosphere thereby influencing how water is utilized by plants. Upsurge in global temperature is therefore directly related to continuous CO₂ emission (Fig. 2). Another issue considered by environmental agencies that need to be drastically addressed is anthropogenic climate change (IPCC, 2005). Carbon capture and storage is one of the many options that are gaining interest. It is a technology with the prospect of abating the anthropogenic emissions of CO₂ emissions and to achieve the target of holding the increase in the global average temperature at or below the critical 2°C threshold (Thomas *et al.*, 2016; Wang and Qie, 2018). CCS from fossil-fired and bioenergy-fired plants was reported by IPCC (2014) mutually contribute in reducing CO₂ emissions by up to 25% till the year 2100 (Pachauri *et al.*, 2014). Decoupling energy use as well as CO₂ release is a very vital long-term way of halting greenhouse gas emissions with the assumption that energy use will continue to grow (Herzog, 2001). This can be achieved by utilizing renewable energy sources such as hydro, nuclear, wind, solar, geothermal and tidal energy. However, these sources cannot fully replace fossil fuels, particularly given the numerous ways in which such fuels are used and the current global framework for energy. The consequence is that fossil-fuel-based energy infrastructure is currently been planned that will remain for decades, continuing to increase atmospheric CO₂ concentration. This article reports an overview of the CCS technology, its relevance as a multi-functional climate change mitigation option for oil and gas companies and the associated challenges of its implementation.

Despite the controversy in the effects of carbon dioxide in the atmosphere, the average temperature of the Earth is rising, especially when measured at the poles. Fig. 2 show good correlation between the average Earth surface temperature correlates with the amount of CO₂ in the atmosphere (i.e., upsurge in the atmospheric CO₂ levels is directly proportional to the increase in surface temperature).

Overview of the CCS Technology

Carbon capture and storage (CCS) is a technology that involved disengagement of CO₂ from industrial and energy related sources (large stationary sources), transport to a permanent storage location and complete isolation from the atmosphere (FAO, 2009). This implies that CO₂ must first be isolated from the emission point(s), emanating from the burning of fossil fuels before being stored permanently in a manner that prevents it from entering the atmosphere. Addressing the sequestration of CO₂ from widely distributed and/or mobile emission sources such as residential heating, automobiles and airplanes, is currently impractical but necessary (Williams, 2006). The process involved three important stages as described below.

Stage 1: Capture process

Before capturing CO₂, separating it from other flue gases that results from combustion and/or other industrial processes must first be achieved. This could be done by post-combustion, pre-combustion or oxy-combustion method or oxyfuel capture (Markewitz *et al.*, 2012).

The post-combustion process (gas scrubbing or flue gas method) involved scrubbing the gas exiting the combustion or production process (Heafeli *et al.*, 2004). The capture process is practised at over a dozen plants all over the world, which is based on chemical absorption. Up to 99% of the gas exiting a boiler or a gas sweetening unit can be captured. Mono ethanolamine (MEA) is the most popular solvent usually employed with the process described in the following equations (Galadima and Garba, 2008).

- (1) $2\text{RNH}_2 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow (\text{RNH}_3)_2\text{CO}_3$
- (2) $(\text{RNH}_3)_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow 2\text{RNH}_3\text{HCO}_3$

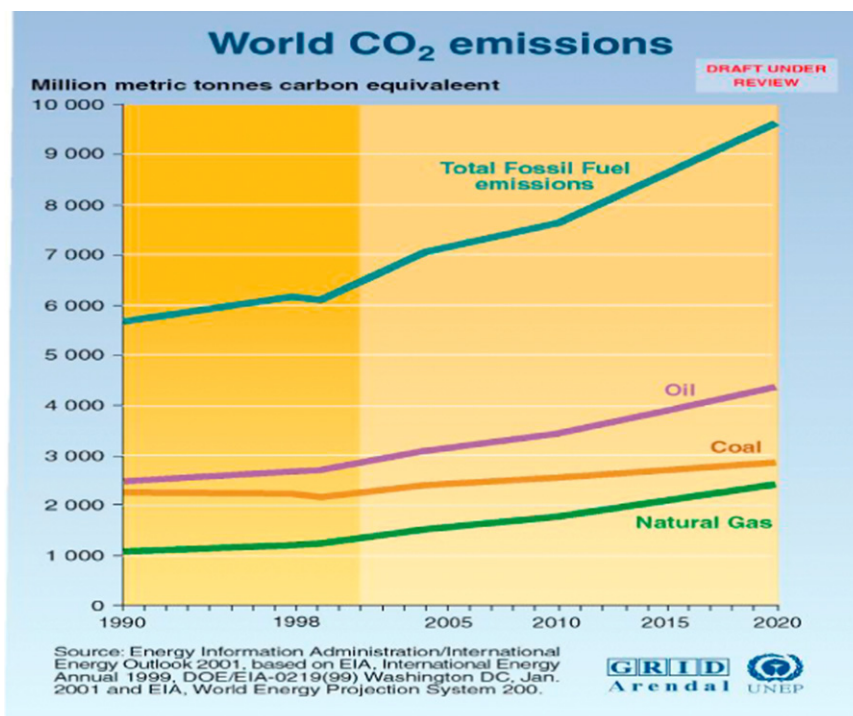


Fig. 1 Global CO₂ emissions. Source: <http://courses.knox.edu/envs101/tempco2.JPG>.

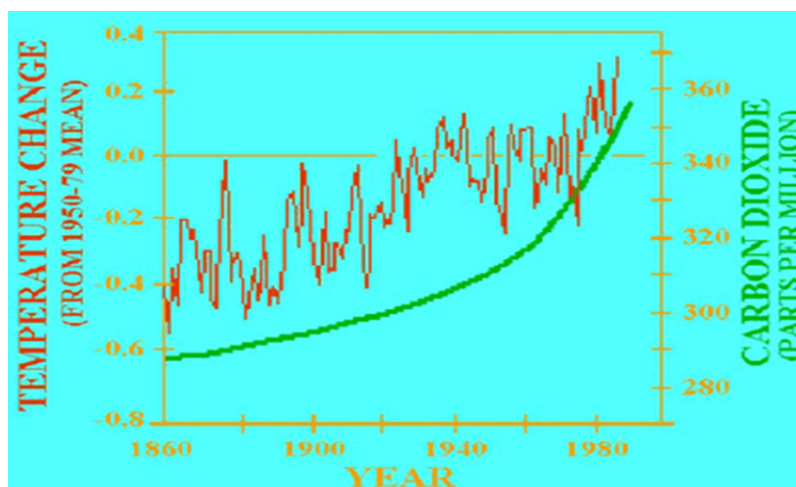


Fig. 2 Effect of CO₂ emissions on global temperature. Source: <http://courses.knox.edu/envs101/tempco2.JPG>.

- (3) $2\text{RNH}_3\text{HCO}_3 \rightarrow 2\text{RNH}_2 + 2\text{H}_2\text{O} + 2\text{CO}_2$ [Amines regeneration and carbon dioxide release for transportation to appropriate geological storage unit]. Alternatively, the process can obey the following mechanism



$\text{R} = \text{C}_2\text{H}_4\text{OH}$ when the employed solvent is MEA.

To date, the chemical absorption processes with monoethanolamine (MEA)-based solvents is being used by all commercial post-combustion CO₂ capture plants. MEA was developed over 70 years ago as a general, non-selective solvent to remove acid gases, such as CO₂ and hydrogen sulfide, from natural gas streams. The process was modified to incorporate inhibitors that reduce solvent degradation and equipment corrosion when applied to CO₂ capture from flue gas. Concerns about degradation and corrosion also kept the solvent strength relatively low (typically 20%–30% amines by weight in water), resulting in relatively large equipment sizes and solvent regeneration costs (Chavez and Guadarrama, 2008).

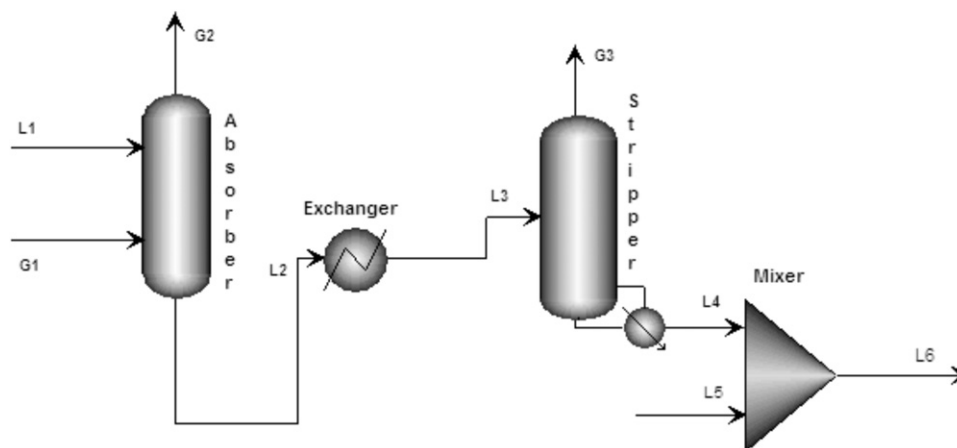


Fig. 3 Flow sheet diagram for post-combustion capture. Source: Chavez, R., Guadarrama, J.J., 2008. Optimized process for post-combustion CO₂ capture in thermoelectric power plant using structured packing. Available at: <http://www.aidic.it/pres11/webpapers/291Chavez.pdf>.

The flow diagram of the main process is depicted in Fig. 3. Gas flow G1 gets entry from the bottom of the absorption column with the liquid flow L1 coming in from the top. The rich liquid amine stream L2 enters to a heat exchanger to raise its temperature and then pass to the stripper where it carries out amine regeneration. For the sake of verifying the mass balance of the whole process, the regenerated liquid flow is mixed with MEA solution at 30% weight L5. Stream L6 is re-circulated to the absorption column. The stability of the stream L5 was due to know the iteration number in the simulator (Chavez and Guadarrama, 2008).

Post-combustion capture has an edge over other capture technologies, having the advantage of being compatible with existing coal-fired power plant infrastructure as well as being retrofitted without requiring tangible change in basic combustion technology. It has the highest priority when it comes to gas-fired power plants. Neither the oxy-combustion nor the pre-combustion approaches are well suited for gas plants.

Another advantage it offers is flexibility as the power plant can still operate even if the capture plant is off but the other two capture options are highly integrated with the power plant: So if capture fails, the entire plant must shut down. It also proffers utilities which allow for increased capacity by temporarily restraining the capture process during periods of peak power demand.

Pre-combustion/syngas method is appropriate to integrated coal gasification combined cycle (ICGCC) plants, where by synthetic H₂ and CO₂ rich gas is produced from the fuel (Heafeli et al., 2004). It first involved the gasification of coal to generate the synthetic gas comprising of CO and H₂ followed by “water-gas shift reaction” of the CO to produce CO₂ for capture and H₂ to a turbine to generate electricity. This clean coal technology has good potential for future generation and is currently practised in few existing facilities in the US and Europe.

Oxy-combustion process involves burning the fossil fuel in pure or enriched oxygen to produce a flue gas consisting mostly of CO₂ and H₂O vapour. The CO₂ can be piped directly to storage unit after being compressed. Cooled flue gases are circulated with the sole purpose of limiting the resulting flame temperatures to levels common during typical combustion and injected into the combustion chamber. The constituents of flue gas are mainly carbon dioxide and water vapour, the latter of which is condensed through cooling. The result is an almost pure carbon dioxide stream that can be transported to the sequestration site and stored. Power plant processes that relies on oxyfuel combustion are also referred to as “zero emission” cycles, because the CO₂ stored is not a fraction removed from the flue gas stream (as in the cases of pre- and post-combustion capture) but the flue gas stream itself. It is also worth noting that no matter how small a fraction of CO₂ generated during combustion, it will inevitably end up in the condensed water. Thus the water would have to be treated or be disposed fittingly to merit the label “zero emission”. The technique is encouraging though the initial air separation step demands a lot of energy. This process is still at the Research and Development (R & D) phase. The main stages of the above-mentioned three carbon capture methods are summarized in Fig. 4 (Agrali et al., 2018).

Chemical looping combustion (CLC) is an alternate method though under development. It is a method based on utilization of a metal oxide as solid oxygen carrier. Metal oxide particles usually produces solid metal particles with a mixture of carbon dioxide and water vapour when reacted with solid, liquid or gaseous fuel in a fluidized bed combustor, condensing the water vapour thereby leaving the pure carbon dioxide ready for sequestration. The solid metal particles are circulated to another fluidized bed where they react with air, producing heat and regenerating metal oxide particles that are recirculated to the fluidized bed combustor.

Eradicating CO₂ from the atmosphere is a form of geoengineering by greenhouse gas remediation. Widespread media coverage was given to techniques of this type due to their upper hand in offering the promise of a comprehensive solution to global warming if they can be coupled with efficient carbon sequestration technologies. It is more common for such techniques to be proposed for air capture, than for flue gas treatment. Carbon dioxide capture and storage (CCS) is more commonly proposed on plants burning coal in oxygen extracted from the air, which means the CO₂ is highly concentrated and no scrubbing process is necessary. A hierarchical and multiscale framework was presented by Hasan et al. (2015) to design CCS and CCU supply chain networks with less investment, operating and material costs by taking into consideration the selection of source plants, capture processes, capture materials, CO₂ pipelines, locations of utilization (for enhanced oil recovery) and sequestration sites, and

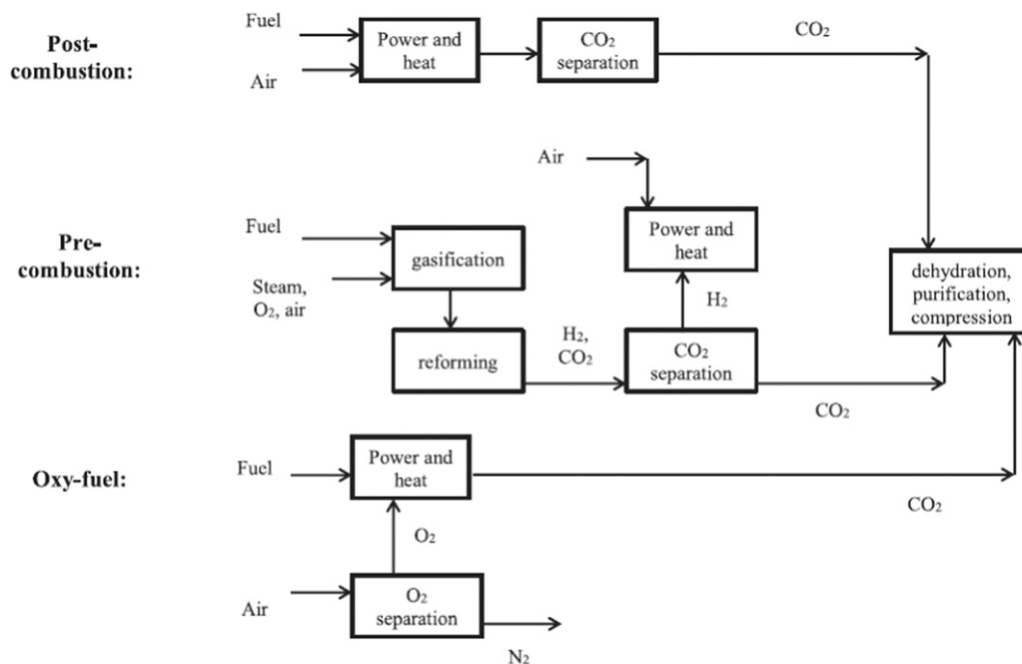


Fig. 4 Basic principles of carbon capture. Reproduced from Agralı, S., Üçtug, F.G., Türkmen, B.A., 2018. An optimization model for carbon capture & storage/utilization vs. carbon trading: A case study of fossil-fired power plants in Turkey. *J. Environ. Manag.* 215, 305–315.

amounts of CO₂ storage. A profit of \$9.23 per ton of CO₂ was achieved by their optimized network. An optimal solution to the problem of choosing between CCS and carbon trading was founded by Üçtug *et al.* (2014) for a hypothetical methanol production facility. A non-linear optimization approach was employed with the objective of maximizing the net returns from pursuing an optimal mix of CCS and carbon trading. The results are sensitive to carbon credit prices and the discount rate, which determines the choices with respect to the future and present. Three alternative CCS configurations to the benchmark process which is absorption by using monoethanolamine, (MEA) as solvent was compared by Schach *et al.* (2010). They concluded that “the process with the highest energy savings is not the lowest cost of CO₂-avoided, and the influence of rising investment costs of more complex configurations cannot be ignored.” A coal-fired power plant was also studied by Cristobal *et al.* (2012a) for which they considered installing four control devices in series. They assumed that bypassing one or more of these devices before the CO₂ discharge point would be possible. They develop a mixed-integer nonlinear programming (MINLP) model that determines which devices to use and the operating condition of each device. MINLP was also developed by Cristobal *et al.* (2012b) for a similar problem where a set of pollution control retrofitting alternatives are considered to be installed in a cap and trade framework.

Stage 2: Transportation process

I was reported by IPCC (2005) that the gas should be transported safely except in the situation when emission point is located directly over the storage unit. Onshore pipelines have been utilized since the 1970s in the USA. About 5800 km of CO₂ pipelines were reported in the United States in 2008, with most of them in the Permian Basin of Texas. CO₂ is being transported to oil production fields by these pipelines where the CO₂ is injected in older low producing fields to enhance oil recovery by EOR. Another option for the gas transportation is by liquidification like liquidified petroleum gas (LPG) and transported through ships or ocean going tankers. In the case of small scale applications, rail cars may also be employed. CO₂-transportation generally depends on distance, quantity and cost.

Stage 3: Storage process

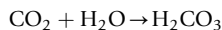
Large quantities of captured CO₂ could be stored in different geological formations, minerals and deep oceans as believed by scientists and engineers.

Ocean storage

Oceans can accommodate CO₂ due to its being appreciably soluble in water. Upon its capture, CO₂ could potentially be injected directly into deep oceans and most of it would remain there for millions of years (IPCC, 2005). It was reported by Herzog (2001) that the ocean embodies the largest storage option for the gas. Already 40,000 Giga tonnes of CO₂ were reported to be confined in the oceans in relation to the atmospheric concentration of only 750 Giga tonnes. Thus, quantities of CO₂ that would double its atmospheric concentration would only change the ocean’s concentration by 2% (Herzog, 2001). As such the countries with better chance of storing large volume of the gas are those that are closed to the oceans. Below are among the various concepts proposed for the ocean storage:

- Injecting CO₂ by ship or pipeline into the water column at depths of 1000 m or more, and the CO₂ subsequently dissolves.
- Depositing CO₂ directly onto the sea floor at depths greater than 3000 m, where CO₂ is denser than water and is expected to form a 'lake' that would delay dissolution of CO₂ into the environment.
- Converting the CO₂ to biocarbonates (using limestone).
- Storing the CO₂ in solid clathrate hydrate already existing on the ocean floor, or growing more solid clathrate.

Negative environmental effects of oceanic storage are usually reported though poorly understood. Living organisms in the ocean are usually killed by high concentration of CO₂ and also the ocean storage is not permanent too as the dissolved CO₂ would eventually equilibrate with the atmosphere. Also, the CO₂ reacts with the water to form carbonic acid, H₂CO₃, hence increasing the acidity of the ocean water.



About 1600 years was the order of time estimated to take water in the deeper oceans to circulate to the surface. The retention of CO₂ in the ocean would be enhanced by the bicarbonate approach which reduce the pH effects, but other environmental effects and cost will also increase.

The inevitability of the effects of making the ocean more acidic are absolute as illustrated by Fig. 5, which are easy to predict due to reliance on simple chemistry, not on complex computer models of climate. The ocean already holds 400 Billion tons of fossil fuel CO₂. Consequently, the ocean is already 0.1 pH units more acid than before industrial CO₂ emissions. This means nutrients for plankton in the North Sea, and all shallow ocean waters, are changing rapidly. This is the base of the food chain for invertebrates, shells and, eventually, economic fishing. By 2050 the ocean will be five times more acid than at any time since glaciation (change pH 8.4 to pH 7.8).

Mineral storage

Another form of carbon sequestration involve the reaction of naturally occurring Mg and Ca containing minerals with CO₂ to produce carbonates as can be seen from the following reactions.



In this process, stable carbonates are produced by exothermically reacting CO₂ with abundantly available metal oxides. This is a process that occurs naturally over many years and is responsible for much of the surface limestone. Reaction at higher temperatures and pressures or pre-treatment of the minerals made the reaction rate to be faster although the method may require additional energy. The IPCC estimates that a power plant equipped with CCS using mineral storage will need 60%–180% more energy than a power plant without CCS.

Geological storage

Several factors such as geological setting, integrity of the hydrocarbon column height (cap rock), quality of the reservoir and possibility of unexpected events like earthquake need to be considered in order to strike a balance between permanent storage and risks of leakage with regards to the geological storage options. Geological storage options involve depleted oil and gas reservoirs, offshore and onshore deep saline formations, use of CO₂ in enhanced hydrocarbon (oil or gas) recovery and in enhanced coal bed methane recovery (Galadima and Garba, 2008). In 2001 according to Herzog and Golomb (2005), about 200 million cubic

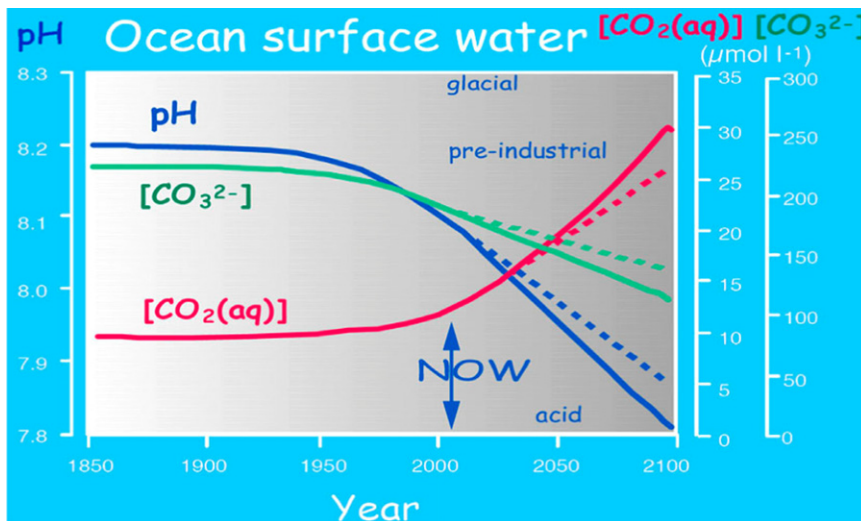


Fig. 5 Effects of CCS on ocean acidity. Source: <http://courses.knox.edu/envs101/tempco2.JPG>.

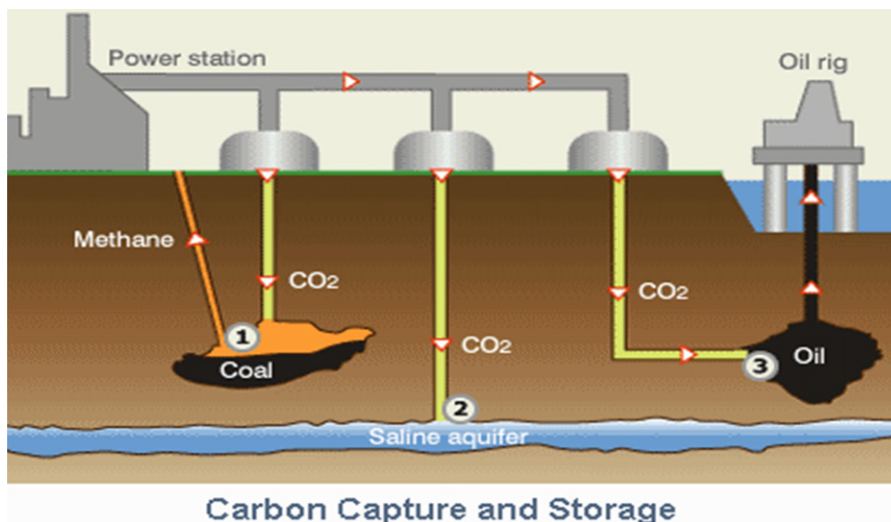


Fig. 6 Application of CCS for EOR and enhanced methane recovery from coal seams.

meters of the gas were believed to be injected into more than 30 different oil and gas fields of Alberta and Columbia. The gas could also be utilized in improving the recovery of coal bed methane especially with the fact that the surface structure of coal has good adsorption affinity for CO_2 . With the possibility of achieving return on investment in short time, EOR becomes an economic option with special interest to many oil and gas companies leading to the availability of more than 80 CO_2 -EOR projects worldwide in the last 9 years, producing 200,772 bbls of oil per day (Herzog and Golomb, 2005). In general, the cheapest and most environmentally friendly storage option is the geological storage.

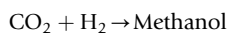
Benefits of CCS Technology

Utilization of the gas for enhanced oil recovery (EOR) is one of the major potential benefits of the CCS. The method has the advantage of increasing the oil amount that is recouped from an underground oil reservoir. By pumping CO_2 into an oil reservoir, previously unrecoverable oil is pushed up through ideal displacement to where the oil can be reached (Fig. 5). Additional 30%–60% of the original amount of recoverable oil was reported by the U.S. Department of Energy (DOE) once all the recoverable oil has been reached, and the depleted reservoir can act as a permanent storage site for the CO_2 (MGA, 2009). As reported by Galadima and Garba (2008), CO_2 has been injected into over 11,000 oil wells for tertiary recovery since late 1970s and the technology already accounted for over 15% of annual oil and gas production in the region in the Permian basin of Texas United States.

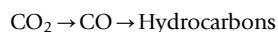
“Sleipner Project”, is an example of the commercial success of the technology. It is a project where the gas is compressed and pumped into 200 m thick Utsira sandstone layer of the Sleipner oil and gas field in the North Sea United Kingdom (Herzog, 2001). The investment was paid back in about one-and-half years only with about 1 million metric tonnes of CO_2 reported to have been sequestered annually since October 1996 (Herzog, 2001). Another project is called the Weyburn- CO_2 monitoring project, Canada which accounts for about \$30 million of gross revenues to the gasification plant’s cash flow each year (Heafeli *et al.*, 2004). Up to 20 million tonnes of CO_2 would be injected and permanently stored, leading to at least 130 million barrels of additional oil recovery for the project life cycle.

As can be seen in Fig. 6 with regard to oil and gas companies involved in methane exploitation from coal beds, studies reported the possibility of injecting up to 173–203 billion tonnes of the gas for enhanced coal bed methane recovery (ECBMR) world-wide. In a country like Nigeria that is developing, the current proven oil and gas reserves (36.22 bbls & 184 tcf) were projected to last for the next 40 years (Galadima *et al.*, 2009), indicating that future CO_2 -enhanced oil recovery is necessary.

The conversion of CO_2 into hydrocarbons is a potentially useful way of dealing with industrial sources where it can be stored or reused as fuel or to make plastics with quite a number of projects investigating that possibility. Currently, biofuels represent the other potentially carbon neutral jet fuel available. Carbon dioxide scrubbing variants exist based on potassium carbonates which can be used to create liquid fuels. Although the creation of fuel from atmospheric CO_2 is not a geoeengineering technique, nor does it actually function as greenhouse gas remediation, it nevertheless is potentially very useful in the creation of a low carbon economy, as transport fuels, especially aviation fuel, are currently hard to make other than by using fossil fuels. A proven process to produce a hydrocarbon is to make methanol. Methanol is rather easily synthesised from CO_2 and H_2 .



By heating CO_2 up to the temperature of 2400°C , it dissociates into carbon monoxide and oxygen. Another important process that can be used to convert CO into hydrocarbons is the Fischer-Tropsch process. The required temperature can be achieved by using a chamber containing a mirror which focuses sunlight on the gas.



In addition to all these, the captured CO₂ can be applied for various other household and industrial applications which include production of carbonated drinks and soda water, electric fire extinguishers, polymers and plastics, industrial welding urea or as a promising solvent for organochlorine in the removal of caffeine from coffee, lipophilic organic compounds as well as an industrial gas laser (CO₂-laser). These therefore give a chance to various oil and gas companies to diversify their investments by establishing related industries

Implementation Limitations and Challenges

It was claimed that even very low leakage rates could undermine any climate mitigation effect, for that safe and permanent storage of CO₂ cannot be guaranteed. However, some geologists argued that the proportion of CO₂ retained in appropriately selected and managed geological reservoirs is likely to exceed 99% over 1000 years. There is major concern here with CCS as to whether the leakage of stored CO₂ may compromise the technology as a climate change mitigation option. For well-selected, designed and managed geological storage sites, IPCC estimates that risks are comparable to those associated with current hydrocarbon activities. For ocean storage, its depth is very crucial in determining the CO₂ retention. It was estimated by IPCC that 30%–85% would be retained after 500 years for depths of 1000–3000 m. With regard to mineral storage on other hand, it is free from any risks of leakage.

The degree of challenges for CCS implementation can be viewed from country perspective. Majority of developing countries cannot successfully adopt the CCS technology in the short term despite certain progress being achieved in terms of its life cycle assessment. Several factors covering technology to regulatory policies could be attributed to this fact.

Technology

Shifting towards low-carbon energy sources (more importantly biofuels) has special interest in many countries; most projections show that the current environmentally undesirable fossil fuels will in the medium term continue to play a crucial role. For example coal demand alone in developing countries will likely increase from 4215 to 5647 million tonnes from 2015 to 2030. In ensuring the successful capture of CO₂ that will be emitted in line with the combustion of these fuels, an effective technology is very vital. For successful “Clean Coal Technology” alone, a range of modern technologies that are currently not available in developing countries are certainly required. These technologies will cover the preparation of coal (washing and briquetting), combustion for example by fluidised bed boilers and gasification, and clean-up of undesirable gases by processes like flue gas desulphurisation and denitrification before the ultimate carbon capture and storage. In fact the whole CCS process involved series of advance technologies, few of which are under early stages of practise in some industrialised countries like United Kingdom and U.S.A. This clearly indicates that inefficient technology will lead to a serious setback in implementing CCS in many regions and most developing countries, who do not have enough technology to provide their citizens with basic amenities (Galadima and Garba, 2008).

Capture and storage cost

The country, technology and fuel types have a big influence on the costs of capture, transport and storage of CO₂. For example, the cost of capture from gas-fired power plants will be lower than from coal power plants due to lower concentration of the gas. Similarly transportation cost varies with applicable options with ships and pipelines emerging as the most viable transport options in many regions. Different authors reported varying cost estimates. In an analysis by Anderson and Newell (2003), they estimated storage costs of \$7 to \$19 per 1000 Kg of CO₂ total transport while Hendriks *et al.* (2000) reported \$13 to \$44 per 1000 Kg of the gas (Galadima and Garba, 2008). The transportation distance of 1000 km was assumed by both authors, implying an upsurge in both transportation cost and risk of corrosion for longer distance (especially for offshore pipelines). In a developing country like Nigeria for example, the costs are much likely to be higher due to metocean conditions, requiring advance pipelines technology and potentially longer transportation distance. This may have an earnest effect in its implementation except otherwise if forced by government or oil and gas companies make use of the gas in enhanced oil recovery (EOR). The consequence will rise in oil and gas consumers cost and when this is connected with the current poverty situation, the masses would be at serious disadvantages (Galadima and Garba, 2008).

Capture and storage policies

For the successful implementation of CCS, the right approach must be developed by the major emitters (oil and gas companies) and other companies permitted by the government to be involved in power distributions and related services as well as other industry participants that integrates important solutions and previous lessons from international sectors like the natural gas company of America. This should include development of government regulatory frame works that ensure unconditional commitment and national support. Putting into consideration the existing environmental policies in many countries that do not address this issue, its implementation will be stuck along the way if the government do not either introduce a new regulatory frame work that encourages its development or modify the current regulations to ensure that capture and storage responsibilities are assigned to the actual emitters. In essence, the oil companies should initiate CCS in addition to the biofuels options based on the current environmental policy (Galadima and Garba, 2008).

Implementation time

Sufficient time and planning is also very crucial when it comes to the implementation of CCS system that can capture desired quantities of greenhouse gases. In order to promote the efficient isolation and capture of CO₂, Each oil and/or gas formation as

well as power generation facility (medium or large) requires unique method innovations (Galadima and Garba, 2008). There is the need for appropriate technology and equipments to be put in place for the transportation of the gas either by pipelines or ships and also the number of capture facilities fully implemented upon the effective capture costs and cost-sharing agreement finalised between companies and appropriate authorities assigned by the government. Other reasons that can lead to the shift of project to a longer period in many countries in addition to lack of efficient technology suitable for CCS include poor planning and implementation policies, potential cost inconsistencies, serious corruption problems and unmitigated insecurity in the oil industry. Early compliance by oil and gas companies being the major emitters is another indicator of how shortly and successfully the implementation will be. However, for CCS project to be successfully executed in the short term, those problems need to be adequately addressed, which will yield positive results though very difficult (Galadima and Garba, 2008).

Conclusion

Carbon Capture and Storage (CCS) is a carbon emissions reduction process receiving special attention globally today. The technology provides a good solution against the global climate change. It also provide low-carbon approach to use non-renewable fuels like coal or natural gas to ensure security of power supply and is a good opportunity for Enhanced Oil Recovery (EOR) from low producing or partly depleted petroleum formations. In this article, an evaluation of CO₂ capture, transportation and storage potential was given, which include storage site screening, storage mechanism analysis, and storage capacity evaluations. Though the current economic situation does not consider the process as financially viable, CCS will play a significant role in mitigating future emissions especially from developing countries. However, careful approach is required to avoid more problems than benefits. Successful implementation of the technology must be planned ahead of time, effective future agreement is required from the sides of both government and oil companies, policies and strategies shall be base on research findings by environmental, geological and policy analysts couple with lessons from prior developed and developing countries. With correct policies, government and financial support, CCS will undoubtedly play more and more important role on sustainable development.

See also: Green Buildings: Risk Factors and Mitigation Measures/Emerging Urban Green Spaces in Dhaka: Planning and Analysis

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Carbon Footprint Reduction Instrument

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Introduction

Carbon foot printing is the process of quantifying the land segment of carbon gas emission interconnected with human activity. Usually, the carbon footprint is related to the production of a product, the delivery of a service or, more generally, the occurrence of some process. The term 'carbon footprint' is commonly used to portray the land unit based on the total amount of CO₂ along with other GHG emissions for which different type of land use is responsible. Thus, carbon footprint has become extensively used term and concept in the public debate on responsibility and abatement action against the threat of global climate change. Over the last few years, a tremendous increase in public appearances across the media, the government and the business world have been seen a wide range of awareness towards it. However, it is difficult to understand what exactly 'carbon footprint' is to the common? Despite its ubiquitous appearance there seems to be no clear definition of this term and there is still some confusion what it actually means and procedures to follow and which unit to be used. While the term itself is originated from 'Ecological Footprint' (Wackernagel and Rees, 1996a,b), the general idea is related to the carbon footprint of some land segment responsible for gaseous emissions, that are also relevant to climate change in connection with production or consumption activities of human society. However, this is almost where the commonality ends. There is no consensus on how to calculate a carbon footprint. The spectrum of definitions ranges from direct CO₂ emissions to full life-cycle GHG emissions and not even the units of measurement are clear. The change in on earth surface which is as a result of anthropogenic activity since the start of the industrial revolution. Scientific evidence proved that the burning of fossil fuels contributes to raising the average temperatures and extreme weather events (Rosenzweig *et al.*, 2001; Mitchell *et al.*, 2006; Solomon *et al.*, 2007).

Carbon footprint or amount of CO₂ emission allied with all the activities of human or other things (e.g., person, building, corporation, land segment, country, etc.) which contain to direct emission results from fossil-fuel combustion in manufacturing system, heating and transportation, as well as emissions required to produce the electricity connected with goods and services consumed. It includes the emissions of other greenhouse gases like methane, nitrous oxide or chlorofluorocarbons (CFCs). Canadian ecologist, William Rees and Swiss-born regional planner Mathis Wackernagel have invented the ecological footprint from which the concept of carbon footprint has been taken out in the early 1990s at the University of British Columbia. An ecological footprint is the total area of land required to maintain an activity or population which comprises environmental impacts, such as water use and the amount of land used for food production. In contrast, a carbon footprint is usually expressed as a measure of weight, as in tons of CO₂ or CO₂ equivalent per year. The carbon footprint of a person, organization or object can be accessed on the basis of the emission of carbon components such as CO₂. In other words, the carbon footprint is the total amount of land responsible for CO₂ and other GHG generation through the life cycle of any product or service. Although the different forms of footprint counting are established in the domain of ecological and environment science, land-use and land-cover controlled assessment of carbon footprint is found in gaps. A person's carbon footprint is calculated in terms of major categories of consumption like housing, travel, food products, and services etc. All these components are directly linked with the land use and land cover (LULC) practices of the urban environment which include various parameters of energy utilization like fuel use, calorie consumption, travel expenditure, distance, and spending behavior. The suitable emission factor takes into account the relevant life cycle as much as possible. In a year, a city-dweller emits 4 ton of carbon dioxide.

Carbon footprint examines the climate change impact of each activity ranging from making a product, living a lifestyle. Generally, a carbon footprint considers not just the CO₂ emission of a particular activity but also escaping of all other GHGs such as methane and nitrous oxide. On the contrary, biomass on the terrestrial systems has the greater potentiality to absorb carbon component that also plays an important role in balancing anthropogenic carbon emissions (Pacala *et al.*, 2001; Pan *et al.*, 2011). Indeed, carbon sink or storage capacity varies between different terrestrial ecosystems, geological formation, and oceanic deposition; on the other hand, changes in land utilization categories from high-vegetated to low-vegetated biomass usually, result in the high amount of carbon emissions into the atmosphere. This type of land-use changes in an urban area not only increases the atmospheric carbon through vegetation biomass directly, but also lowers the amount of vegetation residues returned to the topsoil as an organic matter, which turns to soil humus, by the process of mineralization. This subsystem is the main source of carbon storage as a soil organic carbon (SOC) (Post and Kwon, 2000). Unlike the directly release of Carbon dioxide from fossil fuel into the atmosphere, pests and diseases help to avoid carbon emissions from dead plants; proper fertilization and drainage can also promote vegetation growth, which may increase the accumulation of SOC (Michal and Price, 1996). Thus, globally the LULC changes have a major impact on the extent and distribution of terrestrial carbon emissions (Shevliakova *et al.*, 2009; Van der Werf *et al.*, 2010). It is expected that LULC change has contributed about one-third of all anthropogenic carbon emissions since the industrial revolution (Houghton *et al.*, 1999) and it has a share of 12.5% of total emissions between 2000 and 2009 (Friedlingstein *et al.*, 2010). As a result, the impact of changes within terrestrial ecosystems on carbon balance has been a focus of land dynamics research in recent decades (Houghton *et al.*, 1999; Houghton *et al.*, 2000). Several studies have been investigated the disturbance of carbon pools by human activities using bookkeeping models, which track the changes in areas of different land

utilization types and also used standard growth and decomposition curves to calculate the change in carbon pools (Houghton *et al.*, 1999; Dixon *et al.*, 1994). Others have estimated the effects of LULC change using spatial models that internally computed the carbon density in vegetation and soils of different ecosystems based on climate and other factors (Shevliakova *et al.*, 2009). Carbon emissions caused by deforestation, cultivation, and other land-use changes have been widely reported (Gaston *et al.*, 1998; Delcourt *et al.*, 2001; Houghton, 2003). Compared to biomass carbon pools, soil organic carbon stocks have been shown to undergo much larger changes due to the dynamism of LULC (Pan *et al.*, 2004; Huang and Sun, 2006).

Urban areas have been recorded 76% of CO₂ emissions owing to energy used and shared about 43% of global primary energy-related CO₂ emissions (O'Meara, 1999). In this background, the aim of this article is to understand the ways of reduction of household emissions of CO₂ in Kolkata and its determinants to mitigate CO₂ emissions through appropriate land utilization practices. In this connection, the estimation of LULC based carbon footprint has been emphasized and the study of its temporal changes has been incorporated through the various components of the Geographic Information System (GIS) platform. Detailed ward level data on LULC (as secondary information) and household categories (as primary and empirical information) have been used for understanding the nature of footprint. Know how regarding the household emission patterns in Indian city matters for several reasons. First, urbanization is likely to become the most relevant land transformation process in India for structuring future emission. Hence, it becomes increasingly important to study the specific role of growing cities in shaping GHG emission profiles. Second, on a more detailed level, recent studies have highlighted the aggregated or segmented direction of energy use and GHGs emission of cities but these all are insufficiently examined the household level data (Dhakal, 2009; Marcotullio *et al.*, 2011; Creutzig *et al.*, 2012; Makido *et al.*, 2012; Chavez and Ramaswami, 2013).

India is the second most urban populous country in the world (after China, with about 760 million) with an urban population of 410 million (32% urbanization level) which is projected to reach 814 million (with a 50% urbanization level) in 2050. The current share of India's urban population to the world urban population is 10.5% which is anticipated to grow to 12.8% by mid-century (UNDESA, 2015). Management of the population distribution across urban centers also matters for climate-change improvement. All footprints have a wide range scope for environmental impact assessment, though this carbon footprint is also computed. Since no process is completely isolated, land boundaries must be set regarding what to include in the carbon footprint. For example, carbon footprint could take into account the acquisition of raw materials and the disposal of the products or purely the manufacturing wastes of the product from the raw materials (Lenzen and Dey, 2000).

Changing Dimensions of Land Utilization and Carbon Footprint

Uncontrolled urbanization in connection with excessive population pressure especially in the developing countries generates the drastic alteration of the land utilization practices within the urban area and its immediate surroundings or periphery. Although the alteration process of land use from one type to another is found primarily at the regional or local level, with temporal changes at the local level, various criteria play an important role on the local environment (Ramadan *et al.*, 2004). During last several centuries near about 80% of the earth's land surface area has been prone subjected to change (Vitousek *et al.*, 1997; Ramadan *et al.*, 2004; Pabi, 2007) by the both natural as well as anthropogenic drivers. Human-induced land cover and land use changes have been found near 30% of the earth's surface (Robinson, 2011; Houghton, 1994; Vitousek *et al.*, 1997). Huge population growth and excess demand on land resource causes the dramatical alteration of land's nature and converted the land from one use to others (Dlamini, 2011). In the case of Kolkata, the extension of the built-up horizon is excessively high than the other cities located in North-East India (Haque and Bandyopadhyay, 2012). Within the aerial unit of high population concentration in this metropolitan region, the high rate of demand for services, facilities, and resources have been generated. Geographically 'there is an urgent need for accurate and timely land-based information' (Subudhi, 2001) to facilitate better and smart services. For the decision-making purpose in terms of urban land use alteration, GIS-based spatial models act as powerful tools.

Modern remote sensing technology has already been shown the capability to detect and analyze the LULC changes particularly in the mega-city regions (Kumar *et al.*, 2011; Welch *et al.*, 1998; Harris and Ventura, 1995; Westmoreland and Stow, 1992; Ehlers *et al.*, 1990). Initially, both the term 'Land Use and Land Cover' are closely linked and interchangeable (Anderson *et al.*, 1976). Today, the term 'Land Cover' is being used in association with the term 'Land Use'. But from the geospatial viewpoint 'Land Use' differs from the 'Land Cover' and there are some differences between these two. Almeida (2005) stated that in the domain of spatial science 'there are various definitions to define these terms like land, land use and land use changes; and they vary according to the purpose of application and to the context of their use'.

From the viewpoint of natural science Wolman (1987) and Stewart (1968) made some arguments that the term 'land' is being used in a collective sense because it is considered as a natural, non-renewal and green resource. The extensions of these natural resources are found around the earth surfaces, including 'climate, landform, soil, vegetation, fauna and water' (Almeida, 2005). However, considering only the natural limits may not give sufficient results regarding the concept of 'land'. Therefore, Hoover and Giarratani (1984) considered three different views from the economical side of the 'Land' stated that it is a 'first and foremost denoted space' which integrates 'topographic, structural, agricultural, and mineral properties of the sites', and includes 'the climate, the availability of clean air, water, and immediate environmental characteristics'.

Jones and Clark (1997) and Lambin and Geist (2004) illustrated that there are two different ways to change the land use practices, firstly direct conversion of one type to another type of land use, secondly simultaneous modification of present land use practice (Almeida, 2005). The processes of land use alteration have characterized by the functional as well as structural

complexities. The nature, magnitude, spatial extent and impact of human alteration of the land utilization system have been considered as an unpredictable fact in modern times. In this connection, quantitative and spatially explicit data is more vital in the scientific community for the understanding and systematic analysis of land use related carbon generation and absorption process. 'The modern world is rich in geographic information' (Dekker, 2005), so the spatial dynamics of land utilization facts is being emphasized with the trend of rapid changes regarding the above-mentioned theme. Computer-based modern spatial science techniques provide cost-effective multi-spectral and multi-temporal data for better management, understanding and monitoring the land carbon generation and sequestration. Literally, sequestration is the offset mechanism of trapping the atmospheric carbon in vegetation and in the soil by both natural as well as the human-induced system. Under the control of seasonal variation, carbon sequestration is also a result of capture and storage capacity. Thus, the process of sequestration is more closely linked with the land utilization practices of local people through the utilization of their indigenous know-how. The earth system has a tremendous capacity to retain atmospheric carbon through the geological formation and oceanic depositions but these all are fully controlled by nature's laws. Various scientists have carried out their works to assess the mechanism of carbon sequestration but land use related understanding and measurement the process of urban expansion in the light of CO₂ source-sink is still in paucity. Presently the systematic study on land cover and land use changes have got preferences in the research fields of spatial and change science (Vitousek *et al.*, 1997).

Globally, human society is consuming more resources from natural limits and squeezing the earth's natural assets (Livingstone, 2002). Human consumption among the other dwellers of earth surface is much more and it creates threat condition in environmental burden and risk. This situation has more highlighted in the urban areas where every dweller's security is found in threatening conditions (McManus and Haughton, 2006; Wackernagel, 2001). In this connection, Rees (1997) considered the city as an incomplete ecosystem. These threats crossed the former boundary of the urban places and generated ecological impacts too far beyond the built environment of the urban area (McManus and Haughton, 2006; Rees, 1997; Wackernagel and Rees, 1996a,b). In the urban area ecological footprint also calculates the equivalent land amount for per capita material consumption of inhabitant's functions. The approach of the ecological footprint is being popular dramatically in the developed country for the assessment of urban sustainability and environmental planning. Regarding this, the concept of the ecological footprint is a more successful approach (McManus and Haughton, 2006) and also a vital tool to measure and analyze the sustainable uses of the resource by the individual or population (IWM (EB) 2002). Generally, it measures the impact of resource consumption as well as a waste generation (McManus and Haughton, 2006). Therefore, it is a powerful indicator of demand for resources per global hectare area (gha) which compare with the supply of productive area (IWM (EB) 2002). On the other hand, it is a good technique to measure the impacts of resource utilization at various scales of study; it is suitable at the national level in one hand, works best at the city level (McManus and Haughton, 2006). According to Wackernagel and Murray (2004), ecological footprint considers 'the excess global demand over the global supply of nature's resources for human use' (McManus and Haughton, 2006). McManus *et al.* in their famous paper used the concept of an ecological footprint in a metaphoric way. They believed that it has a deep link with various earlier concepts; as for example, in 1917 Mark Jefferson indirectly used the concept of 'sustenance space of cities'. For the greater dependency of the English industrial cities upon the imported resources, Mahatma Gandhi observed that 'London needs half the world to keep it operating' (McManus and Haughton, 2006). In 1965, the Swedish academician George Borgstrom illustrated the idea of 'ghost acres'.

Expansion of built-up environment is a phenomenon relating to the development of a cultural milieu of the human society as well as it is a 'modern art' of human habitation. In the recent globalizing era, urbanization is occurring throughout the world with rapid changes in the urban morphology to the way of life of people. Concretization of land unit alters the nature of re-radiation from the surface, carbon dioxide (CO₂) generation, the aerosol concentration at a large scale. However, recently Indian cities have grown at an alarming pace and have encroached its surroundings, which accelerated the growth of population in the other surrounding urban centers. As a result, this situation brings forth changes in land use scenario in greater dimensions (Vasconcellos, 2001). As per the World Bank report (2010), the average footprint of CO₂ in India is 1.33 tCO₂e/capita in 1994 and in Kolkata, this scenario is 1.1 tCO₂e/capita in 2000. Although urbanization in India is characterized by many changes and it has a pivotal role in the nation's growth and development, but climate change is now beginning to influence urban development strategy (GoI, 2015). In the coming decades, Indian urban centers will work towards more productive and stronger rural to the urban linkage.

Subsequently, from an economic or market perspective, one has to distinguish between a mandatory market and a voluntary market. Prevalent for both markets is the trade with emission certificates: Certified Emission Reduction (CER), Emission Reduction Unit (ERU) and Verified Emission Reduction (VER). To achieve the goals as defined in the Kyoto Protocol, targeting with the minimal economic costs, the following flexible mechanisms were popularized for the mandatory engineering market i.e., Clean Development Mechanism, Joint Implementation, Emission trading. The Clean Development Mechanism and the Joint Implementation Mechanisms require for projects which cater the supply of emission reduction instruments; while Emissions Trading allows those instruments to be sold on international markets under the guidance of policy instrumentation. In this regard, the projects which are compliant with the requirements of the Clean Development Mechanism are controlled under the CERs process. The projects which are compliant with the requirement of the Joint Implementation Mechanism are monitored under the rules of ERUs.

At present, the status of CERs and ERUs is fully depended on emissions related trading. The demand for the CERs and ERUs being traded under the driver of (a) the crisis in national emission reduction obligations under the Kyoto Protocol and (b) lacuna among the entities obligated under local emissions reduction schemes. Nations which have failed to deliver their Kyoto emissions reduction obligation (United Nation, 1998) can enter Emissions Trading to purchase CERs and ERUs to cover their treaty shortfalls. These nations or group of nations can also create local emission reduction scheme which places mandatory CO₂

emission targets on entities within their national boundaries. Based on the CRS (2012) report, it is advocated that if the rules of treaty allow, the obligated nation/s may be able to cover all or any few reduction strategies by purchasing CERs and ERUs through Emissions Trading. While local emissions reduction rules have no status under the Kyoto Protocol itself, they play a vital role either in creating the demand for CERs and ERUs or stimulating the Emissions Trading and setting a market price for further emissions.

In contrast to the strict rules set out for the mandatory market, the voluntary market provides companies with different options to acquire emissions reductions as well as policy framing. A solution, comparable with the development of the mandatory market, has been prepared for the voluntary market is known as Verified Emission Reductions (VER). This measure has the great advantage to manage the critical result according to the quality standard for any projects but the certificate provisions are not registered by the governments of the host countries or the Executive Board of the UNO. Subsequently, high-quality VERs can be acquired at lower costs for the same project quality. However, at present VERs can't be used in the mandatory market. The voluntary market in North America is divided between members of the Chicago Climate Exchange (CCE) and the Over the Counter (OTC) market. The CCE is a voluntary unit yet has legal binding cap-and-trade emission scheme whereby members were committed to coping up the emission reductions and must purchase allowances from other members or offset excess emissions. The OTC market does not involve with the legal binding scheme and it has a wide array of buyers from the public and private realms, as well as special events that want to go carbon neutral. Being a carbon neutral one country can refer to achieve net zero carbon emission by balancing the measured amount of carbon released with an equivalent amount sequestered or breaching. On the Voluntary market, Renewable Energy Certificates (RECs) sold are quite contentious due to additional concern (Hamilton *et al.*, 2007). Siphoning off industrial gas for sequestration is considered picking the low hanging fruit; which is why credits generated from industrial gas projects and these are the cheapest in the voluntary market. The size and activity of the voluntary carbon market are difficult to measure (Hamilton *et al.*, 2007) and is fully governed by the policy instrumentation. In this framework, the European Commission (EC, 2018) has suggested different possibilities of carbon reduction through the adaptation of policy implementation and green technology.

Global Scenario of Land Utilization as Green Instrumentation

According to Andrew and Kaidons (2011), the concept of policy instrument within the frame of engineering domain acts with the help of three kinds of approaches; *firstly* the capping approach which imposes the quality of carbon emission along with the permissible limits of maximum emission. In this thought, the excess ejection of GHGs should be followed by the market price of emission. *The second* view propagates through the levy approach and it directly imposes of price valued upon the emission and this view also assumed that the excess charge will reduce the volume of emission, and the *third* approach directly controls the outflow of the greenhouse gases and it is known as a regulated approach. But after experiencing the policy and practices since the last two decades many governments have inclined to regulate price on the CO₂ emission in terms of market-based and relative cost adjustment. On the other hand developed countries were basically in favor of 'cap and trade' system; nevertheless, these all are experiencing too slowly and not to up to level with expected result (Carbon Market Data, 2009; Andrew and Kaidons, 2011). The use of pre and post-combustion captures are found in limited in the industrial sectors and oxyfuel combustion for CO₂ is presently in the demonstration stage in the advanced nations (Metz *et al.*, 2005). Besides these all economic instrumentation, parties of the Kyoto Protocol have enforced the policies that enhance the capacity of CO₂ absorb and allow to land through carbon sink process (The Royal Society, 2002). Initially, this protocol was not a comprehensive one in terms of sequestration but this was drawn up in the commitment period of 2008–2012 (Waran and Patwardhan, 2001). On the other hand, the United Nations Framework Convention on Climate Change (UNFCCC) in 1997 has focused the different issues related to the emission of GHGs and associated land utilization. And it is true that many human-induced activities produce far more carbon sink than its credit. However, the court regulation (article 3.4) of the Kyoto Protocol allows the provisions of carbon sequestration through the traditional practices of local people using their indigenous knowledge. Thus, the sequestration of this gas in any form is considered the effective strategy of land use policy but the volume of storage and sequestration permanency is the matter to the concern of people's perception. And in urban sectors, it is more vital to balance the carbon source-sink capacity. Categorically agriculture sector has the highest capability to sequester the CO₂ from the atmosphere. As a result, land-use instrumentation comes to play a vital role in disposing the excess CO₂ from the atmosphere.

The concentration of gaseous carbon in the atmosphere leads to the rise in average temperature in addition to incorporate different kinds of long-term environmental problems. Hence, it is difficult to formulate a universal consensus and adaptation policy to slew this problem (Andrew and Kaidons, 2011). But it is necessary to stay our planet alive. Presently, reduction of CO₂ is cognizant matter in the engineering platform. In every step of technological improvement strategies, it is a prime concern that the greenhouse effect performed gases should be less in the coming future. Most of the leading technological industries in the USA use two types of instrumentation regarding the low GHGs to trap the excess emission and these are either *Offsets instruments* which reduce direct emission of gases; or *Renewable Energy Certified instruments* which manage the indirect emissions. Chicago Climate Action Plan has also been introduced the forum focusing on the enforcement of the energy efficiency buildings. In the report of U.S. Energy Information Administration (2010), it is found that urban trees have increased its capacity to CO₂ sequestration from 57.1 in 1990 to 93.9 million metric tons per year in 2008 (USEIA, 2011). Whereas, the Carbon Tax, a cap-and-trade system, and vintage model are considered prime attempts which controlled carbon emission in the UK for the last two decades (Ingham and Ulph, 1991). On the other hand, various types of policy instruments are performed as new paths of green technology in Australia

under the Carbon Pollution Reduction Scheme (Freebairn, 2016). Apart from 'infrastructure-21 Summit', a new integrated approach was adopted by the national spatial plan of Australia. There was a wide range of planning initiatives incorporating state, regional and local consensus through urban planning in connecting the climate change adaptation like Victorian Climate Change Green Paper, South East Queensland Climate Change Management Plan, North Queensland Regional Plan 2025, Sustainable Sydney 2030 etc. It was the first time in 2008 when built-environment was paid more attention to the community resilience by industrial insurance (Norman, 2010), but CO₂ footprint in association with land use dynamics is still neglected. Canada has also practiced the same adaptation measures along with Building Resilience to Climate Change in Human Settlement Programme in the year of 2009. In developing countries, this is very difficult to run an effective emission controlled scheme. It is true that the problem associated to score the green success lies in social and political inertia as well as economic sacrifices (The Royal Society, 2002). Similarly, only a few have been adapted for the betterment of urban climate. A carbon neutral sustainable city plan was proposed for Shanghai, China. In India, carbon sequester land utilization policy is fully absent but the scientific study regarding its understanding is going on. As for example tree patches in Puna city absorbed only 2% carbon per year and causing 98% overload in its immediate surroundings (Waran and Patwardhan, 2001). Whereas Florence in Italy has contracted 6.2% of the direct carbon emission through its 29.1 sq km green space (Vaccari et al., 2013).

Nature and Scope of Land Instrumentation in Kolkata

Human-induced modification of land cover and land use results in the fragmentation of landscape and large-scale environmental degradation since the last four decades in and around the Kolkata city. So, this is the right time to study the green land transforming the urban environment in the context of the impact of land modification and development of CO₂ source-sink area within the arena of fragile ecosystems like that found in the context of Kolkata. Kolkata, having one-third population residing in the informal settlements is now experiencing rapid spatial as well as economic expansion (Colenbrander et al., 2016). The process of urbanization creates a high rate of energy inflow in urban ecology and alters the nature of surface-air interaction system to create the phenomenological changes of local climate. In the case of Kolkata Municipal Corporation (KMC), leading metropolitan urban center in eastern India, the advancement nature of built-up environment posed threats to the several ecological function of water bodies within as well as immediate surroundings of urban limits, fragile ecological relation and ultimately encroaching upon the green spaces (Haque and Bandyopadhyay, 2012). KMC is not a walled city but it is almost bounded in all sides either by the natural systems (like the Hugli River on its west and the East Kolkata Wetlands to its east). Since the last four decades, the fringe area of this metropolitan center has absorbed more population than it's downtown the city has experienced a rapid outward extension of housing infrastructures and structural modification (Pathak, 2011). Owing to the high rate of population concentration the nature of city limit of KMC is *over-bounded* for a long time i.e its built environment has exceeds its boundary. So, the outer wards of the KMC, compare to the inner-city wards have gained population along with the infrastructural development which creates an environmental cost of urban activities (Haque and Bandyopadhyay, 2012; Shaw, 2015). Thus, the expansion of city limits reveals both spatially and ecologically, that the quasi-natural ecosystem situated in its immediate surroundings has been impacted through the extension of the built-up surfaces. Here 59% of people used modern energy sources and the remaining depends on fossil fuels like kerosene and solid fuels (Colenbrander et al., 2016; ALGAS, 1998). As a result, energy utilization capacity per unit area has increased vigorously which has exaggerated the release of carbon in the local atmospheric system and created different Local Climatic Zones. As per the Central Pollution Control Board daily report, it is observed that the month of November 2018 Kolkata has experienced the highest number of 'red category' days in terms of Air Quality Index (AQI). Sometimes the city's air quality was worse than Delhi's (TOI, 2018). In and around the KMC jurisdiction, the extended built-up space replaced huge numbers of tropical wetlands, agriculture, and open land. The air quality has also been declined because of the high rate consumption of diesel fuel. Besides, the following concepts are playing important roles, which are beneficial to urban land use planners and other adjunct development activities in terms of green land use management system.

- (1) *The implication of 'land instrumentation' analysis at the micro-level study:* Efforts regarding municipal facilities in the process of policy making are now becoming one of the vital principles in urban sustainability and ambitious urban planning. Within the limits of the municipal boundary, intra-zonal variations of urban ecology are also becoming popularized with time especially in the arena of developing the region. While the attention of sustainability and overall urban development is welcome, the spatial distribution of land use scenario should be emphasized from the knowledge of the technocratic solution. Integration of micro-level spatial and spatial data along with the statistical analysis through the soft-computing technologies portrays the contemporary situation of urban ecosystem spatially CO₂ source and sequestration nature of land segments. In this concern 'land use' acts as an instrument. Research regarding the carbon release and sequestration creates the fundamental and scientific know-how underpinning the scope of land instrumentation.
- (2) *Green aspect of the micro-level planning:* In the recent economic and environment relationship, urban center play as a pivotal role regarding the unprecedented flow of resources, wastes, trade products, services, capital, and labor. This interconnected relationship creates environmental problems involving major damage to the tropical ecosystem in the study area, which is basically unprecedented and not replenishable. Ultimately different patches of micro-climate will generate automatically and develop unique types of CO₂ source and sink area. Under this circumstance, this work advocates some strategic ways of land instrumentation planning through integrated urban development planning.

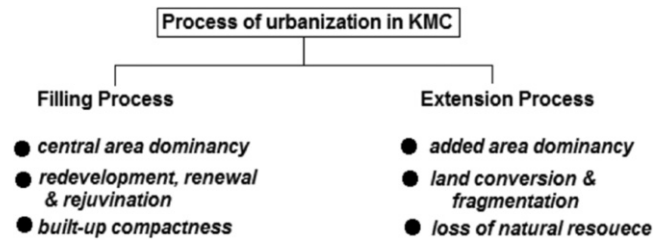


Fig. 1 Major LULC characteristics of urbanization in Kolkata.

- (3) *Controlling the negative characteristics of Urban Land-use:* As KMC has a long experience of colonial history and has grown without any proper planning, its central part has already become a problematic area and started to decay due to numerous negative reasons. The proper and systematic understanding regarding the green land utilization process can revitalize and renew these land segments with the integration of science, technology and society inputs.
- (4) *Management of the ecological cost of land transformation:* The very word 'ecological cost of land transformation' is necessary for the management of urban space into two different ways. *Firstly*, conservation and redevelopment of the existing ecological hot-spots like water-bodies, green spaces, segments of open land and pockets of biological habitat etc. which have already been fragmented in nature, shrinkage in its spatial extent and have a weak ecological function. Because these were all treated as areas of CO₂ sink in the compact urban domain. Secondly, the creation and rejuvenation of CO₂ sequestration spaces within the contiguous built-up environment through which carbon footprint will be maintained. The attempts to create this sequestration should be eco-friendly to the local area in terms of soil, groundwater, and climate. The efforts regarding the beautification and landscape design related activities in the study area have been done with the efforts of super-imposing the foreign species which do not sustain the local ecosystem rather created environmental degradation.

The process of urbanization in Kolkata leads two different styles ([Fig. 1](#)) and it is also characterized by horizontal dominance of built-up extension. [Colenbrander et al. \(2016\)](#) have estimated the increasing nature of GHGs emission in terms of total emission, per unit and per capita energy consumption for the coming decade, although it will be declined with the GDP rate. The land utilization practices during the last five decades in KMC also create different types of changes. The details of major changes are described below:

- (1) A number of *wetlands* in the extended part of KMC have dramatically been consumed by built-up environment under the process of urban extension. Since 1957 near about 50% water bodies including wetlands have been altered to built-up uses. There were two large wetlands in the eastern portion of KMC popularly known as Kadapara (means muddy-hamlet) in ward no 31 and three out of four old wetlands in the central portion of Wattgunge (under ward no 75) have totally vanished owing to the same reason. Wetlands in Paharpur and Taratala region (in Ward No. 80) have utmost (nearly 80%) disappeared due to the encroachment of built-up structures. Rest of the area has transformed their water bodies into either Open Land, Grass Covered area or Tree Covered area. The same situation is also critically found in Anandapur, Patuli, Mukundapur, Garia, Jadavpur area as well as both sides of E. M. Bypass for the urbanization. Wetland in the all most of the wards located in the east and south-eastern periphery of KMC are found with the fragile condition. Land fragmentation, garbage dumping, filling of water bodies through solid waste, illegal encroachments etc. have been sighted during the field investigation in central and northern wards of KMC. As a result, the scope of decarbonification has become limited; only the patches of tree and grass covered area have the carbon intake capacity.
- (2) The process of urbanization through the redevelopment and rejuvenation of the built-up environment grabbed the *ponds* in the KMC. Wards located in the northern portion of the study area filled up most of the ponds. Here maximum ponds have been left neglecting to maintenances and also surrounded by buildings with no natural bank. From the ecological view point, this was more sensitive for the pond ecosystem. Similarly, some big patches of the pond are found in the Port area and the medium or small patches are shown central and south-western area, mainly located at the Metiabridge region. It is remarkable that the total area of Ponds has increased in Taratala (about 1% to total ward area) due to the development of fisheries and aquaculture activity of Mudiali Fisheries Estate but it happened only in the pocket area. This type of change has been mainly noticed on the eastern side of KMC. Eventually, the activity of pond filling still going on basically for the different types of developmental activities. A very negligible portion of earlier Pond segment has converted into Open Land category. Ponds in and around the Sinthi, Maniktala, Kasba, Kalikapur, Jodhpur Park, Bansdroni, Behala, Taratala are found in a stressed condition. During the field observation, it is found that almost the entire numbers of ponds are structured and fenced by concrete banks. Previously ponds associated with its banks performed a unique function of the ecosystem to detain high amount of CO₂ from its surrounding but from the ecological viewpoint presently all these became functionless.
- (3) It is revealed that *Open Land* was the predominant land cover unit in the year of 1957 in all the wards of the added area of KMC. Comparatively, wards situated in the central portion have contained nearly zero open areas. During the 1980s the extensive open land was situated in the south-eastern fringe of the ward, coverage, and utilization of open land for the

Table 1 Ecological footprint in selected wards under different variable

Variable	The ecological footprint of selected wards (cubic metre/person/year)				
	Ward 31	Ward 75	Ward 80	Ward 93	Ward 128
Food	1158.221	966.1535	2562.849	2176.1	2041.604265
Domestic	32.59013	14.13859	45.79795	29.575	20.76184834
Industry	0.0063	0.006182	0.011935	0.0085	0.014218009
Total	1190.817	980.2983	2608.659	2205.7	2062.380332
<i>Ecological footprint under Food item of Selected Wards (cubic metre/person/year)</i>					
Cereal food	613.1264	568.2241	1172.558	923.83	1168.415877
Meat	250.1411	61.36476	674.2387	589.76	541.9170616
Vegetable	17.01015	28.16744	56.96675	46.691	12.95616114
Fruit	11.51108	34.53323	190.4766	144.61	79.41824645
Dairy	74.77809	124.7429	209.4518	243.43	37.96919431
Stimulant	97.10886	22.46265	30.4919	32.106	40.07582938
Egg	10.28106	50.44256	36.72634	33.27	9.280805687
Other	83.9748	70.04946	185.815	157.77	148.0225118
Total food	1158.221	966.1535	2562.849	2176.1	2041.604265

Source: Compiled by authors based on LULC output and primary survey in 2013.

purpose of grass and tree cover maintenance is about very less and it has been used for beautification and recreation purposes, i.e., 'parks and gardens'. During the field study, open land was found to be used for dumping of garbage. An elongated patch of vacant land is found along the western side of D. H. Road. It is located on the south-western side of the study area. Another elongated open land has been napped along the western side of the Becharam Chatterjee Road situated at the Ho-Chi-Minh and Basudebpur crossing. Rest open lands were marked in the isolated condition in the northern portion and situated in the eastern side of KMC. During the last five decades, this class of land utilization has been totally altered its characteristics i.e., became built-up structures. Because of its roadside location in an eastern & south-eastern portion of the Ward this class of land utilization had attracted various developmental activities.

Both Tree Covered, Lawn and Grass Covered condition have found quite environmentally stress situation with a fragile ecosystem. Owing to the developmental programme and renovation activities of roads, the non-native vegetation species have been plated dramatically. Openland has been formed in the new places comparatively previous vegetation area which shows the indication of unplanned land conversation. In one word the uncontrolled extension of the built-up horizon in KMC exaggerates the CO₂ generation source replacing the CO₂ sequestration facilities. The following table shows the ecological footprint of the five selected wards on KMC in the year of 2013. For the discussion of CO₂ footprint, except wards located in the central portion of KMC (ward 75) due to the vegetational occupancy all have a high level of absorption capacity in 1957; but in 2013 carbon generation area has increased dramatically. For example, ward 93 has a drastic change in terms of carbon generation rather absorption. From the ecological viewpoint, it is noted that CO₂ in the atmosphere is fully controlled by the direct process of photosynthesis and respiration, which are also been operated by land utilization practices. In the tropical monsoon climate (the light value of PAR) high rate of photosynthesis is found between 25°C to 35°C and the average temperature of Kolkata is also ranged between these value with high relative humidity condition. Under these circumstances, a strong mesophyll cell contained tree absorbs 20 µmol CO₂ per sq. metre per second by photosynthesis process, on the other hand, it produces 7 µmol CO₂ per sq. metre per second. So the net photosynthesis value is 13 µmol CO₂ per sq. metre per second (Smith and Smith, 2007). Thus the level of CO₂ concentration in and around the Kolkata urban area will be higher along with the other GHGs showing the variety layout of spatial concentration.

The nature of ecological footprint in KMC has been assessed in a few selected wards using both primary (i.e., household variables) and secondary (i.e., LULC) information under the framework of GIS platform. From Table 1, one can understand the ward level scenario of ecological footprint regarding various parameters of LULC category. All the values are showing the average condition of ecological footprint in terms of cubic metres per person per year. As the spatial concentration of population is high in ward no 80 (Port area and Taratala) and most of the people are engaged as daily laborers in port activity and informal service sectors, the total value of ecological footprint is comparatively high than other selected wards. The same condition is also found in the case of ward no 93, having the second highest value this ward shows of high concentration of population in Lake Garden, Jodhpur Park, and South City area. On the other hand, Ward No. 75 (Wattgunge and Hastings area) shows the minimum value of ecological footprint because of the presence of prohibited areas of stables, defense sector, cantonments houses in Hastings area and the existence of slums and warehouses in Wattgunge area. For the consideration of CO₂ footprint and its temporal changes, ward no 93 has shown extreme changes for the remarkable alteration of land utilization system (Table 2). In the year of 1957, the CO₂ absorption area was more than ten times larger than carbon generation area. Presently carbon generation area is nine times larger than its absorption/sinking area. Regarding the LULC change detection, the CO₂ source/generation land area in 2013 have drastically increased to replace the CO₂ sink/absorption capacity bearing area. Vertical use of urban built-up space is also responsible for creating more carbon-dioxide in relation to land utilization. Other than these five selected ward areas, central

Table 2 Temporal variation of CO₂ footprint in selected wards of KMC in terms of LULC

Ward no.	Area in 1957			Area in 2013		
	Absorption (a) sq. metre	Generation (g) sq. metre	Footprint (a/g)	Absorption (a) sq. metre	Generation (g) sq. metre	Footprint (a/g)
31	1,131,809.431	327,465.698	3.46	236,561.3314	1,222,714.331	0.19
75	219,635.01	320,391.37	0.86	86,625.97	453,400.43	0.16
80	7,067,079.777	1,219,296.139	5.8	3,017,699.578	5,268,676.34	0.57
93	1,664,275.151	151,618.1875	10.98	180,787.3	1,635,106.4	0.11
128	1,726,131.645	267,949.8467	6.44	806,734.6626	1,187,346.829	0.68

Source: Compiled by authors based on LULC output from Sol map and primary survey in 2013.

Note: the value a/g indicates the areal dominance for carbon generation or absorption; if the value is 1, then it shows a balance condition; more than 1 value marks the dominance of carbon assimilation and less than 1 value depicts the dominance of carbon generation capacity under land utilization practices in KMC.

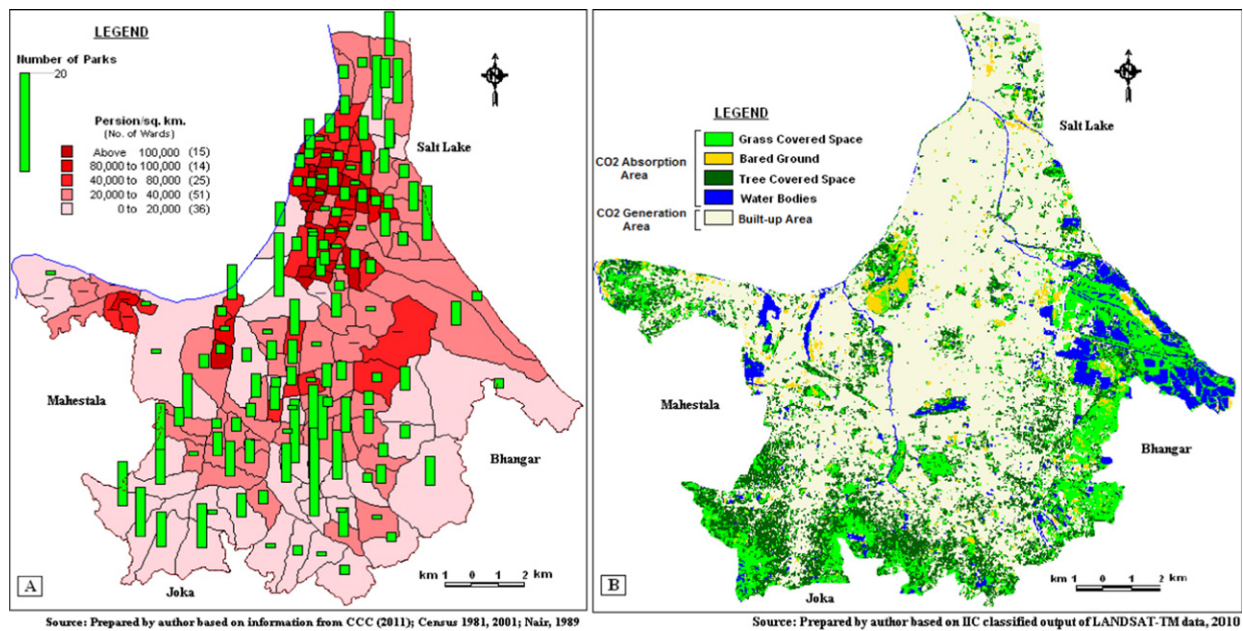


Fig. 2 Distribution of CO₂ absorption area in KMC: (A) spatial variation of parks with population concentration, (B) satellite output of CO₂ absorption area along with generation of the built-up environment. Source: Haque, S.M., 2013. Urbanization around Kolkata Metropolitan Core and Its Impact on Landuse Changes: A Geospatial Analysis (Unpublished PhD Thesis). Central library, University of Calcutta, p. 172.

Kolkata has similar condition depicting compactness of built-up infrastructure (Fig. 2(B)) and high density of population concentration. Owing to the location advantage, KMC did not contain this CO₂ for a long time because of the strong monsoon wind flow from July to October and heavy precipitation. But people in the central Kolkata faced uncomfortable weather during the late winter and early summer. As the immediate surroundings of the built-up surface in this period bear a high amount of CO₂, it absorbs an excessive amount of long-wave surface reradiation which also develop the strong Urban Heat Island effect. Long duration existence of this type of effect creates an unmanageable demand on energy consumption to modify the indoor environment of the buildings and again it could trigger the carbon generation procedure. The situation of this type of local climate and its land-use controlled has already been advocated by Stewart and Oke (2012).

Land Use Sustainability and Balanced Carbon Footprint

Environmentalists, ecologists, and scientists have already been advocating that an urban area has shown climatic differences compared with its immediate surroundings as well as rural areas (Nowak, 2000). Lomas (2006) measures the Carbon Footprint in UK Cities through different types of mapping, modeling tools. The World Bank (2012) shows the probable capacity of carbon sink in the agriculture field and its allied soil segment. Nowak and Crane (2002) estimated that the urban trees have the role of sequestrators in ten USA cities through the carbon storage ranges from 1.2 million ton (in New York, NY) to 19,300 ton (in Jersey city) and the national average is 25.1 ton per hectare to 53.5 ton per hectare. The US Department of Agriculture has advocated the measurement guideline for the sequestration of forest carbon by the public and private entities to register the GHGs (Pearson and Brown, 2007). On the other hand, Aricak et al. (2015) examine the carbon biomass above the ground surface in the dry region of Turkey through

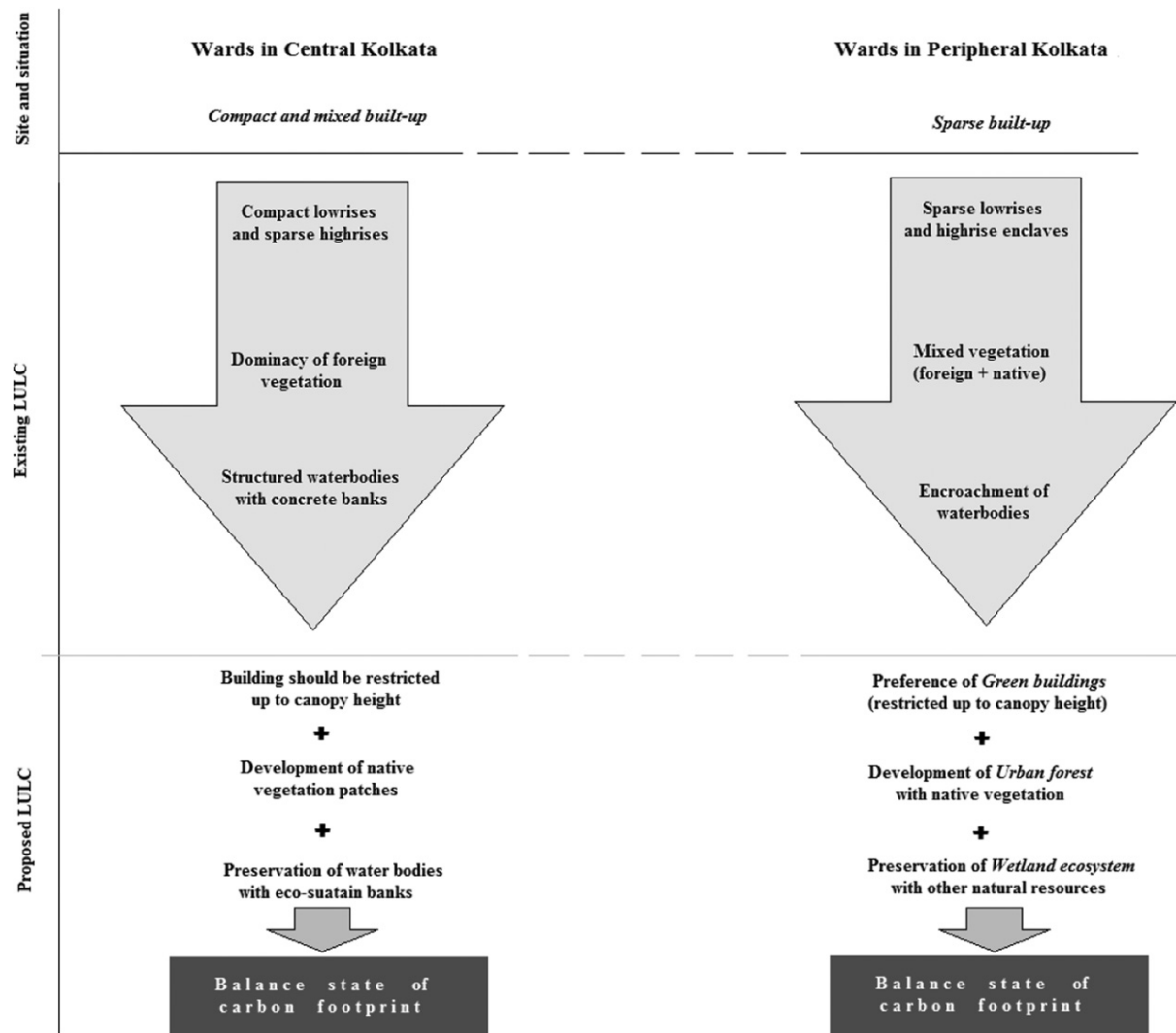


Fig. 3 Conceptual framework of green LULC practices to achieve a balanced carbon footprint in Kolkata through LULC practice. *Source:* Prepared by authors.

the Remote Sensing techniques. [Liu et al. \(2012\)](#) and [Velasco et al. \(2013\)](#) have measured the nature of carbon flux in the urban neighbourhood in the tropical region. The nighttime surface influx along with the seasonal variation of CO_2 along with CH_4 in urban areas of Southern Poland has also been studied by [Zimnoch et al. \(2010\)](#).

Based on the above discussion in the urban development perspective, now scientists are realizing the significance of study the consequences of the carbon footprint for the spatial development of urban infrastructures. Urbanization in the context of climate change is being more vulnerable with the development of carbon source triggered land use practices. Though the different forms of footprint counting are established in the domain of ecological and environmental science, land-use and land-cover controlled assessment of carbon footprint has more vital for the geographical understanding of the micro-level study. India is becoming more urbanized in the coming future with the limited available area and Kolkata is naturally bounded urban center. River Hooghly confined its western limits, an old urban center known as Baranagar is situated its northern side and the eastern boundary is circled by ecologically fragile Ramsar area East Kolkata Wetland. Subsequently, to achieve the sustainability of this metropolitan center it is essential to minimize the carbon generation activity along with its maximum absorption capacity and citizens have to practice the balance strategies of CO_2 footprint reduction. The essential steps to achieve a balanced carbon footprint in Kolkata are sketched below.

Conclusion

In the complex urban landscape, the development induces activity has always promoted the formation of the concrete horizon is associated with the creation of a built-up environment which is basically impervious and flourishes long-wave radiation from the

surface. Besides, the compact built-up area has no scope of CO₂ sequestration capacity except the superimposition of green vegetation in it and it is not easy to accept that all types of vegetation have the equal power to operate CO₂ absorbing capacity even in the same climatic situation. Uncontrolled and unsystematic land transformation in the leading metropolis has experienced significant role in CO₂ generation and thermal energy production. So, the construction activity associated with high rises is not free from all types of environmental as well as ecological constraints. Metropolitan Kolkata, like other leading urban centers, has numerous climatic problems and it has already been faced with different environmental difficulties. For the assessment of these kinds of environmental problems systematically, carbon footprint will consider a vital measuring tool for long term sustainability of a compact urban area. Urban nodes allowing the relationship with its vast hinterland, create the barrier for its green development and have a strong inflow-outflow mechanism of the energy demand as well as resource requirement interaction. On the other hand, the target of green development in the compact urban area will largely control by the introducing of green LULC practices. Where the practices of land instrumentation (Fig. 3) is more suitable for the limited and controlled consumption of energy required infrastructures, symbiotic association with green patches, alternate use of environment degraded materials, promotion of more green building, construction of urban landscape to support local climate and wise use of natural resources etc. Like the other engineering instruments, utilization of land parcel (as prescribed in Fig. 3) should be treated as a green engine to build more carbon absorption. With the smooth opening of this type of enviro-centric and green practice, urban landscape will improve its environmental quality in the coming future. Eventually, the people should be made aware of ways to control the emission with requisite perception change and pursue the green land instrumentation within the compact urban settings.

Acknowledgements

The authors are thankful to Mr. Swasti Vardhan Mishra and Prof. Sumana Bandyopadhyay, Department of Geography, University of Calcutta, Kolkata for their valuable suggestions and continuous encouragement. Also, the authors are thankful to Hewlett Packard for providing research grant of HP Z4 G4 Workstation for compiling the data.

See also: Greenhouse Effect and Carbon Foot Print. Plasma Arc Driven Solid Waste Management: Energy Generation and Greenhouse Gases (GHGs) Mitigation. Power and Other Energy Utilities From Low Grade Waste Heat – Novel Technologies to Reduce Carbon Footprint. Synthesis of Multiwalled Carbon Nanotubes (MWCNTs) From Waste Cooking Oil Catalyzed by Mill-Scale Waste for Development of Microstrip Patch Antenna (MPA)

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Carbon Management and Greenhouse Gas Mitigation

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Introduction

Rapid industrial development and human growth has led to the huge increase in fossil fuel consumption, causing a dramatic CO₂ concentration in earth atmosphere. It leads to significant increase in average global temperatures over the past several decades (Oelkers and Cole, 2008). This temperature increase has been linked to global warming and climate change like heavy precipitation events, including hurricanes (Groisman *et al.*, 2004), and rising sea levels due to melting of ice glaciers (Manabe and Stouffer, 1994). A temperature also leads to ocean acidification, effects on global ecosystems (Cole and Monger, 1994), flora and fauna distribution (Mckenney *et al.*, 2007), extinction of numerous species and human health impacts (Patz *et al.*, 1996). Weather events (Table 1) such as extreme temperature difference as high temperature in Australia recorded in January 2014 (54°C) and Canada faces extreme cold storms (~ -50°C) at the same time. In the 2005–2006, hurricane Katrina in the United States and the droughts, bushfires, snow (almost simultaneously) in Australia makes climate change as global agenda. As a result of that, there were growing scientific, economic and political debates to the issues related to CO₂ management (Table 2). Kyoto protocol (1997) is a keystone document in international climate change policy which aimed at phased reduction of greenhouse gases (GHGs). The targets were to reduce GHGs emissions about 5% below the 90s. In December 2009, interested countries met in COP-15 (the Copenhagen Protocol) to draft for this overarching of determined and direction of long-term changes to limit global warming.

Table 1 Timeline of tragic events related to climate change

Sl. no.	Year	Tragic events	References
1	1889	The Johnstown Flood killed 2200 people when the South Fork Dam holding back Lake Conemaugh broke	(Perkins, 2009)
2	April 26, 1989	The Daulatpur–Saturia, Bangladesh Tornado occurred in the Manikganj District, Bangladesh and was the costliest and deadliest tornado in Bangladesh's history. There is great uncertainty about the death toll, but estimates indicate that it killed around 1300 people	(Cerveny, 2006; Jonathan, 2008)
3	1931	The Huang He (Yellow River) in China floods particularly often. The Great Flood of caused between 800,000 and 4,000,000 deaths	(Pietz, 2002)
4	November 11, 1970	Bhola cyclone struck East Pakistan (now Bangladesh) and India's West Bengal and killed Up to 500,000 people	(Paula Ouderm, 2007)
5	2003	A deadly summer heat wave in Europe kills more than 30,000 people	http://www.pbs.org/newshour/indepth_coverage/science/globalwarming/timeline.html
6	December 26, 2004	The earthquake triggered a series of devastating tsunamis along the coasts of most landmasses bordering the Indian Ocean, killing over 230,000 people in fourteen countries	(Paris <i>et al.</i> , 2007)
7	2005	Awareness and concern about global warming rises in the U.S. after a tough storm season, including <i>Katrina</i>	http://www.pbs.org/newshour/indepth_coverage/science/globalwarming/timeline.html
8	2008	A 60-square-mile section of the Wilkins Ice Shelf breaks from the coast of Antarctica	http://www.pbs.org/newshour/indepth_coverage/science/globalwarming/timeline.html
9	February 27, 2010	The 8.8 magnitude Chile earthquake and tsunami cost 525 lives	http://earthquake.usgs.gov/earthquakes/eqinthe-news/2010/us2010tfan
10	April 27, 2011	One-day record of 188 tornadoes that killed 339 people, including 41 in Tuscaloosa, Alabama	http://towardfreedom.com/environment/2530-lethal-weather-the-rise-of-natural-disasters-due-to-climate-change
11	2011	Tōhoku earthquake and tsunami registered a moment magnitude of 9.0. The death toll from the earthquake and tsunami is over 13,000, and over 12,000 people are still missing	(Chai, 2011)
12	2012	according to The National Climatic Data Centre, Iowa is have more extreme rainstorms – Rainstorms are 35% more frequent in Iowa since 1948	(Willcox, 2012)
13	2012	Every month through August brought record high temperatures in America, with frequent triple-digit heat days	(Wiltgen, 2012)
14	16–17 June 2013	Lake outburst and debris flow disaster at Kedarnath, Uttarakhand, India: Killed more than 6000 people	(Guha-Sapir <i>et al.</i> , 2014)

Table 2 Different treaties related to CO₂ management

<i>Sl. no.</i>	<i>Year</i>	<i>Events</i>	<i>Issues</i>
1	1971	SMIC conference	There is a requirement of organized research effort to prevent serious global change
2	1979	The first World Climate Conference (Geneva)	World Climate Program established
3	1985	Joint UNEP/WMO/ICSU Conference	Role of Carbon Dioxide and other Greenhouse Gases in Climate Variations and Associated Impacts
4	1987	Montreal Protocol of the Vienna Convention	Project international restrictions on emission of ozone-destroying gases
5	1988	Toronto conference	Called for strict, specific limits on greenhouse gas emissions
6	1992	Intergovernmental Panel on Climate Change (IPCC)	192 countries signed for stabilization of greenhouse gas to avoid climate change
7	1992	The United Nations Conference on Environment and Development(Earth Summit)	First unified effort to get to grips with global warming and leads to negotiations
8	1992	UN Framework Convention on Climate Change(Rio de Janeiro)	- Stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system - Ensure food production is not threatened - Enable economic development to proceed in a sustainable manner "A discernible human influence" on the Earth's climate
9	1995	IPCC's Second Assessment Report	Developed nations agree to cut greenhouse gas emissions by at least five per cent by 2012
10	1997	Kyoto Protocol	- US later refuse to take action. Developing nations, including China, have no formal binding targets - Rich countries agree to take action first on the model of the Montreal Protocol - Diplomats did not pay attention to the financial implications of the emission trading
11	November 2000	A two-week conference at the Hague	- Try to produce an agreement on measures to fight global warming - U.S. and EU cannot agree on necessary measures
12	2001	The IPCC's Third Assessment Report	Project is new and stronger evidence that most of the warming observed over the last 50 years is attributable to human activities
13	2007	The IPCC's Fourth Assessment Report	World will have to end its growth of carbon emission within seven years
14	2008	Climate Change Act	UK passed the Climate Change Act committing the country to cut greenhouse gas emissions to 80% of 1990 levels by 2050.
15	2001	Bonn meeting	Develop mechanisms for working towards Kyoto targets
16	2007	Fourth IPCC report	- Warned that serious effects of warming have become evident - Cost of reducing emissions would be far less than the damage they will cause
17	December 2007	UNFCCC meets, Bali, Indonesia	Proposed for a roadmap for a new post-Kyoto climate change treaty
18	December 2009	UN Climate Change Conference, Copenhagen, Denmark	- Try to negotiate binding agreements - Hopes of avoiding dangerous future climate change
19	December 2010	The UN Climate Change Conference, Mexico	- Deep cuts in global emissions in order to limit global average temperature rise to 2°C - Parties agreed to keep the global long-term goal under regular review and consider strengthening it during a review by 2015, including in relation to a proposed 1.5°C target
20	28 November–11 December 2011	The UN Climate Change Conference in Durban, South Africa	- Establishment of a second commitment period under the Kyoto Protocol - Launched the new ADP with a mandate "to develop a protocol, another legal instrument or an agreed outcome with legal force under the Convention applicable to all Parties"
21	August 29–31, 2012	Second Nordic International Conference on Climate Change, Helsinki	- Agreement on the operationalization of the GCF - Identify common ground between adaptation research and adaptation decision-making by comparing experiences
22	2013	Climate Change Conference, Convention Centre, Palmerston North, New Zealand	- Reporting new insights and revealing key gaps in knowledge - Opportunity to consider challenges the research and end user communities face when dealing with climate change
23	June 22–23, 2013	Australian Climate Action Summit, Sydney	- Awareness of the severe impact of coal and coal seam gas industries on climate, health, land, water and air - Benefits of moving to clean renewable energy
24	July 15–16, 2013	ICCCGW 2013 Stockholm, Sweden	Discuss the practical challenges encountered and the solutions adopted

(Continued)

Table 2 Continued

Sl. no.	Year	Events	Issues
25	June 19–21, 2013	Transformation in a Changing Climate, Oslo, Norway	• Diverse perspectives on transformation, and to generate cutting-edge discussions on deliberate, ethical and sustainable transformation • Complex global challenges associated with climate change
26	30 Nov 2015–12 Dec 2015	United Nations Climate Change Conference, COP 21 or CMP 11, Paris, France	• 195 countries agreed on a plan to reduce emissions of CO₂ and other greenhouse gases

Intergovernmental Panel on Climate Change (IPCC, 2000) which proved the GHGs emission was the major cause of global warming and fixed responsibility of major emitters that is developed countries. United Nations Framework Convention on Climate Change (UNFCCC) established in 1992 to provide a framework for policy making to mitigate climate change based on scientific agreement. The ultimate aim of the UNFCCC, as stated in Article 2, is stabilization of atmospheric greenhouse gases at a reduce level to prevent dangerous anthropogenic climatic influence. Hence, need of global effort to reduce the amount of CO₂ emission from the source has become increasingly emphasized as a primary environmental concern and sustainable carbon dioxide management practices are essential to fight long term climatic change issue.

Carbon dioxide is responsible for about half of the observed greenhouse effect (Rodhe, 1990). Arrhenius is the first to quantify the contribution of carbon dioxide to the greenhouse effect in the atmosphere. According to him water vapor and carbonic acid (resultant from the hydration of CO₂) plays dominant role in the absorption of small fraction of the solar radiation. Arrhenius refers to carbon dioxide as “carbonic acid” (Arrhenius, 1896). From experimental carbon management research to industrial and environmental applications, the efficient reduction of CO₂ has attracted growing international interest. The aspects behind the CO₂ transformation to valuable products like chemical and fuel is attractive towards sustainable carbon management, can promote recycles of CO₂ and balances anthropogenic emissions (Milani *et al.*, 2015). Sustainable carbon management plans should have both general and experimental aspects (Pant *et al.*, 2017). Includes: (a) Reduce emission; (b) maximum environmentally sound (3R) reuse, reduce, and recycling; and (c) increase energy efficiency, promoting energy conservation; increasing the usage of low carbon containing fuels (Shove, 2017) (d) turning carbon dioxide into valuable products with atom economy. Experimental carbon management plans involving various physical, chemical and biological approaches with limitation in terms of research level and economic feasibility.

The Global Carbon Cycle

Carbon presents in four different global C pools, namely, atmospheric, oceanic, fossil and terrestrial. Natural and anthropogenic activities can influence the total carbon stock by changing carbon cycle. Its current overall concentration of CO₂ is ~ 400 parts per million (ppm) compared with pre-industrial levels ~ 280 ppm by volume (Wisniak, 2002). Fossil fuel combustion and cement production are the main sources of global emissions of CO₂. Global net CO₂ emissions from human activities such as land-use change, including deforestation agricultural use, including open burning of cleared biomass are more difficult to update annually. Combined evidence from land cover change, fire activity, deforestation lead to net emissions rate were $0.9 \pm 0.5 \text{ Pg C yr}^{-1}$ in 2011 (IPCC, 2005).

The atmosphere containing $\sim 3.0 \times 10^{15} \text{ kg}$ (3000 Gt), of CO₂ and world's oceans contain $\sim 39 \times 10^{15}$ (39,000 Gt) of C, while $\sim 2.0 \times 10^{15} \text{ kg}$ (2000 Gt) C present in soils, vegetation and detritus (Fig. 1). Carbonate rocks (limestone, marble, chalk) contain $\sim 65,000,000 \text{ Gt C}$. So, only $\sim 0.001\%$ of atmosphere–ocean – upper crust system carbon present in the atmosphere (Holland, 1978). Vegetations play an important role in global carbon cycle through fix carbon dioxide *via* photosynthesis process. Land plants contain 250 times more carbon than aquatic plants. It is estimated that the exchange rate of carbon between surface ocean and atmosphere is about 90 Gt and 110 Gt with terrestrial vegetation (Houghton, 2007).

Natural process can lead to the release of CO₂ to the atmosphere from land and water includes animal and plant respiration, and the decay of vegetation where oxygen and nutrients are converted into CO₂ and energy.

Global Carbon Budget

The “global carbon budget” refers to the net C transition due to the uptake and return in the various pools. CO₂ emissions from fuel combustion and cement production (E_{FF}) and the CO₂ emissions from anthropogenic activities on land including land use, land-use change pattern and forest fire are reported here main sources of CO₂ emission (Table 3). The main components of the CO₂ budget are included CO₂ emissions sources like, (1) fossil fuel combustion and cement production (E_{FF}), (2) the CO₂ emissions resulting from land use changes (E_{LUC}) (Figs. 2 and 3) the growth rate of CO₂ in the atmosphere (G_{ATM}), and the uptake of carbon dioxide by the “CO₂ sinks” in the ocean (S_{OCEAN}) and on land (S_{LAND}). The balance between emissions rate of CO₂ and their partitioning among the all pools like atmosphere, ocean and land can be explained by following equation. The decadal mean of the anthropogenic CO₂ budget is given below (Quérel *et al.*, 2012) (Table 4).

$$E_{\text{FF}} + E_{\text{LUC}} = G_{\text{ATM}} + S_{\text{OCEAN}} + S_{\text{LAND}} \quad (1)$$

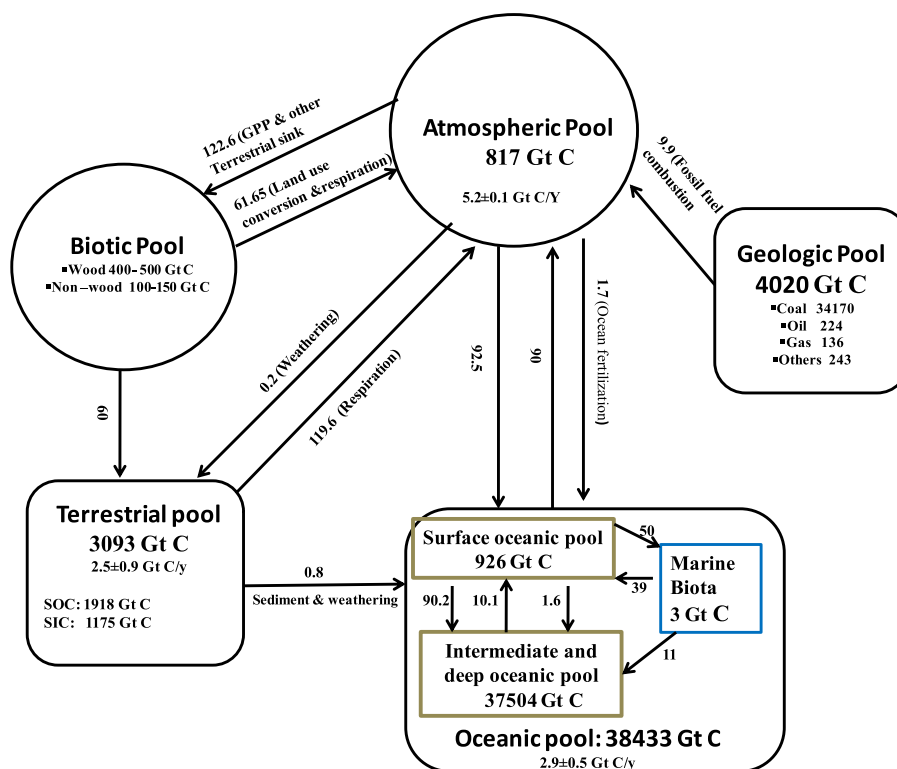


Fig. 1 Estimate of the global pools and fluxes. Reproduced from Pant, D., Sharma, V., Singh, P., *et al.*, 2017. Perturbations and 3R in carbon management. *Environ. Sci. Pollut. Res.* 24(5), 4413–4432.

Table 3 Global Carbon sequestration (Gt C/yr) by different process

Process	Carbon uptake	Carbon return	Net carbon dioxide removal	References
Soil vegetation	123	Plant respiration: 60 Decaying biomass: 60	3	(Farrelly <i>et al.</i> , 2013)
Ocean photosynthetic organisms	92	Respiration + decaying: 90	2	(U.S. Geological Survey, 2010)
Volcanic emission	–	–	0.13	(Scholes <i>et al.</i> , 2009)
Human activities	–	–	4.2	

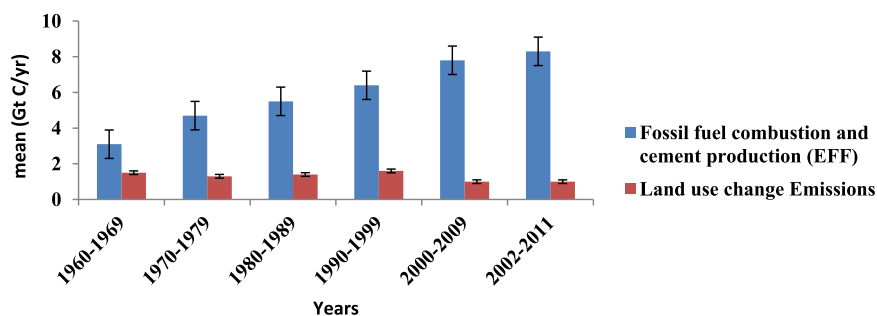


Fig. 2 Decadal mean of the anthropogenic CO₂ emissions. Reproduced from Quéré, C.L., Andres, R.J., Boden, T., *et al.*, 2012. The global carbon budget 1959–2011. *Earth Syst. Sci. Data Discuss* 1107–1157. doi:10.5194/essdd-5-1107-2012.

Fossil fuel emissions of atmospheric carbon dioxide enhanced about 29% in between year of 2000 and 2008 from the fuel combustion and international trade of goods and services. Some other industries are also contributed to global carbon emission (Fig. 4).

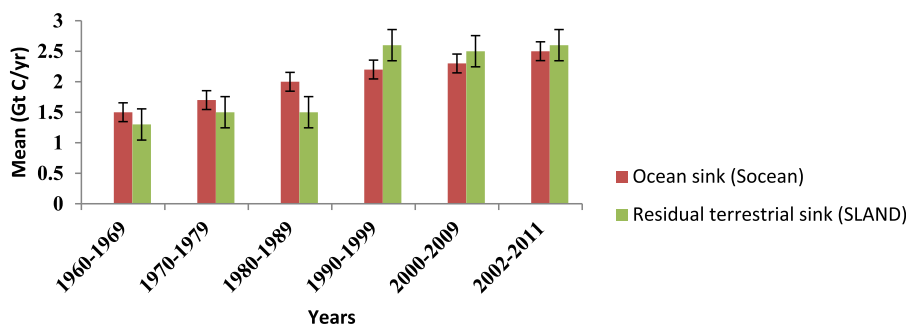


Fig. 3 Decadal mean of the anthropogenic CO₂ sink.

Table 4 Carbon budget from 1980 to 2011

Carbon budget in Gt C/yr						
Emissions	1960–1969	1970–1979	1980–1989	1990–1999	2000–2009	2002–2011
$E_{FF} + E_{LUC}$	4.6	6	6.9	8	8.8	9.3
Sinks						
$S_{OCEAN} + S_{LAND}$	2.8	3.2	3.5	4.8	4.8	5.1
G_{ATM}	1.7	2.8	3.4	3.1	4	4.3

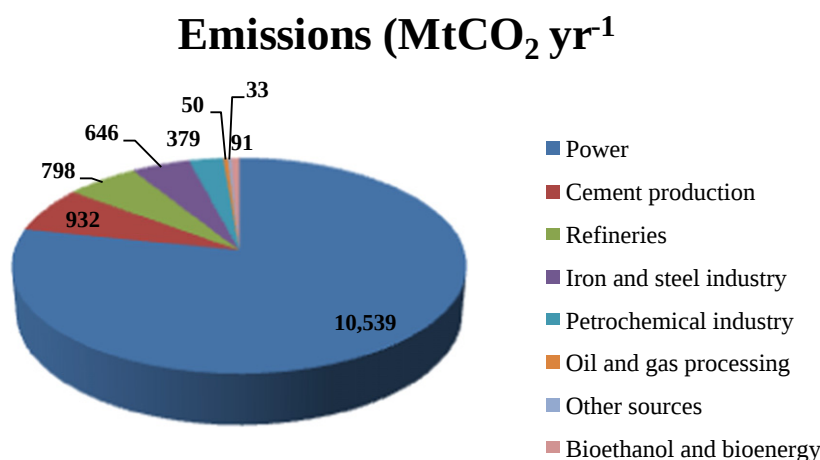


Fig. 4 Profile by process or industrial activity of worldwide large stationary CO₂ sources with emissions of more than 0.1 million tonnes of CO₂ (MtCO₂) per year. Reproduced from Intergovernmental Panel on Climate Change IPCC, 2005. IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change. In: Metz, B., *et al.* (Eds.), Cambridge, U.K: Cambridge University Press.

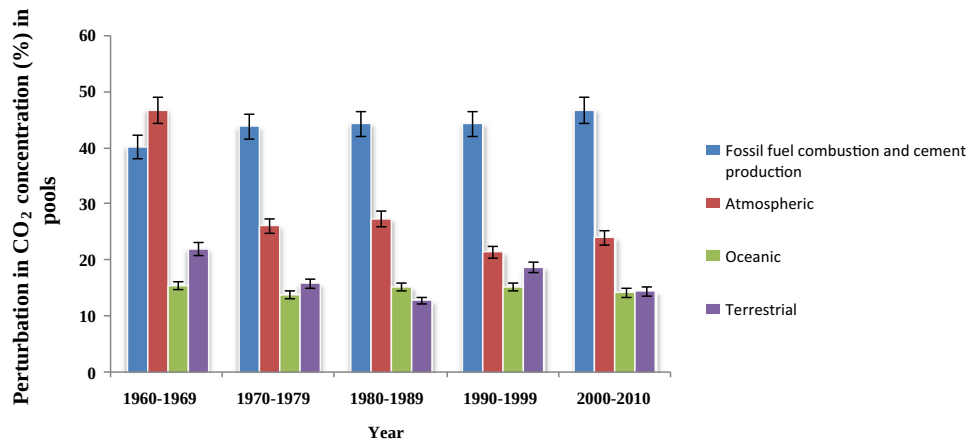
Perturbation

Irregularity in changing the different C pools data cannot be ignored toward carbon mitigation and it creates the perturbation in the global C cycle. The perturbation of global carbon cycle can be categorized into the following categories (**Table 5**).

As per world meteorological organization world data centre for greenhouse gases, perturbation in CO₂ concentration (%) in various pools per decade given in **Fig. 5**. Carbon dioxide perturbation in different pools like atmosphere, oceanic and terrestrial is effecting total atmospheric CO₂ concentrations over the last five decades due to human activities and natural process. Human activities like fossil fuel combustion and cement production takes a major part of the current CO₂ perturbation followed by the atmospheric emissions, while terrestrial and oceanic pools showed less CO₂ perturbation than other pools. So, it is important to consider CO₂ perturbation is also for sustainable carbon management practices (**Fig. 6**).

Table 5 Example of main sources for Carbon dioxide perturbation

Sl. no.	Perturbation	Example
1	Biological perturbation	- Archaea/bacteria population is responsible for converting organic matter to CH₄ via anaerobic reduction and affects the oceanic and terrestrial carbon cycle - Rice paddies amplify the level of CH₄ in the atmosphere through wetland emission - Change in the number of archaea/bacteria, net primary productivity, rice paddies, wetland emissions, and loss of biological diversity are the events responsible for the perturbation in the biological carbon cycle
2	Geological perturbation:	Volcanic eruption and metamorphism of rocks are always uncertain and responsible for carbon cycle perturbation (Fan <i>et al.</i>, 1998; Pearson and Palmer, 2000)
3	Oceanic perturbation	- The enhanced supply of nutrients from land are continuously increasing the coastal productivity, temperature, organic matter burial, and gas hydrate recharge (Dickens, 2003; Lerman <i>et al.</i>, 2004) - Organic matter, dissolved phases, and authigenic carbonate in the oceans (Dickens, 2003) can result in oceanic perturbation
4	Missing carbon sink perturbation	Carbon stock data in tropical forests and northern mid latitude forests
5	Miscellaneous	Forest fire, bush fire, oil fire, leakage of CO₂ from storage sites and pipelines result in accidental emission of CO₂ to the atmosphere and affect carbon concentration

**Fig. 5** Percentage of CO₂ perturbation in different pools.

Carbon Mitigation Pathways

Direct Carbon Sequestration Pathway

This carbon sequestration approach is a most potential technology for reducing large scale CO₂ mitigation from point emission sources before it is released to the atmosphere. Pre combustion capture, post combustion captures and oxyfuel combustion are the main methods for direct carbon sequestration of CO₂ from emission sources. Pre combustion capture involves the removal of carbon from the fuel before the fuel is combusted through gasification and other methods, while post combustion capture is involve removal of CO₂ from gas stream. Oxyfuel method is the combustion of fossil fuel in presence of a purely oxygen environment (Buhre *et al.*, 2005; Hadjipaschalis *et al.*, 2009).

Depending on the removal process, various technologies for CO₂ separation from emission sources can be used, including absorption, adsorption, membranes techniques, and hybrid applications (Fig. 7).

Indirect Carbon Sequestration

Natural sinks like ocean sequestration as well as terrestrial sequestration (photosynthesis in vegetation on the land) played an important role in carbon management and contribute to 55%–65% anthropogenic CO₂ removal (Scholes *et al.*, 2009).

Carbon Capture by Absorption

Physical absorption

The Physical process of CO₂ absorption is based on Henry's law in which efficient CO₂ absorption is mainly in presence of high pressure and a low temperature, while desorption in reduced pressure and high temperature (Yu *et al.*, 2012). There are many

processes like selexol process; rectisol process, purisol process, morphysorb process, and fluor process are used for physical CO₂ absorption.

Chemical absorption – Amine absorption technology

Chemical absorption of CO₂ into reactive solvents system is regarded as a proven technology to CO₂ mitigation (Norouzbahari *et al.*, 2016) (Tables 6–8).

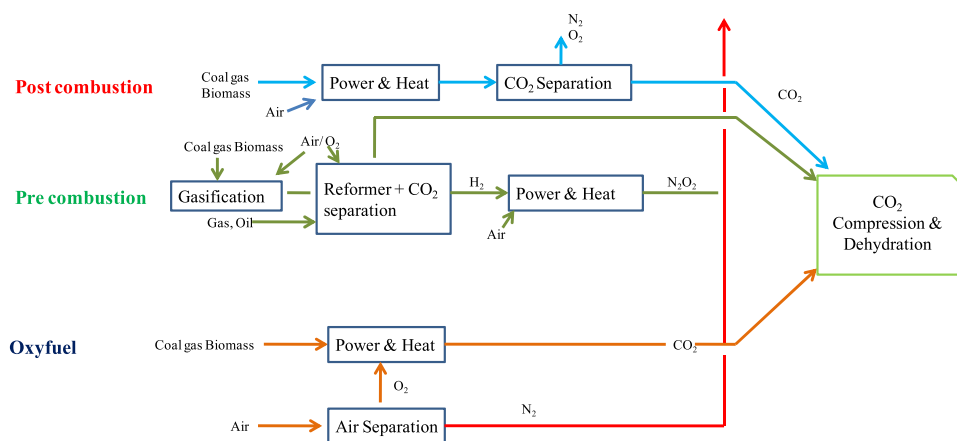


Fig. 6 Overview of different approaches for Carbon capture process and system.

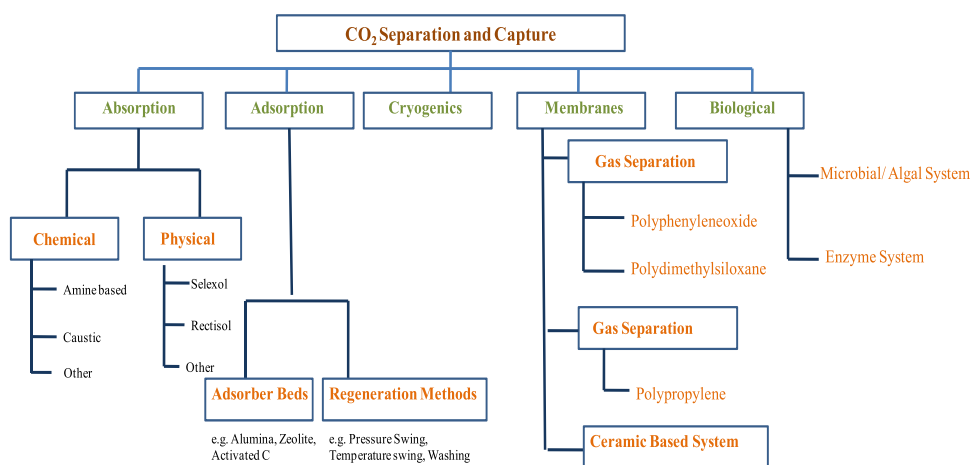


Fig. 7 CO₂ separation and capture techniques.

Table 6 Direct and indirect carbon sequestration

Carbon sink	Total carbon content (Gt)	Carbon mitigation (Gt/yr)	Nat Carbon sequestration (Gt/yr)	Route return to atmosphere	References
Soil Biomass	550	120	0	Plant respiration (60 GtC/yr) microbial decay	(IGBP, 1998; Lal, 2005)
Soil	2000	0	3	Cultivation (20%–40% of stored carbon), Deforestation and conversion to agriculture (20%–50%)	(Batjes, 1999)
Ocean Biomass, Ocean acidification	1000	90	0	Air–Water exchange, Respiration, decay	(Lal, 2005)
Deep ocean	37,000	0	2	Carbon sequestered	(U.S. Department of Energy, 2005)
CCS Aquifers + Enhance Oil recovery (EOR) + Biochar	200	2.4–3 t/t oil	200	Carbon stored	(Bird <i>et al.</i> , 2011)

Table 7 CO₂ absorption performance of the common absorbent

<i>Sorbent</i>	<i>Capacity</i>	<i>References</i>
monoethanolamine (MEA),	0.5 mol CO ₂ /mol	(Mandal <i>et al.</i> , 2001)
N-methyldiethanolamine (MDEA)	1 mol CO ₂ /mol	(Pani <i>et al.</i> , 1997)
2-amino-2-methyl-1-propanol (AMP)	1 mol CO ₂ /mol	(Xiao <i>et al.</i> , 2000)
Piperazine (PZ)	1 mol CO ₂ /mol	(Cullinane and Rochelle, 2004)
diethylenetriamine (DETA)	1 mol CO ₂ /mol	(Hartono <i>et al.</i> , 2009)
2-(2-aminoethylamino) ethanol (AEEA),	1 mol CO ₂ /mol	(Ma'mun <i>et al.</i> , 2007)
Sodium hydroxide (NaOH)	0.5 mol CO ₂ /mol	(Munjal <i>et al.</i> , 1989)
N-(2-aminoethyl)-1,3-propanediamine (AEPDNH ₂)	2.451 mol CO ₂ /mol	(Bonenfant <i>et al.</i> , 2003)
Triethanolamine (TEA)	1.220 mol CO ₂ /mol	
Triethylamine	1.159 mol CO ₂ /mol	
3- piperidino- 1,2-propanediol	1.1 mol CO ₂ /mol	(Puxty <i>et al.</i> , 2009)
3- quinuclidinol	1.1 mol CO ₂ /mol	
Pyrrolidine	1.033 mol CO ₂ /mol	(Bonenfant <i>et al.</i> , 2003)
2- piperidinemethanol	1 mol CO ₂ /mol	(Puxty <i>et al.</i> , 2009)
diisopropanolamine	0.64 mol CO ₂ /mol	(Bosch <i>et al.</i> , 1989)
Ammonia	0.5 mol CO ₂ /mol	(Bonenfant <i>et al.</i> , 2003)
Pyridine	0.229 mol CO ₂ /mol	
Aqueous ammonium	1.20 g CO ₂ /g	(Resnik <i>et al.</i> , 2004)
Aminated mesoporous silica	0.45–0.6 mol CO ₂ /mol	(Knowles <i>et al.</i> , 2005)
Aminated SBA-15	1528–4188 μmol CO ₂ /g	(Gray <i>et al.</i> , 2004)
PEI-impregnated MCM-41	45 ml (STP) CO ₂ /g	(Xu <i>et al.</i> , 2005a)
Anthracite activated carbon	65.7 mg CO ₂ /g	(Maroto-Valer <i>et al.</i> , 2005)

Table 8 CO₂ absorption performance of the Ionic liquid

<i>Ionic liquid</i>	<i>T (K)</i>	<i>P (bar)</i>	<i>χCO₂*</i>	<i>References</i>
N-Butylpyridiniumtetrafluoroborate	323	92.35	0.5810	(Blanchard <i>et al.</i> , 2001)
Trihexyltetradecylphosphonium chloride	302.55	149.95	0.8000	(Carvalho <i>et al.</i> , 2009)
Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide	296.58	721.85	0.8790	
N-Butyl-4-methylpyridinium tetrafluoroborate	303	10	0.1443	(Galan Sanchez, 2008)
N-Butyl-3-Methylpyridinium dicyanamide	303	10	0.1436	
N-Butyl-4-Methylpyridinium thiocyanate	303	10	0.0962	
1-Butyl-1-methylpyrrolidinium trifluoroacetate	303	10	0.1674	
1-Butyl-1-methylpyrrolidinium tri(pentafluoroethyl)trifluorophosphate	283.5	18.00	0.4980	(Zhang <i>et al.</i> , 2008)
Tetrabutylphosphoniumformate	298.1	19.9	0.3480	(Yokozeki <i>et al.</i> , 2008)
1-N-Octyl-3-methylimidazolium hexafluorophosphate	313	92.67	0.7550	(Blanchard <i>et al.</i> , 2001)
1-N-Butyl-3-nethylimidazolium nitrate	323	92.62	0.5300	
1-N-Octyl-3-methylimidazolium tetrafluoroborate	313	92.90	0.7080	
1-Ethyl-3-methylimidazolium ethyl sulfate	333	94.61	0.4570	
1-Butyl,3-methyl-imidazolium hexafluorophosphate	298.15	6.66	0.122	(Kim <i>et al.</i> , 2005)
1-Hexyl-3-methylimidazolium hexafluorophosphate	298.15	9.27	0.167	
1-Ethyl-3-methylimidazolium tetrafluoroborate	298.15	8.75	0.106	
1-Ethyl-3-methylimidazolium trifluoromethane-sulfonate	303.85	149	0.6260	(Shin and Lee, 2008)
1-Butyl-3-methylimidazolium trifluoromethane-sulfonate	303.85	160	0.6720	
1-Hexyl-3-methylimidazoliumtrifluoromethane-sulfonate	303.85	180	0.7170	
1,3-Dimethylimidazolium methylphosphonate	313.35	95	0.4750	(Revelli <i>et al.</i> , 2010)
1-Butyl,3-methyl-imidazolium tetrafluoroborate	293.65	73	0.6100	
1-Ethyl-3-methylimidazolium trifluoroacetate	298.1	19.99	0.2820	(Yokozeki <i>et al.</i> , 2008)
1-Ethyl-3-methylimidazolium acetate	298.1	19.99	0.4280	
1-Hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate	283.5	17.99	0.5170	(Zhang <i>et al.</i> , 2008)
Bis(2-hydroxyethyl)-ammonium acetate	298.15	15.15	0.1076	(Kurnia <i>et al.</i> , 2009)
2-Hydroxy ethyl ammonium formate	303	78.9	0.3083	(Yuan <i>et al.</i> , 2007)
2-Hydroxy ethyl ammonium acetate	303	90.1	0.4009	
2-Hydroxy ethyl ammonium lactate	303	82	0.2422	

Table 9 Adsorbent materials utilized for CO₂ capture

Sorbent	Temp. (°C)	Pressure (kPa)	CO ₂ molar fraction (%)	Uptake CO ₂ capacity	References
<i>Zeolite</i>					
Zeolite 13X	50	100	15	3 mol/kg	(Dantas <i>et al.</i> , 2011)
Zeolite 13X-APG	30	100	15.9	4.3 mol/kg	(Wang <i>et al.</i> , 2012)
Zeolite A5	30	100	16	3 mol/kg	
Clinoptilolite-rich natural zeolite	5	—	—	2.08 mmol/g	(Maurin <i>et al.</i> , 2005)
LEZ-13X	50	101.3	—	4.6 mol/kg	(Cho <i>et al.</i> , 2014)
LEZ -A5	50	101.3	—	5.2 mol/kg	
ZSM- 5	25	120	25	0.7 mol/kg	(Hefti <i>et al.</i> , 2015)
Natural Zeolite	24.8	100	—	0.8 mmol g ⁻¹	(Siriwardane <i>et al.</i> , 2003)
5A	119.85	15	—	0.38 mmol g ⁻¹	(Siriwardane <i>et al.</i> , 2005)
4A	119.85	15	—	0.50 mmol g ⁻¹	
APG-II	119.85	15	—	0.38 mmol g ⁻¹	
Na-Y	99	10	—	4.9 mmol g ⁻¹	(Michelena <i>et al.</i> , 1977)
Na-X	49.8	100	—	2.70 mmol g ⁻¹	(Díaz <i>et al.</i> , 2008)
NaX-h	99	100	—	2.52 mmol g ⁻¹	(Díaz <i>et al.</i> , 2008)
<i>Activated Carbon:</i>					
Carbon	24.8	100	—	3.3 mmol g ⁻¹	(Na <i>et al.</i> , 2001)
Carbon	1.8	100	—	3.5 mmol g ⁻¹	
CN800	24.8	100	—	1.91 mmol g ⁻¹	(Pevida <i>et al.</i> , 2008)
CN800	74.8	100	—	0.61 mmol g ⁻¹	
RN800	74.8	100	—	0.73 mmol g ⁻¹	
GAC	24.8	10	—	0.0057 mmol g ⁻¹	(Lu <i>et al.</i> , 2008)
NCLK3	25	120	—	3.5 mol/kg	(González <i>et al.</i> , 2013a)
NCHA29	25	120	—	2.3 mol/kg	
KL31	25	4000	100	22 mol/kg	(Marco-Lozar <i>et al.</i> , 2014)
KA21	25	4000	100	17.5 mol/kg	
Carbon fiber composites	25	101.3	13	3.1 mol/kg	(Thiruvengkatachari <i>et al.</i> , 2013)
Almond shells	50	120	14	0.58 mol/kg	(González <i>et al.</i> , 2013b)
No1KCl-a-600	25	120	50	2.03 mol/kg	(Gil <i>et al.</i> , 2015)
No1KCl-b-1000	25	120	50	1.91 mol/kg	
No2OS-1000	25	120	50	1.83 mol/kg	
Cu/Zn-16%AC	30	100	15	1.98 mol/kg	(Hosseini <i>et al.</i> , 2015)
Cu/Zn-20%AC	30	100	15	2.26 mol/kg	
Cu-20% AC	30	100	15	1.99 mol/kg	
<i>Oxide of Calcium and Magnesium</i>					
CaO	449	41	—	4.5 mmol g ⁻¹	(Wu <i>et al.</i> , 2007)
Ca(OH) ₂	449	25	—	6.7 mmol g ⁻¹	
Ca(OH) ₂	649	41	—	10.7 mmol g ⁻¹	
CaCO ₃	599	34	—	6.3 mmol g ⁻¹	
CaCO ₃	299	20	—	1.5 mmol g ⁻¹	(Kuramoto <i>et al.</i> , 2003)
CaO/Al ₂ O ₃	650	5	—	6.02 mmol g ⁻¹	(Wu <i>et al.</i> , 2008)
Cs/CaO	450	40	—	4.9 mmol g ⁻¹	(Reddy and Smirniotis, 2004)
Rb/CaO	450	40	—	4.5 mmol g ⁻¹	
K/CaO	450	40	—	3.8 mmol g ⁻¹	
Na/CaO	450	40	—	3.1 mmol g ⁻¹	
MgO	100	20	—	0.64 mmol g ⁻¹	(Gregg and Ramsay, 1970)
MgO,K	60	1	—	2.36 mmol g ⁻¹	(Lee <i>et al.</i> , 2008a)
<i>Lithium Zirconate and Lithium orthosilicates</i>					
Li ₂ ZrO ₃	500	100	—	4.55 mmol g ⁻¹	(Ida and Lin, 2003)
Li ₂ ZrO ₃ , K	400	100	—	3.64 mmol g ⁻¹	
Li ₂ ZrO ₃	550	100	—	4.55 mmol g ⁻¹	
Li ₂ ZrO ₃	550	70	—	4.5 mmol g ⁻¹	(Ochoa-Fernández <i>et al.</i> , 2005)
Li ₂ ZrO ₃	600	80	—	5.7 mmol g ⁻¹	(Guzman-Velderrain <i>et al.</i> , 2008)
Li ₂ ZrO ₃ /Na	600	80	—	3.4 mmol g ⁻¹	(Guzman-Velderrain <i>et al.</i> , 2008)
Li ₄ SiO ₄	500	2	—	6.14 mmol g ⁻¹	(Kato <i>et al.</i> , 2002)
Li ₄ SiO ₄	500	20	—	6.14 mmol g ⁻¹	
<i>Hydrotalcites</i>					
HTLcs	400	45	—	0.59 mmol g ⁻¹	(Ding and Alpay, 2000)
HTLcs	480	58	—	0.48 mmol g ⁻¹	
HTLcs	400	44	—	0.62 mmol g ⁻¹	

Ionic liquid

Recently, ionic liquids (IL) has attracted widespread attention toward carbon dioxide management due to very low vapor pressure, non toxicity, good thermal stability and high polarity (Yu *et al.*, 2012). Table 9 to provide value of different ILs for peak CO₂ solubility.

* χ_{CO_2} is the solubility of CO₂ (mole fraction).

Table 10 CO₂ adsorption capacities for metal organic frameworks

Chemical formula and common name	Surface area (m ² /g) BET	Capacity	Pressure (bar)	Temp. (K)	References
Zn ₄ O(BTE) _{4/3} (BPDC) (MOF-210)	6240	74.2 (%)	50	298	(Furukawa <i>et al.</i> , 2010)
Zn ₄ O(BBC) ₂ (H ₂ O) ₃ (MOF-200)	4530	73.9(%)	50	298	(Furukawa <i>et al.</i> , 2010)
Cu ₃ (TCEPEB)(NU-100)	6143	69.8(%)	40	298	(Farha <i>et al.</i> , 2010)
Zn ₄ O(FMA) ₃ Mg ₂ (dobdc)(Mg-MOF-74, CPO-27-Mg)	1120	69.0(%)	28	300	(Xue <i>et al.</i> , 2009)
Zn ₃₋₁₆ Co _{0.840} (BDC) ₃ (Co21-MOF-5)	–	65.0(%)	10	273	(Botas <i>et al.</i> , 2010)
Be ₁₂ (OH) ₁₂ (BTB) ₄ (Be-BTB)	4030	58.5(%)	40	313	(Herm <i>et al.</i> , 2011)
Zn ₄ O(BDC) ₃ (MOF-5, IRMOF-1)	–	58.0 (%)	10	273	(Botas <i>et al.</i> , 2010)
Zn ₄ O(BTB) _{4/3} (NDC) (MOF-205)	4460	62.6(%)	50	298	(Furukawa <i>et al.</i> , 2010)
Ni ₅ O ₂ (BTB) ₂ (DUT-9)	–	62.1(%)	47	298	(Gedrich <i>et al.</i> , 2010)
Zn ₄ O(BTB) ₂ (MOF-177)	4500	60.8(%)	50	298	(Furukawa <i>et al.</i> , 2010)
[Cu ₃ (H ₂ O)] ₃ (ptei)(PCN-68)	5109	57.2(%)	35	298	(Yuan <i>et al.</i> , 2010)
Ni ₂ (dobdc)(Ni-MOF-74) 9 (CPO-27-Ni)	1218	54.2(%)	22	278	(Dietzel <i>et al.</i> , 2014)
[(Ni ₂ L1)(bptc)] (ethyl-bridged) L1 = ethyl-bridged Ni ₂ macrocyclic complexesbptc = 1,1'-biphenyl-3,3',5,5'-tetracarboxylate	–	9.3%	1 atm	298	(Choi and Suh, 2009)
[Cu(H ₂ O)] ₃ (ntei)(PCN-66)	4000	53.6(%)	35	298	(Yuan <i>et al.</i> , 2010)
Zn ₄ O(BDC)(BTB) _{4/3} (UMCM-1)	4100	52.7(%)	24	298	(Mu <i>et al.</i> , 2010)
Cu ₃ (BTC) ₂ (HKUST-1)	1270	42.8(%)	300	313	(Moellmer <i>et al.</i> , 2011)
H ₃ [(Cu ₄ Cl) ₃ (BTtri) ₈](Cu-BTTri)	1750	42.8(%)	40	313	(Herm <i>et al.</i> , 2011)
Co(BDP)	2030	41.3(%)	40	313	
Zn ₄ O(btb) ₂ (MOF-177) and [Zn ₄ O(bdc) ₃] (MOF-5) btb = 1,3,5-benzenetribenzoate	–	33.5 mmol/g	32	298	(Millward and Yaghi, 2005)
	–	2.10 mmol/g	1 atm	295	
Zn ₂ (BPnDC) ₂ (bpy) (SNU-9)	–	29.9	30	298	(Park and Suh, 2010)
Al(OH)(ndc)(DUT-4)	1308	26.4	10	303	(Senkovska <i>et al.</i> , 2009)
Mn(tpom)(SH) ₂ (MSF-2)	622	25.0	20.3	293	(Zhang <i>et al.</i> , 2010)
<i>Lower-Pressure CO₂ adsorption capacities for metal organic frameworks</i>					
Mg ₂ (dobdc)(Mg-MOF-74, CPO-27-Mg)	1174	27.5 & 27.2	1	298	(Bao <i>et al.</i> , 2011)
Cu ₃ (BTC) ₂ (H ₂ O) _{1.5} (HKUST-1)	–	27.0	1	298	(Yazaydin <i>et al.</i> , 2009a)
Co ₂ (dobdc)(Co-MOF-74)	957	24.9	1	298	(Yazaydin <i>et al.</i> , 2009b)
Zn ₂ (dobdc)(Zn-MOF-74)	–	19.8	1	296	(Yazaydin <i>et al.</i> , 2009b)
Cu ₃ (TATB) ₂ (CuTATB-60, PCN-6)	3811	15.9	1	298	(Kim <i>et al.</i> , 2011)
Co ₂ (adenine) ₂ (CO ₂ CH ₃) ₂ (bio-MOF-11)	1040	15.2	1	298	(An <i>et al.</i> , 2010)
Cu ₂ (bdcppi)(DMF) ₂ (SNU-50)	2300	13.7	1	298	(Prasad <i>et al.</i> , 2010)
Fe ₃ [(Fe ₄ Cl) ₃ (BTT) ₈ (MeOH) ₄] ₂ (Fe-BTT)	2010	13.5	1	298	(Sumida <i>et al.</i> , 2010)
Cu(bpy) ₂ (BF ₄) ₂ (ELM-11)	–	11.7	1	298	(Kano <i>et al.</i> , 2009)
Cu ₂ (bptc)(H ₂ O) ₂ (DMF) ₃ (MOF-505)	1547	12.6	1.1	298	(Millward and Yaghi, 2005)
Ni ₂ (BDC) ₂ (DABCO)(USO-2-Ni)	1925	10	1	298	(Arstad <i>et al.</i> , 2008)
Cu ₂ (TCM)(SNU-21H)	–	9.7	1	298	(Kim and Suh, 2011)
Cu(BDCOH)(H ₂ O)(Cu-BDCOH)	397	9.3	1	296	
Zn(nblm)(nlm)(ZIF-78)	620	9.1	1	298	(Banerjee <i>et al.</i> , 2009)
Zn(cyanlm) ₂ (ZIF-96)	960	8.8	1.1	298	(Morris <i>et al.</i> , 2010)
Zn ₂₀ (cblm) ₃₉ (OH)(ZIF-100)	595	3.8	1	298	(Wang <i>et al.</i> , 2008)
Cu ₂ (abtc) ₃ (SNU-5)	–	38.5	1	273	(Lee <i>et al.</i> , 2008b)
Cu ₂ (EBTC)(H ₂ O) ₂ (Cu-EBTC)	1852	25.9	1	273	(Hu <i>et al.</i> , 2009)
Cu ₂ (TCM)(SNU-21)	–	18.4	1	273	(Kim and Suh, 2011)
[In ₃ O(diazDBC) _{1.5} (H ₂ O) ₃](NO ₃)	892	17.9	1	273	(Moellmer <i>et al.</i> , 2010)
Cu(bpy) ₂ (BF ₄) ₂ (ELM-11)	–	13.8	1	273	(Kondo <i>et al.</i> , 2009)
Zn(Pur) ₂ (ZIF-20)	–	12.4	1	273	(Hayashi <i>et al.</i> , 2007)
Zn ₂ (BTetB)(DMF) ₂	800	12.1	1	273	(Bae <i>et al.</i> , 2009)
Zn ₂ (BDoborDC) ₄	800	12.1	1	273	(Spokoiny <i>et al.</i> , 2010)
Zn ₂ (TCPB)(DPG)	740	11.6	1	273	(Gadzikwa <i>et al.</i> , 2009)
Cu ₃ (2,7-NDC) ₃ (DEF)(H ₂ O) ₂ (MOP-23)	760	8.9	1	273	(Furukawa <i>et al.</i> , 2008)
LiB(4-MIm) ₄ (BIF-9-Li)	1523	6.6	1	273	(Wu <i>et al.</i> , 2009)

Table 11 High-Pressure CO₂ adsorption capacities for metal organic frameworks

Sorbent	Surface area (m ² /g) BET	Uptake CO ₂ (mol/kg)	Temp. (K)	Pressure (kPa)	References
HKUST-1	1326	8.07	303	1000	(Ye <i>et al.</i> , 2013)
MIL-101(Cr)	2549	7.19	303	1000	(Ye <i>et al.</i> , 2013)
Zn ₂ (hfpbb) ₂ (ted)	–	0.45	298	101.3	(Xu <i>et al.</i> , 2005b)
MOF-177	4690	0.65	313	100	(Mason <i>et al.</i> , 2011)
Mg ₂ -MOF-74	1800	7.5	313	100	(Mason <i>et al.</i> , 2011)
IRMOF-1	2833	11.1	298	3500	(Millward and Yaghi, 2005)
IRMOF-3	2160	10.3	298	3500	
IRMOF-6	2516	10.5	298	3500	
IRMOF-11	2096	8.9	298	3500	
HKUST-1	1781	7.3	298	3500	
Zn-MOF-74	816	7.1	298	3500	
MOF-505	1547	0.70	298	3500	
Cu-TDPAT	1938	0.59	298	100	(Li <i>et al.</i> , 2012)
Na-rhoZMOF	–	6.2	298	100	(Nalaparaju <i>et al.</i> , 2014)
MIL-100(Fe)	1894	0.67	303	101.3	(Xian <i>et al.</i> , 2015)

Carbon Capture by Adsorption

Adsorption of CO₂ capture is considered as one of the potential options for CO₂ management. This approach is mainly dependent on (a) kinetics (adsorption/desorption); (b) CO₂ capacity; (c) adsorption and desorption temperatures (low heat capacity) (d) regenerability and (e) impact of common flue gas components such as H₂O, Hg, SO₂, NO and (f) High CO₂ selectivity (Choi *et al.*, 2009). Adsorption processes involving CO₂ capture by liquid media are widely established even in gas separation via selective adsorption (Yang, 2013).

Inorganic adsorbents

Various physical inorganic adsorbents have been used for CO₂ mitigation process including zeolites, carbonaceous adsorbent, metal oxides materials, microporous and mesoporous materials (activated carbon and carbon sieves), metal organic frameworks (MOFs) and chemically modified mesoporous materials (Ben-Mansour *et al.*, 2016). The adsorption capacities of different adsorbents are summarized in Table 9.

CO₂ adsorption in metal organic frameworks

Carbon dioxide adsorption by metal organic frameworks (MOFs) have emerged as an extensive class of CO₂ capture materials with ultra-high porosity and high internal surface areas attracted much recent attention to their potential applications in gas storage, and selective separation etc. (Zhou *et al.*, 2012).

Chemical adsorbent

Many scientific and industrial works have been devoted to improve selective CO₂ adsorption process and enhancing efficiencies and selectivity by chemical changes and design and development of a suitable adsorbent like synthesizing a high nitrogen content carbon -including adsorbents-by carbonization (Yu *et al.*, 2012). According to the interaction type between basic organic group (amine) and support following types of adsorbent can categorized as, (i) amine (-NH₂) impregnated adsorbent and, (ii) amine (-NH₂) grafted adsorbent (Tables 10–12).

The comparisons of various carbon capture technologies tabulated below (Table 13).

Terrestrial Sequestration

Terrestrial C sequestration is alteration of atmospheric carbon dioxide into biotic and soil C pools. According to Fan *et al.* (1998) presently, the concentrate of C sequestration in forest ecosystems is 1.7 ± 0.5 Pg C yr⁻¹. The forest C is sequestered in lignin and other polymeric C compound by the timber, woody debris, and other woody plants and grasslands (Wofsy, 2001). Afforestation is one of the best options of terrestrial C sequestration (Lamb *et al.*, 2005). As per the IPCC report following carbon sequestration potential like 3 MT C yr⁻¹ in Norway, 6 MT C yr⁻¹ in New Zealand, 9 MT C yr⁻¹ in Sweden, 107 MT C yr⁻¹ in Russia and 117 MT C yr⁻¹ in the USA can lead by only afforestation (IPCC, 2005) (Table 14).

Chemical Carbon Mitigation

The atom of carbon and oxygen in CO₂ molecules are susceptible to nucleophilic and electrophilic attack for substitution reaction of chemical reagents. The various chemical processes and their chemical CO₂ sequestration capacities are shown in Table 15.

Table 12 CO₂ adsorption capacities for amine impregnated supports

Amine	Support	T (K)	pCO ₂ (bar)	Adsorption capacity (mmol/g)	References
PEI	Inorganic support	348	1	2.4	(Satyapal <i>et al.</i> , 2001)
DEA	PE-MCM-41	298	0.05	2.93	(Franchi <i>et al.</i> , 2005)
PEI	MCM-41	348	1	3.02	(Xu <i>et al.</i> , 2002)
PEI	MCM-41	348	0.15	2.02	(Xu <i>et al.</i> , 2005a)
PEI	KIT-6	348	1	3.07	(Son <i>et al.</i> , 2008)
PEI	MCM-41	348	1	3.02	(Xu <i>et al.</i> , 2003)
TEPA	SBA-15	348	1	3.93	(Yue <i>et al.</i> , 2006)
DEA/TEPA	SBA-15	348	1	4.0	(Yue <i>et al.</i> , 2008a)
TEPA	MCM-41	308	1	5.02	(Yue <i>et al.</i> , 2008b)
PEI	SBA-15	348	–	3.08	(Ma <i>et al.</i> , 2009)
PEI	Silica gel	348	–	3.07	(Xu <i>et al.</i> , 2003)
PEI	Carbon black	348	–	3.07	(Wang <i>et al.</i> , 2011)
PEI	MCM-48	348	–	2.70	(Son <i>et al.</i> , 2008)
PEI	SBA-16	348	–	2.93	
PEI	HMS	348	–	4.18	(Chen <i>et al.</i> , 2010)
TEPA	as-SBA-15	373	–	3.93	(Yue <i>et al.</i> , 2006)
TEPA	as-MCM-41	348	–	5.39	(Yue <i>et al.</i> , 2008b)
TEPA	Al ₂ O ₃	303	–	0.19	(Fischer II <i>et al.</i> , 2009)
TEPA	SiO ₂	303	–	0.68	(Fischer II <i>et al.</i> , 2009)
TEPA	Beta zeolite	303	–	2.08	
TEPA	Fumed silica	328	–	2.09	(Tanthana and Chuang, 2010)
TEPA/PEG	Fumed silica	328	–	1.11	
DETA	AC	298	–	1.01	(Plaza <i>et al.</i> , 2007)
PEHA	AC	298	–	1.18	
DETA	Meso- Al ₂ O ₃	373	–	1.75	(Plaza <i>et al.</i> , 2008)
PEI	Meso- Al ₂ O ₃	373	–	1.50	
PEHA	Meso- Al ₂ O ₃	370	–	1.03	
DIPA	Meso- Al ₂ O ₃	310	–	0.93	
TEPA	PMMA	296	–	21.45	(Lee <i>et al.</i> , 2008b)
PEI	SiO ₂	333	–	2.80	(Ebner <i>et al.</i> , 2011)
PEI	PMMA	333	–	3.60	(Gray <i>et al.</i> , 2009)
PEI/PSS	PMMA	313	–	1.70	(Jiang <i>et al.</i> , 2011)
<i>CO₂ adsorption capacities of amine with silane</i>					
Di silane	SBA-15	295	0.15	0.57	(Zheng <i>et al.</i> , 2005)
Di silane	SBA-15	303	1	1.95	
Di silane	SBA-16	333	0.15	0.87	(Wei <i>et al.</i> , 2008)
Mono silane	SBA-15	298	0.1	2.01	(Gray <i>et al.</i> , 2004)
Mono silane	HMS	293	0.9	1.59	(Knowles <i>et al.</i> , 2005)
Mono silane	MCM-48	298	0.05	1.14	(Huang <i>et al.</i> , 2003)
Mono silane	SBA-12	298	0.1	1.04	(Zelenak <i>et al.</i> , 2008)
Mono silane	PE- MCM-41	298	0.05	2.05	(Serna-Guerrero <i>et al.</i> , 2008)
Tri silane	SBA-15	333	0.15	1.1	(Hiyoshi <i>et al.</i> , 2004)
Tri silane	HMS	293	0.9	1.34	(Knowles <i>et al.</i> , 2006)
Tri silane	MCM-41	298	0.05	0.97	(Harlick and Sayari, 2006)
Tri silane	PE- MCM-41	298	0.05	1.41	(Harlick and Sayari, 2006)
MAP	SBA-12	298	0.1	0.98	(Zelenak <i>et al.</i> , 2008)
PAP	SBA-12	298	0.1	0.68	
DMAP	SBA-15	333	0.15	0.25	(Hiyoshi <i>et al.</i> , 2005)
<i>CO₂ adsorption capacities of amine supported on solid organic materials</i>					
DETA	Carbon	298	1	0.91	(Plaza <i>et al.</i> , 2007)
PEHA	Carbon	298	1	1.09	
PEI	Carbon	298	1	1.11	
PEI/ECH	Glass fiber	303	0.16	0.26	(Li <i>et al.</i> , 2008)
EDA	Crosslinked VBC/DVB	298	0.14	2.16	(Diaf <i>et al.</i> , 1994)
EDA	Linear VDC	298	0.14	2.62	
Diamine	Linear VDC/styrene	298	1	0.67	(Diaf and Beckman, 1995)
DBN	styrene	298	1	0.76	(Ochiai <i>et al.</i> , 2008)

Table 13 Comparisons of carbon dioxide option

Sl. no.	Technology	CO ₂ recovery (%)	CO ₂ purity achieved (%)	Energy penalty (%)	Capture cost US\$/Ton CO ₂
1	Chemical absorption	90	> 90	36	47
2	Physical Adsorption	90	44	47	61
3	Membrane separation	90	43	52	78

Note: Nanoti, A., Goswami, A.N., 2009. Post combustion CO₂ capture. In: ACBCCS-2009.

Table 14 Estimate of soil Organic carbon pool

Sl. no.	Ecosystem	SOC pool (Gt C)	Total area (10 ⁹ ha)
1	Forests		
	1. Tropical	213–216	1.76
	2. Temperate	100–153	1.04
	3. Boreal	338–471	1.37
2.	Tundra	115–121	0.95
3.	Temperate grassland and scrub land	176–295	1.25
4.	Tropical savannas and grassland	247–264	2.25
5.	Desert and semi desert	159–191	4.55
6.	Cropland	128–165	1.60
7.	Wetland	225	0.35

Note: IPCC, 2000. Land use, land-use change, and forestry. Cambridge University Press, Cambridge, U.K. Lal, R., 2003. Global potential of soil carbon sequestration to mitigate the greenhouse effect. CRC Crit. Rev. Plant Sci. 22, 151–184. doi:10.1080/713610854.

Biological Carbon Mitigation

Several biological processes lead to ocean and terrestrial CO₂ sequestration through photosynthesis like phytoplanktonic photosynthesis mechanisms can fix 45 Gt C yr⁻¹. The world ocean currently accounting for a global net uptake of 2.9 Gt C annually of human caused CO₂ emission (Falkowski, 2012). Following biological media involve in biological carbon mitigation.

Microalgae

Microalgal photosynthesis is can lead to potentially long-term sink of carbon through the precipitation of calcium carbonate (Kurano *et al.*, 1995) (Table 16). Microalgae are fast growing can achieved high carbon dioxide fixation rate like 14.6 g cm⁻²/day at 4% CO₂ concentration (Watanabe and Hall, 1996).

Macroalgae

In the coastal areas macroalgae (autotrophic aquatic plants) are the main primary producers with net NPP of 1521 Mt C yr⁻¹ (Duarte *et al.*, 2004). Krause-jensen and Duarte (2016) estimated macroalgae can sequester about 173 Mt C yr⁻¹ globally. Following selected macroalgae strain can use of carbon sequestration purposes (Table 17).

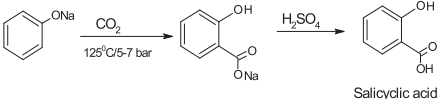
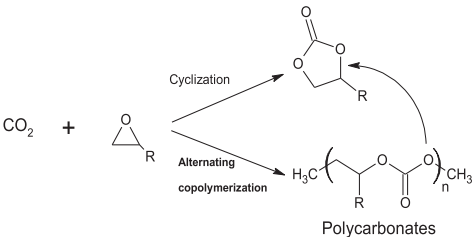
The photosynthetic rate of macroalgae can be used as an indicator of CO₂ capture capacity and can regulated by the enrichment of nutrients, gaseous CO₂ and DIC (Gao and McKinley, 1994). *Enteromorpha compressa* the highest rate of net photosynthetic rate for the green algae range from 400 to 1800 μmol CO₂ g (dry wt)⁻¹ h⁻¹. Similarly *Sargassum muticum* shoes net rates range from 100 to 1670 μmol CO₂ g (dry wt)⁻¹ h⁻¹ (Brown and Tregunna, 1967). The net photosynthetic rate ranges from 250 to 2232 μmol CO₂ g (dry wt)⁻¹ h⁻¹, of *Porphyra* showed highest in the red algae (Smith and Bidwell, 1987). By the adding DIC concentrations (2–10 Mm, pH 8.2) in seawater at the photosynthetic rate of *Porphyra yezoensis* was increased ranges from 1560 to 2230 μmol CO₂ g (dry wt)⁻¹ h⁻¹ and *Gracilaria sp.* increased their photosynthetic rate from 62 to 108 μmol CO₂ g (dry wt)⁻¹ h⁻¹ (Gao *et al.*, 1991).

Cyanobacteria

Cyanobacterias utilize CO₂ as their food source plays important carbon mitigation. Following selected cyanobacterial strains can use direct biological carbon sequestration applications and bio mineralization (Table 18). Cyanobacteria can capture CO₂ by two different modes one via photosynthesis process and Calvin Benson-Bassham process where CO₂ captured and converted into organic compounds and calcium carbonate (Kamennaya *et al.*, 2012).

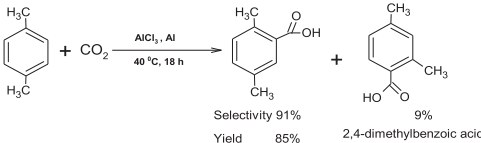
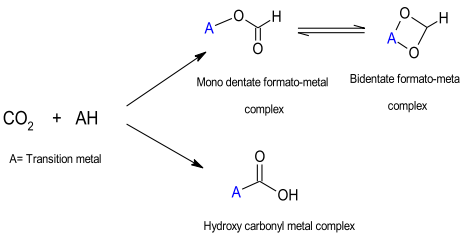
Cyanobacterial carbonate mineralization have major environmental and geological significance like *Synechococcus sp.* PCC 8806 could mineralise around 2.5 MT carbonate per year over an area of 70 km² (Lee *et al.*, 2004, 2006) and *Nannochloris atomus* can precipitate 1.6 × 10³ T of CaCO₃ in 12 h (Yates and Robbins, 1998). Biological fixation can occur through following six major pathways, (1) Calvin- Benson- Bassham cycle, (2) reductive acetyl-CoA pathway, (3) reductive citric acid pathway, (4) 3-hydroxypropionate/malyl-CoA cycle, (5) 3-hydroxypropionate/4-hydroxybutyrate cycle, and (6) dicarboxylate/4-hydroxybutyrate cycle (Berg *et al.*, 2010).

Table 15 Chemical methods for carbon sequestration

Sl. no	Process	Reaction	CO ₂ consumption (Giga tonne)	Uses	References
1	Kolbe-Schmitt Process	 Salicylic acid	0.00002	Skin-care products	(Wilkinson <i>et al.</i> , 1982)
2	Carboxylation	$2\text{NH}_3 + \text{CO}_2 \xrightleftharpoons[150-200^\circ\text{C}]{150-250 \text{ bar}} \text{NH}_2\text{CONH}_2 + \text{H}_2\text{O}$ Urea	0.07	Chemical fertilizer, urea resins, urea-melamine resins	(Mikkelsen <i>et al.</i> , 2010)
ii		$3\text{CO} + 9\text{H}_2 + \text{CO}_2 \xrightarrow{\text{CuO/ZnO}} 4\text{CH}_3\text{OH} + \text{H}_2\text{O}$ Methanol	0.014	Common laboratory solvent, for the production of formaldehyde and other chemicals	(Olah <i>et al.</i> , 2009; Saito <i>et al.</i> , 1996)
iii		$\text{CH}_4 + \text{CO}_2 \xrightarrow[\text{Acetic acid}]{\text{Palladium}} \text{CH}_3\text{COOH}$	0.0016	Production of cellulose acetate for photographic film and polyvinyl acetate for wood glue, as well as synthetic fibers and fabrics	(Mikkelsen <i>et al.</i> , 2010)
iv		$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2 + \text{CO}_2 \xrightarrow[90^\circ\text{C}, 15\text{h}, \text{CH}_3\text{CN}]{0.2 \text{ mol\% Pd}(\text{acetylacetonate})_2, 0.4 \text{ mol\% P}(\text{isopropyl})_3} \text{H}_2\text{C}=\text{CH}-\text{CH}(\text{O}-\text{C}(=\text{O})-\text{CH}=\text{CH}_2)-\text{CH}_2-\text{CH}=\text{CH}_2$ 40% yield lactone		Used in the flavors and fragrances industry	(Nakano <i>et al.</i> , 2014)
v	Organic carbonates				
a	Acyclic Carbonates	$2\text{H}_3\text{C}-\text{OH} + \text{scCO}_2 \xrightleftharpoons{\text{Catalyst}} \text{H}_3\text{C}-\text{O}-\text{C}(=\text{O})-\text{O}-\text{CH}_3 + \text{H}_2\text{O}$ Dimethyl carbonate	0.0002	For the production of polycarbonate, polyurethane etc	(Sakakura and Kohno, 2009)
b	Cyclic carbonates	$\text{CO}_2 + \text{R} \xrightarrow[70-100 \text{ bar/R}_4\text{NX}]{150-170^\circ\text{C}} \text{Organic carbonates}$ (R= H, CH₃)		Used as high-boiling solvents for natural and synthetic polymers such as lignin, cellulose ester, Nylon, PVC and in lithium batteries	(Mikkelsen <i>et al.</i> , 2010; Sakakura and Kohno, 2009)
c	Polycarbonates	 Polycarbonates		Soft drink bottles, building materials, automobile parts and electrical components	(Coates and Moore, 2004)

(Continued)

Table 15 Continued

Sl. no	Process	Reaction	CO ₂ consumption (Giga tonne)	Uses	References
3	Carboxylation-Amination	$\text{CO}_2 \xrightleftharpoons{\text{R-NH}_2} \text{R-NH-COOH} \xrightleftharpoons{\text{R-NH}_2} \text{R-NH-COO}^- \text{RNH}_3^+$ Carbamate		Insecticides	(Chaturvedi and Ray, 2007)
4	Boudouard reaction	$2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$		Fuel, reducing agent in the chemical industry	(Dai <i>et al.</i> , 1996)
5	Friedel-Crafts Acylation	 Selectivity 91% Yield 85% 2,4-dimethylbenzoic acid 9%		Synthesis of other chemicals	(Olah <i>et al.</i> , 2002)
6	Reductive hydrogenation	$\text{Cu/ZnO/Al}_2\text{O}_3$ $\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$	0.014	Common laboratory solvent	(Saito <i>et al.</i> , 1996)
7	Photochemical reduction	$\text{H}_2 + \text{CO}_2 \xrightarrow{\text{Rhodium in DMSO}} \text{HCOOH}$ $\text{CO}_2 \xrightarrow[\text{Triethanolamine}]{\text{Ru(bpy)}_3^{2+}} \text{HCOO}^-$ $\text{CO}_2 \xrightarrow[\text{Triethanolamine}]{\text{ReCl(bpy)(CO)}_3} \text{CO}$	0.67 mt	Preservative and antibacterial agent in livestock feed, production of leather As a preservative and antibacterial agent in livestock feed, production of leather, coagulant in the production of rubber In synthesis of bulk chemicals like aldehyde, phosgene, methanol	(Gassner and Leitner, 1993) (Gassner and Leitner, 1993) (Hawecker <i>et al.</i> , 1986)
8	Formate-Metal complexes	 A= Transition metal Mono dentate formate-metal complex Bidentate formate-metal complex Hydroxy carbonyl metal complex		In production of solar fuels	(Mikkelsen <i>et al.</i> , 2010)

Note: Pant, D., Sharma, V., Singh, P., *et al.*, 2017. Perturbations and 3R in carbon management. Environ. Sci. Pollut. Res. 24, 4413–4432.

Table 16 Carbon mitigation of selected microalgae

Strain	Growth temp (°C)	CO ₂ concentration tolerance (%)	CO ₂ removal (g/l/day)	References
<i>Botryococcus braunii</i> SI-30	25–30	–	1	(Murakami and Ikenouchi, 1997)
<i>Chlorella kessleri</i>	30	0.038	–	(Morais <i>et al.</i> , 2007)
<i>Chlorella</i> sp.	26	2	0.261	(Chiu <i>et al.</i> , 2008)
		5	0.316	
<i>Chlorella</i> sp.KR-1	25	10	–	(Sung <i>et al.</i> , 1999)
<i>Chlorella vulgaris</i>	25	Air	0.075	(Scragg <i>et al.</i> , 2002)
		10	0.25	(Sydney <i>et al.</i> , 2010)
		2	0.43	(Yeh and Chang, 2011)
<i>Chlorococcum littorale</i>	25	5	16.7	(Iwasaki <i>et al.</i> , 1998)
		20	4	(Kurano <i>et al.</i> , 1995)
<i>Dunaliella</i>	–	27	0.313	(Kishimoto <i>et al.</i> , 1994)
<i>Haematococcus pluvialis</i>	16–18	Air	0.143	(Huntley and Redalje, 2007)
<i>Euglena gracilis</i>	27	10	64.8%	(Chae <i>et al.</i> , 2006)
<i>Monoruphidium minutum</i>	25	13.6	90%	(Brown, 1996)
<i>Nannochloropsis oculata</i>	26	2	0.211 g/h	(Chiu <i>et al.</i> , 2009)
		5	0.234 g/h	
		15	0.393 g/h	
<i>Scendesmus obliquus</i>	30	6	28.08%	(de Morais and Costa, 2007)
		12	13.56%	
<i>Spirulina</i> sp.	30	6	53.29%	
		12	45.61%	
<i>Scendesmus dimorphus</i>		0.03	1.27	(Fulke <i>et al.</i> , 2014)
<i>Scendesmus incrassatulus</i>	–	0.03	1.50	
<i>Chlorella</i> sp	–	15	0.46	(Jin <i>et al.</i> , 2006)
<i>Chlorella</i> sp	–	5	0.7	(Ryu <i>et al.</i> , 2009)
<i>Scendesmus</i> sp.	–	15	0.61	(Jin <i>et al.</i> , 2006)
<i>Spirulina platensis</i>	–	15	0.92	(Kumar <i>et al.</i> , 2010)
<i>Scendesmus obliquus</i>	–	10	0.55	(Ho <i>et al.</i> , 2010)
		10	0.29	(Tang <i>et al.</i> , 2011)
		2.5	1.19	(Ho <i>et al.</i> , 2010)
<i>Dunaliella</i> sp.	–	3	0.31	(Kishimoto <i>et al.</i> , 1994)
<i>Chlorella kessleri</i>	–	18	0.16	(de Morais and Costa, 2007)
<i>Haematococcus pluvialis</i>	–	34	0.14	(Huntley and Redalje, 2007)

Table 17 Carbon sequestration by selected macroalgae

Strain	Growth temp. (°C)	CO ₂ concentration in water	CO ₂ removal (ppm)	References
<i>Gracilaria cornea</i>	25	12–15	–	(Israel <i>et al.</i> , 2005)
<i>Gracilaria</i> sp.	20	345	320	(Gao <i>et al.</i> , 1993)
		1050	891	
		1616	1420	
<i>G. chilensis</i>	20	345	292	
		1050	883	
		1616	1280	

Table 18 Carbon mitigation by selected cyanobacteria

Strain	Growth temp (°C)	CO ₂ Conc. (%)	CO ₂ removal	References
<i>Aphanothece microscopic Nageli</i>	35	15	109.2 ^a	(Jacob-lopess <i>et al.</i> , 2009)
<i>Anabaena</i> sp.	27	–	1.45 ^b	(López <i>et al.</i> , 2009)
<i>Chlorogleopsis</i> sp.	50	5	20.45 ^c	(Ono and Cuello, 2007)
<i>Synechococcus elongatus</i>	60	0.04–60	–	(Miyari, 1995)
<i>Fischerella</i> 113	45	0.1	–	(Weissman <i>et al.</i> , 1998)

^aCarbon fixation rate measured in mg/l/h.^bCarbon fixation rate measured in g CO₂^{–1} day^{–1}.^cCarbon fixation rate measured in mgC/l/d.

Table 19 Conversion of CO₂ to Bicarbonate by selected microbes through carbonic anhydrase and other enzymes

Microbes	Growth temp (°C)	CO ₂ conc. (%)	Conversion efficiency of CO ₂ to Bicarbonate	References
<i>Aeribacillus pallidus</i>	80	5–10	42.5 mg	(Bose and Satyanarayana, 2016)
<i>Bacillus sp.</i>	20–55	–	2.26 mg calcite	(Achal and Pan, 2011)
<i>Bacillus subtilis</i>	37	–	480 mg CaCO ₃	(Oviya <i>et al.</i> , 2012)
<i>Bacillus schlegelii</i>	70	5–10	–	(Muley <i>et al.</i> , 2014)
<i>Chorella vulgaris</i>	–	30 ± 2	–	(Morais <i>et al.</i> , 2007)
<i>Chlorogleopsis sp.</i>	50	5	20.45 mgC/l/d	(Ono and Cuello, 2007)
<i>Monoruphidium minutum</i>	25	13.6	90%	(Brown, 1996)
<i>Citrobacter freundii</i>	40	–	–	(Ramanan <i>et al.</i> , 2009)
<i>Pseudomonas fragi</i>	30–55	–	17.8 mg CaCO ₃	(Sharma and Bhattacharya, 2010)
<i>Serratia sp.</i>	40	18	24 mg CaCO ₃	(Bharti <i>et al.</i> , 2014)

Table 20 Role of various enzymes in CO₂ sequestration

Enzyme	Function	References
Oxidoreductases	Converting CO ₂ in oxidation state of the carbon element	(Shi <i>et al.</i> , 2015)
Formate dehydrogenase(F _{ate} DH) or carbon dioxide (CO ₂) reductase	Conversion of CO ₂ to formate	(Tishkov and Popov, 2004)
Carbon monodioxide dehydrogenase (CODH). ([NiFe] CO dehydrogenases [NiFe] CODH)	Conversion of CO ₂ to carbon monodioxide (CO)	(Appel <i>et al.</i> , 2013)
Nitrogenase from <i>Azotobacter vinelandii</i> ,	Catalyze the two-electron reduction of CO ₂	(Seefeldt <i>et al.</i> , 1995)
Remodeled nitrogenase	Conversion of CO ₂ to methane	
Lyases	Michael addition (breaking of chemical bonds and generates a new double bond or a new ring structure)	(Shi <i>et al.</i> , 2015)
Carbonic anhydrase (CA)	Conversion of CO ₂ to bicarbonate	(Giri <i>et al.</i> , 2018)
Decarboxylases e.g.,	Conversion of CO ₂ to biodegradable chemicals	(Aresta and Dibenedetto, 2002)
1. 4-hydroxybenzoate decarboxylases from <i>Chlamydomonas reinhardtii</i> AR39, <i>Enterobacter cloacae</i> P240109 and <i>Clostridium hydroxybenzoicum</i>	● Reversible carboxylation of phenol with CO₂ to yield 4-hydroxybenzoate. ● Carboxylation of phenol with CO₂ to synthesize p-hydroxybenzoic acid. ● Catechol carboxylated into 3,4-dihydroxybenzoate in the presence of bicarbonate.	
2. Phenylphosphate enzymes of <i>Thauera aromatica</i>		
3. 3,4-dihydroxy-benzoate decarboxylase from <i>Clostridium hydroxybenzoicum</i>		
F _{ate} DH and methanol dehydrogenase (MDH)	Conversion of CO ₂ to methanol	(Kuwabata <i>et al.</i> , 1994)
Genetically engineered <i>Synechococcus elongatus</i> PCC7942 through the expression of several key genes (<i>alsS</i> , <i>ilvC</i> and <i>ilvD</i>) Rubisco, acetolactate synthase (<i>AlsS</i>), acetohydroxyacid isomeroreductase (<i>IlvC</i>), dihydroxy-acid dehydratase (<i>IlvD</i>) and 2-ketoacid decarboxylase (<i>Kdc</i>)	Produce isobutyraldehyde from CO ₂	(Atsumi <i>et al.</i> , 2009)

Enzymatic Conversion of CO₂

CO₂ fixation/conversion reaction can occur through directly adopting the single enzyme or multiple enzymes (oxidoreductases, synthases or lyases) to catalyze the conversion of CO₂ In vitro or in Vivo.

- (1) *Carbon monodioxide dehydrogenase (CODH)*: Conversion of CO₂ to carbon monoxide by CODH can also lead production of liquid hydrocarbons (Fischer-Tropsch process), acetic acid (Monsanto and Cativa processes), and methanol has received much attention now a days (Woolerton *et al.*, 2010). Two types of CODHs, [NiFe] CO dehydrogenases ([NiFe] CODH) and [MoCu] CO dehydrogenases ([MoCu] CODH) are containing metal subunit [Fe₄S₄Ni] and [MoSCu] active sites (Appel *et al.*, 2013). In nature, the conversion between CO and CO₂ is primarily catalyzed by [NiFe] CO dehydrogenases ([NiFe] CODH) (Parkin *et al.*, 2007).
- (2) *Conversion of CO₂ to Formic Acid/Formate by formate dehydrogenase*: Conversion of CO₂ into formate by the formate dehydrogenase (FDH or FateDH) is also important CO₂ mitigation pathway like *Syntrophobacter fumaroxidans* FDH has also been used to reduce CO₂ and showed very good activity in formate reduction.

- (3) *Conversion of CO₂ to Methanol by dehydrogenases*: Reduction of CO₂ into methanol used as a important material for many industrial and environmental applications. Multi enzyme system is one of the most promising possible routes for the reduction of CO₂ into methanol with following attributes: (1) recycling of the “GHGs” gas, and (2) the production of renewable or sustainable fuel alternatives (Shi *et al.*, 2015). In the multi enzyme system FateDH and methanol dehydrogenase (MDH) as the catalysts for CO₂ reduction with pyrroloquinolinequinone (PQQ) as a cofactor used as electrochemical reduction of CO₂ to methanol (Kuwabata *et al.*, 1994).
- (4) *Conversion of CO₂ by oxidoreductases*: Oxidoreductase transfer of electrons from one molecule to another like conversion of CO₂ by an oxidoreductase and reduce the oxidation state of carbon (Shi *et al.*, 2015).
- (5) *Conversion of CO₂ to Bicarbonate*: Carbonic anhydrase (CA) catalyze CO₂ to bicarbonate (HCO₃[−]) via catalysis with up to 10⁶ per second turnover rate (Lindskog and Coleman, 1973). Single and multienzyme based CO₂ conversion system is given below (Tables 19 and 20).

Conclusion

Carbon mitigation through physical, chemical and biological sequestration from any point sources offers a great potential in the amelioration of GHG mitigation. Carbon dioxide capture and storage (CCS) and sequestration from industrial and energy-related source can consider as an option for stabilization of atmospheric greenhouse gas concentrations. GHG mitigation using biological and chemical methods has many advantages than other conventional mitigation methods like CO₂ is being utilized to produce value added products, chemicals and high value biomass offers a good opportunity for sustainable development in the energy and environmental sectors. Physical adsorption is a good option for carbon dioxide capture at high pressure and low temperature, therefore it is not suitable for high temperature operation like post combustion CO₂ capture. Chemical adsorbent like amine based adsorbent, metal organic frameworks are the suitable under such conditions with high selectivity. Biological carbon mitigation can convert inorganic C to organic C and many advantages like produce high value biomass has a number of applications in cost effective energy production.

See also: Plasma Arc Driven Solid Waste Management: Energy Generation and Greenhouse Gases (GHGs) Mitigation

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Catalytic Conversion of Greenhouse Gases

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Introduction

Indisputably, greenhouse gases emission has been unfavourable to the eco-system (Nabgan *et al.*, 2016). Methane (CH_4) is a reactive trace gas readily available which can be obtained from natural and anthropogenic sources (University of Oxford, 1998). It is the main constituent of natural gas (Zavala-Araiza *et al.*, 2015). CH_4 and carbon dioxide (CO_2) are the main anthropogenic gases present in the atmosphere (Lauder *et al.*, 2013). The increased development of industries and the abundance of non-renewable carbon and H_2 sources have led to the growing reservoir of greenhouse gases. Generally, CH_4 can be transformed into more valuable product such as; syngas (H_2 and CO) using various reforming techniques which include steam, partial oxidation and CO_2 reforming. In fact, CH_4 reforming has become an accepted procedure for producing syngas which is used in the petrochemical industry (Domínguez *et al.*, 2007; Zahedinezhad *et al.*, 2009). Detailed study have been reported using these various techniques viz; steam reforming by Antzara *et al.* (2016), partial oxidation by Jahangiri and Pahlavanzadeh (2012), CO_2 reforming by Foo *et al.* (2012), Osazuwa *et al.* (2017b) and, (Osazuwa and Cheng, 2017). Combination of CH_4 reforming techniques in order to obtain a much improved product have also being reported previously by, Lim *et al.* (2010), Koo *et al.* (2014), (Choudhary and Mondal, 2006). Apart from the fact that the CO_2 reforming of CH_4 reaction consumes greenhouse gases, its products serve as feed for the Fischer-Tropsch synthesis (syngas ratio below 2.0) (Choudhary and Mondal, 2006). The product (H_2) is employed as fuel cells for transmission of clean energy, electricity generation and production systems (Wang *et al.*, 1996; Hosseini and Wahid, 2016). The need to promote a cleaner environment by minimizing global warming cannot be over emphasized. To reiterate this need, over 195 countries signed an agreement in 2015 to take part in a combined attempt to reduce the emission of greenhouse gases. Naturally, CH_4 reforming with CO_2 (greenhouse gases) is an endothermic reaction that occurs at a very slow rate if allowed to progress un-catalysed. Therefore, catalytic reforming of CH_4 with CO_2 is a reaction, which progresses with H_2 and CO formation as products and carbon as unwanted/by products (Pompeo *et al.*, 2009). This carbon deactivates the catalyst; hence, researchers have tried to develop catalysts with improved performance, which minimizes catalyst deactivation from carbon formation on the surface or pore of the catalyst. Noble metal based catalyst was reported to minimize carbon deposition (Hou *et al.*, 2006; Sutthiumporn and Kawi, 2011). However, nickel (Ni) catalyst is more economical (Hirose *et al.*, 2011; Yentekakis *et al.*, 2015). Reports have shown that as a result of the cost of noble metals coupled with the attraction of Ni to carbon, it makes economic sense to enhance the performance of non-noble metal catalyst. Hence, transition metal based catalyst has shown better performance towards syngas production from CH_4 dry reforming (Valderrama *et al.*, 2005; Gallego *et al.*, 2008b; Rivas *et al.*, 2008; Khajeh Talkhoncheh and Haghighi, 2015). Another effective catalyst for CO_2 reforming/ conversion of CH_4 is the perovskite, which requires the introduction of metals into the perovskite matrix. Perovskite possess a structure with superior reduction-oxidation properties that permits very high distribution of metal elements in a reduced system; hence enhancing the activity of the catalyst (Goldwasser *et al.*, 2005b; Moradi *et al.*, 2012). Moreover, the perovskite has a wide selection of A and/or B cations, enabling combinations of varying oxidation state of its elements (Tienthao *et al.*, 2007). Catalytic conversion of greenhouse gases to valuable products can be effectively achieved via CO_2 reforming of CH_4 . However, catalyst inhibition (deactivation) due to carbon formation has been outlined as the major setback that inhibits the revolution of CO_2 reforming of CH_4 to a commercial process. Reports available in literature have attempted to analyse ways to enhance catalyst activity, catalyst stability, reduce carbon formed and deactivation of catalyst by varying supports, promoters and combining metals to obtain support on metal oxides and perovskite type catalysts. Furthermore, various modifications have been carried out to alter the kinetic behaviour of these catalysts in order to improve these aforementioned qualities. This paper seeks to outline the various methods that have been employed in the catalytic conversion of greenhouse gases into valuable products. More specifically, the effects of various catalyst type on the overall behaviour (conversion, yield and kinetic) of greenhouse gases (CH_4 and CO_2) have been emphasized in this review paper.

Greenhouse Gases

Greenhouse effect is a natural (regular) occurrence modelled to retain gases in the earth crust at equilibrium. However, disturbances to the environment take place when imbalance exists. These disturbances are as a result of artificial greenhouse effect which enhances the regular greenhouse effect. Artificial greenhouse effect results from burnt fossil fuels, natural gas, coal and petroleum, while the regular greenhouse effect results from confined heat waves released from the sun. As a result of the heat energy, the temperature of the greenhouse gases in the atmosphere is increased. Activities of man such as; deforestation, burning of fossil fuels, coal, oil, industrialization and population increase are responsible for the excess greenhouse gases produced. Components of greenhouse gases are; water vapour, nitrous oxide, ozone, CH_4 and CO_2 . CO_2 and CH_4 are readily available in much

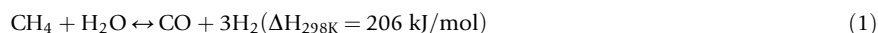
larger amounts (Lim *et al.*, 2010). The global interest to reduce greenhouse gases has resulted in studies aimed at promoting the mitigation of the two main gases; CH₄ and CO₂ into usable products.

Conversion/Reforming of Methane

CH₄ can be produced naturally and artificially by organic process and man-made activities, respectively. Conversion/Reforming of CH₄ is the separation of its molecules by combining it with the molecules of a splitting agent. CH₄ can be converted via different methods depending on the quality of the product stream required; steam, partial oxidation and CO₂ reforming of CH₄ are amongst the several methods recently reported (Arkatova, 2010).

Steam reforming of CH₄

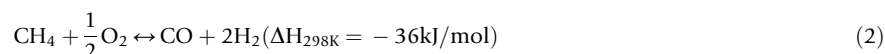
Already commercialized steam reforming is often used industrially and the process is shown in Eq. 1, (Krylov *et al.*, 1998).



Reforming of CH₄ via steam produces H₂ and CO with ratio of about 3.0. Reports have claimed higher H₂: CO ratio is not ideal for the Fischer Tropsch reaction which produces liquid petrochemicals (Tsipouriari and Verykios, 2001). Low temperature steam reforming of CH₄ using metal oxide (MgO, CaO and La₂O₃) promoted Ni-Ce_{0.8}Zr_{0.2}O₂ catalyst in a compact reformer have been investigated by Kim *et al.* (2017). Results from their study showed that metal oxides improved the basic strength of the catalyst, hence, enhancing the resistance to carbon formation and improving the catalytic activity. Amongst all the catalysts prepared, Ni-La₂O₃-Ce_{0.8}Zr_{0.2}O₂ catalyst had the highest performance as a result of the high dispersion of Ni, strong basicity of La₂O₃ and strong interaction between Ni and La₂O₃. Enhanced catalytic performance of Ni/ α -Al₂O₃ catalyst modified with CaZrO₃ nanoparticles in steam methane reforming have been studied by Lertwittayanon *et al.* (2017). The effects of loading CaZrO₃ nanoparticles (0–15 wt%) were investigated after synthesizing the catalyst using the sequential impregnation method. Results from their study showed that 15 wt% CaZrO₃ nanoparticles provided the highest H₂ yield. The activity was linked to the steam adsorption-dissociation at the sites where O₂ vacancies exist on the surface of CaZrO₃ nanoparticles. Stability of the modified and unmodified catalyst was also tested with the modified Ni/ α -Al₂O₃ catalyst showing higher catalytic performance when compared to the unmodified Ni/ α -Al₂O₃. It was also found that at high S/C ratio of 3.0, excess steam adsorption at the oxygen vacancies on the CaZrO₃ particle occurred resulting in adsorptive competition between steam and CH₄, thereby decreasing CH₄ dissociation. Hence, the optimum S/C ratios for the CaZrO₃-modified Ni/ α -Al₂O₃ catalysts were lower than those for the unmodified Ni/ α -Al₂O₃ catalyst as a result of the very good steam reforming capability of the CaZrO₃ particles.

Partial oxidation reforming of CH₄

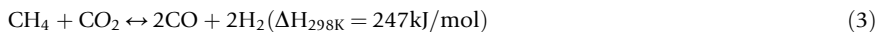
In order to produce liquid fuels, syngas ratio less than 2.0 is required (Sutthiumporn and Kawi, 2011; Ruckenstein and Wang, 2002; Khalesi *et al.*, 2008). Syngas with lower ratio are obtained from partial oxidation of CH₄ as shown in Eq. 2 (Goldwasser *et al.*, 2005b).



Kaddeche *et al.* (2017) investigated the partial oxidation of CH₄ on co-precipitated Ni-Mg/Al catalyst modified with copper or iron. The authors used the co-precipitation method to prepare Fe or Cu promoted (Ni/Mg) Al catalysts. The compositional effects of the catalyst and the pre-treatment conditions were tested on the partial oxidation of CH₄. Results from their study revealed that Fe or Cu promoted (Ni/Mg) Al catalysts had high performance in partial oxidation of CH₄. In addition, as the calcination temperature decreased and Ni and Al contents increased, the results showed increasing activity and selectivity towards the products. In all reactions, the catalyst promoted with Fe was superior in terms of the CH₄ oxidation and for the water-gas shift reaction. Adding Cu also enhanced the performance of the (Ni/Mg) Al catalyst. The performance was linked to the creation of NiM (M=Cu or Fe) alloy which enhanced the distribution of Ni particles. LaNiO₃ and La₂NiO₄ supported on CeO₂ were synthesized using a microwave assisted co-precipitation method and the activity test was carried out in the partial oxidation of methane by La Parola *et al.* (2016). Results from their catalytic study showed that at increased temperature (about 800°C), high CH₄ conversion was obtained with approximately 100% CO selectivity. The LaNiO₃CeO₂ stimulated CH₄ cracking with CO/CO₂ evolving in a large temperature span which was in contrast to LaNiO₃ stimulating CH₄ cracking in a more limited range of temperature. This was attributable to the interaction between Ni and Ce, thereby enhancing the catalyst activity in partial oxidation of CH₄ reaction. Partially oxidized CH₄ with bi-functional catalyst I and the formation of Ni^o/La₂O₃ during temperature programmed partial oxidation of methane reaction over LaNiO₃ perovskite have been studied by Nguyen *et al.* (2014). Several characterization techniques such as XRD, TGA, HRTEM/EDX, and FFT were employed to ascertain the physicochemical properties of the catalyst pre, during and post reaction. Oxidation of CH₄ over LaNiO₃ and La₂O₃, and the syngas production over reduced Ni^o/La₂O₃ catalysts were analysed to understand the transformation of LaNiO₃ to Ni^o/La₂O₃ and proposed kinetic model of POM process over final bi-functional Ni^o/La₂O₃.

CO₂ reforming of CH₄

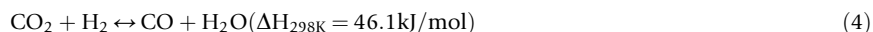
The main challenge of partial oxidation of CH₄ is the exothermicity of the reaction which creates control difficulties during the reaction. Hence, CH₄ dry reforming with H₂: CO ratio less than 2.0 is of higher demand and can be represented by Eq. 3.



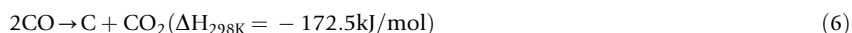
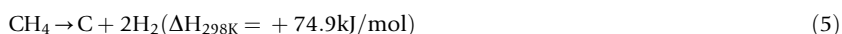
Global industrialization has focused attention on the consumption of CO₂. The excessive release of CO₂ has further worsened the critical problems associated with global warming and climate change (Song, 2006). An attractive way atmospheric CO₂ can be effectively minimized is by reforming of CH₄ via CO₂. Catalytic performance of mesoporous carbons modified with lanthanides in dry conversion of methane have been reported by Goscianska *et al.* (2018). Mesoporous carbon was synthesized using SBA-15 and KIT-6 and sucrose as carbon source. After characterization, the catalysts were tested using 1:1 molar ratio of CH₄ and CO₂ at continuous flow in a stainless steel reactor at 650°C under atmospheric influence. From their results, Ce- and La-based catalysts supported on mesoporous carbons showed better activity and stability when compared to the unmodified catalysts supported on SBA-15 and KIT-6. Osazuwa and Cheng (2017) studied the catalytic performance of samarium-cobalt trioxides perovskite catalyst for the conversion of greenhouse gases into cleaner energy. The various outstanding catalytic properties gave way for an excellent conversion (above 90%) in a 30 h experimental setup with the used catalyst showing evidence of carbon deposits. Syngas production via methane dry reforming over neodymium sesquioxide supported Co catalyst prepared using the wet-impregnation technique have been outlined by Ayodele *et al.* (2016a). Their results showed that conversion of both reactants increased with feed ratio and reaction temperature, hence, leading to an increased syngas yield of 59.91% and 62.02% for H₂ and CO, respectively. The authors' proceeded by proposing CH₄ and CO₂ adsorption, activation of CH₄ from CH₄ decomposition and gasification of carbon deposited on the catalyst surface.

Combined steam and CO₂ (dry) reforming of CH₄

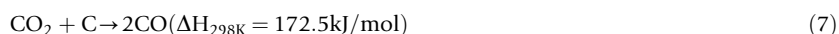
Other researchers have attempted to combine steam and dry reforming process to improve the conversion of greenhouse gases and enhance the end product of the reaction. In a study, an ideal design for combining steam reforming with dry CH₄ reforming and reusing CO₂ as raw material have been investigated by Lim *et al.* (2010). In order to minimize cost and energy consumption, steam and dry reforming was combined to reform CH₄ for CO₂ treatment process. Models for the combined process and the steam reforming process were established and the cost was obtained for the overall process. Their results showed that the combined process reduced the net CO₂ by 67% when compared to the steam reforming process. The production of syngas via steam and CO₂ reforming of CH₄ over Ni-Ce/MgAl₂O₄ catalysts with enhanced coke resistance have been investigated by Koo *et al.* (2014). Ni-Ce/MgAl₂O₄ catalyst was prepared using the co-impregnation method by adjusting the Ce/Ni ratio in a range 0.0–1.0. In their study, pre and post catalyst analysis was carried out to determine the effect of Ce addition. It was found that the addition of Ce to Ni/MgAl₂O₄ catalyst affected the NiO crystallite size, metal dispersion and reduction degree. Ni-Ce/MgAl₂O₄ catalyst with Ce/Ni ratio 0.25 had the smallest NiO crystallite size of 8.3 nm and highest metal dispersion of 4.91%. Ni-Ce/MgAl₂O₄ with Ce/Ni ratio of zero had the largest NiO crystallite size of 11.0 nm and lowest metal dispersion of 3.49%. In terms of catalytic activity, Ni-Ce/MgAl₂O₄ (Ce/Ni=0.25) catalyst had the best activity and coke resistance as a result of the improved metal dispersion, better reducibility and higher surface oxygen transfer. Choudhary and Mondal (2006) combined partial oxidation, CO₂ and steam conversion to syngas catalysed by NdCoO₃ perovskite catalyst. The conversion and yield were affected by CO₂/H₂O feed ratio in the CO₂ and steam reforming process. For the CH₄ reforming process via CO₂ and partial oxidation, reactants conversion, H₂ selectivity and the net heat of reaction are affected by operating constraints like relative O₂ concentration in the feed, temperature and space velocity. Interestingly, their report showed no carbon deposit on the catalyst for both cases, thereby placing reduced NdCoO₃ as a very good catalyst for carbon-free CO₂ combined with steam reforming. Interestingly, CO₂ reforming of CH₄ reaction proceeds with side reactions such as the reverse water-gas shift reaction (RWGS) represented in Eq. 4.



The endothermicity of the RWGS coupled with the formation of H₂ and CO (CO₂ reforming of CH₄) is preferred at high temperature. In contrary views, some writers have argued that temperature increase does not favour the conversion of greenhouse gases (forward reaction) because of the negative effects on the catalyst. The resulting effects are catalyst sintering, unsteady behaviour of the catalyst and catalyst active site engulfment by carbon due to increased CH₄ cracking (Luo *et al.*, 2000). In reforming of CH₄ with CO₂, carbon is produced as a by-product of CH₄ cracking and another side reaction known as the Boudouard reaction represented as Eqs. 5 and 6, respectively, (Richardson and Paripatyadar, 1990).



Another group of writers have argued that CH₄ conversion using CO₂ proceeds at elevated temperature in order to crack CH₄ and minimize the Boudouard reaction side reaction effect. At elevated temperature, the reverse Boudouard reaction is favourable and it is shown in Eq. 7.



Hence, carbon formation can be minimized by carefully selecting the reaction operating conditions such as; reaction temperature and type of catalyst.

Catalyst characterization

Catalyst characterization assesses the catalytic physicochemical properties. The need to characterize the catalyst is to ascertain the connection linking the physicochemical properties and the mechanism of reaction and kinetics as a means of developing a suitable catalyst to enhance greenhouse gases conversion. In catalytic studies, some physical characterizations include N_2 physisorption, SEM, FESEM and TEM. Physical properties are the textural properties and morphology of the catalyst. N_2 physisorption which refer to textural properties such as; pore size, surface area, pore size distribution and pore volume are obtained by N_2 adsorption-desorption isotherms data while the morphology of the catalyst is shown by the scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). Some chemical characterizations include; EDX, XPS, XRD, NH_3 -TPD, CO_2 -TPD, TGA and FTIR. These chemical characterizations can be sub-divided into elemental (EDX and XPS) and surface chemical analysis (XRD, TPD, TGA, FTIR). Captured images from SEM, FESEM and TEM are analysed by the energy dispersive X-ray (EDX) analyser in order to obtain the catalyst elemental composition. X-ray photoelectron spectroscopy (XPS) is method for elemental and surface analysis due to its increased recognition capability of chemical characteristics without any known damage to the catalyst morphology (Tao *et al.*, 2014). XPS analysis is aimed at obtaining the composition at the surface and binding energy of the catalyst. X-ray diffraction (XRD) pattern of the catalyst shows the crystalline structure of the catalyst. Further computation for the crystalline particle size can be carried out using the Debye-Scherrer equation shown in Eq. 8 (Bradford and Vannice, 1996) or the more precise Williamson–Hall equation represented in Eq. 9 (Khorsand Zak *et al.*, 2011).

$$D_{hkl} = \frac{0.9\lambda}{\beta_{hkl} \cos\theta} \quad (8)$$

$$\beta_{hkl} \cos\theta = \frac{k\lambda}{D_{hkl}} + (4\varepsilon \sin\theta) \quad (9)$$

where λ is the wavelength of Cu-K α , θ is the Bragg diffraction angle, k is a constant (0.9), D_{hkl} is the crystallite size of the catalyst, the peak full width with half maximum (FWHM) is β_{hkl} , and ε is the strain. Data from XRD can be linearized in the Williamson-Hall equation to give the y-intercept (y) and slope (s) represented in Eqs. 10 and 11, respectively.

$$y = \frac{k\lambda}{D_{hkl}} \quad (10)$$

$$s = (4\varepsilon \sin\theta) \quad (11)$$

After purging the surface with gases at high temperature, desorbed molecules from a surface are analysed using a technique known as temperature programmed desorption (TPD). In catalysis, the acidic and basic sites/strength can be determined by the amount of gases adsorbed in the sites. In addition, the catalyst reducibility can be determined by employing H_2 - temperature programmed reduction (H_2 -TPR). Adsorbed H_2 , NH_3 and CO_2 gases on the catalyst surface are estimated using a thermal conductivity detector. The solid state thermal profile prior to calcination is obtained using thermo gravimetric analysis (TGA). Furthermore, post reaction (carbon study), the weight loss profile and the derivative weight loss profiles of the catalyst can also be obtained using the TGA. The TPC uses a flow of N_2 , while the TPO uses O_2 . Using infrared light, the functional groups present in the catalyst can also be identified using the Fourier transform infrared spectroscopy (FTIR). This type of analysis presents the absorbance spectra showing the chemical bonds and molecular structure of the catalyst.

Catalyst Type for Conversion of Greenhouse Gases

Good catalysts are required to stimulate the process of CH_4 dry reforming and improve the product under favourable conditions (Lombardo and Ulla, 1998). At high temperature and under reducing conditions, the formation of syngas is favoured. Hence, several researchers reduce the catalyst with H_2 to aid finely dispersed metal particles of the catalyst (Zhu *et al.*, 2014). In CH_4 reforming reactions, the ability to synthesize a catalyst with high performance is of great interest. Hence, it is desirable to obtain a deactivation free catalyst that can effectively combine greenhouse gases (CH_4 and CO_2) to produce valuable products. Researchers have tried to obtain this kind of catalyst by supporting and promoting the active site of the catalyst (Su *et al.*, 2014). CH_4 cracking during the CO_2 reforming of CH_4 is a major source of carbon. Carbon formation during the reforming process has been the major drawback and it is still under investigation up till date (Sutthiumporn *et al.*, 2012). Noble metals show good performance and more importantly are have less affinity for carbon during methane dry reforming (Hou *et al.*, 2006). The use of noble metals is however to advisable due to their high cost and unavailability. To substitute for noble metals, attention have shifted to Group VII transition metals like Nickel (Ni) (Wang *et al.*, 1996). These type of metals are active and selective towards CH_4 dry reforming (Valderrama *et al.*, 2005; Rivas *et al.*, 2008; Khajeh Talkhonchek and Haghighi, 2015; Pichas *et al.*, 2010). Additionally, the low cost of transition metals is another advantage over noble metals (Yentekakis *et al.*, 2015). In terms of superior activity, an effective catalyst for methane dry reforming is the Ni-based catalyst (Gallego *et al.*, 2008a). However, the active site of Ni-based catalyst are readily attacked by carbon, (Gallego *et al.*, 2008b; Ashcroft *et al.*, 1991). Supported cobalt (Co) catalysts (Ruckenstein and Wang, 2000) and Co-La based perovskite catalyst have also been applied in methane dry reforming (Valderrama *et al.*, 2013). In summary, Ni-based catalyst have shown superior catalytic properties in CO_2 reforming of CH_4 , supported Co catalyst have been reported to exhibit better stability towards the reaction as a result of its superior ability to withstand carbon attacks and extreme

temperature changes (Ferreira-Aparicio and Guerrero-Ruiz, 1998). In addition, Co catalyst have also being reported to show good catalytic properties in methane dry reforming (Budiman *et al.*, 2012).

Supported Metal Catalyst for Conversion of Greenhouse Gases

SBA-15 supported mesoporous Ni and Co catalysts with high coke resistance for CO₂ reforming of CH₄ have been investigated by Erdogan *et al.* (2018). In their study, wet-impregnation method was used to synthesize the mesoporous SBA-15 supported Ni and Co and Ni-Co catalysts. From the activity results, it was found that bimetallic 4Ni-1Co@SBA-15 catalyst had good activity with CH₄ conversion 73% and CO₂ conversion of 89% with reaction temperature of 750°C. Coke formation was decreased when Co was combined with SBA-15 supported Ni catalyst. Durability and activity enhancement of Zirconia supported Ru catalyst for methane dry reforming have been studied by Whang *et al.* (2017). In their study, a small amount of Ru (0.13 wt%) supported on ZrO₂-SiO₂ showed good performance for methane dry reforming reaction carried out at 800°C. Ru size increased (6.3 nm) after Ru was placed on the SiO₂ support. In contrast, the size of Ru reduced to 1.4 nm when Ru was incorporated on the ZrO₂-SiO₂ support. Upon testing in methane dry reforming reaction, the Ru/ZrO₂-SiO₂ catalyst showed no carbon deposit while the filamentous carbon was deposited on the Co-Ru/ZrO₂-SiO₂ catalyst. Nickel catalyst particles incorporated on ceria-zirconia were synthesized by different methods and their catalyst performance were evaluated in methane dry reforming by Wolfbeisser *et al.* (2016). The catalyst which they prepared by surfactant assisted co-precipitation was inactive for methane dry reforming due to the engulfment of Ni particle by ceria-zirconia particles. In terms of the catalytic activity, it was found that the catalyst prepared without surfactant was similar to that of Ni-ZrO₂. Ni-ZrO₂ did not show a better performance when compared to ceria-zirconia supported Ni catalyst even though filamentous carbon was reduced during the reaction. In summary, the authors linked the catalyst activity to the method of preparation and phase composition. The effects of support on the activity of Ni-based catalyst in dry methane reforming have been reported by Zhang *et al.* (2015). It was found that support significantly affected NiO species. According to the authors, SiO₂, TiO₂ and ZrO₂ as support have a weak attraction to NiO. These could lead to catalyst inactivity as a result of accumulation of active metal species. In contrast, Al₂O₃ and MgO showed strong interaction with NiO leading to phase modification of NiAl₂O₄ and NiO-MgO, hence, making the reduction process difficult to attain. Therefore, NiO supported on MgO-modified Al₂O₃ exhibited the best catalytic performance (100 h stability) in methane dry reforming. The effects of phosphorus addition to Rh-supported catalysts for conversion of methane with CO₂ have been studied by Cimino *et al.* (2017). Three types of these catalysts were prepared; (i) dispersed phosphorus and rhodium on La-stabilized γ -Al₂O₃; (ii) stabilizing γ -Al₂O₃ with phosphorus and then dispersing rhodium; (iii) dispersing rhodium on AlPO₄ support and Rh incorporated on La-stabilized γ -Al₂O₃ was used a catalyst reference. It was found that the addition of phosphorus to the supports increased the catalyst acidity and suppressed CO₂ activation leading to reduction in activity and carbon resistance during methane dry reforming reaction.

Promoted Metallic Catalyst for Conversion of Greenhouse Gases

Samaria-doped Ni and Co/SBA-15 catalysts for methane reforming with CO₂ has been reported by Taherian *et al.* (2017). It was found that samaria doped Ni/SBA-15 gave the best CH₄ conversion (about 58% at 700°C). However, samaria-doped Co/SBA-15 has very low conversion of methane (about 25% at 700°C). The author related the effects of samaria on Ni/SBA-15 to reduced NiO particles, increased dispersion of NiO and reduced carbon formation. The undesired influence of samaria on Co/SBA-15 catalyst was as a result of Co oxidation and Co particles sintering at elevated temperatures. Károlyi *et al.* (2018) reported methane dry reforming over Ni-in/SiO₂ catalyst free of carbon deposit. Findings from their study showed that carbon deposit on Ni/SiO₂ can be completely eradicated from the process of greenhouse gases conversion by the addition of indium as promoter to the catalyst. Characterizations such as TPR, CO₂-TPD and XPS suggested the interaction between the two metals. According to their report, indium diluted the nickel surface thereby minimizing the formation of carbon species and carbon nanotubes on the catalyst surface in-situ the conversion of methane with CO₂ reaction. Promotional effect of Gd over Ni/Y₂O₃ catalyst for methane dry reforming have been investigated by Al-Fatesh (2017). The effects of calcination temperatures, activation temperature and time were studied. It was found that a maximum H₂ yield of 82.8% was obtained at calcination temperature of 800°C, activation temperature of 800°C and reaction temperature of 700°C. In order to inhibit carbon formation, the catalyst was promoted by Gd. Interestingly, 1 wt% of Gd altered the carbon formation mechanism and reduced the carbon deposited. This property of Gd was linked to the superior basicity of the Gd when compared with non-promoted Ni/Y₂O₃ catalyst. Dispersed Gd-doped Ni/ZSM-5 catalyst for enhanced carbon-resistant for dry reforming of methane have been reported by Sarkar *et al.* (2016). Adding Gd forms GdNi₅ alloy on the ZSM-5 support with particle size ranged 2–10 nm. It was found that Gd enhanced the mass transfer effects of the reactants and products, respectively, while hindering accumulation of the Ni nanoparticles. According to the authors, Gd releases O₂ to oxidize the carbon deposited on the Ni sites. The Gd promoted Ni/ZSM-5 catalyst was able to withstand 100 h of reaction runs without catalyst deactivation. Interestingly, Ni/ZSM-5 catalyst deactivated during the methane dry reforming reaction due to Ni metal sintering. Ghods *et al.* (2016) studied the effects of alkaline earth promoters on the catalytic performance of Ni catalyst supported on mesoporous magnesium silicate in methane dry reforming reaction. The catalysts were characterized by N₂ adsorption, X-ray diffraction, TPR-TPO techniques. It was found that modifying the catalyst decreased the specific surface area and the distribution of the pore sizes. TPR also showed a decrease in the temperature of reduction of the catalyst. From their results, promoting the catalyst with MgO gave the highest catalytic performance. Ni/MgSiO₃ catalysts modified by different contents of MgO were synthesized and results showed that deposited carbon on the catalyst surface decreased with increase in MgO content.

Perovskite Catalyst for Conversion of Greenhouse Gases

The perovskite is a mineral with the configuration of CaTiO_3 (Zhu *et al.*, 2014). It was named after the Russian mineralogist, Count Lev Aleksevich Von Perovski but was actually discovered by Gustav Rose in 1839 (Screen, 2007). 'A' depicts a rare earth or alkaline earth metal, while 'B' depicts the transition metals in the general formula ABO_3 or A_2BO_4 (Mishra and Prasad, 2014). The perovskite structure is cubical with 'A' cation being 12-fold coordinated and 'B' cation 6 fold coordinated with O_2 anions (Peña and Fierro, 2001; Goldwasser *et al.*, 2003). The framework of the perovskite is a ReO_3 type framework configured by adding 'A' cations to the BO_6 octahedral structure (Peña and Fierro, 2001). Various isomorphous solids can be prepared from the perovskite for catalytic studies. The properties and oxidation states of A and B sites are the basis for the catalytic nature of the perovskite. In catalytic studies, perovskites with higher surface area are desirable; however, other factors have played significantly affected the performance of the catalyst. Furthermore, the method of preparation plays an important role in the physical properties of the perovskite. Perovskites prepared using the solid state synthesis method is a very stable solid at extreme temperatures in catalytic reactions. Nonetheless, this synthesis route fails for perovskite employed in surface related studies but are applied mainly in electronic and electrical applications (Labhasetwar *et al.*, 2015). As catalyst, the stability and activity of the perovskite is controlled by the 'A' cation and 'B' cation, respectively (Mishra and Prasad, 2014; Zhong *et al.*, 1997). In another perspective, Zhang (1990) reported that 'A' metals influences the amount of adsorbed O_2 , while 'B-site' influences the quality of adsorbed O_2 . Peña and Fierro (2001) stated that partially substituting the 'A' site with rare earth cations can alter the structural defects and oxidation state such as ionic vacancies. For the 'B' site partial substitution enhances the structural stability and catalytic performance of the catalyst. This claim was supported by Goldwasser *et al.* (2005a) who also reported that the activity of the catalyst could be enhanced by substituting the A and/or B sites leading to slight crystalline structural changes. About 90% of the metals on the periodic table can be incorporated into the A and/or B ionic sites of the perovskite, hence resulting in different stoichiometry and crystalline shapes (Zhu *et al.*, 2014). The major drawback of the perovskite is it relatively low surface area, therefore researchers have focus attention on ways to improve the surface area of the perovskite (Lombardo and Ulla, 1998). The solid state properties of perovskites has further beamed more search light on the use application of perovskite in catalysis (Lombardo and Ulla, 1998). Very recently, more author are using perovskite as catalyst in methane dry reforming by incorporating rare earth or alkaline earth metal into the 'A' site and a transition metal into the 'B' site (Goldwasser *et al.*, 2005b; Hayakawa *et al.*, 1999). Perovskites meets the requirement to be applied in catalysis for reforming reactions because it provides a platform for its constituent's metals to be stable and well dispersed (Goldwasser *et al.*, 2003; Tomishige *et al.*, 2002). The structure of the perovskite is significant in formulating a catalyst that can resist carbon formation during methane dry reforming. La-Ni based perovskites have been reportedly employed for syngas production from methane dry reforming however, for this type of catalyst, structural differences/defects were often observed post reaction as a result of the carbon deposited which leads to catalyst deactivation (Lombardo and Ulla, 1998; Gallego *et al.*, 2006; Jahangiri *et al.*, 2013; Zheng *et al.*, 2015). Perovskite type oxides $\text{LaFe}_{1-x}\text{Co}_x\text{O}_3$ for chemical looping steam methane reforming to syngas and H_2 production have been investigated by Zhao *et al.* (2016). $\text{LaFe}_{1-x}\text{Co}_x\text{O}_3$ with $x=0.1, 0.3, 0.5, 0.7, 1.0$ were employed as O_2 carriers and in effects of Co on the perovskite characteristics were analysed. It was found that the optimal Co required was 0.3. Although, moderate sintering occurred, $\text{LaFe}_{1-x}\text{Co}_x\text{O}_3$ catalyst was able to regenerate in twenty redox reactions. Syngas ratio of 2.0 was obtained with 85% conversion, 43% of CO selectivity and 50% of H_2 selectivity. In the steam oxidation cycle, H_2 production of approximately 4 mmol g^{-1} O_2 carriers was produced. Dama *et al.* (2018) prepared and investigated alkaline earth metal substituted perovskite catalyst for methane dry reforming. From characterizations carried out, it was found that the perovskite A site was responsible for the structure, basicity, O_2 deficiency and Ni dispersion. Results showed that calcium promoted perovskite ($\text{CaZr}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$) showed better CH_4 and CO_2 conversion rate with stability maintained even after 500 h of reaction. In terms of carbon formation, their studies revealed that the type of carbon formed depends on the basicity of the perovskite, metal to support interaction, Ni crystallite size, surface hydroxyl groups and O_2 defects. In summary, the authors successfully proved that $\text{CaZr}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$ was a very good catalyst for methane dry reforming in terms of its activity and stability. The effects of incorporation of perovskite type oxides into a mesoporous SBA-15 silica support in methane dry reforming have been reported by Rivas *et al.* (2010). It was found that incorporating the perovskite into the SBA-15 mesoporous silica increases reactants conversion and selectivity for syngas production but a decrease in reactants conversion were observed when another cation was added to the perovskite active site. A comparative study on methane dry reforming on LaNiO_3 perovskite catalysts supported on mesoporous SBA-15, MCM-41 and silica carrier have been studied by Wang *et al.* (2013). It was found that the pore structure had a direct impact on the catalyst activity and stability. More specifically, $\text{LaNiO}_3/\text{MCM-41}$ had higher activity due to more uniformly dispersed Ni particles in the catalyst. $\text{LaNiO}_3/\text{SBA-15}$ showed better stability when compared with $\text{LaNiO}_3/\text{MCM-41}$ as a result of the stable silica structure which resisted the accumulation of Ni particles. Furthermore, it was reported that the hexagonal matrix of $\text{LaNiO}_3/\text{SBA-15}$ was retained even after reaction unlike the $\text{LaNiO}_3/\text{MCM-41}$ matrix which was completely modified resulting in metal agglomeration.

Catalyst Deactivation in the Conversion of Greenhouse Gases

Efforts have being put in place to enhance the catalyst for conversion of greenhouse gases (CO_2 and CH_4) particularly, for Ni-based catalyst so as to minimize catalyst deactivation due to carbon attacks. In methane dry reforming, catalyst deactivation are triggered by carbon formation which causes reactor pressure build up, carbon attack on metal site and agglomeration of the active metal, thereby reducing and eventually blocking the catalyst pores. Several combinations of La-Ni-Co have been used as catalyst by Yang *et al.* (2013), González *et al.* (2005) and Valderrama *et al.* (2010) try to minimize catalyst deactivation during the conversion of greenhouse gases (CO_2 and CH_4). Due to the increased rate of carbon formation when using transition metals especially Ni catalyst in CO_2 reforming of CH_4 , rare earth metal

oxide rich in lattice O_2 such as CeO_2 , La_2O_3 , TiO_2 and SiO_2 or mixed supported oxide such as ZrO_2-SiO_2 , $La_2O_3-SiO_2$, (Sutthiumporn and Kawi, 2011; Ayodele *et al.*, 2016b), can be used as support for the metallic catalyst. The carbon deposited is gasified by Lattice O_2 released by this oxides, hence, purging the metallic active surface. Recently, researchers have focused attention not only on producing an efficient catalyst but also to reducing carbon deposit on the catalyst surface in the course of the CH_4 reforming reaction. An efficient means of merging transition metals and rare earth oxides is by hosting the metals in the perovskite structure (Moradi *et al.*, 2014). Studies have shown that the superior solid-state properties of the perovskite have presented this type of catalyst as a very good candidate for methane dry reforming (Lombardo and Ulla, 1998). The performance of cobalt aluminate as an O_2 rich catalyst for methane dry reforming have been reported by Wong *et al.* (2017). The catalyst was synthesized via sol-gel method as an O_2 carrier which inhibits the carbon formation rate. Employing this catalyst, the authors successfully obtained a novel mechanism for syngas production via the catalyst reduction by CH_4 and regeneration with CO_2 . They conducted a stability test using the best cobalt aluminate catalyst with 33.33% of Co content. It was found that the catalyst was stable for up to 30 h with 97.2% and 99.7% H_2 and CO yield, respectively with only 1.9% CH_4 converted to carbon. Re-alloy catalysts with improved stability in CO_2 reforming of CH_4 reactions have been investigated by Zubenko *et al.* (2017) Perovskite precursors ($LaFeO_3$) were promoted with Ni and Re. Reducing the perovskite catalyst ex-solved Re-alloy nanoparticles which showed good performance in methane dry reforming. The authors carried out a 70 h reaction study with no carbon deposits or metal particle sintering. Son *et al.* (2014) studied coke formation over $Ni/\gamma-Al_2O_3$, Co- $Ni/\gamma-Al_2O_3$ and Mg-Co- $Ni/\gamma-Al_2O_3$ catalysts for CO_2 reforming of CH_4 . The effects of promoting the catalyst with Mg and Co have been analysed to know the value on coke deposits. Amongst all the catalyst employed for the study, Mg-Co-Ni/ $\gamma-Al_2O_3$ catalyst had the highest performance with CH_4 conversion over 95% for 200 h and minimal coke formation. The increased activity resulted from the addition of Mg and Co which enhanced the cracking of CH_4 and dissociation of CO_2 . High carbon-resistance $Ni/CeAlO_3-Al_2O_3$ catalyst for CH_4/CO_2 reforming was investigated by Chen *et al.* (2013). After reduction at $900^\circ C$, $CeAlO_3$ phase was formed. In their study, it was found that the catalyst showed good activity with or without $CeAlO_3$ for 250 h at $800^\circ C$ and WHSV of $20,000\text{ mLh}^{-1}\text{gcat}^{-1}$. However, as the $CeAlO_3$ phase increased, carbon formation progressively dropped from 0.92 to 0.29 gcat^{-1} . They concluded that $CeAlO_3$ can minimize the formation of graphitic carbon on the metallic surface with the formation of amorphous carbon being independent of the $CeAlO_3$ phase. This phase ($CeAlO_3$) was also responsible for breaking down CO_2 to release O_2 species which aided gasification. Carbon gasification from Fe-Ni catalyst supported on $MgAl_2O_4$ after methane dry reforming was reported by Theofanidis *et al.* (2016). Gasification was obtained using a transient response technique known as temporal analysis of products (TAP). After the reaction, graphitic and amorphous carbons were formed. The oxidation of CO_2 removed some of the carbon species located in the active metal sites. The carbon species removal involves: (1) CO_2 dissociation on the Ni site closely followed by carbon oxidation by surface O_2 . (2) CO_2 oxidation by Fe and carbon oxidation by the lattice O_2 from Fe oxide. The carbon species oxidation by O_2 which was observed in the TPO analysis and the isothermal test included two steps: (1) Surface carbon oxidation by lattice O_2 and (2) the movement of particles to the carbon species deposited away from the active metallic sites followed by the lattice O_2 oxidation of Fe and /or NiO.

Kinetics of conversion of greenhouse gases (methane dry reforming reaction)

The kinetics and mechanism of syngas production from the mitigation of CH_4 using CO_2 over $SmCoO_3$ perovskite catalyst operated in the temperature ranged 973–1073 K was investigated by Osazuwa *et al.* (2017a). The authors carried out detailed study of the mechanism of the reaction and postulated a model for the process. The reaction mechanism predicts CH_4 adsorption on the Co° , CH_4 decomposition and carbon formation. They reported that the mechanism also predicted the formation of $Sm_2O_2CO_3$ which reacted with carbon to form CO.

Conclusions

Various methods exist for the conversion of greenhouse gases to more valuable products. Amongst these methods are the steam reforming, partial oxidation and CO_2 reforming of CH_4 . In terms of the amount of greenhouse gases converted (CO_2 and CH_4) and the usefulness of its products (syngas) in the formation of other petrochemicals, CO_2 reforming of CH_4 is more advantageous. In order to increase this conversion, various support have been used, promoters have been added, bi-metallic catalyst have been developed and even recently perovskite have been employed to mitigate greenhouse gases in various reforming processes. Decomposition of CH_4 on the metallic surface, dissociation of CO_2 on the support, the reduction-oxidation perovskite mechanism coupled with the effects of dopants in inhibiting carbon formation on the surface of the catalyst by introducing O_2 species describes the reaction mechanism. Comparing supported catalyst, with particular interest on Ni-based and Co-based supported catalyst, reports show that perovskite oxides show greater superiority in preventing catalyst deactivation during the conversion of greenhouse gases (CH_4 and CO_2) as a result of the abundance of O_2 species in its structure.

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Challenges of Employing Renewable Energy for Reducing Greenhouse Gases (GHGs) and Carbon Footprint

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Introduction

The responsibility of the reduction of the greenhouse gas emissions lies largely with the industrialized world, though the developing countries are likely to be the source of an increasing proportion of future emissions. The projected climate change under various scenarios is likely to have implications on food production, water supply, coastal settlements, forest ecosystems, health, energy security etc. The survey says that the global mean temperature may increase between 1.4 and 5.8°C by 2100. This unprecedented increase is expected to have severe impacts on the global hydrological system, ecosystems, sea level, crop production and related processes. The impact would be particularly severe in the tropical areas, which mainly consist of developing countries, including India. All the Developing country was not be able to adopt any strategy because it is more concerned to the social economic development. Various sustainable methods and renewable technologies which will be accepted environmentally and globally too. Other than talking about socio economic growth, concentration must be dissipated to the introduction of the green technology into the development of the sustainable technologies for the prevailing problem of the Climate change impact. This work captures and disseminates the impacts and perspectives on climate change from the Global context. Climate change could represent an additional stress on ecological and socioeconomic systems that are already facing tremendous pressures due to rapid urbanization, industrialization and economic development. While talks about the reduction of GHG's between various industrialized countries have not yielded the expected, measures are on the run to put a knot for the problem of Climate Change. Now it is our one of the major responsibilities for cutting down the CO₂ and GHG's emissions. Many Environmental Activists have volunteered to bring out a Green Revolution in the industrialized world. The GHGs and carbon footprint has its adversities in food production, water supply, coastal settlements, forest ecosystems, health, energy security etc. The climatic change is a global concern, but the pressure is upon us as its impact upon us is severe. It's now time to mitigate the impacts of the GHGs and Carbon footprint upon our planet. The livelihood of vast population depends on climate-sensitive economic sectors like agriculture, forestry and fisheries. The costs of not addressing climate change or to adapt to it are very uncertain, but their welfare consequences are enormous. Adaptation is a private or local public good, whereas mitigation is a global public good. The individuals or communities bear the risk wherever there is undersupply of adaptation measures. Adaptation costs are the insurance payments and the costs of not addressing adaptation are the damages from unmitigated climate risks. There are many ways to pursue sustainable development strategies that contribute to mitigation of GHGs and Carbon footprint. So our responsibility is to find a suitable sustainable strategy.

Aspects of Renewable Technology

Renewable technology is a technology that is environment-friendly and ensures that natural resources are conserved. Green technology is the future at large, and the main aim of this innovative technology is to avoid any deterioration to the environmental resources. In a way, green technology helps in reducing the amount of pollution that is being emitted during the process of production and even while consuming the products. It talks about the relationship between human beings and natural resources, and the irreversible hazard that is being caused to the nature and the environment because of the economic activities. One can quote some examples of environmental hazards such as pollution of rivers, global warming resulting in depletion of ozone layer etc.

Both the production and consumption are so massive that one can witness the tremendous amount of damage that is being caused to the environment and natural resources every second. If the trend continues, then one day we may have to zero in on what we have achieved and get into the shoes to rectify our unpardonable mistakes, which are irreparable. Reusable technology is not only essential for sustainable development in the long-run but there are also short-term advantages of using eco-friendly fuels. There are certain crucial issues that need to be focused upon while introducing green technology. For instance, a social awareness about the need for environment-friendly goods and services for production and consumption at a larger scale is required. And, for this, a massive campaign on this issue has to be undertaken. Renewable technology as a subject need to be made mandatory in academics. The industrial segment needs to be pushed forward to come out with more environment-friendly production and consumption processes. Various incentives need to be given to the industrial sector, which is ready to innovate and implement green technology.

Renewable Technology Sources and it's CO₂ Emissions

Here renewable energy sources like hydro, wind, photovoltaic, fuel cell, biomass, ocean thermal energy and geothermal energy sources are considered as eco-friendly technology or green technology ([Table 1](#)).

Table 1 Different renewable technologies and their emissions

Renewable technology	Basic information	Renewable sources ^a	CO ₂ emission ^b (gmCO ₂ eq/kWh)
Fuel cell	Device which converts chemical energy into electrical energy	Methanol (CH ₃ OH), Natural gas, Reforming of CH ₄ to H ₂ leads to decreased efficiency	50
Photovoltaic (Solar PV)	Generates no heat and produces electricity from solar radiation	Sun	Utility scale – 48 Rooftop – 41
Wind	Converts wind energy to electrical energy by wind-turbines.	Wind	Offshore – 12 Onshore – 11
Hydro	Natural Resource of River water	Water	24
Biomass	Biofuel, Waste management system	Biological waste	Dedicated – 230
Geothermal energy	Thermal energy of Earth	Earth Temperature	38
Other renewables	OTEC (Ocean thermal energy conversions)	Temperature difference between cooled water and warm tropical surface waters	17

^aSource: IET Renew. Power Gener., 2016, vol. 10, Iss. 7, pp. 873–884.

^bSource: IPCC, 2014. Global warming potential of selected electricity sources.

Greenhouse Gases

The greenhouse effect is the process by which absorption and emission of infrared radiation by gases in a planet's atmosphere warm its lower atmosphere and surface. It was proposed by Joseph Fourier in 1824, discovered in 1860 by John Tyndall.

On Earth, an atmosphere containing naturally occurring amounts of greenhouse gases causes air temperature near the surface to be warmer by about 33°C (59°F) than it would be in their absence. Without the Earth's atmosphere, the Earth's average temperature would be well below the freezing temperature of water. The major greenhouse gases are water vapor, which causes about 36%–70% of the greenhouse effect; carbon dioxide (CO₂), which causes 9%–26%; methane (CH₄), which causes 4%–9%; and ozone (O₃), which causes 3%–7% (Fig. 1).

Human activity since the Industrial Revolution has increased the amount of greenhouse gases in the atmosphere, leading to increased radiative forcing from CO₂, methane, tropospheric ozone, CFCs, and nitrous oxide. According to work published in 2007, the concentrations of CO₂ and methane had increased by 36% and 148% respectively since 1750. These levels are much higher than at any time during the last 800,000 years, the period for which reliable data has been extracted from ice cores. Less direct geological evidence indicates that CO₂ values higher than this were last seen about 20 million years ago.

Fossil fuel burning has produced about three-quarters of the increase in CO₂ from human activity over the past 20 years. The rest of this increase is caused mostly by changes in land-use, particularly deforestation. Another significant non-fuel source of anthropogenic CO₂ emission is the calcination of limestone for clinker production, a chemical process which releases CO₂. There are efforts to develop types of cement that produce less CO₂ but it is feared not enough is being done. Estimates of global CO₂ emissions in 2011 from fossil fuel combustion, including cement production and gas flaring, was 34.8 billion tones (9.5 ± 0.5 PgC), an increase of 54% above emissions in 1990. Coal burning was responsible for 43% of the total emissions, oil 34%, gas 18%, cement 4.9% and gas flaring 0.7% (Fig. 2).

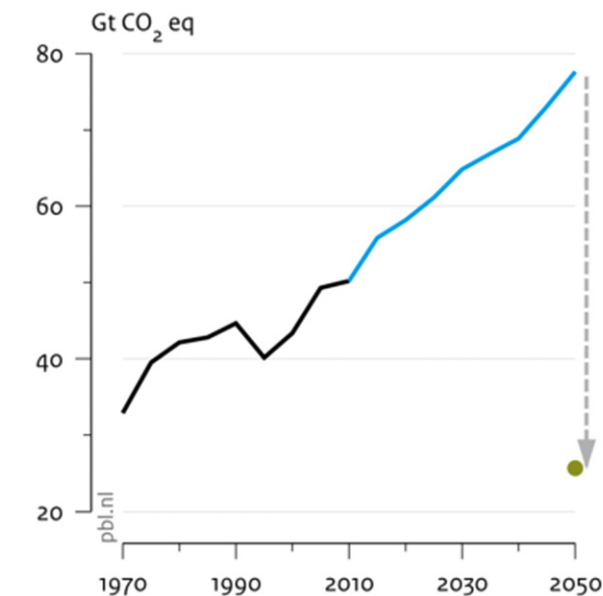
In May 2013, it was reported that readings for CO₂ taken at the world's primary benchmark site in Mauna Loa surpassed 400 ppm. According to professor Brian Hoskins, this is likely the first time CO₂ levels have been this high for about 4.5 million years. Monthly global CO₂ concentrations exceeded 400 ppm in March 2015, probably for the first time in several million years. According to the global carbon project, carbon emission rates plateaued from 2014 to 2016, rose by 1.6% in 2017, then rose again by 2.7% in 2018.

Over the last three decades of the twentieth century, gross domestic product per capita and population growth were the main drivers of increases in greenhouse gas emissions. CO₂ emissions are continuing to rise due to the burning of fossil fuels and land-use change. Emissions can be attributed to different regions. Attributions of emissions due to land-use change are subject to considerable uncertainty.

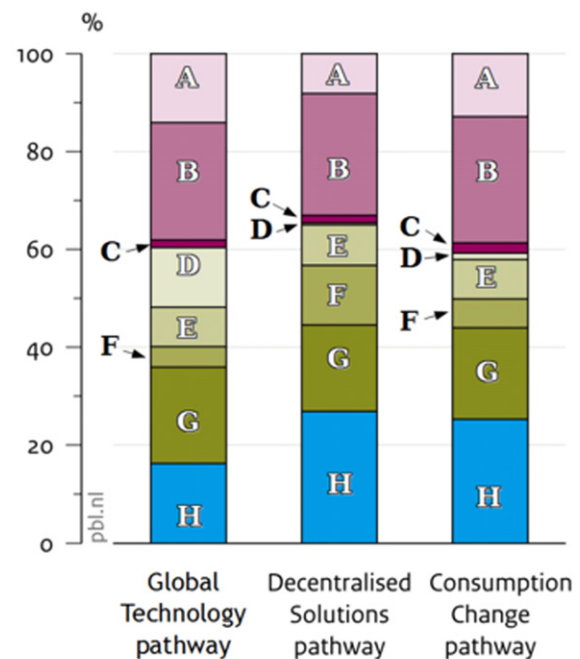
Emissions scenarios, estimates of changes in future emission levels of greenhouse gases, have been projected that depend upon uncertain economic, sociological, technological, and natural developments. In most scenarios, emissions continue to rise over the century, while in a few, emissions are reduced. Fossil fuel reserves are abundant, and will not limit carbon emissions in the 21st century. Emission scenarios, combined with modeling of the carbon cycle, have been used to produce estimates of how atmospheric concentrations of greenhouse gases might change in the future.

In this given Fig. 3 is a simplified, schematic representation of the flows of energy between space, the atmosphere, and the Earth's surface, and shows how these flows combine to trap heat near the surface and create the greenhouse effect. Energy exchanges are expressed in watts per square meter (W/m²). If this is not feasible due to space limitations it should possibly be explained in the image notes that the remaining grey part of the arrow stands for thermic energy transmission by convection of

Greenhouse gas emissions



Contribution to cumulative emission reduction, 2010 – 2050



— History
 — Trend scenario
 ● Goal

↓ Policy gap

A Avoid deforestation
B Reduce other greenhouse gases
C Reduce other energy-related emissions
D Increase nuclear power
E Increase bio-energy
F Increase solar and wind power
G Increase CO₂ capture and storage
H Improve energy efficiency

Fig. 1 The graph on the top shows three “pathways” to meet the UNFCCC’s 2°C target, labelled “global technology”, “decentralized solutions”, and “consumption change”. Each pathway shows how various measures (e.g., improved energy efficiency, increased use of renewable energy) could contribute to emissions reductions. *Source:* PBL Netherlands Environmental Assessment Agency.

sensible and latent heat. The sun is responsible for virtually all energy that reaches the Earth’s surface. Direct overhead sunlight at the top of the atmosphere provides 1366 W/m²; however, geometric effects and reflective surfaces limit the light which is absorbed at the typical location to an annual average of ~235 W/m². If this were the total heat received at the surface, then, neglecting changes in albedo, the Earth’s surface would be expected to have an average temperature of –18°C. Of the surface heat captured by the atmosphere, more than 75% can be attributed to the action of greenhouse gases that absorb thermal radiation emitted by the Earth’s surface. The atmosphere in turn transfers the energy it receives both into space (38%) and back to the Earth’s surface (62%), where the amount transferred in each direction depends on the thermal and density structure of the atmosphere. This process by which energy is recycled in the atmosphere to warm the Earth’s surface is known as the greenhouse effect and is an essential piece of Earth’s climate. Under stable conditions, the total amount of energy entering the system from solar radiation will exactly balance the amount being radiated into space, thus allowing the Earth to maintain a constant average temperature over time. However, recent measurements indicate that the Earth is presently absorbing 0.85 ± 0.15 W/m² more than it emits into space. An overwhelming majority of climate scientists believe that this asymmetry in the flow of energy has been significantly increased by human emissions of greenhouse gases. This figure was created by Robert A. Rohde from published data and is part of the Global Warming Art project.

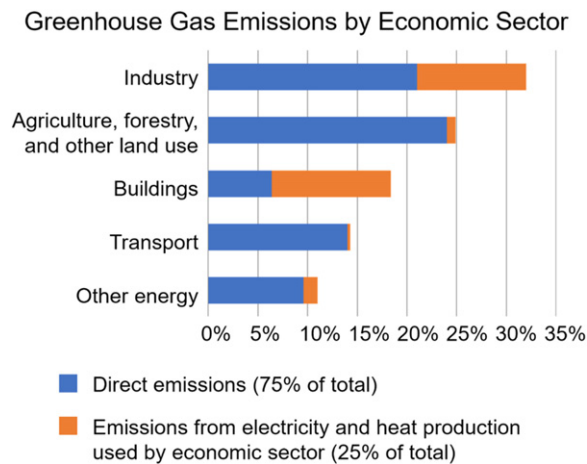


Fig. 2 Annual greenhouse gas emissions attributed to different sectors as of the year 2010. *Source:* Enescot, 2014. Summary for Policymakers. In: Edenhofer, O., *et al.* (Eds.), *Climate Change 2014: Mitigation of Climate Change. Contribution of Working Group III (WG3) to the Fifth Assessment Report (AR5) of the Intergovernmental Panel on Climate Change (IPCC)*, p. 7. Cambridge University Press. Archived 29 June 2014.

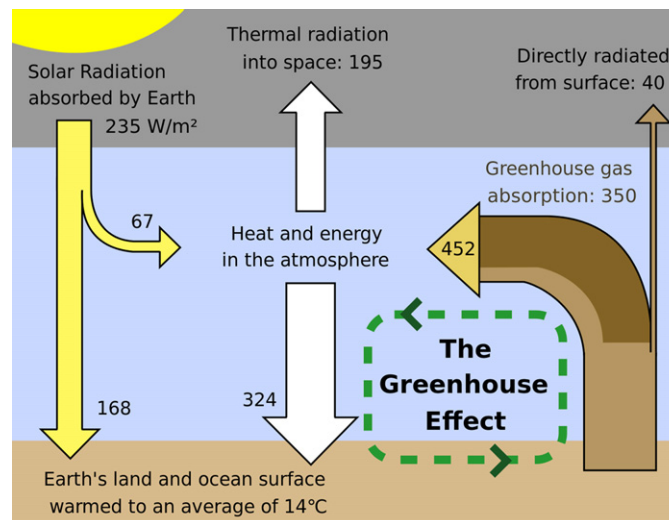


Fig. 3 Greenhouse effect schematic showing energy flows between space, the atmosphere, and Earth's surface. Energy exchanges are expressed in watts per square meter (W/m^2). *Source:* This figure was created by Robert A. Rohde from published data and is part of the Global Warming.

Carbon Footprints

A carbon footprint is historically defined as the total emissions caused by an individual, event, organization, or product, expressed as carbon dioxide equivalent.

In most cases, the total carbon footprint cannot be exactly calculated because of inadequate knowledge of and data about the complex interactions between contributing processes, including the influence of natural processes that store or release carbon dioxide. For this reason, Wright, Kemp, and Williams, have suggested to define the carbon footprint as:

"A measure of the total amount of carbon dioxide (CO_2) and methane (CH_4) emissions of a defined population, system or activity, considering all relevant sources, sinks and storage within the spatial and temporal boundary of the population, system or activity of interest. Calculated as carbon dioxide equivalent using the relevant 100-year global warming potential (GWP100)".

Greenhouse gases (GHGs) can be emitted through land clearance and the production and consumption of food, fuels, manufactured goods, materials, wood, roads, buildings, transportation and other services. For simplicity of reporting, it is often expressed in terms of the amount of carbon dioxide, or its equivalent of other GHGs, emitted (**Fig. 4**).

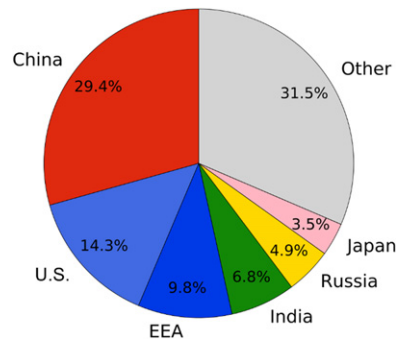


Fig. 4 Global carbon dioxide (CO₂) emissions by countries in 2015.

Most of the carbon footprint emissions for the average household come from “indirect” sources, e.g., fuel burned to produce goods far away from the final consumer. These are distinguished from emissions which come from burning fuel directly in one’s car or stove, commonly referred to as “direct” sources of the consumer’s carbon footprint.

The concept name of the carbon footprint originates from ecological footprint, discussion, which was developed by William E. Rees and Mathis Wackernagel in the 1990s. This accounting approach compares how much people demand compared to what the planet can renew. This allows to assess the number of “earths” that would be required if everyone on the planet consumed resources at the same level as the person calculating their ecological footprint. The carbon Footprint is one part of the ecological footprint. Carbon footprints are more focused than ecological footprints since they measure merely emissions of gases that cause climate change into the atmosphere.

Environmental Pollution

Pollution is the inclusion of several contaminants to the environment causing adverse effects on nature.

Pollution may cause due to natural phenomenon or by foreign particles. It may even be fatal to the life. Death rates are in increasing order for pollution. Presence of greenhouse gases abruptly changing the temperature, climate as well as causes the Global Warming, which is a threat to the society.

Various aspects of environmental pollution are discussed below:

- *Air pollution*: the release of chemicals and particulates into the atmosphere. Common gaseous pollutants include carbon monoxide (CO), sulfur dioxide (SO₂), chlorofluorocarbons (CFCs) and nitrogen oxides produced by industry and motor vehicles. Photochemical ozone and smog are created as nitrogen oxides and hydrocarbons react to sunlight. Particulate matter, or fine dust is characterized by their micrometer size PM10 to PM2.5. Increase of Greenhouse gases.
- *Light pollution*: includes light trespass, over-illumination and astronomical interference.
- *Littering*: the criminal throwing of inappropriate man-made objects, unremoved, onto public and private properties.
- *Noise pollution*: which encompasses roadway noise, aircraft noise, industrial noise as well as high-intensity sonar.
- *Plastic pollution*: It involves the accumulation of plastic products and microplastics in the environment that adversely affects wildlife, wildlife habitat, or humans.
- *Soil pollution*: Soil contamination occurs when chemicals are released by spill or underground leakage. Among the most significant soil contaminants are hydrocarbons, heavy metals, pesticides and chlorinated hydrocarbons.
- *Radioactive pollution*: Radioactive contamination, resulting from 20th century activities in atomic physics, such as nuclear power generation and nuclear weapons research, manufacture and deployment. (See alpha emitters and actinides in the environment).
- *Thermal pollution*: It is a temperature change in natural water bodies caused by human influence, such as use of water as coolant in a power plant.
- *Visual pollution*: In which we can refer to the presence of overhead power lines, motorway billboards, scarred landforms (as from strip mining), open storage of trash, municipal solid waste or space debris.
- *Water pollution*: By the discharge of wastewater from commercial and industrial waste (intentionally or through spills) into surface waters; discharges of untreated domestic sewage, and chemical contaminants, such as chlorine, from treated sewage; release of waste and contaminants into surface runoff flowing to surface waters (including urban runoff and agricultural runoff, which may contain chemical fertilizers and pesticides; also including human feces from open defecation – still a major problem in many developing countries); groundwater pollution from waste disposal and leaching into the ground, including from pit latrines and septic tanks; eutrophication and littering.

Air Pollution

Air pollution is caused whenever concentration of certain detrimental elements increases in the atmosphere to very high level. Air pollution causes objectionable effect on living beings, thereby disturbing natural eco-balance in a significant amount. These

elements can be at any state i.e., solid, liquid or gas. Mostly human related anthropogenic activities such as burning of fossil fuel are responsible for their origin.

Whenever polluting substances are released into the atmosphere, these are transported to the atmosphere. Some of these substances chemically react with other constituents in the atmosphere directly in the presence of sunlight while others are transformed to different substances.

Pollutants which are emitted directly to the atmosphere are termed as primary pollutant while pollutants formed in the atmosphere as a result of transformation are called secondary pollutants.

Source of Air Pollution

Air pollution sources can be of three types. These are discussed below

Point Source

A point source for air pollution is a single entity having one or more than one emission points. A coal-based thermal power plant is a good example of point source.

Area Source

Area source for air pollution is a group of smaller sources confined within a particular geographical area. As an example, it can be stated that emissions from kitchens in a residential zone is treated as a collective source for air pollution. Hence it can be termed as an area source.

Line Source

Line source for air pollution is one-dimensional by nature. A roadway is a good example of line source for air pollution.

It is imperative from the above discussion that emission rates for larger and specific point sources can be directly measured by inserting sampling probes to the concerned chimney or vent. However, this will be a troublesome job for determining pollution from area source. This is because it is always not possible to monitor individual emission in a large area source. To tackle this situation the concept of emission factors plays a vital role. Emission factor is a statistical average or the quantitative estimate of the amount of a particular pollutant emitted from a specific source. Basically, the function of emission factor is to measure total emission from similar sources or on stoichiometric calculations. Once, emission factor is determined for a particular sector of area source, then it is multiplied with the number of sources to estimate the total emission in that particular zone.

Propagation and Transformation of Air Pollution

After emission from sources, air pollutants may be transformed to other substances or may be propagated to the atmosphere depending on the atmospheric stability of the particular pollutant. Again, the stability of a particular pollutant depends on various parameters such as the presence of cloud, fog, precipitation, solubility of the pollutant etc.

Atmospheric stability of a particular pollutant depends on its atmospheric residence time. It has been observed that atmospheric mean residence time for pollutants like NO_x , SO_x etc., is less than a day. Hence, their critical environmental impact usually lies within the close vicinity of the source of emission. So, it can be stated that pollution caused by these sources is a local phenomenon.

Pollutants like CO , CO_2 , CH_4 , N_2O , CFC etc., possesses relatively longer mean residence time and hence they accumulate in the atmosphere uniformly throughout the globe. So, pollution caused by these agents is a global phenomenon.

We often encounter a term 'receptor' while discussing about environmental pollution. A receptor is an entity such as a living being or the whole ecosystem affected by the emission of these pollutants.

Air Pollutants

Oxides of Nitrogen (NO_x)

Any kind of combustion is the main source for various oxides of nitrogen. NO_x can be either fuel NO_x or thermal NO_x . The former is produced during a fuel having nitrogen as a constituent while the latter is produced when temperature for combustion exceeds 1500°C . In this high temperature NO_x is produced as a result of chemical reaction between the atmospheric nitrogen with oxygen. It can form nitric acid by chemical reaction with water vapor present in the atmosphere thereby causing acid rain. NO_x is also responsible for photochemical smog.

Oxides of Sulfur (SO_x)

Main source for sulfur emission is fossil fuel-especially coal. Most of the SO_x emitted in atmosphere is SO₂. A little portion is SO₃ which forms sulfuric acid in presence of water vapor. SO_x is a severe polluting agent causing respiratory problem and causes acid rain along with NO_x.

Particulate Matter PM

Particulate matters are tiny, finely divided solid and liquid particles dispersed in air (aerosols). Concentration of PM in atmosphere is measured through an indicator termed as PM₁₀. It indicates particulate matters of diameter of 10 μm or even smaller than that. The standard of 10 μm was chosen due to the fact that 50% of the particles having diameter equal or less than 10 μm deposits over respiratory tract during breathing. Deposition fraction decreases with increase in the diameter of the particulate matter.

Pollution Measuring Indicators

Environmental pollution is caused by emission from mainly human related activities. This type of emission contributes several polluting agents in the atmosphere. Air pollution can be measured either by concentration measurement or by load measurement. Concentration measurement is basically instantaneous in nature whereas load measurement is carried out over a specified time period.

As an example, it can be stated that, if a measurement technique reports that in a certain emission, the amount of SO₂ is 850 mg/m³. This kind of measurement is known as concentration measurement as discussed.

On the other hand, load measurement can be framed over a certain year such as per year basis. This can be further explained with a simple example. Let us consider the case of a coal based thermal power plant. In such measurement, firstly the emission factor for a particular pollutant is multiplied to obtain total emission of the particular pollutant on unit mass basis. Total pollution over a year can be estimated from total generation of the plant in that particular year.

Global Warming

It is the process through which solar energy is entrapped in earth. Global warming is actually the increase in average temperature of earth due to various natural or human related activities. It is well known fact that the source of energy for earth is the sun. Incoming solar radiation coming in the form of visible light penetrates the atmosphere which consists of greenhouse gases (GHG: which is water vapor, carbon dioxide, methane, chlorofluorocarbon etc.) along with other gases such as nitrogen, oxygen etc., after penetrating the atmosphere, the visible solar radiation reaches earth's surface where it delivers a certain amount of energy contained within it and then reemitted to the atmosphere. As a result of this change in energy level, the wavelength of this reemitted wave is increased so that it becomes infrared radiation (IR). GHG present in the atmosphere are opaque to this infrared radiation and hence the reemitted wave is entrapped within earth. This phenomenon is known as greenhouse effect. As a result of greenhouse effect, more and more amount of infrared is entrapped within earth thereby increasing the average temperature of earth which is more pronounced as global warming.

From the above discussion one may think that greenhouse effect is a harmful phenomenon. On the contrary it must be mentioned that, if greenhouse effect did not occur, then average temperature of earth would have been -23°C. So, global warming is responsible for maintaining a suitable average temperature around 15°C for existence of life in this planet. However, the concern is that average temperature is increasing in an uncontrolled fashion due to pollution. The main reason of this is increase in concentration of greenhouse gases (mainly CO₂) due to various anthropogenic activities. The detrimental effects of global warming involve change in rainfall pattern, increase in severity of storms, different unexpected nature of natural calamity in several places, migration and somewhere extinction of several species and ecosystems, flooding in many coastal regions due to thermal expansion of the oceans, melting of glaciers and polar ice etc. Hence, concern has to be grown in this aspect and proper measures should be taken to tackle this menace.

A Case Study: Recent Natural Disasters in India

Recently, India has suffered a number of natural calamities which includes severe thunderstorms in Rajasthan and Uttar Pradesh as well as devastating flood in Kerala. Somehow, the pollution is responsible to accelerate the above-mentioned concerns.

The phenomenon occurs when a sudden downpour proves so heavy that the underlying ground cannot cope with the sheer amount of water it is exposed to and becomes saturated before it has a chance to drain away. Common in low-lying areas, flash floods can also be caused by an intense concentration of rain from thunderstorms on dry soil, unaccustomed to ready absorption. Just six hours of rainfall can be enough to overwhelm the earth.

In built up areas, this can mean sewers overflow and the streets gush like rivers, ferrying debris and in extreme cases running with enough water to lift and carry away cars.

Ordinarily, the flooding of rivers is a very gradual process as it takes time for enough rainfall to percolate through the ground and cause the water level to rise sufficiently so that it overflows before reaching the sea.

Flash flooding, however, gives no such warning.

In the case of Kerala, the weather is part of the four-month monsoon rainy season that strikes the Indian subcontinent every summer.

Local officials have been blamed for exacerbating the situation by failing to gradually open the dams dotting the state's complex river network, waiting instead until they were already full before unleashing the excess water.

Air pollution particles lead to change in the physical properties of monsoon clouds, which can lead to more intense rainfall, flash floods and unusual gaps in the progression of monsoon rainfall, say scientists from Indian Institute of Technology (IIT), Kanpur, who have used long-term satellite data (2002–2016) and modeling to understand the association between aerosols and cloud properties. Their findings are published in the journal, *Nature*.

The thunderstorm in Rajasthan and Uttar Pradesh that killed more than a 100 people in May and the spate of severe thunderstorms this summer may be attributable to such aerosol-induced changes.

Aerosols, particularly black carbon and dust particles, induce "cloud invigoration", which means cloud cover and thickness increases because of reduction in the size of cloud droplets and other structural modifications during cloud formation.

Enhanced cloudiness reflects more sunlight back to space, leading to a cooling effect of the clouds' surface. The enhanced cloud cover limits reflection of solar energy back to space and traps the energy emitted from the surface at night and decreases the surface diurnal temperature range to make days cooler and nights warmer.

It has been observed that the main sources of aerosols are fossil and bio-fuels combustion from residential and industrial sector, biomass burning and forest fires.

India's Stance on GHG and its Adverse Effect?

Agriculture being the backbone of this country has been put to threat in the recent years. In India nearly 700 million rural populations depend upon climate-sensitive sectors such as agriculture, forests and fisheries. Moreover, natural resources such as water, biodiversity, mangroves, coastal zones, grasslands and their livelihoods have also been put into threat. Increased greenhouse gases are likely to impact all the natural ecosystems as well as socio-economic systems. An annual mean surface temperature rises by the end of century, ranging from 3 to 5°C with warming more pronounced in the northern parts of India. A 20% rise in all India summer monsoon rainfall and further rise in rainfall is projected over all states except Punjab, Rajasthan and Tamil Nadu which show a slight decrease. Extremes in maximum and minimum temperatures are also expected to increase and similarly extreme precipitation also shows substantial increases, particularly over the west coast of India and west central India.

GHG concentrations should be stabilized at levels where food production is not threatened (UN, 1992). Without considering the carbon dioxide fertilization effects yield losses for rice and wheat vary between 32 and 40%, and 41 and 52%, respectively. Their study also showed that even with carbon fertilization effects, losses would be in the same direction but somewhat smaller. For a developing country, these are very large changes which can cause much human misery. From India's point of view, a 2°C increase would be clearly intolerable.

Oxygen levels and its isotopic composition in the atmosphere are stable; it takes a major terrestrial change to affect it very much. These changes were huge. The drop-in vegetation growth must have been dramatic. Ocean circulation patterns also can heavily influence climate, and shift in ways that are not completely understood.

Lives of large population in the coastal areas are now put to threat due to the sea level rise and prone to sub-mergence. This will lead to the migration in large scale especially from the low-lying delta regions in the developing countries. Intrusion of sea-water in the ground water and changes in temperature can reduce agricultural and fishing too. If a one-meter sea level rise were to take place today, it would displace 7 million persons in India (ADB, 1995). If this situation prevails in future, the number would be more and there are chances that 35% of the land in Bangladesh would be submerged by a one-meter rise.

Increase in greenhouse gases such as CO₂ and methane (CH₄), and other anthropogenic emissions into the atmosphere, can be expected to have significant impacts on forest ecology, forest distribution, and productivity. The projected impacts of climate change on forests also have implications for forest product flows and trade and forest management.

Large forest areas of Sundarbans have turned into forest villages with heavy with carbon dioxide in the environment. Local people destroy mangrove forest of the region unknowingly; they do not know the concept of climate change and global warming. India is experiencing some of the very real effects of climate change. Sundarbans is losing 100 km² every year (Tables 2 and 3).

Functioning of Ozone Layer and its Depletion

Ozone is a gaseous substance which is created at the upper part of the atmosphere by photochemical reaction between molecular oxygen, oxygen atom in presence of solar radiation in a continuous fashion. Main function of ozone layer is to protect earth from the dangerous ultraviolet radiation (about 97%–99%) of the sun. On absorption of ultraviolet light, ozone dissociates into oxygen which become ozone again as mentioned earlier maintaining a balanced situation. But the alarming situation is that ozone layer is getting thinner day by day thereby passing a portion of the harmful UV radiation.

Table 2 Precipitation change projections for India due to increasing GHGs

Year	Precipitation change (%)			Sea level rise (cm)
	Annual I	Monsoon	Winter	
2020s	1.36 ± 0.19	1.61 ± 0.16	1.13 ± 0.43	4–8
2050s	6.7 ± 8.9	-2.9 ± 26.3	6.7 ± 8.9	15–38
2080s	11.0 ± 12.3	5.3 ± 34.4	11.0 ± 12.3	46–59

Source: Aggarwal, D., Lal, M., 2001. Vulnerability of Indian Coastline to Sea-level Rise, New Delhi: Centre for Atmospheric Sciences, Indian Institute of Technology.

Table 3 Temperature change projections for India due to increasing GHGs

Year	Temperature change (°C)		
	Annual I	Monsoon	Winter
2020s	1.36 ± 0.19	1.61 ± 0.16	1.13 ± 0.43
2050s	2.69 ± 0.41	3.25 ± 0.36	2.19 ± 0.88
2080s	3.84 ± 0.76	4.52 ± 0.49	3.19 ± 1.42

Source: Aggarwal, D., Lal, M., 2001. Vulnerability of Indian Coastline to Sea-level Rise, New Delhi: Centre for Atmospheric Sciences, Indian Institute of Technology.

Distribution of ozone depends on the geographic location and season. Ozone layer is located in between 10 and 50 km above the surface of the earth. Observations from worldwide ozone monitoring units (also known as Dobson unit, named after British meteorologist G.M.B. Dobson) noted that more than 95% of total atmospheric ozone concentration is found at an altitude ranging between 15 and 20 km is supposed to be in danger. More than 50% ozone content of this zone has been destroyed.

Depletion of ozone layer takes place due to both natural and artificial. However, natural phenomenon such as stratospheric wind or sun-spots is responsible for depletion of ozone layer by not more than 1%–2%.

Main cause of ozone depletion is due to human related activities. Day by day the concentration of chlorine and bromine is increasing from industrial production of chlorofluorocarbon or CFC, halogens, methyl chloroform, carbon tetrachloride, hydro fluorocarbons etc. These chemicals are termed as ozone depleting substances. Chlorine is very destructive for ozone. Every chlorine atom can destroy thousands of ozone molecules. Commercially produced CFC is available in various grades. However, the amount of damage to the ozone layer by any agent is expressed in terms of CFC-1. The equivalence is carried out by ozone depleting potential or ODP. Ozone depleting agents generally possesses a relatively longer life span and hence they continue to deplete ozone layer long after their emission. ODS are relatively stable in atmosphere. Stability of these substances pushes them to the upper portion of the stratosphere where ultraviolet light dissociates them to ultimately form chlorine or bromine.

It is already discussed that ozone filters out harmful UV radiation contained in sunlight. When ozone is depleted, UV rays reaches earth. Exposure to UV radiation has serious impacts on all living being.

Impacts of Ozone Depletion on Living Being

Human and animal

- Chances for skin cancer increases.
- Eye diseases.
- Weakening human immunity system.

Agriculture

- Reduction of growth rate for various crops such as rice, wheat, oats, peas etc.

Other impacts on eco-system

- Planktons (micro-organisms, vital in marine food chain) are damaged on exposure to UV radiation. This reduces fish yields, thereby losing biodiversity.
- Besides, construction materials like wood, rubber etc., are degraded on exposure to UV radiation.

Noting the detrimental effects of ozone depletion, various nations have taken a remarkable step by joining hand together. 194 nations signed an international agreement (Montreal protocol) to stop commercial production of CFC and other ODS. However, more concern as well as awareness is required to forbid usage of ODS.

Kyoto Protocol

Different anthropogenic activities such as extraction of energy from fossil fuels, deforestations, industrial development etc., have resulted in increase in Greenhouse Gas (GHG) level beyond normal values since a long. This is the main reason of increase in the average temperature of earth in an uncontrolled fashion. Carbon dioxide, Methane, Nitrous oxide, Chlorofluorocarbon, oxide of sulfur etc., are generally treated as greenhouse gases (GHGs). Major constituent of GHG is carbon dioxide which mainly originates from combustion of fuels. Kyoto protocol is a treaty between different Nations of the World to commit reduction of greenhouse gas consumption to control the detrimental effects caused due to global warming.

Incoming solar radiation can penetrate the layer of greenhouse gases at the upper layer of atmosphere but gets entrapped when reemitted from earth in the form of infrared radiation. In this way GHG is capturing heat day by day, thereby increasing the average temperature of this planet. This rapid increase in temperature has become a matter of great concern in present day. Keeping this grave situation, awareness is required for proper implementation of sensible strategy at the international level. Basically, Kyoto protocol is based on different obligations particularly for the developed countries on the fact that they are responsible for the present level of greenhouse gases due to their continued emission over a long period.

United Nations Framework Convention on Climate Change (UNFCCC)

The awareness started in 1992. In order to promote sustainable development, a common platform was required so that different nations can act together in order to save environment. The common platform was named as United Nations Framework Convention on Climate Change (UNFCCC). This framework imposed non-binding limits on greenhouse gas emissions for individual nations having no provision for any kind of enforcement mechanism. However, in Earth summit, there was an outline for specifying international treaties or protocols. Presently, there are 192 nations attached with the protocol (Canada withdrew in 2002). This protocol encouraged industrialized nations to stabilize GHG emissions. For each level of different component of GHG, different levels of emission reductions were required to stabilize their concentration on atmosphere.

Flexibility in Meeting Targets

Emission targets for industrialized countries participating in Kyoto protocol are expressed as allowed emission levels over commitment period of 2008–2012 was denominated in tones of CO₂ equivalent emissions.

Economical basis for providing flexibility was that the marginal cost of reducing the emission was different at different parts of the globe. Surveys conducted in this regard suggested that flexibility mechanisms could reduce overall cost of achieving the targets.

Although industrialized countries should take necessary action to reduce the detrimental effects of climate change, however Kyoto protocol allows flexibility in meeting their emission reduction targets through market-based mechanisms mentioned below.

Kyoto Mechanisms

Three mechanisms were adopted in Kyoto protocol, namely: Emission Trading, Joint Implementation and Clean Development Mechanism.

Carbon market used by these mechanisms is a key to monitor reduction of emission worldwide.

CDM and JI were two project-based mechanisms feeding carbon market. CDM involves investment in sustainable development-based project works while JI promotes industrialized countries to join hands among each other.

Although more than 160 countries signed Kyoto protocol, the USA, larger emitter of GHG did not ratified Kyoto Protocol.

International Emission Trading

Emission trading is an innovative market based mechanism proposed at Article 17 of the Kyoto Protocol.

A number of emission trading schemes have been implemented. In different countries, different agencies were given responsibility to take care about this. European Union framed Emission Trading Scheme (EU ETS) allowed trading of national Kyoto obligations between participating countries, known as Carbon Trust.

Generally, the pollutant emission is treated as a commodity and the price for emission is decided on the reduction target or 'emission cap'. The term 'cap' denotes total amount of the regulated pollutant in certain units that is accepted globally to be

emitted on yearly basis. The cap value is set at particular emission values and then divided into allowable levels which are distributed between all the participating units. This allowance can be traded in market.

Main objective of this is to set limit on total emission by the larger emitters of GHG. Individual nations have mandatory emission targets to meet.

If the units emitted in a year is less than its allowance level, then that nation can sell its excess allowance. On the other hand, if the emission is more than the allocation level, then the concerned nation has to buy allowances to cover its excess emission. In this way countries with lesser emission can sell emission units to the countries which have crossed their emission targets. In view of the fact that carbon dioxide is the major GHG constituent, other polluting emissions can be converted in terms of their carbon dioxide equivalence, hence this marketing is known as "Carbon-Market". Countries taking part in carbon market has to meet their commitment on targeted emission per year otherwise they have to buy compliance with a variable rate depending on the situation. If the cost in carbon market is high, then the nations will be either forced to utilize energy efficiency or they have to explore different renewable energy resources. Both this possibilities ultimately reduces the overall GHG emission. Localized emission trading has been already implemented in Europe in order to reduce GHG from industry. Such localized process may intend to link up ultimately in a globalized system, under Kyoto protocol.

Joint Implementation (JI)

Joint Implementation is proposed at Article 6 of Kyoto protocol. The basis of JI is financial as well as technical cooperation between Annex I countries for implementation of clean and renewable energy and promoting energy efficient projects among them. This is another way of mitigation of GHG emission. An Annex-I country can invest in a energy efficient project or renewable energy project in another Annex-I country, thereby reducing carbon dioxide emission in the atmosphere. In this process emission reduction units (ERU) is allotted to the former nation thereby mitigating its emission target.

Clean Development Mechanism (CDM)

Clean development program or CDM is proposed in article 12 of Kyoto Protocol. Basis of CDM is that any Annex-I nation can invest in a sustainable development program in a non-Annex-I nation. CDM allows project based flexible trading between developed and developing countries in order to help each other to mitigate the target for GHG emission. Main difference between JI and CDM is that the former is implemented between Annex-I nations whereas the later involves cooperation between an Annex-I and a non-Annex-I nation. Both of these mechanisms involve energy efficient projects generating emission reduction credits CER (Certified Emission Reduction), directly crediting to investor's account.

Basically, CDM helps both an Annex-I country and a non-annex-I country in a cooperative manner. Utilizing this mechanism an Annex-I nation can achieve its target on emission reduction commitment while a non-Annex-I nation can achieve sustainable development by providing a revenue to the developing countries.

To decide the price of trading many attempts were made. Price estimation is based in the result of economic models and various identification factors. In the carbon market, the price estimation was decided on the basis of emission of per ton of carbon dioxide. Initially, it was decided that the price range should be between 3 \$ and 74 \$ (US dollar) per ton of carbon dioxide.

CDM found its effectiveness in promoting renewable energy projects. This will help the developing nations to enrich their economy. Rural development in developing countries will be enriched by implementing distributed generation. Industries will take part in sustainable development by implementing energy efficient projects through optimal resource allocation. Urban lifestyle will be improved by various waste processing projects. This will help in maintaining balance in ecosystem.

CER generated from CDM projects financially or technically or both have become a source of revenue for developing countries. Mainly clean and renewable energy projects, fuel switching, waste treatment projects, energy efficient techniques, energy management etc., are included CDM projects. Renewable energy-based power projects gained attention because they do not emit any GHG at any stage. So, such projects can earn revenue through carbon market on per unit (kWh) electricity production. It is observed that on an average approximately 1.486 kg carbon dioxide is emitted for per unit electricity production from a coal-based thermal power plant. This is obtained from stoichiometric analysis of coal. If more efficient technologies can bring down the capital investment cost on green energy-based projects, then its carbon profit will be more.

Introduction to Energy Management

Energy is the key factor to for the development of human civilization. Tremendous research works giving birth to newer technologies day by day. With the advancement of technological growth, harnessing energy has become a matter of great concern. Different application of technologies requires energy utilization in different forms. Among all other forms, electrical energy is the most compact form. It is a very good intermediate form of energy and very ease to transmit and distribute. Besides, it can be

converted to any other form of energy with ease. However, a major portion of energy is lost during energy conversion. The term 'energy loss' may sound as misleading because according to the law of conservation of energy cannot be created, nor can be destroyed and only can be transferred from one form to the other. The logic of using the term 'energy loss' is that, during conversion of energy from one form to other or in transmitting and distributing, a certain portion of energy is converted to heat which cannot be utilized to perform any useful work. So, from economics point of view it is a loss because the process is consuming energy but cannot utilize it fully due to inherent *heat loss*.

Energy resources can be categorized as renewable and non-renewable. Non-renewable resources are fossil fuel-based resources and renewable resources include solar, wind, hydel etc.

Basically, fossil fuel-based resources possess very high energy-density than renewable resources and energy extraction from fossil fuel is already existing through well-established popular and developed technologies. But, main problem with these types of resources is that these are finite by nature. Besides, extraction of fossil fuel involves emission of polluting agents, mainly greenhouse gases and is responsible for the detrimental effect of global warming.

On the other hand, renewable resources are clean by nature because they do not emit greenhouse gas or any kind of polluting agent. However, main limitation of renewable resources is low energy density in comparison to fossil fuel-based resources. Extraction from renewable resources is also not popular or well established though tremendous research and development works are carried out globally to find efficient and cheaper techniques to harness renewable resources. However, it is a fact that harnessing of fossil fuel is usual practice.

Per capita energy consumption is an economic indicator to judge the standard of living of the people in a nation. High consumption of energy is correlated with a quality life specified by the term gross national product (GNP). The main problem in present time is the increasing per capita energy consumption on daily basis due to technological development. This is very alarming because if this situation continues, fossil fuel will not sustain in distant future. On the other hand, renewable resources alone cannot meet the need for energy demand due to lower energy-density. But economic growth cannot be sacrificed and hence per capita energy consumption has to be maintained at a reasonable level.

One way to tackle this situation is an optimized mix of renewable and fossil fuel-based resources which are achieved through various techniques such as co-generation, tri-generation, energy conservation, energy efficiency and energy management.

Co-generation system produces multiple forms of useful energy in a single (usually mechanical and thermal), integrated system simultaneously. Mechanical energy is generally used to produce electricity through generators or can be utilized to blow fans and compressors. Thermal energy is utilized in heat processing applications such as to produce steam, hot water or hot air for drying.

On a similar note, tri-generation is the production of electricity, heat and cooling in a single, compact system simultaneously. One example for tri-generation is a gas fired power plant generating electricity and heat with the exhaust heat going to an absorption chiller which produces chilled water and hot water for air conditioning or alternatively the heat is used in process industries. The ratio of electricity produced and exhausts heat for the absorption chiller and then the ratio of cooling to heating can be varied to meet the demand.

Energy conservation denotes efficient and judicious energy consumption. This is synonymously related to energy efficiency which permits consuming lesser energy to achieve the same level of work done. To achieve energy efficiency, total system performance should be considered. This is because with the increase in system components, overall system efficiency goes down, no matter how efficient individual components are.

Energy management comprises of two sides – supply side management and demand side management.

Supply-side management (SSM) refers to measures taken to ensure efficient conversion, transmission and distribution of energy. This has become a matter of great importance with the deregulation of the electricity industry in many countries, where the efficient use of available energy sources becomes essential to remain competitive. SSM is mainly correlated with electricity; however, it can also be applied to actions concerning the supply of other forms of energy. Utility companies always look for a flat load profile for economic operation of their plant. But, unfortunately, due to the continuously varying nature of load, compels them to run peak load power plants running on less efficient equipments which are needed to be operated for as small duration as possible (compared with high efficiency equipment that should be used to the maximum). Utility companies may improve maintenance and control of existing equipment, or upgrade equipment with state-of-the-art technologies for more efficient and economic utilization of energy.

Demand-side management (DSM) or demand-side response (DSR), is the modification of consumer demand for energy through various methods such as financial incentives and behavioral change through education. The term DSM was coined following the time of the 1973 energy crisis and 1979 energy crisis. The main objective of demand side management is to encourage the consumer to use less energy during peak hours, thereby moving the time for energy usage to off-peak hours. This reduces peak loads often supplied by peak load boilers running on more expensive and less sustainable fuel. Peak demand management does not necessarily decrease total energy consumption, but could be expected to reduce the need for investments in networks and/or power plants for meeting peak demands. Latest trend for DSM is to aid grid operators in balancing intermittent generation from wind and solar units, particularly when the timing and magnitude of energy demand does not coincide with the renewable generation. Governments of several countries have mandated performance of various programs for demand management.

Presently, DSM technologies have gained popularity due to the integration of information and communications technology and the power system, thereby resulting in a new term: smart grid. In energy sector, DSM focuses to at reduce the demand for electricity and energy sources. DSM helps to reduce greenhouse gas emissions.

It is evident from the above discussion that major concern should be given to demand-side management methods (DSM). However, some aspects of supply side managements should be considered too. For example, they may look at on-site generation alternatives – including cogeneration – or consider diversifying to alternative fuel sources (such as natural gas, solar, wind, bio-fuels etc).

Environmental Impact Assessment (EIA)

Environmental impact assessment (EIA) is an interdisciplinary procedure to consider environmental implications before making final decision regarding a proposed project.

Purpose of EIA is to inform decision makers and public about the environmental consequences of any proposed project. Basically, EIA is a technical tool that identifies, predicts or analyses several activities proposed in the project and their effect on the environment. The EIA process serves an important procedural role in overall decision making by transparency and involvement of mass.

An effective EIA should predict the possible change in environment due to proposed human activities.

During the planning of a project, EIA can be treated as an essential step to mitigate sensitive socio-economic issues, if any. Benefits of EIA process can be stated as under:

Screening of projects which are not eco-friendly.

- Reduced cost and time of project implementation.
- Avoidance of environmental impacts, if any and obeying existing rules and regulations.
- Prediction of hazardous impacts.
- Improved performance of the concerned project.
- Identification of potentially affected communities or individuals.
- Proposition for any modification on a proposed project to override environmental impacts.
- Achieving socio-economic development but without sacrificing biodiversity.
- Decreased extraction of resources, thereby help to achieve sustainable development.
- Conflict between nature and mankind is minimized.
- Increased community skills and cultural enhancement.

Depending on the EIA system, either by government agency/ministry or proponent for the project is assigned with the responsibility for producing EIA.

Duration of EIA will depend upon the size and complexity of the proposed project, the extent of co-operation of the parties involved in the proposed project, EA techniques employed etc.

It is important to recognize a general principle of assessment relating to the review of environmental impacts that might be obtained from a proposed project.

The following are well recognized processes:

- Social impact assessment
- Risk assessment
- Energy analysis
- Life cycle analysis
- Health impact assessment
- Economic assessment
- Regulatory impact assessment
- Cumulative impact assessment
- Strategic impact assessment

EIA involves several important purposes, which can be enumerated below

- Decision making
- Process to aid development
- Achieving sustainable development

The process of EIA is closely related with sustainable as well as community development **Fig. 5**.

EIA is carried out through a systematic process to check environmental attributes due to the development action in advance. Hence, it is proactive by nature. EIA process involves a number of steps. Few of them are listed below:

- Screening of project
- Scoping and consideration of alternatives
- Baseline data collection
- Impact prediction
- Assessment of alternatives, delineation of mitigation measures and environmental impact statement
- Public hearing
- Environmental management plan (EMP)
- Decision making and preparation of environmental impact statement (EIS)
- Post-decision monitoring and clearance conditions

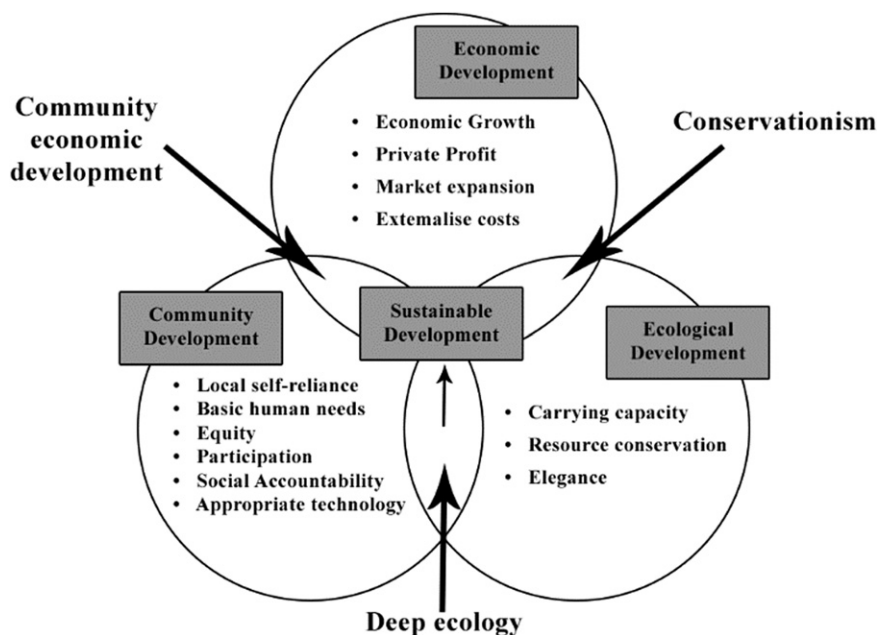


Fig. 5 Illustration of sustainable development. Source: <https://www.semanticscholar.org/paper/EIA-follow-up-Roles-and-stakes-in-environmental-Morrison-Saunders-Arts/0d0ccaa02085a3b6f31ed436f905d23e4502b6b7>.

Steps involved in environmental cleaning can be explained by the following diagram in Fig. 6.

However, procedure involved in EIA can be analyzed with the help of Fig. 7 as given below.

EIA studies are broadly classified as under:

- Site election studies
- Comprehensive studies
- Regional studies
- Carrying capacity studies

EIA cycle can be explained with the following diagram (Fig. 8)

EIS provides valuable information regarding the proposed project. A typical EIS is prepared with the following three parts:

- Part 1 – methods and key issues
- Part 2 – background of the proposed project
- Part 3 – environmental impact assessments on topic areas

Adoption of EIA has evolved since last few decades. USA was the first country in the globe to mandate EIA through NEPA act, 1969. Developed countries adopted EIA in between 1970–1980.

India initiated implementation of EIA in 1976–77 by active cooperation between Planning commission and Department of Science and technology. After thorough monitoring of several projects with environmental angle, Government of India enacted The Environment (Protection) Act, on 23rd May 1986. In 2000, EIA was made statutory for 30 activities.

The ministry of Environment and Forests (MOEF) has prescribed guidelines for different sectors to be addressed during EIA studies. Generally, impacts of air, noise, water, land nature, biodiversity, and socio-economic condition of local people are assessed.

Carbon Sequestration

Carbon Sequestration is a natural or artificial process by which carbon dioxide is removed from the atmosphere and held in solid or liquid form.

Carbon Sequestration is an effective tool for mitigating emission targets as prescribed in the Kyoto protocol. Kyoto protocol allocates CER to promote carbon sequestration activities. This encourages forestation or reforestation or agriculture thereby reducing CO₂ concentration in the atmosphere.

It has been observed that global (both atmospheric as well as marine) accumulation of CO₂ can be absorbed by carbon sequestration.

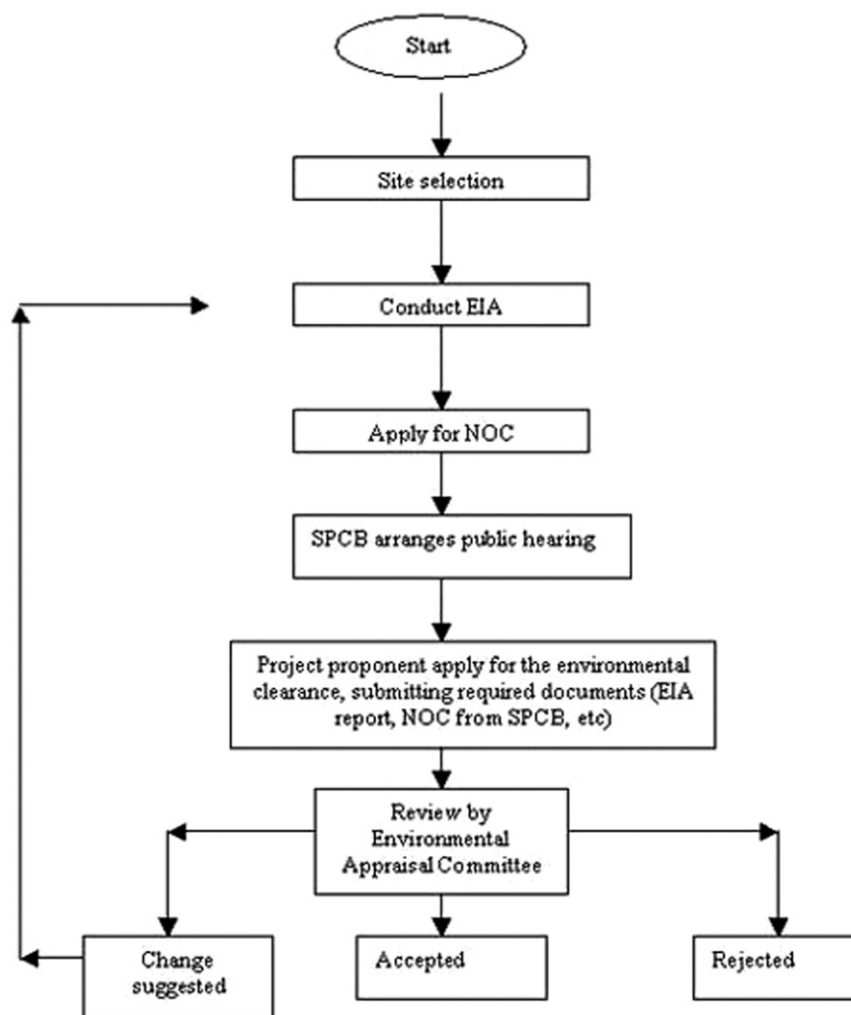


Fig. 6 Step-by-step procedure involved in environmental clearance. *Source:* The manual in perspective, EIA Training Resource Manual, United Nations Environment Program, 2002.

With respect to the growing concerns about global warming resulting from increased concentration of greenhouse gases (GHG) in the atmosphere, considerable interest has been drawn to the possibility of increasing the rate of carbon sequestration. CO₂ is merely responsible for the detrimental effect of global warming which is the increase of average temperature increase of earth by entrapping heat from solar radiation in the form of infrared radiation.

CO₂ can be naturally captured from the atmosphere through natural biological, chemical and physical processes. Various artificial processes also have been incorporated to yield similar results. This includes artificial capture and sequestration of CO₂ originated from various industries using subsurface saline aquifers, reservoirs, ocean water or other carbon sinks.

Carbon sequestration mainly carried out in three ways: post-combustion capture, pre-combustion captures and oxy-combustion.

Carbon sequestration can be effectively implemented through changes in the utilization of land as well as forestry and also through geo-engineering techniques such as carbon capture and storage.

Carbon is released in atmosphere both from human related anthropogenic activities such as the burning of fossil fuels as well as from various natural processes such as the combustion and decomposition of vegetation or animal. On the other hand, carbon sinks are those reservoirs that retain carbon and prevent it from entering in the atmosphere. Water and plant are two main and natural sinks for CO₂. Hence, afforestation or reforestation can effectively reduce concentration of atmospheric CO₂. Plants fix carbon through photosynthesis. It is the process through which a major portion of carbon is transferred naturally from the atmosphere to the biomass reservoir in the presence of solar radiation at chlorophyll. Beyond the natural growth of plants, other terrestrial processes such as of replacement vegetation on cleared land, land-management practices etc., can sequester carbon. It is important to note that carbon sequestered in soils and aboveground vegetation could be released again to the atmosphere through land-use or climatic changes such as combustion (which is caused by fires) or decomposition (which results from microbe infestation).

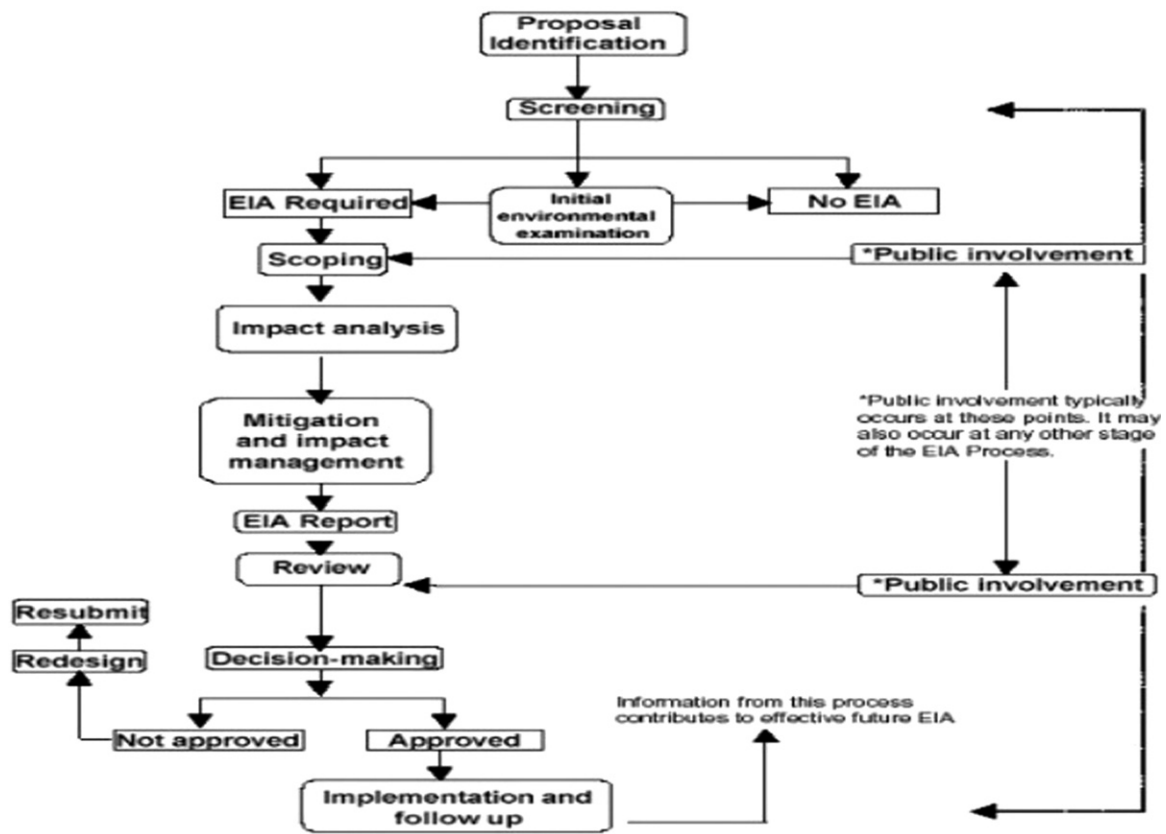


Fig. 7 Procedural steps involved in EIA. *Source:* Prof. Sandeep Hegde's resource material.

Carbon is transported in various forms through the atmosphere, the hydrosphere, and geologic formations. An important link for exchange of carbon is the atmosphere and the oceans. A fraction of the CO_2 combines with water, forming carbonic acid (H_2CO_3).

Carbonate entrapped in soil may become buried in geologic strata and eventually release CO_2 through volcanic eruption. Carbon dioxide is also exchanged through photosynthesis in plants and through respiration in animals. Dead and decaying organic matter may ferment and release CO_2 or methane (CH_4) or may be incorporated into sedimentary rock, where it is converted to fossil fuels. Basically, the biological and anthropogenic activities occur at a faster rate than the geochemical processes and hence possess a greater impact on the composition and temperature of the atmosphere.

Globally, the total amount of carbon sequestered in nature is approximately 2200 gigatons (1 gigatons = 1 billion tons), and it is estimated that the amount of carbon sequestered annually by terrestrial ecosystems is approximately 2.6 gigatons.

Oceans also accumulate carbon, and the amount found just under the surface is roughly 920 gigatons. Various studies showed that amount of carbon stored in the oceanic sink exceed the amount in the atmosphere (about 760 gigatons).

Carbon Capture and Storage

There are many economic as well as technical challenges to implementing carbon capture and storage on a large scale. It has been estimated that carbon capture and storage would increase the cost of electricity production up to five cents per unit, depending on the fuel geographic location of the site. Leakage of carbon from reservoirs is also a matter of great concern. Though various reports show that properly managed geological storage is very reliable (66%–90% retentively) to store 99% of its sequestered carbon dioxide for over 1000 years.

Basically, three types of carbon sequestration techniques are available to implement carbon sequestration. These are terrestrial, geological and mineralization which are discussed below:

Terrestrial Sequestration

Terrestrial sequestration is the removal of existing CO_2 and storage of the same with the help of vegetation and soils through afforestation, reforestation, wetland recovery etc.

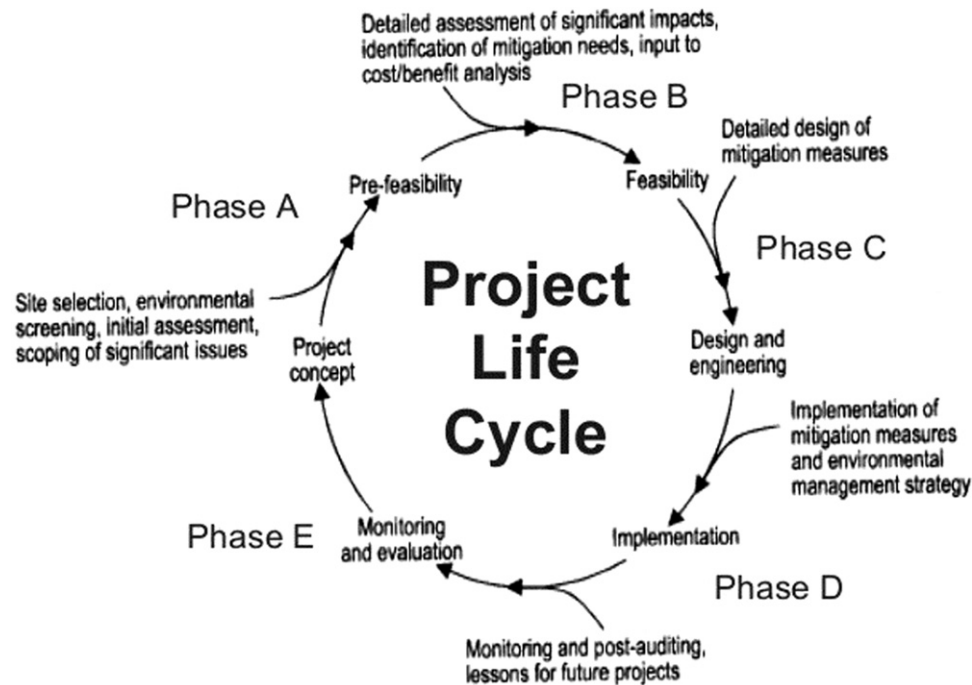


Fig. 8 Representation of EIA in cyclic form. *Source:* Prof. Sandeep Hegde's resource material.

Geologic Sequestration

This involves storage of CO₂ in subsurface structure in oil reservoir, natural gas reservoirs, deep saline formations, shale reach in oil or gas, and in coal beds unsuitable for mining etc.

Mineral Sequestration

It is the process of forming stable carbonate salts by chemical reaction of various substances mainly magnesium and calcium with CO₂. It is a natural process which is responsible for producing limestone.

Geological sequestration among others possesses greater viability due to its substantial storage capacity. Besides, most of the major anthropogenic sources of CO₂ emission are located near potent geological storage sites.

Technologies for Carbon Sequestration

Carbon sequestering technologies include a geo-engineering proposal called carbon capture and storage (CCS). CCS is carried out through two interrelated steps.

Firstly, carbon dioxide is separated from other constituents emitted in various industries. After separation, the CO₂ is compressed and transported through pipelines to a location that is isolated from the atmosphere for long-term storage. Suitable storage locations might include geologic formations such as deep sedimentary rocks whose pore spaces are saturated with water containing high concentrations of dissolved or in depleted oil and gas reservoirs, or in the deep ocean. Although CCS captures carbon dioxide directly at the source of emission before releasing into the atmosphere, it may also include techniques to remove carbon dioxide from the surrounding air. Separation of CO₂ can be done through the following three methods.

- *Pre-combustion capture*

This treatment is carried out before burning of the fuel. The fuel is converted to synthesis gas or syngas and then ultimately to hydrogen and CO₂. After that, hydrogen is separated from CO₂ and is used as fuel.

- *Post-combustion*

After burning of fuel, CO₂ is separated from nitrogen using chemical agents.

- *Oxy-fuel combustion*

Fuel is burnt in pure oxygen so that nitrogen is not present in the emission.

In the second step, CO₂ in supercritical form (liquid stage) is injected into underground geological formations.

Obstruction for Carbon Sequestration

The challenges encountered by carbon sequestration are mainly technical, financial or regulatory by nature.

CO₂ is mainly stored underground by hydraulic pressure so that it is stored in supercritical (liquid) state. In case of minor fault in tank design or any form of even very small leakage will ease the pressure on the liquid CO₂, thereby releasing it into the atmosphere in gaseous form.

CCS techniques would increase the operational cost for energy production. If CCS is mandated through regulatory action, then cost of production of electricity would be nearly double in a coal-based thermal power plant. The cost of CCS technology varies with different types of capture technologies being used. The cost also depends on concerned sites that it is implementing CCS. It is obvious that research and development may reduce the cost for CCS technologies still it would remain slightly higher than costs involved in technologies without CCS.

Energy required for sequestration technique is also a significant factor. As an example, it can be stated that any power plant implementing CCS has to supply a significant amount of energy for pumping of CO₂, thereby reducing its effective output.

Responsibilities of Energy Managers

- (1) Preparation of annual activity plan and present to management concerning financially attractive investments to reduce energy costs.
- (2) Establish an energy conservation cell within the firm with management's consent about the mandate and task of the cell.
- (3) Initiate activities to energy costs.
- (4) Analyzing equipment performance with respect to energy efficiency.
- (5) Checking the functioning and calibration of instrumentation required to conduct energy audit.
- (6) Convey awareness about the importance of energy audit with real time data among the staff members associated with the plant concerned.
- (7) Establish a methodology to calculate the specific energy consumption of various products/services or activity of the plant concerned.
- (8) Develop and manage training program for energy efficiency at operating levels.
- (9) Co-ordinate nomination of management personnel to external programs.
- (10) Develop integrated system of energy efficiency and environmental up gradation.
- (11) Co-ordinate among various implementation techniques of energy audit/efficiency improvement projects through external agencies.
- (12) Establish and/or participate in information exchange with other energy managers of the same sector through association.

Energy Intensive Equipments

Following are energy intensive equipments consuming a large portion of energy for their proper operation

- Industrial drives
- Heating/cooling equipment such as oven or chiller/ cooling tower
- Lighting
- Intra-transport for goods as well as staff members or labors
- Pumping system
- Combustion chamber
- Ventilation and air conditioning equipment
- Purifying equipment such as electrostatic precipitator (ESP) or air filter
- Heat or water treatment plants etc.

Energy Conservation Opportunities

Substitution of fuel (if possible), efficient energy conversion methodologies, economic feasibility etc., are easily identifiable provisions energy conservation.

Proper fuel air ratio or any efficient fuel can decrease the energy consumption level. Similarly, it can be stated that efficient energy conversion methodologies should be adopted in order to achieve economy in energy consumption. Captive power generation, optimal loading of distributed generation, waste heat recovery, flue gas heat recovery, pre-heating etc., are various ways to improve system efficiency wherever applicable. Economic feasibility is the key parameter for adopting energy management policies. This is carried out through various economic tools such as payback period, internal rate of return, net present worth etc. It is mention-worthy that economic feasibility is also depended on technical viability which involves availability of proper techniques, skilled manpower, reliability, safety, quality etc.

Classification of Energy Conservation Opportunities

Based on the report from detailed energy audit, several potent energy saving projects may be figured out. These may be classified as per the following:

- (1) Low cost-high return projects
- (2) Medium cost-medium return projects
- (3) High cost-high return projects

Obviously, projects possessing low cost and high return are prioritized. Other options are analyzed further and implemented in a phase by phase manner. Projects involving high cost with high return are given careful attention before implementing. Commencement time of such projects may be very high.

Energy Efficiency and Conversion Efficiency of Energy

Energy efficiency either refers to efficient usage of energy or efficient conversion of energy.

Efficient usage of energy or simply energy efficiency is consumption of less energy to provide same level of performance than in a normal situation. As an example, it can be stated that installation of LED lights instead of incandescent or fluorescent light will decrease the energy usage level but providing same amount of illumination. Energy efficiency is an essential criterion to achieve energy conservation (Russell, 2006). Energy efficiency is a cost-effective strategy in order to achieve overall economy as well as sustainable development.

Energy conversion efficiency is the ratio between the useful output and the input for an energy conversion device. Due to inherent losses, output energy is always lesser than the input energy. The objective of energy conversion efficiency is to minimize the inherent losses, if possible. Energy conversion efficiency cannot be defined uniquely, because it is case specific.

Conclusion

The effects of global warming are the environmental and social changes caused (directly or indirectly) by human emissions of greenhouse gases. There is a consensus that climate change is occurring, and that anthropogenic activities are mainly responsible for this. Several impacts of climate change have already been observed, including glacier retreat, thermal expansion of large water-bodies and changes in agricultural productivity.

Future effects of climate change will vary depending on climate change policies and social development. The two main policies to address climate change are reducing human greenhouse gas emissions (climate change mitigation) and adapting to the impacts of climate change.

Very short-term climate change policies could significantly affect long-term climate change impacts. Besides, environmental pollution does not follow the boundary of a country and hence it is not a localized phenomenon.

Stringent mitigation policies might be able to limit global warming (in 2100) to around 2°C or below, relative to pre-industrial levels. Without mitigation, increased energy demand and extensive use of fossil fuels might lead to global warming of around 4°C. Higher magnitudes of global warming would be more difficult to adapt to and would increase the risk of detrimental impacts like severe thunderstorms and flash flooding etc.

The effects of global warming include its effects on human health. The observed and projected increased frequency and severity of climate related impacts are mentioned below:

- *Impact on infectious diseases*
- *Impact on respiratory system*
- *Impact on vascular disease*
- *Impact of extreme weather*
- *Malaria*
- *Dengue fever*
- *Psychological impact*

The global health care sector is highly interconnected with industrial activities emitting a significant portion of environmental pollutants. Environmental emissions directly and indirectly attributes to the physical as well as mental health care sector. Negative environmental and public health outcomes were estimated through economic input-output life cycle assessment (EIO-LCA) modeling using National Health Expenditures (NHE) for the decade 2003–2013 and compared to national totals in USA.

Concerted efforts from all corners of people to improve environmental performance of health care could reduce expenditures directly through waste reduction and energy savings, and indirectly through reducing pollution burden on public health, and ought to be included in efforts to improve health care quality and safety and reduction of hospital bills.

Thus, based upon the current impacts of the climate change, it is very clear that the controversies to be created in the future would be really aggravated than thought. Hence, it is now in our hands to take up the responsibility of shaping the planet as it was before. Maybe it is now late in taking decisions but there is very little time to implement it. We have exploited our mother nature

to the maximum as we could and now, we are being repaid. Adhering to the latest technologies available in the market, we have the capability to advance easily into the industrial practices. Indian industry is quite adept at absorbing technology. Most of the technologies are already available. In fact, if you are talking about steps on climate change, almost 90% of the technologies are available. Unless you are talking about clean coal technologies or carbon sequestration, it's not an issue.

See also: Renewability Assessment of a Production System

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Clean Energy Technologies: Hydrogen Power and Fuel Cells

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Introduction

The ever increase demand of energy and power has caused serious irrecoverable damage to our environment. With this continuous demand of energy and the regular increasing usage of fossil fuels to meet the needs of the various industries an increase in the amount of greenhouse gases in the nature has been observed. These greenhouse gases pose serious hazards to our environment and causes consequent climate change. The prominent gases causing greenhouse effect include Carbon Dioxide, Methane, Nitrous Oxide, Ozone and Chlorofluorocarbons (11 and 12). Out of these gases it has been estimated that Carbon Dioxide is the major greenhouse gas. The individual contribution of all these gases to greenhouse effect is shown in [Table 1 \(Rodhe, 1990\)](#).

With these being a serious issue an important and concerning issue is their increasing concentration in our environment. Their increase in concentration every year has been estimated and shown in [Table 2 \(Rodhe, 1990\)](#).

The increase in the greenhouse gases every year has some serious effects on the environment. They have caused global warming to increase at an unappreciable and concerning way due to which the ice capped mountains and peaks have started to melt and an increase in the water level has been noticed. Acid rains is one of the causes of the increase in the concentration of the greenhouse gases ([Jakobsson et al., 2009](#)). Depletion of ozone layer is a very critical issue. 70%–75% of the Carbon Dioxide is produced by consumption of fossil fuels ([Hoel and Kverndokk, 1996](#)). Apart from the effect of greenhouse gases produced by fossil fuels, the increased demand of fossil fuels increases its cost due to its regular demand. Fossil Fuel depletion has been stated as a future challenge. However these non-renewable sources of energy are bound to deplete in a certain period of time and the only alternate solution to such an increasing demand are renewable sources of energy. So in order to limit the use of the fossil fuels and save the planet from increased global warming which will lead to drastic climate changes the use of renewable energy like wind energy, geothermal, solar and hydro energy are very much into use ([Johansson and Burnham, 1993](#)).

However countries like Japan, China is trying to revolutionize by bringing a new renewable source of energy, Hydrogen cells. Hydrogen links the renewable sources of energy to zero emission technologies. These cells would be used to power fuel cells in order to run the vehicles as well as provide electricity at home ([Behling et al., 2015](#)). The primary steps to use Hydrogen as a primary source of renewable energy was taken in the early 1980s by the European Union.

Hydrogen Fuel: Advantages, Production, Delivery, Storage and Conversion

The thought of hydrogen cells as a source of energy came into being because of climate change and the depletion of the fossil fuels. With the aim of decarbonizing the environment, Hydrogen cells could play an important role. The Hydrogen cells provide the following advantages over fossil fuels:

- Hydrogen production from wind, hydropower, solar, biomass and thermal energy are low polluting emission systems.
- Since no extraction and refining is done as in the case of crude oils, winter smog and acidification will be reduced.
- Air pollution will be decreased as no production of Sulphur Oxides, Nitrogen Oxides and other polluting gases will be formed which shall decrease respiratory problems.
- Eco-friendly means of production of Hydrogen ([Koroneos et al., 2005](#)).

With the following advantages of Hydrogen fuels, Hydrogen production is done by following means:

- Pyrolysis and Gasification.
- Water Electrolysis.

The electrolysis of water is done by utilizing electricity produced using some renewable source of energy. The production of hydrogen in this process is from water which is very readily available in nature. Hence this process is cost effective process as it only involves the costing of the electricity required for the splitting of the water molecule. The major drawback of this technique is the use of platinum electrodes which makes it costly.

- High temperature Nuclear Reactor.
- Production from solar, wind and thermal energy sources.

Wind energy is used to produce electricity by affecting the nature to a minimum. Solar energy is the most used renewable source of energy. These energies are used to produce electricity by keeping the environment in a quasi-static state. This electricity is

Table 1 Individual contribution of greenhouse gases

<i>Greenhouse gas</i>	<i>Relative contribution towards greenhouse effect (%)</i>
Carbon dioxide	60
Methane	15
Ozone	8
Nitrous oxide	5
CFC-11	4
CFC-12	8

Table 2 Annual increase in greenhouse gases

<i>Greenhouse gas</i>	<i>Annual increase rate (%)</i>
Carbon dioxide	0.5
Methane	1
Ozone	0.5
Nitrous oxide	0.2
CFC-11	4
CFC-12	4

used to produce hydrogen required in electrolysis of water. Geothermal energy is cheap and is readily available and hence is a good alternative to produce hydrogen. Geothermal energy can be available in electricity or heat form. So hydrogen can be synthesised using electrolysis or hybrid cycles.

- Production from Biomass.

There are two ways to produce hydrogen from biomass: biological and thermochemical. It is produced in the way shown in **Fig. 1** (Hosseini and Wahid, 2016).

- Production from natural gas and coal.

Coal and Natural Gas are used for synthesising hydrogen. Hydrogen is synthesised from Natural Gas by reacting it with water at 20 times the atmospheric pressure and 1000°C. The drawback of this system that for 1 ton of Hydrogen produced almost 2.5 tons of Carbon dioxide is produced which makes it an insignificant process.

Coal produces almost twice the air pollution in comparison to the Natural Gas and it has been shown simultaneously that using coal to produce Hydrogen is uneconomical (Gray and Tomlinson, 2002; DOE, n.d.).

The pyrolysis and gasification hydrogen production when made to mix path with Carbon Capture and Storage aids in removing the Carbon Dioxide from the atmosphere. This is a very important factor in absorption of such technologies. A very important statistics laid by IEA Greenhouse Gases Programme this uptake of this technology could remove 800 million tonnes of Carbon Dioxide on an annual basis in Europe only by replacing fossil fuels (Sgobbi *et al.*, 2016).

Even though this system has so many advantages the main problem lies in the fact that what needs to be established first: the system that would utilize such fuel or the vast infrastructures to produce this eco-friendly fuel.

The increased demand of Hydrogen will lead to its economic manufacturing using the above mentioned processes. However the Hydrogen economy has not gained much attention. Hence for its delivery pipelines only in few places around the world has been established which include Indiana, California, Texas and Louisiana in United States of America and the Ruhr Valley in Germany. It is generally distributed over road transport in cryogenic cylinders which contains Hydrogen in liquid form. Since the volumetric energy density of Hydrogen is very low, hence it needs to be compressed or liquefied for its transportation. However these are not economical processes and research and development team is dedicating their work to optimize the cost in this operations.

Though Hydrogen has the highest gravimetric energy content of any fuel reported till date and is the lightest element, its lower volumetric energy density makes it challenging for its storage purpose. This is one of the most challenging field in comparison to the hydrocarbon fuels which can easily be delivered, stored and carried along. Apart from it needs to be stored in automobile refuelling places which was so easily achieved by hydrocarbon fuels.

Hydrogen so produced can be converted into electrical energy through electrochemical processes by using fuel cells. They can also be converted to thermal energy through thermochemical processes by using turbines and combustion engines. Fuel cells are the future of our world as we aim to provide efficient, clean and fuel-flexible energy to our locality. Fuel cells have proved to be efficient with some cells providing an overall efficiency exceeding 80%. The use of Hydrogen in the engines of Space Shuttle is an old known concept.

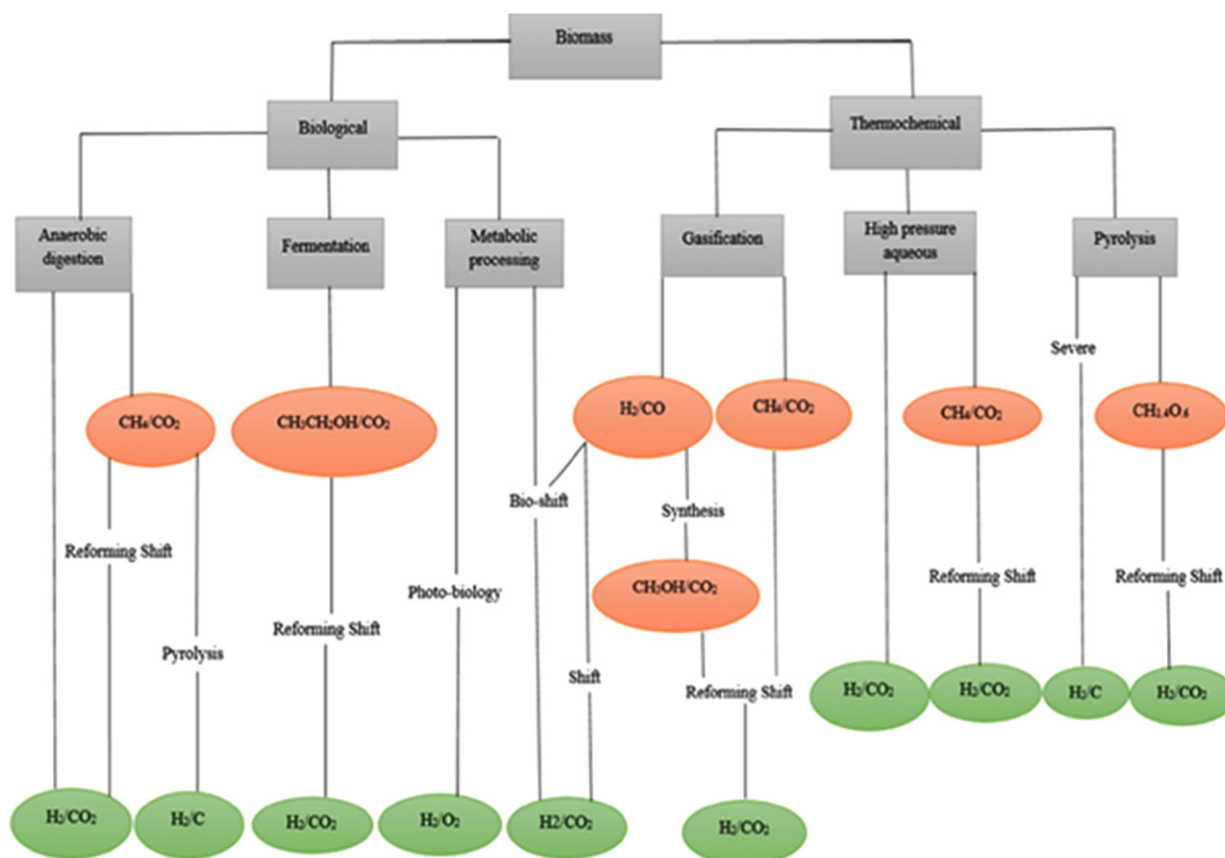


Fig. 1 Hydrogen production from biomass. Reproduced from Hosseini, S.E., Wahid, M.A., 2016. Hydrogen production from renewable and sustainable energy resources: Promising green energy carrier for clean development. *Renewable and Sustainable Energy Reviews* 57, 850–866.

Hydrogen Economy and Utilization of Hydrogen Fuel

Hydrogen Economy has different divisions which deals with production, storage, transportation and distribution of Hydrogen fuel. The Hydrogen fuel has found its way in different sectors which include transportation, residential and commercial sectors and industries (Brandon and Kurban, 2017).

Hydrogen in Automobile/Transportation Sector

A new idea and attitude has been seen by engine manufacturers and oil refineries to the increasing carbon content in the nature. Some major steps taken by them include:

- Hybrid electric vehicles.
- Lightweight materials being used for the transportation purposes.
- Direct-injection compression ignition engines.
- Fuel Cell powered electric vehicles.

In order to render the emissions from the vehicles carbonless initiatives has been taken by leading automobile companies like Toyota, BMW, Hyundai, etc. by producing Fuel Cell Electric Vehicles (FCEV). However they still offer only 30% Carbon Dioxide saving as the Hydrogen fuel cells are made from natural gas and coal derivatives (Sgobbi *et al.*, 2016; Ball and Wietschel, 2009) and are costly in the present scenario. Though the prices are supposedly to come down in the coming future with the increased research and development dedicated to this field but in this present scenario the internal combustion engine vehicles and the plug in electrical vehicles are much cheaper compared to them.

It has been experimentally shown by some researchers in 2003 from MIT that the hybrid engines can reduce greenhouse gases to about 65% by 2020, this shift can be understood as well in 2018, in comparison to the non-hybrid conventional engines (Weiss *et al.*, 2003). Hybrid engines were tested for fuel cells and internal combustion engines with the properties under observation was the efficiency and the emission of the greenhouse gases. Along with the advances in power systems to reduce the greenhouse gas emission and increase the efficiency of the vehicles, the important factors which played an important role were the weight of the vehicle, aerodynamic drag and tire rolling resistances. A comparison has been shown by them between Fuel Cells and

Internal Combustion Engines. The Internal Combustion Engines had greater advantages compared to Fuel Cells. The Internal Combustion Engines are much easier to manufacture compared to Fuel Cells because of the existing infrastructure. However the Fuel Cells operate at a very low noise compared to Internal Combustion Engines.

Hydrogen in Residential and Commercial Sectors

The energy consumed by this sector consists of lighting, heating, cooling and for running appliances and equipment. More than 40% of the global energy is used in the residential sector (Brandon and Kurban, 2017). Also it is necessary to decarbonize heat as it is the third in global energy related Carbon emissions. Decarbonizing heat can be done through Though decarbonizing heat energy has not been the major attention seeking subject in this field in comparison to decarbonizing power, this subject needs to be brought into consideration if we are to meet the climate mitigation targets. Decarbonizing heat is challenging in these fields however if the gas network can be converted to hydrogen it would be cheaper to provide low carbon heating.

Hydrogen in Industries

Almost 25% of the global energy is used by the industries all over the world, hence the emissions produced by them leads to carbonizing the environment to a large extent. Hence it becomes necessary to use renewable sources of energy like fuel cells. Fuel Cell is basically a technology which takes Hydrogen as an input source of energy and produces dc power. But it has been observed that most of the Hydrogen is utilized to prepare fertilizers and then industries and methanol synthesis. In the European Union, industries produce Hydrogen as by-products and only 10% is supplied by merchants. Hydrocracking and Hydro-treating techniques are used by oil refineries to refine crude oil. Hydrogen accounts for near about 20% of the total emissions produced by these refineries (European Technology Platform for Zero Emission Fossil Fuel Power Plants, 2013). The demand of Hydrogen has increased with the increased use of heavy oils with clean high quality fuels with less Sulphur content (International Energy Agency, 2015).

Fuel Cells

With increased demand for energy and decreasing Carbon content in the nature, Fuel Cells seems to be a very good alternative as it uses Hydrogen to produce power. There are three types on the basis of temperature: Low temperature, medium temperature and high temperature (El-Sharkh *et al.*, 2004a,b). The low temperature is further classified into the following: Alkaline Fuel Cells, Solid Polymer fuel Cells and Proton Exchange Member (PEM) Fuel Cells. The Medium temperature has Phosphoric Acid Fuel Cells. The high Temperature can be classified into Molten-Carbonate Fuel Cell and Solid Oxide Fuel Cell.

The Hydrogen Fuel Cell consists of reformer (fuel processing unit), power conditioning unit and the fuel cell stack. The low temperature and medium temperature Fuel Cells have external reformers while the high temperature Fuel Cells have an internal based reformer as hydrocarbons can be processed internally at the high temperature provided by them. The output of this is a dc power, which can be supplied to residential complexes, industries with proper conditioning techniques and use of transformers. The material selection of the fuel cell technologies is subjected to various constraints which are subjected to its performance under various conditions. Minimization of cell resistivity is one such important factor as it ensures high energy densities. Hence the combined resistivity of the anode, cathode and the electrolyte, the cell components, should be a maximum of $0.5 \text{ } \Omega\text{cm}^2$. In order to reduce the combined resistivity of the cell the electrolyte, the electro-catalyst, current collector and the gaseous reactants needs to be brought together in a close contact. In order to further reduce the resistivity the electrode a metallic wire, mesh or screen was introduced in the cell. Further reduction was achieved by incorporating high ionic conductivity electrolytes like molten carbonates, liquid KOH or phosphoric acid. The other important component is the impermeable electronic conducting bipolar plate. This serves two function: One is to provide air and fuel to both the anodic and cathodic plates and second is to provide electric contact between adjacent cells. Due to corrosive effects in some membrane fuel cells (polymetric-electrolyte and phosphoric acid) the material to be chosen is severely restricted to certain elements like graphite. Stainless steel derivatives are used for high temperature fuel cells operating in a temperature range close to 750°C . But for solid oxide fuel cell the different bipolar plate materials are different as the temperature of these fuel cells are around 100 (Steele and Heinzel, 2011). However fabrication of graphite plates are expensive, hence polymeric materials are preferred as they can be machined easily and is more cheaply fabricated using injection moulding or hot pressing. Even graphite can be mixed with different materials to make these bipolar materials. With the increase in graphite the mechanical properties like toughness decreases and brittleness increases and machinability decreases, however the electrical conductivity increases. The best electro-catalyst used for operations with Hydrogen and air is platinum. However platinum is a costly element and hence incorporation of nanoparticles of platinum over Carbon. The platinum content has been reduced over the years without affecting the performance of the electro-catalyst. The material should also have reliability and durability properties. The durability should be at least 1000 h for transportation system while for stationary applications this should extend to over 5 years. However, the materials used for these membran fuel cells are having issues which are further overcome by the upcoming new generation of research and development. These systems would not have gathered interest if not for the discovery of the Naflon (Steele and Heinzel, 2011). Naflon was first introduced as membrane cells for the production of Chlorine. But in order to be used in fuel cells the polymeric membranes should have the following properties in the balanced way:

- Permeability of gases must be low irrespective of the membrane thickness.
- Thermal, mechanical and chemical strengths should be good.
- Moisture content in stack should be controlled.
- The proton conduction should be high.

Polymer electrolyte membrane fuel cell has gained importance over other fuel cells because of its application in a quick start-up. This Fuel Cell gained much importance as an exchange resin was incorporated as an electrolyte for the space application. With this incorporation the Polymer electrolyte membrane proved to be better alternatives compared to solar cells and batteries. The working of the fuel cell depended on the cell membrane thickness and the water content in the membrane. The water content increases the conductivity of the membrane, hence more water should improve the performance of the fuel cell, but cathode may get flooded which will slow down the reaction. This is termed as water drag. In order to reduce the water drag, the thickness of the membrane can be reduced and this lowers the resistance of the membrane, decreases the overall cost and increases hydration (Smitha *et al.*, 2005). The membrane materials can be as follows:

- Perfluorinated membranes.
- Partially fluorinated membranes.
- Acid base blends.
- Non-fluorinated membranes with aromatic backbone.
- Non-fluorinated membranes.

Among all the membranes Naflon produced by DU point had gained popularity as it has high proton conducting property, mechanical strength and chemical stability. However efforts are still being made to improve the properties of Nefflon, like water retention at higher temperatures. Silicon has been used to improve the retention property above 130°C (Watkins *et al.*, 1993). Significant changes in the conductivity were observed when perfluorinated ionomers were incorporated in the Naflon matrix along with doping with heteropolyacids. Many such attempts were made to improve the properties so that the overall performance of the fuel cell increases. However there are a still a lot of limitations with regard to Naflon. They are as follows:

- Safety issues during its manufacture.
- Temperature limitations.
- Supporting Element requirements.
- High Cost of the membranes.

With the shortcomings of this membrane, it is expected that it will be replaced in the coming future (Antonucci *et al.*, 1999; Watkins *et al.*, 1993) with the research to overcome these shortcomings going on.

Challenges in Fuel Cells

The challenges faced by the fuel cells are its high expenses and its durability problems. The cost of the fuel cells is generally due to the electrocatalyst, since it contains precious metals, which increases the cost of the actual fuel cell to be almost seven times the target market value. As said earlier the use of nanoparticles are helping this cause and even the introduction of unique nanostructured thin film have increased the properties as well as reduced the cost. This provides 15–20 times more durability compared to the Membranic Electrode Assembly. The other factors which affect the cost of the cells are bipolar plates and the membranes.

For the durability problems, the target running time should be 5000 h but it has been experimentally observed that after 1000 h of running under heavy loading the performance of the system decreases significantly. The fuel cells performance also decreases due to degradation of the catalyst layers and membranes, which in turn is accelerated by the cell potential variation and humidity of the system. Due to their combined effect chemical and physical stresses are induced in the membranes which eventually results in the formation of the pin holes finally leading to membrane failures. It has also been observed that the fuel cells cannot operate at all vehicle temperatures i.e., -40°C to $+40^{\circ}\text{C}$. This makes it less competitive compared to Internal Combustion Engines (Chalk and Miller, 2006).

Conclusion

With the increase in the greenhouse gases there are various irrecoverable impacts on the nature, like global warming, climates changes, melting of snow caps, etc. Hydrogen being one of the best alternatives has shown much promise in various studies. Its production from renewable sources being the best possible scenario to decarbonize the environment. A number of ways has been suggested by the researchers to produce Hydrogen gases, with production from biomass being the most efficient while the production from natural gas being the most cost effective. The hydrogen economy though seems to be a very promising and reliable idea but the concept to come into existence will take much more years as predicted by the researchers. The use of Hydrogen in the automobile sector is one of the best ways to decarbonize the environment. However the question of durability and efficiency comes into play as Internal Combustion Engines' durability is high and then comes the cost terms, which is very high for Hydrogen based vehicles. The biggest problem faced by this sector is that the transportation, storage and distribution of Hydrogen at cheaper rates. The Fuel Cells are a very important future technology which has a tendency to cause the 'Hydrogen Revolution'.

With the recent progress going on over fuel cells to decrease the cost of the fuel cells and increase its mechanical and electrical properties, this revolution may be far but not impossible because in many parts of the world the Government has taken actions to develop Hydrogen Economy. Hence, Hydrogen Power and the Fuel Cells are the essential tools of clean energy with the help of which mitigation of greenhouse gases can be done and a better and greener future can be ensured.

See also: Use of Clean, Renewable and Alternative Energies in Mitigation of Greenhouse Gases

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CO₂ Sequestration Using Algal Biomass and its Application as Bio Energy

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Introduction

According to the Intergovernmental Panel on Climate Change (IPCC), emissions of global greenhouse gases (GHG) have enhanced the average global temperature at the end of the 21st century by 1.1–6.4°C (Intergovernmental Panel on Climate Change IPCC, 2007), with a proposal of reducing global greenhouse gas (GHG) emissions by 50%–80% by 2050 (Intergovernmental Panel on Climate Change IPCC, 2001). Emissions of anthropogenic CO₂ are generally a consequence of fossil fuels being the most important global energy sources. The demand of energy has been increased significantly in recent years because of the rapid development of modern industries. At present scenario, the most challenging mission for many countries, to find alternative energy resources specifically for those countries lacking fuel resources (Huang *et al.*, 2010). So, for reducing CO₂ emissions, exploration of renewable energy should be emphasised. Therefore, carbon sequestrations are required for balance energy efficiency and renewable energy to reduce global CO₂ emissions. Carbon sequestration is the one of the most effective process of storing atmospheric CO₂ which is removed from the atmosphere. It has also emerging as promising ways of 'geo-engineering' and mitigating the crisis arising global warming. Carbon sequestration involve two important segments namely (i) carbon capture (the capturing of large quantities of CO₂ for carbon sequestration) and (ii) carbon storage (successfully storage of the captured CO₂, finding a safe, protected, and cheap place). This article aims to present an outline of CO₂ sequestration techniques through natural resources as a trail to alternative fuel. This article has explored the potential of algae for CO₂ sequestration and as a source of sustainable alternative fuel source.

CO₂ Sequestration and Associated Facts

Recent studies present that atmospheric carbon dioxide has increased from about 280 ppm in 1750–383 ppm in 2007 and is increasing at an average rate of 2 ppm (parts per million) per year. Carbon sequestration has been recognised as potential way to reduce greenhouse gas emissions. It also complements two other major approaches for greenhouse gas reduction, namely improving energy efficiency and increasing use of non-carbon energy sources. It's emerging as important field of research because of its compatibility with the large energy production and delivery infrastructure. All the potential routes for removal of CO₂ from air or industrialized flue gas stream has been classified as, physicochemical routes, geological routes and biological routes. In physicochemical process, capturing of CO₂ from industrial flue gas streams involves application of several unit operations like absorption, adsorption, gas separation by membranes and cryogenic distillation. Geologic sequestration has been assumed as most perpetual method for carbon sequestration and part of a process frequently referred to as 'carbon capture and storage' or CCS. Geologic sequestration refers to a promising technology to reduce CO₂ emissions to the atmosphere and mitigate climate change. Geologic sequestration process involves the steps of injecting carbon dioxide, captured from an industrial (like, steel and cement production) or energy-related source (like, a power plant or natural gas processing facility), into deep subsurface rock formations for long-term storage. Underground injection of CO₂ also serves the purposes of enhanced oil recovery (EOR) and enhanced gas recovery (EGR) as a long-standing practice. CO₂ injection specifically for GS involves different technical issues and potentially much larger volumes of CO₂ and larger scale framework. This is Geologic sequestration has been considered as reliable and reassuring if the geologic formations embattled for carbon sequestration and can prevent the discharge of carbon dioxide in the environments.

Bio sequestration is the capture and storage of the atmospheric carbon dioxide by biological processes by various routes like, increased photosynthesis (through practices of reforestation or preventing deforestation and genetic engineering; enhanced soil carbon trapping in agriculture; and algal bio sequestration. Biological routes include algal systems and energy crops like corn, oil palm, switch grass which can utilize CO₂ from the atmosphere using photosynthetic pathway. The carbohydrates and polysaccharides can be transformed to hydrocarbon fuels through various thermochemical processes such as pyrolysis, refraction, liquefaction and gasification and several biochemical methods like anaerobic digestion and fermentation (Nanda *et al.*, 2014). Coal bed methanogenesis has also been categorised as biosequestration which involve use of methanogenic bacteria that degrade the coal bed and produce biogenic methane to capture carbon from atmosphere.

Bio sequestration is the process of capturing and storage of CO₂ in living organisms such as plants and algae. It has been given utmost priority being simple, and being responsible for the formation of the extensive coal and oil deposits which have potential fuel application. The term 'biosequestration' was coined for one of the solutions to help balance greenhouse gas and carbon emissions as part of climate change policy. The photosynthetic organisms such as several bacteria, algae which can be inhabited marine as well as freshwater environments are abandoned and the microbial route has been reported more advantageous over other chemical process because of their very spontaneous assimilation methodology. The progressive routes for carbon capture and sequestration can be shown in Fig. 1.

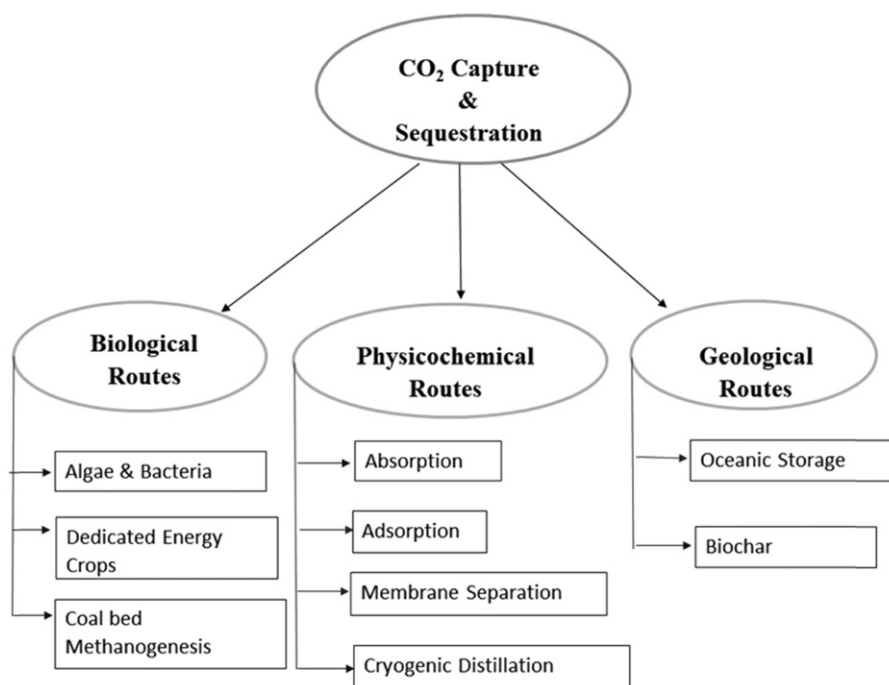


Fig. 1 The routes for carbon capture and sequestration.

Cement plants generate concentrated amounts of carbon dioxide producing 1.25 metric tons of CO₂ for every ton of cement produced. On average each plant produces 100,000 tons of CO₂ per year. According to the Intergovernmental Panel on Climate Change, there are more than 1175 cement production facilities globally that in 2000 collectively generated 932 million tons of CO₂. Because cement plants generate copious amounts of CO₂, and many are located in tropical or subtropical regions of the world, they are ideal candidates to take advantage of algae technology to convert stack gasses to algae oil.

Carbon Sequestration Using Algae as Green Energy Feedstock

Developed and developing nations to meet the demand of energy crisis utilise conventional sources of energy which inevitably increases the CO₂ emissions which ultimately results in increased environmental fouling and pollution. At present the energy, Industry and transportation sectors release the CO₂ in a bulk volume. Under Kyoto Protocol agreement, the targeted value of CO₂ was established to meet the sustainability for a better tomorrow which helps us to mitigate the level of pollution. Thus the concept of green development has come to researcher's mind. As CO₂ is the main contributor to global warming, it must be captured. Recently, lot of different kinds of pathways are available, among them the biological route of CO₂ capture using microalgae is under our immense research attention due to its simplicity in production, less by-product at different stages which reduces the cost of the process as well as the consumption of energy (Nanda *et al.*, 2014). This section has covered the potency of microalgae as fuel alternative, the salient features of algal fuel, details of the CO₂ fixation methodology, different aspects of algae production and optimisation aspects of algal biofuel.

Algae are photosynthetic diversifying organisms which can be found anywhere in the world, and their presence is in aquatic environment in bulk quantity. Algae may be unicellular or may be multi-cellular in nature and the word 'algae' can be denoted as a polyphyletic and collection of synthetic microorganisms (Apt and Behrens, 1999). In presence of sunlight, CO₂ and nutrients; their photosynthetic pigments produce food. Algae are the largest producer of oxygen in the environment. Near about 50% oxygen is produced by the algae (Chisti, 2000, 2007; Gavrilescu and Chisti, 2005; Wijffels, 2007). Being primary producer algae provides the baseline in the aquatic food chain. Due to its wide availability in the environment, it is used as bio indicator which reflects the different kinds of alteration in the environment in different phases of time. Pollution level indexing is done by different kinds of algae. Algae are generally classified in two kinds, namely, microalgae and macro algae. Microalgae are basically microscopic in nature (Scott *et al.*, 2010), while, in case of macro algae, generally they are visible in naked eyes (Smith, 1944). The length of microalgae is basically from few micrometres to few hundred micrometres. But in terms of macro algae they are generally larger than microalgae having thallus like structure. According to various critical factors like pigmentation, thallus structure, reserve food material, flagellation and reproduction; algae are classified in different classes among which *Chlophyceae sp.*, *Cyanophyceae sp.*, *Rhodophyceae sp.*, *Bacillariophyceae sp.* and *Euglenophyceae sp.* are the most commonly found algae in aquatic environment (Benemann *et al.*, 1978). Algae are significant source of

important biomolecules, like (i) lipids, (ii) carbohydrates and (iii) proteins. Lipids and carbohydrates can be used as fuel precursors like biofuels, biodiesel and gasoline and proteins can be used as animal's nutrient (Ferrell and Valerie, 2010). Comparisons of oil yield between different feedstock for production of biofuel has been presented in Table 1. It was studied that microalgae are superior alternative as a feedstock for large scale biofuel production (Metting, 1996; Spolaore *et al.*, 2006). That's why microalgae biomass is preferred for the large scale -biofuel production.

CO₂ Sequestration and Fixation Using Algae

Cultivation of Micro Algal Biomass and Salient Features

Photosynthesis is the most promising process to store CO₂ in form carbohydrates using the solar energy and water. Microalgae have done their photosynthesis process in chloroplast of their cell. Photosynthesis process of sequestering CO₂ by algae may be harnessed either in (i) light dependent photosynthesis process (in this stage the light energy is harnessed and conserved in the form of ATP and NADPH by the chlorophyll and sun light harvesting compound) (ii) light independent photosynthesis process (ATP and NADPH are consumed in the time of carbohydrates synthesis). Algae production typically achieved by (i) Photo autotrophic where inorganic carbon and light are required, (ii) Heterotrophic where organic carbon and light are required in this mechanism and (iii) Mixotrophic mechanism where autotrophic photosynthesis and heterotrophic assimilation are required for production of microalgae.

Usually algae have been cultivated, in either open raceway ponds or closed photo-bioreactors system (Jiménez *et al.*, 2003a). Brennan and Owende (2010) have demonstrated raceway pond a closed loop and oval shaped recirculation channels as presented in Fig. 2. Horizontal tubular photo-bioreactor including arranged straight glass or plastic tubes can be shown in Fig. 3. Ugwu *et al.* (2008) The tubular array structure was made for better capturing of sunlight and to avoid microbial contamination and to assure pure algal cell growth within the system (Huntley and Redalje, 2007; Rodolfi *et al.*, 2009). In 2012, (Ketheesan and Nirmalakhandan, 2012) have considered an airlift-driven raceway reactor for microalgae culture to obtain highest CO₂ consumption. According to Cheng *et al.* (2006), it was observed that retention time of CO₂ has enhanced in photo bioreactor to enhance efficiency of CO₂ fixation. CO₂ fixation using microalgae through closed photo-bioreactors have been reported by several researchers (Fulke *et al.*, 2010; de Moraes and Costa, 2007; Chiu *et al.*, 2008; Giripunje *et al.*, 2013). Various microalgae species like *Chlorella vulgaris*, *Scenedesmus obliquus*, *Chlamydomonas reinhardtii*, *Spirulina sp.* and *Botryococcus braunii* were used for CO₂ fixation and sequestration (de Moraes and Costa, 2007; Chiu *et al.*, 2008; Giripunje *et al.*, 2013; Packer, 2009; Fulke *et al.*, 2013). Numerous numbers of research publications have established the importance of carbon capture using algal biomass and production of biofuels from microalgae as favourable and eco-friendly methodology for carbon dioxide sequestrations (Fulke *et al.*, 2010; Packer, 2009; Shekh *et al.*, 2013; Ramanan *et al.*, 2010, 2012).

Table 1 Comparisons of oil yield between different sources for production of biofuel

Feedstock	Oil yield (L/acre)
Soybean	181.68
Corn	68.13
Rapeseed	480.69
Sunflower	386.07
Canola	495.83
Oil palm	2403.47
Jatropha	788.33
Microalgae	19,000–57,000

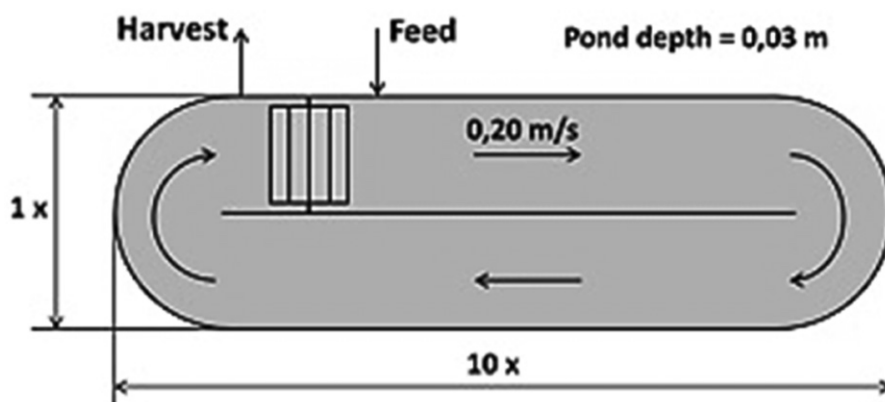


Fig. 2 Artificial system for microalgae cultivation arrangement in open raceway pond.

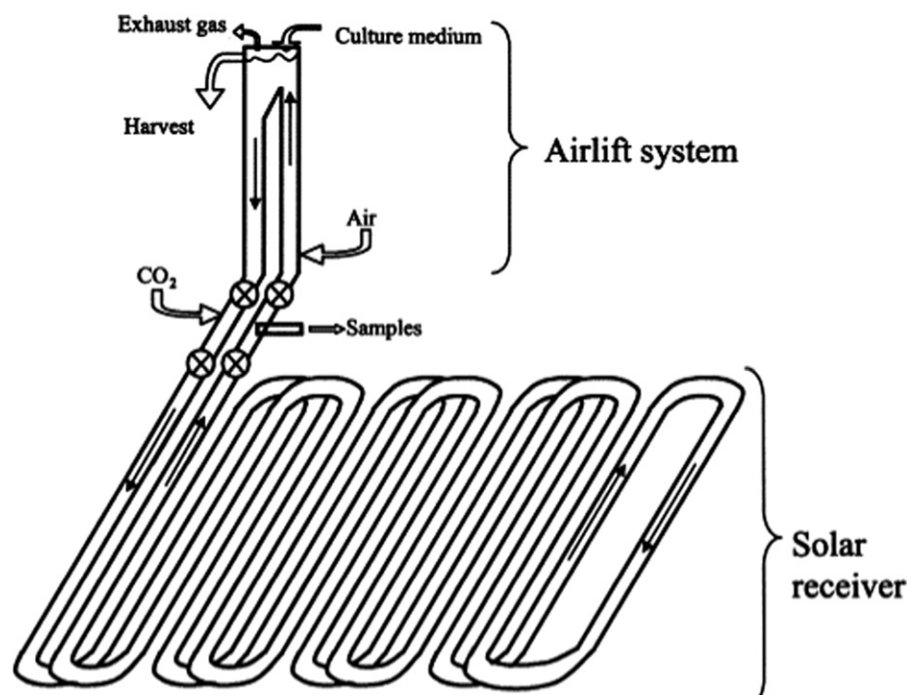


Fig. 3 Horizontal tubular photo-bioreactor including arranged straight glass or plastic tubes.

Table 2 Productivity of biomass and CO₂ fixation rate of different micro-algal species

Name of the algal species	Name and volume capacity of Photo-bioreactor	Biomass productivity from algae ($\text{mg L}^{-1} \text{d}^{-1}$)	CO ₂ Fixation rate using algae ($\text{mg L}^{-1} \text{d}^{-1}$)	References
<i>Aphanothece microscopica</i>	Bubble column (3.2 L)	301	562	Sydney <i>et al.</i> (2010)
<i>Anabaena sp.</i>	Bubble column	310	1450	Lopez <i>et al.</i> (2009)
<i>Chlorella vulgaris</i>	Bioflow fermentor (11 L)	129	252	Jacob-Lopes <i>et al.</i> (2009)
<i>Spirulina platensis</i>	Bioflow fermentor (11 L)	156	319	Jacob-Lopes <i>et al.</i> (2009)
<i>Nanno chloropsisoculata</i>	Cylindrical (0.8 L)	480	902	Chiu <i>et al.</i> (2009)
<i>Chlorococcum littorale</i>	Vertical tubular (20 L)	530	900	Kurano <i>et al.</i> (1995)
<i>Synechocystis aquaticlis</i>	Vertical flat plate (24 L)	78	128	Zhang <i>et al.</i> (2001)

Biofuel Production Using CO₂ Sequestered Algae

CO₂ Fixation Through Algal Biomass Production

The CO₂ is fixed in the growth period of algae through various processes such as formation of biomass, mineralization where atmospheric CO₂ can be converted to chemical compounds such as carbonates and bicarbonates and construction of extracellular products like polysaccharides, unstable organic compounds, various hormones and halogen containing organic compound (Sydney *et al.*, 2014). All of them, biomass formation is the key aspect, where 70% – 88% of total CO₂ fixation was created in the period of algal cultivation (Sydney *et al.*, 2014). Hence, the researchers have explored the potential of biomass for CO₂ fixation. The CO₂ fixation ability of microalgae have been summarized in Table 2.

Advantage and Disadvantages of Algal Biomass for Biofuels Production

Micro algal biotechnology has developed due to the pronounced multiplicity of products of algal biomass. Sustainability is the key factor in production of bioenergy, particularly the biofuels, as a part of future generation of fuel development from algal biomass. Some advantages and disadvantages of biodiesel production using algal biomass have been summarized in Table 3.

Table 3 Advantages and disadvantages of biofuel production using algal biomass

Aspects	Advantages	Disadvantages
Cost	It is made from renewable resources	Currently more expensive than other fossil fuel
Air pollution	Significant reduction of particulate matter (PM) emissions	Caused increases in nitrogen oxide (NO _x)
Greenhouse gas (GHG) emission	Significantly less harmful carbon (CO ₂ , CO) emission using algae	Reduction of fuel economy
Energy security	Viability of the first generation biofuel production	Conflicts with food supply
	Relatively less flammable compared to fossil diesel	Less suitable for use in low temperatures
Usage	Significantly improved lubricating properties	More likely than fossil fuel to attract moisture
	Significantly less harmful carbon emission compared to other fossil fuel	
Energy availability	Fossil fuel is a limited resource, but biofuels can be manufactured from a wide range of materials	Sometimes more fossil fuel energy was required to produce algal bioenergy. Few Life Cycle Analyses (LCA) from algal biomass have shown (–ve) energy balance

Note: Haines-Young, R., Potschin, M., 2010. The links between biodiversity, ecosystem services and human well-being. In: Raffaelli, D., Frid, C. (eds.) *Ecosystem Ecology: A New Synthesis*. Cambridge: Cambridge University Press, 110–139. Sharma, V., Ramawat, K.G., Choudhary, B.L., 2012. Biodiesel production for sustainable agriculture. *Sustainable Agriculture Reviews* 11, 133–160. Xue, J., Grift, T.E., Hansen, A., 2011. Effect of biodiesel on engine performances and emissions. *Renewable and Sustainable Energy Reviews* 15, 1098–1116. Tesfa, B., Gu, F., Mishra, R., Ball, A., 2014. Emission characteristics of a CI engine running with a range of biodiesel feed stocks. *Energies* 7, 334–350.

Factors Affecting Microalgae Growth for Biofuels Production

Several environmental factors which are affected the algal growth for production of biofuel. Energy such as light, carbon abundance, nutrient availability, environmental parameters like temperature, pH, salinity and inhibiting compounds have an impact on algal metabolism and shown in the [Table 4](#).

Harvesting of Algal Biomass for Production of Biofuel

For large scale biofuel of productions from microalgae, selection of efficient harvesting method is recognised as crucial point ([Amaro et al., 2011](#); [Uduman et al., 2010](#)). Selection of the suitable harvesting technique has great importance to the economics of biofuels production. The appropriate technique of harvesting depends on the several micro-algal characteristics like the density and size of algal cells as well as the product derived from the algal biomass ([Amaro et al., 2011](#)). Typical microalgae harvesting methodology involve two-steps. (i) Bulk harvesting, aims to separate micro-algal biomass from the bulk suspension which can be done by several physical methods like, flocculation, flotation, or gravity sedimentation with total solid algal biomass concentration of 2%–7% w/v ([Brennan and Owende, 2010](#)). (ii) Thickening, targets to concentrate the slurry with filtration and centrifugation process, requiring high energy of processing than bulk harvesting ([Brennan and Owende, 2010](#)). Several literatures have briefed the possibility of suitable harvesting strategies based on several unit operations like, centrifugation, sedimentation, flocculation, flotation and micro-filtration ([Amaro et al., 2011](#)). A comparative analysis between different methods of harvesting has been summarized in [Table 5](#).

Algal Biomass Conversion Into Biofuel

The major biofuel products from algal biomass are bioethanol, biodiesel, bio-hydrogen, and biogas ([Singh and Olsen, 2011](#)). In the conversion of biofuel, alcohols are derived from sugars fermentation or conversion of cellulosic biomass through a combination of hydrolysis and fermentation or gasification and synthesis, traditional biodiesel (mono-alkyl esters made from trans-esterification of vegetable or animal triglycerides), and synthesis fuels of alcohols and alkanes (gasoline, diesel) produced from gasification of biomass. Biofuels produced from algae and the respective yield values has been summarized in [Table 6](#).

Algal oil extraction from the biomass involves two steps, namely mechanical extraction and chemical extraction. Mechanical methods include, expression or expeller press and ultrasonic-assisted extraction. Crushing in conjunction with the chemicals also practiced for better extraction for some specific varieties with medium lipid content. The use of ultrasonic reactor (sonochemistry), greatly speed up the extraction processes.

In chemical extraction route, algal lipid extraction is assisted with use of solvents, like benzene, hexane and ether have been well recognised solvent system for extraction of lipid. The technique of hybrid pressing and solvent extraction process has been reported to increase the yield value of the lipid more than 95% of the total oil present in the algae. Supercritical CO₂ extraction method has been developed for extraction of lipid but being highly expensive not practiced industrially.

Table 4 Environmental factors affecting microalgae growth for biofuels production

Factor	Organism	Conditions	Result	References
Carbon Source	<i>Dunaliella salina</i>	CO ₂ concentration increased from 2% to 10% for 7 day	2.7 fold increase in fatty acid	Muradyan <i>et al.</i> (2004)
	<i>Chlorella zofingiensis</i>	under glucose concentration of 5–20 g L ⁻¹ in Heterotrophic culture	Maximum specific growth rate 0.031 h ⁻¹ at glucose concentrations of 20 g L ⁻¹	Ip and Chen (2005)
	<i>Spirulina platensis</i>	Elevated CO ₂ concentrations	Decrease in proteins content and also pigments and increase in carbohydrate content;	Gordillo <i>et al.</i> (1998)
Temperature	<i>Botryococcus braunii</i>	Increased from 25 to 32°C	Decrease in intracellular lipid content from 22% to 5% (dry weight) with significant accumulation of polysaccharides	Kalacheva <i>et al.</i> (2002)
	<i>Chlorella vulgaris</i>	Increased from 20 to 38°C	Decrease in starch component resulting in increase in sucrose	Nakamura and Miyachi (1982)
		Increased from 10 to 38°C	Transformation of L starch (high molecular weight) to S starch (low molecular weight) reversible with temperature	Nakamura and Imamura (1983)
	<i>Haematococcus pluvialis</i>	Increased from 20 to 30°C	3-times increase in fatty acid formation	Tjahjono <i>et al.</i> (1994)
	<i>Nitella mucronata Miquel</i>	Increased from 5 to 20°C	Increase in velocity of cytoplasmic streaming	Raven and Geider (1988)
	<i>Dunaliella viridis</i>	Darkness (No light)	Increase in total lipid content Decrease in free fatty acids, alcohol, sterol	Gordillo <i>et al.</i> (1988)
	<i>Chlorococcum sp</i>	Temperature increase from 20 to 35°C under nitrogen deprivation	Two fold increase in total carotenoid content	Liu and Lee (2000)
Light	<i>Porphyridium cruentum</i>	Red light	Enhanced Photosystem II relative to Photosystem I and phycobilisome	Cunningham <i>et al.</i> (1990)
	<i>Nannochloropsis sp.</i>	Light limited conditions	Increase in lipid content	Sukenik <i>et al.</i> (1989)
	<i>Chlorella vulgaris</i>	Red light	Increase in sucrose and starch formation	Miyachi and Kamiya (1978)
		Blue light	Increase in lipid fraction and alcohol–water insoluble non carbohydrate fraction	
pH	<i>Chlamydomonas acidophila</i>	pH 4.4	Denaturation of V-lysin	Visviki and Palladino (2001)
	<i>Coccochloris penicystis</i>	pH decreased from 7.0 to 5.0 and 6.0	Decrease in total accumulated carbon and oxygen evolution	Coleman and Colman (1981)
Effect of reaction time	<i>Spirogyra</i>	higher the reaction time 10 to 25 min	The higher yield (above 95%) was obtained at 25 min of reaction time.	Shah <i>et al.</i> (2015)
Nitrogen source	<i>Nannochloropsis oculata</i>	75% decrease in Nitrogen	Increase in lipid synthesis from 7.90% to 15.31%	Converti <i>et al.</i> (2009)
	<i>Chlorella vulgaris</i>	75% decrease in Nitrogen	Increase in lipid synthesis from 5.90% to 16.41%	Converti <i>et al.</i> (2009)
	<i>Phaeodactylum tricornutum</i>	Nitrogen limitation	Increase in lipid synthesis; Decrease in protein content	Morris <i>et al.</i> (1974)
	<i>Haematococcus pluvialis</i>	Nitrogen limitation	Increase in carotenoid formation (13% w/w)	Borowitzka <i>et al.</i> (1991)
phosphorus concentration	<i>Chlamydomonas reinhardtii</i>	Limitation of phosphorous	Decrease in phosphatidylglycerol	Sato <i>et al.</i> (2000)
	<i>Ankistrodesmus falcatus</i>	Limitation of phosphorous	Enhance in carbohydrate and lipids	Healey (1982), Healey and Hendzel (1979)
	<i>Selenastrum minutum</i>	Starvation	Reduced rate of respiration; Decreased photosynthetic CO ₂ fixation	Theodorou <i>et al.</i> (1991)
Iron concentration	<i>Dunaliella tertiolecta</i>	Limitation	Decrease in cellular chlorophyll concentration	Greene <i>et al.</i> (1992)
	<i>Chlorella vulgaris</i>	High concentration of iron	Increase in lipid content	Liu <i>et al.</i> (2008)
	<i>Haematococcus pluvialis</i>	High concentration of iron was required	Increase in carotenoid formation	Kobayashi <i>et al.</i> (1993)

(Continued)

Table 4 Continued

Factor	Organism	Conditions	Result	References
Salinity	<i>Dunaliella tertiolecta</i>	increased in NaCl concentration from 0.4 to 4 M	Increased in saturated and mono unsaturated fatty acids	Xu and Beardall (1997)
		increased in NaCl concentration from 0.5 to 1.0 M was observed	Increase in intracellular lipids (60% to 67%) and triglyceride concentration (40% to 56%)	Takagi and Yoshida (2006)
	<i>Tetraselmis suecica</i>	High salinity	reduction in protein content per cell of up to 20% with increasing salinity	Fabregas <i>et al.</i> (1984)

Table 5 Comparative analysis between different methods of harvesting

Harvesting method	Advantages	Disadvantages
Filtration	(1) High recovery efficiency of biomass (2) Can be scaled up (3) Easy for bulk harvesting	(1) Fouling of membranes (2) Energy intensive process
Coagulation flocculation	(1) High efficiency (2) Simple and easy to establish (3) Sustainable and low in energy input	(1) Chemical flocculants cause accumulation of harmful compounds in biomass. (2) Not suitable for high value added products
Screening	(1) Methods of screening are very simple (2) Easy to operate	(1) Clogging of screens due to micro-algal slime (2) High operational cost
Gravity sedimentation	(1) Cost effective process (2) Easy to operate (3) Bulk harvesting	(1) Slow rate of separation (2) Not suitable for very small microalgae
Centrifugations	(1) Highly efficient process (2) Up to 98% recovery of biomass (3) Can be scaled up	(1) Energy intensive process (2) High maintenance costs
Floatation	(1) Simple and effective process (2) Can be made efficient in combination with other harvesting methods	(1) Low harvesting efficiency (2) Some methods may damage the cells
Ultra-sonication	(1) Simultaneous recovery of product possible (2) Easy to operate (3) Can be scaled up	(1) Energy intensive process (2) May lead to damage of cells
Electrophoresis	(1) High efficiency (2) Combines different methods (3) Scale up not possible	(1) Energy intensive process (2) Non-sustainable

Note: Amaro, H.M., Guedes, A.C., Malcata, F.X., 2011. Advances and perspectives in using microalgae to produce biodiesel. *Applied Energy* 88(10), 3402–3410. Uduman, N., Qi, Y., Danquah, M.K., Hoadley, A.F., 2010. Marine microalgae flocculation and focussed beam reflectance measurement. *Chemical Engineering Journal* 162, 935–940.

Table 6 Biofuel produced from algal biomass and respective oil yield value

Algal species	Product	Oil yield
<i>Chlorella vulgaris</i>	Biogas	0.63–0.79 LCH ₄ /gVS
<i>Scenedesmus obliquus</i>		0.59–0.69 LCH ₄ /gVS
<i>Chlorella protothecoides</i>	Bio-oil	57.9%
<i>Dunaliella tertiolecta</i>		43.8%, 34 MJ/Kg
<i>Chlamydomonas reinhardtii</i> (CC124)	Biohydrogen	102 mL/1.2 L
<i>Platymonas subcordiformis</i>		11,720 nL/h
<i>Chlorella pyrenoidosa</i>	Carbohydrates content for bioethanol	26%
<i>Porphyridium cruentum</i>		40%–57%
<i>Botryococcus braunii</i>	Lipid content for Biodiesel	25%–75%
<i>Nitzschia sp</i>		45%–47%

Note: Singh, A., Olsen, S.I., 2011. A critical review of biochemical conversion, sustainability and life cycle assessment of algal biofuels. *Applied Energy* 88, 3548–3555. Chisti, Y., 2007. Biodiesel from microalgae. *Biotechnology Advances* 25, 294–306. Das, D., Veziroglu, T., 2008. Advances in biological hydrogen production processes. *International Journal of Hydrogen Energy* 33, 6046–6057. Gouveia, L., Oliveira, A.C., 2009. Microalgae as a raw material for biofuels production. *Journal of Industrial Microbiology and Biotechnology* 36, 269–274. Marcià, A., Catalá, L., García-Quesada, J.C., Valdés, F.J., Hernández, M.R., 2013. A review of thermochemical conversion of microalgae. *Renew Sustain Energy Review* 27, 11–19. Oncel, S.S., 2013. Microalgae for a macroenergy world. *Energy Review* 26, 241–264. Ramos-Suárez, J.L., Carreras, N., 2014. Use of microalgae residues for biogas. Production. *Chemical Engineering Journal* 242, 86–95. Demirbas, M.F., 2011. Biofuels from algae for sustainable development. *Applied Energy* 88, 3473–3480.

Large Scale Micro Algal Cultivation for Production of Biofuels

Open Pond System for Algal Culture

In 1890, Beijerinck *et al.* (Borowitzk, 1999) has studied the physiology of the plants using the first unialgal cultivation with the microalgae *Chlorella vulgaris*. In Germany algal cultivation has been increased using open ponds for food supplement in the time of Second World War. Most industrially applied cultivation systems are open pond system because of its low cost of investment and working capital. Fig. 4 is the schematic presentation of the open pond system. Although these systems have severe problems associated with control of working environments hence, causes lower biomass productivity and highly susceptible to microbial contaminants from other (Suh and Lee, 2003). Closed photo bioreactors have been reported to produce improved biomass yield value with high efficiency of photosynthesis compared to the open pond system. The most commonly used open pond systems include either raceway ponds or circular ponds (Suh and Lee, 2003; Chiaramonti *et al.*, 2013; Kumar *et al.*, 2015). The sump-assisted raceway ponds have been designed for improved CO₂ - liquid contact period. In this system, CO₂ gas was injected in the counter-current direction to increase the liquid/gas contact time. Since the gas was introduced at the bottom of the sump having greater depth, it preferentially allows an enhanced contact time of gas phase and liquid phase. Better CO₂ utilization efficiency and minimization of the CO₂ loss into the atmosphere has been achieved by this system (Kumar *et al.*, 2015; Mendoza *et al.*, 2013; Craggs *et al.*, 2012). de Godos *et al.* (2014) have reported the biomass productivity through the sump-assisted raceway pond as 17 g m⁻² d⁻¹ with approximately 66 % capturing CO₂ from the inlet gas stream. For further enhancing the period of CO₂ liquid contact, atmospheric air was used to flow and produce velocity of the liquid (de Godos *et al.*, 2014). Lam *et al.* (2018) have published a review highlighting different strategies to control the biological contamination during microalgae cultivation in open pond. Baldev *et al.* (2018) have presented a research article highlighting the prospect of the open raceway pond system for culture of *Chlorella vulgaris* as resource material for biodiesel production.

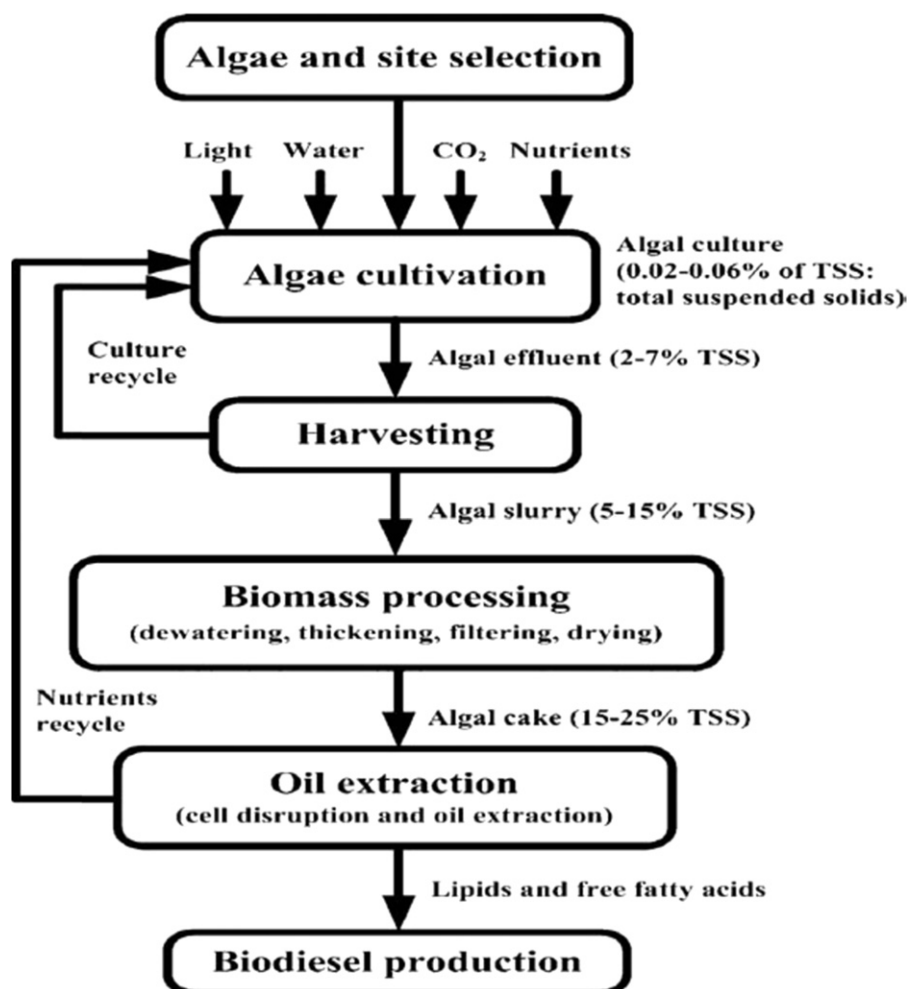


Fig. 4 Schematic representation of the biofuel production from algal biomass.

Closed Pond System and Photobioreactor for Algal Culture

Closed pond system algal culture has been studied in large scale to produce algal biofuel. In closed ponds system the control over the environment being easier than open ponds reduces the chance of contamination but at the expense of reduced light penetration, which affects the cultivation process. Though its initial construction cost is much higher than the open pond system but comparatively lower than photobioreactor. The idea behind the closed pond is to close it off, to cover a pond or pool with a greenhouse. While dimensionally it results smaller system, but evades many of the problems associated with open system. Closed system allows more species to be grown, allows the species that are being grown to stay dominant, and it extends the growing season, only slightly if unheated, and if heated it can produce year round. These systems having the provision of increasing the amount of CO₂ facilitating the algae growth rate.

Photobioreactor (PBR) is closed equipment which provides a controlled environment and enables high productivity of algae. As it is a closed system, all growth requirements of algae are introduced into the system and controlled according to the requirements. PBRs facilitate better control of culture environment such as carbon dioxide supply, water supply, optimal temperature, efficient exposure to light, culture density, pH levels, gas supply rate, mixing regime. Photobioreactors also offer some other advantages like potential for much higher productivity, large surface-to-volume ratio, maximum efficiency in using light and therefore greatly improve productivity (typically the culture density of algae produced is 10–20 times greater than close pond), better control of gas transfer, reduction in evaporation of growth medium, uniform temperature control, space saving (may be placed vertically, horizontally or at an angle, indoors or outdoors), tube self-cleaning mechanisms can dramatically reduce fouling. An enclosed PBR design will enhance commercial algal biomass production by keeping algae genetics pure and reducing the possibility of parasite infestation. Some major limitations in commercialization of the PBR high capital cost, the productivity and production cost in some enclosed photobioreactor systems are not much better than those achievable in open-pond cultures, difficulty in sterilizing these photobioreactors. Design of an ideal high performance PBR involves (i) minimization of the volume of the non-illuminated parts of the reactor, (ii) the design must provide for the uniform illumination of the culture surface and the fast mass transfer of CO₂ and O₂, (iii) mechanical cleaning or sterilization for prevention of fouling of light-transmitting surfaces, (iv) energy consumption required for mass transfer and the arrangement of the light-receiving surface of the algal suspension must be reduced to its minimum possible. Moreover, the commercial microalgae cultivation system depended on growth pattern of algal species for biofuels production are given in Table 7.

Advanced Technologies to Improve Algal Biofuels Production

Utilization of microalgae in bioenergy production have the probability to meet the requirement of a technically and economically viable biofuel resource, because it is economically viable than petroleum fuels, requires no additional land use, enables air quality improvement (e.g., CO₂ sequestration). Microalgae were evaluated as a potential fuel source till 1970s, but the lack of technical knowledge and the production cost have dejected the commercial microalgae-based biodiesel production. The important technical barriers, such as slow growth rate, low biomass production and low lipid contents, need to be overcome before microalgae can be used as an economically viable biofuel feedstock. Hence to make the algal fuel system technologically sound and feasible researchers are concentration on the advanced technologies with an aim to get more biomass and the fuel material from the algal system. To improve the yield value of the of the fuel material (lipid content) of the algae, there different technical modifications have been attempted so far; the first one is the application of genetic engineering approach to improve the lipid yield in algal biomass. The second approach is controlling of the metabolic pathways in microalgae for more biomass and lipid production, and to control the environmental parameters to improve the protein and lipid content of the algae. This section aims to present the effect technological advancement on algal culture and biofuel production.

Genetic Modification of Algae

Application of genetic engineering concept to improve the yield of algal biomass has been studied by several researchers. This section highlights the role of genetic engineering as an ultimate solution of the associated technical problems and also the future prospective of microalgae based biodiesel. Application of genetic engineering approach has been recognised as the best strategy to develop biofuel

Table 7 Growth pattern of different algal strains at mass cultivation prospect

Cultivation system	Name of the algal species	% of Lipid content	Biomass formation	Reference
Raceway pond	<i>Nannochloropsis gaditana</i>	22	19.9 (g m ⁻² d ⁻¹)	Nurra <i>et al.</i> (2014)
	<i>Botryococcus braunii</i>	48.4	1.9(g L ⁻¹)	Ashokkumar <i>et al.</i> (2014)
	<i>Spirulina platensis</i>	–	13.5 (g ⁻² d ⁻¹)	Jiménez <i>et al.</i> (2003b)
Photobioreactors	<i>Chlorella zofingiensis</i>	54.5	58.4 mg L ⁻¹ d ⁻¹	Rodolfi <i>et al.</i> (2009)
	<i>Nannochloropsis sp.</i>	60	0.30 (g L ⁻¹ d – 1)	Feng <i>et al.</i> (2011)
	<i>Chlorella sp</i>	–	4.3 g L ⁻¹ d ⁻¹	Doucha and Lívanský (2009)

production from microalgae in a cost effective way. Due to the absence of cell differentiation, the genetic manipulations of microalgae have become a much simpler system compared with higher plants. Substantial developments in micro algal genomics have been achieved through in depth researches like, an expressed sequence tag (EST) database has been developed, nuclear, mitochondrial, and chloroplast genomes from several microalgae have been sequenced. The knowledge of microalgae genome sequences has greatly simplified the genetic manipulation, and easy access to microalga research. Research publications have summarized several nuclear genome sequencing ventures on a broad range of microalgae (Radakovits *et al.*, 2010). Details on genetic transformation of the microalgae for biofuel production have been reported elsewhere (Radakovits *et al.*, 2010).

Genetic Engineering and Lipid Metabolism

The precursor of biodiesel from algae is the lipid content. The variation in lipid content from various species has driven the research on improvement of the lipid content by controlling the lipid metabolic pathway. The quantity and quality of diesel precursors from algal strain are closely linked to lipid metabolism. This field of research is still at the stage of infancy and lipid biosynthesis, catabolism, the pathway to modify the length and saturation of fatty acids, have not been as thoroughly investigated for algae. The transgenic overexpression strategies have resulted in the increased production of triacylglycerol in seeds and in other plant tissues like soy bean (*Glycine max*), and rapeseed (*Brassica napus*). Since the overexpression strategies to increase storage lipid content was not effective for algal species, an alternative approach have been suggested and reported by a group of researchers based on blocking of metabolic pathway approach. Another approach of increasing the cellular lipid may be achieved by blocking the metabolic pathways which ultimately lead to the accumulation of energy-rich storage compounds, like starch. Starch-deficient strain *C. reinhardtii*, have disruptions in the ADP-glucose pyrophosphorylase and accumulate increased levels of TAG during nitrogen deprivation. Overexpression of the lipid biosynthesis genes (encoding acetyl-CoA carboxylase) and a plant thioesterase, have reportedly to result 20-fold increase in free fatty acid production of *E. coli*, by decreasing lipid catabolism. Inactivation of gene responsible for activation of both TAG and free fatty acids, and those genes involved in β -oxidation of fatty acids, has also reported to increase cellular lipid content.

Another strategy of increasing the biofuel production from algal cell can achieve by modification of lipid characteristics specifically to increase the quality of the lipid with regard to suitability as a diesel fuel feedstock. The carbon chain length and degree of unsaturation of the fatty acids from microalgal species significantly affect the cold flow and oxidative stability properties of biodiesel fuel. Usually, fatty acids from most microalgae offer chain length between 14 and 20, higher percentage being, 16:1, 16:0, and 18:1 fatty acids. Typically, C_{12:0} and C_{14:0} fatty acids are recognised as ideal fatty acids for diesel production. Fatty acid's chain lengths are controlled by acyl-ACP thioesterases activity. There are several acyl-ACP thioesterases from a variety of organisms that are specific for certain fatty acid chain lengths, and transgenic overexpression of thioesterases can be used to change fatty acid chain length. Results have shown that expression of a 12:0-biased thioesterase from *Umbellularia californica* in both *A. thaliana* and *E. coli* drastically have changed the lipid profiles with a great increase in the production of lauric acid (C_{12:0}). Publications have also presented that 14:0-biased thioesterase from *Cinnamomum camphorum* after expressed in *A. thaliana* and *E. coli*, have resulted significantly increased production of myristic acid C_{14:0}. Hence, application of 'thioesterases' for transgenic overexpression in microalgae could improve the suitability of microalga-derived diesel feedstock. Some fatty acids with shorter chain lengths have been recognised as gasoline and jet fuel. Researches have claimed that genetically engineering microalgae directly produce shorter chain lengths of fatty acids. Transgenic overexpression of an 8:0- and 10:0-biased thioesterase from *C. hookeriana* in canola seed has been reported to increase production of short chain fatty acids. Hence the knowledge of gene characteristics, metabolic pathways can effectively be employed for getting more lipids and the fuel precursor from call biomass. Sometimes environmental stress also helps in lipid synthesis hence by creating stress condition in the environmental factors lipid storage in algal biomass have been enhanced. Shortage of nitrogen lowers the proliferation rate consequently energy storage products are produced.

Reutilization of Algal Biomass

In biofuel production process after removing of oil and starch from the microalgal biomass remaining biomass can be used as methane and feed for cattle, used as biofertilizer because of its higher N: P ratio (Wang *et al.*, 2008). Algal biomass has potential application in removing heavy metals, uranium, toxic chemicals and other impurities from wastewater and they can also degrade poisonous poly aromatic hydrocarbons which is usually mixed with petrochemical effluent. Nowadays, the extreme concern in agricultural field is the use of chemical fertilizers which harm the soil and vegetation and algal biomass can resolve the issue serving as green manure. Algal biomass helps in nitrogen fixation, and various microalgae species like Nostoc, Anabaena, Oscillatoria, Cylandrosperrun fix nitrogen by aerobic digestion process and used as biofertilizers (Singh *et al.*, 2016). Algal biomass can be used as bio pigments. Three main pigments namely, chlorophyll (blue light), red carotenoids (blue light and green light) and can be absorbed by phycobilins (green, yellow, and orange light) have been used as natural pigment in food industry. *Phycocerythrin* and *phycocyanin* has pigments which can be provided natural colours in food, pharmaceutical drug, and cosmetics to avoid the carcinogenic synthetic colour (Richmond, 1990). Algal biomass has been used as precursor of antibiotics like acrylic acid found in *Phaeocystis poucht*, which are capable in preventing the growth of gram-positive micro-organisms. The extracts of the diatom species such as *Asterionella notata* has an antifungal and antiviral activity. Toxic algae have been utilized as a depressant vessel (Richmond, 1990). Algal biomasses have also been attempted as biopolymers to produce decomposable plastics depending

on the ecological environments (Jau *et al.*, 2005). The algal biomass having immense value to utilise and need proper exploration for unique green applications like, zooplankton enrichment, bio-energy technology, bio-fertilizer, molecular farming, bioremediation of water and soil and over all environmental protection with green approach. Globally algae are responsible for 50% of the production of photosynthetic biomass and they are abundant feed sources of biofuels.

Conclusion and Future Prospect

Algal biofuels have excellent impact on environmental protection, social and economic sustainability. The bio refinery of algae was aimed for production of an extensive range of biofuels from algal biomasses with reduced environmental pollution at low expense. Biofuel production from algae should assimilate other ecologically sustainable technologies like carbon sequestration, toxic oil degradation from petrochemical industry and the purification of toxic water from agricultural wastes and produced valuable products. Several biofuels can be generated from liquid fuels such as bioethanol, biodiesel, green diesel and jet fuel and biogas, syngas and bio-hydrogen and other gas fuels which can be used in industries and as feedstock for refineries. To frame algae-to-energy systems in reality, substantial research need to be continued in different aspects like, genetic improvements, bio refinery and microbial fuel cell concept development, and integration of alternative energies to CO₂ treatment systems. This algal technology offers a safe and sustainable solution to the problems associated with global warming.

Though algal biofuel is a promising bioenergy source but production of biofuel from algal is too lavish to be commercialized due to the static cost during oil extraction process and biofuel processing and the variability of algal-biomass production. Moreover, utilization of the microalgae for producing value-added products and integration with chemical technologies have now been designed to reducing the cost of algal-biofuel production as future technological development.

See also: Biomass for CO₂ Sequestration

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Co-Firing of Biomass to Reduce CO₂ Emission

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Introduction

Co-firing is the process of burning two different types of fuel simultaneously to generate heat or electricity. Co-firing is generally done to get environmental benefit by using renewable energy without significant cost involvement. Coal is the mostly used fossil fuel in the world and combustion of coal emits greenhouse gases (GHG) which are considered to be detrimental to the Earth's atmosphere. Among these different gases, CO₂ is considered to be contributing the most because of two factors: (i) CO₂ represents the largest emissions of all global anthropogenic GHG emissions and (ii) CO₂ has a very high residence time in the atmosphere. Whereas, biomass is renewable energy source and it does not add net CO₂ to the atmosphere because plants as source of biomass consumes the same amount of CO₂ from the atmosphere during growth as is released during combustion. Therefore, use of biomass with coal for energy production will reduce CO₂ emissions by substituting coal feed with a renewable fuel. Recently, the interest in co-firing has grown due to increasing concern about global warming and GHG emissions leading to new policies on energy and the environment to reduce emissions. Co-firing is regarded as the most attractive option for replacing coal used for power generation with renewable fuels at lower costs to result in direct decrease of greenhouse gas emissions. There are many advantages of co-firing of biomass in coal based power plants and some of the important advantages are discussed below (Verma *et al.*, 2017).

- Co-firing of biomass is the easiest way to increase the use of biomass for power generation
- Co-firing of biomass to the existing coal fired power plants can be done with little modification which implies little investment cost
- Opportunity of using different biomass materials with coal which can diversify the fuel portfolio in existing coal fire power plants
- In case of coal shortage, import substitution with biomass will significantly improve the economy of the nation
- It will lower the CO₂ emission by saving the fossil fuels
- It will also reduce other airborne emission like NO_x and SO_x because most of the biomass contain less amount of nitrogen and sulphur
- It will provide energy security to the nation by producing electricity from locally available fuel like biomass
- Growing of biomass as energy crops will add value to barren lands, improve the landscapes, conserve soil resources and reduce the need for water and fertilizers

Co-firing of biomass is more cost-effective in combined heat and power (CHP) plants which generate electricity and useful thermal energy. CHP, also known as cogeneration, is often used in industrial facilities where there is specific demand for both heat and power. The economics of biomass co-firing is increased when it is used in CHP plants because of higher overall efficiency in CHP compare to normal power plants. Co-firing of biomass to the existing coal based power plants yields negative CO₂ emission to the atmosphere when it is combined with carbon capture and storage (CCS) technology.

Though, the co-firing of biomass has many advantages, it has also some disadvantages which are discussed here. Moisture content of raw biomass is high which may reduce the thermal efficiency of the plant. Ash content in biomass is also high which may lead to the ash deposition on heat exchange surfaces. Chlorine from biomass can accelerate corrosion of combustion system and flue gas cleanup components particularly at high temperature. Besides, the availability of biomass varies with season. However, there is no renewable energy source other than biomass which is chemically as fit as fossil fuel. Almost all biomass fuels can be used in coal based power plants according to the available resources near to the power station.

Power generation by co-firing of biomass to the existing coal based power plants are increasingly gaining importance because it gives the opportunity to replace our precious fossil fuels partially, which may gives extensive support to the growth of power sector. Compare to dedicated biomass based plants, the addition of biomass to the high efficiency coal-fired power plants can greatly increase the efficiency of utilizing biomass (Baxter, 2005). Besides, the cost of retrofitting an existing coal-fired power plant for biomass co-firing is significantly lower than building a new dedicated biomass based power plant (Spliethoff and Hein, 1998). Therefore, research on co-firing of coal and biomass increased considerably during the last few decades which provide very diverse solutions for biomass co-firing with a limited impact on efficiency, operation and lifespan.

This article provides a concise review on co-firing of coal and biomass. Different technical issues like co-firing types, co-firing reactors and effect of fuel characteristics are discussed in detail. In addition, the effect of co-firing of biomass on the GHG emission is also discussed.

Theory of Co-Firing

The basic idea of co-firing of biomass with coal is to replace certain amount of thermal energy input from coal with the same amount of thermal energy input from biomass. Biomass can be utilized in three different ways for providing thermal energy input to the existing coal fire plants. If biomass is combusted directly with coal then it is called direct co-firing. When biomass is converted to fuel gas in a gasifier and subsequently the fuel gas is combusted in the coal furnace then it is called in-direct co-firing. If biomass and coal are combusted in separate furnaces and generate steam separately then it is called parallel co-firing. Direct co-firing is the simplest way which requires minimal investment. But, parallel and indirect co-firing methods are more suitable for biomass materials which have issues in combustion or when the ash quality is of importance for subsequent sale or disposal. These methods of co-firing of coal and biomass are discussed in detail below.

Direct Co-Firing

In direct co-firing, combustion of coal and biomass takes place simultaneously at the same combustion chamber or furnace. Direct co-firing can be done either by pre-mixing coal and biomass and injecting the mixture to the coal handling system or directly injecting them (without physical mixing) into the pulverize coal firing system. In case of pre-mixing, coal and biomass can be mixed either before milling or after milling. In case of direct injection, coal and biomass are burned either using separate burners or combined burners depending principally on the biomass fuel characteristics. Direct co-firing is the simplest and least expensive method of co-firing. Hence, it is the most commonly applied co-firing configuration reported so far. However, the direct co-firing systems are more sensitive to variations in fuel quality and heterogeneity. Ash deposition and corrosion usually increase with the use of biomass which may shorten the lifespan of devices in contact with flue gas. Therefore, the amount of biomass which can replace the coal is limited by the type of biomass to be used. In direct co-firing, approximately 3%–5% of biomass could be co-fired with coal without significant investment costs. However, the co-firing percentage may raise upto 20% when cyclone boilers are used, although the best results are achieved with pulverized coal fires boilers (Basu *et al.*, 2011). The method of direct co-firing is shown schematically in Fig. 1. In most cases, the biomass thermal input in direct co-firing schemes is around 10% owing to technical and economic constrain (Karampinis *et al.*, 2014).

Indirect Co-Firing

In indirect co-firing system, coal and biomass are not burned in the same furnace. It is relatively complex in arrangement and expensive compare to the direct co-firing system. Indirect co-firing can be carried out in different ways. Biomass may be burned in a separate system and the flue gas is injected to the original coal boiler or burning coal and biomass in separate systems and both the systems couple their heating fluid circuits with separate exhaust gas treatment or biomass may be converted into fuel gas in a gasifier and then passing the fuel gas through the coal boiler. The most suitable gasification technology for indirect co-firing is fluidized bed gasification either in the form of bubbling fluidized bed gasification or circulating fluidized bed gasification, since they permit the use of a wide range of biomass fuels. Indirect co-firing reduces the problems associated with corrosion, fouling and slagging as the biomass is not fed directly to the furnace. Therefore, indirect co-firing system has the advantage of better fuel flexibility than direct co-firing and it also allows larger amount of biomass co-firing than direct system. Since, biomass and coal are converted separately, different conversion systems like fluidize bed system for biomass and pulverize system for coal can be used. Biomass materials which are relatively difficult to handle for combustion because of high alkali and chlorine contents can be used here because biomass and coal ashes are kept separately. A typical indirect co-firing system is shown schematically in Fig. 2.

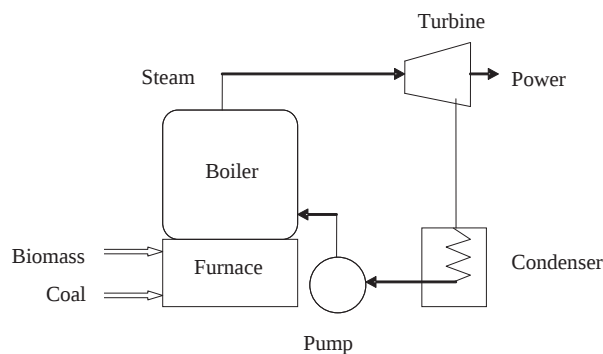


Fig. 1 Schematic diagram of direct co-firing.

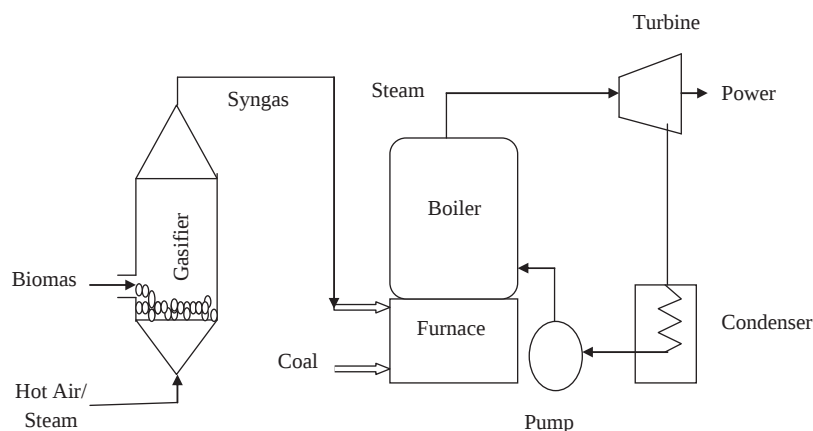


Fig. 2 Schematic diagram of indirect co-firing.

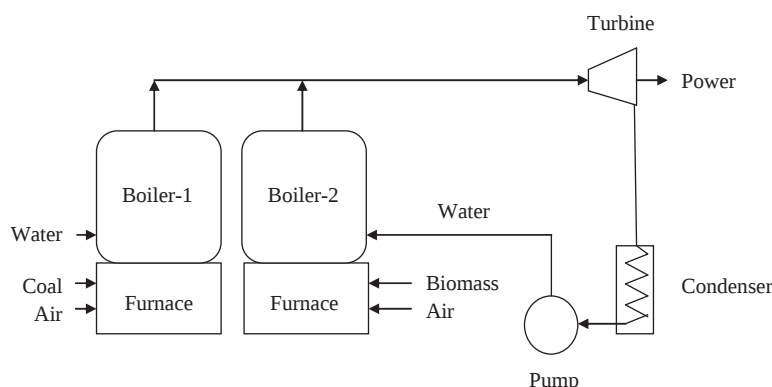


Fig. 3 Schematic diagram of parallel co-firing.

Parallel Co-Firing

In parallel co-firing, separate combustion chambers and boilers are used for coal and biomass. Steam produce by both the boilers are fed into the main power plant system where steam is upgraded to higher temperatures and pressures to give higher energy conversion efficiencies. Therefore, the fuel preparation and feeding system is physically independent here. Parallel co-firing system offers more opportunity for using higher percentages of biomass fuels compare to the direct and the indirect co-firing systems (Thompson, 2006). Here, the maximum amount of energy that can be generated from biomass will depend on the downstream infrastructure of the existing plant such as steam turbine. Like indirect co-firing, biomass ash is separated from coal ash in parallel co-firing which allows using a wide variety of biomass. However, parallel co-firing system is much more expensive than direct and indirect co-firing systems because of additional infrastructure requirement. Parallel co-firing technique is mostly used in paper and pulp industries. The schematic diagram of a typical parallel co-firing is shown in Fig. 3.

These different methods of co-firing of biomass are studied by many researchers experimentally and also implemented commercially in a number of plants. These commercial plants are mainly located in Europe and United States. However, some units are also located in Asia and Australia. Some of the commercial plants where biomass is co-combusted with coal either by direct co-firing method or by indirect co-firing method or by parallel co-firing method are listed in Table 1.

Fuel Characteristics and Their Effect on Co-Firing

Coal and biomass have different fuel properties. These differences in fuel characteristics affect the performance of the co-firing boiler. Ultimate and proximate analysis of coal and different biomass are listed in Table 2. The main differences between coal and biomass properties are listed here.

- Biomass generally contains more moisture than coal
- Biomass contains large amount of volatiles matter compare to coal

Table 1 Notable commercial co-firing plants

<i>Co-firing plant</i>	<i>Type of co-firing</i>	<i>Biomass used</i>	<i>Capacity</i>	<i>Boiler type</i>
Gelderland Power Station, Netherlands	Direct	Wood waste	635 MWe	Pulverized
Wallerawang Power Stations, Australia	Direct	Wet sawdust	–	–
Vales Point Power Stations, Australia	Direct	Wood chips	–	Pulverized
Studstrup Power Plant, Denmark	Direct	Straw	150 MWe and 350 MWe	Pulverized
St Andra Power Plant, Austria	Direct	–	124 MWe	Pulverized
Zeltweg Power Plant, Austria	Indirect	Wood	137 MWe	Pulverized
Amer Power Plant, Netherlands	Indirect	–	600 MWe	Pulverized
Avedøre Power Plant, Denmark	Parallel	Straw	430 MWe	–
Soma Power Plant, Turkey	Direct and Parallel	Olive pits	165 MWe	Pulverized
Atikokan, Station, Ontario, Canada	Direct	Wood	227 MWe	Pulverized
Lambton Station, Ontario, Canada	Direct	Dry distillers and grain	500 MWe	Pulverized
Nanticoke, Station, Ontario, Canada	Direct	Agricultural residues	500 MWe	Pulverized
Mount Poso Cogeneration Plant, Bakersfield, California, USA	–	Urban and agricultural wood waste	44 MWe	–
Schiller Station, Portsmouth, New Hampshire, USA	–	Wood chips	50 MWe	Fluidized Bed
Bay Front Station, Ashland, Wisconsin, USA	–	Waste wood	75 MWe	–
Charter St. Heating Plant, Madison, Wisconsin, USA	–	Variety of biomass	Heating Plant	–

Source: Penninks, F.W.M., 2000. Coal and wood fuel for electricity production. In: Proceedings of the EU Seminar on the Use of Coal in Mixture With Wastes and Residues II, Cottbus. Mory, A., Tauschitz, J., 2000. BIOCOMB – Gasification of biomass and co-combustion of the gas in a PF boiler in Zeltweg power plant. In: Proceedings of the EU Seminar on the Use of Coal in Mixture With Wastes and Residues II, Cottbus. Willeroer, W., 2000. Amergas biomass gasifier starting operation. In: Proceedings of the EU Seminar on the Use of Coal in Mixture With Wastes and Residues II, Cottbus. Amirabedin, E., McIlveen-Wright, D., 2013. A feasibility study of co-firing biomass in the thermal power plant at soma in order to reduce emissions: An exergy approach. International Journal of Environmental Research 7, 139–154.

Table 2 Proximate and Ultimate analysis of different biomass and coal

<i>Fuel</i>	<i>Proximate analysis</i>				<i>Ultimate analysis</i>				
	<i>Volatiles</i>	<i>Fixed carbon</i>	<i>Moisture</i>	<i>Ash</i>	<i>C</i>	<i>H</i>	<i>O</i>	<i>N</i>	<i>S</i>
Indian coal	20.70	63.50	5.98	38.63	78.20	4.93	13.30	1.45	1.69
Indonesian coal	29.79	46.79	9.43	13.99	76.99	5.43	15.52	1.33	0.73
Colombian coal	41.80	54.10	2.60	1.50	75.30	5.40	15.60	1.80	0.40
Pine	71.50	16.00	12.0	0.50	51.60	4.90	42.60	0.90	n.d.
Holm-oak	70.20	17.80	9.50	2.40	51.10	5.30	42.70	0.90	n.d.
Eucalyptus	74.80	13.90	10.6	0.70	52.80	6.40	40.40	0.40	n.d.
Wheat straw	67.77	14.54	4.13	13.56	38.09	6.15	37.31	0.70	0.06
Sawdust	74.60	15.82	6.11	3.47	45.76	6.74	37.85	0.07	n.d.
Rice husk	55.54	14.99	9.95	19.52	49.07	3.79	46.42	0.63	0.09
Bagasse	65.87	17.43	13.05	3.65	46.10	5.26	44.25	0.19	4.20
Groundnut shell	68.96	15.52	10.12	5.40	52.54	5.37	41.01	0.59	0.49
Peanut shell	67.48	17.99	8.84	4.69	43.53	6.54	34.04	2.24	0.12
Palm kernel shell	67.13	17.19	7.37	8.31	51.63	5.52	40.91	1.89	0.05
Coconut shell	29.19	25.18	4.66	40.97	45.24	5.04	48.20	1.46	0.06

Source: Franco, C., Pinto, F., Gulyurtlu, I., Cabrita, I., 2003. The study of reactions influencing the biomass steam gasification process. Fuel 82, 835–842. Hanping, C., Bin, L., Haiping, Y., Guolai, Y., Shihong, Z., 2008. Experimental investigation of biomass gasification in a fluidized bed reactor. Energy and Fuels 22, 3493–3498. Loha, C., Chatterjee, P.K., Chattopadhyay, H., 2011. Performance of fluidized steam gasification of biomass- modeling and experiment. Energy Conversion and Management 52, 1583–1588.
n.d.: not detected.

- Coal contains more fixed carbon than biomass
- Net calorific value of coal is higher than that of biomass
- Density of biomass is lower than coal
- Biomass generally contains more amount of chlorine but very less amount of sulphur
- Pyrolysis of biomass starts earlier than coal
- Biomass char contains more oxygen
- Biomass char is more porous and reactive than coal
- Biomass ash is more alkaline in nature

So, there are many differences in fuel properties which may affect the co-firing performance. Some of the important properties which affect the co-firing performance significantly are discussed below.

Effect of Moisture

Initial moisture content in biomass available from different sources may vary from 10% to 50% which restricts the application of biomass as an alternate fuel. Due to high moisture content, the energy density of biomass is less compare to coal. In order to obtain good performance of boiler and better plant efficiency, the moisture content of biomass should be in a certain range. The optimum moisture content of woody biomass is 10–15 wt% for efficient combustion. If moist biomass is used, a significant amount of heat is used to evaporate the moisture which reduces the lower heating value of the flue gas (Luk *et al.*, 2013). This heat energy cannot be utilized in the power generation process which will increase the energy input to the system for same output if moist biomass is used (Holmberg and Ahtila, 2004). Instead, if dried biomass is used, the product of combustion will result in higher flame temperature which will increase the radiant heat transfer in the boiler. Higher heat transfer will increase the steam production for the same boiler tube. With the higher flame temperature there will be more complete combustion of fuel which will reduce CO emission and less fly ash will leave the boiler. The energy efficiency of a boiler thus could be increased by replacing wet biomass with dry biomass. It is observed that maximum boiler efficiency of 74% is achievable with standard equipment while biomass with 45% moisture is used and it can reaches to 80% with the same equipment while dry biomass of approximately 10%–15% moisture is used (Ross, 2008). Therefore, it is very much important to reduce the amount of moisture in biomass before co-firing. Moisture in biomass can exist in three forms: water vapour, capillary water in the pores and bound water in the solid matrix. Drying of biomass generally occurs at about 100–200°C when water from biomass is released as vapour. However, biomass does not decompose at this temperature because the temperature is not high enough to cause any chemical reaction. Drying of biomass before co-firing has a number of advantages which include but not limited to the better energy efficiency, high combustion temperature, nearly complete combustion, better energy quality, ancillary power reduction and lower emissions (Granstrom and Javeed, 2016; Moreno *et al.*, 2006). Drying is an energy intensive process and a significant amount of energy is consumed for drying. Therefore, even though the drying of biomass provides a number of benefits, they must be balanced against increased capital and operating costs.

Effect of Ash

Ash is another important factor which has significant impact on the boiler performance. The nature of ash left after combustion depends upon the type of co-firing technology employed. For example, direct co-firing produces a mixture of coal and biomass ash and indirect/parallel co-firing produces separate coal and biomass ash (Agbor *et al.*, 2014). In general, the amount of ash produces by burning unit mass of fuel is more in case of biomass compare to coal. At high temperature (>800–1000°C), ash is fused or partially fused and deposited in the furnace refractory or water wall surfaces which may reduce the heat transfer rate in heat exchange surfaces, affect the burner operation and can damage the furnace ash hopper and other components. This high temperature ash deposition process occurs very rapidly, within few minutes or hours, is known as slag formation. Ash deposition at relatively low temperature (<1000°C) on superheater, reheater and evaporator surfaces occurs due to bondage of ash particles with relatively low melting point constituents like alkali metal. This is one of the most important ash related issues associated with the combustion of biomass with coal because biomass ash contain relatively high amount of alkali metal. The corrosion process on the gas-side surface of boiler tube occurs at high temperature underneath ash deposits. Higher amount of alkali metal and lower amount of sulphur/chlorine ratio in biomass compare to coal also have influences related to the high temperature corrosion.

Reactors for Co-Firing

There are three major types of boilers which are used for co-firing of coal and biomass i.e., grate fire boiler, pulverize fuel fire boiler and fluidize bed boiler. The grate fire boiler is the oldest technology for combustion of solid fuel. Though this technology is used in some co-firing plants but it is not very suitable for co-firing application. The pulverize fuel fire boilers are the mostly used boilers for combustion of coal. However, pulverize fuel fire boilers are also used for co-firing of coal and biomass. The fluidize bed boilers are the most preferred technology for co-firing of coal and biomass due to its advantageous feature of fuel flexibility. Under this section, three different types of boilers, their working principles, advantages, disadvantages and their applications are discussed below.

Fluidize Bed Boiler

Fluidization is the operation by which a bed of solid particles is converted into a fluid like state by forcing a gas through it. As the gas velocity is increased, a situation arrives when solid particles are just suspended by the gas and the situation is called the minimum fluidization condition. After increasing the gas velocity beyond the minimum fluidization velocity, bubble formation starts from the bottom. Bubbles grow in size while travelling through the bed by coalescing small bubbles and finally burst at the upper surface of the bed and particles are splashed into freeboard region. This is called bubbling fluidized bed (BFB) boiler or combustor. Fig. 4 shows the schematic representation of a bubbling fluidized bed boiler. If the velocity of gas is increased beyond the bubbling fluidized bed, solid particles are distributed across the whole riser height, bigger particles fall back and smaller particles are entrained by the gas. These entrained particles are separated from the gas with the help of cyclone separator and fed

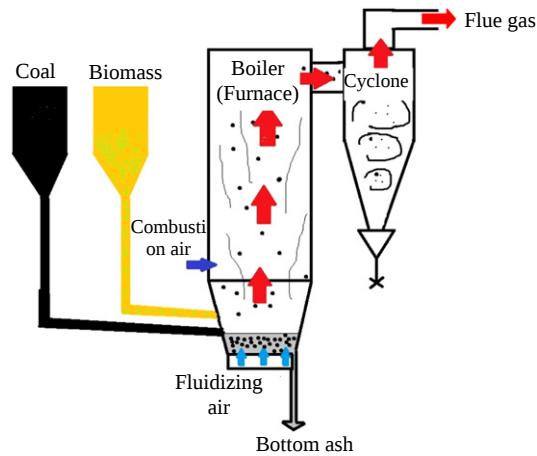


Fig. 4 Bubbling fluidize bed boiler.

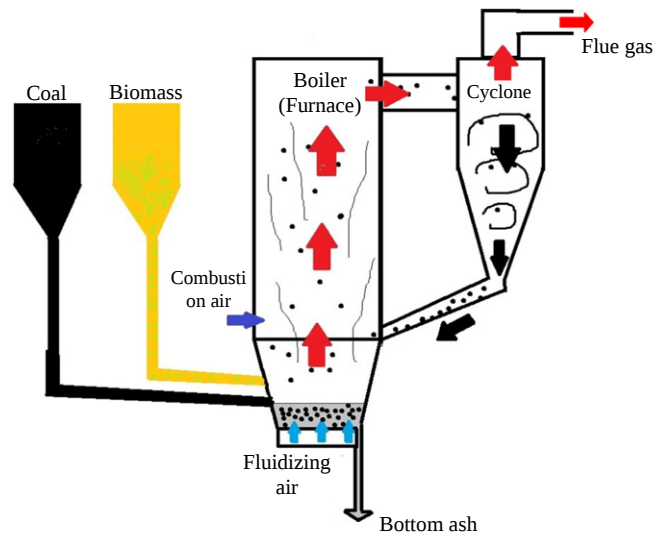


Fig. 5 Circulating fluidize bed boiler.

back to the bed with the help of loop-seal/L-valve. This is called circulating fluidized bed (CFB) boiler or combustor. Fig. 5 shows the schematic representation of a circulating fluidized bed boiler. In CFB combustor the bed and the freeboard regions are no longer separated. The main advantage of fluidized bed boilers is its fuel flexibility in terms of use of different types of fuel, feed rate, particle size and moisture content. Therefore, the fluidised bed boilers designed for coal combustion can also be converted for co-firing of coal and biomass with small retrofitting. The typical fluidization velocity in a bubbling fluidised bed combustor is 1–2 m/s which is about 5–10 m/s for circulating fluidised bed combustor (Loha *et al.*, 2018). In a fluidized bed combustor, it is possible to achieve the fuel-to-steam efficiency over 90% even with low grade fuels. Because of the high amount re-circulation of bed material in CFB, it is possible to burn moist, heterogeneous fuels with low calorific value. However, a support fuel can be used for high moisture content fuels. In fluidized bed combustors, more than 90% of the bed is occupied by sand/ash and the rest is fuel which balances any changes in fuel quality/moisture and prevents combustion disturbances and undesired bed temperature variation. The choice between BFB and CFB technology largely depends upon the plant capacity. BFBs are generally preferred for small scale application upto 20 MWth, whereas, CFBs are preferred for large-scale applications of more than 30 MWth. At this juncture, fluidised bed combustors are the best combustion systems available for co-firing of coal and biomass because of fuel flexibility, high rate of heat and mass transfer and lower emission due to low temperature combustion.

Pulverize Fuel-Fire Boiler

Pulverize fuel combustion is the most commonly used method for combustion of coal. However, it is also used for co-firing of coal and biomass. Here coal and biomass are grounded to fine powder and pneumatically injected into the furnace. Pulverize fuels are blown into the boiler plant through a series of burner with the help of a part of combustion air called primary air. The fuel is burned

by injecting secondary and tertiary air. Air is also injected downstream from the burner to reduce NO_x. Based on the boiler capacity and the capacity of each burner, a number of burners are used. The combustion is initiated with the help of an auxiliary burner. As the combustion temperature reaches a certain value, the auxiliary burner is shut down and the fuel is injected. The residence time of fuel particles in a pulverize fuel fire boiler is typically 2–5 s. Therefore, the particle size needs to be very small ($\sim 100 \mu\text{m}$) so that complete combustion takes place within this time. Due to small particle size and high gas velocities, the ash is mostly carried with the flue gas and is partly precipitated in the post-combustion chamber. Fig. 6 shows the schematic of a pulverized fuel fire boiler. The quality of fuel used for pulverize combustion need to be quite constant. The moisture content of the fuel should not be more than 20% (wb). The capacity of pulverize boiler may be as high as to meet the demands of the steam turbines with outputs 500–700 MWe.

Grate Fire Boiler

Grate fired boiler is the oldest amongst different type of boilers used for solid fuel combustion. Though the grate fire boilers are also used for co-firing of coal and biomass but they are not very common. The construction of grate fire boiler is simpler than pulverize fuel fire boiler and fluidize bed boiler. There are different types of grate fire boiler which are used e.g., fix flat grate, fix sloping grate, mechanical sloping grate and chain grate. The efficiency of grate fire boiler is lower and the flue gas emission is higher compared to pulverize fuel fire boiler and fluidized bed boiler. It also required fuel with uniform size and quality. Fig. 7 shows the schematic of a grate fire boiler.

Effect of Co-Firing on the Greenhouse Gas (GHG) Emissions

CO₂ is the major contributor to the global atmospheric Greenhouse Gas (GHG) emissions. This is because CO₂ has a very high residence time in the atmosphere. CO₂ released from fossil fuel combustion might be presents in the atmosphere upto 300 years.

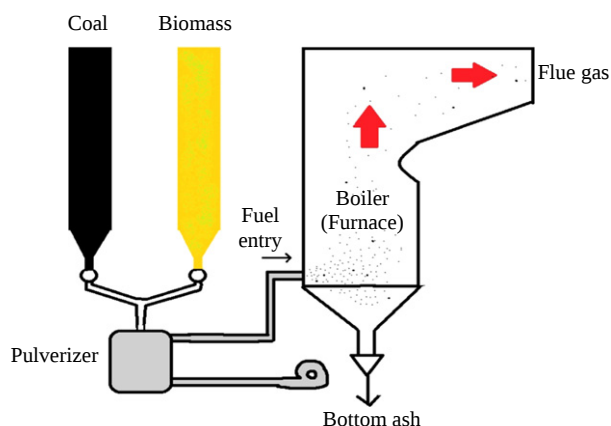


Fig. 6 Pulverized fuel-fire boiler.

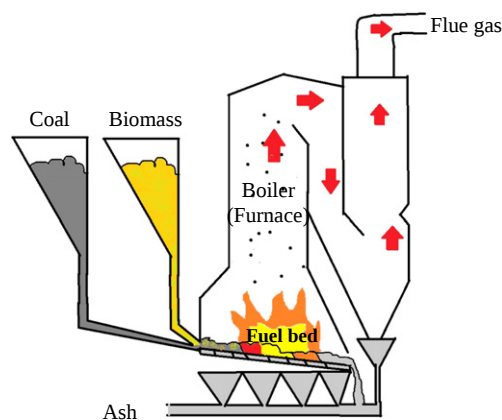


Fig. 7 Grate fire boiler.

In addition 25% of them lasts forever (Adanez *et al.*, 2012). Hence it is the most important anthropogenic greenhouse gases of our concern. The Global atmospheric concentration of CO₂ has increased to 408 ppm in 2018 (Trends in atmospheric CO₂, 2018). The concentration of CO₂ increased every year since scientists started measuring the slopes of the Mauna Loa volcano more than five decades ago. The rate of increase has accelerated from about 0.7 ppm per year in the late 1950s to 2.1 ppm per year during the last decade and now the rate of increase is 100 times faster than the increase that occurred when the last ice age ended. Therefore, it is felt worldwide that reduction of atmospheric GHGs is essential as soon as possible.

Co-firing of biomass in coal fired power plants offers the simplest and cost effective way to reduce greenhouse gas (GHG) emissions. This is because the co-firing of biomass to the existing power plant can be done by minimum retrofitting and the cost associated with the retrofitting is less compared to the other option available for GHG reduction. The CO₂ emission from a coal fired power plant of identical capacity reduces while biomass is co-fired with coal because biomass does not add net CO₂ to the atmosphere owing to the fact that the combustion of biomass releases the same amount of CO₂ which it absorbs during growing. It is estimated that the CO₂ emission could be reduced by 45–450 million tons per year in 2035 if 1%–10% of coal in power plants is replaced by biomass assuming an average CO₂ emission level of 95 kg/GJ from coal combustion (van der Hoeven, 2011).

There are three different routes of NO_x formation; thermal NO_x, prompt NO_x and fuel NO_x. Thermal NO_x is generated at high temperatures from nitrogen present in combustion air. Prompt NO_x is generally formed in rich combustion region through an intermediate species generated from decomposition process of hydrocarbon fuels. Prompt NO_x is formed in the presence of hydrocarbons and fuel NO_x is originated from fuel-bound nitrogen. In most of the combustion cases NO accounts for about 90% of the total NO_x. Reduction of NO_x emission from co-firing of biomass with coal depends upon biomass type, reactor type and operating condition (Baxter, 2005). It is observed that most of the fuel nitrogen in biomass is converted to mainly NH₃ during combustion and NH₃ reduces NO to molecular nitrogen which is one of the reasons reported for the reduction of NO_x emission in co-firing of biomass (Hughes, 2000). Another reason for reduction of NO_x in co-firing of biomass with coal is the quick release of volatiles in biomass particularly in the lower part of the reactor which produces a lot of radicals which consume local oxygen and also de-oxidized NO_x. It is observed that biomass derived from forest residues have a lower tendency because they contain less nitrogen to produce NO_x compared to biomass derived from agricultural residues (Agbor *et al.*, 2014). Lower combustion temperature in fluidised bed boiler compared to pulverized fuel fired boiler reduces the formation of thermal NO_x. However, N₂O emissions seem to be higher in fluidised bed boiler.

Co-firing of biomass also reduces the emission of SO_x because of mainly two reasons. Firstly, most of the biomass contains very less amount of sulphur compared to coal and additionally, due to the retention of sulphur in the ash generally presents in the form of solid alkali sulphates.

Use of biomass residues for co-firing will also gives additional greenhouse gas reduction because these biomass materials will otherwise be used for land filling which will release CH₄ which have 21 times more global warming potential than CO₂ (Hughes, 2000).

However, the emission of particulate matter from combustion of biomass required attention particularly in small-scale power plants with low-efficient particulate filters, which traps fine particles.

Different Biomass Sources for Co-Firing

Biomass available from different sources can be utilized for co-firing. Available biomass resources for co-firing may vary from country to country. However, they can broadly be classified into three groups as wood and wood residues, forest residues and agricultural crop residues.

Wood and wood waste: Wood is the main source of biomass energy in many countries. Wood residues include bark, sawdust, wood chips and wood scrap from wood industries.

Forest residues: Forest harvesting is a major source of biomass for energy. Harvesting may occur as thinning in young stands or cutting in older stands for timber or pulp that also yields tops and branches may serve as potential biomass for co-firing.

Agricultural crop residues: Large quantities of crop residues such as husk, straw, stem, stalk, leaves, shell, pulp etc. are produced which are mostly underutilised could be the potential biomass resource for energy generation.

Different agricultural crops available from major biomass producing countries which can potentially be utilized for co-firing are shown in Table 3.

Future of Co-Firing

Though the co-firing of biomass to the existing coal fire power plants seems to be one of the most efficient and environment friendly option to exploit biomass for energy generation but its future application will depends mostly on the following points.

- It will largely depend on the overall sustainability of biomass. Enough supply of biomass should be ensured to meet the targeted level of biomass co-firing. For this there is an urgent need to assure the ecologically sustainable biomass production. This calls for further technology development, process and infrastructure development to produce/collect more biomass. Subsidies and incentive should be provided to grow biomass in barren lands to fulfil the requirement. It is also required to

Table 3 Potential agricultural crop from major biomass producing countries

Country	Agricultural crops
Australia	Wheat, Rice, Sugarcane, Grape, Agave, Canola, Giant reed, Sorghum
Bangladesh	Rice, Wheat, Pulses, Oil seeds, Tobacco, Sugarcane, Jute, Maize, Barley, Sorghum, Millet
Brazil	Sugarcane, Bamboo, Eucalyptus, Sisal, Wheat, Barley, Oats, Maize
Canada	Corn, Wheat, Straw, Switchgrass, Canola and Sunflower
China	Bamboo, Rice, Bagasse, Rapeseed, Sumac, Chinese goldthread, Sweet broomcorn
Ethiopia	Maize, Coffee, Sorghum, Sugarcane, Wheat, Millet, Barley
Germany	Sugarcane, Rapeseed, Sunflower, Palm, Maize, Wheat
India	Rice, Wheat, Cotton, Sugarcane, Jowar, Bajra, Maize, Coconut, Cashewnut, Groundnut, Banana
Italy	Straw, Pruning, Forestry, Vinasse, Olive, Fruit Shell, Rice
Malaysia	Rubber, Rice, Coconut, Cocoa, Palm
Nigeria	Sugarcane, Cassava, Sorghum, Maize, Oil, Palm, Soybeans, Millet, Cocoa, Coffee, Groundnut, Rice, Cotton, Tobacco, Wheat
Russia	Wheat, Rapeseed, Soybean, Sunflower
South Africa	Sugarcane, Maize, Sorghum, Sweet Sorghum, Soybeans, Groundnuts, Sunflower
Tanzania	Cotton, Sugarcane, Cashew nut, Maize, Cassava, Banana, Sweet potatoes, Groundnut, Sunflower, Simsim
Thailand	Rice, Sugarcane, Corn, Cassava, Palm, Jatropha
UK	Straw, Cereal, Oil crop, Sugarcane, Eucalyptus, Miscanthus, Willow
USA	Corn, Wheat, Sunflower, Corn, Palm, Switchgrass, Miscanthus, Poplar, Willow

identify the appropriate biomass which has the highest potential of sustainable supply depending on economic and geographical factors.

- Cost of biomass will play an important role for the future application of biomass co-firing. Even though the raw material cost is low but the availability of biomass is so diversifier that the cost of collection and transportation become the major issue.
- It is required to develop properly organized biomass market so that every coal fired power plants can take advantage of it.
- Spreading of biomass co-firing technology will depend on the amount of incentive given for reduction of CO₂. It will attract the investors to establish such technology in future.
- Public awareness on environmental pollution and the use of renewable energy will also force to advance the biomass co-firing technology.
- Last but not the least, it will also largely depends on the policy of the individual country like how the country will set their target and what type of promotional scheme they will take to implement it. For example, to promote biomass co-firing the country may decide certain percentage of co-firing mandatory in the existing and upcoming coal based power plants.

Conclusion

This work highlights the contributions of co-firing of biomass with coal in reducing the emissions of greenhouse gases like CO₂, NO₂ and SO_x. Co-firing of biomass in existing coal based power plants is considered as the simplest, most effective and economical short term solution to conserve fossil fuel, increase the use of biomass and reduce net CO₂ emission. Hence, the importance of co-firing of biomass with coal is increasing day-by-day throughout the world. The three different methods of co-firing of biomass namely direct co-firing, indirect co-firing and parallel co-firing are discussed. Direct co-firing is the simplest and most commonly used method which requires minimal investment although the amount of biomass share is limited in direct co-firing. Whereas, indirect and parallel co-firing methods are comparatively complex albeit they are more suitable for biomass fuels containing problematic compounds or when the ash quality is of importance for subsequent sale or disposal. Co-firing of coal and biomass is studied in different types of boilers and it is observed that fluidized bed boiler is most suitable because of its advantageous features like fuel flexibility and low temperature combustion.

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Design and Synthesis of New Ruthenium Coordination Complex as Efficient Dye in DSSC Like Alternative Energy Resources With a Bird's Eye View on Strategies Towards GHGs Mitigation

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Introduction

The quality of human life depends largely on accessibility of energy, eventually; world energy consumption is rising every day. The source of power production in general is mostly from coal. As a consequence, the thermoelectric produced by burning of coal results in tons of carbon dioxide (CO₂) to environment which remarkably increases the *carbon footprint*. Carbon foot print is basically defined as total emissions caused by an event/organization/individual or product as carbon dioxide equivalent. The impact of an energy technology on the climate can be characterized by its carbon emission intensity, a measure of the amount of CO₂ or CO₂ equivalent emitted per unit of energy generated. Here, 'CO₂ equivalent' (CO_{2eq}) refers to non-CO₂ GHGs, notably methane and nitrous oxide, which are released from a number of human activities such as fossil fuel extraction and agriculture. Existing fossil fuel technologies possess large carbon emission intensity through the combustion of carbon rich fuels. Moreover, the amount of emitted CO₂ from thermoelectric plants is higher than produced from transportation or industrial processes. As a consequence of elevated level of greenhouse gases like CO₂, global warming index is rising day by day which badly affects our environment and ecosystem as well.

One of the protective steps against global warming is to minimize the *carbon footprint* along with mitigation of greenhouse gases (GHGs). Several countries have decided different memorandum towards this process. One of the significant processes is utilization of renewable energy like solar energy to limit the scale of future climate risks from fossil fuel use. In such ways, solar energy, along with other low-carbon assisted renewable technologies, plays a vital role in reducing the GHGs and carbon footprint from the environment especially in power sectors. Hence solar energy may help to reduce the carbon foot print by replacing more carbon intensive sources of energy. These consequences have motivated the researchers worldwide to utilize solar energy in terms of different processes. With increasing exhaustion of fossil fuels, attention is being paid to solar energy which supplies average 1.73×10^{17} J of energy to the Earth (Kopp and Lean, 2011) every second, nearly 10^4 times higher than what civilization requires. This renewable energy is also apt for enabling low carbon development in developing or under developed countries, where approximately 1.3 billion people lack access to electricity (World Energy Outlook, International Energy Agency, 2012). In that perspective solar energy is considered one of the most positive ways to decrease the climate change resulting from the use of fossil resources for energy generation.

Origin of Photovoltaic Cell

Technology of the photovoltaic cells actually started back nearly over 160 years. The fundamental science was first exposed in 1839 but the pace of advancement actually accelerated in three major thrusts in the 20th century (see "Relevant Websites section"). The scientific breakthroughs are highlighted in Table 1.

It was not until Albert Einstein wrote his paper in 1905 on the photoelectric effect: "*On a Heuristic Viewpoint Concerning the Production and Transformation of Light*" which was supported by experimentation done by Robert Millikan in 1916. Later on Einstein got Nobel Prize for this concept of photoelectric effect, in 1922. This work created the theoretical basis for all photovoltaic devices, in which photons generally excite the valence electrons out of the valence band and thrives into the higher energy conduction band, where they are collected and transported to the outer circuit. The work of Goldmann and Brodsky (carried out in 1914) was then studied in detail by many researchers, such as Neville Mott and Walter Schottky, in the 1930s. In the year of 1941 Russell Ohl devised a silicon solar cell. With the advancement of silicon in the 1950s, Fuller developed near-surface p-n junctions using a boron tri-chloride incorporation of n-type silicon, which developed charge separation in the device. In 1954, Bell Laboratories exhibited first high-power silicon PV cell with efficiencies exceeding ~6%. However, the possibilities of sensitization were not fully recognized until the early 1960s. Many new research outcomes were reported at the International Conference on Photosensitization of Solids held in Chicago, such as the sensitization of ZnO with cyanine dyes and the necessity of a mono layer dye to get maximum efficiency. Various types of p-n junctions were developed using gallium-arsenide (Ga-As), cadmium-sulfide (Cd-S), cadmium telluride (Cd-Te) and indium-phosphide (In-P). But these systems are very much expensive as well as their applications are also limited (like space applications). The term "*first*

Table 1 Scientific breakthrough at a glance

Year	Scientific breakthrough
1839	French physicist Alexandre Edmond Becquerel observed a physical phenomenon allowing light-electricity conversion when experimenting with metal electrodes and electrolyte
1883	Charles Fritts , an American inventor, described the first solar cells made selenium and thin layer of gold.
1888	Edward Weston received first US patent for “solar cell”
1901	Nikola Tesla received US patent for “method of utilizing, and apparatus for the utilization of, radiant energy”

generation” generally refers to p-n junction photo voltaics, which are made of mono-and poly-crystalline silicon, doped with other elements. Both mono and poly-crystalline photo-voltaics require complicated fabrication procedure and large amounts of silicon. First generation cells, based on single (mono) crystalline silicon, recorded the highest efficiencies of all PV devices. However, these cells comprise complicated compositions and high manufacturing costs. From 1954 to 1960, Hoffman invented a method to increase PV cell efficiency from ~2% to ~14%. In the following years, dye-sensitization was proved to be efficient due to its potential applicability in transfer of electrons or energy. The idea of using dispersed particles to offer a sufficient interface was used to develop efficient semiconductor metals, such as TiO₂ and ZnO etc. Titanium dioxide became the preferred nano-crystalline semiconductor of choice for the researchers due to its advantages like widely accessible, inexpensive, non-toxic and biocompatible. In the mid-1970s, solar cells engrossed considerable attention towards an alternative energy source. Second-generation photo-voltaic cells were developed during this period, these cells are comprised of thin-film of photovoltaic cells that are composed of amorphous poly-crystalline semiconductors. Historically, amorphous silicon (Si), cadmium telluride (CdTe), and copper indium gallium selenite (CIGS), and recently thin-film poly crystalline silicon, have been considered as prime features for thin films, of which CdTe thin film technology is the most expensive. These three types of thin-film cell structures include either mono or single junction/double or twin junction/multiple junctions. The main difference between these structures is the number of p-i-n junction layers. Depositing small thin layers of developed material with different band gaps enhances cell efficiency where as the cost of fabrication increases due to the several steps involved in depositing each layer of material during fabrication. However, the efficiency of these developed cells is lesser compared to the efficiency of wafer-based silicon solar cells, which are currently dominating the commercial PV market. Researchers throughout the world have been trying to develop thin-film devices that are very efficient as well as cost effective. First and second generation PV devices are basically fabricated from semiconductor materials. The design and development of low-cost PV cells has been the topic of interest over the last three decades. Third-generation PV cell technologies are superior compared to the first and second generation technologies by optimizing the efficiency and considerably decreasing the production costs. Most third-generation solar cells are still in the progress stage and tend to contain dye-sensitized solar cells, hetero junction cells, polymer solar cells, quantum dot cells and hot carrier cells. DSSCs are novel devices that adapt visible light into electricity based on wide band gap semiconductor sensitization and belong to a assembly of thin-film cells. The development of DSSCs began in 1972 with the invention of a chlorophyll-sensitized zinc oxide (ZnO) electrode. The group of Carlson and Pankove first invented the amorphous silicon solar cell with an efficiency of 2.4% in 1976; later efficiency was enhanced to 4%. In the subsequent years, DSSCs became an attractive subject of research from both applied and fundamental perspectives. The main problem was that a mono layer of dye molecules on surface absorbs only 1% of incident sunlight. In 1990, at the Ecole Polytechnique Federale de Lausanna (EPFL), Grätzel *et al.* succeeded in fabricating a new type of solar cell that is known as DSSC or Grätzel cell, this cell mimics photosynthesis procedure in plants by sensitizing nano-particulate titanium dioxide (TiO₂) films with a novel ruthenium (Ru) bipyridyl complex. The performance of a DSSC depends primarily on the dye sensitizer. The dye absorption spectrum and the attachment to the surface of the semiconductor (TiO₂) are key parameter for determining the DSSC efficiency. Currently, silicon made inorganic solid-state junction devices, govern the photovoltaic industry due to their cell efficiency. However, the supremacy of solid-state junction devices is now being challenged by the appearance of DSSCs. These conducting thin films and nano-crystalline material based devices can potentially replace conventional solid-state devices. The efficiency of DSSCs comprised of Ru-compounds adsorbed on nano-crystalline TiO₂ semiconductors has remarkably reached ~11%–12%.

Solar Cells

The term “solar cell” is used to refer to a cell that produces electricity from sunlight. Sunlight is essentially the radiation spectrum of a 5800 K black body with differences due to spectral lines and absorption. Cells can be described as photovoltaic or solar cells even when the light source is artificial one. There are mainly two types of solar cells: (i) solid-state devices and (ii) liquid electrochemical cells. The mechanism of all photo voltaic cells may be elucidated in two steps: (i) light absorption followed by electronic excitation and (ii) charge separation and transport of electrons (Bisquert and Vikhrenko, 2004). These actions are accomplished with different pathways in solid-state and electrochemical cells, although the results are the same in both cases. A better concept of dye-sensitized solar cells can be gained through discussions of these different types of photovoltaic cells (Sze and Ng Kwok, 2007).

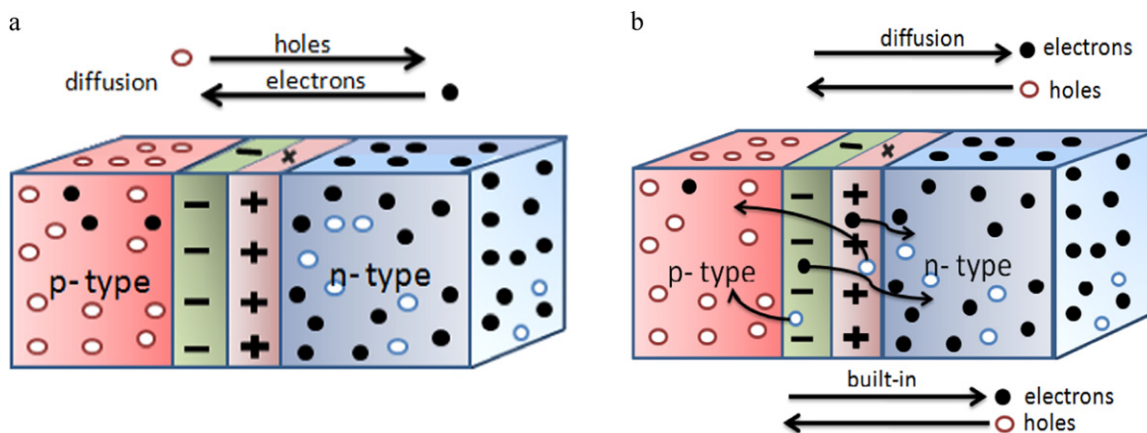


Fig. 1 (a) Schematic diagram of diffusion establishing a “built-in” electric field and (b) the transfer of electrons and holes due to diffusion and the “built-in” electric field.

Silicon Solar Cells

Being the 2nd most plentiful metal in the Earth’s crust, silicon has the advantages of being inexpensive as well as easily available in adequate quantities. Moreover its manufacturing processes are eco-friendly (El-Refi, 2014). The concept of standard silicon solar cell is based on a semiconductor p-n junction. Homo-junction solar cells, like conventional silicon solar cells, have both p-type and n-type semiconductors comprising of the same material, whereas hetero-junction solar cells, like thin-film solar cells are made of cadmium telluride or dye-sensitized solar cells have n-type and p-type semiconductors comprising of different materials. n-type semiconductors are developed through the doping of pentavalent impurity atoms, such as arsenic, phosphorus and antimony, which share free electrons and thereby remarkably increase the conductivity of silicon. The addition of tri-valent impurity atoms, such as boron, aluminum and gallium, which have one lesser valence electron than the silicon atoms, generates p-type semiconductors (McEvoy *et al.*, 2003). **Fig. 1(a)** shows a schematic of silicon cells, which are simply silicon (semiconductor) p–n junctions. When n- and p-type semiconductors are combined, large density gradients form between the sides of the p-n junction as a result free electrons from the n-type silicon impurity atoms (donors) begin to migrate across this newly developed junction to fill the holes in the p-type silicon (acceptor), which generates negative ions. The movement of electrons across the p-n junction from the n-type to the p-type leaves positively charged phosphorous ions on the negative side, while the holes migrate from the p-type acceptor to the n-type region across the p-n junction, where there are many free electrons, leaving the negatively charged boron ions behind. Due to this drive of electrons, the charge density of the p-type conductor along the p-n junction is filled with negative charges, and the charge density of the n-type silicon conductor becomes positive. The free electrons and holes are affected by the built-in electric field, as result the negative electrons are attracted towards the positive phosphorus centers and positive holes are attracted towards the negative boron centres. This transfer of electrons and positive holes across the p-n junction is termed as diffusion. The movement of electrons and holes across the p-n junction occurs until equilibrium (an electrically neutral condition) is attained. At equilibrium, no net charge diffusion occurs, and a depletion region is formed (**Fig. 1(b)**), which is also referred to as a space charge layer. This incident is known as the equalization of the Fermi energy level in the materials. The depletion region becomes highly resistive and acts as crystalline silicone, which is almost like an insulator. By the incorporation of an external electric field to the previous built-in electric field, the resistance of the depletion layer may be customized. At the p-n junction, solar energy absorbed by the semiconductor silicon will dislodge an electron and create an extra mobile electron and an extra mobile hole. The electron field assures the electron flow to the n-type material and the hole flow to the p-type material. This process is known as the *photo generation of charge carriers*, which occurs throughout n-type and p-type semiconductors. The resulting separation of the positive and negative charges across the p-n junction is named as voltage or potential difference. Preplanned connection of a solar cell to an external circuit allows both electrons and holes to travel around the circuit and recombine, which returns the system to its primary condition (**Fig. 2**). Interestingly if positive voltage is applied on n-type cell and negative voltage is applied on p-type cell, there will be no current flow. The resistance in a silicone cell is large at voltages nearly from 0 to 0.6 V due to depletion region, while the resistance is very small at voltages exceeding 0.6V and there will be current flow without any constraint (Gregg and Hanna, 2003).

Dye-Sensitized Solar Cells

The development of photovoltaic cells for the last two decades led to the development of devices that are cost effective and expands the applications of photovoltaic cells to compete with other energy production systems. These technologies are taken as emerging photovoltaics. The use of dye sensitization was limited, rather unsuccessful until 1991, when Grätzel and his co-workers successfully developed a solar cell by successful recombination of nano-structured electrodes with efficient charge donating dyes at the Laboratory of Photonic and Interfaces in the École Polytechnique Fédérale de Lausanne in Switzerland. DSSCs are devices that

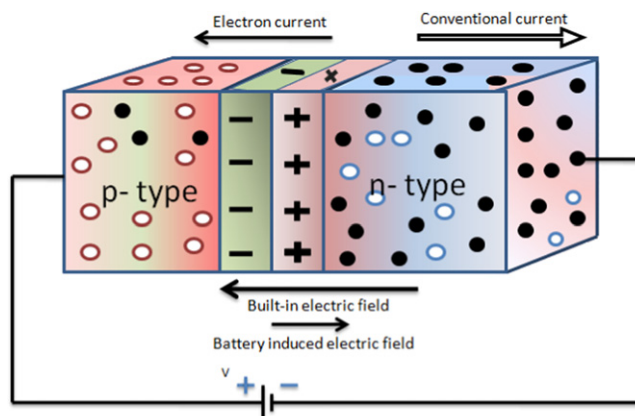


Fig. 2 Schematic diagram of the motion of mobile electrons and holes due to diffusion and the “built-in” electric field.

can convert solar energy to electric energy by light sensitization established on wide energy band semiconductor. Now a days DSSCs have shown a very promising future in the field of photovoltaic cells. These solar cells (DSSCs) differ from other solar cell related devices in their basic constructional and operational point of view. In contrast to first and second-generation PV devices, which are based on solid-state semiconductor materials, the typical arrangement of DSSC combines both solid and liquid phases. Dyes used in solar cells are classified into two broad categories i.e., organic and inorganic dye. Ruthenium (Ru) dyes are presently known to be the most significant inorganic dye for the fabrication of DSSCs with great efficiency.

DSSC Structure

A DSSC is a complex system for light-to-electricity conversion. The basic structure of a DSSC is similar to the original design made by Grätzel *et al.* Economic as well as environmentally friendly properties of dye-sensitized solar cells (DSSC) make the DSSCs one of the most promising classes of photovoltaic cells for the conversion of photon energy to electricity. In general, DSSC contains of a working counter electrode, a redox-coupled electrolyte containing iodide and tri-iodide ions, and a porous semiconductor electrode-absorbed dye of nano-crystalline nature. The dye molecule of the DSSC plays a pivotal role in absorbing sunlight and in the conversion of solar power to electrical energy. The operational mechanism of DSSCs are based on the photo-sensitization created by the dyes on wide band-gap mesoporous metal oxide semiconductors. As a consequence, with time, DSSCs have become more interesting since large collections of dye including natural dye can be used as light harvesting elements to deliver the charge carriers. This review brings the history of DSSC with a focus on the recent advancements of the Ru-dyes in this specific area, the working principle of DSSCs as well as the work done over recent the years on Ru-dye based DSSCs. Apart from DSSC's advantages, there are several disadvantages as well. Efficiency of DSSC is one of the major concerns. The majority of low efficiencies are due to traditional photo-sensitizers undergoing low absorption, narrow absorption spectra along with the loss of energy absorbed by the electrolyte. For this reason, an approach using co-sensitization was investigated to recover the performance of the DSSC. Several research works have been targeted towards the improvement of new and efficient photo-sensitizers, including sensitizers like ruthenium complexes, zinc porphyrins as well as metal-free organic dyes. Ruthenium based sensitizers such as the N3, N719 and black dye etc., were rigorously tested as light harvesters and reached up to a remarkable milestone where overall power conversion efficiency is in the range of $\sim 11\%$ under Air Mass 1.5 (AM 1.5) irradiation while organic photo sensitizers have reached power conversion efficiency (PCE) in the range of $5\text{--}8\%$. As of now, metal-free indoline dye (D149) is the most effective photosensitizer for DSSCs and has attained very high efficiencies up to 9% . Recently, devices are fabricated by using Ru^{II} complexes with $\text{Co}^{\text{III/II}}$ based electrolytes have achieved efficiencies up to 9.4% . Overall a schematic diagram is given based on the successful implementation of the three kind of dyes i.e., Ru-dyes, metal free dyes and natural dyes.

From the graph (Fig. 3) it is observed that, there is a steady progress in Ru-based dyes since 1991 and a maximum efficiency of 13% is achieved in the year 2014. Metal free dyes and organic dyes, on the other hand have started its growth from the year 2004. But the efficiency is very less compared to the Ru-based dyes. A maximum of 10.7% efficiency was reported in the year 2010 which is still lesser than Ru-DSSC. Moreover, the performance of the Ru-complexes based on the conversion yield and long term thermal stability is admirable compared to other dyes. There are huge opportunities regarding further development of the DSSCs in domain of repeatability and reliability of the sensitizers.

In a nutshell continuous development in this DSSC field explores the potential implementation of solar photovoltaic (PV) technologies to deliver rapid transformation of our energy systems to limit the scale of future climate risks from fossil fuel use. In particular, cost reductions, scalability of manufacture and the new science needed are to be kept in mind in order to accelerate the uptake of solar power technologies. Low carbon foot print forecasts that by 2050 some $14\text{--}22\%$ (IEA_{2DS} base Scenario, 2012) or more (Greenpeace International, European Renewable Energy Council, Council GWE, 2012) of electric power should be supplied by solar conversion. In such pathways, solar, along with other low-carbon technologies will play a vital role in decarbonizing the power sector.

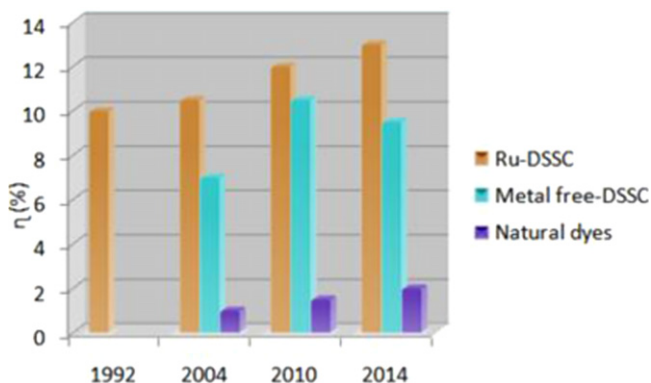


Fig. 3 Plot of progress in efficiency (η) of DSSC up to 2014 based on three different types of sensitizers: Ru-based DSSC, metal free DSSC and natural DSSC.

Characteristics of DSSC

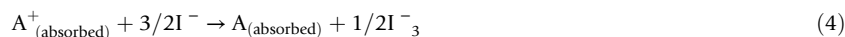
The performance of DSSCs is monitored by two main criterions, i.e., (i) overall efficiency (ii) photochemical as well as thermal stability. Other required parameters are IPCE (Incident Photon to Current Conversion Efficiency also known as Quantum efficiency), I_{sc} (short-circuit current i.e., when the voltage across the solar cell is zero (i.e., when the solar cell is short circuited)), V_{oc} (open circuit voltage i.e., Open Voltage Current is the maximum voltage available from a solar cell and this occurs at zero current), FF (fill factor i.e., the ratio of the maximum power from the actual solar cell to the maximum power from an ideal solar cell). The efficiency of DSSC is remarkably dependent on the following factors:

- (1) The ratio of input energy from the sun to solar cell and the energy output from the solar cell.
- (2) Photovoltaic device should have a serviceable life-time of about 20 years without substantial loss of performance. Efficient dyes like N3 sustained 108 cycles after long time illumination.
- (3) Regeneration is another prime factor here, and it should happen fast to maintain the long term stability of the cell. Common tests are based on 1000 h stability tests at 80°C for evaluating the photochemical stability of the DSSC.

Mechanistic Pathway

The dye-sensitized solar cells are generally comprised of five components: (i) Transparent Conductive Oxide coated a mechanical support; (ii) the semiconductor film, usually TiO_2 ; (iii) a sensitizer adsorbed onto the surface of the semiconductor; (iv) an electrolyte containing a redox mediator; (v) platine like counter electrode capable of regenerating the redox mediator. The Schematic representation is given below (Fig. 4).

The basic operating principle for any DSSC contains absorption, separation and collection. Different types of optimization of these parameters take DSSC to attain better efficiency. Thus, absorption occurs in the very first step of the reactions occurring in the solar cell. Under illumination, sensitizer dye (A) absorbs a photon that may lead to excited sensitizer state (A^*). Photo excitation of this sensitizer is then followed by the electron insertion into the conduction band of the semiconductor (generally mesoporous). This leads sensitizer to an oxidized state A^+ with electron donation from the electrolyte but the original state of the dye restored. Iodide/triiodide system is widely used in DSSC as redox couple for regeneration of the dye. Here, Iodide regenerates the sensitizer, and gets itself reproduced due to the reduction of triiodide at the counter electrode. In this way, the circuit gets completed by transfer of electron via the external load. The following reactions summarize the working mechanism (Gratzel, 2003; Nazeeruddin *et al.*, 2011)



Factors Affecting Absorption Spectrum

Concentration of the dye within the nano-porous TiO_2 surface and the absorption coefficient determines the fraction of light that will be absorbed by the TiO_2 layer. A sensitizer should have

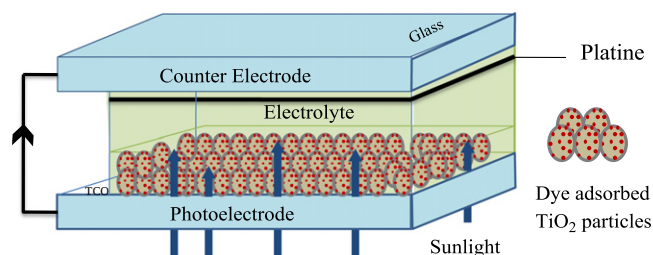


Fig. 4 Schematic diagram of dye-sensitized solar cell.

- (1) high absorption coefficient in the visible region and
- (2) high affinity to the TiO_2 surface in order to ensure a dense coverage of the surface. Also increase in absorbance helps in reducing the thickness of the TiO_2 layer thereby eliminating the probability of recombination.

Generally at longer wavelengths, the absorption decreases significantly, thus a substantial fraction of the solar spectrum will be lost. The absorption of the dye can be described with Beer-Lambert's Law (Eq. (5))

$$\frac{I(x)}{I_0} = 10^{-\alpha(\lambda) \cdot x \cdot C_{\text{dye}}} \quad (5)$$

where $I(x)$ is the light intensity at the point x (W m^{-2})

I_0 is the initial light intensity (W m^{-2}).

α is the absorption coefficient ($\text{M}^{-1} \text{cm}^{-1}$).

λ is the wavelength (nm).

C_{dye} is the concentration of the dye (M).

x is the path length (cm).

Apart from TiO_2 , ZnO and Nb_2O_5 have also been investigated for the use of semiconductor. Sensitizers are mostly metal complex dyes and are formed as a dye. Although a lot of dyes have been studied including natural dyes, Ruthenium complexes have proved to be the most effective due to its photon to current conversion efficiency as well as its thermal efficiency over a wide range of temperature.

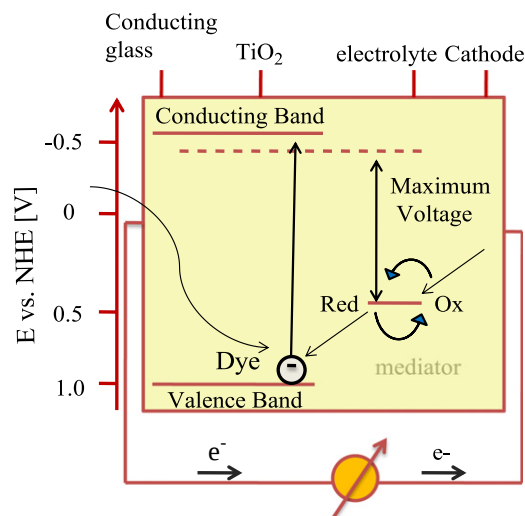
Sensitizers

Sensitizer is a very crucial part of the DSSC and it possess some essential characteristics. The ideal sensitizer for a single junction PV cell converting standard global Air mass (AM) 1.5 sunlight to electricity should absorb all light below a threshold wavelength (~ 920 nm). Moreover, it must be grafted on the semiconductor oxide surface with the assistance of attachment groups like carboxylate or phosphonate. The attachment group of the dye confirms that it spontaneously gathers as a molecular layer after exposing the oxide film to a dye solution. It will make a high prospect that after a photon is absorbed, the excited state of the dye will relax back to its ground state by electron injection to the semiconductor conduction band. It should insert electrons after proper excitation and its energy level must match with the lower bound of the conduction band to avoid any kind of energy loss. It should be rapidly regenerated and be fairly stable, both in the ground and excited states. Also, it must be stable enough to bear about 10^8 turnover cycles. Many different compounds have been examined for semiconductor sensitization, such as porphyrins, coumarin, phthalocyanines, carboxylate derivatives of anthracene and other type of polymeric films. Among the photo-sensitizers studied, transition metal complexes have been the best till date. Photovoltaic performances can be assessed based on conversion yield and long term stability of the dye. Interestingly the polypyridyl complexes of Ruthenium have fulfilled both the criterion. The general structure which is proven best for sensitizers is $\text{ML}_2(\text{X})_2$, where M may be a metal like Ru and L is 2,2'-bipyridyl-4,4' - dicarboxylic acid and X presents a halide, cyanide, thiocyanate, thiocarbamate etc. (Scheme 1).

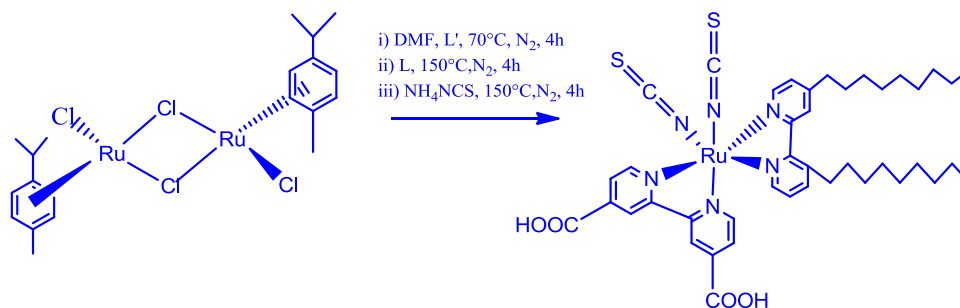
The present review is based on the current research issues in the field of a new dye sensitized solar cell based on charged electron injection from molecular sensitizers into a semiconductor oxide having wide-band-gap of nanocrystalline morphology. Some discussions based on some Ru-complexes, their properties and the principles of solar light energy harvesting and conversion to electric power are done by these systems.

Ru-Complex Dyes

In the year of 1991, Ru-based DSSC exhibited a remarkable success with a conversion efficiency of 7.1%. Ru (II) metal is always an excellent choice for a number of reasons: (1) its octahedral geometrical structure that tolerates extending of specific ligands in a controlled fashion; (2) the photo physical, photochemical and electrochemical properties of Ru (II) complexes can be tuned; (3) it possesses multiple stable and accessible oxidation states from I to IV; (4) possess good solubility in many solvents.



Scheme 1 Schematic operating principles and energy level diagram of DSSC.

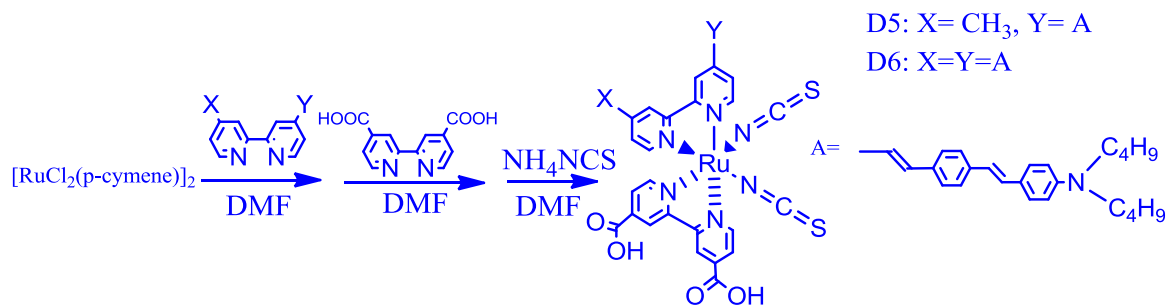


Scheme 2 Post synthetic route for the Ru-dye preparation.

Nazeeruddin *et al.* (1993) prepared *cis*- $X_2\text{Bis}(2,2'\text{-bipyridyl-4,4' dicarboxylate})\text{ruthenium(II)}$ complexes ($X = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{CN}^-$, and SCN^-) and characterized by absorption, luminescence, and redox behavior. These complexes act as very efficient charge transfer sensitizer materials for nanocrystalline TiO_2 films (thickness of film about $\sim 8\text{--}12\ \mu\text{m}$). The thiocyanato derivative *cis*-di(thiocyanato)-*bis*(2,2'-bipyridyl-4,4' dicarboxylate)ruthenium(II) was found to exhibit excellent properties, taking it as a very striking new redox sensitizer compared to other known sensitizer. The four carboxylate groups attached to the two bipyridyl moieties assure rigid adsorption onto the surface of oxides such as TiO_2 . Apart from this, carboxylate groups also provide strong coupling between the two predominating factors i.e., charge-transfer excited state and the conduction band wave function of the semiconductor. As a consequence, ultrafast electron flow from the excited complex into the semiconductor occurs at nearly 100% quantum yield. A solar-to-electric energy conversion efficiency of 10% was gained with this system. The effect of temperature on the power output and the thermal stability of the dye was also examined. It has been claimed that a device based on a simple molecular light absorber module has been designed which attained a conversion efficiency matching with that of conventional silicon-based photovoltaic cells.

Wang *et al.* (2003) have synthesized a new ruthenium sensitizer *cis*- $\text{RuLL'}(\text{SCN})_2$ ($L = 4,4'\text{-dicarboxylic acid-2,2'-bipyridine}$, $L' = 4,4'\text{-dinonyl-2,2'-bipyridine}$) in combination with a quasi-solid-state polymer gel electrolyte. Ultra-microelectrode voltammetric measurements indicate that the triiodide/iodide couple can transport charge freely in the polymer gel. The dye sensitized solar cell has unprecedented high stability under both thermal stress and at the time of absorbing light that matches the durability criteria for outdoor applications. The efficiency of the system is above 6% under sunlight. The solar sensitized device showed excellent thermal stability at $\sim 55^\circ\text{C}$ for $\sim 1000\ \text{h}$ in a solar simulator ($100\ \text{mW cm}^{-2}$) that is equipped with a ultraviolet filter. The complex has been synthesized following the **Scheme 2**.

Significant modifications were done by Jang *et al.* (2006) by changing the anchoring group. Implementing the idea, two ruthenium based sensitizer materials have been synthesized i.e., $\text{Ru}((4,4\text{-dicarboxylic acid-2,2'-bipyridine})(4,4'\text{-bis(p-hexyloxy)styryl)-2,2'-bipyridine})(\text{NCS})_2$ and $\text{Ru}((4,4\text{-dicarboxylic acid-2,2'-bipyridine})(4,4'\text{-bis(p-methoxy)styryl)-2,2'-bipyridine})(\text{NCS})_2$, coded as K-19 and K-73, respectively. The compounds were characterized by various sophisticated spectroscopic tools like $^1\text{H-NMR}$, FT-IR, UV-vis absorption, emission spectroscopy, excited-state lifetime and Spectro electrochemical measurements. It has been claimed that these two ruthenium dyes with (K-19) and without amphiphilic chains (K-73) show very striking features with respect to photovoltaic performance and stability. Devices based on the K-73 dye and a nonvolatile electrolyte yielded an unprecedented overall



Scheme 3 Schematic representation of the reaction and the molecular formulas of D5 and D6.

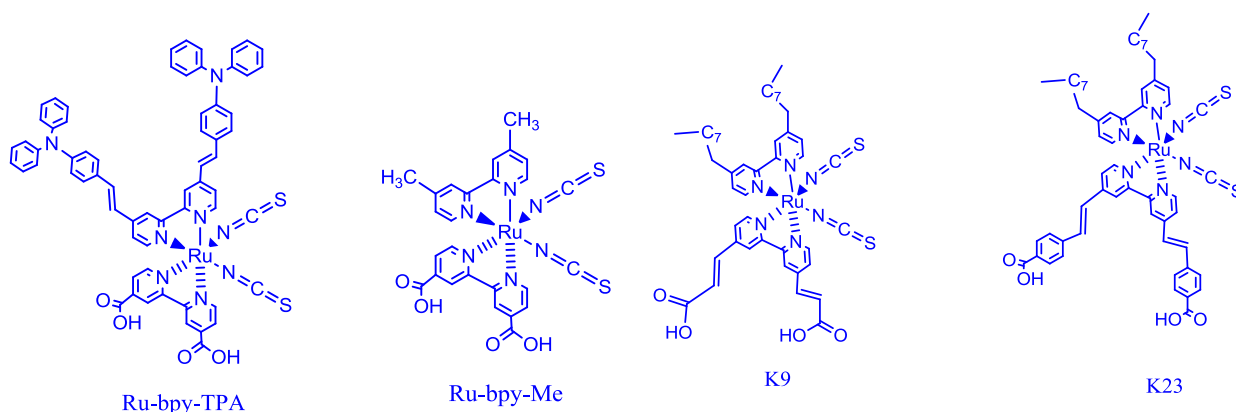


Fig. 5 The structures of Ru-bpy-TPA and Ru-bpy-Me respectively; **Fig. 6** The structures of K9 and K23 respectively.

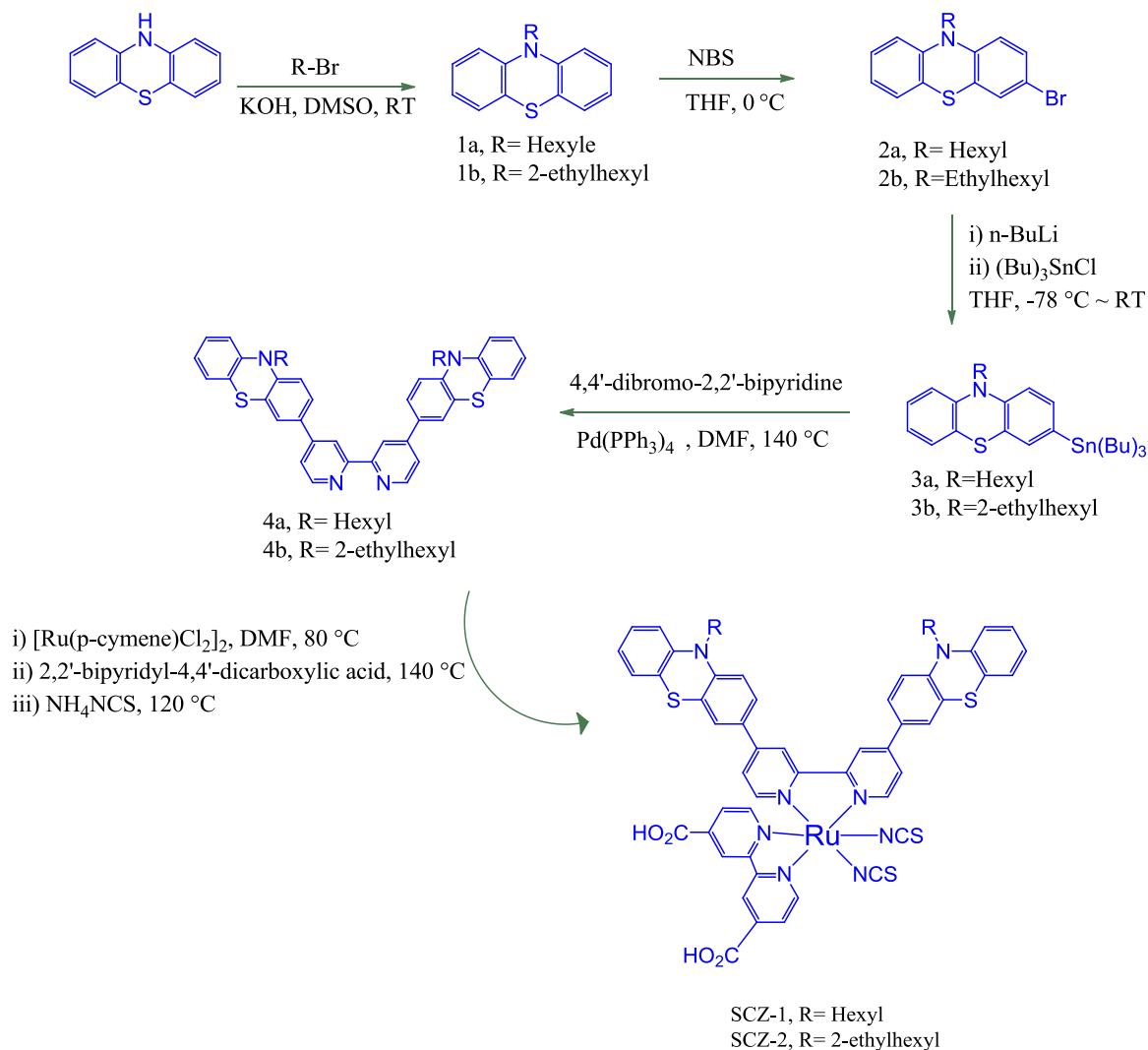
conversion efficiency of 9% under simulated global air mass 1.5 sunlight at 1000 W/m² intensity. The high extinction coefficients of these sensitizers enables these dyes, a new generation thin film dye sensitized solar cells yielding high conversion efficiency even with viscous electrolytes based on ionic liquids or nonvolatile solvents. The incorporation of the alkoxy styryl group helps in the conjugation of the bipyridine donor ligand increasing profusely their molar extinction coefficient and solar light harvesting ability. Dye sensitized solar cells incorporating the K-19 dye in combination with a binary ionic liquid electrolyte gave over 7.0% efficiency and maintained excellent stability under light at ~ 60°C for ~ 1000 h.

Incorporating electron donating group in the anchoring group, Snaith *et al.* (2008) have synthesized two novel 4- and 4,4'-oligophenylenevinylene-functionalized Ru^{II} bipyridine sensitizers materials coded as D5 and D6. Authors claimed that both of these dyes showed higher photocurrents as well as higher efficiencies for their cells compared to those of cells containing N3 dye [Ru (dcbpyH₂)₂(NCS)₂], herein dcbpyH stands for 4,4'-dicarboxy-2,2'-bipyridine. According to the report, the short circuit photocurrent densities for N3, D5, and D6 are 9.8, 10.8, and 11.7 mA/cm², and the efficiencies are 4.1%, 4.6%, and 4.8%, respectively. Corresponding enhancements in photon to current conversion efficiency values are attributed to the oligophenylenevinylene groups of D5 and D6 that contains conjugated double bonds. The Schematic diagram (Scheme 3) of the reaction and the molecular formulas of the complexes are shown below.

Chen *et al.* (2009) have synthesized two novel bipyridyl-NCS ruthenium complex sensitizers, i.e., Ru-bpy-TPA (TPA = triphenyl amine) with extended π conjugation and Ru-bpy-Me without conjugation system. It has been claimed that by incorporating the TPA unit to the backbone of the dye molecule, the molecular extinction coefficient has been remarkably enhanced resulting in high light harvesting and photocurrent generation. The resulting solar power to electricity conversion efficiency for the solar cell has been phenomenally increased from 2.4% to 3.2% when comparing the new sensitizer of an analogy with no conjugating group. The structures (Fig. 5) are drawn below.

Jang *et al.* (2009) have reported two ruthenium based novel sensitizers i.e., Ru(4,4'-dicarboxyvinyl-2,2'-bipyridine)(4,4'-dinonyl-2,2'-bipyridine)(NCS)₂ (coded as K9) and Ru(4,4'-dicarboxy(phenylethenyl)-2,2'-bipyridine)(4,4'-dinonyl-2,2'-bipyridine)(NCS)₂ (coded as K23). The complexes were characterized by spectroscopic, analytical and electrochemical impedance measurements. Incorporation of the conjugated linkers on the anchoring bipyridyl group that enables enhancements in the short-circuit photocurrents of the thin film DSSCs as compared to conventional Z907 dye (Ru(4,4'-dicarboxy-2,2'-bipyridine)(4,4'-dinonyl-2,2'-bipyridine)(NCS)₂) sensitized cells due to increased molar extinction coefficients and enhanced spectral response in the visible light and the near-IR regions. The conversion efficiencies of K9, K23 and Z907 were 4.14%, 4.41% and 4.06% respectively.

Kisserwan and Ghaddar (2011) have synthesized novel heteroleptic ruthenium complex, coded CYC-B11 (Fig. 6), introducing an electron enriched hexylthio-bithiophene antennas. It has been claimed that this ruthenium complex with the new concept of



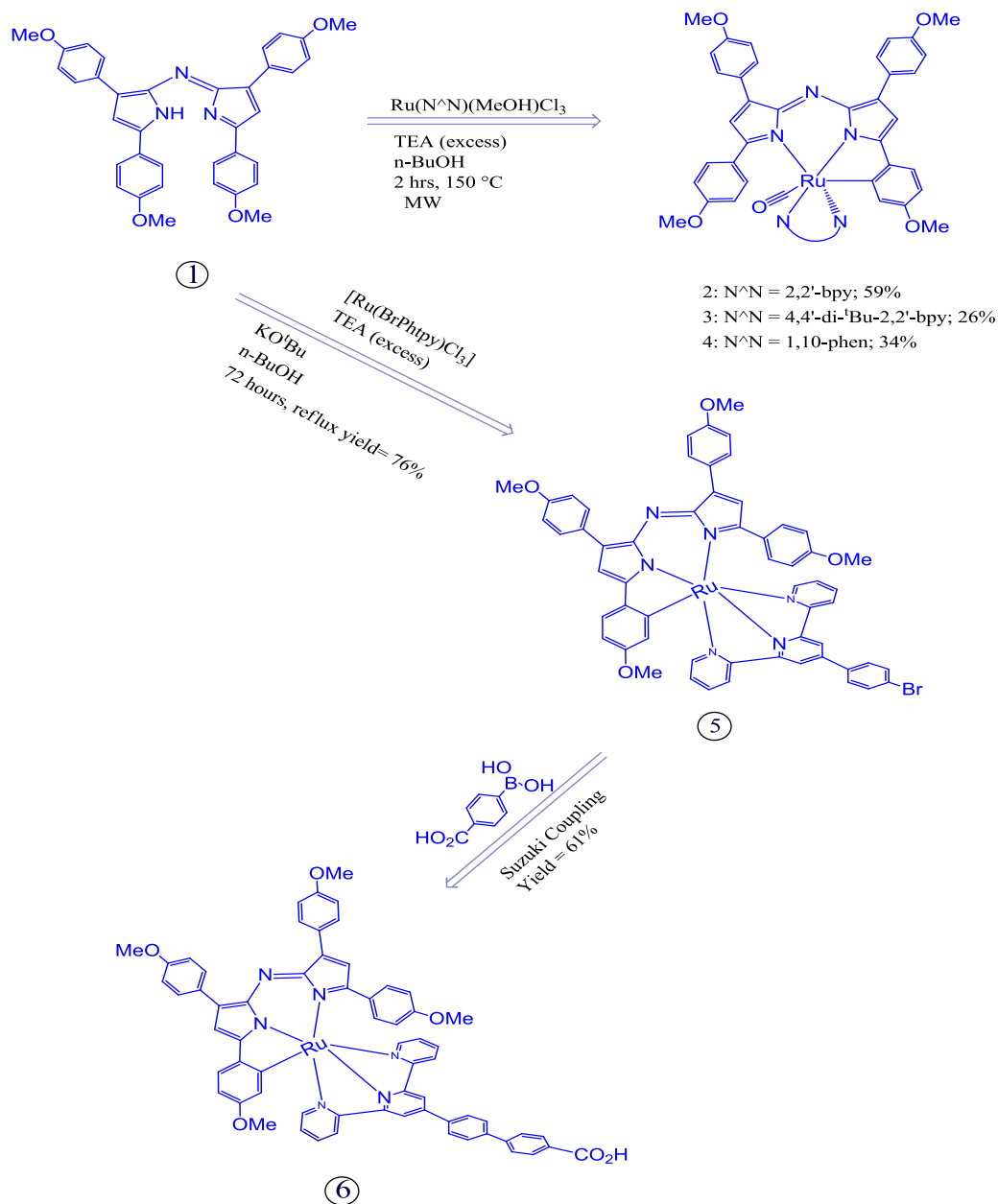
Scheme 4 Schematic representation of synthesis of SCZ-1 & SCZ-2.

Recently, Ashraf *et al.* (2017) have synthesized and characterized two unique tris-heteroleptic thiocyanate-free Ru(II) complexes created on bi-imidazole moiety varying the ancillary ligand. The dye with carbazole was coded as SD-15 and with triphenyl amino group was coded as SD-16. Both the sensitizers gave overall power conversion efficiency of 3.3% (Table 2).

Though there are some disadvantages of the Ruthenium complexes such as their higher costs but polypyridine complexes of Ruthenium have intense charge transfer absorption across the whole visible range and have easy tunable redox properties creating them gain superior to other metal sensitizers. Later on, a modified DSSC has been described which is known to be “e DSSC”. This has come into existence because of the encapsulation problem posed by the use of liquid in the conventional wet type DSSC. With the rising research in the different domains of DSSC including sensitizers, semiconductors, thin films, redox couples, the efficiency has already risen from 7% to ~11% leading to the introduction of DSSCs commercially over the conventional silicon based solar cells, which acutely suffers from degradation due to the well-known Staebler-Wronski effect, in the upcoming future.

DSSCs: A Next Generation Power Source With Strategies Towards GHGs Mitigation and Low Carbon Foot Print Through a Renewability Approach

Urbanization of human civilization is over filling the atmosphere with several toxic pollutants which hampers the balance of our ecosystem. In addition, increasing rate of greenhouse gas emission is enhancing global warming index which results in steady drive up the planet's temperature. The present CO₂ foot print in our atmosphere is approximately 410 ppm. One of the major sources of CO₂ emission is electricity in thermal plants, which accounts more than one-third of world's global warming. Indeed, most of the thermal plants are generating electricity by coal-burning and in some cases by utilizing natural gases. In contrast, renewable energy sources can produce very minuscule amount of carbon footprint. According to a survey of energy supply options, the sun is the only fresh energy resource in sufficiently abundant supply to meet global energy demand, though less than 0.1% of our energy



Scheme 5 Schematic representation of synthesis of Ru (II) sensitizers 2–6.

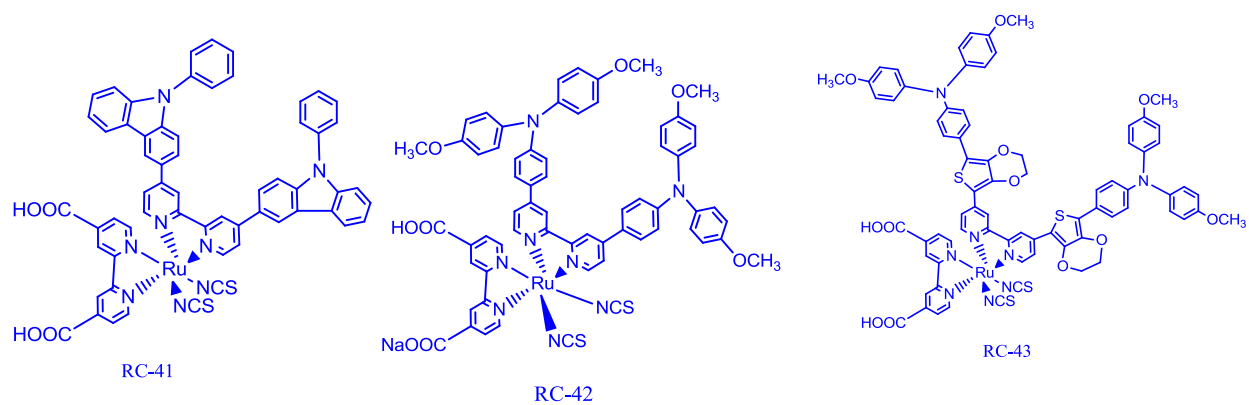


Fig. 7 Structures of Ru sensitizers (RC-41, RC-42 & RC-43).

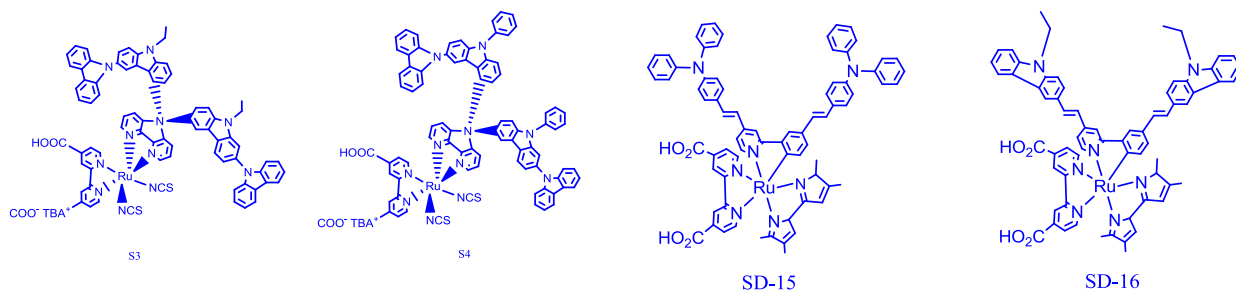
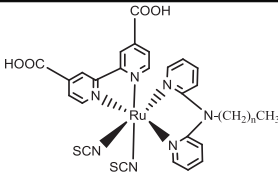
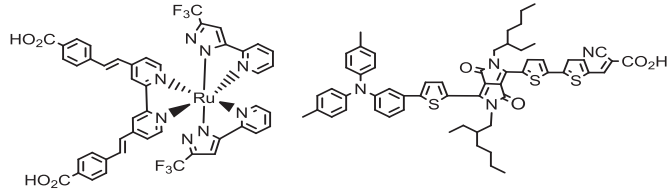
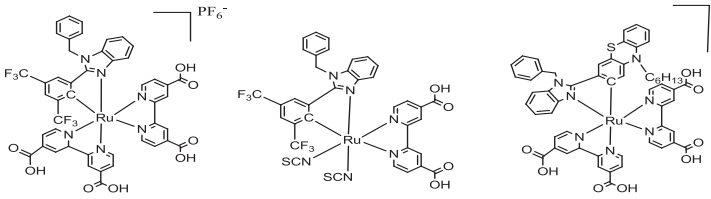
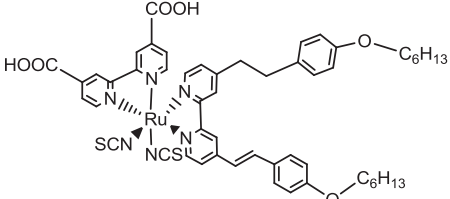
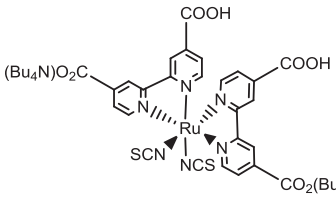
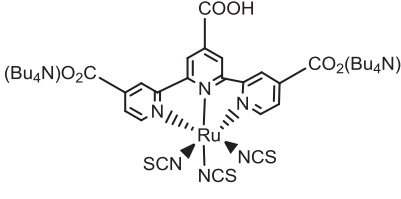


Fig. 8 Structures of Ru sensitizers (S3 and S4).

Table 2 Ruthenium complex based some of the dye sensitizers and their properties

Sl no.	Structure or chemical formula	UV-vis peak	Efficiency	References
1	Ru3 Ru6	306 nm	1.80%	(Younes and Ghaddar, 2008)

Table 2 Continued

Sl no.	Structure or chemical formula	UV-vis peak	Efficiency	References
2	 complex 1, n=13 complex 2, n=11	568 (complex 1) and 426 nm (complex 2)	8.2%	(Wang <i>et al.</i> , 2004)
3	 SPS-01 TDPP	418 nm and 532 nm	6.90 %	(Sharma <i>et al.</i> , 2012)
4	 TC-01 TC-02TC-03	TC-01 & TC-02-400 nm & TC-03-572 nm	(i) TC-1-6.39% (ii) TC-2-7.63% (iii) TC-3-2.87%	(Jella <i>et al.</i> , 2016)
5	 N3	~ 534	10	(Karmakar and Ruparelia, 2011)
6	 N719	~ 532	11.18	(Karmakar and Ruparelia, 2011)
7	 Black Dye	~ 605	10.40	(Karmakar and Ruparelia, 2011)

(Continued)

Table 2 Continued

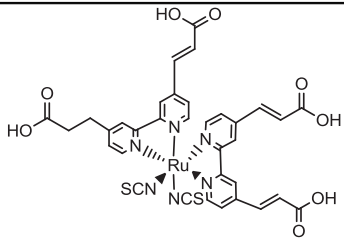
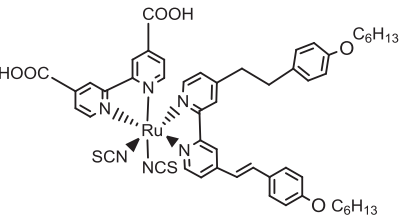
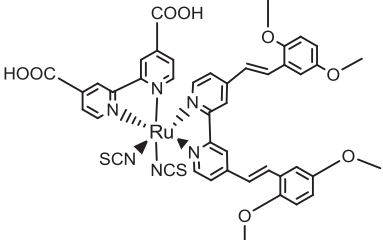
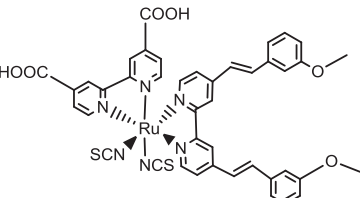
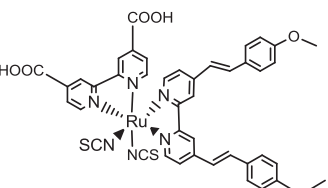
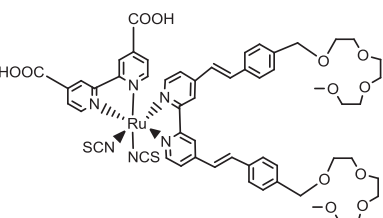
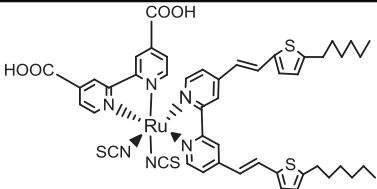
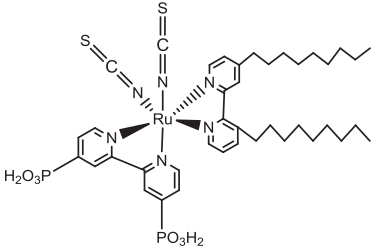
Sl no.	Structure or chemical formula	UV-vis peak	Efficiency	References
8	 K8	~ 555	8.64	(Karmakar and Ruparelia, 2011)
9	 K19	~ 543	7.0	(Karmakar and Ruparelia, 2011)
10	 N945	~ 550	9.60	(Karmakar and Ruparelia, 2011)
11	 Z910	~ 543	10.20	(Karmakar and Ruparelia, 2011)
12	 K73	~ 545	9.00	(Karmakar and Ruparelia, 2011)
13	 K51	~ 530	7.80	(Karmakar and Ruparelia, 2011)

Table 2 Continued

Sl no.	Structure or chemical formula	UV-vis peak	Efficiency	References
14	 HRS-1	~ 542	9.50	(Karmakar and Ruparelia, 2011)
15	 Z955	~ 519	8.00	(Karmakar and Ruparelia, 2011)

needs are met through the direct conversion of sunlight. To meet up this global energy demand, there are a number of “next generation” technologies on harvesting sunlight with more eco-friendly materials. Dye-sensitized solar cells (DSSCs) and organic solar cells are currently showing high efficiency in terms of their efficiency, thermal stability and commercialization though there remains much fundamental information to be learned within this diverse arena. In this perspective solar energy has achieved a massive footprint in India’s energy basket. It has contributed around 39% i.e., over 7100 megawatts (MW) to the overall total capacity additions (according to data from Mercom Capital Group, a US-based research and consulting firm). In a nutshell, the country has a total solar capacity of around 14.7 gigawatts (GW), (1 GW = 1000 MW) as of September 2017 (see “Relevant Websites section”). According to data aggregated by the International Panel on Climate Change, global warming emissions associated with renewable energy which includes fabrication, installation, commissioning and maintenance, and dismantling and decommissioning are minimal. Increasing the supply of renewable energy would allow us to replace carbon-intensive energy sources and significantly reduce greenhouse gas emissions. In addition to reduced GHG emissions, these technologies can provide other important environmental benefits; in particular non-combustion based options can put forward benefits like elimination of air pollution by low emission of suspended particulate matter as well.

Concluding Remarks

Unprecedented hike in the demand of energy along with the awareness about health and environmental hazards of fossil fuels have made researchers to look into different aspects of Dye sensitized solar cells as the alternative clean and renewable energy sources. In this regard, our emphasis has been given on mitigation of greenhouse gases and carbon foot print through renewability approach. With the beginning of nanotechnology it has become increasingly possible to understand, control and direct the material properties in an exceptional manner as a result of which several new concepts and designs of solar cells devices have emerged. Many sensitizers including both inorganic and organic dyes have been used to fulfill the energy demands of future generations in an environment friendly and sustainable way. Among them, Ruthenium complexes have been preferred owing to the high conversion efficiency which now has reached up to ~ 11%.

Recent developments in the area of DSSCs have lead researchers to invent some dyes which absorb across the visible spectrum leading to higher light to energy conversion efficiencies. Apart from these, cost reduction and simplification of the manufacturing procedures of dye solar cells are also to be emphasized. So that in near future, the DSSC will be the only alternative way to fulfill the energy needs of the planet within next few years.

See also: Green Mining of Rare Earth Elements (REE) to Diminish Greenhouse Gas (GHG) Footprint. Renewable Jet-Fuel (RJF): Mitigation of Aviation-Related GHG Emission. Use of Clean, Renewable and Alternative Energies in Mitigation of Greenhouse Gases

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PV History - Sunlight Electric.
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Quartz.

Development of Vapor Absorption Cooling System Driven by Renewable Energy

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Glossary

2DS 2°C Scenario (pathway to a CO₂ trajectory with 50% chance of limiting temperature increase to 2°C by 2100 by using currently available technologies).

AC Air conditioner.

ARS Absorption Refrigeration System (also known as VACS).

B2DS Beyond 2°C scenario (intended as an indication of how far beyond 2°C available and in development technologies could take us).

BAU Business as usual.

BEE Bureau of Energy Efficiency.

CCHP Combined Cooling, Heating, and Power (also known as Tri-generation System).

CDD Cooling degree-days.

CE Cooling effect.

CEC Comparative Energy Consumption (calculated to determine the star rating band and star rating of model of a cooling system employing a correlation involving cardinal parameters as applicable, such as, total adjusted storage volume for household frost free refrigerator).

CFC Chloro-Fluoro-Carbon.

CFHX Counter flow heat exchanger.

CHP Combined Heat and Power (also known as cogeneration).

COP Coefficient of performance (cooling produced per unit of heat or electricity used, W/W, a non-dimensional quantity, calculate as EER divided by 3.412).

DAP Double acting pump.

DC, DCS District cooling, District cooling system.

DEARS Double Effect Absorption Refrigeration System.

DH, DHS District heating, District heating system.

DHC District heating and cooling.

ECBC Energy Conservation Building Code.

EE Energy efficiency.

EER Energy efficiency ratio (cooling produced per unit of heat or electricity used, Btu per h/Input W, calculated as COP multiplied with 3.412, as 1 kW = 3412 Btu per h).

EMPT Emission payback time.

EPT Energy payback time.

ERR Energy return ratio represents how many times the energy saving overcomes the global energy consumption due to the innovative plant.

EWS Economically weaker sections.

GCI Green Cooling Initiative.

GHG Greenhouse gas.

HDD Heating degree-days.

HVAC Heating, ventilating and air conditioning.

IDE Input driving energy.

IESS India Energy Security Scenario

INR Indian rupees.

K-CEP Kigali Cooling Efficiency Program.

LCC Life cycle cost.

LCE Low carbon economy.

LIG Low income groups.

LiBr Lithium bromide.

LPD Litres per Day.

LPT Low pressure turbine.

NZEB Net-Zero Energy Building.

PEE Primary energy exchange

PEX Power exchanger.

PV Photovoltaic.

RAC Room air conditioner.

RCHG-ARS Absorption-Compression Hybrid Refrigeration System Recovering Condensation Heat for Regeneration.

RE Renewable energy [The energy sources available in nature which have the capacity to be renewed or replenished within our lifetime under favorable circumstances or let that happen in natural course. It is sometimes synonymous with CE = Clean Energy (according to '100% RE' "clean energy" mean carbon- and pollution-free energy collected from renewable, sustainably harvested sources, such as wind, solar, hydro, tidal, and geothermal, as well as EE but does not include natural gas, nuclear, or any carbon-based energy source)].

RTS Reference Technology Scenario (based on today's commitments to limit emissions and improve EE and then an extension of current trends, requires further major shifts in policy and technology in the period to 2060).

SDS Sustainable Development Scenario.

SEER Seasonal energy efficiency ratio.

SFPC Solar flat plate collectors.

SPVS Solar photovoltaic system.

SS Strong solution (of refrigerant and absorbent in VACS).

SSGS Solar steam generating system.

SWHS Solar water heating system.

TR Tons of Refrigeration (cooling produced by one Ton of ice per hour, that is, removal of 12,000 Btu per h).

UNDP United Nations Development Program.

VACS Vapor absorption cooling system (also known as ARS and VAMs).

VAM Vapor absorption machine.

VCCS Vapor compression cooling system.

WHR Waste heat recovery.

WS Weak solution (of refrigerant and absorbent in VACS).

Introduction

- Growing cooling need as developing world fast approaches the developed economy

Cooling methods and needs have both been evolving over thousands of years. However, the recent and anticipated rise in cooling need has surpassed all previous records probably because the developing world, where about 70% of the world's population resides, has begun to employ large and small scale application of cooling systems in the commercial as well as domestic sector as if repeating a historic trend of the developed world. Pérez-Lombard *et al.* (2008) pointed out that energy consumption of buildings in developed countries comprises 20%–40% of total energy use and is above industry and transport figures in the EU and USA. With the consolidation of the demand for thermal comfort, HVAC systems (and their associated energy consumption) have become an unavoidable asset, accounting for almost half the energy consumed in buildings, and around 10%–20% of total energy consumption in developed countries. The growing trend in building energy consumption, HVAC in particular, will continue even more so with a similar evolution now happening in the developing world that was earlier experienced in developed world, as total energy consumption is increasing in the larger population as a whole. For example, in India, NITI Aayog (2015) estimated that 70% of the buildings in 2030 would be found to be constructed during 2010–2030 only. Studies have shown that India's domestic sector alone calls for a 40% rise in cooling need for urban India and 21% per annum for rural India, calling for 10,386 MW additional capacity in three years (Choudhury and Ray, 2012) and solar operated VACSs, are feasible (Prabhune and Choudhury, 1995), elaborated in this article. Saastamoinen and Paiho (2018) reported that the global cooling demand is expected to increase sharply by 2050 by almost 150% primarily because of population and economic growth, change in lifestyle and energy system development, global warming, as well as quantity and quality of buildings and urban development. Analysis by Sachar *et al.* (2018) shows that at the current growth trajectory of RACs, by the year 2100 the world may see a more than 50-fold increase in the cooling energy demand since the start of the century, solely contributing to over 0.5°C increase in global surface temperatures. The trend in the global context, mentioned below in this article, could well emphasize the need for holistic development of VACS, which has been identified to be the most promising among the solar cooling systems alternative to conventional cooling systems (Al-Zubaydi, 2011) in spite of several barriers to be overcome. Cases from the EU, USA, and India have been presented toward the end of this article to highlight the global trend of RE operated VACS.

- VACS to play an important role for development in the LCE path

The plot of Energy Consumption per capita versus Human Development Index (HDI) for various countries of the world is parabolic in nature, showing a rise of the former with increment of latter (Fig. 1), but at diminishing rate of return (Steinberger, 2016). This observation is corroborated by UNDP (2018) clearly observing that while most countries of the world are showing an increasing trend of HDI (Fig. 2), business-as-usual approaches must change, with countries at different levels of human development exposed to

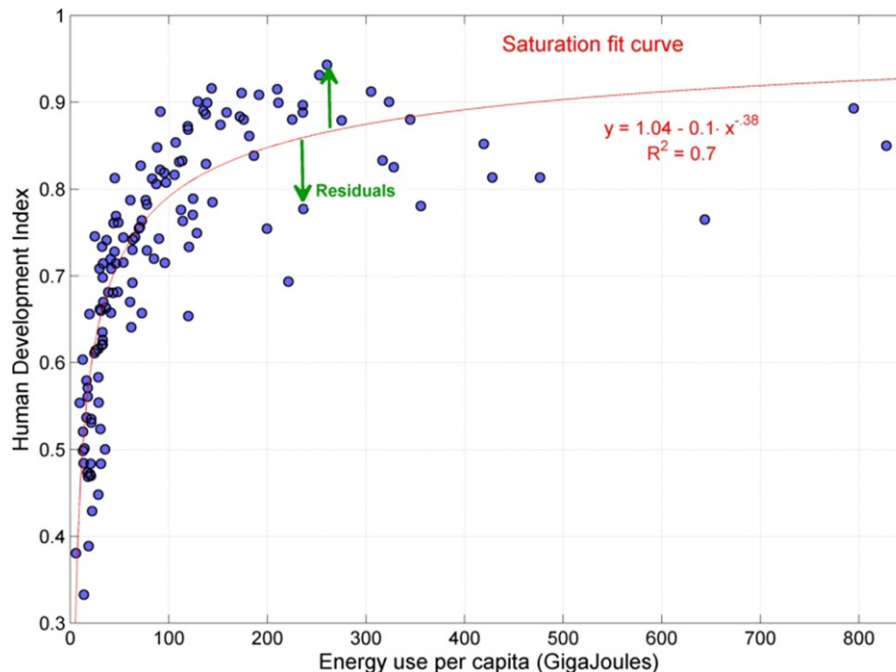


Fig. 1 Energy Consumption per capita vs. Human Development Index. Reproduced from Steinberger, J.K., 2016. Energising Human Development. Dr. Julia K. Steinberger, Associate Professor in Ecological Economics, Sustainability Research Institute, University of Leeds, United Kingdom. United Nations Development Programme, Human Development Reports, April 14, 2016. Available at: <http://hdr.undp.org/en/content/energising-human-development> (accessed 15.04.19).

Human Development Index values, by country grouping, 1990–2017

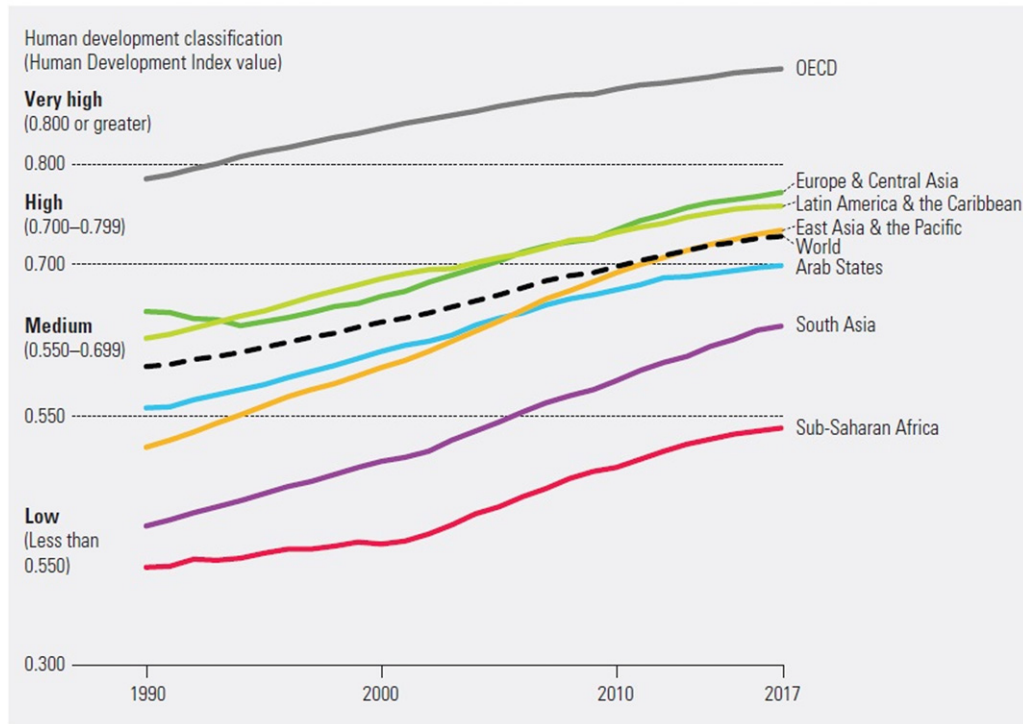


Fig. 2 Most countries of the world showing an increasing trend of Human Development Index. Reproduced from UNDP, 2018. Human Development Indices and Indicators 2018. New York: Statistical Update the United Nations Development Programme. Available at: http://hdr.undp.org/sites/default/files/2018_human_development_statistical_update.pdf. (accessed 30.04.19).

and contributing to environmental degradation in different ways, CO₂ emission in particular. Very high human development countries (HDI ≥ 0.8) are the biggest contributors to climate change, with average carbon dioxide emissions per capita of 10.7 t, compared with 0.3 t in low human development countries (HDI < 0.55) as shown in Fig. 3. The considerable variation within the developed nations reveals the opportunity for developing nations to follow a cleaner path of development: Qatar (HDI 0.856) had the highest carbon dioxide emissions per capita in 2014 (> 45 t per person), while Uruguay (HDI 0.804) released only 2 t per person. Further studies within such countries (viz. Qatar versus Uruguay) help to understand the sectorial issues and opportunities for improvement. The energy sector is the largest contributor to carbon dioxide emission where we burn fossil fuel to produce energy. The developing world cannot become developed by following the average path of development, but by assimilation of the lessons learned and applied depending on location, time as well as users' need, taste, and economic conditions. WICEE and GTZ (2004) emphasize the need to make sustainable energy systems integrating EE and renewable energies an important subject for the discussion and implementation on rapidly intensifying international transfer of know-how. In 2018 and 2019, two landmark steps were taken for the first time (International Energy Agency (IEA), 2019a; "see Relevant Websites section"). First, the Cooling Action Plan – the first of its kind in the world – that has put forth multiple proposed interventions to address cooling across multiple sectors in India, and second, the "First-ever global coalition for clean cooling" by the United Nations. Thus, rapid rise of HVAC calls for urgent action toward LCE in favor of development of VACS driven by renewable energy. also discussed in this article.

- Potential of RE can be fully realized through adaptation of environmentally benign technologies such as VACS

The sun is a smaller star among several hundred billion stars in our Milky Way alone. Earth receives only a tiny fraction (less than a billionth) of energy released from the sun in all directions, yet that is several thousand times more than what even modern human civilization consumes today, which includes the old stock (of solar energy) now explored as fossil fuels, viz. coal, oil, and gas, along with the present forms of renewables, viz. solar and its derivatives, such as wind, biomass, ocean thermal, etc. The energy sources that also play a significant role albeit out of this energy chain, viz. nuclear fission, geothermal, and tidal, having no direct emission of CO₂ in the energy conversion process, are also sometimes termed as renewable though this is debatable. Since the Industrial Revolution, our economy has become too carbonized through rampant consumption of fossil fuels. Decarbonization of the economy is crucial for the survival of modern civilization and calls for judicious use of energy resources through EE and application of RE in all possible ways. Active systems utilize RE directly, such as solar water heaters, renewable energy driven VACSs, etc. Huge potential of REs can further be explored by employing passive systems as well, such as passive architecture in buildings, natural cooling, etc. For example, through passive architecture, the cooling load of a building has been reported to be reduced by 25% (Radhi, 2009). Such initiative can also reduce the size of required active

Carbon dioxide emissions per capita, by human development group, 2014 (tonnes)

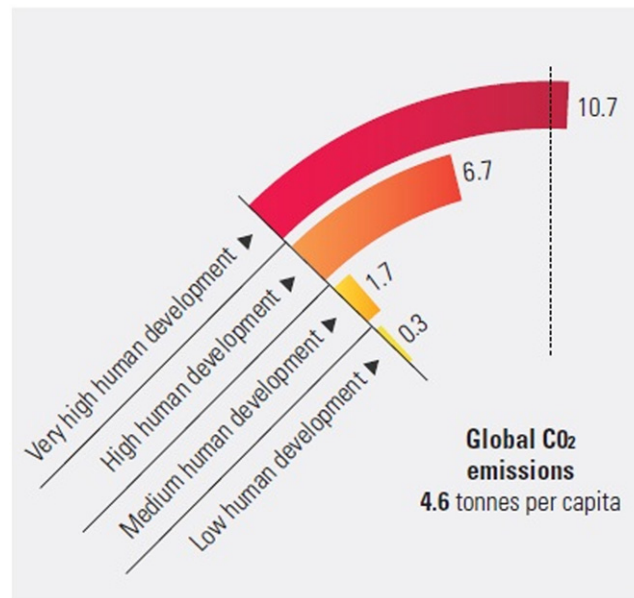


Fig. 3 Carbon dioxide emissions per capita, by human development group, 2014 (t). Reproduced from UNDP, 2018. Human Development Indices and Indicators 2018. New York: Statistical Update the United Nations Development Programme. Available at: http://hdr.undp.org/sites/default/files/2018_human_development_statistical_update.pdf. (accessed 30.04.19).

cooling systems and make the overall economy favorable that can be revealed through application of tools, viz. life cycle cost analysis by Beccali (2010) for solar cooling systems of IEA SHC Task 38 Solar Air Conditioning and Refrigeration, where solar thermal collectors' inclusion caused a reduction of net benefits of about 15%, with a payback time of about 3 years.

Several countries in the world have been successfully implementing 100% RE initiatives. These are already a reality in more than 180 sites around the globe (Kumar *et al.*, 2018). The Sierra Club's 2016 report showcases 10 U.S. cities that have made ambitious commitments to be powered by 100% clean (renewable) energy, that will help save taxpayer dollars, help their residents save money, create good jobs, and foster a better quality of life, in the backdrop that solar and wind energy prices have dropped 80% and 60%, respectively, in recent years. Georgetown, Texas, found that renewables made sound fiscal sense as it could lock in lower rates for solar power, and renewables use far less water than fossil fuels – critical in a state accustomed to drought. Clean energy can bring economic benefits to every American family. Studies by Stanford scientists revealed that the transition to a clean energy economy would save the average American family over \$200 a year in energy costs and \$1500 a year in healthcare costs as clean energy cuts pollution and saves lives. According to a national survey conducted by the University of Texas at Austin in spring of 2016, 90% of American adults agree that the government should be focusing on developing renewable energy. The report also mentioned that Burlington, Vermont; Aspen, Colorado; Columbia, Maryland; and Greensburg, Kansas, had already achieved 100% clean energy, powering their cities entirely with renewable sources, and proclaimed further that a dozen additional cities have made commitments to reach 100% clean energy in the next 15–20 years, and many others were considering similar plans. Sukumaran and Sudhakar (2017) reported the case study of fully solar powered Cochin International airport operating at 87% performance ratio and 20% capacity utilization factor.

The Kigali Amendment to the Montreal Protocol on hydrofluorocarbons, which cause ozone layer depletion, and the subsequent K-CEP launched in 2017 are working closely with partners across multiple countries to promote major EE gains and sustainable cooling solutions, bringing together philanthropic foundations, technical experts, international organizations, and other cooling partners, unleashing the huge potential for faster applications of solutions, such as VACS driven by renewables.

- VACS driven by renewable energy for CO₂ emission reduction toward achieving Sustainable Development Goal (SDG) 7

Among 17 goals set by the United Nations General Assembly in 2015, SDG 7 targets to “ensure access to affordable, reliable, sustainable and modern energy for all” within the year 2030. In support of these efforts, the IEA, the lead custodian agency for SDG 7.2 on renewable energy and 7.3 on EE, developed the SDS in World Energy Outlook 2017. The SDS combines ambitious climate policy (SDG 13) with significant action on achieving energy access (SDG 7.1) and creating cleaner air (SDG 3) – An integrated approach that speaks to energy policy priorities in a very wide range of countries (International Energy Agency (IEA), 2018a). Energy demand for cooling is the fastest growing end-use in buildings. Sales are rising three times faster than efficiency improvements, and more than 10 air conditioners will be sold every second over the next 30 years. Meanwhile, carbon dioxide

(CO₂) emissions from cooling have tripled since 1990 to 1130 million tons (Mt), equivalent to the total emissions of Japan (International Energy Agency (IEA), 2018b). To put cooling on track to meet the SDS target, minimum energy performance standards need to push markets to improve AC performance by more than 50% by 2030. This could cut CO₂ emissions from space cooling in half while reducing local air pollution. The IEA also launched in 2018 the Kigali tracker under its Global Exchange Platform to work with countries and K-CEP partners to track information on EE, refrigerants, investments, and policies. If improvements in the EE of cooling equipment continue to lag behind increases in sales, air-conditioning electricity demand could increase by as much as 60% globally by 2030 – 40% greater than the pace needed to match SDS targets.

This cannot be achieved without attaining EE and switching over to alternative sources such as renewable energy in particular. While launching the Cool Coalition, the United Nations revealed that emissions for cooling sector are set to increase 90% by 2050 if no action is taken. The energy sector happens to be the largest contributor to global CO₂ emission and buildings in EU and USA consume more energy than other sector sectors of economy, viz. transportation and industry. Therefore, to ensure sustainable modern energy for all, both EE and renewable energy use are essential and important. Thus, renewable energy driven VACS, elaborated in this article, are among few that meet both needs. Fahléna *et al.* (2012) pointed out that absorption cooling has potential for cost-effective CO₂ reduction.

Principle of Operation of Vapor Absorption Cooling System

Reversed Heat Engine Cycle for Vapor Absorption Cooling

In a heat engine cycle, flow of heat from a high temperature source to a low temperature sink is utilized to run a working fluid, say, water, through boiler–turbine–condenser–pump–(back to) boiler cycle, as the turbine drives an alternator to produce electricity, essentially from heat produced by combustion of a fuel, say, coal or oil or gas. In a reversed heat engine cycle [popularly known as VCCS, comprising evaporator–compressor–condenser–throttle–(back to) evaporator], heat flow apparently takes place from a low temperature source (sink, in previous case) to a high temperature sink (source, in previous case). Thus, the system is driven by a compressor raising the pressure of working fluid [popularly known as refrigerant, such as ammonia (NH₃), hydrofluorocarbon (HFC), chlorofluorocarbon (CFC), etc.] in gaseous form, that is, large specific volume and hence by consumption of significant amount of electricity to run the compressor, as $p dV$ work will be high. That is the reason why the EER is sought to be higher while selecting such systems with huge running cost of energy consumption, compared with a lower cost of initial investment for the purchase of the system.

Whereas, in vapor absorption cooling, as shown in Fig. 4, the compressor is replaced by another cyclic system of absorber–pump–generator–throttle–(back to) absorber, drastically reducing the need for electricity as pump handling liquid with much lower specific volume has much less $p dV$ work for similar pressure rise and mass flow rate. However, the additional system component, the generator (also known as desorber), would need some heat input, which is made available from the existing system, and could be low pressure steam or hot water generated from locally available renewable energy sources or waste heat. The vapor absorption systems have experienced a comeback nowa days as the savings due to lower electricity consumption outweigh the incremental cost for larger initial investment plus the cost of heat required at the generator. Among a large number of pairs available, techno-commercially most common working pairs are H₂O–LiBr and NH₃–H₂O nowadays (Saastamoinen and Paiho, 2018; Choudhury, 2019); both are non-CFC gases and not listed among the six GHGs as per the Kyoto Protocol. Solar energy driven NH₃–H₂O systems' performances are reported by Brice Le Lostec (2012) and Jawahar and Saravanan (2013). Jawahar and Saravanan have done an experimental study on the ammonia water VACS using a high-pressure and a low-pressure generator–absorber–heat exchanger system and the COP was found to be 0.61. Brice Le Lostec (2012) has done an experimental study on an ammonia water absorption chiller cooled with water–ethylene glycol solution. The required heat source is hot water ranging from 75–85°C and the COP was found out to be 0.6. A theoretical analysis on H₂O–LiBr and NH₃–H₂O VACSs can be obtained at IIT Kharagpur (2014, 2015, 2017).

Gomri (2013) has done a simulation study on the performance of a solar/natural gas operated H₂O–LiBr VACS and shown that the CO₂ emission is reduced by a considerable amount when compared with VCCS. Saleh and Mosa (2014) has done an optimization study on a single effect H₂O–LiBr absorption system powered by flat plate solar collectors and the COP was found to be 0.82. The generator temperature was 80–90°C and so the H₂O–LiBr system was found to be more suitable for solar applications. The present study further reviews several opportunities for improvement of efficiency and performance of renewable energy operated VACS including proposal of an innovative application of double acting reciprocating pumps as power exchanger to further reduce the power consumption thereby increasing the COP and enhancing opportunity for such system to be driven by renewable energy systems – solar energy in particular.

Coefficient of Performance of Cooling Systems

COP of cooling systems may be defined as the ratio of desired output, that is, the cooling effect to necessary input, that is, the power and heat (if any) input to be provided to run the system. COP varies from 2.30 to 3.10 for conventional cooling systems, that is, those running on VCCS. If the electrical input is corrected for its thermal use of primary energy resources, these values assume the range from 0.70 to 1. On the other hand, VACS use only a tenth to seventh part of electricity being used by its VCCS counterpart – the same being compensated by low temperature thermal energy input to its 'generator', and has typical COP of

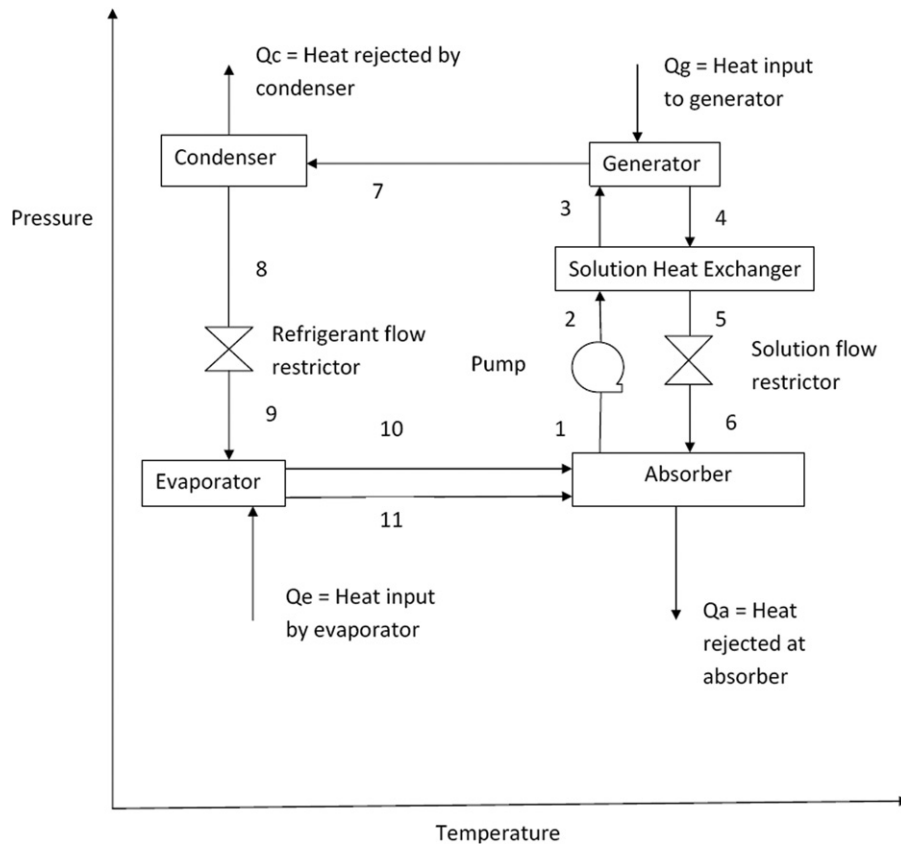


Fig. 4 Schematic diagram of single stage lithium bromide–water vapor absorption cooling system. Reproduced from Florides, G.A., Kalogirou, S.A., Tassou, S.A., Wrobel, L.C., 2003. Design and construction of a LiBr–water absorption machine. *Energy Conversion and Management* 44 (15), 2483–2508. Available at: https://s3.amazonaws.com/academia.edu.documents/47750868/s0196-8904_2803_2900006-220160803-26866-n7qel5.pdf?AWSAccessKeyId=AKIAIWOWYYGZ2Y53UL3A&Expires=1558277831&Signature=Oph6t1klS5Kt%2FYYPxw5ZHfOccE%3D&response-content-disposition=inline%3B%20filename%3DDesign_and_construction_of_a_LiBr_water.pdf.

0.704–0.95 If this COP is corrected to calculate in the same way as was done for VCCSs, it would be found to vary from 2.1 to 2.7. Many such VACS run on waste heat to meet the thermal energy input.

Cooling Systems' Performance Measured in the Market

In the market, cooling systems are generally measured in terms of EER, SEER, and CEC and expressed as follows:

COP is cooling produced per unit of heat or electricity used, $W(W)^{-1}$, a nondimensional quantity, calculated as EER divided by 3.412.

EER is cooling produced per unit of heat or electricity used, Btu per h/Input W, calculated as COP multiplied by 3.412, as $1 \text{ kW} = 3412 \text{ Btu per h}$. However, if EER is expressed as kJ cooling per hour $(W)^{-1}$, $\text{COP} = \text{EER}/3.6$.

The theoretical efficiency limit is the efficiency of a Carnot cycle operating between two temperatures. Considering a typical outside temperature of 35°C and inside temperature of 27°C , the maximum possible efficiency (COP in case of these cycles operating in reversed heat-engine mode) is 37.5 W/W . The best available room air conditioners in the world have a COP of around six or EER 21.6. This calculation for a Carnot cycle is based on the sensible cooling load only (i.e., cooling the air from a source temperature of 35°C to a sink temperature of 27°C) and ignores the latent load impact. In addition, Sachar (2018) observes that latent load, if any, can be met via a desiccant system with 100% theoretical efficiency. This is further in accordance with the BEE, Government of India, standard test conditions for evaluating the cooling capacity of variable capacity room air conditioners in India, where the expression of EER and COP are just interchanged.

SEER is seasonal EER, calculated by dividing total cooling produced in an annual cooling season to the total heat or electricity input to the system during the same period. Thus, if EER is a functional parameter, SEER is an operational parameter. SEER aims to increase the efficiency of ACs, helping consumers get lower bills even in higher temperatures. A SEER rating of 14–22 is considered to be good.

CEC is calculated to determine the star rating band and star rating of the model of a cooling system employing a correlation involving cardinal parameters as applicable, such as total adjusted storage volume for a household frost-free refrigerator.

Concept of Levelized Coefficient of Performance

$$\text{COP of a refrigeration system is} = \frac{\text{Cooling Effect (CE)}}{\text{Input Driving Energy (IDE)}} \quad (1)$$

In case of VCCS (electrically driven)

$$(\text{COP})_{\text{VCCS}} = \frac{\text{CE}}{\text{IDE}(\text{Electrical})} \quad (2)$$

In case of VACS (thermally driven)

$$(\text{COP})_{\text{VACS}} = \frac{\text{CE}}{\text{IDE}(\text{Heat}) + \text{Electricity}(\text{one} - \text{seventh part of normal VCCSs})} \quad (3)$$

Levelized COP is also termed as PEE (taking into consideration the fact that heat is a lower grade energy than electricity with a conversion factor of about 33.9% (Ministry of Power, Government of India, 2015).

$$(\text{COP})_{\text{Levelised VACS}} = \frac{\text{CE}}{\text{IDE}(\text{Heat}) \times (33.9/100)} \quad (4)$$

$$= \frac{2.94 \times \text{CE}}{\text{IDE}(\text{Heat})} \quad (5)$$

$$= 2.94 \times (\text{COP})_{\text{VCCS}} \quad (6)$$

Thus, COP of VACS may be compared with the COP of conventional vapor compression system only after normalizing it as mentioned above, that is, multiplying by 2.94 if they were levelized by making them comparable on a similar plane. Here IDE (Electrical $\times 0.339 / 7$) has been considered to be negligible as applied in the system shown in Fig. 4. Typical values for a single stage (Florides *et al.*, 2003) shown in Table 1 will give an idea why LiBr–H₂O VACSs are often selected for being driven by solar thermal energy (Q_g) input to the generator (at 90°C) for space cooling applications (cooling effect provided at 6°C or above).

Vapor Absorption Cooling System Driven by Renewable Energy

Abu-Zour and Riffat (2007) made a review of the then existing VACS and classified solar driven systems and Al-Zubaydi (2011) showed that VACS is more promising for solar thermal application. However, today, a large number of options are available and more are evolving for efficient use of various renewable energy sources for cooling purposes, as shown in Fig. 5, indicating nonsingularity of the solution, rather keeping the option open for optimization.

VACS driven by RE refers to the systems that procure the necessary thermal energy for heating of generator from one or more renewable energy sources. However, such systems, in addition to thermal energy, may also utilize renewable energy source to meet the (meager or much less than their VCCS counterpart) electrical energy to run the pump. VACS can be driven by various renewable energy sources, as follows:

- (1) Solar thermal energy: SWHSs or SSGSs or solar air heaters can drive any of the five types of the solar thermal cooling systems, viz. absorption, adsorption, ejector systems, desiccant cooling, thermomechanical. Even SFPC are utilized to provide

Table 1 Cardinal parameters for single stage vapor absorption cooling system

Point	Enthalpy (kJ/kg)	Mass flow rates (kg/s)	Pressure (kPa g)	T (°C)	Remarks
1	83.0	0.0530	0.934	34.9	Normal temp low pressure rich solution
2	83.0	0.0530	9.660	34.9	Normal temp high pressure rich solution
3	145.4	0.0530	9.660	65.0	Subcooled liquid
4	212.2	0.0486	9.660	90.0	Warm high pressure lean solution
5	144.2	0.0486	9.660	54.8	Normal temp high press lean solution
6	144.2	0.0486	0.934	44.5	Normal temp low pressure lean solution
7	2628.0	0.0044	9.660	85.0	High pressure superheated steam
8	185.3	0.0044	9.660	44.3	High pressure saturated liquid water
9	185.3	0.0044	0.934	6.0	Low pressure warm refrigerant liquid
10	2511.8	0.0043	0.934	6.0	Saturated vapor
11	23.5	0.0001	0.934	6.0	Saturated liquid water

Note: Florides, G.A., Kalogirou, S.A., Tassou, S.A., Wrobel, L.C., 2003. Design and construction of a LiBr–water absorption machine. *Energy Conversion and Management* 44 (15), 2483–2508. Available at: https://s3.amazonaws.com/academia.edu.documents/47750868/s0196-8904_2803_2900006-220160803-26866-n7qel5.pdf?AWSAccessKeyId=AKIAIWOWYYGZ2Y53UL3A&Expires=1558277831&Signature=Oph6t1kl5SKt%2FYYPXw5ZHfOccE%3D&response-content-disposition=inline%3B%20filename%3DDesign_and_construction_of_a_LiBr_water.pdf.

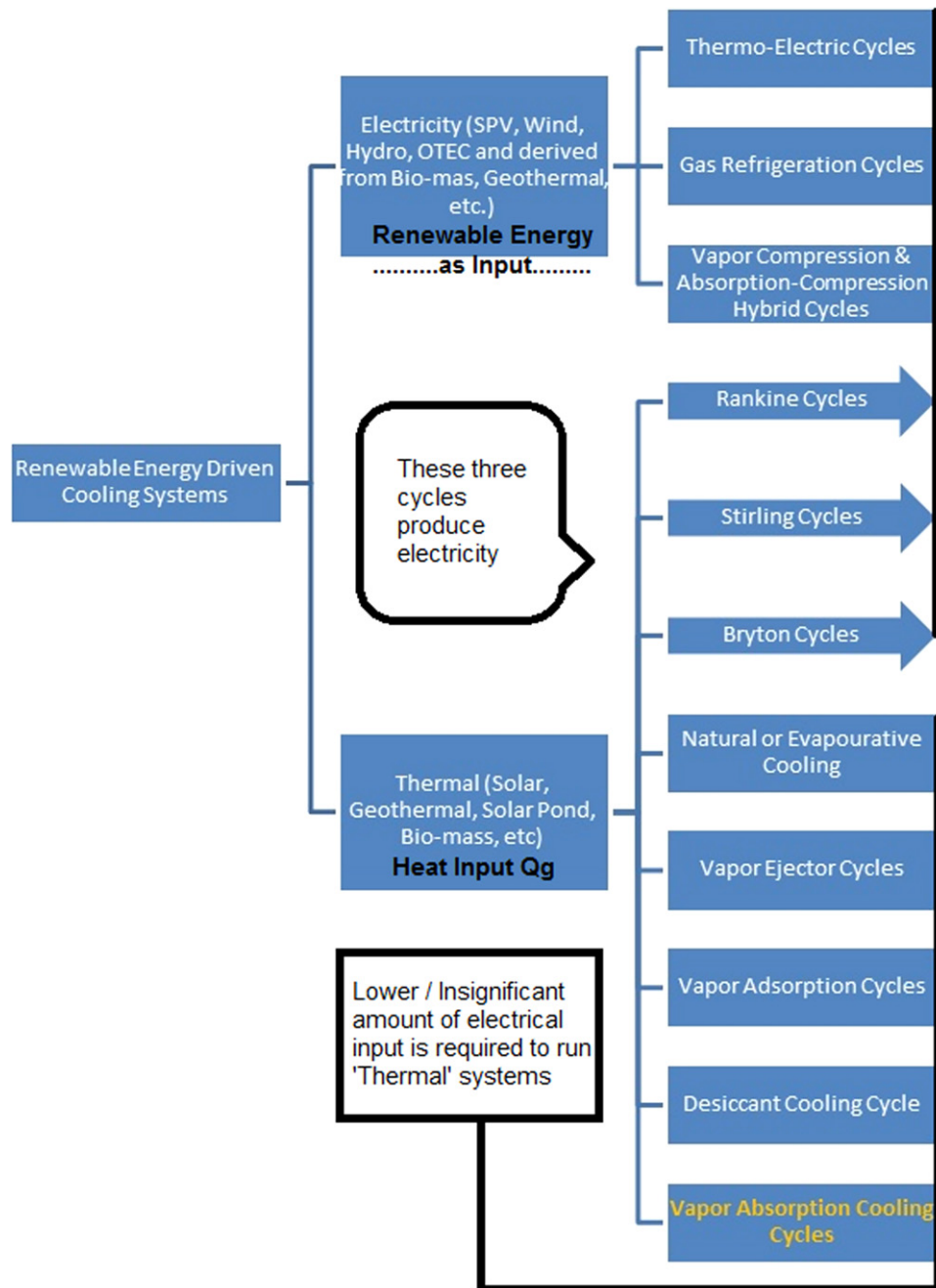


Fig. 5 Classification of cooling systems driven by renewable energy.

necessary heat (Q_g in Figs. 4 and 5) to the generator to meet the cooling load during summer leading to improved utilizability of SFPC, which normally remains underloaded during summer as size is designed on the basis of critical load, which is in winter. A mathematical modeling by Bajpai (2012) revealed that typically such $\text{NH}_3\text{--H}_2\text{O}$ system of 1 TR capacity would require 24 m^2 SFPC, which would make the system costly but technically feasible for even domestic application. Saha *et al.* (2001) found silica gel–water, when taken as the adsorbent refrigerant pair to exploit solar/waste heat of temperatures below 70°C , COP of only 0.36 could be achieved even at two stage chiller.

- (2) Biomass energy: If a sustainable supply of biomass is available at reasonable price, the same may be utilized or burned to produce heat to be transferred to the generator (Q_g in Figs. 4 and 5). For controlled and clean combustion, biogasification may be employed to produce producer gas.
- (3) SPVS: After thermal energy need at the generator has been met by renewable energy sources, electricity produced by SPVS can be utilized to run the pump, as the requirement of electricity is much lower with compared with the requirement to run the compressor in VCCS. In some cases, solar electricity operated VCCS may turn out to be more beneficial than solar thermal energy operated VACS.

- (4) Wind Energy Generator (WEG): Where available at cheaper rate, power from WEGs could be utilized instead of SPVSs in the above cases.
- (5) Hydropower: Similarly, as above, hydroelectricity could be a favored renewable energy source for driving the pump.
- (6) Geothermal: Geothermal power plants can provide bleed steam from LPTs to meet thermal energy need in the generator and electricity to drive the pump of VACS and also the electricity from geothermal power plants could be a favorable option to run a VCCS or any other system mentioned in Fig. 5.

Opportunities and Barriers for Development of Such Systems

A growing rate (15%) of electricity consumption in buildings goes to heating, ventilating, and air conditioning (HVAC). For some CDDs and HDDs, cooling would be costlier than heating. Buildings account for nearly 40% of global energy consumption. About 40% and 15% of that are consumed, respectively, by HVAC and lighting (Sun *et al.*, 2013). Solar cooling has been found to be a good example of addressing climate change and improving efficiency of solar thermally operated cooling technologies is an essential research need of the hour as well as the future (Al-Alilia *et al.*, 2014).

In developing countries, the building sector has a higher growth rate; for example, the highest is in case of India (Sachar *et al.*, 2018), where according to estimates by NITI Aayog (2015), 70% of the building stock in the year 2030 will be built during 2010–2030. Often, there is a match among the needs, as follows:

- (1) Cooling load generally increases directly with solar radiation, that is, availability of solar energy increases when cooling load is greater.
- (2) SWHS are typically designed for winter load, and therefore, remain largely underutilized during summer, when the hot water need will be much lower than that of the need in winter. Since the system size cannot be changed seasonally, SWHS becomes oversized and much of the capital investment is thus blocked. However, the cooling need is greater in summer. VACS are ideal applications to meet such load utilizing the surplus heat from SWHS employing VACS.
- (3) In the developing world, more buildings are upcoming that would be suitable for directly implementing more energy efficient and effective policy, which includes giving higher priority to VACS, thus avoiding the repetition of the mistakes learned previously.
- (4) In the developed world, opportunities of integration with existing systems, such as DHS, SWHS, etc. could be found to be technoeconomically viable as the utilizability of the existing systems would be enhanced.

In spite of increasing importance, the above-mentioned opportunities would be productive through identification of barriers and analysis to overcome the same as explored in the following section.

Overcoming the Barriers: Technology, Economics, Financial, and Social

Overcoming Technology Barriers

Innovation in technology to overcome barriers

International Energy Agency (IEA) (2019a) begun in 2019 the first ever Technology Collaboration Programmes (TCPs) for Heat Pumping Technologies (HPT TCP) and Energy Storage through Energy Conservation (ECES TCP) to seek to develop a prototype 'Climate Comfort Box' for sharing and dissemination of innovations and applications in this one of the fastest growing area for high efficiencies with flexible storage at affordable prices to deliver on ambitions for affordable heating and cooling. This new Innovation Tracking Framework identifies key long-term "technology innovation gaps" across the energy mix that need to be filled to meet long-term clean energy transition goals. The objective is to highlight where R&D investment and other efforts need improvement. The following are a few such innovative solutions.

Employing double acting pump to operate in power exchanger mode

As cooling demand will continue to grow, innovative technologies may be incorporated as quickly as possible. One of the technological innovative approaches would be application of a power exchanger (PEx), as briefly described below:

Working and Employing of Double Acting Pump in Power Exchanger mode

The innovative application of a double acting reciprocating pump, as proposed in the present study, to act as PEx, would further reduce the electricity consumption by nearly 75% and life cycle cost by nearly 10% especially for WHR VACSs. Here the pressure of the high pressure solution coming from the generator is utilized to pump the weak solution from the absorber to the generator. This reduces the pumping power significantly. When the valves V3 and V4 are closed then the piston moves upward forcing the valves V1 and V2 to open leading the inlet of fluid from the absorber and outlet of fluid to the generator.

When the piston moves upward, valves V2 and V3 are open but the valves V1 and V4 get closed, thus the strong solution from the generator gets stored from the lower chamber of the pump (below piston as shown in Fig. 6). In the same stroke the weak solution in the upper chamber (above piston) in the pump that was stored from the absorber in the previous stroke (piston moves downward) is pumped to the generator.

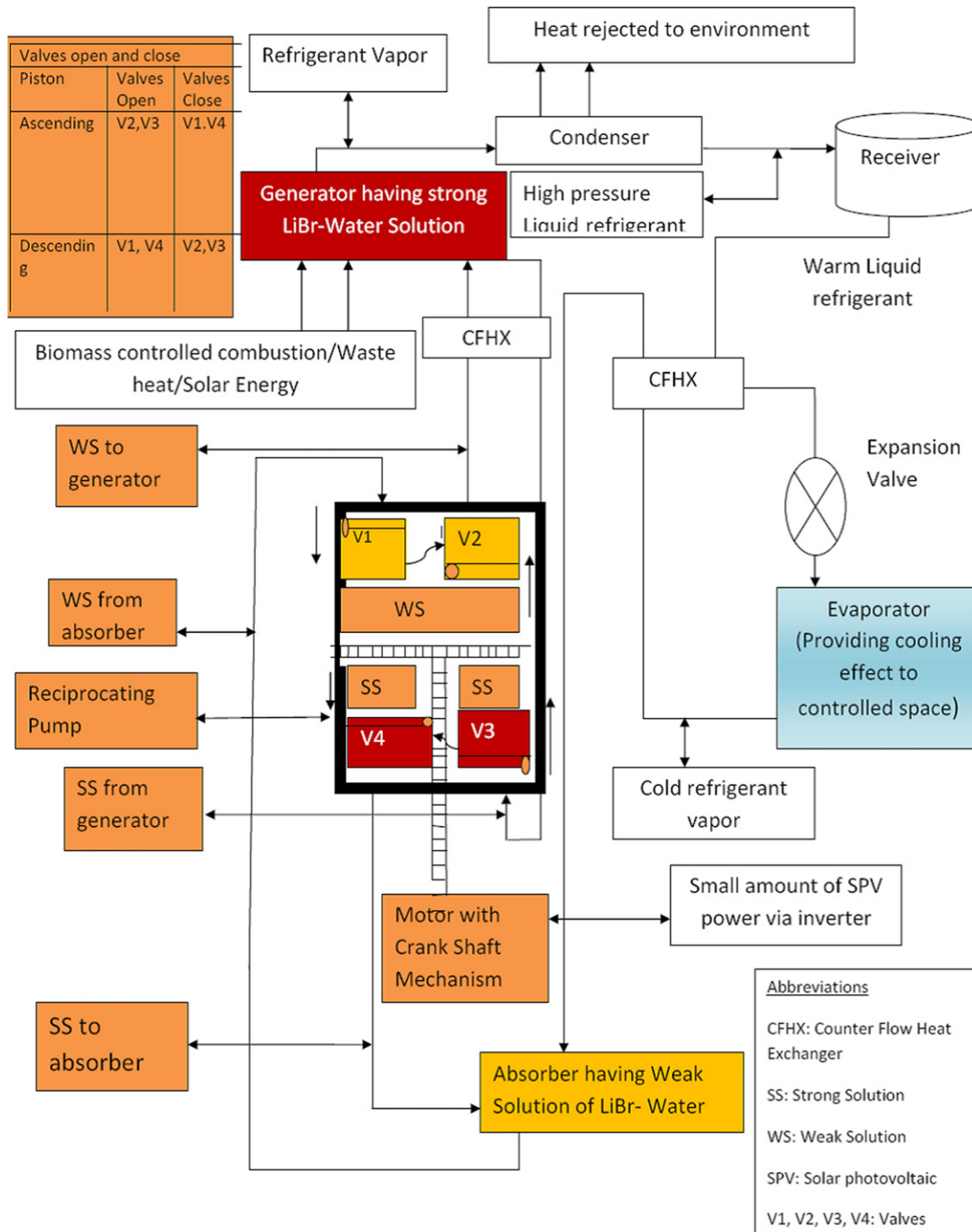


Fig. 6 Schematic diagram of a vapor absorption cooling system (lithium bromide + water) using reciprocating pump (in power exchanger mode).

Similarly when the piston moves downward valves V1 and V4 are open and V2 and V3 are closed. Thus the weak solution from the absorber gets stored in the upper chamber (above piston) in the pump and the strong solution, which was stored from the generator in the previous stroke (piston moves upward), is now pumped into the absorber completing the cycle.

The loss of power due to flow of strong solution from the generator at higher pressure to the absorber at lower pressure is almost recovered with the employment of this double effect reciprocating pump compared with single effect (ordinary) reciprocating pump necessary to transfer the rich solution in low pressure absorber to the high pressure generator. That is why the proposed system is termed as PEx in parity with the working principle and nomenclature of the heat exchanger. Thus by using the reciprocating pump in PEx mode the COP can be increased and the running cost can be lowered as the pump power to the generator is decreased, compared with conventional VACS, and thus makes it more competitive with VCCS.

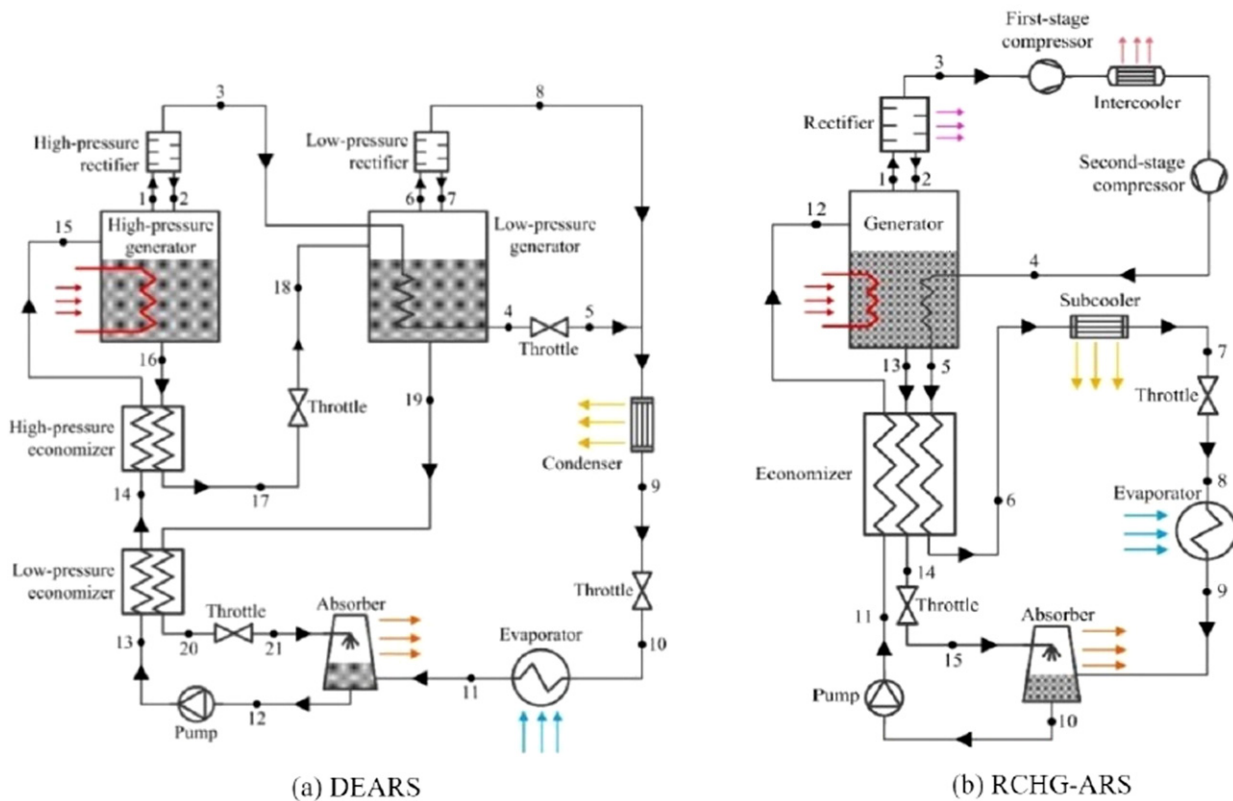


Fig. 7 Principle of operations of double effect absorption refrigeration system and absorption-compression hybrid refrigeration system recovering condensation heat for regeneration systems. *Source:* Wang, J., Li, X., Wang, B., *et al.*, 2017. Performance comparison between an absorption-compression hybrid refrigeration system and a double-effect absorption refrigeration system. *Procedia Engineering* 205, 241–247. Available at: https://www.researchgate.net/publication/320761741_Performance_Comparison_between_an_Absorption-compression_Hybrid_Refrigeration_System_and_a_Double-effect_Absorption_Refrigeration_System.

Employing double effect absorption refrigeration system and absorption-compression hybrid refrigeration system recovering condensation heat for regeneration for more efficient use of renewable power in cooling systems

Wang *et al.* (2017) have shown through simulation the opportunities for improvement of performance in absorption compression hybrid refrigeration system (RCHG-ARS) by 29% with compared with even a DEARS shown in Fig. 7.

Vapor compression cooling system and vapor absorption cooling system hybrid

The heat of condensation rejected by VCCS if integrated and utilized in the generator of VACS, the combined performance of the system run on renewable electricity could be better (than a single VACS, of capacity same that of the proposed combined system, also run on renewable electricity) in larger applications particularly where such electricity generation and cooling need are directly proportional. This would also help stability in the grid and overcome challenges of large-scale grid integration.

Choosing the correct vapor absorption cooling system technology, alone or hybrid

VACSs can be of various types and selection can be made, depending on combinations of various renewable energy resources with suitable VACS technologies, viz. standard, open cycle, turbo-absorption (Trivichachai and Wongwises, 2003), VCCS-VACS hybrid, etc. with appropriate absorbent-absorber solvent pair considering availability of supplier, maintenance, techno-economic viability, etc. Sreeshankar *et al.* (2014) pointed out that the exhaust gas of vehicles when utilized to run a Seebeck cycle for electricity generation and remaining heat for thermal input to VACSs provides all energy to cool automobile space and cold-storage on heavy vehicles.

Heating from cooling

Just like the old technology of VACS is coming back to meet the modern needs, some of our old concepts may be rethought to fetch huge benefits through replicated applications. Instead of using a separate heating system for any chilled substance to bring to normalcy for consumption/use, if the heat of condensation of the refrigerants is appropriately used, it would not only save energy of separate heating system, but also improve COP of the cooling system.

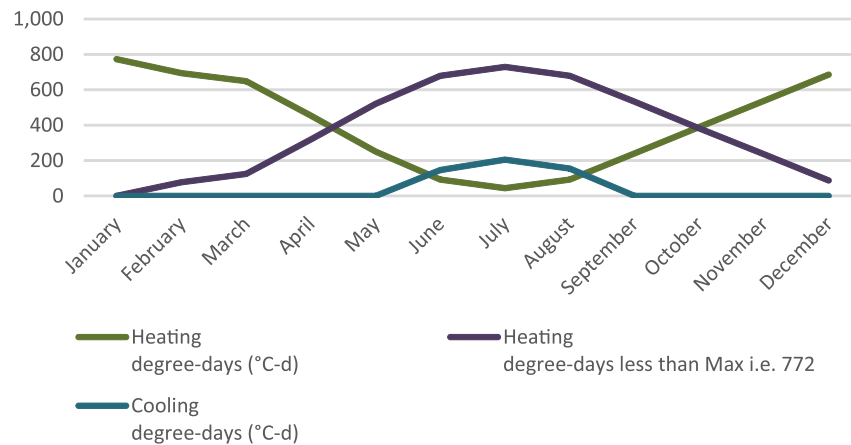


Fig. 8 Monthly variation of heating, differential heating and cooling degree-days in Helsinki, Finland. *Source:* RETScreen. Available at: <https://www.nrcan.gc.ca/energy>.

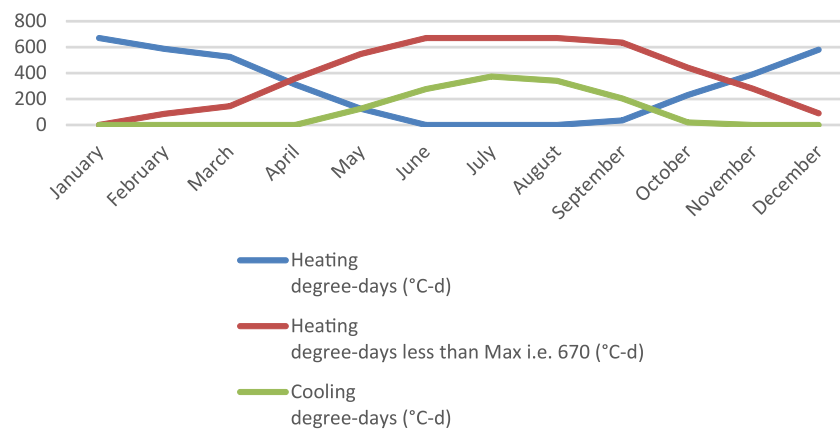


Fig. 9 Monthly variation of heating, differential heating and cooling degree-days in Buffalo, USA. *Source:* RETScreen. Available at: <https://www.nrcan.gc.ca/energy>.

Cooling from heating

VACS are essentially such devices that are being optimally operated to utilize the waste/surplus/unutilized/cheaper/less carbon intensive heat available at/near the point where cooling is required. Studies revealed newer ways and means for taking the fuller advantage of VACS. One such example is DHS, which are normally run on CHP mode. RETScreen data reveals that the HDD and CDD have opposite trends. DHS designed on the basis of HDD would be sized considering the maximum value, that is, in peak winter months. In other months, DHS will remain underutilized and hence away from highest efficiency point in proportion to the differential (maximum HDD – current month's HDD), which shows near perfect variation with CDD as shown in **Figs. 8** and **9** for two locations, viz. Helsinki, Finland and Buffalo, USA.

Also, the solar radiation is available more with cooling DD for most places, including Stockholm, Sweden and Canberra, Australia, as shown in **Figs. 10** and **11**. It is interesting to note that Canberra, being located in the southern hemisphere, has a different pattern of solar radiation (when it is winter in the northern hemisphere, summer prevails in the southern hemisphere, and vice versa) but the availability of solar radiation is again more for months with higher cooling DDs. Thus, opportunity for VACS driven by RE is again more. This is corroborated by the observations of *Ilic (2014)* on the monthly variation of heating load in Sweden as shown in **Fig. 12**.

Potential for drastic improvement of performance levels

Carrier launched in 2018 an air-conditioning unit with a SEER of 12.3, three times the market average efficiency of residential air-conditioning unit sales in the United States in 2017. Such initiatives illustrate the potential for cooling equipment to drastically improve performance levels and also calls for innovative action plans to help dissemination of such innovations. Average efficiencies of new air-conditioning units sold would need to move from a SEER of around 4 today to 7 or higher in 2030 – a task that is not insurmountable but one that would require strong market signals and greater collaboration between countries (*International Energy Agency (IEA), 2019a*).

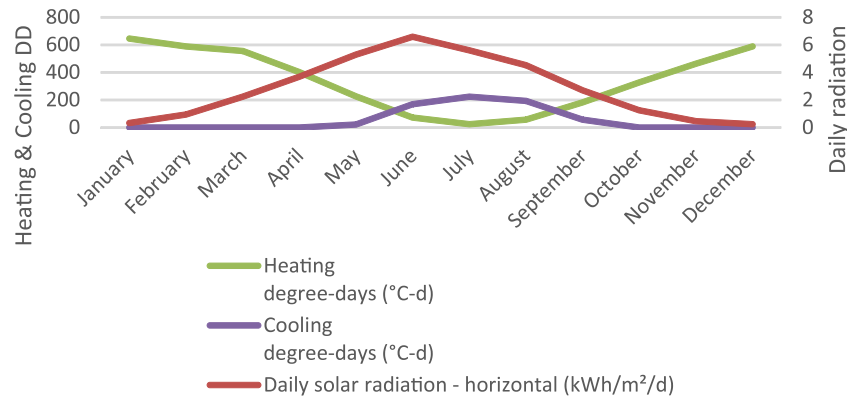


Fig. 10 Monthly variation of heating and cooling degree-days with solar radiation in Stockholm, Sweden. Source: RETScreen. Available at: <https://www.nrcan.gc.ca/energy>.

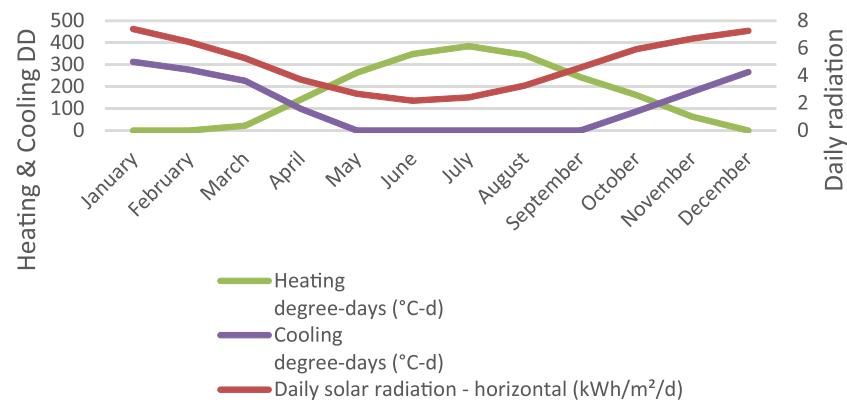


Fig. 11 Monthly variation of heating and cooling degree-days with solar radiation in Canberra, Australia. Source: RETScreen. Available at: <https://www.nrcan.gc.ca/energy>.

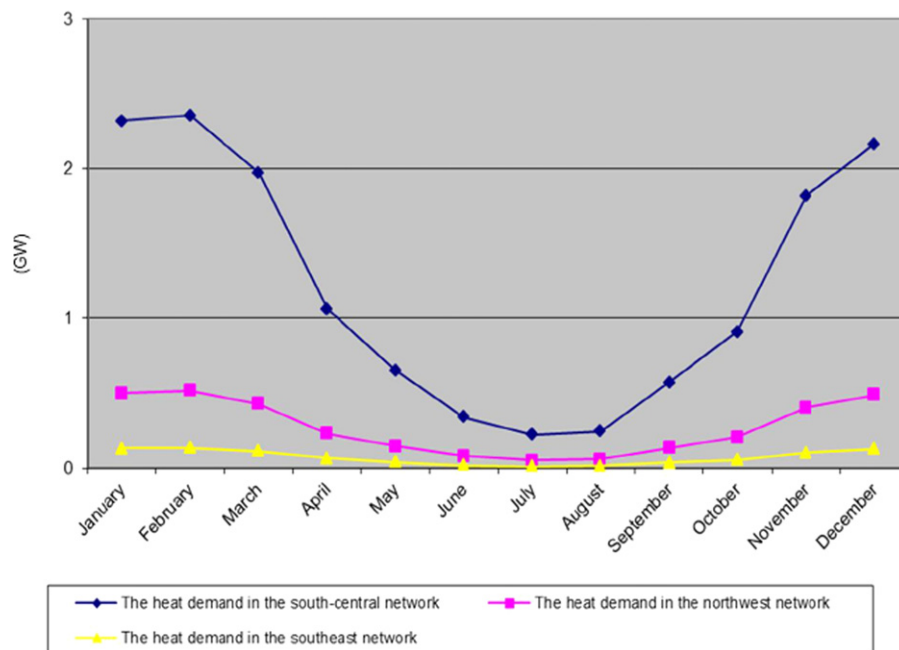


Fig. 12 Monthly average district heating demand in Stockholm, Sweden. Reproduced from Ilıc, D.D., 2014. With district heating toward a sustainable future: System studies of district heating and cooling that interact with power, transport and industrial sectors. Doctoral thesis, Linköping University, Department of Management and Engineering, Energy Systems. Linköping University, The Institute of Technology. Available at: <http://liu.diva-portal.org/smash/get/diva2:719334/FULLTEXT01.pdf> (accessed 29.04.19).

International Energy Agency (IEA) (2019a,b) also launched in 2018 the Kigali tracker under its Global Exchange Platform to work with countries and K-CEP partners to track information on EE, refrigerants, investments, and policies.

Continual innovations is the solution

Various types of renewable energy driven VACS discussed here are still evolving with improvement of performance in the process of gaining more applicability according to the local conditions, as has been reported by various researchers, showing continual development as one key to overcome the barriers. For example, Al-Zubaydi (2011) refers to one type of recently developed small capacity machine capable of operating at partial load with cooling load with a temperature of 65°C and with an estimated COP of around 0.7, a compromise ideal for solar applications. In another study, one of the simulation results showed the possibility of use of the dry type cooling tower in a solar assisted air condition absorption system with hot water driven ammonia/water absorption chillers in case of lack of fresh water, for example, in a high ambient location in Abu Dhabi (UAE).

Overcoming Economic and Financial Barriers

Higher initial investment plays a negative role on economics of VACSs and one of the reasons for its popularity far behind VCCSs today. However, a good number of conditions in its favor have already been identified as follows:

- The refrigerants used are pairs of solvents and solutes in VACSs and there are more than 50 such pairs are possible. Most common pairs in use nowadays are H_2O –LiBr and NH_3 – H_2O – the former for space cooling at more than 5°C and the latter for refrigeration to lower than 5°C, both being non-CFC gases and not listed among the six GHGs as per the Kyoto Protocol. It may be noted that VCCS were developed to operate with CFCs and other GHGs as refrigerants that were the cause of the ozone hole and global warming, which led to ban of their use in most of the world, which had to spent huge amount to tackle the menace. The indirect benefit to society is therefore quite significant and needs to be quantified and reflected in costing to customers.
- The main driving energy being thermal, waste heat available in industrial installations and in larger buildings (diesel or gas exhaust after combustion in generator-sets or such facilities) is not only free but also may help avoid the cost of treatment of waste heat because of prevailing environmental regulations.
- Moreover, wherever larger installations of solar air/water heating systems or DHS exist, invariably it is observed that during summer such systems are underloaded or nonfunctional. Employment of VACSs utilizing the heating capacity of such systems during summer, when the cooling load is significant, would not only ensure a free source of heat, but also, may improve the performance and/or life of such existing systems.
- Since VACSs driven by renewable energy would help avoid the CO_2 emission that would have happened otherwise with cooling systems run on energy from fossil fuels, the emission mitigation needs to be quantified and reflected in costing to customers. Such mechanism exists in some countries asking polluters to pay the social cost.
- While considering available options of cooling systems, often the decision makers are confused with cost to multiple benefits of the alternatives. Multicriteria decision making (MCDM) processes help the investors to choose among alternatives with different pay-back period, return on investment, internal rate of return, initial investment, CO_2 mitigation, energy saving, working life, resale value, etc. (Majumdar and Choudhury, 2017). While taking into consideration criteria for greening of existing buildings also, retrofitting with VACSs climbs up the ladder to assume top priority in the decision making process (Majumdar and Choudhury, 2018).

Overcoming Social Barriers

Social barriers often assume subtle issues in a complex situation involving economic, cultural, political, climatic, and other aspects of a society. Delicate care is required in designing and planning for awareness programs and relevant policies to overcome social barriers. For example, the “top runner” approach in Japan and standardization and labeling have been a huge success in many countries including India. Japan’s Top Runner Program led to an efficiency increase of 100% from 1995 to 2005, while prices dropped over 80% (Sachar *et al.*, 2018). Availability of decision making tools also will play a positive role. With innovations in improvement of performance, reduction of cost, and productive use of locally available resources to meet the need would encourage more people to explore the huge benefits of VACSs taking it to a favorable cycle (more positive initiatives – lower cost at improved performance – more use – realization of benefits – more popularity – more production – more positive initiatives) from a vicious cycle.

NZEBs are expected to play an important role in fighting climate change and reducing the energy use of the built environment (Robert and Kummert, 2012). Baniyounesa *et al.* (2014) points to commercial buildings with large roof areas, such as supermarkets, shopping centers, hotels, hospitals, and convention centers, as most suitable for VACS by solar systems and emphasize on a set of rules that should be undertaken by operators, supervisors, and project managerial teams to ensure occupational health and safety guidelines, site preparation, site security, environmental considerations, and identification of general hazards and their control. Major challenges faced by cities in moving to 100% renewable energy, with need for cooling in place, identified in the dialog held in conjunction with COP 21 at Paris in 2015 (Jacquet *et al.*, 2015), were in order of number of responses (high to low) per thematic challenge: (1) Lack of jurisdictional control, (2) lack of political will at the national level, (3) limited access to sufficient RE resources, (4) transitioning from cheap coal, (5) vested interests in fossil fuels or nuclear, (6) building retrofits and housing, (7) fleet conversion, (8) transportation, (9) transitioning industry from fossil fuels, (10) scaling up RE with limited financial resources, and (11) public support, as shown in Fig. 13.

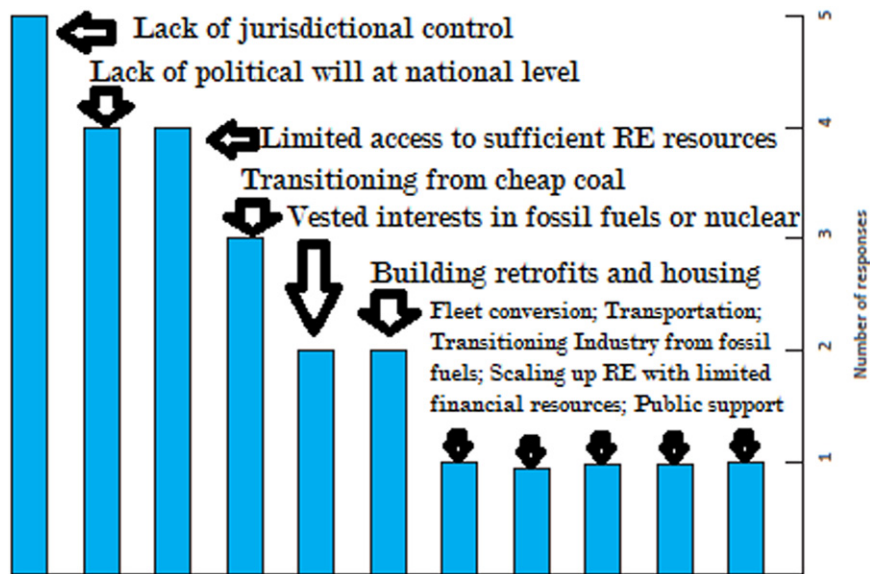


Fig. 13 Major challenges faced by cities in moving to 100% renewable energy. Reproduced from Jacquet, E., Small, M., Marques, A., Leidreiter, A., 2015. Dialogue report: 100% Renewable energy in cities. TAP 2015 – COP21. Le Bourget, Paris. Retrieved from May 11, 2019. Available at: <https://www.renewablecities.ca/rc/wp/wp-content/uploads/North-American-Dialogue-Report-Print.pdf>.

Role of Tools to Overcome Barriers

Standard tools and techniques are available to evaluate existing and proposed systems. Energy audits can evaluate the energy performance of VACSs as well and point out the opportunities for improvement. A number of simulation software programs give the opportunity to assess the performance even at the design stage. With the employment of such tools, cost-benefit and other economic analysis can be faster, unambiguous, and versatile. Postoccupancy evaluation of actual building energy consumption, say in VACSs, is being compared with the design values, and taking users into confidence, significant energy savings have been achieved through improved maintenance, temperature set points, and control.

Ranking among alternative cooling systems with various combinations, viz. high cost – high efficiency, high cost – low efficiency, low cost – high efficiency and low cost – low efficiency, is also possible through such tools and techniques helping the decision making process. Social awareness can be raised significantly by showing various scenarios simulated by such tools (Majumdar and Choudhury, 2017). Many software tools are used to generate and assess alternative scenarios, simulate, and/or assess project alternatives and system performances (technological, financial and social), viz. EnergyPlus, eQUEST, MATLAB, PVSyst, RETScreen, SolarGis, TRNSYS, etc.

Many of the studies reported in this article (Al-Zubaydi, 2011; Fahléna *et al.*, 2012; Gomri, 2013; Robert and Kummert, 2012; Sukumaran and Sudhakar, 2017; Sun *et al.*, 2013) give interesting and conclusive outputs through application of simulation techniques. Peters (2018) emphasizes application of simulation tools and identified six recommendations to overcome barriers:

- (1) Awareness – Among stakeholders to create consensus and intersect about cooling as top of the agenda particularly in view of all three internationally agreed goals that happened for the first time: The Paris Agreement; the SDGs; and the Montreal Protocol's Kigali Amendment.
- (2) More accurately defining cooling needs and targets to meet the SDGs.
- (3) A quantitative intervention roadmap and toolkit.
- (4) Cold Community Networks among stakeholders.
- (5) Cooling Services Methodology and Model – “fit for market” – including “fit for energy source” – and “fit for finance” cooling through simulation before capital intensive investment in on-the-ground deployment.
- (6) Living Labs – An ecosystem for trialing and developing strategy, revenue and financing, and technology mixes at scale and demonstrating impact, providing a launch-pad for accelerated deployment and urges the establishment of a multidisciplinary Center of Excellence for Clean Cooling.

Rhetoric and Realities: Vapor Absorption Cooling System Around the Globe

Snapshots of Vapor Absorption Cooling System in Global Scenario

The global cooling market, since 1990, has been growing in excess of 4% per annum and would reach 80% by 2030 and 150% by 2050 (Saastamoinen and Paiho, 2018; International Energy Agency (IEA), 2013, 2015, 2018a, 2019a). The International Energy Agency (IEA) (2019a) estimated final energy use for cooling is to have increased by 5% globally in 2018, an exceptionally hot year in

It is also interesting to note that both the companies have higher share of their products in the capacity range of 100–200 TR but in terms of total TR of installed capacity, the highest share is assumed by 500–1000 TR VACs as indicated also in Fig. 14.

- CO₂ emission reduction opportunities through utilization of VACSs

Even as solar and wind posted double digit growth, demand for all fuels increased, led by natural gas. Higher electricity demand was responsible for over half of the growth in energy needs. EE saw improvement much lower than expectations. As a result of higher energy consumption in 2018, CO₂ emissions rose 1.7% last year and hit a new record, to a historic high of 33.1 Gt CO₂. While emissions from all fossil fuels increased, the power sector accounted for nearly two-thirds of emissions growth; coal use in power alone surpassed 10 Gt CO₂, mostly in Asia. 85% of the net increase in emissions was from China, India, and the United States. Emissions declined for Germany, Japan, Mexico, France, and the United Kingdom. In China, CO₂ emissions grew by 2.5%, driven by incremental use of coal in power stations and gas being increasingly chosen as a substitute for coal-based heating. In the United States, the emission reductions seen in 2017 were reversed, with an increase of 3.1% in CO₂ emissions in 2018. However, emissions in the United States remain around their 1990 levels, and 14% (or 800 Mt of CO₂) below their peak in 2000, which happens to be the largest absolute decline among all countries since 2000.

Table 2 Excerpts from cases studies of renewable energy driven heating and cooling

<i>Sl. no./Case Study no#</i>	<i>System</i>	<i>Location</i>	<i>Collector area (m²)</i>	<i>Storage volume (m³*)</i>	<i>Capacity (MW_{th})</i>	<i>Project cost (million USD)</i>	<i>Annual avoided CO₂ (tonnes)</i>	<i>Status (Year of completion)</i>
1 & 9	Stand-alone biomass (VACS)	St Paul, Minnesota, US: Local biomass in a centralized heating and (absorption) cooling CHP plant	NA	NA	65	41	91	2004
2 & 11		London Olympic Park, Great Britain (16 km heating and 2 km cooling network)	NA	NA	100 MW heat, 18 MW cooling & 3.5 MW electricity	150	NA	2009
3 & 12	Solar Cooling (VACS)	Phoenix, Arizona, US: Desert Mountain High School	5000	34.5	3.5 (Chiller 1.75)	10	NA	NA
4 & 13		United World College South East Asia	3900	60 (cold) & 7 (hot)	2.73 (Chiller 1.5)	5	NA	NA
5 & 14		Sheikh Zayed Desert Learning Center	1108	5 (cold) & 26 (hot)	(Chiller 0.4)	N/A	NA	NA
6		Experimental trials of LiBr/H ₂ O absorption chiller prototype located in Madrid	42.2	1.5	0.025	N/A	NA	2012
7		NPCIL, Kota, Rajasthan, India (100 nos of PTC)	641		0.35	0.45		2013
8		Honeywell Tech. Hyderabad, India (128 nos of PTC)	821		0.45	0.39		2013
9		NTPC, Noida, UP, India (2 nos of Arun 160)	338		1.13	0.49		2012
10		Turbo Energy Ltd. Chennai, India (2 nos of Arun 160)	338		1.13	0.18		2011
11		Civil Hospital, Thane, India (150 nos of Scheffler Dishes)	2040		0.56	0.89		2011
12		Mahindra Vehicles, Chakan, Pune, India (70 nos of Scheffler Dishes)	1120		0.42	0.28		2010
13		Magneti Marelli, Manesar, Haryana, India (20 nos of Scheffler Dishes)	320		0.11	0.23		2010
14		Cancer Hospital, Muni Seva Ashram, Goraj, Gujarat, India (96 nos. Scheffler Dishes)	1250		0.35	0.25		2008
7 & 15	Natural water cooling	Paris, France: Large cooling network sourced by the river Seine (three locations)	NA	140 MWh, in total	144 MW (45%) of 350 MW total cooling capacity	NA	NA	NA
8 & 16		Bahrain Bay, Manama, Bahrain: Shallow seawater cooling in new development	NA	NA	155	NA	NA	2010
9 & 17		Geneva, Switzerland: Lake water cooling (26389 MWh/yr, only 5.5% for heating)	NA	NA	16.2 MW (cooling) & 3 MW (heating)	34	6000	In expansion
10 & 18		Honolulu, Hawaii, US: Deep seawater cooling	NA	NA	70	250	NA	2017 (completion)
11	Biomass & natural water cooling	Stockholm's DC System	NA	NA	227 MW capacity delivering annual cooling of 350 GWh achieved from VCCS using electricity from CHP operating at 22% electrical efficiency and 59%–69% thermal efficiency			

Abbreviations: VACS, vapor absorption cooling system; VCCS, vapor compression cooling system.

Note: IRENA, 2017. Renewable Energy in District Heating and Cooling – Case Studies. Abu Dhabi: The International Renewable Energy Agency (IRENA). Available at: https://www.irena.org/-/media/Files/IRENA/Agency/Publication/2017/Mar/IRENA_R-Emap_DHC_Case_Studies_2017.pdf?la=en&hash=963DB0F2449088164CAB724EC4CA8BAEB21D1141 (accessed 29.04.19). Ilic, D.D., 2014. With district heating toward a sustainable future: System studies of district heating and cooling that interact with power, transport and industrial sectors. Doctoral thesis, Linköping University, Department of Management and Engineering, Energy Systems. Linköping University, The Institute of Technology. Available at: <http://liu.diva-portal.org/smash/get/diva2:719334/FULLTEXT01.pdf> (accessed 29.04.19). Lizarte, R., Izquierdo, M., Marcos, J.D., Palacios, E., 2012. An innovative solar-driven directly air-cooled LiBr–H₂O absorption chiller prototype for residential use. Energy and Buildings 47, 1–11. Available at: <https://www.sciencedirect.com/science/article/pii/S0378778811005548>. Singhal, A.K., 2014. Status and scope of solar cooling in India. Sun Focus, (4), 6–8. Available at: https://mnre.gov.in/file-manager/UserFiles/Sun-Focus_April-June-2014.pdf.

Table 3 Classification based on types of systems for two manufactures (A and B) taking two samples of sizes of 711 and 535

Description	Up to 100 TR	200 ≥ TR > 100	300 ≥ TR > 200	400 ≥ TR > 300	500 ≥ TR > 400	1000 ≥ TR > 500	1500 ≥ TR > 1000	2000 ≥ TR > 1500	More than 2000 TR
Share (%) Numbers of VACSS of A	15.2	19.8	16.5	14.2	9.4	17.6	4.1	1.0	2.5
Share (%) Installed TR of VACSS of A	3.0	7.1	10.0	11.9	10.1	27.9	11.9	4.0	14.8
Share (%) Numbers of VACSS of B	18.5	22.2	13.3	18.7	11.4	13.1	2.2	0.2	0.0
Share (%) Installed TR of VACSS of B	3.9	10.6	10.6	20.5	16.1	29.5	8.1	0.9	0.0

Abbreviation: VACSS, vapor absorption cooling system.

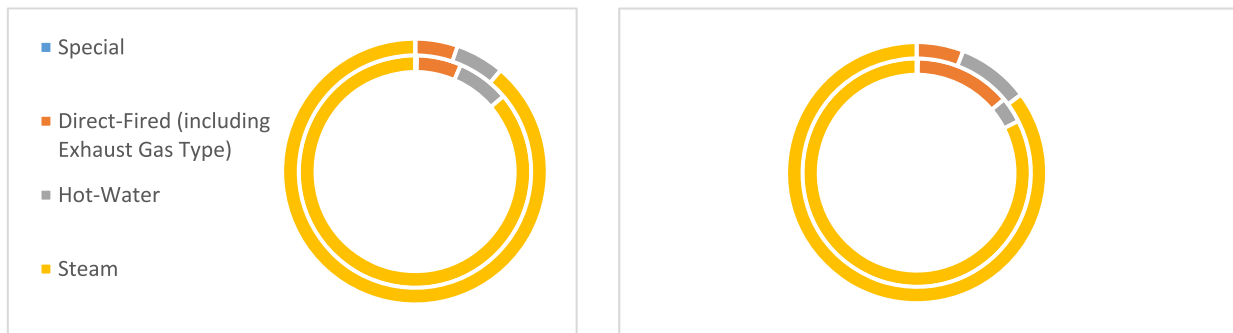


Fig. 14 Production patter of various types of vapor absorption cooling system in Company A (left) and Company B (right): Numbers (inner ring) and TR (outer ring) [Special types are so insignificant as to not be noticeable].

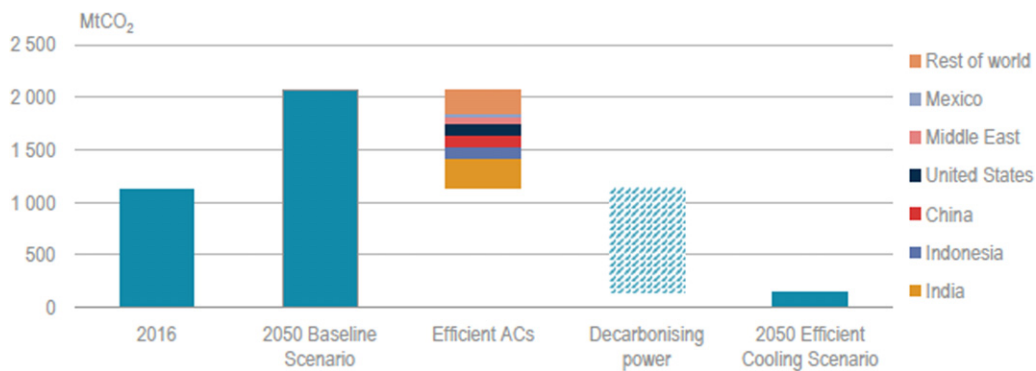


Fig. 15 Estimated contribution to the global reduction in CO₂ emissions from space cooling by country/region in the Efficient Cooling Scenario. Reproduced from International Energy Agency (IEA), 2018b. The Future of Cooling: Opportunities for Energy-Efficient Air Conditioning. Available at: https://www.iea.org/publications/freepublications/publication/The_Future_of_Cooling.pdf (accessed 12.04.19).

Global share of electricity from fossil fuels and that of cooling by VCCS are nearly 70% and more than 90% respectively. Also about 2100 TWh electricity has been reported to be used annually just for cooling purpose and without actions it could become 19,600 TWh in 2050 (International Energy Agency (IEA), 2019b; Peters, 2018). These would lead us to the following understanding:

- (1) The majority of cooling systems operating today are unsustainable and cause emissions as high as 4 GT of CO₂ in 2018, which is almost 11.8% of the global annual emission of 33.1 billion tonnes.
- (2) It is possible to drive present and future cooling needs by renewable energy in a sustainable way, among which VACSS have been found to most economical.

The results of research carried out by Fahléna *et al.* (2012) show that despite recent advances of compression chillers, which are becoming more and more energy efficient, potential for cost-effective CO₂ emission reduction by AC expansion, which is robust with regards to the different scenarios applied of energy market prices and policies, is high. While the effects on annual DHC system results are minor, an increased cooling demand may be met by generation associated with low or even negative net CO₂

emissions – as long as there is high availability of industrial excess heat in the DHC system, or if, for example, new biomass-based CHP capacity is installed, due to the avoided and replaced marginal power generation, as VACSSs need only a fraction of electricity input compared with the conventional counterpart, that is, compression chillers (VCCSSs).

Naukkarinen (2012) also showed that various EE and RE projects may not lead to similar reduction of CO₂ and energy saving. Careful considerations among options are required to achieve more CO₂ reduction than energy saving or vice versa, as per the need and economy. Peters (2018) reported that an aggressive range of technology and operational efficiency improvements can be implemented (GCI demand forecast – accelerated technology progress), then an additional 21% reduction in total sector energy consumption could be achieved by 2050 over and above the current technology improvement trajectory (GCI demand forecast – current technology progress). However, this would still leave consumption from the sector above the IEA 2DS implied energy budget for cooling (Fig. 16(A) and (B)).

Scenario of Renewable Energy Driven Vapor Absorption Cooling System in Developed Nations With Case of Finland

Saastamoinen and Paiho (2018) reported a study by European Commission in 2016 revealed that per capita cooling demand in single family house is more than double with compared with a multifamily building. As the trend moves to single family buildings, the cooling load will continue to increase in developed countries. For example, in Finland, as many as 50% of citizens lived in single family houses at the end of 2015 and since 2000, the heat-pump use has increased by 25-fold, at a rate of as high as 60,000 units annually, mostly in smaller capacity range of up to 6 kW. This indicates the people's intension to reduce the heating cost and would increase the demand of more number of cooling systems in summer but at lower cost of cooling. The cooling demand is estimated to increase from 1–5 kWh/m²/year to 6–39 kWh/m²/year in offices by 2030. The corresponding demand in residential buildings would be 0.5–12 kWh/m²/year. This will lead to a total cooling demand to go as high as 1700 gigawatt hours (GWh) in 2030 from 1300 GWh recently. A 13%–19% increment will be due to climate change in Finland. Out of this only the district cooling share was 178 GWh in total, which is the third largest in Europe after Sweden and Norway. The overall average cooling demand at present in Finland is 28 kWh/m² with a break up of 45 and 20 kWh/m² in the service sector and residential sector respectively.

In 2017, nine companies in Finland provided 223,439 MWh district cooling services to 491 customers, 65% of which were located in the capital area. The most commonly used district cooling technology has been heat pump (i.e., VCCSSs), free cooling, and absorption cooling (i.e., VACSSs) with a share of 60%, 25%, and 10%, respectively, and it is increasing. A good district cooling system can have supply/return water temperature difference of 10°C, which is typically 50°C for a good DHS, leading to about 4–5 times higher flow in the district cooling system calling for higher investment than the DHS. Moreover, in summer, energy fees are much higher than in winter and in 2014 it was 31.11 €/MWh in Helsinki and 36.42 €/MWh in Espoo. In Finland, a cooling tower is not required as the heat from chiller coolant is rejected to natural sources of cold water. The cogeneration DHS when also equipped with cooling services, are termed as tri-generation systems, which are capable of achieving higher energy performances than only cogeneration systems because of better system loading profile. Cogeneration district heating only systems would run at lower efficiency because of underloaded systems during winter. Approximately one-third of district heating is produced by biomass, which shows the potential of VACSSs driven by renewable energy in Finland. Energy saving through higher tri-generation efficiency often leads to attractive payback time when existing CHP site is integrated with absorption chiller. In addition, environmental benefits are obtained as the municipal solid waste-fired power plant is integrated with VACSSs. The losses in DHS are reported to be typically 10%–15% in less populated areas, 5%–8% in dense urban areas, and for the district cooling system within 2% of total delivered energy service.

It is also reported that absorption cooling cost is competitive with the available/existing air conditioning system in the long run, but for the much higher initial investment, its popularity would also depend on collateral benefits. However, until prices

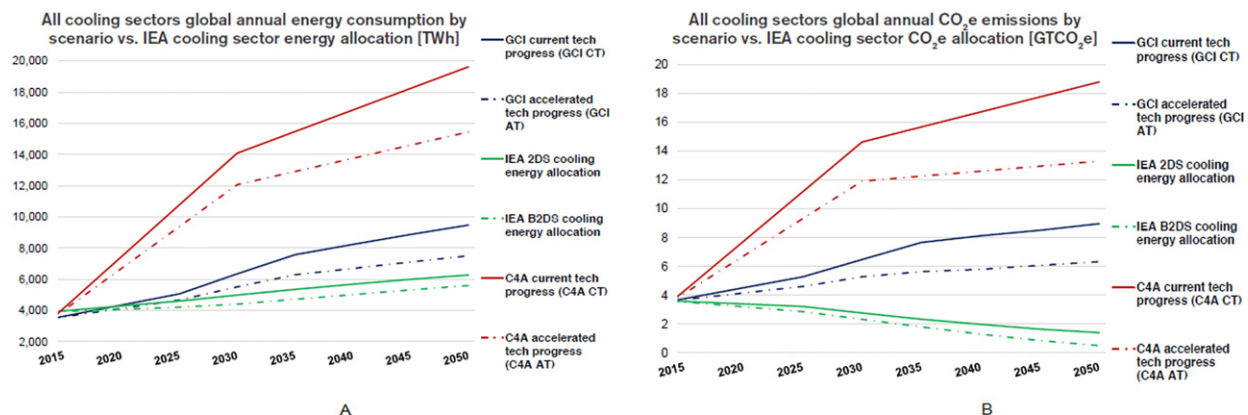


Fig. 16 Cooling for all energy consumption and CO₂e emissions. Reproduced from Peters, T., 2018. A Cool World Defining the Energy Conundrum of Cooling for All. Birmingham Energy Institute – University of Birmingham. Available at: <https://www.birmingham.ac.uk/Documents/college-eps/energy/Publications/2018-clean-cold-report.pdf> (accessed 05.05.19).

reduce, solar thermal cooling would remain unutilized even with major cooling demand and irradiation occurring simultaneously in Finland (Saastamoinen and Paiho, 2018).

In the United States, the cost of district steam varies from \$11 to \$12/Million kJ and the cost of generating steam from solar installations (solar concentrators) needs to be compared based on future data.

- CO₂ Emission Reduction opportunities in Finland through utilization of VACSs

According to the BAU scenario, the total yearly cooling demand for buildings in Finland is going to increase from 1300 GWh to 1700 GWh by 2030 (Saastamoinen, 2018). Considering the emission factor for Finland as 0.24 kg CO₂/kWh electricity, as much as 312,000 t of CO₂ was released in 2017 and in 2030 the amount would be 408,000 t.

Scenario of Renewable Energy Driven Vapor Absorption Cooling System in Developed Nations With Case of Australia

Australia is different from most of the countries in the Northern Hemisphere as the solar radiation characteristics and seasonal pattern are different in the Southern Hemisphere. With a very sunny climate, there is high demand for air conditioning, as most of the cities have more CDD than also significant HDD (ideally suitable for VACS), air conditioning's impacts upon the electricity network and the environment threaten to affect quality of life in Australia, particularly on hot days in summer. Associated with the air conditioning's high use of energy is significant environmental pollution, namely in the form of greenhouse gas emissions with the resultant climate change impacting not only upon environment, but also health and productivity. Australia is one of the top ranked countries in active solar estimated annual yields for glazed flat plate collectors 700 kWh/m² per m², while its 400 kWh/m² per m² in Germany. Al-Zubaydi (2011) points out the huge potential for solar air-conditioning having higher demand when solar radiation is more, but the technology of using the solar thermal assisted air-conditioning system, in spite of suitability in conditions of Australia, is yet to be in focus in Australia as it is in rest of the world. The change is however favorable as new developments as well as the climate changes (50% of Australia's greenhouse gas emissions are from stationary energy, primarily electricity generation), energy prices, and other impacts urge us to call for further studies to investigate the feasibility of the solar thermal air-conditioning system in Australia. A number of cases of solar air-conditioning systems from Australia are included in Table 2.

Scenario of Renewable Energy Driven Vapor Absorption Cooling System in India

Solar energy is the most widely available renewable energy resource in India, where more VACSs applications could be new in terms of challenges and opportunities. Further if only 50% of the upcoming new cooling installations are done by VACSs and out of this 30% are operated by solar energy then the demand for capacity addition will be lessened by 8% of the present installed capacity in India (Choudhury and Ray, 2012). India is going to become the most populous nation in the world and is the fifth largest economy. Many players are striving to lead the growing VACS market in India, viz. Thermax, Voltas, IKON Technologies, Majestic Engineers, Lakshmi Air System, Happy Instruments, etc. The average SEER of conventional air-conditioning units sold in the fastest-growing markets, such as China and India, is typically around 4. Yet products available in those same markets – often at comparable prices – can have SEERs that are 50%–70% better (International Energy Agency (IEA), 2019a). VACSs has the opportunity to directly come out with higher SEER to catch the growing market.

The Energy Conservation Act 2001, amended in 2010, is much more stringent than the first version, and would have a favorable impact on the industry sector. The Perform Achieve and Trade mechanism, applicable to 866 Designated Consumers (DCs) Industrial Units in 13 sectors including larger commercial buildings, would encourage the use of VACSs particularly in cases where waste heat could suitably be utilized to meet ever-increasing cooling needs. DCs consume more than 50% of India's Energy Consumption and contribute significantly to India's growth rate of more than 7%. The Bureau of Energy Efficiency (BEE) (2018), Government of India, has taken pro-active measures in view of the above:

- Comparative Energy Consumption

CEC values for household frost-free refrigerators (mainly VCCSs) manufactured or imported during various period of 2011 till today or (would be) till 2021, as shown in Table 4 and Fig. 17 below, are calculated from the following equation, $CEC = K_{nf}$

$$* V_{adj_tot_nf} + C_{nf}$$

Where,

K_{nf} = Constant multiplier (kWh/Liter/Year)

$V_{adj_tot_nf}$ = Total adjusted storage volume for household frost free refrigerator (liter)

C_{nf} = Constant fixed allowance (kWh/Year)

Depending on the value of CEC, a product is rated on a scale of five stars (1* to 5*****) as shown in the Table 4. This is analogous to five star rating labeling in United States and some other countries.

India is poised for a spiral rise of cooling demand in the building sector for at least two reasons, viz. more than 60% of India's buildings in 2030 are yet to come up and by mid-2020s India is going to be the world's largest growth market (BP, 2019). The ECBC 2017 version is more versatile and optimistic compared with the first version released in 2007 and some of the government initiatives to keep the trajectory toward a low carbon path. VACSs need to be standardized and labeled with a suitable mechanism.

As the transport sector is getting electrified very fast, VACSs would find application in vehicles for at least three reasons, viz. VACS consume only about 1/7th of electricity needed in VACCs of same capacity, solar radiation and cooling demand match each

Table 4 Star level valid in India for household frost free refrigerator from January 1, 2020 to December 31, 2021

Sl. No.	Star rating band during this period	Comparative Energy Consumption (CEC) criteria	Star rating band in immediate past period
(1)	(2)	(3)	(4)
1.	1 Star *	$(0.228 * V_{adj_tot_nf} + 199) \leq CEC < (0.286 * V_{adj_tot_nf} + 249)$	2 Star **
2.	2 Star **	$(0.183 * V_{adj_tot_nf} + 159) \leq CEC < (0.228 * V_{adj_tot_nf} + 199)$	3 Star ***
3.	3 Star ***	$(0.146 * V_{adj_tot_nf} + 127) \leq CEC < (0.183 * V_{adj_tot_nf} + 159)$	4 Star ****
4.	4 Star ****	$(0.117 * V_{adj_tot_nf} + 102) \leq CEC < (0.146 * V_{adj_tot_nf} + 127)$	5 Star *****
5.	5 Star *****	$CEC < (0.117 * V_{adj_tot_nf} + 102)$	Much superior

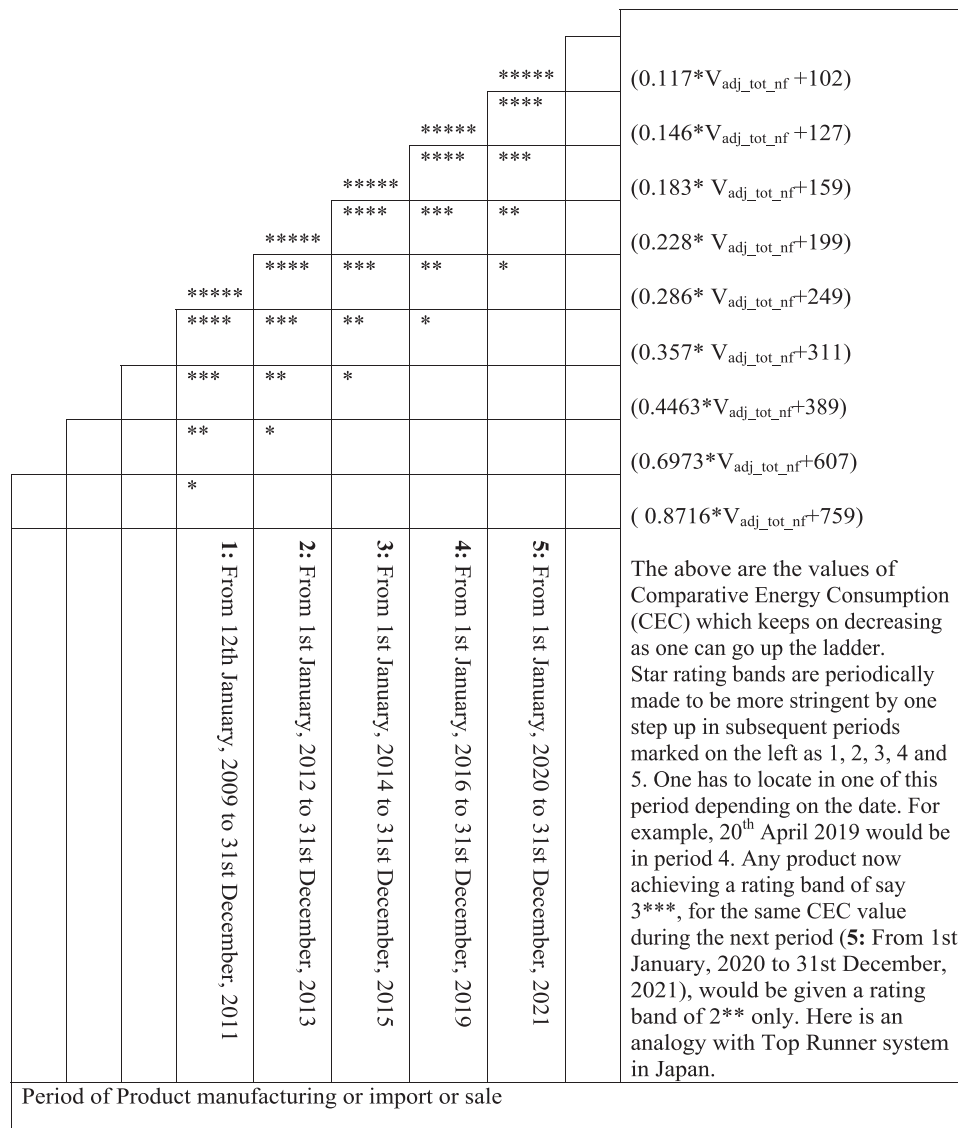


Fig. 17 Identification of applicable star (*) rating of household frost free refrigerators in different periods from January 2009 to December 2021.

other in vehicles, and more stringent environmental norms would be in favor of VACSs. Green mobility mission sets a target of at least 50% electrification of all vehicles on the road by 2030.

MNRE Government of India (2019) has set a target of 175 GW electricity generation capacity from solar (100 GW), wind (60 GW), biomass (10 GW), and small hydro (5 GW) from renewable sources by 2022 when India's electricity demand is estimated to be double that of 2011–2012 value and has reported that about 40% of the target has already been achieved. However, this is low in view of solar energy potential of 750 GW and wind potential higher than 1000 GW. Total electricity generation capacity of 275 GW is significantly higher than India's peak demand of 177 GW. Energy sector, with more than 60% electricity coming from that of coal-based thermal

power plants alone, is the largest contributor to CO₂ emission among all sectors in India. Renewables along with EE are going to play an important role in fulfilling India's commitment to reduce energy intensity by 20% with compared with 1990 level by 2020.

International Energy Agency (IEA) (2018b) observed that the deployment of solar PV in India is expected to grow strongly, up to 1000 GW of installed capacity by 2050. This means there will more often be times when more power is being generated than is required, leading to curtailment of excess PV generation during the sunniest times of the day, which has already been experienced by Germany. As India's growth of cooling demand is being influenced more by the residential sector, typically peaking in the early evening around 7 p.m., when the sun has gone down and solar PV is no longer providing its full capacity, one potential way to address this mismatch is to store cold and then distribute it to buildings through district cooling networks. For instance, heat pumps could produce chilled water or ice when the solar electricity is available, and then use that storage to meet cooling loads later in the evening. To demonstrate the potential benefits of using thermal storage with solar PV and integrated district cooling, the operation of the Indian power system was modeled during a peak cooling week in 2050. The simulation considers a scenario in which India's cities – where the expected growth of cooling demand will be concentrated – would use district cooling networks with thermal storage to partially meet cooling loads from ice or chilled water produced using daytime solar PV. The scenario does not suggest that district cooling would be economically viable in all Indian cities; rather, it provides a sense of the potential and magnitude of the thermal storage needs to meet rapidly growing peak cooling demand in India through the country's large solar generation potential. The model assumes a total thermal storage of 2400 GWh thermal, corresponding to an equivalent of about 600 GWh of electrical storage. The IEA estimates that roughly one-fifth of the total solar PV output could be stored during the day as chilled water or ice, which otherwise would be curtailed and hence lost. That cold storage could then be discharged later in the evening, meeting around 15% of space cooling demand after the sun goes down. The required volume would be comparable to around 20,000 Olympic-sized swimming pools (if the storage medium were ice). Discharge from such a system could meet peak cooling demand between 5 p.m. and 7 p.m., while equally reducing the need for peak generation capacity (e.g., using coal- or gas-fired thermal power generation, shown in dark blue). The model results show a reduction in peak residual demand of 11%, or 80 GW. In addition, the thermal storage adds system flexibility through balancing of supply and demand, which allows provision of electricity from cheaper generation sources throughout the year. Estimates of total system costs reveal a net savings from the use of energy storage to meet cooling loads through excess PV generation, compared with a scenario without storage requiring more peak power generation. The estimated annual system savings are higher for thermal storage (USD 9.7 billion) than battery storage (USD 7.5 billion). This is the result of lower costs for thermal storage capacity at around 10 USD per kWh thermal compared with targets of around USD 300 per kWh electric for battery storage in 2050. Those savings would likely outweigh additional costs for the district cooling system (e.g., network pipes and substations), given the long life of typical district energy networks and investments that can be amortized over time. Of course, the more efficient the AC stock is, the lower the investment is required. While this analysis does not provide a detailed assessment of the specific local conditions or system dynamics that would be required for sound energy system planning and investments, it does suggest that combining different supply and demand-side elements could offer cheaper, cleaner, and more flexible solutions to meet space cooling demand in India. These types of integrated solutions, allowing for greater use of renewable energy sources, could also complement broader economic and social policy objectives – for instance, cutting local air pollution from electricity generation. Thermal storage could take advantage of surplus solar output to alleviate the strain of peak cooling demand on the electricity system in the evenings. Thus, thermal storage could take advantage of surplus solar output to alleviate the strain of peak cooling demand on the electricity system in the evenings.

Aggregate consumption of the commercial sector, growing at 12% annually, stood at 70 TWh in 2012, of which HVAC, lighting, and others comprised 55%, 25%, and 20%, respectively. The relevant quantities are shown in Table 5 (NITI Aayog, 2015) emphasizing the indispensability of VACS driven by renewable energy for this largest democracy in the world.

- CO₂ Emission Reduction opportunities in India through utilization of VACSs

Sachar *et al.* (2018) observed that, with world's largest growth market for cooling, India's cooling-related energy demand from RACs increased 20-fold from just 94 TWh (out of total generation of 938 TWh, that is, almost 10% of total) in 2016 to 1890 TWh in 2050 and thus the country emerges to become the world's largest energy user for space cooling in 2050. The per capita energy use for space cooling from RACs increases from mere 72 kWh (one of the lowest in the world) to 1140 kWh owing to rapid urbanization and a growing affluent middle class that desires a better quality of life and health. India would and need to benefit significantly from the adoption of the 5× solution, that is, five times improvement in EE, adoption of which could reduce India's estimated peak loads by around 400 GW in 2050 while resulting in the curtailment of about 1300 TWh required to operate these units – Almost equivalent to India's total electricity consumption today. Thus, by 2050, India's avoided cumulative emissions would be 16 Gt, which essentially neutralizes the climate impact of total carbon dioxide emissions (from primary energy) of the country over the last decade, and would play an important role to achieve the Nationally Determined Contributions (NDCs) in line with the Paris climate goals and reduce the emission intensity of the Indian economy by 15% in the year 2030 (from 2005 levels) – nearly 40% of the NDC target. This, when combined with the country's renewable energy target of 175 GW by 2022, could achieve a 48% reduction in the emissions intensity, putting the Indian economy on a sustainable pathway. It may be noted that India's air conditioner minimum efficiency performance standards program led by BEE saw an efficiency increase of 30% from 2006 to 2016, 2015, while prices dropped by 20%. As more than 60% of electricity generated in India is from coal, the emission factor is as high as 0.82 kg CO₂/kWh, which means HVAC in the commercial sector alone is responsible for an annual emission of 90 billion tons of CO₂ in India, which is more than 10% of total annual emission, that is, 888 Mt in 2016–2017.

Table 5 Potential of demand reduction from determined effort scenario to heroic effort scenario for India

Sectors	Sector demand in 2012 (TWh)	Demand in 2047 (TWh)			Policy response
		Determined effort	Heroic effort	% Savings	
Buildings	238	2287	1540	33	Energy Conservation Building Code 2017
Industry	2370	10,430	6912	34	Energy Conservation Act 2001 amended in 2010
Others (transport, pumps & tractors, telecom, cooking, etc.)	2321	5918	3984	33	National Electric Mobility Mission Plan
Total	4929	18,635	12,436	33	

Source: NITI Aayog, 2015. India Energy Security Scenarios (IESSs) 2047, Version 2.0. Energy Division, NITI Aayog, Government of India. Available at: <http://indiaenergy.gov.in/> (accessed 19.03.19).

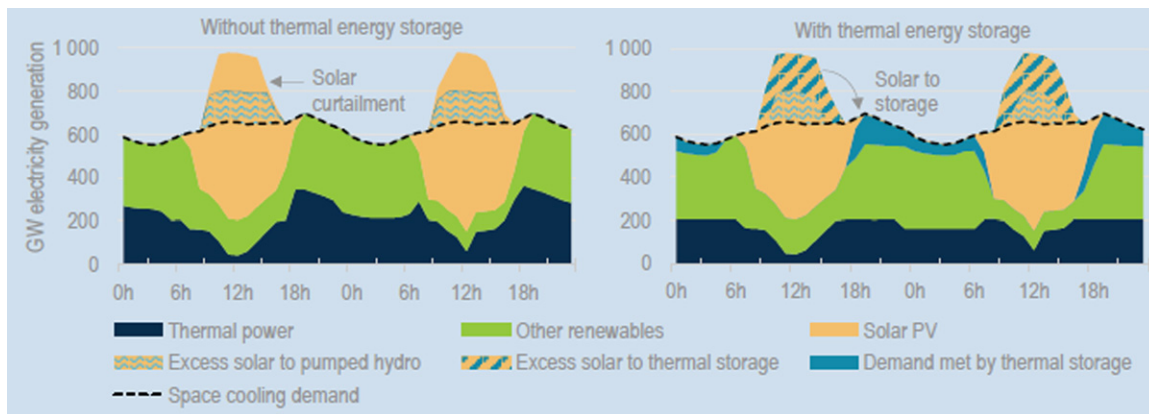


Fig. 18 Illustrative analysis of the potential role of storage using solar photovoltaic for district cooling over two days in April 2050 during the peak cooling period in India. Reproduced from International Energy Agency (IEA), 2018b. *The Future of Cooling: Opportunities for Energy-Efficient Air Conditioning*. Available at: https://www.iea.org/publications/freepublications/publication/The_Future_of_Cooling.pdf (accessed 12.04.19).

The International Energy Agency (IEA) (2019a) pointed out that the Cooling Action Plan, being released in 2018, is the first of its kind in the world and has put forth multiple proposed interventions to address cooling across multiple sectors, following 2018 updates to India's Seasonal Energy Efficiency Ratings (ISEER), which took effect in January 2018. The full version available at website provided in "Relevant Websites section" is said to be in draft form, not to be cited. The Press Information Bureau' (PIB) released the main highlights, which include to look for synergies in actions for securing both environmental and socioeconomic benefits. "The overarching goal of ICAP is to provide sustainable cooling and thermal comfort for all while securing environmental and socio-economic benefits for the society, acknowledging the SDGs. This will also help in reducing both direct and indirect emissions" and aims to provide an integrated vision toward cooling across sectors encompassing inter alia reduction of cooling demand, refrigerant transition, enhancing EE and better technology options with a 20 year time horizon. The India Cooling Action seeks to (1) reduce cooling demand across sectors by 20%–25% by 2037–2038, (2) reduce refrigerant demand by 25%–30% by 2037–2038, (3) reduce cooling energy requirements by 25%–40% by 2037–2038, (4) recognize "cooling and related areas" as a thrust area of research under the national S&T Programme, (5) provide training and certification of 100,000 servicing sector technicians by 2022–2023, synergizing with the Skill India Mission. According to PIB, the following benefits would accrue to the society over and above the environmental benefits: (1) thermal comfort for all – provision for cooling for EWS and LIG housing; (2) sustainable cooling – low GHG emissions related to cooling; (3) doubling farmers income – better cold chain infrastructure, better value of produce to farmers, less wastage of produce; (4) skilled workforce for better livelihoods and environmental protection; (5) make in India – domestic manufacturing of air-conditioning and related cooling equipment; and (6) robust R&D on alternative cooling technologies – to provide push to innovation in cooling sector (Fig. 18).

Conclusion and Way Forward

A number of studies reported in literature are based on simulation and/or laboratory experiments and reveal huge opportunity but point to needs for practical actions to bring the benefit to market as early as possible as the cooling demand is increasing at one of the highest rates among all energy guzzling sectors globally. In response, achieving LCE in cooling through EE and RE would mean

a step toward survival of our civilization threatened by rupture in energy supply and energy demand in the near future, climate change crossing dangerous limits and unstable social-economic structure in many parts of the globe, all three being anthropogenic in nature.

Many of the innovative ideas are yet to come and have the potential to leap-frog the drive, a few being discussed in this article, such as, employing DAP, to operate in PEx mode, drastic improvement of SEER, innovative policy, MCDM, standardization and labeling and VCCS–VACS hybrid driven by renewable power, DH to tri-generation, and so on, with practical examples.

The multiple benefits of VACSs are far from being considered in the purchase and policy decisions at the micro and macro level respectively. Renewable energy driven VACSs bring energy security, environmentally benign non-CFC refrigerants, lowered/abolished CO₂ emission to run the cooling system, reduced/abolished electricity consumption for cooling, and an attractive economy particularly where heat is otherwise wasted/underutilized.

The voice is far and wide through various landmark initiatives, such as, 100%RE, Kigali tracker under its Global Exchange Platform to work with countries and K-CEP partners, Technology Collaboration Programs (TCPs), Cooling Action Plan (in India) – The first of its kind in the world and ‘First-ever global coalition for clean cooling’ by the United Nations. Though well-taken, such global intentions need head and heart to join with hands for practical actions by all local stakeholders to achieve the goal.

Acknowledgment

The authors would like to express sincere thanks and gratitude to Prof. Dr. Rajagopal Dhar Chakraborti, Director and Prof. Dr. K.M. Agrawal, former Dean (Academics) of Indian Institute of Social Welfare & Business Management (IISWBM) for continuous encouragement and support to complete this article in spite of delay and dilemma due to academic and professional commitments to jobs at different parts of the globe.

Sincere acknowledgment is also to the respective institutions and family members, Rhitambhar (Rio), in particular, for without their support and sacrifice, this work would not have been completed.

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Eco-Sustainable Molecular Quantum Dot Cellular Automata Based Radiography in Defect Identification of Industrial Product Using Renewable Energy Source

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Introduction

From the last century fossil fuel, combustion of coal had been fundamental drivers of industrial revolution which lead to technological, social, economic progress globally. These energy sources have negative impacts on environment being dominant sources of carbon dioxide, carbon monoxide and other greenhouse gases. Hence it has become imperative to decarbonize and minimize dependence on coal and fossil fuel and transition towards renewable energy sources.

India currently started relying and building infrastructure on renewable energy sources. It is Electricity sector utilized renewable energy (excluding large hydro) for 20% of the total installed power capacity (71.325 GM) as on 30 June 2018 (Anon). India is the fourth largest wind power in the world having capacity of 34,046 MW as on 31st March 2018. The country is already having strong manufacturing base in wind power with international quality and exporting wind turbine models to other countries (Anon1).

Government of India has taken a big initiative by taking target of achieving 100 GW of solar power by 2022. Second largest solar park in the world is established at Kurnool, Andhra Pradesh, with a capacity of 1000 MW. The country has also four of the top seven largest solar parks worldwide (Anon; Anon1). In our current contribution we avail this opportunity to propose a methodology that enables us avoiding combustion of non-renewable energy such as fossil fuels and using power generated through renewable energy source such as sunlight to run Quantum Dot Cellular Automata based industrial radiography system.

The proposed methodology incorporated here with Quantum dot Cellular Automata paradigm consumes very small amount of power and energy to radiate gamma ray of similar intensity. The present invention relates to Molecular Quantum dot Cellular Automata methodology to electronically radiate gamma rays for industrial radiography system from QCA cell unit.

Discovery of Gamma Rays in the year 1900 by a French chemist and physicist, Paul Villard revolutionized many industrial applications including locating the cracks or flaws in materials such as Gas and oil pipelines, Metal welding, Boilers, Vehicle parts and Aircraft parts etc., such cracks typically are not visible from the outside without damaging the material. The existing convention for production of Gamma Ray (Jacques *et al.*, 1975a; Schneeman, 1944; Pellechia, 2016; Van, 1975; Jacques *et al.*, 1975b) can not turn off the production of the ray when the system is not in use. The radioactive material always produces gamma rays. The only way there to prevent the gamma beam is to place a heavy metal plate at the opening of the device. So worker has to remain very careful even when the device is not in use to avoid exposure. Gamma ray is pointed to the item under consideration. On the other side of the item a detector is lined up. A thick item allows fewer amount of gamma ray to pass through it. Area with crack or flaws allow greater amount of gamma ray to pass through. Detector captures gamma ray and form picture of cracks.

This is worth mentioning that a mathematically monotonic relation seems prevalent while relating voltage consumption and power consumption with generation of greenhouse gas. But to the best of our knowledge, there is hardly any established equation relating this three parameters. As such any device with lesser power/energy requirement is more desirable from the perspective of greenhouse effect. Less the power/energy consumption is, the more environment friendly the device would be. This is primarily because the major source of energy is combustion of fossil fuel and carbon source, in the present day scenario. Accordingly a low power device based on nanotechnology stands in good stead from environmental point of view. Our present proposal appears meritorious in this context.

We shall first analyze the technical feasibility of fabrication of metal dot QCA using electrometer. Accordingly, we ascertain whether it is possible to achieve the same at room temperature. The study in the next three sections establishes that the radius of graphene based metal dot will be in attometer dimension only which is not possible to fabricate in respect of available technology.

The present invention relates to Molecular variant of Quantum dot Cellular Automata methodology for generating gamma ray wave from QCA unit.

Consideration of SET to Determine the Radius of Island of Metal Dot QCA

4 dot 2 electron metal dot QCA is fabricated using single electron transistor due to associated advantages like small size, low power consumption, and ability to perform fast and sensitive charge measurements (Liu *et al.*, 2002; Visconti *et al.*, 2004). Fig. 1 (Visconti *et al.*, 2004; Lu *et al.*, 2006) depicts the schematic of the metal dot QCA realization.

Fig. 2 (Visconti *et al.*, 2004) indicates SET circuit which comprises a dot between the Source and Drain electrodes. The island is separated from these electrodes by a tunnel junction. Each tunnel junction has its resistance and capacitance as shown in Fig. 3. The dot is also capacitively coupled to the Gate electrode which also has a capacitance to regulate current flow. The total capacitance (C) between the dot and outer environment is given below:

$$C = C_1 + C_2 + C_g \quad (1)$$

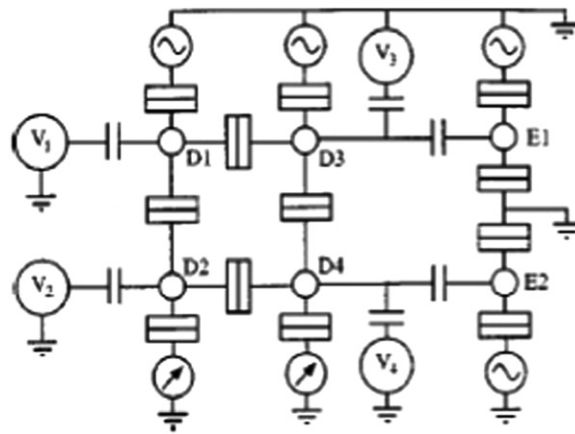


Fig. 1 Simplified schematic of the four-dot QCA cell and electrometers.

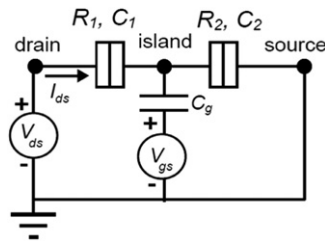


Fig. 2 Single electron transistor.

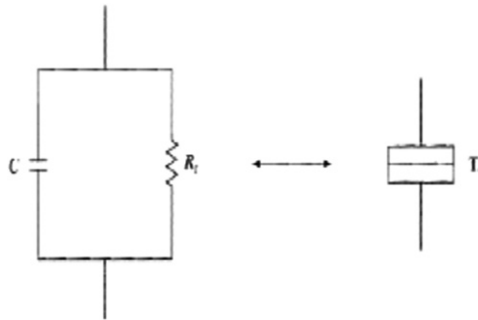


Fig. 3 Tunnel junction.

C_1 , C_2 and C_g denote drain capacitor, source capacitor and gate capacitor respectively. Three conditions need to be met to achieve coulomb blockade.

- (1) $V_{bias} < \frac{e}{C}$
Here V_{bias} denotes bias voltage, e denotes elementary charge and C denotes total capacitance.
- (2) $R_t > \frac{\hbar}{2\pi e^2}$
Here R_t denotes the tunneling resistance and $\hbar$ is plank's constant. This condition is derived from Heisenberg's uncertainty principle.
- (3) $KT < \frac{e^2}{2C}$
Here KT denotes the thermal energy, $K = 1.3806505 \times 10^{-23}$ J/K, $\frac{e^2}{2C}$ denotes the charging energy or coulomb energy and T is temperature. If this condition is not met then the electron will pass the quantum dot via thermal excitation. When one electron overcomes the charging energy and tunnels into the quantum system, it blocks the tunneling of a second one since it would charge additionally the quantum system by an amount $< \frac{e^2}{2C}$. The effect is that a single electron may tunnel through at a time.

In **Fig. 4** the region $-\frac{e}{2C} < V_{dc} < \frac{e}{2C}$ is called coulomb blockade region, with a coulomb gap voltage V_{gap} . In this region the electron's energy is smaller than the repulsive Coulomb energy of the electrons on the island.

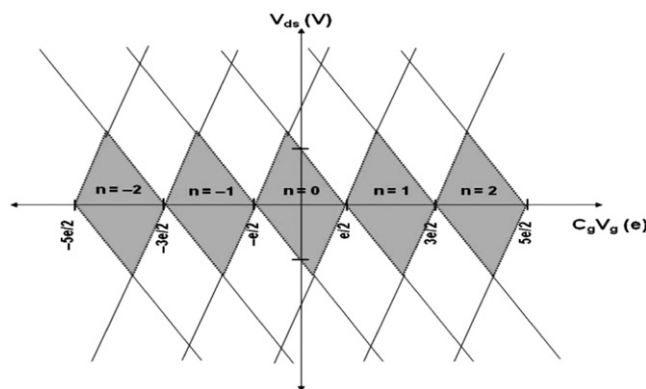


Fig. 4 The stability charge diagram of the source-drain voltage, V_{ds} , across a SET as a function of the gate voltage V_g . The gray regions have zero source-drain currents I_{ds} (Coulomb blockade regions).

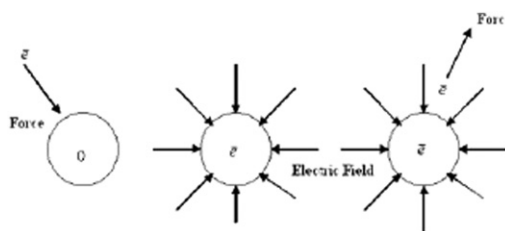


Fig. 5 (a) an electron feeling a small attractive force as it approaches a sphere. (b) Once sphere gets charged negatively by a single electron; other electrons will feel a strong repelling force.

Determining the Radius of Island in Room Temperature

In SET the island can be explained by assuming a small metallic sphere, as shown in **Fig. 5**. This island is initially electro-neutral i.e., the net charge on this island is zero since the number of electrons and protons are same in it. Now, consider that a single electron is placed close to the island. In this situation, it gets attracted towards the island. Thus, this single electron comes into the island and leaves a negative charge of e on it. Now, due to the presence of this negative charge, an electric field is created around the island so that in the event of another electron approaching close to this island, it will face a strong repulsive force induced by the electric field created around the island (Lent, 1997; Lent *et al.*, 1993; Lent and Tougaw, 1993).

The total capacitance (C) corresponds to the self capacitance of island. When the island is a sphere with a radius of R embedded in a dielectric material with a dielectric constant, the self capacitance, (Lent, 1997; Lent *et al.*, 1993; Lent and Tougaw, 1993) is given by

$$C_{\text{self}} = 4\pi\epsilon_0\epsilon_r R \quad (2)$$

Where ϵ_0 and ϵ_r are permittivity of free space and permittivity of dielectric material of capacitor. From the 3rd condition we get $C < \frac{e^2}{2kT}$. Therefore at room temperature (300°K) $C < 3.09 \times 10^{-18}$ F.

Here we use graphene as a metal of island primarily because it is a good conductor. In the 5–40 GHz range encompassing the microwave and the lower part of millimeter wave spectrum, the electrical permittivity of graphene is almost 3 (Toth and Lent, 1999). This experiment was carried out using a coupled coplanar wave guide placed over a graphene mono layer flake, which is deposited on Si/SiO₂. So the relative permittivity of graphene is 3.3882×10^{11} . Now from Eq. (2) we can write,

$$4\pi\epsilon_0\epsilon_r R < 3.09 \times 10^{-18} \text{ F} \quad (3)$$

Thus, $R < 0.819721$ Attometer

Here we performed studies for the radius of island in room temperature. It is seen from Eq. (3) that the radius of island will be in attometer range which is not possible to fabricate using graphene as a metal.

QCA Cell and Molecular Cell Clocking Arrangement

The QCA cell and electromagnetic clock signal are the most vital ingredients in the invention of gamma-rays radiated from QCA cells which consume very less amount of electric energy and power.

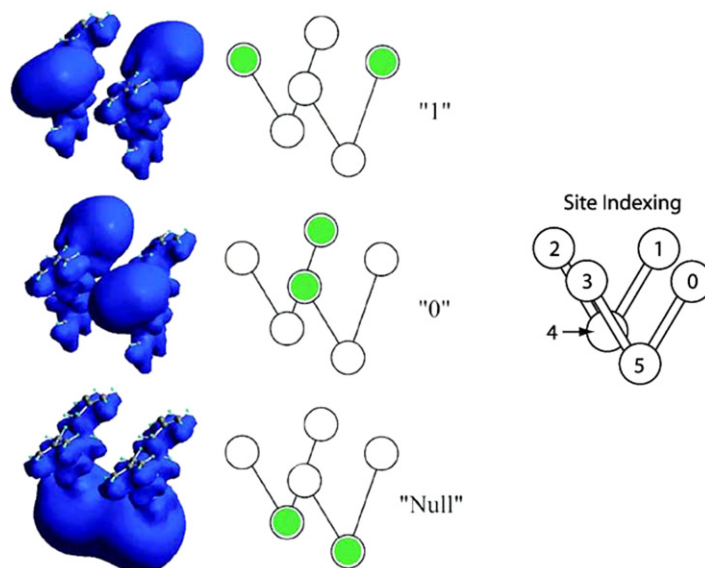


Fig. 6 QCA cell in V shaped molecular form. Reproduced from Anon2, Siemens oem products, www.siemens.com/healthcare. Karim, F., Walus, K., Ivanov, A., 2010. Analysis of field-driven clocking for molecular quantum-dot cellular automata based circuits. J. Comput. Electron. 9, 16–30.

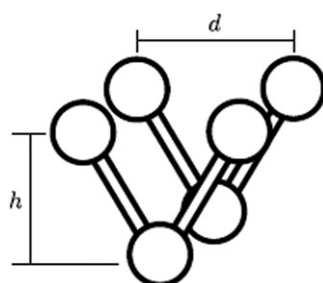


Fig. 7 Molecular cell dimension.

QCA Cell

Each cell is composed of two V shaped molecular structures and has six redox sites. as shown in Fig. 6. The redox sites are considered as quantum dots. The figure depicts three stable configurations of the two mobile electrons within the molecular cell. Mobile electrons establishing themselves at the upper diagonal sites (i.e., either at sites 2 and 0 or 1 and 3) represent ACTIVE states of the cell. These active states carry two polarities of the cells viz. $P = \pm 1$. $P = 1$ is said to represent binary '1' and $P = -1$ represents binary '0'. When the two mobile electrons are positioned at the two sites depicted below, the cell is said to represent 'NULL' state. Fig. 7 indicates molecular cell dimension. Here we employ cell size (d) to be 1 nm and height (h) to be 1 nm (Karim *et al.*, 2010; Lent and Isaksen, 2003; Lu *et al.*, 2006).

Molecular System Clocking Arrangement

Clock signal is applied through submerged electrodes buried in oxide layer (Anon2).

Managing Electrodes

The electrodes carry electromagnetic clock signals and they are placed at the bottom of the oxide layer. The phase shifted sinusoidal signal is applied to each of the electrodes to energize the electrons. Fig. 8 depicts the four phases of the applied sinusoidal signal viz. ϕ_1 , ϕ_2 , ϕ_3 and ϕ_4 with $\phi_1 < \phi_2 < \phi_3 < \phi_4$ such that the data may flow in the direction as indicated in Fig. 8. This electric field

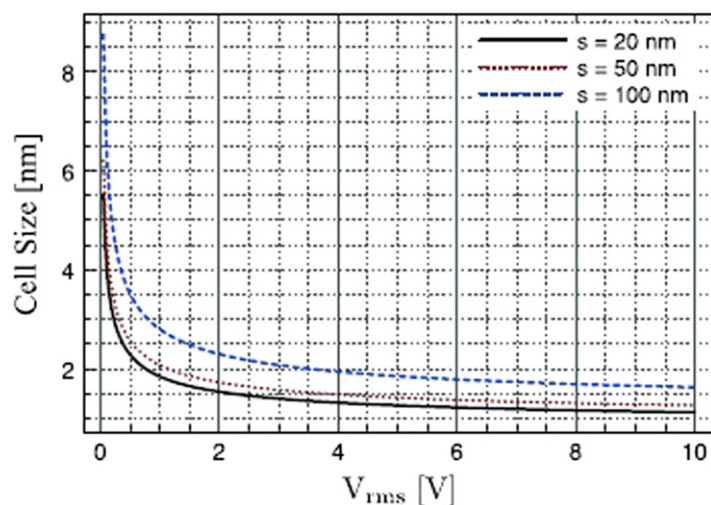


Fig. 8 Plot of cell size (nm) vs. V_{rms} for three different spacing of electrodes. Reproduced from Anon2, Siemens oem products, www.siemens.com/healthcare.

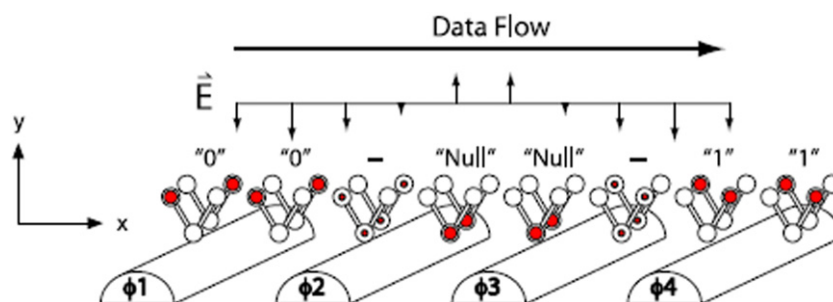


Fig. 9 Submerged electrodes to generate an electric field $\vec{E}$ at the level of molecular cells. Reproduced from Anon2, Siemens oem products, www.siemens.com/healthcare.

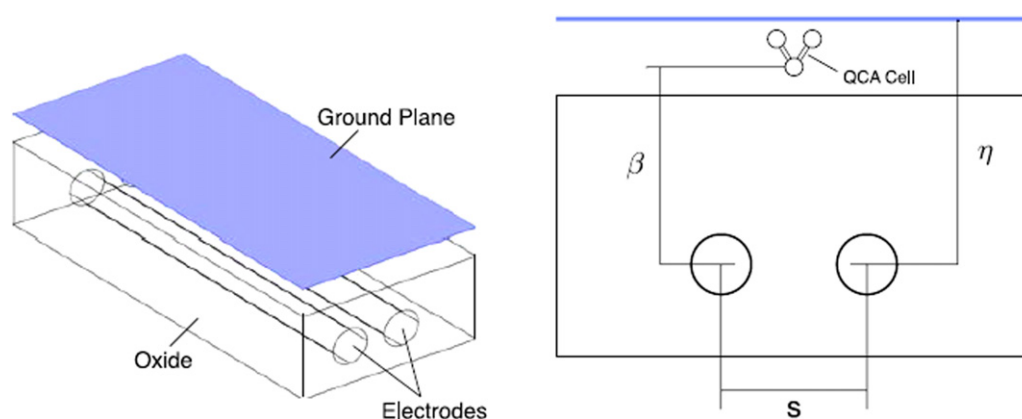


Fig. 10 The figure on the left side shows perspective view of two buried electrodes. The figure also shows the ground plate and the electrodes are buried within oxide. The figure on the right is a cross sectional view of the figure on the left. Reproduced from Karim, F., Walus, K., Ivanov, A., 2010. Analysis of field-driven clocking for molecular quantum-dot cellular automata based circuits. J. Comput. Electron. 9, 16–30.

$\vec{E}$ in the Y and $-Y$ directions switch the molecular cell from ACTIVE state to NULL state and vice-versa. The electrodes have finite radius and potential voltage is applied with respect to grounded plate as per Fig. 9. Average electrode potential (Anon2) is determined as,

$$V_{avg} = \frac{V_{e1} + V_{e2}}{2} \quad (4)$$

where V_{e1} and V_{e2} are the potentials on two adjacent electrodes. The electrode potential difference between these two adjacent electrodes can be given as,

$$\Delta V_e = |V_{e2} - V_{e1}| \quad (5)$$

The RMS voltage V_{rms} can be defined as $\sqrt{(V_1^2 + V_2^2)}$. Where V_1 is maximum allowable V_{avg} and V_2 is minimum allowable V_{avg} (Anon2).

The interdependence between cell size and RMS voltage is studied and analyzed in Fig. 10. A spacing of 20 nm (Anon2) is applied while selecting V_{rms} and cell size. While selecting the above two parameters we need to analyze the temperature issues also.

Now maximum applicable phase difference ϕ_{max} between two adjacent electrodes having maximum potential difference ΔV_{emax} can be expressed as,

$$\phi_{max} = \pm 2\sin^{-1}\left(\frac{\Delta V_{emax}}{2V_0}\right) \text{ radians} \quad (6)$$

Here, V_0 is peak potential value of clock signal applied to adjacent electrodes and the minimum RMS voltage should be applied (Anon2; Karim *et al.*, 2010). The inter-electrode spacing is maintained at 20 nm. The ground plate is placed $\eta = 25$ nm above the electrodes and cells are placed $\beta = 23$ nm above the electrodes as depicted in Fig. 10. The length and radius of electrode are chosen to be 100 nm and 5 nm respectively as justified in Lu *et al.* (2007), Visconti *et al.* (2004) and Dutta and Mukhopadhyay (2019). Dielectric like SiO_2 is used between electrodes and molecules whose dielectric constant is 4.2. The electrodes shall be buried inside the dielectric (SiO_2) (Liu *et al.*, 2002).

Gamma-Ray Generation Methodology for Portable Industrial Radiography System

Tunneling electrons exhibit dual wave particle behaviour. During the act of tunneling, electrons attain the nature of sinusoidal wave (Fock, 1986) as supported in Born's Probabilistic Interpretation (Timler and Lenta, 2002). It demonstrates "particle has a greater probability of being found near $x = 0$, i.e., at dots and reduces chance of being found away from $x = 0$ ". At dots electrons behave as particles. The electron wave ($\psi(x)$) tunneling through the positive X direction with associated finite potential energy $V(x)$ can be represented using time independent Schrödinger wave equation as given in Eq. (7) below,

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}(E - V(x))\psi(x) = 0 \quad (7)$$

where, E is discrete energy of an electron. m is mass of an electron and $\hbar$ is reduced plank constant. This equation (Fock, 1986) reduces to

$$E_n = \frac{\pi^2 n^2 \hbar^2}{2md^2} + V(x) \quad (8)$$

where E_n is infinite sequence of discrete energy levels corresponding to all possible nonnegative integral values of n , the electron quantum number and d is molecular cell dimension. Electrons acquire energy from the applied clock and jump up to higher energy state. On the contrary, while losing energy they move down to lower energy state. Movement of electrons from higher to lower energy levels leads to radiation of energy. This radiation is of our interest and it is tuned to generate Gamma ray for industrial radiography system. The transitions between these energy states are possible if sum or difference of quantum numbers is an odd number (Orlov *et al.*, 1997; Anderson, 1979; Baym, 1969; Fock, 1986). Transitions are strictly forbidden if both the quantum numbers are even (Orlov *et al.*, 1997; Anderson, 1979; Baym, 1969; Fock, 1986).

Any transition of an electron from higher energy state (n th state) to ground state can be expressed with the help of Eq. (9) as,

$$\Delta E_n = \frac{\pi^2 \hbar^2}{2md^2}(n^2 - 1) \quad (9)$$

Industrial radiography system (Jacques *et al.*, 1975a) requires Gamma ray energy in the range of 1.24 MeV. Considering this energy radiation i.e., 1.24 MeV and equating it to ΔE_n in Eq. (9), the relation between electron quantum number n and molecular cell dimension d can be expressed as,

$$1.65 \times 10^{24} d^2 = (n^2 - 1) \quad (10)$$

A careful study of Fig. 11 reveals that at temperature of 1200°K and at 2.12 V_{rms} operating voltage the cells attain a dimension of 1 nm. If molecular cell dimension is considered to be 1 nm, Gamma ray radiation for radiography system, Eq. (10) produces the

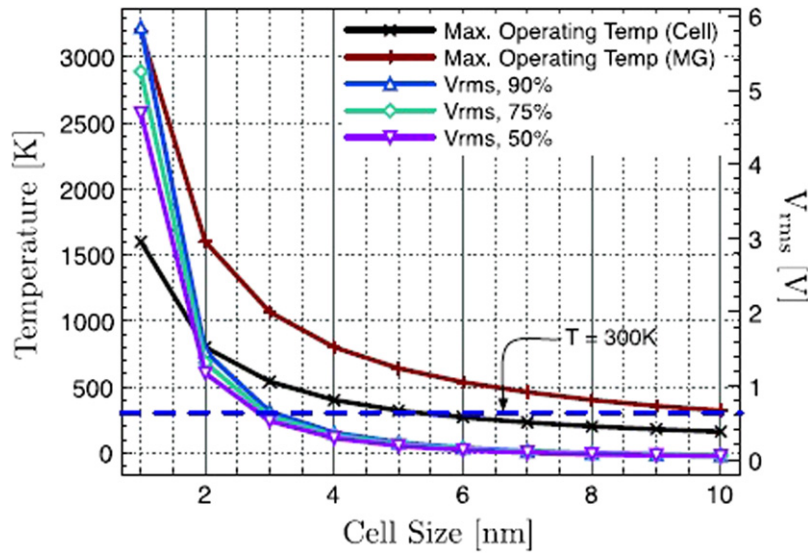


Fig. 11 The plot depicts a trade off between maximum operating temperature in K, cell size in nm and RMS voltage in volt. Reproduced from Anon2, Siemens oem products, www.siemens.com/healthcare.

Table 1 Comparative study on existing and proposed molecular QCA industrial radiography system

Technical specifications	Existing technology	Proposed technology
Power supply	Not applicable	2.12 RMS Voltage
Operating temperature	Normal temperature	1200°K
Power generation	Not applicable	In the range of Watt
Transformer	Not applicable	Step down supply
Compact cooling system	Not required	Required
Radiation	Not controllable	Controllable

value of n to be 1286. For a single molecular cell Eq. (9) can be reformed as,

$$\nu_2 = \frac{\pi \hbar}{2md^2}(n^2 - 1) \quad (11)$$

where, ν_2 is radiation frequency.

Eq. (11) produces a result of 300.73×10^{18} Hz with $n = 1286$ and $d = 1$ nm, which falls within the frequency range of existing Gamma ray for Industrial radiography system. Expression in Eq. (8) should be greater than or equal to $\frac{CV^2}{2}$, where C is barrier capacitance and V is applied voltage (Fock, 1986). A voltage of $2.12 V_{RMS}$ is applied to a barrier capacitance of 0.043 pF and this voltage is enough to cross the barrier. The above calculations are for single molecular cell. The radiation energy strength for N number of molecular cells arranged in cascade is computed as 1.24×10^6 N eV.

Proposed Gamma-Ray Generator for Industrial Radiography System

Our present disclosure is the Gamma ray generating part of Industrial radiography system. The existing Gamma ray generator works without electricity and radiates all the time even when the device is not in use. Whereas the current disclosure works at $2.12 V_{RMS}$ supply, consumes power in the range of Watt only and running at an operating temperature of 1200°K and is able to be electrically switched off the radiation (Table 1).

Proposed QCA Based Gamma Ray Industrial Radiography System

The primary unit of our proposed system is a Gamma-ray plate containing an array of molecular cells arranged in sequence as shown in Fig. 12(a). Each cell in the plate may be replaced by the molecular counterpart as shown in Fig. 12(b). Fig. 13 depicts the electrodes at the bottom of the section. They are buried under SiO_2 layer. The molecular cells are arranged over the layer as they are

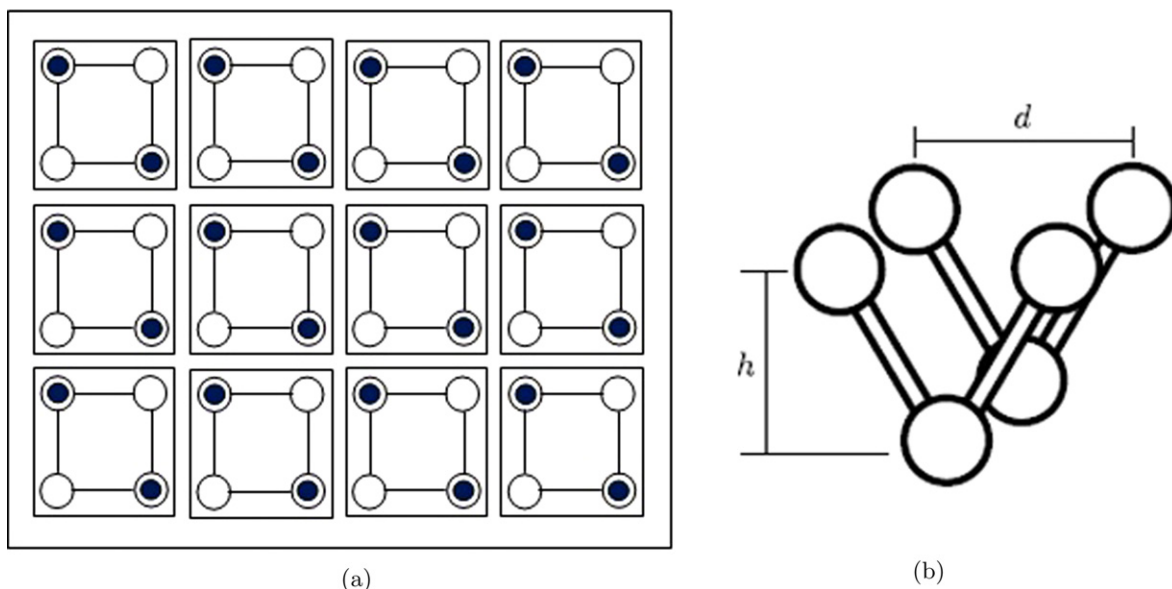


Fig. 12 (a) Gamma-ray plate containing an array of square cells. (b) Molecular cell that will replace the square cells in Gamma-ray plate. h is cell height and d is cell dimension.

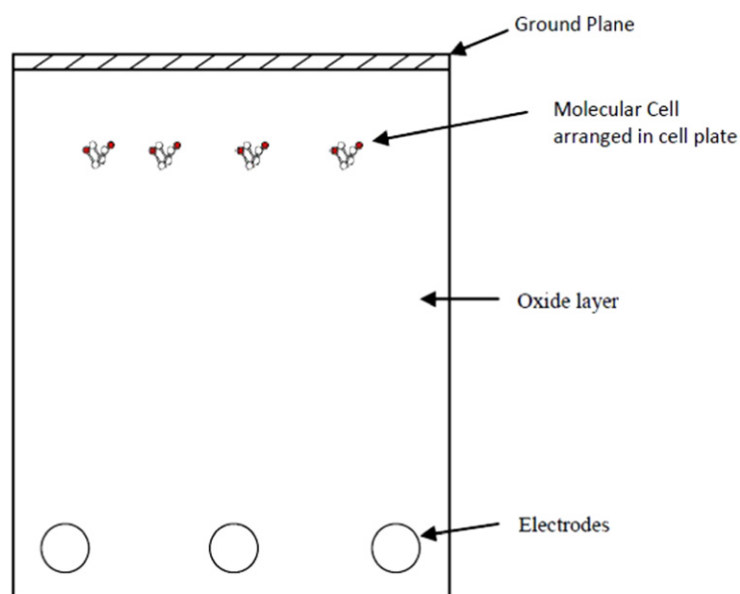


Fig. 13 Cross section view of the proposed Gamma-ray generator Unit for Gamma Ray Generation.

arranged over the plate. One grounded plate is placed above the cell level. All the molecular cells are having a size of 1 nm. It may work at temperature of 1200K and execute at an applied voltage of 2.12 RMS voltage. This value of RMS voltage might be supplied to the electrodes buried under the dielectric through step down transformer. The Gamma-ray generator in Fig. 13 is housed within the Gamma-ray radiography system as in Fig. 14. It contains a power supply section at the bottom, Gamma ray plate as in Fig. 12(a). The power supply section is consisting of electrodes, oxide layer and grounded plate. The Gamma-ray generator runs at a temperature of 1200K. So there is need to control the temperature inside. Our contribution here is the molecular QCA Gamma-ray tube that runs on electricity, runs in 1200K temperature, execute with the supply voltage of 2.12 RMS Voltage and no radiation while switched off.

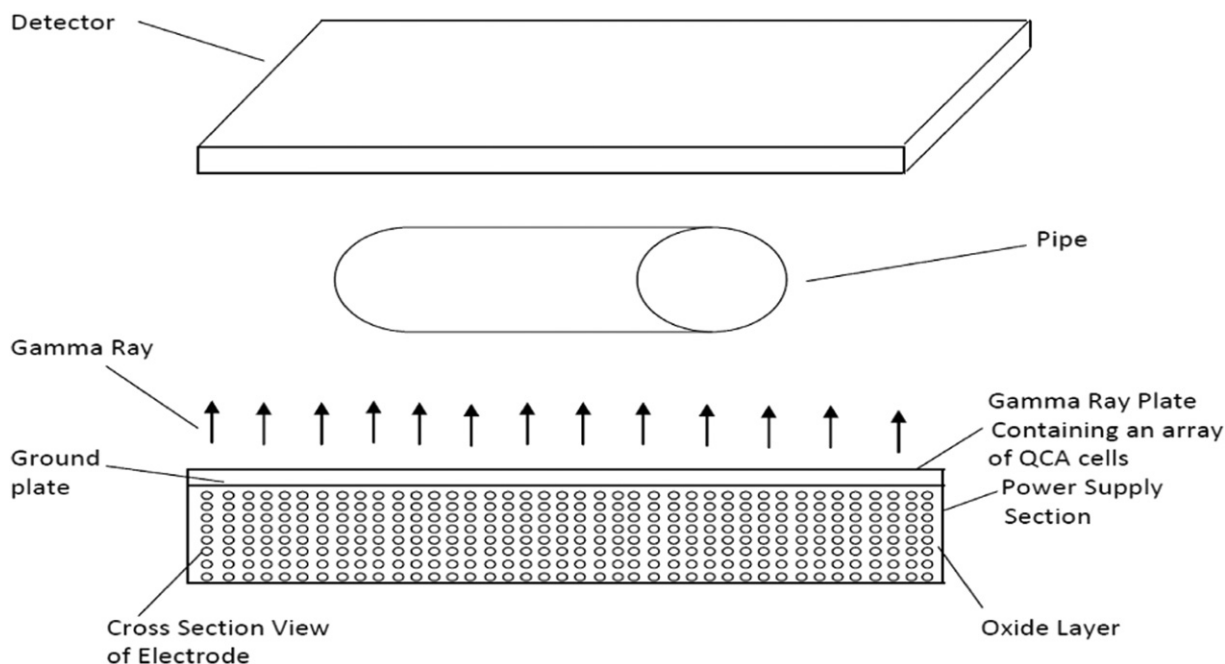


Fig. 14 Quantum dot cellular automata based industrial radiography system.

Conclusion

The article discloses a proposal of nature friendly Gamma-ray generating system used for the purpose of industrial radiography. This technology can be operative by consuming energy generated from harness natural processes such as geothermal energy, wind energy, biomass energy, solar energy, hydro-electric power etc., for system execution. Existing industrial radiography solution technologies being typically power hungry seem unsuitable for use of such eco-friendly power generating sources. The nano-technology based system places itself as appropriate from environmental point of view. As a result it may be found to eliminate any chances of generation of greenhouse gases and keeps the environment clean and worth living.

See also: An Ultra Low Power Molecular Quantum Dot Cellular Automata Based X-ray (QX-ray) Generating System Using Renewable Energy Source

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Fermentative Production of Optically Pure Lactic Acid From Renewable Materials

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Introduction

It is well known that in the coming years of globalisation of commodity products due to rise in human consumption will result in depletion of the planet's natural reserves. The use of the unsustainable natural resource, crude oil leads to an increase in carbon dioxide (CO₂) and methane (CH₄) in the environment (Sukan *et al.*, 2015). Again, worldwide the plastics that are used nowadays are synthesized from these fossil fuels and their depletion after use from the environment will take great amount of time and will be hazardous for the planet (Chen and Patel, 2012; Blanco *et al.*, 2011, 2013, 2014).

Since, plastics or rather polymers have become an important part of our lives various technologies are used to improve it and make it more environment friendly. But with the depletion of its source materials novel resources are being sought after. Along with scarcity of resource with polymer production a great deal of its usage results in increase of atmospheric greenhouse gases (GHGs). This results in global warming and increase usage of this non-renewable resource increases the carbon footprint as well (Hottle *et al.*, 2013; Colwill *et al.*, 2012). These escalating environmental problems over the recent years have led to the microbial synthesis of commercially valuable products, i.e., by adopting "green methods" (Abdel-Rahman *et al.*, 2013). Emission of greenhouse gases (GHGs) and increase in the carbon footprint have driven the world towards adopting such techniques. The urge for the synthesis of biopolymers have lead to a search from "green chemicals" from renewable resources (Flieger *et al.*, 2003; Du and Yu, 2002; Landis *et al.*, 2007).

It is well known, that lactic acid (LA) is a commercially important chemical product owing to its wide application in various industries like cosmetic, food, pharmaceutical and chemical industries. Nowadays LA is used in the synthesis of the polymer poly lactic acid (PLA). PLA has great potential in production of various products ranging from fibers to foam (Abdel-Rahman *et al.*, 2013). In global estimates demand for PLA was 360.8 kilo tons in 2013 which is assumed to grow upto 18.8% by 2020 and reach 1960.1. Consequently, in 2013, 714.2 kilo ton of LA was produced which is could reach 1205.3 kilo ton by the year 2020 with a growth rate of 15.5% (Abdel-Rahman *et al.*, 2013; Abdel-Rahman and Sonomoto, 2016). LA production is generally achieved through two routes (i) chemical synthesis and (ii) fermentative routes. Chemical synthesis is done mainly by the hydrolysis of Lactonitrile which produces a racemic mixture of D-(-)- LA and L-(+)- LA. The fermentative production produces optically pure D-(-)-LA or L-(+)-LA when the suitable microorganism is used for the synthesis of Lactic acid through fermentative routes. This results in use of substrates from renewable resources. At present most of the lactic acid produced in the world comes from this fermentative routes. About 90% of LA is produced through this fermentative route (Okino *et al.*, 2008; Abdel-Rahman *et al.*, 2013; Abdel-Rahman and Sonomoto, 2016). Thus, for the production of optically pure lactic acid, suitable biotechnological innovations are required. Lactic acid production through fermentative route has been done mainly from sugar substrates like glucose, lactose, maltose, sucrose etc., procured from barley, malt, molasses and beet sugar.

However, production of lactic acid from economically viable resources such as rice bran, green microalga and paper sludge have also been achieved (Wang *et al.*, 2015). In recent times lignocellulosic starch from agricultural residues and also from forest materials have been sought by researchers for synthesis of lactic acid (Wang *et al.*, 2015). Wide arrays of microorganisms have been used applying various optimum conditions to achieve the desired results by the researchers for production of optically pure lactic acid. Among the microorganisms commercially important lactic acid bacteria i.e., lactobacillus have been used mostly. These strains are advantageous due to their ability of high acid concentration tolerance. They are also able to generate selective synthesis of optically pure D-(-)-LA or L-(+)- LA through genetic engineering. However, they possess disadvantages such as requirement for complex nutrients and little pentose utilization (Zhou *et al.*, 2003). Other microorganisms used for this purpose include *Rhizopus*, *Escherichia*, *Saccharomyces*, *Bacillus* and *Kluyveromyces*. These microorganisms require improvements in substrate range for improved productivity and enhanced optical purity of the product (Zhou *et al.*, 2003; Saitoh *et al.*, 2005). However, there are various constraints in LA production, such as most of the substrates requires pretreatment of its renewable source due to removal of lignin and lack of hydrolytic enzymes in LA producing strains. Purification of LA from broth is also a concern. So such challenges are persistent in production of optically pure LA.

Lactic Acid

Lactic acid in recent times have emerged as a great product for production of various industrially desirable materials and also for the production of bioplastics from renewable resources. Lactic acid (2-hydroxypropanoic acid) is a hydroxycarboxylic acid which occurs naturally and present in L form in humans. Swedish chemist Scheele in the year 1780 first refined it from sour milk. Then it was used majorly in the food industry for enhancing flavour, as an acidulant and also as a preservative. Gradually it emerged as an important chemical to be used in cosmetic, pharmaceutical and chemical industries. Recently its use for synthesis of PLA has been widely sought for. Among, the optical isomers of lactic acid L-(+)- LA is preferred in drug and food industries as this form of LA could be easily assimilated in human body. Copolymerisation of both the isomers leads to an amorphous structure whereas homopolymers are crystalline in nature having regular structures (Wang *et al.*, 2015).

Synthesis of Optically Pure Lactic Acid

As discussed earlier there are two routes for the synthesis of optically pure LA. However, batch fermentation method is the widely used for LA synthesis. The conditions for the fermentation processes are different as per their industrial requirements. For example, in case of organism *Lactobacillus delbrueckii*, LA is produced at temperature range of 45–60°C within a pH range of 5–6.5 whereas when *Lactobacillus bulgaricus* is used temperature is maintained at 43°C within a pH 6–7. LA synthesized by batch fermentation has a yield of 90%–95% based on initial substrate concentration and depending on various parameters of pH, concentration of nitrogenous nutrients, temperature and initial substrate concentration (Ghaffar *et al.*, 2014; Meng *et al.*, 2012).

Chemical Synthesis of Lactic Acid

As discussed earlier, lactonitrile is used for the chemical synthesis of LA. Lactonitrile is synthesized by adding hydrogen cyanide to acetaldehyde at high atmospheric pressure. The synthesized lactonitrile is purified by distillation followed by hydrolysis by concentrated H₂SO₄/HCL to get the desired LA and the ammonium salt. Then it is esterified by methanol to form methyl lactate and further purified before second hydrolysis to form LA and methanol. Consequently, a racemic mixture of L and D-LA is formed (Ghaffar *et al.*, 2014).

Fermentative Synthesis of Lactic Acid

Fermentative synthesis is the most preferred route. It is an energy generating procedure in which the organic molecules involved in the synthesis act as both the electron acceptor and electron donor. Thus, in this chemical synthesis the molecule produced does not possess its own entire potential energy. Generally, LAB are used for this fermentation where no or very less amount of heat is required. In batch fermentation procedure the cultures are first made to grow in number of inoculum vessels and then transferred to the fermenter. In general the inoculum volume is 5%–10% of the liquid volume of the fermenter. It is kept at a temperature of 35–45°C and kept at a pH of 6.5. Bacterial fermentation occurs in fed-batch, continuous batch and repeated batch methods. Higher LA concentration is found in fed-batch and batch methods and higher productivity is achieved through continuous cultures. Again continuous cultures could be run for greater periods of time (Ghaffar *et al.*, 2014; Benthin and Villadsen, 1995). Advantages and disadvantages of this fermentative process of LA synthesis is given in Table 1.

Apart from bacteria various other microorganisms can produce lactic acid. The fungus *rhizopus sp.* synthesizes L-(+)-LA at lower yield from starch when compared to LAB. In this case if airlift bioreactor is used 85% of the yield under optimal conditions could be achieved. In this case of fungal mycelia hinder lactic acid production as they increase the medium's viscosity. Thus, lactic acid bacteria which have complex nutrient requirements are used mainly industrially for fermentation processes. Again, product recovery after fermentation is an important step which is done through separation and purification of LA from the broth. For this purpose various methods have been studied including ion exchange, membrane technology, reactive extrusion electro-dialysis, distillation etc (Ghaffar *et al.*, 2014).

Microorganisms Involved in Fermentative Synthesis of Lactic Acid

As discussed earlier, gram positive Lactic acid bacteria (LAB) are used for fermentation of LA. These bacteria are non-spore forming cocci and rods and non-motile. They do not possess cytochromes and porphyrins as a result of which they do not generate ATP.

Table 1 Comparison of advantages and disadvantages of fermentation processes

Fermentation mode	Advantages	Disadvantages
Batch fermentation	Simple operation High product concentration Reduced risk of contamination	Low productivity Substrate and/or end product inhibition
Fed-batch fermentation	Overcome substrate inhibition problem High product concentration	End product inhibition Difficult to conduct optimal design
Repeated fermentation	Time saving process	Requirement of special devices (e.g., hollow fiber module) or special connection lines used for cell concentration
Continuous fermentation	Labour-saving Omission of seed preparation time High growth rates Short main culture High productivity Control growth rates Less frequency shut down process	Incomplete utilization of carbon source

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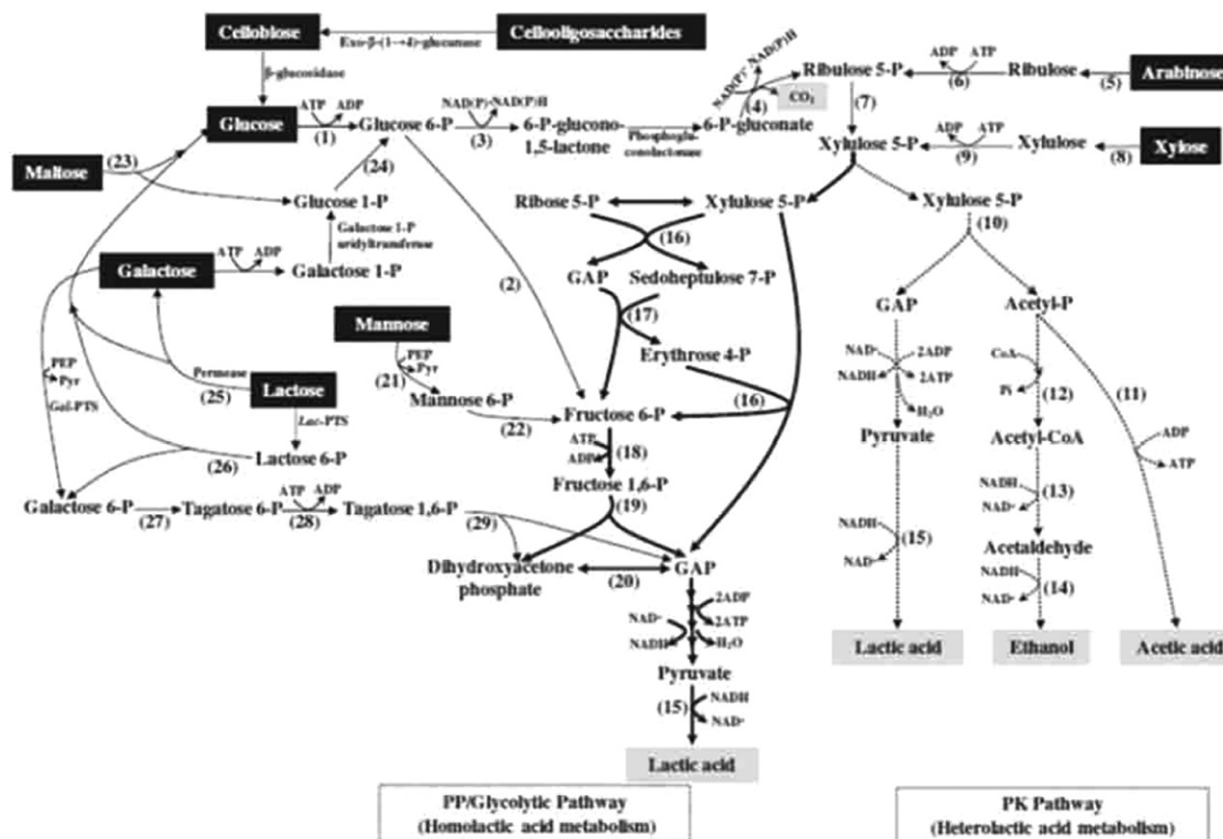


Fig. 1 Metabolic pathways for LA synthesis by LAB. Reproduced with permission from Abdel-Rahman, M.A., Tashiro, Y., Sonomoto, K., 2013. Recent advances in lactic acid production by microbial fermentation processes. *Biotechnology Advances* 31, 877–902.

Thus they grow under anaerobic condition and do not require oxygen for survival but they are facultative anaerobes and are can grow when oxygen is present. These aero tolerant anaerobes are thus protected from the harmful effects of oxygen by-products like hydrogen peroxidase. They also have the ability to ferment hexose to lactic acid which many organisms do not have (Ghaffar *et al.*, 2014). A schematic representation of the metabolic pathways used by LAB in LA synthesis is given in Fig. 1.

Lactic acid bacteria present in the genera of *Lactobacillus*, *Enterococcus*, *Leuconostoc*, *Lactococcus*, *Carnobacterium* etc., ferment carbohydrates through homo, hetero and mixed fermentation pathways to produce LA but homofermentative pathways gives less by products such as formic acid, acetic acid etc., and better yield of LA. However few LA bacteria such as *L. helveticus*, *L. amylophilus*, *L. delbrueckii* and *L. bulgaricus* can produces optically pure L-(+)-LA (Yun *et al.*, 2003).

A comparative account of homo and hetero fermentative LAB is given in Table 2.

These microorganisms have the ability to use cheap raw materials for fermentation and require very little amount of nitrogenous nutrients and have the capability to produce high amount of stereo specific LA under optimal conditions of low pH and high temperature. In this process they produce little amounts of cell mass generating low amount of by products which are industrially desirable. The filamentous fungi *rhizopus sp.* also produce lactic acid.

R. oryzae and *R. arrhizus* directly converts starch into L-(+)-LA owing to their amylolytic activity. These fungi have drawn great interest industrially as their immobilization property had resulted in better yield of the desired products. Nowadays, genetic engineering have also been employed to produce LA. For example *Saccharomyces cerevisiae* have low pH resistance compared to LA bacteria. Thus on experimental basis genetically engineered yeast have been preferred. Again, mixed culture of *Lactobacillus brevis* and *Lactobacillus pentosus* were used to synthesize LA from wheat straw hemicelluloses. *Enterococcus faecalis* RKY1 have also been used to produce LA from sugars. *Escherichia coli* were also used for the generation L-lactate and D-lactate. The strain JP203 was reported as the strain of *E. coli* for good production of D-lactate. This strain also possessed various antibiotic resistant genes (eg., TET and KAN). Repeated batch fermentation process also produced LA from *Enterococcus faecium*. A *Bacillus sp.* strain was also reported to produce L-(+)-LA. This strain possessed thermo-philic properties and optically pure L-(+)-LA can be formed from this strain (Okano *et al.*, 2009).

The synthesized stereocomplex PLA is made of both poly D-(−)-LA and poly L-(+)-LA and has high thermal stability with a melting point of 230°C. This is 50°C higher than the single polymers individually. Thus, this has resulted in the synthesis of pure D-(−)-LA. It has been reported that through the construction of *Lactobacillus plantarum* which is L-lactate dehydrogenase gene (*ldhL1*)-deficient through plasmid insertion pure D-(−)-LA could be synthesized from corn starch encoding *Streptococcus bovis* 148-amyase (AmyA). A high yield of optical purity of about 99.6% was achieved (Mazumdar *et al.*, 2010).

Table 2 Comparative account of homo and heterofermentative bacteria

Characterization	Homofermentative LAB	Heterofermentative LAB
Products	Lactic acid	Lactic acid, ethanol, diacetyl, formate, acetoin or acetic acid and carbon dioxide
Metabolic pathways	Hexose: Embden-Meyerhof pathway Pentose: Pentose phosphate pathway	Hexose: Phosphogluconate and phosphoketolase pathway Pentose: Phosphoketolase pathway
Theoretical yield of lactic acid to sugars	Hexose: 1.0 g/g (2.0 mol/mol) Pentose: 1.0 g/g (1.67 mol/mol)	Hexose: 0.5 g/g (1.0 mol/mol) Pentose: 0.6 g/g (1.0 mol/mol)
Genera	<i>Lactococcus</i> , <i>Streptococcus</i> , <i>Pediococcus</i> , <i>Enterococcus</i> , some <i>Lactobacillus</i> .	<i>Leuconostoc</i> , <i>Oenococcus</i> , some <i>Lactobacillus</i> species.
Availability for commercial lactic acid production	Available due to high selectivity	Not available due to high by-product formation

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Again, genetic engineering in *Escherichia coli* both the microanaerobic and aerobic conditions has achieved a conversion of D-(–)-LA from glycerol (a cheap, easily available source). This was achieved by over expressing pathways for this conversion and consequently blocking of those pathways leading to the synthesis of by-products. In this homo fermentative route overexpression of genes encoding the glycolytic intermediates (GldA-DHAK and GlpK-GlpD and pathways) alongwith that of the synthesis of D-lactate from pyruvate (D-lactate dehydrogenase) was done. Again the for the synthesis of acetate, ethanol and succinate was reduced by engineering those pathways (Mazumdar *et al.*, 2010).

Synthesis of Optically Pure Lactic Acid From Various Renewable Resources

Agricultural wastes or crop residues is an important renewable source. Globally every year approximately 3.5 billion tons of wastes from agriculture are produced. Carbohydrate feedstocks requirement are costly and availability lacks abundance. However, the agro industrial wastes thus produced are rich in carbohydrate sources. However, they are not utilized owing to poor protein content and are also not digestible. Conventionally, the carbon source for LA production has been sucrose, lactose, glucose or molasses, starchy materials (carrot, barley, tapioca, potato), whey, sugarcane bagasse, cassava bagasse etc. The raw material for substrate for LA synthesis is very important. Purified sugars are very expensive. Different agro wastes are more economically viable alternatives. Molasses are often exploited for this purpose. Again, starchy materials are also often used. Agricultural by products like corn starch, cassava starch also can be used. Lignocellulosic materials like hemicellulose hydrolyzates, corn cob, Jerusalem artichokes, corn stalks, wheat bran, beet molasses, sweet sorghum, rye flour, sugarcane press mud, cellulose, carrot processing wastes, molasses spent ash, carrot waste hydrolyzates are also being reported to be sources for LA production (Hofvendahl and Hahn-Hägerdal, 2000; John *et al.*, 2007).

A list of renewable resources which are used for LA production and the microorganisms involved along with the processes is given in Table 3.

As it is well known that LAB does not have amylolytic and cellulolytic enzymes, thus hydrolysis of cellulosic and starchy wastes are required. Enzymatic, steam treatment or acid hydrolysis or by lignocellulosic enzymes are preferred for pre treating the raw materials.

Woody materials are mechanically broken down and bisulfates are used to release the carbohydrates and sugars. This sulphite filtrate could be then used by LAB (John *et al.*, 2007). Acid or enzyme hydrolysed starchy wastes have also been reported. Prior to hydrolysis these materials are often gelatinized. Enzymes like glucoamylase are used for saccharification and alpha amylase for liquefaction. However of all the treatments done on starchy and lignocellulosic materials acid hydrolysis is found to be more economical and less energy is consumed when compared with enzyme hydrolysis. Hemicellulose and cellulose are often hydrolysed with 72% sulphuric acid. This is then further diluted to extract its sugars. Sometimes co- immobilization with starch degrading enzymes of starch-degrading and LAB are also done to get simultaneous sugar generation and saccharification (John *et al.*, 2007). Waste materials are also used for LA generation. The by products from cheese industry whey is often used. Mussel processing wastes from industries also used (John *et al.*, 2007). Li *et al.* (2015) had reported the use of food waste for production of optically pure L-(+)-LA. Again, excessive sludge have been used for open fermentative synthesis of L-(+)-LA by thermophilic bacteria (Ma *et al.*, 2014). Neu *et al.* (2016) had reported the use of coffee mucilage by *Bacillus* sp. for synthesis of optically pure LA.

Applications of Lactic Acid (LA) in Various Industries

The applications of Lactic acid (LA) accounts for about 85% of its usage in food industrial applications and the rest of its production is used in other industries. As mentioned earlier, LA has found its use as an acidulant and preservative in industries (food and beverages) for several years. Chemicals from lactic acid such as calcium lactate and sodium lactate is known to be used

Table 3 Recent investigations on lactic acid production from renewable materials by different fermentation modes and methods

Microorganism	Substrate	Fermentation mode	Lactic acid γ (g L ⁻¹)	Yield γ (gg ⁻¹)	Productivity P(g L ⁻¹ h ⁻¹)
<i>Bacillus</i> sp. strain XZL9	Carob mollases	Fed batch	74.7	0.50	0.38
<i>Enterococcus faecium</i> No.78	Sago starch	Batch	166 ± 0.8	0.93	1.105 ± 0.06
		Continuous	10.4	–	1.56
		Continuous (with high cell density)	11.7	0.76	3.04
<i>E. faecalis</i>	Wood hydrozylate	Batch	93.0	0.93	1.7
<i>Lactobacillus bifementans</i> DSM 20003	Wheat bran hydrozylate	Batch	62.8	0.83	1.2
<i>L. brevis</i> S3F4	Corn cob	Batch	39.1	0.70	0.81
<i>L. casei</i> NCIMB 3254	Cassava bagasse	SSF	83.8	0.96	1.40
<i>L. casei</i> G-02	Jerusalem artichoke tubers	Fed batch, SSF	141.5	0.936	4.7
<i>L. casei</i> LA-04-1	Soybean meal hydrozylate	Fed batch (fed with CSL)	162.5	0.897	1.69
		Fed batch (fed with YE)	180	0.903	2.14
<i>L. delbrueckii</i> NRRL B-455	Alfalfa fibers	SSF	35.4	0.35	0.75
<i>L. delbrueckii</i> mutant Uc -3	Cellobiose and celotriose	Batch	90.0	0.90	2.3
<i>L. delbrueckii</i> ZU-S2	Corn cob residue	Batch	48.7	0.95	1.01
		Continuous	44.2	0.92	5.7
<i>L. delbrueckii</i> mutant Uc -3	Mollases	Batch	166	0.87	4.2
<i>L. delbrueckii</i> IFO 3202	Rice bran	SSF	28.0	0.28	0.78
<i>L. paracasei</i> LA104	Green microalga	SSF	37.11	0.46	1.03
<i>L. pentosus</i> CECT-4023T	Trimming vine shoots	Batch	24.0	0.76	0.51
<i>L. plantarum</i> 14431	Alfalfa fibers	SSF	46.4	0.46	0.64
<i>L. rhamnosus</i> CECT-288	Apple pomace	Batch	32.5	0.88	5.4
<i>L. rhamnosus</i> HG 09	Hydrolysed acorn starch	Batch	57.61 ± 1.37	0.46	1.60 ± 0.12
<i>Lactobacillus</i> sp. MKT-878 NCAIM B02375	Wheat starch	SHF	118	0.94	1.71
<i>Lactobacillus</i> sp. RKY2	Rice and wheat bran Lignocellulosic hydrozylates	SSF	97	0.89	1.74
		Batch	129	0.95	3.1
		Cell-recycle	27	0.90	6.7
<i>Lactobacillus lactis</i> IO-1	Sugarcane bagasse	Batch	10.9	0.36	0.17

SSF, simultaneous saccharification and fermentation; SHF, separate hydrolysis and fermentation; CSL, corn steep liquor; YE, yeast extract; –, not determined.

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for conditioning and emulsifying purposes. LA is used in food for flavouring purposes, as acidulant and also as for pH buffering. Presence of LA in food inhibits bacterial spoilage in many processed foods and beverages (Datta et al., 1995).

LA and its salts also acts as disinfectants in packaging industry for storing of fish, poultry etc. This is mainly done to reduce spoilage by *Clostridium botulinum* (Datta et al., 1995). It is used extensively in bakery products for emulsifying and conditioning purposes. Cosmetic industry also uses this natural ingredient in creams used for skincare purposes like acne removal (Datta et al., 1995; Wee et al., 2006). Pharmaceutical industry also used it in various topical creams and lotions (Wee et al., 2006). As, mentioned before it is now been used extensively for biopolymer synthesis which have a wide variety of applicability ranging from commodity products to medical prostheses (John et al., 2007). The biopolymer PLA synthesized from LA mainly by condensation polymerization can be degraded biotically by simple hydrolysis of the ester bonds of the molecules (Vijayakumar et al., 2008). Thus synthesis and use of PLA is environmentally sustainable. LA being a green chemical synthesized from renewable resources and PLA is a bioplastic which could be degraded effectively after its use biologically, makes it a product which will reduce GHGs and carbon footprint of this planet. In spite of its various application potential and environmental benefits, the production of PLA is considerably lower than the plastics produced from non-renewable resources. Various limiting factors ranging from economic factors to procurement of renewable resources have been the limiting factors in its production. However, in recent times these limitations are being made to overcome to increase PLA production fro LA (Åkerberg and Zacchi, 2000; Christensen et al., 2008; Pacheco et al., 2012).

Conclusions

Lactic acid (LA) is known to be an important chemical which is required in various industries like chemical, pharmaceutical etc. However, with the rising concerns of increasing greenhouse gases and more use of bio-products from renewable resources is sought after. Bioplastics is one such developing sector industrially in our recent times. Among the various bioplastics being used poly lactic acid (PLA) is one such plastic which is now being industrially produced. These recent advents in PLA productions have

considerably put the focus on synthesis of LA. LA is generally produced by fermentative route by using microorganisms to get optically pure forms of LA. Genetic engineering coupled with newer substrates is now being sought after for LA production. Conventional use of sugars is now being replaced by renewable resources like agro wastes and lignocellulosic materials. These require various pre-treatments before extraction of the sugars from them to produce the optically pure LA by microorganisms. However, they are a cheap, economical and environmentally friendly source for this purpose. Research is now being focussed in this area to produce LA from renewable cheap resources. The use of this chemical for synthesis of PLA is the current focuses for researchers vying for synthesis of economically viable biopolymers. Since, the use of PLA as mentioned earlier, will result in mitigation of GHGs and reduce carbon footprint of this world it is a widely sought after material in today's time and its process of synthesis from renewable materials is also an important field of study (Drumright *et al.*, 2000; John *et al.*, 2007).

Acknowledgement

SS would like to acknowledge UGC D.S. Kothari Post doctoral Fellowship scheme for financial assistance during writing of this article [CH/15-16/0163].

See also: Manufacturing of Biodegradable Poly Lactic Acid (PLA): Green Alternatives to Petroleum Derived Plastics

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Gasification of Hospital Waste by Thermal Plasma: A Relevant Technology Towards Mitigation of Greenhouse Gases in India[☆]

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Introduction

India is the second most populated country in the world after China. According to sensuous in 2011 its population was 1.21 billion, and according to United Nations of Organizations its population was 1.32 billion in 2016. It has been studied that India's population will reach around 1.40 billion in 2020 and it will surpass China in population at 2022. Due to this growth in population, improper utilization of natural resources has been increased to such an extent that has put adverse effect on ecological balance and as a result nature has been changed largely. Environment has been polluted, nature has lost its purity, and people became sick and going to lose their immunity power.

Due to the massive growth in population, generation of waste has been raised to a very high level. As a result there is an uncontrolled increase in the number of patients and generation of Hospital Waste, (abbreviated as HW) in India. Hospital waste is generated from Government and Private Hospitals, nursing homes, pathological centers, health checkup centers, veterinary hospitals, medical camps, blood donation camps, and in research laboratories. Generation of Hospital Waste is recorded 1–1.5 kg/day per patient in an average in India. According to Press Information Bureau, (Govt. of India, Ministry of Environment and Forest) 2016, it is known that 0.17 million ton Hospital Waste is generated every year in India. The generation of Hospital Waste is increased in a rapid rate throughout the country and has become a threat and impose a mammoth task to dispose it in proper and scientific manner without affecting the environment and human health. Hospital Waste can cause serious diseases if not managed and disposed properly. The infectious germs, pathogens and chemicals can cause health hazard if one comes in direct contact of it without having adequate precautionary measures. It emits toxic gases into environment if burned or put abundantly in open ground for land filling. So a suitable technology is very much required as soon as possible which can dispose HW without affecting our environment. Plasma being the fourth state of matter can generate temperature about 3000–6000°C and is a reliable and viable technology for safe and complete disposal of HW. It can completely destroy pathogens, infectious molecules and emits neither toxin nor greenhouse gases into atmosphere. The volume reduction of HW is about 99% in plasma arc gasification process and gas produced here is mainly a mixture of H₂ and CO which is known to be Synthetic Natural Gas (Syn gas).

A Burden to Modern Age: Hospital Waste and its Classification

Hospital Waste generated from treatment and health-care activities consists of 85% non-hazardous and 15% hazardous wastes. The hazardous HW is mainly infectious, toxic in nature and sometimes, holding radioactive properties too ([HWO Healthcare Waste, 2018](#)). The amount of hazardous waste material is increased when there is not proper segregation of generated waste in hospitals. As a result when non-hazardous HW is mixed with hazardous HW, the entire waste becomes hazardous. There is a variety in generated Hospital Waste, such as:

Infectious Waste

This consists of pathogens which can cause fatal diseases, blood and other body fluids, culture and research of infected body parts and cells, and waste generated from treatment of infectious patients. Diagnostic samples, bandages, some medical treatment devices are mainly infectious during treatment of chronic disease patients ([HWO Healthcare Waste, 2018](#)).

Pathological Waste

These wastes are mainly tissues, body parts, blood, and other body fluids.

[☆]A. Hazra and S. Das have contributed equal share.

Sharps

Needles, syringes, nail, broken glass, blades, disposable and discarded scalpels, saws etc., are sharp HW which may cause serious injuries and contamination if impinged to body.

Pharmaceutical Waste

These are expired drugs, vaccines etc.

Chemical Waste

It include chemicals discarded after being used for cleaning, disinfection etc. Moreover, chemical waste is generated in research work of tissue culture. Heavy metals used in medical devices and instruments are also became a source of chemical waste (as mercury in a broken thermometer).

Genotoxic Waste

These waste materials are highly hazardous in their nature, these are mainly carcinogenic, mutagenic waste products produced in the treatment of patients suffering from chronic diseases like cancer. e.g., cytotoxic drugs used for the treatment of cancer patient.

Radioactive Waste

These wastes are generated through radioactive diagnostic materials which are used for *in-vitro* analysis like tissue, *in-vivo* imaging studies of organ, tumor analysis etc and their related treatment.

Non-Hazardous Waste

These are general wastes which are less hazardous in nature, kitchen wastes, food grain, papers, plastics, wrapper, fruit peels, vegetables etc are some kinds of non-hazardous waste.

Hospital Waste Generation and Treatment: A Brief Survey in India

In most of the cases, Hospital Waste is dumped in open land or sometimes burnt in dumped yards in many places without taking much concern about environment. People come in contact with such contaminated HW experiences potential health hazard. A very few hospitals have proper infrastructure for waste disposal and monitoring system for management of hospital waste (Nema and Ganeshprasad, 2002).

Hospital waste is treated through Incinerator, Autoclave, Microwave, and Shredder at the waste generation site. As per the reports published by Central Pollution Control Board (CPCB) in 2014 it has been found that Incinerator, Autoclave and Shredder are the common methods used in different hospitals in different states of India (Vide Table 1). The other processes are rare to be used.

Existing Conventional Methods for Hospital Waste Treatment in India's Perspective

Till date, Hospital Waste once collected from hospitals is disposed commonly through Land filling, Autoclave, Microwave, Shredder and Incineration processes in India.

In Autoclave technology water vapor at a very high temperature (superheated) is utilized to sterilize the pathogens, infectious germs and other contaminated medical instruments into a closed chamber. A boiler is used to produce saturated steam, which is surrounded through a steam jacket at the Autoclave chamber. Air being an insulator is removed from Autoclave chamber through air suction process. This process is fruitful for disinfection of hazardous hospital waste but the waste remains in its original position. Surgical instruments can be reutilized after being sterilized by this process but hospital waste is not totally treated here, the volume of HW remains unaltered after the treatment. Besides this, this procedure can never be used for radioactive waste, volatile and semi volatile materials, mercury, and waste produced from chemotherapy. However this process is not that much prospective and henceforth useful towards complete and safe disposal of any kind of hospital wastes (Diaz *et al.*, 2005). For complete disposal of HW incineration process is performed after treatment through Autoclave, it makes the entire procedure more costly and critical (Nema and Ganeshprasad, 2002).

Land filling is a frequently and widely used technology for waste disposal in the world and also in India. Hospital wastes collected from different sources are dumped in open land far away from the locality (in general outskirts of a city). Various bio-degradable and bio-non degradable infectious, hazardous waste materials came in direct contact of the environment and causes environment pollution. The bio degradable waste materials produce NH_3 , CH_4 , and CO_2 like greenhouse gases. It causes harmful

Table 1 Hospital waste generation and waste treatment scenario in India

Sl. No.	Name of state/union territory	Govt. hospitals & health care centers	Total quantity of HW generation (kg/day)	Treatment (%)	Waste treatment process			
					Incinerator	Autoclave	Microwave	Shredder
1.	Andaman & Nicobar Island	29	230	100	06	Nil	Nil	Nil
2.	Andhra Pradesh	7213	22,187	77	17	16	Nil	Nil
3.	Arunachal Pradesh	44	85	100	02	10	Nil	Nil
4.	Assam	1009	4293	99	334	118	38	118
5.	Bihar	174	624	100	18	10	Nil	09
6.	Chandigarh	681	2039	100	02	01	Nil	04
7.	Chhattisgarh	740	4492	100	14	305	07	358
8.	Daman & Diu and Dadra & Nagar Haveli	76	133	100	01	01	Nil	01
9.	Delhi	3941	13,912	100	09	19	02	22
10.	Goa	371	5720	100	01	177	01	Nil
11.	Gujarat	27,021	23,500	100	17	16	Nil	19
12.	Haryana	2375	8695	100	14	168	Nil	1008
13.	Himachal Pradesh	570	2858	100	06	06	Nil	04
14.	Jammu & Kashmir	838	4359	70	10	66	Nil	04
15.	Jharkhand	1136	4810	100	18	356	Nil	01
16.	Karnataka	26,788	82,812	92	31	17	Nil	15
17.	Kerala	3399	40,252	92	93	306	12	526
18.	Lakshadweep	11	50	100	01	10	Nil	Nil
19.	Madhya Pradesh	2663	9405	95	23	321	Nil	810
20.	Maharashtra	51,185	45,090	100	18	1085	40	2840
21.	Manipur	577	415	85	04	26	Nil	Nil
22.	Meghalaya	699	652	100	06	Nil	Nil	01
23.	Mizoram and Nagaland	94	2039	37	04	07	02	Nil
24.	Odisha	1415	5772	81	12	856	11	45
25.	Puducherry	127	9152	100	04	01	01	02
26.	Punjab	2935	9300	100	05	05	Nil	08
27.	Rajasthan	3566	15,570	80	12	12	Nil	12
28.	Sikkim	48	208	100	06	01	Nil	Nil
29.	TamilNadu	5563	33,024	100	09	11	Nil	13
30.	Tripura	1157	1251	85	02	Nil	Nil	Nil
31.	Uttar Pradesh	5711	23,000	93	35	28	Nil	26
32.	Uttarakhand	623	2070	100	07	82	22	95
33.	West Bengal	6440	31,400	63	07	18	03	17

Source: Modified from CPCB Report on 26.06.2014. Available at: <http://cpcb.nic.in/displaypdf.php?id=aHdtZC9BUl8yMDEyLnBkZg=>.

effect on the entire eco system of that area. Bio non degradable waste products remain unaltered at the land. Cattle and human being come in direct contact of it or indirectly get in touch of the contaminated hospital waste consisting infectious pathogens became seriously ill. In one hand this process emits greenhouse gases into the environment and in other hand it causes serious health problems and diseases.

Incineration is another process used for hospital waste disposal in different countries and in different hospitals. Hospital waste is combusted into a closed chamber in presence of oxygen. The temperature is about 700–900°C. Waste materials are put into the closed chamber where through an ignition system it is combusted in presence of oxygen. The problem associated with it is the formation of extremely toxins like dioxin and furan at the final outlet. The temperature is not so high as to remove dioxin and furan completely from the combustion of waste materials (Nema and Ganeshprasad, 2002). Besides this, the final gas outlet consists of CO₂, CO, SO₂, NO₂, NO, CH₄, hydrocarbons, water vapor etc (Rajor *et al.*, 2012; Gidarakos *et al.*, 2009). Produced CO₂, CH₄, SO₂, N₂O act as greenhouse gases and are apparently responsible for global warming (Javied *et al.*, 2008). So at one side incineration can't be a great solution for complete disposal of infectious bio medical waste and at another side it causes greenhouse gas emission to the atmosphere too.

Microwave disinfection process is also used to sterilize microorganisms, pathogens present at hospital waste. By using magnetrons, electromagnetic microwave is generated. Microwave is of very short wavelength and high frequency usually results higher friction and as a consequence sustainable heat is generated inside the microwave chamber. Waste materials put inside the microwave chamber is disinfected at a temperature range of 95–100°C (Diaz *et al.*, 2005). However volume of waste remains same here without having much change at the composition of waste. Microwave disinfection can be used for sterilization of infectious pathogens generated through medical treatment but this process is quite inappropriate towards complete disposal of HW. After the disinfection process through microwave, waste materials are either land filled or put in an incinerator for further treatment and disposal (Nema and Ganeshprasad, 2002).

Shredders are used in different health care facilities to reduce the size of produced hospital wastes. This process is helpful towards transportation of HW and reducing the size of waste, whereas it is not a process of disposal or treatment of HW.

Greenhouse Gas (GHG) Emission and its Effect on Environment

In Earth's atmosphere troposphere lies between the earth-surface and about ~16 km above it where dense air is present. In this region some gaseous molecules are present which can efficiently trap heat reflected from the earth surface. Presence of such gases beyond a certain limit causes an increase in temperature of the earth's atmosphere. The gases responsible for this are greenhouse gas and it causes Global Warming which is of a major concern in today's perspective. Adverse effect of global warming can be seen throughout the year in different parts of the globe.

Global warming and emission of greenhouse gases at the atmosphere have become a severe problem in front of the whole world. Certain steps are required to be adopted to reduce the emission of GHGs, in order to reduce the adverse impact of Global Warming. The GHGs are Carbon dioxide (CO₂), Nitrous Oxide (N₂O), Methane (CH₄), Perfluoro-carbon (PFC), Hydro-fluor-oarbon (HFC), etc. The rate of generation of such greenhouse gases is increased due to rapid industrialization and growth in population which enhances the growth in industrial, automobile, construction sectors etc. The uncontrolled direct emission of GHGs into the atmosphere by different industries, emission of unburned hydrocarbons and emission of GHGs from motor vehicles have made the situation more ridiculous.

Carbon dioxide is the most important greenhouse gas contributing about 70% of the total heat absorption of the atmospheric earth surface. Methane contributes about 20% of heat absorption of the total heat absorbed at the atmosphere.

In the last hundred years (reported from 1905 to 2005) the earth's temperature at the surface has been increased about 0.4–0.8°C, water level at sea has increased about 1–2 mm annually. As a consequence climate has been changed and eco-system has been badly affected. In 1990, developed nations as USA, EU, Russia, Australia, Canada and Japan have together contributed about 66% of total GHG emission in the world, meanwhile in 2000, these countries emission of GHG was 54% when China put a greater contribution for GHG emission (Sharma *et al.*, 2006). In the year of 1994, India's contribution was merely 3% (1228 million tons) in terms of GHG emission in atmosphere in the world in which 63% was CO₂ emission, 33% was CH₄ emission and the rest was N₂O (Sharma *et al.*, 2006; Diaz *et al.*, 2005). CO₂ emission was increased about 4.2% per annum between 1990 and 2000. In this decade GHG emission from industry and waste has been increased at a rate of 21.3% and 7.3% per annum respectively. With this pace the emission of CO₂ is expected to reach about 3000 million tons by 2020. With such increase in GHG emissions the Earth's mean temperature is estimated to raise 1.5–5.5°C by the year 2050 and the sea level may increase 0.2–1.5 m in an average within coming 50–100 years (Roop Ganesh, 2011).

Major GHG, CO₂ can stay about 500 years in the Earth's atmosphere and it contributes about 55% towards Global Warming. In the year 1990 the concentration of CO₂ was 355 ppm which has been increasing at a rate of 1.5 ppm in every year. CH₄ has a potential contribution about 18% towards Global Warming which can stay about 7–10 years in Earth's atmosphere. It traps heat even 25 times more than that of CO₂ which made it a very strong contributor for Global Warming. CFC, another GHG is responsible for depletion of Ozone layer at Stratosphere. It can stay in that atmospheric layer for about 65–100 years and traps heat about 1500–7000 times than that of CO₂. The concentration and accumulation of CFC is increasing at a rate of 0.5% every year (Roop Ganesh, 2011).

GHG Impact in Indian Perspective

It has been reported that in 2007 the emission of CO₂ from India was 1728 million tons, where major contributors were energy sector (contributing about 58%), industry (contributing about 22%), agriculture sector (contributing about 17%), and waste products (contributing about 03%). Between the year 1994 and 2007 the rate of generation of GHG per year has been observed increasing at a rate below 6% in electricity, energy, transport, residential, cement, iron and steel plant, agriculture while an increase about 7.3% in GHG emission have been seen in waste disposal. It is estimated that per capita emission of CO₂ will reach 2.1 ton in 2020 and 3.5 ton in 2030 in India (INCCA, 2010).

China holds the first position for total emission of CO₂ (Fig. 1) in the environment with 4.58 tons per capita emission whereas India being the second most populated country in the world emits 1.18 tons CO₂ per capita. USA, Russia, Germany, Japan emits significantly higher amount of per capita CO₂ than India. (Fig. 2) In terms of total emission of CO₂ China, USA, Russia, Japan, India and Germany play the leading role (Table 2).

Generation of GHGs by HW

Waste materials contribute about 3% towards the emission of greenhouse gases. Hospital waste beholds about 15% in an average of the total waste generated per day in the globe. Keeping pace with the growth in population, number of hospitals, nursing homes, health care centers are increasing day by day and as a result hospital waste generation per day is also increasing with an enormous hike. When generated Bio medical or Hospital wastes are land filled or put burned at open atmosphere greenhouse gases produce and affect a poisonous, deleterious atmosphere which renders environmental cleanliness. Land filling is a common technology for waste disposal in India which causes a serious environmental degradation and bio organic infectious waste materials produce methane gas which is considered a major greenhouse gas. Whereas autoclave, microwave disinfection and shredding procedures require additional disposal methods like incineration which cause additional adverse environmental impact

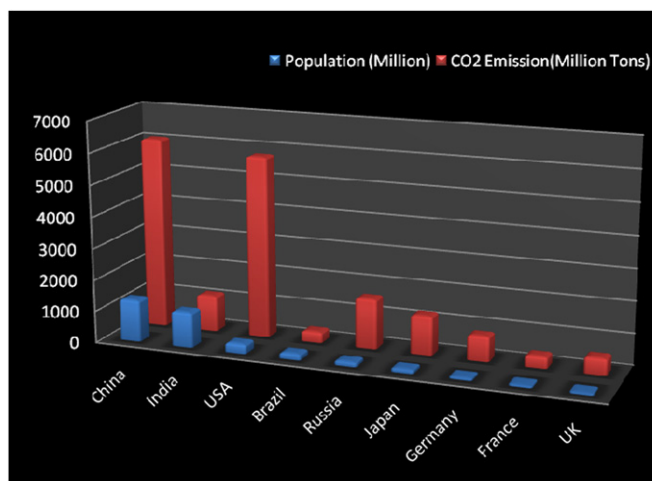


Fig. 1 Million ton CO₂ emission with respect to population. A few desirable data are collected from Statistics related to Climate Change-India 2015 vide table 2.1.1. Available at: http://www.mospi.gov.in/sites/default/files/publication_reports/climateChangeStat2015.pdf.

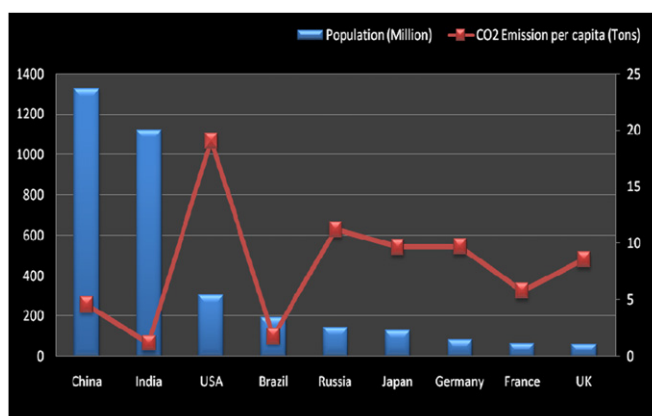


Fig. 2 Per capita CO₂ emission with respect to population. A few desirable data are collected from Statistics related to Climate Change-India 2015 vide table 2.1.1. Available at: http://www.mospi.gov.in/sites/default/files/publication_reports/climateChangeStat2015.pdf.

Table 2 Greenhouse Gas emission from different sources in India (2007)

Sl. No.	Sources	CO ₂ emission (thousand tons)	CH ₄ emission (thousand tons)	N ₂ O emission (thousand tons)
1.	Energy sector	992,837	4266	57
2.	Industrial sector	405,863	15	20
3.	Agriculture		13,768	146
4.	Land-use change and forestry	98,330		
5.	Waste	—	2516	16

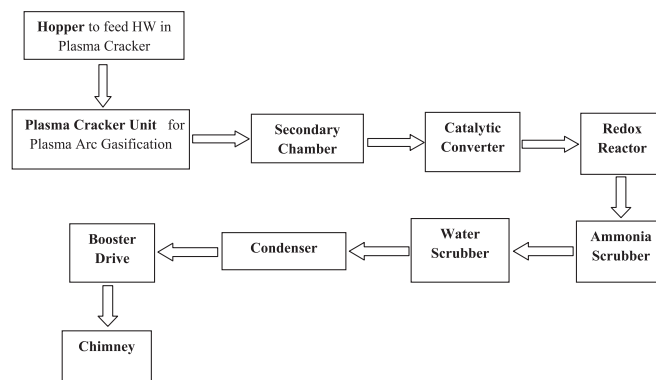
Source: Data are collected from Statistics related to Climate Change-India 2015 report vide Table 2.1.3 (b) Available at: http://www.mospi.gov.in/sites/default/files/publication_reports/climateChangeStat2015.pdf.

and make it more polluted. As greenhouse gases are also produced through incineration process it causes harmful effect on our environment and its impact is enormous with respect to global warming.

Results and Discussions

Plasma Driven Arc: A Viable Approach in HW Management and Treatment in India

Plasma is considered as the fourth state of matter, which consists of positively charged ions, electrons and neutral particles, that make a collective behavior but maintaining the whole system electrically neutral (Leal-Quir'os, 2004; Dighe *et al.*, 2001). The



Scheme 1 Schematic diagram of HW disposal plant at CSIR-CMERI. Reproduced from our own developed set up.

temperature of plasma is as high as 5000–10,000°C. Plasma arc is generated in a closed chamber utilizing high velocity high temperature fluid medium and also by generating arc between two terminals of cathode and anode electrodes. Such high temperature is capable enough to destroy pathogens, infectious hazardous molecules, contaminated hospital waste etc. completely. Moreover the advantage of plasma arc treatment is the generation of significantly less amount of toxic products like dioxin and furan which is much below the standard limit of toxic emission in the environment. Waste materials need not get segregated in plasma arc treatment process, organic materials are completely gasified and inorganic materials are turned into non leachable high density vitrified slag. Here the volume reduction of organic materials is about 99% (Nema and Ganeshprasad, 2002). Generated plasma plume is capable to produce and maintain a very high thermal atmosphere inside the plasma reactor which makes the applicability of plasma arc technology towards complete and safe disposal of HW and this phenomenon makes the difference between thermal plasma and other processes available for waste disposal.

A Small Scale Plasma Arc Driven HW Treatment Plant in Remediation of Generated HW: An Attempt Towards HW Mitigation

A mini plant of a few 10 kg/h has been set up at CSIR-CMERI, Durgapur (vide [scheme 1](#)) for disposal of Hospital Waste by utilizing high temperature electric arc plasma. It is completely a new process to treat HW in India. The waste material is fed into plasma cracker unit where three plasma torches are utilized for gasification of waste materials. The plasma torches are made of graphite cathode and tungsten impregnated carbon anode. Superheated water vapor is used as carrier fluid for generation of plasma plume. The plasma cracker unit is designed in such a manner so that plasma electrodes can also be used for plasma arc generation instead of plasma torch. It might be a rare combination of using plasma torch as well as plasma electrode together for plasma arc generation in plasma cracker unit. The waste gets gasified inside the plasma cracker unit in absence of oxygen. Thus produced gas consists of mainly a mixture of CO, H₂ which is synthetic natural gas (Syn gas). From the plasma cracker unit in the next stage the gas mixture is passed through a secondary chamber of incineration where it is combusted in presence of oxygen. Then the produced gas mixture is passed through catalytic converter and redox reactor. Here the higher hydrocarbon present in waste materials, reacting with nickel mesh present at catalytic converter becomes lower hydrocarbon i.e., if CH₄ is present in the gas mixture it becomes CO, CO₂ and H₂. Then gas passes through the redox reactor which comprises of carbon sieves. Here steam present in the gas mixture usually reacts with carbon sieves and produce CO, CO₂, and a little amount of H₂O.

After that the produced gas passes through an ammonia scrubber followed by a water scrubber. The toxic gases as HCl, SO₂ (if present at the gas mixture) are removed by simultaneous treatment from ammonia and water scrubbers. The evolved gas mixture is passed through condenser where the temperature of the gas mixture is lowered down using a water cooling fan. Finally the generated gas mixture is released to the atmosphere through a 30 m height chimney to the open air. The toxin free combusted gas is harmless to open air.

Plasma Arc Generation and Secondary Treatment in HW Plant: A Real Day Solution in Modern Age

Utilizing plasma arc technology for safe disposal of Hospital Waste (HW) is hitherto less explored R & D domain in India. Here not only the HW gets completely destroyed but also the final emissive gas mixture released in air holds lesser extent of greenhouse gases, also non toxic gases. The infectious and hazardous HW is gasified at plasma cracker unit through a star shape three numbers of transferred plasma torches. A newer and greener technology is simultaneously utilized and adopted for generation of plasma arc. Using a rarefied combination of mechanical components like catalytic converter, redox reactor, ammonia scrubber, water scrubber, condenser, secondary chamber, and chimney ~ 30 m are assembled which is an innovative approach for HW treatment. Here secondary chamber is additionally utilized for making sure that there should not be any infectious pathogens; dioxin or furan remains at the exhaust gas mixture. The gas mixture takes residence time of about 3 s to pass through secondary chamber which is of national standard protocols for waste disposal through incinerator. To be in safer side, this particular Secondary Chamber is

placed just after the primary plasma cracking chamber. In continuation catalytic converter and redox reactor are improvised within the system to produce less carbon and high calorific value synthetic natural gas ($\text{CO} + \text{H}_2$) abbreviated as syn gas.

Secondary Chamber Treatment @ Viable Route for Pathogen Destruction

Plasma electrodes and torches are operated in 30–50 V and in 200 Amp DC current supply of main source. Superheated water vapor about temperature 300–400°C, pressure at 4 kg/cm² is used as carrier gas for plasma arc generation at plasma torch. The temperature generated through plasma torch inside the plasma cracker lies in between 3000 and 6000°C which is capable enough to completely destroy the pathogens present in HW. The organic waste materials are gasified and it produces syn gas while the inorganic components (metal, ceramics, glass etc.) are melted and are stored at the bottom of the plasma cracker as a slag material which is recovered in timely basis and furthermore is utilized for producing building construction materials like bricks.

Through electric spark, ignition is performed into the secondary chamber and the temperature inside it varies between 1000°C and 1500°C. If any unburned pathogens remain there at the gas mixture, it will be completely get burned and destroyed in this secondary chamber due to its higher temperature. The hospital waste is no way directly incinerated in this chamber, but the gas mixture produced by plasma arc gasification of HW is incinerated here. So the problem associated with the direct incineration of waste material and emission of greenhouse gases are not laying here. Only the gas mixture gets combusted here. Through this primary plasma arc gasification chamber followed by incineration treatment in secondary chamber it makes sure that HW is completely destroyed.

To make sure of that there is significantly nominal emission of toxic gases from HW plant, a study has been done. Detection of toxins like dioxin and furan concentration requires sophisticated instruments like GC-MS. This cannot be afforded in online system, so the gas mixture is adsorbed primarily in porous materials then is analyzed.

The Gas Collection Procedure for Dioxin and Furan Analysis Form HW Disposal Plant

After plasma treatment of HW, produced gas is further burned inside secondary chamber. After successive burning the gas is lead through a 30 m chimney. The analysis of emitting gas mixture is highly needed from the environmental concern. In analysis, measurement of dioxin and furan contents in emitting gas mixture is very much important. As the adverse toxicity and higher possibility of generation of dioxin and furan lies in waste management plants, the analysis of gas component is having the utmost necessity.

Detection of dioxin and furan concentration requires sophisticated instruments like GC-MS. This cannot be afforded in online system, for which a porous adsorption material is required for encapsulation of the desire gases. In this case, porous resin is used for adsorption purpose. In collection process of gas sample, interventions of other impurities like soot, moisture are prevented with a specially designed sample collection system. In the above diagram (Fig. 3) the soot trapper and the sample collection box work as a suitable system in an integrated manner. Inside the box, gases are forced to be trapped inside the porous material and after saturated adsorption the material is sent for the GC-MS analysis.

In gas collection process, (vide scheme 2) the gas mixture is flown through a shoot trapper where the unwanted shoot particles are trapped. This is done so as the shoot particles may not interfere in collection of desired gas mixture through sampling box. In sampling box the gas mixture is passed through a condenser where the temperature is getting lowered down by introduction of cold water inside the condenser chamber. Through this condensation method the moisture content in gas mixture gets sorted and is being collected differently in the sampling box. Then the gas is passed through a sampling chamber, where the gas is driven through porous resin and been adsorbed in porous resin. Finally from the sampling box, it is flown through a flow meter where the flow velocity of gas is measured. The gas adsorbed in porous resin is then tested in GC-MS.

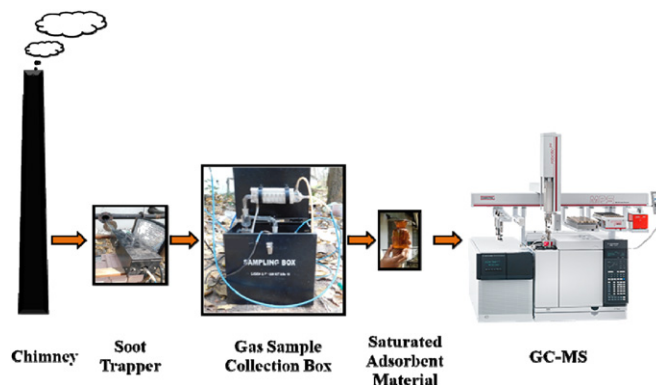
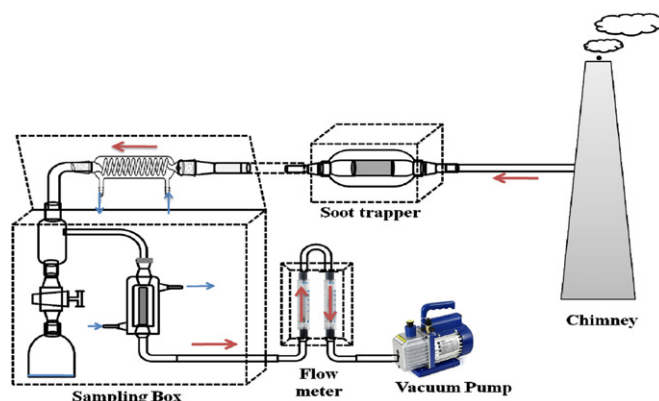


Fig. 3 Flow diagram of gas collection process. Figure is constructed based on our own working process.



Scheme 2 Schematic diagram of gas collection process from chimney. Fully schematic, not reproduced from anywhere.

Table 3 Dioxin and Furan analysis report

Sl. No.	Parameter	Results (ng.TEQ)
1.	1 2 3 4 6 7 8-Heptachlorodibenzo-p-dioxin	< 0.00024
2.	1 2 3 4 7 8-Hexachlorodibenzo-p-dioxin	< 0.0024
3.	1 2 3 7 8 9-Hexachlorodibenzo-p-dioxin	< 0.0024
4.	1 2 3 7 8-Pentachlorodibenzo-p-dioxin	< 0.024
5.	2 3 7 8-Tetrachlorodibenzo-p-dioxin	< 0.005
6.	1 2 3 6 7 8-Hexachlorodibenzo-p-dioxin	< 0.0024
7.	Octachlorodibenzo-p-dioxin	< 0.000015
8.	2 3 4 7 8-Pentachlorodibenzofuran	< 0.0072
9.	1 2 3 4 6 7 8-Heptachlorodibenzofuran	< 0.00024
10.	1 2 3 4 7 8 9-Heptachlorodibenzofuran	< 0.00024
11.	1 2 3 4 7 8-Hexachlorodibenzofuran	< 0.0024
12.	1 2 3 6 7 8-Hexachlorodibenzofuran	< 0.0024
13.	1 2 3 7 8 9-Hexachlorodibenzofuran	< 0.0024
14.	1 2 3 7 8-Pentachlorodibenzofuran	< 0.00072
15.	2 3 4 6 7 8-Hexachlorodibenzofuran	< 0.0024
16.	2 3 7 8-Tetrachlorodibenzofuran	< 0.0005
17.	Octachlorodibenzofuran	< 0.000015
	Total Dioxins & Furans	< 0.01

Note: Our own R&D result.

Table 4 Gas analysis report after being treated in Secondary Chamber

Sl. No.	Parameter	Unit of measurement	Results
1.	Carbon Monoxide(CO)	mg/m ³	<1.0
2.	Carbon dioxide (CO ₂)	%	9.2
3.	Sulphur Dioxide(SO ₂)	mg/m ³	2.0
4.	Oxides Of Nitrogen(NO _x)	mg/m ³	53.0
5.	Particulate Matter	mg/Nm ³	29.0
6.	Oxygen (O ₂)	%	11.0

Note: Our own R&D result.

Analysis of Emission of Toxin as Dioxin and Furan after Being Treated in Secondary Chamber

The analysis shows that the total presence of toxins like dioxin and furans are less than 0.01 mg.TEG (**Table 3**) in the produced gas mixture after being treated in plasma cracker unit and then in secondary chamber is below than the national standards set by Central Pollution Control Board. Also the final emission of GHGs holds lesser amount of CO, SO₂, NO_x into atmosphere (**Table 4**). Thus plasma arc driven system is the most viable recently developed HW disposal technology where the treatment plant

emits less toxic gases into atmosphere that makes it a real day solution for disposal of waste and maintain an eco-logical balance of the surrounding.

Conclusion

In summary, disposal of HW, maintaining a green and clean environment is a real challenge all over the world. In India, Central as well as different State Governments has taken several impressive and noteworthy initiatives for cleanliness, safe disposal of waste materials and environment protection. The general public awareness has been roused through campaigns like "Swatch Bharat Mission". Safe handling, safe transportation, and finally safe disposal of hospital waste by several R&D organizations, NGOs and self help group throughout India are taken care keeping in mind of the 2020 vision of waking India to give birth a clean, eco-friendly, and healthy environment for its mankind. In present days out of other noteworthy initiatives for disposal of HW, plasma arc driven technology is perhaps the most reliable and authentic technology keeping it in mind that this technology is viable for drastic volume reduction of generated HWs, lesser extent of toxin and dioxin like gas emission and above all an user-friendly green technology in a viable manner.

See also: Reducing Greenhouse Gas Emission From Waste Landfill

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Geological Storage of CO₂ to Reduce Greenhouse Gases

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Introduction

Modern society consumes tremendous amount of energy. For example, the worldwide energy consumption was 168,519 TWh or 6.07×10^{20} J in 2015 (World Energy Consumption, 2015). Moreover, energy demand in the future will keep on increasing due to the growing population, economy and standards of living. A prediction from US Energy Information Administration (EIA) indicates that by year 2035, worldwide energy consumption will reach approximately 7.8×10^{20} J, a 50% increase from year 2008 (U.S. Energy Information Administration, 2010). Prediction and analysis also suggest that the majority of this energy demand will be met by utilizing the fossil fuels. About 80%–90% of worldwide energy in 2008 was derived from the combustion of fossil fuels. Currently, utilization of fossil fuels provides the most affordable solution for the world's energy demand; however various undesirable byproducts are generated by the combustion process. One of the major by-products of combustion is the greenhouse gas carbon dioxide (CO₂), which has been shown to be directly related to increase in global mean temperature of the surface of the Earth, potentially giving rise to global warming.

Three approaches have been identified by the scientists for mitigating global warming caused by CO₂ emissions from fossil fuel consumption: (1) capture CO₂ from the emission source and permanently sequester it; (2) improve combustion efficiency and employ techniques to convert CO₂ to non-greenhouse products, and (3) switch the energy generation from greenhouse gas producing sources to renewable carbon free sources. Among all these approaches, carbon capture and geological carbon sequestration (GCS) is considered to be most promising in the near term. GCS can provide quick, efficient and economical solution to the excessive anthropogenic carbon emission without drastic change in energy generating sources and technologies (Intergovernmental Panel on Climate Change, 2005).

Various geological structures have been identified for possible deployment of geological carbon sequestration (GCS) – deep saline aquifers, depleted oil/gas reservoirs, un-mineable coal seams, etc. According to the estimates by the US Energy Information Administration (EIA), deep saline aquifers appear to be the most viable candidates since their storage potential is sufficiently large to achieve the required carbon emission reduction target. Geological surveys and pilot studies of Saline Aquifer Geological Carbon Sequestration (SAGCS) can be dated back to 1990s'. Although some promising results have been obtained, this technology is still not considered mature for large scale industrial deployment since many uncertainties about sequestration efficiency and safety still exist. Concisely, SAGCS is an activity with coupled physical and chemical phenomena, such as hydrostatics, fluid dynamics, geological physics and chemical reactions, which occur over many spatial (from nano to macro) and temporal scales (from nano to macro). Therefore, the experimental study of SAGCS at all scales is simply not feasible and is likely to be very costly. However, numerical simulations can be performed at all scales to study SAGCS. Thus, numerical simulation approach offers a promising avenue for the purpose of quick screening, evaluation, and prediction of strategies for GCS.

Over the last decade, numerical simulation programs have been developed in US, Europe and Japan to determine a priori CO₂ storage capacity of a saline aquifer and to provide risk assessment with reasonable confidence before the actual deployment of CO₂ sequestration can proceed with enormous investment. In US, TOUGH2 (Transport of Unsaturated Groundwater and Heat, version 2.0) numerical simulator has been widely used for such purpose. Numerical simulations using TOUGH2 can help in determining the influence of uncertainties in SAGCS practice such as the hydrogeological properties of the aquifer (Pruess, 1999; Pruess *et al.*, 2011). Additionally, they can provide insights into the reservoir performance and the flow transport phenomena. More advanced versions of TOUGH2 include TOUGHREACT (Xu *et al.*, 2004) and TOUGH + codes (Moridis *et al.*, 2008).

The objective of this chapter is to provide information and insights into the flow transport in SAGCS for improved understanding and estimation of reservoir performance, including its pressure response, leakage risk, and in situ CO₂ footprint by providing two examples of large scale industrial projects. It is hoped that this review of modeling and simulation studies related SAGCS should be beneficial for better understanding of in situ CO₂ migration and trapping mechanisms, as well as the CO₂ mitigation and commercialization potential of SAGCS.

Basic Ideas and Fluid Dynamics Behind GCS

The earth crust consists of layers of geological formations, which are generally quite distinct from each other in hydrogeological properties and in situ conditions. A geological reservoir forms when one layer of formation with large void space is bounded by other formations with less void space. Existing oil and gas reservoirs can all be characterized in this manner. Analogously, with proper hydrogeological properties and in situ conditions, highly concentrated CO₂ captured from large stationary emission sources can be injected into such formation and is likely to be confined underground for thousands of years without major concerns of its leakage. Following such idea, GCS process can be described as follows. CO₂ is first separated at the emission source (the process is known as carbon capture), then compressed and transported to the storage site, and finally injected into the selected

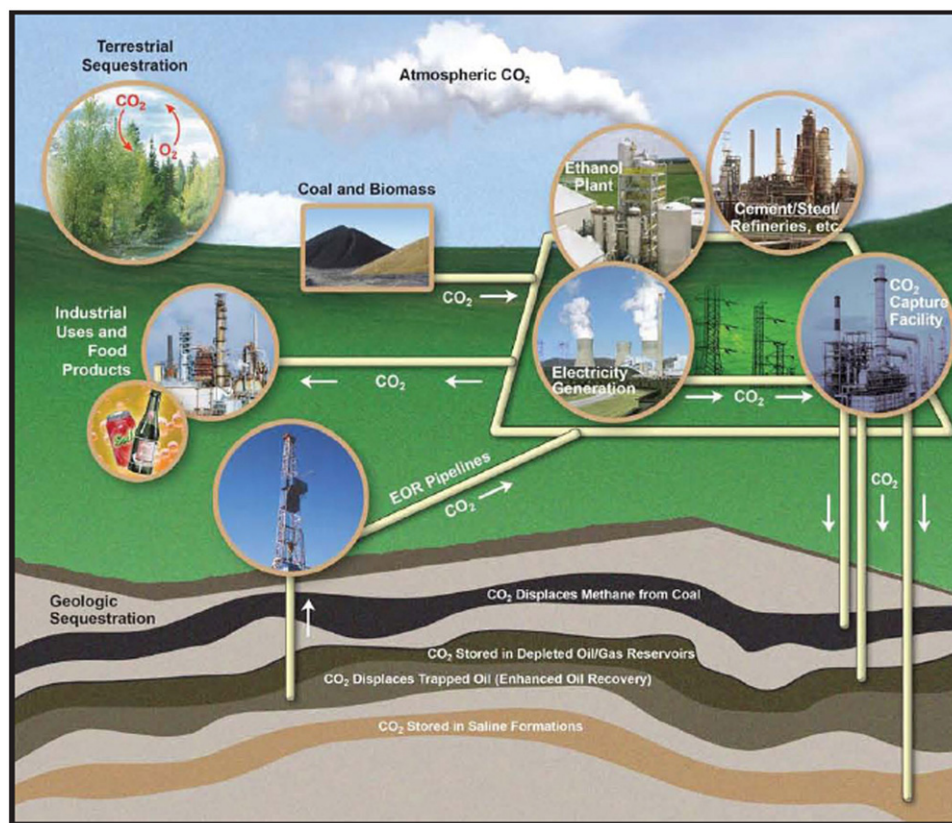


Fig. 1 Schematic of carbon capture and sequestration. Reproduced from National Mining Association, 2015. Fact Sheet on Carbon Capture and Storage. (online) Available at: http://www.nma.org/pdf/fact_sheets/ccs.pdf (accessed 15.08.18).

geological formation for permanent sequestration (the process is known as GCS). **Fig. 1** shows the schematic of GCS process (National Mining Association, 2015). Since the CO₂ capture process and devices are generally complex and highly energy consuming, large stationary CO₂ sources are more suitable for deployment of carbon capture technology and sequestration. A good example of a large stationary carbon source is the large coal-fired power plant.

In GCS, four major trapping mechanisms can be identified which are responsible for confining the injected CO₂ in the sequestration site for large time period of thousands of years (Herzog and Golomb, 2004; Johnson *et al.*, 2004). These trapping mechanisms are described below.

- **Structural and stratigraphic trapping.** The geological formations selected for GCS can be considered as a CO₂-tight geological container underground. Therefore, three structures recognized as upper, lower and lateral confining formations must be present to keep the in-situ CO₂ confined within the sequestration formation. The lateral extent of the sequestration formation is generally very large. Due to buoyancy, anticline formed by topography of the upper confining formation is usually the preferred location for structural trapping. Structural trapping occurs very quickly and is responsible for trapping the majority of in situ CO₂ during the early stage of GCS project when most of the in-situ CO₂ is still mobile. However, it provides least amount of security in sequestration due to the relatively high risk of leakage. An illustration of structural trapping is shown in **Fig. 2** (upper-left).
- **Residual trapping.** The void space of the storage formation is originally filled with formation fluid, such as impotable saline water in deep saline formations. When CO₂ is injected into the formation, pressure driven Darcy flow will occur and the original fluid in the formation is displaced as in situ CO₂ moves through the porous formation. As CO₂ continues to migrate away from the injection well, some of it is left behind in the form of disconnected droplets in the pore spaces, which is called residually trapped CO₂. These isolated residual droplets remain immobile due to the capillary pressure. Residual trapping therefore provides better immobility in sequestration; however, the amount of residually trapped CO₂ is relatively small and furthermore the development of faults/cracks in the formation may cause its release. An illustration of residual trapping is shown in **Fig. 2** (upper-right).
- **Solubility trapping.** The injected CO₂ can be considered as the solute and the original formation fluid (usually brine) as the solvent. In situ CO₂ gradually dissolves into the formation fluid at the contact surface. Because the formation fluid with dissolved CO₂ is slightly denser than the surrounding fluid, it tends to sink to the bottom of the formation over time, trapping

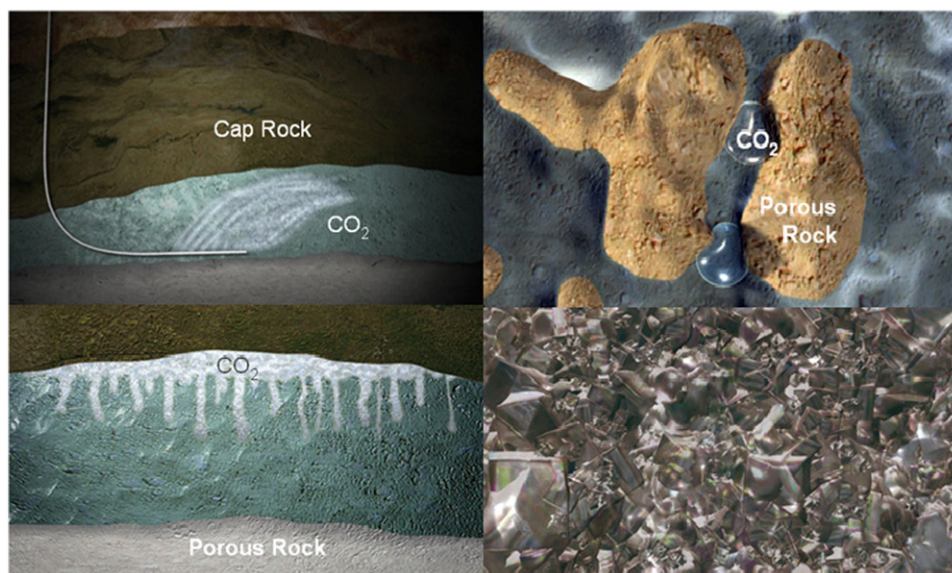


Fig. 2 Four major trapping mechanisms of GCS. Reproduced from National Mining Association, 2015. Fact Sheet on Carbon Capture and Storage. (online) Available at: http://www.nma.org/pdf/fact_sheets/ccs.pdf (accessed 15.08.18).

the dissolved CO₂ more securely. However, the dissolution of CO₂ into brine water tends to be a process that occurs very slowly. An illustration of solubility trapping is shown in Fig. 2 (lower-left).

- **Mineral trapping.** The dissolved CO₂ results in weak carbonic acid formation fluid. Over a long period (hundreds to millions of years), however, the carbonic acid fluid may react with minerals in the formation matrix and form carbonate minerals as precipitates. Once such carbonate minerals are formed, the in situ CO₂ can be considered to be sequestered with ultimate security. An illustration of mineral trapping is shown in Fig. 2 (lower-right).

Thus, the ultimate sequestration of captured CO₂ is expected to be complete after a considerably long period of time. Each of the above four trapping mechanisms dominates during different time periods in the complete GCS process, therefore having a different level of sequestration security in various time periods. Fig. 3 illustrates the dominant timeframes, storage contribution, storage security, and governing principles of various trapping mechanisms (Intergovernmental Panel on Climate Change, 2005).

The sequestered CO₂ needs to be isolated from the drinking water supply and must be prevented from releasing into the atmosphere, by effectively utilizing all four trapping mechanisms. Monitoring is needed throughout the life cycle of the GCS process to ensure sequestration security. When conducting research on GCS, the time scale of interest as well as the spatial scale of interest must be determined prior to carrying out any substantial work, since different physical principles govern the fate of in situ CO₂ for different trapping mechanisms.

Saline Aquifer Geological Carbon Sequestration (SAGCS)

Studies on GCS have suggested that various geological structures can serve as potential CO₂ storage sites. The major geological carbon sinks include the following structures: (1) conventional hydrocarbon reservoirs, (2) un-minable coal seams, (3) matured oil/gas reservoirs, and (4) deep saline formations. Among these candidates, US DOE has determined that the carbon sequestration in saline aquifers has the greatest potential considering the following facts.

- Concentrated locations of major sources of CO₂ (such as power plants) are close to the existing saline aquifers in US.
- Geological survey has confirmed vast geological distribution of deep saline formations possibly suitable for GCS in US and Canada.
- Preliminary estimates have suggested large storage capacity of the existing deep saline formations. The US DOE estimates an aggregate storage capacity of approximately 919–3378 billion metric tons of CO₂ for SAGCS in US, which accounts for 80%–90% of US overall GCS potential (U.S. Department of Energy, Office of Fossil Energy, 2008).
- Since most of the saline formations are located deep underground, i.e., at least 800 m below the sea level, they provide great potential for secured long-term sequestration.
- Many surveys, research projects and commercial projects have already been conducted for SAGCS, making it attractive for further research and technical contributions.

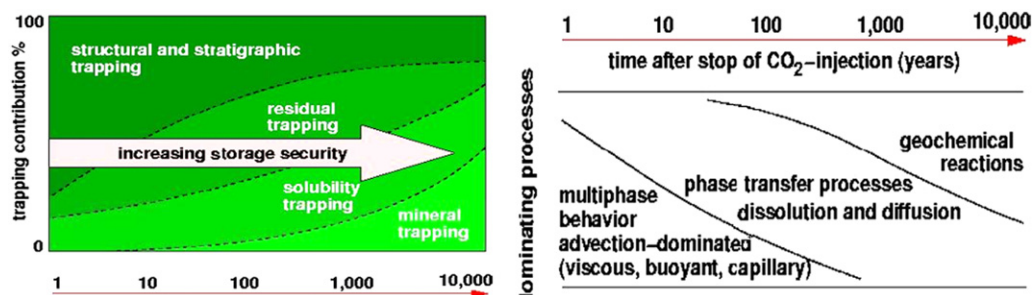


Fig. 3 Trapping mechanisms and their dominant timeframes a, storage contribution a, storage security and governing principles. Reproduced from Intergovernmental Panel on Climate Change, 2005. IPCC Special Report on Carbon Dioxide Capture and Storage. Cambridge: Cambridge University Press.

Numerical Simulations of SAGCS

The large spatial extent of the order of kilometers and time duration of the order of centuries for CO₂ plume migration after injection makes the study of SAGCS very difficult at these large spatial and temporal macro-scales by using the laboratory scale experiments which can be conducted only on relatively small spatial and temporal scales varying from nanometers to a few meters and from nanoseconds to a few days/months. Conducting field tests in large scale formations before the actual deployment takes place can be very expensive. However numerical simulations using computation fluid dynamics (CFD) technology can be employed at industrial scale to determine the fate of injected CO₂ in a reservoir. With the development over four decades, CFD technology has now become mature and has been widely and successfully applied to various engineering problems. With the proper modeling of the storage formation and ground water transportation, CFD is capable of providing accurate enough analysis for quick estimation of reservoir performance at considerably lower cost. The governing equations of mass/energy transportation and numerical representations of the formation properties have been well explained in the TOUGH2 User's Guide (Pruess *et al.*, 2011) and are not presented here for the sake of brevity. Another important benefit of numerical simulations is that one can investigate the effect of various injection parameters such as injection rate, injection duration, and injection well orientation and displacement on CO₂ storage efficiency and plume migration in a given reservoir.

In a complex simulation like that of SAGCS, it is impractical to integrate all geophysical and geochemical effects into one single model while retaining acceptable computational efficiency. Therefore, careful examination of physical phenomenon of interest in SAGCS is essential to determine simplifications in modeling of features of interest. Celia and Nordbotten describe various spatial and temporal scales in SAGCS and the associated processes and their features as shown in Figs. 4 and 5 (Celia and Nordbotten, 2001, 2009).

Additional advantage of numerical simulations is that they make it possible to perform optimization studies of various injection parameters for achieving the highest possible storage efficiency and minimum plume migration.

Some Examples of Simulations of GCS in Large Scale Saline Aquifers

The accurate large-scale simulations of existing (completed/continuing) SAGCS projects for identified known aquifers are crucial to create confidence in the future deployment of SAGCS projects. Although detailed history-matching simulations of existing SAGCS projects are challenging due to various uncertainties, e.g., in the reservoir topography and hydrogeology, the simulations can still provide informative insights in several aspects of SAGCS, such as the variance in multiphase flow properties, integrity of the geological seals, and the mechanism of CO₂ trapping. Such insights are essential for better understanding of the nature of SAGCS and its best practices for deployment. Detailed history-matching simulations have always been an important part in the SAGCS research activity. In the following two sections "SAGCS Simulation for Mt. Simon Formation" and "SAGCS Simulation for Utsira Formation", SAGCS simulations for two large scale industrial GCS projects are provided (Zhang, 2013)

SAGCS Simulation for Mt. Simon Formation

Located at Illinois basin, Mt. Simon sandstone formation is a huge saline aquifer that covers most of Illinois, southwestern Indiana, southern Ohio, and western Kentucky. The estimated storage capacity of Mt. Simon formation ranges from 27,000 to 109,000 million tons of CO₂ (Leetaru *et al.*, 2008; Barnes *et al.*, 2009). Midwest Geological Sequestration Consortium (MGSC) is the regional consortium conducting studies of the possibility of large scale GCS throughout the Illinois basin (Midwest Regional Carbon Sequestration Partnership, 2011). Decatur GCS Project and FutureGen 2.0 Project are two most well-known SAGCS projects being currently carried out at Mt. Simon formation.

The depth of Mt. Simon formation varies significantly throughout its coverage (Leetaru *et al.*, 2008; Barnes *et al.*, 2009). In the southern part, it reaches as deep as 4300 m below the mean sea level (MSL); while it increases to 80 m below the MSL in the north.

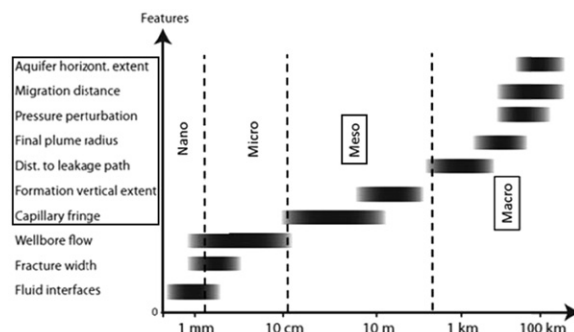


Fig. 4 Spatial scale of different processes and features for GCS. Reproduced from Celia, M., Nordbotten, J., 2001. How simple can we make models for CO₂ injection, migration, and leakage? *Energy Procedia* 4, 3857–3864. Celia, M., Nordbotten, J., 2009. Practical modeling approaches for geological storage of carbon dioxide. *Underground Water* 47(5), 627–638.

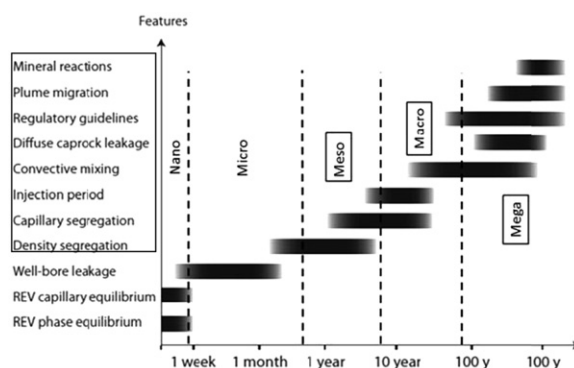


Fig. 5 Time scale of different processes and features for GCS. Reproduced from Celia, M., Nordbotten, J., 2001. How simple can we make models for CO₂ injection, migration, and leakage? *Energy Procedia* 4, 3857–3864. Celia, M., Nordbotten, J., 2009. Practical modeling approaches for geological storage of carbon dioxide. *Underground Water* 47(5), 627–638.

Consequently, a south-north geological slope of approximately 8 m/km has been estimated. The thickness of Mt. Simon formation also changes significantly. A maximum thickness of 800 m in the north has been measured while it diminishes to zero in the further south. Furthermore, the variance in topography and analysis of rock samples has suggested strong anisotropy in the formation's hydrogeological properties, with porosity ranging from 0.062 to 0.2 and permeability ranging from 5 mDarcy to 1000 mDarcy. Low permeable Eau Claire shale which sits above the Mt. Simon formation serves as the caprock. Except for some small regions near Mississippi river, Eau Claire shale is considerably thick (more than 90 m) throughout most of the Illinois basin. The security of SAGCS over Mt. Simon formation is therefore assured by the continuous coverage of Eau Claire shale. Precambrian granite formation stretches beneath Mt. Simon saline aquifer.

Recent geological survey has suggested an area in the center of the Mt. Simon formation to be the core injection area – an area in which future storage sites are likely to be located. This core injection area is indicated as the area compressed by white boundary in [Fig. 6](#), along with the elevation information of Mt. Simon formation. As can be seen from [Fig. 6](#), both ADM project and FutureGen 2.0 project are located in the core injection area.

Mt. Simon sandstone is a typical stratified saline formation. According to the geological survey, strong anisotropy in porosity, permeability, and capillary pressure exists through the entire depth of the formation. Based on variance of porosity, Mt. Simon formation can be distinguished as four subunits, namely an upper unit with sandstone and shale tidally influenced and deposited, a middle unit with relatively clean sandstone, an Arkosic unit with highly porous and permeable sandstone, and a lower unit with decreased porosity and permeability. The high porosity and permeability of Arkosic unit makes it an ideal candidate for the injection to take place. When modeling, these four subunits of Mt. Simon are further divided into 24 layers, each of which has a layer-averaged porosity and permeability value ([Leetaru et al., 2008](#); [Zhou et al., 2010](#)). With the consideration of data availability, a candidate site for future sequestration project, the Weaber-Horn #1 well (WH #1 well shown as the red dot in [Fig. 6](#)), has been chosen in the simulation study. The detailed well log of WH #1 is summarized in [Table 1](#) ([Midwest Regional Carbon Sequestration Partnership, 2011](#)). It is important to model the anisotropy of hydrogeological properties as accurately as possible to capture its effect on in situ CO₂ transport. It should be noted that the lower unit of Mt. Simon formation is not considered in the modeling due to its absence near WH #1 well. Both Eau Claire shale and Precambrian granite are modeled as impermeable formations.

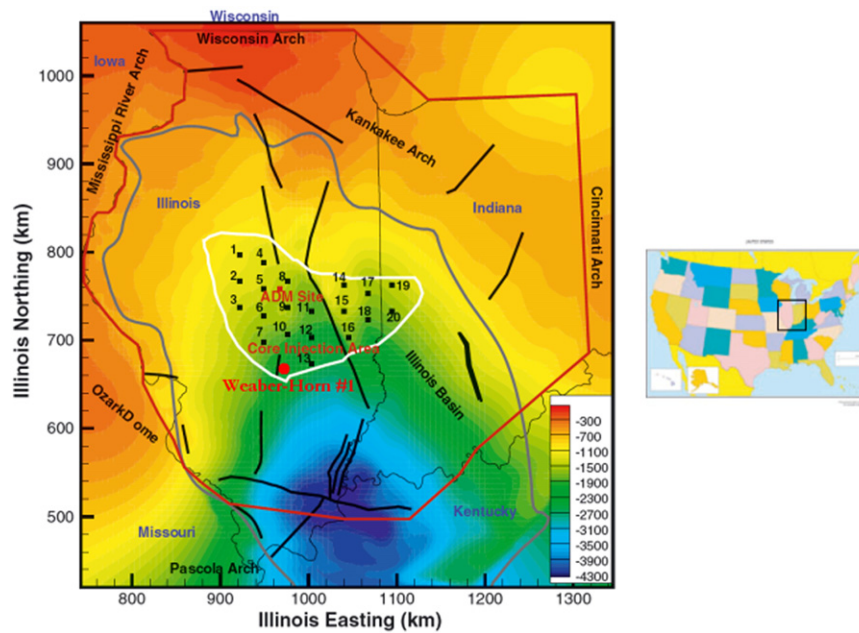


Fig. 6 Core injection area and elevation of Mt. Simon Sandstone.

Table 1 Porosity, permeability, and characteristic capillary pressure of the 24 layers of Mt. Simon at injection site WH #1

Sub-unit	Sub-layer	Layer depth (m)	Mean porosity	Mean permeability (mDarcy)	Characteristic capillary pressure (bar)
Upper Unit	1	2140–2150	0.061	5	0.37
	2	2150–2182	0.109	300	0.06
	3	2182–2197	0.074	10	0.28
	4	2197–2203	0.083	3.6	0.4875
	5	2203–2230	0.195	110	0.1
	6	2230–2232	0.071	1.1	0.8
	7	2232–2280	0.13	210	0.083
Middle Unit	8	2280–2322	0.083	5.4	0.4125
	9	2322–2331	0.24	150	0.0875
	10	2331–2340	0.088	8	0.35
	11	2340–2350	0.156	800	0.095
	12	2350–2370	0.25	80	0.125
	13	2370–2378	0.163	900	0.095
	14	2378–2385	0.195	105	0.1007
	15	2385–2399	0.163	800	0.05
	16	2399–2406	0.136	72	0.1167
	17	2406–2412	0.156	700	0.05
	18	2412–2424	0.129	160	0.09
	19	2424–2430	0.161	850	0.05
	20	2430–2462	0.128	60	0.15
Arkosic Unit	21	2462–2500	0.202	1000	0.05
	22	2500–2502	0.14	190	0.09
	23	2502–2537	0.151	1000	0.04

Note: Midwest Regional Carbon Sequestration Partnership, 2011. CO₂ Injection Test in the Cambrian-Age Mt. Simon Formation, Final Report. 'Battelle, Columbus, OH'.

A cylindrical model of Mt. Simon formation is constructed. For thermal condition the model uses calculated values with a thermal gradient of 9.2°C/km. The reservoir pressure is assumed to be hydrostatic pressure with a gradient of about 10.8 MPa/km from the ground surface. Salinity is assumed to increase with the depth, starting from 235 mg/L at 450 m below ground surface with a gradient of 12.8 mg/L per meter in depth. A north-south geological slope of 8 m/km is also considered in the modeling. "No-flux" boundary condition is applied at top and bottom of the model, representing the impermeable upper and lower bounding formations. "Fixed-state" boundary condition is imposed at the lateral boundary to represent an essentially "open" reservoir. The permeability and porosity of the 24 sublayers can be noted in Fig. 7.

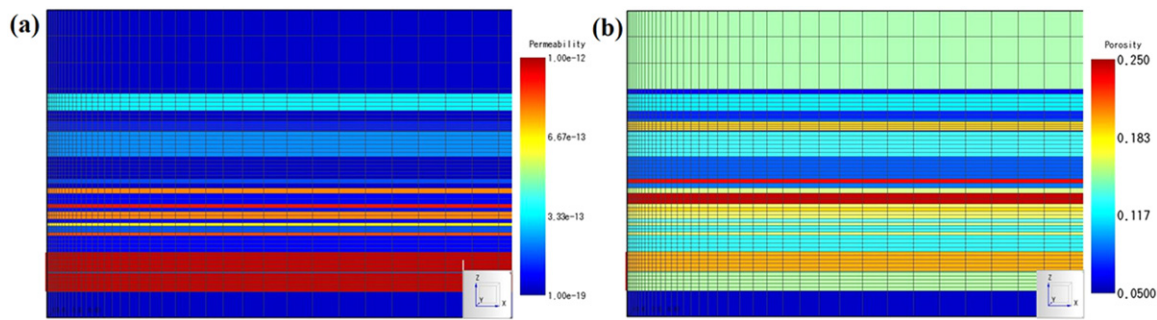


Fig. 7 (a) Permeability, (b) porosity and computational mesh of the 24 sub-layers of the Mt1 well.

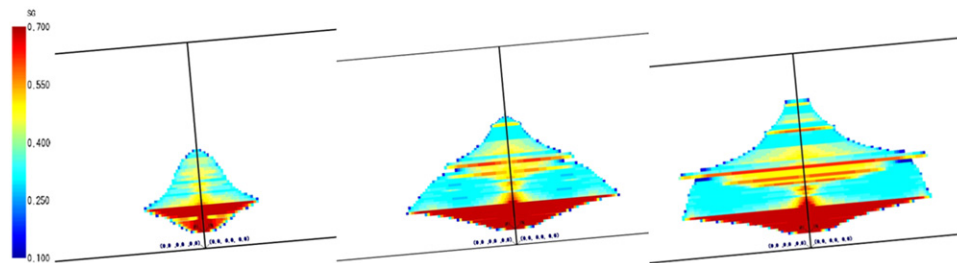


Fig. 8 Saturation of gaseous CO₂ at (a) 5th, (b) 25th, and (c) 50th year of injection.

Due to the relatively high porosity and permeability, CO₂ injection is assigned at the bottom of Arkosic unit (bottom three sub-layers). The injection rate is assigned to be 5 million tons per year and injection lasts for 50 years. CO₂ footprint at 5th year, 25th year, and 50th year since the beginning of injection is examined. **Fig. 8** shows the saturation of gaseous CO₂ at (a) 5th (b) 25th and (c) 50th year of injection.

As can be seen in **Fig. 8**, CO₂ plume evolves with a complex spatial pattern during the 50 years of injection. Within the Arkosic unit where the injector is located, extensive lateral migration with relatively higher concentration of gaseous CO₂ can be observed. In the overlying sub-layers, however, strong secondary sealing effect that retards the vertical migration of gaseous CO₂ is observed as the pyramid-shaped subplume. Detailed analysis of secondary sealing effect is made as follows. As shown in **Fig. 8**, the injected CO₂ migrates laterally away from the injector within the highly permeable Arkosic unit in the first 5 years since the beginning of injection. Simultaneously, buoyancy also leads to upward movement of CO₂ until it encounters the immediately overlying low permeability sublayer (sublayer #20). The low permeability of sublayer #20 directly results into higher capillary pressure experienced by mobile CO₂, and thus stronger vertical pressure gradient is required for mobile CO₂ to penetrate sublayer #20. When the capillary pressure is greater than the phase pressure of CO₂, sublayer #20 appears to be “impermeable” to the underlying CO₂ plume. Consequently, gaseous CO₂ accumulates under this layer and continues spreading out laterally, finally reaching a maximum extent of approximately 3000 m. Meanwhile, the increased CO₂ column under sublayer #20 brings up its phase pressure. Once the phase pressure of CO₂ exceeds the entry pressure of the sublayer #20, mobile CO₂ breaks the capillary barrier of its overlying layer and starts to penetrate it. Such accumulation-penetration-breakthrough behavior of gaseous CO₂ occurs each time the upward migrating CO₂ encounters an overlying sublayer with lower permeability. Because the high capillary entry pressure of the overlying layer temporarily prevents CO₂ migrating upwards, such phenomenon is identified as secondary sealing effect. As can be seen from **Fig. 8**, secondary sealing effect is a very effective means to retard the upward migration of in situ CO₂. Its contribution makes gaseous CO₂ barely reach the Eau Clair shale even after 50 years of injection.

SAGCS Simulation for Utsira Formation

The Sleipner project near the Norwegian coast at North Sea is probably the most prestigious, important and successful SAGCS demonstration so far. It has the most complete topographic description, industrial-scale injection amount, and long-term monitoring data. Nevertheless, great uncertainties still exist for accurate reservoir-scale simulation of the Sleipner SAGCS project. Simulation studies of this project can provide helpful insights in understanding the transport behavior of in situ CO₂ and the reservoir performance.

Starting from 1996, the Sleipner field in the North Sea has been the host of the world’s first commercial SAGCS project. CO₂ is captured from the gas mixture produced from a nearby deeper natural gas reservoir. Until today, approximately 1 million tons of supercritical CO₂ has been sequestered annually. Utsira saline aquifer is the target formation for permanent carbon sequestration for the Sleipner SAGCS project. Utsira formation is located at a depth of 800–1100 m from the seabed with thickness of about

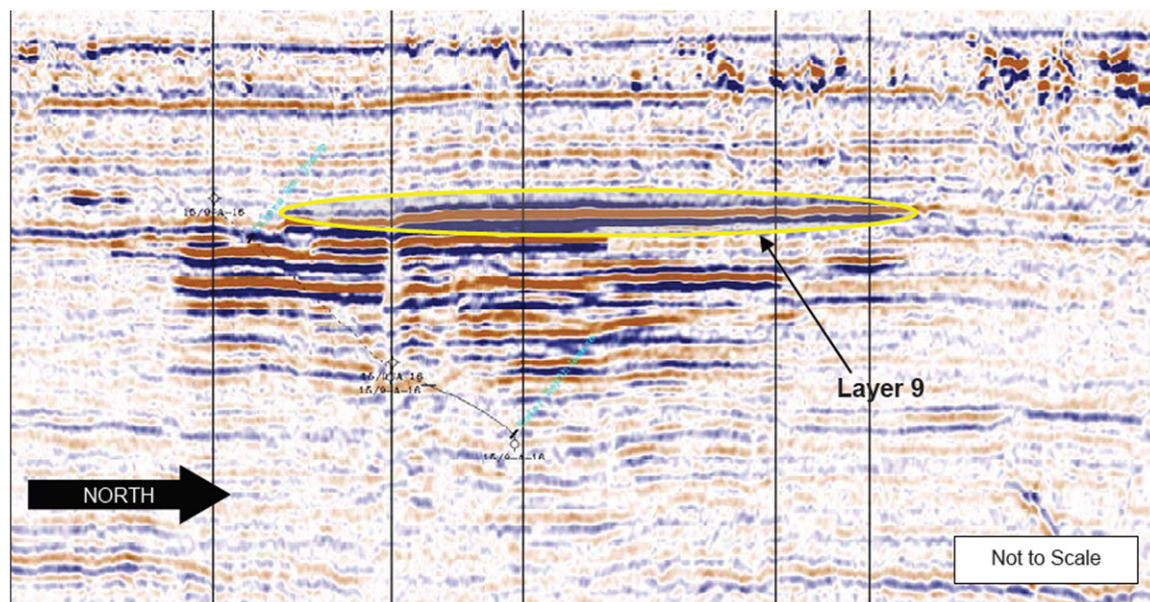


Fig. 9 Seismic image of Utsira formation after 9-years of injection, S–N cross-section. Reproduced from Leetaru, H., Frailey, S., Damico, J., *et al.*, 2008. Developing a geological model for the phase III (ADM) saline sequestration validation site. In: Proceedings of the 7th Annual Conference on Carbon Capture and Sequestration.

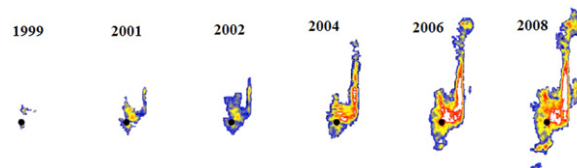


Fig. 10 Amplitude maps of Layer 9 from 1999 to 2008. Reproduced from Singh, V., Cavanagh, A., Hansen, H., *et al.*, 2010. Reservoir modeling of CO₂ plume behavior calibrated against monitoring data from Sleipner, Norway. In: Proceedings of the SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers.

200–250 m. The injection site is located at the southern portion of Utsira formation. A 250–330 m thick shale layer known as the Nordland Formation serves as the caprock, and core testing has suggested its potential of bearing CO₂ column of at least 100 m but perhaps up to 400 m (depending on the in situ conditions). It is estimated that Utsira formation has permeability of about 1 Darcy – 8 Darcy, porosity of about 0.35–0.4, and temperature of about 34–37°C. It is also estimated that the reservoir bears hydrostatic pressure from its overburden formations. Similar to Mt. Simon formation, Utsira formation is also highly stratified, consisting of sublayers with high-permeability sandstone and low-permeability shale. Therefore, it is expected that secondary sealing effect will occur. Fig. 9 shows a 2-D seismic image taken in 2008 revealing CO₂ plume in Utsira formation. Multiple layers can be distinctly identified from the seismic image.

Here we describe a model of Utsira formation which only considers a total area of 48 km² of detailed topmost sandstone layer (marked as Layer #9 in Fig. 9). Layer #9 is of particular interest regarding the safety of this sequestration project, as it is the layer within which highest concentration of gaseous CO₂ exists and most significant plume migration occurs. Detailed topography of Layer #9 makes it a complicated 3D model as shown in Fig. 10. The 3D Layer #9 model is considered to investigate the effect of actual topography on in situ CO₂ migration, while avoiding intensive computational effort associated with full 3D modeling and simulation of the entire Utsira formation. Seismic survey has shown striking growth of CO₂ accumulation in Layer #9 between 1999 and 2006 as shown in Fig. 10 (Singh *et al.*, 2010).

The black dot in Fig. 10 marks the location of the injection well, which is roughly 200 m under Layer #9. Two distinct local CO₂ accumulations appeared after about three years of injection (recall that injection began in 1996), indicating CO₂ began to accumulate under the caprock. However, CO₂ migration in Layer #9 was not symmetric due to the topography of the caprock. The northward migration of initially impacted CO₂, seen as the “body” of the plume in Fig. 10, implies a local topographic dome; a prominent north-tending migration, seen as the “finger” of the plume in Fig. 10. It implies the spill of local structurally trapped CO₂ along a north-tending topographic ridge. CO₂ migration along the north-tending ridge is rather fast at about 1 m/day between 2001 and 2004 (Chadwick and Noy, 2010).

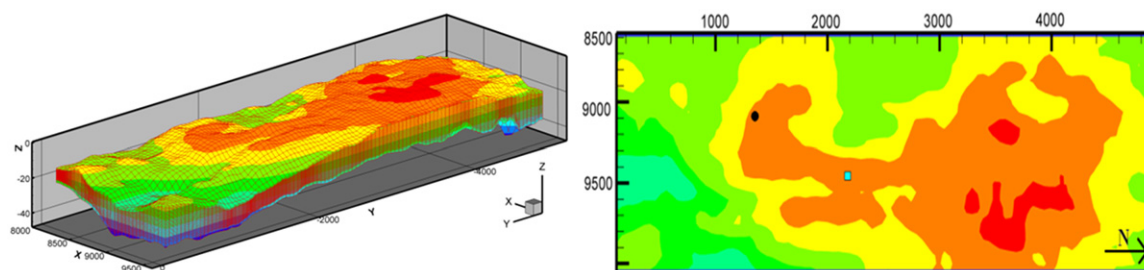


Fig. 11 3D overview and plan-view of the 3D Layer 9 model of Utsira indicating feeder locations, black dot – main feeder, cyan square – secondary feeder.

Table 2 Hydrogeological properties of the Utsira Layer #9 model

Temperature	33°C
Pressure	8.6 MPa
Total Utsira formation area	26,100 km ²
Total Utsira formation Thickness	50–300 m
Layer#9 area	1600 m × 4900 m
Layer#9 thickness	3.5–26.3 m
Shale permeability	W–E: 0.001 mDarcy, N–S: 0.001 mDarcy, Vertical: 0.0001 mDarcy
Mudstone permeability	W–E: 2 Darcy, N–S: 10 Darcy, Vertical: 200 mDarcy
Utsira porosity (shale/mudstone)	35.7%
Residual CO ₂ saturation	0.02
Residual brine saturation	0.11
Relative permeability type	Corey/van Genuchten–Muller
Capillary pressure	None
Porewater salinity	3.3%
North–South geological slope	8.2 m/km, 5.8 m/km
CO ₂ feeder location	Main feeder: W–E: 516 m, N–S: 1210 m, bottom mudstone Secondary feeder: W–E: 925 m, N–S: 2250 m, bottom mudstone

In order to examine the plume evolution within the topmost layer more closely, a 3D model of Utsira Layer #9 is created with detailed topography. It should be noted that only Layer #9, not the entire depth, is modeled because of the following considerations. To ensure the accurate capture of topographic effect on plume shaping, computational domain with considerable fine mesh resolution has to be modeled based on geological survey data. The computational effort and thus the feasibility of highly detailed model of the entire Utsira formation is very intensive and time consuming. Secondly, CO₂ has to breakthrough several layers of relatively low permeability shale prior to reaching the topmost layer. While it is difficult to quantify the breakthrough of gaseous CO₂, the quantification of CO₂ feeding into the topmost layer (Layer #9) is rather reliable. Therefore, a model of only the topmost layer (Layer #9) could provide an ideal platform to investigate the effect of various parameters such as topography on the shaping of CO₂ plume, as well as it could be used for optimization purpose to achieve high efficiency sequestration while maintaining an affordable computational effort and cost.

A reservoir model with dimension of 1600 m × 4900 m with varying thickness is constructed. It covers the portion of Utsira formation where the plume, shown in Fig. 11, resides. As mentioned earlier, the topography of this portion of Utsira formation is accurately modeled based on seismic geological survey data provided by Zhu and Lu of the University of Indiana with 50 m × 50 m mesh resolution (Zhu and Lu, 2012). Because only Layer #9 is modeled, the thickness of the computational domain varies from 3.5 to 26.3 m with an average thickness of 11.3 m. However to accurately capture the accumulation and upward and lateral movement of CO₂, 37 layers are used along the thickness. The topmost layer and the bottom two layers are designated to represent the low permeability shale, while the 34 layers in the middle are assigned the properties of mudstone. In the 3D Layer #9 model, permeability anisotropy is considered with west-east permeability of 2 Darcy, north-south permeability of 10 Darcy, and vertical permeability of 200 mDarcy. 3D overview of the Layer #9 model is shown in Fig. 11.

Table 2 summarizes the hydrogeological properties of the Layer #9 model.

It should be noted that in the 3D Layer #9 model, the source of CO₂ is identified as “feeder” but not “injector” to emphasize that CO₂ is supplied from the lower aquifer through leakage pathways rather than by direct injection. Since the actual CO₂ injector is located at about 200 m under Layer #9, information of injection rate recorded at the injector is not applicable for the CO₂ feeders in Layer #9 model. To determine the CO₂ feeding rate to Layer #9, seismic surveys of CO₂ distribution are used to obtain its volume under in situ conditions, and then converted to mass flow rate. Information of CO₂ accumulative mass provided by Zhu and Lu is summarized in Table 3 (Zhu and Lu, 2012).

Table 3 Accumulative CO₂ mass in Layer #9, 1999–2008

Year	Accumulative mass (kg)	Yearly feeding mass (kg)	Feeding rate (kg/s)
1999	0.00	0.00	0.00
2000	1.82×10^7	1.82×10^7	0.577
2001	5.52×10^7	3.70×10^7	1.17
2002	9.49×10^7	3.97×10^7	1.26
2003	1.45×10^8	5.01×10^7	1.59
2004	2.13×10^8	6.80×10^7	2.16
2005	3.07×10^8	9.40×10^7	2.98
2006	4.34×10^8	1.27×10^8	4.03
2007	6.03×10^8	1.69×10^8	5.36
2008	8.20×10^8	2.17×10^8	6.88

Note: Zhu, C., Lu, P., 2012. Indiana University (Private communication).

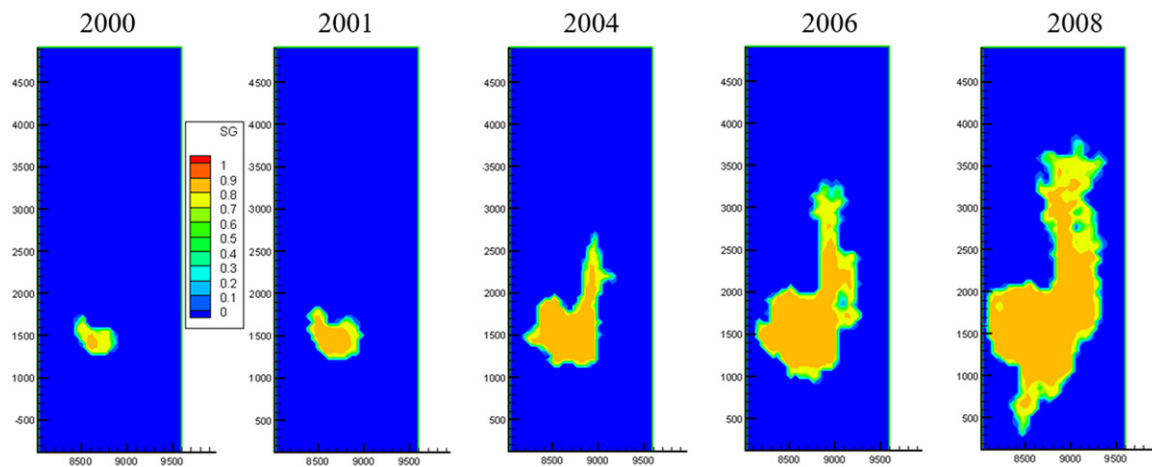
**Fig. 12** Simulated CO₂ migration in Layer 9 of Utsira formation, 2000–2008.

Table 3 gives the CO₂ accumulation in Layer #9 from 1999 to 2008. It can be seen that CO₂ feeding rate to Layer #9 keeps on increasing for the recorded nine years. Recalling the analysis of secondary sealing effect given for the previous cases, it is the pressure gradient between the gaseous CO₂ phase pressure at lower aquifer and the capillary pressure of the overlying shale layer that determines the breakthrough of CO₂ and its flow rate. When breakthrough first occurs, the pressure gradient just breaks the equilibrium state, resulting in relatively low breakthrough mass flux to Layer #9. However, as more CO₂ accumulates, the pressure gradient gradually increases and leads to increasing breakthrough mass flux as depicted in **Table 3**. A nine-year average feeding rate of about 2.89 kg/s can be obtained from **Table 3**. Both the nine-year average value and the values in **Table 3** have been considered in the simulations.

The significant north-trending plume finger is rather perplexing for regular pressure-gradient driven Darcy flow. Analysis suggests three possible explanations to the cause of prominent north-trending CO₂ fingering along the ridge: (1) significantly higher permeability applied to the ridge, (2) existence of north-south geological slope which enhances the buoyancy-driven migration along the ridge, and (3) existence of a secondary (or even multiple) CO₂ pathways under the ridge. The hypothesis of significantly higher permeability at the ridge can be easily ruled out since no such evidence is obtained from the geological survey. It is still under debate whether geological slope should be considered when analyzing the CO₂ migration in Utsira formation. Chadwick and Noy's work has suggested two possible values of geological slope based on the seismic images of the cross-section of the Utsira formation, which are 8.2 m/km and 5.8 m/km (Chadwick and Noy, 2010).

The simulation time is set at nine years, which corresponds to the injection period of 1999–2008. CO₂ plume migration at the topmost layer is examined for each year. Considering all the uncertainties mentioned above, a total of nine simulations are performed until a good history-matching is obtained, as shown in **Fig. 12**.

As can be seen by history matching, the 3D detailed Utsira Layer #9 model has generated satisfactory simulation results. In summary, five major conclusions can be made as follows. First, the simulations show that the permeability anisotropy should be accurately modeled. Vertical-to-horizontal anisotropy close to 10:1 is needed to accurately capture the upward migration of CO₂. Horizontal anisotropy of 2:10 is needed to capture the northern spill of CO₂ into the north-trending ridge. Secondly, a secondary feeder is likely to exist directly under the north-trending ridge to generate sufficient plume migration along the ridge. It suggests multiple pathways for CO₂ breakthrough from the lower aquifer structure. Thirdly, the fact that injection gas being CO₂–methane mixture is very important in modeling since the presence of 2% methane enhances the buoyancy. Fourthly, it is critical that time-

dependent feeding of CO₂ is modeled. This is consistent with the behavior of CO₂ path flow breaking the capillary pressure barrier, as noted before for the secondary-sealing effect in case of Mt. Simon formation. And finally, simulation results suggest strong mobility of gaseous CO₂ under the caprock (shale) without major leakage, implying that the caprock serves quite well as the non-permeable CO₂ barrier while exerting little resistance for the lateral flow of CO₂ underneath.

The simulation studies of the two actual large scale identified deep saline aquifers provide important insights and best practices for obtaining accurate simulations of GCS using TOUGH2.

Conclusion

In this chapter, first the multi-phase fluid mechanics and other mechanisms relevant to geological sequestration of CO₂ are discussed including the processes and features of GCS that become important at various spatial and temporal scales. Then rest of the chapter is devoted to the modeling and simulation of saline aquifer geological carbon sequestration (SAGCS) for two large scale industrial projects, namely the Mt. Simon in Illinois and Sleipner/Utsira in Norway. The numerical simulations are based on the DOE simulator TOUGH2. The simulations show that they can provide satisfactory information about the plume migration in the formations over large spatial and time scales and therefore can be used to assess the viability of large GCS projects a priori before actual deployment. As to the recommendations for the future work in GCS, the real-life SAGCS projects such as the ADM Mt. Simon project, Sleipner project and others should be continually studied over the years as more detailed field data becomes available. In addition, optimization studies for large scale SAGCS projects should be performed for greater storage efficiency and reduced plume migration.

Acknowledgements

The author is grateful to his former graduate student Dr. Zheming Zhang who performed many of the numerical simulations reported in this paper.

See also: Biomass for CO₂ Sequestration. CO₂ Capture, Storage, and Enhanced Oil Recovery Applications. CO₂ Sequestration Using Algal Biomass and its Application as Bio Energy. Overview of CCS: A Strategy of Meeting CO₂ Emission Targets. Sustainable Carbon Di-Oxide Sequestration Using Photosynthetic Reactions

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Green and Sustainable Manufacturing of Metallic, Ceramic and Composite Materials

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Introduction

Composite materials are defined as the combination of two or more different materials to produce unique and superior materials. But now a day's composites are described as reinforced plastics. Composites are the most widely used materials due to their special characters like adaptability to different situation while combine to other materials to serve various purpose and exhibit desirable properties. There are so many composites like metal matrix composites, nano composites, fiber reinforced composites and hybrid composites commonly used in various industries. Composite materials can provide unique advantages in comparison with materials like metals, wood. The primary driver and advantage in the adoption of composites is the lightweight properties. In transportation, these light weight composites can save more fuel and improve acceleration. In sporting equipment, these materials allow for longer drives in golf, faster swings in tennis, and straighter shots in archery. In production of wind energy, if the blade weight is less, more power the turbine can produce. Besides these composites acquires more beneficial properties like: Non-corrosive, Non-conductive, Flexible, will not dent, Low maintenance, Long life, Design flexibility. Based on structures there are three main classifications of composites we have:

- (1) Particle-reinforced (large-particle and dispersion-strengthened) – These are composed of particle of one or more material is dispersed in a matrix of another material to make it strong and stable.
- (2) Fiber-reinforced (continuous (aligned) and short fibers (aligned or random) – In this case long fiber of one material is incorporated in the matrix of other material like polymer, which turns out to be extremely strong.
- (3) Structural (laminates and sandwich panels) – While there are layers of two or more different material are bonded together by sandwiching two layers of strong materials.

The most common type matrix is like polymer matrix, metal matrix and ceramic matrix composites, as are natural composites such as wood. There are so many research work has done for the production of suitable composite materials, but they are all hazardous and emitting materials, harmful for environment. Hence ecological concerns have resulted in renewed interest in natural materials and recyclability and environmental safety are becoming increasingly important issue in the case of composite production. Now our attention is focused on sustainable manufacturing of composites which may be green composites and are environment friendly.

Manufacturing is a word derived from middle French in Medieval Latin Manufactura (Manu + Factura) which means made by hand. From the very early stage ancient humans are applying different manufacturing techniques and developed gradually. But the first signs of modernization in manufacturing method were seen in the mid of sixteenth to seventeenth century. Manufacturing is a series of processes which includes selection of raw materials, production or fabrication of objects, building or constructing, assembling the parts, inspection or examination and finally dispatching, [Fig. 1](#).

Modernization is going at faster rates so as to meet the needs of human beings the Industrial sectors of many of the countries are following modern manufacturing techniques. Along with the modernization and development of techniques, human being should see that new or existing method is not harming the natural resources and is not disturbing the balance of the ecosystem. Since the natural resources are not in adequate amount, their utilization should be optimized for future generations. The use of natural sources and hence energy by the human resource is increased exponentially [Fig. 2](#).

There are so many conventional manufacturing process are there like casting, moulding, forming, machining, joining, additive manufacturing, rapid manufacturing etc. During these different modern methods of manufacturing of composites, the waste disposed are very harmful and has an enormous detrimental effect on the environment. For manufacturing of composite materials, workers have to handle very harmful heavy metals like lead, zinc, cadmium and also hazardous air pollutants including carbon materials, gaseous pollutant, benzene is released from cupola furnace, very harmful to health. For cutting purpose, fluids used such as water based – emulsions (soluble oil), chemical solutions (or synthetic fluids), mineral oils – fatty oils, composed oils, extreme pressure oils (EP). These metal working fluids can be used once and thus after the work they are thrown into water bodies, land causing hazardous pollution. Hence there should be continuous examination of pollutant levels at each and every stage of manufacturing. Now a days in any developing country a common word is being echoed in every industrial sector i.e., "Green Technology". Due to different types of production techniques there have been many greenhouse gases released into the atmosphere since 100 years. This is the main cause of the phenomena 'global warming'. And now for our sustainability, it's the time to save our planet from the effect of these harmful gases. Hence many sustainable techniques and environment-friendly operations have been standardized in every industry. Again a huge amount of energy is consumed during conventional manufacturing methods. In order to reduce that usage, industries are adopting green technologies. Green technologies are based on four R factor,

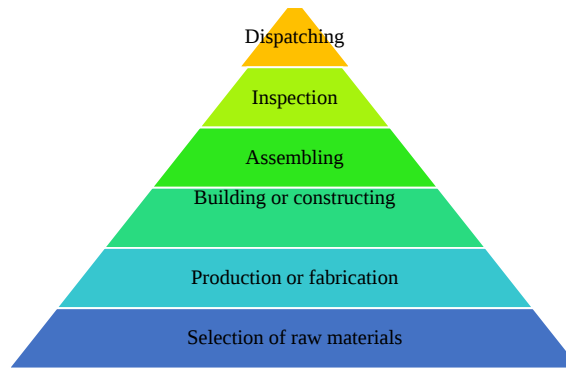


Fig. 1 Sequence of manufacturing.

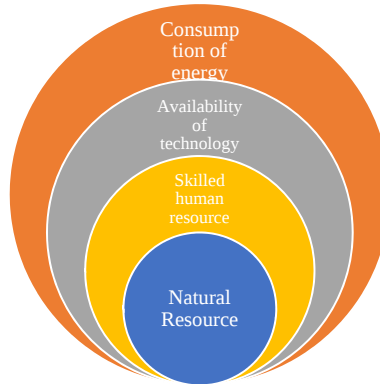


Fig. 2 Comparison between energy consumption and availability of resources.

Refuse, Reduce, Reuse and Recycle which can optimize resource consumption, reduce wastage, adopt recycling and reuse techniques, so that the cost of production can also be optimized.

There are so many different ways can be adopted for green manufacturing technologies.

Operation of Energy Audits-The important step for green sustainable manufacturing is conducting the energy audit on day to day basis for checking where energy is consumed in higher amount. After that it will be replaced with green technical equipment. As there is limited availability of fossil fuels and the global ecological balance is also being disturbed, hence the only survival strategy is to minimize the energy consumption. Hence use of green products in manufacturing, contributes towards use of less energy and production would enhance the reduction in carbon emissions.

Use of Renewable and alternative energy – Instead of using conventional power, produced by fossil fuels, the need of hour is to use renewable energy resources like solar, wind, tides, biomass etc. Many governments provide incentives and tax free production for production of power from green technologies.

Application of 3 R's (Reduce, Reuse and Recycle) –The production cost can also be reduced by recycling the waste left after manufacturing of materials.

Minimize the usage of water – There are so many industries like textile, leather and construction discharge their waste directly to the water bodies which again polluting the water and also harmful for us.

The real meaning of green technology is not only regulate the pollution or recycling process but also reduces the energy consumption and emission of harmful materials in each and every stage of manufacturing. Green Manufacturing focuses on primary goals such as minimization of emissions, effluents, accidents, use of virgin and non -renewable, energy resources, life cycle cost, product and services. The following diagram, **Fig. 3**, represents the development of an industry and hence A country or a industry said to be developed only that time when it will adopt modern green technology with highest production rates. Its development is achieved step wise.

Green Manufacture of Metal Composites

Metal matrix composites are not used widely as polymer composites but at present it generates an wide interest due to its high strength, fracture toughness and stiffness. They can withstand elevated temperature than polymer composites. While most of the metals are used as matrix for the composite, a reinforcement material should use to stabilize the composite over a range of

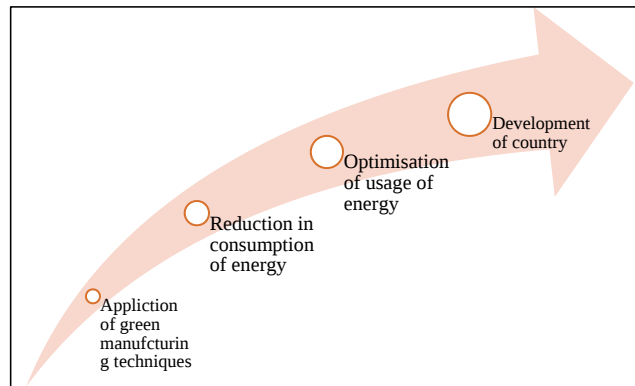


Fig. 3 Result of green manufacture.

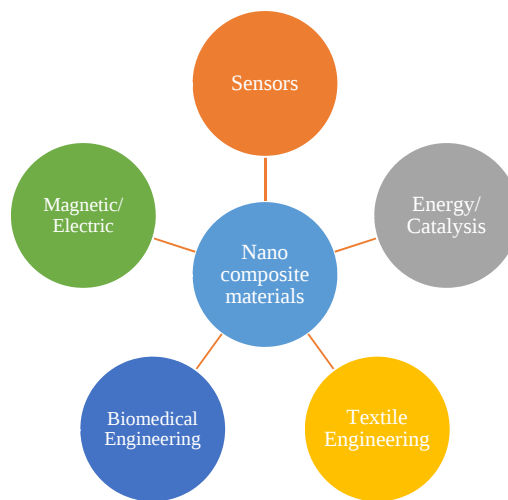


Fig. 4 Characterization of Nano composites based on application.

temperature and non-reactive also. Generally light metals are responsive for low temperature applications. For aircraft applications titanium, aluminum and magnesium are the popular matrix. High modulus reinforcements are used for the metal matrix where it has to offer high strength. The strength-to-weight ratios of resulting composites can be higher than most alloys.

The purpose of using reinforcing constituent in composites is to serve as heat resistance or conduction, corrosion resistance and also provide rigidity. A reinforcement that embellishes the matrix strength must be stronger and stiffer than the matrix and capable of changing failure mechanism to the advantage of the composite. This means that the ductility should be minimal or even nil the composite must behave as brittle as possible. As reinforcing agents fibers, fabrics particles or whiskers can be used for the metal composites. Fibers are essentially characterized by one very long axis with other two axes either often circular or near circular.

Metal Nano- Composites

Nano-composites are a new generation of improved materials, can be formed by mixing one or more different materials at the nano scale in order to control and develop new and improved structures as well as properties (Fig. 4). The term nano-composite includes a wide range of materials from three-dimensional metal matrix composites, two-dimensional lamellar composites, and nanowires of single dimension to zero-dimensional core shells.

The properties of nano-composites depend not only upon the individual components used, but also upon the morphology and the interface characteristics. As compared to individual materials, nano-composites can enrich the properties such as improved friction and abrasion resistance, fouling resistance, super hydrophobicity, super hydrophilicity, thermal energy transport, electronic and ionic transport, and liquid transport displayed for a wide range of engineering applications. As per (Freedonia, 2008), the demand for nano-composites in 2011 reached 150,000 TPA in USA. The use of nano composites will be huge by reducing the price of nano materials and increase in production. It is expected that nano-composites by 2025 will be the US \$9 billion market, with volumes nearing 5 million tons.

Multifunctional nano-composites are of great interest due to their synergy and developed properties compared to their base counterparts (Akbulut *et al.*, 2009; Gobin *et al.*, 2004; Yang and Ko, 2008). Noble metal-based systems are incorporating frequently to obtain the desired functional nano-materials. Research has been made in incorporating noble metals on semiconductor metal oxides such as TiO₂ and highly conductive nanomaterial such as CNTs using any surfactant or linkers (Jose *et al.*, 2009; Peining *et al.*, 2011). It is proved that at nano scale a vast changes of physical, chemical and biological properties of any materials occurred from their bulk counterpart because of the quantum confinement. For instance, gold and silver nanoparticles have the ability to absorb visible light at certain wavelengths, which depend on the size and shape of the nano – materials.

There are so many different methods are invented for the synthesis of nano materials like chemical, physical, and biological methods. But some these chemical or physical methods have resulted environment contamination by producing a large amount of hazardous byproducts and gases (Amato *et al.*, 2011).

Hence most of the research works are focused on Green Technology, including a clean, safe, nontoxic and eco-friendly synthesis methods, without the use of high pressure, energy, temperature, and toxic chemicals (Pallavicini *et al.*, 2010). Through the biological methods nano-materials can be synthesized from the extracts of plant, bacterial, fungal species, and so forth (Dallas *et al.*, 2011).

Nanoparticles of silver have been found to exhibit interesting antibacterial activity (Deshmukh and Composto, 2006). Recently, materials have been developed (mainly textiles) incorporating silver nanoparticles, which possess very interesting antimicrobial activity. For this unique property of Ag, the plastic containing silver can be used in medicines to reduce infections and also preventing bacteria colonization on plastic devices such as prostheses, catheters, vascular grafts, and dental materials (Damm and Munstedt, 2008). The generation and propagation of micro-organisms on plastic medium can occur under ideal temperature and humidity conditions causing irritation and infection. Hence the materials made of polymers can protect against micro-organisms in order to suppress their growth and dissemination. There are so many research work has reported the use of silver nanoparticles (AgNPs) to form composites with polymers such as polyvinyl alcohol, polypyrrole, poly-vinylidene fluoride, chitosan, and cellulose. But for the formation of polymer-silver nano-composites, it is required to control the size of the nano particles and the distribution of nano particles should be uniform (Mohan *et al.*, 2006).

Ag – Polystyrene nano composite

Green synthesis of Ag nano particles was done by using orange peel as reducing agent and then these nano particles were incorporated in polystyrene matrix forming Ag- polystyrene nano composite film.

Experimental

Green Synthesis of Silver Nanoparticles: 200mg of orange peel was taken to crush and 20 ml of toluene was added to it with continuous vigorous stirring at 600C to prepare the orange peel extract. After this the extract was centrifuged at room temperature for 5 min at 7000 rpm. In another flask 1 mmol/ml silver nitrate was dissolved in 20 ml of toluene with again vigorous stirring at the temperature of 700C for 5 min. Then 5 ml of orange peel extract was added to silver nitrate solution which changes to brown colour indicating reduction of silver ion.

Synthesis of Green AgNPs/PS Nano-composite Film: Various methods are employed to prepare antimicrobial AgNPs/PS nano-composite (Tripathi *et al.*, 2011). Here solution method is used to synthesize antimicrobial AgNPs/PS films. 2 gm of polystyrene was mixed with silver nano particles, dispersed in toluene. During the addition of polystyrene the solution was stirred vigorously and continuously at 600C. Finally the solution was cast in a glass plate and keep it at room temperature for 24 h. to evaporate the toluene. Thus nano composite film was prepared.

Characterization

Nano-composite film was characterized spectro-photometrically using X-ray diffraction, Bruker D8 Discover, the size of green synthesized AgNPs was analyzed through Zetasizer, Nano series, HT Laser, ZEN3600 (Molven Instrument, UK).

Transmission Electron Microscopy (JEM-1011, JEOL, Japan) was employed to characterize the size, shape, and morphologies of formed nano-composite at voltage of 80–100 KV, while Thermo Scientific, Nicolet 6700, FT-IR spectrophotometer was used for recording the infrared (IR) spectrum.

With the help of Energy Dispersive Spectroscopy (EDS) analysis the formation of elemental silver was confirmed. Elemental analysis on single particles was carried out by Oxford Instrument, Incax-act, equipped with Scanning Electron Microscopy using (JEOL-FE SEM, Japan).

Ag- Chitogannano – Composite

Ag nano particles are becoming significant and important to all scientist as it attributes towards biological activities such as antitumor activity, antimicrobial activity and enhance the immunity system (Gu *et al.*, 2003; Dutta *et al.*, 2011). There are so many methods are applied for producing silver nanoparticles (Ag NPs) like both physical and chemical approaches such as sono-chemical and electro-chemical methods, thermal decomposition, laser ablation, microwave irradiation, etc. (Kim *et al.*, 2005; Bae *et al.*, 2002; Zhang *et al.*, 2004). But these methods have some limitations as using toxic and hazardous chemicals, consuming high energy. So interests are grown to synthesis of Ag- nano composites by green technologies (Panigrahi *et al.*, 2005; Qian and Yang, 2005; Huang *et al.*, 2006; Pal *et al.*, 2008, 2007). Therefore, green synthesis is eco-friendly processes in chemistry, in chemical technology and engineering. These processes are becoming more popular and essential to reduce the environment pollution (Thuesombat *et al.*, 2014). In green synthesis

of these nano composites, mainly natural polymers (chitosan, etc), sugars, enzymes, microorganisms, plant extracts as reductants (e.g., lemon aqueous extract, Azadirachita indica aqueous leaf extract, kumquat aqueous extract, and capping agents are used (Mittal *et al.*, 2013; Prabhu and Poulouse, 2012; Gopinath *et al.*, 2013; Bar *et al.*, 2009; Rafique *et al.*, 2016). These natural sources are abandoned and reactions are also simple, one step, cost-effective, energy efficient, forming more stable and environment friendly composite materials (Kharissova *et al.*, 2013; Badawy and Rabea, 2011; Kong *et al.*, 2010; Ahmed and Saiqa, 2015; Benelli, 2016; Ahmed *et al.*, 2016).

Experimental

River leaf creeper extract was used for green synthesis of Chitosan- Ag nano particles with the help of microwave without using any hazardous chemicals. At low concentration of River leaf creeper extract, nano composites are produced. Moreover, the synthesized chitosan/Ag nano-composites also showed their anti-bacterial activity on E. Coli bacteria.

Fresh River leaf creeper first boiled with de-ionised water at 100°C for 10 min and filtered to obtain a juice extract from river leaf. This extract is used as reducing agent. 0.01 M 1 ml AgNO₃ solution was mixed with chitosan solution, 1.5 mg/ml of which is in 2% acetic acid solution. Then in this solution river leaf creeper extract was added for reduction of Ag metals at 70°C with constant stirring for 90 min. During the reaction the colour of the solution changes time by time. Finally the solution was centrifuged at 10,000 rpm for 15 min and washed with DI water to remove undesired products. The average particle size of the as-prepared chitosan/Ag nano-composite is ~15–41 nm.

Characterization

The absorbance spectra of particle solutions were analyzed by UV–vis spectrophotometry (UV-675; Shimadzu). Fourier transform infrared spectroscopy (FTIR) of chitosan/Ag nano-composites were done by using a Renishaw 2000 confocal Raman microscope system. The phase structure of chitosan/Ag nano-composite was obtained, using X-ray diffractometer (Rigaku Dmax-B, Japan) with Cu K α source operated at 40 kV and 100 mA. A scan rate of 0.05°–1° was used for 2 θ between 10° and 80°. The particle size and surface morphology of chitosan/Ag nano-composites were analyzed by transmission electron microscope (TEM) with a Philips Tecnai F20 G2 FEI-TEM microscope (accelerating voltage 200 kV).

Graphene based Ag nano composites

The main constituent of graphene is carbon atom and they are bonded with each other in a repeating pattern of hexagon (Grigorenko *et al.*, 2012). For this reason graphene has a wide range of application in the field of electronic, energy storage and super capacitor, batteries (fuel cells, solar cells), and bioscience/biotechnologies. Graphene-based nano-composites again shows unique properties, which are useful for various biomedical applications including drug/gene delivery, imaging, antibacterial and anti-cancer activities (Khan *et al.*, 2015a,b). The important role of graphene in the composites is acting either as a functional element or a substrate for immobilizing the other constituents such as metal likes silver, gold, zinc oxide, copper etc (Xu *et al.*, 2008). In recent years, it was investigated that (GO) based Ag nano-composites are also very useful for many applications and several methods like chemical. (Nossol *et al.*, 2014), thermal (Chen *et al.*, 2011), microwave (Hassan *et al.*, 2009), and green methods have been reported for the synthesis of GO- Ag nano composites. While GO-Ag nano composites are synthesized through chemicals reduction method, some of the chemicals such as Hydrazine (N₂H₄), Sodium borohydride (NaBH₄), Dimethyl hydrazine (C₂H₈N₂), Hydroquinone (C₆H₆O₂), Sulphuric acid (H₂SO₄), and Aluminum powder (Al), involved in the reduction and functionalization of graphene oxide, have highest number of toxicity. Hence here also Green technologies are adopted for reduction of graphene oxide. Natural reducing agents like plant extracts have been considerably exploited due to their low cost, bulk availability and biocompatibility for these metal nano-composite (Khan *et al.*, 2015a,b).

Experimental

Silver nano materials have excellent anti-microbial activity. Hence these nano materials incorporated in graphene network for packaging and bio-medical applications (Sahu *et al.*, 2015).

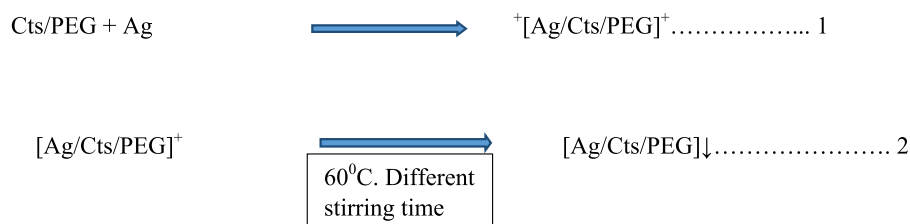
GO was prepared by the oxidation of natural graphite powder according to modified Hummers method (Chen *et al.*, 2013).

Sapodilla fruit was washed with first distilled water and peeled off manually. Then the peels were cut into very small pieces. About 10 gm of this sapodilla peels were dipped into distilled water around 1h. Thus the extract obtained, filtered for further experiment.

Another flask contained 100 ml 0.1 M solution of AgNO₃ mixed with 200 ml of 0.1 M aqueous ammonia solution to prepare 0.1 M of silver Ammonia solution. Then 1 ml of GO (0.1 mg/ml) and 20 ml of this silver ammonia solution are mixed properly with constant stirring. Next 2 ml of sapodilla peel extract was added to the mixture with stirring and treated with sunlight. Within a few seconds, the brown coloured solution changed to dark yellowish brown solution indicating the formation of the composite materials. Finally the solution was covered with aluminum foil and kept it into dark place for complete and uniform deposition of Ag nano particles on GO sheet. After that the solution was centrifuged for 10 min at 4000 rpm and the final compound was washed with distilled water again and again.

Characterization

The absorbance spectra of the prepared sample was analyzed by UV–vis spectrophotometry (UV-675; Shimadzu). Fourier transform infrared spectroscopy (FTIR) of GO/Ag nano-composites were done by using a Renishaw 2000 confocal Raman microscope



Scheme 1 Reaction mechanism for synthesis of Ag- Chitosan- polyethylene glycol nano Composites.

system characterized by UV, FT- IR, SEM and TEM spectra. The surface morphology of composite materials can observed through TEM spectra.

Ag- Chitosan- polyethylene glycol nano composites

The green synthesis method can be used to synthesize Ag- Chitosan- polyethylene glycol also. The concept of green synthesis was adopted to reduce the pollution of environment as in conventional method so many toxic reagents were used. Besides, it also utilizes a non-toxic stabilizer in forming Ag NPs (Raveendran *et al.*, 2003; Shameli *et al.*, 2010). It is reported that the exclusion of NaBH₄ in the synthesis made it “greener” as compared to the method reported by Huang *et al.* (2004).

After formation of nano particles, a stabilizer should use to control the formation and dispersion of metal nanoparticles. Many research work established that polymer can be used as stabilizer to control the particle growth, stabilize the metal dispersions and limit the oxidation of the particle (Sun *et al.*, 2001; Pimpang *et al.*, 2008). Chitosan(Cts) is excellent biocompatible, biodegradable, non-toxic and bioactive material. Polyethylene Glycol (PEG) is a water-soluble polymer with a general formula H(OCH₂CH₂)_nOH. This polymer is widely used in the mechanical as well as pharmaceutical and cosmetic industries. This is also a good stabilizer for the nano composites where Ag nano particles are used.

Experimental

In this green synthesis AgNO₃ solution was stirred with different times at moderate temperature, reducing the Ag metal to Ag⁺ ions. Chitosan solution was mixed to PEG solution to produce Cts/PEG solution. Next, to this solution Ag⁺ ion containing solution was added which reacted with the Cts/PEG to form metallo-polymer [Ag/Cts/PEG]⁺ (Equation 1). This metallo polymer was stirred at a moderate temperature of 60°C according to varying stirring times to form Ag/Cts/PEG nano-composites (Equation 2). In this process, Ag⁺ was successfully reduced to Ag⁰ to form Ag NPs **Scheme 1**.

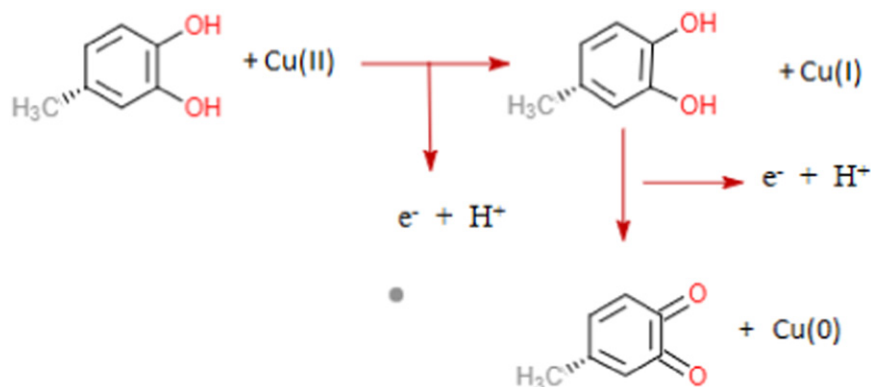
Characterization

The influence of the stirring times on the optical properties, structures and morphologies of silver nanoparticles was characterized by the ultraviolet-visible (UV-vis) spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR).

Cu- magnesium oxide nano composite

The MNPs are more active than their particulate metal counterparts due to their properties, small sizes and large surface areas. Among MNPs, copper nanoparticles (Cu NPs) have attained a particular attention due to cheapness and availability compared to other metal nanoparticles (Pourtehdal *et al.*, 2009; Karunakaran *et al.*, 2010; Ghosh *et al.*, 2015). Despite the advantages of Cu NPs, the stability of nano particles were inevitable. The synthesis of these nano particles through heterogeneous catalysts is one of the best ways to overcome the agglomeration of MNPs (Panin *et al.*, 2004; Panin *et al.*, 2005; Jung *et al.*, 2005; Takada *et al.*, 2008; Dhineshbabu *et al.*, 2014). Recently, various research groups reported the green synthesis of MNPs such as TiO₂ (Khade *et al.*, 2015) graphene oxide (Choi *et al.*, 2015), Fe₃O₄ (Fekri *et al.*, 2015), bentonite (Issaabadi *et al.*, 2017), perlite (Vartooni *et al.*, 2016) and etc. In this regard, MgO has been used widely as an efficient heterogeneous catalyst in organic reactions due to its good chemical and thermal stability, low cost, high surface area, ease of handling and high catalytic activity reusability (Julkapli and Bagheri, 2016). Plants extract mediated synthesis of NPs can be beneficial for preparing nano-metals to control the size, shape and distribution size. The green approach for the synthesis of Cu nano particles by using plants extract were eco-friendly, compared to other physical and chemical methods. This green methods included the use of nontoxic solvents, simple work-up procedure, very mild reaction conditions, cleaner reaction profiles. These reactions involved limited emission of toxic and dangerous materials, without using of surfactant, capping agent and or template, elimination of high pressure, energy, temperature and very cost effective (Sathishkumar *et al.*, 2009; Bordbar *et al.*, 2017; Bordbar, 2017).

Cassythafliformis L. from the Cassythaceae family was a medicinal plant of tropical region of Asia and America which mainly well known for the treatment of cancer. In modern medical research, C. filiformis has been reported to constitute so many number of different biologically active chemical compounds can be used for human health applications. The aqueous extract of Cassythafliformis L was used for reduction of metal particles into stable nanoparticles without application of poisonous chemicals and harsh reaction conditions.



Scheme 2 Reaction mechanism for synthesis of Cu- Magnesium Oxide Nano Composite.

Experimental

Cu/MgO nano-composite via a new, fast, simple, green, cost effective and ecofriendly process by using *Cassipoupa grandiflora* L. extract as stabilizing and reducing agent for the reduction of Cu^{2+} ion to Cu^0 .

50 gm of dried powder of *Cassipoupa grandiflora* L fruit was added to 250 ml of double distilled water with constant stirring at 70°C for 30 min in magnetic heating stirrer. Then the extract was centrifuged at 7000 rpm and filtered.

To 10 ml of 5 mM $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 100 ml of freshly prepared plant extract was added with vigorous shaking until the colour of the solution was changed to yellow to dark. After that the solution was centrifuged for 30 min at 7000 rpm and filtered. The filtrate then washed thoroughly with n-hexane and ethanol to remove impurities, **Scheme 2**.

Next 25 ml of 5 mM $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was added drop wise to the plant extract and also 1 gm of MgO was added to the mixture with constant stirring at 80°C for 4 h. Then the solution was centrifuged to separate Cu-MgO nano composite and washed with distilled water and then dried at 90°C for 2 h.

Characterization

FT-IR spectra were recorded on a Nicolet 370 FT/IR spectrometer (Thermo Nicolet, USA) using pressed KBr pellets. The formation and the size of nanoparticles was analyzed by UV-Visible spectral analysis on a double-beam spectrophotometer (Hitachi, U-2900). The morphology of the Cu/MgO nano-composite were identified by transmission electron microscope (TEM) using a Philips EM208 microscope operating at an accelerating voltage of 90 kV. Field emission scanning electron microscopy (FE-SEM) was performed on a cam scan MV2300. The Chemical analysis of prepared nanostructures was analyzed with EDS (energy dispersive X-ray spectroscopy). X-ray diffraction (XRD) mensuration were done by using a Philips powder diffractometer type PW 1373 goniometer ($\text{Cu K}\alpha = 1.5406 \text{ \AA}$). The scanning rate was 2° min^{-1} in the 2θ range from 10 to 90° .

Metal Oxide nano composites from solid waste

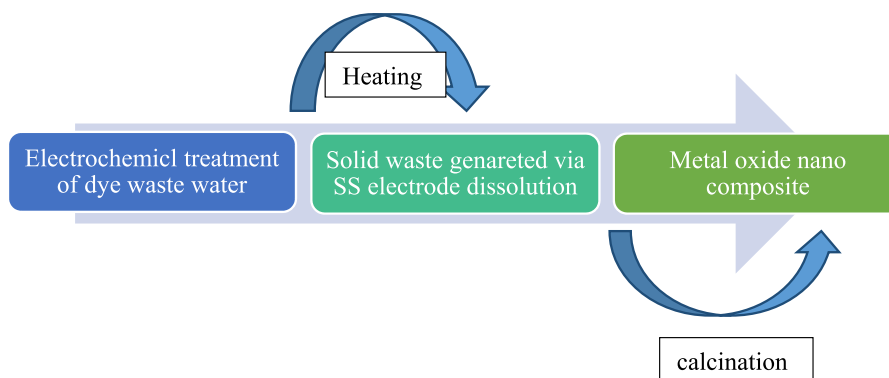
Recently there are so many research work has been reported on synthesizing nano sized metal oxide based catalysts prepared by very simple, versatile and ecofriendly methods to get the suitable texture and chemical composition of catalysts. In this purpose solid waste can be used for green synthesis of nano composites (Fan *et al.*, 2008; Kargbo, 2010; Matos *et al.*, 2011; Esparza *et al.*, 2011; Zhuo *et al.*, 2012). Some of the composites produced from sewage sludge based can be used as an adsorbent for adsorbing NO_2 (Pietrzak and Bandosz, 2008).

Iron oxide nano composites, having variable surface area and different size of porous sites, facilitate the adsorption and transport of various species in the reacting system. They also contain a large number of active sites which can provide superior adaptability and sustainability for various applications in the field of energy and environment, semiconductors, medicinal use. They are also useful for inorganic and organic contaminant degradation (Cao *et al.*, 2007; Oha and Park, 2011; Xu and Wang, 2011). There are so many work has been done to produce iron oxide nano composites. But mostly they used hazardous chemicals and sophisticated instruments. The treatment of solid industrial waste to synthesis of nano composites by Electro chemical method is one of the economic, simple and short treatment. Theory of EC methodology is described in the supporting information (SI).

Experimental

Iron oxide nano composites were prepared from solid waste, calcined at different temperatures. The composites were then characterized by using different methods to evaluate their structures and morphology.

At first the solid waste was spread over a glass plate to dry for 2–3 days, until the mass became constant. Then 5 gm of this waste was taken into a silica crucible for calcination at different temperatures for 3h in muffle furnace, **Scheme 3**, shows the graphical representation of the preparation of iron oxide NCMs from EC solid waste. Experimental procedure for EC treatment and generation of sludge is given in supporting information (SI). The solid waste heated to 100°C and then the temperature was gradually increases from 100°C to 300°C , up to 1000°C . After that the calcined waste was furnace cooled.



Scheme 3 Synthesis of metal oxide nano composite from solid waste.

Characterization

Thermo-gravimetric and differential thermal analysis (TGA and DTA) were carried out using Perkin ElemerPyris Diamond thermo-gravimetric (TG) analyzer in air atmosphere at the heating rate of $10^{\circ}\text{C}/\text{min}$ with air flow rate of 20 ml min^{-1} in the temperature range $20\text{--}1000^{\circ}\text{C}$. Powder X-ray diffraction (PXD) patterns were recorded on a Bruker AXES D8 advance powder X-ray diffractometer operating at 40 kV and 30 mA using Cu K α radiation ($\lambda = 1.5418\text{ \AA}$) in the angular range $10^{\circ}\text{--}90^{\circ}$. The experiment was done at a scan rate of $0.02^{\circ}/\text{step}$ and 0.5 s per step. The observed PXD patterns were analyzed by comparing with the powder diffraction files available in the joint committee on powder diffraction standards (JCPDS) database. Field emission scanning electron microscope (FE-SEM: QUANTA 200-FEG) was used to analyze the surface topography. The elemental analysis of the prepared iron oxide NCMs was performed using energy dispersive X-ray analysis (EDX) accessory by 5%–10% error of element contents.

Au- Iron oxide nano composite

In many cases super magnetic iron oxide nano particles were often coated with Ag or Au metal, supporting a localized plasmon resonance and also protects the magnetic core from many chemicals. These metallic core played an important role in surface chemistry or enhancing the dispersion and compatibility in biological media (Yu *et al.*, 2005; Wei *et al.*, 2008; Levin *et al.*, 2009; Wei *et al.*, 2009; Song *et al.*, 2010; Kim *et al.*, 2011; Miao *et al.*, 2011; Bhana *et al.*, 2012). Hence Au- Fe_xO_y nano particles can be used as multimodal contrast agents for isolating and purifying the protein molecules like DNA in biomedical imaging. These nano particles also played important role as photothermal agents for hyperthermia-mediated cancer therapies (Mandal *et al.*, 2005; Smolensky *et al.*, 2011; Meledandri *et al.*, 2011; Jin *et al.*, 2010; Aaron *et al.*, 2006; Park *et al.*, 2007; Ma *et al.*, 2009; Mohammad *et al.*, 2010; Xie *et al.*, 2010; Wang *et al.*, 2009; Huang *et al.*, 2009). Despite their strong technological potential, in most of the studies, organic non-polar solvents, high temperatures or high concentration of non-bio-degradable surfactants were used for the production of Au- Fe_xO_y nano composites. All of these are negative factors from the perspective of sustainable manufacturing and lifecycle assessment, causing significant pollution of the environment, consumption of energy and increasing production costs (Kralisch *et al.*, 2015). Hence we must seek an alternative, greener methods for synthesizing Au- Fe_xO_y NPs, with minimum concerns for environmental impact upon scaled production.

Experimental

This is an optimized and highly reproducible method for synthesizing MGNs in aqueous alcohol, based on systematic adjustments in reagent concentrations and reaction conditions.

648 mg of 4 mmol FeCl_3 and 398 mg of 2 mmol $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ solutions were mixed in 5 ml de-aerated de-ionized water. To this solution 15 ml of 28% NH_4OH solution was added drop wise over a period of 10 min. and immersed the solution in ultrasonic bath. Immediately Fe_3O_4 was formed as suspension. While iron salts were added to the NH_4OH solution, the anaerobic condition must be maintained. The mixture was then removed from ultrasonic bath and agitated for 2 min by vortex mixing to generate a homogeneous dispersion. Colloidal Fe_3O_4 was precipitated keeping an external handheld magnet along the walls of the reaction tube, then re-dispersed in deionized water. This process was repeated again and again to remove weakly magnetized colloidal oxides. Finally the precipitation was separated and dried to take the weight.

20 mg of 5 kDa mPEG- NH_2 was dissolved in 1 ml of dry de-aerated methanol with stirring for 10 min. Then to this solution 4 μmol of CS2 (one equivalent, diluted with methanol) was added with stirring for 10 min. Then 4 μmol triethylamine was added to the mixture with continuous stirring for again 10 min, resulting in mPEG-dithiocarbamate (DTC). Absorption spectroscopy confirmed DTC formation by the appearance of a doublet at 255–295 nm (Zhu *et al.*, 2008). Then freshly prepared mPEG-DTC solution was mixed with 1 ml of colloidal Fe_3O_4 , dispersed in water (8 mg ml^{-1}) and incubated at room temperature for 1h. Aliquots were removed and air-dried for analytical characterization.

A 0.25-ml aliquot of freshly prepared dispersion of mPEG-DTC-treated colloidal Fe_3O_4 (1 mg) was taken and added to 4 ml of an aqueous solution of L-histidine (1 mg ml^{-1}). The pH of the solution was adjusted to 5–6 using 0.1 M HCl, then incubated at room temperature for 1 h. After that 0.6 ml of 1% w/v HAuCl_4 was diluted by 14.8 ml distilled water. The pH of this solution was

maintained at 9–10 by using 5 M NaOH. To the colloidal Fe_3O_4 – histidine solution, diluted HAuCl_4 solution was added with constant stirring for 20 min. Now the reaction mixture was treated with 20 mM N-methylhydroxylamine (NMH) for initiating the reduction. The NMH solution was added in 5 portion to the reaction mixture of 0.2 ml with constant stirring in each 5 min. During the reaction noticeable change in colour occurred. The magnetic nano composites were finally formed after 12 h at room temperature. The final range of pH would be 6–7. The produced MGNCs were separated by selective precipitation using a handheld NdFeB magnet producing linear field gradients of $1\text{--}3\text{ kG cm}^{-1}$. After 15–20 min magnetically unresponsive materials was removed by decantation. The residue was the again and again re-dispersed into water at twice the original volume with mild sonication, followed by magnetic precipitation, to yield MGNCs that were essentially devoid of non-magnetic gold NPs.

Finally 0.5 M solution of diethanol – DTC in methanol (DE-DTC; final concentration 2 mM) is used for removal of excess Fe_3O_4 from nano-composites. In a typical cleansing procedure, 20 μl of 0.5 M DE-DTC was added to 5 ml of final compound MGNCs (O.D. 0.4), followed by vortex mixing, keeping it in ultra sonicator for several seconds, incubation for 1h at room temperature, then two rounds of magnetic precipitation and re-dispersion in water.

Characterization

The prepared metal oxide nano composites was characterized by using transmission electron microscopy (TEM) using a Tecnai-T20 microscope (FEL, Hillsboro, OR, USA). TEM samples were prepared by floating carbon-coated grids on top of an aqueous NP dispersion for 30 min, followed by removal of the grid and drying in air for at least 60 min prior to analysis. Energy-dispersive X-ray (EDX) analysis by scanning transmission electron microscopy (STEM) was done by using a Tecnai G2 T20 microscope (FEL) equipped with a LaB6 filament and X-Max 80 silicon drift detector (Oxford, UK), with data collected by a high-angle annular dark field (HAADF) detector (Fischione, Export, PA, USA) and recorded by a $2\text{ k} \times 2\text{ k}$ CCD imaging camera (Gatan, Pleasanton, CA, USA) using Inca software (ETAS, Stuttgart, Germany). Atomic absorption spectroscopy (AAS) was performed with a Perkin-Elmer (Waltham, MA, USA) 3110 spectrometer, using materials dissolved in aqua regia.

Ceramic Composite

Now a days it has been reported that carbon fiber reinforced silicon carbide matrix composites were applicable in the field where high specific strength with suitable fracture toughness at elevated temperature were required like automotive breaks, high efficiency engine systems, chemical reactor and space vehicle (Rak, 2001; Naslain, 2005; Zhang *et al.*, 2008). But there were so many limitations for synthesizing these composites such as difficulties in reproducibility, use of expensive equipment and involvements of hazardous chemicals.

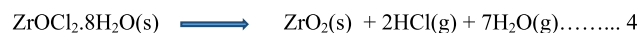
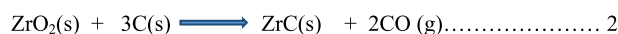
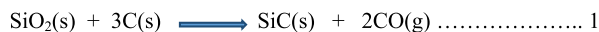
Several methods can be use to fabricate carbon- silicon carbide composite materials like carbon vapor infiltration, polymer impregnation and pyrolysis, liquid silicon infiltration, sol-gel method etc. But all these methods have merits and demerits. According to a research work this composites can synthesize by soft solution approach which is simple, rapid and eco-friendly process.

Carbon Fiber Reinforced SiC

Experimental

Water soluble colloidal 40% by wt silica, sucrose, boric acid and zirconiumoxychloride were taken as raw materials for the production of silica, carbon, boron oxide and zirconium di-oxide. In this soft solution approach, The first step was the preparation of green precursor solution by dissolving the raw materials. Then the precursor solution was dried at room temperature for 2 days and heated to 338K for 12 h. After that it was heated at 773K for 1 h. for carbonization of the dried powder. Thus in this step sucrose converted to carbon, zirconiumoxychloride to zirconia and boric acid to boria. Finally carbothermal reduction of oxides to carbides and borides was taken place by heating at 1873 and 1973K for 3 h. **Scheme 4**.

For the preparation of carbon fiber reinforced silicon carbide, carbon fiber tow was washed properly with acetone. Next these fibers were vacuum impregnated with precursor solution of different matrices like SiC, SiC + ZrB_2 , SiC + ZrC , SiC + ZrO_2 . Then



Scheme 4 Reaction mechanism of production of Carbon fiber reinforced silicon carbide composite.

SiC + TiO₂ (Mixture), 3:1 and 6:1



Co milling	
BPR:	10:1
rpm:	1100
time:	5h
medium:	Ar



TiO₂/SiC, ceramic mixture

Scheme 5 Experimental set up for high energy ball milling process.

it was dried at room temperature for 6 h and after that at 338k for 2 h for removal of excess water. Then the dried samples were carbonized at 773k for 1 h for the conversion of sucrose to carbon. This sequence of vacuum in pregation, drying and carbonisation were repeating for 6 times to improve the density of the composites. The samples were heated at 1873k and 1973k for 3 h in argon atmosphere. The density of the prepared composites has been measured using Archimedes principle.

Characterization

First thermogravimetric analysis was done for the green powder to know the change of reactants on heating. With the lowering of temperature, the green precursor attributed towards the amorphous nature of obtained carbon materials. The crystalline characteristics was reported by using XRD. SEM analysis of the compound was also done to know the structure.

SiC- TiO₂ Ceramic Composites

In another research work ceramic composites were again synthesize by environment sustainable method for tribological studies (Briscoe and Sinha, 2008). Polymers have very interesting properties and lighter than metal and ceramics. But pure polymer was not suitable for tribological application due to its low strength and low wear resistant. The high hardness of SiC were able to reduce polymer wear. The toughness of SiC can be improved by adding TiO₂ which can also improve the wear resistant (Zum Gahr, 1998). In this work a mechanochemical method was applied for preparation of SiC- TiO₂ ceramic powder which can be used as filler in polymer tribosystem.

Experimental

A Novosibirsk Corp. Activator 2S mill (Novosibirsk, Russia) was used for all high-velocity ball milling experiments. The steel reaction vessels(10 mm diameter) were taken to dry in argon atmosphere with a ball to powder ratio is 10:1.Milling time was 5 h and conducted at 1100 rpm. 10 gm of sample were taken into each reaction vessels. Series A composed of 6:1 weight ratio of SiC- TiO₂ and in series B the ratio was 3:1 **Scheme 5**.

Characterization

The obtained final products were used in powder X-ray diffraction (XRD) on a Philips X'Pert instrument with CuK α source between 10 and 90° 2 θ with a step size of 0.05° to analyze the morphology. SEM-EDS measurements were also done by using Hitachi S 4700 instrument at 20 kV and at a magnification of 10,000 X. For EDS analysis a Noron VANTAGE microanalysis system was used.

Conclusion

Now a days in any developing country a common word is being echoed in every industrial sector i.e., "Green Technology". Due to different types of production techniques there have been many greenhouse gases released into the atmosphere since 100 years. This is the main cause of the phenomena 'global warming'. And now for our sustainability, it's the time to save our planet from the effect of these harmful gases. In a near future the industries around the world would achieve a development in production which

has less impact on environment. Green synthesis of materials not only reduce the pollution of environment, also it can lower the impact of manufacturing at each and every stage. Environment sustainable production focuses on mitigation of greenhouse gas emissions, effluents, accidents, use of virgin and nonrenewable energy resources, life cycle cost, product and services.

See also: Green Manufacturing: Progress and Future Prospect. Quality of Environment and Clean Manufacturing

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Green Fuel Blending: A Pollution Reduction Approach

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Nomenclature

ABE Acetone-butanol-ethanol
B Biodiesel
BBD Butanol blended diesel
BE Bioethanol
BM Biomethanol
BSFC Brake specific fuel consumption
BTDC Before top dead center
BTE Brake thermal efficiency
Bu Biobutanol
CA Canola
CC Coconut
CF Chicken fat
CI Compression Ignition
CO Corn
EGT Exhaust gas temperature
FO Fish oil

GBu Gasoline-biobutanol
GHG Greenhouse gas
GMB Gasoline-methanol blend
GME Gasoline-bioethanol
HVO Hydrogenated vegetable oil
LCA Life cycle assessments
M Mustard
OECD The organization for economic corporation and development
P Palm
PM Particulate matter
SB Soybean
SCF Swine and chicken fat
SI Spark Ignition
SU Sunflower
THC Total hydrocarbon
WCB Waste cooking biodiesel

Introduction

Global Transport Scenario

The entire world's day to day transport (including light-duty and heavy-duty vehicles) vastly depends on two important fuel resource viz. diesel and gasoline. The world's statistical data portray that 947 million light-duty cars and 335 million commercial vehicles were operational in 2015 which was 2 times higher compared to the number of vehicles ten years back ([Annual Energy Outlook, 2018, EIA](#)); thus, indicating a significant demand growth of such automobile liquid fuels.

Moreover, an article published in [International Energy Outlook \(2016\)](#) disclosed that energy consumption has been 30.472 trillion kWh in 2012 and will reach to 45.415 trillion kWh in 2040 ([IEO, 2016, EIA](#)) in the transport sector. Countries like India, Africa, China and other parts of Asia accounted for about 61% share in global transportation energy. The published report also encompasses the fact that among the personal mobility modes of transport, light-duty vehicles occupied 44% of global transportation energy; while heavy transports (cargo/shipment) consumed 39% of total energy; whereas goods trucks shared 23% followed by marine vessels (12%), rail and pipeline (a combined 4%). Aircraft and buses including 2 or 3 wheeler vehicles consumed 11% and 6% of global transportation energy ([IEO, 2016, EIA](#)). Therefore, it is quite evident that road transportation sector has major share in global transport energy.

Fuel Prices, Fuel Depletion and Climate Change

The whopping mandate of liquid fuel in public transport, growth in the financial market and global trade has elevated the price of crude oil vis-à-vis petroleum products viz. gasoline and diesel. It has been reported elsewhere that the key fuel source in surface transport is gasoline in OECD (The Organization for Economic Co-operation and Development) countries; whereas, in non-OECD countries like India and China, diesel has been the major transport fuel. Likewise, statistics show that China and India became world's largest crude oil importer; this depicts the fact that these countries are most affected by the market prices of the crude oil.

The present scenario also illustrates the imbalance between demand and supply chain caused due to high exploitation of fossil fuel for technological and economic advancements. Since oil, natural gas and coal are finite natural resources and its declination is inevitable from the geological point of view, a concern existed regarding exhaustion of these non-renewable fuels. Furthermore, if the same extraction rate continued the worldwide crude oil reserve will last for only another 50 years.

Moreover, the environmental stability was not only disturbed due to depletion of fossil fuel, but the dreadful emission resulting from these natural fuels, possesses a grave threat to the entire mankind. Consequent greenhouse gas (GHG) emission leading to global warming and climate change has become global apprehension in the present situation. The average universal temperature has increased from 1.8 to 4.0°C owing to GHG emissions. Thus, it could be well understood from the statistical data

that with the increase in the existing fleet to satisfy the comfort of the society, the fossil fuel consumption will increase which will also putrefy the atmosphere proportionately.

Additionally, other toxic engine emissions involving NO_x (nitrous oxides), SO_x (sulfur oxides), HCs (hydrocarbons) and PM (particulate matter) causes harm to the environment by depleting the ozone layer, causing acid rain, contributing to smog formation and disturbing human health profoundly. Therefore, various countries implemented environmental policies viz., United National Framework Convention on Climate Change (UNFCCC) and the Kyoto Protocol that mandated engine modifications or alterations in fuel quality to overcome these detrimental effects. Thus, the researchers are struggling to find efficient fuel substitutes or investing to develop energy-efficient equipment in order to tackle ever-increasing oil prices and environmental pollution.

Fuel Blending

Green Fuel Blending With Gasoline

To restrict the polluting emission from gasoline (for example 1098 million metric tons of CO₂ only in US), gasoline blending with green fuel has recently attracted the attention of various researchers and policy makers.

Green gasoline derived from fermentable sugars of corn, sugarcane, sugar beets, barley, sorghum, cassava and other agricultural biomass acted as an efficient green fuel substitute in the spark-ignition engine by virtue of its high octane value, thereby reducing emission of harmful pollutants compared to conventional gasoline. In 2007, legislation was enforced by Renewables Fuels Standard that necessitated blending of gasoline with 10% of bioethanol without engine modifications; statistics also showed that 96% of all gasoline vehicles in the USA could run on gasoline blended with 10% bioethanol (derived from corn).

The United States became the largest fuel-ethanol producer (15.8 billion gallons) followed by Brazil (7.6 billion gallons), China (0.87 billion gallons), India (0.28 billion gallons) in 2017 ([Ethanol fuel production in top countries, 2017](#)). More recently, a report by the International Energy Agency ([IEA predicts growth in global ethanol production through 2023, 2018](#)) on market analyses of renewable fuels predicted that ethanol would occupy two-third global share in the growth of conventional biofuels within 2023.

Similarly, bio-methanol (BM) is also known for its blending synchronization with gasoline in SI engines. An article published by IEA reported the tradition of methanol use as a transportation fuel in the US and China where many refueling stations employ M3 (3% methanol) to M85 (85% methanol) blends for road transports.

Therefore, BM can serve as an efficient fuel additive which can be produced from chemical/biochemical conversion routes using different feedstocks viz., animal trash (cattle manure) and agricultural wastes.

However, production of BM through chemical route involves gasification of carbohydrates into carbon monoxide and hydrogen that undergo catalytic reaction to produce methanol. Moreover, BM production from biomass gasification requires additional steps like pretreatment, gas cleaning (removing tar, soot, alkali metals) and gas conditioning (removing methane and other hydrocarbons). Unlike gasification, methanol can also be directly obtained from fermentation of sugars and starch (biochemical route) without incurring additional processing costs.

Green Fuel Blending With Diesel

Biodiesel is a competent renewable, green substitute for conventional diesel fuel that can effectively reduce the harmful engine exhausts. Sources of biodiesel production are transesterification of vegetable oil and esterification of fatty acids using methanol/ethanol for generation of methyl/ethyl esters of fatty acids ([Pradhan and Chakraborty, 2018](#)). Biodiesel is well known for its increased oxygenation ability that facilitates complete combustion of fuel, thereby reducing the detrimental emanation of CO from the diesel engine. According to the statistical data published, USA projected a production of 1 billion gallons of biodiesel within 2025 ([Leading biodiesel producers worldwide in 2017, by country in billion liters, 2017](#)). It has been also reported that in 2050, green-fuels like biodiesel would significantly replace petroleum-based fuel and would be able to meet 40%–60% of the total energy demand of the world. This growth will not only improve the economy of the non-oil producing countries by plummeting their needs on imported crude petroleum fuel but will also offer great enticements to the agricultural sectors and rural economy.

On the other hand, bio-alcohols viz. ethanol and butanol not only serve as gasoline additives in SI engines but can also improve the burning characteristics of diesel fuel in CI engine. Alcohol-diesel blends have efficacy in heightening fuel cetane number, reduces particulate matter (PM) emission and also helps demand suppression of petroleum-based fuel.

However, the response for hydrotreated vegetable oil (HVO) or green diesel is competitive to bio-alcohol and biodiesel. They have better shelf life i.e., less susceptible to oxidation, has the potential to be used as unblended feedstock without any alterations to the existing engine designs and a high calorific value similar to diesel. Besides propane is the by-product of this hydrotreated vegetable oil which has huge market demand. Therefore the catalytic hydrotreating of waste and residue feedstock holds a significant share in the production of valuable green fuel.

Pyrolytic oil (Pyro-oil/bio-oil) is yet another example of a diesel substitute that finds its effective application in the diesel engine. The extensive sources of pyro-oil are waste tires and plastics which have effectively controlled the solid waste management problems. Pyro-oil showed promising engine performance when blended with diesel/gasoline up to 15–20 vol% in

Table 1 Impact of methanol blending with gasoline on fuel properties, engine performance and emission attributes

Blend with gasoline vol%	Impact on engine emission	Impact on engine performance	Remarks	Citation
10 and 20	1. Lessens particulate matter emission. 2. Lower exhaust gas temperature. 3. Higher HC emission at lower engine loads	1. High cylinder pressure due to good methanol combustion. 2. Lower heat release rate of blends 3. The duration for combustion of blended fuel was higher. 4. Higher BSFC due to lower calorific value.	1. Lower heating value of methanol (20 MJ/kg) compared to gasoline (44 MJ/kg).	Agarwal <i>et al.</i> (2014)
3, 5, 7	1. Reduction in CO emission. 2. Lower HC emission	1. Higher volumetric efficiency of methanol due to higher latent heat of vaporization 2. Lesser output power due to lower heating value.	2. Addition of excess methanol provokes the emission of unburned CH₃OH	Elfasakhany (2015)

compression/spark ignition engines. This alternative fuel has the capability of reducing GHG emissions and deliver similar engine performance as conventional diesel.

Therefore, the present article emphasizes on application of different green fuel alternatives/additives that can be effectively blended with conventional gasoline and diesel in improving the fuel properties without any engine modifications. The survey also meticulously investigates the efficacy of these additives in mitigating the adverse effects of petroleum fuel on global climate.

Effect of Alcohol Blending on Gasoline and Diesel

Bio-Methanol Blending

Gasoline-bio-methanol blend

Bio-methanol (BM) acts as an alternative chemical to conventional gasoline that can reduce the consumption of fossil fuel and has also beneficial effects on the environment because of its low carbon emission. The octane number of 5% BM and 95% gasoline (BM5) is 98 which make BM5 almost equivalent to the neat fuel with respect to engine performance while providing reduced emission of harmful pollutants (e.g., CO, HC, PM); however, the brake specific fuel consumption (BSFC) is higher compared to neat gasoline.

Moreover, the performance and cost analyses indicated that BM5 could substitute neat gasoline and was comparatively more environment-friendly (lower reactivity of the organic emissions) and cost-effective than conventional gasoline. **Table 1** illustrates the effects of methanol-gasoline blending on SI engine emission and performance. The addition of methanol has immensely influenced the SI engine performance and has also controlled the harmful emanations of GHGs. BM demonstrated superior performance in terms of CO and HC reduction due to the higher oxygen content of the fuel. Again, greater methanol blends facilitated lower NO_x emission. Nevertheless, excess methanol deteriorates the heating value of the fuel which causes late burning of the fuel and increases BSFC and lowers brake thermal efficiency (BTE).

Also, it exceeds the unburnt methanol emission, therefore; excess methanol (85% methanol) should be avoided in consideration of gasoline-methanol blending.

Diesel-bio-methanol blend

The high oxygen content of BM has also favored its use as a green diesel fuel blends in CI engine. **Table 2** describes the behavior of diesel-methanol fuel blend in CI engines.

It could be observed from **Table 2** that the addition of methanol has effectively reduced the GHG emission in comparison with neat diesel. However, similar difficulties (as in gasoline-methanol blend) were also faced in the diesel-methanol fuel blend. At higher methanol proportion, decreased cetane number reduces the calorific value of the fuel that causes the deterioration in the engine performance.

Recent practices in bio-methanol blending

Current practices (**Table 2**) enumerate the addition of long chain alcohols to the diesel-methanol blend that can increase the capacity to hold water, thereby improving the stability of the blended fuel (Chen *et al.*, 2019). A similar technique for the improvement of gasoline-methanol blended fuel can also be effective. Since lower carbon alcohols are not completely miscible in conventional fuel owing to phase separation issues in presence of water; therefore, the addition of branched-chain alcohols to gasoline-methanol blend would make the overall blend more homogeneous. The branched alcohols viz. isobutanol has been observed to be as less polluting fuels with smooth operational capability due to nullification of separation problem of gasoline-methanol blend (GMB) in presence of water. Furthermore, the leaning effect on addition of alcohol can appreciably facilitate combustion behavior of the fuel (Elfasakhany, 2018).

Table 2 Effects of alcohol blending on diesel properties, engine performance and emission profiles

Blends	Impact on engine emission	Impact on engine performance	Remarks	Citation
Methanol and Diesel	1. Alcohol content reduces exhaust gas temperature. 2. Higher methanol content above 30% results increase in THC emission. 3. 80% reduction in CO emission. 4. High NOx emission with increase in alcohol blend.	1. Above 25% blend result in substantial ignition delay. 2. Increase in heat release rate. 3. Above 30% load results in reduction of in-cylinder pressure	1. Lean fuel decreases NOx emission but deteriorates engine performance. 2. Presence of water increases the immiscibility of methanol in diesel. 3. Higher blends lower the cetane number and heating value of fuel thereby reducing ignitability.	Jamrozik (2017)
Diesel, Methanol and n-pentanol	Lowers soot emission and increases NOx emission.	Shortens combustion duration.	1. Presence of long chain alcohols in diesel-methanol blend increases the stability and solubility of methanol in diesel. 2. Increases the heating value of the fuel.	Chen <i>et al.</i> (2019)

Bioethanol Blending

Diesel-bioethanol blending

European Parliament Directive (2009/28/EC) passed a regulation of using 10% of renewable green fuels in transport by 2020. Bioethanol (BE) amongst the common renewable fuels has gained major attention due to its positive influence in lowering NOx emission (Park *et al.*, 2012). However, from the exhaust emission analyses presented in Fig. 1(A and B), the blending of BE beyond a proportion has least impact on the CO emission (Fig. 1(A)) while it aggravates HC emission (Fig. 1(B)). The higher values of HC emission may result lower cetane number (value 11) that extends the ignition delay, eventually rendering decomposition of the blended fuel (Tutak *et al.*, 2017; Jamrozik, 2017) in engine bore. Notably, the lower NOx emission at higher BE blends (Fig. 1(C)) is due to the leaning effect during the air-fuel premixing prior to its induction into cylinder of CI engine for combustion.

Another usual problem related to the engine exhaust of petroleum diesel is the high emission of particulate matter (PM)/soot, which causes severe health damages. To regulate PM, engine modifications involving diesel particulate filter can be considered; however, these kinds of additional facilities increases the manufacturing cost of the diesel engine. In this context, BE provides an immense benefit as blending stock for diesel owing to its capability in retarding soot/PM emission.

Table 3 describes the soot/PM emission values for diesel blended with different proportions of BE. It could be observed in a study conducted by Lee *et al.* (2018) that with the application of BE in diesel, the size distribution of PM decreases from 1000 nm to 50 nm which advocated for the beneficial effect of blending BE with diesel. Nonetheless, from the aspect of the engine performance, bioethanol blended diesel resulted in higher exhaust gas temperature, lower combustion duration of 22° and lower thermal efficiency due to a lower calorific value that restricts the use of bioethanol at higher blend percentages.

Gasoline-bioethanol-gasoline (GBE) blending

BE blended gasoline also serves as an important green fuel substitute that is capable of providing improved brake power and higher thermal efficiency in SI engine. The octane number of 30% BE blend was reported 13% higher than that of neat gasoline (Costagliola *et al.*, 2016) indicating compatibility of BE as a suitable green blending component for gasoline in SI engine.

Notably, the oxygen content of bioethanol is 35% which renders lower PM emission ($1.7 \times e^{12}$) during the combustion of GBE fuel. Other properties e.g., lesser flame luminosity and lower vapor pressure make it efficient during cold start-ups of the engine. It has been also observed that for higher BE blend percentage; the fuel consumption remains identical to gasoline during cold condition; whereas, fuel consumption increases at warmer ambient with an increase in BE proportions. Yet another important aspect of BE as represented by Fig. 2, is the reduction of exhaust emission of the engine including NOx, CO and HC. It has been reported (according to Worldwide Motorcycle Emissions Test Cycle, Costagliola *et al.*, 2016) that increase in BE blend could substantially reduce HC and CO emissions; however, an enhancement (nearly 40%) in NOx emissions may be observed with respect to the engine types having different kinds of fuel injection systems (carburetor/electronic multi point fuel injection).

LCA case study for GBE blending

LCA and environmental life cycle costing assessments have been illustrated in this article to give a clear concept about the sustainability of BE (wheat straw/corn stover derived) use as a green additive to gasoline. The case study was based on the emission profile/km of a middle sized passenger car (Daylan and Ciliz, 2016). The study was conducted 'from cradle to grave' perspective considering parameters viz., feedstock acquisition, BE/gasoline production and fuel blending with fuel storage. LCA for GBE10, GBE85 and G100 blends demonstrated that with increase in BE blend, GHG emissions including CO and CO₂ could be considerably reduced from 522 mg/km to 341 mg/km and 0.273 kg/km to 0.129 kg/km respectively. Similar results were also observed for SO₂ discharge where the emission values mitigated from 420 mg/km to 227 mg/km. However, the NOx emission was found to increase by 19.7% and fuel economy was decreased by 24% in case of GBE85 compared to G100. Besides, LCA study has

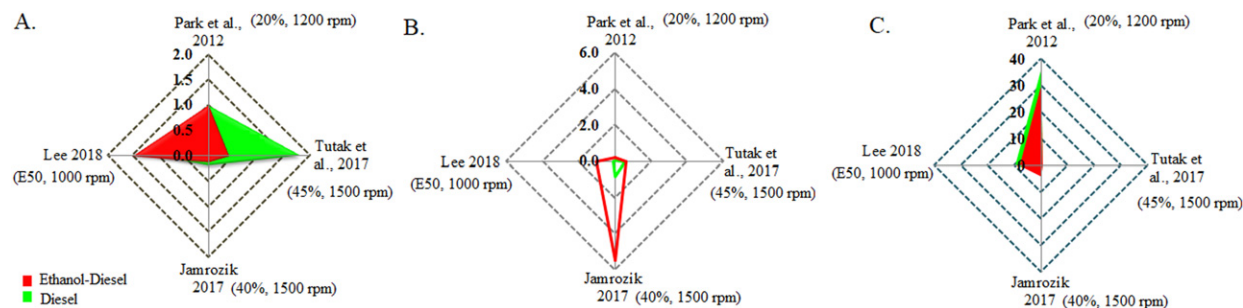


Fig. 1 Exhaust emission analyses of bioethanol blended diesel.

Table 3 Soot emission from CI engine using bioethanol blended diesel

Blend combination	Engine condition	Soot/PM emission	Reference
Ethanol (20)	Speed: 1200 rpm	D100: 0.05 g/kWh	Park et al. (2012)
Diesel (80)	Engine Pressure: 40MPa	E20: 0.025 g/kWh	
Ethanol (50)	Speed: 1000 rpm	Reduction in PM molecules during combustion.	Lee et al. (2018)
Diesel (50)	Engine Pressure: 0.8 MPa		

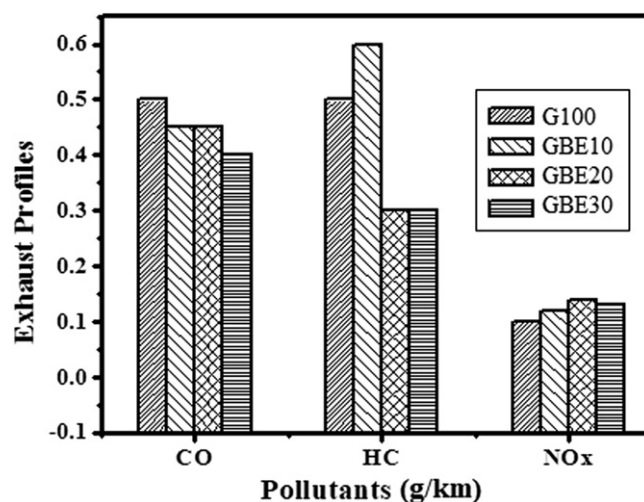


Fig. 2 Exhaust emission attributes from SI engine using bioethanol blended gasoline. Reproduced from Costagliola, M.A., Prati, M.V., Murena, F., 2016. Bioethanol/gasoline blends for fuelling conventional and hybrid scooter. Regulated and unregulated exhaust emissions. Atmospheric Environment 132, 133–140.

also concluded minimal stratospheric ozone layer depletion for GBE85 compared to GBE10 and G100 due to lower GHG emission from GBE85.

This study therefore infers that GBE85 has significantly lower environmental impact (global warming, ozone layer depletion, acidification, crude oil consumption) compared to G100 and GBE10. Again cost assessments for GBE85 results in 23% lower driving costs for in road transports which also advocate its economic sustainability over conventional gasoline.

However, BE blending above a threshold limit possess certain considerable drawbacks. The inclusion of BE as blends with gasoline above a specified threshold limit generates another spectrum of emissions involving acetaldehyde, VOCs, formaldehyde, benzaldehyde and significant levels of vaporized ethanol during combustion. Acetaldehydes are known for provoking respiratory irritation, bronchitis and asthma; while, benzaldehydes were considered as nerve toxins which could cause nerve failure and brain impairment. Formaldehyde is also associated with the carcinogenic effects on human body. Therefore, the release of such toxins with the exhaust emanation can cause serious damage to the human health and environment which restrains its use as a neat fuel in SI engine.

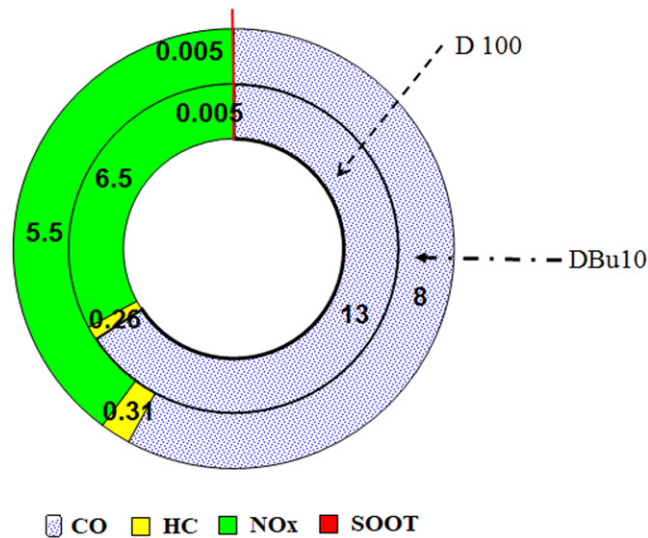


Fig. 3 Effects of butanol addition on diesel engine emission at 30 Nm load and 60° BTDC. Reproduced from Yun, H., Choi, K., Lee, C.S., 2016. Effects of biobutanol and biobutanol–diesel blends on combustion and emission characteristics in a passenger car diesel engine with pilot injection strategies. *Energy Conversion and Management* 111, 79–88.

Biobutanol Blending

Biobutanol blending with conventional fuel is another pollution reduction approach which could be competently used in both SI and CI engines without any engine modifications. The higher heating value of butanol (18.46%) renders reduced specific fuel consumption in engine compared to ethanol. Additionally, the higher knock resistance characteristic of butanol has helped improving the ignition timing resulting in more efficient combustion of the blended fuel. The leaner fuel/air ratio and higher oxygen content are further contributor to better burning of the fuel (Feng *et al.*, 2015).

Gasoline-biobutanol (GBu) blending

To explain the influence of biobutanol (Bu) addition in gasoline, an example has been cited from the work of Feng *et al.* (2015). The experimental investigation demonstrated that within the speed range of 2500–8500 rpm, an increase in Bu percentage from 30 (GBu 30) to 35 (GBu 35) vol% has curtailed the unburnt HC emission (3750–2600 ppm) compared to pure gasoline. The improved combustion efficiency, lower carbon content and higher air-to-fuel ratio were the reasons behind the suppression of HC emission. Moreover, in this study, CO emission was also reported to become reduced from 8×10^4 ppm (neat gasoline) to 5×10^4 ppm (GBu 35). The aforementioned reasons holds good in this case also. Unfortunately, NOx emission has a completely reverse scenario. An increase in Bu blend led to augmented NOx emission to 2000 ppm from 1000 ppm. The higher residence time and combustion gas temperature along with greater oxygen content contribute to more NOx emission according to the Zeldovich mechanism.

Diesel-biobutanol (DBu) blending

Bu showed similar blending efficacy when mixed with conventional diesel. The higher oxygen concentration in Bu (2.34 times more) compared to diesel prompted the clean burning of the green fuel. Even biobutanol blend is also efficient in impeding PM and nano-level particulate emission.

To explain the fact a reported work by Yun *et al.* (2016) may be considered wherein 10% and 20% Bu was premixed with diesel for a passenger car engine running at a speed of 1500 rpm with a varying load of 30 Nm and 60 Nm and the pilot injection timing has ranged between 20° and 60° before the top dead center (BTDC). It could be observed from Fig. 3 that, addition of Bu could lower the NOx discharge by virtue of maintenance of lower gas temperature in the burning chamber and higher ignition delay of the blended green fuel.

Similarly, soot formation could also be hindered by increasing Bu proportion in blended fuel at higher load while identical values were recorded at lower engine load (30 Nm). CO emission was greatly reduced with an increment in butanol content which could be ascribed to the leaning effect of Bu rendering such improvement. However, HC emission depends differently on several factors:

- Fuel Quality: Extended ignition delay; inferior cetane number and high heat of vaporization.
- Engine Attributes: Geometry of the combustion chamber; wall wetting of engine cylinder and engine piston surface.

Table 4 Properties of biodiesel obtained from different edible oil feedstocks

Feed stock	Oil content (%) ^a	wt% fatty acid	Name	Pour point (°C)	Cetane no
Canola oil, <i>Brassica campestris</i>	35	56.6	C18:1	−7	61.5
Mustard, <i>Brassica juncea</i>	30	20.5	C18:2	5	53
Soybean, <i>Glycine max</i>	21	53.7	C18:2	−4	46
Palm kernel, <i>Elaeis oleifera</i>	40	56.1	C18:1	10	56.5
Palm olein		41.9	C18:1	7.22	62
Palm stearin		61.1	C16:0	13.48	74.3
Sunflower, <i>Helianthus annuus</i>	44–51	56.5	C18:2	1	49
Corn, <i>Zea mays</i> (germ)	40–50	44.7	C18:2		
Olive, <i>Olea europea</i>	55–83	71.6	C18:1	2	
Coconut, <i>Cocos nucifera</i>	63	50.9	C12:0	−8.47	45–55
Ricebran, <i>Oryza sativa</i>	14.7–19.10	38.9	C18:1	5.8	
Groundnut, <i>Arachis hypogea</i>	36–56	41.1	C18:1		54
Sesame, <i>Sesamum</i>	44.6–53.1	41.2	C18:2	18	38.2

Note: Issariyakul, T., Dalai, A.K., 2014. Biodiesel from vegetable oils. *Renewable and Sustainable Energy Reviews* 31, 446–471.

Furthermore, Bu blended diesel (DBu) demonstrates advantages from the aspect of the engine performance. The DBu exhibited comparable engine performance as that of the neat diesel both at higher and lower injection timing along with higher BSFC and lower EGT under all operating conditions.

Demerits of biobutanol blending

The acrolein emission is a major issue of butanol blended fuels that causes impaired metabolism, edema while longtime exposure triggers cancer to humans. Moreover, Bu is generally produced by biochemical route; and the downstream purification process is cost extensive because of additional by-product formation viz., hydrogen, acetic, lactic and propionic acids, acetone, isopropanol and ethanol etc. Besides, the lower yield of Bu through fermentation makes it more challenging for its commercial application as a green fuel.

Emerging trends

Recent practices involve triple blend i.e., combination of acetone-butanol-ethanol (ABE) which can nullify the individual disadvantages of ethanol and butanol. ABE (10–30 vol%) can be blended both with gasoline and diesel that could effectively reduce CO, NO_x, HC and soot emissions; nevertheless, the flipside of ABE is its lower calorific value that increases the BSFC while higher ABE concentration augments CO and NO_x emissions.

Biodiesel Blending

Biodiesel (B) is made of monoalkyl esters (derived from long chain fatty acids) which can be usually produced by esterification/transesterification reaction of waste/refined vegetable oil and animal fat with short-chain alcohols (methanol, ethanol) in presence of a homogeneous or heterogeneous catalyst (Banerjee and Chakraborty, 2009). The feedstock could be further categorized into vegetable oils (including edible and non-edible oil), animal fats and organisms like microalgae and cyanobacteria (*Cyanobium* sp., *Limnothrix* sp. and *Nostoc* sp).

Notably, biodiesel possesses various positive attributes that can control the emission of harmful GHGs and PM from CI engines. Nevertheless, the biodiesel has to satisfy the American Society of Testing and Materials (ASTM) standard specifications which has been designated as ASTM D-6751 and European standards (EN14214). Therefore, in the following section, the application of biodiesel as green diesel blends has been discussed for mitigation of harmful pollution concerning CI engines.

Edible oil biodiesel: Properties, emission and performance characteristics

Table 4 presents different edible oil feedstocks with fatty acids present in different extents. However, the production of biodiesel using this vegetable oil feedstock chiefly depends on the regional availability. For example, biodiesel production from rapeseed oil was highest in Europe, soybean oil in the USA, palm oil in Malaysia and coconut oil in the coastal areas. Depending on the type of feedstock and fatty acid content, properties of biodiesel viz., cetane number and pour point (Table 4) of fuel vary; this also affects the engine performance and exhaust emission.

Fig. 4 exhibits emission assessments for neat biodiesel derived from four important types of edible oil viz., coconut (CC), soybean (SB), sunflower (SU) and canola (CA); correspondingly, the PM, smoke and NO_x emissions have been compared with that of petroleum-based diesel. It could be observed from Fig. 4 that CC, CA and SB derived biodiesel could effectively reduce the PM discharge whereas SU derived biodiesel has augmented the emission.

Noticeably, CO emission can be reduced in case of all types of biodiesel. Interestingly, NO_x emission has been found to be lesser in SU and SB oil derived biodiesel which was due to higher C18:1 content of the fuel.

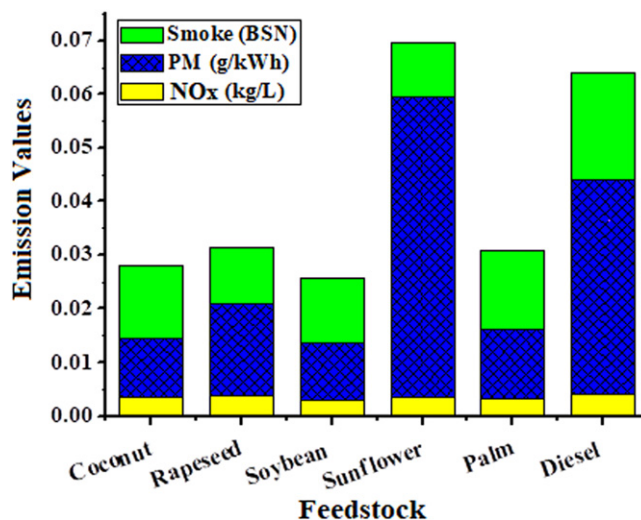


Fig. 4 Exhaust emission attributes of biodiesel derived from different edible feedstocks. Reproduced from Rajak, U., Verma, T.N., 2018. Effect of emission from ethylic biodiesel of edible and non-edible vegetable oil, animal fats, waste oil and alcohol in CI engine. *Energy Conversion and Management* 166, 704–718.

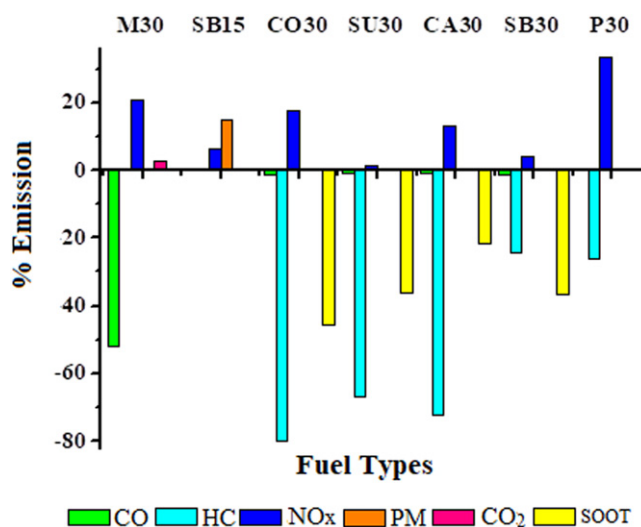


Fig. 5 Emission results of diesel-biodiesel (edible oil) blend. Reproduced from Uyaroglu, A., Uyumaz, A., Çelikten, I., 2018. Comparison of the combustion, performance, and emission characteristics of inedible *Crambe abyssinica* biodiesel and edible hazelnut, corn, soybean, sunflower, and canola biodiesels. *Environmental Progress and Sustainable Energy* 37, 1438–1447. Uyumaz, A., 2018. Combustion, performance and emission characteristics of a DI diesel engine fueled with mustard oil biodiesel fuel blends at different engine loads. *Fuel* 212, 256–267.

To further analyze the exhaust features of the diesel-biodiesel blend, a bar chart (Fig. 5) has been constructed, compiling emission results collected from different scientific articles in order to show the proficiency of different kinds of biodiesel. Maximum soot and HC declination were observed in corn-derived biodiesel (CO30) and SU30 showed well depreciation in NOx emanation, while mustard biodiesel (M30) enumerated much lower CO emission (Uyumaz, 2018).

The lower NOx emission in SU30 (Fig. 5) could be attributed to the comparatively higher air-fuel ratio that could suitably regulate the temperature of the combustion chamber, thereby causing lesser NOx release (Uyaroglu et al., 2018). Likewise, the greater oxygen content and higher cetane number were responsible for lower GHG emission. Again, the specific fuel consumption of all kinds of biodiesel was higher than conventional diesel due to higher viscosity and lower heating value; thus, delivering lower brake power.

Nonetheless, it is meaningful to mention that no single kind of biodiesel can control all types of engine emission which require further advancements (such as addition of suitable additives) in order to meet the desired specifications. Moreover, special attention should be given on feedstock selection which must be on the basis of surplus availability, lower production cost and suitable fuel properties with less market demand as edible oil to avoid food-fuel nexus.

Table 5 Properties of different non-edible vegetable oil sources

Feedstock	Oil content (%)	Major fatty acid	Cetane no	Flash point (°C)	Calorific value (MJ/kg)	Non-edibility
Jatropha	35–40	Oleic and Linoleic	57.2–63	238	39.8–42	Contains a toxin, curcin
Karanja	9–46		52–58	187	36–38	Contains toxic flavonoids
Cottonseed	18		41.2–59.5	243	39.5–40.1	Gossypol, a toxic compound
Jajoba curcas	25–30	Arachidic	63.5	292	42.76–47.38	Contains erucic acid
Waste cooking oil	–		60.4	70.6	38.73	Chemical and Physical degradation of oil

Note: Issariyakul, T., Dalai, A.K., 2014. Biodiesel from vegetable oils. *Renewable and Sustainable Energy Reviews* 31, 446–471. Rajak, U., Verma, T.N., 2018. Effect of emission from ethylic biodiesel of edible and non-edible vegetable oil, animal fats, waste oil and alcohol in CI engine. *Energy Conversion and Management* 166, 704–718.

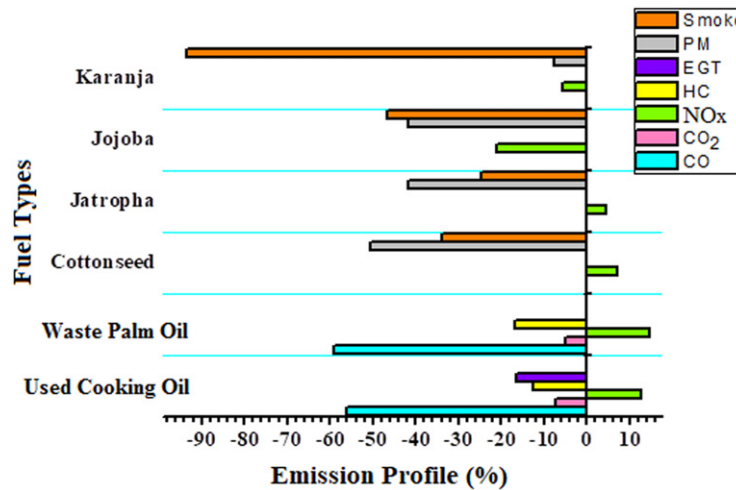


Fig. 6 Emission assessments of diesel-biodiesel (non-edible oil derived) blend. Reproduced from Rajak, U., Verma, T.N., 2018. Effect of emission from ethylic biodiesel of edible and non-edible vegetable oil, animal fats, waste oil and alcohol in CI engine. *Energy Conversion and Management* 166, 704–718. Pradhan, P., Chakraborty, R., 2018. Optimal efficient biodiesel synthesis from used oil employing low-cost ram bone supported Cr catalyst: Engine performance and exhaust assessment. *Energy* 164, 35–45.

Non-edible oil biodiesel properties, emission and performance characteristics

Biodiesel from non-edible oil resources (jatropha, mahua, karanja, cottonseed) has gained immense attention which has effectively reduced the utilization of edible oil feedstock. Reports also revealed that the non-edible oil sources could replace diesel completely in the CI engines (Rajak and Verma, 2018). Besides, waste oil including both waste cooking/frying oil and grease procured from different restaurants, household and food industries also serve as a cost-effective source for biodiesel synthesis.

The research reported in the same study also highlighted the fact that waste cooking biodiesel (WCB) can effectively reduce particulate emission via reducing its mass concentration and mean particle diameter. Further 75% WCB in CI engine showed performance equivalent to conventional diesel, thus advocating its efficacy. Table 5 depicts the properties of some of the non-edible feedstock for biodiesel production. The high flash points and acceptable calorific value make biodiesel appropriate for its use in CI engines.

Furthermore, a review of previous studies has been elaborated in Fig. 6. It can be observed that, NO_x production can be effectively reduced through employment of jojoba and karanja oil derived biodiesel. This is because of higher calorific value and satisfactory air-fuel ratio that can reduce the cylinder bore temperature of the engine resulting in lower NO_x emission. It has been also identified from Fig. 6 that jojoba and karanja derived biodiesel deliver equivalent engine performance similar to diesel in CI engine (appreciable BTE at higher compression ratio). Noticeably, a higher presence of oxygen in cottonseed and jatropha oil derived biodiesel raised the in-cylinder temperature, thereby, rendering complete oxidation with the curtailment of PM, CO and HC emission. Nevertheless lower PM emission has been compromised with a poorer reduction in NO_x emission.

Biodiesel obtained from used cooking oil is also efficient in depreciating CO and HC emissions while marginally higher NO_x emission may result due to faster burning of the biodiesel-diesel blend (Pradhan and Chakraborty, 2018). Other non-edible resources include rubber seed oil, neem tree oil, kusum seed oil, oleander oil which have also found their applications for biodiesel production and can effectively control harmful emission from the diesel engine. Similarly, microalgae e.g., *Calophyllum inophyllum* derived methyl ester (i.e., biodiesel) also acted as a suitable green fuel substitute due to higher cetane number and significant calorific value that facilitated a reduction in NO_x, PM and smoke emission (Rajak and Verma, 2018).

LCA case-study of biodiesel blending

To analyze the economic sustainability and environmental impacts of biodiesel as a green fuel alternative for diesel, LCA serves as the best methodology to find the options for sustainable transport systems. Therefore, a case-study has been considered where biodiesel has been used as fuel for cars, buses and municipal fleets in Greece (Nanaki and Koroneos, 2012). It has been reported that biodiesel (derived from rapeseed oil) fueled cars emit 94% lesser CO₂ while showing equivalent energy consumption of 183.1 MJ/100 km like diesel cars. This signifies lower GHG emission, lessens respiratory impairments and carcinogenic hazards along with reduction in fossil fuel consumption. However, 10% higher NO_x emission has been noted in the study which indicates eutrophication as the major drawback of biodiesel use as fuel alternative. Again, biodiesel production cost is higher which has been accounted for the higher prices of feedstocks that restricts its applications at larger scales. This can be avoided through use of feedstocks available in larger quantities that will not only increase the economic sustainability but will also reduce the environmental impact to the maximum extent. Moreover, suitable fuel additives can be used to substantially reduce NO_x emission while meeting standard fuel specifications.

Animal source derived biodiesel properties, emission and performance assessments

To overcome the cost pertaining to biodiesel feedstock, another alternative that has gained huge consideration is waste animal fats and oils available mainly in densely populated regions. The surplus availability of inedible animal fats has generally been much more compared to waste frying oils globally. In the earlier literature, it has been found that only in the US 2.5 million pounds of waste lipids are generated from restaurants which could be effectively transformed into valuable biodiesel (Rajak and Verma, 2018).

Animal fat resources (Chakraborty *et al.*, 2014) for biodiesel production include:

- Slaughter house animal fats: beef and goat tallow, pork lard, fleshing oil, lamb meat, goat fat and veal stock.
- Poultry farm animal fats: chicken or turkey fat, goose fat; duck tallow and feather meal.
- Waste fish oil.

Rendered animal fats and tallows, fish oil and other waste oil generate renewable and eco-friendly fuels. Again, fish oil generated from different fish processing industries were either discarded or sold at low prices as fertilizers or animal feeds. The optimum utilization of fish oil is in the field of biodiesel manufacturing. Furthermore, the presence of very low or zero toxins like sulfur, nitrogen and other harmful components in fish oil render clean-burning fuel that has also emerged as a cost-effective green alternative for diesel.

Table 6 illustrates the properties of fatty acid esters/biodiesel obtained from different animal sources. The competitive calorific value with diesel, higher cetane number and flash point make such biodiesel appropriate for CI engine. However, it cannot directly replace diesel owing to its higher viscosity and pour point, which would adversely influence engine performance. Again, kinematic viscosity values of some of the esters viz., poultry fat exceeds the limit set by EN14214 which thereby gets rejected as fuel blend in the diesel engine. Therefore, animal fat derived biodiesel has been generally used in the blended form with conventional diesel. Fig. 7 highlights the desired reduction in cloud point and kinematic viscosity through addition of diesel into poultry fat based biodiesel.

Likewise, researchers (Chakraborty *et al.*, 2014; Rajak and Verma, 2018) have tested animal fats and tallow derived biodiesel in CI engine and observed a significant reduction in emission compared to petroleum-based diesel. Fig. 8(a) indicated the emission from the diesel-biodiesel (from fish oil (FO) derived biodiesel (B20)) blend resulted the lowest HC emission followed by chicken fat (CF) based biodiesel due to the higher oxygen content of the fuel. The biodiesel obtained from mixed swine and chicken fat (SCF) produced lowest NO_x emission at lowest biodiesel blend and under full load condition with comparatively lesser CO and CO₂ emission than conventional diesel. Similarly, the smoke reduction was also achieved using blended fuel at low and medium engine loads.

Besides, waste animal oils and fats derived neat biodiesel was also tested in the CI engine (Fig. 8(b)). Results were compared with diesel and it was observed that NO_x, smoke and PM emission could be diminished in case of all kinds of biodiesel except poultry fat where rise in NO_x emission was noticed.

Notably, animal waste-derived biodiesel can serve as an efficient green diesel blend for effective management of waste oils/fats disposal problem in a sustainable way while benefitting the environment with comparatively much cleaner emission.

Table 6 Properties of biodiesel obtained from different feedstocks

Biodiesel source	Flash point, °C	Cetane no	Calorific value MJ/kg	Pour point, °C	Kinematic viscosity, mm ² /s
Beef fat		57.8	38.9	12	4.637
Beef oil	156.7	60.23	39.93	12	5.3
Lard oil	143.5	57.8	36.5		4.85
Veal		52.34	39.93		6.3
Chicken fat	177	54.8	39.93	– 5	4.94
Poultry fat	172		38.5		6.86
Fish oil	155	52.4	40.54		4.45
Pork lard		74	39.5	8	3.95

Note: Chakraborty, R., Gupta, A.K., Chowdhury, R., 2014. Conversion of slaughterhouse and poultry farm animal fats and wastes to biodiesel: Parametric sensitivity and fuel quality assessment. *Renewable and Sustainable Energy Reviews* 29, 120–134. Rajak, U., Verma, T.N., 2018. Effect of emission from ethylic biodiesel of edible and non-edible vegetable oil, animal fats, waste oil and alcohol in CI engine. *Energy Conversion and Management* 166, 704–718.

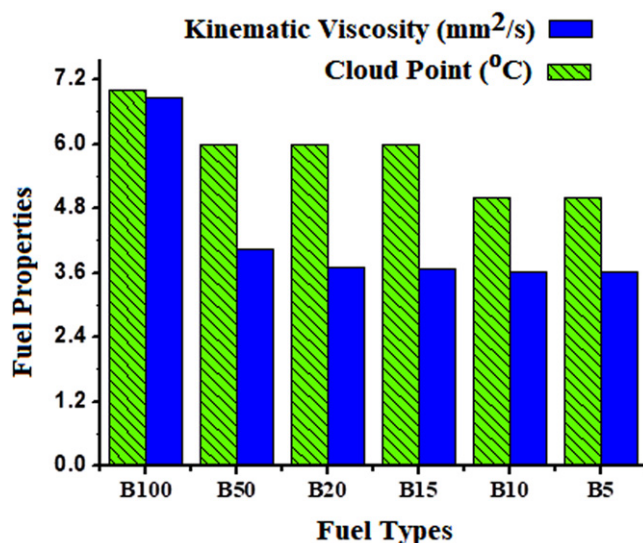


Fig. 7 Effects of addition of poultry fat derived biodiesel on diesel fuel properties. Reproduced from Chakraborty, R., Gupta, A.K., Chowdhury, R., 2014. Conversion of slaughterhouse and poultry farm animal fats and wastes to biodiesel: Parametric sensitivity and fuel quality assessment. *Renewable and Sustainable Energy Reviews* 29, 120–134.

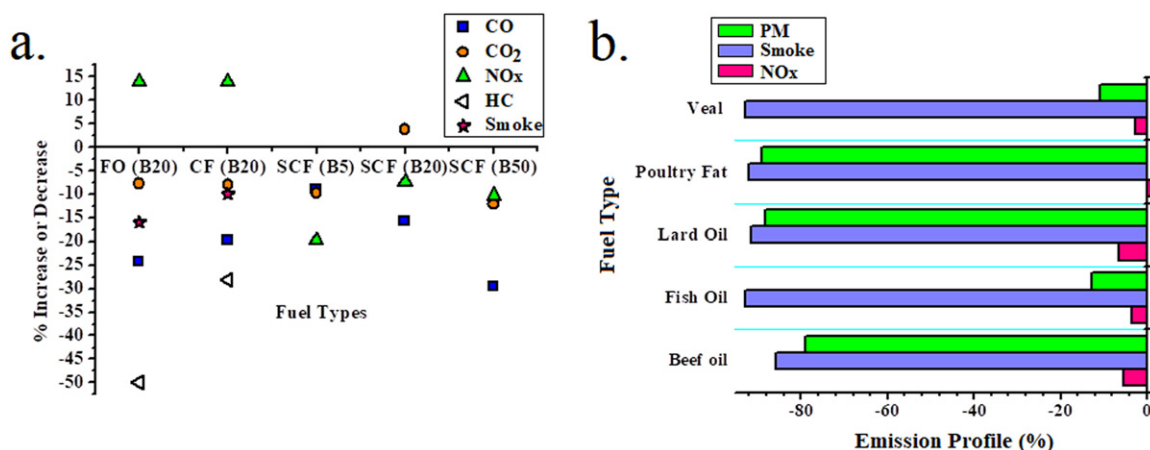


Fig. 8 Emission profile of a. Blended and b. Neat biodiesel in CI engines. Reproduced from Chakraborty, R., Gupta, A.K., Chowdhury, R., 2014. Conversion of slaughterhouse and poultry farm animal fats and wastes to biodiesel: Parametric sensitivity and fuel quality assessment. *Renewable and Sustainable Energy Reviews* 29, 120–134. Rajak, U., Verma, T.N., 2018. Effect of emission from ethylic biodiesel of edible and non-edible vegetable oil, animal fats, waste oil and alcohol in CI engine. *Energy Conversion and Management* 166, 704–718.

However, there are certain issues which need immediate resolution in order to facilitate its maximum use. The fuel property could be enhanced by reducing the viscosity of biodiesel. On the other hand, animal waste oils/fats derived biodiesel contains approximately 50%–70% unsaturated hydrocarbons which deteriorate its shelf life and make it susceptible to oxidation. Recent studies portray the application of long-chain alcohols like n-propanol and n-octanol which can improve the oxidation stability as well as depress the pour point to certain extents. Therefore, application of animal fat derived biodiesel along with long chain alcohols should be meticulously studied in order to gain perfect insight and to achieve a perfect blend that would not only have satisfactory fuel properties (meeting ASTM and EN standard) but will also nullify harmful emissions to the maximum extent.

Effect of HVO blending

HVO, a sulfur free liquid fuel, has similar chemical structure like conventional diesel. Therefore, application of HVO does not require any engine modification. The higher cetane number (79.5), lower CFPP (–35°C) and comparable viscosity (2.9 mm²/s) advocate for its suitability as a green diesel blend rendering minimal CO and THC emissions. HVO can be used in 20, 30, 50 and 100 vol% proportions. Notably, the NO_x emission for HVO blended fuel also depends on engine types; it has been found that NO_x emission is lower for vehicles equipped with selective catalytic reduction system compared to vehicles without any additional facility. Nevertheless, the exhaust emission profiles also depend on the characteristics of feedstocks used for production of HVO.

Table 7 Pyrolyzed oil (bio-oil) as diesel fuel alternative

<i>Fuel Source</i>	<i>Blends (%)</i>	<i>Engine characteristics</i>	<i>Citation</i>
Waste tires	20	1. BTE: Similar wrt diesel. 2. BSFC: 4% higher 3. HC: 14.2% lesser discharge 4. CO: 4.7% lower emission. 5. NOx: 40% more release	Sharma & Murugan (2015)
Municipal plastic	100	6. EGT: 8.3% higher temperature 1. BTE: 6% greater than diesel. 2. BSFC: 20% higher 3. HC: 3.12 times higher 4. CO: 40% more emission. 5. NOx: 42.85% lesser emission 6. Smoke: 25% more discharge	Chintala <i>et al.</i> (2018)

Effect of pyrolyzed oil blending

Plastic waste accumulated due to day-to-day activities raises a major environmental concern. Therefore, researchers attempted to tackle the issue by transforming mixed plastic waste into fuel through a thermochemical route that could be effectively used in transportation or industrial and other energy sectors. Varieties of plastics include HDPE, LDPE, PP, PET and PVC. However, since they occur in mixed form their separation techniques are cost intensive. Thus, in recent times electrostatic separation protocols were used to separate mixed plastics and served as the most cost-effective protocol. [Table 7](#) presents the performance of pyrolyzed oil either used directly or blended with diesel in CI engines.

It can be apparent from [Table 7](#) that, 100% of municipal plastic oil in CI engine renders a promising reduction in NO_x; however, other engine characteristics have deteriorated significantly. On the other hand, pyrolyzed tyre oil as 20% blend with diesel showed good performance except for higher NO_x emission. Again, the agricultural residue derived bio-oil (pyro-oil) also has a positive influence on engine performance and emission. Most common residues as feedstocks for pyrolysis include wood, coffee bean residue, mustard de-oiled cake, coconut shell, waste plant resources like mahua seeds, cotton seeds, karanja seeds, pine seeds etc., these also aids in the reduction of NO_x and HC emission.

Therefore more researches should be conducted to find out the optimum fuel blend that can advantageously affect all the fuel properties to render superior engine performance while achieving to the emission norms.

Commercialization of Green Fuel Blends

Blending of aforementioned green fuels with conventional fuel has tangible benefits on the environment owing to reduced GHG emissions and lower carbon footprint. Therefore, to commercialize the use of green fuel additives for the goodwill of mankind, the requirement of public awareness has become mandatory. With an ever increasing biofuel acceptance, the market growth of renewable green fuels is poised to increase; thereby, boosting the sales revenue and profit of the stakeholders. However, there are certain constraints that could act as a barrier in the commercialization of biofuel.

[Chen and Smith \(2017\)](#) elaborated about the hindrance faced by first-generation BE due to “food-vs-fuel” controversy along with the acceptance of second-generation cellulosic bioethanol in the U.S. This report also illustrated the three important barriers viz., biofuel production cost, competition between biofuels and petroleum fuels and policy uncertainty. The study also projected the fact that to overcome these existing barriers, additional focus would be required for further advancement in production technology along with involvement of more funding agencies for endorsing biofuel synthesis at commercial scales.

According to the EIA report, in 2017 approximately 14.39 billion gallons of BE was consumed with motor gasoline in the US; this depicts the huge market demand for BE alone ([Biofuels: Ethanol and Biodiesel, 2018](#)). Various commercial-scale bioethanol producers viz. POET-DSM Advanced Biofuels, Abengoa Bioenergy Biomass of Kansas, GranBio, Alagoas, are operational only in the U.S. which produce an average 75,000 tons of BE annually. Similarly, the Asian countries viz. Bangladesh, China, India, Indonesia, Malaysia, Myanmar and many others showed equal interests and have participated in the “Ethanol Summit of the Asia Pacific” to promote the large-scale ethanol production ([Ethanol Summit of the Asia Pacific Highlights Global Ethanol Use Opportunities, 2018](#)). Besides, Government of India also declared projects for setting up BE plants having production capacity of 1 billion liters per year ([India-proposes-new-bio-ethanol-policy-to-spur-rs-5000-crore-investments, 2017](#)). Indian Petro giants viz., Bharat Petroleum Corporation Limited (BPCL) and Hindustan Petroleum Corporation Limited (HPCL) have also signed MOUs to build commercial plants which will be operational in near future.

Likewise, global market size of BM is projected to flourish from 34 million \$ (2017) to 105 million \$ by 2022; thus, indicating a huge market demand of BM as the next-generation green fuel. Recently, BASF-SE has commercialized BM production and sales to customers in the brand name of EU-REDcert-methanol. Notably, EU-REDcert-methanol has been recognized by the European Commission under the Renewable Energy Directive (RED) as a standard to be used as a green fuel. Other multinational units e.g., BioMCN, Enerkem are pioneers in BM manufacturing where bio-methanol has been used as a building block for a range of synthetic alternative fuels.

Further, Bu being a potential green fuel blending stock, has gained equivalent attention like bioethanol and its global demand has reached 1.2 billion gallons per year. A joint venture of DuPont and BP Plc has invested in biobutanol production in large scale.

Biodiesel also occupies a major share in the renewable automotive fuel's market. The eco-friendly nature of biodiesel has increased its demand as alternative fuel in road and water transport sectors. The projected consumption of biodiesel will approximately reach 1 billion gallons only in the U.S. as per the forecasted data ([Biodiesel consumption in the United States from 2010 to 2025 \(in million gallons\), 2011](#)). At present, in the US alone, there are 124 commercial plants producing biodiesel with 2513.61 MMgy capacity. Thus, this ever growing commercialization of green fuel could eventually reduce carbon footprint through mitigation of GHG emissions from combustion of automotive fuels.

Conclusions

CI and SI engines have occupied a large market in on-road transport sectors because of high power output, durability and thermal efficiency of the fuel. Unfortunately, conventional diesel and gasoline emanate detrimental engine exhausts (greenhouse gases) which pose a potential hazard to humans causing life-threatening ailments due to enhanced carbon footprint leading to adverse global climate changes.

The present article illustrates the applications of different green fuel blends that can effectively reduce harmful engine exhausts while also improving the engine performance. Use of bio-alcohols as fuel-additives finds great attention due to its fuel efficiency and cleaner burning characteristics with extensive reduction in CO, CO₂ and HC emission. Even, bioethanol showed promising environmental and economic sustainability evaluated through LCA methodology. However, NO_x emission problem was not resolved at higher proportions of alcohol that renders benzaldehydes and formaldehyde emission causing severe damage to human health. Thus, more research should be conducted to find the optimal blending proportion along with selection of other oxygenates viz., acetone and higher alcohol (e.g., n-pentanol) for further benefits.

The inherent limitations were further attenuated by use of biodiesel derived from edible and non-edible resources including plants and animals. Animal-derived biodiesel alleviated NO_x emission to a greater extent compared to the biodiesel derived from plant resources while biodiesel derived from edible oil (e.g., soybean or sunflower oil) can completely substitute diesel in CI engines accordingly as revealed from LCA. In spite of several advantages of biodiesel as a green diesel blends for pollution reduction, still, the higher viscosity and pour point restrains its use as a neat fuel in CI engines which can be avoided by using long chain alcohols.

Again pyro-oil derived from waste plastics depicted good performance in improving exhaust emission (CO, HC and NO_x) attributes although the engine performance get deteriorated significantly with its use.

Thus, it may be concluded that blending of a specific kind of green fuel with conventional fuel may not favourably regulate all types of detrimental emissions and cannot simultaneously improve the engine performances. Accordingly, this field requires further extensive studies and experimental analyses that will facilitate in finding an optimum blend that will eventually serve as the most proficient green fuel alternative to mitigate global climate changes. Eventually, the ever rising public awareness has greatly encouraged a massive industrial production of green renewable fuels and their consequent utilizations in transport sectors which could significantly contribute in lessening carbon footprint and adverse climate changes through reduced greenhouse gas emissions.

See also: Is the Production of Biofuels Environmentally Sustainable?

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Green Manufacturing: Progress and Future Prospect

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Introduction

The term “green manufacturing” reflects the new manufacturing paradigm which supplies a variety of green policies, design and techniques to become more eco-efficient. The green strategies create products that consume minimum material and energy, alternating input materials, reducing unwanted outputs and converting outputs to inputs for creating recycling. This new paradigm “green manufacturing” is a result of market and technological drivers in the previous manufacturing paradigms. Advanced global warming, climate change awareness of the environmental risks is a result of the new green movement. The green technology with more eco-friendly product planned which helps to understand the green manufacturing aims in real practice. But nowadays, it has been seen that the interest of green manufacturing is mounting more among the research, policy makers and industrial communities a clear explanation of this term which is becoming much necessary. In this expanding urban era of the challenging world, resources and population has been found out major tribulations. The change and transform in environment through climatic change results to the imbalance of the earth. The ISO (International Organization for Standardization) has projected the new quality management system for products and environment. The main allowance is in reducing the environmental damage due to the industries. For suitable and sustainable development strategies, the new manufacturing procedure i.e., Green Manufacturing is very much necessary (Tan *et al.*, 2002). The rising demand and limited supply is the result of increasing cost of energy and resources but the trend of rising price can be projected for reaching successfully target of the companies among high price of energy and resources. While a price score may need the improvement is made to the product. On the other hand, stable prices may be assisted with mounted production efficiency, which can be achieved by diminishing resource consumption and refining the manufacturing system (Diaz-Elsayed *et al.*, 2013). Environmental issues and sustainability are very burning topics for planned business, manufacturing, product development decisions and management. In the recent year, awareness of the natural environment has return in environmentally conscious products. For lowering the environmental problem, concept of environmental management including green marketing, green organization and green production etc., are now being followed. Increasing international environmental conventions like Kyoto Protocol, Montreal Convention, Restriction of Hazardous Substances Directive(RoHS), Waste Electronics and Electrical Equipment (WEEE) and popular environmental consciousness of consumers would bring noteworthy impacts to businesses in the world (Chen *et al.*, 2006). For achieving the sustainable development, enterprises must adopt new technological process and redesign products for the problems of environmental solution (Nidumolu *et al.*, 2009). Liu *et al.* (1999) established the decision making model for green manufacturing. He examined the decision- making aim in green manufacturing, planned the decision- making objective system with five major variables. Xu *et al.* (2003) developed the green manufacturing model related meaning, mechanism, and implementation driving force.

Background

The concept of Green Manufacturing invented in Germany during the late 1980s and early 1990s. Bylinsky (1995) said that they had developed a global manufacturing standard instilling that any company willing to struggle globally must made products which can accomplish with the Green rules of European market. Programs or function regarding to sustainable manufacturing for reducing waste in production and pollution started from the 1980s. All concerned with sustainable manufacturing have been altered from process to product oriented which mainly focuses on reduction of resources, and toxic materials, energy and use of renewable materials (Seliger *et al.*, 2008). Fischer *et al.* (1997) who supported numbers of ways organizations have addressed these concerns like reducing waste, designed for recycling, and raw material consumption. In 1800s manufacturing has started from a small-scale production which developed to large scale mass production line to flexible production till 1980s. The era of customized, computerized and personalized manufacturing systems in 2000s, came into existence for mass production lines which benefited for the consumers with low cost and customized varieties of goods in mass production volumes (Jian, 2013). From the past century the demand of energy has been augmented a lot and to convert greener become a noteworthy topic in the research field for establishing more sustainable products locally and globally. Researchers, policymakers find the solutions concerning the green manufacturing in various fields have been taking places since 2011. For the solution concerning green manufacturing advised for adopting Additive Manufacturing (AM) processes including 3D printing to practice green process which reduces production steps and saves materials. The Additive Manufacturing, which is 90% energy efficient because of material loss (Ahn *et al.*, 2013). Baxter in 2001 finds out and examined the water consumption by measuring volume of daily wasted waters which regarded as one of the world's best ‘green’ strategic examples. These findings helped the company to rethink and redesign their water processing units in order to improve the wasted waters usage (Pirraglia and Saloni, 2012). Porter and Linde (1995) suggested that green manufacturing technique can be used for green industrial facilities through from workplace to improve the environmental outcomes of production processes. As per their result the green manufacturing can be adept by reducing the cost of raw material and reusing the recycled wastes, measuring the efficiency difference of production received by reducing the water usage and energy consumption and declining the environmental

impact on the public. They developed a tool as Life Cycle Inventory (LCI) for green manufacturing process which measures the compilation and quantification of the raw materials (inputs) and their emissions (outputs) for test production material throughout its life cycle. [Lele \(2009\)](#) analyzed the need for meeting individualistic customer demands brought about the introduction of flexible and mass customization techniques. Environmental protection laws, regulations and tax implications are already in put in many countries ([Gungor and Gupta, 1999](#)). While environmental regulations and public pressure, coupled with economic and technological factors have prejudiced industry worldwide to become more environmentally conscious and Green urged ([Shrivastava, 2003](#)). Green Manufacturing is gathering the needs of the present generation without giving concession to the ability of future generations to meet their own needs ([Mendler et al., 2005](#)). Green Manufacturing decreased to waste and pollution which measured the reduction of natural resources ([Cortellini, 2001](#)).

[Florida et al. \(2000\)](#) demonstrated the Green packing, distribution and EOL use into GM. [Atlas and Florida \(1998\)](#) examined that Green Manufacturing involves efficient production processes including source reduction, Green Design and recycling. [Gutowski \(2002\)](#) demand manufacturer's consideration for the environmental impact at all stages of the production process through resource saving, and components recycling. [Zhang et al. \(1997\)](#) analyses that Green Manufacturing technologies and design practices will permit manufacturers to turn waste into a gainful product. [Chien and Shih \(2007\)](#) Green Manufacturing technology through sustainable design of products and processes save energy and diminishes dependence on non-replaceable raw materials. Green Manufacturing is more than using Green resources which is based on manufacturing for reuse ([Bylinsky, 1995](#); [Norberg-Bohm, 1999](#)).

Importance of Green Manufacturing

The Green Manufacturing plant ends to reduce the Greenhouse gases produced by human activities on the environment which can range from complex industrial production processes ([Thurner and Roud, 2016](#)), associate with global warming, sustainability of cities, air contamination, waste, pollution, scarcity of energy sources and population growth. The greenhouse effect which caused by engorged greenhouse gas emissions including Carbon-di-oxide, Methane, Nitrous oxide and Fluorinated gases which originate trap heat in the Earth's atmosphere. Human actions like deforestation and burning of fossil fuels have provoked the greenhouse effect, resulting global warming which is affecting the environment in different ways like desertification, increased melting of snow and ice, sea level rise and stronger storms and extreme events, other effects are contain ocean acidification, variation in plant growth and nutrition levels, smog and ozone pollution and ozone layer depletion. Hence, we can infer that Green means ecological sustainability. Green innovation has also turned into one of the crucial strategic parameters to obtain sustainable developments in manufacturing industries caused by the escalating environmental pressure. In present day, strict environmental regulations and famous environmentalist have changed the competitive laws, rules and patterns for companies, whereas in previous, spending in environmental activities was considered as needless.

[Zhang et al. \(1997\)](#) has explained that if products lifecycle shift from the drawing board into the production line while the environmental attributes of it are basically fixed. Thus for estimation of the environmental consequences in each sector, support the design function with tools and methodologies is very necessary. [Liu et al. \(2005\)](#) advocated that Sustainable development is a key approach which environmental control and resource usage can be done, despite continuous expansion. Green technology is much needed for understanding the causal relationship between Green Manufacturing and corporate environmental performance. Rising industrial activities led to the global problem of unfavorable environmental impact. In order to get rid of it from the very source, Green Manufacturing. Life cycle analysis (LCA) are now being pursued urges [Rivera-Becerra and Lin \(1999\)](#). Thus Green Manufacturing is the only obvious solution for today's manufacturing scenario while many manufacturers consider environmental management as an integral part of economic development and a need for residual competitive in business ([Sawhney et al., 2007](#)). [Allen et al. \(2002\)](#) find out many relevant and related program of action and boost many aspects for the problem like waste, emission, energy usage, Greenhouse gases, and product recycling. [Seliger et al. \(2008\)](#) demonstrated that use of Green Manufacturing, proper use of resources and Green treatment are currently very significant issues for governments and industries worldwide. The scientific approaches have also been focused on the material level recycling. [Tseng et al. \(2006\)](#) advocated that minimizing wastes and emissions at source can improve the environmental and economic performance of an organization. Thus, it can be concluded that Green Manufacturing is an importance issue and it needs to be explored in detail at world level.

Transformation to Green Manufacturing

Green Manufacturing is an idea or a process which is a method for manufacturing that control pollution and reduces waste by proper design and process of product. It is the mandatory and responsibility of individual to conserve the resources for future generation which is main objective green manufacturing. They should also be aware related environmental sustainability and ascertain the acceptable level of toxic emission to the environment. Green manufacturing creates a status for public's savings on useless cost and promotes research and design where the process of green manufacturing involves investing in production process development rather than control technology, substitute renewable sources for finite ones, product recycling, and the companies must decide whether to make or buy the product. The mounting global environmental change and other features of environmental misconduct have given go up to concerns about economic enlargement more than the Earth's carrying capacity. Government's environmental aims should be accomplished in parallel with positive economic development; a transformation of the industry is needed. Most of the international organizations and developed countries have proposed various ideas and initiatives such as green economy, green growth, green transformation, sustainable transformation and green industrial strategy ([Luitkenhorst et al., 2014](#);

OECD, 2013; UNEP, 2011; World Bank, 2012). Green structural transformation means to change in the national economy in which carbon intensive industrial sectors minimized their share of the gross domestic product (GDP). Green transformation refers to processes within industries which lead to minimized environmental change impact (Growth Analysis, 2014).

There are three areas for the Manufacturing Companies to be focused including green energy, green products and green process.

Green Energy which created energy by natural sources including rain, tides, algae, sunlight, wind and plants and recycled it. Fossil fuels are a specific reserve which have been developed before millions of years and will continue to reducing with use. There are five energy sources like Municipal solid waste, Biomass- wood and wood waste, Landfill gas and biogas.

Green Products means “sustainable” which refer to products and service that utilized for economic betterment for sustainable development. Green products is characterized by Energy efficient and precaution for Ozone depleting chemicals, toxic compounds and nontoxic byproducts, plan for using recycled materials/content or from renewable and sustainable sources, acquired from local manufacturers or resources and easily reused either in part or as a whole.

Green Processes in business Operations: A green environment is a burning issue among social and business aspects. A large part of the global community is grateful to make actions toward an environmentally sustainable operation which reflects their social responsibility. This reengineering of business processes is characterized by areas of green which containing to efficient, effective, agile, necessary and measurable with life cycles. Therefore, framework includes five aspects focused on business processes with green process characteristics, merging business processes with the environmental standards, green business process redesign, training programs development and change management, performance monitoring and process improvement (Lan, 2013).

Environmental impact of all stages of production is essential for considering green manufacturing. The manufacturer should avoid from using any materials which are harmful to the ecosystem in the design, production, field application and end of life disposal stages of the product. Green manufacturing is also the expression of the sustainable development policy and the cycle economy mode in modern manufacturing. The following sphere are needed for green manufacturing including Recycling, Bio-degradable Materials, Alternative Energy (Wind, Solar), Waste-to-Resource (Biomass Pellet Fuel), Product and Packaging Design and Energy Efficiency (LEED and Automatic Doors). Implementation of green manufacturing needed the following principles: which contains eco-friendly materials and energy, prevent waste, specific separation and purification process, optimized utilization of mass, energy, space and time efficiency, design for durability not immortality, Minimization of material diversity, Utilization of local materials and energy flows, Using renewable resources (Pirraglia and Saloni, 2012)

Hence forces driving Green Manufacturing are related with five factors:

- (1) Increasing energy and input costs.
- (2) Awareness to consumer for Green products of the company.
- (3) Forcing regulatory environmental and waste management laws for the companies and pressurized to policy makers for following the same.
- (4) The companies must make technological advances for new business benefit.
- (5) Requirement for enhancing competitive differentiation between companies, particularly for first movers or those who are able to break the compromise between short-term higher costs and numerous benefits (example: brand premium, new customer segments) (Turner and Roud, 2016).

Green Manufacturing in Developing Nations With Special Reference to India

It has been seen that after the World War-II, industrial advancement has given a new dimension in the process of urbanization in developing countries, which also resulted in the human development. It is recorded that only 160 million people (one tenth of the then population) were living in the urban areas in 1900 but almost 3.2 billion people are expected to inhabit the urban areas in 2016. Most of this projected growth will be increased in the developing countries due to economic affluence, better social and civic amenities, degradation of rural areas and population increase. The industrialization has totally changed to the human settlement pattern and livelihood. It has been accounted that most of the jobs were in the agriculture fields only, confining the population to rural areas during the period up to about 1950, but now most of the jobs are in service sector which as a result of industrialization, pushed the people towards urban centers. Cities occupied about 2% of the world's available surface area. About 78% of carbon emissions estimated from fossil fuel combustion and cement manufacturing while 76% of industrial wood use occur in urban areas. It has been recorded that 60% of the total water tapped in the world for human consumption which consumed by the cities. It is also found that almost half of this water is used for irrigating the food crops consumed by city dwellers, roughly a third used for city industries and the rest used to meet the requirement of sanitation and drinking water (O'Meara, 1999).

The most serious problems facing the world today are: scarcity of water and food supply, extreme instability in energy and food prices, augmenting greenhouse gas emissions, severe income difference, chronic fiscal imbalances and terrorism (World Economic Forum, 2012) either from environmental mismanagement or dissimilarity, or both. Aside from the chronic economic imbalances that mostly concern the developed economies while developing countries are the most susceptible to all of these risks. The key question is if environmental aim can be resigned with growth and poverty reduction in the developing world. This report states that these objectives can indeed be pursued simultaneously in a mutually reinforcing way through green and inclusive enlargement. Advanced countries boards on huge industrialization through manufacturing for more benefits. Developing countries are also taking on similar plan to make the most of their natural resources. Nations have begun improvement their manufacturing methods through the adoption of eco-friendly processes. All over the world manufacturing companies have resorted to save

environment enterprise and marketing activities due to the expansion in the environmental complexity and mounting public demand to reflect on the effects of their activities in the environment (Kotler, 2011). In manufacturing industries, strategic approaches have been accepted by several firms to meet the concerns of stakeholders while producing goods that meet customer expectation related environmental safety (Hult, 2011). Customer expectations is the alteration in current products while bringing on board new products and processes objective for reducing environmental effect, but instead get better the environmental protection by firms (Cronin *et al.*, 2011). Studies have been conducted under various titles by academicians to find out the motives and processes adopted by firms to innovate in their product lines. Among these titles include green product innovation (Dangelico *et al.*, 2017), environmentally conscious product strategies (Pujari and Wright, 1996; Katsikeas *et al.*, 2016), eco-design practices (Sarkis *et al.*, 2010; Yu *et al.*, 2017), green product development (Chen, 2001; Johansson and Sundin, 2014) and environmental new product development (Pujari *et al.*, 2003; Jabbour *et al.*, 2015).

It is regarded that natural ecosystem and manufacturing have always been associated in some method. Enhancing output of manufacturing firms is the capacity to augment market sector for these products with making high profits on manufacturing. The ability of some on the other hand few firms ability like in those agro-industry to effect taken demand the operations of other manufacturers is likely to create sideway linkages, which originate from one firm making use of the by production waste taken out from initial production processes according to the Food and Agriculture Organization (FAO, 1997; Al-hassan *et al.*, 2013). FAO (1997) demonstrated that how manufacturing firms such as those in the agro processing sector add to the general enlargement of economies throughout the world. In spite of these advantages, the manufacturing sector also has pessimistic environmental impact including release of toxic waste into water bodies, and the release of toxic gasses into the air, thus affecting the clean air. Though these challenges exist, several nations lack the vision, plans and structures that are capable of overcoming these ecological challenges.

The rapid economic and industrial growth of India result to urbanization has come at the high cost of increasing Green Hough Gases emissions, growing demand for scarce resources such as mounting waste generation from urban centers. Today, India is the fourth largest economy in Purchasing Power Parity terms and the fifth largest Greenhouse Gases emitter in the world. In India, CO₂ emissions augmented more than 150% after China during 1990–2008. As per Confederation of Indian Industry (CII) and the Boston Consulting Group (BCG) report, India produced close to 4 million tons of hazardous waste from industrial and bio-medical sources which cause water and land pollution, while on the other hand e-waste is also becoming a major area of concern for India. Estimates suggest that only 3% of e-waste makes it to endorsed recycling facilities, with the rest either going into landfills or being processed at informal recycling yards. The said report advised that to overcome these challenges or at the very least to reduced their impact, the Indian manufacturing sector will need to take concerted action on all three areas containing Green energy, Green products and Green processes in business operations.

In Asia India is a third largest economy in Growth Domestic Production and as the one of the fastest growing economies in the world. In India, the gross national income was 105.27 trillion with an annual growth rate of 7.4% during the period of for 2014–15 (Economic Survey, 2014–15). It has been reported that services sector was the largest share in total GDP of India i.e., 57% (2013), followed by industrial sector 25%, and agriculture sector 18% (World Bank Development Indicators, 2015). Total population of India has been counted as 1.29 billion and its share was around 17.84% in the world population. At the global level in 2014 the economic growth has been noticed picked up in the last one year and it has been expected to further increase during 2015–16.

Table 1 shows the distribution of development in India and select countries. The economy in India should be develop for its achievement and further advancement but for developing countries like India, environmental consequences can be significant as it will place serious restraints on natural resources like land, water, minerals, and fossil fuels, driving up energy and commodity

Table 1 Distribution of development in India and selected countries

Country	GDP in billion (constant 2005 US\$) ^a	GDP per capita (constant 2005 US\$) ^a	CO ₂ emissions (MT) ^a	CO ₂ emissions (metric tons per capita) ^a	Energy use (kilograms of oil equivalent per capita) ^a	International Trade Balance in Goods ^a	Cash surplus/ deficit (% of GDP) ^a
Brazil	1206	5853	439.41	2.19	1391.90	– 4.13	– 1.84
China	5274	3866	9019.52	6.17	2142.81	370.02	–
European Union	15,372	30,241	3574.10	7.07	3253.82	134.78	– 3.63
India	1600	1235	2074.34	1.66	623.82	– 139.88	– 3.81
Japan	4780	37,595	1187.66	9.29	3545.60	– 120.64	– 7.97
Russian Federation	1000	6844	1808.07	12.65	5283.41	188.04	2.67
United States	14,797	46,405	5305.57	17.02	6814.82	– 727.15	– 7.56
South Africa	329	6086	477.24	9.26	2674.82	– 18.1	– 4.47
World	58,055	7996	34,649.483	4.94	1897.95	–	– 4.94

^aAl-hassan, S., Yussif, A-R., Mohammed, F., 2013. New ways of protecting the environment: The case of agro-processors in Ghana. *Journal of Economics and Sustainable Development* 4 (7), 83–91. Jindal, G., Manisha, G., 2012. Green computing future of computers. *International Journal of Emerging Research in Management & Technology* 12, 14–18 (ISSN-2278-9359).

Note: Data for various years: a2014, b2011, c2012.

Source: World development indicators (data.worldbank.org); from ORCD.

prices. The extent to which its economy “grow green” will depend on its ability for carrying economic growth which leads to enhancement of social equity and job creation. Green growth could play an important role in balancing this priority. However, managing economic shortage and public debts are two key challenges for national policy making, which could make technological change required for green growth more complicated. Hence, it becomes essential to understand and maximize the development benefits, such as income, energy access, and trade, of green growth involvement across all sectors.

As per Central Pollution Control Board, recorded that class I cities and class II towns in the country produced around 38,254 million liters per day (MLD) of sewage which only 11,787 MLD (31%) is treated and balance is discharged untreated. Forest Survey of India, 78.92 million hectares covered by forest and tree cover spreads across and represents 24.01% of the geographical area of the country. It has been accounted that rise in forest covered area by 5871 sq. km compared to 2011 assessment but there has been slight decline in moderately dense, and mount in open forest category. The decline in mounting stock of the country as 389 cu. m has been noticed during 2011–2013, which suggests a reduced in quality of forest in spite of the increase in forest and tree cover.

India has only 2.4% of the world's land area and harbors a significant proportion of recorded species. Of the 34 global biodiversity hotspots, four are present in India that including the Himalayas, the Western Ghats, the Northeast, and the Andaman and Nicobar Islands. International Union for Conservation of Nature Red List, 1039 species was categorized as threatened species for India in 2015. The National Institute of Hydrology estimates India is affecting towards perennial water shortage and found out that water availability in India to be 938 cubic meters per capita per year, which with less than 1700 cubic meters per capita per year is considered as water stressed. Additional water demand will increased from the domestic and industrial sectors where is an urgent need for water efficiency measures in all sectors, especially in irrigation, which is projected to be so even in 2025 and 2050. It has been found out from past studies and observations that the annual mean temperature of India has showed noteworthy warming trend of 0.51°C per 100 year, during the period 1901–2007 with augmented warming during 1971–2007 (Kothawale *et al.*, 2010). Warming trend in the Indian sub-continent and the ecological impacts expected with even 2°C of warming are quite intense in it where the situation could be much worse due to higher temperature rise as per projection of 2030. Energy supply in India is heavily dependent on fossil fuels with petroleum products and coal which accounting about 88% of the total primary energy supply. In 2012 as per International Energy Agency, India had more than 300 million people who were deprived of electricity and more than 800 million people were dependent on solid biomass as fuel for cooking. As per census of 2011, 43% of rural households used kerosene as primary energy source for lighting. Since energy access has strong growth implication, this is a serious challenge that the government is currently trying to address. Cities contribute to almost 2/3 of India's GDP (MOUD, 2015) and will assume even greater role as India embarks on higher economic growth. Indian cities faced severe challenges associated to quality and availability of infrastructure, such as power, telecom, roads, water supply, and mass transportation, which could pose serious constraints to economic growth if left unaddressed. It has been seen that the Government of India would like the manufacturing sector to play a bigger role in the economy of country. The Ministry of Commerce and Industry, Government of India has set a target to increase the sector's contribution to the Growth Domestic Production to 25%, from the current level of about 16% for growth strategy in green manufacture. The said growth is very much necessary for the country's environmental concerns need to be mitigated the manufacturing sector must use energy and resources efficiently for minimizing generations of waste. It is found out that even if every factory, power plant, car and airplane is shut down, the average global temperature would still increase by 0.6°C in this century. Green manufacturing engaged transformation of industrial operations in three ways: (1) Using Green energy, (2) developing and selling Green products and (3) employing Green processes in business operations. 92% of the companies surveyed are engaged in Green initiatives recorded as per a recent global survey by BCG.

There are disparities regarding for adopting Green across the sectors. Few sectors take it up due to regulatory compulsions (power), while others see it as an opportunity to build a stronger brand with consumers (retail). Steel manufacturers have adopted Green projected to stabilize mounting energy costs on the other hand automobile companies launch electric and hybrid cars to meet increasingly stringent emission regulations. The impact of Green initiatives also varies by the industry sector like green initiatives in the power sector have the greatest impact on reducing CO₂ emissions followed by transportation and then the industrial sector. Green manufacturing in India has been significant policy development and adoption by the manufacturing industry in the area of Green energy, there is substantial scope on both the policy front and its adoption in the areas of Green products and Green processes. Successful transformation into Green manufacturing will bring fabulous advantages for the nation development.

Green Manufacturing and Industry Perspective

Green as an Integral Part of Business leading Sustainable Development: At the same time, businesses can find approaches that will move towards social wellbeing, environmental protection and economic development. Sustainable development leads to adopt business strategies and activities to meet the requirement of the enterprise and its stakeholders today, while protecting, sustaining and enhancing the human and natural resources (Yang, 2017). But it has become a cliché that environmental problems are substantial, and that economic growth contributes to them. The common approach is stricter environmental regulation, which generally constrains expansion. Sustainable development in good business opens new ways for supplier as green consumers, environmentally safer materials and processes that invest in eco-efficiency and those that lead themselves in social well-being. Environmental challenges are forcing to alter the regulatory and market landscape of businesses tending towards green business and energy-efficient companies will be better able to navigate these regulatory changes and be better positioned to climate negative events like energy price spikes.

Also, nowadays end users like to buy safe, non-toxic, green products. Consumers are becoming more educated about their choices and are willing to invest more in a green product to participate in environment movement and to protect their family.

Recently, many of the world's leading organizations are investing billions of dollars into environmental sustainability programs which is a good indication that small business owners should follow these with following steps: Making green thinking a part of company culture, Swapping to LED Lighting, Eliminate plastic, Doing business with green vendors, Organizing a fund-raising event and Recycle and reuse.

Green Manufacturing in Traditional Industries

Nowadays relating with environmental movement, generally the relative impact and performance considering green energy vary significantly, depending on the intensity of energy and carbon footprint of the industry segment. Considering the emission of greenhouse gas, power generation is the highest emitter, followed by transportation and manufacturing. So, green initiating influencing the three sectors.

- (1) *Power generation*: Globally in 2008 average 20,000 TWH of electricity has been used, it is expecting this amount will be increased approximately 2.8% per year and in 2020 it will reach 28,000 TWH ([International Energy Agency, 2012](#)). Fossil sources such as coal, oil and gas produce three quarters of the current electricity which poses several challenges for human being.

(A) It is projected by 2020 that increasing global warming with greenhouse gas emission levels already exceeding 380 parts per million (ppm) and expected to reach 400–430 ppm (Inter-governmental Panel on Climate Change (IPCC)). (B) Energy prices are expected to rise, with scarcity of fossil sources, and creates global economic crisis. (C) The political instability in resource-rich countries has the industrialized nations worried about energy security ([Bhattacharya et al., 2011](#)).

In present days power-generation industries are adopting many green energy technologies which are becoming competitive with fossil fuels while others are still expensive (BCG report on potential of solar power generation: "Solar Storm", BCG report on alternate energy: "What's Next for Alternate Energy?"). The power sector need to develop a detailed understanding of the cost and development trajectories for renewable (Water, Biomass, Solar etc.) and include them in their fuel portfolios.

- (2) *Transportation*: It is another 'non-Green' industry problem for which governments around the world are aware. Due to strict Government policies, concerns of energy security and higher oil prices, and equally demand of enhanced public approval of Green brands, virtually all leading automobile manufacturing companies are in the path to control the CO₂ emissions of their vehicles and making it fuel efficient. Thus, the new clean propulsion technologies are adopted by the automotive industry containing power trains, electric cars and fuel cells. If the industry starts to control on the cost-benefit trade-offs in creating and owning a Green car and offering consumers an attractive value proposition, the share of these products could well reach close to 50% by 2020 (BCG report on increasing the potential of Green vehicle technology: "The Comeback of Electric Car?") ([Bhattacharya et al., 2011](#)).
- (3) *Manufacturing*: This sector also needs Green Initiative. Based mainly on fossil fuels, Steel is an energy-and-emissions-intensive manufacturing industry. The iron and steel industries account for close to 20% of all energy consumed by industries worldwide and about 30% of the world's direct industrial CO₂ (Greenhouse Gas) emissions, as per International Energy Agency (BCG report on sustainable steel manufacturing: "Sustainable Steelmaking") ([Bhattacharya et al., 2011](#)). Industry- caused CO₂ emissions aggregate about 25% of the total worldwide emissions with following:

Iron and Steel Industry 30%, Non-metallic minerals (e.g., Cement) 27%, Chemicals and Petrochemicals 16%, As per energy consumption 14%, Chemicals and Petrochemicals 28%, Iron and Steel Industry 20% and non-metallic minerals production 10%. Thus, for reducing Greenhouse gas emissions at the global level, improving energy efficiency of the manufacturing sector is very crucial. Policy makers are tightening controls and charging fines on GHG emissions and waste disposal and also nowadays financiers prefer companies maintaining environmental sustainability. Increasing energy prices also have influenced the competitive positioning of many industry. In case of rising fuel prices coupled with tightening environmental regulations and the challenge of maintaining competitiveness, must be forced that steelmakers should change their working conditions by both minimizing their energy intensity, and controlling environmental pollution. Energy-demanding industries always cost low levels of R&D spending rather than other industries such as semiconductors and pharmaceuticals. In spite of this challenge, quiet developments in energy efficiency continue to proceed within these industries. GHG emissions from the industries can be reduced with following three main ways: Enhancements in efficiency that can be applied through the recycling of waste materials and changes in the product design, Replacement of feedback, for e.g., Greater use of biomass and GHG capture and storage such as CCS. For sustainable energy consumption there are two main pillars:

- Energy efficiency
- Renewable energy use

These two pillars are deeply rooted in the foundations of energy policy in case of manufacturing and production. A multidisciplinary challenge combining science, ecology, information technology, technology and common sense, is achieving energy efficiency.

Emerging Technologies for Green Manufacturing

For making the traditional businesses Greener, and creating new business setup, emerging new technologies must be needed. Generally, there are five broad categories of technologies for reducing GHG:

Carbon sinks: With this developing technology, Carbon Capture and Storage (CCS) are made for using in power plants which are fired by fossil fuels such as coal. This technology enables capturing and storing CO₂ from fossil fuels, being trapped and stored in underground wells under severe pressure as liquefied form. Thus, it does not pollute the atmosphere. Efficient fuels: Using cleaner fuels such as hydro power, biomass, Integrated Gas Combined Cycle (IGCC), etc., for generating power also need some technology. Consumer Green: At the user end have to use clean and efficient fuels, for example, off-grid solar power applications like solar water heating and building insulation and solutions. Green transportation: Pollution less fuel cells, electric vehicles, and bio-diesel may use for green transportation. Industry efficiency: In traditional industries such as iron and steel, cement, refining, chemicals, etc., have to use green production methods and technologies (Jian, 2013).

Categorizing technologies based on two dimensions (maturity and availability), provides guidance in making business model choices. For example, based on relative technological and commercial maturity some technologies such as biomass, hydro and off-grid solar score higher, whereas other technologies like tidal waves, wind offshore and concentrated solar power are relatively nascent. Again, some are globally available technologies (IGCC and CCS), others (geo-thermal and waste to energy) are available in selected geographical places. Solar energy is generally cost effective, and in the areas of water and waste management many mature as well as emerging Green technologies are available.

Green Manufacturing From the Perspective of Green Information Technology

Today weather change, environment and climate change very big problems, there is no easy solution to minimize and control it, which is a big challenge in front of business world and it is impossible to ignore the ongoing awareness related same. Thus, the IT community have a significant role on the worldwide carbon footprint by adopting a 'greener' approach to computing. Green Information Technology is a collection of strategic which minimize to the carbon footprint of an organization's computing operation. Green Information Technology is not only practiced on minimizing the impact of the ICT industry but also using the services of ICT for reducing the organization's overall carbon footprint. The Green Computing, as defined in the Official Journal of the French Republic on July 12, 2009, the ESTs of information and communication for short eco-ICT, are information technology and communication which design or use can decrease the negative effects of human bustle on the environment. About 60%–70% energy is consumed by computers which are not in use but still turned on and that consumed energy is the main reason of CO₂ emission (Mittal and Kaur, 2013). Considering Jevons's paradox technological progress that increases the efficiency with which a resource is used tends to increase (rather than decrease) the rate of consumption of that resource. This paradox is well supported by Moore's law, 2005 which predicts exponential growth in the power density, and total power used for IT. On the contrary there is linear growth in power generation mechanisms (Harbla et al., 2013). The Grid Computing as a rising technology is a pivotal instrument that bridges the gap between being remote and industrialized. One of the prime movers in the technology that we have these days is the use of the grid computing. This technology allows for the distribution of the PC effectiveness where there is an extraordinary computing device with resources comparable to a super computer that acts as a "server" for a group of computers that then act as work stations which methodically work as a group in order to achieve a common goal.

In case of Green IT (green information technology) which is environmentally sustainable computing, procedure is to minimize the negative impact of IT operations on the environment by designing, manufacturing, operating and disposing of computers and computer-related products in an environmentally-friendly manner. It reduces the use of hazardous materials, maximizing energy efficiency during the product's lifetime and promoting the biodegradability of unused and outdated products. Green IT is also used technologies for redesigning of data centers and the growing popularity of virtualization, green networking and cloud computing (Xiang et al., 2016). Being Green means different things to different peoples. For some, it might mean buying technology that's more energy efficient than what they have & reducing the amount of electricity a data centers consumes. For others, it means buying hardware that is made of environmental friendly components. Yet others might seem at the end of hardware life and suggest that Green IT means proper disposal. The global green mantra is 3 R's that is "Reduce, Reuse, and Recycle" (Velte et al., 2008).

Technologies Green Computing: A VIA Technologies Taiwanese company which manufactures motherboard chipsets, CPUs and other computer hardware, that introduced its initiative for "green computing" in 2001. With this green vision, the company has been showing on power effectiveness throughout the design and manufacturing process of its products. Carbon-free computing: According to one of the VIA Technologies' ideas, is indicating to decrease the "carbon footprint" of users – the amount of greenhouse gases produced, measured in units of carbon dioxide (CO₂). Greenhouse gases are responsible for earth's more or less stable temperature as because it naturally blankets the Earth. For increasing the concentration of the main greenhouse gases – carbon dioxide, methane, nitrous oxide, and fluorocarbons – Earth's temperature is increased, which could lead to severe floods and droughts, rising sea levels, and other environmental effects, affecting both life, society and the world's economy.

Solar Computing: For solar computing, VIA partnered with Motech Industries, one of the largest producers of solar cells worldwide. As sun is rich source of alternative energy, amid the international race toward alternative-energy sources, VIA is setting its eyes on the sun, and the company's Solar Computing initiative plays an important role for its green-computing projects. Lead-Free and RoHS computing: No requirement of a lead bead, VIA's lead-free manufacturing technologies and the solder balls now consist of a tin, silver, and copper composite. Energy-efficient computing: The development of energy-efficient platforms for low-power, small-form-factor (SFF) computing devices (Jindal and Gupta, 2012) is a central goal of VIA's green-computing initiative.

Green Principles: Eco-Friendly Approach: It was realized that the conventional computers take much energy and produce heat. The main aim of the manufacturer is to decrease the e-waste in the environment. In these computers, hazardous material such as PVC's

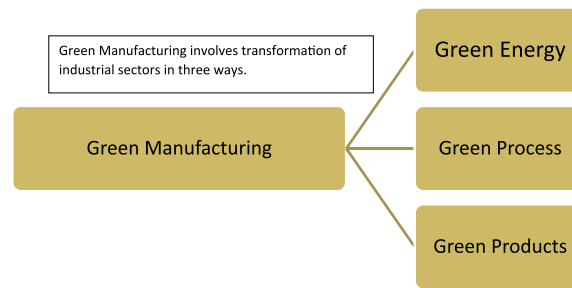


Fig. 1 Green manufacturing focus.

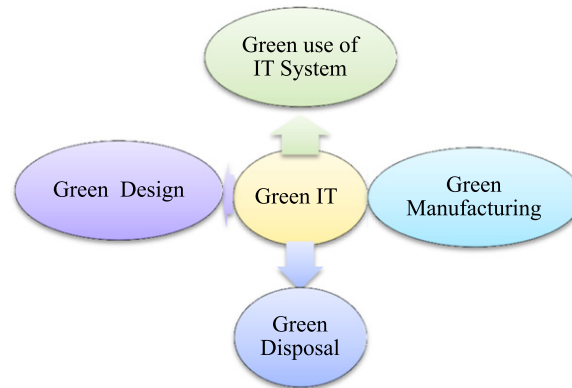


Fig. 2 Domains of Green IT. Reproduced from Murugesan, S., 2008. Harnessing Green IT: Principles and practices. IEEE IT Professional, 24–33.

brominated flame-retardants and heavy metals such as Cadmium, Mercury and Lead are not used like commonly used computers (Masood Anwar, 2013). The Green IT principles show the concepts of reducing the environmental impact. The Fig. 1 focused on different areas and activities. It presents the four green holistic principles. These principles are focused on different sectors and activities as follows: Green use – Decrease the energy consumption of data centers, computers and other information systems by using them in the environmental ways e.g., virtualization, turning off computer when not in use, etc., Green design – Energy efficient and environmentally sound components, computers, servers and equipment's have to be designed and also concern more on the future of electronic parts e.g., eco-friendly design, LED monitor, etc., Green manufacturing – A low or no impact on the environment should make an important factor in every process in manufacturing electronic components, computers and other associate subsystems. Green disposal –The plan should be made by company for refurbishment and reuse of old computers. Also, rules of recycling process for unwanted computers or other electronics components should be prepared (Fig. 2).

Benefits of environmental protection and cost reduction: Murugesan (2008) has identified the three drivers of Green IT as economical, regulatory and ethical. Bose and Luo (2011) also demonstrates that “the three primary drivers of Green IT” initiatives according to the literature including reducing costs due to budget cuts, decreasing consumption due to resource restrictions, and complying with the local law. Therefore, it is evident that Green IT aims at cost reduction as well as environmental protection (Tushi et al., 2015). Green IT Personalities, through discussion with IT and business decision-makers, four predominant Green IT Personalities emerge. The Green IT Personality Matrix plots Green Attitudes & Action on the vertical axis and implemented Green IT initiatives on the horizontal. The four personalities are Green Advocates, Smart Spenders, Green Seekers and Green Observers as Fig. 3 depicts this.

Green Awareness, Green Consumption: There are two major factors of consumer green awareness and green purchasing behavior: (1). Consumer's environmental concern, and (2). products functional attributes. Environmentally responsible purchasing is important for day to day life. People are changing their trends and way of lifestyle in a more conscious way paying more attention towards green consumption, relating with the environmental significance of purchasing, using, and disposing of various products, or adopting various green services. The social values of consumers are directly co-related with consumer's awareness of green products. Companies are used to adopt green advertisement strategies for creating positive green brand awareness. Relating with green awareness, green marketing also changes a wide range of activities such as modification of product, production process, packaging changes, as well as modifying advertising etc., for making business success and fulfill consumer's need.

Barriers to consumer's higher green consumption: For motivating consumers towards adopting sustainable green consumption, only a basic understanding of ecological and social problems might not be enough. For environment protection and a deeper thinking of the consequences of irresponsible consumption should play more effective role in making the consumer shift towards green consumption.

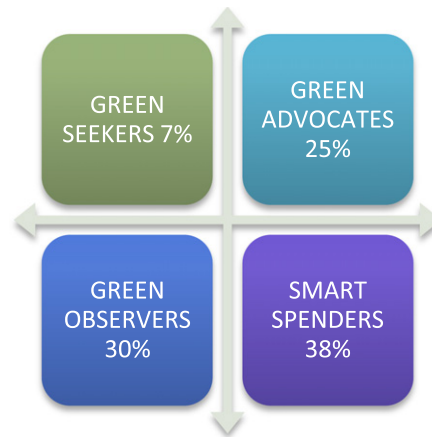


Fig. 3 IBM and Info-Tech Research Group, 2016.

Barriers to Consumer's higher Green consumption are related with some factors like Individual factors, Emotions, Habit, Recognized consumer effectiveness, Observed behavioral control, Values and personal norms, Trust, Knowledge, Situational factors, Price, Product availability, Product attributes and quality, Brand image and Eco labeling and certification etc.

Framework for adopting green manufacturing: Advantages and disadvantages of Green Manufacturing: At the time of converting the business into a green or environmental friendly, manufacturer, it obviously, decides to maintain certain values aiming towards the goal of protecting the environment as well as focusing on things viz technological innovation and progress. Serving to the Environment which can be directly protected by green manufacturing through reducing waste and harmful emissions and work toward protecting resources that are finite and nonrenewable. By green manufacturing, a business can also gain new customers as many customers want to support businesses which implement green manufacturing.

Improving the business: A company should improve its public relations by implementing green manufacturing as the end users are feeling the need of protecting the environment. As a result, it can lower costs for the business over the long term through the implementation of more efficient systems and fostering a company culture dedicated to innovation in processes. Also, these more efficient processes must result in lowering the amount of waste a business produces.

Remaining the transition: A business can experience relates to the transition to green manufacturing which is disadvantages of green manufacturing. Manufacturer has to continuously look for funding sources to finance for converting to green manufacturing. In a nutshell implementing green manufacturing can cost business significant amounts of money, although the process may save the business money at end. Over and above, this new movement requires not only the implementation of new manufacturing processes, but also the ability to design and build the necessary technology and machinery to support green manufacturing. Also, a business will discover new talent to come in and educate current employees on how to work in the new green manufacturing environment (Rusinko, 2007).

Disadvantages relating international trade: For going green, another important disadvantage relates to international trade. Many businesses stumble to implement a green manufacturing system because they scared about that this process will become a burden to the free flow of goods and profitable trade deals. This restriction can apply to a wide range of manufactured products and industries. For example, a business might restrict to start green manufacturing in anticipation of losing an international supplier who does not participate in green manufacturing.

Economic assessment and making strategic choices: An economic assessment requires estimating the 'value' generated over the long term through the green initiatives in case of adopting green manufacturing. It should maintain all parameters of value creation – from quantitative metrics like pricing power and cost savings, to qualitative ones like employee recruitment and engagement. Companies will get long term benefits of Green by following these. For an optimistic solution, companies have to be very clear vision about their strategic choice on how green manufacturing they want to be, and why. The potential impact (Bhattacharya et al., 2011) of sustainability efforts containing powerful brand and greater pricing power, Better operational efficiencies, More effective use of resources, Optimization of supply chain, Reduced costs and taxes, Increased ability to attract, retain, and motivate employees, Higher employee productivity, Enhanced customer loyalty, Improved ability to enter new markets, Promising sources of revenue, Operational risks, lower market, balance-sheet, Decreased cost of capital and Better access to capital, financing, and insurance.

Implementation Framework for Green Manufacturing

Plan, Execute, Communicate: There are approaches (Rusinko, 2007) to environmental practices: Pollution Control, Pollution Prevention and Product Stewardship. Pollution control, "end of pipe" approach, refers to the methods to trap, store, treat, and/or dispose of pollution. It is viewed as costly and non-productive as it represents an expense that yields no potential for competitive advantage. Pollution prevention reduces or prevents pollution and can result in lower costs, reducing the usage of resources, reducing

the amount of waste generated and recycling. So, resource productivity and competitiveness can be improved by product and process innovations which reduce or prevent pollution. Generally, pollution prevention is defined here as mainly manufacturing and operation oriented, Product Stewardship boosts the environmental outlook to the whole value chain and includes other internal and external stakeholders such as R&D, product designers and suppliers. It includes reconstructing products and processes to be more environment companionable, by using renewable resources and reassuring suppliers to practice pollution avoidance and product stewardship. Product Stewardship may grant the companies to gain competitive benefit through competitive preemption. With this, green manufacturer's reputation may attract new customers, and manufacturing quality will be enhanced. Thus pollution prevention and product stewardship can be specified to as environmentally sustainable manufacturing practices. There are some methodological limitations are found as competitive outcomes of empirical research on environmental manufacturing practices.

There are three-step implementation framework has to be maintained. *Plan*–Companies require to plan broadly to increase the use of Green energy, shift the product portfolio to Green products and business operations towards Green processes and future gain or loss. These are related to long term business. Green targets and metrics must be related with a sustainability charter, based on short term and long-term goals. Companies should develop Green indices or scorecards specifying the significance of the Green initiatives they have maintained. With this company's should agree for specific targets on those indices and point out progress against those targets (Eunsung and Sung-Yong, 2016). *Execute* – With green energy, green product, and green processes in business operation, a robust plan must be opted and targets clearly defined and monitored.

Conclusion

Generally, information about production, work planning and real-time information in manufacturing is actively related with energy management. For this, infrastructure for related information sharing, integrated monitoring, planning, control and analysis are necessary. So, integration of the energy management system with the information network is the requirement of Green Manufacturing system. Also, manufacturers would become not only consumers, but also suppliers by using their own energy resources. Prevention of environmental pollution, using renewable energy, applying legal regulations and fulfillment of stakeholders and customers' requirements are necessary tools to improve the performance of Green Manufacturing. Generally large manufacturing industries have capacity can heavily invest on the green awareness than small manufacturing capacity industry because larger industry invest much on green concept. In a nutshell, green manufacturing is more than a social issue. The benefits of adopting this technique and concerned costs are easily justified relating the benefits of adoption.

Implementation of Green Manufacturing technologies is not just a social compulsion but a growth catalyst. Adoption to green manufacturing has the possible to achieve sustainable development and eliminate poverty. So the leaders, society and leading businesses should be collaboratively engage in this conversion which will require a continued attempt on the part of policy makers and their constituents to re think and redefine traditional measures of wealth prosperity and wellbeing. It has been find out that a green manufacturing economy substitutes clean energy and low carbon technologies for fossil fuels, which addresses climate change, creates jobs and decrease import dependencies. However there are many perils and challenges along the way for the industries and for the government therefore taking these risks and facing these challenges would certainly assist any country to become a green economy with mounted manufacturing would also help in bringing about sustainable development.

See also: Green Energy Fuel From Biomass and Sea Water

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Green Mining of Rare Earth Elements (REE) to Diminish Greenhouse Gas (GHG) Footprint

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Introduction

The value of “Rare Earth Elements (REE)” which are often referred as rare earth metals is increasingly rising due to its many uses in today's high-tech world. Actually, REEs are used starting from miniaturization of electronics, to the enabling of green energy and medical technologies, supporting numerous of essential telecommunications and defense systems (Charalampides *et al.*, 2015; Dutta *et al.*, 2016; Schreiber *et al.*, 2016). REEs are the key ingredients of Cellular telephones, computer hard drives, electric and hybrid vehicles, and flat-screen monitors and televisions, significant defense applications include electronic displays, guidance systems, lasers, and radar and sonar systems. The amount of REEs used in high tech equipment is nominal but almost always significant to the unit's performance. REEs are called “technology metals” or “the seeds of technology” because of their unique magnetic, phosphorescent and catalytic properties. As per International Union of Pure and Applied Chemistry (IUPAC), rare earth elements are a set of seventeen chemical elements in the periodic table, specifically the fifteen lanthanides plus scandium and yttrium. Specific and compulsory uses of each rare earth elements are described in Table 1. Basically, REEs are divided into two categories based on their atomic number (Schreiber *et al.*, 2016; Suli *et al.*, 2017): Light Rare Earth Elements (LREE) having atomic number 57–63 (La to Eu) and Heavy Rare Earth Elements (HREE) having atomic number 64–71 (Gd to Lu). Minerals containing largely yttrium and HREEs include gadolinite, xenotime, samarskite, euxenite, fergusonite, yttrialite. Minerals containing predominantly LREEs include bastnasite, monazite, allanite, loparite, lanthanite, fluocerite, cerianite (Haque *et al.*, 2014). But, commercially used minerals or ore containing operable mines are bastnasite, monazite and xenotime. Rare earths are not actually rare rather they are available with broad geological distribution and their average level on earth crust is 150–220 ppm (Dutta *et al.*, 2016) which is almost equal or sometimes greater than any other metals mined for industries. Poor supply chain to fulfill the demand of rare earth elements for a nation creates the scarcity of REEs and make them as rare. The reasons are various. First of all, rare earth present in geological deposits in combination with other mineral, which makes the extraction process complicated, challenging and expensive. On the other hand, radioactive element like thorium and uranium co-exist with them; results radioactive emission on extraction of rare earth elements. Some mines are closed and not in use due to the environmental threat associated with exploration of REEs. Environmental concern is also associated with the processing steps of REE ore from mine into their elemental state. Use of acids and organic chemicals are the source of greenhouse gas (GHG) emission and environment footprint. Therefore, life cycle impact assessment (LCIA) is a necessary component of to operate REE production unit. Table 2 shows the few selected life cycle based environmental impact of few rare earth elements. Prediction and as well as speculation

Table 1 Industrial applications of REEs

Sl. No.	REE	Symbol	Atomic number	Use
1	Scandium	Sc	21	High-strength Al-Sc alloy, electron beam tubes
2	Yttrium	Y	39	Capacitors, microwave filters, glasses, oxygen sensors, radars, lasers, superconductors
3	Lanthanum	La	57	Glasses, ceramics, car catalysts, pigments, accumulators
4	Cerium	Ce	58	Polishing powders, ceramics, phosphors, catalysts, pigments, misch metals, U V filters
5	Praseodymium	Pr	59	Ceramics, glasses, pigments
6	Neodymium	Nd	60	Permanent magnets, catalysts, IR filter, lases
7	Promethium	Pm	61	Sources of measuring devices, miniature nuclear batteries, phosphors
8	Samarium	Sm	62	Permanent magnets, microwave filters, nuclear industry
9	Europium	Eu	63	Phosphors
10	Gadolinium	Gd	64	Visualization of images in medicine, optical and magnetic detection, ceramics, glasses, crystal scintillators
11	Terbium	Tb	65	Phosphors
12	Dysprosium	Dy	66	Phosphors, ceramics, nuclear industry
13	Holmium	Ho	67	Lasers, ceramics, nuclear industry
14	Erbium	Er	68	Dyes for glasses, optical fibers, lasers, ceramics, nuclear industry
15	Thulium	Tm	69	Electron beam tubes, visualization of images in medicine
16	Ytterbium	Yb	70	Metallurgy, chemical industry
17	Lutetium	Lu	71	Single crystal scintillators

Note: Charalampides, G., Vatalis, K., Apostoloplos, B., Ploutarch-Nikolas, B., 2015. Rare earth elements: Industrial applications and economic dependency of Europe. *Proceeda Economics and Finance*, 126–135. Dutta, T., Kim, K., Uchimiya, M., *et al.*, 2016. Global demand for rare earth resources and strategies for green mining. *Environmental Research*, 182–190.

Table 2 Carbon footprint of selected rare earth oxide production (impact analysis as per Australian indicator)

REOs	Primary energy (MJ/kg)	GHG (kg CO _{2-e} /kg)	Toxicity (^a DALY/kg) × 10 ⁻⁶
La	177	9.3	1.65
Ce	157	8.3	1.46
Pr	798	41.4	7.36
Nd	743	38.5	6.86
Sm, Eu, Gd (mixed oxides)	1074	55.6	9.89

^aDALY – Disability adjusted life years (unit of toxicity).

Note: Haque, N., Hughes, A., Lim, S., Vernon, C., 2014. Rare earth elements: Overview of mining, mineralogy, uses, sustainability and environmental impact. Resources, 614–635.

about the “peak oil” i.e., the theorized point in time when the maximum rate of extraction of petroleum is reached, after which it is expected to enter deadly turn down; but, similar type of study is also becomes inevitable for REEs and REOs because of increasing demand of rare earth elements and limited reserve of it. However, most of REE and REO are expected to be utilized in energy reduction, energy efficiency and renewable energy technologies. Consequently, most nations are motivated to secure REE by recycling or other preservation techniques and some countries relied totally on REE import. However, this trend is rapidly changing as China (largest producer and Supplier of REEs) government imposed restrictions on REE import (Haque *et al.*, 2014).

Recently, scarcity of energy and problems of environment become the major focus of global concern and thrust has been directed towards “sustainable development” in every nations. High and specified demand of rare earth elements for technological improvements and mitigation of energy issues are also acknowledged. But, problems related to abolishment between demand and supply of REEs creates large concern now-a-days. Moreover, environmental threats related to mining of REEs become the focus area. Practice of ‘green mining’ methodologies may result ‘green industries’ of REE. The objective of the article is to describe the review of the overview of green mining methodologies for REEs to overcome the threatening environmental aspect and to diminish GHG footprint.

Application of REEs

Use of REE in various sectors is considered as important tool for today’s advanced technological progress. The developed REO end-users markets consume mainly cerium (45%), lanthanum (39%) and yttrium (8.0%) (Charalampides *et al.*, 2015). Dysprosium, gadolinium, neodymium, and praseodymium oxides contribute the remaining 7.0% of total REOs demand (Charalampides *et al.*, 2015). REEs are used everywhere like in cell phones, laptops, televisions, hybrid cars, wind turbines, solar cells, hard disks and other many high-tech applications. Rare earth elements make the world’s strongest permanent magnets. These magnets are used in electronic motors to produce high power magnets in hybrid vehicles with smaller and light weight car. Miniaturization of hard disks used in electrical devices is also made by these powerful magnets. Neodymium and praseodymium are the REEs used in powerful magnets with little amount of dysprosium and terbium to allow them to retain their properties to higher temperatures too. REEs like europium, terbium and yttrium are used in energy efficient lighting (compact fluorescent lamps) and display panes (LEDs, plasma, LCDs) as phosphors. Cerium is used in catalytic converters which results better emission quality from a combustion engine used in automobiles. Emission of toxic gases like nitrogen oxides gets reduced by the use of RE in catalytic converter which helps to convert toxic nitrogen oxides to harmless nitrogen and oxygen, carbon monoxide to carbon dioxide and moreover oxidize unburnt hydrocarbons. Most of the cars now have these types of catalytic converters. Another important use of REEs is in rechargeable batteries. A mixed rare earth metal alloy is used as anode in NiMH battery; lanthanum is most widely used rare earth element in NiMH battery. Rare earths are directly used as catalyst in crackers used in oil refinery industries. On addition with glass, REO has the capability to enhance the glass property to absorb ultraviolet light by altering the refractive index. Yttrium is used in lasers. Neodymium and other REEs are used as dopants for the production of YAG lasers. The main industrial applications are described briefly listed in Fig. 1 (Dutta *et al.*, 2016). Even REs are added to aluminum, iron, steel and other metals to improve specific physical properties of alloys. REEs are doped with various compounds like ceramic glaze, barium titanate powder, ferrites for various types of improvement in their quality. REEs has great role in clean energy technologies like wind turbines, electric cars, solar cells and energy efficient lightening and rechargeable batteries. US department of energy (USDoE) assessed that REEs are widely used in various clean energy technologies and predicted (2010) that it need to grow significantly in next few decades for enhancement of use of renewable energy in different sectors. In order to evaluate the demand of REE using the present state of four technologies in 2016/2020/2025/2030, eight market scenarios are forecast including wind power, linear fluorescent lamps (LFLs), compact fluorescent lamps (CFLs), light-emitting diode (LED), electric vehicles (EV), electric bicycles, NiMH batteries, and catalytic converter (Kamenopoulos, 2016). The overview of the clean energy demand is presented in Table 3 (Kamenopoulos, 2016).

Distribution of REE

Though REE are relatively abundant in the upper part of earth crust but not always easy to exploration them commercially. The viability of exploitation usually depends on the geology, grade, tonnage, available processing technology and on associated cost.

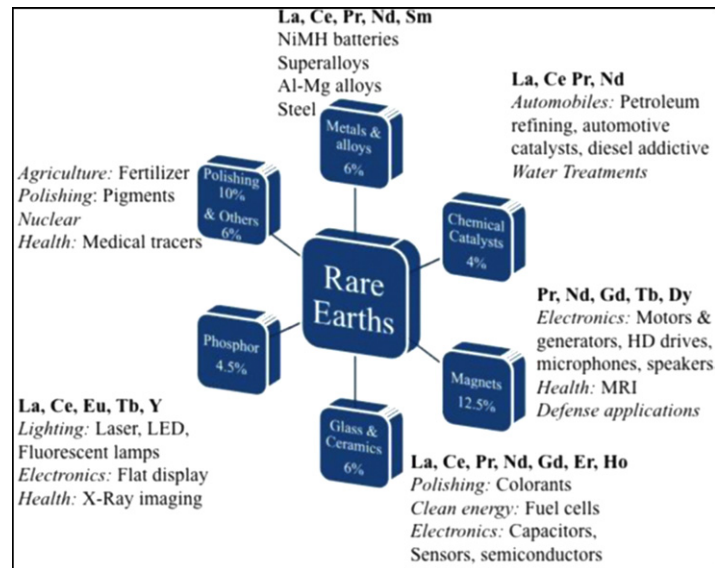


Fig. 1 Commercial applications of REEs. *Source:* Dutta, T., Kim, K., Uchimiya, M., *et al.*, 2016. Global demand for rare earth resources and strategies for green mining. *Environmental Research* 182–190.

Table 3 Overview of global clean technology demand in 2016/2020/2025/2030

Year	Wind power (MW)	Lighting			Electric vehicle		Batteries	Catalytic converter (MW) (Million cars)
		LFL (Million Cps)	CFL	LED	Electric cars (car)	Electric bicycles	NiMH batteries (battery)	
2016	63,350	2142	1903	2675	750,000	35,000,000	580,125	95
2020	79,005	1604	1491	4828	21,400,000	35,500,000	1,252,900	110
2025	76,810	1116	662	5874	7,953,375	36,300,000	715,803	111
2030	107,488	776	294	7146	29,523,323	37,000,000	2,657,729	171

Note: Zhang, F., Dongyuan, Z., 2008. Synthesis of uniform rare earth fluoride (NaMF₄) nanotubes by in situ ion exchange from their hydroxide [M(OH)₃] parents, *ACS Nano* 3, 159–164.

The global reserves of REEs are estimated at 130 million tones (as per report of United States Geological Survey, USGS, 2016); but only 0.1% of total reserve is now in use (Kamenopoulos, 2016). China is the biggest player in REE production; control 99.8% of world REE production. United States, Brazil, Australia, India, Malaysia are the important producer of REE in world market scenario. An approximate recent estimate about REE reserves by country is shown in Fig. 2 and estimated capacity of world reserve country wise is depicted in Fig. 3. The majority of the global REE production comes from four minerals: Bastnasite, Monazite, Xenotime and Loparite (Zhou *et al.*, 2017). Bastnasite in China comprises the largest percentage of global REE production, followed by monazite in Australia and India, loparite in Russia, and xenotime in Malaysia (Zhou *et al.*, 2017). The world's most popular and largest RE mine in China, Bayan Obo (Inner Mongolia), was initially identified as iron ore mine; was mined REE for long time; but production has been reduced its major ecological and environmental impact. Actually, REE has potential market in different sectors like catalysis, polishing, glass, phosphorous and pigments, metallurgy, batteries, magnets, ceramics and others. Considering all aspects, operation in Bayan Obo started production in huge scale with some steps for environmental remediation. Another biggest RE mine is situated in US, located in Mountain Pass, California. Though environmental issues are there also, but recently it is undergoing expansion and modernization. As per USGS report, a gigantic REE reserve was identified in the Helmand Province, Afghanistan. Ion-adsorption clay deposits, alternative REE reserve, are available in Southern China which marks environmental footprint in Jiangxi which has 2.3 Mt ion-adsorption RE reserves (Zhou *et al.*, 2017). Environmental impact is comparatively lower than Bayan Obo and Mountain Pass in the Mount Weld mine in Western Australia and in Malaysia.

Rare Earths Production Steps

REE production can generally be divided into the following steps (refer Fig. 4):

- (1) Mining and extraction: Removal of REE containing ore or specific waste fraction.
- (2) Concentration and purification: To produce pure REE containing mixture for separation.

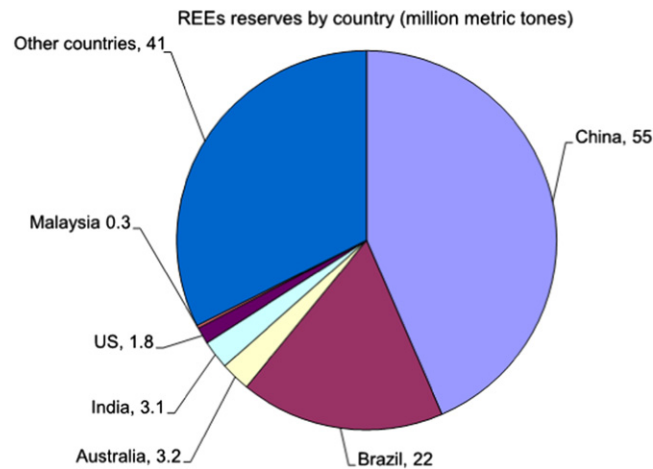


Fig. 2 Global REE reserve by country. *Source:* Kamenopoulos, S., 2016. Development of a framework and a decision support system for the sustainable exploitation of rare earth elements. Doctoral Dissertation.

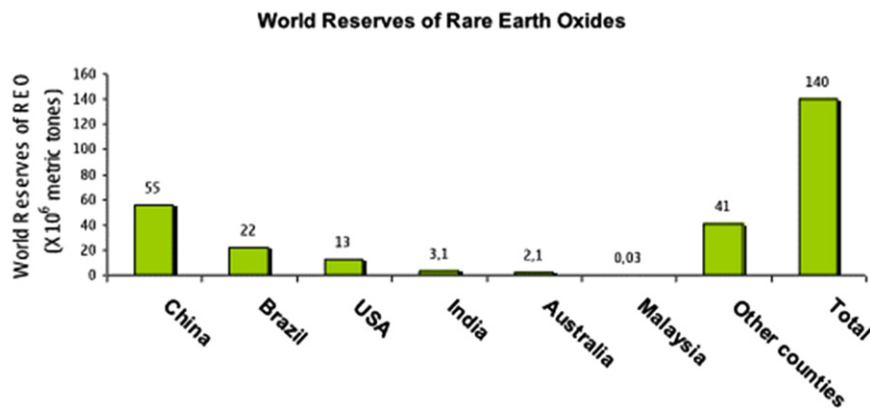


Fig. 3 The global rare earth reserves by country estimated by USGS, 2014. *Source:* Charalampides, G., Vatalis, K., Apostoplos, B., Ploutarch-Nikolas, B., 2015. Rare earth elements: Industrial applications and economic dependency of Europe. *Procedia Economics and Finance* 126–135.

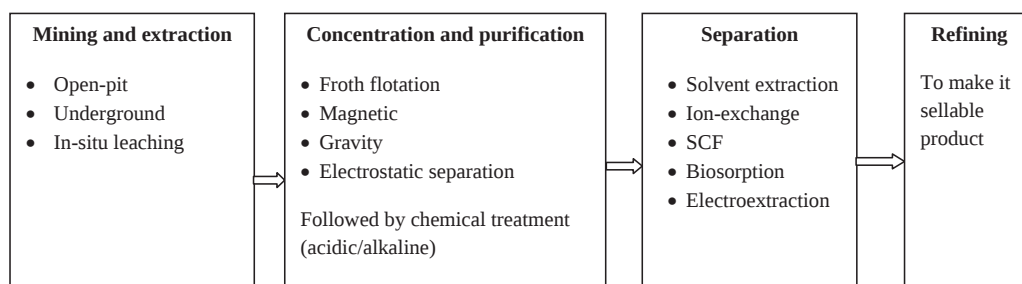


Fig. 4 Schematic of REE processing step. Reproduced from Haque, N., Hughes, A., Lim, S., Vernon, C., 2014. Rare earth elements: overview of mining, mineralogy, uses, sustainability and environmental impact. *Resources* 614–635. Reproduced from Schreiber, A., Marx, J., Zapp, P., *et al.*, 2016. Environmental impacts of rare earth mining and separation based on eudialyte: A new European way. *Resources* 5, 1–22. Reproduced from Suli, L., Ibrahim, W., Aziz, B., Deraman, I., 2017. A review of rare earth mineral processing technology. *Chemical Engineering Research Bulletin* 19, 20–35.

(3) Separation: To have different REE fractions.

(4) Refining: To produce a sellable product.

Rare earth resources are varied in their geology, mineralogy, and REE contents. A series of precise techniques are required to process various REE resources to extract commercially viable elements.

Mining and Extraction

Generally, rare earth mining can be open pit or surface mining, underground or leached in-situ (Haque *et al.*, 2014; Schreiber *et al.*, 2016; Suli *et al.*, 2017). A typical open pit mining is done considering ore composition, mining rate, stripping rate and rare earth oxide (REO) content. It is commonly employed in China, United States, and Australia. It involves taking out ores from the tunnels by blasting and transporting them to the surface for concentration of ore. If the ores are 100 m from the surface (Suli *et al.*, 2017) then only open pit method can be employed. Though this method is less expensive but usually not followed it leads large scars to the land surface and harmful to the environment too. It involves huge amount of water and energy usage. A large number of waste streams are also produced. In case of hard rock, both open-pit and underground techniques are followed like in Lovozero complex in Russia (Suli *et al.*, 2017). If the mineral is monazite type deposit then wet dredging is followed instead of dry mining. Though underground mines are considered as more expensive and unsafe than open-pit but still it is in use in some cases. In-situ leaching technique is followed in some special cases like for deposits in Southern China (Suli *et al.*, 2017).

Concentration and Purification

It is basically beneficiation process of RE bearing minerals for removal of undesired impurities from desired product by some physical means. Magnetic separation, froth floatation, gravity separation and followed by dewatering of minerals (thickening or drying) are followed in a sequential manner (as per the specification of the ores) to have purified ore sample for RE. All the physical separation is preceded by size reduction process. Suitable single or multiple physical separation steps are followed case wise as per composition of ore available. Table 4 indicates composition of an ore of Norra Korreudialite. It is evident that the RE ores are usually found to be combined with barite, fluorite, calcite, silicates and iron minerals which can be quite challenging to separate. The ores are crushed using double-stage jaw crusher first to a size less than 2 cm (Schreiber *et al.*, 2016; Suli *et al.*, 2017) and followed by grinding in a ball mill to finer size (40–100 μm) (Suli *et al.*, 2017). These finely ground materials are ready for next beneficiation steps like froth floatation, magnetic separation, electrostatic separation, gravity concentration, or a combination of all. According to Spedding's theory (Spedding, 1975), REEs have a series of electrons involving a shielded 4f sub-shell and these electrons have magnetic charge, and may results some degree of magnetism. If magnetic particles are present, magnetic separation becomes important before froth floatation unit. The ore-water slurry is prepared in a mixer and passed to froth floatation cell to separate the valuable metals and impurities. The depressant (include sodium silicate, sodium hexafluorosilicate, lignin sulfonate, or sodium carbonate) and collector chemicals (like hydroxamates, fatty acids, dicarboxylic acids, and organic phosphoric acids) are added respectively to prevent floating of unwanted mineral and to attach desired minerals with air bubbles respectively (Refer Fig. 5) The RE particles may require at least an estimated 40–100 μm size diameter for better attachment with the air bubbles and optimum froth floatation feed. If the minerals has huge specific gravity (from 4 to 7) (Suli *et al.*, 2017) then gravity separation is suitable to be applied. The enrichment in gravity settler or froth floatation cells may be up to 62%. The ore-water slurry is then de-watered using thickener and flowed by thermal process (e.g., drying) in rotary dryers or spray dryers.

The concentrated ore is then purified using chemical treatment methods to produce at least 90% purified product. There are two routes: acid treatment and alkaline treatment; combined known as 'cracking processes'. Sulphuric acid (H_2SO_4), hydrochloric acid (HCL) and nitric acid (HNO_3) are used in acid treatment process, while NaOH and Na_2CO_3 are commonly used in alkaline treatment. It is found that (Suli *et al.*, 2017) alkaline treatment is mostly applied in monazite and bastnasite (Suli *et al.*, 2017; Royen

Table 4 Ore composition of Nooakorr

Component	Mean value (%)
SiO_2	55.1
Al_2O_3	17.17
Fe_2O_3	5.35
CaO	3.17
MgO	1.31
Na_2O	9.00
K_2O	3.99
Cr_2O_3	0.01
TiO_2	0.33
MnO_2	0.27
P_2O_5	0.06
SrO	0.04
BaO	0.03
ZrO_2	1.18
LOI (loss on ignition)	2.7
REO (all rare earth oxides)	0.59

Note: Schreiber, A., Marx, J., Zapp, P., *et al.*, 2016. Environmental impacts of rare earth mining and separation based on eudialyte: A new European way. Resources 5, 1–22.

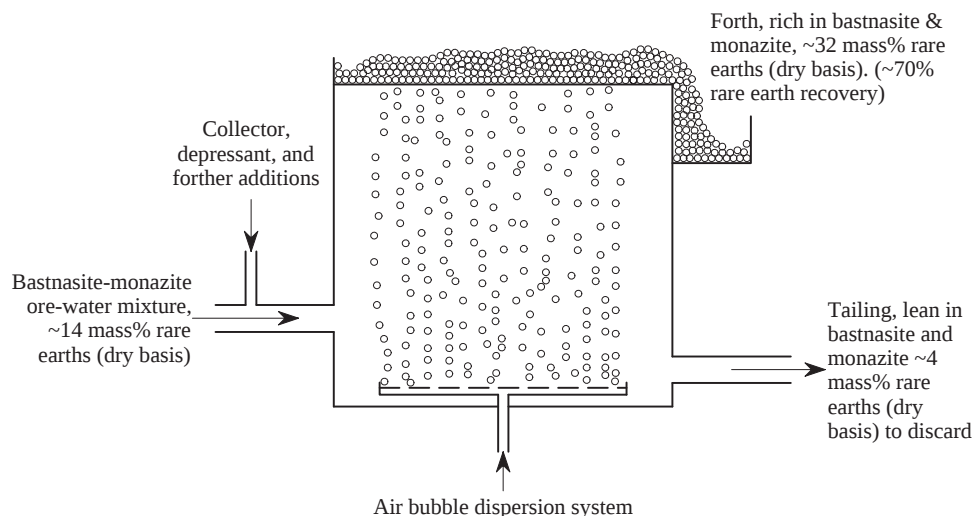


Fig. 5 Schematic diagram of Froth floatation cell. Reproduced from Suli, L., Ibrahim, W., Aziz, B., Deraman, I., 2017. A review of rare earth mineral processing technology. *Chemical Engineering Research Bulletin* 19, 20–35.

and Fortkamp, 2016) due to its phosphate and carbonate–fluoride content. Acid-roasting with sulphuric acid (H_2SO_4) at high temperature is used to remove fluoride (HF), sulfur dioxide (SO_2), sulfur trioxide (SO_3), and silicon tetrafluoride (SiF_4). Hazardous gasses including hydrofluoric acid (HF), acid sulphuric (H_2SO_4) and hexafluorosilicic acid (H_2SiF_6) will be adsorbed during the first and second scrubber before being released to the atmosphere. As acid treatment does not give a sufficiently clean product and does not recover phosphate of the minerals, caustic soda method becomes popular one. The acid treatment is currently apply at the Bayan Obo mine in China, but the alkaline treatment was apply by Molycorp at the Mountain Pass mine before the company closed in 2002. Various applied routes for various types' ore are described in Fig. 6 (Royen and Fortkamp, 2016). The leach solution from sulphuric acid digestion, contains other elements namely uranium (U), thorium (Th) and ferum (Fe). Thorium (Th) and uranium (U) are removed by following steps like sodium double sulphate precipitation, neutralization by ammonia hydroxide and neutralization by sodium oxalate. The caustic soda method begins with dissolving the mineral in concentrated sodium hydroxide at $140\text{--}150^\circ\text{C}$ to convert REE and thorium into their hydroxides (Suli *et al.*, 2017; Royen and Fortkamp, 2016). The solution is diluted with water which results precipitation of REE and thorium but phosphate remains in solution and can be recovered as tri-sodium phosphate (Royen and Fortkamp, 2016). Hydrochloric acid is used to precipitate REE selectively and thorium and other suspended material are removed by filtration.

Separation

The purified REE mixtures then undergo separation techniques to produce individual REEs. Due to having alike physical and chemical properties, it is very challenging to separate individual RE from each other. Some methods are followed to separate RE from the ores which are namely chemical precipitation (de Vasconcellos *et al.*, 2004; Panchula and Akinc, 1996; Queiroz *et al.*, 2002), reduction (Uda *et al.*, 2000), bio-sorption (Diniz and Volesky, 2005; Palmieri *et al.*, 2002; Kazy *et al.*, 2006), membrane extraction (Sugiura *et al.*, 1989; Kubota *et al.*, 1995), liquid membranes, solvent extraction (Yongqi *et al.*, 2008; Zhang and Dongyuan, 2008), ion exchange (Zhang and Dongyuan, 2008) and electro-winning (Enghag, 2004). However, supercritical, bio-sorption, electro-winning, solvent extraction and ion exchange are the five most standard methods for extracting REE. Solvent extraction or liquid-liquid extraction is the most popular large-scale separation method, usually carried out as a continuous multi-stage process of repetitive fractionation in a group of mixer settlers called “batteries” (Royen and Fortkamp, 2016). The REE-containing aqueous feed solution is first passed to a mixer to mix with an organic phase containing an organic solvation agent that forms complexes with REE ions. The ions are then extracted from the REE-enriched organic phase by moving it into contact with an aqueous solution where the ions have higher solubility. By adjusting the pH of the solution, scrubbing action can be done followed by solvent extraction to remove co-extracted contaminants from the organic phase. The most economical ion exchange techniques are employed to obtain high quality RE products either for electronic or analytical application. The organic extractant which are commonly used are di-2-ethylhexyl-phosphoric acid and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (Suli *et al.*, 2017). Most researchers are interested in REEs by supercritical fluid (SCF) technique, in which, REEs extraction are expected to be improved by means of increasing the mass transfer between CO_2 and REEs and the rapid and complete removal of the solute from the solvent is reached by means of gasification of carbon dioxide at atmospheric pressure, after the extraction. Ion exchange can be used in the next to produce very pure REE. An ion exchange resin captures the REE ions and the elution of REE from them is done using suitable eluent solutions, often containing certain complexing or chelating agents with different affinities for different REE. But, ion-exchange methods are time consuming and commercially it is only used to produce a few of the heavy REE (HREE).

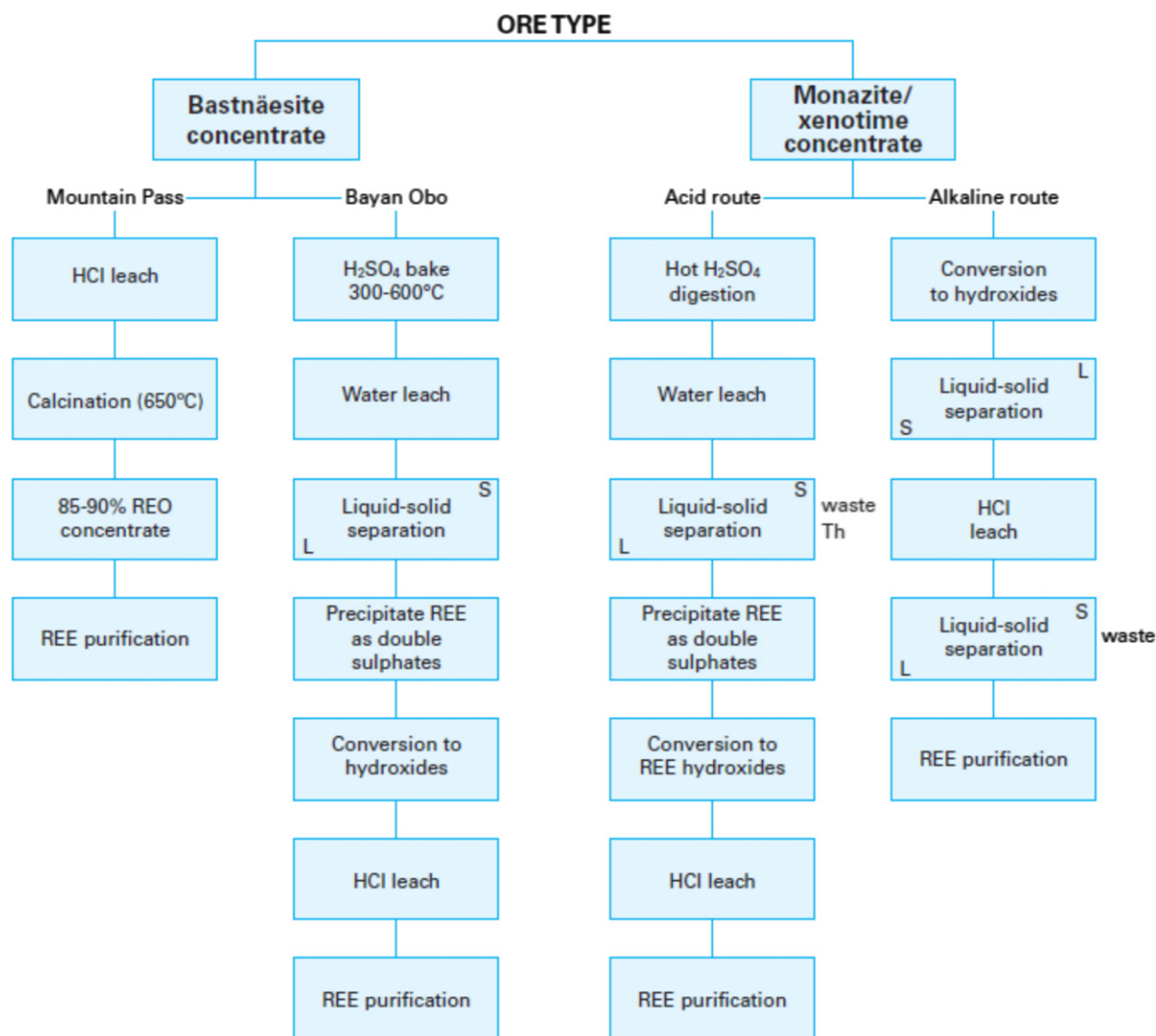


Fig. 6 Processing routes of extracting REE from different type's ore. *Source:* Royen, H., Fortkamp, U., 2016. Rare earth elements – Purification, separation and recycling. Report by IVL Swedish Environmental Research Institute.

Refining

It is basically a step of production of RE metal. Metals are produced by molten salt electrolysis and by metallothermic reduction methods (Enghag, 2004). It can results 99.99% purity of RE metals. Though the process is technically complicated and requires huge amount of electricity, but it is practiced well in China (Royen and Fortkamp, 2016). In metallothermic reduction, REO is treated with HF to form fluoride and removed along with calcium as liquid calcium fluoride. However, Sm, Eu, Tm and Yb have to low boiling points, so this process is not followed in this case and their oxides are reduced in a melt with metallic La, which has a very low vapor pressure. The reduced metals are vaporized and deposit on the walls of the tantalum container where the reaction takes place (Royen and Fortkamp, 2016). Barium can be used in place of calcium and mischmetal (i.e., a REE alloy typically composed of mostly of Ce and La with smaller amounts of Nd, Pr, other REE and iron) can be used instead of pure La. The main outputs of electrolysis process are CO, CO₂, C₂F₆, HF, CF₄ and dust (PM 2,5) with maximum amount of CO and high amount of CO₂ and dust too (Schreiber *et al.*, 2016).

Consequences of REE Mining and Processing

Rare earth mining and extraction procedures create enormous exploitation of earth's resources which results destabilization of soil and water ecosystems. One of the major concerns of REE mining from the primary ore deposits such as bastnasite and monazite is the resultant of radiological effects as REEs co-exist with radioactive minerals like thorium and uranium (Dutta *et al.*, 2016). REE mining directly affects some concerns like soil erosion, biodiversity loss, land use change, flooding, pollution of air, water and soil,

crop uptake of REEs and consequently leading to human health issues. It is worthy to mention that in-situ leaching lowers the ground water contamination, protects soil and vegetation. On the contrary, the expected environmental impact in relation to rare earth processing particularly linked with waste management and disposal of tailings which dictates importance to change in processing to recover rare earths from ores and other sources. The global warming potential impact or greenhouse gas (GHG) footprint of REE production is a serious concern today. The major donor to total GHG footprint is hydrochloric acid, followed by steam use and electricity. Overall 51% of GHG is due to use of energy in various forms (i.e., diesel, steam, fuel oil and electricity) (Haque *et al.*, 2014). The remaining minor elements are from other chemicals and transport. One report indicates that for the production of 1 tonne of REO in China are 60,000 m³ of waste gases, 200 m³ acidified water and 1.4 tonnes of radioactive waste (as most REE deposits contain uranium or thorium) (Royen and Fortkamp, 2016) are formed. The other important factor in relation with GHG footprint is the massive use of organic chemicals in solvent extraction step; requires the effort to reduce the use of organic chemicals to minimize disposal issues. Radioactive substance laden gases produced like sulfur oxides, hydrogen chloride, hydrogen fluoride and dust are the possible emission from REE processing unit which causes air pollution. Similarly, water contaminants are radioactive substances, heavy metals, acids, fluorides and large amounts of ammonium (Royen and Fortkamp, 2016). Aquatic eco-toxicity has a share around 22%–30% of the total impacts (Schreiber *et al.*, 2016). Above all, the environmental impacts depend on the ore grade and recovery of the particular REEs. The GHG footprint of separated oxides of REE from respective materials is shown in Fig. 7 (Haque *et al.*, 2014). Improvements on technologies starting from mining to processing of REEs are inevitable to sustain the REE industries in future days with minimal degree of environmental threats.

Mining of REE

The mining process of REE differs based on the type of ore being processed and the range of associated minerals. Bastnasite, Monazite and Xenotime are three significant rock forming minerals from which REE are extracted out. Bastnasite is a magma-derived fluorocarbonate mineral containing 65–75 wt% LREO and serves as major source of REE (Papangelakis and Moldoveanu, 2014). The two major sources in the world for lanthanides are bastnasite deposits at Mountain Pass, California, USA (devoted solely to REE production), and Bayun-Obo, Inner Mongolia, China (mined primarily for iron ore and REE as by-product). Monazite is a light phosphate containing rock associated with granites and beach sands in Australia, Brazil, India; comprising 55–65 wt% REO (Papangelakis and Moldoveanu, 2014). But, use of Monazite is decreasing due to radioactivity of thorium and radium. Xenotime is an yttrium rich phosphate containing rock with 25–60 wt% yttrium oxides; actually recovered as by-product of titanium, zirconium mining in Malaysia, Indonesia and Thailand (Papangelakis and Moldoveanu, 2014). Rare earth mining from its own ore (e.g., bastnasite and monazite) is not generally practiced because they occur as solid sediment and often lace up with radioactive element such as uranium and thorium. Radioactive elements production may occur simultaneously with extraction of rare earth elements. Thorium extraction always accompanies alpha particle emission, which can cause cellular damage when inhaled. Therefore, it is mandatory to have particular monitoring plan on REE extraction process.

Sedimentary Phosphate Deposits (Phosphorites)

Significant amount of REEs are found in marine sedimentary phosphate rock which entirely contained in francolite (Dutta *et al.*, 2016; Emsbo *et al.*, 2015). Compared to Chinese clay-type deposits, U.S. phosphate rock and its beneficiated equivalent are more

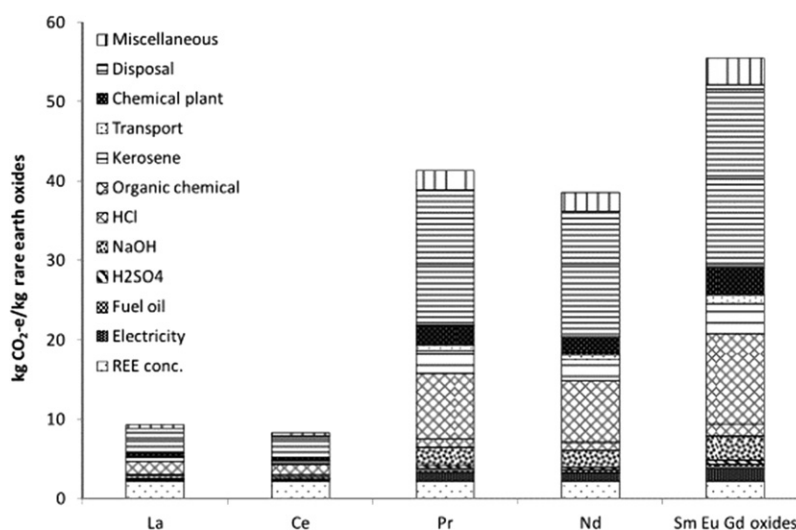


Fig. 7 Greenhouse gas footprint of some selected rare earth products. *Source:* Haque, N., Hughes, A., Lim, S., Vernon, C., 2014. Rare earth elements: Overview of mining, mineralogy, uses, sustainability and environmental impact. Resources 614–635.

enriched with REEs (total 500–2000 ppm of which 50–200 ppm HREs) (Dutta *et al.*, 2016). REE extraction from phosphate mining is encouraged now-a-days it does not associated with radioactive emission and radioactive waste production. On the other hand, REEs are easily extractable and extracted out concurrently when phosphate rock is dissolved in dilute sulphuric acid to produce phosphoric acid used for manufacture of fertilizers. Huge demand of phosphate fertilizers ensures the production of significant amount of REEs in an environmental friendly manner. Recently, apatite, another ore of phosphate deposits are investigated for production of REEs and results 0.1–1.0 mg/kg REO content. It is reported that 15% of total U.S. REE demand and specifically 65% of total U.S. HREE demand of 2014 is fulfilled by U.S. phosphate industry (Emsbo *et al.*, 2015). Actually, production of phosphate fertilizer from phosphate rock is in tough competition with REE production from phosphate rock because some phosphate occurrences suggest that REE can be mined more economically than phosphate fertilizers. In U.S., Palaeozoic phosphate deposits were identified (but not mined) (Emsbo *et al.*, 2015) which can be a future resource of REE. In Arkansas Love Hollow phosphorite deposits, 235 Mt of phosphate rock contains 1.3 Mt of extractable REEs of which 0.37 Mt are HREE which is roughly twice of HREE estimated for the South China clays (Emsbo *et al.*, 2015) and 60 times than Bokan deposit which yields 50% of REE projected global demand (Emsbo *et al.*, 2015). Therefore, abundance of phosphate rock and low-cost economic processing to produce phosphate fertilizer along with REEs manufacture in an environmentally friendly way makes the phosphate rock potential source to meet the global REE demand.

Ion-Adsorption Clays

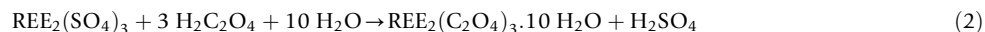
In 1969, the ion-adsorption clays were first identified as novel rare earth ore in Jiangxi province (southern China) (Papangelakis and Moldoveanu, 2014; Refer: Fig. 8). Actually, three types of industrial grade REE ore (mixed bastnaesite and monazite, bastnaesite and ion-adsorption clays) are available in China among which 2.9% of total REE reserves comes from ion-adsorption clay (JinYang *et al.*, 2013); which meets 26% of China's total demand which has reached 35% in 2009 (JinYang *et al.*, 2013). Ion-adsorption clays have different REE content from that of bastnaesite and monazite and its REE distribution varies significantly from location to location, but they all appear to have much higher content of some highly valuable HREEs than bastnaesite and monazite. REEs present in ion adsorption clays are in the form of trivalent cations adsorbed on kaolin, which brings the relative simple and ease of extraction.

Ion-adsorption clays are formed due to physical, chemical and biological weathering of REE rich granite and volcanic rocks under humid, warm and slightly acidic conditions in subtropical zones. As per the report (Papangelakis and Moldoveanu, 2014), weathering crust are divided into four layers; (a) an upper humic layer of quartz, organic matter and soil with very low REE content, (b) strongly weathered layer enriched with REE along with kaolinite, halloysite, quartz and mica, (c) semi-weathered layer with kaolinite and sericite and (d) weakly weathered bottom layer with same mineral composition a host rock. Layer (b) contains most of the REE and layer (c) also contains REE but less in extent. Ion-adsorption clays contains 0.05–0.3 wt% rare earths out of which 60%–90% occurs as physically adsorbed trivalent cations which are easily extractable by ion-exchange leaching using inorganic salt solution of monovalent cations (JinYang *et al.*, 2013). Various methods of mining and corresponding leaching methods are followed in different cases. Heap, tank/pool leaching and in-situ leaching both are practiced in various places. In a specific inorganic salt solution, REEs are desorbed by substitution reaction forming monovalent ions and transferred into the solution as sulphates or chlorides, following a 3:1 stoichiometry and then precipitated as oxalate which then converts to REO and individual REEs are separated by dissolution in HCl and fractional solvent extraction. Sometimes ammonium bicarbonates are also used for precipitation of



Fig. 8 Ion-adsorption rare earth mining in Ganzhou, Jiangxi Province. Source: JinYang, X., Lin, A., Li, X., *et al.*, 2013. China's ion-adsorption rare earth resources, mining consequences and preservation. *Environmental Development* 8, 131–136.

REEs. Following Eqs. (1–3) are followed sequentially to convert REE containing ore to extracted REEs (Dutta *et al.*, 2016; Papangelakis and Moldoveanu, 2014):



Initially, opencast mining was followed with NaCl solution followed by oxalic acid precipitation (Papangelakis and Moldoveanu, 2014). But it resulted poor yield, poor product quality along with enormous overwhelming environmental impact like severe loss of vegetation and biodiversity, soil erosion and water contamination. Next, in batch and heap leaching, ammonium sulphate was used instead of NaCl which requires less in amount than NaCl due to increased desorption capabilities of NH_4^+ as compared to Na^+ and led to improved final product purity. But, this technology is also discarded as it is based on batch, heap leaching which lead to environmental problems due to mining-related deforestation and discharge of wastes. Continuous practice of heap leaching outcomes a great ecological and health damage in southern China. In-situ leaching replaces the heap leaching in China first and which is currently practiced to overcome the problems associated with it. In-situ leaching using ammonium sulphate gives best product quality and yield without surface vegetation clearing and soil disturbance. Fig. 9 describes the various routes of in-situ leaching methods followed in Southern China (Vahidi *et al.*, 2016). The basic principle of in-situ leaching is addition of leaching solution by injection directly into the natural orebody and recovery of the pregnant solutions for precipitation of REEs. Leaching holes with a depth of 1.5–3 m and diameter of ~ 0.8 m are drilled 2–3 m apart for injection of $(\text{NH}_4)_2\text{SO}_4$ (Papangelakis and Moldoveanu, 2014) at high pressure. It takes up to 400 days and ultimately 85%–90% of REE is extracted. Therefore, a comprehensive geological study of the site in order to determine hydrological structure of area, ore characteristics, grade and rock infiltration properties are prerequisite to carry out in-situ leaching.

Coal and Coal By-Products

There are different types of coals available and have their different types of ashes. Certain types of coal have fairly high concentration of REEs, on the order of 100 ppm. Coal and coal by-products are a potential source of REEs estimated amount in the range of 50 million metric tons (Charalampides *et al.*, 2015). It is reported by the researchers from West Virginia University and National Technology

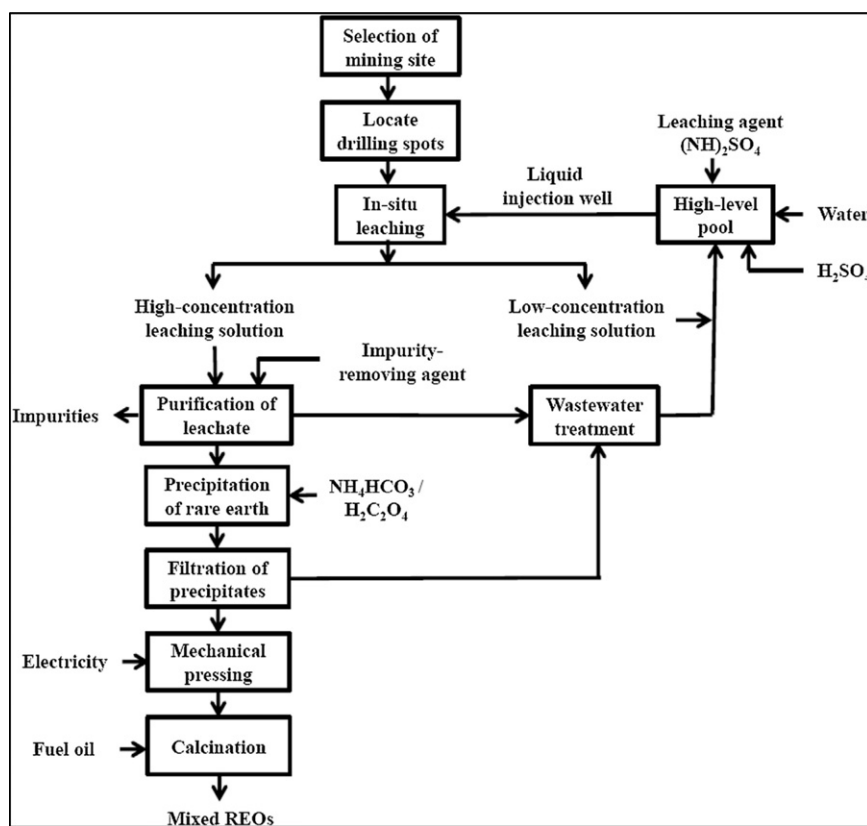


Fig. 9 Flow diagram of ion-adsorption process followed in Southern China. Source: Vahidi, E., Navarro, J., Zhao, F., 2016. An initial life cycle assessment of rare earth oxides production from ion-adsorption clays. Resources, Conservation and Recycling 1–11.

laboratory that various valuable REOs are available in the acid mine drainage found at various coal mines. REEs are recovered (around 89%) by ionic-solvent extraction technique using ammonium sulphate and is then mixed the leached and filtered solution with an ionic liquid (1-butyl 3-methyl imidazolium chloride) and a deep eutectic solvent (2:1 urea/choline chloride, M/M) as lixiviants resulted in 80% and 71% recovery of REEs respectively (Dutta *et al.*, 2016). This ion exchange is more environmentally friendly and requires a reduced amount of energy. Ion exchange comprises rinsing the coal with a solution that releases the REEs that are bound to the coal. Actually, REEs can be obtained in cleaner way using coal and coal mine waste. The U.S. could soon decrease its dependence on importing valuable rare-earth elements that are widely used in many industries, according to a team of Penn State and U.S. Department of Energy researchers who set up a cost-effective and environmentally friendly way to extract these REEs from coal by-products.

Fly Ash From Fossil Fuels and Other Wastes

REE extraction process from fly ash of fossil fuels is recognized as less cost intensive than that mining from a raw product. Moreover, coal fly ash (CFA) contains full range of REE, whereas most mines have only a few types of these elements. This is why; many companies are discovering methods to extract REE from coal fly ash and considered the CFA processing as more economical and environmental friendly routes over traditional mining (Mayfield and Lewis, 2013). Study of fly ash from Jungar power plant, Inner Mongolia, China discovered that the concentration of REEs were greater in the finer sized fractions of fly ash than coarser one (Dutta *et al.*, 2016; Dai *et al.*, 2014). Still, the feasibility of recovering REEs from fly ash of fossil fuels are needed to be investigated more. Though there is no commercial leaching technology to leach REEs from coal ash but various laboratory methods are reported already. In acid leaching method, dilute sulphuric acid is used to dissolve REEs from fly ash. But, the efficiency of extraction is not good enough (highest leaching efficiency 45% and lowest 8%). Sometimes, instead of sulphuric acid, hot nitric acid may be used followed by solvent extraction using a mixture of tri-butyl phosphate and kerosene. In alkali leaching method, ammonium carbonate can be used to leach mainly yttrium.

Actually, South Korea has deficiency of REEs and imports of that from China are inevitable. Export of REEs from China is now limited; so alternative routes are devised in South Korea. Actually, coal ash samples from various industries like coal power plant has higher quantity of yttrium than coal. Therefore, coal ash samples are investigated already to find out higher range of REEs in South Korea (Thriveni *et al.*, 2013).

Sustainable Methods of Mining of REEs

Sustainable mining practices are nothing but to address the environmental, economic, health and social impacts and benefits of mining through the participation of investors. In the United Nations RIO + 20 conference (2012), resolution was taken that mining activities should maximize social, economic benefits and as well as effectively consider the negative environmental and social issues. Therefore, government needs strong initiative to develop, manage and regulate their mining industries for sustainable development. 'Green Mining' is best solution as it follows economic cycle and reduces environmentally objectionable emission. Demand of use of REEs in various applications is increasing day by day and mining of REEs has a long disagreeable past of environmental damage. Therefore, sustainable methods of mining (along with 'Green Mining') need to be practiced in a bigger shape.

REE Waste Management and Recycling Methods From Magnets, Batteries and Phosphor

Recovery of REEs from waste during production, landfills and end of life consumer products is referred as 'urban mining' (Dutta *et al.*, 2016) and recycling is needed to satisfy the increasing demand of REE and shortage of materials associated with supply issues and more specifically restriction imposed by Chinese authority. It ensures several benefits like lower environmental impact, less dependency on Chinese export and availability of radioactive contaminants free feed materials (Haque *et al.*, 2014). Moreover, it is experimented that discharge of REE waste causes deadly contamination of surface water and soil which can be minimized by 'urban mining'. A great challenge in recycling method lies in its low yield due to lack of established design or methodology to recover REE from wastes and it is believed that REE cannot be recycled back as it is always used in minute quantities. Among the post production waste or post-consumer disposed goods, used magnets, batteries, phosphor lightening and spent catalysts are important. Table 5 indicates the possible end-of use products to recycle specific REEs and their percentage recovery from the products.

Permanent magnets consist of neodymium-rich alloy with smaller amounts of Pr, Gd, Tb, Dy and other metals (Royen and Fortkamp, 2016). 30% of magnetic alloy simply become waste during production which is invariably recycled back. Permanent magnet containing electronic waste always shredded and melted down for recycling of other metals; REE present in it are oxidized and removed as smelter slag (Royen and Fortkamp, 2016). Various lab scale experiments are reported for efficient removal of REEs from NiMH batteries. In 2013, Honda and Japan Metals and Chemicals (JMC) proposed the recovering technique of REEs by use of molten salt electrolytes from NiMH batteries (Royen and Fortkamp, 2016). After collection of scraps, they dismantled and calcined-pulverized those into powder which are separated as different fractions. REEs are recovered as a dissolved phase in acid. Molten salt electrolysis is followed then to produce REE in metal form. In 2012, Rhodia (part of Solvay Group) took initiative to

Table 5 List of REEs recovered from end of use products (studied in 2016)

Order	Recycle	REE	% Recovery
1	Motors	Nd, Pr, Dy	82
2	Permanent magnets	Nd, Pr	93
3	Fuel cell catalysts	Pt	76
4	Phosphor lamps	Eu, Y	100
5	Oil refining catalyst	La, Ce	NA
6	NiMH battery	Nd, Sm, Pr, Ce	98.1
7	Fluorescent lamps	Eu, Y	99.9

Note: Dutta, T., Kim, K., Uchimiya, M., *et al.*, 2016. Global demand for rare earth resources and strategies for green mining. *Environmental Research*, 182–190.

recycle REE from old lamp phosphors in France (Royen and Fortkamp, 2016). Series of methods are followed to separate REEs from phosphor lamps like (Royen and Fortkamp, 2016);

- Froth floatation and physiochemical method: Under a controlled pH values (below 4.5), halophosphates are efficiently separates phosphor using this method. Though floatation is more difficult for separation of phosphors powders than mineral processing because of its complicated components and lower size, still it is in use. Density based separation also can be used using diiodomethane which has intermediate density among heavy phosphors and light halophosphates. Difference in magnetic susceptibility and photochemical reduction are also used for separation.
- Acid extraction method: It is an wet technique to recover REEs from waste spent fluorescent tubes. Nitric acid, hydrochloric acid or sulphuric acid are used as leaching agent. But, sulphuric acid is the most preferred among three acids. Some reports are (Hu *et al.*, 2017) available on use of supercritical carbondioxide containing tri-*n*-butylphosphate, nitric acid and water to separate yttrium and europium up to 100% (Hu *et al.*, 2017).
- Alkali fusion: it is basically high temperature, high pressure process. It is used after the acid leaching step to disintegrate the substances to prepare soluble fraction. NaOH, Na₂CO₃ and Na₂O₂ are commonly used fusion reagent.
- Solvent extraction: When water containing REE substance comes in contact with suitable solvent, REEs are separated very efficiently. It is reported that lanthanum (III), europium (III), and lutetium(III) were extracted by bis(4-acyl-5-hydroxypyrazoles) derivatives (Hu *et al.*, 2017). High recovery rate and good purity of the product are obtained by this method. A study in China reveals that to recover REEs from phosphor are 25% naphthenic acid ratio, 20% isooctyl alcohol, 55% sulfonated kerosene, phase comparison 1:1, and balance water phase pH 4.5; under such conditions, the REEs extraction yield is nearly 99.78% (Hu *et al.*, 2017). A new type of solvent, ionic liquid (IL) like functionalized IL betainiumbis (trifluoromethylsulfonyl)imide, [Hbet][Tf₂N] is recently used for selective dissolution of phosphor without leaching other constituents of waste powder like glass particles, alumina etc. ILs provide environmentally friendly and efficient alternative to traditional acid leaching.

There is no report yet to recycle REEs from spent catalysts. It is also regarded that substitution possibilities from energy efficient lightening systems (compact fluorescent lamp, LED, plasma display, LCD display) or catalysts in automotive and petroleum refinery are still complex and need further research.

Strategies for Promoting the Preservation of REEs

Rare earth elements are important constituent for clean energy technologies. Apart from energy sector, REEs are essential element for defense related technologies and weapons. Continuous supplies of REEs are absolute necessary for sustainable growth of a country. China is the only dominant global supplier of REEs. But, recently China has begun to close the export of REEs which creates shortage in supply of REEs in global market. It is reported that projected global shortage of essential REEs has started in 2014 and gradually it is increasing day by day. To tackle the China's monopoly in REE trading, administrative policies are developed and implemented to enhance recycling and preservation of the resources. Community awareness programs are also devised to improve the recycling and preservation of REEs. Several strategies are followed to preserve REE resources (Dutta *et al.*, 2016) like (i) developing strict industrial standards and laws for REE, (ii) avoiding illegal mining and centralized management of REE resources, (iii) developing integrated REE market pricing and distribution, (iv) arrangement of various programme to combat environmental problems associated with REE industries, (v) encouraging and implementing laws for recycling of REE from their potential waste and (vi) use of electro recovery solution using ionic liquids instead of acid leaching in conventional mining of REEs. All the strategies are basically judged based on diminishing carbon footprint by REE industries and balance between focused demand and supply of REEs.

Conclusion and Recommendation

The recent technological advancement is with the help of unique characteristics of REEs. Use of REEs in renewable energy applications is one of the most important aspects for growth of REE industries. Till date, China controls the global market of REE;

so it is necessary to identify alternative producers of REE to create competition in trading and as well as to fix the market price. Immediate adverse effects of REE mining like soil erosion, loss of biodiversity, flooding, pollution of air, soil, and water, and crop uptake of REEs, consequentially leading to human health issues; proposes the need of framework for sustainable development of REE mining projects which refers to five basic “overlapping” circles: economy, society, environment, technology, and geopolitics. Research is carried out to overcome the environmental issues related with conventional mining of REEs. Moreover, ‘green mining’ strategies are in practice which refers to “low production, high efficiency, low emission”. Recent global agenda is “exploitation of resources-environmental protection-sustainable development of mining area” for resource handling (Shi, 2012). According to ‘green mining’ initiative, 2012, millions of dollars are invested in mining research in countries like Australia, US. Exploring other sources of REE apart from its ore becomes the prime research topic in this area. It is worthy to mention that recycling and recovery of REE poses challenges in terms of energy to collection, reprocessing and reproducing products at specifications. It is sure that REE or products from REE will be the decisive factor of global economy in near future. But, over a longer time, nanotechnology may replace various critical materials like REEs or it may happen as they will require in lesser quantity. The exclusively environmental perspective of this review research paper is therefore addressing only one aspect of decision making and needs supplemented by economic and social assessment.

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Hybrid Renewable Multigeneration: Low Carbon Sustainable Solution With Optimum Resource Utilization

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Introduction

According to the report of the Brundtland Commission, sustainable development is said to be “the development that meets the demand of the present without compromising the need of the future generations.” Presently, sustainable development is an important goal in the present days globally. But the scientists and the policy makers are facing severe challenges to find out the appropriate means to achieve the sustainable development goals. It is very difficult challenge for the energy sector to attain these sustainable development goals. This is because till date the entire world is dependent mainly on coal for electricity generation. Nearly 41% of the world's electricity is generated by coal. On the contrary the coal reserves of the world are depleting fast. Coal based power emits 0.975 kg of CO₂ for 1 kWh of electricity generated even in best practices (Hammond and Spargo, 2014). So continuous efforts are made to find out alternate sources of energy. The renewable sources of energy may be a better sustainable option than fossil fuels. However, renewable resources have serious limitations. The most prominent limitations are their generally dilute nature and intermittent availability. Developed technology till date is also not suitable to substitute fossil fuel based systems in full to meet the electricity demand of the world.

To develop a useful renewable energy system at a locality, the resource estimation of that particular location is very important. Battery storage may be integrated with renewable energy systems to accommodate intermittency. However, battery storage have limitations like high initial cost, lower capacity, lower life and disposal problem due to detrimental environmental effects. For a sustainable energy system cost effectiveness and environmental friendliness are two most important priorities. The term “greenization” of energy systems addresses simultaneously the issues of increasing the energy efficiency and the introduction of new energy systems under 3S criteria where 3S stands for “Source, Systems and Service” (Dincer, 2016). Service means the utility service which a particular form of energy gives to the society. Say for example the energy stored in oil is used in the transportation purpose. In this case oil is the source, using it in an engine is the system and transportation is the service. The greenization of the source includes the introduction of renewable. The greenization of systems includes process integration and better efficiency of the system. Thus a renewable based multigeneration addresses both of these issues simultaneously. Moreover multigeneration is also viewed as a more efficient method of utilization of natural resources (Serra et al., 2009).

In this article, the emergence of multigeneration as a low carbon technology is reported. Various aspects of design of multigeneration system is discussed. The importance of multigeneration as a potential option of sustainable energy system is also discussed.

Review of Low Carbon Technologies

In present practice, most of the secondary energy generation is through combustion of fossil fuels. These fossil fuels emit carbon dioxide and other greenhouse gases during combustion resulting to global warming. Hence, to reduce the global warming effect, low carbon technologies are inevitable. The low carbon energy technologies are mostly renewable using resources like solar, wind, biomass, tidal, geothermal etc. Till now renewable energy harvesting technologies are not so matured to meet the energy demand of the whole world. Moreover, renewable energy sources suffer from the serious limitations of generally dilute nature and intermittency. Technology is yet to be matured enough with proper devices for capturing and harvesting these resources of energy in a large scale. The share of different types of energy in the global energy mix is shown in Fig. 1. Though presently most important fuels in the generation of electricity worldwide are coal natural gas and oil, all of these resources are depleting fast and they emit greenhouse gases (GHG). Even the demand for coal increased at a rate of 6% per annum and the demand for oil by about 12% per annum in the last five years. So it is a need to develop alternate low carbon technologies for future energy sustainability. Prospective methods, presently visible for transforming the energy sector to be low carbon are shown in Fig. 2. Decarbonization, i.e., making the energy sectors a low carbon one may be done in a number of ways. More use of renewable resources of energy generally helps to achieve low carbon energy sector as renewable resources are either carbon negative (say solar, wind etc.) or carbon neutral, say biomass.

Higher energy efficiency, specifically for using fossil fuels is a decarbonizing measure as it helps to consume fewer amounts of input fuels for a required output utility. For fossil fuel based power plants efficiency improvement measures reduce the carbon footprint. On the other hand, renewable resources of energy are mostly intermittent in nature. These may not be available at the time when these are required. So either through storage or by means of hybridization the gap between demand and supply may be accommodated. At a particular time of the day, one or more resources may not be available but the others may be available for use. At night the solar energy may be absent but the biomass resources may be utilized for electricity generation at that time.

What is Multigeneration?

Multigeneration is the process of generating multiple utility outputs from one or more inputs. In multigeneration, process integration and intensification increase the efficiency of such an energy system. Several attempts have been made for

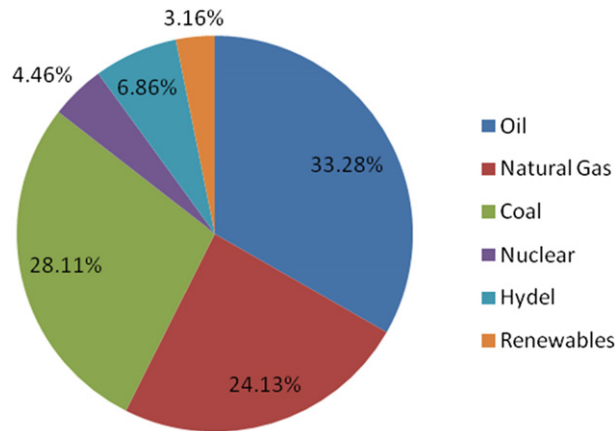


Fig. 1 Percentage share of different shares of energy in the global energy mix.

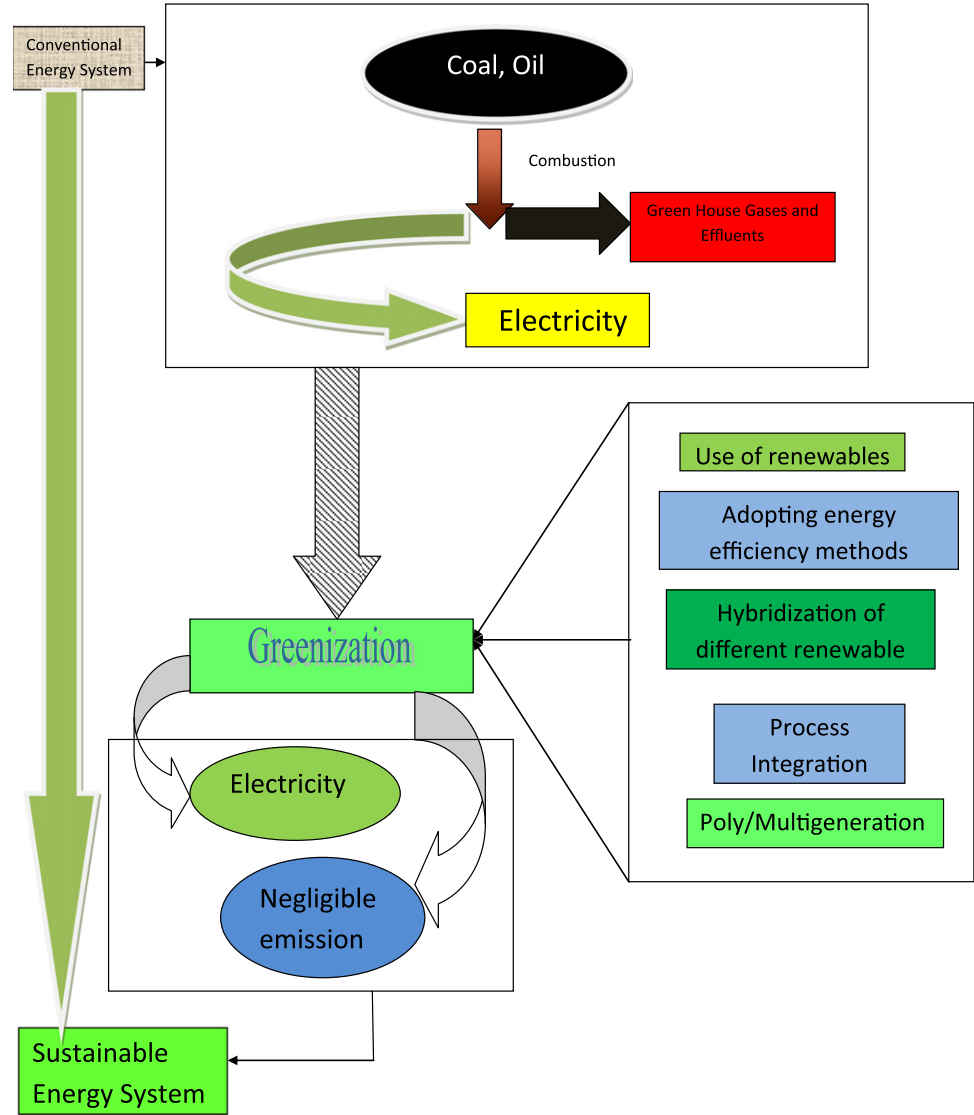


Fig. 2 Transition from Conventional Energy System to Sustainable Energy.

process integration for decarbonizing energy systems. Multi generation is one such advanced development of process integration. Fig. 3 shows the different development of multigeneration process through process integration at different levels. In a multigeneration system, there are multiple inputs and multiple outputs. Inputs are various sources of energy or material. Different types of inputs and outputs of a multi generation system are discussed in the later part of this article.

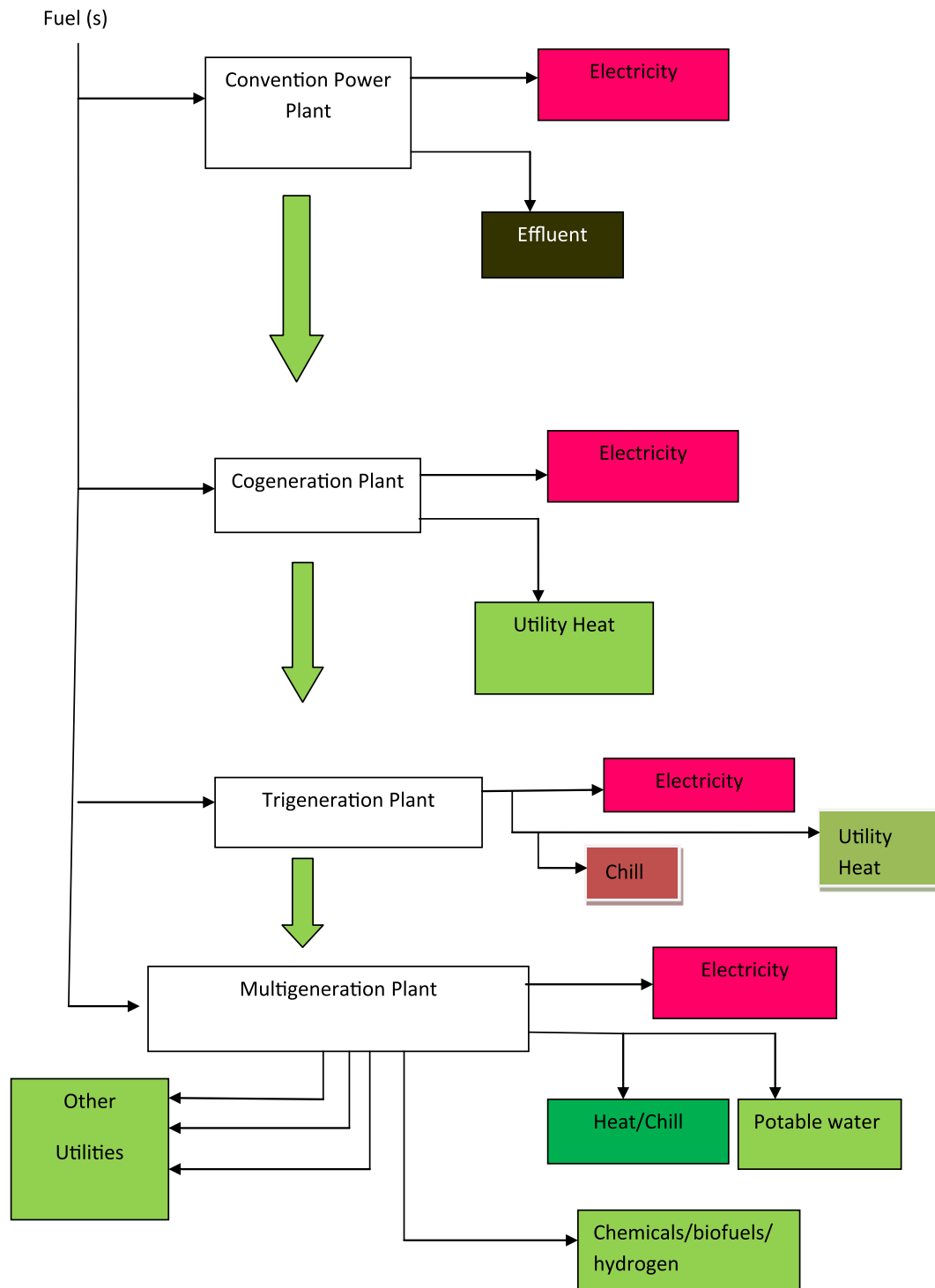


Fig. 3 Development of Multigeneration Concept.

Though electricity is a basic need, it is not the only need of the people. Several other utilities like potable water, fuels etc are also needs of the people. In coastal areas, drinking water is scarce. In many places due to remote terrain conditions it is very difficult to transport transportation fuels like diesel, petrol etc. Villages lying in the humid tropical regions also in need of cooling utility for temporary storage of perishable agricultural crops before selling in the market. So if all of these utilities can be combined in a single efficiently integrated system, then it is very beneficial from the societal point of view. Multigeneration systems if suitably designed may serve this purpose. Thus, multigeneration also finds its significance as a potential option of distributed generation to meet the local needs through optimum utilization of local resources.

Multigeneration as a Low Carbon Technology

Life cycle assessment (LCA) is considered as a potential tool for assessing the environmental impact of an energy system. Jana and De compared a multigeneration system with corresponding stand alone systems generating the same utility outputs for overall environmental impacts including carbon foot print (Jana and De, 2017). In multigeneration systems the process integration and the process intensification increase the energy efficiency of those systems. The high energy efficiency leads to the better utilization of resources and thereby reducing the carbon footprint of the system.

Planning and Design of Distributed Multigeneration Systems

In distributed multigeneration systems local resources are used as inputs. Suitable conversion technologies to deliver utility outputs from these inputs are efficiently integrated in multigeneration systems. Basic factors and steps to be considered for the design of a multigeneration system are illustrated in Fig. 4. For designing renewable energy based multigeneration systems, locally available resources at a particular place have to be assessed. After the resource assessment, suitable available technologies are to be identified that can be integrated efficiently for conversion of available resources to desired utility outputs is chosen. After this the electricity demand as well as the other utility demands like potable water, bio fuels etc are assessed.

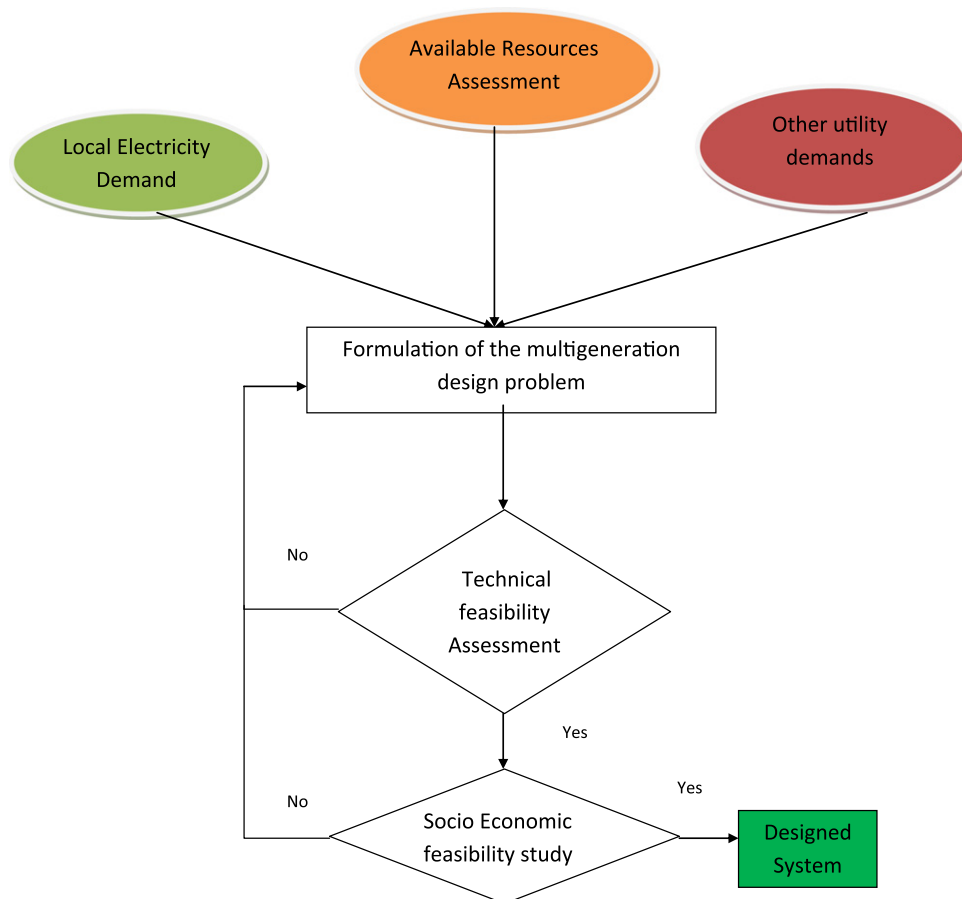


Fig. 4 Formulation of a multigeneration design problem.

Then, the feasibility of the system is studied in that particular location from the environmental and the socio economic viewpoints. The final design of the system thus evolves based on the combined technical, environmental and the socio economic optimum performance of the system.

Possible Options of Renewable Energy Based Systems

The possible renewable energy resources available for input to the multigeneration systems are shown in Fig. 5. Unlike the fossil fuels, these are not feasible to be transported for distant use. So, the renewable based systems have to be designed only after assessing the duration and the amount of availability of the locally available renewable resources. Moreover, renewable resources are mostly intermittent and may not be always available when there is a demand for it, i.e., at the time of need. The demand of energy services identified in the load curve does not always match with the availability of renewable resources. The need of storage and/or hybridization of several renewable resources depending on the local needs thus arise.

Resource Utilization and its Relation With Low Carbon Energy Systems

Energy is an essential service for the growth of any community. Useful secondary energy is generated from naturally available primary resources. Resources are harvested using suitable conversion technologies to yield secondary energy. The maximization of the resource utilization is the key issue for the design of green and sustainable energy systems. This maximization of resource utilization may be achieved through increasing the efficiency of the energy conversion methods, more utilization of locally available resources available at a particular location etc.

Advantages and disadvantages of renewable energy systems

Renewable energy systems have following general advantages.

- (1) The renewable energy systems emit no or low greenhouse gases (GHG) for generation of energy.
- (2) The renewable resources are not depleting.
- (3) It is almost available at all parts of the globe though in different forms and concentrations at different locations.

In spite of all these advantages, the renewable sources of energy suffer from severe limitations like intermittency of availability and dilute intensity. For renewable energy systems, energy can be generated only when the resources are available but not necessarily when it is demanded. Hence storage is inevitably required to get 100% reliable power supply utilizing renewable sources. Till now the mostly used form of electricity storage is the electrochemical storage i.e. to store

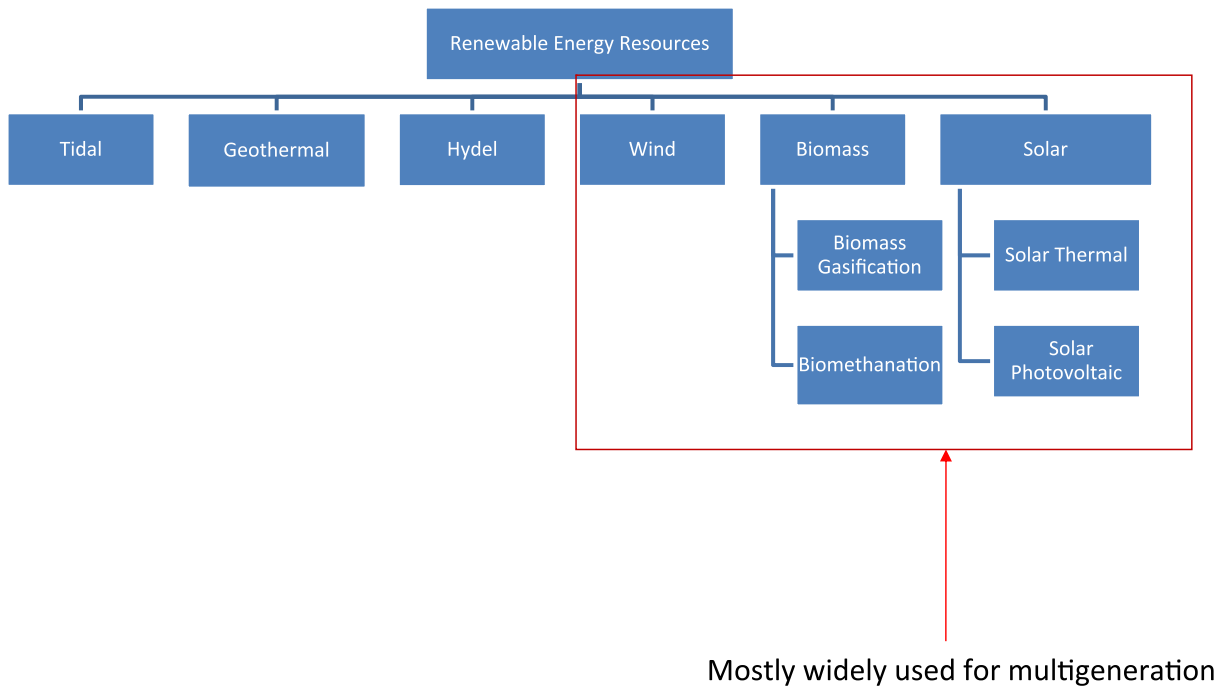


Fig. 5 Possible options of renewable energy inputs for multigeneration.

electricity in a battery. But the electrochemical storage has capacity as well as environmental and economic limitations. High cost of the batteries makes the system cost high. Batteries are to be generally replaced after five years whereas most of the renewable energy systems have a life of about twenty years or more. Moreover, the disposal of the batteries is also not environmentally benign. Due to intermittency of availability of primary energies, renewable energy systems are not capable to deliver energy services as per the load curve. Using a single type of energy, Fig. 6 shows links between supply-demand, storage and hybridization in renewable based multigeneration systems. More demand than supply in a renewable based multigeneration in any time may be accommodated by power from a storage device like battery. Alternatively non availability of one form of renewable energy may be compensated by another available form if several forms of inputs are integrated i.e., 'hybridized' in a multigeneration. For example, during evening hours the sun is absent but the demand is high. At this time the electricity may be supplied from the battery or from other sources like wind, biomass etc which is available at that particular site. On the contrary, another situation may arise that the electricity generated from the available resources is higher than the instantaneous demand. In this case either the electricity may be diverted to any storage device to be used later during higher demand of it or the resource may be utilized to produce some other utilities like chemicals, biofuels etc. For example, the biomass gasifier generates syngas for power generation. The size of the gasifier and the biomass feed rate is fixed. But if the electricity demand is low, then the total amount of syngas generated at that instant may not be needed to produce electricity. For such cases a fraction of the syngas may be diverted to produce bio fuel like ethanol. This is done in a system called multigeneration.

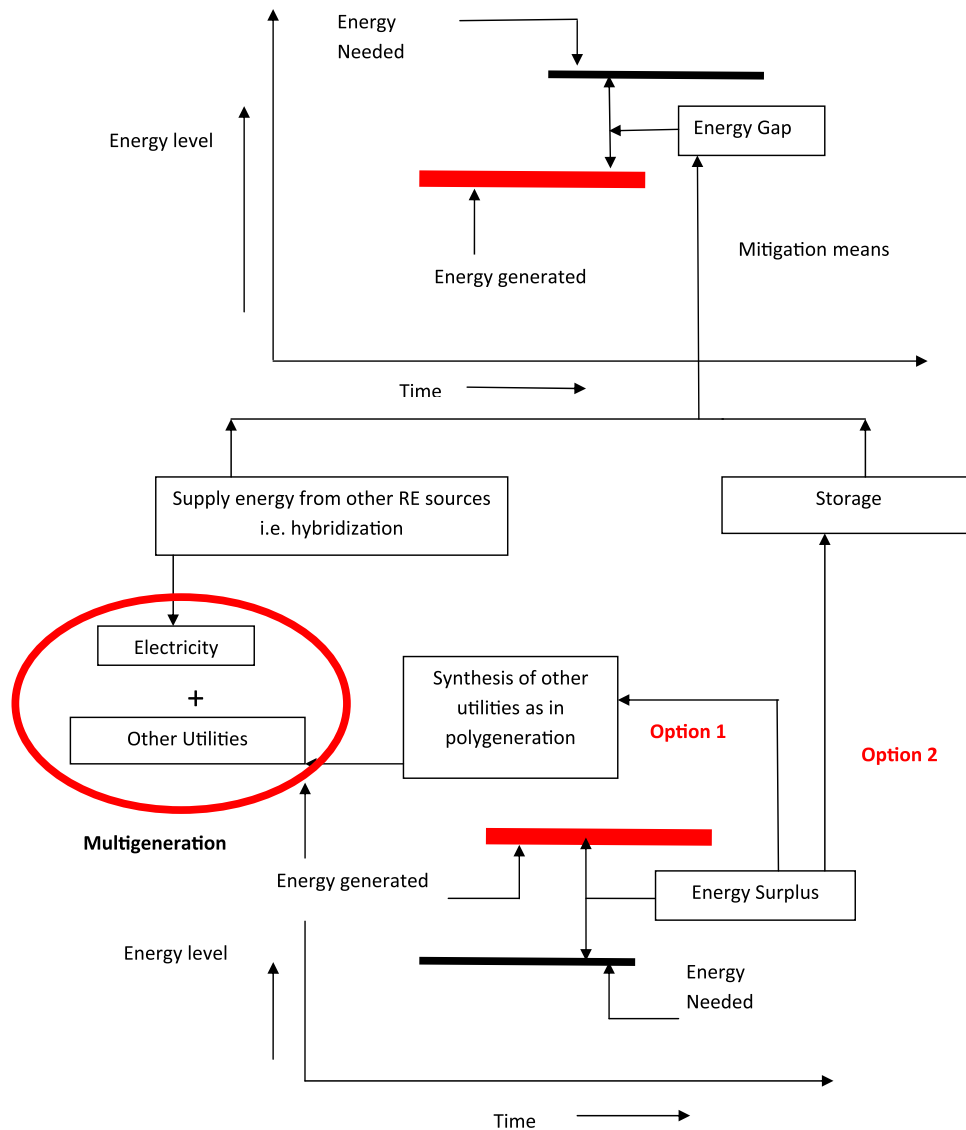


Fig. 6 Schematic diagram showing links of storage, hybridization and multigeneration.

Table 1 Application of numerical algorithms in renewable based polygeneration systems

Author (year)	Algorithm used	Input	Output
Fazlollahi and Marechal (2011)	Multi objective optimization using MILP and Multi objective evolutionary algorithm (MOEA)	Biomass	Electricity and heat
Sigarchain <i>et al.</i> (2016)	Particle Swarm Optimization (PSO)	Solar, LPG	Electricity and heat
El-Emam and Dincer (2017)	Multi objective evolutionary algorithm	Solar, biomass	Electricity, cooling and hydrogen

Table 2 Some examples of polygeneration systems with inputs and outputs

Author	Inputs	Outputs
Spencer <i>et al.</i> (2013)	Solid waste	Heat, hydrogen, and power
Hossain <i>et al.</i> (2013)	Jatropha and Pongamia	Electricity, food preparation, cold storage and pure water
Salomón <i>et al.</i> (2013)	Residue of palm oil mill	Bio-diesel, pellet, electricity, steam
Jana and De (2015)	Agricultural waste	Power, heat, chill, ethanol
Yang <i>et al.</i> (2016)	Cotton stalk, rice husk	Charcoal, biogas, woody vinegar, woody tar
Chen <i>et al.</i> (2016)	Tobacco waste	Char, oil, gas
Leiva-Illanes <i>et al.</i> (2017)	Solar energy (Thermal)	Electricity, fresh water, heating and cooling
Siddiqui and Dincer (2018)	Solar energy (Thermal)	Electricity, Potable water and hydrogen

Optimization of Multigeneration System

The economic operation of a multigeneration system needs a proper sizing of components considering the availability of local resources. Thus application of suitable optimization algorithms for the proper sizing of the multigeneration system is also important from the resource utilization point of view. In [Table 1](#), a few optimization algorithms used in renewable energy based multigeneration systems is shown. For optimization of renewable based multigeneration system, both linear programming and mixed integer linear programming are found suitable. Also, heuristic optimization methods like particle swarm optimization algorithm and multi objective evolutionary algorithm have also found its application. In majority of the multigeneration problems, multi criteria optimization is used.

Case Studies

Renewable based multigenerations mainly uses solar, biomass, wind and in some cases geothermal energy or a combination of these forms of energy i.e., several energy resources are hybridized. The outputs are electricity, heating, cooling, hydrogen, potable water and others. In [Table 2](#), a few examples of multigeneration systems with the inputs and outputs are given. The inputs are dependent on the resources available at a particular place and the outputs are decided to cater to needs of people based on socio-economic status of the local people. Suitable technologies are selected to for harvesting the resources into useful energy services. In the renewable based multigeneration systems, mostly solar and biomass resources are used. Mostly solar thermal route of energy conversion is used for the multigeneration systems as it is the convenient solar energy form for system integration. The biomass conversion technology mainly depends on the type of biomass available. The wet biomass is subjected to biochemical conversion i.e., bio-methanation and the dry biomass is subjected to thermo chemical conversion say, gasification.

Conclusion

Energy generation is done from naturally available resources. Resource management is an important aspect for the proper energy management and greenization of energy systems. Process integration is an efficient way for the proper energy management of a system. The levelized cost of electricity is also decreased by the application of the multigeneration system. The life cycle assessment is considered as an efficient tool for the assessment of the environmental performance of a system. The life cycle assessment of a multigeneration system also shows that the environmental load of a multigeneration system is lower than the sum of the environmental loads generating the same utilities. Moreover electricity is not the only need of the villagers. Other utilities like potable water, biofuels etc are also needed. If a single integrated system can give all these utilities along with electricity then it is a low carbon sustainable solution and beneficial from the socio economic point of view too.

See also: Biochar as Sustainable Reinforcement for Polymer Composites. Evaluating the Sustainability Performance of Building Systems and Technologies for Mainstreaming Sustainable Social Housing in India. Power and Other Energy Utilities From Low Grade Waste Heat – Novel Technologies to Reduce Carbon Footprint. Sustainability and Green Building Rating Systems: A Critical Analysis to Advance Sustainable Performance. Sustainability Issues in Bioplastics

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Innovations in Variable Frequency Drives and its Implication in Reducing Carbon Footprint

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Introduction

As reference to U.S. Energy statistics, industry accounts for more than 40% of the world 14,400 TWh (billion kilowatt hours) electricity. In Industrial sector above 50% of all electricity consumption is generally due to electrical drives (Hopper, 2007, 2006; Siemens, 2019a; see "Relevant Websites section"; Hossain *et al.*, 2017; SEEMP, 2012; Shahan, 2011; Siemens, 2019b; Su *et al.*, 2014b; Swamy, 2017; Verma *et al.*, 2010). United States, the distribution of industrial motor- system energy is 25% for pumps, 14% for fans, and 16% for compressed air (Su *et al.*, 2014a; Neufeld *et al.*, 2014; Hopper, 2007; Su and Yu, 2013). A case study reported in 2011 that globally 45% of all electricity used by electric motors (Shahan, 2011; Siemens, 2019b; Su *et al.*, 2014b; Swamy, 2017; Verma *et al.*, 2010). Besides industry, motors are major energy consumption electrical devices in HVAC in buildings, electric traction, electric vehicles, and many house hold utilities, such as, mixer, grinders, washing machines, etc (Su and Yu, 2013). As many of such uses have been increasing exponentially in recent years, the share of motors' electricity use would be increasing unless it is managed through efficient control such as VFDs (Hopper, 2007; Drews *et al.*, 2012a; Hopper, 2006; Schmehl *et al.*, 2014; Verma *et al.*, 2010; Hart, 2012; Rasanen *et al.*, 2012; Verma *et al.*, 2010; Yaskawa, 2019). 50% of world motors are installed in USA, European Union and China. Smart motor systems single-handedly could save 1718 TWh of electricity annually which is counterpart to the total electricity generation of 286 nuclear power plants globally (Hopper, 2007, 2006; Siemens, 2019a; see "Relevant Websites section"; Shahan, 2011; Siemens, 2019b; Su *et al.*, 2014b; Swamy, 2017; Verma *et al.*, 2010).

Variable speed drives for industrial utilities and applications are used for two main focal points: significantly to improve the efficiency of motor by driving the equipment by reference speed to variable load and to allow precise and continuous process control over a broad variety of speeds (Hopper, 2007; Drews *et al.*, 2012a; Hopper, 2006; Schmehl *et al.*, 2014; Verma *et al.*, 2010; Yaskawa, 2019). Centrifugal fans, blowers and pumps have been premeditated to meet the maximum load but actually function at reduced load after extended period of time leading to energy inefficiency (Shahan, 2011; Siemens, 2019b; Su *et al.*, 2014b; Swamy, 2017). Reports have stated that carbon dioxide is the important factor of the process. Carbon dioxide (CO₂) generated as the consequence of electrically operated industrial machines predominantly leads to global warming (Liu, 2018; Carbon trust, 2018; Price *et al.*, 2001, 1999; Jindal Steel Works, 2019). In an effort to minimise CO₂ emissions from industry, this article is analysing industrial electric motors equipped with variable frequency drives as the means of reducing CO₂ emissions (Price *et al.*, 2001, 1999; Shahan, 2011; Siemens, 2019b; Su *et al.*, 2014b). Electrical operated machines such as pumps, fans or compressors used in an industrial applications, are obsessed by electric drives. Thus, mitigating the efficiency and saving the energy usage of as well as mitigating CO₂ foot prints and its effects generated by the use of electrically operated devices like motors, pumps and motors are vital factor in recuperating and mitigating overall industrial performance and utility (Jindal Steel Works, 2019). Article give a learning paradigm and in depth study of carbon footprint and its negative effects, with significant features of variable frequency drives (MEFCC, 2018, 2015; Liu, 2018; Carbon trust, 2018; Olivetti *et al.*, 2013; see "Relevant Websites section"). High end applications of technologies have significant prospective to reduce significantly industrial energy use. Industrial energy use could be more efficient with the judicious application of latest energy conservation technologies, such as, variable speed drives in motors, energy efficient motors, energy-smart controls & systems for compressors and waste-heat in processes, etc. A variable frequency drive is an electronic driven power converter that predominantly generates a multi-phase, variable frequency output that can be used to operate a standard AC induction motor, and to transform and control the motor's speed, torque and mechanical power output. Variable frequency control technology has been proposed and applied to ship power pump load energy efficiency optimization (Giannoutsos and Manias, 2015a, 2013; SEEMP, 2012; Harrington, 1992; Brater *et al.*, 1996; Rishel, 2002; Su *et al.*, 2014a; Drews *et al.*, 2012b; Shahan, 2011; Siemens, 2019b; Su *et al.*, 2014b, 2016b; Su and Yu, 2013; Swamy, 2017; Su *et al.*, 2016a; Gaerke and Hernandez, 2015) in order to meet international electrical standards law and regulations, as well as energy conservation management requirements (SEEMP, 2012). Marine engineering systems are electrically complex system however, when sensing element fails, the workload of engineers for reliability and electrical safety increase. This is especially true when power pump equipment stops functioning due to a motor fault and the ship operation and navigational safety are negatively affected (Brater *et al.*, 1996; Rishel, 2002; Neufeld *et al.*, 2014; Siemens, 2019a). The efficient operation characteristics of power pumps under variable frequency control and drives will assist operators in smooth running and minimum outage time for marine engineering equipment operations and high reliability (SEEMP, 2012). The ship power pump load can be divided into deck machinery and engine room machinery according to the specific objectives (Harrington, 1992). The pumps, which can be categorised into four types according to their operating characteristics, include the centrifugal pump; rotary pump, piston pump and ejection pump (Brater *et al.*, 1996). The centrifugal pump is the one most commonly used on ships, and its operation methodology can be categorised as open or closed systems (Rishel, 2002). In an open system centrifugal pump, the fluid communicated by the pump performs an external flow between the equipment and the outside environment. Typical open marine pumps include the ballast pump and the seawater cooling pump. In a closed centrifugal pump, the flipper forms an internal circulation between a pipeline system and the equipment (Neufeld *et al.*, 2014).

These pumps include the fresh water cooling pump, M/E jacket cooling fresh water pump, lubrication oil pump and auxiliary boiler feed water pump. Various methods have been proposed for controlling open pumps by means of variable frequency drives (VFDs) (Hopper, 2006; Schmehl *et al.*, 2014; Su *et al.*, 2014a; Verma *et al.*, 2010; Giannoutsos and Manias, 2015a; Brater *et al.*, 1996; Siemens, 2019a; IEEE, 2014, 2010; Liu, 2018; Carbon trust, 2018; Rasanen *et al.*, 2012; Yaskawa, 2019; Hart, 2012; Shahan, 2011), those proposed for closed pumps (Rishel, 2002; Neufeld *et al.*, 2014; Su *et al.*, 2014a) have mainly focused on onshore power applications, with in depth literature regarding problems for closed pumps driven by VFDs in marine vessels or offshore power systems. This specific application offers major energy savings if applied in many industrial applications. Policy and strategic makers responded by introducing restrictions on carbon dioxide (CO₂) as it is the largest constituent of anthropogenic GHG emissions. This creates challenges for the energy intensive industrial sectors to manage their carbon footprint.

Different technologies related to CO₂ emissions as per Indian perspective are mitigated and discuss and Iron and steel industry as designated consumer is taken as case study in this article (MEFCC, 2015, 2018; Jindal Steel Works, 2019).

Carbon Foot Prints With Energy Use and Carbon Dioxide Emissions by Process in U.S. Steelmaking

For our detailed referral case study of the U.S. iron and steel industry, we focus on a small subsystem of the industry, blast furnaces and steel mills (SIC 3312) (IEEE, 2014; MEFCC, 2015; MEFCC, 2018). The main energy usage processes for integrated steel production are sinter-making, coke-making, iron-making, steel-making. Only the steelmaking step is used for production of secondary steel. Following steel production, energy is used for casting, hot rolling, cold rolling, and finishing. In 1994, integrated steel mills in the U.S. produced 55.4 Mt of steel and secondary steel mills produced 35.87 Mt, for a total U.S. production of 91.3 Mt. **Table 1** gives the referral view of Energy saving synergy major with different energy management strategies in iron and steel industry as per USA statistics **Table 2** gives Primary energy use for integrated steel making was about three times more than energy use in secondary steelmaking, consuming 1439 PJ compared to 425 PJ. The primary energy intensity of integrated and secondary steel production in 1994 was 26.0 GJ/t and 11.8 GJ/t, respectively, for a total sector primary energy intensity of 20.4 GJ/t. Total carbon dioxide emissions from steel-making in 1994 were 34.4 Mt C, with 80% of these emissions from integrated steelmaking. The carbon dioxide intensity of integrated steelmaking was 0.5 tC/t crude steel while the carbon dioxide intensity for secondary steelmaking was 0.2 tC/t crude steel, resulting in a total sector carbon dioxide intensity of 0.4 tC/t crude steel (Su *et al.* 2016a,b; IEEE, 2014). The above facts and figures give a specific data of carbon foot prints in Iron and steel industry and its effects. Iron and steel industry plays a vital role and major focus area in the field energy saving strategies by using variable frequency drives and its effects by CO₂. Implementation of VFD for Industrial process plant and carbon dioxide emissions can be reduced in one of the three methods, reducing energy and carbon produced from combustion by energy integration, reducing carbon from the fuel itself by the use of low footprint fuels and carbon storage and sequestration.

Operating and capital costs are calculated on a crude steel basis according to the same procedures as fuel and electricity savings. Allocation of the share of production to which each assess is applied was based on a multiplicity of information sources on the U.S. iron and steel industry in 1994 and expert decision. Finally, carbon dioxide emissions minimization and reductions for each measure were calculated based on a weighted average carbon dioxide emissions coefficient (tC/GJ) for each procedural step.

Variable Speed Drives for Flue Gas Control, Pumps, Fans

Based on referral studies in the UK, we assume that electricity savings of 42% are feasible through the use of variable speed drives (VSDs) on pumps and fans (Energy Star, 2019). Previous studies reveals that this technology can be applied to 5% of electricity use in integrated steel making, resulting in a savings of 0.04 GJ/t crude steel. Based on a 3.25 year payback of an installed system in the UK and assuming an electricity price of 3 pence/kWh, we calculate the costs to be \$1.3/t product. This equals a payback period of 3.4 years under U.S. 1994 conditions. Programmed heating instead of conventional constant heating of the coke ovens ensures optimization of the fuel gas supply to the oven at the various stages of the coking process and reduces the heat content of the coke before charging. Use of programmed heat can lead to fuel savings of about 10%, estimated to be 0.17 GJ/t coke. Small capital costs regarding the computer control system for the coke oven are included. Review studies reveals that the costs to be \$75K per coke battery for a large energy management system, which is equivalent to approximately \$0.23/t coke for the coking capacity of the integrated steel mills (excluding merchant coke producers). This measure is also applied to 100% of U.S. coke production in 1994.

Variable Speed Drive Coke Oven Gas Compressors

Variable speed drive coke oven gas compressors can be installed to reduce and minimise compression energy. Coke oven gas is generated at low pressures and is pressurized for transport in the internal gas grid. The coke oven gas flows vary over time due to the coking reactions. Installing a variable speed drive system on a compressor at a coke plant in the Netherlands saved 6–8 MJ/t coke, at an investment of \$ 0.3/t coke. Coke dry quenching is an alternative to the traditional wet quenching of the coke, and this process reduces dust emissions, improves the working climate, and recovers the sensible heat of the coke. Dry coke quenching is typically implemented as an environmental control technology. Various systems are used in Brazil, Finland, Germany, Japan, and Taiwan, but all essentially

Table 1 State-of-the-art energy efficiency measures in the U.S. iron and steel industry

Preventative maintenance	
Energy monitoring and management systems	
Variable speed drives for flue gas control, pumps, and fans	
Cogeneration	
Integrated steel making measures	Secondary steel making measures
<i>Iron ore preparation (Sinter making)</i>	<i>Electric arc furnace</i>
Sinter plant heat recovery	Improved process control (neural networks)
Use of waste fuels in the sinter plant	Flue gas monitoring and control
Reduction of air leakage	Transformer efficiency measures
Increasing bed depth	Bottom stirring/gas injection
Improved process control	Foamy slag practices
<i>Coke making</i>	Oxy-fuel burners/lancing
Coal moisture control	Post-combustion
Programmed heating	Eccentric bottom tapping (EBT)
Variable speed drive on coke oven gas compressors	Direct current (DC) arc furnaces
Coke dry quenching	Scrap preheating
<i>Iron making - blast furnace</i>	Consteel process
Pulverized coal injection (medium and high levels)	Fuchs shaft furnace
Injection of natural gas	Twin shell DC arc furnace
Top pressure recovery turbines (wet type)	
Recovery of blast furnace gas	
Hot blast stove automation	
Recuperator on the hot blast stove	
Improved blast furnace control	
<i>Steel making - basic oxygen furnace</i>	
BOF gas & sensible heat recovery (suppressed combustion)	
Variable speed drive on ventilation fans	
Casting and rolling (measures apply to integrated and secondary plants unless otherwise specified)	
<i>Casting</i>	
Adopt continuous casting	
Efficient ladle preheating	
Thin slab casting	
<i>Rolling</i>	
Hot charging	
Recuperative burners in the reheating furnace	
Controlling oxygen levels and variable speed drives on combustion air fans	
Process control in the hot strip mill	
Insulation of furnaces	
Energy efficient drives in the hot rolling mill	
Waste heat recovery from cooling water	
Heat recovery on the annealing line (integrated only)	
Automated monitoring & targeting system	
Reduced steam use in the pickling line	

recover the heat in a vessel where the coke is quenched with an inert gas (nitrogen). The heat is used to produce steam (approximately 400–500 kg steam/t), equivalent to 800–1200 MJ/t coke. The steam can be used on site or to generate electricity. For new coke plants the costs are estimated to be \$50/t coke, based on the construction costs of a plant in Germany.

Variable Speed Drive on Ventilation Fans

The BOF process is basically a batch process. The volumes of flue gases vary widely over time, making variable speed drives an option. Large fans are used in the BOF plant to control air quality. At Hoogovens the use of variable speed drives has been shown to save power (Energy Star, 2019) in the BOF, reducing the power demand by approximately 20%, or 0.9 kWh/t crude steel. With total costs of \$1M (1988) the investment costs are \$0.2/t crude steel. We assume that such variable speed drives could be used in all U.S. BOF steelmaking facilities. Improved process control (neural networks) can help to reduce electricity consumption beyond that achieved through classical control systems. For example, neural networks or “fuzzy logic” systems analyze data and emulate the best controller. For EAFs, the first “fuzzy logic” control systems have been developed using current, power factor and power use to control the electrodes in the bath. The average power savings are estimated to be up to 8% (or 38 kWh/t), with an average increase in productivity of 9%–12% and reduced electrode consumption of 25%. The actual savings depend on the scrap used and the furnace operation. Furnace maintenance costs are reduced as well. We assume an average efficiency improvement of 30 kWh/t (or 0.1 GJ/t).

Table 2 Energy use and carbon dioxide emissions by process in U.S. steel production, 1994

Process stage	Fuel (PJ)	Electricity (PJ)	Final energy (PJ)	Primary energy (PJ)	Carbon dioxide emissions (MtC)
Integrated steelmaking					
Sinter making	26	2	28	31	0.8
Coke making	74	2	76	81	0.6
Iron making	676	4	680	689	11.0
Steelmaking (Basic oxygen furnace)	19	6	25	36	0.5
Casting	15	11	27	50	0.9
Hot rolling	157	34	191	263	3.7
Cold rolling and finishing	43	15	58	89	1.3
Boilers (integrated steelmaking)	167	0	167	167	7.8
Cogeneration (integrated steelmaking)	101	−22	79	101	0.4
Total integrated steelmaking	1280	52	1332	1439	27.0
Secondary steelmaking					
Steelmaking (electric arc furnace)	6	62	68	197	2.8
Casting	1	4	5	12	0.2
Hot rolling	102	22	124	170	2.4
Cold rolling and finishing	0	0	0	0	0.0
Boilers (secondary steelmaking)	42	0	42	42	2.0
Cogeneration (secondary steelmaking)	11	−2	9	11	0.04
Total secondary steelmaking	162	85	248	425	7.4
Total primary and secondary steelmaking	1443	137	1580	1864	34.4

Note: Available at: www.clarkpublicutilities.com. Energy Star, 2019. Available at: www.energystar.gov (accessed February 2019).

Flue Gas Monitoring and Control

Flue gas monitoring and control using variable speed drives can reduce the energy use for the flue gas fans, reducing the heat losses in the flue gas. The flue gas flow varies over time, which makes the use of variable speed drives possible. Flue gas VSDs have been installed in various countries (e.g., Germany, UK). The electricity savings are estimated to be 15 kWh/t, with a payback period of 2–3 years (Energy Star, 2019; Hart, 2012; Siemens, 2019a,b). We estimate the capital investments to be \$2/t, and apply this measure to all furnaces with a size of 100 t or larger, equivalent to 50% of the U.S.

Controlling Oxygen Levels and Variable Speed Drives on Combustion Air Fans

Controlling oxygen levels and variable speed drives on combustion air fans on the reheating furnace helps to control the oxygen level, and hence optimize the combustion in the furnace, especially as the load is variable. The savings depend on the load factor of the furnace and control synergy applied. Two cases from the UK steel industry demonstrate the various techniques. Implementing a variable speed drive combustion fan on a walking beam furnace at Cardiff Rod Mill (UK) reduced the fuel consumption by 48% with a payback period of 16 months (1985 UK conditions). Another example (without installing variable speed drives) is a walking beam furnace for reheating billets, saving approximately 2% on fuel use, with a payback of one year (Energy Star, 2019). Reported referral energy savings of 10% equivalent to 0.33 GJ/t product, at an investment of 0.5\$/t product. A systematic approach to integrate reduced carbon dioxide after implementing VFD within an industrial park with manifold carbon emitting streams and the potential carbon utilization options (sinks) that may exist. The technique identifies the least possible cost integration options to attain a given footprint reduction target and decides which sources are preeminent captured together with their provision to the various utilization options. It determines if the captured carbon dioxide should be purified and takes into account costs of carbon capture, carbon transportation between sources and sinks as well as costs associated with the utilization processes.

Some of the main cost-effective energy saving measures for secondary steelmaking includes improved process control and carbon dioxide reduction is given in Table 3. Energy integration on an individual process or across multiple units that is primary steel making and secondary steel making has been applied to reduce carbon footprint. Many strategies used graphical methods to apply energy integration in order to achieve carbon emission target.

We identified cost-effective energy savings of 104 PJ and carbon dioxide emissions reductions of 1.5 MtC of carbon dioxide for secondary steelmaking in 1994 which represents 6% of total U.S. steelmaking energy use and 4% of total carbon dioxide emissions as shown in Table 4. More in depth work has emerged in terms of solving the problem of carbon dioxide generation mainly focus from energy integration point of view that later expanded to include multiple processes for Iron and steel plants or for different Industrial plants.

In the hot strip mill, recuperative burners in the rolling mill, improved process control in the EAF, and preventative maintenance.

These methods were aimed to reduce carbon dioxide generation as results of combustion thus targeting a reduced amount of energy use and new efficient designs. Other methods looked at cutting carbon dioxide from the resource itself while maintaining the energy condition. Nevertheless, these methods try to limit carbon production; they do not pact with the expected produced carbon. While the prospects of applying renewables into the energy grid is appealing, the move in industry towards their

Table 3 Energy saving measures and carbon dioxide reduction for iron and steel process plant

Option	Production (Mt)	Fuel savings (GJ/t crude steel)	Electricity savings (GJ/t crude steel)	Primary energy savings (GJ/t crude steel)	Annual operating costs (US\$/t crude steel)	Retrofit capital cost (US\$/t crude steel)	Carbon dioxide emissions reduction (kgc/l)	Share of production measure applied (%)
Iron ore preparation (sintering)								
Sinter plant heat recovery	12.1	0.12	0.00	0.12	0.00	0.66	3.41	100%
Reduction of air leakage	12.1	0.00	0.00	0.01	0.00	0.02	0.12	100%
Increasing bed depth	12.1	0.02	0.00	0.02	0.00	0.00	0.59	100%
Improved process control	12.1	0.01	0.00	0.01	0.00	0.03	0.30	100%
Use of waste fuels in sinter plant	12.1	0.04	0.00	0.04	0.00	0.04	1.16	74%
Coke making								
Coal moisture control	16.6	0.09	0.00	0.09	0.00	14.69	0.55	100%
Programmed heating	16.6	0.05	0.00	0.05	0.00	0.07	0.31	100%
Variable speed drive coke oven gas compressors	16.6	0.00	0.00	0.00	0.00	0.09	0.01	100%
Coke dry quenching	16.6	0.37	0.00	0.37	0.15	20.99	2.25	100%
Iron making-blast furnace								
Pulverized coal injection to 130 kg/thm	49.4	0.69	0.00	0.69	-1.78	6.24	11.42	80%
Pulverized coal injection to 225 kg/thm	49.4	0.51	0.00	0.51	-0.89	4.64	8.45	30%
Injection of natural gas to 140 kg/thm	49.4	0.80	0.00	0.80	-1.78	4.46	13.35	20%
Top pressure recovery turbines (wet type)	49.4	0.00	0.10	0.30	0.00	17.84	4.29	20%
Recovery of blast furnace gas	49.4	0.06	0.00	0.06	0.00	0.27	0.98	60%
Hot blast stove automation	49.4	0.33	0.00	0.33	0.00	1.25	5.49	60%
Recuperator bot blast stove	49.4	0.07	0.00	0.07	0.00	0.32	1.19	100%
Improved blast furnace control systems	49.4	0.36	0.00	0.36	0.00		5.93	50%
Steelmaking-basic oxygen furnace								
BOF gas+sensible heat recovery	55.4	0.92	0.00	0.92	0.00	22.00	12.55	100%
Variable speed drive on ventilation fans	55.4	0.00	0.00	0.01	0.00	0.20	0.14	100%
Integrated casting								
Adopt continuous casting	49.5	0.24	0.08	0.49	-5.35	11.95	36.06	9%
Efficient ladle preheating	49.5	0.02	0.00	0.02	0.00	0.05	0.27	84%
Thin slab casting	49.5	3.13	0.57	4.89	-31.33	134.25	177.60	20%
Integrated hot rolling								
Hot charging	48.3	0.52	0.00	0.52	-1.15	13.09	7.18	22%
Process control in hot strip mill	48.3	0.26	0.00	0.26	0.00	0.61	3.59	69%
Recuperative burners	48.3	0.61	0.00	0.61	0.00	2.18	8.38	20%
Insulation of furnaces	48.3	0.14	0.00	0.14	0.00	8.73	1.91	30%

Table 3 Continued

<i>Option</i>	<i>Production (Mt)</i>	<i>Fuel savings (GJ/t crude steel)</i>	<i>Electricity savings (GJ/t crude steel)</i>	<i>Primary energy savings (GJ/t crude steel)</i>	<i>Annual operating costs (US\$/t crude steel)</i>	<i>Retrofit capital cost (US\$/t crude steel)</i>	<i>Carbon dioxide emissions reduction (kgC/l)</i>	<i>Share of production measure applied (%)</i>
Controlling oxygen levels and VSDs on combustion air fans	48.3	0.29	0.00	0.29	0.00	0.44	3.95	50%
Energy efficient drives (rolling mill)	48.3	0.00	0.00	0.03	0.00	0.17	0.39	50%
Waste heat recovery (cooling water)	48.3	0.03	0.00	0.03	0.06	0.70	0.46	69%
Integrated cold rolling and finishing								
Heat recovery on the annealing line	31.7	0.17	0.01	0.19	0.00	1.55	2.73	50%
Reduced steam use (pickling line)	31.7	0.11	0.00	0.11	0.00	1.61	1.55	80%
Automated monitoring and targeting system	31.7	0.00	0.12	0.38	0.00	0.63	5.51	50%
General								
Preventative maintenance	55.4	0.43	0.02	0.49	0.02	0.01	9.74	100%
Energy monitoring and management system	55.4	0.11	0.01	0.14	0.00	0.15	2.60	100%
Cogeneration	55.4	0.03	0.35	1.1	0.00	14.52	22.39	100%
Variable speed drive: flue gas control, pumps, fans	55.4	0.00	0.02	0.06	0.00	1.30	0.040	50%

Note: Available at: www.clarkpublicutilities.com. Energy Star, 2019. Available at: www.energystar.gov (accessed February 2019).

Table 4 Summary of cost-effective 1994 energy savings and carbon dioxide emission reductions

<i>Steelmaking sector</i>	<i>Crude steel production (Mt)</i>	<i>Reduction in energy intensity (GJ/t)</i>	<i>Reduction in primary energy use^a (PJ)</i>	<i>Share of total U.S. iron and steel primary energy use (%)</i>	<i>Reduction in carbon dioxide emissions (MtC)</i>	<i>Share of total U.S. iron and steel carbon dioxide emissions (%)</i>
Integrated	55.4	4.3	236	13%	5.0	15%
Secondary	35.9	2.9	104	6%	1.5	4%
Total	91.2	3.8	341	18%	6.5	19%

^aPrimary energy is calculated using a conversion rate from final to primary electricity of 3.08, reflecting the difference between an average power plant heat rate of 10,500 Btu/kWh and a site rate of 3412 Btu/kWh, including transmission and distribution losses.

Note: Energy Star, 2019. Available at: www.energystar.gov (accessed February 2019).

adaptation might be slow as fossil fuels are currently the most used energy sources. Therefore, there is a requirement to apply a methodology that resolves the carbon production issue. This has been demonstrated through the study of carbon capture allocation between sources and sequestration sinks.

Attempts to allocate carbon dioxide in utilization sinks across processes have not been studied before. The concept of using the waste or emissions elsewhere as in natural ecological systems stems from Industrial Ecology's (IE), Eco-Industrial Parks (EIP).

Variable Frequency Drives in Motors

The macro field of Motor Drives has gained significant importance in recent years. One reason is the availability of high speed processors needed for extensive analytical calculations to achieve good performance and control of AC motors. In addition, extraordinary progress in power semiconductor devices cannot be ignored. An important reason for the extensive use of variable frequency drives (VFDs) in industrial and commercial applications is the significant energy savings that it enables due to the possibility of operating AC motors at variable speeds. However, in much industrial application, motors are made to run at rated speed with no need for speed control. Such operations do not capitulate any energy savings and in turn one has to account for the power loss in the VFD. A Silicon controlled rectifier (SCR) based

technology soft starter may be a better option in such cases. There are other applications where the use of VFD yields significant energy savings. In these applications, there is ample opportunity for improving system efficiency as will be discussed in the article.

In addition to brainstorming ideas to improve system efficiency in a cost effective manner, innovative topologies will be put forward that can result in optimal use of power semiconductor devices to achieve multiple tasks as will be explained in this article. In regenerative or bidirectional power flow applications, typically an LCL filter is used for interfacing the PWM frontend rectifier to the AC grid. In these industrial applications, predictably there is large circulating current through the filter capacitor even when the regenerative unit is not in working. There is power loss associated with this circulating current and in some cases, this current can also interact with other nonlinear loads on the system and can trigger system resonance. In many applications, VFDs need output filters to reduce the dv/dt experienced by the motors at large distances from the drives. In addition, common mode issues need to be taken care of to reduce radiated and conducted EMI noise. Ideas to achieve these multiple demands in an integrated filter section have been also discussed in the article.

Input Current Harmonics and System Efficiency

VFDs depicts nonlinear current from the AC source because of the presence of a three-phase AC to DC rectifier front end and a large DC bus filter capacitor. When distorted current flows through the system impedance, there is distorted voltage drop across the impedance, especially in weak AC systems. When distorted voltage drop across the system impedance is added to the system voltage, it results in voltage distortion. Many researchers have sought to reduce the effect of voltage and current harmonics in the power system (Swamy, 2017; Giannoutsos and Manias, 2013,2015a; SEEMP, 2012; Gaerke and Hernandez, 2015; Harrington, 1992; Brater *et al.*, 1996; Rishel, 2002; Su, *et al.*, 2014a; Neufeld *et al.*, 2014).

Voltage harmonics can negatively affect other sensitive loads on a given AC system. Current harmonics results more power loss in the power delivery equipment. Examples of power delivery equipment include power system transformers, feeders, circuit breakers, etc., around the world. Pumps and fans are by far the largest application of variable and constant frequency AC drives. The applications include boiler ID/FD fans and feed pumps, tunnel ventilation, sewage and water pumps, variable fluid flow in process control, drying or cooling by air, compressors and fans in air conditioning and refrigeration, ship propulsion, gas and fuel line compressors, etc. Presently, the artificial intelligence tools, such as expert system, fuzzy logic and neural network are showing performance impact on variable frequency drives. Designing of Filters with correct insulation is key points for study and professional using VFD's in Industries should have technical discussion with vendors.

The affinity Laws (also called the cubic Laws) states that pump output or flow are directly proportional to the speed of the pump. Therefore, to produce 50% flow, the pump would be run at 50% speed. At this operating point, the pump would require only 12.5% of rated horsepower ($0.5 * 0.5 * 0.5 = 0.125$ or 12.5%). From a mechanical point of view, bearings run at reduced speeds typically last much longer than their full speed counter-parts. "Soft Start" is a mechanism which can be achieve after installation of Variable frequency drives and for the operation of mechanical dynamic equipment (Su *et al.*, 2014a). A electrical load covers various types of electrical equipment, including power pumps, lighting equipment, communication and equipment load. The power pump and motors is the major user, accounting for about 70% of the total power consumption in Industries. Before deciding which motor VFD to use, information on the control system design and control parameter settings is required. It is essential that a proper VFD closed pump system be designed which will increase energy savings, enhance control performance and improve system operations. In this article we will discuss typical methods of flow control by industrial fans and power which are very dominant in industrial application and in the field of Industrial automation and control. Fans, blowers and pumps constitute a large application of motors. In such application how flow is to be controlled by driving a pump. If driving a pump by a motor it will extract certain amount of air. Demand of air and water is not same at all time. It depends upon pump characteristics and machine characteristics that is how operating point is determined. Flow is to be varied by varying the operating point. The most common characteristics we will demonstrate the energy saving with variable speed drive method of flow control. Variable speed drive method is the most vital technology in industrial and automation control. On Off control method is not used in industrial process.Because in on off control method there is pulsating flow.

$$\text{Average flow rate} = Q_{\max} \times t_{\text{on}} / (t_{\text{on}} + t_{\text{off}})$$

In industrial processes the air fuel ratio should be perfect that is full combustion of fuel. Pulsating value of flow is not good for combustion. Similarly for industrial cooling processes the on off control method is not appropriate. When discussing energy savings and variable frequency drives (VFD) the attention often focuses on a centrifugal fan or pump application. However, you should not overlook other applications which also have large potential energy savings and energy recovery.

Centrifugal Applications

When a centrifugal fan or pump is used with mechanical flow control, converting the application to an adjustable speed AC drive can reduce energy costs by 10%–55% if the fan or pump is designed to operate between 40% and 75% of full speed. This usually provides a return on investment which is in the 6–20 month time frame. The Laws of Affinity, which shows an operating range that produces the most flow or pressure per horsepower. The increasing potential benefit from VFD can be estimated from the table below. This is particularly important as "When considering total cost of ownership for an industrial electric motor system, 95%–99% cost is expended on motor energy requirements" (Hart, 2012).

Table 5 shows Estimation of Electrical Energy saving potential through speed control with ratio of actual to full load quantities and percentage reduction in power saving potential. In real life, say in case of one of the leading iron and steel industry in India, the motor loading is generally lower than 80%, as shown in **Table 7**, and so the energy saving potential is up to 49%. When comparing the different methods of mechanical flow control it is clear to see only a VFD gets close to the maximum efficiency of the theoretical fan curve or Pump Flow.

Case Study of India

Table 6 gives sector wise contribution to India GHG emission profile (MEFCC, 2018, 2015; Liu, 2018; Carbon trust, 2018). Energy contributes to as much as 71% of India's carbon emissions and share is shown to be increasing. Therefore, the Government of India has taken up National Action Plans on Climate Change to meet the Sustainable Development Goals of the United Nations. Energy tops the list with first two missions are aiming to enhance use of renewable energy and energy efficiency, all to reduce the carbon emission intensity as India is a signatory to UNFCCC and committed to achieve the set goals.

National Action Plan on Climate Change: Eight National Missions

- (1) Jawaharlal Nehru National Solar Mission.
- (2) National Mission for Enhance Energy Efficiency.
- (3) National Mission on Sustainable Habitat.
- (4) National Water Mission.
- (5) National Mission for Sustaining the Himalayan Ecosystem.
- (6) National Mission for a Green India.
- (7) National Mission for Sustainable Agriculture.
- (8) National Mission for Strategic Knowledge for Climate Change.

Table 5 Estimation of electrical energy saving potential through speed control

Sr. no.	Ratio of actual to full load quantities				% reduction in power saving potential
	Speed	Volume flow rate	Pressure head	Input power	
1	1	1	1	1	0%
2	0.9	0.9	0.81	0.729	27%
3	0.8	0.8	0.64	0.512	49%
4	0.7	0.7	0.49	0.343	66%
5	0.6	0.6	0.36	0.216	78%
6	0.5	0.5	0.25	0.125	88%
7	0.4	0.4	0.16	0.064	94%
8	0.3	0.3	0.09	0.027	97%
9	0.2	0.2	0.04	0.008	99%

Note: Hart, T., 2012. Case Study: Hart Variable Frequency Drives Cut Energy Cost. Siemens Industry, Inc. Available at: https://w3.usa.siemens.com/drives/us/en/formsdocs/Documents/VariableFrequencyDrives_Cut-energy-costs.pdf (accessed 06.12.18).

Table 6 Sector wise contribution to India GHG emission profile

GHG emission (Gg CO ₂ eq)						
Year	1994		2004		2010	
Sector	Emission	Share (%)	Emission	Share (%)	Emission	Share (%)
Energy	743,820	62	1,027,016	67	1,510,121	71%
Industrial process & product use	102,710	7	88,608	6	171,503	8
Agriculture	344,485	29	355,600	23	390,165	18
LUCF	14,292	1.16	– 222,567	–17	– 252,532	–12
Waste	23,233	2	52,552	4	65,052	3
Total (without LUCF)	1,214,248		1,523,777		2,136,841	
Total (net emission)	1,228,540		1,301,209		1,884,309	

Source: MEFCC, 2015. India's First Biennial Update Report to the United Nations Framework Convention on Climate Change. Ministry of Environment, Forest and Climate Change, Government of India, December 2015. Found at: <https://unfccc.int/resource/docs/natc/indbur1.pdf> (accessed 27.12.18).

Table 7 Energy conservation opportunities for iron and steel Industry for Ispat India Ltd at Dolvi Mumbai

Energy conservation opportunities recommended for implementation	Estimated annual savings (INR)	Probable investment (INR)	Simple payback in months	Estimated life of the proposed system (Yrs)	Depreciation charge (INR/Yr)	RoI (%/Yr)
Installation of demand fluctuation Controller system in central Compressed air system at Dolvi	23,212,800	4,050,000	2	10	405,000	563%
Installation of intelligent cooling tower energy saver at Dolvi	6,429,327	1,480,251	3	6	246,709	418%
Installation of VFD's in pumps at Kalmeshwar	5,203,875	1,747,575	4	8	218,447	285%
Application of intelligent/variable drive based on-off system & multi-cell system for cooling tower at Kalmeshwar	1,260,705	356,696	3	6	59,449	337%

Table 8 Hourly CO₂ emission savings with VFD (https://www.lehigh.edu/~inesei/images/posterpdfs/09-10_Wei%20Jung.pdf)

LOAD	CO ₂ emission(t/h) for 10,000 HP motor		
	Without VFD	With VFD	CO ₂ emission saving
100%	5.4506	5.24296	0.20764 (3.809%)
80%	4.2566	3.06271	1.19389 (28.048%)
50%	3.27036	1.03821	2.23215 (68.254%)

Table 9 Annual CO₂ emission savings with VFD (https://www.lehigh.edu/~inesei/images/posterpdfs/09-10_Wei%20Jung.pdf)

LOAD	CO ₂ Emission(t/h) for 10,000 HP motor		
	Without VFD	With VFD	CO ₂ emission saving
100%	47,747	45,928	1819 (3.809%)
80%	37,287	26,829	10,458 (28.048%)
50%	28,648	9094	19,554 (68.254%)

Iron and Steel Industry in India ranks second after power industry in terms of energy use and hence emission of carbon and therefore the Government of India has Designated Consumer with very high target to reduce specific energy consumption and hence emission through an innovative mechanism called Perform Achieve and Trade (PAT). A large number of energy audits has been conducted and huge savings have been achieved through implementation of the recommendations of such studies. In Summary, a few examples of case studies at JSW Works (erstwhile ISPAT Industries Ltd), at Dolvi and Kalmeshwar, Maharashtra, India (based on Energy Audit conducted by IISWBM, Kolkata, India), are placed below:

Table 7 highlights Energy conservation opportunities for Iron and steel Industry for Ispat India Ltd at Dolvi Mumbai. It may be noted that in most of the cases where VFD has been found to be techno-economically viable, the opportunities are favourable over time as the cost of electricity has been increasing at much higher rate than the cost of equipment. In some cases, the cost of VFD has practically come down. Thus, in all the four cases taken from a leading industry unit of 5 TPA capacity of steel production in India have simple payback period less than half-an-year and Return on Investment (RoI) more than 160% per annum. Use of VFD has found its significance even in India's First Biennial Update Report to the United Nations Framework Convention on Climate Change (MEFCC, 2015) where in another leading Industry house, for example, 'Balmer Lawrie & Company (BL)', pointed out the savings achieved through VFD.

Carbon dioxide (CO₂) generated as the consequence of electrically driven industrial machines contributes to global warming. In an effort to reduce CO₂ emissions from industry, this article focus on industrial electric motors equipped with variable frequency drives as the resources of reducing CO₂ emissions. Many machines such as pumps, fans or compressors used in an industrial applications, no matter if they are big or small, are driven by electric drives. Thus, improving the efficiency and saving the energy use of electricity as well as reducing the CO₂ emissions generated by the use of these motors are paramount factor in improving industrial usage. The intensity of CO₂ Emission Savings with for 10,000 HP motors, are shown in **Tables 8** and **9** (see "Relevant Websites section").

The above result shows significant CO₂ Emission reduction with VFD. Applying VFD decrease the emissions of carbon dioxide for use of fans. When the load is half, the savings are significant in comparison with 100% load.

Conclusion

Carbon footprint of industry is one of the vital issue in mitigating the impact of global warming. Industry accounts for more than 40% of world electricity consumptions and out of which more than half is due to electrical motors. From the above evidences it is clearly visible that applying variable frequency drives does decrease CO₂ emission significantly besides increasing energy efficiency. In this article overview of different case study of industrial sector as per USA and Indian perspective are analyzed with respect to carbon footprint and its environmental implications. In India Iron and steel Industry is considered to be designated consumer with synergy to reduce specific energy consumption and hence CO₂ emission through harbinger of technology known as Performance Achievement and Trade (PAT) scheme with respect to carbon dioxide emissions and its synergy of minimization is discussed. Article give in depth study related to harmonics and system efficiency for variable Frequency Drives. Environmental degradation due to carbon footprints are to mitigate and previous data are interpolated for future research. Latest trends and technology as per Indian perspective are of broad area of research for carbon footprints and it can be mitigated by technical awareness and up gradation of technology. Thus applying variable frequency drives are not only to improve the efficiency of motor driven equipments to control load and flow but also significantly reduce carbon footprint.

See also: Greenhouse Effect and Carbon Foot Print

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The Impact of Variable Speed Drives on the Carbon Footprint of Electric Motors Used in Industry.

Is the Production of Biofuels Environmentally Sustainable?

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Introduction (Zinoviev *et al.*, 2010; Reijnders, 2018, 2019)

This article deals with the production of biofuels. Biofuels are renewable. They are based on recently generated biomass. This contrasts fossil fuels which are based on very old, converted biomass. The focus here is on modern biofuels, biofuels which are applied using advanced conversion technologies. Current commercial modern biofuels include gasified biomass and wood pellets applied in advanced power generators and biogas produced by anaerobic conversion and applied in advanced combustion (whether or not after purification). Liquid biofuels applied in modern cars are also included. Modern biofuels are mainly generated on the basis of plant-derived biomass. They can be made from terrestrial lignocellulosic biomass (e.g., woody biomass or harvest residues), from algae, from non-edible oils derived from terrestrial plants, or from terrestrial food (including feed) crops, such as sugarcane, corn, oil palm, rapeseed and wheat.

Use of biomass for electricity generation is currently mainly based on forestry. Cultivation of fast growing plants (e.g., willow) and harvest residues from agriculture (e.g., straw) can also be a source of biomass for power generation. Production of liquid biofuels from substances generated by terrestrial plants that can also be sources of foodstuffs, such as starch, sugar and oil, predominates so far the production of modern liquid biofuels. Currently, about 5% of worldwide food (including feed) production serves the generation of liquid biofuels. Biogas production is based on a wide variety of substrates, including excrements, production residues and crops. Biofuels based on the cultivation of microalgae are under development but as yet not commercially produced. Biofuels that are under discussion include liquid biofuels produced by thermochemical treatment of biomass and bio-hydrogen. There are ambitious plans for the expansion of modern biofuel production.

In this article the question will be raised whether modern biofuels are environmentally sustainable. Environmental regards here: Natural resources, living nature and pollution. Sustainability is a concept which has many operational definitions. Here environmental sustainability will be defined in terms of nearly no decrease of natural capital and resources derived from natural capital that are to be transferred to future (human) generations. *Ceteris paribus*, this would allow for the near indefinite availability of current natural capital and resources derived thereof. Natural capital is defined as the stock of natural assets providing, or able to provide, services to mankind. Such services include the provision with natural resources such as clean fresh water, ores and fossil fuels. Also included are: soil fertility, environments conducive to health, the pollination of crops and climate regulation. The requirement that natural capital and resources derived thereof should not decrease is in line with early definitions of sustainability and with justice between generations. Constancy of natural capital and resources derived thereof fit a steady state economy, an economy in equilibrium with its environment. The qualification 'nearly' in 'nearly no decrease of natural capital and resources derived thereof' is linked to the usage of natural resources which are generated by slow geological processes, such as ores and fossil fuels. No decrease of natural capital would imply that only the ongoing addition to stocks of such resources could be consumed. In the case of many human generations, justice between the generations, however, would allow for limited consumption of natural capital and resources derived thereof beyond the current addition to stocks of natural resources generated in slow geological processes.

A focus on natural capital does not mean that social and economic matters are not important for sustainable development. On the contrary, such matters are highly relevant, also in the context of modern biofuels. The emergence of modern biofuels is linked to socio-economic considerations regarding energy security and farmer's income. Indirect land use change following from the use of food crops for biofuel production due to the economic inelasticity of the demand for food is an important impact of modern liquid biofuel production. Another important impact concerns the displacement of people with insecure land rights by large scale plantations used for modern biofuel production and the effects of using marginal soils for producing biofuels on people currently using such marginal soils for their livelihood. However, there is a case for considering the conservation of natural capital and resources derived thereof as a pre-condition for sustainable development.

Natural capital has many components, reflecting in part the diversity of environmental factors and of natural resources on which an economy depends. In this article a selection of contributions to natural capital will be discussed, based on their relevance to biofuel production. They are important for the production of biofuels and/or substantially affected by the production of biofuels. The contributions to natural capital that will be discussed here are:

- Clean fresh water,
- Soil and soil organic carbon,
- Plant nutrients,
- Living nature providing ecosystem services,
- Fossil fuels,
- Climate as affected by the emission of greenhouse gases and other atmospheric impacts of biofuel production.

These contributions to natural capital will be considered in the following sections.

Clean Fresh Water (Reijnders, 2014a,b; Filoso *et al.*, 2015; Reijnders, 2019)

If compared, per unit of energy produced, with fossil fuels, with solar energy and wind energy, biofuels based on terrestrial crops are characterized by a relatively large consumption of fresh water (surface water, ground water and precipitation such as rainwater). Per unit of energy produced, the fresh water consumption linked to biofuel production from terrestrial crops can be a factor 10^3 – 10^4 larger than the fresh water consumption linked to production of fossil fuels, of solar energy and wind energy. Water consumption per unit of energy produced linked to forestry-based and algal biofuel production is also much larger than the fresh water consumption linked to production of fossil fuels, of solar energy and wind energy. A large consumption of fresh water is problematic when there is fresh water stress (not sufficient sustainably available water to meet demand). Worldwide fresh water stress is increasing. It is estimated that fresh water stress will affect about two-thirds of mankind by the year 2025. Water stress is closely bound up with food production, climate change and population pressure. In practice reversal thereof is very hard, which suggests that current water stress is important to the inter-generational transfer of natural capital linked to fresh water. Ecosystem services (see Section “Living Nature Providing Ecosystem Services” (Reijnders and Huijbregts, 2009; Curran *et al.*, 2014; Reijnders, 2014a; Verdade *et al.*, 2015; Gasparatos *et al.*, 2018)) can be negatively affected by exacerbating fresh water stress.

In practice biofuel production has contributed to increased fresh water stress. An increase in biofuel production may further exacerbate fresh water stress. There is, however, scope for improving water efficiency in biofuel production. Improved water efficiency can reduce water consumption, but it would seem widely beyond the scope of technology to reduce fresh water consumption per unit of energy produced to levels in the order of fresh water consumption linked to the production of fossil fuels, of wind energy and solar energy.

Apart from water pollution linked to erosion, which will be considered in the next section, the cultivation of terrestrial biofuel crops may lead to the pollution of surface and ground water by added plant nutrients (fertilizers) and pesticides. When such substances are persistent (for instance in groundwater and sediments) natural capital to be transferred to future generations may be negatively affected. For instance, in Brazil elevated concentrations of heavy metals such as Cd have been found in aquatic organisms and sediments affected by sugarcane cultivation. This is presumably caused by the presence of heavy metals in added plant nutrients. Such heavy metals may have a longstanding negative impact on natural capital. Their removal from fertilizers before application is preferable.

High inputs of plant nutrients tend to be conducive to large biomass yields, and these are often preferred by cultivators. Pesticide use tend to be larger for food (including feed) crops than for lignocellulosic crops, but it is not certain whether this difference will persist when lignocellulosic crops are further domesticated. Persistent nitrate and pesticide concentrations in groundwater used for the production of drinking water resulting from intensive crop cultivation may exceed standards safeguarding human health. The concentration of phosphorus- and nitrogen- based nutrients in surface water affected by the cultivation of biofuel crops may negatively affect water ecosystem quality and may be conducive to blooms of cyanobacteria which can be a nuisance and may be detrimental to human health. Eutrophication of water systems, including persistent elevated concentrations of plant nutrients in sediments, may have longstanding negative effects on biodiversity in ecosystems and thereby on natural capital.

Conversion of biomass into liquid biofuels can be linked to the generation of waste water containing large amounts of organic substances and plant nutrients. Treatment options exist which can sharply reduce waste water concentrations of plant nutrients and organic substances, but when these are not used, surface water quality may be seriously affected. This is well documented for the wet processing of fruit bunches of oil palm to generate palm oil. Insufficient treatment of palm oil mill waste water is linked to large negative impacts of mill effluents on surface waters. In the case of Brazilian sugarcane processing to ethanol, large volumes of watery vinasse, containing organic substances and plant nutrients, are generated as by-product. In Brazil vinasse tends to be applied to sugarcane fields. This may e.g., lead to excessive K concentrations in groundwater, in which K may persist for a long time, and in surface water.

In the case of biofuels from cultivated fresh water algae, much depends on the recycling of water used for algal cultivation. Such recycling may well be partial in view of preventing the accumulation of substances and pests which can negatively affect subsequent production of freshwater algae. The environmental burden of algal biofuel production for water will be dependent on the treatment of non-recycled water.

Both increased fresh water stress and persistent water pollution can be considered a reduction of natural capital. This does not mean that there can be presently no biofuels, without a negative effect on fresh water related natural capital. A case in point regards biofuels based on forestry with no or very low inputs of plant nutrients and pesticides in areas which are not subject to fresh water stress.

Soil and Soil Organic Carbon (Blanco-Canqui and Lal, 2009; Reijnders, 2014a; Filoso *et al.*, 2015; Lal, 2018)

Erosion of soils under cultivation as arable land may exceed erosion in natural ecosystems by one to two orders of magnitude. Soils of sloping arable land are more at risk of erosion than horizontal soils. *Ceteris paribus*, soils under multiannual cover of crops are less prone to erosion than those under annual crops. Harvesting operations in forestry may also cause increased erosion.

Both wind and water erosion may be caused by biofuel feedstock production. Compaction of soils linked to the use of heavy machinery in biofuel production is conducive to increased water erosion. After deposition from air or water part of eroded soil may contribute to the future production of biomass, but a net loss of productive soil, which is loss of natural capital, is very likely. Sustainable use of mineral soils would require that the net loss of productive soil due to erosion does not exceed productive

mineral soil formation due to natural processes such as weathering. Current biofuel feedstock cropping practices often do not meet this requirement.

Much can be done to limit erosion. In the case of cultivation on arable land, reduced tillage, cover crops, addition of harvest residues, windbreaks to reduce wind erosion and traps for water-eroded soil such as vegetation buffers may contribute to reduced soil losses due to erosion. Selective harvesting in forestry may cause a lower loss of natural capital due to erosion than clear cutting.

Soil organic carbon is of major importance in the limitation of erosion. Also soil organic carbon contributes to water conservation, soil productivity, soil biodiversity, nutrient supply and the reduction of nutrient emissions. The net emission of carbonaceous greenhouse gases from soils is dependent on changes in soil organic carbon stocks. Thus, maintaining levels of soil organic carbon in productive soils and restoring soil organic carbon in depleted soils is relevant to natural capital. Environmental sustainability requires that soil organic matter stocks should not decrease in quality or quantity.

Relatively productive crops, reduced tillage, cover crops and the addition of harvest residues, manure and compost to soils are conducive to the maintenance and restoration of soil organic carbon. The removal of harvest residues for biofuel production may be detrimental to soil organic carbon stocks in mineral soils. Whether this indeed occurs depends on cultivation practices. In the case of reduced tillage, highly productive crops, the use of continuous crop cover, and the addition of manure and compost there may be scope for removal of harvest residues without compromising soil organic carbon stocks. Cultivating bioenergy feedstocks on peat is usually unsustainable because of the net loss of soil organic matter due to cultivation practices such as drainage.

Current cultivation practices may lead to accumulation of heavy metals in soils. The uses of plant nutrients present in sewage sludges, combustion ashes, synthetic P fertilizer (in which substantial amounts of cadmium and uranium may be present) and swine manure (which may contain elevated levels of Cu) have been noted to contribute accumulation of heavy metals that may have a longstanding negative impact on natural capital linked to soil quality. Selective use of sources of plant nutrients on the basis of low bioavailable heavy metal concentrations and better purification in the processing of phosphate ores to synthetic fertilizer are obvious antidotes against accumulation of heavy metals in soils.

Plant Nutrients (Reijnders and Huijbregts, 2009; Reijnders, 2014a,b, 2019)

The indefinite availability of adequate amounts of plant nutrients, such as Ca, Cu, K, Mg, N, P, S and Zn, is important for the environmentally sustainable production of biofuels. Natural processes such as weathering and N-fixation provide addition to nutrient stocks in soils. When biomass is harvested from production systems fed by natural processes, withdrawal of nutrients may exceed natural additions to stocks, leading to decreasing stocks over periods of time relevant to generating new biomass from the same soils. These decreases may be counteracted by recycling nutrients associated with biofuel production to new biomass production. Such recycling practice is, however, rare. Also, in practice such recycling is not without problems. Ashes originating in biomass combustion may show deficiencies in N and S and may induce increased leaching of N-compounds and inhibit plant growth. Cd may accumulate in soils due to the recycling of biomass combustion ashes. For such reasons addition of biomass combustion ashes to soils is restricted or prohibited in several European countries.

Biomass production in systems which are only fed by natural processes is often considered too low for profitable exploitation. This in turn leads to inputs of fertilizers to achieve elevated levels of nutrients such as K, N and P. As noted in Section "Soil and Soil Organic Carbon" (Blanco-Canqui and Lal, 2009; Reijnders, 2014a; Filoso *et al.*, 2015; Lal, 2018), use of those fertilizers may lead to concentrations of substances in soils that have negative impacts. Large inputs of fertilizers may also be associated with relatively high losses of plant nutrients from biomass production systems. These losses may be partly counteracted by cultivation practices conducive to soil- and soil carbon conservation and by the use of deep-rooting plants.

In practice, the production of modern biofuels often tends to be characterized by substantial to high losses of plant nutrients. It might be argued that such losses of natural capital are not a major problem for plant nutrients such as Ca, K and Mg as these nutrients are geochemically abundant. N is abundant in the atmosphere and synthetic N fixation may be powered by wind and solar energy which are characterized by practically indefinite availability. However, plant nutrients such as Cu, P and Zn are not geochemically abundant. For instance, much of P used in biofuel feedstock production is currently provided from ore stocks that have been generated in slow geological processes and are in practice limited. It has been estimated that when mankind runs out of such stocks, natural processes combined with a 90% efficiency of recycling of P in harvested biomass can only supply 3.10^9 people with food. It has been argued that in view thereof the use of ore-derived P should presently only serve its essential use in food production. All in all, the current use of plant nutrients for biofuel feedstock production negatively affects natural capital to be transferred to future generations.

Living Nature Providing Ecosystem Services (Reijnders and Huijbregts, 2009; Curran *et al.*, 2014; Reijnders, 2014a; Verdade *et al.*, 2015; Gasparatos *et al.*, 2018)

Living nature provides mankind with a variety of ecosystem services. These include the provision of food and wood, cleansing of air and water, the provision of pest predators, pollination, ecotourism, climate regulation, protection against 'dustbowls' caused by wind erosion and against natural hazards. Ecosystem services provided by nature are linked to biodiversity: The diversity of species in natural ecosystems. The relation between ecosystem services and biodiversity may be non-linear, e.g., due to the presence of

keystone species, that have a relatively large impact on ecosystem services. The impact of biofuel production on ecosystem services provided by nature is dependent on the nature of the biomass involved, land use and production practices.

Replacement of living nature by food (including feed) crops for biofuel production has occurred on a substantial scale. Examples are the replacement of biodiverse Cerrado natural ecosystems by sugarcane production in Brazil, the replacement of miombo woodland in sub-Saharan Africa for sugarcane production and the replacement of tropical forest by oil palm plantations in South East Asia. In these replacements biodiversity has been substantially reduced.

In the case of cultivating lignocellulosic feedstocks the reduction of biodiversity may be less than in the case of conventional food and feed crops. The presence of buffer zones adjacent to biomass-for-biofuel cultivation may mitigate the reduction of biodiversity.

The inelasticity of demand for food implies that replacement of living nature may also be indirect. In this case diverting food crops on existing agricultural land to biofuel production leads to extra cultivation for food elsewhere, where living nature may be replaced.

Fallow and abandoned land has also been used for the expansion of modern biofuel production and there has been advocacy for more extensive use of fallow and abandoned land to produce biofuel feedstocks. When agricultural land becomes fallow or abandoned, living nature can make inroads, leading to increases in biodiversity. Such increases are, however, not general. A case in point is provided by *Cylindrica imperata* grasslands that cover parts of abandoned agricultural land in the tropics but show little biodiversity. However, often biodiversity is much increased after long periods of fallow or abandonment. When biodiverse fallow or abandoned lands are taken into production to generate biofuel feedstock, biodiversity may be much decreased, with a negative impact on ecosystem services.

Biodiversity of living nature may be negatively affected by additional water consumption related to terrestrial biofuel production in areas subject to water stress. Emissions of plant nutrients, pesticides and organic substances linked to biofuel production may also negatively affect biodiversity of natural ecosystems. Sometimes such negative impacts may occur far away from their source. An example is the increased loading of the Mississippi river with nutrients originating in terrestrial crop production for biofuels, which leads to increased hypoxia in the Gulf of Mexico. In view of the impacts caused by added inputs of nutrients, pesticides and water, which often characterize intensification of cropping, it is uncertain whether such intensification, leading to higher yields per hectare and thus to reduced land use per unit of energy produced, will benefit ecosystem services provided by living nature.

The production of fresh water-based microalgal biofuels may negatively affect ecosystem services by land use change, impact on fresh water availability and waste water emissions. The use of forestry residues for biofuel production is likely to negatively affect animals, plants and fungi which are dependent on the presence of dead wood in forests.

It would seem that the expansion of modern biofuel production so far has had a substantial negative effect on biodiversity and ecosystem services provided by living nature. Reversal thereof tends to take long time spans (more than one human generation) and may well be incomplete. Thus, a negative effect of current biofuel production on natural capital to be transferred to future generations is likely.

The impact of non-fossil energy supply on ecosystem services provided by living nature may be much reduced by replacing bioenergy by other types of energy supply. The net energy production from a hectare of solar cells in the tropics exceeds the net energy generation of biofuels based on oil palm and sugarcane by roughly a factor 40–80. For wind energy the land requirement tends to be even lower than for solar cells. Though both wind and solar energy may negatively affect ecosystem services, their impact per unit of net energy produced is likely to be much lower than the negative impact associated with terrestrial biofuels.

Fossil Fuels (Reijnders and Huijbregts, 2009; Reijnders, 2014a, 2019)

Fossil fuels currently dominate worldwide energy supply, so it will come as no surprise that there are currently fossil fuel inputs in biofuel production. Fossil fuels are generated in slow geological processes. Their formation is ongoing but the addition to stocks is very small, if compared with worldwide fossil fuel consumption.

Fossil fuel inputs in biofuel production are currently e.g., linked to the input of synthetic fertilizers, the use of machinery in harvesting and transport and can also be substantial in biomass processing. Ratios of energy embodied in fossil fuel inputs to biofuel energy outputs can vary strongly: from relatively low for harvested wood to relatively large for European rapeseed-based biodiesel and US corn-ethanol. As current worldwide fossil fuel consumption massively exceeds the additions to stocks, the consumption of fossil fuels in biofuel production adds to the reduction of natural capital. Fossil fuel inputs can be much reduced and even eliminated by the replacement of fossil fuels as energy source by wind and solar energy. Fossil methane that serves as hydrogen donor in the synthesis of N-based fertilizers used in crop cultivation may be partly replaced by increased use of biological N-fixation and by hydrogen generated in solar- or wind power driven electrolysis of water.

Climate as Affected by Greenhouse Gases and Other Atmospheric Impacts of Biofuel Life Cycles (Reijnders, 2014a,b; Filoso *et al.*, 2015; Reijnders, 2019)

The consumption of fossil fuels discussed in Section “Fossil Fuels” (Reijnders and Huijbregts, 2009; Reijnders, 2014a, 2019) impacts climate, but is not the only impact of biofuel production on climate, as affected by greenhouse gases. Another impact of terrestrial biofuel production on climate is associated with changes in above-ground and soil carbon stocks, which in turn can

affect atmospheric CO₂ concentrations. Changes in soil carbon stocks in biofuel feedstock cultivation can be linked to tillage, to burning practices and to cultivation of crops on drained peat. Land use change directly linked to biofuel production can impact carbon stocks (e.g., in case of the replacement of tropical forests by oil palm plantations or the conversion of grasslands to plantations for the production of woody biomass). In the case of new oil palm plantations on peat which replace tropical rain forest, the life cycle CO₂ emission for palm oil-based biodiesel during the lifetime of the plantation is larger than the life cycle CO₂ emission for fossil diesel. Thus, biofuels do not necessarily mitigate the greenhouse effect or carbon footprint if compared with fossil fuels. Carbon stocks may decrease or increase due to direct land use change. An increase of aboveground carbon stocks can e.g., occur when grasslands are converted to plantations for woody biomass, whereas in the case of replacement of tropical forest by oil palm plantations the opposite occurs. Land use change can also be indirectly linked to biofuel production. In the latter case the use of food crops for biofuel production is associated with land use change elsewhere because the demand for food is inelastic. CO₂ is emitted when biofuel production residues and/or biofuels are burned. The latter emission is often valued at zero, because it is assumed to be compensated by sequestration of the same amount of CO₂ by new photosynthesis. However, in the real world new photosynthesis in part sequesters CO₂ that is emitted by the combustion of fossil fuels and due to land use change. Moreover, permanent sequestration of CO₂ emitted by biofuel combustion is not assured.

The emission of other greenhouse gases than CO₂ can also be linked to the production of biofuels. Crop-based biofuel production is associated with substantial emissions of the greenhouse gas N₂O. High inputs of N- and K-based nutrients can be conducive to high emissions of N₂O. In the case of biogas production from biomass, there can be substantial fugitive emissions of the greenhouse gas methane (CH₄).

When the emissions of CO₂, N₂O and CH₄ linked to biofuel life cycles are considered, it is often far from certain that claimed climate benefits of liquid biofuels and biogas, if compared with fossil fuels, do indeed occur.

All in all, biofuel production significantly contributes to the emission of greenhouse gases. As the effect of increased atmospheric concentrations of these greenhouse gases, which is predominantly negative, persists for a long time, this negatively affects natural capital to be transferred to future generations.

Significant negative impacts of biofuel production on air quality may follow from burning practices associated with feedstock cultivation. Such practices have been well documented in case of Brazilian sugarcane cultivation (where they show a diminishing trend). Exposures negatively affecting human health associated with such burning practices have been noted. Particulates and polycyclic aromatic hydrocarbons (PAH) have been implicated in negative impacts of burning practices to human health. As PAH tend to be poorly degradable and may retain bioavailability, there may be a longstanding negative impact of burning practices on natural capital. Another type of emission associated with biofuel production which may have long lasting negative effects on natural capital is the emission of volatile N-compounds that may lead to acidification and eutrophication.

Conclusion

It emerges from the previous sections that current biofuel production is often at variance with the conservation of natural capital that is to be transferred to future generations. In part this is linked to the 'background' of the present state of the world, as related to other human activities. The fresh water consumption associated with biofuels would probably not be a problem in the absence of widespread man-made fresh water stress. The use of fossil fuels in biofuel production is linked to the current dominance of fossil fuels in the world economy. Large scale use of phosphate ores is strongly connected to feeding the present large world population. Thus the answer to the question 'are biofuels environmentally sustainable?' can be highly context-dependent. On the other hand, there is not always strong context-dependency of environmental sustainability of biofuel production. Burning practices in sugarcane production are far from general. Both dry processes and efficient waste water treatment are practiced in parts of palm oil production, and this matters for water pollution. Plant nutrients can be purified before addition to biofuel feedstock cultivation and this can prevent accumulation of heavy metals in soils. Commercial agricultural systems managed in ways that prevent reduction of soil organic carbon stocks are operational. Also the context of biofuel production can change, with benefits to the conservation of natural capital. Fossil fuels may, for instance, be replaced by solar and wind energy systems (in which geochemically scarce elements are subjected to highly efficient recycling).

In conclusion: Presently the answer to the question whether current modern biofuels are environmentally sustainable should often be: No. However, there are options available to make biofuels less environmentally unsustainable.

See also: Green Fuel Blending: A Pollution Reduction Approach. Renewable Biofuels and Their By-Products for Automotive Applications

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Low Carbon Economy for Sustainable Development

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Nomenclature

ASEAN Association of Southeast Asian Nations
CO₂ Carbon dioxide
COP Conference of Parties
DCs Designated Consumers
GHG Greenhouse Gas
HDI Human Development Index
INDC Intended Nationally Determined Contributions
IPCC Intergovernmental Panel on Climate Change

IREDA Indian Renewable Energy Development Agency
NDCs Nationally Determined Contributions
PAT Perform Achieve and Trade
P-D-C-A cycle Plan-Do-Study-Act Cycle
SDG Sustainable Development Goals
UNDP United Nations Development Programme
UNEP United Nations Environment Programme
UNFCCC United Nation Framework for Climate Change

Introduction

United Nation Framework Convention for Climate Change's (UNFCCC) latest Climate Change Conferences (Conference of Parties) – COP24 as well as international climate change agreements are aimed to meet ultimate target of low-carbon economy and tackle global warming to achieve goal of sustainable development. After COP24, the new international regulation suggested that all countries should report their emission cutting progress every two years from 2014 (Carbon Brief, 2018).

The increasing concentrations of carbon dioxide (CO₂) is a serious threat to the earth's environment and to tackle number of new concepts and policies like “carbon footprint”, “low-carbon economy”, “low carbon technology”, “low carbon development”, “a low-carbon lifestyle”, “low carbon city” are coming but unfortunately low carbon became a fashion than real actions. Scientific modeling of climate change suggested that if the growth in global temperatures held below two degrees, there is some hope that negative outcomes of global warming can be avoided (IPCC, 2007). An essential part of climate change mitigation involves replacing fossil fuel-based energy production systems with low or zero-carbon energy sources (Snell and Schmitt, 2012).

The low carbon economy defined as ‘the activities which generate products or services which deliver low carbon outputs’ (DBIS, 2015). The European Commission (2016) has a roadmap which states that by 2050, the EU should reduce emissions to 80% below 1990 levels. The Paris Agreement establishes a new mechanism for post-2020 global climate governance and sets long-term goals to accelerate worldwide low-carbon transformation of economic development, promote the revolutionary reform of energy system which helps to develop industrial civilization to eco-civilization (He, 2016). To date, very few countries have demonstrated the willingness or capacity to make these necessary changes.

Based on the recent development of low carbon economy, this article highlighted the existing problems of low-carbon economy in developing countries and some alternatives to overcome the problem including the energy efficiency, technology modification and country level carbon financial system and suggestions to achieve at country level.

Low Carbon Economy Status – Worldwide

The IPCC's Fifth Assessment Report (IPCC, 2014) confirmed that the impacts of climate change are increasing, largely driven by anthropogenic Greenhouse Gas (GHG) emissions. New innovations along with demand-focused policies favouring low-carbon economy are vital for every country worldwide. To know what amount of attention a particular country must provide, it is required to know how much a particular country is contributing and to what extent the country is willing to engage to keep global temperature below 1.5°C. Historically developing countries contributing less to GHG emission than developed countries. They need to concentrate more in carbon-intensive investment with the aim to reduce poverty. For example, countries in East and South Asia and the Pacific which have reduced their levels of poverty have in turn increased their emissions over 200%, while regions like Sub-Saharan Africa (which have experienced increases in poverty) have in turn had decreases in carbon emissions (Goldstein, 2015). Research shows that while urbanization in developing countries is decoupled from industrialization, suggesting a different trajectory for increases in carbon emissions (Vollrath et al., 2016). Developing countries are more energy intensive than developed countries (Fankhauser and Jotzo, 2018). Therefore the role of developing countries is very much essential to limit global temperature increase.

Low Carbon Development and Developing Country

Stabilizing the world's climate change and successfully addressing Sustainable Development Goals (SDGs) would not be possible without effective planning and implementation of low carbon economy by developing countries. The effective policy to address

Table 1 Comparative analysis of low carbon policy and development – China vis-a-vis India

Theme	China	India
Copenhagen accord target	40%–45% by 2020 in comparison to 2005 levels	20%–25% by 2020 in comparison to 2005 levels
INDC target (emission intensity)	60%–65% by 2030 in comparison to 2005 levels	33%–35% by 2030 in comparison to 2005 levels
INDC: peaking	2030 or earlier	–
INDC: non-fossil fuel	Non-fossil fuels in primary energy consumption to be around 20% by 2030	To achieve 40% cumulative electric power installed capacity from non-fossil fuel based energy resources by 2030
INDC: forestry and land use	To increase the forest stock volume by around 4.5 billion m ³ on the 2005 level by 2030	Create additional carbon sink of 2.5–3 billion tonnes of CO ₂ equivalent through additional forest and tree cover by 2030
INDC: financing needs	–	US\$ 2.5 trillion (at 2014–2015 prices) will be required for meeting India's climate change actions between now and 2030
National climate policy	China's Policies and Actions on Climate Change (2014)	National Action Plan on Climate Change (2008)
Key national agency coordinating climate change	National Strategy for Climate Adaptation The National Development and Reform Commission	National Adaptation Fund Ministry of Environment, Forest and Climate Change
Sub-national initiatives	Low carbon Pilot Projects in Provinces and Cities	State Action Plan on Climate Change
Emissions/energy trading	Carbon Emissions Trading Pilot Programme	Energy Saving Certificate and Renewable Energy Certificates
Technology development	China's Science and Technology Actions on Climate Change	Climate Change Centres in states
South–South cooperation	Fund for South–South Cooperation on Climate Change	International Solar Alliance

Abbreviation: INDC, intended nationally determined contributions.

Source: He, J.-K., 2016. Global low-carbon transition and China's response strategies. *Advances in Climate Change Research* 7 (4), 213–221.

three dimensions of sustainability with an integrated model and a realistic approach is the solution to make it effective within 2030. According to [Steckel et al. \(2017\)](#), the main challenge is to avoid future emission in different energy consuming sectors through emission-intensive technologies. Though policy instrument like 'carbon prices' was often rejected by developing nations, new comparative sustainable economic growth policy is required. [Jakob et al. \(2016\)](#) proposes use of revenues from carbon pricing to finance infrastructure investment. In many countries, the revenues which a government can collect from taxing CO₂, can then be utilized to finance measures for achieving the SDGs, e.g., access to water, sanitation or electricity. [Dorband \(2016\)](#) shows that a carbon tax applications turns out to be largely progressive and minimizing emission concerns. Many fast developing countries have developed targets for near future and to achieve low-carbon economy. **Table 1** presents comparative analysis of low carbon policy and development – China vis-a-vis India.

Innovation, Financing and Sub-National Actions

Along with policy initiative, new innovative practices in low-carbon technologies, financing, and actions are focus areas that will enable China and India to achieve their emission reduction goals (**Table 2**).

Low Carbon Green Growth in Asia

Clean renewable energy approach and low-carbon technology is widely viewed as the next step of development and economic growth. Most governments are aware of innovation and new technological growth. For example, the Government of Republic of Korea recognized offshore wind power as its next big global player ([GGGI, 2011](#)). Globally, various governments and businesses have adopted green and clean energy solutions with an aim to deduce carbon emission. The involvement of different sectors like power, manufacturing, energy, environment, transportation is vital to develop low-carbon economy in Indian scenario.

The ASEAN region which is usually known as a rich natural energy region in the world, some countries in ASEAN perform quite poorly with regard to energy resources. According to [The World Bank Database \(2016\)](#), 4 out of 10 countries in ASEAN are energy importing countries including Singapore (98%), the Philippines (46%), Thailand (42%) and Cambodia (33%). Other countries such as Brunei, Indonesia, Myanmar and Vietnam whose main source of income is commercial energy, will continue to provide important energy resources to other countries in the region.

Policy Framework for Low Carbon Economy

The policy framework of low-carbon economy is basically based on policy instruments that governments are using to meet the climate change mitigation targets.

Table 2 Key practices on low carbon development in China and India

Strategy	China	India
Technology and Innovation	Market based demonstration and deployment National Scientific and Technological Plan on Climate Change	National Mission on Strategic Knowledge for Climate Change National Mission for Sustaining Himalayan Ecosystem
Innovative Financing	Green Fiscal Stimulus Green Credit Guidelines Emission Trading Scheme	Clean Energy Fund Renewable energy certificates Priority sector lending norms Green Bonds Fiscal transfers
Informing Sub-national Actions	Low carbon pilots	State Action Plan on Climate Change

Source: Based on China-India Low Carbon Study – Publication links: TERI-NCSC-CUFE-ZU-UNDP, 2016. Low Carbon Development in China and India: Issues and Strategies. Available at: <http://www.teriin.org/projects/locci>. It is available in Chinese at www.cn.undp.org.

Table 3 Climate change mitigation instruments

Carbon pricing	Technology-based	
Fiscal	Fiscal	Regulatory
Emission trading	Demonstration grants	Technology performance standards
Carbon tax	Public Research and development	Renewable fuel /energy standards
Hybrid trading-tax scheme	Investment subsidies	Building regulations
	Preferential tax treatment	Automobile regulations
	Government investment in venture capital	Information standards
	Public investment vehicles	
	Feed-in traffic	
	Tax credits	
	Public procurement	
	Renewable energy certificate trading	
	Subsidies for energy-efficiency purchases	

Source: Howes, S., Dobes, L., 2011. Climate Change and Fiscal Policy: A Report for APEC. Washington DC: World Bank: Office of the Chief Economist, East Asia and Specific Region.

Howes and Dobes (2011), had an analysis and the discussion was divided into two sections – technology based policies and carbon-pricing policies. Technology-based policies are in favor of a particular technology or a group of policies. On the other hand, carbon-policies are based on how emission reduction occurs to market forces, technology policies or research and development funding involve in favor of a particular technology or project. Both carbon pricing and technology policies are aimed to evaluate market failure in different ways. Table 3 detailed climate change policy instruments under these two categorization.

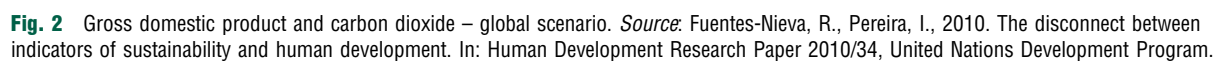
Low Carbon Development Strategy and Lifestyle Choices

Asia is the most populous continent accounting for 60% of the world population where the world's two most populated countries, China and India, together constitute about 36% of the world's population (World Population Review, 2018). Energy consumption was increased in most of Asian countries, such as China, India, Indonesia, Malaysia and South Korea. Chinese energy consumption rose twice as fast as in 2016, pulled-up by a strong industrial demand, energy efficiency gains in the industry and national policies to decarbonize the economy (Global Energy Statistics Year Book, 2018).

World's growth patterns have demonstrated that it is not necessary to consume excess energy in order to improve the Human Development Index (HDI) of the United Nations Development Programme (UNDP), which is used as a measuring level of development of a country. But along with the development, there is a trend to depend on more resources, products and so produce more waste. Along with technological development, it is now possible to find solutions that are decentralized, energy efficient, cost-effective and some of them are well-suited for developing nations.

Human Development Index (HDI) of any country is influenced by their per capita energy consumption. Fig. 1 present the status of energy consumption and HDI. Three important observations from the Fig. 1 emphasize the need to focus on India and China as developing nations:

- (1) Improvement in Human Development Index (HDI) calls for higher per capita electricity consumption
- (2) After a certain level (say 4000 units/head/year) of electricity consumption, the HDI does not increase significantly and rather shows a diminishing rate of impact on HDI.



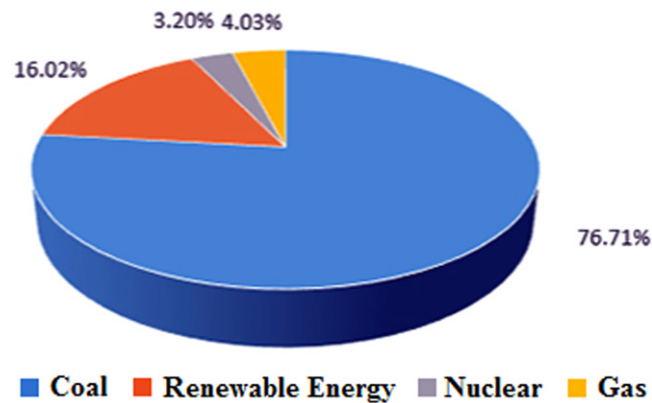


Fig. 3 Sources of electricity generation in India (as on April 2017). *Source:* Central Electricity Authority – Growth of electricity in India from sector from 1947 to 2015.

Table 4 Lifestyle changes and related factors – Energy

<i>Lifestyle change</i>	<i>Hurdles</i>	<i>Policies</i>	<i>Level</i>	<i>Example</i>
Optimizing setting in household appliances	Lack of knowledge and awareness	Awareness campaigns, training programs, support energy service companies	Local	
Use energy efficient appliances	High up-front investment, lack of awareness, lack of uniform standard	National standards and labeling, product service systems as market mechanism, tax incentives	National and middle and high income class	Energy labeling programme for appliances and houses, promotion of energy efficiency in
Use of solar appliances such as water heaters, solar cookers, solar lamps, solar photovoltaic panels	High initial investment, lack of awareness, lack of availability	Loan systems, provide tax incentives, other government initiatives	Local and national	Sustainable financing mechanisms for delivering renewable energy system

Source: Asian Development Bank, 2015. Managing the Transition to a Low-Carbon Economy, ISBN 978-4-89974-057-5, Japan.

Table 5 Lifestyle changes and related factors – Waste

<i>Lifestyle change</i>	<i>Hurdles</i>	<i>Policies</i>	<i>Level</i>	<i>Example</i>
Avoid heavy packaging	Packaging design of products	Awards for companies that reduce packaging material, awareness campaign	National	
Buy in bulk	Not available in supermarkets	Legislation and incentives for supermarkets to offer certain food items in bulk	Local and national	eFoodsDirect sells groceries in Utah, US (eFoodsDirect, 2012)
Send back old appliances such as laptops to the company	Inconvenient, awareness	Awareness campaigns	National	Dell (2012) and Apple (Price, 2011) buy back old products from customers. Both refurbish and resell their own computers with a 1-year warranty.
Reuse cans, bags, and containers	Inconvenient	Tax on waste, refund for cans, bags, and containers	Local and national	Most EU countries have introduced landfill taxes (Economic Instruments in Environment Policy, 2010)

Source: Asian Development Bank, 2015. Managing the Transition to a Low-Carbon Economy, ISBN 978-4-89974-057-5, Japan.

- (3) If India and China would follow the average path assuming to become developed economy at average electricity consumption rate of about 8000 kWh/head/year, another earth without population but full resources, besides our mother earth, would have been necessary for sustainable development. On the other hand, if India and China apply all learning worldwide to apply locally as per appropriate, in the process of becoming developed nation, it could be possible at around 2000 kWh/head/year. Hence our special attention in this article has been India and China, along with global issues.

Table 6 Potential of demand reduction from determined effort scenario to heroic effort scenario for India

Sectors	Sector demand in 2012 (TWh)	Demand in 2047 (TWh)			Policy response
		Determined effort	Heroic effort	% Savings	
Buildings	238	2287	1540	33%	Energy Conservation Building Code 2017 version is more versatile and optimistic with compared to the first version released in 2007
Industry	2370	10,430	6912	34%	Energy Conservation Act 2001 amended in 2010 is much more stringent than the first version. The Perform Achieve and Trade (PAT) mechanism applicable to 866 Designated Consumers Industrial Units in 13 sectors including larger commercial buildings. DCs consume more than 50% of India's Energy Consumption
Transport	929	4414	2975	33%	Green Mobility Mission: by the year 2030, 100% of the vehicles will run on electricity, later reduced to 50%
Pumps and Tractors	237	798	533	33%	Large utility in Agricultural Sector feeding the large is fast undergoing mechanization
Telecom	83	184	66	64%	Highest % saving opportunity in this high growth sector
Cooking	1072	522	410	21%	A consistent improvement is in place because of increasing awareness and government policy to shift to more cleaner safer and efficient mode of cooking, which was earlier based on direct burning of fire-wood in rural sector where almost 70% population lived
Total	4929	18,635	12,436	33%	

Source: India Energy Scenario 2047 version 2, NityAayog, Government of India, from <http://indiaenergy.gov.in/> (accessed 15.03.19).

Table 7 Policy response to look urban economy in India

Emissions in 2047 (MTCO ₂ Eq)			
Sector	Determined effort pathway	Maximum renewable and clean energy pathway	% Savings
Industry	5935	3559	40%
Transport	1118	709	37%
Agriculture	72	43	40%
Telecom	37	3	92%
Thermal Generation	2678	1409	47%
Bioenergy	–304	–363	(19%)
Fossil Fuel Production	93	93	–
Fossil Fuel Transfer	109	73	33%
Total	9738	5526	43%

Source: NITI Aayog, Government of India, 2018. Handbook of Indian Energy Security Scenario 2047, Version 2.0. Available at: <http://www.niti.gov.in/> (accessed 15.04.19).

Fig. 2 presents the global scenario gross domestic product – purchasing power parity and carbon dioxide emission.

This section attempts to highlight some policies development recommendations to improve awareness and decision making of people to change their lifestyle and help to minimize climate change.

Power Sector

Global electricity production and consumption are not sustainable. The main source of energy are fossil fuels such as coal, oil and gas which are the fastest growing contributor of carbon di-oxide contributor (**Fig. 3**). As of 2015, power generation in India accounted for 44% of domestic GHG emissions (**Ministry of Environment, Forest and Climate Change, 2015**).

Organizational standardized approach to account their GHG emissions and carbon footprint are implementing in many ways. Renewable energy certificates (RECs) which is used to manage indirect emissions and offsets which is used to reduce direct global emissions few approaches which are used to track and substantiate emissions reductions. The carbon footprint study is the basis of any low-carbon research and has been utilized by organizations to measure their product's carbon and take proper measures to reduce carbon emission and meet sustainable development goals.

Transport and Mobility

Transport is the key component of today's economic development and along with e-commerce the volume and intensity increasing around the world. The problems and challenges associated with transport are growing large amount of air pollution,

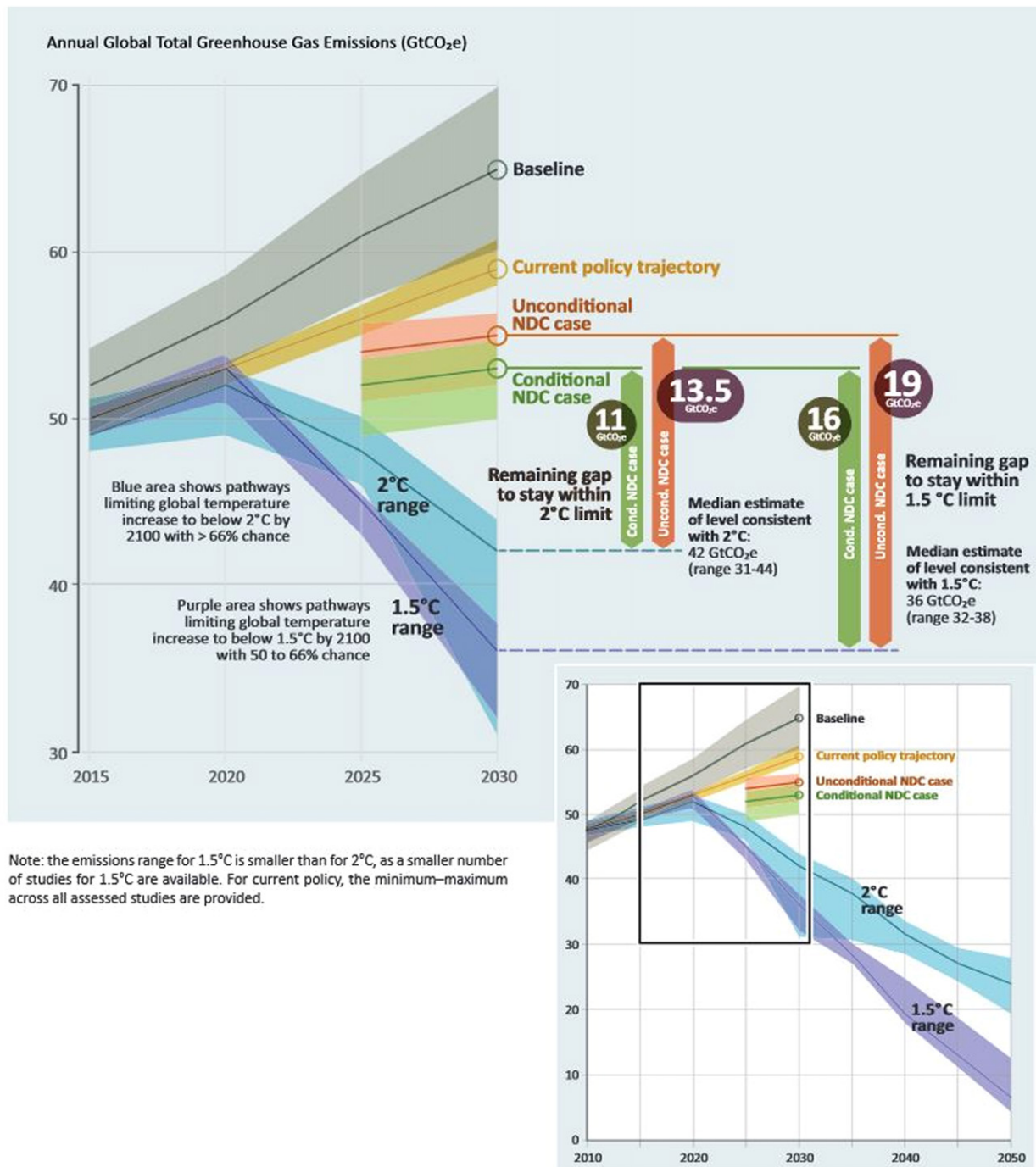


Fig. 4 Global GHG emissions under different scenarios and emissions gap in 2030. *Source:* The Emissions Gap Report 2017, UNEP, November 2017.

GHG emissions, petroleum dependency, traffic congestion, infrastructure cost and packaging waste. These are rapidly growing in developing countries where economic development and population is also growing rapidly.

It was mentioned in the document of Government of the Republic of India and the Government of the People's Republic of China in a Joint Statement on Climate Change between India and China that "climate change and its adverse effects are the common concern of mankind and one of the greatest global challenges of the 21st century, which needs to be addressed through international cooperation in the context of sustainable development". China and India reiterated that their bilateral partnership on the issue of climate change is mutually beneficial as well as globally significant (Kedia and Jain, 2015).

Table 8 Low carbon financial mechanisms in India

<i>Description</i>	<i>Type</i>	<i>Mechanisms in India</i>
Public finance and fiscal instruments	Tax revenue	Coal cess
	Coal cess Budgetary allocations and fiscal transfers	Annual budgetary allocations, center-state fiscal transfers
	Subsidies	Example include subsidies on solar heaters, electric vehicles, energy efficient appliances
Financing mechanisms	Fiscal instruments	Tax rebates
	Special Funds / Institutions	National Clean Energy Fund, state energy conservation fund, IREDA, sub-national funds
	Markets innovations	Indices such as Greenex and Carbonex
	Traditional market instruments	Green bonds for renewable energy, energy efficiency and green infrastructure projects
	Climate / energy market instruments	Clean Development Mechanism, Renewable Energy Certificates, Energy Saving Certificates
Risk management	Banking provisions	Special provisions for MSME, priority sector lending norms by the Reserve Bank of India
	Risk management mechanisms	The Partial Risk Guarantee Fund under the National Mission on Enhanced Energy Efficiency, Credit Guarantee Fund Trust for Micro and Small Enterprises
International sources	Grants	Bilateral and multilateral sources
	International climate finance	Green Climate Fund, Adaptation Fund

Source: Based on Kedia, S., Jain, N., 2015. Financing for Low Carbon Development in India (Policy Brief). Available at: http://www.teriin.org/projects/loci/pdf/res/Policy_Brief_LCD_Finance.pdf (accessed 21.01.19).

Waste Management

In the past, when the definition of waste was different that today, it was reused, transmuting into a new resource. This attitude of resource management still exists in villages in developing countries, where material cycle is completed, intimating the ecosystem. Every year we dump a massive 2.12 billion tons of waste and global waste to grow by 70% by 2050 unless urgent action is taken (The World Bank Report, 2018).

Low-Carbon Green Growth in Asia

Low-carbon green growth is provided recently whether in developed country or in developing country. But the different is quite similar with a large-scale industry and a small-scale industry. With changes there are many lifestyle change factors which are applicable in different levels (Tables 4 and 5).

Low Carbon Economy – Indian Perspectives

Sustainable Low Carbon Strategies in India

A relevant observation on opportunities while meeting the fundamental needs of people of India is placed below (Table 6).

Food: Harmonic development has been proved to be possible through growing number of successful organic farming. Bio-gas plant also produces green fertilizer besides providing energy from waste.

Cloths: The textile industry accounts for 14% of industrial production, which is 4% of gross domestic product employs 45 million people, and accounts for 13% of the country's total export basket.

Buildings: India's 2/3 of buildings yet to come up by 2030 to provide shelter then largest populous country. India can directly apply the latest advancement taken in this sector worldwide. Going green can reduce emission and help resource conservation by more than 50% in this sector.

Sustainability Challenges and Policy Response to Low Carbon Economy in India

Many natural species has become extinct for which they or their activities may not be responsible at all. Modern research also revealed that if this human civilization becomes extinct, it would be mainly due to anthropogenic intervention to nature. Supply side analysis of impact on Primary Energy Supply as a result of changes in demand pathways reveals the sustainability challenges in low carbon economy. The intervention cause, challenge and policy response are shown in the Table 7. Fig. 4 presents global GHG emissions under different scenarios and emissions gap in 2030.

Low Carbon Financial Mechanisms in India

Financial mechanisms for low carbon development in practice in India include public finance, traditional finance, risk management instruments, market-based tradable instruments, and international sources (Table 8). While there is no domestic carbon market

developed in India, instruments such as renewable energy certificates are traded at the Power Exchange India Limited. In terms of mechanisms developed by the central banking regulatory authority, there is a scope for the issuance of green credit guidelines.

Conclusion

It is revealed in this article that mitigation GHG emission and carbon footprint through Low Carbon Economy along with renewable energy approach is not an option but compulsion for sustainable development. The recent global economy growth also witnessed a considerable increase in global energy demand matched by overall increase in CO₂ emissions despite, some emissions have been prevented by switching from coal to gas that helped to avoid 60 million tonnes CO₂ emissions that would have come from coal. Additionally, a greater shift towards renewable energy in 2018 helped the world avoid 215 Mt in emissions. China and Europe led the global push for green energy. Increase efficiency of energy sources was the biggest saver in emissions, helping to avoid nearly 275 Mt in CO₂ emissions. An opportunity in the commercialization of low-carbon solutions, including energy efficiency and clean energy technologies, can support the transformation of the global energy sector. Simultaneously, this transition presents an enormous challenge given the significant capital required to transform economies that have been reliant on an energy system that has been largely fossil-fuel based. All the key objectives of MDGs are directly or indirectly related to low carbon economy, as it is one of the main drivers towards achievement of sustainability. The initiatives taken worldwide are worthy of praise but far from actual need, particularly in terms of practical actions. Some of the key findings to take this mission forward include awareness at all walks of life, inclusion in topics in syllabus from school level to all subjects of study in appropriately significant manner for strengthening awareness regarding implications of energy intensity and efficiency, innovative green technologies and techniques appropriate to the need, short-medium-and-long term policy and action plan in a P-D-C-A cycle to attain continual progress, as indicated in this article. To achieve the goal of low carbon economy for long term sustainability, the key potential areas has been found to be power, steel, cement and other industrial sectors including transportation and waste management, etc.

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Manufacturing of Biodegradable Poly Lactic Acid (PLA): Green Alternatives to Petroleum Derived Plastics

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Introduction

Climate change mitigation and reduction in carbon footprint requires lowering of the emissions of greenhouse gases (GHG's). Petroleum based plastic production industrially in industries is responsible for GHG emissions and since they are non-biodegradable their incineration after use also contributes to the emissions. These growing environmental problems have led researchers to develop novel environment friendly materials from renewable resources which could be easily which will reduce emissions as well as be biodegraded after their use. The next generation of materials are now being developed keeping this environmental sustainability in mind. This has resulted in the development of biodegradable polymers which can replace the polymers from petrochemical sources effectively (An *et al.*, 2013). Polylactic acid (PLA) is one such polymer which can be used to produce environment friendly biodegradable materials for various industrial applications like automobile and electronics manufacturing owing to its enhanced mechanical properties (Huda *et al.*, 2008). PLA is a hydroxyacid derived polymer belonging to a family of aliphatic polyesters. The monomer lactic acid (2-hydroxy propionic acid) exist in optically active L- or D-enantiomers. The proportion of enantiomers results in the production of PLA with variable properties. Thus, PLA polymers can be produced in wide variety catering to various requirements of the materials produced. Since, PLA has good mechanical, optical and barrier properties in comparison with the commonly used petroleum based polymers it can be effectively used to replace them (Lim *et al.*, 2008).

Poly lactide (PLA) is one of the most promising biodegradable polymers owing to its mechanical property profile, thermoplastic processibility and biological properties, such as biocompatibility and biodegradability. Moreover, the degradation products of polylactides are nontoxic which enhances practical applications in biomedicine. PLA is currently being commercialized for a wide spectrum of applications. The polymer was first obtained by Carothers in 1932 as a low molecular weight product by heating lactic acid in vacuum. Although the initial work did not produce a high molecular weight polymer, DuPont was awarded a patent for a process to produce high molecular weight materials. The commercialization of the polymer for the bioabsorbable high strength suture VICRYL was taken up by Ethicon in 1972 (Avérous, 2008). This suture is a copolymer of glycolic acid and lactic acid in 90:10 ratio and undergoes relatively fast hydrolytic cleavage of the backbone ester linkage under alkaline or acidic conditions. is accelerated by in-situ formation of carboxyl end groups (Jamshidian *et al.*, 2010). This polymer in combination with other comonomers, such as caprolactone or glycolic acid, has produced interesting materials that could provide requisite behavior and performance as biomaterials (Gupta *et al.*, 2007).

PLA in comparison to other biopolymers has several advantages. These are: (1) The lactide monomer from lactic acid is obtained by fermentation from renewable resources, (2) The source i.e., corn's production results in fixation of carbon dioxide by the corn plant, (3) The manufacturing is energy saving, (4) It could be recycled back by alcoholysis or hydrolysis to lactic acid. (5) PLA could be used in manufacturing compostable hybrid paper-plastic packaging material, (6) Use of PLA materials in turn reduces landfill volumes, (7) it improves agricultural economy. (8) It could be used to make tailor made consumer products (Jamshidian *et al.*, 2010).

PLA has wide application in biomedical field due to its biocompatibility characteristics. PLA has been studied extensively for tissue engineering and drug delivery system and has been widely used in human medicine. Many of the PLA properties are compared to those polyethylene, polypropylene, polystyrene, and polyethylene terephthalate (such as stiffness, tensile strength, and gas permeability), turning PLA into a potential substitutes to petroleum based products such as trash bags, table utensils, films, paper coating, fiber, and cloth (Carlotta, 2001).

Poly lactic Acid (PLA)

Chemistry of Poly lactic Acid

The polymer PLA is processed by polymerizing lactic acid monomer. As discussed earlier lactic acid ($\text{HOCH}_2\text{CHCOOH}$) is a simple chiral molecule existing in two enantiomeric forms of D-lactic acid and L-lactic acid, differing in their effect on polarized light. The D and L isomer rotates the plane of light counter clockwise and clockwise respectively. D, L or meso form is racemic (equimolar) mixture of D and L isomers and is optically inactive. Lactic acid is produced in mammalian body is involved in Kreb's cycle through pyruvic acid and acetyl CoA synthesis and produced in muscles during glycogenolysis. Lactic acid is prepared by fermentation of molasses or dextrose of corn or potato starch. The structure of PLA is given in (Fig. 1).

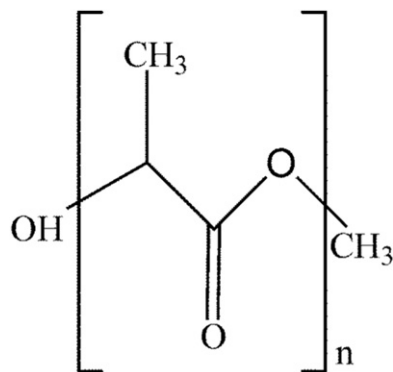


Fig. 1 Structure of PLA.

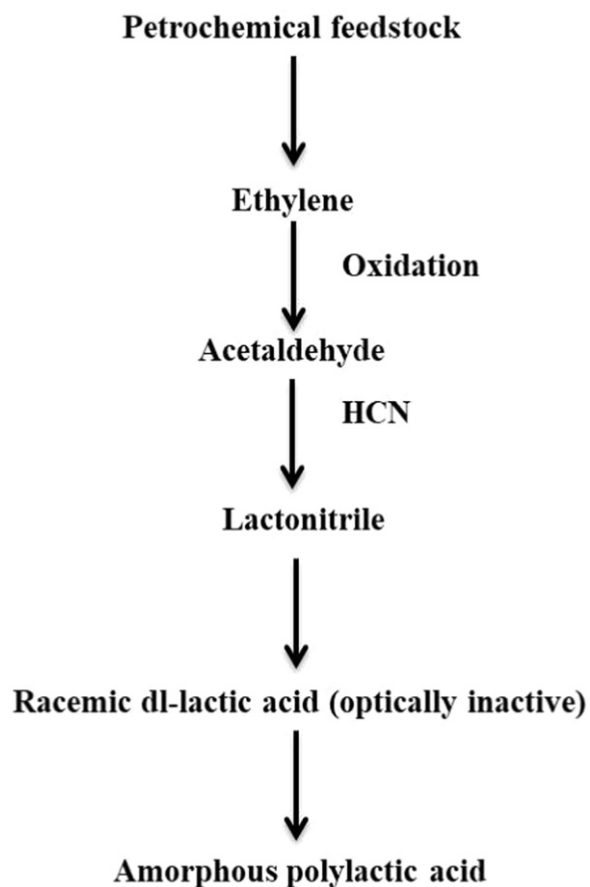


Fig. 2 Schematic representation of petrochemical route of PLA synthesis. Reproduced from Gupta, B., Revagade, N., Hilborn, J., 2007. Poly (lactic acid) fiber: An overview. *Progress in Polymer Science* 32, 455–482.

Synthesis of Polylactic Acid

The basic building block of PLA is lactic acid. This can be produced by carbohydrate fermentation or by chemical synthesis. At present the majority of lactic acid production is done by the fermentation route. However different technologies have been developed to purify the products (Datta and Henry, 2006).

In the past another route of lactic acid production was prevalent upto 1990s where lactic acid monomer was produced from petrochemical feedstock. The produced lactic acid is an optically inactive racemic mixture of D and L enantiomers. Nowadays the more economic fermentation approach is used (Gupta *et al.*, 2007). A schematic representation is given below in (Fig. 2).

In recent years more usage of PLA could be attributed to the economical production of high molecular weight PLA polymers (100,000 Da). Several techniques have been adopted for their production which includes direct condensation polymerization, azeotropic dehydrative polymerization and/or polymerization through lactide formation. The commercially available PLA polymers are produced mainly by the lactide ring-opening polymerization route (Lim *et al.*, 2008).

Biosynthesis of PLA

Biosynthesis of PLA for commercial production utilizes corn as a feedstock. The corn first undergoes traditional milling in order to produce glucose/dextrose. Then glucose is fermented to form lactic acid. Many studies have been conducted to find other sources of carbohydrates for lactic acid production. The availability, purity and price of the carbohydrate feedstock determine its use. The agricultural by products used for lactic acid production include starch, cassava, lignocellulose/hemicellulose hydrolysates, Jerusalem artichokes, cotton seed hulls, beet molasses, cornstalks, sugarcane press mud, rye flour, wheat bran, barley starch, sweet sorghum, molasses, carrot processing waste, corn fiber hydrosylates and potato starch. Alternative sources of carbohydrate production includes fish meal wastes, Kitchen waste and paper sludge. Using kitchen wastes for PLA synthesis could help significantly in reducing domestic waste disposal problems in the cities. This will also reduce large amount of corn consumption (Jamshidian *et al.*, 2010; Carlotta, 2001).

The fermentation process for obtaining lactic acid for PLA synthesis is anaerobic. Anaerobic fermentations have more advantage over aerobic fermentation with respect to CO₂ balance. In industries homofermentive method is used more because of greater yields and small amount of byproduct generation (Jamshidian *et al.*, 2010). The bacteria lactobacillus is used in this process and the organisms commonly used are *L. leichmanii*, *L. amylophilus*, *L. bulgaricus*, *L. delbrueckii* at temperature range of 38–42°C and pH range of 5.4–6.4 with low oxygen concentration.

Fermentation is conducted in batch process commercially which takes about three to six days to complete. 5%–10% of sugar concentrations are used which produces about 2 gm of acid per 1 L of broth in 1 h. Finally, a high concentration of lactic acid is required to give maximum efficiency. In order to maintain the bacterial cell growth different methods of neutralization or extraction of the lactic acid is required to produce either all hydroxyl or all carboxyl groups (Carlotta, 2001).

After lactic acid synthesis it is dimerized and purified using reactive distillation. The separation of lactic acid from the broth is done by adding calcium hydroxide or calcium carbonate in the presence of a small amount of multifunctional hydroxyl compounds such as 2-butene in order to neutralize the fermented acid and give the soluble calcium lactate solutions. This calcium lactate solution is filtered with addition of 1,4-diol, glycerol, or 1,4-butanediol in order to get preferential hydroxyl end-groups. The purification can also be conducted post condensation to remove all the cell biomass alongwith other insolubles, after which the solutions are evaporated, recrystallized, and acidified yield the crude lactic acid (Carlotta, 2001).

PLA is then formed by polymerization. The two general polymer synthesis routes for PLA include the condensation polymerization of lactic acid and the ring-opening polymerization of lactide (Jamshidian *et al.*, 2010). The biosynthesis of PLA is given below in (Fig. 3).

Polymerization of Lactic Acid

As discussed earlier synthesis of high –molecular weight PLA follows different routes. The polymerization methods are given below in (Fig. 4).

Condensation polymerized lactic acid has low molecular weight which could be increased to high molecular weight by using chain extending agents. Esterification and use of coupling agents are also used to increase the molecular weight. However these addition products used for increase of molecular weight of the PLA generates byproducts which should be removed or neutralized. The method of ring opening polymerization or ROP also yields high molecular weight PLA. This method was the only method of producing pure, high-molecular-weight PLA until Mitsui Toatsu Chemicals recently commercialized a process wherein lactic azeotropically dehydrated in a refluxing, high-boiling, aprotic solvent under reduced pressures in order to obtain PLA with an weight-average molecular > 300,000 (Carlotta, 2001).

Processing of PLA

The main conversion methods used nowadays is melt processing. Melt processing involves heating of the polymer over its melting point and then shaping the melt material in desired shapes and sizes and then cooling it into required dimensions. The melt rheological,

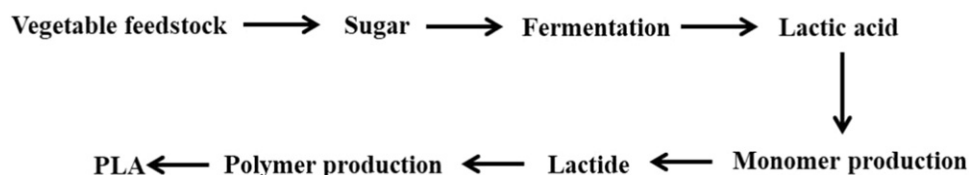


Fig. 3 Schematic representation of biosynthesis of PLA. Reproduced from Gupta, B., Revagade, N., Hilborn, J., 2007. Poly (lactic acid) fiber: An overview. Progress in Polymer Science 32, 455–482.

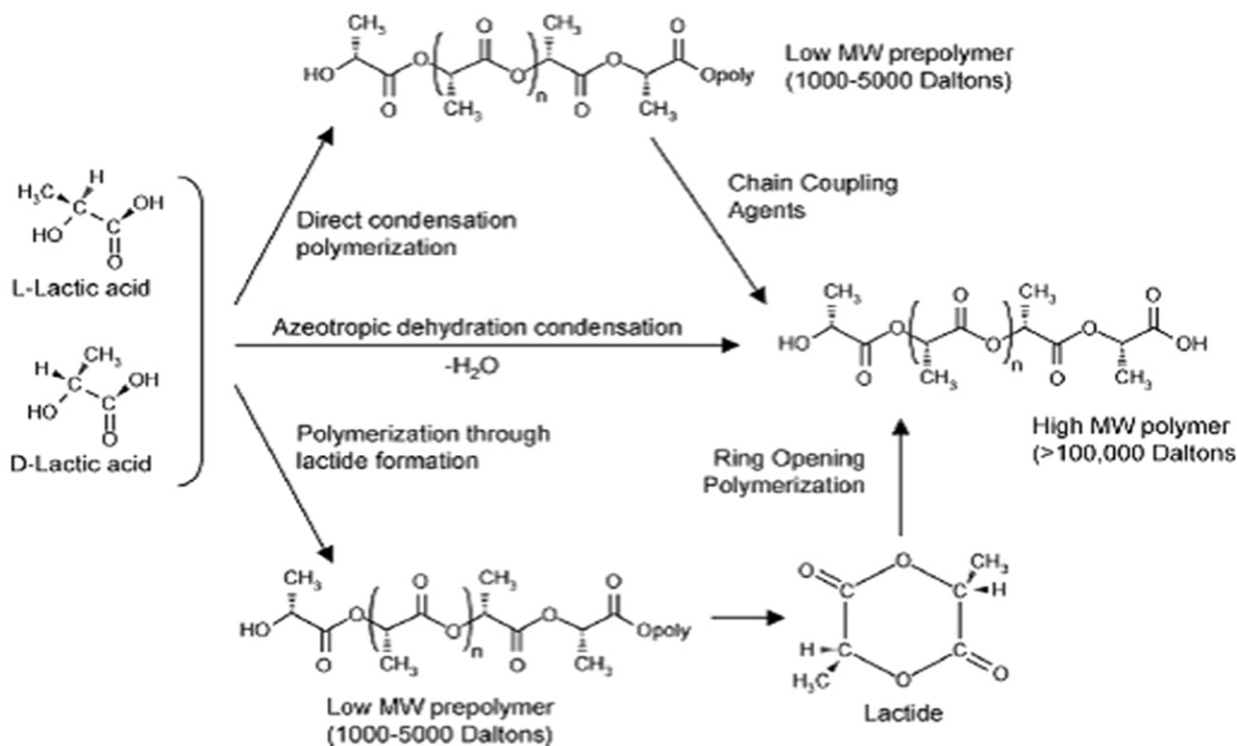


Fig. 4 General methods of PLA polymerization. Reproduced with permissions from Lim, L.T., Auras, R., Rubino, M., 2008. Processing technologies for poly (lactic acid). *Progress in Polymer Science* 33, 820–852.

thermal, crystallization behaviours of the polymer should be known properly in order to process and optimize the products. Melt processed PLA products include injection molded disposable cutlery, meltspun fibers for nonwovens, extruded cast and oriented films, textiles and carpets thermoformed containers and cups, injection stretch blown bottles. The less conventional products made from PLA includes housing for laptop computers electronic. A processing of PLA bottle by Injection stretch blow molding is given in Fig. 5.

PLA is also used with other polymers to form blends and with fillers like nanoclays, biofibers, cellulose, glass fibers etc. to form composites which possess various unique properties.

Applications of PLA

PLA has great application potential for packaging materials ideally for fresh products whose quality will not be damaged by oxygen permeability of PLA. It is the new “green food packaging polymer”. PLA containers which are thermoformed could be used in markets for containing fruits, vegetables and salads. 70% of PLA used today are in packaging. By 2020 PLA is seen to be use more in manufacturing of fibers and fabrics. PLA being a biocompatible polymer has usage in various biomedical applications, mainly used as internal body components like screws in ankle, knee and hands. It is also used as tacks and pins for ligament attachment, plates and screws for craniomaxillofacial bone fixation, interference screws in ankle, knee and hand, rods and pins for bones, and also for surgical sutures, implants, and drug delivery systems (Jamshidian *et al.*, 2010).

PLA Blends

Blends have great application potential in polymer industry. Many studies have been conducted where PLA has been blended with poly (vinyl acetate), thermoplastic starch, poly (ethylene glycol), poly (ethylene oxide), poly (ϵ -caprolactone), poly (hydroxy butyrate), cellulose acetate, poly (butylene succinate) and poly (hexamethylene succinate). Plasticizer like low molecular weight oligomeric lactic acid, glycerol, triacetine, and low molecular weight citrates have been used in these blends. The polymers are chosen depending on the requirements of application. Depending on the applications only non-toxic substances should be used in these blends. The plasticizer used should be miscible with PLA in order to create a homogeneous blend. The plasticizer should also be non-volatile so that it does not cause evaporation at higher temperature during processing. Again the plasticizer should not be prone to migration of materials when in contact. Sometimes plasticizers migrate to the surface of the polymer which could be averted by increasing the molecular weight of the plasticizer. The final properties of the blends depends on various factors mainly the chemical structure of the components, the mixing ratio and the processing parameters (Jamshidian *et al.*, 2010).

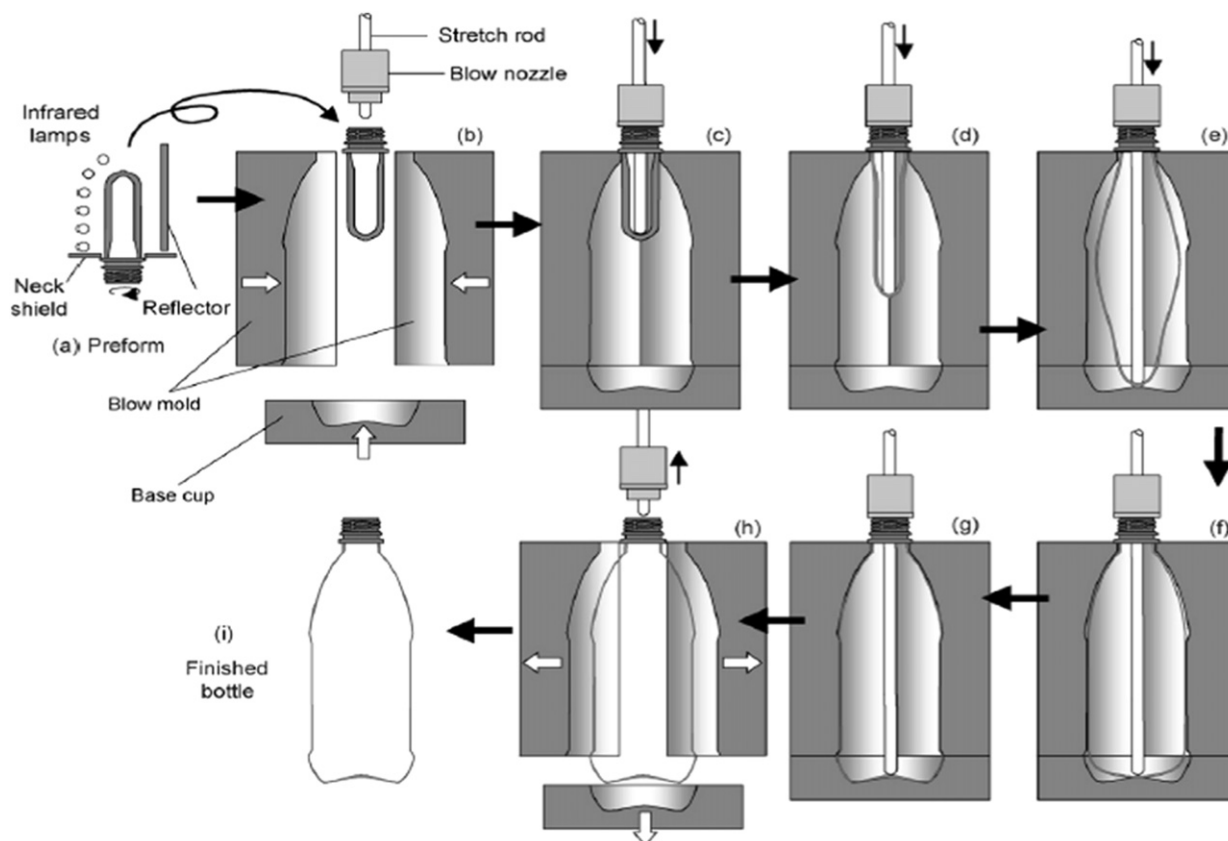


Fig. 5 Injection stretch blow molding of PLA bottle. Reproduced with permissions from Lim, L.T., Auras, R., Rubino, M., 2008. Processing technologies for poly (lactic acid). *Progress in Polymer Science* 33, 820–852.

PLA Composites

As discussed earlier, rapid use of plastic based products specially polymer composites in almost all aspect of human activities leads to contamination of environmental components like water resources and soil with residual plastic. Thus, researchers are trying to find an alternative renewable solution to these polymer composites by producing bio based polymer composites like PLA composites. Various types of these composites depending on the reinforcement used having various applications can be manufactured. Research work on different types of PLA composites and their potential applications are discussed in detail in the following sections. Manufacturing of these bio-based composites from a biopolymer leads to reduction in conventional polymer production and in return mitigates the GHG's emissions.

PLA-Natural Fiber Composites

Natural fibers are have been used as raw materials to produce biocomposite for replacing the plastic. Copious amount of literature are available where natural fibers has been used to produce reinforced bio-based polymeric composite (Pracella *et al.*, 2016; Pickering *et al.*, 2016). This becomes trends due to inexpensive nature of natural fibers than the synthetic fibers. Also, natural fibers have low density, high specific strength and stiffness, and they contain different types of functional groups easy to modification (Pickering *et al.*, 2016). Mechanical properties of different natural fibers are presented in (Table 1). However, hydrophobicity of natural fibers makes them less useful for preparation of hydrophobic composite. Thus it is necessary either to use some hydrophobic agent or modification of the natural fibers surface to increase the hydrophobicity. Poly-lactic acid (PLA) has been used by many researchers to prepare hydrophobic natural fiber reinforced composites. Selected examples of natural fiber reinforced PLA composite have been discussed below in (Table 1).

Flax Reinforced PLA Composite

Possibility of using flax fiber reinforced PLA composites in automotive industries is monitored in a recent study. To prepare flax-PLA composite, 30% (volume fraction) flax fibers were scatter randomly within PLA polymer and the mixture was used to

Table 1 Mechanical properties of natural

<i>Types of fibers</i>	<i>Density (g/cm²)</i>	<i>Young's modulus (GPa)</i>	<i>Tensile strength (MPa)</i>	<i>Elongation at break (%)</i>
Bamboo	0.6–1.1	11–17	140–230	NA
Carbon	1.4	230–240	4000	1.4–1.8
Coconut	1.15	4–6	131–175	15–40
E-glass	2.5	70	2000–3500	2.5
Flax	1.54	27.5–85	345–2000	1.2–3.8
Hemp	1.47	17–70	368–800	1.6
Jute	1.44	10–30	393–773	1.5–1.8
Kenaf	1.2	14–53	240–930	1.6
Nettle	1.51	24.5–87	560–1600	2.1–2.5
Ramie	1.5–1.56	27–128	400–1000	1.2–3.8
Sisal	1.45–1.5	9–22	350–700	2–7

prepare the composite by film stacking technique (Bodros *et al.*, 2007). The composite were then compared with polypropylene (PP)–flax composites by monitoring the tensile strength and Young's modulus. The report indicated that the mechanical properties of flax-PLA composite were better than the PP–flax composites. Even the properties were very close to mechanical properties of glass fiber polyester composites. In another study, PLA was first modified with Biomax Thermal 300 and Palaroid BPM-500 through melt-compounding and then used to prepare composite with nonwoven flax fibers mat (220 g/m²) (Siengchin, 2014) via hot compression molding. The results indicated that the stiffness of the composite was increased due to flax mat incorporation. Also the composite was resistant to high impact. Researchers have also modified flax fibers to improve their physico-chemical properties by modifying them by alkali treatment, corona discharge, maleic anhydride grafting and aminopropyltriethoxysilane treatment (Xia *et al.*, 2015), and interstitial polymerization (Shanks *et al.*, 2006).

Kenaf-Pla Composites

Kenaf-based PLA composites have been developed by many researchers till date. These types of composites are being used by Toyota for automotive applications. Lee *et al.* (2009) fabricated PLA–kenaf composites by carding PLA with up to 70 wt% kenaf fibers followed by treatment with 3-glycidoxypopyltrimethoxysilane. Thereafter, it was hot-pressed to obtain composites. The report indicated that use of silane coupling agent improve heat deflection temperature and mechanical properties, and reduce water swelling in comparison to the raw PLA. Also it was noticed that fiber diameter has significant effects on thermo-mechanical properties and crystallization rate of the composites.

Glass Fibers-Pla and Carbon Fiber-Pla

Glass fiber is the most common and widely use reinforcement used in composite industries. However, it is noticed that very few literatures are available where glass fibers has been used for composite preparation using PLA. Glass fibers (GF) reinforced composite of PLA could overcome the shortcoming of raw PLA composites as GF-PLA composite has very high mechanical and thermal properties can could replace the petroleum-based plastics (see “Relevant Websites Section”, last accessed Dec 15, 205). These composites due to their performances overcome partially the shortcomings of unmodified PLA because they have the mechanical and thermal properties necessary to allow their using as eco-friendly alternative to reinforced. It has been reported that bioactive glass fibers (BGF) have been used to prepare composites for biomedical application. Studies indicated that use of 40% BGF as reinforcement could improve the mechanical properties of PLA composites by two times (Ahtiainen *et al.*, 2015). The report also indicated that the mechanical strength is comparable to the bone tissue.

Carbon fibers (CF) could be a promising reinforcement agent for preparation of biomedical composites as it has excellent tensile strength, low density, high thermal and chemical stability and electrical conductivity. Carbon fiber has been used extensively for preparation of composite with PLA for use in biomedical application.

Pla-Cellulose and Other PLA Composites

Cellulose extracted from different natural fibers in different forms like micro fibers, microcrystalline, Nano whisker and nanocrystal had been used as reinforcement for preparation of PLA composites (Ambrosio-Martín *et al.*, 2015; Graupner *et al.*, 2016; Oksman *et al.*, 2016; Dhar *et al.*, 2015). Cellulose-reinforced composites are lightweight, biodegradable, non-toxic, low cost and recyclable. However, use of cellulose as reinforcement has drawbacks like hydrophilicity and low processing ability. But, the promising part of cellulose fibers is that the surface hydroxyl groups are easily modifiable. In a study, recycled wood fibers have been utilized to prepare PLA based composites with small amount of silane using injection molding machine. The results indicated that the tensile modulus and the storage modulus of composites increased with the RWF content. Costes *et al.* (2016) have used phosphorylated nano cellulose for preparation of composites with fire retardant properties. They introduced

phosphorus into the nanocellulose either by chemical grafting or by co-additive melt blending using aluminum phytate. This study reported that composites prepared with 20 wt% phosphorylated nanocellulose had better fire retardant properties than the other composites.

PLA Composites With Inorganic Fillers

Fillers are combined with the polymer either for reduction of the cost or for modification of physical, mechanical, rheological, and other properties (see "Relevant Websites Section" last accessed on April 16, 2018). However, the addition of filler should not decrease the molecular, thermal and mechanical characteristics of the composites. Different types of fillers such as talc, carbonaceous fillers, hydroxyapatite, inorganic carbonates and sulfates, mica, kaolin, organo-modified layered silicates, graphite derivatives, carbon nanotubes, sepiolite, halloysite, polyhedral oligomeric silsesquioxanes, silica, ZnO had been used to modify PLA (Murariu and Dubois, 2016; Ojijo *et al.*, 2014; Matusik *et al.*, 2011). Few examples of the filler modified PLA based composites have been described in the following subsections.

PLA-talc composites

Talc is one of the most considered filler material have been used to modify PLA composites. Addition of talc in PLA, increase stiffness, heat resistance, dimensional stability and, reduce crystallization and molding time, and production costs of PLA composite preparation. Copious amount of literature are available where talc has been used as filler to improve the properties of PLA composites (Ouchiar *et al.*, 2015; Kaynak and Erdogan, 2015; Joseph *et al.*, 2015; Refaa *et al.*, 2014a,b; Nofar, 2016; Zhu and Avakian, 2015; Hoekstra *et al.*, 2014). From many reports it is evident that whatever loading amount, talc has nucleating effect which enhance the PLA crystallization (Ouchiar *et al.*, 2016). It is noted that isothermal crystallization halftimes of PLA were decrease almost 65-times by addition of only 2% talc. Due to faster crystallization the processing of composite need less time, key-parameter for determining the level of resistance at high temperature. Also, talc has reinforcing effect which enhances the thermal stability and heat distortion temperature of highly filled composites. In a recent study 30 wt% ultra-fine talc has been used to prepare PLA composites (Shakoor and Thomas, 2014). The mechanical and thermo mechanical characterization of the composites indicated that Young's modulus was increased from 4.1 to 9.8 GPa after the PLA was modified with 30 wt% talc. The enhanced storage moduli of the 30 wt% talc-PLA composite also confirm the reinforcing effect of talc based filler.

PLA-carbonaceous fillers

Technological potential of carbonaceous fillers like carbon black, graphite derivatives, carbon nanotubes, for different applications makes them a promising and attractive alternative to modify polymer based composites (Kasgoz *et al.*, 2014). Large numbers of reviews are available on carbonaceous fillers based composite synthesis and their structural and mechanical characterizations (Mittal *et al.*, 2015). PLA had been used very often as polymeric matrix for production of micro or nano filler based composites (Wu *et al.*, 2015). It is reported that the composites prepared with PLA and carbonaceous fillers had improved nucleating, mechanical, and thermal and fire retardant properties (Murariu and Dubois, 2016). In addition, it was also reported that combination of two or more nano fillers with different geometry showed dramatic improvement of specific properties of PLA composites. For example, Wu *et al.* (2015), enhance conductivity of PLA foams by combining CNT and CB with PLA in different proportion. The CNT form a bridge for connecting CB and forming a better structure network for electrical conductivity. However, the dispersion state and surface functionality of CNT has very important role for the final morphology, electrical percolation threshold and thermal stability of these types of PLA composites.

Recently graphite and its derivatives have been gaining much attention to the composite industries for preparation of micro or nano composites with specified properties (Sullivan *et al.*, 2014). Graphite derivatives like graphene or graphene oxides are exotic materials of 21st century with exceptional charge transport, thermal, optical, and mechanical properties. These types of fillers can be used when properties like heat stability, lubricant ability, thermal and electrical conductivity need to be increased into the composites (Xiao *et al.*, 2014). The study reported by Kim and Jeong (2010) indicated the preparation of PLA nano composites with graphite and exfoliated graphite via melt-blending method. From the report it is evident that the nano-composites had better morphology, thermal, mechanical and electrical properties than the raw PLA composites.

PLA-hydroxyapatite

Hydroxyapatite (HA) has very high bone bonding ability and osteoconductivity. These properties led the use of this filler in the composite industries for biomedical applications (Water *et al.*, 2015) affect copolymer type, HA loading and surface modification HA on the mechanical and microstructural properties of the composites had been studied. The report indicated that surface modified HA containing PLA composites had the better mechanical properties than the raw PLA composites. However, it is fact that the mechanical properties of the composite with HA fillers are still the below the required demand.

PLA composites with other fillers

Apart from the above filler, many other micro or nano fillers such as layered silicates, mica, kaolin, zeolites, glass beads/microspheres (Malinowski *et al.*, 2015), wollastonite, boehmite alumina (Hao *et al.*, 2016; Agwuncha *et al.*, 2015), has been used to prepare PLA based composite with better thermal and mechanical properties.

Nevertheless, it should be mentioned that not all types of filler could improve the properties of PLA based composites. There are many metal oxide based fillers, such as CaO, MgO, ZnO, or layered double hydroxides, which leads to advanced degradation of PLA chains and sharp reduction of thermo-mechanical properties of the matrix.

Conclusions

PLA is a biodegradable, biocompatible polymer derived from renewable sources. Its polymer component lactic acid is derived from vegetable feedstocks by fermentation by microorganisms (*Lactobacillus sp.*) which is then purified and made to undergo polymerization processes like condensation and ring opening polymerization to synthesize the polymer of desired molecular weights. These polymers could be melt extruded or injection molded to form various materials with tailor made properties. They find applications in packaging industries and also in produces biomedical devices, implants etc. PLA could be blended with other polymers using plasticizers to get materials with desired properties and also could be reinforced with various fibers and fillers to form composites. Thus this green polymer and its composites and blends gives a world a wide array of plastic products which can easily replace the conventional non-biodegradable plastics from petroleum sources. Thus, its production from a bio-source reduces GHG's emissions, as in the case of petroleum based polymers. It also recycles renewable feedstocks. The PLA products are also biodegradable after its use and do not require incineration. This also further reduces GHG's emissions. Therefore, use of PLA products will offer the world a way of mitigating GHG's emissions and reduce carbon footprint.

Acknowledgements

SM would like to thank SERB-DST, New Delhi for the financial support he is receiving as National Post-doctoral Fellow during writing of this chapter (PDF/2016/000062). SS would like to acknowledge UGC D. S. Kothari Post-doctoral Fellowship scheme for financial assistance during writing of this chapter [CH/15–16/0163].

Contribution

SS and SM has contributed equally in this book chapter.

See also: Fermentative Production of Optically Pure Lactic Acid From Renewable Materials

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Polylactic Acid Containing Fillers and Fibers.

Nanofluid in Energy Harvesting and Related Applications

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Nomenclature

EJ Exajoule, Unit of energy, 1 Exajoule = 10^{18} joules

GWth Gigawatts-thermal

Kg min⁻¹ Kilogram per minute, Unit of mass flow rate

L min⁻¹ Liter per minute

Mb d⁻¹ Millions of Barrels per day, Unit of volume,
1 barrel = 159.0 L

MTOE Million tonnes of oil equivalent, TOE: tonne of oil
equivalent, unit of energy, 1 TOE = 41,868,000,000 joule

Nm Nano-meter, Unit of length

Petawatts Unit of power measurement,

1 petawatt = 10^{15} watt

PPM Parts per million, also expressed as milligrams
perliter, Unit of concentration

W m⁻² Watts per square meter, Unit of irradiance

W/m-K Watts per meter-kelvin, Unit of thermal
conductivity

Wh m⁻² Watt hour per square meter, Unit of irradiance
over a time period (1 h)

Wt. Unit to measure weight

Introduction

Energy is the primary mainstay of modern civilization. The proper utilization of available energy resources is the key of the development of society. Most of the energy sources which are non-renewable in nature are depleting gradually whereas the consumption of energy rises exponentially with the widespread urbanization throughout the globe. For example ancient people used wood as the major resource of their energy need. Later transition to coal as a major fuel took place. Since the last century widespread use of liquid fuel and gaseous fuel in different purposes has been witnessed. Several reviews (see "Relevant Websites section") indicate that the consumption of energy will increase continuously and this seems logical as more and more urbanization and energy consuming industries are coming up. Progress of civilization will continue and it is one of the aims of modern science and technology to bring the under privileged sections of the society in to the main stream civilization. However all these developments must be sustainable otherwise in near future we will witness extreme dearth of fuels and energy resources. We do not have any right also to exhaust the storage of fossil fuels for our own need without caring for the future. It is high time to think about the alternative energy resources to meet the ever-increasing demand of energy and at the same time should be sustainable. Each of the statistical review (see "Relevant Websites section") indicates a huge difference between consumption and production thus a severe problem of energy crisis for near future is predicted. Besides, air pollution, acid rain, ozone-layer depletion and climate changes are resulted from rapid consumption of fossil fuels which cause disasters like droughts, heat waves, flood causing serious problems like global warming (Gorji and Ranjbar, 2017a).

We need to think of the renewable energy technologies in order to compensate the ever-growing energy demand and also to produce energy in an environment friendly way. There are different renewable energy resources which can be naturally replenished on a human timescale, such as (1) wind energy (2) tidal energy (3) solar energy (4) geothermal heat waves (5) naturally occurring energy that are wasted as mechanical energy. In several areas mostly for electricity generation, air and water heating/cooling, transportation, non-conventional energy resources are explored by the scientists now a days (see "Relevant Websites section").

In a recent survey report it is shown that renewable resources have contributed 19.2% to global energy consumption and 23.7% to generation of electricity in 2014 and 2015 respectively (see "Relevant Websites section"). According to BP Statistical review, Asia is the leading consumer of oil, coal, hydroelectricity and for the first time in 2016, it has become the leading consumer of different renewable resources of energy in power generation, overtaking Europe and Eurasia (see "Relevant Websites section"). This shows the increasing demand for renewable energy in all over the world. The statistical results indicate the growth of renewable in different countries indicating China to be the leading country on the basis of renewable growth (see "Relevant Websites section").

Amongst all other non-conventional sources, solar energy is the most abundant permanent source of energy on the earth. It is reported that solar radiation coming to the surface of the earth in one year is approximately 3,400,000 EJ which is 7500 times the world's total annual primary energy consumption of 450 EJ (see "Relevant Websites section"). Owing to the unlimited availability and environmental safe nature, solar energy can be sustainably utilized in near future instead of other energy forms and prediction says that, solar energy would supply almost 70% of the world energy consumption by 2100 (see "Relevant Websites section").

Energy Harvesting

The environment surrounding us consists of different forms of energy like thermal, light, wind, mechanical energies etc. but energy available from these sources is often too insufficient in quantity to provide adequate power for variable purposes. Most of the part of

these energies is lost as heat or mechanical energies which cannot be converted to any useful work. It has not been possible to capture such ambient energy efficiently to utilize it in useful purposes till now. Energy harvesting is a procedure to derive and store energy from different external ambient energy resources like solar power, thermal energy sources, kinetic energy, wind energy, salinity gradient etc (see “Relevant Websites section”). Energy harvesting devices are used to capture, accumulate, store, condition and manage energies coming from different ambient resources efficiently and effectively and supply it in an useful form. The concept of crystal radio is one of the earliest ways of deriving ambient power from ambient electromagnetic radiation (see “Relevant Websites section”).

The storage of fossil fuels is limited and the extensive use of fossil fuels causes hazardous diseases along with environmental pollution. Now-a-days, instead of utilizing fossil fuels, energy harvesting through ambient energy resources is motivated by the need of energy production in an environment friendly way besides, efficient utilization of energy derived from renewable energy sources can meet the enhanced demand of energy. The places where remote application is deployed and natural energy sources are inexhaustible in nature, energy harvesting from natural sources is an attractive alternative to wall plug or costly battery installation (see “Relevant Websites section”). Energy harvesting-controlled remote control node is able to be implemented as a self-powered electronic system and multiple energy sources can be utilized to enhance the overall efficiency of the system (see “Relevant Websites section”).

Different Types of Energy Harvesting Techniques

The environment represents an infinite number of ambient energy resources. Through proper utilization of modern technologies, useful power is scavenged from different ambient sources which have attracted the researchers due to its pollution-free energy production in a cost-effective way. Available ambient resources and corresponding energy harvesting technologies are demonstrated at Fig. 1 (see “Relevant Websites section”), (Yildiz, 2009).

After extensive researches, Nanotechnology has been identified as an efficient tool in case of harnessing energy. It has opened many new horizons in field of energy production in efficient but cheapest ways. Researchers are trying to achieve highest conversion from electricity to light with the help of quantum dots (Yang *et al.*, 2014), whereas Nano wire solar cell designed by GASPSOLAR shows two times more light entrapment efficiency compared to the commercial solar cells available in market and this Nano wire made solar cell is 10 times cheaper than PV-solar cells (Anis *et al.*, 2017). The processing of Nano materials is very easy thus energy harvesting through nanotechnology is cost-effective at the same time. Solar Botanic Ltd. has designed an artificial tree made of tiny solar cells, the movements due to wind has been converted to electricity with the help of piezoelectric Nano elements, this new technology has been able to achieve 50% enhancement in efficiency in converting solar and wind energy to electricity (Anis *et al.*, 2017). Spire solar utilizes Nano structured materials along with quantum dots to fabricate efficient Building integrated photovoltaic and Chicago implemented the cost effective solar energy systems thus was named as number one green city by business facilities magazine (Anis *et al.*, 2017). ROYAL DSM KHEPRICOAT invented a new Nano porous anti-reflecting coating to avoid the solar energy losses by reflection thus enhancing the efficiency of solar cells (Anis *et al.*, 2017). California based Phoenix motor uses Nano-structured Lithium Titanate to facilitate the high electrical-charge transfer (Anis *et al.*, 2017), the nanotechnology implemented in such Nano- safe batteries produced high performance vehicles which can be charged in less than 10 min using a 480 V circuit thus indicating the effect of nanotechnology in future vehicles. Recent researches shows that Nano particles while dispersed in a base fluid shows enhanced thermal conductivity thus capable of harvesting energy efficiently from incoming solar light compared to conventional solar cell collectors (Bhalla and Tyagi, 2017).

In 1905, Max Weber mentioned the possibility of ending of fossil fuels in his *Die protestantische Ethik und der Geist des Kapitalismus* (see “Relevant Websites section”). Recent trends shows that the growth in consumption of coal and oil could end by 2020 due to enhanced utilization of renewable energy sources (see “Relevant Websites section”).

The demand of utilization of renewable energy sources has enhanced due to its recyclable, pollution free ways of energy harvesting. Recent reports say that wind power met 42% of electricity demand in Denmark, 23.2% in Portugal and 15.5% in Uruguay whereas solar water heating meets 70% of the global total, 180 GWh in China, hydropower generated 16.6% of worlds total electricity in 2015 and 70% of all renewable energies (see “Relevant Websites section”). Very recent British Petroleum

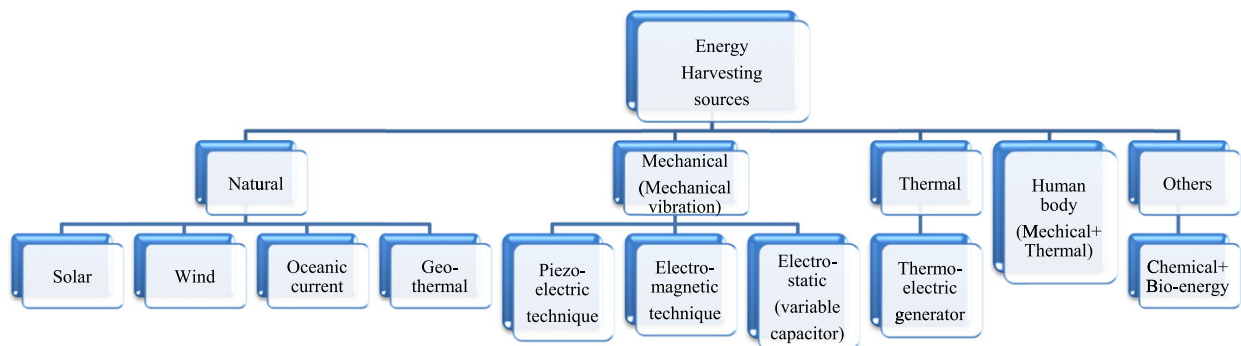


Fig. 1 A list of available energy harvesting sources. Modified from https://en.wikipedia.org/wiki/Renewable_energy. Yildiz, F., 2009. Potential ambient energy-harvesting sources and techniques. Available at: <http://www.energyharvesting.net/>.

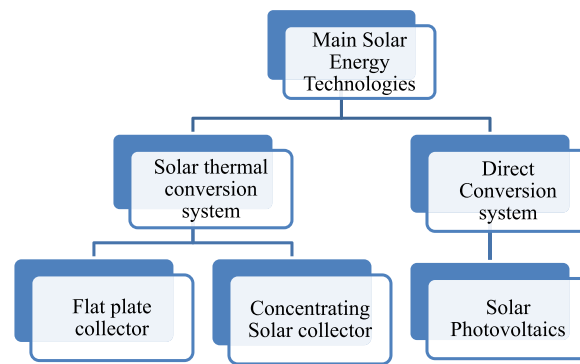


Fig. 2 A list of major solar energy technologies. Modified from https://en.wikipedia.org/wiki/Solar_energy and https://en.wikipedia.org/wiki/Energy_harvesting.

statistical reviews show that power generation through renewable resources enhanced up to 14.1% in 2016 except hydropower thus showing the largest increment on record (52.9 mtoe), Asia Pacific contributed 60% of the growth and China has become the world's largest renewable power producer (see "Relevant Websites section"). Amongst the different sources of renewable energy the much explored and researched one is power generation through solar energy.

Solar Energy Harvesting

At the upper atmosphere, the earth receives 174 petawatts of insolation, 30% of which is reflected back to space while rest of the part is absorbed by clouds, oceans and masses (see "Relevant Websites section"). Now-a-days, this huge amount of inexhaustible, clean and abundant radiant energy is harnessed using different technologies such as solar heating, solar architecture, solar heating, molten solar power plants, photovoltaic and artificial photosynthesis technologies. Depending upon how the solar energy is being captured and converted into effective solar power the solar harvesting technologies are broadly classified into active and passive, the active solar techniques include energy harnessing through the use of photovoltaic systems, concentrated solar power and solar heating systems (see "Relevant Websites section"). **Fig. 2** indicates different kinds of solar harvesting technologies (see "Relevant Websites section"; see "Relevant Websites section").

Solar collectors are the key components of solar thermal utilization systems as its efficiency depends entirely upon efficiency of collector. **Fig. 3** represents different solar collectors (Selvakumar *et al.*, 2010).

United Nations Development Program found annual potential of solar energy was 1575–49,837 EJ on its 2000 World energy assessment indicating annual potential to be several times larger than world energy consumption (see "Relevant Websites section"). Photovoltaic systems uses photoelectric effect to convert light into Direct current. Concentrated solar power systems uses lens or mirror arrangements to focus solar light of a large area into a small beam where a working fluid is used to concentrate the heat and that concentrated heat is used in power plants as heat source. Commercial concentrating power plants were first developed in 1980 s (see "Relevant Websites section"). There are wide range of technologies available for concentrating solar light such as, parabolic trough, linear Fresnel's reflector, Stirling dish and solar power tower amongst which, Stirling shows the highest efficiency (see "Relevant Websites section"). Amongst the non-concentrating collectors, most of the evacuated tube systems are considered to be more efficient per square meter than equivalent flat plate systems based on absorber plate area (see "Relevant Websites section"). Recent reports say that solar generated almost 1.3% of the global power in 2016 indicating the increase of the utilization of solar energy to produce electricity in an efficient way (see "Relevant Websites section"). Direct absorption solar collectors utilize heat transfer fluid to absorb radiant energy and to convert it into thermal energy directly. It has been proved to provide higher receiver efficiency compared to others since it was designed in 1970 (Minardi and Chuang, 1975). To achieve highly efficient Direct absorption solar collector (DASC), we need to improve the optical and thermo-physical properties of the heat transfer fluids. Recent researches have introduced a new working fluid called Nanofluid to be utilized as heat transfer fluid in DASCs. Theoretical predictions and experimental investigations show that nanofluid based DASC shows better collector efficiency compared to flat plate collectors due to enhanced thermo-physical properties of Nano fluid (Liu *et al.*, 2017). This is evident that utilization of Nano fluid efficiently transforms the low grade, dispersed solar energy into high grade thermal energy.

Energy Harvesting Using Nanofluid

Nanofluid

In many industrial applications, traditional fluids such as water, ethylene glycol etc. are utilized for power generation, heat transfer and cooling purposes. Owing to the low thermal conductivity, these fluids cannot be used for high heat exchange rates in thermal

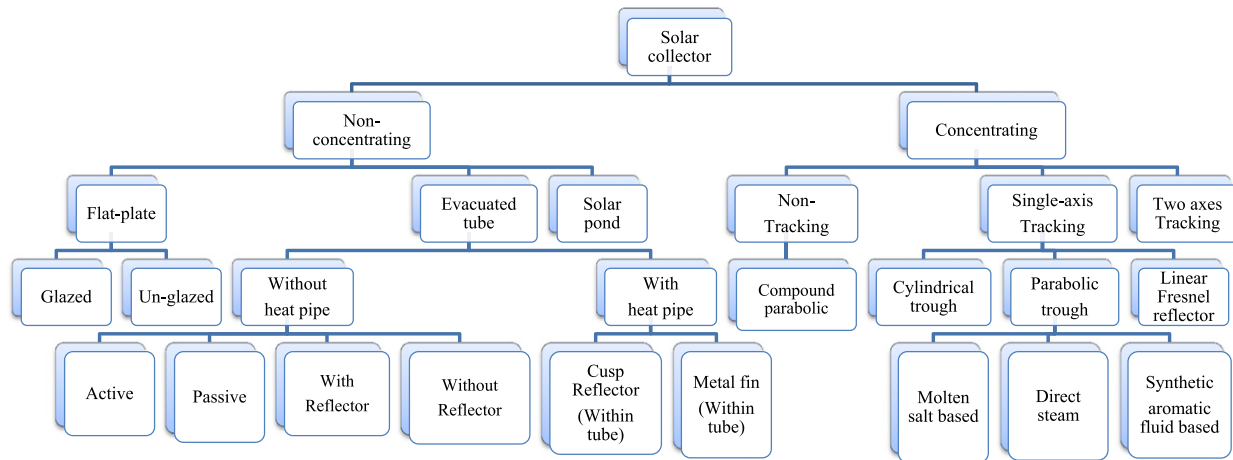


Fig. 3 Different types of solar collectors.

engineering devices. Nanofluid is a new class of fluid that contains Nano-sized particles having one of their principle dimension less than 100 nm suspended in a base liquid, the concept of nanofluid was introduced by Choi in 1995 in Argonne National Laboratory (Choi and Eastman, 1995). Nanofluids find its application in diverse field like energy harvesting, thermal management, Chiller, Power sectors, heat exchanger in grinding due to its novel properties like enhanced thermal conductivity, high surface to volume ratio of the Nano-particles compared to their bulk form, good convective heat transfer coefficient (see "Relevant Websites section"). It has been reported that Nano-sized particles mostly carry their atoms on the surface instead of volume thus allowing thermal interactions between tiny sized particles thus inducing micro-convection which in turn enhances the heat transfer (Das et al., 2006). Particle size, shape material nature, viscosity, Brownian motion, acidity, agglomeration, base fluid nature and temperature influences the heat transfer properties of nanofluid significantly (Reddy and Chamkha, 2016). Different experimental observations indicate nanofluid has an enhanced thermal conducting nature compared to base fluid and this thermal conductivity enhances with particle concentration and temperature (Kim et al., 2007; Beck et al., 2009; Williams et al., 2008; Das et al., 2003; Chon and Kihm, 2005).

Effect of Base Fluid

Different types of base fluids are used to formulate Nanofluid. Thermo-physical properties of base fluid are the key features for determining its impact in forming nanofluid for enhanced heat transferring phenomenon. Amongst three kinds of motion called Thermophoretic, Osmophoretic and Brownian motion, Brownian motion affects the thermal conductivity of nanofluid effectively. It has been found from literature that the possible reasons for enhancement of thermal conductivity of nanofluid are Brownian motion of Nano-particles, liquid layering at liquid-particle interface, Nano-particle clustering effect (Murshed et al., 2008). The base fluids generally used are: De-ionized Water (DI), Ethylene Glycol (EG), Mixture of DI and EG, Therminol VP-1, Syltherm-800, Therminol 55, Engine oil, Ionic liquid etc. Table 1 shows a comparison of Thermo-physical properties of some base fluids affecting nanofluidic heat transfer (Sadeghinezhad et al., 2016), (see "Relevant Websites section"; see "Relevant Websites section").

To be a good base fluid to form effective nanofluid with good thermo-physical properties, it should have high thermal conductivity, low viscosity coefficient, low density and small heat capacity. Amongst these base fluids, Therminol VP-1 is a liquid-vapour phase heat transfer fluid possessing high thermal stability and is suitable to be operated over long periods up to 370–400°C. It is an eutectic mixture of 73.5% diphenyl oxide and 26.5% diphenyl (see "Relevant Websites section").

Therminol 55 is used to be utilized in non-pressurized indirect heating systems. This can be utilized up to 315°C showing good thermal stability, it also possess a wide operating range from – 15 to 550°F (see "Relevant Websites section").

Another heat transfer synthetic fluid that is used to formulate nanofluid is Syltherm 800 which is highly stable, long lasting Silicone fluid utilized for high temperature liquid phase operations. The range of operation for Syltherm 800 is from – 40 to 400°C (see "Relevant Websites section").

Apart from the quality of base fluid another important feature which is essential to form good nanofluid is the dispersion stability of nanoparticles. Strong Van der Waals interaction between nanoparticles causes agglomeration which degrades the stability of Nanofluid. To achieve homogeneous and long-term stable Nanofluid is the greatest problem till now. Chemical and physical treatments like addition of surfactant, pH control, and ultrasonic vibration are the techniques to attain stable Nanofluid. Surfactants like Gum Arabic (GA), Sodium dodecyl sulphate (SDS), Hexadecyltrimethylammonium bromide (CTAB), Polyvinylpyrrolidone (PVP), Oleic acid, Triton X 100 etc. helps to modify the stability of dispersion by its amphiphilic nature.

Nano Materials

Energy harvesting using nanofluid is mainly based on its key feature of enhanced heat transfer capability. Previous literature reviews indicate a strong dependence of heat transfer capacity of nanofluid on morphological variation and phase distribution

Table 1 Thermo-physical properties of common base fluids

Fluid type	C_p (J/Kg-K)	ρ (Kg/m ³)	K (W/m-k)	μ (N s/m ²)/viscosity	Ref.
Water (20°C)	4184	998	0.599	0.1×10^{-3}	Sadeghinezhad <i>et al.</i> (2016)
EG (20°C)	2383	1117	0.250	0.22×10^{-1}	Sadeghinezhad <i>et al.</i> (2016)
Engine oil (20°C)	1881	888	0.145	0.84	Sadeghinezhad <i>et al.</i> (2016)
R-134a (20°C)	1405	1125	0.083	0.21×10^{-3}	Sadeghinezhad <i>et al.</i> (2016)
Therminol VP-1 (20°C)	1546	1064	0.136	4.29 mPa.s (viscosity)	https://www.sintelub.com/files/therminol_vp1.pdf
Therminol 55 (16°C)	1890	875	0.1289	53.1 mPa.s (Viscosity)	http://blueoceanoil.com/wp-content/uploads/2015/04/therminol_55.pdf

Note: Modified from Sadeghinezhad, E., Mehrali, M., Saidur, R., *et al.*, 2016. A comprehensive review on graphene nanofluids: Recent research, development and applications. Energy Conversion and Management 111, 466–487. Available at: https://www.sintelub.com/files/therminol_vp1.pdf. Available at: http://blueoceanoil.com/wp-content/uploads/2015/04/therminol_55.pdf.

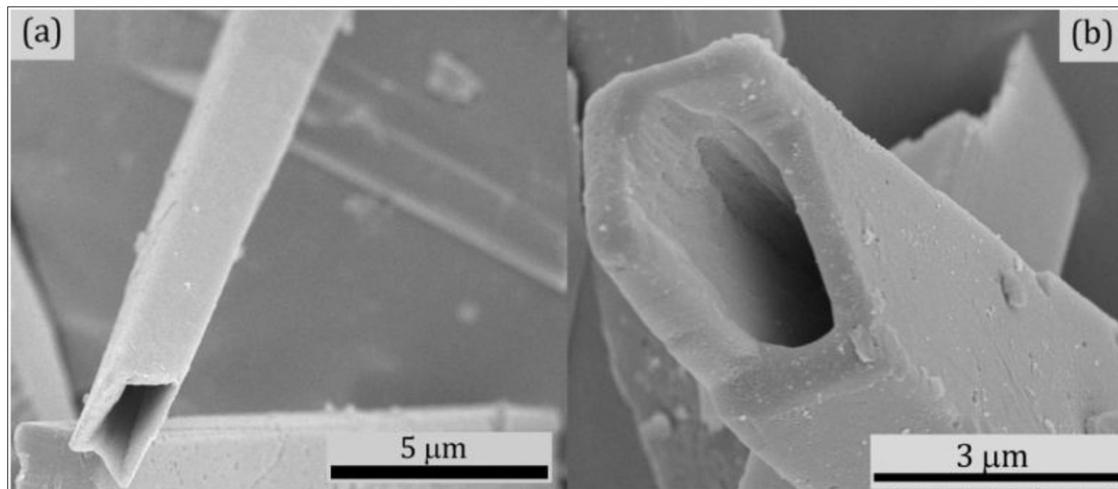


Fig. 4 Nanotube morphology of ZnPc nanomaterial through Solvo-thermal synthesis procedure. From Mukherjee, M., Samanta, M., Ghorai, U.K., *et al.*, 2018. One pot solvothermal synthesis of ZnPc nanotube and its composite with RGO: A high performance ORR catalyst in alkaline medium. Applied Surface Science 449, 144–151.

(Amin *et al.*, 2015; Xie *et al.*, 2002a; Murshed *et al.*, 2005; Maheshwary *et al.*, 2017). Prominent morphological variation of different nanostructures can be observed by varying experimental conditions of different Top-down and Bottom-up synthesis procedures. Some examples of the dependence of morphological variations on variation of synthesis procedures and experimental conditions have been shown below. Fig. 4 presents the FESEM (Field emission scanning electron microscope) image of Nanotube morphology of ZnPc nanomaterial through Solvo-thermal synthesis procedure (Mukherjee *et al.*, 2018).

Fig. 5 shows variation of morphology of graphitic carbon nitride synthesized at various temperature (350–650°C) indicating the effect of temperature on morphological changes (Das *et al.*, 2017).

Fig. 6 shows Morphological changes of Co₃O₄ nanowire grown on carbon fabric for variation of hydrothermal reaction time ((a) and (b) for 3 h and (c) and (d) for 6 h) (Howli *et al.*, 2016).

Fig. 7 represents rGO wrapped Bi₂Se₃ flower like morphology through easy hydrothermal procedure (Das *et al.*, 2016).

Morphological effect on nanofluid

Fig. 8 shows a basic classification of various nanostructures based on the different shapes (see “Relevant Websites section”).

Amin *et al.* (2015) has shown the shape effect on the efficiency of nanofluid based flat plate solar collector using spherical, cylindrical, Blade, Brick, and platelet- shaped Nano materials. Through Timofeeva model, they have shown the thermal conductivity enhancement of Alumina nanofluid corresponding to various shapes. The results obtained by Amin *et al.* indicate the largest thermal conductivity enhancement for Blade shaped Alumina particle based nanofluid.

They have compared their results using Hamilton-Crosser and Timofeeva models. Both results follow the same trend but efficiency enhancement trend remains constant in higher particle concentration in case of Timofeeva model whereas in Hamilton-Crosser, trend raises at higher concentrations.

Xie *et al.* (2002a) showed higher rise in thermal conductivity about 23% for cylindrical shaped particles (600 nm) whereas spherical (26 nm) size gives only 15% for a volume concentration of about 4%. Maheshwary *et al.* studied the effect of size,

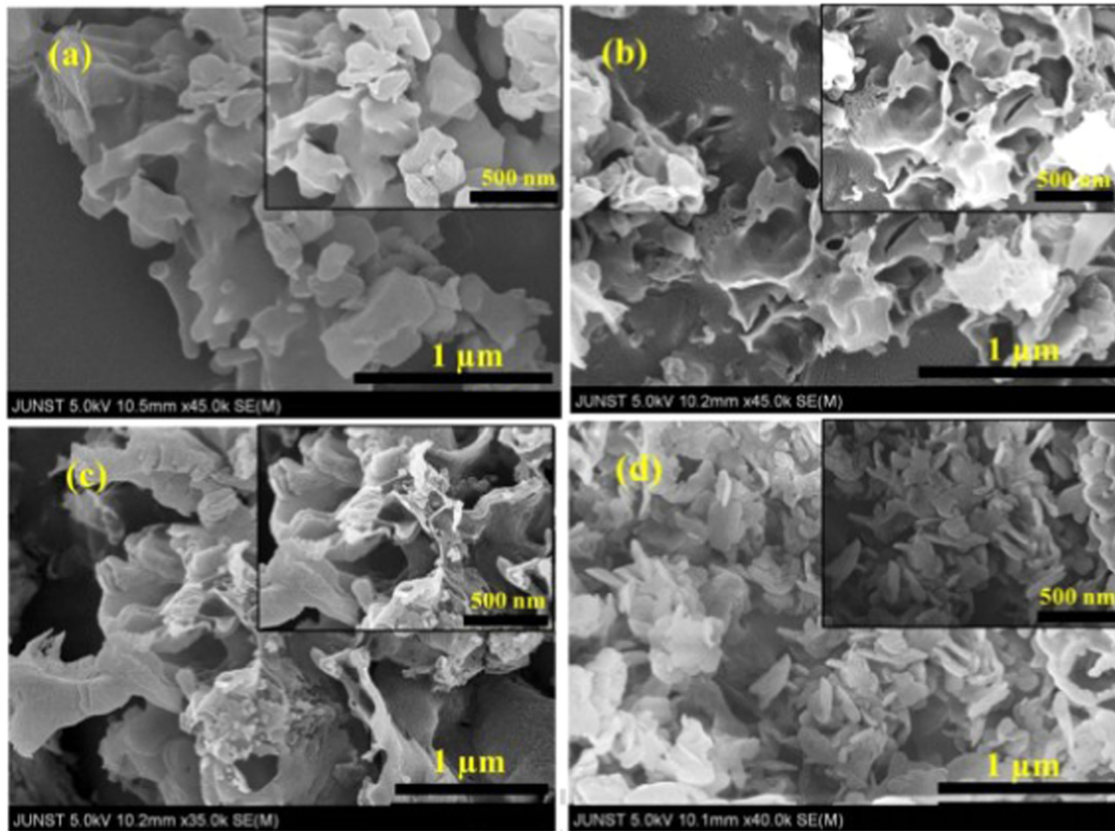


Fig. 5 Variation of morphology of graphitic carbon nitride synthesized at various temperature (350–650°C). From Das, D., Banerjee, D., Pahari, D., *et al.*, 2017. Defect induced tuning of photoluminescence property in graphitic carbon nitride nanosheets through synthesis conditions. *Journal of Luminescence* 185, 155–165.

concentration and shape on thermal conductivity of TiO_2 -water nanofluid. Amongst rod, cubic and spherical shaped nanoparticles, cubic shaped morphology with 51.87 nm particle sizes and with 2.5 wt% shows highest thermal conductivity effect due to its high surface area (Maheshwary *et al.*, 2017). Results show that at temperature 353K, thermal conductivity ratio reaches 2.69 for cubic shaped morphology whereas it becomes 1.765 for spherical and 1.966 for rod shaped indicating a prominent relationship of morphology with heat enhancement. Their results indicate a 5.54% contribution of shape factor in thermal conductivity enhancement. Fig. 9 shows FESEM images of different morphology of nanoparticles.

Murshed *et al.* (2005) showed high impact of rod morphology compared to sphere in thermal conductivity enhancement with TiO_2 -DI system. Akbar *et al.* (2017) shows shape effect on heat transfer of nanofluid. Fig. 10 represents the shape and volume fraction effect on effective thermal conductivity variations which indicates platelet shaped nanoparticle shows better thermal conductivity compared to brick and cylinder.

By tuning the optical properties of nanoparticles with variable geometry, solar energy harvesting through collector is a recent trend. Table 2 shows variation of solar absorption efficiency factor with variable geometry of nanoparticles having same surface area equal to a Nano sphere of radius 50 nm (Wang *et al.*, 2018).

Particle size is also an important factor. Relationship of effective thermal conductivity with particle size shows different trends. Kim *et al.* Li *et al.* and Peterson *et al.* showed increasing trend of thermal conductivity with particle size while Yu *et al.* showed negative trend (Kim *et al.*, 2007; Li and Peterson, 2007; Yu *et al.*, 2007). Xie *et al.* (2002b) showed decreasing trend of thermal conductivity with particle size both for ethylene glycol and pump oil for alumina based nanofluid. Beck *et al.* (2009) studied influence of particle size on thermal conductivity by using nanofluid of alumina nanoparticles of wide range of diameter ranging from 8 to 282 nm in diameter and showed a decreasing nature of thermal conductivity with size below 50 nm. But according to Mints *et al.* (2009) at higher temperature smaller sized alumina based nanofluid shows greater thermal conductivity. Chopkar *et al.* (2006) and Colangelo *et al.* (2012) showed enhanced thermal conductivity with reduced particle size.

Material effect

Material is also another important parameter to be considered while preparing nanofluid. In Flat plate solar collector the effect of CeO_2 shows highest Exergy efficiency compared to other oxides like NiO , CoO and ZnO (Alim *et al.*, 2014). Metal nanoparticle unlike oxides show surface Plasmon resonance effect that helps to improve the efficiency of solar collector efficiency by modifying

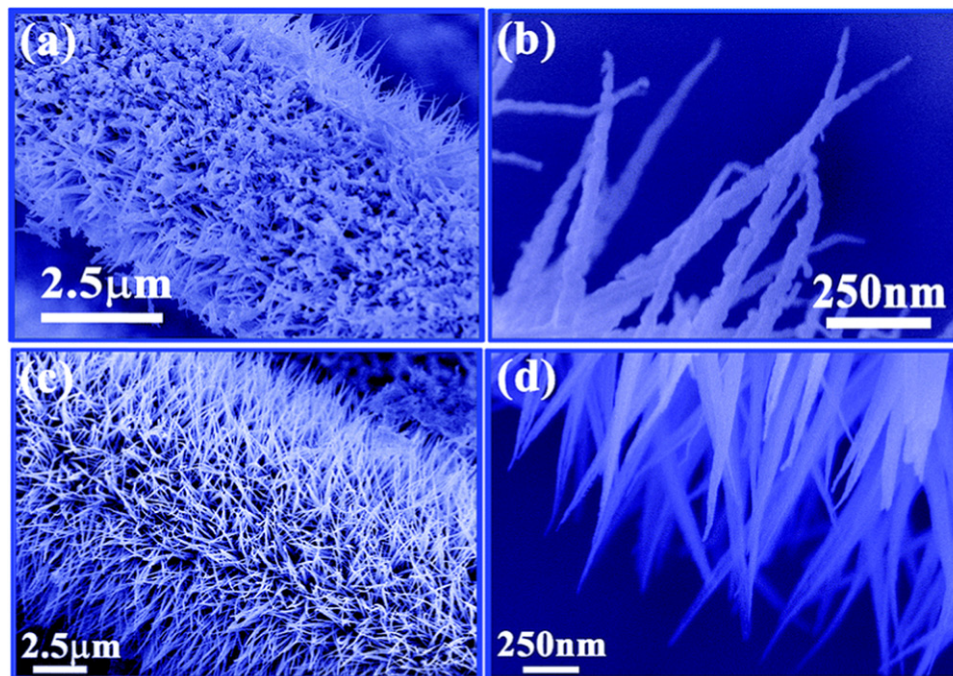


Fig. 6 Morphological changes of Co_3O_4 nanowire grown on carbon fabric for variation of hydrothermal reaction time ((a) and (b) for 3 h and (c) and (d) for 6 h). Reproduced from Howli, P., Das, S., Saha, S., *et al.*, 2016. RGO enveloped vertically aligned Co_3O_4 nanowires on carbon fabric: A highly efficient prototype for flexible field emitter arrays. RSC Advances 6 (94), 91860–91869.

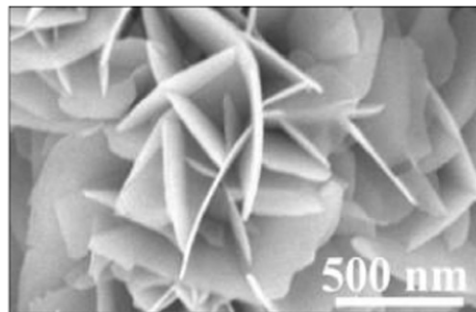


Fig. 7 RGO wrapped Bi_2Se_3 flower like morphology through easy hydrothermal procedure. Das, B., Sarkar, S., Khan, R., *et al.*, 2016. rGO-Wrapped flowerlike Bi_2Se_3 nanocomposite: Synthesis, experimental and simulation-based investigation on cold cathode applications. RSC Advances 6 (31), 25900–25912.

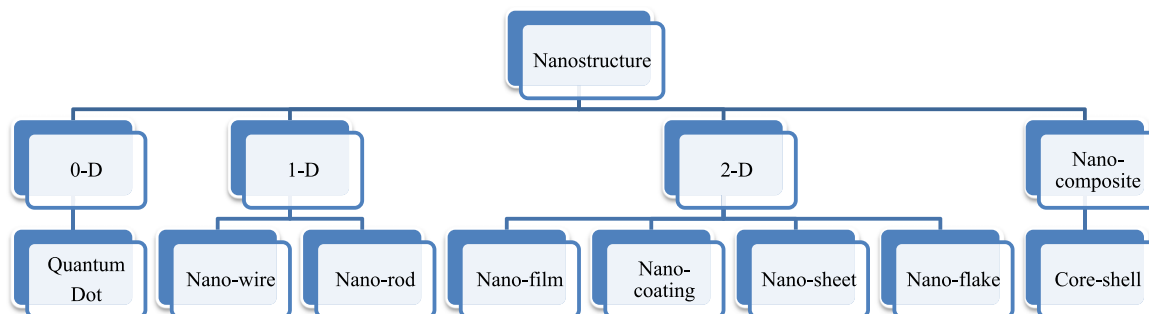


Fig. 8 Classification of nanostructures based on morphology. Modified from <https://en.wikipedia.org/wiki/Nanostructure>.

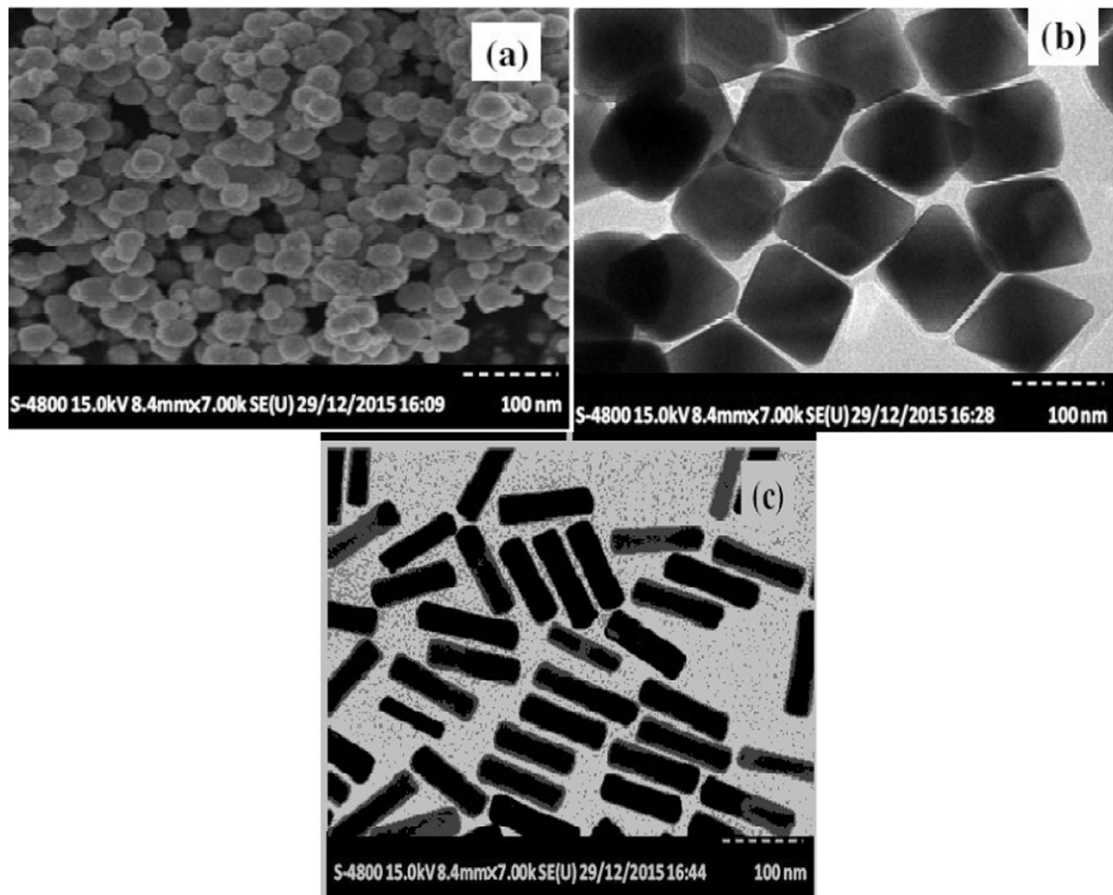


Fig. 9 FESEM image of different geometries of TiO_2 nanoparticle (a) spherical, (b) cubic, (c) rod-shaped. Reproduced from Maheshwary, P.B., Handa, C.C., Nemade, K.R., 2017. A comprehensive study of effect of concentration, particle size and particle shape on thermal conductivity of titania/water based nanofluid. *Applied Thermal Engineering* 119, 79–88.

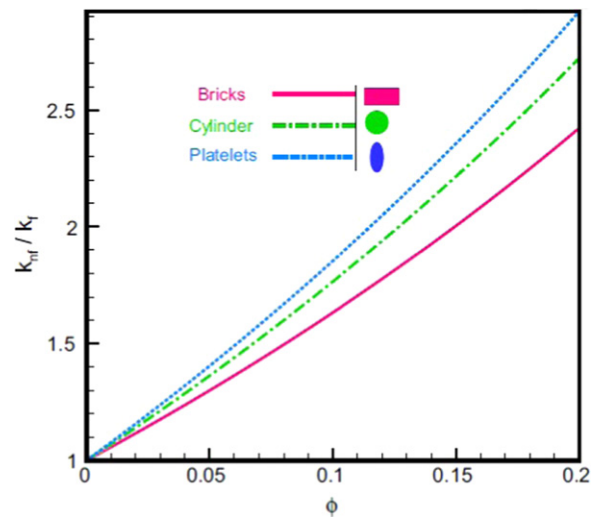


Fig. 10 Effect of shape and volume fraction on effective thermal conductivity. Reproduced from Akbar, N.S., Tripathi, D., Bég, O.A., 2017. MHD convective heat transfer of nanofluids through a flexible tube with buoyancy: A study of nano-particle shape effects. *Advanced Powder Technology* 28 (2), 453–462.

Table 2 Solar absorption efficiency factor for variable geometry each having same surface area equal to that of a 50 nm nanosphere

Shape	Ellipse	Tetrahedron	Triangular	5-sided equilateral polygon	Octahedron	Cross	Star
SAEF	0.53338	2.5827	0.58321	1.4312	1.4317	1.7993	2.597

Source: Wang, Z., Zhang, Z.M., Quan, X., Cheng, P., 2018. A numerical study on effects of surrounding medium, material, and geometry of nanoparticles on solar absorption efficiencies. *International Journal of Heat and Mass Transfer* 116, 825–832.

the optical behaviour. Core-shell arrangement is a new addition to this. Various reviews indicate strong dependence of solar collector efficiency of heat transfer capacity of nanofluidic system on the material choice (Gorji and Ranjbar, 2017b; Kim *et al.*, 2016; Al-Shamani *et al.*, 2016; Alashkar and Gadalla, 2015; Alim *et al.*, 2012).

Nanofluidic Energy Harvesting

Energy harvesting is the efficient conversion of any other form of energy to electricity. The striking enhancement of thermal conductivity of nanofluid attracts researchers to utilize it as heat transfer fluid in different solar collectors instead of less efficient, more costly PV collectors.

Effectiveness of Nano Fluid in Solar Collectors

Nanofluid based solar thermal collector uses nanofluid for efficient heat transfer to harness solar energy more efficiently than conventional solar collectors. A recent report shows 92.9% thermal efficiency whereas water shows only 36.2% as a working fluid (see “Relevant Websites section”).

The benefits of using nanofluid are:

- Entrapping of solar light can be enhanced by tuning and changing the size, shape, volume fraction efficiently.
- Suspended Nano-particles enhances thermal conductivity of entire system due to high surface to volume ratio but at the same time decreases the heat capacity of fluid due to very small particle size.
- Nanofluid can be made optically selective by using the Localized surface plasmon resonance (LSPR) effect of metal Nano-particles, thus can be utilized as an optical filter.

Various ways of energy scavenging through tuneable nanofluidic properties are schematically represented in Fig. 11.

The efficiency of carbon coated cobalt dispersed Therminol VP-1 nanofluid based DASC system is found to be 35% indicating the utility of nanofluid based DASC instead of fossil fuels in near future (Liu *et al.*, 2017). Incorporation of Phase change materials into heat transfer fluid enhances the specific heat of it and thus enhancing the energy harvesting (Liu *et al.*, 2017). Metal Nano-particles owing to their LSPR effect shows effectiveness in enhancing the collector efficiency (Jeon *et al.*, 2016) whereas, spectrum splitting nanofluid based Photovoltaic thermal hybrid solar (PV/T) collectors are well-known for better efficiency than stand-alone PV system (Crisostomo *et al.*, 2017).

Solar collectors in energy harvesting

Solar collectors are designed to collect solar radiation effectively and to convert it into heat which is eventually transferred to the working fluid of a system which is either water or air generally. Nanofluid as working fluid improves the efficiency in a great way. Solar collectors are generally of two kinds- Stationary and Concentrating Solar collectors. Flat plate solar collector (FPSC), DASC, Evacuated tube solar collector (ETSC) are widely used stationary solar collectors which are installed at particular tilt and orientation angles to maximize solar energy harnessing. FPSC are widely used and of less thermal efficiency and outlet temperature but of less complicated in nature. These were first developed by Hottel and Whillier in 1950s (Florschuetz, 1979). A FPSC consists of glass, absorber, insulation, backsheet, riser, header pipes and aluminium rails. Many researchers have investigated the effective way to enhance the collector efficiency as much as possible which leads to the use of nanofluid as working material in collector due to their unique property of enhanced heat transfer. Theoretical investigation of FPSC with alumina-water nanofluid at different concentration (0.5%–2.0%) and at different flow rates (0.5–2 L min⁻¹) shows a maximum 31.6% enhancement in efficiency for 1.5% concentration indicating huge enhancement in efficiency compared to that of pure water as working fluid (Dubey, 2017). Use of hybrid nanofluid instead of nanofluid containing only one kind of nanoparticle is proved to be better in maximizing collector efficiency. Tahat *et al.* used Aluminium oxide and copper oxide based hybrid nanofluid as collector medium (Tahat and Benim, 2017). A mixture of EG and water (25:75 by weight) has been used. Experiment has been conducted for various volume concentrations varying from 0.5% to 2%. Results indicate rise of thermal conductivity with rise of concentration.

The functionalization of alumina nanoparticle with copper causes rise in thermal conductivity as copper has higher thermal conductivity compared to alumina. FPSC efficiency shows a maximum of 52% at 2 vol%. A rise of collector efficiency about 45% in average is observed with hybrid nanofluid having 25: 75 EG and water compared to pure water indicating the utility of hybrid nanofluid compared to normal nanofluid. Said *et al.* analysed the effect of pH controlled nanofluid on collector efficiency (Said *et al.*, 2016b). Both exergy and energy efficiencies are studied for alumina-water nanofluidic system with 0.1 and 0.3 vol% for

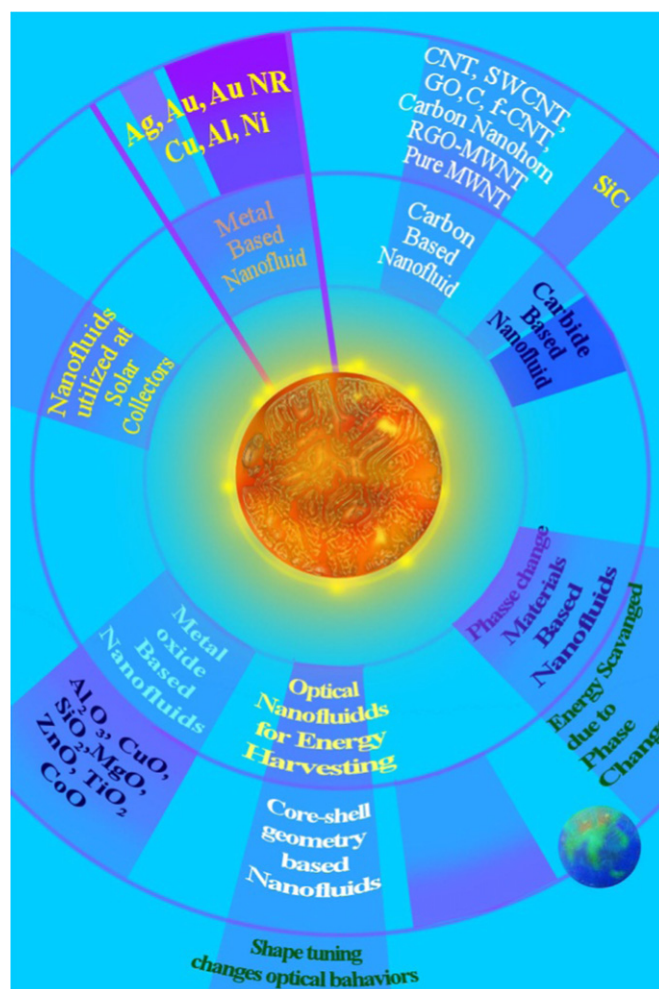


Fig. 11 Schematic representation of different ways of energy harvesting through nanofluid of various kinds. Artwork done by Nirmalya S. Das.

13 nm sized nanoparticles. They formulate a stable nanofluid by controlling the pH for 30 days. Flow rates were varied from 0.5 to 1.5 kg min⁻¹. Their results revealed an enhancement about 83.5% of energy efficiency for 0.3 vol% and flow rate 1.5 kg min⁻¹ whereas exergy efficiency reaches to 20.3% for 0.1 vol% and 1 kg/min flow rate. [Table 3](#) shows improvement of stability by pH treatment. As stability is a prime factor for enhancing thermal conductivity of nanofluid so, pH controlling can be effective as is seen from this result.

[Zambolin and Del Col \(2010\)](#) and [Ayompe *et al.* \(2011\)](#) showed that the performance of ETSC is far better than FPSC under same condition. An U tube solar collector consisting of a two-layered glass evacuated tube and a U tube which showed a max of 62.8% efficiency with MWCNT for 0.2 vol% with 20% Propylene glycol (PG) water amongst oxides ([Kim *et al.*, 2016](#)). [Sabiha *et al.* \(2015\)](#) proposed the use of water based Single-walled carbon nanotube (SWCNT) in ETSC where 93.43 % collector efficiency has been found for 0.2 vol% much higher (about 71.84%) than water.

Unlike FPSC and ETSC, in DASC, solar radiation is first absorbed by the outer surface of tube and then is transferred directly to a working fluid through heat transfer by conduction and convection. It shows better efficiency with nanofluid as working fluid. Fang *et al.* explored the effect of GO dispersed nanofluid in DASC ([Chen *et al.*, 2017c](#)). Both thermo-physical and optical-absorption properties are investigated. Photo-thermal conversion efficiency is highest (97.45%) for 0.02% of GO at 30°C. Thermal conductivity of GO sheet-water was explored at 30°C. [Fig. 12\(a\)](#) shows their results on variation of thermal conductivity with mass fraction which indicates an enhancement in conductivity with rise of mass fraction. At 0.1 wt%, thermal conductivity approaches to 0.73 W/m-K whereas, [Fig. 12\(b\)](#) shows enhancement of thermal conductivity with temperature. At 0.02 wt%, thermal conductivity enhances from 0.6718 to 0.8656 W/m-K while temperature is varied from 30 to 80°C.

Thus GO sheet is promising in formulating effective working fluid for DASC for better efficiency. Gorji *et al.* observed the effect of different nanofluids (Graphite, magnetite, Silver based) on DASC ([Gorji and Ranjbar, 2017b](#)). Experiments were carried out under variable volume fraction (5–40 ppm), Flow rates (5–10 ml min⁻¹) and incident fluxes (600–1000 W m⁻²). Results showed maximum thermal and Exergy efficiency for magnetite at optimum volume fraction 40 ppm, flow rate 10 ml min⁻¹ and flux-884 W m⁻² followed by the results of graphite and silver nanofluids.

Table 3 Results showing improvement of stability of Alumina – Water based nanofluid by controlling pH of the solution

Nominal particle size	Zeta potential (mV)	Particle size(nm) from DLS using high pressure homogenizer	pH
13 nm	58.4	106	9.0
13 nm	54.3	109	8.1
13 nm	49.5	123.9	7.0
13 nm	35.9	126.4	6.1

Source: Said, Z., Saidur, R., Sabiha, M.A., Hepbasli, A., Rahim, N.A., 2016b. Energy and exergy efficiency of a flat plate solar collector using pH treated Al_2O_3 nanofluid. Journal of Cleaner Production 112, 3915–3926.

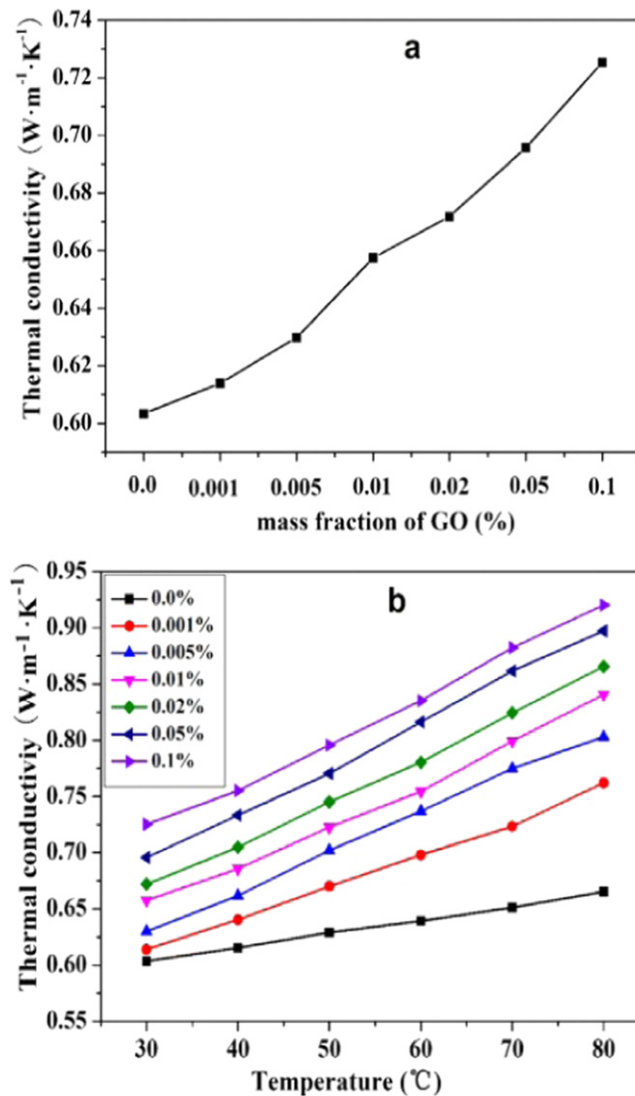


Fig. 12 Experimental results of GO based nanofluid showing variation of (a) thermal conductivity with mass fraction, (b) effect of temperature variation on thermal conductivity. Reproduced from Chen, L., Xu, C., Liu, J., Fang, X., Zhang, Z., 2017c. Optical absorption property and photo-thermal conversion performance of graphene oxide/water nanofluids with excellent dispersion stability, Solar Energy 148, 17–24.

Kasaeian *et al.* utilized parabolic trough collector in a bare glass tube, non-evacuated glass-glass tube and Vacuumed absorber tube based receivers (Kasaeian *et al.*, 2017). Ethylene glycol was taken as a base fluid and 0.2% of silica (inner dia: 6 nm and outer dia: 15 nm) and 0.3% of CNT (inner dia: 4 nm and outer: 10 nm) were taken to form different nanofluidic systems. Amongst all, CNT shows maximum outlet temperature 338.3K and highest efficiency 74.9% in vacuumed glass-glass absorber tube. Compared to bare glass tube, 20% higher efficiency has been noted for vacuum glass-glass absorber. They also calculated optimum volume fraction for highest efficiency in vacuumed glass-glass absorber. For, Nano-silica, it is 70.9% at 0.4 optimum volume fractions and

for CNT, it is 80.7% at 0.5. The detailed studies and results of different researchers on the application of nanofluid in different solar collectors are furnished in [Table 4](#).

Optical Nanofluids in Energy Harvesting

Radiant energy from incoming solar insolation should be efficiently captured and converted into thermal or electrical energy in order to harvest useful energy from solar energy which can be done by modifying the dispersed phase of a nanofluidic energy system or combining different Nano-materials having complimentary optical properties together to produce broadband absorption capability or by utilizing some special optical properties of some Nano-particles it is possible to harvest energy efficiently.

Surface plasmon resonance effect

A resonant oscillation of conducting electrons is seen at the interface of negative and positive permittivity material while stimulated by incident light energy, this effect is known as surface Plasmon resonance effect (SPR), a non-radiative electromagnetic surface wave called surface Plasmon polariton propagates in a parallel direction to the interface between negative and positive interface i.e., metal and dielectric interface, the condition for surface Plasmon to exist is the real part of the dielectric constant of conductor should be negative and its magnitude should be greater than that of dielectric, this condition is seen to be satisfied in case of Infra-red-Visible region for air-metal and metal-metal interfaces (see "Relevant Websites section"). In case of metallic Nano-particles, the phenomenon of collective electron charge oscillation due to optical excitation is known as Localized surface Plasmon resonance effect.

Energy harvesting with metal nanoparticles

The metal Nano-particles which are known as plasmonic Nano-particles are capable of entrapping light energy when excited by LSPR effect. Electric field around these Nano-particles is enhanced significantly causing a considerable amount of heat energy generated in particles ([Duan et al., 2017](#)). Utilizing LSPR effect, solar energy harvesting is possible by solar thermal collector. Nanofluids, while used as working fluid provides an alternating way to enhance light absorption due to LSPR effect thereby enhancing the incoming solar light absorption resulting an enhanced temperature of nanofluid, thus energy can be more efficiently harvested as Photo-thermal conversion efficiency depends sharply on absorption properties of nanofluid. The absorption peak induced by LSPR is highly particle size, shape and concentration dependent so, it is possible to enhance photo-thermal efficiency by proper tuning of these parameters ([Duan et al., 2017](#)).

Du *et al.* investigated the rise of collector efficiency of a DASC due to the LSPR effect induced red-shift at the surface of gold nanoparticles based blended plasmonic nanofluid ([Du and Tang, 2016](#)). Numerical representations of the dependence of variation of morphology and concentration on optical properties are presented here. Results indicate a prominent dependence of enhanced LSPR effect of gold Nano-rods and Nano-ellipsoids on increased aspect ratio (AR). Broad-band absorption covering both visible and near infra-red region, is reported to be achieved with gold nanofluid blended with 20% Nano-ellipsoids of AR=2 and 60% of Nano-rods of AR=5 and 20% of Nano-sheets of l/h (length/height) equal to 7. Nano-sheet is reported to have great potential in solar thermal conversion. Blended system shows an enhancement in solar energy harvesting about 104% compared to gold sphere at low particle concentration. [Fig. 13](#) shows the result of absorption efficiency versus wavelength nature for (a) ellipsoid and (b) rod morphologies.

[Fig. 14](#) shows absorption efficiency of Nano-sheets for different ARs. Results indicate that thinner sheet is more effective in exciting LSPR effect.

Chen *et al.* conducted an experimental study on the size effect of gold nanofluid which shows LSPR effect on the efficiency of both flat and cubic shaped DASC ([Chen et al., 2016b](#)). They have reported an average enhancement of 19.9% in photo-thermal conversion efficiency for cubic while a 21.3% enhancement of the same for flat shaped DASC at a very low particle concentration (0.000008 wt%) indicating a geometry dependence of collector on efficiency. [Fig. 15](#) shows the size dependence on absorbance spectra of gold nanofluid.

The result indicates better absorbance with reduced particle size for flat shaped DASC.

[Jin et al. \(2016\)](#) reported an enhancement of photo-thermal efficiency about 76% for gold based nanofluid at 5.8 ppm and a non-linear increasing trend of it for enhanced particle concentration. [Jeon et al. \(2016\)](#) studied the effect of blended plasmonic nanofluid made of gold Nano-rods at flat plate volumetric solar collector. Amongst three different AR (1.77, 2.73, 4.17), highest extinction coefficient was achieved by 4.17 AR based nanofluid depicted in [Fig. 16](#).

Chen *et al.* reported the effect of Au, Ag and Au-Ag bended plasmonic nanofluid on photo-thermal conversion efficiency due to LSPR effect on metal surface ([Chen et al., 2016a](#)). Both temperature and photo-thermal conversion efficiency was observed to rise with concentration. At 1.75–0.15 ppm, Au-Ag blended nanofluid shows enhanced photo-thermal conversion efficiency 30.97% which is almost arithmetic sum of individual Au and Ag nanoparticles. Au (10 nm) and Ag (30 nm) were slightly spherical and slightly spherical-cylindrical in morphology respectively. [Fig. 17](#) shows the solar radiation spectral intensity and absorbance of Au, Ag and Au-Ag based nanofluid.

Energy harvesting through core-shell geometry

Core-shell structure is a kind of biphasic material which has an inner core structure and outer shell made of different materials. These are well-known for their unique tuneable optical property by choosing appropriate material for core and shell and tuning

Table 4 Solar energy harvesting through different solar collectors utilizing nanofluid

Type of solar collector	Base fluid	Nano-material	Shape and size (nm)	Concentration (%) / flow rate	Heat transfer coefficient/thermal efficiency/nusselt number	Ref
PTSC	Ethylene glycol	Silica and CNT	Cylindrical	Optimum conc. (MWCNT)-0.5 vol (%) (Nano-silicon)-0.4 vol (%)	At optimum conc., thermal efficiency is: (MWCNT)-80.7% (Nano-silicon)-70.9%	Kasaeian <i>et al.</i> (2017)
	DI	α -Al ₂ O ₃	Spherical 20 nm	0.05–0.125 vol%	Overall efficiency: 13.98% (80 LPH/0.125 vol %)	Ajay and Lal (2016)
	Water	Al ₂ O ₃	Spherical	0.1 vol% and 0.3 vol%	Nusselt number enhances by 20% at 0.3 vol%	Jafar and Sivaraman (2015)
	Water	CuO	Spherical Outer dia: 100 nm	0.002–0.008 vol%	Thermal efficiency 52% (at 0.008 vol%)	Menbari <i>et al.</i> (2016)
	DI	CuO	Spherical	0.01% Flow rate: 20 L/h	Efficiency reaches 7.4% (Expt. Result)	Ajay and Lal (2015)
	Water	Al ₂ O ₃ CuO	Spherical 20–30 nm	0.01–0.05 vol% Flow rate: 20–60 L/h	Max efficiency (CuO): 18.4% (at 0.05 vol% & 60 L/h)	Sharma and Lal (2014)
	Water EG	CuO	Spherical 25–55 nm	0.01–0.1 vol% Flow rate: 100–160 L/h	Max efficiency: 6.6% (for CuO-Water)	Kandwal and Lal (2015)
	Water	CuO SiO ₂	Spherical 20–30 nm (SiO ₂) 40 nm (CuO)	0.01 and 0.05 vol% Flow rate: 20, 40, 60 L/h	Max overall thermal efficiency (CuO –based system): 9.57%	Kumar <i>et al.</i> (2014)
	Therminol VP 1 Syltherm-800	Al ₂ O ₃ Cu SWCNT	Spherical cylindrical	–	Max rise in annual energy output: 3.1% (Cu- Syltherm-800)	Alashkar and Gadalla (2017)
	Syltherm-800	Al ₂ O ₃	Spherical	1%–10% (Molar fraction)	Convection coefficient rises by 18% at 5%	Basbous <i>et al.</i> (2015)
	Therminol-VP1	Al ₂ O ₃ Cu CNT	Spherical Cylindrical	0–5 vol%	Thermal conductivity enhancement: 98% (CNT) at 3 vol%	Alashkar and Gadalla (2015)
FPSC	Water	Al ₂ O ₃	Spherical	1.5 vol (%)	Max Efficiency: 31.6%	Dubey (2017)
	EG: water 25:75 (by weight)	Al ₂ O ₃ -CuO (Hybrid)	Spherical	0.5–2 vol (%)	Max efficiency: 52% (For 2 vol%)	Tahat and Benim (2017)
	DI (pH-controlled)	Al ₂ O ₃	Spherical 13 nm	0.1–0.3 vol%	Energy efficiency: 83.5% (0.3 vol%) Exergy efficiency: 20.3% (0.1 vol%) Thermal conductivity: 6.8% (0.3 vol%)	Said <i>et al.</i> (2016b)
	Water	MgO	Spherical 40 nm	0.25–1.5 vol%	Thermal efficiency: 9.34% At 0.75 vol%	Verma <i>et al.</i> (2016)
	Water	Al ₂ O ₃	Spherical 13–20 nm	0.1 vol%	Max Energy efficiency: 73.7% (for 13 nm)	Said <i>et al.</i> (2016a)
	DI	Al ₂ O ₃	Spherical 45 nm	3.0 vol%	Efficiency: 11.7%	Colangelo <i>et al.</i> (2015)

DASC	Water	ZnO CeO ₂ NiO CoO	Spherical	1–4 vol%	CeO ₂ shows highest exergy efficiency	Alim <i>et al.</i> (2014)
	50:50 (EG: Water)	Al ₂ O ₃	Spherical, Platelet, Blade, Cylinder, Brick. 15–80 nm (for spherical)	0–5 vol%	Max efficiency: 60% at 1.0 vol% (For 15 nm)	Amin <i>et al.</i> (2015)
	Water	CuO Al ₂ O ₃ TiO ₂ SiO ₂	Spherical	1–4 vol% (Flow rate:1–4 lit/min)	Highest Thermal conductivity: 43% (at 5 vol%) Highest collector efficiency (at 0.8 vol%) for Blade Highest energy efficiency:38.46% At 2 vol% (CuO)	Alim <i>et al.</i> (2012)
	Water	Graphene oxide	Nano-sheet 0.55–1.2 nm (thickness)	0.02%	Thermal conductivity rises: 84% (30–80°C)	Chen <i>et al.</i> (2017c)
	DI	Graphite Magnetite Silver	Spherical C(40 nm) Fe ₃ O ₄ (15 nm) Ag(20 nm)	5–40 ppm	Max Thermal efficiency: 94.57% (Fe ₃ O ₄)	Gorji and Ranjbar (2017b)
	(H2O:EG) Surfactant Pvp: CuO	CuO	Spherical <40 nm	12.5–100 ppm	Thermal conductivity enhancement: 5.6–13.7% (25–60°C)	Karami <i>et al.</i> (2016)
	DI, EG	PUMWNT	Tubular Outer dia:40 nm Inner dia:8 nm	0.005–0.03 vol%	Thermal conductivity enhancement: 27% (at 0.03 vol %) for DI	Shende and Ramaprabhu (2016)
	(H2O:EG)	CuO	Spherical	100 ppm (Flow rate 0.015–0.025 kg/s)	Collector efficiency enhancement: 17% (at 0.025 kg/s rate)	Karami <i>et al.</i> (2015)
	DI	f-CNT	Cylindrical 10 nm	5–150 ppm	Thermal conductivity enhances by 32% at 150 ppm	Karami <i>et al.</i> (2014a)
	DI EG	N-(RGO-MWNTs)	–	0.005–0.03 vol%	Max thermal conductivity enhancement: 17.7% at 0.02 vol% (DI)	Shende and Sundara (2015)
GCPVT	Water	Carbon-Nano-horn	–	Flow rate: 0–0.06 (g/L)	Max Efficiency: 17% at 0.05g/L	Karami <i>et al.</i> (2014b)
	Water	Graphite	Spherical 50–300 nm	0.0025–0.000025 vol%	At 0.000025 vol% 23% enhancement in energy absorption compared to water	Ladjevardi <i>et al.</i> (2013)
	Ionic liquid	Paraffin –(core) Graphite embedded melamine formaldehyde –(shell)	Micro-encapsulated	20 wt%	13% enhancement in Thermal conductivity	Liu <i>et al.</i> (2017)
	Ionic liquid	SiC	Spherical 30 nm	0.06 wt%	10.2% rise in Thermal conductivity	Chen <i>et al.</i> (2017d)
	–	SiC	–	–	Max Electrical efficiency-13.5%	Al-Shamani <i>et al.</i> (2017)
	20% PG-Water	MWCNT,Al ₂ O ₃ , CuO,TiO ₂ ,SiO ₂	Nanotube and nano-particle	3 vol% for Al ₂ O ₃ ,CuO, TiO ₂ ,SiO ₂ 0.2vol% for MWCNT	For 0.2 vol% MWCNT: 62.8% (Max)	Kim <i>et al.</i> (2016)
	DI	CuO	Spherical	0.03–0.06 vol%	Efficiency enhanced up to 51.4% at 0.06 vol%	Ghaderian <i>et al.</i> (2017)
	DI	SWCNT (90%-CNT + 60% SWCNT)	Cylindrical Average dia:1–2 nm	0.05–0.2 vol%	Efficiency:93.43% at 0.2 vol% & 0.025 kg/s rate	Sabiha <i>et al.</i> (2015)
	Water	TiO ₂	Spherical	0.05–1 vol%		

(Continued)

Table 4 Continued

Type of solar collector	Base fluid	Nano-material	Shape and size (nm)	Concentration (%) / flow rate	Heat transfer coefficient / thermal efficiency / nusselt number	Ref
Hybrid PV/T	Pure water	Polypyrrole	Spherical	–	Max heat transfer enhancement is seen at 0.5 vol% & 30° inclination angle	Jamil <i>et al.</i> (2016)
Rectangular tube absorber PVT	DI	SiO ₂ , TiO ₂ , SiC	Spherical	Mass flow rate: 0.068–0.17 kg/s	Thermal efficiency 13.3% higher without filter	An <i>et al.</i> (2016b)
Fresnel lens based solar thermal collector	Therminol 55	Al ₂ O ₃	Spherical	Up to 0.1 vol%	Thermal efficiency: 81.73% At 0.17 kg/s & 1000 w/cm ² (SiC)	Al-Shamani <i>et al.</i> (2016)
Concentrated solar thermal collector	DI + 0.45 g KPS + KOH	MWCNT	Cylindrical (Dia: 6–13 nm) (Length: 2.5–2.0 μm)	–	Thermal efficiency: 52.2% at 0.1 vol%	Muraleedharan <i>et al.</i> (2016)
Cylindrical Solar collector	Water	Al ₂ O ₃ , CuO	Spherical	0.1 wt% of CuO and 0.2 wt% Al ₂ O ₃	Efficiency of copper coated tube: 85% at ambient whereas efficiency of nanofluid absorber: 73% at ambient	Li <i>et al.</i> (2015)
					Max Efficiency: 64.5% (for pH-10.5, Al ₂ O ₃)	Goudarzi <i>et al.</i> (2015)

Note: Modified from multiple sources [Ref. has been incorporated in the list of tables].

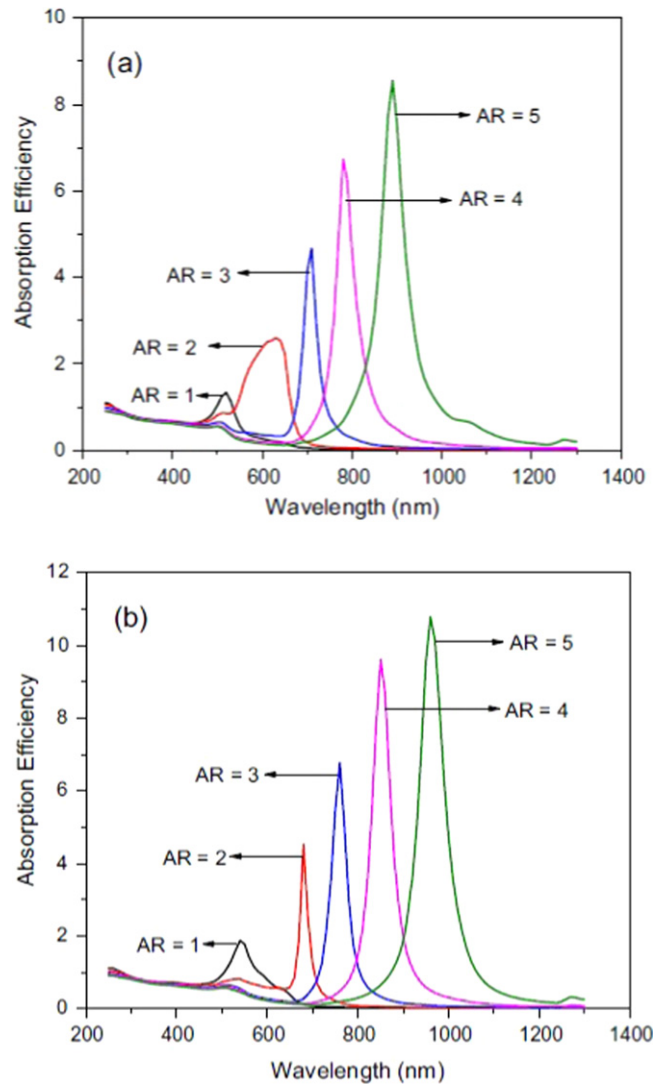


Fig. 13 Results showing absorption efficiency variation with wavelength for gold nanomaterial having (a) ellipsoid and (b) Rod morphology for different aspect ratios. Source: Du, M., Tang, G.H., 2016. Plasmonic nanofluids based on gold nanorods/nano ellipsoids/nanosheets for solar energy harvesting, *Solar Energy* 137, 393–400.

other parameters. Controlled tuning of shape, size and material of both core and shell of a Nano-composite enables the emission wavelength to be tuned over a wide range of wavelengths. Duan *et al.* (2017) developed a hybrid nanofluid made of core-shell nanoparticles of various sizes to observe the overall absorbing performance due to enhanced plasmonic resonance effect. To observe the shift in plasmonic resonance frequency, three different sizes of core-shell are chosen and volume fraction is kept at 0.01. Core is made of SiO_2 and Shell is of Ag. First observation was the effect of fixed shell size (5 nm) and variable core sized (15 nm, 30 nm, 45 nm) particles blended together to form a hybrid nanofluid. Fig. 18 shows the absorbance spectra of variable core sized-structure.

The result indicates that the blended form of different core sized particles allows a broadband absorption compared to single core-shell dispersed nanofluid. Wu *et al.* (2015) explored different composite structures (Si/SiC as core and Au, Ag, Cu and Al as shell) based plasmonic fluid to observe both the optical and radiative phenomenon by varying radius ratio, outer radius and type of material. They reported about the coupling effect induced by the structure capable of influencing the average and near field radiation of plasmonic nanofluid simultaneously. Fig. 19 shows the variation of absorption efficiency while changing the radius ratio t for Si/Au composite at 0.7 vol%.

Result indicates that while enhancing the shell thickness keeping the outer radius fixed, the wavelength of resonance peaks approach towards the resonance peak of pure Au nanoparticle hence, optical absorption is enhanced by the enhanced electric field at resonance wavelength of gold Nano-shell thus by adjusting the radius ratio, LSPR effect can be successfully utilized to absorb solar energy efficiently. Fig. 20(a) represents the dependence of shell material on extinction coefficient with outer radii fixed at 5 nm while Fig. 20(b) shows the effect of core material.

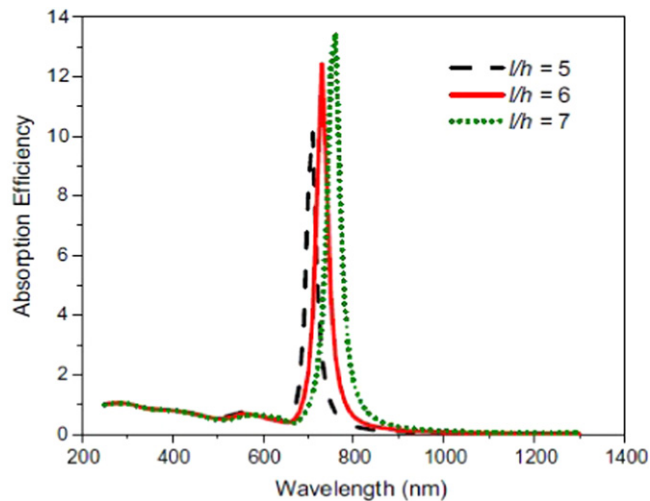


Fig. 14 Experimental results showing dependence of aspect ratio on absorption efficiency of gold Nano sheet. Reproduced from: Du, M., Tang, G.H., 2016. Plasmonic nanofluids based on gold nanorods/nano ellipsoids/nanosheets for solar energy harvesting, *Solar Energy* 137, 393–400.

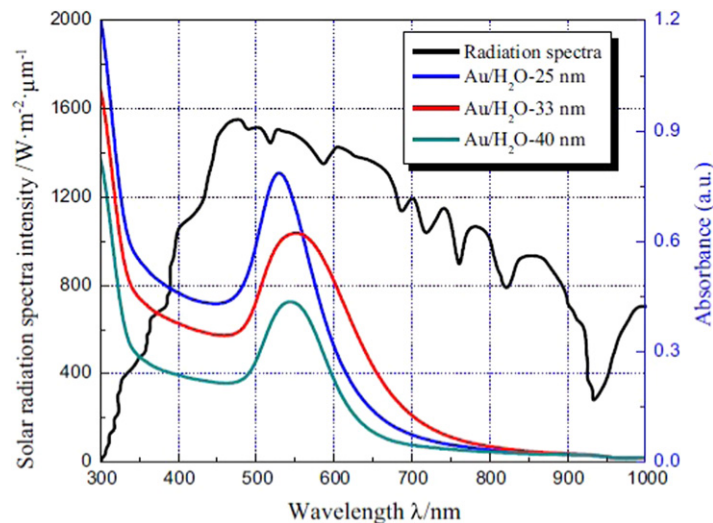


Fig. 15 Results indicating nanoparticle size dependence of absorbance spectra of gold-water nanofluid. Reproduced from Chen, M., He, Y., Zhu, J., Kim, D.R., 2016b. Enhancement of photo-thermal conversion using gold nanofluids with different particle sizes, *Energy Conversion and Management* 112, 21–30.

The researcher concluded that SiC/Al, Si/Al and Si/Cu are the best candidates for photo-thermal application in solar collector.

Use of complementary combination of nano-materials

Broad-band solar thermal conversion is a must in effective solar energy harvesting. Some of the researchers have introduced the use of a combination of Nano-materials to realize it. They chose two different materials such a way that one of them has a strong optical absorption effect in one region while the other has strong absorption capability in another region thus covering the desired portion of incoming solar spectra that enhances absorption causing efficient energy harvesting. [Chen et al. \(2017b\)](#) introduced the concept of choosing materials having complementary optical absorbing properties and combining them to form two-component nanofluid to access an optical absorption over a broad-range. To utilize the whole of the visible and near-infra-red region, they opted CuO which shows strong absorption in visible region and ATO which shows good absorption in near infra-red region. The solar weighted absorption of the two component fluid was reported 99.6% at 0.1 vol% and the solar utilization efficiency was observed to be 92.5% compared to 81.3% for CuO and 80.7% for ATO nanofluids individually. For two-component system, the ratio of CuO and ATO has been shown as an important factor, if the ratio is 4:6 then [Fig. 21](#) indicates almost 100% absorption of solar irradiation.

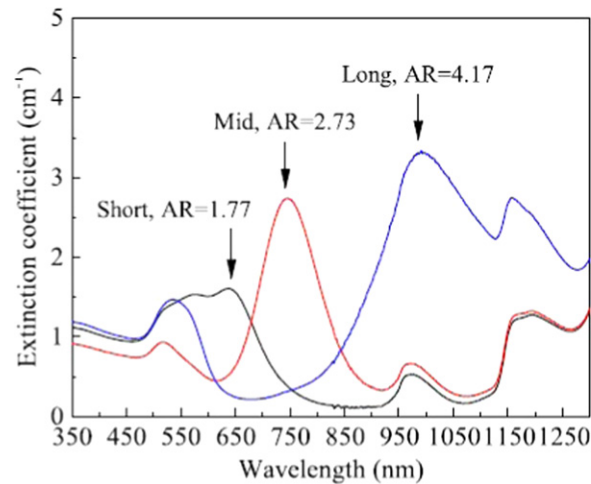


Fig. 16 Dependence of Extinction coefficient (cm^{-1}) on aspect-ratio of nanorod structure. Reproduced from Jeon, J., Park, S., Lee, B.J., 2016. Analysis on the performance of a flat-plate volumetric solar collector using blended plasmonic nanofluid, *Solar Energy* 132, 247–256.

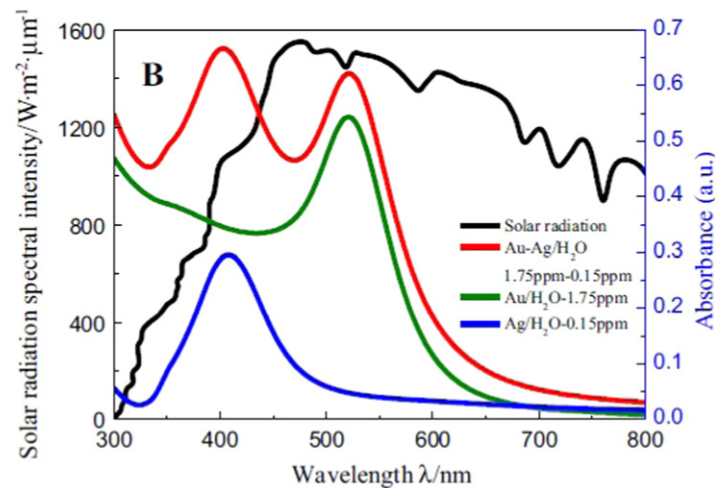


Fig. 17 Variation of solar radiation spectral intensity and absorbance of Au, Ag and Au-Ag based nanofluids. Reproduced from Chen, M., He, Y., Huang, J., Zhu, J., 2016a. Synthesis and solar photo-thermal conversion of Au, Ag, and Au-Ag blended plasmonic nanoparticles, *Energy Conversion and Management* 127, 293–300.

Spectrally selective optical filter

The solar energy application where absorption of light from a particular portion of solar spectra is needed for a better efficiency, highly efficient Nanofluid with optically selective nature is a very recent finding of researchers. Using such nanofluids as working fluid in solar collectors such as hybrid PV/T collector an efficient energy harvesting can be obtained (Crisostomo *et al.*, 2017). Tuning particle shape, size and material is the way to achieve spectrally selective optical filter. To overcome the temperature limitations in traditional PV/T collector, An *et al.* introduced the concept of using concentrating PV/T collector with spectral splitting filter (An *et al.*, 2016a). Here Oleylamine based Cu_9S_5 nanofluid works as optical filter in collector. The maximum overall efficiency achieved was reported 34.2%, 17.9% more than that of without filters with a collector temperature more than 100°C . Cu_2S is a kind of nanoparticles that always possess the intense effect of SPR at visible to near infra-red region. The spectral properties can be well-tuned by controlling proportion of Cu defect in crystals. Cu_9S_5 is a representative of this kind of materials able to be utilized for efficient spectral modulation. For spectral-splitting hybrid system, liquid should have large transmittance at visible wavelength and at the same time intensive absorption at Ultra-violet and near-infra-red range. Due to Cu_9S_5 addition, absorption of nanofluid is reported to be enhanced up to 800–1600 nm and lightly at 400–800 nm, as the solar radiation in the range 280–2500 nm accounts for 96% total solar radiation so, the use of Oleylamine based Cu_9S_5 nanofluid proves to be a good spectral-selective filter fluid. Hassani *et al.* (2016a) explored the use of nanofluid as a coolant and optical filter to improve the energetic and ecological performance of a hybrid PV/T system. Here, Ag nanoparticles suspended in water acts as a nanofluid based optical filter as the water molecules absorbs longer wavelengths whereas silver nanoparticles absorbs shorter thus as a whole

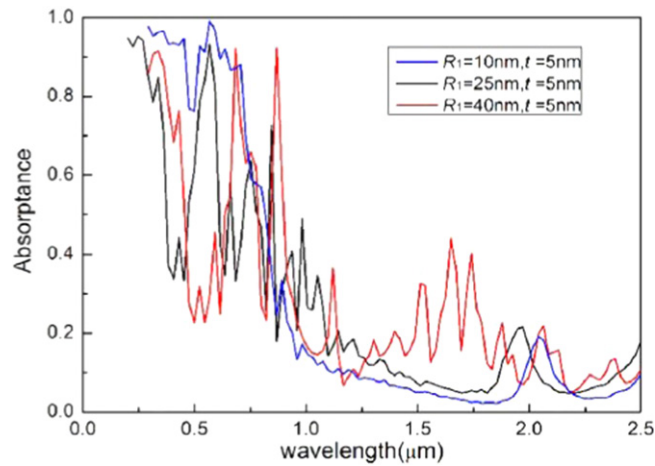


Fig. 18 Influence of core size variation on absorbance spectra for a fixed shell thickness of 5 nm. Reproduced from Duan, H., Tang, L., Zheng, Y., 2017. Optical properties of hybrid plasmonic nanofluid based on core/shell nanoparticles, *Physica E Low-dimensional Systems and Nanostructures* 91, 88–92.

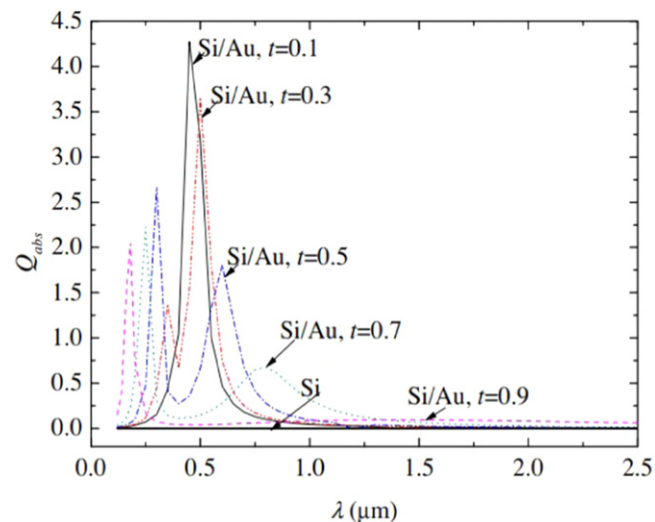


Fig. 19 Dependence of absorption efficiency on absorbance spectra for Si-Au composite at 0.7 vol%. Reproduced from Wu, Y., Zhou, L., Du, X., Yang, Y., 2015. Optical and thermal radiative properties of plasmonic nanofluids containing core-shell composite nanoparticles for efficient photothermal conversion. *International Journal of Heat and Mass Transfer* 82, 545–554.

provides a broad band absorption capacity and CNT based water nanofluid serves as coolant. Ag-water absorbs 38% of incident radiation while pure water absorbs only 21% and annual Exergy efficiency is reported to be 1.3 MWhm^{-2} with payback time of 2 years. [Hassani et al. \(2016b\)](#) showed the efficiency of hybrid PV/T collector with thermal and optical nanofluids. Ag-Therminol VP1 forms optical filter to allow absorption of radiation from UV and IR region efficiently and with volume fraction enhancement, electrical efficiency is reported to have enhancement up to 9% (GaAs) and 5.6% (Si-PV Cells). Faiz et al. investigated that by varying nanofluidic layer thickness, Hematite nanoparticle based nanofluid shows most resistance to optical transmittance and Gd and TiN based nanofluid are mostly affected with a rise in volume concentration ([Faiz and Zahir, 2014](#)). Faiz et al. also showed the use of Hematite based nanofluid to serve as long-pass tuneable filter ([Faiz and Zahir](#)). Hematite nanofluid shows great similarity with performance of solid thin film Hematite filter at small particle size and high volume fraction and transmittance is reported to improve at mid and high infra-red region. With enhanced volume fraction, level of transmittance raises.

Solar energy harvesting using different optical properties of Nano-particles has been furnished in [Table 5](#).

Phase change material based nanofluid

A phase change material is a material of high heat of fusion and is capable of storing and releasing large amount of energy while the material undergoes a phase change from solid to liquid and vice-versa (see “Relevant Websites section”). Nanoparticles used to prepare PCM nanofluids/composite are metallic materials like aluminium, copper, silver etc. and non-metallic materials such as

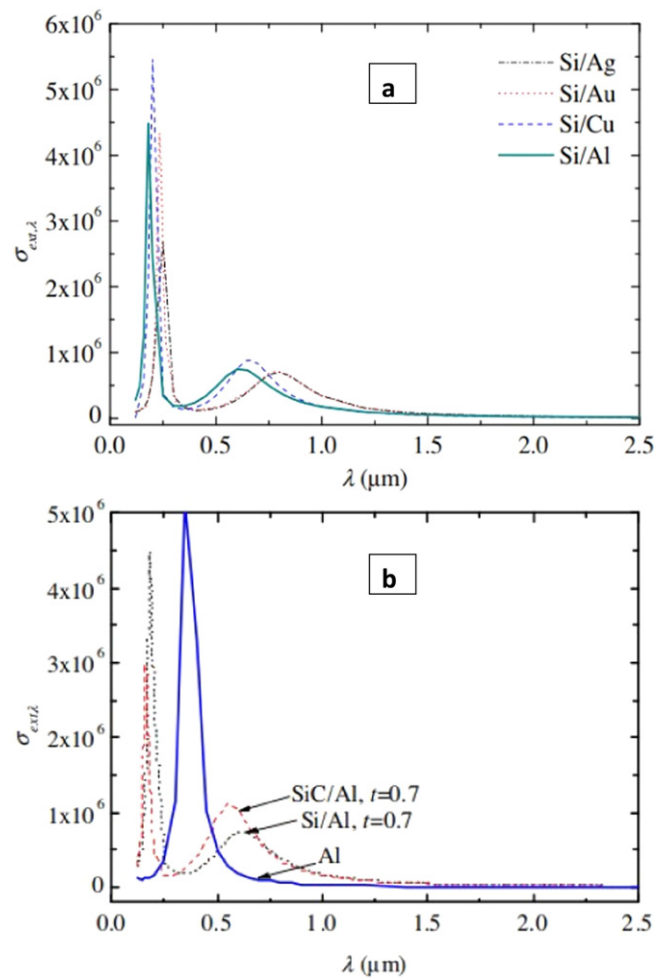


Fig. 20 Results indicating impact on (a) shell, (b) core material variation on extinction co-efficient. Reproduced from Wu, Y., Zhou, L., Du, X., Yang, Y., 2015. Optical and thermal radiative properties of plasmonic nanofluids containing core-shell composite nanoparticles for efficient photothermal conversion. *International Journal of Heat and Mass Transfer* 82, 545–554.

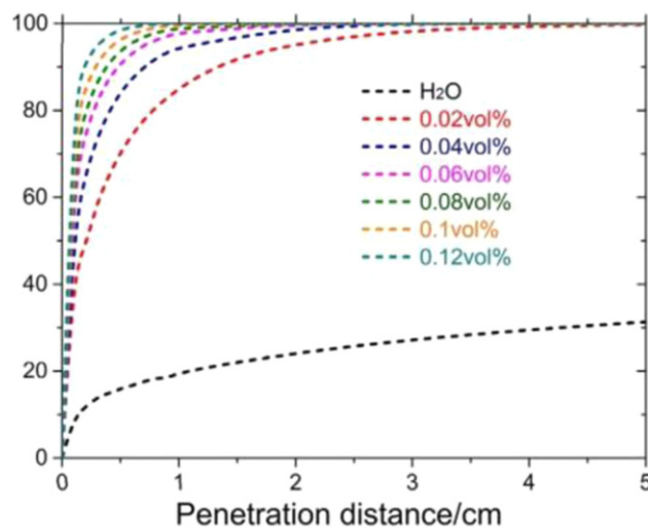


Fig. 21 Variation of solar weighted absorption fraction (%) with penetration depth (cm) for CuO-ATO based two-component system. Reproduced from Chen, N., Ma, H., Li, Y., *et al.*, 2017b. Complementary optical absorption and enhanced solar thermal conversion of CuO-ATO nanofluids, *Solar Energy Materials and Solar Cells* 162, 83–92.

Table 5 List of different optical phenomenon of nanofluid used for solar energy harvesting

Nature of nano fluid	Nano-material	Base fluid	Size (nm)	Shape	Concentration	Result showing Photo-thermal conversion efficiency/Abs. coeff./Extinction coeff./ Evaporation efficiency	Solar collector	Phenomenon involved	Ref
Hybrid	SiO ₂ -Core Ag-shell	Water	Shell:5 nm Core:15–45 nm	Shell	0.01 vol%	With the rise of amount of larger particles, absorption peak enhances from 1.1–2.5 μ m	–	Broadband optical absorption due to blending	Duan <i>et al.</i> (2017)
Two-component Hybrid	CuO ATO	Water	–	–	0.1 vol%	Solar-thermal utilization efficiency: 92.5%	–	Complementary optical absorption	Chen <i>et al.</i> (2017b)
Hybrid	TiO ₂ -core Ag-shell	Water	–	Shell	–	Presence of defects enhances solar weighted absorption coefficient by 12 %	–	LSPR effect	Liu and Xuan (2017)
–	GO	Water	0.55–1.2 nm (width)	Sheet	0.05–0.001 wt%	Photo-thermal efficiency: 97.45% (at 0.02%)	–	Photo-thermal conversion	Chen <i>et al.</i> (2017c)
Nano-composite	Ag-core SiO ₂ -shell	water	–	Core-shell	2.5, 1.9, 1.3, 0.6 [wt%10 ⁻²]	9% more weighted thermal + electrical output is obtained for two most concentrated nanofluids having concentration [At 2.5 wt%10 ⁻² & 1.9 wt %10 ⁻²] Compared to same PV cell at full solar spectrum	Hybrid PV/T	Spectrally selective absorption of solar radiation	Crisostomo <i>et al.</i> (2017)
–	RGO	Water	0.55–1.2 nm (width)	Sheet	0.02 wt%	Photo-thermal conversion efficiency:96.9%	–	Enhanced absorption and photo-thermal conversion	Chen <i>et al.</i> (2017a)
Ionanofluid	SiC	[HMIM] BF ₄	30 nm	Sphere	0.03 wt%	Extinction coefficient rises by 5.8 cm ⁻¹	–	Solar absorption by Ionanofluid	Chen <i>et al.</i> (2017d)
Blended	Au	water	AR (ellipsoid): 2 AR(rod): 5 l/h (sheet): 7	Rod Sheet Ellipsoid	20% of Ellipsoid, 60% of Rod, 20% Sheets	104% enhancement in solar energy harvesting for blended system	–	LSPR effect	Du and Tang (2016)
Oleylamine based	Cu ₉ S ₅	Oleylamine	60.2 nm	Sphere	(22.3 $\pm$ 1.1) to (89.2 $\pm$ 4.5) ppm	Efficiency: 34.2% at 89.2 $\pm$ 4.5 ppm	–	SPR Effect	An <i>et al.</i> (2016a)
Hybrid	Ag-Core TiO ₂ -shell	Water	Ag: (19.7 $\pm$ 1.4) nm TiO ₂ : (2.2 $\pm$ 0.7) nm	Core-shell	25–400 ppm	Evaporation efficiency: 53.9% at 200 ppm	–	Broadband solar absorption due to LSPR effect	Li <i>et al.</i> (2017)
Plasmonic	Au	Water	25 nm 33 nm 40 nm	Sphere	0.000008 wt%	Photo-thermal efficiency: 19.9%(Cubic) & 21.3%(Flat)	Flat and Cubic DASC	LSPR effect	Chen <i>et al.</i> (2016b)
Metal Based	Au	DI	20 nm	Sphere	0–5.8 ppm	Photo thermal efficiency: 76% at 5.8 ppm	–	High solar light absorbing capacity due to LSPR effect of Au	Jin <i>et al.</i> (2016)
Blended	AuNR	CTAB	Average dia:16 nm	Rod shaped	<0.0001 vol%	Extinction coeff is highest in largest AR 4.17	FPSC	Broad band absorption over near-IR & Vis spectra due to LSPR effect	Jeon <i>et al.</i> (2016)

Hybrid	Au Cu Al Graphite SiO ₂ /Au	Water	Dia:10–150 nm	Sphere and Shell	Concentration of Au:52% And SiO ₂ /Au: 48%	Enhanced solar light absorption due to hybrid nature	–	LSPR effect	Tullius and Bayazitoglu (2016)
–	Si	Water	40–250 nm (TEM)	Sphere	0.1–0.0001 vol%	Vaporization rate is higher for higher concentration At 1200 s, vaporized weight for 0.01 vol% enhances 1.6 fold relative to pure water & temperature rises 1.8 fold than pure water Si –based nanofluid covers 70% of solar spectrum due to broadband absorption	–	Absorption due to Mie resonance of Nano- particles	Ishii <i>et al.</i> (2016a)
–	CNT Ag	Water	CNT: 15 nm Ag: 10 nm	Cylinder and Sphere	0.0104 wt%	Ag/water absorbs almost 38% of the incident radiation	Hybrid PV/T	Nanofluid serves both as optical filter and coolant	Hassani <i>et al.</i> (2016a)
Plasmonic	Au Ag Au-Ag	Water	Au (10 nm) Ag (30 nm)	Sphere and Cylinder	Ag (0.5 ppm) Au (2.5 ppm)	Photo-thermal conversion efficiency of Ag- Au blended: 30.97% (1.75–0.15 ppm)	–	LSPR effect	Chen <i>et al.</i> (2016a)
Plasmonic	Au	Water	Dia:18.5 nm	Sphere	15 mg/L	At low concentration, an absorption of 80% is obtained after a 10 cm propagation length which is twice than pure water	–	LSPR effect	Mondragón <i>et al.</i> (2016)
Plasmonic	TiN C(Black) Au	Water	TiN:30 nm Carbon: – 40 nm	–	0.0001–0.1 vol%	TiN shows better solar light absorption than others At 0.1 vol%, TiN nanofluid produces almost 240 mg vaporized weight whereas that of carbon, it is less than 220 mg	–	Lossy plasmonic resonance of Nano- particles	Ishii <i>et al.</i> (2016b)
–	Ag	Water	10 nm	Sphere	0.001–1.5 vol%	Optical filter transmits almost 82% of the desired spectrum	PV/T hybrid system	Optical filter	Hassani <i>et al.</i> (2016b)
Plasmonic	TiO ₂ Ag	Water	Shell:30 nm Core size: variable	Core-shell	0.005–0.015 vol%	20.9% photo-thermal efficiency at 0.005 vol% whereas that of water: 15.52%.	–	LSPR effect	Xuan <i>et al.</i> (2014)
Plasmonic	Au	CTAB	AR: 1.77, 2.73,4.17	Cylinder	0.0001vol%	Extinction coefficient: 1.77 cm ⁻¹ in visible spectrum	–	LSPR Effect And Broadband absorption in VIS and Near-IR	Jeon <i>et al.</i> (2014)
Metal oxide based	Al ₂ O ₃ TiO ₂	DI	13 nm 21 nm	Sphere	0.1 vol% 0.3 vol%	Max Extinction coefficient: 11.4 cm ⁻¹ at 400 nm at 0.1 vol% (TiO ₂)	–	Energy absorption depending upon size, shape & different scattering modes	Said <i>et al.</i> (2014)
Metal oxide based	TiO ₂ C- TiO ₂	Water EG	TiO ₂ :42.77 nm C- TiO ₂ : 49.74 nm	Sphere	0.04–0.08 wt%	C- TiO ₂ shows full absorption compared to TiO ₂ in the range 460–800 nm	DASC	Carbon enhances absorption in C-TiO ₂ nanofluid	Subramaniyan <i>et al.</i> (2016)
Metal oxide based	Al ₂ O ₃	0.0001 M aqueous Solution of HCl	13 nm	Sphere	0.03–0.08 vol%	Extinction coefficient reduces more rapidly for 0.05 vol% samples than others within 6 h of nanofluid preparation.	–	Time varying optical behaviour of nanofluid	Sajid <i>et al.</i> (2014)
						Transparency of EM waves raises by 10%–35% within 6 h after preparation within Vis to near IR range			

(Continued)

Table 5 Continued

Nature of nano fluid	Nano-material	Base fluid	Size (nm)	Shape	Concentration	Result showing Photo-thermal conversion efficiency/Abs. coeff./Extinction coeff./Evaporation efficiency	Solar collector	Phenomenon involved	Ref
Plasmonic	Ag	DI	10 nm	Nearly spherical	0.0001625–0.065 vol%	144% enhancement in thermal energy storage is obtained at peak temperature at 6.5 ppm	DASC	SPR effect	Bandarra Filho <i>et al.</i> (2014)
–	Hematite silicon gadolinium TiN	Water	Variable	–	Variable	Maximum transmittance of Gd: 98.9% at thickness 1 μm & 50 vol%	–	Nanofluid acting as tuneable optical filter	Faiz and Zahir (2014)
Plasmonic	Ag	Water	Average size: 49 nm	Near-spherical	20.24–80.94 ppm	After 5 min irradiation the efficiency of Ag nanofluid reaches to 84.61% at 80.94 ppm	–	LSPR effect	Chen <i>et al.</i> (2015)
Plasmonic	Ag Au	Water	Dia: 5 nm (Au & Ag both)	spherical	0.00019 vol% 0.00025 vol% (Experimental)	Ag based nanofluid shows highest thermal, PV & overall efficiency	PV/T Hybrid collector	Optical Filtration of Nanofluid	Saroja <i>et al.</i> (2015)
Hybrid	Au Silica	Water	–	Nano-shell: Silica core & Au shell Nano-matryoshka: Core-Au, Silica-shell & Au-shell	Variable	Ratio of scattering to absorption efficiency: 10 (Nano-shell) and 0.167 for nano-matryoshka multiple scattering begins to effect fractional light absorption for Nano-shell & Nano-matryoshka at 10^9 & 10^{10} NP/ml respectively	–	Large temperature is obtained due to concentrated light obtained by multiple interactions due to strong optical scattering	Hogan (2014)
Plasmonic	Si/SiC Au Ag Cu Al	Water	Outer radius: 5 nm Core Size: variable	Core: Si/SiC Shell: Au, Ag, Cu or Al	0.1–0.7 vol%	Si/Al & SiC/Al Nano-particles are considered to be the best in efficient photo-thermal conversion efficiency	–	LSPR effect	Wu <i>et al.</i> (2015)
–	TiN	Water	30 nm	Spherical	0.0001–0.1 vol%	Evaporation rate enhances four times compared to water whereas heating rate enhances twice at 0.1 vol%	–	SPR effect of TiN	Ishii <i>et al.</i> (2015)
Plasmonic	Au, Ag, Al or Cu and Si	Water	Variable	Core: Si Shell: Au, Ag, Al, Cu	Variable	Al & Cu based core-shell suspension shows better Solar weighted efficiency compared to Nobel metal core-shell	–	SPR effect	Lv <i>et al.</i> (2013)
–	Hematite Fe_3O_4	Water	Dia: 0.005–0.2 μm	–	70–0.1 vol%	Small size, higher concentration & lower thickness of liquid layer shows best transmittance effect	–	Nanofluid as Long-pass tunable filter	Faiz and Zahir (2013)
Plasmonic	Shell: C Ag, Au, Al, Cu, Ni and Core: Si	Water	For core-shell (r1/r2): 0.5, 0.7, 0.83, 0.88 (variable)	Core-shell	0.004–0.008 vol%	Core-shell structure shows highest solar weighted absorption efficiency: At 0.008 vol% and 18 nm net size with 3 nm shell thickness	DACS	Plasmon resonance effect	Lv <i>et al.</i> (2012)
Plasmonic	Au Ag Si	Water	Relative core-radius varies from (0.01–0.99)	Core-shell	9E^{-6} to 7.8E^{-6}	Au/Si with core radius 37.6 nm & 2.4 nm shell thickness & Ag/Si of 10.8 nm & 49.2 nm shell thickness causes 95% of total extinction at a least volume fraction 9E^{-6} to 7.8E^{-6}	–	Plasmon resonance effect	Hewakuruppu <i>et al.</i> (2013)

Note: Modified from multiple sources [Ref. has been incorporated in the list of tables].

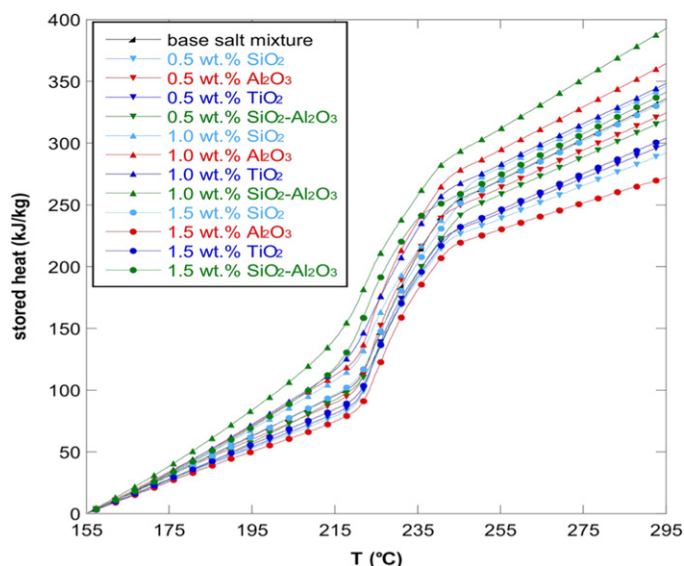


Fig. 22 Variation of stored heat (KJ/Kg) with temperature for base salt mixture $\text{NaNO}_3\text{-KNO}_3$ and other nanofluids. Reproduced from Chieruzzi, M., Cerritelli, G.F., Miliozzi, A., Kenny, J.M., 2013. Effect of nanoparticles on heat capacity of nanofluids based on molten salts as PCM for thermal energy storage, *Nanoscale Research Letters* 8 (1), 448.

alumina, copper oxide, titanium oxide and carbon nanotubes etc. Kumaresan *et al.* (2012) prepared a new class of nanofluid called NFPCM system by dispersing Multi-walled carbon nanotube (MWCNT) in water with Sodium Dodecyl Benzene sulphonate (SDBS) as surfactant. Results indicate the enhancement of thermal conductivity about 15% at 0.6 vol% of MWCNT thus indicating enhancement of heat transfer phenomenon with concentration. Navarrete *et al.* (2017) introduced the phenomenon of enhancement of both thermal conductivity and heat capacity of nanofluid containing Nano encapsulated Phase change materials (NEPCM). It has been shown here that metal and metal -alloy nanoparticles can be used as self-encapsulated NEPCM system using the metal oxide layer. Therminol-66 has been taken as base fluid. A prominent difference between the performance of base fluid and NEPCM nanofluid with Sn (<300 nm) both in thermal storage and conductivity rise has been presented here. Results showed a significant enhancement in thermal conductivity at 50°C and 100°C at 5 vol% loading.

Chieruzzi *et al.* (2013) developed different nanofluids with phase change behaviour by mixing molten salt base fluid with nanoparticles to study the phase change nature of them and to use them efficiently in concentrating solar plants. The base salt material taken as phase change material was $\text{NaNO}_3\text{-KNO}_3$ (60:40) binary mixture. SiO_2 , TiO_2 , Al_2O_3 , $\text{SiO}_2\text{-Al}_2\text{O}_3$ nanoparticles were used to form nanofluid each in water solution. Results indicate that addition of 1.0 wt% of nanoparticles enhances specific heat of 15%–57% in solid state and of 1%–22% in liquid state. Fig. 22 shows the results representing stored heat versus temperature for $\text{NaNO}_3\text{-KNO}_3$ mixture and nanofluids.

Harikrishnan *et al.* (2013) developed steric acid- TiO_2 nanofluid (average size of nanoparticle was 23 nm) as a composite phase change material to investigate the effect of phase change on solar heating systems. Zhichao *et al.* (2015) explored the heat capacity enhancement of Nano-titania(20 nm) doped erythritol forming Phase change material. The heat capacity of nePCM enhanced by 45% in solid state while 14% in liquid state at 0.2 vol% Nano-titania, thus 8% overall enhancement in total heat capacity storage was reported.

Energy harvesting in a different way

Researchers are paving the path of nanofluidic research with some simple but innovative ideas thus the field of nanofluid in energy harvesting gets wider as time is passing by. Nanofluidic battery is an interesting energy generation system converting mechanical energy to electric power which is possible by the acoustic phonons to drive the condensed ions across a matrix to have sustainable current. Yan *et al.* (2013) studied the effect of slip length and access Ohmic resistance on the energy conversion of nanofluidic battery.

From both the theoretical and experimental analysis, maximum conversion efficiency was found to be as high as 50% for a slip length of 90 nm for a pore radius of 5 nm and pore length of 4 μm . Ouyang *et al.* (2013) designed a Nanofluidic crystal, a high-efficiency and high power density scheme for energy harvesting through reverse electro- dialysis technique.

In predefined microstructure, self-assembly of mono-dispersed nanoparticles forms Nanofluidic crystal (NFC) capable of providing high power output.

The proposed NFC provides a maximum efficiency of $42.3 \pm 1.84\%$ and maximum power density of $2.82 \pm 0.22 \text{ W m}^{-2}$.

Conclusion

More and more use of energy intensive devices and rapid industrialisation all over the world have started taking its toll in terms of increasing greenhouse gas and over all carbon footprint. For a sustainable socio economic development alternative and efficient

energy harvesting technologies have to be developed which can provide clean energy and mitigate the above threats. Use of nanotechnology in the energy fields have already shown enormous promise in this direction. The exciting features of Nanofluid have attracted the minds of researchers to utilize it in harvesting energy from ambient energy sources. Use of Nanofluid as heat transfer fluid in solar collectors has replaced many of the commercial solar cells with its extremely good solar thermal conversion efficiency due to enhanced heat transfer capability of nanofluid. Metal nanoparticle with its unique LSPR effect is able to form an efficient optical nanofluid to capture and absorb incoming solar light effectively and convert it into useful thermal energy. By proper tuning of shape, size and material of a core-shell hybrid nanostructure based nanofluid has proved to be a very good alternative of commercial heat transfer fluid. Besides, blended plasmonic nanofluid is explored extensively now-a-days. Researchers are incorporating different sized metal and core-shell geometry based nanofluid to achieve the broadband solar light absorption both in VIS and NIR region to have enhanced solar energy harvesting. In the present scenario of high energy demand, it is very difficult to fulfil it with only fossil fuel based resources which are depleting gradually. It is high time to think over an alternative way to harvest energy from natural resources in a pollution-free way. Nanofluid is the best option to achieve it economically, without harming our atmosphere. Poor stability, low conversion efficiency are the barriers. Extensive research is needed in this field to achieve higher efficiency and meet the ever-increasing energy demand.

See also: Application of Nanofluids for Radiator Cooling

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Nanomaterial for CO₂ Sequestration

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Introduction

Carbon dioxide is considered as a primary greenhouse gas (GHG) of the recent decade as it accounts for 77% of greenhouse effect resulting from anthropogenic activities and 26%–30% of total CO₂ emissions. Burning of fossil fuel is the main source of anthropogenic CO₂ emission. Concentration of CO₂ in flue gas varies with the type of fuel like 12–15 mol% in case of coal, 3–4 mol% in case of natural gas, etc. CO₂ concentration in industrial exhausts are found to vary with the industrial process generating the same and are recorded to be 8–9 mol%, 14–33 mol%, and 20–44 mol% for oil refining, cement production and manufacturing of iron and steel respectively as reported by Songolzadeh *et al.* (2014). Worldwide CO₂ emissions have demonstrated an increase of 26% between 2004 and 2011. Power plants, transportation and industrial processes are respectively responsible for 55%, 23% and 19% of CO₂ emissions in USA. Cement and petrochemical industries are considered as major contributors of global CO₂ emissions (Songolzadeh *et al.*, 2014). According to Intergovernmental Panel on Climate Change (IPCC), the atmospheric CO₂ concentration is expected to reach 570 ppmv by 2100, thereby causing an increase of mean global temperature and sea level rise by 1.9°C and 38 m, respectively (Crombie *et al.*, 2011; Mohammadi *et al.*, 2013). Owing to the rising trend revealed by mean global temperature, IPCC has recommended a reduction in global GHG emissions by 50%–80% to be achieved by 2050 in order to avoid the intense consequences of global warming (Songolzadeh *et al.*, 2014).

In recent times, development of technologies for efficient carbon capture and storage (CCS) is the primary strategy for reducing CO₂ emissions resulting from combustion of fossil fuels and other industrial processes. CO₂ isolated from flue gases may be further reused for advanced oil recovery (Pires *et al.*, 2011). Pure CO₂ is widely utilized in various other industries like food/beverage, production of urea, fertilizer and dry ice, foam blowing and even as a supercritical solvent (Dave *et al.*, 2009; Zangeneh *et al.*, 2011). Therefore, research for CCS is growing by the day. However, most technologies reported so far necessitate improvement in terms of efficiency and reduction of cost incurred (Ben-Mansour *et al.*, 2016). Different post combustion carbon capture processes reported so far have been shown in Fig. 1.

The major challenges limiting conventional strategies of CCS are enlisted as follows:

- Massive consumption of energy (recorded for supplying pure O₂ in case of oxy-fuel combustion capture and compression of captured CO₂ as well as sorbent regeneration in case of post-combustion capture),
- High expense incurred for pre-combustion capture,
- Insufficient technical proficiency,
- Dearth of single compact process with holistic approach for CCS, and
- Non investigation of these technologies for their commercial feasibility and application on industrial scale.

Of all other processes of CCS reported so far, post-combustion carbon capture is considered more advantageous as it is easier to incorporate the same within existing industrial configuration and/or combustion technology of any type and its flexibility exhibited for maintenance and monitoring (Ben-Mansour *et al.*, 2016). Recent research have established nanoporous solids (of both microporous and mesoporous nature), having high surface area and pore volume, as ideal adsorbents for selective separation of CO₂ from a mixture of gases as post-combustion carbon capture (Sneddon *et al.*, 2014). These solids are easy to handle and known to cause fewer corrosion related issues. The schematic comparison of pore sizes of reported nanoporous materials applied for CO₂ capture has been shown in Fig. 2.

Moreover, these materials demonstrate thermal stability up to 150–200°C. This renders them suitable for post-combustion CO₂ capture as the temperature of flue gas generated from a power plant may measure between 40 and 120°C (Sneddon *et al.*, 2014). Nanosorbents prepared from such solids and applied for CO₂ capture have been reviewed in details in the following segments of the article.

Nanosorbents for CO₂ Capture

Metal organic frameworks (MOFs), nanotubes (made up of carbon, silicon carbide, etc.) and nanosheets (prepared from graphene, aluminum nitride, etc.) have been previously reported for CCS with highly reduced energy consumption (Guo *et al.*, 2015). For efficient CO₂ capture, these sorbents are expected to exhibit high surface areas and robust adsorption sites which in turn facilitate high selectivity (Guo *et al.*, 2015). However, interaction between CO₂ and sorbent surface is often weak. Furthermore, in real time scenarios, water vapor often out-competes CO₂ for bonding with active sorbent sites. Some sorbents also reportedly exhibit instability in presence of water vapor (Guo *et al.*, 2015). Efficient nanosorbents for CCS reported in recent studies have been discussed below.

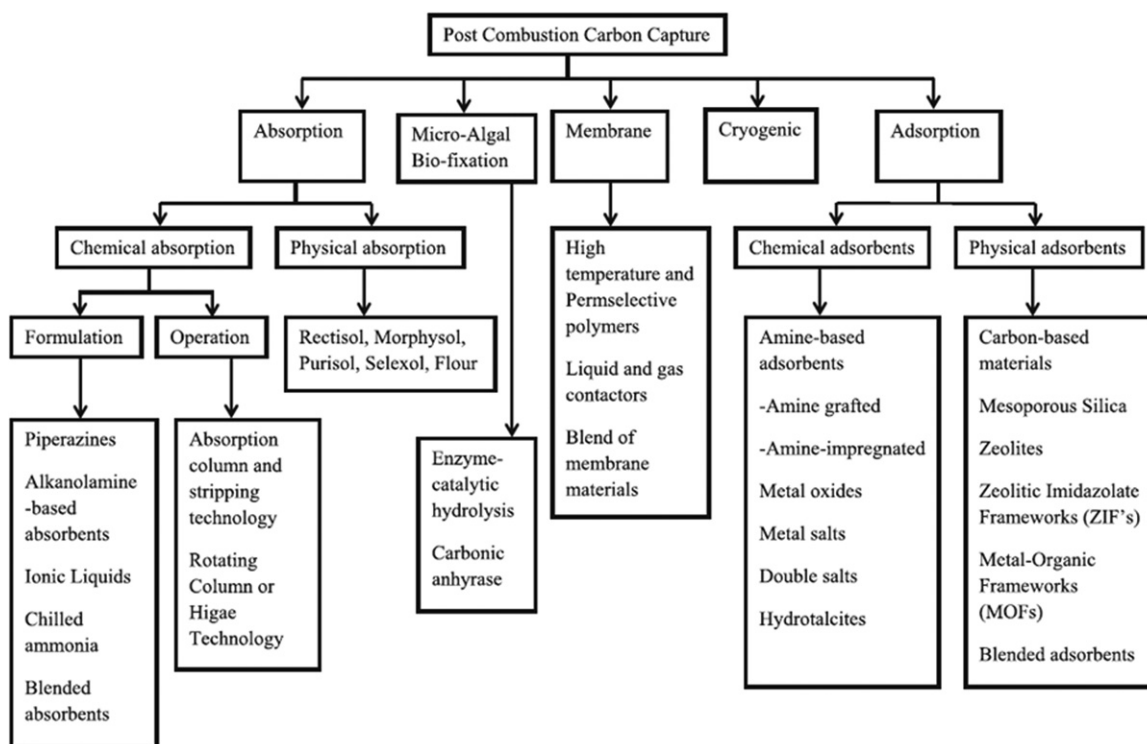


Fig. 1 Post combustion carbon capture processes. Reprinted with permission from Ben-Mansour, R., Habib, M.A., Bamidele, O.E., *et al.*, 2016. Carbon capture by physical adsorption: Materials, experimental investigations and numerical modeling and simulations—a review. *Applied Energy* 161, 225–255. Copyright 2015 Elsevier Ltd.

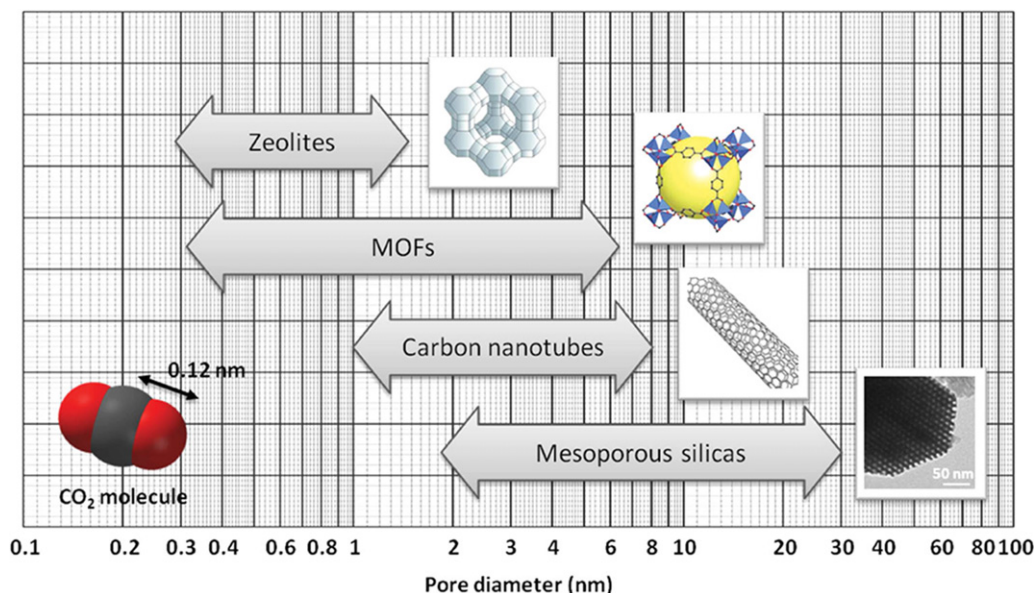


Fig. 2 Illustrative comparison on the pore sizes of several common nanoporous materials. Reprinted with permission from Sneddon, G., Greenaway, A., Yiu, H.H., 2014. The potential applications of nanoporous materials for the adsorption, separation, and catalytic conversion of carbon dioxide. *Advanced Energy Materials* 4 (10), 1301873. Copyright 2014 The Authors. Published by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Metal Oxide Nanoparticle

According to contemporary studies, metal dioxides are reportedly exhibit high affinity for uptake of gases like H₂, CO₂, NH₃, etc. due to unsaturated atoms present on their surface (Li *et al.*, 2016). Recent studies have investigated mesoporous transition metal dioxides (like TiO₂, MnO₂, ZnO, etc.) for gas adsorption and sensing (Pawar *et al.*, 2010; Wei *et al.*, 2011). In a recent study by Liao *et al.* (2015), amine-functionalized ZnO nanosheets were investigated for CO₂ capture. In this study, ZnO nanosheets were functionalized with monoethanolamine. The terminal amine groups present on ZnO surfaces were found to facilitate higher CO₂ capture as a result of chemisorption and thereby result in CO₂ activation. The excited ZnO further liberated photogenerated electrons which in turn augmented photocatalytic reduction of CO₂ (Liao *et al.*, 2015).

Some researchers have also suggested that composites of metal oxides formed with carbonaceous materials exhibit improved efficiency for size-selective adsorption of gaseous molecules (Chowdhury *et al.*, 2015; Hong *et al.*, 2012; Li *et al.*, 2015a; Mishra and Ramaprabhu, 2014). In a recent study, Li *et al.* (2016) reported a novel porous nanomaterial consisting of ZnO and N-doped reduced graphene oxide (rGO) referred to as N-rGO-ZnO. N-rGO-ZnO reported in this study was examined for its pore size and adsorption-desorption efficiency for CO₂ and N₂. Addition of ZnO was found to increase the microporous diameter as well as CO₂ and N₂ uptake efficiency of rGO. The CO₂ and N₂ uptake efficiency of N-rGO-ZnO was found to increase with a corresponding rise in temperature and was recorded to be high at 35.84°C rendering the same applicable for capturing CO₂ from flue gas emitted by power plants (Li *et al.*, 2016).

Controlled synthesis and assembly of colloidal clusters of metal oxides nanoparticles are presently being considered as novel building blocks for advanced functional materials (Harada and Hatton, 2015). These clustered nanoparticles are also known as colloidal atoms (Wang, 2010) or supraparticles (Xia *et al.*, 2011) and demonstrate potential efficiency as catalysts (Chen *et al.*, 2011) and high density magnetic storage media (Harada and Hatton, 2015). Harada and Hatton (2015) have reported colloidal clusters of MgO nanoparticles coated with alkali metal nitrates and mixtures of nitrate/nitrite capable of rapid and significant uptake of CO₂. These adsorbents demonstrated significant adsorption of CO₂ at ~300°C and were successfully regenerated at ~400°C rendering the same highly appropriate for treatment of hot gaseous discharges (Harada and Hatton, 2015). The nitrite salts used to coat the MgO nanoclusters were also considered responsible for preventing detrimental morphological alterations resulting from recurring cycles of adsorption and desorption by increasing critical thickness of the sorbent surface.

Mesoporous Materials

Mesoporous substrates (like zeolites, carbonaceous and siliceous materials, MOFs, etc.) having fine structural and chemical properties are considered highly advantageous for carbon capture (Kamimura *et al.*, 2014). These materials have facilitated pressure/temperature swing adsorption of CO₂ from diverse sources of emissions. Synthetic zeolites and mesoporous materials modified with amines demonstrate high selectivity and interact strongly with CO₂. Such materials are therefore considered appropriate for capturing CO₂ from flue gas emitted post-combustion having low pressure and low CO₂ concentration (D'Alessandro *et al.*, 2010; Samanta *et al.*, 2011). Kamimura *et al.* (2014) reported the fabrication of novel mesoporous ceria having a surface area of 200 m² g⁻¹ and investigated the same for CO₂ adsorption. This mesoporous ceria was found to demonstrate significantly higher CO₂ uptake capacity per volume in comparison to commercially obtainable non-porous ceria, activated carbon and zeolite under conditions of high pressure (3000 kPa) and moderate temperature (25°C). The mesoporous ceria reported by Kamimura *et al.* (2014) was found to be highly stable and could be conveniently regenerated after multiple cycles of adsorption-desorption. Results of this study also indicated that a further rise in surface area of mesoporous ceria could facilitate higher CO₂ uptake. The simple and cost effective process of synthesis of mesoporous ceria reported in this study was also considered more advantageous than mass production of other contemporary adsorbents.

In a separate study by Niu *et al.* (2016), authors reported mesoporous silica nanotubes impregnated with polyethenimine as an emerging nanomaterial for CO₂ capture. The specific surface area and pore volume of these silica nanotubes was found to be higher than those of parent halloysite nanotubes by six and two times respectively. Impregnation with polyethenimine was found to facilitate higher CO₂ uptake capacity (around 2.75 mmol g⁻¹ at 85°C for two hours) in the mesoporous silica nanotubes. These polyethenimine bearing mesoporous silica nanotubes demonstrated rapid kinetics and improved stability even after ten recurrent cycles of adsorption-desorption. Authors claimed these nanotubes to be heat stable, ecofriendly, cost effective and highly efficient for CO₂ capture.

Metal Organic Frameworks

MOFs are microporous materials consisting of metal ions or metal clusters bearing organic ligands assembled in suitable solvents (Furukawa *et al.*, 2013; Qiu and Zhu, 2009). MOFs offer high surface areas as well as uniform pore features and are thus widely applied for chemical separation and catalysis (Chen *et al.*, 2010; Lee *et al.*, 2009). MOFs have also been previously investigated for CO₂ capture and clean energy storage. Recent studies have focused on developing novel materials with higher surface areas having enhanced gas loading abilities (Anbia and Hoseini, 2012; Sumida *et al.*, 2011; Xiang *et al.*, 2011). Such materials generally exhibit high sorption enthalpy that renders the same suitable for adsorption of gas molecules. Due to the presence of diverse metal centers

and functional ligands in structures of MOFs these materials are widely considered for development of novel composite materials having improved gas storage ability and properties differing from parent MOFs (Kang *et al.*, 2015).

Improvisation of MOF has been primarily achieved via catenation and interpenetration, enhancement of chemical bonding as well as involvement of electrostatic force (Liu *et al.*, 2012). In a study by Kang *et al.* (2015), adsorption enthalpy of MOF (JUC-32) was reportedly enhanced by composite formation with carboxyl-modified multi-wall carbon nanotubes. Results obtained in this study suggested that composite materials absorbed larger quantities of CO₂ and CH₄ with increased adsorption enthalpies in comparison to individual parent materials.

Other recent studies have also reported different strategies like multipoint interactions, partitioning of pore space, cooperative crystallization (in case of heterometallic MOFs), ion exchange, ligand exchange (post synthesis) and charge polarization, trapping of single molecules, encapsulation of ionic liquids, enhancement of local electric field, controlled morphology, interpenetration of partial framework, controlled co-adsorption of water, etc. for enhancing the capacity of CO₂ adsorption of MOFs (Yu *et al.*, 2017).

Nanoporous Polymers

Metal nanoparticles discussed previously have gained considerable focus owing to their potential utilization for conversion of energy, pollution remediation and catalysis (Kim *et al.*, 2013; Zaera, 2013). However, these nanoparticles tend to aggregate due to high surface energy and thereby suffer from loss of reactivity (Myers *et al.*, 2011). Previous studies have investigated immobilization of nanoparticles on MOFs for fabrication of catalytic systems having high selectivity and reactivity (Aijaz *et al.*, 2012; Roberts *et al.*, 2012; Saha *et al.*, 2013; Zhu *et al.*, 2013). However, reversibility of metal coordination of MOFs renders them unstable in different liquid-phase catalysis (Li *et al.*, 2015b). Recent reports have suggested porous organic polymers (POPs) as a suitable alternative to MOFs for immobilization of nanoparticles due to the similarity of both materials (Dalapati *et al.*, 2013; Hasell *et al.*, 2009; Zhou *et al.*, 2013). The catalytically active sites of POPs can be adjusted and altered with a broad range of organic and synthetic compounds for enhancing their catalytic potentials (Fang *et al.*, 2014; Suresh *et al.*, 2014). The porosity of POPs depends upon the method of POP synthesis as well as the geometry and size of constituting monomers and also influences the catalytic activity of the POPs (Smith and Dichtel, 2014; Wang *et al.*, 2013; Xu and Jiang, 2014). Recent studies have reported the incorporation of functional groups like triazolyl, imine, urea, etc. as linkages in POP for stabilization of immobilized metal ions and nanoparticles (Bhunia *et al.*, 2012; Du *et al.*, 2010; Li *et al.*, 2014).

In a recent study by Li *et al.* (2015b), researchers reported ultrafine palladium nanoparticles separately immobilized on two triazolyl functionalized POPs (CPP-C and CPP-Y) for hydrogenation of olefins. Results indicated good stabilization of immobilized palladium nanoparticles due to combined effect of entrapment in polymer matrix and coordination interaction with triazolyl groups.

In a separate study, Talapaneni *et al.* (2015) reported the confinement of N-heterocyclic carbenes (by virtue of steric interactions) in nanoporous polymer (NP-NHCs) and its subsequent application for CO₂ capture at room temperature. NP-NHCs exhibited highest CO₂ capture efficiency than any other solid carbene based material reported so far. The NP-NHC also demonstrated high activity and selectivity for formation of cyclic carbonates from CO₂. Moreover, results obtained in this study established the reported NP-NHC as a heterogeneous organocatalyst having good recyclability. The metal free integrated approach for CO₂ fixation and conversion reported by Talapaneni *et al.* (2015) was also found to be a novel cost effective approach for CO₂ capture.

Graphene Based Sorbents

A survey of existing literature revealed that carbonaceous materials like activated carbons and carbon nanotubes have already demonstrated promising CO₂ adsorption (Mishra and Ramaprabhu, 2011a; Pevida *et al.*, 2008). In comparison to other carbonaceous materials, graphene reportedly has cost-effective and feasible production procedures, greater surface area, mechanical strength, stability (both thermal and chemical) as well as recyclability and offers good tolerance to chemical alterations (Dai *et al.*, 2009; Ghosh *et al.*, 2008). Recent studies have reported chemically modified graphene to possess excellent CO₂ adsorption capacities (Chandra *et al.*, 2012; Mishra and Ramaprabhu, 2011b). Studies have also suggested deletion or substitution (with nitrogen bearing functional groups) of acidic groups present on the surface of carbonaceous materials for enhancing the CO₂ uptake efficiency of the adsorbent (Oh *et al.*, 2014; Zhao *et al.*, 2012).

In a recent study, Oh *et al.* (2014) have reported borane modified graphene-based sorbents (B-rG-O) for CO₂ adsorption. The B atoms are Lewis acid in nature and their electron deficiency reportedly demonstrate high affinity for the electron-rich O atoms present in CO₂ (Choi *et al.*, 2011). CO₂ adsorption capacity of the reported sorbent was found to be 1.82 mmol g⁻¹ under a pressure of 1 atm. Authors also reported that the charge distribution of the sorbent could be altered by introducing boron defects in the sorbent architecture. The carbon atoms neighboring this defect were found to exhibit improved selectivity towards CO₂.

Similar results were also reported by Sun *et al.* (2014) who had investigated CO₂, N₂, CH₄, and H₂ adsorption using amphoteric B₈₀ fullerene. Results obtained in this study indicated that CO₂ molecules strongly interacted with basic domains of B₈₀ via Lewis acid–base interactions. However, the other gases were found to develop only weak interactions with B₈₀ fullerene. Thus, results suggested that B₈₀ fullerene could be effectively used to separate CO₂ from a mixture of gases.

In a separate study, Mishra and Ramaprabhu (2014) reported Fe₃O₄ decorated graphene nanocomposite for CO₂ capture. The composite reported in this study demonstrated good CO₂ uptake even under conditions of elevated pressure and temperature where graphene usually undergo desorption of adsorbed gases. Adsorption of CO₂ by this composite was chemisorption in nature which in turn promoted higher CO₂ uptake.

Monolayer Boron Nitride

In recent studies, novel hexagonal boron nitride (h-BN) occurring as monolayers has been considered as an alternative to graphene due to similar properties like high stability (both chemical and thermal) and conductivity that rendered the same suitable for catalytic activity (Guo *et al.*, 2015). Owing to the intrinsic iconicity of B–N bonds and high specific surface areas, h-BN sheets are being investigated for separation and storage of gases. According to the results obtained by Guo *et al.* (2015), h-BN sheets can efficiently separate and capture CO₂ from a mixture of H₂, CH₄, N₂, CO, and H₂O in presence of a vertical electric field. In absence of the electric field, h-BN sheets are unable to capture CO₂ due to reduced binding energy and loss of entropy. Hence, it could be concluded that h-BN sheets hold potential for application in field controlled separation and storage of CO₂.

Ionic Liquids

Recent studies have contributed significant attention to imbibition and stabilization of ionic liquids (IL) within channels of different porous substrate for purposes of catalysis and separation (Kasahara *et al.*, 2014; Ramdin *et al.*, 2012; Steinrück *et al.*, 2011). The IL-modified pore structure of supported IL phase materials (SILPs) and membranes (SILMs) are tailored according to their application type (catalytic or separation) (Romanos *et al.*, 2014). Use of nanoporous materials as supports for IL reportedly provides high surface area and stabilizes the IL phase entrapped in the nanopores. For achieving simultaneous dispersion of catalysts and adsorption of gases, the layer of the catalyst bearing the IL phase should be kept as thin as possible for ensuring that the gas reactants are able to access the whole IL surface while passing through the pores. Leaving the core space of nanopores open in SILPs is found to lead to reduced absorption specificity whereas complete pore filling is known to result in diffusivity. Besides nanoporous materials with ordered pore structure (like nanotubes, mesoporous silicas, zeolites, etc.) are rather expensive. Those having complex pore architecture exhibit high tortuosity which in turn hinders efficient gas absorption (Romanos *et al.*, 2014). Romanos *et al.* (2014) have reported “inverse” SILPs in their study whereby micro IL droplets are enveloped by silica nanoparticles. These inverse SILPs were found to demonstrate efficient separation of a mixture bearing CO₂ and N₂. These inverse SILPs were capable of 1.5–3.0 mmol g^{−1} CO₂ absorption under pressure and temperature conditions of 1 bar and 40°C respectively. The kinetics of CO₂ absorption was found to be higher for inverse SILPs in comparison to contemporary conventional SILPs. The significant aspects of these inverse SILPs included convenient handling, reduced cost as well as high CO₂ separation efficiency and absorption capacity. The stability of these inverse SILPs at high temperature and pressure indicated its applicability on an industrial scale for treatment of real flue gas. Moreover these inverse SILPs were completely regenerated at 60°C without any structural alteration.

Nano-Biocatalysts for CO₂ Sequestration

Recent studies have proposed novel methods for CO₂ reduction of which biomimetic CO₂ capture has been considered as one of the most promising approaches due to its low cost and green nature (Jo *et al.*, 2014). In a recent study, Jo *et al.* (2014) reported a biosilica encapsulated carbonic anhydrase biocatalyst for application in environmental CO₂ capture. No leaching of the enzyme was recorded from the biosilica matrix thereby confirming the efficiency of the process. Besides good reusability, these biocatalysts demonstrated good thermostability by withholding 80% of its activity after being stored at 50°C for five days. This biocatalyst exhibited highly compact morphology with low surface area while its outermost surface performed catalytic activities. This biocatalyst was found to exhibit a maximum of almost 60% of CO₂ capturing efficiency of that demonstrated by the free enzyme. Therefore, results obtained in this study suggested that the biocatalysts reported herein could be successfully investigated for biomimetic capture and storage of the CO₂.

In another recent study, Liu *et al.* (2015) reported an artificial process simulating the scheme of photosynthesis facilitating reduction of CO₂ for formation of various biochemical products. In this study, a biocompatible nanowire array capable of capturing light was developed that supported direct interaction with microbial systems. This hybrid semiconductor was investigated for reduction of CO₂ to form different end products like fuels, polymers, pharmaceutical precursors, etc. with only consumption of solar energy. The silicon nanowire array used in this study provided high surface area for trapping light energy required for providing reducing equivalents to *Sporomusa ovate*, an anaerobic bacterium, in order to achieve acetic acid produced photoelectrochemically under aerobic conditions. The acetate so produced was activated to yield acetyl coenzyme A using genetically modified *Escherichia coli* for synthesis of value-added products like n-butanol, polyhydroxybutyrate, and three different isoprenoids. Development of such a biocompatible nanodevice supporting living cells paved the path for designing a programmable system for chemical production entirely powered by solar energy. Results obtained in this study also established a process of

conversion of solar power by integrating nanoscale semiconductors with bacterial biocatalysts. Primary advantages of this device included improved oxygen tolerance, direct utilization of exhaust gas in the system and efficient CO₂ sequestration in nano-wire – bacteria hybrid. Furthermore, this modular design facilitated the synthesis of various molecular targets by a simple integrated system without any changes in the setup used for capturing solar energy and reduction of CO₂ to acetate by altering only the specie of microorganism present downstream.

Conclusion

An efficient adsorbent forms a vital part of almost all CCS technologies developed for separation of CO₂ from pre/post combustion sources like fossil fuels and flue gas respectively. Recent research has devoted significant attention for fabrication of efficient adsorbents having enhanced capacity, stability as well as recyclability. Owing to their high specific surface area, porosity and stability, different nanoporous materials have been investigated for their CCS efficiencies. The present review has covered both advantages and limitations of different nanoporous catalysts reported in the recent decade for their carbon capture efficiency. The nanomaterials discussed in this review may be implemented as sorbents, membranes or molecular sieves for CCS. Biocatalytic conversion of CO₂ for yielding valuable byproducts has also been discussed in this study. The biomimetic carbon capture and utilization technologies discussed in this review was completely devoid of any significant hazard related to CO₂ storage and also provided an opportunity to recover a part of the cost incurred for maintenance of the proposed device by producing value added products. In spite of all endeavors, technologies for carbon capture and storage/utilization are still reckoned as temporary solutions for managing the ever increasing discharge of CO₂ in the environment. In the long run the human thirst for energy has to be satiated by alternative energies instead of fossil fuels. Sources of energy like solar power, wind power, tidal power, hydropower, etc. are considered as potential alternatives of fossil fuel but necessitate caution prior to rapid implementation on wide scale in order to avoid any unforeseen detrimental and significantly irreversible effects. Nevertheless, current technologies for CCS and utilization play a vital role in remediating current environmental conditions till scientists develop novel efficient technologies for generating power with reduced carbon consumption. The nanomaterials discussed in this study may be considered as the most recent and efficient technology for addressing and arresting anthropogenic climate change.

See also: Overview of CCS: A Strategy of Meeting CO₂ Emission Targets

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Nanomaterials for Alternative Energy

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Introduction

From the dawn of civilization, energy has been the sole reason for creating the trajectory of advancement and innovation of the human race. Since 1000 BCE fossil fuels have served as the citadel for civilization and industrialization consecutively. The earth had enough natural fuel reserves to cater to our needs all these centuries but the rapid growth of population and the modern industrial revolution since the past few centuries have cumulatively questioned the sustainability of the natural reserves.

Present studies according to the World Coal Association have given an estimate of 1.1 trillion tonnes of proven coal reserves worldwide. The implication being that the coal reserve can last us around 150 years at current rates of production and consumption. Whereas the world is left with meager 53.3 years to find an alternative to oil and natural gas before the proved reserves run dry according to British Petroleum. Inevitably, the nations are excavating for new reserves and scouting for new methods, but the cost-effectiveness is an elephant in the room. Necessity being the mother of invention has led to the discovery and experimentation of using renewable sources of energy in the form of solar, wind, wave, hydrogen, geothermal etc. to balance the demand-supply ratio. Given the present trends of research in the field of renewable energy, it is expected that almost 50% of the world's energy demands will be satisfied with the aid of green energy by 2040. Moreover, almost 70% of the reduction of excess greenhouse gases can be achieved with this target.

Nanoscience and nanotechnology with their vast and diverse applications have been another rapidly growing area of research and in fact, have shown promising results in experimentations on renewable energy. Nanoparticles being in the size range of <100 nm have a vast impact on the fabrication and utility due to their reduced size. The most notable effects being:

- (1) Lower consumption and dissipation of energy due to a smaller size.
- (2) Ease of synthesis in large quantity.
- (3) Enhanced capability of energy storage.
- (4) Clean and green technology with significantly less waste generated.
- (5) Faster production and easy disposability.

The incorporation of nanotechnology in the alternative forms of energy has improved the efficiency of generation and durability quite remarkably. For example, the use of nanoparticles in solar cells have improved the capacity for energy storage and retainability. The use of nanoparticles adds to the lightness of the rotor blades, hence increasing the efficiency of wind energy generation. Nano-coatings on the surface of the tidal energy generating equipment results in significant corrosion resistance whereas the infusion of nanocomposites in manufacturing drilling machines for the geothermal energy has resulted in an increase of the life-span of machines. Moreover, nanotechnology also paved a path for controlled growth of biomass with proper shielding against the danger of pest and hence creating an increased number of plants for biofuel extraction. This article aims to provide an insight into the diversified applications and impact of nanoscience and nanotechnology in the field of renewable energy generation.

Applications of Nanotechnology in the Energy Sector

Solar Energy Sector

Studies show that the surface of the earth receives about 124 EXA (10^{18}) Watts or 3850 Zetta (10^{24}) Joules of solar power annually (Chapin *et al.*, 1954). The range of solar power spectrum varies from 250 nm to about 2500 nm in wavelength. The chief usage of solar energy is the derivation of electrical energy from it. The two primary methods for the conversion of solar energy to electrical energy are concentrating the solar power by reflectors and using photovoltaic cells.

Nanotechnology is the future of fabricating more efficient and low-cost systems to generate, store and transport energy. Nanoscale level synthesis and designs combined with thin films offer economical solutions to the otherwise sophisticated methods of hydrogen production, photovoltaics, fuel cells, solar thermal systems etc. The solar economy comprises of the various ways by which the solar energy can be used, for example, in PV (photovoltaic) technology for conversion of light to electricity directly, solar collectors, artificial photosynthesis for producing carbohydrates and hydrogen by the water-splitting method, Biomass technology for generating complex carbohydrates to generate biofuels etc (Bailey, 1972).

The photoelectric effect is the principle behind the production of electricity by PV cells. Presently, silicon wafer-based solar cells (thick cells of around 150–300 nm made of crystalline silicon) is the prime available type in the real world. This technology, coined as the first-generation photovoltaic cell, accounts for more than 86% of the global solar cell market. The second-generation

of photovoltaic materials is primarily based on the inculcation of thin film layers (1–2 nm) of semiconductor materials. Nano-crystal quantum dots, which are nanoparticles made of direct bandgap semiconductors serves as the basis to thin film solar cells on silicon or conductive transparent oxide (CTO), such as indium-tin-oxide (ITO) substrate with nanocrystal coating. Photo-catalyzed decomposition of pollutants at various titania surfaces is also of great interest to the present scientists. Electron transfer reactions are the governing factors for these photoinduced processes and hence also the subject of one of the theoretical contributions for the next generation solar cells. Harvesting of light photons in a semiconductor (most commonly TiO_2) and subsequent conversion of these photons to electronic excitations is the typical scheme of photocatalysis which then induces the desired chemical reaction on the semiconductor surface.

The major benefits of incorporating nanotechnology for manufacturing solar cells are:

- (1) Reduction of manufacturing costs of conventional solar cells made of crystalline semiconductor material due to the implementation of low-temperature processes similar to the novel technique of high-temperature vacuum deposition printing.
- (2) Reduction in the installation cost with the aid nanotechnology since it fosters the manufacturing of flexible rolls instead of rigid crystal panels.

Solar Cell Structures and Infusion of Nanoparticles

P-N junction solar cells

The solar spectrum comprises of photons with energies ranging from about 0.5–3.5 eV. Conventional solar-cell technology or the first-generation solar cell generation is based on a single p–n junction that is utilizing one electron-hole pair for each absorbed photon. Electron-hole pairs are generated when light quanta are absorbed and they can reach the junction if their recombination is prevented, where they are separated by an electric field. Large crystals of silicon, or thin films of amorphous silicon, cadmium telluride or copper indium gallium selenide etc. are the chief components of the current photovoltaic technologies. A large part of the solar spectrum is absorbed by the semiconductor material determined by its band gap. For instance, amorphous silicon has a higher bandgap (1.7 eV) than crystalline silicon (1.1 eV), which implies the absorbance of the visible part of the solar spectrum more strongly than the infrared portion of the spectrum (Corkish *et al.*, 2002; Miskovsky *et al.*, 2012).

The p–n junction solar cells based on crystalline silicon currently achieve an efficiency of 22% approximately (Conibeer, 2007; Goetzberger *et al.*, 2003). According to the Shockley–Queisser limit, the maximum thermodynamic efficiency for single bandgap devices, assuming detailed balance is 31% (Shockley and Queisser, 1961). It is obvious that one can improve the efficiency by layering materials with different bandgaps. This is the underlying idea of the multi-layer ‘tandem’ cells, which are highly efficient, but very expensive (Conibeer, 2007). The energy conversion efficiency of solar cells based on bulk silicon is higher than that of thin-film silicon.

These limitations have been countered by employing light-trapping techniques (Goetzberger *et al.*, 2003). The incoming light is obliquely coupled into the silicon film and the absorption is increased multiple folds as the light is made to traverse the film several times (Goetzberger *et al.*, 2003). The thermodynamic limit on light trapping determines the minimum thickness of the material for fabricating the film (Yablonovitch, 1982). However, recent findings reveal that in principle, any semiconductor material can exceed the light-trapping limit if the local density of optical states (LDOS) of its absorbing layer is greater than the LDOS of the bulk semiconductor material (Callahan *et al.*, 2012). This may potentially allow for designing novel solar cells that are approximately 10 nm thick but can absorb light from the entire solar spectrum (Callahan *et al.*, 2012).

Utilization of the electric field effect provides another method to create the p–n junctions in semiconductors, where the application of an electric field alters the concentration of charge carriers (Regan *et al.*, 2012). The major factors that limit the efficiency of conversion are the inability to absorb photons with energy level lower than the bandgap, thermalization of photon energies exceeding the bandgap and the recombination losses due to radiation (Conibeer, 2007). The approaches to counter the loss of efficiency can be attributed as:

- (1) To increase the number of energy levels by stacking of multiple p–n junctions in different semiconductor materials resulting in the absorbance of higher-energy photons in the higher-bandgap semiconductors and lower-energy photons in the lower-bandgap semiconductor (Regan *et al.*, 2012).
- (2) To capture the carriers before thermalization hence yielding a higher photovoltage.
- (3) Multiple-carrier-pair generation per high-energy photon or single-carrier-pair generation with multiple low-energy photons, leading to the enhancement of the photocurrent.

Intermediate-band solar cells (IBSCs)

The main concept behind IBSCs is to introduce one or more energy levels within the bandgap so that they can absorb photons in parallel with the normal operation of a single-bandgap cell (Conibeer, 2007; Luque *et al.*, 2012; Luque and Martí, 2011, 1997; Lopez *et al.*, 2011). The transitions from the valence band (VB) to the intermediate band (IB) and from the IB to the conduction band (CB) result in the absorbance of the sub-bandgap energy photons, thus enabling IBSCs to achieve both high current and high voltage. To enable absorption from the VB into the empty states of the IB, the IB has to be partially occupied and from occupied states of the IB to the CB [811]. To preserve the high output voltage of the cell, the Fermi level is split into three separate quasi-Fermi levels (Luque *et al.*, 2012).

The theoretical limiting efficiency of IBSC is calculated to be 63%, derived at isotropic sunlight illumination and assuming the temperatures of the Sun and Earth to be 6000 K and 300 K, respectively (Luque and Marti, 1997). The maximum efficiency of a single-gap solar cell was 41% under the same conditions (Luque and Marti, 1997). The research on finding optimal sub-bandgap absorbers has been concentrated on alloys that naturally exhibit an IB and nanostructures, in particular, arrays of quantum dots (QDs) that form an IB (Luque *et al.*, 2012; Luque and Marti, 2011; Palacios *et al.*, 2008).

To exhibit three electronically isolated energy bands, the electronic band structure of highly mismatched semiconductor alloys can be tuned both experimentally and theoretically (Luque and Marti, 2011). By substituting a relatively small fraction of host atoms with an element of very different electronegativity, this can be achieved in the highly mismatched alloys. For example; III-V and II-VI alloys, in which group V and VI anions are replaced with the isovalent N and O, respectively (Yu *et al.*, 2003, 2006). The interaction between localized states associated with N or O atoms and the extended states of the host semiconductor matrix determine the electronic structure of such alloys. As a result, the conduction band gets subdivided into two sub-bands with clear non-parabolic dispersion relations, thus changing the optical and electrical properties of these alloys (Yu *et al.*, 2003). If the localized states lie well below the conduction band edge, only then a narrow lower band can be formed (Yu *et al.*, 2006). Consequently, by adding two new absorption edges, the absorption spectrum is modified, which can be tuned to lie within the spectrum of solar energy. Experimental examples include the IB formation within the bandgap of highly mismatched semiconductor alloys, for instance, $\text{Zn}_{1-y}\text{Mn}_y\text{O}_x\text{Te}_{1-x}$ and $\text{GaN}_x\text{As}_{1-x-y}\text{Py}$ (Yu *et al.*, 2003, 2006).

Spectral photoreflectance measurements detected the IB and its formation was attributed to band anti-crossing. Blocking layers were incorporated in order to obstruct electron tunneling between the IB and CB, and hence maintaining a high open-circuit voltage. From theoretical and computational perspectives, various calculations have been performed in the search for optimal IB materials. The most promising discovery of the quest has been $\text{V}_{0.25}\text{In}_{1.75}\text{S}_3$, because of its strong sub-bandgap absorption and the inherent partially filled IB. This implies that the IB is already partially filled without the necessity to rely on impurity doping, thus reducing densities and consequently lowering the absorption levels (Palacios *et al.*, 2008). Bulk IBSCs have so far exhibited efficiencies way below their promised potential, and the issue of finding the best candidate materials for this technology is extremely crucial if IBSC research is to be introduced to the mainstream solar cell generation.

Quantum dot IBSCs

From the confined states of QDs situated within the bandgap of a host semiconductor, an IB can also be formed. To enable the strong wave function overlap and the formation of minibands, QDs should be closely spaced and with high-quality interfaces. A high concentration of QDs is required to achieve strong absorption to and from IB. By engineering the parameters such as QD geometry (size and shape), inter-dot separation, and dot arrangement, IB position and width can be optimized for achieving the maximum efficiency (Shao *et al.*, 2007; Levy *et al.*, 2005; Laghumavarapu *et al.*, 2007). Typically, self-assembled (In, Ga) As QDs embedded in a GaAs matrix have been used as an IB (Luque *et al.*, 2012; Suraprapich *et al.*, 2006). Interestingly, features of IBSC operation have been demonstrated by some of these devices, and have achieved efficiencies over 18% (Luque *et al.*, 2012; Blokhin *et al.*, 2009).

Self-assembled QDs consist of approximately 10^4 – 10^6 atoms of a semiconductor such as (In, Ga) As embedded in another semiconductor matrix GaAs. They are synthesized by the Stranski–Krastanov (SK) growth mode, which uses the principle of natural lattice mismatch between the substrate and the deposited material (Shchukin and Bimberg, 1999; Shchukin *et al.*, 2003). The strain intensity in the layer as related to the misfit of the lattice constants, the temperature at which the growth occurs, and the growth rate are the contributing factors for the shape and average size of the QDs. The island emerges to the state of quasi-equilibrium in which they take the shape of pyramids or lenses formed on a thin wetting layer and then capped by the barrier material. The main advantages of the SK growth mode are a synthesis of defect-free QDs of small sizes, homogeneous sizes, and shapes of QDs, the formation of ordered uniform arrays of 3D coherent islands and quite convenient growth processes (Shchukin and Bimberg, 1999; Shchukin *et al.*, 2003). Their structural perfectness (absence of impurities, dislocations, and defects), the remarkable isolation from the environment and the ability to charge the system with a few electrons or holes (multiexcitons), have made them important in studying the arena of particle physics in confined spaces (Mlinar *et al.*, 2009; Mlinar and Zunger, 2009). In self-assembled QDs the multiexcitons survive and decay radiatively unlike colloidal QDs, where nonradiative decay channels rapidly destroy multiexcitons and cause blinking in photoluminescence (Efros and Rosen, 1997; Wang *et al.*, 2009). The self-assembled QDs are not influenced by the photo-corrosion and photostability of colloidal QDs, where QDs stability depends on the solution (e.g., it was found that CdS QDs in nonpolar solvent were significantly stable even under UV light exposition) (Sato *et al.*, 2007) (Fig. 1).

Some measure of homogeneity must exist between the successive quantum dot layers in order to create a mini-band. However, the number of QD layers are limited as a consequence of strain accumulation which in turn leads to the prevention information of quantum dots (Mlinar and Peeters, 2007a, 2006, 2007b). The strain symmetrization within the structure can help to lift the strain-induced limit of the number of QD layers. It was found that, even if the number of QD layers were increased, the absorption intensity between QD-confined electron states and the host CB remained weak because of their localized-to-delocalized character and the position of the IB within the matrix bandgap could not satisfy the suitable energetic locations for the IB (Popescu *et al.*, 2008).

Furthermore, the loss of output voltage at room temperature compared to reference solar cells without an IB has been one of the major challenges in the QD IBSC design (Luque *et al.*, 2012). The thermal escape of electrons from the IB to the CB (in addition to the tunneling of electrons from the IB to the CB) is the primary reason for the loss of voltage at room temperature (Luque *et al.*, 2012; Luque and Marti, 2011).

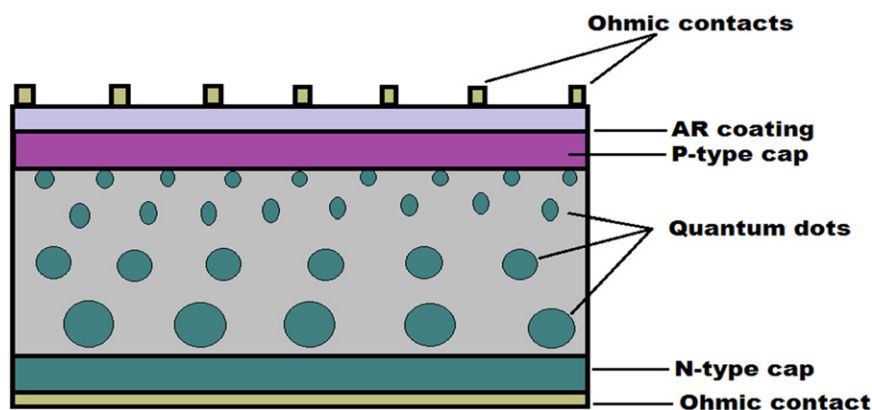


Fig. 1 Schematic diagram of a quantum dot intermediate band solar cell.

Thus, from a fundamental point of view, a better understanding of the nature of the IB (localized versus extended), and carrier relaxation processes is necessary for further exploration. From a purely technological perspective, the research for advanced fabrication techniques and more optimal materials (strain symmetrization and strong absorption between the IB and CB) is at the budding stage and has a lot of room for growth and development. As an insight into the sensitivity of the problem, significant elimination of output-voltage reduction was achieved by careful fabrication of InAs/GaAs IBSCs, potentially opening pathways for room temperature IBSCs (Bailey *et al.*, 2011).

Multiple exciton generation solar cells

The generation of more than one electron-hole pair (exciton) by absorption of one photon is known as Multiple exciton generations (MEG) or carrier multiplication (Nair *et al.*, 2011; Pijpers *et al.*, 2009; Beard *et al.*, 2010). Through a scattering process, known as impact ionization (the inverse of Auger recombination), high-energy photons, at least twice the bandgap energy, absorbed in a bulk semiconductor can generate one or more additional electron-hole pairs close to the bandgap energy (Conibeer, 2007; Nair *et al.*, 2011; Pijpers *et al.*, 2009; Beard *et al.*, 2010). Previously bulk Si, PbS, PbSe, Ge, InSb, etc., exhibited the impact ionization. Since the rate of impact ionization is much slower than the rate of radiative recombination at low electron energies (in visible and near IR spectrum) and the necessity to conserve momentum, this effect is inefficient in bulk concentration. In addition, as the required photon energies lie outside the solar spectrum (3.5 eV) the impact ionization in bulk is not useful for energy conversion purposes; for e.g., it requires approximately 7 eV photons to produce one extra carrier in silicon (Conibeer, 2007; Nair *et al.*, 2011; Semonin *et al.*, 2011).

Thus, it was proposed that MEG can be more efficient in semiconducting nanocrystals (Nozik, 2002; McGuire *et al.*, 2008). It was suggested that the relaxation dynamics of photogenerated carriers may be affected by quantization effects given the unique electronic structure properties of nanocrystals—atomic-like electronic structure and size-dependent bandgap energies, and thus lead to more efficient solar cells (Mlinar and Zunger, 2009; McGuire *et al.*, 2008). For example, hot carrier cooling rates of impact ionization could become competitive with the rate of carrier cooling (Conibeer, 2007; Ellingson *et al.*, 2005).

Numerous experiments have affirmed the existence of MEG in nanocrystals (although not undisputedly) by revealing that excitation of a semiconductor nanocrystal by a single, high-energy photon which may result in the formation of a few electron-hole pairs (Conibeer, 2007; Semonin *et al.*, 2011; Nozik, 2002, 2008; McGuire *et al.*, 2008; Ellingson *et al.*, 2005; Beard and Ellingson, 2008; Nair *et al.*, 2008; Ji *et al.*, 2009). The generation of multiple excitons from a single photon occurs on a very short time scale following photon absorption, where the efficiency increases with the energy of the photon (Fig. 2).

The number of excitons generated by absorption of a photon is defined by the efficiency " η " (Nair *et al.*, 2011; Beard *et al.*, 2010). Using the detailed balance model under the assumptions that all photons with energies above the bandgap were absorbed and those with energies less than the bandgap were not absorbed, that the only loss is the radiative recombination and that all photogenerated carriers are collected, the calculations are done (Beard *et al.*, 2010).

The ultrafast transient absorption spectroscopy is used to determine the number of electron-hole pairs produced per absorbed photon in a typical MEG experiment. Samples are irradiated with a low-intensity beam of high-energy photons, and the dynamics of multiexciton decay versus single exciton decay are measured. If a fast component with a lifetime same as that of a multiexciton lifetime is observed along with exciton decay, it is attributed to multiexciton. However, the existence of MEG artifacts can give 'false positive' signatures of MEG (Nair *et al.*, 2011). For example, due to the opening of nonradiative channels, the single exciton decay can acquire a fast component, e.g., electron or hole traps in a nanocrystal surface.

Furthermore, the role of quantum confinement for MEG has garnered certain disagreements and disputes. Interpretations ranging from those stating that the efficiency of MEG of the PbSe nanocrystal is about twice the efficiency observed in bulk PbSe to those stating that the advantage of nanocrystal MEG is only due to a possibly larger photovoltage because of the quantum confinement (Nair *et al.*, 2011; Beard *et al.*, 2010; Semonin *et al.*, 2011). Finally, there is also an issue of the impact that MEG can have on solar energy conversion.

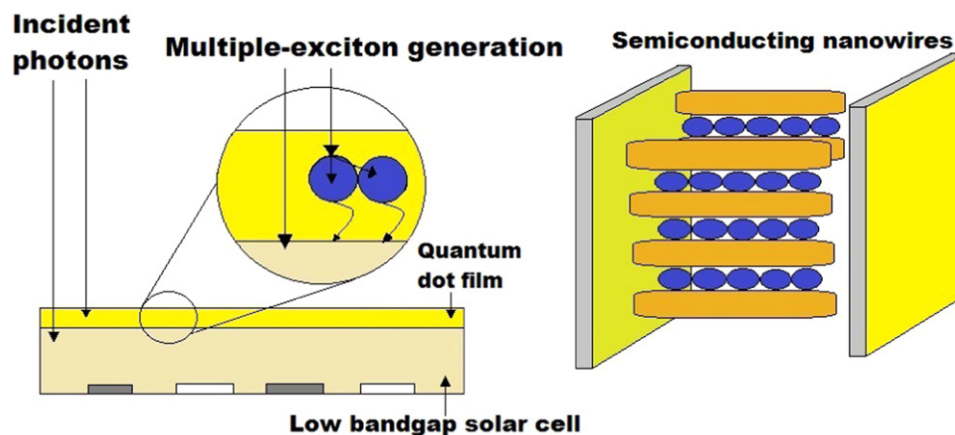


Fig. 2 Development of a multiple exciton generation solar cell by using nanowires.

Theoretical studies related to the basic mechanisms of MEG gives ambiguous results. Theoretical models giving explanations of MEG ranging from a coherent superposition of single and multiple exciton states to excitations of virtual multiexciton states is still a matter of further delving into advanced research (Brown, 1970; Service, 2004). Additional constraints on the set of initial parameters are required in order to distinguish between different interpretations. The set of primary parameters include the coupling strength between excitons and multiexcitons, decay rates and density of states (Semonin *et al.*, 2011; Mlinar, 2012). This is yet to be addressed and resolved.

Hydrogen Economy

The predominantly identified renewable sources of energy available in nature, such as solar, wind, geothermal or tidal need to be converted to some other form of energy preferably electricity and transported from one place to other. Whereas, hydrogen needs to be generated and itself acts as both energy as well as a medium of transporting and storing energy. Hydrogen can be synthesized from renewable sources of energy and can be converted into electricity mainly using fuel cell technology with much ease. All these reasons attribute hydrogen, like any other fuel, to be considered a developing arena for energy studies and hence can claim to be the pivotal point of developing an economy.

One of the most promising and optimistic characteristic features of hydrogen is that the only product of its combustion is water. The production of hydrogen from renewable energies with its use in fuel cells combining with the utilization of the product of its combustion makes hydrogen a perfect candidate for leading the sustainable greener economy.

Hydrogen Production

Though hydrogen production, storage, and transformation into electricity have been ongoing since decades, we are still lacking efficient economical techniques to use this light gas in such a way that it makes the future hydrogen economy viable and relevant for commercialization. Being a vector than just a source, hydrogen is as clean as the way used to produce it. At present, the maximum production of hydrogen globally is done by steam reforming of natural gas (Service, 2004). Though this method has an efficiency ranging from 7%–80% but the production of CO₂ is a huge setback. Because of its inexpensive nature, it is speculated that this process will account for the bulk of hydrogen for the next 30–50 years until more cost-effective sustainable solutions are developed and implemented successfully.

Clean and sustainable electricity can be provided by renewable energy sources such as photovoltaic, wind, biomass, hydrothermal, and geothermal energies. However, these renewable energy sources, predominantly water electrolysis account for only around 5% of the commercial hydrogen production (Serrano *et al.*, 2009). In spite of the efficiency ranging higher than 70%, consumption of a significant amount of electricity, which inadvertently increases the costs is the prime reason for the absence of its commercialization.

The future of hydrogen production is its direct production from renewable sources avoiding electrical, heat and mechanical losses in a cost-effective manner. These include solar, thermal, wind energy, thermochemical cycles or biomass gasification and proton exchange membrane fuel cells. Apart from these, water splitting by Nano-photocatalysis one of the most promising alternatives for direct hydrogen generation via a renewable energy source in an economical and environmentally friendly manner (Züttel *et al.*, 2002). Unfortunately, according to the Royal Society of Chemistry report; new, clean and sustainable new pathways for the replacement of hydrocarbon-based hydrogen production processes are not expected before the year 2035.

Hydrogen Transport and Storage

Most of the presently available hydrogen storage systems are quite inefficient. For example, pressure vessels for the storage of hydrogen are not efficient enough as pressurized gas is bulky and heavy, low-temperature requirements of hydrogen storage in a

liquid state, the gravimetric storage density is low, etc. These disadvantages of transport and storage thus result in the loss of a great part of the energy produced. According to the Department of Energy of the United State of America, the threshold for a sustainable hydrogen storage system is a gravimetric storage density of 6.5 wt% and 62 kg H₂/m³ (Serrano *et al.*, 2009).

For the above-mentioned reasons, extensive research is being carried out to increase the capacity of existing hydrogen storage systems cumulatively with the aim to develop in parallel good hydrogen transport devices. Presently, hydrogen adsorption (chemisorption or physisorption) is considered to be one of the most efficient and sustainable ways to store a light gas like hydrogen.

The main drawback of Chemisorption techniques is binding hydrogen too tightly. Along with this, for discharge, the storage system must operate above ambient temperatures (>400K), while recharge is highly exothermic in nature. On the contrary, most physisorption techniques suffer from the reverse problem where significant adsorption can only be achieved at very low temperatures (<100K).

The use of activated carbon materials for hydrogen storage testing several carbon structures at cryogenic temperatures was suggested by Carpetis and Peschka (1980, 1976). Since then, these materials have been the subject of experimentation in the past decades. The wide pore size distribution and their inadequate pore size, which allows very small storage efficiency as most of the pores present higher sizes than those corresponding to hydrogen atoms or molecules are the main limitations (Schwartz and Amankwah, 1993; Dillon and Heben, 2001). Values of around 48 g H₂ per kg of carbon at 186°C under a pressure of 6 MPa have been reported (Schulz *et al.*, 1999). In both cases of chemisorption as well as physisorption, hydrogen adsorption kinetics can be improved by reducing the size of the adsorbing material to the nanosize range (Schwartz and Amankwah, 1993; Dillon and Heben, 2001; Schulz *et al.*, 1999).

Controlled pore size, shape and architecture and large surface areas, in many cases, in excess of 1000 m²/g are exhibited by mesoporous materials. In this manner, high adsorption capacities of hydrogen can be obtained by using nanomaterials that meet the criteria of high surface area, optimized pore size, and shape, high storage capacity, controlled desorption, and safety.

The physisorption of hydrogen on activated carbon with a controlled pore size distribution and the right surface chemistry is one of the novel alternatives to efficiently store hydrogen. Other alternate techniques to activate carbon involve various nanostructures such as carbon nanotubes, graphite nanofibers, and zeolites, to name a few (Züttel *et al.*, 2002; Schimmel *et al.*, 2003). Carbon nanotubes both multi-wall (MWCNT) and single-wall (SWCNT) carbon nanotubes have been suggested as potential candidates for efficient and economical hydrogen storage (Dresselhaus *et al.*, 1999; Hao *et al.*, 2003; Pinkerton *et al.*, 2000; Liu *et al.*, 2003; Shaijumon and Ramaprabhu, 2003).

Research findings of hydrogen adsorption by using SWCNT was first published dating back to 1998 and it was reported by Ye *et al.* (1999). The effect of the synthesis procedure by comparing laser-generated with those purified were analyzed by the authors. To describe these processes, various mechanisms of both physisorption and chemisorption of hydrogen on nanotubes have been suggested (Dai *et al.*, 2002; Gundiah *et al.*, 2003; Gao *et al.*, 2001; Zhang *et al.*, 2002). Nilsson *et al.* successfully reported the hydrogenation of single-walled carbon nanotubes (SWCNTs) using atomic hydrogen as the hydrogenation agent (Nikitin *et al.*, 2008). These authors have inferred that the nanotube diameter plays a key role in the maximal degree of nanotube hydrogenation. Nanotube-hydrogen complexes with close to 100% hydrogenation exist for approximately 2.0 nm diameter values and are stable at room temperature. This corresponds to 7 wt% of hydrogen storage capacity, which is higher than the one proposed as the goal for 2010 by the U.S. DOE (Serrano *et al.*, 2009). In a few years, other carbon materials, like graphite particles, have also been proposed as materials with great potential for hydrogen storage (Serrano *et al.*, 2009) (Fig. 3).

For hydrogen storage both at room temperature and cryogenic conditions and at different pressures, both zeolites and mesoporous materials with various nanostructures, have been tried as adsorbents. Their storage capacities being still too low

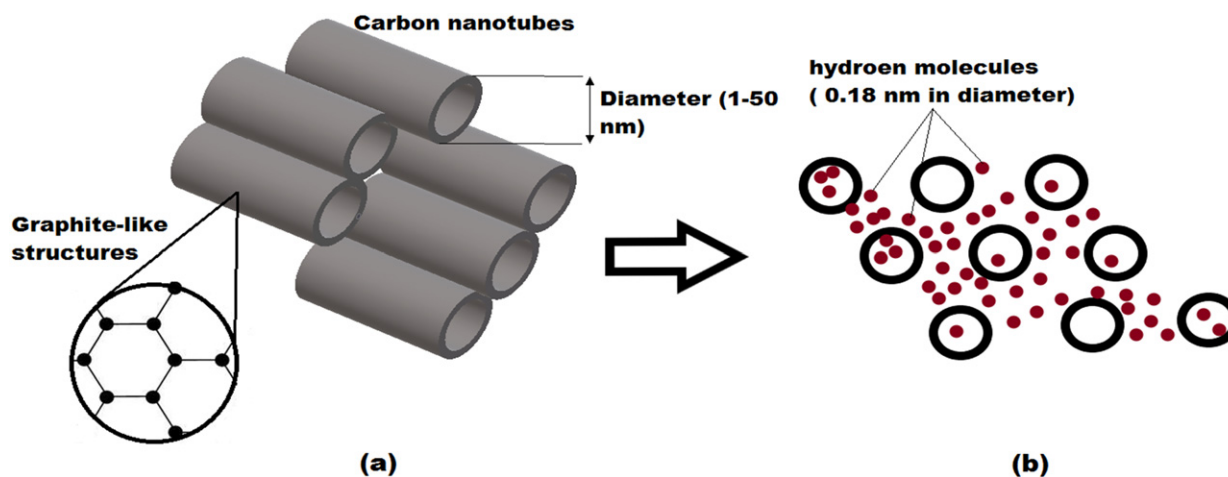


Fig. 3 (a) Structure of Carbon nanotubes. (b) Storage of hydrogen molecules in CNT.

(1.6 wt% at 77K at 36 bar in MCM-41), yet the inclusion of metal oxide dopants and incorporation of organic groups in the silica walls (organo-silicas) have a positive effect to increase the hydrogen storage capacity of these materials (Ramachandran *et al.*, 2007; Sheppard and Buckley, 2008; Jung *et al.*, 2006; García-Martínez *et al.*, 2007; Danilov *et al.*, 2008).

More efficient hydrogen adsorbents can be obtained with the aid of new mesoporous materials with hierarchical structures and controlled pore size. The use of biomolecules to produce bio-inspired porous silica is one of the most promising alternatives. For example, radically new hierarchical nanostructure with concentrically arranged pores assembled in a hexagonal array is produced by the addition of lecithin to a conventional synthesis of MCM-41 (García-Martínez *et al.*, 2007).

Noteworthy, Danilov *et al.* (2008) have recently synthesized porous carbon nanofibers proving its ability to efficiently store hydrogen. Thus, it can now be successfully treated as an alternative to hydride metals for its use in batteries. Nanofibers showed a surface area of 1700 m²/g after activation with KOH. Further modification and developments of the activated nanofibers enhance the discharge characteristics of the negative electrode. Moreover, through the modification of highly porous carbon nanofibers (surface area of 2000 m²/g) with Ni nanoparticles, nanomaterials with high hydrogen storage capacities were obtained by Kim and Park (2007).

Currently, a lot of attention is given to other hybrid materials based on coordination polymers, known as metal-organic frameworks (MOF) which are used as scaffolds for metals. These are being proposed as highly efficient hydrogen storage materials (Collins and Zho, 2007).

Metal or alloy hydrides are potential candidates to replace the more conventional methods for hydrogen storage (cryogenic liquid, compressed gas, and metal hydrides) taking into account both safety and cost. In these systems, the lattice of the metals or the alloys contain the hydrogen atoms thus achieving a storage capacity similar to the liquid hydrogen or pressurized hydrogen, chiefly depending on metal/alloy mass. Alloys like ZrV₂, Mg₂Ni, FeTi or LaNi₅ are used for storage purposes while in case of metal hydrides, MgH₂ also known as a high-temperature hydride with gravimetric storage of 0.07 kg of H₂/kg of metal also show true potential to successfully store hydrogen (Sherif *et al.*, 2005).

The three most crucial factors for the storage of hydrogen in metal or alloy hydrides are (1) Their capacity to store hydrogen, (2) the recycle and the reversible storage, and (3) hydrogen absorption/desorption kinetics. All of the above-mentioned reasons attribute to the alloy microstructure. In this light, nanostructured features in powder particles form have very distinct advantages. Some of the potential optimal materials for hydrogen storage in a few years' time can be envisioned in the Magnesium, aluminum or Mg-Al alloys either in the form of bulk materials with nanograins, or Mg-Ni alloys (nanocrystalline powders) (Serrano *et al.*, 2009). For example, Mg-Ni alloys not only have conventional sizes but their nanostructured interior confers efficient hydrogen absorption without the need for long activation treatment. It is also lightweight and relatively inexpensive material. The doping of metal hydrides with titanium nanoparticles is another feasible pathway but comes with certain drawbacks. Though sodium aluminum hydrides (NaAlH₄) doped with titanium nanoparticles can be treated as a sustainable and low-cost hydrogen transport and storage method, but the adversity is the limited market of Ti production hence inadequate development in the storage technique field.

The implementation of porous supports is a widely used technique to maintain the small size of nanoparticles. Usually, after the porous material has been prepared, the metal is loaded on its surface. A novel method of the incorporation of metal nanoparticles in high-quality mesoporous materials by functionalizing Pd nanoparticles with tri-alkoxysilane terminal groups has been developed recently (García-Martínez *et al.*, 2009). By copolymerization with tetra-alkoxysilanes in the presence of a surfactant, these modified nanoparticles are diffused into the porous structure of the silica. In this manner, the hydrogen adsorption performance of silica supported by palladium has been enhanced due to the obtaining of highly dispersed nanoparticles.

Boranes provide the citadel for the test of other chemical hydrogen storage materials. Recent studies show that the combination of boron and nitrogen can be treated as the potential solid-state hydrogen storage materials for onboard applications. A scaffold having 6–7 nm wide channels to hold ammonia borane (NH₃BH₃) in the nano-phase of silica mesoporous has been used by Brown *et al.* (2006). The hydrogen release kinetics at lower temperature was enhanced after the addition of saturated ammonia borane when embedded in a scaffold.

Fuel Cells

Hydrogen conversion has been the field of concentration of many researchers across the globe and over the years many new methods have been invented and developed. Both engines and fuel cells can burn hydrogen for generating energy. Like gasoline or natural gas, hydrogen can also undergo combustion in engines. Whereas fuel cells are electrochemical devices that basically transform the chemical energy of hydrogen into electrical energy. Fuel cells are among the most attractive and promising green technologies since electrochemical reactions are more controlled and efficient than combustion at generating energy (Sherif *et al.*, 2005; García-Martínez *et al.*, 2009). In a hydrogen fuel cell, hydrogen combines with oxygen in an electrochemical reaction (reverse of electrolysis) and produces direct electric current.

The various types of hydrogen fuel cells are classified on the basis of electrolytes as Polymer Electrolyte Membrane Fuel Cell (PEMFC), Phosphoric Acid Fuel Cell (PAFC), Alkaline Fuel Cell (AFC), Molten Carbonate Fuel Cell (MCFC) and Solid Oxide Fuel Cell (SOFC) (García-Martínez *et al.*, 2009).

The manufacturing costs are extremely high because of the expensive materials used for the manufacturing of electrodes' bipolar plates, the electrolytes, membranes, and catalysts where platinum is used. Hence, the cost of installation, as well as

production, is very high than the prevalent modes of electricity generation, fuel cells are being confined only to the laboratories. As a silver lining, the contribution of nanotechnology has considerably reduced the cost by improving efficiency even more. The huge number of research papers focused on nanotechnology applied to fuel cells that have been published in scientific journals since the last decade implies the extraordinary impact of this subject on the energy sector (Serrano *et al.*, 2009).

The automobile industry, power generation industries for both home and electronic applications have especially focused on works related to PEMFC for generation of zero-emission clean vehicles to tackle the alarming rate in which global warming is increasing. The clean and efficient green systems being a major solution to cut down the carbon dioxide and carbon monoxide content have always been a subject of high priority. But the two main obstacles that prevent its commercialization are the high cost of Pt/support electrodes and the low performance of the membrane, mainly at high temperatures.

The cost of the electrodes could be reduced significantly by decreasing the quantity as well as the durability of Pt catalyst needed for the application, is directly related to the support and catalytic influence. Carbon nanotubes-based electrodes for PEMFC fuel cells have been successfully synthesized by Wang *et al.* (2004) and Rajalakshmi *et al.* (2008). The authors found that instead of carbon powder, MWNT can be used as catalyst support thus allowing the reduction of the Pt used in comparison with the traditional PEMFC fuel cells by almost 2/3 times. For membrane electrode assemblies, higher performance and durability was observed while the electrodes showed higher thermal stability and higher catalytic activity. In his review "Novel catalyst support materials for PEM fuel cells: current status and future prospects", Shao *et al.* (2009) summarized the list of most feasible candidates for supporting the catalyst in the area of nanotechnology. For an alternative to the anode, tungsten carbides were proposed while diamond materials, in both conductive doped and nano-diamonds forms, were scouted for its use as a cathode. Carbon nanotubes, carbon nanofibers, mesoporous carbon and conductive oxides such as SnO_x/ITO , Ti_xO_y , TiO_2/ITO or WO_x are also projected to be used in commercial electrodes, in both cathode and anode. Doping is the main strategy for most of the mentioned in order to further escalate their application as supports of catalyst for the membrane fuel cells.

Synthesis of metallic nanostructured electrocatalysts with the aid of different self-assembled templates as structure-directing agents, capping agents are other alternatives that have been considered with importance. A silica-based template comprising of nanosized holes and bimetallic Pt–Ru nanowire networks, to be used as anodes of Direct Methanol Fuel Cells (DMFC) is experimented by Choi and Woo (2003). Chien and Jeng (2007) developed a new class of nano-catalysts based on three-dimensional Pt and Pt–Ru nano-structures with interconnected holes by using the same concept. Although they have been tested as a cathode (Pt) and anode (Pt–Ru) of specifically DMFC, these electrodes have potential applications on all membrane fuel cells in general. In a relatively newer study, using hexagonal self-assembled Ti/Si template, mesoporous Pt nanowire array has been prepared which shows potential applications in portable fuel cells (Zhong *et al.*, 2008).

One of the major contributions of nanotechnology with respect to the membrane performance is the use of nanoscale hydrophilic inorganic materials in electrolytes inorganic lithium salts. This has helped in improving the membrane's hydrogen ion conductivity at relatively high temperatures (the inorganic materials show a high affinity towards water and the salts function in the right temperature range). The use of capillary fuel cells instead of flat cell membranes is another growing alternative. The capillary cells are considerably cheaper than the flat cell membranes. Moreover, the closely packed construction results in approximately three to six times higher power density and allows to cut off the expenditure on the bipolar plates of the electrodes. In addition to this, the production of capillary fuel cells is fully automated and its miniature size makes it readily possible for portable applications. Additionally, the synthesis of nanoporous films of polybenzimidazole (PBI) doped with phosphoric acid has been mentioned by Mecerreyes *et al.* (2004). PBI doped with phosphoric acid already has its application as an electrolyte for methanol fuel cells (Wang *et al.*, 1995). With the introduction of nanoporosity in PBI, the increase in conductivity results in the betterment of the membrane performance as well. To obtain an enhanced performance mainly at high temperatures, the conventional Nafion membrane has been modified with titanium and tin dioxide nanoparticles by Abbaraju *et al.* (2008). Deposition of silica nanoparticles on sulfonated poly(aryl ether sulfone) has resulted in the fabrication of nanostructured membranes with special attention towards proton and ethanol fuel cells (Magno de Carvalho *et al.*, 2008).

Parallely, advances in SOFC are also in process with a heavy reliance on nanotechnology. Ignatiev *et al.* (2008) fabricated a nanoengineered SOFC with ultra-thin films supported by metallic foils. There was a remarkable decrease in the operating temperature in comparison with traditional SOFC. The efficiency of these nanoengineered and nano-structured fuel cells was found out to be above 50% with a maximum power density of 140 mW/cm² at 575°C.

Rechargeable Batteries

The rechargeable lithium battery is the prime focus of the research in this sector presently. In comparison to the aqueous batteries, the Li-ion batteries have shown an increase ranging between 100%–150% on the storage capability of energy per unit weight and volume. The major limitations are related to low energy and power density, a large change in volume on reaction, safety and cost of manufacture. The aforesaid shortcomings are tackled by the infusion of nanotechnology into the field of rechargeable batteries.

A tin-based anode nanobattery, trade named "Nexelion" has been commercialized by Sony Corporation. For the first time, the graphite electrode in the battery was replaced by a nano-alloy (Serrano *et al.*, 2009; Inoue, 2006). In the same line, Toshiba Corporation's claim of the new nanobattery that can recharge 80% of a battery's energy capacity in only 1 min has been a matter of great discussion. According to the company's model, this is approximately 60 times faster than the typical lithium-ion batteries and on a further note combines this fast recharge time with performance-boosting improvements in energy density.

Introduction of nanoparticles of alumina, silicon or zirconium to non-aqueous liquid electrolytes have increased the conductivity of the electrolyte up to six times. Solid state electrolytes, solid polymer electrolytes (SPE) have been the focus of most of the efforts. Since PEO is safe, green and can make flexible films, Poly(ethylene oxide)-based (PEO-based) SPE gathered most attention. As polymers have a low conductivity in room temperatures and are not mechanically stable enough, nanocomposite polymer electrolytes act as the best replacement in the fabrication of highly efficient, safe and green batteries. For instance, the electrical conductivity of the polymer electrolytes at room temperature increased by 10–100 times compared to the corresponding undispersed SPE system due to the inclusion of ceramic nanomaterials as separators. Out of TiO_2 , Al_2O_3 and SiO_2 and S-ZrO₂ (sulfate-promoted superacid zirconia) used for this purpose, the incorporation of S-ZrO₂ led to the best performance (Bruce *et al.*, 2008; Agrawal and Pandey, 2008; Whittingham, 2008; Patil *et al.*, 2008).

The substitution of LiC_6 electrode, with storage capacities of 340 mAh/g, by graphite nanoparticles and carbon nanotubes, is an important replacement in the structure of anode of the lithium batteries. Further replacement by nanosized metal oxides (i.e., titanium, aluminum, vanadium, cobalt, tin as well as silicon oxides) mostly in the form of nanotubes and nanowires have brought a solution to both depositions as well as some safety problems (Nam *et al.*, 2006; Park *et al.*, 2007; Chan *et al.*, 2007). For instance, the silicon nanowire synthesis harbored to the substrate act as a current collector to obtain a charge capacity of ca. 3000 mAh/g during 10 cycles after the first one, losing around one-third of capacity in the first cycle as inferred by Chan *et al.* (2008).

To increase the life cycle of nanocomposites through the reduction of volume change caused during the formation of the alloy, nano-scaled metal alloy composites are employed. For example, out of all Lithium alloys, Li_4Si has the highest gravimetric energy density, 4200 mAh/g, and the change in volume during alloy formation is around 400%. With this perspective, the most potential applications can be accounted for as: (i) thenano-architected anode construction in a variety of nanoforms (ii) deposition of nanoparticles on nanostructured copper roads (i.e., Ni_3Sn_4 for $\text{Li}_{4.4}\text{Sn}$) by displacement reactions to fabricate intermetallic electrodes as nanoparticles and (iii) the applications of nanostructured alloys in amorphous forms (titanium, vanadium, chrome or cobalt in amorphous tin phase) (Green *et al.*, 2003; Taberna *et al.*, 2006; Timmons and Dahn, 2007; Hassoun *et al.*, 2007).

For cathode reconstruction with the help of nanotechnology, it has been found that main suitable candidates for both environmental and economic reasons are manganese oxides, LiMn_2O_4 in bulk and vanadium oxides. Since nanoparticles are required to be coated to avoid sintering and increasing conductivity, they are not preferred. In this case, nanotubes and nanowires of vanadium oxide or lithium intercalation host including manganese oxides have shown a good performance. The very fact that storage and rate capability of V_2O_5 depends on the morphology and nanocables showed better performance than nanotubes or nanorods was proven by Wang *et al.* (2006). Other architectures involve fabrication of ordered mesoporous cathodes (which could arrange the electrolyte inside the pores) by using mesoporous silica templates as well as liquid crystalline electrolytes notably increase the battery performance LiMn_2O_4 , LiCoO_2 or NiOOH are to name a few recently studied mesoporous cathodes.

Wind Energy

The other booming energy sector of this era is the wind energy sector. The main governing principle behind a wind energy system (i.e., wind turbine) is to convert the kinetic (moving) energy of the wind into mechanical or electrical energy which is then used for practical purposes. Since wind energy does not deal with the combustion of any sort, hence it is environment-friendly and can be treated as green energy. Moreover, wind energy being a natural resource which is renewable in nature, it serves as a long-term solution to the current energy crisis. In comparison to the other power resources, the effects of wind energy on the environment are generally less adverse.

To fully utilize a wind power plant to its perfect effect, the wind speed should be at least 13–15 m/s. For comparatively smaller wind power, the wind speed can be approximately 10 m/s. The efficiency of wind power plants varies from 30% to 60% on average since wind speed is not uniform throughout the day. The energy generated by a wind turbine is directly proportional to the square of its blade length (Mostafaeipour *et al.*, 2011; Burton *et al.*, 2001).

Nano-composite materials exhibit extraordinary strength to weight and stiffness to weight ratios. Therefore, the construction of longer, stronger blades is recommended. The reduction of energy losses caused by some tribological issues like micro-pitting, wear, scuffing and spalling in gearboxes can be attributed as one of the effects of incorporating nanotechnology. Hence the wind turbine efficiency increases significantly. Some promising solutions to counter the energy loss problems are nano-lubricants and low-friction coatings (Sherif *et al.*, 2005). Using a sliding contact linear reciprocating rig to estimate the wear behavior and friction of a boron nitride-based surface and nano-particle lubricant additives for wind turbine gearbox applications were experimentally calculated by Greco *et al.* (Dalili *et al.*, 2009). The studies were mainly focused to adjust to severe operating conditions and mitigate surface originated failure.

To form a wear protective tribo-film, nano-colloidal boron nitride based lubricant additives are considered as an alternative technology to react with the borided surface. The boro-carburized surface showed much less wearing track and even the surface within the wear track was smoother than the surrounding surface. The conclusion was that a wear resistive tribo-film was formed by a chemical reaction due to the infusion of nano-colloidal boron nitride additive in commercial gear oil. Moreover, the mechanical properties of the surface layer were improved by the borided surfaces thus leading to increased wear resistance (Greco *et al.*, 2011).

Geothermal Energy

The thermal energy originating from the earth's crust is termed as Geothermal Energy. This varies between 5 and 10 km in length. The temperature is very high in the depths of the earth's crust. So, to cool the pipes which were exposed to the extremely high temperatures, nanofluids can be used as a cooling-agents to cool the pipes. Sensors and electronics in drilling machines which operate under high friction and high-temperature conditions are also cooled by using these nanofluids.

The sources of geothermal energy are classified in three main categories with respect to the measured temperature as low ($<100^{\circ}\text{C}$), medium ($100\text{--}150^{\circ}\text{C}$) and high temperature ($>150^{\circ}\text{C}$). A ground heat exchanger is mainly employed for the extraction of the energy (Kalagirou, 2005). The driving force for the conduction of thermal energy is the geothermal gradient. A geothermal gradient is defined as the difference in temperature between the core of the earth and its surface. On the other hand, the extraction energy from the core of the earth until the processing of it into a power plant system can be done by nanofluids as well. Thus, a large amount of work energy can be generated with the aid of nanotechnology in the geothermal sector as well.

Since the last few decades, geothermal energy has gained wide popularity for its varied applications. Household heating and electricity generation in small industries are the primary applications for the geothermal energy procured from the natural reserves. It has been reported that more than 72 countries have already started proper usage of geothermal energy. Almost 93% of the homes in Iceland are heated by geothermal energy, thus making it a global leader in the geothermal energy sector. Inevitably, Iceland is saving over 100 million dollars annually by substituting oil imports with geothermal energy. Since the generation of geothermal energy and its conversion to heat and electrical energy does not require any combustion, Iceland has also emerged as one of the cleanest countries thus making an exemplary difference in the global sustainable economy (Pahl, 2007).

As geothermal power plants can operate 24 h per day unlike tidal, solar, wind, it has been identified as a promising candidate to replace fossil fuels. With the current base-load capacity, the global potential for geothermal power generation is roughly estimated to be 85 GW within the next 30 years. But geothermal power is highly topography centric and the reserve is not distributed uniformly over the surface of the earth. Hence making it accessible in mainly the United States, Central America, East Africa, Iceland, Indonesia, and the Philippines (Hussein, 2015).

However, the major challenge encountered in the procurement of geothermal energy is the necessity for deep borings. The drilling is identified as the major reason for the triggered tremors or earthquakes in geographically weak areas. The research on nanofluids which is capable of encapsulating energy of higher orders in comparison to the other thermal fluids has opened up a portal of future research possibilities to counter the threat of digging deep borings (Ganguly *et al.*, 2012).

Conclusion

To cater to the world's increasing demand for energy, alternative forms of energy is slowly and steadily reaching the mainstream energy sector due to their wide availability, renewable nature and significant compatibility with the environment. The limitations of sustainability have led researchers and scientists to delve into studies of nanotechnology which promise optimistic ways to troubleshoot the major concerns.

The solar economy, which dominates the renewable energy sector has not achieved the expected efficiency or the economic feasibility with the traditional silicon based solar cells. Material science in the form of nanotechnology has been inculcated in the solar energy sector with the objective of increasing efficiency, ease of manufacturing thus broadening the acceptance in the market. The PV solar cells or the first-generation solar cells have experienced a rise in controlling the band-gap and interchangeability with the aid of quantum dots which have a close to 40% of the total efficiency of the present solar cells. Moreover, the inclusion of a vertically aligned nanowire array deal with the problems of exciton diffusion.

Hydrogen, on the other hand, has caught the attention of the scientists for its use as clean energy as it leaves only water as the by-product after combustion. But the generation and the storage of this green energy has faced some serious challenges with the prevalent techniques. Thanks to nanotechnology, single-walled and multiple-walled carbon nanotubes with the principles of physisorption and chemisorption as well as mesoporous materials with hierarchical structures and controlled pore size are gaining popularity for potential ways to store hydrogen. The development of graphene based membranes, as well as carbon nanotubes, carbon nanofibers, mesoporous carbon and conductive oxides for substituting the expensive platinum electrodes, aim to bring down the manufacturing costs of fuel cells with the aid of nanotechnology.

The inclusion of nanocomposites, nano-solvent coatings on the walls of the wind turbine blades are proposedly helping to reduce the friction and increase efficiency. Nanofluid which can function as both thermal fluid and coolant is emerging as a suitable alternative to the present drilling methods for procuring geothermal energy. The review discusses the various proposed as well as implemented ways by which nanotechnology can make a difference to the prevalent renewable energy sector and scientists in unanimity believe that these are just glimpses of what nanoscience and nanotechnology are actually capable of achieving.

See also: Nanomaterial for CO₂ Sequestration

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Optimal Operation of Renewable Distributed Generators (DGs) and its Environmental Benefits

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Introduction

Renewable distributed generation is expected to become more important in the future generation system. Renewable Distributed electricity generation, is a kind of new concept in the literature of pricing about markets of electricity, although the idea behind this is not new at all. At early days when there was no AC generation, DC distributed generation was ruling the electricity markets. The first power plants only supplied electricity to near customers of the generating plant. The first grid established were DC based, and therefore, the supply voltage was limited, as was the distance that could be used between generator and consumer. Balancing demand and supply was partially done using local storage, i.e., batteries, which could be directly coupled to the DC grid. Along with distributed generation, local storage is also returning to the scene. Later, technological evolutions, such as the emergence of AC grids (Thanks to scientist Tesla), allowed for electricity to be transported over longer distances lead to an increase in the power output of the generation units. All this resulted in increased convenience and lower per unit costs and massive electricity systems were constructed, consisting of huge transmission and distribution grids and large generation plants. Balancing demand and supply was done by the averaging effect of the combination of large amounts of instantaneous variation of loads. Reliability and security of supply was increased as the failure of one power plant was compensated by the other power plants in the interconnected system. In fact this interconnected high voltage system made the economy of scale in generation possible. In the last decade, sharp technological innovations and a changing economic and regulatory environment have resulted in a renewed interest for distributed generation. This is confirmed by the IEA (2002), who lists five major factors that contribute to this evolution, i.e., developments in distributed generation technologies, constraints on the construction of new transmission lines, increased customer demand for highly reliable electricity, the electricity market liberalization and concerns about global climate change.

Here we present general ideas of renewable distributed generation. Definition and different technologies, which are allowed dispersed generation of electricity, are discussed in Part-1. The important characteristics of every technology are summarized in Table 1. Then we discuss the major benefits that are offered by the use of distributed generation. Part-3 focuses on the major issues that are raised in the distributed generation literature. This illustrates that many of the benefits and issues depend on the renewable distributed generation technology used. In Part-4 the resilience of such networks is being shown and one flowchart (Fig. 1) is being prepared for the intentional cyber-attacks to the network. Part-5 then tries to show the environmental aspects of dispersed generation. The impacts due to the renewable distributed generation is summarized in Table 2. Finally, Part-6 is the conclusive part of the discussion.

Distributed Generation: Brief Description

In the previous sections, renewable distributed generation was loosely defined as small-scale electricity generation. The different technologies that can be used for it were listed in Table 1. A short survey of the literature shows that there is no consensus. This is confirmed by CIRED (1999), on the basis of a questionnaire submitted to the member countries. Some countries define distributed generation on the basis of the voltage level, whereas others start from the principle that distributed generation is connected to circuits from which consumer loads are supplied directly. Other countries define distributed generation as having some basic characteristic. The European Renewable Energy Study (TERES), commissioned by the European Union (EU) to examine the feasibility of EU CO₂-reduction goals and the EU renewable energy targets, found that around 60% of the renewable energy potential that can be utilized until 2010 can be categorized as decentralized power sources. Thus, generation units built by the transmission grid operator as a substitute for grid expansion and that have measures implemented for dispatching are not considered to be distributed generation according to this philosophy.

The IEEE defines distributed generation as the generation of electricity by facilities that are sufficiently smaller than central generating plants so as to allow interconnection at nearly any point in a power system 10. On the basis of the definitions surveyed in their paper, Dondi *et al.* (2002) define distributed generation as a small source of electric power generation or storage (typically ranging from less than a kW to tens of MW) that is not a part of a large central power system and is located close to the load. These authors also include storage facilities in the definition of distributed generation, which is not conventional. Furthermore, their definition emphasizes the relatively small scale of the generation units as opposed to CIRED and CIGRE. Chambers (2001) also defines distributed generation as relatively small generation units of 30 MW or less. These units are sited at or near customer sites to meet specific customer needs, to support economic operation of the distribution grid, or both.

With the exception of the CIGRE definition, all definitions assume that distributed generation units are connected to the distribution network. This is also the case for the definition used by IEA (2002), which sees distributed generation as units

Table 1 Different technologies of renewable distributed generations

Name	Basic information	Generation range ^a	Efficiency of electric conversion ^b	Renewable sources ^b	Application ^b	Remarks
Fuel cell	Device which converts chemical energy into electrical energy	50 kW–2 MW	35%–55%	Methanol (CH ₃ OH) Natural gas Reforming of CH ₄ to H ₂ leads to decreased efficiency	IC engines or dc batteries.	If the H ₂ comes out from electrolysis of water. energy, it reduces CO ₂ and CH ₄ gases emission
Photovoltaic	Generates no heat and produces electricity from solar radiation	1–5 kW Every range possible when using more cells	25%–30%	Sun	Home appliances application and a few commercial applications Isolated-grid applications Developing countries	Non predictable output
Wind	Converts wind energy to electrical energy by wind-turbines	Every range possible when using more windmill	50%–60%	Wind	Household In a few scale applications	Non predictable output
Hydro	Natural resource of river water	100 kW–30 MW	80%–85%	Water	Household and smallcommercial applications Off-grid/grid applications Countries which are developing Small applications in houses Household and small industrial applications	A very high value of output; capacity factor ~80%–85% in Western Europe
Biomass	Biofuel, Waste management system		30%–40%	Biological waste	Smallcommercial applications Developing countries	
Geothermal energy	Thermal energy of Earth		2%–5%	Earth temperature	Smallcommercial applications Developing countries	
Other	renewables	OTEC (Ocean thermal energy conversions)		Not applicable	Temperature difference between cooled water and warm tropical surface waters.	Smallcommercial applications
Developing countries						

^aSource: Linden *et al.*, IEA, p. 64; Duffie *et al.*, p. 638 and author.^bSource: IET Renew. Power Gener., 2016, 10 (7), pp. 873–884.

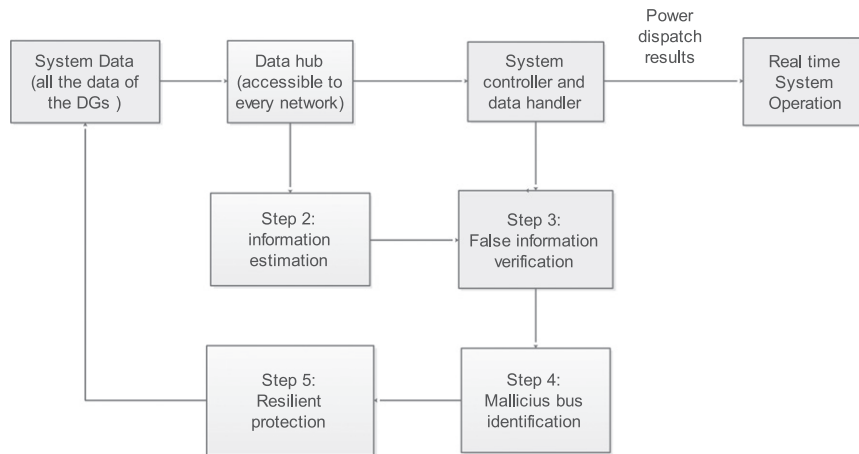


Fig. 1 Block diagram of the attack resilient distributed generation.

producing power on a customer's site or within local distribution utilities, and supplying power directly to the local distribution network. The Electric Power Research Institute defines distributed generation as generation from 'a few kilowatts up to 50 MW'.

IEA, however, makes no reference to the generation capacity level as opposed to all other definitions. It should be clear by now, that many definitions of distributed generation exist, allowing for a wide range of possible generation schemes. Some definitions allow for the inclusion of larger-scale cogeneration units or large wind farms connected to the transmission grid, others put the focus on small-scale generation units connected to the distribution grid. All these definitions suggest that at least the small-scale generation units connected to the distribution grid are to be considered as part of distributed generation. Moreover, generation units installed close to the load or at the customer side of the meter are also commonly identified as distributed generation. This latter criterion partially overlaps with the first, as most of the generation units on customer sites are also connected to the distribution grid. However, it also includes somewhat larger generation units, installed on customer sites, but connected to the transmission grid. This leads to the definition proposed by Ackermann *et al.* (2001), who define distributed generation in terms of connection and location rather than in terms of generation capacity. They define a distributed generation source as an electric power generation source connected directly to the distribution network or on the customer side of the meter. We favor this definition, even though it is rather broad. Indeed, it puts no limit on technology or capacity (relative: in % of the country) of the potential distributed generation applications.

Therefore, some additional criteria can be helpful and necessary to further narrow the definition in function of the research question that is tackled. The following paragraphs list a (no exhaustive) number of these criteria along with a short discussion. Voltage level at grid connection (transmission/distribution) Although some authors allow distributed generation to be connected to the transmission grid, most authors see distributed generation as being connected to the distribution network, either on the distribution or on the consumers' side of the meter. In all cases, the idea is accepted that distributed generation should be located closely to the load. The problem is that a distinction between distribution and transmission grid, based on voltage levels, is not always useful, because of the existing overlap of these voltage levels for lines in the transmission and distribution grid. Moreover, the 'legal' voltage level that distinguishes distribution from transmission can differ from region to region. Therefore, it is best not to use the voltage level as an element of the definition of distributed generation. It would be more appropriate to use the concepts 'distribution network' (usually radial) and 'transmission network' (usually meshed) and to refer to the legal definition of these networks as they are used in the country under consideration.

Different Technologies of Distributed Generation

Here we presented in a tabular form of the different technologies which can be implemented for renewable distributed electricity generation. All the technologies are not analyzed in great detail. From this discussion the advantages and disadvantages of dispersed generation are given below in Table 1.

Utility of Renewable Distributed Generation

It was mentioned in the above section, the IEA identifies five major aspects which are contributing to the interest in dispersed generation. We describes five factors which can be further more reduced to 2 main actuating forces, i.e., open electricity market and concerns about environment. We doubt that decentralized generation is adept of intermitted, and certainly maintain, the employment of new transmission lines. Reliability being the third most important element and resiliency must be accounted for the hazards like natural disaster or cyber terrorism in constructing the plants of renewable generations.

The De-Regulation of Markets for Electricity

An increment in interest of electricity suppliers in renewable distributed generation as market suppliers make it as a tool which could help them to create niches in an open market. Customers will look into in such a market; customers will look for the electricity service best suited for them. Different customers attach different weights to features of electricity supply, and distributed generation technologies can help electricity suppliers to supply to the electricity customers the type of electricity service they prefer. In short, distributed generation allows players in the electricity sector to respond in a flexible way to changing market conditions. Some major examples are discussed below.

In open markets, it is important to adapt to the changing economic environment in the most flexible way. Distributed generation technologies generally provide this flexibility because of their small sizes and the short construction lead times compared to most types of larger central power plants. According to the IEA (2002), the value of their flexibility is probably understated when economic assessments of distributed generation are made³. It should be stated that the lead time reduction is not always that evident. Public resistance to for instance wind energy and use of landfill gasses may be very high.

Backup Capacity

Many distributed generation technologies are indeed flexible in several respects: operation, size and expandability. For example, making use of distributed generation allows reacting in a flexible way to electricity price evolutions. Distributed generation then serves as a hedge against these price fluctuations.

Apparently, the demand for distributed generation is mainly driven by price volatility, i.e., using distributed generation for continuous use or for peaking use (peak shaving). In the market demand for distributed generation is, for the moment, driven by heat applications, introduction of renewables and by potential efficiency improvements. These will be discussed below.

High Installation Cost

The IEA (2002) and many others claim that one of the major remaining issues is the relatively high capital costs per kW installed power compared to large central plants. Moreover, differences in capital costs between the different distributed generation technologies are also quite large, ranging from €1000 per kW to over €20,000 per kW for solar, wind and fuel cells, respectively.

More Choice Between Renewable Sources

An increasing share of renewable distributed generation in the installed generation capacity, implies more choice between renewable sources. Given that most distributed generation technologies are (primarily) based on solar and wind. We expect an increased demand for and dependency on solar. The importance of this argument crucially depends on the market share of distributed generation in the total generation capacity, but also, for example, on the amount of cogeneration that is installed, as this will lead to increased pricing but lower environmental pollution.

Another claim is that the primary fuel supply for renewable distributed generation applications will usually be less costly than that for central coal based generation. In the demand for renewable energy sources that can be used to obtain some more efficient technologies.

Economic Efficiency

Economic efficiency refers to the principle that wasting valuable resources should be avoided. The extent to which distributed generation is integrated efficiently in the electricity market things upon the market structure, the market operation and upon pricing. In many countries, the structure of the electricity market is revised through the de-regulation process. The final market structure will have an influence on the penetration potential of renewable distributed generation. An economically efficient deployment would require an open scope of the retail market in the sense that electricity customers then have the option to generate their own electricity in response to price if a dispatchable DG technology is used. If only wholesale market liberalization is achieved, electricity customers would essentially be faced with a monopolist at the distribution level. This monopolist can easily discourage the installation of distributed generation, for example by charging high prices for ancillary services or by offering very low prices for distributed power supplied to the grid. Clearly, the regulator could play a role here, for example by fixing (minimum) buy-back prices, but these prices risk to be set at inefficient levels such that either too much or too little distributed generation capacity is installed. Liberalization at the retail level is not a sufficient condition for non-discriminatory access of distributed generation to the grid. Grid operators that own generation capacity also have an incentive to discriminate against distributed generation. A separation of generation and distribution transport activities is necessary to remove this incentive. In the latter case, some potential benefits mentioned in the next part will be more difficult to realize (renewable distributed generation as an alternative to grid expansion).

Often, the liberalization of the electricity market has led to the introduction of spot markets for electricity. These markets play an important role in the balancing of supply and demand. Retailers unable to meet their forecasted output or demand must turn

to the balancing market where they pay high prices for their imbalances. Clearly, distributed generators are adversely affected by this evolution because they typically have difficulties to forecast their output (renewable). In principle, prices should reflect underlying demand and supply conditions, which can vary overtime and place. In practice, electricity prices are rarely sensitive to location, except when there are important technical reasons for price differences found in the grid, and in many cases they are also not sensitive to time, except for corrections for day/night or weekend and seasonal. Pricing mechanisms based on varying demand and supply conditions will encourage an efficient use and deployment of (distributed) generation. The use of time based pricing schemes is increasing, but location based pricing schemes are apparently more difficult to implement.

Cheap Renewable Fuel Opportunities

Setting up renewable distributed generation allows the exploitation of cheap fuel opportunities. For example, in the proximity of landfills, distributed generation units could burn landfill gasses. Also, other locally available biomass may be used. In short, the decentralization of the electricity market and increased environmental concerns both induce an enhanced interest in distributed generation applications and thus also in innovations in the appropriate technologies. However, the economic as well as technical challenge will be to optimally integrate this increasing number of small generation units in an electricity system that up to now has been very centralized and integrated and planned.

Geographical Diversities

The modular nature of renewable energy technologies, such as wind turbines and solar photovoltaic (PV), allows greater geographical diversification of energy supplies compared to conventional power generation systems, which deliver power from a concentrated point or central location. This increased regional diversification reduces the vulnerability of the energy supply to cause damage from a single event or a single critical location, which increases overall energy system resilience.

Micro Grids

Microgrids capable of islanding based on renewable distributed generation (DG) can disconnect from the central grid during a major climate event to allow energy to be diverted to critical loads. This allows utilities flexibility in restoring generation stations, responding to critical outages, and shutting down systems before a major event to prevent damage. Islanded DG systems ensure consumers have access to power during long-term power outages that severely impact central grid systems, which can occur after major natural disasters.

Strategy

New Jersey had more than 1000 megawatts (MW) of installed solar capacity when “Hurricane Sandy” hit the Northeast United States. However, only 2 solar PV systems provided power in the days following the “hurricane” (Stout and Hotchkiss, 2017). At the time, a combination of interconnection strategy and a lack of dynamic controls or transfer switches prevented the islanding of systems. Without appropriate strategy and codes, the installed DG capacity could not do a little to aid resiliency. Selected locations to enhance resiliency through DG may adopt appropriate policy on interconnection and islanding to realize the full benefits of these energy generation systems.

Redundancy

Redundancy is critical to most operations, but is essential for resiliency. The increased stress on infrastructure systems as a result of changing climate or other threats has the potential to increase the likelihood of failure of one or more parts of a system. Communities served by only one power line has limited resilience. Increasing supplies, routes, or incorporating redundancy to overall systems will reduce the risks of those systems. In an analysis conducted for a community in New England, it is determined that pairing renewable energy and energy storage technologies with conventional backup power systems increased the number of days a system could operate without grid connection.

Generation Capacity (MW)

One of the most obvious criteria would be the generation capacity of the units installed. However, the short survey of definitions illustrated that there is no agreement on maximum generation capacity levels and the conclusion is that generation capacity is not a relevant criterion. The major argument is that the maximum distributed generation capacity that can be connected to the distribution grid is a function of the capacity of the distribution grid itself. Because this latter capacity can differ widely, it is not possible to include it as an element of the definition of distributed generation. However, this does not imply that the capacity of

the connected generation units is not important. Thus, a narrowed definition of distributed generation could, among other things, be based on the generation capacity criterion. Services supplied Generation units should by definition at least supply active power in order to be considered as distributed generation. The supply of reactive power and/or other ancillary services is possible and may represent an added value, but is not necessary.

Generation Technology

In some cases, it can be helpful to clarify the general definition of distributed generation by summing up the generation technologies that are taken into account. It would however be difficult to use this approach to come to a definition because the availability of (scalable) technologies and of capacities, especially in the field of renewable, differs between countries. Also conventional systems such as gas turbines are available over wide ranges (a few kW to 500 MW). Sometimes, it is claimed that distributed generation technologies should be renewable. On the other hand, not all plants using 'green' technologies are supplying distributed generation. This would, for example, depend on the plant size or on the grid to which the installation is connected (transmission or distribution).

Mode of Operation

Ackermann *et al.* (2001) had not taken account the mode of operation as an important element in the definition of small scale generation. The corrected view, at that time must be considered more problems regarding distributed generation, especially the fact on that these units are beyond control from grid operations. Converging to the definition, the criterion, mode of operation is appropriately used. Within the same distribution network area, power generation and consumption may take place simultaneously.

Benefits of Renewable Distributed Generation

Several benefits of introducing renewable distributed generation in consonance with existing distributed networks are economical, environment-friendly and many technical implications are interrelated. Hence, it is classified the benefits into three groups – technical, environmental and economical.

The major technical benefits are:

- Line losses will be reduced;
- Improvement of Voltage profile;
- Overall energy efficiency will be increased;
- Enhancement of system reliability and security;
- Power quality will be improved.

The major environmental benefits are:

- Emissions of pollutants will be reduced;
- Due to environmental improvement health care costs will be reduced.

The major economic benefits are:

- For up-gradation of facilities investments will be very high;
- Productivity enhancement;
- Due to increment in overall efficiency fuel costs will be reduced;
- Operating costs will be very much less;
- Security for critical loads will be increased.

An approach to technical benefits of introducing renewable DGs can accrue in one of two broad categories:

- (1) Improvement of a certain aspect such as reliability, power quality, voltage profile, resiliency, environmental issues, healthcare assessment etc.
- (2) Reduce of an aspect such as emissions, congestion, pollution, line losses etc.

Resilient Operation of Power Network Having Renewable Distributed Generation

By the looming decentralized environment confront by the electric industry, many renewable distributed generation options are attaining its great economical viabilities by the help of some advancement in technologies. Magnitudes of recent natural hazards have created a new situation for the power industry. In below they are presented.

- Open market of the power generation industry and the subsequent breakup of the hierarchy of that system.
- Constructing new power network over the environmental ground opposes by the public.
- Electric power generation impacts on environment, makes the people aware.
- In some parts of the country the demand in electric power increases rapidly.
- Significant advancement in various generation technologies which are much more eco-friendly such that wind to electricity generation, hydro generation, solar generation, fuel cell, biomass and ocean thermal electricity conversion than conventional oil, coal and gas-fired plants.
- Increasing desires of public to promote green or eco friendly technologies which are based on renewable energy sources.
- Awareness for these opportunities of distributed generation for enhancement of the resiliency on power supply, especially to highly important loads, by promoting mini and micro grids in case of emergencies and/or terrorist attacks, cyber-attacks and/or embargoes of energy supplies.

All these factors discussed above have incremented interest for the development and usefulness of renewable DGs. There are various technologies which utilizes renewable energy resources. Hence forth the individual that show promise for DG applications are: wind energy, biomass systems, photovoltaic, solar-thermal-electric systems, Fuel cells, and geothermal systems. The DGs can range from a few kilowatts up to 300 MW. Capacity credit, energy cost saving and energy value are quantified and evaluated as the important part of DGs.

Distributed Generation Considering Attack Resilient Power Flow

Discussing attack resilient power flow over the natural hazards and cyber-terrorism to quantifying some technical benefits. The block diagram is shown below in [Fig. 1](#).

Resiliency: A Protective Approach to Power System

Globally it is initiated by the governments to be adopted and implemented various actions regarding climate change and reducing global warming effects. By adapting some resilient actions with the renewable distributed generations to overcome environmental degradation as well as natural hazards and intentional cyber attacks. Analytical and technical support provided all over the world for important lessons on resilience associated with renewable power generation. Renewable distributed energy generation is a huge factor in development of resilience with green energy technologies and its solutions. There are some key points discussed below.

- Power sector vulnerabilities and potential hazards may impede the provision of the energy services necessary to achieve economic growth and development goals.
- Planning for resilience can help communities avoid and recover from potential threats and vulnerabilities to the power sector.
- Renewable energy-based generation can enhance resilience due to its modular nature, ability to operate in severe weather when designed to do so, and lack of fossil fuel requirements.
- Decision makers may consider enacting policies that enable resilience strategies; coordinate their implementation; and evaluate their effectiveness on a regular basis.

The Resilience Roadmap is to be prepared for federal, state, and local entities to effectively convince at the regional level for adaptable and holistic planning. A step-by-step process offers guidance, exercises and aggregated data lists to support decision makers. The descriptions of data and hemorrhages report during any natural calamity or at any cyber-terrorism.

Methods Used to Designing the Resilience Roadmap and Some Case Study

From the zero level, the ability of recovering the stress from the application and retains its original state very quickly is termed as resilience. Increment in resilience means it reduces vulnerabilities and various threats to the power system having renewable distributed generations. In consonance with the effects of natural disasters and cyber attacks in power network, planning for resilient actions to be employed. The resilience planning methodology for developing and implementing an action plan can include community engagement, policy analysis, vulnerability and risk assessments microgrid modeling, and renewable energy feasibility studies.

International Case Study – Colombia

Power sector resilience is a concern to decision makers around the globe. In 1992, droughts caused by the El Niño effect resulted in widespread power shortages across hydropower-dependent Colombia. The severe shortages precipitated planned blackouts from 8 to 10 h daily across the country. The power rationing was called an “economic crisis” as the estimated cost of the blackouts

Table 2 Environmental impact on using different renewable distributed generations

Name of the methods of distributed generation	CO ₂ gas generation (g/kWh) ^(a)	Water pollution (kg/KWh) ^(a)	Chemical pollutants ^(b)	Land requirement (K m ² /TWh) ^(b)
Fuel cell	50	NA	Very less	NA
Solar	90	10	NA	28–64
Wind	25	1	NA	72
Hydro	41	36	NA	750
Geothermal	170	12–300	NA	18–74
OTEC	NA	NA	NA	NA

^aSource: Kaltschmitt *et al.*^bSource: Lewin, Fritsch *et al.*, also Ackermann; All figures include direct and indirect emissions based on average German energy mix, technology efficiency, solar radiation and typical lifetime.

reached \$35 million per week in lost productivity. The Colombian president at the time, Cesar Gaviria, famously noted that “We will never suffer like this again”. The president even temporarily changed the time zone to take better advantage of daylight hours.

Echoes of the 1992 crisis were heard in 2016 when severe El Niño-caused droughts impacted hydropower availability in Colombia. Through a concerted effort of energy savings and new billing practices, Colombia avoided blackouts despite a 63% reduction in water storage in hydroelectric dams.

Colombia is now preparing for the next El Niño event. The country, which depends on hydropower for over 70% of electricity generation, is seeking to diversify its energy portfolio. Colombia has updated its grid codes to incorporate greater levels of non-hydropower renewable energy-based generation. A new regulation creates a pathway to interconnect distributed generation resources to the grid to provide spatially-diverse, locally-produced power. The first ever, large-scale energy auction in Colombia that incorporates non-hydropower renewable energy was announced in early 2018. The goal of these projects is to provide reliable, cost-effective power to Colombia and to minimize the impacts of El Niño droughts on the Colombia energy sector.

Concerns Regarding Environment

Presently, the policies on environment are the key point for driving force to the demand for renewable distributed electricity generation throughout the world. The regulations on environmental policies play an important role to the electricity market for looking after cost efficient and clean energy generation. Hence, dispersed generation also allows optimization of the energy utilization of industries which have a huge demand for both electricity and heat. Moreover, all the government policies which aim at promoting the practice of renewable will resulting in an increased effect of distributed generation technologies, as renewable, in an integrated nature. The environmental impact of the Renewable distributed generation is presented below in a tabular form (Table 2).

Environmental Impact on Renewable Distributed Generation

The environmental impact of renewable distributed generations like CO₂ generation, Water pollution, Chemical pollutants and also the requirement of land for setting up the Renewable DG plants are discussed below in Table 2.

Conclusions

We initiated the observation on renewable energies as decentralize electricity generation. Prevailing dispersed generation technologies have been discussed so far, its gain and problems of using these technologies are also accounted. More precisely we define the concept of renewable distributed generations. In different environments it appears that many technologies encompasses these new concept by some precise attributes. In a dispersed network, consumer side end directly connected to a power generating source, best explanation of this generation. Resilient, reliable power output is essential for social and economic development. Nonetheless, renewable electricity generation plays a significant role in reducing emissions of greenhouse gas globally and contributing its effect on climate change too. Contemporarily, power systems are very sensible to climate changes. Stubborn challenges are to provide resilient, affordable, reliable power to the consumers. In consonance with this, we identified the challenges and probable solutions in the section considering the need for resilient and reliable output to meet increasing electricity demands for all the countries which are developing and growing, implementing the ideas of renewable generation, enlarge energy

accessibility, while improving distributed generation structure for lowering the emission and improve the environmental aspects and electricity transmission for climate resilience.

See also: Renewable Electricity Generation – Effect on GHG Emission

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Overview of CCS: A Strategy of Meeting CO₂ Emission Targets

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Introduction

Presently, use of fossil fuels is the major source of global anthropogenic greenhouse gas emission and this trend is expected to continue over a significant period in future. Coal and natural gas continue as the main primary source of energy for electricity production (IEA, 2015) (Fig. 1).

Hence, replacement of these fossil fuels is not practically feasible in near future though greenhouse gas (GHG) emission from these fossil fuels is the main source of global warming. Use of fossil fuels is mostly responsible for the climate change due to greenhouse gas emission from these fuels (Hansen *et al.*, 2010).

From Fig. 2, it is noted that CO₂ emission from the fossil fuels and industrial processes contributes significantly to the total GHG emission. At the same time, electricity and heat production sector is the largest source of this GHG emission (IPCC, 2014). Reduction of this GHG emission is the global challenge at present for survival of life on earth. Thus, utilization of fossil fuels in a better sustainable way than existing one is a possible way out from this crisis.

Under these circumstances, almost all countries were determined to limit the rise in global average temperature well below 2°C of pre-industrial levels at COP21, Paris in 2015. Several countries adopted different steps to reduce the consumption of fossil fuels and to promote clean technology for power generation as well as other industrial processes. Different Governments are imposing additional tax on carbon based fuel production or use to discourage its use. For example, Government of India imposed carbon tax on coal at a rate of INR 400 per tonne to raise funds for research on clean energy and to promote the clean environment. At the same time, many countries are in transition phase towards low carbon economy. They are promoting for low carbon life style and communities for sustainable development. Thus, coal and natural gas are not considered as clean fuels from the viewpoint of sustainable energy. Several technologies are explored to utilize coal in a more sustainable way. Carbon capture and storage (CCS) is considered to be the option of using fossil fuels with low GHG emission. CCS has good potential to mitigate carbon footprint of fossil fuel use as well as it has the potential of net carbon negative electricity generation through biomass based energy system integrated with CCS. However, significant cost increase is inevitable due to CCS. For CCS technology, CO₂ is captured before or after the combustion of fossil fuels and from other industrial processes e.g., iron and steel production, cement production etc. In this article, different CO₂ capture technologies e.g., post-combustion, pre-combustion, oxy-fuel combustion and chemical looping are discussed. Different aspects of CO₂ compression, transportation and storage are included. Application and integration of CCS in power industry, iron and steel industry, chemical process are shown in this article. Advanced carbon capture technology like carbon capture and utilization (CCU), BECCS are also explored. Finally, challenges and opportunities of CCS are also mentioned.

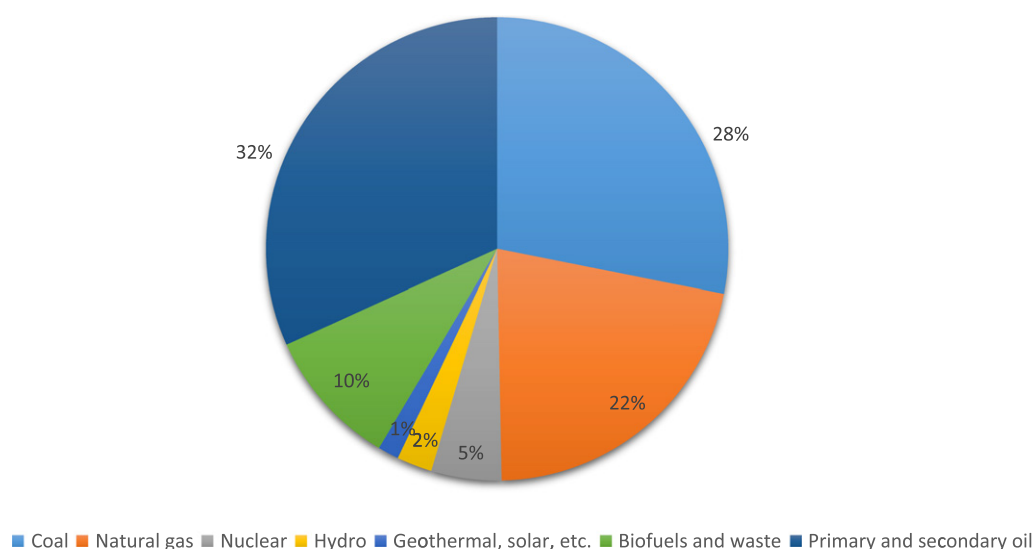


Fig. 1 Fuel wise primary energy supply of world in 2015. Reproduced from IEA, 2015. World Energy Outlook 2015, Paris: International Energy Agency.

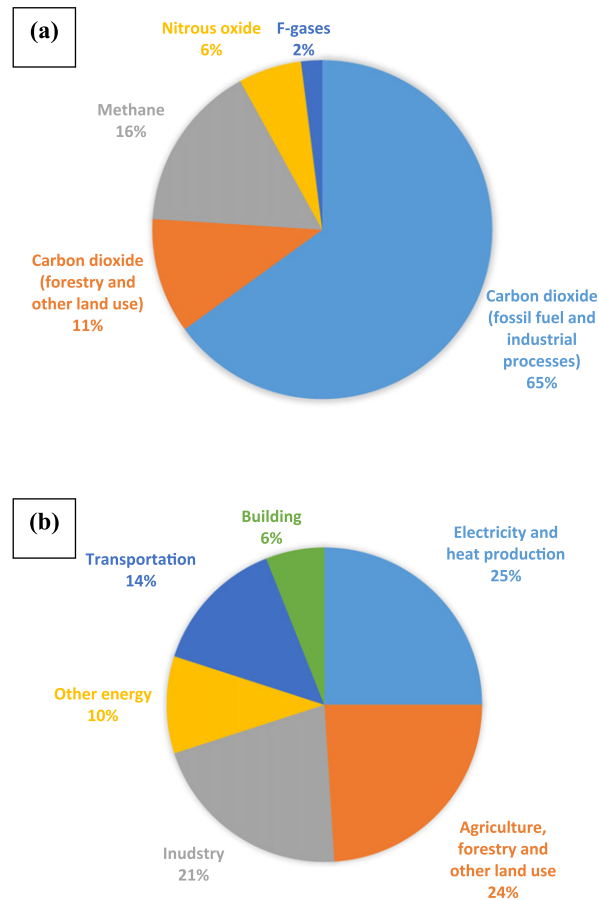


Fig. 2 (a) Contribution of different gases to global GHG emission (b) Global GHG emission by different economic sectors. Reproduced from IPCC, 2014. Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Core Writing Team, Pachauri, R.K., Meyer, L.A. (eds.), Geneva: IPCC, 151.

Properties of Carbon Dioxide

Properties of CO₂ are necessary to model the processes of carbon dioxide capture, compression, liquefaction, transport and storage. In Table 1, different thermodynamic and transport properties of CO₂ are given (IPCC, 2005). To simulate the carbon capture by amine, thermodynamic properties as well as viscosity are required. As CO₂ is compressed and liquefied before transportation through different mode, thermodynamic properties of CO₂ determine the optimum pressure of liquefaction. Also density of CO₂ has significant impact on storage volume. There are significant effects of impurities (say, SO₂) on the property of CO₂.

Overview of Carbon Capture Technology

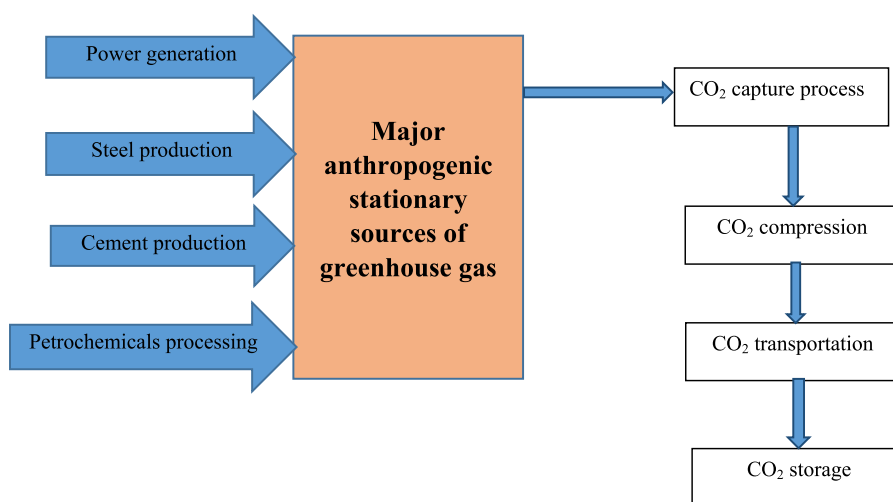
Electricity sector is the main source of anthropogenic greenhouse gases. Apart from power generation other sources of GHG emission are iron and steel production, cement production and petro-chemical processing where CCS technology may be implemented as shown in Fig. 3. Iron and steel industry contributes 31% of industrial emissions (IEA, 2013). For each ton of cement production around 880 kg of CO₂ is emitted. Petrochemical processing is another important sector responsible for GHG emission. From these sectors CO₂ can be captured and stored as shown in Fig. 3. Detail of CO₂ emission and potential of CCS is discussed later.

In Fig. 4, basic principle of a power plant with different methods of carbon capture against that without any carbon capture is shown. In a basic power plant, fuel and oxidizer (say, air) are the inputs and power is the output. Flue gas containing CO₂ is a hazardous effluent of the power plant. Efficient separation and storage of this CO₂ in different ways is the main research challenge. Basic overview of post-combustion CO₂ capture is shown in Fig. 4(b). In this process CO₂ is captured after the complete combustion of fuels. In pre-combustion process, CO₂ is captured subsequent to gasification process i.e., before the complete combustion of syngas as shown in Fig. 4(c). In oxy-fuel combustion process, combustion of fuel takes place in

Table 1 Properties of carbon dioxide (CO₂)

Property name	Value
Molecular weight	44.01
Critical temperature	31.1°C
Critical pressure	73.9 bar
Triple point temperature	− 56.5°C
Triple point pressure	5.18 bar
Boiling point (sublimation) at 1.013 bar	− 78.5°C
<i>Gaseous phase</i>	
Gas density at standard temperature and pressure (STP)	1.976 kg/m ³
Specific volume at STP	0.506 m ³ /kg
C _p at STP	0.0364 kg/mol-K
C _v at STP	0.0278 kg/mol-K
Specific heat ratio (C _p /C _v) at STP	1.308
Viscosity at STP	13.72 μPa s
Thermal conductivity at STP	14.65 mW (m/K)
Solubility in water at STP	1.716 vol/vol
Enthalpy at STP	21.34 kJ/mol
Entropy at STP	117.2 J mol/K
Enthalpy of formation at STP	213.8 J mol/K
<i>Liquid phase</i>	
Vapor pressure at 20°C	58.5 bar
Liquid density at − 20°C and 19.7 bar	1032 kg/m ³
Viscosity at STP	99 μPa s

Note: IPCC, 2005. IPCC Special Report on Carbon dioxide Capture and Storage. New York: Cambridge University Press.

**Fig. 3** Various anthropogenic sources of CO₂ with overview of CCS.

presence of pure (90%–95%) oxygen. Hence, flue gas contains mainly CO₂ and H₂O. CO₂ can be separated by condensing moisture in the flue gas and simple purification process as shown in Fig. 4(d). More details of these processes are discussed later.

Overview of Materials for Carbon Capture

The most matured technology for low partial pressure CO₂ capture is done by amine solvents. It is the most matured technology till date. It is benchmarked against pilot scale setup. Three types of amines are used in CO₂ capture process as shown in Fig. 5.

However, most commonly used amine is monoethanol amine (MEA). In present benchmarked technology 30% aqueous MEA solvent is used to capture CO₂ from the flue gas. In this process 90% CO₂ of the flue gas may be captured. Though energy penalty

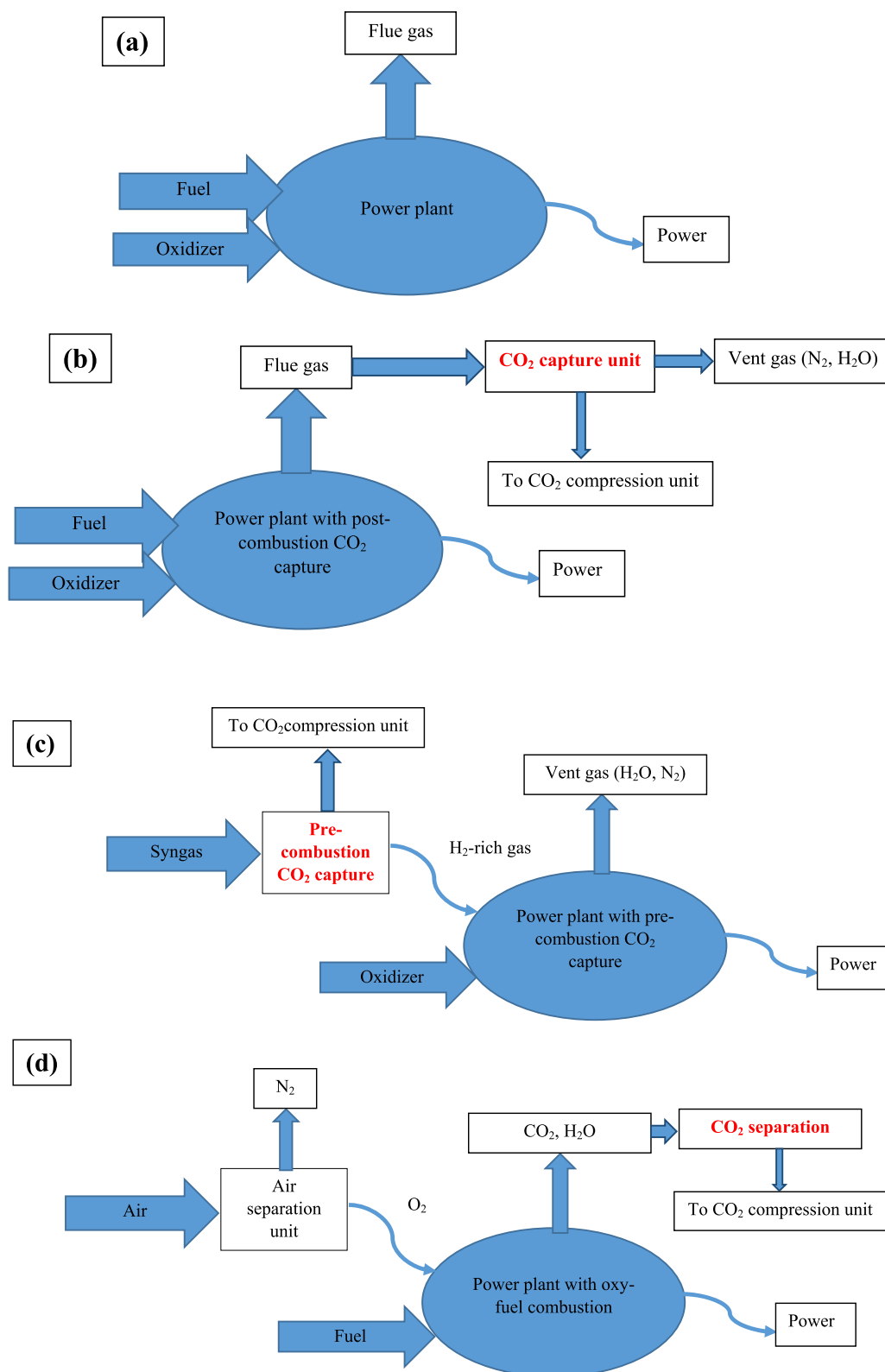


Fig. 4 Overview of power plant (a) without carbon capture, (b) with post-combustion carbon capture, (c) with pre-combustion carbon capture and (d) with oxy-fuel combustion.

Primary amine R^1NH_2

•e.g. Monoethanol amine (MEA)

Secondary amine R^1R^2NH

•e.g. Diethanol amine (DEA)

Tertiary amine $R^1R^2R^3N$

•e.g. Methyl-diethanol amine (MDEA)

Fig. 5 Types of amines used for CO₂ capture.

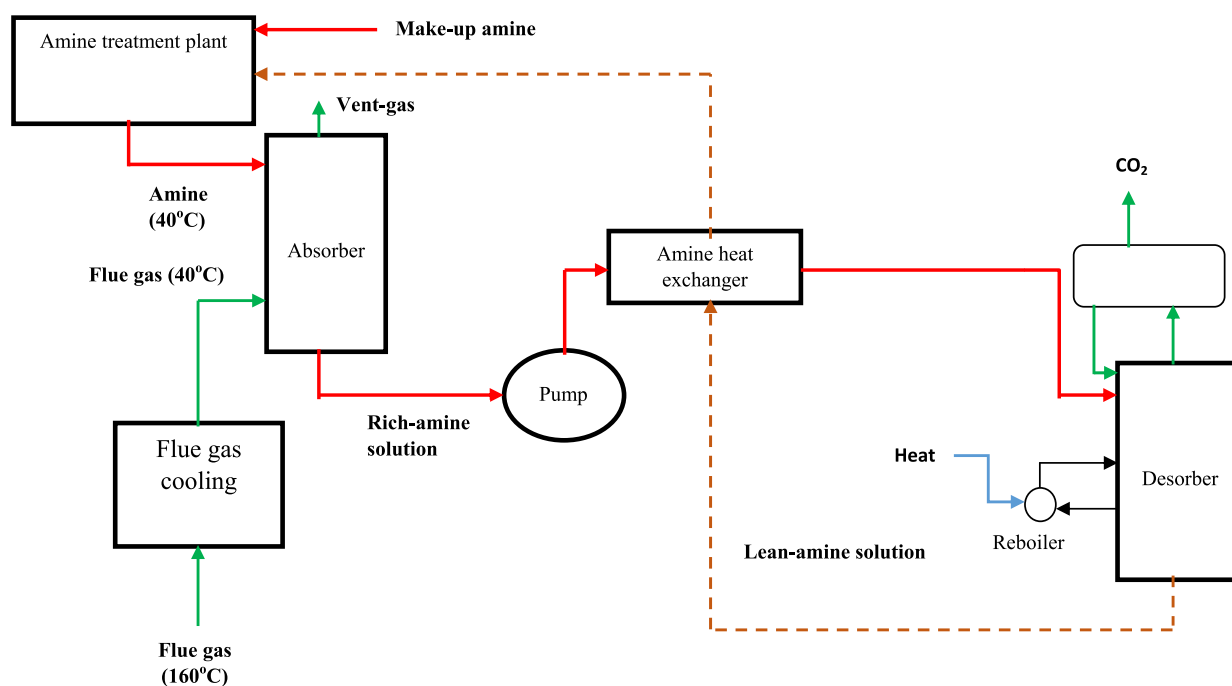
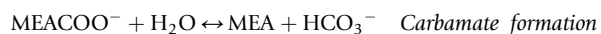
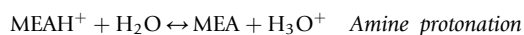


Fig. 6 Basic schematic of amine based CO₂ capture process. Reproduced from Jana, K., De S., 2016. Utilizing waste heat of the flue gas for post combustion CO₂ capture – A comparative study for different process layouts. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* 38, 960–966.

is observed in form of reboiler heat duty at a rate of 3.6–4 GJ per tonne of CO₂ captured. Detailed reaction of aqueous MEA solution with CO₂ is given below.



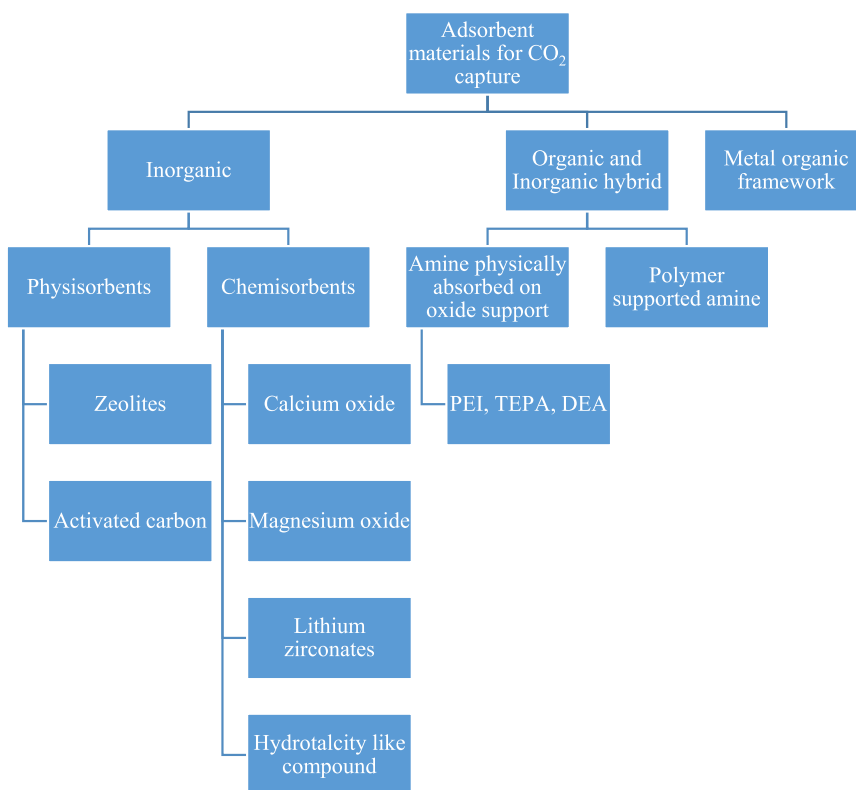


Fig. 7 Type of adsorbents for CO₂ capture.

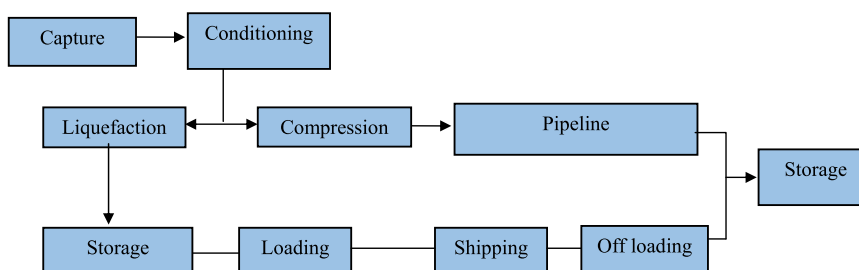


Fig. 8 Schematic of CO₂ compression, transportation and storage. Reproduced from Rackley, S.A., 2017. Carbon Capture and Storage, second ed. UK: Butterworth-Heinemann.

One of the primary objectives for development of amine properties is to reduce reboiler heat duty. Thermal degradation and oxidative degradation as well as moderate toxicity are the major disadvantages of MEA based CO₂ capture. For these reasons, development of novel sorbents is being explored. Aqueous piparazine (PZ) and 2-amino-2-methyl-1-propanol (AMP) has been studied for CO₂ capture. In some cases, blending of amines is used for experiment where one amine may complement other(s) and blending will be decided accordingly. As MEA is the most matured technology, schematic of MEA based CO₂ capture is shown in Fig. 6.

In this process, initially flue gas is cooled to 40°C. SO₂ may be removed from flue gas before entering into the absorber column. In absorber column, CO₂ is absorbed by aqueous amine solution at 40°C. Then the solution becomes rich with amine. Pressure loss in the absorber column and stripper column is compensated by pressurizing the solution using pump. Before entering to stripper column, the rich amine solution is preheated by returning lean amine solution. In stripper column, rich amine solution is heated in reboiler section. In this column, CO₂ is separated from amine solution and CO₂ is obtained in the condenser section of the stripper column.

Apart from absorption process, adsorption is a promising option for CO₂ capture from flue gas (Choi *et al.*, 2009). In this process CO₂ is held on the surface of adsorbing material and it is regenerated by applying various techniques like pressure swing adsorption (PSA) or temperature swing adsorption (TSA). Better selectivity, higher capacity and better tolerance to the impurities are the main research area of adsorption based CO₂ capture. Also reducing the energy intensity of the process is another area of

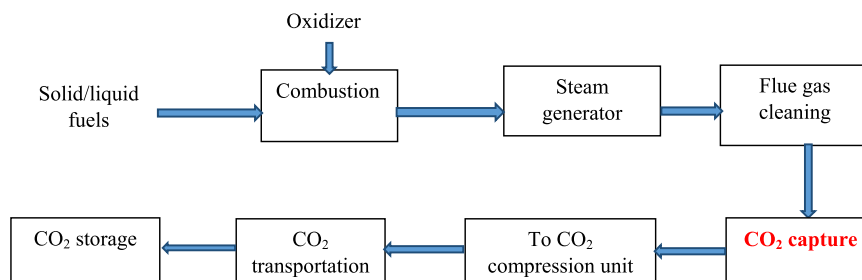


Fig. 9 Schematic of power generation with post-combustion CCS.

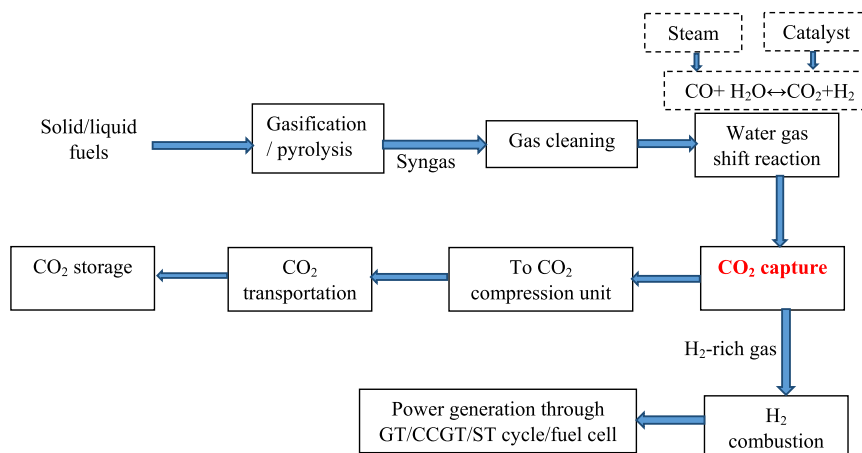


Fig. 10 Schematic of power generation with pre-combustion CCS.

research. Different types of adsorbent are shown in Fig. 7. In general, adsorbent materials are organic, inorganic, inorganic hybrid and metal organic framework. However, this adsorption process for CO₂ capture is yet to be commercially available. It is at the research and development stage.

CO₂ Transportation and Storage

After capturing CO₂, it has to be transported to the suitable sites for storage. Transportation may be done by pipeline, by container or by ships. Transportation technology is matured for gas transportation, oil transportation or water transportation. Transportation of CO₂ at atmospheric pressure is difficult due to its large volume. The schematic of various steps of CO₂ compression, transportation and storage is shown in Fig. 8. Before CO₂ is compressed, it is conditioned to remove impurities like H₂S and other corrosion elements. Then it is compressed and transported to the desired site. The compression may be done in multiple steps of intercooling to reduce the energy consumption. However, pressure of CO₂ transportation is maintained between 10 and 80 MPa. Otherwise it is liquefied and transported through container and then by ships. Pipeline should be avoided from populated area to avoid the risk of leakage.

After transportation, CO₂ is stored in various ways like geological storage, ocean storage and mineral carbonation. It may be used for value added services like enhanced oil recovery (EOR), enhanced coal bed methane (ECBM) recovery etc. These are the geological storage options for CO₂ capture. However, EOR and ECBM are commercially available. In geological storage, CO₂ is stored under suitable impermeable rock formations (caprock). However, cost of CO₂ storage depends on site and it may vary widely from 0.6 to 8.3 US\$ per tonne of CO₂ (IPCC, 2005). CO₂ may be stored in depleted oil and gas reservoir where oil and gas was stored due to suitable geological formation. However, leakage should be avoided. It may create health hazards for local plant or may affect local minerals. Ocean can be a great storage option for CO₂. In this process CO₂ is injected into the ocean from ship or suitable pipeline at a certain depth. In ocean, CO₂ may be kept away from the atmosphere for centuries. CO₂ may be stored in the form of inorganic carbonates or may be utilized for value added products as discussed later.

Integration of CCS

In Fig. 9, schematic of carbon path in post-combustion CO₂ capture is shown. From the figure it is noted that combustion of carbon containing solid or liquid fuel (mainly coal) takes place in combustion chamber or in furnace with an oxidizer like air.

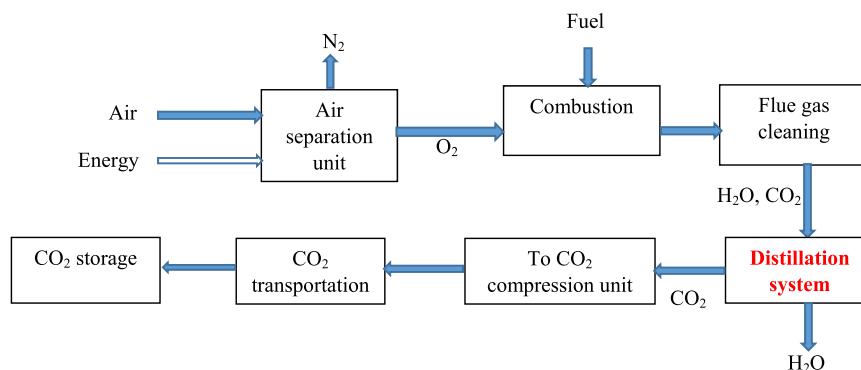


Fig. 11 Schematic of power generation with oxy-fuel combustion.

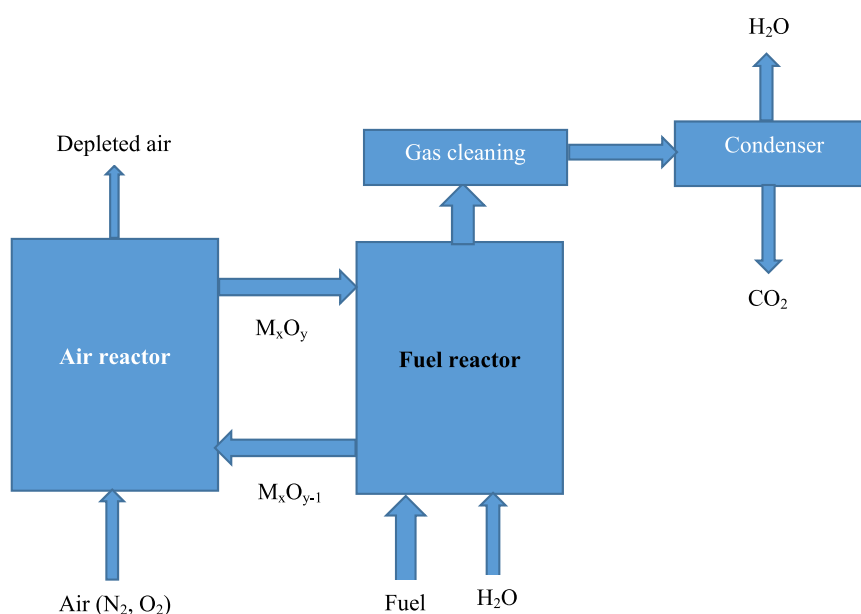


Fig. 12 Chemical looping combustion for CO₂ separation.

Then hot flue gas passes through the steam generator or boiler. It transfers heat to generate steam which is used in steam turbine for power generation. Then flue gas is cleaned for solid particles with filters or electrostatic precipitator (ESP) for coal based power plant. After that flue gas is cooled down to 40°C for applying MEA based CO₂ capture process as discussed earlier. After capturing the CO₂, it is compressed, then transported and stored in suitable site. However, this carbon capture process may be integrated with newly designed plant or it may be retrofitted with existing plant. Hence, for existing plant post combustion CO₂ capture process is preferred.

In **Fig. 10**, power generation with pre combustion carbon capture process is shown. In this process carbon containing fuel is not directly combusted. It is gasified or pyrolyzed to produce a syngas. Depending on the fuel properties and operating condition of the gasifier, syngas may contain H₂, CO₂, CO, H₂O, CH₄ with varying fractions. To decrease the CO percentage and to increase the CO₂ content in the syngas, water gas shift (WGS) reaction is executed in the WGS reactor as shown in **Fig. 10**. In this process, steam is the input to convert CO and to produce H₂ in the presence of suitable catalyst. To avoid catalyst poisoning, depending on the type of catalyst gas cleaning process is done before the WGS reaction. After WGS reaction, CO₂ content in syngas becomes high and it may be captured by various commercial solvents like Selexol[®], Rectisol[®] etc., CO₂ is further transported and stored at suitable location. After capturing CO₂, syngas becomes H₂-rich. This H₂ may be directly used in fuel cells or may be used for combustion in gas turbines (GT), combined cycle gas turbines (CCGT) or in steam generators of steam turbine (ST) cycles.

Another option for CO₂ capture is oxy-fuel combustion. The schematic of power generation through oxy-fuel combustion is shown in **Fig. 11**. In this process, combustion takes place with almost pure oxygen. To produce pure oxygen (90%–95%), air separation unit (ASU) is integrated. It requires significant amount of energy. It is the main drawback of this process. After

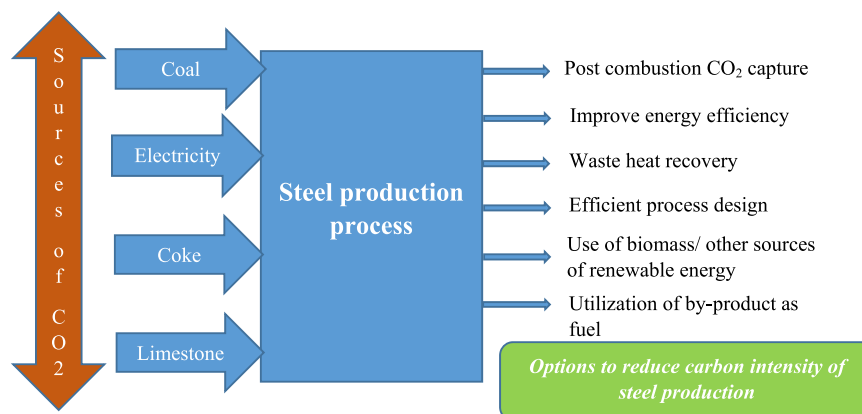


Fig. 13 Sources and options for CO₂ emission reduction in steel production process.

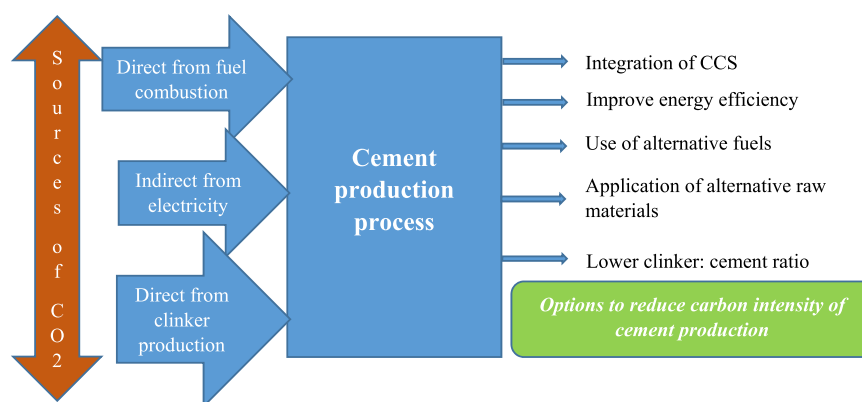


Fig. 14 Sources and options for CO₂ emission reduction in cement production process.

combustion flue gas contains mainly H₂O and CO₂. CO₂ is separated after the condensation and further distillation of the flue gas. Then separated CO₂ is compressed, transported and stored at the desired location.

Chemical looping combustion process is shown in Fig. 12. In this process oxygen is carried by metal oxides. In air reactor, metal oxide reacts with air and becomes oxidized. Then it is transported to the fuel reactor. However, in this reactor, fuel is oxidized and metal oxide is reduced. Then the reduced metal oxide is fed to the air reactor for oxidation. Similar to oxy-fuel combustion, in this process, flue gas contains only H₂O and CO₂. By condensing the flue gas, CO₂ may be separated in a comparatively easier process.

In steel production, significant amount of CO₂ is emitted. In 2010, total CO₂ emission was 2500 million tonnes from steel industry. In this process several sources of direct and indirect CO₂ emission are observed. In Fig. 13, sources as well as potential for reduction of CO₂ is shown. The main source of CO₂ emission is coking coal which is used to reduce iron ore. To produce 1 tonne of steel 770 kg of coking coal is required (ULCOS, 2013). Apart from coking coal, electricity and limestone inputs are the other sources of CO₂ emission in steel production. To reduce the carbon intensity of steel production, post combustion CO₂ capture may be integrated with steel production process. Increase in energy efficiency and/or waste heat recovery is other option. Apart from these, use of renewable energy, efficient process design and utilization of products may reduce carbon emission from steel production. Another significant carbon intensive process is cement production. The sources and potential options to reduce CO₂ emission is shown in Fig. 14 (IEAGHG, 2013). In cement production process clinker is the main source of CO₂. Indirect emission due to electricity use and direct emission due to fuel combustion are the other two sources of CO₂ emission. To reduce CO₂ emission, integration of CCS and improvement in energy efficiency may be implemented. Use of alternative fuels and materials and low clinker to cement ratio may improve carbon intensity of the cement production process.

Options for Carbon Capture and Utilization

As stated earlier, carbon capture is energy intensive process and it is reflected on the economic performance of the plant. It reduces the output electricity. As a result, per unit electricity prices increases. Also significant economic investment is required. This may be offset by utilizing the captured CO₂ to value added product and services (Hu et al., 2013). In Fig. 15, different source of CO₂ and its utilization pathways are shown. The captured CO₂ may be used directly in enhanced oil recovery, enhanced gas recovery. In

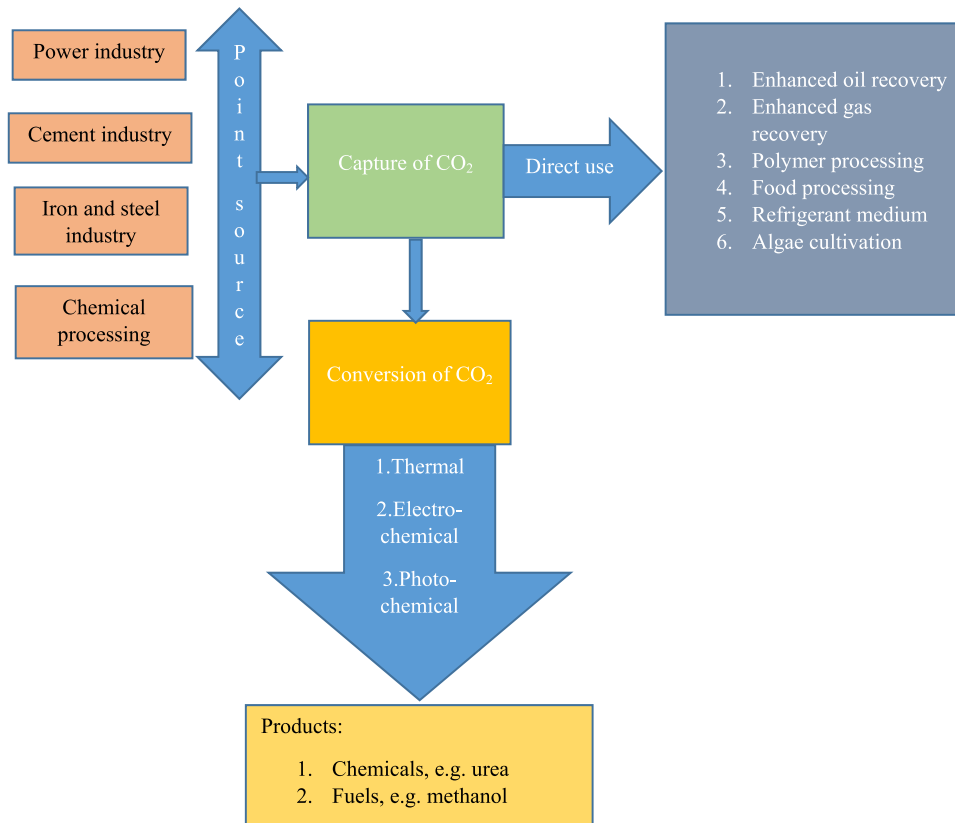


Fig. 15 CO₂ capture and utilization (CCU) pathways.

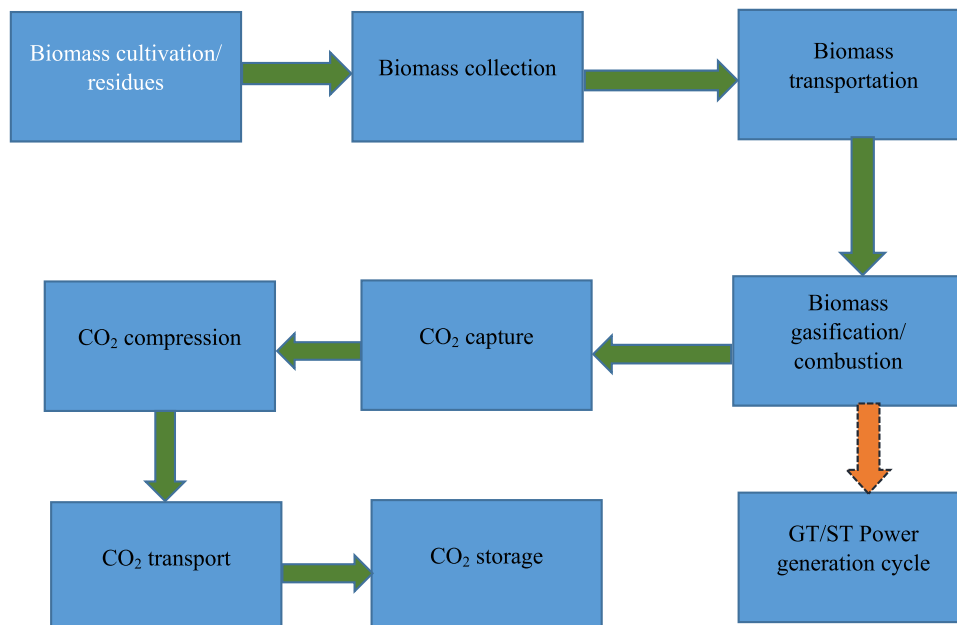


Fig. 16 Biomass based power generation integrated with carbon capture and storage.

these cases, CO₂ is transported and injected into the geological rocks where recovery of oil and gas are enhanced. CO₂ may be used in polymer processing, food processing. It may be used as refrigerant media also. Algae cultivation is one of the promising areas of CO₂ utilization. For this case the growth of algae is enhanced by consuming captured CO₂. There are mainly three routes for conversion of CO₂ into value added products. These are thermal, electro-chemical and photo-chemical. The conversion of CO₂

Table 2 Present status of different carbon capture and storage technology

Formulation	Lab test	Lab prototype	Lab scale plant	Pilot plant	Demonstration	Commercial
Ocean storage ^a	Post-combustion ionic liquids ^b	Oxy-combustion gas turbine ^b	Inorganic membranes for H ₂ separation ^b	Polymeric membranes ^b	Pre-combustion IGCC + CCS ^b	Post-combustion amines ^b
	BECCS			Chemical carbonate looping ^b	Oxy combustion coal power plant ^b	Pre-combustion NG processing ^b
	Material storage ^c			Chemical looping combustion ^b	Post-combustion adsorption ^b	Onshore and off-shore pipelines for transport ^c
				Non EOR CO ₂ utilization ^d	Direct air capture ^b	Ship transport ^c
					CO ₂ EGR ^d	Saline formation ^a
						CO ₂ -EOR ^d

^aStorage.^bCapture.^cTransport.^dUtilization.Note: Bui, M., *et al.*, 2018. Carbon capture and storage (CCS): the way forward. Energy and Environmental Science 11, 1062–1176.**Table 3** Performance of new power plant based on current technology

Parameters	New pulverized coal plant	New IGCC plant	New NGCC plant
Emission without CO ₂ capture (kg CO ₂ /MWh)	736–811	682–846	344–379
Emission with CO ₂ capture (kg CO ₂ /MWh)	92–145	65–108	40–66
Plant efficiency with capture, LHV basis (%)	30–35	31–40	47–50
Percentage increase in capital cost with carbon capture	44–74	19–66	64–100
Cost of electricity without carbon capture (US\$/MWh)	43–52	41–61	31–50
Cost of electricity with carbon capture (US\$/MWh)	62–86	54–79	43–72
Cost of CO ₂ captured (US\$/t CO ₂)	23–35	11–32	33–57
Cost of CO ₂ avoided (US\$/t CO ₂)	29–51	13–37	37–74

Note: IPCC, 2005. IPCC Special Report on Carbon dioxide Capture and Storage. New York: Cambridge University Press.

mainly depends on the catalyst development. Good energy efficiency, high conversion rates are other parameters to consider successful applications of CO₂ utilization. To convert CO₂, input energy is preferred from renewable resources like solar energy, wind, biomass to reduce the overall life cycle CO₂ emission. In this conversion, CO₂ may produce fuels like CO, CH₃OH, HCOOH etc., or it may produce chemicals like urea, polymers etc., as shown in Fig. 15.

Negative-CO₂ Emission Technology

To reach the 'goal of 2°C', net-CO₂ negative plant can be a suitable option. When CO₂-neutral fuel is used with CO₂ capture, then net life cycle CO₂ emission may become negative. Biomass is a suitable net-CO₂ neutral fuel. In this case, CO₂ absorbed during its growth phase is equivalent to the CO₂ emission during its use. However, transport and other logistics of biomass may add some CO₂ to the environment. Otherwise, direct air capture (DAC) of CO₂ may be a net negative-CO₂ emission technology. In Fig. 16, schematic of a biomass based power generation with carbon capture and storage is shown. In this process, firstly, woody biomass or agricultural residues are collected. Then it is pre-processed and transported. After that combustion or gasification process is done to produce hot flue gas or syngas. Flue gas or syngas is utilized for gas turbine or steam turbine power generation. CO₂ is captured from the flue gas (post combustion capture) or H₂-rich syngas (pre combustion capture). Then the captured CO₂ is compressed, transported and stored. Direct air capture (DAC) is another net negative CO₂ technology. In this process CO₂ is captured from the air and stored.

Status of Present Carbon Capture and Storage Technology

In the context of COP21 and Paris agreement, carbon capture and storage technology will have significant impact to keep the temperature rise below 2°C of pre-industrial age. Though a few projects are commercially operating, many areas need suitable research and development for successful implementation of CCS. The different stages associated with CO₂ capture, transport, storage and utilization technology are given in Table 2. From the table, it is noted that CO₂ capture by aqueous amine

solution was commercially available for natural gas processing. Also on-shore and off-shore pipeline is commercially available for EOR projects. Transportation by ship and saline formation technologies are also commercialized. However, pre-combustion CCS for IGCC, adsorption CO₂ capture, direct air capture etc., are in demonstration stage only. Chemical looping, non-EOR CO₂ utilization etc., are in pilot plant stage. Further research is needed to commercialize these technologies. Other technologies of CCS and utilization are at lab scale. Suitable research and development is necessary to scale-up and successful implementation of these technologies through commercialization. However, performance of newly built plant with or without CCS is given in Table 3. In this table, potential of CCS to reduce CO₂ emission and its economic penalty are given. It is noted that significant amount of CO₂ emission can be avoided through CO₂ capture. However, it decreases the overall plant efficiency and hence cost of electricity increases. As a result, significant economic penalty is generally inevitable to avoid CO₂ emission.

Conclusion

Anthropogenic CO₂ emission is the main reason behind global warming. CCS may play an important role in this context to reduce the anthropogenic CO₂ emission from the energy sector. Though CCS is facing many challenges, a few technologies of CCS are commercialized, say, amine based post combustion CO₂ capture was in operation previously in the case of natural gas processing. However, many advanced CCS technology are in the stage of research and development or in laboratory scale. Absorption, adsorption, oxy-fuel combustion and chemical looping are mostly the available technologies of CO₂ capture. However, monoethanol amine (MEA) based post combustion CO₂ capture is the most matured technology. Off-shore and on-shore pipeline transportation and transportation by ships are commercially available technologies. Utilization of CO₂ for enhanced oil recovery is presently being used in practical operation. However, other CO₂ utilization technologies such as chemical production, fuel production need further research and development. Bioenergy with CCS and direct CO₂ capture from air are the options for net negative CO₂ emission. Apart from energy sector, CCS may be integrated with carbon intensive industries like iron, steel, cement industries also.

See also: Biomass for CO₂ Sequestration. Carbon Management and Greenhouse Gas Mitigation. CO₂ Capture, Storage, and Enhanced Oil Recovery Applications. Geological Storage of CO₂ to Reduce Greenhouse Gases. Nanomaterial for CO₂ Sequestration. Sustainable Carbon Di-Oxide Sequestration Using Photosynthetic Reactions

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Plasma Arc Driven Solid Waste Management: Energy Generation and Greenhouse Gases (GHGs) Mitigation

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Introduction

Industrial revolution and economic growth are accumulatively accelerating the urbanization and change in societal way of living. This factor along with population explosion is directing the whole community towards the consumption of non-renewable resources. The shifting trend from renewable to non-renewable resources is leading to the generation of waste mountains and addition of a large volume of long-lived Greenhouse Gases (GHGs) e.g., (CO_2 , CH_4 , N_2O) and several other fluorinated gases into the atmosphere ([Environmental Protection Agency \(EPA\), 2016a](#)). Solid wastes make an entry into the main stream in the form of MSW and creates various environmental and health hazardous issues ([Environmental Protection Agency \(EPA\), 2009](#)). In 2011, worldwide the amount of MSW is around 2 billion tones and the growing rate is faster than urbanization. It is expected that this faster growing rate will accelerate the waste generation which will touch 10 billion tons within 2050 ([Chen, 2016](#)). Thus, proper handling and disposal of MSW through an environmental friendly, economically viable system is an utmost necessity for every nation in this world ([Intergovernmental Panel on Climate Change \(IPCC\), 2006a](#); [Rajaeifar et al., 2017](#)). Now days, waste disposal system is categorised in regular (like landfilling, incineration) and proximal (like Refuse derived fuel, gasification) methods. In general, regular processes are found to work more in number than the proximal ones, however, the harmful impact on environment is also more prominent in case of regular ones. Incineration and landfilling are the more common practices among the waste disposal systems. Presently, landfilling is executed to minimize the waste amount from our living space by simply dumping in a particular area. Subsequently, Incineration is become another frequent practice to minimize the waste volume by simple burning in a concise place or chamber. These practices are effectively causing high amount of greenhouse gas emission and health hazard issues for livelihood as well as for the environment. Despite of requirement of large land and transportation cost, most frequently landfilling is used for waste disposal but it is also responsible for adding high extent of GHGs to the atmosphere. Similarly, incineration can be beneficial in line with waste volume destruction but in addition it releases environmentally toxic greenhouse gases like SO_x , NO_x ([Wanga et al., 2017](#)) too and other hazardous chlorinated dioxins and furans ([Rajaeifar et al., 2017](#)).

In greenhouse gas emission related issues, it was estimated that globally around 46 billion metric tons of greenhouse gases were emitted in our environment during 2010 by only human activities ([Environmental Protection Agency \(EPA\), 2016b](#)). The energy generation sectors are one of the major contributors of GHGs to the atmosphere. In 2010, annual CO_2 emissions from these sectors were about 25% of total CO_2 emissions throughout the world. Some other sectors like agriculture, forestry, other land use together contribute 24% while industry alone contributes about 21% ([Intergovernmental Panel on Climate Change \(IPCC\), 2014](#)). Waste and waste disposal methods contribute a 3%–4% share of total GHGs emission ([Intergovernmental Panel on Climate Change \(IPCC\), 2006b](#)). However on the basis of per capita GHGs emission India stands on the fourth position in GHGs release throughout the world. After China, USA and European Union, at present India is holding this position releasing around 3000 metric tons of GHGs which is only 6.5% of total GHG emission. Similarly, continuous economic growth and population expulsion directed towards rapid urbanization which makes Indonesia, Brazil, Mexico and Iran a bigger contributor to the total world GHGs emission ([Baumert, 2017](#)). But it has been observed that during 1994 and 2007 the rate of GHG generation from waste products disposal has increased to about 7.3% while total 6% increase has been observed in the others sectors like electricity, transport, energy, residential, agriculture, cement, iron and steel plant ([INCCA: Indian Network for Climate Change Assessment, 2010](#)).

Reduction of waste generation at source is very much less effective that makes the waste generation and resource consumption a parallel process. Improper waste management and GHGs emission are the inevitable process. Thus proper waste management can minimize the waste quantity and as well as can reduce the GHGs emission for the waste sectors. In this regard, the proximal process plays an efficient role with high volume reduction efficiency and minimal release of toxins ([Rajaeifar et al., 2017](#)).

Accounting for suitable methods, Plasma arc technology is marked as most efficient methods with high waste destruction efficacy, negligible amount of toxin release, producer of high calorific value syngas which assists in energy recovery. The residual part is vitrified into a non-leachable inert material like slag which is very good constituent in developing building as constructional materials ([Janajreh et al., 2013](#)). In the wastes generated the main counterparts of MSW are solid combustible materials like plastic, textile, paper which has high energy recovery potential ([Rajaeifar et al., 2017](#)). In this technology, organic materials directly come in to contact with the high temperature plasma flame operated by plasma torches. In this plasma driven operation CO_2 emission is

reasonably less owing to the absence of O₂ like oxidant (Byun *et al.*, 2010). It also restricts the formation of various toxic pollutants like dioxin, furan (Gomez *et al.*, 2009; Moustakas, 2005). Oxygen starved condition also helps to break down the waste material into gases which have high content of syngas (CO, H₂). It can be utilised in a gas engine for electricity generation or used as a feed stock for generation of bio-fuels like methanol, which is a next generation fuel. Methanol is always a suitable option for fuel cells as a source of hydrogen. In production of some important synthetic fuels like dimethyl ether (DME), methanol is used as an intermediate chemical (Ma *et al.*, 2009). In future, methanol can help to meet the energy requirement either through direct use or as indirect feed stock. It clearly indicates the necessity of methanol production in cost effective way which is of utmost necessity. Syngas is a prime feedstock for methanol production due to high content of carbon monoxide (CO) and hydrogen (H₂). Conventionally, natural gas and oil are the main source of syngas but uninterrupted supply of these sources is not affordable in coming days. Exhaustive use and uncontrollable burning of fossil fuel has already stood our environment in facing a serious threat about Global warming due to massive GHGs emission (Bermúdez *et al.*, 2010). Syngas production from MSW through gasification by a plasma arc driven system is an energy efficient method. Herein the feedstock comprises of discarded waste materials, indicates its cost effectiveness in production of syngas as well as in production of methanol. This approach could be a solution to reduce the use of fossil fuel and finally a significant reduction in GHGs emission.

Implementation of plasma arc technology in MSW destruction with energy recovery could be an effective solution towards GHGs emission. The significance of this method is that the outcome products can be further utilised for electricity, heat or fuel generation. This concept has unique points like reducing the dependency on renewable resources, decreasing the fossil fuel consumption which leads to lessening the emission of Greenhouse Gases (GHGs). Accordingly, waste consumption in energy recovery process leads to high volume reduction and reduces the load on landfilling. Waste to energy generation is now-a-days a rising process path throughout the world for producing energy (Rajaeifar *et al.*, 2017).

Results and Discussions

Municipal Solid Waste

Municipal solid waste is the most frequently generated waste around the world. Its composition depends on geographical position, population, people's life style, economic growth, urbanization, *etc.* For this reason there is a significant variation in MSW composition and total waste generation. In respect of waste generation, United States of America (USA) comes first in the list with 254.1 million tons of MSW generated in 2013. A sudden surge in waste generation has been observed from 1960 to 2013 *vide* (Table 1; Rajaeifar *et al.*, 2017).

In this timeline, there is a significant increase in population which results in increment of quantity of MSW generation as well as the per capita MSW generation. During the same period, there is two-third time increment in Per capita MSW generation (Environmental Protection Agency (EPA), 2013, 2015; United States Census Bureau, 2015). Accordingly, European Union (EU) with its 27 member in 2013 generates around 241 million tons of MSW. From 1995, population and waste generation increases abnormally in a linear fashion, while there is slight increase in average per capita waste generation (0.2 kg/person/day) (Table 2; Rajaeifar *et al.*, 2017). However, the variation rang of per capita waste generation is very much wide (747–272 kg) depending upon the population distribution, global position and waste management processes *etc* (European Commission statistics (Eurostat), 2015a, 2015b; European Environment Agency (EEA), 2015).

In respect of per capita MSW generation, Australia is one of the major contributors. But surprisingly; there is a fall (7.6%) in per capita MSW generation during 1980–2013 (Table 3). This value of per capita generation reside at 1.77 (kg/person/ day) in 2013 which is also significantly high (Statista, 2015; Australian Bureau of Statistics, 2015; Organisation for Economic Co-operation and Development (OECD), 2015a, 2015b).

Table 1 Total MSWs generation (in million tons) in the USA with increasing Population (in million) during 1960–2013

Year	Population (million)	Total MSW generation (million tons)	Per capita generation(kg/person/day)
1960	180.7	88.1	1.22
1965	194.3	104.4	1.34
1970	205.1	121.1	1.47
1975	216	127.8	1.47
1980	226.5	151.6	1.66
1985	237.9	166.3	1.74
1990	249.6	208.3	2.07
1995	266.3	217.3	2.05
2000	282.2	243.5	2.15
2005	295.3	253.7	2.13
2010	309.3	250.6	2.01
2013	316.5	254.1	2.00

Data Source: Rajaeifar, M.A., Ghanavati H., Dashti, B.B., *et al.*, 2017. Electricity generation and GHG emission reduction potentials through different municipal solid waste management technologies: A comparative review. Renewable & Sustainable Energy Reviews 79, 414–439.

Table 2 Total MSWs generation (in million tons) in the European Union (EU)-27 with increasing Population (in million) during 1960–2013

Year	Population (million)	Total MSW generation (million tons)	Per capita generation(kg/person/day)
1995	476.96	225.60	1.30
1999	481.63	246.11	1.40
2003	486.33	249.98	1.41
2005	491.39	253.56	1.41
2006	493.00	257.35	1.43
2007	494.78	259.26	1.44
2008	496.75	258.81	1.43
2009	498.96	254.97	1.40
2010	499.93	251.96	1.38
2011	500.51	249.25	1.36
2012	499.95	244.48	1.34
2013	502.16	241.54	1.32

Data Source: Rajaeifar, M.A., Ghanavati H., Dashti, B.B., *et al.*, 2017. Electricity generation and GHG emission reduction potentials through different municipal solid waste management technologies: A comparative review. *Renewable & Sustainable Energy Reviews* 79, 414–439.

Table 3 Total MSWs generation (in million tons) in the Australia with increasing Population (in million) during 1960–2013

Year	Population (million)	Total MSW generation (million tons)	Per capita generation(kg/person/day)
1980	14.69	10.28	1.92
1999	17.07	11.78	1.89
2000	19.15	13.22	1.89
2009	21.78	14.09	1.77
2010	22.07	14.30	1.78
2013	23.10	14.95	1.77

Data Source: Rajaeifar, M.A., Ghanavati H., Dashti, B.B., *et al.*, 2017. Electricity generation and GHG emission reduction potentials through different municipal solid waste management technologies: A comparative review. *Renewable & Sustainable Energy Reviews* 79, 414–439.

Continent wise, most wide range of variation in per capita waste generation is observed in Asia due to largest land area and diversity in population density. There is large difference in amount of annual waste generation and average per capita generation among the different regions of Asia. Almost 270 million tons of MSW generated from the East Asia and the Pacific Region with an average of 0.95 per capita (kg /person/day) generation. Though this per capita value is varies from 0.44 to 4.3 kg over 15 major countries of this region (**Fig. 4**) (Rajaeifar *et al.*, 2017). Among these countries, China contributes around 70% of total waste generation by this region. Eastern Europe & Central Asia region and South Asia region are on the verge of becoming the next two major contributing domain of Asia with an annual generation of 93 million tons and 70 million tons of MSW respectively. Whereas, Middle East & North Africa region generates around 63 million tons of MSW per year but the average per capita generation (1.1 kg/ person/day) is similar to Eastern Europe & Central Asia region and higher than South Asia region (0.45 kg/ person/day). The average per capita MSW generation of these regions are mainly dependant on the average per capita MSW generation by the countries depicted in the respective regions (**Fig. 1**; Rajaeifar *et al.*, 2017).

In 2012, Sri Lanka holds the highest average per capita MSW generation (5.1 kg/Capita/day) in south Asian region of Asia (**Table 4**; Hoorweg and Bhada-Tata, 2012). Comparatively in case of total MSW generation, very unfortunately India holds the leading role with 109,589 ton per day. This clearly indicates there is a sharp increase in the total annual MSW generation in every region as well as countries around this globe (Hoorweg *et al.*, 2005; Hoorweg and Bhada-Tata, 2012).

In Indian context, the situations are becoming worse considering its uncontrolled growth in population, and economical growth. brief survey reflect, India in his mid ninety's has very lesser extent of MSW (6 Million tons), however uncontrolled waste generation and unscientific waste management, mass level unawareness leads India to a huge crisis of piling near about 50 million tonnes of MSW in its 50th independence anniversary. Shockingly, in it's coming diamond jubilee it might approximately attain 300 million tons (Sharholly *et al.*, 2006). A brief sketch of total waste generation in a limited time frame is depicted for India's forty six major metro cities (**Table 5**) (CPCB: Solid waste generation in metrocities, 2017). The analysis that clearly reveals that the mega cities like Mumbai, Delhi, Kolkata, Chennai *etc.* are gathering MSWs at an alarmingly rate in the last ten years. Proper initiatives and timely action in stopping uncontrolled waste generation is the urge of the present century.

Waste Composition

Worldwide composition of MSW can be categorised in nine different types which are generated from various sources with the relative proportion *vide* (**Table 6**; Hoorweg and Bhada-Tata, 2012).

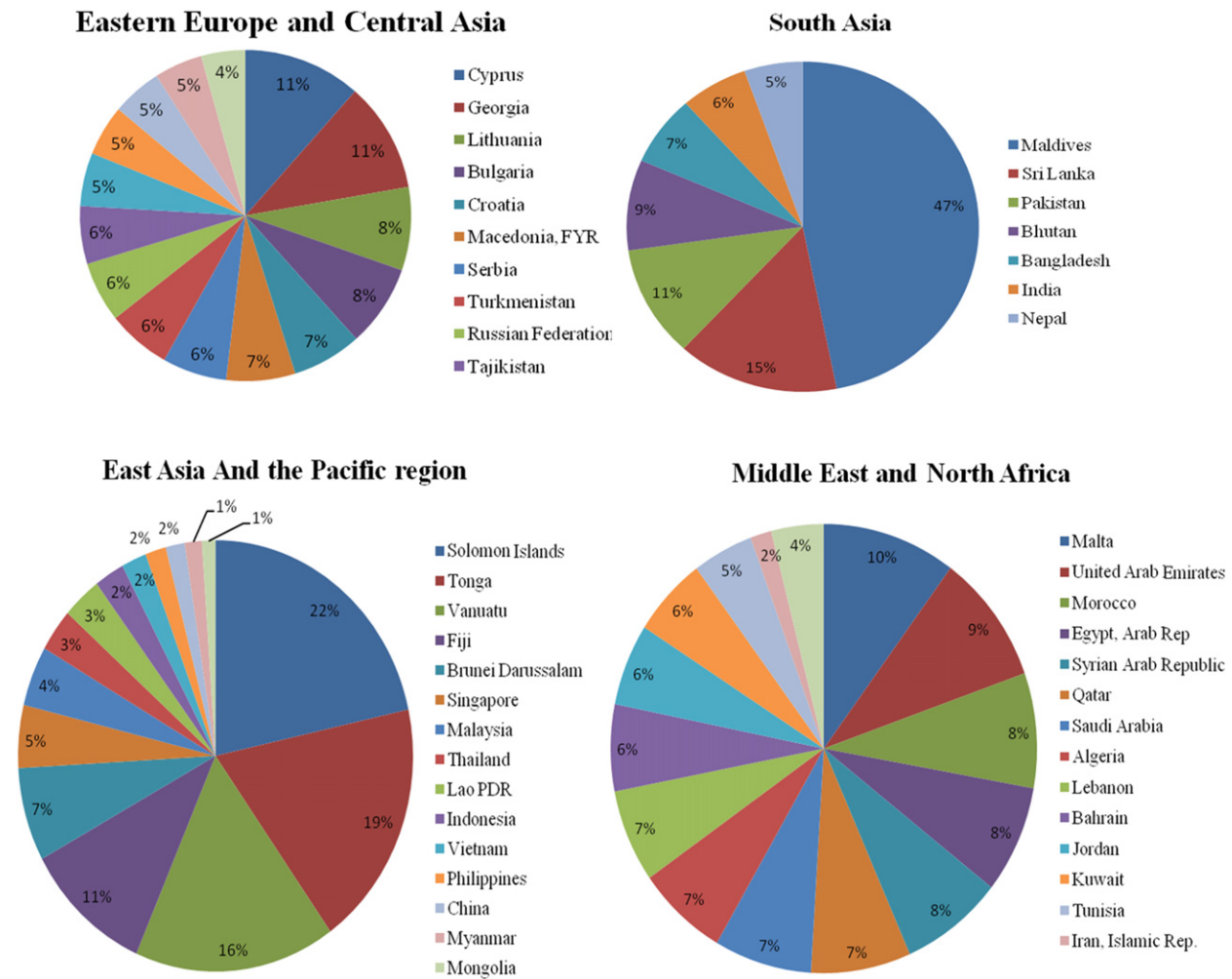


Fig. 1 Per capita MSWs generation in different regions in Asia. Data Source: Rajaeifar, M.A., Ghanavati H., Dashti, B.B., *et al.*, 2017. Electricity generation and GHG emission reduction potentials through different municipal solid waste management technologies: A comparative review. *Renewable & Sustainable Energy Reviews* 79, 414–439.

Table 4 Variation of waste generation in different countries of South Asian region

Sl no.	Countries	Total MSW generation (tonnes/day)	MSW generation per capita (kg/ capita/day)
1.	India	109,589	0.34
2.	Pakistan	50,438	0.84
3.	Nepal	427	0.12
4.	Maldives	175	2.48
5.	Sri Lanka	15,068	5.10
6.	Bangladesh	16,384	0.43
7.	Bhutan	329	329

Data Source: Hoornweg, D., Bhada-Tata, P., 2012. What a waste: A Global Review of Solid Waste Management. Washington, D.C: Urban Development & Local Government Unit, World Bank.

The variations of proportion in waste composition are also highly influenced by populations, economic development, geographical location, climate and cultural versatility *etc.* An urbanised country with economically rich people generates more inorganic fraction than organic ones in MSW. Similarly, percentage of these 6 types also effectively varies with income and shows that countries that possess higher income level are having lower organic fraction in comparison to the other income levels (Fig. 2; Rajaeifar *et al.*, 2017). Construction and demolition waste (C&D) like debris, concrete are also noticeable composition in waste materials. Here, construction and demolition waste is not taken in consideration due to its ineffectively in energy recovery process.

Table 5 Variation of waste generation in Indian cities during 1999–2016

Rank	City	Waste Generation (TPD)			
		1999–2000	2004–2005	2010–2011	2015–2016
1	Mumbai	5355	5320	6500	11,000
2	Delhi	400	5922	6800	8700
3	Bangalore	200	1669	3700	3700
4	Chennai	3124	3036	4500	5000
5	Hyderabad	1566	2187	4200	4000
6	Ahmadabad	1683	1302	2300	2500
7	Kolkata	3692	2653	3670	4000
8	Surat	900	1000	1200	1680
9	Pune(Mah)	700	1175	1300	1600
10	Jaipur (Raj)	580	904	310	1000
11	Luck now (UP)	1010	475	1200	1200
12	Kanpur (UP)	1200	1100	1600	1500
13	Nagpur (Mh)	443	504	650	1000
14	Visakhapatnam (AP)	300	584	334	350
15	Indore (MP)	350	557	720	850
16	Thane (Mh)	–	–	–	700
17	Bhopal (MP)	546	574	350	700
18	Pimpri-chinchwad (Mh)	–	–	–	700
19	Patna (Bhr)	330	511	220	450
20	Vadodara (Guj)	400	357	600	700
21	Ghaziabad (UP)	–	–	–	–
22	Ludhiana (Pb)	400	735	850	850
23	Coimbatore (TN)	350	530	700	850
24	Agra (UP)	–	654	520	790
25	Madurai (TN)	370	275	450	450
26	Nashik (Mh)	–	200	350	500
27	Vijayawada (AP)	–	374	600	550
28	Faridabad (Hr)	–	448	700	400
29	Meerut (UP)	–	490	520	500
30	Rajkot (Guj)	–	207	230	450
31	Kalian-dombivali (Mh)	–	–	510	650
32	Vasai-virar (Mh)	–	–	–	600
33	Varanasi (UP)	412	425	450	500
34	Srinagar (JK)	–	428	550	550
35	Aurangabad (Mh)	–	–	–	–
36	Dhanbad (Jh)	–	77	150	180
37	Amritsar (Pb)	–	438	550	600
38	Navi Mumbai (Mh)	–	–	–	675
39	Allahabad (UP)	–	509	350	450
40	Ranchi (Jh)	–	208	140	150
41	Howrah (WB)	–	–	–	740
42	Jabalpur (MP)	–	216	400	550
43	Gwalior (MP)	–	–	285	300
44	Jodhpur (Rj)	–	–	–	–
45	Raipur (Chh)	–	184	224	230
46	Kota (Rj)	–	–	–	–

Data Source: CPCB: Solid waste generation in metrocities, 2017 Solid waste generation in 46 metrocities: Central Pollution Control Board, India. Available at: http://cpcb.nic.in/uploads/hwmd/trend_46_cities_list.pdf.

This type of variation in MSW composition is usually deviated from region to region across the globe. In country wise material is a common phenomenon. For example in India, MSW mainly comprises of organic fractions along with waste paper, synthetic materials, waste glass, metal, inert material. This variation of MSW composition is mainly influenced by population variation in cities *vide* (Table 7; Gupta *et al.*, 2015).

On the other hand, MSW can also be classified into compostable matters and recyclable materials. Bio-Organic wastes like fruit and vegetable peels, food wastes are mainly considered as compostable matters. In this context, recyclables materials are enriched with plastic, paper, glass and metals *etc.* and moreover toxic substances like used batteries, paints, medicines, pesticides, *etc.* are common contaminants. Physical characteristics also varying from place to place and in Indian megacities (Delhi, Mumbai, Kolkata, Bangalore, Chennai) and these variations are clearly visible. Other cities and capital are having

Table 6 Different type of MSW and composition generated from different sources

Sl No.	Types	Sources	Composition
1.	Organic	Food scraps, yard (leaves, grass, brush) waste, wood, process residues	46%
2.	Paper	Paper scraps, cardboard, newspapers, magazines, bags, boxes, wrapping paper, telephone books, shredded paper, paper beverage cups. Strictly speaking paper is organic but unless it is contaminated by food residue, paper is not classified as organic	17%
3.	Plastic	Bottles, packaging, containers, bags, lids, cups	10%
4.	Glass	Bottles, broken glassware, light bulbs, colored glass	5%
5.	Metal	Cans, foil, tins, non-hazardous aerosol cans, appliances (white goods), railings, bicycles	4%
6.	Other	Textiles, leather, rubber, multi-laminates, e-waste, appliances, ash, other inert materials	18%

Data source: Hoornweg, D., Bhada-Tata, P., 2012. What a waste: A Global Review of Solid Waste Management. Washington, D.C: Urban Development & Local Government Unit, World Bank.

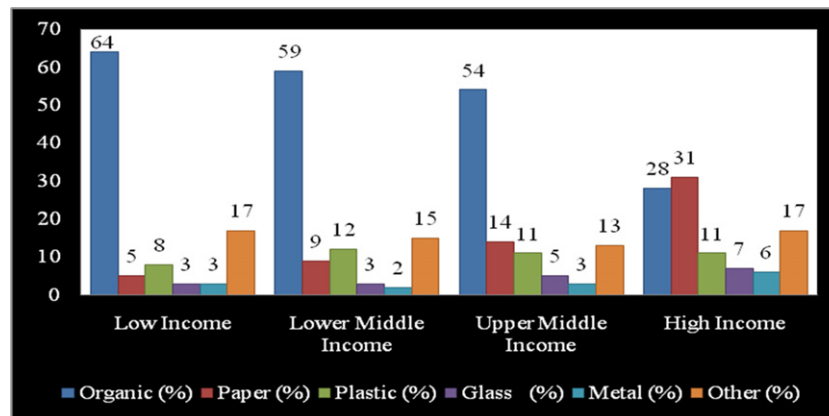


Fig. 2 Variation of MSW composition with different level of income. Data Source: Hoornweg, D., Bhada-Tata, P., 2012. What a waste: A Global Review of Solid Waste Management. Washington, D.C.: Urban Development & Local Government Unit, World Bank.

Table 7 Waste composition variation with population in India

Population series (in millions)	Cities surveyed	Organic materials	Waste paper	Synthetics materials	Waste glass	Metal	Inert material
0.1–0.5	12	44.57	2.91	0.78	0.56	0.33	43.59
0.5–1.0	15	40.04	2.95	0.73	0.56	0.32	48.38
1.0–2.0	9	38.95	4.71	0.71	0.46	0.49	44.73
2.0–5.0	3	56.57	3.18	0.48	0.48	0.59	49.07
5.0 and above	4	30.84	6.43	0.28	0.28	0.8	53.9

Data Source: Gupta, N., Yadav, K.K., Kumar, V., 2015. A review on current status of municipal solid waste management in India. Journal of Environmental Sciences 37, 206–217.

different proportion of compostable and recyclables materials (**Fig. 3; Waste Generation and Composition: Central Pollution Control Board, India, 2017**). Depending on the sources, generated MSW may be comprised of soiled waste like waste cotton, blood stained clothes, disposable syringes, sanitary napkins *etc.* which are highly infectious in line with spreading various types of diseases (Jha *et al.*, 2003).

Conventional Methods of MSW Disposal

Safe disposal of MSW is the most crucial and challenging part of waste management maintaining the environment balance and a healthy human life. Accordingly, an efficient technology for safe disposal of MSW is required to meet the environmental cleanliness. There are so many remedial methods to dispose generated MSW but no one of the existing methods is suitable enough to consider all aspects of MSW disposal. Here first of all, composting and vermi-composting are most general techniques to deal with the compostable parts of MSW. The generated manure with some amount of bio-methane (bio-gas) is one of the value added end products of this technology. Nature of wastes materials is an important factor for commercial applicability of these methods. Besides, landfilling is the most common waste disposal method for worldwide disposal of generated MSW which is also due to low cost of such technology. Landfilling is an open field where wastes are only dumped

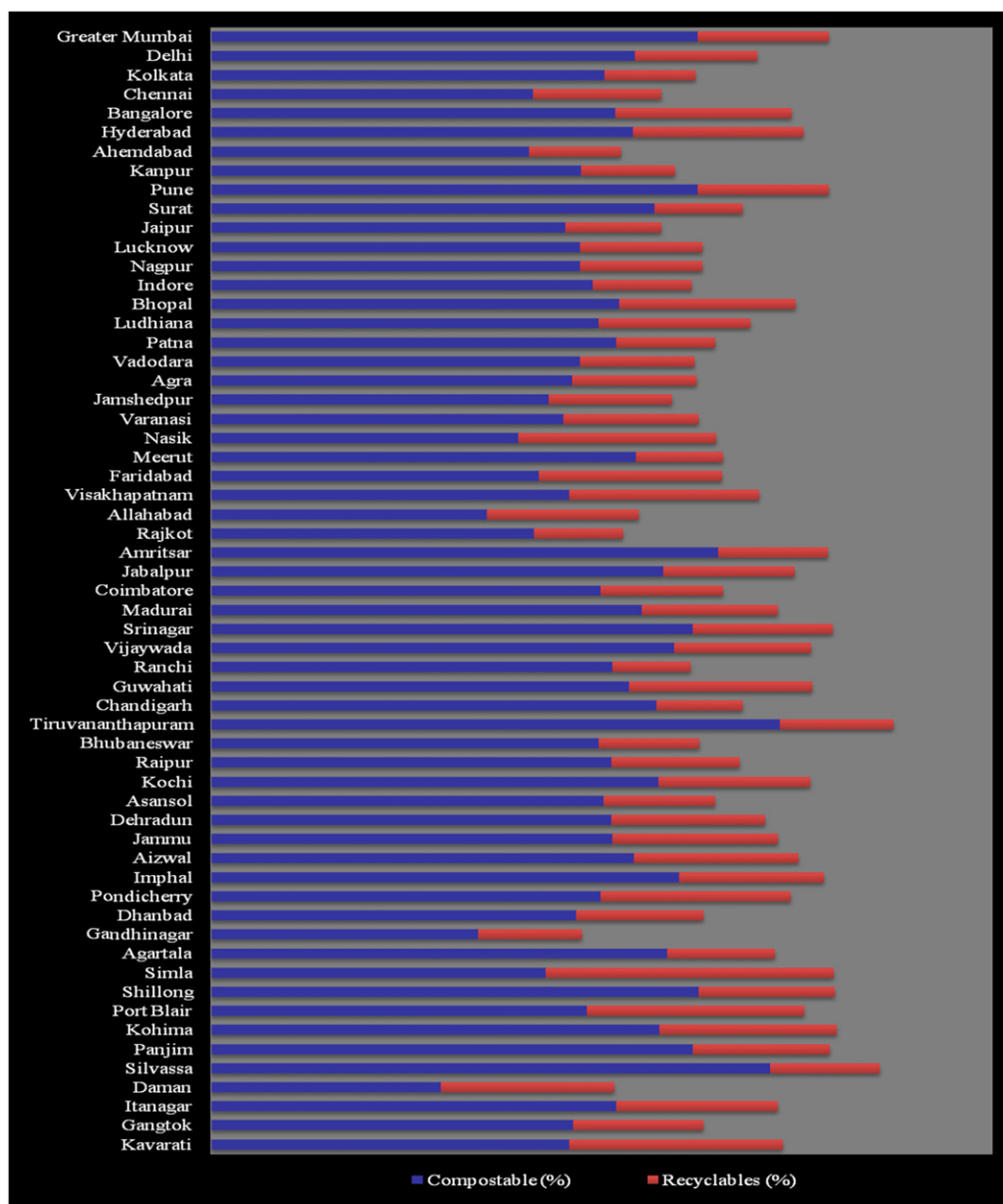


Fig. 3 Variation of compostable and recyclable material in MSW in Indian cities. Data Source: Waste Generation and Composition: Central Pollution Control Board, India, 2017. Available at: <http://cpcb.nic.in/waste-generation-composition/>.

periodically and consequently it becomes a breeding place for insects, vermin or a snitching place for rag pickers. Contaminants and toxins are exposed to the environment by these type of carriers (insects, vermin, rag pickers) (Gupta *et al.*, 1998; Giusti, 2009). In addition, Landfilling is a well known source of greenhouse gases (GHGs) among the other man made sources of greenhouse gases (GHGs). Carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) like gases is the major contributor of GHGs (Intergovernmental Panel on Climate Change (IPCC), 2013). It is estimated that in 2004, CH_4 emissions from landfills is approximately 18% of global anthropogenic CH_4 emissions. Analysis of different collective data indicates that there is a wide variation in landfill CH_4 emission during 1990–2015 (Fig. 4; Bogner *et al.*, 2008). Furthermore, it is estimated that the amount of CH_4 emission will be increased by more than three times by the middle of this century from the cities where landfilling is the major way of waste mitigation (Bogner *et al.*, 2008).

Based on reported emissions from national inventories and national communications, and (for non-reporting countries) on 1996 inventory guidelines and extrapolations (US EPA, 2006).

Based on 2006 inventory guidelines and BAU projection (Monni *et al.*, 2006).

However the requirement of large dumping space restricts the application of landfilling in many places. Here also the non-biodegradable parts of MSW are creating more problem than the compostable ones. some of non-biodegradable parts are further

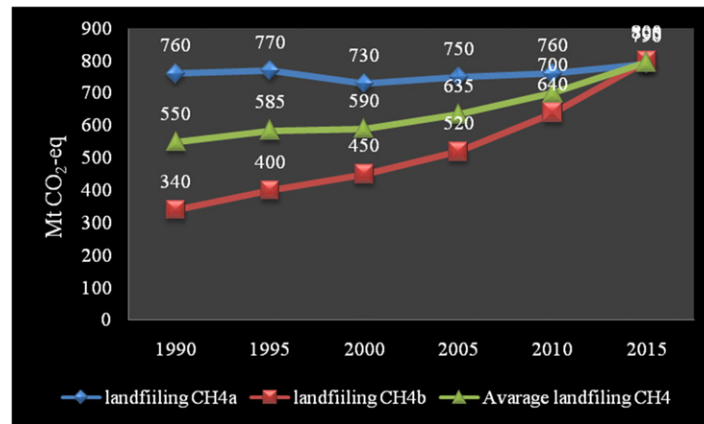


Fig. 4 CH₄ generation from landfilling. Data Source: Bogner, J., Pipatti, R., Hashimoto, S., *et al.*, 2008. Mitigation of global greenhouse gas emissions from waste: Conclusions and strategies from the Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report. Intergovernmental Panel on Climate Change (IPCC): Working Group III (Mitigation). Waste Management & Research 26, pp. 11–32.

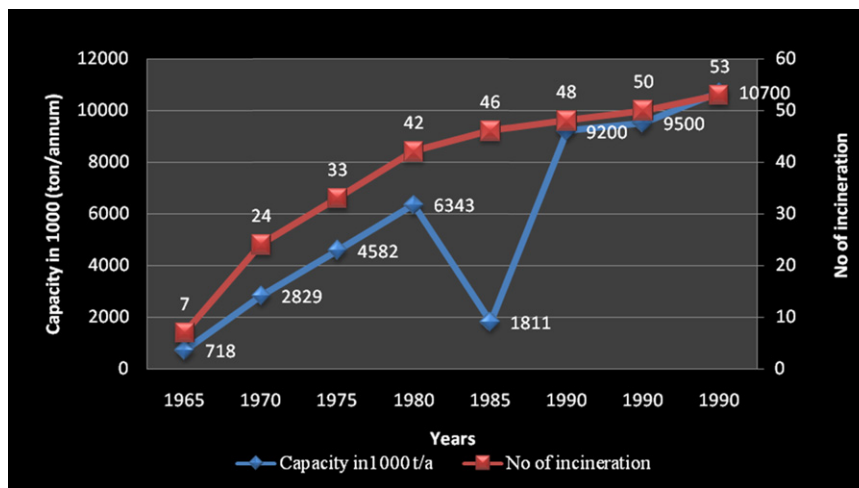


Fig. 5 Number of incineration in operation during 1968–1990 in European countries. Data Source: McKay, G., 1996. Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration: Review. Chemical Engineering Journal 86, 343–368.

recycled and rest are dumped in an unscientific manner. Their long lifetime and large volume of generation makes these wastes a threat to the environment. Consequently, incineration is one of the most frequently use method for drastic volume reduction of MSW. There is a significant increase in the number of incineration plants used and there operating capacities during 1965–1990 in Europe (Fig. 5; McKay, 1996). Incineration is a thermal treatment process where waste materials are combusted in presence of oxygen in a confined system. Herein, presence of air helps in releasing toxic gases comprising of high extent of GHGs. Apart from high percentage of CO, CO₂, HCl, SO₂, some other toxic elements like dioxins, furans and particulate matter *etc.* are generated. Particularly, the CO₂ emission from incineration varies significantly in comparison to total GHG emission in waste sectors since 1990–2015 (Fig. 6; Bogner *et al.*, 2008). The char or ash residue of Incineration usually carries toxic contaminants that make a facile entry in our food chain through aquatic bodies and other water sources. In India, usage of large and small scale incineration systems are quite familiar for MSW disposal and also in some cases a small extent of energy is recovered (United States Census Bureau, 2015).

Environment friendly waste disposal technologies with prior provision for wastes to energy recovery concepts are getting importance in India. Some technologies like Refuse-derived fuel (RDF), pyrolysis and gasification have a good efficiency in waste to energy production. In RDF, MSW are converted to pellets which act as solid fuel. These pellets are further utilised for power generation. This approach is a good attempt towards reducing the load of wastes that are dumped on landfill sites. MSW having very wide range of composition variation restricts the commercial viability of RDF (Sharholy *et al.*, 2008).

In waste to energy recovery process, Pyrolysis is considered to be an efficient thermo-chemical process where waste materials are destructed and as by-products bio-oil, gas and char is produced through application of heat. This method is generally maintained

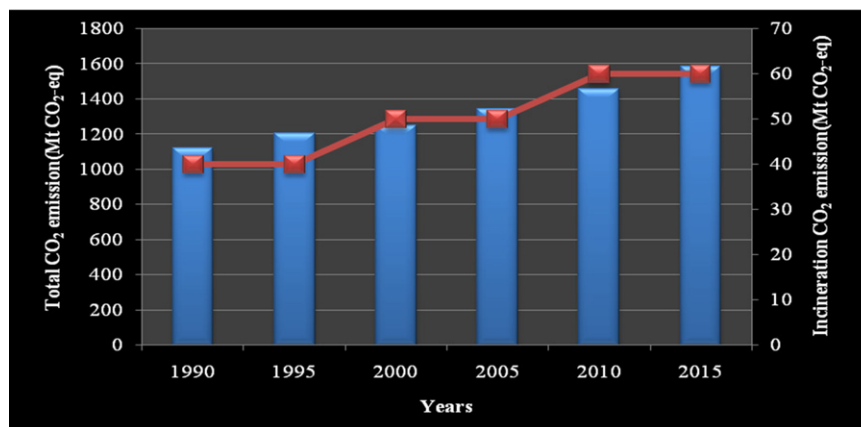


Fig. 6 Comparison between total CO₂ emission from waste and emission from incineration. Data source: Bogner, J., Pipatti, R., Hashimoto, S., *et al.*, 2008. Mitigation of global greenhouse gas emissions from waste: Conclusions and strategies from the Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report. Intergovernmental Panel on Climate Change (IPCC): Working Group III (Mitigation). Waste Management & Research 26, pp. 11–32.

in an oxygen starved system but it readily generates high concentration GHGs like CO and some other toxins due to low temperature conversion (Sharholy *et al.*, 2008; Rogner *et al.*, 2007).

Greenhouse Effect and Its Impact

Global Warming has emerged as a threat to the civilized world in the last century. The developing as well as developed countries has made their significant contribution for controlling of Global Warming. The emerging GHGs as carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), hydro-fluorocarbon (HFC), perfluoro-carbon (PFC) *etc* have adverse effects such as global warming. The techno-economic growth, rapid industrialization, urban lifestyle of people has roused the level of GHGs in the atmosphere. The unburned hydrocarbons from motor vehicles, open burning of fossil fuels, also the dumping of waste materials in open land are the major sources of GHGs.

Carbon dioxide is considered to be the most common GHGs which contribute about 70% of the total heat absorption from the earth surface. Methane contributes about 20% of heat absorption of the total heat absorbed in the atmosphere. Surprisingly, the earth's atmospheric temperature has been increased about 0.4–0.8°C during the last century; the most alarming issue is that the sea water level has increased to 2 mm per year. The ecological balance and environmental purity has been drastically altered. Developed nations of western world along with Russia and China have contributed about 54% of total GHG emission in 2000. Globally emission of GHG emission has been increased about 4.2% per annum from the year 1990–2000. During this time the rapid growth in industrialization and automobile sectors had enhanced the GHG emission with a rate of 21.3% and 7.3% per annum respectively. As a result of such GHG emission and Global Warming the Earth's temperature might increase by 5.5°C by the year 2050 if not controlled properly (Sharma *et al.*, 2006).

A tentative estimation in 2004 summit suggested that the amount GHG emission is around 49 Gt CO₂ eq. CO₂, CH₄, N₂O and fluorinated gases are also contributed significantly in this total amount. In 1990 total annual emissions of GHGs is increased by 24% which further enhanced by approximately 70% from 1970 (Rogner *et al.*, 2007). Among this, CO₂ can absorb about 55% of the heat reflected from the Earth's surface. It's a major GHG contributor which can stay unaltered about 500 years in the Earth's atmosphere. From the late twentieth century the concentration of CO₂ has been increased at the rate of 1.5 ppm per annum which is an alarming fact too. In comparison to other GHGs, the generation of CO₂ increases about 77% of emissions with the rapid enhancement rate of fossil fuel combustion in 2004 (Rogner *et al.*, 2007). CH₄ is another potent GHG contributor with 18% in an average. It is even more harmful towards global warming because it obviously absorb heat 25 times more than that of CO₂ and also its sustainability in atmosphere is about 10 years. Meanwhile, presence of 8% share of N₂O becomes one of the higher GHGs contributors. Another gas causing serious Global Warming is CFC, which can absorb heat about 1500–7000 times than that of CO₂. Its concentration in atmosphere is increasing by 0.5% every year. It also causes Ozone layer depletion and remains in the atmosphere unaltered for about 100 years (Roop Ganesh, 2011).

GHG Emission in India

In India, study on the regional distribution of major contributors of CO₂ emission shows that energy sector is contributing more than half (~58%) of the total CO₂ emission. Whereas other sectors like industry and agriculture also hold significant share of

Table 8 Major CO₂ emitting countries in 2008

Sl. no.	Country	Population (million)	CO ₂ emission (million tons)	CO ₂ emission per capita (tons)
1.	China	1327	6071	4.58
2.	India	1123	1146	1.18
3.	USA	302	5769	19.10
4.	Brazil	192	347	1.8
5.	Russia	142	1593	11.24
6.	Japan	128	1236	9.68
7.	Germany	82	798	9.71
8.	France	64	369	5.81
9.	UK	61	523	8.6
10.	World	6609	28,962	4.38

Data Source: Climate Change status-India, 2015. Statistics Related to Climate Change – India 2015, Government of India Ministry of Statistics and Programme Implementation, Central Statistics Office Social Statistics Division, New Delhi. Available at: http://www.mospi.gov.in/sites/default/files/publication_reports/climateChangeStat2015.pdf.

Table 9 Greenhouse Gas emission from different sources in India in 2007

Sl. no.	Sources	CO ₂ emission (thousand tons)	CH ₄ emission (thousand tons)	N ₂ O emission (thousand tons)
1.	Energy Sector	992,837	4266	57
2.	Industrial Sector	405,863	15	20
3.	Agriculture		13,768	146
4.	Land-use change and forestry	98,330		
5.	Waste		2516	16

Data source: Climate Change status-India, 2015. Statistics Related to Climate Change – India 2015, Government of India Ministry of Statistics and Programme Implementation, Central Statistics Office Social Statistics Division, New Delhi. Available at: http://www.mospi.gov.in/sites/default/files/publication_reports/climateChangeStat2015.pdf.

about 22% and 17% respectively. In comparison, waste sector is contributing only 3% in total emission. Quantitatively, in future (2020) per capita CO₂ emission in India will reach 2.1 ton and after that within 10 years that value reach approximately 3.5 ton (INCCA: Indian Network for Climate Change Assessment, 2010) (Tables 8 and 9; Climate Change status-India, 2015).

Plasma

Plasma is considered to be the fourth state of matter and it consists of neutral particles, electrons, and ions. However, as a whole it is electrically neutral (Byun *et al.*, 2010). On classifications of plasma, there are three of it: Thermal, cold and warm plasma. Thermal plasma is considered as thermally equilibrium plasma and the other is considered to be non-thermal equilibrium plasma. High temperature profile of thermal plasma indicates its efficiency towards various field of application (Gomez *et al.*, 2009; Ruj and Ghosh, 2014). Transferred and non-transferred arc torches are mainly used to generate plasma for different types of application. Non-transferred arc torch generates a high temperature plasma plume which is directly applied to the working substrate. Application of such type of torch is more generalised in various industrial applications like plasma cutting, welding, spraying *etc.* In plasma plume generation process, inside the arcing zone of plasma torch carrier gases like N₂, Ar, are transformed into plasma. The plasma arcing zone is generated between the anode and cathode gap through application of high electric potential difference. The phenomenon of arcing is quite similar in transferred torch but here the arcing zone is outside the plasma torch. Also the reacting materials act as an electronic linker between cathode and electronically grounded anode (Huang and Tang, 2007; Tang *et al.*, 2013). Some other classifications like direct current (DC)/alternating current (AC), radio frequency (RF), Microwave (MW) and DC-RF hybrid arc plasma system are also utilised as plasma generation systems (Tang *et al.*, 2013). All are considered in design and development of gasification systems. Plasma Arc driven gasification technology is one of the most emerging waste disposal technique. Owing to the high waste destruction efficiency and eminent energy recovery potential, plasma gasification is considered an emerging system of waste disposal throughout the world. Some countries have also used this technology in diverse applications.

It is found that plasma gasification generates more syn gas than the ordinary gasification and emits significantly less amount of CO₂ (Table 10; Janajreh *et al.*, 2013). The emission of SO_x, NO_x and other toxins like dioxin, furan is usual in an ordinary gasification plant. Plasma gasification holds a very low level (below permissible limit) of toxins emission (Janajreh *et al.*, 2013). Keeping the advantageous points of plasma technology, it is commercialised in various parts of the world. But in India the technology is still confined in some pilot plants in few sectors. Navreet Energy Research and Information (NERI) took the first attempt to install one plant (NERIFIER) at Nohar, Hanungarh, Rajasthan. Waste treatment rate of NERIFIER is about 50–150 kg per hour which shows its efficiency of waste destruction is about 70%–80%. Tata Energy Research Institute (TERI) gasification unit is the second plasma gasification plant in India installed at Gaul Pahari campus of Tata Energy Research Institute (TERI), New Delhi (Sharholly *et al.*, 2008).

Table 10 Comparison between plasma gasifier and ordinary gasifier

<i>Syn gas mole fraction</i>	<i>MSW gasification with ordinary gasifier</i>	<i>MSW gasification with plasma gasifier</i>
H ₂	17.04	43.50
CO	22.70	34.50
CO ₂	4.92	0.03
H ₂ O	0.00	16.22
CH ₄	0.00	0.01
H ₂ S	0.00	0.09
N ₂	48.49	5.63
HCN	0.00	0.00
S	0.06	0.00
SO ₂	0.00	0.00
COS	0.01	0.00
NH ₃	0.00	0.00
C ₂ H ₂	0.00	0.00
C(Solid)	1.12	0.00
Syngas LHV ^a (MJ/kg)	22.78	13.44
Syngas HHV ^b (MJ/kg)	26.45	14.71
Feedstock flow (kg/s)	1.00	1.00

^aLHV- Lower heating value.

^bHHV- Higher heating value.

Data Source: Janajreh, I., Raza, S.S., Valmundsson, A.S., 2013. Plasma gasification process: Modeling, simulation and comparison with conventional air gasification. *Energy Conversion and Management* 65, 801–809.

Plasma arc technology directed our society that MSW could be utilised as a source of renewable energy. Production of clean syn gas with very low emission of toxins validates the smooth operation and implementation of plasma arc technology for safe waste management.

Potential of Energy Recovery

Beside the organic part, combustible materials (papers, plastics, food waste, wood, textiles, disposable diapers, leather) are the larger components of MSW. It could be used as a feedstock in energy recovery. To get an idea about efficiency of MSW towards the energy recovery some parameters like carbon and nitrogen (C/N) ratio, calorific value (CV), moisture content of MSW are important. However, parameters of MSW largely depend upon the compositions, place of generation *etc.* of MSW. In India, The C/N ratio of waste ranges from 15 to 45 (Fig. 7) and the calorific value (CV) lies between 500 and 4000 kcal/kg (Fig. 8) due to wide variation in the composition of MSW. Higher extent of moisture content in MSW indicates very low energy recovery efficiency as it directly affects the heating value of MSW. Moisture content also varies widely in Indian cities (Fig. 7; *Waste Generation and Composition: Central Pollution Control Board, India, 2017*) as some places in northern India have very high moisture content in MSW and also the C/N ratio and calorific value (HCV) are comparatively high. Whereas, densely populated mega cities like Greater Mumbai, Delhi, Kolkata, Chennai, Hyderabad *etc.* have moderate range of parameters and also generating high amount of MSW. In India, Energy recovery from waste can be commercially viable approach due to considerable parameter range and huge availability feedstock. All facts show that MSW could be a potential feedstock for waste to energy recovery systems (Sharholy *et al.*, 2008).

Potential of GHG Emission Mitigation

Improper treatment of MSW can cause emission of GHGs which have high content of CH₄, CO₂, and N₂O. Generally, waste materials are improperly disposed off into land filling sites or burnt in open land without paying much attention towards environmental pollution. The most common practices like land filling, open burning are increasing day by day and as a result the extent of GHGs emission in the environment has been increased with a very high intensity. Incineration of waste also emits GHGs along with other toxins into the atmosphere (EIPPC Bureau, 2006).

Now, it is necessary to find the best possible option for GHGs mitigation especially in the field of waste disposal. Considering environmental and societal health, reduction of GHGs emission could be possible through material and energy recovery from waste. It is estimated that around 1.83×10^6 kg CO₂-eq/year could effectively be reduced by only recovering metal parts form waste. For paper waste, value of GHGs reduction is seven times higher than the recovery of metal. It's also true that every component in waste material cannot be recovered or recycled; some will remain as solid waste which could be disposed off through energy recovery pathway. The waste to energy generation process can be an alternative for traditional fuels and also it can reduce the demand of fossil fuel to some extent. The emission of GHGs could also be reduced by the application of plasma arc

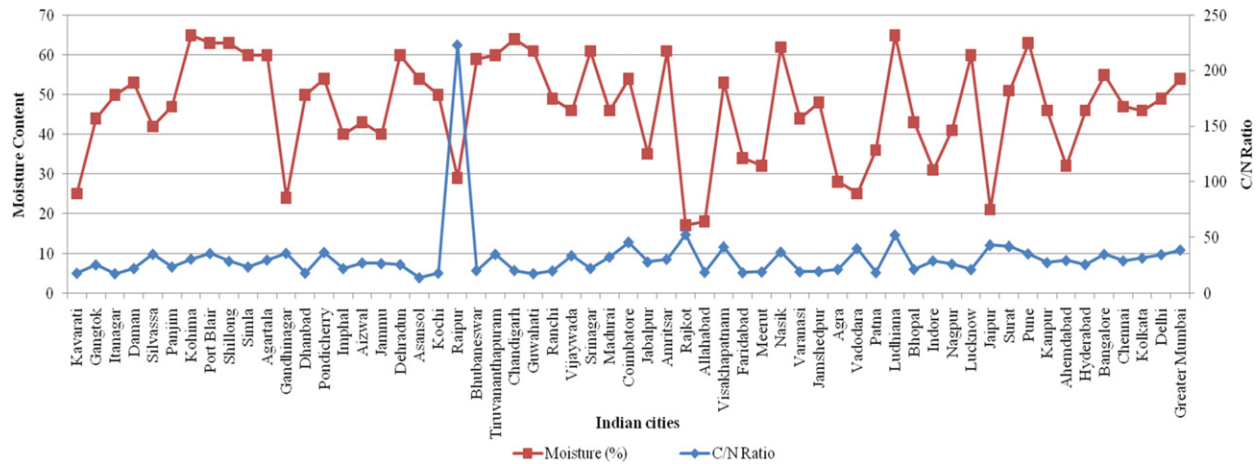


Fig. 7 Indian scenario of moisture content and C/N ratio variation in India. Data Source: Waste Generation and Composition: Central Pollution Control Board, India, 2017. Available at: <http://cpcb.nic.in/waste-generation-composition/>.

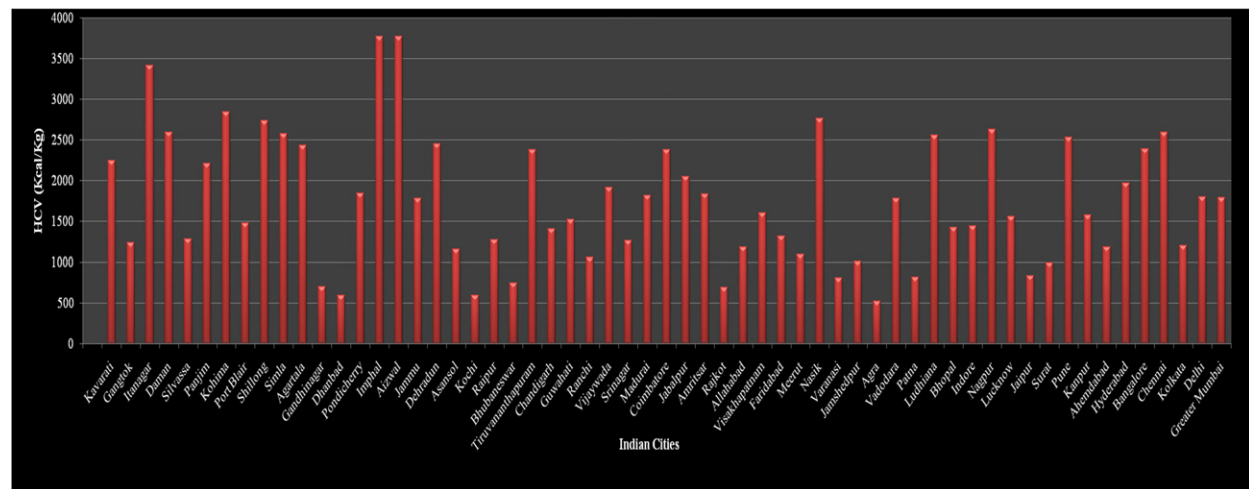
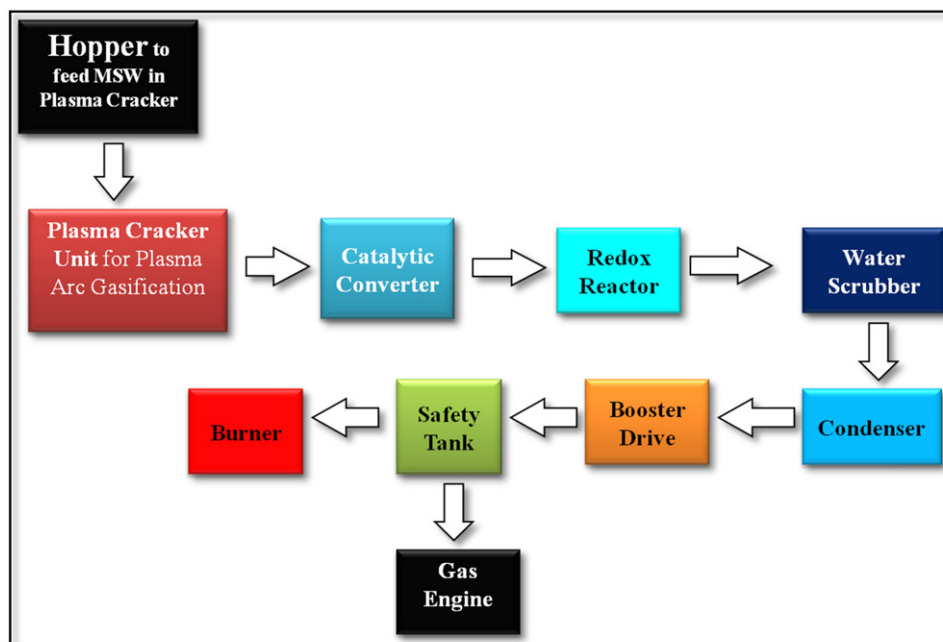


Fig. 8 Calorific value variation in Indian Cities. Data Source: Waste Generation and Composition: Central Pollution Control Board, India, 2017. Available at: <http://cpcb.nic.in/waste-generation-composition/>.

gasification process and also the produced fuels like syn gas and methanol could reduce GHGs emission as compared with the burning of other conventional fuels. Moreover, waste to energy conversion concept through material recovery could be a solution to deal with the GHGs emission as well as climate change. Subsequently, plasma arc technology becomes the valuable method for safe waste management through generation of green energy with suppression in consumption of fossil fuel (Bogner *et al.*, 2008).

Plasma Arc Driven MSW Treatment Plant

A mini plant has been designed and installed at CSIR-CMERI, Durgapur for the safe disposal of MSW (Scheme 1). Waste materials are collected from different sources and then fed into the plasma hearth for its safe disposal. Two valves are put in the plasma chamber so that waste materials can be channelized properly and air can't enter into the hearth and also the produced gas cannot move out of the hearth. Plasma is being generated through three plasma electrodes placed at a star shape 120° apart in the plasma hearth for generating plasma arc. Through the transferred plasma electrode, plasma plume is generated inside the plasma hearth. The temperature generated here is about 1500–3000°C. At this higher temperature the waste materials are completely gasified and as a by-product non leachable slag is generated which is stored at the slag collector present at the bottom of plasma hearth. The waste volume reduction is about 95% and that clearly signifies that the waste materials are totally disposed and only 5% slag product remains there. The produced gas is then passed through a catalytic converter and a redox reactor through which the produced gas mixture is cleaned. Nickel catalyst is present in catalytic converter which reacts with the higher hydrocarbons present in the gas generated in plasma hearth and converts it to simplified lower hydrocarbons. If CH₄ is present in the gas coming after



Scheme 1 Process Flow diagram of MSW disposal plant.

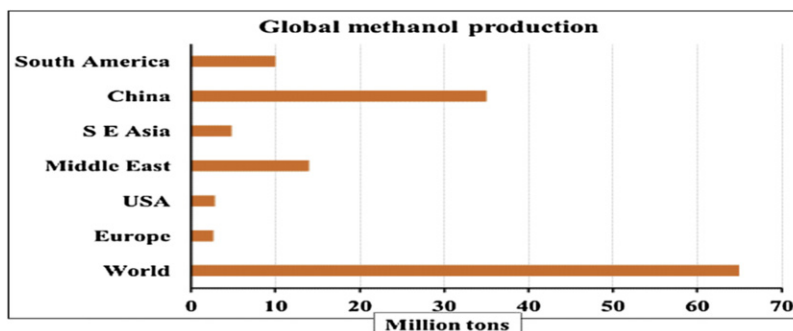


Fig. 9 Global production of methanol by the year 2014. Data source: Methanol Market Services Asia (MMSA), 2014. Methanol, Methanol uses. The Essential Chemical Industry Online. Article, the University of York. Data adopted from Methanol Market Services Asia (MMSA); Galadima, A., Muraza, O., 2015. From synthesis gas production to methanol synthesis and potential upgrade to gasoline range hydrocarbons: A review. *Journal of Natural Gas Science and Engineering* 25, 303–316.

being treated in catalytic converter it becomes CO, CO₂ and H₂. It actually enhances the presence of syn gas as the final output of plasma treatment procedure. Carbon sieve is present in redox reactor which helps to convert steam and water vapour into CO, CO₂, and a little amount of H₂O.

After that the gaseous mixture is passed through a dry water scrubber where water is sprayed into the scrubber chamber so that the toxic gas (HCl) may get dissolved in it and a toxin free gas gets out. Then the gas is made to flow through a condenser where the temperature is lowered down by introduction of water. This gaseous mixture is then utilised for energy generation. This gas mixture mainly comprises of CO and Hydrogen (Synthetic natural gas). Because of the presence of higher contents of Synthetic natural gas or syn gas, the gas has a very high calorific value. The produced gas is used as fuel to run gas engine and also to generate electricity.

Methanol Production From Syngas

Methanol is an important chemical for industrial sectors due to its very wide range of application. In paint and pigment industry methanol act as solvent whereas in fuel cell it acts as source of hydrogen (Reubroycharoen *et al.*, 2003). In production of bio-diesel

and synthetic fuel methanol also plays an important role. In recent days, to meet the energy demand industries are looking for alternative sources of hydrocarbons. Keeping this fact, gasoline production from methanol is nowadays becoming a forefront technology in energy production sectors. Consecutively, worldwide the methanol production is considerably high (Fig. 9; Methanol Market Services Asia (MMSA), 2014) and in future the demand will increase enormously (Galadima and Muraza, 2015).

Production of methanol from syngas is a well established phenomenon and the major source of syngas is natural gas and oil. Gasification of coal in a controlled system can also produce syngas. In coming days for continuous supply of syngas we have to look for an alternative source as the conventional sources are drastically diminished (Bermúdez *et al.*, 2010). Production of syngas from MSW utilising plasma arc technology become a solution for continuous supply of syngas.

Plasma gasification can simultaneously produce syngas with drastic suppression of MSW in a safe and environment friendly way. Herein, methanol production from syngas could be commercially viable because the feedstock is MSW. Production of methanol following this path could be an aid towards “waste to wealth generation” (CanPete *et al.*, 2014).

Conclusion

Greenhouse gas emission is evident towards global warming and degradation of social and ecological balance. In relevance to this, huge accumulation of MSW and improper waste management causes serious issue to the mankind. So, there is a need of such a scientific process which could destroy waste, mitigate GHGs and also produce new sources of energy. Plasma arc driven MSW disposal system has emerged as a suitable process to fulfil these requirements. Waste to syngas generation and syngas to methanol production from waste without any harmful effects on the environment has made this technology viable. This technology is safe, easy to operate and eco-friendly. Waste to wealth recovery without harming our ecosystem is always a better option towards the sustainable development of our society.

Acknowledgement

Department of Science and Technology, Govt. of INDIA sponsored DST-TSG (vide letter no.-DST/TSG/WM/2015/459) (GAP-211712) project is hereby acknowledged. SD and AH are thankful to DST (GAP-211712) for their fellowship.

See also: Carbon Management and Greenhouse Gas Mitigation

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Further Reading

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Polygeneration as Efficient and De-Carbonized Energy Solution

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Introduction

In the context of limited fossil resources and energy sustainability, maximum resource utilization is the possible way towards sustainable energy solution (Bundgaard *et al.*, 2017). Better utilization of energy resources gives better economic performance and reduces carbon footprint of the energy system. It also minimizes the harmful emission to the environment. Another possible way to achieve sustainable energy goal is to increase energy efficiency both in generation and in demand side. Polygeneration is an option to utilize energy resources efficiently (Jana *et al.*, 2017). By properly designed polygeneration, improved energy efficiency can be achieved. Also energy efficiency in demand side is improved due to distributed supply of utilities. In distributed polygeneration, utilities are supplied in locality. Long distance transportation and transmission is not feasible. Hence, it reduces transportation and transmission loss in demand side and increases efficiency in demand side.

Another critical challenge to the human being is global warming. Presently climate change due to global warming is an inevitable fact. Anthropogenic greenhouse gas emission is the main reason for global warming (IPCC, 2015). Country wise highest greenhouse gas emitter is shown in Fig. 1. It is noted that China, United States and India are the highest greenhouse gas emitter. Hence, many countries decided to limit the GHG emission at COP21. To reduce the CO₂ emission associated with the fossil fuel used in energy sector, carbon capture and storage (CCS) is a possible option. But significant amount of energy penalty and economic penalty is observed due to CCS. It reduces overall energy efficiency of the plant. It also requires significant economic investment. Thus, polygeneration with carbon capture and utilization (CCU) emerges as possible solution to this (Koytsoumpa *et al.*, 2018). Utilization of captured CO₂ may offset the economic penalty of CCS (Dowell *et al.*, 2017). Hence, proper system integration is required for efficient polygeneration to deliver utility efficiently. In this article, polygeneration is defined and its advantages are shown. Inputs and outputs of polygeneration along with its classification are given. Thermodynamic schematics of various utility deliveries are shown. Different parameters to assess a polygeneration are indicated in this article. Integration of CCS and CCU, possible output utilities production are mentioned along with literature survey.

Definition and Advantages of Polygeneration

To achieve the goal of 'sustainable development', resource utilization efficiency is one of the important pillars. Multi-generation or polygeneration is a designation to use input energy resources efficiently. Polygeneration is the system of integrating multiple processes to obtain multiple utility outputs through an efficient (viz. thermodynamic, economic, environmental, social) energy system by single or multiple sources of energy inputs. At the same time, maximum resource utilization reduces the carbon footprint for unit output and gives maximum utilization of materials also. On the other hand, it reduces the harmful waste to the environment.

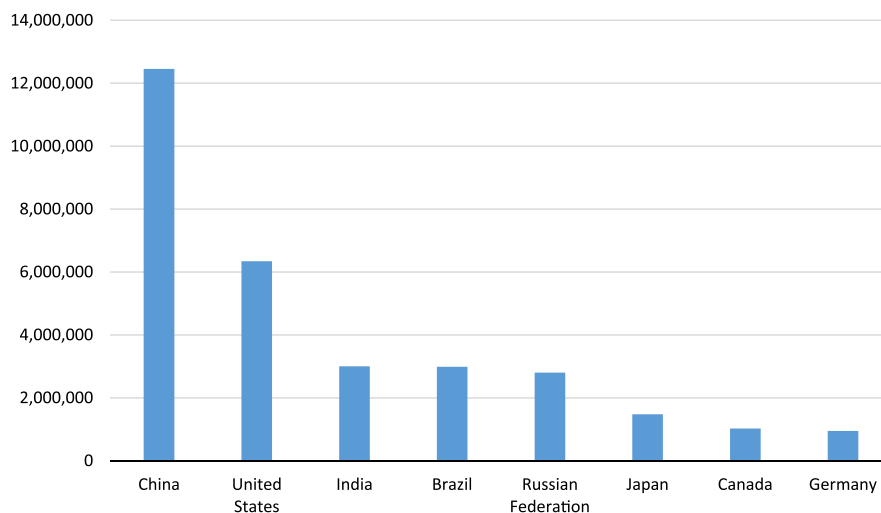


Fig. 1 Greenhouse gas emission of different countries (kt/y of CO₂ equivalent). Reproduced from World Bank Data, 2012. Total Greenhouse gas emission. Available at: https://data.worldbank.org/indicator/EN.ATM.GHGT.KT.CE?year_high_desc=true

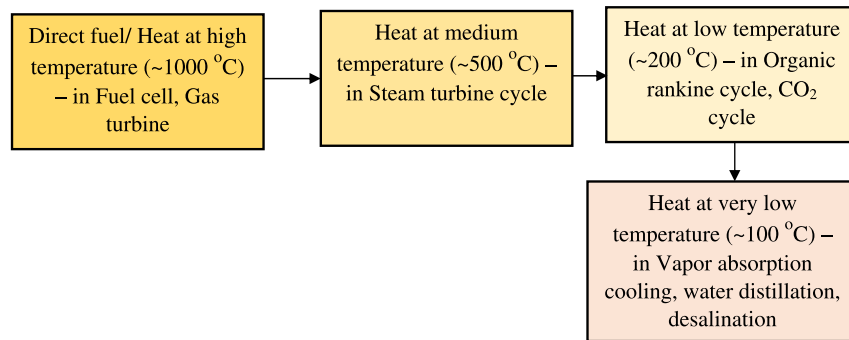


Fig. 2 Energy cascading of heat at different temperature.

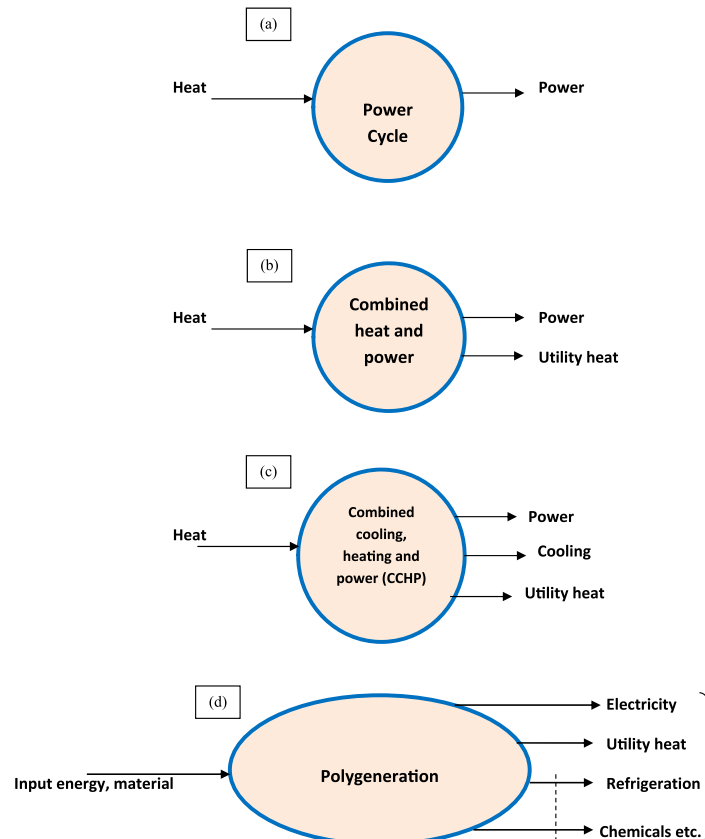


Fig. 3 (a) Power generation, (b) cogeneration, (c) trigeneration and (d) polygeneration.

Energy cascading is a thermodynamic way of getting maximum output from a definite input. It gives the opportunity to utilize heat source according to their thermodynamic quality. In energy cascading output of one energy system is the input to other downstream system as shown in Fig. 2. Fuel may be utilized directly in fuel cell or after combustion the hot flue gas may be utilized as input to the gas turbine. Then exhaust of the gas turbine may be used for steam generation in the downstream steam turbine cycle. However, low temperature flue gas may be utilized in organic Rankine cycle or in CO₂ power cycle for power generation. Several criteria have to be considered to find the suitable organic fluids for ORC including thermodynamic properties, fluid stability and chemical reactivity, safety, health and environmental hazards. Availability and costs of the fluid is also important for long run operation of ORC. Then, low temperature heat (say, at 100°C) can be used for vapor absorption cooling or water desalination process. Thus, input energy can be used by energy cascading for different utility outputs viz., power, heating, cooling, desalinated water etc.

In conventional power generation, input heat is converted to the power through different power cycles as shown in Fig. 3(a). Details of different power cycles are discussed later. In combined heat and power (CHP) or cogeneration, utility outputs are heat

and power as shown in Fig. 3(b). It increases the energy efficiency as compare to power generation only. However, along with heat and power, cooling is another utility which is produced in combined cooling, heating and power or trigeneration as shown in Fig. 3(c). Apart from power, heating, cooling, production of other utilities (say, chemicals, liquid fuels etc.) is possible by polygeneration plant as shown in Fig. 3(d).

There are several advantages of polygeneration. Some of those are- (a) it increases energy efficiency, (b) it minimizes waste, (c) gives better economic performance, (d) gives better environmental performance, (e) properly designed poly-generation increases social acceptance as it may meet the needs of local areas. However, disadvantages of polygeneration are that it increases complexity of the system and it increases inter-dependency of different sub-processes within the poly-generation. Hence, failure of one process may affect the performance of the downstream processes. Another important aspect of polygeneration is that it can be integrated with carbon capture process. The captured carbon may be utilized for other processes as discussed later.

Inputs and Outputs of Polygeneration

Inputs of a polygeneration are selected according to availability of fuel, size of the plant and desired outputs of the plant. In general, polygeneration may be classified as decentralized or centralized plants as shown in Fig. 4(a and b) respectively. The catchment area or supply area and capacity of decentralized plant is smaller. Hence, number of plants is more for a particular area as compared to centralized plant. On the other hand, capacity and supply area of centralized plant is larger as shown in Fig. 4. Centralized plant can be renewable or non-renewable energy based. However, the decentralized plan is generally renewable energy based as shown in Fig. 5. Centralized plants are always grid connected. However, decentralized plants may be on-grid, micro-grid or off-grid.

Different possible inputs to a polygeneration plant are shown in Fig. 6. For maximum utilization of coal, polygeneration is a possible option. Coal is a high energy density fuel with good source of hydrogen and carbon. Coal may be utilized through combustion or gasification of fuel. After direct combustion of coal, hot flue gas is produced and this flue gas may be used in downstream process for generation of power, heating or cooling. Coal may also be used after gasification process. In gasification process, coal is converted to syngas. This syngas may be utilized for gaseous or liquid fuels like FT fuel, dimethyl ether (DME), methanol etc. Coal based polygeneration may be integrated with carbon capture process to reduce its carbon footprint for secondary energy generation. Hence, it has the possibility to decarbonize the energy system through carbon capture and storage (CCS) or carbon capture and utilization (CCU).

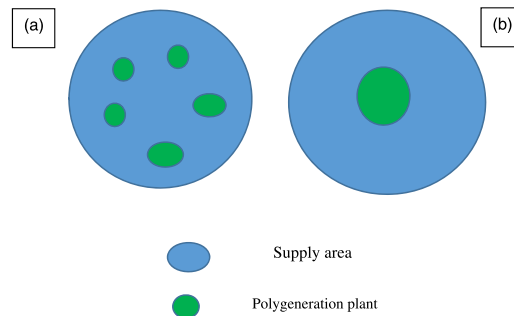


Fig. 4 (a) Decentralized and (b) centralized polygeneration.

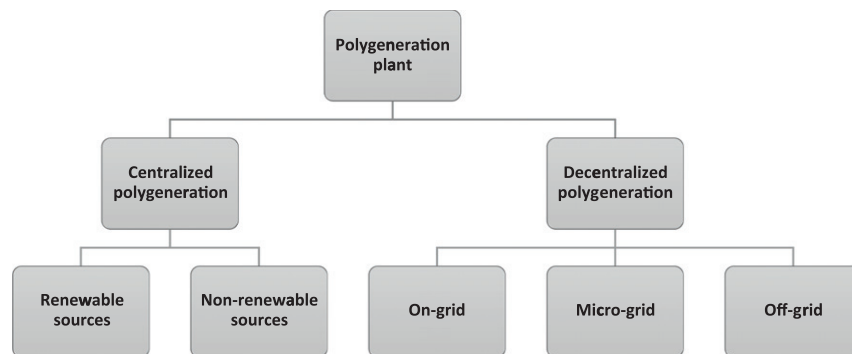


Fig. 5 Classification of polygeneration.

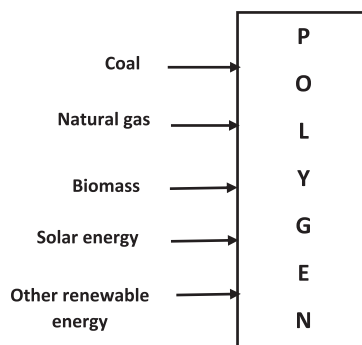


Fig. 6 Inputs of polygeneration.

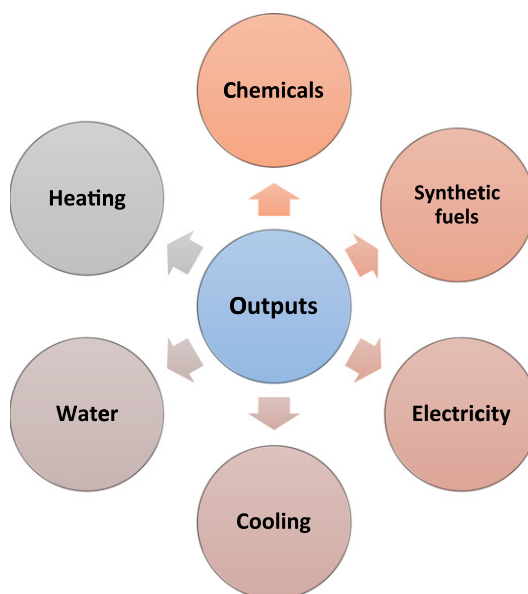


Fig. 7 Outputs of polygeneration.

Another important fuel input to polygeneration is biomass. Similar to the coal, biomass is also solid fuel consist of hydrocarbons e.g., cellulose, ligno-cellulose. But its hydrocarbons are complex in nature. Hence, conversion of biomass is more critical due to its low conversion rate, tar formation and ash fusion. As energy density of biomass is less and it is a scattered resource, distributed polygeneration plant is preferred for biomass based plants. Biomass may be converted through thermo-chemical or bio-chemical route. Gasification, pyrolysis, torrefaction are the options for thermo-chemical conversions. In first generation biomass conversion, soyabean oil, rapeseed oil, jatropha etc were converted to bio-fuels. This challenges the 'food security'. In second generation biomass conversion, waste from wood, agriculture etc are converted to useful form of secondary energy e.g., liquid fuels, electricity etc. In third-generation biomass conversion, the rate of conversion is enhanced by improved catalysts or by improved processes. In fourth generation, carbon capture is integrated with polygeneration to get negative net-negative carbon emission. One of the greatest sources of biomass is agricultural waste. Other sources are plantation crop waste (say, coconut fiber) and waste of food processing industry (say, sugarcane bagasse).

Another important source of renewable energy is solar energy. It can also be used as input to the polygeneration. However, solar energy is hybridized with other sources of energy as its energy density is low for multi-generation. Biomass gasifier and fuel cell are mostly hybridized with solar energy for polygeneration as noted from open literature. When biomass is hybridized with fuel cell, heating, cooling and electricity are the outputs. Additional outputs like alcohols, liquid fuels etc are obtainable when solar based polygeneration is integrated with biomass. Other forms of energy like wind, geothermal etc. can also be hybridized in polygenerations. Hybridized systems help to reduce the storage capacity required for intermittent energy sources.

Polygeneration is designated to deliver multiple utilities from a single unit. Possible outputs are shown in [Fig. 7](#) as obtained from literature. Electricity is the most widely used form of secondary energy. Hence, electricity is the most significant output of a polygeneration. For centralized polygeneration, utilities are transmitted or transported. However, long distance transportation or

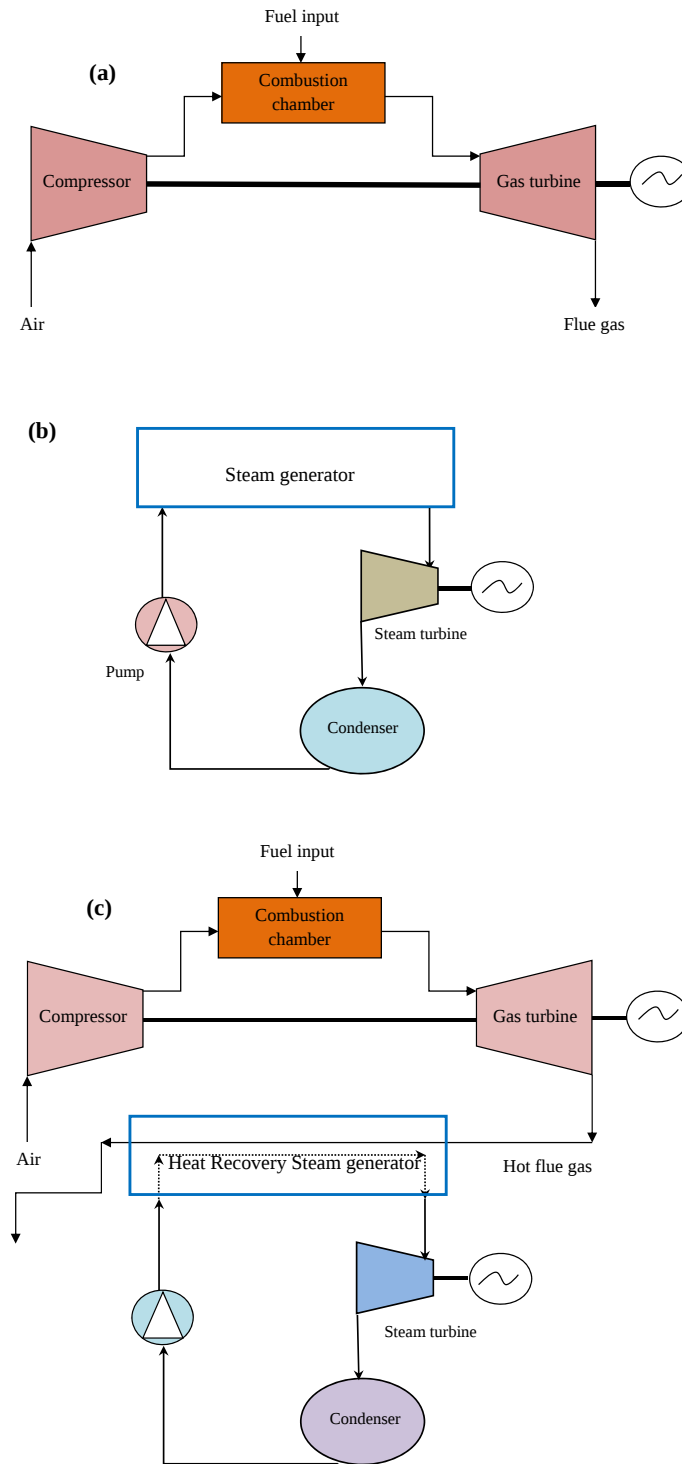


Fig. 8 (a) Gas turbine cycle, (b) steam turbine cycle, (c) combined cycle.

transmission is not economically feasible for decentralized polygeneration. Hence, output utilities are consumed locally and distributed polygeneration are designed to cater to the needs of local people only. Heating and cooling are other two outputs of polygeneration. Heating may be used for room heating or industrial process heating. In polygeneration cooling is generally heat driven. Waste heat available in polygeneration is used for vapor absorption cooling process. Water is another important output of polygeneration. In the present context of water scarcity and water contamination, production of drinking water is significant. Production of drinking water from naturally available water may be heat driven or power driven. In heat driven process, low

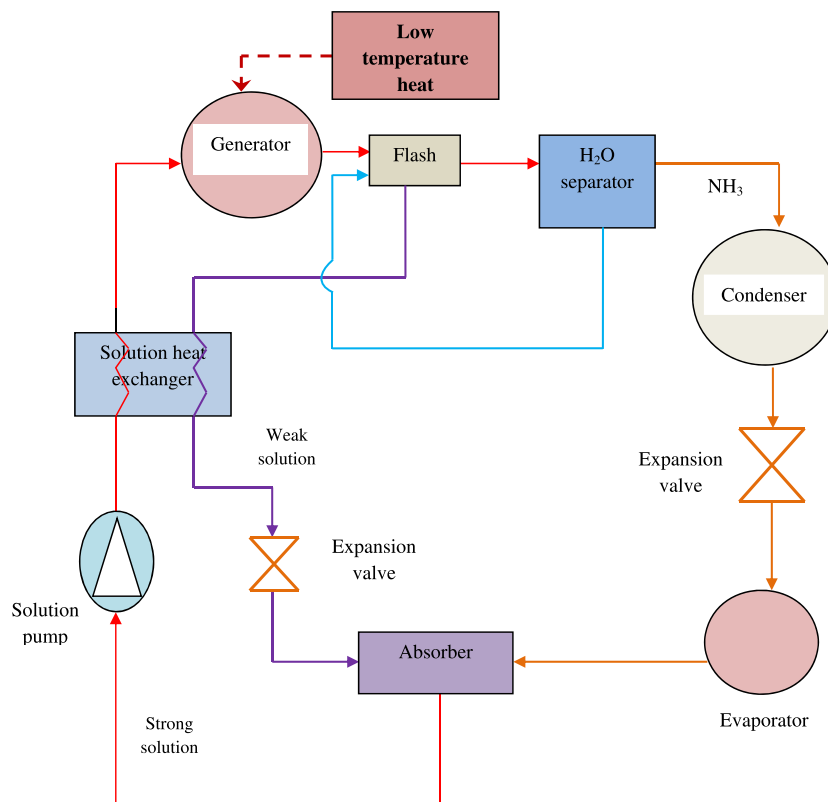


Fig. 9 Vapor absorption refrigeration.

temperature waste heat is used in multi stage flash or multi effect distillation. To control the fluctuating load (electricity) and intermittent source of energy, power driven water purification may be applied to a polygeneration.

Synthetic fuel is another important output of polygeneration. As stated earlier, biomass and coal are sources of hydrogen and carbon. In polygeneration, hydrogen and carbon are synthesized to liquid or gaseous fuel. The possible fuel outputs are ethanol, methanol, higher alcohols, DME, Fischer-Tropsch liquids etc. The production process of each fuel is different and it needs significant amount of input energy in the form of power. Integration with polygeneration increases the efficiency as compared to standalone units. Apart from fuel, polygeneration has also the capability of delivering different chemicals like ammonia, urea, etc. When polygeneration is integrated with carbon capture and utilization process, different fuels and liquids production is possible as discussed later.

Thermodynamics of Utility Production

As stated earlier, electricity is the most important utility of polygeneration. There are several energy conversion devices or prime movers for electricity generation. Fuel cell can produce electricity directly from fuel. However, it needs novel material. Impurities in input fuel should be very less for fuel cells.

Gas turbine is another energy conversion device for producing power. However, for gas turbine, input should be gaseous i.e. natural gas or derived syngas from gasification. The impurity level should be within the specified limit. The schematic of gas turbine cycle is shown in Fig. 8(a). However, micro gas turbine is also available for decentralized polygeneration. For directly fired coal or biomass, steam turbine cycle converts the input heat to power as shown in Fig. 8(b). In this cycle, steam is generated by heat of combustion of fuel. This steam is expanded through steam turbine to produce power. The steam turbine is coupled with generator to produce electricity. To increase the efficiency of gas turbine cycle, it is combined with bottoming steam turbine cycle as shown in Fig. 8(c). For decentralized power generation, internal combustion engine is a good option due to its robustness. However, the selection of this device is based on capacity, input fuels, economy etc.

Another important output of polygeneration is cooling. Cooling in polygeneration is generally heat driven. Schematic of vapor absorption refrigeration is shown in Fig. 9. In this refrigeration process, heat is the input energy at $\sim 100^{\circ}\text{C}$ to the generator of vapor absorption refrigeration cycle. The substances used may be $\text{NH}_3\text{-H}_2\text{O}$ or $\text{H}_2\text{O-LiBr}$ solution. Drinking water is another important output of polygeneration. Schematic of multi stage flash desalination is shown in Fig. 10. This is a heat driven water desalination process. Number of stage may vary from 2 to 12. Though number of staging increases the yield of water production, it also increases the economic investment. Hence, the stages are optimized according to the inputs and outputs.

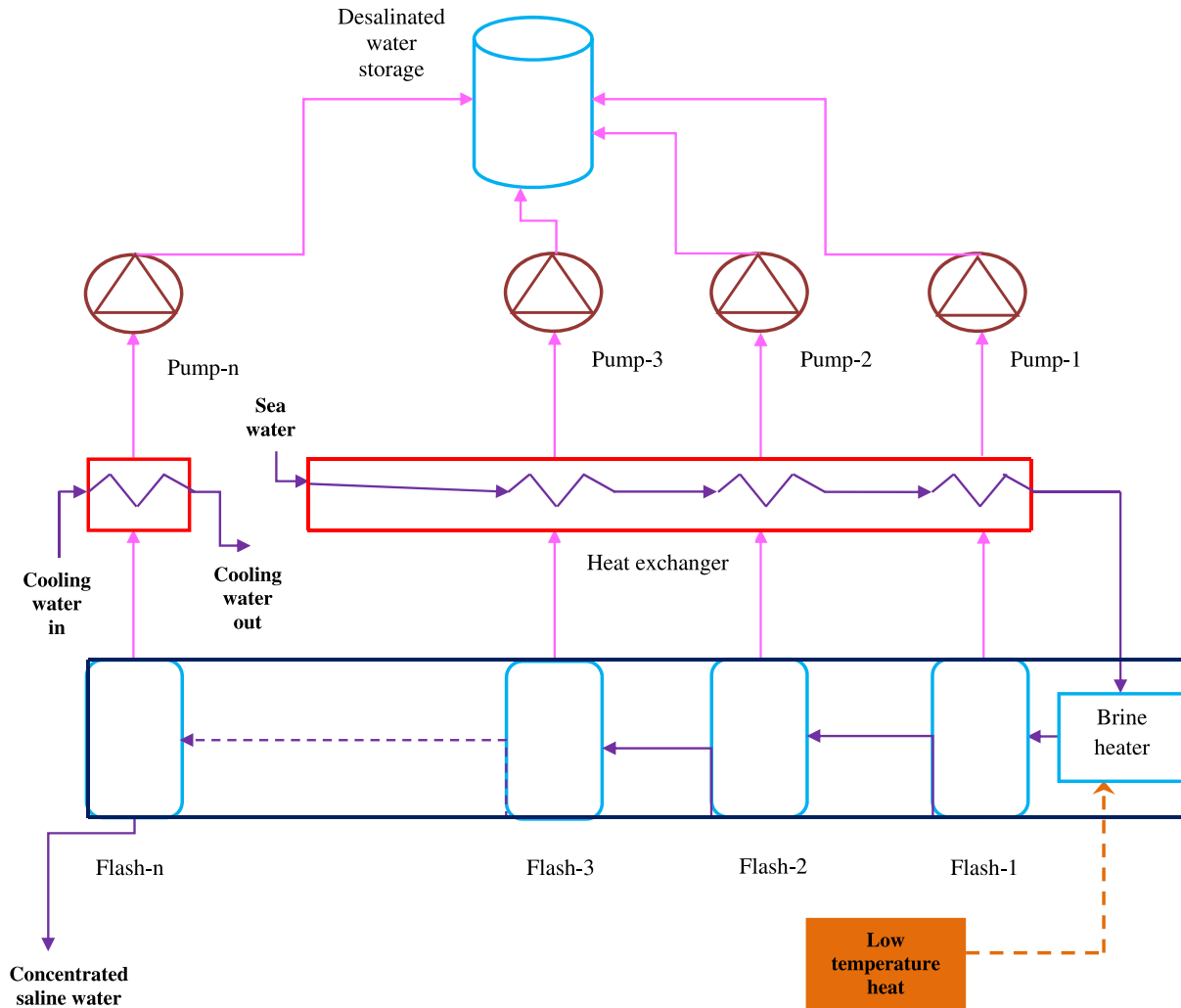


Fig. 10 Multi stage flash desalination.

Performance Parameters

Assessment through analysis is important to examine the sustainability aspects of polygeneration. To be a sustainable energy solution, polygeneration should be economically feasible, socially and environmentally acceptable. Various assessment methods are there for polygeneration. Different parameters are shown in [Fig. 11](#). Thermodynamic parameters show the technological aspects and possible improvements within the process. Thermodynamic assessment is done based on 1st law and 2nd law of thermodynamics. Economic assessment shows the economic feasibility and economic benefits of the polygeneration. Several parameters like return on investment (ROI), payback period, net present value (NPV) are used for economic analysis of polygeneration. Polygeneration may be assessed by social parameters too as it should be socially acceptable. For environmental assessment, life cycle assessment (LCA) is the most scientific approach.

A few assessment parameters are given below ([Jana and De, 2015a](#)):

$$\text{energetic efficiency} = \frac{\text{energy equivalent of utility outputs}}{\text{fuel energy input} + \text{other from of energy input}} \quad (1)$$

$$\text{exergetic efficiency (energy utilization efficiency)} = \frac{\text{exergy of output utilities}}{\text{exergy of input utilities}} \quad (2)$$

$$\text{Cost utilization factor} = \frac{\text{market price of output utilities and materials}}{\text{market price of input utilities and materials}} \quad (3)$$

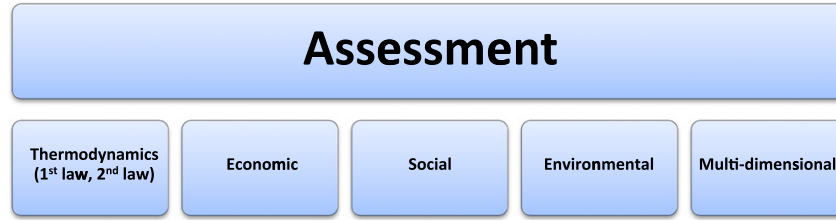


Fig. 11 Various bases for polygeneration assessment.

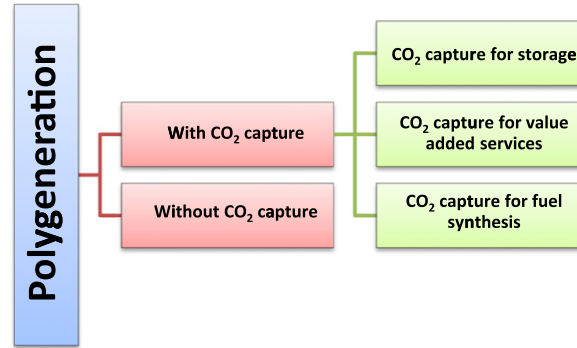


Fig. 12 Carbon capture option for polygeneration.

$$\begin{aligned}
 &\text{Usefulness of polygeneration with relative priority} \\
 &= \sum_i \left(\frac{1}{N} \times x_i \times \frac{\text{production of output utilities and materials}}{\text{demand of output utilities in the locality and materials}} \right) \\
 &x_i = \frac{(\text{price}_i \times \text{demand}_i)}{\sum_i (\text{price}_i \times \text{demand}_i)} \quad (4)
 \end{aligned}$$

$$\text{Carbon emission factor} = \frac{\text{CO}_2 \text{ emission from the polygeneration plant with CO}_2 \text{ capture}}{\text{total CO}_2 \text{ emission from individual units delivering same utilities}} \quad (5)$$

$$\text{Carbon emission factor} = \frac{\text{CO}_2 \text{ emission from the polygeneration plant with CO}_2 \text{ capture}}{\text{total CO}_2 \text{ emission from individual units delivering same utilities}} \quad (6)$$

$$\text{land or water utilization factor} = \frac{\text{land or water used in stand alone units}}{\text{land or water used in polygeneration} - \text{water produced (in case of desalination)}} \quad (7)$$

Polygeneration With Carbon Capture

In the present context of global warming, CO₂ emission reduction from the energy sector is an urgent need. There are many ways of CO₂ reduction from energy sector as observed from the literature. CO₂ capture and storage is one of the established options of carbon emission reduction. But it requires significant amount of input energy in the form of both heat and power. Hence, it reduces overall efficiency of secondary energy generation.

Integration of carbon capture with polygeneration may decrease the energy and economic penalty. Captured CO₂ in polygeneration process may be stored, or may be utilized for value added services and fuel synthesis as shown in Fig. 12. There are various options for CO₂ capture and utilization as discussed below.

Carbon Emission Reduction and Utilization Potential Through Polygeneration

In general, carbon capture process may be of three type, viz., (a) oxy-fuel combustion, (b) pre-combustion capture and (c) post-combustion capture as shown in Fig. 13. In oxy-fuel combustion process, combustion of fuel is done by oxygen only in absence of N₂. Hence, the product gas of combustion mostly contains H₂O and CO₂. By condensing the H₂O, CO₂ is separated from the

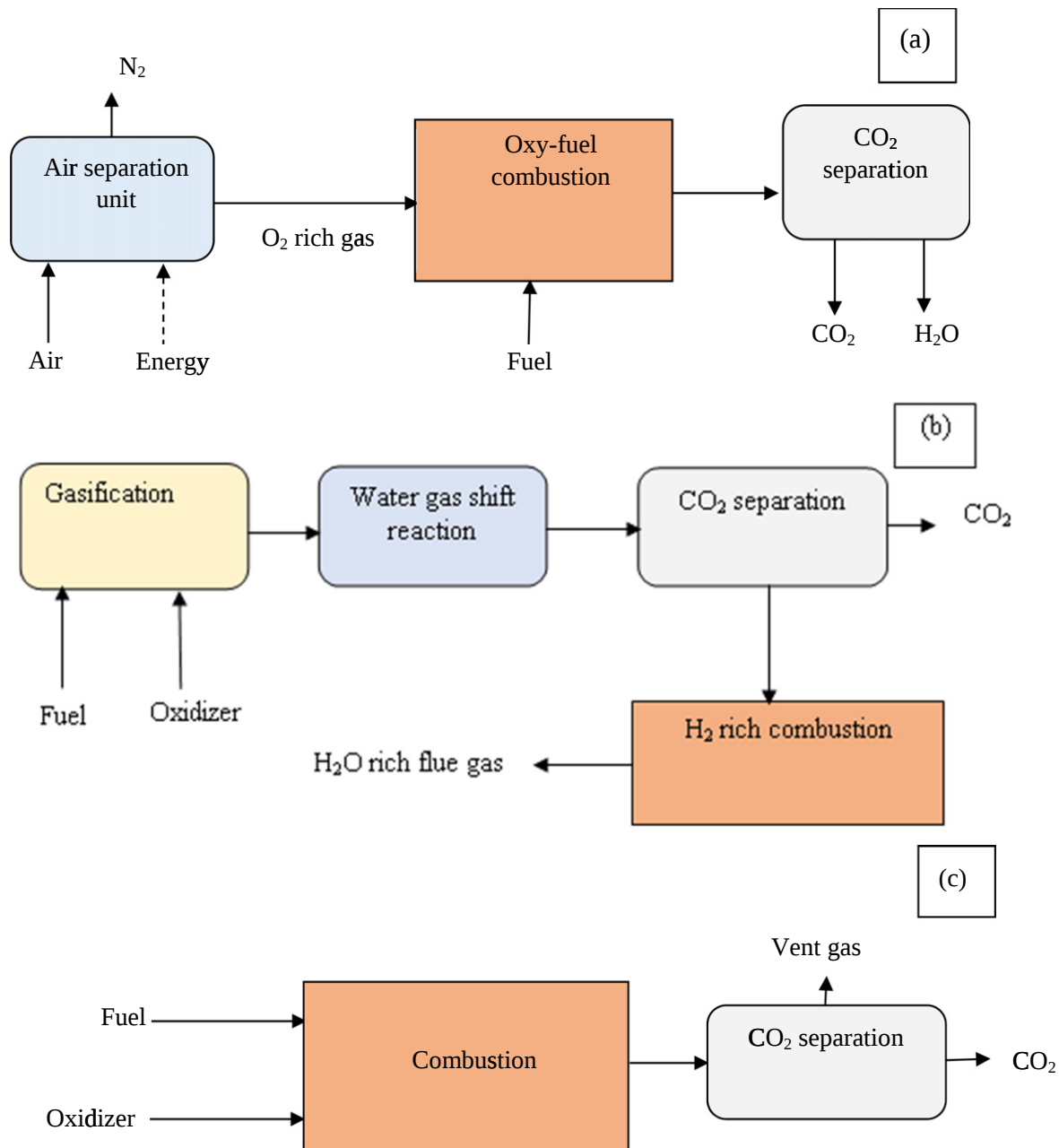


Fig. 13 (a) Oxy-fuel combustion, (b) pre-combustion CO₂ capture (c) post-combustion CO₂ capture.

product gas. But for production of oxygen from air, air separation unit (ASU) is required. The air separation process is also energy intensive. Another option for capturing CO₂ is pre-combustion capture. In this process, fuel is gasified by partial oxidation. Then water gas shift reaction is done to increase the CO₂ and H₂ contents. Then CO₂ is separated by various chemical absorption or adsorption process. Hence, this process too requires additional energy. Post-combustion CO₂ capture is another option. In this process CO₂ is separated after combustion by suitable chemical absorption process. After that it may be stored or utilized for various subsequent processes. After capturing CO₂, it may be used for value added products as shown in Fig. 14. Additional value added products increase the material utilization efficiency and minimize the waste. It also reduces and may even offset the economic penalty due to CO₂ capture. There are mostly three significant methods of CO₂ conversion as shown in Fig. 15. In photochemical process, solar radiation is used to convert CO₂ to value added products. Electricity from various renewable sources (wind, solar) is used in electrochemical process to convert CO₂ and store intermittent renewable energy in form of chemicals. In thermal process heat energy is used to convert CO₂ e.g., plasma may be used for the reduction of CO₂ to convert it to CO. Apart from chemicals and fuels, CO₂ may be used for different value added services as shown in Fig. 16. It may also be used for enhanced

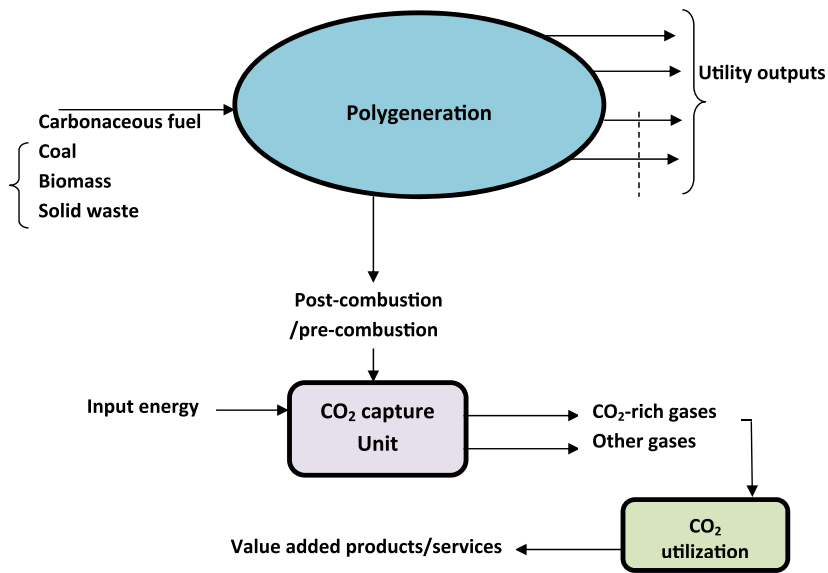


Fig. 14 Schematic of carbon capture and utilization process in polygeneration.

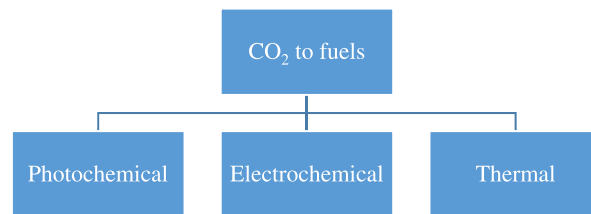


Fig. 15 Conversion route of CO₂ to fuels and value added products. Reproduced from Hu, B., Guild, C., Suib, S.L., 2013. Thermal, electrochemical, and photochemical conversion of CO₂ to fuels and value-added products. *Journal of CO₂ Utilization* 1, 18-27.

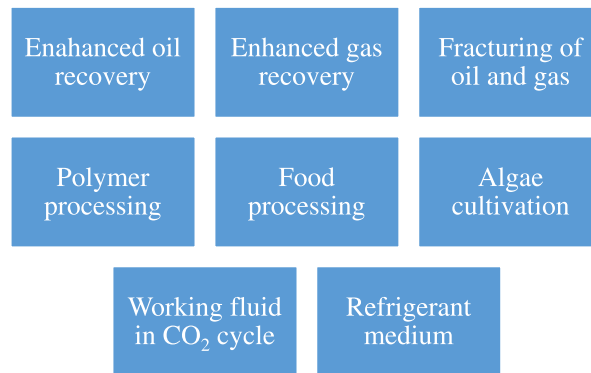


Fig. 16 CO₂ to different value added services. Reproduced from Koytsoumpa, E.I., Berginsa, C., Kakarasa, E., 2018. The CO₂ economy: Review of CO₂ capture and reuse technologies. *Journal of Supercritical Fluids* 132, 3–16.

oil and gas recovery which increases the production of oil and gas from its reservoir. In polymer processing, urea production from CO₂ may be used as the chemical feedstock. In food processing industry, it may be used in beverages, for wine production, for horticulture etc. CO₂ may be used for algae production which is used for advanced biofuel production. Another important use of CO₂ is that it may be utilized as the working medium for different thermal processes. For power generation from low temperature waste heat, it is used in supercritical and transcritical power cycles. It can also be used as working medium for refrigeration cycle. In literature, several authors reported about CO₂ capture and storage including utilization processes. Summary of those is given in

Table 1 Summary of polygeneration with CO₂ capture and storage/utilization

Author	Inputs	Carbon capture	CO ₂ capture technology	CO ₂ captured for	Outputs
Yu <i>et al.</i> (2010)	Coal	Pre-combustion	Rectisol	Fuel Synthesis	FT liquids, power
Meerman <i>et al.</i> (2011)	Biomass, coal, heavy oil, gas	Pre-combustion	Rectisol	Methanol synthesis	H ₂ , electricity, FT liquids, methanol, urea
Hu <i>et al.</i> (2011)	Coal	Pre-combustion	Chemical absorption	CO ₂ recovery and methanol synthesis	Power, methanol
Li <i>et al.</i> (2011)	Syngas, coke oven gas	Pre-combustion	–	CO ₂ recovery and methanol synthesis	Power, methanol, DME
Adams and Barton (2011)	Coal, natural gas	Pre-combustion	Chemical absorption	Fuel input to SOFC, natural gas reforming, methanol synthesis	Electricity, methanol, FT fuel
Ng <i>et al.</i> (2013)	Coal, bio-oil	Pre-combustion, post-combustion	Rectisol	CCU for methanol synthesis	Power, methanol, hydrogen, acetic acid
Li <i>et al.</i> (2014)	Coal	Pre-combustion	Selexol	Methanol synthesis	Power, methanol
Bose <i>et al.</i> (2015)	Coal	Pre-combustion	Chemical absorption	H ₂ production	Power, urea
Jana and De (2015b)	Biomass	Pre-combustion	Chemical absorption (MEA)	Desired H ₂ and CO ratio	Power, ethanol, chill, heat
Fan and Zhu (2015)	Methane	Pre-combustion	Chemical absorption (MEA)	Increasing H ₂ concentration	Power, hydrogen
Yu and Chien (2015)	Coal	Pre-combustion	Selexol	Increasing H ₂ concentration	SNG, ammonia, electricity
Guo <i>et al.</i> (2015)	Lignite	Post-combustion	–	CCS	Electricity, tar
Zhu <i>et al.</i> (2016)	Coal	Oxy-fuel combustion	Chemical looping CO ₂ absorption	CCS	Power, H ₂
Farhat and Reichelstein (2016)	Coal, hydrogen	Pre-combustion	–	H ₂ separation, urea synthesis	Power, H ₂ , ammonia, urea

Note: Jana, K., Ray, A., Majoumerd, M.M., Assadi, M., De, S., 2017. Polygeneration as a future sustainable energy solution – A comprehensive review. *Applied Energy* 202, 88–111.

Table 1. From the table, it is noted that CO₂ capture is used for wide range of coal and biomass inputs. Rectisol, selexol, monoethanol amine are mainly used for the CO₂ capture process. Captured CO₂ may be utilized for fuel synthesis, oil recovery and storage.

Conclusion

CO₂ emission from fossil fuel (mostly coal) based power plants is the major source of greenhouse gas for climate change. Ever increasing demand of energy with population growth and improved life style has also made the problem even more complicated. With huge demand of energy worldwide and available renewable technologies, it is impossible to replace fossil fuel based systems by renewable alternatives overnight. Distributed generation with locally available renewable resources may be a good interim option for mitigating greenhouse gas and carbon footprint. Polygeneration is emerging as an efficient and decarbonized energy solution. In polygeneration, optimum system integration increases the different performances viz., thermodynamic, economic and environmental performances of the plant. Distributed polygeneration utilizing locally available resources to cater to the secondary energy and other utility needs of the local people, increases the social acceptability. Polygeneration integrated with carbon capture gives better performance than standalone carbon capture process. Also polygeneration with carbon capture and utilization emerges as the most promising option to even offset the penalty of carbon capture process.

Acknowledgement

Dr. Kuntal Jana gratefully acknowledges to the Science and Engineering Research Board (SERB, DST), India for awarding National Post-Doctoral Fellowship.

See also: Hybrid Renewable Multigeneration: Low Carbon Sustainable Solution With Optimum Resource Utilization. Power and Other Energy Utilities From Low Grade Waste Heat – Novel Technologies to Reduce Carbon Footprint

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Power and Other Energy Utilities From Low Grade Waste Heat – Novel Technologies to Reduce Carbon Footprint

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Nomenclature

c_p Specific heat at constant pressure (kJ/kg K)
 e_g Exergy of flue gas (kJ/kg)

T_0 Ambient temperature (K)
 T_g Flue gas temperature (K)

Introduction

The rise of global average temperature due to excessive emission of greenhouse gases (specifically CO_2) due to combustion of fossil fuel is an issue of great concern for the survival of future generation. Fossil fuel based power plants are responsible for the majority of this CO_2 emission. However, fossil fuel burning is unavoidable for a considerable period to maintain a desirable industrial growth and living standard.

Though renewable power generation is increasing worldwide, the majority of the global demand for electricity is still from coal based power plants. There is a major gap between generations of secondary energy using renewable resources and corresponding global demand for a sustainable development. In this situation, replacement of older coal based power plants with an improved natural gas based power plants, retrofitting of existing low efficient power plant, incorporating CO_2 capture and sequestrations are possible options to continue with fossil fuel and simultaneously to fight against the threat of global warming. However, all of these are long term and capital intensive options.

On the other hand, a large part of all industrial energy inputs through combustion of fuels is finally released to the local atmosphere as waste heat for existing technologies. This waste heat may be utilized to produce more electricity introducing suitable technology for this purpose. Thus, the amount of fossil fuel burning required for generating an equal amount of power will be reduced and corresponding CO_2 production will be eliminated due to adoption of these waste heat recovery schemes.

It is observed in the literature that if waste heat is available above 250°C , steam based Rankine cycle is the well established technology for converting waste heat into secondary energy. Steam based CCGT (Combined Cycle Gas Turbine) may be cited as an example in this respect. However; innovation is required to generate secondary energy from waste heat available below 250°C .

Some of the refrigeration cycles are heat driven. Replacement of vapour compression refrigeration system with such low grade waste heat driven refrigeration systems will also lead to lesser fossil fuel consumption. Ejector based refrigeration cycles are capable of producing refrigeration effects using low grade waste heat even when waste heat temperature is as low as 100°C .

Due to over use and even with climate change available water for human consumption is fast decreasing. Desalination technology is an important need for future sustainability. Low grade waste heat may also be utilized for the purpose of desalination adding more sustainability. In the middle-east countries, substantial amount of drinking water is produced by the process of desalination.

Review of Energy Scenario Worldwide and Share of Fossil Fuel

Global energy consumption is ever increasing. It is reported in [International energy outlook IEO \(2017\)](#) that between 2015 and 2040 world energy consumption will increase by 28%. More than half of this increment in energy consumption will be in non-OECD Asia (including India and China) due to the rapid economic growth of these countries. It is predicted in this report that there will be 51% increment in energy demand in non-OECD Asia. In Africa and Middle East, this growth will be 51% and 45% respectively. Industrial sector that consumes more than 50% of the world energy production appears to be a major end user of global energy supply.

Though, global contributions of renewable energy are increasing sharply, fossil fuels like liquid fuel (including petroleum), coal and natural gas are the major sources that still contribute to most of the global energy demand. [World energy council/ resources, 2016 summary \(2016\)](#) that oil accounts for 32.9% of global energy demand. On the other hand, coal accounts for close to 30% of global basic energy consumption. 40% of the global secondary energy demand is by coal based power plants. Natural gas is the third major contributor to global primary and secondary energy demands. Presently it contributes to 24% of the global primary energy demand and 22% of the global electricity demand.

Impact of Fossil Fuel on Carbon Footprint

Though fossil fuel contributes to the majority of the global demand for energy, fast depleting resources of fossil fuels and greenhouse gas emissions due to the burning of these fossil fuels are two major concerns. According to [IEA Statistics \(2015\)](#), in the year 2013 global CO₂ emission due to combustion of different fuels had been 32,189.7 million tonnes. 46% of this total emission was due to combustion of coal. The corresponding share of oil and natural gas had been close to 34% and 19.8% respectively. It is critical to note that CO₂ emission due to fuel combustion in the year 2013 was 56.1% higher than that of year 1990. Sector wise, electricity and heat production together contributed to 42.4 % of Global CO₂ emission of the year 2013. Transportation sector was responsible for 23% of global CO₂ emission in that year.

To reduce CO₂ emission, various emission trading schemes have been implemented by various countries. These schemes set prices for CO₂ emission. Some of the countries introduced carbon tax, tax on fuels responsible for emission etc. Currently the EU emission trading system (ETS) includes Norway, Iceland, Liechtenstein and twenty seven members of states. However, it is projected in [International energy outlook IEO \(2017\)](#) that between 2015 and 2040 CO₂ emissions related to Coal, Oil and natural gas will increase by 0.1%, 0.7% and 1.4% respectively. These increments are appreciably small compared to the increment of CO₂ emissions observed between 1990 and 2015 – corresponding values during this period were 2.3%, 1.2% and 2.2% respectively.

It should be noted that in the year 2015, China and USA deducted CO₂ emission by 0.7% and 2.6 % respectively compared to that of 2014. However, these decrements have been nullified by 5.1% and 1.3% increment in emission by India and European Union.

Status of Renewable Energy and Gap between Demand and Supply

As discussed in the previous section, it is clear that the power sector is responsible for more than 40% of the global CO₂ emission. So instead of burning fossil fuels it is better to concentrate on renewable resources like Solar, wind, hydro power etc. Wind, solar and nuclear energy are the forms of energy that can effectively reduce global CO₂ emission. However, improved technology for large power generation at lower cost is the critical challenge for wide spread power harvesting from renewable sources.

It was reported by [IEA Statistics \(2016\)](#) that in the year 2014 only 13.8% of global primary energy was produced from Renewable resources. For electrical energy supply, corresponding value was 22.3% of global electricity production. Out of this 22.3%, 16.4% were only from hydro power and 1.8% was from bio fuel and waste. Thus, in the year 2014, only 4.1% of global demand of electricity was from geothermal, solar, wind and tidal resources.

[International energy outlook IEO \(2017\)](#) reported that between 2015 and 2040 renewable use will grow at an average rate of 2.8% per year. During this period global share of coal based power will decline from 40% in 2015 to 31% in 2040. In the year 2040, renewable resources will contribute 31% of the global demand for secondary energy. Among non hydro-power renewable resources, solar and wind are two fastest growing sectors- global capacity of these two resources will be 2.5 and 1.4 trillion kWh respectively in the year 2040. However, global electricity demand will rise from about 22 trillion kWh in 2015 to about 33 trillion kWh in 2040 and about 57% of this demand will be from coal and natural gas based power plants. Corresponding CO₂ emission will also be an issue of great concern. More over the availability of renewable resources greatly depends on location and environmental condition. Fluctuating supply of electricity from renewable resources is a great challenge for its successful utilization. Thus, in addition to the progress of renewable power generation technology other possible options are to be explored to reduce carbon footprint resulting from burning of fossil fuels. Innovation for improved utilization of fossil fuels for lower CO₂ emission appears to be critical at present.

Improved Utilization of Limited Fossil Fuel

As according to present situation, utilization of renewable resources alone cannot replace fossil fuel based power generation completely, CO₂ emission may be reduced by cutting down fossil fuel consumption with improved utilization efficiency of fossil fuel based power generation. Cogeneration, trigeneration and polygeneration are the technologies available for improved fossil fuel utilization.

Delivering two forms of energy utilities simultaneously using the same energy resource is known as cogeneration. Most widely used cogeneration systems are combined heat and power (CHP) systems in which simultaneous power and process heat are supplied from a single unit. By using a CHP system, it is possible to achieve even 80% overall energy utilization.

Tri generation delivers three utilities (say, power, process heat and refrigeration effect) from a single system. In a tri-generation system, generally an absorption-chiller is integrated with the CHP system. In the early phase of 1980s cooling, heating and power generation were integrated to form a tri-generation unit for serving the purpose of municipal cooling and heating ([Emho, 2003](#)).

When more than three energy services are combined together, the scheme is generally referred to as poly generation. For example, a desalination plant can also be integrated with production of process heat, power and refrigeration effects.

Besides improving thermal efficiency, carbon capture and storage is the direct way to reduce carbon footprint. There are three different pathways of capturing CO₂ before its storage:

- (1) Post combustion CO₂ capture: In this method CO₂ is captured after the combustion of fuel. This is a preferred technology for retrofitting of existing power plants. Larger energy penalty and higher cost are two major constraints for commercial implementation of post combustion CO₂ capture. Implementation of post combustion CO₂ capture may increase electricity generation cost even by 70% (Leung *et al.*, 2014).
- (2) Pre combustion CO₂ capture: In this method the fuel is pre-treated to remove carbon from it before the final combustion of rest combustible, mainly hydrogen. For an example, before the actual combustion of coal, a gasification process may produce a syngas, which is mainly a combination of CO and H₂. This syngas is then converted to a mixture of H₂ and CO₂ through a water gas shift reaction. High concentration of CO₂ in the mixture of CO₂ and H₂ results in better separation efficiency for absorption and adsorption. Pre combustion CO₂ capture is a suitable option that can be used for an integrated gasification combined cycle (IGCC) power plant.
- (3) Oxy fuel combustion: in this process, pure oxygen is used as the oxidant instead of air during the combustion process. This results in flue gas free from nitrogen and its oxides. Particulate matters and SO₂ are separated from the flue gas by electrostatic precipitation and desulphurization methods respectively. Finally flue gas that contains about 80%–98% CO₂ is compressed, transported and stored. Requirement of a large air separation unit results in higher costing and about 7% energy penalty (Leung *et al.*, 2014). Corrosion of equipment due to high SO₂ concentration is another issue of concern for its implementation.

After separation of CO₂ from flue gas it is to be transported to a storage site through road tanker, ship or pipeline. The pipeline is the most viable option for offshore transportation of CO₂.

Finally, CO₂ is to be stored in geological reservoir. Depleted oil and gas reservoir, un-mineable coal beds, saline aquifer are possible geological reservoirs for storage of CO₂.

As a substantial part of the energy input is finally rejected as waste heat it can be utilized to produce secondary energy or utilities that consume the secondary energy. Thus, additional requisite fuel burning for supplying this amount of electricity and corresponding CO₂ emission may be avoided.

Energy Efficiency Through Waste Heat Recovery

Most of the industrial units require thermal energy input for their operation. It was presented by Rosen (2013) that in the year 2005 total industrial energy input was about 87.6 Exa Joule (EJ). Out of this energy input only 44.6 EJ was utilized. Thus, nearly 50% of the industrial energy input remained un-utilized and ultimately released into the environment as waste heat. Obviously there is wide variation in quality and quantity of waste heat released from different industries.

Utilization of industrial waste heat to meet a part of localized electricity demand or to supply auxiliary power to run equipment may enhance overall utilization efficiency of fossil fuel input and reduce carbon footprint through less fossil fuel consumption. It should be noted that energy performance of waste heat recovery unit greatly depends on quality of waste heat and environmental condition. Proper selection of technology and suitable working fluid are also very important factors for the successful implementation of waste heat recovery process.

Classification of Waste Heat Recovery and its Challenges and Issues

It is important to note that majority of waste heat is carried away by the flue gas streams and released finally to the local atmosphere. Depending on the temperature of the waste heat, it can be classified into three different categories as shown in Table 1.

The quality of waste heat depends on flue gas temperature and can be represented by its exergy value. Exergy is the theoretically maximum useful work obtainable from a given heat source. It depends on flue gas temperature as well as the temperature of the immediate surroundings as shown in Eq. (1):

$$e_g = c_{pg}(T_g - T_0) - c_{pg} \ln \left(\frac{T_g}{T_0} \right) \quad (1)$$

Variation of exergy of flue gas stream with a varying flue gas temperature at different ambient temperatures is demonstrated in Fig. 1. It is evident from Fig. 1 that exergy or the quality of the flue gas decreases with a decrease in flue gas temperature.

Table 1 Waste heat classification

Flue gas temperature (°C)	Category waste heat	% of total global waste heat
> 300	High temperature	21
100–299	Medium temperature	16
< 100	Low temperature	63

Note: Forman, C., Muritala, I.K., Pardemann, R., Meyer, B., 2016. Estimating the global waste heat potential. *Renewable and Sustainable Energy Reviews* 57, 1568–1579.

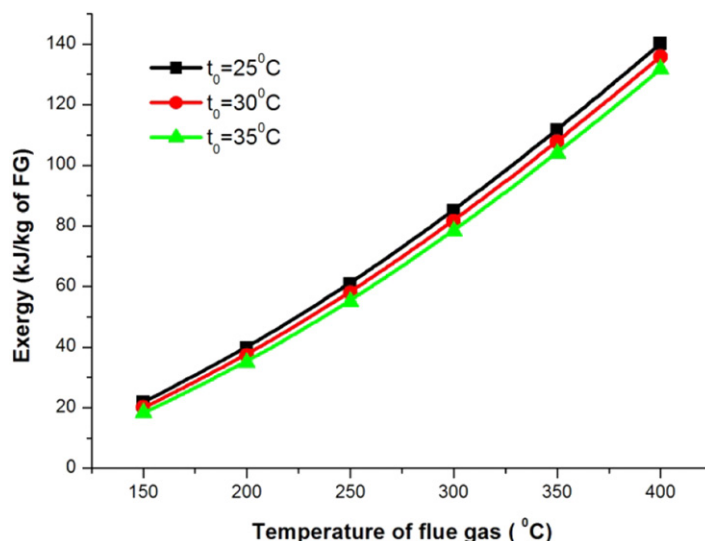
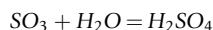
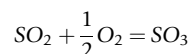


Fig. 1 Exergy variation with varying temperature of flue gas.

The most effective way of utilizing waste heat is to produce secondary energy through some thermodynamic cycles. For fixed heat source and sink temperatures, theoretically most efficient thermodynamic cycle for generating power is Carnot cycle. As during the execution of any real cycle, certain finite temperature difference between the flue gas and the working fluid during heat transfer is always be there, the efficiency of the any actually executed cycle is always less than that of the Carnot cycle. Efficiency of any power cycle sharply decreases with a decrease in heat source temperature. As a result waste heat recovery becomes more challenging as flue gas temperature decreases. This challenge is even more for the ambient temperature being higher.

Besides flue gas temperature, composition of the flue gas is another major factor for the selection of suitable waste heat recovery scheme. If some amount of SO_2 is present in the flue gas then SO_2 reacts with moisture and produces sulphuric acid. Reaction of sulphuric acid formation is presented as follows:



Acid dew point temperature (i.e., sulphuric acid condensation temperature) of the flue gas varies between 115° and 160°C depending on the SO_2 content in the flue gas. As sulphuric acid is highly corrosive, cooling of the flue gas in the waste heat recovery unit (HRU) below the acid dew point temperature must be avoided to ensure longer life. Improving 1st law or thermal efficiency of a thermodynamic cycle is the prime objective as for a specified mass flow rate and temperature of the flue gas, waste heat available is fixed. However, if the flue gas is free from SO_2 , it is better to cool it to a much lower temperature as it would increase the power output from same available heat of the flue gas. Thus, for SO_2 free flue gas, maximizing work output per kg of flue gas flow is the objective instead of improving thermal efficiency of conversion of waste heat to work. While improving cycle performance, economical aspect must also be considered.

Need of Innovation in Low Grade Waste Heat Recovery

The technology available for converting available waste heat at a temperature higher than 250°C is well established. Steam based Rankine cycle is the best option for utilizing this heat source from thermodynamic as well as environmental point of view. Steam based Combined cycle gas turbine power plant may be cited as an example for utilizing available waste heat above 250°C . However, appreciable amount of flue gas is coming out from different industries at a temperature lower than 200°C .

Most commonly available technology for converting low grade heat into power is by using an Organic Rankine cycle (ORC). However, for subcritical ORCs at least 20° – 30°C terminal temperature difference is to be maintained at the higher temperature end of the HRU to maintain a feasible size of the HRU. This results in lower turbine inlet temperature and smaller thermal efficiency of the ORC. Generally the pinch point temperature difference occurs at the exit of the economizer as shown in Fig. 2. For maintaining the feasible size of the HRU, there should be 5° – 10°C pinch point temperature difference between the flue gas and the working fluid streams. Due to this pinch limitation of ORC, flue gas cannot be cooled below a certain temperature. This leads to a bad utilization of waste heat of flue gas free from SO_2 as the cycle power output decreases due to a smaller heat input to the cycle. Thus innovations are required to improve thermodynamic performance by addressing these two issues.

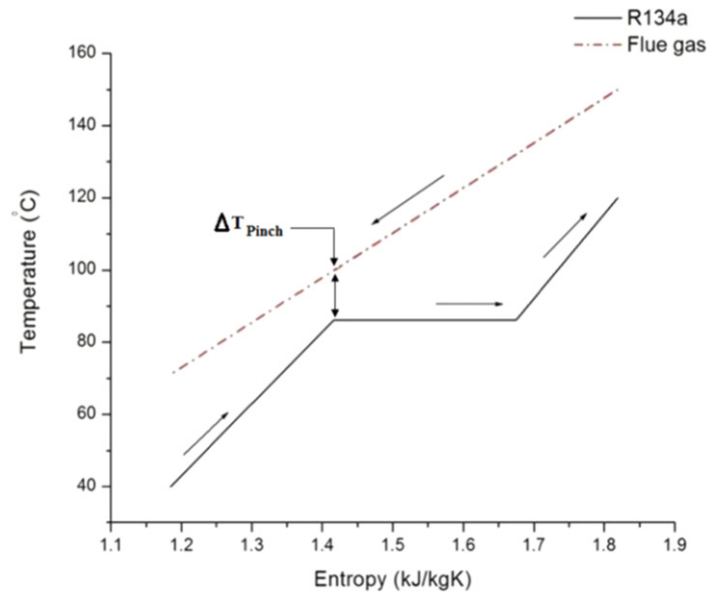


Fig. 2 Temperature profiles for working fluid and flue gas of an ORC.

Table 2 Environmental and safety data of selected refrigerant

Category	Refrigerant	Critical temperature (°C)	Critical pressure (MPa)	ODP	GWP in 100years	ASHRAE safety group
Natural refrigerant	CO ₂ (R744)	30.978	7.38	0	1	A1
	Ammonia (R717)			0	0	B2
HC	N ₂ O (R744A)	36.425	7.254	0.017	298	A1
	Butane (R600)	152.01	3.796	0		A3
	Isobutane (R600A)	134.7	3.64	0	~20	A3
	Pentane (R601)	196.56	3.358	0	~20	A3
	Isopentane (R601A)	187.78	3.358	0	~20	A3
HFC	Propane (R290)	96.7	4.248	0	~20	A3
	Difluoromethane (R32)	78.11	5.782	0	675	A2L
	1,1,1,2-tetrafluoroethene (R134a)	101.06	4.059	0	1430	A1
	1,1-Difluoroethene (R152a)	113.26	4.517	0	124	A2
	Fluoroethane (R161)	102.22	4.702	0	12	-
	1,1,1,3,3,3-Hexafluoropropane (R236ea)	139.29	3.502	0	1370	-
	1,1,1,3,3-Pentafluoropropane R245fa	154.05	3.64	0	1030	B1

Note: Calm, J.M., Hourahan, G.C., 2011. Physical, safety, and environmental data for current and alternative refrigerants. In: Proceedings of the 23rd International Congress of Refrigeration. Prague, Czech Republic.

Selection of Working Fluid for Low Temperature Waste Heat Recovery

Selection of suitable working fluid with zero ODP, low GWP and reasonable thermodynamic performance is another challenging task. CFCs (Chlorofluorocarbons) had been most preferred working fluids since 1930. However, Montreal protocol decided to phase out production of CFCs by 2010 due to high ozone depletion potential of CFCs. Soon HCFCs (Hydrochlorofluorocarbons) appeared as alternatives of CFCs. But due to very high GWP use of HCFCs will not be permitted after 2030 in developed countries and after 2040 in developing countries (Powell, 2002). HFCs are to be phased out by the year 2047 according to Kigali amendment to the Montreal protocol introduced in 2016. In this situation, natural refrigerants, Hydrocarbons, and some of the HFCs (Hydrofluorocarbons) with low GWP are the possible working fluids for waste heat recovery as listed in Table 2 (Calm and Hourahan, 2011).

Both CO₂ and NH₃ are in use since the 19th century. However, high toxicity of ammonia is an issue of great concern for their utilization in the HRU. On the other hand, CO₂ is a non-flammable and non toxic working fluid. Due to lower critical temperature, CO₂ at supercritical state can be utilized for the recovery of low grade waste heat. This eliminates the pinch limitation of

the subcritical HRU. Supercritical CO_2 has a concave shaped temperature profile as shown in Fig. 3. This allows operation of the HRU with smaller terminal temperature differences by maintaining a feasible size of the HRU. Thus, CO_2 can be heated closer to the flue gas inlet temperature to achieve higher 1st law efficiency. High operating pressure ($> 10\text{MPa}$) of CO_2 inside the HRU is a disadvantage of the CO_2 power cycle. However, CO_2 may be considered as the most preferable working fluid after steam if thermodynamic, environmental and safety issues are considered together. For low grade waste heat recovery, CO_2 is emerging as a better option than steam.

Hydrocarbons yield satisfactory thermodynamic performance for low temperature waste heat recovery. They are non toxic and with zero ODP and negligible GWP. However, they fall in A3 safety category which means they are highly flammable gases. Thus, possible safety measures are to be ensured to eliminate the accidental explosion while using HCs as working fluids.

HFCs are having higher GWP compared to HCs. However, they are favoured due to their excellent thermodynamic properties and less chance of explosion. For an example R32 is slightly flammable and R245fa is non flammable. But R245fa is toxic to some extent.

Besides refrigerants listed in Table 2, recently some of the HFOs (Hydrofluoroolefins) may be considered for future use as working fluids. As listed in Table 3 these working fluids are less flammable compared to hydrocarbon as well as having zero ODP and lower GWP. However, they are still not available commercially.

Finally, it should be noted that saturated vapour lines of some of the working fluids (R600, R600a, and R245fa etc.) have positive slope. These working fluids are known as dry working fluids. Some of the working fluids which are having almost vertical vapour lines are known as isentropic working fluids. With the use of dry or isentropic working fluids, compulsory requirement of a super heater in conventional ORC can be eliminated.

Some Case Studies and Current Status

Low grade waste heat recovery through innovative power cycle is recently gaining importance. According to recent studies, transcritical CO_2 power cycle, Organic flash cycle, ORC with a blend of hydrocarbon and inert compounds are possible options for the conversion of low grade waste heat (i.e., $120^\circ\text{C} < t_g < 200^\circ\text{C}$) to power. Besides vapour absorption refrigeration cycle, ejector refrigeration cycle is also emerging as another option for the utilization of low grade heat below 150°C . A few case studies for such low grade waste heat recovery are discussed here.

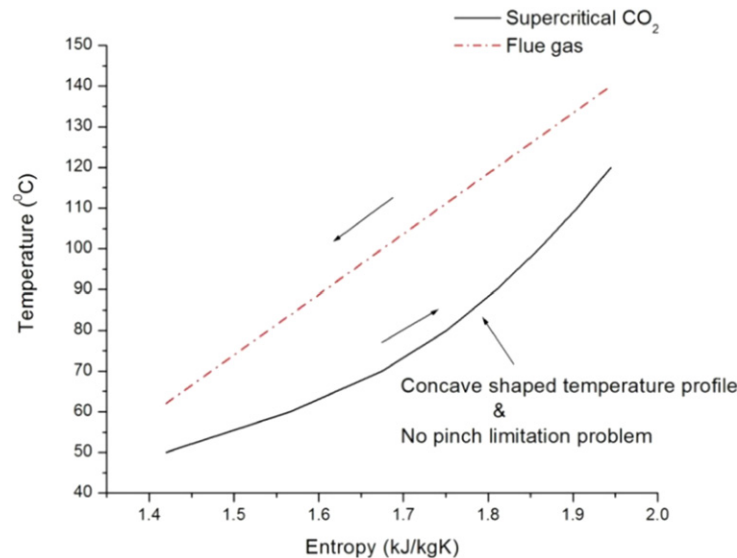


Fig. 3 Temperature profile of supercritical CO_2 .

Table 3 Environmental and safety data for HFO refrigerant

Refrigerant	Critical temperature($^\circ\text{C}$)	Critical pressure(MPa)	ODP	GWP in 100years	ASHRAE safety group
R1234yf	94.7	3.3822	0	04	A2L
R1234ze(E)	109.36	3.6349	0	06	A2L
R1234ze(Z)	150.12	3.53	0	<10	A2L

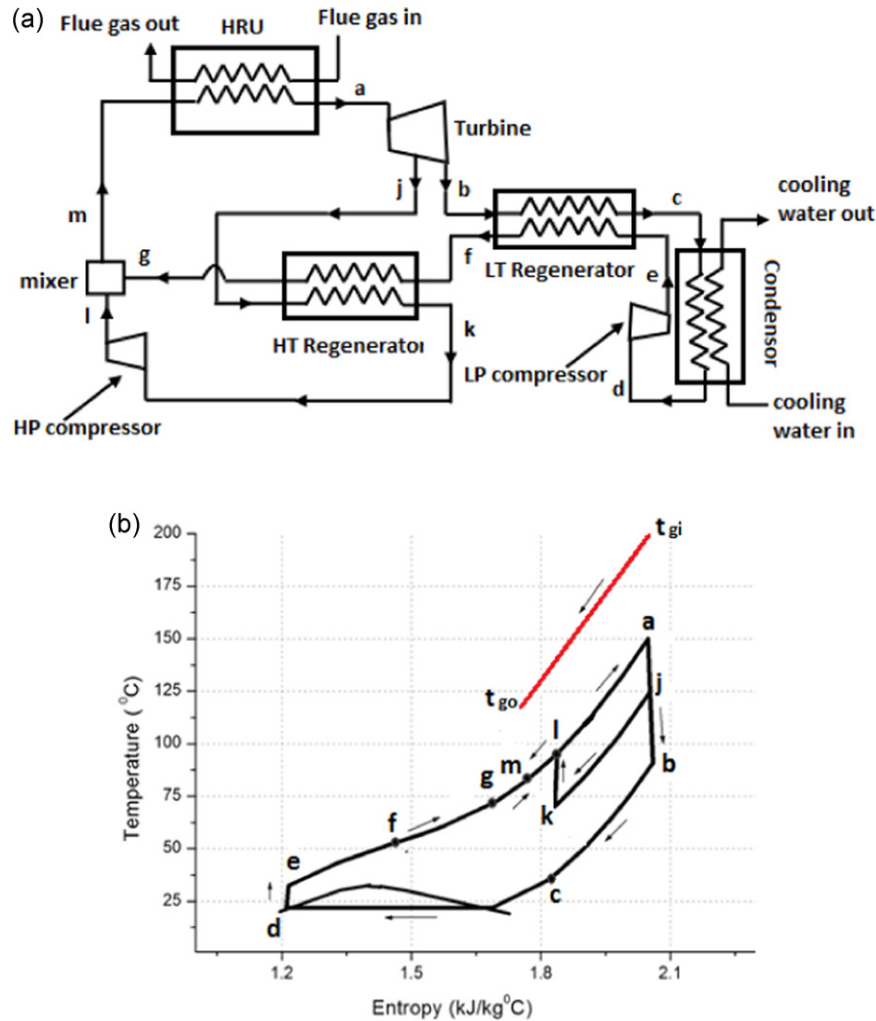


Fig. 4 (a) Lay out of the regenerative T-CO₂ power cycle. (b) T-s diagram of the regenerative T-CO₂ power cycle. Reproduced from Mondal, S., De, S., 2015. Transcritical CO₂ power cycle – Effects of regenerative heating using turbine bleed gas at intermediate pressure. *Energy* 87, 95–103.

Case study-1, Regenerative CO₂ power cycle – A scheme for utilization of low grade waste heat of flue gas containing SO₂ (Mondal and De, 2015)

In this study, the available flue gas temperature was 200°C and flue gas could not be cooled below 120°C in the HRU to avoid sulphuric acid condensation. Thus, in this study improvement of 1st law efficiency was the basic objective as the recoverable heat was a constant quantity for specified mass flow rate of the flue gas. To achieve higher 1st law efficiency two regenerators were introduced into the system as shown in [Fig. 4\(a\)](#). The T-s diagram of the proposed layout is presented in [Fig. 4\(b\)](#). The CO₂ stream coming out from the compressor at state-e initially was heated in the low temperature (LT) regenerator by the heat of exhaust CO₂ stream of the turbine. Then the CO₂ stream entered into the High temperature (HT) regenerator at state-f and was heated further to state-g by the heat of the bleed CO₂ stream extracted at some intermediate pressure (i.e., state-j) of turbine expansion. After being cooled (process j-k) in the HT regenerator bleed CO₂ mass was pressurized to turbine inlet pressure (i.e., state-l) and mixed with the main CO₂ stream. After the mixing, total mass of CO₂ mass was heated (i.e., process m-a) to turbine inlet temperature by the waste heat of flue gas. Various input parameters considered during the analysis are listed in [Table 4](#).

It was observed that the 1st law efficiency as well as the 2nd law efficiency increased monotonically as more and more mass of CO_2 was extracted from the turbine for the purpose of heating of the main CO_2 stream in the regenerator. With larger bleed mass of CO_2 , total CO_2 mass entered into the HRU at some higher temperature. Thus, the larger mass of CO_2 was heated in the HRU by using the same mass of flue gas as well as irreversibility of the HRU reduced with the introduction of additional regenerator. Finally, it was concluded in this study that efficiencies could not be improved beyond a certain level as an increment of bleeding CO_2 mass beyond a certain value resulted in exponential increment in the size (i.e., NTU) of the HT regenerator.

This analysis also considered the effects of varying isentropic efficiency of the compressor on cycle performance. It was observed that cycle performance improved more significantly with a higher isentropic efficiency of the compressor for higher values of bleed

Table 4 Operating condition of the regenerative T-CO₂ power cycle with turbine bleeding

Operating parameters	Values
Turbine inlet pressure	12 MPa
Turbine Inlet temperature	150°C
Turbine exit pressure	6 MPa
Flue gas inlet temperature	200°C
Isentropic efficiency of the turbine	90%

Note: Mondal, S., De, S., 2015. Transcritical CO₂ power cycle – Effects of regenerative heating using turbine bleed gas at intermediate pressure. Energy 87, 95–103.

ratio. An optimum bleed pressure corresponding to maximum 1st and 2nd law efficiency was identified during the operation of the proposed cycle for any specified bleed mass of CO₂ from the turbine.

Case study-2, a comparison between T-CO₂ cycle and Organic flash cycle (OFC) while utilizing low grade heat of flue gas free from SO₂ (Mondal and De, 2017a)

Due to the smaller thermal efficiency of power cycles driven by low grade heat sources, only larger heat input would result in satisfactory power output. Thus, if flue gas is free from SO₂, it is better to cool the flue gas down to some lower temperature to enhance power output from a given mass of flue gas available at a temperature below 200°C. Transcritical CO₂ power cycle without regeneration and Organic flash cycle (OFC) are two cycles that allow cooling of the flue gas down to a temperature which is much smaller than the acid dew point.

T-s diagrams of these two cycles are presented in Figs. 5(a) and 5(b) respectively. As shown in Fig. 5(b) in organic flash cycle working fluid undergoes a throttling process after being heated (i.e., process e-f) to saturated liquid state in the HRU. After throttling (i.e., process f-g), wet stream of working fluid enters into the vapour separator (State-g). Dry saturated vapour coming out from the separator is expanded (i.e., process a-b) in turbine to produce power output. It is important to note that selected working fluid for OFC should be a dry or isentropic working fluid.

Mondal and De conducted thermodynamic as well as economic comparison of these two cycles to explore the better option for utilizing low grade heat of flue gas free from SO₂. They considered R245fa and R600 as working fluids of OFCs taking environmental factors in consideration. In that analysis working fluids for all cycles were heated to 140°C using the waste heat of the flue gas at 150°C. The working fluid temperature at the exit of the condenser was 30°C for each of these two cycles.

It was reported that work output per kg of flue gas flow of OFCs were slightly lower compared to that of the T-CO₂ power cycle if 10°C terminal temperature difference was maintained at the low temperature end of the HRU. However, this difference reduced gradually as the terminal temperature difference at the low temperature end of the HRU increased gradually.

As maximum operating pressure of the T-CO₂ power cycle was much higher compared that of the OFC, the economic comparison of these cycles in terms of bare module cost (BMC) per kW of power output were also required. The analysis revealed that the T-CO₂ power cycle could produce unit power output at smaller BMC compared to that of the OFCs for 10°C terminal temperature difference at the low temperature end of the HRU. However, BMC kW⁻¹ could be reduced appreciably for OFCs by increasing the terminal temperature difference at the low temperature end of the HRU. It was concluded that T-CO₂ power cycle would be a better option for low grade waste heat recovery if thermodynamic and environmental issues are only taken into consideration. However, OFCs appeared to be an economically better option if lesser work output per kg of flue gas is acceptable. Out of OFCs, OFC with R600 was a better option due to smaller GWP of R600. However, it was suggested to take suitable safety precautions to avoid possible accident due to the high flammability of R600.

Case study-3, low grade heat recovery from SO₂ free flue gas through ejector base combined power refrigeration cycle (Mondal and De, 2017b)

Organic flash cycle (OFC) is capable of converting low grade waste heat into power effectively if flue gas is free from SO₂. However, in an OFC, appreciable amount of energy remains un-utilized due to throttling of saturated liquid stream exiting the vapour separator.

Mondal and De proposed to utilize the energy of this saturated liquid stream to run an ejector based refrigeration cycle as shown in Fig. 6. Saturated liquid stream exiting the vapour separator entered as the primary flow to the ejector. Saturated vapour stream leaving the refrigerator evaporator entered into the ejector as the secondary flow.

The ratio between the secondary mass flow and the primary mass flow was maintained in such a manner that the total refrigerant mass leaving the ejector was at condenser pressure. R245fa was considered as the working fluid due to zero ODP and non-flammable nature. This cycle exhibited appreciably higher first and second law efficiency compared to an ordinary OFC. For condenser temperature more than 40°C, an additional compressor was introduced into the system for achieving reasonable amount of refrigeration effect.

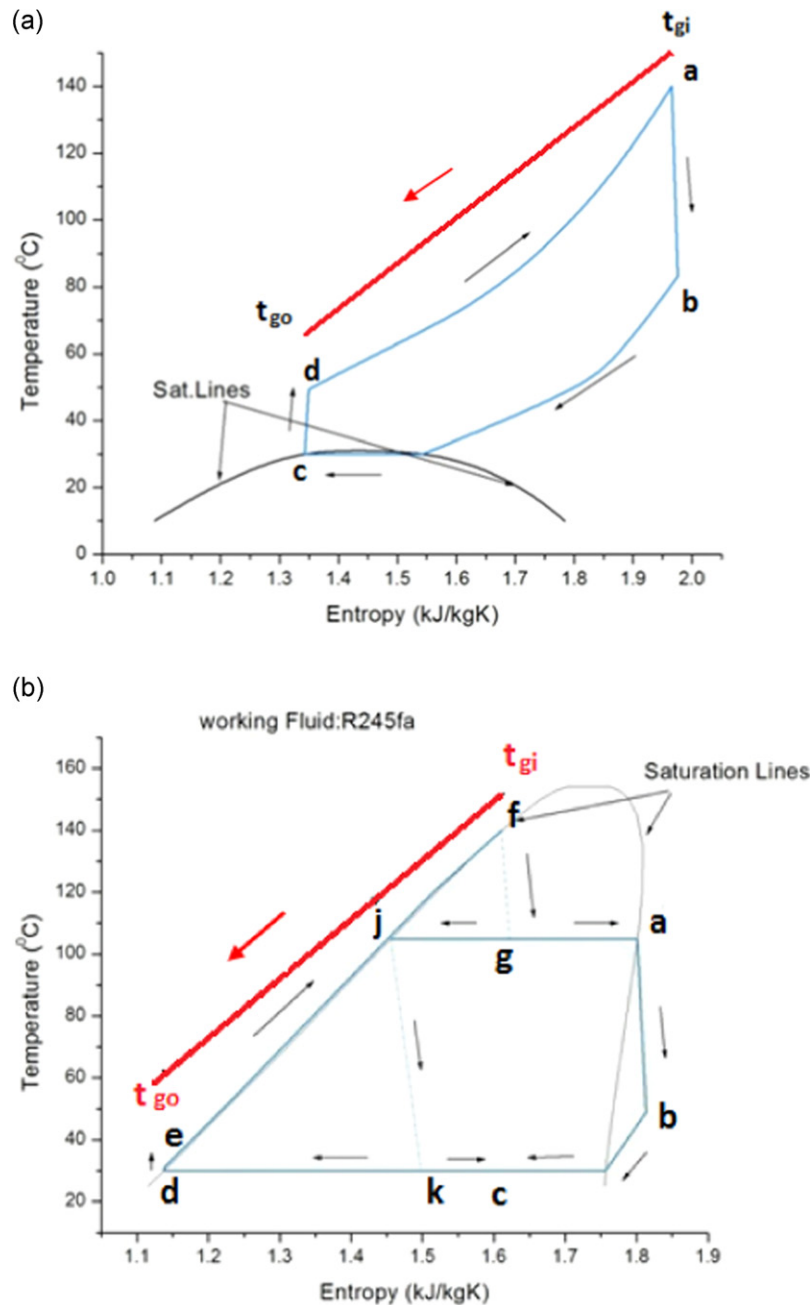


Fig. 5 (a) T-s diagram of T-CO₂ power cycle. (b) T-s diagram of OFC. Reproduced from Mondal, S., De, S., 2017a. Power by waste heat recovery from low temperature industrial flue gas by Organic Flash Cycle (OFC) and Transcritical-CO₂ power cycle: A comparative study through combined thermodynamic and economic analysis. Energy 121, 832–840.

Case study-4. Desalination using low grade heat source (Hamieh *et al.*, 2001)

Hamieh *et al.* (2001) demonstrated desalination of mild brackish water containing about 800 PPM of dissolved solids. They applied dew evaporation technique for this purpose – this device could be operated even when the heat source temperature is in between 65° to 100°C.

The working principle of the dew evaporation technique may be explained with the help of Fig. 7. The dew evaporation system consists of an evaporation tower and a dew formation tower. In the evaporation tower, air is allowed to pass from bottom to top and saline water is allowed to come down through the wall of the tower at some higher temperature. The air absorbs the water and comes out through the top portion with high moisture content. The air is further heated before entering into the dew formation tower and humidified to increase humidity. While coming down through dew formation tower, air is cooled and dehumidified by

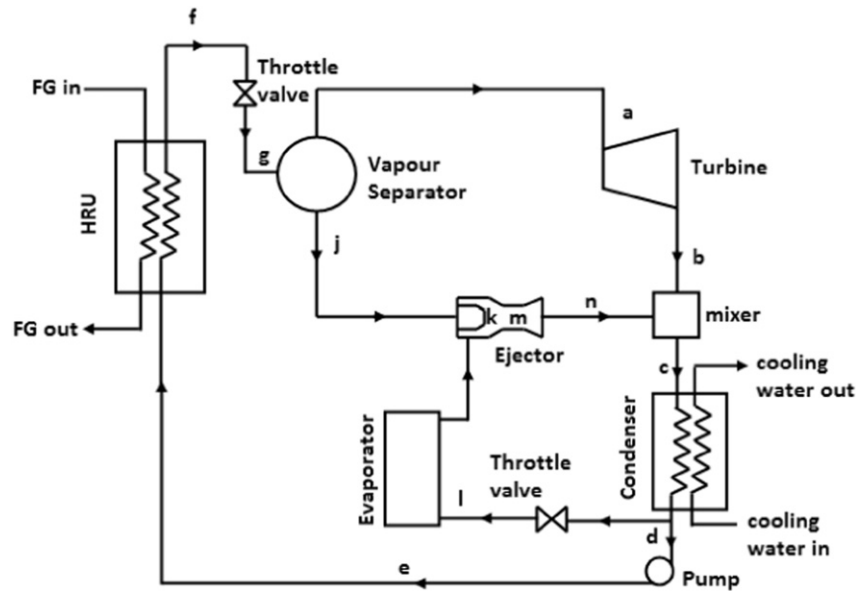


Fig. 6 Layout of ejector based combined power and refrigeration cycle. Reproduced from Mondal, S., De, S., 2017b. Ejector based organic flash combined power and refrigeration cycle (EBOFCP&RC) – A scheme for low grade waste heat recovery. *Energy* 134, 638–648.

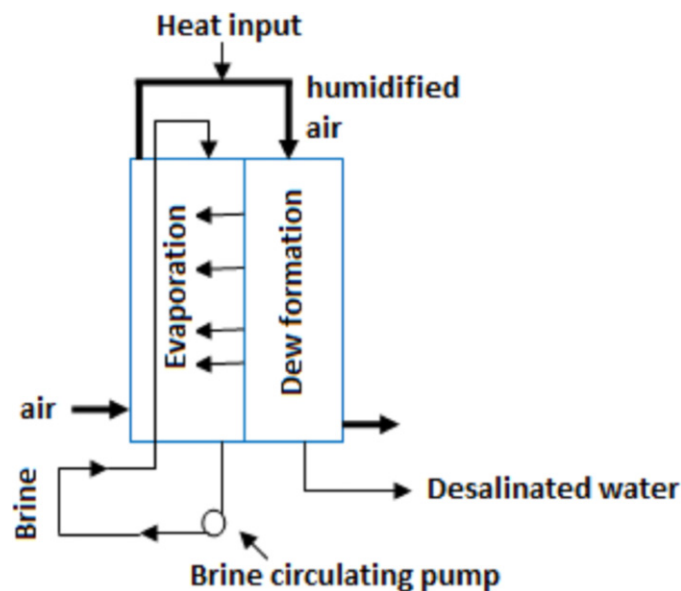


Fig. 7 Heat driven dew evaporation system. Reproduced from Hamieh, B.M., Beckman, J.R., Ybarra, M.D., 2001. Brackish and seawater desalination using a 20 ft² dewvaporation tower. *Desalination* 140, 217–226.

rejecting heat to air and water passing through the evaporation tower. Fresh water getting separated from the air is collected at the bottom of the dew formation tower.

Most of the heat driven desalination system suffers from the problem of formation of scales on the heat transfer wall. The experimental setup developed by Hamieh *et al.* (2001) not only eliminated this problem, but also was capable of producing desalinated water with an energy reuse factor of 11. Energy reuse factor is defined as energy recovered by re-circulating the brine to that of supplied from the external source.

Conclusions

As CO₂ emission due to fossil fuel combustion is mainly responsible for global warming, it is necessary to reduce global consumption of fossil fuel. However, global consumption of primary and secondary energy is increasing steadily with time. Though technologies of

producing power from renewable sources like solar, wind, geothermal, etc. are improving; still there is an enormous gap between global demand of secondary energy and installed capacity of power from renewable resources. As more than 50% of the industrial energy input as heat remains unutilized and finally rejected to atmosphere as waste heat, utilization of this waste heat for producing power and other energy utilities may be a significant sustainable options for reducing global carbon footprint.

Technology for producing power using high temperature (i.e., above 250°C) industrial waste heat is a well established. However, this conversion becomes very challenging as the waste heat temperature is below 200°C. Suitable working fluid selection based on thermodynamic, environmental and safety issues together is another challenging task. CO₂ may be considered as the most suitable working fluid for low grade waste heat recovery if thermodynamic performance, safety issues and environmental issues are preferred aspects.

In this article, four case studies are reported to explore possible ways of utilizing low grade waste heat of available industrial flue gases. The first case study illustrates suitability of CO₂ power cycle for utilization of low grade waste heat of flue gas containing SO₂. In the second case study it was demonstrated that CO₂ power cycle without regeneration as well as OFC were effective to convert low grade SO₂ free waste heat into power. In the third case study working principle of a low grade waste heat driven combined power and refrigeration cycle was demonstrated. In the fourth case study, possible use of low grade waste heat driven dew evaporation desalination system was explored. The temperature of this waste heat was as low as 100°C. These case studies demonstrate that there is a huge potential of effective utilization of low grade waste heat for producing power and other energy services adding to lesser consumption of fossil fuel and corresponding lower CO₂ emission for same energy services. However, further research is necessary for commercial utilization of low grade waste heat for producing power and other energy utilities.

See also: Hybrid Renewable Multigeneration: Low Carbon Sustainable Solution With Optimum Resource Utilization. Plasma Arc Driven Solid Waste Management: Energy Generation and Greenhouse Gases (GHGs) Mitigation. Synthesis of Multiwalled Carbon Nanotubes (MWCNTs) From Waste Cooking Oil Catalyzed by Mill-Scale Waste for Development of Microstrip Patch Antenna (MPA)

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Quality of Environment and Clean Manufacturing

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Introduction

Cleaner manufacturing plays a vital role in the day to day life of mankind, it is a continuous preventive environmental strategy applied to processes, products and services to increase overall efficiency, and reduce risks to humans and the environment. Cleaner production can be functional to the processes used in any industry, to products and to various services provided in society. The mission of cleaner production can be achieved from preserving raw materials and energy, replacing toxic/hazardous materials and reducing the quantity and/or toxicity of all emissions and wastes before they leave a production process (see “Relevant Websites” section). The manufacturing industry aim should be to improve productivity and product quality at the same time as maintaining clean and sustainable environment (Aghion *et al.*, 2009). Environment awareness is of the utmost importance to all socially responsible manufacturers. A strict environmental regulation has to be regulated into the industry keeping increasing global competition in the world. The change in environment are indicated through CO₂ emissions per capita, change in forest area, consumption of ozone depleting substances, and lack of access to improved sources of water (Ayouty *et al.*, 2017). The automobile industry is under pressure to take action at its product carbon footprint. The wide use of fossil fuels is gradually more renowned as unsustainable as a result of depletion of supplies and the input of these fuels to climate change by GHG (greenhouse gas) emissions into the atmosphere (Maity *et al.*, 2014). It is very important to understand that the future of industry depends upon how we channelized today (Aghion *et al.*, 2009), therefore mitigation of greenhouse gases can only be achieved by adopting sustainable techniques of manufacturing which include minimizing the number of manufacturing steps by employing advanced and alternative methods (Gupta *et al.*, 2016). Increased energy efficiency, optimization of energy structure and the generation of a sustainable consumption and production patterns will provide opportunities to resolve regional and the global environmental problems (Yia *et al.*, 2007). With the increasing report on environment and energy shortage, the world have understood the importance of its prevention, therefore this task of promoting education in energy conservation and environment effect has been taken actively. Many countries have started to identify their responsibility for decreasing the unfavorable effect of high energy use on the environment (Bilgen and Sankaya, 2018). Most of the industry are examining the flow of materials and energy in a company and tries to identify options to minimize waste and emissions out of industrial processes through source reduction strategies. For better selection in use of materials and energy, and to avoid waste, waste water generation, and gaseous emissions, and also waste heat and noise the development of organization, technology and ethics of company should be correct which will help in mitigation of greenhouse gases (see “Relevant Websites” section). Waste Management and consumption patterns will continue to be important activities for many years to come (Kjaerheim, 2005) (Figs. 1–3).

The Evolution of Cleaner Manufacturing

The concept of clean manufacturing was developed under the leadership of Jacqueline Aloisi de Lardere, the former Assistant Executive Director of UNEP, during the preparation of the Rio Summit as a programme of UNEP (United Nations Environmental Programme) and UNIDO (United Nations Industrial Development Organization). The programme was meant to reduce the environmental impact of industry. It built on ideas used by 3 M (Man, Machine and Material) in its 3P programme (Pollution Prevention and Pays). It has found more international support than all other comparable programmes. The programme idea was describe to assist developing nations to progress from pollution to less pollution using available technologies. Clean production was developed with simple idea to increase the resource efficiency of production by less waste. UNIDO has been operating National Cleaner Production Centers and Programmes (NCPCs/NCPPs) with centers in Latin America, Africa, Asia and Europe (see “Relevant Websites” section). At first, productivity improvement focused only on quantity; i.e., outputs. As the markets developed and competition increased, cost effectiveness became the key factor towards success. Therefore, a cost reduction approach was used to improve profitability or organizational effectiveness; viz. productivity. Next, growing consumer preferences and competition lead in the era of the quality drive. The consistency of delivering the utmost quantity of a product at the desired level of quality in a cost-effective manner became the third generation concept in the productivity movement and hence a number of management systems emerged – Total Quality Management (TQM), Total Preventive Maintenance (TPM) and subsequently, the international standard on Quality Systems viz. the ISO 9000 series. While the productivity concept expanded, the field of environmental management also matured and broadened (see “Relevant Websites” section) (Table 1).

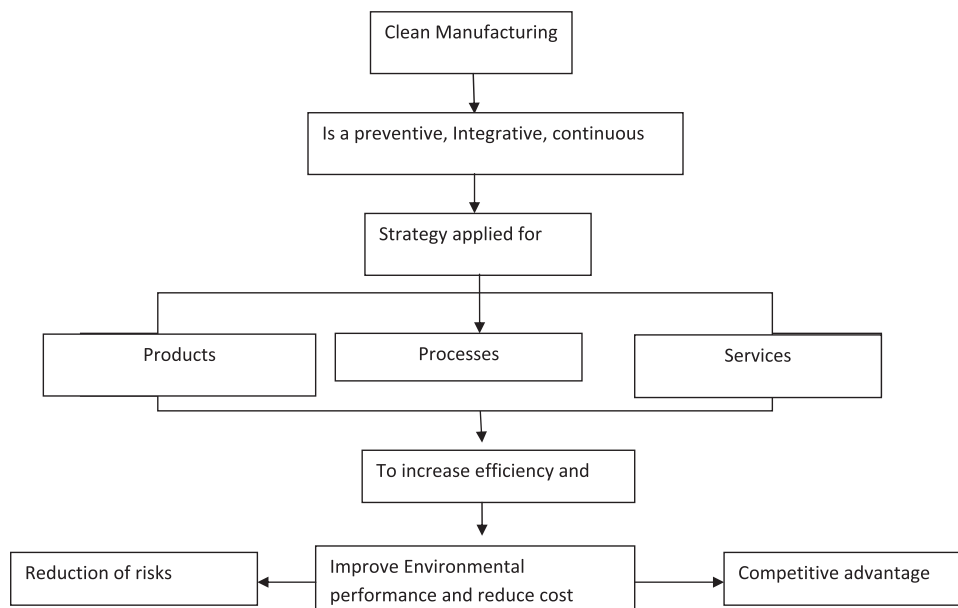


Fig. 1 Definition of clean manufacturing.

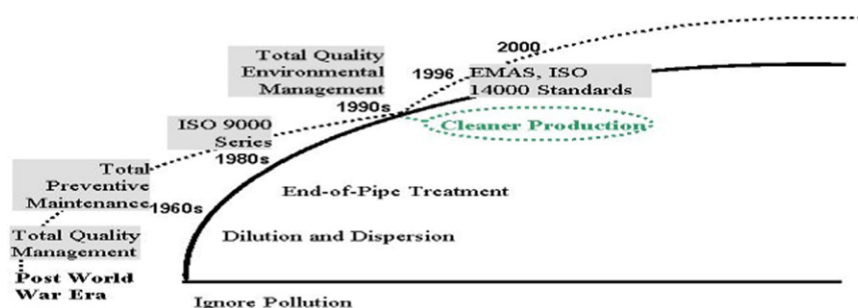


Fig. 2 Tracking the influence of quality programmes on productivity (<http://www.unep.fr/shared/publications/other> – How to establish and operate cleaner production centres).

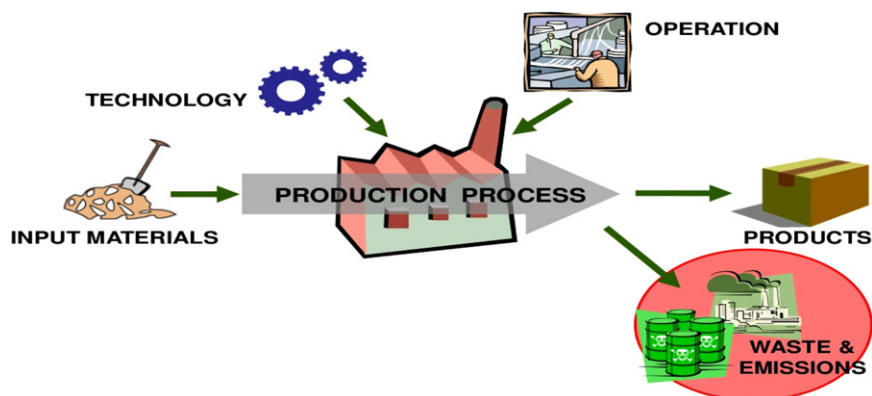


Fig. 3 Categories of manufacturing unit. Reproduced from Anon, Applying cleaner production to multilateral environmental agreements. Basics of cleaner production.

Table 1 Environmental impacts linked with manufacturing waste

<i>Waste type</i>	<i>Environmental impact</i>
Defects	Raw materials consumed in making defective products, defective components require recycling or disposal. More space required for rework and repair, increasing energy use for heating, cooling, and lighting
Waiting	Potential material spoilage or component damage causing waste. Wasted energy from heating, cooling, and lighting during production downtime.
Overproduction	More raw materials consumed in making the unneeded products Extra products may spoil or become obsolete requiring disposal.
Movement and transportation	More energy use for transport Emissions from transport More space required for work-in-process (WIP) movement, increasing lighting, heating, and cooling demand and energy consumption. More packaging required to protect components during movement.
Inventory	More packaging to store WIP Waste from deterioration or damage to stored WIP More materials needed to replace damaged WIP More energy used to heat, cool, and light inventory space.
Complexity and over processing	More parts and raw materials consumed per unit of production, Unnecessary processing increases wastes, energy use, and emissions.
Unused creativity	Fewer suggestions of pollution and waste minimization opportunities.

Source: EPA, 2003. Draft Report on the Environment Technical Document. Washington, DC: United States Environment Protection Agency.

Components of Clean Manufacturing

The six main components of CM are:

- **Waste Reduction:** the term waste refers to all types of waste including both hazardous and solid waste, liquid and gaseous wastes, waste heat, etc. The goal of CM is to achieve zero waste discharge.
- **Non-Polluting Production:** Ideal production processes, within the concept of CM, take place in a closed loop with zero contaminant release (no greenhouse gases or harmful products which endangers the environment).
- **Production Energy Efficiency:** CM requires the highest levels of energy efficiency and conservation. Energy efficiency is determined by the highest ratio of energy consumption to product output. Energy conservation, on the other hand, refers to the reduction of energy usage.
- **Safe and Healthy Work Environments:** CM strives to minimize the risks of workers in order to make the workplace a cleaner, safer, and healthier environment.
- **Environmentally Sound Products:** The final product and all marketable by-products should be as environmentally appropriate as possible. Health and environmental factors must be addressed at the earliest point of product and process design and must be considered over the full product life-cycle, from production through use and disposal.
- **Environmentally Sound Packaging.** Product packaging should be minimized wherever possible. Where packaging is necessary to protect the product, to market the product, or to facilitate ease of consumption, it should be as environmentally appropriate as possible (Kjaerheim, 2005).

Benefits of Clean Manufacturing

- The benefits of cleaner production comprises lessen waste, the improvement of valuable by-products, enhanced environmental performance, better resource productivity, increased efficiency, minimized energy consumption, reduces greenhouse gases and an overall reduction in costs (see "Relevant Websites" section).
- Clean manufacturing reduces operation costs for example, the costs involved with waste treatment, storage, and disposal are often reduced and the savings can be used to counterbalance the development and implementation costs of the program.
- It helps to save the raw material and refining operations which will decrease the ecological damage, and also reduces the risk of emissions during the production process and during recycling, treatment, and disposal operations.
- Clean manufacturing not only reduces effects but also enhanced company image and reputation. It improves the working environment in the organization; employees are likely to feel more positive toward their company when they recognize that management is committed to providing a safe working environment (Kjaerheim, 2005).

Clean Manufacturing Techniques

- **Change input materials:** substituting toxic or harmful materials with less toxic, employ of renewable materials, use of materials with longer lifetime and material purification.
- **Technology change:** by replacing, equipment modification, optimal process conditions, increased automation, improve process control and improve equipment layout.

- Improve operation practices: Product scheduling, energy management, maintenance programmes, working instructions and procedure, training and incentive program, adequate process control operations, proper maintenance and cleaning.
- Production Modifications: recycling friendly design, product life extension, more efficient, less material intensive packaging and reducing of harmful substances.
- On-site reuse and recycling: On-site revival and re-use of raw materials in the process, waste water, waste cooling water, converting waste into useful by-production waste segregation and storage.

Barriers to Clean Manufacturing Implementation

- Internal barriers: Low awareness of CEOs, internal constraints in organization and communication, Limited information, lack of data and knowledge on waste and emissions, Focus on short term profits by a industry, in the race of cost/profit calculations somewhere clean manufacturing options is missing, obsolete or untrustworthy process instrumentation, no or inadequate support of middle management, to achieve persistent there is no proper Environment Management System (EMS).
- External barriers: Availability of investment capital, Availability of clean manufacturing technologies and lack of effective government policies (Anon).

Clean Manufacturing Strategies

It is not sufficient to observe and decrease the residuals and emissions from the machining processes, in order to provide assurance for clean manufacturing process in the future it is essential to scrutinize and solve the core issues which increases unwanted residuals and emissions and their sources have to be identified and eliminated. A further possibility for the improvement of the environmental impact in manufacturing is through the development and introduction of new technologies as a replacement for the traditional technologies examples using machine like new cutting tool materials, rapid prototyping, laser machining, etc. keeping in the view that new technologies do not lead to environmental contamination of a different nature. Fig. 4 shows the strategies for clean manufacturing process.

- Raising awareness of environment-related activities at the facility and providing training. A training program should include all levels of personnel within the organization. The goal of such training is to make every employee aware of waste generation, its impact on the site and the environment, and ways waste can be reduced, pollution prevented, mitigation of greenhouse gases and cleaner production achieved. Provide ongoing staff education programmes, make clean manufacturing awareness program a part of new employee orientation.
- R&D, engineering, productions, strategy, the environmental department and top management all of them should re-enforced together. The discharge of carbon dioxide (CO₂) and other greenhouse gases (GHGs) due to human action is rising global

Present <i>Residual, emission from manufacturing.</i> <i>-Evaluation</i> <i>-Minimisation</i> <i>-Disposal</i> SYMPTOMS	Current status <i>Significant deficit in the consideration of effects of manufacturing processes on the environment</i>	Future <i>Clean manufacturing process in order to minimized eliminate negative environmental effects</i> CORE
Research Objectives: - Deficit elimination - Process Understanding - Environmentally friendly factory		

Fig. 4 Strategy for clean manufacturing process.

average surface air temperatures, disrupting weather patterns, and acidifying the ocean. Unawareness and ignores could cause global average temperatures to increase by another 4°C or more by 2100 and by 1.5–2 times as much in many midcontinent and far northern locations (Obama, 2017). Perseverance of top management, the development of a long-term technology strategy (25–50 years), and the integration of environmental management in business activities is especially important for accomplishment of more essential cleaner technologies. The Research and Development department should be more involved in the laying down of long-term technology strategies.

- Formation of inter-firm knowledge networks. At least three or more manufacturing firms work together in joint research projects. These joint research projects are especially productive in the pre-competitive stage. Relations between firms should be prepared to include mutual education and training, risk sharing agreements and joint agreement on performance measurements.
- Offer financial and technical incentives. Recognizing an individual's efforts in the field of clean production. Recognition of effort is also a powerful tool in maintaining a clean production program. Coordinating environmental policy incentives programmes.
- Provide public outreach and education about clean production advantages, Submit press release on innovations to local media and to industry journals read by prospective clients, arrange for employees to speak publicly about clean manufacturing measures in schools and civic organizations.
- Governments could directly interfere in the existing polluting production process by imposing more strict environmental legislation. Stimulation of government-industry partnerships. The government could introduce incentives or subsidy to the industry to encourage cleaner technology development (see "Relevant Websites" section) (Moors *et al.*, 2005; Sarkis, 1995).

Clean Manufacturing Tools

- Value Stream Map (VSM) can be used as a tool for mapping and identifying environmental impacts in the processes of the plant layout. It demonstrates the linked processes for making a family of products, from the raw material to the shipping to the customers. Below each process there is a data box which contains the environmental impacts of the process.
- The implementation of 5S in a company has an environmental impact in a positive way. 5S is usually ordered by five precise steps. These steps are: separating, setting in order, shining and cleaning up, standardizing and sustaining. By means of 5S, the companies initiate a specific identification of the different kinds of garbage using extremely visible and identifiable bins. Each bin is coded with different color and it is positioned in a precise area bounded by colored strips on the ground. In order to avoid movements of the operators the bins are placed close to the workplace.
- Cellular manufacturing is a clean manufacturing tool which has huge impact in enhancing environment performance. In cellular manufacturing methods the workplaces, machine and staff are grouped in a single cell which work in a similar products, which is arranged in a particular U-shape rather than having them in random places of the plant layout. The workplaces and machines in the cell are positioned very close to one another to save space and time. The handling and transportation of materials can, in this way, be easily reduced, which automatically affect environmental impacts in a positive way.
- Total Productive Maintenance (TPM) is cleaning and maintenance practices in an industry, which again helps to improve environment impacts. Its main intention is to keep all equipments in top functioning condition to avoid breakdowns and delays in manufacturing processes. It is managed at two important levels. Operators every day have to clean the machine and perform basic maintenance such as topping up oil levels, cleaning filters and checking pressure, temperature, and so on of the machine. It reduces the atmosphere emissions in terms of dusts and fumes (Chiarini, 2014).

Environmental Management Systems

International standardized Environmental Management Systems (EMS) should be implemented to construct a systematic environmental plan. In present condition it has become more and more important for different companies all over the world (Ljungberg, 2007; Graedel and Allenby, 1995). Actually EMSs can normally be considered as a voluntary system. Environment Management system can be seen as a tool for management that can be used to guide and control environmental efforts by computer controlling or performed by a particular organization. All company that has taken steps towards environmental concern has in fact implemented an EMS (Coglianese and Nash, 2001). There are five main mechanism of an EMS: Environmental Policy, Planning, Implementation and Operation; Checking and Corrective Action; and Management review (see "Relevant Websites" section). In an organization the Environment Management System is designed to achieve environmental goals, manage environmental issues, and continually improve environmental performance (Fig. 5).

It was World Business Council for Sustainable Development (WBCSD) during 1990s issued a statement about the relationship between environmental protection, economic growth and fulfillment of human needs (Schmidheiny, 1992). The statement has a huge impact and later there was an establishment of an international standard ISO 14001, which was released in 1996 by the International Standardization for Organization (ISO) in Switzerland (Graedel and Allenby, 1995). ISO 14000 consists of a entire series of environmental standards based on the 14001 standard (Sheldon, 1997). ISO 14001 is one of the corner stone and most well recognized standard of the ISO 14000 series. It is the only ISO 14000 standard against which it is currently possible to be certified by an external certification authority (see "Relevant Websites" section). It is important to note that the EMS as per ISO 14001 does not itself affirm specific environmental performance criteria.

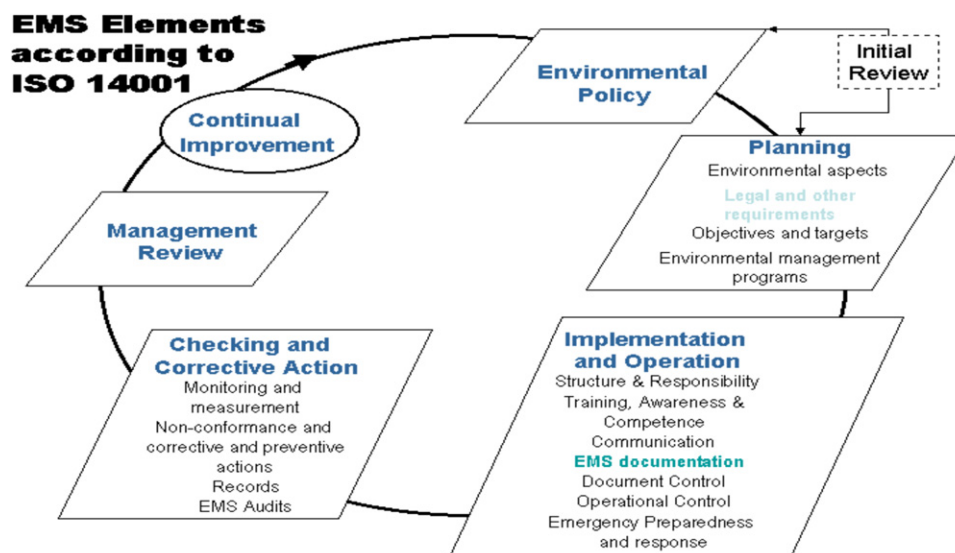


Fig. 5 Environment management system model (<http://www.unep.fr/shared/publications/other> – How to establish and operate cleaner production centres).

Some of the benefits of an EMS are improved control and efficiency, reliable regulatory compliance, reduced environmental liabilities, easier access to loans, enhanced corporate image, reduced insurance premiums. An environmental policy should have the following characteristics such as suitable to nature, scale, and environmental impacts, provides framework for setting and evaluation of environmental objectives and targets; documentation, implementation procedure, maintenance procedure, and communication to all employees available to the public (see “Relevant Websites” section).

Cleaner Manufacturing in India

Clean Manufacturing has been put into practice across various industrial sectors in India. We know that growing population and rapid economic development in India has tarnished the environment, exhausted the resources + – and harshly spoiled the ecosystem. So to meet both the environmental and economic challenges, India understand the requirement for clean manufacturing and progress has been made through framing various eco-friendly policies (Manju and Sagar, 2017). The first systematic investigations, Project DESIRE was introduced for waste minimization along with pollution prevention for developing countries, it was implemented between 1993–1995, through this project it was come to know that many companies like textile and paper industries had a drastic improvement in environment performance (Unnikrishnan and Hegde, 2007). It reduces heat consumption in the range of 25%–44%, electricity consumption 5%–34%, wastewater volume 39%–41% and chemical oxygen demand 39%–51% (Berkel, 2004). In the garment sector cleaner technologies it helps to eliminate redundant washes, substitution of hazardous chemicals, water consumption and energy consumption leading to lot of benefits (Venkatesan and Scott, 2001).

The UNIDO has started national and regional cleaner production centers in India. The basic premise of the UNIDO/UNEP NCPC programme believes that sustainability of clean manufacturing is only possible if the country have right intention and capacity to adopt it. It can be successful if it is promoted by professionals by taking advantages of the local conditions. To achieve that many centre are build, which provides training and advise their clients on how to find the best solution for their specific problems rather than ready-made solutions (Ralph and Jaroslav, 2004). Important activities of the cleaner production centers (CPCs) are to provide training under capacity building. It provides in-depth modular training as well as short courses on different topics related to clean manufacturing. Most of the Courses were designed mainly for company staff and consultants, still some specific courses were also targeted towards policy makers (Unnikrishnan and Hegde, 2007). Through many case studies we can say that in India is contributing to improve the environment by implementing the clean manufacturing policies and many cooperate is also tie-up with certain such organization to improve the environment in positive way.

Conclusion

This review article outlines the overall aspects of environment and clean manufacturing as a whole. It focuses on the relationship between the quality of the environment and clean manufacturing industries and the mission of cleaner manufacturing and how it can be achieved. It helps to understand the affect of different types of manufacturing waste to the ecological balance of the environment. Article gave brief knowledge about the six main components of CM and also discuss about the benefits of CM implementation. In order to provide assurance for clean manufacturing process in the future it is essential to scrutinize and solve the core issues which increase unwanted residuals and emissions of greenhouse gases and carbon footprint, their sources have to

be identified and eliminated. This article has discussed about the strategies of identification and elimination of core issues and how different types of tools of CM helps to achieve the objectives. The CM process had a vital role to play in keeping the environment safe by mitigating of greenhouse gases in coming future. The mitigation of greenhouse gases is only be achieved by adopting sustainable techniques of manufacturing. This article also discussed about the EMS and its advantage of implementation.

For implementing national and international policies/strategies it is very important to measure and report their Carbon Footprint (CF) aimed at mitigating and adapting the environmental concerns. The information given in this article will contribute to improve environment policies for a more clean and sustainable future. As policy has an important role in supporting energy conservation in any society because not only can it produce an adequate economic environment that finally leads to savings, but it may also impose regulations for proper energy management, promote recycling and energy recovery, and encourage suitable education of the society.

See also: Green and Sustainable Manufacturing of Metallic, Ceramic and Composite Materials. Green Manufacturing: Progress and Future Prospect

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Principles of pollution prevention and cleaner production.

Reducing Greenhouse Gas Emission From Waste Landfill

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Introduction

The rampant increase of municipal solid waste (MSW) along with rapid population growth, urbanization, and improper waste management options has created an unavoidable situation in the whole world. The economic prosperity and socio-economic development is the index for the rate of waste generation. Therefore, it is evident from the fact that the whole world is experiencing a high rate of a waste generation with the rapid unplanned urbanization of the cities and towns (<http://dx.doi.org/10.1080/23311843.2016.1139434>). The increased income and advanced living standard of people have considerably augmented the average waste generation rate of 0.5 Kg or g per person/day (https://www.worldenergy.org/wpcontent/uploads/2013/10/WER_2013_7b_Waste_to_Energy.pdf). Landfill gas from waste contains a high concentration of methane, which has about 30 times higher global warming impact compared to carbon dioxide (Pawlowski *et al.*, 1996). Anthropogenic sources account for 70% of total annual Methane (CH_4) (Pawlowski *et al.*, 1996), emission from rice fields, domestic ruminants, agricultural, biomass burning in the tropics, organic waste in the sewage system and landfills, fossil fuels production, transportation and utilization (Bousquet *et al.*, 2006). Fossil fuel energy is responsible for about 37% of human-caused CH_4 emissions (Tubiello *et al.*, 2014). MSW landfills are among the third largest anthropogenic sources of methane emission. Sanitary landfill is an engineered, in-ground facility for the safe and secure disposal of waste (<https://www.epa.nsw.gov.au/publications/waste/solid-waste-landfill-g259uidelines-160>) designed to reduce environmental hazards and ensures to protect human health. However, MSW at landfills has measured to be one of the major contributors to anthropogenic GHG emission and a key component in global warming (<https://www.ipcc.ch/meetings/session12/twelfth-session-report.pdf>). Landfills are supposed to produce the pollution streams, such as leachate, storm water runoff, LFG, offensive odor, dust, noise and litter thereby degrading the quality of surrounding surface water bodies, groundwater, soil, and air. Majority of MSW both in the US and globally is placed in landfills. As per the estimate US, alone releases around 92.7 MMT of CO_2 equivalents to the atmosphere in 2016 (<https://www.epa.nsw.gov.au/publications/waste/solid-waste-landfill-g259uidelines-160>). In developed countries, well designed sanitary landfills are used which typically include well-lined bottoms for leachate collection and treatment systems, gas collection, and its treatment, final covers, and air and water monitoring systems (<https://www.regulations.gov/document?D=EPA-HQ-OAR-2003-0215-0045>). Landfill undergoes in a sequence of complex physical, chemical and biological processes that lead to waste degradation. However, the process that occurs at the landfill is a natural though it can be either triggered or altered by controlling internal conditions in a landfill. The waste received at the landfill consists a large fraction of organic wastes like paper, food and green wastes that undergo degradation under anaerobic conditions and produces LFG including 50% CH_4 , 50% CO_2 and non-methane organic compounds. The existing landfills, i.e., open dumps, conventional landfill, and landfills with low-organic-waste along with adopted technologies and processes depict the amount of GHG emissions into the environment (Manfredi *et al.*, 2009). The major contributors are the direct emissions from the landfill that account to 1000 kg CO_2 -eq tonne^{-1} for the open dump (Manfredi *et al.*, 2009), 300 kg CO_2 -eq tonne^{-1} for conventional landfilling and 70 kg CO_2 -eq tonne^{-1} for low-organic-waste (Manfredi *et al.*, 2009). However, the methane generation largely depends on various factors, such as the amount of waste being received at the landfill, concerning its age, its physicochemical characteristics, including its biodegradability, and other abiotic factors, such as topography, climate, rainfall patterns, and humidity.

Hence, more sustainable and feasible methods are required to be addressed for alleviating the CH_4 emissions into the environment, through an enhanced degree of CH_4 oxidation in the landfill cover soil, and it can be achieved by optimizing the oxidation process in landfill based on parameters, such as the depth of soil cover, pH, and gas circulation coefficient.

Brief Introduction to the Landfill

A trend of significant increase worldwide has been observed in waste generation due to factors including high population growth rate, industrialization, urbanization and other. According to the report of World Bank on solid waste management, the worlds' cities generated 1.3 billion tonnes of solid waste per year amounting to a footprint of 1.2 kilograms per person per day in 2012 which is expected to rise to 2.2 billion tonnes by 2025 (<http://www.worldbank.org/en/topic/urbandevelopment/brief/solid-waste-management>). The landfill has remained as the oldest and the most common treatment method of waste disposal throughout the globe. It is an area of land that is specifically allocated for controlled disposal of waste on or beneath the surface of land with the aim of isolating the waste from the surrounding environment.

With the realization of the detrimental effects of past waste handling methods, sustainable waste management is gaining more and more attention. It emphasizes more on reducing, reusing and recycling waste and considers landfill disposal of waste as the least preferred option. All types of waste treatment options have a certain amount of residue that requires to be disposed of in a landfill. Thus, landfill persists as the primary means of waste disposal method. It also has the advantage of being the most economical option for managing waste. Landfills in use can be broadly classified in two ways, i.e., by engineering facilities

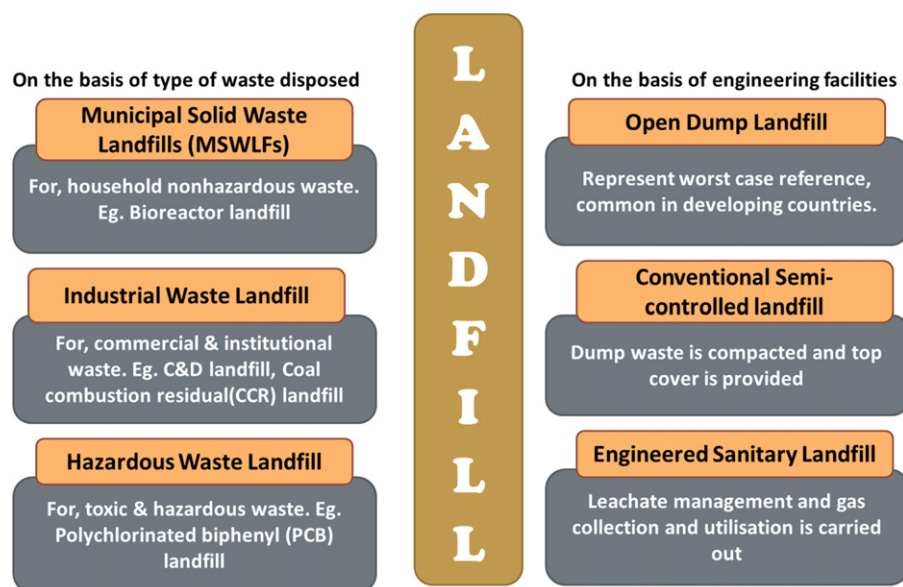


Fig. 1 Classification of landfill.

Table 1 CH₄ & CO₂ emissions and GWF as estimated using IPCC guidelines

Landfill types	CH ₄ (kg CO ₂ per tonne w/w)	CO ₂ (kg CO ₂ per tonne w/w)	GWF(LFG) (kg CO ₂ -eq per tonne w/w)
Open dump (mixed waste)	27.5–38.5	61.9–86.6	561–786
Conventional landfill (mixed waste)	2.3–13.1	85.3–228.2	– 69 to 162
Engineered landfill (mixed waste)	2.3–13.1	85.3–228.2	– 74 to 26
Engineered landfill (low organic waste)	0.8–3.0	24.7–54.2	– 48 to – 3

Note: Manfredi, S., Tonini, D., Christensen, T. H., Scharff, H., 2009. Landfilling of waste: Accounting of greenhouse gases and global warming contributions. Waste Management & Research 27 (8), 825–836.

employed (Tchobanoglous *et al.*, 1993) or by the type of waste disposed of (US EPA, 1995). Fig. 1 shows the classification of the landfill.

The major contributors of environmental pollution from a landfill are the landfill leachate and gas. Landfill leachate is the percolating water that reaches the waste due to precipitation, irrigation and to some extent, water that is generated from the waste of the landfill resulting in a liquid consisting suspended solids, soluble components of the waste and degradation products of the waste due to microbial activity. The composition and amount of the leachate will highly depend on the site conditions, heterogeneity, and composition of the waste, and, the stage of fermentation reached by the waste, the moisture content and the operational procedures. The various pollutants in leachate can be (Kjeldsen *et al.*, 2002), dissolved organic material (COD and TOC, volatile fatty acids and fulvic and humic-like material), inorganic macro-components (like calcium, magnesium, sodium, potassium, ammonium, iron, manganese, chloride, sulphate and bicarbonate compounds), heavy metals (cadmium, chromium, copper, lead, nickel, zinc) and compounds not degraded by organisms (aromatic hydrocarbons, pesticides, plasticizers, chlorinated aliphatic compounds, etc.). Several studies have reported that ammonia, chloride, acidity or alkalinity and heavy metal concentrations highly contribute to landfill leachate toxicity. Toxic leachates from solid waste landfill sites may also be mutagenic and carcinogenic (Kjeldsen *et al.*, 2002). Leachate collection and removal systems (LCRS) are incorporated in landfills for collecting the leachate and employing leachate treatment and management technologies like leachate recirculation, evaporation, neutralization (Warith, 2003), activated carbon adsorption process (Foo and Hameed, 2009), etc.

LFG emission is the other major environmental concern associated with landfill waste disposal method. Due to anaerobic conditions prevailing underneath, the biological degradation of biodegradable waste components produces LFGs. The quality and quantity of gas produced depend on the characteristics of waste, aerobic/anaerobic conditions and site conditions like pH, moisture, temperature, etc. Among others, methane and carbon dioxide contribute to 90% of total LFG (El-Fadel *et al.*, 1997). CH₄ from landfills represents 12% of total global methane emissions (El-Fadel *et al.*, 1997). Total European emissions are about 2% of the total GHG of 5000 Million ton per year (EEA, 2009). In the US, landfills are the main source of CH₄ emissions and emitted nearly 37% of total US carbon emissions in 1997 (EPA, 1999).

The greenhouse gases GHG emissions from landfills have been estimated using IPCC guidelines, 2006 considering 1 tonne of waste for 100 years (Manfredi *et al.*, 2009). **Table 1** provides an insight into the individual CH₄ and CO₂ emissions and Global warming factor (GWF) for landfill gases from various landfill types (Manfredi *et al.*, 2009).

Many efforts have been made to mitigate the CH₄ from the landfill.

About GHG Emission

Emission of GHGs from conventional waste practices in the developing countries contributed considerably to global warming. GHG emissions from waste management activities such as waste handling & processing, operational activities, and transportation are contributed indirectly especially due to fossil fuel consumption. Also, there are many possibilities for indirect GHG emissions from materials and energy use. Unfortunately, municipalities responsible for municipal solid waste management (MSWM) do not recognize the link between waste management and GHG emission.

Since many, decade's management of waste has been only correlated with human health and sanitation. GHG emission linked with the waste handling and disposal practices was recognized as a burning issue in the last few years only, before that it was not considered as a major issue in the context of global warming (Singh *et al.*, 2018).

Municipal solid waste (MSW) has been identified as a significant contributor to global warming because of GHG emissions from each of the functional waste management system. The rise in average global temperature due to GHG emissions has altered the global climatic pattern and created a threat to human and animal health. GHGs have distorted global temperature pattern & negatively affected the global environment (Singh *et al.*, 2018).

MSW is considered as the 3rd largest anthropogenic source of CH₄ emissions; it contributes to about 11% of total CH₄ emissions all over the globe (Stocker *et al.*, 2013). CH₄ emitted from landfills is identified as major contributors to GHGs. CH₄ has twenty-eight times more global warming potential than that of CO₂ on a horizon of 100 years' period (Stocker *et al.*, 2013).

Over the last decades, the concentration of CH₄ in the atmosphere has more than doubled (Sunarto *et al.*, 2017). Fast growth in industrial development and rise in population have increased the potential anthropogenic CH₄ emissions (Sunarto *et al.*, 2017). Waste disposed into landfills undergoes aerobic decomposition, which produces a considerable amount of CH₄ (Singh *et al.*, 2018; Chynoweth *et al.*, 2001).

Waste treatment or disposal approach through landfilling is most common and is expected to increase in low and middle countries. Their many alternatives are identified for open landfills such as aerob landfills, pre-composting, and energy recovery, but all these options also emit GHG emissions.

Complexity in the quantification of indirect GHGs emission from waste management sector has become a general problem. GHG emission has a strong correlation with per capita waste generation and economic development. All functional aspects of MSWM system, such as waste generation, segregation, collection, handling, storage, transfer and transport, treatment and final disposal emits GHGs both directly and indirectly (Singh *et al.*, 2018).

Developing economy and advancement in urban cities have led to a rise in a solid waste generation, and landfill waste quantity and subsequently increased GHGs emission. Therefore, quantification of CH₄ emissions from MSW landfills is a need of the hour. Studies reported that the developmental and industrial activities caused an accumulation of GHGs in the overall environment. GHG emissions are quantified during manufacturing of products, but also related to its end-of-life phase, i.e., waste treatment processes. All over the globe, emissions from solid waste disposal sites are responsible for about 3%–4% of anthropogenic GHG emissions (https://www.ipcc-nggip.iges.or.jp/public/2006gl/pdf/5_Volume5/V5_3_Ch3_SWDS.pdf). Solid waste management has been getting importance in the global GHG emissions scene.

Several studies revealed that MSW is a major contributor to GHGs through biological waste decomposition.

General sources of GHG emission from waste management sector

- CH₄ from anaerobic decomposition of organic waste.
- CO₂ from fossil fuel combustion and electricity consumption (Indirect source of emission from waste management activities).
- Nitrous Oxide (N₂O) from leachate treatment.

Summary of GHE of Different Countries (Sector Wise)

Tables 2–15 presents a summary of GHE of different countries from 1990 to 2016.

Table 2 Change in GHG emissions/reductions from 1990 to 2016: Austria

Name	Name of the sources	Amount (%)
Austria	Energy	– 47.45
	Energy industries	– 54.03
	Fugitive emissions from the fuel	– 31.73
	Agriculture	– 115.39
	Waste	– 38.53

Note: Available at: http://di.unfccc.int/ghg_profiles/annexOne/AUS/AUS_ghg_profile.pdf (accessed 05.08.18).

Table 3 Change in GHG emissions/reductions from 1990 to 2016: Belgium

<i>Name</i>	<i>Name of the sources</i>	<i>Amount (%)</i>
Belgium	Energy	– 17.23
	Energy industries	– 33.53
	Fugitive emissions from the fuel	– 48.00
	Agriculture	– 19.46
	Waste	– 65.53

Note: Available at: http://di.unfccc.int/ghg_profiles/annexOne/BEL/BEL_ghg_profile.pdf
(accessed 05.08.18).

Table 4 Change in GHG emissions/reductions from 1990 to 2016: Cyprus

<i>Name</i>	<i>Name of the sources</i>	<i>Amount (%)</i>
Cyprus	Energy	63.81
	Energy industries	87.33
	Fugitive emissions from the fuel	7.26
	Agriculture	2.76
	Waste	42.98

Note: Available at: http://di.unfccc.int/ghg_profiles/annexOne/CYP/CYP_ghg_profile.pdf
(accessed 05.08.18).

Table 5 Change in GHG emissions/reductions from 1990 to 2016: Estonia

<i>Name</i>	<i>Name of the sources</i>	<i>Amount (%)</i>
Estonia	Energy	– 51.85
	Energy industries	– 52.78
	Fugitive emissions from the fuel	– 66.03
	Agriculture	– 51.37
	Waste	– 17.21

Note: Available at: http://di.unfccc.int/ghg_profiles/annexOne/EST/EST_ghg_profile.pdf
(accessed 05.08.18).

Table 6 Change in GHG emissions/reductions from 1990 to 2016: Greece

<i>Name</i>	<i>Name of the sources</i>	<i>Amount (%)</i>
Greece	Energy	– 13.07
	Energy industries	– 14.41
	Fugitive emissions from the fuel	– 31.65
	Agriculture	– 22.62
	Waste	– 6.66

Note: Available at: http://di.unfccc.int/ghg_profiles/annexOne/GRC/GRC_ghg_profile.pdf
(accessed 05.08.18).

Table 7 Change in GHG emissions/reductions from 1985 to 87–2016: Hungary

<i>Name</i>	<i>Name of the sources</i>	<i>Amount (%)</i>
Hungary	Energy	– 43.53
	Energy industries	– 47.75
	Fugitive emissions from the fuel	– 74.24
	Agriculture	– 42.04
	Waste	– 3.66

Note: Available at: http://di.unfccc.int/ghg_profiles/annexOne/HUN/HUN_ghg_profile.pdf
(accessed 05.08.18).

Table 8 Change in GHG emissions/reductions from 1990 to 2016: Iceland

<i>Name</i>	<i>Name of the sources</i>	<i>Amount (%)</i>
Iceland	Energy	– 0.56
	Energy industries	– 84.00
	Fugitive emissions from the fuel	– 145.79
	Agriculture	– 4.30
	Waste	– 31.20

Note: Available at: http://di.unfccc.int/ghg_profiles/annexOne/ISL/ISL_ghg_profile.pdf
(accessed 05.08.18).

Table 9 Change in GHG emissions/reductions from 1990 to 2016: Ireland

<i>Name</i>	<i>Name of the sources</i>	<i>Amount (%)</i>
Ireland	Energy	– 21.85
	Energy industries	– 11.51
	Fugitive emissions from the fuel	– 80.52
	Agriculture	– 1.35
	Waste	– 38.08

Note: Available at: http://di.unfccc.int/ghg_profiles/annexOne/IRL/IRL_ghg_profile.pdf
(accessed 05.08.18).

Table 10 Change in GHG emissions/reductions from 1990 to 2016: Latvia

<i>Name</i>	<i>Name of the sources</i>	<i>Amount (%)</i>
Latvia	Energy	– 62.68
	Energy industries	– 70.37
	Fugitive emissions from the fuel	– 52.91
	Agriculture	– 52.54
	Waste	3.75

Note: Available at: http://di.unfccc.int/ghg_profiles/annexOne/LVA/LVA_ghg_profile.pdf
(accessed 05.08.18).

Table 11 Change in GHG emissions/reductions from 1990 to 2016: Lithuania

<i>Name</i>	<i>Name of the sources</i>	<i>Amount (%)</i>
Lithuania	Energy	– 65.66
	Energy industries	– 78.19
	Fugitive emissions from the fuel	– 15.90
	Agriculture	– 50.28
	Waste	– 36.46

Note: Available at: http://di.unfccc.int/ghg_profiles/annexOne/LTU/LTU_ghg_profile.pdf
(accessed 05.08.18).

Table 12 Change in GHG emissions/reductions from 1990 to 2016: Netherlands

<i>Name</i>	<i>Name of the sources</i>	<i>Amount (%)</i>
Netherlands	Energy	2.09
	Energy industries	26.83
	Fugitive emissions from the fuel	– 39.46
	Agriculture	– 23.38
	Waste	– 77.07

Note: Available at: http://di.unfccc.int/ghg_profiles/annexOne/NLD/NLD_ghg_profile.pdf
(accessed 05.08.18).

Table 13 Change in GHG emissions/reductions from 1990 to 2016: Malta

Name	Name of the sources	Amount (%)
Malta	Energy	– 26.80
	Energy industries	– 57.46
	Fugitive emissions from the fuel	– 0.00
	Agriculture	– 15.23
	Waste	– 132.15

Note: Available at: http://di.unfccc.int/ghg_profiles/annexOne/MLT/MLT_ghg_profile.pdf (accessed 05.08.18).

Table 14 Change in GHG emissions/reductions from 1990 to 2016: Norway

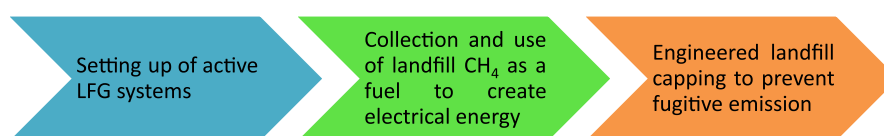
Name	Name of the sources	Amount (%)
Norway	Energy	28.85
	Energy industries	107.28
	Fugitive emissions from the fuel	– 2.92
	Agriculture	– 6.04
	Waste	– 44.23

Note: Available at: http://di.unfccc.int/ghg_profiles/annexOne/NOR/NOR_ghg_profile.pdf (accessed 05.08.18).

Table 15 Change in GHG emissions/reductions from 1990 to 2016: Spain

Name	Name of the sources	Amount (%)
Malta	Energy	– 26.80
	Energy industries	– 57.46
	Fugitive emissions from the fuel	– 0.00
	Agriculture	– 15.23
	Waste	– 132.15

Note: Available at: http://di.unfccc.int/ghg_profiles/annexOne/ESP/ESP_ghg_profile.pdf (accessed 05.08.18).

**Fig. 2** Showing general mitigation step to reduce GHEs.

GHE Reduction Through the Different Treatment Options

Waste management sector has great potential for GHG reduction and climate change mitigation. Waste management sector can considerably contribute to the national GHG emission reduction targets. At present, GHGs, emission and global warming is a burning issue for people all over the globe (<http://www.unep.or.jp/ietc/Publications/spc/Waste&ClimateChange/Waste&ClimateChange.pdf>). The rate of fossil fuel consumption & industrialization has been accelerated for many decades which has caused a rise in earth average temperature (http://www.grida.no/graphicslib/detail/contribution-from-waste-to-climate-change_1033). As an outcome, additional methods or tools are anticipated in the waste management sector to mitigate GHG emissions, especially for new emerging economies. **Fig. 2** shows the steps required to mitigate GHG.

The general concept of capturing CH_4 and reducing GHE is not much benefit as a collection of CH_4 does not occur over the complete duration of emission generated by anaerobic decomposition (<https://www.americanprogress.org/issues/green/reports/2013/04/17/60712/energy-from-waste-can-help-curb-greenhouse-gas-emissions/>). The methane gas is not collected immediately, thus, only a fraction of gas is being trapped and EPA's waste reduction Model reports that on an average only 34% of CH_4 is being

recovered which in turn produces electricity, 38% of CH₄ emission is used for flare in a landfill, rest 28% of methane released into the atmosphere. Thus, only 62% of CH₄ is being captured and hence to reduce GHE from landfills, it is more beneficial to divert the waste to different treatment options available to treat waste (<https://www.americanprogress.org/issues/green/reports/2013/04/17/60712/energy-from-waste-can-help-curb-greenhouse-gas-emissions/>).

The quantity of GHE from a variety of solid waste treatment processes highly depends upon the type of treatment used, the distance between waste collection and waste treatment site & physical composition of waste to be treated. Decentralized waste treatment processes have less GHG emission due to onsite treatment without any transportation, less energy consumption and on-site use of end products. It indicates that the choice of the method for waste treatment process plays a vital role in reducing GHE (<https://www.americanprogress.org/issues/green/reports/2013/04/17/60712/energy-from-waste-can-help-curb-greenhouse-gas-emissions/>).

Therefore, selection of appropriate solid waste treatment process is very important to reduce the load of MSW along with the reduction of GHE for mitigating global warming (Yuan *et al.*, 2012). Integrated strategies involving recycling, composting, waste-to-energy combustion and landfills with gas collection and energy recovery play a significant role in reducing GHG emissions by recovering materials and energy from the MSW stream.

GHE Reduction Potential of Composting

Solid waste treatment through the composting process has been well established in developing countries. Most of the municipalities prefer composting for MSW treatment because it is very simple and cost-effective. The end product from solid waste composting can be used as an organic fertilizer, which is having a huge potential for reduction of GHG emission. One tone of compost from solid waste treatment can be used as a replacement for chemical fertilizer. Along with this, solid waste treatment through the composting process can reduce a load of organic waste from waste dumping sites and can minimize associated GHE by avoiding the organic waste decomposition in landfills.

GHE Reduction Potential of Anaerobic Digestion

Solid waste treatment through anaerobic digestion (AD) is also having great potential for the treatment of biodegradable waste. Among the biological treatment methods, the AD is the most popular and economical due to its cost-benefits. Biogas generated from bio-methanation of solid waste contains high calorific value & heat energy. Biogas generated from anaerobic digestion of solid waste can produce a major quantity of electrical energy. The energy generated from the AD process can be used as an alternative for conventional energy sources, and thereby solid waste can contribute to lowering GHG emission. The AD can also reduce the quantity of biodegradable waste going to landfills and thereby reduces associated GHGs emission.

GHE Reduction Potential of Mechanical Biological Treatment (MBT)

MBT has been commonly utilized as a preliminary solid waste treatment or before final waste disposal. MBT reduces the total waste quantity by biological decomposition of organic waste and ultimately reduces the GHG emission. MBT can reduce GHGs in several ways. According to composting or anaerobic digestion, MBT can reduce the quantity of organic waste from landfilling and lowers the associated GHG emissions that would otherwise occur during the decomposition of biodegradable waste in landfills.

GHE Reduction Potential of Incineration

Solid waste treatment through incineration has been extensively used all over the globe. It has reported that more than 130 million tons of MSWs are treated annually in an around 600 incineration plants (Themelis, 2003). As compared to conventional landfilling incineration reduces the GHG emission by avoiding CH₄ emissions from the landfills. Huge of the amount of electricity and steam generated in the incineration plant can be used as an alternative for fossil fuels. Additionally, incineration plant reduced the transportation of MSW to the distant landfill sites and associated GHGs emission (Kaplan *et al.*, 2009; Weitz *et al.*, 2002; Hefa and Yuanan, 2010; http://ledsgp.org/wp-content/uploads/09/User_Manual_for_GHG-waste-calculator.pdf).

Compared to the option of landfilling, WTE can curb the contribution of MSW on GHG emissions by avoiding the release of methane from landfills and offsetting emissions from fossil fuel power plants. In a comparative study of incineration and landfilling of solid waste, it has been observed that incineration process can reduce up to 1.3 tons of CO₂ equivalent emission per ton of waste by avoiding CH₄ emission from convention landfills.

EPA has reported that every 1 ton of processed garbage reduces approximately 1 ton of CO₂ emissions (<https://www.americanprogress.org/issues/green/reports/2013/04/17/60712/energy-from-waste-can-help-curb-greenhouse-gas-emissions/>). This happens because each treatment options forbid the amount of GHE emission. The recyclable are segregated and are recycled which is another benefit of using treatment options also the electricity generated through waste offsets the GHG emissions which generate from burning coal or natural gas.

Case Studies of Landfill Mitigation Programs

Ulsan Landfill Site

Ulsan is a fully successful pilot project under Climate Technology Partnership (CTP) and has been operating for nearly four years. The methane gas recovery system at Ulsan is designed to capture the gas from the landfill and transport it to local industrial sites where it is burned in boilers without being purified. The Ulsan landfill gas facility reduces GHG emissions, offsets natural gas as a fuel source and builds Korea's capabilities to install similar projects (<https://www.nrel.gov/docs/fy07osti/40428.pdf>).

Fresno Municipal Sanitary Landfill

The Sanitary Landfill in the United States named Fresno Municipal Sanitary Landfill opened in Fresno, California in 1937 is the first modern engineered sanitary landfill. It is designated as a National Historic Landmark though involving the innovating techniques, such as compacting, daily coverage of waste with soil and trenching. It underlies the importance of waste disposal in urban society (<https://cumulis.epa.gov/supercpad/cursites/csinfo.cfm?id=0901854>).

Massachusetts Municipalities

It has turned their towns and communities waste burden through proper assessment and closing their old landfills into a rehabilitated settlement for their respective communities:

The town, located north of Boston, has obtained a long-term layout for reclamation of the existing landfill site into useful areas such as business park containing a hotel, two office buildings and a sports/country club complex concerning the landfill closure. The municipality also rehabilitated one more community located at 10 miles to the west of Boston that was found for open space and recreational fields (<https://corporate.findlaw.com/law-library/landfill-closure-and-redevelopment-three-case-studies.html>). The landfill was procured with an aim to develop the landfill into wetlands and sports field. In a predicament with closure activities, the town also coupled to figure out the associated issues with the reclamation of landfill site including the transformation of the existing drainage system within the landfill site followed by new drainage construction around the landfill site (<https://corporate.findlaw.com/law-library/landfill-closure-and-redevelopment-three-case-studies.html>).

Ghazipur Landfill Delhi

"The Ghazipur Landfill is one of the biggest and oldest landfill areas of Delhi with continuous and indiscriminate MSW disposal since last 34 years (Ranjan *et al.*, 2014). Various strategies have been undertaken to minimize and reduce the negative impacts of landfill gas emissions from the landfill area. As the study reported methane and nitrous oxide were analyzed in Ghazipur landfill area (Ranjan *et al.*, 2014). However, the landfill area was converted into waste to energy plant, where the garbage was mined to convert refuse derived fuel (RDF) to be used for energy generation and ten acres of landfill area supposed to handover to Gas Authority of India (GAI) for mining methane and other gases to be used as fuel. Estimations done at field explored that the methane generated during summer was highest, i.e., 264 mg/m² h and concluded that the emitted gas has large enough calorific value that could be utilized to generate electricity" (Ranjan *et al.*, 2014).

Landfill Regulations and Program Related to GHG Mitigation

The amount of GHG emission is rising day by day. To control the emission of enormous GHG from waste landfill certain protocol, act and projects are formulated to resolve the issue. To achieve the purpose United Nations, a Climate Change conference under the framework of the United Nations Framework Convention on Climate Change (UNFCCC) hold annual Conference of Parties (COP) to implement and reviews the issues of GHG emissions. The very first COP came into force in the year 1995. Since then various meeting held which is listed below (<https://www.epa.gov/laws-regulations/summary-clean-air-act>).

- 1995: COP 1, Berlin, Germany
- 1996: COP 2, Geneva, Switzerland
- 1997: COP 3, Kyoto, Japan
- 1998: COP 4, Buenos Aires, Argentina
- 1999: COP 5, Bonn, Germany
- 2000: COP 6, The Hague, Netherlands
- 2001: COP 7, Marrakech, Morocco
- 2002: COP 8, New Delhi, India

- 2003: COP 9, Milan, Italy
- 2004: COP 10, Buenos Aires, Argentina
- 2005: COP 11/ CMP 1, Montreal, Canada
- 2006: COP12/CMP 2, Nairobi, Kenya
- 2007: COP 13/CMP 3, Bali, Indonesia
- 2008: COP 14/CMP 4, Poznan, Poland
- 2009: COP 15/ CMP 5, Bali, Indonesia
- 2010: COP 16/CMP 6, Cancun, Mexico
- 2011: COP 17/ CMP 7, Durban, South Africa
- 2012: COP 18/CMP 8, Doha, Qatar
- 2013: COP 19/CMP 9, Warsaw, Poland
- 2014: COP 20/CMP 10, Lima, Peru
- 2015: COP 21/ CMP 11, Paris, France
- 2016: COP 22/ CMP 12/ CMA 1–1, Marrakech, Morocco
- 2017: COP 23/CMP 13/ CMA 1–2, Bonn, Germany
- 2018: COP 24/CMP 14/ CMA 1–3, Katowice, Poland

For a landfill, there are specific regulations designed by USEPA (<https://www.epa.gov/laws-regulations/summary-clean-air-act>). Also, there are certain programs and projects which is used to reduce GHG emissions.

Clean Air Act (CAA)

To protect the environment and to ensure a sound public health CAA regulations were framed. It is a set of comprehensive federal law that regulates air emission from stationary and mobile source (<https://www.epa.gov/laws-regulations/summary-clean-air-act>).

EPA Rules for GHE

Municipal solid waste landfills: New source performance standards (NSPS) (<https://www.epa.gov/stationary-sources-air-pollution/municipal-solid-waste-landfills-new-source-performance-standards>)

- This rule came into force in 1991 after a series of the amendment in different year final updated rule came in the year 2016. This regulation focused on the reduction of methane emission from new modified and reconstructed MSW landfill which is rich in methane gas. It is formulated guidelines to reduce emission from existing MSW landfill (<https://www.epa.gov/stationary-sources-air-pollution/municipal-solid-waste-landfills-national-emission-standards>).

Municipal solid waste landfill: National emission standards for hazardous air pollutants (NESHAP) (<https://www.epa.gov/stationary-sources-air-pollution/municipal-solid-waste-landfills-national-emission-standards>)

- This rule was proposed in the year 2000 and focusses on the same principle of emission guidelines and new performance standards (EG/NSPS).
- The update rule came in the year 2006. This result focusses on the hazardous air pollutant (HAP) which is generated from the landfill along with CH₄ and CO₂.
- To collect and control LFG.
- Collection and control system.
- It also checks semi-annual compliance reporting (<https://www.epa.gov/stationary-sources-air-pollution/municipal-solid-waste-landfills-national-emission-standards>).

Neshap for internal combustion engine (<https://www.epa.gov/stationary-engines/national-emission-standards-hazardous-air-pollutants-reciprocating-internal-0>; <https://www.gpo.gov/fdsys/pkg/FR-2013-01-30/pdf/2013-01288.pdf>; <https://www.gpo.gov/fdsys/pkg/FR-2014-08-15/pdf/2014-19062.pdf>)

This rule came into force in the year 2004. After several amendments, EPA finalized the amendment in the regulation. The final decision and reconsideration came in the year 2014.

This rules specifically focusses on the LFG-fired internal combustion engines at major and area resources of hazardous emissions. This regulation provides measurement system performance specifications and sampling protocol to ensure reliable data.

This regulation also has guidelines for the measurement system, data recorders, electrochemical cell, moisture removal system calibration and standardization.

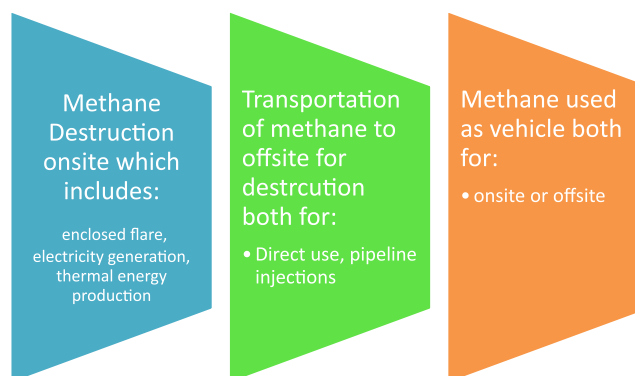


Fig. 3 Boundaries United States Landfill Project Protocol V4.0. Reproduced from Available at: <http://www.climateactionreserve.org/how/protocols/us-landfill/> (accessed 12.06.18).

Industrial, commercial and industrial boilers and process heaters: National emission standards for hazardous air pollutants (NESHAP) for major sources (<https://www.epa.gov/stationary-sources-air-pollution/industrial-commercial-and-institutional-boilers-and-process-heaters>; <https://www.epa.gov/stationary-sources-air-pollution/industrial-commercial-and-institutional-boilers-and-process-0>)

The rule was proposed in the year 2003. This rule is articulated mainly for major sources such as industrial boilers, commercial and institutional boilers which emit hazardous air pollutants. This rule has certain guidelines for LFGs collection and distribution system which are as:

- (1) The firing unit which is either infrequent in operation or works at very low-temperature loads is subjected to tune-up the practice.
- (2) The fire gas stream should be within limits and should maintain the emission limit of Hydrochloric acid (HCL), Mercury (Hg), and Carbon Monoxide (CO) as set up by the EPA.
- (3) The gas which is generated should meet the minimum methane content criterion also the heating value should not exceed the maximum mercury concentration.

Protocol Related to Landfill GHG (United States Landfill Project Protol V4.0) (<http://www.climateactionreserve.org/how/protocols/us-landfill/>)

This protocol is formulated for installation of a system used for capturing and destroying methane gas emitted from U.S landfill. This protocol includes a wide range of boundaries depicted in **Fig. 3**.

Project eligibility criteria: United States Landfill Project Protocol V4.0 (<http://www.climateactionreserve.org/how/protocols/us-landfill/>)

Compliances are considered for sanctioning any project under United States Landfill project Protol V4.0 is shown in **Fig. 4**.

Performance standard

The compliances of Performance standard of United States Landfill Project Protocol V4.0. is shown in **Fig. 5**.

Project exclusions

Projects extrusions of United States Landfill Project Protol V4.0 is shown in **Fig. 6**.

Landfill Methane Outreach Program (LMOP) (<https://www.epa.gov/lmop/basic-information-about-landfill-gas>)

To reduce the emission of CH₄ from landfill EPA has formulated the Landfill Methane Outreach Program (LMOP). **Fig. 7** shows different activities of LMOP.

Programs Related to GHG Emissions

There are certain programs which are formulated to reduce GHG emissions. Some of the programs are listed below:

Canada and Chile collaborative program to reduce GHGs emission from landfill (<http://www.ccacoalition.org/en/news/Canada-chile-join-forces-reduce-greenhouse-gas-emissions-landfills>)

Canada and Chile join forces to support clean innovation which reduces the methane emissions from landfills. Its based on bilateral co-operation formulated to deliver significant direct environmental and health issues and help Chile to use LFG as an alternative clean energy source. The project is running from 2017 and estimated to be completed by 2021.



Fig. 4 Compliances of the project under the United States Landfill Project Protocol V4.0. Reproduced from Available at: <http://www.climateactionreserve.org/how/protocols/us-landfill/> (accessed 12.06.18).

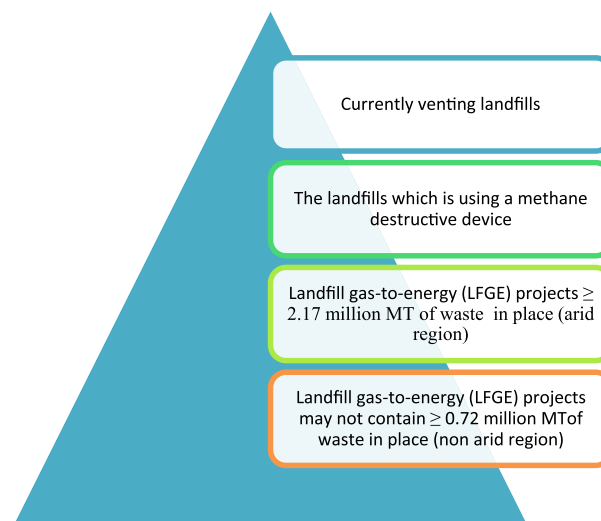


Fig. 5 A performance standard of United States Landfill Project Protocol V4.0. Reproduced from Available at: <http://www.climateactionreserve.org/how/protocols/us-landfill/> (accessed 12.06.18).

India GHG programme (<http://www.indiaghgp.org/>)

This program was launched in July 2013 by founding member companies viz., World Energy Institute (WRI), The Energy Resources Institute (TERI), and the Confederation of Indian Industry (CII).

The aim and scope of this program are to deal with assists large-scale reduction of emission and also to mitigate the Impacts of climate change.

The effort of this program is depicted in Fig. 8.

There are certain arrays of service of this program. It is listed in Fig. 9.

Landfill Gas Projects and Energy Projects Worldwide

To establish long-term success with end users, the landfill owners and operators ensure contractual agreements for the sale of LFG, electricity and other attributes generated by landfill an energy project that relies on financial side for these agreements. Hence, the

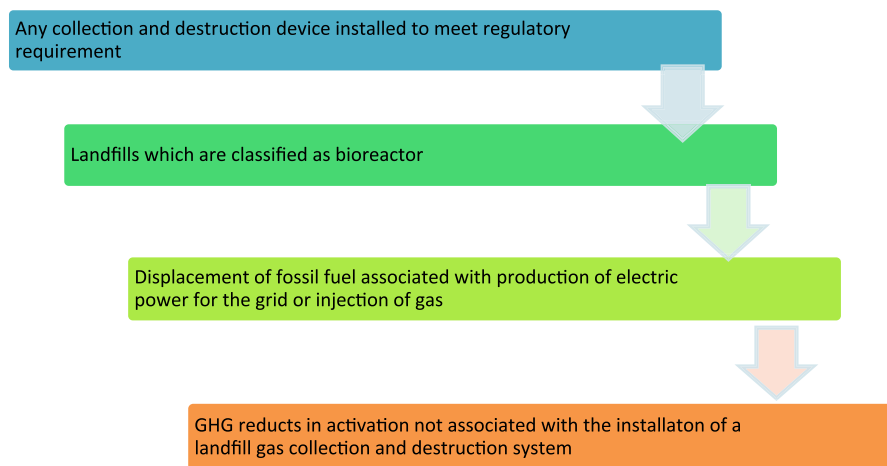


Fig. 6 Compliance of the Project Exclusions United States Landfill Project Protocol V4.0. Reproduced from Available at: <http://www.climateactionreserve.org/how/protocols/us-landfill/> (accessed 12.06.18).

LMOP includes the following activities:

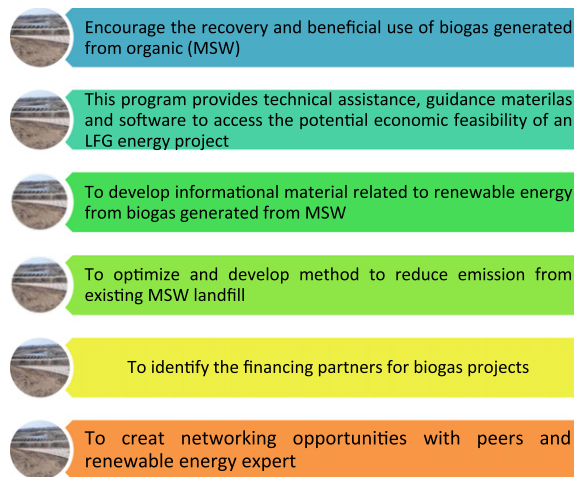


Fig. 7 Different activities of LMOP. Reproduced from Available at: <https://www.epa.gov/lmop/basic-information-about-landfill-gas> (accessed 12.06.18).

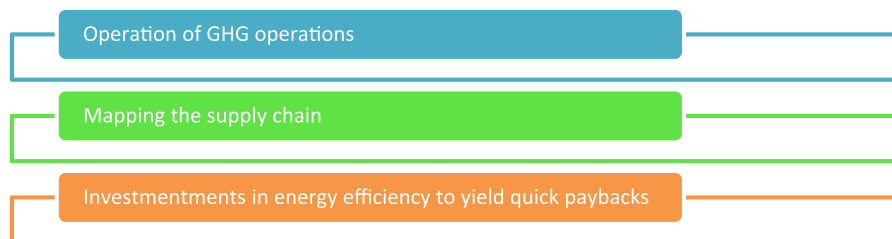


Fig. 8 The Effort of India GHG programme. Reproduced from Available at: <http://www.indiaghgp.org/> (accessed 10.06.18).

owners and LFG project developers require immense information and knowledge to implement or lay out the elements of LFG contractual agreements. The different categories of the contacts are presented in **Table 16**.

LFG projects are aimed towards generating energy and reduced CH_4 emissions also, embark to bring positive outcomes for all and sundry. It also creates a partnership among citizens, NGOs, ULB's, government, and industrial partners. However, **Fig. 10** shows the LFG projects are significant and have potential benefits regarding energy, economy, and environment.

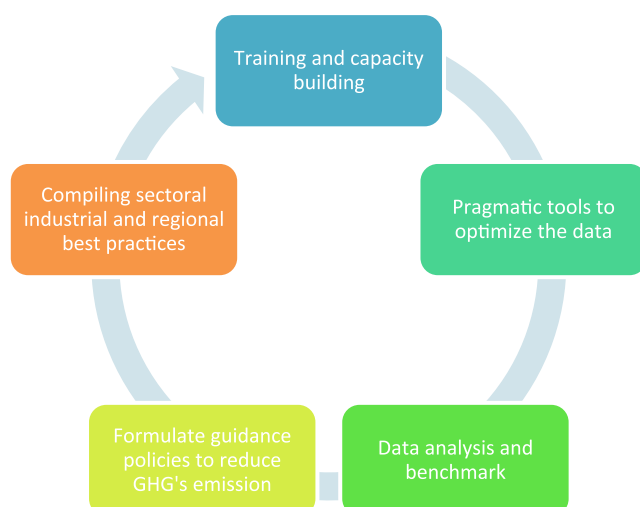


Fig. 9 Arrays of India GHG programme. Reproduced from Available at: <http://www.indiaghgp.org/> (accessed 10.06.18).

Table 16 Different categories of the contacts

Landfill gas regulations and contracts

Power sales agreements	Landfill purchase agreement	Environmental attribute agreements	Regulations and permitting
Power purchase agreement with an Investor Owned Utilities	Direct use sales of medium-Btu LFG	Direct environmental attributes i.e., destruction of methane (a potent GHG emission)	Applicable Clean Air Act (CAA) regulations
Power sales contract to a power marketer or whole sale buyer	LFG sales to an electrical generation project	Indirect environmental attributes i.e., displacement of fossil fuel use by LFG use, a renewable energy resource	Applicable Resource Conservation and Recovery Act (RCRA) regulations
Selling directly into market	High Btu sales		National Pollutant Discharge Elimination System Permit
Net metering			Applicable Clean Water Act (CWA) regulations

(https://www.epa.gov/sites/production/files/2016-11/documents/pdh_full.pdf)

Note: Available at: https://www.epa.gov/sites/production/files/2016-11/documents/pdh_full.pdf (accessed 13.06.18).

The solid waste landfills in the US are regulated by the Environmental Protection Agency (EPA) and other states environmental agencies. The regulatory authorities are aimed for safe and sound s SWM through the technical framework, monitoring, compliance, regulations, and enforcement to protect the environment from toxins that might be present in the waste. It also ensures the restriction in the entry of some banned materials from the disposal of hazardous wastes. It ensures that all the landfills envisages complying with federal regulations in 40 CFR Part 258 and are designed to protect human health and environment by controlling the emissions at the landfill. Some of the key features of the federal regulations include: setting buffer zones, for waste landfills, mandating the requirements for composite liners requirement, leachate collection and removal systems, operating practices, groundwater monitoring, closure, and post-closure care equipment. The landfill regulations in India is facilitated through Central Pollution Control Board (CPCB) that ensures the guidelines for the urban local bodies (ULB's) in dropping the nuisance value of waste management along with to enhance the aesthetic appeal. To reduce the negative impact of landfills on public health and environment, the CPCB has come out with guideline that ensures to maintain the buffer zones including a 10 m green belt around the landfill sites specified that the selected plant species should be fast growing, have a thick canopy, perennial and evergreen and act as high CO₂ sink, thereby contributing on the reduced GHG emissions, such as, Babul, Shisham, Australian babul, Neem, Jamun and Karanj.

Landfill Gas Energy Projects

To convert LFG into usable energy form, the projects are grouped into three categories: Electricity generation, Direct Use of Medium-Btu Gas and Upgraded LFG. **Table 17** shows landfill gas energy projects.

Technology: Turbines, micro-turbines, and fuel cells.

Reciprocating engine Gas turbines: Used, while micro-turbines.

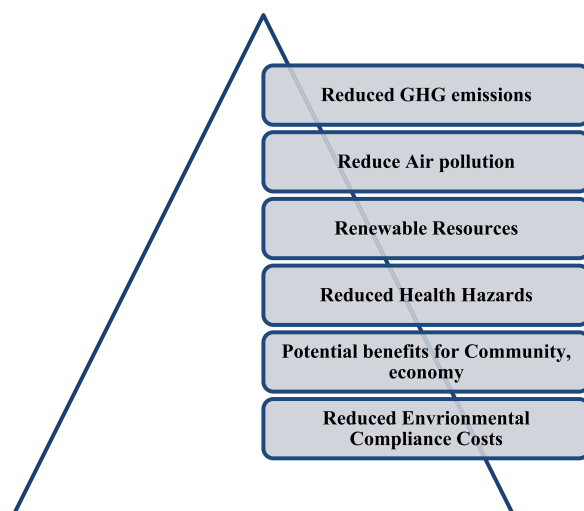


Fig. 10 LFG projects and their significant benefits.

Table 17 Landfill gas energy projects

Type	Technology	Comments
Electricity Generation: ¾ of LFG generates electricity from existing LFG projects in the US	Reciprocating internal combustion engines It is most commonly used technology for converting LFG to electricity due to its relatively low cost, high efficiency and size ranges complementing the gas output of many landfills. Turbines are used in larger LFG energy projects Microturbines are applicable for smaller LFG volumes and in niche applications.	Several Combined Heat and Power (CHP) under LFG projects have been installed to convert LFG to generate both electricity and thermal energy in the form of steam or hot water using the technologies.
Direct use of Medium-Btu Gas replaces the use of another fuel like natural gas or fossil fuel, and it occurs between 1/4th of currently operational projects	The LFG produced here is piped directly to the customer	It is used directly in various industrial applications such as boiler, dryer, kiln, etc., as a substitute for other fuel consumption. It is also used to evaporate the landfill leachate
Upgraded LFG It ensures the production of equivalent pipeline-quality gas (natural gas), compressed natural gas (CNG) or Liquefied Natural Gas (LNG)	High upgraded- Btu LFG through the treatment process by the reverse mechanism of increased methane content and reduced CO ₂ , nitrogen and oxygen content.	Used as CNG or LNG in Vehicles itself at landfill sites

Note: Available at: https://www.epa.gov/sites/production/files/2016-11/documents/pdh_full.pdf (accessed 13.06.18).

Feasibility of Using LFG as a Liquefied Natural Gas (LNG) Source for the Heavy-Duty Trucks Operating Landfills in Texas

Acrion Technologies Inc. in association with Mack Trucks Inc. developed a technology to generate LNG from the gases at landfills using CO₂ WASHTM Process. The process is successfully implemented at the Eco-Complex in Burlington County, PA, in which two refuse trucks were operated for 600 h each using LNG produced from the landfill (Zeitmans *et al.*, 2008).

Landfill Gas Capture and Utilization Project at VEOLIA Environmental Services

It is a division of employs nearly 83,000 staffs operating in 35 countries around the world specialized in the management, treatment, and disposal of waste including recycling, reclamation and reuse of waste products. In 2006, the project at Veolia Environmental Services avoided 23% emissions in the volume of direct GHG emissions. It converted the CH₄ generated from landfills as a useful commodity in Thermal Energy and Electricity form. The services have ensured the LFG utilization projects at various sites as shown in Table 18.

Table 18 Landfill gas projects

<i>Site</i>	<i>Technology</i>	<i>Benefits</i>	<i>Reference</i> (http://siteresources.worldbank.org/INTUWM/Resources/340232-1208964677407/Veolia_4-9-08.pdf)
Brazil: SASA Landfill	Leachate evaporator treats up to 19 m ³ /day of leachate using LFG as fuel for the evaporator	First registered project and carbon transaction developed as a clean development mechanism and ensured reduced GHG emission at 700,000 t CO ₂ e over ten years	Tremembé Landfill Brazil
US: Cranberry Creek Landfill, USA	Direct use compressed, filtered and dried LFG is conveyed from the landfill to the plant through a 2.4 km pipeline, i.e., the methane gas from the pipeline powers the Ocean spray's steam boilers, that the energize the cranberry concentrator	Reduced GHG emissions, i.e., 6300 tonnes a year significantly reduced fuel costs by 25% at Ocean spray achievement: the site was awarded GOLD STAR AWARD from SWANA (Solid Waste Association of North America)	Cranberry Creek Landfill Wisconsin, USA
China: Xingfeng Landfill	Two 970 kW is reciprocating engines/gensets for electricity production thereby adding additional modular units with increased landfill gas.	Alleviate electricity shortage developed as clean development mechanism and reduced methane emissions	Xingfeng Landfill, Guangzhou, China
France REP, Energie	Combined cycle in 2005 nominated under French Government for renewable energy project from Biomass/Biogas to meet European Union Target i.e., 11 MW 9300 N m ³ LFG/h recovered further extended its efficiency to total 25 MW 17,000 N m ³ LFG/hr recovered since 2006	Reduced GHG emissions 74,000 tonnes CO ₂ avoided emissions reduced fuel consumption 16,400 tonnes saved. The installed capacity of 25 MW is equivalent to the consumption of 80,000 inhabitants	REP Landfill, Claye Souilly France
Greentree Landfill USA	Pipeline Quality Conversion of landfill gas (17,000 m ³ /h) into natural gas	Reduced GHG emissions green energy produced as electricity equivalent of 40 MW and is enough to satisfy the needs of 45,000 homes	Greentree Landfill, Pennsylvania, USA

Conclusions and Perspectives

Disposal of MSW being practiced all across the world leads to continues emission of GHGs and ultimately to climate change and global warming. Climate change has accelerated the need to find measures to reduce and manage the waste being disposed at landfill sites. The Challenges associated with mitigating the GHG emanating from landfills have sought to be a mammoth task, especially methane. Since many investigations have done so far yet, the technical difficulties and high cost in combination with conventional possibilities are needed to be addressed to overcome the issues on the financial side. Hence, microbial oxidation of methane can emerge as a cost-effective candidate to minimize the GHG emission from landfills to the environment. LFG projects are aimed towards generating energy and reduced methane emissions also, embark on bringing positive outcomes for all and sundry. It also creates a partnership among citizens, NGOs, ULB's, government, and industrial partners. However, the LFG projects are significant and have potential benefits in terms of energy, economy, and environment.

See also: Biochar as Sustainable Reinforcement for Polymer Composites. Evaluating the Sustainability Performance of Building Systems and Technologies for Mainstreaming Sustainable Social Housing in India. Gasification of Hospital Waste by Thermal Plasma: A Relevant Technology Towards Mitigation of Greenhouse Gases in India. Sustainability and Green Building Rating Systems: A Critical Analysis to Advance Sustainable Performance. Sustainability Issues in Bioplastics. Synthesis of Multiwalled Carbon Nanotubes (MWCNTs) From Waste Cooking Oil Catalyzed by Mill-Scale Waste for Development of Microstrip Patch Antenna (MPA)

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Further Reading

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Renewability Assessment of a Production System

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Introduction

Mitigation of greenhouse gas emission is one of the most critical responses to climate change, as it plays a central role in implementing the Carbon and Climate Commitments. The direct reductions of on-spot emissions are often a tangible and highly successful demonstration of sustainability policy. The key ingredients lie inherently in all possible production systems active on this planet. Setting a bold aspiration to carbon neutrality often drives deeper cuts in emissions beyond what would be achieved with the simple desires of wise resource usage and cost saving. Higher education is one of society's driving forces of innovation and new ideas. It is in this spirit of discovery and learning that one can start to address the challenge of carbon neutrality. Carbon neutrality is defined as having no net greenhouse gas (GHG) emissions, to be achieved by minimizing GHG emissions as much as possible, and using carbon offsets or other measures to mitigate the remaining emissions. This is an exciting time to undertake a path to a low-carbon future. Each year new technologies and applications appear in the point of becoming economical for wide-scale implementation. The majority of such technologies require achieving carbon neutrality on a national scale. To help focus planning and determine a starting point for carbon mitigation efforts, it is often useful to follow a carbon management hierarchy. A carbon management hierarchy generally outlines broad categories of mitigation strategies like avoiding or reducing emissions through Efficiency and Conservation, eliminating emissions through switching to Renewable (zero carbon) sources of energy and offsetting any remaining emissions. Efficiency and Conservation are often low-cost or cost-saving endeavors and so can be placed as the first-choice solutions. Efficiency generally involves technological improvements to equipment and infrastructure of a production system. The advantage of boosting efficiency typically lies in a very high return on investment and does not require major changes in the behavior of a local community. The drawback is that it typically requires a certain expenditure of up-front capital against the cost savings over the lifetime of the production system. A Green Revolving Fund (GRF), described in financing, is a great method for overcoming this challenge. Another perspective of mitigating carbon footprint is the culture of conservation which typically may not include major capital investments. According to the Intergovernmental Panel on Climate Change (IPCC), in order to limit the global mean temperature increase over 2–2.4°C, global emissions need to be reduced 50%–85% below 2000 levels by 2050. Keeping this broader context in mind, emission reductions must be initiated as soon as possible in order to slow down the adverse effects of greenhouse gases including carbon dioxide and chlorofluorocarbons. Shifting to low-carbon sources of energy typically requires significant advance planning particularly when involving changes to a production system infrastructure. Therefore a detailed analysis of the production system is highly essential to set the optimum strategy of renewability approach.

In the present era an awareness of renewable energy is a common aspect irrespective of branch or streams of engineering and science. A source of energy can be called renewable if natural processes are constantly replenishing it. For example, sunrays, wind, wave energy, geothermal heat and wood are considered renewable resources. Even fossil fuels can be renewable over many millions of years, as geological processes are continually generating new petroleum. But the process is not fast enough to refill oil fields as they are drawn down. For the aforementioned reasons, the term renewability is rather defined on the basis of continued human relationship with a given energy resource i.e., the rate at which humans exploit it compared to the rate at which nature renews again. If the resource is regenerated at a higher rate than it is used, it is considered renewable, but if it is exploited at a higher rate than it is regenerated, it is considered nonrenewable. The more renewable an energy resource is (that is, the faster it can be regenerated at the level it is being used), the less of an environmental impact it has. Wind electricity, has high renewability, as there is essentially no time lag between its use and regeneration. Forest exploitation at rates low enough to permit renewal should be expected to have less environmental impact than exploitation above renewal rates. It is therefore a matter of concern to examine energy technologies having intermittent renewability that can be realistically increased. While an efficient use of a resource can increase renewability, an innovation in the process of turning a non-resource renewable material into a useful resource can be more proficient. Literatures suggest that several presently available energy systems having low renewability may become more renewable in the future (Manzini and Martinez, 1999).

Renewability is a key parameter for evaluating energy technologies according to their environmental impact. Consequently Renewability assessment is of great importance for sustainable development of systems and processes concerned with human welfare. On one hand it deals with calculations of input/output ratio for a specific renewable resource based on benefit analysis. The same is applicable to the systems like wind energy generation farms and wastewater treatment plants (Malca and Freire, 2006). On the other hand such assessments aim to investigate the sustainability of a concerned system by identifying the renewable resource components from its total historical resources use. The second role has a much larger domain of importance in the perspective of mitigating carbon footprints. For various kinds of production systems it can be carried out to find the specific renewability index for each final product (Shao and Chen, 2016a,b). For all products a tag of renewability can be attached so as to distinguish them qualitatively in the perspective of sustainable development. Most of such assessments rely upon thermodynamic accounting methods based on exergy. However, emergy analysis developed by Odum (1996), has been a historical breakthrough regarding the renewability assessment of a wide variety of production systems. Initially it emerged from the analysis of historical resource uses of various systems (Vassallo *et al.*, 2009). Within many of the quality indicators proposed in the literature, the renewability index (RI) is mostly significant due to its concern with original use of renewable resources. In most cases, only a part

of the natural renewable resources are directly utilized by the concerned system. Likely sunlight and rain, are generally identified as renewable resources. But various purchased products are encompassed within nonrenewable resource category, the historical use of renewable resources for the product are often ignored. Almost all the economic products and social services, both renewable and nonrenewable resources have been consumed during their productions. To assess the overall renewability of a production system aided by various kinds of social products, the renewable resources use of each product or service input should be analyzed.

A Review of Renewability Assessments

The renewability assessment of continually replenishing energy sources like the solar energy, wind power and biofuels have been intensively carried out in many literatures. Most of these studies were based on embodied energy analysis where the historical energy use of an energy system has been traced and accounted by net energy analysis or thermodynamic methods, such as energy analysis and exergy analysis. The renewability has been judged by either the input/output ratio of a specific renewable energy source or the proportion of renewable energy use to total energy use (Chen *et al.*, 2011). Solar energy is conventionally believed to be the primary driving force of the ecosphere. Based on these facts energy analysis was first proposed by famous ecologist Odum to quantify the direct and indirect work previously done to make a product or service (Odum, 1988). It conceptualized the 'solar energy' analysis to evaluate the solar energy required directly and indirectly to make a product or service. This approach translates each environmental and economic input, including energy, materials, labor and currency, into solar energy equivalents by utilizing a conversion factor called transformity. Therefore it illustrates the total previous resource use of each product. Till now, the energy analysis has been widely employed to evaluate resources used by various production systems at different times and regional scales (Ulgiate *et al.*, 1995). To illustrate the sustainability, environmental cost and benefit for a particular production system, lot of indicators have been contributed by energy analysis. Like many other exergy based studies, the Renewable Index (RI) is one of the important indicators which express the proportion of total renewable resources. Later such indicators were improved to include the renewable resource consumption triggered by the economic products inputs like those embedded in social products (Yang *et al.*, 2013). In order to assess the overall renewability of a production system, the use of renewable and nonrenewable resource as well as their components of each social product input should be properly identified. Actually, apart from a few essentially natural resources, each material, especially social product or service has consumed both renewable and nonrenewable resources through its supply chain, which cannot simply be classified as total renewable or nonrenewable source. A modified framework proposed by Chen *et al.* (2009) involves an improved indicator for renewability assessment of a production system.

Freshwater is often considered as renewable resources but it was not in the limelight for a long time because of the common perception of considering fossil energy as the only nonrenewable resource in human civilization. The availability of water resources is limited against a specific eco-geographical and socio-economic background. Although there is a wide range of renewable water resource points which don't appear with same production rates. While for the river water it's roughly two to three weeks, for groundwater aquifers it may take several hundred or even thousands of years (Li, 2009). Moreover, the extraction rate is larger in comparison to the underground accumulation and availability of river water throughout the world. Therefore it becomes necessary to account such varying resource points where a lot of extraction has already been done. The term "fossil water" is developed to refer the water from such ground aquifers since their accumulation time is measured at a human time scale (Oki and Kanae, 2006). From the economic perspective it needs a great deal of cost to make the water resources available for end use. Not only the cost of extraction from natural environment, but also the costs involved in treating them before and after use are important in assuring a safe and hygienic environment for the human society. The sustainability characteristics of wastewater treatment have been analyzed from economic, environmental and social perspective in many literatures (Muga and Mihelcic, 2008).

Various methods, for instance, life cycle analysis, energy analysis, exergy analysis, and some integrated approaches (Hellström *et al.*, 2000) have been applied to assess various sustainability indexes in relation with carbon footprints. The demand of water would continue to increase along with the fast growing population and ever growing living standard. Therefore the renewability assessment of water related system is highly crucial in the perspective of its efficiency and policy making. Transformity, defined as the energy required for making a unit of product or service, has been calculated by a plenty of scholars (Odum *et al.*, 2000). The transformity data for environment inputs such as sunlight and wind power are relatively constant where Odum's database (Odum *et al.*, 1988) is applicable. For the social products and services, energy was estimated by multiplying the monetary cost by a single energy to money ratio (Ukidwe and Bakshi, 2004). Process analysis tries to analyze each individual stage to trace the historical energy of the concerned product. But it deals with truncation error and data inconsistency jeopardizing the reliability of energy studies. In contrast with process analysis, the input-output analysis is a top-down approach (Leontief, 1970). By integrating the consistent statistics with various ecological impacts, the input-output analysis can efficiently provide up-to-date data for ecological accounting studies. It has been successfully applied to study the environmental implications of natural resources use and environmental emissions like energy, carbon, pollutant etc., within an economy (Zhou, 2008).

Methods of Renewability Assessments

Evaluation of Exergy Based Renewability Index

The search for thermodynamic quality standards is one of the most interesting challenges of the Engineering Thermodynamics. In the last decades, this concern is no more restricted to the performance quantification of a given process or equipment, but it

extends to all the boundaries of any energy conversion process, including its energy inputs and wastes. For every process, equipment and a given output, two major drawbacks can be identified

- A larger energy input utilization as smaller is the conversion efficiency,
- A larger quantity of wastes and consequently a higher potential to generate environmental impacts, as smaller is the conversion efficiency.

The concept of exergy was originated from the formulation presented by Gouy (1889) and Stodola (1898), which shows that the maximum potential for a system to perform work is a function of its internal energy and the ambient conditions. For a prolonged period of time the concept of renewability has been associated to mass and energy balances, not taking into account the reduction of the quality of the energy i.e., exergy destruction related to energy conversion processes. The traditional definition of sustainability, that calls for policies and strategies that meet society's present needs without compromising the ability of future generations to meet their own needs, Odum (1996) does not provide a rational way to quantify this ability. Exergy originating from the contrast between sun and space drives flows of energy and matter on the surface of Earth. This exergy input is destroyed in order to keep the natural cycles responsible for recycling materials on earth, and a small part is stored as fossil fuels and mineral ores. Recycling again takes time and exergy to be accomplished, but total recycling is not possible due to the second Law of Thermodynamics. Therefore the Origin of its energy source and Efficiency of the energy conversion processes should be taken into account whenever discussing renewability of any product (De Oliveira, 2012). Based on these facts a renewability exergy index can be defined which accounts the exergy associated to the useful products of a given energy conversion process or a set of processes, the destroyed exergy, the exergy associated to the fossil fuels required, the needed exergy to deactivate the wastes, and the exergy of by-products and not treated wastes.

Exergy flow rate $\dot{B}$ can be calculated by the following general equation in which four components are considered: kinetic exergy (k), potential exergy (p), physical exergy (ph), and chemical exergy (ch).

$$\dot{B} = \dot{B}_k + \dot{B}_p + \dot{B}_{ph} + \dot{B}_{ch} \quad (1)$$

Where, specific physical exergy is

$$\dot{B}_{ph} = (h-h_0) - T_0(s-s_0) \quad (2)$$

Here h is the specific enthalpy, s is the specific entropy and the subscript 0 is referred to the dead state. The exergy balance for a control volume (CV) operating in steady state express the destroyed exergy

$$B_{destroyed} = \sum_{in} \dot{B}_i - \sum_{out} \dot{B}_i + \sum \dot{B}^Q - \dot{W} \quad (3)$$

Where, $\sum_{in} \dot{B}_i$ and $\sum_{out} \dot{B}_i$ are the sum of inlet and outlet exergy flow rates respectively. $\sum \dot{B}^Q$ is the sum of thermal exergies, and $\dot{W}$ is the power in the CV.

Exergy efficiency η_B measures the ratio between the exergy outflow rate and the exergy inlet rate. Exergy product consists in the difference between the exergy content of the separated products $\dot{B}_p$ and that of the mixture $\dot{B}_M$. The exergy inlet rate is given by the exergy flow rate $\dot{B}_U$ used to provide the exergy flow rate output. The utilized exergy $\dot{B}_U$ is the exergy content of the fuel used to satisfy the requirements of the processes

$$\eta_B = \frac{\sum \dot{B}_p - \sum \dot{B}_M}{\dot{B}_U} \quad (4)$$

The renewability exergy index λ measures the ratio between the exergy associated with the useful product of the process and the sum of the exergy associated to the fossil fuels required, the destroyed exergy, the needed exergy to deactivate the wastes, the exergy related to waste disposal and the exergy of wastes that are not treated or deactivated (Sánchez and De Oliveira, 2015)

$$\lambda = \frac{\sum B_{product}}{B_{fossil} + B_{destroyed} + B_{deactivation} + B_{disposal} + B_{emission}} \quad (5)$$

Where,

- $B_{product}$ represents the net exergy associated to the products and by-products.
- B_{fossil} is the non-renewable exergy consumed on production processes chain.
- $B_{destroyed}$ is the exergy destroyed inside the system, punishing the process for its inefficiencies.
- $B_{deactivation}$ is the deactivation exergy for treating wastes, when they are carried to equilibrium conditions with the environment.
- $B_{disposal}$ is exergy rate or flow rate related to waste disposal of the process.
- $B_{emission}$ is the exergy of wastes that are not treated or deactivated.

Depending on the value of the renewability exergy index (De Oliveira, 2012), it indicates that

- Processes with $0 \leq \lambda \leq 1$ are environmentally unfavorable.
- For internal and externally reversible processes with non-renewable inputs, $\lambda = 1$.
- If $\lambda > 1$ the process is environmentally favorable, and additionally, increasing implies that the process is more environmentally friendly.
- When $\lambda \rightarrow \infty$ it means that the process is reversible with renewable inputs and no wastes are generated.

Energy Return on Investment (EROI) Method

In physical assessment of renewable and sustainable energy technologies for mitigating greenhouse gasses and overall carbon footprint, system indicators play an essential role during the evaluation (Chen *et al.*, 2011). Although theoretically a totally renewable energy should not involve any fossil energy requirement, in a practical scenario it requires both renewable and nonrenewable energy inputs. In this regard a remarkable breakthrough is the basic concept of energy return on investment (EROI). It is defined as the ratio of energy extracted or delivered by a process to the energy used directly and indirectly in that process (Cleveland, 2007).

EROI is calculated from the following equation, although the details are really involved:

$$\text{EROI} = \frac{\text{Energy returned to society}}{\text{Energy required to get the energy}} \quad (6)$$

The numerator and denominator are necessarily assessed in the same units so that the ratio derived is dimensionless. This example means that a particular process yields 30 joules per investment of 1 J. EROI is usually applied where the energy resource leaves a production facility like the mine-mouth, wellhead or a farm gate. So it can be denoted more explicitly as EROI_{mm} . In another approach EROI is the standardized energy output divided by the summation of direct energy used at production site and indirect energy used to manufacture the machinery and products used, consumed to generate that output. This results in a measurement of standard EROI i.e., EROI_{st} . The numerator of the EROI equation is the product of the quantity of energy produced and the energy content per unit. Determining the energy content of the denominator is usually difficult. The energy used on site may be manifold like the energy used to rotate the drilling bit when drilling for oil, the energy used to excavate when mining for coal, or the energy used to operate the farm tractor when harvesting corn for ethanol. The energy involved in the manufacturing of concerned equipments is also under the purview (Hall, 2011). EROI values for our most important fuels, liquid and gaseous petroleum, tend to be relatively high. World oil and gas has a mean EROI of about 20:1 (Lambert *et al.*, 2012). Analysis of EROI values for nuclear energy suggests a mean EROI of about 14:1. Hydroelectric power generation systems have the highest mean EROI value, 84:1. Nearly all renewable energy systems appear to have relatively low EROI values when compared with conventional fossil fuels. A question remains as to the degree to which total energy costs can be reduced in the future, but as it stands most “renewable” energy systems appear to be still heavily supported by fossil fuels. They are considerably more efficient at turning fossil fuels into electricity than are thermal power plants, although it takes many years to get all the energy back (Fig. 1).

The reciprocal of EROI has been addressed as energy cost indicator to denote how many energy times of cost used in the whole manufacturing process over the energy are contained in the final product. Fossil energy ratio, defined as the ratio between the biofuel energy content and the fossil energy input, has been used to identify whether a biomass derived fuel is renewable (Chen and Chen, 2011). Few literatures has reported flaws about EROI, such as varying answers to the same question, controversial boundaries of the analysis and dependence upon monetary data. Despite these limitations, EROI is still a basic concept to indicate renewability when considering energy policy and the future prospects for modern civilization.

Net Energy Analysis

During the worldwide energy crisis in 1970s, the net energy analysis was first proposed to assess the energy exploitation efficiency of a conventional energy supply system (Berthiaume *et al.*, 2001). To assess the renewability of a sample production unit having possible carbon footprints, an indicator called NEIED (nonrenewable energy investment in energy delivered) was proposed (Cleveland, 2007). At early stages only fossil energy was concerned to deal with conventional energy system. Subsequent studies made some progresses by additionally concerning the specific renewable energy sources. However its historic consumption embodied in the production of the material inputs was not assessed in many cases. For example, in a sustainability assessment of a 1.5 MW solar power tower plant in China (Wall and Gong, 2001), while accounting a nonrenewable energy cost only the fossil energy cost of the material inputs were accounted. However with the previous solar energy cost for the geophysical formation of the fossil fuel was not mentioned. A lot of existing renewability assessment studies has used thermodynamic analysis to trace and

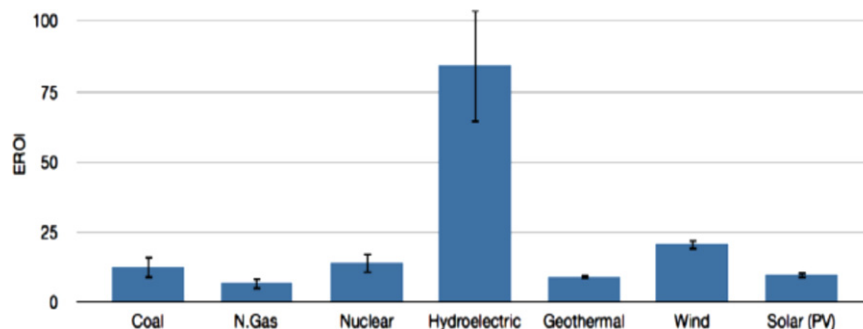


Fig. 1 Mean EROI with standard error values of power production systems. Reproduced from Hall, C.A.S., 2011. Introduction to special issue on new studies in EROI (energy return on investment). Sustainability 3 (10), 1773–1777.

measure the embodied energy of a production system especially while considering the energy inside soil and water. Therefore, the term 'nonrenewable energy investment in energy delivered' (NEIED) is expressed as

$$\text{NEIED} = \frac{\text{NE}}{E_{\text{OUT}}} \quad (7)$$

Where, NE is the nonrenewable energy used directly and indirectly in the production process, and E_{out} is the net output energy. NE can be calculated as,

$$\text{NE} = \sum \text{NE}_i = \sum \text{Input}_i \times C_i \quad (8)$$

Where, NE_i denotes the nonrenewable energy used directly and indirectly in the production of the i th input, Input_i to the whole chain of a production farm. C_i is defined as the nonrenewable energy-intensity coefficient which indexes the proportion of direct or indirect nonrenewable energy demand for the production process. Such coefficients can be measured by one of two general methods: namely process analysis or input–output (I–O) analysis. Both methods require the same data and would yield the same result in most cases. The more nonrenewable energy required to produce an output, the less we can say that this output is renewable. Significant cases could be identified for different ranges of NEIED values. $\text{NEIED} < 1$ is for a renewable process in which more energy is produced than NE invested, while $\text{NEIED} > 1$ is for a nonrenewable process in which more NE is consumed than energy produced (Yang and Chen, 2012). Smaller the NEIED, higher is the renewability of the production system. Similarly, the Greenhouse Gas (GHG) emissions associated with NE cost can be calculated as

$$\text{GHG} = \sum \text{GHG}_i = \sum (\text{INPUT}_i \times G_i) \quad (9)$$

Where, GHG_i denotes the direct and indirect Greenhouse Gas emissions in the production of i th inputs, G_i is defined as the GHG-intensity coefficient of the i th input (Zhou, 2008). Lesser GHG emission of a production system is indicative of higher renewability.

Emergy Analysis

Emergy is the availability of energy or exergy that is used up in transformations directly and indirectly to make a product or service. The unit of emergy is the emjoule. For example, sunlight, fuel, electricity, and human service can be put on a common basis by expressing them all in the emjoules of solar energy that is required to produce each (Brown and Ulgiati, 2004). Solar emergy is expressed in solar emjoules or sej. The more work that is done to produce something, the more energy must be transformed to perform that work, and higher the emergy value stored in the product. Emergy is therefore a global measure of the sum of the energy flows in the processes required to produce something. Few basic block diagrams describe emergy systems. Relevant symbols used in the energy systems diagram have been depicted in Fig. 2.

Fig. 3 illustrates the pathways (flows) and conservation of energy within a typical production system. The key aspects include flows of energy into and out of the system, transformation of energy and its storage in various pools within the system, consumption of energy by a process to do work, and flows of energy between storage pools.

Exergy represents the real proportion of the energy that is available to perform mechanical work:

$$E_x = (\text{Gibbs free energy}) + (\text{Gravitational energy}) + (\text{kinetic energy}) \quad (10)$$

Brown and Ulgiati (2002) defined the solar emergy (E_m) of the flow from a given process as the solar energy that is directly or indirectly required to drive the process. The unit of solar emergy is the solar emjoule (sej):

$$E_m = \sum E_i \text{Tr}_i \quad (11)$$

Where, E_i is the available energy (free energy) content of the i th independent input flow into the process and Tr_i is the solar transformity of the i th input flow. Transformity is the emergy of one type required to create a unit of energy of another type. An important concept in emergy analysis is the solar transformity, which represents the solar emergy (in solar emjoules, sej) required to provide 1 J of a service or product (Odum, 1996). Solar transformity is therefore measured in sej J^{-1} . For example, 159,000 J of solar energy can be transformed into a quantity of wood through photosynthesis, with some loss during transformation processes. If that wood can release 1 J of energy by combustion, the transformity of the wood will be 159,000 sej J^{-1} (Fig. 4). Transformity captures the emergy invested per unit of product or useful output (Brown and Ulgiati, 2004). Transformity (Tr) can therefore be specified as the ratio of used up input emergy or available energy to the output exergy as follows,

$$\text{Tr} = \frac{E_m}{E_x} \quad (12)$$

Fig. 5 is a generic example of the emergy diagram which describes the interactions between the different stages of a system involved in the production of a product whether a good or service. Independent Sources represented by circles can be three types: (local) renewable resources R, (local) non-renewable resources N, and flows passing through the economic system S (Wilfart and Corson, 2012) synthesized the sources as shown in Table 1. Varying interpretations may exist when classifying a resource, for example "nonrenewable" or "service". Although it depends on the given modeler's choice, the choices made in the analysis should be explicit. Emergy analysis is governed by a set of rules which connects them. The (total) emergy of co-products is equal to the input emergy E_{mi} and the total input emergy within a junction is distributed in proportion to energy outputs. Two systems with the same production process may have different transformities like $\text{TR1} < \text{TR2}$. If the second system uses more renewable resources

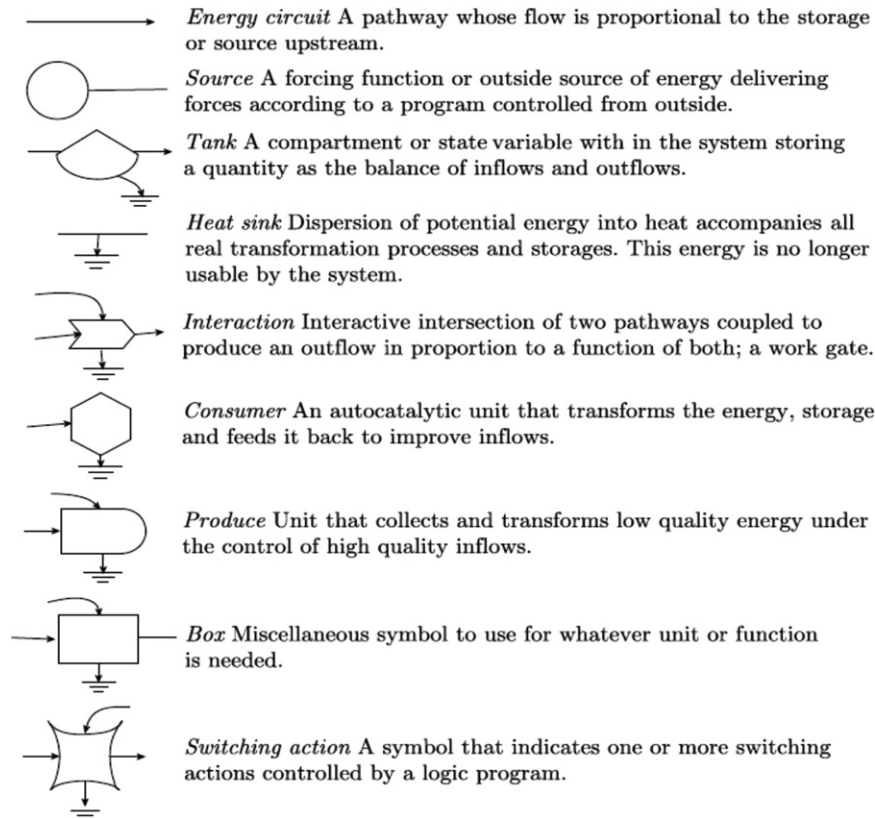


Fig. 2 Symbols used in the energy systems diagrams. Based on Odum, H.T., 1996. Environmental Accounting: Energy and Environmental Decision Making. New York: Wiley.

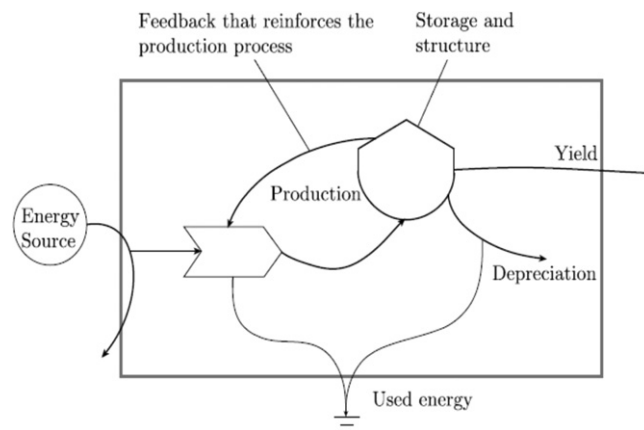


Fig. 3 Energy transformation within a production system. Based on Odum, H.T., 1996. Environmental Accounting: Energy and Environmental Decision Making. New York: Wiley.

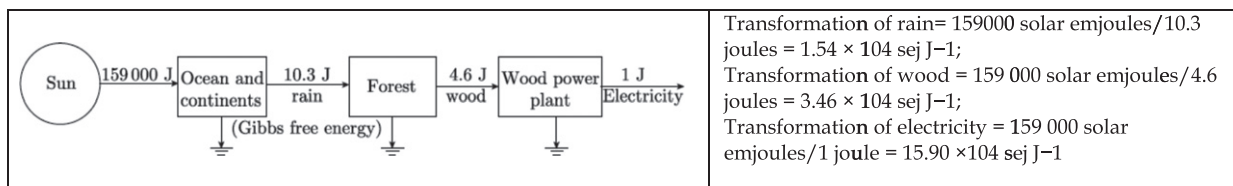


Fig. 4 An example of the chain of energy transformations required to generate a product like electricity After Odum, H.T., 1996. Environmental Accounting: Energy and Environmental Decision Making. New York: Wiley.

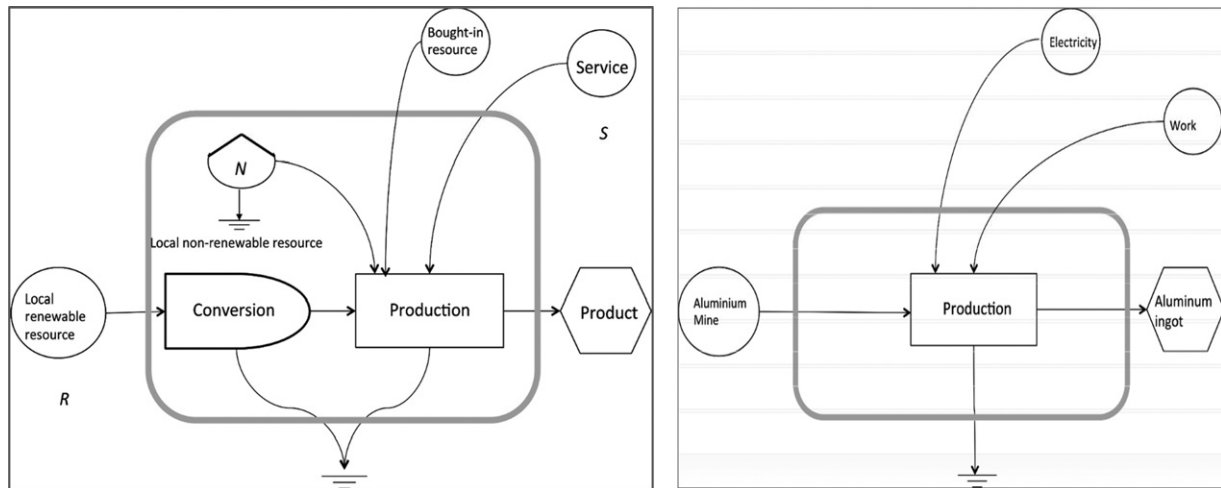


Fig. 5 Example of an emergy diagram of a production system.

Table 1 Classification of sources for emergy evaluation

Description		Unit UEV	Notation
Environmental contribution (local)			
Renewable resource	Sun, tidal, wind and other natural sources	seJ/J	R
Non-renewable resources	Fossil fuel, minerals and other fuels	seJ/unit	NR
Interaction with the economic system (external)			
Equipment (good)	Machine	seJ/\$	S
Service	Electricity, employees labor	seJ/\$	S
Input emergy which is modified to outputs = $R+NR+S$			

Table 2 Emergy ratios used as different renewability index

Emergy ratio	Formulation	Implication
Emergy Yield Ratio (EYR)	$EYR = \frac{Em_p}{Em_s}$	The larger the EYR or Production ratio, the lower the service contribution
Emergy Loading Ratio (ELR)	$ELR = \frac{Em_r + Em_n}{Em_r}$	Smaller ELR indicate more significant emergy portion of local renewable resources. An increased value demonstrates a production system mainly using non-renewable resources
Emergy Investment ratio (EIR)	$EIR = \frac{Em_s}{Em_r + Em_n}$	Lower EIR shows more tendency of a product obtained from local resources (renewable or non-renewable) and consequently more emergy cost or investment flow through the economic system
The Emergy Sustainability Index (ESI) is defined as:	$ESI = \frac{EYR}{ELR}$	An increased ESI value corresponds to a production system which uses local renewable resources and is therefore considered to be sustainable
The recycling fraction %R	$\%R = \frac{Em_r + Em_{sr}}{Em_p}$	This fraction takes account of the share of local renewable emergy, but also connects the renewable part coming from the economic system

for its production, then even if its transformity is higher than that of the first system, the second system should be retained. In extension with transformity evaluation, another important parameter of interest is the unit emergy value (UEV) which is expressed as the emergy value for a product unit in seJ/g. Fossil resources (coal, natural gas and oil) from different geological eras can also be analyzed to judge their renewability. Minerals are assessed from a so-called (natural) enrichment factor. For interactions between the studied system and the economic environment, the emergy value of a given currency is also needed (Lei *et al.*, 2014).

The first step of emergy analysis is gathering all inputs which cross the boundaries of a given system as shown in Fig. 5. This information is generally presented in the form of a table. Each constituent is referred to an identifier with an associated unit, the quantity of the constituent used and the unit emergy content. The last column calculates the total emergy of the constituent. Local resources can be separated as renewable or non-renewable which are imported or transported within the market based system. To compare renewability of two production systems concerned to the same output product, five major emergy ratios are defined in Table 2. For example in the production of Aluminum, it is first extracted from a mine, then refined and finally converted into an ingot (Olivier, 2016). For simplification, let's assume that electricity is the only given source of energy during the production process. The emergy diagram

associated with this process is given in Fig. 5. For a case study of production, Buranakarn (1998) indicated that a quantity of $4.17\text{E}+5$ tons of minerals were used. From a database, he obtained the unit energy content ($1.17\text{E}+10$ seJ/g) as well as the total energy. Through similar analysis for electricity and human labor, he calculated the total quantity of emergy. Table 3 summarizes the above approach exploiting the annual production of aluminum ingots in USA and the unit energy content of this product.

Modified Emergy Analysis Based on Input-Output Analysis

As discussed earlier, emergy analysis translates all goods, services, environmental inputs like sunlight, wind, rain and tides, into a common unit of available energy. However for social products, transformity database is dependent upon time-consuming process analysis which traces the historical emergy of a concerned product at each stage of the production system. Leontief (1970) introduced the input–output analysis based on economic statistics. It organizes matrices of all the intermediate inputs into goods and services by integrating the consistent statistics with various ecological impacts. The input–output analysis can efficiently avoid the truncation errors of process analysis and provide unified data for renewability studies. It has been successfully in the assessment of environmental implications regarding natural resources use and environmental emissions. The modified diagram for the emergy based renewability assessment of a production system is shown in Fig. 6, following the methods developed by Odum (1988). Natural resources accounted by emergy can be classified into renewable resources (RR) such as sunlight, wind power etc., and nonrenewable resources (NR) such as soil, fuels, and minerals. Besides directly utilizing natural resources from the environment (L), a production system also indirectly utilizes resources by purchasing products and services from the economy (P). Since the human society consumes both renewable and nonrenewable resources in its evolution, each product and service consists of both renewable (RP) and nonrenewable (NP) components. Following steps demonstrate the resource accounting procedure as the basis of renewability assessment of a production system (Shao and Chen, 2016a).

- (1) Itemize all the inputs of the concerned system, including both environmental inputs as local sources and social products and services as purchased sources to form an inputs inventory of the concerned system. The quantity of environmental inputs (QE) should be in Joule and transformity in seJ/J. The quantity of purchased input (QP) is in monetary unit.
- (2) Determine the transformities of all inputs of the concerned system. For environmental inputs transformity (TE) are relatively constant as per data contributed by Odum (1996). To trace the previous resources consumption of a social product, the transformity database should cover both renewable and nonrenewable transformity data of each product or service input to

Table 3 Emergy table for annual production of USA aluminum

Sl. no.	Element	Unit/year	Quantity	UEV (seJ/unit)	Emergy (seJ/year)
1	Aluminum mineral	g	$4.17\text{E}+11$	$1.17\text{E}+10$	$4.88\text{E}+21$
2	Electricity	J	$1.08\text{E}+15$	$1.74\text{E}+05$	$1.88\text{E}+20$
3	Labor	\$	$2.09\text{E}+07$	$1.15\text{E}+12$	$2.40\text{E}+19$
Annual quantity		g	$4.00\text{E}+11$	$1.27\text{E}+10$	$5.08\text{E}+21$

Note: Buranakarn, V., 1998. Evaluation of Recycling and Reuse of Building Materials Using the Emergy Evaluation Method (Ph.D. Dissertation). Gainesville, FL: Department of Architecture, University of Florida.

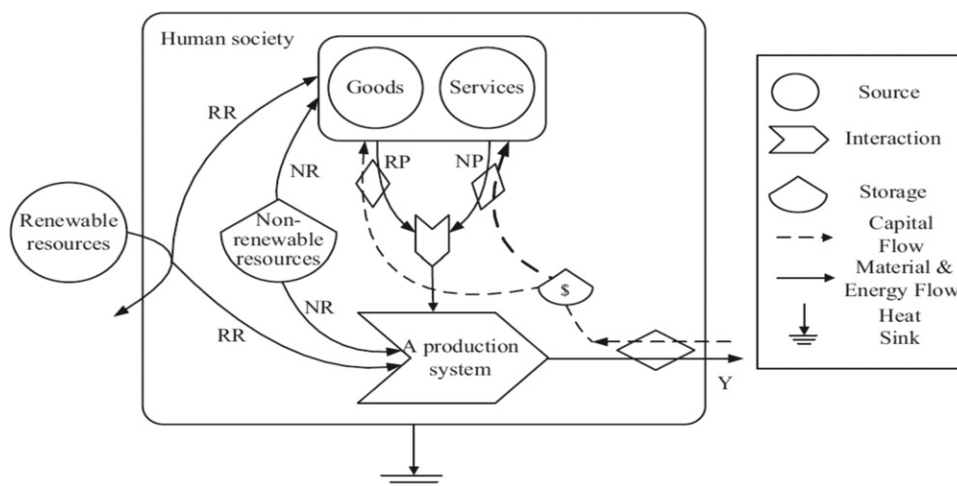


Fig. 6 Diagram for emergy analysis of a production system. Reproduced from Shao, L., Chen, G.Q., 2016b. Renewability assessment of a production system: Based on embodied energy as emergy. *Renewable and Sustainable Energy Reviews* 57, 380–392.

make subsequent renewability assessment possible. After preparing the database the corresponding transformity for each product or service input (TP) is calculated from corresponding economy input–output table.

- (3) The energy as energy embodied in the supply chain of each input can be calculated by multiplying the transformity by its quantity. By adding up the energy of both environmental and social product inputs, the total resource use of the concerned system is given as:

$$U = \sum_{i=1}^n TE_i \times QE_i + \sum_{i=1}^n TP_i \times QP_i \quad (13)$$

According to the energy theory, the related energy flows of a production system and the indicators used for assessing the renewability, efficiency and performance are respectively described in Table 4. The previous energy studies used to consider a product or service as completely renewable or completely nonrenewable. As for the natural resources that can be true. But for products or services, this perception is inappropriate (Shao and Chen, 2016a). The production of a product or service needs both renewable and nonrenewable resources in its making which makes the estimation more complicated. In general cases with heavy economic investment, the input–output analysis is necessary for energy analysis especial the renewability assessment studies considering that it realizes the complete modeling of the whole economy as organizing matrices of all intermediate inputs.

Case Studies

Renewability Assessment for Biofuel Production

Biofuel is one of promising option to reduce carbon footprints and reducing greenhouse gas emission. This study presents an efficiency and renewability analysis of the production of three biofuels: rapeseed methyl ester (RME), soybean methyl ester (SME) and corn based ethanol (EtOH). The overall production chain to transform the crops into biofuels, including the crop production, industrial conversion into biofuels, production of agricultural resources like pesticides, fertilizers, fuel, seeding material and industrial resources like energy and chemicals were taken into consideration. Simultaneously, byproducts of the agricultural and industrial processes have been taken into account when resources have to be allocated to the biofuels.

Three production chains were quantified in exergy terms. The reference state considered was temperature at 298K and pressure at 1 atm with composition as per standard literature (Szargut *et al.*, 1988). In Fig. 7, the overall production chains of RME, SME, and EtOH are represented where allocation of renewable and nonrenewable resources to the delivered biofuels and byproducts are done on exergy basis. The thermodynamic second law analysis revealed that corn-based EtOH results in the highest production

Table 4 Energy indicators of renewability assessment of a production system

Item	Symbol and algorithm	Item	Symbol and algorithm
Local Energy	$L = RR + NR$	Environmental Loading Ratio (stress on the environment)	$ELR = (NR + NP) / (RR + RP)$
Local Renewable / Nonrenewable Energy	RR / NR	Energy Yield Ratio (for purchased resources)	$EYR = U / P$
Purchased Energy	$P = RP + NP$	Locality Index (for environmental contribution)	$LI = L / U$
Purchased Renewable / Nonrenewable Energy	RP / NP	Environmental Sustainability Index (ecological sustainability)	$ESI = EYR / ELR$
Total Resources Use	$U = L + P$	Renewability Index (percent renewability)	$RI = (RR + RP)$

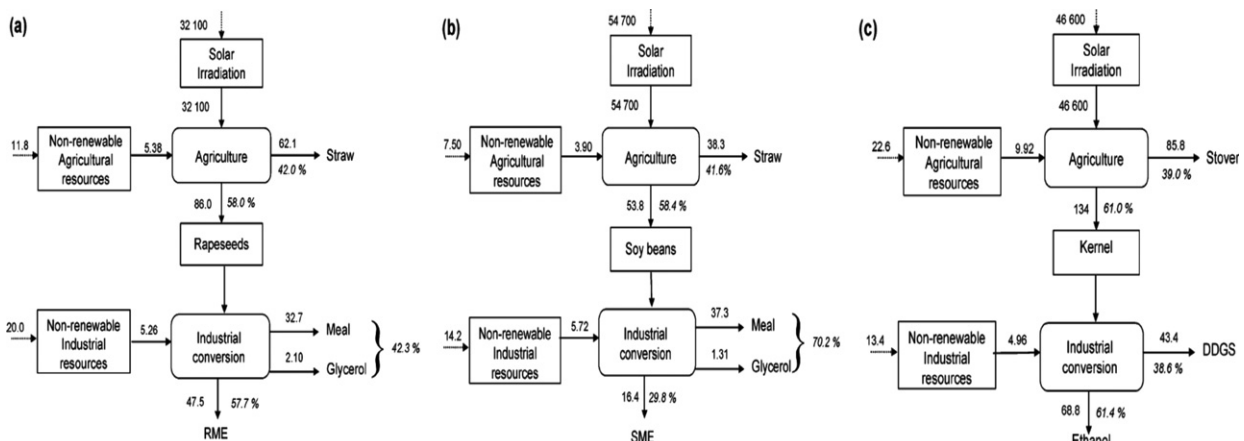


Fig. 7 Exergy flow for annual production of biofuels on 1 ha ($\text{GJ ha}^{-1} \text{yr}^{-1}$), including byproducts. Percentages show the shares in the output of respective process on exergy basis (a) RME, (b) SME, (c) EtOH. DDGS- Distiller's dried grain. Reproduced from Dewulf, J., Vanlangenhove, H., Vandeveld, B., 2005. Exergy-based efficiency and renewability assessment of biofuel production. *Environ. Sci. Technol.* 39, 3878–3882.

rate with an exergetic fuel content of $68.8 \text{ GJ ha}^{-1} \text{ yr}^{-1}$, whereas the RME and SME results were limited to 47.5 and $16.4 \text{ GJ ha}^{-1} \text{ yr}^{-1}$. The allocated nonrenewable resource inputs are 16.5, 15.4 and $5.6 \text{ MJ ha}^{-1} \text{ yr}^{-1}$ respectively. This means that these biofuels, generally considered as renewable resources, embed a nonrenewable fraction of one-quarter for EtOH and even one-third for RME and SME. The renewability can also be judged in terms of exergy breeding. The energy or exergy breeding factor (BF_{ex}) and the net energy or exergy value (NEnV or NExV) assesses how much renewable resources are bred from nonrenewable resources. It turns out from the detailed analysis that not only for the overall production chain, corn-based ethanol proves to be the most suitable biofuel in terms of efficiency and renewability (Dewulf *et al.*, 2005). The analysis reveals an overall industrial metabolism exergy breeding factor i.e., overall BF_{ex} of 4.1 for EtOH based production with lowest nonrenewable fraction of 24.3%. RME and SME show overall BF_{ex} values close to 3 and a nonrenewable fraction of about one-third.

Renewability of Various Power Production Systems

Renewability of power production systems can be analyzed by many of the methods outlined earlier. The first step is to devise the Emergy diagram through detailed analysis of the system. Input data for each item in the evaluation tables are the operational data of each plant and are converted into appropriate units by suitable conversion coefficients. Unit oil equivalents (goil/unit) are used for energy evaluation and transformities (sej/unit) for emergy evaluation, to yield net energy and emergy values for each input item. Energy values are initially expressed as grams of oil equivalent followed by grams of released carbon dioxide, by means of an average oil-to-carbon dioxide conversion coefficient. Energy, emergy, and CO₂ flows are then summed, yielding a total that is divided by the amount of the product of each plant to calculate its energy cost, its transformity, and its associated carbon emissions. This evaluation offers an opportunity to evaluate the effects of greenhouse gas emissions in the concerned process. Finally to get an overall picture of plant performance, energy, emergy and carbon-flow related indicators are assessed. All inputs and outputs of the production systems are expressed on a yearly basis. Fixed capital equipment, machinery, buildings, and so on are divided by their estimated useful life (10–30 years). CO₂ production is calculated for direct fuel combustion in thermal plants using multipliers of indirect energy consumption for their production. These multipliers are derived from a standardized comparison of literature in this field (Brown and Ulgiati, 2004).

The case study is based on data provided by Italian National Electric Company (ENEL) on the average performance of Piombino 1280 MWe power plant situated at Tuscany, Italy. The plant consists of four 320 MWe boiler-turbine-generator groups, cooled by the seawater from nearby Mediterranean Sea. A conventional oil fuelled thermal power plant consists of a fuel inventory, boilers with pumps for steam generation, steam turbines, electric generators, set of transformers for easier transport to end users, chimneys for the release of combustion gases to atmosphere, and finally a set of heat exchangers to condense the steam by means of sea water (approx $44 \text{ m}^3/\text{s}$). Fuel desulfurization devices along with antipollution filters and scrubbers at the chimney mouth are also considered. As per the material components all inputs were sorted and suitable transformity were chosen from available literature. Labor and services are also accounted. Waste heat and chemicals released to the environment are quantified. The amount of environmental services (cooling water, wind, etc.) needed for dispersal, dilution and abatement is calculated through emergy accounting procedure. Fig. 8 shows the direct and indirect annual environmental flows to run the plant structure (assuming a lifetime of 25 years). The assessment automatically reflects the GHG emissions and its routes in the production system.

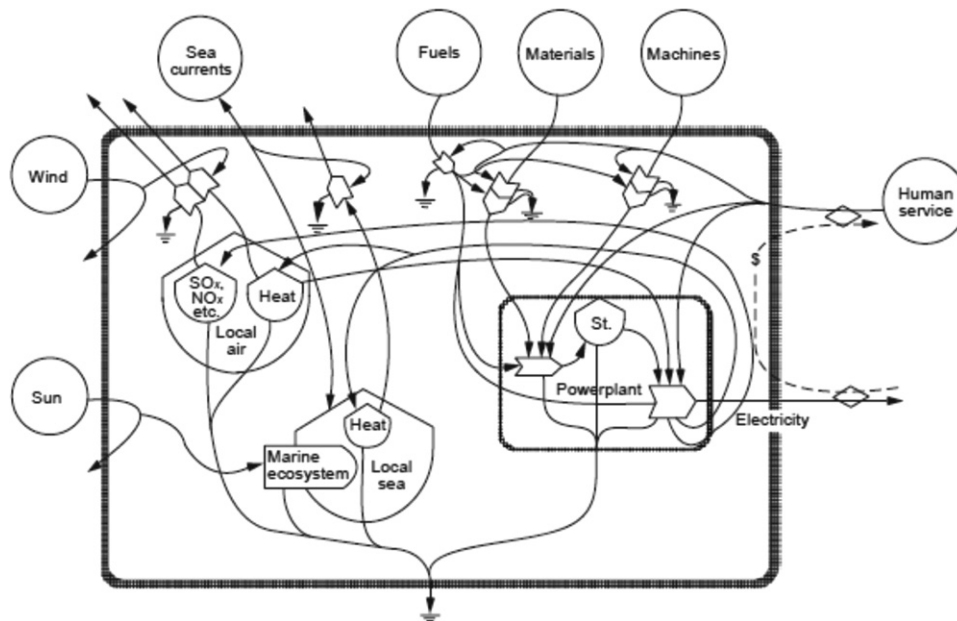


Fig. 8 System diagram of a thermal power plant and its environment demonstrating the use of environment and nonrenewable energy sources. Reproduced from Brown, M.T., Ulgiati, S., 2004. Emergy analysis and environmental accounting, Encyclopedia of Energy 2, Elsevier Inc.

Another investigation consists of a 2.5 MW wind powered field, composed with 10 single-blade, 250 kW, wind turbines M30-A, sited in southern Italy. The wind field was installed in the year 1995 by the Riva Calzoni Company. The distance between two generators is 150 m. Each turbine is located on the top of a 33 m support tower. Operating wind speeds are between 4 and 25 m/s. The turbine automatically stops in off design conditions. This remote controlled wind field does not require any local labor for its daily activity. The energy systems diagram of this case is elaborated in Fig. 9. Net Energy analysis (NEA) or Embodied Energy Analysis (EEA) typically evaluates energy sources and the process outputs in their heat equivalents. In this regard EROI is considered as a measure of the first law energy efficiency of a production unit. The total input energy in this case is derived by multiplying all goods and materials consumed in the construction per year of the average life span added with the annual maintenance of plants by energy equivalent multipliers and the annual energy consumed directly and indirectly. The output as electricity is converted to joules using the standard conversion of 3.6×10^6 J/kWh. Table 5 shows the energy accounting for the wind turbine case. Each item related to the investigated case study is multiplied by an appropriate transformity to get the emergy input. The total emergy is a measure of the total environmental support or ecological footprint to the process (Bargigli and Ulgiati, 2003). Finally, a new transformity for the process output is calculated by dividing the total emergy by the exergy of the product. Further renewability indicators like emergy yield ratio, environmental loading ratio, emergy density and renewability or emergy

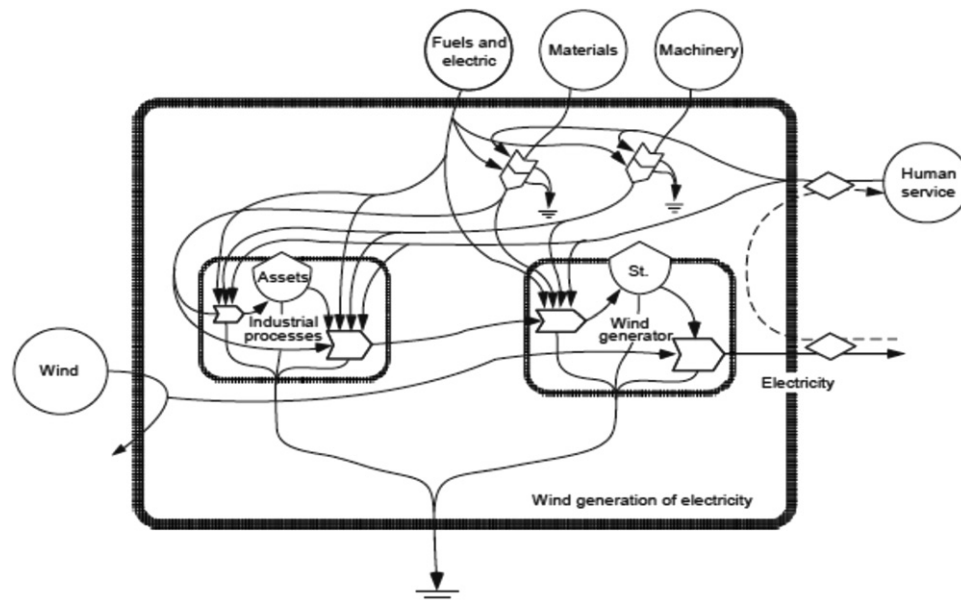


Fig. 9 System diagram of wind power plant showing the industrial processes required to produce the generator, associated structure and use of wind energy in power production. Reproduced from Brown, M.T., Ulgiati, S., 2004. Emergy analysis and environmental accounting, Encyclopedia of Energy 2, Elsevier Inc.

Table 5 Emergy accounting of wind power production in Italy

Item	Unit	Amount	Unit emergy value (seJ/unit)	Solar emergy (seJ)
<i>Direct renewable inputs</i>				
Wind	J	$4.85\text{E} + 13$	$2.52\text{E} + 03$	$1.22\text{E} + 17$
<i>Nonrenewable and purchased inputs</i>				
Concrete (basement)	g	$5.62\text{E} + 06$	$2.59\text{E} + 09$	$1.45\text{E} + 16$
Iron (Machinery)	g	$2.65\text{E} + 06$	$2.50\text{E} + 09$	$6.63\text{E} + 14$
Steel	g	$8.61\text{E} + 06$	$5.31\text{E} + 09$	$4.57\text{E} + 15$
Pig Iron	g	$1.56\text{E} + 04$	$5.43\text{E} + 09$	$8.47\text{E} + 14$
copper	g	$8.76\text{E} + 04$	$3.36\text{E} + 09$	$2.94\text{E} + 14$
Insulating and other plastic materials	g	$1.01\text{E} + 06$	$2.52\text{E} + 09$	$2.55\text{E} + 13$
Lube Oil	J	$3.10\text{E} + 09$	$1.11\text{E} + 05$	$3.44\text{E} + 14$
Labor	years	$8.33\text{E} - 02$	$6.32\text{E} + 16$	$5.26\text{E} + 15$
Services	US \$	$2.94\text{E} + 01$	$2.00\text{E} + 12$	$5.88\text{E} + 13$
<i>Electricity generated</i>				
Electricity with labor and services	J	$1.35\text{E} + 06$	$1.11\text{E} + 05$	$1.49\text{E} + 17$
Electricity with labor and services	J	$1.35\text{E} + 06$	$1.06\text{E} + 05$	$1.49\text{E} + 17$

Note: Modified from Odum, H.T., 1996. Environmental Accounting: Emergy and Environmental Decision Making. New York: Wiley.

Item		Unit	Oil plant (1280 MWe) ^a	Wind (2.5 MWe) ^a
Energy indicators				
E _{out}	Total electric energy delivered per year	J/year	2.35E + 16	1.35E + 13
E _{in}	Total energy invested per year	J/year	7.84E + 16	1.76E + 12
GWP	CO ₂ released/unit of energy delivered ^c	g/MJ	260.22	10.17
ER	Energy return on investment (energy output/input)		0.30	7.67
Emergy indicators				
R ₁	Renewable input from the local scale	seJ/year	3.43E + 20	1.22E + 18
R ₂	Renewable input from the global scale ^d	seJ/year	1.72E + 21	0.00E + 00
N	Locally nonrenewable input ^e	seJ/year	0.00E + 00	0.00E + 00
F	Purchased plant inputs, including fuel	seJ/year	5.71E + 21	2.13E + 17
L	Labor and services ^f	seJ/year	5.36E + 20	5.33E + 16
Y	Yield (R ₁ + R ₂ + N + F), without labor and services	seJ/year	7.78E + 21	1.44E + 18
Y _L	Yield (R ₁ + R ₂ + N + F + L), with labor and services	seJ/year	8.32E + 21	1.49E + 18
Indices (including services for fuel supply and plant manufacturing)				
Tr ₁	Solar transformity of electricity, with labor and services	sej/J	3.54E + 05	1.10E + 05
Tr ₂	Solar transformity of electricity, w/out labor and services	sej/J	3.31E + 05	1.06E + 05
EYR	Emergy yield ratio, EYR = (Y _s)/(F + L)		1.33	5.59
ELR	Environmental loading ratio, ELR = (R ₂ + N + F + L)/R ₁		23.26	0.22
ED	Emergy density, ED = (Y _L)/area of plant	sej/m ²	4.33E + 15	2.12E + 12
EIS	EYR/ELR		0.057	25.64

Fig. 10 Energy and emergy-based indicators and renewability of power plants. Reproduced from Brown, M.T., Ulgiati, S., 2002. Emergy evaluation and environmental loading of electricity production systems. *J. Clean. Prod.* 10, 321–334. Odum, H.T., 2000. Emergy evaluation of an OTEC electrical power system. *Energy* 25, 389–393.

index of sustainability are calculated. A relative comparison on the two aforementioned case studies has been depicted in Fig. 10 where all type of renewability indicators has been assessed.

Table 5 shows that wind emergy accounts for about 82% of the total emergy input, while labor and services (4%) and goods and machinery (14%) play a much smaller role. Emergy analysis demonstrates the whole process by considering hidden environmental flows and evaluating their role by means of a common measure of environmental quality. Allied literature shows that the EROI of a hydel plant is quite high in the range of 7.67 in comparison to the oil fired power plant with 0.30. A production system having lower environmental loading ratio also indicates higher energy density along with higher renewability index. A series of emergy performance indicators show that the main contributions to any electricity generation process are the driving forces of fuels or renewable sources, followed by the emergy associated with plant components. The other emergy indicators support this point by showing low Emergy Yield Ratios for oil-powered plants. High ELRs characterize oil-based patterns, as well as bioethanol electricity, while very low ELRs shown by the processes signify a larger degree on renewable. As a consequence, the aggregated sustainability measure expressed by the EIS ranges from a low 0.06 for oil based processes up to a significantly high 25 for wind-based ones.

Conclusion

This article is a brief synopsis of several types of renewability assessments possible for a production system. Starting with the basic exergy based calculations, the evolution of several important indicators have been discussed as per relevance. Methods detailed here, have been applied successfully by many researchers to account the sustainability of various production processes for example harnessing geo-thermal energy or just a simple recycling of wastewater for everyday use. Emergy accounting methodology has been discussed in details to understand versatile energy system diagrams for assessing almost all kind of production systems and affixing a renewability index to every product. Systematic analysis reveals the exergetic efficiency of each element and process used in the whole production unit to identify a resource which might contribute increasing the renewability index. Case studies have been incorporated to clarify the usefulness of emergy concept as well as the application of input output based transformity database. EROI based Case studies have exploited the use of net energy analysis for biofuels production systems through stage-wise process analysis. Ecologically best process was identified to minimize the possible carbon footprints of the production system. Emergy-based case studies of electricity productions system are presented for a better understanding of emergy indicators as well as decision making for prolonged future use. With the renewability approach presented here, a huge number of case studies can be assessed which varies from ecosystems to socioeconomic systems, biosphere, agriculture, industry, tourism, recycling patterns and generation. In all cases, the common aspect is to evaluate all forms of energy inputs, materials and human services directly or indirectly related with carbon footprints which help to measure the past and present environmental support to any production system. The obtained renewability of various products is crucial to promote sustainable economic development as people and firms can prioritize their options with regard to product's renewability label. It is

expected that a perfect scrutiny of production systems in terms of renewability will certainly minimize the overall level of carbon footprints and at the same time will integrate systems leading to least contribution in global warming.

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Further Reading

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Renewable Biomass: A Candidate for Mitigating Global Warming

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Introduction

The rapid growth of industrialization and simultaneous increase in population all over the world have elevated the air pollution to a very critical level, which threatens public health, deteriorates the environment, and damages property and landscape. The combustion of fossil fuel has led to increase in greenhouse gases (GHGs) and carbon footprint, which has resulted in higher global temperature and climate change. It is expected that the global temperature will rise from 1°C to 6.4°C by 2100 as a consequence of increase in the concentration of GHGs by consumption of fossil fuels in the atmosphere (Pachauri, 2007). Realizing the impact of global warming, almost all countries over the last few decades have introduced increasingly stringent legislation restricting permissible levels of pollutant emission from major combustion systems such as electricity generating power stations, furnaces, and industrial plants as well as from automobiles and aircrafts using fossil fuels. To mitigate greenhouse gases and carbon footprint, it is expected that the use of new and cleaner methods and fuels particularly from renewable energy sources will play a significant role. Amongst different sources of renewable energies, a very promising future energy source is biomass. This is because biomass has distinct advantages over the use of other renewable energies like solar energy and wind power, which are restricted because of their intermittent power generation. While biomass energy is the only renewable energy that can be used in the form of gas, liquid, or solid, it could as well replace the fossil fuel. Besides, if biomass is used as fuel, net carbon emission to the environment is zero because biomass absorbs the same amount of carbon in growing as it releases when consumed as fuel. Also because of very low sulfur content, the emission of sulfur dioxide (SO₂) is low from biomass. Biomass has remained a major source of energy for mankind since the inception of the civilization. Currently biomass accounts for about 10% of the global energy supply, of which two-thirds is used in developing countries for cooking and heating (IEA Task 40, 2003). Although trees and plantations are the main sustainable source of biomass, a number of other sources of biomass also exist. These include but are not limited to agricultural residues, forest residue, animal manure, industrial waste, and municipal/household solid waste. The majority of the biomass materials available in developing countries are used inefficiently in traditional ways, which causes extensive pollution to the environment. Incomplete combustion leads to the formation of extensive smoke. Exposure to smoke from indoor biomass burning is a known major cause of acute respiratory infection and chronic lung disease. However, biomass fuels currently used in traditional energy systems could potentially provide a much more extensive energy service than at present if these are used efficiently. Recently, there is a renewed interest in biomass-based energy because of the following reasons: (1) recent developments relating to the conversion technology and biomass production that made bioenergy competitive with fossil fuel-based energy generation in some situations, (2) environmental benefits provided by the modern biomass energy, (3) increasing concern over energy security and diversity of energy supply, (4) employment generation and rural development, and (5) restoration of degraded lands as a result of plantations and possibility of increase in biodiversity. Since biomass could be used for off-grid power generation, it could provide energy access to all sections of society while addressing the issue of mitigation of GHGs and carbon footprint. Scientists and researchers throughout the world have investigated different methods of converting biomass into useful energy. These methods are broadly classified into three routes: The biochemical conversion route, thermochemical conversion route, and physical conversion route. In the biochemical conversion route, biomass can be converted into either biogas through the anaerobic digestion process or ethanol through fermentation process. In the thermochemical conversion route, there are mainly three processes, namely, pyrolysis, gasification, and combustion. In pyrolysis, biomass is converted into a liquid fuel popularly known as bio-oil. In gasification, biomass is converted into a gaseous fuel known as syngas or producer gas. In combustion, biomass is converted into heat energy in the form of flue gas. On the other hand, in the physical conversion route, biomass is squeezed and oil is extracted that is further processed to use as diesel, and this is known as biodiesel. Different routes of converting biomass into useful energy are shown in Fig. 1.

Different Routes of Converting Biomass into Useful Energy

There are three different routes for converting biomass into useful energy: Biochemical conversion, thermochemical conversion, and physical conversion. Each process has its own advantages and limitations. These processes are described in detail below.

Biochemical Conversion Route

There are two different biochemical process routes for conversion of biomass: Anaerobic digestion and fermentation. These two processes are discussed below.

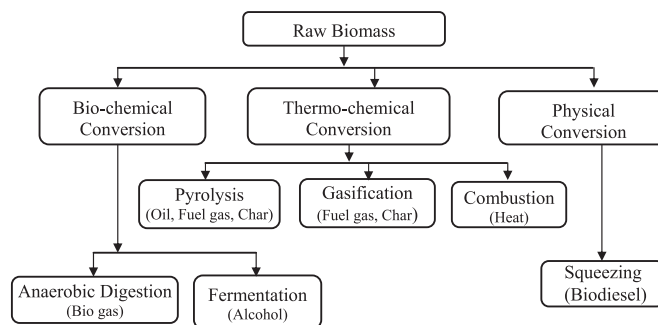


Fig. 1 Different routes of biomass conversion.

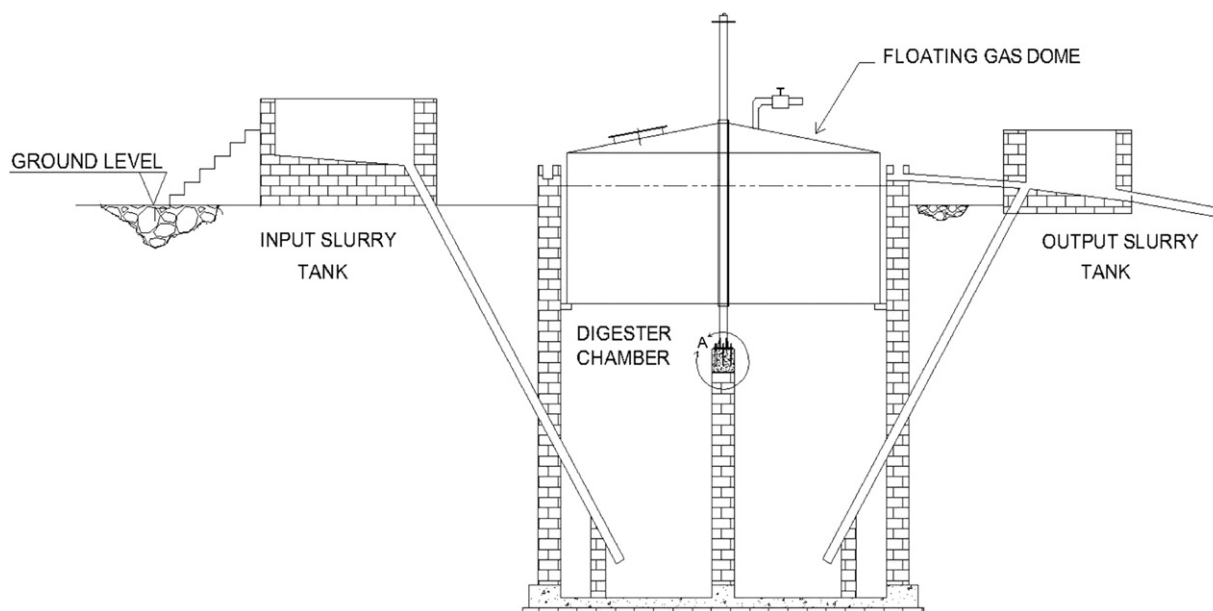


Fig. 2 Schematic diagram of a typical biogas digester.

Anaerobic digestion

Anaerobic digestion is the process by which biomass is converted into biogas and other energy-rich organic compounds through biological process in the absence of oxygen. The diverse microorganisms break down organic material and convert it into other forms through a series of metabolic reactions such as hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Biogas produced from anaerobic digestion of biomass is primarily a mixture of methane and carbon dioxide. It also has small amounts of hydrogen sulfide and moisture. The high amount of methane in biogas allows biogas to be used as a replacement for fossil fuel to generate heat or electricity (Pellera and Gidarakos, 2017). This process has the advantage of low energy requirement for operation compared with other biomass conversion routes. The anaerobic digestion of biomass reduces the environmental pollution because the sealed environment of the process prevents exit of methane into the atmosphere and burning of the methane will release carbon dioxide. The main disadvantages of anaerobic digestion are the long retention times and the low removal efficiencies of organic compounds. Anaerobic digestion of biomass has potential application to reduce the environmental load as compared with conventional sanitary landfills. The design of the reactor has a strong influence on the performance of the digester. Different types of reactor design have been proposed by the researchers in the view of improving the rate of reaction for the treatment of biomass. Fig. 2 shows the schematic of a basic anaerobic digester unit. It has different components as discussed below.

Input slurry tank: Initially the entire feed material would be collected and blended with water in the tank. After blending the ready feed material would be fed in the digester chamber. The feeding is a routine process to be followed up once daily to extract the maximum efficiency from the digester.

Digester chamber: Here the input slurry along with water is fermented and as a result methane and other gases will be produced in the chamber. The gas generated in the chamber will get accumulated at the top in a floating dome. Floating type dome is generally used to give extra storage space without requiring any extra land or incurring any additional cost for the gas storage tank. It also maintains uniform output gas pressure with the help of its metal dome's weight without using any additional compressor or blower.

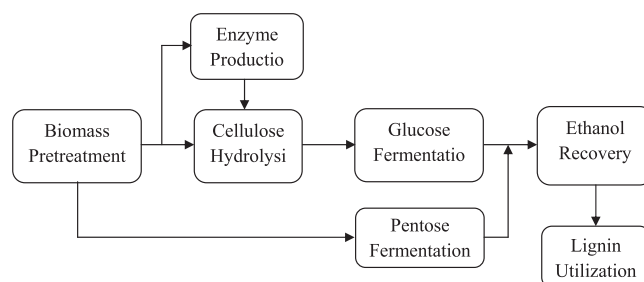


Fig. 3 Ethanol production from biomass through fermentation.

Output collection chamber: This chamber is used to collect the final output, which is in the form of semiliquid state and is also a by-product of this process. This by-product is enriched organic manure and can be directly used in the agriculture farming.

Anaerobic digestion is a simple process for converting organic waste into energy and simultaneously reduces the environmental pollution. However, it can suffer from process instability, which limits wider application of the process for energy production. Recent studies indicate that process monitoring is the best method of achieving improved process stability and higher conversion efficiency.

Fermentation

Fermentation is a metabolic process in which biomass is converted into ethanol through the action of enzymes. Ethanol can be produced from any biomass feedstock that contains appreciable amounts of sugar or materials that can be converted into sugar such as starch or cellulose. Ethanol is considered as the cleanest liquid fuel alternative to fossil fuels for transportation because it contains 35% oxygen that helps complete combustion of fuel and thus reduces harmful tailpipe emissions. It also reduces particulate emissions. In recent years, growing attention has been devoted to the conversion of biomass into ethanol and significant advances have been made towards the technology of ethanol fermentation. Ethanol can be produced from any biological feedstock that contains appreciable amounts of sugar or materials that can be converted into sugar such as starch or cellulose (Manochio *et al.*, 2017). The process of ethanol production from lignocellulosic biomass involves three major steps, which are pretreatment, enzymatic hydrolysis, and fermentation as shown in Fig. 3. Biomass is pretreated to improve the accessibility of enzymes. After pretreatment, biomass undergoes enzymatic hydrolysis for conversion of polysaccharides into monomer sugars, such as glucose and xylose. Subsequently, sugars are fermented to ethanol by the use of different micro-organisms. The solid residue from the fermentation process can be used as cattle feed.

The choice of biomass is important as feedstock costs typically make up 55%–80% of the final alcohol price (Kulkarni and Dalai, 2006). Raw materials containing sugars, or materials that can be transformed into sugars, can be used as fermentation substrates. The fermentable raw materials can be grouped as directly fermentable sugary materials, starchy, lignocellulosic materials, and urban/industrial wastes. Sugar-containing materials require the least costly pretreatment. But, starch-based biomass is usually cheaper than sugar-based materials but requires additional processing. On the other hand lignocellulosic materials (such as wood and straw) are readily available. But, the conversion of lignocellulosic biomass is more complex due to presence of long-chain polysaccharide molecules, which require enzymatic hydrolysis before resulting in sugar for fermentation.

Due to rapid growth in population and industrialization, worldwide ethanol demand is increasing continuously. Conventional crops such as corn and sugarcane are unable to meet the global demand of bioethanol production due to their primary value of food and feed. Therefore, in recent years, more attention has been given to lignocellulosic biomass like forest residue, agriculture waste, industrial residues, and municipal waste, which could be used as ideally inexpensive biomass materials for production of ethanol by fermentation. Bioethanol production from rice straw, wheat straw, corn straw, and sugarcane bagasse is a matter of interest worldwide now. Rice straw is the most abundant waste, and has the potential of producing the maximum amount of ethanol among these four mentioned agricultural wastes.

Thermochemical Conversion

Thermochemical conversion may of three types: Pyrolysis, gasification, and combustion, as discussed in detail below.

Pyrolysis

Pyrolysis is a thermochemical conversion process in which volatile component of a solid biomass is vaporized by heating without presence of any oxidizing agent and leaves behind a residue consisting of char and ash. The condensable part of pyrolysis vapor is collected as a liquid after condensation, which is commonly known as biooil and the remaining noncondensable gases leaves the system can be used as fuel gas. The main objective of pyrolysis process is to produce as much liquid fuel from biomass s possible. Liquid fuel has a number of advantages over gaseous fuel like storage, transportation, and versatility in application such as IC engine, boilers, turbines, etc. The product distribution of the biooil depends upon the amount of cellulose, hemicellulose, and lignin present in biomass (Mythili *et al.*, 2013). It was observed from the literature that the decomposition of hemicelluloses,

cellulose and lignin occur at 220–315°C, 314–400°C, and 160–900°C respectively. In addition to the quantitative composition of cellulose, hemicelluloses, and lignin in biomass, the interaction between these components also determines the product distribution in the biooil. The nature of pyrolysis product depending upon the operating conditions used like temperature, heating rate, residence time, pressure, catalysts etc. For example, high temperatures and short residence times favor the formation of condensable products, while high temperatures and longer residence times favor the formation of noncondensable gaseous products. Depending on the operating conditions, the pyrolysis process can be classified into three categories: Fast pyrolysis, intermediate pyrolysis, and slow pyrolysis (Dhyani and Bhaskar, 2018). Recently, pyrolysis of biomass has gained more attention compared with combustion and gasification because of its above-mentioned advantages. Different types of reactors are used by the researchers to carry out different pyrolysis processes, such as fixed bed reactor, fluidized bed reactor, rotating cone reactor, vacuum reactor, auger reactor, etc. However, it is still at an early stage in development and more research and development works are needed to overcome the technical and economic issues to compete with traditional fossil fuel-based techniques.

Fast pyrolysis

Fast pyrolysis is an advanced process where biomass is heated rapidly in controlled temperature to result in high yields of biooil. In fast pyrolysis, the production of biooil can be obtained as high as 80 wt% on dry feed. The essential features of a fast pyrolysis process are given below.

- Very high heating and heat transfer rate are required.
- Nearly ground biomass feed is needed for fast conversion.
- Carefully controlled temperature.
- Rapid cooling of the pyrolysis vapors to maximize the biooil production.

The typical heating rate in fast pyrolysis varies from 100 to 1000°C/s and the residence time is 1–2 s. It is carried out at moderate temperature of 450–600°C. It is reported in the literature that the liquid yield as high as 75% on dry feed basis can be obtained in fast pyrolysis of wood (Bridgwater *et al.*, 2009).

Intermediate pyrolysis

Intermediate pyrolysis is similar to fast pyrolysis process but has a bit longer residence time (10–20 s). The main objective of intermediate pyrolysis is to use more hard-to-handle feedstock such as sewage sludge, grass, or algae. Intermediate pyrolysis offers working conditions preventing formation of high molecular tars and offers dry and brittle chars suitable for fertilization or combustion. In this type of processing, larger sized feedstock may be used without milling. This offers the opportunity to separate char from vapors easily.

Slow pyrolysis

In slow pyrolysis, the heating rate is very slow and the process is carried out for relatively longer residence time. Slow pyrolysis is carried out in the temperature range from 400 to 800°C. Heating rates as low as 0.1–2°C, have been reported (Antal and Grønli, 2003). The slow pyrolysis process may continue from few hours to a number of days. Here the main objective is to produce biochar from biomass. Generally, vapor is not condensed in this process but it can be used for providing heat required for the pyrolysis process through combustion. Biomass with large particle size can be used provided the feeding system can handle it. Slow pyrolysis process is more tolerant to the moisture content in biomass compared with fast pyrolysis and intermediate pyrolysis process.

Therefore, higher temperatures and longer residence time promote gas and vapor production, while higher char yield is obtained at lower temperatures and slower heating rates. The product slate is similar for each feedstock at a given temperature, although the yields of gas, pyrolysis oil, and char can be quite different. Table 1 shows the comparison between three different pyrolysis processes.

Gasification

Biomass gasification is the thermochemical conversion of solid biomass into the fuel gas, which contains mainly hydrogen, carbon monoxide, carbon dioxide, methane, and nitrogen. A limited supply of oxygen, air, steam, or a combination of these serves as gasifying agent. Fuel gas produced from biomass gasification can be used in boiler, gas engine, gas turbine, etc. In general, three

Table 1 Comparison of fast pyrolysis, intermediate pyrolysis, and slow pyrolysis

Parameters	Fast pyrolysis	Intermediate pyrolysis	Slow pyrolysis
Heating rate	> 100°C/s	> 10°C/min and < 100°C/min	< 10°C/min
Operating Temperature	~ 500°C	~ 500°C	~ 400°C
Residence time	1–2 s	10–20 s	Hours to days
Biooil	75%	50%	30%
Biochar	12%	20%	35%
Fuel gas	13%	30%	35%

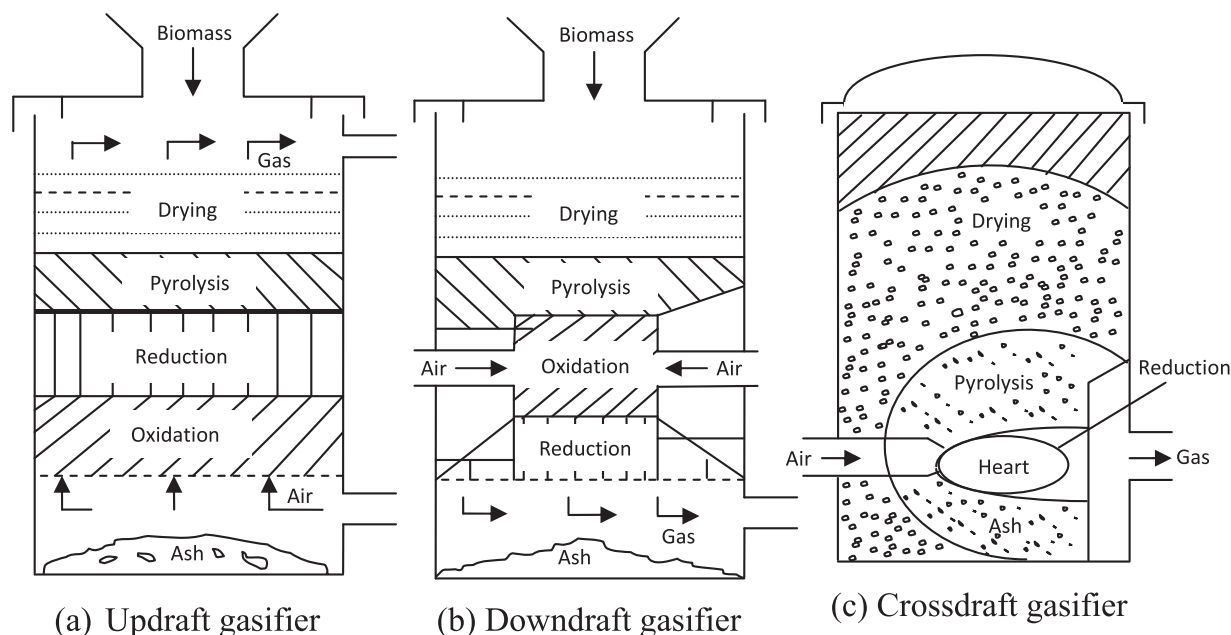


Fig. 4 Schematic diagram of fixed bed gasifiers.

different gasification technologies are used for biomass gasification: Fixed bed, fluidized bed, and entrained bed (Loha *et al.*, 2018a,b). The principle of operation, merits, and demerits of different types of gasifiers are described below.

Fixed bed gasification:

Depending upon the way the solid fuel and the gas interact, the fixed bed gasifiers are classified into three types: Updraft, downdraft, and crossdraft gasifiers. Fig. 4 shows the schematic diagram of fixed bed gasifiers. In an updraft gasifier (Fig. 4(a)) air passes through the biomass from the bottom and the product gas comes out from the gasifier at the top. As the oxidant is supplied at the bottom, the exothermic combustion reactions take place there. Therefore, the highest temperature is at the bottom for updraft gasifier. From the bottom to the top the temperature decreases. Hence, the fuel enters at the top and there is first a drying zone, then the pyrolysis zone, reduction zone, and finally the oxidation zone, before the remaining ash is removed from the reactor (Basu, 2006). The produced gas moves upward through the fixed bed of solids. It transports the heat from the hot combustion region to the inlet region of the solids. Thus it cools down so that the main problem for the updraft gasifier is the high tar content in the produced gas, as the tar once formed is not cracked in the reactor.

In comparison, the product gas from a downdraft gasifier has the lowest tar content received. The fuel enters the reactor again at the top and moves downward. The gas is added some way down the fuel path where the reactor cross section is narrowed (Fig. 4(b)). It moves concurrent with the particles downward to the grate at the bottom where the product gas and also the ash are retained. So not only the fuel but also the pyrolysis gas produced passes the oxidation zone. Therefore, the tars can be cracked and the tar content of the product gas is very low (Basu, 2006). The drawback of the downdraft gasifier is the high demand on the fuel particle size and carbon conversion is lower than in other gasifier types.

In crossdraft gasifier (Fig. 4(c)), the fuel is introduced from the top and the air from the side of the gasifier. The fuel moves down as it gets dried, devolatilized, pyrolyzed, and finally gasified, while the air exits from opposite side of the unit. The exit for the gas is more or less at the same level as that of entrance. The combustion and gasification zone is located near the entrance of the air while the drying and pyrolysis zones are at a higher level than the entrance and exit. Although the crossdraft gasifier has certain advantages over updraft and downdraft gasifier, it poses serious limitations. The disadvantages such as high exit gas temperature, poor CO₂ reduction, and high gas velocity are the consequence of the design. Unlike downdraft and updraft gasifiers, the ash bin, fire, and reduction zone in crossdraft gasifiers are separated. These design characteristics limit the type of fuel for operation to low ash fuels such as wood, charcoal, and coke. The load following ability of crossdraft gasifier is quite good due to the concentrated partial zone, which operates at temperatures up to 2000°C. Start up time (5–10 min) is much faster than that of downdraft and updraft units. The relatively higher temperature in crossdraft gasifiers has an obvious effect on gas composition such as high carbon monoxide, and low hydrogen and methane content when dry fuel such as charcoal is used.

Fluidized bed gasification:

Fluidization is the operation by which the solid particles are transformed into a fluid like state by the application of gas. In a fluidized bed gasifier, the oxidant also acts as the fluidizing agent to fluidize the inert solid particles and biomass mixture. The distinct advantages of fluidized bed over fixed bed are uniform temperature distribution in the reactor due to excellent gas–solid

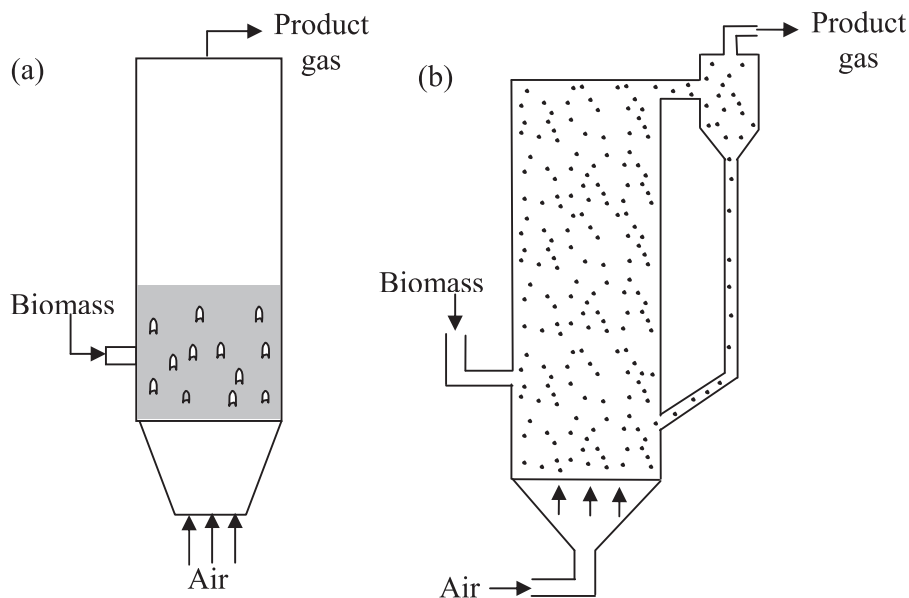


Fig. 5 Schematic diagram of (a) bubbling fluidized bed gasifier and (b) circulating fluidized bed gasifier.

mixing, high carbon conversion with low tar production and flexibility in terms of fuel type, feed rate, particle size, and moisture content (Kunii and Levenspiel, 1991). Typical capacity of the fixed bed gasifier is 50–500 kW. However, due to the above-mentioned features, scale-up and operation of the fluidized bed gasifiers for electricity generation in MW scale is much easier. There are two main types of fluidized bed gasification systems: Bubbling fluidized bed and circulating fluidized bed. Fig. 5 presents the schematic diagram of bubbling and circulating fluidized bed gasifiers.

In a typical gasifier, when the gas velocity is increased, a situation is reached when the particles are just suspended in the upward flowing gas. At this situation the frictional force between a particle and fluid counterbalance the weight of particle, the vertical component of the compressive force between adjacent particles disappears, and the pressure drop through any section of the bed equals the weight of fluid and particles in that section. At this instance, the bed is considered to be at minimum fluidization. With an increase in velocity beyond minimum fluidization, large instabilities with bubbling and channeling of the gas are observed. At higher flow rates agitation becomes more violent and the movement of solids becomes more vigorous. However, the bed does not expand much beyond its volume at minimum fluidization. Such a bed is called bubbling fluidized bed (Loha, 2013). Fig. 5(a) shows the schematic of a bubbling fluidized bed reactor. In a bubbling fluidized bed, the gas velocity is low. The gas moves through the bed in the void and in bubbles with higher velocity. Some of the particles are entrained into the freeboard along with these fast moving bubbles, and some fly ash is transported with the product gas and leaves the reactor at the top. But most of the entrained particles fall back and can be continuously removed from the fluidized bed with the remaining ash at the bottom. When the gas velocity is increased further, the solids will be distributed across the whole riser height and entrained by the gas at the riser top. The particles are separated from the gas in a cyclone, and are returned to the fluid bed near the bottom. Then it becomes a circulating fluidized bed (Fig. 5(b)). The advantage of circulating fluidized beds is mainly due to the longer overall residence time. The solids circulate in the outer loop, going up in the riser, leaving at the top, going down in the return leg, and entering the riser again at the bottom. But there is also internal circulation of the solids, which fall back from the higher region of the riser and move downwards at the riser wall. The tar content from fluidized bed gasifier is less than that from fixed bed updraft gasifier, but higher compared with the tar content from fixed bed downdraft gasifier.

Entrained flow gasification:

In entrained flow gasifiers, the gas velocity is even higher than in circulating fluidized bed (Ghassemi *et al.*, 2016). Fig. 6 shows the schematic diagram of an entrained flow gasifier. No inert bed material is used. Normally, the feedstock must be in the form of very fine particles (100–400 μm). The reaction temperature is high (about 1200–1500°C) depending on whether air or oxygen is used as oxidant. Therefore, the product gas has a low content of tars and condensable gases. However, there can be problems with ash melting and reactor materials. Entrained flow gasifiers are more commonly used for fossil fuels like coal, refinery waste, etc. Their use for biomass gasification is rather limited, as it requires the fuel particles to be very fine.

Combustion

Biomass can be combusted alone in a dedicated plant, which is called direct combustion, or it can be cocombusted with coal in existing coal-based power plants, that is, cofiring, as discussed below.

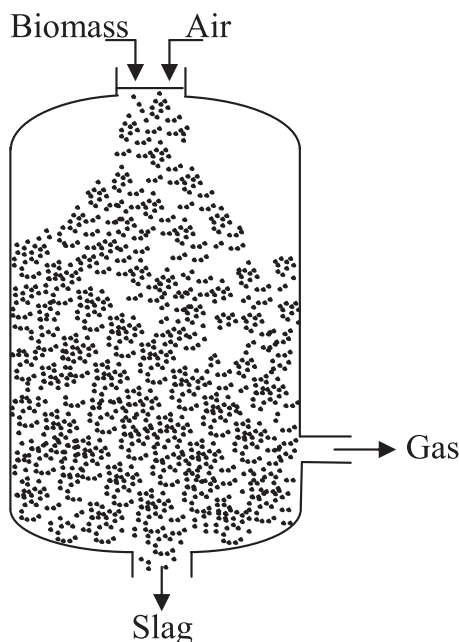


Fig. 6 Schematic diagram of entrained flow gasifier.

Direct combustion:

The combustion of solid biomass is fully established and widely used in biomass applications. The combustion properties of biomass are well understood. The most popular combustors for 100% biomass applications are stoker-fired or fluidized bed designs. In stoker-fired combustors the feed burns as it moves through the furnace while resting on a stationary or moving grate. Fluidized bed designs burn the feed in a turbulent bed of inert material that is fluidized by combustion air flowing through it from underneath. Although grate-fired combustors are the form of older biomass-fired plant, fluidized bed combustors are rapidly becoming the preferred technology for biomass combustion because of their high heat transfer rate, fuel flexibility, and low NO_x emissions. Direct biomass combustion-based plants are mostly used for small-scale application in many industries as cogeneration units. But, large-scale dedicated biomass combustion plants are still not popular because of the constraint of continuous supply of the enormous amounts of biomass required for such large-scale dedicated biomass combustion plants. The availability of biomass resources is generally distributed and the transportation cost for such enormous amounts of biomass to a centralized location where the plant is located becomes the major factor. Therefore, instead of dedicated biomass plant, cofiring of biomass to the existing power plants has emerged as a more economical short-term option for biomass utilization.

Cofiring:

Cofiring is the process of burning two different types of fuel simultaneously to generate heat or electricity. Cofiring of biomass in coal-based power plants is generally done to get environmental benefit by using renewable energy without significant cost involvement. Compared with dedicated biomass-based plants, the addition of biomass to the high efficiency coal-fired power plants can greatly increase the efficiency of utilizing biomass (Baxter, 2005). Besides, the cost of retrofitting an existing coal-fired power plant for biomass cofiring is significantly lower than building a new dedicated biomass-based power plant (Spliethoff and Hein, 1998). Recently, the interest in cofiring has grown due to increasing concern about global warming and GHG emissions leading to new policies on energy and the environment to reduce emissions. Cofiring is regarded as the most attractive short-term option for replacing coal used for power generation with renewable fuels at lower costs to result in direct decrease of greenhouse gas emissions. There are many advantages of cofiring of biomass in coal-based power plants and some of the important advantages are discussed below (Verma *et al.*, 2017).

- Cofiring of biomass is the easiest way to increase the use of biomass for power generation.
- Cofiring of biomass to the existing coal-fired power plants can be done with little modification which implies little investment cost.
- Opportunity of using different biomass materials with coal, which can diversify the fuel portfolio in existing coal-fired power plants.
- In case of coal shortage, import substitution with biomass will significantly improve the economy of the nation.
- It will lower the CO₂ emission by saving the fossil fuels.
- It will also reduce other airborne emission like NO_x and SO_x because most of the biomass contains less nitrogen and sulfur.

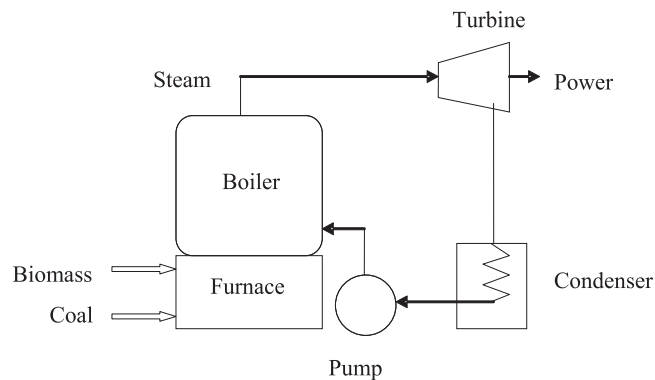


Fig. 7 Schematic diagram of direct cofiring.

- It will provide energy security to the nation by producing electricity from locally available fuel like biomass.
- Growing of biomass as energy crops will add value to barren lands, improve the landscapes, conserve soil resources, and reduce the need for water and fertilizers.

Cofiring of biomass is more cost-effective in combined heat and power (CHP) plants, which generate electricity and useful thermal energy. CHP, also known as cogeneration, is often used in industrial facilities where there is specific demand for both heat and power. The economics of biomass cofiring is increased when it is used in CHP plants because of higher overall efficiency in CHP compared with normal power plants. Cofiring of biomass to the existing coal-based power plants yields negative CO₂ emission to the atmosphere when it is combined with carbon capture and storage technology. Cofiring of biomass to the coal-fired power plants can be done in three different ways. If biomass is combusted directly with coal then it is called direct cofiring. In direct cofiring, combustion of coal and biomass takes place simultaneously at the same combustion chamber or furnace.

Direct cofiring:

Direct cofiring can be done either by premixing coal and biomass and injecting the mixture to the coal handling system or directly injecting them (without physical mixing) into the pulverize coal firing system. In case of premixing, coal and biomass can be mixed either before milling or after milling. In case of direct injection, coal and biomass are burned either using separate burners or combined burners depending principally on the biomass fuel characteristics. Direct cofiring is the simplest and least expensive method of cofiring. Hence, it is the most commonly applied cofiring configuration reported so far. However, the direct cofiring systems are more sensitive to variations in fuel quality and heterogeneity. **Fig. 7** shows the schematic diagram of direct cofiring system.

Indirect cofiring:

When biomass is converted to fuel gas in a gasifier and subsequently the fuel gas is combusted in the coal furnace then it is called indirect cofiring. It is relatively complex in arrangement and expensive compared with the direct cofiring system. Indirect cofiring can be carried out in different ways. Biomass may be burned in a separate system and the flue gas is injected to the original coal boiler or burning coal and biomass in separate systems and both the systems couple their heating fluid circuits with separate exhaust gas treatment or biomass may be converted into fuel gas in a gasifier and then the fuel gas passed through the coal boiler. Indirect cofiring reduces the problems associated with corrosion, fouling, and slagging, as the biomass is not fed directly to the furnace. Therefore, the indirect cofiring system has the advantage of better fuel flexibility than direct cofiring and it also allows larger amount of biomass cofiring than the direct system. **Fig. 8** shows the schematic diagram of an indirect cofiring system.

Parallel cofiring:

If biomass and coal are combusted in separate furnaces and generate steam separately then it is called parallel cofiring. In parallel cofiring, separate combustion chambers and boilers are used for coal and biomass. Steam produced by both the boilers are fed into the main power plant system where steam is upgraded to higher temperatures and pressures to give higher energy conversion efficiencies. Therefore, the fuel preparation and feeding system is physically independent here. Parallel cofiring system offers more opportunity for using higher percentages of biomass fuels compared with the direct and the indirect cofiring systems (Thompson, 2006). Here, the maximum amount of energy that can be generated from biomass will depend on the downstream infrastructure of the existing plant such as for steam turbines. Like indirect cofiring, biomass ash is separated from coal ash in parallel cofiring, which allows using a wide variety of biomass. However, the parallel cofiring system is much more expensive than direct and indirect cofiring systems because of additional infrastructure requirements. Parallel cofiring technique is mostly used in the paper and pulp industries. The schematic diagram of parallel cofiring is shown in **Fig. 9**.

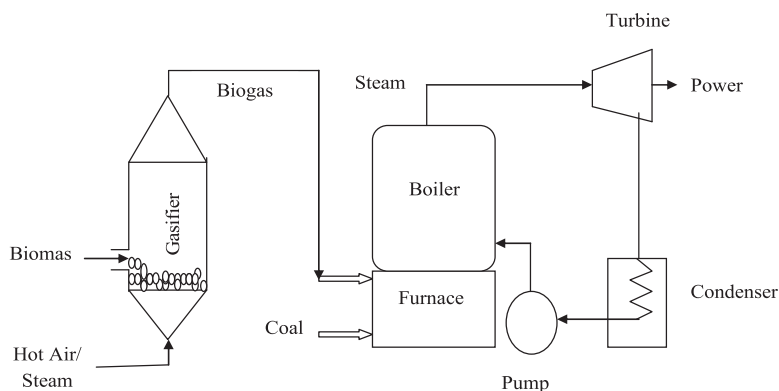


Fig. 8 Schematic diagram of indirect cofiring.

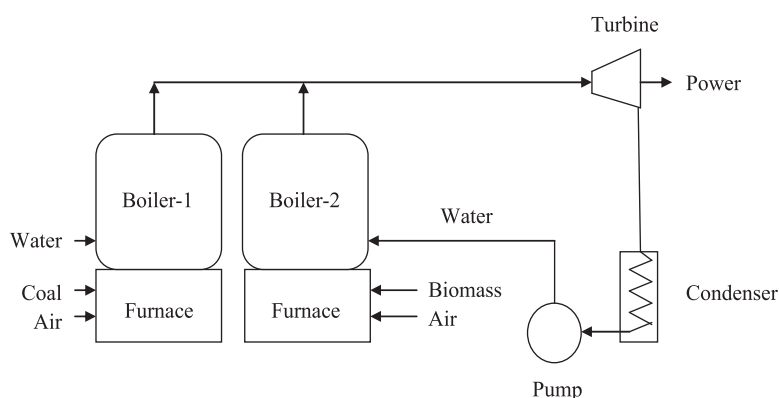


Fig. 9 Schematic diagram of parallel cofiring.

Physical Conversion

In the physical conversion process, oil is extracted mechanically by squeezing the seeds of various biomass seeds. The process produces not only oil but also a solid residue called deoiled cake, which can be used for animal fodder. The oil extracted is further processed by reacting with alcohol using a process called esterification to obtain biodiesel. Biodiesel can be a potential alternative to petroleum diesel. It has a number of advantages, for example, it is nontoxic, it degrades four times faster than diesel, it has higher flash point, it contains no sulfur, etc. Emissions of (PAH) compounds are substantially lower with biodiesel. Initially, biodiesel is produced from edible oils in most of countries. But, converting edible oils into biodiesel means converting food resources into automotive fuels. Therefore, it is envisaged that large-scale production of biodiesel from edible oils may bring global imbalance to the food supply and demand market. Therefore, the focus has shifted from edible oil to nonedible seeds like *Jatropha curcas*, *Madhuca indica*, *Pongamia pinnata*, etc. But, the expansion of nonedible oil crop plantations for biodiesel production on a large scale may increase deforestation. Moreover, it may also happen that the land that would otherwise have been used to grow food will be used to grow fuel and this trend is already being observed in many parts of the world. In that situation, biodiesel production from animal fat or waste oil from restaurants may be a good option. However, these limited resources may not meet the increasing demand of biodiesel. Recently, the research and development throughout the world have been focused to generate biodiesel from lignocellulosic biomass residues.

Properties of Biomass Affecting the Conversion Process

Properties of biomass are important for converting biomass into other forms like fuels, heat, and power. These properties include bulk density, particle density, particle size, moisture content, volatiles content, fixed carbon, ash content, and heating value.

Biomass materials are mostly available in loose form. Therefore, the bulk density of biomass is an important parameter for designing the biomass handling system in biomass processing unit. Bulk density is defined as the weight of biomass material in bulk per unit volume. The bulk density of loose biomass varies from 60 to 150 kg/m³. The nonuniform particle size and shape of

the raw biomass materials in loose form have very low bulk density, which leads to high costs for transportation, storage, and feeding into the processing plant. Besides, if biomass materials in their loose form are converted to energy, they will create more pollution by emitting fine particulate matter to the atmosphere. Therefore, loose biomass materials are generally densified by making briquettes before using for conversion. Since briquettes are created by compressing loose biomass materials, they are denser, harder, and more compact. The bulk density of briquettes varies from 350 to 400 kg/m³. Therefore, compacting biomass into briquettes can reduce the volume of biomass up to 70%, thus storage, transportation, and handling costs is reduced by almost 7 times, making it much easier to store and transport than loose biomass. These briquettes can readily be piled up in several heaps. They are likewise clean to handle and to be packed into bags. Thus, biomass briquettes offer a more concentrated form of energy. Along with the compactness, the heating value is increased in briquettes. Briquettes can relatively produce more intense energy than other fuel. They have longer shelf-life due to lower moisture content. Uniform physical property of briquettes leads to more efficient energy conversion.

Particle density is defined as the mass of an individual particle over its volume. Particle density for a group of particles is the ratio between mass of all particles and the volume occupied by all particles (excluding the pore space volume).

Numerous biomass materials available for energy conversion have irregular shapes. Some are of a needle shape with high aspect ratio and the finely ground particles have a round shape with aspect ratio close to 1. Therefore, the particle size range of biomass materials available from nature is huge, and may vary from microns to centimeters or even meters. However, depending on the requirement of different processes they are converted into either powder or granules or blocks.

Biomass materials generally contain a higher amount of moisture, which affects their conversion process. Higher amount of moisture in biomass materials increases the cost of production in any biomass conversion process. Therefore, it needs to be dried properly before being used for any conversion process.

Volatile matter is the amount of the gases formed except water vapor while biomass material is heated in an oxygen-free environment. The volatile matter from biomass generally contains hydrogen, carbon monoxide, carbon dioxide, hydrocarbons, and nitrogen dioxide. After realizing the volatile matter, the remaining solid combustible residue is called the fixed carbon and remaining noncombustible residue is called ash. The quality of biomass for thermochemical conversion depends upon the amount of volatile matter, fixed carbon, and ash contained in the biomass. Volatile matter has the opposite trend of fixed carbon. Generally, biomass contains higher amount of volatile matter and lower amount of fixed carbon compared with coal. The ash content in biomass has special significance because it causes lots of operational problems during biomass combustion. For example, silicon from biomass ash is the main contributor to wear. Potassium and calcium cause fouling of heat exchangers and slagging in the bottom of the furnace. This requires shutting down the units regularly, reducing the operating time of the production units and also increasing the maintenance cost. The calorific value is the amount of heat released from unit mass of biomass while it is burned with oxygen. It is the indicator that determines the amount of energy that can be recovered during its thermochemical conversion. The calorific value depends upon the amount of combustible present and different elements present within the combustible in biomass. [Table 2](#) shows the ultimate and proximate analysis of different biomass materials.

Effect on Global Warming by Using Biomass as Energy Source

Coal, oil, and natural gas are the three different forms of fossil fuels that are widely used in the electricity generation, transportation, and chemical industries. Large-scale use of fossil fuels started around the Industrial Revolution. Today, these are the most

Table 2 Proximate and ultimate analysis of different biomass materials

Fuel	Proximate analysis				Ultimate analysis				
	Volatiles	Fixed carbon	Moisture	Ash	C	H	O	N	S
Pine	71.50	16.00	12.0	0.50	51.60	4.90	42.60	0.90	n.d.
Holm-oak	70.20	17.80	9.50	2.40	51.10	5.30	42.70	0.90	n.d.
Eucalyptus	74.80	13.90	10.6	0.70	52.80	6.40	40.40	0.40	n.d.
Wheat straw	67.77	14.54	4.13	13.56	38.09	6.15	37.31	0.70	0.06
Sawdust	74.60	15.82	6.11	3.47	45.76	6.74	37.85	0.07	n.d.
Rice husk	55.54	14.99	9.95	19.52	49.07	3.79	46.42	0.63	0.09
Bagasse	65.87	17.43	13.05	3.65	46.10	5.26	44.25	0.19	4.20
Groundnut shell	68.96	15.52	10.12	5.40	52.54	5.37	41.01	0.59	0.49
Peanut shell	67.48	17.99	8.84	4.69	43.53	6.54	34.04	2.24	0.12
Palm kernel shell	67.13	17.19	7.37	8.31	51.63	5.52	40.91	1.89	0.05
Coconut shell	29.19	25.18	4.66	40.97	45.24	5.04	48.20	1.46	0.06

Note: Loha, C., Karmakar, M.K., De, S., Chatterjee, P.K., 2018a. Gasifiers: Types, operational principles and commercial forms, Chapter 1.3. In: Coal and Biomass Gasification. Singapore: Springer Nature, pp. 63–91.

Loha, C., Chattopadhyay, H., Chatterjee P.K., Gautam, M., 2018b. Co-firing of biomass to reduce CO₂ emission. Encyclopedia of Renewable and Sustainable Materials. Elsevier, doi:10.1016/B978-0-12-803581-8.11006-9.

widely used sources of energy available for the use of both personal as well as commercial purposes. To date, almost three-fourths of the demands of the energy in the world is fulfilled by fossil fuels. Combustion of these fossil fuels emits gases, mainly carbon dioxide (CO₂), sulfur oxides (SO_x), nitrogen oxides (NO_x), chlorofluorocarbons (CFCs), and other trace gases. Most of the gases emitted during combustion, known as greenhouse gases, are considered to be detrimental to the Earth's atmosphere as these gases absorb radiation within the thermal infrared range and then reradiate it back to the surface resulting in an elevation of Earth's surface temperature, which is known as global warming. Among different gases, the gas considered to be contributing the most to the GHE is CO₂ because of two factors: (1) CO₂ represent the largest emissions of all global anthropogenic GHG emissions (around 75% of all GHGs), and (2) CO₂ has a very high residence time in the atmosphere. Hence, CO₂ is the most important anthropogenic greenhouse gases of our concern. The global atmospheric concentration of CO₂ has increased to 408 ppm in 2018 (NOAA, 2018). The concentration of CO₂ increased every year since scientists started measuring the slopes of the Mauna Loa volcano more than five decades ago. The rate of increase has accelerated from about 0.7 ppm per year in the late 1950s to 2.1 ppm per year during the last decade and now the rate of increase is 100 times faster than the increase that occurred when the last ice age ended. Therefore, it is felt worldwide that mitigation of GHGs is essential as soon as possible. Use of biomass as an energy source will definitely have a positive effect on environment because of its low CO₂ and SO₂ emissions. CO₂ is the major contributor to GHG emission and SO₂ is the main reason for acid rain. Hence, there is a worldwide trend toward increasing the use of biomass as an energy source in different ways. Using biomass as fuel for energy generation through different routes has many advantages. For example, biomass combustion or cofiring with coal is an attractive option with a relatively low need for additional investments when used in the power generation sector. The use of biomass in power generation instead of fossil fuels will result in significant decrease in the release of particulate matters to the atmosphere because of low ash content in biomass (2%–6%) compared with coal (20%–50%). Sulfur emission is also reduced compared with fossil fuel because of low sulfur content in biomass. Utilizing biomass wastes for biogas production through anaerobic digestion or production of ethanol via fermentation prevents the accumulation of these wastes and eliminates their cause of serious environmental concerns. The use of animal dung to produce biogas by controlled anaerobic digestion can solve the environmental issues concerning GHGs, nitrogen, and unpleasant odors. It also helps in intensifying the recycling of nutrients within agriculture. Further, biogas has lower carbon to hydrogen ratio and it is a better fuel than these wastes and is a much cleaner, odorless, and smokeless fuel that can be used for household cooking, heating, and lighting requirements. Similarly, ethanol produced from biomass fermentation can serve as the cleanest liquid fuel alternative to fossil fuels. In gasification, syngas is produced from biomass, and can be used to run internal combustion engines, as a substitute for furnace oil in direct heat applications, and to produce methanol – An extremely attractive chemical that is useful both as fuel for heat engines as well as chemical feedstock for industries.

However, to precisely calculate the net CO₂ emission from biomass energy, it is necessary to monitor and observe the whole carbon cycle caused by the biomass energy development and consumption. For example, deforestation or destroying local vegetation to grow crops and thereafter producing energy from those crops will result in larger net CO₂ emission than the fossil fuel. Nevertheless, utilizing locally available biomass or agricultural waste or forest residues for generating bioenergy will reduce CO₂ emission.

Potential of Biomass to Meet the Global Bioenergy Demand

Global production of biomass and biofuel is growing rapidly due to the increasing price of fossil fuels, concerns over greenhouse gas emission and carbon footprint, and considerations regarding the security and diversification of energy supply. The ways biomass is currently used will not continue for long and are expected to change significantly in the next few years. At present, traditional methods of space heating and cooking, such as burning firewood, account for two-thirds of total biomass use. But, in the near future, this would give way to modern biomass consumption, including substantially larger shares for power and transport applications. The global biomass potential is sufficient to meet the growing demand. It is estimated that the total biomass supply worldwide in 2030 could range from 97 to 147 EJ/yr among which about 38%–40% would originate from agricultural residues and waste and the remaining supply potential is shared between energy crops and forest products, including forestry residues (IRENA, 2014). Recently, there have been a number of studies performed to estimate the future demand and supply of biomass. The availability and expected future potential of major biomass producing countries are discussed below. Biomass is one of the largest renewable energy resources in sub-Saharan Africa (SSA). About 90% people in SSA use biomass, such as wood or residues, for cooking and heating which means about 265 million tons of wood equivalent of energy is required for cooking. The estimated forest residues available in SSA comprise about 444 million tons and the crop residues comprise about 140 million tons. Therefore, the power generation potential by using 30% of agroresidues and 10% of forest residues is 5000 MW and 10,000 MW respectively (Stecher *et al.*, 2013). In the United States, it is estimated that the demand for biomass in 2030 will be 100 million tons if the state Renewable Portfolio Standards (RPSs) are implemented and it will reach to 262 million tons if the federal Renewable Fuel Standard (RFS) is implemented. The crop and forest residues could meet more than 70% of the demand under the policy scenarios considered above. The remaining supply of biomass can be achieved by converting 0.7 million hectares of land under the RPS and 4.3 million hectares of land under the RFS (Oliver and Khanna, 2017). A study on the potential availability of biomass resources in Brazil shows that it produces around 1500 million tons of biomass and it is expected to increase to 2500 million tons by 2030. The bioenergy potential from Brazilian Resource is 8902.2 EJ, which will increase to 17,299 EJ by 2030 (Welfle, 2017). Biomass is a significant source of energy in China, particularly in rural areas. In China, the total amount of annual residue biomass, averaged over 2003–2007, is around 15.519 EJ among which 10.818 EJ comes

from agriculture residues (70%) and 4.701 EJ from forestry residues (30%). Total 12.693 EJ of biomass is available for energy production, with 66% derived from agricultural residue and 34% from forestry residue. Most of the available residue comes from south central China (3.347 EJ), east China (2.862 EJ) and southwest China (2.229 EJ) (Gao *et al.*, 2015). India is also blessed with substantial biomass resources. The estimated annual biomass production in India is 500 million tons, which can generate around 17,500 MW power. In addition, around 120–150 million tons of surplus biomass can be collected from waste of various industries, which can generate another 5000 MW power (Loha, 2013). A broad assessment of the potential availability of biomass in Australia reveals that approximately 80 million tons/yr of biomass are available with the major contribution from crop stubble (27.7 million tons/yr), grasses (19.7 million tons/yr), and forest plantations (10.9 million tons/yr) (Crawford *et al.*, 2016). It is also estimated that over the next 20–40 years, total potentially available biomass could increase to 100–115 million tons per year, with new plantings of short-rotation trees being the major source of the increase. In the European region, the bioenergy potential from dedicated bioenergy crops varies between 1.7 and 12.8 EJ/yr. In addition, agricultural residues and forestry residues can potentially add 3.1–3.9 EJ/yr and 1.4–5.4 EJ/yr respectively (De-Wit and Faaij, 2010). However, large variation exists in biomass production potential and costs. Regions that have high potential and low costs are large parts of Poland, the Baltic States, Romania, Bulgaria, and Ukraine. On the other hand, regions like Western Europe, France, Spain, and Italy are moderately attractive following the low cost high potential criterion. Biomass could also play a major role in Russia to increase its renewable energy share by 2030. Renewable energy consumption could rise from 3.6% of the current energy mix to more than 11% by 2030. It is estimated that the demand of bioenergy in Russia could reach 2.4 EJ by 2030 whereas the country has the potential to supply up to 14 EJ per year from biomass feedstocks (IRENA, 2014).

Conclusion

It is observed from the above study that biomass has the significant potential of mitigating greenhouse gases and carbon footprints if it is used scientifically. There are three different processes by which biomass can be converted into useful energy, namely biochemical, thermochemical, and physical conversion. All the conversion processes have their merits and demerits. Biochemical processes have the advantage of low energy requirement for operation. But the main drawback is that the biochemical processes are very slow. Whereas, thermochemical conversion processes are very fast. Any type of biomass can undergo thermochemical processes whereas only selected biomass materials can be processed through biochemical and physical routes. Hence, thermochemical routes of biomass conversion are much more attractive. Among thermochemical processes, cofiring of biomass with the existing coal-based power plants is the most promising near-term application of biomass. On the other hand, biomass gasification with sophisticated downstream application like gas turbine/fuel cell and biomass pyrolysis with upgradation of biooil offer the greatest potential for developing countries. Therefore, different types of gasifiers are developed and used for gasification of biomass. However, under present conditions, economic factors seem to provide the main constraint for wider application of biomass gasification. In many situations where the price of petroleum fuels is high or supplies are unreliable, the biomass gasification can provide an economically viable system, provided the suitable biomass feedstock is easily available.

See also: Traditional Biomass: A Replacement for Petro-Fuels

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Renewable Electricity Generation – Effect on GHG Emission

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Introduction

Energy is the basic need for human civilization. Men started harnessing energy from ancient days by burning dried leaves, logs of wood etc. Heat generated was mostly used for roasting meat. Conversion of heat to work or movement subsequently transformed the human civilization to a new dimension. Men began to use energy for locomotion. Subsequently the industrial revolution happened. It was the age of automation when the human power or the animal power was replaced by the “power of machines”. Electricity is the most convenient and useful form of secondary energy in the modern world. It can be transported over a long distance with high efficiency and then may be converted into all other forms of energy with suitable conversion technologies. Moreover, the electrical gadgets can be controlled more precisely than the thermal gadgets. However, being a secondary form of energy, it has to be generated from some other naturally available energy resources, called primary energy. Demand for electricity is ever increasing with increased population and improvement of living standard. From the beginning till date electricity is mostly generated from the combustion of fossil fuels like coal, oil, gas etc. These fossil fuels were created by conversion of submerged biomass under the ground over a long period. These are all basically hydrocarbons in different forms with some other combustible and incombustible materials. The combustible parts of these hydrocarbons are both hydrogen and carbon. Heat energy is released from these hydrocarbons through oxidation of both of these. For maximum energy release from these fuels, complete combustion of both hydrogen and carbon is desired. Hydrogen is converted to water vapor during its complete combustion which has almost no effect on the environment and the living ecosystem as a whole. However, the product of complete combustion of carbon of the fossil fuel is carbon dioxide (CO_2) which is released to the atmosphere from the fossil fuels stored under the ground in this process. Like many other gases, CO_2 in the atmosphere has a special effect of reflecting back the emitted radiation from the earth and thus retaining more heat from the sun in the atmosphere. This leads to the rise in average temperature of the earth's atmosphere. As the effect is similar to trapping of heat in greenhouse during winter, this effect is called the greenhouse effect and CO_2 is one of such greenhouse gases responsible for this effect. As electricity has been generated over centuries using mostly fossil fuels, CO_2 concentration in the atmosphere has increased in this process of power generation from fossil fuels, leading to observed increase in average atmospheric temperature. This is formally called ‘global warming’. It has several disastrous effects on the environment and the most critical among those is the rise of sea level due to melting of polar ice. In fact, global warming is considered to be the most critical threat to human survival including many other species on the earth. As this anthropogenic CO_2 emission is leading to a possible destruction of human civilization and even living on earth, several measures are adopted internationally beyond political boundaries to fight this menace. Intergovernmental Panel on Climate Change (IPCC) assess the effects of global warming regularly, suggest measures to be adopted and possible future scenario with different measures adopted through international negotiations in different conventions. Different conventions in this regard initially suggested possible measures to be adopted to mitigate climate change only. However, over the years it was realized that more meaningful measures would be towards overall ‘sustainable development’ rather than addressing climate change only as an isolated phenomenon. According to the report of the United Nations’ Brundtland Commission, sustainable development is defined to be “the development that meets the demand of the present generation without compromising the need of the future generations.” Supplying ever increasing need for electricity is one of the critical challenges for sustainable development. Presently, the whole world is mostly dependent on fossil fuels like coal, oil, natural gas etc for energy generation. Presently 38% of the world's primary energy consumption is from oil followed by coal (24%) and the rest comes from natural gas, nuclear and renewable (Tester *et al.*, 2006). The fossil fuels emit carbon dioxide and other greenhouse gases in the process of combustion as shown in Fig. 1. The generation of power is mostly dominated by coal and oil. The share of each type of fuel in the global energy mix is shown in Fig. 2. Presently, the power sector is the single largest sector for the emission of GHG amongst all the sectors owing to the maximum use of these fossil fuels. On the other hand, electricity from the renewable resources generally does not generate greenhouse gases during operation, though installation and final disposal of some such plants may cause some GHG emission. So, more use of renewable electricity will definitely reduce the emission of these harmful gases thereby reducing the detrimental effect on human survival. Also per capita energy consumption is grossly related to the living standard and gross domestic product (GDP) of a nation. Per capita energy consumption is generally much higher in the developed countries than in the developing countries. For example, per capita electricity consumption in India is 805.60 kWh whereas that of USA is 12,984 kWh in the year 2015 which is almost four times the world average of per capita electricity consumption. But still India is the fourth largest emitter of GHG gases in the world due to its huge population and mostly fossil fuel based electricity generation (World Bank, 2018). As energy sector is one of the largest contributors of the global GHG emission, various means have to be thought out to reduce the GHG emission from this sector. The energy sector emits about 400 Mt of CO_2 /year (European Commission, 2018). Proper energy management i.e., planned, efficient and judicious use of energy and more use of renewable energy are considered as the two most suitable options for the reduction of GHG.

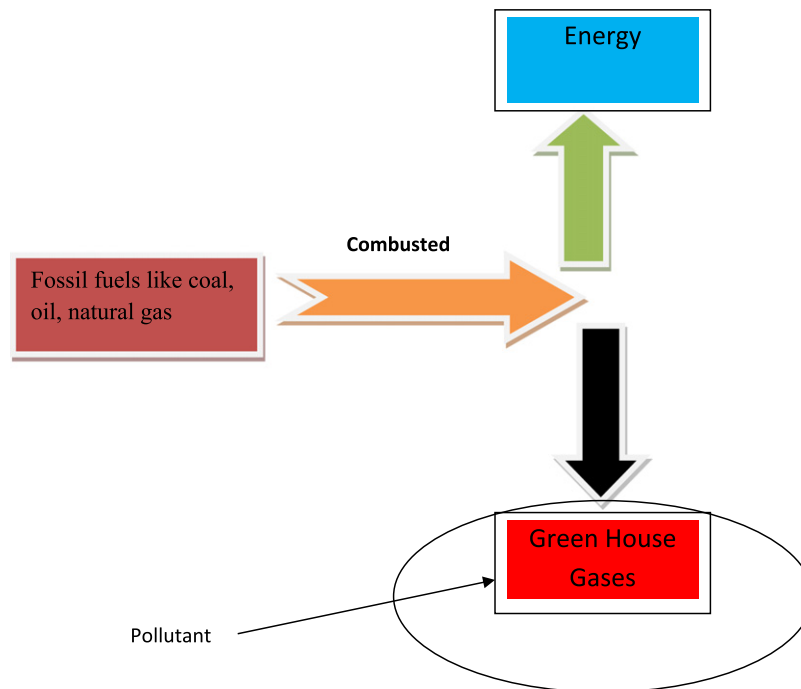


Fig. 1 GHG emission from combustion of fossil fuels.

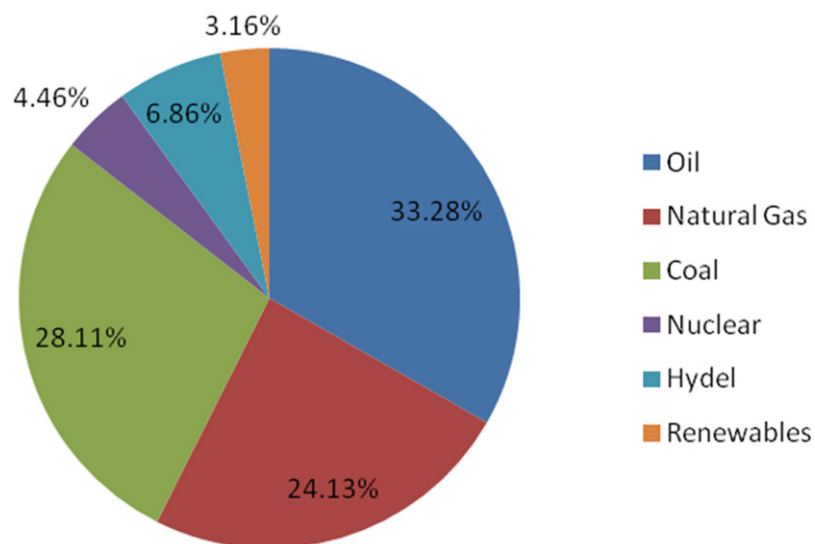


Fig. 2 Percentage share of different energy resources in the global energy mix.

International Initiatives for the Reduction of GHG Emission and Identified Relevance of Renewable Energy Introduction

The reduction of the GHG emission was a global concern for every stakeholder since the onset of the 20th Century. All countries need to work together for reducing the GHG emission and meeting the target to protect the earth. With this view, global leaders negotiated in joint meetings to decide committed action plans to mitigate the climate change with possible minimum compromise with their national economic growth, if any. As effects of GHG emission is global, though sources may be local, climate change has to be addressed globally beyond political boundaries and actions may be either local or global. In order to reach consensus on scientific facts of climate change, an Intergovernmental Panel on Climate Change

Table 1 Some important international climate change mitigation initiatives

Serial no.	Protocol name	Place	Year	Main feature
1	Kyoto Protocol	Kyoto, Japan	1997	Emission targets were set to the participating nations.
2	Cancun Agreements	Mexico	2010	It was decided that the developed nations will mobilize 100 billion USD to developing nations as climate protection fund.
3	Durban Platform for enhanced Action	South Africa	2011	Opinion of legal framework formulation was considered to all members of the United Nations.
4	Paris Agreement	Paris, France	2016	The climate change is considered as an urgent threat. The specific areas of fund and technology transfer of the developing nations are identified.

(IPCC) was formed in 1988. Renowned multi-disciplinary experts from many countries are working in IPCC. Function of IPCC is to scientifically monitor, assess climate change, disseminate these facts for the public and recommend possible measures with specific target of maximum rise of average temperature over a specific period. This assessment and recommendations need interdisciplinary experts to study interrelated effects. Also actions have several impacts on individual countries depending on their socio-economic conditions. Specifically actions to mitigate climate change have economic impacts in most cases and poor countries are affected most with it. The diplomatic negotiations are thus very important for actions of climate change. According to the assessment of the IPCC, increase in use of renewable energy replacing fossil fuels is a possible option for reducing GHG emission. Though electricity generation with fossil fuels may not be replaced in very near future, the same with carbon capture and storage may be the possible option to reach acceptable target of maximum CO₂ emission. Unfortunately, the technology of CO₂ capture from the power plants is still cost intensive process and even affects the efficiency of the overall plant leading to increase in cost of electricity significantly. Moreover, the storage of captured CO₂ at a high pressure needs to be explored more for future possible catastrophes. On the other hand, reducing GHG emission through renewable electricity generation is a rather safer path and will also add better long term energy security and sustainability. For reducing the GHG emission, more use of renewable energy is inevitable. But the initial cost of installation of the renewable energy devices is also generally high. This is a major issue against wide acceptance of renewable energy systems. So, in most of the international conventions, decisions were taken to incentivize the introduction of renewable energy projects through competitive financing. This helped adoption of renewable energy projects more rapidly. Some of the landmark international conventions for collective negotiations of most of the countries of the world to identify possible committed/voluntary actions to address the climate change issue are listed in [Table 1](#). The first important convention was the Kyoto protocol in 1997. In this protocol only the emission targets were set but the means to reduce the emission was left to the stakeholders and no monetary incentive was also decided in this protocol. The next significant convention was the Cancun Agreements. In this agreement it was decided that the developed nations will fund the carbon emission mitigation projects of the developing nations. In spite of these accepted resolutions, responses from the stakeholders were not commendable. So, in the next international convention, i.e., Durban Platform for enhanced action, a legal framework was constituted and there was a provision for measures to be taken against a nation or a stakeholder if the committed target was unmet. There was a legal framework to bring all the countries to a “renewable power target” phasing out the fossil fuel options. From this meeting emerged the concept of “Renewable Power Purchase Obligation Issues”. This made it compulsory for all stakeholders to implement renewable energy projects. In these meetings the use of renewable power was recognized as a potential way to mitigate the GHG emission targets. The next convention was Paris Agreement. In this agreement, climate change was considered as an urgent threat to the entire world. Here, specific areas were identified where the technology transfer or the fund transfer might take place in between the developed nations and the developing nations for the promotion of carbon free energy. The next summit was COP 21. This Conference was held in Paris, France and this was a convention where the issue of sustainable development was emphasized. The specific areas were identified where the technology growths as well as financial incentives were required to make the development sustainable in the long run. From these conventions the concept of low carbon business models like carbon trading, renewable energy certificates, power purchase obligation and many others emerged. These business models have catalyzed the growth of renewable energy projects as a potential means for mitigating GHG emission. The monetary benefit comes from the government incentives and also there is very low operational cost, if any, as most of the renewable resources like solar, wind etc., are available in the nature at no/low cost. Presently, with rapid development of renewable technologies and suitable policy adoption, payback periods for most of the renewable energy projects are below five years. The urgent need for increased use of renewable energies replacing fossil fuel based energies to reduce carbon emission is now accepted as an international mission through global cooperation.

Relation Between Conventional Electricity Generation and GHG Emission

For conventional electricity generation, fossil fuels are combusted to release heat energy. In this process, GHG and a number of harmful effluents for the environment are also emitted. The fossil fuels are mainly the long chain hydrocarbons and containing

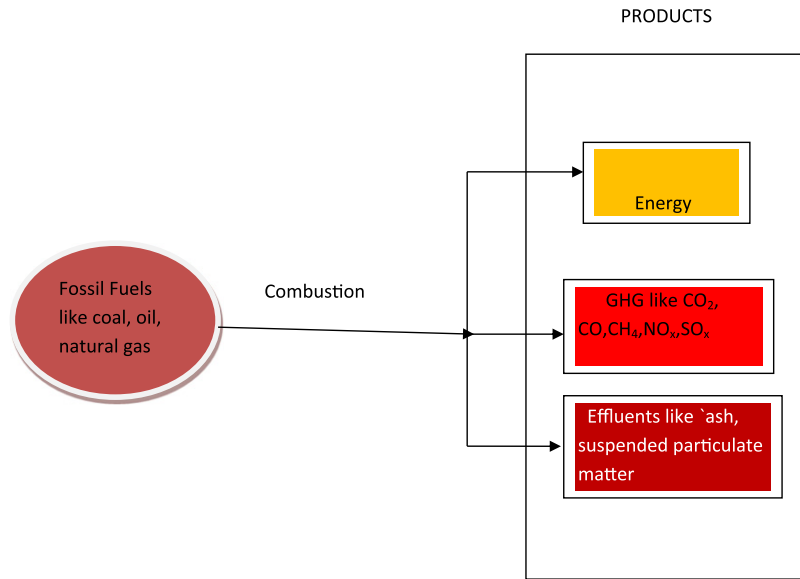


Fig. 3 Products of combustion of fossil fuels.

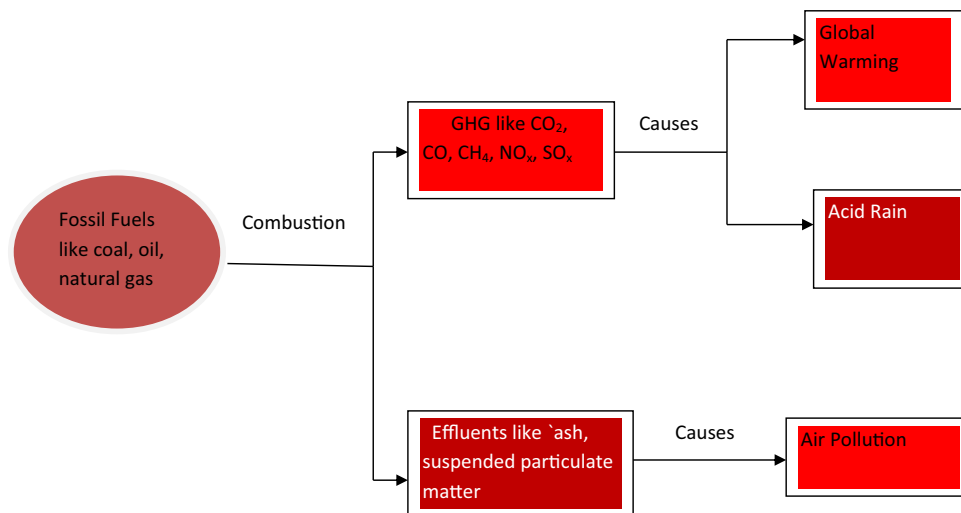


Fig. 4 Pollution effects caused by the combustion of fossil fuels.

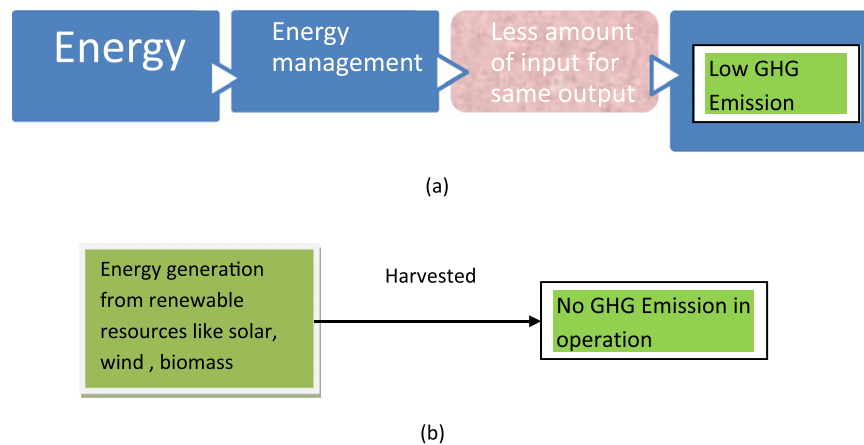
sometimes some amount of sulfur, nitrogen oxygen too. Also some incombustible component, called ash, is also present in solid fossil fuel, i.e., coal. Through gasification and partial combustion, the carbon gets oxidized to form carbon dioxide, carbon mono oxide and even small amount of methane. These are greenhouse gases causing global warming. On the other hand, sulfur and the nitrogen compounds get oxidized to form harmful gases like sulfur dioxide and nitrogen dioxides which not only causes global warming but also have other environmental detrimental effects like acid rain etc., **Fig. 3** shows the relationship between the electricity generated and the effluents produced. The combustion of the hydrocarbons is an exothermic reaction. Here, the heat is released along with the oxides of carbon and hydrogen. The oxide of hydrogen i.e., water vapor is released in the atmosphere but it has no harmful effect. But the oxides of nitrogen, hydrogen and sulfur have environmental degradation effects causing multiple problems like global warming, diseases to humans etc. The dust particles and other by products of the energy generation have adverse effects on the ambient air quality of the environment. The possible effluents from the different fossil fuel based power plants are greenhouse gases like CO_2 , CH_4 , N_2O . **Fig. 4** shows the possible environmental hazards which may take place due to the generation of energy from the different types of fossil fuels. The GHG emission potential of different renewable fuel based power plants is shown in **Table 2** (Agarwal *et al.*, 2013). It has been noted that the GHG emission potential of the renewable energy systems is much less than that of the fossil fuels. **Table 3** shows the comparative analysis of the GHG emission potential of common fossil fuel based power plants. It is observed that the emission potential of renewable energy resources is much less than

Table 2 Emission potential for renewable based power plants

Serial No	Name of component	Emission potential (g-CO ₂ /kWh)
1	Solar photovoltaic	98
2	Biogas system	70
3	Wind	100
4	Fuel cell	20
5	Biomass gasifier systems	65

Table 3 Emission potential for fossil fuel based power plants

Serial No	Name of component	Emission potential (g-CO ₂ /kWh)
1	Coal	950
2	Natural gas	455
3	Oil	600

**Fig. 5** (a) Reducing GHG emission by energy management. (b) Reducing GHG emission by use of renewable energy.

the fossil fuel based power plants. In the coal based or the oil based power plants, the fuel is fed to the furnace/chamber for the combustion. During combustion, the fossil fuels release heat as well as GHGs. The heat carried by the flue gases generated from the combustion is used to heat the working fluid of the power cycle, say water in steam power plants to generate steam from water. The steam is then used to run a turbine and generate power. So, in this system effluents and flue gases are generated during operation. So, the GHG emission potential per unit of electricity for the fossil fuel based power plants is very high. On the other hand, in case of the renewable energy based power plants the fuel is the renewable energy like solar, wind, biomass, hydro, tidal, geothermal etc. In case of solar photovoltaic cells, the electricity is generated with the help of semiconducting materials. In the solar photovoltaic (PV) cells, the light energy is directly converted to electricity. When the photons are incident on a semiconductor junction, the voltage is produced due to the barrier potential of the semiconductor device leading to the generation of a potential (voltage). Charge is also produced as electrons begin to flow leading to the flow of current. The product of the current and the voltage gives the amount of power generated by the photovoltaic modules. Thus the PV modules emit no carbon during its actual operation for generating electricity. Similarly in the solar thermal power plants the steam is produced by concentrating the solar heat by the help of suitable collectors. This heat is used to run the turbine used for generating electricity. In the wind based power generating units the wind turbine is rotated by naturally flowing wind. In biomass gasification systems, syngas is generated by incomplete combustion of biomass with sub-stoichiometric oxygen supply. Though GHGs are generated during gasification, these gases like carbon monoxide and methane are either converted subsequently or used for generating energy. Moreover biomass absorbs environmental carbon dioxide during its growth and releases the same during its gasification/combustion. So, the net carbon emission for biomass is zero, though some net 'logistic' CO₂ may be there for transportation of biomass etc. Thus it is clear

from the above discussion that the renewable resources of energy emit no/low carbon during its operation phase while generating electricity. Hence it has much low overall GHG emission potential than the fossil fuel based power plants.

Possible Means to Mitigate GHG Emission

Fig. 5(a) and (b) shows the possible means to mitigate the GHG emission. The two ways are energy management and the use of renewable resources of energy. The energy management reduces the energy consumption by the judicious use of energy. The energy management leads to maximum energy efficiency. If the energy used is less for a particular utility service, the GHG emission is also less. For example, a LED lamp consumes one fifth power than a filament lamp for the same lumen. When running in part load conditions the boiler efficiency falls. So, more input energy is to be supplied for generating 1 unit of electricity. More energy use from fossil fuel based power plants means more fuel will be combusted leading to more emission of GHG. Thus judicious use of energy with proper planning lowers the GHG emission. The renewable source of energy like solar, biomass, wind etc emits no/negligible GHG gases during its operation. However, life cycle GHG emission should be considerable as it may be due to the emission during manufacturing, installation and final disposal of the system. For renewable energy systems, the initial installation cost is high. The cost rises with the capacity increase. By energy management, the consumption of energy is reduced for the same utility service. Though the initial cost may be higher, renewable energy systems can be used with reduced carbon emission. Economics of the system will however depend on several factors including subsidy as a policy. Even if the overall energy efficiency of a fossil fuel based plant can be improved, carbon emission will also be reduced. Presently the main research challenge is to reduce the initial cost of renewable energy systems.

LCA Approach Regarding GHG Emission by Renewable

GHG emission from a renewable energy system may be assessed during operation. However, more relevant and accurate assessment of it will be throughout its life cycle, i.e., ‘cradle to grave’ means for the entire life period starting from manufacturing/ installation to final disposal of the system/plant. Life cycle assessment is a tool for the environmental impact assessment of any system based on the ISO 14040 and ISO 14044 methods (ISO, 2019). The life cycle assessment (LCA) methods include all the emissions of the system from cradle to grave. The various steps of the LCA are shown in Fig. 6. In life cycle assessment, at first the goal of the assessment has to be decided. Then the inventory analysis is done i.e., the source of materials needed to form that particular material has to be decided. The GHG emission and other environmental impacts are then assessed and analyzed. The life cycle emission potential of some renewable energy sources is given in Table 2 (Ray *et al.*, 2018). The GHG emission may take place during the production phase of the renewable energy equipment as well as the operation phase of the renewable energy gadgets and the disposal phase too. This process is shown in Fig. 6. In the renewable energy systems, the GHG emission in the production phase of the gadgets is due to the energy involved in mining the materials needed etc., for the fabrication of the devices. In the fabrication of photovoltaic panels, silicon is needed. Huge energy is needed to convert metallurgical grade silicon to solar grade silicon. At the same time the disposal of modules along with iron frames and all have a carbon loading effect on the environment. In case of the solar photovoltaic panels huge energy is needed to convert the metallurgical grade silicon to the solar grade silicon in an arc furnace. The sources of CO₂ emission at different stages of renewable electricity generation is shown in Fig. 7. In the perspective planning of choosing the energy options, the LCA approach is an important one. The Life Cycle approach gives the total scenario of the GHG emission from fabrication to utility and disposal. The renewable energy devices emit almost no GHG during its operation. But it emits some or more during the fabrication process. So in assessment of GHG emission for renewable electricity generation, life cycle assessment is more rational and accurate.

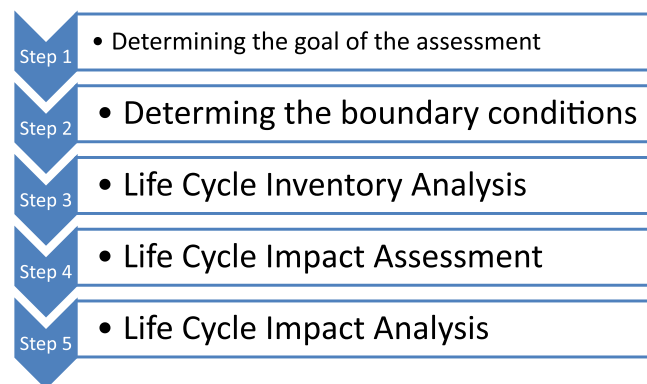


Fig. 6 Steps of life cycle assessment.

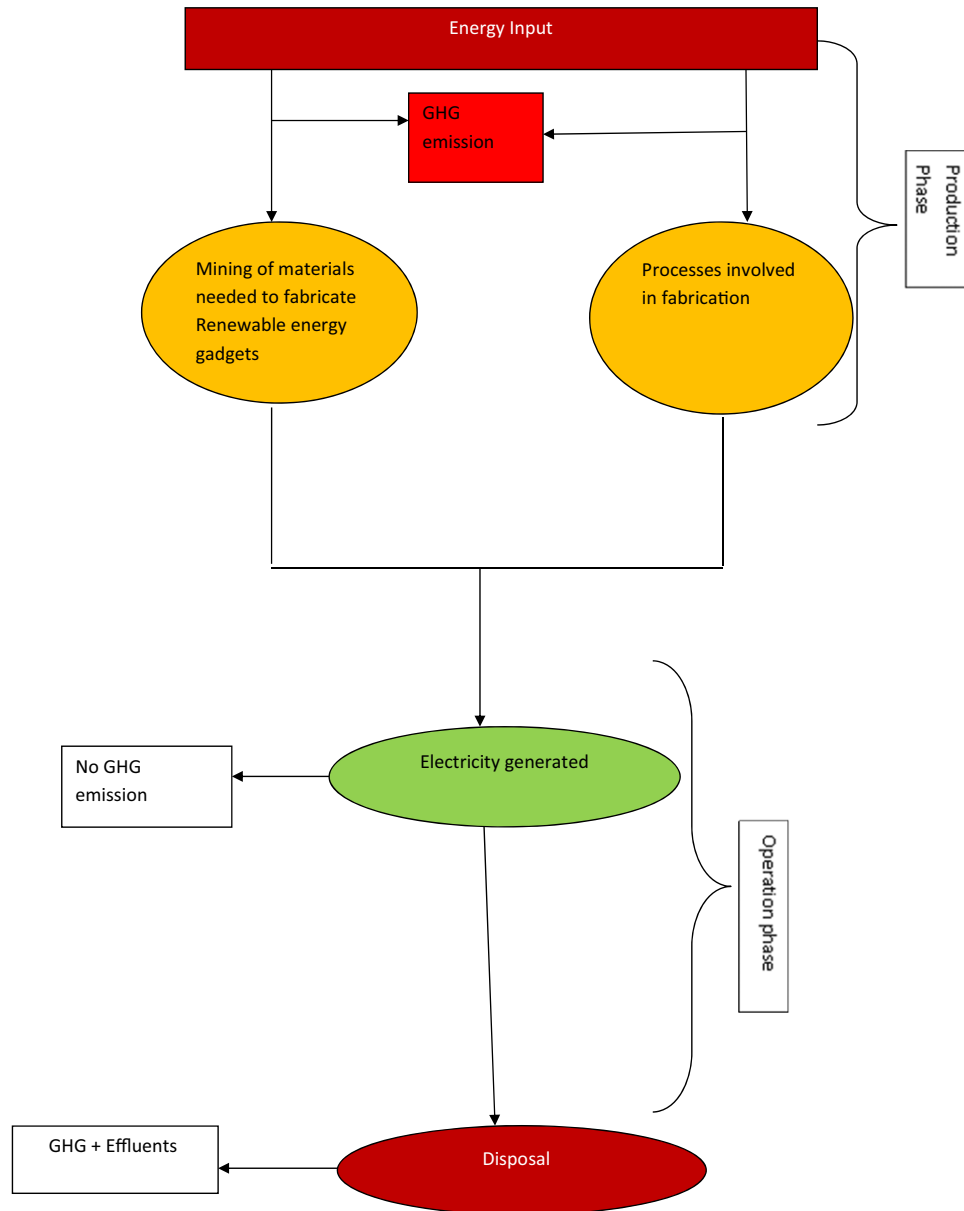


Fig. 7 Sources of GHG emission in life cycle of renewable electricity generation.

Conclusion

Fossil fuels have been dominating over centuries for generation of electricity. These fuels were economic and suitable technology for these fuels is matured over centuries. However, fossil fuel based electricity generation caused increased concentration of CO₂ in the earth's atmosphere. It being a GHG, the average temperature of the earth increased leading to the problem of the climate change. It is the greatest threat for survival of life on earth. As the effect of GHG emission is global though sources may be local, policies are to be decided globally though measures are to be adopted both locally and globally through international agreement. Several international agreements were signed and measures adopted internationally to fight this climate change. GHG emission due to electricity generation from fossil fuels is a serious concern globally. As renewable electricity generation generally emits no net CO₂, replacing fossil fuels by renewables for electricity generation may help reduction of GHG emission. As complete replacement of fossil fuels for electricity generation is not feasible due to several reasons, phasing it out over some period is an international mission. However, depending on available natural resources, different countries have varied constraints for this mission. Also, consideration of the CO₂ emission during operation only may not be the right method of concluding about the GHG emission due to electricity generation. The life cycle GHG emission should be estimated for the environmental impact due to CO₂ emission. It is noted that the life cycle GHG emission of the renewable electricity plants is much less than that of the fossil

fuel based power plants. Thus more use of renewable power generally reduces GHG emission. But the GHG emission by the renewable based power plants is not zero if the LCA methodology is applied. So, while considering the environmental impact of a system the LCA methodology must be applied to get a total estimation during entire life time of the operation of the plant or device. So, switching over to renewable power may be a better sustainable option if suitable economic technology can be developed to cater the electricity demand as a whole.

See also: Optimal Operation of Renewable Distributed Generators (DGs) and its Environmental Benefits

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Renewable Jet-Fuel (RJF): Mitigation of Aviation-Related GHG Emission

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Introduction

Jet fuel (JF) also known as aviation turbine fuel is traditionally of two types viz. kerosene type and naphtha type. Kerosene based JF is a combination of several hydrocarbons having carbon range from 8 to 16 and Naphtha based JF having carbon range from 5 to 15. Over the years, the naphtha based JF has gradually been replaced by kerosene based JF.

With the growing population the demand for JF has also increased thereby increasing the utilization of crude oil and resulting in the depletion of natural resources. According to the US energy information administration, the supply of kerosene type JF has remarkably increased from 53,263 thousand barrels in March 2018 to 57,548 thousand barrels in August 2018. JF has market of 22-billion gallon per year in US and 80 billion gallon per year in the whole world (EIA International Energy Statistics, 2010). The consumption and price of JF have also been projected to increase by 40% by 2040 (Radich, 2015). The International Civil Aviation Organization (ICAO) predicted that there would be an augmentation in JF consumption in commercial flights from 140 million tons to 850 million tons over the years 2010–2050. Corresponding to the increase in JF consumption, an estimated six fold increments (i.e., from 442 million tons to 2686 million tons) in GHG emissions would occur during 2010–2050.

Notably, the emission of GHGs due to combustion of petroleum derived JF leads to environmental pollution and is also responsible for ozone layer depletion resulting in global warming and adverse climatic changes. The CO₂ emission from aviation industry globally has been projected by Business-as-usual (BAU) to be 3.1% every year, thereby causing 300% increase in emission by 2050 (IEA, 2008). It has also been set as a goal by the International Civil Aviation organization to accomplish carbon-neutral growth of aviation fuel by 2020 (International Air Transport Association press release, 2013).

The European Union (EU) has targeted 40% reduction in GHG emission by 2030 in comparison with that in 1990. Moreover, the bio-jet fuels (bio-JF) developed should emit 60% less GHGs than petroleum derived JF.

Renewable Jet Fuel (RJF)

RJF is the term used for JF being developed from different renewable feedstocks and which can be blended with petroleum JF at definite proportions to run jet engines. Development of RJF is being carried out to have a greener environment and sustainable fuel source. It is very essential to maintain the standard specifications prescribed by ASTM while formulating RJF viz. viscosity, pour point, calorific value etc. Due to JF's exposure to different temperatures like very low temperature at high altitude and in winter season or hot temperatures in summer or humid areas; it is essential to maintain the viscosity and pour point of the RJF otherwise it will be difficult for the aviation fuel to maintain its fluidity. A term "drop in" is commonly used for RJF in aviation industry which means a blend of 50% of RJF can be mixed with commercial JF according to ASTM7566 standards. The property of kerosene based JF (Jet A-1) according to ASTM standard is given in Table 1 (Abhari et al., 2010).

Production of Renewable Jet Fuel (RJF)

Initially the focus was on production of RJF from coal, natural gas, biomass which also included municipal solid waste, lignocellulosic agricultural and forest wastes using Fischer–Tropsch (FT) synthesis method. The coal derived RJF was referred

Table 1 ASTM specifications of conventional Jet Fuel (JF)

Properties	ASTM D-1655 Jet A-1
Flash point	38 min°C
Distillation EP	300 max°C
Viscosity @ – 20°C	8 max cSt
Freezing point	– 47 max°C
Density	0.775–0.840 g/ml
Heat of combustion	42.8 min MJ/kg
Smoke point	25 min Mm
Sulfur	3000 max ppm
Hydrogen	None mass %
Carbon (Saybolt)	None

to as “iso-paraffinic kerosene” (IPK) and was developed by Sasol in South Africa. “Synthetic-paraffinic kerosene” (SPK) derived from FT was employed for blending in military flights early in 2008 and in commercial flights in 2009. Another method for production of RJF being presently widely studied is hydroprocessed renewable jet (HRJ) in which RJF is produced from plant sources viz. jatropha oil, palm oil, rapeseed oil, salicornia oil, camelina, algae and also from animal fat e.g., rendered tallow. The RJFs produced from hydroprocessing of vegetable oil and animal fat have been given the name bio-SPK and “green jet”. RJF produced from lignocellulosic feedstock viz. switch grass, corn stover, short rotation woody crops etc., are also categorized as bio-SPK (Corporan *et al.*, 2011). Hydroprocessing renders hydroprocessed esters and fatty acids (HEFA) that may be deployed as RJF through processing of soybean and depolymerized cellulosic jet fuel (HDCJF). Corn stover, fermented sugars (HFS) besides RJF can also be produced from sugarcane and corn grain processing and hydrothermal liquefaction (HL). One more method for production of RJF is aqueous phase processing (APP). APP is used generally for conversion of woody biomass and alcohol to RJF in which sugar is first converted to ethanol which is subsequently converted to RJF. The U.S. Federal Aviation Administration has given approval to RJF developed from technologies viz. Alcohol to Jet SPK, HFS, HEFA, FT and FT synthesis with aromatics.

Recently, algae have achieved importance as feedstock for production of RJF, firstly, because it is possible to cultivate algae in nonarable land which minimizes the competition with agricultural land. Moreover, the productivity of algae per acre is high, its cultivation can utilize waste water and it has the potential to recycle carbon from industrial emissions. Importantly, it has demonstrated the ability to produce biofuels and valuable co-products.

In FT process the synthesis gas (syngas) is converted to paraffinic hydrocarbons which are further refined through processes like cracking, isomerization and fractionation to produce liquid fuel (Corporan *et al.*, 2007). The use of iron or cobalt supported chemical catalyst in FT process have also been carried out to meet the temperature and time requirements and thereby reducing energy involvement (Baliban *et al.*, 2013). As heteroatoms and aromatics are present in fewer amounts in this liquid fuel, it has been used as a green blend with conventional JF. This blend is termed as “semisynthetic” fuel.

Although the ‘semisynthetic’ fuel showed improved thermal oxidative stability and favorable emission properties; nonetheless, could not fulfill other specifications viz. density, lubrication property etc. The gas chromatogram of the synthetic JF and conventional JF (Corporan *et al.*, 2007) depicted that the synthetic/renewable JF contains less amount of aromatic compounds than conventional JF. With 50% blend of the synthetic JF with conventional JF, the aromatic content could be beneficially reduced to only 9.25 vol% (Lobo *et al.*, 2011).

Another technology which has gained significant importance is fermentation of suitable biomass feedstock. In this case, monomeric forms of sugars are converted to certain molecules using microorganisms e.g., yeast which are responsible for degradation of cellulosic feedstock which are further chemically upgraded to RJF.

Yet another method of production of RJF is ‘Ethanol to Jet’. Corn grain and corn stover are the two different feedstocks which have been used to produce ethanol and finally converted to RJF (Tao *et al.*, 2017). Ethanol can be derived from feedstock either through thermochemical route such as catalytic hydration of ethylene or through biological route which includes employment of enzymes and microorganisms responsible for fermentation. Companies like Byogy in Bryan Texas in U.S. are deriving ethanol biologically from the feedstock followed by conversion to RJF catalytically. During this conversion process the ethanol is dehydrated to ethylene which is oligomerized and the products are separated by distillation and then hydrotreating is carried out. It is necessary that the RJF being produced from ethanol meets the standard specifications for JF. Therefore, the first step dehydration is carried out to remove oxygen present in ethanol. After that catalytic dehydration of ethanol is carried out to form ethylene. The second important step is the formation of α -olefins. Through catalytic oligomerization process, ethylene is converted into linear and branched olefins. Depending on the operating conditions and the catalyst used, α -olefins produced ranges from C_4 to C_{32} hydrocarbons. Dimerization is also sometimes carried out to form a dimer of lighter hydrocarbons like C_8 to C_{16} olefins. Dimerization and oligomerization processes are carried out in a single reactor. Subsequently, the olefins are hydrogenated to form paraffins which are used as RJF. Green diesel and gasoline are also produced as co-products from biomass feedstocks viz. corn grain and corn stover.

Commercialization of RJF

RJF is already being used in commercial flights. Virgin Atlantic on 24th February 2008 used a blend of fatty acid methyl ester derived RJF with kerosene in the ratio of 20:80 to run B747-400 engine between London and Amsterdam. United Airlines on 11th March 2016 were the first to regularize the use of RJF as 30% blend with conventional Jet A1/8 fuel for running commercial flights from Los Angeles International Airport. The RJF was produced from non-edible feedstocks viz. agricultural wastes and vegetable oils. According to the International Air Transport Association (IATA), the United Airlines has planned to utilize RJF from 2019 for the next ten years targeting an anticipated consumption of 270,000 tons per year. It is being expected that there will be a 50% reduction in CO_2 emission by 2020 in comparison with 2005. Honeywell UOP utilized grant of U.S. Defense Advanced Research Projects Agency (DARPA) to develop technology for production of green JF. Algae, camelina etc., were utilized as feedstock for production of green JF. More than 1 million gallons of RJF has been produced by Honeywell for usage by U.S. military and commercial flights for mitigation of GHG emission and carbon footprint.

Indian standard RJF (17081:2019) consists of synthesized hydrocarbons developed from different feedstocks e.g., non-edible vegetable oil and tree borne oil. Indian Air Force has indigenously developed RJF that has been given trials and has eventually been approved by Centre for Military Airworthiness and Certification (CEMILAC) for utilization as a green blend with conventional JF. Bureau of Indian Standards (BIS) has worked in collaboration with Indian Air Force to produce RJF and use it as Aviation turbine fuel (ATF). According to 'Business As Usual', it is anticipated that 1/5th of the present GHG emission would be reduced due to the use of RJF as a green blending component with conventional JF.

RJF has been utilized by European countries over the recent years for both civil and defense aviation transport sector. The commercial production of drop-in biofuels has been projected to attain approximately two million tons by 2020 in coordination with companies viz. Biomass Technology Group, Neste Oil and UOP. In concurrence with European Union analysis, there would be a possible 95% life-cycle GHG reduction through employment of RJF as compared to conventional JF.

The global increase in demand of RJF has necessitated enhanced agricultural activities for cultivation of different non-edible feedstocks for RJF production. This would further improve employment opportunities and rural economy encompassing all stake holders.

Effects of RJF on Aviation Emission

The combustion of RJF in aircraft engine has profound effect on air-environment through mitigation of GHG emission. The jet engine exhaust components have different lifetime, viz. water vapor (9 days); CO₂ (approximately 20% for thousands of years) and NO_x (about 114 years). The longer lifetime of components like CO₂ results in the accumulation of these components in the earth's atmosphere. They are responsible for reducing the solar radiations returning to the atmosphere which in turn increase the reflection of solar radiations from the atmosphere. This eventually results in the increase in temperature of Earth's surface which is commonly referred to as 'global warming'. Individual components affect the climate differently; e.g., accumulation of NO_x components is responsible for the depletion of ozone layer. It has been found that 10% depletion in ozone layer can lead to 45% penetration of harmful UV rays to the earth's atmosphere, thereby, causing serious health issues like skin cancer. Other components like SO_x also accumulate in the atmosphere and when reacts with water form acid rain. Smog formation also results due to emission of non-methane hydrocarbons (NMHC). PM (Particulate Matter) emission and its reaction with water results in condensation and thereby forming contrails which contribute towards global warming; although their life expectancy in the atmosphere is short (Janic, 2018).

The PM emission of JF has been observed to be $2.25 \times 10^8 \pm 5\%$ particles cm⁻³ (Corporan *et al.*, 2007). It has been found that with the increase in the percentage of blend of RJF with conventional JF reduction of PM emission occurs up to approximately 97.5%–99.9% (Janic, 2018). The blend of RJF with conventional JF results in the release of smaller size PM and the smaller size make PM easily oxidizable. This is due to the presence of fewer amounts of aromatic compounds in RJF in comparison with conventional JF. The formation of soot nuclei also becomes less because of meager content of aromatics in RJF. It has also been revealed that RJF comprises of normal and branched aliphatic compounds which are less hazardous in terms of soot formation. Evidently, soot formation is unacceptable with respect to environment safety. Moreover, the RJF has high hydrogen (H) to carbon (C) (H-C) content which also helps in soot reduction. It has also been showed that there is a relation between the aromatic content and hydrogen content of fuel. Less than 5% polycyclic aromatics exhibit good correlations with H-C content and reduce soot formation. However, it's just the opposite with polycyclic content more than 5%.

Further, the sulfur content of RJF has also been found to be low as compared to conventional JF and therefore it helps in reducing particle formation by reducing the nucleation mode. It has been demonstrated that the oxidized sulfur compounds do not interfere in the PM formation and emission.

Besides, a strong relation has been observed in between the mean particle diameter and the concentration of RJF in RJF blended JF. The increase in concentration of RJF reduces the mean particle diameter from 28 nm to 17 nm thereby reducing the formation of soot nuclei. This ultimately reduces the availability of nascent particles for coagulation and facilitates reduction in PM emission.

Smoke number (SN) is another important fuel property which comes into consideration while discussing emission. SN is basically a parameter which reflects soot formation. Soot formation causes blackening of the smoke filter which is responsible for reflectance. In case of blend with RJF, as the soot formation is less there is a considerable decrease in SN. Moreover, SN is also associated with mean particle diameter. As the nanometer sized particle decreases in diameter with the increase in blend of RJF with conventional JF, SN decreases further. SN can therefore be said to have relation with PM emission and particle size decrement.

In case of gaseous emissions, NO_x emission decreases by approximately 11%–22% (Janic, 2018) after blending RJF with conventional JF. A slight decrease in CO₂ emission (approximately 2%) (Janic, 2018) was observed due to the presence of higher hydrogen to carbon (C-H) content in RJF. As the RJF is usually sulfur free, a considerable reduction in SO_x emission can be possible. Further, NMHC also reduces by approximately 18%–25% (Janic, 2018).

It has also been observed that the emission of components is dependent upon the feedstock chosen along with the location from where the feedstock is procured viz. rapeseed collected from different places of U.S. showed different NO_x emission. Although rapeseed has been found to be a better feedstock for RJF production than camelina, *Jatropha curcus* and soybean because of 40%–44% of oil content; however, the NO_x emission increases on usage of rapeseed as feedstock when overall process is considered starting from cultivation to utilization of rapeseed as feedstock. This is due to the fact that during cultivation of rapeseed, fertilizers are being used which contain N and are therefore harmful for the environment (Ukaew *et al.*, 2014).

The technology adopted for production of RJF also affects the GHG emission profiles. With application of fermentation technology on sugarcane, corn grain and switch grass the GHG emission rates could be reduced significantly as compared to conventional chemical conversion technologies (Staples *et al.*, 2014).

Life Cycle Analyses of GHG Pertaining to RJF

The life cycle of GHG emission of RJF is usually described using a term “Well to wake”. This term has been used to study both CO₂ and non-CO₂ combustion effects. It is expressed in the unit of energy. As per previous reports, 73.2 g CO₂/MJ is emitted when combustion of conventional JF occurs whereas the combustion of RJF emits 70.4 g CO₂/MJ (Stratton *et al.*, 2011). Notably, It has been observed that when RJF is produced from cellulosic biomass through APP technique, the ‘Well to wake’ GHG emission varies from 31.6 to 104.5 g CO₂e per MJ (Olcay *et al.*, 2018). Importantly, in case of application of fermentation technology for production of RJF from sugarcane, switch grass and corn grain, the ‘Well to wake’ GHG emission was found to vary from – 27.0 to 19.7, 11.7–89.8 and 47.5–117.5 g CO₂e per MJ respectively in comparison with 90.0 g CO₂e per MJ from conventional JF (Staples *et al.*, 2014). Evidently, the RJF results in much less GHG emission relative to conventional JF; and thus, facilitates mitigation of global climate change.

Generally 100 years is considered as the time span for analyses of impact of GHG on climate considering mainly those components which have longer lifetime in the atmosphere. 500 year time span is also considered in some cases. It has been found that atmospheric cooling occurs when there is reduction in ambient NO_x and soot over a time span of 100 and 500 years. This ultimately leads to reduced global warming. There has also been reduction of sulfur components which will lead to reduced global warming.

The life cycle analyses of the RJF utilized as blend with conventional JF, encompasses the impact of various steps on emission, viz. the cultivation of the feedstock, its transportation, processing, conversion to RJF and utilization as RJF (Bailis and Baka, 2010). One such well known feedstock is *Jatropha curcus*. The first stage is the acquisition of land and its preparation for *Jatropha curcus* cultivation. This step includes tilling, sowing, cropping, and seed harvest. During this step, proper irrigation is required which is also responsible for GHG emission. Further, limestone (CaCO₃) is also mixed with soil in some countries (e.g., Brazil), where the acidity of soil is high. This limestone when comes in contact with water forms solution of bicarbonates; and eventually results in the emission of CO₂ and water. Next component is the use of fertilizers to increase the yield of *Jatropha* seeds. The most commonly used fertilizer viz. urea breaks down and results in the emission of N₂O and CO₂; thus further contributing towards increment in GHGs emission.

The second stage is the transportation of the cultivated *Jatropha* seeds to the point where oil will be processed and converted to RJF. For transportation, vehicles are used which involve burning of fuel and therefore the second stage also adds to the emission of GHGs.

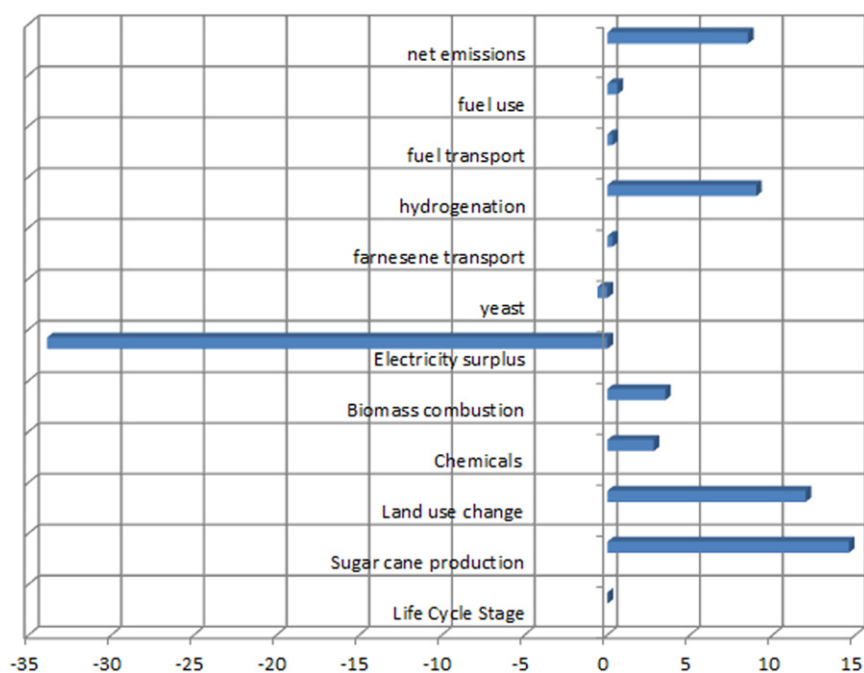


Fig. 1 Life cycle GHG emission concerning RJF derived from sugarcane.

The third stage is the production of RJF from the processed oil. In this step hydrogen is being utilized to get bio-SPK from refined Jatrophia seed oil. In this step also additional emission occurs which contributes towards global warming.

The fourth stage is the transportation of RJF from the refinery to the aircraft for its utilization as a green fuel blend with conventional JF. In this step also as vehicles are being used for transportation of RJF, the combustion of fuel in the vehicle will also lead to further emission of GHGs.

The final stage of life cycle analyses includes the blending of RJF with conventional JF and its utilization as liquid fuel in operating aircraft engine rendering additional emission of GHGs. Thus, the overall emission of GHGs would include the emissions of GHGs from all the stages.

Another important feedstock for production of RJF is sugarcane. Sugarcane is first converted into a compound namely farnesene through fermentation carried out using yeast. In the fermentation broth this compound is available as a separate phase as the top layer which facilitates its recovery. Farnesene is consequently carried to hydrogenation plant where it is catalytically hydrogenated to a compound referred to as 'farnesane' which acts as RJF and used as a green blend with conventional JF.

In the preceding process, the net GHG emission in g CO₂e/MJ would include all the emissions occurring starting from cultivation of sugarcane, its milling, syrup production, conversion of syrup to farnesene and finally to farnesane. The GHG emission is shown in Fig. 1 for production of RJF when sugarcane is deployed as feedstock. From Fig. 1, it is evident that maximum GHG emission (CO₂e) occurs during sugarcane production and land use change. Notably, it becomes negative when electricity and yeast are taken into account concerning GHG emission. Other factors which contribute towards GHG emission are also exhibited in the figure along with corresponding percentage of contribution (Moreira *et al.*, 2014).

It should be emphasized that, accounting the emission of GHGs in all the stages of RJF production and utilization would facilitate prediction of the life cycle analyses of any feedstock as illustrated in Fig. 2. The data of GHG emission corresponding to each step in life cycle analyses can be utilized for the development of sustainable technology for RJF production and end use.

A comparison of the GHG emission in g CO₂e/ MJ occurring due to several factors considered in the life cycle analyses has been exhibited in Fig. 3 for different feedstocks. From Fig. 3, it is evident that during utilization of fertilizers and chemicals for production of feedstocks, their transportation and their conversion into RJF using catalyst the GHG emission are relatively higher whereas in case of consideration of land carbon net emission, the GHG emission values obtained were negative.

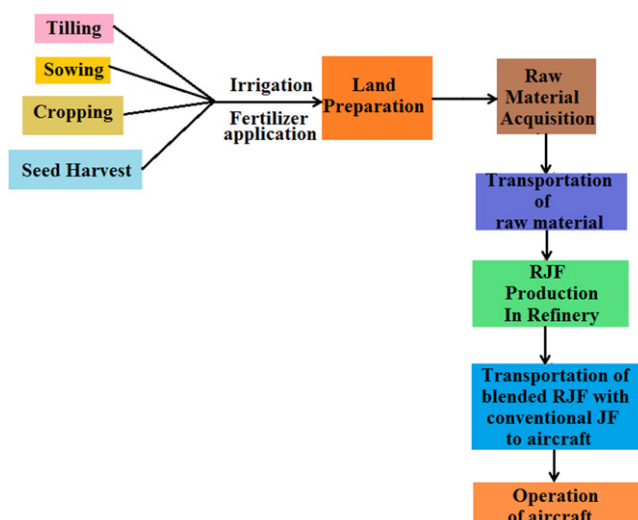


Fig. 2 Life cycle analyses steps for net GHG emission for any feedstock.

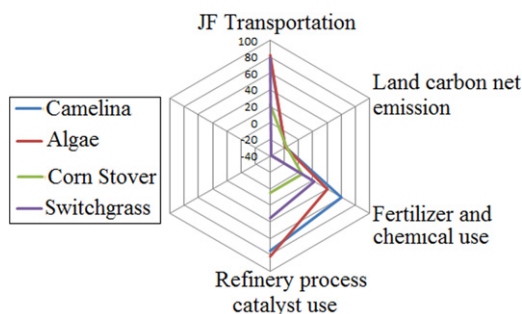


Fig. 3 Comparison of GHG emission in g CO₂e/MJ RJF for different feedstocks.

Conclusions

This study emphasized on the mitigation of GHGs emission by employing RJF as a blending stock for conventional JF. It is apparent that the increasing population is leading to an augmented demand of JF. The more the utilization of JF the more will be depletion of our natural fossil fuels. Further, the burning of JF also leads to substantial emission of GHGs which are responsible for ozone layer depletion, global warming and eventual environmental pollution. This has led to the necessity for production of cleaner JF i.e., greener alternative RJF. At present, RJF is being commercially produced from various feedstocks like jatropha, sugarcane, algae and other lignocellulosic feedstocks through different processing technologies like Fischer-tropsch synthesis, hydroprocessing, aqueous phase processing, alcohol to jet conversion and fermentation technology. Commercialization of RJF is in progress globally through different public and private sector stakeholders. The public and private enterprises produce RJF employing proprietary technologies utilizing predominantly non-edible feedstocks e.g., tree borne oil, algae, camelina etc. The RJF should conform to specified standards and obtain necessary clearances from standard aviation regulatory authorities for employment as a green blending stock with conventional JF in military aircrafts and civilian flights for air transport.

From the present study, it can be concluded that RJF is efficient in mitigating GHGs emission and higher blending percentage of RJF with conventional JF can render further reduction of GHG emission in air transport. At present maximum 50% RJF blended with conventional JF is utilized to run aircraft engines. It is evident that the GHG emission of RJF produced from different feedstock is different. The net GHG emission combines all the emissions occurring due to cultivation of the feedstock, its processing, and transportation to refinery, conversion into RJF, blending with JF and utilization to run aircraft engine. This concludes that selection of feed stock and all processing steps are one vital for sustainable RJF production. It should be taken care of that the feedstock selected does not compete with food products for agricultural land for its cultivation. Moreover, waste management is also a vital issue in terms of land acquisition and overall environmental pollution. There is utmost need for development of sustainable technology to efficiently utilize all types of waste viz. solid waste, municipal waste, agro-waste, food industry waste etc., to produce RJF through energy-efficient and inexpensive pathway. RJF can also be produced from bio resources e.g., algae which can also be efficiently cultivated. Further, the increasing demand of RJF would lead to a boost in requirement of the feedstocks for RJF production. The increment in demand of non-edible plant based feedstocks would eventually lead to an enhanced growth in agricultural activities. Concurrently, new employment generation would facilitate enhanced economic growth.

The processing technologies currently utilized for production of RJF are energy intensive and makes the RJF costly. Therefore it has not become possible to commercialize it completely. The production process of RJF is still undergoing pilot scale development to achieve superior sustainability. There is an utmost need for the development of processing technology for formulation of RJF from lignocellulosic feedstock to make it more cost-effective. Moreover, RJF produced should be such that it meets the specified fuel standards as per ASTM or EU. It should have the ability to be blended with conventional JF at a percentage more than 50%. Importance should be given to reduce PM emission, aromatic compound formation, soot formation, release of harmful gaseous compounds viz. SOx and NOx, C-H content so as to effectively mitigate the net GHG emission reduction and achieve the target of carbon-neutral growth. Mitigation of GHGs could be possible through proper selection of feedstock and application of cost-efficient technology for conversion of the selected feed stock to RJF to have a greener, cleaner and healthier climate.

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Selected Issues in Economics of Greenhouse Gas Emission Mitigation

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Introduction

Global warming and climate change have emerged as unavoidable components of any discourse related to growth in economic activities. Greenhouse gases (GHGs) that are at the heart of the concerns, absorb a part of solar energy that comes to the earth and radiates it back as heat. Increased concentration of these gases implies an increase in the amount of infrared radiation (heat energy) trapped in the atmosphere. This trapped heat energy in turn leads to an increase in the global mean temperature. While this was known to the scientific community since nineteenth century, there is augmented concern with regard to the same as it was realized that the anthropogenic emissions of GHGs can go beyond natural assimilative capacity and interfere with the bio-physical system on earth. Although the exact one to one correspondence between increase in GHG concentration in the atmosphere and increase in global mean temperature is yet to be established, several studies indicated likelihoods of exceeding a certain degree of temperature for a given level of stabilization of these gases. The 'hockey stick' plot of temperature rise that shows drastic increase in global mean temperature since the beginning of the 20th century following a flat pattern, by [Mann et al. \(1999\)](#) is now considered to be an evidence of global warming beyond doubt. According to the Fifth Assessment Report of Intergovernmental Panel on Climate Change ([IPCC, 2014](#)), under baseline scenario, without additional efforts to mitigate GHG emissions, global mean surface temperature can increase between 3.7 and 4.8°C in 2100 as compared to the pre-industrial level. A large portion of this emission is anthropogenic in nature and caused by combustion of fossil fuel to produce power and other economic goods to meet the growing consumer demand with population growth. Besides, land use change for e.g., clearing of forest reduces carbon sequestration capacity and contributes to the increase in GHG concentration in the atmosphere. Since the major cause of emission is anthropogenic, a coordinated human effort towards mitigation is the key to the solution.

Anthropogenic GHG induced climate change can be seen as a case of transboundary pollution leading to transnational externalities. So, the debate and dilemma over the questions of 'efficiency' of mitigation and 'equity' in burden sharing are expected to continue in a fragmented and unequal world. Economic efficiency in emission mitigation relates to minimization of abatement cost at the margin. Given the long lifetimes of the GHGs in the atmosphere, the efficiency also needs to be inter-temporal in nature. However, economic efficiency is a necessary but not the sufficient condition for sustainable development. It further requires achieving intra- as well as inter-generational equity and therefore raises a plethora of questions such as 'who will mitigate?', 'what should be the scale of mitigation?', 'during what time period?', 'who will pay for it?' etc. All these questions geared to seeking a strategy towards governing transboundary pollution and internalization of transnational externalities in a politically fragmented world, especially in the absence of a supranational government. Needless to mention the challenge is complex. The scope of Economics as a discipline has significantly expanded to deal with such complex questions of inter-temporal efficiency and equity related to emission mitigation. The issue is addressed based on the concepts of negative transnational externality created by emission, its impact on global commons, global public good characteristic of benefits from emission mitigation and the related free rider problem.

The current article addresses two issues: First, it introduces the readers to the fundamental argument that frames the concepts of economics of climate change mitigation. Second, based on empirical examples, it explains the complexity of solutions towards mitigation compared to standard economic problems. The rest of the article is arranged in the following manner: Section "GHGs Emission and Mitigation: Using the Lens of Economics" gives an overview of the basic concept of 'good' and 'bad' in economics, why market fails as an institution to govern a 'bad' creating 'negative externality' and how government can intervene to internalize the externality. It also discusses the additional challenges created by a 'bad' that is global, since there is neither a market nor a global government to internalize the externalities. Section "From Kyoto to Paris" provides a brief note on the nature of international agreements evolved over time to address climate change mitigation under such circumstances. This is to provide a glimpse of the role of supra-national bodies to surrogate market mechanisms and/or to create a form of global governance to internalize the externality. Although mitigation goal is a global goal, in a politically fragmented world policy instruments are mostly designed and implemented by national governments. This leads to Section "Designing Tax for Multiple Greenhouse Gases" that shows optimal design of policy instruments requires careful consideration of several facts – including the fact that emission mitigation involves not only carbon dioxide (CO₂), but of a number of GHGs with different implications towards climate change. Section "Levelized Cost of Conserved Carbon" talks about the levelized cost of conserved carbon (LCCC) and what additional information does it capture beyond near term cost-benefit assessments. Finally, the debate of managing GHG emissions by looking at the production based approach vis-à-vis consumption based approach has been addressed by focusing on measurement of carbon footprints using an empirical example in Section "Measuring Carbon Footprint".

GHGs Emission and Mitigation: Using the Lens of Economics

Negative Externality and Public Good

Human activity induced GHG emissions can be conceptualized as 'negative externality' created by a 'bad'. The identification of 'externality' dates back to 1920 when A. C. Pigou (Pigou, 1920) wrote about the problem of a smoke emitting factory causing damage to nearby business/residents. Clearly, the production behavior (This is applicable also in case of consumption activities) of one entity (the factory) here affects the production and/or consumption behavior of other entities. Here the externality is said to be 'negative' since the effect is damaging. If we continue with the example of smoke emitting factory, the question is how to ensure that such emission does not go beyond an optimal level or more generally, how to govern a 'bad' creating negative externality at a local level. In traditional economics, market as an institution facilitates exchange of 'goods' and services with well-defined property rights through price mechanism. The interaction of demand and supply of 'goods' determine an agreeable price where demand equates supply, an exchange takes place and the market clears. An overproduction relative to demand pulls the price down while any underproduction pushes it up. Market mechanism that helps managing 'good' is missing in case of a 'bad' in absence of demand. The 'bad' remains un-priced in the absence of a market that would otherwise generate a negative price of such pollutants. Had there been a market for 'bad', the producer of such 'bad' would have been liable to pay the market determined price to the consumer i.e., the affected entity. Over production of 'bad' would have implied more payment by the producer to the consumer generating some kind of disincentive to produce 'bad' (here the polluter/emitter) beyond the optimal level. This, if remains unpaid by the producer of 'bad', drives the gap between the 'social cost' and 'private cost'. Think of the same smoke emitting factory. The out of the pocket cost that the producer has to bear will include payments to various fixed and variable factors of production such as wage payment to labors, payment for raw material and fuel, payment for services such as transportation etc. These costs constitute the 'private cost', the cost that the producer has to pay as a private entity. In order to arrive at a 'social cost' one has to add to it all kind of costs inflicted upon the society by the production activity, including the cost of emission and pollution caused by the production process. As long the producer doesn't internalize the externality the divergence between social and private cost remains.

In absence of market mechanism, government often intervenes and uses appropriate fiscal instruments to internalize the externality. In the context of local pollutants, they are often in line with Pigou's solution to internalize the externality through imposing a per unit tax (equal to the difference between the social marginal cost and the private marginal cost corresponding to the social optimal output) on output of the polluting firm. The government can also impose restrictions through command and control. By doing so the government recognizes the 'public good' character of mitigation of 'bad'. Here the concept of 'public good' needs further clarification. In economic literature, a commodity or service is categorized based on two attributes: consumption rivalry and excludability. A piece of cake that is purchased from the market is characterized by both excludability as well as consumption rivalry and is called a 'private good'. It is excludable because if one doesn't have a certain amount of money to buy it, he/she will be excluded from the consumption. The consumption rivalry arises from the fact that if one person consumes it, less will remain for any other person to consume. This is however not the case for a service such as street lights. Once the provision is made, nobody can be denied of the service. Also, one person's consumption doesn't affect other's share. Similarly, if the smoke emitting factory reduces the pollution the benefit of pollution reduction will be felt in the entire locality in a similar manner and hence has a 'public good' character.

The phenomenon of climate change is a special case of externality with layers of complexity. First, negative externality caused by GHGs is transboundary in nature- the effects of emission are not restricted within the geographical boundary of the emitting country (Hanley et al., 2006). GHG emitted by one production/consumption entity accumulates in the global atmosphere, irrespective of its source and creates negative externality such as increase in global mean temperature, climate change etc. in a global scale. What is unique about these gases is the uniformity of mixing i.e. they spread relatively evenly in the atmosphere around the globe. The impacts of accumulated GHGs are felt on global commons such as atmosphere, ocean, biodiversity reserve etc. and stands for a case of transnational externality. That is the reason why they are called 'global pollutant' in contrary to their local counterparts such as SO_x, NO_x, particulate matters etc. The uniformity of mixing and the impact over the globe makes the problem extremely complex. So far for local pollutants, although the market didn't exist, national governments could either take up a command-and-control policy to cap the emission or use fiscal instruments to generate optimal solution. But to manage GHG emission, neither market nor a supra-national government exists. Fiscal instruments of national governments are not capable of internalizing externality since decrease in welfare of one country may well be a result of actions propagated by some other country. As the impact of emission is transboundary, so is the impact of emission mitigation. This is simply because if country A undertakes some mitigation actions, the climate benefit or the safe-guard to global common will be available to the entire world. If the mean temperature stabilizes and climatic condition over the globe is improved due to emission mitigation, then no one can be denied to be a beneficiary of the same. Also, one person enjoying the benefit of climate change mitigation doesn't reduce the scope of it by anyone else. So, climate benefit derived from emission mitigation is 'non-excludable' and 'non-rival' at an international scale and is therefore a 'global public good'. This has a tendency to lead to a situation where no one is willing to pay for mitigation as everyone will assume that the others will pay while he/she can enjoy the benefit. The tendency of such 'free riding' is at the heart of market failure for anything with the public good characteristic. The problem becomes even more complex if intergenerational equity is brought into the picture. Since accumulation of GHG in atmosphere is likely to render adverse climatic consequences in

future, the main demand from emission mitigation should have come from them, which is again non-existent at present. Any discussion on this is however, beyond the scope of this paper.

Given such circumstances, efforts are extended in two directions: first to augment the role of international cooperation and establishment of supranational bodies such as United Nations Framework Convention on Climate Change (UNFCCC); second, to augment the application of policy instruments that may seem to be useful in addressing this complex problem. The frontier of economic research has also been expanded to address these issues in the context of climate change mitigation. In the sections we discuss such international negotiations as new global order to manage GHG emission.

From Kyoto to Paris

The role of international cooperation is often considered to be the key to climate change mitigation in absence of supra-national government in a politically fragmented world. Beginning in 1992 through the establishment of UNFCCC followed by Kyoto Protocol in 1997, the nature of international negotiation and cooperation with regard to climate change has experienced significant evolution. The Kyoto Protocol classified countries based on their historical emissions in terms of Annex I and non-Annex I countries. While Annex I i.e., the developed countries faced a target of emission reduction, though legally non-binding in nature, there was no such mitigation target for non-Annex I countries. The protocol, this way, recognized the equity issue of burden sharing by stating that the heavier burden was placed on the developed countries for the 'current high levels of greenhouse gas emissions in the atmosphere as a result of more than 150 years of industrial activity'. This was coined as the principle of 'common but differentiated responsibilities'. However, several efficiency factors including the perception about the impact of climate change, cost of emission reduction, domestic and international policies – all shaped the emission mitigation activity profile of countries (see "Relevant Websites section"). The dynamics however, changed significantly over the years as learning by doing is increasing. Several direct and indirect policies are getting implemented while countries are learning from past mitigation experiences. In order to bring more countries on board, to achieve the target mitigation in a least cost manner, the idea of 'common but differentiated responsibilities' was reformulated in terms of 'Intended Nationally Determined Contribution' to climate change mitigation. In 2016, the Paris Agreement intended to 'strengthen the global response to the threat of climate change, in the context of sustainable development' to restrict the increase in the global mean temperature to 1.5°C above pre-industrial levels.

Designing Tax for Multiple Greenhouse Gases

As a policy instrument for emission mitigation, global carbon tax is widely discussed and has also been tested in some parts of the world. However, while talking about emission mitigation one needs to be careful to take into account a group of GHGs and not CO₂ alone. It is a case of multiple pollutants, such as CO₂, Methane (CH₄), Nitrous oxide (N₂O), several Fluorocarbons (such as CFC11, CFC12, HFC23) etc. What is important is to note that the sources of such pollutants are significantly diverse. While fossil fuel burning and deforestation is the primary source of CO₂ emission; livestock, rice cultivation and manure management are major sources of Methane. Nitrous Oxide emission, on the other hand, mostly comes from the agricultural activities and the use of fertilizer. Even if the problem caused by over concentration of each of these gases is similar in nature, the degree of the effect is not identical. So, 'how many tons of CO₂ would lead to similar impact caused by a ton of CH₄?' is a question of immense importance to design efficient economic instruments such as emission tax. As soon the concern is to tax a group of pollutants, and not CO₂ alone, the issue of relative taxation becomes important (Michaelis, 1992). What should be the optimal tax on CH₄ relative to CO₂? To answer this question it is important to know two scientific characteristic of these gases: the capacity of absorption of the infrared radiation and its natural rate of degradation in the atmosphere or inversely, their atmospheric lifetime. The first one gives an idea about the amount of CO₂ equivalent to one unit of the other GHG in terms of its greenhouse impact and the second one provides information on how fast does the natural removal of the gas from the atmosphere take place. It is therefore important to have a knowledge of accurate values of these natural parameters to have a multiple pollutant tax policy in place. Higher the capacity of absorption of the infrared radiation and lower the rate of degradation (or longer the atmospheric lifetime), higher will be contribution of the gas to global warming. Michaelis (1992) in his paper "Global Warming: Effective Policies in the Case of Multiple Pollutants" developed a model to design optimal tax policy for multiple pollutants. This model has its own merits to solve for the efficient level of relative taxes for multiple GHGs in a simplified manner. The model also formulates the optimal time path for taxes on each of the gases from a dynamic optimization perspective. It shows that if the economic objective is to minimize the discounted flow of abatement costs (C) (i.e., the cost of mitigation) subject to the warming constraint (for example, not letting the mean surface temperature of the earth to go beyond 1.5°C over and above the pre-industrial level), then the problem of a central planner would be:

$$\begin{aligned} \text{Min } C &= \sum_{t=0}^T \sum_{i=1}^n C_i(v_i(t)) / (1+r)^t \\ \text{Subject to : } S(t) &\leq S^0 \\ \text{or, } (\Sigma)_i (\Sigma)_j \alpha_i (1 - q_i)^{T-t} e_i(t) &\leq S^0 \end{aligned} \quad (1)$$

Table 1 Global warming potential (100 year time horizon) and atmospheric lifetime (http://www.ghgprotocol.org/sites/default/files/ghgp/Global-Warming-Potential-Values%20%28Feb%2016%202016%29_1.pdf)

	1995 IPCC second assessment report	2001 IPCC third assessment report	2007 IPCC fourth assessment report	2014 IPCC fifth assessment report	Atmospheric lifetime
Carbon dioxide (CO ₂)	1	1	1	1	100
Methane (CH ₄)	21	23	25	28	12
Nitrous oxide (N ₂ O)	310	296	298	265	114
HFC 23	11,700	12,000	14,800	12,400	260

Where, $C_i(v_i(t))$ is the cost of the mitigation measure v_i (related to gas i) at period t and r is the social rate of discount. So, C gives the present value of the stream of abatement costs over time horizon T . The constraint implies that the stock of all GHGs measured in terms of their CO₂ equivalence $S(t)$ should not exceed the threshold S° . Two scaling parameters α_i , to capture the amount of CO₂ which is equivalent to one unit of GHG i.e., the warming potential in terms of its greenhouse impact and q_i to capture the natural rate of degradation are used to derive the equivalence. Solving the problem for two GHGs i and j gives the static optimum for each period as

$$\frac{C'_i[v_i(t)]}{C'_j[v_j(t)]} = \frac{\alpha_i}{\alpha_j} \left[\frac{1 - q_i}{1 - q_j} \right]^{T-t}$$

$$C'_i[v_i(t+1)] = \frac{1+r}{1-q_i} C'_i[v_i(t)] \quad (2)$$

This implies that the mitigation activities are to be combined in such a way that the ratio of marginal abatement costs of two GHGs should be equal to the ratio of their warming potentials adjusted for the rate of natural decay. The implications are similar in case of a decentralized planner. So, higher the global warming potential of a GHG, higher will be the relative tax and quicker it degrades the lower will be the relative tax rate. Michaelis calculated the paths of the tax rates based on α_i , q_i depicted in IPCC Report, 1990, taking social discount rate=4% for a twenty year time period. However, certain complexities exist in estimating these natural parameters. These values are estimated on the basis of scientific understanding and the precision of such estimation changes over time. While the most widely accepted definition and figures for the GWPs are presented by IPCC but the values are continuously being modified with increased precision of scientific modeling. As a result, no two Assessment Reports of the Panel could furnish the same value for warming potential of these GHGs. Table 1 gives a glimpse of changing reported GWP of three GHGs over time: Methane (CH₄), Nitrous Oxide (N₂O) and a fluorocarbon- HFC23.

In this article, an attempt has been made to see the effect of such changes in the values of natural parameters on the optimal tax path. The optimum tax paths are calculated based on Eq. (2). While the atmospheric lifetimes are assumed to be constant over time, (100, 12, 114 and 260 years for Carbon Dioxide, Methane, Nitrous oxide and HFC 23 respectively), GWP is varied based on IPCC reports. The rate of discount is assumed to be 4% and the time period considered is twenty, as assumed by Michaelis. Further, the tax on CO₂ in the first period is assumed to be unity.

The optimum tax paths for these pollutants are depicted in Fig. 1. CH₄ 1995, in the north east box in Fig. 1, shows the optimal tax path calculated for methane based on the warming potential reported in 1995. Other graphs have similar implications for other gases and other years. There are few important matters that need attention. First, if at the first period the tax on CO₂ is unity, then the relative tax on methane, nitrous oxide and HFC 23 should be approximately 7281 and 13,938 respectively (considering the global warming potential reported in 2014). Further, the optimal tax paths will be different if the warming potential is changed. This explains the gaps between the curves in each diagram calculated on the basis of different warming potentials. It also shows that in the short run, the divergence may not be significant (for initial periods tax rates being almost equal irrespective of the warming potential), but it increases over time. Therefore, it has significant implications towards long term decision making with regard to climate change mitigation. This also has serious policy implication as the sources are different for different GHGs implying different degrees of burden on different sectors. So, implementation of any tax for a reasonably longer period of time calculated on the basis of inaccurate GWP or atmospheric lifetime will distribute tax burdens on sectors in a sub-optimal way following the essence of the model. Any policy designed for very long run always has less flexibility to incorporate modified values of these parameters. This limitation has a very important role to play in deciding the length of a policy, especially in the global context. So, there is a need for constant reformulation of tax rates based on new parameters.

Levelized Cost of Conserved Carbon

The literature on climate change mitigation has been moving beyond usual cost benefit analysis as expected benefits of mitigation policies often ignores the irreversibility of climate change and related risks. This leads to cases where estimated cost exceeds the

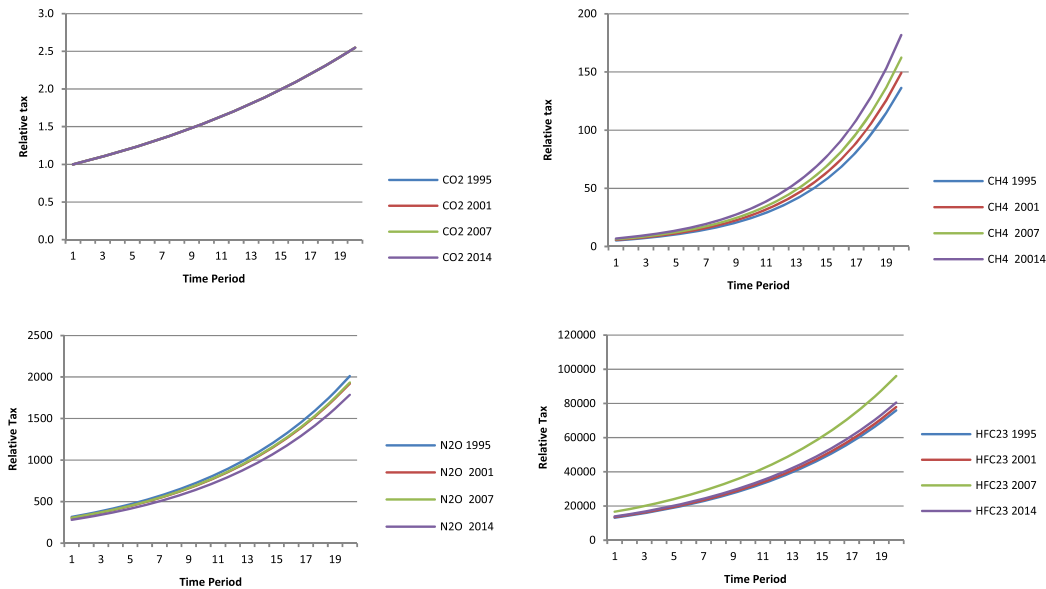


Fig. 1 Optimum tax paths for Carbon Dioxide (CO₂), Methane (CH₄), Nitrous oxide (N₂O) and HFC 23.

estimated benefit in a shorter time frame. However, if one can see to the fact that the impacts of climate change are irreversible, the benefit derived from climate change mitigation seems to be extremely high though unquantifiable. The appropriate objective therefore, is not to implement a mitigation measure where benefit exceeds cost, but to choose the least cost mitigation option to achieve the target of climate stabilization (see “Relevant Websites section”). LCCC gives a good methodological base in this context. This section is based on a related study where the concept of LCCC was deployed to assess a range of energy efficiency measures implemented in a set of Indian industries (Fischedick *et al.*, 2014). The analyses of the cost of such energy efficiency measures and the resultant emission mitigation provide an opportunity to come up with the effective mitigation cost per unit of CO₂.

Assuming, annual emission reduction, annual operation & maintenance costs and annual benefits to be constant over the lifetime of the technological option, LCCC can be represented as:

$$LCCC = \frac{(CRF * \Delta I) + \Delta O \& M}{\Delta C} - \frac{\Delta B}{\Delta C} \quad (3)$$

Where,

$CRF = \left(\frac{i}{(1+i)^n - 1} + i \right)$, i is rate of interest and n is the lifetime of the option in years

ΔI is the investment to deploy the energy efficiency measure

$\Delta O \& M$ is annual operation and maintenance costs

ΔB is the annual benefits compared to a baseline for which no such measure is implemented (for example, avoided cost of energy, cost of avoided emission etc.)

ΔC is annual emission reduction.

To arrive at LCCC, data are required on the annualized investment cost of the measures, annual operation and maintenance cost of the measures and energy saved and/or emission avoided per year as compared to the no policy scenario. Bureau of Energy Efficiency (under Ministry of Power) in India publishes the investment cost of the energy efficiency measures adopted by the winners of the National Awards on Energy Conservations (One of the innovative voluntary schemes initiated by the Government of India, Ministry of Power, to promote energy efficiency and conservation is the Energy Conservation Awards to the industrial units) in different years. To compute the annualized investment cost the rate of interest has been assumed to be 8% per annum. The lifetime of the technology/measures are determined on the basis of expert consultations. Once the annualized investment cost is computed, the operation and maintenance cost is assumed to be equal to 10% of the annualized investment cost. The dataset also mentions the energy-saving potential of each of the measures in either of the two following ways (i) avoided energy cost per year in INR or (ii) avoided energy use per year in kWh. For some measures, both (i) and (ii) are mentioned in the dataset and based on that the cost incurred by the industrial units per kWh is calculated and it is found that on an average the value is close to INR 4.99 (USD 0.1) (1 USD = 45.67 INR; source: see “Relevant Websites section”). Using this conversion ratio the avoided energy use per year is obtained for the measures where only (i) is furnished in the dataset. Further, in India, an average of 0.94 Kilogram of CO₂ is emitted per kWh of electricity generation (Raghuvanshi *et al.*, 2006). Using this emission factor we also estimate how much CO₂ emission is mitigated when a particular amount of energy use is avoided through implementation of an energy efficiency measure.

A wide variety of energy efficiency measures implemented by Aluminium (26), Cement (42), Chemical (62), Integrated Steel Plant (ISP) (30), Pulp and Paper (46) and Textile (75) industries during the period 2007–2012 in India are considered. These measures have been implemented at varying costs. The technologies/measures are divided into six categories based on the cost per

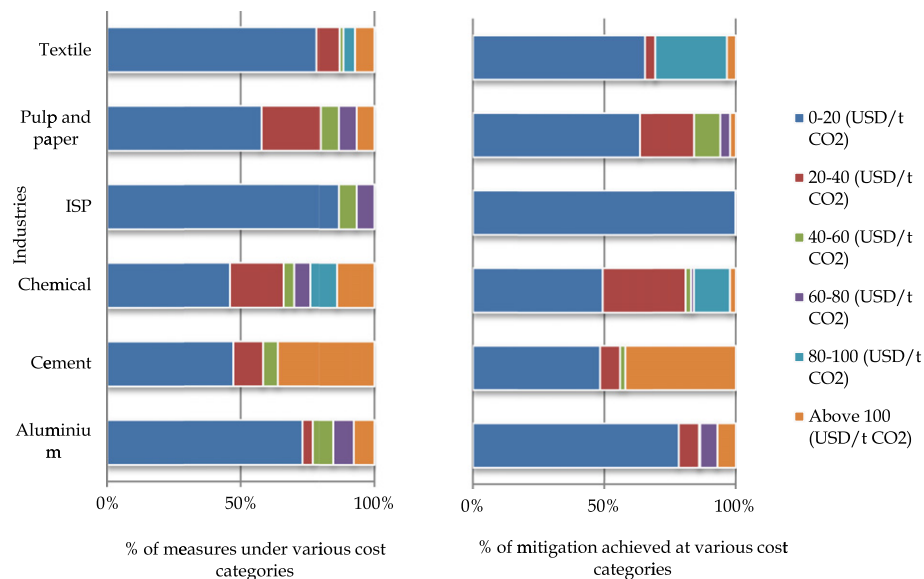


Fig. 2 Energy efficiency measures taken and mitigation achieved by Indian industries under various cost (USD₂₀₁₀/tCO₂) categories.

ton of avoided CO₂ emission. It ranges from '0–20 USD per ton of avoided CO₂ emission' to 'more than 100 USD per ton of avoided CO₂ emission'. The distribution of the measures among the cost categories is represented in the left hand panel of Fig. 2. It shows that 87%, 73%, 47%, 46%, 58% and 78% of the measures adopted in the Integrated Steel Plants, Aluminium, Cement, Chemical, Pulp and Paper and Textile industries, respectively, fall under the least cost category '0–20 USD per ton of avoided CO₂ emission'. In fact 63% of all measures across industries fall under this category. To understand the mitigation potential of the measures under various cost categories, the distribution of total mitigation achieved over six cost categories (right hand panel of Fig. 2) is presented. It shows that those 63% under the cost category '0–20 USD per ton of avoided CO₂ emission' are associated with 93% of total avoided CO₂ emission. For Integrated Steel Plants, Aluminium, Cement, Chemical, Pulp and Paper and Textile industries 100%, 78%, 48%, 49%, 63% and 65%, respectively, of avoided CO₂ emission are associated with the least cost category. This shows that most of the energy efficiency measures and the related emission mitigation are associated with low per unit costs of avoided emission. However, some high cost options have also been implemented by some production units.

Eq. (3) also shows that LCCC will be negative when the benefit derived from the energy efficiency measures exceeds the cost of the same for each unit of avoided emission. Now the benefit can be derived from two sources: avoided energy cost and revenue derived from avoided emission in presence of a functional carbon market. Most of the measures under consideration, however, yield a negative value of LCCC even without consideration of any carbon price. This implies that the energy bills saved through implementation of these measures are high enough to offset the cost of the measures in this example. There are, however, few high cost measures (all of them falling under the cost category 'more than 100 USD per ton of avoided CO₂ emission') for which the LCCC is positive and the cost of the measure exceeds the benefit derived if only the avoided energy bill is considered. Next, we try to add the second component of benefit i.e., the revenue that can be derived out of the avoided emission in presence of a carbon market. The trend of volume weighted average price of CO₂ (USD/tCO₂) in the global carbon market (Fig. 3), shows that during 2007–2011, it peaked in 2008 to touch the value 30USD/tCO₂ (Bloomberg, 2012).

So even if the highest carbon price (30USD/tCO₂) is added as benefit derived from the energy efficiency measures through avoided emission, the positive sign of LCCC of these high cost measures remains unchanged. In other words, in our example 94% of avoided CO₂ emission achieved through 65% of measures is associated with a negative LCCC with carbon price greater than or equal to 30 USD/tCO₂. This leads the way towards a discussion how a low carbon price will fail to capture the social benefit derived from emission mitigation.

Measuring Carbon Footprint

Traditional economics conceptualizes consumer's equilibrium as the highest level of satisfaction that she can derive from the consumption of goods and services given the price and income constraint. This implies with an increase in population, leading to increase in the number of consumers and an increase in average income across world, demand for goods and services will grow, if the real prices do not go up significantly. However, if climate change is taken into consideration, income is not the only constraint, there are also global bio-physical constraints. GHG assimilation capacity of the atmosphere is one such example. Therefore, new indicators are emerging to see the implications of production and consumption to address such bio-physical constraints.

In addition to traditional economic performance indices, recent literature therefore suggests several alternative performance indicators to monitor resource use pattern in bio-physical terms (Chakraborty and Roy, 2013): Ecological Footprint (EF), Energy Footprint (EnF), Water Footprint (WF) and Carbon Footprint (CF). Among these four measures, the oldest is EF, introduced in the 1990s by William Rees

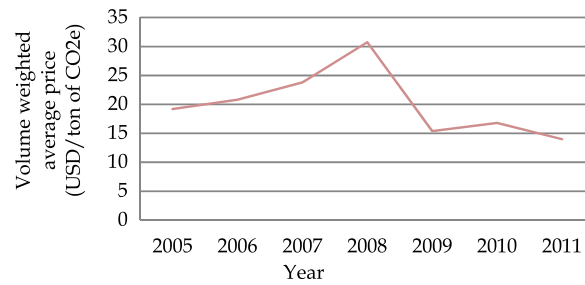


Fig. 3 Volume weighted average CO₂ price in global carbon market. Derived from Bloomberg, 2012. Bloomberg new energy finance. The future of energy 2012 results book. New York. Available at: <https://about.newenergyfinance.com/blog/bloomberg-new-energy-finance-2012-summit-results-book/>. (accessed 26.07.2018).

and Mathis Wackernagel (Rees and Wackernagel, 1994). It measures the use of available bio-productive space (in hectares) to the entity. EnF (in hectares), accounts for the bio-productive space needed as a 'sink' for assimilating the waste generated by human induced activities. WF is a measure of the volume of freshwater used at the place where the actual production and water use take place. It is normally expressed as green, blue and grey WFs: the green WF refers to the consumption of rainwater stored in the soil as soil moisture; the blue one refers to the evaporated surface and ground water and the grey WF refers to volume of freshwater required to assimilate the load of pollutants. Finally, the concept of CF originated from the concept of EF and came to be widely known since the year 2005 (Safire, 2008). It refers to the sum of GHG emissions caused by an organization, due to event or production and is expressed in terms of CO₂ equivalent. CF can be measured for a product or supply chain of a product; public or private institutions, such as universities; industry/business houses or companies including small and medium enterprises (SMEs), service agencies, data centres etc., or for a country or some parts of a country. While the concept of CF is relatively new, it has gained immense importance in the domain of climate change mitigation. This section discusses measurement of CF based on a related case-study in India.

Product Carbon Footprint (PCF) is one of the emerging environmental performance indicators that work as a part of larger contributory effort to expedite the move toward a low carbon economy. It estimates the extent to which products and activities of a business house along the supply chains contribute to carbon emissions. It is also useful to cater to the growing demand of the stakeholders for low-carbon products along with associated carbon information. It provides an opportunity for the businesses to identify the drivers behind emissions, scope to reduce emissions across the product life cycle leading to cost savings, supporting the development of future low-carbon products, and thereby contributing in emission mitigation. Direct and indirect emissions from three main sources are usually included for calculating the overall Carbon Footprint as per Life-Cycle Assessment (LCA) GHG Protocol Standard (WRI and WBCSD, 2008), namely: Scope 1 – only direct GHG emissions i.e., emissions that are owned or controlled by the entity, e.g. emission from own power generation (including back-up power generation), fuel used in the canteen of any institution, where kitchen is attached, emission resulting from the use of company/entity-owned vehicles etc., Scope 2 – indirect emissions occurring from consumption of purchased electricity or steam, and Scope 3 – all indirect emissions other than under Scope 2. Examples of indirect emissions under Scope 3 include emissions from distance traveled and fuel burnt for employees traveling for business purpose, transportation of input, output and disposal of wastes etc. (Rothberg, 2011).

The present case study is related to measurement of PCF of a ton of newsprint paper manufactured from wastepaper by a paper production unit in West Bengal, an eastern state in India and is reported from the work of Chakraborty (2015). The calculation is based on PAS 2050 method that includes GHG emissions from energy use, combustion processes, chemical reactions, refrigerant losses and other fugitive gases, operations, service provisions and delivery, land use change, livestock, other agricultural processes and wastes in the assessment (Plassmann et al., 2010). Capital goods are not taken into consideration in the PAS 2050; emissions related to human energy inputs, transport of consumers to and from shops, transport of employees to and from work are also excluded. In the present case study organizational boundaries encompasses both the operations over which the organization can exercise its control and also those like transportation of raw materials, wastes and finished goods. GHG emitted for producing a ton of paper measured in terms of kg CO₂e has been considered as the main operation in this case study. The product related GHG emissions have been classified under six stages or heads, taking into consideration the consumption of electricity, freshwater, wastewater and generation of wastes: pulping stage, paper making stage, finishing and conversion stage, steam generation, water treatment and distribution of finished products.

While activity data are collected through primary surveys, data on emission factors are obtained from secondary sources. The data collection process was as per PAS 2050 analysis requirements. For each activity PCF has been calculated based on the following equation:

$$\text{Activity (kg/litres/kWh/tkm etc.)} \times \text{emission factor (kg CO}_2\text{e per kg/litres/kWh/tkm)} \quad (4)$$

Emission figures obtained from each activity are then summed up to calculate total CF.

Results suggested that total emissions produced by the production unit for the year 2013–14 was 33,788,800 kg CO₂e for producing 18,000 tons of paper. PCF of a tone of paper was 1877.16 kg CO₂e. The breakdown of the unit's carbon footprint (in kg of CO₂e) shown under the various stages of production reveals that the largest source of emission for producing a tone of paper resulted from steam generation process, followed by paper making and then pulping. The remaining emission resulted from distribution of finished goods (occupying the fourth largest segment) and emission from finishing & conversion being the least

contributor. An analysis of percentage-wise contribution of production and distribution components towards greenhouse gas emissions (in kg CO₂e) per ton of paper production revealed that grid energy was on the top of the list followed by fuel (non – coking coal grade C&D) consumption and waste. Transportation of raw materials, wastes and finished goods, freshwater and wastewater were in the fourth, fifth and sixth position in the contribution league.

The study was useful to identify the emission hotspots of the industrial unit and to develop recommendations accordingly. From the calculation of the value and analysis of results of product carbon footprint it may be inferred that this footprint calculation results in communicating information on the environmental impacts to the business, its stakeholders and to the public at large. The results obtained by using this new performance footprint indicator, provide an assessment of the production unit's environmental impacts over time and in developing an assessment of sustainable limits for the product manufactured by the case study unit.

Summary

This article introduces readers to the fundamental concepts of economics that are used to address the issue of climate change mitigation. It discusses how GHG emission can be conceptualized as a 'bad' generating 'negative externality', that too transboundary in nature, and why market fails as an institution to govern a 'bad'. It also discusses why intervention by national governments in absence of a supra-national government is not able to internalize negative externalities created by GHG emission. However, international agreements evolved over time to address climate change mitigation in a politically fragmented world. The roles of such supra-national bodies to surrogate market mechanisms and/or to create a form of global governance to internalize the externality had been important. Designing instruments for emission mitigation is a challenge since there are several layers of complexities. This article demonstrates how optimal design of policy instruments requires careful consideration of several facts – including the fact that emission mitigation involves not only carbon dioxide (CO₂), but of a number of GHGs with different implications towards climate change. Emission mitigation involves cost. The LCCC method allows industries or other economic units to get a clear comparison of the cost of emission mitigation measures vis-à-vis their mitigation potential. Finally, it shows how in a bio-physically constrained system, new indicators related to carbon footprint can provide a useful measurement tool. Needless to mention that this article is not an exhaustive attempt to apply economic lens to GHG emissions issue but just a modest beginning.

See also: Advanced Vehicle Systems and Technologies: Economic and Environmental Implications. The Applicability of the Inflection Point in the Environmental Correction Process

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Solar Geoengineering

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Introduction

Emissions of phylogeny greenhouse gases changing Earth's climate and enforce substantial risks for current and future generation. To manage these climate hazards what are the strategies to be followed which are scientifically sound, economically strong, and ethically defensible. Seriously addressing temperature change due to climatic conditions suggests that cutting carbon emissions and, ultimately, reducing the carbon already within the atmosphere. There's no means around it. Another sort of involvement, however progressively gathering attention: Solar Geoengineering, which is a process where sun rays are reflected back to space and make earth's surface cool. For climate change it's not a permanent solution, and having a drawback of alarming environmental and political risks which are caused by its own, however, it's a tough price exploring (Wagner and Weitzman, 2018). The principle underlying solar geoengineering is easy enough: Brighter colors reflect more light. That's why houses in Mediterranean villages are usually painted white. Because of this situation scientists are concerned about the loss of polar ice, which have a sensible surface that reflects the incident solar radiation. Where open water will absorb sunlight and heat. In 1965 a suggestion was given to US president for solving the problem is solar geoengineering. First attempt has made to brighten ocean surface on a grand scale by using solar geoengineering.

As the research is shifted from oceans to the skies, the first important and widely discussed basic scheme is solar geoengineering which involves spreading small reflected particles within upper portion of the atmosphere. Answer to the question that solar geoengineering will work or not is given by the nature. Large volcanic eruption usually decreases the mean average global temperature. On 1991 in Philippines eruption of Mt. Pinatubo released almost 20 million tons of sulfur dioxide into the stratosphere. The global mean temperature in 1992 has decreased almost a degree Fahrenheit because of the eruption (Wagner and Weitzman, 2018).

But volcanic eruptions are generally large natural events, providing a rapid and temporary global cooling. Temperatures shortly return to previous levels. Solar geoengineering would need further careful and long-term approach. When we are doing practical problem and solving that problem it should start slowly and the effect could be considerable for long term. The scientists framed out a research hypothesis the basis of a proposal to decrease half of the increase in global average warming from a specific date onward. The situation is like that they are preparing up for after a decade a million tons of sulfate aerosol is to deliver in the stratosphere each year. We can't notice the impact of that work with our naked eye where 1% of solar radiation reflects back in to space (Wagner and Weitzman, 2018).

The burning of fossil fuels releases 25 Pg of CO₂ per year into the atmosphere, which is leading to global warming. It also emits 55 Tg Sulfate as SO₂ per year (Stern, 2005), in which half of this is converting into sub-micrometer size sulfate particles, the remainder being a dry deposit. Sulfate particles partially counter the concentration of greenhouse gases by backscattering solar radiation into space. Sulfate particle acts as cloud condensation nuclei and it also influences properties of the cloud likely micro-physical properties and optical properties which increase cloud albedo (Crutzen, 2006a,b).

There is a problem that we can't simply make such decision responsibly because we don't know enough about which material would be the safest and most effective when we use them. Sulfate aerosols used in most plans, largely because they are matching with the known effects which are observed in volcanic eruptions. But there is a problem with these aerosols they play a role in depleting stratospheric ozone. By some preliminary research points, calcium carbonate has a possible use as an alternative. Making the planet more reflective is not a replacement for cutting carbon-based pollution. Solar geoengineering is not a substitute for cutting emissions. It is at best a supplement (Wagner and Weitzman, 2018).

If we combine cutting of greenhouse-gas emissions and solar geoengineering then we can keep the temperatures of the planet under 1.5°C. Decreasing the emissions alone cannot bring the temperature down. As the emissions are stopped inertia of the climate and uncertain feedback such as loss of permafrost carbon, there will be a significant change but the world continues to warm for more than a century. Reducing the effect of heat-trapping greenhouse gases by reflecting a small fraction of sunlight back to the atmosphere is a process done by humans is called solar geoengineering. In a future large range of research efforts can yield quick progress because development in the technology of solar geoengineering would be a great exercise in the application of existing tools of aerosol science, atmospheric science, climate research, and applied aerospace engineering (Keith et al., 2017).

We cannot judge the results of solar geoengineering meaningfully without a scenario of implementation practically. It is now common to assess the balance between the risks and benefits of solar geoengineering effectively more scientific research is needed, here after it can be called solar radiation management (SRM). Any technology will have a set of technology-specific impacts for producing radiative, such as ozone loss arising from the introduction of aerosol particles in the stratosphere. A risk listed occur by SRM is ocean acidification, yet acidification depends almost solely on cumulative CO₂ emissions and is unaffected by SRM. If

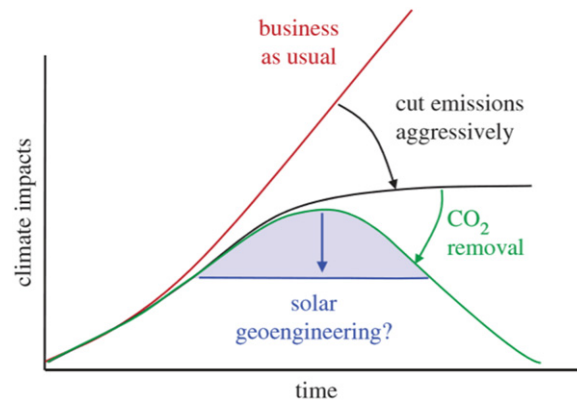


Fig. 1 Impact on climate by the time with reduction in CO₂. Reproduced from MacMartin, D.G., Ricke, K.L., Keith, D.W., 2018. Solar geoengineering as part of an overall strategy for meeting the 1.5°C Paris target. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 376, 20160454.

SRM is used as a substitute for emissions mitigation then ocean acidification is a risk of SRM but in this case, the risk derives from the increase in emissions not from SRM (Keith and MacMartin, 2015).

SRM scenario combines three elements: a specific method of altering solar forcing, an initial trajectory for SRM radiative forcing over time, and a plan for altering the trajectory based on new information. SRM scenario is chosen to meet the following criteria (Keith and MacMartin, 2015):

- (1) It is temporary in that the endpoint is zero SRM.
- (2) It is moderate in that it does not offset all of the global mean temperature change due to increased greenhouse gases.
- (3) It is responsive in that it explicitly recognizes that the amount of SRM will be adjusted in light of new information (Fig. 1).

As mentioned in previous discussion which is to decrease the atmospheric temperature there is agreement done in Paris which has a specific goal of holding the increase in the global average temperature to well below 2°C which is above pre-industrial levels and to study to limit the increase in temperatures to 1.5°C, to achieve this in less time there is process immediate reduction to net-zero emissions (MacMartin *et al.*, 2018). To this things are happening quite opposite that present commitments decreasing of CO₂ emissions are projected to result in warming closer to 3°C (Rogelj *et al.*, 2015). Approaches for ‘net-negative emissions’ carbon dioxide removal (CDR) is already impinged in future emission process, which is a strongly unrealistic scale. Nonetheless, over the period of overshoot, the technologies which are adopted now might bring the temperature to rise back below 1.5°C (Ricke *et al.*, 2017).

As per the figure, it is clear that solar geoengineering (or solar radiation management, SRM) could be considered as an alternative possibility to the other methods for maintaining long term climate damages. The purpose of solar geoengineering is to reduce climate changes by reflecting some sunlight back to space. The most frequently discussed approach is to inject aerosols or their precursors (e.g., SO₂) into the stratosphere the same mechanism by which large volcanic eruptions cool the planet. Another approach is marine cloud brightening (MCB), which aims to increase cloud albedo through injection of sea-salt aerosols the effectiveness of this is less certain (Latham *et al.*, 2012) (Table 1).

Other techniques have also been proposed, from space-based that are likely too expensive to land- or ocean-albedo modification that are either less scalable, have other environmental concerns (such as adding surfactants to the ocean), or are simply less well studied (MacMartin *et al.*, 2018).

Sulfate geoengineering is a proposed method to partially counteract the global radiative forcing from accumulated greenhouse gases, potentially mitigating some impacts of climate change. While likely to be effective in slowing increases in average temperatures and extreme precipitation, there are known side-effects and potential unintended consequences which have not been quantified. One such consequence is the direct human health impact (Pitari *et al.*, 2014; Effiong and Neitzel, 2016). Given the significant uncertainties, we take a sensitivity approach to explore the mechanisms and range of potential impacts. Using a chemistry-transport model, we quantify the steady-state response of three public health risks to 1°C global mean surface cooling (Eastham *et al.*, 2018).

The mechanisms by which an SRM proposal affects these outcomes can be separated into two categories: the “direct” impacts of the method, and the “RF (radiative-forcing)-driven” impacts. The figure below gives a conceptual overview of how these categories apply to the impact pathways between stratospheric injection of sulfate aerosol and human health impacts. “Direct impacts”, shown in black, include any effects of the technique which would occur even if there were no effect on the climate. For sulfate geoengineering, an example would be the descent of injected aerosol to the surface (Fig. 2).

SRM (solar radiation management) is not designed for reducing the concentration of GHGs (greenhouse gases) in the atmosphere; it only makes the warming effect. So, if SRM is used to make high-level warming and its distribution occur suddenly, temperatures would come towards the levels they would have reached without the geoengineering (McCusker *et al.*, 2012, 2014). This effect is known as “termination shock” or “termination effect”. This effect could be very damaging for nature and human

Table 1 Advantages and disadvantages of stratospheric geoengineering

Method	Confidence that substantial global ΔRF (e.g. $> 3 \text{ W m}^{-2}$) is achievable	Advantages	Disadvantages relative to stratospheric sulfate
Stratospheric sulfates	Very high: current technologies can likely be adapted to loft materials and disperse SO_2 at relevant scales	Similarly, volcanic sulfate gives an empirical basis for estimating efficacy and risks	
Other stratospheric aerosols	Moderate: depends on aerosol, lofting similar to sulfate but aerosol dispersal much more uncertain	Some solid aerosols have less start. heating and minimal ozone loss	Harder to bound uncertainty since not naturally occurring in the stratosphere
Marine cloud brightening	Uncertain: observations support wide range of CCN impact on albedo; substantial process uncertainty	Ability to make local alterations of albedo; and modulate on short timescales.	Only application on marine stratus covering approximately 10% of the Earth means RF inherently patchy
Cirrus thinning	Uncertain: deep uncertainty about a fraction of cirrus strongly dependent on homogeneous nucleation; no studies examining the diffusion of CCN	Works on longwave radiation so could provide better compensation	Maximum potential cooling limited; zonal distribution of RF constrained by the distribution of cirrus
Space-based	Low physical uncertainty, but deep technological uncertainties	The possibility of near 'perfect' alteration of the solar constant	Sustainably more expensive

Note: MacMartin, D.G., Ricke, K.L., Keith, D.W., 2018. Solar geoengineering as part of an overall strategy for meeting the 1.5°C Paris target. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 376, 20160454.

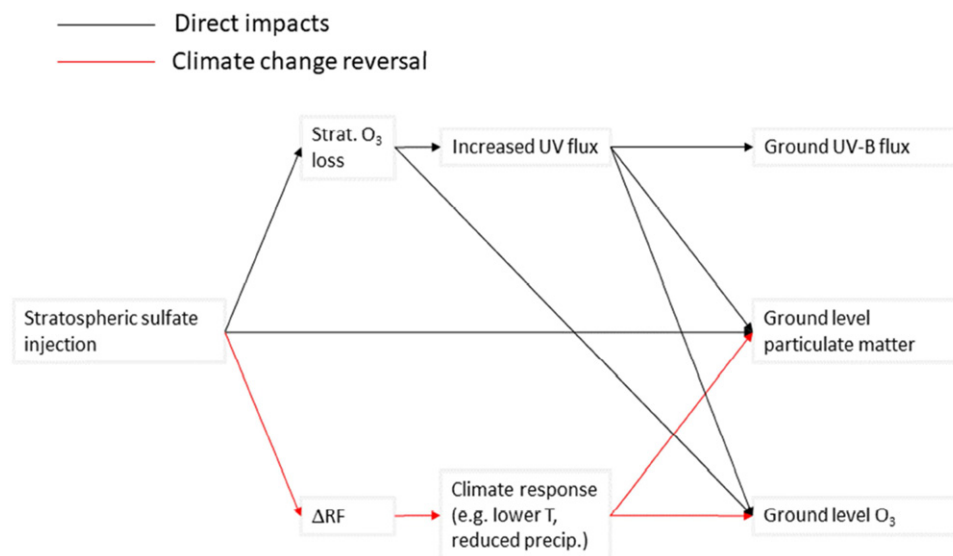


Fig. 2 Impacts of sulfate geoengineering on humans. Reproduced from Eastham, S.D., Weisenstein, D.K., Keith, D.W., Barrett, S.R.H., 2018. Quantifying the impact of sulfate geoengineering on mortality from air quality and UV-B exposure. *Atmospheric Environment* 187, 424–434.

systems as the rate of warming is more than regularly expected climate under phylogeny climate change that means both human and ecosystems have less time to adopt that rapidly changing climatic conditions (McCormack *et al.*, 2016; Trisos *et al.*, 2018). Thermal shock can be defined as a rapid and strong rise in global temperatures that do the termination of SRM distribution (Parker and Irvine, 2018).

The United Nations Framework Convention on Climate Change has been working for reduction of greenhouse gas emissions to “avoid unsafe phylogeny interference with the climate system” (UNFCCC, 1992). Aerosol geoengineering links on offsetting the forces effects of greenhouse gas emissions with the forcing effects of aerosol emissions. The possibility of intermittent aerosol geoengineering forcing as well as negative impacts of the aerosol forcing itself may cause economic damages that far exceed the benefits (Goes *et al.*, 2011).

Models

In previous confer scientists gave their absolution on SG and to performed examinations using some models ensemble to know the agreement and disagreement of the models to following questions (Kravitz *et al.*, 2011).

- (1) Do CO₂ induced regional temperatures and precipitation values can be restored by global level geoengineering to diligence level?
- (2) Does the global scale geoengineering effectiveness depend on the amount of geoengineering?
- (3) Does an assessment of the effectiveness of global-scale solar geoengineering depend upon the relative weighting between temperature and precipitation?
- (4) Can we achieve the same effect as a transient one with continuous stratospheric aerosol and what extent precipitation would be compensated by a regional change in evapotranspiration?

To answer these questions some models are proposed which suites to standardized climate modeling experiment. For coordinating such experiments one framework is proposed that is known as Geoengineering Model Intercomparison Project (GeoMIP) (Kravitz *et al.*, 2011). The Program for Climate Model Diagnosis and Intercomparison (PCMDI) has consented to archive results from these experiments, so they can be openly studied. A number of simulations to be performed should be small because the Climate Model Intercomparison Project 5 (CMIP5; Taylor *et al.*, 2008) is already spreading the proficiencies of the modeling group.

Kravitz *et al.* (2011) used G1, G2, G3 and G4 codes to a suite of experiments. Simplest conceivable probes of balancing increased long-wave forcing with short-wave forcing are G1 and G2, i.e., by decreasing solar constant. From these experiments which are idealized to disclose the basic model retorts to the forcing balance without the added intricacies of conflicting treatments of stratospheric aerosol in various models. In this experiment, the author is trying to attain a perfect balance in radiative forcing but they are aiming to get the net balance as close to zero. From the results of this simulation validation of model has done as a part of GeoMIP runs. From a model control run, G1 experiment is introduced and will build on a CMIP5 simulation in which quadrupled CO₂ concentration can be observed promptly. Reduction in solar constant will balance global average radiative forcing from CO₂ this is done in G1. Radiative forcing of CO₂ is measured during CMIP5 quadrupled CO₂ run and the reduction in solar constant needed to compensate for force is done by a simple calculation using global average planetary albedo (Figs. 3 and 4).

After simulating a few years and monitoring radiative balance correction to this first estimation of the solar constant can be made. Both CO₂ radiative forcing and planetary albedo differ from one model to another so a different solar constant change may be needed. This change in solar constant is applied in G2 experiment (Figs. 5 and 6).

Experiment G3 is comparable with G1 and G2 but more realistic, that means it will give a scenario of execution of stratospheric geoengineering.

G3 assumes an RCP4.5 outline (representative concentration pathway, with a radiative forcing of 4.5 W m⁻² in the year 2100; Moss *et al.*, 2008) but with additional stratospheric aerosol added starting in the year 2020, which is a reasonable estimate of when the delivery systems needed to inject the aerosols, might be ready. To keep the planetary temperature about constant and balance phylogeny forcing stratospheric aerosol will be added progressively.

Experiment G4 similar to experiment G3 simulates a stratospheric sulfate aerosol layer. G4 involves the injection of stratospheric aerosols at a specific constant annual rate instead of attaining radiative balance, turned on precipitously in the year 2020. When uncertainties that can arise in evaluating the impact of geoengineering then results of G4 experiment will be helpful in assessing when the models are used to transmute emission ratio into concentrations. Authors base the proposed injection of aerosol rate is 5 Tg SO₂ per year on several considerations. Several estimates (Rasch *et al.*, 2008; Robock *et al.*, 2009) have implied that 3–5 Tg per year of SO₂ into lower stratosphere compensate a doubling of CO₂ concentration. 5 Tg SO₂ rate of injection per year interprets into 0.0137 Tg SO₂ per day as Crutzen (2006a,b), and Robock *et al.* (2009). Rasch *et al.* (2008) suggest 1.5 Tg of sulfur per year would be enough but Kravitz *et al.* (2011) proposed using 5 Tg SO₂ per year, to reduce the global average temperature to about 1980 values.

A group of simulations will be performed for each geoengineering experiment. The suggested method of generating each group and recommended size of groups will closely arrange with the protocol set by CMIP5 for simulations without geoengineering, additional group members will be developed if the results show in size of groups is insufficient to obtain statistically significant

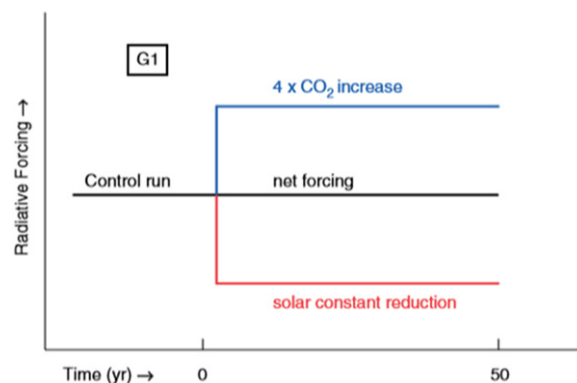


Fig. 3 Schematic of experiment G1.

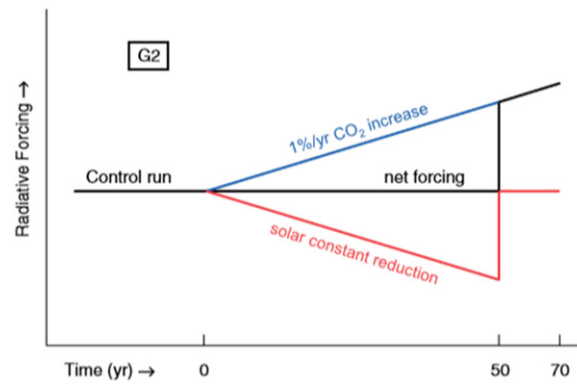


Fig. 4 Schematic of experiment G2.

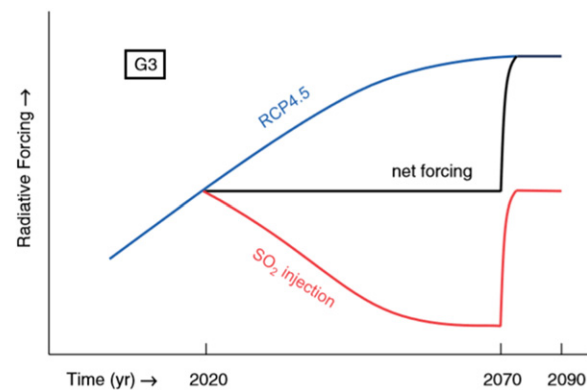


Fig. 5 Schematic of experiment G3.

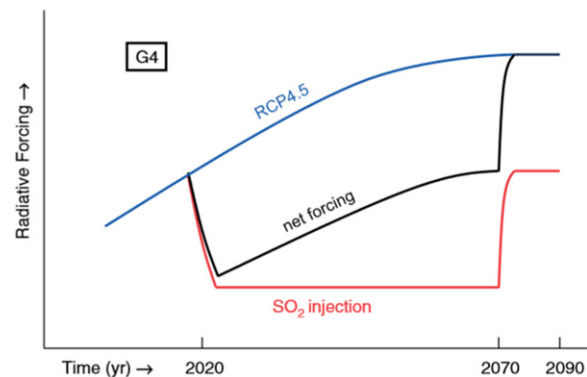


Fig. 6 Schematic of experiment G4.

results. In experiments G2, G3, and G4, the geoengineering will be applied for only the first 50 years, but with the courses extended an additional 20 years to examine the response to discontinuance of geoengineering.

Kravitz *et al.* (2011) used 12 models to obtain output for three simulations:

- (1) pi Control: a stable preindustrial control simulation.
- (2) Abrupt 4xCO₂: from the climate of pi Control, CO₂ concentrations are instantaneously quadrupled.
- (3) G1: the top-of-atmosphere net radiation changes in abrupt 4xCO₂ are offset by a uniform reduction in solar irradiance.

In each of these simulations, we carry out 12 models as well as we take the mean of 12 models to assemble. Temperature and perspiration average values over 11–50 are taken from the simulations. The climate in Abrupt 4xCO₂ continues to develop as well as in piControl and G1 has approximately reached steady state (Kravitz *et al.*, 2011; Tilmes *et al.*, 2013).

To calculate temperature and temperature and precipitation changes at the grid scale, both in absolute terms and normalized by the standard deviation of interannual natural variability in the piControl simulation $\sigma_{T, \text{piControl}}$, $\sigma_{P, \text{piControl}}$ (Kravitz *et al.*, 2011).

$$\Delta T_{\text{abrupt4} \times \text{CO}_2} = \frac{T_{\text{abrupt4} \times \text{CO}_2} - T_{\text{piControl}}}{\sigma_{T, \text{piControl}}} \quad (1)$$

$$\Delta P_{\text{abrupt4} \times \text{CO}_2} = \frac{P_{\text{abrupt4} \times \text{CO}_2} - P_{\text{piControl}}}{\sigma_{P, \text{piControl}}} \quad (2)$$

From Eqs. (1) and (2) where T (units of °C) and P (units of mm day⁻¹) are absolute values of temperature and precipitation, respectively, and ΔT and ΔP (unit less) are the absolute changes normalized by the standard deviation. To determine the temperature and precipitation partings from preindustrial levels for an arbitrary level of solar reduction g , denoted $\Delta T(g)$ and $\Delta P(g)$, we linearly interpolated between $\Delta T_{\text{abrupt4} \times \text{CO}_2}$ and ΔT_{G1} and between $\Delta P_{\text{abrupt4} \times \text{CO}_2}$ and ΔP_{G1} .

The response of temperature and perspiration to CO₂ and global – scale solar geoengineering had shown in this model closely linear in the range of forcing by doing the interpolation of the climate metric to different modes of solar reduction. The linear trend disdained levels of geoengineering that crossed the solar reduction in G1. Normalized level of solar reduction is defined as $g = \Delta S / \Delta S_{4 \times \text{CO}_2}$, where ΔS is a solar reduction, and the denominator denotes the reduction in solar irradiance that returns the globally averaged temperature to its preindustrial value ($g = 1$) (Kravitz *et al.*, 2011). 12-model ensemble average has been taken after calculating each model. In all calculations, g ranges between 0 (no geoengineering) and 2 (twice the required amount of geoengineering to return global mean temperature to its preindustrial value; also see Supplemental section 1).

The climate change metric D in a given Giorgi region I for a particular level of geoengineering g and weight w is defined by (Kravitz *et al.*, 2011):

$$D_i(w; g) = \sqrt{(1 - w)[\Delta T(g)]^2 + w[\Delta P(g)]^2} \quad (3)$$

w is a dimensionless weight parameter with values in $[0, 1]$. An equal weighting of ΔT and ΔP in calculating D corresponds to $w = 0.5$.

The dimensional quantities only make sense for the special cases of $w = 0$ and $w = 1$. In these cases, the equations for D degenerate into (Kravitz *et al.*, 2011):

$$D_i(g) = |g\Delta T_{G1} + (1 - g)\Delta T_{\text{abrupt} \times \text{CO}_2}| (w = 0) \quad (4)$$

$$D_i(g) = |g\Delta P_{G1} + (1 - g)\Delta P_{\text{abrupt} \times \text{CO}_2}| (w = 1) \quad (5)$$

For ease of assessing the results, one can also express D for precipitation changes in terms of percent change (Kravitz *et al.*, 2011):

$$D_i(g) = \left| g \left(\frac{P_{G1} - P_{\text{piControl}}}{P_{\text{piControl}}} \right) + (1 - g) \left(\frac{P_{\text{abrupt4} \times \text{CO}_2} - P_{\text{piControl}}}{P_{\text{piControl}}} \right) \right| \times 100 (w = 1) \quad (6)$$

Using the above model's calculations have done which were statistically not significant, i.e., a sign of change due to either CO₂ increases or solar reductions.

Effects of Solar Geoengineering

SRM (solar radiation management) can make a warming effect of GHGs (greenhouse gases) but not to reduce their concentration in the atmosphere. Therefore, if SRM deployment terminated suddenly while using to make high-level warming, the temperatures can be reduced by the levels that they would reach by the absence of geoengineering. This effect is known as “termination shock” or “termination effect” (Brovkin *et al.*, 2009). Natural and human systems will damage due to this termination shocks as the rate of increase in warming much higher than normal, as a result, both ecosystems and human systems have less time to adapt to the quick change in climatic conditions (McCormack *et al.*, 2016). By this, we can define a termination shock is a sudden and tolerable rise in global temperatures follows the termination of SRM deployment.

To occur termination shock there must be three criteria that need be satisfied: a large amount of SRM cooling, termination should be done suddenly, and SRM deployment should stay for a minimum period of time. To know better what would form a termination shock, we have to know answers to the following questions (Parker and Irvine, 2018):

- What is the time period for SRM cooling effect before possibility of termination shock?
- At what pace large scale SRM should be scheduled to avoid occurrence of rapid warming?
- For large scale SRM what should be the time length for causing substantial warming?

What is the Time Period for SRM Cooling Effect Before Possibility of Termination Shock?

Terminating SRM suddenly follows rapid warming. At the time of termination, the magnitude of warming will depend on the amount of cooling employed. Most of the modeling studies up to now have similar terminating scenarios, where SRM compensates the warming effect of GHG from decades, at the time of termination so that a sudden rise in global

temperature follows. At the same time, if the magnitude of deployment in SRM is very small, the risk will be a little and substantial rise in global temperature will not appear. The termination shock is defined with a threshold; it is possible to define a cooling threshold under which instantaneous termination of SRM will lead to less than the above threshold at the rate of warming addition. With evaluating the response of global temperature for an instantaneous change in forcing, leads to estimate threshold magnitude of cooling forcing. With simulations of Earth system model indicates that quadrupling of CO₂ concentration (an instant change in radiative forcing of about 7.4 W m^{-2}) instantaneously will respond around one half of equilibrium temperature response occurs within a decade, meanwhile three quarters within 100 years (Parker and Irvine, 2018).

At What Pace Large Scale SRM Should be Scheduled to Avoid Occurrence of Rapid Warming?

SRM deployment was stepped out adequately slow, then the warming rate could be limited, and we can avoid termination shock, even though it causes a very large cooling effect. By RCP 8.5 scenario limiting the rate of warming will imply stepping out SRM at a rate of 0.5°C per decade, but generally, it will be taken as dangerously rapid. With optimistic RCP 2.6 scenario limiting warming rate can expect minimum, 0.2°C per decade which shows stepping out of 50 years per degree Celsius cooling (Parker and Irvine, 2018).

For Large Scale SRM What Should be the Time Length for Causing Substantial Warming?

Rapid warming will follow; if something disturbs activities of large forming SRM deployment they were not stopped. Impact of disturbance would be much less for a full termination shock if SRM deployments were starts before a rapid increase in temperature. "Buffer period" length during the restoration of forcing would be determined by three factors:

- (1) Timescale of radiative forcing where decays of deployment activities starts.
- (2) Timescale for global temperature respond for radiative forcing changes.
- (3) Magnitude of forcing.

First, by sudden stoppage of deployment would not stop the aerosol to scatter the light which has been released in stratosphere, so radiative forcing on the climate is applied. For the observation of stratospheric aerosol the life time of aerosol is calculated which is approximately days, before they are washed out or fallen to the ground.

Second, for change in radiative forcing surface air temperature takes some time to adjust because earth's atmosphere and oceans will take time to warm. The whole process can't able to described by a simple e-folding time, but by observing we noted that for instantaneous change in forcing for one year the response of equilibrium warming is one quarter, for decade response is half and three quarters with in 100 years.

Third, if magnitude of forcing is smaller at the time of termination to cross the given threshold of warming it will take more time. For very large scale deployments which are leading to substantial rapid warming will take some time to cause some effect for the reasons mentioned above.

To classify physical dimensions that are responsible to lead termination shock to finalize that three conditions are followed to occurring of termination shocks

- (1) Deployment of SRM should cause a substantial cooling.
- (2) SRM deployment should be terminated suddenly.
- (3) Disturbance for deployment of SRM should continue for months or longer.

Considering physical characteristics of termination shock and analysis of schemes which are leading to termination statements below will describe them

- (1) To stop termination shock SRM should be maintained with a strong support.
- (2) Characteristics to make a robust and resilient SRM be relatively easy than most proposed elements of termination.

Global-scale solar geoengineering is the deliberate modification in climate system to balance some amount of manmade climate changes. By these changes differential effects in regional climate are resulting.

Conclusion

Partial restoration of global mean temperature to its preindustrial level could reduce the level of temperatures produced by mankind and also the perspiration changes by using a moderate amount of global scale solar geoengineering. Coming to Aerosol geoengineering it depends on counteracting the forcing effect by the emission of greenhouse gas with aerosol emission forcing effect. By the occasional aerosol geoengineering as well as the negative impacts causes economic damage which exceeds the benefits of aerosol forcing. More work in future to be needed to estimate the positives and negative consequences of solar geoengineering on biosphere and society, using more appropriate models and realistic problems.

Appendix A Supplementary Material

Supplementary data associated with this article can be found in the online version at doi:10.1016/B978-0-12-803581-8.11009-4.

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Sustainable Carbon Di-Oxide Sequestration Using Photosynthetic Reactions

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Introduction

Mother earth is unique among planets since she has a suitable environment for the survival of living beings. The atmospheric conditions including temperature are maintained as such that life can exist comfortably here. But in the recent era several challenges have come upon humans to maintain these sustainable environmental conditions. One of the major challenges to mankind is to control climate change for which the responsible components are the greenhouse gases. The main contribution towards greenhouse effect comes from carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and chlorofluorocarbons (CFCs) (Mikkelsen *et al.*, 2010). All these gases are released in the environment due to human activities like burning of hydrocarbons in the engines of automobiles or production of electricity by combustion. CO_2 is one of the major greenhouse gas (GHG) in respect to its contribution to the global warming. Although Methane (CH_4) and Chlorofluorocarbons (CFCs) show much higher greenhouse effect as per unit mass basis, but CO_2 has about 60% contribution on the basis of its amount which is increasing continuously.

The main cause of CO_2 emissions is the increasing demand of energy requirement which is fulfilled by fossil fuel based electric power plants. Rapid industrialization includes enormous increase in the number of chemical plants which manufactures hydrogen, ammonia, cement, limestone and soda ash as well as implements fermentation processes and chemical oxidation processes. Urbanization, deforestation, over population, increasing automobile exhaust also contribute towards the increasing emissions of CO_2 .

One of the possible ways to control climate change is to minimize the amount of CO_2 present in the environment since CO_2 has a major contribution towards greenhouse effect. Though the capture of CO_2 has always been a challenging issue, it can be done by removal of carbon dioxide from the environment and its sequestration for purposes like several purposes. The probable methods of CO_2 capture includes three types of capture technologies namely pre-combustion capture, post-combustion capture and oxyfuel capture. One such process is the capture of CO_2 and its usage for generation of electricity by scrubbing with amines. Another method is by using molecular sieves or by membrane separation. These methods reduce the amount of CO_2 present but are either not cost effective or are not sustainable. Moreover, there are several barriers like energy requirements for chemical conversion of CO_2 , cost of co-reactants, limitations in market along with costs of capture, treatment, and transportation. As a solution, photosynthetic processes for sequestration of CO_2 have been considered in this study.

To reduce CO_2 emission three sustainable preventive measures can be opted. The first being reduction of energy intensity by its efficient use which is very difficult. The second requires use of non-fossil fuel such as hydrogen and renewable energy. The third one involves development of technologies to capture and sequester CO_2 . The technologies available for use of renewable energy sources are not mature enough, so still today fossil fuel dependency is unavoidable to meet the increasing demand of electricity. This makes the third option most viable to protect earth from the expected climatic changes.

Different Ways for Carbon-Di-Oxide Sequestration (CCS)

According to IPCC report 2005, Carbon Capture and Sequestration can be applied to large point sources. The captured CO_2 can be compressed and transported for storage in geological formations, in ocean, in mineral carbonates, or can be used as feedstock for industrial processes. Basically, there are three main routes of CO_2 capture systems: post-combustion, pre-combustion, and oxy-fuel combustion (Figueroa *et al.*, 2008). For post-combustion capture, CO_2 is sequestered from flue gas after the fuels being completely burned. Pre-combustion capture involves the so-called integrated gasification combined cycle (IGCC) system, i.e., the syngas generated from coal gasification consisting of CO and H_2 , is reformed by steam to produce a mixture of CO_2 and H_2 . The CO_2 is removed before H_2 is burnt in the combustion chamber of the gas turbine. In case of oxy-fuel combustion, coal is burned in nearly pure oxygen environment to produce flue gas having high concentration of CO_2 which can be stored or transported directly. Figueroa *et al.* (2008) summarized the advantages and disadvantages for all the three pathways. They believed that pre-combustion capture is applicable to gasification plants and oxy-fuel combustion can be applied to the newly built power plants. Presently all conventional coal-fired power plants combust fuels directly in a boiler to generate power (Merkel *et al.*, 2010). So post combustion capture as an "end-of-pipe" technology is more viable option for existing coal-fired power plants.

Many post-combustion capture technologies like chemical absorption (Rochelle, 2009), adsorption (Harlick and Tezel, 2003), membrane separation (Zhao *et al.*, 2008), Ca-Looping technology (Martínez *et al.*, 2016) and cryogenic fractionation (Hart and Gnanendran, 2009) etc., are proposed and being investigated these years.

Some of these are illustrated here.

Short Term Injection

Carbon-di-oxide can be relocated by direct injection into the sink capable of holding many mega-tones of gas over a period of time. Although this process helps to reduce global warming with immediate effect, most sinks will leak the sequestered CO₂ after a certain period of time.

Ocean injection

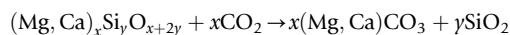
Ocean stores more CO₂ (estimated 38,000 Gt-carbon) than atmosphere (estimated 750 Gt-carbon) and terrestrial biosphere (estimated 2200 Gt-carbon). Annually ocean absorbs 1.7 ± 0.5 Gt from atmosphere. This natural process can be enhanced by direct injection. Depending on economic as well as technological grounds, "Droplet plume" and "Towed pipe" methods are suggested as most viable techniques for CO₂ injection in which liquid CO₂ is injected from a manifold below 1000 m, resulting in a rising plume or CO₂ is injected from a boat at a depth of 1000 m, resulting in a rising plume (Stewart and Hessami, 2005).

But this way of sequestration reduces the pH value of the deep ocean which affects the species like zooplankton, bacteria and benthos that are present in the non-swimming marine ecosystem at a depth of 1000 m or more (Stewart and Hessami, 2005). To resolve this problem and to utilize the delocalized CO₂ ocean fertilization can be opted. In this process the delocalized CO₂ is absorbed by the photosynthetic organisms. Their growth is stimulated by addition of nutrients. The dead organisms are decomposed by the microorganisms through the process of re-mineralization. But the resulting change in phytoplankton structure challenges the marine ecosystem. Additionally, the sinking organic matters decomposes anaerobic which may release other greenhouse gases like methane, nitrogen monoxide etc. which counteract the beneficial effects of carbon fixation (Yang *et al.*, 2008).

Geologic injection

Geologic injection refers to the process of fixation of CO₂ by converting the silicates to carbonates.

Mineral carbonation: This process involves chemical weathering that ensures the long term fixation rather than temporary storage and also reduces the risk of any accidental release of stored CO₂ from underground. In this process the CO₂ converts the silicates to carbonates by following reaction (Maroto-Valer *et al.*, 2005a,b).



The mineral carbonation happens naturally over geologic time scale. The process can also be accelerated by different artificial methods:

- (1) The reaction rate can be increased by enhancing the rate of dissolution of mineral ions by using strong acids. But the strong acids may cause damage to both the reaction facilities and environment (Yang *et al.*, 2008).
- (2) The reaction can also be operated under higher CO₂ pressure. But the higher CO₂ pressure will require intensive energy thereby increasing the cost of operation (Yang *et al.*, 2008).
- (3) The carbonation has also been studied by mechano-chemical process by University of Utah and University of Idaho (Nelson, 2004; Nelson and Prisbrey, 2004). In this process the natural silicates like forsterite, lizardite, wollastonite and synthetic materials like magnesium silicates were ground for a number of times in presence of gaseous CO₂. But the amount of carbon fixation was insignificant with respect to energy input for grinding activity (Nelson, 2004; Nelson and Prisbrey, 2004).
- (4) Mineral carbonation was also studied by surface activation to accelerate the reaction rate. Chemical activation was found to be more effective than physical activation in terms of increasing the surface area. The most effective chemical available for chemical carbonation was sulfuric acid and the process of steam activation was found to be the most effective one (Maroto-Valer *et al.*, 2005a,b).
- (5) Biomimetic process that involves biological catalyst was also studied for carbonation. The enzyme carbonic anhydrase increased the rate of precipitation of carbonate mineral significantly using industrial waste water as a source of calcium cation (Liu *et al.*, 2005).

Overall, mineral carbonation has limited scope as this technology requires a huge supply of metal oxides which will have a major impact on mineral industries (Yang *et al.*, 2008).

Enhanced oil recovery (EOR)

CO₂ can be injected in oil reservoirs to enforce the oil movement. The out-coming CO₂ can be recaptured and recycled for oil extraction. But the process of EOR is not feasible economically as it requires huge amount of energy for CO₂ removal. If the CO₂ recovery plant is combined with EOR, then the transportation cost can be reduced, still the process remains uneconomical (Stewart and Hessami, 2005).

Coal seams

Coal beds often contain methane gas. If CO₂ is adsorbed physically by porous structure of coal, then permanent retention of carbon is possible (Herzog, 2001). Reports has shown that using CO₂ instead water to flood the bed can recover methane more efficiently and sequester CO₂ as well (Beecy and Kuuskraa, 2001).

Technical Approach

The main problem for carbon capture and sequestration (CCS) is the increased cost of electricity that is required for the processes. In order to be accepted industrially, the cost of carbon capture should be minimum. Thus to obtain a cost effective process, different technologies like absorption, adsorption, membrane technology, hybrid treatment, biotechnology have been studied to compare the cost of chemical conversion and power generation.

Absorption process

Amine absorption process

- Absorption by amines is the most commercialized, mature and widely studied absorption technology. Different solvents like monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), etc. are generally used in this process. Among these monoethanolamine (MEA) is mostly preferred because it reacts faster with CO₂ compared to other secondary or tertiary amines which allows absorption to take place in a smaller column. Reaction of mixed amines with CO₂ has also been studied and the cost of regeneration was found to be reduced. A comparison of performance between MEA with MEA/MDEA mixture (4:1 molar ratio) indicated that huge heat duty reduction can be achieved by using mixed solution instead of single MEA solution (Idem *et al.*, 2006).

Process description: During the chemical absorption process, flue gas enters a packed bed absorber from the bottom and counter-currently contacts with CO₂ lean solvent for absorption, then the CO₂ rich solvent flows into a stripper for thermal regeneration (Freguia and Rochelle, 2003).

After solvent regeneration, the produced CO₂ lean solvent is pumped back to the absorber to absorb CO₂ again. And the pure CO₂ is released from the top of the stripper which is then compressed to about 15 MPa for subsequent transportation and storage. The operational pressure for the whole system is approximately equal to the atmospheric pressure and the temperatures of the absorber and the stripper are generally in the range of 40–50°C and 100°–140° respectively (Metz *et al.*, 2005; Ciferno *et al.*, 2009). Theoretically, the minimum energy requirement for CO₂ recovery from power plants flue gas and for compression of CO₂ to 150 bar is 0.396 GJ/tonne CO₂. For operation in a power plant in real practice, 0.72 GJ/tonne CO₂ is to be achieved hopefully (Rochelle, 2009).

The proposed mechanism for CO₂ capture using amine is as follows:

Main problems and improving methods

Typical MEA process suffers the following disadvantages during separation of CO₂ from flue gas (Kittel *et al.*, 2009):

- (1) Low carbon dioxide capture capacity (g CO₂/g absorbent);
- (2) Amine degradation by SO₂, NO_x and oxygen in flue gas which induces a high absorbent makeup rate;
- (3) High equipment corrosion rate; and
- (4) High energy consumption for solvent regeneration.

To make the process more efficient, several promising investigations were done and improvements were considered:

- (i) Solvent utilization can be increased by increasing the gas-liquid contact area per unit volume with structured packing. The bed absorber was packed in a new structured way with different materials (like BX gauze, Flexipac, intalox saddle etc.) to improve the absorption efficiency and absorption rate compared to the traditional random packing. For structural packing 43.9% of solvent was utilized whereas in random packing it was only 28.6% (Yeh *et al.*, 2001).
 - (ii) Investigations were also done to develop promising solvents to enhance CO₂ absorption. Piperazine (PZ), a cyclic amine with two secondary amine nitrogen atoms is one of the promising solvents that have high absorption rate (Dugas and Rochelle, 2009), good capacity (Freeman *et al.*, 2010a,b) and good resistance towards thermal and oxidative degradation (Freeman *et al.*, 2010a,b). 2-amino-2-methyl-1-Propanol (AMP) and methyldiethanolamine (MDEA) were also considered because of relatively low energy consumption for solvent regeneration. But their reaction rate is low (Park *et al.*, 2006; Li and Lie, 1994). Blending of different alkanolamines was also done as it combined the advantages of different solvents and suppressed the disadvantages. Proper blending can result in high absorption rate for primary and secondary amines and lower solvent regeneration cost for tertiary and sterically hindered amines (Hagewiesche *et al.*, 1995).
 - (iii) Dilution of the aqueous fraction with organic solvents like methanol or ethylene glycol can also reduce the energy requirement for solvent regeneration as the organic solvents has lower heat capacity than water (Xiaomei *et al.*, 2014).
- Ammonium absorption process:

Aqua ammonium process can overcome the drawbacks of MEA process. In this process the flue gas is oxidized to convert SO₂ and NO into SO₃ and NO₂ respectively. After pre-treatment the flue gas is treated with aqueous ammonia in a wet scrubber. The byproducts of this reaction like ammonium sulfate and ammonium nitrate can be used as fertilizers but the use of ammonium

carbonate and ammonium bicarbonate is uncertain. So heat input is required to recycle ammonium from them. It was estimated that the process saves up to 60% energy compared to MEA process (Resnik *et al.*, 2004; Yeh *et al.*, 2005).

Adsorption process

The adsorption process is based on the same principle but uses porous adsorbents like zeolites, activated carbon, etc; chemical reaction between adsorbents and CO₂ may or may not occur.

- Molecular sieve adsorbent:

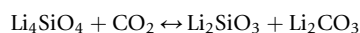
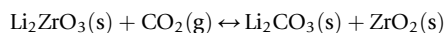
Molecular sieves are specially designed sieves used to separate molecules on the basis of their molecular weight or molecular size. Being mesoporous substrate the sieves have high surface area which incorporates organic adsorbent groups (generally amines). Then, the basic surface interacts with acidic CO₂ to form surface ammonium carbamate under anhydrous conditions and produces ammonium bicarbonate and ammonium carbonate in presence of water. Studies have been carried out with silica and MCM-48 as porous substrate and the CO₂ adsorption capacity was 0.5 mol CO₂/mol surface-bound amine group in absence of water (Yang *et al.*, 2008).

- Adsorption by activated carbon:

Anthracite, the best grade coal is capable of producing high surface area activated carbon. Studies have revealed that CO₂ capture does not show a linear relationship with increasing surface area. The highest CO₂ adsorption capacity was 65.7 mg CO₂/g adsorbent for the anthracite activated at 800°C for 2 h with a surface area of 540 m²/g. The anthracite with the highest surface area of 1071 m²/g only had a CO₂ adsorption capacity of 40 mg CO₂/g adsorbent. This could be explained by certain size pores being effective for CO₂ adsorption. Also the NH₃ treatment and PEI impregnation increased the CO₂ capture capacity of the activated anthracites at higher temperature due to the introduction of alkaline nitrogen groups on the surface (Maroto-Valer *et al.*, 2005a,b).

- Lithium compounds based adsorbents:

Lithium zirconate (Li₂ZrO₃) (Fauth *et al.*, 2005) and Lithium silicate (Li₄SiO₄) (Essaki *et al.*, 2004; Kato *et al.*, 2005) also exhibits CO₂ adsorption capability.



Among these lithium silicate is more desirable since it has larger capacity and rapid absorption. It also exhibits a wide range of temperature, concentration of CO₂ and stability (Essaki *et al.*, 2004; Kato *et al.*, 2005).

Membrane separation

Membrane separation depends on permeability and selectivity. Different membrane materials commonly uses ceramic (inorganic), polymeric (organic) and hybrid (mixed: organic and inorganic) membranes. Different modules also used spiral wound or hollow fibres. In this process, the flue gas is cooled by a wet scrubber before entering the membrane module. A portion of CO₂ permeates through the membrane and a stream (permeate gas) with higher concentration of CO₂ remains on the permeate side. The remaining part in the left side is called retentate gas. Compressor and vacuum pump are used to create pressure gradient between feed and permeate.

Although very few studies have been done on membrane separation compared to amine absorption, it has been concluded that the membrane-based separation process does not have apparent advantages over chemical absorption technology in terms of energy and cost at 90% separation degree (Wang *et al.*, 2017). Hybrid membrane-absorption capture system also has been studied. In the series arrangement, the flue gas is firstly treated in the chemical absorption unit and approximately 50% of the CO₂ can be removed. Exiting stream from the stripper with 10% CO₂ goes to the membrane unit. By this parallel set up 90% removal can be achieved and the volume of the flue gas decreases in the chemical absorption system due to which the absorber becomes half of the normal size. It is concluded that in this case the energy required for solvent regeneration is less and the capital cost is also less compared to conventional absorption process (Wang *et al.*, 2017).

Economic Concern and Environmental Issues

Most of the carbon capture and sequestration methods suffer from drawbacks. For example, oceanic and geologic injection can only delays the release of CO₂ in the atmosphere up to a certain time. Cost is also a major concern, as the carbon capture and sequestration increases the cost of electricity production. For example, MEA absorption leads to an increased cost of electricity by about 80% due to capture and storage of CO₂ (Mohamed *et al.*, 2017).

About the investment cost, for post-combustion it was estimated to be increased by 50% and for oxy-combustion by 65%, whereas for pre-combustion by 90% (Mohamed *et al.*, 2017). CO₂ capture process not only has to be economical but also environmentally and socially accepted.

In post combustion the ash particle emission gets decreased as the flue gas is washed by solvent and water. Still the process is not eco-friendly as amines can lead to gaseous, solid and liquid emissions which are potentially toxic for human beings and environment.

In amine absorption process there are three types of risks-

- (1) Solvent leakage and degradation of products;
- (2) Traces of emission of amine into the atmosphere;
- (3) Waste production in the solvent reclaimed.

Among these emission issue is most dangerous. Treated flue gas can contain traces of amine as a gas or aerosols which cannot be trapped by the flue gas water wash downstream in the absorption columns. The emitted amines and degraded amines may react in the atmosphere by complex mechanisms like photolysis, degradation and form more toxic elements like nitrosoamines (Shao *et al.*, 2009; Rohr and Show, 2012; Bratten *et al.*, 2009). Further, amines as a solvent not only reacts with CO₂, but also with NO_x and SO_x leading to form volatile compounds harmful to the environment.

Pre-combustion faces the same problems as post-combustion depending on the used solvent. However, unlike post-combustion, the treated syngas undergoes further combustion in the gas turbine. The issues of combustion of the pollutants that are generated by pre-combustion are not yet studied.

Considering all these facts, it is clear that the sustainable way of CCS is photosynthetic sequestration of CO₂.

Photosynthetic Sequestration

The most abundant and sustainable source of energy for Earth is the sun. More than 3800 zettajoules (1 zettajoule = 1×10^{21} joules) of solar energy are absorbed by Earth's atmosphere and surface annually. About 0.05% of this energy is captured in biomass each year through the process of photosynthesis (Hill *et al.*, 2006; Lewis and Nocera, 2006; Zhu *et al.*, 2008). The production, decomposition, and accumulation of biomass play a central role in the global carbon cycle. In a well-balanced ecosystem, carbon capture from photosynthesis, carbon deposition in the soil and oceans, and carbon release from biological and geological sources are in equilibrium. Since the beginning of the industrial age (in the 1850s), however, this equilibrium has been perturbed by increasing carbon emissions from the combustion of fossil fuel and biomass, and from reduced carbon uptake as a result of global deforestation and the loss of arable land.

Direct carbon combustion for energy production generates more than 24 gigatons of carbon dioxide (CO₂) annually (Lewis and Nocera, 2006) that causes rise in atmospheric CO₂ level leading to Global Warming. Hence it is very important to develop new method of CO₂ sequestration. It is also very important to develop a clean energy source which does not depend on fossil fuel and which have a tolerable environmental impact.

The first generation of biofuel production systems (starch- and sugar-based ethanol production) demonstrated the feasibility of generating liquid transportation fuels from renewable sources, but at initially low energy-conversion efficiencies and high cost. Fermentation of biomass to produce ethanol emits substantial carbon and yields a fuel that has only about half the energy density of oil-based fuels.

Hemicellulosic and cellulosic biofuel production systems enable the conversion of nearly all sugar-based plant polymers into fuels (ethanol, butanol, diesel). Plants that produce high levels of cellulosic biomass, such as *Miscanthus* and switchgrass, are being developed as second-generation biofuel crops. These biofuel crops do not compete directly with food production, require less agronomic (fertilizer, plowing, pesticide) inputs, and have lower environmental impacts than first-generation biofuels. However, some biofuel crops (*Miscanthus*) have the potential to be invasive species that may disrupt the biological integrity of local ecosystems (Raghu *et al.*, 2006). Overall, the energy efficiency, environmental sustainability, and economics of various renewable fuel production systems must be collectively evaluated to make informed decisions to identify the best energy production systems for each location and market. From the recent researches the scientists had come across the technique of carbon dioxide sequestration and biofuel production from micro and macro algae. This method becomes one of the alternatives to combat climate change as higher plants have various limitations to be used as a model system for carbon sequestration and biofuel production.

CO₂ Sequestration Using Algae

- What is algae:

Algae are eukaryotic organisms. Algae are recognized as one of the oldest life-forms. The true roots, stems or leaves are absent, they have no sterile covering of cells around the reproductive cells. Presence of chlorophyll and other pigments help in carrying out photosynthesis. Algae can be multicellular or unicellular. Depending on the species, algae can range from 1 micron (μm) to a few hundred microns in size. Microalgae are one of the most important groups of organisms on the planet. Mostly they are photoautotrophic and carry on photo-synthesis, some of these are chemo heterotrophic and obtain energy from chemical reactions as well as nutrients from pre-formed organic matter. Microalgae can fix CO₂ using solar energy with efficiency ten times greater than terrestrial plants (Wang *et al.*, 2011). Many species of algae are present such as; green, red and brown algae

which belong to the group of Chlorophyta, Rhodophyta and Phaeophyta, respectively. Algae belong to a wide range of habitat like freshwater, marine water, in deep oceans and in rocky shores. The Planktonic and benthic algae can become important constituents of soil flora and can exist even in such extreme conditions as in snow, sands/desert or in hot springs (temperatures above 80°C).

- Importance of algae:

It is estimated that microalgae produce approximately half of the atmospheric oxygen on earth, while consuming vast amounts of the greenhouse gas carbon dioxide. Microalgae have a rapid growth potential and many species have oil content in the range of 20%–50% dry weight of biomass (Falkowski *et al.*, 1996; Chisti, 2007; Metting, 1996). With respect to air quality maintenance and improvement, microalgae biomass production can effect bio fixation of waste CO₂ (1 kg of dry algal biomass utilize about 1.83 kg of CO₂) (Falkowski *et al.*, 1996). Nutrients for microalgae cultivation can be obtained from wastewater as a growth medium, thereby treating the organic effluent from the agro-food industry (Cantrell *et al.*, 2008). Algae can be grown under conditions which are unsuitable for conventional crop production like soybean and others. Algal cultivation does not require herbicides or pesticides application (Rodolfi *et al.*, 2008).

Algae is used as a source of food, fuel (oil, biodiesel, bioethanol, biohydrogen, and biogas), stabilizing agent (carrageen), fertilizer, chemical and in waste water treatment as well as in power plants to reduce CO₂ emissions and more. Algae provide much higher yields of biomass and fuels. Certain species of algae accumulated up to 60% intracellular lipid of their total biomass, it increases their heat of combustion and fuel value. Micro algae contain lipids and fatty acids are membrane components, storage products and as a sources of energy. More than 70,000 species of algae have been identified but all of them are not fit for human requirement. 50% of weight of algae is oil. The biofuel derived from Algae is non-toxic, contains no sulfur and is highly biodegradable (Singh and Singh, 2014). Fifty percent of the photosynthesis process takes place on Earth by algae (Goldman *et al.*, 1971). It removes inorganic carbon from the environment. Genetic engineering methods are improved micro algal photosynthetic rate to enhance CO₂ fixation and gain higher quantity of biomass to produce biodiesel and other important alternatives (Zeng *et al.*, 2011). They can also produce valuable co-products such as proteins and also biomass residue after oil extraction which may be used as fermented to produce ethanol or methane (Hirano *et al.*, 1997) or fertilizer (Cantrell *et al.*, 2008).

- Carbon capture by algae:

Cultivation of autotrophic microalgae on land in large ponds or in enclosed photo bioreactors using enriched carbon dioxide can help recycle this specific greenhouse gas. Algal growth is directly or indirectly gets affected various physical and chemical parameters such as light/irradiance/temperature/carbon-dioxide/pH/mixing; aeration, salinity etc. These autotrophic micro organisms are capable of converting CO₂ into carbohydrates and lipids in the presence of light by photosynthesis. Thus cultivation of microalgae can help to reduce the overall greenhouse gas emission when the algal biomass is converted into biofuel. Current research on oil extraction is focused on microalgae to produce biodiesel from algal oil.

Photosynthesis–fermentation model with double CO₂ fixation in both photosynthesis and fermentation stages has enhanced carbon conversion ratio of sugar to oil and thus provided an efficient approach for the production of algal lipid (Wei *et al.*, 2010).

The enriched carbon dioxide stream may come in the form of flue gases from power plant or may be obtained from other fossil fuel combustion and biological processes. Microalgae can be extensively used to capture CO₂ from power plants, steel, cement, oil, automobiles and many other industries and the resulting algal biomass can not only be used for biofuel production but also for various industrial products. Algae can reproduce very rapidly as compared to any other plants. With the cultivation of tens of thousands of algae, numerous CO₂ sinks can be developed which could be used to sequester CO₂ effectively through photosynthesis.

In general microalgae can be produced in open ponds or closed systems (such as photobioreactors) and the culturing methods used can be continuous, semi- continuous or batch (Jorquera *et al.*, 2010) (Table 1).

Direct utilization of power plant flue gas has been considered for CO₂ sequestration systems (Benemann, 1993). The

Table 1 CO₂ Tolerance of various species

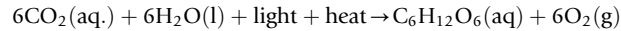
Species	Known maximum CO ₂ uptake concentration	References
<i>Cyanidium caldarium</i>	100%	Seckbach and Kaplan (1973)
<i>Scenedesmus</i> sp.	80%	Sung <i>et al.</i> (1992)
<i>Chlorococcum littorale</i>	60%	Kodama <i>et al.</i> (1993)
<i>Synechococcus elongatus</i>	60%	Miyairi (1995)
<i>Euglena gracilis</i>	45%	Nakano <i>et al.</i> (1996)
<i>Chlorella</i> sp.	40%	Sung <i>et al.</i> (1992)
<i>Eudorina</i> spp.	20%	Sung <i>et al.</i> (1992)
<i>Dunaliella tertiolecta</i>	15%	Tsuji <i>et al.</i> (2003)
<i>Nannochloris</i> sp.	15%	Yoshihara <i>et al.</i> (1996)
<i>Chlamydomonas</i> sp.	15%	Miura <i>et al.</i> (1993)
<i>Tetraselmis</i> sp.	14%	Matsumoto <i>et al.</i> (1995)

advantage of direct utilization of flue is the reduction of the cost of separating CO₂ gas. Since power plant flue gas contains higher concentration of CO₂, identifying high CO₂ tolerant species is important. Although CO₂ concentrations vary depending on the flue gas source, 15%–20% v/v is typically assumed. Several species have been tested under CO₂ concentrations of over 15% (Sharmila *et al.*, 2014). In Table 2, various algae are reported that easily grow at very high CO₂ concentration (Table 3).

- Photoautotrophic Production:

For large scale production of algae biomass for non-energy production, photoautotrophic production is the only technically and economically feasible method. Two systems based on open pond and closed photo-bioreactor are deployed for this purpose.

These systems make use of the natural process known as photosynthesis to convert light, heat and carbon dioxide to useful products, such as carbohydrates, hydrogen and oxygen.



The above equation illustrates a photosynthetic reaction. The type of product produced, in this case glucose, depends highly on the biological strain used in the photo-bioreactor (Figs. 1–2).

- Open pond system

Open ponds were extensively used in the past for the cultivation of algae (Fig. 3). Open ponds can be grouped into natural waters bodies such as lakes, lagoons, ponds and artificial ponds. Shallow Ponds are effective in algal growth as more sunlight penetrates into the shallow water. Shallow water also tends to be warmer, and this favors algae growth. In stagnant ponds, algae growth is favoured. The ponds in which the algae are cultivated are usually what are called the “raceway ponds”. In these ponds, the algae, water & nutrients circulate around a racetrack. With paddlewheels providing the flow, algae are kept suspended in the

Table 2 CO₂ fixation rate and amount of CO₂ used in Biomass generation

Sl. no	Algae	CO ₂ fixation rate (mg/L/day)	% to Biomass	References
1.	<i>Dunaliella tertiolecta</i>	272.4	70.42	Sydney <i>et al.</i> (2010)
2.	<i>Chlorella vulgaris</i>	251.64	86.68	Sydney <i>et al.</i> (2010)
3.	<i>Spirulina platensis</i>	318.61	80.40	Sydney <i>et al.</i> (2010)
4.	<i>Botryococcus braunii</i>	496.98	87.96	Sydney <i>et al.</i> (2010)
5.	<i>Chlorella vulgaris</i>	865	N/A	Hirata <i>et al.</i> (1996)
6.	<i>Chlorella vulgaris</i>	624	N/A	Yeoung-Sang <i>et al.</i> (1997)
7.	<i>Botryococcus braunii</i>	1100	N/A	Murakami and Ikenouchi (1997)
8.	<i>Spirulina platensis</i>	413	N/A	De Moraiss and Costa (2007)
9.	<i>Dunaliella tertiolecta</i>	313	N/A	Kishimoto <i>et al.</i> (1994)
10.	<i>Chlorella sp. UK001</i>	31.8	4.3	Hirata <i>et al.</i> (1996)
11.	<i>Synechocystis aquatilis</i>	1500	N/A	Murakami and Ikenouchi (1997)

Source: N/A=biomass produced at particular CO₂ fixation rate was not mentioned by these investigators.

Table 3 Biomass produced by microalgae species at particular CO₂ concentration

Sl. no	Algae	Amount of CO ₂ supply (% CO ₂)	Biomass produced (gm/L/day)	References
1.	<i>Chlorella vulgaris</i>	6	0.21	Chinnasamy <i>et al.</i> (2009)
2.	<i>Chlorococum littorale</i>	N/A	9.2	Hu <i>et al.</i> (2009)
3.	<i>Chlorella kessleri</i>	6	0.087	De Moraiss and Costa (2007)
4.	<i>Scenedesmus obliquus</i>	12	1.14	De Moraiss and Costa (2007)
5.	<i>Chlorella KR-1</i>	70	0.71 (Given at 5th day)	Sung <i>et al.</i> (1999)
6.	<i>Chlorella KR-1</i>	10	0.667	Sung <i>et al.</i> (1999)
7.	<i>Spirulina platensis</i>	10	2.91	Ramanan <i>et al.</i> (2010)
8.	<i>Chlorella sp.</i>	10	2.25	Ramanan <i>et al.</i> (2010)
9.	<i>Scenedesmus obliquus</i>	5	1.7	Pakawadee <i>et al.</i> (2012)
10.	<i>Scenedesmus obliquus</i>	15	2.3	Pakawadee <i>et al.</i> (2012)
11.	<i>Chlorella vulgaris</i>	0.03	0.226	Bhola <i>et al.</i> (2011)
12.	<i>Chlorella vulgaris</i>	4	1.222	Bhola <i>et al.</i> (2011)
13.	<i>Scenedesmus obliquus</i>	15	0.145	Pakawadee <i>et al.</i> (2012)
14.	<i>Nannochloropsis oculata</i>	2	0.480	Sheng <i>et al.</i> (2009)
15.	<i>Nannochloropsis oculata</i>	5	0.441	Sheng <i>et al.</i> (2009)
16.	<i>Nannochloropsis oculata</i>	10	0.398	Sheng <i>et al.</i> (2009)
17.	<i>Nannochloropsis oculata</i>	15	0.372	Sheng <i>et al.</i> (2009)

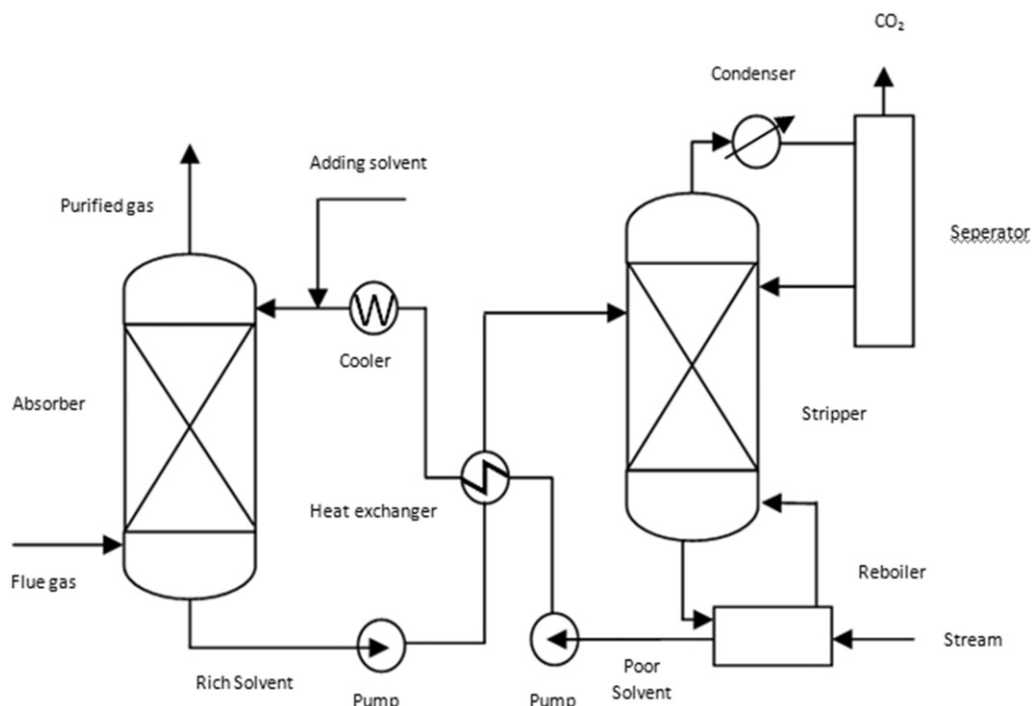


Fig. 1 Flow Diagram of Amine absorption process. Reproduced from Xiaomei, W., *et al.*, 2014. The advances of post-combustion CO₂ capture with chemical solvents: Review and guidelines. *Energy Procedia* 63, 1339–1346.

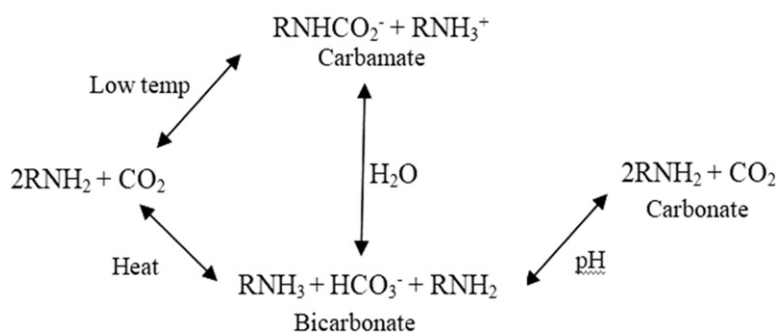


Fig. 2 Proposed reaction sequence for the capture of CO₂ by liquid amine based systems. Reproduced from Gray, M.L, Soong, Y., Champagne, K.J, *et al.*, 2005. Improved immobilized carbon dioxide capture sorbents. *Fuel Processing Technology* 86 (14-15), 1449–1455.

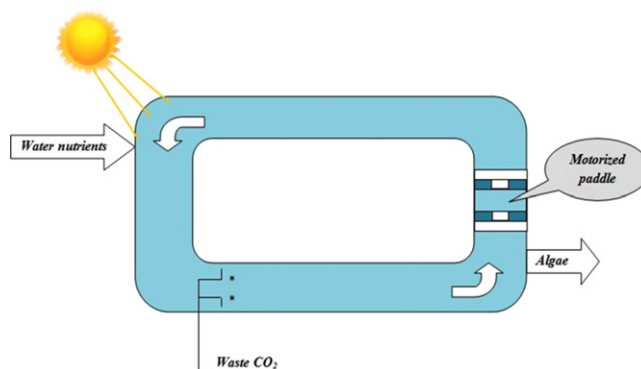


Fig. 3 Open pond system. Reproduced from Sharmila, K., Ramya, S., Babu Ponnusami, A., 2014. Carbon sequestration using microalgae-a review. *International Journal of ChemTech Research* 6 (9), 4128–4133. (CODEN (USA): IJCRGG ISSN: 0974-4290).

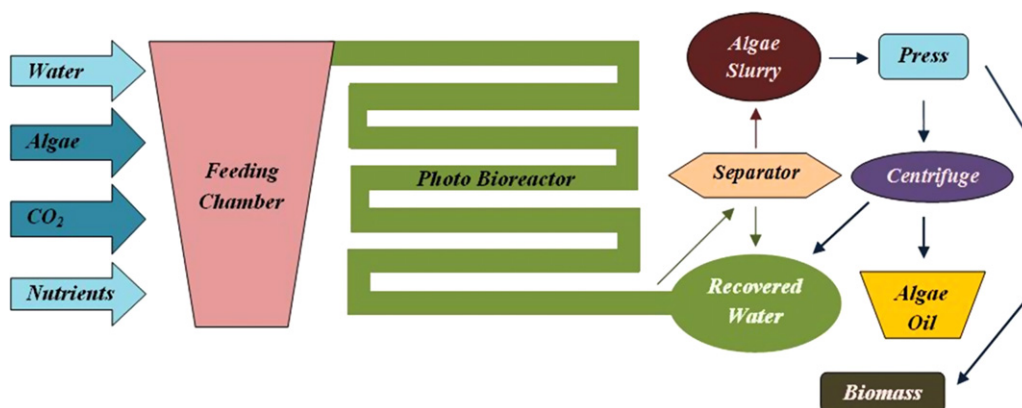


Fig. 4 Cultivation of Algae in Photobioreactor (<http://www.oilgae.com/algae/cult/pbr/pbr.html>).

water, and are circulated back to the surface on a regular frequency. Though open ponds are easier to construct, operate and easy to clean after cultivation, they have certain disadvantages. These disadvantages include poor light utilization by the cells, high evaporation rate, diffusion of carbon-dioxide into atmosphere resulting low biomass productivity (Fig. 4).

- Cultivation of Algae in Photobioreactor:

A photobioreactor (PBR) is closed equipment which provides a controlled environment and enables high productivity of algae. As it is a closed system, all growth requirements of algae are introduced into the system and controlled according to the requirements. PBRs facilitate better control of culture environment such as carbon dioxide supply, water supply, optimal temperature, efficient exposure to light, culture density, pH levels, gas supply rate, mixing regime, etc.

From the feeding vessel, the flow progresses to the diaphragm pump which moderates the flow of the algae into the actual tube.

The photobioreactor itself is used to promote biological growth by controlling environmental parameters including light. The tubes are made of acrylic and are designed to have light and dark intervals to enhance the growth rate. The photobioreactor has a built-in cleaning system that internally cleans the tubes without stopping the production. After the algae have completed the flow through the photobioreactor, it passes back to the feeding vessel. As it progresses through the hoses, the oxygen sensors determine how much oxygen has built up in the plant and this oxygen is released in the feeding vessel itself. It is also at this stage that the optical Cell Density sensor determines the harvesting rate. When the algae are ready for harvesting, they pass through the connected filtering system. This filter collects the algae that are ready for processing, while the remaining algae passes back to the feeding vessel.

Various researchers have investigated algal cultivation by changing various parameters.

Usui and Ikenouchi (1997) used a concave mirror to collect the light and passed the IR radiation to the bioreactor by fibre optics. The authors realized an improvement of 55% in overall efficiency by developing the light transmission system. These included developing a more sophisticated protective cover for the system, selecting an appropriate fibre optic diameter and optimising the ratio of fibre core area to bundle size. The light was distributed throughout the reactor by means of illumination plates consisting of a lattice of strips between two frosted acrylic plates. The experimental system experienced illumination of 10 h a day with 14 h darkness and achieved a CO₂ fixation rate almost 10 times that of a tree undergoing a natural photosynthetic process.

In designing a photo-bioreactor, Degen *et al.* (2001) made use of the “flashing light effect”. This is when the conversion of light to biomass can be enhanced by repeatedly cycling cells from the dimly lit interior of the reactor to the higher illumination of the exterior. Random cycling is not too effective. Degen *et al.* (2001) recommended a light-dark cycle of 1 Hz frequency with a light versus dark residence time of 1:10. In order to increase productivity, baffles were added.

Cultivation of algae in PBRs allows cultivation of algae in controlled environment, which leads to higher productivity. The other major advantages are – large surface to volume ratio, better control of gas transfer, reduction in evaporation of growth medium, attainment of more uniform temperature, much lesser probability of contamination, space savings.

The major drawbacks of using photobioreactor in algae cultivation are huge capital cost. Despite higher biomass concentration and better control of culture parameters, experimental data obtained in the last two decades have shown that the productivity in some enclosed photobioreactor systems are not very encouraging compared to those achievable in open-pond cultures. The technical difficulty in sterilizing these photobioreactors has hindered their application for algae culture for specific end-products such as high value pharmaceutical products.

- CO₂ fixation with wastewater treatment:

Microalgae feedstock production can be integrated with wastewater and industrial sources of carbon dioxide. CO₂ mitigation by microalgae production in wastewater is a beneficial technology to produce nutraceuticals, specifically beta- carotene, extracted from *Dunaliella* and *Spirulina* biomass (Benemann and Oswald, 1996). At the 272.40 mg/L/day CO₂ fixation rate, 70.42% biomass

was *Dunaliella Chlorella vulgaris* was cultivated in wastewater discharged from a steel-making plant with the aim of developing an economically feasible system to remove ammonia from wastewater and CO₂ from flue gas simultaneously. CO₂ fixation and ammonia removal rates were estimated as 26.0 g CO₂ m⁻³ h⁻¹ and 0.92 g NH₃ m⁻³ h⁻¹, respectively, when the alga was cultivated in wastewater supplemented with 46.0 g PO₄³⁻ m⁻³ without pH control at 15% (v/v) CO₂ (Sang Yun *et al.*, 1999). In another study, the feedstock potential of the Howard F. Curren Advanced Wastewater Treatment Plant (HFC AWTP) in Tampa, and the Wetland Treatment System of city of Lakeland, Florida have been estimated to be approximately 71 tons ha⁻¹ yr⁻¹ of algal biomass, 270,000 gal hr⁻¹ of liquid biofuel, and 415,000 kg yr⁻¹ of methane. Renewable energy derived from algae will play a significant role in providing energy security while important services such as water treatment can be synergistically achieved by these systems.

Conclusion

The world is faced with an intrinsic environmental responsibility, i.e., the minimization of greenhouse gas emission to acceptable levels. The mitigation of emissions of greenhouse gases, particularly CO₂, and their effective utilization present to the world both a difficult challenge and a major opportunity for sustainable development in energy and environment.

This study presented here attempted to explain the methods of carbon dioxide capture and sequestration and to discuss a line of research that may, in the future, help to reduce the greenhouse effect in a sustainable manner.

Different carbon dioxide capture techniques, such as amine scrubbing to treat flue gases, membrane separation methods, molecular sieve and desiccant adsorption technologies are proven technologies related to CO₂ sequestration but these capture and sequestration techniques would not have been economically feasible. Geologic and oceanic injection techniques also would not be sustainable. CO₂ conversion and utilization research is important and should be an integral part of research and development for carbon management and sustainable development.

Global strategy for control of CO₂ should begin with energy issues since the problem originates from the way the energy sources are selected and used. Among all processes of CO₂ sequestration, the natural process of photosynthesis, can be utilized to fix carbon dioxide and produce useful by-products in a sustainable fashion. The production of algae is identified as one of the solutions of carbon sequestration along with production of renewable fuel. It has been found that microalgae is capable to fix CO₂ from different sources such as from atmosphere, from flue gases discharged from industry as well as from soluble carbonates. The impact of various concentrations of CO₂ applied and its effect on algal lipid accumulation has been presented here which manifests a two-fold achievements namely reduction of an environmental problem by reducing one potential greenhouse emission as well as giving rise to a new form of renewable fuel, a valuable byproduct.

See also: Overview of CCS: A Strategy of Meeting CO₂ Emission Targets

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The Applicability of the Inflection Point in the Environmental Correction Process

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Introduction

It is not now that environmental problem has become relevant in economic growth theories (Since the Club of Rome was founded, a recurring economic problem has been the relationship between economic growth and public concern for environmental issues. The empirical EKC model is a popular means of analyzing the relationship between economic growth and environmental pollution. There is currently a large body of literature on EKC's ([Grossman and Krueger, 1991](#); [Selden and Song, 1994](#); [Hilton and Levinson, 1998](#))). Since the [Grossman and Krueger \(1991\)](#) established the existence of an inverted U-shaped relationship between environmental pollution and income, extensive research has been conducted in the field of Environmental Economics under the phenomenon of Environmental Kuznets Curve (EKC) ([Grossman and Krueger, 1991](#); [Stern et al., 1996](#); [Stern, 2004](#); [Dasgupta et al., 2002](#); [Dinda, 2004](#)). This has led to different theoretical argument on potential existence of a relationship between income and environmental pollution. The EKC model proposes a relationship between environmental quality and per capita income. This empirical hypothesis allows the incorporation of a set of additional variables that help to explain the EKC's behavior (e.g., how the potential impacts of public incentives on energy efficiency and energy innovation). In Addition, the EKC hypothesis shows that economic growth is friendly with environmental improvements. So, under the empirical evidence of a link between income and carbon pollution, we consider that analysis of inflection point provides an additional argument in order to accelerate the incorporation or regulatory measures, linked with energy efficiency and innovations, to control environmental degradation ([Balsalobre and Alvarez, 2016](#); [Álvarez et al., 2017](#); [Balsalobre et al., 2018](#)).

This approach seeks to incorporate a complementary exploration in the relationship between economic growth and environmental degradation, where regulatory policies that enhance energy innovations, many times requires public intervention aimed at improving economic growth and environment quality ([Iwata et al., 2010](#); [Turner and Hanley, 2011](#); [Balsalobre et al., 2015](#)). So, the implementation of innovation processes will contribute positively to environmental quality, placing countries on a path of sustainable economic growth ([Balsalobre et al., 2015](#)). To demonstrate this hypothesis, [Balsalobre et al. \(2015\)](#) employed the EKC model where they included additional explanatory variables linked with energy innovations.

Literature Review

While many studies have reported an inverted U-shaped relationship between economic growth and environmental degradation, there has been extensive research on the EKC hypothesis ([Shafik and Bandyopadhyay, 1992](#); [Ekins, 1997](#); [Grossman and Krueger, 1991](#); [Stern et al., 1996](#); [Stern, 2004](#); [Dinda, 2004](#); [Luzzati and Orsini, 2009](#); [Halicioglu, 2009](#); [Acaravci and Ozturk, 2010](#)). Since [Grossman and Krueger \(1991\)](#) reported inverted U-shaped between pollution and income relationship which is termed as EKC hypothesis. The empirical research on the EKC hypothesis has been extensively conducted and provided inconclusive empirical findings ([Shafik and Bandyopadhyay, 1992](#); [Stern et al., 1996](#); [Stern, 2004](#); [Dinda, 2004](#), among others). The EKC's analytic scheme, proposes a relationship between economic growth and environmental quality which implies that environmental degradation is an increasing function of economic activity, until it reaches a critical level, and then higher income levels lead to improve environmental quality, inverted-U shaped ([Selden and Song, 1994](#)). [Fig. 1](#), shows how environmental pollution increases till an economy reaches a certain income level (highest point) and thereafter economy experiences decreases in environmental pollution as the income level continues to grow.

[Fig. 2](#) represents a dynamic process where structural changes appears linked with economic growth ([Dinda, 2004](#)) which suggests that economic growth affects environmental quality via three channels such as scale effect, composition effect and technique effect ([Grossman and Krueger, 1991](#)). The *scale effect* asserts that, an increase in production will result in decreased environmental quality. This effect refers to the margin for new improvements to create increasing returns in terms of reducing contamination ([Torrás and Boyce, 1998](#)). The *composition effect* contains the impact on environment, since in the early stages of economic development, pollution increases as economic structure shifts from agriculture to more resource-intensive heavy manufacturing industries, whereas in later stages, pollution decreases as structure shifts toward services and light manufacturing industries. Otherwise, the *technical effect* refers to productivity gains and adoption of cleaner technologies, leading to increased environmental quality ([Andreoni and Levinson, 1998](#) argue that as economic activity increases, the level of environmental contamination is corrected, mainly through technological factors). This perspective links the EKC hypothesis with technological development, as the technical effect is stronger than the composition and scale effects. The technical effect refers to technological improvements that enable the use of less input per unit of output or the adoption of cleaner technologies to replace obsolete ones in the production of goods. Finally, [Andreoni and Levinson \(2001\)](#) argue that decontamination processes mainly depend on

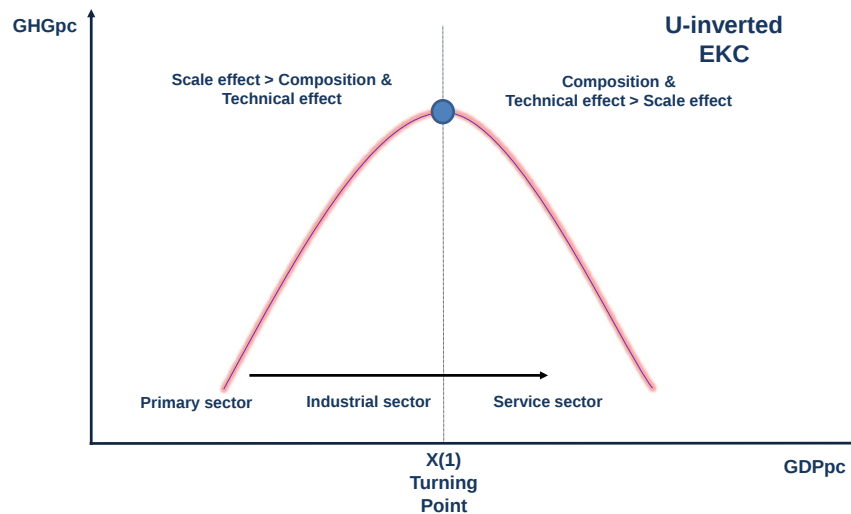


Fig. 1 Inverted U-shaped EKC: Scale, Technical and Composition Effects.

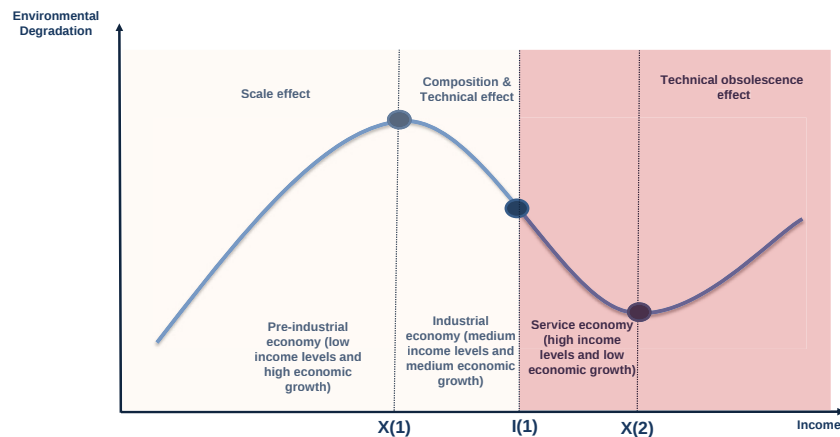


Fig. 2 N-shaped EKC: Scale composition, technical and technical obsolescence effect. *Source:* Prepared by the authors based on Halkos, G.E., 2003. Environmental Kuznets Curve for Sulphur: Evidence Using GMM estimation, *Environment and Development Economics*. vol. 8, pp. 581–601. Cambridge University Press. Kaika, D., Zervas, E., 2013. The Environmental Kuznets Curve (EKC) theory- part A: Concepts, causes and the CO₂ emissions case. *Energy Policy* 62, 1392–1402. And Balsalobre, D., Alvarez, A., 2016. An approach to the effect of energy innovation on environmental Kuznets curve: An introduction to inflection point. *Bulletin of Energy Economics* 4, 224–233.

“technical effect”, as investment in innovation is going to contribute positively to reduce carbon emissions. Therefore, when the economies increase their income levels, it leads to higher energy consumption and lower rates of environmental pollution, due to a strategy of innovation with increasing returns to scale enable to improve energy efficiency. Recent studies reflect the existence of a technical obsolescence effect that appears when, in the long-run, the *scale effect* overcomes again the *technical* and *composition effects* (Balsalobre and Alvarez, 2016; Sinha *et al.*, 2017; Balsalobre *et al.*, 2018).

Among these different EKC shapes, our analysis focuses on the N-shaped pattern (Grossman and Krueger, 1995; Torras and Boyce, 1998; Shafik and Bandyopadhyay, 1992; List and Gallet, 1999; Álvarez *et al.*, 2017; Balsalobre *et al.*, 2018). In long-run, the N-shaped EKC hypothesis incorporates an extensive analysis, where technical obsolescence and inflection points can be explored (Balsalobre *et al.*, 2015; Álvarez *et al.*, 2017). This view was proposed by Opschoor and Vos (1989), who consider that, once the potential for technological improvement has been exhausted or becomes too expensive, increased income results in net environmental degradation. Otherwise, Torras and Boyce (1998) support the possibility of an N-shaped path of increasing contamination that could become manifest at reasonably high income levels. Economies might reach a path of increasing contamination if the scale effect overcomes the composition and technical effects when the margin for continuous improvement in distribution is exhausted or when the diminishing returns on technological changes to reduce contamination have been depleted.

The EKC also suggests the potential of public intervention in environmental affairs, and energy RD&D helps to understand this phenomenon. Thus, the regulatory processes involved in technological innovation offer an additional explanation, backed by the

endogenous theory: the income level/environment nexus is changed due to improvements in the production process as a result of technological change (Gradus and Smulders, 1993). Therefore, the technology used to reduce contamination also affects the EKC analysis, such that economic growth alone cannot solve contamination issues. When the effect of technological innovation is incorporated, thereby reinforcing the endogenous aspect of our hypothesis technological progress can be said to condition the income level-environmental contamination relationship, so that as energy technology improves, replacement with less contaminating energy sources and more efficient processes take place (Verdier, 1993).

In addition, the inflection point between first turning point X(1) and second turning point X(2) (Fig. 1) indicates that when the economy reaches a certain income level, society begins to pay less attention to environmental protection, and the scale effect can become dominant (Antweiler et al., 2001; Song et al., 2013; Balsalobre and Alvarez, 2016; Balsalobre et al., 2018). This pattern implies that economies are in a scenario where scale effects are stronger than composition and technical effects. Goklany (2012) argues that the inflection point indicates the peak corresponding to environmental transition is likely to move over time because of technical change and increased problems due to environmental degradation. In Fig. 3, the inflection point determines the income level at which scale effects start to overcome composition and technical effects, although these economies are decreasing carbon emissions (Balsalobre et al., 2018).

An Empirical Approach to Inflection Point in the EKC

The analysis presents the following reduced-form of the EKC model to test the presence of any potential relationship between income and environmental pollution:

$$ED_{it} = \alpha + \beta_1 GDP_{pc_{it}} + \beta_2 GDP_{pc_{it}}^2 + \beta_3 GDP_{pc_{it}}^3 + \beta_4 Z_{it} + \varepsilon_{it} \quad (1)$$

where ED refers to environmental degradation, GDP_{pc} is per capita income, and Z_{it} denotes a vector defining other factors that can potentially drive environmental degradation. The coefficient α shows the environmental degradation average when income has no special relevance for environmental degradation, while the coefficient β represents the relative importance of exogenous variables; ε_{it} is the error term, normally distributed with a zero mean and constant variance. A sub-index i indicates the country i , and t denotes the time dimension. The relationship between income and some measure of environmental quality is not monotonic and may present different shapes. Many studies that consider the link between economic growth and environmental degradation recommend an inverted U-shaped relationship (Fig. 1) (Grossman and Krueger, 1991; Selden and Song, 1994; Shafik, 1994, Panayotou, 1997). The EKC model can identify different relationship between environmental degradation and income, depending of β_1 , β_2 and β_3 coefficients ($\beta_1 = \beta_2 = \beta_3 = 0$ indicates a flat pattern or no relationship between x and y . $\beta_1 > 0$, $\beta_2 = \beta_3 = 0$ denotes a monotonic increasing relationship or a linear relationship between x and y . $\beta_1 < 0$, $\beta_2 = \beta_3 = 0$ indicates a monotonic decreasing relationship between x and y . $\beta_1 > 0$, $\beta_2 < 0$, $\beta_3 = 0$ denotes an inverted U-shaped relationship, i.e., EKC. $\beta_1 < 0$, $\beta_2 > 0$, $\beta_3 = 0$ supports a U-shaped relationship, while $\beta_1 > 0$, $\beta_2 < 0$, $\beta_3 > 0$ denotes an N-shaped curve. Finally, $\beta_1 < 0$, $\beta_2 > 0$, $\beta_3 < 0$ supports an inverted N-shaped curve). The EKC may not hold even in the long run (De Bruyn and Heintz, 1999). A so called N-shaped curve (Fig. 4) which exhibits the inverted-U shaped curve initially but beyond a certain income level the relationship between environmental pollution and income turns out to be positive, suggesting that the re-linking hypothesis may be plausible (Sengupta, 1996; De Bruyn and Opschoor, 1997).

The EKC's N-shaped behavior illustrates how an economy that reaches a certain income level (i.e., first turning point) also experiences decreases in its environmental pollution, with continued growth in income. Across the different shapes of the EKC,

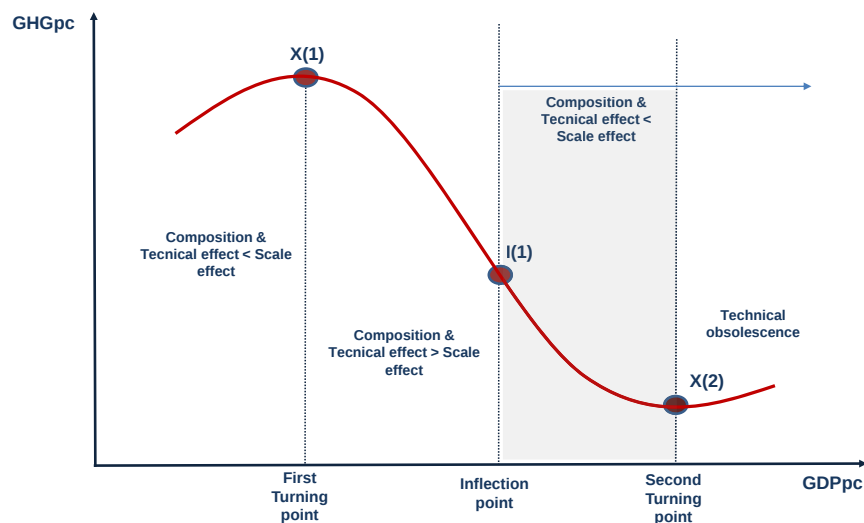


Fig. 3 Inflection Point and Technical Obsolescence Effect.

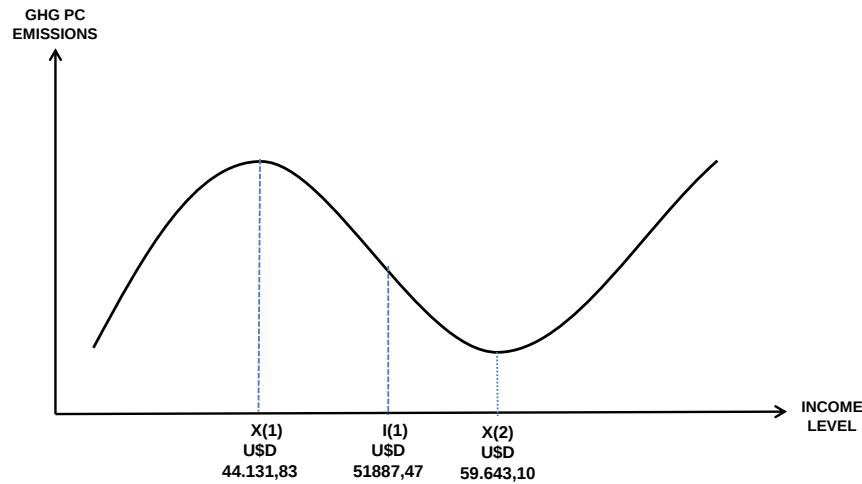


Fig. 4 Turning points of the EKC model with regulatory variables and globalization. *Note:* The coefficients $\beta_1 > 0$, $\beta_2 < 0$, and $\beta_3 > 0$ indicate a cubic polynomial in an N-shaped EKC. The coefficients β_1 , β_2 , and β_3 also allow us to calculate the turning points in the cubic EKC model. (X_1) represents the first turning point and (X_2), the second.

Table 1 Summary Statistics

Variables	GHGPC	GDPpc	GLOB	RDD	RNW
Mean	10.91015	41,495.94	82.26402	316.8111	1.01E + 10
Median	11.05155	38,280.17	83.46196	158.9520	4.79E + 09
Maximum	17.42656	91,593.67	92.34386	1,514.235	1.22E + 11
Minimum	6.048545	16,688.26	54.86887	1.501000	2.09E + 08
Std. Dev.	2.698881	15,637.41	6.166734	329.4268	1.63E + 10
Skewness	0.106376	1.317136	- 1.145916	1.565749	3.701200
Kurtosis	1.845586	4.926923	5.026608	4.935795	19.44496
Jarque-Bera	14.52575	112.2943	98.66619	142.8774	3,428.489
Probability	0.000701	0.000000	0.000000	0.000000	0.000000
Sum	2,760.267	10,498,472	20,812.80	80,153.22	2.56E + 12
Sum Sq. Dev.	1,835.557	6.16E + 10	9,583.208	27,347,546	6.70E + 22
Observations	253	253	253	253	253

this study focuses on N-shaped type of the curve (Grossman and Krueger, 1995; Torras and Boyce, 1998; List and Gallet, 1999). This N-shaped pattern is attuned with the consideration about the fact that technological improvements turn to be very expensive, with net environmental degradation resulting from increased income. An adequate environmental regulation policy could effectively accelerate technological changes, capable of decreasing contamination levels (Torras and Boyce, 1998).

Our study proposes an estimation of the relationship between income level and carbon emissions, including in the model a set of variables linked to energy regulation and environmental degradation. This model, which uses panel data for selected European countries (Denmark, Finland, France, Germany, Italy, Netherlands, Norway, Portugal, Spain, Sweden, United Kingdom) between 1990 and 2012, combines time-period and cross-sectional data. Using econometric techniques with panel data is adequate and extremely useful if there are non-observable heterogeneities in any specific country or during any time period. In our case, not every country makes decisions similarly, even if they share the same observable characteristics.

We therefore propose the following equation:

$$GHGpc_{it} = \alpha_i + \beta_1 GDPpc_{it} + \beta_2 GDPpc_{it}^2 + \beta_3 GDPpc_{it}^3 + \beta_4 RDD_{it} + \beta_5 RNW_{it} + \beta_6 GLOB_{it} + \varepsilon_{it} \quad (2a)$$

where: $GHGpc_{it}$ is CO₂ emissions, measured in metric tons (per capita) in country i and year t (WDI, 2017), $GDPpc_{it}$ is income per capita, measured in USD, at current prices and current PPPs, for country i and year t (WDI, 2017), RDD_{it} is public spending on energy RD&D, measured in USD, at current prices and current PPPs, for country i and year t (OECD, 2017) RNW_{it} is electric consumption (per capita) to each country's final, measured in ktop, for country i and year t (WDI, 2017). $GLOB_{it}$ is globalization. The descriptive statistics of the variables used are shown in Table 1.

It is necessary to pay attention to empirical results when the EKC N-shaped model is estimated for selected European countries between 1990 and 2012. The N-shaped behavior in the EKC means that when a cubic pattern equation is applied, a second turning point appears, where, beyond a given income level, carbon emissions once again begin to increase. This empirical approach shows how the income level ($GDPpc$) is needed to reduce carbon emissions ($GHGpc$) when a set of regulatory variables that help to

Table 2 Heteroskedasticity-corrected, using 253 observations

Dependent variable: GHGpc	Coefficient	Std. Error	T-ratio	P-value
const	−17.988	3.85236	−4.6693	<0.0001***
GDPpc	0.00250774	0.000309785	8.0951	<0.0001***
GDPpc ²	−4.94348e−08	7.26243e−09	−6.8069	<0.0001***
GDPpc ³	3.17577e−013	0.0000	5.8321	<0.0001***
RDD	−0.00303199	0.000189026	−16.0401	<0.0001***
RNW	−2.42106e−011	7.95101e−012	−3.0450	0.0026***
GLOB	−0.125631	0.0283179	−4.4364	<0.0001***
Statistics based on the weighted data:				
Sum squared resid	597.0611	S.E. of regression	1.557908	
R-squared	0.774896	Adjusted R-squared	0.769405	
F(6, 246)	141.1377	P-value(F)	1.03e−76	
Log-likelihood	−467.6081	Akaike criterion	949.2163	
Schwarz criterion	973.9500	Hannan-Quinn	959.1675	
Statistics based on the original data:				
Mean dependent var	10.91015	S.D. dependent var	2.698881	
Sum squared resid	1310.348	S.E. of regression	2.307946	

explain the evolution of carbon emissions is also included. These exogenous and complementary variables are the replacement of conventional energy sources with renewable ones (RNW) and public spending on energy innovation (RDDPC). For the result of the estimations, this study tries to verify the positive influence of energy innovation and electric use on carbon emissions. Otherwise, we hypothesizes that globalization entails a reduction in the CO₂ emissions.

The analysis of the income-pollution relationship poses certain potential problems. One such problem is the possible two-way causality between income and environmental degradation (Stern, 2004). Otherwise, it is known as an endogeneity problem, which means that some floating and explanatory variable correlates with the error term i.e. ε_{it} . We thus built a model, with instrumental variables for both regressions, without fixed effects in order to determine the correct coefficients of income (GDPpc_{it}, GDPpc_{it}², and GDPpc_{it}³). To capture the non-observables specific to each country that do not vary with time, the fifth regression is a fixed effects regression where GDPpc, GDPpc², and GDPpc³ are implemented with regard to age dependence and inflation, including both the square and cube of each instrument (Table 2).

In a first step, Model-1 is estimated, by *heteroskedasticity-corrected method*. The reduced form of the endogenous explanatory variable is obtained in function of the exogenous variables:

$$\text{GHGpc}_{it} = \alpha_i + \beta_1 \text{GDPpc}_{it} + \beta_2 \text{GDPpc}_{it}^2 + \beta_3 \text{GDPpc}_{it}^3 + \beta_4 \text{RDDPC}_{it} + \beta_5 \text{RNW}_{it} + \beta_6 \text{GLOB}_{it} + \varepsilon_{it} \quad (2b)$$

Discussion of the Results

This study examines the validity of the EKC hypothesis for selected European countries between 1990- and 2012 using heteroskedasticity-corrected method. We also check the relationship between energy innovations, renewable energy consumption, globalization and CO₂ emissions. The empirical results evidence that all variables are significant, confirming the robustness of the proposed model in Eqs. (2a,b).

The estimation of the coefficients (Eqs. (2a,b)) reveals that $\beta_1 > 0$, $\beta_2 < 0$, and $\beta_3 > 0$, confirming an N-shaped EKC pattern in Model-1 (Fig. 4). The first three coefficients β_i determine the cubic shaped of the EKC; the behavior of remaining coefficients also helps explain carbon emissions. This result indicates that initial stage of economic growth, GHGpc levels increase until GDPpc reaches a threshold point ($X_1 = \text{USD } 44,131.83$). Beyond that point, GHGpc levels start to decrease until GDPpc reaches a second turning point ($X_2 = \text{USD } 59,643.10$), (The estimation of the turning points for the cubic model used the following formulation (Diao *et al.*, 2009; Balsalobre and Alvarez, 2016)):

$$X_j = \frac{-\beta_2 \pm \sqrt{\beta_2^2 - 3\beta_1\beta_3}}{3\beta_3}, \forall j = 1, 2$$

To estimate the inflection point:

$$I_j = \frac{-\beta_2}{3\beta_3}, \forall j = 1$$

beyond which GHGpc levels start to rise again. Between first and second turning points appear Inflection $I(1) = \text{USD } 51,887.47$, which suggests that scale effect is able to overcome again composition and technical effects. This inflection point suggests that

economic systems need to accelerate innovation measures (technical effect) to delay scale effect, before these economies reach again a new stage of ascending emission levels (technical obsolescence).

To analyze this EKC's behavior and explain how energy regulations can help to delay the return to increasing GHGpc levels. The coefficient β_4 (Eqs. (2a,b)) represents energy innovations (RDD); the negative sign ($\beta_4 < 0$) suggests that innovation processes reduce GHGpc emissions. This result indicates that the implementation of regulatory policies in the field of energy innovations positively affects the correction of per capita GHG emissions (Balsalobre and Alvarez, 2016). In addition, the coefficient $\beta_5 < 0$ linked with renewable energy use (RNW) indicates that an increase in renewable electric consumption contributes positively to reduce GHGpc emissions. Therefore when economies stimulate innovation processes and renewable electricity use, by extension, the level of energy intensity decreases, helping to reduce GHG emissions (Lin and Polenske, 1995; Balsalobre and Alvarez, 2016; Álvarez et al., 2017).

An additional effect that has been explored in Eqs. (2a,b) is how globalization (GLOB) helps to control emissions. The coefficient $\beta_6 < 0$, which is negative and statistically significant, indicates that globalization process in selected European countries helps to reduce carbon emissions (Shahbaz et al., 2016a). We note that an increase in globalization leads to a decrease in CO₂ emissions. Cavlovic et al. (2000) establishes the existence of a direct relationship between low levels of globalization and high pollution intensity levels. Therefore our study suggest that both energy regulations and globalization help to control emission and delay technical obsolescence. This results also suggests that in the long-term, globalization might be expected to have a positive impact on economic efficiency (technique effect) and improve environment quality. Therefore, increased competition, which is shaped by globalization, will reduce technical inefficiency and pollution levels (Tisdell, 2001; Shahbaz et al., 2016b). This empirical evidence suggests that globalization process is environmentally friendly. This result is in line with previous empirical literature that considers the globalization process in terms of instruments of efficiency and technical progress.

The main objective of this study is to reflect the necessity of examine the inflection point, in order to improve the EKC analysis. According to the results obtained in this study, the scale effect in the EKC, specified by Torras and Boyce (1998), is justified. The way to solve the scale effect is by promoting energy innovation (RDD). When technical obsolescence appears, increasing income levels will lead to increasing environmental degradation (scale effect), which, in turn, will lead to the reemergence of an upward trend in carbon emissions per capita. The estimation of Model-1 incorporates public spending on energy RD&D, a variable that is compatible with our main hypothesis, which suggests that it is necessary to undertake measures to improve energy innovation, whether to correct or prevent environmental degradation. The N-shaped EKC relationship between income and environmental degradation suggests that, in the absence of measures to improve technical innovations, technological obsolescence leads to a return to a state of increasing environmental degradation. Andreoni and Levinson (1998, 2001) consider that the decontamination processes depend mainly on technical innovation. Therefore we suppose that technical effect dominance will depend on the incentives offered to policy makers and energy innovation measures (Heerink et al., 2001; Balsalobre and Alvarez, 2016).

Fig. 5 shows how the inflection point appears when, in long-term, scale effect overcomes composition and technical effect. This behavior is linked with technical obsolescence that implies that without the correct regulation process in the long term will be appear again an ascending stage of emissions (Balsalobre and Alvarez, 2016; Balsalobre et al., 2018). According with the results, $I(1) = \text{USD } 51,887.47$, when selected economies arise that inflection points starts there is a reduction in the positive effect of technical effect and composition effect on environmental quality. This point suggests that economies have to star to accelerate innovation processes before they reach that point. On the other hand, when scale effect overcomes composition and technical

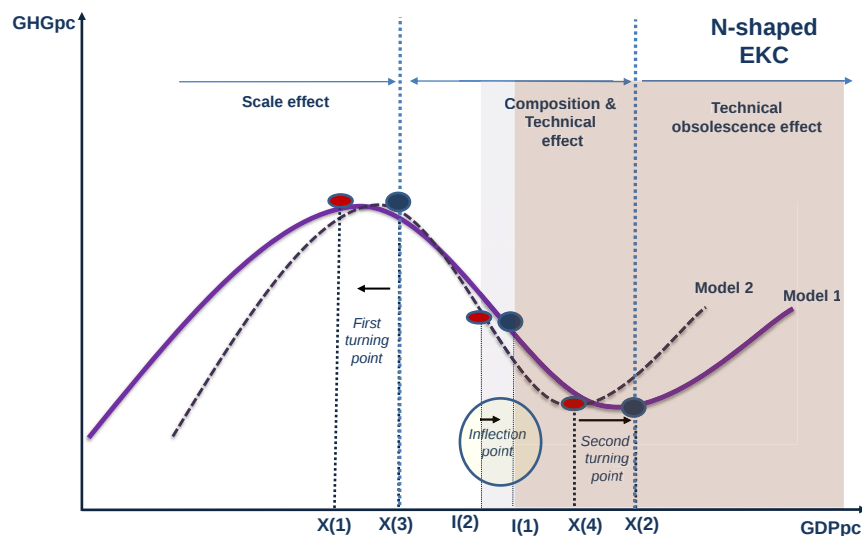


Fig. 5 Comparison of Models: Isolation of Energy Regulation Variables.

Table 3 Comparison between Model 1, Model 2 and Model 3

Dependent variable: GHGpc Variable	Model 1 Coefficient	Model 2 Coefficient	Model 2 Coefficient
Const	− 17.988 (3.85236)*	− 13.7525 (3.87371)*	− 14.7735 (4.19043)*
GDPpppp	0.00250774 (0.000309785)*	0.00175474 (0.000321526)*	0.00157954 (0.000336109)*
GDPpppp2	− 4.94348e−08 (7.26243e−09)*	− 3.49211e−08 (7.65953e−09)*	− 3.08613e−08 (8.31221e−09)*
GDPpppp3	3.17577e−013 (0)*	2.28182e−013 (0)*	1.97884e−013 (0)*
RDD	− 0.00303199 (0.000189026)*	−	−
RNW	− 2.42106e−011 (7.95101e−012)*	−	−
GLOB	− 0.125631 (0.0283179)*	− 0.0422619 (0.030239)*	−
R-squared	0.774896	0.499114	0.474975
Adjusted R-squared	0.769405	0.491036	0.468650
F-statistic	141.1377	61.78077	75.08782
P-value(F)	1.03e−76	3.68e−36	1.27e−34

effects, there is a deceleration of environmental correction process. In advanced economies, growth rates are generally low, such that technological change may overcome the scale effect implies that the quality of environment and technology are public goods, which makes government involvement necessary to keep a market economy on a socially optimal path.

Any strategy that seeks to reduce contamination levels must thus assume increasing returns to scale. In turn, we can infer that technical innovation is fundamental to control carbon emissions. When societies assume innovation processes it make environmental correction possible at lower incomes (Arrow *et al.*, 1995; Stigl, 1999; Unruh and Moomaw, 1998; Balsalobre *et al.*, 2015). Therefore, the implementation of measures related to energy innovation and the replacement of conventional sources with renewable ones results in a deviation from the diminishing technological returns, leading to a reversal in the upward trajectory of the EKC (Opschoor and Vos, 1989; Torras and Boyce, 1998; Balsalobre *et al.*, 2015).

To validate this hypothesis, we isolate the effect of energy regulation, omitting the variables RDD and RNW (Table 3) to demonstrate how the EKC performs (Model-2) and whether the turning points reflect the omission of the regulatory variable. This step is important in order to show how energy regulation and innovation policies are relevant to solve technical obsolescence.

$$\text{GHGpc}_{it} = \alpha_i + \beta_1 \text{GDPpc}_{it} + \beta_2 \text{GDPpc}_{it}^2 + \beta_3 \text{GDPpc}_{it}^3 + \beta_6 \text{GLOB}_{it} + \varepsilon_{it} \quad (3)$$

$$\text{GHGpc}_{it} = \alpha_i + \beta_1 \text{GDPpc}_{it} + \beta_2 \text{GDPpc}_{it}^2 + \beta_3 \text{GDPpc}_{it}^3 + \varepsilon_{it} \quad (4)$$

Model 2 (Eq. 3) omits the variables RDD_{it} and RNW_{it} is estimated, the turning points change, while model 3 (Eq. 4) just confirms the N-shaped model for selected countries between 1990 and 2012.

When we compare Model 1 (Eqs. (2a,b)) and Model 2 (Eq. 3), which omit the regulatory variables (RDD_{it} and RNW_{it}), in the main model (Model 1), the income requirements necessary to achieve reductions in carbon emissions per capita are lower ($X_1 = \text{USD } 44,131.83 < X_3 = \text{USD } 44,767.25$). Another consequence of the application of energy regulations is that income required to reach the second turning point, and, thus, to return to increasing pollution levels, is higher ($X_2 = \text{USD } 59,643.10 > X_4 = \text{USD } 57,259.79$). Another consequence of the estimation and comparison between Model 1 and Model 2 is that the former model can include a breakthrough in Fig. 1. Model 1 suggests the appearance of a new effect, which we define as the technical obsolescence effect (Balsalobre and Alvarez, 2016) that occurs as result of inadequate energy regulation strategy. When economies reach the state of technical obsolescence, it leads once again to an increase in environmental pollution levels. Otherwise, the inflection point of Model 2 (Eq. 3) reflects $I_2 = 51,013, 52 < I(1) = \text{USD } 51,887.47$, which implies that without regulatory measures scale effect appears sooner. So, the inflection point shows the income level necessary to take energy measures before economies reach the second turning point, and scale effect overcomes again composition and technical effect (technical obsolescence effect).

Conclusions and Policy Implications

Although the environmental Kuznets curve has been widely studied from both a theoretical and an empirical perspective, the various studies on EKC in the last decade have not been sufficient to provide a unanimous response in this field of study. This study constitutes an improvement in the analysis of the EKC pattern. The main objective of this paper is to analyze the inflection point between turning points and how it affects to carbon emissions. Our study including additional variables linked to energy

regulation, in order to validate that, in addition to economic growth, measures in the fields of energy innovations and the replacement of conventional energy sources with renewable ones are required to reduce carbon emissions. The results show an N-shaped relationship between income and environmental degradation.

This study demonstrates, through a heteroskedasticity-corrected econometric estimation for selected countries in the years 1990–2012 that regulatory measures and globalization help to reduce carbon emissions. The main model (Eqs. (2a,b)) proposed in this study demonstrates the relevance of environmental regulation measures to keeping countries on a path of decreasing carbon emissions per capita, even once they have attained high income levels. When economies' income levels increase, early on in the process of economic development, pollution levels rise. When income levels reach the first turning point, economies begin to experience corrections in their emissions. In a second stage, pollution levels begin to fall, in keeping with further increases in economies' income levels. This behavior is sustained until a second turning point is reached, after which economies once again begin to experience increases in pollution levels. Fig. 5 shows that without energy regulations (energy innovation and renewable energy promotion), economies may return to a pattern of increasing environmental degradation, a phenomenon that this study defines as the technological obsolescence effect, where inflection point has an essential role on this process. Consequently, to avoid this return to a path of increasing contamination, measures must be taken to encourage technological innovations and promotion of renewable sources, as not to fall into the trap of technical obsolescence.

This study tries to verify whether implementing environmental regulations has any effects beyond the EKC. In this regard, we have confirmed that, with the incorporation of energy regulations, second turning point, which is the consequence of technological obsolescence, can be pushed back. For this reason, regulations of energy innovation and renewable energy promotion help to delay the scale effect, according to which in the absence of regulatory measures, economies will once again see diminishing returns and increases in environmental pollution. The results also support the positive effect that globalization contributes positively to the reduction of carbon emissions.

Finally, the results obtained support the how the inflection point helps to advances in the analysis of the EKC. Finally, the results validate that environmental regulations should aim to provide incentives for innovation and the adoption of better abatement technologies. This study also points to the need for greater nuance in policy approaches aimed at energy innovation. Our results indicate that advances in energy processes are necessary to improve environmental quality. One of the most important conclusions that can be drawn from the EKC analysis is that environmental quality cannot wait until per capita income rises, as pollution will not automatically disappear with economic growth. This leads us to conclude that there is a strong need for European countries to develop specific policies in energy RD&D, energy replacement and globalization to reduce environmental pollution.

See also: Selected Issues in Economics of Greenhouse Gas Emission Mitigation

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Thermoelectric Materials: Improving Energy Efficiency and Decreasing CO₂ Emissions

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Introduction

From the year of 1760 onward Great Britain witnessed the industrial boom regarding the nature of machines where some particular works have been shifted to highly profiled special purpose machines from general purpose applications comprising of simple hand tools and basic home-made machines. Since then coal emerged to be the main source of energy in the entire world. It is an established fact that the energy sources may broadly be classified into conventional energy sources like coal, oil or natural gas, and renewable energy. The latter includes hydro power (water energy), wind energy, geothermal energy, solar power, and tidal energy, which are inexhaustible, clean, pollution free, and environmentally friendly. The source of electricity generation has been slowly shifting from conventional to renewable energy for the different advantages associated, with China, the United States, and the European Union as the frontline leaders in this respect.

The energy crisis that the earth is witnessing now is mainly related to limited use of the alternative energy sources and excessive dependence on the fossil fuel sources, which are supposed to be depleted within the next few decades. It is an alarming fact that despite several atmosphere threatening facts regarding the use of fossil fuel, 41% of the electricity generated worldwide uses coal as the source material causing emission of huge amounts of greenhouse gases. Also surprising is the fact that such unscientific use of fossil fuel is most acute in several developed countries like China, Australia, and other European states.

Now with the increasing environmental awareness, several countries having significant contribution towards greenhouse gases have stepped forward and discussed resolving the issues with severe climate change. In that list China is a mention-worthy country, which according to the United Nations Organization report is one of the main carbon dioxide contributors. Fig. 1 shows the current and projected energy consumption worldwide between 1990 and 2040 for both OECD and non OECD countries (see "Relevant Websites section").

The mechanical division extends to share the highest part of distributed power usage; global industries are expected to use more than 50% of energy in 2040. Though there are different international policies that impose critical limits on use of conventional energy, still it is predicted that there will be a 46% increase of CO ranging from 31 billion metric tons in 2010 to 36 billion metric

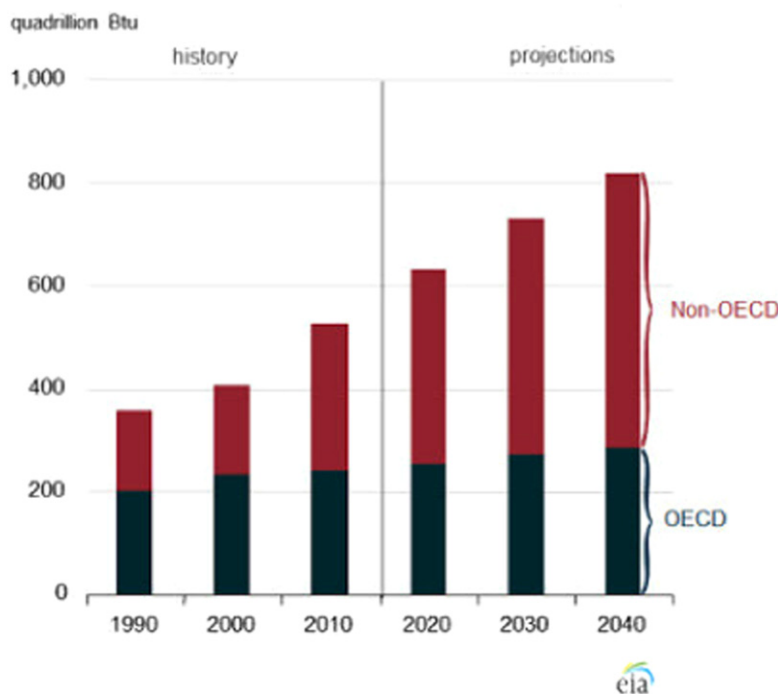


Fig. 1 World energy consumption, 1990–2040 (<https://www.linkedin.com/pulse/energy-crisis-causes-effects-remedies-naveed-ahmed-unar>).

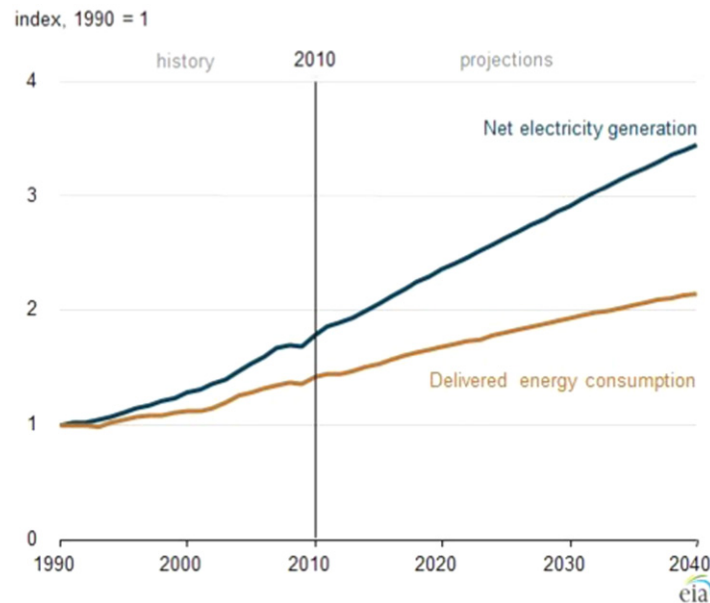


Fig. 2 Growth in total electricity generation and total delivered energy consumption, 1990–2040 (<https://www.linkedin.com/pulse/energy-crisis-causes-effects-remedies-naveed-ahmed-unar>).

tons in 2020 and 45 billion metric tons in 2040. An aggregate of global power usage jumps from 524 quadrillion British Thermal Units (BTUs) in 2010 to 630 quadrillion BTUs in 2020 and 820 quadrillion BTUs in 2040.

It is no wonder that there is a tremendous effort worldwide to use renewable energy sources for the entire electricity needed, and in this aspect Denmark has achieved a commendable effort and produced 140% of their total electricity needed from wind power alone. Also the Scottish government has set an aim to generate 100% of the electrical energy needed with renewable sources by 2020.

In 2013, in a report entitled “International Energy Outlook 2013” the United States Energy Information Administration predicted that around 11% of the energy consumption is from renewable sources worldwide, which should be increased to 15% by the year 2040. On the other hand about 21% of the global power generation was from alternative sources like nuclear or other clean sources, which will be increased up to 25% by the same year. **Fig. 2** shows the corresponding statistics graphically (both existing and projected).

It is to be noted that there is always an imbalance between the energy consumed and energy generated associated with every country, which leads to the energy crisis. The situation can be understood if one analyzes the fact that the United States only has less than 3% of the global oil reserves and only 3.5% of gas reserves whereas Japan and China extract the major portion of their required energy from outside. On the other hand, the major raw energies are found in the vicinity of Gulf countries and Russia, which are however not big consumers of these. **Fig. 3** shows the existing and projected electricity generation from different sources up to 2040.

In another Asian country, like Pakistan, the distribution of energy is also mostly dependent upon the fossil fuel like gas (47.5%), oil (30.5%), coal (11.07%), and LPG (1.53%), which are of great concern. Presently the country is generating 35% of electrical power via hydel energy.

It would not be out of place to mention here that the alternative/renewable energies may be associated with greater installation cost and other installation hazards compared with the fossil fuels; however, they are associated with the pragmatic solution of the environmental issue as well as a gateway to balanced energy mix. It is to be noted that with the daily increasing demand of energy with limited supply of it this energy crisis brings economic demise enclosed with regional conflicts. Thus it is the perfect time to go for renewable energy to recuperate the global energy market.

Looking again back to the statistical analysis it can be seen that a country like China has done better than any other with investment of \$51 billion in alternative energy technologies and led the world in renewable power capacity with 70 total giga-Watts whereas in the same year that two figures for the United States are \$48 billion and 68 GW respectively. Germany took the third place in this aspect with \$31 billion investment with the total output capacity of 61 GW.

Germany's production of alternative energy, which provides nearly 11% of the country's energy needs, leads G-20 members (a group of finance ministers and central bank governors from 20 major economies), as stated by a 2012 report by the National Resources Defence Council. Indonesia follows, with roughly 6%, and next is the United Kingdom, at about 4%. The United States came in seventh, with only 3% of its electricity coming from renewable sources.

An extensive research led by Cutler Cleveland and team predicts that in the coming 50 years no country can produce renewable energy that alone can meet the entire energy requirement; however they also saw some commendable growth in some particular

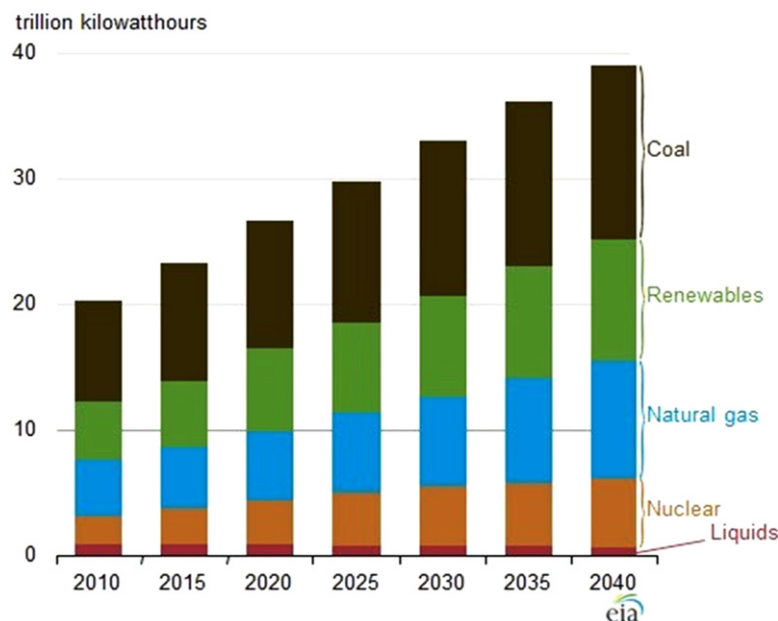


Fig. 3 World net electricity generation by fuels (<https://www.linkedin.com/pulse/energy-crisis-causes-effects-remedies-naveed-ahmed-unar>).

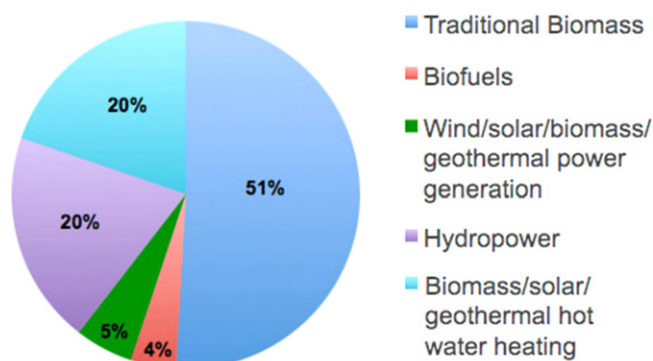


Fig. 4 A look at the world renewable energy consumption in 2010. *Source:* Energy Transitions by Cutler Cleveland (https://file:///H:/Chapter%204/The%20Climate%20Crisis_%20Breaking%20the%20Fossil%20Fuel%20Habit%20_%20BU%20Today%20_%20Boston%20University.html).

sectors. For instance the cost of wind energy has decreased much due to the government subsidies and other improved technologies used. However another very promising energy sector, that is, solar energy needs to contribute substantially to the renewable energy sector.

Nuclear power, even though there are other low carbon energy sources, provides only 3% of the current world energy however it has an inherent drawback related to hazardous waste disposal and safety use making it less acceptable compared with wind or solar energy. In the developed countries like the United States, which has 65 operating nuclear power plants, people are not very keen on accepting it near their land because of the radioactive waste associated. Thus it may raise political issues if any government put extra effort in establishing new power plants.

Biomass such as switch grass, corn, or sugar cane converted to biofuel is another alternative source of energy, however, it associated with carbon exchange and thus again is not very environment friendly. **Fig. 4** shows the distribution in the use of renewable energy.

As per the extensive research work of Cleveland, it can be concluded that the best way to break the fossil fuel habit is developing a sustainable energy infrastructure using fossil fuel and with the help of these developed infrastructure one has to move slowly from coal and oil to renewable energy (see "Relevant Websites section"). Other associated policies taken by different governments like gas tax hikes, mandatory car-pooling to office/school/college, or mass awareness increase towards use of renewable energy can dramatically change the situation.

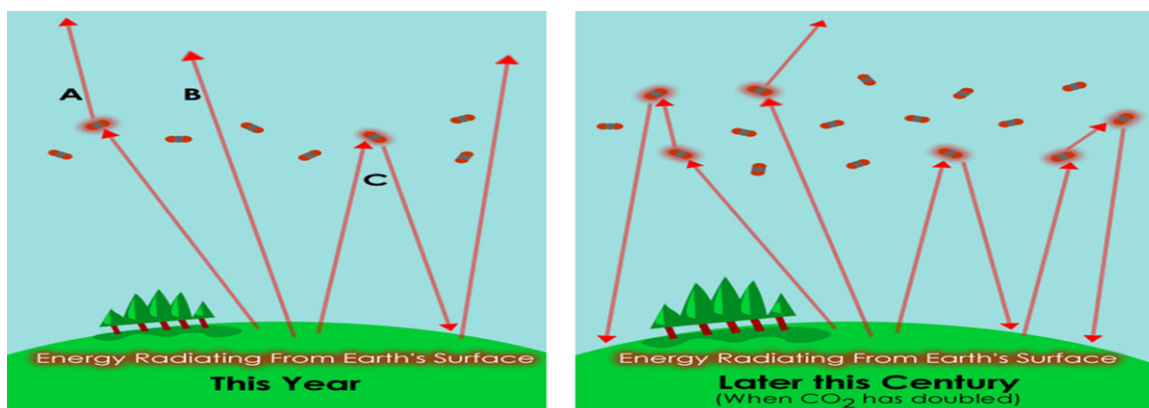


Fig. 5 Earth's surface, warmed by the sun, radiates heat into the atmosphere. Some heat is absorbed by greenhouse gases like carbon dioxide and then radiated to space (A). Some heat makes its way to space directly (B). Some heat is absorbed by greenhouse gases and then radiated back towards Earth's surface (C). With more carbon dioxide in the atmosphere later this century, more heat will be stopped by greenhouse gases, warming the planet (<https://scied.ucar.edu/longcontent/greenhouse-effect>).

Greenhouse Effect

The greenhouse effect is a phenomenon that causes the natural temperature of the planet to be above freezing. In principle the greenhouse effect is the net imbalance of the energy that comes from the sun into the planet and goes back into space. This effect results in imbalanced energy being absorbed and released by greenhouse gases. Though the effect is quite natural in our climate, the situation has grown alarming as due to basic human activity more and more greenhouse gases are generated and the atmosphere of the planet is getting warmer day by day (see "Relevant Websites section").

As mentioned before, Earth absorbs solar energy and reemits it into atmosphere in the form of heat. Due to the special molecular arrangement, a few gases called greenhouse gases can absorb much of it, which in turn they radiate back either to Earth's surface, to the atmosphere, or to another greenhouse gas molecule. Some typical examples of greenhouse gases are carbon dioxide, water vapor, methane, and nitrous oxide. The major constituent atmospheric gases nitrogen, oxygen, and argon, which are all diatomic and monoatomic, are not greenhouse gases. This is due to the fact that diatomic molecules like O₂ or N₂ have no net change in the distribution of their electrical charges or dipole moment when they vibrate. Also for monoatomic gas like argon there is no vibrational mode. Hence they are almost totally unaffected by infrared radiation. The heteroatomic molecules like carbon monoxide or hydrogen chloride absorb infrared radiation. However these molecules are short-lived in the atmosphere owing to their reactivity and solubility and this is the reason these gases do not significantly contribute to the greenhouse effect.

Fig. 5 shows the distribution of solar energy into Earth's surface.

It is to be noted that though the total amount of all the greenhouse gases is still very small as compared with the total atmospheric gases but they have tremendous effect on the climate of the planet. More alarmingly it can be predicted with perfection that due to excessive exhaustion of fossil fuel in the coming years the amount of carbon containing greenhouse gases will be doubled. Some farm animals release methane as they digest food, and during manufacturing of cement from limestone, carbon dioxide gases also gets released. The effect of presence of greenhouse gases is as follows. With more greenhouse gases in the air, heat passing through its way out of the atmosphere is more likely to be stopped. The added greenhouse gases absorb the heat. They then radiate this heat. Some of the heat will head away from the Earth, some of it will be absorbed by another greenhouse gas molecule, and some of it will wind up back at the planet's surface again. With more greenhouse gases, heat will stick around, warming the planet.

Energy Harvesting

What is Energy Harvesting

The process is alternatively known as energy scavenging or microenergy harvesting and is actually associated with capturing and reusing of readily available energy in the universe. The conversion is mainly into electrical energy, which can be of instantaneous use or can be stored for future applications. This process is useful mainly in places where it is difficult to install wind turbines or solar panels and power grids are not available. The captured energy can mainly be used for various applications like wireless applications, remote sensing, body implants, radio-frequency identification (RFID), and other applications at the lower segments of the power spectrum. When the energy harvested is not sufficient in making a small device run independently it can still make a battery run with longer lifetime (see "Relevant Websites section").

Why Harvest Energy

It is to be noted that the changing of batteries after a certain period is one of the major problems associated with low-power electronic devices. The problem mainly involves cost especially when there are hundreds of such devices like sensors involved, especially in remote locations. Energy harvesting technology on the other hand eliminates the need of replacing batteries regularly, providing almost infinite operating time to the battery. Thus the battery replacement becomes unnecessary where it is costly or not feasible or dangerous. Most energy harvesting systems are self-sustaining and practically require no servicing for many years. In addition, the power is used closest to the source, hence eliminating transmission losses and long cables. If the energy is enough to power the device directly, the application or device powered by the energy can operate batteryless.

Energy Harvesting Technologies

As mentioned before there are dedicated power conversion circuits that will be required for efficient collection, managing, and conversion of energy from different nontraditional power sources into usable electrical energy for different microelectronic devices like remote sensing, body implants, RFID, and others. The harvesting will be with the help of thermoelectric generators, piezoelectric transducers, and solar cells or others.

Harvesting kinetic energy

Kinetic energy originating from different vibrations, mechanical movement, etc. is collected and converted into electrical energy by a transducer, which is then rectified, regulated, and stored in certain thin film battery or supercapacitors. A few examples of proper harvesting and utilization of mechanical energy include a batteryless remote control unit where power is harvested from the force that one uses in pressing the button. The harvested energy is enough to power the low-power circuit and transmit the infrared or wireless radio signal. Another example is pressure sensors for car tires. In this application piezoelectric sensors are placed inside car tires from which they monitor the pressure and send information to the dashboard for the driver to see.

Harvesting RF energy

Here also the basic mechanism is the same. The antenna dedicated for receiving radio frequency signals pass the same to the associated transducer and thus the radio frequency gets converted to a DC voltage of 5.25 V capable of generating a current of 50 mA. In this way development of complete battery-free wireless sensor is possible, which finds applications in various fields like building automation, smart grid, defense, industrial monitoring, and more.

Harvesting solar energy

In this case light energy is converted to electrical energy with the help of photovoltaic cell. Here due to the intermittent nature of light the proper storage of energy is required. Thus the energy is used to charge a supercapacitor or battery to ensure a stable supply to the application.

The system found its applications in both industrial and domestic purposes, which include satellites, portable power supplies, streetlights, toys, calculators, and more. For indoor applications the typical intensity of the light used is not more than $10 \mu\text{W}/\text{cm}^2$. For indoor applications, light is usually not very strong and typical intensity is about $10 \mu\text{W}/\text{cm}^2$. It is to be noted that the power from an indoor energy harvesting system thus depends on the size of the solar module as well as the intensity or spectral composition of the light.

Harvesting thermal energy

Excess heat from industry is an abundant resource of unutilized energy that is primarily considered as a waste. The effective utilization of this heat energy, even up to a small percentage, may have significant effect on the energy efficiency of the fossil fuel utilization and also thereby mitigation of carbon dioxide, which would ultimately lead to a low carbon society. From the basic law of thermodynamics, whenever work is obtained from some resource such as fossil fuel, heat will be generated as a by-product. This heat energy remains untapped.

There are various innovative attempts to harness the waste heat to convert it into usable form of energy such as electricity. Various heat conversion technologies have already been developed with varying efficiencies. These include Rankine cycle, phase change material engine, thermophotovoltaics, and thermoelectricity.

Alternative Effective Fuel Generation

Even before 20th century, in 1896, Swedish researcher Svante Arrhenius was the first who predicted that constant use of fossil fuel can cause major problems like global warming. However nobody paid serious attention in this matter until the beginning of the 21st century.

When people realize that the use of fossil fuel should be decreased, the very obvious question that one has to face is what can be the possible replacement for conventional fossil fuel. All these alternative sources have their individual merits and demerits,

however, they all have substantial contribution towards the fields of alternative energy. These merits are related to the feasibility, efficiency, or cost (see “Relevant Websites section”). Considering all these, a few sources of alternative energy have been mentioned below.

Hydrogen Gas

Hydrogen gas is one of the most important alternative forms of energy, which is mainly associated with clean burning fuel producing only water vapor and warm air upon use, unlike other natural gases. It can either be extracted as the by-product of natural gases and fossil fuel emissions or can be generated by splitting of water through electrolysis. The first process denies its advantage due to the associated use of fossil fuel whereas the second one lacks the adequate generation of the product as per requirement. Present research has concentrated in generating hydrogen with much more efficiency to meet the supply/demand ratio properly.

Tidal Energy

Tidal energy has enormous potential to be one of the major contributors in the field of alternative energy. It can satisfy 20% of total electricity needed in UK. Mainly tidal stream generators are used to produce electricity from the kinetic energy of ocean without producing any waste. This is nothing but the production of electricity from tidal energy, resembling hydroelectricity generation.

Biomass Energy

Biomass energy is associated with the carbon emission; however, the rate of emission is lower than that from fossil fuel combustion. For domestic use, the maintenance cost is higher and one has to get permission from local government. This energy is not only associated with wood burning at low temperature but also associated with landfills and alcohol products.

Wind Energy

As the name suggests this energy is generated by using natural wind by means of wind turbine. This also produces no waste, keeping all other advantages regarding energy production the same. It is interesting to know that in the United States there are more than 20 million homes where only wind energy supplies all the required power and the number is increasing every day. Most of the nation here has some kind of wind energy set up and they have substantial investment regarding the growth of this particular technology.

Geothermal Power

Geothermal power has great potential to meet the energy requirements of around 40 countries and this particular energy sector has experienced a massive growth of 5% worldwide in the year 2015. This power is all about extracting energies from the ground around us without doing any acute harm to the land. However the sector has inherent drawbacks regarding the huge initial cost associated with the installation of power plants. This is the main reason that this form of energy with so much potential has not spread at the expected pace.

Natural Gas

Natural gas though has potential in different fields of applications like the vehicle industry for reduced rate of carbon emission; it also has the biggest negative issues compared with all other alternative energy sources associated with pollution. Further, natural gases emit greenhouse gases though the emission level is lower than that of fossil fuel. In last few years the demand for this form of energy has increased at a massive rate. In 2016, the lower 48 states of the United States reached record levels of demand and consumption.

Biofuels

This kind of alternative energy also has found its application mainly in the United States with around 7% of the transport fuel consumption supplied from this form of energy in the year 2012 and its use is increasing day by day. This energy, unlike biomass energy, uses animal and plant life to produce energy. The drawback is that the machinery needed for the proper extraction of the energy emits a considerable amount carbon.

Wave Energy

Wave energy also uses water energy like tidal energy, going further in that they can be placed in the ocean in various situations and locations. Like tidal energy its inherent advantage is the absence of any waste product associated with it. It is also more reliable than many other forms of alternative energy and has enormous potential when used properly. There are two major shortcomings regarding the extensive use of this form of energy: First is obviously the cost, and second is related to less knowledge regarding its effects on natural ecosystems.

Hydroelectric Energy

Hydroelectric energy is one of the oldest forms of energy where the electricity is generated by means of water turbine. However due to the rise of fossil fuel the use of this form of energy has been decreased rapidly still they supply the 7% of total energy produced in the United States. It has advantages of being renewable as well as a clean source of energy. Also it has some associated advantages like flood control by the dams raised for generating electricity.

Nuclear Power

Nuclear power plants generate a quarter of the electricity in 12 countries around the world with more than 450 plants working worldwide. It is mention-worthy that this power is amongst the most abundant forms of alternative energy. This has advantages regarding emission, efficiency, and moreover regarding the creation of jobs in the field of power plant development and maintenance. However, it has drawbacks regarding the definite catastrophe associated with sudden breakdown of the plant.

Solar Energy

Solar energy is the most popular form of alternative energy and has shown tremendous potential in solving the energy issue. In the last couple of decades much of the alternative energy related research has been focused on this form of such energy. A number of countries have introduced initiatives to promote the growth of solar power. The United Kingdom's Feed-in Tariff is one example, as is the United State's Solar Investment Tax Credit.

This energy source is renewable in all senses and though it seems costly at the time of installation, this cost can be counter-balanced by the money saved in energy bills compared with the traditional energy sources. Nevertheless, solar cells are prone to deterioration over large periods of time and are not as effective in unideal weather conditions.

An Introduction to Thermoelectric Phenomena

Thermoelectric effect involves generation of electricity due to temperature gradient existing over a thermocouple. The effect can be classified into three categories: Seebeck effect, Peltier effect, and Thomson effect.

Seebeck effect is associated with the generation of electricity in a thermocouple when one junction is kept at lower temperature while the temperature of the other junction is raised.

Peltier effect is completely different from Joule heating, and involves generation of temperature gradient when current is applied.

In contrast with the previous two effects the *Thomson effect* involves single conductor instead of thermocouple. Here, if two points of a conductor of the same material are maintained at different temperatures then there exists an e.m.f between these points. So there will be evolution or absorption of heat in excess of Joule heat when a direct current passes through a non-uniformly heated conductor. It is also a reversible phenomenon.

The efficiency of a thermoelectric material is determined by the dimensionless figure of merit, where S is the thermoelectric power, defined as the

$$ZT = \frac{S^2 \sigma}{\kappa} T \quad (1)$$

Here, σ is the Seebeck coefficient, κ is the total thermal conductivity consisting of both phonon and electronic contributions, and T is the temperature. The efficiency is related to ZT by the following equation:

$$\eta = \frac{\Delta T}{T_{Hot}} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_{Cold}}{T_{Hot}}} \quad (2)$$

where T_{Hot} is the temperature of the hot junction and T_{Cold} is the temperature of the cold junction. One immediately sees that the efficiency tends towards the Carnot limit when ZT approaches infinity. To compete with modern-day compressor based refrigerators, a thermoelectric device must have a $ZT > 3$.

There is no theoretical limit to ZT . To maximize ZT , P must be large so that a small temperature difference can create a large voltage, σ must be large to minimize joule heating losses, and κ must be small to reduce heat leakage and maintain a temperature

difference. P , S , and κ are not, however, mutually exclusive. For instance in a bulk material, the Weidmann–Franz law limits the ratio σ/κ_e , where κ_e is the electronic contribution to the total thermal conductivity. Also, a sharply peaked density of states favors large S , but the density of states is a smoothly varying function for bulk materials. Nanowires may offer the possibility to circumvent some of the materials limitations found in bulk. First, the thermal conductivity has been shown to decrease when the size of a material is reduced to the nanoscale. Second, the thermopower is sensitive to the density of states and phonon–electron scattering, which may be very different in certain materials at the nanoscale. To increase ZT , a better understanding of the interplay between the three materials parameters, P , S , and κ , must be developed.

Electronic Theory for the Generation of Thermoelectricity

The reason behind thermoelectricity is mainly dependent upon the transport phenomena of the charge carrier, that is, electron. When two metals are brought into contact with one another the electrons from one metal start to flow into the other one, making first one positive and the second metal negative. Thus an e.m.f. gets developed across the junction trying to prevent the further electron diffusion. This e.m.f., also known as contact e.m.f., is equal to the difference between the work function of the two metals. Now, if both the junctions of the thermocouple are kept at the same temperature the as-grown contact e.m.f. nullifies each other and no net electron flow occurs.

However the contact e.m.f. depends slightly on temperature and thus a net e.m.f. gets developed when two junctions of the system are kept at different temperature. Also due to the higher thermal energy the electrons diffuse more rapidly from the hot end to cold end than from the cold to hot end, and give rise to the volume component of the thermo e.m.f. Also at low temperature another component of thermo e.m.f. may contribute, which comes from the phonon assisted drag of electron from hot to cold end.

The Peltier effect can be explained with the assumption of using an external battery to send current through the junctions maintained at same temperature. In one junction the current is flown against the contact e.m.f. and thus the work has to be done against it and heat gets generated. Similarly in the other junction the current flows down along the direction of the contact potential, hence the work is done by it and as consequence the junction gets cooled.

The effect can alternately be explained in other ways. Let the average carrier energy of metal I and metal II be w_1 and w_2 ($w_1 > w_2$) and let the direction of current be such that carrier passes from metal I to II at one junction. Then the carriers of metal I give up excess energy at a region very near to the junction and thus the junction gets hot. Similarly in the other junction carrier moves from II to I and the less energized carriers absorb energy and consequently the junction gets cold. This accounts for the observed Peltier effect.

Thomson effect can also be explained from the same point of view. It should be noted that the electrons from the hot end thus would diffuse into the metal faster than those from the cold side. Thus during the passage of electrons from the hot side it loses energy due to collision with the lattice in the colder side and causes evolution of Thomson effect. However this theory is too simple and cannot account for the fact that for some metals, the effect is positive, whereas for others it is negative.

Band theory of solids can explain the work more vividly. Electrons from the hot end have more energy and higher wave number value. Their velocity depends on the shape of E – k curve near the top of a band. If $\frac{d^2E}{dk^2}$ is negative then the velocity $v = \frac{2\pi}{h} \frac{dE}{dk}$ of the electrons from the hot end would be lower compared with that from the cold end and as a consequence the electron would diffuse more rapidly from the cold end contrary to the previous expression. This would give rise to an e.m.f. of opposite sign to that we should expect from free electrons.

Some Efficient Thermoelectric Materials

So far a number of potentially important thermoelectric materials have been discovered and studied widely. From the long list only some important materials are mentioned below. In this context, the material Bi_2Te_3 is mention-worthy at the beginning.

The material has strong anisotropy associated with its properties and a strong correlation between electrical conductivity and the stoichiometric composition of the material can be observed. It has very high vacancy induced defect density, as high as 10^{21} cm^{-3} . This has direct consequences with strong scattering of carriers causing substantial decrease of the mobility. The inherent low melting point (585°C) and small bandgap (0.16 eV at 300K) makes it suitable for using it in low temperature region ($\leq 150^\circ\text{C}$). A suitable substitution can make the material p-type (As, Sb, Pb) or n type (I and Cu). Bi_2Te_3 based materials have low band gap (0.16 eV at 300K) and thus are used at low temperature in thermoelectric cooling devices. The band gap and hence the operating temperature of the material can be increased up to 950K with suitable replacement of Te by Se ($\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$), which may double the band gap of the material for optimum value of x .

The materials operated between temperature ranges 450–950K are medium-temperature thermoelectric materials for which an optimum band gap of ≈ 0.6 eV is needed; however some exceptions of lower band gap materials can also be seen. Chalcogenide materials like PbTe, PbSe, and GeTe are good examples of medium-temperature thermoelectric materials having operating temperature between ambient and 625°C . Fig. 6 shows the temperature variation of ZT values for medium-temperature thermoelectric materials.

Semiconductors like silicon or germanium in their elementary forms have high thermal conductivity and low figure of merit values and thus are not much suitable for thermoelectric applications. However a Si–Ge solid solution thermal conductivity decreases substantially and thus they can be used as high temperature thermoelectric material with operating temperature $\sim 1000\text{K}$.

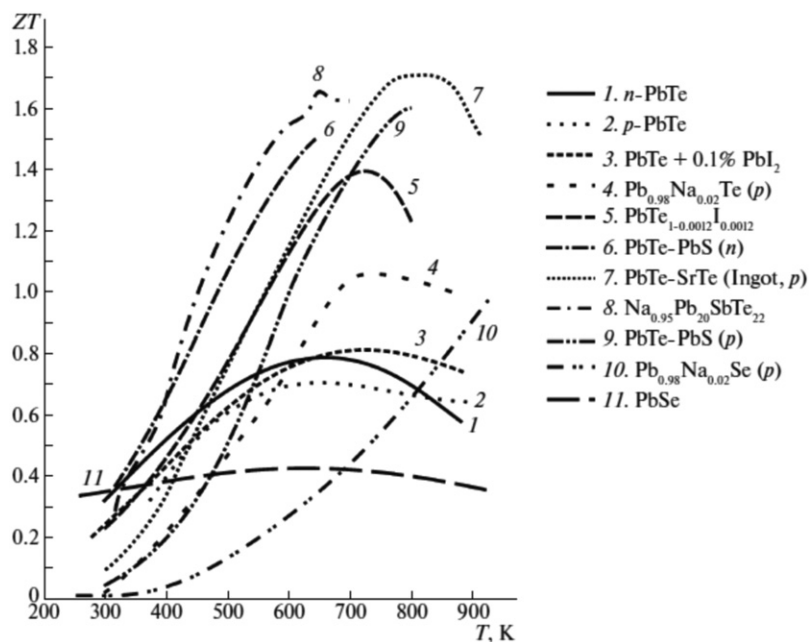


Fig. 6 Temperature variation of ZT values for medium-temperature thermoelectric materials. Reproduced from Sherchenkov, A.A., Shtern, Y.I., Mironov, R.E., Shtern, M.Y., Rogachev, M.S., 2015. Current state of thermoelectric material science and the search for new effective materials. *Nanotechnologies in Russia* 10 (11–12), 827–840.

Also there is search for a new material that has strong scattering of phonons with low thermal conductivity and high transport properties (Slack, 1995). This kind of material is called phonon glass–electronic crystal (PGEC), having less thermal conductivity high transport properties of charge carrier. The concept was proposed by J.A. Slack in 1995.

As per Slack's idea, in PGEC one atom is weakly attached to the other atoms of the unit cell experiencing nonharmonic oscillation, which is independent of the fluctuation of the other atoms in the unit cell. This oscillation reduces the phonon components of the thermal conductivity and thus the value of the latter reduces significantly while keeping the electrical property of the material almost unchanged significantly enhancing the figure of merit value.

A set of materials that belongs to PGEC category are called skutterudites, which came from the mineral based on CoAs_3 . Other skutterudites include the materials with similar structures like CoP_3 , CoAs_3 , CoSb_3 , RhP_3 , RhAs_3 , RhSb_3 , IrP_3 , IrAs_3 , and IrSb_3 , having the general formula of MX_3 . Fig. 7 shows that at room temperature these kinds of materials have small ZT value ~ 0.2 , however, at 1000K ZT has a value ~ 1.4 exceeding that of SiGe solid solution.

Another set of materials analogous to PGEC are called clathrates, which are in principle composed of ten to hundred atoms of crystalline materials. Here the structure is formed by the formation of covalently bound frame of atoms and loosely connected with the frame of atoms or molecules located in the cavities. In case of semiconductor clathrates the framework is formed with different group IV elements like Si, Ge, and Sn, which can be substituted by nontransition elements like P, As, Sb, Bi, Al, Ga, In, and Te or transition metals like Ni, Pd, Pt, Cu, Ag, or Au. However substitution should be in small amounts in the case of transition elements.

So far clathrate $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ is reported to have the highest ZT values at 0.35, which is however much less compared with the values of established thermoelectric materials.

An abnormally high ZT value of ~ 2.3 along the c -axis and ~ 0.8 along the a -axis has been reported for the material SnSe at 923K (Zhao *et al.*, 2014). Also high value of ZT can be found for the material Zn_4Sb_3 . A set of materials with modified Bi_2Te_3 structures with the structure of tetradymite and blocks of tellurides of arsenic, lead, or germanium with the adjusting structure attracted the current researchers as efficient thermoelectric material. $\text{Ge}_2\text{Bi}_3\text{Te}_5$, GeBi_2Te_4 , GeBi_4Te_7 , and $\text{GeBi}_5\text{Te}_{10}$ are few examples of such materials.

Some other promising thermoelectric materials are Na_2CoO_4 , CaMnO_3 , $(\text{ZnO})(\text{In}_2\text{O}_3)$, ZnO , and CuAlO_2 (Sugihara, 2005). Among these, CuAlO_2 has been discussed in detail in the next section. All of them are stable at high temperature, but the problem in dealing with them as thermoelectric materials lies in the fact that it is not easy to ensure low contact resistance and there may be cracking due to large mismatching of coefficient of thermal linear expansion between working material and that of the electrode.

CuAlO₂: An Efficient Thermoelectric Material

As mentioned before, the conventional thermoelectric materials like Bi_2Te_3 , PbTe , and SiGe alloys have limitations with use over 1000K. At the same time, materials like doped FeSi_2 remain active over 1000K, but their performance is not satisfactory. Thus to

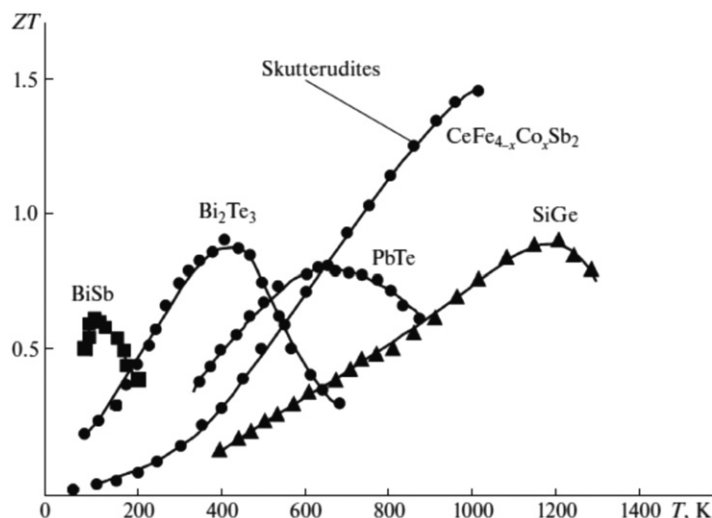


Fig. 7 Temperature dependence of ZT for some thermoelectric materials. Reproduced from Sherchenkov, A.A., Shtern, Y.I., Mironov, R.E., Shtern, M.Y., Rogachev, M.S., 2015. Current state of thermoelectric material science and the search for new effective materials. *Nanotechnologies in Russia* 10 (11–12), 827–840.

make a balance, other conducting oxide materials like $(\text{Zn}_{1-x}\text{Al}_x)\text{O}$, $(\text{Zn}_{1-y}\text{Mg}_y)_{1-x}\text{Al}_x\text{O}$, $(\text{Ca}_{1-x}\text{Bi}_x)\text{MnO}_3$, $\text{CdIn}_{2-x}\text{Sn}_x\text{O}_4$, Cd_2SnO_3 , $\text{Cd}_2\text{Sn}_{1-x}\text{Sb}_x\text{O}_4$, $\text{In}_2\text{Te}_{1-x}\text{Re}_x\text{O}_6$, etc. have received much attention for possible applications over a wide temperature range.

Also we have seen the dimensionless figure of merit, which is the measure of the performance of the material as thermoelectric material increases with higher values of σ and λ . However when σ and λ increase the thermal conductivity also changes as per Wiedemann–Franz law and thus figure of merit remains almost constant.

Materials with delafossite structure MIMIIIO_2 (where $\text{MI}=\text{Cu, Ag, Pt, Pd}$; $\text{MIII}=\text{Al, Ga, In, Cr, Fe, Co, etc.}$) possess natural layered structure. Thus it can be used as promising thermoelectric material as per Hicks' model. Like the materials mentioned above, polycrystalline CuAlO_2 thin film is a p-type transparent conducting oxide, which has tremendous potential to be used in optoelectronic device technology. A few years back Koumoto *et al.* (2001) reported the efficient thermoelectric properties of CuAlO_2 single crystal.

Also there are reports regarding the same from different researchers worldwide. For instance, Ruttanapun *et al.* (2014) found ZT of solid state synthesized bulk CuAlO_2 powder to be 0.017 at a 960K. In the same year Suriwong *et al.* (2014) synthesized the same material by direct microwave heating and found the value of ZT to be 0.009 at 1073K. Akyildiz (2015) reported the synthesis of the material by coprecipitation method and studied its electrical property. In 2015, Lu *et al.* reported the fabrication of thermoelectric CuAlO_2 and performance enhancement by high density and found the highest value of ZT to be $5 \times 10^{-3} \text{ K}^{-1}$ at optimum density value.

Electronic structures and thermoelectric properties of delafossite 2H-CuAlO_2 have been theoretically investigated by Poopanya (2015) using first principles calculations and Boltzmann transport equation. Sakulkalavek and Sakdanuphab (2016) reported doped p-type oxide with Ag_2O to enhance the thermoelectric properties of CuAlO_2 and got the highest value of ZT as 5×10^{-3} at 873K. The same substitution into the same material gives the value of ZT as 0.0044 at 573K, from a sample containing 0.2 at% Ag_2O as reported by Pantian *et al.* (2017). CuAlO_2 thermoelectric compacts by spark plasma sintering and thermoelectric performance improvement by orientation control has been reported by Hao *et al.* (2017). Temperature dependency of thermoelectric properties of CuAlO_2 has been studied by Feng *et al.* (2019) who found the highest values of ZT to be 0.27×10^{-2} at 780K.

Synthesis of CuAlO_2

There are numbers of ways for the synthesis of the material, a few of which has been invented and reported in the author's previous work. The experimental includes simple solid-state reaction (Banerjee *et al.*, 2005a), sol-gel synthesis (Ding *et al.*, 2010), or dc-sputtering (Banerjee *et al.*, 2005b). Apart from that, there are others methods like pulsed laser deposition (Yousheng *et al.*, 2014), chemical vapor deposition (Cai and Gong, 2005), reactive solid-phase epitaxy (Ohta *et al.*, 2003), thermal coevaporation (Jayaraj *et al.*, 2001), electron beam evaporation (Bobeico *et al.*, 2003), etc.

As reported in our previous work, solid-state reaction between stoichiometric mixture of Cu_2O and Al_2O_3 at 1400K in air produced CuAlO_2 powder (Banerjee *et al.*, 2005b). This powder was then placed into a grooved aluminum holder ($\sim 5 \text{ cm}$ diameter) and pressed into pellets by hydrostatic pressure and used as target for dc-sputtering. The sputtering unit was evacuated by standard rotary-diffusion pump arrangement to a base pressure of 10^{-4} Pa . The target was arranged as an upper

Table 1 Summary of deposition parameters regarding dc-sputtering

Electrode distance	1.8 cm
Sputtering voltage	1.1 kV
Current density	10 mA cm ⁻²
Substrates	Si (4 0 0), glass
Sputtering gases	Ar and O ₂ (3:2 volume ratio)
Deposition pressure	0.2 mbar
Substrate temperature	453 K
Deposition time	4 h

Note: Banerjee, A.N., Kundoo, S., Chattopadhyay, K.K., 2003. Synthesis and characterization of p-type transparent conducting CuAlO₂ thin film by DC sputtering. *Thin Solid Films* 440 (1–2), 5–10.

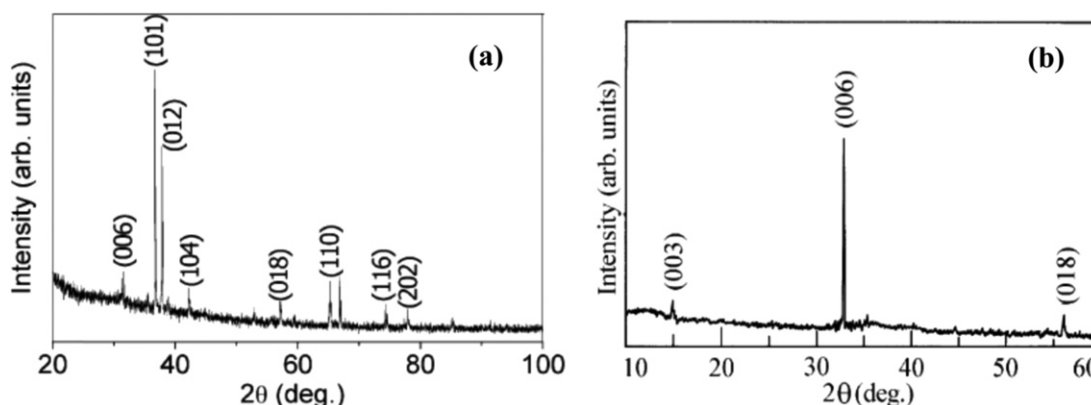


Fig. 8 XRD pattern of CuAlO₂ powder (a) and sputtered CuAlO₂ thin film deposited on Si (4 0 0) substrates. Reproduced from Banerjee, A.N., Kundoo, S., Chattopadhyay, K.K., 2003. Synthesis and characterization of p-type transparent conducting CuAlO₂ thin film by DC sputtering. *Thin Solid Films* 440 (1–2), 5–10.

electrode and negative bias was applied to it. Ultrasonically cleaned glass and Si substrates were placed on the lower electrode and connected to the ground of the power supply. The electrode distance was taken as 1.8 cm. Ar and O₂ (40 vol%) were taken as sputtering gas and the sputtering was done in an elevated substrate temperature (~ 453 K) to achieve high crystallinity in the film. Postdeposition annealing of the films (at 473 K) in an O₂ atmosphere (20 Pa pressure) for different annealing times (ta) ranging from 30 to 150 min were performed to induce nonstoichiometry in the films for enhancing p-type conductivity. Details of the deposition conditions were reported in other work (Yanagi *et al.*, 2000) and summarized here in the following Table 1.

The target was presputtered for 10 min to remove contamination, if any, from the surface and then the shutter was displaced to expose the substrates in the sputtering plasma. Si (4 0 0) and glass were used as substrates. Before placing into the deposition chamber, the glass substrates were cleaned first by mild soap solution, then washed thoroughly in deionized water and also in boiling water. Finally, they were ultrasonically cleaned in acetone for 15 min. Si substrates were immersed in 20% HF solution for 5 min for removing surface oxide layers. Then they were cleaned in deionized water and finally with alcohol in an ultrasonic cleaner. After the deposition was over, the films were postannealed in the same vacuum chamber at 473 K for 1 h (at pressure 0.2 mbar), maintaining the oxygen flow.

For the sol–gel synthesis the experimental is as follows (Ghosh *et al.*, 2009): copper nitrate, [Cu(NO₃)₂], aluminum nitrate [Al(NO₃)₃], and methanol (CH₃OH) were used as precursors for the material synthesis. In a typical run of experiment 7 mM of Cu(NO₃)₂ and Al(NO₃)₃ were stirred in 30 mL of methanol at room temperature for 45 min. This process was followed by addition of citric acid solution and the total solution was again stirred at room temperature for 1 h to obtain well-mixed precursor solution. When temperature was raised at 70°C with continuous stirring jellification of the solution got started after around two hours. The final products were obtained when the gels were heated at different temperature at several hundred degrees of temperature for six hours in open atmosphere.

The phase formation of the as-synthesized sample can clearly be understood from the X-ray diffraction pattern shown in Fig. 8. Fig. 9 shows the SEM image of a CuAlO₂ film deposited on Si substrate. It is seen that there is no particular structure that has been formed during the deposition. Only clustered type deposition has been taken place with irregular sizes. It is seen that the sizes of the small particles are beyond the limits of SEM resolution however bigger clusters are in the micrometer range, which is due to the higher formation temperature.

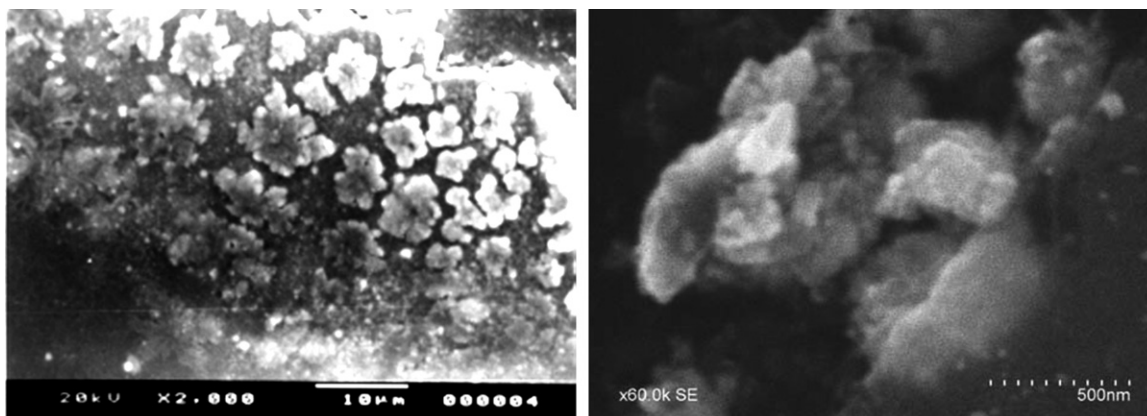


Fig. 9 XRD pattern of CuAlO₂ powder (a) and sputtered CuAlO₂ thin film deposited on Si (4 0 0) substrates and (b) SEM image of CuAlO₂ sol-gel powder sample synthesized at 1000°C for 6 h. Reproduced from (a) Banerjee, A.N., Kundoo, S., Chattopadhyay, K.K., 2003. Synthesis and characterization of p-type transparent conducting CuAlO₂ thin film by DC sputtering. *Thin Solid Films* 440 (1–2), 5–10. (b) Ghosh, C.K., Popuri, S.R., Mahesh, T.U., Chattopadhyay, K.K., 2009, Preparation of nanocrystalline CuAlO₂ through sol-gel route. *Journal of Sol-Gel Science and Technology* 52 (1), 75–81.

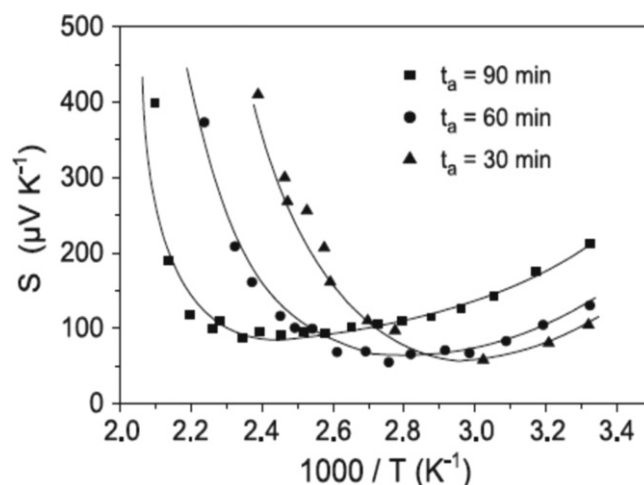


Fig. 10 Seebeck coefficient vs. $1000/T$ of CuAlO₂ thin films.

Thermoelectric Properties of CuAlO₂

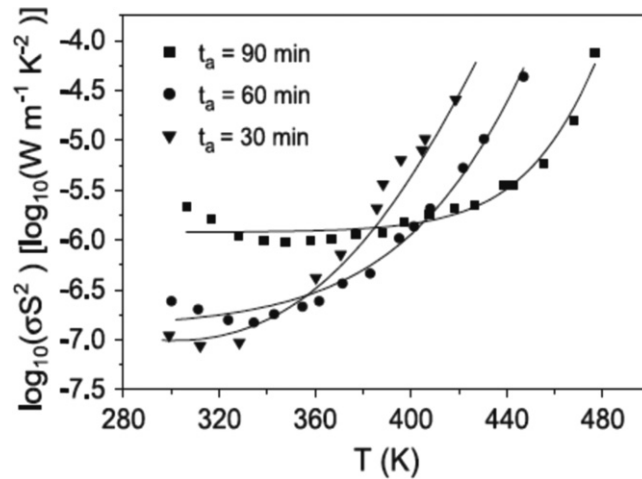
The performance of CuAlO₂ thin film, synthesized by dc sputtering, as thermoelectric material has been tested from room temperature (300K) to 550K. It is to be noted that postdeposition the thin films were annealed at 473K in oxygen atmosphere for different time (t_a), from 30 to 150 min. **Fig. 10** shows the temperature dependence of S for three types of films. It is seen that S is positive for all the samples, which confirms the p-type nature of the sample. It can be seen that the value of σ_{RT} comes out to be 230 $\mu\text{V K}^{-1}$ (for $t_a = 90$ min), 141 $\mu\text{V K}^{-1}$ (for $t_a = 60$ min), and 120 $\mu\text{V K}^{-1}$ (for $t_a = 30$ min). The figure shows that the value of Seebeck coefficient initially decreases from room temperature to around 390 K and then increases to almost 400 $\mu\text{V K}^{-1}$, for further increase in temperature. Also there are reports of the same material having values of σ_{RT} to be 183 and 214 $\mu\text{V K}^{-1}$ (Kawazoe *et al.*, 1997; Yanagi *et al.*, 2000), which are comparable to the values obtained in the author's laboratory.

Also there is a report from Koumoto *et al.* regarding the values of σ of CuAlO₂ single crystal as well as polycrystal at 600K around 180 and 150 $\mu\text{V K}^{-1}$, respectively (Akyildiz, 2015). A relatively high value of S_{RT} (670 $\mu\text{V K}^{-1}$) of CuAlO₂ powdered pellets has been reported by Benko and Koffyberg (1984). They have shown that σ_{RT} varies directly with conductivity of the sputtered deposited film, which shows consistency with the available Hicks model that predicts high ZT values of natural superlattice due to increase in both S and σ (Hicks and Dresselhaus, 1993).

It is to be noted that the structure of CuAlO₂ delafossite consists of alternative stacking of Cu^I and Al-O₆ octahedra edge shared AlO₂ layers. Here a c -axis oriented dumbbell shaped O-Cu-O bond gets formed due to coordination of one Cu atoms with two oxygen atoms. The O-Cu-O bonds all the Cu layers gets linked with all the AlO₂ layers (Ishiguro *et al.*, 1982). Thus a layered structure of CuAlO₂ gets formed where the charge carriers can more easily move in the two-dimensional ab plane than in the Al-O insulating layers.

Table 2 Different thermoelectric and electrical parameters of CuAlO₂ thin films, deposited at different annealing times

Sample	t_a (min)	σ_{RT} ($S\ cm^{-1}$)	S_{RT} ($\mu V\ K^{-1}$)	E_a (meV)	E_f (meV)
S1	90	0.39	+230	196	130
S2	60	0.16	+141	245	151
S3	30	0.09	+120	270	200

**Fig. 11** Thermoelectric power factor vs. temperature of CuAlO₂ thin films.**Table 3** Relative thermoelectric performance of different materials in terms of ZT values

Sl. no.	Material	Synthesis methods	ZT _{max} values	@ Temperature (K)	Refs.
1	p-type FeNb _{1-x} Ti _x Sb	Levitation melting	1.1	1100	(Fu <i>et al.</i> , 2015b)
2	SnSe	Chemical	2.6 ± 0.3	923	(Zhao <i>et al.</i> , 2014)
3	FeNb _{1-x} Hf _x Sb	Levitation melting	1.5	1200	(Fu <i>et al.</i> , 2015a)
4	Bi _{0.3} Sb _{1.7} Te ₃	Solid-state reaction	1.3	380	(Hu <i>et al.</i> , 2014)
5	(Nb _{1-x} Ta _x) _{0.8} Ti _{0.2} FeSb	Levitation melting	1.6	1200	(Yu <i>et al.</i> , 2018)
6	PbTe–SrTe	Hydrothermal	2.5	923	(Tan <i>et al.</i> , 2016)
7	Fe _{1.05} Nb _{0.75} Ti _{0.25} Sb	Levitation melting	1.34	1150	(Fu <i>et al.</i> , 2016a)
8	Ag _{0.01} Sb _{1.85} In _{0.15} Te ₃	Solid-state reaction	0.92	710	(Hu <i>et al.</i> , 2015)
9	PbTe _{0.7} Se _{0.3}	Solid-state reaction	2.2	923	(Wu <i>et al.</i> , 2014)
10	Na doped SnSe	Solid-state reaction	0.8	773	(Chere <i>et al.</i> , 2016)
11	TiS ₂ by organic interaction	Chemical vapor transport method	0.28	373	(Wan <i>et al.</i> , 2015)
12	Cu _{10.5} Ni _{1.5-x} Zn _x Sb ₄ S ₁₃	Direct melting method	> 1	723	(Lu <i>et al.</i> , 2015)
13	Hole doped single crystal SnSe	Solid-state reaction	2	773	(Zhao <i>et al.</i> , 2015)
14	Pb _{1-x} Mg _x Te _{0.8} Se _{0.2}	Solid-state reaction	2.2	820	(Fu <i>et al.</i> , 2016b)
15	Na doped SrTe _{1-x} O _x	Spark plasma sintering method	2.1	800	(Kim <i>et al.</i> , 2017)
16	Sb ₂ Te ₃ /Ag ₂ Te	Solid-state reaction	1.5	700	(Lee <i>et al.</i> , 2015)
17	Al _x Yb _{0.25} Co ₄ Sb ₁₂	Mechanical alloying	1.56	850	(Elsheikh <i>et al.</i> , 2017)
18	Nb doped SrTiO ₃	Solid-state reaction	0.33	900	(Li <i>et al.</i> , 2016)
19	Bi ₂ Te _{2.5} Se _{0.5}	Solution-phase route	1.0	488	(Xu <i>et al.</i> , 2017)
20	(Hf _{0.6} Zr _{0.4}) _{0.99} V _{0.01} NiSn _{0.995} Sb _{0.005}	Solid-state reaction	1.3	850	(Chang <i>et al.</i> , 2016)
21	CuAlO ₂	Sol–gel	0.035	> 500	(Banerjee and Joo, 2018)

However, all this structural information cannot account for the efficient thermoelectric properties of the as-synthesized material. There are some proposed theories behind this phenomenon. Koumoto *et al.* (2001) predicts that low dimensionality of the crystal structure and the behavior of electrons and phonons in an anisotropic structural environment may be the reasons behind this. Also there is a report by Wang *et al.* (2003) that suggests spin entropy may be the reason for enhanced thermoelectric property seen in similar layered structured material like Na_xCo₂O₄. However it is still a subject of debate whether these reasons are responsible for the enhanced thermoelectric properties of layered CuAlO₂.

The variation of thermoelectric power (S) with temperature given by (Willardson and Beer, 1971):

$$P = \frac{k}{e} \left(A + \frac{\Delta E_f}{kT} \right) \quad (3)$$

$$\text{with } A = 5/2 - s \quad (4a)$$

$$\text{and } \tau = \tau_0 e^{-s} \quad (4b)$$

where k is the Boltzmann constant, e is the electronic charge, ΔE_f is the energy difference between Fermi level and the upper edge of the valence band, τ is the relaxation time for electron scattering, s is a constant that is different for different scattering mechanism, and τ_0 is a constant that is a function of temperature but independent of the electronic charge, e .

The above equation can be used to find the Fermi level from the plot between S and $1/T$, which comes out to be 130, 151, and 200 meV for $t_a = 90, 60$, and 30 min, respectively as obtained from Fig. 10, which is comparable to the value as reported by Benko and Koffyberg (1984) (190 meV).

Table 2 summarizes different electrical and thermoelectric parameters.

Fig. 11 represents the temperature dependence of thermoelectric power factor (σS^2) of CuAlO₂ thin film for the temperature range of 300–500K. The values come out to be $1.1 \times 10^{-7} \text{ W m}^{-1} \text{ K}^{-2}$ and $7.5 \times 10^{-5} \text{ W m}^{-1} \text{ K}^{-2}$ for the samples annealed for 30 and 90 min respectively, which is comparable to the previously reported values. Thus it can be concluded that the material CuAlO₂ may be a good candidate for use as thermoelectric material.

Table 3 summarizes the performance of different thermoelectric materials with respect to the figure of merit values

Conclusions

The worldwide energy crisis caused by increasing use of fossil fuel due to enhanced energy consumption and thereby generation of huge quantity of greenhouse gas like CO₂ is one of the most severe problems faced by human beings. The article discusses some aspects of the present energy crisis worldwide with possible solutions and also thereby mitigation of CO₂ emission. This problem is actually multifaceted and hence discussions on many other aspects are necessary. The different forms of alternative and renewable energies with their associated merits demerits have been discussed. Methods of waste heat energies are discussed in detail. The role of thermoelectricity in addressing the energy problems and associated CO₂ emission reduction is emphasized. The basic principles of thermoelectric effect and its corresponding theory have been discussed in detail. Materials aspects of efficient thermoelectricity generation are discussed and some published results are summarized. The features of some conventional thermoelectric materials are presented and the potential of a comparatively novel thermoelectric material, that is, copper aluminum oxide, has been presented. These discussions may be helpful particularly for the young researchers in this field.

Acknowledgments

One of us (KKC) wishes to thank the University Grants Commission (UGC), the Govt. of India for the University with potential for excellence scheme. The authors also wish to thank the DST Nanomission, the Govt. of India.

See also: Alternate Photovoltaic Material: Its Environmental Consequences

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The How and Why of Energy Harvesting for Low-Power Applications.

Traditional Biomass: A Replacement for Petro-Fuels

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Introduction

Biomass is nothing but the plant or animal based material the main constituents of which are carbon, oxygen and hydrogen. Plant-based biomasses such as tree leaves, barks, stumps, and other parts are generally classified as lignocellulosic biomass. Biomasses are long being used since ancient time for heat and energy production during cooking and other general purposes worldwide. In recent time, the use of biomass is not only limited to cooking but also many processes have been developed to use it more economically such as production of biofuel in developed and developing countries all over the world. Different sources of traditional biomass (wood, eucalyptus, bamboo, *Jatropha curcas* (Raja *et al.*, 2011)); agricultural waste (sugarcane bagasse); industrial waste wastes (black liquor from pulp and paper industry; waste cooking oil, palm oil, soybean oil, sunflower oil, rapeseed and different vegetable oils, animal fat; algae; municipality solid waste) have already been reviewed. In recent few years, the scarcity of petro-fuels and the pollution originated from petro-fuels is an important topic of concern. Hence, the scientists are focusing on the production of clean energy sources and one of the main promising source of this type of energy is the biofuel which is comparable with those of conventional petroleum fuels with reduced emission of carbon monoxide (CO), carbon dioxide (CO₂), sulfur dioxide (SO₂), nitrogen oxides (NO_x) and other toxic gases and particulate matter (PM), unburned hydrocarbon thus resulting in reduction of Greenhouse Effect (GHE) and environmental pollution. A survey on Greenhouse Gases (GHGs) emission shows that 25% GHGs release throughout the world is caused by liquid fuels that are used in vehicles (Isa and Ganda, 2018). Another main problem with petro-fuels is their non-renewable nature and the continuous and rapid depletion of these fuel-reservoirs. Coal-gasification may be considered as an effective way to produce liquid petroleum range hydrocarbons but are not categorized as non-renewable source of energy. On the other hand, the use of fuel oil for mass transportation such as buses, cars, and ships, heavy duty engines in industries is increasing at fast pace. According to The United States Energy Information Administration report, the annual average increase in oil consumption was about 2.7% per annum in between 2009 and 2015 worldwide. Hence, a replacement of petro-fuels with some renewable energy resource appeals an urgent attention. In this case, biomass is a readily available renewable source of carbon mainly the lignocellulosic biomass as they are reproduced naturally by photosynthesis cycle. The main issue governing the biofuel production and commercialization has been reported as the discovery of novel procedure to produce biofuels that suits the economy of any nation. Based on the type of resource material biofuel are categorized as (i) first-generation biofuels (typically produced from food grade biomass like, starch, different type of waste vegetable oil). (ii) Second-generation biofuels (generally non-food biomass which mainly includes waste from agricultural farms), and (iii) third generation biofuel (algal biofuel) (Saladini *et al.*, 2016). In commercialization of biofuel the main factor is its source and in this case algae and palm oil have been proven to be very promising (Isa and Ganda, 2018). Lignocellulosic biomass having the propensity to produce transportation fuel as an alternative to petro-fuels (Addepally and Thulluri, 2015) hiking the popularity of bio based fuels and different state governments and federals are encouraging the production of biofuel. A contemporary survey report on production scenario of biodiesel in European countries prevails that its production rate is about 20–25 million gallon per year which is deviating to a large extent from expected production rate of 500 million to 1 billion per year (Gerpen, 2005). This exploration endorses the growing popularity of biofuel as an alternative to petro-fuels.

Traditional Biomass: An Unexplored Boon of Nature

Biomass is organic matter having wide spectrum of applications for both food and nonfood sectors. The harvested energy in the biomass has immense potential to be utilized as fuel resource. 'Traditional' or 'modern' biomass classification is based on the utilization over period of time. Traditional biomass refers the use of biomass that is long-established and is followed for centuries without any modifications, which mostly practiced in developing countries. Developed countries have recommended innovative idea for economic utilization of biomass such as for production of biogas (H₂, CH₄), liquid fuel, electricity generation and different type of fertilizer production. These activities have brought a breakthrough in the arena of energy research and developments and have endorsed traditional biomass to modern biomass. Sustainability of biomass is the key feature for exploiting it to energy production sectors. Studies have reported the complications associated in the sustainable biomass production processes (Anon, 2012) those are allied to availability of land for production and cultivation of biomass and environment suitability (Anon, 2012; Anon, 2012). Availability of land is directly or indirectly related with bioenergy generation. First generation biomass which are mainly the cultivated plants store about 1%–3% of solar energy by photosynthesis-process requiring a wide spread land area for fulfilling the energy demand of modern age. Hence the sustainability of biofuels greatly depends on sustainable land uses as replacement of natural vegetation with the cultivated one without affecting the eco-system. Oeko institute, Freiburg, Germany (2012) has calculated the 'minimum net energy requirement' for bioenergy carrier in details (Anon, 2012). Biodiversity is also considered as another important factor for sustainability of biomass. To ensure the sustainability of biomass, biofuel must be

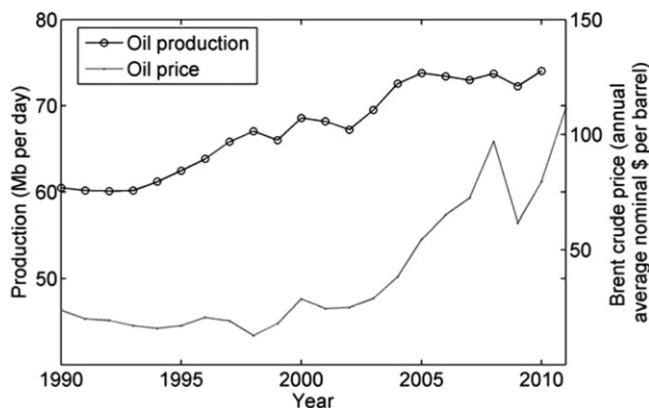


Fig. 1 The global petroleum oil production scenario (<https://www.diva-portal.org/smash/get/diva2:476153/FULLTEXT01.pdf>).

confirming zero or close to zero emission of Greenhouse Gases (GHGs) and other pollutants (cause by disposal of the biofuel waste). Water & soil quality protection is also crucial factor during the cultivation of the biomass as energy stock.

Importance and Current Consumption Scenario of Petro-Fuels

Petroleum which is also known as 'Rock Oil' is a naturally occurring fossil fuel containing a wide range of hydrocarbons with different boiling point. Fuels are generally produced from this petroleum by refining this crude oil. After fractionation or distillation different liquid fuels are produced from this crude oil such as diesel, gasoline, kerosene, LPG, coal tar, naphtha, ethanol. This oil dominates the market in the area of road transportation and petrochemical industry as it has become one of the leading tradable commodities, but this oil source is finite and use of the petro-derived fuels have a negative effect on the environmental ecology, climate and is mainly responsible for Greenhouse Effect. Sulfur dioxide (SO_2) which is produced when petro-fuel containing sulfur is burned emits through different vehicles causes air pollution which is detrimental for human health. The production of petroleum oil worldwide is given by the Fig. 1 (see "Relevant Websites section"). The exploitation of oil globally was reported about 98.3 million barrels per day ($15,630,000 \text{ m}^3 \text{ d}^{-1}$) in the year of 2015 and estimated about 118 million barrels per day in upcoming year of 2030 (Energy Information Administration, 2006 prognosis). Since petroleum is unsustainable source of energy and hence exploration of alternative fuel sources have become crucial topic of research to energy sectors and environmental technologist. Though petroleum fuels are indispensable for community development but its scarcity and adverse environmental impact like global warming associated with emission of GHGs, acid rain, climate changing, and aquifer contamination, are highly threatening to the all kind of living beings and ecosystems. The present scenario about petroleum consumption presents a high rising of fuel price, making the fuel crisis protuberant and the necessity of alternative fuel as urgent and foremost crucial topic to maintain clean environmental.

Bio-Based Petro- Alternative-Fuels

Alternative fuels, are defined as non-conventional and advanced fuels, those are any materials other than conventional fuels like fossil fuels, nuclear materials as well as artificial radioisotope fuels those are used in nuclear reactors. Some of the most potential resources of alternative fuel explored till date and well recognized as alternative petroleum fuel are classified as biodiesel, bio alcohol, refuse derived fuel, fuel cells, hydrogen, non-fossil methane and natural gas vegetable oil though and abounded biomass resources are still waiting for exploration and recognition as alternative biofuel. The United States government has produced a 'data center' for the six most common alternatives of petroleum oil (biodiesel, bioethanol, hydrogen, natural gas, propane, electricity), summarizing the benefits and the challenges that still exist to bring them to a larger market.

Biodiesel

Bio diesel, resource material, production and utilization scenario

Biodiesel is a renewable fuel which can be made from vegetable oils, animal fats, or recycled restaurant grease. This can be used in diesel vehicles already on the road because of its similar fuel characteristics like petroleum diesel, but it burns much more cleanly and safely. It's totally biodegradable and friendly to the environment if spilled, but it has a flashpoint of over 130°C , compared to 52°C for normal diesel. Experimental studies have established that pure biodiesel (B100) reduces carbon dioxide emissions by more than 75% compared with normal diesel. The chemical nature of biodiesel is defined as mono-alkyl esters which can be produced from any potential lipid sources such as vegetable oil, animal fat or different type algal

biomass. Biodiesel is a promising renewable alternative fuel for conventional petro diesel. It reduces the carbon dioxide emission by 70%–75% in comparison with those conventional fossil fuels (Hillion *et al.*, 2003). The sulfur and nitrogen content of this fuel being less reduce the GHG emission and the toxic NO_x and SO_x with excellent lubrication efficiency. It entails little or no modification of the engine when it is used in place of petro diesel. This biodiesel can be used alone or can be blended with conventional diesel fuel to various recommended ratio to get various fuel grades. The most common are B5 (up to 5% biodiesel) and B20 (6%–20% biodiesel). B100 (pure biodiesel) is typically used as a blend stock to produce lower blends and is rarely used as a transportation fuel (see “Relevant Websites sections”). B20 is a common biodiesel blend used in the United States, because of its good balance of cost, emissions, cold-weather performance, materials compatibility, and ability to act as a solvent. Regulated fleets use biodiesel blends of 20% (B20) or higher qualify for biodiesel fuel use credits under the Energy Policy Act of 1992. Engines operating on B20 have similar fuel consumption, horsepower, and torque to engines running on petroleum diesel. B20 with 20% biodiesel content will have 1%–2% less energy per gallon than petroleum diesel, but most B20 users report no noticeable difference in performance or fuel economy. Many diesel engine original equipment manufacturers (OEMs) approve the use of B20.

Other high level biodiesel blends (B100) are less common than B20 and lower blends due to a lack of regulatory incentives and pricing. Biodiesel-compatible materials (as hoses and gaskets), allow B100 to be used in some engines built since 1994. B100 has good solvent effect, which help in cleaning vehicle's fuel system and releasing deposits accumulated from petroleum diesel use. The release of these deposits may initially clog filters and require frequent filter replacement in the first few tanks of high-level blends. While using high-level blends, a number of issue regulate its use is ‘energy value’ which is much less on a volumetric basis than petroleum diesel. Therefore, the higher the percentage of biodiesel (above 20%), the lower the energy content per gallon. High-level biodiesel blends impart negative aspect on engine performance, like gelling in cold temperatures. Some studies have reported that use of B100 could also increase nitrogen oxides emissions, requires special handling and require equipment modifications. Key features of the biodiesel for its well acceptability has been summarized as, its renewable, can be used in most diesel equipment with no or only minor modifications, can reduce global warming greenhouse gas emissions, compatible with new technology diesel engines (NTDE) and emissions control devices, can reduce tailpipe emissions from older vehicles, including air toxics, nontoxic, biodegradable, and suitable for sensitive environments, can be produced domestically from agricultural or recycled resources.

As presented in experimental research publications, the several potential raw materials for biodiesel production are waste cooking oil (WCO) (Raqeeb and R, 2015), animal fats (chicken or poultry fat, beef tallow and pork lard (Othman *et al.*, 2017)), waste vegetable oil (Refaat, 2010), Jatropha oil (Raja *et al.*, 2011), different types of vegetable oil such as soybean oil, palm oil, coconut oil, sunflower oil, algal biomass (Rawat *et al.*, 2013; Chisti, 2007; Kumar *et al.*, 2018), lipid containing waste slurry (Chena *et al.*, 2018).

The chemical method involve in the production of biodiesel has been classified as trans-esterification reaction of oil with alcohol in presence of catalyst. In literature trans-esterification process has been described as a simple reaction between triglyceride of any oil and fat material and low molecular weight alcohol such as methanol or ethanol (anhydrous or maximum water content of 2%) in presence of catalyst. The reaction stoichiometry has been presented in Fig. 2 (Hillion *et al.*, 2003).

The main advantage of methanol uses was reported due to ease of separation of the methyl ester by simple decantation process as compared to ethanolic derivative (Duarte *et al.*, 2007). Various catalyst system has been reported in literatures for efficient conversion of triglyceride oil and the fatty matter to respective methyl ester derivatives ranging from alkaline to acidic one, micro size to nano size and homogeneous to heterogeneous type. As typical homogeneous catalyst system sodium hydroxide (NaOH), potassium hydroxide (KOH) (Othman *et al.*, 2017; Nagi *et al.*, 2008), sodium methylate and many acid catalysts (Hillion *et al.*, 2003) have been attempted by eminent research groups. The system has significant drawback due to

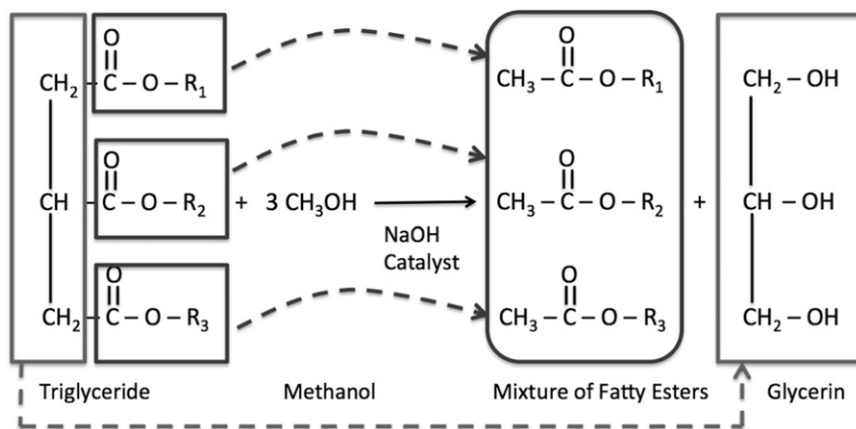


Fig. 2 Process schematic of trans-esterification reaction for biodiesel production (<https://www.e-education.psu.edu/egee439/node/684>).

Table 1 Some important experimental work demonstrating the significance of nano photo catalyst in trans-esterification reaction

Name of the nano catalysts produced or utilized	Nature of feed stock	Reference
Carbon Nanohorn catalysts ($\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH}$, CaO-CNH)	Various oils extracted from seeds or kernels of non-edible crops were used as potential feed	Sano <i>et al.</i> (2016)
Calcium oxide combined with aluminum oxide ($\text{CaO-Al}_2\text{O}_3$)	Biodiesel production from beef tallow	Hashmi <i>et al.</i> (2016)
Iron Nano catalyst	Biodiesel production from <i>Pongamia pinnata</i> oil	Rengasamy <i>et al.</i> (2014)
Titanium based nano-catalyst $[\text{Ti}(\text{SO}_4)_2\text{O}]$	Biodiesel production from used cooking oil.	Gardy <i>et al.</i> (2016)
Nano-sized magnesium oxide (MgO)	Rancid vegetable oil.	Sivakumar <i>et al.</i> (2013)
CuO-Mg Heterogeneous Nano catalyst	Biodiesel from Sunflower Oil	Nagi <i>et al.</i> (2008)
CaO and MgO nanocatalysts	Biodiesel from recycled cooking oil	Tahvildari <i>et al.</i> (2015)

low purity level of glycerol (80%–95%) (Hillion *et al.*, 2003) as byproduct because of the soap contamination in presence of moisture in reaction system. Hence, highly anhydrous (water content less than 1%) reaction condition has been recommended in few publications. Several acid catalysts like, strong sulfuric acid, hydrochloric acid, phosphoric acid and acids containing sulfonic group are typical with minimal chance of saponification reaction leading soap formation. The main restraint of the use of acidic catalyst system is the production of water as byproduct that constrains the yield of trans-esterification reaction (Marchetti *et al.*, 2007), requires high temperature ($> 100^\circ\text{C}$) and very slow reaction rate leading to few days of completion. Process efficiency has also been studied in details for the role of enzymatic catalyst (lipase) in trans-esterification reaction. Lipase catalyzed trans-esterification reactions require simple operational conditions compared to typical acid and alkali catalysts. The enzymatic catalyst was reported more effective with ethanol rather than methanol, the yield of ester is 75% for ethanol and only 15% for methanol when treated with PS30 lipase (Othman *et al.*, 2017; Enujiugha *et al.*, 2004). The deactivation and removal of catalyst system steps in homogeneous catalyst system have efficiently been eliminated by switching the method to heterogeneous catalyst system. A researchers' team has studied a heterogeneous catalyst system (consist of mixture of aluminum and zinc oxide) with rapeseed and soybean oil as raw material that requires high temperature of operation and excess methanol in comparison to the homogeneous system but gives a relatively pure, moisture free biodiesel product and recoverable alcohol system (Nage *et al.*, 2012).

At present scenario about 90% of biodiesel has been reported to produce by trans-esterification process of triglycerides with low molecular weight alcohols using homogenous acid or base catalysts. However, the biodiesel industries experiencing some significant challenges due to (i) high cost of biodiesel feedstock (70%–85% of the overall production cost) and (ii) cost of biodiesel processing, including separation, purification and neutralization of by-products. The use of nano catalyst in trans-esterification reaction offers comparatively high surface area and the catalyst displayed low catalytic activity for glycerin at reaction temperature. Moreover, the employments of heterogeneous catalysts offer easy separation from the products and reutilization facilities. Obadijah *et al.* (2012), have reported the use of Nano hydrotalcite (Mg-Al) for preparation of biodiesel from *Pongamia* oil with maximum conversion of about 90.8% for methanol to *Pongamia* oil molar ratio of 6.0, 1.5% catalyst (w/w of oil) for 4 h reaction time and an optimum temperature of 65°C . A number of researchers have studied the preparation of nano sized heterogeneous catalysts to increase the catalytic activity. Some important experimental works have been summarized in Table 1 demonstrating the significance of nano photo catalyst in trans-esterification reaction.

Algal lipid can also be used as resource of biodiesel production due to high triglyceride content. Some of the potential microalgae (freshwater) used for biodiesel production have been studied are *Cladophora*, *Enteromorpha*, *Mougeotia*, *Hydrodictyon*, *Oedogonium*, *Spirogyra*, *Microspora* (Kumar *et al.*, 2018), surface-floating microalga, such as *Botryo sphaerellusdetica* (Nage *et al.*, 2012). The schematic for production of algal biodiesel has been presented on Fig. 3. Though biodiesel can be used as fuel for the engines in place of conventional petro-fuel, but solely can't be utilized because of poor oxidation stability, lower calorific value and poor cetane index. It is usually blended with fossil fuel like, n-butanol in wide range ratio to get a better fuel quality (Kumar *et al.*, 2018).

Bio Hydrogen

Hydrogen is considered to be one of the cleanest sources of fuel which on burning it generally produces heat and clean water and it has high gravimetric energy density almost 143 MJ Kg^{-1} (Khan *et al.*, 2017) but low volumetric energy density nearly 12 MJ m^{-3} (at NTP) (Singh *et al.*, 2015). Electrolysis of water and steam reforming of water are the common methods for hydrogen gas production. Current world is in the phase of energy crisis due to extensive exploitation of fossil fuel reservoirs and rapid depletion of petroleum and others gas and solid fuel sources. One of the main disadvantages of this petroleum or other fossil fuels is the anthropogenic CO_2 emission and Greenhouse Effect. Bio hydrogen production is environmental friendly approach from the area of utilization of waste biomass to produce energy with minimal pollution emission.

Bio hydrogen resource material, production and utilization scenario

To solve the issue of energy crisis several group of researchers have explored different techniques to utilize waste biomass to produce petroleum alternative fuels. Different types of biomass can be used to produce bio hydrogen like, marine biomass (mainly

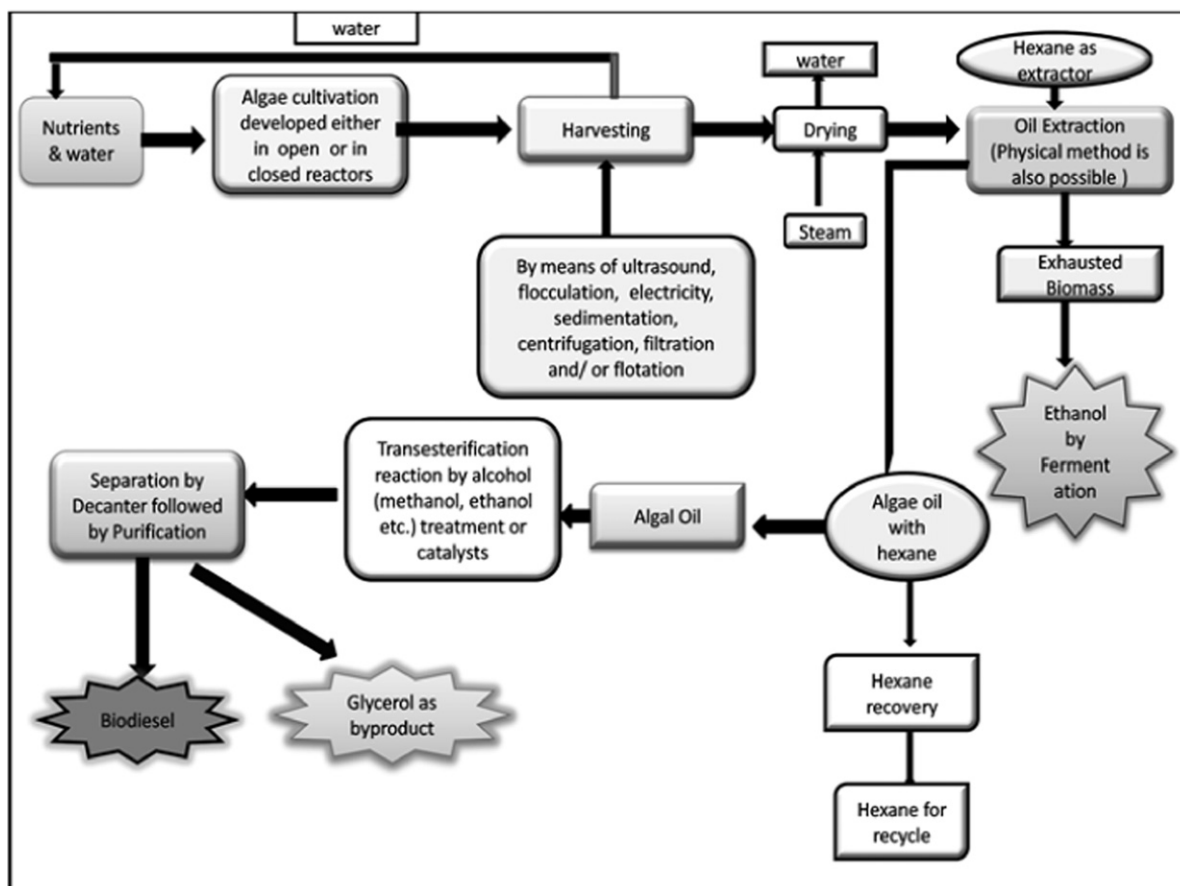
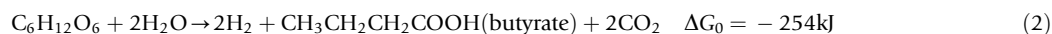
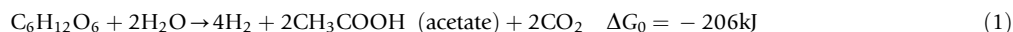


Fig. 3 The schematic presentation of algal biodiesel.

agar polysaccharide which mainly contains galactose) (Wu *et al.*, 2017), sugarcane bagasse (Hu *et al.*, 2018), agricultural residues, organic waste from industries (Lin *et al.*, 2018), sewage sludge, lignocellulosic biomass (Boodhun *et al.*, 2017), cheese whey waste (Patel *et al.*, 2016), Cow dung compost (Wu *et al.*, 2010), food waste (Moon *et al.*, 2015) etc. different biomass and organic wastes are treated in different methods to produce bio hydrogen.

Hydrogen/bio hydrogen are considered as future source of alternative fuel due to its salient features of non-polluting emission, high energy density and sustainability. As per recent reports, the amount of hydrogen production worldwide is about 700 billion N m^3 which solely depends on fossil fuel (Ball and Wietschel, 2009). This renewable source of fuel caters high energy yield (almost 122 kJ g^{-1}) compared to fossil hydrocarbon fuel (nearly 2.75 times higher) (Singh *et al.*, 2015). Current reports present that about 50 million ton of hydrogen is marketed per annum and with trade off growth rate of 10% annually (Winter, 2005). Various techniques and methodologies have been summarized (dark Fermentation, photo Fermentation, sequential dark and photo fermentation, combined dark and photo fermentation) in publications and further developments are under way to produce bio hydrogen as part of waste biomass utilization (Argun *et al.*, 2016).

The principle of dark fermentation is based on anaerobic process of hydrogen gas production and mainly produces a mixed gas which contains mainly hydrogen and carbon dioxide (Kim, 2003). The biomass feedstock for dark fermentation has been broadly classified in five groups such as simple sugar containing waste, starch containing waste, waste having cellulose content, waste from various food industry and waste water, bio solids or waste sludge (Kapdan and Kargi, 2006). Glucose, sucrose and lactose are the simple sugars from which bio hydrogen can be generated. H_2 yield per mol glucose is 4 mol with acetate while 2 mol H_2 per mol glucose with butyrate (Kapdan and Kargi, 2006). The reaction scheme has been summarized in Eqs. (1) and (2) (Kim, 2003).

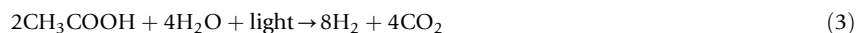


A study has reported that the yield of hydrogen from sucrose is much higher about 4.52 mol H_2 per mol sucrose when operated in CSTR for 8 h hydraulic residence time (Chen and Lin, 2003) but another study by same researchers has been proved that the amount of hydrogen obtained for the same condition in CSTR is only 0.91 mol H_2 per mole glucose (Chen and Lin, 2000). In case of lactose a maximum of 3 mol H_2 can be obtained from 1 mol of lactose (Collet *et al.*, 2004). Researchers have concluded that bio hydrogen production was maximum for sugar waste containing sucrose. Starch which is another abundant source of substrate for

dark fermentation can yield 553 mL of hydrogen gas from 1 g of starch through acetate as intermediate (Zhang *et al.*, 2003). Cellulose which is available in plenty from agricultural waste, industrial waste such as paper and pulp industries, food industries is also capable of producing hydrogen under certain condition. It has been reported that for increasing concentration of cellulose the yield of bio hydrogen decreases (Kapdan and Kargi, 2006). Ample amount of carbohydrate was found in waste water coming from food processing industries, household activities, municipal sewers and solid wastes are rich in polysaccharides and protein hence having the potential to be utilized in hydrogen production with proper pathways. In dark fermentation process, several bacterial systems are involved like, aerobes (*Alcaligene* etc.), mainly anaerobes (bacteria belonging to genus *Clostridium*) and facultative anaerobes (*Enterobacter aerogenes*) (Kim, 2003). The temperature was maintained in different range depending on the nature of the bacterial systems utilized like mesophilic (25–40°C), thermophilic (40–65°C), extreme thermophilic (65–80°C) and hyperthermophilic (>80°C) (Kim, 2003; Levin *et al.*, 2004) under pH range of 6.5–7.5 (Boodhun *et al.*, 2017). The major challenges in bio hydrogen production are those have been identified as the selection of the potential resource material and the underlying pathways to be followed for the production as well as the microbial system selection. Side reactions such as methane and alcohol production are also responsible for low yield of hydrogen (Khan *et al.*, 2017).

Single stage photo fermentation has been reported in several other publications as bio hydrogen system method from polysaccharides. In this technique, waste stream containing polysaccharides cannot be directly used as feedstock hence was converted to monosaccharide prior to the treatment with photo fermentative bacteria. Some bacterial system has been reported to produce hydrogen gas from acids such as lactic, acetic and butyric, propionic, malic acids (which are produced during dark fermentation process) using wide spectra of light with CO₂ as a byproduct (Kapdan and Kargi, 2006). They are called photosynthetic bacteria and main type of such bacteria includes purple bacteria (non-sulfur) such *Rhodobacter capsulatus* (Kapdan and Kargi, 2006), *Rhodobacter sphaeroides* (Argun *et al.*, 2016). With this second bacterium, at a sugar concentration of 5 gL⁻¹, the yield of H₂ was 1.23 mol per mol glucose (Kapdan *et al.*, 2009). The production rate of hydrogen for this type of process greatly depends on composition of media such as concentration of Mo, Fe and other nutrients, pH, temperature.

In sequential dark and photo fermentation process, production was achieved in two stages of operation. The first stage organic acid substrate produced in dark fermentation process and then the photo fermentative bacteria culture is used to break down those organic acids to hydrogen and carbon dioxide in second stage. Same bacteria are used as for the single stage photo fermentation process. The optimum condition maintained for bio hydrogen production summarized as 30–35°C and 7 respectively (Kim *et al.*, 2006; Molino *et al.*, 2013).



The process schematic for the production of bio hydrogen utilizing wastes from agricultural farms and food industries as source of starch and cellulose has been presented in Fig. 4(a and b) (Kapdan and Kargi, 2006).

In combined dark and photo fermentation technique, production was achieved in single stage. In single reactor both the dark fermentative and photo fermentative microorganisms are cultured for the effective production of hydrogen. The first type of microorganism dissociates the complex carbohydrates into hydrogen and organic acids and then the second type of microorganism convert those acids into further hydrogen and carbon dioxide thus, inhibiting the accumulation of organic acids in the reactor. The main challenges of this method lie upon the conditions of the reactor such as temperature, pH, nutrient composition, intensity of the light source applied and so on.

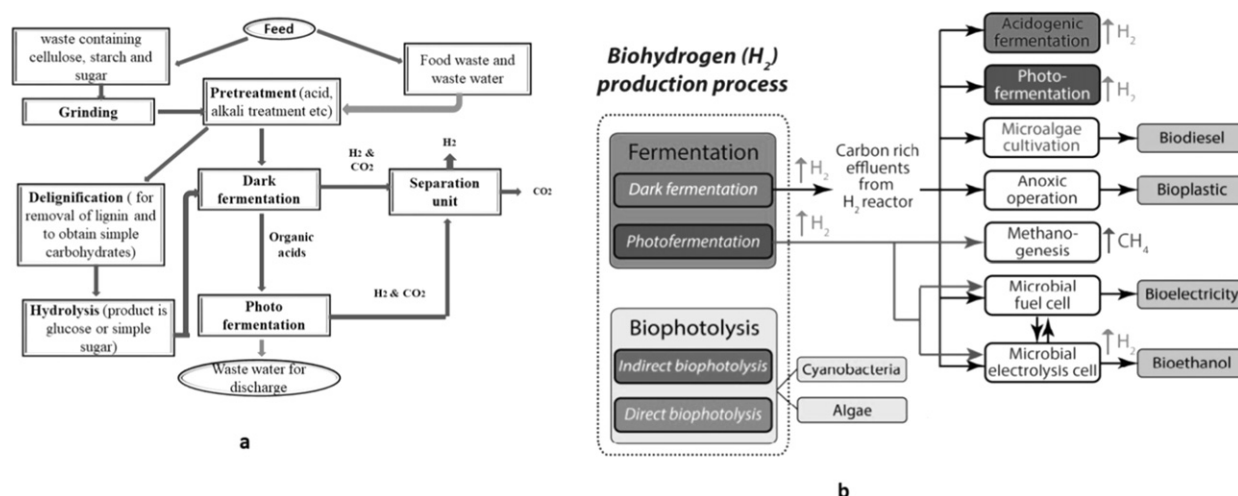


Fig. 4 (a) The process schematic for the biohydrogen production steps utilizing wastes from agricultural farms and food industries; (b) schematic presentation of different biohydrogen production processes. Reproduced from Chandrasekhar, K., Lee, Y.-J., Lee, D.-W., 2015. Biohydrogen Production: Strategies to Improve Process Efficiency through Microbial Routes, International Journal of Molecular Sciences 16 (4), 8266–8293. Available at: [doi:10.3390/ijms1604826](https://doi.org/10.3390/ijms1604826).

Bio hydrogen is clean sustainable renewable energy supply that plays a key role in all sectors of the economy. The proper realization of the technological potential of hydrogen may be helpful in contributing sustainable growth of the world economy, a stable supply of energy with reduced future emissions of greenhouse gases. For H₂ to be renewable fuel it must come from renewable sources and bio hydrogen production need to be economically feasible. However, extensive research and technological developments are needed bio hydrogen production methods for commercialization.

Bio Methane

Methane is a nontoxic gas and it is generally lighter than air. Methane can be used as a powerful fuel as its net heating value is 11946 MJ kg⁻¹. Since methane is well recognized as greenhouse gas hence, from environmental safety issue control of its emission and effective utilization is appearing as emerging research topic with economic value.

Bio methane resource material, production and utilization scenario

Typical resource materials for bio methane production are characterized as organic matter with sufficient carbon content (Molino *et al.*, 2013). A wide range of organic matter such as fecal waste of animal and human being; food waste such as fruit peel (Pisutpaisal *et al.*, 2014), waste vegetable, crops and cereals (Negri *et al.*, 2014), domestic wastes such as leftover foods, industrial waste water, sewage waste have been already attempted as feed stock for bio methane production.

The method of production of methane from organic waste is the anaerobic digestion (AD) of biomass (Mishima *et al.*, 2006; Molino *et al.*, 2013; Moodley and Kana, 2017). Anaerobic digestion is generally a biological process with assistance of micro-organism to breakdown organic matter significantly in absence of oxygen or with little amount of oxygen. The end product of this process is generally methane containing biogas, hydrogen and solid sludge (Roati *et al.*, 2012). Three sequential steps namely hydrolysis, acidogenesis and methanogenesis comprise the anaerobic digestion process (Winter and Temper, 1987). The first stage hydrolysis is also known as liquefaction and in this step the microorganism reacts with the organic complex matters to break down them into simpler forms by secreting appropriate hydrolytic enzyme for the reactions. For lipid to fatty acid conversion enzyme secrete lipase enzyme, for protein to amino acid the secreted enzyme is amylase enzyme (Molino *et al.*, 2013). In acidogenesis stage, bacteria act on those simpler soluble organics which are the product of previous stage and gives volatile organic acids such as acetic acid, propionic acid, hydrogen and carbon dioxide, little amount of ammonia is sometime also produced depending on the feedstock composition. Ethanol is another important product during acidogenesis process. The bacteria involved in these steps are *Syntrophomonas wolfei*, *Clostridium spp.*, *Syntrophobacter uolinii* (Molino *et al.*, 2013). Third step is the methane production, bacteria facilitates the methane production from organic acid (such as CH₃COOH) or inorganic carbon dioxide and hydrogen (CO₂/H₂); these bacteria are called methanogens such as, *methano coccus*, *methano bacillus*, *methano sarcina*, *methano bacterium* (Molino *et al.*, 2013). This methanogenesis is an anaerobic process and oxygen acts as an inhibitor for action of the microorganism. The basic reaction stoichiometry is presented in Eqs. (4) and (5).



The final raw biogas obtained from anaerobic digestion not only contains methane but also contains different types of impurities such as moisture, hydrogen sulphide (H₂S), carbon dioxide (CO₂), ammonia, sulfuric acid etc. Biogas produced in this case contains roughly 60% methane (Vijay and Kapdi, 2006) and rest of the impurities mainly consists of carbon dioxide. Our motive should be to make methane rich biogas by removing the impurities as much as possible to increase the energy density of biomass, to reduce the corrosion and improve the efficiency of biogas system. H₂S is a hazardous gas for our health and environment as H₂S (in biogas) on burning produces SO₂ which in turn combines with water vapor to give sulfuric acid (H₂SO₄) causing corrosion of entire biogas system (such as pipeline, valve, vessels, reactors, regulators) and contamination of the material under use (Shah and Nagarseeth, 2015). CO₂ which is the major impurity of biogas is undesirable as it reduces the energy efficiency of biogas and causes environmental pollution. H₂S can be removed from the raw biogas by various ways such as addition of different metal oxide solution to the anaerobic digester to get nearly insoluble metal oxides; biological treatment such as sulphide oxidation by chemoautotrophic microorganisms mainly of species *Sulfolobus* and *Thiobacillus*; usual method of chemical treatment with caustic solution; utilization of adsorption technology (Ramaraj and Dussadee, 2015). Recently another novel technique has been come into play to purify the biogas to improve its calorific value by removing the impurities and increasing the methane concentration and this technique is the membrane processing. A special type of polymeric membrane that is very stable and durable towards the untreated biogas that contains ammonia, water, carbon dioxide, hydrogen sulphide and capable of giving almost 95% pure methane as retentate in a single run (Molino *et al.*, 2013). Hence biogas can be purified by both chemical and physical processes to get bio methane.

Bio methane can be used as a replacement for natural gas after its purification and can be used as fuel for transportation purpose instead of Compressed Natural Gas (CNG) or Liquid Natural Gas (LNG); it can be used as fuel for heat and power such as electricity production (see "Relevant Websites sections"). A typical bio methane production route with potential application pattern has been presented in Fig. 5.

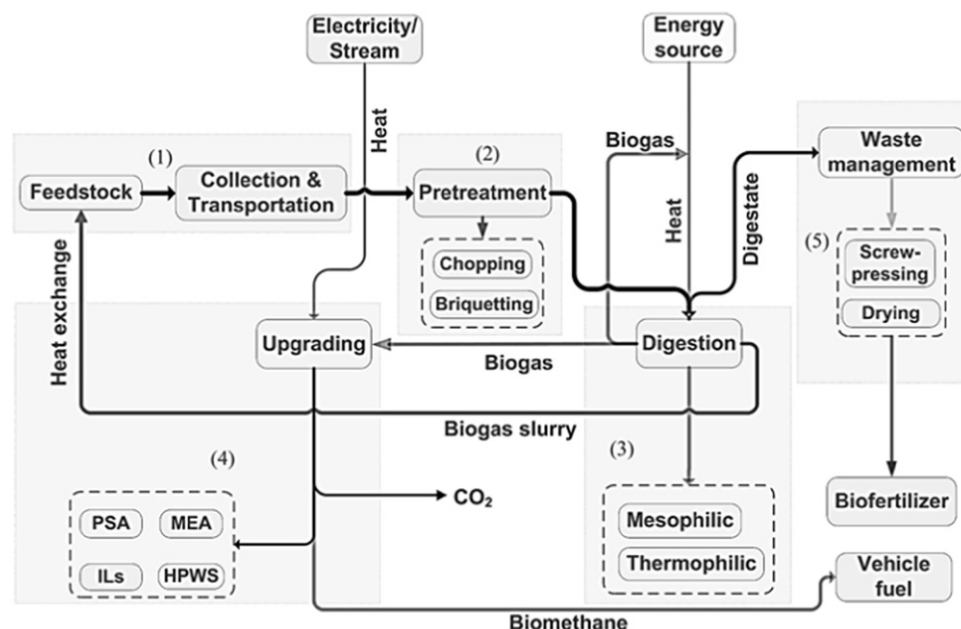


Fig. 5 Process schematic of bio methane production route with potential application pattern. Reproduced from Wu, B., Zhang, X., Bao, Di., *et al.*, 2016. Biomethane production system: Energetic analysis of various scenarios. *Bioresource Technology* 206, 155–163.

Bio Alcohol

Bio methanol (CH_3OH), bioethanol ($\text{C}_2\text{H}_5\text{OH}$), bio propanol ($\text{C}_3\text{H}_7\text{OH}$) and bio butanol ($\text{C}_4\text{H}_9\text{OH}$) (Demirbas, 2008) are collectively known as bio alcohol among which most common and abundantly producible bio alcohol is the bioethanol and last two are less common from the area of production and utilization. Bio alcohols of two types first generation and second generation bio alcohol; in the production of first one human or animal consumable plant parts are used and in the generation of the second one non-edible parts of plants are used (see “Relevant Websites sections”). Bioethanol can replace the conventional gasoline in the transportation vehicles as its energy efficiency (heating value is 26.4 MJ kg^{-1}) is comparable to petrol and it produces less amount of CO and other pollutants after burning or can be mixed with gasoline because of its octane rating is high.

Bio alcohol resource material, production and utilization scenario

The main feedstock for bio alcohol production are bio crops for both first (starch and sugar plants) and second generation (grass, bagasse) bio alcohol; industrial waste such as waste from paper and pulp industries that contains ‘kraft lignin’ and liginosulfonates, agricultural waste such as lignocellulosic wastes, wet manure, oil crop wastes such as waste from coconut, olive, rapeseed oil plant (Kasmuri *et al.*, 2017).

Pretreatment of lignocellulosic biomass is always necessary before the main course of production. The main purpose of pretreatment of biomass is the fractionation of lignocellulose into different components such as lignin, cellulose, hemicellulose (Chen *et al.*, 2017) and to breakdown the bond between them to release sugar easily without or with less degradation of the sugar (Bhatia *et al.*, 2017). Generally, four different type of pretreatment can be done with the biomasses which are physical, chemical, physiochemical and biological (Bhatia *et al.*, 2017).

The main physical pretreatment method consists of washing of the biomass material to remove dust and dirt and then drying followed by grinding and screening. Grinding helps the starch or sugar containing part of any biomass to be free to interact and it also increases the surface area for reactions involved in the later steps. Microwave irradiation (Moodley and Kana, 2017) and sonication are other two pretreatment methods. Pyrolysis which is nothing but the exposure of biomass at high temperature without presence of oxygen can also be included as an effective pretreatment for the biomass.

Chemical treatment is the most widely used method of pretreatment. Chemical treatment is usually done to enhance the biodegradability of cellulose material by the removal of hemicellulose or lignin from it (Zheng *et al.*, 2009). The chemical pretreatment methods comprise acid treatment, alkali treatment, utilization of oxidizing and ionic liquids, ammonia treatment (Bhatia *et al.*, 2017; Zheng *et al.*, 2009). Acid or alkali treatments are sometimes performed for the rupture of the fibrous materials so that they can be easily accessible by the enzymes during hydrolysis (Elemikea *et al.*, 2015). Generally, two types of acid treatment are in use one is the concentrated acid treatment and another one is the dilute acid treatment. Concentrated inorganic acids such as HCl and H_2SO_4 (Vedernikov *et al.*, 1991) are generally used. Other acids such as per acetic acid (Zhao *et al.*, 2007), phosphoric acid (Israilides *et al.*, 1978), and nitric acid (Brink, 1993) are also used during dilute acid treatment. Alkali treatment is generally performed to solubilize hemicellulose, lignin and cellulose from biomass and it is also capable of removing acetyl and

Table 2 Advantage and disadvantages of sustainable petroleum alternative fuels

Advantage	Disadvantage
Biohydrogen: Biohydrogen is a clean source of energy having higher energy density and environmental friendly as there is zero emission of GHGs when it is used as fuel in fuel cell (Argun <i>et al.</i>, 2016) and during its production less amount of chemicals are required as it is produced by microorganism. Conventional production methods such as steam reforming of methane, other hydrocarbon requires very high energy during operation ($>850^{\circ}\text{C}$) whereas biohydrogen can be produced around 24h by dark fermentation and less energy intensive. One of the main advantages of biohydrogen production is that a wide range of biomass feedstock of low cost (Anon) can be used in dark fermentation and being an anaerobic process it does not claim oxygen during reactions (Vijay and Kapdi, 2006). Biohydrogen can be produced by photo fermentation which when combined with dark fermentation process yields higher hydrogen productivity (Vijay and Kapdi, 2006).	Oxygen acts an inhibitor for fermentation process. During combined and sequential fermentation process continuous light is necessary for smooth operation; maintaining of this condition is very difficult when it is used in large industrial scale (Anon). The yield of hydrogen by fermentation process is very low and the resulting hydrogen gas contains many impurities such as CO_2 etc hence post treatment is a mandatory operation (Argun <i>et al.</i>, 2016; Vijay and Kapdi, 2006). –
Bio methane: Bio methane is considered to carbon neutral source of energy and as it is generally produced by biological method (Anaerobic Digestion) by means of microorganism, it is environmental friendly (nonpolluting and reduces GHG) and requires very less energy to be produced hence very much energy efficient (Azwar <i>et al.</i>, 2014). It is a renewable source of energy as waste biomass produced from living being is the feedstock for this bio methane aka biogas production.	Industrialization is one of the main constraints in the advancement of the bio methane production. Large scale production of bio methane is still requiring improvements. Many technologies must be developed and improved in order to make this energy cost effective.
Capital investment in the bio methane production is very insignificant compared to the profit acquired (Pandu and Joseph, 2012).	Another big limitation of bio methane production is its level of impurity. As raw untreated bio methane contains H_2S, H_2O, CO_2 and many other impurities hence its purification needs modern equipment and assembly and thus adds another cost to the production cost. Bio methane is very liable to suffer from oxidation when exposed to air or any other oxidizing medium hence unstable in nature and some can cause serious problem like explosion (Li <i>et al.</i>, 2017).
Bio alcohol: Bio alcohol is a renewable source of energy; carbon neutral and it reduces the environmental pollution and emission of Greenhouse Gases when blended to conventional gasoline in various ratios. The product (exhaust gases) of combustion of ethanol is purer as it undergoes complete combustion during burning. As the fuel is nontoxic and biodegradable accidental spills will not cause any considerable environmental hazards. Bio alcohol production is economic as it gives valuable side products during its preparation which could be profitable (Garba <i>et al.</i>, 1996).	Bio crops cultivation for bioethanol production is expensive and may cause scarcity of food. Proper knowledge for the optimum production of bio alcohol is required and capital cost laboratory set up is quite high (Ganiyu, 2005). –
Biodiesel: Biodiesel is nontoxic, biodegradable that means does not make accumulation in land or water if exposed (Sitepu <i>et al.</i>, 2014). Upon combustion biodiesel does not emit sulfur compounds, carbon mono or di oxides, polyaromatics thus subscribe to the minimization of global warming and environmental pollution (Komonkiat and Cheirsilp, 2013). Biodiesel has higher cetane number hence ignites fast and more completely which ensures the smooth performance of compression ignition engine (diesel engine) and reduces the extent of harmful gases generated by inadequate combustion reaction. For biodiesel application modification of engine is not necessary (Othman <i>et al.</i>, 2017). As biodiesel is dense oil it provides proper and apposite amount of lubrication to the engine parts. As it possesses indistinguishable properties like conventional fossil fuels and hence can be blended with them or can be used unassisted (Nagi <i>et al.</i>, 2008).	As the origin of feedstock for biodiesel production varies from country to country and type to type hence the petro-chemical properties thus the exhaust gas composition is not homogeneous (Othman <i>et al.</i>, 2017). The cost of production of biodiesel is higher and it is one and half time higher than the fossil diesel. Vehicles using biodiesel as the energy source requires perennial change of filter of the engine (Firoz, 2017). –

different uronic acid groups resulting in enhanced accessibility of enzyme towards cellulose or hemicellulose (Chang and Holtzapple, 2000). Chemicals used for this purpose are sodium hydroxide (NaOH) (Abdi *et al.*, 2000), potassium hydroxide (KOH) (Chang and Holtzapple, 2000), calcium hydroxide [$\text{Ca}(\text{OH})_2$] (Kim and Holtzapple, 2005), ammonium hydroxides (NH_4OH) (Prior and Day, 2008). Hydrogen peroxide (H_2O_2) (Mishima *et al.*, 2006) and ozone (O_3) (Maurya *et al.*, 2015) which

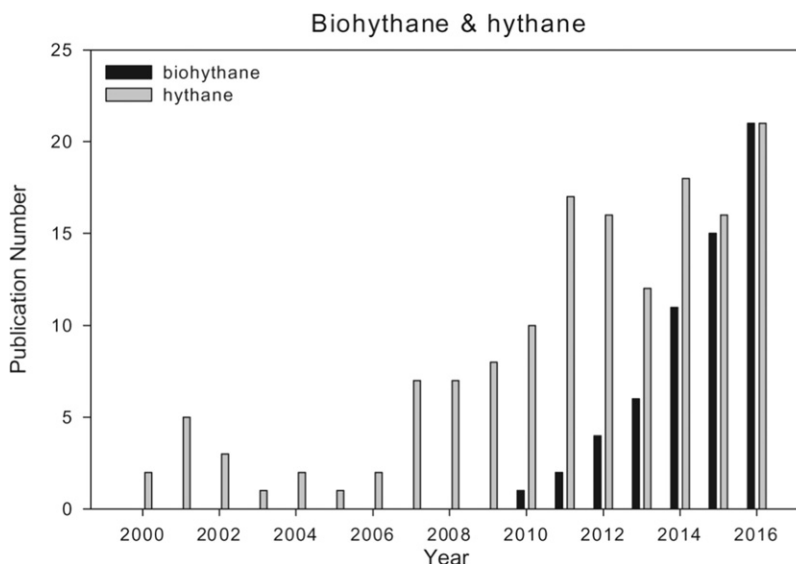


Fig. 6 Research scenario of the combined production of hydrogen and methane (biohythane). Lin, C-Y., Nguyen, T. M-L., Chu, C-Y., Leu, H-J., Lay, C-H., 2018. Fermentative biohydrogen production and its byproducts: A mini review of current technology developments. *Renewable and Sustainable Energy Reviews* 82, 4215–4220.

are oxidizing agents can also modify the biomass structure. Ionic liquids are “green” novel solvents that cater a high solubility and extraction of cellulose and with this it is almost possible to recover 100% of the solvent (Zheng *et al.*, 2009). Examples of ionic liquids include N-methylmorpholine-N-oxide monohydrate (NMMO), 1-ethyl-3-methylimidazolium [EMIM], 1-allyl-3-methylimidazolium chloride (AMIMCl) (Prashant, 2015).

Physiochemical processes of pretreatment of biomass include catalyzed steam explosion, ammonia fiber/freeze explosion (AFEX) etc. In catalyzed steam explosion some catalyst such as SO_2 , H_2SO_4 are reacted with biomass before the conventional steam explosion which offers additional advantages of steam explosion method (Zheng *et al.*, 2009). The mechanism of AFEX is that biomass is treated with hot ammonia under high pressure for a certain period of time and after it a sudden release in the pressure takes place causing decrystallization of cellulose structure and improved enzyme activity and digestibility towards it (Agbor *et al.*, 2011). One other physicochemical pretreatment of biomass can be the combination of steam with hydrogen peroxide (Verardi *et al.*, 2018).

As the name suggest biological method of pretreatment is more environment friendly compared to those chemical or physical methods. Both fungi (soft rot, white rot, brown rot) and bacteria are involved in this biological treatment. Among these microorganisms soft and brown rot fungi are more effective for disruption of cellulose while white rot fungi (*Cyathus stercolerus*, *Ceriporia lacerate*, *Phanerochaete chrysosporium*) are more prone to attack the lignin in the biomass (Mauya *et al.*, 2015; Schurz, 1978).

After hydrolysis of the biomass material the next step is the saccharification to produce reduced sugar. This is an important step in ethanol production. According to a recent study amyloglucosidase is used at pH 4.6 and with a temperature 50–60°C for 2 h for this saccharification purpose (Elemikea *et al.*, 2015). Next important step in ethanol production is fermentation by *Saccharomyces cerevisiae* yeast followed by distillation (Mushimiyimana and Tallapragada, 2016). As ethanol forms an azeotrope with water during distillation the distillation is generally extractive distillation and in this process the extracting solvent are generally cyclohexane, heptane, and benzene (Sarkar *et al.*, 2012). Bio methanol can be produced by fermentation and can be recovered by distillation as it does not produce azeotrope with water in the mixture (Voloshin *et al.*, 2016), by oxidation of carbohydrate in biomass aided by water and oxygen (Demirbas, 2009). Butanol is another alcohol produced during fermentation and in this process of fermentation *Clostridium spp.* is very much effective and a study reveals that approximate 14.4 g L⁻¹ of butanol can be possible with this conditions (Komonkiat and Cheirsilp, 2013). Bio butanol is a very promising renewable source of future world as it possesses energy content which is comparable with gasoline and it can be directly be applied in the engine as a replacement for petrol. Its octane number is also nearly equal to gasoline. Its handling is very comfortable as compared to bioethanol as it offers very low vapor pressure (Szulczyk, 2010; Jin *et al.*, 2011). Bio propanol is less popular bio alcohol and limited research works are involved with this fuel. Bio alcohol can be used as the fuel for gasoline engine or can be mixed to various ratios with gasoline to make transportation fuel. Bioethanol may be used to produce biodiesel by required processing.

Advantages and Disadvantages of Biofuel as a Replacement for Petro-Fuel

Since the term “biofuel” first entered the energy lexicon of the average consumer, there has been a steady stream of advancements to this technology. While general perceptions on biofuels may have changed over the years, quite a lot of interest in the pros and cons of this fuel source still remain. It is important for all to seriously consider both the positive and negative aspects of this

still-emerging technology. This section aims to briefly summarize all the pros and cons associated with the various alternative fuels commercially available and under exploration. The advantages and disadvantages are summarized in Table 2.

Future Prospect

Bio hydrogen, bio methane, bio alcohol, biodiesel all are sustainable and renewable source of energy of the future world providing a clean environment to all living being. Different associations and committees have been established to find out the regular and continuous inventions and development regarding these green energy technologies; such associations include Asia Bio-HyLinks (ABHL) [established in 2006] and APEC Research Center for Advanced Bio hydrogen Technology (ACABT) [established in 2009] for Asian countries. They arrange different events to explore the current pattern of research technologies available for bio hydrogen and bio methane energy efficiency (Schievano *et al.*, 2014). This combined production of hydrogen and methane via two stage fermentation is immensely famous as “biohythane” (Sen *et al.*, 2016). The research work regarding “biohythane” is increasing gradually and Fig. 6 (Boodhun *et al.*, 2017) shows this increasing trend. Though cost of raw material for bio hydrogen production is slightly high, biological way many dark and photo fermentation processes are most promising way of bio hydrogen production. The efficiency and yield of dark fermentation is low and it is considered to be one of the slowest process but when combined with photo fermentation it gives high hydrogen yield and lower the cost, time, energy expenditure; and all these is possible only by the utilization of optimum parameter conditions such as temperature, pH, biomass concentration (C/N ratio), microorganism utilization, hydraulic retention time (HRT) (Boodhun *et al.*, 2017; Kapdan and Kargi, 2006). Bio hydrogen production commercialization is a great constraint towards the development of industry regarding it. The global production rate of hydrogen per annum is around 50 million metric tons in which bio hydrogen or in turn hydrogen from biomass or renewable source accounts only 3%–4% and remaining from fossil raw material sources such as coal (19%–20%) and natural gas and naphtha (76%–77%) (Bakkenne *et al.*, 2016). From a current economic assessment, it has been come to know that the cost of hydrogen production by biomass gasification is USD\$ 4.60–7.86 per kg of H₂ produced (Dowaki *et al.*, 2007) and by pyrolysis it accounts USD\$ 1.3–2.2 per kg of H₂ produced (Khan *et al.*, 2017). Furthermore, a study shows that the cost of bio hydrogen production by dark fermentation processes with a 95 m³ photo-bioreactor was estimated to USD\$ 2.74 per kg H₂ when lignocellulogic material was its main raw material (Ljunggren and Zacchi, 2010). Different experts performed different benefit-cost ratio for this biohydrogen to check out its feasibility in large scale and one such result gives the ratio values for three different plants 3.85, 3.37 and 2.20 (Lee, 2016) which shows a satisfactory result.

Anaerobic digestion which is the main production procedure of biomethane has now improved by integration with other processes. One study shows that anaerobic digestion (AD) with upgrading gives 62%–64% bio methane production efficiency whereas gasification coupled with methanation which is also known as Göteborg biomass gasification project (GoBiGas) gives 65% efficiency which are nearly equal (Li *et al.*, 2017). Another study also shows that combination instead of competition will yield better result where anaerobic digestion gives an efficiency of bio methane production of 52% only when operated alone and this efficiency increases to a value of 67% when it is integrated with pyrolysis which gives 1.2 volumetric increase in the resulting bio methane (Salman *et al.*, 2017). While carrying out the economic analysis of this coupled process it prevails that the process is economically profitable and delivers a payback period of approximately six years with an annual rate of return of 16.5%. The presence of different studies and research works regarding bio methane production give the evidence for blooming future of bio methane. An observation of a research team compares the potential of various cereal crops for bio methane production; in their work they took two different kind of crops one is the single crop (maize only) and another one is the double crops (maize along with winter cereals) (Negri *et al.*, 2014). In their study they studied five different maize hybrid classes (300, 400, 500, 600, and 700); among them bio methane yield per hectare was highest for classes 600 and 700 and the among the winter crops triticale shows much liability than wheat. In our current stage of civilization second generation biofuels are more desirable for the healthy balance of the environment through eradication of food scarcity and proper management of bio waste materials. Such a work of second generation bio hydrogen and bio methane production was carried out by a research team where they use three types of waste material under study namely a blend of waste vegetable materials referred as “Mix”; ACV15, an un matured compost sample; and three different kinds of green composts to be specific ACV1, ACV2 and ACV3 (Arizzi *et al.*, 2016). All these studies show that bio methane is an attractive source of renewable energy and all we need it is proper industrialization for the future energy crisis concerns.

Bio alcohol which is another sustainable biofuel suffers from many drawbacks from different sectors mainly economic and social zones. Bio alcohol production will be profitable and will offer economic return if we bother with the side products during its production which are valuable (Hassan and Kalam, 2013). Bio methanol is an important bio alcohol but the production of bio methanol has some limitations. According to a recent study the feedstock for the bio methanol production such as corncob or sugarcane bagasse should contain less moisture generally less than 10% to get a higher yield; again the real conversion is very low such as 0.67% and 5.93% respectively; hence it requires large amount of biomass for effective commercialization (Shamsul *et al.*, 2014). Another study shows that Cassava cellulosic waste gives a yield of 2.7 g ethanol/15 g waste (32.4% alcohol) which is very low but can be improved if this second generation bioethanol process can be combined with the first generation technique which will satisfy the economic value (Elemikea *et al.*, 2015). As the first generation bio alcohol production is not warrantable hence more and more pressure is given on second generation bio alcohol production. Bioethanol is generally used as E10 grade where

there is 90% gasoline and 10% bioethanol present in the blend. The cost of bioethanol is also profitable; which was \$ 80 per barrel in November 2007 (Sen *et al.*, 2016). Hence bio alcohol can be treated as a promising clean fuel of future.

Different research works are continuously taking active participation in the refinement of the biodiesel production day by day. One such work shows that algal biomass accommodated from a river having fresh water which has low lipid content of 18.6% gives fatty acid methyl ester (FAME) whose characteristics are similar to those conventional fossil diesel (Kumar *et al.*, 2018). This biodiesel gives low carbon dioxide (CO₂) and nitrogen oxides (NO_x) in the exhaust gas when blended with butanol and conventional diesel and applied in a four stroke four-cylinder diesel engine. A research team conducted another interesting work on the biodiesel where they used waste cooking oil (WCO) on to which yeast *Yarrowia lipolytica* was made to be grown (Katre *et al.*, 2018). This experiment showed by means of a Plackett-Burman statistical design this biomass *Yarrowia lipolytica* was the key strand for the FAME production. Keeping all variable constant, with the increase of the biomass loaded the rate of production of FAME increases like 4 g of biomass applied yields 0.88 g of FAME in 8 h keeping all variable at a specific condition. This is a very prospecting work to be considered. Photo bioreactor is utilized all around there in the world for biodiesel production but an extraordinary photo bioreactor was developed by a research team to accelerate the rate of production of algal biodiesel (Pham *et al.*, 2017). In this work three different type of bioreactor were designed X-Shape, H-Shape, and serial-column among which X-Shape delivers most optimistic characteristics. Biomass and lipid production obtained for X-Shape photo bioreactor were 30.05% ($1.359 \pm 0.007 \text{ g L}^{-1}$) and 23.49% ($117.624 \pm 3.522 \text{ mg L}^{-1}$) more than those from the control photo bioreactor respectively. Thus the process shows that this can be accepted industrially for the production of biodiesel in future effectively. Many other trending inventions are present regarding the commercialization of biodiesel which proves a luminous future of this sustainable clean fuel.

Conclusion

As this article epitomizes, the potential of biofuel as an alternative of petro-fuel as an efficient path for sustainable fuel economy. The concern arising from the depleting availability of the petroleum and environmental issues have driven scientists and researchers to explore alternative fuel resources with development of green energy-economy system. Biomass being renewable matter have drawn surveillance of the researchers for exploration of its potential. Though woody fuels or plant based fuels have been cultivated mostly for fuel applications, as mentioned in major sections of this article but other alternative biomass resources are also emerging as potential resources for fuel applications like, animal wastes and municipal solid waste (MSW). In connection to the challenges arising from effective management of the increasing amount of produced municipal solid wastes and remediation of environmental hazard issue in concurrence to energy crisis issue, MSW can be the ultimate solution. The approaches to turn waste to energy have gained ground as methods for waste management. Both biological and thermochemical conversions of conventional plant based biomass and nonconventional MSW has been conducted in the last few decades to improved yield of product or energy formation together with decreased environmental impact. Presently, the society is facing a serious challenge for the effective alternative fuel with reasonable price value and economy of the biofuel has become the critical issue to address this connection. Economics of the biomass based fuel are strongly associated with fuel supply, including the total quantities available, the stability of the supply or of the industry generating the fuel, competitive uses and markets for the fuel. The low energy density of biofuel with cost of fuel collection and transportation can outweigh the value of the fuel hence, economy of the fuel is pivoted on the precise selection of the biomass. So, biomass need conservation and through scrutiny for societal wellness.

See also: Renewable Biomass: A Candidate for Mitigating Global Warming

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An Ultra Low Power Molecular Quantum Dot Cellular Automata Based X-ray (QX-ray) Generating System Using Renewable Energy Source

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Introduction

Industrial revolution that got full swing in the 19th century initiated use of increasing amount of fossil fuels such as coal, oil, gasoline, natural gas etc.

Power station generates power by combustion of fossil fuels. These non renewable energy source generates gases like CO_2 , CH_4 etc., which are greenhouse gases. With higher concentration of CO_2 and CH_4 in the atmosphere the infrared radiation from earth is not able to find free passage through Oxygen and Nitrogen, the major transparent ingredient of atmosphere. Solar radiation mostly in the form of visible light causes generation of heat while absorbed into the earth surface. This heat is radiated as infrared radiation. This infrared radiation gets absorbed by these greenhouse gases and does not get easy passage into space. This absorbed heat causes global warming.

Use of sources of green energy or clean energy may be the future solution for global warming. The energy is derived from natural processes that do not radiate greenhouse gases and replenished also by nature. This energy is derived from various natural sources such as sunlight, wind, rain and tides. It can replace fossil fuels in almost all major areas of utilization.

The most common source of renewable energy is solar power. Photovoltaic cells produce solar power capturing sunlight turning subsequently into electricity. After commercialization, this technology has become inexpensive and utilized in daily needs.

Air flow through surface is another source of renewable energy that pushes turbines and generates power.

Hydroelectric power may be generated through earth's water cycle, rainfall, force of water running through a dam etc.

Our current contribution here is to propose a methodology that enables us avoiding combustion of non-renewable energy such as fossil fuels and using power through renewable energy source such as sunlight to run Quantum Dot Cellular Automata based X-ray generating system.

The use of sunlight as energy source enables us to avoid the application of huge amount of voltage and consumption of huge power and energy in existing technology. The Quantum Dot Cellular Automata paradigm reveals a methodology that requires the application of small amount of voltage and consumption of less amount of energy and power as compared to existing technology to radiate X ray with same intensity.

The existing digital X ray needs the use of approximately 80 kV of voltage and 80 kW of power whereas the proposed X ray system needs application of voltage in the range of 2–2.81 V_{rms} and power in the range of watt only. So, proposed methodology ensures power generation through renewable energy source, debarring the use of sources of greenhouse gases and radiates X ray with minimum application of voltage and power.

One of the biggest discovery in the 19th century was the discovery of X-ray by Wilhelm Röntgen. That time it was an unknown type of radiation and termed as X-radiation or X-ray. The existing convention for production of X-ray requires X-ray tube. It is a vacuum tube that employs a high voltage (see "Relevant Website section") to accelerate the electrons released by a hot cathode plate. These high velocity electrons colliding with metal anode radiate X-rays. While colliding with anode, electrons knock an orbital electron out of inner electron shell of anode atom. The electrons from higher energy level then fill up the vacancy and radiate X-ray. The existing process of generating X-ray is inefficient with production efficiency of only one percent (Jerrold *et al.*, 2002; Camara *et al.*, 2008). The process encompasses good amount of power to produce the required flux of X-ray. Digital X-ray generator employs 440 VAC, 50/60 Hz supply with three to single phase transformer. Here around 80 kVA amount of power is generated during the process of X-ray generation. Most of this amount is lost and consumed by the tube as waste heat. The existing X-ray tube is designed in such a way that it can dissipate the excess heat. Energy and power loss are big concerns while generating X-ray and plenty of research efforts are going on around the globe. Around 2500°C of temperature is generated in the existing process imperatively requiring associated cooling system. Quantum dot Cellular Automata (Lent, 1997) paradigm can be employed to generate X-ray wave with very less amount of supply voltage in the range of 2–2.81 V_{rms} and very small amount of power consumption in the range of watt only.

This is worth saying that a mathematically monotonic relation seem prevalent while relating voltage consumption and power consumption with generation of greenhouse gas. But to the best of our knowledge, there is hardly any established equation relating this three parameters. As such any device with lesser power/energy requirement is more desirable from the perspective of greenhouse effect. Less the power/energy consumption, is the more environment friendly the device would be. This is primarily because the major source of energy is combustion of fossil fuel and carbon source. in the present day scenario. Accordingly a low power device based on nano-technology stands in good stead from environmental point of view. Our present proposal appears meritorious in this context.

We will analyze first the technical feasibility of fabrication of metal dot QCA using electrometer. Accordingly, we ascertain whether it is possible to achieve the same at room temperature. The study in the next three sections establishes that the radius of graphene based metal dot will be in attometer dimension only which is not possible to fabricate in respect of available technology.

The present invention (Roy *et al.*, 2018, 2017) relates to Molecular Quantum Dot Cellular Automata methodology for generating X-ray wave from QCA unit.

Consideration of SET to Determine the Radius of Island of Metal Dot QCA

4 Dot 2 electron metal dot QCA is fabricated using single electron transistor due to associated advantages like small size, low power consumption, and ability to perform fast and sensitive charge measurements (Devoret and Schoelkopf, 2000). Fig. 1 (Snider *et al.*, 1999) depicts the schematic of the metal dot QCA realization. Fig. 2 (Durrani and Ahmed, 2008) indicates SET circuit which comprises a dot between the Source and Drain electrodes. The island is separated from these electrodes by a tunnel junction. Each tunnel junction has its resistance and capacitance as shown in Fig. 3. The dot is also capacitively coupled to the Gate electrode which also has a capacitance to control current flow. The total capacitance (C) between the dot and outer environment is given below:

$$C = C_1 + C_2 + C_g \quad (1)$$

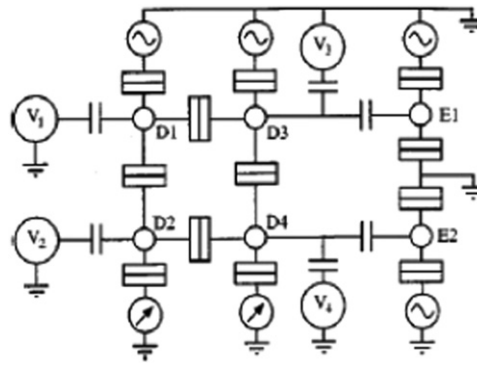


Fig. 1 Simplified schematic of the four-dot QCA cell and electrometers.

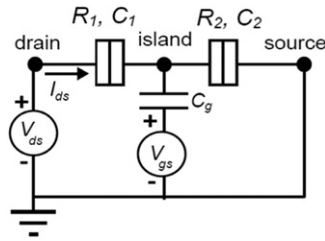


Fig. 2 Single electron transistor.

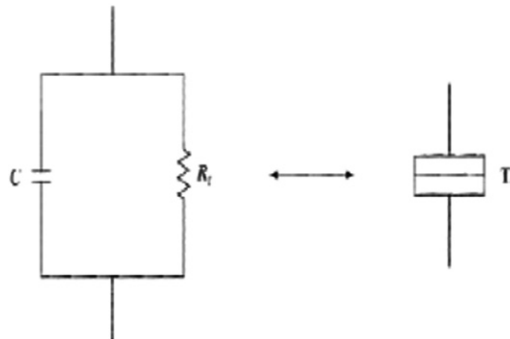


Fig. 3 Tunnel junction.

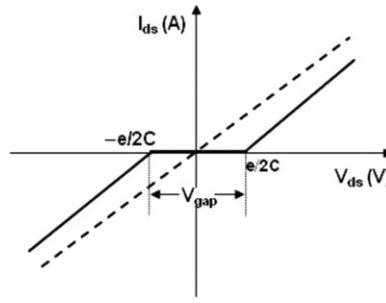


Fig. 4 The drain-source current, I_{ds} , V_s the source-drain voltage, V_{ds} , characteristics of this system in the presence of single electron charging effects (solid line) and in the absence of single electron charging effects (dashed line).

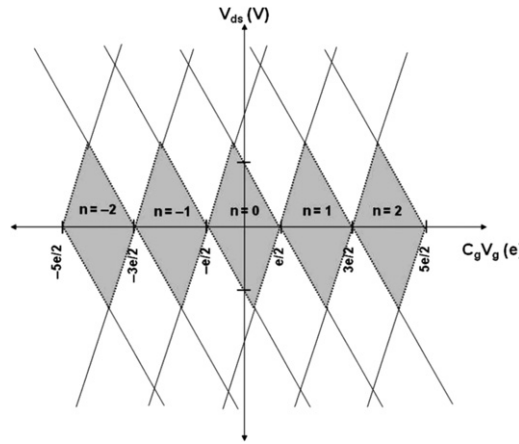


Fig. 5 The stability charge diagram of the source-drain voltage, V_{ds} , across a SET as a function of the gate voltage V_g . The gray regions have zero source-drain currents I_{ds} (Coulomb blockade regions).

C_1 , C_2 and C_g denote drain capacitor, source capacitor and gate capacitor respectively. Three conditions need to be met to achieve coulomb blockade.

$$(1) V_{bias} < \frac{e}{C}$$

Here V_{bias} denotes bias voltage, e denotes elementary charge and C denotes total capacitance.

$$(2) R_t > \frac{\hbar}{2\pi e^2}$$

Here R_t denotes the tunneling resistance and $\hbar$ is plank's constant. This condition is derived from Heisenberg's uncertainty principle.

$$(3) KT < \frac{e^2}{2C}$$

Here KT denotes the thermal energy, $K = 1.3806505 \times 10^{-23}$ joules/kelvin, $\frac{e^2}{2C}$ denotes the charging energy or coulomb energy. If this condition is not met then the electron will pass the quantum dot via thermal excitation. When one electron overcomes the charging energy and tunnels into the quantum system, it blocks the tunneling of a second one since it would charge additionally the quantum system by an amount $< \frac{e^2}{2C}$. The effect is that a single electron may tunnel through at a time.

In **Fig. 4** the region $-\frac{e}{2C} < V_{dc} < \frac{e}{2C}$ is called coulomb blockade region, with a coulomb gap voltage V_{gap} . In this region the electron's energy is smaller than the repulsive Coulomb energy of the electrons on the island as shown in **Fig. 5**.

Determining the Radius of Island in Room Temperature

In SET the island can be explained by assuming a small metallic sphere, as shown in **Fig. 6**. This island is initially electro-neutral i.e., the net charge on this island is zero since the number of electrons and protons are same in it. Now, consider that a single electron is placed close to the island. In this situation, it gets attracted by the island. Thus, this single electron comes into the island and leaves a negative charge of e on it. Now, due to the presence of this negative charge, an electric field is created around the island so that in the event of another electron approaching close to this island, it will face a strong repulsive force induced by the electric field created around the island (Sinha and Sanjay, 2014). The total capacitance(C) corresponds to the self capacitance of island. When the island is a sphere with a radius of R embedded in a dielectric material with a dielectric constant, the self capacitance (Weis, 2004; Gupta, 2016) is given by

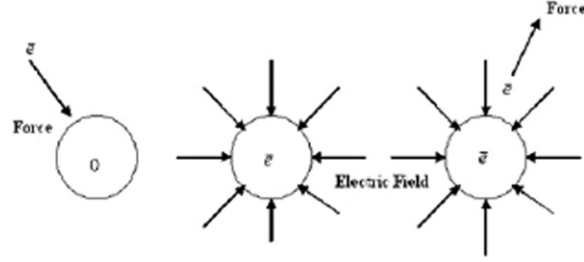


Fig. 6 (a) An electron feeling a small attractive force as it approaches a sphere. (b) Once sphere gets charged negatively by a single electron; other electrons will feel a strong repelling force.

$$C_{self} = 4\pi\epsilon_0\epsilon_r R \quad (2)$$

Where ϵ_0 and ϵ_r are permittivity of free space and permittivity of dielectric material of capacitor. From the 3rd condition we get $C < \frac{e^2}{2kT}$. Therefore at room temperature (300° kelvin) $C < 3.09 \times 10^{-18} F$.

Here we use graphene as a metal of island as graphene is a good conductor. In the 5–40 GHz range encompassing the microwave and the lower part of millimeter wave spectrum, the electrical permittivity of graphene is almost 3 (Cismaru *et al.*, 2013). This experiment was carried out using a coupled co planar wave guide placed over a graphene mono layer flake, which is deposited on Si/SiO₂. So the relative permittivity of graphene is 3.3882×10^{11} . Now from Eq. (2) we can write,

$$4\pi\epsilon_0\epsilon_r R < 3.09 \times 10^{-18} F \quad (3)$$

Thus, $R < 0.819721$ Auttometer

Here we performed studies for the radius of island in room temperature. It is seen from Eq. (3) that the radius of island will be in auttometer range which is not possible to fabricate using graphene as a metal.

QCA Cell and Molecular Cell Clocking Arrangement

The QCA cell and electromagnetic clock signal are the most vital ingredients in the invention of X-rays radiated from QCA cells which consume very less amount of electric energy and power.

QCA Cell

Each cell is composed of two V shaped molecular structures and has six redox sites. as shown in Fig. 7. The redox sites are considered as quantum dots. The figure depicts three stable configurations of the two mobile electrons within the molecular cell. Mobile electrons establishing themselves at the upper diagonal sites (i.e., either at cites 2 and 0 or 1 and 3) represent ACTIVE states of the cell. These active states carry two polarities of the cells viz. $P = \pm 1$. $P = 1$ is said to represent binary '1' and $P = -1$ represents binary '0'. When the two mobile electrons are positioned at the two sites depicted below, the cell is said to represent 'NULL' state. Fig. 8 indicates molecular cell dimension. Here we employ cell size (d) to be 1 nm and height (h) to be 1 nm (Lu *et al.*, 2006; Lu *et al.*, 2007).

Molecular System Clocking Arrangement

Clock signal is applied through submerged electrodes buried in oxide layer (Karim *et al.*, 2010).

Managing Electrodes

The electrodes carry electromagnetic clock signals and they are placed at the bottom of the oxide layer. The phase shifted sinusoidal signal is applied to each of the electrodes to energize the electrons. Fig. 9 depicts the four phases of the applied sinusoidal signal viz. ϕ_1, ϕ_2, ϕ_3 and ϕ_4 with $\phi_1 < \phi_2 < \phi_3 < \phi_4$ such that the data may flow in the direction as indicated in Fig. 9. This electric field $\vec{E}$ in the Y and $-Y$ directions switch the molecular cell from ACTIVE state to NULL state and vice-versa. The electrodes have finite radius and potential voltage is applied with respect to grounded plate as per Fig. 11. Average electrode potential (Karim *et al.*, 2010) is determined as,

$$V_{avg} = \frac{V_{e1} + V_{e2}}{2} \quad (4)$$

where V_{e1} and V_{e2} are the potentials on two adjacent electrodes. The electrode potential difference between these two adjacent electrodes can be given as,

$$\Delta V_e = |V_{e2} - V_{e1}| \quad (5)$$

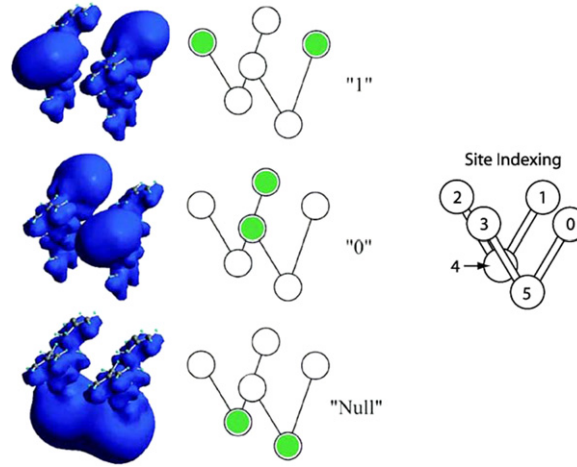


Fig. 7 QCA cell in V shaped molecular form. Reproduced from Karim, F., Walus, K., Ivanov, A., 2010. Analysis of field-driven clocking for molecular quantum-dot cellular automata based circuits. *Journal of Computational Electronics* 9, 16–30. Lent, C., Isaksen, B., 2003. Clocked molecular quantum-dot cellular automata *IEEE Transactions on Electron Devices* 50, 1890–1896.

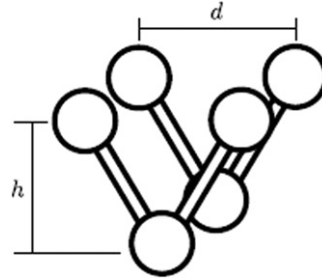


Fig. 8 Molecular cell dimension.

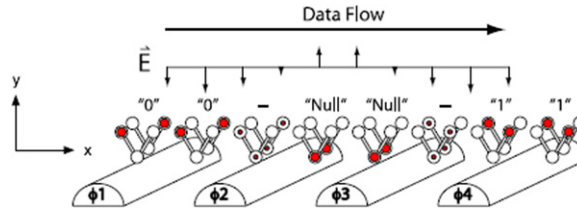


Fig. 9 Plot of cell size (nm) Vs V_{rms} for three different spacing of electrodes. Reproduced from Karim, F., Walus, K., Ivanov, A., 2010. Analysis of field-driven clocking for molecular quantum-dot cellular automata based circuits. *Journal of Computational Electronics* 9, 16–30.

The RMS voltage V_{rms} can be defined as $\sqrt{(V_1^2 + V_2^2)}$. Where V_1 is maximum allowable V_{avg} and V_2 is minimum allowable V_{avg} (Karim *et al.*, 2010). The interdependency between cell size and RMS voltage is studied and analyzed in Fig. 10. A spacing of 20 nm (Karim *et al.*, 2010) is applied while selecting V_{rms} and cell size. While selecting the above two parameters we need to analyze the temperature issues also. Now maximum applicable phase difference ϕ_{max} between two adjacent electrodes having maximum potential difference ΔV_{emax} can be expressed as,

$$(\phi)_{max} = \pm 2\sin^{-1}\left(\frac{\Delta V_{emax}}{2V_0}\right) \text{ radians} \quad (6)$$

Here, V_0 is peak potential value of clock signal applied to adjacent electrodes and the minimum RMS voltage should be applied (Karim *et al.*, 2010). The inter-electrode spacing is maintained at 20 nm. The ground plate is placed $\eta = 25$ nm above the electrodes and cells are placed $\beta = 23$ nm above the electrodes as depicted in Fig. 11. The length and radius of electrode are chosen to be 100 nm and 5 nm respectively as justified in article (Visconti *et al.*, 2004; Liu *et al.*, 2002). Dielectric like SiO_2 is used between electrodes and molecules whose dielectric constant is 4.2. The electrodes shall be buried inside the dielectric (SiO_2) (Nojeh *et al.*, 2004).

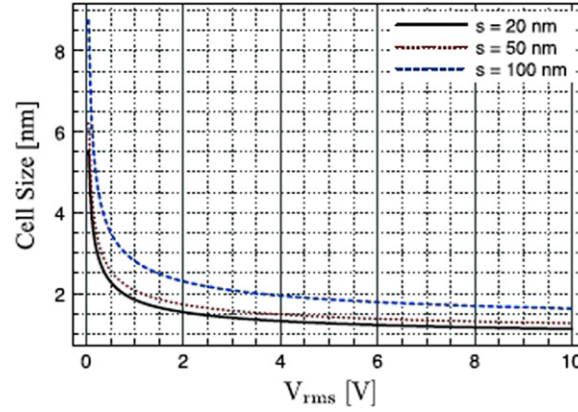


Fig. 10 Submerged electrodes to generate an electric field $\vec{E}$ at the level of molecular cells. Reproduced from Karim, F., Walus, K., Ivanov, A., 2010. Analysis of field-driven clocking for molecular quantum-dot cellular automata based circuits. *Journal of Computational Electronics* 9, 16–30.

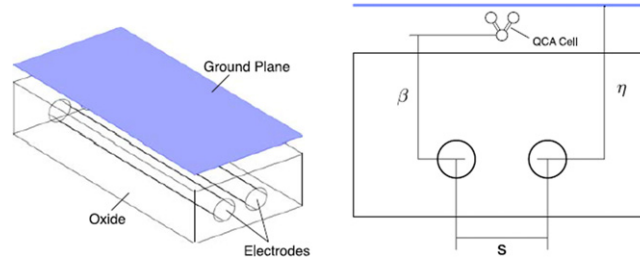


Fig. 11 The figure on the left side shows perspective view of two buried electrodes. The figure also shows the ground plate and the electrodes are buried within oxide. The figure on the right is a cross sectional view of the figure on the left. Reproduced from Karim, F., Walus, K., Ivanov, A., 2010. Analysis of field-driven clocking for molecular quantum-dot cellular automata based circuits. *Journal of Computational Electronics* 9, 16–30.

Proposed Methodology for the Generation of X-ray

If cell size is allowed to decrease, reduced RMS voltage and maximum operating temperature can be regulated as analyzed in Fig. 12. At 1000–1300K, an array of cells having dimension of 1 nm can be employed with an RMS value of 2–2.81 V_{rms} voltage magnitude approximately (Karim *et al.*, 2010). Application of clock signal energizes the electrons and bring them to the NULL state. Application of input signal decides polarity when applying simultaneously with the clock signal. Tunneling electrons possess dual wave particle property (Zetili, 2009; Blum, 2012). Each electron particle, while moving through the tunnel, behaves as a group of waves as per de-Broglies hypothesis on matter waves (Zetili, 2009; Blum, 2012). According to this hypothesis this group of waves is nothing but superposition of several monochromatic waves with same amplitude and phase but marginally different wavelength (Baym, 1969; Fock, 1986). Let $\psi(x)$ be the superposition state of an electron tunneling between the dots in the x direction. Fourier transform expresses the superposition state $\psi(x)$ of an electron as (Fig. 13),

$$\psi(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} (\phi)(k) e^{i(kx)} dk \quad (7)$$

where $\phi(k)$ is the amplitude of the superposition wave. $k = \frac{2\pi}{\lambda}$ is the wave propagation velocity. λ is the wavelength and $i = \sqrt{-1}$. Fig. 14 shows the characteristic curve of an electron wave while moving through channels (Mukhopadhyay and Dutta, 2015). Whenever electron is localized, it is positioning at $x=0$ and at this position $e^{i(kx)} = 1$. It means electron waves of different frequencies interfere constructively and no oscillations are reported. Hence $\psi(x)$ attains peak at $x=0$. At other values of x , the components of $e^{i(kx)}$ are added up as in Eq. 7. Thus resulting in oscillations and the value of $\psi(x)$ is obtained. At $\frac{x}{2}$, $e^{i(kx)}$ attains minimum value and characteristic curve achieves the negative peak. When x grows from this point, the value of $e^{i(kx)}$ also grows resulting in growth of $\psi(x)$.

As stated earlier, clock signal in QCA is the energy supplier for the electrons to change their state. We assume that inter-dot channels are experiencing finite potential energy $V(x)$ in the positive x direction. Then time independent Schrödinger wave equation is,

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} (E_n - V(x))\psi(x) = 0 \quad (8)$$

where m is the mass of electron, $\hbar$ is reduced plank constant, E_n is the infinite sequence of discrete energy levels corresponding to all possible nonnegative integral values of n . Here, n is representing the quantum number. Eq. (8) can be reduced to

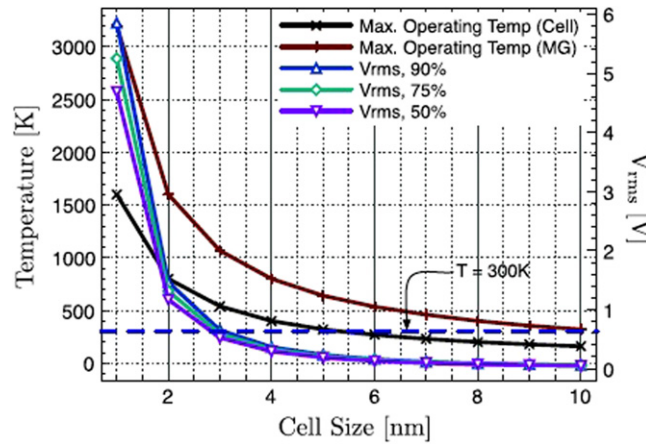


Fig. 12 The plot depicts a trade off between maximum operating temperature in K, cell size in nm and RMS voltage in volt. Reproduced from Karim, F., Walus, K., Ivanov, A., 2010. Analysis of field-driven clocking for molecular quantum-dot cellular automata based circuits. *Journal of Computational Electronics* 9, 16–30.

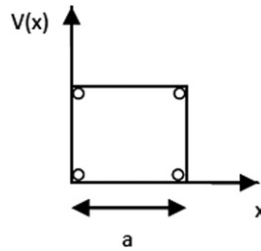


Fig. 13 QCA cell in 2D representation. Reproduced from Mukhopadhyay, D., Dutta, P., 2015. A study on energy optimized 4 dot 2 electron two dimensional quantum dot cellular automata logical reversible flip-flops. *Microelectronics Journal* 46, 519–530.

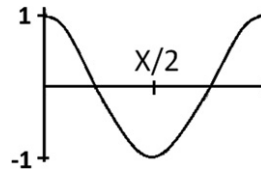


Fig. 14 Characteristic curve Reproduced from Mukhopadhyay, D., Dutta, P., 2015. A study on energy optimized 4 dot 2 electron two dimensional quantum dot cellular automata logical reversible flip-flops. *Microelectronics Journal* 46, 519–530.

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2md^2} + V(x) \quad (9)$$

where d is the molecular cell dimension (Mukhopadhyay and Dutta, 2015). If applied voltage to the molecule is V volt and junction capacitance is C then, an expression can be generated as (Mukhopadhyay and Dutta, 2015),

$$\frac{\pi^2 n^2 \hbar^2}{2md^2} + V(x) = \frac{1}{2} CV^2 \quad (10)$$

This expression will eventually be useful in calculating operating RMS voltage of the system.

We assume that two discrete energy states E_{n_1} and E_{n_2} correspond to two quantum numbers n_1 and n_2 . Electron may transit from one energy state to another if sum or difference of quantum numbers is an odd number (Mukhopadhyay and Dutta, 2015). We need to find out the n th quantum number such that while transiting from this state to ground state, a cell radiates energy between 5×10^3 eV to 10^4 eV. This transition is expressed as,

$$\Delta E_n = E_n - E_1 = \frac{\pi^2 \hbar^2}{ma^2} (n^2 - 1) \quad (11)$$

X-ray generating system requires to radiate X-ray energy in the range between 5×10^3 eV to 10^4 eV. Considering lowest energy value i.e., 5×10^3 eV to be equal to ΔE in Eq. (11), we deduce a relation between electron quantum number (n) and cell dimension (d) as,

$$n^2 - 1 = 13.29 \times 10^{21} d^2 \quad (12)$$

Again considering the highest energy radiation i.e., 10^4 eV and equating it to ΔE_n in Eq. (11), the relation between electron quantum number n and molecular cell dimension d can be expressed as,

$$n^2 - 1 = 2.66 \times 10^{22} d^2 \quad (13)$$

A careful study of Fig. 12 reveals that at temperature of 1000K and at 2 V_{rms} operating voltage the cells attain a dimension of 1 nm considering potential energy of an electron to be 5.82×10^{-20} Joules and junction capacitance to be 200 atto-farad. If molecular cell dimension is considered to be 1 nm, for lowest level of X-ray radiation, Eq. (9) produces the value of n to be 116. If we apply the same methodology in Eq. (11) for highest limit of X-ray radiation, the value of electron quantum number n can be deduced to be 162, the temperature is modified to 1300°C at 2.81 V_{rms} applied voltage. For a single molecular cell the Eq. (11) can be reformed as,

$$(v)_2 = \frac{\pi \hbar}{2md^2} (n^2 - 1) \quad (14)$$

where v_2 is radiation frequency.

Eq. 14 derives $v_2 = 4.8 \times 10^{18}$ Hz with $n=162$ and $d=1$ nm and $v_2 = 2.446 \times 10^{18}$ Hz with $n=116$ and $d=1$ nm which lies between 1×10^{18} Hz to 3×10^{19} Hz, the frequency range of existing X-ray for X-ray system. The above calculations are for single molecular cell. The radiation energy strength for N number of molecular cells arranged in cascade is computed between $5 \times 10^3 \times N$ to $10^4 \times N$.

QCA Molecular X-ray (QX-ray) System

Our finding is a portable X-ray system consisting of X-ray generator and X-ray detector. We are going to propose X-ray generator only. Portable X-ray detectors are already available. The existing X-ray generator is huge in size and permanently housed in a room. The patients are to be brought physically to the X-ray room for imaging. Sometimes this movement becomes very painful for patients having fractures and/or bone disorders. Our invention is directed towards these kind of patients to give them some relief from additional pain of movement. The proposed X-ray generator system along with X-ray detector will be brought to the patient site. The image taken in digital form will be stored temporarily with the detector and later it will be analyzed at the laboratory.

Proposed X-ray Generator System

Existing X-ray systems suffer from many drawbacks. The focal spot at anode may attain a temperature level of approximately 2500°C and anode assembly may reach a temperature of around 1000°C. They use a high voltage power source of approximately 150 kilo volt (kV) (Coolidge, 1917; Langmuir, 1917). Another major drawback observed in the existing generation methodology is that approximately about 1% of the energy is radiated as X-ray and the rest is released as heat (Donnelly, 2005; Jens and Des, 2001). Our proposed system should overcome these drawbacks. Table 1 lists comparative studies on existing and our proposed X-ray system. The list suggests the superiority of the proposed system against the existing counter part.

The invention consists of an X-ray plate containing an array of cells as shown in Fig. 16(a). Each cell in the plate will be replaced by the molecular counter part as shown in Fig. 16(b). The cross section of X-ray generator is depicted in Fig. 15. At the lowest level

Table 1 Comparative study on existing and proposed X-ray system

Patent no.	Voltage supply	Temperature	Power generation	X-ray generation efficiency	Cooling system	Vacuum Chamber
US20110280371 (Molloi and Alivov, 2011)	600 kV	High(Data not available)	270 kW	1%–2%	Present	Present
US20120207269 (Behling, 2012)	1 kV external, – 120 kV cathode voltage	High(Data not available)	High power	1%–2%	Present	Present
US20120219118 (Tolt, 2012)	High(Data not available)	High(Data not available)	High(Data not available)	1%–2%	Present	Present
US20120027173 (Duerr, 2012)	10 kV/mm applied	More than 1000°C	High(Data not available)	1%–2%	Present	Present
US20110051895 (Vogtmeier et al., 2011)	40–160 kV	High(Data not available)	High(Data not available)	1%–2%	Present	Present
US7289602 (Raulf et al., 2007)	200–240 line voltage, 40–125 kV operating voltage	High(Data not available)	750 Watt	1%–2%	Present	Present
Proposed Technology	2–2.82 V_{rms} Voltage	1000–1300K	In the range of Watt	Nearly 100%	Required	Required

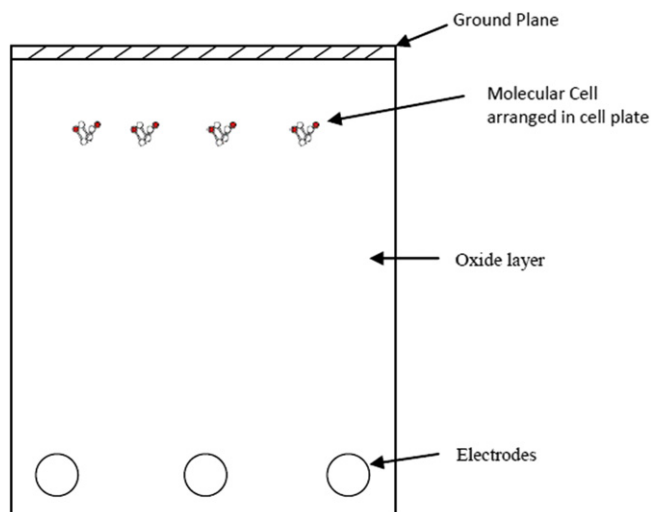
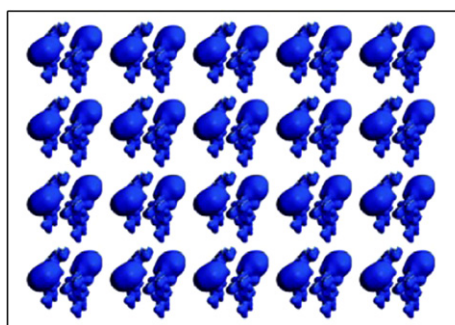
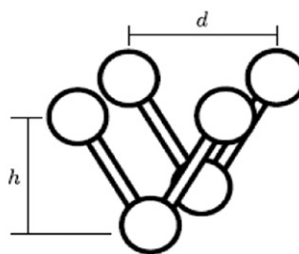


Fig. 15 X-ray system. Reproduced from Karim, F., Walus, K., Ivanov, A., 2010. Analysis of field-driven clocking for molecular quantum-dot cellular automata based circuits. *Journal of Computational Electronics* 9, 16–30.



(a) X-Ray plate



(b) Molecular cell that will replace the square cells in X-ray plate

Fig. 16 X-ray system.

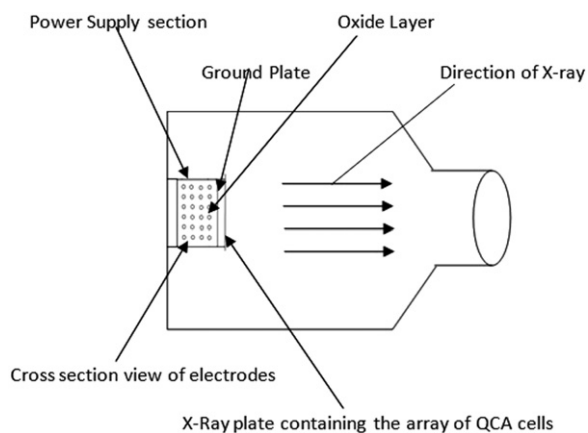


Fig. 17 (a) X-ray plate. (b) Molecular cell that will replace the square cells in X-ray plate.

electrodes are arranged. These are buried under oxide layer. The details about electrodes and dielectric are provided in Section “Molecular System Clocking Arrangement”. The molecular cells are arranged over this layer as in Fig. 16(a). Above this layer of cells, ground plane is placed. The cell size of 1 nm may work at temperature between 1000K and 1300K at 2–2.81 RMS voltage. So there is need for temperature control and electrodes might be supplied with the required RMS voltage employing step down

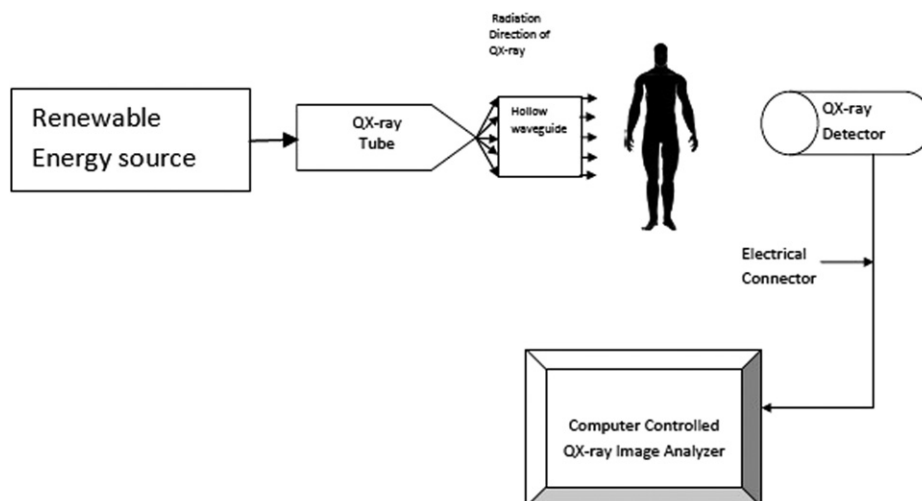


Fig. 18 X-ray tube containing power supply section.

transformer. **Fig. 17** depicts X ray tube containing power supply. Power supply is housed at the back of the tube. It contains electrodes and oxide layer. A ground plate will be located at the top of electrodes. X ray plate containing an array of QCA cells is placed at the top of power supply section. Radiation coming out from plate is directed towards radiation head.

Portable X-ray Detector

Portable X-ray detector (Lanca and Silva, 2009; Uffmann and Schaefer-Prokop, 2009) is already available in the market. The proposed X-ray system as shown in **Fig. 18** consisting of the X-ray generator and X-ray detector may be brought to the patient site. The image created will be detected by the proposed X-ray detector. The detector will convert it into electrical signal and may store information temporarily.

Hollow Waveguide or Capillaries

X-ray wave is difficult to direct. Different techniques are employed to direct X-ray beams such as optics based on total reflection principle such as capillary, natural crystals and multilayer optics i.e., man made layered structures etc. X-ray after generation are scattered everywhere unless we place an hollow parabolic waveguide just after X-ray tube as apparent in **Fig. 18**. The hollow parabolic wave guide may be made from Carbon Nano Tube (CNT) or glass as reported in patents (Verman and Jiang, 2011; Aharon Bar-David and Harel, 2014).

Conclusion

The present disclosure is a proposal of nature friendly X-ray generating system. This technology may consume green energy generated from harness natural processes such as geothermal energy, wind energy, biomass energy, solar energy, Hydro-electric power etc for system execution. This nano-technology based system places itself as appropriate for environmental point of view. Thus the proposed methodology may eliminate any chances of generation of greenhouse gases and keeps the environment clean and worth living.

See also: Eco-Sustainable Molecular Quantum Dot Cellular Automata Based Radiography in Defect Identification of Industrial Product Using Renewable Energy Source

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Use of Clean, Renewable and Alternative Energies in Mitigation of Greenhouse Gases

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Introduction

Climate change is now a global concern because it has deep repercussion on both human and natural systems. The impacts of climate change are observed in occurrence of floods, storms, snowstorms, tsunamis, droughts, tornados in greater frequency, stretch of infectious pests, pathogens and heat waves. It also results alarming rate of extinction of species and biodiversity loss. Climate change is basically based on global warming due to augmented concentration of greenhouse gases (GHGs) in the Earth's atmosphere (Elum and Momodu, 2017). The attempt to mitigate the causes of high concentration of greenhouse gases (GHGs) is accepted throughout the world as one of the best approaches to arresting climate change. To keep global warming well below 2°C or even below 1.5°C requires a fundamental restructuring of important areas in the economy and society. Solution to the problem lies in the implication of clean air policies by using renewable energies, increasing energy efficiency, reducing extremely climate-damaging fluorinated greenhouse gases (F-gases) and as well as sustainable mobility and city planning (Owusu and Asumadu-Sarkodie, 2016; Kang and Holbrook, 2015; Raghuvanshi *et al.*, 2008). On the other hand, sustainable development for prevention of climate change is also global concern which can be duly handled by use of renewable energy resources.

Renewable energy refers to harnessing energy from natural sources like solar, wind, hydro, geothermal energy and even rivers, biomass which produces very small amounts of greenhouse gases during combustion. Therefore, it refers as sustainable route of energy production and as well as clean energy source. The dominance of fossil-fuel based power generation (coal, oil & gas) and exponential increase in energy demand due to huge population growth results global challenges associated with rapid increase in concentration of carbon dioxide, which is an important greenhouse gas. In a developing country like India, the growth rate of electricity generation is 5.5%; it increased to 212 GW from 106 GW within 1996–2010 (Raghuvanshi *et al.*, 2008). It is predicted that globally energy related emission would increase by about 16% by 2040 (Elum and Momodu, 2017). Second big contributor to GHGs emission in the environment is the combustion of conventional transport fuel which is derived from fossil fuels. In 2010, transportation sector contributed 27% of total GHGs emission in United States (Kang and Holbrook, 2015). Actually, United States, Australia and Canada are identified as world's highest per capita carbon emitter (Elum and Momodu, 2017). Major portion of CO₂ and other GHGs are emitted from cars and trucks. It is reported that around 62% transport sector emission comes from light-duty vehicles (LDVs) including cars and trucks (Kang and Holbrook, 2015). Use of renewable energy may be a valuable solution to all these problems. Renewable energy can be utilized to produce electricity, vehicles fuels and as well as heat.

This study actually identifies the sources of renewable energy and their potential applications in support of GHGs mitigation attempts for climate change alleviation and sustainable development. Next section of the research focuses on greenhouse effect and greenhouse gases and their abatement policies with global and national perspective. Third section describes the various types of renewable energy options and their mode of uses.

Background

Greenhouse Effect

The 'greenhouse effect' is an atmospheric, natural heating phenomenon in which the Earth atmosphere and surface experiences heating because of presence of certain gases in the atmosphere. Part of incoming solar radiation is reflected back to the space and rest is absorbed by earth surface. Earth emits absorbed energy as infrared radiation (heat) which is partly trapped and re-emitted in all directions by greenhouse gases (GHGs). Some portion of emitted radiation from GHGs absorbed by earth surface again which makes earth warmer. This natural process is called 'Greenhouse effect'. If these gases wouldn't trap heat and emit radiation in the atmosphere, the temperature of the earth would be about 33°C colder on average. Therefore, 'Greenhouse effect' is the key factor to sustain life on earth. In global scale, the key greenhouse gases are carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O) and Fluorinated gases (F-gases). Among them, CO₂ is the most responsible gas for the phenomena because of its larger quantity in atmosphere. Although the greenhouse effect is a natural phenomenon and is one of the reasons that life can exist on Earth, the greenhouse effect is getting worse day by day. At the present, temperature of the earth is steadily rising over the years and causes global warming. The problem of climate change and global warming occurs when enormous amount of GHGs accumulate in the atmosphere, increasing the amount of radiation that is absorbed by the atmosphere and re-emitted back to the Earth's surface. The "enhanced" greenhouse effect is caused by anthropogenically produced GHGs. Combustion of fossil fuel is the primary source of CO₂. It can also be produced from direct human-induced impacts on forestry and other land use, such as through deforestation, land clearing for agriculture. Agricultural activities, waste management, energy use, and biomass burning all add to CH₄ emissions in the atmosphere. The main sources of N₂O emissions are agricultural activities, such as use of fertilizers. Fossil fuel combustion also generates N₂O. F-gases are mainly formed from various industrial processes, refrigeration, and due to the use of a variety of consumer products.

To avoid an irreversible build-up of GHGs and eventually global warming and climate change, we should act immediately because only few years are left as our “breathing space” (Mac Kinnon *et al.*, 2018; Fernandez *et al.*, 2005). Like other countries with developing economies, India faces the dual challenge of merging its rapid economic growth with a persistent need to address climate change. India is a large developing country with huge rural population directly depending on natural resources like water, mangroves, coastal zones, grasslands and their survival & existence depends on forestry, agriculture and fisheries. The potential impacts of climate change are often various and different regions have differential vulnerabilities to climate change. ‘The Climate Modeling Forum’ of India (consists of several independent research institutions, e.g., NCAER, TERI, IRADe, and Jadavpur University) supported by the Ministry of Environment & Forests, Government of India published a report (see “Relevant Websites section”) in September 2009 indicating the GHG emissions trajectory of India for the next two decades, using a number of different techniques. One report (see “Relevant Websites section”) shows that India’s per-capita CO₂ emissions in 2030/31 would be between 2.77 and 3.9 tons per-capita, or little higher like 5 tons per-capita. Another report was published under the umbrella of “MAIN – Mitigation and Adaptation Information Network” for Sustainable communities by Development Alternatives (DA) in association with UNEP/GRID-Arendal named as “Climate Change Mitigation in India” which focuses on the efforts taken up by the Government of India towards climate change mitigation and how the environmental concerns have been integrated in Indian planning process (see “Relevant Websites section”). The basic findings of the report indicates that main contributor sector of GHGs emission are energy, industry, agriculture and waste (Fig. 1) (see “Relevant Websites section”) and per capita CO₂ emissions was 1.5 tonnes in 2007. The energy sector is broadly divided into sub-section: electricity generation and transport where the first sector is the giant supplier.

In global perspective, in 2014, the top carbon dioxide (CO₂) emitters were China, the United States, the European Union, India, the Russian Federation, and Japan (Fig. 2). These data include CO₂ emissions from fossil fuel combustion, as well as cement manufacturing and gas flaring and presented in Fig. 2.

GHG Mitigation and Abatement Options

Mitigation and abatement activities aims to either reduce releases of GHGs or increase removals of GHGs from the atmosphere. Initiatives involving to substitute GHG-producing activities with non-GHG producing activities are reduction approaches (Pahuja *et al.*, 2014; see “Relevant Websites section”; Reck and Hoag, 1997).

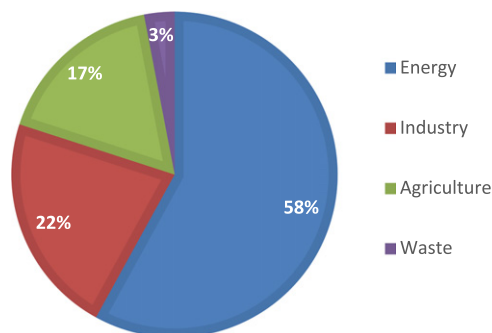


Fig. 1 Sectoral GHG emission in 2007 [http://www.devalit.org/knowledgebase/pdf/CDM_Report.pdf,\(2011\).](http://www.devalit.org/knowledgebase/pdf/CDM_Report.pdf,(2011).)

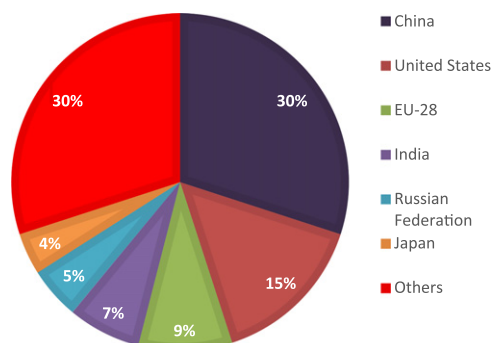


Fig. 2 Global CO₂ emissions from fossil fuel combustion and some industrial processes. Reproduced from Boden, T.A., Marland, G., Andres, R. J., 2017. National CO₂ Emissions From Fossil-fuel Burning, Cement Manufacture, and Gas Flaring, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, pp. 1751–2014.

Reduction option can be implemented by:

- Industrial process modifications,
- Renewable energy transitions,
- Demand side efficiency improvement,
- Prevention of deforestation.

On the other hand, approaches of capturing GHGs that have already been produced by various sequestration technique (i.e., storage of captured gas) is the second possible route of mitigation and abatement of GHGs.

Sequestration of various types:

- Forest sequestration,
- Agricultural sequestration,
- Geological sequestration,
- Ocean sequestration,
- Mineral sequestration.

Capturing and use is the last but best possible route of mitigation of GHGs. This includes:

- Methane capture,
- Biomass to energy,
- Biomass to product.

Under this category, GHGs are captured from atmosphere and then converted into products and used as energy sources that substitute for GHG-producing activities. For example, a crop such as corn might be grown to produce ethanol, which then replaces the use of fossil fuels.

Clean and Renewable Energy Options

Renewable energy can be defined initially as any energy source that is converted directly or indirectly from solar energy. In the broadest sense, however, almost all of the energy, including fossil fuels, can be considered a form of solar energy. The most widely used forms of non-renewable energy, such as wood, oil, gas, and coal, are embodied forms of solar energy collected, stored, and converted by natural processes. Till date approaches to energy are non-sustainable and non-renewable and the world's energy supply is largely based on fossil fuels and nuclear power. These sources of energy will not last endlessly and have proven to be contributors to our environmental problems like emission of GHGs. Due to continuous increment of global need of energy associated with economic growth and industrial revolution; mankind has already exhausted roughly half of the fossil fuels that accumulated under the earth's surface over hundreds of millions of years. Availability of nuclear power is also depends on a limited resource (uranium) and the use of nuclear power creates such countless risks that nuclear power plants cannot be considered as reliable source of energy. Therefore, the main problem of 'scarcity' will remain, and this represents the greatest challenge to mankind in next decades onwards. Renewable energy can now be defined as forms of solar energy that are available and replenished in time scales no longer than human lifetimes.

Renewable energy basically comes from the sun directly or indirectly. These sources of energy supply opportunities for countless, sustainable and replenishable energy supply with almost no environmental effect. Renewable energy offers to reduce carbon emissions, clean the air, and put our civilization a sustainable solution of energy demand. On the other hand, it helps to reduce dependence of energy imports, thereby ensuring an obvious economic growth via sustainable supply and climate protection. Renewable energies will offer a more diversified, balanced, and steady pool of energy sources.

There are several renewable energy sources that are in use today (Sathaye and Meyers, 1995; Alrikabi, 2014):

- Solar energy,
- Wind power,
- Hydropower and tidal energy,
- Geothermal energy,
- Biomass energy,
- Fuel cell.

The major technologies available to harness various forms of renewable energy from their sources and its applications are listed in **Table 1** (Sathaye and Meyers, 1995; Alrikabi, 2014). Although many of these technologies are still under development, most have come in commercial markets around the world. Research and development activities continue to improve all of these systems to enhance their ability to meet future energy demands.

Renewable Energy Sources and Technologies

Renewable energy is called as alternative energy, an alternative to fossil fuels from 1980s. In 2009, about 18% of global final energy consumption came from renewables, with 13% coming from traditional biomass and 3% from hydroelectricity (**Fig. 3**)

Table 1 Renewable energy sources and relevant energy technologies available with their end-use applications

Resource	Technology	End-use applications			
		Electricity	Industry	Building	Transport
Solar energy	Photovoltaics – Flat plate	✓			
	Photovoltaics – concentrator	✓			
	Solar thermal parabolic through	✓	✓		
	Solar thermal dish	✓			
	Solar thermal central receiver	✓	✓		
	Solar ponds	✓	✓	✓	
	Active heating		✓		
	Day lighting		✓		
Wind energy	Horizontal axis turbine	✓			
	Vertical axis turbine	✓			
Biomass energy	Direct combustion	✓	✓	✓	
	Gasification/pyrolysis	✓	✓		✓
	Anaerobic digestion	✓	✓	✓	
	Fermentation				✓
Geothermal	Dry steam	✓			
	Flash steam	✓			
	Binary cycle	✓			
	Heat pump			✓	
	Direct use		✓	✓	
Hydropower	Conventional	✓			
	Pumped storage	✓			
	Micro-hydro	✓			
Ocean energy	Tidal energy	✓			
	Thermal energy conversion	✓			

Note: Sathaye, J.A., Meyers, S., 1995. Renewable energy supply (Chapter 9). In: Sathaye, J.A., Meyers, S. (Eds.), Greenhouse Gas Mitigation Assessment: A Guidebook. Springer, pp. 133–149.

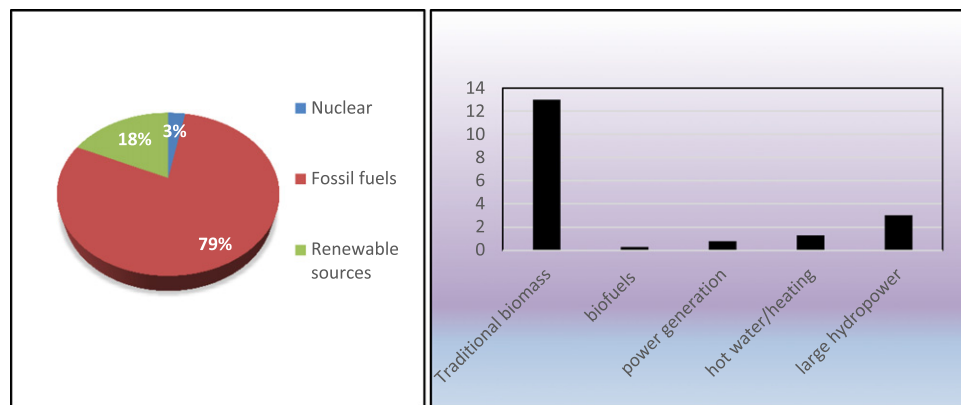


Fig. 3 Global Final Energy Consumption, 2006 (REN21, 2007, Global Status report). Reproduced from El Bassam, N., 2011. Renewable Energy Sources and Their Applications (Chapter 1). Agrobios International.

(El Bassam, 2011). New renewables (small hydro, modern biomass, wind, solar, geothermal, and biofuels) accounted for another 2.8% and is growing very rapidly. The share of renewables in electricity generation was around 19.4%, with 16.1% of global electricity coming from hydroelectricity and 3.3% from new renewable (El Bassam, 2011). In the country like India, the potential capacity of renewable energy source is estimated to be 126,000 MW including ocean, tidal, thermal power (Raghuvanshi *et al.*, 2008). Maximum potential is available as wind power (45,000 MW (Raghuvanshi *et al.*, 2008)) but achievement is highest in exploiting hydro power capacity (Raghuvanshi *et al.*, 2008).

Solar Energy

Solar energy is abundant, it has the greatest potential for providing clean, safe, and reliable power. Both usable electricity and heat can be produced from sun's light. Statistics indicates that the annual total solar energy is 1×10^{18} kWh, which is just equivalent to

13 trillion tons of standard coal and about 1000 times more than the oil reserves. Total available solar energy is ten thousand times more than the world's energy necessity. Solar Energy can be classified into two types: active solar and passive solar or photovoltaic and thermal. Electricity can be produced directly from photovoltaic, while solar thermal systems produce heat for buildings, industrial processes or domestic hot water. Thermal systems can also be utilized to generate electricity by operating heat engines or by producing steam to spin electric turbines. Solar energy systems have no fuel costs, so there is only original investment in the equipment. The main types of solar energy technologies are (Sathaye and Meyers, 1995):

- Photovoltaic (PV) systems convert sunlight directly to electricity by means of PV cells made of semiconductor materials.
- Concentrating solar power (CSP) systems concentrate the sun's energy using reflective devices such as troughs or mirror panels to produce heat that is then used to generate electricity.
- Solar water heating systems contain a solar collector that faces the sun and either heats water directly or heats a "working fluid" that, in turn, is used to heat water.
- Transpired solar collectors, or "solar walls" use solar energy to preheat ventilation air for a building.

Photovoltaic systems

A photovoltaic system uses photovoltaic cells (PV) to directly convert sunlight into electricity using modules composed of multiple PV cells. The photoelectric effect was first noted by a French physicist, Edmund Becquerel, in 1839, who found that certain materials on exposure to light would produce small amounts of electric current. In 1905, Albert Einstein described the photoelectric effect. PV generates power on a much smaller scale than traditional utility power plants, so they can often provide high-value electricity exactly where and when it is needed. PVs are often the best choice for supplying power for remote, "off-grid" sites (refer Fig. 4).

The method of conversion of light energy to electrical energy is based on photovoltaic effect. On exposure to light, semiconductor materials can absorb some of the photons and which results some free electrons in the crystal. This is the basis of electricity generation by photovoltaic effect. Silicon is the widely used semiconductor material for constructing photovoltaic cell. A typical PV cell consists of thin two layers: ultra-thin layer of phosphorus-doped (N-type) silicon on top and thicker layer of boron-doped (P-type) silicon (Schumm, 2010). In the top junction, electrical field is generated. When sun light strikes the PV cell, electrical field is produced and results flow of electricity when solar cell is connected to an electrical load. A typical silicon PV cell produces about 0.5–0.6 volt DC under open-circuit, no-load conditions; it does not depend on size of cell. The current (and power) output of a PV cell depends on its efficiency and size (available surface area), and is proportional to the intensity of sun light.

PV devices are used as modules composed of multiple PV cells. Two distinct categories of PV devices are available: flat-plate and concentrating. Flat plate type has huge surface area and utilizes the whole of the incident solar radiation including diffused part. A concentrator system uses lenses to focus radiation on few efficient PV cells and only use direct beam sun-light. Concentrating solar power (CSP) technologies requires mirrors for reflecting and concentrating sunlight onto a point where it is stored as heat and then converted to electricity.

Solar thermal – Electric

Solar thermal technologies collect the sun's radiant energy to create a high-temperature heat source that can be converted into electricity via a number of thermodynamic conversion cycles (Fig. 5).

Parabolic trough technologies employ a field of parabolically-shaped solar collectors. The collectors accept sun's energy and focus onto specially-coated metal pipes surrounded by heat transfer fluid filled glass tubes. The fluid passes through the sunlight collector and becomes very hot. Typical heat carrier fluids are water or steam, oil, or molten salt. Then the fluid is transferred to the heat engine, which converts the heat to electricity. Parabolic dish systems use a modular mirror system that approximates a

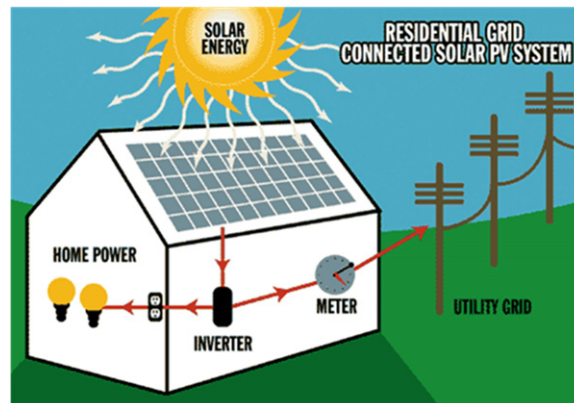


Fig. 4 Solar energy in small unit. Pic: Wikipedia, Alrikabi, N.K.M.A., 2014. Renewable energy types. Journal of Clean Energy Technologies 2, 61–64.

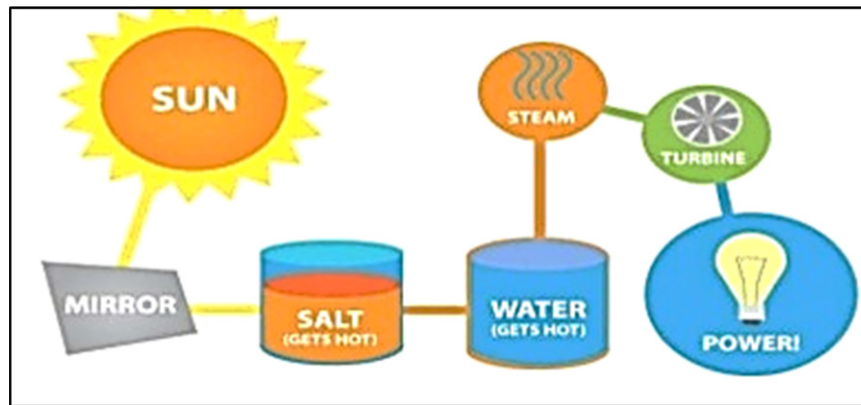


Fig. 5 Solar thermal electric conversion system. (Pic: Wikipedia).

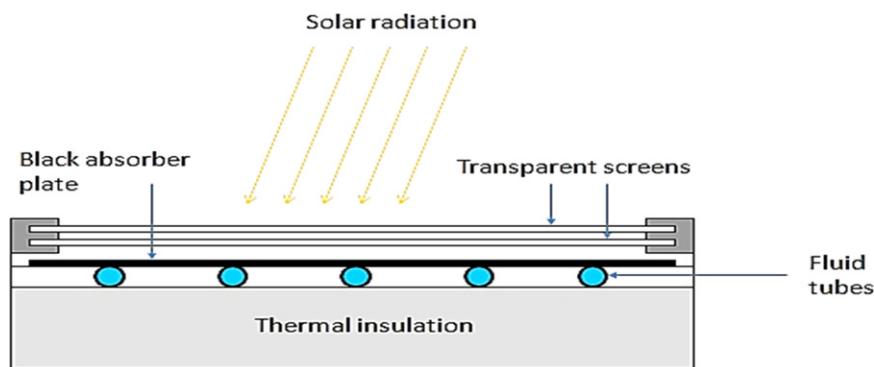


Fig. 6 Schematic of a flat plate solar collector. (Pic: <https://www.e-education.psu.edu/eme81>).

parabola and creates a high energy flux at the focal point where an external combustion converts the heat into electricity. Central receivers use a large field of sun-tracking mirrors (heliostats) that reflect the incident radiation onto a tower-mounted thermal receiver. Finally, solar pond systems collect and store solar energy in a liquid medium (usually a large basin of water with a salt gradient), which can then be converted to electricity using a closed Rankine Cycle engine (Sathaye and Meyers, 1995). Two types of collectors are described schematically in Figs. 6 and 7.

Some typical collectors are used which to a bigger energy conversion system. The following designs are used as utility scale solar thermal systems:

- (1) Linear reflectors (heating temperatures $\sim 280^{\circ}\text{C}$),
- (2) Parabolic trough (heating temperatures $\sim 400^{\circ}\text{C}$),
- (3) Dish/engine systems (heating temperatures $\sim 650^{\circ}\text{C}$),
- (4) Solar tower (heating temperatures $\sim > 1000^{\circ}\text{C}$).

Solar building technologies

Building energy consumption is growing day by day. Solar energy, as a type of renewable energy, will greatly alleviate the pressure of the building energy consumption. Heating, cooling or day lightening of buildings can be done using active and passive solar building technologies. Appreciable number of solar water heaters is available in Japan; some other countries like United States, China, Turkey, Kenya and Guinea are also using this technology (Sathaye and Meyers, 1995). Both active and passive solar building designs (Fig. 8) are used though passive is more popular. In case of active design, solar energy collectors receive energy and transfer to a working fluid (water, oil or air) for direct use or storage. This system can provide hot water or heating/cooling of interior space. Cooling technologies include solar desiccant systems that use a drying agent to adsorb water vapour in circulating air to make cooling effect in interior space and solar heat is then used to dry or regenerate the desiccant for re-use (Sathaye and Meyers, 1995). Passive solar design is practiced throughout the world to make buildings with low energy cost and low maintenance cost. No mechanical means are used in this technology; rather, it exploits the thermal energy flow associated with radiation, convection and conduction. Actually, building material can absorb, reflect or transmit solar radiation and air flow is also governed by solar heat; thus living space of the building itself can get heating or cooling effect by itself. Whole success of the technology based upon the choice of building material, placements that can provide heating and cooling effect at home and some

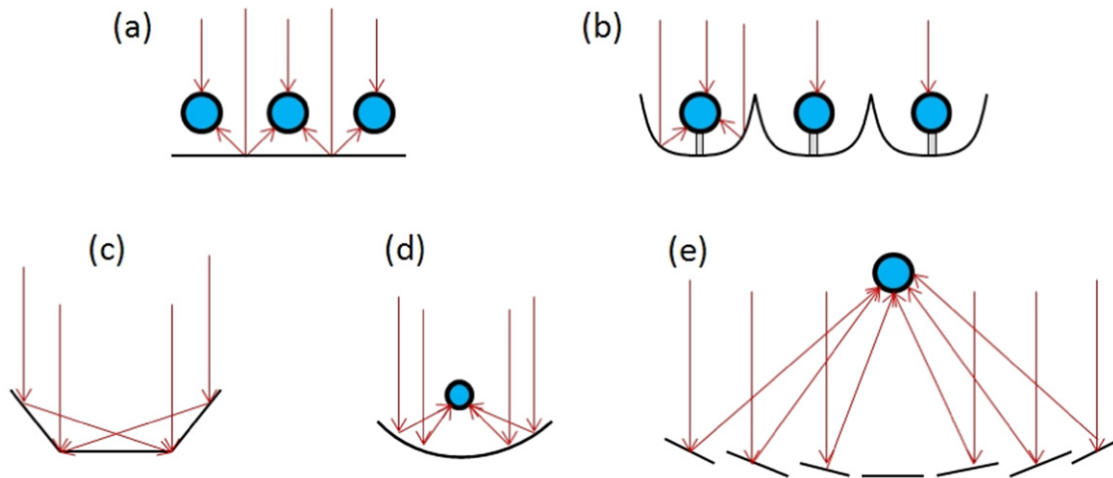


Fig. 7 Types of concentrating sunlight collectors: (a) Tubular absorbers with diffuse back reflector, (b) tubular absorbers with specular cusp reflectors, (c) plane receiver with plain reflectors, (d) parabolic concentrator, (e) array reflectors (heliostats) with central receiver. (Pic: <https://www.e-education.psu.edu/eme81>).

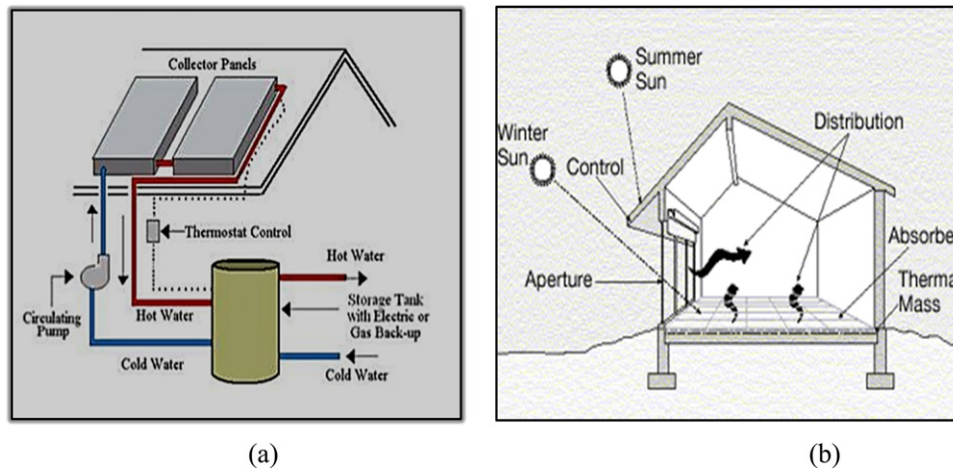


Fig. 8 Solar building technologies (a) Active solar heating; (b) Passive solar heating. (Pic: Wikipedia).

design elements. For passive solar heating, two primary requirements are south facing glass and thermal mass to absorb, store and distribute heat. Passive cooling is done using natural ventilation. Thermal chimneys can create or reinforce the effect hot air rising to induce air movement for cooling purposes.

Therefore, efficiency of active solar design depends on external storage system which captures and store solar energy like heat pumps, radiators. Active solar systems include the following features (Sathaye and Meyers, 1995):

- Flat-plate PV collector panels or modules (many connected panels), usually mounted and stationary are used to collect sunlight.
- The hydronic collectors use liquid and air collectors use air as conductors to store and convert energy.
- Liquid conductors are more common than those that are air-based, as liquid is generally more efficient at conducting heat, though air-based solar systems have the benefit of not freezing characteristics.

In contrast to active solar systems, external devices are not used for passive systems to operate. Generally, south facing glass windows are used to allow sunlight to enter the home and thermal mass like greenhouses, solariums and sunrooms, solar energy captures sunbeams and retain heat. Passive solar systems include following features (Sathaye and Meyers, 1995):

- It usually relies on south-facing windows to convert rays into sunlight.
- Design of passive solar collectors is based on the law of thermodynamics, which suggests that heat transfers from warm to cool surfaces, such as through convection.
- The success of the passive solar system depends on its orientation and the thermal mass of its walls.

Wind Energy

Wind energy actually an indirect form of sun's energy which is always reloaded by sun and formed by differential heating of earth's surface by sun. Around 10 million MW of energy are continuously available from wind energy. Wind energy provides a flexible and environmental friendly option and national energy security at a time when decreasing global reserves of fossil fuels threatens the long-term sustainability of global energy supply. Rotating shaft of wind turbines convert the kinetic energy of the wind to directly mechanical energy (e.g., milling or water pumping) or converted to electric power in a generator. At good windy sites, it is already competitive with that of traditional fossil fuel generation technologies. Like solar energy resource, one of the main challenges with wind power is its intermittence and high inconsistency in availability. But it can be resolved by systematic adjustment in operation cycle and correct strategies to store wind power into grid.

A wind farm actually a set of wind turbines that are linked together to supply electricity to local large population. Wind turbines should be located where there are steady strong winds – though not so strong they would damage the turbines. Ideal sites for wind turbines therefore are (Thresher *et al.*, 2008):

- Away from obstructions such as forests, towers and rocky outcrops. (These would cause the air to swirl around).
- At the highest point possible.

Newer wind turbines are mainly three bladed rotors with diameters of 70–80 m mounted on top 60–80 m towers (Thresher *et al.*, 2008) shown in Fig. 9. The typical turbine installed in United States in 2007 can produce 1.5 MW of electrical power (Thresher *et al.*, 2008). Wind turbines will not work in winds below 13 Km per hour. They work best where the wind speed averages 22 km per hour (Alrikabi, 2014). Though some greenhouse gases and other pollutants are produced during manufacture, transportation and installation of wind turbines but operating wind farm do not emit greenhouse gases or other pollutants. It is less costly than other energy sources and can be installed remote areas too.

Hydroelectric Power and Tidal Power

Hydroelectricity refers to the electricity produced by conversion of energy from flowing water. River or ocean water is used to produce hydropower. It is basically a renewable energy source as (see “Relevant Websites section”) water cycle constantly renewed by the sun. Generation of hydropower is achieved by damming a river or running a pipe (‘Penstock’) from a high water to lower water body (lake, river, sea). The schematic process diagram of hydroelectric power plant is presented in Fig. 10. Water released from the reservoir spins the turbine and using a connected generator, electricity is produced. Pumped storage plants are also operating to supply power during peak hours. Recycled water generally stored into an upper reservoir which in turn used during peak hours. Hydropower technology is now sufficiently developed and widely used. Currently, worldwide around 15% of total electricity demand is fulfilled by hydroelectric power (Sathaye and Meyers, 1995). Though there is limitations of use of hydropower like concern about impact on regional ecosystem near damming area on river, flooding susceptibility in the nearby landscapes; carbon dioxide emission during construction of dam and methane gas emission from lost vegetation of flooded area, but operation of hydropower plants are totally free of GHGs emissions. As per World Energy Council report (2016) (see “Relevant Websites section”) global hydropower installed capacity is 1.21 TW and they reported the list of top hydropower producing countries (refer Fig. 11).

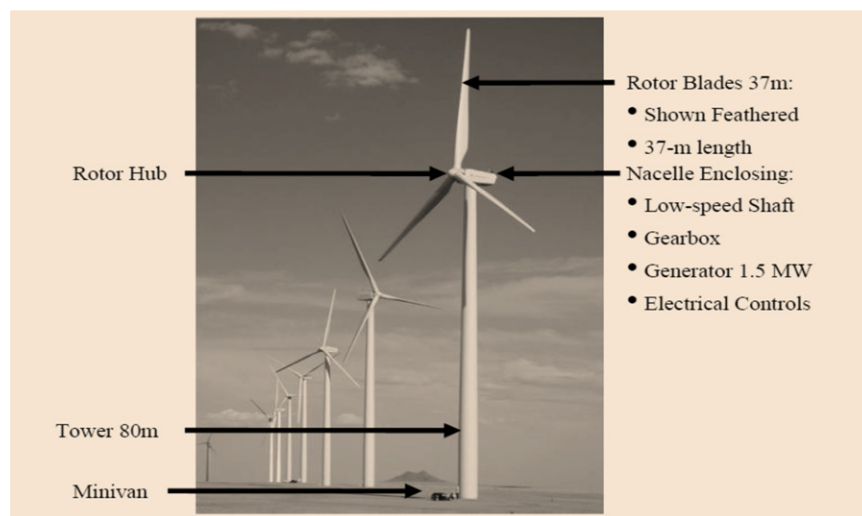


Fig. 9 Close-up view of modern wind turbine in a wind farm. Source: Thresher, R., Robinson, M., Veers, P., 2008. Wind energy technology: Current status and R&D future. In: Proceedings of the Physics of Sustainable Energy Conference, pp. 1–21.

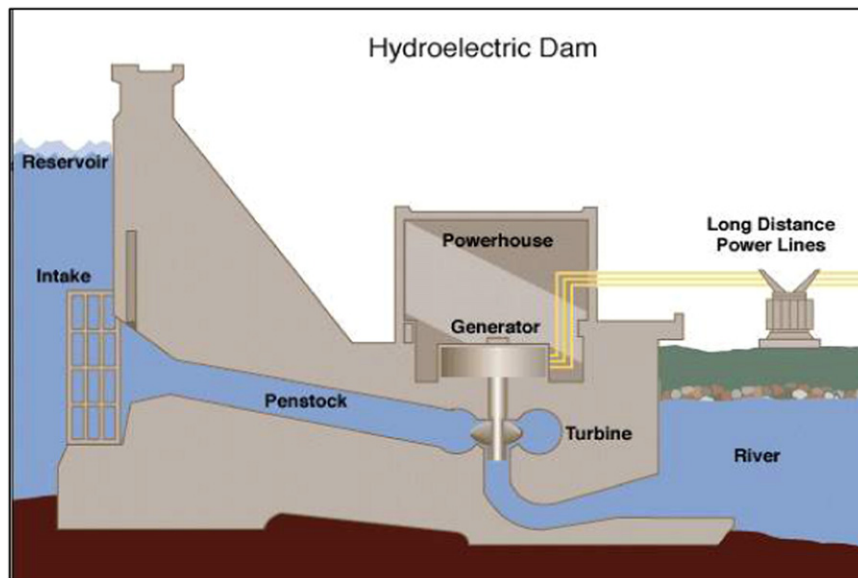


Fig. 10 Schematic of hydroelectric power plant (Pic: Wikipedia).

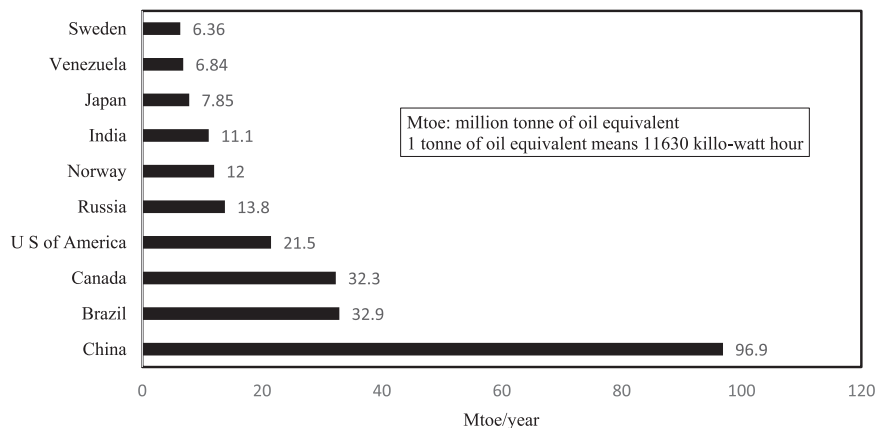


Fig. 11 Top hydropower producing countries. (Source: World Energy Council, <https://www.worldenergy.org/data/resources/resource/hydropower>).

Like hydropower, Tidal power also uses moving water to spin turbine and produce electricity; but the difference lies on the fact that here hydrostatic liquid head is created due to tides which is controlled by natural gravitational pull of sun and moon. As tides are generated by continuous movement of our planet, it can be considered as renewable source of energy. It is the oldest form of energy generation. Just like dam, tidal barrage is formed to utilize the potential energy generated by the change in height of water between high and low tides, which energy turns the turbine to produce electricity. Like wind turbines, turbine stream generator (TSG) are also used to make use of kinetic energy of moving tides. Coastal area and seashore is abundant in the world which is the source of clean, free, renewable and sustainable energy. But, tidal power plants are expensive to install and it cannot act as consistent supply of energy as it is dependent of tapping of tidal energy. France came up with first tidal power plant and followed by only few countries like China, Russia, South Korea, Canada set up plants. It is reported in the assessment of The Ministry of New and Renewable energy of India that Khambhat in Gujrat, Kutch in Gujrat and Gangetic delta of Sundarbans, West Bengal are the high potential (total around 8300 MW) places for setting up tidal power plant but, the existing plant in Gujrat is of very low in capacity.

Geothermal Energy

In traditional power plants, steam is used to rotate turbine to produce electricity and required steam is produced by burning of fossil fuels. But in geothermal energy plant, used steam is produced from hot water available in the reservoirs few miles or more in the earth surface. Actually, geothermal power plant uses heat of deep inside of the earth. Hot water is pumped from deep underground of earth at high pressure or high temperature steam is directly pumped. At the ground, due to huge pressure drop, hot water converts to

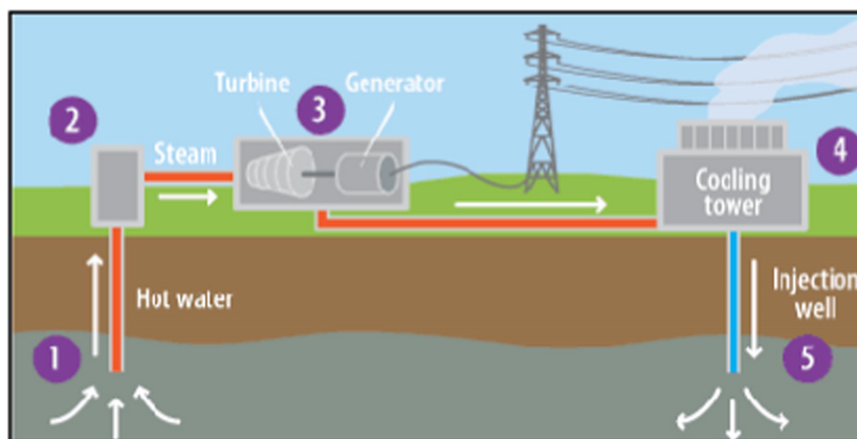


Fig. 12 Schematic diagram of geothermal power plant (Pic: Google image).

steam (or directly produced steam) which in turn spins turbine and produce electricity using connected generator. Then the steams cools off and condenses into a cooling tower and sent back to the ground to complete the cycle (refer Fig. 12).

Geothermal energy, based on high temperature difference between earth core and earth surface, is so called renewable source of energy because the core of the earth will cool after hundreds of millions of years. Unlike other renewable sources of energy, it does not depend on specific weather condition because heat is constantly radiating outward from earth's core to warm up rock, water, gas and other geological material. But, only some portions of earth's interior are accessible by drilling and geothermal gradient is higher than average, act as 'hydrothermal reservoir' (Owusu and Asumadu-Sarkodie, 2016). Basically, three types of geo-thermal power plants are available: dry steam, flash steam and binary cycle (Sathaye and Meyers, 1995). Dry steam power plant produce steam from the reservoir to form electricity, no liquid water will be with steam; requires no steam separator. But, in flash steam plant, hot liquid water is pumped at high pressure and flashed at surface at low pressure; vapour-liquid separator is used to use only steam in the turbine. In binary cycle, slightly cooler water (at around 57°C) is used to heat separate binary fluid that has lower boiling point (Sathaye and Meyers, 1995). Geothermal energy generation units are already installed in California (US), Philippines, Mexico, Japan, Italy, New Zealand and other countries (Sathaye and Meyers, 1995). The world's largest geothermal power station was set up in California, The Geysers with capacity around 750 MW (El Bassam, 2011). Geothermal electric capacity is touched more than 3000 MW in United States. As per report of EAI, India's leading consulting and research firm, Iceland has a big capacity geothermal unit which contribute 25% of total electricity demand and they reported that India has good potential (10,600 MW), but only 100 MW capacity has been utilized yet. Due to limited size and location of reservoirs, recently engineered geothermal system (formally, hot, dry rock geothermal) which are called as 'Enhanced Geothermal Systems (EGS)' (Reck and Hoag, 1997) are in use.

Biomass and Bioenergy

Bio-energy which is in principle derived from biomass includes any kind of energy obtained from plant materials that range from agricultural and forestry waste, food industry waste, sewage, municipal solid waste to dedicated woody energy crops (Sathaye and Meyers, 1995) and as well as from animal waste. Since biomass (refer Fig. 13) is available in abundance in any country, it can be considered as potential alternatives for energy problem. There are various technologies to harness bioenergy from their feedstock based on digestion, combustion or decomposition. Bioenergy is a significant source of energy which can be used for transport fuel using biodiesel, electricity generation, cooking and heating. It is reported that biomass promises for 79.4% of the total renewable energy supply (Boyle, 2004; Foster, 2007) and comprehensive study of World Energy council (Faaij, 2008) indicates that almost 30% of total world energy demand in 2100 will come from bioenergy. With biomass, lot of research work is aiming to produce sustainable and environmentally acceptable source of energy. Bioenergy has the potential to cut CO₂ emission and decrease global warming. Though, sustainability of the bio-fuel sources (refer Fig. 13) is ensured but debate has been raised between *first generation* and *second generation* bio-fuel. Basically, *1st generation* bio-fuels are those which comes from the feedstock directly; like mainly food crops as oil seeds (rapeseed, palm oil), starch crops (cereals, maize) or sugar crops (sugar beet, sugarcane) (see "Relevant Websites section", Naik et al., 2010; Alam et al., 2015). It is mainly characterized by its capability to produce biodiesel, bio-ethanol and biogas which can be blended with petroleum based fuels and combusted in conventional combustion engines (Dellomonaco et al., 2010). But, recently, use of *1st generation* bio-fuel is under some challenges. Food-versus-fuel debate is the first concern about *1st generation* bio-fuel due to rising food prices and competition of land use with food crops when the feedstock is non-food type crops. Not only that, relatively low GHGs abatement, relatively high marginal carbon abatement cost make threat to commercial use of *1st generation* bio-fuel (see "Relevant Websites section"). Therefore, *2nd generation* bio-fuel produced from lignocellulosic feedstock, become more attractive in commercial use. But, in lignocelluloses, sugars are present as complexly bind as chain and type of sugar is also different from that present in sugar crops. Therefore, conventional fermentation using microorganisms is not

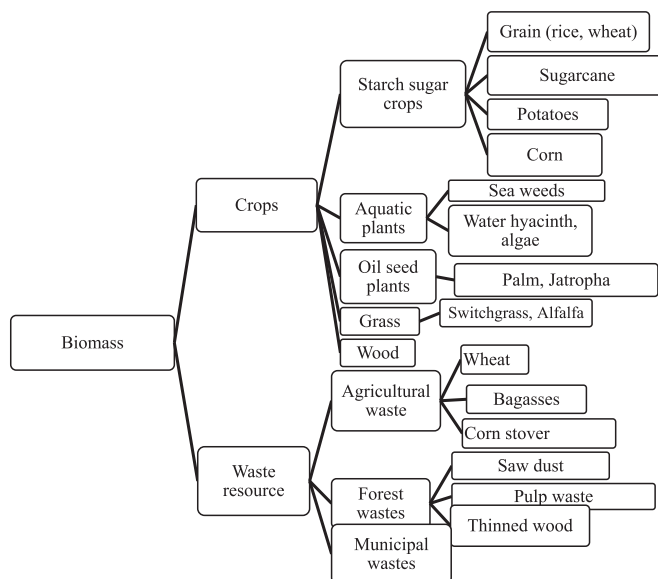


Fig. 13 Source of biomass used as feedstock for bio-refineries. Reproduced from Sikarwar, V.S., Zhao, M., Fennell, S., Shah, N., Anthony, E., 2017. Progress in biofuel production from gasification. *Progress in Energy and Combustion Science* 61, 189–248.

sufficient to produce bio-ethanol and appropriate method of bio-ethanol production should be supported by suitable pretreatment process which helps to remove the unconvertible lignin part. Fermentation process is preceded by advanced pretreatment and enzymatic hydrolysis processes to remove out sugar. Though it is non-competitive with food but advanced technologies are still under development to reduce the cost of conversion. Latest reports suggest that microalgae are recently promoted as 3rd generation bio-fuel (Larson, 2008; Sikarwar *et al.*, 2017). Starting from methane, biodiesel, bio-hydrogen type of renewable bio-fuels can be obtained from microalgae (Larson, 2008). It is reported that it can give 15–300 times more biodiesel than traditional crop on area basis (Larson, 2008). Moreover, it does not require high quality agricultural land to grow and its growth rate is too fast. Therefore, it may be a viable alternative. The various routes for production of bio-fuels are described in Fig. 14.

Conversion processes for 1st generation bio-fuels

Transesterification

Oil seed crops are mainly used to produce bio-oil containing triglyceride which converts to fatty acid methyl esters (FAME) in presence of alcohol and catalyst (homogeneous/heterogeneous) by saponification reaction. This conversion step is based on transesterification. The FAMES of bio-oils are popularly known as biodiesel. Biodiesel can easily replace diesel fuels due to having comparable or rather superior fuel quality (Alam *et al.*, 2015; Sikarwar *et al.*, 2017; Dellomonaco *et al.*, 2010). The Transesterification (alcoholysis) reaction is shown in Fig. 15 where catalyst may be a liquid acid/liquid base or solid catalyst. Basically, homogeneous catalysis using liquid catalyst is preferable with high triglyceride containing oil but heterogeneous catalysis using solid catalyst is performed when oil contains less triglycerides and high free fatty acids. In the both the cases final products are same. Catalysts are regenerated and use of excess alcohol favours the ester formation.

Ethanol conversion process

Ethanol production is obtained by enzymatic hydrolysis of starch containing crops and specifically fermentation process of sugar containing crops and cellulosic biomass too. The alcohol produced from food crops is known as grain alcohol and ethanol produced from lignocellulosic biomass is termed as bio-ethanol (Alam *et al.*, 2015). Grains like wheat, barely, rice, corn etc., are starch containing crops and sugar cane, beet root, fruits etc. are sugar containing crops. In fermentation process, organic substrate undergoes chemical changes in presence of enzymes secreted by micro-organisms which are available in nature.



Though stoichiometrically, ethanol conversion efficiency is 51% on weight basis, but roughly 40%–48% efficiency is available (considering consumption of glucose by microorganism itself), i.e., 583 lit of pure ethanol can be obtained from 1000 kg fermentable sugar (Alam *et al.*, 2015).

Conversion processes for 2nd generation bio-fuels

Thermo-chemical conversion

Pyrolysis, gasification and liquefaction are three important routes of thermo-chemical conversion technologies to synthesize bio-fuels from biomass. All the processes are high temperature and sometimes high pressure process. Biomass is generally heated

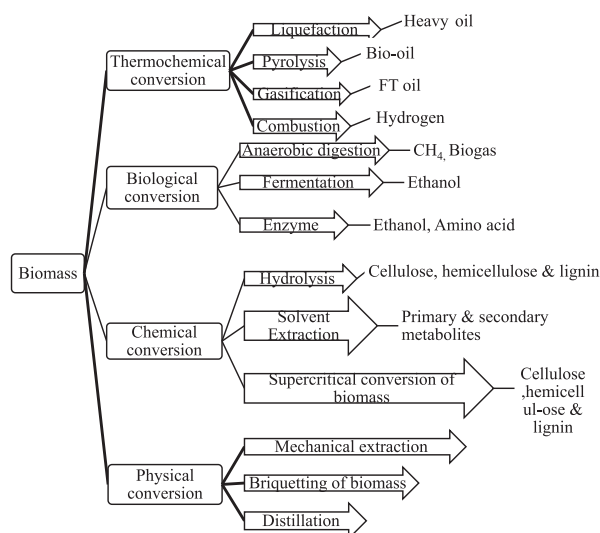


Fig. 14 Existing and possible bio-fuel production routes. Reproduced from Naik, S.N., Goud, V.V., Rout, P., Dalai, A.K., 2010. Production of first and second generation biofuels: A comprehensive review. *Renewable and Sustainable Energy Reviews* 14, 578–594. Sikarwar, V.S., Zhao, M., Fennell, S., Shah, N., Anthony, E., 2017. Progress in biofuel production from gasification. *Progress in Energy and Combustion Science* 61, 189–248.

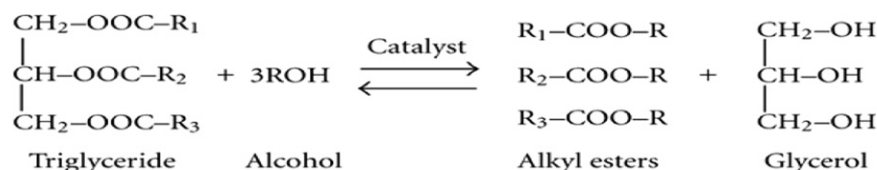


Fig. 15 Transesterification reaction. Source: Wikipedia.

under oxygen deficient condition to reduce oxygen content of biomass and enhance fuel quality. Syngas is a obvious by-product of the processes which can be used as fuel directly or can be processed to produce other products.

Pyrolysis is basically thermal degradation of biomass at high temperature (300–500°C) in absence of oxygen. It results charcoal (solid), bio-oil (liquid) and fuel gaseous products). Significant amount of bio-oil can be produced without pre-treatment of raw material; but produced bio-oil requires extensive treatment prior to use as bio-fuel oil.

Thermo-chemical conversion of lignocellulosic biomass by reacting with synthesis gas at comparatively lower temperature range 250–450°C and high pressure (5–20 bar) gives liquefaction of biomass and results water insoluble bio-oils (Alam *et al.*, 2015; Dellomonaco *et al.*, 2010). Bio-oil produced by liquefaction has lower oxygen content than oil produced by pyrolysis; so it requires less extensive treatment.

Gasification is the oldest technology among them. It is the thermochemical conversion of solid or liquid biomass into a mixture of carbon monoxide, carbon dioxide, methane, hydrogen, nitrogen, tar, water vapour, hydrogen sulfide at very high temperature (1300°C). it involves reaction between biomass with air, oxygen or steam. Producer gas and syn gas are directly used as fuel. Using Fischer-Tropsch synthesis, syn gas can be converted to hydrocarbon fuels.

Conversion processes for 3rd generation bio-fuels

Microalgal biomass can be converted to energy sources by various ways like biochemical conversion, thermo-chemical conversion; chemical reaction and even direct combustion (refer Fig. 16). Oil content of algal biomass is around 30% (Alam *et al.*, 2015) and around 70% algal by-products are formed which are used as raw materials in some other industries. Both biodiesel and bio-ethanol are from algal lipids (and free fatty acids) and algal starch (and proteins) respectively. Lots of challenges remain in commercialization of this bio-fuel conversion route.

Fuel Cell

Fuel cell combines hydrogen and oxygen to form electricity, heat and water. Like batteries, fuel cell produces electricity in cost of chemical reaction. Fuel cell can power tiny microchips to buildings to buses. Fuel can use a variety of fuel like hydrogen, ethanol, methanol, various acids and even various bases but it run best by hydrogen. Unlike batteries, it does not get exhausted, gives continues supply of electricity. In future, it may be a viable alternative fuel.

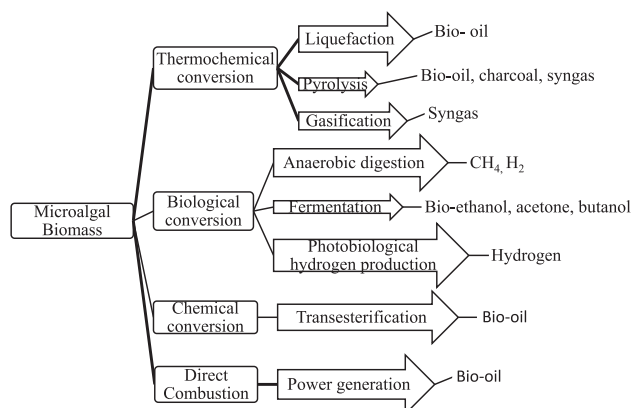


Fig. 16 Bio-fuel production processes from microalgal biomass. Reproduced from Dellomonaco, C., Fava, F., Gonzaliz, R., 2010. The path to next generation biofuels: Successes and challenges in the era of synthetic biology. *Microbial Cell Factories* 9, 3.

Use of residential fuel cell is being popular now-a-days. It is very efficient since it can convert chemical energy to electrical energy directly; without combustion and with clean emission. If hydrogen is used in fuel cell, in presence of reformer, converts fuels to hydrogen and emits water vapour and carbon dioxide. Fuel cells are compatible with other renewable sources of energy. It can be run by chosen fossil fuel and as well renewably generated hydrogen. This particular source of energy is very much flexible and can be easily maintained. But the main limitation of using is high cost of the source.

Conclusion

Within this review, it has been demonstrated that renewable energy resources have adequate potential to support sustainable energy strategies over time that can achieve the GHG reduction and air quality improvement sought by society. Energy is a requirement of everyday life and demand for energy is growing exponentially with progression of technologies, up gradation of lifestyle and augmented attention towards economic growth and productivity. Renewable energy not only improves health and environmental quality rather it gives economic benefits too. Harnessing of renewable energies is basically labor-intensive than fossil fuels; creates job opportunities in utility companies. Basically, renewable energy is the stable and abundant resource for energy need. Though renewable energy sources are acknowledged as alternative fuels to fossil fuels, but use of them is still limited and infrastructure development to use them is still need to cross some barriers like cost, political environment, market condition and awareness. Renewable energy has significant contribution to heat and transport fuel but the progress is slower. Few basic disadvantages of use of renewable energies are identified already. Many forms of renewable energies are not commercially viable like tidal power, geothermal power and some forms of renewable energies are location specific or weather specific like solar power, wind power which needs storage capabilities for constant supply of them. Complete pollution free status can not be attained by use of renewable energies because the technologies and services that are used to build renewable energy resources require burning of fossil fuels. Some forms of renewable energies require enormous space also. Renewable energy policies for transport sector are focused in bio-fuel blending mandates, subsidies or combination of both. Now, a systematic approach for tracking the progress and impact of mitigation actions for GHG inventory system at corporate, city, state, nation and international levels is an important way to ensure effective implementation of the planning for clean and green 'Earth'.

See also: Clean Energy Technologies: Hydrogen Power and Fuel Cells

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Utilizing the Greenhouse Effect as a Source to Produce Renewable Energy

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Introduction

Man's Hunt for Energy

Civilization has always been driven by the energy where as resource handling for energy has transformed over the time. Previously, people and their domestic animals relied on food as a resource for energy. Worldwide, the social order is determined on a novel and sustainable food sources. New processing methods for the preservation of food could also be utilized with increased effectiveness and producing less waste. Individuals relocated across the continents in the light of complex societal demands, but certainly, search for a constant supply of energy was a general feature in those migrations (<http://www.extremetech.com/extreme/124383-bacteria-converts-carbon-dioxide-into-liquid-fuel>). Likewise, there is rather an endless search of mankind for the recovery of energy from the substances that once would have been viewed as nourishment, yet now are exclusively planned to create energy like biofuels (David and Wiegman, 2010). These consequent advancements caused cutting of the trees and contended with once likely just for agricultural practices. By 13th Century, Europeans had acquired the knowledge regarding the Chinese gunpowder; this made a further interest for charcoal once more (Medina-Ramos *et al.*, 2014). The exploitation of gunpowder dictated by the military for chucking of guns has needed a lot more of charcoal (Medina-Ramos *et al.*, 2014). These elements influenced the necessities of time required for charcoal creation, prompting presentation of boundaries in specific nations. By the 18th century, the interest in charcoal that promoting iron business was huge to the point and option was appealing, which was started coke as an alternative fuel (Medina-Ramos *et al.*, 2014). The recorded connection between coke and coal showed how single energy source could lead to numerous collaborating uses along with its constraints and the resultant trade that associates the difficulties in the usage. Aside from searching for new arrangements and growing new techniques for resource creation, energy engineers have a reasonable response to help the approach creators and the overall residents of the upsides and downsides of every means of energy generation (Hu *et al.*, 2018).

Fossil Fuels

In the course of the past, fossil fuels are framed by usual routes, for example, the anaerobic disintegration of buried dead-living beings, for the period of the revelation of high temperature and pressure of earth's scab over the period. Due to soaring carbon proportions, fossil fuel takes account of coal, oil, and natural gas. The carbon to hydrogen (C/H) ratios, composition varies like methane (CH₄), to oils. Non-volatile materials are made out of an unadulterated carbon, for example, anthracite coal (Liu *et al.*, 2015; Nick, 2009). In 2011, petroleum derivative utilization on the planet totaled eighty quadrillion British thermal units (Btu). The US Energy Information Administration (EIA) ball park reported that 80% of the vitality was imitative from non-renewable energy sources, particularly 35.3% arising of oil, 19.6% from coal, and 26.8% from petroleum gas. Nuclear power and sustainable power source represented 8.3% and 9.1%, respectively (Nick, 2009). Fossil fuels also known as non-renewable resources since they seize a long time to form and crude materials being dwindled substantially quicker than new ones. Fuel blazing generates more than 22 billion tons of CO₂ yearly, yet it is evaluated that typical techniques can just splash up about a portion of that quantity. This makes a net rise of 11 billion tons of barometrical CO₂ every year (Dandekar, 2005).

Coal

It is earth's most regarded common resources; it has been a source of heat and energy to the world for many years. Coal is formed due to decomposition of forest and other flora for several years. Coal essentially made up of carbon, while additionally containing components of hydrogen, oxygen, nitrogen, aluminum, silicon, iron, sulphur and calcium (Dandekar, 2005). Coal is the world's main profuse and broadly disseminated fossil fuel that fulfills more than one-fourth of essential energy demand worldwide (http://www.eia.gov/energyexplained/index.cfm?page=natural_gas_home). In the course of the last few decades, coal has out-paced by the use of gas, oil, atomic power, and renewable energy sources. North America, previously the Soviet Union, and the Asia Pacific United recorded more than 80% of set up coal holds. Worldwide coal creation in past decade topped 6.9 billion tons, with China delivering around 46%, the US 16%, and Australia and India measure up to makers at roughly 6%. 60% of coal is obtained using underground mining (<http://www.eia.gov/totalenergy/>). Coal-terminated power plants, presently, are confronting new difficulties inferable from an expanded challenge of petroleum and novel air toxin controls progressed by the EPA (<http://epa.gov/mats>). Regular CO₂ outflows from fuels control foliage are roughly two fold than that from natural gas plants (<http://epa.gov/mats>).

Petroleum

Petroleum, also known as crude-oil, consists of hydrocarbons and few biodegradable compounds in traces. It is obtained from the characteristic arrangements underneath Earth's surface. It is obtained through primitive natural materials, for example, algae and zooplankton. Oil is recouped generally from oil dreary. Due to the fast development of the car business leads to accessibility and contribution of gasoline (Gold, 2012; <http://www.epa.gov/climatechange/ghgemissions/gases.html>). Nowadays, petroleum is obtained in refined form and made its way into a scope of shopper items, including fuel (oil), lamp oil (paraffin), black-top (bitumen), and concoction ingredients required for plastics and pharmaceuticals manufacturing (<http://www.epa.gov/climatechange/ghgemissions/gases.html>). The term petroleum entirely alludes to the raw petroleum that incorporates all fluid, vaporous, and strong hydrocarbons. At typical conditions of temperature and pressure, lighter hydrocarbons including CH₄, ethane, propane, and butane subsisting gaseous state, while pentane (C₅H₁₂) and heavier organic compounds exist in liquids or solid state (Howell, 1979).

Because of the atmospheric conditions at the surface, these gases condense out to form natural-gas condensate. The quantity of lighter hydrocarbons present in petroleum varies from 97% (weight by weight) to merely 46% (Hunter *et al.*, 2005). Among Organization of Petroleum Exporting Countries (OPEC), the Five nations from Middle-East namely Iran, Saudi Arabia, Iraq, United Arab Emirates, and Kuwait, considered to have almost 70% of the aggregate oil holds in 2009, while lone Saudi Arabia claimed to have 26% of total OPEC reservoirs (http://www.eurekalert.org/pub_releases/2013-06/ultgt062013.php). Non-OPEC generation of oils is around 60% of the total global oil supply. China is emerging as the prevalent oil-overriding nation in the globe with a 7% annual growth rate. Worldwide petroleum utilization raised by 0.6 million barrels per day (b/d) in 2012, which is 88 million b/d. OECD utilization in-fact reduced by 1.2% corresponding to drift in recent past while Non-OECD utilization raised by 2.8% (<http://www.worldenergyoutlook.org/media/weo, 2010.pdf>).

Natural Gas

Natural gas originates in profound dissident innate rock pattern development or linked with trace hydrocarbon basins in coal reserves and as CH₄ catharses. As mentioned previously, oil is established in propinquity with natural gases well. Generally, natural gases were produced over a long period by biogenic or thermogenic means. Gas produced by biogenic means is resultant of the methanogenic activity of microbes (microbes that generates methane as a result of their metabolism in an anaerobic environment). Thermogenic gas is formed deep inside the earth at high temperatures and pressure from the dormant organic material (<http://dx.doi.org/10.1787/9789264095243-en>). Natural gas is frequently known as gas particularly in comparison with other available energy sources like coal or oil. A few decades back, natural-gas was acquired as a result of delivering oil. On the other hand, undesirable petroleum gas was parched in the oil field (<http://dx.doi.org/10.1787/9789264095243-en>).

The world's biggest gas reservoirs are situated in Russia having 48 trillion m³ of gas (Irby-Massie and Keyser, 2002). Russia is leading natural gas extractor worldwide. Erstwhile foremost verified resources of the natural gas exist in Iran, Qatar, Saudi Arabia, and the United Arab Emirates. The major gas field in the world is located in Qatar's North offshore. It is having approximately 25 trillion m³ of primed gas (<http://epa.gov/mats>).

Due to the over-exploitation of these resources, non-renewable sources of energy are vanishing rapidly. At the same time, its uncontrolled utilization is resulting in the huge growing concern of 'global warming' and increased 'greenhouse effect.'

Earth's Atmosphere and Greenhouse Gases

Changeability of climate is the greatest arguments and is the biggest apprehension nowadays for the human race. Advancement in studies of climate and meteorological research is well-known. Therefore, it is fitting to momentarily reconsider the writings of particular revolutionary consideration of previous centuries in consideration of the make-up of the atmosphere. In the 1820s, Jean Baptiste Joseph Fourier computed by the mass and distance from the sun; earth must have been significantly colder than in fact it is, considering the impact of inward solar waves (<http://www.whitehouse.gov/share/climate-action-plan>). The study by Jean Baptiste Joseph Fourier may be considered the most primitive scientific input of the greenhouse effect (<http://www.whitehouse.gov/share/climate-action-plan>). Four decades afterward John Tyndall recognized the irradiative nature of water vapor and CO₂ in controlling temperature of the surface (Rajaram, 2012). The study reported that humid air could soak up heat 13 times more than that of dry, purified air (<http://ocean.nationalgeographic.com/ocean/photos/sea-level-rise/>). Arrhenius became the first person to study the effect of doubling atmospheric CO₂ on overall climate and was honored with the Nobel Prize (1903) for Chemistry (<http://pubs.usgs.gov/circ/c1143/html/text.html>; Smith, 1997). Stretching out from earth's surface, the climate ensures life on earth by engrossing bright sun-powered radiation, warming the surface through temperature with-holding (the greenhouse effect), and diminishing temperature limits among day and night through a procedure called diurnal variety. The air comprised of 78.1% nitrogen, 20.9% oxygen, 0.9% argon, 0.04% carbon and little measures of different gases approximately (Rajaram, 2012). These different gases frequently alluded to as trace-gases, additionally contain the GHGs. GHGs can ingest and emanate radiation inside the warm infrared (IR) scope of the electromagnetic range of light (Stevens, 2012). The prime GHGs are water vapor, CO₂, CH₄, N₂O, and tropospheric ozone (Dandekar, 2005). Solar radiation short lived through the atmosphere which warms up the surface of the Earth. A portion of the energy comes back to the climate as long-wave warm radiation, some energy caught by the layer of

gases that encompasses the Earth, and the leftovers go into space. The fixation and a relative blend of these gases in the environment influence atmosphere dependability and changes in composition can result in climate change. Since the commencement of the modern transformation, human reliance on non-renewable energy sources, the release of mechanical synthetic concoctions, the reasoning of backwoods that would make some way or another assimilate CO₂, and their supplanting with animals farming, has changed the nature and amounts of gases in the atmosphere (http://www.chathamhouse.org/sites/default/files/public/Research/Energy,%20Environment%20and%20Development/bp_0812_stevens.pdf).

How Human Activities Produce GHGs

Generally, significant human actions emanate GHGs. Emissions are underway to ascend radically in the past centuries because of the industrial revolution and alteration in land use. Most of the GHG releasing actions are indispensable to the worldwide market and a crucial portion of the present existence.

CO₂ from blazing the fossil fuels is a major cause of GHG emanations from day-to-day activities. The utilization of fossil fuels contributes about 3/4th of CO₂ emanation, 1/5th of the CH₄, along with a noteworthy amount of N₂O (http://www.chathamhouse.org/sites/default/files/public/Research/Energy,%20Environment%20and%20Development/bp_0812_stevens.pdf). It gives rise to nitrogen oxides (NO_x), hydrocarbons (HC), and carbon monoxide (CO), which are not counted as GHG but persuades chemical reactions in an environment which gives rise to other GHGs, such as tropospheric ozone. For the meantime, fuel-related discharges of aerosols are momentarily making-up for the warming effect of GHGs (Rajaram, 2012).

The greater part of the GHG emissions is related to energy utilization resulting from the burning of fossil fuels. Oil, natural gas, and coal convey the majority of the energy used to deliver power, run cars, and power processing plants. If fuel consumed altogether, the main result controlling carbon would be CO₂ (Rajaram, 2012). However, most of the times burning is incomplete resulting in the emission of CO and other hydrocarbons. Nitrogen present in fuel gets combined with the oxygen which generates N₂O and other NO_x whereas, sulphur gets combine with oxygen to generate sulphur oxides (SO_x) (Smith, 1997).

GHG emissions take place through extortion, dispensation, transportation, and distribution of fossil fuels. These emissions can be conscious while flaring the natural gas, discharging mainly CO₂ and CH₄ (http://www.pseg.com/info/media/newsreleases/2011/attachments/njclean_air_council10-12-2011.pdf). Emissions likewise may result from mischance, poor support, and little breaks in well-heads, pipe fittings, and pipelines. CH₄ is taking place physically in coal and discharged when coal is pulverized. Hydrocarbons enter the atmosphere because of oil slicks from tanker boats or little misfortunes amid the routine fuelling of engine vehicles (Stevens, 2012).

The second largest source of CO₂ is deforestation. At the point when jungles were cleared for agricultural or industrial advancement, the vast majority of the carbon in the consumed or decaying trees breaks to the environment. In any case, when new backwoods are planted, the developing trees retain carbon dioxide, expelling it from the atmosphere (Turner and O'Connell, 2001). Late net deforestation has happened mostly in the tropics. There is a lot of logical vulnerability about emanations from deforestation, yet it is assessed that from 600 million to 2.6 billion tons of carbon are discharged all around consistently (http://www.chathamhouse.org/sites/default/files/public/Research/Energy,%20Environment%20and%20Development/bp_0812_stevens.pdf).

Lime production (calcium oxide) in cement manufacturing accounts for 2.5% of CO₂ emissions. CO₂ emissions are pre-dominant through cement manufacturing and principally from the biomass sector as well as sea-shell concealed in pre-historic marine sediments (http://www.pseg.com/info/media/newsreleases/2011/attachments/njclean_air_council10-12-2011.pdf).

Tamed creatures release of CH₄ which is another critical GHG after CO₂. CH₄ is formed from the excreta of the animals. Most domesticated animals related CH₄ emissions are resulting from the bacterial actions which cause fermentation of food in the digestive tracts of animals; while decomposition of animal manure also releases CH₄ (http://www.chathamhouse.org/sites/default/files/public/Research/Energy,%20Environment%20and%20Development/bp_0812_stevens.pdf). Livestock represents around one-fourth of the CH₄ discharges from human exercises, totaling somewhere in the range of 100 million tonnes a year (http://www.pseg.com/info/media/newsreleases/2011/attachments/njclean_air_council10-12-2011.pdf).

Rice cultivation additionally discharges CH₄, wetland or paddy rice cultivating produces approximately one-fifth to one-fourth of worldwide CH₄ outflows from human exercises. Representing more than 90% of all rice creation, wetland rice is developed in fields that are overflowed or flooded for a great part of the rainy season (Dandekar, 2005). Microorganisms in the dirt of the overwhelmed rice paddy break down organic compounds and emit CH₄ (Dandekar, 2005).

Disposal and treatment of waste additionally release GHGs. At the point when waste is disposed of in a landfill, it undergoes decomposition in prevailing anaerobic conditions and emanates CH₄. Except the gas is trapped and utilized as a fuel, the remaining CH₄, in the long run, disappears to the air. This CH₄ sink is more typical in urban communities, where rubbish from numerous homes is conveyed to the landfill than in rural areas where refuse is ordinarily burned or left to decay in the outside (<http://dx.doi.org/10.1787/9789264095243-en>). CH₄ is discharged additionally from the biological treatment of the sewage.

Excessive use of fertilizer results in emissions of No_x. The presence of nitrogen in a lot of fertilizers augments the bacterial action resulted in the nitrification and denitrification in the soil (http://www.eurekalert.org/pub_releases/2013-06/ultgt062013.php). The amount of N₂O emanated based on the nitrogen content of fertilizer and soil circumstances.

Chlorofluorocarbons (CFCs) are generally released from the industrial processes. Shaped in the 1920s, CFCs have been discharged in extensive amounts since 1950 (<https://www.epa.gov/nscep>). They have been utilized as charges in vaporized jars, in the fabricated of plastic froths for pads and different items. These are also used in the cooling curls of fridges and temperature control systems, as flame quenching materials, and also as solvents for cleaning. Most of the CFCs are used as a result of the

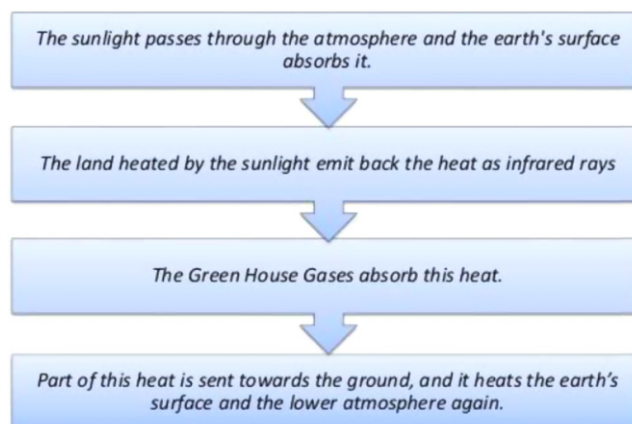


Fig. 1 The greenhouse effect.

Montreal Protocol on materials that reduce the Ozone Layer, barometrical centralizations of, e.g., CFC-11 have almost balanced out and are relied upon to decay over the coming decades. A few compounds being presented as CFC substitutes, for example, HCFCs, cause less harm to the ozone layer however these are yet powerful as GHGs (<https://www.epa.gov/nscep>).

Human activity has incredibly expanded the measure of GHG discharges in the environment. Rather than the worldwide impacts of ozone-depleting substances, the effect of anthropogenic pressurized canned products is limited principally toward the northern hemisphere, where the greater part of the world's modern action occurs. The example of increments in anthropogenic vaporized after some time is likewise fairly not the same as that of ozone-depleting substances. Amid the center of the twentieth century, there was a considerable increment in vaporized emanations. This seems to have been at any rate incompletely in charge of discontinuance of surface warming that occurred in the northern hemisphere during the 1940s to 1970s. Since that time, aerosols emanations have leveled off because antipollution measures were embraced in the industrialized nations since the 1960s. Vaporized discharges may ascend later on, nonetheless, because of the quick rise of coal-let go electric power age in China and India (<https://www.epa.gov/nscep>).

Greenhouse Effect

The greenhouse effect is a characteristic procedure that warms the Earth's surface. At the point when the Sun's energy reaches the earth's environment, some of it is replicated into space, and the rest gets absorbed by GHGs. The greenhouse effect in the atmosphere of the earth is depicted in [Fig. 1](#).

Most prominent GHGs can be listed as water vapor, CO₂, CH₄, N₂O, ozone (O₃) and some artificial chemicals such as CFCs. The engrossed energy heats the surface of the Earth. This course of warming upholds the Earth's temperature at around 33°C, favorable consent conditions for life on earth ([Smith, 1997](#)).

The Greenhouse Effect

The normal surface temperature of the planet is kept up by equalization of different types of sunlight based and earthbound radiation. Solar radiation is frequently called shortwave radiation because the frequencies of the radiation are moderately high and the wavelengths generally short – near the noticeable bit of the electromagnetic spectrum. Earthbound radiation, then again, is regularly called long-wave radiation because the frequencies are generally low and the wavelengths moderately long somewhere in the infrared piece of the range. Downward moving solar energy is typically measured in watts per square meter. The energy of the total incoming solar radiation is commonly estimated in watts per square meter. Modifying for the way that just a single portion of the planet's surface gets solar radiations, the normal surface insulation is 342 watts per square meter every year (http://www.pseg.com/info/media/newsreleases/2011/attachments/njclean_air_council10-12-2011.pdf).

The measure of sun-powered radiation consumed by the earth's surface is just a little part of the aggregate solar radiation entering the air. For every 100 units of approaching sun-based radiation, around 30 units are reflected back to space by cloud or intelligent areas of earth's surface (http://www.pseg.com/info/media/newsreleases/2011/attachments/njclean_air_council10-12-2011.pdf). This intelligent limit is alluded to as earth's planetary albino, and it requires not to stay settled after some time, due to the spatial degree and appropriation of intelligent arrangements, for example, mists and ice cover can change. The 70 units of sun based radiation that is not reflected might be consumed by the climate, mists, or the surface (<https://www.epa.gov/nscep>). Without further intricacies, to keep up thermodynamic harmony, earth's surface and air must emanate these equivalent 70 units back to space (<http://www.aip.org/history/climate/co2.htm>). Earth's surface temperature is joined with the scale of the emissions of outgoing radiation as reported by Stefan-Boltzmann law ([Turner and O'Connell, 2001](#)).

Earth's energy spending plan is additionally convoluted by the nursery impact. Follow gases with certain synthetic properties—the claimed GHGs, for the most part, CO_2 , CH_4 , and N_2O absorb a portion of the infrared radiation delivered by earth's surface. On account of this retention, some part of the initial 70 units does not specifically run away to space (http://www.pseg.com/info/media/newsreleases/2011/attachments/njclean_air_council10-12-2011.pdf). Since GHGs transmit a similar measure of radiation they retain and in light of the fact that this radiation is produced similarly every which way (that is, as much descending as upward), the net impact of ingestion by GHGs is to expand the aggregate sum of radiation discharged descending toward Earth's surface and lower climate (<http://www.aip.org/history/climate/co2.htm>). To look after balance, earth's surface and lower air must transmit more radiation than the initial 70 units. Subsequently, the surface temperature must be higher. This procedure isn't exactly the equivalent as that which oversees a genuine nursery, yet the end impact is comparable (<https://www.epa.gov/nscep>). The nearness of GHGs in the climate prompts warming of the surface and lowers some portion of the environment concerning what might be normal without GHGs.

It is basic to recognize the characteristic, or foundation, nursery impact from the improved nursery impact related to human movement. The common nursery impact is related to surface warming properties of regular constituents of the earth's environment, particularly water vapor, CO_2 , and CH_4 . The presence of this impact is acknowledged by all the researchers. For sure, in its nonattendance, earth's normal temperature would be colder than today, and earth would be a solidified planet.

In light of the article, evidence of the warmth of the earth's facade and beneath may be tailored in the following ways:

1. By a net increment in the sun oriented radiation entering at the highest point of earth's environment,
2. By an adjustment in the part of the radiation achieving the surface, and
3. By an adjustment in the grouping of greenhouse gases in the air.

For situation, the progressions can be thought of in regards to radioactive constraining. As defined by the IPCC (<https://www.epa.gov/nscep>), Irradiative compelling is a proportion of the impact of a given climatic factor on the measure of descending corresponding radiant energy impinging upon earth's surface. Climatic variables are isolated between those caused basically by human society and those caused by characteristic powers; at that point, for each factor, supposed constraining qualities are computed for the period among 1750 and the present day positive driving applied by climatic variables that add to the warming of earth's surface, while negative forcing applied by elements that cool earth's surface (<https://www.epa.gov/nscep>).

The Influences of Human Activity on Climate

Anthropogenic activities have a significant impact on the global temperatures by altering the radiative equilibrium leading the Earth on a variety of timescales and at shifting spatial scales. The anthropogenic activities are eminent in the increasing concentration. These activities influence climate change by altering the aerosols release and O_3 and thereby transforming the land cover pattern.

GHGs heat the surface of the earth by increasing the retention of long-wave radiations. The connection between air grouping of ozone-depleting substances and the related positive radiative driving of the surface is diverse for every gas. A confused relationship exists between the compound properties of every GHG and the relative measure of long-wave radiation that each can retain (<https://www.epa.gov/nscep>).

Water vapor is the most potent of the GHG in Earth's atmosphere, but its behavior is in a general sense not the same as that of the other GHGs. The essential role of water vapor isn't as an immediate specialist of radiative driving yet rather as atmosphere feedback that seems to be, as a reaction inside the atmosphere framework that impacts the framework's proceeded with activity. This distinction emerges from the way that the measure of water vapor in the environment can't when all is said in done, be specifically changed by human conduct, however, is rather set via air temperatures: the hotter the surface, the more prominent the dissipation rate of water from the surface. Accordingly, expanded dissipation prompts a more noteworthy centralization of water vapor in the lower climate equipped for engrossing long wave radiation and emanating it descending (<http://www.epa.gov/climatechange/EPAactivities.html>).

Some of the marine processes additionally go about as carbon sinks. One such process, called the solubility pump, involves the drop of surface seawater containing broke up CO_2 . Another procedure, the biological-pump consists of the take-up of broke up CO_2 by marine vegetation and phytoplankton (little free-skimming photosynthetic living beings) living in the upper sea or by other marine living beings that utilization CO_2 to assemble skeletons and different structures made of calcium carbonate (CaCO_3) (Smith, 1997). As these creatures' lapse and tumble to the sea depths, the carbon they contain is transported descending and, in the end, covered at profundity. A long haul balance between these regular sources and sinks prompts the foundation, or characteristic, level of CO_2 in the environment (Rajaram, 2012).

Conversely, human exercises increment air CO_2 levels basically through the consumption of fossil fuel principally oil and coal and optionally gaseous petrol, for use in transportation, warming, and the age of electrical power and through the creation of bond (<https://www.epa.gov/nscep>). Other anthropogenic sources incorporate the consuming of backwoods and the clearing of land. Anthropogenic discharges at present record for the yearly arrival of around 7 billion tons of carbon into the air. Anthropogenic emanations are equivalent to around 3% of the aggregate outflows of CO_2 by characteristic sources, and this increased carbon stack from human exercises far surpasses the counterbalancing limit of regular sinks (http://www.pseg.com/info/media/newsreleases/2011/attachments/njclean_air_council10-12-2011.pdf).

CO₂ subsequently aggregated in the air at a normal rate of 1.4 sections for every million by volume (ppmv) every year somewhere in the range of 1959 and 2006, and somewhere in the range 2007 and 2017, the rate of CO₂ gathering expanded to around 2.25 ppmv every year (<http://www.eia.gov/totalenergy/>). Considering the entire dataset, the development in air carbon focuses has been genuinely straight. However, this could change. A certain flow sinks, for example, the seas, could move toward becoming sources later on. This may prompt a circumstance in which the centralization of environmental CO₂ works at an exponential rate (Rajaram, 2012).

The regular foundation level of CO₂ fluctuates on timescales of a great many year's given moderate changes in out-gassing through volcanic action. For instance, about 100 million years back, amid the Cretaceous Period (145 million to 66 million years prior), CO₂ fixations seem to have been a few times higher than they are today (maybe near 2000 ppm) (<http://epa.gov/mats>). In recent years, CO₂ fixations have fluctuated over a far littler range (between around 180 and 300 ppm) in a relationship with a similar Earth orbital impacts connected to the traveling every which way of the Pleistocene ice ages (see underneath Natural effects on atmosphere) (http://www.pseg.com/info/media/newsreleases/2011/attachments/njclean_air_council10-12-2011.pdf). In 2017 CO₂ levels achieved 403 ppm, or, in other words, percent over the characteristic foundation level of about 280 ppm that existed toward the start of the industrial revolution (http://www.pseg.com/info/media/newsreleases/2011/attachments/njclean_air_council10-12-2011.pdf). According to ice core measurements, this level (403 ppm) is believed to be the highest in at least 800,000 years and, according to other lines of evidence, may be the highest in at least 5 million years (Turner and O'Connell, 2001).

Methane

CH₄ is another largely significant GHG. CH₄ is more intense than CO₂ because the radiative compelling delivered per particle is greater. In any case, CH₄ subsists in lower fixations as compared to CO₂ and focuses by volume and large estimated in ppb as opposed to ppm (<http://dx.doi.org/10.1787/9789264095243-en>). CH₄ additionally has an impressively shorter habitation time as compared to CO₂ yet having 23 times more global warming potential than CO₂ (<http://www.epa.gov/climatechange/ghgemissions/gases.html>).

Common sources of CH₄ include tropical wetlands, anaerobic microorganisms that nourishes on natural material. These microbes releases CH₄ as a natural residue, and CH₄ leaks from the mainland racks of the seas and polar permafrost. The essential regular sink for methane is simply the climate, as CH₄ responds promptly with the hydroxyl radical (OH) inside the troposphere to frame CO₂ and water vapor (<http://www.epa.gov/climatechange/ghgemissions/gases.html>). At the point when CH₄ achieves the stratosphere, it is devastated. Bacteria present in soil can also be brought the CH₄ oxidation. The overall methane cycle is shown in Fig. 2.

Alongside CO₂, human action is expanding the CH₄ fixation quicker than it may be balanced by regular sinks. Anthropogenic sources as of now represent around 70% of yearly discharges, prompting generous increments in fixation after some time (<https://www.epa.gov/nscap>). The major anthropogenic wellsprings of environmental CH₄ are development in rice cultivation, domesticated animals cultivating, the consuming of coal and gaseous petrol, the burning of biomass, and the disintegration of a natural issue in landfills (http://www.pseg.com/info/media/newsreleases/2011/attachments/njclean_air_council10-12-2011.pdf). Future patterns are especially hard to anticipate. This is to some extent because of an uneven knowledge of the atmosphere inputs related with CH₄ outflows. Likewise, it is hard to anticipate how human populaces develop, conceivable changes in domesticated animals rising, advancement in rice cultivation, and vitality usage will impact CH₄ emanations (<http://www.aip.org/history/climate/co2.htm>).

The Environmental Challenge

CH₄ and CO₂ are discharged both from landfills, and agricultural sectors which ultimately results in climate change. Sustainable ways for its safe and ecologically stable transfer is a noteworthy test for large-scale agricultural practices. Utilizing petroleum derivatives for vitality adds to a dangerous atmospheric deviation, and vitality needs are developing in numerous nations. Catching waste gases and changing over them to vitality can relieve environmental change by bringing down the utilization of petroleum derivatives, in the meantime diminishing the arrival of hurtful gases. As indicated by the United Nations Environment Program (UNEP, 2011), with the end goal to guarantee the normal worldwide temperature does not ascend by more than 2°C by 2020, the level of essential vitality that is created from non-petroleum derivative vitality sources, for example, biogas, should increment by as much as 28% by 2020 (Dandekar, 2005).

Mitigation of Greenhouse Gasses

The awareness of GHG and their potential harm have been known for along time. In the nineteenth century, researchers understood that gases in the environment cause greenhouse effect which influences the temperature of the planet. The researchers were interested mostly in the probability that a lower level of CO₂ gas might explain the ice times of the disconnected past. When the new century rolled over, Svante Arrhenius figured out that emanations from human industry might sometime bring a global warming. He found that the gas assumes an essential job in environmental change with the goal that the rising level could gravely influence our future (http://www.pseg.com/info/media/newsreleases/2011/attachments/njclean_air_council10-12-2011.pdf).

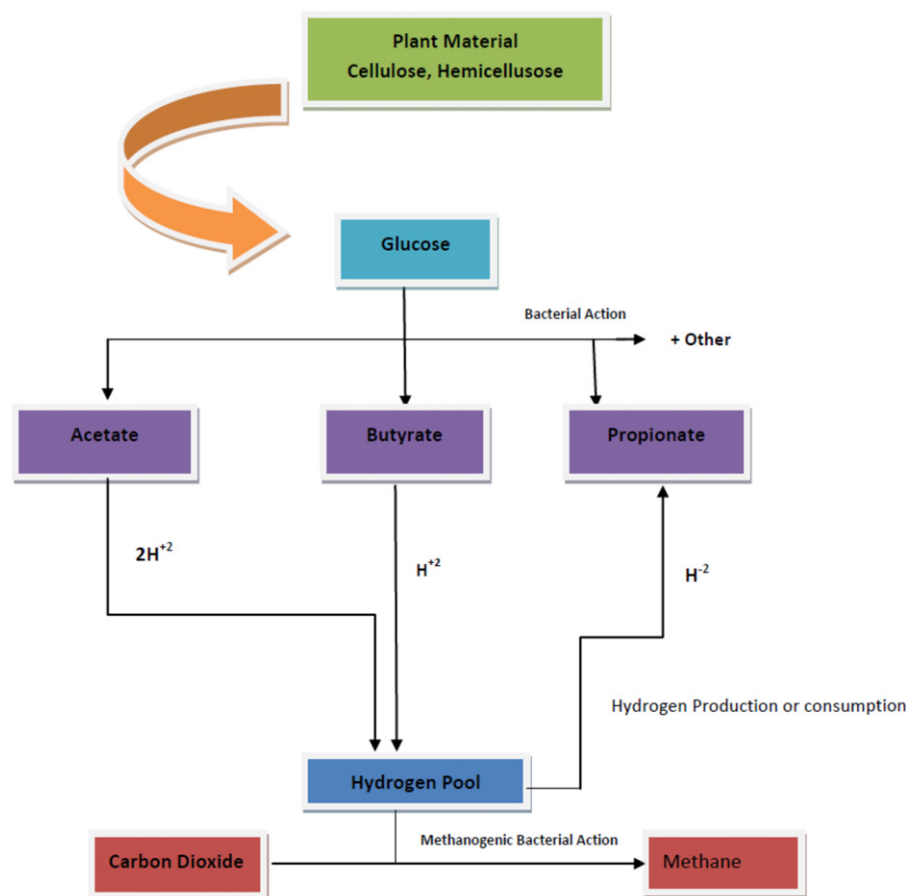


Fig. 2 Flow chart: methane cycle.

China is currently the leading culprit of producing excessive CO_2 . Before China; the United States had been the most significant contributor to the problem; hence the United States government has taken strides to tackle this issue. For example, on June 25, 2013, President Obama announced a plan to continue to reduce carbon emissions and to expedite resolutions for GHGs. The United States has made efforts through the EPA ([Environmental Protection Agency, 2013](http://www.epa.gov/climatechange/ghgemissions/gases.html)) to address the problem; these include collection emissions data, getting reductions, evaluating policy options, costs, and benefits, advancing the science, partner in an internationally, partnering with states, localities, and tribes, and helping communities adapt (<http://www.epa.gov/climatechange/ghgemissions/gases.html>).

It is encouraging to see that steps are being taken to mitigate greenhouse gasses both nationally and internationally and to try to reduce the harmful consequences that already exist. Unfortunately, the beneficial progress continues to meet resistance. A factor that usually causes such delays is the motivation to persuade people to participate. Therefore, it is proposed to mitigate GHGs by converting the GHGs into energy (http://pubs.usgs.gov/circ/c_1143/html/text.html). Energy is an easy conversion into money, and economic gain is a great motivator. By converting GHGs into energy, we can remove the existing excess GHGs and capture the newly-produced gasses, and in turn profit from the mitigation of these gasses. The profit generated would hopefully be an incentive to motivate action.

Utilizing Greenhouse Effect as a Source of Energy

While the human race will always leave its carbon footprint on the Earth, it must continue to find ways to lessen the impact of its fossil fuel consumption. There has been growing interest over recent years regarding the carbon capture and utilization (CCU) in GHE mitigation (<http://www.worldenergyoutlook.org/media/weo2010.pdf>). Despite its potential, their significant uncertainties persist with regards to CCU's ability to achieve real and measurable emissions reductions within carbon reduction support schemes (<http://www.worldenergyoutlook.org/media/weo2010.pdf>).

Carbon capture advances: one approach is to catch CO_2 synthetically before its discharge into the environment. Research conducted in Cornell University uncovers new approach for capturing GHGs transforming it into a valuable item along with the electrical supply. Nowadays the majority of CCU models utilizes liquids (as fluids), followed by vaporization or depressurization to discharge CO_2 (Howell, 1979). The resolute gas can be packed for transportation, and various ventures can reuse it readily, or subjected to underground sequestration. The discoveries in investigation speak to a conceivable change in perspective (**Fig. 3**).

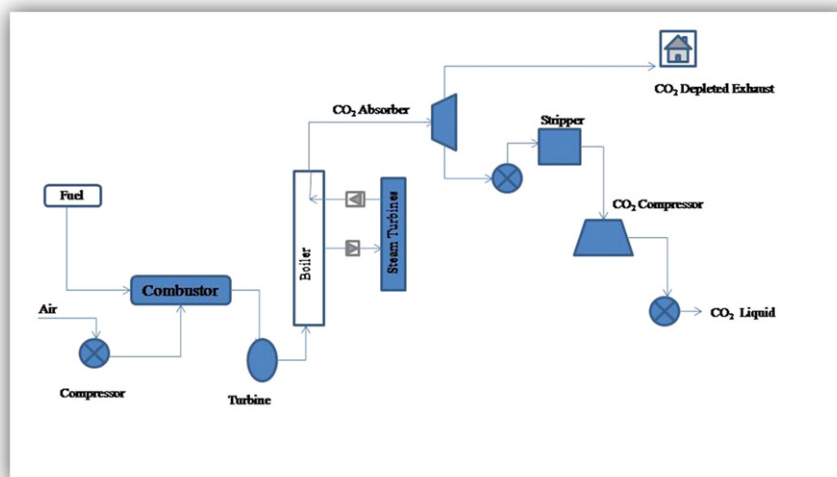


Fig. 3 Utilizing GHGs as energy.

A novel way of generating fuels like gasoline, jet fuel, and diesel from CO₂ can be attained by the new catalyst. Adaptation of such technology for conversion of CO₂ into fuel at large scale can solve the predicted energy crisis shortly. This novel technology can also be worked on the existing facilities of energy storage and transportation without any net GHG emissions to the environment (<http://www.aip.org/history/climate/co2.htm>).

The innovative approach like using porous silver electrode which can be able to transform CO₂ and water into CO and hydrogen is also being practiced. Transforming CO₂ into CO itself is the biggest achievement in the utilization of GHG for producing energy and other value-added products (<http://www.epa.gov/climatechange/EPAactivities.html>). Presently, CO and Hydrogen mixture is used widely as a source of energy. The major issue of CO₂ transformation is its selective conversion to yield and hydrogen in the required amount which can act as a precursor for further chemical processing. The unique system hence developed will provide the selective and specific pathway for CO₂ to CO conversion. Desired CO proportion can be obtained in the system through the modifications in the meso structure of the porous material (<http://www.epa.gov/climatechange/EPAactivities.html>).

A Cell Full of Water, Air, and CO₂

An innovative fuel cell utilizing air water and CO₂ (composite air) is proving to be the best energy source using GHGs. The advancement was attained with modification in fuel cells and adaptation of a capacitive electrochemical cell. A battery like an assembly of this cell is provided with two porous electrodes: anode which attracts H⁺ ions, and a cathode that attracts the bicarbonate ions. The inflow in the cell was maintained by bubbling CO₂ in the water (<http://www.epa.gov/climatechange/EPAactivities.html>). Initially, this CO₂-packed water is pumped through the cell which results into the increased flow of each ion from the water towards cathode and anode – the ion-flow results into the charge separation that creates the potential to drive an electrical current. In a later stage where maximum ions are absorbed by the electrodes, air is bubbled into the water that leads to the backflow of ions from electrodes to the cell. Due to the continuous alternation of these processes the cell can provide continuous electrical supply (<http://www.aip.org/history/climate/co2.htm>).

Making the Mix

This concept is evolved from the released energy of fluids (e.g., with different densities) when mixed in an appropriate ratio. This fundamental material science idea holds for the two gases and fluids, however, till date; no innovation existed for adequately harvesting the energy released from mixing of fluids like (Hydrogen & CO) (<http://epa.gov/mats>). It can help in developing the relatively simple and cost-effective technology which could present an energy source with an aggregate yearly (worldwide) limit of 1570 TWh (terawatt hours) potential (<http://epa.gov/mats>).

When Researchers and policymakers are in search of the permanent solution to reduce this GHG and its adverse impacts, the shift in the trends of global research to figure out a way to use GHG for generating renewable energy and it seems the study can provide a sustainable solution to the alarming issue of GHG emissions and greenhouse effect (<http://epa.gov/mats>).

Methane Capture and Utilization

Landfills and tropical wetlands are reportedly the significant sources of CH₄ emissions. CH₄ is a major GHG found in the environment. CH₄ can be used as fuel because of CH₄ capture and utilization to produce electricity, heat buildings, or power garbage trucks. Landfills are the major source of CH₄. Confining CH₄ prior to the release into the atmosphere can be the key to

reduce the effects of CH₄ on climate change (<http://www.aip.org/history/climate/co2.htm>). CH₄ capture from ranch digesters that are large cisterns that restraint with household waste (biodegradable) along with cattle. Thousands of landfill-to-energy projects are presently functional across the globe, and many more landfills can also be considered to harvest methane and convert it into a suitable form of energy. If the total energy balance is taken into account, overall methane being produced from the landfills will generate electricity which concurs the need of 688,000 households per day (<http://www.aip.org/history/climate/co2.htm>).

These technologies cannot be termed as 'renewable energy technology' at least in the very long-term, but these technologies are perhaps cleaner, and certainly adaptation of these novel cleaner technologies will definitely play a vital role in GHE reduction targets in coming years.

Conclusions and Perspectives

By providing a succinct source of information about GHGs, and the resulting harmful effects caused along with the significance of their mitigation will produce the motivation to decrease these gasses by transforming them into a beneficial energy source.

Detailed cost-benefit analysis and economic profile of the various ways to alleviate the greenhouse effect needs to systematically and succinctly comply, so that a logical way for implementation of the processes can be chalked out. The combination of this initial information and financially-focused study will hopefully motivate the performance of GHG generated energy. The performance of greenhouse generated energy will develop the job prospects in a newly invented commercial market, which will be ecological and economically advantageous. At the same time, these energy companies will be extenuating the existing greenhouse effect and avert any dangerous auxiliary consequences. It is a win-win situation for the earth and mankind.

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Wind Farm Repowering Using WAsP Software – An Approach for Reducing CO₂ Emissions in the Environment

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Glossary

Micro-siting Process of choosing the type of wind turbine and its exact position

Plant load factor Output of a power plant compared to the maximum output it could produce

Re-powering Process of replacing older power stations with newer, more efficient ones

Wind power density A quantitative measure of wind energy available at any location

Introduction

Energy is an enabling medium for economic development, technological advancement and a necessary factor for production. The need for energy and its related services to satisfy human social and economic development, welfare and health is increasing. But there are many regions in the world with a limited accessibility to grid based electricity due to economic, geographic and other factors making conventional grid unviable. Turning to renewable energy sources is an excellent approach which needs to be sustainable in order to meet energy demand of future generations. Since they are obtained naturally from ongoing flows of energy in our surroundings, they are considered clean sources of energy. Optimal use of these resources decreases environmental impacts, produces minimum secondary waste and provides non-harmful delivery of environmental goods and services. Also these resources are limitless and thus sustainable based on the current and future economic and social needs.

Considering that the major component of greenhouse gases is carbon dioxide, there is global concern to reduce carbon emissions. In this regard, different policies could be applied to reduce carbon emissions, such as enhancing renewable energy deployment and encouraging technological innovations. Renewable energy technologies provide an exceptional opportunity for mitigation of greenhouse gas emission (like CO₂) and reducing global warming through substituting conventional energy sources (fossil fuel based).

Greenhouse gases (GHGs) concentrations in the earth's atmosphere need to be limited to mitigate significant changes to natural systems which in turn could effect resource use, production & economic activities. Identifying & then reducing the sources of emission relies on proper assessment, monitoring and verification of GHG emissions and removals of which carbon footprint is an important element. A carbon footprint relates to the amount of GHGs produced through burning fossil fuels for electricity, heating and transportation etc. It calculates the volume of the produced greenhouse gases in CO₂ equivalents for any particular activity; which is used to compare the greenhouse gas emissions between companies, institutions and other bodies. Then appropriate reduction measures can be considered and introduced like the use of green energy sources, reduction of fossil fuel consumption, appropriate waste management and recycling to save material cost and energy.

Among the green energy sources, wind energy has great potential to reduce GHG emissions resulting from energy services. Also, wind energy has a comparatively small environmental footprint when relative impacts of various energy supply technologies are measured. Repowering in wind energy has significant potential in this regard and contributes to a more secure energy supply. Along with reduced GHG emissions, it provides additional environmental benefits depending on the advanced technology, management and site characteristics of the proposed wind farm for repowering project. Though average wind speeds in different locations vary considerably, enough technical potential is there in most parts of the world for significant use of wind energy. Repowering further reduces the cost and improves wind energy's footprint reduction potential. Wind energy has taken a commanding lead among other renewable energy sources. Wind exists everywhere in the world, in some places with considerable energy density which can be harnessed by means of kinetic energy from moving air. The primary application is to produce electricity from large turbines located onshore (land) or offshore (in sea or fresh water). Production of electricity using wind energy saves a considerable amount of CO₂ emission which may be discharged in the environment if the same power is generated using conventional sources of energy.

Recent developments in technology open new pathways to creating more power. Re-powering is one of the methods to increase the total available power of existing wind farms. It means replacement of installed old wind turbines of lower capacity by modern turbines of higher capacity normally in lesser numbers. It also refers to replace first generation turbines installed for more than twenty years back. It has generally been accomplished by installing fewer, larger capacity turbines. The modern commercial grid connected wind turbines are multi-megawatt machines equipped with advanced operation and control systems. As per a study carried out at Riso Laboratory, Denmark, the process of re-powering will double the capacity and triple the energy yield with half the infrastructure. Another report of Leonardo Energy outlines the repowering program for following factors (Verma *et al.*, 2015):



Fig. 1 Wind farm at Jamgodrani Hills, Madhya Pradesh, India.

- Without adding more land to the wind farm its capacity can be multiplied which gives more annual energy production from the same site and land area.
- Reduction in cost of per unit generation due to higher efficiency of individual turbines.
- Better grid integration due to improved power electronics.
- Appearance of the landscape is improved due to fewer wind turbines than earlier. The hub height is also increased after repowering.
- Better prediction of wind characteristics and annual energy generation of an existing site.
- Visual appearance is better as modern wind turbines rotate with lower rotational speeds. (Figs. 1 and 2).

Indian Scenario

According to Indian Wind Energy Institute the gross wind power capacity in the country is estimated to be about 49 GW at 50 m elevation and 102 GW at 80 m elevation with the assumption of 2% land availability. The installed capacity of wind power is more than 32 GW up to February 2018 (Central Electricity Authority Report-2018). It contributes more than 50% of total renewable energy capacity of the country. More than 90% of wind power potential is concentrated in southern and western states like Tamilnadu, Karnataka, Andhra Pradesh, Maharashtra, Gujarat and Rajasthan. Wind energy development in India started in early 1990s and the wind farms were developed in the areas where the wind regime is often very good. Therefore, the old or first generation wind turbines occupy the best windy locations. These turbines are also of lower hub height (about 30–40 m), lower capacity and lower efficiency and fitted with old technology in terms of generator, control mechanisms, power quality etc. These sites with the best wind can be utilized more efficiently by replacing old turbines by modern machines of hub height of more than 80 m. New locations for wind farms are becoming scarcely available due to non-availability of useful land, environmental protection, green belt requirements and sometimes resistance from the local populace. Re-powering can contribute to achieve national target of achieving installed capacity of 100 GW by year 2022 under National Mission for Wind Energy of Ministry of New and Renewable Energy, Government of India. It also contributes to reducing the level of CO₂ emission. In India about 25% of the old installed turbines have rating below 500 kW of the total installed capacity to date which is in the order of 22,000 MW. Most of these turbines are hardly in efficient working conditions. It offers a great opportunity and huge technical and economical challenge to replace roughly 5500 MW capacity of old turbines. Re-powering priority is to be given for wind farms with a plant load factor (PLF) less than 12% (Ahmed, 2015; Sharma *et al.*, 2012).

Issues and Challenges

Wind turbines are generally designed for a service life of 20–25 years. After replacement due to re-powering, the old turbines are usually not installed on the same site. These can be sold for installation at some other location for their remaining service life or

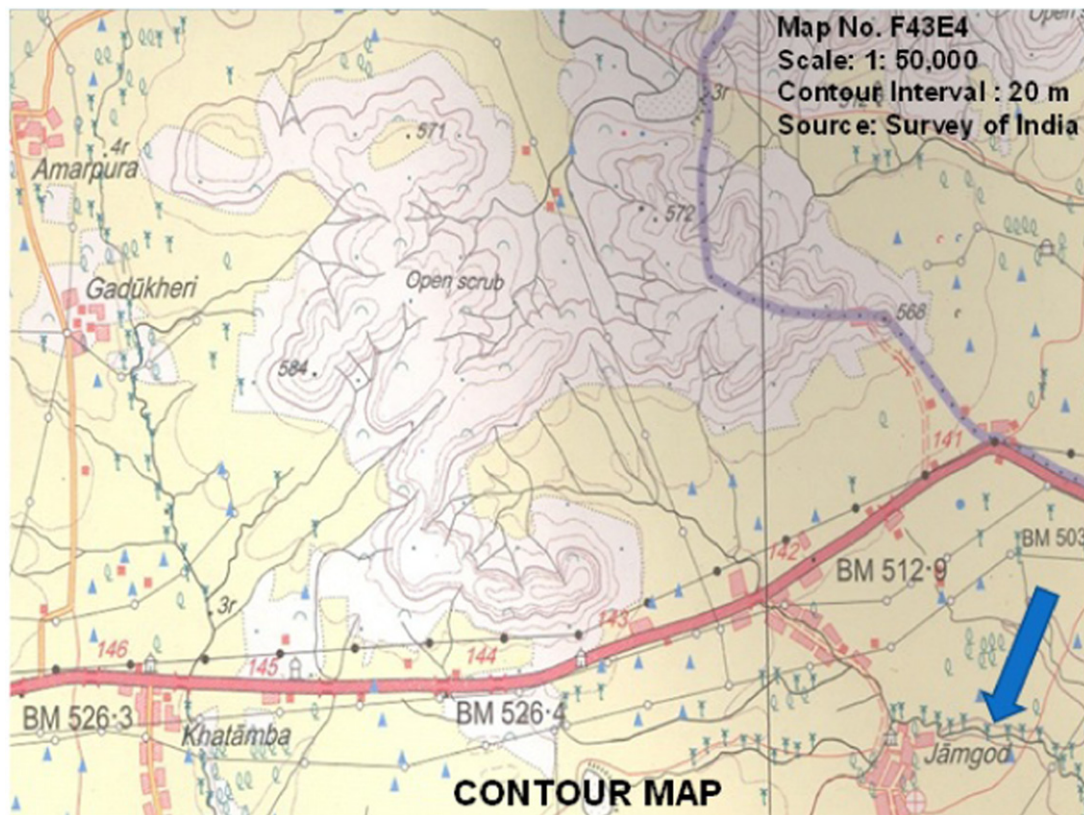


Fig. 2 Topo sheet of Jamgodrani Hills. Source: Survey of India, Jabalpur.

can be sold for scrap for recycling of different parts. Turbines are placed in rows in a wind farm, typically perpendicular to prevailing wind direction by micro-siting process involving flow modeling, micro surveys and wind monitoring and by determining array efficiency and turbulence in the downstream (Verma *et al.*, 2016; Goyal, 2010).

There are many challenges for re-powering such as:

Turbine ownership: More numbers of turbines are replaced by fewer numbers due to which the matter of ownership becomes an issue to be resolved in cases where one to one replacement is not possible.

Land ownership: There is an issue of multiple ownership of wind farm land to be resolved.

Power purchase agreement: PPA might have been signed for long duration, before the end of which re-powering may pose difficulties.

Electricity evacuation: Enhanced power output due to re-powering may require modification or replacement of current equipments and systems of the grid as it is designed to handle current power supply.

Additional cost: The decommissioning cost of existing turbines is to be estimated.

Disposal of existing turbines: Many options for disposal of old, to be replaced turbines are to be analyzed like scrap value, buy-back by manufacturer, relocation cost etc.

Re-Powering Approach

There are certain technical aspects to be considered to determine the re-powering potential of an existing wind farm site:

- Characteristics of the wind resource of the site are to be studied such as speed frequency distribution curve of past several years, Weibull parameters, wind power density, turbulence intensity, power law index, wind rose, prevailing wind direction etc.
- Everything about the existing wind turbines is considered like the number of turbines, their capacity, power curve, cut-in, rated and cut-out speed, rotational speed per minute, hub height, type of generator, rating, thrust and power coefficient etc.
- Proposed modern wind turbine, its capacity and detailed specifications are to be analyzed.
- Available area with necessary off-set from approaching roads and dwellings is to be determined.
- Estimation of annual energy production, gross and net energy production and array efficiency from proposed re-powering turbines at new hub height is to be done.
- Proper planning of proposed wind turbines with micro-siting and turbine array spacing is to be done.
- Re-powering ratio of proposed turbines to existing turbines is to be determined first.

- Energy yield ratio of proposed turbines to existing turbines for same site or area is to be calculated.
- Dismantling cost of existing wind turbines, cost of installation and commissioning of new turbines, unit cost of energy after re-powering and cost of other modified facilities is to be included in the overall economic analysis.

In the next 10 years, it is expected that off-shore wind farms will be developed in select wind zones on Indian Ocean and Arabian Sea. These wind farms will be repowered in next 15–20 years in future. Therefore it requires master plan approach to make the re-powering process a dynamic exercise (Karoui *et al.*, 2017).

High capacity wind turbines are particularly well adapted for sites with higher average wind speeds. Report of Leonardo Energy outlines that: For utilities trying to scale-up their capacity to achieve set target put preference for larger wind turbines. The practical reason is that power output of a wind turbine is depending on square of rotor diameter therefore larger wind turbine is better than two smaller wind turbine of same capacity. The larger wind turbines are preferred for off-shore applications as it minimizes installation cost per MW in terms of foundation cost which takes significant proportion of total cost of installation.

Need for Repowering

Development of the wind power projects in India started off more than two decades ago, and thousands of mega-watts of new capacities are being added on every year. Thus one can find plenty of wind farms that have operated for more than 12 years by now. The turbines that have been installed in these old farms have either already completed their service lives or are nearing the end of it; however generation should continue further and possibly increase in the future. Given the worn out turbines, the generation is likely to drop, and thus, the project developers are now facing with end-of-life decisions. Now during these decades technology has gone ahead big time, and today not only has the hub heights, but also the efficiencies of the turbines doubled. The old PPAs also have either ended or are nearing the end dates. The solution to this issue is repowering (Indian Wind Turbine Manufacturers Association IWTMA, 2015; Tripathi, 2017).

The main salient features of the repowering policy are enumerated as follows:

- As part of the policy, wind turbine generators of capacity 1 MW and below will be eligible for repowering.
- Indian Renewable Energy Development Agency will provide an additional interest rate rebate of 0.25% for repowering projects.
- Benefits available to the new wind projects, that is, accelerated depreciation or Generation Based Incentives (GBI) as per applicable conditions will also be available.
- In case augmentation of transmission system from pooling station onwards is required, the same would be carried out by the respective state transmission utility.
- Additional generation could either be purchased by Distribution Companies at feed-in-tariff applicable in the state at the time of commissioning of the repowering project or allowed for third party sale.

Techno-Economic Analysis

Flow modeling requires three essential set of technical data related to wind, site and turbine:

- Wind characteristics
- Site characteristics, and
- Wind turbine characteristics

Wind Characteristics

For the development of wind energy, the site characterization has to include following major parameters and information: Annual average wind speed (WAsP requires the wind data measured at 10 min intervals by a meteorological mast in the same region), wind power density, wind rose, wind resource map, prevailing wind direction, speed frequency distribution and persistence, vertical wind speed profile, wind shear exponent, Weibull shape parameter (k), scale parameter (c), turbulence intensity, wind density and its variation vertically and seasonally, historical wind data (including frequency and intensity of past storms) etc.

Site Characteristics

Location (latitude, longitude and mean sea level), topographic maps provide the analyst with a preliminary look at site attributes, including available land area, contour map, roughness class of the site, grid related data, transmission line map, positions of existing roads and dwellings, land cover (e.g., forests), political and administrative boundaries, parks, national parks, forest reserves, restricted areas, proximity to transmission lines, location of significant obstructions, potential impact on local aesthetics, cellular phone service reliability for data transfers, other infrastructural facilities.

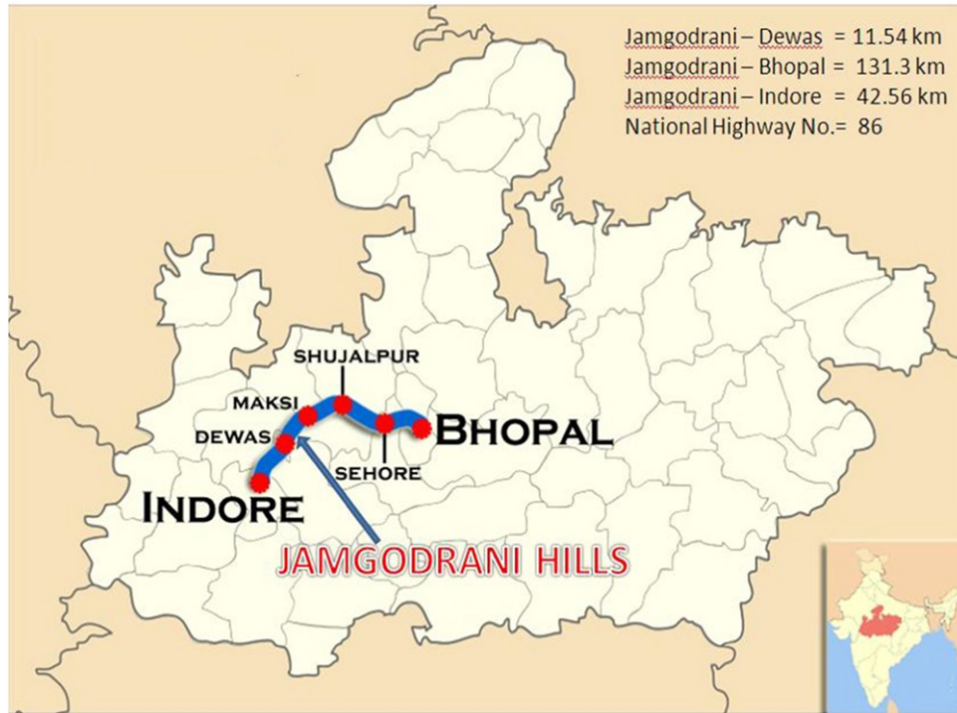


Fig. 3 Research Site location. *Source:* Maps of India.

The Jamgodrani wind farm is located in district Dewas of state Madhya Pradesh in central India. The geographical coordinates of the farm is latitude of 22° 59' 9", longitude of 76° 9' 5 6.5" and at an altitude of 580 m from the sea level. The factors which may impact the characteristics of wind are urban cities Indore and Ujjain which are closest to the wind farm and the Kshipra River. The wind farm covers an area of approximately 12,000 sq m which has non-uniform surfaces and contains a number of small water pools, farm lands and some manmade developments as shown in Fig. 3.

Wind Turbine and Farm Characteristics

Wind farm layout of existing and after re-powering, power and thrust curve of the turbine(s), hub height, rotor diameter, pitch mechanism, braking mechanism, generator type, gear or gearless machine, type of power electronics, cut-in, rated and cut-out speeds, capacity factor etc (Figs. 4–6).

In addition to above, the parameters related to machine availability, grid availability, transmission losses and WAsP prediction error is to be considered for arriving at annual energy production value. The annual energy production (AEP) of the wind farm after re-powering can be predicted by using industry standard WAsP (Wind Atlas Analysis and Application Programme) and simulation can be performed by using MATLAB. Following parameters are to be determined after analysis for re-powering (Ganesan and Ahmed, 2008; Diwakar *et al.*, 2010):

- Improvement in plant load factor (PLF),
- Increase in annual energy production (AEP) or energy yield,
- Increase in installed capacity of wind farm,
- Change in reactive power consumption.

Wind power density

Wind power available per unit area swept by the turbine blades is called as Wind Power density.

Where,

$$\text{Wind Power Density} = \frac{1}{2n} \sum_{i=1}^n \rho V_i^3 \quad (1)$$

n = number of records in averaging interval

ρ = air density (kg/m³),

v = wind speed value (m/s)

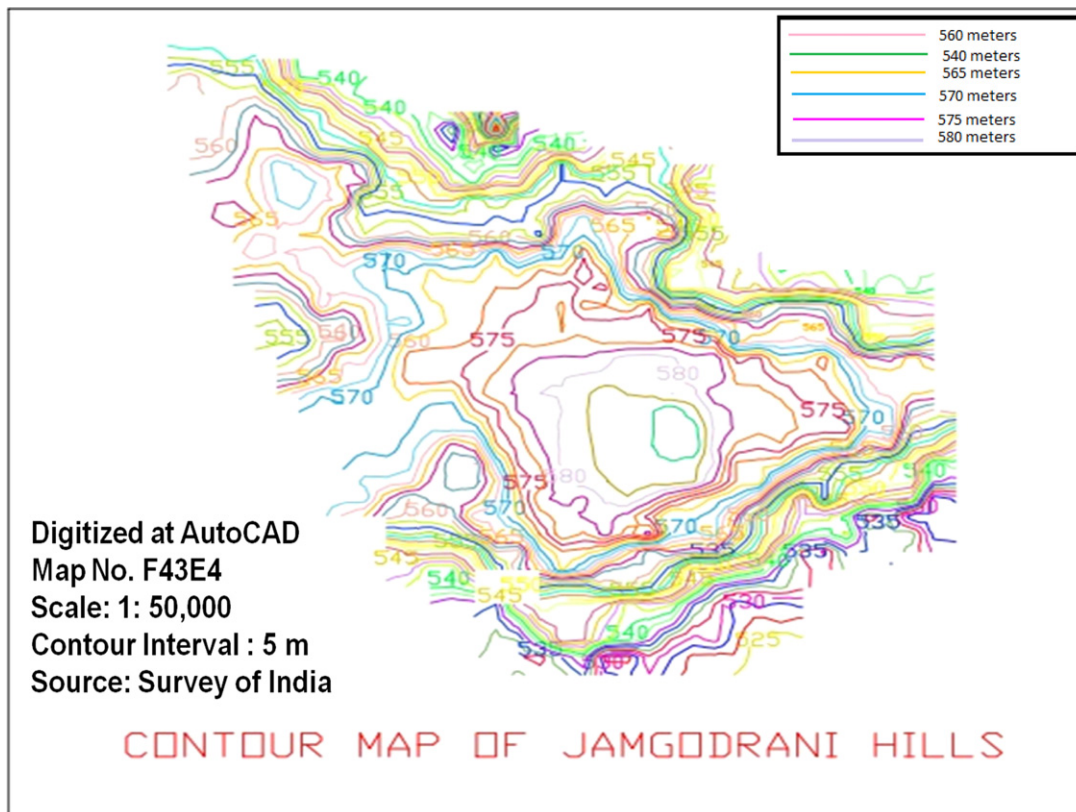


Fig. 4 Contour Map of Jamgodrani Hills.



Fig. 5 Existing Research Site location at Jamgodrani Hills. Source: Google Earth Image.



Fig. 6 Proposed Research Site location at Jamgodrani Hills.

Power law equation

$$\frac{V_2}{V_1} = \left(\frac{Z_2}{Z_1} \right)^\alpha \quad (2)$$

Where,

V_2, V_1 = wind speeds,

Z_2, Z_1 = heights,

And α = power law index or empirical wind shear

Where,

$$\alpha = \frac{\log \frac{V_2}{V_1}}{\log \frac{Z_2}{Z_1}} \quad (3)$$

Energy production analysis

The theoretical maximum annual energy production is given by

$$AEP_{max} = \frac{(R \times N \times 24 \times 365)}{1000} kWhr \quad (4)$$

While the actual annual energy production is given by

$$AEP = \left(\sum_{m \in M} W(m) \times P(m) \right) \times \frac{N \times 24 \times 365}{1000} kWhr \quad (5)$$

Where,

R = Rating of turbine.

N = Number of turbines.

W = Weibull distribution.

P = Power curve of turbine.

Weibull distribution

The Weibull is a two parameter distribution function and is represented by a dimensionless shape parameter k and scale parameter c in units of wind speed (m/s) and it can be described by its probability density function $f(v)$ and cumulative distribution function $F(v)$ as given below:

$$f(v) = \frac{k}{c} \left(\frac{v}{c}\right)^{k-1} \times \exp\left[-\left(\frac{v}{c}\right)^k\right] \quad (1')$$

$$F(v) = 1 - \exp\left[-\left(\frac{v}{c}\right)^k\right] \quad (2')$$

Where v is the wind speed, k is the dimensionless shape parameter, and c is the scale parameter having the same unit as v (m/s). The distribution is termed as Rayleigh distribution when its shape parameter k is 2. For calculating the parameters of the Weibull distribution nine different numerical methods are used in this study (Diwakar *et al.*, 2010).

Actual Methodology for Proposed Research Work

- (1) Select the research site.
- (2) Collect the wind data from National Institute of Wind Energy from Chennai, Tamilnadu.
- (3) Extrapolation of data at different heights to optimize the results.
- (4) Replacing existing wind turbine with new modern wind turbines.
- (5) Analysis of site (Jamgodrani Hills) by meteorological data.
- (6) Draw wind rose pattern of the research site using WAsP software and MATLAB software.
- (7) Evaluate and analyze technical data of research site with economical study.
- (8) Compare current technical data with modern wind turbines data to enhance the efficiency and net increase power generation through repowering.

Data Interpretation Through WAsP and MATLAB

WAsP Based Software Analysis

WAsP (Version 8.0) is a complete software package for wind data analysis, map editing, wind atlas generation, wind resource assessment and siting of wind turbines. Working with wind resource assessment and WAsP in practice, however, requires other software as well.

In 1987 the Wind Energy and Atmospheric Physics Department at Riso National Laboratory introduced WAsP – A powerful tool for wind data analysis, wind atlas generation, wind climate estimation and siting of wind turbines.

MATLAB Based Software Analysis

MATLAB (Matrix Laboratory) is basically a high level language which has many specialized toolboxes for making things easier. MATLAB allows matrix manipulations, plotting of functions and data, implementation of algorithms and creation of user interfaces

- WAsP Version: 8.0
- MATLAB Version: R2012b

Data Interpretation Through WAsP and MATLAB

Roughness effect, Orographic effect, power density curve for individual turbines are analyzed for existing wind turbines using WAsP software as shown in Figs. 7–9.

Roughness effect, Orographic effect, power density curve for individual turbines are analyzed for proposed wind turbines using WAsP software as shown in figures below. Wind rose distribution and probability distribution function (PDF) at 20 m height in WAsP is also drawn to obtain wind rose pattern and predominant wind direction of the research site (Figs. 10–12).

Wind Speed Probability Distribution Function (PDF) and Weibull Cumulative Distribution Function (CDF) at different heights (30 m and 80 m) are plotted through MATLAB based programming to obtain the probability and wind flow distribution of existing and proposed site of Jamgodrani hills as shown in Fig. 13.

Results and Discussions

Re-Powering Outcomes

The analysis shows that the repowering can increase the capacity utilization factor from 12.26% to 22.61% hence about 10% boost could be achieved.

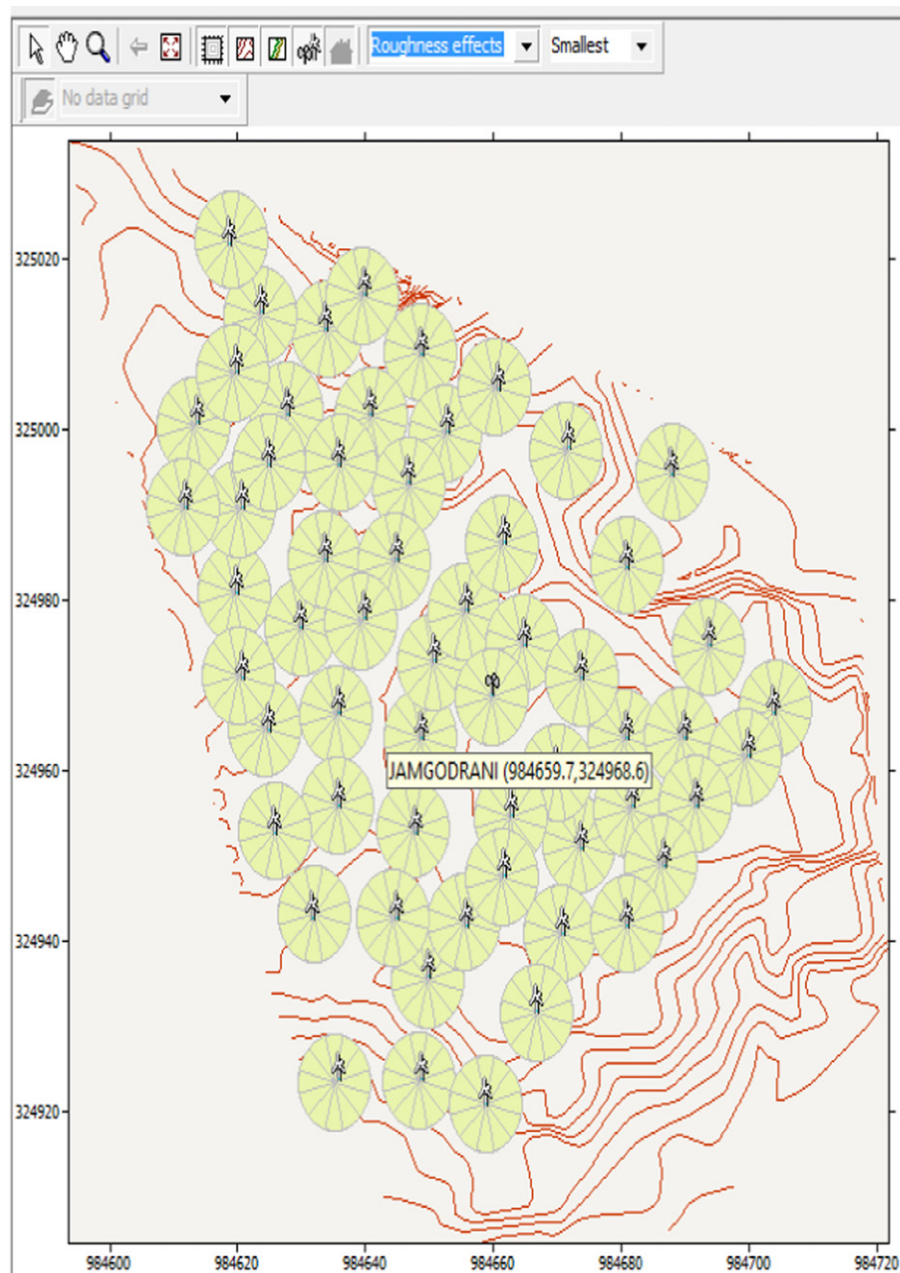


Fig. 7 Roughness effect on existing wind turbines using WAsP.

Energy Production Analysis

See [Table 1](#).

Cost Analysis

Considering the tariff of 4.35 INR per units with no escalation for 25 years the repowered wind farm can be recovered within

$$\frac{1050000000}{27716640} = 8.7 \text{ years}$$

The payback period/recovery can be further decreased by considering the reselling of old turbines, finance rate and the government subsidies ([Table 2](#)).

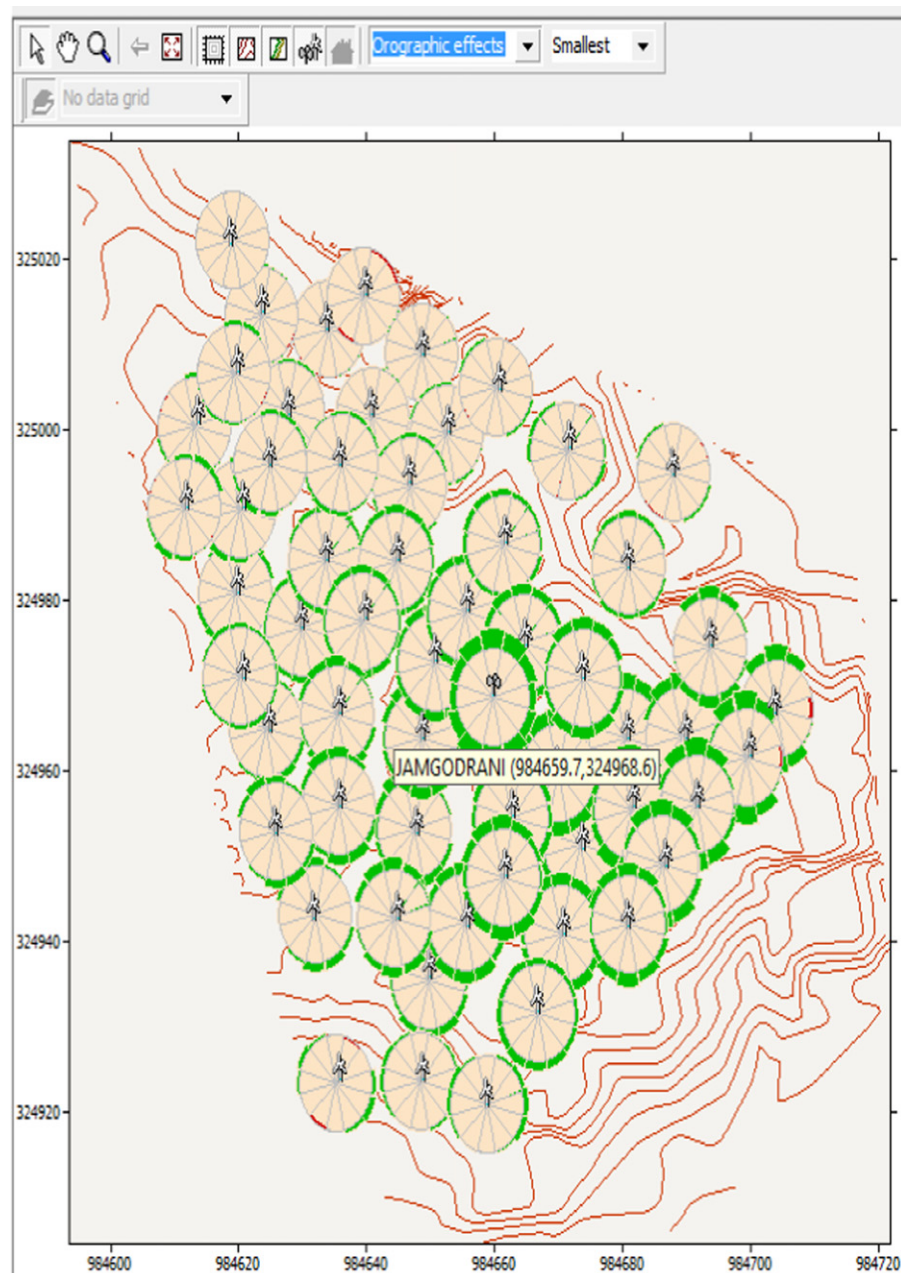


Fig. 8 Orographic effect on existing wind turbines using WAsP.

Environmental Analysis

The repowering causes a significant reduction in the total number of wind generators from 58 to 7, which are also located at much greater heights. This greatly reduces the visual and acoustic impact.

Suggestions and Recommendations With Possible Solutions (for a Case Study in Southern Region of India)

The study identifies key challenges which are likely to be faced by the re-powering project in Muppandal region of Tamil Nadu State. Following are the key challenges and their possible solutions:

New Power Purchase Agreements (PPA)

For sale to Executive Board (EB) projects, many if not most of the projects are under the old PPA rates and in case the projects are to be set up by dismantling of old Wind Turbine Generators (WTG), it is recommended for financial viability of the projects that

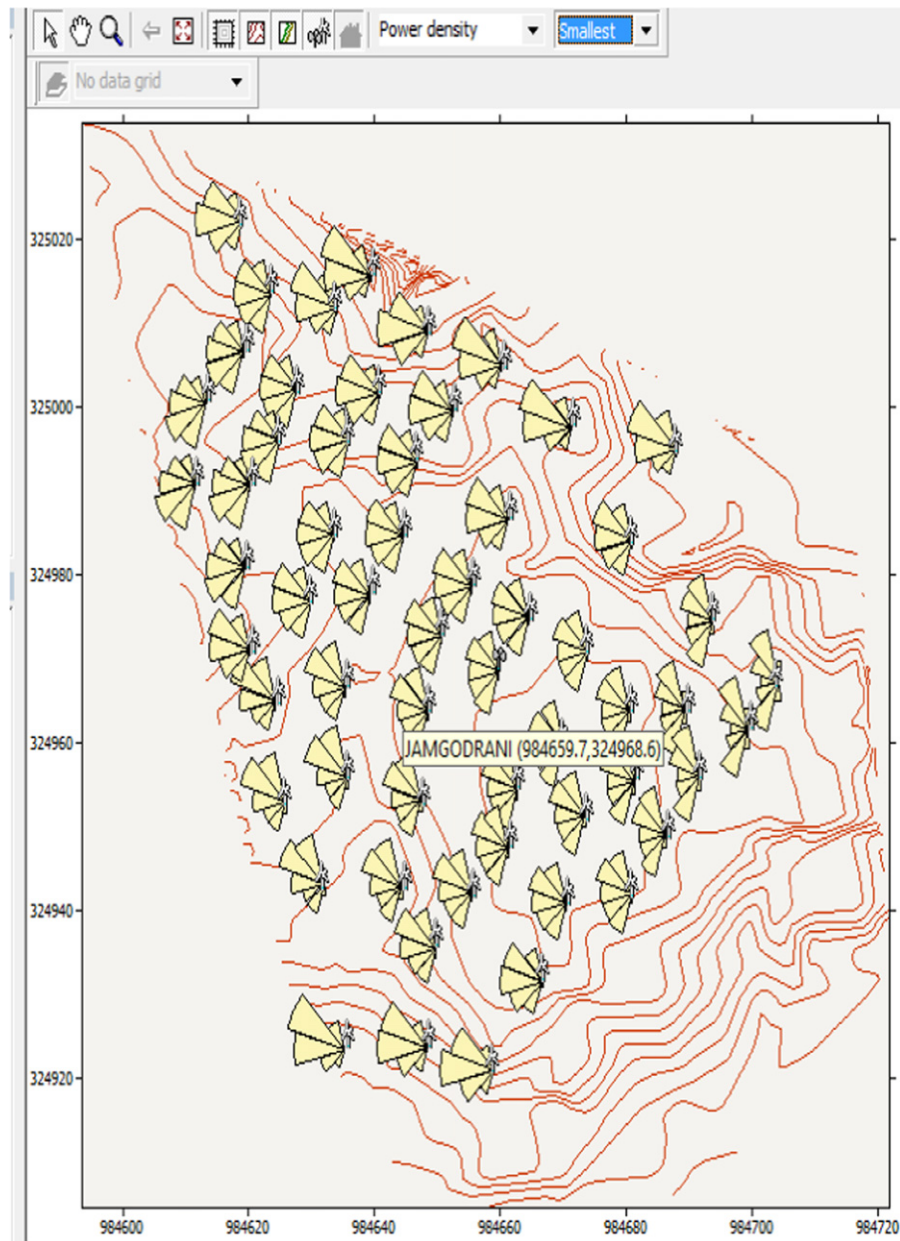


Fig. 9 Power density on existing wind turbines using WAsP.

Tamil Nadu Generation and Distribution Corporation Limited (TANGEDCO) should allow developers to sell power under current FiT (Feed in Tariff) rates. It is possible TANGEDCO will not be willing to come out of such PPAs where they are buying power at much cheaper rate than that of current tariff. Few of the existing project proponents may have a PPA with private consumers (industrial/commercial) at the indexed tariff, who will not be willing to come out of the existing short term PPA because of power deficiency in the state. But since the Third-party sale rates are very high, PPAs should be allowed to lapse after giving a notice of six months which will give existing power buyers the required time to find new sellers.

Possible solution

There should be a provision of “Right of First Refusal to Purchase” to the existing group of captive PPA holders to buy power from the repowered projects at competitive rates. In this case the existing power purchaser should have the right to opt the electricity generated from repowered project at the price determined by the state regulatory body and if existing purchaser refuses to opt then only power producer may opt to go for other option of sale of electricity. This way interest of existing power purchaser will be safeguarded. In another option each repowered project can be considered as a new project in terms of PPA rates and the existing PPA should lapse with a notice period of 6–12 months.

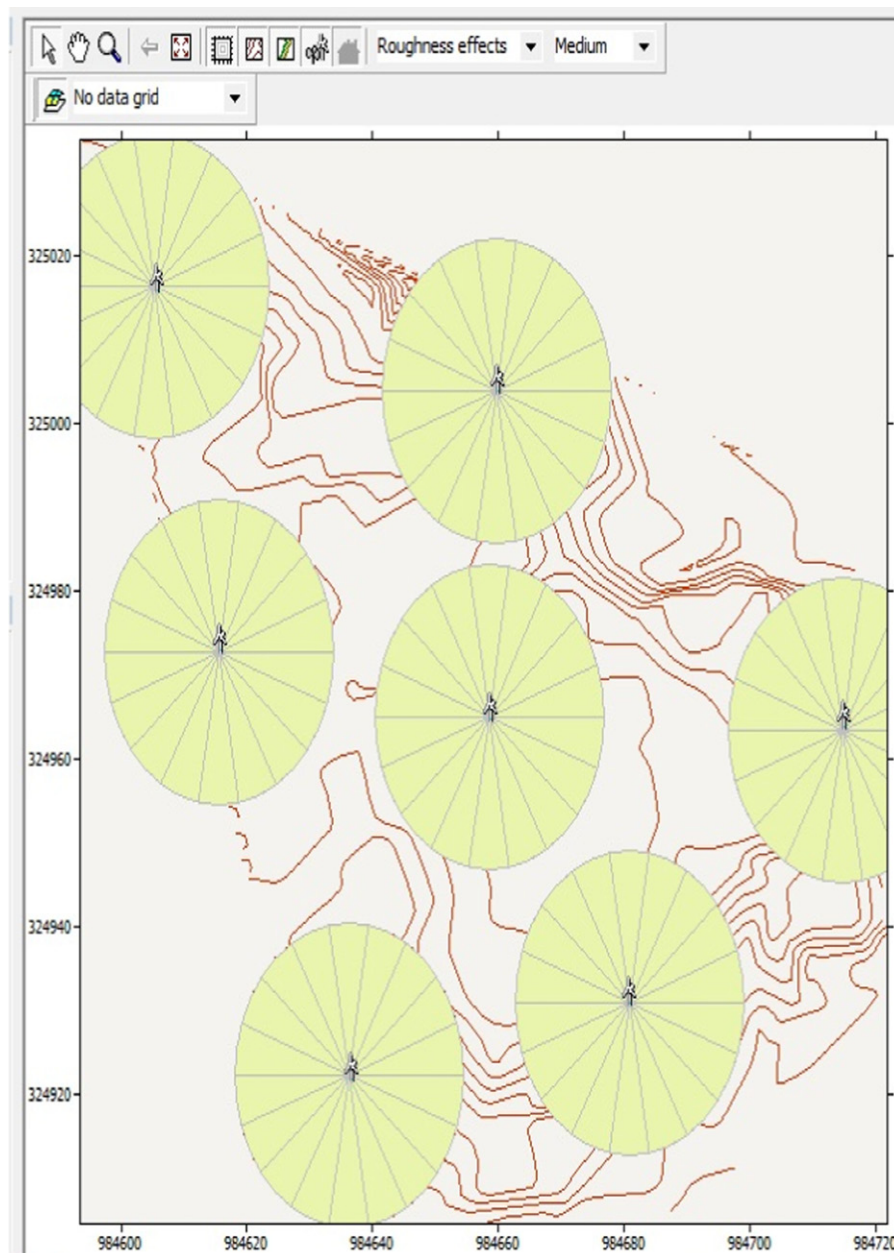


Fig. 10 Roughness effect on proposed wind turbines using WAsP.

Turbine and Project Ownership

Multiple owners of wind farm land may create complications for repowering projects in terms of obtaining permission. The wind turbines are maintained by different agencies and Original Equipment Manufacturers (OEM). Repowering will reduce the number of turbines and there may not be one-to-one replacement. Thus, the issue of ownership needs to be handled carefully.

Possible solution

It is necessary to identify and engage concerned stakeholders such as owners of the wind farms, OEMs, project developers, financial institutions, regulatory bodies, nodal agencies, land owners, operation and management agencies etc. to arrive at a workable business model. All existing stakeholders willing to re-power can be made partners in a Special Purpose Vehicle (SPV) company and profits can be shared in the ratio of equity shareholding in the SPV.

Disposal of Wind Turbine

The disposal of the old WTG is an important factor which is a challenge in itself for repowering projects.

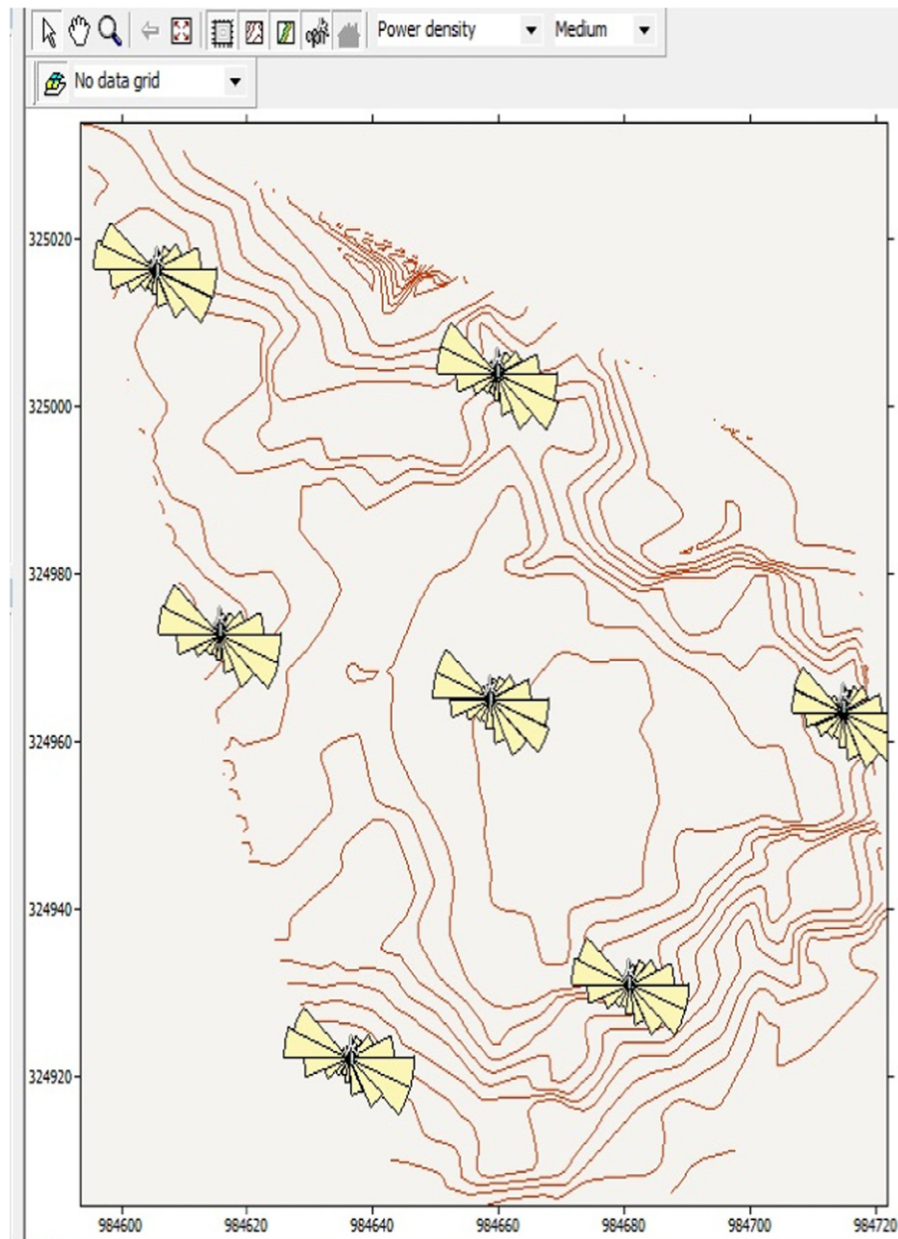


Fig. 11 Power Density on proposed wind turbines using WAsP.

Possible solution

There are various options such as scrapping to recycle usable parts, buy-back by the government or manufacturer and reusing at some other location. Local capacity may need to be developed. But most of the turbines may be too old and in unusable condition and can be just sold as scrap to be scavenged for usable spare parts, copper and other expensive metals.

Incentives

One of the primary barriers of re-powering is the general lack of economic incentive to replace the older WTGs.

Possible solution

Appropriate incentives are necessary in order to compensate for the additional cost of re-powering. To encourage repowering, financial incentives need to be extended by the Government. The following are some of the incentives which can boost repowering in the country.

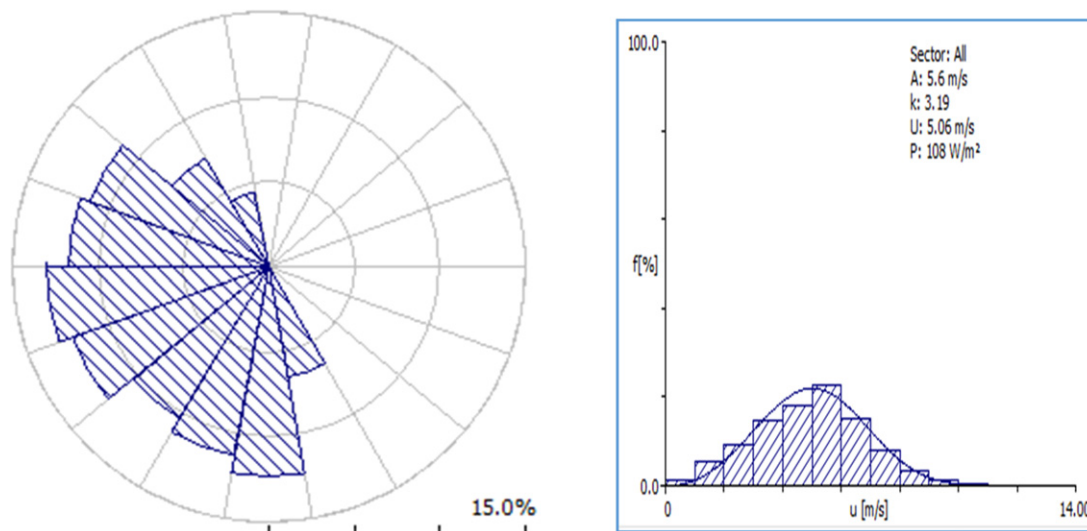
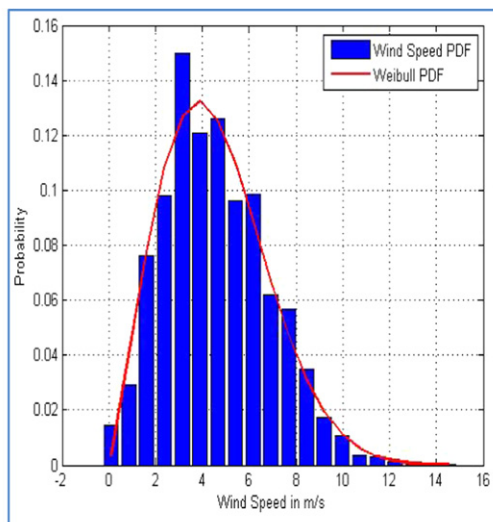
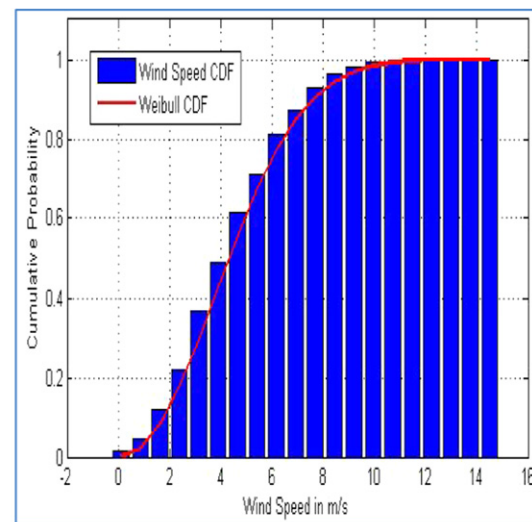


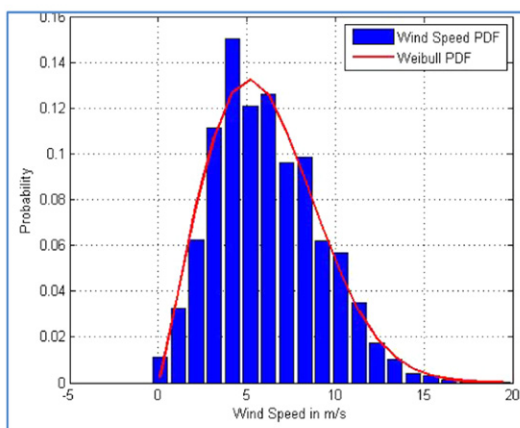
Fig. 12 Wind rose distribution and probability distribution function (PDF) at 20 m height in WASP.



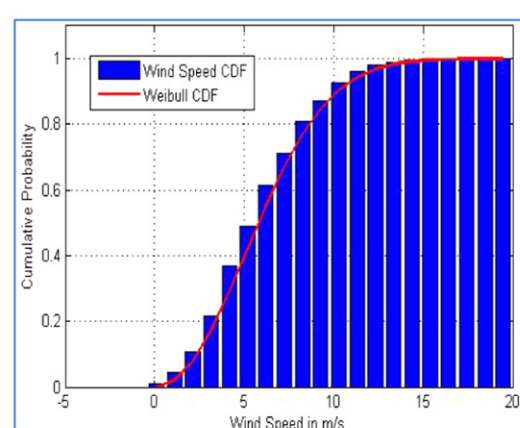
(a) Wind speed function at 30 meter height



(b) Wind speed function at 30 meter height



(c) Wind speed function at 80 meter height



(d) Wind speed function at 80 meter height

Fig. 13 Wind Speed Probability Distribution Function (PDF) and Weibull Cumulative Distribution Function (CDF).

Table 1 Energy production analysis

<i>Before repowering</i>		
<i>Parameters</i>		
a.	Annual Energy Production (AEP)	114.186 <i>GWhr per year</i>
b.	The actual Annual Energy Output is	14.003 <i>GWhr per year</i>
c.	Capacity Utilization Factor (CUF) [c = b/a]	12.26%
AFTER REPOWERING		
<i>Parameters</i>		
a.	Annual Energy Production (AEP)	122.6400 <i>GWhr per year</i>
b.	The actual Annual Energy Output is	27.727 <i>GWhr per year</i>
c.	Capacity Utilization Factor (CUF) [c = b/a]	22.61%

Table 2 Cost Analysis of Research Site

<i>Parameters</i>	<i>Generation per year (MWhr per year)</i>	<i>Capital Expenditure (INR)</i>	<i>Total Generation in 25 years @1% degradation</i>	<i>Cost of per unit generation (INR)</i>
Existing Wind farm	14003.955	696,000,000	311137968.5	2.25
Proposed Wind farm	27716.640	1050,000,000	618394646.1	1.70

- IPPs (Independent Power Producers) and FDI (Foreign Direct Investment) needs to be encouraged by the government;
- Old project owners needs to be given freedom to choose alternate option for sale of power i.e. REC Mechanism, third party sale etc.

Grid Augmentation

All the WTGs in Muppandal are connected at 11/33/66 KV rural feeder level and most of the WTGs available in the market today are designed as per 33 KV/ 220 KV level as it minimizes losses due to step-up and transmission. For new projects, TRANSCO/TANGEDCO needs to allow interconnection at higher (110/220) KV levels. Considering the congestion of grid lines at Muppandal Pass, it would be advisable to allow interconnectivity at 220 KV level.

NIWE Certification

The wind regime at Muppandal Pass is suitable for Class IIIA / IIA turbines and in certain cases even Class IB turbines can be used. But most of the current WTGs sold in India are suitable for low wind sites i.e. class IIIA/IIIB sites and manufacturers like Suzlon who have higher class turbines (class I/II) in their portfolio have stopped manufacturing such turbines due to either lack of demand or lapsing of their NIWE (National Institute of wind energy, formerly CWET) certifications. NIWE needs to allow fast-track revival of such types of certificates for manufacturing of higher class turbines of limited numbers for these repowering Projects.

The additional decommissioning cost for old turbines (such as transport charges) needs to be assessed.

Conclusion

The interdependence of economic growth and energy consumption cannot be denied, so access to a stable energy supply is important to the political world and a technical and monetary challenge for both developed and developing countries, because prolonged interferences can generate serious economic and basic functionality difficulties for most societies. Renewable energy sources are evenly distributed around the globe as compared to fossils and generally less traded. Conventional sources of energy are unsustainable from economic and environmental aspects whereas renewable sources like wind and solar energy are limitless and create almost no pollution.

Renewable sources also reduce energy imports and contribute to the diversification of energy supply options, reducing an economy's vulnerability to price volatility and at the same time representing opportunities to enhance energy security across the globe. They can contribute towards increasing the reliability of energy services in areas that often suffer from insufficient grid access. A diverse portfolio of energy sources together with good management and system design can help to enhance energy security. Also, renewable energy technologies enable countries to utilize renewable energy sources to meet their domestic demand and even have long-term export potential.

Renewable energy technologies could reduce CO₂ emissions by replacing fossil fuels in the power generation industry and transportation sector. Enhancing energy efficiency regardless of type is also crucial for climate change mitigation and reduction of environmental and health impacts.

This article focuses on wind energy technology and the way to optimize the efficiency of old wind farms through repowering method. It presented the repowering aspects both financial and electrical of Jamgodrani wind farm. The research work pointed out a number of advantages in this analysis which shows that the Repowering of considered farm could increase its annual energy production by 10% (from 12.26% to 22.61%) while using only 7 turbines instead of 58 turbines presently in used which also reduces the environmental impact. Furthermore the financing of repowering and government subsidies could also reduce the cost burden of repowering. Overall it can be said that these are strong evidences that repowering is a profitable investment in electrical, economic and environmental aspects.

Future Scope of the Research Work

The field of wind energy has a tremendous scope for innovation and large economic opportunities. The advanced wind modeling software such as windPRO, WindFarmer, Windographer and WAsP can be used for micro-siting, wind resource assessment, predicting annual energy production and wake analysis for obtaining better results for repowering at higher heights and as well as at complex terrain. These advanced software consist of several modules which enables to create wind statistics, perform simple or complex energy calculations and generate resource maps.

See also: Application of Remote Sensing in Wind Resource Assessment

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Library of Congress Cataloging-in-Publication Data

A catalog record for this book is available from the Library of Congress

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library

ISBN 978-0-12-813195-4

For information on all publications visit our
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PREFACE

The *Encyclopedia of Renewable and Sustainable Materials* is a novel initiative, launched to cater for researchers, industrial practitioners and environmental conservationists to bring to the fore the issues of renewability, regeneration, recyclability and sustainability of natural material resources for the greater good of the environment, society and renewable resources. With these objectives the project was constituted of 11 sections, led by one Section Editor each. There are about 4,000 printed pages, accommodated in five volumes ranging from 600 to 1000 pages each.

This encyclopedia is the primary reference source for researchers at different levels and stages in their career in academia and industry and those with an interest in environmental protection and sustainability, including re-use and recycling of natural and synthetic materials and regeneration of natural materials. The work encompasses the knowledge and understanding of many experts into a single, comprehensive work of about 370 articles comprising a combination of review articles, case studies and research findings resulting from research and development activities in both industrial and academic domains. The encyclopedia, focuses on how some of these topics bring advantages for a broad range of technologies and environmental protectionists. These include harnessing existing materials both natural and synthetic, their re-usability and regeneration possibilities for the greater good of society and the environment. The aspects of feasibility, conservational objectives and practicability of implementation have been addressed through a number of relevant articles.

As Editors in Chief of this five-volume comprehensive publication, a truly collaborative work, we are greatly indebted to the 11 Section Editors who are internationally renowned experts in their fields, for guiding and selecting the topics for their respective sections which constitute the five volumes, commissioning authors and reviewing the contents so meticulously. Their true dedication to the scientific community and society is reflected in the time and energy they have given to this project. My sincerest thanks are due to all the authors – researchers, environmental protectionists and practitioners who have contributed extensive coverage of literature review as well as recent works of research to this substantial five volume encyclopedia. The excellent insight and specialist knowledge in their respective fields is reflected in the high quality content of this unique work.

Both of us and all the section editors are greatly appreciative of all the hard work undertaken by all concerned to turn this concept of the *Encyclopedia of Renewable and Sustainable Materials* into a publishable work. Our special thanks go to Ruth Rhodes and Michael Nicholls, the Project Manager, along with Kshitija Iyer and the rest of the team at Elsevier who served successively to keep the project on track through friendly nudges in order to ensure timely completion. We are also hugely grateful to other colleagues at Elsevier production unit for the coordination of the proofs.

The extensive research treatment of core ethos of renewability, recyclability and regeneration, supplemented by applied case studies has drawn together many areas of research and we sincerely hope that this work will prove to be of great help to both the young and experienced members of the international research community, academics and industrial practitioners associated with sensible utilization of natural and synthetic materials for many years to come.

Saleem Hashmi and Imtiaz Ahmed Choudhury
Editors in Chief – *Encyclopedia of Renewable and Sustainable Materials*

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Analysis of the Thermal Performance and Comfort Conditions of Vernacular Rammed Earth Architecture From Southern Portugal

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Introduction

From the beginning, humans had to look for shelters to protect themselves from other animals and the climatic elements. But it was in the Neolithic, when humans moved from a nomadic to a sedentary life, that they decided to build permanent shelters. These shelters evolved over thousands of years and generations, across the world, and diverse vernacular techniques and forms have been developed and improved to better respond to climate constraints and to provide the best comfort conditions possible.

To attain thermal comfort conditions vernacular buildings were built using low-tech passive strategies that take advantage of available endogenous resources and other criteria such as sun exposure, geometry, form, and materials, among others (Coch, 1998; Singh *et al.*, 2011; Fernandes *et al.*, 2015a,b). With the industrialization of the building sector, the vernacular knowledge was often forgotten in building design and its use declined. Moreover, nowadays, buildings too often rely on heating, ventilation, and air conditioning (HVAC) systems to ensure indoor thermal comfort conditions (Fernandes *et al.*, 2015a,b). Thus, the relevance of vernacular features is still valid today in the scope of sustainability, being the basis of what is now defined as sustainable building design (Cardinale *et al.*, 2013).

Environmental awareness is increasing and underlining the problems related to energy efficiency and environmental impacts in buildings. The building sector is one of the largest energy and natural resources consuming sectors, being responsible for a third of global total CO₂ emissions and primary energy use (Ürge-Vorsatz *et al.*, 2015). Therefore, new high-performance building concepts have been defined, such as the “nearly zero-energy buildings” (nZEB). An nZEB is a building with a very high energy performance (due to an improved envelope and use of very efficient HVAC systems) and where the very low energy demand must be covered by energy from renewable energy sources.

The awareness of vernacular architecture regarding passive and low energy architecture is increasing, since it is intrinsically related to the local climate, uses passive, low-tech techniques, and is not dependent on nonrenewable energy sources (Kimura, 1994; Singh *et al.*, 2011; Fernandes *et al.*, 2013), which makes these strategies suitable and valuable to achieve the nZEB level in different climate contexts.

Several studies have shown that vernacular buildings have a good thermal performance, allowing achieving acceptable thermal comfort levels during most of the year by passive means only, reducing the energy demand for heating and cooling (Martín *et al.*, 2010; Singh *et al.*, 2010; Priya *et al.*, 2012; Cardinale *et al.*, 2013; Fernandes *et al.*, 2015a,b).

In Portugal, there are some studies focusing on the passive strategies used in the vernacular building, but there is a lack of results showing the influence of these strategies on the thermal performance of vernacular buildings, namely of rammed earth buildings.

Portugal is a relatively small country, but it is a territory full of contrasts. Even though the variation in climatic factors is rather small, they are sufficient to justify significant variations in air temperature and rainfall, as can be seen in Fig. 1, which shows the differences in mean air temperature for mainland Portugal during winter and summer.

As Fig. 1 shows, the northern part of the country has cold winter and dry and mild summers, while in the southern part, the winters are mild, and summers are warm and dry. As a response to these differences, Portuguese vernacular architecture developed specific and different strategies in both regions. In the north, these strategies are more oriented to increase heat gains and reduce heat losses during winter, while in the south they are more focused on passive cooling during summer. A more detailed explanation about the characteristics of these vernacular strategies can be seen in the following sections.

As vernacular architecture has shown, a building solution/strategy does not fit all contexts. The diversity of vernacular construction systems that exist in Portugal leads to the necessity of understanding the actual performance of these buildings. In this study, the main goal was to measure the hygrothermal parameters that characterize the indoor thermal environment and that affect the heat exchanges in vernacular rammed earth buildings from Southern Portugal.

Vernacular Architecture in Inland Southern Portugal

Vernacular architecture from the southern part of Portugal has developed specific mitigation strategies to suit the local climatic conditions mentioned above. As seen in Fig. 1, summer is the most demanding season in the region due to the intense heat. Therefore, in general, the strategies present in this type of building are more oriented for passive cooling (Fernandes *et al.*, 2015a,b). From these, the more common and frequent are (Fig. 2(a–h)) as follows:

- (1) To minimize the size and number of windows exposed to the outdoor environment to reduce solar gains. Also frequent is taking advantage of the wall's thickness to recess the window in the facade, allowing depth to act as a shading system (Fig. 2(a)).
- (2) The use of heavy weight building elements, with a high thermal inertia, as rammed earth walls and domes, to dampen the flow of the thermal wave and to increase the height and thermal stratification, respectively (Fig. 2(b)).

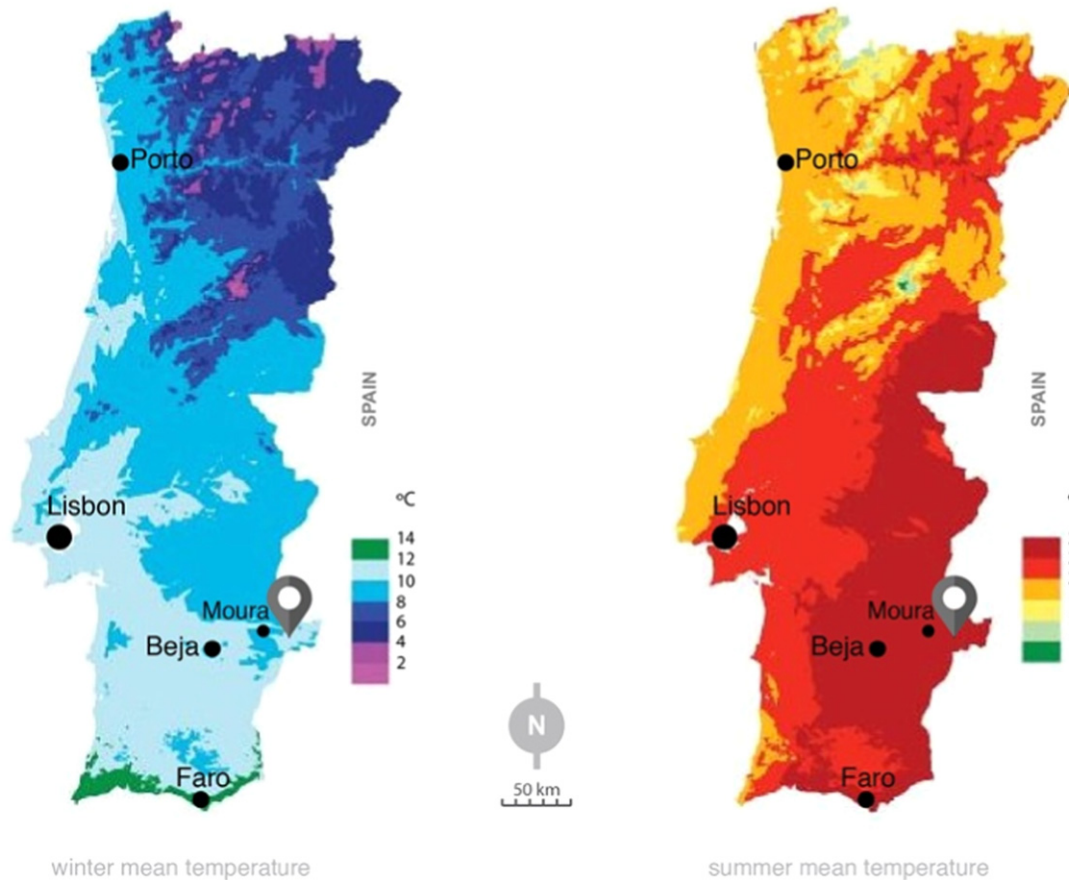


Fig. 1 (left) Winter and (right) summer mean air temperature maps for mainland Portugal. Adapted from Fernandes, J., Pimenta, C., Mateus, R., Silva, S.M., Bragança, L., 2015b. Contribution of Portuguese vernacular building strategies to indoor thermal comfort and occupants' perception. Buildings 5, 1242–1264.

- (3) The use of white-washed surfaces, to reflect the incident solar radiation (Fig. 2(a)).
- (4) Ventilation openings integrated into windows and/or walls, to foster air circulation and night cooling to remove diurnal thermal loads (Fig. 2(c–d)). In some cases, these ventilation openings have gridded shutters, like the *mashrabiya*. These techniques allow simultaneously ventilation and shading from intense light and radiation without compromising privacy and security.
- (5) The use of patios (courtyards), usually containing vegetation and/or water, useful to generate a cool microclimate through evapotranspiration and water evaporation, respectively (Fig. 2(e)).
- (6) Vegetation is also frequently used as a shading system (Fig. 2(f)).
- (7) In an urban context, the use of a compact and irregular layout with narrow streets is also frequent, allowing for reducing the surface area exposed to the sun's rays and enabling buildings to provide shade for one another, thereby reducing solar gains by the building envelope (Fig. 2(g–h)).

These strategies are often combined to maximize their effectiveness to achieve a comfortable thermal environment, as shown in other studies (Fernandes *et al.*, 2015a,b). From these strategies, there is one that stands out for being the building element that characterizes Portuguese southern vernacular architecture. The heavy walls made of rammed earth are the most widespread vernacular construction technique in the southern, and mainly in the Alentejo region (the major area of all the southern part of Portugal). The heavy mass and the good heat storage capacity of rammed earth walls allow them to react appropriately to the hot summer of Alentejo, dampening the outdoor thermal wave and keeping indoor temperature and relative humidity stable (Martín *et al.*, 2010; Fernandes *et al.*, 2015a,b). The use of rammed earth in the region is ancient and there are several possible factors to explain it, such as the flat terrain, dry climate, the abundance of clayey material, and cultural influences from Romans and Moors.

The continued use for centuries of these strategies indicates the effectiveness in mitigating the effects of the climate and, therefore, the quantitative study is useful to discuss their potential nowadays in scope of energy efficiency and sustainability.

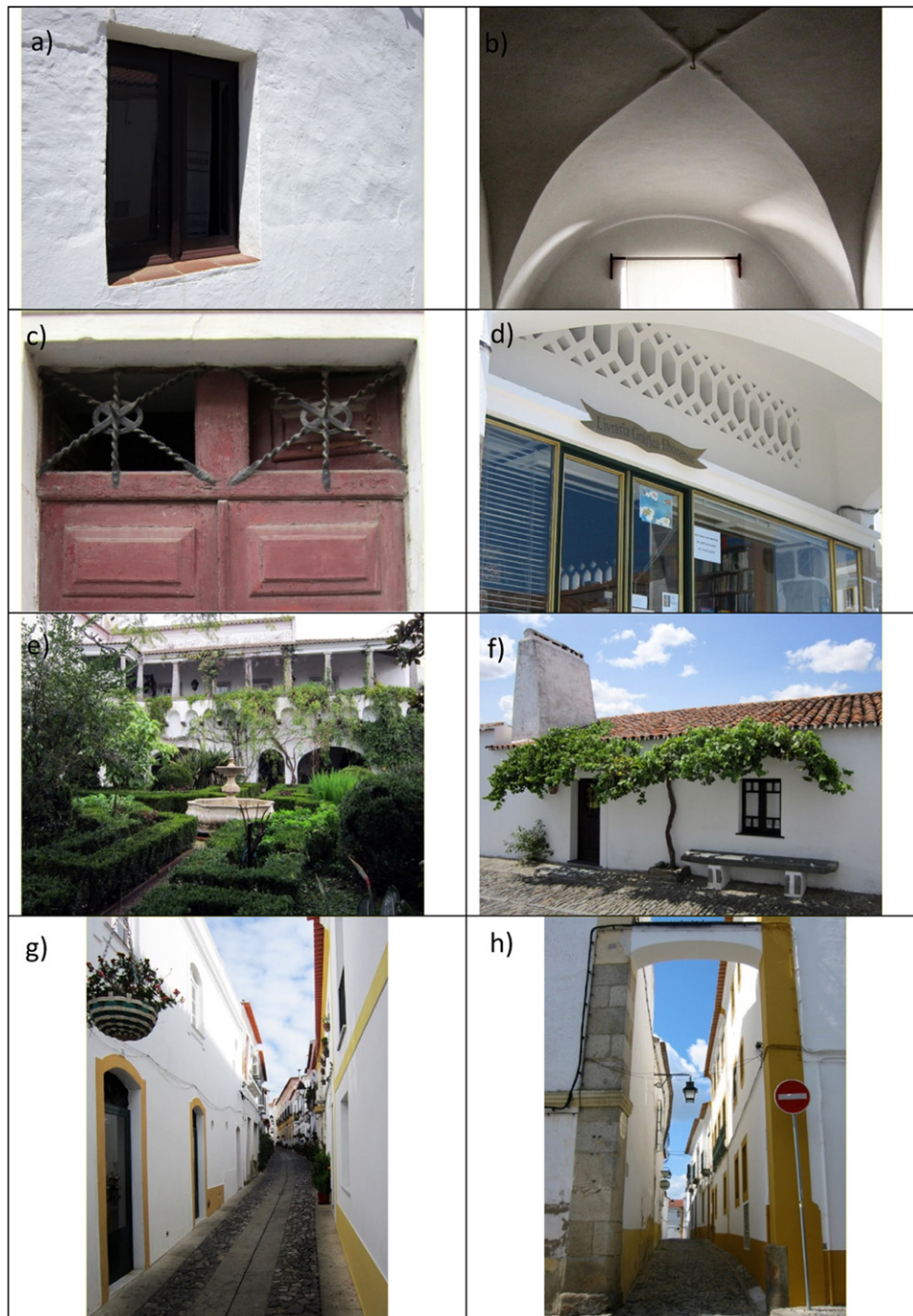


Fig. 2 (a) Small window recessed in a white-washed façade; (b) vaulted ceiling; (c) ventilation shutter integrated into window frame; (d) ventilation openings integrated into wall; (e) a patio containing vegetation and fountain; (f) vegetation shading the façade; (g–h) compact layout with shaded narrow streets.

Case Study Description

The case study is a rammed earth building located in the center of an old village, in the municipality of Moura, southern Portugal (Fig. 1). The Safara territory has an ancient occupation, with some archeological remains dating back to the 2nd Iron Age. The Romans (3rd century BCE to 5th century CE) and the Arabs (8th to 13th century CE) had a long dominion on this territory, having been integrated into the kingdom of Portugal in the 13th century. The origin of the village name has been attributed to the Arabs and means extensive plain without trees, but also adjectives such as *desert*, *arid*, and *harsh*.

This region is characterized by having a Mediterranean climate (subtype Csa), with a hot and dry summer (AEMET and IM, 2011). Summer is the most demanding season in this area, with an average maximum air temperature between 32 and 35°C, but sometimes the maximum temperatures can reach 40–45°C. July and August are the hottest months (AEMET and IM, 2011). The number of days in the year with a maximum temperature above or equal to 25°C is greater than 110 days in a large part of the southern area (AEMET and IM, 2011). In summer, the inland has more than 80 days with a maximum temperature above or equal to 25°C (AEMET and IM, 2011). In terms of precipitation is one of the Portuguese regions with less rainfall (the average value is less than 500 mm), July being the driest month (less than 5 mm) (AEMET and IM, 2011).

To cope with this climate, vernacular buildings from this region have several strategies to minimize heat gains and to promote passive cooling, such as small and few windows and doors, the use of high thermal inertia construction solutions, the use of patios (courtyards), the use of light colors on the envelope to reflect solar radiation, and ventilation openings. Regarding the latter, these are usually integrated into the upper part of windows and doors to promote air circulation, and are particularly useful for night-time cooling without compromising the safety of the building (Fernandes *et al.*, 2015a,b).

The village is strategically implanted next to the confluence between a river and two streams. It is located in a plain area of fertile agricultural land (abundant in cereals and olive trees). However, it is implanted in the transition area to the rugged terrain of streams' valleys and on the less fertile soil (lithosols), in border limit of the fertile land (Fig. 3(a)). Additionally, the characteristics of the surrounding soils show that they are rich in clay (luvisols and vertisols) (Fig. 3(b)), and at a lithological level there is presence of limestone and calcareous formations (Fig. 3(c)). These features were favorable factors in this site for using earth as a building material – The clayey soils for rammed earth, tiles, and bricks; and the limestone to produce lime for plasters, whitewash, etc. For example, the former military walls of Safara were built in rammed earth.

The village's urban layout is compact with a mix of narrow and wide streets, composed mostly of single-story buildings. Most of the buildings have a private courtyard, with vegetation that acts as thermal regulator, as explained in previous sections. The irregular and compact urban layout of narrow streets, with almost no streets and facades facing south, allows for reducing heat gains by the building envelope.

The case study building has an approximate gross floor area of 200 m² divided into two floors; however, the upper floor is just a small attic (originally a granary), usually not occupied. The living areas and the bedrooms are located in the southeast part of the ground floor, and the kitchen and the bathroom are located in the northern part (Fig. 4).

The envelope of the case study building consists of white-washed heavy weight external walls made of rammed earth with an average thickness of 60 cm (as the heavy thermal inertia delays the effect of outdoor temperature variation and stabilizes indoor temperature), pitched roof with ceramic tiles and reeds on timber structure (a small insulation layer of sprayed polyurethane foam was added a few years ago), wooden doors and wooden framed single glazed windows (Fig. 5). Indoor partition walls are in rammed earth and several of the indoor spaces are vaulted and the floor is paved with *baldosa* – a sun-dried clay tile. The building does not have an air-conditioning system and the only heating "system" is a wood-burning stove (in the living room) and the sporadic use of electric fan heaters (in the other rooms).

Materials and Methods for the Evaluation of Thermal Comfort Conditions

The purpose of the study was to assess indoor thermal performance and comfort conditions of a rammed earth building, measuring hygrothermal parameters that characterize indoor thermal environment and affect the body/environment heat exchange (air temperature, relative humidity, mean radiant temperature, and air velocity). In this study, to assess indoor thermal performance, the in situ measurements were divided into short- and long-term monitoring.

The first were carried out at least one time (usually one day) per season and were performed with the purpose of quantitatively assessing the thermal conditions within a specific room using a thermal micro-climate station (model Delta OHM 32.1) equipped with the probes required, namely, globe temperature probe Ø150 mm (range from –10°C to 100°C); two-sensor probes for measuring natural wet bulb temperature and dry bulb temperature (range from 4°C to 80°C); combined temperature and relative humidity probe (range from –10°C to 80°C and 5–98%RH); and omnidirectional hot-wire probe for wind speed measurement (range from 0 to 5 m/s). This data is used in the analysis of the thermal comfort conditions to determine the operative temperature, namely in the adaptive model of comfort, as explained below. Simultaneously, occupants were surveyed to evaluate their satisfaction with the indoor thermal environment, according to ASHRAE survey and thermal sensation scale (ASHRAE, 2004). The results of both procedures were then compared to conclude if converged or diverged.

Long-term monitoring had the aim of understanding fluctuations of air temperature and relative humidity, indoors and outdoors, throughout the various seasons. Therefore, combined temperature and humidity sensors were installed outdoors and indoors (in the most relevant rooms) for the assessment of thermal performance. The equipment used was composed by a thermohygrometer with datalogger (model Klimalogg Pro, TFA 30.3039.IT) (temperature range between 0 and 50°C with accuracy of ±1°C; humidity range from 1% to 99% and accuracy of ±3%), and a set of wireless thermohygrometer transmitters (model 30.3180.IT) connected to the datalogger (the transmitters have the same accuracy values; temperature range from –39.6°C and +59.9°C and relative humidity range from 1% to 99%).

The air temperature and relative humidity measurements were carried out for periods of at least 25 days in each season and with the different thermohygrometer sensors recording data at 30-min intervals. Results on indoor environmental climate parameters were correlated with the outdoor parameters. During these measurements, occupants filled an occupancy schedule where

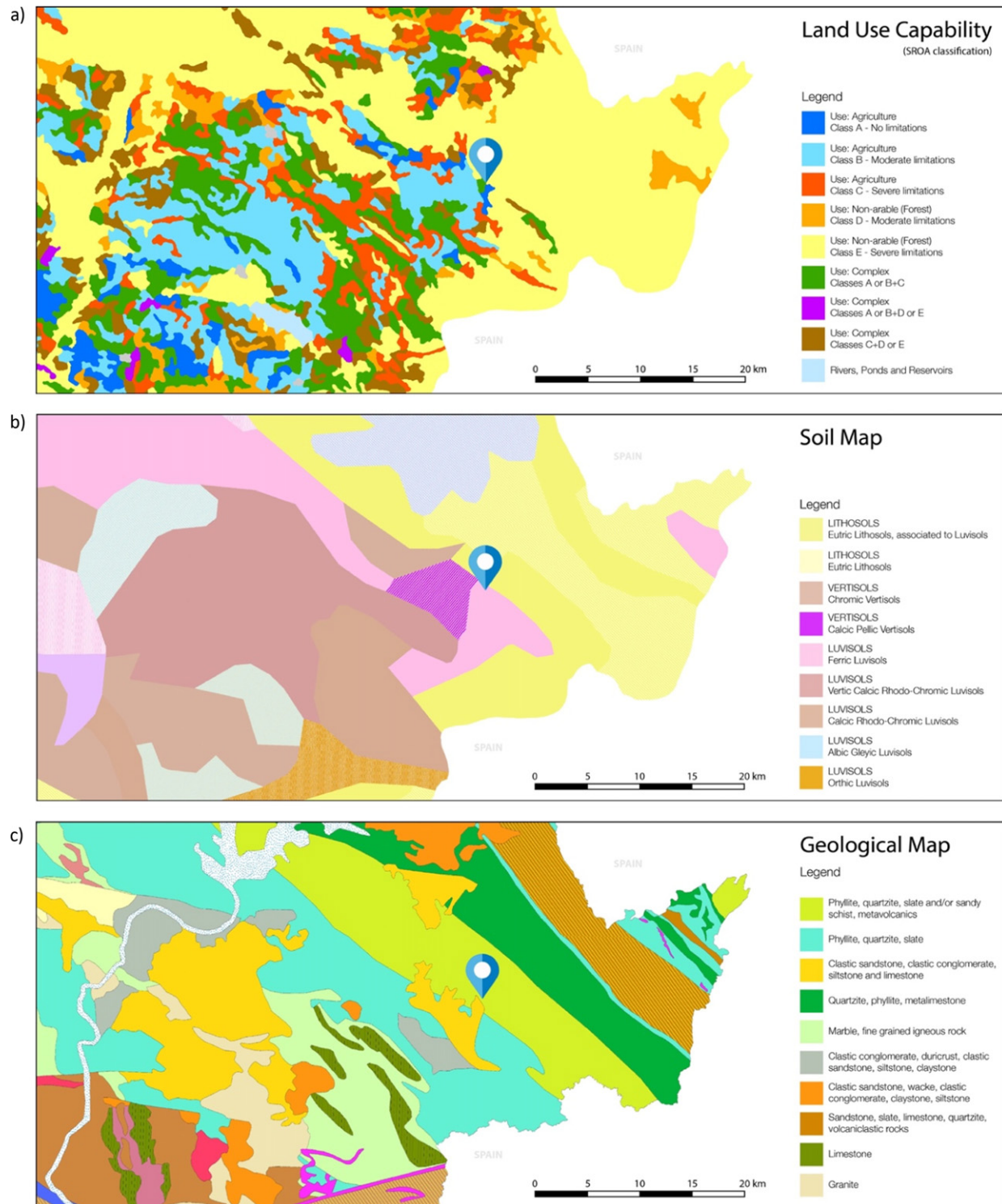


Fig. 3 (a) land use capability map of Safara area. (b) Soil Map of Safara area. (c) Geological map of Safara area. Adapted from APA-SNIAmb, 2018. Environment Atlas – SNIAmb – Agência Portuguesa do Ambiente (online). Available from: <https://sniamb.apambiente.pt/content/geo-visualizador?language=pt-pt> (accessed 14.06.18).

they documented how they used the building (occupation periods, opening windows pattern, for example). These occupancy records were useful to understand, for example, sudden changes in air temperature and relative humidity profiles. The weather data used in the study was collected from the nearest weather station (approximately 5 km). All the measurements were carried out according to standards ISO7726 (2002), ISO7730 (2005), and ASHRAE 55 (2004).

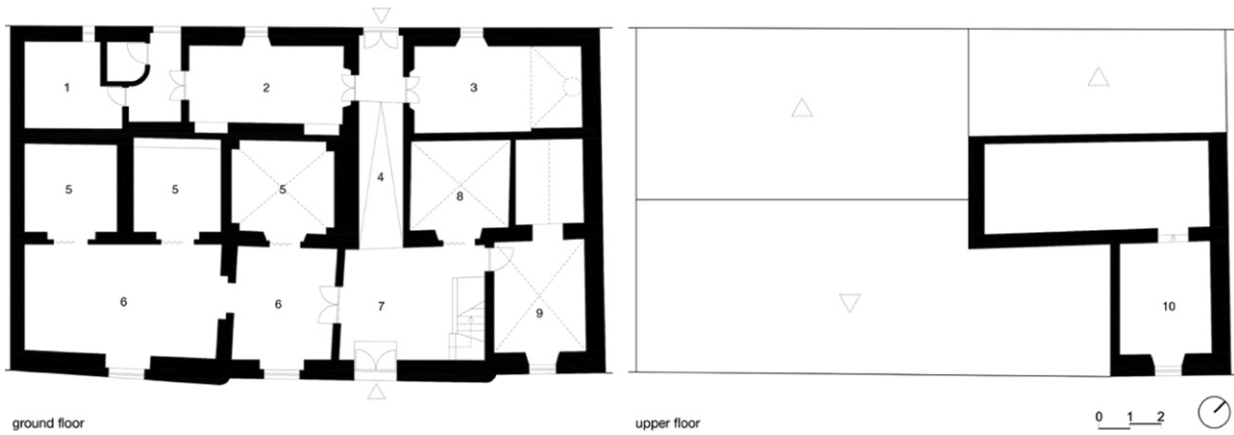


Fig. 4 Floor plans (1 – bathroom; 2 – kitchen; 3 – living room (the kitchen was previously located here); 4 – corridor; 5 – alcove; 6 – living room; 7 – hall; 8 – library; 9 – bedroom; 10 – attic). Adapted from Fernandes, J., Pimenta, C., Mateus, R., Silva, S.M., Bragança, L., 2015b. Contribution of Portuguese vernacular building strategies to indoor thermal comfort and occupants' perception. *Buildings* 5, 1242–1264.



Fig. 5 External view (left), living room (right), with the micro-climate station measuring.

In the analysis of thermal comfort conditions, the relation between indoor comfort temperature and outdoor temperature was evaluated using an adaptive model of comfort, since this is the most adequate model for naturally conditioned areas. To be more representative of the Portuguese reality, the chosen model was the Portuguese adaptive model of thermal comfort (Matias, 2010) developed in the Portuguese National Laboratory of Civil Engineering (LNEC), which is an adaptation to the Portuguese context of the adaptive comfort model of ASHRAE 55 (2004) and EN15251 (2007). The Portuguese model takes into consideration the Portuguese climate (temperate climate Type C according to Köppen-Geiger Climate Classification), typical ways of living and operating buildings. It also considers that occupants may tolerate broader temperature ranges than those usually mentioned in standards and that outdoor temperature highly influences occupants' thermal sensation. A more detailed explanation of the model can be seen in Matias (2010) and Fernandes *et al.* (2015a,b).

The operative temperature was calculated based on the results obtained in the measurements from the Thermal Micro-Climate Station. With the operative temperature (Θ_o) and the outdoor running mean temperature (Θ_{rm}) it is possible to represent in the adaptive chart the point that characterizes the thermal environment condition in the moment of measurement.

Results and Discussion

The analysis of the thermal performance focused on the two most demanding seasons in terms of thermal comfort in the Portuguese context, namely winter and summer.

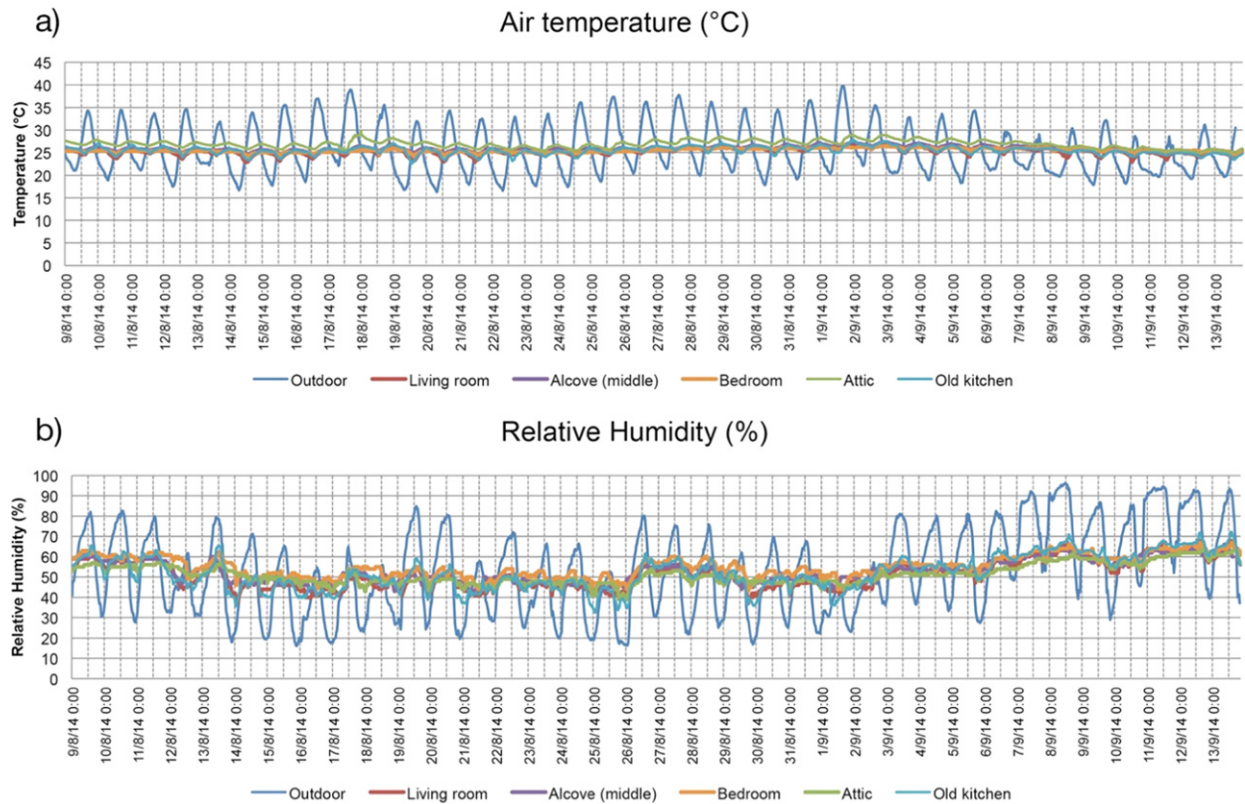


Fig. 6 Thermal performance during summer. (a) Indoor and outdoor air temperature profiles; (b) indoor and outdoor relative humidity profiles. Adapted from Fernandes, J., Pimenta, C., Mateus, R., Silva, S.M., Bragança, L., 2015b. Contribution of Portuguese vernacular building strategies to indoor thermal comfort and occupants' perception. Buildings 5, 1242–1264.

Summer Monitoring

The summer monitoring was carried out from August 9 to September 13, 2014, and the results are presented in Fig. 6. It is possible to verify that during this period the outdoor mean air temperature was of about 26°C. During the day, the maximum air temperature was often higher than 35°C, reaching, in some days, nearly 40°C. The minimum air temperature was usually around 20°C. Although the daily outdoor temperature variation is high, the indoor temperature remained very stable during the monitoring period, with temperature values around 25°C (Fig. 6(a)). Due to its location near the roof, the attic was the room that recorded the highest temperature (27°C), while outdoor peak temperature was around 40°C. The indoor temperature profile shows that the high thermal inertia of the building envelope (e.g., thick rammed earth walls and vaulted ceilings) provides a high capacity to delay the effect of outdoor temperature variation and to stabilize indoor temperature.

The relative humidity profile also presented high outdoor day/night variation, presenting minimum values lower than 20% and maximum values of approximately 95% (Fig. 6(b)). On the other hand, indoor spaces had more stable relative humidity profiles varying between 40% and 60%. These differences were due to the hygroscopic inertia of the building systems, such as the rammed earth walls and the lime plaster, which have a moisture regulation capacity (Fernandes *et al.*, 2015a,b), by absorbing when it is excessive and releasing it when the air is dryer.

Fig. 7 shows the results of the thermal comfort conditions assessment in the living room. This room was chosen because it is where the occupants remain for longer periods during the day. The results showed that the thermal comfort conditions in the building are in the center of the limits defined for the Portuguese adaptive thermal comfort model, i.e., in a condition of thermal comfort. In the survey, one occupant answered as being “slightly cool” and two occupants answered as being “neutral” (comfortable), confirming the measurements.

Winter Monitoring

The winter monitoring was carried out from December 22, 2014 to February 7, 2015. From the results obtained it can be seen that outdoor air temperature presented several fluctuations, with maximum temperature rarely reaching 15°C during the day and minimum values frequently lower than 5°C during the night (Fig. 8). As observed for summer, the indoor temperature remained very stable with a temperature of approximately 15°C (Fig. 8(a)). The indoor rooms with higher temperature variation were the

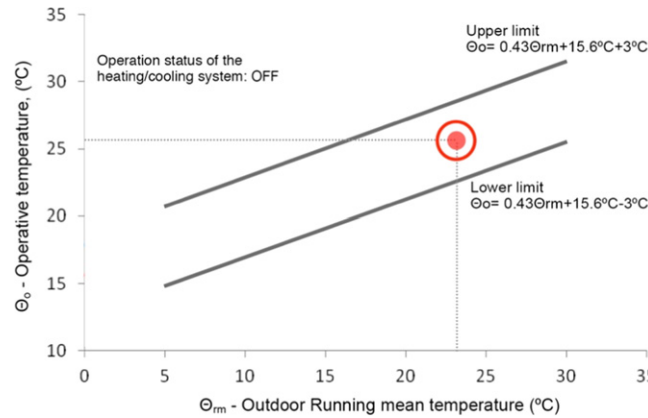


Fig. 7 Thermal comfort temperature (operative temperature) in the living room during summer monitoring, based on the relation between the limits of the indoor operative temperature (Θ_o) for buildings without mechanical air-conditioning systems as a function of the exponentially weighted running mean of the outdoor temperature (Θ_{rm}). Adapted from Fernandes, J., Pimenta, C., Mateus, R., Silva, S.M., Bragança, L., 2015b. Contribution of Portuguese vernacular building strategies to indoor thermal comfort and occupants' perception. Buildings 5, 1242–1264.

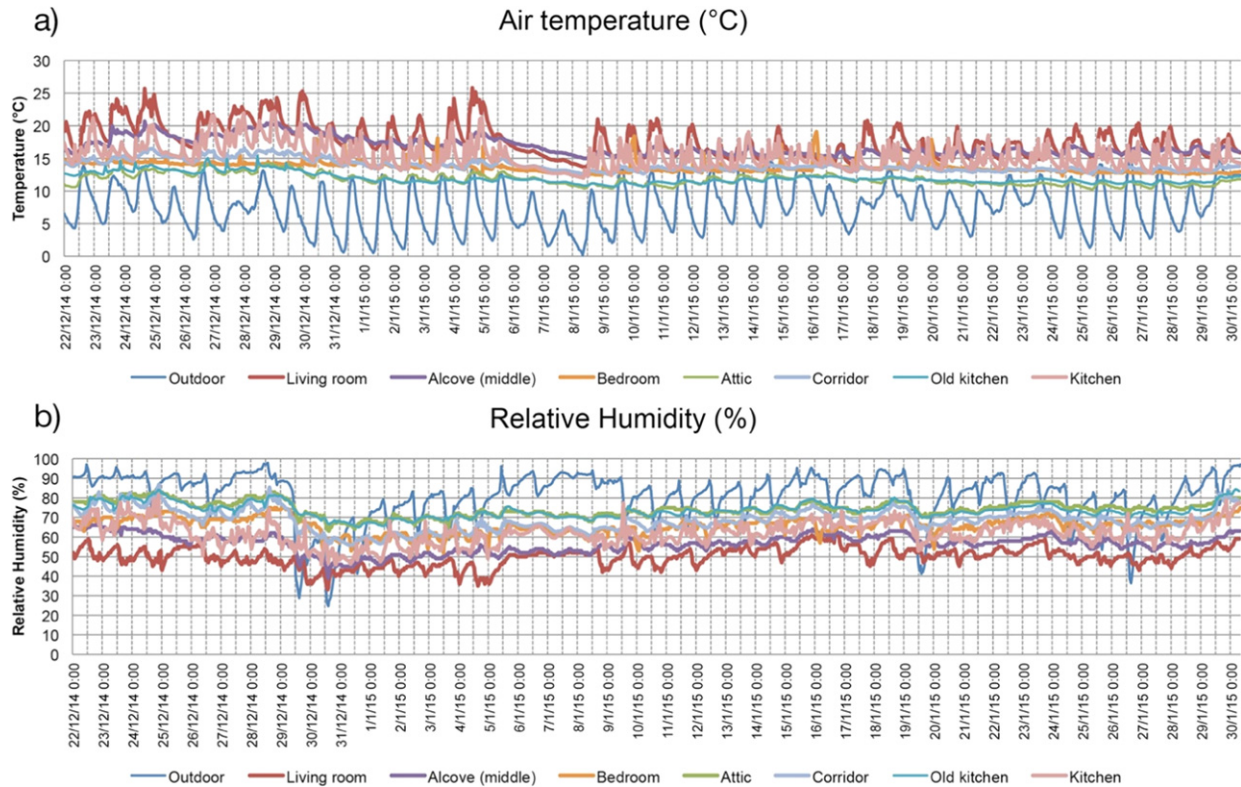


Fig. 8 Performance during the winter. (a) Indoor and outdoor air temperature profile; (b) indoor and outdoor relative humidity profile.

ones where the occupants frequently use heating equipment (stove and electric heating fan), namely in the living room and kitchen. These were also the rooms with better comfort conditions, since the other rooms were not heated and although they had stable temperatures, they were below 18°C. Nevertheless, in **Fig. 8(a)** it is possible to see that when rooms are heated it is relatively easy to increase, and maintain, the indoor temperature above 18°C, and in some situations up to 25°C.

In winter, the relative humidity indoors was very stable, though with values above 60%, with the exception of the living room and alcove (around 50%) (**Fig. 8(b)**). The decrease observed in the living room could be associated with the use of heating (a wood-burning stove).

The evaluation of thermal comfort was carried out with the stove in operation. In the living room the comfort conditions are in the center of the comfort range (**Fig. 9**). However, the thermal sensation in the rooms without heating was

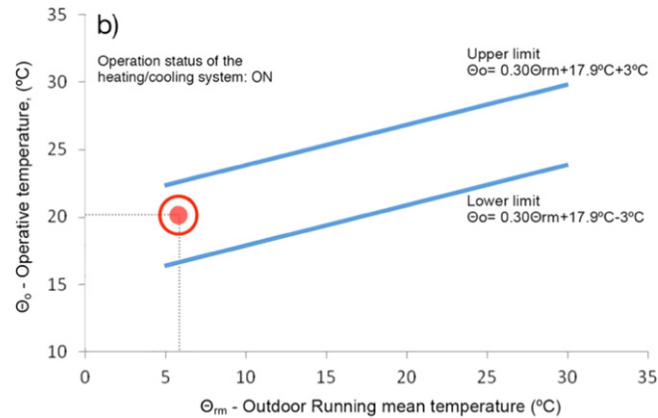


Fig. 9 Thermal comfort temperature (operative temperature) in the living room during winter monitoring when the heating system was on, based in the relation between the limits of the indoor operative temperature (Θ_o) as a function of the exponentially weighted running mean of the outdoor temperature (Θ_{rm}). Adapted from Fernandes, J., Pimenta, C., Mateus, R., Silva, S.M., Bragança, L., 2015b. Contribution of Portuguese vernacular building strategies to indoor thermal comfort and occupants' perception. Buildings 5, 1242–1264.

considerably below the thermal comfort range. Although the indoor temperature was considerably higher and more stable than outdoors, it was not possible to achieve thermal comfort conditions without heating. Nevertheless, it was verified that a simple heating system is sufficient to achieve thermal comfort conditions. The results from survey to the occupants supported the measurements, with three occupants answered as being “neutral” (comfortable) and one as being “slightly cool.”

Conclusions

The results of the thermal performance and comfort conditions assessment of the rammed earth building showed that is possible to achieve indoor thermal comfort just with passive means, confirming a strong relation of cause and consequence between vernacular architecture and the climatic context. The building had a high thermohygrometric performance during summer, the harshest season in this climatic zone, confirming the effectiveness of the passive cooling strategies. In winter, it was not possible to maintain thermal comfort conditions only with passive strategies. However, the thermal discomfort situations were overcome using a simple heating “system” (wood-burning stove).

It was noticed that the thermal inertia of the building, the solar exposure, the shading and natural ventilation devices, the adequate organization of the rooms taking into consideration solar orientation, and the action of occupants are significant aspects that have a positive influence in the indoor temperature and humidity profiles (e.g., promoting passive cooling by natural ventilation during the night and early morning, shutting doors and windows during the periods with incident radiation, etc.).

The results observed in this study allow concluding that with the use of a combined set of passive strategies, such as the passive cooling strategies during summer, it is possible to ensure thermal comfort conditions without using HVAC systems. The adoption of such strategies in buildings in this region can greatly contribute to reducing energy needs for cooling and therefore to reducing energy use and potential environmental impacts during the operation phase.

Considering the results and taking into consideration that the case study is an old building with building elements that are not optimized, it can be stated that the passive strategies used in vernacular architecture have high potential to be improved and adapted to new buildings, allowing thermal comfort while reducing energy demand.

Acknowledgments

The authors would like to acknowledge the support granted by the FEDER funds through the Competitiveness and Internationalization Operational Programme (POCI) and by national funds through FCT – Foundation for Science and Technology within the scope of the project with the reference POCI-01-0145-FEDER-029328, and of the PhD grant with the reference PD/BD/113641/2015, that were fundamental for the development of this study. The authors also wish to thank Mr. João Cordovil and Mrs. Isabel Gaivão for supporting this research work.

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Architecture Follows the Sun: Climatically Responsive Architecture and Process of Design

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Good meaningful architecture emerges at the meeting point when art becomes science and science becomes art - Arvind Krishan

Part I: Unfolding Scenario

These are indeed exciting times to be alive; the moon has been “conquered,” and may pave the way for waves of immigrants from Planet Earth to colonize the moon. Mars is next. And to be part of building higher ever above the clouds, creating architecture that hitherto was not possible. While the Leaning Tower of Pisa (Italy) ([Fig. 1](#)) has been an attraction due to its tilt, perhaps because of a lack of understanding of foundation–soil behavior, now buildings are designed and built to lean as much as 18.5°, designed as “imperfect on purpose” ([Figs. 2 and 3](#)).

Emboldened by what technology can do in design and construction, architecture is reaching ever higher, becoming ever more curvaceous, twisting the logical into a questionable torso. “Smart” buildings, “smart” cities (whatever “smart” means) controlled by artificial intelligence will not only control the habitat and environment we live in, it seems to some that they may provide solutions to all ills of human habitation.

Algorithms produce architecture. They are increasingly becoming a critical part of the process of design. Architecture is formed/deformed by these complex algorithms that are fed into large capacity computing machines ([Fig. 4](#)).

The fundamental question: Is a holistic approach to sustainability based on ecology and the human condition part of any of these algorithms? Can an algorithm be generated based on amorphous issues of sustainable human habitat? ([Fig. 5](#)).

Importantly, a driving force behind change is how people are/will be using buildings of the future. Sensorial adaptive design, supported by technology, robotics, automation, new materials such as carbon nanotubes integrated with glass and new approaches to energy creation, such as solar glass use and storage, is shaping the buildings and cities of tomorrow.

In this era driven by technology, governed by rapid change, human habitat is changing in a manner that is no less than any cataclysm that humanity might have experienced.



Fig. 1 Leaning Tower of Pisa.



Fig. 2 Capital Gate Abu Dhabi.



Fig. 3 Cayan Tower Dubai.

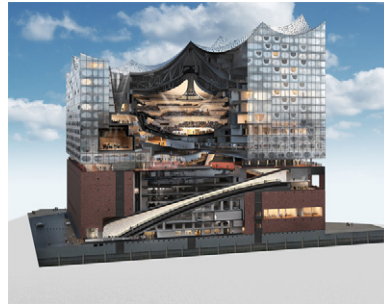


Fig. 4 Elbphilharmonie in Hamburg.

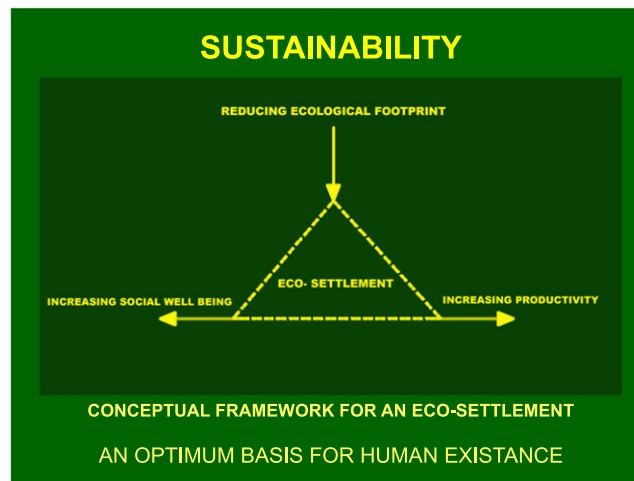


Fig. 5 Sustainability.

The surge to urbanize, a policy adopted by the most populated parts of Planet Earth, India and China (2.74 billion people), which represent 40% of the 7.7 billion world population, as a solution to resolve conflicting issues that human habitat creates and faces, is translating habitat into questionable vertical expansion at unprecedented rate.

Steel and Glass Monoliths

Steel and glass monoliths are marching into every urban development on the planet.

"There's a creepy transformation taking over our cities," says architecture critic Justin Davidson in his TED Talk. From Houston, Texas to Guangzhou, China, shiny towers of concrete and steel covered with glass are cropping up like an invasive species (**Fig. 6**).

Having created megacities and urban spaces that are sterile and lack human scale these shiny steel and glass robots are increasingly creating inhuman living conditions and losing their value, other than creating expensive real estate for the rich and few who build these to live in or use (**Figs. 7 and 8**).



Fig. 6 Glass-steel & concrete towers underway: New York City.



Fig. 7 Tokyo.

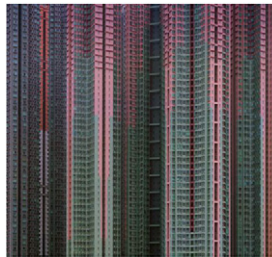


Fig. 8 Hong Kong.

Principles of Design

In principle, fundamentals of planning and design remain: There is a structure, there is a building envelope, and there are services.

Le Corbusier's Brise Soleil

This evolved with a concrete frame structure wrapped by glass envelope bound together by modulating glass mullions in a proportion determined by “musical score.” This was in turn protected by concrete: Brise Soleil.

As contemporary buildings increasingly use glass as a significant cladding material, architectural designers are focusing more on functionality and the aesthetic qualities of glass. While transparency was, and remains, the dominant attribute for most projects in a glass envelope, many designs now use a more complete materiality palette encompassing reflectivity, color, thermal behavior, and surface materiality (Fig. 9).

Ubiquitous use of glass façades has turned these buildings into “glass boxes,” creating uninhabitable spaces both inside and outside. While the glass industry is evolving rapidly, it is still struggling to provide solutions to the basic parameters of architectural design: Daylight, heat transmission, and ventilation (Figs. 10–14).

A New Age “Brise Soleil” has Emerged

The design team sought to create an elegant, eye-catching tower by exploring interactions between simple form, light, and shadow.

The big questions are:

- (1) If control of heat transmittance is the real issue, why the glass envelope tower with a complex solid façade control over the glass envelope?



Fig. 9 High-Court Building Chandigarh (Le Corbusier).



Fig. 10 Capital Market Center – HOK.

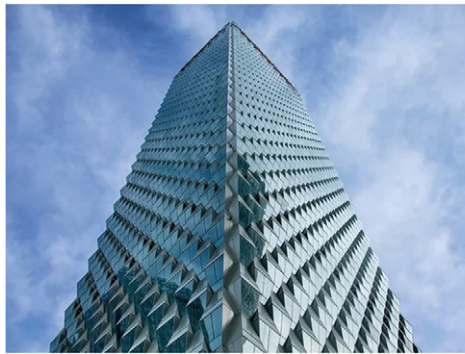


Fig. 11 Green Land Center, Beijing.



Fig. 12 Smithsonian African American History National Museum.



Fig. 13 Al Bahr Tower UAE – Abu Dhabi.

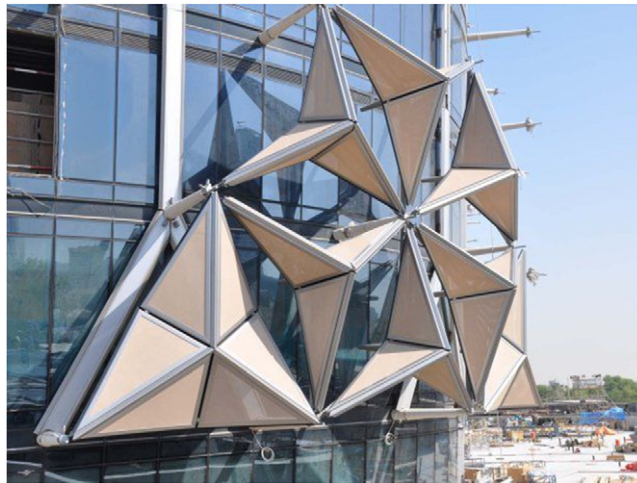


Fig. 14 Al Bahr Towers: The real facade.

- (2) When heat transmittance can be controlled through a traditional/conventional solid envelope and fenestration pattern with controls that can be designed in response to solar geometry, in a simpler manner of construction and effectively, where is the need of Glass envelope?

Conclusion

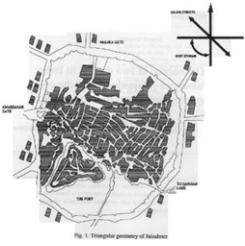
Despite the enormous computing power of super computers, moving from glass towers of different shape, size, and color, realization finally dawned: A glass envelope is not an ideal solution. The glass envelope is now protected with different shapes and sizes, increasing their complexity, where planning and architecture of human habitat are begging for a true solution to generate a truly sustainable habitat. Once again, the past – Indigenous habitat – Is a repository of knowledge that offers the parameters for a solution.

Part II: Lessons From Indigenous Architecture

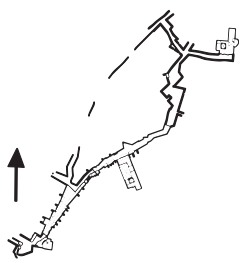
Indigenous architecture has evolved over a long period of time, in response to climatic conditions and socioeconomic parameters, which are largely amorphous. It is a repository of knowledge. A detailed study of two desert habitats, two deserts in India, the hot, dry desert of Jaisalmer (Rajasthan) and the cold, dry high altitude mountainous desert of Leh (Ladakh) was conducted by the author and his teams over period of 3 years (Krishan, 1996).

Jaisalmer and Leh are two cities unique as artifacts of human endeavor in extreme climates. They offer effective solutions to the extreme climates and the terrain.

Planning and design parameters derived from this study are presented here. These are critical for the process of planning and design of human habitat.

S. no.	Description	Jaisalmer: Hot dry desert of Rajasthan	Leh: Cold dry high altitude mountainous desert
1.0	Climate context	Climate of Jaisalmer is a typical hot dry desert. There is very little and unreliable rainfall (average annual precipitation < 200 mm). Two seasons are predominant: Summer and winter. In summer, the daytime temperature can reach up to 48°C (some peak conditions of 50°C have also been observed) and down to 25°C at night. Similarly in winter, temperature varies between 25°C and 5°C. The diurnal range of temperature is between 15°C and 20°C. Relative humidity in summer can be less than 10% in daytime. The sky is mostly clear and solar radiation is intense throughout the year. During the summer months the wind velocity is usually high and there are dust storms during May and June.	Climatic context of Leh is a very cold dry climate. There is very little rainfall; average annual precipitation is less than 115 mm. There is basically one season that is predominant in this area, that is, winter, which becomes very acute for a long period from November to March. The summer, that is, June and July, does offer a comparatively mild climate. The diurnal range of ambient temperatures in winter is about 16°C with the maximum mean recorded as –2.8°C (although a maximum of +3.2°C has also been recorded) and the minimum mean recorded as –14°C (although a minimum of –30°C has also been recorded). The summer diurnal range is above 15°C with the mean maximum recorded as +24.7°C (although +37°C has also been recorded). A diurnal range of 30°C has also been observed by us in the month of October. The relative humidity drops to an average of 30% in summer and rises to an average of 50% in winter.
2.0	Settlement patterns: Is the first level of control in response to climate.	Settlement pattern Jaisalmer  City is served by a triangular fortification and is characterized by narrow winding streets with densely built construction on both sides. It has reasonably large open spaces to serve the community. House planning and design is characterized by a courtyard-type house with an underground level. The house opens onto narrow streets through a hierarchy of spaces that becomes the interface between the street and the house. The entire city ranging from the small house to the Palace of the King is built in locally available light-yellow Jaisalmer's stone, which is basically a sandstone.	 Settlement pattern, Spituk Spituk is a very old monastic settlement dating back 700 years. It is located on a carefully chosen hillock in the valley reasonably close to the Indus River. The entire settlement has been developed on the southern steeply sloping face of the hillock to maximize exposure to the sun. The entire settlement is a very fine example of architectural planning and design. Where exposure to solar radiation is a primary determinant of the settlement pattern and its form. The design of all buildings is carefully controlled in their siting, orientation, plan-form, and total three-dimensional configuration, that is, height, volume, and form. To obtain maximum heat gain through solar exposure the hierarchy of spaces at the community level and individual house level have been so designed and provided such that maximum solar exposure is obtained.

3.0 Street layout



Street layout

Street section mutual shading

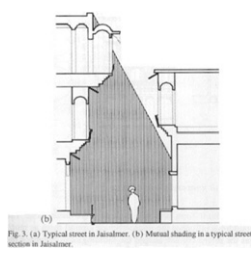


Fig. 3. (a) Typical street in Jaisalmer. (b) Mutual shading in a typical street section in Jaisalmer.

All major streets are oriented almost in the east/west direction at right angles to the direction of dust storms.

The famous Havelies with Jharokas and decorative facades are located on these streets. The streets are relatively narrow and winding. The height of the building compared with the width of the streets is large to create shaded environment for the pedestrians, and social activities on the streets.

Street photograph



Solar access Haliodone study

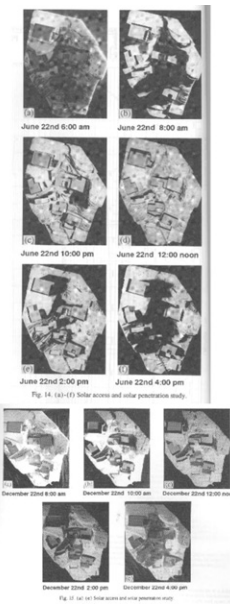


Fig. 14. (a)-(f) Solar access and solar penetration study.

Settlement of Spituk and other indigenous settlements do not have a street layout per se.

However, public circulation areas are clearly defined and a hierarchy of public/semiprivate/private is clearly defined.

Building mass orientation and spatial orientation are so organized that Solar access is maximized and privacy is respected.

A solar access study was done through Heliodon based photographic study. This clearly shows solar access on public and private, exterior spaces during two clear climate seasons, summer and winter, and at different times of the day.

4.0 Generic house

The generic house type in Jaisalmer is courtyard-type of house with unenclosed verandah around the courtyard, a rear enclosed room and an underground space used for storage and living. Variations of the courtyard house occur in the form of a simple single story house and elaborate havelies. A haveli belonging to the Vyas family has been studied in detail and monitored for thermal performance. The more elaborate havelies are normally two- to three- story structures with an underground living space.

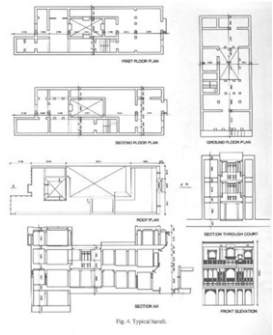


Fig. 4 Typical haveli.

Generic house, Jaisalmer



Generic house, Leh

The generic house in Spituk as well as Old Leh is a compact two- to three-story house constructed in sun-dried mud blocks. The walls are made of dry stone masonry; they are very thick, tapering in thickness from ground floor to the top with average thickness being almost 1 m. The doors and window fenestrations are quite small. The houses provide hierarchy of spaces both enclosed and unenclosed where a good solar exposure is available. The buildings typically do not have any overhangs thus preventing any shading of the surfaces thereby maximizing the heat gain from direct solar radiation.

(Continued)

Chapter 11312 Continued

S. no.	Description	Jaisalmar: Hot dry desert of Rajasthan	Leh: Cold dry high altitude mountainous desert
5.0	Thermal performance	(i) Thermal performance of the haveli type is very good; in this type of building the maximum fluctuation of ground floor temperature was not more than 3.0°C while the outdoor temperature fluctuation was in the order of 15°C. The maximum indoor temperature was 8–9°C lower than the corresponding outdoor temperature. (ii) Ventilation fenestrations that are normally kept open throughout the day causes the building to be warmed up but they increased the air movement providing a greater sensible comfort. (iii) The combined effect of a greater time lag and a small decrement factor reduces the heat flux entering the building. (iv) The courtyard system ensures ventilation through the building even during the calm outdoor conditions. (v) Due to shadow patterns, the buildings receive minimum radiation from direct solar exposure. In the summer, this serves in reducing peak heat flux into.	Thermal performance of the typical Ladakhi houses is represented by the monitored thermal variation for both winter and late October condition (Fig. 13(a) and (b)). The winter monitoring is still in progress. The results are: (i) The thermal performance of the typical Ladakhi house is very good even against the very harsh winter climate. Whereas the ambient conditions fluctuate between minimum low of –20 to –5°C in winter and a minimum low temperature of 3–14.7°C in summer. The internal temperatures stay very stable and at best fluctuate between 12 and 15°C; although this is not in the comfort zone, stability in indoor temperature allows the temperature to be increased by a minimum auxiliary energy source, mostly in the kitchen which is, for this purpose, centrally located within the main living spaces. (ii) The thick mud walls provide a large thermal mass leading to a large time lag and small decrement factor, thereby effectively attenuating the external ambient conditions. (iii) Small window and door fenestrations provide the minimum aperture area for ingress of cold winds. (iv) Windows are typically splayed in the thick mud walls so as to provide minimal area of exposure on the outside and much larger area on the inside face of the wall. The mythical answer to this, given by the local people is that this keeps the evil spirits out of the dwellings. But there is a scientific reason behind this, that is, the splayed window allows a greater distribution of daylight inside the space, thereby minimizing the use of auxiliary energy for lighting spaces in daytime.
6.0	Thermal mass	Thick walls made of local stone effectively control thermal performance of the buildings. It keeps the daytime heat out.	Thick walls made of sun-dried mud blocks effectively control thermal performance of the buildings. It keeps the heat contained inside.
7.0	Conclusions	While indigenous habitats may be considered as old solutions, an in-depth study of thermal performance and analysis has proven they are highly sophisticated solutions to the complex issues of human habitat. Above study of two situations in extreme climates has lessons to teach us for modern planning and design issues. Settlement pattern in both extreme situations is unique response to solar access, wind/dust storm orientation, yet they provide for ample community level open space. Thermal mass–fenestration pattern ratios are very effective solutions. Natural ventilation can be achieved by fenestration location/shading and courtyards. Mutual shading at the entire settlement, street, and house levels is a very effective solution. For reference and detailed study see Krishan (1996).	

Part III: Climate Responsive Architecture: Scientific Process of Design

This section examines the process of design and presents generic approach to design.

Climate Responsive Architecture: The Tool and the Process

The process of architectural design is a complex exercise, involving interactive relationships between parameters of diverse nature and varying magnitude (Fig. 15). Yet, it is the prime generator of architecture as we see and experience.

Ecological process of design (Fig. 16)

Various ideas have dominated architectural thought from time to time. Yet, the fundamental issue of energy as an embodiment of sun, wind, and light – The ecological context – have not been a basic paradigm of design. Therefore, relationship between the built-form and ecology should become the driving force behind the process, based on a scientific methodology – Leading to climate responsive architecture.

The ideal climatic design: Successive modulation of ambient conditions so as to bring internal conditions within the comfort zone.

The relationship between built form and the environment should become the driving force behind this scientific process, based on a scientific methodology.

Available tools of analysis allow critical performance and evaluation of built and overall space network. It seems logical to develop a process, almost in the form of an algorithm, which will help find the optimal form/solution for a given set of requirements and constraints. Evidently based on a design hypothesis, it is possible to generate a set of solutions through this process/algorithm. From this set of solutions, the optimal solution can be arrived at. However, the reverse is not true.

Given a case (the design hypothesis) and a rule (the simulation model) one may obtain by deductive inference the unique possible result (the performance characteristics of the given hypothesis). If instead, one defines the required result (the performance characteristics)

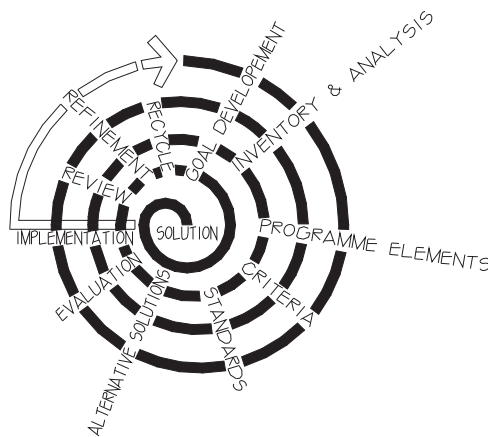


Fig. 15 Process of design graphic representation.

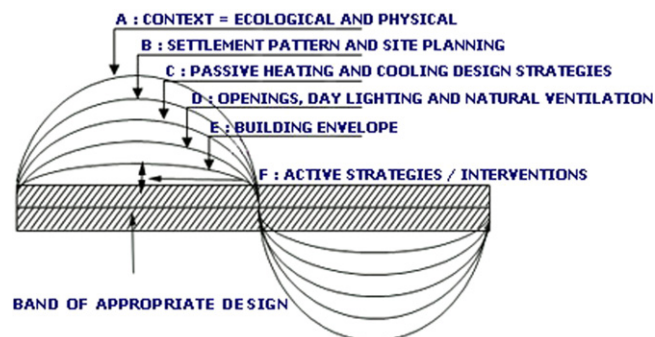


Fig. 16 Ecological process of design graphic representation.

there does not exist a mode of inference by which, using a given rule (a specific algorithm), one may determine uniquely the case (the design solution).

The idea of climatically responsive design is to modulate the conditions such that they are always within or as close as possible to the comfort zone. The ambient conditions over a 24-h period are shown by the line A. For a majority of the time it is outside the comfort zone. Modulations introduced by the landscape, built form, envelope, materials, and other control measures bring the conditions within the comfort range throughout the 24-h cycle. This is the goal of climate responsive design.

However, unlike industrial manufacture, designing is not a linear process. Parameters are interrelated and interactive. Often, they need to be considered simultaneously and in a cyclical manner. Any process of design must, therefore, allow for this flexibility and dynamism. This process and the design tool are outlined in later sections. The basis of our attempt at climate responsive design involves considering climate as a parameter of design in every aspect of the building and built environment. Our first task is to put forth these various aspects in a logical sequence. In effect, we are dissecting the design into its constituent elements so that we can act upon each in turn. The sequence proceeds from macro level details to micro level details.

A qualitative study of these modulations, at each level, is an essential prerequisite to climatic design. What follows is just that. Each level is explained in terms of its climatic implication, the conceptual understanding thereof and its effect on the building design. The various levels together provide an extensive understanding of the interaction of the building and the microclimate. To enable the qualitative and quantitative analysis of landform the energy balance at the surface should be analyzed and the consequent effect of this be taken into account in the design process.

The information given in the preceding text is linked together into a comprehensive design aid by the *design tool*. On the face of it the tool is simply a color-coded ready reckoner. It helps in the formation of a conceptual design strategy. However, it is also linked to the qualitative and quantitative information. It, thereby, draws the reader into a more comprehensive and precise understanding of the requirements towards the design input.

The idea is to optimize the input of the designer and to direct the output of the aid into clear pointers for design. As a result the design-aid package seldom requires the designer to know much more than the basic climatic conditions and the latitude of the place. Only at an advanced stage of design (for instance, while determining glazing areas of sun spaces in a cold climate is more specific data required.

So how does the design tool work anyway? The tool displays the different levels and the broad options available within each. These options are color coded, with the colors indicating the zone they are appropriate for. (There is also a gradation of shades within the colors themselves. The darkest shade indicates the most desirable and the lightest shade indicates the least desirable option.) The color code is as follows:

- Yellow options for hot (overheated conditions)
- Blue options for cold (underheated conditions)
- Green options for moderate conditions

Climates that experience more than one extreme season have to be designed resolving the contradictions as far as possible.

A basic design strategy can be formulated by simply following the appropriate color path. At each level the reference for supporting qualitative and quantitative information is given. These can be referred to, to refine and translate the basic strategy into a design solution. Of course, this is simplifying the case. Each design would have a context of its own which needs to be acknowledged and accounted for. The tool evaluates landform variations but not all projects would have the scope for this. The cause of climatic design would, therefore, not be aided by a gospel like the Ten Commandments for each zone. Like the Commandments they would be seldom followed due to practical problems in doing so. What is needed is a guiding framework that allows each to find their optimum solution. The design tool does just that. The tool indicates the climatic imperative for the options. Therefore, not only are certain options highlighted but the climatic factor and its effect are also indicated. While the options have primary implications they may also have a secondary one, too. This also appears. As a result the user need not work blindly. Knowing the reason for the options being appropriate and the possible implications of each option, the designer need not just follow the color path downwards.

Design Matrix

The tool indicates the climatic imperative for the options. Therefore, not only are options highlighted but the climatic factor and its role is also indicated.

The web link below ties it to a very comprehensive analytical and design method.

<http://new-learn.info/learn/packages/clear/index.html>.

CLEAR Home > Thermal Comfort > DESIGN MATRIX (Climatically Responsive Process of Design >

(This process was developed independently by author and later integrated as part of EU research project by author along-with a team from UK, Greece, and India. It is available in the public domain) (Fig. 17).

Knowledge Based Expert System for Design Decisions

Note: The design matrix-climatic responsive process of design was developed by the author independently and published as part of the book *Climate Responsive Architecture* by Krishan *et al.* published by McGraw-Hill. It was later incorporated as part of an EU project as well.

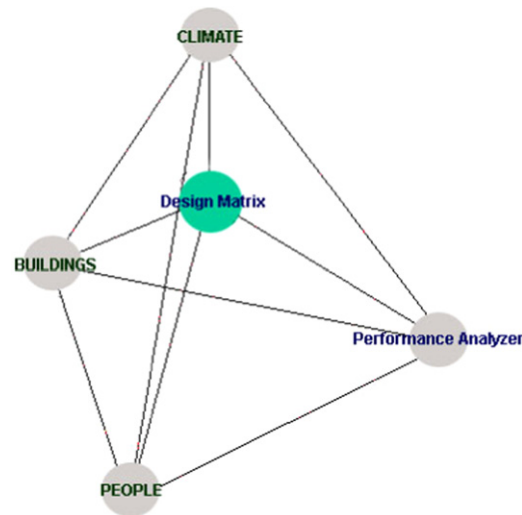


Fig. 17 Design matrix and climatic responsive architecture.

Conclusion

Architectural designs (Part IV) generated by the ecological process of design have responded well to climate.

Part IV: Some Contemporary Solutions

Sustainability and architecture are synonymous terms. While sustainability physically and economically is to a large extent manifest in the habitat built form, it is the scientific temper that will lend a design methodology and process, in order to render architecture sustainable. To achieve this, an energy resource flow–ecological footprint model is suggested, which can help optimize input/output parameters and their relationship. Possible formulation of these parameters leading to a sustainability indicator is also suggested. This leads to a process of design and various actual projects in response to critical issues. Thus, suggesting a new language of architecture.

Preamble

Sustainability, a keyword and catchphrase used by professionals and politicians alike, is an issue that will determine decision making for the next millennium, and it has been an integral part of the life cycle since humankind took charge of its destiny. Although then, it did not have the high-profile definition that it has now. Human habitat and nature were synonymous – habitat of cold deserts of Ladakh (India), the hot deserts of Jaisalmer (India), the plains of Hyderabad (Sind) stand as testimony (Part 2). Yet, today with a technology that can put man on the moon, and clone sheep, we find ourselves on the verge of a global environmental catastrophe.

When the entire planet seems to be hurtling perhaps towards an unsustainable future: Architecture – the human habitat, which is the largest consumer of natural and manmade resources, in my considered opinion – offers a potent tool for moving towards a sustainable future. It more than ever calls for a new language of architecture.

Present Scenario: Urban Dilemma

Central to the issue of sustainability at the global scale is the human-habitat condition that now prevails in large and highly populated countries such as India and China, which together make up 40% of the total world population.

Urbanization in India has risen from 11.4% in 1940 to 28.52% in 1991, is currently 33.56%, and is planned to grow to 75%; this is a phenomenon that is changing the urban context at a very fast rate.

Indigenous cities of Indian civilization, which bear witness to human history of many a millennium – Mohenjodaro, Harrapa, Jaisalmer – are home to architecture of excellence. Yet, the indigenous city in the context of today is virtually overwhelmed by population explosion. Any of the modern developmental/infrastructural solutions prove counterproductive.

Emerging Scenario

A literal crisis situation in urban areas and an alarming depletion in natural resources in India prevail. The environmental conditions thus prevailing demand a radical shift in planning and design paradigm.

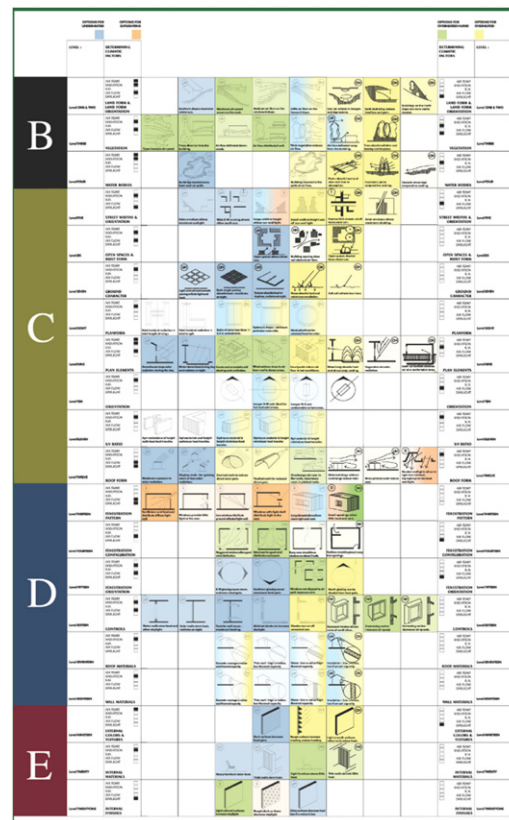


Fig. 18 Knowledge based Expert System for Design Decisions.

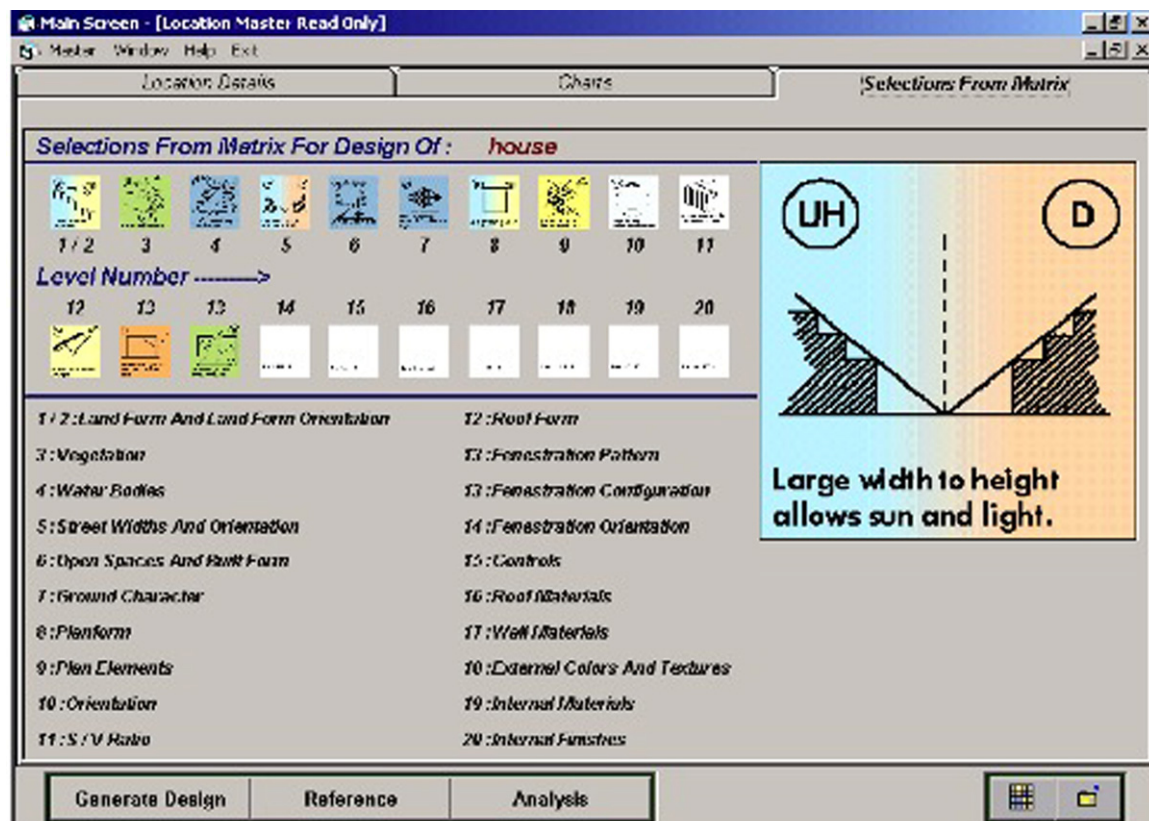


Fig. 19 Design Decision Matrix.

Energy Resource Flow–Ecological FootPrint Model

Human habitat, a physical manifestation of socioeconomic ecological context, is the major consumer and generator of energy and resource. The energy resource flow model presented below illustrates the input–output relationships.

While air, water, and land are the environmental major resource inputs; materials (embodied energy), fossil fuels (primary energy) are the major natural resource inputs. Outputs, that is, emissions, are the major source that modify the environmental context. This input-output intrinsic relationship determines the ecological footprint: The community, city or the region/country – the ultimate determinant of sustainability.

Whereas, direct intervention in the reduction of environmental and natural resource inputs can be made by coupling with renewable energy systems, waste processing and energy extraction offer recycling of energy and resources.

Yet, central to this entire flow model is the habitat/building. It is both in the construction and operation of this habitat/building that energy resource flow can be optimized (Fig. 18).

Outlining the criticality of planning and design of the habitat/building, energy resource flow model becomes systemic basis for design. Wherein, climate-responsive architectural design and ecological planning become the determinants of energy resource flow and offer a powerful tool for optimization (Figs. 19 and 20).

Some Contemporary Solutions

One single parameter that embodies the state and use of natural resources in their various forms is energy. The author presents some contemporary solutions that optimize energy use/consumption through architectural design.

Design principles elicited from analysis of indigenous architecture and the scientific process of design have been translated into design of the following modern buildings at various locations in the country with diverse ecological context, outlining critical architectural responses to key issues.

How Do We Build in a High Altitude, Extreme Cold Dry Ecological Context?

Sustainable solutions for these projects incorporate the following elements and features achieved through architectural design:

- Architectural design optimizes solar exposure throughout the daily and annual solar cycle.
- Daylight distribution is optimized by three-dimensional configuration of the building and reflecting it off design elements: Light shelves and ceiling, providing a uniform and glare-free distribution.
- Embodied energy consumption in building construction is optimized by the use of local materials and relevant technology of construction.

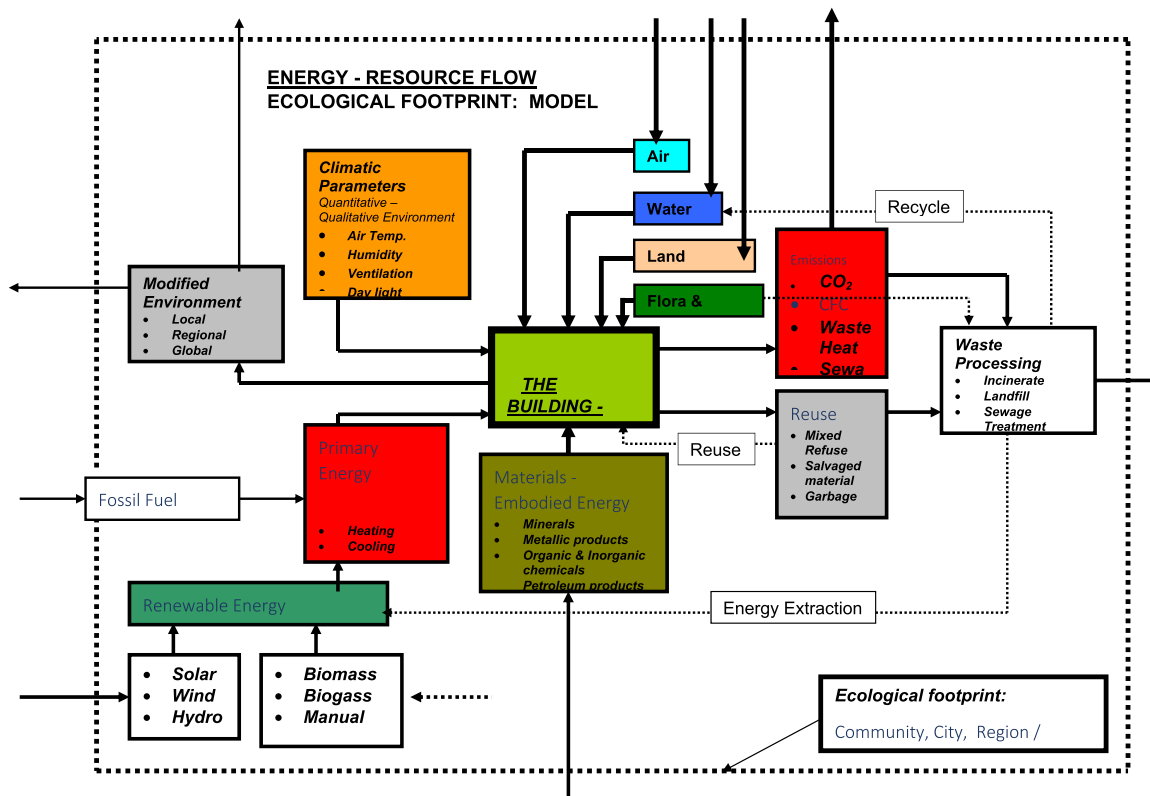


Fig. 20 Energy resource flow–ecological footprint model.

Hill council complex, Leh, India

A major civic structure designed and built as architectural design solutions for this context (Figs. 21–25). Located at 3514 M above M.S.L. in cold dry climate with a severe long winter: October to March end (Min. DBT -30°C).

The main objectives and features of the design besides elements as sustainable solutions are:

- The complex has been designed for the severe winter period. Earth sheltering and earth-berming on the north side and a sunken lobby reduces northern exposure and stabilizes internal temperatures even in critical periods.
- Optimize solar heat gain to office and assembly hall during critical periods of the year, with adequate penetration of sun. While heat gain is optimized, its absorption in the judiciously designed thermal mass provides heat in the spaces over the diurnal cycle.
- Glare-free daylight to minimize lighting load, thereby consumption of energy in the building.
- A new expression of Ladakhi architecture by harmonizing indigenous with modern, incorporating local materials, has been created. This helps sustain the artisan and local art of construction also.

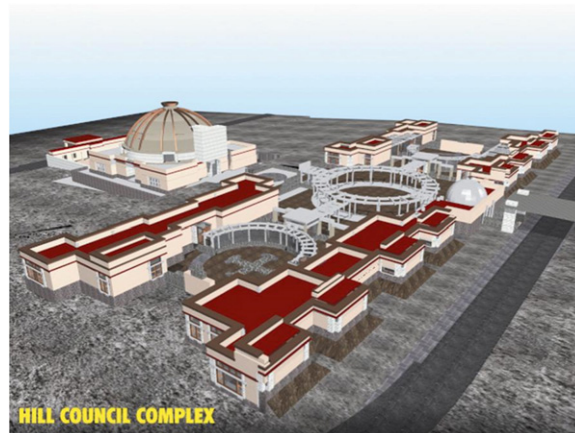


Fig. 21 Bird's-eye view of the complex.



Fig. 22 Section through Council Hall – rendered image.

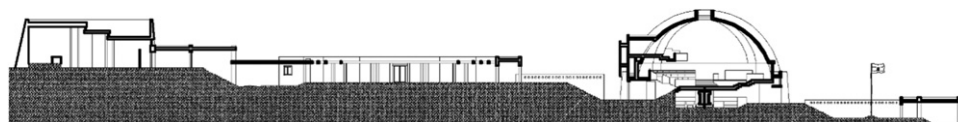


Fig. 23 Section through complex.



Fig. 24 Hill Council Front.



Fig. 25 Hill Council Dome.

What Possible Architectural Responses Can Be Evolved for a Composite Climate and the Context of Urbanity of Chandigarh?

PEDA office complex, Chandigarh, India

Located at Chandigarh, on a flat practically square site with no major topographical variations. Chandigarh as a city lies on the planes at the foot of Lower Himalayas, in a composite climate context.

- Here there are climate swings over the year, that is, very hot and dry period of almost two and a half months (Max. DBT 44°C) and a quite cold period of shorter duration (Min. DBT 3°C). The hot dry period is followed by a hot humid monsoon period (Max DBT 38°C and Max R.H. 90%) of about two months with intervening periods of milder climate.
- Equally important for Chandigarh is the context in space and time. Chandigarh, a bold experiment in city planning and architecture, was based on the professed ethos of design: Build with climate. Le Corbusier put into practice his theory on Brise Soleil. While the major buildings of the Capitol Complex extensively employed Brise Soleil in its various forms and applications, many residences designed by Pierre Jeanneret, Maxwell Fry, and Jane Drew made solar shading devices as a major element of design and expression. Yet, in its application both the method and device lack a scientific basis. Many times its repetitive use on buildings irrespective of orientation and the use of similar devices on different facade belie the claim.
- Can the design of a building be based on a scientific process of design, which responds to the ecological context and yet does not violate the urbanity of Chandigarh and its urban palette, that is, the material, texture, and color?
- That is the unparalleled professional challenge to which we have addressed ourselves.
- While the three-dimensional form of the building has been developed in response to solar geometry, that is, minimizing solar heat gain in the hot dry period and maximizing it in winters, to achieve a climate responsive building an innovative concept in architectural design has been developed. In place of the central loaded corridor plan stacked on top of each other to make various floors, which has virtually become the generic form for an office, the PEDA building is a series of overlapping floors at different levels in space floating in a large volume of air, with interpenetrating large vertical cutouts. These cutouts are integrated with light wells and solar activated naturally ventilating domical structures (**Figs. 26–32**). Consequently, the design is

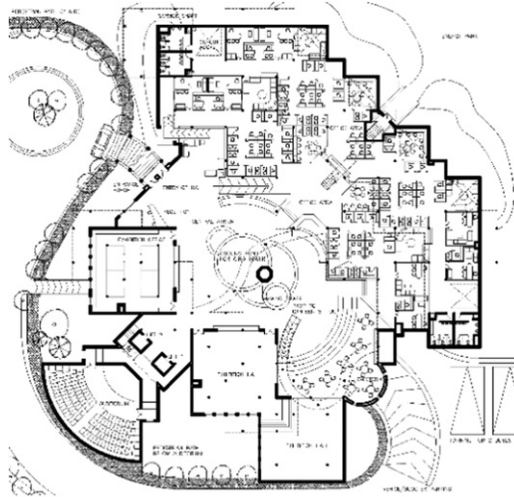


Fig. 26 Plan of complex.

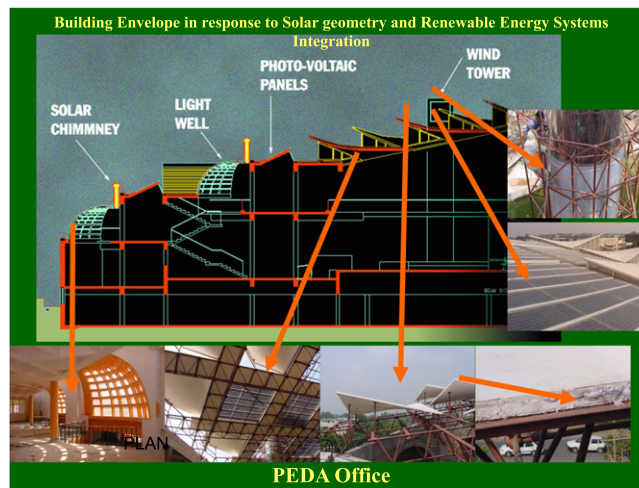


Fig. 27 Building envelope in response to solar geometry and renewable energy systems.



Fig. 28 Interior open plan, integrating wind tower, cooling water pond, integrating PV roof system.



Fig. 29 Central water tank cooling system coupled with wind tower.



Fig. 30 Domical vault, designed in response to solar geometry for daylight efficiency natural ventilation system.



Fig. 31 Office floor with domical day light system.



Fig. 32 HRH Prince Charles visited the project.

thermally responsive to its climatic context and very good daylight distribution is achieved, thereby minimizing consumption of electrical energy.

Awards

The PEDDA building project has been awarded the Star Award several times ([Fig. 33](#)) and the Sustainable Architecture Exemplary Project Award ([Fig. 34](#)).

Conclusion

When we were designing and building this project, neither Griha Council India, nor LEED in the United States, existed. We were designing and producing good, meaningful architecture, which is what sustainable architecture is all about.



Fig. 33 5 Star Award by Bureau of Energy Efficiency as the most energy efficient building in the country.

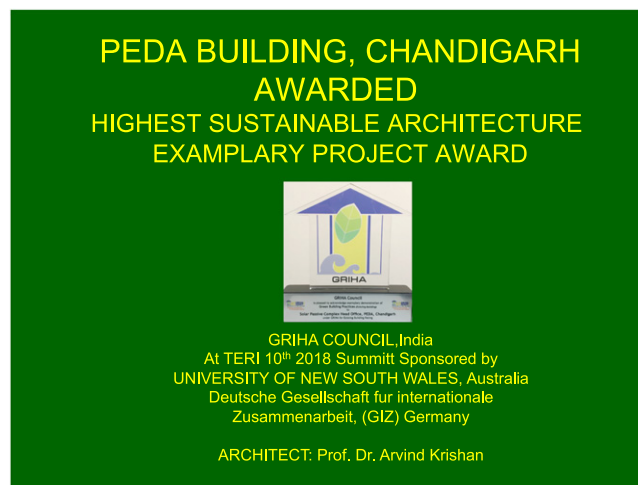


Fig. 34 Sustainable Architecture Exemplary Project Award Griha Council, India, at TERI 10th 2018 summit.

What Can We Do With the Existing (Retrofit)?

There is the equally important issue of the existing stock of buildings that consume a disproportionate amount of natural resources in the form of energy in various forms. If by retrofitting we can render these buildings energy efficient, that will indeed be a great step towards sustainability.

Himurja building, Shimla, India: Limitations converted into opportunities

This perhaps is a befitting example of a solution in retrofitting and redesignation of use. A two-storied existing building being used for shops and warehouse use was handed over to us to be redesigned as a climate responsive building and converted into offices (Figs. 35–42).

- The building was redesigned as a four and half storied building with a hybrid R.C.C. frame (existing) and steel structure for the additional floors.
- Solar heat gain was optimized to all office during critical periods of the year, with adequate penetration of sun and protection from mutual shading achieved through architectural design.
- Glare-free daylight was used to minimize lighting load thereby consumption of energy in the building.
- Distribution of heat within the building is achieved through a double convective loop.

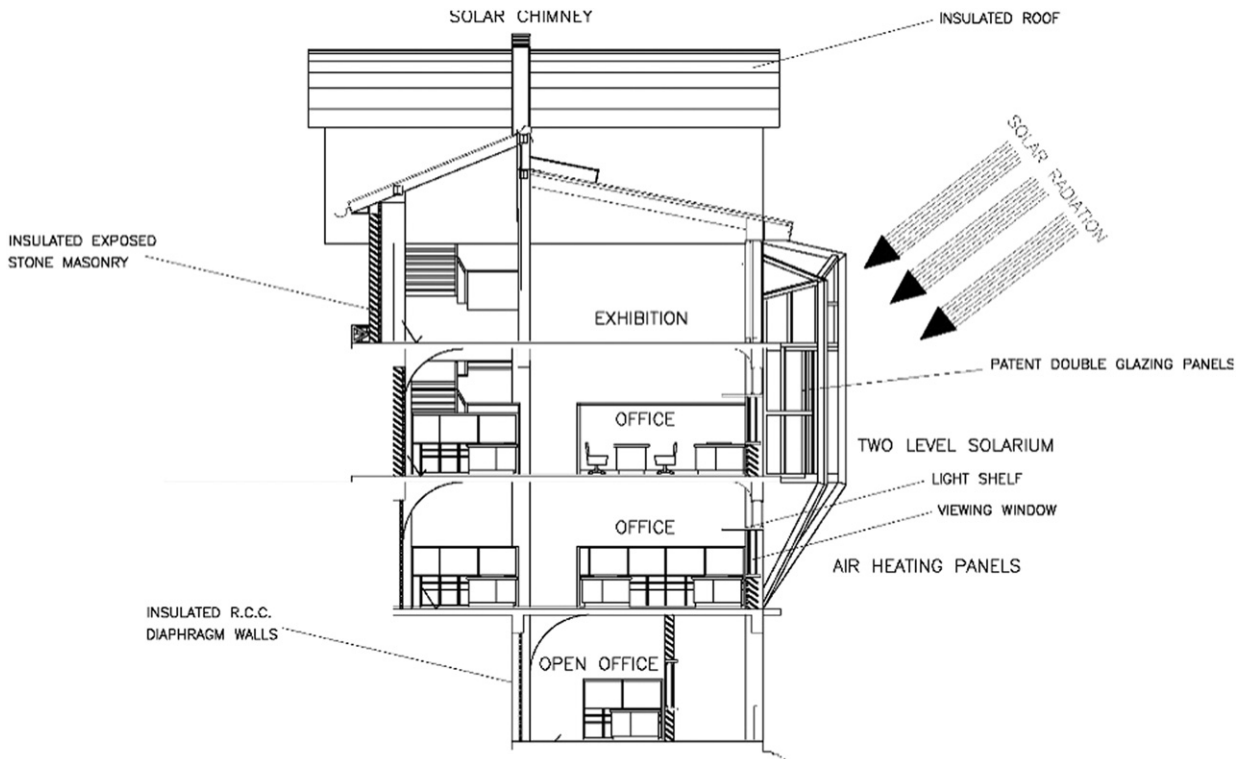


Fig. 35 Final redesign.



Fig. 36 Before retrofit.

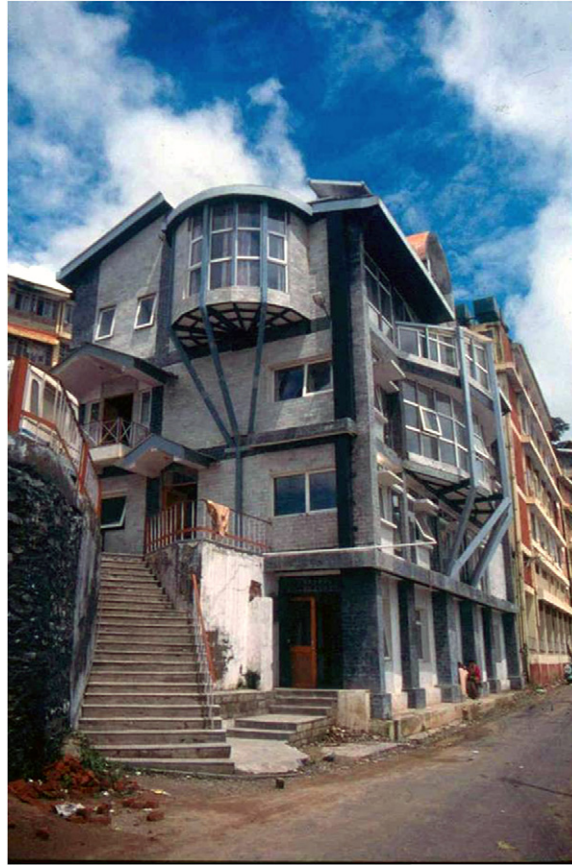


Fig. 37 After retrofit.

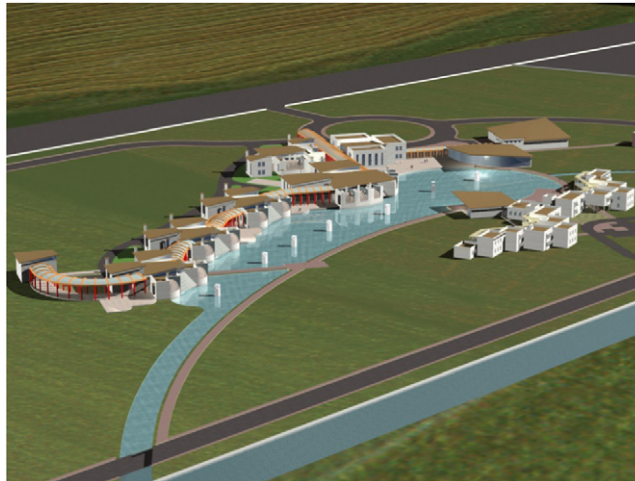


Fig. 38 Sardar Swaran Singh – National Institute of Renewable Energy, Ministry of Non-Conventional Energy sources, Government of India. View of the Complex.

Can We Evolve a New Language of Ecological Architecture for an Innovative Institute?

The author was invited to participate in a limited competition for the above project (Fig. 38). An innovative architectural design evolving a language of ecological architecture presented by the author was selected by the jury for implementation of the project.



Fig. 39 Site/master plan.

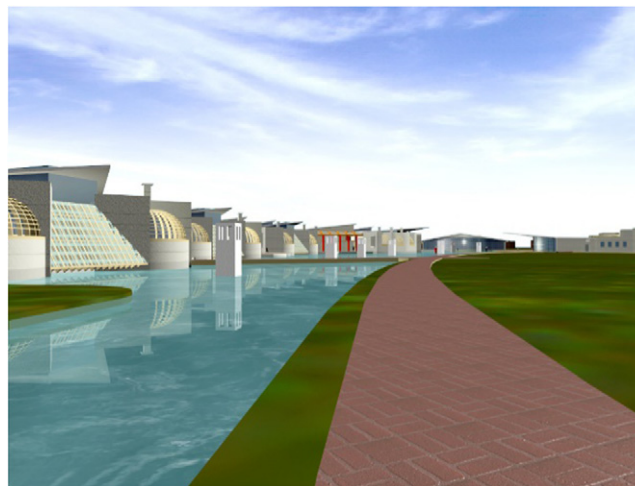


Fig. 40 View from water-body.

Strategies for planning and design

- Control of microclimate of the site by generating a water-body drawn of the canal and by forestation of the site.
- Entire complex and each building designed as a climate responsive-solar passive building.
- Architectural design: The primary generator/tool for developing a low energy building design.
- Maximize environmental control through naturally conditioned laboratories and spaces.
- Maximize use of daylight to minimize electricity consumption in daytime.
- Couple evaporative cooling from water-body with building design.

Ecological architectural design of R&D wings

Since sophisticated R & D work is to be carried out in these wings, it is envisaged that three types of laboratories will be required, that is:

- Naturally conditioned laboratory
- Hybrid

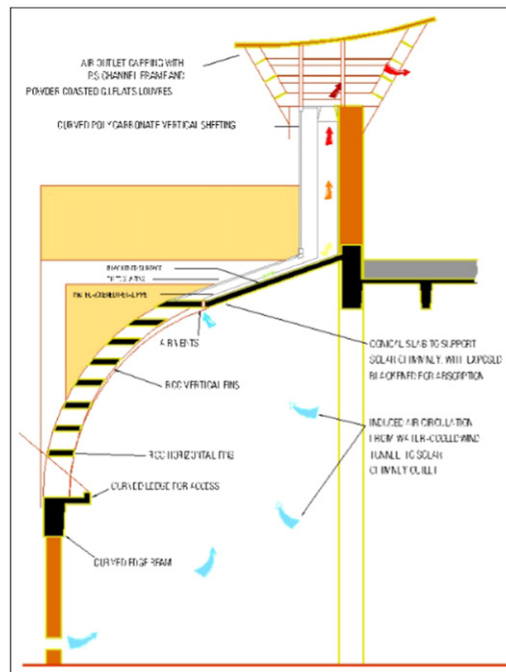


Fig. 41 Solar chimney.

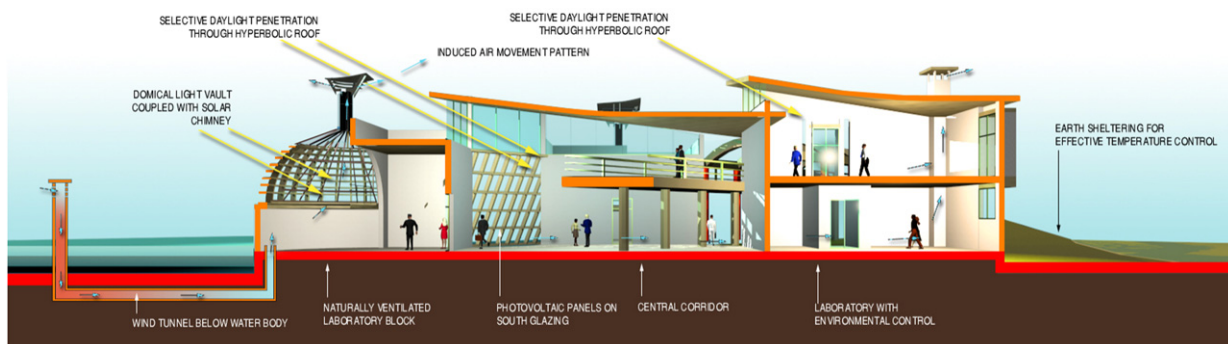


Fig. 42 Typical section through domical vault and solar chimney.

- Environmentally controlled through HVAC systems.
- The R&D wing has therefore been designed to couple the naturally conditioned laboratories and spaces to the water-body through wind towers coupled with earth tunnels to the laboratory and building spaces.
- Domical light vault designed for adequate daylight distribution integrated with solar chimney on domical vault coupled to wind towers.

Roof system

- The roof forms the critical element of the building design since it attracts the maximum solar heat gain and can be used as an element to generate efficient daylight distribution.
Hyperbolic paraboloid used as the structural element for the roof to:
- Optimize on structural design since this is the only doubly curved surface generated by a straight line, making it simple to construct since it generates only direct stresses.
- Double curved surface responds naturally to solar geometry cutting of solar heat gain due to summer sun and allowing penetration solar heat gain for winters.

Integration of renewable energy systems

- Solar chimneys integrated with building design for natural ventilation.
- Photovoltaic panels sandwiched in translucent panels on the south-facing central spaces for generating electricity and allowing penetration of diffused daylight.
- Water management system to be coupled with entire building complex for recycling of water and waste management.

Phase 1 of the project has been built

Photographs are not available yet.

See also: Insulation Materials for the Building Sector: A Review and Comparative Analysis

Reference

Krishan, A., 1996. The habitat of two deserts in India: Hot-dry desert of Jaisalmer (Rajasthan) and the cold-dry high altitude mountainous desert of Leh (Ladakh). *Energy and Buildings* 23 (3), 217–229.

Bamboo Structural Technology

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Divya Chand, Indian Institute for Human Settlements, Bengaluru, India

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Traditions and Rationale for Use

Though bamboo has been widely used in construction of ordinary houses and small structures traditionally, it has always been seen as the “poor man’s timber”, probably because of its being cheap and available, and being usually worked upon with less sophisticated tools as compared to carpenter’s tools used for timber. Bamboo is usually split, laced and lashed, rather than sawn, planed and nailed or bolted. The geometry of the surface that can be created with a bamboo framework is less true than that can be created with timber, leading to the larger possibility of leaks in tiled roofs when compared with timber. Bamboo treatment technology languished, practically non-existent, while developments in timber continued to dominate the building industry. This has created an unfortunate bias against the use of bamboo that persists even with modern techniques of construction described in this section. As with all such biases, bamboo has to often prove itself much better than industrially processed material in order to become accepted in the mainstream.

However, with increasing stress on timber resources globally and limitations on the felling of trees, bamboo has become an attractive wood substitute. As a wood substitute it is preferred to be supplied as treated and compressed sleepers rather than as poles, which is the more natural way to work with bamboo. With modern treatment and preservation techniques, the last quarter of the twentieth century is an era which can be termed as the age of development of engineered bamboo.

Bamboo, botanically a grass, represented by a thousand-odd species, is woody, strong, and very versatile in its applications. It is an abundantly available natural resource, especially in the tropics. Probably more significantly, it grows extremely quickly (at least in areas with sufficient water, even marshes), is tolerant of most qualities of water for its growth, and the plantations sustainably produce much more timber per unit area sown per year as compared to trees. Bamboo, being a grass, is amongst the fastest growing plants in the world. Trees can take 30 years to grow to the same height that a bamboo plant may achieve in just 90 days. Some bamboo species are known to grow even 90 cm in a day. Bamboo can be harvested in 3–5 years from its planting, which makes it a rapidly renewable resource.

Bamboo roots are strong and the clumps can hold soil and prevent its erosion. The fast growth of the plant utilizes carbon dioxide and releases oxygen, making it efficient in sequestering carbon. If we compare the carbon sequestering potential of bamboo with tree forests, the scientific opinion of their relative potentials is divided. While [Seethalakshmi et al. \(2009\)](#) argued for bamboo forests to be seen as a major climate change mitigation strategy, based mainly on their very large overall biomass productivity, recent studies in South America cited by the [National University of Misiones \(2017\)](#) point out that bamboo forests may even halve carbon storage in comparison to tree forests. However, all studies point out bamboo’s socioeconomic and soil conservation benefits.

Raw bamboo is abundant and extremely low cost, even after treatment. By way of example, a 50 mm dia., 4 m long, plain age graded pole of *Dendrocalamus Stocksii* in central India costs USD 2, and it doubles in price after pressure treatment with Copper-Chrome-Boron (CCB), while a roughly equivalent steel pole 40 mm dia. and 3 mm wall thickness of the same length costs USD 6 and if treated by galvanisation, USD 14. Thus, bamboo costs can be significantly lower than that of steel or timber. Therefore, the technology needs to be developed with the confidence that, barring a demand that outstrips supply too soon, this material might be a disruptive material for structures for the better part of this century.

Properties and Applications

Bamboo’s structural properties have been compared with steel mainly due to the fact that its mechanical properties per unit density are better than the same properties for steel. The maximum net density of bamboos is at most about 900 kg/m³ whereas steel has a standard density 8.72 times as much at 7850 kg/m³. Compared to that, typical values of strength of these two materials are summarized in [Table 1](#).

This simple comparison puts bamboo (per unit weight) higher than steel on important tensile and shear behavior properties. The poor figures on compression and bending are partly caused by the extra conservative factors of safety taken by the Code makers of IS 15912. All this doesn’t, of course, make bamboo “stronger than steel” as often claimed by bamboo apologists and the lay public, but definitely categorizes it as a very good natural material ([Awalluddin et al., 2017](#)) able to take considerable longitudinal compression and tension mainly due to the longitudinal bundling of its fibers. Bamboo also has reasonable ability to take bending compressions and tensions.

In any case, IS 15912 says: “Unlike timber, bamboo properties do not relate well to species, being dependent among other factors, on position of the culm, geographic location and age. The practice...to base designs on safe working stresses...may be

Table 1 Comparison of approximate design properties of natural bamboo with mild steel – taking poor properties for bamboo

	Density (kg/m ³)	Compression strength (N/mm ²)	Tensile strength (N/mm ²)	Bending strength (N/mm ²)	Shear strength (N/mm ²)
Poorest bamboo	900	10.5	~100	13.2	~20
Mild steel ($f_y=400$)	7850	260	400	350	160
Ratio bamboo/steel	11.5%	4%	25%	4%	12.5%
Ratio bamboo/steel per unit weight	100%	35%	218%	33%	109%

Note: Adapted from Wei Wen, D.T., 2015. The strength of bamboo in comparison with other construction materials. Available at: <http://danieltiongweiwen.blogspot.com/2015/05/research-question-how-does-properties.html> (accessed 20.01.19). IS 15912 2012 (17): Structural Design Using Bamboo – Code of Practice (Indian Standard Code by Bureau of Indian Standards).

adopted to bamboo with the limitations that *traditional experience rather than precise calculations* generally govern the detailing.” (emphasis added).

The strength of bamboo seems to lie in the silicone like outer skin that covers the culm, which therefore cannot be removed, but is unfortunately too smooth for it to be coated. Thus, most bamboo treatments are effected by hot dipping under atmospheric or higher pressure, so that the preservative material (often boric-borax or CCB, but also other materials) may steep into the fibers of the bamboo.

Due to its structural properties, bamboo can be used in a large number of superstructure applications in building and construction, for columns, beams, floors, roofs, etc. It can also be used for finishing, such as in floors, wall panels, and ceilings. Its limitations are a lack of sufficient research into the variability of its properties according to age, species, and other environmental conditions, lack of research on the performance of joints and junctions, its tendency to leach preservatives when exposed to rain, making it prone to attack by borer or fire, and, so far, its inability to provide the same level of “stiffness” as concrete when it comes to the fabrication of multi-floor buildings. Though bamboo exhibits borer infestation caused by the presence of eggs in the material as it grows, it is considered termite-resistant, which is a common misconception since termites thrive on woody cellulose.

Bamboo construction can be mechanized and prefabricated, making on-site installation very rapid and reliable. Some work to codify bamboo for structural use has been initiated in India and in California, and this area may probably develop rapidly with advances in development of bamboo structural technology in the coming decades. Until that happens, bamboo use remains outside the domain of “formal” structures and is used as an upgraded traditional material in areas where its use is common (such as Vietnam, parts of South America, parts of southeast Asia, and especially the island of Bali, Indonesia).

As a natural and rapidly renewable material, bamboo has the potential to replace both wood and industrial metals such as steel used in construction, after sufficient engineering advances have been developed and integrated into its harvesting, treatment, preparation and fabrication.

Forms

Bamboo can be used *whole*, or by laminating multiple slats of bamboo from wide-diameter and thick-walled species such as well-known Chinese moso (*Phyllostachys edulis*) to create a timber/board like workable material called *bamboo-wood* or bamboo strip-board, or by weaving strips into a mat and using them like timber veneers by hot pressing these into multiple thicknesses of bamboo mats or *bamboo ply* (this is generally better than timber plywood and board, being stronger, with better dimensional stability, smoothness, and resistance to humidity, fire and insects).

The following sections outline the forms and methods of use of bamboo in various building elements.

Foundations. Being an organic material, bamboo foundations are not recommended. Bamboo buildings are designed with conventional (masonry or concrete) foundations. Bamboo has been traditionally used as a pile material for driven pile foundations of buildings (similar to the wooden pile foundations of the Taj Mahal in Agra) as well as to prevent soil erosion along banks of earthen waterways.

Walls. The easiest and most common use of bamboo is to split low-diameter species and use half bamboo lashed into a grid as wattle and daub it (plastered on both sides) with raw or stabilized earth. This is a common type found in many low-income settlements in south Asia, and though very easy to make and affordable, these walls are not very durable, with a tendency to not resist flood and to decay by organic impurities.

Columns and beams. Traditionally, these have been erected with (untreated) whole bamboo with lashed or laced junctions, nailed or bolted together. In some modern applications, fiber-reinforced plastics have been used to cover lashed joints. The techniques for bolting and grouting junctions with a cement or concrete slurry pioneered in south America has allowed much larger spans to be attempted in the last few decades.

Bamboo columns and beams can be integrated into single structures displaying characteristically signature shapes, such that the difference between a column and its beam become meaningless, and the whole assembly may be considered a frame. Bamboo in a heated state is easier to bend to shape as compared to timber (even though it has a tendency to blow-back when released from its jig). This technique in fact has given rise to bamboo structures being *expected* to be curved in form in the minds of most commentators and critics, with single-curvature shapes (vaulted, arched, domed) or double-curvature shapes (shells, twisted surfaces).

Floors. Though the structure of a floor can be formed by trussing and framing techniques as developed for columns and beams above, the floor plate or covering or finish that is increasingly used in modern buildings (even mainstream ones) is bamboo strip-board flooring, which acts as an alternative to wooden plank flooring, with similar details. In traditional work, the framework was also covered by flattened, split bamboo culms or bamboo mats, though both do not create a fully sealed surface.

Roof coverings. Though the structure of a roof can be formed by trussing and framing techniques as developed for columns and beams above, the roof coverings can be made from halved bamboo large-diameter culms (used in an alternating up-down configuration, every alternate culm acting as a drain), or overlapped bamboo mats, or nailed shingles made of bamboo, slate or timber. For better class of buildings, a separate waterproofing layer is usually added below the shingles mats or culms. Roof coverings can also be formed by nailing chicken wire-mesh and steel weld mesh on the bamboo framework and slapping ferrocement on this armature.

Contemporary Technologies

Despite its remarkable structural properties, bamboo use has been greatly restricted to interiors, such as flooring and roofing elements and temporary structures. This is probably due to a perception bias about the material and lack of knowledge about its properties. Even assured practitioners may face difficulties in working with bamboo due to the natural variability of the material, vanishing local skills, a lack of thumb rules and guidebooks of structural design data and exclusion from building codes and manuals, but most importantly, the tendency for modern engineering to be based on processed, artificially manufactured materials as against natural ones because of their relative predictability in behavior.

While bamboo has been used for making houses and sheds for centuries, recent advancements in horticulture (such as the development and propagation of species that show very little nodal prominence, so geometrically more like poles) and treatment has allowed for a leap in architectural possibilities using bamboo. With the right kind of treatments, the right thickness of bamboo poles, complex joints made employing fiberglass and metals, bending technologies, and complex 3D-modeling using computers, it is now possible to create large span and multi-story structures using bamboo. Such practices can be observed across the world today from south American to southeast Asian countries. The method of design and construction adopted in each part of the world is unique, using locally available species, deriving from the local traditions and available technologies while being inspired by best practices around the world. Many case studies can be observed today where large span structures are built using bamboo poles that are bunched to create columns and frames for arches, vaults, domes etc. There have been experiments in low rise multi-storey structures in bamboo as well, with some remarkable examples in Bali.

Limitations

The above examples are exceptions though, and what holds back the widespread use of bamboo are some technical issues that still need much work from the structural and technical science.

Fire retardance. Since bamboo is a kind of timber, the tendency for the structure to catch fire is more. Though, like timber, it behaves “better-than-steel” in conditions of fire, retaining its resistance to forces over a longer period than steel, it is not easy to coat or encase in concrete to provide a fire-proof layer without losing its characteristic elegance. Hollow poles of bamboo also represent a high fire risk. Though the skin of bamboo stems create silicates that make it not highly flammable, this is often sanded off to create a smoother look for interior elements in a building increasing the fire risk. In exterior elements, the possibility of fire coatings and treatments leaching out of the material is real.

Fire prone-ness becomes even more critical in case of multi-storey and high rise buildings. In this context, the multi-storey timber code in Canada (that accepts buildings up to six storeys high) can be adapted to bamboo structures.

There is no standard practice to increase the fire safety in buildings. Around the world different practices are adopted such as filling the cavities with concrete, adding a panelling or plastering over bamboo elements to retard fire. The boron and boric acid treatments done on bamboo to increase the pest resistance also provide an added advantage as fire retardants. Recently, various proprietary fire resistant coating materials have been tried out on lightly sanded bamboo poles and provided good results.

Crack control. Bamboo has a round cross section, often with a variable internal and external diameter. This complicates the execution of joints between different poles since multiple drillings and tightening of bolts may be mismatched and may cause cracks in the vertical fibers. The heating and bending of bamboo may also cause cracks.

It is difficult to avoid these cracks unless the craftsmen working are extremely skilled and experienced. Because bamboo is mostly used in longitudinal stresses, in trusses and columns, often the cracks do not cause any structural disruption unless they are close to the horizontal nodes. It is difficult to ascertain the fatality of cracks since there is no set quality parameter for this and it may differ according to species, and on the function of said bamboo pole in the completed structure.

Brittleness. The Young’s modulus of bamboo is about one-tenth of steel (therefore making it poor even per unit weight compared to steel) and the linear portion of its elastic behavior is small compared to steel. Therefore, it deflects more and tends to exhibit sudden fracture, compared to a ductile material like steel. This limits its use until better research can be brought to bear upon the issue.

Natural Variability. Since the properties of bamboo may exhibit even greater standard deviation than other natural materials like wood, the concept of characteristic strength is not useful since these strengths may be very small as the standard deviation is high. What is required is to create standardized methods of harvesting and treatment by age and species, to bring the natural variation to acceptable limits (such as in timber). This area needs tremendous research work; however, Institutes of technology still treat bamboo as a secondary material and exhibit selection bias when it comes to topics for path-breaking research.

Design of joints. Bamboo joints are relatively untested and not standardized. Their structural performance, ability to withstand and transfer shear, compression, tension, or bending, depends on the species, age and conditions of the harvesting of the pole and treatment thereafter, the details and material of the joints, and above all the workmanship, thus making it a difficult issue to characterize. This area is expected to see a lot of expansion of research work in Institutes of technology.

See also: Study of Junctions With Bamboo: An Attempt Towards Their Classification

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Conservation of Material, Technology and Practice in Heritage Structure and its Relevance in Today's Context

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Introduction

India has a large number of heritage structures made of different types of stone, brick, and plastering materials. Built heritage located in different parts of the country exposed to different climatic conditions in equally varied and each building material is affected in its own unique way. With the imminent need to cope with the conservation of heritage buildings, current knowledge though extensive is by no means complete.

India has over 15,000 historical buildings out of which ASI has declared 3570 buildings as national monuments and approximately same number has been declared by state governments as state important monuments and rest is being maintained by voluntary organizations, Wakf boards, Trusts etc. (Lakhani and Sharma, 2018).

Most of the heritage structures in India are in dilapidated conditions and main cause of their deterioration is environmental conditions.

Significant gaps still can be seen in the understanding of nature of restoration problem and their remedial measures. So far lime mortars have received less attention than that of the conservation of stone because lime mortar takes longer time to settle than cement mortar. In the case of restoration case People Place and Time should be of prime importance. This lack of attention leads to a series of unfortunate consequences which reduces the value and respect for the heritage. After closely observed mortar is the weakest link and easily reacts with the pollutants and other deteriorating agencies available in the environment. There is still significant gap in the understanding of nature of restoration problems and other remedial measures.

Understanding materials and the way they were used is crucial to the care and conservation of historic buildings. Traditional materials were often produced or extracted close to a building site, giving a strong sense of local identity.

Historical buildings are the most important ruins to describe history of a society. Historic buildings, which are the most important parts of our cultural heritage, must be best protected and repaired (Surlaker, 2018).

One of the key problems arising in the conservation field is finding materials compatible to the existing structure. Structures in India were mostly built in stone or brick masonry using locally available stones and mortars based on mud, clay and lime. Considering a dearth of the old material sources, craftsmanship and techniques, it becomes imperative to use new age available materials with properties matched to the ones used in the heritage structures.

Methodology

A Literature study was undertaken, to study the features and characteristics of the heritage structures in India. Case study of Sinhagad fort, Pune and Shahajanabad Gate, Bhopal, built in 2000 and 148 years ago respectively was undertaken to find out various material aspects in historic and present day context and with. A case representing change in the materials used for restoration of both the structure. Documentation and condition assessment of both the structure and comparative analysis on the basis of material has been done. Two cases from different regions with their past and present have been compared in this study. Analysis has been done on the basis of archival photographs, present day condition and various other elements to understand how authenticity criteria should contribute for the conservation of historic buildings.

Case Study Sinhagad Fort, Pune

Sinhagad is a fortress located roughly 30 km southwest of the city of Pune, India. Previously called as Kondhana, the fort has been the site of many important battles, Most notably the battle of Sinhagad in 1670.

It was also strategically located at the center of a string of other fort such as Raigad, Purandar and Torna. Perched on an isolated cliff of the Bhuleswar ranges of the Sahyadri mountains, it is situated on a hill rising 1312 m above sea level (Birodkar, 2008).

Given natural protection by its very steep slopes, the walls and bastions were constructed at only key places; it has two gates – the *Kalyan Darwaza* in the South-East and the *Pune Darwaza* in the North-East (Figs. 1–5).

Sinhagad Fort is greatly located atop on the Bhuleswar Hill range at an altitude of 1312 m. It is built on the plateaus of this hill peak. There is a full length of main ramparts surrounded on this plain land surface bordering its ridges. The fort is constructed of originally of Basalt stone which is locally available in the Deccan plateau fixed with the traditional material Lime mortar. There is a full length of main ramparts surrounded on this plain land surface bordering its ridges. It has got a very good defensive natural trench, since it has very steep slopes on major sides of this hill. These ramparts have two main gateways named as Pune Gate placed towards north-eastern side and the Kalyan Gate on south eastern side of this hill Rock. Few Hindu temples are also found here and the famous one is named Kaundinyeshwar temple. There are also few minor structures found in the ruined stages. The tombs of Tanaji Malusare and Rajaram are built here (Birodkar, 2008).



Fig. 1 Map of Maharashtra locating Pune. Source: <http://worldhindunews.com>.

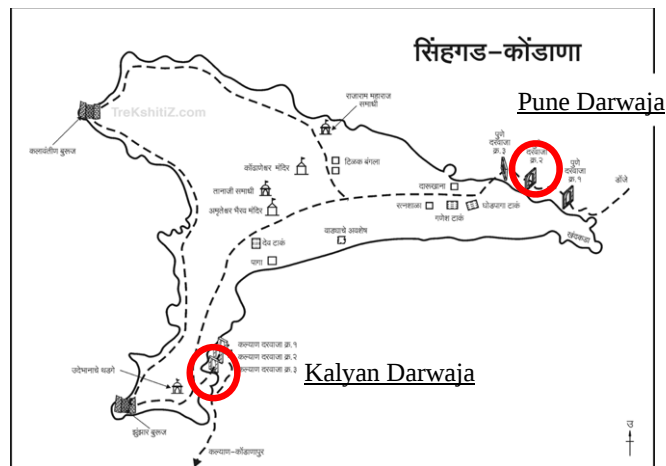


Fig. 2 Plan of Sinhgad fort locating Pune & Kalyan Darwaja. Source: <http://trekshiti.com>.

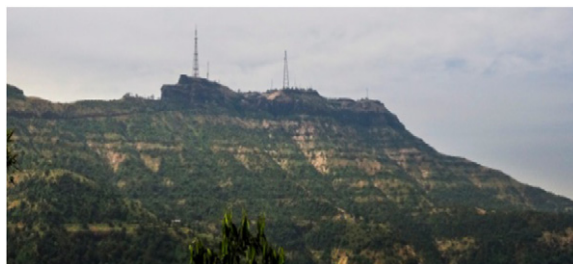


Fig. 3 Image showing Sinhgad Fort, Pune. Source: <http://double-dolphin.blogspot.com>.

Sinhgad Fort being under the Archaeology Survey of India (ASI) property. No heritage Management Plan was prepared due to divided ownership and the area being extremely large to manage and to maintain therefore no such serious action were taken. Restoration of the Fort was done previously in the year 2013 and 2015 by the state archaeological department which did not meet the parameters prescribed to conserve a heritage structure leaving it in a dismal state even after faulty repair. The stone work was utterly substandard and inconsistent with the original work.



Fig. 4 Image showing Kalyan Darwaja. Source: <https://www.nativeplanet.com>.



Fig. 5 Image showing Pune Darwaja. Source: Author.

As no archaeological expert was involved in the restoration work no respect to the authenticity of the heritage was given which is why we can see the use of Concrete, use of inappropriate size of the stone, inadequate shape and Size of the battlement are seen (Figs. 6–8).

Architectural Documentation

Mortars & renderings are an important source of historical information which is insufficiently exploited, their study is neglected and original materials are often destroyed without preservation of samples and proper documentation. Proper documentation is the need of the hour. Fig. 9 is the documentation of the Pune darwaja and the staircase leading towards. Entire fort is constructed of basalt stone and lime mortar. Proportion of the stone vegetation Growth, traces of cement, missing stone were not taken into consideration during the previous restoration done in 2012 and 2015 (Figs. 10–13).

The site needs to be conserved considering the faulty aspects respecting the authenticity and integrity of the 200 yr old heritage. This fort is the major visitors' attraction good restoration should be kept intact the legacy of the Maratha Tradition through these old built structures.

Case Study Shahajanabad Gate, Madhya Pradesh, Bhopal

Bhopal the capital of Madhya Pradesh and so started the process of 'Development'. Large scale migration and big investments in the infrastructure suddenly transported this small principality into a town of National importance. The expansion was so fast and enormous that the original character and dace go got lost and marginalized in the process.

Location Shahajanabad Gate, Madhya Pradesh, Bhopal

Situated in the Shahajanabad area of the city, the construction of this edifice had been initiated by Nawab Shahajahan Begum in the year 1871 CE. This gate was constructed for the protection of Taj Mahal palace which served the grand entrance to the Palace. A three storied structure built with stone and brick is currently in a dilapidated condition (Figs. 14 and 15).

The original town was a conglomeration of six distinct areas, some of them with fortification wall with gates for entry and exit and Shahajanabad gate located in the Shahajanabad area, a fortified area was added to the main city. It consisted of gates, masjid, lakes, palaces and all. This 150 old heritage structure is restored with contemporary material and has lost the Authenticity and its heritage value. It can be well stated as the "Dying heritage of India" (Figs. 16 and 17).

The complete structure is plastered with cement whereas the interior of the structure is of the original construction constructed during the period of Shahajahan begum.

Stone Arch motifs in the Fig. 18 in the interior are constructed using sandstone and brick and bonded with the lime mortar. The base of the structure is constructed with stone and the above floor is constructed with brick and was plastered with lime mortar.



Fig. 6 Image showing restored battlement of Pune Darwaja. From Yash Gaikwad. Available at: [blogspot.com](https://www.blogspot.com).



Fig. 7 Image showing restored image of Bastion of Pune Darwaja. *Soruce:* Author.



Fig. 8 Image showing the restored image of Kalyan Darwaja. From Yash Gaikwad. Available at: [blogspot.com](https://www.blogspot.com).

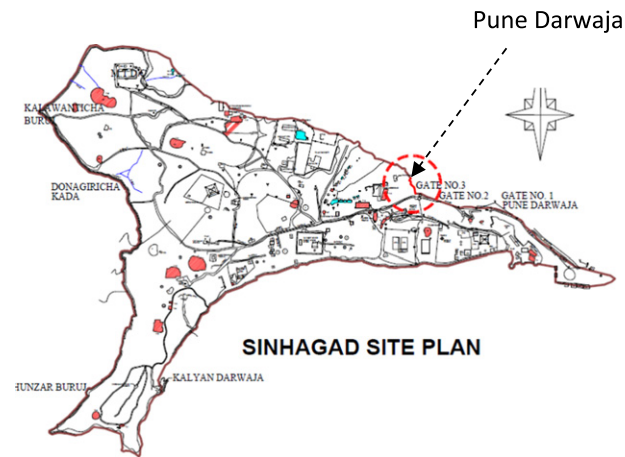
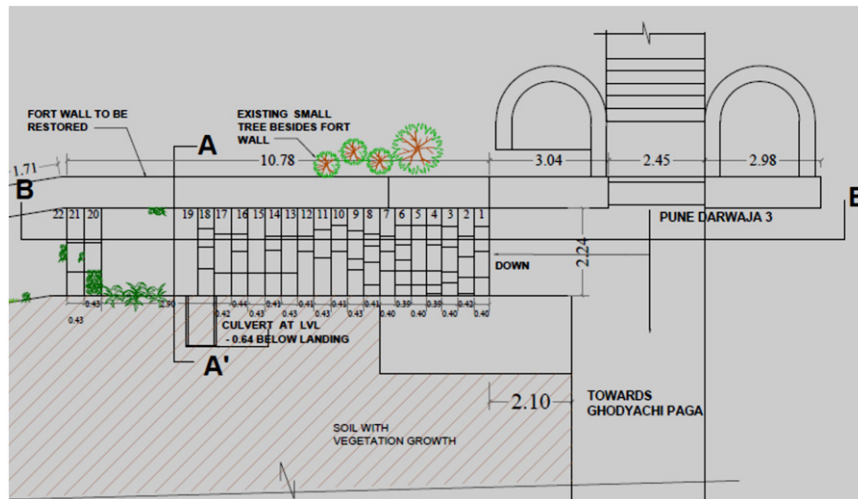


Fig. 9 Site plan Sinhagad Fort, Pune. *Source:* Author.



PLAN, PUNE DARWAJA,

Fig. 10 Plan, Pune Darwaja, Sinhagad Fort, Pune. *Source:* Author.

The structure today is completely ignored and human vandalism is the major cause of deterioration as at one period of time this served the main entrance to the Shahajanhnan Begum Taj Mahal Palace (Figs. 19 and 20).

When deteriorated, damaged, or lost features of a historic building it needs repair or replacement, it is almost always best to use historic materials. In limited circumstances substitute materials that imitate historic materials may be used if the appearance and properties of the historic materials can be matched closely and no damage to the remaining historic fabric will result. Survey of the defects in the building.

Analysis and Observation

Historical buildings are the most important ruins to describe history of a society. Buildings exposed to harsh effects of years and to natural disasters are generally under effect of very serious problems and they have risk of collapse and extinction. Historic buildings, which are the most important parts of our cultural heritage, must be best protected and repaired. The building materials play a decisive role in the behaviors of the structures they use. Historical agglomerations use different materials such as natural stone, brick, wood, mortar.

Understanding the two above case studies the use of lime mortar for plastering in historic structure's offers several advantages, specially a longer life to the structure, as has been proved by the longevity of historic building and monuments.

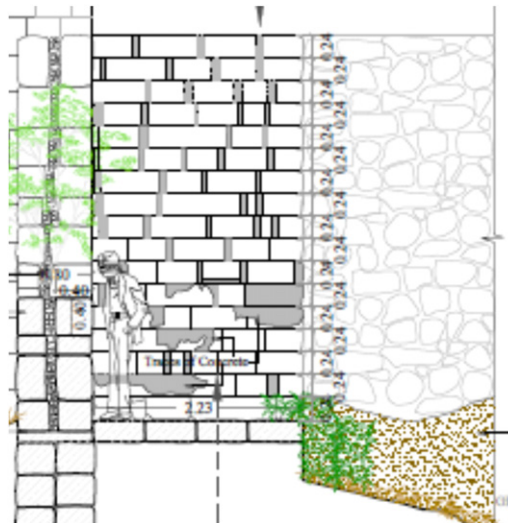


Fig. 11 Trace of concrete and vegetation growth in the staircase. *Source:* Author.

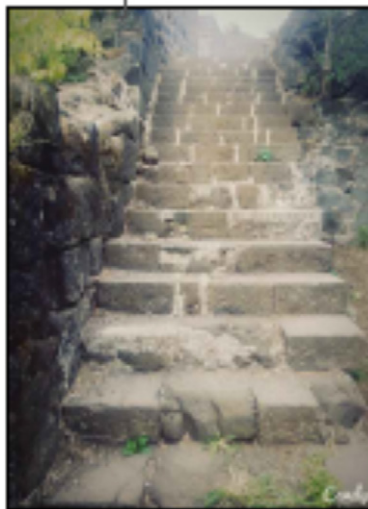


Fig. 12 Images showing damaged stone. *Source:* Author.

Lime is natural occurring, less susceptible to ageing and adjusts to temperature variation and is also less prone to cracking. The lime mortar allows the structure to breathe due to its porosity and permeability and hence maintain the temperature and reduces dampness and other problem. In this particular above case study lime mortar is used as a binding material which a traditional technique and material. The main reason for not using lime as a binding & plastering material is the time constrain. Use of Traditional materials takes longer time to set as compared to cement mortar, other such factor is Workmanship, as it is the physical material and construction technology has lost its importance due to less availability of time and skilled workmanship which is therefore the result seen in the above two restoration.

Case Study 1: Observation

Detriment and Distortion in Structure

Damaged masonry

Before the restoration of the fort wall the exposed stone masonry was found to be damaged with gaps, cracks running along the length of the fort. Layers of mute was the exposed stone masonry and remains of the original plaster surface are found to be covered with layers of white wash and cement plastered. Extensive use of cement for fixing of stone and plasterer has been used to restored the fort wall. The missing stones are not fixed and is still in poor condition (Figs. 21–23).

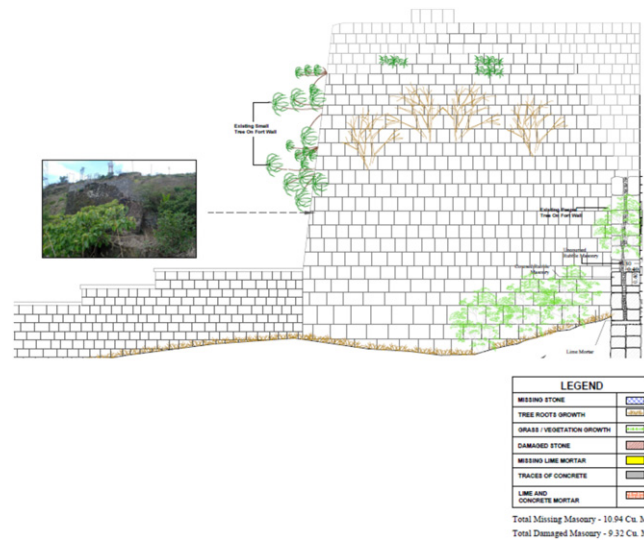


Fig. 13 Vegetation growths in the bastion of Pune Darwaja. *Source:* Author.



Fig. 14 Map showing location of Bhopal. *Source:* <http://office.incometaxindia.gov.in>.

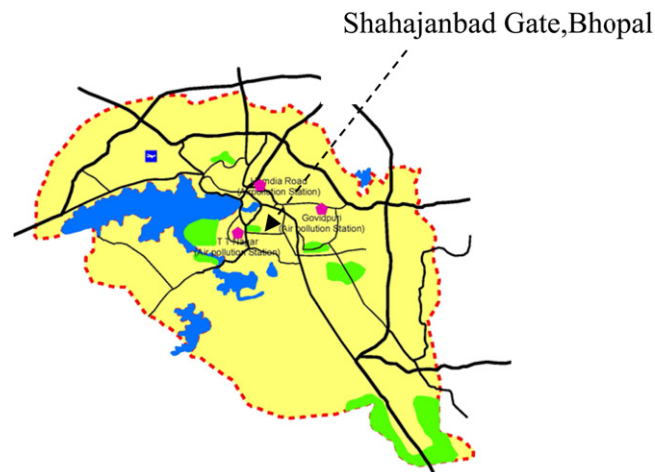


Fig. 15 Plan showing location of Shahajanabad Gate, Bhopal. *Source:* <http://www.spaenviis.nic.in>.

Case Study 2: Observation

This particular front elevation depicts the use of cement plaster in the structure whereas originally lime plaster was used. Due to this intervention Authenticity of the structure has been reduced though the Gate is structurally stable in present condition. **Fig. 24**



Fig. 16 Archival image, Shahajanabad Gate, Bhopal. *Source:* National Archive of India, Bhopal.



Fig. 17 Present condition of Shahajanabad, Bhopal. *Source:* Author.



Fig. 18 Stone arch Motif, Shahajanabad Gate. *Source:* Author.



Fig. 19 Brick Masonry with cement plaster. *Source:* Author.



Fig. 20 Arch detail. *Source:* Author.

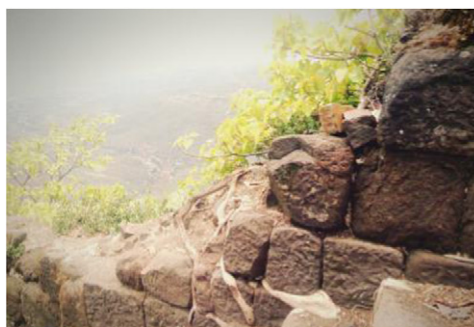


Fig. 21 Vegetation growth in the stone wall. *Source:* Author.

depicts the condition of the structure before Restoration. The structure was in dilapidated condition with exposed masonry, flaking, Algae Growth, Black water stain which was reducing the structural strength. The Restoration was done by using cement which managed to withstand the strength of the structure but lost its identity. Conservation of Heritage structure has a certain process in which it has to match conserving parameter which this structure has not achieved.

A documentation study was done in each of these case studies for understanding the seven criteria of Authenticity which are:

- (1) Location
- (2) Design



Fig. 22 Missing stone, Fort Wall. *Source:* Author.



Fig. 23 Damaged masonry, Fort Wall. *Source:* Author.

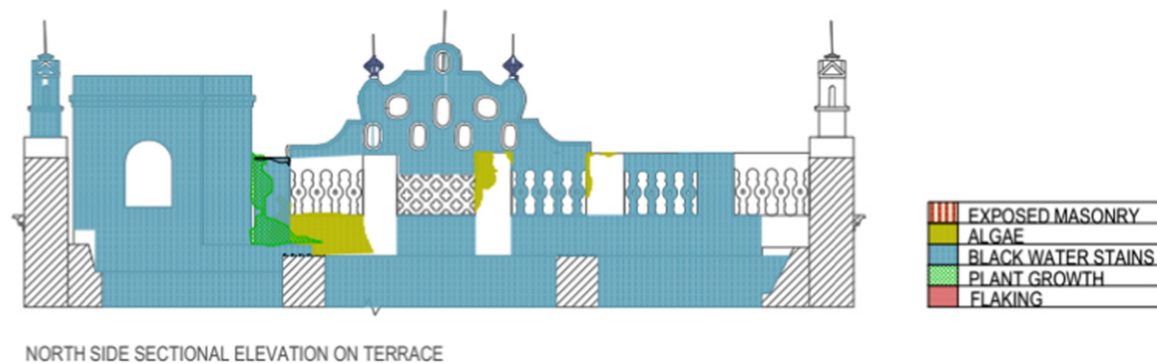


Fig. 24 Condition assessment of Shahjanabad Gate, Bhopal. *Source:* Self.

- (3) Setting
- (4) Materials
- (5) Workmanship
- (6) Feeling
- (7) Association.

Out of the seven criteria of Authentication Material criteria was discussed mainly by documenting the two heritage structure in different regions of India.

Whereas location refers to the specific place where a property was built or an event occurred, setting refers to the character of the place in which the property played its historical role. It involves how, not just where, the property is situated and its relationship to surrounding features and open space E. Function/Use Is the degree of continuity of original or significant uses in a property. An

Table 1 Material analysis

Sr. No	Case study	Age of the structure	Original construction material	Restored building material
1.	Pune darwaja, Sinhagad Fort, Pune	2000 year old	Basalt stone with lime mortar	Restored using cement mortar
2.	Shahajnapad Gate, Bhopal	150 year old	Brick and stone with lime mortar	Cement concrete

Source: Author.

historic area and its surroundings form a coherent whole including associated human activities and constructions; continuation of original or compatible uses minimizes negative impact on authenticity.

The material criteria state that the physical elements that were combined or deposited during a particular period of time and in a particular pattern or configuration to form a historic property. The choice and combination of materials reveal the preferences of those who created the property and indicate the availability of particular types of materials and technologies. Indigenous materials are often the focus of regional building traditions and thereby help define an area's sense of time and place (Alho and Morais, 2000).

Following the above criteria for authenticity material condition assessment and its relevance in today's context was studied following is the case study analysis (Table 1):

Conclusion

The most common reason for considering substitute materials is the difficulty in finding a good match for the historic material (particularly a problem for masonry materials where the color and texture are derived from the material itself).

For example, the same material shall be no longer be in operation so all efforts should be made to locate another material that could supply a satisfactory match. Care should be taken to ensure that the detail, color and texture of the original material are matched and no visual differences should be seen.

Great care must be taken if substitute materials are used on the exteriors of historic buildings. Only after consideration of all options, in consultation with qualified professionals, and development of carefully written specifications should of any conservation work is undertaken.

The use of local materials and traditional technologies must invariably be preferred and respected. Decision must be founded on the accessibility and the availability of traditional knowledge systems. Modern substitutes should be considered only after their use is proven efficient and judicious, and must not compromise the integrity and continuity of local building traditions.

Rehabilitation of old buildings with historic significance is different compared to normal repair of concrete structures as the materials used in construction are natural and the restoration is to be done by maintaining the architectural aesthetics and ambience. One should be able to blend new materials with old building materials. It should be borne in mind that primary responsibility is not only to regain the architectural aesthetics respect the old buildings perform their new roles for future generations.

See also: Energy Efficiency and Thermal Comfort in Heritage Buildings

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Constructing a PV-Integrated Permanent Bamboo Building – An Experience

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Introduction

Bamboo is a low-cost building material, widely available in the world; it is lightweight, durable, flexible, and easily cultivated and processed. The use of bamboo as a structural material is well-known in constructive traditions. Bamboo construction is mainly associated with poor rural housing as a low cost alternative building material. The bamboo has appropriate structural and mechanical properties and high strength/weight ratio. In its natural form, it has a high moisture resistance and is widely used for flooring as well as in making furniture also with some modification. Moreover, the capability of protecting the environment, due to its sustainability, is a relevant aspect to consider and its ability to mitigate constructive emergencies in developing countries. However, with the advent of a new era of exploring the traditional building materials, it became an important area of research to use the bamboo as permanent cost-optimized, energy efficient solution to mass housing projects especially in regions where seismic activity and cyclonic weather is a threat. Despite of its enormous potential, it is still not considered as a permanent building material in most countries.

The National Mission on Bamboo Applications (structured as a Technology Mission) is one of the key initiatives of the Department of Science & Technology (DST), Government of India for enhancing the bamboo construction sector, towards augmenting economic opportunity, income and employment generation. It may be mentioned here that in India, more than 100 species of bamboo grass are available out of which few species are of solid nature and the majority are of hollow types. Though it is an accepted fact that Bamboo is an exceptional structural material but in absence of appropriate design guidelines, its acceptance as an permanent building material is not well recognized. The research project under TIFAC (Technology, Information, Forecasting and Assessment Council), from NMBA (National Mission on Bamboo Application), government of India embarked upon the intention to justify the feasibility of a bamboo structure and to include the different parameters in the different standard. It may be mentioned here that the use of bamboo as a natural construction material is also regulated in several countries by specific standards. Finally an attempt has been made to enhance the prospects of use of bamboo as an alternative mass scale permanent building material as a cost effective, environment friendly as well as esthetically appealing. The latest version of National Building Code has included the general principles involved with the Bamboo construction in its Subsection 3B of Part 6: Structural Design – Timber and Bamboo ([Fig. 1](#)).



Fig. 1 Samples prepared for lab testing.



Fig. 2 The site after clearance.

Site Location and Features

Due to severe space crunch within the campus of Jadavpur University, a damping ground near the Guest House has been taken for the experimental project on a building made up of fully using structural bamboo considering the architectural and structural features. The site (**Fig. 2**) had several fully grown trees along with a few shrubs and samplings leaving limited space for construction, which became a cause of concern. Also there were limitation on the visibility factor and the lack of sense of arrival for the location. The streets approaching the site were narrow and the surrounding areas were cloistered with 3–4 stories building which further deteriorated the sense of place for the building. But the most impressive quality of the site (**Fig. 3**) was rendered by the presence of the water body in its proximity. The water body added to the much desired break of monotony. All these factors had been thoughtfully addressed in order to ensure that the effort that went into conjuring up the new architectural vocabulary was not lost to the banality of the surroundings.

The adjacent guest house mainly houses the Faculty Club, a place for refreshments. It is also regularly used to host seminars and conferences also. The guest house rooms are also under considerable use owing to the proliferation of academic conferences at the University. Being located next to the University Guest House, the project posed immense opportunities but also had several functional issues. The dilemma had been about the kind of functions that could be incorporated to this new experimental building that could adduce the functioning of the guest house but also be an important point of academic discourse in terms of architectural genius. The functions of rooms for the guest were thought to be a tad bit trite for the new building. Again, there were other issues of safety has been considered. Finally, it was decided that the new building would not only be a paradigm shift in terms of building materials, but would also be an innovative way of showing the limits of the material. A multi-functional building was suggested that could also address to the esthetic value of the building. A fully functional seminar facility and an extension of the Faculty club were decided upon (**Fig. 4**).

Architectural Paradigm

The project involves design of a stilted two storied demonstrative bamboo structure with simple innovative bamboo joineries and local techniques to enable engagement of local semi-skilled workers for such construction. The idea was to use locally available bamboo species to enable widespread acceptance and to create a built form of high esthetic standards which can be rendered as an attractive liveable space consequently leading to greater acceptance by the masses. The project also aimed to test the durability of the bamboo boards as well as the performance of the whole bamboo sections as permanent structural building material. The whole building appears to be a single one but horizontally it is divided into three parts and vertically into two levels. The purpose



Fig. 3 The site plan.



Fig. 4 The Bamboo Building-the way it was conceptualized.

of the horizontal division was to carry out experiment of three types of foundations with bamboo and the differences in levels were done mainly to carry out energy related experiments (Figs. 5-7).

The whole bamboo poles are left exposed to enhance the esthetics, lending a natural aura to the space while the free flowing interiors merge seamlessly with the outdoors and the huge water body lying on the rear portion of the site. The fenestrations were



Fig. 5 The Bamboo Building under construction with thatch roofing.



Fig. 6 Hollow pipes inserted into concrete base.

designed very carefully to create intricate, light-filled building. The landscape was done consciously displaying all local varieties of bamboo available in the region. The interiors need not require any further touch up other than placing some bamboo furniture & fittings ([Fig. 11](#)).

Structural Aspects

The whole building is designed and modeled as a frame-structure with bamboo columns and bamboo beams. All typical load like Dead Load, Live Load, Seismic Load and Wind load has been considered in the design process. Each of the column and beam is

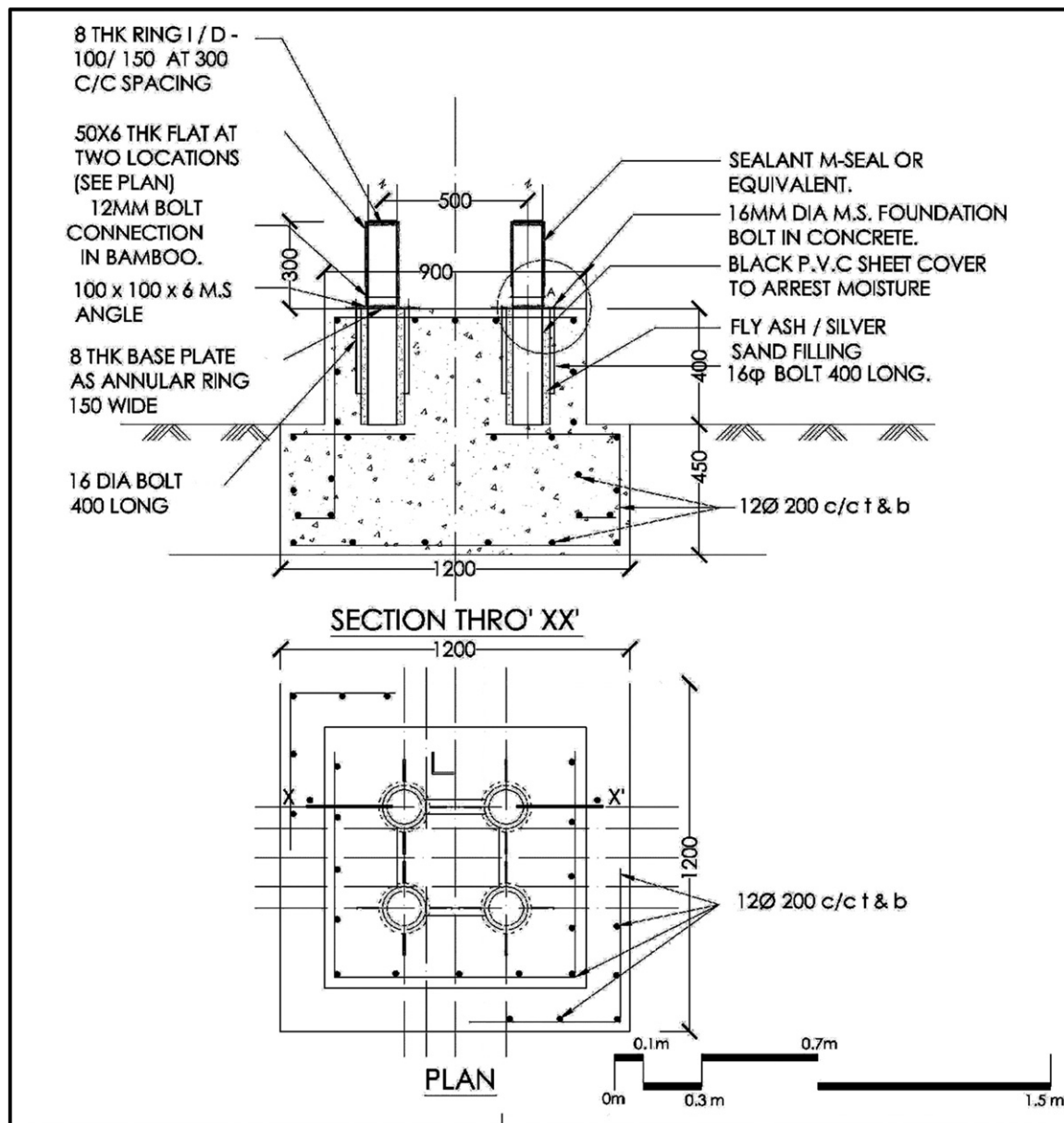


Fig. 7 Column details.

made up of four inter connected whole bamboos. The interconnection has been made with bamboo also at a suitable spacing. The spacing of the main bamboo is fixed based on the design load applied. The floor is consisting of commercially available bamboo board resting on beams. Based on the capacity of the bamboo board the spacing of the beams has been fixed. The columns are also braced with bamboo member to strengthen the structure against lateral load like wind and seismic load. The ground floor of the front portion is stilted at a height of 600 mm so that the portion below the floor can be cleaned easily. The Ground floor is completely open with no walls and thus the air allows the house to catch every breeze that comes through. The structural grid was chosen in such a manner so as to accommodate the 2400 mm × 1200 mm bamboo boards as flooring material on whole bamboo beams (Fig. 9). The central portion is frame structure which is resting on a sand bed. The rear portion is entirely with bamboo board with brick foundation. Two toilets are placed in this rear portion at ground floor level and the pantry is at the first floor level. The first floor of the front and the middle portions are covered with wall panels made of bamboo boards. The boards used in the western and southern facades are insulated ones. The roofs are designed at different angles suitable enough to have covering with both thatch and solar panels for two specific reasons; (1) to protect against rain (2) to give a good esthetic appearance.

The foundation of the structure is designed as typical isolated footing type (refer Figs. 8 and 9). Size of the footing is fixed at 1200 mm × 1200 mm for each column. Four steel tubes of diameter 150 mm is inserted in the isolated footing at a spacing of 500 mm within the pedestal of size 900 mm × 900 mm. The four bamboos used in a column are inserted in the four steel tubes.

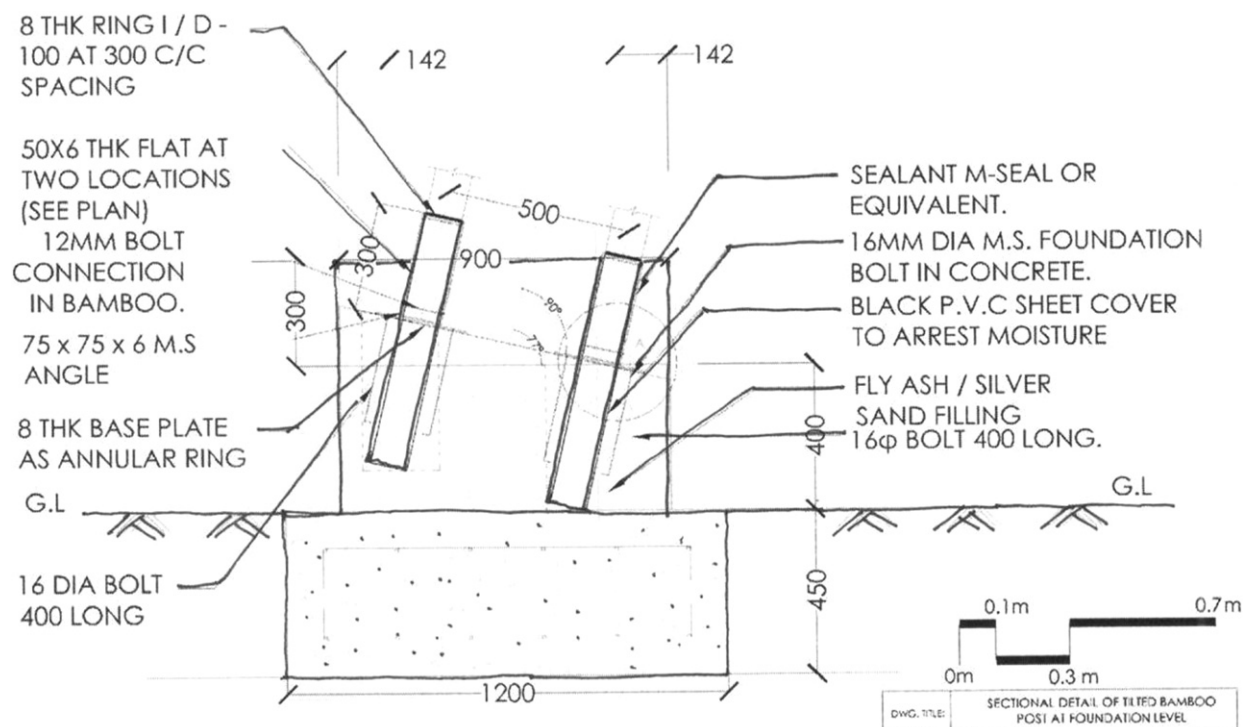


Fig. 8 Details of inclined column.



Fig. 9 Bamboo boards inserted into the pillars.

The gaps between the tube and the bamboo have been filled up fly ash or sand and finally sealed with sealant M-seal or equivalent. The bamboo is connected to the steel tube by 12 mm diameter pin. The tube is connected to the footing with foundation bolts of 16 mm diameter with four angle section. For inclined columns the tubes are inserted in inclined position (**Fig. 8**). All the materials used in the building are of low technology and easy to apply. Different types of joineries were explored, prepared and the testing were carried out in the lab before its actual application (**Fig. 1**). Examples of bamboo usage in the present structure as a composite material demonstrate its full potential as a structural and environmental friendly material. Finally the set of plan schemes from the presented project is an attempt to transfer the technology into the practical applications, offering suggestions for possible destinations.

A 'Zero Energy-Zero-Waste' Building

This research project aimed to be a 'zero energy-zero-waste' demonstration project for students, professionals in the country. A 20 kW grid connected solar PV integrated roof (**Fig. 10**) has been installed replacing the thatch roof under the funding of MNRE



Fig. 10 Integration with solar.



Fig. 11 Solar lanterns.

(Ministry of New and Renewable Energy) through WBREDA (West Bengal Renewable Energy Development Authority) in the phase-II of the research project to reduce the dependence of conventional power. Bamboo was chosen as the main material because, as a natural resource that fixes carbon into the soil and also minimizes CO₂ emissions throughout the whole production phase (Fig. 11).

Conclusion

The application of the proposed technique of construction is not exclusive for developing countries. It can be also adopted in all the areas with environmental and technological features for the use of bamboo. Further investigations should be conducted to protect the façade walls (here not considered) from the risk of rocking falls from the movements of the roof, as in due to earthquakes. It will be carried out on additional structural schemes and corresponding experiments constructions, in view of its eco-friendly characteristics. Moreover the structural system involves only natural materials (bamboo canes, plywood plate, wooden pins, canapé ropes) with strong reduction of environmental impact in those areas where the natural materials are available.

Acknowledgment

I sincerely extend my gratitude towards the then Vice Chancellor for his outstanding support and encouragement by allowing us to carry out such a difficult experiment in an institutional set up. Acknowledgments to all the research fellows of the 'Energy Efficient Built Environment' Lab and students of the Department of Architecture who have worked in the project from time to time for their tremendous effort in implementing the project. Also, I would like to thank all the staffs of Jadavpur University for rendering so much support during the implementation phase of the project.

See also: Expediting Faster Housing Supply in India Using Straw Bale as Prefab Building Material

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Energy Efficiency and Thermal Comfort in Heritage Buildings

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Introduction

Energy is a major factor for development. The building sector is the highest consumer next to transportation, followed by others in the cities, and requires an uninterrupted supply of energy. These consume about 75% of global primary energy and emit between 50% and 60% of the world's total greenhouse gases. In 2012, the global energy supply consisted of 81.3% fossil fuels (oil, coal, and gas), 9.7% nuclear power, and only 9% renewable energy sources (such as hydro, wind, biomass, and solar). Unfortunately, this widespread use of fossil fuels causes a number of challenges. Carbon-based energy generation has a large ecological footprint, not only due to rising greenhouse gas emissions and pollution caused by burning fuels, but also because of extraction techniques that contaminate the environment, and frequent production or delivery accidents (see "Relevant Webiste section").

With limited energy available on the planet *efficiency* is crucial. Energy is required for its production, transporting/transmissions through grids (nature and type of grids) to consumption for lighting and appliances (use of level of technology) and related losses and emissions that add to the GHG gases and carbon emissions at large. The concern is actively addressed for new construction but the existing old buildings especially with heritage value are a challenge. These building stocks are a huge resource of sociocultural connotation, and thus a sensitive issue to be attended with care.

Energy Consumption in Buildings

By 2050 68% of people are expected to be living in urban areas [UN], which means the necessary building stock should be in place, and if it is not energy efficient the implications will be far-reaching globally. Energy consumption is essentially governed by:

- Climate: Parameters: geographical location, water, temperature, humidity, and features of land.
- Climate responsive building design: Thresholds of thermal comfort/standards/norms, local, regional, and global.
- Building performance, technology, and behavior changes, social connotation.

Further due to global warming the need for cooling is on the rise globally. Use of air-conditioners/central cooling or heating affects the microclimate too, largely seen in cities.

Cities account for 75% of total global energy demand and produce 80% of our CO₂ emissions, driving climate change. This figure rises to approximately 80% when the indirect emissions generated by urban inhabitants are included. Buildings also consume vast amounts of energy at all stages of their existence. Energy is needed for the raw materials, construction process, and maintenance and daily operational needs such as lighting, air conditioning, and cleaning. In addition, urban sprawl, increasing distances between destinations, and inefficient public transport systems prompt overall reliance on private motorized transport, such as cars, which have a high energy consumption, mostly of petroleum products (see "Relevant Webiste section"). With urbanization energy consumption shall rise due to the planning and building sectors. Also with the high rate of urbanization in Asian and African cities the implications are far-reaching, as the built-up areas required in these cities are huge. Further, being closer to the equator, the demand for cooling for thermal comfort shall be equally high but the hope is there if the building stock is built in a sustainable manner (Dulac and Hinge, 2016). Currently global use of energy in buildings has grown by 1% per year, global use of electricity in buildings has grown by 2.5% per year, and global building-related CO₂ emissions continues to rise by nearly 1% per year (Dulac and Hinge, 2016).

Energy Efficiency and Thermal Comfort

With limited energy available on the planet *efficiency* is crucial. The law of thermodynamics clearly states that energy can neither be created nor destroyed but *only* can be changed from one form to another, clearly reinforcing the limitation. Thus efficiency is the key word. In buildings thermal comfort followed by lighting are major energy consumers irrespective of the type of building (Figs. 1 and 2). Typically the energy consumption in buildings is due to heating and cooling, followed by illumination or lighting, irrespective of the type of building (D&R International, Ltd., 2011) (Fig. 3).

To achieve energy efficiency there should be a three-pronged approach: (1) to reduce the demand (Gupta and Gregg, 2018) being the foremost followed by (2) optimum consumption of energy and (3) consumption within the limits of energy produced by renewable sources only. Such an approach reduces the carbon emissions and moves towards net zero and sustainable development at large.

Often the norms and standards in the developing nations are not in place and invariably not updated for technology as it is getting updated regularly making the execution of buildings and the building envelope too. Delay in implementation and enforcement of building envelope measures results in additional energy consumption. Building performance evaluation studies too are integral to improve on the design and detailing of buildings. Cooling is the fastest growing use of energy globally and thus

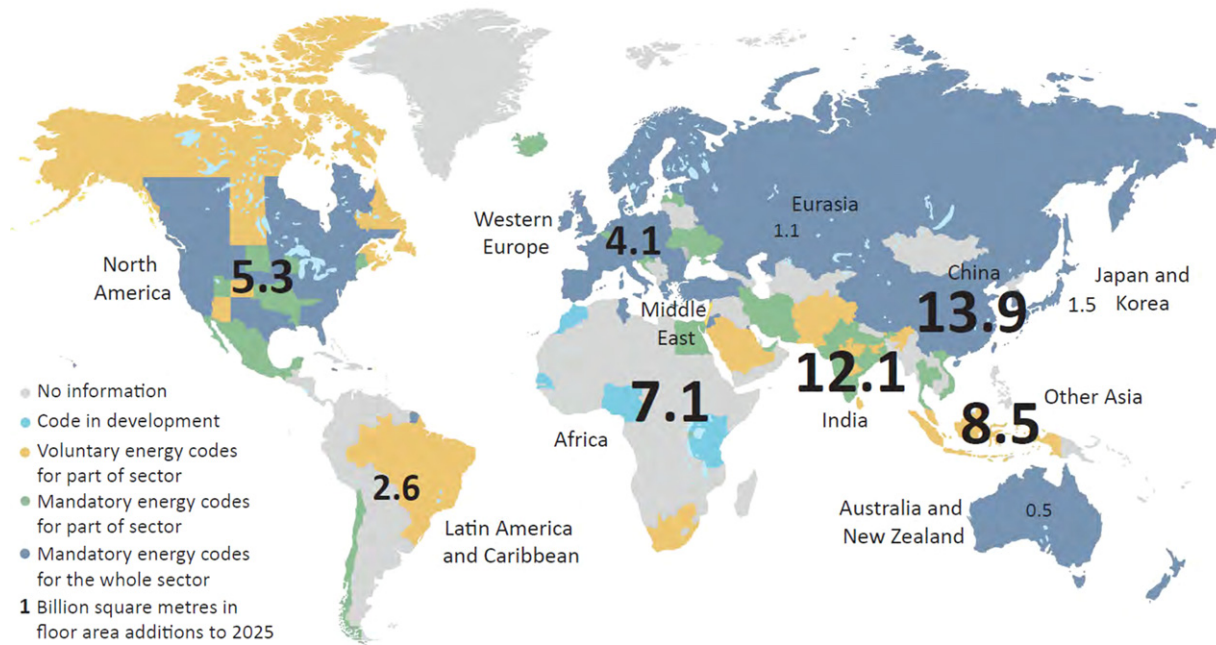


Fig. 1 Global map floor area additions by 2025 (in billion square meters). Source: IEA.

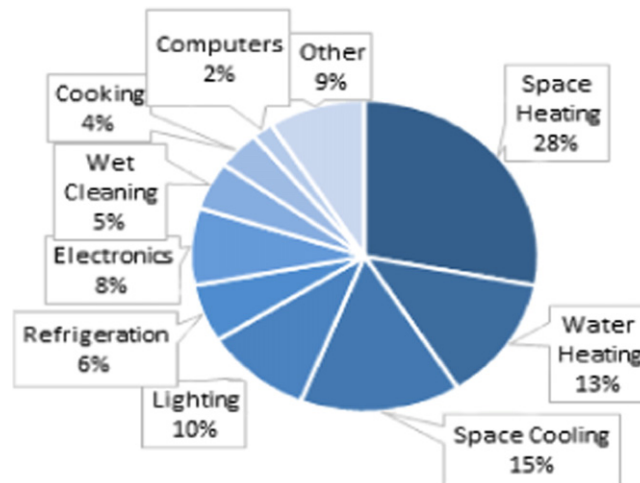


Fig. 2 Residential buildings energy consumption by end use (2010). "Other" includes small electric devices and heating elements.

the focus on air-conditioning. Energy efficiency improves energy security. Typically appliances and building equipment typically need to be replaced every 15 years or so as buildings' major source of GHG.

Energy and Heritage Buildings

Typically, historic building stock was built next to available natural resources: Water and landforms that provided security. Thus the heritage buildings are indigenous to the locally available resources and therefore the desire to be authentic at the expense of the local was not the norm. Most of the traditional heritage built environs were governed by frameworks outlined in ancient scriptures and texts in various cultures that acknowledged natural resources, and are strongly reflected in our heritage buildings in planning and detailing. For example: Ancient Indian concern for environmental protection is found in Kautilya's "Arthashastra." It was the Dharma of each individual in the society to protect nature. People worshiped natural elements: Sun, air, water, and land. Thus recognition and acknowledgment led to protection and preservation of the environment. Similar ideologies are also depicted in Buddhism and Jainism, which propagate nonviolence, minimum destruction of natural resources, and simple living with minimal needs (minimum consumption of energy). While Muslims and Christians consider water sacred and pure. Such a backdrop

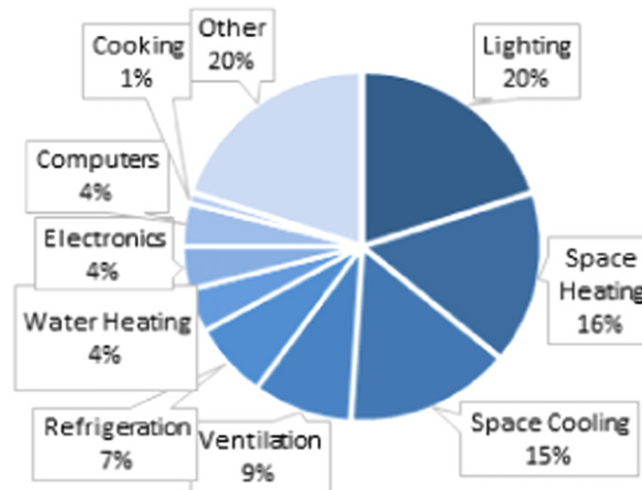


Fig. 3 Commercial buildings energy consumption by end use (2010). “Other” refers to miscellaneous sources like medical equipment, ATM machines, and telecommunications.

outlined a framework of development that respected the natural resources and optimum use of them was integral. But currently the high rate of urbanization coupled with the nature of development ignores the traditional approach; also fast construction facilitated by technology uses the resources quite indiscriminately.

Considering urbanization is a historical trend. Historic records indicate that cities existed over 8000 years ago. Important urban centers developed around the 13th century with the Silk Route stretching halfway around the globe, from Italy through Central Asia, Mongolia, to China and Japan. It left behind a precious strand of heritage cities, including Samarkand, Bukhara, and Kaifeng.

With the Industrial Revolution cities experienced exponential growth setting up so-called modern lifestyles, standards, and norms of city life. This assumed the status of the contemporary lifestyle the world over and governed development across the nations, and this deviation from the contextual living has accelerated climate change and is not sustainable. In Jay Inslee’s words “we are the first generation to feel the impact of climate change and last generation that can do something about it.”

Interestingly the global south, where the majority of the development is expected to occur, has the bulk of existing heritage and thus its relevance, contribution, and learning cannot be negated. In fact the World Urban Forum’s six big ideas recognizes that the integration of Historic Urban Landscape and Values (HUL)-based community values in the planning and design professions is fundamental.

Current Status of Heritage Buildings

Heritage buildings are a huge resource of contextual building frameworks that are environmentally friendly and thus sustainable. But the perception of the heritage environs by the architects and planners is to view them as a page of history and thus addressed as such: Either as a conservation project by a set of professionals or as a dimension of issues in planning exercises – A layer acknowledged but not necessarily integrated in the planning at large. However, they are a strong contextual resource with time tested solutions for design, planning, and construction. Seldom are they integrated such in mainstream design and planning, considering these contextual approaches typically demonstrate a strong relationship with nature underpinned by local cultures that have had minimum impact on the environment and thereby climate change. Further they had a distinct identity of their own that is significant from a sociocultural point of view, enabling people to connect to their roots, bringing in harmony and well-being in societies.

The heritage buildings stocks in various countries have a distinct take based on their socioeconomic status, as environmental degradation is uniform to all. Where these economies are strong they are preserved, often conserved as cultural landscapes. While in some cases where they are in abundance with developing economies they act as resources and used through revitalization, adaptive reuse, additions and alterations, etc. essentially based on their heritage value: Age, architectural style, elements, features to design, and planning merit. Sometimes if the location of the heritage structure is strategic in the city, then it is even demolished, a permanent loss.

Unfortunately heritage buildings are looked upon by the city planners and architects either to be preserved or conserved as such. But they are a timeline layer in the planning of a city/place and need to be acknowledged as such and integrated as another dimension of design in developing city plans. The current parallel approach inhibits the heritage buildings from being mainstream assets.

Characteristically each heritage building has a framework of development as follows:

- **Site and surroundings:** The framework of development based on the respective cultures governs location of each building: For public buildings adequate open spaces to account for spillover activities and others. Further based on the nature of building proximity to water, sociocultural issues were addressed. The topography of land, flora, fauna, and other natural features are acknowledged and retained as such, essentially in line with the environment. Next manmade structures especially related to religion, having significance to local communities, are integrated in the overall planning and resultant sites selected for use.

- Design principles: Typically the sociocultural connotations governed the design and planning of buildings; thus the spaces delivered over and above the functional aspect. Often the texts and literature specific to the communities abided by, for example, orientation, distribution of the built mass with respect of the open spaces, scale proportions, and systems at large. Such an inherent discipline structured the design and planning at large making it in harmony with itself rather than an architectural feat for a building. Therefore the heritage buildings are intrinsic to the development or city's fabric.
- Selection of architectural style: Archetypally each of the historic buildings are distinct for some land use type. All dimensions of space, from its disposition, spans, and relationships between covered and open, system of fenestrations, scale proportions, order in section, and elevations of the buildings. As most of the historic buildings were built when public infrastructure services were not in place, invariably they utilized daylight judiciously and thus were low on energy consumption even for the standards of today. These buildings were designed with passive systems for thermal comfort, and were fairly effective thus energy efficient by nature, as the cost of air-conditioning is high in buildings. From structural systems to embellishments the architectural style is insightful.
- Choice of building material and technology for its execution: Conventionally the selection of building material was what was locally available, as that proved to be environmentally friendly with no transportation costs and was in line with the natural environs. The context played a crucial role in determining the choice of materials that were locally available, and technology was often indigenous thus environmentally friendly and often low on energy as well, as when these technologies were in place in history they were labor intensive, unlike current technology that uses energy.

This clearly enumerates the holistic approach that contributes for energy efficiency and thermal comfort addressed within the sociocultural milieu, a significant measure for well-being.

Heritage Buildings: Energy Efficiency and Thermal Comfort

All heritage buildings are strongly contextual thus the framework of development too is contextual, implying also indigenous and localized thresholds and norms. Use of passive systems was a predominant design criterion for most of the buildings, for example, based on the geographical location and climate typology; the locally available material of requisite due thickness for walls was selected, for example, for a hot and dry climate, if the locally available material was stone, then based on its characteristics the wall thickness was decided. If it was adobe, then thickness was revised to have adequate time lag to ensure the transmission of heat indoors. Further, the outer surface was finished to reflect maximum heat or vertical surfaces protected with deep overhanging projections so that direct heat was avoided.

The fenestrations openings too were detailed such that in a hot and dry climate, if there were strong winds, then dust would be a concern for which the size of openings should be minimum and small; also the shape had to be with maximum area with minimum perimeter (for example, a circle). But for thermal comfort movement of air is important, so there should be a number of openings with a certain hierarchy of openings to ensure such air circulation and take into consideration basic principles like hot air's tendency to move upwards, leading to high ceilings for habitable spaces. Additionally the most efficient system of fenestrations became integral to the architectural style of that place, eventually contributing to the heritage buildings' identity. Such approach was used for the roof and intermediate floors, thus ensuring the least energy demand for the building. Selection of locally available material by default defined the spans and structural systems for roofing but wherever large spans were required then technology was resorted to, while some of the indigenous solutions were strongly contextual; this reduces the energy for transportation while spans assure optimum energy use. The construction technology used was labor intensive; although time consuming, it was environmentally friendly. Extensive use of lime is labor intensive, fire resistant, and termite resistant; it can be used for foundations/roofing/mortars, with time weathers into a strong material, consumes much less energy when compared with concrete; and is biodegradable as well. Also the thermal properties are such that for certain climatic conditions it makes indoor spaces thermally comfortable. Next, design fundamentals like symmetry, compact development, perimeter blocks, etc., make sure that the energy demand is limited.

Similarly for various climatic zones heritage buildings demonstrate such features for thermal comfort and energy efficiency at large. Therefore significance of heritage buildings cannot be negated; unfortunately not many studies have been conducted to document such empirical data. One of the main reasons may be because most heritage buildings are in Asian countries, which have extremely low research bases coupled with poor economies.

Conclusions

The global concern of sustainability and climate change over the last three decades has picked up momentum, essentially becoming the need of the hour. Developing Asia can make a significant contribution to global efforts to reach the objective of the Paris Agreement, which is to restrict global warming to well below 2°C urbanization in Asia: Energy Efficiency Initiative and Sustainable Transport Initiative (ADB, 2017). Although various continents are at varying stages of development, with Asia urbanizing the fastest it ever has, the issue is very crucial.

Considering civilizations have been centuries old, cities were built inhabited few still continuing; it is interesting to note that centuries old cultures that shaped up civilizations sustained for so long. Thermal comfort has always been the foremost concern for habitable spaces and heritage buildings have demonstrated that through their respective solutions: Which meant that the construction of building design responded to the respective climate, and this may be interpreted as a framework of the context. Thermal comfort through energy efficiency can be achieved with wisdom that hinges upon traditional knowledge while the technology base upgraded with time can be gauged with empirical data. Thus it can be now scientifically argued through climatic responsive building design to energy efficient building design; in essence both address the issue of thermal comfort of inhabitants indoors.

See also: Conservation of Material, Technology and Practice in Heritage Structure and its Relevance in Today's Context

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Environmental Life Cycle Analysis of Earthen Building Materials

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Introduction

The building industry is one of the largest consumers of natural resources, both renewable and non-renewable, being responsible for almost a third of all carbon emissions and for consuming more energy and raw materials than any other economic sector (Mota *et al.*, 2012).

During the last decades, architecture has been based on the use of industrially-produced materials, with a low thermal resistance, e.g., large glass surfaces, making buildings extremely vulnerable to outdoor temperature fluctuations. The result was the construction of buildings with a high level of dependence on air-conditioning systems to ensure adequate indoor comfort conditions (Petter, 2011), raising the significance of the building sector in the overall energy consumption. Beyond this, industrially-produced materials are normally produced through energy-intensive manufacturing processes and have considerable environmental impacts, while natural materials, such as timber and earth, normally have low or neutral potential environmental impacts in a life cycle perspective (Mota *et al.*, 2012).

Modern buildings generate important externalities on the environment at local, regional, national and global scales (Ingrao *et al.*, 2018). Nowadays, energy efficiency and sustainability of buildings are important research issues. In the life cycle assessment of buildings, the environmental impacts linked to all life cycle stages of products are estimated (Ingrao *et al.*, 2018). One of the environmental parameters of major relevance in this assessment is the Global Warming Potential, related to greenhouse gases (GHG) emissions, in particular, carbon dioxide, which is closely related to the operational energy consumption and embodied energy of building elements (Stephan and Stephan, 2016). Embodied energy is the amount of energy used to manufacture, transport, assemble and maintain the different building elements, from cradle to the end of the life cycle. The operational energy is the energy used in heating and cooling systems, lighting and in the operation of building's integrated systems (Stephan and Stephan, 2016). To achieve a carbon neutral built environment, it is necessary to optimize both the embodied and operational energy (Dixit, 2019). Nowadays, most of the focus to reduce the life cycle energy consumption in the building sector is put in increasing the energy efficiency during the operation phase. For instance, the European Union is promoting the construction of nearly Zero Energy Buildings (nZEB), by targeting that by 2020 on all new European buildings must be nZEB. While buildings become more energy efficient during the operation phase, the importance of the amount of embodied energy in the life cycle energy balance is increasing, thus pushing the need to find alternative materials to those with high embodied energy (Ramesh, 2012) and more efficient manufacturing processes.

The life cycle assessment (LCA) method allows the evaluation of the potential life cycle environmental impacts and of the total embodied energy of a product or service. The implementation of an LCA study in the product stage is very important since it allows evaluating which are the processes with higher impact and how changing them can contribute to improving the environmental performance of the product. One way to communicate the results from an LCA analysis is to develop the Environmental Product Declaration (EPD) of the product under study. EPDs follow a business-to-business communication format but can also be used by architects, engineers, owners, constructors and consumers to support decision-making in the choice for products with lower potential environmental impact.

In Portugal, it has been estimated for a conventional building (with a lifetime of 50 years) that the embodied energy in building materials is about 6%–20% of the total energy consumed during the buildings' life cycle (Mateus *et al.*, 2007). Additionally, the study carried out by Mota *et al.* (2012) has shown that materials like ceramic tiles, concrete and alkyd paint are the ones that contribute most to the overall life cycle environmental impacts. In this sense, reducing the embodied energy in materials is a premise to reduce the environmental impacts and achieve more efficient and sustainable buildings. It can also contribute to decreasing the cost of materials and in particular of the life cycle cost of a building as a whole (Ramesh, 2012).

Using alternative materials and techniques, like the vernacular ones (lime, earth, adobe, vaulted ceilings, etc.), it is possible to significantly reduce the total embodied energy of a building, as well as the environmental impacts (Fernandes *et al.*, 2013). Understanding that construction materials have important environmental impacts, vernacular materials have, from the sustainability point of view, several advantages. Usually, the most environmental advantages related to this type of materials are: no need for transportation, since they are local materials; lower energy-intensive production processes; and, consequently, lower embodied energy and CO₂ emissions. Furthermore, they are natural materials, often organic, renewable and biodegradable, with better adaptability to the local climate conditions and durability, allowing to improve the environmental performance of a building also in a cradle-to-cradle approach (Singh *et al.*, 2011).

Besides the environmental advantages, these materials allow for social and economic benefits. The local production of materials is not only economically cheaper but also creates jobs (Fernandes *et al.*, 2013). The need for skilled workmanship will result on education and training opportunities on these vernacular building systems, contributing to improve the qualifications of the several construction stakeholders, being also crucial for policymakers (e.g., politicians, sociologists and economists) who take decisions about the built environment (Oliver, 2006). In terms of creating a healthy indoor environment, these materials have low

toxicity, no volatile organic compounds and, some of them, have properties that contribute to regulating the temperature and indoor air quality (Berge, 2009), as referred in the example of earthen architecture. In terms of economy, Goodman (Berge, 2009) argues that an industry of ecological construction must have their production units near the place of consumption, using local renewable resources, focusing on processes that require little energy and produce reduced pollution. In order to promote and implement this goal, it is necessary to involve the local authorities. Each side has its own idiosyncrasies that must be taken into consideration in the definition of specific policies adapted to the different contexts (Dumreicher and Kolb, 2008). Supporting sustainable local development means also preserving the cultural heritage of construction knowledge that is characteristic of a certain region.

Nowadays, the interest in vernacular materials is rising in the construction sector, and slowly they are being reintroduced again in the design of buildings, through an optimised combination between the knowledge of the past with the current scientific and technological developments. In this sense, this study presents an environmental LCA of two earthen building techniques: the rammed earth, a technique that was widely used in the past in Southern Portugal; and the compressed earth block (CEB), which can be considered a technical evolution of the vernacular construction material adobe. The LCA is based on specific life cycle inventory data of the product stage of these two building materials. The specific data is from a company located in Alentejo, a region in the South of Portugal.

Use of Rammed Earth and Compressed Earth Block in Portuguese Building Construction

In the past, in Portugal, the materials used for building construction were obtained from the geographical area of the construction site. The industrialisation promoted the use of industrially-produced materials, which are normally produced very far away from the construction site, implying the transportation for long distances and the related potential environmental impacts. Due to the industrialisation, from the beginning of the twentieth century to a recent past, the use of traditional materials and techniques was very limited and an important part of the associated knowledge was lost.

Portugal is a small country, but it is full of contrasts in climate, with significant variations in air temperature and precipitation and in lithology. In Portuguese vernacular architecture, it is particularly evident that there is an almost perfect correlation between the distribution of the building materials used and the lithological characteristics of Portuguese territory (Fernandes *et al.*, 2015b) and one of these materials is earth.

The rammed earth is a building technique that consists of infilling a formwork with soil with a wet consistency that is then compacted in layers. Rammed earth is still now the most prevalent construction technique in existing buildings of the Alentejo region. In this region, the good quality of soil for this type of construction technique is the main justification for its wide use (Fernandes *et al.*, 2015a). Buildings with rammed earth walls have high thermal inertia, which allows them to respond appropriately to the scorching summer heat of Alentejo.

The compressed earth block (CEB) is a technical evolution of the adobe blocks and is obtained by manually or mechanically compressing the earth within a formwork. These blocks can be done only with earth or contain additives to achieve better mechanical performance. Since the earth is compacted directly in the formwork, the blocks can have different shapes, ranging from massive to perforated. The use of earth in architecture continues to make sense in the Portuguese context, due to its several advantages (Fernandes *et al.*, 2015b): strong thermal inertia; ability to influence the quality of indoor air; hygroscopic inertia, contributing to regulate the indoor relative humidity; low embodied energy; low potential cradle-to-grave environmental impact; low-cost material; and at the end of the lifetime it can be recycled and used again in a new life cycle. Buildings made with earth have great durability, since there are a lot of examples with hundreds of years old, and some with a lifetime over than one thousand years, which are still in operation. Although this construction system needs some periodic maintenance, the interventions are normally low cost. Despite these materials have some advantages compared to conventionally used building materials, some of their functional properties, as for instance the thermal insulation, can still be improved. Pereira and Correia da Silva (2012) reported the possibility of improving the thermal insulation of rammed earth walls, in order to comply with the Portuguese regulation on thermal performance, without changing their environmental characteristics, by adding granulated cork in the soil mixture.

Materials and Methods

The Life Cycle Assessment (LCA) of rammed earth and compressed earth blocks (CEB) is based on the specific life cycle inventory data provided by a Portuguese company located in the south of the country. The used method complies with the standards ISO 14040, ISO 14044 and EN 15804.

Functional Unit and System Boundaries

In this study, the objects of analysis are rammed earth and CEB. The declared functional unit is dependent on the goal of the life cycle analysis and in this case the impacts resulting from the production of 1 m³ of rammed earth and 1 block of compressed earth

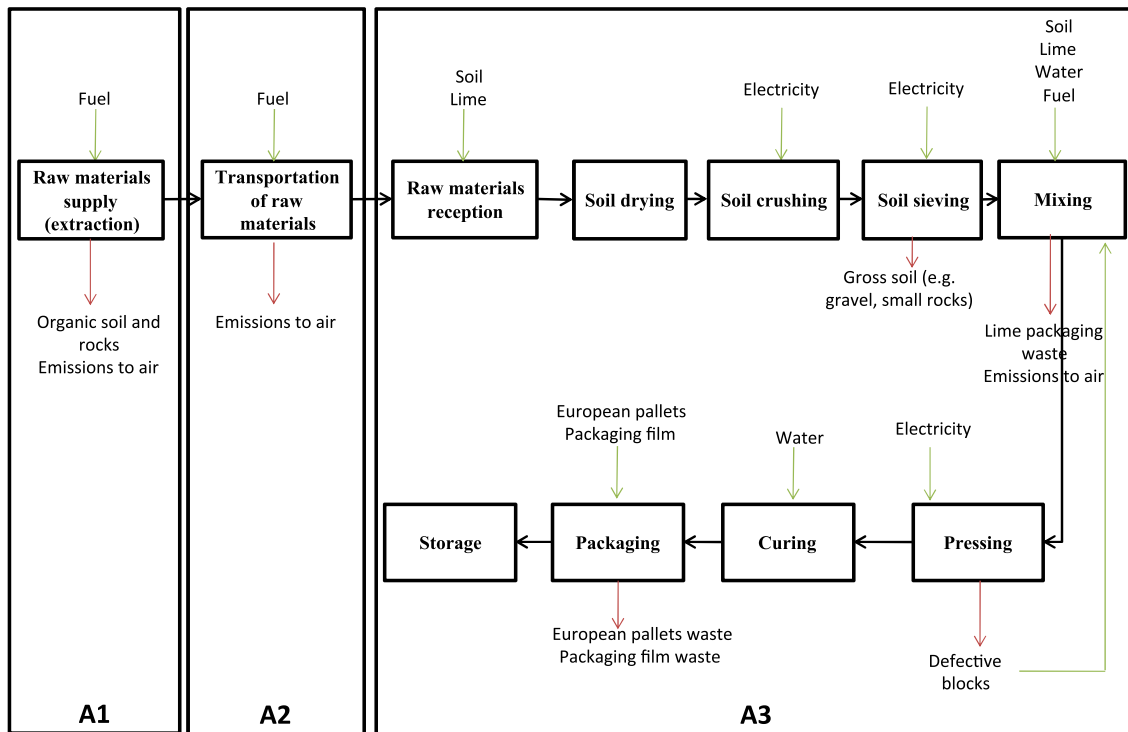


Fig. 1 Diagram of the manufacturing processes of compressed earth block (CEB).

blocks are estimated. This will allow comparisons with other building materials. The boundaries of this work consider the embodied (cradle-to-gate) environmental impacts of the two studied materials. This means that the study takes into account the impacts resulting from the extraction of raw materials, production of secondary products produced by other companies, transportation of the materials to the facility and manufacturing processes. **Figs. 1** and **2** present, in a simplified way, the processes that were included in the LCA analysis and the boundaries of the study.

Inventory Analysis

To quantify the environmental indicators it is necessary to first develop the inventory analysis (Teixeira *et al.*, 2016). The inventory is used to quantify the inputs (e.g., energy, raw materials and chemicals) and the outputs (e.g., emissions and wastes) of the product system.

Data used for the modulation of input and output flows of energy and mass is based on a quantitative and qualitative analysis of information received from the manufacturer and of technical documentation of the mechanical and electric equipment used. Generic data was used for the processes in which the manufacturer does not have direct influence or specific information. Therefore, generic data from the Ecoinvent v3.3 database were used for the production of fuels, electricity, tap water, hydrated lime, packaging plastic, wooden pallets and transportation processes. The following processes are excluded from this study: (i) environmental loads resulting from the construction of industrial infrastructures and production of used equipment; and (ii) environmental loads related to the transportation infrastructures of pre-products (e.g., production and maintenance of vehicles and production and maintenance of roads).

The life cycle of the two products was modulated using the SimaPro v.8.4.0 software. Since this study is focused on the analysis of two environmental indicators (Global Warming Potential – GWP and the Total Embodied Energy – EE, tot), the following two lifecycle impact assessment methods were used, respectively: CML-IA v.3.4 method and Cumulative Energy Demand v.1.9 method.

Results and Discussion

Table 1 presents the results from the quantification of the potential environmental impacts related to the production of 1 block of CEB and 1 m³ of rammed earth and the contribution of different information modules of the product life cycle stage: A1 – raw materials supply; A2 – transportation; and A3 – manufacturing. Since the rammed earth is only materialized in the construction site, the construction process stage was also included. Therefore, the transportation of materials and equipment (information module A4) and the construction process (A5) were considered in the life cycle analysis of rammed earth.

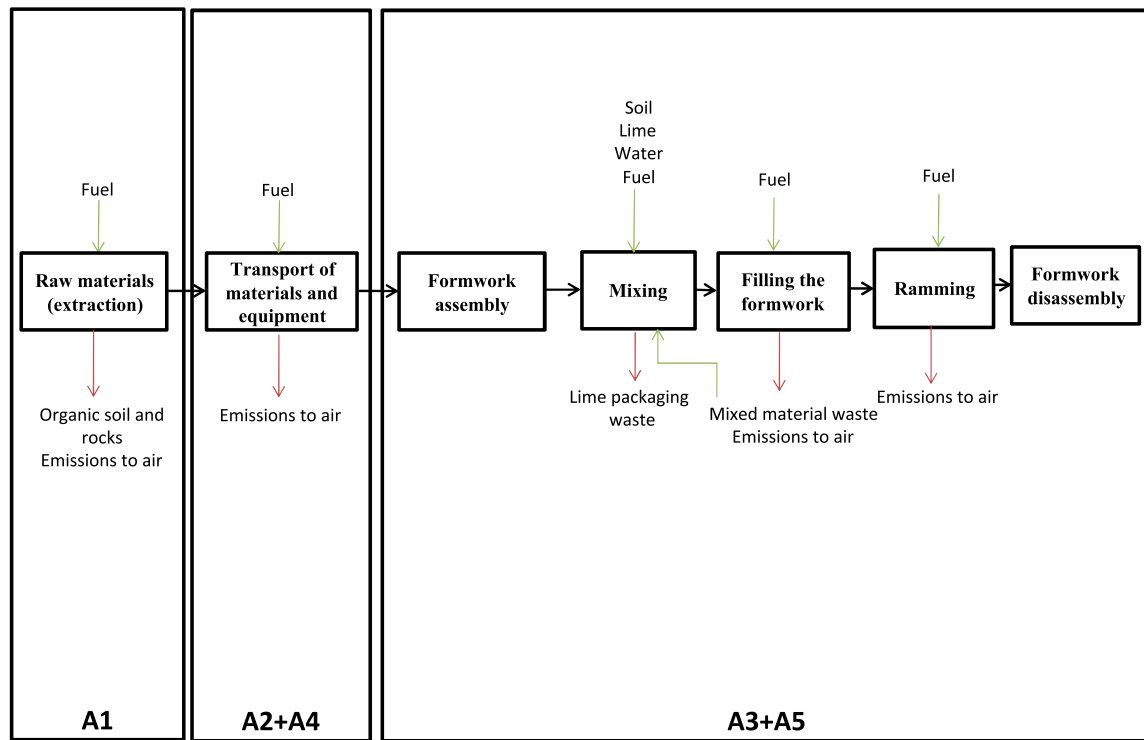


Fig. 2 Diagram of the manufacturing processes of rammed earth.

Table 1 GWP and EE, tot related to the product life cycle stage of 1 m³ of rammed earth and 1 block of CEB

Information modules of the product stage	Rammed earth (1 m ³)		CEB (1 block)	
	GWP (kg CO ₂ eq)	EE, tot (MJ)	GWP (kg CO ₂ eq)	EE, tot (MJ)
A1	3.14	48.84	0.02	0.26
A2/(A2 + A4, in the case of rammed earth)	2.89	48.30	0.11	1.74
A3/(A3 + A5, in the case of rammed earth)	44.26	529.04	0.26	1.93
Total	50.28	626.18	0.39	3.94

Analysing the results it is possible to conclude that the manufacturing stage is the one that most contributes to the environmental impacts of both materials. Additionally, the production of CEB has higher potential environmental impacts than the production of 1 m³ of rammed earth. This is mainly due to the higher impacts resulting from the transportation and manufacturing stages of this material and could be minimised if the production of CEB was done in the same place of earth extraction/preparation, which is the case in the rammed earth.

In order to understand if these two materials have a good environmental performance, it is also necessary to compare these results with the ones of conventionally used building materials. In this case, the results were compared with the ones of the ceramic brick, the most used material in Portugal to build walls and the declared functional unit is 1 kg. In the calculation of the potential environmental impacts of the ceramic brick, the generic LCI data from Ecoinvent v3.3 database and the transportation distance from the nearest brick manufacturer were considered.

Fig. 3 presents the cradle-to-gate environmental impacts resulting from the production of 1 kg of each material. The differences between the three materials are similar for the two environmental impact parameters, being the rammed earth the one that presented the lowest values. Additionally, both earthen materials have substantially lower potential environmental impacts than brick.

Nevertheless, it is important to highlight that the comparison presented in **Fig. 3** is based on the same amount (1 kg) of material, but when they are used in the construction, different kilograms of each material are necessary to satisfy the same function. Therefore, it is necessary to compare these three materials when they are used to fulfil the same function. In the case of this study, the comparison is made considering the amount of material that is needed to build 1 m² of common walls. Six alternatives for walls were considered: 15 cm thick CEB wall with and without plaster since CEB does not need plaster to be finished; 60 cm thick rammed earth wall without plaster; 22 cm thick hollow brick wall finished with plaster in both surfaces; and

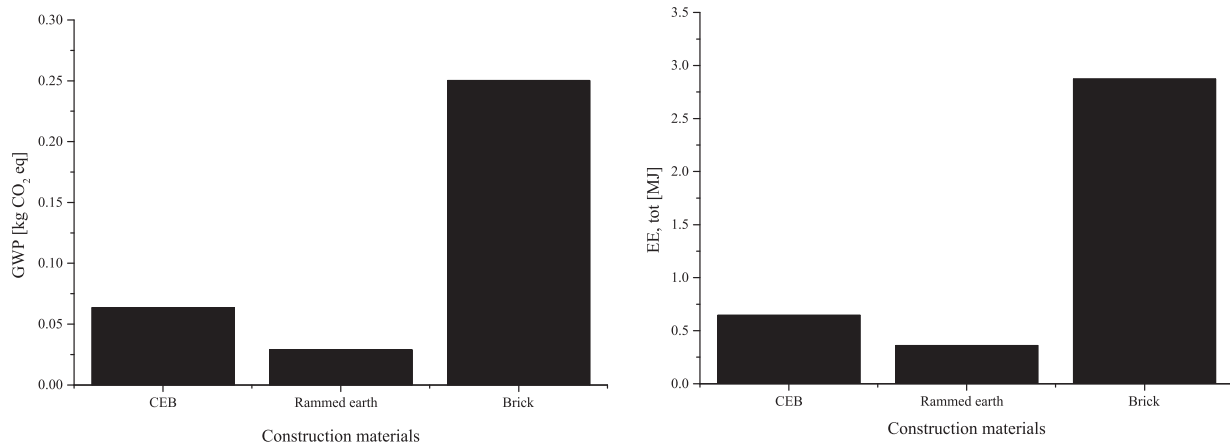


Fig. 3 *GWP and EE, tot* related to the product life cycle stage of 1 kg of CEB, rammed earth and ceramic brick.

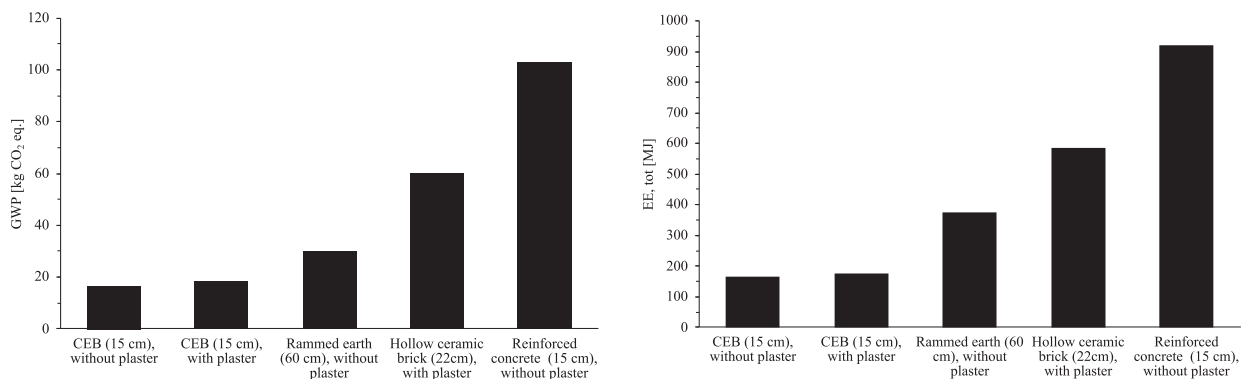


Fig. 4 *GWP and EE, tot* for 1 m² of each alternative wall.

15 cm thick reinforced concrete wall. The considered plaster is the same for the different walls and is made with Portland cement. In the calculation of the potential environmental impacts of the ceramic brick, cement mortar, concrete and reinforced steel, generic LCI data from Ecoinvent v3.3 database and the transportation distances from the nearest producers were considered.

Fig. 4 presents for the six alternative walls mentioned before the values of the two impact categories. It can be observed that the CEB wall without plaster presented the lowest values for both impact categories. One interesting observation is that when the comparison is made at the scale of the building element, CEB is the material with the lowest potential environmental impact, but when comparing 1 kg of each material, the best material is the rammed earth. This is because the weight of CEB needed to build 1 m² of wall is much lower than the weight of a rammed earth wall.

Conclusions

The life cycle assessment results presented in this study are based on specific data from a Portuguese manufacturer of earthen materials (compressed earth blocks – CEB and rammed earth) and showed the substantial environmental savings resulting from the use of these materials in comparison to the use of ceramic brick and reinforced concrete. The comparisons are made at the level of 1 kg of material and also for 1 m² of an equivalent wall, considering the cradle-to-gate life cycle stages. Although the end-of-life impacts are not considered in this study, it is necessary to highlight that earthen materials would also have lower potential environmental impact in that stage, compared to ceramic bricks and concrete, since they can be easily recycled to be used in the production of new earthen materials or they can be simply disaggregated and returned to the natural environment at an insignificant environmental impact.

In the case of the compressed earth block there are two major contributors to the value of the analysed environmental parameters: (i) the transportation of raw materials (soil mixture from the extraction site to the manufacturing site and hydraulic lime from the producer to the manufacturing site); (ii) and the manufacturing process of the block, mainly due to the electricity and fuel consumption in the soil sieving, mixing and pressing processes. For the rammed earth, the major contributor is the manufacturing process, mainly due to the fuel consumed in the mechanical ramming process. The potential impacts of the CEB would be lower if the production facility was closer to the place where the extraction of soil is made.

Results of this study show that the two studied vernacular materials have substantially lower environmental impacts when compared to the equivalent materials that are currently used today in the construction sector. Vernacular materials are locally available and therefore they do not need to be transported for long distances. Additionally, they need very low intensive energy manufacturing processes and therefore they have lower embodied energy than conventional building materials. From the analysis of the results, it is evident that the use of the two earthen materials can contribute to decreasing the embodied impacts of a building, but further studies are needed in order to consider other life cycle stages, such as the use stage.

Thus, to achieve the goals for a more sustainable built environment, architecture and construction industry should seek an optimised integration between tradition and modernity, using the best of both at the level of know-how, techniques and materials. Beyond the environmental issues, promoting the use of local materials may have a positive impact on the local social and economic developments. It is up to designers to use their creativity to improve and adapt these vernacular techniques to the new functional requirements. Nevertheless, internationally there is still a lack of quantitative information of most of vernacular materials and techniques. Therefore, more studies are needed to analyse and identify the best vernacular techniques and materials so that they can be improved and scientifically validated in light of the actual technological and scientific knowledge. This will give credibility to those materials and will promote their use by the different stakeholders of the building sector.

Acknowledgements

The authors would like to acknowledge the support granted by the FEDER funds through the Competitivity and Internationalization Operational Programme (POCI) and by national funds through FCT – Foundation for Science and Technology within the scope of the project with the reference POCI-01-0145-FEDER-029328, and of the PhD grant with the reference PD/BD/113641/2015, that were fundamental for the development of this study. The authors also wish to thank the construction company for providing the life cycle inventory data and supporting this research work.

See also: Evaluating the Sustainability Performance of Building Systems and Technologies for Mainstreaming Sustainable Social Housing in India

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Evaluating the Sustainability Performance of Building Systems and Technologies for Mainstreaming Sustainable Social Housing in India

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Background and Context

India is urbanising at a rapid pace and is projected to add 416 million new urban dwellers by 2050 (UN DESA, 2018). The majority of this is attributed to the growing rate of rural to urban migration, which in turn has rendered stress on the existing basic amenities and infrastructure. According to a recent estimate by the Ministry of Housing and Urban Affairs (MoHUA), the total urban housing shortage at the end of 2017 was about 10 million, with majority of this pertaining to the houses for the Economically Weaker Sections (EWS) and Low-Income Groups (LIG) (PIB Gov. of India MoHUA, 2017). Through its “Housing for All by 2022” mission, the Government of India intends to close this gap by aiming to construct 12 million housing units over the programme duration (2015–2022) through a combination of slum upgradation projects in partnership with the private sector, direct government-led housing delivery, a credit-linked subsidy scheme as well as support to beneficiary-led construction (MoHUA, Govt. of India, 2017). However, such a focus has multiple implications.

First, housing construction must factor in the environmental risks embedded in its processes. For example, increase in building construction is associated with a rise in energy consumption at an annual rate of 9% compared to the increase in overall national energy consumption of 4.3% (UN-Habitat, 2015a). Residential construction consists of the largest portion of this growth (AEEE, 2015). Continued energy consumption in an inefficient manner runs the risk of increased greenhouse gas emissions. Furthermore, the demand for raw materials, such as sand and soil, are expected to grow as construction rises. This can increase the risk of land and riparian degradation. Given the criticality of such resources in sustaining other sectors such as agriculture, increased competition can cause social conflict (Caleb *et al.*, 2017).

Second, the speed at which housing is to be delivered must not only prioritize the provision of shelter at affordable rates, but also incorporate the adequacy of a home as well as the international Human Right to Adequate Housing, and include its seven criteria: tenure security, affordability, habitability, availability of services, accessibility, location, and cultural adequacy. This means housing policies and construction practices should account for multiple factors, including, *inter alia*, and access to basic facilities, infrastructure, and employment opportunities (UN-Habitat, 2017). Poor access to adequate housing is associated with several measures of well-being such as health and chronic poverty (UN-Habitat, 2015b).

Third, housing construction should harness the job creation potential of the construction sector. In 2013–2014, the real estate sector contributed to 6.3% of GDP and employed approximately 7.6 million people (Gopalan and Venkataraman, 2015). The sector's output value is expected to grow at a compound annual growth rate (CAGR) of 4.16% for the 2017–2021 period compared to 3.95% between 2012 and 2016 (Global Data, 2017). These projections are promising. However, rapid housing delivery may also involve utilization of less labor intensive, and more mechanized, and efficient building systems for construction. Neglecting the sector's potential could deepen the country's ongoing challenges with meeting the employment needs of the country's burgeoning youth population.

Furthermore, there is India's commitment at the global level regarding mitigating climate change and resource efficiency in particular. Also, under the 2030 Agenda for Sustainable Development that proposed 17 Sustainable Development Goals, Goal 11: Make cities and human settlements inclusive, safe, resilient and sustainable and Goal 12: Ensure sustainable consumption and production patterns - particularly focus on the impacts of the rapid pace of urbanization and growth in the construction sector. While the Government of India has allocated tremendous resources to ‘ensure access for all to adequate, safe and affordable housing and basic services and upgrade slums, by 2030’ (Goal 11-target 11.1), the delivery of less sustainable housing still represents a challenge to other sustainability dimensions. Although there is increasing knowledge about sustainable development in India, sustainability is yet to become mainstream in housing construction, evident by the limited uptake of alternative construction materials that are environment friendly and cost effective.

Given this context, the “Mainstreaming Sustainable Social Housing in India project (MaS-SHIP)” was designed to build upon work previously undertaken in the field of sustainable social housing globally and India in particular, while recognizing the priorities set by the Government of India, as well as their inherent constraints. In India, social housing is a rarely used term (Herda *et al.*, 2017). Instead, government and the private sector typically use affordable housing to frame housing policy and practice. However, this term can be applied to any income group whereas social housing applies to a country's most economically vulnerable section.

This study was framed within the parameters of social housing because it focused on India's poorest segments – the Economically Weaker Segments (EWSs) and Low Income Groups (LIGs) (Fig. 1) – because the majority of the country's housing shortage, estimated to be between 10 million (MoHUA, 2017) to 12 million units (FSG, 2018), is concentrated amongst such

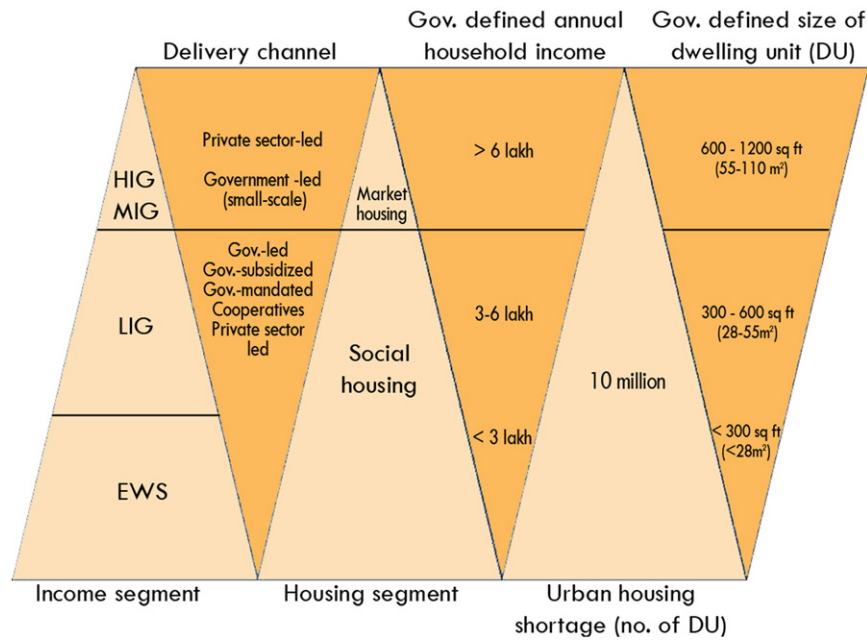


Fig. 1 Social housing definitions as implied by the research.

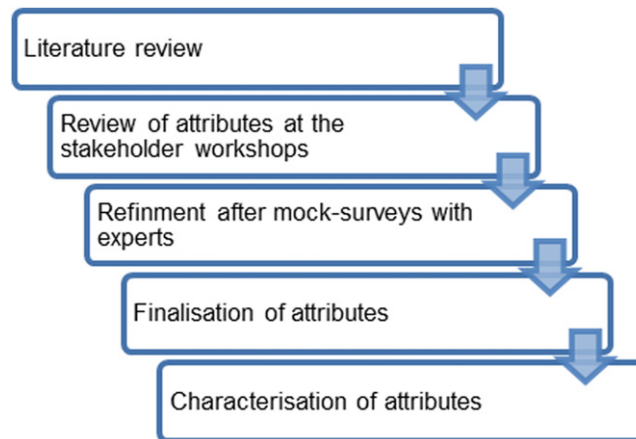


Fig. 2 Attributes selection process.

segments. The study was designed to integrate sustainability in social housing projects in India through the adoption of sustainable building materials and systems, as well as design and management practices by:

- Identifying and selecting a set of 'attributes' to define the sustainability performance of 'established' and 'emerging' building materials and systems for social housing projects, in consensus with experts.
- Developing and testing interactive tools to enable developers, practitioners and policy-makers make informed decisions about integrating sustainability in the design and specification of building systems in social housing projects.

Methodological Approach

The study adopted a socio-technical approach bringing together lessons from previous research, stakeholder engagement methods, with field surveys and statistical analysis. A review of literature helped to define the extent and scale of challenges and opportunities for mainstreaming sustainability in social housing in India. It also helped to identify a list of established and emerging building materials and systems appropriate for the social housing sector, as well as attributes to assess their sustainability performance in terms of environment, resource efficiency, user experience and economic impact. The methodological approach is shown in [Fig. 2](#).



Fig. 3 Level of participation at MaS-SHIP stakeholder events by different types of organizations.

Literature Review

An extensive review of relevant literature (policy documents, journal articles, reports) was conducted to analyze the problem of (social) housing shortage and provision in India, along with the Government's response at the national and state level. National and international case studies of social housing projects were used to derive learning that could positively influence the Government of India's prerogative to provide housing for all. The literature review helped to gather background evidence about policy drivers (and barriers) for integrating sustainability into low-income housing and the development of tools to help in making such decisions. It also informed the selection of attributes to evaluate sustainability performance of selected building materials and systems.

Stakeholder Workshops

Stakeholder engagement through workshops formed a key research tool to gather collective opinions from experts during the course of the study. These events allowed an interactive exchange between the MaS-SHIP team, and various experts associated with the housing and sustainability sector. A total of eight stakeholder engagement workshops were held in three different cities in India at various stages of the study that led to engagement with 112 organizations that included policy-makers, academics, housing developers (public and private), building material manufacturers, architects, building consultants and the voluntary sector. Various organizations from voluntary sector working towards promoting sustainable practices in the Indian construction industry were also well-represented (Fig. 3).

Surveys

In order to address the data gaps, primary data were gathered using interview-based questionnaire surveys to enumerate the qualitative and quantitative sustainability attributes of the selected building systems. Stakeholders included building practitioners (architects, consultants); building material manufacturers and social housing residents. An online survey of experts was also conducted to establish the relative weightings of the selected attributes of sustainability.

Online survey: In order to assign relative weightings to selected attributes of sustainability, the research team conducted an online survey of experts relevant to the housing and sustainability sector in India. The respondents provided weightings to the selected attributes according to their preference or relative importance given to an attribute while selecting building materials and systems for any housing project. The survey was designed based on the Analytic Hierarchy Process (AHP). A total of about 200 responses were gathered, the statistical analysis of which allowed the research team to establish the relative weighting of the selected attributes. The three survey forms are available within the DST that is accessible on the MaS-SHIP website.

Selecting Sustainability Attributes

A key aspect of MaS-SHIP research was to systematically select relevant attributes that can be used for characterising the sustainability performance of building materials and systems. This enabled a comparative evaluation for their application in social housing projects. The literature review along with deliberations with experts during the MaS-SHIP stakeholder engagement workshops enabled the development of the selected 18 attributes. The multistep approach led to progressive iterations to reach the final set of 18 attributes (Fig. 4) that holistically defined the sustainability character of the building material and systems being evaluated.

Their units of measurement were finalized for indicating sustainability, and categorized under four main-criteria namely:

- *Resource Efficiency*: to comprehensively account for the energy consumed and resources extracted throughout the entire life cycle of the construction process.
- *Operational Performance*: to factor in traditional efficiency metrics to ensure high quality building construction.
- *User Experience*: to factor in the role of residents and building practitioners in terms of their familiarity and experiences with existing options and sustainable alternatives.
- *Economic Impacts*: to link better environmental choices with a comprehensive set of economic indicators, including cost and job creation potential.

The list of all the selected attributes along with their description and units of measurements is available in the Annex.

Assigning Relative Weightings to the Attributes

To avoid any bias towards an attribute, it was necessary to assess the attributes with respect to each other rather than assigning equal weightings. This helped to establish the relative importance or preference for the 18 attributes. To assign weightings to the attributes, a survey based on Multi-Criteria Decision Making (MCDM) system was designed to evaluate the attributes with respect to each other. The mathematical technique finalized for MCDM was Analytical Hierarchy Process (AHP), which was selected to assign relative weightings to the selected attributes.

An online nationwide survey based on the AHP technique was conducted to evaluate the relative importance of the 18 attributes. The selection and finalization of the survey design was primarily done by reviewing similar AHP studies. Based on the rankings given by the experts as per the study, the following design was finalized (Table 1).

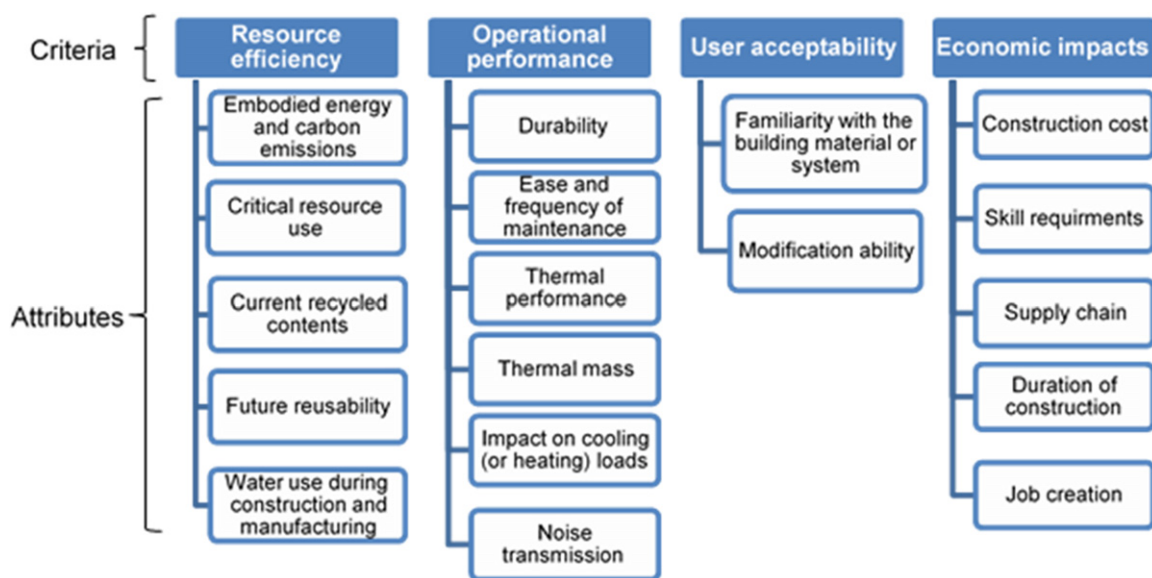


Fig. 4 Final list of attributes.

Table 1 Defining the nominal ratio scale for the AHP survey

Attribute	Left side scale				Center	Right side scale				Attribute
	Very high effect	High effect	Moderate effect	Slight effect		Slight effect	Moderate effect	High effect	Very high effect	
A	9	7	5	3	1	3	5	7	9	B

Note: If A has higher effect, use left side of the scale.

If both, A and B have equal effect, the center of the scale is to be selected.

If B has higher effect, use right side of the scale.

**Fig. 5** Different user groups for the AHP survey.

The nominal ratio scale of 1–9 (Saaty, 1990) was adopted for doing the pairwise comparisons. The formulated decision hierarchy and the above design were then tested through different MaS-SHIP stakeholder events and subsequently improved. The final decision hierarchy comprised of the four main criteria: Resource efficiency, Operational performance, User acceptability and Economic impacts. Pairwise comparison of the attributes grouped under each main criterion was followed by pairwise comparison of all the four main criteria with each other. The final decision hierarchy was the basis on which the attributes and criteria were compared for evaluating final weightings.

The Analytic Hierarchy Process is one of the pre-eminent approaches for formal decision-making techniques. It is critical to select the correct data sample size which is required for a comparative analysis to provide tangible results. The key to arriving at a statistically valid result is finalizing an appropriate sample size.

Determining Sample Size

There is no limitation on the population size that one can take up for a survey. Also, the greater number of different user groups that are represented in the survey, the better it is. For the MaS-SHIP AHP survey the different user groups are shown in Fig. 5. In response to the MaS-SHIP survey, it was imperative to select the representative sample size as this would then become the population set and sampling of the responses would become a key parameter of the analysis to remove any biases from the survey results.

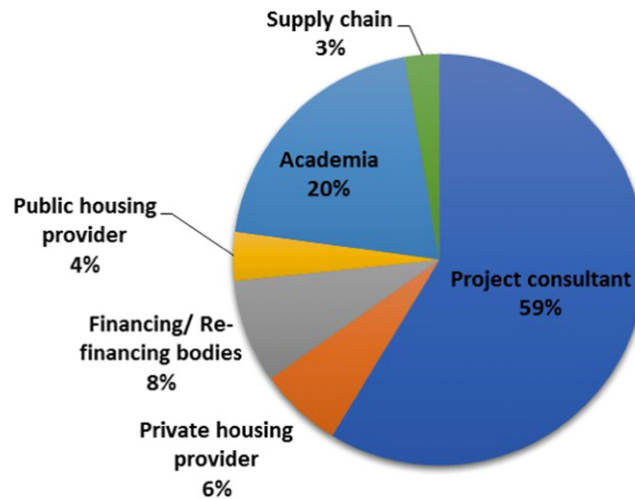


Fig. 6 User groups of respondents.

Targeting the Representative Sample Size From the Population

Selecting the representative sample out of the population set is of utmost importance and various factors such as respondent's age, experience in sustainability, profession, qualification etc., had to be considered while sampling the responses received from the AHP Survey. To avoid any skewed results that may occur during sampling the responses, a Stratified Random Sampling process was adopted where the sampling frame was divided into smaller sub groups. Thereafter, the groups were stratified based on the relevant years of experience in sustainability.

Confidence Level and Confidence Interval

Once the required sample size was arrived at, finalizing the required confidence level of the survey and the confidence interval was essential. The confidence level is expressed as a percentage and represents how often the true percentage of the population who would pick an answer lies within the confidence interval. The confidence interval is also called margin of error.

The margin of error in a survey is approximately equal to the inverse of the square root of the sample size. However, a margin of error more than 10% is not recommended while conducting the surveys. The MaS-SHIP AHP surveys targeted an error margin in between 5%–10%. This implied that a sample of 100–400 responses was desired.

Expert Survey Results

The survey helped in establishing relative weightings of the 18 attributes comprising the Sustainability Assessment Tool (SAT). A total of 200 responses were received from leading experts in the building industry across India. All 200 responses were checked for consistency and the weightings for the attributes were eventually derived from the consistent responses of 184 experts. The 184 consistent survey respondents were categorized into user groups as per their area of expertise (**Fig. 6**).

About 108 respondents out of the 184 belonged to the project consultant group contributing to nearly 59% of the responses. The respondents were also assessed in terms of their experience in the field of housing sector and/or sustainability (**Fig. 7**). The research team assessed the difference in responses of the respondents having 0–2 years (56) of experience in sustainability as opposed to the ones with experience of 3 years (52) and above. Since there were no significant disparities observed in the responses of both groups, the MaS-SHIP team decided to use all 184 responses to evaluate final weightings of the attributes.

Based on the analysis of the survey results, weightings were obtained for the 18 attributes (**Fig. 8**). It was evident from the AHP survey that each respondent group had their bias towards certain attributes. As expected, the private housing providers preferred 'construction cost' over all other attributes. However, it was encouraging to note that attributes such as 'familiarity', and 'modification ability' were also highly preferred. These results were no different from the overall weightings of the attributes evaluated.

Even though residents of social housing were not a part of this expert survey, it was interesting to find that attributes affecting them such as 'familiarity', and 'modification ability', came second in terms of preference, after 'construction cost'. 'Impact on cooling (or heating) loads' was also among the most preferred attributes.

It was evident that the performance of building materials and systems against the most preferred attributes namely 'construction cost', 'familiarity', 'modification ability' and 'Impact on cooling (or heating) loads' would have maximum impact on their final scores.

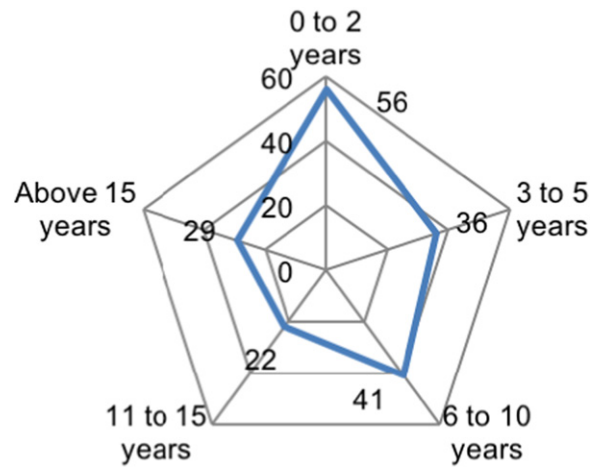


Fig. 7 Experience (in years) of the survey respondents.

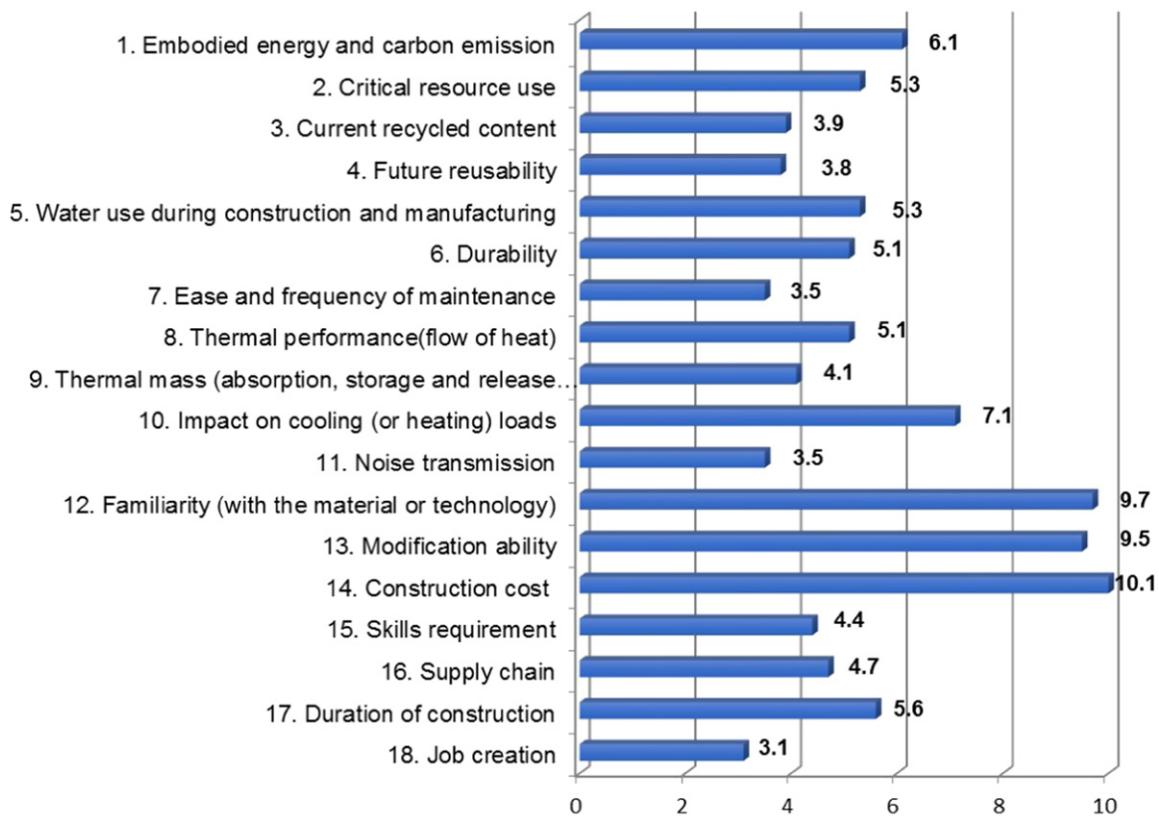


Fig. 8 Final weightings of the 18 attributes.

Decision Support Toolkit (DST)

The data and knowledge assimilated in the study was brought together in the form of a web-based Decision Support Toolkit (DST) with embedded tools, to enable practitioners, housing developers and policy-makers for integrating sustainability concepts in the planning, design and selection of building systems in social housing projects. The Decision Support Toolkit (DST) is an interactive web-based toolkit that not only helps to bring together the outputs and insights from the research, but also provides a unique platform in the social housing sector with data and knowledge on various aspects of sustainable (social) housing. The DST is developed with an aim to enable developers, practitioners and policy-makers to integrate sustainability concepts in the planning, design and specification of social housing projects in India.



Fig. 9 Snapshot of decision support toolkit (DST).

The web-based DST (**Fig. 9**) was designed to address the requirements of different stakeholders involved in the social housing sector. It was organized around the following key themes to maximize engagement with different stakeholders:

Why should sustainability be integrated in social housing projects?

Before delving into ways of incorporating sustainability measures in housing, the DST helps the user understand why this should be done. This section helps the users of the toolkit to familiarize themselves with the social housing sector through its realities today, national policy scenario, best practice examples and opportunities for sustainability in the Indian housing sector.

How should sustainability be integrated into the design of social housing across different climatic zones in India?

The practice of sustainability is still at an early stage in the Indian housing sector. The most efficient way for achieving sustainability is to incorporate its principles in the planning and design stage of the project. There is information available to guide practitioners in this aspect, but this is largely fragmented and available in different versions pertaining to different sources. This section of the toolkit collates the principal design guidelines for sustainable housing in five climatic zones in India. These guidelines drawn from existing literature in the Indian context such as the National Building Code of India (NBC), Design guidelines for Multi-storeyed residential buildings developed by BEEP India and various similar works, data collected in the study as well as findings from the resident's experiences gathered from surveys of housing projects. The guidelines provide an overview of different aspects to be addressed at project conception stage, including passive design strategies, material use and its impact on energy consumption for indoor comfort, maintenance and up-keep of the site and water conservation measures. The guidelines though brief, serve the purpose of directing the user's thoughts towards different aspects and ways of integrating sustainability in social housing projects.

What sustainable building materials and systems are appropriate for social housing projects? What criteria should be used to evaluate their performance?

This section is the core part of the DST and brings together all data collected on building materials and systems which can be considered for social housing. The data for each building system is organized as pertaining to a set of attributes identified and defined by the study. This is intended to assist the user in making an informed choice of building materials and systems by evaluating their sustainability through multiple criteria. The following information is available in this section:

- Sustainability attributes for evaluating building materials and systems,
- Seventeen catalogs for building materials and systems providing data on their performance against the framework of 18 sustainability attributes,
- Analysis of comparative performance of these building systems with respect to sustainability,
- A User guide to using the Sustainability Assessment Tool (SAT),
- The Sustainability Assessment Tool.



Fig. 10 SAT embedded in the DST.

Where are these sustainable building materials available?

The construction sector in India is very diverse and unorganized in nature. About 98% of the construction companies are small and medium scale enterprises. Unlike the manufacturing industry, it is not always repetitive and is project specific and dependent on the source of the local material. A key aspect which governs selection of building materials and systems is transportation distance for delivering materials to construction site and the associated transportation cost. This section provides a guide to the user to locate existing building material manufacturers across the country, with basic information given on each manufacturer for ease of communication. Thus, the user can make an informed decision on the choice of material or system to be used, based on the estimated distance and scale of supply of the manufacturing unit to the proposed construction site.

Also given in this section are formats for recording basic information about building material/system and for specific details of a social housing project. This is to enable the addition of new materials to the DST and to the GIS-based database to maintain the dynamic nature

Who are the residents of social housing and what are their experiences of living in such developments?

This section provides the users, access to the findings from the case study of the five social housing developments in different climatic zones. The case studies are based on surveys of 723 residents belonging to the five housing developments. The resident surveys gather user experience with indoor environment (air temperature, air quality, air movement, overall experience), natural light, problems of dampness, quality of construction and accessibility to amenities.

Sustainability Assessment Tool (SAT)

The Sustainability Assessment Tool (SAT) is one of the key components of DST (Fig. 10) and was developed using a Multi-Criteria Decision Making (MCDM) method to enable developers and designers make informed decisions regarding the selection of building materials and systems for walling and roofing, for deploying in social housing projects in India. Currently, SAT evaluates 12 established and 5 emerging building materials and systems against the 18 attributes. It is an easy-to-use, interactive excel tool that is available through the DST. Presently a beta version of the tool has been developed which can be reviewed, tested and modified progressively.

This section describes the development and potential application of SAT using the results of the AHP survey conducted among 200 experts. This was combined with the data gathered for the 17 building systems against each of the 18 attributes.

Methodology underpinning SAT

Given the difference in the nature of the data gathered against the 18 attributes (qualitative and quantitative), their units of measurements and gaps in the data, it was important to select a methodology that would capacitate both qualitative and quantitative datasets and cater for data gaps while evaluating building systems. All the attributes and the building materials and systems had to be assessed on a level plane to achieve precise scores.

Resource Efficiency				
Attributes	1. Embodied energy and carbon emission	2. Critical Resource use	3. Current recycled content	4. Future reu:
Evaluation scale	MJ/Sq. M	High-Medium-Low	%	High-Medium
Evaluate - Yes/No	No	No	No	No
	Yes No			

Fig. 11 Selection of attributes to evaluate the building materials and systems.

The Multi Criteria Decision Making (MCDM) approach was selected to bring together the quantitative and qualitative data to derive the relative weightings of the attributes for each of the 17 building systems. The approach and methodology were developed so that they provide tangible outcomes and trade-offs as a measure of sustainability.

An extensive literature review was carried out to identify a Multi Criteria Decision Making (MCDM) method which would address all the above challenges to give credible results. MCDM methods such as Analytic Hierarchy Process (AHP), Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS), Multi-Attribute Utility Theory (MAUT), Preference Ranking Organization METHod for Enrichment Evaluation (PROMETHEE) and Weighted Sum Model (WSM) were studied. While some of these could help in overcoming the above challenge, most of them were unable to address the issue of missing data under different attributes.

The MCDM problem considered at the building material and system level in SAT was categorized as a non-classical MCDM problem as it accounts for the missing data under the attributes. The non-classical MCDM method used in SAT is Belief Function based TOPSIS. The Analytic Hierarchy Process (AHP) was selected as the MCDM method to evaluate the attributes and as a result, relative weightings were ascribed to them, to determine the order of preference at criteria level. The data collected for the 17 building materials and systems against the 18 attributes defined the problem statement to select a suitable method for evaluating them under the existing challenges.

The proposed Belief Function based TOPSIS was classified as MCDM tool (Dezert *et al.*, 2016) as its purpose is to help the 'user' to choose a building material or systems among a known set of 17 based on their numerical scores calculated with respect to data collected under 18 attributes.

This new approach offered the advantage to deal directly with negative, zero and positive data values, missing data values, and unreliable sources of information related to each attribute as well. This process assigned belief, plausibility and uncertainty for the missing data values to which TOPSIS was applied subsequently to obtain final scores of the building materials and systems.

Although this MCDM problem was easily formulated, there were difficulties in solving it because the data under various attributes was expressed in different units and scales. Such differences in the unit and scale of data gathered necessitated a normalization step that could have yielded further problems like rank reversal. A rank reversal is a change in rank ordering due to addition or deletion of a building material or systems from the list.

The process for developing SAT calculations involved creating a 'base matrix' comprising of 18 attributes with data populated for 17 building systems. The matrix had both qualitative and quantitative sets of data. The missing values in the matrix were denoted by 'NA'. These missing values were addressed by adopting a theory of belief functions or the Dempster Shafer's Theory which involves assigning probabilistic values of belief, plausibility and uncertainty to data values. After calculating the belief, plausibility and uncertainty, TOPSIS method is applied to the matrix to arrive at the final scores of the building systems.

Interpretation of SAT scores

The SAT enables the user to make an informed choice by providing the order of preference of the 17 walling and roofing systems against all 18 attributes. The user can select the attribute or attributes grouped under the four main criteria (Resource Efficiency, Operational Performance, User Experience and Economic Impacts) to evaluate a total of 17 walling and roofing systems. The selection can be completed by picking a 'Yes' from the dropdown list placed under each attribute (Fig. 11).

Fig. 12 shows the walling and roofing systems evaluated for the attributes under the criterion 'Resource efficiency'. Higher score of a building material or systems with respect to others is an indicator of its better performance. A high score is better and independent of the nature of the attribute. For instance, a high score of a building material or system for an attribute 'Embodied energy and carbon emissions' indicates that it has a low absolute value (MJ/m^2) which has led to its high score. In simpler terms, the higher the graph spikes, the better the score gets, hence the better the performance. Similarly, results for other criteria (Operational performance, User experience and Economic impacts) can be evaluated using SAT. The holistic score across all or selected attributes is also displayed towards the bottom of the SAT under 'Sustainability Assessment – Holistic' (Fig. 13). A detailed guidance document on 'how-to-use' SAT is available as part of the DST.

While SAT is a novel tool for appraising the performance of building systems against a wide range of attributes, it is important to remember that presently, it provides comparative analysis of 17 selected building systems against the 18 attributes of

Sustainability Assessment Tool - Criteria wise

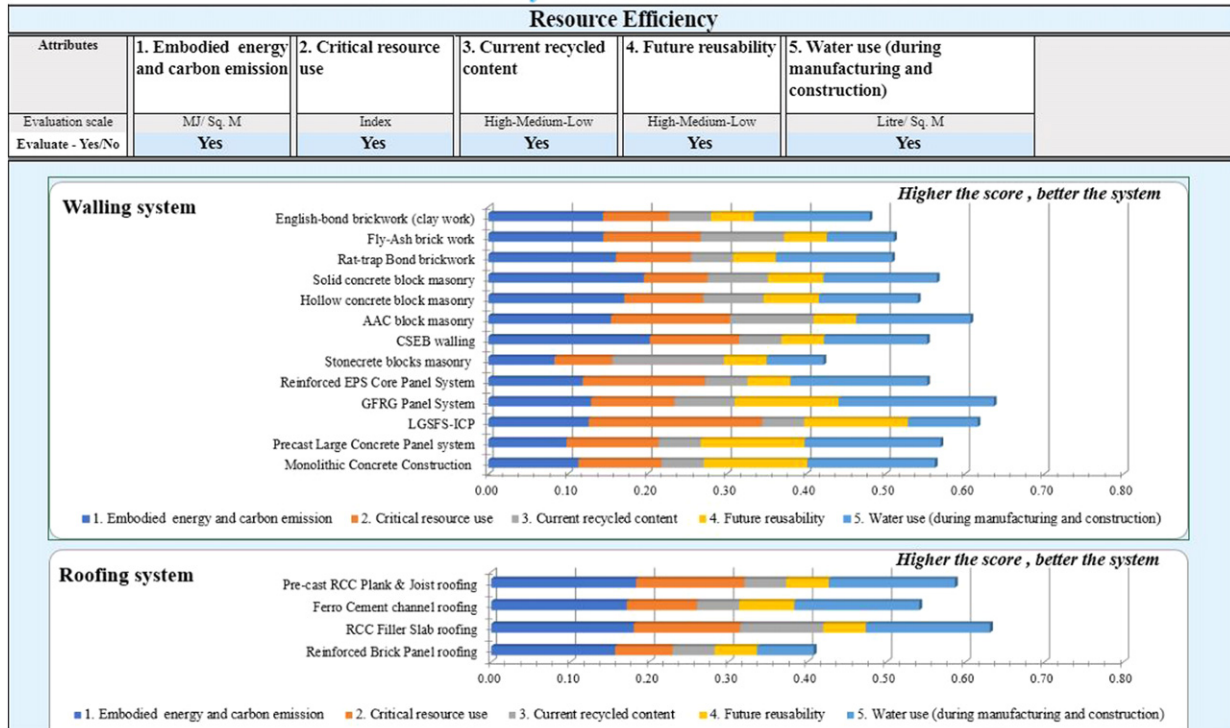


Fig. 12 Order of preference across all attributes under 'Resource efficiency'.

sustainability identified for housing units only up to four storeys high. Also, SAT does not give absolute data or values for the building systems evaluated by it under 18 attributes. It only provides a score which has been calculated using the absolute data for building systems under weighted attributes. The 'score' calculated for any particular building system against the 18 attributes is the 'relative weighting' of that particular building system against the other 16 building systems listed in SAT.

Discussion: Wider Application of DST

It is clear that DST can function as a common reference point to overcome knowledge gaps pertaining to the widespread application of sustainability in the Indian housing industry. It can help prospective users meet their individual priorities while factoring into their decision making, broader systemic goals when selecting building materials, making housing design decisions, and understanding why it is important to mainstream sustainable social housing. For example, decision makers have lacked an appropriate framework to measure the performance of existing and new building materials against its socio-economic and operational benefits and environmental risks. To address this gap, SAT was developed as part of the DST. The tool consists of four broad criteria, some of which were missing in the various earlier sustainability assessment tools, including resource efficiency, operational performance, user experience and economic impact.

The DST also contributes to filling the current lack of data that has inhibited decision makers from making informed policies and investments related to sustainable construction practices. For example, the SAT is populated with the performance of 17 building materials and systems to compare available options. Lack of available information has also affected the development of the green materials supply chain. To this end, a GIS mapping of materials offers a platform to promote the location and performance of materials that are not widely known.

The limited availability of high quality, educational materials has also inhibited the implementation of sustainable design and construction practices. The DST's climate specific design guidelines help ensure sustainable material selection is grounded in construction practices that strengthen the quality and adequacy of the home.

In addition, the DST's background on the policy context for housing in India provides important insights into the institutional environment within which sustainability can be mainstreamed. Its documentation of resident experience can also help refine policies to better incorporate the preferences and concerns of the consumer.

Users of DST

Mainstreaming sustainable social housing will require a coordinated effort from multiple actors who may have individual and sometimes, conflicting priorities. What is common among most construction stakeholders is that they lack an



Fig. 13 Holistic sustainability assessment of the given building system using SAT.

appreciation for the concept of sustainable social housing. As consumer preferences and building standards and rules evolve to mandate adoption of more sustainable building materials, social housing developers will need to adjust their practices accordingly.

In this context, the DST can assist developers in calculating the costs of sustainable alternatives and locate the requisite suppliers. As such, the DST could conceivably help capital constrained developers efficiently manage costs and adhere to sustainability criteria. By extension, the tool could be used by developers to promote their commitment to high sustainability standards. In addition, materials manufacturers and suppliers could leverage the materials map to promote their products, form linkages with prospective clients and strengthen the supply chain.

Building practitioners could also benefit from the DST in terms of making incremental, but important, improvements to their design practices. This, in turn would enhance resident comfort. Given that many practitioners train their workers on site, with no consistent approach, the DST could also enable a more systemic way of monitoring workers' performance. This has the potential of realizing construction standards delivered by a largely unskilled cohort of construction workers.

Public sector housing finance and alternative finance institutions, seeking to make impact investments in green, affordable housing, could use the DST to structure their funds. The data on costs and sustainability of various materials can be used to make linkages between returns on investments with socio-economic and environmental impacts.

For universities and students involved in architecture, planning, and civil engineering, DST can function as an important educational tool by establishing an important framework to understand sustainability in social housing. The listing of the attributes can be used by educators as an entry point in developing lessons that explore issues that range from sustainable water practices to supply chain management.

The DST can also potentially assist local government bodies by functioning as a supplementary guide for monitoring and evaluating the quality of buildings. Its free design guidelines, in particular, provide a useful basis for officials with limited technical

resources to make informed decisions. The DST can also be used by state housing agencies planning to incorporate sustainability criteria into procurement guidelines to induce greater adoption of sustainable building materials.

Numerous central government ministries could also find utility in the DST. The potential of the DST in supporting the Building Materials and Technology Promotion Council's (BMTPC) research and promotional endeavors is indicative. For example, the DST could assist in refining the BMTPC's third party "Performance Appraisal Certification Scheme (PACS)". PACS is a voluntary programme that evaluates the performance of emerging materials based on traditional metrics pertaining to cost effectiveness and efficiency. The certified products are promoted to help them gain a foothold in the market. In addition, PACS assist the Central Public Works Department (CPWD) in incorporating findings into its procurement guidelines for building materials. They also support the Bureau of Indian Standards (BIS) such that findings help in reviewing or formulating relevant Indian Standards (BMTPC, 2016). As such, incorporating the DST's evaluation framework could widen the basis of performance and potentially influence codification.

Conclusions and Recommendations

As the Government of India aims to construct 12 million social housing dwelling units through the Housing for All by 2022 programme, the pressure to deliver in a timely and cost-effective way will increase. It is vital to identify what the impacts and benefits of housing production at such a massive scale and speed could be, especially when there is limited evidence of coherent strategies to decouple the socio-economic benefits arising from housing construction and provision from its negative environmental impacts, such as the deleterious effects of resource extraction. In particular, this shortfall applies to how building materials and systems are not selected in a sustainable manner. Research from MaS-SHIP has produced a comprehensive data framework, datasets, tools, evidence-based knowledge and insights for mainstreaming sustainable social housing in India.

A key output from the MaS-SHIP research has been the creation of the DST, an interactive and online toolkit comprising a range of outputs, datasets, tools and insights that can help prospective users in choosing sustainable building materials and making and monitoring sustainable design interventions and construction practices in social housing projects. The DST not only addresses the absence of a comprehensive measurement framework to assess sustainable materials, through the development of SAT it fills missing data that is needed to quantify the performance, and using Material mapping application, spatially maps the availability of sustainable building systems options. DST also includes design guidelines to ensure sustainability is embedded at the conception stage of a housing project. Filling these knowledge gaps can also assist in prioritizing sustainability considerations in housing policy and implementation.

SAT as a key component of the DST has the capability to measure the relative performance of building materials and systems for social housing projects that do not exceed four stories, using the framework of 18 attributes. The multiplicity of attributes requires rationalized valuations relative to each other. SAT establishes consistency by drawing on the inputs of a representative sample of housing experts in India to weigh each attribute. That is, a widely accepted "Analytic Hierarchy Process (AHP)" was applied to survey 200 experts including project consultants, private and public housing providers, academics, manufacturers, and building practitioners. A weighting process affords a rigorous evidence base for prospective users to prioritize their interventions, appropriately allocate resources, and potentially mitigate preconceived biases.

More data is also needed to support initiatives that promote small, sustainable building system companies with a small client base. For example, the Building Materials and Technology Promotion Council (BMTPC), housed within the Ministry of Housing and Urban Affairs (MoHUA) studies and showcases innovative building systems. It is also responsible for a Technology Sub-Mission, which is involved in such pursuits as part of the PMAY. However, the current focus on materials and systems tend to focus on cost and speed. Missing data on criteria such as a building system's job creation potential inhibits systematic efforts to promote such options against broader metrics. Resolving this shortfall could enable evidence based promotional campaigns, to build awareness and induce demand for more sustainable alternatives amongst prospective clients.

Acknowledgment

The MaS-SHIP project has been funded by the Sustainable Building and Construction (SBC) Trust Fund which is one of the means of implementation of the Ten-Year Framework of Programmes on Sustainable Consumption and Production (SCP) Patterns (10YFP) managed by United Nations Environment (UNE). The goal of the SBC programme is to promote resource efficiency, mitigation and adaptation efforts, and the shift to SCP patterns in the buildings and construction sector of developing countries and countries with economies in transition.

Appendix A

See [Table A1](#)

Table A1 Detailing the 18 attributes

Sl. No.	Attribute	What is being measured	Unit	Calculation/Source
1	Embodied Energy and Carbon Emission	It is the total energy expended for implementing a building system, from extraction of material up until the point of installation in a building. This includes energy consumed in: Manufacture of raw material (example-cement, steel); construction/ installation at site; and transportation of materials/ components from manufacturing facility/ material vendor to the construction site.	MJ/m ² of wall or roof assembly	Calculation: Normalized data readily available. Calculations for the embodied energy per m² of wall or roof assembly of each systems have been made in three stages: Raw material → Component → System. Source: Tier 1 level data on embodied energy and emission factors of material on which the calculations for building components and systems are based on.
2	Critical Resource Use	It is the overall impact created critically from the quality of resource usage measured in terms of: A. Scarcity Index: The creation of criticality due to impact on ecology because of the process of extraction of the various raw materials used in the product/building material (e.g., river ecology, forest ecology, mountainous ecology etc.) B. Environmental Impact (soil and water pollution): The degree of water and soil pollution caused during the process of extraction, manufacture and construction. C. Sectorial conflicts/Conflict of use between different sectors: The degree of criticality created due the conflict of use of raw materials in the production of building component or system (e.g., soil is important for food sector, terracotta handicrafts, etc.)	Normalized numeric index Criticality score: Low: 1, Medium: 2, High: 3 The Low-Medium-High ranking refers to severity of the three parameters of Environmental impact, Scarcity and Conflict of use. <i>The rankings are based on a research study conducted by Development Alternatives on Resource Efficiency in the Indian Construction Sector (2015).</i>	Calculation: The calculations have been done using the weights of the critical resources per m² of the wall or roof assembly multiplied by the criticality score of the respective resource. These values are normalized on a 0–100 scale. The formula for calculation can be referred to in the data framework report available from the project website. Source: Weightings given according to Tier 1 data at primary level, with resulting calculations involving T1, T2 and T3 data at assembly level.
3	Current Recycled Content	Quantum of recycled content utilized in the building material which may be achieved by usage of materials which utilize, for instance, industrial waste. The intent is to reduce the dependency on virgin materials such as top soil, sand etc., or on materials with a high environmental impact such as cement.	Scale of High, Medium and Low Low: 0%–20% High: > 40%–100% Medium: 20%–40%	Calculation: Scale derived from percentage of recycled content in the manufacturing of the material. Source: Calculations based on T1 and T3 data, using inputs from manufacturer surveys and prevalent system/ material specifications.
4	Future Reusability	Ability of a material to be used in its second life cycle without any structural changes. The intent is to reduce the generation of C&D (Construction and Demolition) waste at source.	Scale of High, Medium and Low. Low: 0%–20% Medium: 20%–40% High: > 40%–100%	Calculation: The scale has been derived from percentage of constituent materials of the wall/roof, which may be reusable. Source: Tier 3 data from manufacturer surveys and material specifications.

5	Water use (during manufacturing and construction)	Amount of water consumed by building systems including both embodied water content of raw materials as well as process water consumed in production and construction.	Litres per m ²
6	Durability	Time period for which the building material or system is stated to last by its manufacturer under specified conditions of use. Water resistance and compressive strength determine the durability of the material.	Scale of High, Medium and Low
7	Ease and Frequency of Maintenance	Frequency of maintenance works required (regular or occasional). Could involve the following indicators: ● Extra products required for the maintenance ● External help required ● Mandatory frequent services	Scale of High, Medium and Low
8	Thermal Performance (flow of heat)	Thermal performance of a material is a measure of the thermal transmittance (also known as the U-value) which is the property of heat transmission in unit time through unit area of a building material or assembly and the boundary air films, induced by unit temperature difference between the environments on each side. The lower the U-value of a material, the better is its heat insulating capacity.	W/m ² K
9	Thermal Mass (absorption, storage and release of heat)	Thermal mass or thermal admittance quantifies a material's ability to absorb and release heat from a space as the indoor temperature changes through a period of time. In climates with large diurnal swings, admittance values can be a useful tool when assessing heat flows into and out of thermal storage.	kg per m ²
10	Impact on Cooling (or heating) Loads	Impact of the building system used in the construction of any dwelling on the energy consumed for space cooling and/or heating. The intent was to inform the user of the potential savings associated with the use of a building material or system with respect to a specific climatic zone in India.	kWh/m ² /year

Calculation: Calculations are based on embodied water of raw materials, taken according to composition ratios of these materials in the final wall/roof assembly. The final amount includes water for production (on site/off-site) and curing (on-site).

Source: Tier 1 data on embodied water in material have been used as the base for the calculations.

Calculation: Tier 3 data was collected through material catalogs.

Source: Tier 3 data from manufacturer surveys and material specifications.

Calculation: Tier 3 data was collected through material specifications and catalogs regarding the maintenance of the building system. Households were questioned on the ease and frequency of maintenance required in the houses. The scale of high, medium and low comes from the responses of the householders and building practitioners towards these questions.

Source: Tier 3 data from manufacturer surveys and material specifications.

Calculation: Normalized data readily available.

Source: Tier 1 data from published reports and articles, Tier 2 calculations from the CEPT CARBSE Assembly U-factor calculator³, based on the selected walling and roofing assembly

Calculation: The terms heavy-weight, medium-weight and light-weight are often used to describe buildings with different thermal mass strategies.

Source: Tier 1 and Tier 3 data on material specifications, with calculation for change in unit.

Calculation: Simulation based results using DesignBuilder.

Source: Tier – 2 data based on simulations

(Continued)

Table A1 Continued

Sl. No.	Attribute	What is being measured	Unit	Calculation/Source
11	Noise Transmission	Refers to airborne insulation values of walls and airborne and impact insulation values of floors.	Decibel (dB)	Calculation: Normalized data readily available Sound Transmission loss as per IS 1950:1962 30 dB or less – Poor 40 dB – Fair 45 dB – Good 50 dB - Very good 60 dB - Excellent Source: Tier 1 data from published reports and articles.
12	Familiarity (with the material or system)	Degree of inclination towards a building material or system based on user acceptance.	Scale of High, Medium and Low	Calculation: Tier 3 data was collected through household and building practitioner surveys. Household were questioned on their experience with the building system used, while the building practitioners were questioned on their likeliness towards using a certain building system. The scale of high, medium and low comes directly from the responses of the householders and building practitioners towards these questions. Source: Tier 3 data inputs from manufacturer and household surveys.
13	Modification Ability	Suitability of constructed building for adopting changes after construction by occupant, including nail-ability. To be able to make changes like- Concealed piping, electrical, and plumbing services, and provision for incorporating the mechanical, electrical and plumbing services within the proposed building component thickness.	Scale of High, Medium and Low	Calculation: Qualitative tier 3 data was collected through material specifications and catalogs regarding the maintenance of the building system. Households were questioned on the modification ability of the materials used in the structures of the households. Source: Tier 3 data inputs from manufacturer and household surveys.
14	Construction Cost	Cost per m ² of the building system (wall and/or roof). This includes primary material, labor, water and equipment charges. <i>This is not the cost per m² of built up area.</i>	Cost per m ²	Calculation: The cost analysis has been done first through calculation of the cost per component (e.g., solid concrete block) using rates from CPWD's Delhi Schedule of Rates 2016. The cost analysis of the final assembly is done using the above calculated costs of components. Source: Calculation based on combination of Tier 1 data from Delhi Schedule of Rates 2016 and Tier 3 data from practitioners and manufacturers/suppliers.
15	Skill Requirement	Level of skill needed during production and construction of a building material or system.	<20%: Low; 20%–40%: Medium; >40%: High	Calculation: Percentage of skilled personnel required in the construction process. Source: Calculations based on Tier 3 data from practitioners and manufacturers/suppliers.

16	Supply Chain	The availability of number of reliable suppliers for a particular building material or system in the very initial stage of construction of the project and in proximity to the project site.	Scale of High, Medium and Low	Calculation: GIS mapping of building materials and system suppliers Source: Mapping geographic locations of manufacturers and suppliers of building materials and systems (GIS mapping of building materials)
17	Duration of Construction	Time consumed on site in construction, assembly and installation of a building material or system.	m ² of built-up area per day.	Calculation: Tier 3 values from project details, practitioners and developers. Source: Tier 3 values from project details, practitioners and developers.
18	Job creation	Quantum of jobs created per m ² of wall/roof construction in terms of man-days.	Man-days per m ²	Calculation: Man-days per m² have been calculated as a sum of work required per m² of wall/roof assembly by the skilled and unskilled labor in each step of the assembly process. Source: Calculations based on T3 data, values from projects, practitioners and developers.

^a<http://www.carbse.org/resource/tools/>.

See also: Environmental Life Cycle Analysis of Earthen Building Materials

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Evaluation of Sustainability Indicators of Buildings

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Introduction

The development across the globe needs to be sustainable only then the earth shall be a liveable place. Although various efforts are on by each of the nations in their own way to address the issue but isolated approaches shall not yield the desired result unless and until a common platform is drawn up. The developed and developing nations divide is still on and the developing nations are urbanising rapidly and construction of large builtup area is underway. This is inevitable but if not done in a sustainable manner shall have farreaching implications globally. Thus a check and monitoring the same is of utmost importance. Currently, the efforts are on by each of the nations in their own respective ways but if the baselines vary and a holistic approach is missing then the results might be difficult to measure. Therefore resources required for this urban population are important especially from sustainability viewpoint for example, nearly 1.1 billion people had no access to electricity in 2014, and more than 3 billion had no access to clean fuels and technologies. Goal 7 recognizes that extending access to electricity and other forms of energy is fundamental to improving people's lives and communities (SDG, 2018). The numbers are a strong pointer for optimum usage of resources thus the need for evaluation and that too standard as much as possible.

The rating system for evaluation started with BREEAM; UK way back in 1990, with USA initiating LEED in 1998 and Canada, Australia and others followed, while China has adopted few of the existing ones and added on real estate development. Each of the systems has a separate rating system for the building typology and scale. Although most of them address the overall aspects but do have gaps that may be perceived as strongly contextual but has an impact when overall evaluation occurs. The system of evaluation needs to be such that when the buildings are at design stage, few indicators may be addressed, then at detailing stage followed by monitoring when the execution of the project happens and evaluation to continue as Building Performance Evaluation (BPE) over time with room for technology up gradation for appliances and even for the buildings.

The canvas of sustainability indicators is broad-based over rating system of buildings but with time the rating system has evolved to address and quantify the carbon emissions, energy issues with immediate effect however each of the rating system touches upon social and economic aspects in their own limited way often customised. Therefore the need for a system of evaluation of sustainability indicators for buildings need to be in place; to gauge interventions at a global level and for the output to be measured effectively.

Sustainability Indicators

UN developed Sustainability indicators for Sustainable Cities Program (SCP) created in 1992 after the UN Conference on Environment and Development (UNCED), the Commission on Sustainable Development through Agenda 21, included "the implementation of the Earth Summit agreements at the local, national, regional and international levels. Over fifty-five countries experimented the Commission on Sustainable Development program in 1992 each initiative has its own success rate; additionally, as feedback, they put forth some recommendations of indicators to be included in the existing framework. Now fourth implementation cycle on with learning's from the previous cycles the structure is more robust and precise and making it circular in nature.

To arrive at the sustainability indicators for buildings understanding of the said backdrop and the standard UN SDG are a good reference, to begin with and narrows it down for the buildings. List of 17 UN Sustainable Development Goals (Fig. 1), have 232 sustainability indicators, address the said goals, while for buildings only a few are directly applicable. (Is it possible to list down the indicators which directly/indirectly/partially deals with buildings under each UN Goal as listed below?) Of the UN Sustainability Development Goals and their sub-indicators the ones that are related to built environs are goal no: 3, 6, 7, 11, 12, and 13. Considering the rating system tackles few of the sustainability issues based on the rating system at large. The key goals that need to be mapped parallel to rating system are as follows:

Backdrop of Rating Systems of Buildings

To evaluate sustainability indicators for a building, the system needs to be comprehensive in nature as the rating systems validate the building's performance but for it to be sustainable and to be a part of the urban fabric the impact of the building on its immediate surroundings and other related aspects is a concern and needs to be part of the evaluation system as well. Thus a comprehensive understanding of the rating system is documented hereby as follows:

1990 saw BREEAM framed up as BRE – Environmental assessment method started in the UK for new and existing buildings, later that was taken up by other countries as well: Canada, Hong Kong and New Zealand. In 1996 fourteen countries started two year program called it as the green building challenge with the agenda to gauge building performance and energy efficiency by: Austria, Canada, Denmark, Finland, France, Germany, Japan, Netherlands, Norway, Poland, Sweden, Switzerland, United Kingdom and United States and advanced to BEAM – evolved as Building Environmental assessment method. In 1998 LEED – leadership in Energy and Environmental

SUSTAINABILITY INDICATORS FOR BUILDINGS	
UN Goals	UN Goal- Attributes
GOAL 3	Ensure healthy lives and promote well-being for all at all ages. <i>{for Sustainability indicator for Evaluation - The larger context of the goal refers to good health and well being but none of its sub-goals speaks off relating it with productivity; the impact of materials with weathering on the health, that needs attention}</i>
GOAL 6.4	By 2030 substantially increase water -use efficiency all sectors and ensure sustainable withdrawals and supply of freshwater scarcity and substantially reduce the number of people suffering from water scarcity.
GOAL 6.5	By 2030 implement integrated water resource management at all levels including transboundries cooperation as appropriate.
GOAL 6.6	By 2030 protect and restore water related ecosystems including mountains, forests, wetlands, rivers, aquifers and lake.
GOAL 7.1	By 2030 ensure universal access to affordable, reliable and modern energy services.
GOAL 7.2	By 2030 increasingly substantially share of renewable energy in the global energy mix.
GOAL 7.3	By 2030 double the global rate of energy efficiency.
GOAL 11.1	By 2030 ensure access for all adequate, safe and affordable housing and basic services and slums upgrade.
GOAL 11.6	By 2030 Reduce the adverse per capita environmental impacts of cities, including by paying attention to air quality and municipal and other waste management.
GOAL 11.b	By 2020 substantially increase the number of cities and human settlements adopting and implementing integrated policies and plans towards inclusion, resource efficiency and mitigation and adaptation to climate change, resilience to disasters, and develop and implement, inline with the Sendai framework for disaster risk reduction 2015-2030, holistic disaster risk management at all levels.
GOAL 12.2	By 2030 achieve the sustainable management and efficient use of natural resources.
GOAL 12.4	By 2020 achieve the environmentally sound management of chemicals and all wastes throughout their life cycle, in accordance to the agreed international framework, and significantly reduce their release of sir, water and soil in order to minimize their adverse impact on human health and environment.
GOAL 13.1	Strengthen resilience and adaptive capacity to climate related hazards and natural disasters in all countries.

Fig. 1 UN sustainable development goals.

design, 1999 EEWH – Ecology saving. Waste reduction and health, 2000 GREEN GLOBES (Canada), 2002 Green Building certification system and Green Star, 2004 CASBEE (Japan) Comprehensive assessment system for built environment efficiency, 2005 Green mark, Green building standards, 2006 GRIHA (India) Green rating for integrated habitat assessment. With each of the rating system, a dimension has got added from stand-alone building to energy issue to ecology to integrated systems at large. It is meaningful to see the progression in the sustainability indicators from their identification, to recognition to its application.

Technology has shrunk the world and with awareness of rating system the data can be assimilated at various levels till global. Such information shall not only be insightful but shall enable one to take precise measures for sustainable development. Next important initiative is to set up base lines, norms and standards based on geographical, climatic zones with technology aid.

Parallel is the existing building stock that has served for centuries on when the resources were limited and the indigenous technology demonstrates a range of passive systems of which some can be continued even today reducing on the energy demand and ensure the continuity of the traditional architectural styles of the buildings. Conventionally these buildings are looked upon as heritage structures to be valued for its age and architectural style but continuing the time-tested solutions are worthwhile and may be measured for as innovation value too with few modifications if so required with help of technology. Conventionally these buildings are an integral part of the socio-cultural strength of the local population that over time local economies too are dovetailed with them. This inherent balance between the social, economic and the existing built environs proved to be sustainable and therefore are a resource by themselves. Thus it may be noteworthy that the framework of the development of such existing building stock can be evaluated largely for sustainability indicators for buildings as well. Next, the economic dimension of sustainability is seen, limited to buildings only.

Understanding Issues for the Framework of Sustainability Indicators for Buildings

The intent of the paper is to arrive at issues for a standard framework of sustainability indicators for buildings at large. The UN format is universal but the nations are developing across the globe at their own pace. The local negotiations have certain

repercussions as the base line may be common but the thresholds vary with each nation and climate for the people who are the end user of buildings. Therefore this gap/range is significant and needs to acknowledge with reference to socio-economic aspects, as they are key to sustainability.

As building elements are standard for all typologies of buildings that are taken criterion, also tabulating the data shall be faster and even the communication of data for its implications shall be simple to translate irrespective of its geographical location. The vital issues for sustainability indicators of buildings in urban areas are as follows:

- Site and its immediate surroundings – the building to be viewed with respect to its surroundings for planning viewpoint – existing urban tissue, services that may be shared i.e., smart grid/load shifting; mixed land use, response to open spaces, landscape and other design-related decisions.
- Building design – based on typology, architectural style, spans, services-HVAC, Electrical, water, sanitation, waste, security, cost effective with specifications, and most significant the design development stages wherein the rating systems/sustainability concerns are inherent to the design rather than being an add on at a later stage as that gets reflected in the performance at large for it various services that are energy consuming.
- Building materials – selection of materials for foundations, walls, infill walls, all types of fenestrations and roofing as that determines the structural system and need to use of technology. Subsequently the selection of finishes for flooring, walls, service areas and others are crucial as they are a major component of the cost of the building and since it deals with cosmetic aspect of the buildings the options are many and not necessarily environmentally friendly in fact the focus is largely on visual and aesthetics.
- Construction technology and commissioning – implementation of project is typically influenced by the local construction systems at place, use of technology and its related impact. Use of indigenous technology, to handing over to the owner/users and maintenance logistics and data records.

Understanding Evaluation With Rating Systems

The initiative for rating system was taken up by the developed nations first followed by developing nations. When one speaks of sustainability indicators then the three pillars of sustainability are inherent. Having shared the key UN sustainability indicators relevant for buildings an overview of rating system shall enable to put issues in correct perspective for the said agenda of this paper. Each of the rating system are a reflection of the countries where they developed thus for a standard system the regional or local contextual issues also need to be accounted for such along with the socio-economic framework.

To evaluate sustainability indicator of buildings with rating system as well there may appear few gaps that exist may be because of issues, are not contextual/local, regional, political or economic. An attempt to understand the most frequently used rating system and highlighting their respective strengths that are not reflected such in other rating systems but are significant from sustainability viewpoint. Further few issues shared herein are random but directly related to the sustainability aspect for buildings. Beginning with site selection LEED has extensive thrust on natural features, water, and others. While BREEAM has a structured outline for duties and responsibilities during execution of the project and thrust on management is 11% relatively high when compared with other rating systems. Next mixed land use is not recognized by GSAS, GRIHA considering the traditional cities establishes such land use as it reduces on transportation, as production, retail and residence are in same building that demonstrates compact city planning therefore economizing on energy consumption also enjoys inherent social security in the streets they are the life line of the city. Use of transportation is recognized, as 10% by BREEAM while the GRIHA has no mention of that. Globally single residences are large in number but the GSAS have exempted them from the rating system also the noise and light pollution as well. Furthermore they accept the passive systems and recommend them but they are quantified. Use of technology is largely responsible for energy consumption at site during execution of the projects and technology is updated regularly. Often the upgraded technology costs more and efficient as well but among the developing nations there is a tendency to use less upgraded version as that is relatively cheaper but may not be sustainable from environmental viewpoint. Like technology Innovation needs to encouraged as LEED emphasizes a substantially on it to the extent for use of energy modeling technology with versions as well whereas BREEAM gives an over and above credit for the same, rather than being inherent to the rating system. There is ample thrust on energy but no baseline defined by quite among the rating systems. Infrastructure facilities especially HVAC is a major energy consumer over electrical, plumbing, waste, sanitation to mapping of indoor air quality and relating that to productivity, health and well-being is insightful from sustainability point of view. By an large number of users and relating them with defining base line is missing considering although in BPE energy consumption per user is documented but with lack of baselines the data is just another number. Similarly there are other issues as well but an extensive study is beyond the scope of this paper thus the above mentioned text is to enumerate the issues of rating system that are a concern for sustainability indicators of buildings at large.

Issues for the Framework of Sustainability Indicators for Buildings

To arrive at the framework of issues for sustainability indicators for buildings the approach was to draw parallel sustainability indicators with rating systems. The outputs of issues are compiled under three sub categories as common for the buildings followed by the geographical location of the project within the socio-economic framework of the building is as follows:

Common indicators

Common indicators of the *four key issues* of a building are: the building design, architectural vocabulary, construction technology and maintenance and technology up gradation. As the cities with their master plans may govern the site selection and that may not be essentially acknowledging the natural features and resources; as land is a premium and invariably the major component of any project. Ideally the site selection to be considered keeping in mind with socio-economic aspects as well: who the users shall be? number of users? daily costs of travelling? gender connotation? security? earnings to savings? financial viability as social equity rather than befitting a chosen few and others. Although it may not within the purview of the architect but role of planner is significant or else it shall be a built stock neither used nor occupied. There are quite a few such examples in Asian cities and thus one has metropolitan cities with no limitation for extent of the city. So it is important that the building that one builds is integrated within the city's fabric or urban tissue and an asset at large. Furthermore the building to have a symbiotic relation with its immediate surroundings be it open space or built environs such that resources may be shared and is an asset to its location.

- (1) The Building design is key but the rating systems have a framework to account for that with few gaps based on the countries where they are implemented. But during the design development stages the inclusion of issues if monitored could yield improved results. The baselines be defined for the respective geographical zones as thresholds of thermal comfort varies with ethnic groups/communities and recognizing their thresholds such shall ensure optimum use of resources.
- (2) The global architectural vocabulary is cloning the high end of buildings in cities irrespective of the climatic condition creating buildings that are un-necessary for example glass façade buildings are not called for hot and dry climate so by building such the energy demand multiplies; a price that the city pays to have such built environs and adding heat islands, adding carbon emissions, altering the micro climate and related climate impacts.
- (3) Among developing nations majority of the construction sector has labours that are in farming and migrate during non-farming duration, a social phenomenon related to economic activity. Such labour is not formally trained but cheap: this implies that the quantity of material used may be more and execution of the task may not be accurate at the cost of quality and such a setup has been in operation for years and continuing. Also in such a situation the use of technology may be used judiciously and relying more as labour intensive.
- (4) After execution of the project at handing over stage is formal as maintenance, facility management with up gradation of technology regularly for commercial buildings, high-end housings, malls etc but limited. This needs to be a norm for all the buildings.

Geographical Indictors: Are These Issues or Indicators?

Often the same climatic zones have varied response by the nations and people at large essentially governed by their economies and social setup. For example Asian civilizations is one of the oldest thus their living built environs time tested for use of locally available building materials, indigenous construction technology and typical architectural vocabulary sustainable; an alternative to global construction option. As transportation is rule out in the former one but the only challenge is the scale of development with densities and mega cities one needs to be innovative to continue with the traditional solutions but technology does come in handy. Next for a climatic zone the local population is adapted to it thus their thresholds of thermal comfort also vary. For example use of air-conditioning is the highest consumption in buildings and the global standard of 20 + degrees makes sense for countries of temperate zone but tropical zone population the threshold of 30° when shaded and moderate humidity is comfortable. And as most of the urbanization is to happen in tropical zone and if they decide to go the global way then the energy demands could be catastrophic and jeopardies the sustainability at large. As the UN - SDG vouches health and well being for all, its logical to accept the varying baselines such as that shall be the sustainable approach for future. One may conclude that the energy consumption for the two sets of people shall vary either for heating or cooling, wherein the traditional solutions may help in reducing the energy demands. As a matter of fact there shall be other nations with varying needs for thermal comfort and they too should be dealt such.

Thus key issues may be summarized as follows:

- (1) Climatic zone to be grouped with their historical backdrops that are rich in architecture.
- (2) Thresholds/Baseline for uses of resources – water and energy an offshoot of local DNA.
- (3) For selection of construction to be gauged for its immediate surroundings, urban fabric and regional tissue; as a group of sustainable buildings does not ensure a sustainable tissue.

Socio-Economic Indicators: Are These Issues or Indicators?

The socio-economic context for the nations vary as they all at varying stages of development i.e., for African countries, India and China where pace of urbanization is highest a balance between labour intensive and technology driven execution of buildings etc may be logical; while for the developed nations it may vice versa. Further in the recent past the trend has been developing nations following the 'nature' of development of developed nations and that is alarming; as the solutions adopted by developed nations are in line for their context while duplication in another context shall never be sustainability. When the local economies of

developing nations are growing then the thrust should be contextual – based on circular economy, regenerative economy, and others.

With globalization the economies have diluted the political boundaries and the process is on for social as well. But for the global communities to shape up is a gradual process as it deals with people, their cultures, traditions, their identities and so on. Interestingly the developing nations have young population who are relatively more receptive to changes thus the paradigm shift in some nations faster than the others. Such a volatile situation needs sensitive handling especially from resource consumption point of view.

To sum up the key issue would be:

- (1) Socially acceptable thresholds for resource consumption as they vary from the laid out norms often less than the prescribed ones especially among the developing nations, as they are use to less are more.
- (2) To be aware of their buying capacities and priorities- for example if an air-conditioner is costing more for better rating and technology over a cheaper one with poor rating more often they shall opt for the latter one.
- (3) Lack of awareness and easy access to information too dilutes the intent therefore a standard system recommended with sub sections to address respective issues.

Conclusions and Way Forward

The paper focused on key issues of sustainability indicators of buildings to develop such a framework is an exhaustive exercise and cannot be limited to a paper.

Therefore as a step forward is to on record the key issues which could be carried forward. As UN Sustainable development goals already in place with its fourth revision in place is evolving for efficiency and effectiveness is universally measured. As for the buildings rating systems that essentially focuses on energy issue at large also the output cannot be standardized thus the need to have a universal system that accounts for the three pillars of sustainability. The paper opens up with an overview of the concern with approach to tackle the same by drawing up a matrix of UN SDG and the rating system those have been implemented for maximum buildings. The intention is to be rational in approach so that the evaluation of sustainability indicators to be universal in nature with implementation across the globe.

The way forward shall be to implement the said approach and arrive at a set of sustainability indicators for buildings that can be applied for all type of buildings irrespective of its typology, scale, context and even the climatic zone. The draft cut is in place argued and put out such in the paper but may include the rest of the rating systems as well.

See also: LCCA and Environmental Impact of Buildings

Reference

SDG, 2018. UN report.

Further Reading

CSD-UN Sustainability Indicators.

GRIHA Version, 2015, India.

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LEED BD + C: Homes v4, LEED BD + C: Multifamily Midrise v4, Verification and Submittal Guidelines.

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United Nations Sustainable Development: Issues – Indicators.

Expediting Faster Housing Supply in India Using Straw Bale as Prefab Building Material

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One thing we do know, that we dare not forget, is that better solutions than ours have at times been made by people with much less information than we have.
Wendell Berry

Introduction

Human activities have contributed to global warming and the deterioration of the environment and the planet. These are some of the facts which are being already established by number of studies. It is extremely likely that (95%) human activity is the main cause for global warming since the mid-20th century as stated by intergovernmental panel on Climate Change, IPCC. The three traditional principles like Utility, Beauty and Stability in defining 'Good architecture' are no more enough at the present day context. Architecture has gained a new dimension with an additional term called 'sustainability' as we are entering into a more environmentally-conscious age. Consciousness and appropriate actions are required at each and every stage by all stakeholders involved with the building activities. In India, it is reported that *"India needs to build 31,000 new houses a day over the next 15-years to meet the needs of its rapidly growing and urbanising population"*. One can assess the preparedness regarding management, stock of building materials, availability of proper technology and manpower required in order to attain the target. On the other hand, most of Affordable Housing schemes in majority states are coming up in peri-urban areas or in rural areas in absence of ready, cheap, bulk land in urban areas. The involvement of time, energy and cost in the transportation of so-called conventional building materials like brick, cement, steel, glass, etc., is an issue for these low-budget projects. Moreover, all these materials are either energy intensive and major Embodied energy (EE) contributor. EE is the sum of all energy used in the construction process – right from extraction of raw materials, manufacture of products to their transportation and incorporation into buildings. About 25% of the India's total primary energy demand is because of manufacturing building materials. Government bans on mining of stone, sand and earth, among others will further enhance a major crisis in near future. There is an urgent need to think in a different way by all the stakeholders involved in the building sector in India (Figs. 1 and 2).

On the other hand, India, the largest rice growing country produces around 125 million tonnes of rice with a comparatively low yield level at around 2.85 t/ha. India accounts for almost 20% of all world rice production. This huge production of paddy leaves a substantial quantity of straw on the field at the end of the yield. The farmers burn their field stubble because they do not have the ready options to dispose the straw residuals. The simplest way they find is to burn it locally. The problem of pollution caused by burning of straws in the agricultural states of India is so severe that the US National Aeronautics and Space Administration released a satellite image showing fires across millions of hectares of agricultural fields in the region. The smog and haze it causes even affects the nearby cities. Straw burning not only affects the immediate environment also by generating tremendous amount of heat and by killing the soil microorganisms affecting the soil productivity level but also causes pollution to the overall environment grossly.

Straw is a sustainable construction material that is not extracted from the ground like other materials and does not produce any toxins or pollutions during its production. India being one of the largest rice growing country accounts for almost 20% of all world rice production. Thus the quantum of production of straw is understandable especially in the rural belt where availability of conventional building material is an issue. Generally, in absence of any quick and cheaper option, farmers prefer to burn these straws in order to prepare the ground for the next crop very quickly. The most important benefits of straw bales are environment friendly and low cost due to the availability in abundance as agricultural residues and its reuse as building material.

About Straw Bale

Aiming a more holistic approach towards using sustainable materials in construction, this study examines the viability of straw bale as building material to satisfy our future construction needs in Indian context. As architects, our decision regarding selection of appropriate materials can bring a substantial impact on the environment. Straw bale as a material in construction is the most appropriate answer in handling all issues. Straw is nontoxic, low-cost and carbon-sequestering in nature.

Straw

Straw refers to agricultural byproduct consisting of the yellow dry, dead stems of cereal plants after the grain and chaff have been removed. The cereal grains include wheat, rice, barley, etc. It is different from hay. Straw is the woody hollow stalk of the plant



Fig. 1 Straw bale house at University of Bath, UK Campus. Source: Available at: www.bath.ac.uk/.



Fig. 2 Straw bale Home in Missouri. Source: Available at: <https://blog.shelterpub.com>.

whereas hay is the upper part of it where the grain is located. Straw is rarely used in feeding livestock because of its low nutritional value. Straw is generally used as a waste by-product. It is readily available after every harvesting season and 're-generative' in nature. These straws are very common to soft woods and very similar in chemical composition. It consists of cellulose, hemi-cellulose and lignin. It is estimated that 97.19 MT rice straw is produced in India per annum of which 23% is surplus and left as uncollected.

Straw is a versatile material, has good thermal properties, biodegradable, it is a by-product from agricultural practices with low embodied energy compared to other building materials. Straw can be used as building material in the field where it grows (**Fig. 3**), which is unique for any building material and does not emit poisonous fumes in case of fire. Forever rising inflated housing needs this agro-waste material in the current shortage of wood is a good alternative building material.

Straw Bale

Straw bale usually means a variously-sized, rectangular bundle of plant stems, held together by two or three ties of wire or baling twine and weighing from about 16–43 kg. Bales are rectangular compressed block of straws tied by wire, polypropylene twine or natural fiber twine mostly using mechanical baling equipment preferably at moisture content less than 20%. According to [Myhrman and MacDonald \(2012\)](#), bales are available in two different sizes based on dimensions and number of ties in **Table 1**. The 3-ties bales are more compact denser than 2-ties bales.

Straw bales are available in various other sizes, shapes and weights also meant for various other purposes. These bales can be used laid both 'flat' and 'on edge'. For using straw bales for construction purpose, it is necessary to determine the 'calculated density' (CD) of the bale if it exceeds the minimum standard value. Moisture content is normally expressed as a percentage of the total weight of the "damp" bale, and is calculated by dividing the weight of free water in a bale by the total weight of the bale including water, then multiplying that by 100. The dry weight is used as CD. The densities can vary according to the type of grains, moisture content and the compaction provided by the baler. Most of the US codes specify that a minimum density of 100 kg/m³ is desirable for the purpose of building construction. Bales are usually produced during a short period and it makes sense to buy and



Fig. 3 Straw: an alternative building material. *Source:* Available at: www.thespruce.com.

Table 1 Standard dimension of Straw bales

<i>Number of ties</i>	<i>Length</i>	<i>Width</i>	<i>Height</i>	<i>Weight</i>
2-Ties	35–40 in. (89–102 cm)	18 in. (46 cm)	14 in. (35 cm)	40–50 lbs (18.2–22.7 kgs)
3-Ties	43–47 in. (109–119 cm)	23 in. (58 cm)	14–16 in. (35–41 cm)	75–85 lbs (34–38.6 kgs)

Source: Available at: <https://www.strawbale.com/straw-bale-design-choosing-your-bales/>.

Table 2 Harvesting season of different varieties of paddy in India

		<i>Autumn</i>	<i>Winter</i>	<i>Summer</i>
Northern Region	Punjab, Haryana, West UP, HP J & K	Sep-Nov	Sep-Dec	
Western Region	Rajasthan, Gujarat, Maharashtra		Oct-Dec	
North East Region	Assam	Jun-Jul	Nov-Dec	May-Jun
Eastern Region	Bihar	Sep-Oct	Nov-Dec	May-Jun
	East M.P	Mid Sep-mid Dec		
	Orissa	Sep-Oct	Dec-Jan	May-Jun
	East U.P	Sep-Nov	Nov-Dec	Apr-jun
	West Bengal	Jul-nov	Nov-Dec	Apr-may
Southern Region	Andhra Pradesh	Jul-Aug	Nov-Dec	Apr-may
	Karnataka	Sep-Dec	Nov-Mar	Apr-Jul
	Kerala	Aug-Oct	Jan-Feb	Mar-Apr
	Sonavari	Jul-Aug	Nov-Dec	Mar-Apr
	Kar	Aug-Sep	Dec-Jan	Apr-May
	Kuruvai	Sep-Oct	Dec-Jan	

Source: Available at: <http://drd.dacnet.nic.in/> (Directorate of Rice Development, Patna).

build soon after the new batch becomes available. The bales are not homogenous in nature. **Table 2** shows the harvesting season of different varieties of paddy can give an idea of the possible construction period using straw bales in different locations in India.

Embodied Energy of Straw Bale

Straw has very low embodied energy as compared to most of the conventional building materials (**Fig. 4**) that have high embodied energy, which is the total energy required for producing it; for extracting, processing, transporting etc. This construction method has minimal impact on the environment as the production and transport to the building site of straw bales consumes very little

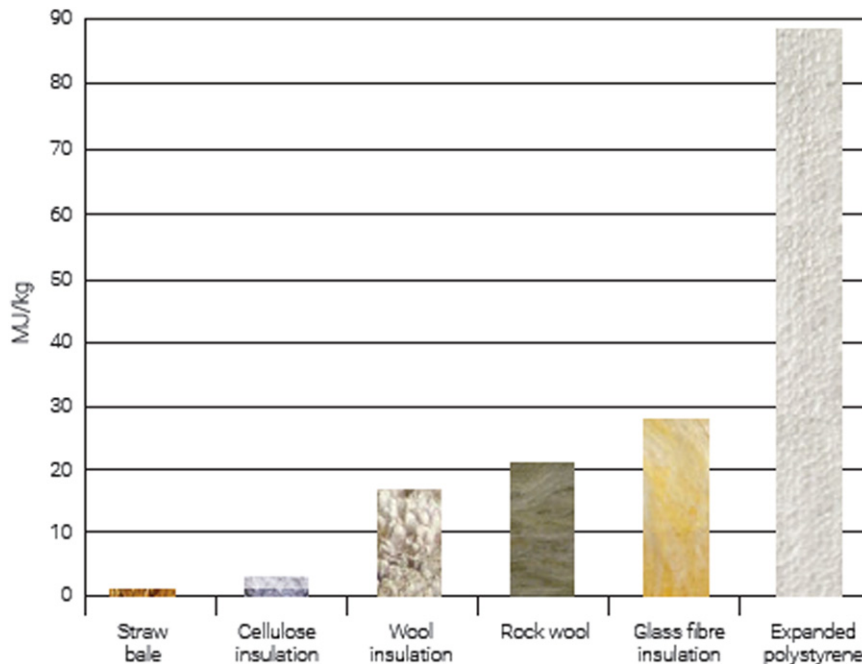


Fig. 4 Embodied energy in building materials. *Source:* SERT-Sustainable Energy Research Team.

energy. The embodied energy of straw bale is six times lesser than that of the most common material used in conventional construction. Moreover, in a study it is found that by adopting local materials like straw bale the amount of energy used in building decreased upto 215% and the impact of transportation by 453% compared to a concrete building.

The findings can be utilized both in conventional construction industry as a guide in making environmentally mindful decisions, as well as for natural building construction in order to further improve the performance of straw bale structures.

Embodied energy assessment can be done in two stages:

- (1) Measure all the energy requirements and outputs of the process. At this stage sufficient information can be obtained from the technical specifications of a mechanical baler. The efficiency of the baler (meaning how many bales are produced per fuel unit) can be obtained from the manufacturer. Fuel used by the baler is the direct energy requirement of the process.
- (2) Indirect input into the value of embodied energy of straw bales can be identified as energy required for manufacturing of the mechanical equipment- the baler. The composition of the baler has to be established. The second indirect energy input is associated with the construction of shelter needed to keep the bales dry. The energy inputs into the construction of the storage facility must be added.

Thermal Capability

The thermal properties of straw bales depend upon the density of the bales. Load-bearing straw bale walls will require the bales to have a higher density, typically more than 110 kg/m^3 . Non-load-bearing straw bales used for infill can tolerate lower densities, often in the range $80\text{--}100 \text{ kg/m}^3$. Straw bale can have a wide range of densities. Most straw bale codes in the US have chosen to use a minimum density of 7 pounds per cubic foot, (110 kg/m^3) since it is generally agreed that higher density bales are superior (e.g., bales up to 12 pcf are available). Various researches has proved that straw bale has excellent insulation properties. From another study done by the students of Worcester Polytechnic Institute, it is stated that the earthen-based plasters are more thermally resistant than lime-and-cement plasters when applied onto bales. The R-Value of the earthen-plastered bale was calculated to be 10.97 per inch whereas the lime-and-cement-plastered bale was calculated to have an R-value of 7.39 per inch. R-value is the measure of resistance to heat flow through a given thickness of material which actually determine the effectiveness of an insulation material.

Moisture Performance

Despite all its advantages the biggest obstacle to widespread acceptance is the moisture behavior within the straw bale construction, especially as it concerns mold growth. Moisture transfer may cause primarily because of the following reasons:

- Direct wetting from precipitation;
- Water vapour diffusion due to differential pressure across the wall;

- Absorption of rising moisture from the ground;
- Accidental exposure.

Precipitation in the form of rain and snow can be a major cause of concern to straw bale construction if not properly addressed from the very beginning. This will lead to poor durability. Poor durability may again create safety concerns for the occupants and will increase the lifecycle costs of the building. Thermal and moisture performance of straw bale wall systems are intimately related. Moisture performance requires knowledge of heat transfer as some moisture parameters depend upon temperature. Rice is mainly grown in rain fed areas that receive heavy annual rainfall, the reason for which availability of straw will be easy. Thus, adequate attention and precautions need to be taken in the preparation of the straw bales ready for construction and also both in the design and method of construction. As stated by Thomson and Walker (2013), there are several ways to monitor the moisture content of straw bales used in buildings:

- Electrical resistance measurements of timber blocks buried within the wall;
- Indirectly using measured %RH and temperature and determining equivalent straw
- moisture content;
- Direct measurement of the straw electrical resistance with a purpose built probe;
- Gravimetric determination of moisture content through removal and oven drying.

Fire Resistance

The potential for fire lies in the loose straw but not in the straw bales prepared for construction purpose. A compact bale surface normally does not support combustion once the 'fuzz' has burned off. With plaster on both sides, the risk of fire for straw bales reduces significantly. Fire retardant solutions may be applied to straw bale walls with the help of spraying equipment. A study conducted by the students of University of Berkeley shows that the straw bale reflects good fire resistance performance reaches to 30 min fire resistance for non-plastered straw bale and to 2 h fire resistance for plastered straw bale.

Mice and Other Pest Problems

Unlike hays, straws do not have any food content and hence are not an attractive resource for vermin. If plastered properly, the chances of the entry of any kind of vermin is completely eliminated. Since there are voids and gaps in between straws in the bales, there are chances of penetration of mice and other insects. Attention should be there to seal the surface properly.

Structural Stability

The structural components of a building are the foundation, frames, walls and roof. A straw bale building can be constructed in three ways, (1) Load bearing (2) Non load bearing and (3) Hybrid structure. Most of the examples which are available world wide in straw bale construction are low rise buildings with a maximum of two floors. In Indian context, the buildings in rural areas like community buildings, houses, school buildings, health shelters can be designed using straw bale techniques. In peri-urban areas, straw bale walls can be used in frame structures in mass housing schemes. A study says that it takes about 260 three-tie bales to build the six-course high walls (about 8 ft, or 2.44 m) of a modestly rectangular house having an interior square footage of 1500 sq. ft (about 139 sq. m).

Structural load bearing straw bale walls can withstand loads of more than 48,826 kg/m². A wall of "conventional field bales" is able to support a roof load of 600 pounds per foot (900 kg/m), the high-density bales can support up to 3000–4500 pounds per foot (4500–7000 kg/m). The stiffness (E-modulus) of found to be between 0.1 and 0.2 MPa (15–30 psi), depending on density. The bales did not fail or crush in tests which subjected them to over 25% compression, but the useful level of stress was approximately 0.01–0.02 MPa (1.5–3 psi). These values are based on tests conducted by TUNS on oat, barley, and wheat bales from various suppliers, with a density of 55 kg/m³ (3.4 pcf) to 115 kg/m³ (7 pcf). Higher density bales are stiffer.

Acoustic Performance

Straw bale walls are super insulative acoustically. For example, even recording studios in the USA and elsewhere were built of straw bales for their soundproofing quality and insulation. Straw bale wall systems have also been used near airport runways and motorways in US and Europe as sound barriers.

Weather-Resistance

If a straw bale is left out in the field during rain it will become very heavy that can't be lifted due to its weight and will be of no use then. Bales must be stacked off the ground by raising them and covering with a roof they will withstand the weather and the outside edges simply get wet and dry out. Straw does not suck water into itself as concrete does. It simply gets wet as far as the force of the wind can drive the rain into it. When the rain stops, the natural movement of air or wind around the bales dries them out. This cycle of wetting and drying does not damage the bale.

Service Life and Durability

The time period is not certain but it can surely last for at least a century, as there are some straw houses that were built more than one hundred years ago and are still in perfect health. A pre-compressed bale assumes the same characteristics of wood and it can look like a normal brick house.

Design and Construction of Buildings Using Straw Bale

It will be pertinent to discuss few elements related to design and construction in the context of prefabricated construction the design and construction is best suitable in a modular pattern using straw bale. Therefore the scope of modularity and commensurate construction is required. It needs flexibility, user-friendliness and efficiency of space, cost and time to be effective. A general note is given below:

Flexibility

Straw is a flexible material and requires to be work with it somewhat differently than if it was rigid. It is very self-supporting, can resist tipping keep out the wind, inhibiting air or moisture infiltration, resist heat transfer (insulation), reduce water intrusion and migration by storing moisture within the wall, keep the assembly from buckling, under a compressive load and from deflecting in a strong wind, keep the plaster from cracking after it is cured of shrinkage and support the plaster skins from buckling, reduce damage or failure from high winds and earthquakes and stops bullets. In the load-bearing straw bale method, walls of up to 3 stories have been constructed, with infill walls, in post and beam type structures; the straw does not take weight anyway.

End-User-Friendliness

Organic straw is a healthy alternative to modern materials natural and harmless. Living within straw walls can enhance the quality of the air we breathe because it is a breathable material and does not give off harmful fumes such as formaldehyde, as many modern materials do so it helps to keep the inside air fresh. Another health benefit is that when it is coupled with the use of non-toxic organic finishes such as clay, natural pigments, paints, and with opening windows, it can provide one of the safest and most comfortable atmospheres to live and also the ambiance inside a straw bale house is calm, cozy and peaceful. A beautiful, nurturing and safe environment to inhabit needs a high level of sound insulation, air quality and the organic feel to the house. Bales are a healthy choice.

Efficiency

A saving of approximately 10% in the direct cost of the walls is achieved when building with straw bales due to the elimination of formwork the quantity of materials needed is reduced. Due to precast construction lesser waste is generated because of utilization of cheap sources far from the construction site and the shuttering is eliminated with a saving. Similar components when produced repetitively results in faster execution, plenty of productivity and economy. This direct saving in prices is else to the environmental profit of reducing the energy consumption as compared to cement and reinforcing production.

Construction

The construction time for straw bale based buildings is less due to the construction of the prefabricated parts since structural work is confined to constructing the foundations. The building dries out quicker than a building of conventional construction due to low wetness content in the precast modules and is sooner prepared for service. In ready-made housing system, time is saved by the employment of precast elements that are casted off-site as the finishes and services could also be done below the block directly tends to save of money. The construction with prefabricated components takes less time resulting in less expenditure on labor. Up to one-third cost can be saved as compared to a conventionally built home of the same size through prefabrication.

For construction, labor needed to be trained to work on straw bale as the process is different from the conventional process. The baling machine is the most important and foremost equipment that is required before starting the construction. The degree of risk is less than the conventional method as it is not a high rise construction and straw bale can be handled easily. Electric supply is required initially for running baling machine. Water will only be required at the time of foundation casting. Curved walls can be easily made using straw bale blocks but arches and domes are not possible. The mechanical, electrical and plumbing services can be easily installed. Big overhangs are needed to be provided for preventing them from the rain.

A Comparative Statement

Building Materials and Technology Promotion Council (BMTPC) has been identifying and evaluating new materials and construction technologies. These mandatory and desirable criteria should be studied and adapted by implementing agencies to suit their needs.

A number of rapid construction techniques developed both within the country and abroad have been found to be suitable for mass housing projects in the country. Some states have taken initiative to introduce technologies in their projects. BMTPC has also identified, evaluated and recommended technologies: (1) Monolithic Concrete Construction System Using Plastic-Aluminium Formwork, (2) Expanded Polystyrene Core Panel System, (3) Glass Fiber Reinforced Gypsum (GFRG) Panel Building System, (4) Factory Made Fast Track Modular Building System. The reason behind selecting these four prefabrication technologies is that these are technologies which are mostly implemented in housing projects in the India. They are the technologies that are implemented for constructing prefabricated walls and Straw bale construction is also implemented in constructing walls. Above all the parameters like Time Efficiency, Cost Efficiency, Versatility, Structure Behavior and Thermal Behavior on bases of straw bale construction can be analyzed are common in these materials also (Table 3). After comparing straw bale prefabrication housing from other prefabrication techniques the benefits are clear. If the growth of straw bale construction continues, the amount of money and energy that can be saved could reach millions, even billions. If cities began using straw bale as affordable housing, their energy consumption could be reduced by 60%–70%. Moreover, if straw bale construction is used, costs of the building could be greatly reduced. Money saved by using straw bale construction could be applied towards other initiatives in cities. We could easily implement straw bale prefabricated housing for low-income housing. Beyond monetary benefits, its time efficiency, its Versatility the environmental advantages are evident. The use of straw bale rids an agricultural waste that ultimately results in major pollutants. The possibilities of straw bale construction are endless.

Table 3 Comparison of Straw bale with selected prefab materials

1	<i>Straw bale construction</i>	<i>Monolithic concrete construction system using plastic – aluminium formwork</i>	<i>Expanded polystyrene core panel system</i>	<i>Glass fiber reinforced gypsum (gfrg) panel building system</i>	<i>Factory made fast track modular building system</i>
Time efficiency	1/3rd time of conventional construction	1/6th of the X time	One building of two storied (total 1981 sq. ft) was constructed in IIT Madras in one month. <i>Source: www.bmtpc.org</i>	40%	15%–20%
Cost efficiency	10% direct cost saving in walls	15% Cost saving	40% Cost saving	20%–30%	30% cost saving
Versatility	By-product from agricultural practices, bio-degradable, good thermal properties and low embodied energy	Designed for any condition/ component of building such as bay windows, stairs, balconies, and special architectural features. <i>Source: aluminiumformwoktechnology.blogspot.in</i>	Panels can be easily anchored to other construction elements, such as steel, wood, and pre-stressed concrete. <i>Source: naredco.in</i>	Panels can be used not only as walls but also as floors, roofs and staircase. <i>Source: naredco.in</i>	Structure can be transported and erected fast due to its lightweight.
Structure behavior	Straw bale walls can withstand loads of more than 48,826 kg/m ²	Resistant to earthquakes than the traditional RCC column and beam designs. <i>Source: aluminiumformwoktechnology.blogspot.in</i>	Withstand a maximum load of up to 1530 KN/m $\approx$ 153 ton/m, have a low seismic mass. <i>Source: naredco.in</i>	Filled with reinforced concrete, possess the substantial strength to act not only as load-bearing elements, but also as the shear wall. <i>Source: www.bmtpc.org</i>	Less earthquake force generation is due to light weight. Highly ductile and load carrying nature of closely spaced studs/joists. Very light structure does not require the heavy foundation.
Thermal behavior	R-value between 40 and 60. A good thermal performance than the other walling materials	100 mm RCC Walls and Roof has thermal transmittance value as 3.59 W/m ² K (as per IS 3792:1978)	80 mm core and finished thickness of about 15 cm provides the same thermal insulation as an insulated solid masonry wall of about 40 cm. <i>Source: www.bmtpc.org</i>	Compared the traditional system with GFRG system, the thermal comfort performance was almost the same	

Source: Available at: drdpai.bih.nic.in/Status%20Paper%20-%202002.htm.

Production of Straw Bale Prefab Components

Using any material as prefab material is different than the conventional construction. It needs systematic planning of the prefabrication process. General process of prefabrication is given as, design (modular coordination), production, supply, assembly and quality controls. However, for doing this, there are many offsite and onsite conditions. The materials suitability for modular construction in the given geo-climatic region could be the onsite construction related elements taken care prior to production of components. Following that it needs land, investment, offsite infrastructure, skill development and quality control for a successful prefabrication process of building components. Few of those concerns for prefabrication is discussed below:

Land for Setting up Prefab Plant

Apart from the comparative advantage on structural behavior, thermal behavior, versatility and efficiency as shown in the table on the preceding page it is also to be mentioned that straw bale will be more affective in rural areas when considered off site considerations of prefab productions. Firstly, the supply of land for setting up of manufacturing plant will be cheaper in rural areas than urban areas. The quantum of land required for agro based factories for straw bale will be small mid-sized and not some large industries. This makes it more feasible options. It is highly possible that the straw growers make cooperatives as in the other agricultural cooperatives and makes smaller plants. This in fact could be more viable options if right kind of government facilitation is provided. The existing land acquisition act (RIFCTLARR Act 2013) provides much ease of any such land related investment when land owners offer mutual consent. Nevertheless, we find a win-win possibility of such prefab plant since the whole life cycle of the materials is rural and agro based. In return the adjoining areas and villages will be benefitted with more employment and jobs. This should motivate the policy and decision makers.

Investment for Prefabrication

The land requirement is directly related to the capital investment for the setting up of plant. The initial investment thus will be much lesser than any prefab plant in the cities and peri-urban areas. The cost of raw material is almost negligible since straw bale is essential byproduct of agriculture. As mentioned earlier, it will maintain the sustainability of use and reuse of straw bale. A very important evidence of this sustainability of this material could be taken from large tract of Himalayan belt in India where straw mixed clay is used as filler materials in the framed construction. the easy availability of straw and its sustainable supply due to food production is the unique reason for its popularity in rural areas of India and elsewhere. Thus the advantage can be taken for the prefab panel productions. The initiatives by farmer's cooperatives and other community based organization can also explore such opportunity. The industrialization of building components thus, could be much different in rural India than the urban counterpart in the country and other industrialised countries where mainly it came through the private investment.

Training and Skill Development

We find a gradual depletion of the sustainable construction practices in rural areas and hilly areas in India in spite of such abundant supply of agri-based raw materials. One of the reason for this is the changing economic dimensions in the country. The cases of migration from rural to urban and cities to large cities are common. The tradition practices of construction are forgotten. Traditional and indigenous practices of sustainability are on the back seat. The concrete and steel has taken over the vernacular practices in most of the indigenously rich regions of India. One of the silent reason for this is the absence of organized practice of the traditional construction systems and continuity in training and academics. The straw bale as prefab materials will be successful if it is connected to a suitable training mechanism along with the investment and manufacturing. There is a great concerns of prefabrication worldwide are the acceptance of the product. In this case if the people are involved in the whole life cycle of the materials and building construction there is a high possibility of successful prefabrication. The training and ICT ecosystems at the village panchayat level in the country could be linked with such training. It is to be noted that the training has to be linked with the practice. In 70s the setting up of building centers in the country by HUDCO failed to the missing link between the training and practice. That lesson must be considered. Inclusion of straw-bale as prefab construction in the academic courses of architecture and civil engineering will also be needed.

Quality Control

Quality control in prefab construction is great concern. In a closed system the whole quality control is maintained by a single manufacturer. The city authority and quality control authority as the case may be provided technical norms and guidelines. In India, the required step could be the formulation to relevant building codes for straw bale construction. It is highly recommended to have a semi-prefabrication in the case of straw-bale construction. The quality control has to be linked with the training, institutional mechanism and involvement of local governance set up to get the maximum benefit.



Fig. 5 A straw bale house construction with pre fab construction. *Source:* Available at: <https://in.pinterest.com>.

Offsite Infrastructure

In the prefabricated building component supply chain the offsite infrastructure takes a major role. The transportation of raw material and supply of finished materials need finished road to withstand the load of prefabricated transporters. In this case the need for offsite road infrastructure will be minimal. The catchment of raw materials seems not more than 5–10 km which can be transported with metalled rural roads in India as built during PMGSY and with the basic vehicles including animal driven carts. For the supply of finished product, the same network can be used through the use of animal driven cart and small vehicle. This definitely makes straw bale as unique than the other prefabricated materials. The onsite and near site movement can be even manual since the weight of components are not heavy (see earlier sections).

Straw bale prefabricated modules are needed to be carefully designed so that they will be accepted as any other conventional alternatives that exist on the construction market today before introducing them to the construction market emphasizing on that they will perform as they are supposed to. The new material must be easier to manufacture, transport and assemble as existing systems and methods and also needs to be economical as compared to the existing materials (Fig. 5).

Keeping in view the present Indian context regarding the other prefabricated materials discussed above it is proposed to have straw bale construction housing consisting framed structures and made of prefabricated components to achieve a cost-effective and socially acceptable housing supply for Economically Weaker Sections and Lower Income Group who mainly forms slums or unauthorized construction in urban areas. Straw is an answer to solve the housing demand for the growing population in India. Enough to build millions of homes as it is available abundantly due to its production every year with the production of cereals all over the country so incorporating straw in home construction. The straw bale can accommodate the future need of construction if it will enter the industrial construction market and it is capable of reducing emissions, storing carbon, reducing waste and saving both energy and non-renewable resources.

Straw bale construction is capable of ticking all of those boxes if approached properly. Straw edges from intrinsic 'green' values, inaccessibility while not the requirement for specialist skills and a robust support network. It is proved that straw bale building has a good thermal performance than the other walling materials in tropical climatic conditions. It was found that the straw bale construction is a good alternative for common walling materials and also this will be a cost-effective construction method.

Conclusion

Strawbale is ideally suited to dry hot climates, cold climates and temperate climates with hot/cold seasonal swings. Wide wrap-around porches, trees for shade, capturing breezes, natural ventilation, good design to guard against roof leaks, and other factors are important considerations to be kept in mind while designing the site plan with straw bale construction. Straw-bale construction is an excellent choice for cold climates. Its ability to provide affordable super insulation is unsurpassed. Building of Straw bale houses are possible in rainy climates also, and if properly detailed, will last for many years without moisture problems. In India, some of the states are 3-crop regions where bulk straw is produced as a waste-by product. There is a promising possibility of using this stock as a pre fab material in the construction in meeting the huge demand of built up area for different purposes in the country.

See also: Constructing a PV-Integrated Permanent Bamboo Building – An Experience

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Improving Building Technologies With a Sustainable Strategy

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The daily headlines scream of the looming energy and water crisis. Accelerated urbanization, supplementary spending power and a desire for an improved life style demand buildings, which are increasingly complex and insensitive to the context of contemporary environmental concerns. The lifestyle, attitude and demands of the urban populations all over the world, display a voracious appetite for material affluence which is directly proportional to dependency on existing energy resources.

Traditional architecture has been constantly innovative, so that structures have presented a series of logical solutions to the problems of the climatic conditions, while attempting to enhance human comfort and productivity. On the other hand the practice of design, construction, operation and maintenance of buildings in present times, utilizes colossal amounts of energy, water and raw materials, and at the same time generates large quantities of waste, causing severe environmental pollution. Designers, in an effort to meet the growing demands of lighting, ventilating, cooling and heating are regularly providing solutions which are energy intensive and inflict tremendous pressure on the rapidly diminishing energy resources. Excessive consumption of land, water and energy resources during the construction of buildings and their life span is having a negative impact on the fragile ecosystems leading to environmental degradation.

At this stage it may be appropriate to examine the meaning of the term 'sustainable development'. There are various definitions in use but it is difficult to put a precise meaning to the term. Development is about improving the well-being of people, raising living standards and increasing facilities whereas the closest explanation of the term sustainable would probably be 'long lasting'. Today, it appears that development is proving detrimental to sustainability. Spiraling energy prices too accentuate the significance of material and resource conservation. There is, therefore, an urgent need to foster thinking which redefines a cordial relationship between the building and the environment such that practical solutions given against traditional patterns of social and economic development circumvent set parameters to improve the quality of the surroundings, produce surplus power and food, and convert waste into nutrients and useful products.

Buildings are integrated systems that continuously interact with their surroundings. The process of architectural design is complex and involves interaction amongst parameters of diverse nature and varying magnitude. It is therefore mandatory to develop and define a process of architectural design that is scientific and leads to sustainability. In the present scenario, the energy and water crises would continue to worsen, and so will the associated negative impacts of pollution and environmental degradation, unless urgent steps are taken to control unsustainable design practices.

Sustainable building practices and technologies seek to reduce and decelerate the depletion of natural resources of energy, water and ground cover and promote the process of eco-friendly habitat. Intelligent architectural design strategies can enhance building performance. It is very important, therefore, to develop and implement specific design strategies and construction techniques in order to decrease energy consumption and move towards sustainability. It is equally important to consider the mode of designing buildings with an integrated approach which simultaneously incorporates climate responsive design strategies using eco-friendly materials to create 'Sustainable' buildings that enhance users' comfort. Further, varied materials and methods of construction can be used to establish a harmonious co-relation between sustainability, affordability and the contemporary built environment.

An integrated approach to design, incorporating bio-climatic architectural design principles, responsive to the climate of that region goes a long way towards minimizing the load on conventional heating, cooling, ventilating and lighting systems. 'Sustainable' buildings so designed, minimize the negative impacts on our fragile environment while enhancing users' comfort and productivity. The overall energy performance of buildings can be substantially enhanced by adopting sustainable principles promoting the use of efficient design strategies, renewable energy systems, and environmentally friendly materials and technologies. This results in a substantially reduced ecological footprint (Fig. 1).

The process of sustainable building design needs to be addressed right from the schematic design stage using scientific methods of:

Analysis	Understanding the problem and its context.
	Characterizing important requirements.
	Establishing relative priorities.
	Determining desired objectives.
Application	Formulating climate responsive, sustainable design strategies.
	Applying strategies which simultaneously establish relationships between architectural form, space and energy consumption.
Evaluation	Monitoring the performance of the building.
	Evaluating the performance against established priorities and objectives.

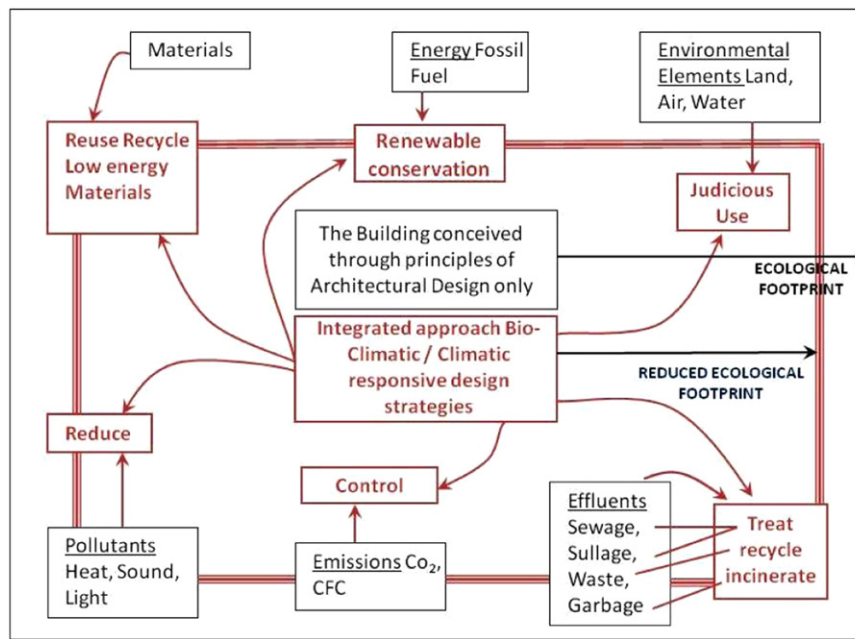


Fig. 1 The ecological footprint.

Concerns for the Designer

One of the most challenging problems associated with design and construction of a sustainable built environment is the optimal energy management with respect to manifold and often contradictory objectives. In order to establish a meaningful balance between energy saving and a comfortable lifestyle, designers are continuously innovating to develop techniques capable of providing a high level of comfort for users, together with a lower energy consumption needed to meet environmental regulations and minimize electricity bills. To minimize power consumption, the energy used by the building has to be optimized and effectively managed right from the stages of the initial design, period of construction and throughout its entire life cycle. Techniques for reducing consumption in high-use buildings and upgrading the comfort levels of users with optimum consumption of energy need to be consciously implemented. Integrating devices and components in the architectural fabric, providing optimum light and ventilation using centralized/active or decentralized/passive renewable technologies, reducing the water and energy embodied in materials and construction, and reducing waste and reusing or recycling building materials are some of the important concerns for designers.

Efficient Design Strategies

To increase the sustainability quotient of a building, a variety of active and passive design strategies can be incorporated. Active strategies involve the direct use of heating and cooling systems, while passive design measures include working on building orientation, air sealing, continuous insulation, openings and daylighting calculations at the initial design stage of a building to take advantage of natural lighting and ventilation opportunities during the useful life of the building. Some of such measures could be:

- Astute application of design principles for orientation, building envelope, design of fenestration and shading devices, building form and shape, surface-volume ratio, passive solar design, conducive to the availability of natural lighting and ventilation to help in minimizing energy loads.
- Use of advanced concepts of passive heating like use of direct or indirect gain systems, sunspaces or passive cooling concepts like evaporative cooling, wind tower, earth air tunnel etc. may be considered in lower operating costs.
- The landscaping character can greatly alter the microclimate of the place and serve to reduce direct sun striking and subsequent heat build-up. Appropriate treatment of landscaping elements, vegetation and water bodies can decrease temperatures by evaporative cooling and create advantageous air-flow patterns resulting in desirable ventilation.
- Use of solar energy for water heating, wind energy for electricity, water conservation, rain water harvesting for ground water recharge, solid waste management can further contribute to the aim of reducing the strain on conventional energy sources.

Such design strategies, if adopted judiciously can go a long way in the creation of affordable, sustainable habitat.



Fig. 2 Properties of environment friendly building materials.

Environment Friendly Building Materials

Traditionally man has depended heavily on nature to provide the basic materials for the construction of his dwellings. The cost of conventional building materials like burnt bricks, steel and cement is high and they utilize large amounts of non-renewable natural resources like minerals, top-soil, forest cover etc. They increase the dependence on external materials and manpower, harm the local ecology and are generally polluting in nature (Fig. 2).

The materials and technologies chosen for construction, should, in addition to functional efficiency, fulfill some or more of the following criteria, for the cause of sustainability and a better quality environment. These technologies should:

- not endanger bio-reserves
- be non-polluting
- recycle polluting waste into usable materials
- utilize locally available materials
- utilize renewable energy sources
- be accessible to the people
- utilize local skills, manpower and management systems
- be self-sustaining and promote self-reliance
- benefit local economy by being income generating
- be low in monetary cost

Embodied energy consumption in building construction is optimized by the use of locally available or recycled materials and new materials with desired properties. Environment friendly materials demonstrate one or more of the characteristics like renewable source, high reused or recycled content, low level of emissions, smaller toxicity content, durability, longevity and local production. Judicious choice of building materials can be made by evaluating several characteristics on a comparative scale. An understanding of the lifespan of a material, the energy input and waste output at each stage can form the base analysis in the selection process. Use of low-energy materials contributes significantly to materials efficiency. Ferro-crete, substituting steel with wire mesh and eliminating aggregates, bamboo reinforced concrete components, terrazzo flooring tiles using waste chips of broken tiles, stones and ceramic articles, interlocking porous concrete paving blocks, bricks and building blocks manufactured using industrial waste, mine wastes and rejects, fly ash in combination with burnt clay, cellular concrete, pulverized debris are few of the available eco friendly materials.

Appropriate Building Technology

Although a range of environment friendly materials is now available in the market, there is a need today, for developing cost-effective, sustainable, building techniques using locally available materials which are strong and durable yet esthetically pleasant. Over the years, innovations and developments in construction technology have provided the impetus to create relevant tools and techniques of construction such as the inverted saucer foundation, universal building blocks for internal and external walls and filler slabs. Moreover, the use of solar energy for electricity, bio gas for cooking and hot water, rain water harvesting for ground water recharge, water conservation methods and solid waste management play a significant role in reducing the strain on conventional energy sources.



Fig. 3 (a, b) Filler slab using overburnt bricks.

Indigenously Developed Brick Bonds

Substantial reduction in unnecessary use of excess building material in the construction of brickwork, while maintaining required strength, can be achieved by the use of indigenously developed brick bonds. Variations of the traditionally used brick bonds have been developed and used in various parts of Maharashtra, India. The indigenously developed 'Joshi bond', for one brick thick walls, can save up to 20% by the use of bricks laid on bed. The Joshi cavity bond, (modified rat trap bond), for one and half brick thick walls can effect a saving of up to 35.7% for bricks laid on edge, while the Joshi cavity bond, for one brick thick walls, used for internal partition walls can effect a saving of 25% in the quantity of brick used.

Filler Slabs

A unique modification of the filler slab construction technique, replaces the redundant concrete in the slab with light weight, damaged and therefore discarded or reused, clay tiles (Mangalore tiles) and ordinary bricks bats. The use of Mangalore tiles as a filler serves the dual purpose of providing thermal insulation from the heat of sunlight while simultaneously reducing the weight of the slab due to reduced quantity of the concrete. As a result of reduction in the dead weight of the slab, the spacing of the steel can be increased, effecting a reduction in the consumption of steel. Experiments in using filler slab instead of regular slab show an effective saving of 30%–40% on steel & concrete (**Fig. 3**).

Shutter Less and Frameless Windows

Specially designed cement concrete window panels prove to be very economical in terms of cost of material and construction. They can be used to form shutter less, frame less windows without weather shade (Chhajja). The special cement panel pattern is designed and cast locally. The panel is designed to have horizontal strips having a downwards slope on the external face with a provision to fix 6 in. wide glass strips. Rainwater will slide down over the glass and flow away easily without penetrating into the room. The glass strips also allow penetration of light into the room while preventing glare and providing privacy. These window panels when placed on the windward side permit even distribution of air in the interiors. The use of this type of narrow and extra height windows without frame and shutter, eliminating the use of chhajja costs only about 10%–15% of the total cost of a normal window with shutters & chhajja (**Fig. 4**).



Fig. 4 Pre cast cement concrete window panel.



Fig. 5 (a, b, c) The inverted saucer foundation.



Fig. 6 Biogas plant.



Fig. 7 Wall constructed using universal blocks.

Inverted Saucer Foundation

This form of foundation is ideal for black cotton soil. A large proportion of the load of building is spread on the upper surface of the ground and expenditure on piles and deep foundations can be avoided. Additionally, each footing requires only one third the quantity of cement as against the total quantity of cement required for a normal footing. Inverted saucer footings are also resistant to earthquakes as the cavity formed inside the hollow of the footing is filled with loose sand which can absorb seismic movements ([Fig. 5](#)).

Use of Bio Gas

As an alternative to unhygienic soak-pits or septic tanks, toilets can be connected to Cowdung (gobar)gas plants or biogas plants. Depending on quantity of flow, a constant or regulated intermittent flow of gas can be available for purposes of cooking or heating. Additionally good quality organic manure can be generated. The bio gas plants require minimal regular maintenance ([Fig. 6](#)).



Fig. 8 (a, b, c, d) Bamboo as substitute to steel reinforcement in slab, parapet, staircase and piles.

Universal Cement-Aggregate Blocks

Conventionally, bricks used for building construction have three dimensions namely the header, the stretcher and the height. While using in traditionally preferred English or Flemish bonds, variation in dimensions, requires trained and skillful masons, and also considerably reduces the speed of the construction subsequently increasing use of mortar. Universal blocks of size 20 cm × 20 cm × 20 cm cast out of 25% cement mortar and aggregate reduces the quantity of cement used in the construction considerably. The ease of laying the blocks increases the speed of construction. No continuous joints, vertical or horizontal should be allowed throughout the length and height of the wall unit. This block standing on its edge has the maximum load bearing strength and maximum resistance to buckling. It also has a good

lateral stability due to optimal slenderness ratio. The complimentary units derived from the basic block above are $10\text{ cm} \times 20\text{ cm} \times 20\text{ cm}$ and $10\text{ cm} \times 10\text{ cm} \times 20\text{ cm}$. These serve as bats and/or closers. By eliminating the use of some blocks a perforated wall can be designed. These small openings if arranged in sufficient number by precise calculation, can serve as ventilators allowing desirable ventilation and reducing the glare, which is highly preferred in the tropical climates. This construction detail helps to eliminate lintels, chhajjas and grills for windows, thereby effectively reducing the cost. The time of construction is substantially reduced, as time for fixing the windows, casting the lintels etc. is eliminated. The bond using the universal blocks is named as “Universal Bond” and has several documented variations. Almost 216 variations are possible with these three units. In practice it is seen, that if a mason goes wrong, he changes the design but does no harm to the strength of the wall. All the waste material obtained from demolished buildings can be recycled irrespective of type or size and utilized in the universal blocks. About 8%–10% cement by weight is required for each block. They can be cast by hand or with the help of a machine. Intelligent use of a wood piece as a rough ground, while casting the specific blocks to be used on the peripheries of openings, helps to eliminate the need of doorframes. Documented examples have shown that small self supporting walls of approximately 8 feet height and 10 feet length can be erected without any lateral supports, columns etc. using universal blocks (Fig. 7).

Use of Bamboo as a Reinforcement Material in RCC

Bamboo as a natural material is renewable and biodegradable in nature. It is energy efficient on account of its natural origin and environmentally sustainable nature. These properties have encouraged the use of bamboo in the construction field for several years. Bamboo has been used for scaffolding works, formwork supporting stands and in many medium and large building construction projects. Bamboo based products like bamboo based particle boards and ply boards, bamboo matting are considered environmentally friendly and are used regularly in construction. Bamboo has been used mainly as a strength bearing construction material for building shelters for centuries in certain regions. However, its application as reinforcement in concrete is fairly recent. It is observed that bamboo reinforced concrete construction can follow the same design, mix proportions and construction techniques as used for steel reinforced concrete. Only steel reinforcement is replaced with bamboo reinforcement. On account of high demand of steel as a reinforcing material in developing countries, there are situations when the production of steel is inadequate to meet the demand. It is noted that the property of tensile strength which is the main requirement of a reinforcing material is quite appreciable for bamboo as compared to other materials. Fast growing bamboo can be cultivated in abundance and can probably satisfy the demand as a reinforcing material to become an ideal replacement for steel (Fig. 8).

Conclusion

Climate responsive design strategies using eco-friendly materials and technologies can become the means to create ‘Sustainable’ buildings. Although a range of environment friendly materials is available in the market, efforts at innovation, seeking to provide logical solutions to the problems of the climatic conditions, in order to enhance human comfort and productivity should be promoted. Generating an awareness in the masses, documenting and acknowledging efforts of individual practitioners of sustainable techniques, encouragement to industrial units by way of incentives from local bodies, and educating clients and builders in areas of sustainable practices can go a long way to help protect the environment.

See also: Sustainability of Advanced Materials in Construction

Improving Energy Efficiency in Buildings Through Responsible Design: Optimizing Use and Careful Selection of Building Materials

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"The world we have made as a result of the level of thinking we have done thus far creates problems that we cannot solve at the same level at which we have created them...We shall require a substantially new manner of thinking if humankind is to survive" Albert Einstein

Introduction

"The future is not some place we are going to, but one we are creating. The paths to it are not found, but made; and the activity of making them changes both the maker and the destination" says John Schaar. It is no denying a fact that technological innovations have contributed a lot in the field of Architecture and the benefits are being enjoyed by the people for couple of decades. These emerging technologies not only affect the user behavior but also have an overall impact on society. Collingridge says 'The social consequences of a technology cannot be predicted early in the life of the technology. By the time undesirable consequences are discovered, however, the technology is often so much part of the whole economics and social fabric that its control is extremely difficult'. Today the world can witness the tallest (163 floor storied) structure only because elevators were invented in the year 1853. Researchers from University of Missouri-Columbia have found in a study 'Taking The Elevator Could Be Worse For Your Body' that a reduction in daily physical activity is an actual cause of many of the risk factors for chronic diseases, including diabetes and cardiovascular disease. Because of the availability of the elevators, the concept of 'walk-up' apartment is vanished from the society. Even for a double storied building also, people are preferring to install an elevator at the cost of one's health. The installation of an elevator is not only inviting the health problem of the occupant but also involves huge amount of energy cost. The energy component is quantifiable whereas the impact of other components like health, social, behavioral, etc., is not. Designers need to understand the dynamics between technology and society. A piece of technology attain its meaning and stable function in a society, thereby providing a conceptual foundation for design methodology. At present, there are few rating systems available in most of the countries which have become a framework of reference to assess and measure the sustainability of buildings. But there are no mechanisms available by which the quantification of other factors can be done.

All design projects have certain forces (as mentioned in Fig. 1) which are always pulling them in different directions. Among these forces, some are 'definite' in nature (in purple and brown) and some are 'indefinite' (in black) in nature. For the purpose of this study, we will limit our discussion regarding 'usability' and 'material selection' only.

Universal Values and Design

Architecture is the discipline dealing with design focusing on the creation of physical environments. Designing a built environment is not merely satisfying the functional space requirements of the user. Integration of the individual and social values into the design process has become equally important to meet the sustainability goals. In architecture, a firm relation between values and design is present throughout the history. 'Architecture can communicate memory, but it can also communicate values and a sense of place.....Architecture is an expression of values – the way we build is a reflection of the way we live.' says Norman Foster. Values underline all the acts which we feel we have chosen. The question is 'Can moral values be considered as universal?' A value can be called a universal value if it has the same value or worth for all, or almost all people. At the same time, it is interesting to note that the design values and perception as read by the architecture fraternity often varies from that of the civil society. On the other hand, there are certain universal values which are accepted by all in a similar manner.

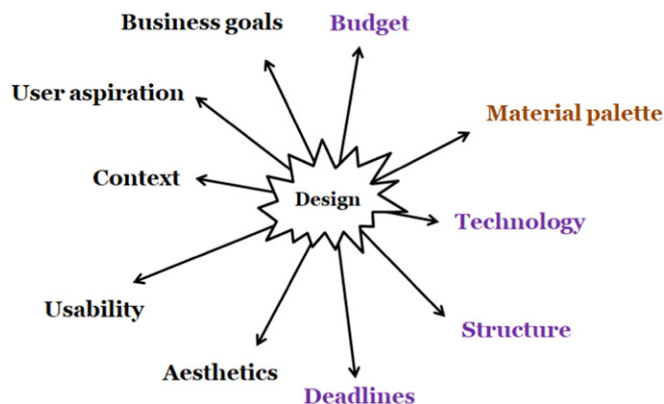


Fig. 1 Different forces in Design process.

'Satyam-Shivam-Sundaram' which means Truth-Goodness-Beauty is considered as universal values by everyone since time immemorial. A rose appears to be a beautiful creation in nature is an accepted fact by everyone which can be considered as an universal value.

Values become deeply embedded into the architectural design process. Thus if the universal values are similarly understood or recognized by all, then how the interpretations by the architecture fraternity and the civil society are different? Sharon Knoll says 'The domain of interpretation contains how we label or describe our experience. It includes analysis, evaluation, assessment, "knowledge", opinion, stories, etc. It also contains reflexive responses/reactions, unconsciously inherited perspectives, and the foundation/justification for saying that someone or something is "right" or "wrong".'

The preservation of options for the future can be readily linked to notions of equity if it is agreed that "the future ought not to face, as a result of our actions today, a seriously reduced range of options and choices, as they try to adapt to the environment that they face".

Concept of Responsible Building

What is 'Responsibility'? Sharon Knoll says 'For most of us, responsibility is held as burden, blame or guilt. Responsibility has become something to be avoided.....Responsibility can be embraced as a powerful relationship to circumstances.' In this context, it would be pertinent to mention that till date there is no such proper definition about Responsible Building. On the other hand, lot of definitions of 'Sustainable buildings' are found available over the last few decades. The U.S. Environmental Protection Agency (EPA) stated that sustainable building is the practice of creating structures by using processes that are environmentally responsible, resource efficient and impact minimizing in their life cycle from siting to deconstruction. In absence of any such definition of responsible building, an effort is taken to find out how other disciplines are capturing the concept in today's context. It is found that 'Responsible Innovation' is defined by Jack Stilgoe and co researchers as "taking care of the future through collective stewardship of science and innovation in the present". In a training workshop 'Designing for Socio-Ecological Transformation' organized by ECO-LOGICAL Foundation in collaboration with FES, India the discussions on 'Responsible Building' were held and after several deliberations the concept (Fig. 2) was developed. It is clear that a responsible building needs to be responsible throughout its existence on the mother Earth right from the beginning. Responsibility starts with the design process and gradually

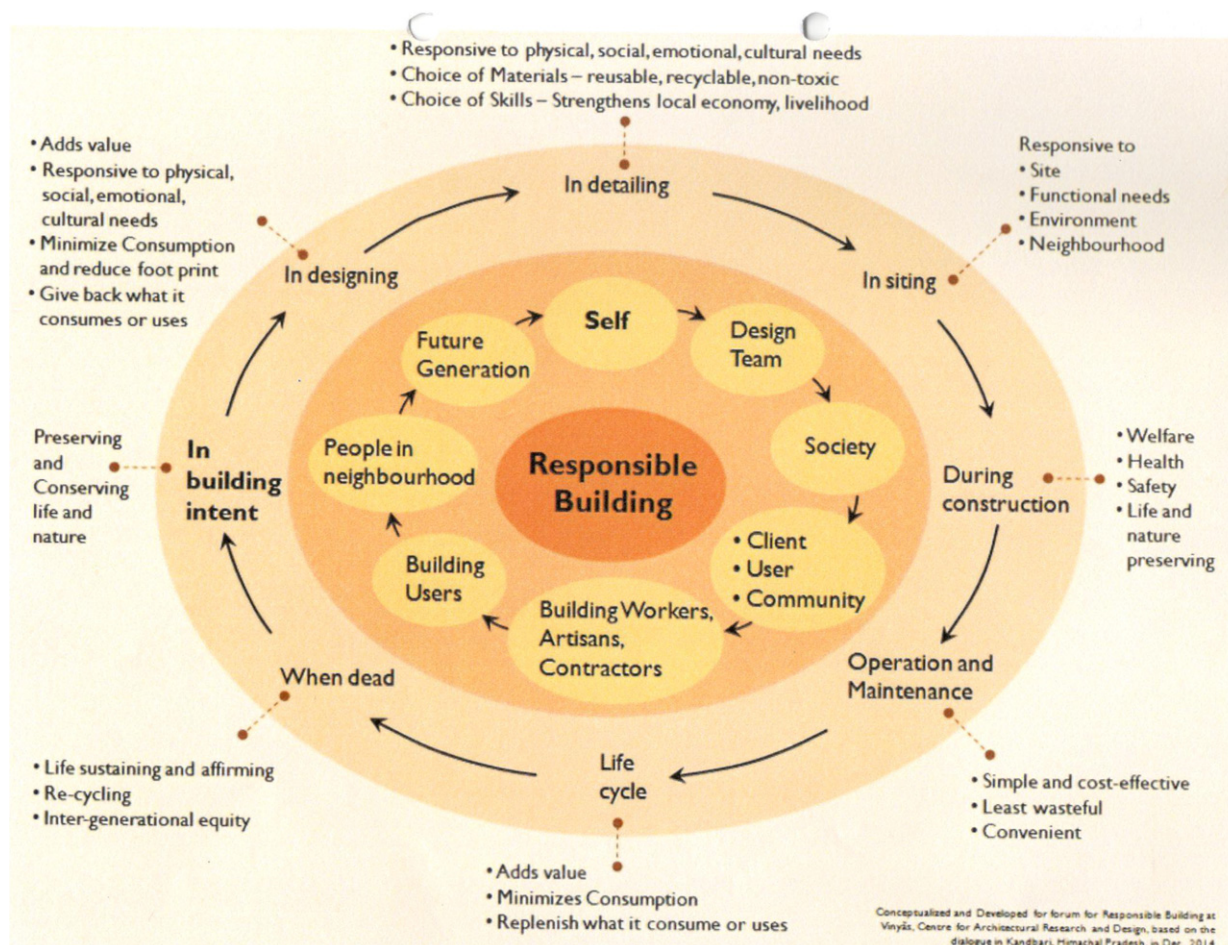


Fig. 2 Responsible Building. Conceptualized and developed by Vinyas based on the dialogue in Kandbari, Himachal Pradesh, 2014.

it increases at each and every stage even after its death also, a building has to be responsible. It means the thought process involved with the building activities has to be responsible.

Value Judgement: Way Towards Responsible Design

When we are discussing about universal values in the context of taking design decisions for achieving energy efficiency in buildings, it is imperative to understand what is 'value judgment' and how it can lead to create responsible design. A value judgment is a judgment of the rightness or wrongness of something, or of the usefulness of something, based on a comparison. Different theories on engineering ethics have defined value as a principle that promotes well-being or prevents harm. Values are the scales we use to weigh our choices for our actions, whether to move towards or away from something. Through value judgment one can be sensitive towards the beliefs, values and identity of society that has usually been acquired through layers of experience and actions, which can enable to take responsible environment responsive design decisions.

While focusing on responsible design, knowledge about social, ethical, environmental, economic values and issues involved in design is required to make informed, considered and sensitive value judgments. Design quality can be evaluated as an overall value judgement of stakeholders involved in the entire process of design, construction and use of the built space, which is based on their respective interaction with different aspects of the built environment. As a result of the interaction between the individual and the product, a value judgement is always accompanied by an emotional response and an assessment about the level of quality or value of a product.

Responsible design focuses on creating functional feedback loops between social and environmental systems, while avoiding superimposition of preconceived stereotype ideas. Before providing the building design for construction, several field studies, stakeholder discussions, assumptions, conceptual plans, design and redesign, and climatic efficiency test by using different computational simulation technique are conducted several times till the design fulfills all functions satisfactorily. Different materials and construction techniques are tried and tested in the design process. Building design should be an iterative process to enable value judgment in creating an environment responsive built space.

Right Environmental Actions: Ethical Approach for Responsible Designing

Ethical theories and principles stresses upon how to live, to respond to issues, through the duties, rights, responsibilities, and obligations. The principles and practices have varied over different geography, climate, period of history and society. But, ethical behavior that focuses on responsible actions is being advocated beyond the limits mentioned above and these principles and practices have universal value and inclusive applications. Two basic questions are in the forefront in the discourse on environmental values (a) What kinds of thing are intrinsically valuable? (b) What makes an action right or wrong for the sustenance of environment.

Environmental ethics often draws conceptual thinking from traditional ethical systems and theories. "Human-environmental interaction in a specific place, including the management of common pool resources, needs to be situated within the historical, ecological and cultural narrative of its human ecology" (Rourke, 2005). Environmental principles acknowledge the moral relationship of human beings towards environment, and also the value of environment and its non-human contents. Pro-Environmental actions include the attempt to apply traditional ethical theories, preservation of biodiversity as an ethical goal, and broader concerns of the built environment along with the politics of poverty; and climate change (Brennan and Yeuk-Sze, 2016).

The consciousness and emergence of activism for right environmental actions brought in the slogan of 'Sustainability' into most of the development agenda. The Brundtland report depicts sustainability as a challenge and opportunity for the world to become more socially, politically and environmentally fair. In pursuit of intergenerational justice, it suggests that there should be new human rights added to the standard list, for example, that "All human beings have the fundamental right to an environment adequate for their health and well being" (WCED, 1987). With depleting natural resource and impending climate change, it is important to examine 'How much is adequate?' and 'What is the optimum level?'. The term 'Utilitarianism' conceptualized in the 19th century by Jeremy Bentham and John Stuart Mill which suggested that the standard of right conduct is maximization of good consequences. But, to find a solution to the above posed questions, the good consequential effects drawn by utilitarian approach are required to be achieved with minimalist ideas and techniques. Herein, the principles of reduce, reuse, recycle, recover and replenish coined by Bwrgkamp *et al.* (2015) for sustainable development and discussed in the Directive [2008/98/EC] of the European Parliament and of the Council on waste have meaning in the context of right environmental action, and which can be the guiding principles for responsible design.

Naagarazan (2006) puts forth the following points while analyzing an issue with an utilitarian approach:

- Various courses of action that are available are to be identified.
- Next it is to be examined who will be affected by each action and what benefits or harms will be derived from each of these actions.
- Then the action that will produce the greatest benefits and the least harm is to be selected. The ethical action is the one that provides the greatest good for the greatest number.

Fig. 3 shows the issues and requisites a professional has to act upon for making environmental sensitive responsible design decisions.

OBJECTIVITY
Cost and benefits of all possible alternative means in objective manner. Skill in comprehending, clarifying, and critical assessment of contested ideas.
BACKGROUND KNOWLEDGE
Understanding of economic and functional viability (effectiveness), environmental and technical achievability (efficiency), operational feasibility (post occupancy) and social acceptability, which include environmental and ethical aspects. Awareness of alternate responses to issues and creative solutions.
VALUE
Qualities, such as <i>competence (skills and expertise), diligence in delivering decisions, loyalty in meeting the interests of users, public trust, and respect for the common good, rather than serving only the interests of the clients or the political interests.</i>
TECHNICAL COMPLEXITY
Unrealistic assumptions and frivolous design decisions goes against environmental ethics, and increase in embodied energy. Energy options, assumptions on population increase, life style, urbanization, availability of local fossil resources, projected costs of generating alternative forms of energy and adoption of alternative construction technology may increase the complexity in judgment on future. Sensitivity to genuine difficulties, including willingness to tolerate uncertainties while making decisions.

Fig. 3 Professional issues and requirement. *Source:* Naagarazan, R.S., 2006. Professional Ethics and Human Values. New Delhi: New Age International Publishers.

Usability in Architecture

In software engineering, usability is the degree to which a software can be used by specified consumers to achieve quantified objectives with effectiveness, efficiency, and satisfaction in a quantified context of use. Usability in Architecture is based on the prevailing norms and standards for each building functional use. The amount of air, daylight and the space per person are also mentioned in the Architectural standards. Standards might change with time and context. An efficient building should be able to adapt to all the upcoming changes which might be required by its users in future. Usability is present in all interactions between user and object. Architects need to think about the solutions which can create an adaptable intervention so that it becomes easy to incorporate future modifications within enclosures. At present, a majority of architectural creations is based on studying human behavior and patterns. Architectural designs are mostly carried out based on past experiences following certain norms and standards. In most cases, the design briefs are generally prepared by the architects in consultation with the client. The outcome often comes as a product where it is found a certain amount spaces are either un-utilized or under-utilized. A space when remains un-utilized or under-utilized in turn is a wastage of energy and resources. Thus thinking of optimizing space requirements in design will also help in reducing the carbon footprint on the globe and a responsible way to look at it.

Integrated Holistic Process: Enabling Sustainable Design

Meeting the ever expanding human needs in the face of declining resources and changing climate is a challenge posed to all the stakeholders involved in taking decisions regarding building design and construction. As more issues, perspectives, models, codes and metrics are incorporated into the planning and building process, the roles of engineers and designers are increasingly being fused (Sarté, 2010). Designers are to be equipped with expertise to incorporate systems thinking, take account of material flows, and infuse environmental performance concepts into their work. Engineers are to be more involved from the initial stage by applying their technical and infrastructure related expertise earlier and more comprehensively as an integral part of a holistic design process. There is a need to address critical questions regarding planning, designing, and building healthy, cities, homes and communities for a growing and demanding population, along with the provision of efficient utilities and infrastructure in ecologically sustainable manner.

There is a need of integrated creative technological approaches for designing, redesigning and retrofitting the built environment, where the role of architects, engineers, building science experts, ecologists, landscape architect are elucidated at different stages in the collaborative design process necessary for developing effective integrated solutions. Recently these types of integrated design team are working together around the world by incorporating ecological infrastructure into buildings by using different environmental approaches and techniques; eg. reuse of storm-water, recycle of grey water, solid waste, application of alternative building construction techniques in an aesthetically environmental friendly way, incorporating creative solar passive design ideas to build more beautiful communities and by designing urban environments that respect and engage natural systems. (Table 1) The infrastructure solutions can emerge from a process of on- and off-site collaborative thinking involving a wide array of stakeholders.

Table 1 Framework for five pillars of sustainability for optimizing system synergies and advancing towards regenerative designs

	<i>Level one: Reduce Harm</i>	<i>Level Two: Sustainability sourcing</i>	<i>Level Three: Systems Integration</i>	<i>Level Four: Regenerative Design</i>
Community	(1) Integrate project into local context (2) Minimize infrastructure impacts (3) Reduce air pollution	Education and employment (1) Improve local training and workforce development (2) Access to health care	Capital improvements (1) Develop infrastructure in surrounding communities (2) Generate additional tax based revenue for local community	(1) Achieve lasting economic and social benefit (2) Optimize system of learning and education (3) Expand and enable cooperative network
Ecology	Mitigate Disturbed Areas (1) Mitigate wetland impacts (2) Incorporate open space (3) Minimize negative impact on habitat	Conserve and protect natural systems (1) Monitor sensitive species (2) Preserve wild life corridors (3) Improve natural hydrology (4) Landscape with native plants	On-site restoration (1) Regenerate native systems (2) Restore native species in wildlife corridors (3) Coral reef propagation (4) On-site and off-site reforestation	(5) Maximise biodiversity and restore when necessary (6) Model on ecosystem, Biomimicry at macro and micro scale (7) Appropriate use of environmentally sound technologies
Energy	Efficiency (1) Reduce carbon emission (2) Energy efficient appliance (3) Building-scale energy demand reduction strategies (4) Promote public transportation	Active high performance system (1) Application of renewable energy systems (2) Transit- oriented development (3) Energy monitoring systems (4) Promote passive energy design	Renewable energy generation (1) Photovoltaic cells (2) Wind power (3) Zero emission transportation (4) Carbon sequestration	Carbon Zero (1) Continually minimize energy use through aggressive auditing
Water	Water efficiency (1) Water conservation (2) Xeriscaping (3) Low impact development	Water reclamation (1) Grey water recycling (2) On-site waste water treatment (3) Retaining water on-site	Water reuse (1) Onsite rainwater harvesting (2) Use of water recovery systems (3) Ground water recharge	Water balance (1) Effective demand management (2) Strive for net zero use (3) Match pre-development hydrologic conditions
Materials	National material sourcing (1) Active recycling (2) Reduce toxic materials	Regional material sourcing (1) Active reuse of materials (2) Onsite composting	Local material sourcing (1) Design consideration (2) Onsite agricultural production	(1) Minimize ecological footprint through construction and operations (2) Minimize waste production and promote responsible recycle and reuse

Source: Sarté, S.B., 2010. Sustainable Infrastructure: The Guide to Green Engineering and Design. USA: John Wiley & Sons, Inc.

Along with technical challenges, this kind of integration enables a softer approach that helps to bring in opportunities to celebrate the human experience of making greener, healthier, more beautiful and more efficient communities. This multidimensional approach has the potential to weave in together different priorities and requirement to achieve design synergies and cost savings. This holistic design process makes it possible to rethink on alternative approaches using fundamental building science and material technology concepts that will be distinct, and can be appropriate and effective for different, geography, climate and culture. With this background the subsequent sections of the paper will highlight on building materials that has different energy impacts in different context and the transitions of vernacular communities with respect to adoption of conventional modern building engineering practices.

Responsible Selection of Building Materials: Significant Impact on Energy Efficiency of Buildings

Construction, operation and maintenance of buildings consume the largest energy, while globally accounting to one third of the world's resources (Atkinson, 1994). including approximately one third of primary energy supply with maximum ecological footprint (Pulselli *et al.*, 2007). The general breakup of energy consumption in buildings globally is 16:84, the former being the percentage attributed to manufacturing, construction material transport, and maintenance and renovation of a building, while the latter includes the energy share attributed to appliances and space conditioning and operation. (WBCSD, 2008) Manufacture of materials for building sector attributes to 20%–25% of India's total energy demand (Sanyal *et al.*, 2009). It is crucial to note that these estimates are related primarily to highly developed urban areas.

Careful selection of environmentally sustainable building materials is the easiest way to begin incorporating environment friendly design principles in buildings. Retrofitting buildings for energy-efficient performance can yield significant result in regulating Greenhouse Gas (GHG) emissions (Levine *et al.*, 2007). Cost of material has been the primary guiding factor for choice of specific building material. The market price of a building component represents only the manufacturing and transportation costs, while ignoring the social or environmental costs. Past studies on cost effective technology and low energy materials have attributed five modes of energy consumption to buildings; energy for extraction of material, energy for transport, energy for construction, energy for operation and maintenance, and finally energy for the demolition, and recycling or disposal (Sengupta, 2008). This is referred as the 'embodied energy' of a material.

A life cycle cost analysis of building products, from the gathering of raw materials to their ultimate disposal, provides a better understanding of the long-term costs of materials, which is paid not only by the owner, but also by the environment. Each step of the manufacturing process, from extraction of raw materials, manufacturing, distribution, and installation, to ultimate reuse or disposal, is examined for its environmental impact. This principles of Life Cycle Design provide important guidelines for the selection of building materials. A material's life cycle can be organized into three phases: Pre-Building; Building; and Post-Building. These three life-cycle phases relate to the flow of materials through the life of the building (see Fig. 4).

Building materials are to be selected based on these three building phases. With respect to Pre-building phase the selection of materials should be based on reduction of waste, pollution prevention, recycled content of the materials and reduction of embodied energy. The primary considerations for selection of materials with respect to Building phase is reduction in construction

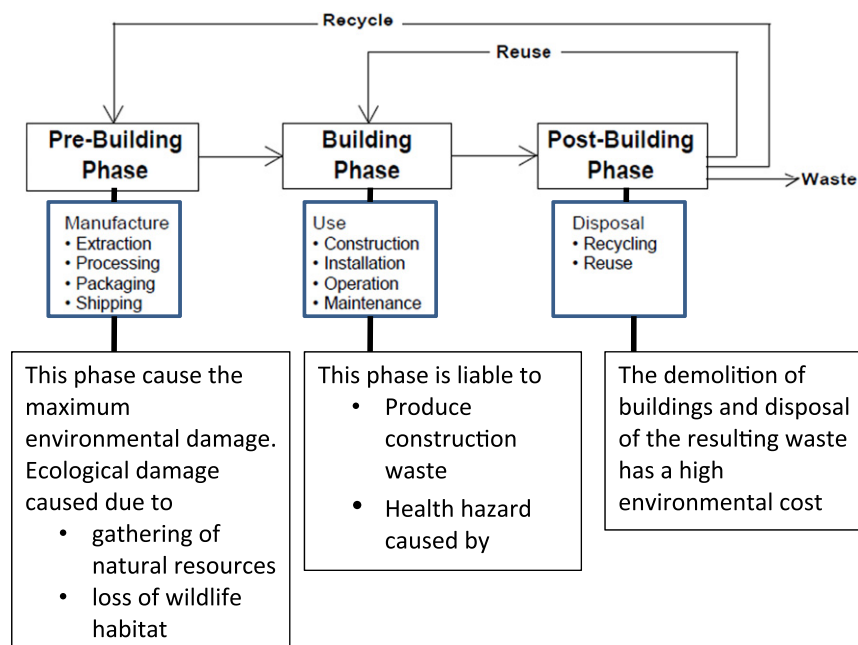


Fig. 4 Three phases of the building material life cycle. Adopted from Kim, J.J., Rigdon, B., 1998. Sustainable Architecture Module: Qualities, Use, and Examples of Sustainable Building Materials. Ann Arbor, MI: National Pollution Prevention Center for Higher Education.

Table 2 Energy and environmental effectiveness

Initial embodied energy per m ³ of wall		Pollution emission (kg of CO ₂) per m ³ of wall	
CSEB wall	631 MJ/m ³	CSEB wall	56.79 kg/m ³
Kiln Fired Brick (KFB)	2,356 MJ/m ³	Kiln Fired Brick (KFB)	230.06 kg/m ³
Country Fired Brick (CFB)	6,358 MJ/m ³	Country Fired Brick (CFB)	547.30 kg/m ³

Source: Building with Earth, Auroville – Earth Institute.

waste, energy efficiency, use of non-toxic or less-toxic materials, and durability. Reusability, recyclability, biodegradability characteristics of materials are important for the Post-building phase.

Life Cycle Analysis (LCA) is the tool to measure the environmental performance of a particular building material, which provide-

- Comprehensive understanding of its environmental impact
- Improvement ideas that can be offered at each stage in the life cycle of a material
- Decision system to compare and select materials
- Efficient alternatives and qualitative judgments to choose based on environmental and economic performance.

Life Cycle Cost (LCC) estimate apply

- Method to assess the cost effectiveness of a material
- Set of techniques to evaluate the present value of the asset over its operating life including initial capital cost, operational cost and the cost of salvage value.

The presence of certain features in building materials based on the material life cycle make it environmentally sustainable. The recycled content of a material reduces the waste stream and the demand on virgin natural resources. By recycling materials, the embodied energy they contain is preserved. Aluminum, for example, can be recycled with only 10%–20% of the energy that is required to transform its raw ore into finished goods. Glass, plastics, metals, concrete or brick, and wood have potential for recycling. Reduction of embodied energy of material by revision of manufacturing process reduces the amount of energy required to produce it, implying less ecological consequences.

Minimization in use of natural resources by minimizing resource quantity through optimization of quantity of materials used for building can also give good result. This can be achieved by building less, such as reducing wall thickness and optimized utilization of built spaces. Examples of reducing embodied energy by replacing conventional materials are; replacement of cement in concrete with coal fly ash or ground granulated blast furnace slag, use of lime pozzolana mortars in place of cement mortars, soil or stabilized soil blocks over burnt clay bricks, light weight concrete blocks over dense concrete blocks, gypsum plaster over cement plaster, load bearing masonry in place of framed structure wherever possible.

Researchers around the world are working on new scientific ideas and techniques to improve the strength and durability of structures made of earth. Use of Compressed Stabilized Earth Blocks (CSEB) and Rammed Earth construction are being promoted across the world. Use of locally available natural materials are generally lower in embodied energy and toxicity than man-made materials (Table 2).

Use of energy efficient materials is an important selection criteria for making the building environment responsive. The long-term energy costs of operating a building are heavily dependent on the materials used in its construction. The energy-efficiency of building materials can be quantitatively measured using factors such as R-value (Resistance), shading coefficient or Solar Heat Gain Coefficient (SHGC), U-value (Transmittance), thermal conductivity, luminous efficiency, or fuel efficiency. Effective selection of materials reduces the transfer of heat through a building's envelope and consequently reducing the need for heating or cooling. Quantitative measurements of a building material's efficiency are available to help in the comparison of building materials and determining appropriateness for certain installations. The shading coefficient (SC) or SHGC comparatively evaluates the sun-blocking effectiveness of various glass types, shading devices, and glazing patterns. Past literature also suggests that energy related environmental impacts on buildings is to be considered through their life-cycle and environmental analysis by focusing on factors that influence energy consumption. Evaluation of building envelope, glazing and fenestrations, thermal mass and insulation of buildings, daylighting and artificial lighting, natural versus mechanical ventilation, energy-recovery opportunities, indoor and outdoor air quality and environmental protection (Todorovi, 2019).

Environmental Impacts of Transition in Rural Settlement

Architectural Design is a complex art, rooted in strong intellectual, cultural and spiritual traditions, but also modified through technological development and intelligent application (Bundgaard, 2011). The inevitability of change and dynamism attributed to the built environment must be recognized within the discourse on responsible design principles. Rural areas are undergoing transformation while responding to the modernizing aspirations of its inhabitants. Significant transitions in the rural fabric has brought about a paradigm shift in the theology of traditional building practices. Traditional building practices used to adhere to the physical and metaphysical context of the place it belonged to and suited to the social, cultural and environmental need of the

inhabitants. The performance evaluation of such buildings would rank high in the efficiency index, considering the four aspects; self-built or community-built, use of local resource for materials, utilization of traditional technologies and synergy with environmental context.

It has been found that there exist a significant relation between the community's lifestyle and environmental sustainability (UNCHS, 1990). The so called 'Development' of traditional settlement meant to describe the human act of improving, or attempting to improve well-being is being recently examined from different directions; as indicating fading culture (Mani and Reddy, 2012), contested lifestyles, sustainability issues and environmental impacts. Steadily changing pattern of actions, rules, values and norms have altered the traditional ways of life, which has impacted the environmental quality of vernacular settlements. Modern aspirations are resulting in transitions from low energy local resource dependent habitations to energy intensive non-local resource based modern style habitations. Further, these transitions are resulting in the habitations becoming increasingly unsuited to the local climatic conditions with increasing discomfort and environmental disruption. It is estimated that adoption of modern building materials in rural dwellings have a clear potential to increase GHG (Greenhouse Gas) emission between 8.5 and 10% of projected 2031 national emissions of India (MoEF, 2009).

Recent ideologies of zero-energy and low carbon footprint much advocated as means to achieve sustainability in urban areas are intrinsic practices in vernacular settlements, as they are less dependent on active energy systems. Only 60.2% of rural households use electricity as the primary source of lighting. Energy requirement for thermal comfort is negligible, as the vernacular dwellings have incredible ability to passively regulate the indoor environment to achieve thermal comfort. The building materials used are less energy intensive and community led construction activity is adopted.

Studies on rural transition in India have found that the roofs of vernacular dwellings have undergone significant transformation. It was seen that within 15 years the use of Reinforced Cement Concrete (RCC) roofs was on the rise, along with Asbestos Corrugated (AC) sheets or Galvanised Iron (GI) corrugated sheets, as well as houses with a combination of old and new roof types and materials have increased by almost 50%. They found that this transition was due to the aspiration to live in a safe and maintenance free house, and it has resulted in less thermal comfort with 7–10°C rise in indoor air temperature during summer. All the criteria of well-being could not be achieved as there was less satisfaction from meeting physical, mental and environmental needs.

A study conducted in the heritage village of Raghurajpur in Odisha, shows that over the past decade transitions in their dwellings, is primarily seen in the building materials adopted, while building layout still remain the same. The community lived on minimum resource for basic survival within the natural setting of the village with negligible demands on energy and process-intensive materials for sustenance. Earlier building materials used were mud, bamboo, thatch, laterite stone blocks and bricks, which were locally available. Walls and attic roof of some of the houses which still exist used wattle daub construction, where mud reinforced with bamboo and wooden twigs is used as a composite material, which is made by the community in response to the prevalent climatic and environmental conditions (Fig. 5). These vernacular dwelling regulate the indoor thermal environment and provided adequate occupant comfort without the need of mechanical cooling system like fan.

The transitions can be observed in progressive phases, first phase involved the replacement of traditional thatch roof by either a corrugated asbestos cement or tin sheet roof; in the second phase burnt clay brick wall with mud mortar replaced traditional earthen walls; third phase, which is the present trend involves a total transition to burnt clay brick walls with cement mortar and corrugated tin sheet roof or reinforced cement concrete roof (Fig. 6). These transitions in the rural setting have altered the indoor and outdoor environmental conditions. The integration of concrete and asbestos roof in the traditional compact form of the dwelling, has resulted in the dwellings becoming increasingly unequipped to maintain comfortable indoor conditions. From the survey conducted in the village it was observed that there is unanimous response of increasing thermal discomfort within the altered dwellings and outside due to increased built footprints and reduction in natural environment.

The earthen structures of rural West Bengal which have evolved over generations use locally available building materials: thatch, earth and bamboo and constructed by the community. The built form, orientation, and preparation of materials all follow simple, well-established rules in response to local climatic conditions. Past studies shows that although the external diurnal



Fig. 5 Traditional Building construction technique used earlier for the houses. *Source:* Mohapatra, B., 2015. Transition, adaptation and continuity: The narratives of a modernizing heritage village. In: Proceedings of the International Conference on South Asian Vernacular Architecture (SAVA). Bhopal: School of Planning and Architecture.



Fig. 6 Transition from thatch roof to the use of corrugated sheets and then to RCC roof. *Source:* Mohapatra, B., 2015. Transition, adaptation and continuity: The narratives of a modernizing heritage village. In: Proceedings of the International Conference on South Asian Vernacular Architecture (SAVA). Bhopal: School of Planning and Architecture.



Fig. 7 Transition in vernacular dwelling of West Bengal. *Source:* Mani, M., Reddy, B.V., 2012. Sustainability in human settlements: Imminent material and energy challenges for buildings in India *Journal of the Indian Institute of Science* 92 (1), 145–162.



Fig. 8 Transformation of dwellings and use of modern construction materials. *Source:* Moothedath, C.K., Nallaval, C.B., Monto, M., 2015. Well-being and sustainable design: A case study of building typology transition in a rural settlement in India. In: Mani, M., Kandachar, P. (Eds.), Design for Sustainable Well-Being and Empowerment. IISc Press and TU Delft, 207–226.

temperature varies between 10 and 15°C, indoor temperature variations are maintained within 3°C, which is well within physiological resilience of the inhabitants (Mani and Reddy, 2012). Transformation in their dwellings is primarily in the use of modern building materials, like corrugated asbestos/cement (AC) sheet roofs (Fig. 7). Although the inhabitants agreed upon the indoor discomfort conditions, the community is still drawn towards adopting modernized methods of building construction.

The traditional building typology of the villages in Karnataka is characterized by a single-room space with a thatched roof, and very few roofs of stone slabs, walls constructed from adobe or sundried bricks or straw bamboo reinforced adobe, and floors plastered with cow dung or mud. Random rubble (RR) masonry and stone flooring with clay- tiled roofing are also in practice.

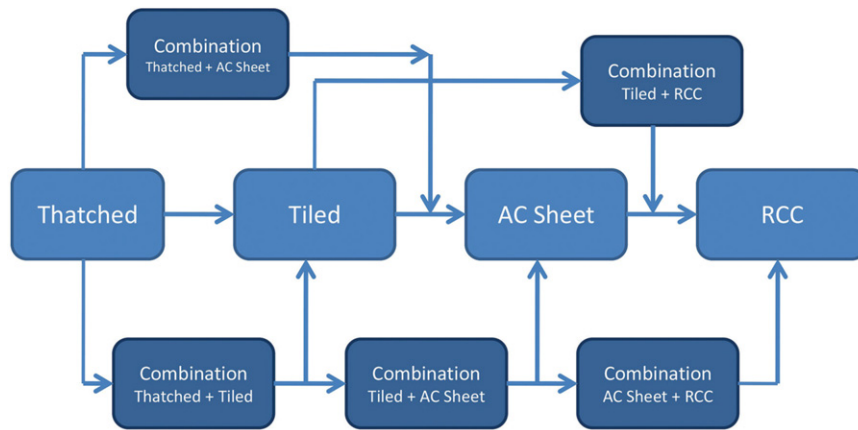


Fig. 9 Transition trend of vernacular roof. *Source:* Moothedath, C.K., Nallaval, C.B., Monto, M., 2015. Well-being and sustainable design: A case study of building typology transition in a rural settlement in India. In: Mani, M., Kandachar, P. (Eds.), *Design for Sustainable Well-Being and Empowerment*. IISc Press and TU Delft, 207–226.

Similar to the first two cases the aerial picture of the area reflect the increase in built-spaces of the villages as well as the transition of the roof materials. The use of Reinforced Cement Concrete (RCC) roofs is on the rise, along with Asbestos Corrugated (AC) sheets or Galvanised Iron (GI) corrugated sheets, as well as houses with a combination of old and new roof types and materials (Figs. 8 and 9).

Conclusion

Instilling environmental ethics and responsibility for sustaining the environment are means to recognize the place and make commitment to the natural environment. Across the world, in every sphere people are talking about ‘sustainability’. For varied reasons, though there is wide usage of the very term, yet the true understanding of the term ‘sustainability’ is often not reflected in the day to day practices done by the people. Building activities are a major contributor to the world’s total pollution. Talking about ‘Sustainable’ Buildings is no more enough in handling the burgeoning environmental pollution issue. As a human being, since our childhood we grew up with certain universal values and we are taught to become responsible. Are we behaving very responsibly as an user or as an architect in the society? The aim of this paper is not to provide any toolkit or database rather opening up an agenda for further discussion in order to create avenues for further research leading to policy framing in future.

“There is, it seems to us at best, only a limited value in the knowledge derived from experience.

The knowledge imposes a pattern, and falsifies, for the pattern is new in every moment is a new and shocking valuation of all we have been”. -T.S. Eliot

See also: Thermal Adaptation and Sustainable Housing in Cold Climates

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Insulation Materials for the Building Sector: A Review and Comparative Analysis

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Thermal Insulation of Buildings

The twenty-first century's challenge for energy and environmental efficiency of buildings requires the thermo-hygrometric characteristics of the building envelope to be adequate to the climate, in order to guarantee the best thermal comfort for the inhabitants with the lowest energy consumption and greenhouse gas emissions. Space heating and cooling account for over 30% of all energy globally consumed in buildings, rising to as much as 50% in cold climate countries. In the residential sector, the share of energy consumption used for heating and cooling in cold climate countries is over 60% (IEA, 2015).

Therefore, the goal to achieve buildings with very high energy performance, characterized by a very low or almost zero annual energy requirement, has made it essential to provide, with specific insulation materials, an adequate thermal insulation of the walls, roofs and floors of new and existing buildings in order to reduce heat losses in winter and heat gains in summer.

Research and development on insulation materials are now focusing on two main areas. On the one hand, the increasingly important goal to promote the use of environmentally friendly building materials and products is leading to the development of insulation materials with a lower environmental impact along the whole life cycle, preferring those rapidly renewable, of vegetable or animal origin, possibly recycled and recyclable, non toxic and with low energy production techniques (bio-based insulation materials).

On the other hand, the necessity of rapidly carrying out the energy renovation of the existing buildings stock is leading to a new class of high performance insulation materials able to guarantee the required thermal resistance with minimal thickness (nano-porous insulation materials – NIMs).

The choice of the most suitable insulation material depends on the type of application and the operating conditions. In addition to the thermal performances, insulation materials have now to be evaluated for other aspects such as limited impact on living space, acoustic behavior, fire reaction, compressive resistance and behavior in the presence of water and vapor. Resistance to damaging agents such as moisture and rodents should also be considered when relevant for the application.

The choice should also consider aspects like lightweight construction and ease of installation, competitive price, full compatibility with all relevant material combinations, enhanced durability for increased operative life, reduced maintenance and reduced costs.

Finally, particular attention must be paid to the life cycle sustainability of selected materials in terms of energy incorporated in the product, emission of substances harmful to the health and the environment, ease of deconstruction and reusability/recyclability at end of life, evaluated via specific life cycle assessment studies.

Classification of Building Insulation Materials

In building construction, we define as “insulation materials (or insulating materials)” those materials that show a thermal conductivity $\lambda \leq 0.065 \text{ W m}^{-1} \text{ K}^{-1}$ and that are consequently employed as functional layer to increase the thermal resistance, or R-value ($\text{m}^2 \text{ K}^{-1} \text{ W}^{-1}$), of the components of the building envelope.

The thermal behavior of insulation materials is explained by the fact that the base material occupies only a small part of their entire volume – as is shown clearly by the comparison between their apparent density and the density of the base material itself – while the rest is constituted by air. This, on the other hand, is distributed in pores or capillaries, arranged in many cavities so small as to exclude the presence of convective motions. The transmission of the pores is therefore to be attributed to the internal conductivity of the air, which, like all other gases, is modest at ordinary temperatures ($0.026 \text{ W m}^{-1} \text{ K}^{-1}$). Below are the values of thermal conductivity, density and specific heat of main construction materials (Table 1).

Based on their origin, either organic or inorganic, insulation materials are classified into 4 main categories (Table 2): vegetal (cork, wood fiber, hemp fiber, coconut fiber, etc.), animal (sheep's wool), mineral (glass fiber, mineral wool, expanded vermiculite, pumice, aerogel, etc.) or synthetic insulators (polyurethane, polystyrene, polyethylene foam, etc.).

The structure of insulation materials can be fibrous (mineral wool, wood fiber), porous (cork, expanded vermiculite, pumice) or cellular (polyurethane, polystyrene, polyethylene foams). These cavities may be intercommunicating (open cell insulators), as in the case of fibrous materials, or non-communicating (closed cell insulators), as in the case of synthetic insulators with cellular structure (expanded polystyrene or polyurethane).

Products available on the market can come in form of panels, rolls, mats, felt, bands, with different sizes and thickness from 5 to over 200 mm, or in bulk to be applied on site by blowing, injection or spraying. Depending on material, shape and application, insulating products can be installed by simply laying rolls, mats or fillers above roofs and floors, by fixing panels on walls or ceilings with adhesives, nails, screws or anchors, or by blowing beads, flakes or granules inside interspaces or attics.

Table 1 Thermal conductivity, volume mass and specific heat of main construction materials

Materials	Thermal conductivity ($W\ m^{-1}\ K^{-1}$)	Volume mass ($Kg\ m^{-3}$)	Specific heat ($J\ Kg^{-1}\ K^{-1}$)
Metals	420 ÷ 17	11300 ÷ 2700	880–380
Natural stones	4.1 ÷ 0.63	3000 ÷ 1500	1000
Plaster and mortars	1.40 ÷ 0.29	2000 ÷ 600	1000
Close structure concrete	1.16 ÷ 0.75	2000 ÷ 1700	1000
Open structure concrete	1.06 ÷ 0.13	1900 ÷ 250	1000
Glass	1	2500	750
Porcelain	1	2300	840
Bricks	0.90 ÷ 0.25	2000 ÷ 600	840
Waterproofing materials	0.70 ÷ 0.23	2100 ÷ 1100	1000
Compact plastic materials	0.50 ÷ 0.28	2000 ÷ 1050	2200–900
Water (calm at 293K)	0.6	1000	4190
Wood	0.22 ÷ 0.12	850 ÷ 450	1600
Cellular plastic materials	0.059 ÷ 0.032	80 ÷ 10	1450
Still air	0.026	1.025	1005

Note: UNI 10351, Materiali da costruzione e Conduttività termica e permeabilità al vapore.

Table 2 Classification of main building insulation materials

Origin	Material	Structure			Available products
		Fibrous	Cellular	Porous	
Vegetable	Bagasse	■			Panels
	Cellulose fibers	■			Spray, blowing filler, panels
	Coir fibers	■			Panels, bands
	Cork		■		Filler, panels
	Corn fibers	■			Panels, rolls, mats
	Flax fibers	■			Panels, rolls, felt, bands
	Hemp fibers	■			Panels
	Jute fibers	■			Panels
	Kenaf fibers	■			Panels, rolls
	Mineralized wood wool	■			Panels
	Mushroom	■			Filler, panels
	Reed	■			Mats
	Rice hull	■			Filler
	Seaweed	■			Filler, panels
	Straw bale	■			Blocks
	Wood fiber	■			Panels
	Wood wool	■			Panels
	Sheep wool	■			Rolls, felt, bands
Animal	Natural pumice			■	Filler
	Expanded clay			■	Filler
	Expanded perlite			■	Panels, filler
	Expanded vermiculite			■	Filler
	Cellular glass		■		Panels
	Expanded glass granules		■		Panels, filler
	Silicate calcium			■	Panels
	Stone wool	■			Panels, rolls, mats
	Glass wool	■			Panels, rolls, mats
	Aerogel			■	Panels, rolls, mats
Synthetic	Sintered expanded polystyrene (EPS)		■		Panels
	Extruded expanded polystyrene (XPS)		■		Panels
	Expanded polyurethane (PUR)		■		Panels, spraying foam
	Expanded phenolic resins		■		Panels
	Expanded polyethylene foam		■		Panels, Rolls
	Polyester fibers	■			Panels, Rolls

Beyond this main classification, several insulation products available on the market are actually a combination of more materials, usually of different origin. These composite solutions are normally made of a main insulation material to provide the bulk of the thermal resistance, and additional materials to improve the mechanical characteristics (such as polyester fibers in sheep wool for reinforcement), as

Table 3 Thermal conductivity of main insulation material

Insulation material	Thickness (mm) for achieving $U = 0.25 \text{ W m}^{-2} \text{ K}^{-1}$	Thermal conductivity λ , $\text{mW m}^{-1} \text{ K}^{-1}$
<i>Innovative high performance products</i>		
Vacuum Insulating Panels	30	8
Aerogel	50–55	13–15
<i>Polyurethane (PUR)</i>		
Polyurethane with pentane up to 32 kg m^{-3}	105–115	27–30
Soy based polyurethane	100–145	26–38
Coated polyurethane with pentane up to 32 kg m^{-3} coated	75	22
Polyurethane with CO_2	130	35
On site applied polyurethane (sprayed/injected)	80–100	23–28
<i>Polyisocyanurate (PIR)</i>		
Polyisocyanurate up to 32 kg m^{-3}	95–105	25–28
Coated polyisocyanurate up to 32 kg m^{-3}	80–85	22–23
On site applied polyisocyanurate (sprayed/injected)	80–100	23–28
Polyisocyanurate up to 32 kg m^{-3}	95–105	25–28
Coated polyisocyanurate up to 32 kg m^{-3}	80–85	22–23
On site applied polyisocyanurate (sprayed/injected)	80–100	23–28
<i>Phenolic foam</i>		
Phenolic foam	80–95	20–25
Coated Phenolic foam	75–85	20–23
<i>Expanded polystyrene foam (EPS)</i>		
Expanded polystyrene foam up to 30 kg m^{-3}	115–165	30–45
Expanded polystyrene foam with graphite (grey)	115–120	30–32
<i>Extruded polystyrene foam (XPS)</i>		
Extruded polystyrene foam with CO_2	95–140	25–37
Extruded polystyrene foam with HFC 35 kg m^{-3}	110–120	29–31
<i>Mineral insulating materials</i>		
Glass wool	135–180	30–44
Rock wool up to 160 kg m^{-3}	150–170	34–40
Vermiculite	235	39–60
Cellular glass	140–185	38–50
Expanded perlite panels	190	51
<i>Bio-based insulating materials</i>		
Cotton	165–170	39–40
Cork 120 kg m^{-3}	155–200	41–55
Wood fiber	145–225	39–61
Sheep wool 25 kg m^{-3}	150–215	34–54
Injected cellulose fiber 24 kg m^{-3}	150–190	35–46
Hemp fiber	165	39

Note: Energy Saving Trust, 2012. CE71 – Insulation Material Chart – Thermal properties and environmental ratings. London: Energy Saving Trust.

binders (such as cement in mineralized wood fibers), to form a support matrix (FRABs) or to convey desirable properties such as resistance to fire (via fire retardant additives) or to water (with a bitumen or fiberglass sheet) or vapor tightness (with aluminum foils).

Thermal Properties

Thermal conductivity (λ) values of most common insulation materials available on the market typically range from 0.032 to $0.045 \text{ W m}^{-1} \text{ K}^{-1}$. Best performance can currently be achieved with EPS boards integrated with graphite with a thermal conductivity of $0.030 \text{ W m}^{-1} \text{ K}^{-1}$ (20% lower than conventional EPS) and with PUR foams that go as low as $0.022 \text{ W m}^{-1} \text{ K}^{-1}$, or with advanced nanoporous insulation products such as vacuum insulating panels or aerogels that allow to reach λ values lower than $0.015 \text{ W m}^{-1} \text{ K}^{-1}$ (Table 3).

The thermal resistance (R) of a homogenous layer of insulation material of thickness (d) can be calculated by the expression:

$$R = \frac{d}{\lambda} \left[\frac{\text{m}^2 \cdot \text{K}}{\text{W}} \right] \quad (1)$$

in which:

R = thermal resistance ($\text{m}^2 \text{ K W}^{-1}$)

d = thickness (m)

λ = thermal conductivity ($\text{W m}^{-1} \text{ K}^{-1}$)

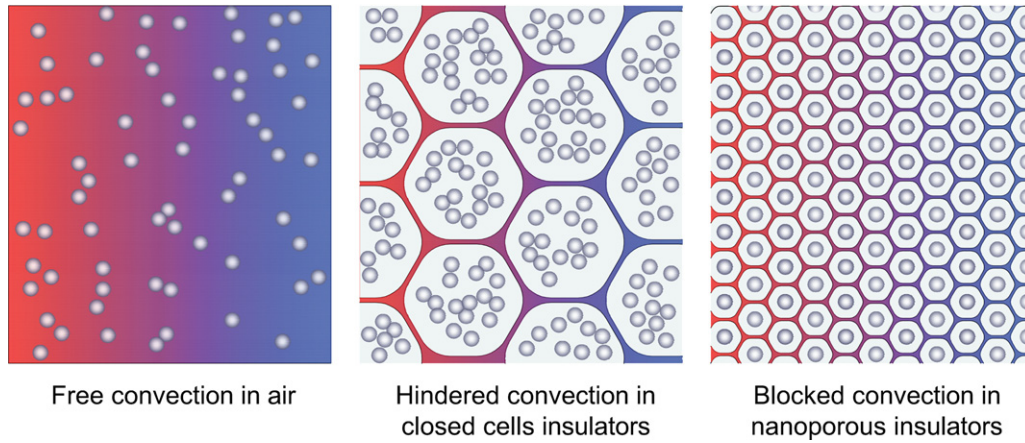


Fig. 1 Knudsen effect in nanoporous insulators. Reproduced from Casini, M., 2016. Smart buildings: Advanced materials and nanotechnology to improve energy-efficiency and environmental performance. Cambridge: Woodhead Publishing Limited.

Envelopes of existing buildings without thermal insulation materials show on average thermal resistance values (R) comprised between 0.28 and 1.00 $\text{m}^2 \text{K W}^{-1}$ in relation to thickness, constituting materials and the presence of any air gap. Current European standards oriented to the achievement of zero energy buildings require, in relation to the climate area, minimum values comprised between 2.22 and 5 $\text{m}^2 \text{K W}^{-1}$, making the use of insulation materials absolutely necessary. According to (IEA, 2015), 6 centimeters of a conventional insulation material with a thermal conductivity of 0.030 $\text{W m}^{-1} \text{K}^{-1}$ are able in fact to provide by themselves a thermal resistance of 2 $\text{m}^2 \text{K W}^{-1}$, whereas more than 1.5 m of bricks ($\lambda = 0.75 \text{ W m}^{-1} \text{K}^{-1}$) are required to achieve the same performance.

Recent advancement in the development of insulation materials is due to the progress in nanotechnology and material sciences, and has allowed to obtain high performance thermal insulators (HPTIs) with a thermal conductivity well below 0.020 $\text{W m}^{-1} \text{K}^{-1}$, making them particularly suitable for energy retrofit interventions. Such performance is achieved thanks to the higher rarefaction of air inside the insulation materials due to their nanoporous solid structures. These nanotechnological insulating products are made of aerogel (air + gel), a solid nanoporous material with ultra-low density obtained through the dehydration of a colloidal gel by replacing the liquid component with a gaseous one, integrated in a fibrous support structure (Fiber Reinforced Aerogel Blankets – FRAB).

In nanoporous materials such as aerogel, high porosity reduces heat conduction through the solid part, while the small size of the pores, typically ranging from 5 to 100 nm and an average pore diameter between 20 and 40 nm, reduces the radiation and the conduction in the gas. By reducing the pore size to nanoscale level, air molecules collide with the pore walls more often than with each other dispersing most energy within the porous structure (see Fig. 1) leading to suppressed gas conduction (Knudsen effect) and to thermal conductivity values typically of 0.015 $\text{W m}^{-1} \text{K}^{-1}$.

The values of thermal conductivity indicated in the product sheets of insulation materials are usually calculated at a temperature of 10°C. However, the thermal conductivity is greatly affected by the actual temperature of the material, which, in summer, can easily exceed 50°C when exposed to the outside. It is therefore important to know, in relation to the methods of application, the actual performance of each material at the operating temperature, as the increased mobility of air molecules inside porous, fibrous or cellular materials usually decreases thermal resistance. From this point of view, Fiber reinforced Aerogel blankets present, compared to all other insulation materials, a constant thermal performance regardless of operating temperature (Fig. 2).

Concerning the growing importance of the building behavior in the summer period, in addition to the thermal conductivity parameter, a further parameter useful to characterize the performance of the insulation material in a dynamic regime, in order to delay and dampen the incoming thermal wave and to reduce the phenomena of overheating of internal environments is that of thermal diffusivity (a), obtained from the relation:

$$a = \frac{\lambda}{\rho \cdot c} \left[\frac{\text{m}^2}{\text{s}} \right] \quad (2)$$

in which

a = thermal diffusivity ($\text{m}^2 \text{s}^{-1}$)

λ = thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)

ρ = density (kg m^{-3})

c = specific heat ($\text{J kg}^{-1} \text{K}^{-1}$)

This parameter allows to take into account not only the insulating properties, but also those of heat accumulation in a certain volume of material. The lower the diffusivity of a material, the quicker and for short distances it will extinguish the thermal wave produced on its surface. Given an equal thermal conductivity, the insulators that behave better in the summer are those that have

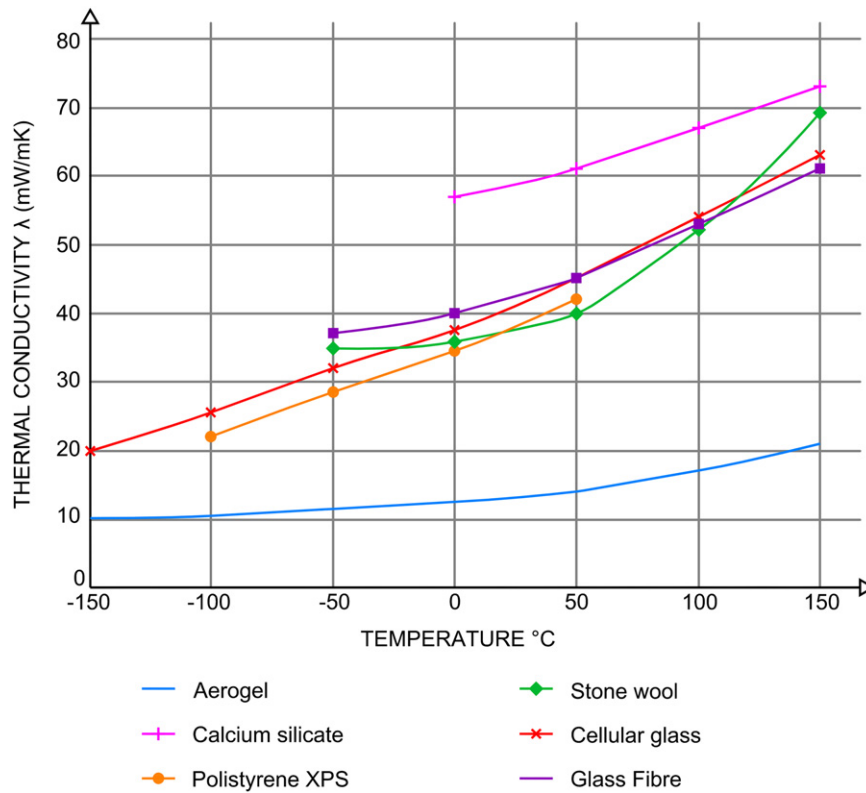


Fig. 2 Thermal conductivity of insulation materials related to operating temperature. Reproduced from Reproduced from Casini, M., 2016. Smart buildings: Advanced materials and nanotechnology to improve energy-efficiency and environmental performance. Cambridge: Woodhead Publishing Limited.

high values of specific heat and density. From this point of view, a good behavior in summer characterizes insulators such as mineralized wood fiber, cork and high density mineral wool (Table 4).

Application and Comparative Analysis

The choice of the type of material or product to use for the thermal insulation of a building and the related methods of installation depends on numerous factors including, in particular:

- The type of building intervention, whether new construction or renovation, on which depend the possibilities of application in terms of compatibility of materials, installation methods and thicknesses allowed;
- The technological unit of the affected building (vertical closure, horizontal closure, etc.) and the functional model of the technical element (external insulation, internal insulation, interspace, ventilated wall (see Fig. 3), which determine the minimum performance that the insulation must guarantee, the categories of suitable insulators and the related application technologies;
- The operating conditions (external climatic conditions, exposure to atmospheric agents, thermo-hygrometric values of the environments, loads, exposure to fire, available space, etc.) on which depend the performance that the insulation must provide;
- The environmental sustainability objectives that are to be achieved with the intervention and with the materials and products used.

As consequence, parameters for selection concern (Hilla *et al.*, 2018; Adityaa *et al.*, 2017):

- Thermo-hygrometric behavior (thermal conductivity and thermal diffusivity);
- Behavior in the presence of water (imbibition coefficient) and resistance to vapor diffusion (water vapor diffusion resistance factor);
- Mechanical behavior (compressive strength);
- Fire reaction, including the possible emission of fumes and toxic substances during combustion (Euroclass);
- Acoustic behavior (weighted sound reduction index, sound absorption coefficient);
- Ease of installation and workability on site, including dust emissions during processing;
- Durability, including resistance to biological agents, insects and rodents;
- Cost to obtain a given thermal resistance;

Table 4 Comparative analysis of main insulation materials on the market

Material	λ ($W\ m^{-1}\ K^{-1}$)	Thermal diffusivity ($mm^2\ s^{-1}$)	Operating temperature ($^{\circ}C$)	Compressive strength at 10% compression (kPa)	Vapor diffusion resistance μ	Fire reaction (Euroclass)	Primary energy PEI n.r. ($MJ\ m^{-2}$)	GWP ($Kg\ CO_2\ m^{-2}$)	Thickness for $R=2$ $m^2\ K\ W^{-1}$ (cm)	Cost for $R=2$ $m^2\ K\ W^{-1}$ (%)
Synthetic										
PUR	0.022	0.421	− 40/ + 110	150	148	F	147	10.35	4.4	115
XPS medium load	0.034	0.837	− 50/ + 75	250	150	E	144	5.52	6.8	130
XPS high load ^a	0.034	0.521	− 50/ + 75	700	150	E	144	5.52	6.8	255
EPS medium load	0.031	1.069	− 40/ + 85	100	70	E	147	4.52	6.2	100
EPS high load ^a	0.032	1.103	− 40/ + 85	250	70	E	147	4.52	6.2	110
Vegetal										
Wood wool ^b	0.038	0.113	n.d.	100	5	E	82	4.56	7.6	335
Mineralized wood wool ^b	0.065	0.090	n.d.	150	5	B	377	13.82	13.0	360
Cork ^b	0.039	0.171	n.d.	100	20	E	175	0.49	7.8	470
Animal										
Sheep wool ^c	0.035	0.440	− 60/ + 80	n.d.	2	E	17	0.39	7.0	220
Mineral										
Medium density rock wool ^c	0.033	0.458	n.d.	n.d.	1	A1	63	3.62	6.6	105
High density rock wool ^d	0.036	0.250	n.d.	50	1	A1	63	3.62	7.2	155
Medium density glass wool ^c	0.032	0.777	n.d.	n.d.	1	A1	37	1.62	6.4	105
High density glass wool ^d	0.037	0.370	n.d.	50	1	A2	37	1.62	7.4	175
Aerogel	0.015	0.100	− 200/ + 200	80	5	C	242	12.50	3.0	1300

^aRecommended for high load underfloor and walkable roof applications.^bNot suitable for inverted roof applications.^cSuitable only for pitched roof and cavity wall applications.^dDesigned for ETICS and pitched roof applications, walkable during installation.

- Environmental sustainability of the life cycle, in terms of energy incorporated into the product (embodied energy), renewability and recyclability of the material, content of recycled material in the product, absence of release of hazardous substances during processing and use, etc.

The embodied energy indicates the non-renewable energy used to transform raw materials into building products, measured in energy per mass unit (MJ kg^{-1}) or, for insulation materials, in energy per surface unit with a given thermal resistance (MJ m^{-2}). It refers to overall energy consumed during raw materials acquisition, transportation to the factory, transformation into finished products. Insulators of animal and vegetable origin, with the exception of cork and mineralized wood fiber, are those with the lowest embodied energy values, whereas highest values characterize insulators of synthetic origin (Table 4).

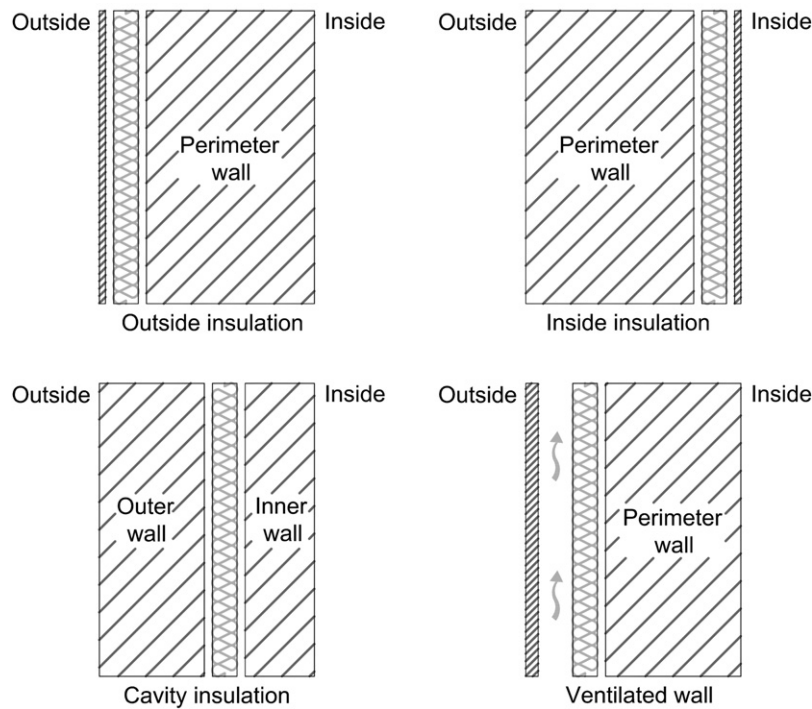


Fig. 3 Perimeter wall insulation functional models.

Table 5 Suitable insulation products for different building envelope functional models

Functional model	Suitable insulation products
Wall with outside insulation (ETICS)	Panels with high rigidity to allow the application of sheet cladding or external plaster (External Thermal Insulation Composite System – ETICS). Insulation materials of synthetic origin (polyurethane, polystyrene, expanded polyethylene, aerogel) or closed cell vegetables (cork), which can also offer greater water resistance. Mineral wool panels with increased density and mechanical resistance are also suitable to allow greater passage of vapor.
Wall with interspace insulation	Panels, or rolls, of all types, or loose materials (cellulose flakes, granulated perlite and expanded vermiculite, cork granules) poured or blown with specific tools. Recommended products are panels or rolls with open cells, loose fillers.
Wall with inside insulation	Panels, or rolls, of all types (synthetic, mineral, vegetable and animal) with the application of gypsum wall boards, fiberboards or cement panels. Open cell types are the most suitable, with FRABs recommended for intervening on existing buildings to minimize loss of floor area.
Ventilated and insulated wall	Closed cell panels or ETICS compliant mineral wool panels
Insulated flat roof	Materials with high compressive strength, such as extruded polystyrene (XPS), polyurethane foam (PUR), mineralized wood fiber, FRABs.
Inverted flat roof	Waterproof and weather resistant materials such as extruded polystyrene (XPS) or polyurethane (PUR) in panels of a smaller size, or FRABs.
Pitched roof	All types of insulating rolls or panels. In case of ventilated roofs, open cells insulators are recommended to allow free vapor flow from the inside.
Green roof	Closed cell materials with high compression resistance such as extruded polystyrene (XPS) or polyurethane (PUR).
Interfloor slab with acoustic insulation	Thin layer of fibrous materials able to absorb the vibrations passing through and convert them to heat, such as coir, kenaf, polyester fibers.

Open cell, porous or fibrous insulators (expanded melamine resin, wood fiber, stone or glass wool) exhibit higher thermal conductivity and poor behavior in presence of water, but on the other hand perform better in terms of possibilities of acoustic insulation of the building, offering a greater resistance to the passage of noise, and of breathability, making them particularly suitable for the insulation in cavity walls and for the insulation of pitched roofs (Table 5).

XPS is the insulation material that has the highest compressive strength values and is therefore recommended to insulate floors that have to withstand high loads. Mineral wools are the insulators that present the best fire behavior and are therefore used also for building fire closures. Closed cell synthetic insulators such as EPS, XPS and PUR have the best water behavior and therefore suitable for applications exposed to atmospheric agents (ETICS, ventilated walls, inverted roofs). Insulators such as cork, coir or wood fiber are instead used as a thin mats for the reduction of walking noise in inter-floor slabs.

FRAB's, as well as offering greater thermal insulation values ($\lambda = 0.015 \text{ W/mK}$) with a constant thermal performance regardless of operating temperature, compared to conventional insulation materials, show the following main advantages: high hydrophobicity values with high vapor permeability; low flammability (Euroclass C to A2); mould proofing, UV and weather resistance; ease of installation thanks to their lightness and ease of adaptation; ease of handling and storage. In view of these advantages, aerogel insulation materials' cost per square meter is however still high, about 8–10 times higher than traditional insulation, whereas the most economical insulation materials on the market are actually mineral wools and sintered expanded polyester (EPS).

Sustainability

Sustainability of insulation materials, as for all building products, must be evaluated through the analysis of their impact on health and on the environment throughout the entire life cycle (from cradle to cradle), from the acquisition of raw materials, through manufacture, transport, and use until their disposal (see Table 6 and 7). Green building designers are increasingly focused on choosing environmentally friendly products, certified (Eco-label) or with environmental product declaration (EPD), supplied by

Table 6 Life cycle sustainability features of insulation materials

<i>Life cycle stage/Environmental risk factors</i>	<i>Sustainable features of insulation materials</i>
<i>Raw materials supply</i> ● Consumption of non-renewable natural resources ● Land deterioration ● Pollution from transport	<i>Designed for resource and environment conservation</i> ● Renewable or vastly available raw materials ● Recycled or recovered raw materials ● Environment and biodiversity protection ● Use of natural techniques ● Certified cultivation and extraction systems
<i>Manufacturing process and distribution</i> ● Energy consumption due to manufacturing process, transport and distribution ● Air, water and soil pollution ● Health risks for production workers	<i>Designed for cleaner production and for efficient distribution</i> ● Absence of hazardous raw materials ● Certified environmental management system (EMAS, ISO 14001, ISO 50001) ● Low energy consumption in the manufacturing phase ● Low pollutant emissions ● Absence of risks for production workers ● Low distance from the construction site to the manufacturing plant (km 0)
<i>On-site works and installation</i> ● Harmful emissions during handling ● Production of procession scraps and waste	<i>Designed for easier and cleaner installation</i> ● Absence of harmful emissions hazards ● Ease of installation and workability on site ● Instructions for on-site operations and installation
<i>Building operation</i> ● Short and long term hazardous emissions ● Low durability of performance ● Low resistance to atmospheric and biological agents	<i>Designed for green use and maintenance</i> ● Absence of harmful emissions hazards ● High durability ● High resistance
<i>Decommissioning</i> ● Partial or total loss of natural resources following the impossibility to reuse, recover, recycle or reintroduce materials to the environment. ● Air, water and soil pollution for disposal	<i>Designed for re-use, re-manufacture, disassembly, recycling, safe disposal</i> ● Use of recyclable materials ● Ease of disassembly ● Absence of additives or substances that impede recycling ● Ease of treatment and disposal

Table 7 Comparative analysis of main environmental risk factors of insulation materials

Life cycle stage/Environmental risk factors	Insulating materials			
	Organic synthetic	Inorganic	Bio-based	Fabs
<i>Raw materials supply</i>				
● Consumption of fossil resources	■ ■ ■	□	□	■
● Land deterioration	■ ■	■ ■ ■	□	■ ■ ■
<i>Manufacturing process</i>				
● Energy consumption	■ ■ ■	■ ■	■	■ ■ ■
● Greenhouse effect	■ ■ ■	■ ■	■	■ ■ ■
● Ozone depletion	■ ■	□	□	□
● Acid rain	■ ■	■	□	■
● Photochemical smog	■ ■	■	□	■
● Health risks for production workers	■ ■ ■	■	□	■
<i>On-site works and installation</i>				
● Harmful emissions during handling	■	■ ■	□	■ ■
<i>Building operation</i>				
● Short term hazardous emissions	■ ■	■ ■	□	■
● Low durability of performance	■ ■ ■	■	■ ■	□
● Low resistance to atmospheric and biological agents	■ ■	■	■ ■ ■	□
<i>Decommissioning</i>				
● Partial or total loss of natural resources following the impossibility to reuse, recover, recycle or reintroduce materials to the environment.	■ ■ ■	■ ■	□	■ ■ ■
● Air, water and soil pollution for disposal	■ ■	□	□	■

Note: □ None; ■ Low; ■ ■ Medium; ■ ■ ■ High.

companies holding an ISO 14001 or EMAS certificated environmental management system, or finally that participate on an extended producer responsibility program or are directly responsible for extended producer responsibility. The objective of construction sustainability also requires the designer to focus towards the use of local materials and products (so-called zero km material), in order to reduce the environmental impacts due to the transport to the building site.

While selecting building insulation materials in view of the sustainability, it is important to remind that there are no ecological materials in an absolute term, as the life of a building component is inextricably linked to the life of the building, influencing and in turn being influenced by it. The overall sustainability of the life cycle of insulation materials is therefore dependent on the distance between the place of manufacture and that of installation, on the characteristics of the context in which the intervention will be carried out, on the application methods of the product into the building, on the use conditions and on the method of disposal. For instance, the real possibility of recovering insulation materials is linked to not only the recyclability of the single products, but also to the construction techniques used and the method of demolition at the end of the building life. All these variables are not known to the scale of the product, and are definable only from time to time on the basis of the context and building characteristics and of the project requirements.

Furthermore, it is a fundamental principle to insulate to the greatest level that is justified, based on life-cycle costs, when constructing a building or when retrofitting an existing building. The marginal cost of installing additional insulation is generally low. Higher levels of insulation can be justified during new construction or deep renovation by considering full-system impacts that allow for downsizing of mechanical equipment in accordance with life-cycle cost assessment. The primary drivers that determine optimal levels of insulation are climate, the cost of energy, the heating system type and efficiency, and the installed cost of the insulation.

Synthetic Insulation Materials

This category of insulators presents a very high impact in terms of consumption of non-renewable natural resources, as they derive from the extraction and processing of petroleum. Some, such as insulating products made of polyester fiber, have a lower impact as they derive from recycled polyester from waste sorting of PET bottles.

Expanded polystyrene (EPS) is manufactured by adding pentane (C_5H_{12}) to polystyrene beads, which is then evaporated off to foam the beads. Extruded polystyrene (XPS) is made by melting polystyrene beads and passing the melt through an extruder with the addition of a blowing agent (HFC, C_6H_{12} or CO_2). Polyurethane foam (PUR) is produced by a reaction between a polyisocyanate and a polyether backbone polyol (alcohols containing multiple hydroxyl groups). During the expansion process, the closed pores are filled with an expansion gas (HFC, C_6H_{12} or CO_2). This production process, despite being long and complex, it does not have energy requirements higher than those of insulators of mineral origin, but nevertheless presents a strong impact in terms of atmospheric pollution as regards the reduction of the stratospheric ozone layer, the greenhouse effect, the formation of acid rain and photochemical smog. In particular, the greatest impact on the atmosphere by synthetic insulators has always been due to the use of

the blowing agents such as CFCs and later HCFC and HFC for achieving their cellular structure (EPS, XPS and PUR/PIR), but these are being discontinued due to their high Ozone Depletion Potential (ODP) and Global Warming Potential (GWP). Nowadays, hydrocarbons foaming agents (pentane, isopentane, cyclopentane) are widely used, characterized by zero ODP and a reduced GWP (isopentane's GWP value is 11, compared to 4750 of CFC-11 or 782 of HFC-365mfc). Currently the industry is shifting towards CO₂ and Nitrogen as foaming agents, which advantages compared to hydrocarbons include lower environmental impact (no ODP and reduced GWP), low gas consumption due to their high degree of foaming, low price, non-flammability, non-toxicity and no residue in the finished product. Among those, CO₂ is emerging as the blowing agent of choice since it has much higher solubility in polymers. A further improvement in the reduction of environmental impacts is represented today by the use as raw material of plastics derived from biogas and bio-fuel produced from organic waste or vegetable oils, instead of petroleum, with a saving of CO₂ emissions up to 70% compared to the use of fossil raw materials.

Production of expanded materials still poses a high risk for the health of workers due to possible contact or inhalation of highly toxic substances, such as styrene, benzene, isocyanates, phosgene or phenols, and due to the risk of fires and explosions due to their high flammability.

Regarding the working and installation phase, this does not involve health hazards provided that no hot works are carried out, since the high temperature at which the material is subjected can cause the release of styrene and other decomposition products. On the other hand, the application of polyurethane foams can be extremely harmful, as it causes the release of free isocyanates during in-situ expansion and in the following hours with acute effects on the respiratory tract.

During the operating life of the building, organic compounds can be released in interiors in the first few months after installation, and special attention must be given to the release in case of fire of dense and opaque fumes with highly toxic substances (styrene, benzene, phenols and, in case of PUR, hydrogen cyanide and isocyanates).

If correctly installed, insulators of synthetic origin can have a life span between 30 and 50 years. Re-use is possible whenever the material is not coupled, glued or dirty. Fusion recycling is possible for EPS and XPS but, in fact, only happens in rare cases. Polyurethane, on the other hand, cannot be subjected to a melting process. Expanded insulators are normally recycled by granulation for filling materials or for agglomerates, or subjected to waste-to-energy treatment. Polyester fiber, itself already coming from recycled polyester, is 100% recyclable.

Mineral Insulation Materials

This category of insulators does not present particular impacts from the point of view of the consumption of natural resources, as they derive from raw materials very widespread in nature and available in abundance (quartz sand, clay, minerals of volcanic origin). On the contrary, the mining activity from quarries, if not well managed, can have a strong impact on the territory. Glass wool is normally manufactured with 80% recycled glass (50% of which post-consumption).

The manufacturing process is instead very energy-intensive, due to the thermal production processes at high temperatures (1600°C for stone wool, 1400°C for glass wool and 850–1200°C for expanded granular minerals) which are also responsible for atmospheric emissions from the combustion process. Stone wool is manufactured by melting different kinds of rocks, such as dolostone, basalt and diabase, obtaining fibers that are then bound together with resins, food-grade starches or oils. Glass wool is produced by mixing natural sand and glass (usually recycled). The transformation in fibers occurs via centrifugation and blowing processes then bound with resins.

Since 1995, the health risks for workers and installers of mineral wool manufacture resulting from the inhalation of volatile fibers have been mitigated by the introduction of biosoluble fibers, with limited permanence in the human body and officially considered non-carcinogenic.

During the operating phase of the building, mineral wool can emit volatile organic compounds such as phenols or formaldehyde deriving from the glues and the phenolic or melamine resins used for production. Several glass wool products already employ low-VOC binding agents, of vegetal origin and without added formaldehyde, and stone wool with this technology is currently entering the market. Stone and glass wool are both long lasting and fully recyclable without any reduction in quality.

Bio-Based Insulation Materials

Along with the development of high-tech insulation products, the proposal of natural materials, in the vein of the so-called green architecture, has been growing over time. These materials are expected to be rapidly renewable, of vegetable or animal origin (bio-based materials), possibly recycled or recovered and reused (Schiavoni *et al.*, 2015, 2016). This trend addresses the scope of using environmentally friendly building materials and products that ensure the reuse or recyclability of the construction works, of their materials and of their parts after demolition. The use of bio-ecological insulation is also encouraged by the main environmental buildings certification systems (LEED, BREEAM, Living Building Challenge, etc.), that in fact award points to the project in case of use of renewable, recyclable, recycled materials or materials with recycled content. Using these products aims to reduce the environmental impact of the whole life cycle of materials through greater resource conservation and a reduction of energy consumption and pollutant emissions during production and disposal.

Compared to insulation materials of synthetic and of mineral origin, bio-based insulation materials (animal or vegetable) have, with a comparable performance, lower environmental impact at every stage of the life cycle of the product and a lower embodied energy value (Table 7).

Table 8 Thermal properties of unconventional bio-based insulation materials

Insulation materials	Volume mass Kg m^{-3}	Thermal conductivity $\text{W m}^{-1} \text{K}^{-1}$
Bagasse	70–350	0.046–0.055
Cattail	200–400	0.043–0.060
Cotton (recycled denim)	NA	0.036–0.038
Cotton (stalks)	150–450	0.059–0.082
Cotton (recycled)	25–45	0.039–0.044
Date palm	187–389	0.072–0.085
Durian	357–907	0.064–0.185
Mushrooms	120	0.039
Oil palm	20–120	0.055–0.091
Posidonia seaweed	65–75	0.041–0.044
Pineapple leaves	178–232	0.035–0.042
Reeds	130–190	0.045–0.056
Recycled textile (commercial)	30–80	0.036–0.042
Recycled textile fibers (polyester and polyurethane)	440	0.044
Recycled textile fibers (synthetic)	200–500	0.041–0.053
Rice	154–168	0.046–0.566
Sunflower (pitch)	36–152	0.039–0.050
Straw bale	50–150	0.038–0.067

Note: Schiavoni, S., D'Alessandro, F., Bianchi, F., Asdrubali, F., 2016. Insulation materials for the building sector: A review and comparative analysis, *Renewable and Sustainable Energy Reviews* 62, 988–1011.

Some materials of vegetable origin such as hemp, kenaf, flax, corn, reed, coir and jute derive from easily renewable raw materials, others from recycled raw materials and processing waste (cellulose and wood). Cork is a renewable raw material but of limited availability (the plant can be decorticated only every 8–10 years). For the production of some particular products (hemp, kenaf, cellulose, flax, sheep wool), a percentage of synthetic fiber, generally polyester, may be added to the main fiber in a measure of 10%–15% up to 50% for support or reinforcement.

In addition to the more traditional renewable insulation materials, innovative products made with fungi roots, wood foam, marine algae or the fibers of recycled jeans are currently being researched (Casini, 2016) (Table 8). Mushrooms roots (mycelium) insulation materials are grown from agricultural and food waste, obtaining a material with good thermal performance, inherently flame retardant and stable over time that does not need chemical additives, thus containing VOC emissions. Among the insulators of vegetal origin deriving from recycled raw materials or processing wastes, in addition to wood, particularly interesting are those that use textile fibers or recycled cellulose. Recycled cellulose comes from waste and by-products of paper processing as well as returned newspapers. Recycled textile insulation materials are also gaining interest, in particular referring to fibers of jeans recycled pre-consumer (waste from the production) or post-consumer (denim insulation). Regarding sheep wool, the one used in building applications comes from flocks bred for meat and milk production, not for the textile industry, and would otherwise be wasted.

The production process generally has a low or almost zero environmental impact, with the exception of those insulators requiring a heat treatment such as mineralized wood fiber and expanded cork. In particular, mineralized wood fiber panels have a significant consumption determined by the production of the Portland cement binder used to manufacture the panels that account around 50% weight (the production process provides the mixing of fir wood fibers with cement followed by a drying phase).

As far as the operating phase is concerned, possible health risks may derive from the emission of powders and fibers, or from the release of any toxic substances used for adhesives (cork, wood fiber). Furthermore, for some materials, the presence of residual insecticide or pesticide used in intensive cultivation and farming (flax, hemp, sheep's wool) or preserving treatments to protect the material during long-distance transport (coconut, jute) may be an issue. Substances contained in sheep wool fibers are instead able to absorb indoor pollutants such as formaldehyde, VOCs, nitrogen oxides (NO_x) and sulfur oxides (SO_x). This is due to the presence of keratin, a base component of the albumin protein that constitutes the wool: molecules from lateral groups of its amino acids can bond with polluting agents and degrade them into harmless substances.

Regarding the recovery or recycling of materials after the phase of disposal, this can be made problematic, if not impossible, by the presence of binders (mineralized wood fiber), additives (addition of synthetic fibers), fireproofing or anti-parasitic treatments (sheep wool), or glues or adhesives used for installation (cork and wood fiber).

Fiber Reinforced Aerogel Blankets

FRAB composition is made normally of 40%–55% silica, 20%–45% PET/glass fiber and 0%–15% additives. The manufacturing process first impregnates a fibrous felt with silica sol-gel solution (sol-gel casting); when impregnation is complete, felts are rolled and placed in a controlled environment for chemical ageing of the gel. Finally, supercritical extraction of the solvent is carried out in large autoclaves with CO_2 recovered from other external industrial processes. As the gel dries, aerogel particles are firmly

Table 9 FRAB environmental characteristics

<i>Component</i>	<i>Embodied energy (MJ/kg)</i>	<i>Embodied CO₂ (kg/kg)</i>
Silica precursor and other raw materials	35.5	3.2
Fibrous reinforcement	12.1	0.6
Production process	3.5	0.4
Supercritical extraction	2.1	Recovered from other industrial processes
Pollution control equipment	0.7	0.03
Total	53.9	4.23
International transport (from US to Europe)	2.2	0.14

Note: ASPEN AEROGELS, 2015. Spaceloft[®] Aerogel Insulation Environmental Product Declaration According to ISO 14025 and EN 15804. Declaration Number S-P-00725. Anglesey: Renuables Ltd.

embedded into the mat fibers. After a final drying step an aerogel saturated mat, easy to transport and install, is achieved. FRABs can then be coupled with support materials such as rigid PP panels.

From an environmental point of view, FRABs require a relatively modest 53.9 MJ/kg for manufacturing (embodied energy), compared to 88.6 MJ/kg for expanded polystyrene and 101.5 for polyurethane foam. Most energy is needed for obtaining and mixing silica precursor and other raw materials for the sol gel solution. Conversely, embodied CO₂ amounts to 4.23 kg per kg of finished product, of which 3.2 kg are required by solution preparation alone (see [Table 9](#)).

Moreover, FRABs are completely innocuous to the ozone layer (Ozone Depletion Potential ODP = 0), employ recycled materials and are further completely recyclable, are lead free and ROHS compliant and release zero VOC ([ASPEN AEROGELS, 2015](#)). Finally, their excellent aging resistance, measured by accelerating aging techniques (12 weeks at 90°C, equal to 60 years in real world conditions, showed no decay in insulating performance) ensure maintenance free operating life and the possibility of further reuse of the products.

Regarding the installation phase, FRABs tend to produce dust during movement and installation, but this is not considered harmful to health as it contains silica in amorphous and not crystalline form, posing no carcinogenicity concerns according to the International Agency for Research on Cancer (IARC). However, dust coming from aerogel blankets manipulation may cause mechanical irritation to the upper respiratory tract and its high hydrophobicity strongly dries skin and may damage lubricated parts of machines used for processing and installation. Mats encapsulation with rolled flame retardant polymers was proved as a viable solution of this issue causing little increase of thermal conductivity (from 0.018 to 0.020 W/mK).

Conclusions

The role of thermal insulation is fundamental to achieve the objectives of zero energy building in both new constructions and retrofit interventions and of the consequent reduction of global CO₂ emissions. A more effective insulation of buildings will also bring significant environmental, economic as well as social benefits for both public administrations and for citizens.

Many different solutions are currently available on the market. The choice of the most suitable insulation material or installation technology depends on the type of application and the operating conditions and have to take into account technical, economic and environmental aspects.

Future scope concerns the development and characterization of improved insulation materials and solutions based on advanced sustainable materials and/or nanotechnologies to provide enhanced insulation properties and environmental performance, addressing issues such as thermal bridges correction and ensuring the best architectural quality. In particular, room for improvement regards reduced embodied energy, that, in perspective of more and more energy efficient buildings, will assume a greater weight in the overall lifetime energy balance.

See also: Architecture Follows the Sun: Climatically Responsive Architecture and Process of Design

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LCCA and Environmental Impact of Buildings

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Introduction

Globally, countries increasingly recognize the relevance and importance of mainstreaming green buildings for various reasons, one of them being this happens to be a low hanging fruit when it comes to carbon mitigation efforts and the additional benefits of low operational costs and other associated benefits. In spite of the wide recognition and relatively larger adoption of various environmental rating systems and building energy codes (voluntary or mandatory) by different countries all over the world, green buildings as part of the total new/existing building stock continues to be low. As per a recent report released by [IEA and UNEP \(2018\)](#) the spending on energy efficiency and greening of buildings has been slowing down with incremental energy efficiency investment increasing by only 4.7% in 2017 compared to 6%–11% annual growth rates observed from 2014 to 2016. There continues to be a prevailing perception of high (initial) costs associated with green buildings. LCCA or Life Cycle Cost Analysis is one of several methods to rationally look at the potential cost savings of a product, system or building as a whole over its assumed life compared to various alternatives. What sets it apart from simple payback calculation (and therefore an effective decision making tool) is it not just considers the enhanced cost of the product/system/building component but also accounts for hidden costs such as future costs of maintenance, operation costs, energy use, salvage and replacement value. It thus gives a logical way of taking decisions and has the potential (if applied extensively) to largely get over the myth that green buildings cost more. If LCCA is made more popular, it will be more convincing for acceptance by the financier/banker on identifying the more valuable buildings.

There is another similar sounding (yet different) popular tool called LCA or Life Cycle Analysis which provides an assessment of a product, system or building's sustainability over the entire life cycle. It looks at more accurate assessment of materials true environmental impact over the entire life cycle. LCA estimates the environment impact in terms of greenhouse gas emissions, wastes, toxins, and particulate matter. LEED v4 has given a new impetus to considering LCA by including them in the Materials and Resources section.

LCA when combined with LCCA gives the most rounded analysis. Given the spurt of activities already going on around LCA (and the materials section in LEED), there is a need specially in developing economies like India where initial costs and payback are the key drivers for decision making to look at LCCA more rigorously and actively.

Aim

The paper attempts to analyse the incremental costs of select residential (multi-family high-rise) projects in India certified under the Energy Efficient Homes (EE-Homes) programme between 2012–2015 and to assess the economic feasibility of energy-efficient buildings using the LCCA approach. The German development bank, *KfW Entwicklungsbank*, provided a line of credit in 2012 to the *National Housing Bank of India (NHB)* to promote energy efficiency in the residential building sector in India. This credit line was used by NHB for refinancing individual home buyer loans for energy-efficient new residential housing under the *Energy Efficient Homes Programme*. Apartments eligible for refinancing had to meet a minimum standard of 30% improvement over the benchmark building in energy efficiency if active Energy Efficiency measures are implemented, and 18% improvement if only passive Energy Efficiency measures are applied. Projects meeting the target received an official certificate under the programme.

There are two important perspectives when looking at the incremental costs of energy-efficient buildings:

- (1) From the construction point of view EE is particularly relevant for the investors of buildings, since their overall goal is to construct in a cost-efficient way.
- (2) From a macroeconomic point of view it is more relevant to not only look at the incremental costs in the construction phase, but to also look at the incremental costs over the entire life cycle.

Therefore, future streams of benefits arising from energy savings were also evaluated and reflected in the lifecycle assessment of incremental costs in order to assess the economic viability of investments made towards improving the energy performance of buildings.

Life Cycle Costing-Concept

Life-cycle costing (LCC) is a method for assessing the total cost of facility ownership. It takes into account all costs of acquiring, owning, and disposing of a building or building system. LCC is especially useful when project alternatives that fulfill the same performance requirements, but differ with respect to initial costs and operating costs, have to be compared in order to select the one that maximizes net savings ([Fuller and Petersen, 1995](#)).

LCC can be implemented at any level of the design process and can also be an effective tool for evaluation of existing building systems. LCC can be used to evaluate the cost of a full range of projects, from an entire site complex to a specific building system component.

Methodology

Using the standard methodology (Fuller and Petersen, 1995) to analyse the incremental costs of EE measures for the four buildings studied, all costs for the actually constructed buildings, i.e., the “green” (actual) case, were compared to the costs of the benchmark buildings, i.e., the “reference” case. Both incremental costs for the construction itself and over the entire life cycle of the building were assessed. Also, the financial indicator, Discounted Payback Period was determined for the implemented measures, in order to assess the economic viability of the Energy Conservation Measures (ECMs).

Multiple realistic assumptions have been made, the case (i.e., the actual/green case and the reference case) has been defined, and sources for data have been chosen. The following sections describe the methodology applied in detail.

Green (actual) case and reference case

More than 15 residential projects located in various climatic zones of the country participated in the Energy Efficient Homes programme and were able to achieve the minimum desired level of energy savings as prescribed in the programme. Of the various projects situated in different representative climate zones, four specific projects have been selected to study the incremental costs of these energy-efficient buildings using the LCC approach. These projects are:

- (1) Ganga Skies, Pune (Moderate climate)
- (2) Spire Wood, Gurgaon (Composite climate)
- (3) Apollo HIRCO, Mumbai (Warm and Humid climate)
- (4) Lotus Boulevard, Noida (Composite climate)

The parameters for building design, system, lighting power density, use of solar water heaters, and thermo-physical properties of building envelope were assessed during the certification of these projects. For conducting the comparative analysis, parameters regarding the way of construction of the reference case were used as defined during the IT Toolkit development. The parameters of the reference buildings (as of the IT Toolkit) can be found in Annexure A. **Table 1** below illustrates the ECMs implemented in these four buildings (green case):

Costs included in life cycle costing and data sources

There are numerous costs associated with acquiring, operating, maintaining, and disposing of a building or building system. Building-related costs usually fall into the following categories:

Table 1 Energy conservation measures used in the projects which added to the incremental capital investments

Ganga skies^a	● Use of Autoclaved Aerated Concrete (AAC) block instead of brick masonry for walls ● Roof insulation and reflective paints on the roof ● Use of 6 mm reflective glass
Spire woods^b	● Use of AAC block instead of brick masonry for walls ● Roof insulation and reflective paints on the roof ● Use of 6 mm reflective glass ● Provision of solar hot water systems ● Provision of 4-star AC
Apollo HIRCO^b	● Use of AAC block instead of brick masonry for walls ● Roof insulation and reflective paints on the roof ● Use of 6 mm reflective glass ● Provision of solar hot water systems ● Provision of 4-star AC
Lotus boulevard^a	● Use of AAC block instead of brick masonry for walls ● Roof insulation and reflective paints on the roof ● Use of 6 mm reflective glass

^aAny reduction/addition of incremental costs due to reduced common area lighting power density and reduced structural load (due to AAC) has not been considered.

^bAny reduction/addition of incremental costs due to reduced common area lighting power density, internal lighting power density and reduced structural load (due to AAC) has not been considered.

Source: Author.

Table 2 Data sources/definitions of different costs

Costs	Green (Actual) case/Reference case
Construction costs/investment costs	CPWD Plinth area rates and Schedule of Rates, market rates for components such as SWH, AC
Energy costs	Average tariff rates for domestic sector
Operating, maintenance and repair costs	Assumed to be 2% of the capital costs per year (based on discussions with sectoral experts)
Residual costs	Residual costs are the remaining value of the initial investment cost (excluding the land cost) at the end of 15 years. It has been assumed as 6% of the initial investment cost which increases @8% per year (This information was provided by financial experts)

Source: Author.

- Initial Costs – Purchase, Acquisition, Construction Costs
- Operation, Maintenance, and Repair Costs
- Replacement Costs
- Residual Values – Resale or Salvage Values or Disposal Costs
- Energy Costs

Only those costs within each category that are relevant to the decision and significant in amount are needed to make a valid investment decision. Costs are relevant when they are different for one alternative compared with another; costs are significant when they are large enough to make a credible difference in the LCC of a project alternative. All costs are entered as base-year amounts in today's currency; the LCCA method escalates all amounts to their future year of occurrence and discounts them back to the base date to convert them to present values (Gluch and Baumann, 2003).

Following categories have been used for the calculations in this study: (1) construction/ investment costs, (2) operating, maintenance and repair costs, (3) residual costs (4) energy costs, which are derived from specific data sources. Table 2 provides a summary of the data sources of these four different cost categories:

The following subsections describe the data sources used for calculation of incremental construction costs and Life Cycle Costs (LCC) of both the green and the reference case in more detail.

Construction costs

In the absence of the actual Bill of Quantities (BOQ) and rates used by these projects, the following data sources were used to calculate overall construction costs from different cost components:

- Civil construction: Plinth Area Rates as given by Central Public Works Department (CPWD) were used for the calculation of civil construction costs (see "Relevant Websites section").
- Masonry, glazing, roof insulation and paints: The CPWD Schedule of Rates 2012 was used (see "Relevant Websites section").
- SWH rates and star ACs: Average available market rates from vendors were used.
- Thumb rules were used for calculation of other costs such as (This information was provided by sectoral experts):
 - Internal water supply and sanitary installations (12% of civil construction costs);
 - External service connections (5% of civil construction costs); and
 - Internal electric installations (12.5% of civil construction costs).

There may be variations in the actual rates depending on regional markets; however, CPWD seems to be the best available, most comprehensive and most current schedule prepared by a government entity (The escalation cost due to reduced lighting power density on account of possible better lighting fixtures is not considered due to absence of detailed information on fixture types, number, etc).

Energy costs

An average tariff rate of 5.5 Rs/KWh is assumed for all the cases considered (for a consumption volume of 201–400 kWh/month for the residential sector), although from state to state these rates differ and change every financial year (For more details please refer to the different state regulatory commissions' websites available at "Relevant Websites section"). Please note that applying fixed (discounted) electricity prices for the calculations is rather a conservative approach, since the (net) energy price is expected to increase significantly over the next years and decades.

Operating, maintenance and repair costs

Operating, maintenance and repair costs are assumed to be 2% of the investment cost per year (This assumption is based on discussions with experts from the sector). This reflects higher expected operating, maintenance and repair costs for the ECM.

Residual costs

The resale value (excluding the land cost) for the project is assumed to be 6% of the initial investment cost, which increases by about 8% annually. Other residual costs have not been considered. Since a LCC is a summation of costs, a negative residual value indicates that there is value associated with the building at the end of the study period. Perhaps, the value is a roof that was recently replaced or it is the building's superstructure that could function for another thirty years. Whatever the reason for the remaining value, it is a tangible asset of building ownership and should be included in the LCCA.

A positive residual value indicates that there are disposal costs associated with the building at the end of the study period. Perhaps, the costs are related to abatement of hazardous material or demolition of the structure. Whatever the cause, these are costs of building ownership and should be included in the LCCA.

Zero residual value indicates that there is no value or cost associated with the building at the end of the study period. This rare instance occurs if the intended use of the building terminates concurrent to the end of the study period, the owner is unable to sell the building, and the owner is able to abandon the building at no expense.

Formulas applied

In order to calculate the incremental costs for initial incremental investments, the discounted payback period of projects and the incremental costs over the life cycle, the following formulas have been applied based on The National Institute of Standards and Technology (NIST) Handbook 135 (1995 edition):

Assessment of initial incremental investment

$$\text{Initial incremental investment} = I_{\text{energy efficient case}} - I_{\text{conventional case}}$$

Where,

$I_{\text{energy efficient case}}$ = all costs occurred for the construction of the EE building as specified above

$I_{\text{conventional case}}$ = all costs occurred for the construction of the reference building as specified above

Discounted payback period

Discounted payback period = time required for cumulative savings to recover initial incremental investment, taking the time value of money into account

Where,

$$\text{Annual savings}_t = (\Delta E_t + \Delta \text{OM\&R}_t + \Delta \text{Res}_t)$$

$$t = 1, 2, \dots, 15$$

The life time of buildings is assumed to be 15 years in these calculations, although the actual life time of a building is much longer, potentially in the range of 25–50 years. However, since it is expected that buildings undergo major repair after 15 years, this time period is considered here.

Life cycle cost calculation

Life cycle cost (LCC) analysis is a measure to calculate the total cost of a building over its entire life time. It is a useful tool to compare cost-effectiveness of EE projects with that of conventional projects as it estimates the total cost of a building over its entire life. The general formula used for LCC calculation is:

$$LCC = I + E + \text{OM\&R} - \text{Res}$$

LCC = Total Life cycle cost of the building in current value rupees

I = Present value investment costs (All initial investments costs are considered to be incurred at the beginning of the study period)

E = Present value of energy costs

$\text{OM\&R}$ = Present value of non-fuel operating, maintenance and repair costs

Res = Present value of residual costs value (Residual costs refer to the net worth of a building at the end of the LCCA study period.

Unlike other future expenses, an alternative's residual value can be positive or negative, a cost or a value)

In order to calculate the present values (Refer Annexure B) for energy, OM&R costs, and resale value, the following parameters are used ([Table 3](#)):

Table 3 Discount, inflation and escalation rates used

Parameters	Values
Nominal discount rate (D)	16%
Real discount rate (d)	10.6%
Inflation rate (I)	4.9%
Nominal escalation rate (E)	7.6%
Real escalation rate (e)	2.6%

Source: Author.

Sensitivity analysis to study the impact of change in discount rates and escalation rate of energy prices has not been done in the current study due to time constraint.

Incremental Costs for Construction of EE Buildings

The following **Table 4** presents the results of the incremental costs analysis of the buildings studied regarding investment costs, energy costs and respective energy savings through ECMs as well as the payback periods for these four projects. It can be highlighted that the green (actual) cases of the Spire Woods and the Apollo HIRCO projects cause the highest incremental investment costs – with 2.02% and 2.8% respectively – but at the same time also achieve the greatest energy savings (36% and 32% respectively).

If further analysis is done regarding the incremental capital costs incurred per sq. m in case of an energy efficient building versus a conventionally built building, it is observed that the incremental costs per sq. m ranges between Rs 232–942 in the studied four projects. The average selling price of residential apartments in Class 1 towns and cities in India is Rs 55,000/sq. m. Hence, the incremental costs compared to the selling price are relatively low (**Fig. 1**).

The following **Table 5** gives the list of Energy Conservation measures (ECMs) used in the studied projects which are responsible for the incremental capital costs.

It is further seen that the incremental costs for using more efficient AAC blocks are very low. Only in-cremental costs of about 1% have to be invested using AAC instead of conventional bricks. Costs for improving the thermo-physical properties of the roof are also rather small, whereas costs for use of more energy-efficient glazing and provision of solar water heaters are rather substantial.

Table 4 Results of incremental costs analysis

Building name	Climate zone	Cases (reference/green)	EPI (kWh/m ² /yr)	Energy savings (%)	Investment costs (in crore rupees)	Incremental investment cost (%)	Energy costs per year	Payback period (years)
Ganga skies	Moderate	Reference case	71	–	Rs12.37	–	Rs 1,727,963	
		Actual (green) case	55	23%	Rs 12.48	0.9%	Rs 1,338,563	1.5
Spire woods	Composite	Reference case	69	–	Rs 18.49		Rs 3,092,958	
		Actual (green) case	44	36%	Rs 18.85	2.02%	Rs 1,519,760	2.2
Apollo HIRCO	Warm and Humid	Reference case	95	–	Rs 12.39		Rs 1,848,605	
		Actual (green) case	65	32%	Rs 12.73	2.8%	Rs 1,264,835	3
Lotus boulevard	Composite	Reference case	102		Rs 23.20		Rs 3,847,338	
		Actual (green) case	82	20%	Rs 23.38	0.8%	Rs 3,092,958	1.3

Source: Author.

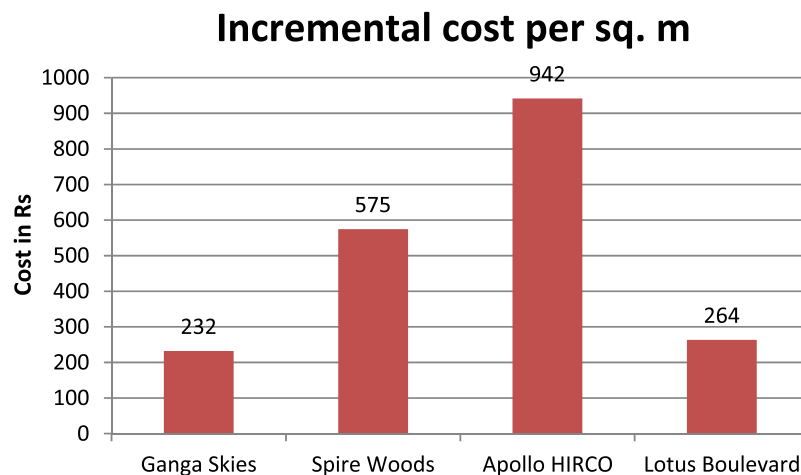


Fig. 1 Incremental cost per sq. m for the studied projects. Source: Author.

Table 5 Energy conservation measures used in the projects which added to the Incremental capital investments

Ganga skies	● Use of AAC block instead of brick masonry for walls ● Roof insulation and reflective paints on the roof ● Use of 6 mm reflective glass <i>Note:</i> any reduction/addition of incremental costs due to reduced common area lighting power density and reduced structural load (due to AAC) has not been considered
Spire woods	● Use of AAC block instead of brick masonry for walls ● Roof insulation and reflective paints on the roof ● Use of 6 mm reflective glass ● Provision of solar hot water systems ● Provision of 4-star AC <i>Note:</i> any reduction/addition of incremental costs due to reduced common area lighting power density, internal lighting power density and reduced structural load (due to AAC) has not been considered
Apollo HIRCO	● Use of AAC block instead of brick masonry for walls ● Roof insulation and reflective paints on the roof ● Use of 6 mm reflective glass ● Provision of solar hot water systems ● Provision of 4-star AC <i>Note:</i> any reduction/addition of incremental costs due to reduced common area lighting power density, internal lighting power density and reduced structural load (due to AAC) has not been considered
Lotus boulevard	● Use of AAC block instead of brick masonry for walls ● Roof insulation and reflective paints on the roof ● Use of 6 mm reflective glass <i>Note:</i> any reduction/addition of incremental costs due to reduced common area lighting power density, and reduced structural load (due to AAC) has not been considered

Source: Author.

Table 6 Overall incremental construction costs

	<i>Ganga skies</i>	<i>Spire woods</i>	<i>Apollo HIRCO</i>	<i>Lotus boulevard</i>
Incremental costs	Rs. 1,027,438	Rs. 3,608,938	Rs. 3,331,842	Rs. 1,807,180
(% of investment costs)	0.87%	2.02%	2.83%	0.80%

Source: Author.

Overall, the incremental construction costs for the four buildings ranged from 0.8% to 2.83% compared to the costs of the reference case (Table 6). Higher incremental costs in Spire woods and Apollo HIRCO is due to the provision of solar water heaters and 4-star AC.

Incremental Costs for EE Buildings Over Entire Life-Cycle

The following Table 7 gives an overview of all cost categories, the overall LCC as well as the total LCC savings over the reference cases.

In all cases it can be observed that the LCC of the energy-efficient building is lower than the LCC of the same building built with conventional construction practices. Even though the initial investment costs for energy-efficient buildings is higher than that of conventional buildings, over the life span of 15 years (the actual life span of a building is more likely 25–50 years, but 15 years were used for the calculations in this study) an energy-efficient building turns out to be significantly cheaper than a conventionally built building. The annual savings realized in an energy-efficient building more than compensate for the initial incremental costs incurred by incorporating ECMs in a building's construction.

Fig. 2 shows the comparison between LCC of energy-efficient cases and those of the respective reference cases for the four case studies.

Discounted Payback Period

Discounted payback period (DPP) is the time required to recover the initial incremental investment from the discounted future savings. To calculate the DPP, present values of annual savings are cumulated until they equate with the initial incremental

Table 7 Overview of different costs and LCC savings of studied projects

<i>Building name</i>	<i>Climate Zone</i>	<i>Case (reference/green)</i>	<i>Investment costs</i>	<i>Energy consumption over lifecycle</i>	<i>Operating, maintenance and repair costs over lifecycle</i>	<i>Residual value over lifecycle</i>	<i>Overall LCC</i>	<i>LCC savings total (and in % of investment cost of reference case)</i>
Ganga skies	Moderate	Reference case	Rs. 123,737,908	Rs. 15,059,166	Rs. 20,042,591	Rs. 6,537,093	Rs. 152,302,573	–
		Green (actual) case	Rs. 124,765,346	Rs. 11,665,551	Rs. 20,209,012	Rs. 6,591,372	Rs. 150,048,537	Rs. 2,254,036 (1.48%)
Spire woods	Composite	Reference case	Rs. 184,887,570	Rs. 20,642,470	Rs. 27,215,893	Rs. 7,783,551	Rs. 224,962,383	–
		Green (actual) case	Rs. 188,496,508	Rs. 13,163,314	Rs. 27,747,137	Rs. 7,935,483	Rs. 221,471,477	Rs. 3,490,906 (1.55%)
Apollo HIRCO	Warm and humid	Reference case	Rs. 123,941,025	Rs. 16,011,587	Rs. 18,244,416	Rs. 5,217,773	Rs. 152,979,255	–
		Green (actual) case	Rs. 127,272,867	Rs. 10,955,296	Rs. 18,734,871	Rs. 5,358,039	Rs. 151,604,994	Rs. 1,374,261 (0.9%)
Lotus boulevard	Composite	Reference case	Rs. 231,945,173	Rs. 33,323,498	Rs. 34,142,885	Rs. 9,764,621	Rs. 289,646,936	–
		Green (actual) case	Rs. 233,752,353	Rs. 26,789,479	Rs. 34,408,906	Rs. 9,840,702	Rs. 285,110,037	Rs. 4,536,899 (1.57%)

Source: Author.

Comparison of Life Cycle costs over 15 years: EE vs conventional case

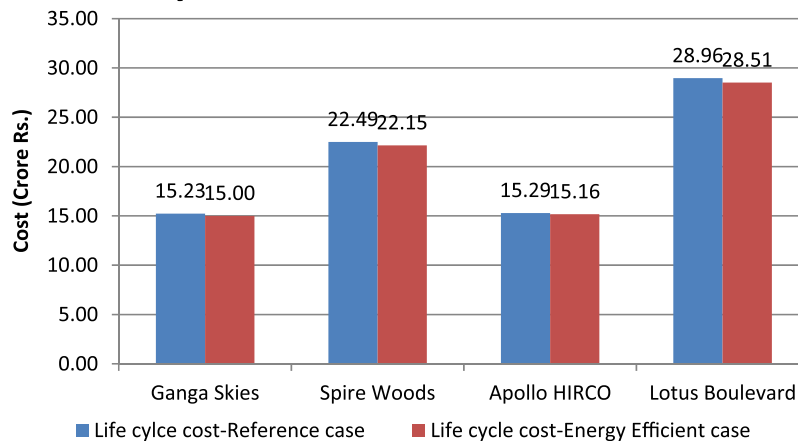


Fig. 2 Life cycle costs comparison of EE vs conventional case. *Source:* Author.

Discounted payback period

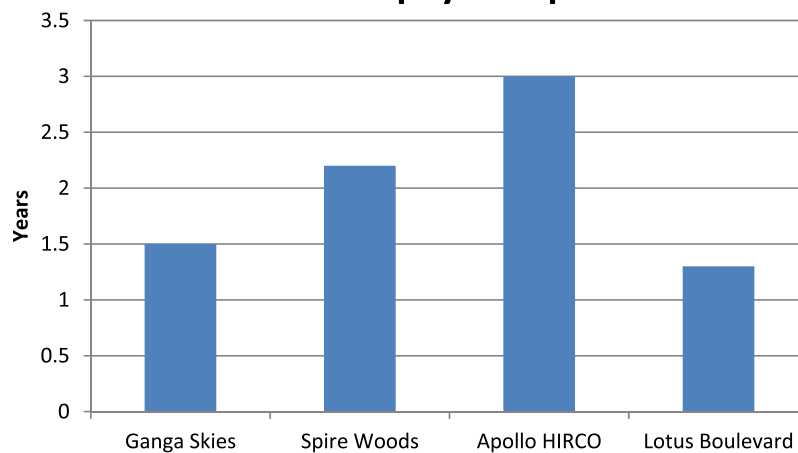


Fig. 3 Discounted payback period of studied projects. *Source:* Author.

investment. When using DPP as an assessment criterion, an investment is profitable if its discounted payback is lower than the life of the product (15 years considered in this study although it is higher in the range of 25–50 years).

Fig. 3 clearly illustrated that all the four cases have DPP between 0.8 and 2.8 years.

Summary

The study shows that investing in EE buildings is a profitable venture and use of LCCA gives a better perspective of taking right decisions. Using the LCCA for the selected four projects, all the energy-efficient projects have proved to be financially attractive.

Incremental costs for using better walling and roofing alternatives such as AAC and insulation/reflective paints for the roofs are relatively small, while EE glazing is much more costly. However, total incremental costs of the green case over the reference case are in the range of 232–942 Rs/sqm, which are very low compared to an average selling price of 55,000 Rs/sqm.

With incremental costs ranging between 0.8% and 2.8% of the initial capital investment, the discounted payback periods are notably attractive ranging between 1.3 and 3 years. Overall, cash savings accrued from these energy-efficient apartments not only compensate for this initial cost increment but provide benefits to the owners throughout the life time of the building.

In the developer driven (residential) market, there is often a debate between split incentives with the developer bearing the incremental costs whereas dividends through conserved energy are reaped by the home buyers/owners. This remains one of the key

barriers in the market of green construction. However, this obstacle can be overcome with enhanced awareness, incentive schemes, policy support, and other promoting measures for energy efficiency among the buyers, as developers have to respond to user needs and demand, while potentially charging a premium for the higher costs incurred. The KfW-NHB EE Homes programme attempted to achieve this through various measures including financial incentives. Lessons learnt from such programmes can be replicated and integrated with mainstream policies and programmes at the Federal and State level for larger uptake.

With the launch of the new Eco-Niwas Samhita 2018 in India, also known as Energy Conservation Building Code for Residential Buildings, adopting LCC approach as shown by this study to overcome the perceived barrier of high costs associated with green/energy efficient buildings particularly in residential sector is even more relevant and pertinent. It is strongly recommended to make LCCA a formal part of construction process as is the practice in some parts of the world to let various stakeholders take more rational decisions of investing in green building and energy efficiency features.

Acknowledgement

The author would like to thank Adelphi for giving the permission to reproduce the work she did with other colleagues during their collaborative work for the KfW-NHB work on Promotional Programme on Energy Efficient Homes.

Annexure A

Reference Building Parameters

For the reference case, the tool includes pre-defined values for the building envelope and systems which represent the common building practice for urban residential housing construction. In order to calculate and certify an actual “energy efficient building”, the Assessment Tool user enters all active and passive energy efficiency measures applied in the building. Through the tool, the energy consumption of the reference case and of the actual energy efficient building are simultaneously being calculated and compared.

The tool reference case, against which the actual building is being assessed, is currently defined as:

Building envelope

External Wall

Conventional External Wall

U-Value 1.57 W/(sq. m K)

Roof

Flat Roof (conventional roof)

U-Value 1.77 W/(sq. m K)

Floor (floor of the lower most apartment)

Lowest Level Apartment Floor

U-Value 2.03 W/(sq. m K)

Glazing

Single clear

U-Value 6.17 W/(sq. m K)

SHGC (Solar Heat Gain Coefficient) 0.81

Window frame

Aluminium without thermal break

U-value 13.51 W/(sq. m K)

Shading by overhangs and fins

SHGC (Solar Heat Gain Coefficient) 0.9

Lighting

Lighting Power Density for the general lighting scheme shall be taken as 7.5 W/m² for the apartment area, 6.5 W/m² for common area lighting and 2.2 W/m² for parking area lighting.

No occupancy/daylight controls

Lighting operation schedule – 6–9 morning, 17:30–23:00 evening, 60% diversity

Space cooling

The base case cooling system shall be BEE 1 star rated product having minimum EER of 2.5 W/W for decentralized cooling systems.

A central (VRF) system shall have an EER of 3.9 as there is not yet a star rating available.
 Cooling operation schedule – 8 h/day, 70% diversity, 1st May – 15th October
 Cooling set point temperature – 25°C

Space heating

The space heating is not changed in the reference building.

Hot water system

The hot water systems are left as they are except for electric geyser which shall have a BEE 1 star rating.
 If the actual building has SWH it will be removed in the reference building.

Annexure B

Present Value Factors (Fuller and Petersen, 1995)

Single Present Value is used to discount the single costs of the project i.e., initial investment cost, and resale value of the project. Uniform Present Value is used to discount the uniformly annually recurring costs of the project i.e., OM&R costs of the project. Uniform Present value-non-escalating is used to discount the non-uniform annually recurring costs of the project i.e., energy costs that change from year to year at a constant escalation rate.

Single Present Value PV of a future cash amount occurring at the end of year t , F_t , given a discount rate d :

$$PV = F_t \times \frac{1}{(1+d)^t}$$

Uniform Present value PV of a series of equal cash amounts, A_0 , that recur annually over a period of n years, given d :

$$PV = A_0 \times \sum_{t=1}^n \frac{1}{(1+d)^t} = A_0 \times \frac{(1+d)^n - 1}{d(1+d)^n}$$

Uniform Present value non-escalating PV recurring annual amounts that change from year to year at a constant escalation rate, e over n years, given d :

$$PV = A_0 \times \sum_{t=1}^n \left(\frac{1+e}{1+d} \right)^t = A_0 \frac{(1+e)}{(d-e)} \left[1 - \left(\frac{1+e}{1+d} \right)^n \right]$$

The different Present value factors calculated and used for LCC in this study is given as under (Table B1):

Table B1 Present value factors calculated and used for LCC

Year	Uniform present value factor-escalating	Single present value factor (SPV)	Uniform present value factor-non escalating
1	0.9043	0.9043	0.9276
2	1.7221	0.8178	1.7880
3	2.4616	0.7395	2.5861
4	3.1304	0.6688	3.3264
5	3.7351	0.6048	4.0131
6	4.2820	0.5469	4.6501
7	4.7766	0.4946	5.2410
8	5.2238	0.4472	5.7890
9	5.6283	0.4044	6.2974
10	5.9940	0.3657	6.7690
11	6.3248	0.3307	7.2064
12	6.6239	0.2991	7.6121
13	6.8943	0.2705	7.9885
14	7.1389	0.2446	8.3376
15	7.3601	0.2212	8.6614

Source: Author.

See also: Evaluation of Sustainability Indicators of Buildings

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Leadership in Energy and Environmental Design Rating System: A Global Tool to Assess Sustainability in Buildings, Communities and Cities

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LEED, Leadership in Energy and Environmental Design stands for the most globally relevant and accepted green building rating system designed and administered to transform buildings to be sustainable and healthier, change behavior and facilitate healthy spaces that do no harm to people. Developed by U.S. Green Building Council, LEED has been applied in 167 countries. USGBC leads by example and has a strong vision that buildings and communities will regenerate and sustain the health and vitality of all life within a generation. LEED has set global benchmark and standard for facilitating design, construction and operation of green and sustainable buildings, communities and cities and most importantly addressing health aspects of people working in or living in their buildings. LEED, is a performance driven rating system that holistically addresses all aspects of building or project life cycle from how conveniently it is located to intrinsic aspects of indoor environmental quality such as daylight, quality views and indoor air quality and acoustics.

The LEED Rating System is a voluntary, consensus driven, internationally recognized green building certification system providing third-party verification that a building or community was designed and built using strategies aimed at improving performance across metrics such as energy savings, water efficiency, CO₂ emissions reduction, improved indoor environmental quality, and resource stewardship. LEED provides building owners, design teams, and operators a concise framework for identifying and implementing practical and measurable green building design, construction, operations and maintenance solutions. Project teams use LEED both as a design guide and verification system to measure progress towards defined performance goals. LEED is structured to encourage interdisciplinary project teams to engage in an integrated project delivery process. By combining mandatory and optional strategies in a framework that rewards successful projects with a third party certification, LEED motivates project teams to take action which results in higher performing buildings.

LEED is structured into a set of prerequisites and credits organised in six key areas namely:-

- Location and transportation
- Sustainable sites
- Water efficiency
- Energy and atmosphere
- Materials and Resources
- Indoor environmental quality

There are a collection of mandatory and optional strategies in each credit category. Mandatory strategies or prerequisites are necessary to qualify for rating. Optional strategies or credits can be selectively attempted and complied with to get to desired level of certification. Four levels of certification are available for LEED rating namely certified, silver, gold and platinum corresponding to 40, 50, 60, 80 points, respectively. Prerequisites do not carry any points.

Allocation of points or relative weightage of points is based on seven impact categories that a LEED project should accomplish. The highest weightage is awarded to credits that address climate change and human health. The impact categories also address issues on protection and restoration of water resources, biodiversity, material resources and including waste, greener economy and quality of life of occupants and visitors (Internal paper on LEED V4: Impact category and point allocation development process by Brendan Owens *et al.*) (Fig. 1).

LEED has now transcended beyond buildings into communities and cities. Quality of life and human experience are central to any city and community. Issues influencing quality of life stretch beyond environmental goals and hence LEED Rating System for cities and communities have a significant focus on equitable education, jobs, prosperity, environmental justices, quality of outdoor air, access to healthy living and food, affordability of housing, avoidance of gentrification, among many other issues.

Genesis of LEED (see “Relevant Websites section”)

With as few as with 19 pilot projects way back in 1998 under its earliest version, LEED has grown immensely, as the economic, human health and environmental benefits of achieving certification have become well known. And the numbers are outstanding.

As of October 2018, total commercial projects participating in LEED are more than 95,600, totaling to total square feet of over 20.59 billion, total certified commercial projects are nearly 44,000 and certified commercial square feet is more than 7.28 billion, residential units (registered and certified) being more than 1.6 million and certified LEED for Neighborhood Development projects totaling at 200. There are more than 201,000 LEED professionals. These numbers demonstrate the phenomenal influence that LEED has had in the green building industry globally in over more than two decades of its inception and existence.



Fig. 1 LEED impact category.

LEED has transcended beyond the commercial office space, the sector in which it originated, with market-specific offerings for schools, healthcare, homes, neighborhood developments, campuses, entire corporate building portfolios and retail settings, acknowledging the unique considerations for each of these space types. LEED has also pushed far beyond new construction projects, its original focus, with LEED for Commercial Interiors, LEED for Core and Shell and LEED for Existing Buildings: Operations and Maintenance, which offers older structures the opportunity to dramatically reduce their environmental impact.

LEED projects can be found in all 50 states of USA and 167 countries and territories, buoyed by local U.S. chapters, the LEED International Roundtable as well as green building councils around the world, united behind the World Green Building Council in a truly global mission.

USGBC also counts nearly 11,000 member organizations representing all their employees among LEED's supporters, including Fortune 500 companies, architecture firms, contractors and builders, product manufacturers, nonprofit organizations, government institutions and many others. These organizations, large and small, represent a broad cross-section of economic and societal interests.

The infographic below provides a snapshot of various milestones in history of LEED, including references to names of "firsts" in key categories of certification (Image courtesy: Neha Koul, Technical Manager, Green Business Certification Institute, India and Mili Majumdar, Author) ([Fig. 2](#)).

Variants in LEED Rating

LEED is a versatile rating system that applies to buildings, spaces communities and cities, both new and existing. Needs and functions of buildings vary based on type of use. There are about 21 adaptations available to suit different building typologies. For example, a hospital building is distinct in use from a school or retail or office building. Although the sustainability framework remains similar irrespective of variations of building functions, credit requirements i.e., technical requirements to meet intent of a specific credit may vary depending of the typology, or number of available points in a credit may vary based on typology or variant. For examples LEED for school encourages community integration through sharing of spaces between the school and surrounding community. This credit on joint use of spaces is specific to LEED for schools. LEED for Buildings is available for both new and existing buildings and the most recent version is *LEED v4.1*. LEED is about leadership and as a rating system, it has set industry benchmarks for high performance buildings. *LEED Zero*, (see "Relevant Websites section") the latest addition to LEED rating thus rewards a complement to LEED that verifies the achievement of net zero goals with *LEED Zero Carbon* recognizing buildings or spaces operating with net zero carbon emissions from energy consumption and occupant transportation to carbon emissions avoided or offset over a period of 12 months or, *LEED Zero resources*:

- *Energy* recognizes buildings or spaces that achieve a source energy use balance of zero over a period of 12 months.
- *Water* recognizes buildings that achieve a potable water use balance of zero over a period of 12 months.
- *Waste* recognizes buildings that achieve GBCI's TRUE Zero Waste certification at the Platinum level.

LEED also has variant for certification of new and existing transit stations, *LEED for Transit*. While the rating system certification of new transit system is modelled after LEED for new construction of buildings, with variations that apply to transit station, LEED for existing transit stations builds on performance of stations tracked through Arc, as its foundation. Measuring performance on critical parameters such as energy used, water consumed, waste generated and diverted, transportation of commuters and quality of indoor environment, on a regular basis provides insight into actual performance of the building and provides opportunity to

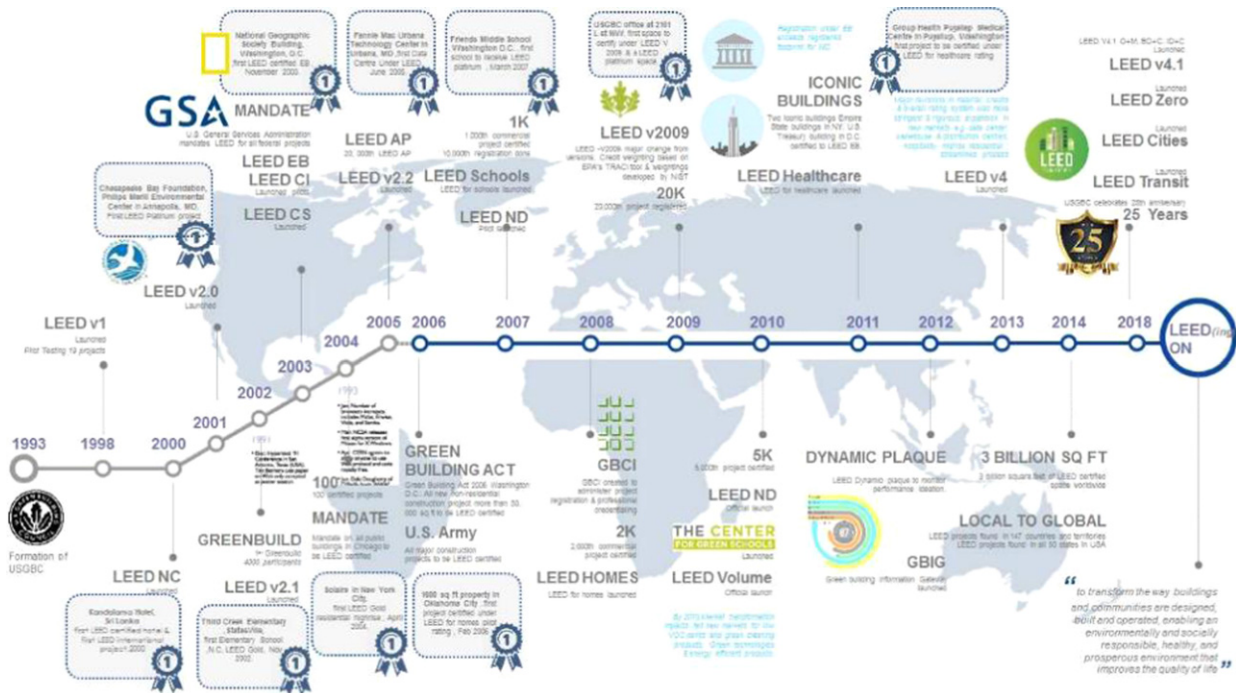


Fig. 2 History of LEED and list of firsts.

improve performance on continuous basis. It also allows peer to peer benchmarking and help projects realize tangible savings through retrofits and improvements in operation and management. Powered by Arc, a digital platform to track performance, LEED v4.1 for existing buildings, transit stations, cities and communities provides unique opportunity to measure, track and improve performance and continue to do so over its lifetime.

Cities and communities are very diverse entities with a long life cycle of development and operation. People are central to any city and community and quality of life of residents are very important for a city being recognized as liveable, sustainable and green. *LEED for Cities and Communities* program is developed to revolutionize city planning, development and operations, while also improving life for citizens around the world. In addition to setting credits and technical parameters and policy frameworks for enabling better utilization of energy, water, ecosystems, land, transportation and waste management, this rating system has significant focus of citizens' quality of life. Thus, equity, access, quality of outdoor air, access to education, jobs, poverty reduction, affordability in housing, crime prevention, resilience, environmental justice, healthful food etc., are some critical aspects that have been integrated through appropriate credits in the rating system. Similar to other variants of LEED, performance tracking and monitoring, is central to the system, particularly for existing cities.

Global Rating System

Versatility of LEED in the way it is written and followed has allowed its adoption globally. LEED is the most popular and widely accepted green building rating system and is adopted in over 167 countries, though its origin lies in USA. LEED follows a unique way of measuring greenness or sustainability in projects. Each credit or prerequisite has an intent that defines why a project should meet the intent and the environmental, social and/or economic benefits associated with the intent. The credit defines outcomes that a project needs to derive by following it. Though typically a U.S. code or standard or best practice is referenced, LEED allows international equivalents to be followed to meet the credit intent. Thus, a project gets flexibility to adopt a local code or standard (after due approval from USGBC) without compromising on intent of the credit.

LEED also regularly publishes alternative compliance paths and regional priorities to recognize global best practices, standards and codes. It is thus a flexible and globally applicable system.

Performance Holds the Key

Design and construction of greener and healthier buildings, communities and cities have significantly gained traction over last decades. While design intent can be met through a well-designed green building and its certification, it is critical that these

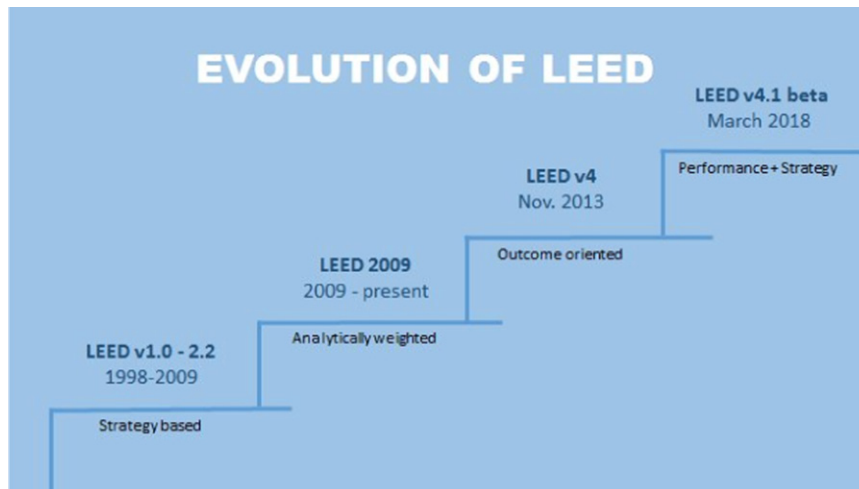


Fig. 3 Evolution of LEED.

buildings perform as designed. LEED has transformed itself from a purely prescriptive and strategy based system to a performance cum outcome oriented system over the years. The figure below captures the evolution of LEED credit structure in a timeline (Fig. 3).

Performance of any building or any entity is heavily dependent on operation and maintenance and often there is a gap in this area. Green buildings are designed to operate as energy and water efficient buildings with better quality of indoor environment for healthy and productive occupants. However many a times a well-designed green building may fail to operate as a green building, due to lack of maintenance, operational failures and lack of knowledge and understanding over the years.

LEED has evolved itself from a prescriptive and strategy, oriented rating system to strategy and performance driven rating system. With experience from over 94,000 participating projects globally, LEED has gathered immense experience on technologies that work, strategies that are effective, behaviors that can be influenced and failures that are common and avoidable. Every new version of LEED is based on market experience from earlier version and cumulative knowledge sharing by many volunteers and groups of LEED. With launch of the newest version, LEED v4.1 LEED has again raised the bar to increase the impact on our built environment. From improving energy performance to emphasizing human health and integrative building design, LEED is encouraging project teams to operate beyond the status quo. LEED v4.1 is the most inclusive and transparent system to date. It is more inclusive with updated referenced standards and allows projects to earn LEED points through building performance monitoring through use of Arc platform; it continues to drive performance, fully integrating performance outcomes supported by new methodologies and a simple data-driven path so that one can measure performance on an ongoing basis and includes lessons learnt from the market using LEED. The reach of LEED is ever expanding and now also applies to existing buildings, residential projects, transit stations and cities/communities (Fig. 4).

LEED v4.1 for existing entities such as buildings, cities, communities, transit stations is driven by data provided on a digital platform namely Arc. Arc provides a unique platform to track performance of buildings, cities, communities, spaces so that they can perform as designed and set new benchmarks for better performance. The Arc platform was launched in 2016 by Green Business Certification Inc. (GBCI), it helps connecting people all over the world to take appropriate actions and inspire them to make the most informed decisions related to sustainability of our built environment. It is a transformational initiative that has a huge leverage effect on tracking and reducing emissions and other environmental impacts from buildings. It provides the building owner and the building facility manager with a tool to engage with the occupants to create healthier and efficient working and living spaces. It also promotes healthy competition among spaces to raise the bar on performance and set new standards of performance. It thus indirectly promotes newer technology development and helps users to participate in maintaining or betterment of building performance. For example, energy performance in an office space can be improved by regulating thermostat set point, or switching off lights that are not required. Arc helps track both parameters i.e., energy performance and human experience and thus ensuring that thermal or visual comfort is not compromised at the cost of efficiency.

Today more than ever before, the green construction drive depends on technology and data, and the future of green building is concentrated on performance. Powered by Arc, everyone using a space can be involved in its improvement e.g., commercial buildings, residences, retail, hospitals, schools, shopping malls, education institutes, industrial facilities, districts, cities, etc. LEED v4.1 for existing entities leverages heavily on Arc for data tracking and scoring of buildings for certification. For new constructions undergoing LEED certification, projects have to commit to provide data on Arc once they start operations. This shall ensure continuity of performance as promised and committed during certification.



Fig. 4 Performance Tracking Using Arc platform.

LEED and Integrative Design (see “Relevant Websites section”)

Integrative design forms first principles in any design that allows project teams to come together, collaborate and evolve solutions that cut across multiple disciplines. The Integrative Design Process begins at the earliest stages of project planning. It is a collaborative process that focuses on a building’s design, construction, operations and occupancy over its complete life-cycle. The entire team, from client, to architect, to engineering, to landscaping, and so on – identifies goals and establishes performance objectives for the building and its systems during the earliest design stages.

The newest iteration of LEED – LEED v4 and LEED v4.1 – facilitates the Integrative Design Process with an IDP credit requirement. A project attempting to earn this credit must set goals and expectations involving the performance of energy and water systems.

Energy modeling on preliminary base design is done to evaluate advantages of site conditions, all with an eye on HVAC sizing. The impacts of building orientation, and interior and envelope design elements – such as insulation, high-performance glazing, window-to-wall ratios, shading, optimal lighting levels, indoor design temperatures – are collectively and individually assessed in the energy modeling exercise (Fig. 5).

Taking the example of Daikin Industries, Ltd., that has achieved the highest rank of Platinum Certification in the LEED for New Construction (LEED-NC) rating system for the Technology and Innovation Center (hereinafter referred to as “TIC”), in Japan in 2016 has deployed innovative and integrative design methods to arrive at net zero energy consumption. The TIC is a building structure that combines Daikin technologies for achieving a zero energy building (ZEB). Here new energy-saving technologies are constantly being tested and verified with the building serving as a solution model for sustainability. The building uses structural elements as conduits for heating and cooling systems, thus demonstrating principles of integrative design. A combination of passive strategies such as high performance thermal envelope, long and narrow building shape, geothermal energy utilization, outdoor units installed in well-ventilated area thus allowing better heat dissipation and a balanced mix of active technologies such as High-efficiency HVAC, free-cooling HVAC, Glass duct + ventilation system, High-efficiency water-source package HVAC system, Automatic variable-flow water spray system and integration of renewable energy technologies, enabled the building to be net zero, a true leadership level outcome (Fig. 6).

A similar analysis is recommended for water systems. The planned integration of plumbing fixtures, landscaping species, roofing systems, and rain water capture systems can cohesively and efficiently reduce and optimize water use.

Additionally, in the built form there is often a nexus between energy and water systems. For example, a roof garden provides a cooling effect and helps to reduce HVAC loads in hot climates. At the same time, water is required to maintain that roof garden. In the Integrative Design Process, an optimization between energy and water requirements is determined before deciding on final designs for, by way of example, either the roof-garden or the HVAC system.

LEED as a Market Transformative Initiative

LEED is a market transformation initiative. LEED has been instrumental in bringing out critical issues related to buildings and occupants and how building systems and strategies have a large impact on health of people, utilization of resources such as energy



Fig. 5 Team members in integrative design.

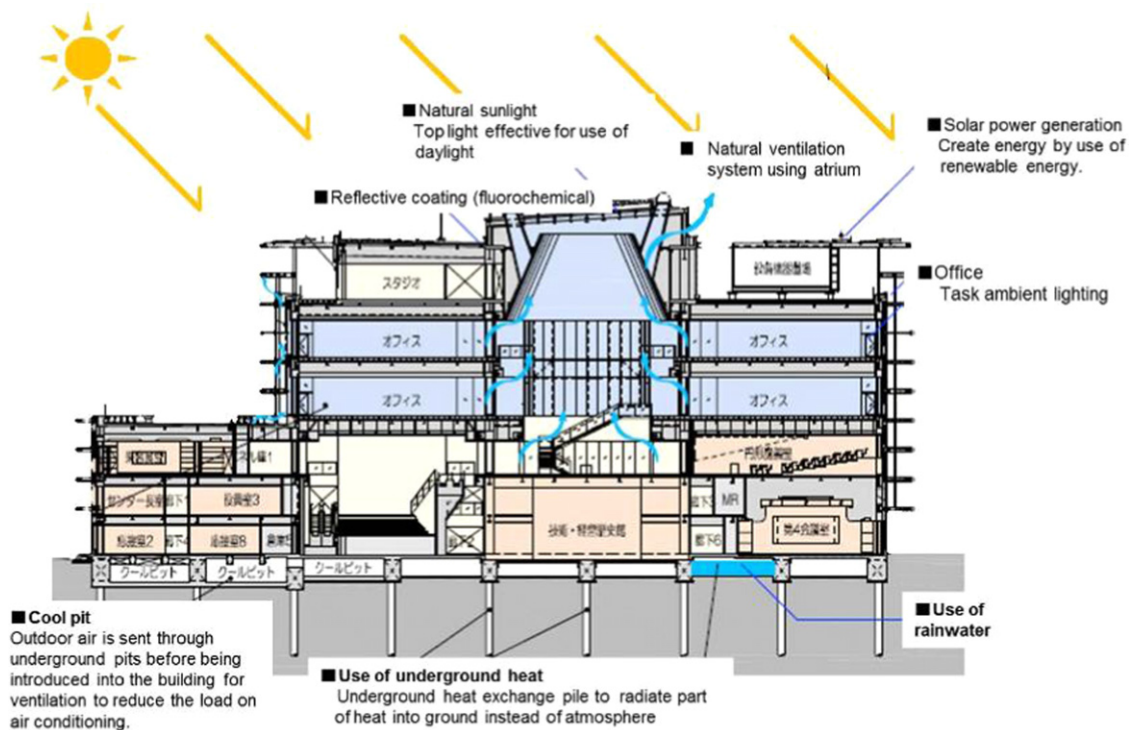


Fig. 6 Daikin technology and innovation center, Osaka, Japan. (https://www.daikin.com/press/2016/160908_2/press_20160908_2.pdf).

and water. Energy efficiency in buildings and use of progressive codes and standards to push boundaries in this area has been a significant contribution of LEED. LEED has adopted the ASHRAE 90.1 as the base standard for driving energy efficiency (Fig. 7).

ASHRAE 90.1 has been made more stringent over years and LEED has progressively aligned itself to the latest version. The 2010 version of the standard is over 40% more stringent than the first version of 1975. The stringency is representative of market progression in energy efficiency and evolution of better and energy efficiency technologies, for HVAC, lighting, building insulation and glazing systems among others. The latest version LEED v4.1 references ASHRAE 90.1-2016. Adoption of progressively stringent energy codes as a baseline and making efforts to be better than the code by up to 50%–60% certainly creates great market push on adoption of energy efficient products. There are several markets that have received push due to LEED. Some significant examples

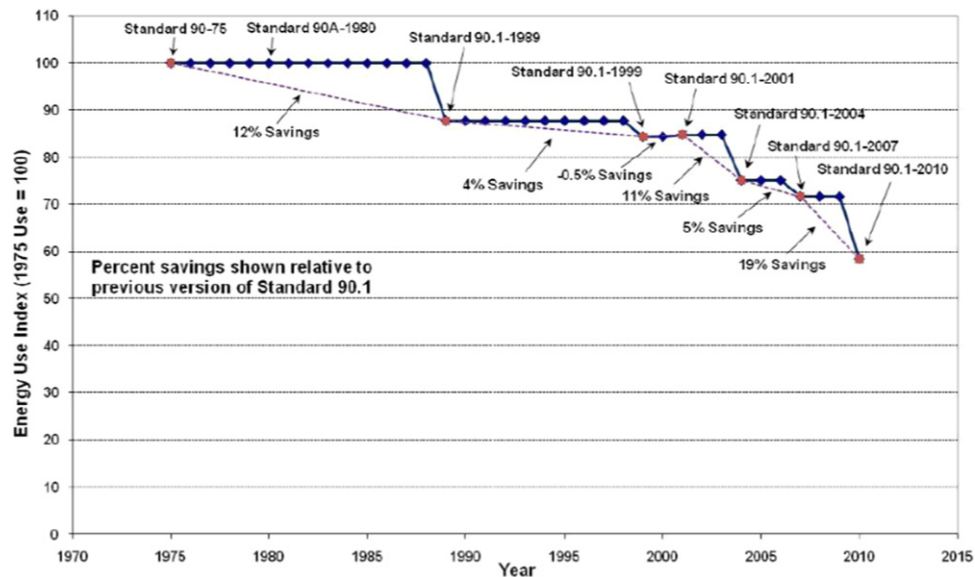


Fig. 7 Energy code stringency progress.

are low VOC paints and finishes, low flow water fixtures, and irrigation devices, controls for systems among others. LEED has also raised awareness on critical health issues such as impact of smoking on health and has introduced mandates on prohibiting smoking in LEED certified projects.

LEED and Human Health

A LEED certified project means a lot: energy efficient and possibly powered by clean and green energy, uses less water, reduced waste, better indoor quality of light, air, acoustics; use of environmentally responsible safer and healthier materials and much more. Human health and well-being has been embedded in LEED from its earliest version. Direct impacts on health and well-being are achieved through credits in indoor environmental quality. Improved daylighting, access to quality views, improved *air quality*, better ventilation strategies, thermal comfort, acoustics, choice of low emitting materials etc. There are several credits that also indirectly contribute to improved health and well-being of occupants e.g., credits on energy and atmosphere that lead to energy savings contribute to emission reduction impacting human health. Use of public transportation and mass transit facilities lower emissions from vehicular sources, which has impact on human health. Likewise, LEED pilot credits on *social equity* address disparities within communities; enables residents with diverse economic backgrounds, age groups etc., to live together; encourage development on site with developmental challenges, all these progressively contributing to social well-being. LEED provides for *mental well-being* through accessibility to open and outdoor spaces, daylighting and enhancing liveability in communities and so on. LEED promotes *fitness* through credits on shared facilities such as gymnasiums or encouraging walking, cycling and non-motorized means of transportation. Issues related to *Toxicity* is addressed through credits on minimizing use of harmful chemicals in building materials, disclosure on human health impacts of products, prohibiting smoking, discouraging use of harmful chemicals on plots and so on (Fig. 8).

LEED for cities and communities have a significant focus on quality of life and address well-being at a larger level as well. Reduction of poverty, access to education and job or healthful food, access to and equitable supply of clean water and power, clean air are addressed through the system to ensure enhanced quality of life for residents.

LEED and Sustainable Development Goals

The 17 sustainable development goals are a call for action by all countries to promote prosperity while protecting the planet. They recognize holistic economic and social progress while tackling climate change and environmental protection. They recognize that ending poverty, and doing so hand in hand with balanced and sustainable development, is crucial to survival of mankind. As a leadership organization, USGBC has been at forefront of meeting Goal 17. By fostering and nurturing several partnerships to realize its global vision on sustainable habitats and buildings, makes USGBC a unique organization. And LEED has been instrumental in contributing to all goals through its credit achievements. A high level correlation between SDGS and LEED credit categories is mapped in the Fig. 9. By way of example, reversing the contribution of buildings to global climate change is a core



Fig. 8 Health impacts of LEED credits. Image Courtesy; Neha Koul, Technical Manager, GBCI, India.



Fig. 9 LEED and sustainable development goals Image Courtesy: Richa Prasad, Technical Specialist, Green Business Certification Institute, India.

goal in LEED. High performing green buildings, particularly LEED certified ones, can significantly reduce greenhouses gases emissions thus directly contributing to achievement of goal 13. This also has highest weightage in LEED followed by weightage on human health that directly contributes to achievement of goal three, good health and well-being.

Examples of Outstanding LEED Certified Projects Globally

CityLife

Milan

Targeting LEED gold

Covering an overall area of 366,000 square meters, CityLife is a new urban renewal project consisting of residences, offices and shopping and has attracted some of the biggest names in architecture such as Zaha Hadid, Daniel Libeskind and Arata Isozaki. Early on, the team behind CityLife conducted a feasibility study of the project. One million Euros, equivalent to 0.07% of the construction cost, was devoted to improve their score to LEED Gold. Another selling point to investors of the project was energy modeling. The model suggested a zero cost improvement, saving 50% of cooling costs (Fig. 10).



Fig. 10 CityLife (Milan).

Vodafone Village

Milan

LEED silver

With 127,000 square meters Vodafone Village is the world's largest LEED for Commercial Interiors certified building and the largest in Italy. Vodafone, one of the world's leading mobile companies with over 406 million global customers, built their new headquarters on an unused industrial area in Milan that has led to the environmental rehabilitation of the site and surrounding area. The roof includes a photovoltaic garden of 800 square meters producing more than 8000 kWh of clean energy every year ([Fig. 11](#)).

Lilla Bommen

Gothenburg, Sweden

LEED for existing buildings: operations and maintenance (gold) Jan 2013

Popularly referred to as L ppstiftet or "Lipstick" because of its red top. History The name Lilla Bommen, or Little Boom, is derived from Gothenburg's proud seafaring history, which dates to the 1600s. Because of its location, on the banks of the G ta River, the city had become a shipping center, with ready access to the Kattegatt, the North Sea, and the Atlantic. For fortification, city leaders constructed high walls and a moat with channels. At the time, those channels were the only passage ways into the city and so, for added security, each channel was equipped with a boom that was lowered at night. In 1989, when Lilla Bommen was completed, there were few tall buildings in Gothenburg. Consequently, it was considered a daring design, albeit one that was tied closely to the city's rich history and current status as Sweden's chief seaport. Most notably, many who have sailed past Lilla Bommen remark that, from the water, it resembles the mast of a ship ([Fig. 12](#)).

Built: 1986–1989 by Skanska Property West AB Purchased: in 2001 by Vasakronan, Sweden's largest property management company Designer: Ralph Erskine, renowned British-Swedish architect LEED Consultant: Piacon, Pia  hrling with sub-consultant ThorntonTomasetti Project Size: 442,160 square feet (41,078.0082 square meters); 22 stories.

Taipei 101

Taipei, Taiwan

LEED for existing buildings: operations and maintenance – platinum certified on July 7, 2011

With 101 floors and nearly 186,000 gross square meters, TAIPEI 101 is one of the tallest buildings in the world. Since its completion in 2004, it has become an icon for Taipei City, Taiwan and has set the quality and performance benchmark for supertall buildings in Asia. From 2008–2010, TAIPEI 101 invested in significant energy efficiency retrofit projects to generate energy and water savings. A review of public lighting was undertaken and resulted in the conversion to more energy efficient luminaires and lighting controls ([Fig. 13](#)). By utilizing Energy Management and Control Systems (EMCS), building managers are able to adjust operating temperatures, modify chiller plant operating schedules and modify chilled water distribution according to actual tenant needs. TAIPEI 101 earned LEED for Existing Buildings: Operations and Maintenance certification and succeeded in:

- Decreasing potable water usage by at least 30% compared to average building consumption
- Saving 28,000,000 L of potable water annually
- Being ranked in the top 30% of high-rise office buildings as benchmarked by the U.S. ENERGY STAR database
- Reducing energy consumption by 33.41 million kWh per year
- Saving more than \$2 million per year

Verdant Place

Shanghai, China

LEED platinum certified

With 22 floors and about 30,000 gross square meters, Verdant Place is one of the landmark buildings in Shanghai city. From 2008–2012, Verdant Place invested in significant energy and water efficiency retrofit projects to achieve energy and water savings.



Fig. 11 Vodafone village (Milan).



Fig. 12 Lilla Bommen (Gothenburg, Sweden).



Fig. 13 Taipei 101 (Taipei City, Taiwan).

The entire existing structural element was kept, but the single panel glass was replaced with double layer laminated low-e glass. The whole, old low-efficient MEP systems (including chiller, pump, fan, boiler, sanitary fixture, lighting fixture, and lift machine) were replaced with new equipment. A review of public lighting was undertaken and resulted in the conversion to more energy efficient luminaires and lighting controls. By utilizing Energy Management and Control Systems (EMCS), building managers are able to adjust operating temperatures, modify chiller plant operating schedules and modify chilled water distribution according to actual tenant needs. Verdant Place succeeded in:

- Decreasing potable water usage by at least 40% compared to average building consumption.
- Saving 2,861,770 L of potable water annually.
- Being ranked in the top 30% of office buildings as benchmarked by the U.S. ENERGY STAR database.
- Reducing energy consumption by 989,839 kWh per year.
- Saving more than \$128,495 per year (USD).



Fig. 14 Hysan place (Hong Kong).

Shanghai Pratt and Whitney Aircraft Engine Maintenance Co., Ltd. (Shanghai engine center)

LEED platinum located in the Qingpu district

The Shanghai Engine Center officially opened in September 2009 as an environmentally friendly and highly efficient CFM56® engine maintenance, repair and overhaul facility. The first LEED Platinum facility in China, the Shanghai Engine Center is a joint venture between China Eastern Airlines and Pratt and Whitney, the latter being a United Technologies Corporation company. The facility incorporates high-performance building solutions from other UTC businesses such as Carrier. Key LEED features at the 26,000 gross square meter facility include:

- At least 12.5% of the facility's energy is being produced from renewable sources such as solar thermal, photovoltaic, wind, geothermal and canal water sources.
- High performance, energy efficient windows contribute to the facility's daylighting system, reducing electricity requirements and the need for additional cooling.
- At least 20% of all construction materials were sourced locally, and 10%–20% of materials contained recycled content. Use of certified stewarded wood products.
- About 70% of construction waste was diverted from landfills.
- Reduced usage of potable water and the construction of a large pond on site capture and stores rain water to meet all sanitary needs

Hysan Place, Hong Kong

LEED platinum

LEED certification has resulted in:

- 22% total energy reduction compared to the ASHRAE 90.1 baseline.
- 30% increase in ventilation rate for the AC system.
- Providing vertical sky gardens that not only reintroduce public green space to residents of Causeway Bay, but also offer light, air, and views not usually available in the region
- A value increase in the entire Causeway Bay portfolio.
- By developing design and operations targets, monitoring changes, reviewing strategies, and reporting progress publicly, we strive to continually improve the firm and increase our positive contribution to the environment through business and design practices that are consistent with our broader social and environmental values, such as future LEED projects (Fig. 14).

Jaypee Vasant Continental Hotel

New Delhi

LEED platinum

The Jaypee Vasant Continental Hotel is strategically located within New Delhi's Diplomatic Enclave. Known for its easy approachability and premium hospitality services, the Continental takes great pride in its many sustainable features and practices. Among them, the hotel recycles 99% of its total solid waste. The project team has managed to reduce the cooling demand by



Fig. 15 Jaypee vasant continental hotel, New Delhi.

having over 75% of the roof area covered with paints having a high Solar Reflective Index. In regard to natural resource conservation, this LEED certified hotel saves approximately INR 7 million in energy and water savings and reclaims 44% of its potable water. Its total GHG reduction is 123 MT of CO₂ (Fig. 15).

**EDS Global
New Delhi
LEED platinum**

Since 2002, the staff and management of Environmental Design Solutions has worked on hundreds of green building projects worldwide. Their deep experience was amply rewarded when EDS pursued LEED Platinum for its New Delhi headquarters. During construction, the project diverted 97% of all waste from landfills, while pursuing high-efficiency performance and superior indoor environmental quality. Important highlights included the installation of three-foot tall windows that spread natural light evenly throughout the open office, thereby promoting visual comfort and occupant well-being. Operational improvements yielded a significant 42% reduction in water consumption, and overall savings of 35% in energy use.

**K. Raheja Corp. Mindspace Buildings No. 5 and 6
Navi Mumbai
LEED gold**

K. Raheja's Mindspace Buildings No. 5 and 6 was built on expansive space and surrounded by 14,000 square feet of professionally landscaped grounds. Its park-like gardens represent nearly 15% of the site's total area. Other sustainable innovations included 100% on-site treatment of wastewater to tertiary standards, allowing reuse for gardening and flushing. Efficiency was a fundamental requirement, and this building produces annual energy savings of INR 34 million and water savings of INR 2.8 million.

**ITC Sankhya Data Center
Bengaluru
LEED v4 platinum**

ITC Sankhya Data Center recently became the world's first data center to earn LEED Platinum, ranking it among the most energy efficient data centers in the world. ITC Sankhya is fully powered by renewable energy. It also incorporates variable capacity technology and a sophisticated sensor network that automatically adjusts cooling, heating, humidification, and dehumidification. The resultant combined energy savings last year were INR 121 million. Other performance highlights include PM10 in the range of 10–20 Ug/m³, Carbon Monoxide below detectable limits, Formaldehyde below 27 ppb, Ozone below detectable limits for most regularly occupied spaces, along with water savings of INR 0.2 million per year.

**Starbucks
Chhatrapati Shivaji International Airport, Terminal 2, Departures Mumbai
LEED silver**

This project is the champion of three prestigious milestones: it's the first LEED-certified Starbucks store in India, it's the 900th LEED-certified Starbucks store overall, and it makes India Starbucks' 20th country with a LEED store. The green features in the store include water efficient plumbing fixtures, energy-efficient appliances and LED lighting that not only reduce the demand on the water supply and energy grid, but help save money over the life of the lease. Integrating sustainable building practices and conserving precious resources is critical as India's population grows. The certification of the first Starbucks store in India represents the company's commitment to conserving resources and green retail but also a strong partnership between Starbucks and Tata.

**Infosys EC-53 Building
Bengaluru
LEED platinum**

Infosys has designed efficient buildings for many years, and they have learned much. The EC-53 Building is one example. It boasts a custom radiant panel-based cooling system that is 30% more efficient than conventional systems. Its building envelope is fully insulated to minimize heat ingress. Over 90% of the occupied space enjoys natural light and outside views. Self-powered,



Fig. 16 Surat city.



Fig. 17 Washington DC.

peel-and stick wireless switches and sensors reclaim energy from the indoor environment. Rainwater harvesting and an onsite sewage treatment plant reduce water consumption. Indoor air quality is continually monitored and balanced at the granular level. These interventions and others cut energy consumption by 42% over baseline, and reduced water use by 50% over LEED requirements.

Surat City

LEED platinum city

Surat city located in Gujarat state of India, with an area of 326 square km and a population of 5.32 million is the first Platinum certified city in Asia. It is the 8th largest and fastest growing city in India and is known for industries such as textile processing, diamond cutting and polishing, petrochemical, thermal power, fertilizer and heavy engineering. Surat has taken crucial initiatives to address the elevation in energy demand due to increase in commercial and industrial activities making it one of the progressive cities in India. These initiatives based on committed target of 10% reduction in energy demand by 2016, entails energy efficiency measures like adopting ESCO model, smart grid application and demand response as well as increase in renewable energy production from solar, wind and biogas. Additionally, Surat has been successful in providing quality water to 96% of the population and treats millions of wastewater to meet water demand in industries and landscaping. The city has also adopted City Resilience Strategy and has been declared as the 4th cleanest city in India ([Fig. 16](#)).

Washington, D.C.

LEED platinum city

Washington, D.C., the U.S capital located in the East Coast expands up to 68.34 square miles with a population of 0.67 million and is the first LEED Platinum city in the world. With its progressive energy goals DC has been able to achieve a reduction of 31.2% by 2013 and aims to achieve 50% reduction in GHG emissions from 2006 levels and 50% renewables in the energy mix by 2032 through wind and solar energy production. DC is also the national leader in green building movement with highest number of square footage per capita of LEED certified buildings. The city has been successful in reducing potable water consumption by

13.5% from 2012 to 2017 and aims at reducing it further by increase in storm water reuse. Waste is well managed in the city with 51% diversion rate from landfill and aggressive strategies in waste reduction such as pricing incentives and ban on plastics. Washington, D.C. has remarkably low per capita vehicle miles travelled and aims to reduce it further through improved public transit systems and safe and secure walking and biking infrastructure (Fig. 17).

See also: LCCA and Environmental Impact of Buildings. Roof Gardens to Vertical Farming

Relevant Websites

<https://www.usgbc.org/articles/simple-idea-several-hundred-billion-dollar-industry>

From a simple idea to a several-hundred-billion-dollar industry
USGBC.

<https://www.gbj.or.jp/integrativedesignprocessi201706/>

Green Building Japan.

<https://new.usgbc.org/leed-zero>

LEED Zero
USGBC.

Life Cycle Assessment Methods and Procedures and Their Role in Measuring the Sustainability Component of a Construction Technology

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Introduction

The development path that humans have taken, particularly since the Industrial Revolution, has proven to be detrimental to the health of ecological context of the world. The rapid change in the global environment linked to the Industrial Revolution is referred to as global change. Global change is likely to be further accelerated through globalization of the economy. Because of global change, which can be termed as environmental damage, the issues to be resolved are global warming due to greenhouse gas emissions; acidification of soil and water; drastic decline in the quality of air, soil, and water; reckless exploitation of natural resources stored in the soil through mining activities, drastic changes in land-use and land-cover through overexploitation of natural resources leading to desertification of landscapes, associated rapid depletion of biodiversity, etc. All this demands an exploration of a variety of additional pathways for development. There is an increasing awareness worldwide about the state of environment, caused by overexploitation of natural resources for economic development. The issues relevant to conservation of natural resources have to be addressed differently depending upon the ecological, social, economic, and cultural framework in which one is operating. This has led to the evolution of new concepts including that of sustainable development as a basis for overcoming the environmental, social, and economic challenges. Sustainability concerns have gained international acceptance to devise and implement sustainable development policies that can eventually halt and hopefully reverse the effect of global warming.

The term *sustainable* development can be described as enhancing quality of life; and thus, allowing the human beings to live a healthy environment and improve social, economic, and environmental conditions for present and future generations. Improving social, economic, and environmental indicators of sustainable development is drawing attention to the construction industry, which is a globally emerging economic sector and is a highly active industry in both developed and developing countries.

For the construction industry specifically, achieving true sustainability will require a paradigm shift, similar to the one faced by manufacturing industry that strives toward a sustainable approach to development by integrating sustainable strategies at all phases (Vanegas *et al.*, 1995). To overcome the increasing concerns of today's resource depletion and to address environmental considerations in both developing and developed countries, life cycle analysis/assessment (LCA) can be applied to decision making to improve sustainability in the construction industry. This may become possible only when at least some of the stages of that construction technology are quantified to prove its contribution in making that construction technology sustainable. LCA attempts to measure the "cradle to grave" impact on an ecosystem.

Life Cycle Assessment

LCA is a process to evaluate the environmental burdens associated with a product, process, or activity by identifying and *quantifying* energy and materials used and wastes released to the environment; to *assess* the impact of those energy and materials used and releases to the environment; and to identify and *evaluate* opportunities to affect environmental improvements (Asif *et al.*, 2007). The assessment includes the entire life cycle of the product, process, or activity, encompassing extracting and processing raw materials; manufacturing, transportation, and distribution; use, reuse, and maintenance; recycling; and final disposal.

In this study, the LCA is used as a tool to measure the environmental performance of a particular construction technique and to demonstrate the suggestions that can be offered for improvement at each stage in the life cycle of a building.

The LCA caters to the wide array of impact in a stage specific process, where each stage poses an opportunity as well as a constraint to improve the environmental effects. This provides a set of efficient alternatives and qualitative judgment that can help a designer to choose from a range of construction technologies depending on their respective environmental and economic performances. According to ISO 14040, there are four interactive steps necessary for a complete life cycle study: Planning, inventory analysis, impact assessment, and improvement analysis; these are graphically interrelated in Fig. 1. These steps are further elaborated in ISO 14041, 14042, and in 14043 as per Fig. 1.

The first step defines the *goals* and objectives of the LCA framework and its scope (including investigation boundaries or system boundaries). This step establishes a relationship between the purposes of the study, decides boundary conditions of the LCA, and procedure for quality assurance of the study.

The second step is *inventory analysis*. The life cycle inventory (LCI) involves collecting data for each unit process regarding all relevant inputs and outputs of energy and mass flow, as well as data on emissions to air, water, and land. This phase includes calculating both the material and the energy input and output of a building system. It provides a quantitative input/output account of the product or system as shown in Fig. 2.

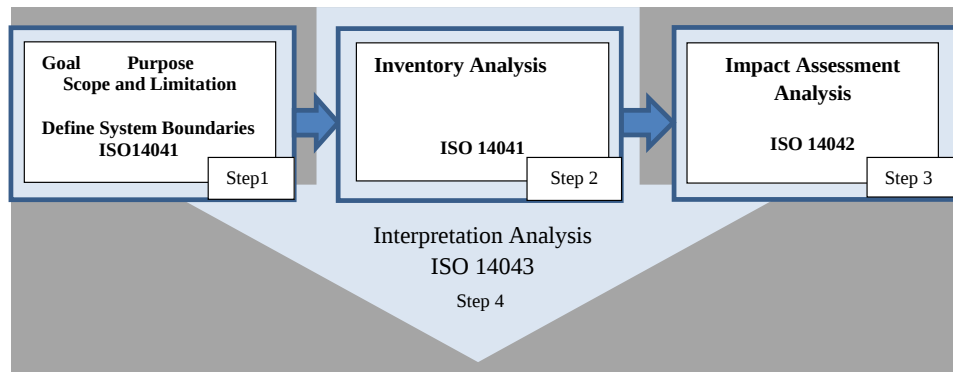


Fig. 1 Steps for life cycle assessment. *Source:* Authors.

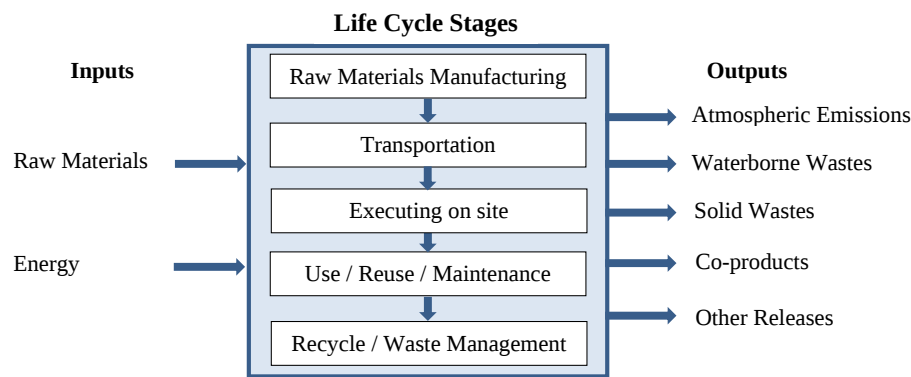


Fig. 2 Life cycle stages, inputs and outputs for life cycle assessment. *Source:* Authors.

Each of these input–output categories comprise of simple materials, specific energy input, or some processes like for kiln burnt brick or cement manufacturing process, which need to be broken down and analyzed in the same way as the main material life cycle process.

The third step is *impact assessment analysis*. It is a quantitative and/or qualitative process to characterize and assess the effects of the environmental burdens quantified in the inventory, the life cycle impact assessment (LCIA) phase evaluates potential environmental impacts and estimates the resources used in the modeled system. This phase consists of three mandatory elements: Selection of impact categories, assignment of LCI results (classifications), and modeling category indicators (characterization). The process may be divided into three steps: Classification, characterization, and valuation. This is to analyze how raw materials used, energy generation, water usage, effluent output, air emission, and solid waste affect the environment.

Finally, the last step of ISO 14040 is the *improvement/interpretation analysis*. This stage identifies significant issues, evaluates findings to reach conclusions, and formulates recommendations. This improvement assessment would allow identification or making changes in the construction life cycle, improving its environmental performance. For example replacing highly processed, nonrenewable resource consumed as building material with renewable resources.

Construction Industry and Environmental Sustainability

The construction industry is one of the largest sectors, which consumes an enormous amount of natural resources, manpower, energy, and money. The process of construction of buildings consumes a huge amount of energy and in turn produces a large volume of GHG. Among the top seven sectors contributing to CO₂ emission in India, the construction sector tops the list with about 17% of the total share, when both direct and indirect emissions are considered (Asif *et al.*, 2007). This emission comes from production and transportation of building materials. Manufactured building materials, which consume a large quantity of energy, are commonly used for building construction. Increased use of these energy intensive materials not only depletes the energy resources, but they also produce adverse environmental effects. The main aim of sustainable construction is to minimize natural resource consumption and also minimize the impacts on ecological systems (Charles, 2013).

In sustainable development discourse, there seems to be general consistency in the presentation of environmental aspects, whereby the environment is viewed both as a *source* and a *sink*. The environment is a source of natural resources. The resources can be categorized into renewal, nonrenewable, and other resources. Renewable resources can be regenerated in a timescale relevant to

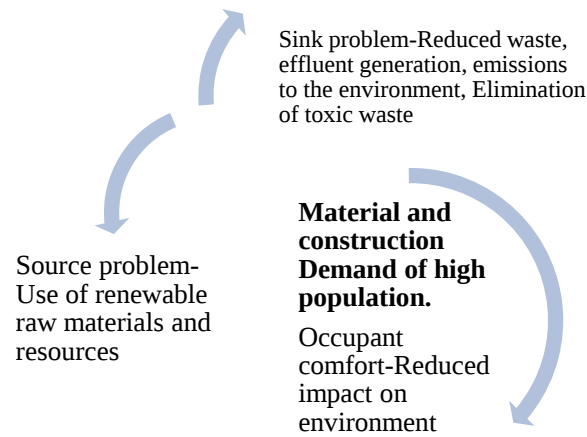


Fig. 3 Environmental Sustainability- 'Source' and 'Sink' side. *Source:* Authors.

man. Nonrenewable resources are those that have taken millions of years to form and can, therefore, not be regenerated on a timescale relevant to man. Other resources include biodiversity, climate (rain, sunshine, wind, etc.), water bodies, landscapes, and terrains. The environment is also a sink for waste resulting from humans and their activities. It absorbs gaseous, liquid, and solid waste as well as the heat resulting from human activity.

Today's increasing demands on environmental resources emanate from high population growth on one hand, and environmentally destructive production and consumption patterns on the other (Meadows *et al.*, 1972). A big population requires more materials from the environment and generates big waste streams. In addition, wasteful production and materialist consumption patterns create a spiraling demand for resources and generate lots of waste. Based on reasonable assumptions about social and a technological condition, the environment imposes limits on economic growth (Gupta, 2008).

Sustainability and its relationship with construction industry considering the environmental dimension of sustainable development is related in Fig. 3.

Construction Technology and Building Life Cycle

Construction technology involves study of the methods of construction to successfully achieve the structural design with recommended specifications. The construction technology entails (1) natural capital: Building materials and water used in construction technique; (2) human capital: Human resource like skilled and unskilled labor; and (3) manufactured capital: Tools and equipment used to execute the technology.

Understanding the sustainability component of any construction technology would involve quantifying, assessing, and evaluating all the aspects of LCA explained above at every stage of construction, such as foundation, superstructure, walls roofs, etc., and interior detailing also. Choices made at every stage offer a plethora of options. The entire spectrum is quite wide and complex. Construction technology involves the choice of building materials and the technique and means used to erect a residential building. Development decisions regarding technology and infrastructure are a major determinant of consumption patterns. It is therefore important to evaluate and make development decisions that structurally contribute to sustainable development. Technologies exist through which substantial reduction in consumption of resources is possible. Efforts to identify, evaluate, introduce, and use these technologies must be made.

This paper demonstrates the possibilities of calculating the sustainability component of wall construction in stone. Basalt stone is locally available in the Vidarbha region and was widely used in rural area of Vidarbha. This technology has its own limitations. It is best suitable for construction of buildings that are not very high, up to three stories, because of its weight. The aim for selecting stone wall construction technology is to demonstrate calculations (partial) for arriving at the sustainable component of this construction technology.

According to Agenda 21 for Sustainable Construction in Developing Countries, "Sustainable construction means that the principles of sustainable development are applied to the comprehensive construction cycle from the extraction and beneficiation of raw materials, through the planning, design and construction of buildings and infrastructure, until their final deconstruction and management of the resultant waste" (Plessis, 2002). The growing significance of the sustainability concept throughout the world has resulted in attitude change in consumption of natural resources for infrastructure development projects. Utilization of large quantity of natural resources for meeting the fast growing building activities and generation of waste has exerted unavoidable pressures on the natural environment with the growing significance in green building concept and the mandatory inclusion evaluation of LCA in building design standards.

By referring to the concept of systems theory, this study proposes that construction technology, when standing in a particular temporal and spatial sequence constitutes the building. The temporal sequence is the requirement that certain activities related to

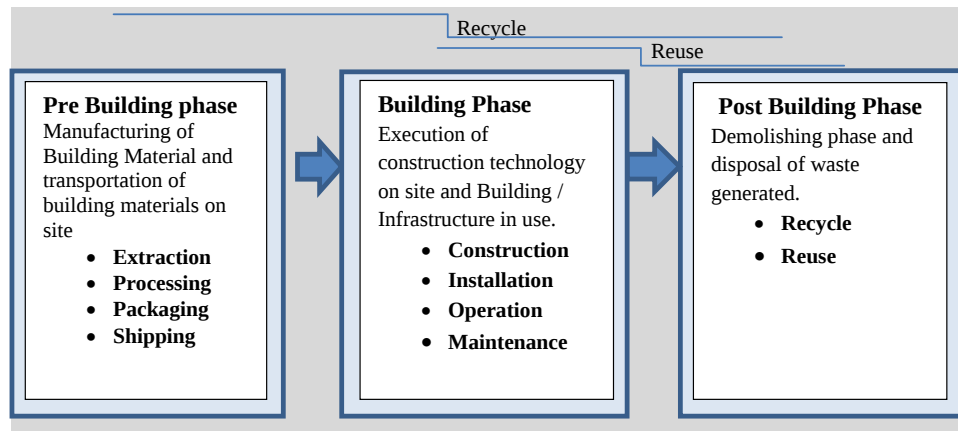


Fig. 4 Three phases of building life cycle in relation with construction technology. *Source:* Authors.

construction of buildings must be done before others. For example, every building must undergo the following series of stages respectively: (1) raw-material extraction, building material manufacture, assembly on site, use/maintenance, demolition, and disposal/recycling; (2) the spatial aspect is included because of the distance that has to be covered within and between the stages identified above, which involves transport; and (3) onsite, the materials must be placed in certain spatial relationship to each other according to the requirement of the construction techniques to form a building. The discussions are aimed at linking building materials and construction technology to the LCA and environmental sustainability.

The comprehensive construction cycle starts from the process of extraction and beneficiation of the raw materials, through planning, design, and construction on site of building and infrastructure and ends with their final deconstruction and management of final resultant wastes. Thus, the construction process could be divided into three distinct building phases: Prebuilding phase, building phase, and postbuilding phase as shown in Fig. 4.

Prebuilding phase includes manufacturing of raw materials, which includes processes like extraction, transportation of raw material, processing, and packaging. The energy consumed in manufacturing of building material is termed as *embodied energy* of the material. The energy required for transportation of raw material from the production unit to construction site is called as *gray energy*.

Building phase includes execution/installation of construction technology by skilled and unskilled labor using required tools and equipment for the execution/erection process. This phase also includes performance of construction technique during the operational phase when the building is functional or in use. Maintenance of the structure during the use of the built space by the occupancy is included in the building phase.

Postbuilding phase includes demolition of construction technology and disposal of waste generated after dismantling of the built structure. Depending upon the building materials and the composition of building materials used in the construction technique the waste generated can be recycled and reused or biodegraded or dumped in landfills.

Considering these three phases of building life cycle, an environmentally sustainable construction technology can be assessed by applying LCA method. Further part of the study focuses on the LCA of stone masonry, the selected construction technology practiced in the Vidarbha region to demonstrate the possibility of a methodology that can be adopted to showcase the judicious choices so that the construction technology is sustainable.

The Integrated Life Cycle Assessment Applicability to Stone Masonry

The principles of life cycle design provide important guidelines for the selection of construction technology. Each step of the manufacturing process, from gathering raw materials, manufacturing, distribution, and installation on site, to ultimate reuse or disposal, is examined for its environmental impact.

Step 1: Defining System Boundaries

The construction technology selected for application of LCA method is stone masonry as the technology is developed and practiced in the region considering regional constraints and it has strong relevance to vernacular construction technology practiced in Vidarbha region. This study focuses on identified criteria relating with environmental sustainability and construction technology considering the building life cycle.

Step 2: Inventory Analysis

The data and information collected to make an inventory analysis for environmental impact of a construction technology over the life cycle of a building at each stage are (1) material input, (2) energy input required, (3) environmental release and by-product or waste generated, (4) total nonenergy natural resources consumption, and (5) cost input.

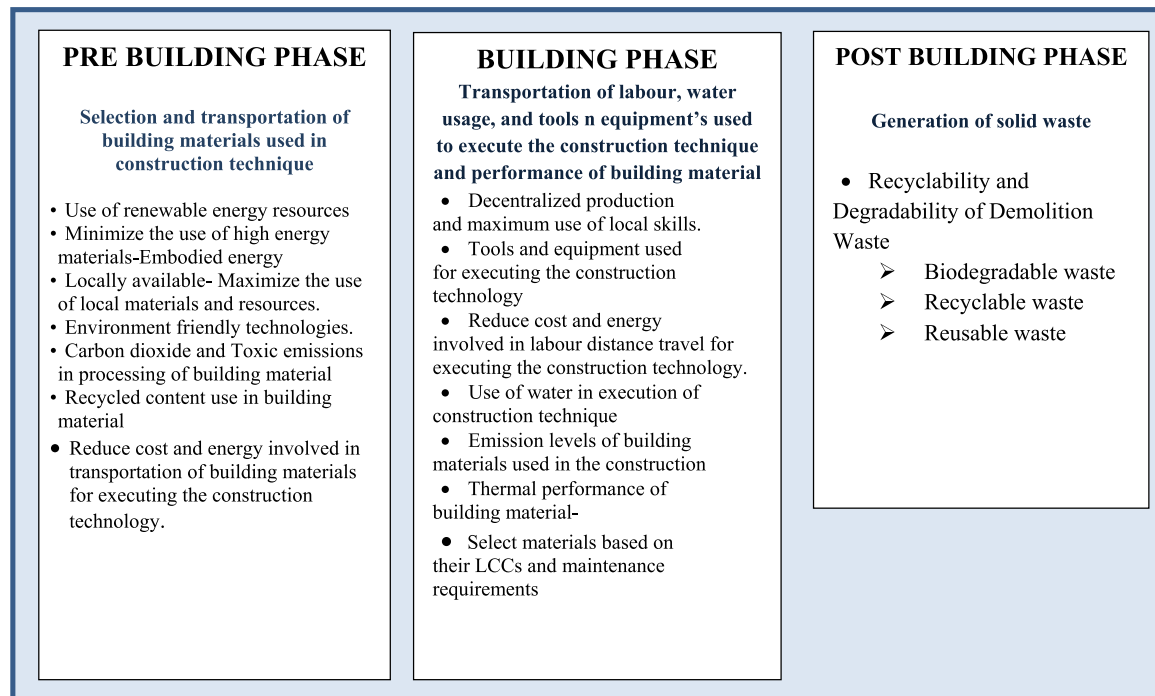


Fig. 5 Building life cycle stages criteria with construction technology. *Source:* Authors.

The materials and energy used in construction technology life cycle are organized into three phases: Prebuilding, building, and postbuilding. These stages are parallel to the life cycle phases of the building itself. **Fig. 5** represents the energy and material consumption at different phases by the concerned construction technology.

Further study elaborates the criteria related to stone masonry at the three different building phases. This stage describes the mathematical simulation and presents the quantitative data resulting from the actualization of the calculations. The data for input into the simulations is a combination of empirical findings and relevant literature. To simplify calculations, the wall-strip component is specified as partition wall.

Prebuilding phase

Renewable resources: Basalt stone used in stone masonry is a locally available material at the selected site location. Stones replenish themselves to some extent in natural form and do not have adverse environmental impact. The energy content in processing the stone as building material is lower than that of artificial materials.

Embodied energy of construction technique: The embodied energy or the energy content of a building material comprises of all the energy consumed in acquiring and transforming the raw materials into finished products. It symbolizes the quotient of its environmental friendliness, reflecting the material's closeness to the earth; the more it is refined or processed the more energy it contains, and hence, more environmentally expensive. In this study, embodied energy of construction technique is calculated. Steps to calculate embodied energy of construction technique involves ([Praseeda et al., 2015](#)):

- Identifying the construction technique from various items of work like walling technique, roofing technique, flooring, door window, etc., in the building.
- Calculation of energy value/unit for each item of work based on the material involved and specification.
- Obtaining the total energy value for each item of work.
- The cumulative energy value of all the items.
- Obtaining the energy value/square meter of the construction technique (**Table 1**).

Regional availability of resources: Using locally manufactured products allows significant reduction in transportation (within 100-km delivery radius). Increased use of locally available materials ensures equity in access to environmental resources by all the people as availability of local resources differs according to the topography and climatic conditions. In stone masonry, basalt stone is locally available material within 10-km distance, sand is brought from 50-km distance from selected site and cement from 185 km. The major material used in stone masonry is basalt stone, which is locally available in the region. Secondly, basalt stone masonry is a traditional construction technique used in vernacular architecture and historical structures.

Elimination of toxic waste or by-product pollutant released in the surrounding in manufacturing process of building material: In stone masonry, the building materials used are stone, sand, and cement; cement is the only material that is highly processed but is used

Table 1 Embodied energy calculation for stone masonry

Random rubble stone masonry in super structure with 1:6 cement sand mortar-unit 1 m³

Take 10 m³

if thickness is 0.4 m for 1 m³ = wall surface area is 2.5 m²

Embodied energy calculation for stone masonry

Materials	Quantity cubic meter	Embodied energy/Unit	Total EE (MJ)
Stone including through bond stone and wastage	12.5 m ³	203 MJ m ⁻³	2537.5
Cement (21 bags)	0.7 m ³ (1050 kg)	5.25 MJ Kg ⁻¹	5512.5
Sand (local)	4.2 m ³	0	0
EE for 10 m ³ -stone masonry			8050
EE for 1 m³-stone masonry			805
Embodied energy calculation for cement pointing 1:2-unit 1 m ² take – 100 m ²			
Cement (6 bags)	0.20 m ³ (300 kg)	5.25 MJ Kg ⁻¹	1575
Sand (local)	0.40 m ³		0
EE for 100 m ² cement pointing			1575
EE for 1 m ² cement pointing			15.76
EE for 2.5 m ² ×2 cement pointing on both sides			78.8
For 1 m³-stone masonry and cement pointing on both sides EE			883.8

Note: Method adopted from Jayasinghe, C., 2011. Embodied energy of alternative building materials and their impact on life cycle cost parameters. In: Proceedings of the International Conference on Structural Engineering and Construction Management (ICSECM). Kandy, Sri Lanka: Department of Civil Engineering, University of Moratuwa.

Table 2 Steps for calculation of CO₂ emission due to transportation of building material

1		A	B	C
2	Material name	Basalt stone	Cement	Sand
3	Quantity used (m ³)	m ³	bags	m ³
4	Density (kg m ⁻³)			
5	Quantity (kg)	Row 3 × Row 4		
6	Fuel type	Diesel	Diesel	Diesel
7	One time carrying capacity	10 m ³	250 bags	10 m ³
8	No. of trips	Row 5/Row 7	1	1
9	One trip distance	10 km	185 km	50 km
10	Total distance traveled	Row 8 × Row 9	10 km	50 km
11	Average of the vehicle	4 km liter ⁻¹	4 km liter ⁻¹	4 km liter ⁻¹
12	Fuel consumption	Row 10 × Row 11	0.25 liter diesel km ⁻¹	0.25 liter diesel km ⁻¹
13	Fuel emission conversion factor	2.62 kg CO ₂ per liter diesel	2.62 kg CO ₂ per liter diesel	2.62 kg CO ₂ per liter diesel
14	CO ₂ emission in kg	Row 9 × Row 12 × Row 13	6.55 kg CO ₂ for 2.5 liter-25 km dist	32.75 kg CO ₂ for 12.5 liter-50 km
	CO₂ emission for materials required for 1 m³ of stone masonry and 5 m² of cement pointing		3.42303 kg	

Note: Method adopted from Shreya, D., 2014. Low Carbon Footprint Homes-Futuristic Homes; Architecture + Design, March 2014, pp. 96–97.

in very small quantity. Stone used for masonry is the least processed material; hence, there is no emission of toxic waste. However the weight of stone is heavy; hence, it impacts the carrying capacity per trip of the vehicle.

Carbon emission due to transportation of building material: Local materials should be used available in the region to reduce carbon emission due to transportation (TERI, 2004). The main benefit of using regional construction techniques is the reduced environmental impact due to shorter distance required for transporting locally available materials. The calculation of carbon emission due to transportation of building materials used in selected construction technology can be done by the method (Sengupta, 2010) given in the Table 2 as shown below for materials used in stone masonry.

Building phase

Technical execution of construction technique

Tools and equipment used for executing the construction technology

In stone masonry, simple tools manually operated and locally manufactured are used in the manufacturing process of building materials as used in construction techniques as well as executing it on site. Simple tools locally manufactured contribute to the

Table 3 Number of skilled and unskilled workers to execute stone masonry

Quantity and cost of material for stone masonry in super structure with 1:6 cement sand mortar-unit 1 m³ take 10 m³
 1 m³ masonry, if thickness is 0.40 m. $1/0.40 = 2.5 \text{ m}^2$
 Wall area of 1 m³ = 2.5 m²

Materials	Quantity or Nos.	
Stone including through bond stone and wastage	12.5 m ³	
Cement (21 bags)	0.7 m ³	
Sand (local)	4.2 m ³	
Labor calculation for random rubble masonry		
Type of Labor	Number of workers	
Mistri (Head mason)	4	Skilled labor
Boy or woman coolie	12	Unskilled labor
Labor for stone masonry: For 10 m ³		
No. of skilled workers – 4; No. of unskilled workers – 12		
Labor for stone masonry: For 1 m ³		
No. of skilled workers – 0.4; No. of unskilled workers – 1.2		

Note: Dutta, B.N., 2016. Calculation of quantity of building material to execute the technique. Estimating and Costing in Civil Engineering (Theory and Practice). New Delhi: UBS Publisher.

economy of the region uplifting the socioeconomic status of the region. This can be achieved because the simple technology-based techniques defining characteristics of local production based on local resources necessarily decentralize the production activity. Decentralized production systems and small scale operations generate local employment.

No. of skilled and unskilled workers used for executing the technique

In stone masonry, the nature of the processes of production and assembly of building materials will also have an impact whereby labor-intensive approaches will generate more employment than capital-intensive methods. The skills required are been readily available in local communities as the material stone has been used since ancient times. **Table 3** gives the quantitative analysis of the number of skilled and unskilled workers required to execute the stone masonry on site.

Water usage

Efficient use of water in construction/low consumption of resource water: In stone masonry, construction requires comparatively less water for execution as well as for curing to reach required strength. This technique uses quarried and seasoned stone with no further processing. This technique uses cement mortar for joint and pointing as finished surface; hence, it needs curing.

Operational building phase: When structure is in use

The check on emission levels of certain building products will reduce the effect on the occupants' health and productivity as well as air quality. In stone masonry no products or materials are used that emit pollutants exceeding the capacity of the building ventilation or filtration equipment to remove them to an acceptable level as the material does not need external finishing coats, such as paints.

Thermal performance of building material: Energy required in building is mostly toward providing thermal comfort. Energy savings in a building can be achieved by appropriate energy efficient design of building envelopes. The building envelope configuration and its thermophysical properties such as heat capacity and thermal diffusivity of the building wall material affect the time lag and decrement factor. Building walls with lower thermal transmittance (U) value has better capability to reduce indoor surface temperature variations (Balaji et al., 2013). Stone wall thickness is more; hence, thermal performance of the technique is better.

Low maintenance requirement: Materials selected to execute the construction technique should respond to the local climatic condition. Secondly, low quality building materials reduce the built structure lifespans and increase the need for maintenance interventions. Stone is intense hard material and its bond with cement-sand mortar is hardwearing and is resistant to damage by abrasion, scratches, or impact. Because of this resistance, the wall is not easily susceptible to damage. For this reason, the stone wall is assessed as having the lowest maintenance requirements. This fact is also proven in the historical structures and vernacular techniques in the region.

Postbuilding phase

Generation of solid waste: Minimal construction waste during installation reduces the need for landfill space and also provides cost savings. The wastage of resources due to inefficient processes or tools causes an increase in investment costs of around 12%. But, beyond the negative influence on costs, wastage also causes negative impacts on resource consumption (Wallbaum et al., 2012). It is observed on site that there is minimum solid waste generated in execution of stone masonry as wet mix mortar is prepared and utilized in proportion per cubic meter masonry to be executed per day on site.

Reusable waste: Material waste generated after demolition of construction technique can be reused as it is without having undergone any type of reprocessing. Reusability is a function of the age and durability of a material. Very durable materials may have many useful years of service left when the building in which they are installed is decommissioned, and may be easily extracted and reinstalled in a new site. When demolished, stone wall can be reused as a building material.

Table 4 Quantified data from inventory analysis used for impact assessment

<i>Environmental impact</i>	<i>Particulars</i>	<i>Quantity</i>	<i>Reference: For 1 m³ stone masonry and 2.5 m² *2 of cement pointing on both sides of masonry</i>
Source side	Stone	1.25 m ³	Building materials for stone wall including cement pointing on both sides
	Cement	0.08 m ³ /117.65 kg	
	Sand	0.440 m ³	
	Skilled workers	0.4	No. of skilled and unskilled workers (Ref. from Table 3)
	Unskilled workers	1.2	
Sink side	Embodied energy of construction technique	883.8 MJ	(Ref. from Table 1)
	Carbon emission due to transportation of building materials	3.42303 kg	(Ref. from Table 2)

Step 3: Impact Assessment Analysis

The third step, impact assessment analysis, is a quantitative and qualitative process to characterize and assess the effects of the environmental burdens quantified in the inventory. More so, the LCIA phase evaluates potential environmental impacts and estimates the resources used in the modeled system. For further analysis the criteria and subcriteria selected for inventory analysis are presented in a hierarchical structure known as value tree, followed by consequential steps such as problem identification, generation of options, assigning relative weights, assessment of consequences, and final decision for impact assessment analysis.

In this study it is categorized on the sink and source side of the environment. On the source side it focuses on consumption of resources and on the sink side it refers to emissions or pollutants released in the environment. The quantified data is used to evaluate environmental impact. CO₂ emissions by use of cement considering the manufacturing process of cement, transportation of raw material, and embodied carbon emission values can be summed and can quantify the contribution to the global warming impact category.

The following table represents the quantity of raw material used in construction of 1cu. m. stone masonry with 2.5 m² wall surface area of wall thickness 0.40 m and cement pointing on both sides of the wall, cost of construction, number of skilled and unskilled workers used in execution of construction technology, embodied energy, and carbon emission due to transportation of building materials. Stone Masonry Results of Mathematical Simulation can be used for impact assessment (Table 4).

Step 4: Improvement/Interpretation Analysis

A simple and effective measure to reduce the environmental impact of construction is responsible materials management at the construction stage. There is, thus, ample scope for energy reduction and carbon dioxide abatement within the construction life cycle. Embodied energy and carbon estimates, of the type provided by the database, are one aspect in the process of evaluating the life-cycle impact of construction. It is also important to evaluate the operational lifetime and maintenance requirements of building materials to enable the construction of true low embodied energy and carbon construction emission. Adopting these simple steps and considering entire building life cycle phases, construction technology selection criteria can be applied at the design phase.

Discussion and Conclusion

Construction technology is the core subject of focus in this study, which has a strong link with sustainable development. This link is explicated by referring to environmental sustainability issues to building life cycle stages of construction technology. This linkage addresses the case in an illuminated manner that the identified criteria are applicable to LCA of construction technology. There is a need to give reasonable rationale for using sustainable construction criteria suited to analyze the construction technology. This paper aims to establish a link between environmental sustainability issues with LCA method as interpreted with building life cycle stages for analysis of construction technology. The link developed so far is used stepwise in LCA of construction technology in the selected site context. Steps, procedures, and precautions to be taken in calculations, related to the LCA of a selected construction technology, are demonstrated in this paper. The same procedure can thus be applied to other elements of building from foundation to roof and also to the finishing materials used in the interiors of the building. Cumulative effect is important. Thus an emphasis is on developing the strategy for calculation at every step of construction and presenting a ready reckoner to the building industry for making judicious choices while undertaking a construction project.

The LCA methodology globally accepted to quantify the multiple criteria existing for evaluating the sustainability of a construction technology is expensive and entails a specific knowledge on this topic, but constitutes the most reliable tool to evaluate the environmental load associated to a construction technology. Consequently, there is a need in the building sector for the classification and characterization of all construction technology employed in a building to prescribe the most suitable construction technique in a selected site context to be incorporated in architectural projects.

See also: Traditional Crafts as Materials in Placemaking: Application and Sustainability in Aesthetic Transformation of Geometry of Urban Public Spaces

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Material Culture and Sustainability: Traditional Versus Modern in a Case of Northeast India

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Introduction

In the past several years, the concept of sustainable architecture has evolved significantly. It cannot be denied that traditional architecture of any region has been a source of knowledge and inspiration in practicing sustainable architecture. Traditional architectural design is an extraordinarily perceptive practice that has evolved through interpretation of past knowledge and experience and has been tailored to meet the needs of time, and this evolution has happened through trial and error without being based on any scientific research or study (Upton, 1993).

Today in the unsustainable world of architecture and planning, we have high regards for sustainability. It is considered as a fresh idea that has made people conscious about concepts of ecology, energy efficiency, cost efficiency, etc. However, we often fail to see that this concept has prevailed throughout the ages and only needs to be understood and rediscovered.

Sustainability – A Traditional Concept

As mentioned before, it is believed that the concept of sustainability is a relatively new idea. The Brundtland Commission's final report, *Our Common Future*, famously defines sustainable development as: "development that meets the needs of the present without compromising the ability of future generations to meet their own needs." Whether we consider this definition or any other and study the traditional architectural and planning practices, the fact would be undeniable that sustainability has been followed as a very important concept in the past.

There is nothing extraordinary in traditional architecture. Traditional architecture and planning has been just a solution to the needs and problems of the society. And these solutions have been a result of years of experience and knowledge. In fact, traditional architecture is not just an individual entity; it always has a particular relationship with the surrounding, as the surrounding environment is also the source of life for all those living there (Oliver, 2006).

The traditional settlements in India have all evolved as a sensitive response to the surrounding, the ecology, climate, and also culture. Spiritual beliefs are another factor that has helped to conserve many natural elements like trees and rivers and water bodies.

For example, in Ladakh, a region in the Indian state of Jammu and Kashmir, which has a cold and dry climate, the traditional houses are built on two levels. The lower level being reserved for cattle, wood, fodder, etc., for winters, whereas the upper level consists of the livable space. Ovens are sometimes placed in the corners, which also help in keeping the interiors warm. The houses are made entirely of mud, sometimes reinforced with horizontal timber members. The sundried brick or rammed earth walls are often mud plastered. The ceiling height is kept low. Thus, every possible care is taken to trap the heat and maintain the temperature inside for comfortable living (Sharma and Sharma, 2016).

Similarly in the hot and dry climate of Jaisalmer of Rajasthan, which is a state in the northwestern part of India, the heat inside the building is controlled by using textures organized at two levels, the town level and the building level. At the town level the buildings are built with unequal heights with parapets and high walls. This creates irregular skylines, which make the buildings shade each other. The roads are also kept narrow so that they are shaded most of the daytime. At the building level, the facades are designed with numerous projections, like *jharokhas*, which are overhanging, semi-enclosed small balconies and *chajjas*, which are small overhangs or canopies over the openings. Such projections not only make the facade visually appealing but also act as a shading device for the facade (Arora, 2018).

Material Culture

"Material culture" refers to the physical or technological aspects of our daily lives, including food items, houses, factories and new materials, etc. Studying the elements of material culture gives us an insight about the people who interacted with or used those objects.

The term *material culture* emphasizes how apparently inanimate things within the environment act on people, and are acted upon by people, for the purposes of carrying out social functions, regulating social relations, and giving symbolic meaning to human activity (Woodward, 2007).

Architecture is a very important element of material culture and also probably the most complex of all. It is also a dynamic component of material culture that should not be studied in isolation from other material assemblages. Thus while studying the architecture of an area, it is very important to understand the preceding social, environmental, and cultural conditions that contributed to the type of architecture in the particular area.

Keeping that in mind when we study the traditional architecture of a place or region, we can see that it connects to every component of the setting very carefully whether it is the surrounding, climate, or culture.

Traditional Architecture in Northeast India

The Northeast of India comprises of eight states, namely Arunachal Pradesh, Assam, Meghalaya, Manipur, Mizoram, Nagaland, Sikkim, and Tripura. This region is very distinct in terms of its customs, rituals, and ethnic culture, which are abundant here. Geographically the region is a combination of plains and mountains both, which makes it abundant in natural resources as well. Most of these states have a humid subtropical climate with hot and humid summers, severe monsoons, and moderate winters. The states of Arunachal Pradesh and Sikkim, however, have a montane ecosystem with cold, snowy winters and mild summers.

The traditional structures are time tested, sustainable, and show great respect to the existing microclimatic conditions and are also sensitive to the natural calamities, including earthquakes and floods, which the Northeast region is extremely prone to.

This region of India is one of the most seismically active regions in the world; three great earthquakes and several big earthquakes have struck this and adjoining regions in the last 110 years. The region experiences severe shaking due to subduction of the Indian plate under the Eurasian plate along the northeastern direction at a rate of about 40 mm per year (Kaushik and Babu, 2009).

The architecture in these areas has developed over the ages as aspects of tradition, climate, topography, and function. Locally available materials like bamboo, cane, mud, and lime are generally used for construction. Influence of the British style has also added to the tradition where bricks, wood, stone, rock slabs, etc., are also being used. As these areas are susceptible to heavy rainfall, sloping roofs are a common architectural feature in all the structures.

Although the traditional architecture in these areas differs from each other as the traditions, culture, and function differ from area to area, there are certain similarities. Based on those similarities the traditional architecture can be categorized in two broad sections: *Kachcha* structures and *pukka* or semi *pukka* structures (Nag and Gondane, 2014).

Kachcha construction

Kachcha, meaning raw or uncooked, is an adjective used for structures made of natural and locally available materials such as mud, bamboo, and thatch. Consolidated earth with timber or bamboo posts are used for the plinth and footing and the walls are made with bamboo frames and mat. The roof is usually thatched with hay, cane, and palm leaves with split bamboo frames. In some regions the walls and floor are also plastered with a mixture of mud and cow dung. In colder areas such as Arunachal Pradesh, the bamboo in the walls is taken over by wood or stone, which helps in retaining the heat.

Similar houses are sometimes built on stilts. Called *Chang ghar* locally (Fig. 1), these stilted houses are built in areas that have high precipitation and moisture content in the soil. The basic idea is to keep away the effects of monsoons. Bamboo being a bad conductor of heat also helps to keep the interior cool in summers and the permeable bamboo surfaces of the walls and floors keep the moisture content low inside (Kaushik and Babu, 2009). The lower level of the *chang ghar* is also used to shelter the cattle, which helps in keeping the interiors warm.

Another variation in *kachcha* structures is the high pitched roof, which is again built with slight variations based on tribal identities. Such structures are mostly built in Nagaland, which is a comparative hilly and colder region. The steep slope of the roof ensures that no water enters the building. The fenestrations are minimal to trap the heat as much as possible (Nag and Gondane, 2014).

Pukka construction

On the other hand the *pukka* or semi-*pukka* structures are made with a combination of organic and inorganic materials. These are a result of the influence of the British colonial architecture to the local architecture.

The most common type of *pukka*, which means cooked or that which is not raw, is the *Ikra* type of construction, which is also known as the Assam type house. Buildings of *Ikra* type of construction are found in most of the northeastern states. The



Fig. 1 A *chang ghar* in a village in Dhemaji district, Assam. Reproduced from Karmakar, S., 2014. Flood control, the missing way – Dispur falls back on 'Coping Practices' of indigenous communities to tackle annual disaster. The telegraph. Available at: https://www.telegraphindia.com/1140717/jsp/northeast/story_18623734.jsp (online) (accessed 16.08.18).

name *Ikra* is derived from the locally available reed known as *Ikra* and it is used extensively in walls and roofs of such houses. Generally, it is a single-story house; however, two-story houses are also found in some places. Based on local requirements, small variations are present in different areas. *Ikra* houses are built on raised plinths to avoid marshy grounds and surface run-off during rains and also stray animals and reptiles. The vertical columns and roof truss are made of wood, usually *Sal* wood.

The wall panels are made of either wood or bamboo frames and are then infilled with the shoots of the *Ikra* reed oriented in the vertical direction; the *Ikra* reed shoots are plastered from either side with mud–dung mixture. In some cases slitted bamboo is also used for the infill instead of *Ikra*.

The covering on the roof truss is a thick stack of *Ikra* reed. However, many such buildings use corrugated GI sheets that are more durable. The roof is pitched with a high gable to cater to the heavy rainfall in the region over many months (Alhasani, 1996). The slope of the roof varies from one-third to one-fifth of the span. Thatched roofs have steeper slopes than the GI sheet roofs.

One major drawback of such construction is the fire hazard. Therefore precautions are taken in terms of design and planning. The kitchen, which is the main source of fire accidents, is built away from the main house or an open veranda of about 3 m is generally provided between the kitchen and the rest of the house to prevent fire accidents.

Ikra-type of construction is not restricted only to dwelling units but also it is implemented in commercial, institutional, and religious structures. The composition of the spaces and also the building elements may differ based on the functional requirements. For example, the shape and slope of roof, windows, doors, etc., for a church will be completely different than a school or college building, and that again will be different from a residential building. Fig 2 is an example of an old institutional building constructed with *ikra* which has survived the tests of time. The architecture follows a general norm of having at least one door in the rear of the house that can act as an escape route in case of any emergency.

This construction technique has been in use for at least 200 years and has proved to be extremely good in several past earthquakes in the region. The lightweight materials used for walls and roofs, flexible connections between the elements, and also the planning are some of the factors that have improved its performance during natural calamities (Kaushik and Babu, 2009).

Sualkuchi – Identifying a Typical Site of Northeast India

Located 36 km away from the city of Guwahati in Assam, is the historic settlement of Sualkuchi. The importance of this settlement throughout history is because of the production of silk and this significance is reflected in the settlement with distinguishing features demonstrating ecological, social, and economic examples for sustainability.

Sualkuchi has been known since the 4th century BCE as a center for silk weaving and is the busiest silk textile center of the northeastern region of India. It used to be a major contributor in the production of the most expensive *Muga* silk. This particular golden silk is a very important part of the Assamese culture. Historically its importance can be determined by the fact that sericulture was exempted from payment of land revenue as the kings of Assam patronized the development of sericulture (Baishya, 2005).

Sualkuchi is a traditional village of weavers, which has preserved, sustained, and transmitted a cultural system. The structure of the heritage settlement as it is today was basically established by Momai Tamuli Barbarua, an administrator of the Ahom kingdom during the reign of Swargadeo Pratap Singha (1603–1641). This patronage led to the advancement and development of sericulture in Assam (Morol, 1979).

The sociocultural institutions like the *Satras* (monasteries), located within played an important role in the survival of the system. This system was sustainable and is reflected in the planning of the settlement as well as in the traditional architecture. The traditional architecture of the settlement had developed as a response to the natural environment and most importantly to



Fig. 2 A more than a century old traditional building of the Cotton College in Guwahati, Assam (Author, 2012. Photograph by Farha Shermin).

accommodate the function of silk production. This sustainable cultural system has not only supported the process of silk weaving but had also led to the advancement of silk production in the region.

Even today, it is sustaining the tradition, although in many cases in a transformed form. This settlement has been chosen because at present it is on the verge of transformation. The settlement is an amalgamation of reminiscence of ancient history and modern culture and thus is a perfect example to study the transformation, which has directly or indirectly affected the aspects of being a sustainable development.

Sualkuchi as a Sustainable Settlement

The historic settlement of Sualkuchi can be explicitly considered as a sustainable one. The concept of sustainability can be defined as having three independent spheres of influence, which are ecological, socioeconomic, and physical sustainability (Tipnis, 2012).

Ecological Sustainability – The setting of Sualkuchi is ecologically very significant. The settlement is located between natural features that form its boundaries, the Bor-beel, which is a wet land, to the northwest, the Gandhmou hills to the east, the river Brahmaputra to the south, and the Siddeshwar hills to the west (Fig. 3). Other than the hills and the water bodies, the settlement lies in a gently sloping land, which slopes down towards the Bor-beel and the river. This ensures good water drainage. The expansion of the settlement is regulated by these natural features.

Also, a small valley is formed between the Siddeshwar hills, which connects the Bor-beel and the Brahmaputra River. A number of manmade ponds are located in this valley. This whole system ensured drainage of the water to the river.

There are number of manmade ponds or *pukhurs* as they are locally called, which act as water reservoirs during dry seasons and also recharge the ground water. The locations of the *pukhurs* were also decided based on the natural drainage. Another interesting feature is the presence of a natural embankment in the east, which benefits a portion of the settlement by obstructing the water and thus preventing the floods. The settlement has restricted its growth towards the river to safeguard the flood plains. The overall ecological setting favors the production of silk.

Socioeconomic Sustainability – A very crucial aspect of sustainability is the social and cultural significance. The local society and culture is best expressed in the way they manage their environment. The built environment in such a sustainable area is thus shaped by the social values and beliefs of the community.

Socioeconomic sustainability in Sualkuchi is prevalent in Sualkuchi from the time it was established. This is evident from the fact that the settlement was deliberately planned on the basis of the communities who were to reside there. Based on oral history and present context, Fig. 4 shows an estimated location of the communities as per the original settlement plan.

The main community was the *Tanti* or weavers' community and the rest were placed to support the Tanti community. The communities were mainly occupation based. They were placed on the site according to hierarchy and also feasibility of workplace. For example, the *Koiborto Para*, which is the fishermen's community, is located near the river bank, whereas the *Mahanta Para*, which is the priest's community, was placed in the heart of the settlement. A water canal was later added, which was not only a source of water but also a physical demarcation that divided the weavers and nonweavers' communities. The same exists even today.

The weavers' communities settled on the west of the canal were very interestingly planned in a grid iron pattern, which formed small clusters. Each cluster is bounded by roads on all four sides. All the houses faced the roads and the central area of the cluster was an open space to grow mulberry trees. The heart of the settlement where the two axial roads meet formed the market place.

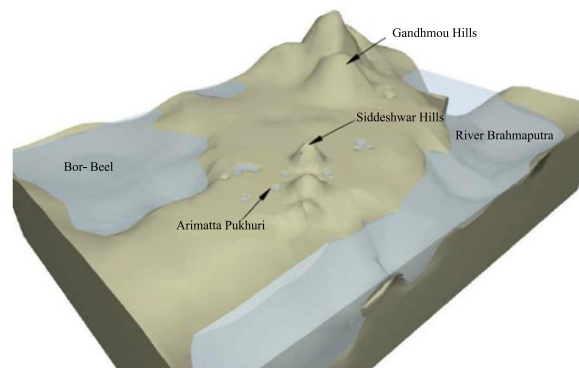


Fig. 3 The natural setting of the settlement. Reproduced from Shermin, F., 2017. Impacts of rural tourism on architectural and cultural heritage – The cases of Sualkuchi and Mawlynnong, Northeast India. International Research Journal of Engineering and Technology 4 (11), 318–322. Available at: <https://www.irjet.net/archives/V4/i11/IRJET-V4I1156.pdf> (online) (accessed 10.06.18).

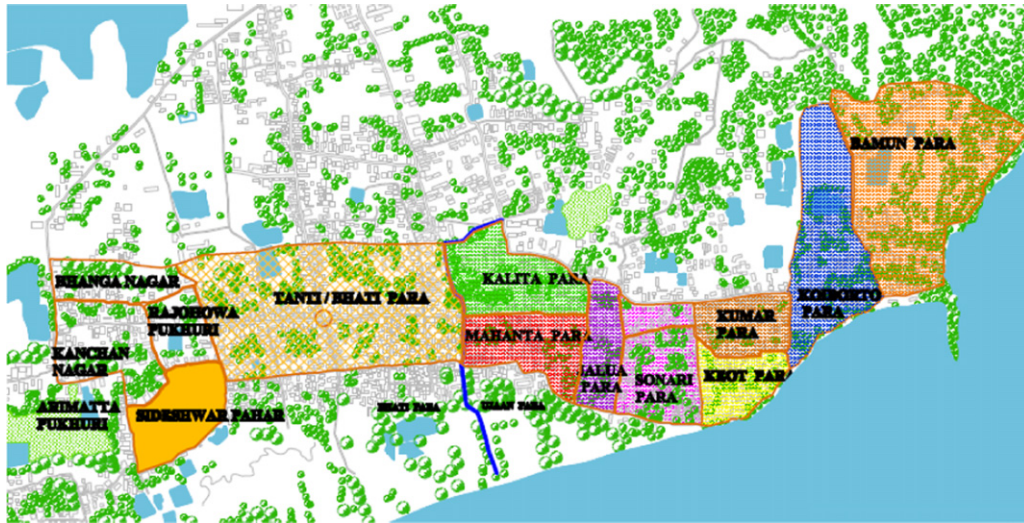


Fig. 4 The occupation based communities of Sualkuchi. Reproduced from Shermin, F., n.d. Conservation of the Vernacular Residential Architecture of the Historic Crafts Settlement of Sualkuchi. New Delhi: School of Planning and Architecture (Postgraduate in Architecture).



Fig. 5 A traditional house at Sualkuchi. Reproduced from Shermin, F., 2017. Impacts of rural tourism on architectural and cultural heritage – The cases of Sualkuchi and Mawlynnong, Northeast India. International Research Journal of Engineering and Technology 4 (11), 318–322. Available at: <https://www.irjet.net/archives/V4/i11/IRJET-V4I1156.pdf> (online) (accessed 10.06.18).

All the communities were interdependent; the Koiborto community supported by providing fish, which is a staple diet of the region; the *Jalua keot* (net makers) community supported the Koiborto community by providing nets for fishing; the basket makers provided bamboo baskets, which are necessary for rearing of silkworms, and so on.

Further, when we consider a cluster, it has been observed that each cluster functions as an individual unit that combines with other clusters to form a system. This has been discussed later in the article.

The contemplative planning and functioning of the settlement and cluster creates an intricate system that functions as a whole to directly or indirectly sustain silk production. This system also ensured community participation or involvement in the overall process.

Physical Sustainability – Physical sustainability is the most tangible aspect of sustainability. With the change in needs and values of the society, the physical built environment either adapts itself to suit the new demands, is abandoned, neglected, or is replaced. Physical sustainability is that quality of a building that allows it to adapt itself to the changing needs (Tipnis, 2012).

Sualkuchi as a built environment has been growing and developing throughout the ages. Traditional architecture of the settlement is a result of the quality and value that this particular culture has produced. It is typified by durable bamboo framework, and mud plaster. Ikra houses are the common typology seen in the whole of the settlement (Fig. 5). The significance of the architecture has a lot to do with the environment, climate, and weaving other than esthetics.

The ikra houses are generally single dwelling units and do not have common walls with adjacent buildings. The ikra and bamboo construction material keeps the interiors cool in summer and warm in winter and also helps in sustaining during earthquakes. The plinth was constructed in stone or brick. The walls in some of the dwellings were partially constructed in brick, which formed a sturdier base and is extended with bamboo or ikra with mud plaster. The basic structure of the wall is the timber framework. The framework is then filled with ikra and bamboo woven panels. The ikra is cut in size of the panel and laid vertically. Bamboo is used as the horizontal member, which is woven with the ikra. After a few days when the ikra is dry, the wall is plastered on both sides with mud plaster. The finished coat is usually a mix of mud and cow dung, which gives a smooth finish.

The roof can be single or it can be in various levels and multicornered. Initially thatched roofs were used, which were later replaced with corrugated iron sheets.

Weaving, being the main occupation and an important aspect of the culture, plays a dominant role in shaping the architecture of the settlement. Every traditional household has tried to accommodate weaving inside the house.

As most of the communities today have taken up weaving as their means of livelihood, the residential architecture has been altered to accommodate this change in their occupation. The original weavers had a separate area dedicated to weaving inside their house, whereas the residences of those who became weavers later had either an area modified to accommodate the looms or had a separate space outside the house for the same.

As discussed before, a traditional cluster was designed to accommodate the various activities of silk weaving. Similarly, a traditional weaver's house was also designed to accommodate the same. The loom, being the most important element in a weaving room, was the basis of the design of the weaving area. The height of the fenestrations was based on the height of the loom as constant daylight was required for weaving. The weaving rooms had a bamboo *jaali* (latticed screen) running from the sill to lintel level for undisturbed lighting and ventilation throughout the room. The sloping roof is covered mostly with corrugated GI sheet, which helps in easy draining of the rain water but in summer heats up the interiors. This issue is resolved by placing a false ceiling made with woven bamboo mats. Most of these houses also have an attic space, which is the space between the false ceiling, and the sloping roof, which is used as the storage. Fig. 6 shows an illustration of traditional weaver's house and images of a typical false ceiling and access to the attic.

Settlement History and Changes Today

As mentioned before, the settlement was planned during the Ahom rule. But from historic records it is known that the settlement existed since the 4th century BCE on the basis of Kautilya's (a scholar of the Mauryan Empire, who authored the ancient Indian political treatise, the *Arthashastra*) reference to *Suvarnakudya* of ancient *Kamrupa* (historical kingdom of Assam) where the best quality of *patorma* (Pat silk) was produced. The presence of a 400-year-old monastery called as the *Hati Satra* and a temple called as the *Siddeshwar Devalaya*, which is known to have been built in the 14th century BCE by king Arimatta, and several historic manmade water bodies, shows that the earliest existing settlement must have been along the road from Siddeshwar Devalaya. Most of the old buildings are found in and around this area. During the Ahom rule, the settlement became a commercial hub. It was due to this reason the market area gained significance.

The most recent phase, which has drastically changed the settlement, is the construction of the outer road along the Bor-beel, and the Hospital road. These roads gave a new dimension to the settlement, but ignored the natural system of drainage, unlike the historic settlement. There is also an extension towards the east, where new institutional buildings have been constructed (Fig. 8).

Traditional Versus Modern

The new areas along the outer road display a complete different planning and design, which partially or in some cases completely disregards the aspects of sustainability. To understand this, two clusters have been selected for study: One from the historic core and the other from the new developed areas.



Fig. 6 A traditional weaver's house at Sualkuchi. Reproduced from Shermin, F., n.d. Conservation of the Vernacular Residential Architecture of the Historic Crafts Settlement of Sualkuchi. New Delhi: School of Planning and Architecture (Postgraduate in Architecture).

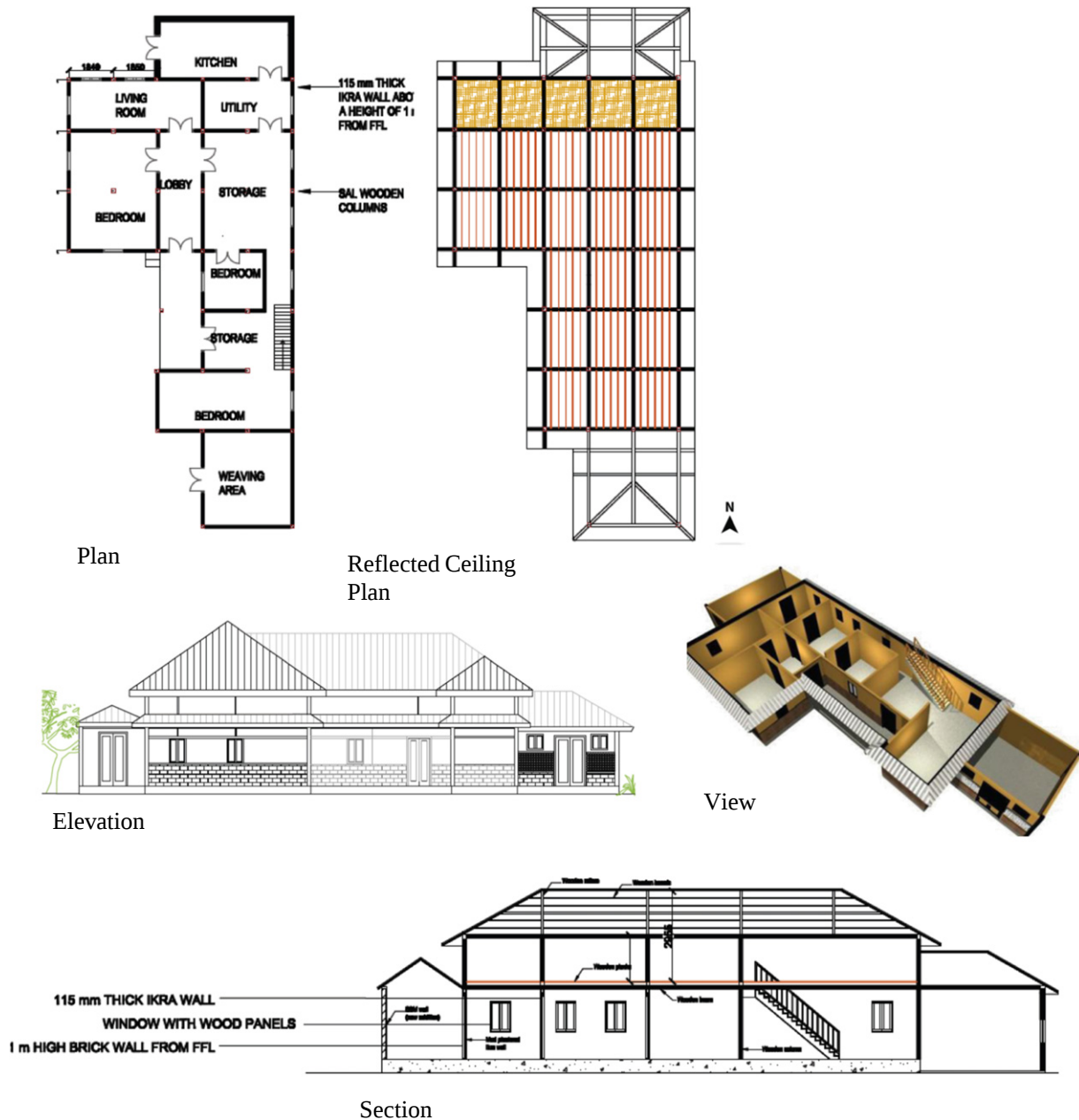


Fig. 7 Documentation of a traditional weaver's house at Sualkuchi. Reproduced from Shermin, F., n.d. Conservation of the Vernacular Residential Architecture of the Historic Crafts Settlement of Sualkuchi. New Delhi: School of Planning and Architecture (Postgraduate in Architecture).

A traditional cluster

Each cluster functions as an individual unit, which combines with other clusters to form a system. With reference to the Fig. 9, it is clearly seen that the spaces for every activity related to silk weaving are clearly designated. Linear spaces along the roads are used for drying the silk yarn and the finished fabric. The common open spaces bounded by two or more dwellings are used for silk reeling. The weaving of the silk takes place inside the house and the central core of the cluster is used for silk rearing in the mulberry plants. This proximity helped the members to look after the silkworms to ensure their safety from birds and other predators. The clusters were also in close proximity to the market, which enhanced the efficiency of silk production and supply.

The traditional buildings were also designed to be climate responsive and low cost and could sustain natural calamities.

Newly developed cluster

As the settlement expands towards the north, the vernacular character of the clusters changes drastically. Apart from loss of the function of the traditional cluster, a new cluster seems to have developed randomly without any concern to the natural ecology, climate, or even function (Fig. 10).

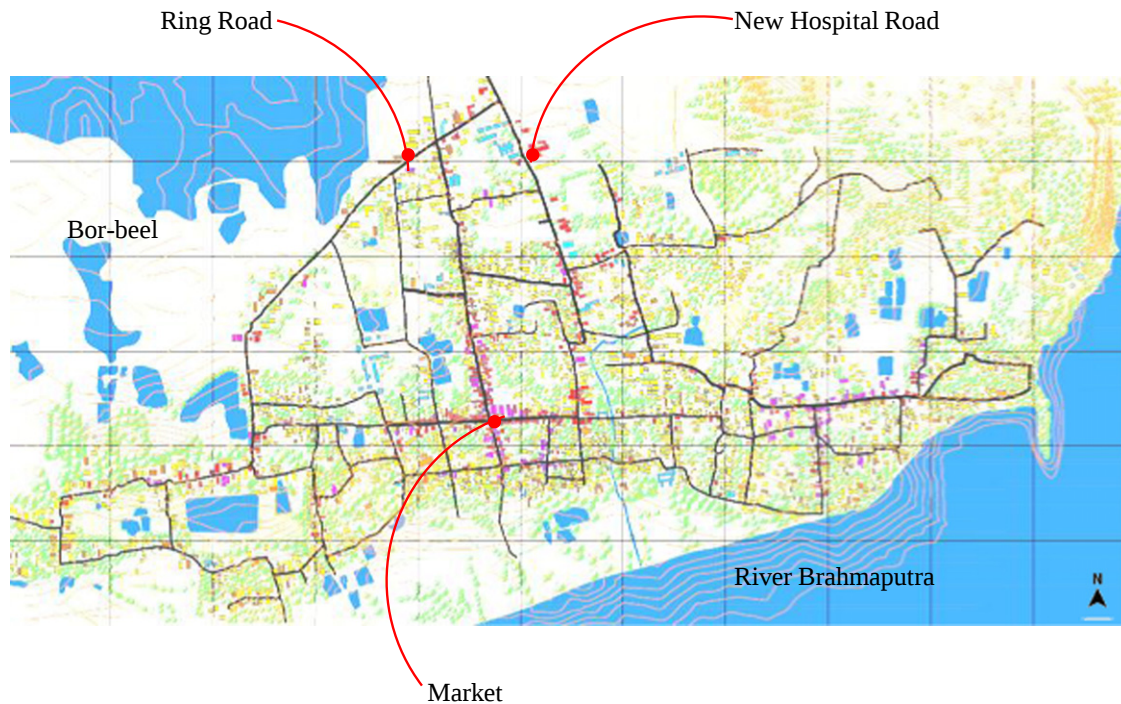


Fig. 8 Sualkuchi. Reproduced from Shermin, F., n.d. Conservation of the Vernacular Residential Architecture of the Historic Crafts Settlement of Sualkuchi. New Delhi: School of Planning and Architecture (Postgraduate in Architecture).



Fig. 9 Traditional clusters. Reproduced from Shermin, F., 2017. Impacts of rural tourism on architectural and cultural heritage – The cases of Sualkuchi and Mawlynnong, Northeast India. *International Research Journal of Engineering and Technology* 4 (11), 318–322. Available at: <https://www.irjet.net/archives/V4/i11/IRJET-V4I1156.pdf> (online) (accessed 10.06.18).

In addition to that, a new typology of residences can be seen in the newly developed areas. This typology is of linear temporary houses for the wage-based workers who work as hired weavers. The linear houses mainly consist of continuous rooms, with each family occupying a room. The standard of living of these people is very low. This has created a social hierarchy in the new clusters that completely disturbs the social sustainability that existed in the past.

The weaving areas are temporary structures made with bamboo with a flat bamboo roof. Fenestrations hardly exist and therefore artificial lighting is required throughout the day. The flat roof, low plinth, and unstable structure disrespect the concept of sustainability in that area.

The other new structures are concrete buildings, which are of two forms. One that follows the traditional vocabulary but uses modern materials like concrete and glass and the other, which is completely a modern structure that is similar to any other building and can exist in any part of the world. The performance of these materials in earthquakes and in maintaining the temperature inside is much less than that of a traditional ikra or bamboo structure.

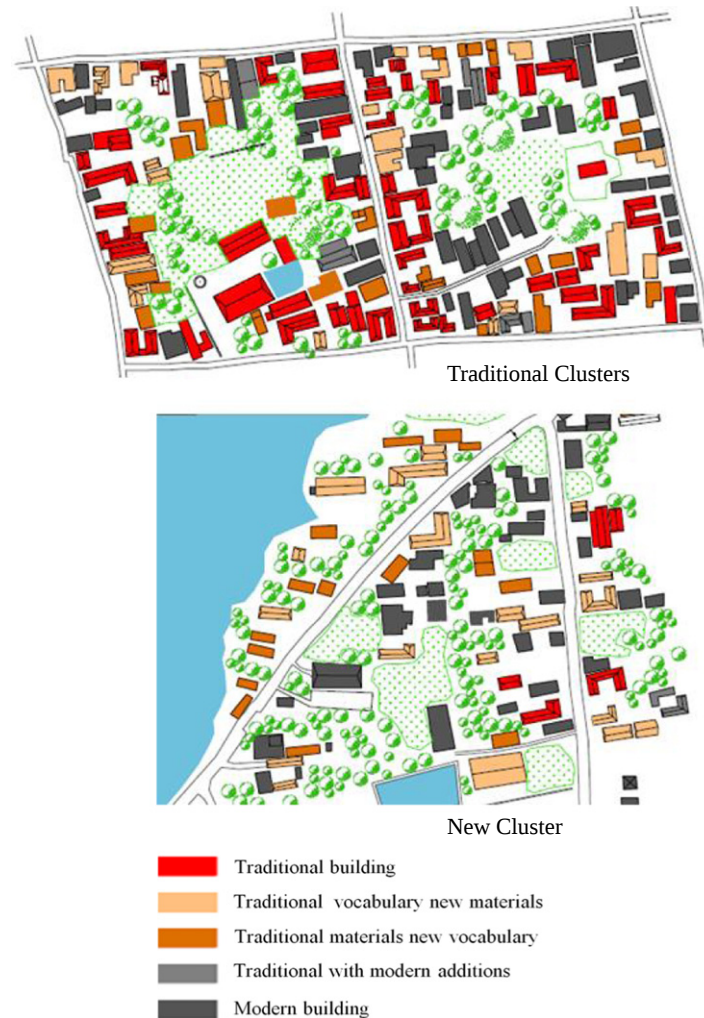


Fig. 10 Traditional planning vs. modern planning. Reproduced from Shermin, F., n.d. Conservation of the Vernacular Residential Architecture of the Historic Crafts Settlement of Sualkuchi. New Delhi: School of Planning and Architecture (Postgraduate in Architecture).

The energy consumption is also considerably high as artificial lighting and ventilation are required. Silk rearing is limited to a few farms, which are not able to fulfill the market demand of Assam silk. The production of Muga silk has reduced considerably, which has not only made it very expensive but has also invited the use of low quality silk from other parts of the world for making the traditional garments.

Findings and Discussion

The study of the settlement of Sualkuchi has been carried out to understand the importance of the relation between material culture and the concept of sustainability with respect to traditional architecture. However, this study inspects a specific type of traditional architecture that is consistently present in most of the areas of Assam, a state in Northeast India. The findings are based on a primary fieldwork conducted in the settlement, which is discussed below.

Sustainable Features of the Traditional Architecture and Planning of Sualkuchi

When the features of the traditional architecture and sustainable design are compared, it is clear that there are several common characteristics in terms of design criteria.

The term *sustainability* may not be known in the history of the settlement but it had been very well manifested in traditional buildings. The natural, economic, and sociocultural conditions of the region have a tremendous influence on the traditional architecture. The settlement planning is an outcome of the physical and environmental factors; the planning of the clusters and the religious architecture is shaped by the social factors and emerging of the temporary bamboo dwellings

is an impact of the economic factors. Also the climatic conditions have very evidently been responsible for shaping the housing as well.

The buildings were designed by their own users and thus the users used all the possibilities and prospects that were offered by their surroundings. They also tried to avoid anything that could make a negative impact in their lives. As a natural result of this process, the traditional buildings incorporated the values of today's concept of sustainability.

Below are two comparative tables showing the materials used in traditional and modern constructions simultaneously, which are listed against the previously discussed three spheres of influence of sustainability – physical sustainability, ecological sustainability, and socioeconomic sustainability (Table 1).

The basic objective of traditional architecture has been to meet the needs through creating simple and functional buildings. Therefore it is very sensible to choose building materials that were readily available in the surroundings, which in this case were mainly bamboo, wood, ikra, and stone (Figs. 11 and 12) (Tables 2 and 3).

From the tables above, it can be clearly concluded that the natural and locally available materials used in traditional construction are much more sustainable than the ones used in modern construction. In terms of today's idea of sustainability, regarding the traditional building culture of Sualkuchi, the following can be observed.

Table 1 Table showing the materials used in traditional constructions

Sl. no.	Architectural components	Materials used	Remarks
1	Foundation	Timber	Locally available and organic though increase in demand can have ecological impacts
2	Plinth	Brick/mud	Locally available bricks and the mud excavated on site for the foundation are used for the plinth
3	Framework	Wood	Wooden framework with bracings supports the structure during earthquakes
4	Walls	Ikra/bamboo/brick	Light weight, low cost and locally available and has insulating properties which keeps the interiors cool in summer and warm in winter
5	Wall finish	Mud plaster with lime wash	Locally available and adds to the insulating properties of bamboo or Ikra
6	Ceiling	Bamboo	Locally available, low cost, and supports local bamboo craftsmen
7	Roof	Clay tiles/thatch	Locally made, low cost, and supports local craftsmen



Fig. 11 Examples of traditional architecture at Sualkuchi. Reproduced from Shermin, F., n.d. Conservation of the Vernacular Residential Architecture of the Historic Crafts Settlement of Sualkuchi. New Delhi: School of Planning and Architecture (Postgraduate in Architecture).



Fig. 12 Examples of modern architecture at Sualkuchi. Reproduced from Shermin, F., n.d. Conservation of the Vernacular Residential Architecture of the Historic Crafts Settlement of Sualkuchi. New Delhi: School of Planning and Architecture (Postgraduate in Architecture).

Table 2 Table showing the materials used in modern constructions

Sl. no.	Architectural components	Materials used	Remarks
1	Foundation	Concrete/steel	Durable and allows multiple stories but high cost; materials are not locally available
2	Plinth	Concrete	Faster construction and low maintenance but high cost
3	Framework	Concrete/steel	Faster construction and allows multiple stories but high cost and risky during earthquakes
4	Walls	Brick	Locally made and easily available
5	Wall finish	Cement plaster with synthetic paint	Faster application
6	Ceiling	Plaster of paris/gypsum	Easy and quick installation but high cost and skilled labor required
7	Roof	Concrete/GI sheet	Comparatively low maintenance and high cost but being nonresponsive to Local climate it increases the consumption of energy

Table 3 Table comparing the aspects of sustainability in traditional and modern construction materials

Sl no.	Architectural elements		Ecological sensitivity	Respect for socioeconomic values	Reduction in energy consumption	Response to climate	Local availability	Cost	Supports creative economy	Overall sustainability
1	Foundation	Traditional	Average	Average	High	High	High	Low	Average	High
		Modern	Low	Average	Low	High	Low	Very high	Very low	Low
2	Plinth	Traditional	High	Average	High	High	Very high	Very low	High	High
		Modern	Low	Low	Low	Low	Very high	Very high	Very low	Low
3	Framework	Traditional	Average	Average	Average	Very high	High	Low	Average	Average
		Modern	Low	Low	Very low	Very low	Very low	Very high	Very low	Very low
4	Wall	Traditional	Very high	Very high	Very high	Very high	Very high	Very low	High	Very high
		Modern	Low	Low	Low	Very low	Average	High	Very low	Low
5	Wall finish	Traditional	High	Average	High	High	Very high	Very low	Average	High
		Modern	Low	Low	Very low	Low	Very low	High	Very low	Very low
6	Ceiling	Traditional	Very high	Very high	Very high	Very high	Very high	Very low	Very high	Very high
		Modern	Low	Low	Low	Average	Very low	High	Very low	Low
7	Roof	Traditional	High	High	High	Very high	High	Average	High	High
		Modern	Very low	Low	Very low	Very low	Very low	Very high	Very low	Very low

Sustainable design culture

The designing of enclosed and semienclosed spaces in a dwelling unit was done keeping in mind the function of silk production and the functioning of the cluster as a whole. All these factors not only made an impact on the production of silk but also facilitated interaction among the people. The proficiency in construction methods and materials offers solutions for construction as well as natural disaster issues.

They have efficiently used the natural resources and materials provided by the surroundings and have designed their own environment using local materials to suit their needs, specifically to suit silk production. Thus a building culture very typical to the region has evolved throughout history.

Sustainable land use

The planning and designing of the structures in a traditional historic cluster was done so as to meet the needs of the local weavers. As already discussed before, the other occupation-based communities were made to settle in Sualkuchi to support the weaving community. The planning ensured feasibility and ease of movement of the different communities according to their occupation and thus guaranteeing efficiency.

Instead of treating nature as an obstacle like we do today, they made use of the best out of nature. Measures like avoiding construction along the flood plains and along the natural drainage helped the settlement to check the seasonal floods. Natural water drainage was also made easy by the addition of manmade water bodies. The settlement was also very strategically planned keeping in mind the access routes through land and water.

Designing for durability

The common locally available materials like bamboo may not be as durable as stone or brick but the traditional buildings incorporated suitable protective measures or design features/solutions to prevent damage. Being in an earthquake prone area where safety is the main concern, the lightweight traditional structures serve the purpose very well. However, the important structures like temples and monasteries were built in stone and wood to ensure durability.

Energy efficiency

It is already known that the Ikra and bamboo construction material keeps the interiors cool in summer and warm in winter, which is a necessity for the hot and humid summer months and the harsh winter months in the region. When it comes to silk production, lighting plays the most important role. And as we have seen, the fenestrations were designed to make sure that proper daylight reaches the weaving areas in the structure.

Another factor that makes the settlement energy efficient is the proximity to the workplaces. Locating occupation-based communities close to their place of work, for example fishermen close to the river, and fishnet making close to the fishing community, and also the central location of the market place, made the work-home distances considerably short thus reducing the carbon footprint of the transportation.

Summary of Findings and Discussion

In the past Sualkuchi has evolved in harmony with the surroundings while serving the sole purpose of silk production. The utilization of easily available local materials for construction and the strategic planning serve to support environmental sustainability.

The solutions for disasters, whether it is a natural calamity like flood or earthquake or a fire, have been well thought of, developed, and mastered. The settlement as a whole had achieved not only environmental sustainability but also had directly or indirectly achieved social and economic sustainability. For example the use of local materials by the local people is important in terms of energy efficiency, cost efficiency, and also helps in supporting the local economy.

The enthusiasm with which communities work and support each other to fulfill the objectives of silk production is also an important part of sustainability and that has been possible only through achieving all the factors of sustainability that we have discussed.

Conclusion

This study aimed at investigating and understanding the relation between traditional architecture as a material culture and sustainability. It was also an attempt to determine the potential of traditional architecture in the concept of sustainability today. It has been observed that the main principles of traditional architecture and the basis of sustainability are both in the same track.

Social, economic, and environmental concerns that are the basis of sustainability can be seen in the traditional construction methods and planning of Sualkuchi in the Northeast of India. With this study it has been made quite clear that the local people of the settlement had mindfully taken into consideration the ideas of a sustainable living. The living spaces were designed to improve their lives and enhance the means of their livelihood, which directly or indirectly followed a sustainable design. Today we take sustainability as a solution to the issues we have created where as back then it was a way of life.

The study makes it clear that sustainability has been inbuilt in our culture and recognizing and transferring this knowledge system of the past to the future generations can ensure a more sustainable future.

See also: Bamboo Structural Technology

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Retrofitting of Buildings/Built Environment – A Sustainable Development Model

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Introduction

In context of a landscape of growing urbanization, rise of inequity and social injustice, design practices, particularly in the urban realms have taken on an increased value. This value is not only reflective of a drive to create more equitable and just spaces in cities, they also need to be carefully attuned to the nuances of space-making and place-making that learn from and evolve in response to a diverse set of tools, technologies and experiences. Urban design practices thus need to not only respond to complex intersecting needs of various stakeholders, disciplines and methods, but also need to be responsibly spatially grounded in the realities of a particular context (in its social, economic, and political manifestations).

This article attempts to unpack the realities of urbanization and development using India as a symptomatic case of other developing contexts. It elaborates on the overall pattern of development and urban transformation, the polarizing inequalities and the uneven landscape of population concentration to talk about the major challenges and dilemmas that are intrinsically linked to such development. Within this context, it discusses the prevalent notion of sustainable development to foreground the key features that lie at the core of this principle. At this point, the article tries to make a case for expanding the domain of what is meant by sustainable development using cases of realized/idea level retrofitting projects successfully implemented across various scales and typologies of the built environment. The focus on elaboration of actual cases has a twofold purpose. Firstly, it's an attempt to illustrate retrofitting as a spatial concept that at the same time can successfully negotiate complex interlinked spatial-political economies of a particular context. Secondly, it is an attempt at understanding the limits and potentials of retrofitting as a concept that could enable grounded, sustainable, and responsible trajectories of development.

The article concludes with a call for a paradigm shift in the way current spatial practices attempt to fragment and implement projects. In this process, there is an implicit rejection of values of the existing and a rationalization of the economic value as the dominant value. Retrofitting, however, could enable a shift in this thought-action process – one that at its core tries to see a wider gamut of values and assets that are otherwise seen as waste.

Urbanization and Indian Cities – Realities, Policies, Practices

Cities have been seen through multiple lenses from multiple perspectives. They have been seen as agglomeration of global capital (Sassen, 2013), as networks as flows (Castells, 2009), as social space (Lefebvre, 1970/2003), as difference and contestation (Sandercock, 2003; Simone, 2010). They have been characterized according to scale (small, medium, large) and physical features (green, garden, compact, transit, virtual) (see Pacione, 2001). This article does not attempt to privilege one view over another, but rather accept that the city itself is a site of multiple representations, narratives, and actions. Tonkiss (2013) aptly captures this, in saying that “cities are not merely by-products of the operation of capital [...] Cities are the sites of intense struggles between disparate interests and multiple stakeholders, whose ideas, influences and actions together ultimately shape today's urban realities” (p. 24). Cities then have been a subject of various debates, elaborations, and discussions – and have been widely investigated by urban practitioners, economists, sociologists, anthropologists, and ethnographers. They are, in fact, spaces that become places – imbued with a particular character, a particular image (Lynch, 1960). A city is thus shaped, reshaped, and transformed in a continuously temporal process and acts, a la Lefebvre, as a dialectical object – existing both in its image and its materiality. Cities thus become cynosures of people, a collective container that is a manifestation of hopes, dreams, and desires for a better future. Migration to the city-space is therefore an act that is simultaneously physical, aspirational, and political.

Increased migration affects urbanization. The reality is that the human population will be largely concentrated in cities in the near future. Based on 2018 population data, 55% of the world's population is concentrated in urban centers and is projected to grow to 68% by 2050 (UN DESA, 2018). This growth is projected to be concentrated mainly in a few countries in Asia and Africa – such as India, China, and Nigeria. These are fast growing countries, characterized by high population growth, increased urban migration, and high economic growth. India tops these projections, adding approximately 416 million people in its urban centers within these years.

Bhattacharya (2002) discusses the implications of such growth – the rise of mega-cities, issues of urban primacy and sprawl, rise of informality, amongst others. Much of what he discusses holds true today. According to Indian Census Data (2017), India's total population is 1330 million. Of this, 34% is concentrated in 468 (> 100,000 population) urban centers. However, almost a quarter of that number reside in just the top 10 biggest cities. These cities are predominantly of two kinds – the four major metropolises with colonial imprints and the other significant historic urban centers of the country. The explosive growth and urbanization has significant implications for development – provision of civic amenities, infrastructures, services, and shelter in the urban areas (Bhagat, 2011).

What Does It Mean in Reality?

Let us look at the metropolises, which have grown at various times to support the massive influx of people. In Delhi, there has been a physical extension in Dwarka for an intended population of one million residents. Similarly, Mumbai has extended itself into Navi Mumbai. Kolkata too has extended its hinterland and has gone from 100 wards to 144 wards. It subsequently grew into Newtown Rajarhat and virtually has become a large urban metropolitan region. The city has reached a stage where the patterns of physical growth now threaten the East Kolkata Wetlands (The East Kolkata Wetlands were designated as “Wetlands of International Importance” under the RAMSAR Convention on August 19, 2002). In all these cities, the physical boundary extends itself at a high rate. In the process, agricultural lands get converted in real estate; small towns become rural islands in the city, which are subsequently redeveloped; and land is reclaimed from the sea at great cost. New typologies for workplaces, institutions, and housing have emerged, further complexifying the situation. The development of urban areas have thus become a critical management issue.

These sprawling metropolises suffer from an acute scarcity of infrastructure, amenities, and services. There are two major kinds of manifestation. In the peripheries, areas reel from lack of circulation space, services, playgrounds, and community amenities. People improvise and often survive by coping with makeshift infrastructure. On the other hand, are the inner cities. Dating back 200 years or more, these are repositories that hold the uniqueness of the city – its character. The character is derived from the way citizens behave, levels of tolerance, opportunities for all classes of people, etc. These are manifested through spatial arrangements, functional mixes, operational networks, informal networks and many others. However, the intense pressure of development and the high influx of migrants slowly degrade the inner cores into slumlike conditions. Characterized by high density, informal organization, low maintenance, abuse of the built form, poor and unplanned urban services, etc., these areas are ripe for redevelopment. In addition, these areas have higher land value, are heavily contested, and extremely politically active. As the city grows, these areas are often developed through mechanisms that displace – be it the old inhabitants, the existing social structure, lifestyles, built form, ecological balance, environmental quality, etc.

In recent years, various policies and programs have been conceptualized in India to support development. Major critiques of these programs are that they are conceptualized at a scale and translated into siloed projects that they are inherently exclusionary and biased towards a particular form of development. They are also thought to lack nuanced mechanisms for actual implementation and are usually easily co-opted by other intentions during the implementation process. For example – let us take *Pradhanmantri Awas Yojana* (PMAY), which has the promise of providing *Housing for All* in India. [Bhan \(2018\)](#) critiques PMAY from the very basis that should ideally be its foundation and shows that despite best intentions the policy fails to create tangible impact. Even through the Ministry of Housing’s campaign says that “[w]e have constructed 6 million houses under the PMAY,” deeper investigations into the use, the value, and the benefits from these houses are hugely debatable.

Towards Sustainable Development

It needs to be understood that in a country like India, development equates to growth and is often evaluated from the perspective of a single parameter- that of financial profit. This means a focus on quantity over quality, and the prioritization of the most economic methods of production of space, provision of services, and amenities. Consequently large, often-complex urban issues are split to be addressed by a series of different projects – each comfortably couched within a particular discipline. Hence, there are the housing projects, the infrastructure projects, the park projects, and so on. A deeper investigation of the motivations, the benefits, and the stakeholders of the project reveals deep-seated inequalities, and vested interests of a few (powerful) actors as the key driving agenda. For example, [Desai \(2008\)](#) unpacks the Sabarmati Riverfront Development Project to foreground the political and neoliberal intentions that underlie and co-opt what has been discursively described as a project for the city and the people of Ahmedabad.

To facilitate these co-options, the development agenda has adopted a few apparently sustainable buzzwords like *eco-friendly*, *green building*, and *smart cities*. These concepts are usually addressed superficially, and engagement with the urban environment becomes an act of image making. This is possibly the biggest reason behind the reality that while India has continued to develop in a ‘sustainable’ way – actual existing environments, sociospatial practices, cultural diversities, and the built environment in urban areas have been destroyed at an alarming rate.

At this juncture there is a need to critically rethink how urban spatial practices can have more holistic, systemwide impacts. [Jacobs \(2016\)](#) strongly argued for a need to reorient urban renewal practices in context of existing socioeconomic patterns, informal networks and connections, and the implications of their displacement as part of renewal strategies. Only with such perspectives can one start to make cities livable. This can support an essential readjustment of present sustainable development approaches that are predominantly measured through quantitative parameters of efficiency, material use, and techniques to a more qualitative, interdisciplinary, and equitable understanding. [Pacione \(2001\)](#) elaborated such a concept of sustainable development that takes steps to preserve needs and resources for future generations, that propounds fair and equitable use of resources, and that does not shy away from taking responsibility for damage caused due to one’s own activities. At the core of this understanding lies a perspective of viewing resources as collective (space, environment, energy) and of valuing the existing assets of a particular place (economic, material, social, and cultural). Any act of development would thus entail a careful analysis of existing assets, a strategic vision for qualitative improvement of the system, and careful implementation of the vision through evolved, context-specific spatial practices that understand, prioritize and negotiate trade-offs.

Retrofitting – A Concept

This article discusses an expanded understanding of retrofitting as a possible concept to further sustainable development trajectories.

Retrofitting has been broadly understood to be the process of critical replacement/addition of components to an existing system. It has been widely used in the fields of manufacturing, environmental management, etc. It has also been used in the fields related to the built environment such as sustainable architecture and conservation (Paradis, 2016; Dave and Prasad, 2010). In these contexts, retrofitting has generally been employed as a method of engagement with the existing – a process that maximizes efficiency and resource utilization. That itself makes use of this method extremely relevant to spatial practices in the urban Indian context – which is replete with extensive preexisting built form, especially in the urban cores. The method of retrofitting is essentially nonstandard, based on a keen awareness of existing assets, resources and a comprehension of their value. The approach concentrates on reduction of waste wherever possible by using appropriate design strategies. In this sense, the first step to retrofitting can be compared to a medical diagnosis of a patient. The process acknowledges that that total systems rarely collapse as a whole; rather some of its components fail to meet the required needs or performance standards and can be addressed as such. It also operates with an understanding that the built environment and buildings are dynamic systems that are capable of adapting and adjusting to the changed circumstances, albeit up to a limit. With new inputs over time, this system might be stressed/destabilized – preventing optimal performance. Retrofitting engages in holistic diagnostic and strategic interventions within the existing system (in this case the built environment) – and can potentially enable value added interventions that would not have been otherwise possible if the method started with a rejection of the existing assets and values.

An even further expansion is an awareness that ‘value’ could be aspects of the system that are invisible upon cursory diagnosis. In engaging with the built environment, the most apparent asset of value is the building. But concurrently, there exists a whole other set of values: Social, cultural, lived experiences, collective memories, lifestyles, heritage, skills or occupations, natural resources etc. The sum total of all these values is a truer representation of the system – and not just the economic or the material value of the tangible assets. If retrofitting is engagement based on existing values, it becomes a much more powerful concept if employed from this perspective. In this form, it becomes a concept – a search for a context specific spatially grounded and appropriate solution that is also inclusive, responsible, smart, green, and sustainable.

Retrofitting could thus enable a shift in the thought-action process behind sustainable development – a concept that tries to see and respond to a wider gamut of values and assets that are otherwise either invisible or seen as waste. As a concept, its applicability is expanded to wider contexts. It essentially becomes an analytical approach to understanding and responding to urban issues and is versatile enough to be adopted at various scales – from that of a city to a neighborhood, a building, or an institution, to the microscale of private residences. Even if employed as a concept, retrofitting in the domain of the built environment must have the following two characteristics. Firstly, it must be extremely rooted to the particularities of a system. The methodology of engagement and implementation must not be prescriptive or generic, but a product of a thorough diagnostic of the system. Secondly, the strategies must be spatially grounded in the place, as only then can there be lasting tangible impact. As such the implementation could take up various forms, such as but not limited to restoration, conservation, revitalization, infill development, etc.

The authors have been engaged in several cases where they have tried to practically implement this concept of retrofitting as a possible trajectory towards sustainable spatially grounded urban practice. The following section elaborates a few demonstrations, across scales and types.

Case 1: Retrofitting a traditional residential typology in North Kolkata.

This case is that of a house, located at *Durgacharan Mitra Street* in *Darjeepara*, a traditional neighborhood in North Kolkata. Dating to almost 300 years, this house is characteristic of the typical residential typology in the old core of Kolkata. The existing house had a partially open to sky inner space with other spaces arranged around it. It's a three-story load-bearing brick structure with a narrow brick staircase for access. The floors have also been constructed in the traditional system using the *Kari-Bargah* (beam and rafter) technique, over which there are two layers of terracotta tiles and lime concrete. The house had the old wooden louver windows, cast iron railings, and other finishes and materials that had aged gracefully. Over time, a separate toilet block was added into this space, and the kitchen occupied part of the verandah. The house had a 300-year-old family deity of *Radha-Krishna*. There were regular religious ceremonies, and this was an actual matter of pride for the family (Figs. 1 and 2).

The owner of the house is a retired life insurance agent and lives with his son on the premises. The family have been long-term residents in the same location and as such, the owner has built up an intimate wider social network in the neighborhood. Apart from the owner, parts of the house were being used by other entities. The ground floor was used by the local club, and there was a small daily needs shop on the porch of the house. The family was in significant financial hardship, which prompted the owner to think about his home as a financial asset (Fig. 3).

Due to a strong social link to his neighborhood, the owner did not want to adopt the standardized practice adopted by homeowners in such cases, which is to outsource the (re)development of the premise to a private developer (*promoter*). In this arrangement, the promoter funds the development of the property, and the owner provides the lands. In return, the owner gets a share of the new built-up area as compensation. After project completion, the owner is free to continue staying in his share of area in the new building, or free to relocate and sell this area for financial gain. Because the model is driven primarily by financial gain (from the promoter's perspective), such redevelopment has a lot of issues. Almost always, the old building is torn down to make space for a new one – as this process is apparently easier. The agreements in terms of benefits always tend to be skewed in favor of the promoter. The project timeline is usually very short (as the promoter also needs to compensate the owners for accommodation

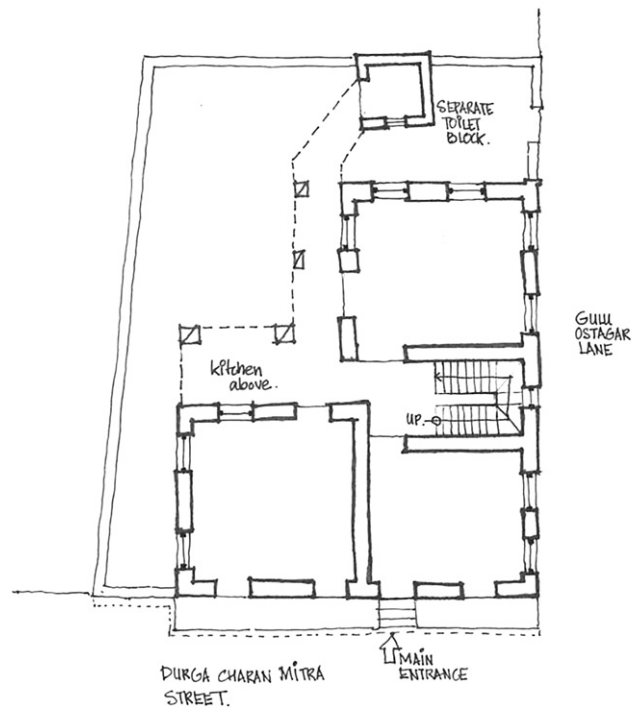


Fig. 1 Ground floor plan I before.



Fig. 2 The building I before.



Fig. 3 Internal condition I before.

during the project) and the quality of construction is also questionable. Also, these new constructions in the old neighborhoods tend to be architecturally incongruous insertions in terms of typology, materials, and treatment.

The initial hesitation of the owner prompted him to engage us in the project. Primarily we tried to figure out an alternative development model following the concept of retrofitting for this project, in which we tried to prioritize the following factors: The owner would not have to forgo his ownership, he would get major benefits from the (re)development, there would be financial benefits, he would retain his existing social networks and the family deity would still remain in the same premises. For us, the most practical and plausible solution lay in the realization that the building structure was in good condition, with minor typological shifts, and conservation and reorganization of the built form could accommodate all these requirements.

Our strategy was to retain most of the original structure and strategically add vertical access and services. With these additions the building was converted into three self-contained double-bedroom apartment units with services and infrastructure matching levels of new construction. Moreover, these apartments retained the feel and flavor of the old spaces and enjoyed all its built-in advantages – high ceilings, larger space, good natural ventilation, connection to the street, etc. A small addition on the roof was conceptualized as a permanent temple that could house the family deity, and also accommodate daily rituals and practices. A small niche was even conceptualized on the ground floor where the preexisting shop still functions (Fig. 4).

To make the entire implementation process cost effective and compatible with the existing, the project stressed reusing old materials, sourcing materials from second-hand markets, recycling available materials on site, etc. Added to the fact that we newly built very little, this significantly affected final costs which were approximately half of the cost of standardized construction. Furthermore, we avoided creation of much demolition waste, minimized the embodied energy of our intervention and ensured that the (re)developed building integrated seamlessly into the neighboring context. Finally, there was careful project management and planning to ensure that the implementation was done in a way that the owners could still remain on the premises during the entire period.

The conserved building opened up alternative trajectories to financial stability for the family. Being essentially three self-contained units, the owner was free to rent or sell two and still keep staying on the premises. In the end, he kept the first floor and sold the other two. Compared with a promoter driven process, all the gains from the sale were his, which made the project financially successful. It has been 10 years since this project, and the building has had a new lease on life that is at the same time safe, comfortable, and congruous with its surroundings. But we believe that the real gain is also in the fact that the project did not disrupt but in fact strengthened a 300-year-old social network while at the same time minimized environmental damage and destruction. This model of retrofitting to facilitate a sensitive development approach is time consuming and takes a lot more effort – mainly because it is a process of inclusive and negotiated spatial practice. In this process it is important to build on trust and value, and practitioners need to go beyond norms of formal engagement as dictated by terms of professional consultancy.

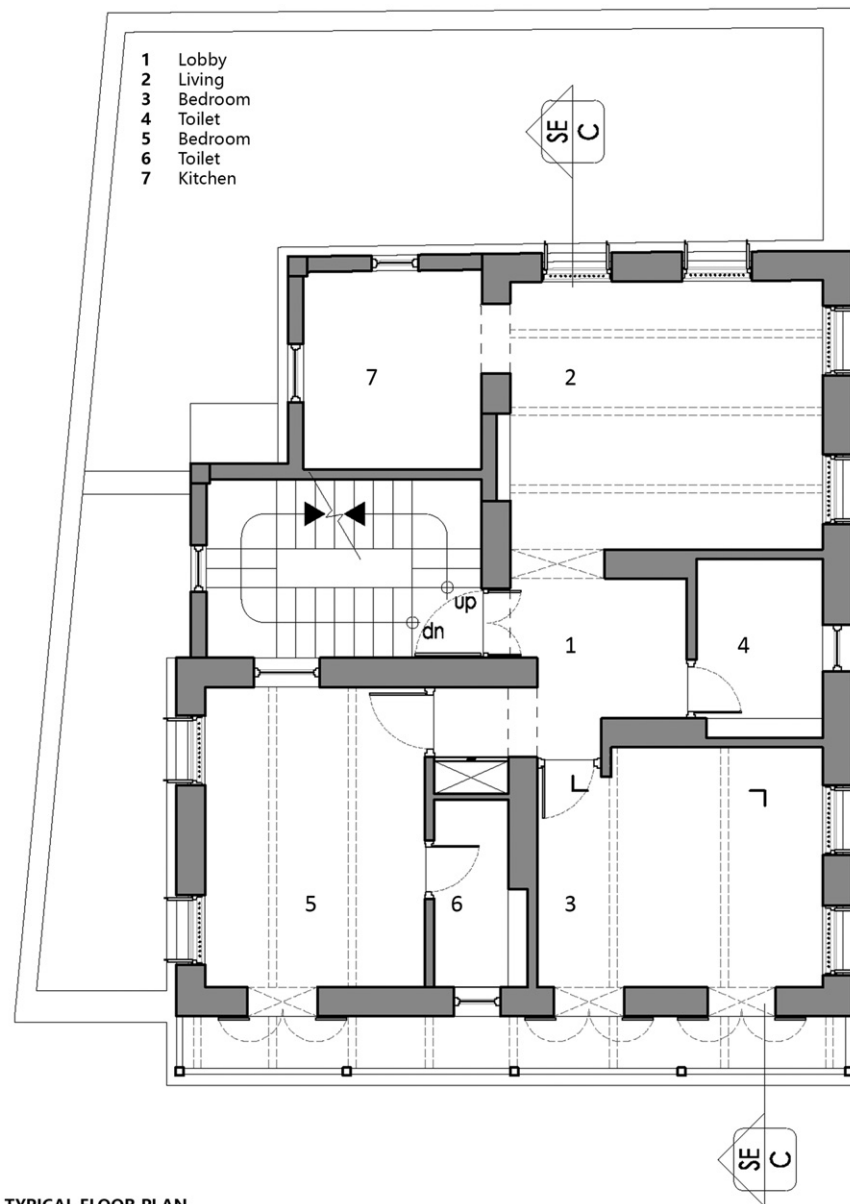


Fig. 4 Transformed floor plan.

But the benefits are many, specifically in terms of a trajectory of development that is not just environmentally but socially sustainable (Figs. 5–8).

Case 2: Transforming an old tannery in Chinatown into a sustainable enterprise.

The case is located in *Tangra*, in the eastern part of Kolkata. *Tangra* was historically developed by the Chinese community who migrated here in the 19th century, and the area gradually became the Chinatown of Kolkata. Chinatown subsequently grew to become an integral part of Kolkata city's cultural heritage with a different ethos, and set of social and cultural values.

The area had a concentration of tanneries and a host of small industries and services like carpentry workshops, beauticians, etc. The dominant typology of the area has uniquely developed to suit the requirements of tanning, featuring large span structures that have residential spaces, storage spaces, and a variety of workspaces. These spaces usually occupy huge footprints. However, the West Bengal Government has given orders to move all the tanneries from the city to the outskirts and suburban regions to reduce environmental pollution. This led to a sudden emptying out of the tanneries and the displacement of workplaces for the resident Chinese population. Physically, a number of physical structures and warehouses were left in an empty and abandoned state. The process also led to fragmentation of the social structure of the local Chinese population who eventually sought to shift their base to other places. The future of Chinatown in Kolkata has become a serious urban concern from financial, environmental, and social terms.



Fig. 5 Internal stair using wood and cast iron | after.



Fig. 6 Transformed building.

Current developments in the area have been those of high-rise residential gated communities that cause large-scale displacement and change the landscape of the entire neighborhood. It was within this context that we collaborated with i-LEAD (an educational institution based in Chinatown) to revitalize a part of Chinatown through the redevelopment of an old, vacant tannery warehouse. For us, the key assets in the place were its historic associations with the Chinese community, the unique small businesses, and the characteristic architectural typology comprised of different scales and volumes. We also identified the gaps in



Fig. 7 Transformed building within the urban fabric.



Fig. 8 The proud owner I after rehabilitation.

the sociospatial fabric in the neighborhood: The huge percentage of built-up and the lack of open public spaces, and the void in work-related opportunities for the local residents (Figs. 9 and 10).

Developing an architectural program was a key task for this case. This was done in a collaborative manner, keeping in mind that different stakeholders had different needs and priorities. There were three major stakeholder groups – the institute (iLEAD), the people from Chinatown who would study/work at this institute, and the wider community. The final program was derived from a mix of the needs of these stakeholders and of an analysis of the existing spatial conditions in and around the warehouse. There were three major components that capitalized on existing assets, values, and demands in the area: entrepreneurship development, education, and skill development spaces; small business opportunity spaces; and community spaces. These took various forms, such as a training center, a school, a skill development center, a bakery, a beauty parlor, rooftop open public spaces, etc. (Figs. 11 and 12).



Fig. 9 Old tannery building | before.



Fig. 10 Ad-hoc developments over the period | interior volume.

The program had to then be integrated within the building in a sensitive way. As with other cases, we adopted an approach of minimal intervention, frugality of material use, and recycled, repurposed, and upcycled products. The multiplicity of programs with their own specific needs fit perfectly in the existing tannery, which had different scales and volumes of space to begin with. However, some practical spatial reconfigurations were needed to further increase space use efficiency. In one area, a combination of structural steel inserts with prefabricated papercrete (wastepaper mixed with cement) was used to create an intermediate floor. Services such as fire, security, accessibility systems, and PHE systems were inserted into the building to make it fit for use in its new purpose. As far as possible, waste and scrap material were repurposed in their original configurations – and design was used as a tool to integrate these within the space. For example, thermocol from packing crates was repurposed as false ceiling panels, tires were repurposed as swings, plastic bottles as vertical planters. All these small elements work to humanize the environment, and soften the harshness of the existing building (**Fig. 13**).

As clear from the description, retrofitting and use of appropriate techniques made the process of repurposing of the tannery much less expensive (in terms of finance, embodied energy, material use, etc.). In addition, the tannery now has created several spaces that have the potential to connect to the wider neighborhood – directly and indirectly. The open-air rooftop sports complex and the multipurpose hall and food court are valuable facilities for the neighborhood, which has otherwise no access to open spaces. These spaces are made to be accessed and used by the community free of any cost or condition. The beauty parlor, bakery, and the utility store employ and also serve the local community in addition to students of the institute. A large number of tannery workers and other kids from the hinterlands are either students or enrolled in the institute's skill development or entrepreneurial training programs. Together, all these activities make the institute a thriving, vibrant place that is at the same time extremely grounded in the sociospatial realities of Chinatown (**Fig. 14**).

Retrofitting here is both spatial as well as programmatic – and addresses sustainability from varying perspectives. However, this was only made possible through the collaborative effort of a willing and passionate investor, who believes that a good business must also have aspects of social and environmental equity for it to become sustainable.



Fig. 11 Transformed tannery and the street.



Fig. 12 Transformed interior space.

Case 3: Retrofitting (Revitalization) of a popular sacred cultural destination: Kalighat Temple Precinct.

The Kalighat temple is a prominent sacred and cultural destination of Kolkata. Kalighat predates the history of Kolkata itself, and is influential in shaping development of the city. It is almost 400 years old and is the most important sacred site beside the Adi Ganga River (now named Tolly's Nullah) (Fig. 15). As such, it occupies a key position in the Bengal mindscape. The complexity of the built/natural fabric, the multitude of stakeholders, and its long history make Kalighat a politically and culturally sensitive historic area. The temple itself has an area of only 16,000 square feet (out of which 80% is built) but caters to an average of 30,000 visitors daily. On special days, this number can reach 100,000. This places extreme stress on the temple and its hinterland, making it vulnerable in terms of safety, security, and environmental quality. In 2013 the High Court passed an order for safety and security of the pilgrims visiting the Temple as well as its environmental improvement (Fig. 16).



Fig. 13 Meaningful reuse of waste.



Fig. 14 Community facility, sports center on the roof of the tannery.



Fig. 15 Kalighat | historic image.

To respond to the High Court order and also the growing development needs of this precinct, Chief Minister of West Bengal Mamata Banerjee initiated the Beautification of the Kalighat Temple Area project. She appointed the Kolkata Municipal Corporation (KMC) to coordinate the entire process. Subsequently, the KMC formed a project monitoring committee involving the Mayor, KMC, KMDA, MLA, MP, local councilors, police, traffic, and local stakeholders. The purpose of this committee was to oversee the entire process. Based on our previous experience with conservation and cultural tourism, the KMC appointed us to the project as architects/development consultants.

We started with a diagnostic assessment of the area, traced daily established practices and interviewed stakeholders to foreground their emotions and concerns. This went hand in hand with an assessment of environmental issues, livelihoods, pilgrim facilities, the local economy and the *dala* shops (ritualistic ingredient shops), legal complications, etc. We looked at historical references to trace morphological transformation, tried to understand the importance of Kalighat as a *Sati-Peeth* according to



Fig. 16 Kundapukur, Kalighat historic image.



Fig. 17 Proposed image of revitalised Kalighat precinct.

Hindu mythology, studied Kalighat *pata* – the indigenous craft, the sacred rituals of the temple, temple management practices and its economy, associated roles of *sebait* families (groups responsible for overseeing management). What we realized is that there are several layers of complexities that involve a wide range of stakeholders that manifest in this space, coupled with an overwhelming daily influx of people. We realized that waste disposal is a serious issue, and that Kalighat is an environmental hotspot due to regular flooding of the Adi Ganga that inundates a large part of the precinct (Fig. 17).

The exercise led to a belief that instead of beautification what Kalighat needs is an inclusive planning exercise to come up with strategies for a negotiated development of the area. This would be akin to what Patrick Geddes suggested as ‘conservative surgery’ – small changes in the sociospatial context that ultimately create a cascading effect of structural change in the area. Moreover, in light of the existing complexity, these small solutions cannot be imposed but need to evolve from the area itself. The first step to a workable inclusive solution lies in expanding the scope of the project from the temple precinct to a larger hinterland – the *Kalikhsetra*. This can be then followed by the collaborative enactment of certain strategic planning provisions. We identified certain thrust areas for intervention, as below.

The first set of interventions concern the temple precinct and its immediate surroundings and linkages, including the *dala* shops, which are essentially in encroached spaces within and outside the temple complex (Fig. 18). They make the area congested, unsafe and insecure. At the same time, these shops are an essential component of the sacred rituals and the core of everyday traditional practices. The system has been operational for generations, providing livelihoods for *sebait* families and direct dependents associated with the temple. The High Court ruling categorically mentions that the temple be cleared of such obstructions and alternate provisions for their rehabilitation be created in an amicable manner. In addition, as the temple has grown, so have the requirements of space. The temple area is restricted and inadequate for carrying out sacred rituals and daily activities. There is a general lack of public space and the *Bhog* kitchen and allied services are too small to sustain the activities. Furthermore, certain activities, such as the ritualistic sacrifice of animals on auspicious days, create hazardous waste, and there is at present no safe way to dispose of such waste. All these issues necessitated major structural and service reorganization of the temple – conceptualized as a series of collaborative, negotiated implementation strategies.

Another layer of interventions were conceptualized that address the larger scale of the precinct and its links to the socio-economic structures. This relates to the informal networks around the precinct and the large number of poor, specially abled people who flock here in hopes of alms and charitable donations. It addresses issues of legibility, ease of movement and access for both vehicles and pedestrians in the area. Finally, it tries to respond to the historic cultural landscape links of Kalighat and Adi Ganga. This is conceptualized in the form of a religious circumambulatory route (*parikrama*) around the area that sanctifies and



Fig. 18 Kalighat temple at present.

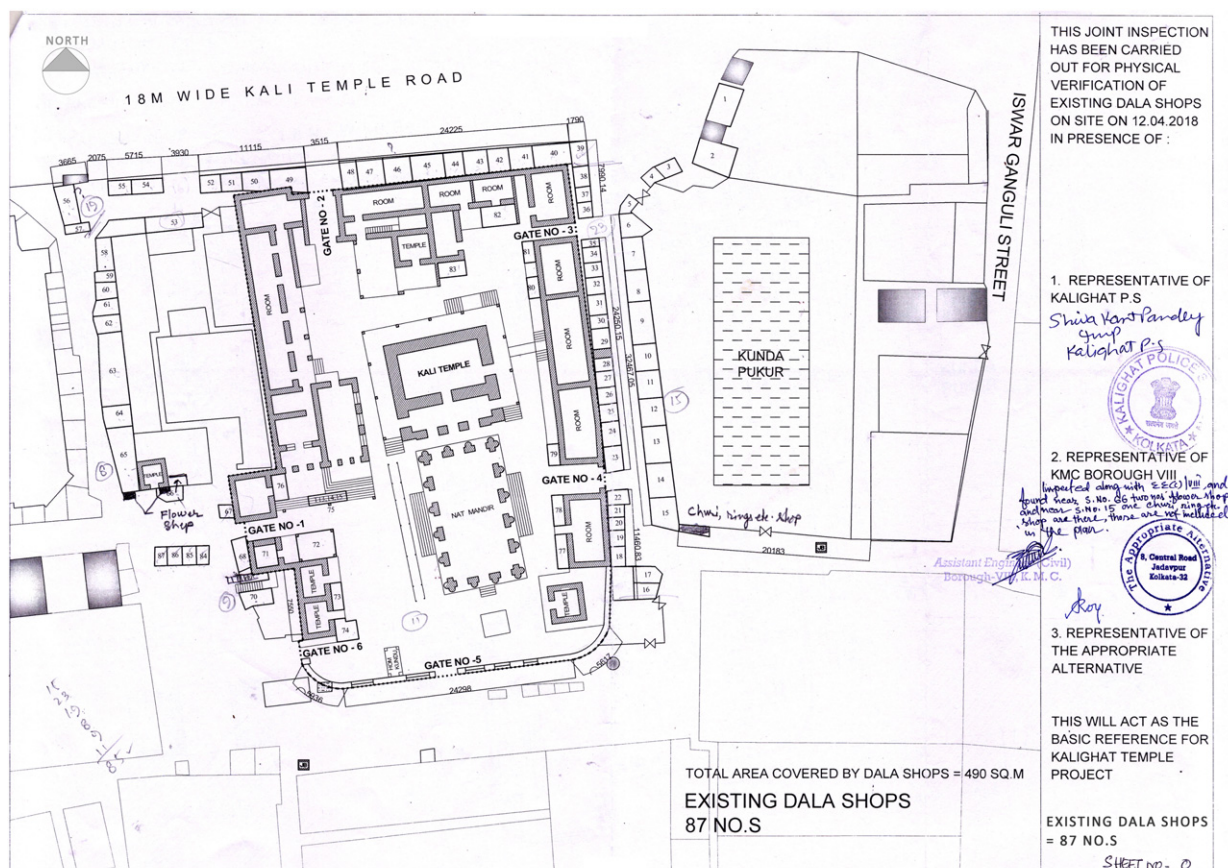


Fig. 19 Joint survey plan of the existing precinct submitted to the High Court.

restores the foreground of the temple. Together, these interventions are aimed at strengthening the resilience, robustness, and efficiency of the precinct while at the same time acknowledging its histories and collective memory.

In both these cases, the idea of retrofitting played a central role. It was an important concept that helped us design the strategic interventions that added on and strengthened the existing sociospatial networks. It was also the main method of engagement. This is because the precinct has a high heritage value, complex legalities and ownership issues and is extremely politically charged. Furthermore, new land for construction is virtually unavailable and even public land is difficult to reclaim without mass evictions and displacement. Retrofitting here gave us a unique trajectory of thought-action to negotiate these potential challenges.

We put these across to the monitoring committee in the form of a preliminary revitalization plan for the area. The approach in the form of a revitalization plan has been appreciated. The public departments tactically wanted to break the project down into

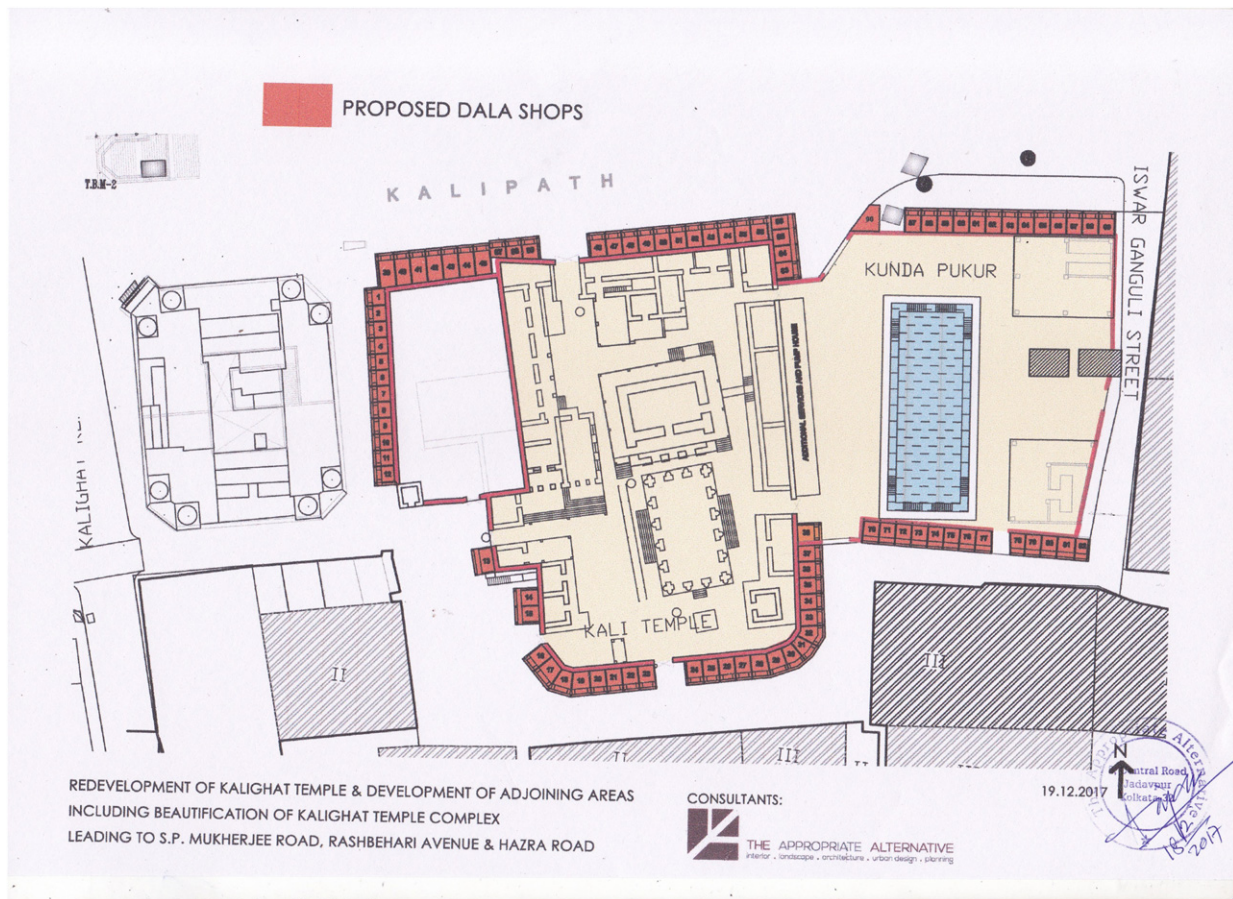


Fig. 20 Revitalization scheme.



Fig. 21 Proposed view of the revitalised Kalighat temple.

phases, and resolved to tackle the first set of issues in Phase I. This also ensured that the project would comply with the directives of the High Court order.

The main strategies for this phase involved rehabilitation of *dala* shops, increase in temple precinct space, and adequate service upgradation. Planning for this stage has been initiated by identifying the exact number of *dala* shops affected and their sizes and types for the purpose of relocation and reorganization. To address the issue of space the strategy adopted would be to group the available temple land along with the intervening public space (that of the adjacent Kundapukur, which was originally connected to the temple as per our historic research). This would provide much needed relief within the temple and generate additional areas that could be retrofitted to make room for service upgradations. The proposed temple would be made safe and secure with proper delineations, access points, and crowd management mechanisms. Once this idea was presented to the stakeholder groups, all groups understood the potential benefits and accepted the suggestion (Figs. 19 and 20).



Fig. 22 Design development involving local craftspeople and stakeholders.

Having established the main temple area, we concentrated on an appropriate rehabilitation strategy for the *dala* shop owners. This was accompanied at all stages by conversations, discussions, and negotiations with the beneficiaries. The focus was on fairness and a uniform shop module was designed based on the average existing footprint. It was then checked for workability through multiple consultations with the users. Some compromises were made to improve safety, such as absence of kitchens in the relocated shops to reduce fire hazard. To eliminate any kind of preferential bias it was decided that the reorganized shops would be allotted on the basis of a common public lottery. Approval was obtained from the stakeholders in a final joint meeting, which was held in presence of the administrators and local public representatives. There was universal acceptance, and this document has been submitted to the High Court and has been endorsed for working out an immediate action plan.

The proposed first phase interventions have been agreed to by KMC, local councilors, stakeholders, and even political leaders. This is because the strategy took the path of least resistance between varied interests in a process of negotiated coproduction. In a historic area loaded with complex sociocultural and political issues, this project validates retrofitting as a sustainable development approach even within a largely conventional planning setup, creating a strong substrate of interaction, collaboration, and agreements between entities that oftentimes are at odds and have confrontational stances. This maximizes the probabilities of sustained and continued efforts towards developing the precinct following a development trajectory that is sociospatially inclusive and sustainable (Fig. 21).

Case 4: A strategy to sustain an orphanage through community based tourism.

This is a case that has its roots in the Incredible India campaign promoted by the Ministry of Tourism, Government of India and supported by United Nations Development Program. The campaign is basically a community-based tourism initiative, where the unique experiences of living with and within a community are shared with tourists who are looking for an immersive travel experience in the country. This is done by developing appropriate hardware (tourism infrastructure) through sensitive architectural and design inputs and matching software (capacity building, management, and operation) through local NGOs/CBOs having exposure in the community building and tourism sector. As part of this campaign, we were involved in a community based rural tourism project in Mukutmanipur, Bankura, West Bengal, where we worked with a like-minded partner NGO.

We got an opportunity to get engaged in this project when we met with Antodaya Ashram (an orphanage) in the village Paoshi in Paschim Medinipur, West Bengal. This orphanage was going through a period of extreme financial liability and was finding it difficult to sustain itself. However, it was a valuable institution in the village and hosted almost 60 girls of various age groups. Apart from being a significant institution in the area, their other asset was that they owned ample land, picturesquely situated at



Fig. 23 Local skills and craftsmanship using locally sourced traditional materials.



Fig. 24 Multipurpose space for dining and activities in an improvised vernacular setting.

the bend of the Orissa-Bengal tidal canal. Our engagement with the situation was to find an appropriate strategy to add to the existing sociocultural linkages that the ashram already had with the local community, while at the same time find a way to alleviate the ashram's lack of assured financial capability to keep doing their work effectively.

The resultant conceptualization – *Mon Chasha* (Cultivator of Mind) – has been conceived as a tripartite arrangement comprising of a design partner, a tourism partner, and a community partner. The mechanism we designed borrowed from our experience of similar development processes during the Incredible India campaign. *Mon Chasha* was imagined as a community-led tourism initiative that highlighted and intimately curated the rural Bengal experience. As such, *Mon Chasha* is a process – the beginning of which is spread across a two-acre parcel of land. The process began with developing the right hardware (accommodation, facilities, etc.) and appropriate supporting software (cultivation of local skills, curation of myths, and an authentic Bengali cuisine).



Fig. 25 Improved typology to suit the rural Bengal context.



Fig. 26 Appropriate interiors involving local materials and skills.



Fig. 27 Evolved cultural space.

Since the focus was on promoting rural experience, the required hardware was conceptualized in a way that is essentially local (Fig. 22). The process started with the identification of a critical mass- the minimum facilities and amenities that needed to be built, and the quality of space that was necessary to sustain and support the other activities. Imagined as a space that is quintessentially rural Bengal, the architectural program started with four cottages (for four people each) with attached services and enough add-on spaces where people can relax, interact, and engage with each other. In addition, there was a decision to create a multifunctional community space in the form of a *Baithak* (lounge), a dining space, and a kitchen (Figs. 23–26). While the programming was important, its translation in terms of materials, techniques, and detailing was equally important. The architectural style was thus derived out of traditional skills and constructed using local skills and materials such as bamboo, thatch, *tal*,



Fig. 28 Authentic traditional Bengali cuisine | intangible heritage of rural Bengal.



Fig. 29 Rural craft and interpretation center.



Fig. 30 A traditional rural Bengal experience.

hogla, etc. The Chang typology was adopted as a base reference, as it is seen in similar climatic conditions, is efficient in using passive methods to increase user comfort and uses similar material and skill palates. However, modern materials have been adopted as they are practical, for example, in the toilets and sanitary fittings. The whole intervention also has systems of gray water management, waste recycling, etc., to minimize the environmental footprint.

Added to the hardware is the software, at whose core lies the ethos of Mon Chasha. It is a place where waste segregation and recycling are part of everyday practice. There is a deep-seated engagement with the natural cycles – ingredients for food is sourced from seasonal vegetables and locally grown produce. The community in the village have also been engaged with the place – in not only working at Mon Chasha, but in taking tourists around, showcasing their crafts, conducting boat trips, and performing in the evenings. There are certain implicit codes of conduct here, which have an uncanny way of making sense even to first time visitors (Figs. 27 and 28).

The space and the relationships have evolved, even transformed over time. Mon Chasha was meant to be an insertion into an existing sociocultural network to strengthen it, but in some ways, it has also started making its own sociocultural networks – with the ashram, the village, and the myriad tourists that come here. This network is ever increasing. The space has also evolved to have a richer experience – the campus now has a *goshala* (cow-shed), a *khamar* (granary), workspaces for local crafts, a sacred space for rituals, vegetable gardens, decks, a pond, and many others.

Being a process, we would like to believe that there is no definitive end. However, the process started from very humble beginnings, from financial paucity and a lack of any definitive idea. The implementation process was phased keeping in mind two things. One was the very low capital cost for the first intervention, and the second was building in periodic maintenance, additions, and alterations so that there are periodic opportunities to engage with the surrounding community. Mon Chasha has been running for six years now. It has approximately 85% occupancy and enjoys a unique position as one of the six must-see tourism projects of West Bengal.

The place has helped in sponsoring the Ashram for their activities and has also enhanced village livelihoods. In addition, it has become a landmark space of the surrounding areas. We believe that behind all these successes was the key idea of building onto and maximizing the existing value of a system – in this case the unique relationship of the ashram and the village, available land, picturesque settings, and ample local skills. Retrofitting in this process started not in the spatial realm, but in figuring out strategic interventions within the existing sociocultural milieu. It was then necessary to follow up the thought with an appropriate and nuanced spatial manifestation.

Mon Chasha is thus essentially different than a conventional tourism resort in an idyllic destination, in the way it is conceived, built, operated, and managed. It is a development process that is collaborative, coproduced, and inclusive. It's a process that is financially viable, yet at no point considers that as the only value. That is the reason it grows – naturally, efficiently, and inclusively. This nuanced natural growth is the real proof of its long-term sustainability (Figs. 29 and 30).

It is important to note that even though the above process showcases a trajectory towards sustainable spatial interventions, one needs to understand that the case is extremely specific and dependent on multiple factors, which is a major limitation. A process like this needs a collaboration between stakeholders with implicit trust, sensibility, and sensitivity to comprehend contexts holistically. It also needs a diverse range of expertise, skills, and capacities for implementation. This makes such processes difficult to replicate or scale.

Conclusion

The case of retrofitting a traditional house engaged not only with the conservation of a heritage residence but also the owner's struggle with growing financial pressure, compromised lifestyles and fear of disconnect from his existing social network. Where traditional spatial practices saw his heritage as a liability that is best demolished, the trajectories adopted showcase how it in fact has created additional financial and social security and has improved his quality of life.

In the revitalization of the old tannery, the key challenge was that an urban typology with strong cultural and occupational roots was suddenly perceived as useless, wasted space that was ill-suited to positive transformation within the overall planning and development framework of the city. The adoption of retrofitting as the process was able to transform this discarded space into something that created new community space in the neighborhood, strong bonds with the local community and trained and prepared future generations to successfully cope with the loss of the traditional occupations in the areas. The process has even created ripple effects of positive change through its indirect influence in the area.

In the case of the redevelopment of the Kalighat temple precinct, retrofitting has enabled an essential reframing of a beautification project with a short-term public (political) agenda into a case of negotiated development grounded in traditional practices, wisdom and collective memory. This has also led to equally grounded spatial solutions that successfully negotiate the complex morphology of spaces, activities, environment, safety, and security to suggest a development alternative that has been deemed viable and has been agreed to by all stakeholders. Furthermore, the process has, for the first time, been able to bring together different stakeholders at the same table. Together, these create a sociospatial context that has an increased probability of being holistically sustainable in the long run.

While the above approaches have a strong existing base scenario, the case of Mon Chasha delves in explorations at a different scale. Here, the intervention can be seen as the retrofitting of an existing structural relationship between different actors in a context, using space, design, and mutual dependencies to kickstart processes of positive change. This process foregrounds several values and experiences as assets, such as traditional wisdom, tangible and intangible unique experiences, available skills, passion, etc. These values are at the core around which is created an authentic experience of rural Bengal that at the same time is firmly grounded in the realities of Paoshi and the Antodaya Ashram. This process is able to highlight shared memories, lived experiences, disappearing crafts, and dialogs that are lost in current urbanization and development trends. In the process there are benefits that are accrued to all stakeholders: Sponsorship to the Ashram, work for local villagers, a secure future for kids, revenue for the resort and so on. These closed loop cycles and holistic dependencies make this whole exercise sustainable.

In summary, the cases illustrate the myriad contexts, issues, challenges and trajectories involved in the practical application of retrofitting, as both a concept and an idea to shape development projects. In each case, retrofitting creates a more holistic understanding and opens up alternative trajectories of design and implementation that are otherwise difficult in traditional forms of spatial practices. It also enhances the flexibility and effectiveness of the engagement to achieve positive change and adds value to

an existing circumstance. These interventions are at an appropriate scale, spatially grounded, and socioculturally relevant. The approach acknowledges the value of the existing (economic, physical, social, cultural, tangible, intangible, natural, etc.) and reinterprets them in an appropriate way so that they become more meaningful. The process looks at finding solutions that start from an immersion within an existing scenario and a natural process of evolution leading to appropriate trajectories of action. At its core, these trajectories reframe different forms of unacknowledged, unrealized, wasted assets into mechanisms that add value to the existing system in a collaborative, coproduced method that cuts across domains of conventional disciplines.

These examples illustrate the wider need for transformation of thought that drive current development attitudes. This needs to percolate and create a paradigmatic shift in the way spatial practices currently implements a wider development vision as a collection of fragmented, siloed, unidirectional projects. Only then can one move past the current conceptualization of sustainable development as efficient growth into something that can go beyond buzzwords to imagine a vision for the future that values the existing assets, is people-centered, inclusive, just, and equitable. Sustainable development would mean more than quantitative growth – it would mean qualitative betterment of human life in a responsible way, for now and for the future.

See also: Using Construction and Demolition Waste Materials as Construction Materials for a New Building

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Roof Gardens to Vertical Farming

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Introduction to the Development of Roof Gardens

Gardens are more than intrinsically related to mankind and an early reference can be found in the Bible in the story of creation in *Genesis the Garden of Eden in Genesis 2:8* (Bible, 1989). The reference to a garden, indeed roof garden or a terrace garden, could be traced back to the Hanging Gardens of Babylonia, which was built by King Nebuchadnezzar, who ruled Babylon for 43 years starting in 605 BCE. The Hanging Gardens consisted of vaulted terraces raised one above another, resting on cube-shaped pillars and the hollows filled with earth to allow trees of the largest size to be planted. The pillars, the vaults, and terraces are constructed of baked brick and asphalt. The existing oldest and best-preserved roof garden is from the Renaissance, located in the town of Pienza in Sienna, Italy. On the roof, a formal garden was erected for Aeneas Silvius Piccolomini to hold audiences. Now it is a UNESCO World Heritage site and its palace has remained virtually untouched since the 15th century.

In the modern era, roof gardens developed into social hubs for the public. Prior to the advent of air conditioning in the 19th century, they were a choice way to cool off in the evenings. The Casino Theater was the first theater to be completely electrified when it opened in 1882; however, the biggest draw was not the bright lights, but rather the roof garden theater. It quickly became the people's choicest destination during hot summer nights, which set off a roof garden craze in Manhattan and nationwide. At a time when most theaters were forced to close down for the summer due to the heat, these open-air theaters performed successfully to offer comfort and kept the businesses going.

In today's context, rooftop garden increases the percentage of greenery in built-up urban areas and brings back the vanishing urban green space; other than that, there are other benefits such as environmental, esthetics, social, and economic benefits. Added greenery in a cityscape also performs as the lungs of the city, cleaning off the carbon dioxide and illness-causing dust from the city atmosphere. Further, it contributes heavily to reduce the urban heat island effect and the related discomfort. From the behavioral point of view, these green spaces are also shaded and offer cooled space within the city's hot environment, furthering human interaction and livability. It retains and manages storm water, improves air quality, modifies urban microclimate, and creates biodiversity. Green roofs modify building behavior in terms of solar radiation, external temperature, relative humidity, and winds. These factors are slowed down and reduced as they pass through the foliage that covers the roof.

Developers are often held back from including rooftop gardens in their designs mainly due to concerns like high initial cost, chemical resistance of roof concrete to chemicals, and structural loading capacity. Lower initial cost solution is not the cost-effective alternative in a normal rooftop garden, since the resulting consequences become unbearable at a later date. A higher first cost and appropriate solution may be thus justified many times over for a durable product with minimal maintenance. Green roofs generally have longer life than exposed roofs because the additional layers of substrata and vegetation act as protection for the roof membrane. Other economic benefits include increased property values, increased marketability of a property, and opportunity to assist in LEED and GRIHA certification in several functional categories.

Design Principles

Design of rooftop gardens or its various types as discussed primarily depends on the investment potential of the developer or owner. However, in any form rooftop gardens offer a multitude of benefits including comfort and pleasing environments to avoid boredom. If one does not intend to invest higher initial costs, then it is advisable to go for planters, grow bags, and containers that are made of high grade plastic. This reduces the loading and water requirements when combined with drip irrigation. A plastic house or shade house as appropriate to the climatic context enables the plants to thrive in any season. The intent of the rooftop design must be clearly specified also the context in which the design is made to stand. Plants in containers offer better chances for relocation and differing mix patterns. On the other hand fixed rooftop gardens neither offer varying mix nor freedom from heavy maintenance and repair if not done for appropriate load bearing, chemical effects resulting from fertilizers, and corrosion due to dampness. Designing a rooftop garden for floriculture is advisable, since it brings a bit of return on investment.

Design is not restricted to genius, nor is it a uniform or simple process, nor is it distinct from practicality or detail. Practicing designers are aware of its convolutions, but they also half believe in the lightning flash (Lynch and Hack, 1984). The method's influence on the design should match the design intent (Jones, 1992). Understanding the methods in the design process allows a landscape architect to evaluate the end result of his or her design and to quickly construct changes in the design by applying different methods. Balcony and façade gardens with mulch, getting ready for planting, and how to integrate the horizontal and vertical landscapes are shown in Figs. 1 and 2 respectively. Planters in balcony gardens,



Fig. 1 Balcony and façade gardens with mulch, getting ready for planting, Wailea Marriot, Maui, Hawaii. *Source:* Prof. Abraham George.



Fig. 2 Balcony and façade gardens: Integration of horizontal and vertical landscapes, Wailea Marriot, Maui, Hawaii. *Source:* Prof. Abraham George.

indicating the importance of size of plant to pot and space, are shown in [Fig. 3](#). One must be careful to choose and maintain proportions in this case. Balcony and pathways gardens and integration of horizontal and vertical landscapes are best explained in [Fig. 4](#). While the penetrating light and water are most important, one must be careful to keep water from passages as it might lead to aquaplating and accidents to the splashing of water on surfaces like corridor floor. The same in principle is to be observed in placing water fountains and jets of water in landscaping. Roof gardens ensure protection from solar radiation and improve environmental esthetics by integration of plants with the right proportions, color, texture, and branching habits as illustrated in [Fig. 5](#). Organization of plants with their soft features and color and texture celebrates a built structure, as illustrated in [Fig. 6](#). These examples are a few eye openers to the value of rooftop and terrace landscapes if designed and maintained properly. Design is often guided by heuristic reasoning involving solution images, analogies, or restricted sets of form-giving rules that partially and provisionally define the solution for a problem; that is, what it should be like ([Rowe, 1982](#)). This approach is from an architect's perspective where forms of reasoning are analogous to Lynch and Hack's methods.



Fig. 3 Planters in balcony gardens, Four Seasons resort, Maui, Hawaii. *Source:* Prof. Abraham George.



Fig. 4 Balcony and pathways gardens: Integration of horizontal and vertical landscapes, Wailea Marriot, Maui, Hawaii. *Source:* Prof. Abraham George.

Vertical Farming

A swift turn to rooftop gardens is happening in today's world as the population explosion due to increased longevity has brought serious problems to the nation, particularly regarding the elderly. As people age their mobility declines, which leads to declined social interaction, activity, dignity, and self-respect. Urbanization with vertical housing blocks also poses a threat to the aging society because land and environment is a major concern in the urban environment, so too safety and security. Wellbeing, which is a measure of mental and physical health, will decline with aging. Environmental concerns, including issues of ecological justice, sustainability, and a focus on issues of food and security have also increased. Hence a community incorporating vertical farming



Fig. 5 Roof gardens: Protection from solar radiation and improved aesthetics by integration, Wailea Marriot, Maui, Hawaii. *Source:* Prof. Abraham George.



Fig. 6 Seasons depicted in pathways gardens: Integration of horizontal and vertical landscapes, Wailea Marriot, Maui, Hawaii. *Source:* Prof. Abraham George.

will enhance the wellbeing of the elderly with additional engagement and the pleasure of being with nature, which adds to the participation of the elderly in sustainability of urban agriculture, which adds to their value (Fig. 7).

Relevance of Vertical Farming

The significant increase in urban population will have greater impact on the availability of food, engagement of free time with nature, and participation of producing daily use vegetables for the elderly. This impact is due to shrinkage of arable land as a result of urban development and the lack of time and resources, along with weakening of the bond among family members in terms of nuclear families and pressures of job and work environments. One major solution to prevent this shrinkage is the high-density development that is now practiced all over the world with its own associated problems and advantages, such as vertical farming. The amount of arable land per capita has decreased from 5100 m² in 1950 to estimated 1600 m² in 2050. An estimated 10⁹ ha of more land will be needed for cultivation, if traditional farming practices are to continue as they are practiced. In India, changes in rain patterns and temperature could diminish its agricultural output by 30% by the end of the century. To overcome the scarcity of land and to maintain the constant productivity in urban area, vertical farming is to be incorporated into the vertical housing blocks of the contemporary world, which also can be seen as a viable solution for the engagement and participation of elderly and increasing their self-worth (Sashi Bhusan Raut, Research Scholar, Dept of Architecture and Regional Planning, IIT Kharagpur under the guidance of Prof. Abraham George). A comparison of soil-based versus soil-less agriculture is shown in Table 1, while the technologies employed in vertical farming are given in Fig. 8.



Fig. 7 Tomatoes growing in soil and Swiss chard growing in a soil-less system. *Source:* Public domain: <http://www.fao.org/3/a-i4021e/i4021e06.pdf>.

Table 1 Soil-based vs. soil-less agriculture

Category		Soil-based agriculture	Soil-less agriculture
Production	Production quality	Depends on management and soil characteristics. Cannot be fully controlled because of exposure to natural environments.	Fully controlled by appropriate use of nutrients at different stages of plant growth and creation of artificial environment suitable for plant growth.
	Yield	Not constant because of soil characteristics and management.	Constant because free from soil and varies by management practice.
	Sanitation	Unhealthy condition because of water being contaminated by use of fertilizer and pesticides.	Healthy condition because of minimal risk of contamination of water.
Nutrition	Nutrient delivery	Cannot be controlled at the root zone because of soil characteristics and structure.	Fully controlled at the root zone because of soil-less water medium.
	Efficiency of nutrient use	High loss of nutrients due to leaching and runoff.	Much less loss of nutrients because of uniform and real time adjustable flow of nutrients.
Water use	System efficiency	Maximum loss of water due to soil characteristics.	Efficient use of water by the help of sensors. Less labor cost for watering.
	Salinity	Water becomes more saline and requires large amount of water to make it usable.	Saline water can be used. Also requires large amount of water when dilution is required.
Management	Labor and equipment	Less investment because of standard machines. More manpower needed for operations.	High investment in equipment and high initial set up cost. Less manual labor required for operation.

Source: Prof. Abraham George.

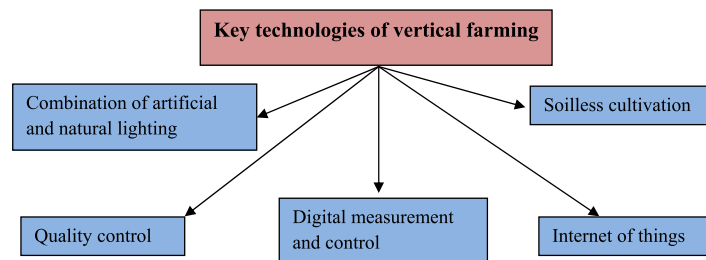


Fig. 8 Technology associated with vertical farming. *Source:* Prof. Abraham George.

Conclusion

Rooftop gardens are an enchanting design opportunity combined with energy efficiency and a welcome design solution to enhance coherence of urban life and enhancement of property value. Vertical farming is a method to increase physical participation, psychological benefits, and social cohesiveness among elderly, which in turn enhances their self-worth and wellbeing. It is one of the sustainable methods of food production and lends a feel of involvement in making one's own food. Vertical farms are easy to

maintain, convenient to harvest, and keep the pollution at lower levels. The elderly feel connected with their families, friends, and neighbors not only at the social level but also at the environmental level and can improve their quality of life. To fulfill these objectives, we need to develop the models, methods, and systems of vertical farming at affordable limits. The immediate attention shall be focused on urban multistoried housing and other amenities.

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Study of Junctions With Bamboo: An Attempt Towards Their Classification

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Introduction

Bamboo has been used in construction for ages; however, the practice has been primarily artisanal. The engineered material for similar construction practices has been timber. As awareness increases about the environment, engineers and technologists look for sustainable construction materials, alternative to timber, where bamboo stands out as a forerunner. [Mukhopadhyay and Dutta \(2015\)](#) states the following major advantages of using this natural construction material.

- Bamboo take about 3–5 years to mature whereas timber take about 15–25 years.
- It produces 35% more O₂ than equivalent stands of trees.
- Some species of bamboo sequester up to 12 metric tons of CO₂ from air per hectare.
- Bamboo forestry assists in soil conservation, watershed development, and wasteland reclamation.
- Its fibrous morphology and natural lightness helps bamboo structures to absorb more strain energy released during earthquakes than timber.

However, bamboo has a few disadvantages for which it is not used as widely as timber. One of the major reasons is its geometry, which imposes certain restrictions on the workability; this restriction is essentially experienced while designing junctions with bamboo. Less availability of data about strength properties of different bamboo species that are deemed fit for building construction, is another limitation. These are some of the key reasons for which use of bamboo has remained, by and large, traditional. Amidst this, sustainability of bamboo has created interest regarding this building material beyond its traditional users, among architects and designers. Subsequent experimentation has resulted in attempts towards improved practices in bamboo junctions.

Need for Documenting Bamboo Junctions

Junctions in bamboo structures are at the interphase of different structural members and they play the important role of effectively transferring force between members, and to achieve continuity between elements with controlled displacements. This load includes self-weight of the structures, the external forces acting on them, and various internal and external stresses due to changes in temperature and humidity. In response to different structural challenges, a number of unique bamboo junctions have been innovated. The design solutions have generally been arrived at, through trial and error; and they are rather specific as opposed to being general. Lack of documentation of these solutions along with limited scope of communication between design-innovators, artisanal or otherwise, have led to the creation of unstructured knowledge, which has a lesser probability of getting re-used.

This article, therefore, attempts to classify the standard bamboo junctions to help their utilization and application for constructions which are yet to come. This would also encourage and initiate dialog between architects and designers from various places to take the work ahead in utilizing this sustainable building material.

Classification of Bamboo Junctions

Observations of bamboo at junctions of different building elements, like roofs, walls etc., reveal varied application of bamboo. One would observe that both whole bamboo and split bamboo pieces have been used in traditional, as well as, in improved practices of fabrication of junctions. Occasionally the constituent member elements of a bamboo junction are observed to be in the same plane, and sometimes they are skewed. Again, the method of jointing varies considerably in each of the above mentioned cases. Based on these observations, an attempt has been made in the following sub-sections to classify bamboo junctions into four main heads. The sub-sections investigate and illustrate these four core types through examples.

- (1) Shape and form of structural members,
- (2) Level of technology applied,
- (3) Planarity of the structural members, and
- (4) Method of jointing.

Shape and Form of Structural Members

Round or whole bamboo culms ([Fig. 1\(a\)](#)) are typically tubular hollow cylinders, which are longer than their diameter. For different construction purposes, the whole bamboo pieces are slit along their vertical axis to produce split bamboo pieces

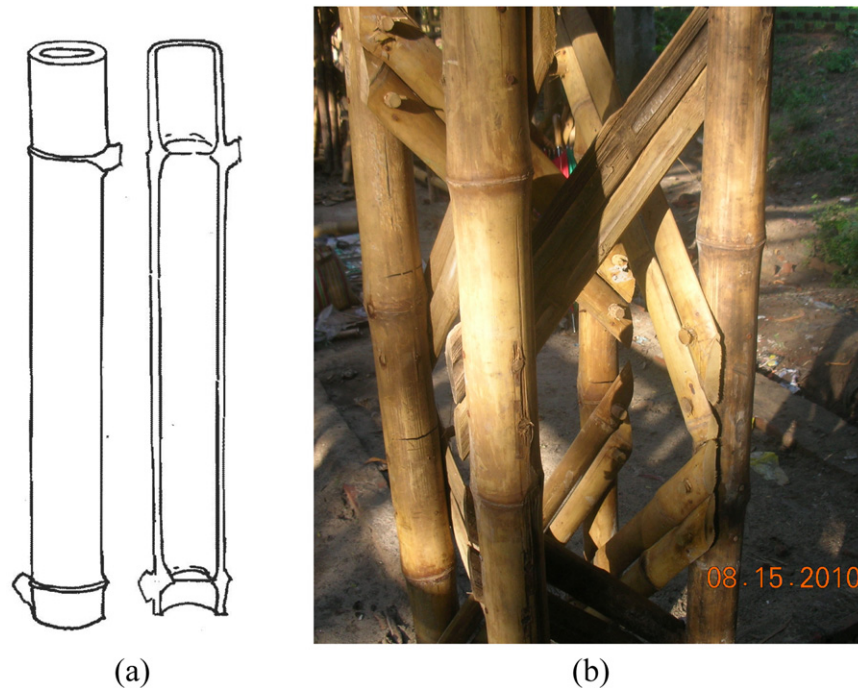


Fig. 1 Classification of bamboo based on shape and form: (a) round or whole bamboo, and split bamboo; (b) bamboo column made of combination of whole and split bamboo. Reproduced from (a) Janssen, J.J.A., 1981. *Bamboo in Building Structures*. Eindhoven: Eindhoven University of Technology.

(Fig. 1(a)). In fact, there has been contradictory claims regarding strength of whole and split bamboo pieces. Whereas National Building Code (NBC) of India (BIS, 2016) states “strength of split bamboo is more than that of round bamboo”, Mukhopadhyay and Dutta (2015) reports that round specimens of the species *Bambusa balcooa* are stronger than their split counterparts. They explained their finding by the fact that donut geometry of hollow round specimens provides it with enough section modulus to offer more moment of resistance than the solid split ones. In practice, combination of whole and split bamboo pieces are used (Fig. 1(b)). Thus, based on shape and form of constituent members, bamboo junctions may be classified into:

- Round or whole bamboo junctions,
- Split bamboo junctions, and
- Round-split junctions.

Level of Technology Applied

Based on the level of technology applied, bamboo junctions may be classified into two broad types:

- Low-tech bamboo junctions, and
- Hi-tech bamboo junctions.

The traditional junctions with bamboo, which are simple, inexpensive and fabricated with easy-to-obtain technology, are commonly referred to as low technology junctions or abbreviated as low-tech junctions (Fig. 2). The simple methods of fabrication may refer to tying with ropes or nailing together. Low-tech junctions can be easily comprehended, free from specialization, and can typically be fabricated with a minimum of capital investment. Because of their ease of construction, these are simple to construct and does not involve much of a technical input. They are rather products of human intuition and common sense.

The use of bamboo, as an alternative to timber, of late, has spread beyond low-tech genre. Different architects and designers have adopted the approach of combining other engineered materials with bamboo to solve specific design needs. In the given example (Fig. 3), bamboo has undergone a formal treatment process and the assembly is a calculated engineered approach. Such junctions and assembly are, therefore, complex and involve a high level of technology. High technology, abbreviated as hi-tech, is conceptually opposite to low-tech, intrinsically non-traditional and innovative.

Planarity of the Structural Members

During fabrication of bamboo structures, it is observed that constituent members require to be joined together to create a framework or a structure. The members may lie in the same plane or in different planes. Variation in planarity of the structural members

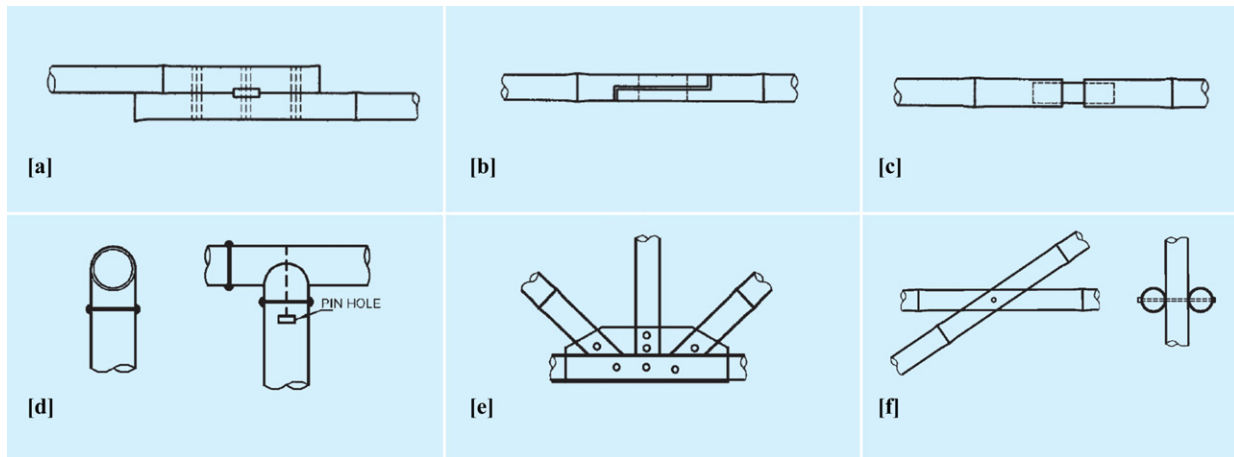


Fig. 2 Typical low-tech bamboo junctions: (a) full-lapped joint; (b) half-lapped joint; (c) spliced joint with inserts; (d) saddle joint with lashing; (e) gusset-plated joint; (f) simple bolted connection with mild-steel washers. Reproduced from Bureau of Indian Standards (BIS), 2016. Part 6: Structural Design, Section 3, Timber and Bamboo. New Delhi: BIS.



Fig. 3 Example of a hi-tech bamboo junction. Reproduced from Yu, X., 2007. *Bamboo: Structure and Culture – Utilizing Bamboo in the Industrial Context with Reference to its Structural and Cultural Dimensions*. Essen: University of Duisburg-Essen.

of a bamboo junction causes variation in the bending moment generated at that junction. Based on the planarity of the bamboo structures, they may be classified as:

- Coplanar bamboo junctions, and
- Non-coplanar bamboo junctions.

In order to appreciate a coplanar bamboo junction, one may consider a rectangular frame-work fabricated using four pieces of bamboo lying in the same plane; again, sometimes a diagonal member is added as a cross-bracing to strengthen the frame-work. Another example of coplanar bamboo junction has been illustrated in [Fig. 4\(a\)](#) where six bamboo members, lying in the same plane, are bolted to a circular ring. [Fig. 4\(b\)](#) illustrates a classic example of non-coplanar bamboo junctions, where a number of small triangular bamboo pyramids have been joined together forming a bigger one.

Method of Jointing

Any and all of the above mentioned three types of bamboo junctions and their sub-classes employ different methods of jointing and fastening, which are specific to the specific application. The end goal is to retain the pieces in their desired or predicted positions. The popular methods used for fastening and joining bamboo members are as follows:

- Use of ropes,
- Use of bolts and nuts,

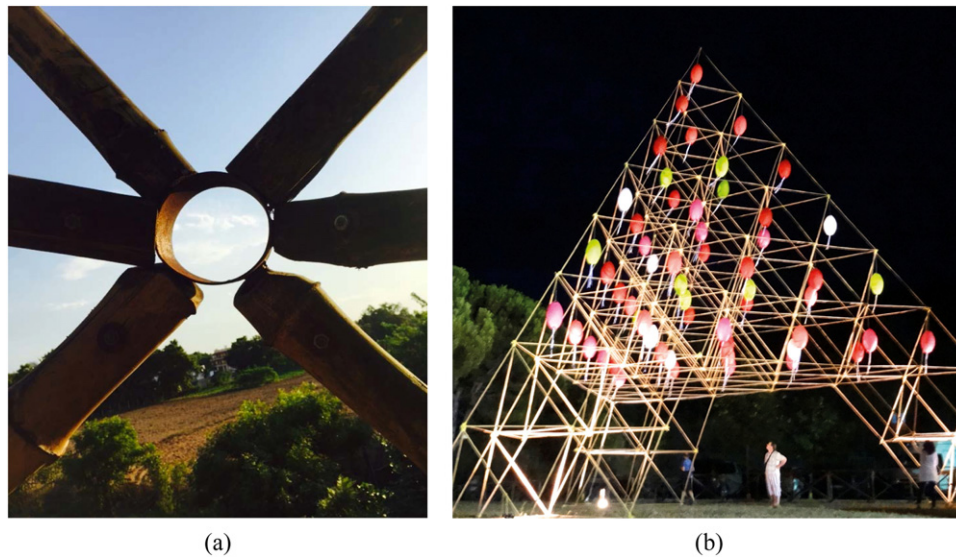


Fig. 4 Planarity of bamboo junctions: (a) several bamboo members in the same plane forming a coplanar junction; (b) Casalini's Cultural Pyramid, Lago Trasimeno, Italy by Antoon Versteegde – an example of use of several non-planar junctions in a bamboo structure. Reproduced from (a) Auroville bamboo center, 2019. Available at: <https://aurovillebamboocentre.org/growing-tower-shalini/>, (b) Versteegde, A., 2013. Available at: https://commons.wikimedia.org/wiki/File:Antoon_Versteegde_Casalini.jpg.



Fig. 5 Bamboo junctions using ropes. Reproduced from Larry, 2010. Bamboo construction from big bambu on met rooftop. Available at: <https://www.flickr.com/photos/muyyum/4850823894>.

- Use of plates,
- Use of carpentry joints,
- Use of glue.

Use of ropes

Tying with a rope is a simple mechanism that does not require much of engineering knowledge (Fig. 5). However, the choice of the material of the rope and the kind of knot applied is important to secure the members in place so that the junction does not slip and fail. Coconut fiber ropes, hemp fiber ropes, jute ropes or even old clothes are used for tying. However, ropes when exposed to the weather may decay and fail, hence would require to be replaced from time to time.

Use of bolts and nuts

Using bolts and nuts involve drilling holes in the members to be joined. However, drilling holes in bamboo is different from that in timber. In bamboo holes are drilled through constituent members in the internodal regions, and not in the nodes. It may be noted here that nodes in bamboo are very strong zones, unlike in wood, hence even trying to drill holes through them would be impractical.

Once the members are ready with properly drilled holes; bolts are driven through them and secured with nuts to achieve a junction. Overlapping of the constituent bamboo members is mandatory for such junctions (Fig. 6).



Fig. 6 Joining bamboo by means of bolts and nuts. Reproduced from Smithsonian Cooper-Hewitt, National Design Museum, 2010. Millennium school bamboo project. Available at: <https://www.designother90.org/solution/millennium-school-bamboo-project/>.



Fig. 7 Bamboo junction by Renzo Piano using plates. Reproduced from Georg-Christof, V.B., 2009. Bambú brasileiro or the future of a material. Stylepark. Available at: <https://www.stylepark.com/en/news/bambu-brasileiro-or-the-future-of-a-material>.



Fig. 8 Joining of bamboo using industrial glue. Reproduced from Wisdom, T., 2012. Natural fiber rope and epoxy joints. Available at: <https://www.flickr.com/photos/thomwisdom/7358920860>.

Use of plates

In the above mentioned two bamboo jointing methods, involving use of ropes and bolts and nuts, bamboo members forming a junction needs to be overlapped. However, there are situations when one needs to avoid the overlapping. Forming bamboo junctions using plates is a jointing method that allow one to achieve junctions avoiding overlap. Plates are also used in bamboo junctions to achieve longer lengths in bamboo where two members are joined tip to tip. Such junctions are also used to accommodate two bamboo members meeting at an angle in the same plane. Again, plates can be used to form complex junctions where the design of the plate is modified to act like florets to achieve joining of more than two members lying on various planes (Fig. 7).

Use of carpentry joints

Standard carpentry joints which involve cutting a groove, interlocking two members etc. can be used in bamboo with intuitive modifications. Lap joint, dovetail joint, and mortise and tenon joints are examples of some of the widely used carpentry joints, used in design of bamboo junctions.

Use of glue

Industrial adhesives are mostly used in combination with bolts or rope made junctions for further securing the joint. PVC glues are also used which form a protective membrane or layer over the junction and protect the underlying material from wear and tear, thus extending its life. Designing bicycles (Fig. 8) and furniture using industrial glue are two of the extensive uses of glue in industrial design.

Apart from securing bamboo junctions, as mentioned above, industrial glues are also extensively used in making bamboo boards, bamboo doors-windows and utensils made from bamboo dust.

Conclusion

The search for sustainable building material has brought bamboo from the fold of age old artisanal use to the arena of engineered investigation. Observing its similarity with timber, the artisans has initially adapted timber fastening and jointing methods to develop bamboo junctions. Use of ropes and carpentry joints in low-tech bamboo junctions represent this stage of development, which has its own area of requirement and is still continuing. However, rise in its engineered application has resulted in the development of the hi-tech bamboo junctions using bolts and nuts, plates and industrial glue.

Apart from the above often-used ones, architects and designers have often created special bamboo junctions addressing specific design needs. These are custom solutions and are mostly not generic in nature. Further, some of these junctions may find wider use in future. However, a generic lack of documentation, variation in bamboo from region to region, lack of strength data and other factors hinders their application. Bamboo is still undergoing a lot of research and there are newer junctions which are yet to be tested for stability, ease of fabrication and longevity. These research heavily bring into use modern industrial design principles of modularity, fabrication standardization and mix material usage.

See also: Bamboo Structural Technology

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Sustainability and Green Building Rating Systems: A Critical Analysis to Advance Sustainable Performance

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Green Building Rating Systems

Green buildings are structures that aim to minimize the environmental, economic, and social impacts of construction and optimize the use of resources. Green buildings use more environmentally friendly materials and ensure efficient use of natural resources such as water and energy with minimal generation of waste. Technologies and innovative systems such as efficient cooling, lighting, and energy operators that automatically adjust room temperature, control internal lighting, reuse water, and consume less energy are also implemented in green buildings. Additionally, green buildings improve indoor environmental quality and thermal comfort reducing the sick building syndrome and increasing the well-being of its occupants and their quality of life.

Green building rating systems are methods used to certify green buildings and serve as a means of reducing construction impacts along the entire life cycle. Rating systems measure performance of building assets across a range of sustainability principles. These require an integrated design process to build projects that are environmentally responsible and resource-efficient from concept to design, construction, operation, maintenance, renovation, and demolition. A primary reason for the creation of rating systems was the need to more clearly define, implement, and measure green goals. Some rating systems are single-attribute, focusing exclusively on water or energy, while others are multi-attribute addressing not only water and energy but emissions, toxicity, and overall environmental, economic and social performance. Even though the philosophy, approach, and certification method vary among rating systems, a shared objective is that certified projects are designed to reduce the overall impact of the built environment, the natural environment, and enhance human health and well-being.

There are multiple factors that should be considered to determine which rating system should be used to certify a building. Firstly, identify what organization is making the assessment and is it being done by a first, second or third party. A first-party assessment is one that comes directly from an organization that is associated with the entity applying for certification or who may benefit from it. An interested party such as a trade association performs a second-party assessment. A third-party assessment is conducted by an independent party that has no financial interest or ties to the outcome of the assessment. Secondly, the type of certification system pursued for a project depends upon that singular project since none of these certification systems are one-size-fits all. Some rating systems address project types such as single-family houses and commercial buildings while others address entire neighbourhoods and communities. There are rating systems available for new construction and major renovations, which focus on decisions made in the planning and design process and actions taken through construction. Other systems are developed for existing buildings, which focus on operations and maintenance throughout the life of the building. The dynamic nature of projects might prohibit one system but favour another. Ultimately, the choice is dependent upon the uniqueness of each project and the project needs and requirements such as the location, size, budget, and overall goals. By comparing essential requirements such as cost, ease of use, and building performance, decisions can be made regarding, which building rating system is applicable and what level of certification is possible.

Pursuing a Green Building Certification

There are various reasons for pursuing a green building certification for a project. Certification provides verification of the accomplishment of green goals, and can be a valuable marketing tool for owners, and design and construction teams through the process of developing a sustainable building. Certification can also be a way to provide an incentive for clients, owners and users to promote highly sustainable construction practices and minimize the environmental and social impacts of construction projects. Rating systems also outline what green standards need to be followed and what type of products should be included in construction specifications. Economic and environmental benefits to sustainable design, often achieved through green building rating certification, have also been quantified and have served to promote new projects. Multiple studies have found that energy, carbon, water, and waste can be reduced, resulting in savings of 40%–60% in costs. Operating costs of green buildings can also be reduced by 8%–13% while increasing its value up to 7.5% compared to regular buildings. Many sustainable buildings have also seen increases of up to 10% on return on investment, 6% in occupancy, and 3% in rent. Other benefits of green buildings such as higher productivity and increased occupant health have been attributed to better indoor environmental quality, increase in natural daylighting, and healthier materials and products. While these benefits are possible, it is important to note that they are dependent upon factors such as climate, topography, timing, credit synergies, and local building standards (GhaffarianHoseini *et al.*, 2013). Additionally, it is worth noting that a building can be sustainable and can be built according to green specifications, but not necessarily needs to be certified to achieve or comply sustainable goals. Certification in most cases is a voluntary process, but recently it has become a standard for construction projects and a requirement for some private and government-owned buildings.

Performance Evaluation in Rating Systems

Two kinds of approaches have been followed to develop performance metrics for rating systems. The first is based on a multi-criteria credit system in which several credits in prescribed categories evaluate the level of sustainability and the project is awarded points. This system follows a prescriptive path by evaluating whether the project implements features or not. The second approach is based on indicators quantified by means of a life-cycle assessment (LCA) procedure. The LCA analysis is a scientific method and is more complex. This system follows a performance path by looking at the functioning and operation of the project. Building sustainability can be assessed using several methods and labelling tools, which are characterized by different credits, weights, calculation procedures, and performance analyses. These differences can impact the final scores and the level of sustainability achieved by each project. Furthermore, rating methods are defined according to local climate and geographical conditions resulting in the adaptation of sustainability to a local or national level. Even the ranking of criteria is also adapted to local conditions and may not be similar at the international level. However, at the global level, building sustainability should be comparable among different conditions and countries despite the differences in features and methods and that poses a challenge.

Building rating systems are in a state of change and evolution and continue to be refined to reflect new standards and goals for achieving ever-higher levels of sustainability at the global level. Therefore, it is essential to investigate the most current versions of these systems to gain an understanding of requirements that must be met in order to achieve the best results. There are approximately 600 rating systems around the world (Vierira, 2011). Very comprehensive inventories of rating systems and tools for green assessment and certification can be found in the Whole Building Design Guide (WBDG), the Global Reporting Initiative (GRI), and the World Green Building Council (WGBC), which is an organization that gathers the national green building councils around the world. The BREEAM was the first rating system developed in the early 1990s and numerous other methodologies have followed it.

This review focuses on the United Kingdom's BREEAM, the United States' LEED, the Arab States' GSAS and India's GRIHA. The rationale for selecting these rating systems is based on comparing two well-established rating systems that were developed to be adaptable to different regions (BREEAM and LEED) to two rating systems that are region-specific, are in their earlier stages, and have seen an increase in their use (GSAS and GRIHA). Future directions and alternatives are also discussed that advance rating systems and sustainable performance measurement alternatives.

BREEAM

The BREEAM was developed in 1990 in the U.K. and it was the first green building rating system in the world. Operated by the Building Research Establishment (BRE), it is widely used throughout the UK the EU, EFTA member states, and EU candidates. Due to its longevity, its use is widespread, and its certification has highly been recognized as influential to almost all later green building rating systems developed such as LEED. BREEAM evaluates a building's lifecycle in view to design, built, operation, and refurbishment and it is widely used because of its flexibility. It assesses not only local codes and conditions, but also allows application in international buildings. As of 2018, BREEAM has issued over 560,000 certifications in over 80 countries and it is expected that both the number of projects certified as well as the countries adapting it will follow an incremental pattern. BREEAM is a multi-attribute rating and certification system that follows a multi-tiered process with pre-assessment and third-party consultant guidance. It is used for the assessment of new construction, communities, in-use buildings, and eco-homes and widely used by planners, local authorities, developers and investors. The assessment process uses recognized measures of performance to compare them against a set of established benchmarks in the areas of energy and water use, internal environment (health and well-being), pollution, transport, materials, waste, ecology, and management processes. Even though all the sustainability criteria are assessed by BREEAM, the environmental factor is still predominant with eight main categories.

LEED

The United States Green Building Council (USGBC) created the LEED in 1998. LEED has been accepted as the most widespread and recognized rating system in the United States, after having established strong credibility among the experts. It is widely used by architects, engineers, and designers that want to earn LEED certification. Since its creation as a voluntary standard measure, the LEED system has become an appropriate tool for the assessment of green buildings, becoming a reference system for the design, construction, and operation of green buildings beyond the United States. The WGBC states that adaptations of the LEED system have been developed or are in the process of implementation in Central and South America, Asia, Middle East, and India among others. As of 2018, LEED has issued over 78,000 certifications in more than 150 countries and it is considered the world's most widely adopted rating system based on the number of countries that have adapted it. LEED is a multi-attribute rating and certification system, which assesses different building types such as new construction, existing buildings, commercial interiors, core and shell, schools, retail, healthcare, homes, and neighbourhood development. LEED has mandatory prerequisites such as minimum energy and water-use reduction, recycling collection, and tobacco smoke control. If the prerequisites are achieved, then a project can earn points in seven categories: site selection, water efficiency, energy and atmosphere, materials and resources, indoor environmental quality, regional priority, and innovation in design. Within each category there are credits that pertain to specific strategies for sustainability, such as the use of low-emitting products, reduced water consumption, energy efficiency, access

to public transportation, recycled content, renewable energy, and daylighting. It uses a prescriptive and feature-oriented approach rather than a performance approach. There are no on-site visits required and certification can occur upon completion of a project. Even though all the sustainability criteria are assessed by LEED, the environmental factors are predominant within the seven categories. Additionally, some economic factors are also considered and play a key role within the categories.

GSAS

The Global Sustainability Assessment System (GSAS) is the first performance-based system in the Middle East and North Africa (MENA) region and Qatar, developed for rating green buildings and infrastructure. GSAS was established by the Gulf Organization for Research and Development (GORD) through collaboration with the University of Pennsylvania and Georgia Tech for the development of a sustainable built environment that minimizes the ecological impact while addressing specific environmental, social, and cultural needs of the region. GSAS was developed in 2007 by drawing best practices adopted from a comprehensive review of more than 40 regional and international building rating systems, tools, and guidelines. The review was later narrowed to six well-known rating systems including BREEAM and LEED, in which MENA's specific needs and regional requirements were integrated with sustainability goals. By combining the best features from the most well-established rating systems with new facets and dimensions, GSAS offers a more comprehensive approach to sustainability requirements and goals from a macro level to a micro level. It uses a quantifiable and result-oriented approach rather than a prescriptive and feature-oriented approach. As of 2018, GSAS has issued over 200 certifications in the MENA region.

GSAS is a multi-attribute rating and certification system, which assesses different building types such as districts and infrastructure, commercial, mosques, neighbourhoods, parks, residential, schools, hotels, light industry and healthcare among others. Through the life cycle approach, GSAS evaluates performance in eight categories: urban connectivity, site, energy, water, materials, indoor/outdoor environment, cultural and economic value, and management and operations. Even though all the sustainability criteria are assessed by GSAS, the environmental factors are predominant with four categories. Additionally, a considerable number of points are awarded to management and operations.

GRIHA

The Green Rating for Integrated Habitat Assessment (GRIHA) is the rating system for green buildings and infrastructure developed in India in 2007. The GRIHA was established by the government and the Ministry of New and Renewable Energy (MNRE) and the Energy and Resources Institute (TERI) to assess the performance of buildings against nationally acceptable benchmarks. It evaluates the environmental performance of a building holistically over its entire life cycle, providing a standard for green buildings. The GRIHA, based on accepted energy and environmental principles, balances established practices and emerging concepts at both national and international levels. It has been developed to design and evaluate new buildings and buildings that are still at the inception stages with a minimum area of 2500 m². The latest version published in 2015 assesses performance or predicted performance over the life cycle from pre-construction to planning, construction, operation, and maintenance. As of 2018, GRIHA has issued over 500 certifications in India and it is expected that the number of projects certified will follow an incremental pattern.

GRIHA is a performance-oriented system, where points are earned for meeting the design and performance intent of the criteria. There are six criteria: site planning, energy and occupant comfort, water savings, waste management, sustainable building material, and social aspects. Each criterion has certain points assigned to it and a project demonstrating compliance with a criterion would receive the associated points. There are 100 points available within these categories with mandatory and optional criteria. Mandatory prerequisites include water quality, tobacco smoke control, and zero ozone-depletion-potential materials. Within each category there are criteria that pertain to specific strategies for sustainability such as low impact design, water reutilization, reduced embodied energy, labor safety and sanitation, air and water pollution control, reduction in waste during construction, and operation and maintenance. GRIHA assesses different building types such as affordable housing, offices, retail spaces, institutional buildings, hotels, hospitals, healthcare facilities, residential, and multi-family high rise buildings among others. Even though all the sustainability criteria are assessed by GRIHA, the environmental factors are predominant. In the next section, the four rating systems are analysed and compared in detail.

Features of BREEAM, LEED, GSAS, and GRIHA

Table 1 shows the main features of the four rating systems including coverage, first and latest version, rating method, rating level, and main categories. BREEAM served as a basis for the development of the later rating systems, while LEED continues to be the most-used rating system around the world. As shown in **Table 1**, all four rating systems released their latest versions recently, which shows that the organisations responsible for their management and release are making efforts to revise and update its criteria to follow with the newest developments in green buildings.

Table 1 Main features of rating systems

Rating system	Coverage	First and last version	Rating method	Rating level	Categories	
BREEAM	80 countries	1990 2016	Pre-weighted categories	Pass ≥ 30 Good ≥ 45 Very good ≥ 55 Excellent ≥ 70 Outstanding ≥ 85	Management Health & wellbeing Energy Transport Water	Material Waste Land use & ecology Pollution Innovation
LEED	150 countries	1998 2013	Credits and points	Certified ≥ 40 Silver ≥ 50 Gold ≥ 60 Platinum ≥ 80	Integrative process Indoor environment quality Energy & atmosphere Location & transportation	Water efficiency Material & resources Sustainable sites Regional priority
GSAS	MENA region	2007 2017	Score and criteria with weights	1 star $0.00 < x \leq 0.50$ 2 stars $0.50 < x \leq 1.00$ 3 stars $1.00 < x \leq 1.50$ 4 stars $1.50 < x \leq 2.00$ 5 stars $2.00 < x \leq 2.50$ 6 stars $2.50 < x \leq 3.00$	Urban connectivity Site Energy Water	Innovation Materials Indoor/outdoor environment Cultural & economic value Management & operations
GRIHA	India	2007 2015	Score and criteria with weights	1 star 50–60 2 stars 61–70 3 stars 71–80 4 stars 81–90 5 stars 91–100	Site planning Construction management Occupant comfort and wellbeing Sustainable building materials Performance monitoring and validation Innovation	

BREEAM and LEED were developed only by non-profit third-party organisations. In addition to third party organisations, GSAS was established with significant input from best practices of previous rating systems and collaboration from academia and industry.

GRIHA was also developed by third-party organisations and with a dominant role from the government and the ministry of energy. It is worth noting that the four rating systems are voluntary tools. However, certification has become a mandatory requirement in some regions or for specific purposes. BREEAM is a mandatory requirement to achieve funding from the Department of Health and Education in the UK. California is the first state in the US that requires high-rise residential projects to be certified LEED silver since 2010. GRIHA rating is mandatory for government buildings as a precondition for departments to get subsidies and other financial assistance for green development since 2011. The GSAS rating is becoming mandatory for new developments funded by the government. The following comparison is focused on new construction manuals, as all the rating systems have a certification for this type of project. For GRIHA, the affordable housing guidelines were used for the comparison.

Coverage

BREEAM and LEED have a significant number of green certified buildings globally. Although both rating systems consider regional characteristics, climate, and culture, other countries besides the UK and the US have adopted (and could adopt) BREEAM and LEED. The flexibility and applicability of GSAS and GRIHA is still limited because they were established only about a decade ago. They were developed to be more region-specific and towards certifying domestic projects leading to fewer number of certifications.

Rating Method

The rating method differs among the green building rating systems. BREEAM has 134 available points (excluding the non-residential building items). It is a multi-attribute certification system that follows a multi-tiered process with pre-assessment and third-party consultant guidance. During the assessment process, the project's metrics of performance are compared against a set of established benchmarks. If the performance is achieved, a score is given. The final scoring level is determined by considering the

score achieved and the pre-weight factor given to each category. BREEAM scoring is based on performance and weights so it is more complex. Additionally, it is stricter in its criteria for achieving credits as it sets absolute parameters.

LEED has 100 available points and it is based on prerequisites and credits. The prerequisites are mandatory; thus, all projects must meet these in order to achieve certification. To earn certification, LEED follows a prescriptive approach in which the project is evaluated to determine whether it has specific features or not. If the project has the features prescribed in the credits, the points are achieved. All the points are added to calculate the final score and certification level. Only a few credits evaluate performance. LEED is considered a transparent approach for calculating points as the evaluation determines whether the project has a feature or not, without requiring a quantifiable measure. Additionally, it is simpler in its criteria for achieving credits as it sets relative percentage improvements or reduction targets.

GSAS is a system with a maximum scoring level of 3.00 and uses key performance indicators to score the project and assess the criteria on each category. The categories have a designated pre-weighted rank based on the analytical hierarchy process (AHP). There is a maximum value the project can achieve, within each category, and based on its compliance and the weight assigned, the project is awarded a score for each criterion. The sum of the scores determine the certification level. GSAS is a performance-based approach in which results are quantified and has designated an importance factor for each category. Like BREEAM, the scoring is more complex as it is based on weights.

GRIHA has 100 points available and it combines a prescriptive and performance path. While the intent of some of the criteria is based on compliance, there are others which need to be validated on-site through performance monitoring. The points evaluated through performance are awarded provisionally while certification is in process and are converted into firm points after monitoring, validation, and evidence. Points achieved in each category are added to determine the certification score. GRIHA combines the transparent approach of compliance and the stricter approach requiring quantifiable measures.

Certification Process

BREEAM certification process starts with the project's registration with the BRE and appointment of an assessor to assess the project. A pre-assessment process is carried out with the assessor and the project's documentation and information are prepared. The assessor reviews the documentation and determines the compliance with the standard. Later the documentation is sent to the BRE to establish the certification level. Certification is awarded for the entire life of the building.

LEED follows an online certification process. Project teams are required to compile documentation to show compliance with its requirements and upload this documentation to the LEED Online website. The Green Building Certification Institute (GBCI) then reviews the documentation and a certification is earned if all prerequisites and enough credits are earned. There are no on-site visits required and certification can occur upon completion of construction and as-built documentation showing compliance. Certification is awarded for the entire life of the building.

GSAS certification process is handled through the online certification management portal and all projects aiming to obtain the certification must register on the GSAS gate. The gate portal is the main database where all the required documents and evidence are prepared and submitted. The review follows a two-step process: a desk review to ensure submission of the requirements and an on-site audit to verify compliance. Additionally, there is a 12-month assessment period in which building operations are monitored to evaluate the sustainability of the project. Even though a building can still obtain the certification based on the as-built specifications without submission of data, the scores will be based on submissions and the data (if provided) can lower the overall rating achieved. Certification is awarded for four years upon which re-certification can be applied.

GRIHA compliance, as specified in the relevant criterion, must be submitted in the prescribed format. The certification follows the GRIHA online process. Project teams are required to register the project before conception and to show compliance with its requirements by uploading this documentation to the website. The documentation shall be sent for a third-party review and three on-site visits are required during the project execution for auditing the green features and on-site performance monitoring. The GRIHA council then reviews the documentation and gives provisional points with an option to resubmit the documentation if there is a desire to increase the certification. The certification is awarded for five years and there is an audit after the first year of commissioning the building. GRIHA reserves the right to conduct random visits and audit any credit that has been awarded.

It is worth noting that BREEAM, LEED, and GSAS can be used to certify new construction and existing buildings and infrastructure while GRIHA can only be used to certify new construction, as projects must apply for certification as early as the design stage.

Life-Cycle Phases and Evaluation Approach

The project's life-cycle phases considered in each rating system vary. GSAS considers design, construction, and operation while BREEAM and LEED consider design, construction, operation, and refurbishment. GRIHA has a more holistic approach that considers pre-construction, pre-design, design, construction, operations, and maintenance.

Regarding the evaluation approach, whether is prescriptive-based or performance-based, there are some differences as well. BREEAM follows a combination of prescriptive and performance based evaluation. LEED follows a prescriptive approach in which the compliance of a project is evaluated one time, that is, if a project has a determined feature then points are awarded towards

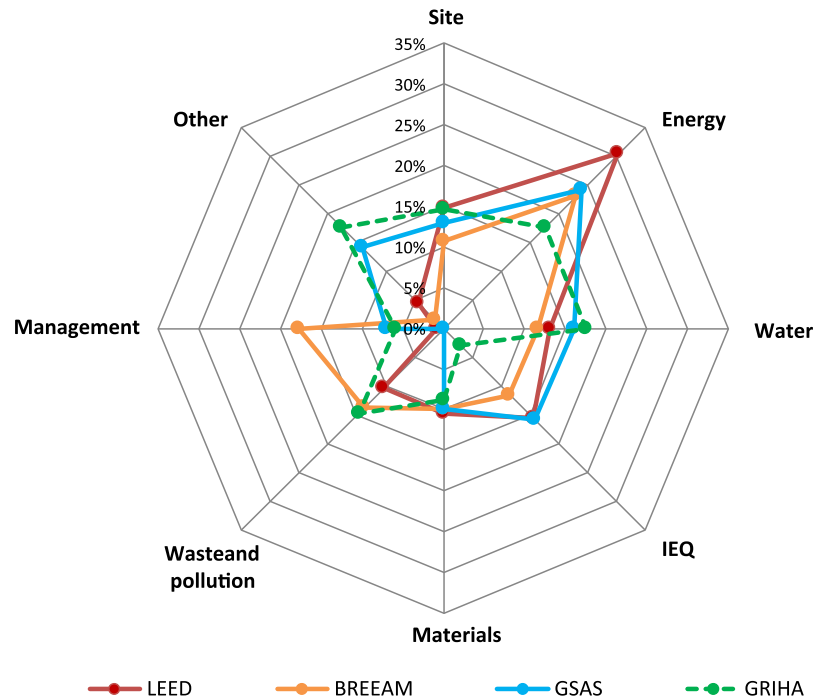


Fig. 1 Distribution of key categories.

certification. GRIHA is a prescriptive and performance-based system. Some criteria are evaluated through compliance, whereas others need to be validated on-site through verification, monitoring and validation. The LCA is considered only by BREEAM and GSAS.

Categories

Regarding the number of categories, BREEAM has the maximum number (10), which is slightly higher than the nine of LEED, eight of GSAS, and six from GRIHA. BREEAM, LEED, and GSAS share a similar pattern in the characteristics of the categories. GSAS has a strong influence and is based on BREEAM and LEED (among other rating systems) hence its similarities. Although GRIHA has an indirect influence from BREEAM, it was established through the cooperation of third-party organisations, the government and the ministry of energy leading to the difference and a reduced number of categories.

Key Categories

Multiple studies have used key categories to compare rating systems. In this article, eight categories are used in the comparison: site, energy, water, indoor environmental quality (IEQ), material, waste and pollution, management, and other. **Fig. 1** shows a radar diagram for the distribution of key categories for each rating system. Energy is still the most prevalent category among the rating systems: LEED has the maximum credits related to it (30%), while GRIHA has the least credits (18%). It is worth noting that all rating systems have a specific energy category: BREEAM has “Energy”, LEED has “Energy and Atmosphere”, GSAS has “Energy performance”, and GRIHA has “Energy and occupant comfort”.

Water is the second most important as all the rating systems have a water-designated category: BREEAM and GSAS have “Water”, while LEED has “Water efficiency”. GRIHA has “Water savings” and it is the rating system that gives more importance to water, as it accounts for 18% of its credits. All the four rating systems follow similar water-saving indicators such as reduction in water consumption, innovative water technology, and water-efficient systems and technologies. GRIHA has an additional consideration aiming to reduce water consumption during construction.

The third most prevalent category is site. All the rating systems have a similar distribution of criteria related to this category: LEED (14.78%), BREEAM (10.77%), GSAS (13.00%), and GRIHA (14.71%). All the rating systems consider similar site characteristics related to the preservation and conservation of species and local environmental features, site amenities, and the influence of the design. BREEAM has an additional consideration aiming to reduce natural and risk hazards.

BREEAM, LEED and GSAS have a similar distribution for IEQ-related criteria (between 12% and 15%) while GRIHA has only 2.94%. The main reason for the IEQ consideration is the increasing concern about the sick building syndrome, tobacco smoke control, and toxic air pollutants. BREEAM is by far the rating system that considers more criteria related to management (17.89%)

by encouraging projects to integrate practices in the design stage and focus on performance targets early to influence decision making and reduce unnecessary costs. GSAS has not criteria directly related to waste and pollution.

The materials category has the same pattern of credit/point allocation among the rating systems: LEED (10.43%), BREEAM (10%), GSAS (10%), and GRIHA (8.82%). LEED materials criteria focuses on improving the recycling rate of building materials and use of local materials, while BREEAM main concerns are on adopting a method of purchasing as to save materials consumption by controlling the material procurement channels. GRIHA material criteria focus on using materials with low emissions and materials for energy efficiency. GSAS main concern is on increasing the use of regional and recycled materials, and materials reuse and design for disassembly.

Three Pillars of Sustainability

Another interesting comparison is to look at the three pillars of sustainability and determine the distribution among the rating systems. Environment is the main factor for all rating systems. More than 60% of the subcategories are related to environmental aspects. Two different environmental effects have been considered across the rating systems. One effect is related to the influence of the site characteristics on the building, which is typically accounted for with site-related criteria. Site considers aspects related to the preservation and conservation of species and local environmental features, natural hazards and risks associated to the site characteristics, site amenities and the influence of the design on the building. All the rating systems consider the mentioned environmental effects except for natural hazards and risks that are only accounted for in BREEAM. The second effect is related to the building impacts on the outdoor environment, both during construction and operational phases, which is typically accounted for in outdoor quality criteria. BREEAM has a management criterion mainly focused on indoor quality. GSAS has a category for indoor and outdoor environment and GRIHA for construction management. Although the number of categories addressing social factors has increased with a focus in culture, comfort, health, and well-being, this aspect is still modest. GSAS has some criterion related to minimum level of safety facilities for construction workers.

BREEAM is the only rating system that addresses economic factors. In addition to the environmental, economic, and social aspects, some rating systems share similar categories to address operations and account for exemplary performance. For instance, BREEAM and GSAS have a category that addresses operations and management while GRIHA goes further and has a category that evaluates performance monitoring. LEED is the only rating system that does not have a category related to operations and management, although indirectly assesses some aspects through the integrative process category. BREEAM, LEED, and GRIHA have an innovation category that promotes new developments and strategies to achieving sustainability that go beyond the minimal standards. GSAS has an education category that aims to raise awareness of energy uses by its occupants by pointing out behavioural changes that minimize the resource consumption. BREEAM, GSAS and GRIHA have criteria that considers visual comfort and adequate noise. LEED is the only rating system that does not assess visual and acoustic aspects.

Meeting Targets

Since all of these rating systems are operational for a substantial time, it is relevant to determine whether these rating systems are meeting the quantifiable targets for which they were developed. BREEAM sets absolute parameters for achieving credits, which sets stricter measures for compliance. For instance, it specifies exact targets for energy performance ratios such as 0.06 for achieving one credit and 0.09 for 15 credits. As it is a one time metric, the evaluation does not consider improvements or benchmarking values. On the contrary, LEED establishes relative percentage improvement or reduction targets, thus it is easier for projects to meet the targets for achieving points. For instance, a table is provided in which the energy simulation results of the building are evaluated against benchmarks for existing buildings. Thus if the simulation shows that there is a 42% improvement then 16 points could be awarded (Doan *et al.*, 2017). With these standards, note that BREEAM helps to achieve certified projects while LEED helps to develop green buildings at the global level.

GRIHA uses a similar approach to LEED. It establishes relative percentage improvement or reduction targets, thus it is easier for projects to meet the targets for achieving points. For instance, a table is provided in which the energy consumption of the building is compared against the GRIHA benchmark. Thus if there is a reduction of 10% compared to the base case then 2 points are awarded and for a reduction of 50% a maximum of 10 points are awarded. One challenge to achieving points is that consumption depends on the number of occupants on the building and the benchmark does not differentiate between a high or low occupancy building hence, it has a direct impact on buildings with many occupants.

GSAS has a mixed approach in which some credits are performance-based and some are prescriptive. In addition, it has a weighting system for credits similar to BREEAM. For instance, an energy compliance requirement states that air-conditioning equipment should have a minimum EER of 10 or better equivalent in the market and light fixtures should be LED, CFL, T5 or similar efficient in the market. Note that the use of products depends on what is available in the market, thus if some products become unavailable then it makes it impossible for designers to achieve these points or becomes increasingly challenging to demonstrate compliance. The performance-based credits evaluate the energy consumption of the building. For instance, a building's energy consumption after the simulation is compared to the benchmark of other buildings. However, this approach does not consider that both buildings are functionally equivalent. The comparison should be on the basis of normative assumptions of their usage and internal processes so designers have a challenge in establishing a fair comparison.

Discussion

This article provided a critical review on four rating systems for green buildings and explored its considerations, similarities, advantages, and challenges. The review included the BREEAM, LEED, GSAS, and GRIHA. The review confirms that BREEAM and LEED continue to be the most established and well-known rating systems across the world, not only by the number of projects certified, but also in terms of the number of countries that have adapted and use them as a reference for certification of green buildings. BREEAM and LEED also provide a great marketing value for buildings and their strict and straightforward approach has contributed to their increased use. BREEAM is the first rating system developed which has established its credibility among the experts and continues to be the most used rating system across the world with about 550,000 project certifications. BREEAM is stricter in its criteria for achieving credits as it sets absolute parameters. LEED has a transparent system that uses a relative percentage improvement or reduction targets. It is easy to use and adapt to specific conditions given its flexible scheme. With over 150 countries, LEED is the most-widely used rating system based on the number of countries. GSAS is a new rating system for the MENA region, and has adapted the transparency of LEED and strictness of BREEAM. It includes criteria related to performance, operations, quantification of results. GRIHA is also a new rating system that operates only in India with a focus on new construction that includes performance and operations.

Because of their adaptability to different conditions, BREEAM and LEED use international standards, so it is argued that they are not designed for specific local conditions. For instance, LEED has energy considerations primarily based on per capita energy consumption in developed nations like the US, which does not reflect per capita energy conditions in developing countries, which have a low consumption compared to developed nations. Additionally, the international codes implemented in BREEAM and LEED usually take a hypothetical case while rating systems adaptable to local conditions work with an absolute number, which is easily understood. LEED promotes the use of certain products like glass and air-conditioning equipment while BREEAM promotes the use of energy solar panels. GRIHA and GSAS have the advantage to be very comprehensive and adaptable to specific conditions, which makes it more suitable for local projects and realities. However, the newest rating systems do not have a higher exposure from other parts of the world, so LEED and BREEAM continue to be more acceptable because of their rigour and trajectory to multinationals and owners who are prime investors and are looking for developing globally recognized projects.

Although BREEAM, LEED, GRIHA and GSAS have environmental and social aspects, the economic aspect is still under-represented. BREEAM has a sub category related to economic (management) aspects, but no considerations on the costs. Economic and financial aspects are determinant for the success of a building. Research in sustainable buildings has stated that costs and the scarce budget are common reasons for the bankruptcy of many green buildings so there is a pressing need for a more holistic approach that accounts for the economic aspects of the building, evaluates life-cycle cost performance and minimizes costs (Pagliaro *et al.*, 2015). Land costs, occupancy costs, construction costs, demolition costs, and professional fees are some of the economic considerations that should be included in rating systems. Furthermore, it is necessary to pay attention to the relationship between environmental performance and economic performance and the interrelationship between these two aspects. A sustainable building should account for economic performance and costs.

Another aspect that has a minimal consideration is the sustainability performance of the construction phase. During the construction phase in which the project is built, numerous stakeholders and participants are directly involved, and this can have a direct impact on their needs and well-being. GRIHA has three criteria related to providing sanitation and safety facilities for construction workers, efficient water use, and air pollution reduction during construction. However, none of the rating systems has considered a broader approach of sustainability of construction operations. For instance, social sustainability is an opportunity to achieve better standards of living by promoting practices and responsible ways to manage people by considering people's needs and expectations (Alwaer and Clements-Croome, 2010). Employment and training opportunities for workers can be assessed to determine whether the project is increasing the well-being of workers and providing job continuity. The economic impact of construction can also be assessed by quantifying the financial costs of the project while minimizing the costs (reducing errors and omissions). The environmental factor could be addressed by reducing the embodied energy of the project and the pollution and emissions of equipment and machinery.

Although site conditions are considered in the rating systems, culture is another criterion that has not been included in the rating systems. This is a key aspect in relation to local conditions of the project, the preservation of intangible attributes and specific conditions that enhance inhabitant's quality of life. Credit criteria focusing on social sustainability such as education and awareness have only been considered in GSAS. Other aspects that have not been included and that are key to achieve a complete level of sustainability are employment, stakeholder inclusion, and resilience for adaptation and mitigation (Fernandez-Sanchez and Rodriguez-Lopez, 2010; Chandratilake and Dias, 2015).

The review confirms that no rating scheme from the four that were evaluated can assess a building project in all aspects of sustainability. Therefore, a question that must be raised is the following: Are rating systems effective tools to realize substantial reductions on the impacts of buildings and infrastructure? Some researchers agree that there is no definition of what constitutes sustainable performance (Lee, 2013). The list may include for instance energy efficiency, water reduction, low contaminants, people's well-being and many others. How many criteria should be included in the list for it to be comprehensive? The acceptance of a definition of sustainable performance is critical to creating a common language and facilitating communication to establish rating tools that measure performance. Consequently, developing indicators becomes critical as these serve to evaluate and measure performance. Indicators highlight trends and are used to quantify sustainability across a range of sustainable principles (Singh *et al.*, 2009). As buildings become systems (and in some cases part of a larger system), rating tools may consider integrating

indicators into models to evaluate trade-offs and the interrelationships and overlapping dimensions of sustainability criteria and building components (Florez, 2012). If rating systems integrate indicators into models to measure performance, a more holistic and realistic approach can be implemented to advance sustainable performance metrics. A model in which, sets of building components become building systems and building systems become part of larger systems, allows comprehensively measuring and assessing sustainable performance. This can be a novel approach to the way rating systems become effective tools to reduce impacts of buildings and infrastructure.

Conclusions

A critical review of four rating systems for green buildings was conducted including BREEAM, LEED, GRIHA and GSAS. It was found that the environmental factors are still predominant in the evaluation of green buildings. Energy is the main category while water is the less evaluated criteria followed by materials. The consideration of social aspects is increasing, although are still marginally considered. Economic aspects and financial considerations are mostly neglected in all the rating systems. The reader is referred to Illankoon *et al.* (2017), Zuo and Zao (2014), Berardi (2013), and Mattoni *et al.* (2018) for critical reviews on other rating systems.

Well-established rating systems (BREEAM and LEED) and new rating systems (GSAS and GRIHA) have some differences regarding the inclusion of a more comprehensive life-cycle perspective and the evaluation of performance and operations. While BREEAM and LEED evaluate a building based on the documentation provided and as-built evidence to determine the certification level, GSAS and GRIHA evaluate a project based on documentation, as-built evidence, and on-site audits to verify that real-time operations match the evidence. A certification level is then awarded to the project. Note that GRIHA also allows a project to revise the documentation and re-apply for certification if a higher level of certification is desired. BREEAM and LEED award a one-time certification while GSAS and GRIHA award a limited-time certification after which the building must be reassessed to maintain its certificate.

This analysis also shows that there are still sustainability issues that are only included in a few rating systems but should be considered in all ratings in order to provide a certification that includes all aspects of sustainability. For instance, environmental hazards and risks, LCA aspects, global warming, noise and light pollution in outdoor environment should be included. There are also limitations in the way the criteria are formulated and evaluated. All the rating systems focus on building features or the final building and infrastructure project and its performance, with little attention being paid to the performance and the impact of the building during the construction phase.

Rating systems need to perform an assessment of its principles: (1) science-based-decision and results must be reproduced by others using the same standard; (2) transparent-standards and process for awarding the certification should be transparent and open for examination; (3) objective-certification body should not have any conflict; (4) progressive-standards should advance industry practices not simply reward business as usual.

Global sustainability and local sustainability are also concepts that need to be considered when evaluating rating systems (Illankoon *et al.*, 2017). Although global sustainability should lead to include in every rating system the same fundamental credits, the non-homogeneous assignment of weights is a natural consequence of local sustainability. BREEAM and LEED were developed to be global standards for green buildings and provide a broader consideration of sustainability aspects, while GSAS and GRIHA have included specific rankings in the criteria aiming to focus on local considerations and conditions. This review is a practical reference of building rating systems and could be valuable for both green practitioners and researchers to have an overall understanding of BREEAM, LEED, GRIHA and GSAS. Differences, advantages and strengths were identified.

The growing need to deal with economic, environmental, and social impacts in construction poses a challenge to develop rating systems that help implement sustainable practices. Sustainability is realized when a building and infrastructure project meets economic, environmental, and social factors. Green building rating systems have been developed across the world to implement sustainability principles and promote the use of features and systems that reduce construction impacts. This article is a practical reference of building rating systems and establishes the extent to which these methods assess green buildings in all aspects of sustainability. The analysis conducted gives practitioners in the built environment and construction industry a deeper knowledge and understanding of the aspects included in BREEAM, LEED, GRIHA, and GSAS. Although the rating systems reviewed in this article have incorporated key criteria to measure sustainability, no rating scheme can assess a project in all aspects of sustainability. The acceptance of a definition of sustainability is critical to creating a common language and facilitating communication, while minimizing the impacts of buildings and infrastructure. Additionally, there is a need to integrate indicators from rating systems into models to provide more useful guidance for efforts to a transition towards sustainability (Singh *et al.*, 2009). By integrating indicators into models, the interrelationships and the overlapping dimensions of the criteria could be covered (Florez, 2012). Models can be used to identify the way in which tasks are unsustainable, assist decision makers to determine which actions should or should not be taken (Singh *et al.*, 2009), give effective feedback (Alwaer and Clements-Croome, 2010) and provide useful evidence to support project administration (Fernandez-Sanchez and Rodriguez-Lopez, 2010).

The analysis performed in this review gives green building users and researchers a deeper knowledge of the aspects included in rating systems, methods of calculation and awards. It also lays the groundwork for identifying common issues that should be included in rating systems for a comprehensive analysis of green goals throughout the life cycle of buildings and infrastructure. This review of the four selected rating schemes may not reflect the overall trend of rating systems that have been developed

worldwide. A comprehensive review of the hundreds of systems could provide a background of such advances. Further research is needed to determine worldwide sustainability and assessing the issues that have more influence on performance. If rating systems integrate performance indicators into models, a more holistic and realistic approach can be implemented to advance sustainable performance metrics. A model in which, sets of building components become building systems and building systems become part of larger systems, allows comprehensively measuring and assessing sustainable performance. This can be a novel approach to the way rating systems become effective tools to reduce impacts of buildings and infrastructure.

See also: Analysis of the Thermal Performance and Comfort Conditions of Vernacular Rammed Earth Architecture From Southern Portugal

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Introduction

The introduction of advanced construction materials is contributing substantially to the improvement of buildings' energy and environmental efficiency throughout their entire life cycle. By introducing new functionalities and improved properties, advanced materials add value to existing products and processes, in a sustainable integrated approach from cradle to cradle. Some of these advanced materials and technologies are already commercially available and have proven cost effective, with payback periods of less than five years. Others are more costly and will require government intervention if they are to achieve a wider market uptake.

Nanotechnology is certainly offering essential innovations for the development and formulation of innovative building products with increased mechanical, physical and chemical properties, with application potential in all technical elements, from structures, to opaque and transparent closures, internal partitions, to systems and appliances.

A new class of highly innovative materials able to perceive stimuli from the external environment and to react immediately to such stimuli, adapting to the changed environmental conditions, so called "smart materials" are finding application in architecture in a high number of products and systems, especially in building envelope components which can most take advantage of their properties of adaptation to different use conditions.

The development of a new generation of multifunctional coatings synthesized by nanotechnology, such as nanocomposite coatings, nanoscale multilayer coatings, super lattice coatings, nanograded coatings, with passive functionality but the capacity to actively respond to changes in their surroundings, is currently a hot technological topic. These coatings will provide key technology for the fabrication of future high-tech 'smart' coatings. Future approaches will focus on tailor-made coatings for specific functions, with particular attention to self healing coatings designed with the ability to repair themselves after chemical or mechanical degradation, based on nanocontainers or nanocapsules that can be filled with inhibitors to protect the substrate from corrosion upon damage or scratching in the coating layer.

In order to foster diffusion of advanced materials, and nanomaterials in particular, a number of barriers still need to be addressed not only related to costs, but mostly to health and environmental concerns basing on reliable and sufficient scientific data. For this purpose, short, medium and long term effects of nanomaterials on health and environment are to be investigated, taking into account the transport mechanism between boundaries as well as levels and type of exposure (direct ingestion, inhalation, dermal intake). The issue of nanomaterials eventually entering the human body is closely related to the form in which they are used in products, with particular concern on their ease of becoming unbound: for instance, nanoparticles covalently bound between them are less likely to become free, as are those firmly embedded in a metal matrix in nanometallic composites (Pacheco-Torgal *et al.*, 2013; Michael *et al.*, 2009; Smith and Granqvist, 2011; Finnish Institute of Occupational Health, 2013). Once detached, free nanoparticles hazard would depend on their mobility, inherent toxicity or potential to carry other pollutants. Environmental concerns also tend to indistinctly merge nanoparticles with the ill-famed ultrafine particles and particulates; while the former are the specific result of an engineering process and serve specific purposes, and thus come in a great variety of sizes, compositions, coatings, the latter are an uncontrolled and unwanted by-product of other activities and processes, and are as such more difficult to assess (Pacheco-Torgal *et al.*, 2013; Michael *et al.*, 2009; Smith and Granqvist, 2011; Finnish Institute of Occupational Health, 2013).

Concluding, most important nanotechnology challenges relate primarily to establishing univocal methods and tools for detecting, characterizing and analyse nanomaterials, to investigating their potential hazard and to assessing the effective exposure. In this picture, regulations shall guarantee high levels of health, safety and environmental protection, while at the same time allowing market uptake of advanced products and fostering innovation and competitiveness in this crucial sector of the industry.

Advanced Materials for Building Sector

Advanced materials are defined as those (both new and deriving from the modification of existing materials) specifically designed to possess new or improved technical properties (structural or functional) or environmental features compared to materials traditionally used to perform the same functions (Featherston and O'sullivan, 2014).

The introduction of advanced materials in the construction industry is contributing substantially to the achievement of energy and environmental efficiency improvements of buildings throughout their life cycle and is leading to profound changes in the whole construction process, from design to implementation. Advanced materials are in fact a key enabling technology for a number of other technologies, and have a key role in enabling advanced/high value manufacturing and in addressing key socio-economic society's grand challenges like climate change and improved efficiency in using resources, supporting and enabling the

[☆]Article adapted from the Chapter 2: Advanced Materials for Architecture of the book "Casini, M., 2016. Smart Buildings: Advanced Materials and Nanotechnology to Improve Energy-Efficiency and Environmental Performance. Cambridge: Woodhead Publishing Limited".

Table 1 Advanced materials for architecture: Enhanced and new properties

Enhanced properties	
● Mechanical resistance ● Hardness (abrasion-resistant) ● Shock resistance ● Weldability ● Quick compacting and Curing time ● Corrosion and Oxidation resistance ● UV resistance and control ● Water-protection ● Fire behavior	● Insulation properties ● Thermal conductivity ● Light transmission or reflectance ● Thermal radiation reflectance ● Surface energy ● Electrical conductivity ● Photoelectric effect ● Energy storage
New properties	
● Self-healing ● Air purifying ● Easy to clean ● Anti graffiti and Anti stain ● Scratch-resistant ● Anti-reflection ● Anti-icing and fogging	● Biocidal activity ● Electromagnetic radiation block ● Light emission (LED/OLED, Photol.) ● Chromogenism (dynamic glass) ● Thermotropism (PCM) ● Real-time structural health monitoring

Note: Casini, M., 2016. Smart Buildings: Advanced Materials and Nanotechnology to Improve Energy-Efficiency and Environmental Performance. Cambridge: Woodhead Publishing Limited.

development of new products through radically different and unique functionality, including low carbon technologies. Advanced materials can introduce new functionalities and improved properties, while adding value to existing products and processes, in a sustainable approach oriented to resource conservation, low-impact materials, cleaner production, efficient distribution, green use and maintenance, re-use, re-manufacture, disassembly, recycling and safe disposal. This is particularly advisable with the building sector, characterized by high environmental impacts in terms of resources consumption and waste production (Table 1).

Advanced materials in architecture can be characterized by a fixed, high performance response or by a dynamic behavior in response to external stimuli; the latter characterizes the so-called *smart materials*. These new or improved properties are the result of an engineering process at the nanoscale (nanomaterials) or at larger scale levels (micromaterials or macromaterials). In particular, the nanometric scale offers today higher potential in developing innovative materials and products and in improving performance of existing ones (Pacheco-Torgal *et al.*, 2013; Michael *et al.*, 2009; Smith and Granqvist, 2011). In fact, fundamental properties of matter at the nanoscale level can be significantly different from the same material in its bulk state. These property variations at the nanoscale level can potentially be exploited by embedding these materials with others either at the micro or macro scale level, improving the performance of the bulk material to the desired extent in real-life applications. Advanced materials may be applied by themselves as end products or be integrated in other products or devices, both during the manufacturing process and in the final unit to enter the market.

Concerning the construction sector in particular, most interesting and innovative developments in the field of advanced materials regard nanocomposite materials and coatings (thin films, nano-coatings, nano-paints), thin coverings deposited on a base material in order to provide new or improved surface qualities or appearance. The application of advanced coatings is in fact allowing to improve mechanical, physical and chemical performance of building materials and components, and glazing in particular, by imparting them new properties, both fixed (anti reflection, scratch resistance, etc.) and dynamic (chromogenics, self cleaning effect, shape memory alloys, etc.).

Applications of Nanotechnology

Nanotechnology is bringing many benefits in the construction sector by improving energy and environmental performance of buildings, with application potential in all technical elements, from structures, to opaque and transparent closures, internal partitions, to systems and appliances (Pacheco-Torgal *et al.*, 2013; Sev and Ezel, 2014).

Main applications of nanotechnology are in fact:

- The creation of nanostructured materials by the addition of free or embedded nano-objects within the composition of traditional materials and products, both solid (nano-composites) and liquid (nano-suspensions), such as cement, metals, ceramics, plastics, textiles, paints, adhesives and lubricants, as well as the modification of their internal structure to make it nanocrystalline;
- The use of nanocoatings for the surface treatment of traditional products such as glass, wood, ceramics, textile materials or photovoltaic cells;
- The modification of the surface structure of traditional products to make it nanostructured;

- The creation of new nanoporous materials (nanoporous insulating materials, nano-filters, nano-membranes, etc.);
- The development of nano-devices such as nano electrical and mechanical systems (NEMS).

Several applications are now available for the building industry to increase the mechanical, physical and chemical properties of materials, products and equipment, as well as their durability over time, with the aim of improving environmental comfort, safety, energy efficiency of buildings and at the same time reduce operating and maintenance costs and environmental impacts (Michael *et al.*, 2009; Sev and Ezel, 2014; Sobolev, 2015) (Table 2 and 3).

In particular, the use of nanomaterials in architecture may allow important improvements in:

- Performance of load bearing structures, with the realization of lightweight nanocomposite construction materials (carbon nanotubes, metal-matrix composites, nanocoated light materials, ultra high performance concrete, polymer composites, etc.);
- Thermal and lighting control, with the realization of high performance nanoporous insulating materials (aerogels, VIP, TIM), high reflective coatings (cool roofs), along with low-e, antireflective, passive and dynamic solar control and self-cleaning nano-coatings for glazing;
- Surface characteristics of building elements, with the application of specific nanocoatings or nanopaints (self-healing, air purifying, self-cleaning, antibacterial, anti graffiti and anti stain, photo luminous, scratch-resistant, anti-reflection, anti-icing anti-fogging, fouling-resistant, oxidation and corrosion resistant, UV resistant, fire resistant, etc.);

Table 2 Main building materials properties improved through nanotechnology

<i>Enhanced properties</i>	<i>Nanotechnology</i>	<i>Building products</i>
Durability	Al ₂ O ₃ , SiO ₂ , ZnO particles	Concrete
Mechanical resistance and crack prevention	Polymers, SiO ₂ , FeO and CaCO ₃ particles, CNT Cu particles	Concrete Steel
	CaSO ₄ , SiO ₂ particles	Gypsum drywalls and ceilings
Hardness (abrasion-resistant)	CNT, FeO particles	Concrete
Shock resistance	V, Mb particles	Steel
	Al ₂ O ₃ particles	Concrete
Weldability	CuO, Ca, Mg	Steel
Formability	Nanopolymers	Concrete
Quick compacting	TiO ₂ , particles, CSH nanocrystals	Concrete
Curing time	TiO ₂ , CaCO ₃ particles, CSH nanocrystals	Concrete
Corrosion resistance	SiO ₂ particles	Paints
	Al ₂ O ₃ , SiO ₂ coating	Steel
Oxidation resistance	CuO particles	Steel
UV resistance	ZnO, CeO ₂ Coating	Wood
Moisture resistance	C ₆ H ₁₀ O ₅	Concrete
Water-protection	Fatty acids coating	Wood
	SiO ₂ particles	Concrete
Fire behavior	SiO ₂ particles	Glass
	TiO ₂ , particles	Concrete
Insulation properties	SiO ₂ Aerogel, SiO ₂ particles	Insulating materials
	Hydro-NM-Oxide particles	Paints
Thermal conductivity	Carbon nanotubes	Polymers and plastics
	Metal oxides coating	Glass
Visible and Near infrared Light transmission or reflectance	VO ₂ , FeO, SiO ₂ , ITO coating	Glass
	Nanoceramics coating	Solar films
UV control	TiO ₂ , ZnO coating	Coating
Thermal radiation absorption or reflectance	Ceramic Nanoparticles	Paints
Adhesion	SiO ₂ or SiH ₄ particles	Adhesives
Rheology	SiO ₂ particles	Paints
Surface energy	SiO ₂ particles	Paints
Electrical conductivity	Carbon nanotubes	Polymers and plastics
Photoelectric effect	Quantum dots, Graphene, CNT	Thin film solar cells
	TiO ₂ particles	DSSC
	Si particles	Silicon solar cells
Energy storage	Graphene, carbon aerogel, CNT	Batteries, capacitors
	Zeolite particles	Wood
Friction	Fullerene	Lubricants
	Ceramic coating	Steel

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Table 3 Main new building materials properties provided through nanotechnology

<i>New properties</i>	<i>Nanotechnology</i>	<i>Building products</i>
Self-healing	Nanopolymers	Concrete, gypsum
Air purifying	TiO ₂ , ZnO coating	Ceramic tiles, Glass
	TiO ₂ particles	Paints, Concrete
	Zeolite particles	Gypsum drywalls, ceilings, Plaster
Easy to clean	SiO ₂ coating	Glass
Anti graffiti	TiO ₂ , SiO ₂ coating	Concrete
Anti stain	TiO ₂ , SiO ₂ coating	Concrete
Scratch-resistant	Al ₂ O ₃ coating	Ceramic tiles and sanitary ware
	SiO ₂ particles	paints
Anti-reflection	SiO ₂ coating	Glass
Anti-icing	CNT	Glass
Anti-fogging	TiO ₂ coating	Glass
Fouling-resistance	TiO ₂ , Ag coating	Ceramic tiles, Glass
	TiO ₂ particles	Paint
Biocidal activity	Ag, ZrO ₂ CuO coatings	Ceramic tiles and sanitary ware
	Ag particles	Paints
	Ag, Cu, Zn particles	Wood
Electromagnetic radiation block		
Light emission	Graphene	OLED lighting
	Quantum dots	LED lighting
Artificial photosynthesis	TiO ₂ particles	Hydrogen production
Dynamic response	Semiconductive metal oxides	Dynamic glazing
Real-time structural health monitoring	CNT	Concrete

Note: Casini, M., 2016. Smart Buildings: Advanced Materials and Nanotechnology to Improve Energy-Efficiency and Environmental Performance. Cambridge: Woodhead Publishing Limited.

- Energy efficiency in lighting (LED/QLED, OLED);
- More efficient and integrated renewable energy systems (polymeric, dye sensitized, quantum dots, thin-film and multi-junction PV solar cells, fuel cells, etc.);
- Building and environmental monitoring and control, with the realization of nano embedded sensor, actuation and control systems (NEMS).

Within these construction materials, elements and systems, nanomaterials can be integrated in the form of solid nanocomposite materials, solid materials enhanced with nano-coatings or characterized by nanostructured surfaces, nanoporous materials and fluid nanodispersion as nanopaints, nanoadhesives or nanolubricants.

More specifically, in the nanocomposite class of materials one or more phases at the nanoscale dimensions (3-D, 2-D, 1-D) are embedded in a polymeric, metallic, or ceramic matrix. Nano-objects embedded in the matrix (usually a few percentage by weight) can be made of various primary materials and their addition can provide the material with unique and enhanced properties compared to conventional composite materials.

Nanocoatings, or nanofilms, are thin films which incorporate nanomaterials, or have a thickness at the nanoscale (< 100 nm), deposited on a substrate material to enhance its surface properties (durability, abrasion or corrosion resistance, electrical, magnetic or optical behavior, etc.) without having to alter its entire mass. Multiple nanoscale layers can be built up to form multilayered or laminate nanostructures. Using thin nano-based coatings is a very convenient way of exploiting the remarkable properties of nanomaterials without the high production cost associated with manufacturing large components fully out of nanocomposites. This gives them one of the greater overall market potentials for any kind of nano-based product or device. Among nano-objects used as a standalone end product, one of the most interesting and promising ones is certainly the graphene, aptly surnamed “wonders material”.

Concrete

Nanotechnology application to the concrete industry allows to obtain products with unprecedented performance regarding both mechanical properties and durability over time, along with improvements in the construction process (ease of mixing, rate of setting, workability etc.) and a reduction of carbon emissions of cement manufacturing (reduced kiln temperatures and durations that occur during processing) (Hossain and Rameeja, 2015; Leone, 2011). Environmental benefit potential is indeed very high, as cement production generates over 1.6 billion tons of carbon worldwide, more than 8% of total carbon emissions. Concrete also accounts for more than two thirds of construction and demolition waste with only 5% currently recycled (Pacheco-Torgal *et al.*, 2013).

Nano-enhanced concrete products may be both nanocomposites, as cement blend added with nanoparticles to enhance its properties, and nano-coated for modifying its surface properties and its interaction with the environment.

Nanocomposite concrete can become impermeable through the addition of inorganic solutions that during curing fill its capillary void with nanocrystals, and can cure much faster due to silicate hydrates nanoparticles that accelerate hydration process without requiring energy intensive treatments such as hot steam or hazardous additives. Addition of TiO_2 nanoparticles makes it photocatalytic, allowing for improved durability, self cleaning action and also air purifying effect, with the added benefit of improved fire behavior. Regarding mechanical performance improvement, currently available Ultra High Performance Concrete (UHPC), added with metal and silicon oxide nanoparticles, require much less material to achieve the same structural strength compared to traditional products thus allowing for a much reduced environmental impact with 6 times reduction in raw materials, 50% reduction in GHG emission and 40% reduction in manufacturing energy. Carbon nanotubes addition is being researched and will allow a 90% reduction in material use.

Concerning concrete nanocoatings, anti-graffiti and anti-stain effects can be achieved by the application of SiO_2 nanoparticles solutions to form a nanothin layer of glass on its surface, preventing moisture or graffiti paint from penetrating the pores and dirt or algae from attaching to the surface. TiO_2 coatings impart self healing and air purifying effect as well.

Metals

Nanotechnology allows for improving a number of properties in all metal applications, being them structural steel, metal piping or interior/exterior surfaces (Michael *et al.*, 2009). The properties of many common metals can be greatly enhanced by the addition of relatively small amounts of nanomaterials – Normally in the form of nanoparticles, nanowires, and nanotubes – As well as by the application of specific nanocoatings.

High performance steel for most demanding applications, such as bridge supporting cables or precast concrete, undergo specific manufacturing processes to reduce their crystalline structure to the nanoscale (nanostructured steel).

Nanocomposite steel develops instead improved properties concerning oxidation resistance and workability (addition of copper nanoparticles), fatigue resilience (addition of vanadium and molybdenum) and welding behavior (through calcium and magnesium particles).

Several nanocoatings allow for improved corrosion resistance thanks to alumina and silica nanoparticles, or employ polymer nano dispersions to promote acrylic coatings adhesion. These nanocoatings constitute more durable and environmentally friendly alternatives to traditional chromating baths. Steel used in highly hygienic environments such as healthcare facilities, as well as medical grade tools, develops an anti microbial effect with the addition of silver or copper nanocoatings. Metal employed in mechanical gears can greatly reduce surface friction through the use of nanoceramic coatings. Finally Architectural metal surfaces can also be protected with anti scratch coatings based on the addition of aluminium oxide nanoparticles (Al_2O_3) in 1%–5% concentration in aqueous coating systems, acrylate dispersions or aliphatic polyurethane dispersions.

Plastics

Plastics and polymers (thermoplastics, thermosets and elastomers) can also take advantage of the benefits of nano-objects integration (polymer-matrix nanocomposites) or nano-coatings deposition on their surface (Michael *et al.*, 2009).

Many kinds of nanofillers (silicas, clays, carbon nanotubes, carbon blacks) are suitable for integration in polymer nanocomposites. The use of a small quantity of nanoparticles, nanotubes or nanoplates – A few percentage by weight – As a reinforcing second-phase material can in fact dramatically alter the properties of the different polymers. For instance, both strength and modulus of elasticity values can be either increased or decreased depending on the polymer host and the nanoscale reinforcing phase: materials such as polystyrene reinforced with silica nanoparticles show an elastic modulus increase while carbon nanoparticles can increase toughness and wear resistance.

Carbon nanotubes can sensibly increase compression strength if dispersed in thermoset epoxies (in the 30% range), with only 0.5%–2.0% wt proportions. Many types of widely used thermoplastics such as polycarbonates can also be added with CNTs with the aim of increasing compressive and impact strength, toughness, elongation, and other properties.

Regarding nano-coatings application to plastics, it is challenging to carry out because of polymers' organic nature and low heat resistance. An effective, transparent scratch resistant coating (+ 55% abrasion resistance) has however been obtained by chemically growing zirconia nanoparticles on top of the polymeric surface.

Ceramics

Ceramic materials in architecture include tiles both for interior and exterior application as well as sanitary ware. All of these applications may benefit from nanotechnology, improving their durability and ease of maintenance characteristics or giving them new properties altogether (Michael *et al.*, 2009). Through the application of nanocoatings, ceramic surfaces can repel dirt and water by becoming superhydrophobic (coatings with SiO_2 nanoparticles that fill surface pores and give an ultra-smooth surface) or superhydrophilic and photocatalytic (TiO_2 coating). SiO_2 coatings also provide anti scratch properties without impeding gloss. Nanosilver coatings finally provide a biocidal effect both on ceramic tiles and sanitary ware.

Glazing

Glazing is indeed one of the fields in which nanotechnology is having the widest impact, with several nano-enhanced products already on the market with much improved performance or altogether new properties. In architecture, glass is mostly employed to achieve natural lighting of interiors, and nanotechnology allows to realize extremely thin coatings with multiple functions that do not hinder excessively its most sought after characteristic, visible light transparency. In particular, nanocoatings may increase glass transparency through anti-reflective effect (multiple nanosized polymer layers with different refractive angles) or by preventing dirt build-up by making its surface superhydrophobic (nanosilica coatings) or superhydrophilic and photocatalytic (TiO_2 coatings). These high transparency levels ensure maximum daylighting levels and, in the case of building integrated photovoltaics, maximum efficiency in harvesting solar energy. SiO_2 nanoparticles intumescent interlayers also allow for fireproof glazing without loss of transparency. Glass fogging as well as snow or ice accumulation can be prevented by self heating glass, obtained by metal or carbon nanotubes coatings that make its surface electrically conductive.

From the energy efficiency point of view, nanocoatings are widely used to improve glazing thermal transmittance (low-e coatings using metal oxides nanoparticles) or filter and absorb UV or NIR radiation (silicon or metal oxides nanocoatings, nanoceramic solar films), avoiding heat loss in winter and excessive heat loads in summer months. In addition to static solar protection glazing, are now available dynamic solar control coatings that can vary their transparency to visible or IR light reacting passively to light (photochromic glass) or heat (thermochromic glass). Electrochromic glazing allows active dynamic control of light and heat transmission thanks to a thin film coating comprised of several extremely miniaturized conductive layers.

Insulating Materials

Nanotechnology can be also used to create new advanced high performance insulating materials able to provide exceptional heat flow resistance performance thanks to their nanoporous structure achieved via sol-gel processing (silica aerogel), also in vacuum applications (VIP) or additionally providing solar radiation transparency (TIM) (Casini, 2016).

Due to their low thermal conductivity ($\lambda < 0.02 \text{ W m}^{-1} \text{ K}^{-1}$) it is possible to obtain high thermal resistance values of building envelope with extremely thin insulating layers (less than a third compared to conventional insulating materials). These products are thus particularly suitable for the correction of thermal bridges and for energy retrofit of existing buildings, especially of historic buildings subjected to architectural constraints, and in all cases in which it is necessary to increase energy efficiency and comfort with minimum space loss.

Near infrared reflecting coatings such as nanopaints can also be used for roof and wall applications in order to reduce the summer overheating and Urban Heat Island Effect (Cool roofs).

Finally, nanomaterials addition can significantly alter the thermophysical properties of heat storage materials, especially in phase change materials (PCMs) for latent thermal energy storage (LTES) applications. There, the incorporation of specified proportions of nanomaterials can increase thermal conductivity, accelerate freezing and melting rates, improve thermal stability, and ensure thermal reliability over time.

Adhesives

Most used adhesives today are based on elastomers, thermosetting or thermoplastic polymers and other materials, and current research on increasing performance and ease of application is being spurred by the advent of nanoscience and nanomaterials.

Nanomaterials as now are mostly added to improve rheology characteristics, such as viscosity and anti sagging, allowing for thinner, more uniform adhesive coating applications: most used in this regard are nano-sized silicates. The inclusion of metal or carbon nanoparticles such as iron oxide allows to obtain electrical conductive adhesives that allow electricity transfer in electronic applications and electromagnetic induced curing (Michael *et al.*, 2009).

Nanoscience is also taking inspiration by naturally occurring nanosized structures to mimic their behavior: in this sector, research has focused on the adhesive ability of mussels and geckos. Regarding the gecko, it has been observed that its excellent clinging ability stems from the nano structured surface on its feet, which feature many small hairs each split in even smaller hairs at the end, called satae. Each of these is covered by cuplike spatulae 200 nm in size, which radically increase the contact area between the hairs and the surface, achieving up to billions contact points that take advantage of both Van der Waals forces and capillary action. Mimicking this behavior shall allow for powerful and reversible adhesive action, and this is carried out by nanostructured surfaces with patterns akin to those of the gecko's soles, such as PMMA nanopillars arrays obtained by electron beam lithography or CNTs. Promising results were obtained, but a decrease of adhesion in wet environments was noted. Research on wet adhesion turned instead to mussels and their ability to reversibly cling to virtually any underwater surface. It was discovered that these unique capability stems from a specialized protein secretion, rich in the amino acid L-Dopa, which is known to provide underwater adhesion and self-healing capabilities. This was mimicked in engineered polymers with an analogue synthesized protein, obtaining an high performance underwater glue applicable in thin films and 10 times more effective than conventional wet adhesives (Kollbe Ahn *et al.*, 2015). By coating gecko inspired nanopatterns with this mussel-inspired adhesive, exceptional, reversible performance both in dry and wet environments was finally achieved.

Paints

Nanotechnology influence in paints sector has been successful, and the addition of nanoparticles in their solution has led to the development of a whole range of innovative and high performing nanodispersed products (Michael *et al.*, 2009). In particular, nano dispersions can show improved characteristics of rheology, settling and viscosity, improving paints' behavior during application, through the addition of nanoclays and silica or aluminium nanoparticles. Photocatalytic paints include dispersed TiO₂ nanoparticles to achieve a self cleaning, anti fouling and air purifying effect if exposed to UV rays, while other self cleaning paints instead exploit the lotus effect, caused by a bumpy surface nanopattern which is small enough to prevent water drops from attaching, causing them to roll away taking dirt particles with them. Interior environments healthiness can be raised by biocidal paints, comprised of nanodispersed silver particles that prevent bacteria and microorganisms from developing. Similarly, metal nanoparticles or carbon nanotubes can make surfaces antistatic or block unwanted electro magnetical radiation.

Lifetime and colour fastness of organic paints exposed to UV degradation can be increased by the addition of metal oxides nanoparticles such as zinc, cerium or titanium, and transparent protective paints (clear coats) for furniture and wood protection can increase their scratch and abrasion resistance with no gloss alteration by the inclusion of silica nanoparticles. Furthermore, interesting colour effects can be achieved on any surface by adding multiple polymer nanolayers with different refractive angles, this varying the wavelength and colour of reflected light according to the viewer position (dichroic effect). Lastly, nanoparticles addition to paints can improve their reflectance to solar radiation for cool roof applications.

Lighting

The energy efficiency of lighting systems is very important due to their high electrical consumption in both residential and tertiary buildings. Last generation incandescent lamps, still widely used in existing buildings, were characterized by low efficiency and heat release and overheating issues, especially in hot climates during summer months.

Solid state lighting technologies such as Light Emitting Diodes (LED) have allowed to greatly improve energy efficiency of lighting systems, superseding at the same time also fluorescent lamps. However, despite their high energy efficiency, actual emission wavelengths that can be generated remain limited and not easily adjustable, and the production of full-spectrum "white light" is still equally problematic since it requires a final adjustment via the addition of phosphors with still unsatisfactory results.

In this picture, existing LED technologies can be widely improved with the integration of a variety of nanostructures, with several beneficial effects including:

- Increasing light extraction or out-coupling from LED chips;
- Enhancing luminescent output by increasing emitters' surface areas;
- Improving the efficiency of injected electrons by using nanostructured electrodes;
- Improving light control by using novel nano-phosphors;
- Exploiting surface fluorescence of quantum dots.

Among these, quantum dots networks integration in LEDs is particularly interesting, paving the way for highly efficient and performing innovative QLEDs. Quantum dots (QDs) consist in nanocrystals of semiconductor materials such as germanium or silicon, which electronic and luminous properties are directly related to their diminutive size. Advantages include high efficiency, better control of emitted light as well as further miniaturization of form factors. Concerning light control, the actual emitted wavelength, thus the colour, does not strictly depend on the semiconductor material as in conventional LEDs, but can be finely tuned by acting on the nanocrystals. Nanoparticle size in fact dictates energy separation levels, which in turn vary the wavelength of emitted photons. This way, precise colour emittance to match specific needs, even in the case of full spectrum white light, can be achieved by directly mixing the right kinds of constituent blue, green and red emitting quantum dots. Quantum dots also benefit from a more convenient manufacturing process: nanocrystals can be grown in large quantities with colloidal approaches, instead of being precisely shaped and cut from germanium or silicon wafers as in macroscale semiconductors.

Further research on LEDs manufacturing by using QDs regards instead the use of carbon made QDs, so called Carbon Dots (CDs); these can even be produced from waste bread and alcohol-free sugar beverages, allowing a further reduction in raw materials costs and environmental impacts (Casini, 2016). Design flexibility potential is also exceptional, as quantum dots may be incorporated into various types of polymeric materials, rigid, flexible and even transparent, through depositing, casting or painting processes. Moreover, potentially longer operating life and improved stability make QLEDs effectively competitive with the other breakthrough evolution in lighting technology, organic light emitting diodes (OLED).

Smart Materials

"Smart materials" are a new class of highly innovative materials able to perceive stimuli from the external environment and to react immediately to such stimuli, adapting to the changed environmental conditions (Schwartz, 2009; Ritter, 2007). This reaction is usually caused by a change in the values of the surrounding energy field (change in potential, electrical, thermal, mechanical, chemical, nuclear or kinetic energy) that triggers in the material a chemical reaction, a change in the molecular or crystallographic

Table 4 Smart materials classification

<i>Type of smart material</i>	<i>Environmental stimulus</i>	<i>Reaction/effect</i>
Property changing materials		
Thermochromics	Temperature difference	Colour change
Photochromics	UV radiation	Colour change
Mechanochromics	Deformation	Colour change
Chemochromics	Chemical concentration	Colour change
Electrochromics	Electrical tension	Colour change
Liquid Crystals	Electrical tension	Colour change
Suspended particles	Electrical tension	Colour change
Photocatalytics	UV radiation	Chemical reaction
Thermotropics	Temperature difference	Phase change
Electrorheological	Electrical tension	Viscosity change
Magnetorheological	Magnetic field	Viscosity change
Shape memory	Temperature difference	Crystalline phase change
Energy exchanging materials		
Electroluminescents	Electrical tension	Visible light emission
Photoluminescents	Radiation	Visible light emission
Chemiluminescents	Chemical concentration	Visible light emission
Thermoluminescent	Temperature difference	Visible light emission
Photovoltaics	Solar radiation	Electrical tension
Bidirectional energy exchanging materials		
Piezoelectric	Deformation	Electrical tension
Thermoelectric	Temperature difference	Electrical tension
Pyroelectric	Temperature difference	Electrical tension
Electrochemical	Chemical concentration	Electrical tension
Electrostrictive	Electrical tension	Deformation
Magnetostrictive	Magnetic field	Deformation

Note: Casini, M., 2016. Smart Buildings: Advanced Materials and Nanotechnology to Improve Energy-Efficiency and Environmental Performance. Cambridge: Woodhead Publishing Limited.

structure, an alteration of the voltage ranges, the absorption of a proton, and other phenomena. The effects may show in phenomena such as a change in colour, a change in volume, a change in the distribution of stress and deformation or a change of the refractive index.

Compared to traditional materials, smart materials are characterized by the following properties (Featherston and O'sullivan, 2014):

- Immediacy, as they respond to stimuli in real time;
- Transiency, as they respond to multiple environmental states;
- Self-actuation, as the ability to react is internal to the material, rather than external;
- Selectivity, as the reaction is discrete and predictable;
- Directness, as the reaction is internal to the event triggering it.

Depending on the type of reaction to the external energy field, smart materials are generally divided into Property Changing Materials and Energy-exchanging Materials (Table 4). Smart materials may come in the micrometer, micrometer or nanometer scale (smart nanomaterials).

The ability of smart materials to produce a useful effect in response to external stimuli makes them greatly interesting for their application in the fields of design and architecture in particular, both characterized by changing and dynamic needs (Table 5). Both types may also find application as sensors or actuators in smart devices or systems directly integrated into the building body.

As defined above, "smart materials" are qualified based in their "smart" behavior, as in a dynamic response which includes all the properties mentioned above. However, the term "smart" is still vague, so in general terminology is often used more widely to describe materials or behaviors with high or unique performance and properties, for instance easy to clean surfaces or self healing materials, even if they don't exactly fit in the "smart materials" category.

Property Changing Materials

The first category includes materials which autonomously and reversibly change one of their mechanical, chemical, optical, electrical, magnetic, or thermal properties in response to a stimulus. They include different types of materials such as chromogenic materials (thermochromics, photochromics, mechanochromics, chemochromics, electrochromics, liquid crystals and suspended particles), phase change materials, photocatalytic materials, electrorheological and magnetorheological materials, as well as shape memory alloys.

Table 5 Main applications of smart materials in the building sector

<i>Requirement class</i>	<i>Specific need</i>	<i>Smart material</i>
Controlling solar radiation transmittance through the building envelope	Control of spectral absorbance and transmittance of transparent closures	Electrochromic glass Photochromic glass LCD glass SPD glass
	Dynamic control of screening systems	External radiation sensors (photovoltaics) Interior daylighting sensors (photovoltaics) Actuators (shape-memory alloys)
Controlling heat flows through the building envelope	Control of thermal conductivity of building envelope materials according to climatic conditions	Thermotropic materials
Controlling temperature of interiors	Increase of thermal capacity of closures and internal partitions	Phase change materials
	Placement of heat sources outside the environment	Optical fibre systems Thermoelectric materials
Controlling air quality	Increase the lighting/heat ratio	LED/OLED Photoluminescent materials
	Monitoring of CO ₂ and pollutant agents	Sensors
Producing energy from renewable sources	Air purification	Photocatalytic materials
	Conversion of environmental energy into electric energy	Photovoltaics Piezoelectric materials
Optimizing lighting systems	Environment lighting monitoring	Photovoltaics
	Interiors daylighting monitoring	Photoelectric materials
Optimizing HVAC systems	Interiors occupancy monitoring	Optical fibres Electroluminescent materials
	Lighting sources placement	Pyroelectric materials
Controlling structural vibration	Temperature monitoring	Hygrometers
	Humidity monitoring	Photoelectric materials
	Interiors occupancy monitoring	Biosensors
	Monitoring of CO ₂ and pollutant agents	Thermoelectric materials
	Heat sources and storage placement	Phase change materials
	Eulerian buckling control	Piezoelectric materials
	Inertial damping control	Magnetorheological materials
		Electrorheological materials
		Shape-memory alloys
	Stress monitoring	Optical fibres

Note: Casini, M., 2016. Smart Buildings: Advanced Materials and Nanotechnology to Improve Energy-Efficiency and Environmental Performance. Cambridge: Woodhead Publishing Limited.

To date, these materials already found application in architecture in a high number of products and systems, especially in building envelope components which can most take advantage of their properties of adaptation to different use conditions. In particular, property changing materials are used:

- In transparent closures for dynamic control of solar radiation (chromogenic materials);
- In closures and in internal partitions to increase their thermal inertia (phase change materials);
- In mortars, paints or coatings of external and internal surfaces of the building in order to achieve a self-cleaning and at the same time atmospheric air purifying effect (photocatalytic materials).

As for transparent closures, these are certainly the most interesting application field of property changing materials, both for new constructions and for existing buildings. The need to combine vision and daylighting through glazed closures with incoming solar radiation control via conventional fixed sun screening systems has led to compromise solutions, skewed toward only one of these requirements and unable to guarantee the best operation along all four seasons. The integration of chromogenic materials in transparent closures instead allows to adapt the characteristics of light transmission and solar shading to external conditions, either with passive systems, completely self-sufficient and not user-controllable (such as thermochromic and photochromic glazing), or with active systems, freely configurable by users or by an integrated management system with the trade off of needing an electrical power supply (electrochromic, LCD, SPD glazing).

Equally interesting is the application in opaque closures and partitions of phase change materials (PCM), capable of reacting to changes in temperature with a state transition able to exponentially increase their thermal capacity. Available in different shapes

and packages (macroencapsulated panels, beads, bags, or microencapsulated in bulk form or integrated in various components such as bricks, gypsum, mortar and plaster), they are used as components in low inertia building systems such as lightweight opaque closures and interior partitions or translucent closures.

As regards photocatalytic materials, they have been finding large use in the building industry since the early 1990s: semiconductor metal compounds such as zinc oxide (ZnO), tungsten oxide (WO₃), cadmium selenide (CdSe) and titanium dioxide (TiO₂) by reacting to ultraviolet (UV) radiation lead to the formation of high reactive agents with the ability to oxidize and decompose many types of bacteria, organic and inorganic materials by photo-induced redox reactions of adsorbed substances.

Among photocatalytic construction and building materials, titanium dioxide (TiO₂) is the most widely used photocatalyst for its numerous advantages: it is chemically stable, safe, widely available and relatively inexpensive; it presents a higher photocatalytic activity compared with other metal oxide photocatalysts; it is compatible with most traditional construction materials, such as cement, without changing any original performance; it is also effective under weak solar irradiation in ambient atmospheric environment (Chen and Poon, 2009). Applied to the construction industry TiO₂ has allowed the development of paints for external or internal applications, mortars and cements, tiles and other construction products able to perform due to solar radiation a self-cleaning and depolluting action. TiO₂ induced photocatalysis is a promising technology also for self-cleaning applications. Besides its photocatalytic properties, TiO₂ demonstrates an intrinsic photo-induced surface super-hydrophilicity. In fact, differently from other photocatalytic materials, when water is adsorbed on this semiconductor material irradiated by UV light, it spreads forming a thin film instead of grouping in water droplets. When water is rinsed over the surface, contaminations like oil can be washed away.

Photocatalytic properties also characterize tungsten trioxide nanoparticles (WO₃). Tungsten based Renecat photocatalytic agent, manufactured by Toshiba, claims superior performance compared to TiO₂ regarding deodorant and antibacterial effect even with fluorescent or white LED artificial light, making it viable for interiors use. Furthermore it can also be applied on polymeric surfaces, such as PMMA or polycarbonate glazing, if provided with an inorganic binder.

Finally, shape-memory alloys can have interesting applications in the construction of buildings and architectural elements able to self-adapt to ambient temperature or assembled with the only supply of electricity or heat. When an object made of shape memory alloy such as nitinol (nickel titanium – NiTi) is deformed from an initial shape to a new one, it will keep this last configuration. If however heated to a certain temperature, either directly or by electric current, it will revert to its initial shape without any mechanical aid, as if it remembered its base configuration. This unique shape-memory effect is caused by the internal phase changes that the material undergoes during the deformation and shape return processes (from martensite to austenite upon heating and vice versa upon cooling). This process is generally reversible, although some shape deterioration over time may occur if the bending and heating are not carefully controlled. Shape memory alloys are applied in several industry sectors: they are used in simple release mechanisms to reduce the need for moving parts, and shape memory superelasticity allows metals to undergo extreme deformation (up to 8%) without consequences, and is for instance used in high end eyeglass frames. Shape-memory have also been developed in the form of rigid plastics or relatively porous foams, with a wide application scope, including self unrolling surfaces, knots that tie themselves for medical applications or consumer customizable furniture.

Energy-Exchanging Materials

The second category of smart materials instead includes those materials capable of converting more or less reversibly an input energy into another form of energy in accordance with the first law of thermodynamics. They include photovoltaic, luminescent (LED, OLED), piezoelectric, thermal and pyroelectric, electrostrictive and magnetostrictive materials. Main applications of energy exchanging materials in construction certainly concern photovoltaic materials and electro and photoluminescent materials.

Photovoltaic materials enable the production of electrical energy by transforming the incident solar radiation (photoelectric effect). Photovoltaic technology has reached the third generation of solar cells and boasts decades of applications. Research trends today are focusing on the development of processing techniques that would allow the production of high efficiency, low cost and high yield solar cells made of CIGS, CdTe and organic materials (polymer composites and dye sensitized solar cells). Further promising smart technologies for solar energy capture regard the direct conversion of light waves into DC current. Using multiwall carbon nanotubes and tiny rectifiers fabricated onto them, researchers have recently demonstrated the first “optical rectenna”, a device that combines the functions of an antenna and a rectifier diode to convert light directly into electricity, for now with a conversion efficiency of 1% but with good growth potential (Sharma *et al.*, 2015).

Regarding luminescent materials, they are commonly classified as chemiluminescent, electroluminescent, or photoluminescent according to the excitation energy source, albeit light emission can depend other energy mechanisms (such as friction).

Electroluminescent materials are the basis of the solid-state lighting technology used in Light Emitting Diodes (LED) systems, characterized by high efficiency, small size of light sources and application versatility. A new generation of solid state lighting is constituted by quantum dots light-emitting-diodes (QLEDs), made of quantum dots networks. These work similarly to conventional LEDs but show greatly improved functionality and even wider applications.

Photoluminescent materials are capable of absorbing solar light and re-emit it at a different wavelength in the visible spectrum (fluorescent and phosphorescent materials).

Lastly, as regards the piezoelectric effect, it consists in the property of some crystalline materials to polarize when subjected to a mechanical deformation (direct piezoelectric effect), generating a potential difference, and at the same time to deform in an elastic

manner when traversed by electrical current (inverse piezoelectric effect). The piezoelectric effect occurs only along one direction and deformations associated with it are the order of nanometers. Many common devices, including doorbells, speakers and microphones or quartz watches are based on piezoelectric technologies. Piezoelectric elements are also the key of recent proposals for harvesting energy from pavements and roads by exploiting kinetic stress.

Conclusions

Thanks to the huge progress in the field of materials science, technology solutions available today for buildings allow to harmonize the architectural quality with the new challenges of sustainability, offering new opportunities in terms of greener and smarter buildings. The goal of reducing energy consumption and environmental impacts in the use and maintenance phases of new and existing buildings is in fact being facilitated by the progressive introduction of advanced nanotechnology materials, which physical and mechanical properties greatly exceed those of traditional materials, and of active components and devices, so-called “smart materials”, able to modify their own characteristics in relation to different operating conditions determined by the climatic agents or by the users, allowing the realization of dynamic building elements and opening up important new possibilities in the way of design and renovate buildings in the twenty-first century.

See also: Improving Building Technologies With a Sustainable Strategy

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Sustainable Architecture, Alternative Concepts and Waste Reduction

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Concepts of Sustainability

Sustainable design and development is defined as; “design and development that meets the needs of the present without compromising the ability of future generations to meet their own needs” (World Commission on Environment and Development, 1987). The need for finding long-term solutions that warrant continuing human existence and well-being is far more compelling in these days of depleting resources and catastrophic climate change, than in the former days (Papanek, 1995). The need for waste reduction is of prime importance since materials saved is equivalent to materials produced. Though, it is Green and sustainable that are the catch words of design, in the contemporary helpless climatic scenario which is worsening over the passage of time, these have also created ample ambivalence and confusion. Thanks to the urgency of the situation, debates on the terms green, sustainable or ecological architecture has become almost meaningless, but the kernel matter lies with addressing the needs of harmonic and ecologically sustaining design and development, emphasizing on material waste reduction, that would assure the future of the earth with all its myriad of living and nonliving systems.

During a building's actualization process, its construction affects the local and global environments by way of interconnected human activities and natural processes. In the beginning stages, site development and construction influence the local ecology and its characteristics. The influx of heavy construction equipments and personnel onto a building site and various processes involved, disrupt the local ecology to a considerable extent, though it may be improved as the construction gets expedited (Ngowi, 2001; Spence and Mulligan, 1995). Needless to state that manufacture, transport and procurement of materials at various stages never fail to leave their impact on the global environment. Completed buildings require resources and energy in various forms for their useful performance. These, in turn, give rise to pollution and add to the mammoth problem of waste and environmental degradation which inflicts long-term impact on the environment. For instance, fuels and water used by its inhabitants produce toxic gases and sewage. Similarly, the process of extracting, refining, and transporting all the resources used in building operation and maintenance also has negative impacts on environment. Further, construction waste produced poses a great problem which could be avoided if creatively looked at it. This needs careful planning, dimensional; Modular, coordination and management that would result in the resource waste reduction.

Global ecosystem is essentially made up of three group namely inorganic substances, living organisms, and human beings (Çelebý, 2003). Built forms contribute to the compounded impact of architecture on global ecosystems. It is therefore, important to study the impact of built forms on the totality of the environment, throughout various stages. Developments should be facilitated taking into consideration the entirety of the systems; *resource, energy and transport etc., and the myriad of population of the Nation*, along with the specific characteristics of the region being developed. Although the general rule is to use the available materials at closer proximity to the site, it may not work out to be feasible when it comes to new and appropriate expressions sought by architects.

Though, it is *green* and *sustainable* that are the catch words, an examination of the meaning of ‘sustainable’ is required to avoid the avoidable confusion these words tend to generate, knowingly or otherwise (Andrew, 1992). Sustainable architecture describes the fact that ‘we receive what we need, from the nature’. Sustainable architecture, then, is a *farsighted positive response to awareness that everything we need is received from nature*, not a prescriptive formula just for our survival (Bergen et al., 1997). In other words, the goal of sustainable design is to find architectural solutions that warrant the well-being and coexistence of constituent groups (Kim and Rigdon, 2000). Therefore, a conceptual approach to framework is to be developed in order to meet the goal of well-being and coexistence together with resource waste reduction in an effort to attain sustainability. Three fundamental concepts of the framework proposed are; *Objectives, Strategies and Achievement*. These relate to the environmental responsibilities, creating environmental awareness, explaining the building ecosystem and designing sustainable built forms with care and efficiency, for the future (Çelebý, 2003).

Why Sustainable Architecture

Sustainable architecture aims at the *Protection of Resources – (PR)*, is the primary response to the awareness which influences all the following stages. Architects have to be mindful of the efficiency of forms, flexibility in designs and potential to reuse the components or the building itself on a later date. *Life Cycle Design – (LCD)* and *Livability Design – (LD)* facilitate healthy habitation for humans. Protection of natural resources is proposed at the inception stage of building process, to be achieved through the reduction and reuse; *direct reuse or recycling*, of the physical resources involved (Çelebý, 2003). While *Life Cycle Designs* provide a methodology for analyzing the building process and its impact on the environment in an effort to decide on the effectiveness of designer's choices, *Livability Design* focuses on the interactions between human beings and the natural environment (American Institute of Architects, 1996) (Fig. 1).

A sympathetic attitude from architects is extremely important as they interact primarily with users and environment in the establishment of a harmonious, healthy and sustainable built environment. Hence, understanding the above objectives which

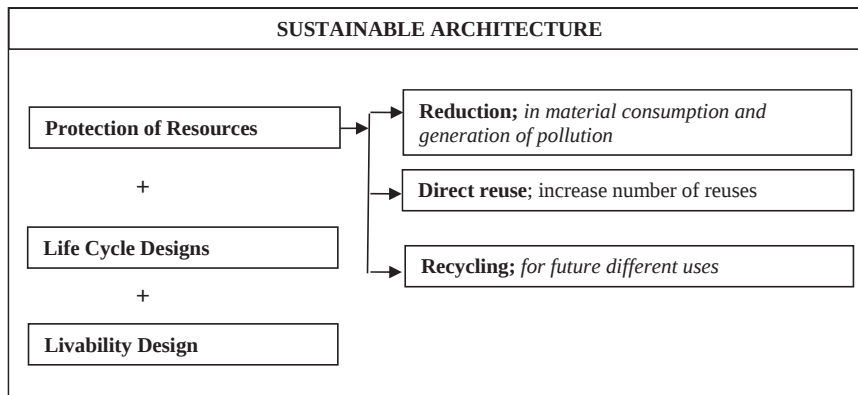


Fig. 1 Framework of concepts and strategies for sustainable architecture.

embodies a unique set of intentions is important to develop a more thorough understanding of the designer's positive interaction with the environment. The genesis of a project leading to its geographic location is one of the extremely important phases in the effort to reduce the load on infrastructure and consumption of resources and generation of waste and pollution. Locating a sustainable built form far away from the supporting or depending facilities would generate unnecessary traffic perils associated with commutation which is avoidable. Moreover, developing countries like India has the major part of 60% of its population living in rural areas. Appropriately rated economic magnets like Special Economic Zone – (SEZ), IT parks, industries or the like may be effectively used in order to achieve balanced development in rural areas which would retard the unhealthy migration to already congested urban areas. Moreover, as a strategy, develop automobile free, 'walk to work' rural or peri-urban communities, self-sufficient in water and energy requirements, equipped with appropriate waste management systems. Such sustainable communities may be the hubs that are effectively connected to others by means of high speed, ecologically friendly mass transit systems.

Protection of Resources – (PR)

It is the responsibility of an architect to reduce the use of nonrenewable resources in the construction and operation process of buildings in an effort to protect the resources and to preserve these for the future generations (Kua and Lee, 2002). Natural and manufactured resources, as is seen, are in a continuous flow in and out of any building which begins with the production of building materials, continues throughout the building's effective life sustaining intended functions. A critical examination of a building process reveals two essential streams of resource flow as shown in Fig. 2.

Intake resources flow into the building as input to the building ecosystem while *Outcome* is resources that flow out of the building to the ecosystem (Kim and Rigdon, 2000). Strategies of protection of resources are multi thronged as given below.

(1) Energy conservation:

It is achieved through the overall built form design, incorporating the principles of energy efficient design in orientation, organization of spaces, form of building, materials of construction particularly glazing, improved technology and intelligent building systems. The motto '*energy conserved is energy generated*' is worth adopting. Further, the design of the built form shall consider integration of energy generation by way of photovoltaic panels, small wind turbines etc. Energy reduction may be achieved by the use of atriums, double roof, shorter span, external shading, terrace and vertical landscapes or even by the use of trombe walls. These consists of a vertical wall, built of a material such as stone or concrete with glazing on its outside. Sunlight incident on the glazing generates heat which is conducted through the wall also, warms up the air between the glazing and the Trombe wall surface. This warm air may be channeled for use depending on the heating needs of the built form. It is important to comply with the GRIHA or other effective sustainability codes in force in the country.

(2) Water conservation:

Any building requires large quantities of water for various purposes that range from domestic uses to irrigation. Water requires treatments at various levels for specific uses. These treatments along with its transportation and delivery consume energy. Conservation of water is of increasing importance in these days of climate change and scarcity of water. It is the basic responsibility of every designer to address this issue seriously. Strategies for conservation of water may be made by the use of intelligent and improved water supply and sanitation systems, introduction of intelligent water management and control, change of life habits, and the use of intelligent design and detailing. Water recycling is important and every built form design shall include water recycling system in order to reduce consumption of treated water. Equally important is water harvesting from roof top and paved areas for the use for supplemental requirements. Every attempt shall be made to harness and treat roof water and its useful storage. Replenishing the underground water sources is vital to sustainability. Every attempt shall be made to increase percolation of rain water to the site soil. Landscaping schemes shall address this issue successfully by the

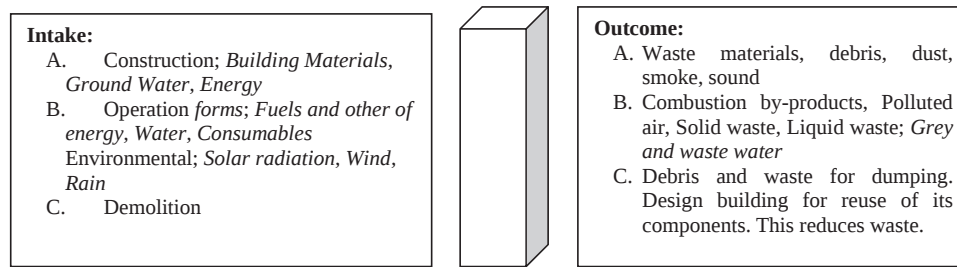


Fig. 2 The input and output streams of resource flow.

integration of roof gardens, perforated pavements or even by the appropriate use of rain pits. Personal use of water is the responsibility of every citizen and shall be practiced on a daily basis to limit and reduce waste water.

(3) *Material conservation:*

Material conservation focuses on every particular resource necessity for building construction and operation. Procurement, production and transportation of materials consume energy which is embodied in these. Major influx of building materials occurs during the construction stage. The waste generated by the construction and installation process is significant. Flow of materials continues even after construction that is used for maintenance, replacement and renovation. Consumer goods flow into the building to support human activities. All of the construction materials, in the end, *are outcome raw materials or waste*, either to be recycled or dumped in a landfill (Federle, 1993). Responsible design is the outcome of a thoughtful attitude to waste reduction at all stages of built form design and use.

Environmental impacts of energy consumption by buildings occur primarily away from the building site, through mining or harvesting energy sources and generating power. The energy consumed by a building in the process of heating, cooling, lighting and equipment operation cannot be recovered and these gets added up. Strategies for material conservation include intelligent form design, stringent area and space requirement calculations, effective management and use of technology in the performance of intended functions. Further, every attempt shall be made to avoid wastefulness through efficient planning and detailing. It is worthwhile considering appropriate legislation for levying tax; *luxury or green*, on buildings that exceeds the material and energy limits prescribed.

Life Cycle Design (LCD)

As it is seen in Fig. 3, the life cycle process of the building is a linear process consisting of three major stages (Curran, 1996). Each of these stages calls for sustainable approaches and strategies in an effort to achieve the goals envisioned.

Life cycle design (LCD) is not prescriptive, but suggestive in nature. However, LCD can contribute information and facilitate the effective decision making process. This approach accounts for the environmental consequences during the entire life cycle of construction materials; *from procurement to return to nature* (Burall, 1996). Life cycle of a building can be brought into three phases namely *Pre-building, Building, and Post-building*. The phases can be developed into LCD means that focus on minimizing the environmental impact of a building. Analysis of the building processes in each of these three phases throws light to the dynamics of design of the built form, its construction, operation, and effects of disposal from it to the ecosystem. Pre-building phase includes site selection, building design, and building material processes. However, this phase does not include the construction or installation of the building. Sustainable design approach considers meticulously the environmental consequences of construction materials, design of the structure, its orientation and impact on the landscape (Dimson, 1996). The procurement of building materials impacts the environment in various ways; *unscrupulous felling of trees leads to deforestation, mining mineral resources disturbs the nature and creates environmental pollution or the like*. Building phase refers to the stage in the life cycle of a building when it is physically constructed and operated. In the sustainable design, the construction and operation processes shall embrace means to reduce environmental impact, resource consumption and sick-building syndrome. Post-building phase refers to the stage which begins when the useful life of a building has ended and its building materials are turned in to resources for other buildings or waste to be recycled or returned to nature. The strategy is to reduce construction waste by recycling and reusing buildings and building materials.

Livable Design – (LD)

Livable Design refers to the livability of all constituent spaces in built forms and spaces that form various groups in the global ecosystem (Celebi and Aydýn, 2001). The livable design is concerned about the healthy coexistence among buildings, their environment and their respective occupants. Its broad objectives are intended to preserve the elements of the ecosystems in an effort to facilitate human survival. Built forms are intended to provide safe and healthy environments that are comfortable for their occupants which in turn enhance their satisfaction and productivity. Livable design objectives, therefore, could be evaluated under *Generation and sustenance of natural conditions, Creation of satisfactory urban design and site, Generation of human comfort* (Table 1).

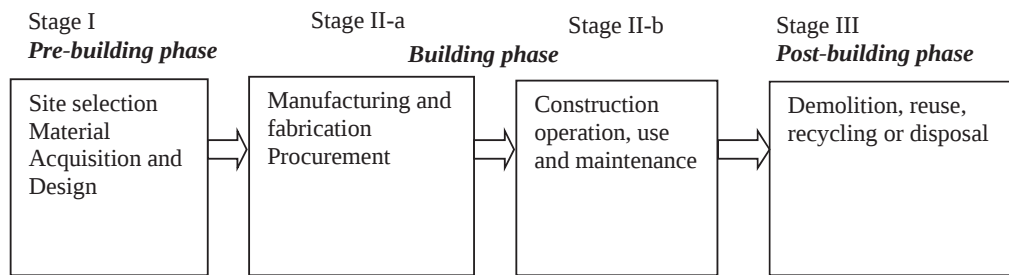


Fig. 3 The life cycle process of building.

Table 1 Conceptual framework of sustainable design

Objective	Protection of resources – PR	Lifecycle designs – LCD	Livable designs – LD
Strategy	Energy, Water and Material Conservation	Pre-building, Building Post-building phases	Generation and sustenance natural conditions Creation of satisfactory urban design and site Generation of human comfort
Achievement	Optimized space and systems, Materials Conserved	Total approach to Built form design, Lower energy consumption, waste generation	Acceptable and healthy exteriors and interiors, Improved performance and health of users

It is important to minimize the impact of a built form on its local ecosystem. The totality of neighborhoods, cities and entire geographic regions can reap the positive benefit from harmonious and complimentary planning on all fronts of resource, energy and pollution. Such a coordinated effort leads to an appropriate urban environment accommodating the specific needs of its context. Needless to state that sustainable design shall offer human comfort; both internal and external, in the interest of individuals and the nation at large.

Strategies for Creating Sustainable Architecture

The prime intension of strategies of sustainable architecture is to generate beneficial solutions in terms of quantity and quality which lead to physical and psychological comfort. The three objectives of sustainable architecture; *Protection of Resources*, *Life Cycle Designs* and *Livable Designs*, gives a comprehensive understanding of the environmental issues related to architecture.

Protection of Resources – PR

Resource demands of a built form are directly related to its utilization efficiency of resources. Concern for conservation of energy, water and building materials would yield specific design methods that would reduce the need for nonrenewable resources in built forms. Built form *outcome* management reduces its effect on environmental by lowering the level of waste generation and appropriate waste management (Thormark, 2001) (Fig. 4).

Energy conservation

Energy consumption by built forms accounts for a major share of energy requirement of any country. Therefore, one of the main objectives is to reduce energy requirement and consumption of fossil fuels used in the generation of energy. Operational phase of buildings consume energy for heating, ventilation and air-conditioning, lighting and transportation. Strategies to be adopted to achieve energy conservation shall be holistic and include energy conscious urban planning with emphasis on eco-cities with its neighborhoods and built forms that are sustainable and planned for public transportation, pedestrian walkways and walk-up work places. Favour mixed use for such cities with zoning laws facilitating balanced developments and walk-up work places. Ensure balanced development of rural areas and avoid migration and urban sprawl by encouraging redevelopment of existing sites and adaptive reuse. Do not encourage unscrupulous development and heavy generators of traffic without efficient integration with public transport networks (Table 2 and Figs. 5 and 6).

Materials conservation

Sustainable designs get realized in terms of building materials, components and products, the choice of which poses a tremendous task which requires understanding of materials and standards of performance. Cost and availability are likely dominant factors in normal building projects. It is also important to have the general awareness regarding the diverse implications of production, consumption and recycling on the environment. Therefore, adopt a lowered consumption which in turn reduces the need for production and generation of waste (Table 3 and Fig. 7).



Fig. 4 Grid and glass form for cultural sustainability in built form. Gable implies the presence of atrium and the influence of traditional Kerala architecture. *Architect: Dr. Abraham George.*

Table 2 Strategies for sustainable design – PR

Strategy	Description – Energy conservation
Energy conservation Energy-conscious site planning	It optimizes the use of natural resources on the site. Southern exposure for passive solar heating, use of trees for shade in summer and solar heat gain in winter. Planting of evergreens on the north of a building for protection from winter winds and improved energy efficiency. Use of water in various forms to provide natural cooling and humidification. Use of passive heating and cooling through the use of trombe walls, atriums for heat, light, and ultraviolet radiation necessary for photosynthesis of indoor planting. Passive solar architecture offers design schemes to control the flow of solar radiation using building structure through the use of intelligent shading devices, active and passive solar heating systems, and use of photo voltaic panels.
Glazing, cladding and insulation	Use of high-performance glazing and wall insulation in cladding to prevent both heat gain and loss. Reduction of heat transfer reduces the building's heating and cooling loads and energy requirement. Compounded benefits of smaller systems are many; smaller HVAC equipments needs lower initial investment, generates lesser mechanical noise and increases sonic quality of indoors and system reliability.
Day lighting and ventilation	Proper orientation of built form, organization of spaces and intelligent fenestration design maximizes the use of natural light in an effort to conserving electrical energy, reduces peak electric loads and cooling needs. Moreover, day lighting enhances the illumination quality of indoors, increases physical and psychological well-being and productivity. The qualitative benefits of day lighting are far more significant than its energy-savings potential.
Energy-efficient equipment	Operation and maintenance of equipments are the longest activities whose costs exceed construction costs over a building's lifetime. Scrupulous selection of high-efficiency lighting, heating, cooling, and ventilation systems is critical. Consideration to energy saving is to be given over initial costs.
Embodied energy building materials	Use materials with low embodied energy; <i>how much energy is needed for production</i> . The embodied energy of a material attempts to measure the energy that goes into the entire life cycle of building material. Use local materials, over transported materials to save transportation energy and reduce pollution (Burali, 1996).
Water conservation	Holistic view on water conservation is essential with all efforts for achieving self sufficiency namely; <i>reduction in requirement, reuse and recycling, water harvesting and practice of water management</i> . Adopt recycling of both grey water and sewage. Though grey water is not of drinking-water quality, it does not require intense treatment as equivalent to sewage therefore, can be recycled within a building, to be used for irrigation or for sanitary purposes. Efficient water supply systems and fixtures can reduce consumption of water and generation waste water. Vacuum-assisted and biocomposting toilets and water-less urinals reduce water consumption. Biocomposting toilets treat sewage on site, eliminating the need for energy-intensive municipal treatment. Encourage the use of indigenous and discriminatory landscaping for reducing water consumption.
Alternative energy sources	Incorporate solar, wind, water, and geothermal energy systems to reduce or eliminate the need for external energy sources. Use of low speed wind turbines could prove to be beneficial if, the built form design is done aerodynamically to channel and generate wind speed to generators.

Lowered consumption in building α Lowered production of waste and Need for production
Optimization of space requirement α Material Requirement, and Lowered operational costs

Life Cycle Design – LCD

The objectives of Life Cycle Design with its three stages; *pre-building, building, and post-building*, calls for the design strategies designed to achieve sustainability in the design of built forms (Table 4).



Fig. 5 Atrium-lit central courtyard of Chemical Engineering Block, NIT Calicut. *Architect:* Dr. Abraham George.



Fig. 6 Atrium-lit central courtyard of Students' Center, NIT Calicut. *Architect:* Dr. Abraham George.

Table 3 Strategies for sustainable design-material conservation

Strategy	Description – Materials conservation
Building material conservation	Attempt to optimize space requirement and estimate scrupulously the built-up area need. Attempt additional discussions with clients, even at the cost of inconvenience on the part of architect. Floor to floor heights multiplies the material requirement which often goes unnoticed. Determine floor to floor height meticulously with proper detailing and efficient system design and intelligent ceiling designs. Avoid excess trimming of materials to fit non-modular spaces that generates more waste.
Direct material reduction	
Reuse of built form	Accommodating existing buildings that are designed for specific functions to new uses, is one of the most effective methods of material conservation. Larger free spans, <i>within the prescribed reach of day lighting</i> , enhances the adaptability of built form. Combining the reclaimed or recycled materials obtained from demolished buildings in new is another method of material conservation (Kua and Lee, 2002). Many construction materials, such as wood, steel, and glass, could be easily recycled into new materials. Proper documentation of carefully dismantled joinery would facilitate its direct reuse in new buildings, particularly those built intentionally to generate heritage images. These attempts preserve embodied energy.
Consumer goods in buildings	Consumer goods lose their original usefulness in time and amounts to waste; <i>goods that have lost their original usefulness</i> . The useful life quantifies the time of conversion of goods from the usefulness to waste. It needs careful consideration in recycling short-life consumer goods since shorter the useful life of consumer goods, greater the volume of useless goods. As a rule of thumb, avoid the recycling of shorter life building materials.



Fig. 7 High performance structural glazing enhances lighting and transparency while reducing thermal load. School of Chemical Engineering, NIT Calicut. Architect: Dr. Abraham George.

Table 4 Strategies for sustainable design

Strategy	Description – LCD
Life cycle design:	Design and detailing are extremely important which are to be combined with building materials to express architectural forms.
Pre-building	Material production and related processes can produce global-level impact that can have long-term consequences. Therefore, architectural designs together with the building materials chosen are examined for their environmental impact at the Pre-Building Phase. All efforts shall be made to avoid wasteful expressions using high-embodied energy materials. Instead, care shall be exercised to use reusable materials intelligently and efficiently integrated with architectural design.
Building materials	Prefer to use sustainable materials made from renewable resources since renewable resources could be replenished at a faster rate exceeding that of consumption. Materials produced from nonrenewable materials like petroleum, metals or the like ultimately amount to no sustainability even if current supply seems adequate. Argument favouring the use of steel and glass based on their implied potential for reuse shall be favoured with careful detailing and effective specifications. It is important for designers to have knowledge of the harvesting of raw materials and the material processes in order to make right selections to ensure sustainability. Adopt materials produced without causing ecological damage which are locally available and cause least negative environmental impact. Though mud is a traditional building material which appears to be sustainable, a careful examination would prove it, not, since the same mud is good for sustenance of flora and retention of essential topographical feature. Adopt the use of recycled materials to reduce waste and save scarce landfill space. Moreover, recycled materials preserve embodied energy of their original form and reduce consumption of raw materials. Many building materials like steel are easily recyclable thereby eliminating the need for more mining and milling operations. Further, use durable materials with longer life and less maintenance, in order to limit the exposure to irritant cleaning chemicals.
Building phase	Strategies to be adopted for achieving sustainability in the Building Phase address the impact of construction and operation processes on environment.
Building materials	Avoid felling of trees by meticulous designing, integrating trees into the built form. Plant additional trees in order to account for damages and depletion of flora. Choose to minimize ecosystem damage on the site by careful planning and minimizing the use of heavy equipment. Topographical modifications and site excavations should not alter or block the flow of prevailing surface and groundwater flows. Use nontoxic materials to ensure health of occupants of built form since they spend more than three-quarters of their life indoors. Adhesives used in interior works produce toxic emissions for prolonged time, even after construction is over. Use only nontoxic cleansers since toxic airborne cleaners tend to remain in the ventilation system for extended periods.
Post-building phase	Examination of the environmental consequence of structures that has outlived their useful life is done, in order to decide on the future course of action; <i>reuse, recycling or disposal</i> .
Building materials	Resort to direct reuse or recycle in order to allow an existing building to become a resource for new one, since disposal requires incineration or landfill dumping, that adds up to the overburden of environment (Ngowi, 2001). Reuse of building as it is important, since the embodied energy which includes the sum of energy embodied in the materials and that went into its construction is considerable. Adaptive re-use is another viable option for energy conservation. When both these approaches fail, try reuse of building components. Discourage the inconsiderate suburbia in favour of reuse of existing built forms and infrastructure since, developing new suburbs from virgin woods or fertile fields destroys the agricultural land and dislocates the rural population which might result in tension and unrest as witnessed in <i>Singur</i> in West Bengal.

Table 5 Strategies for sustainable design – LD

Strategy	Description – LD
Livable design	Retain existing topographical contours by sympathetic design with a view to enhance microclimate. Moreover, unscrupulous alteration of contours will adversely affect existing water courses microclimatic and microclimatic wind movement. Prefer not to disturb site water table by avoiding excavation below water table since large obstructions like buildings, into the water table will disturb the natural flow. Avoid exposing water table during construction since it will increase chances for contamination.
Preservation of natural conditions	Do not spoil the existing flora and fauna, but preserve these vital elements of the site and environment. Native plants and animals; <i>if treated as resources to be conserved rather than as an obstacle to overcome</i> , will compliment the completed built form and make it a more enjoyable space.
Urban design and site	Urban design and planning strategies brings in sustainability at a larger scale, in the totality. It is important for the balanced geographic positioning and distribution of green zones considering the specific nature of the context and the special aspects of the nation to which it is applied. Avoid indiscriminate concentration in urban areas, especially in the Indian context, but encourage sustained growth of both rural and urban areas. Adopt to integrate design with public transportation, especially walk-up work places, or nodes, since sustainable architecture on an urban scale must be supported with efficient public transport networks. Avoidance of public transport results in the use of individual transport means which create problems of pollution, smog, traffic bottlenecks and parking. Encourage mixed use development including residential, commercial, office, retail and institutional spaces. It reduces the use of vehicles, encourages community feeling, dynamism and security with reduced tendency for vandalism.
Design for human comfort	Potential subjects of environmental impact in regard to human health include labourers; <i>both skilled and unskilled</i> , building users and the community in general (Osso <i>et al.</i> , 1996). It is important to provide comfort in terms of thermal, visual, and acoustic environments in order to enhance the performance output of users. Insist on the use of nontoxic materials with low or no VOC emissions to reduce health hazards and avoid sick building syndrome. Studies have established the importance of visual connections to exteriors; <i>the biological clock synchronized with the periodic cycle of day and night, which gets connected to the ever-changing dynamic natural exteriors by way of open or glazed atriums open vertical zones in built form</i> , that link the interiors with exteriors, in an effort to boost the performance and wellbeing of occupants. Similarly integration of operable windows is essential for the occupants to have proper management of openings in an effort to have passive energy efficiency by periodical opening or closing as per favorable outdoor conditions (Abraham, 1997).
Social responsibility	Honour <i>Equal Opportunity Act</i> and design for accessibility by the physically challenged for all spaces in the built form. Once the built form is designed for the physically challenged; <i>wheel chair bound, people with crutches, visually challenged, hearing deficient, children, pregnant and people with ailments</i> , its usefulness life and sustainability gets enhanced.

Livable Design – (LD)

Objectives enshrined at the three levels; *ecology, urban design, and human comfort*, and the social responsibility of sustainable architecture are achieved through the following specific strategies (Table 5).

Need for Alternative Concepts

It is important to understand the limitation of traditional design models to generate unique built forms that meet the requirements of sustainable designs. Mostly, the inherent inability in the traditional models is manifest by way of stereotyped thinking which leads to no atypical designs. It is worthwhile to ponder the words of Albert Einstein “*We cannot solve the problems by the same thinking that created them*”. Due to the lack of novelty in conceptualization and approach, such designs offer very little scope for optimization, lowering energy and resource consumption. This problem of stereotype could be resolved creatively by a search for alternate models in designs. Nature, at this juncture, presents itself with harmonious designs that are sustainable, self-supporting and self organizing. Solutions that are found in the harmonious natural systems are always in evolution, perfecting and adapting to their contexts. Thus, what is seen today has been working over billions of years for evolving a reliable and sustainable model. Adoption of these evolved models in human designs would facilitate the making of future systems better sustainable; environmentally, ecologically and economically. Hence, Biomimicing reveals itself as a fine model to follow in the generation of alternative sustainable design solutions.

Biomimicry

Biomimicry is a new science that studies nature’s best ideas and principles and imitates these designs and processes to solve human problems. In other words Biomimicry leads to *innovations inspired by nature* (Biomimicry Institute). Though some of nature’s basic

configurations and designs can be copied, most ideas from nature are best adapted when they serve as *inspiration for human-made designs and productions* (Bar-Cohen, 2006). Adaptation of natural systems and organisms has facilitated better understanding of related phenomena and principles in the design of novel designs, devices with better features and capability. For example, the cell-based structure that is the building block of biological systems has the ability to grow with fault-tolerance and self-repair. With the adaptation of Biomimic structures based on nano-technologies, such designs and devices are possible in human-made designs, but not with traditional materials and processes. On a different level, there exists the evident, inspirational link between the design of tongs and bird's beaks. The same inspiration is evident in the foldable hand-held fan design and the peacock feather display; *a magnificent attempt to impress the female*. Further, there are organisms like spider that feeds on its own saliva; which otherwise would be a waste, nurturing itself.

One of the important features of nature is its evolution by responding to the system needs and generating solutions that work. Nature remains in an open, dynamic system establishing balance and continuous refinement in all its productions. Each of the successful natural creation that passes to the following generation has to withstand the test of survival, establishing the 'best fit' for the following generation. Nature's laboratory through evolution generates information that is coded in genes and transferred to the following generation through the process of self replication. Nature thus, is perfecting models worth copying and inspiring novel engineering methods, processes, materials, algorithms, and designs. In a similar way production of designs and the elements and their organization in the design produced shall remain in a continuum of evolutionary changes, permitting adaptation and attainment of the 'best fit'. Mimicking of nature may be done at various levels beginning with the full and complete appearance of the natural system to its every system detail in part or full. On the other extreme, natural models are interpreted and transformed in the making of human-made designs. Such mimicking of life-systems demands the full capacity and intelligence of humans.

Principle of 3Ms

Model

Accept nature as the standard and imitate its system designs, processes and strategies at any level as deem fit, to live sustainably. Investigations of such natural systems reveal the details of system composition and their organization at the general level and the details of elements, processes and strategies at the specific level. Biomimic designer has the freedom of choice to operate at the level of optimum advantage, in tune with the technological capabilities and resources available.

Mentor

Nature is the finest teacher and mentor for the designers of all the times. Genius designers like Leonardo da Vinci, mathematician Leonardo Fibonacci to architect F. L. Wright have looked to nature for inspiration, ordering and performance of their productions (Knott *et al.*, 1997). Learning from the vast 3.85 billion years of research experience gained through the nature's lab and evolutionary process would immensely benefit the future designers (Lowman, 2002). One has to be, therefore, intelligent enough to understand, interpret and adopt the nature's time-tested, creative and sustainable solutions and ordered processes for sustainability individual built forms or in collective urban forms.

Measure

Biomimic designers view nature as an ecological and sustainable standard and accept what it does. Nature with its organisms maintains sustainability and survival through constant adaptation and satisfying of just needs without causing congestion and contamination. Unlike organisms, humans plunder the nature for pleasure and satisfy their greed, causing imbalance and violent repercussions at times. Human adaptations rarely follow biological laws; instead, *attempt to change the very constraints that force their own adaptation*. Hence, the antithesis of biological laws is prescribed in the industrial, financial and civil systems. It is worthwhile to recall the statement of Mahatma Gandhi *"The nature has enough to satisfy our need but not greed"*. It is therefore, imperative for a Biomimic designer to comply with nature's standards in the maintenance of sustainability and adapt to the forces of natural transformation rather than aggressive living.

Goal

Biomimic designs imitate life systems that learn, grow and adapt incorporating continuous feedback, inheriting innovation and refinement for effecting evolution and the best fit. This might offer the possibility of a self evolving system having the capability of production, growth and consumption of waste. In this process the problem of waste would be converted to generation of raw materials!

Seven Point Strategy

Optimize rather than maximize

Natural systems are programmed to optimize, never maximize their system output. Every natural system and corresponding elements are designed to be *multifunctional in design* thus enhancing versatility of design and avoid multiplying need for specifics.

A visible example is human hand. Versatility further, reduces consumption of resources and inconveniences. Further natural systems exhibits extreme '*form to function*' fit.

Act independently

Natural systems are self reliant with no need for dependence at all levels of production consumption and disposal. Natural system is equipped for recycling all materials on expiry of useful life and turns *waste to food*. On the contrary, waste production is inherent to all human productions chocking every disposal system. Adopting the natural position of '*waste to useful stuff*' would inspire Biomimic designers to generate individual or collective built forms that would facilitate useful spaces that are *re-transformable* and avoid the need for fresh raw materials, other resources and energy. A Biomimic design shall therefore, *enable independent performance, foster cooperative relationships and facilitate retransformation*. Often built forms meets with the need for self organizing and remain in balance. A simple example is a corporate building designed for a specific set of functions faces the need to get transformed to house altogether different set of functions and users due to changes in economy or other formative forces in order to stay fit. If a built form is designed to be rigid without any scope for readjustment in an effort to be transformed in self organization, it leads to unfit and extinction. Cases of demolition of high-rise apartment buildings that fail to generate acceptable living conditions within and exterior environments endorse the necessity for self organization and retransformation when situations call for it in an effort to maintain balance and harmony (Jacobs, 1961; Newman, 1973).

Manufactures own needs

Traditional models do consume but never produce for the needs it has; be it energy or any other resource. Whereas, through Biomimic designs many if not all of the needs of a built form may be generated fully or partially. Power for example, to be generated by alternate means by creatively using wind, sun or even geothermal, multiple use, involvement of human and animal power or the like in an effort to meet the built form needs. A built form in isolation could be used to tap the wind energy by way of its aerodynamic design and integrated wind turbines. Similarly, built forms could be designed meticulously to tap solar energy; both passive and active, through passive and appropriate courtyard designs or photovoltaic integrated designs. Developments in material science and photovoltaic designs present the designers with transparent thin film options amounting to sustainable and creative built forms. At city level collective built forms of cities could be creatively composed to generate self shading, light and ventilation within and around with appropriate reradiation specified, in an effort to counter the increased energy demand resulting from heat island formation and ill-lit designs.

Imbibing the lesson of consuming what is made by own, locally not brought from elsewhere, Biomimic designers have to begin with the use of locally available and self generated resources, rather than using those brought from afar, at higher cost and energy consumption. Preferring to be in harmony with nature and the context of design would immensely benefit Biomimic designs.

Resourceful and opportunistic

Biomimic designs shall derive its uniqueness and strength from shape rather than the material, and building from the bottom-up. While using simple and common building blocks, creatively explore the possibilities inherent in forms rather than simply bogged-down with materiality and available technology. It simply means choosing the 3D form advantage over 2D traditional models, beginning with the preference for frames over post and lintel. Biomimic designs shall prove to be resourceful and creative naturally in diminishing consumption and enhancing self generation, even by reducing need exercising preference to intelligent built forms.

Cyclical processes over linear

Traditional models of designs are inherently linear and additive in nature. Linear additive models have proved to be ineffective with larger consumption and wastage of resources at all stages of built forms, beginning with erection through operation and maintenance, leaving behind wastage and byproducts. On the contrary, cyclic processes tend to be inherently effective and efficient at all levels proving to be naturally sustainable as in the example of falling leaves turned in to fertilizers for the tree through biological involvement.

In the evolutionary Biomimic designing feedback loops are inevitable. These loops are to be effectively incorporated in the continuous refinement of the process resulting in better designs. In doing so the natural cycles; *Carbon cycle, Water cycle and Seasons*, are to be honoured for maintaining sustainability.

Durable and tough

Biomimic designs are to be as durable and tough in tune with the diverse natural law to be '*operating at low-risk*' as in the preference for a forest against a single agricultural crop. In such a rugged system each of its components systems shall be complimenting one another.

Decentralized and distributed

Nature operates at surplus mode having back-up maintained operational and maintains itself even in the failure of a component system. Multi-supported design increases the operational reliability and earns credibility.

Biomimic Thought Process

- *Identify the real challenge*
 - What do you want to “do” (not make)? Be open, rational and creative. Learn inquisitiveness from kitten!
- *Interpret*
 - Identify the functions / purpose
 - How nature does perform function?
- *Discover Nature’s Genius*
 - Go for a walk outside and observe and brainstorm. Look for the precious stones!
- *Abstract*
 - What patterns and principles work for your problem? Be creative and prudent.
- *Emulate or Imitate*
 - Play and design
 - Brainstorm and converse
- *Evaluate*
 - Revaluate and Re-Imagine the design deeper and rigorous each time with holistic thinking in order to solve the entire problem. It might be necessary to redefine to solve the problem as a whole, not in parts.

Formula for Sustainable Future That Offer Waste Reduction

Intellectual Capital + Nature’s Genius = Innovative, Sustainable solutions

If we are limited, it is by our own dreams! Therefore, dream great and be a B₂, *Beautiful Biomimic*.

Conclusion

Concepts and strategies aim to generate sustainable architecture which is the need of the hour and vital to the existence of life forms on earth. In this process, waste reduction or no waste production shall be attained through adopting alternative concepts to rescue a world that is already choked. There exists confusion from multiple mushrooming agencies and competing visions trying to define and establish what ecologically sustainable architecture is, especially of its scope, application and end result. The scientific and technical complexity involved along with the commercial and political interests amalgamated to its objectives make ‘defining sustainable architecture’ a delicate issue. These approaches lack a real concern for the unique survival and special needs of the context to which such prescriptions are applied. Further, it is important to understand the limitation of traditional design models and look for better alternatives including Biomimicry.

Sustainable architecture can be achieved primarily by reducing the consumption of materials, energy requirement involved both directly and indirectly and the generation pollution. Space and area optimization warrant an effective strategy in the achievement of reduction of the need which lowers the generation of pollution. Architects have a greater role to play, therefore, at this important issue. Engineers have an equally important role in the design and selection of optimized systems; *mechanical, electrical, transport and disposal*, which are vital for the efficient performance of the built forms.

It is important to consider necessary legislation to impose ‘green tax’ on buildings that exceed the limits of material and waste generation; to be stipulated for unit area of foot print on site. Further, those designs that comply with the norms shall be encouraged through incentives. Architectural schools shall promote creative designs instead of stereotypes.

Additional thrust is to be exercised in regard to the generation of environmental awareness, waste reduction and the design detailing and practice for sustainability in order to achieve this vital responsibility we owe to the posterity and ourselves. Education in architecture and allied fields shall impart rigor and soundness to design professionals engaged in the design, production, operation and reuse of built forms (Celebi and Aydýn, 2001). It is also important to accept the relationships and interconnectedness within the ecosystem and the built forms that designers develop. It is the vital responsibility of architects to find creative design solutions that facilitate well-being and harmonious coexistence of organic and inorganic groups (Yeang, 1995). A conceptual layout and an array of feasible strategies are elucidated for appropriation as any project demands. It is important to view these strategies as a positive response to the awareness of the finiteness of the limits of ecosystem.

There is inherent inability in the traditional models and stereotyped thinking leads to atypical designs. The problem of stereotype could be resolved creatively by alternate models wherein mimicking natural systems holds great potential. Natural systems are always in evolution, perfecting and adapting to their contexts over billions of years. Adopting the natural models through Biomimicing facilitates the making of future systems better sustainable. The principle of 3M and the Seven-point strategy is elucidated in generating Biomimic designs. Further, the Biomimic thought process is illustrated in evolving a formula for sustainable future.

It is right time that the Government sets-up a *Project Sustainability Authority* for both public and private sector projects in the wake of the numerous agencies mushrooming with the sustainability and green agendas with no eye for the real needs and special

nature of developing nations like India. Premier research and educational institutions could be made a vital part of the 'Authority' wherein the Nation can expect fairness without outweighed importance assigned to the concerns of corporate sector, forgetting the balanced development of rural sections of the country.

See also: Material Culture and Sustainability: Traditional Versus Modern in a Case of Northeast India

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Further Reading

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Thermal Adaptation and Sustainable Housing in Cold Climates

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Nomenclature

I_{μ}	Annual mean solar radiation	T_{hot}	Temperature of the hottest month
PMV	Predicted Mean Vote	T_{in}	Indoor dry-bulb temperature
RH_{μ}	Annual mean relative humidity	T_{in}	Indoor dry-bulb temperature (instantaneous)
$T_{A\mu}$	Annual mean outdoor dry-bulb temperature	T_{mmax}	Monthly maximum outdoor dry-bulb temperature
T_{amax}	Annual maximum outdoor dry-bulb temperature	T_{mmin}	Monthly minimum outdoor dry-bulb temperature
T_{amin}	Annual minimum outdoor dry-bulb temperature	T_n	Neutral temperature
T_{cold}	Temperature of the coldest month	T_{out}	Outdoor dry-bulb temperature (instantaneous)
T_{comf}	Comfort temperature	T_{rm}	Running mean temperature
		TSV	Thermal sensation vote (subjective)

Introduction

According to ASHRAE Standard 55 (ANSI/ASHRAE, 2004) thermal comfort is defined as “the condition of mind which expresses satisfaction with the thermal environment”. The perception of thermal comfort varies from person to person due to physiological and psychosomatic differences in people. Primarily, thermal comfort is affected by climatic factors such as temperature, air speed, humidity, and radiant temperature; human factors of level of activity and behavioral factor of clothing insulation (Fanger, 1973). Building enclosure acts as a medium, which moderates the outdoor weather changes and facilitates comfortable indoor climate. As a corollary, we infer that the role of the enclosure is crucial when the outdoor thermal boundary conditions are severe. Cold climate zones characterized by low temperatures for the majority of the year are typically prevalent in high latitudes regions or higher altitudes of middle and low latitudes. The role of enclosure is hence a critical factor in ensuring comfortable living conditions indoors. Buildings in cold climates are required to minimize heat loss through the envelope. Traditional buildings in cold regions incorporate passive solar heat gain strategies such as high thermal mass of walls and roofs (Stevens *et al.*, 2016). Apart from physiological heat balance, thermal comfort, by definition, is associated with the “condition of mind”. According to adaptive comfort principle, if a change occurs to produce discomfort, people react in ways which tends to restore their comfort (Nicol and Humphreys, 2002). This change can be physiological, psychological and behavioral adaptation. In countries such as India, centralized heating systems are not an integral part of majority of the housing stock. Comfort conditioning is primarily through conventional and localized heating systems. Design of buildings, enclosure and thermal adaptation are hence crucial for sustainable living conditions in such building types.

The chapter sets to (a) present a characterization of cold climate in India; (b) discuss sustainable design practices and compare the existing housing typologies in cold climate; and (c) discuss thermal adaptation in cold climate of India and its implication on building thermal design. The study focusses on cold climate of North India and specific examples of Himalayan hill settlements is presented. The study employs geo-spatial analysis of thermal conditions using the data from worldclim (2016) and CRU CL v. 2.0 (a high-resolution data set of surface climate over global land areas) (New *et al.*, 2002). Section “Cold Climate of India” of the chapter presents a statistical characterization of cold climate based on the thermal severity variations. Thermal comfort assessment of four representative locations is presented. Section “Thermal Adaptation in Cold Climate” discusses the thermal comfort and adaptation in this region. Thermal adaptation analyzed through longitudinal and transverse surveys conducted in these four locations during summer and winter is discussed. Neutral temperature isotherm generated for the study region is presented. Section “Buildings in Cold Climate” describes the building design requirements and presents a bio-climatic classification of the cold climate zone based on Mahoney’s method. Thermal performance of the existing housing measured through real-time field studies are discussed. The study highlights the role of climate responsive design in order to achieve sustainability.

Cold Climate of India

Definitions of cold temperature vary across different climate classification methods. According to the modified Köppen climate classification by Peel *et al.* (2007) cold climates are those having $T_{hot} > 10^{\circ}\text{C}$, and $T_{cold} < 0^{\circ}\text{C}$. Fig. 1 presents the Köppen Geiger climate zones of the Indian cold regions. Large swathes of Himalayas are classified under very cold (EF, ET) conditions while others have milder (Dfa, Dfb, Dfc, Dsb, Dsc, Dwb, and Dwc) environments.

According to the National Building Code of India (NBC), the cold climate zone is a region that has a mean monthly maximum temperature less than 25°C for more than six months (Bureau of Indian Standards, 2016). By this definition the entire Himalayan region is encompassed in a single cold climate zone.

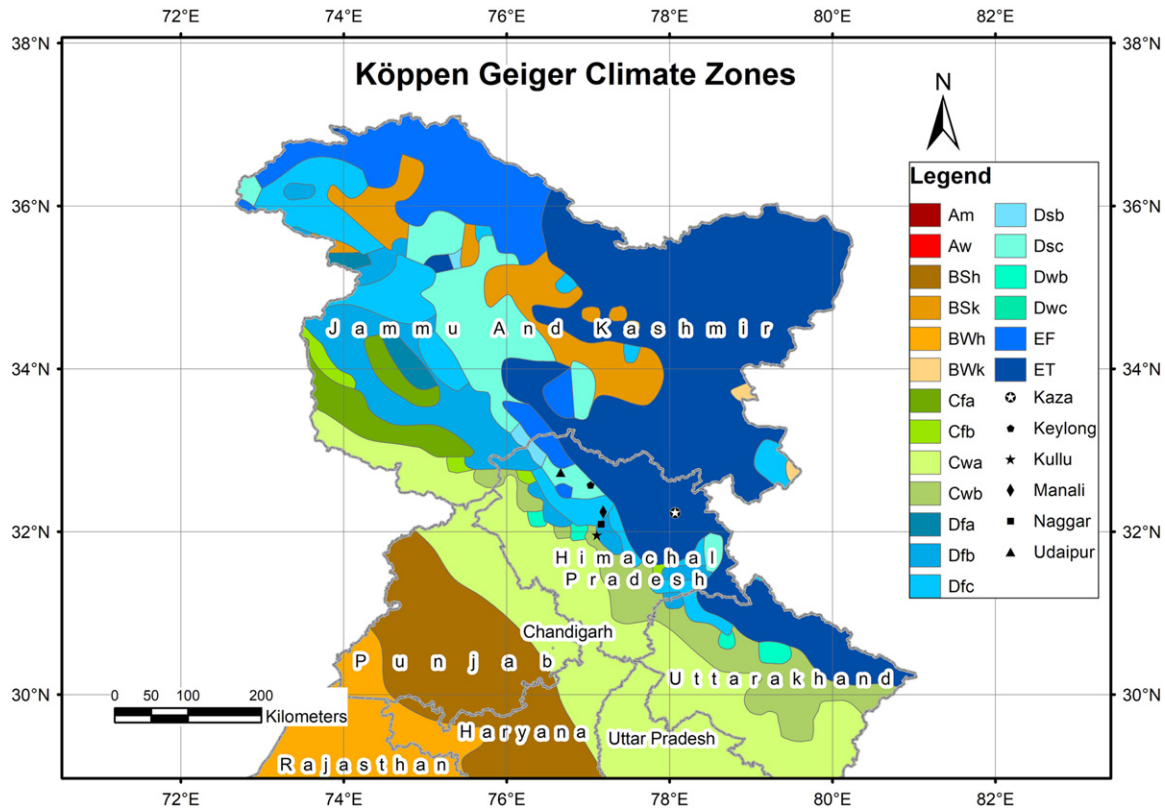


Fig. 1 Köppen-Geiger classification of the study region.

Sub-Classification of Indian Cold Climate

A sub-classification of the Indian cold climate is required to address the variations of temperature, humidity, and solar radiation. Using a high-resolution (30'') spatial dataset of temperature from worldclim and 10' resolution data from CRU (Fick and Hijmans, 2017; New *et al.*, 2002), the NBC's cold climate is re-created in detail. Fig. 2 presents the distribution of annual maximum (T_{amax}) and minimum temperature (T_{amin}) and mean solar radiation (I_{μ}).

The range of annual mean temperature spans from 23°C to as low as -34°C. The extreme temperature ranges from 25°C to -42°C. Similarly, a wide variation is observed in solar radiation availability as shown in Fig. 2. These intra-climate zone variations highlight the need for a climate zone sub-classification. This will facilitate effective regulatory control over thermal performance and energy use of buildings in this region. A rational sub-classification is discussed further.

Three variables (a) annual mean temperature (T_{au}), (b) annual mean relative humidity (RH_{μ}), and (c) annual mean solar radiation (I_{μ}) are used in the sub-classification. The 30'' spatial resolution data points of the above variables in cold climate zone are statistically classified. T_{au} values are classified into three groups (cutoffs at the 20th percentile and 80th percentile). Relative humidity (RH_{μ}) and I_{μ} are classified into two groups (cutoff at the 50th percentile value). The T_{au} , RH_{μ} and I_{μ} groups are spatially overlaid to obtain 11 subgroups referred as CZ(n). Table 1 shows the details of 11 sub-groups characterized by high, medium or low temperatures and high or low relative humidity and solar radiation.

Root Mean Square Error (RMSE) associated with the maximum temperature, minimum temperature, and average temperature are 1.39°C, 1.29°C, and 1.12°C respectively. However, the actual errors differ depending on the "complexity of the terrain" and the "density" of the weather stations. Absolute RMSE for solar radiation is slightly higher at 1.45 MJ/m² (Fick and Hijmans, 2017). Estimated relative humidity has errors up to ±15% (New *et al.*, 1999). Fig. 3 presents the spatial map of the sub-classified cold climate zone.

The north and north-east peripheral regions fall under CZ1 which experience low T_{au} , RH_{μ} and I_{μ} . The southern fringes fall under CZ11 which experience T_{au} , RH_{μ} and I_{μ} . CZ11 further merges with the composite climate zone of the National Building Code. The relevance of the sub-climate zones is validated using the ground station data obtained from the Indian Meteorological Department. The thermal severities, heating and cooling degree hours, relative humidity and solar radiation variables showed a statistically significant difference. The above method of classification provides a simple, reliable and precise estimate of intra climate zone thermal severities. This enables regionalization of the thermal performance regulations of the major climate zone provided by national and international codes. For instance, the sub climate zones can be regionalized to district administrative boundaries in order to facilitate effective implementation of building thermal regulation and energy efficiency codes.

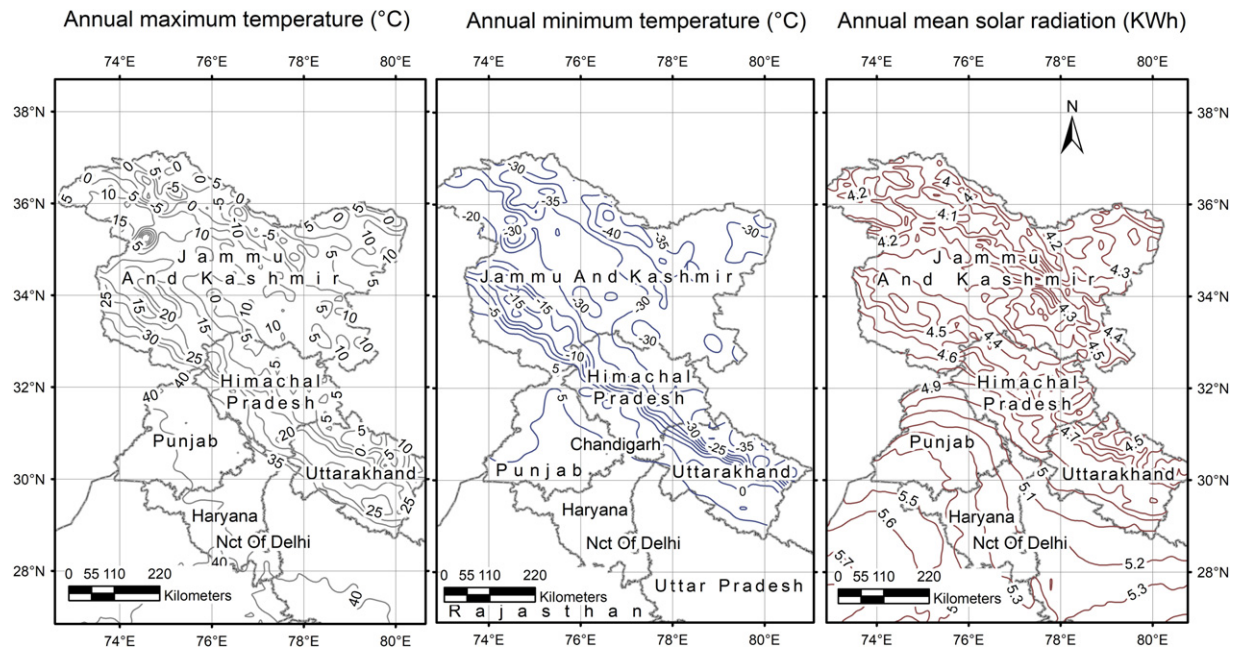


Fig. 2 Iso-line map of T_{amax} (left), T_{amin} (middle) and I_{μ} (right).

Table 1 Temperature, RH, and solar radiation profile of the cold climate zones

Climate zone	T_{am} ($^{\circ}\text{C}$)	RH_{μ} (%)	I_{μ} (KWh/M2/Day)	Area (sq km)
CZ1	(−33.9) to (−2.4)	45.6–56.9	3.66–4.49	69,023.9
	Low	Low	Low	
CZ2	(−20.7) to (−3.7)	51–56.9	4.28–4.7	2138.3
	Low	Low	High	
CZ3	(−30.7) to (−7.2)	56.7–62.4	4.03–4.67	234.3
	Low	High	High	
CZ4	(−17.3) to (19.2)	45.7–57.6	3.85–4.51	83,944.5
	Medium	Low	Low	
CZ5	(−21.4) to (16.8)	45.7–57.2	3.92–4.81	60,862.2
	Medium	Low	High	
CZ6	(−14.6) to (18.5)	55.6–81.4	3.97–4.58	46,578.4
	Medium	High	Low	
CZ7	(−22.7) to (18.8)	55.8–80.3	4.22–5.46	33,223.4
	Medium	High	High	
CZ8	(11.6) to (18)	53.4–56.4	4.25–4.46	363.5
	High	Low	Low	
CZ9	(11.8) to (19.3)	54.4–57	4.36–4.87	624.7
	High	Low	High	
CZ10	(9.9) to (20.1)	58.8–79.9	4.15–4.48	16,633.1
	High	High	Low	
CZ11	(7.5) to (22.9)	56.2–81.4	4.26–5.64	65,327.5
	High	High	High	
Total				378,953.8

Climatic Analysis for Representative Locations

From the above sub-classification (**Fig. 3**) four geographical locations are selected on the basis of climatic severity. The locations Keylong (32.58°N 77.03°E), Manali (32.27°N 77.17°E), Naggar (32.12°N 77.17°E) and Kullu (31°56'42"N 77°6'56"E) represent CZ5, CZ5, CZ9 and CZ11 respectively. A statistical clustering of the daily mean temperature, humidity ratio and solar radiation is performed for the four locations. The two step clustering yielded four clusters. **Table 2** presents the details of the clusters and the cluster mean values of temperature, humidity ratio and solar radiation. As shown in **Table 2**, Keylong (CZ5) experiences sub-zero

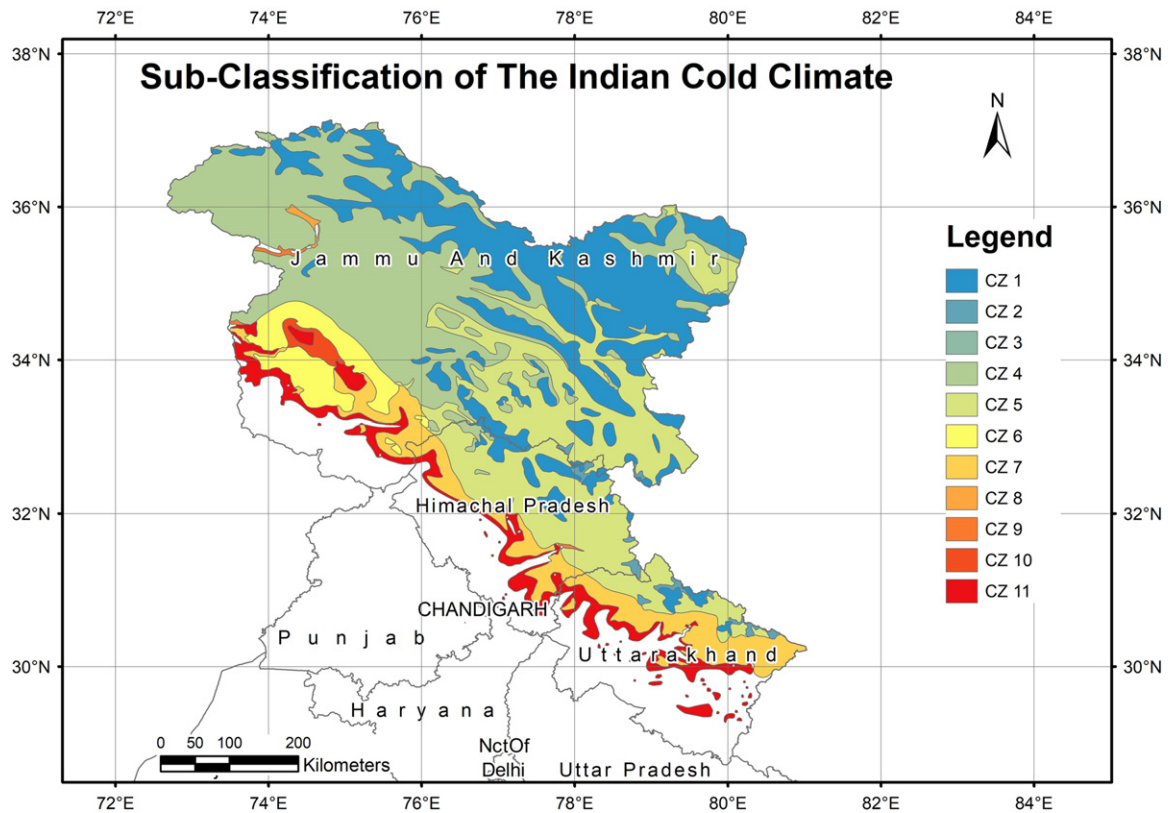


Fig. 3 Sub-zones in the cold climate of India. (CZ=Cold Zone).

Table 2 Seasonal climate clusters of representative locations

City	Cluster	Size (%) <i>N</i> = 365	Humidity ratio (g/kg)	<i>T</i> (°C)	GHI (KWh/m ² /day)
Keylong	CL1	25.2	0.6	−6.68	488
	CL2	19.2	0.8	−4.24	613
	CL3	30.4	1.78	6.08	730
	CL4	25.2	4.29	15.02	747
Kullu	CL1	33.2	5.65	12.25	534
	CL2	9.3	8.61	18.9	573
	CL3	25.5	8.67	22.98	737
	CL4	32.1	14.89	24.84	740
Manali	CL1	23.3	3.28	3.38	490
	CL2	20	3.98	7.52	603
	CL3	32.3	6.67	15.66	730
	CL4	24.4	10.89	21.99	749
Naggar	CL1	17.5	3.92	5.49	480
	CL2	22.5	4.86	9.53	579
	CL3	27.7	6.96	17.92	719
	CL4	32.3	12.27	23.97	747

cluster mean values during winter (cluster 1 and 2) and is prevalent for about 44% of the year. This season is accompanied by low solar radiation (cluster mean of 488 KWh/m²/day) and very low humidity. On the other hand, Kullu (CZ11) experiences moderately cool winters with cluster mean value of 12.25°C (cluster 1) which is prevalent for about 33% of the year. However, the daily minimum temperatures dip below zero during a few days in this cluster.

Fig. 4(a) presents the statistical summary of daily mean temperatures with respect to the climate clusters for the four representative locations. **Fig. 4(b)** presents the statistical summary of solar radiation with respect to the climate clusters for these locations.

Fig. 4(c) shows a psychrometric plot of daily mean temperature and humidity data of Keylong and Kullu. Keylong (CZ5) experience a dry severe cold weather. Kullu (CZ11), which borders the composite climate zone to its south, experiences moderate and cool weather.

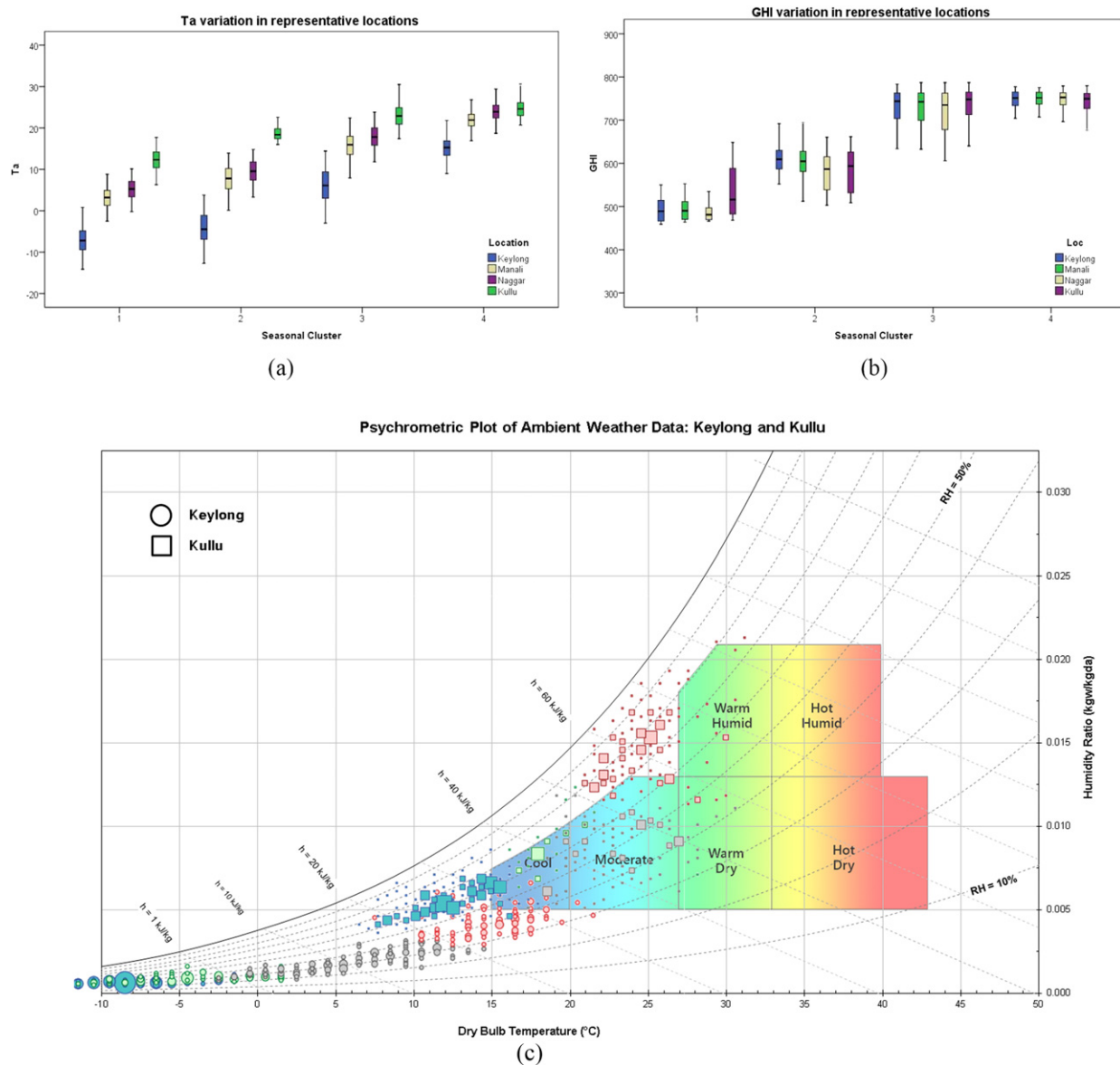


Fig. 4 Statistical summary of (a) daily mean T_a (b) daily mean solar radiation, for seasonal clusters. (c) Psychrometric plot of clustered ambient weather data for Keylong and Kullu.

Thermal Adaptation in Cold Climate

In last few decades, researchers around the globe started questioning the rationale of static comfort models developed in laboratories and gave rise to alternate theories. This resulted in the theory of adaptive thermal comfort (Brager and de Dear, 1998). The adaptive comfort theory is based upon the approach that if change occurs such as to produce discomfort, people react in ways which tend to restore their comfort (Nicol and Humphreys, 2002). This approach is based upon the field studies surveys in the real world. Thermal comfort field studies conducted across the globe established that people are flexible and adapt their behavior to make them thermally comfortable. The adaptive hypothesis states that one's satisfaction with an indoor climate is achieved by matching the actual thermal environmental conditions prevailing at that point in time and space with one's thermal expectations of what the indoor climate should be like (EN15251, CEN Standard, 2007). In field studies, surveyors collect the thermal responses from the subjects. Simultaneously environmental data is recorded based on class I, II, III protocols. This information needs to be statistically evaluated and validated for the significant relationships between neutral temperature and air temperature (EN15251, CEN Standard, 2007). Humphreys found that indoor air temperature is an outcome of outdoor temperature. In naturally ventilated buildings static comfort models predicts thermal sensations different than the occupants actually feel. Adaptive comfort model reveals that the thermal comfort temperature is a function relating to the outdoor air temperature

Table 3 Adaptive equations

Comfort equation	Source
$T_{comf} = 0.31T_{out} + 17.8$ (1)	ANSI/ASHRAE (2004)
$T_{comf} = 0.33T_{rm} + 18.8$ (2)	EN15251, CEN Standard (2007)
$T_n = 0.22T_{out} + 17.86$ (3)	Singh <i>et al.</i> (2011)
$T_n = 0.54 * (30 \text{ day } T_{rm}) + 12.86$ (4)	Manu <i>et al.</i> (2016)
$T_{rm} = (1 - \alpha)\{T_{od-1} + \alpha T_{od-2} + \alpha^2 T_{od-3} \dots\}$ (5)	Nicol and Humphreys (2010)

(Yao *et al.*, 2009). Fanger (1993) states that the best buildings for overall comfort either provide conditions that are within the accepted comfort range for most occupants most of the time (so people do not need to change things that much) and/or people have the facilities to alleviate discomfort quickly when it occurs. Chappells and Shove (2001) state that "Comfort is a highly negotiable socio-cultural construct". This provides a classic definition of adaptive thermal comfort criteria. With the changing outdoor temperature from season to season use of adaptive models in naturally ventilated buildings gains significance. Researchers across the globe have conducted such studies in a variety of climates to establish comfort limits. A review of literature reveals that adaptation is affected by their cultural and socio-economic lineaments.

Empirical equations for estimation of adaptive thermo-neutral temperature and comfort temperatures are presented by ASHRAE based on the extensive studies by de Dear and Brager (Eq. (1)). Similarly, EN15251 came up with an equation based on exponentially weighted averaged running mean temperature, which takes people past thermal history into account for the estimation of T_n (Eq. (2)). The concept of running mean temperature (Eq. (5)) is based on Nicol and Humphreys (2010). The authors state that the exponential weighting system results in a decay in the importance of any past temperature with a half-life in days. They emphasize that monthly mean temperature can be variable within a month, resulting in changes in the neutral temperature through short-term adaptation. Hence, the use of the running mean outdoor temperature provides a realistic representation to adaptive comfort model (Table 3).

An equation for operative comfort temperature indoors for buildings by Singh *et al.* (Eq. (3)) for cold climate of Northeast India based on field study for naturally ventilated buildings is used for determining the neutral temperature. The study was based on vernacular buildings of northeast India. Manu *et al.* carried out adaptive thermal comfort studies for multi climatic zones including cold climate of India and estimated the T_n based on equation (Eq. (4)). The T_n varied from 19.6°C to 28.5°C.

Factors Affecting Thermal Adaptation

Physiological adaptation

The core temperature of human body needs to be maintained within close limit of 37°C for the proper functioning of human body. The brain sends or receives the signal, which acts as a controlling mechanism in case of thermal discomfort. Vasoconstriction is initiated when the body temperature falls. Similarly, vasodilation happens when the body temperature gets high. Over a period of time, the effect of strain caused by heat and cold gradually decreases by exposure to these extreme temperatures by human body in order to be in thermal balance. This physiological adaptation is a result of long time and short time physiological adaptation. Long time physiological adaptation is a result of genetic adaptation, which is developed from generation to generation. Short time physiological adaptation is result of acclimatization, which happens within one generation. However, time required to acclimatize may differ from a single day to years.

Psychological adaptation

People's past and current thermal history has a great role on their thermal expectation. It is the unconscious thermoregulatory reaction. The thermal sensitivity diminishes if repeatedly exposed to a certain thermal environment, which induces relaxation in thermal expectation.

Behavioral adjustment

Behavioral adjustment is an outcome of people's cultural habits, social and economic status. It accounts for clothing's that they wear, food they eat, activities they do. This can be consciously or unconsciously done on a daily basis to keep their body in thermal balance. These adjustments are classified in three subcategories-Personal (putting on or taking off the clothing), technological (turning on/off radiators or tandoors) and cultural (traditional woolen attire, evening tea) Fig. 5.

Adaptive Limit in Cold Climate of India

Adaptive thermal comfort limits

Fig. 6(a-d) shows the thermal comfort limits for the representative locations estimated on exponentially weighted running mean temperature (Eq. (5)) (Nicol and Humphreys, 2010).

Category II represents the moderate thermal expectations of $T_n \pm 3^\circ\text{C}$ and UL (Upper limit) and LL (Lower limit) provides the comfort limits for this category (EN15251, CEN Standard, 2007). Considering the ambient temperatures prevalent at these



Fig. 5 (a) A typical living room in contemporary building in Manali (Cz5), (b) A living room cum kitchen in a traditional building in Keylong (CZ5), (c) A living room cum kitchen in contemporary building.

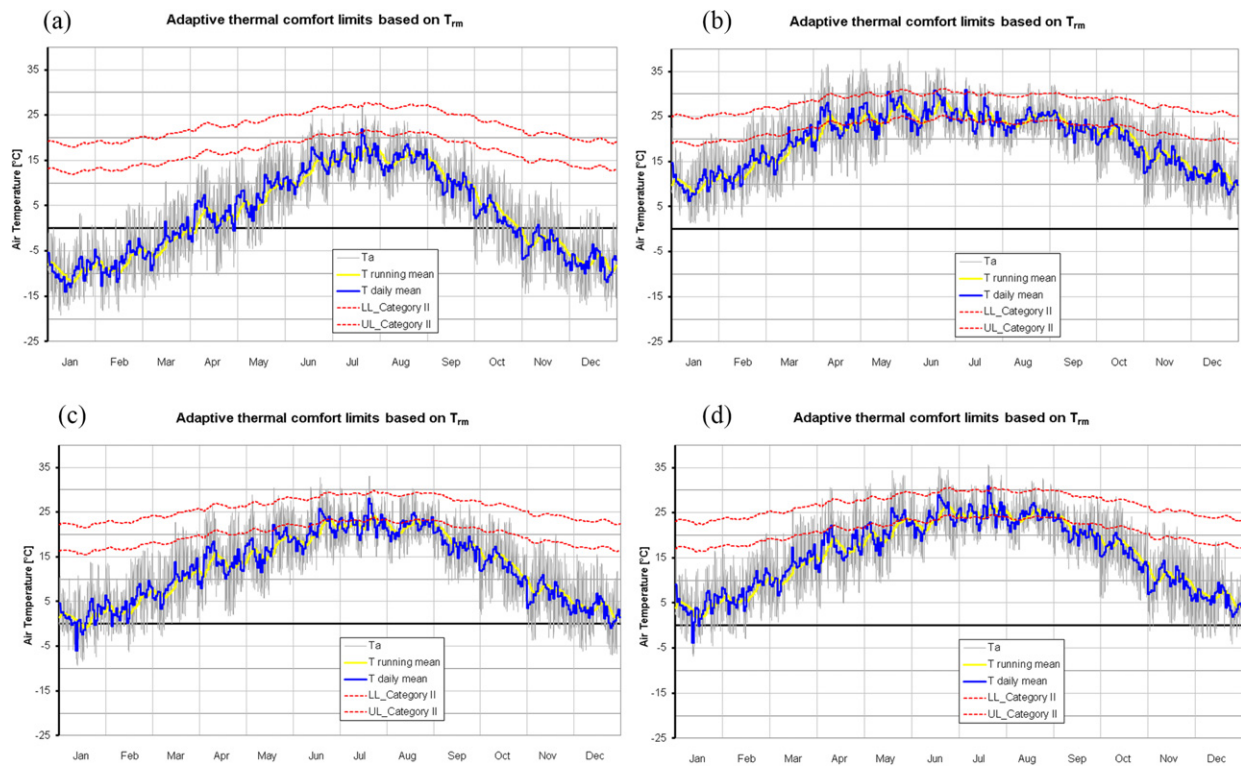


Fig. 6 Adaptive thermal comfort limits for (a) Keylong (b) Kullu (c) Manali (d) Naggar.

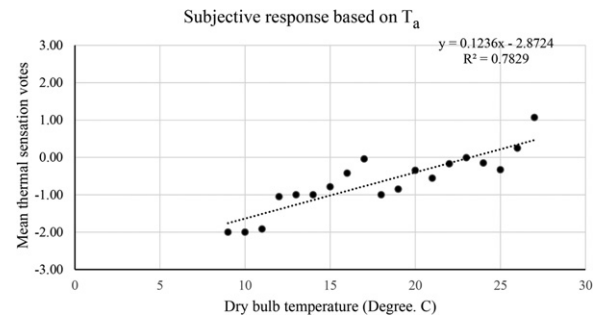


Fig. 7 Correlation between mean TSV and the corresponding T_{in} .

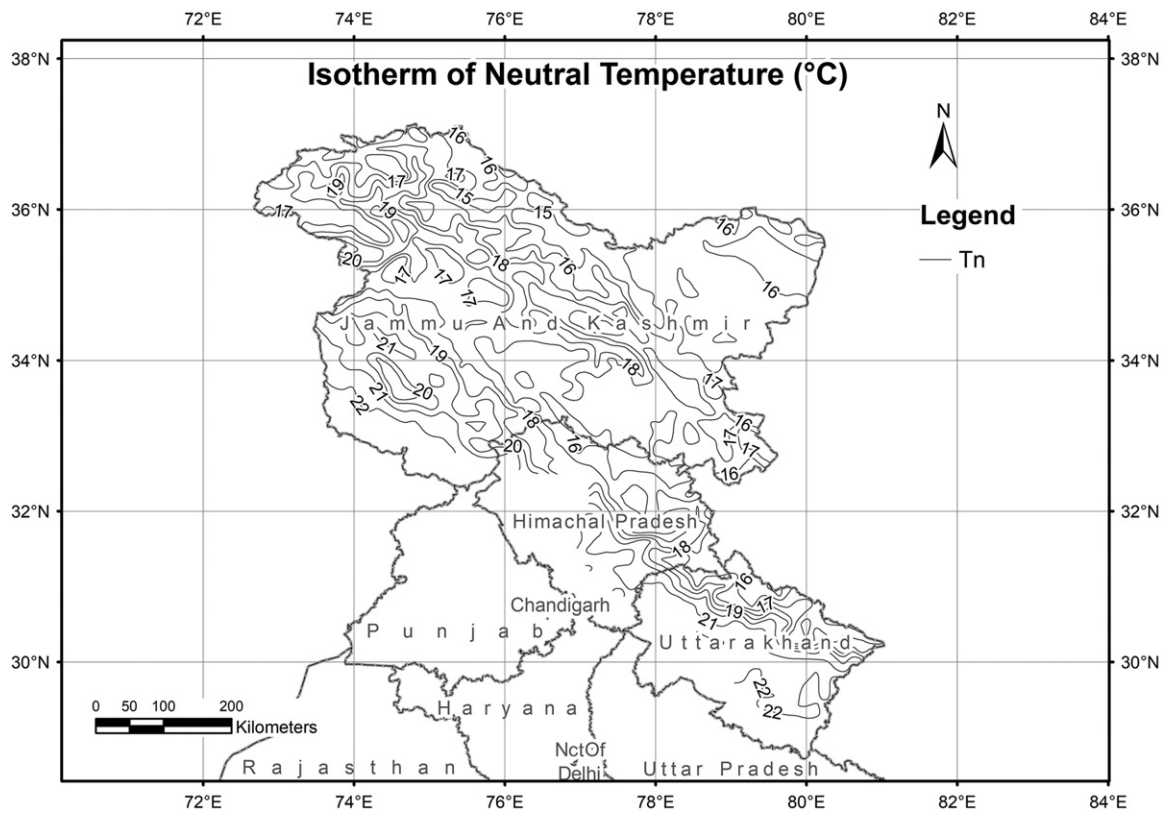


Fig. 8 Isoline map of the T_n , estimated for cold climate of North India.



Fig. 9 (a) Traditional and (b) Contemporary settlements in cold climate (CZ5).

locations, the indoor temperature needs to be within these bands as per the adaptive comfort model. The category I and category III that represents high and low thermal expectation. In order to make dwellings thermally comfortable, thermal performance of buildings needs to be regulated to keep indoor temperature inside these comfort bands.

Field Surveys to Evaluate Thermal Adaptation

To check the extent of thermal adaptation in the Indian cold climate, a field study has been conducted in Kullu (CZ11), Naggar (CZ9), Manali and Keylong (CZ5). The studies were undertaken during post-summer (September to October 2017), winters (November 2017 to February 2018) and summer (June 2018). Two types of surveys – Longitudinal and transverse surveys are administered along with physical measurement of indoor and outdoor thermal variables. In longitudinal surveys, the selected respondents are surveyed over one-week duration on thrice-daily basis (during morning, noon and evening). Transverse surveys are right-now, right-here kind of surveys, which are administered to ensure a wider coverage of samples. The bilingual questionnaire was prepared in Hindi (native language) and English. Surveys have been administered while they were seated indoors. Simultaneously environmental data including indoor temperature T_a , relative humidity (RH), air velocity (V_a) and globe temperature (T_g) were measured. The readings were recorded at 1.1 m from floor level using Delta OHM thermal comfort meters (Fig. 5) (accuracy $\pm 0.35^\circ\text{C}$, $\pm 2.5\%$ RH, ± 0.05 m/s for 0–1 m/s V_a and ± 0.15 m/s for 1–5 m/s V_a). A total of 1561 samples were



Fig. 10 A typical traditional Kath-kuni dwelling in cold climate, Manali (CZ5).



Fig. 11 (a) Typical vernacular and (b) Modern dwelling in cold climate, (CZ5).

collected from residential buildings in Kullu, Naggar, Manali and Keylong. A stratified random sampling method was adopted to include all of the prevalent building (traditional and contemporary) typologies.

The thermal sensation votes are averaged for every 1°C of indoor temperature bins. Fig. 7 shows the correlation between mean thermal sensation votes (TSV) and the corresponding mean indoor air temperature (T_{in}) for the Indian cold climate. The neutral temperature is determined by obtaining regression equation at mean TSV equal to zero. T_n established through this study is 23°C which is similar to the already conducted studies in cold climate of northeast part of India (Singh *et al.*, 2011).

Fig. 8 shows the iso-lines of neutral temperature evaluated on the basis of estimated neutral temperature. The range of T_n is found between 13 and 24.5°C for whole of cold region. Except for extreme cold climate of upper Lahaul and Spiti and some parts of Kinnaur in Himachal Pradesh, most of the settlements has neutral temperature in the range of 17–22°C. For upper Himalayan settlements having extreme winters T_n is found to be on lower side than most of the settlements (CZ5, CZ9, CZ11) within range of 18–23.5°C. It needs to be noted that, ground studies in the extreme cold desert regions are essential to validate the above estimates.

Buildings in Cold Climate

Vernacular buildings in cold climate of India exhibit an evolved climate response. They offer time-tested examples in terms of construction materials, techniques and spatial design, which are further customized with people's adaptive life style. This section focuses on residential settlements in the state of Himachal Pradesh, India, which displays CZ1 to CZ11 sub classification of cold climate described earlier in this chapter. The terrain of upper Himachal Pradesh is mountainous in nature making its elevation variable throughout the state.

Fig. 9 shows (a) the traditional and (b) contemporary settlements. These buildings are located in compact clusters, which restricts the flow of cold winds. The building materials and techniques vary based on the local thermal severities. However, climate responsive strategies such as use of thermal mass, orientation to garner winter solar gain are identical across the region. The traditional construction technology like "Kath-Kuni" (Fig. 10) is prevalent in most of the rural dwellings in which alternate layers of wood and stone masonry in an interlocking manner.

Kath-Kuni structures are prevalent in CZ11, CZ9 and parts of CZ5 deodar wood and stone is being used in abundance. These dwelling have a sloping roof covered with thick stone slates supported by wooden beams. These building are generally of 2+1 floors.



Fig. 12 A contemporary dwelling in severe cold climate, Keylong (CZ5).

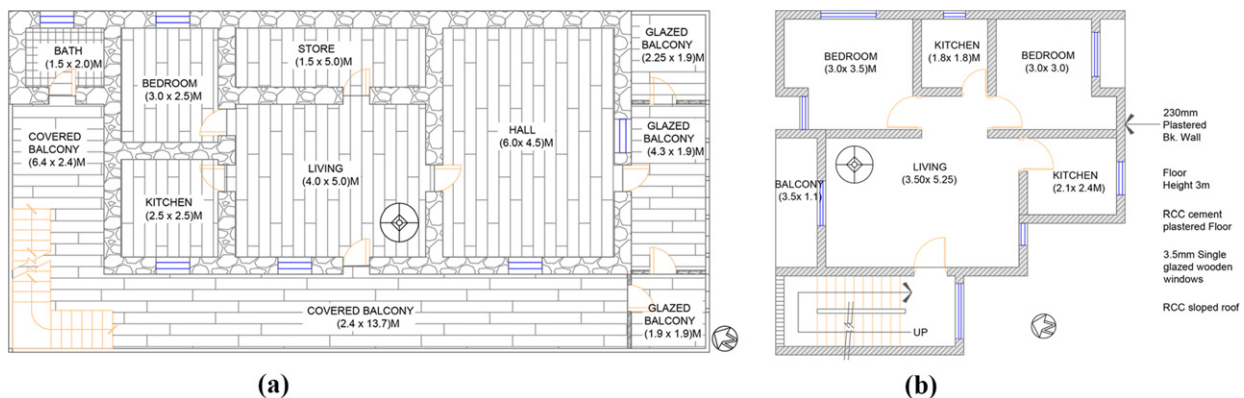


Fig. 13 Plan of (a) traditional house (b) contemporary house in Naggar (CZ9).

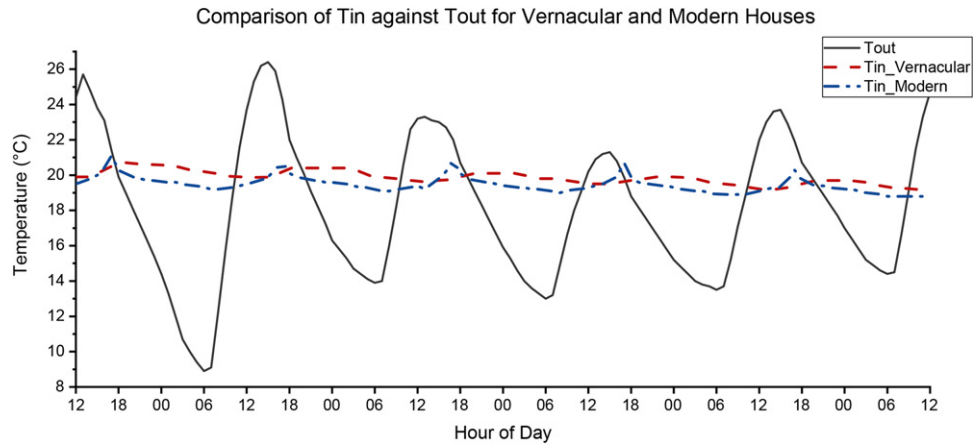


Fig. 14 Comparison of T_{in} and T_{out} for a vernacular and modern house in Naggar (CZ9).

Table 4 Climate responsive design applied in traditional dwellings in Indian cold climate

Region Illustration	Climatic zone	Strategies	Climate responsive design
L&S	CZ5	Trapping heat during the day and release during the night ● Reduce time to warm up area ● Reduce heat loss to exterior environment Passive solar gain	
	Cold winds	● Compact form ● Low floor to floor height ● Small opening in other than north wall ● South orientation ● Large opening in south wall ● Dark colored wall ● No sunshades	Large South Facing Windows
Kullu and Manali	CZ11, CZ9 and CZ5	Cold Winds ● Unilateral window to avoid cross-ventilation	Unilateral Opening (Limits Wind Flow) Bilateral Opening (Enhances Cross-ventilation)
		● Wooden screen to outside walls ● Low floor height ● Compact form ● Heat generation from livestock through the infiltration and internal gains to subsequent floors	

The floors are of wooden planks rested on wooden beams which are cantilevered to all sides to provide balcony space which is used as a storage as well as semi-outdoor space. The ground floor generally used as cattle shed and to keep fodder. This shed also helps to keep adjacent floors warm during winters. The buildings have very narrow openings to resist heat loss. The middle floors serve as living and bedroom. The attic space generally has kitchen and granary store and also provides thermal barriers to the other floors. The 600 mm

Kath Kuni wall with alternate layers of wood and stone provides high thermal mass. Some buildings also incorporated mud plastering to make them more efficient. Moreover, the floor height is less than 2.7 m so as to reduce the air volume inside.

In severe cold zone (CZ5) (Fig. 11) building are made of thick mud plastered stone masonry wall construction. Buildings in CZ5 (Lahaul and Spiti region) have high thermal mass and are made up of minimum of 600 mm stone masonry with mud mortar. These walls are mud plastered and need occasional maintenance. The houses do not use much of wood like kath-kuni houses as the region lacks in good quality of wood suitable for construction. These houses differ in roof constructions as majority of them has a flat roof. These roofs are made up of thick mud mortar and gravel mixture casted into a slab that rest on wooden beams. This roof provides high thermal mass, which also restricts heat loss when these are covered with more than 700 mm of snow during winter.

The contemporary buildings (Fig. 12) have adapted the RCC framed construction technique with stone masonry cement plastered wall insulated with wooden paneling from inside. The building with 230 mm Brick plastered wall generally has stone cladding from outside. The thickness of cladding varies from place to place. Generally, people go for 7–10 cm thick dressed stone as clad (including mortar). Some houses also incorporate wooden paneling over ceiling. In these houses' roofs are generally Reinforced concrete exposed or covered with galvanized iron sheets. The wooden openings are bigger in comparison to traditional buildings.

A real-time monitoring of indoor and outdoor thermal conditions performed during summer and winters in CZ9 (Naggar) is presented further. The measurements correspond to a vernacular house (H1, Fig. 13(a)) and a contemporary house (H2, Fig. 13(b)). H1 has a traditional Kath-Kuni system with 600 mm thick external walls with mud plastering. Floors and ceilings are constructed with 25–30 mm thick wooden planks, which allows some infiltration between adjacent floors. The roof consists of stone slates rested on wooden beams, which absorbs solar radiations and traps that into attic. The floor-to-floor height is 2.7 m. H2 is a reinforced concrete frame construction with 230 mm brick plastered external walls and internal wood cladding. The floor-to-floor height is 3.5 m.

Fig. 14 shows the measured T_{in} and T_{out} of H1 and H2 during 5–10 October in 2017. Diurnal range of T_{out} varies between 9°C and 16°C. The maximum temperature during the day rise up to 25°C while it drops till 9°C in early morning hours.

Despite this fluctuation in T_{out} , T_{in} remains stable within both of the houses; however, vernacular kath-kuni dwelling, H1 experiences less temperature swing than H2. H1 has a longer time lag (about 8 h) compared to H2 (3–4 h). In terms of overall thermal comfort measured in terms of Fanger's PMV, the vernacular house (H1) outperformed the modern house (H2). During winter, PMV varied between –0.3 and –0.9 while in summer it varied between +0.6 and +1 in the vernacular house. In the contemporary residence PMV varied between –0.6 and –1.5 during winter and +0.6 and +1.5 during summer. This depicts the suitability and performance of the vernacular buildings and the importance of bioclimatic strategies adopted in these buildings to suit in this particular climate. Table 4 summarizes the climate responsive design strategies used in this region.

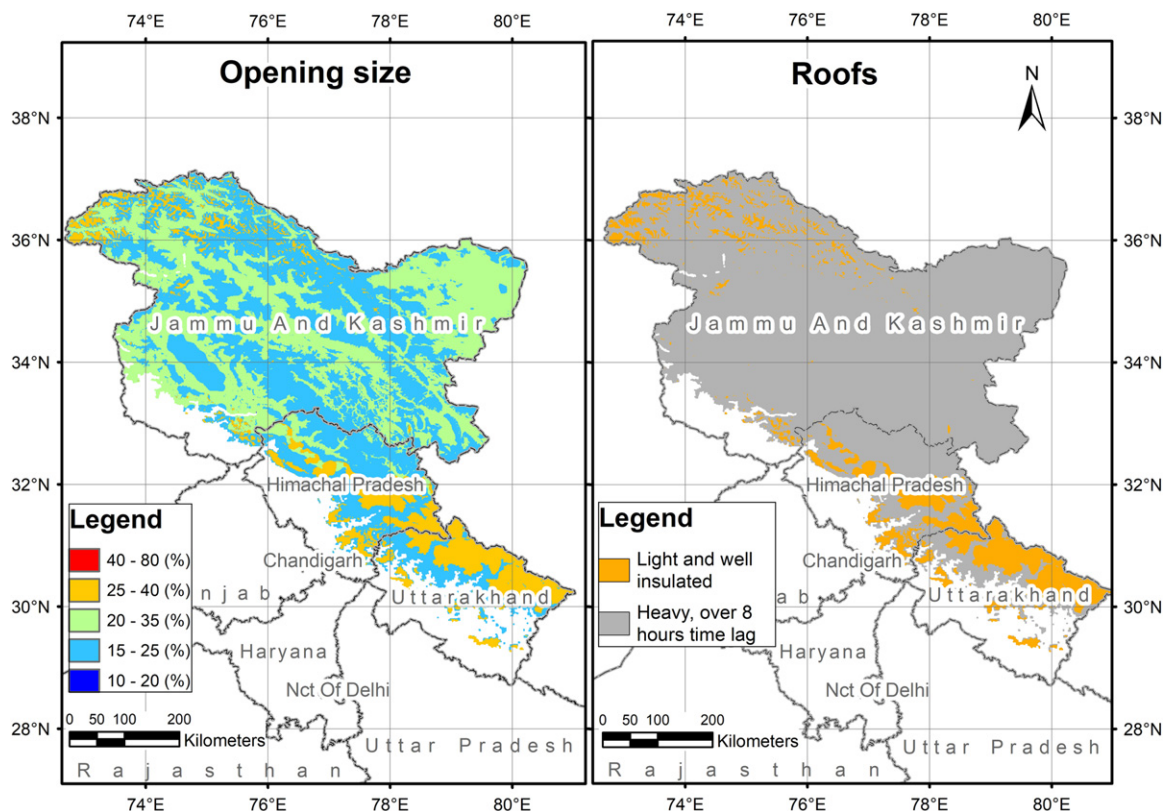


Fig. 15 Required strategies based on Mahoney's method (a) Opening size, and (b) Roof.

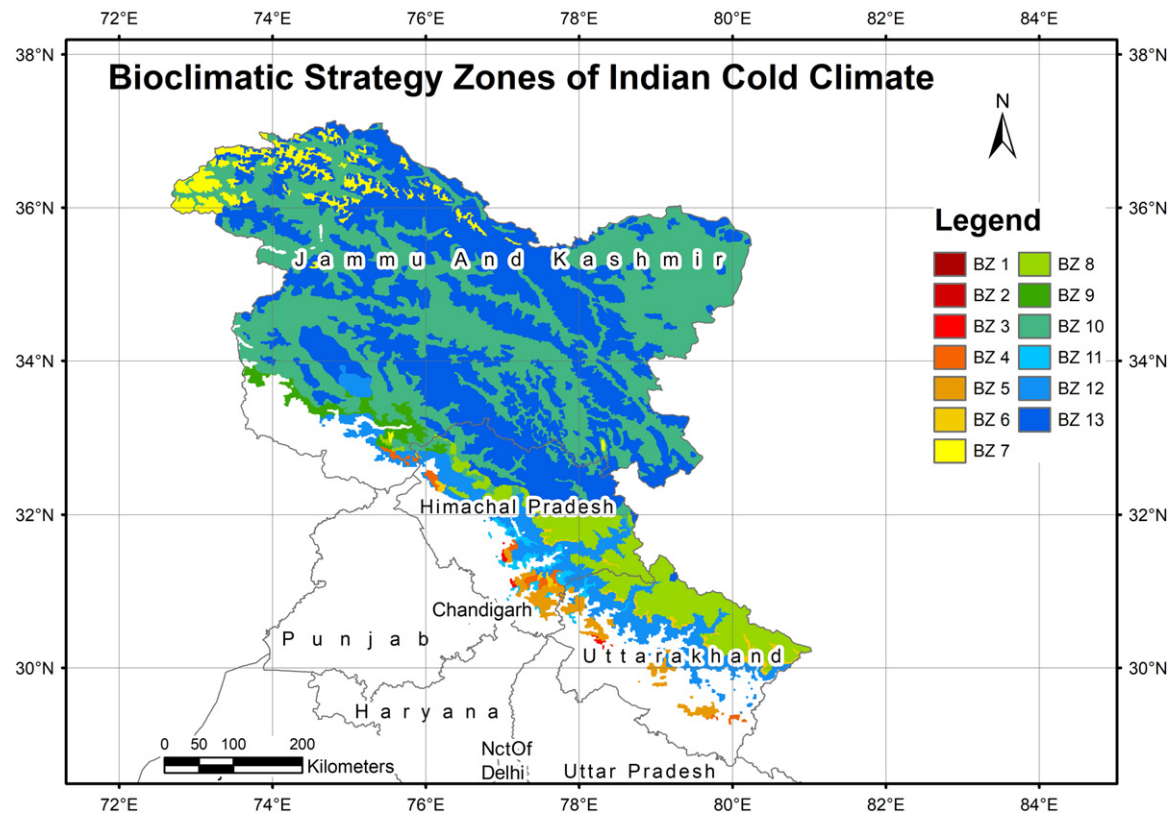


Fig. 16 Bioclimatic design strategy zones of the north indian cold region.

Table 5 Climate zone and bioclimatic strategies of selected locations in the Indian cold climate

City	Climate zone	Bio-climate Zone	Window size	Position of openings	Walls/Floors (Heavy, > 8 h time-lag)	Roofs (Heavy, > 8 h time-lag)
Keylong (L&S)	CZ 5	BZ 10	Composite (20%–35%)	Has no climate related values	Yes	Yes
Udaipur (L&S)	CZ 5	BZ 10	Composite (20%–35%)	Has no climate related values	Yes	Yes
Kaza (L&S)	CZ 5	BZ 10	Composite (20%–35%)	Has no climate related values	Yes	Yes
Manali (Kullu)	CZ 5	BZ 9	Composite (20%–35%)	In N and S walls at body height including Internal walls	Yes	Yes
New Manali (Kullu)	CZ 5	BZ 12	Small (15%–25%)	In N and S walls at body height including Internal walls	Yes	Yes
Jana (Kullu)	CZ 5	BZ 12	Small (15%–25%)	In N and S walls at body height including Internal walls	Yes	Yes
Naggar (Kullu)	CZ 9	BZ 12	Small (15%–25%)	In N and S walls at body height including Internal walls	Yes	Yes
Kullu	CZ 11	BZ 12	Small (15%–25%)	In N and S walls at body height including Internal walls	Yes	Yes

Bioclimatic Classification

Olgyay *et al.* (2015) emphasized that general forms of buildings are more influenced by the climate. Bioclimatic design refers to the careful selection and application of passive & energy efficient building strategies to provide a comfortable indoor environment under given climate conditions (Labaki and Kowaltowski, 1998). It aims to take advantage of the climate conditions and delineate recommended building strategies for a certain region (Wan *et al.*, 2010; Pawar *et al.*, 2015). Since the term bioclimatic design came to use in the domain of architecture, it adopted various methods of assessing the interaction between human comfort requirements, climate conditions and building design. Most notable are the bio-climatic charts by Olgyay (1963), the building bioclimatic charts (Givoni, 1976) and the Mahoney tables (Mahoney *et al.*, 1971). In this section we present a Mahoney method based bioclimatic classification of the study region.

This comprises of three steps. Step one involved computation of annual mean temperature (T_{Au}) from mean of the annual maximum and annual minimum temperatures. The outside monthly maximum and minimum temperature, mean monthly relative humidity, and monthly precipitation data (30'' spatial resolution) are referred from worldclim (Fick and Hijmans, 2017; New *et al.*, 2002). Step two involved

- (1) Calculating monthly temperature range ($T_{\text{max}} - T_{\text{min}}$),
- (2) Creating T_{Au} groups ($< 15^{\circ}\text{C}$, $15\text{--}20^{\circ}\text{C}$, and $> 20^{\circ}\text{C}$),
- (3) Categorizing the relative humidity into four groups (below 30% = G1, 30%–50% = G2, 50%–70% = G3, and above 70% = G4,
- (4) Determining upper and lower temperature limits for daytime and nighttime comfort by comparing humidity groups with T_{Au} groups,
- (5) Diagnosing thermal stress through comparing temperature values with the upper and lower comfort limits (C=cold, O=comfortable, H=hot) and
- (6) Identifying three humidity (H1, H2, H3) and three aridity (A1, A2, A3) indicators.

Step three involved identification of design recommendations from the annual summaries of humidity and aridity indicators. For example, the layout (orientation) of a building can be north to south either if A1 occurs for less than 11 months or if A1 happens for 11 or more months followed by A3 more than four months.

Fig. 15(a) presents the required window-to-wall ratio. As shown, neither large nor very small windows are necessary. Fig. 15(b) shows the required thermal mass of roofs. It is clear that light roofs are not suitable across all cold climate regions.

Individual bioclimatic strategies tend to show uniformity across vast areas with the exception of opening size (strategy-d), position of openings (strategy-e), walls and floors (strategy-g), and roofs (strategy-h) which are responsible for the huge variabilities in the final output (Fig. 16). Table 5 presents the detail climatic and bioclimatic characteristics of selected locations. It also highlights detail strategies of size and position of openings, and envelope thermal properties. Due to the geographical proximity of the selected locations, most of them appear in the same zone.

Summary and Conclusions

The chapter discussed the thermal severities and climatic diversities in cold climate of north Himalayan region. A rational approach was presented through which the cold climate zone was sub-classified into eleven sub-zones (Fig. 3). Climate data of representative locations were statistically analyzed to verify the significance of diversities (Fig. 4(c)). Such sub-climate zones can be regionalized to district administrative boundaries in order to facilitate effective implementation of building thermal regulation and energy efficiency codes. Physiological, psychological and behavioral thermal adaptation in cold climates was presented with relevant field examples. Adaptive comfort limits based on T_{rm} was discussed for representative locations. Results of adaptive comfort field study carried out in this region was presented. T_n established through this study is 23°C which agrees well with similar such studies conducted in cold climates. T_n isopleths were presented (Fig. 8) for the cold climate region based on this study. Vernacular housing practices including construction systems were presented and their thermal performance were compared with contemporary houses through real-time measurements. Geo-spatial data of this region was used to create a bioclimatic classification based on Mahoney's method. Based on this analysis, the study area was classified into thirteen bioclimatic zones. A comparison of some of the vernacular housing practices with that of the bioclimatic strategies was presented. The bioclimatic architecture adapted in vernacular housing provides a learning to adopt these strategies in contemporary buildings to make them suitable for the habitants in this climate.

See also: Improving Energy Efficiency in Buildings Through Responsible Design: Optimizing Use and Careful Selection of Building Materials

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Traditional Crafts as Materials in Placemaking: Application and Sustainability in Aesthetic Transformation of Geometry of Urban Public Spaces

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Traditional Crafts and Materials

Crafts are as inherent to any traditional society like food, shelter and clothing. It gives it the cultural identity which is uniquely identifiable by its aesthetics and materials. Crafts and craftsmanship remains one of the oldest occupations which a community used for fulfilling purpose and also to create appealing spatial compositions. Settlements that go well into various historic periods are treasure trove of these crafts. The significance of crafts as materials will be discussed in the context of India, being one of the oldest settlements with a heritage of amalgamation of cultures across periods and retaining its ethnic identity manifested through harmonious coexistence of religious and social practices (Balaram, 2011).

History of the Crafts – Tradition and Relevance in Social Context

The socio cultural heritage of all civilizations manifest through their crafts. Rooted in social practices and traditions, it becomes part of the aesthetic expression of a community. As knowledge is handed over from generation to generation, crafts become a part of its intangible heritage. Going back into the evolution of the human race, all activities, be it hunting or farming, building shelter or making clothes, crafted objects have fulfilled the basic needs-every product an expression of creation. The artisanship worked on indigenous materials, form and function going hand in hand on the need to design-within the parameters of the locale and the society. Social practices in terms of religion, culture, ethnicity helped retain the identity of a craft, allowing it to survive through ages (Ranjan and Ranjan, 2014).

Across cultures, the crafts have enriched communities with their aesthetics although the purpose may have been similar. These aesthetics give the identity of the community and being distinctly differentiable from one to the other. Considering a strongly material based craft such as Woodcraft. We see it manifested in the various cultures whether in the form of the Noah's Ark or the Temple of King Solomon. Egyptian Pyramids hold them in various forms of furniture with a protective finish as well. Wood was even imported to compensate local resource. The Romans used it more as a construction material or furniture with carvings. In the Middle ages it turns to entire buildings and large sculptures. In Central Asia, we find building elements and intricate crafting which later was adopted for stonework. The skill varies in the Orient where, while in China we get exquisite precision based small day to day objects, in Japan it is best expressed in intricate scenery and curved or bent wood work and special joinery is seen. With the development in hand tools, techniques and the property of timber available, we see the variety in wood craft across the world. But the objective across the cultures remained to create elements to improve the space with objects which were durable, usable and good to look at. These objects defined the space and gave it its character through the craft. So the design identity remained the same within a region though materials differed- as seen in the motifs from China engraved in wood and stone (Figs. 1 and 2).

Practices and Applications – Materials and Process

The ethnocentric characteristic of many old societies and communities have relied on traditional wisdom which shaped over generations of using the five elements in materials. Thus, whether we use a material in raw form for daily use or process it for products developed for keeping for generations, depended on the knowledge of daily practices and the trial and error methods of ages.

Each community gave shape to its crafts in the way that suited their lifestyle. While the objects of daily need remains similar in form and use, like a pot, the materials, tools and physical environment largely determined the form. The crafts bore the signature of the culture and varied across the section of this vast land. However, strangely remaining united in the purpose but differing in motifs and designs. Thus, although they both use natural elements for jewellery making, the Maoris of New Zealand carve it into organic forms while the Native Americans would use it to embellish metal jewellery (Sentance and Sentance, 2009) (Figs. 3 and 4).

According to the definition adopted by the CCI Symposium/CCI Symposium "Crafts and the International Market: Trade and Customs Codification", Manila, 1997 "handicrafts are the ones produced by artisans, either completely handmade or with the help of manual or mechanical tools, as long as the direct manual contribution of the artisan remains the most substantial component of the finished product. Handicrafts are made without restriction in terms of quantity and using raw materials from sustainable resources. The special nature of artisanal products derives from their distinctive features, which can be utilitarian, aesthetic, artistic, creative, culturally significant, decorative, functional, traditional, religiously and socially symbolic and significant." This is an expression of the materials and the creative process of arriving at the optimum solution by indigenous routes. For all traditional crafts, local materials and techniques are the only mode of expressions, crafted by hand. The artisan communities work like guilds. A bamboo is cut raw for daily use container produced instantly, but naturally processed to make boxes or pouches for storing valuables able to withstand natural decay of centuries. Materials that are available in a region remain the primary material for prototype and tools and techniques appropriate to shaping the same has varied degrees of craftsmanship. It is the ingenuity of the creator, the artisan, which elevates the form from ordinary to a revered one-each product



Fig. 1 Wood craft – Wild Goose Pagoda, China. Courtesy Prof. Rupkatha Mukherjee, BKG College, Kolkata.



Fig. 2 Stonecraft – Forbidden city, China. Courtesy Prof. Rupkatha Mukherjee, BKG College, Kolkata.

speaking its purpose. The traditional and time tested processes reveal in the survival of the product form over all these years. The terracotta pot survives side by side with stone pottery as a successful design appropriate to the locale.

Decadence – Sustainability

Traditional crafts are less adaptive to industrialization and contemporary aesthetics. Urbanization and advance of modernity leads to marginalization of something as ethnic that may be confused with rural. New materials and newer processes lead to greater production and saves time too. New generation of traditional clusters digressing to newer pastures for better life leads to slow death of the traditional wisdom which needs nurturing and practice for continuity. Contemporary lifestyle and spaces opt for modern products and tradition is thrown to winds. In the process enlarging the carbon footprint left behind. People tend to choose these appropriate to the purpose of the times which have evolved largely away from the tradition. The clay pot or metal jug being replaced by the bottle, an industrial product. Apart from Industrialization, Globalization acts as a leveller in erasing ethnic characteristics and creating a global society uniform across the earth (Jaitly, 2012).

Renewal/Diversification – Crafts as Resource

Crafts remain a regional activity and grow with the regionality. It imbibes the essence of the climate, geology, flora and fauna of the locale, as also the colours, patterns, language, practices, activities that are part of the ethnicity of the community practicing the craft. The older the heritage of a region, more diverse is its crafts. These crafts become essential to the way of life. The reason why Oriental societies exhibit the vibrancy of crafts in daily life and space. Regions not having indigenous races are bound to lack this identity as settlements from



Fig. 3 Maori fish hook pendant – New Zealand. From Wikipedia & Creative Commons.org.



Fig. 4 Navajo stone & metal Jewellery – USA. From Wikipedia & Creative Commons.org.

outside the region would take longer time to build its heritage. Crafts need to grow over time, which is only possible in civilizations which have a larger span of survival in history. It may have several cultures merging, but in order to be an integral part of the lifestyle, manifesting in all possible ways, it needs the consistency and stable progress to become the identity. This is perceptible as seen in the visual character of traditional houses in Kyoto varying distinctively from those in Venice, lining up on water channels (Figs. 5 and 6).

In spite of rampant Industrialised growth of societies, moving from villages to cities, there is a natural tendency in human minds to retain their ethnic identity. And this is largely possible by retention of crafts in human spaces and life. In a contemporary world, crafts are needed, but in order to survive the times, crafts need to be expressed differently. Craft materials need to venture in new avenues and create appropriate solution. The renewable characteristics of the materials helps in building a resource with longer life which is environment friendly. The same logic plays in using the traditional products in new uses seeking new areas where technology can help in its inclusion in innovative way (Ranjan and Ranjan, 2014).

As crafts are expression of frozen time, it is the same way that it needs to be viewed as an exploration and solution for present needs. After all, we cannot see a modern glass clad skyscraper in China with Pagoda style roofs, except as an Architectural disaster. There lies the need to attain a balanced state of the old and the modern standing side by side, not necessarily mixed. Regional identity is visible in the rock cut Architecture of two world locations cited below (Figs. 7 and 8).

Significance of Traditionally Craft Rich Regions – Example, India

India is diverse in its socio cultural systems as well as bio-diversity, climate etc. Resulting in varied use of materials in the crafts symbolic to the region it belongs to. Thus the boldness of the artefacts of Jammu and Kashmir reflects the hardship of crossing the mountains, while the mica in the sands of Gujrat initiates exquisite mirror work of the region (Jaitly, 2012) (Figs. 9 and 10).

And the use of material varies from place to place as seen in distinctly different forms like the geometric iron tribal figurine of the Bastar region standing apart from the ornate bronze Chola temple figurines (Ranjan and Ranjan, 2014) (Figs. 11 and 12).



Fig. 5 Houses – Kyoto. Available at: <https://in.pinterest.com>.



Fig. 6 Houses – Venice. Available at: <https://jamesbondlocations.blogspot.com/2017/03>.



Fig. 7 Facade of residences at Petra. Courtesy Mr. Diptarag Bhattacharya, COO, Amway, Gurugram.

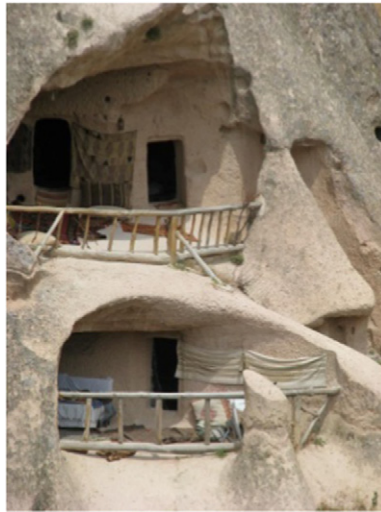


Fig. 8 Cave houses Cappadocia. Courtesy Prof. Rupkatha Mukherjee, BKG College, Kolkata.

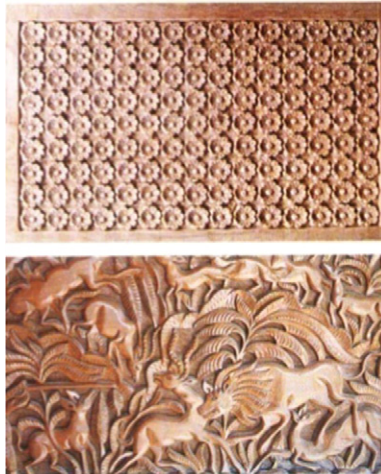


Fig. 9 Walnut craft, Kashmir. Sourced from Ranjan, M.P., Ranjan, A., 2014. Handmade in India. Mapin Publishing, p. 34, pdf – Scribd.



Fig. 10 Mirror work, Gujrat. Available at: <http://gaatha.com>.

In a country of myriad hues and forms, India remains a treasure trove of crafts generated out of languages and dialects, religions, ethnic groups, tribes, castes and sub-castes, festivals and over 1 billion people, half of them living in the villages, spread from the ocean to the Himalayas, with mountains, valleys, plateaus, deserts, backwaters, forests and even inhospitable regions. With millions of craftsmen and innumerable craft clusters, traditional crafts remain till date the biggest experience with indigenous materials and their sustainability. The versatility of use of these materials for appropriate applications speak largely of the ingenuity of its creators (Ranjan and Ranjan, 2014).

Although most of the crafts may be termed as people's art, more stylized forms have generated out of religious practices. The Hindu caste system have indirectly retained the identity of each craft by segregating the artisans in professional groups. Although socially marginalizing, it restrained craft practices and skills within selective social groups, and transmission of the knowledge from generation to generation. Instead of losing out to evolving times, this helped retain the identity of the craft, its materials, tools and techniques, with gradual changes infiltrating with Industrialization and globalization only. This has broad based the crafts from major practices like pottery, weaving, metal craft, stone craft, bamboo craft etc. which are largely material based, to more skill oriented ones like mural, painting, glass work etc. India lives in its villages. So a craft practiced today may be sidetracked later but will continue to sustain in a locality to support local need. It is this fluidity and reach of a craft combined with the expanse of the practice of crafts in India, which makes it nearly impossible to encompass its possibilities and reach (Jaitly, 2012).



Fig. 11 Tribal figure, Bastar. Available at: <https://www.outlookindia.com/outlooktraveller>.



Fig. 12 Bronze figures, Chola temples. From Wikipedia & Creative Commons.org.

Being a civilization dating more than 5000 years, with multiple invasions leading to amalgamation of cultures, the crafts of India have sustained its essence and process, evolving over the inclusive nature of society adopting other cultures and keeping up to the pace of change. The crafted goods remain testimony to the cultures and practices imprinted in the materials reflecting the roots of the social system that produced or used the object. Crafted forms developed for daily use has remained as basic material manipulation with functionality. While the ceremonial ones reflected the intricate aesthetics again as possible with the available resource of materials and tools used to its finest expression (Ranjan and Ranjan, 2014). Moving between regions of the country one gets to see the similarity of practice while differences in manifestation- as seen in the Alpana in the East to Rangoli of North or Kolam in the South, all three being ritualistic creative patterns on the floor, done by hand, with materials differing (Figs. 13–15).

In this age we have crafts dying for various factors. Stone carving remains restricted to temples only as transportation is a deterrent. Hence the craftsmen shift to other occupations. Without patronage and also due to conservation and preservation, many of the expensive materials like Ivory, Sandal wood crafts have become near extinct (Ranjan and Ranjan, 2014).

Tradition and modernity need to co-exist side by side in the modern times. Indian crafts are designed with ecological sense, based on renewable or eco friendly materials, resulting in aesthetics befitting natural surroundings. In keeping pace with modernity, these need to transform into contemporary design and use. While tradition retains its values, newer expressions are required for market acceptance. Being a rich culture of festivals, traditional crafts still occupy the bazaars in and around religious activities as the aesthetics go hand in hand with the cultural actions. It is this aspect that needs to be worked upon to make the craft viable, marketed through contemporary platforms of fairs, trade shows illustrating their diverse possibilities.



Fig. 13 Alpana – West Bengal. Available at: <https://in.pinterest.com>.



Fig. 14 Rangoli – Delhi. Available at: <https://in.pinterest.com>.



Fig. 15 Kolam – Tamil Nadu. Available at: <https://in.pinterest.com>.

Being a land of paradoxes, social patterns remain deep rooted and cannot be standardized. Physical diversity differs from mental perceptions, leading to completely different sensibility in terms of colour, aesthetics etc., may it be the sober palette of the southern lush green states to the vibrant hues of the western arid regions, India defies all norms of standardization. Growth and evolution in society has led to change in the caste system to the class system, bringing in the need for appropriate design solutions to the new necessities. In a country with agriculture as a primary economic activity, crafts play a major role in exports. As a renewable resource material, crafts can play a vital role in diverse uses. Rural spaces have always had an aesthetic legacy using indigenous techniques and judicious use of local materials. In urban spaces, use of crafts gives direction to Architectural design and planning of spaces. Crafts can be used in urban spaces with ingenuity as shown below using mud-mirror craft of Kutchh, also known as 'Lipan Kaam' (Balaram, 2011) (Figs. 16 and 17).

Experimental uses of clay plates in ceilings or natural textile based wall panels have yielded in improving micro environment within the closed spaces. Diversifying into the public spaces and its aesthetics to reduce the mundane character, adding vibrancy that only crafts can bring, is commonly seen in shaping the cultural ethos of Indian society through its festive celebration.

Methodology of Study

The methodology adopted for the research activity conducted may be illustrated as below

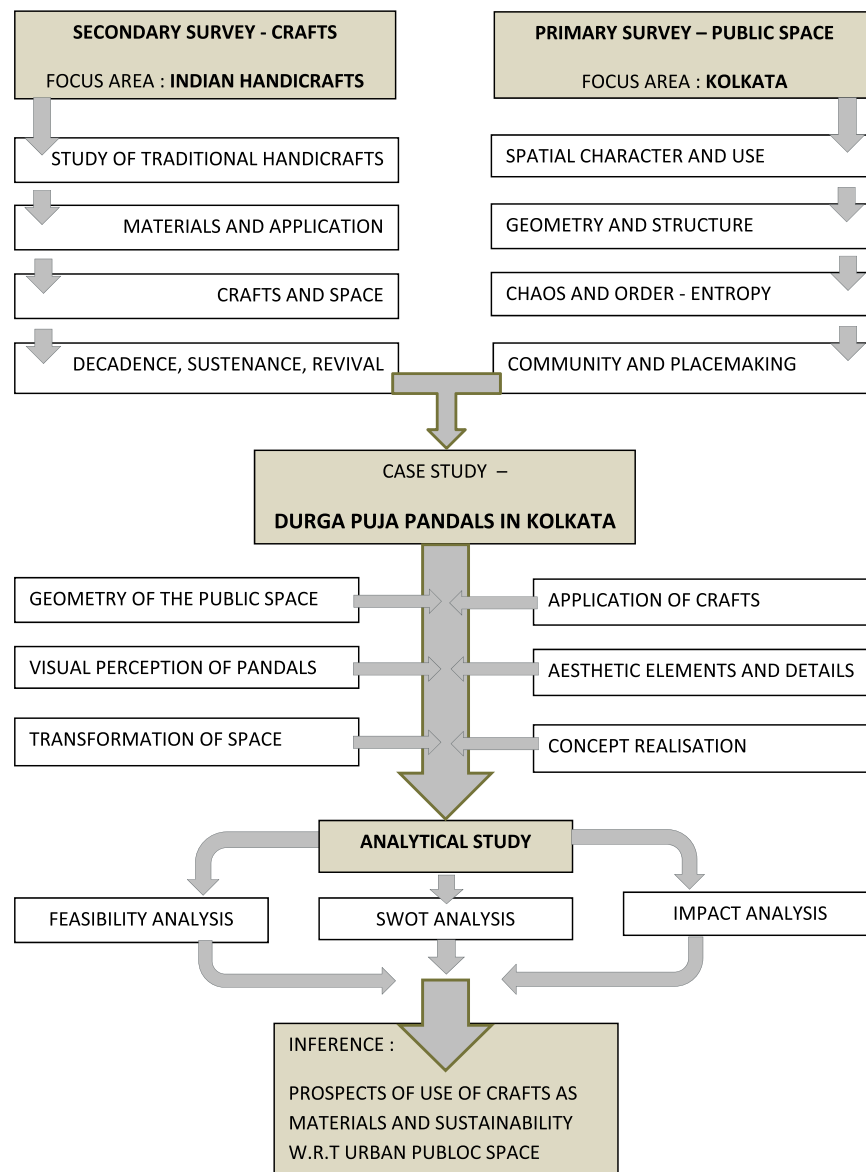




Fig. 16 Traditional house interior. Available at: <http://gaatha.com>.



Fig. 17 Office exterior. Available at: <https://engrave.in/blog>.

Application and Relevance of Traditional Crafts and Materials in Spaces

Traditional crafts have always been a part of creating spaces, as the elements that make a space, were crafted only. The locale and its resources always defined the space in terms of its form and the materials and techniques generated the look. In the Indian context, the diversity is stunning and all encompassing, leading to unique experiences as one moves from one region to another (Ranjan and Ranjan, 2014).

Selection of Craft – Relevance w.r.t. Aesthetics

Indian crafts suit Indian conditions of climate, handling etc. It is optimum in terms of use of resource and meeting the purpose. Traditionally art and craft work as a unified whole. Through these crafts, rural spaces transformed into reflection of the culture. Thus every craft had its own identity expressed through its looks and the character given to the space it belonged to. It also is an expression of the craftsmanship. The refined and cultivated products such as wood carving are classic while the basic forms like papier mache toys remain equally delightful. Their individual visual character makes it appropriate to its application and characterising space in turn.

Each regional culture has its objects, colours, outlines defining its spatial character. It ranges from deep interiors to open outdoors. The space created reflecting the geographical and climatic needs of the community as well as the cultural identity built over ages. Mythology plays a significant role as religion remains embedded deep in the hearts of the people. Hence aesthetics of the craft emerges in objects which reflect this association in form and spirit. The walnut wood carvings or products, the motifs of leaves and flowers derived from the nature around, or the motifs derived from the silk trade woven into the carpets makes it an identity as Kashmir beyond question. Naturally a wooden house as theirs or the house boat is expectedly adorned with these crafts. While just some distance away in a similar regional location, Ladakh remains distinctly different in terms of the colour and motifs of its pile carpets, metal embossed objects to stitched boots. The crafts complementing the spaces created out of stone. The essence of religion creating the so perceptible diversity. Thus when selecting an object of either region brings with it its unique identity stamped into the crafted product and demands or enriches spaces to imbibe similar aesthetics (Ranjan and Ranjan, 2014) (Figs. 18 and 19).

Diversification of Design and Use – Sustainability

Traditional crafts have remained in the locality of origin naturally for the sake of availability of as the resource material. But it has also moved out to other corners of the country or across the world seeking newer markets for generating employment by practice of the craft.



Fig. 18 Knotted carpet – Kashmir. Sourced from Ranjan, M.P., Ranjan, A., 2014. Handmade in India. Mapin Publishing. pp. 31, 41, pdf – Scribd.



Fig. 19 Pile carpet – Ladakh Sourced from Ranjan, M.P., Ranjan, A., 2014. Handmade in India. Mapin Publishing. pp. 31, 41, pdf – Scribd.

The global shift towards indigenous and organic products and the green movement has forced attention back to crafts as alternative to industrialised products. May it be spatial structure or system, or decorative value addition, or cosmetic changes, physical spaces have undergone changes with reintroduction of crafts. The vibrancy and natural feel of the material is easy to associate with. It is the physical form which needs to be contemporised to adapt to the changed social system. Thus the jute gunny bags and handicrafts modify to wall panels or murals transforming the interior into a simplistic modern space with a rustic feel good in insulation.

With a populace as diverse as possible in its mentality, the demands, both physical and aesthetic, are a myriad of choices, colourful or colourless, vibrant or sober, hard or soft, detailed or flat, and so on. It is only crafts which are readily available, as a multifarious form suiting personal demands, to transform the spaces as envisaged by design intervention, diversification or simple alternate use. Crafts are generally used in interior spaces as accessory or cosmetic change, selected from product displays from craft bazaars at random to match the decor or as a wish. Such collection is bound to have short life of use, likely to be thrown away after a time. Such products are also made with lack of sincerity by the crafts person as it fails to be considered a heritage. But if the entire space is conceived to recreate an ethnic identity, the craft item becomes an integral component. It becomes structural to the aesthetics, not a value addition to a somewhat related interior or space. Craft materials can sustain in the future when we start looking at it as a component of built space- as it was at the inception and for centuries down. This needs a complete reorientation of the design, contemporising the look and purpose, using newer techniques for quality and longer life span, yet not compromising on the essence of the craft itself. The Art of Craft needs to move out of one's own room to the public domain for greater acceptance and reach.

Environmental Implications – Recycling Materials

Industrialization and non bio degradable objects are the biggest threat to the human race. Though we have replaced the glass in the chandelier with acrylic, we did not learn what to do with the waste when we throw it away. Crafts are built on materials born out of the region or nature. Hence, it is from the soil, is tolerant to the climate and goes back to the elements after living its life. The craftsman understands the material with fondness and has the necessary rapport as he or she grows up moulding it in their hands

and feels. The attachment is so strong that the material also unfolds itself in the hands. The creation is built to die a natural death after its purpose is complete. Thus the environmental impact of crafts have always followed the green code. As the production has been need based, there has been little surplus to consider a wastage. This is so contrary to the mass production of industrialised items (Jaitly, 2012).

India is a country of up cycling and down cycling. It is common to households to pass down objects and utilise it to the full, until it dies its death. Indian philosophy of saving resources and austerity has always been integral to lifestyle. The example of a Saree converted to Kantha for longer sustenance of the material is just one example. Crafts have always been the avenue for recycling materials and components into daily use objects. For ceremonial purpose, purity of the product remains primary though. But post celebration, the same artefacts can be reused as inherent to the objectivity of the craft (Figs. 20–22).

Urban Public Spaces

Public spaces are different from culture to culture, in terms of its use. Irrespective of their background, they are used as social spaces which is naturally accepted by the community around. In urban areas, it is more of defining the purpose and segregating the spaces



Fig. 20 Traditional Bengali saree. Courtesy Ms. Jayati Mukherjee, Assoc. Prof., NIFT.



Fig. 21 Recycled saree to Kantha throw. From Wikipedia & Creative Commons.org.



Fig. 22 Designer Nakshi Kantha saree. Courtesy Ms. Jayati Mukherjee, Assoc. Prof., NIFT.

as per activity. It is expected to generate social interaction, for festivities and celebrations where cultures intermix. It is these interaction and engagement of citizens in public domain that makes the space come alive. Public spaces are inclusive. But in countries like India with deep cultural heritage, we see the traditional city remaining side by side with the formal city. So, in absolute harmony, the planned geometric public spaces of the new city with specific uses co-exist with the organic free flowing ones of the old city with multiple uses. Walking the streets in Delhi, one can savour the lineage of the Mughal era in Old Delhi with its organic planning and meandering lanes, while in stark contrast New Delhi carries the stamp of the colonial Era in Lutyens' grid layout with vistas and strict geometric planning (Gupta and Gupta, 2016).

Spatial Structure – Activities and Uses

Public spaces are defined by UN-Habitat as “all places, including streets, publicly owned or of public use, accessible an enjoyable by all for free and without a profit motive”.

Urban public spaces in developing countries are free flowing organic conglomeration of shapes. It has its memories and nostalgia of its own. It is a direct opposite to the urban planning of the West and defies rigidity of boundaries. Urban public spaces are dehumanised in terms of use as compared to rural multifunctional public spaces.

As Architect Charles Correa said – ‘a City without shared public spaces is a City without culture, without history.’

In an urban context, space is a resource-used for functional, ritualistic, social, political and cultural interchanges. Public spaces, which developed naturally, are pockets of activities arising out of the need of the surrounding built environment. The unplanned growth results in interesting volumes and shapes which can be assigned separate functions which are more personal and can induce closer interaction. Public spaces transform itself to suit different activities at different time of the day. A busy business area by the day transforms itself into a sleeping quarter for the urban poor at night. This is in contrast to the urban spaces of planned cities which have pre-determined uses and shape, lacking the versatility in terms of its use. Irrespective of its origin, the space remains a place where complete strangers can participate in camaraderie, forgetting their social or community positions (Correa, 1985).

Chaos and Order – Identifying Aesthetic Entropy

Urban public places have always been a place to meet and exchange, may it be Greece, Italy, Africa or India. In order to celebrate the interaction, all public places have always been a composition of aesthetically appealing built elements. So from the proportion of the Agora, to the beautifully crafted column capitals, to the flea markets or to the neighbourhood square, aesthetics and its associative factors have always been the limits which create order and disorder combined to a vibrant composition. This array in disarray tend to leave a longer mark in the heart of the viewer. In the context of urban areas, one needs to appreciate the order in this chaos which allows the space to break the monotony. Under this chaos, communities live and organize themselves. It marks its physicality within its own set of social conventions (Correa, 1985).

The variety of activities result in a multiple stack of objects and elements in a public place as in India. Lack of Defined Symmetry, Ordered Geometry of the space results in sets created as if out of different planes, opening, boundaries. To this adds the various objects correlated to the activities performed. So a linear space such as a road through business area lined with shops and bustling with people from outside in the daytime, turns into a sleeping quarter for the pavement dwellers, vendors, porters of the locality or maybe the vagabond, by night (Critchlow, 1976).

But the visual space remains studded with the store hoardings, shutters, waste bins in tandem with the covered boxes of the street dwellers' belongings, with an occasional towel or shirt hanging on a hook. A bustling work space in the day turns into an open residence after business closes. On weekly day off, with shutters drawn, the same space changes its aesthetics with maybe the entire laundry of the users hanging from temporary clothes line or owing to an activity camp for the street children (Fig. 23).

The dynamics of these Indian organic urban public spaces produce an aesthetic entropy of the highest level as nothing remains constant. The absence of rigid defined vertical or horizontal lines, grids, helps to bring in transition of visual movement from one point to another. Multiple persons, activities, objects of use together create visual frames that is never constant and keeps on changing. The chaos adds vibrancy to an otherwise mundane urban space. Sub spaces within the space are created by different materials. A flex banner becomes a shade from rains. Apparently chaotic and unsystematic and random arrangements of these finally attain a state of repose. It is a different aspect whether the inherent entropy creates aesthetically pleasant compositions (McCall *et al.*, 2005).



Fig. 23 The entropy of public spaces in Kolkata. Courtesy Mr. Diptarag Bhattacharya, COO, Amway, Gurugram.

Role of Community in Placemaking – Culture and Use of Public Space

The result of the chaos and eventual order also induces a need to improve on visual quality which is difficult to achieve within a regular daily schedule. Indian culture is inclusive. Indians embrace all religions and communities with the same warmth and festivals are celebrated together. Indian community is an interactive one, equally in good and bad times. Public spaces transform into Community spaces during the festivals. Durga Puja of Kolkata being the biggest testimony to this transformation. During this festival the community participates in the Placemaking as a reflection of the local community's assets, inspiration or expression. It results in complete transformation of a mundane daily work/living space to quality spaces which contribute to the happiness and well being of the people who use it. People collectively visualize and reinvent the public space and gives it a new feel for a few days, when festivals happen. Everyday dull spaces are transformed into a different realm, based on the potential of the space in terms of its geometric structure scale and built volume. Reflection of specific culture comes out through the common Theme (Spreiregen, 1965).

Any festival celebration is done in the public spaces as per its own parameters and norms. Culture plays a strong role in redefining the space Durga Puja being the biggest of all in India, especially its eastern region, it brings in participation of all communities- following Hindu traditions with modern expressions. With time and the change in urban culture, it is expected to transform with modernity in looks with deep rooted religious ethos. The transformation may represent another space and time, creating a new aesthetic entropy (Montgomery, 2003).

Geometry of Urban Public Space Inducing Aesthetic Transformation With Crafts

The rigid geometry of a planned city differs from the fluidity of an organic space in a traditional settlement. This allows the latter to undergo a variety of aesthetic transformations as would be needed for social purposes. The transformation in consideration of festivals is to be discussed in the context of Durga Puja in Kolkata, which is majorly an organic city, with major shortage of community spaces. This is significant as the festival is a minimum 5 day ritual and the festivities and the associated transformation remains for a period of 10 days with pre and post festival activities. It is indeed remarkable to see an urban public space with a completely different purpose temporarily transforming itself for that many days with complete community acceptance. Such an exercise remains rare and unparalleled across nations (Maslow, 2013).

Geometric Structure of the Public Space w.r.t. Space Transformation

Urban Public spaces can be classified into some common shapes, which defines the transformation for Placemaking of pandals during Durga Puja. The city in consideration for the study being Kolkata (Correa, 1985).

These would be –

- (1) *Linear: broad* – A main street-passage lined with boundaries created out of buildings, railings, walls. The side structures characterized according to residential, commercial, business, industrial, institutional uses. The feel of space as narrow or long characterized by the scale of built structures around. Passage for pedestrians and vehicles, even buses, need to be left. This allows the visual frames to be created for appreciation, majorly from inside and also outside (Fig. 24).
- (2) *Linear: narrow* – A lane-passage lined with boundaries residences and walls, in a predominantly residential space. The feel of space being narrow and private, generally blocked to vehicles with narrow passage for pedestrian entry into the houses around. For enjoying at close distance, very personal (Fig. 25).
- (3) *Rectilinear: on thoroughfare* – A wider space at crossroads-roads or lanes allowing bigger congregation. Passage for movement to be maintained and visual compositions can be directional. Can be a focal point from outside (Fig. 26).
- (4) *Rectilinear: at dead end* – A community space in use-directional movement to reach the structure. Both vertical or horizontal emphasis may be given to form (Fig. 27).
- (5) *Junction: T shaped* – Roads or lanes on 3 sides-visibility needed from all sides but the back. Passage of people and cars in the front creates directional viewing. The built structure should remain closer to eye level for observation (Fig. 28).
- (6) *Junction: L shaped* – Street corner. Importance as Node and structural aesthetics will demand angular viewing (Fig. 29).
- (7) *Free: closed* – A park or community space with walls or railings. Boundaries and gates define the passage within the transformed space (Fig. 30).
- (8) *Free: open* – A field or vacant plot in locality with or without boundaries. The pandal structure can be located at convenience with activities around. Such partitions allow for asymmetric arrangements. Existing built space around decides the direction and focal points (Fig. 31).

Identifying Entropy for Application of Crafts/Materials

Each of the above spaces already have their own aesthetics. In the transformative activity of crafting the theme pandals, the physical boundaries may or may not be put to use, but the horizontal free space is marked as usable space and structures created around them. The vertical elements at the side can be interestingly included and merged into the design theme. The created entropy is vibrant and dynamic enough to deserve attention for the duration of the pujas and leave a lasting impression

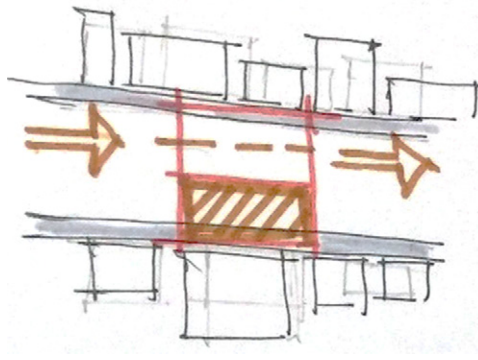


Fig. 24 The structures allow movement through or on one side. From Ms. Jayati Mukherjee, Assoc. Prof., NIFT.

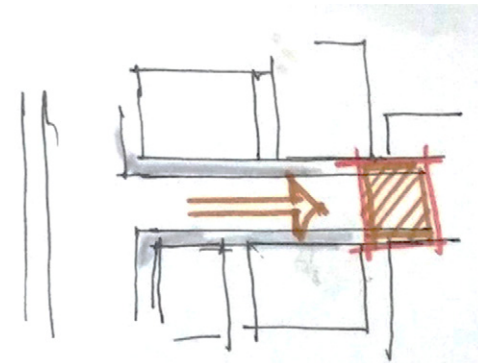


Fig. 25 The space would always appear vertically taller. From Ms. Jayati Mukherjee, Assoc. Prof., NIFT.

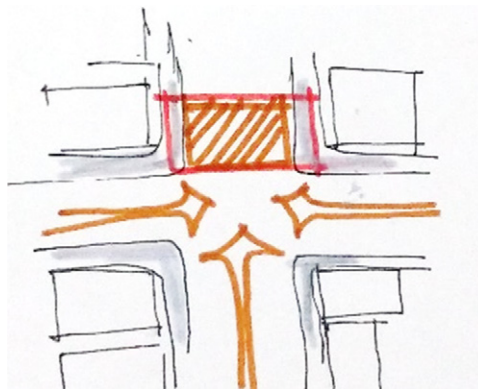


Fig. 26 A larger built form with visibility from all directions. From Ms. Jayati Mukherjee, Assoc. Prof., NIFT.

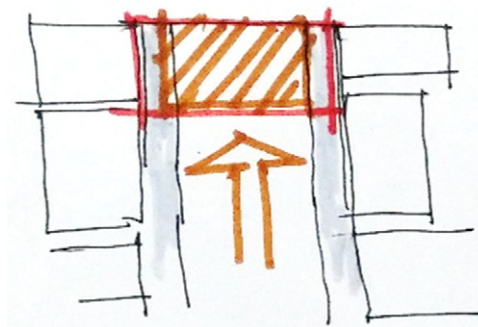


Fig. 27 Importance of façade. Passage leading to like an axis. From Ms. Jayati Mukherjee, Assoc. Prof., NIFT.

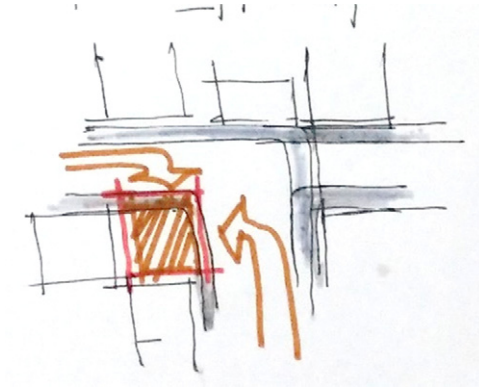


Fig. 28 Much of the vision remaining in transit. From Ms. Jayati Mukherjee, Assoc. Prof., NIFT.

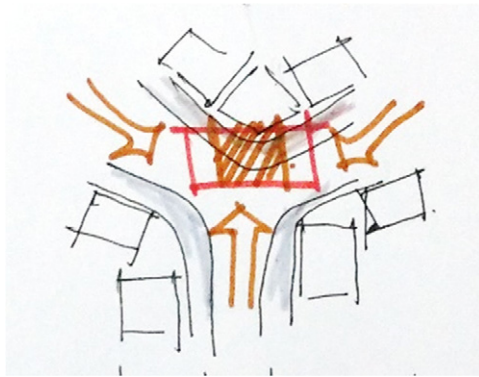


Fig. 29 Visibility from all directions. From Ms. Jayati Mukherjee, Assoc. Prof., NIFT.

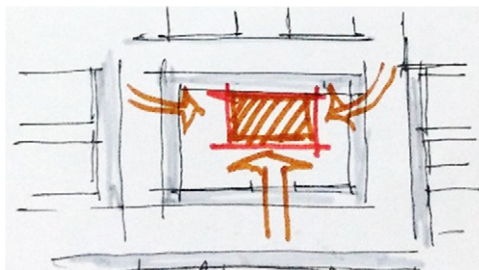


Fig. 30 Allowing small micro spaces created with purpose. From Ms. Jayati Mukherjee, Assoc. Prof., NIFT.

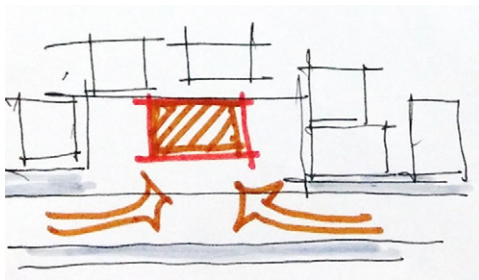


Fig. 31 Boundaries or borders are created for defining limits. From Ms. Jayati Mukherjee, Assoc. Prof., NIFT.



Fig. 32 Concept of theme Pandals reflecting materiality. Courtesy Dr. Bishnupriya Basak, CU, Kolkata.

beyond the period too. People tend to remember for long the compositions by virtue of the ordered arrangement of elements implanted into a completely different visual space as also the entropy generated by the movements of visitors. The static sets built with crafts and the dynamics of human movements with a purpose completely different to the public space concerned leaves a lasting impression of cultural experience, of chaos and order (Gupta and Gupta, 2016).

As the intended placemaking involves recreating a different space, built on crafts, the concept evolves on the craft and its elements and colours. Hence each horizontal or vertical space represents a composition with the crafted products. The material of a craft being its foundation of expression or the process of shaping the material into the end product, the space eventually reflects the material property in all possible forms and becomes a creation on material property only (Weeks, 2010) (Fig. 32).

Use of Materials for Creative Placemaking

Crafts and crafted products are entirely dependent on its material and technique of manipulating the same into feasible products of use. The use may be utilitarian or decorative, which is also a use. Crafts come in various forms. But there are some general ways of using or creating which is visible in these pandals (Ching, 1996).

The types which are largely seen being—

- (1) *Structural elements* – Beams, columns, pillars, posts, joists, trusses, roofs.
- (2) *Units* – Walls, partitions, panels, tiles, ceiling, backdrop.
- (3) *Frames* – Entrances, openings, objects, patterns, racks.
- (4) *Lighting* – Chandeliers, spot, focal, illumination.
- (5) *Hanging* – Bells, ceiling decor, flying objects.
- (6) *Lifestyle* – Pots, utensils, mats, furniture.
- (7) *Recreated* – Real life objects in other forms like weapons, tools, books, instruments.
- (8) *Decorative* – Patterns, textures, shapes, forms, artwork.
- (9) *Communicative* – Real life models, material manipulation, graphics, semiotics, narrative.

Some creative material usage of traditional crafts are illustrated below Figs. 33–40:

In the above typologies the crafts are used in traditional forms as well as modified contemporary designs. Scale of prototypes remain close to the craft practiced as the artisans working on this recreation is deft with the practice passed through generations, their craft remaining cultivated and well-honed to meet the taste of urban clientele. Although design modifications or diversification are introduced, it is difficult for them to change the techniques much for improvised products. Neither is it essential as the essence and flavour of the craft would then go away. Thus, retaining the tradition of the craft, the design takes its shape in the skilled hands of these craftspersons (Balaram, 2011).

Feasibility Study of Application of Crafts and Materials in Transformation of Urban Public Spaces

In a multicultural country like India, religion remains integral to urban spaces, mutually influencing community activities. Contrary to being a secular space, a Contemporary city is a cross religious visual realm. In turn imbibing the need to create a physical space and structure serving as key focal point, even if temporary (Gupta and Gupta, 2016). The product semantics of India remain as ancient as the vedas. The artefacts derive from everyday life and have become part of the cultural and hence religious identity. The crafts became an identity of territoriality and symbolic of the ritualistic character of space for application



Fig. 33 Bamboo. Courtesy Mr. Arnab Paul & Mr. Rupayan Biswas, Alumni, NIFT.



Fig. 34 Wood. Courtesy Dr. Bishnupriya Basak, CU, Kolkata.



Fig. 35 Metal utensils. Courtesy Mr. Arnab Paul & Mr. Rupayan Biswas, Alumni, NIFT.

(Balaram, 2011). Hence for any religious space created, even temporary, like a Durga Puja Pandal, crafts become integral to create a space for attention and reverence which is not achievable through Industrial materials.

Urban spaces are often given makeovers with craft objects added as decoration only during events or promotions. Urban areas have become spaces which lack the identity which is typical of a traditional space where crafts remain integral to the space. In this context, it needs to be reviewed how much transformation of an urban space may be possible using crafts and materials to create a uniqueness which stands apart from the adjoining brick, glass, plastic clad mechanical aesthetics. The geometry of the spaces need to be worked upon to understand the application of the crafts and how interesting spaces emerge from it (Carmona *et al.*, 2010).

Case Study – Community Durga Puja Pandals, Kolkata

A study of Durga Puja in Kolkata conducted over years show how a location in the busy City of Joy changes its aesthetics in so many different ways by use of crafts. It is interesting to note that every year the concept changes dramatically for the same space



Fig. 36 Terracota. Courtesy Dr. Bishnupriya Basak, CU, Kolkata.

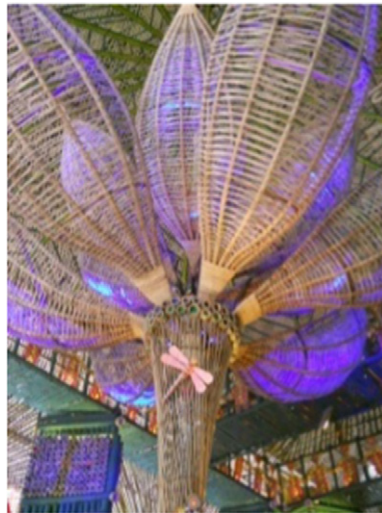


Fig. 37 Cane. Courtesy Mr. Arnab Paul & Mr. Rupayan Biswas, Alumni, NIFT.



Fig. 38 Coconut. Courtesy Mr. Arnab Paul & Mr. Rupayan Biswas, Alumni, NIFT

and the visual perception of the space based on use of these crafts create an identity so diverse from other years, while the geometric structure remains the same.

Crafts and materials are used in creative and varied ways. Traditional Materials used primarily being Wood, Bamboo, Cane, Metal, Fabric, Yarn, Clay, Plaster of Paris, Glass, Paper along with thermocol, plastic and recycled material.

Geometric structure of the space

It gives the direction of visualizing the change possible in that space and the final realisation of the composition leading to a transformation of the physical spatial volume introducing crafts and materials. The case studies cited below pertains to leading



Fig. 39 Wooden toys. Courtesy Dr. Bishnupriya Basak, CU, Kolkata.



Fig. 40 Patachitra. Courtesy Dr. Bishnupriya Basak, CU, Kolkata.

Durga Puja Pandals in Kolkata and the periodic change in forms over years will show the transformation in terms of the geometry of the space perceptually viewed in varying manner in the same urban space context (Ching, 1996).

- (1) Tridhara Sammilani–
Visually wider space in 2013 by using intricate crafts, enhancing verticality (Figs. 41 and 42).
- (2) Mudiali Club–
Experimenting with space enclosures and scale (Figs. 43 and 44).
- (3) Badamtala Ashar Sangha–
To bring uniqueness in a general residential neighbourhood (Figs. 45 and 46).
- (4) Barisha Club–
Complete change in format – open and closed (Figs. 47 and 48).
- (5) Ballygunge Cultural Association–
Focus shifted from viewing from outside in 2013, highlighting external space in 2014 to highlighting interiors in 2016.
Scale enhanced (Figs. 49 and 50).
- (6) Shibmandir–
Playing with creative use of materials (Figs. 51 and 52).
- (7) Nalini Sarkar Street–
Very narrow lane requiring creative space design (Figs. 53 and 54).
- (8) Jodhpur Park–
From community Puja pandal with basic decoration to crafted spaces (Figs. 55 and 56).

Other factors related to transformation

Apart from physical space, the placemaking considers some other factors which are inclusive in the transformation of the space. It includes the built and unbuilt aspects of the space.

- (1) *Scale* – When wider space or visibility from a distance is possible, majestic scales are introduced, while in other spaces more human scale is applied (Figs. 57 and 58).
- (2) *Surrounding elements* – These are included in the conceptualization and become a component in the space created Fig. 59.



(a)



(b)

Fig. 41 (a) Location of Tridhara Sammilani (courtesy Google Maps). (b) Direction of geometric transformation. Courtesy Ms. Jayati Mukherjee, Assoc. Prof., NIFT.



(a)



(b)

Fig. 42 Tridhara Sammilani in (a) 2012 and (b) 2013. Courtesy Ms. Anwesha Mukherjee, Student, NIFT.



(a)



(b)

Fig. 43 (a) Location of Mudiali Club (courtesy Google Maps) (b) Direction of Geometric transformation. Courtesy Ms. Jayati Mukherjee, Assoc. Prof., NIFT.



Fig. 44 Mudiali Club in (a) 2010. (b) 2012. (c) 2013. (d) 2016. Courtesy Dr. Bishnupriya Basak, CU, Kolkata.



Fig. 45 (a) Location of Badamtala Ashar (courtesy Google Maps). (b) Direction of Geometric transformation (Courtesy Ms. Jayati Mukherjee, Assoc. Prof., NIFT).



Fig. 46 Badamtala Ashar in (a) 2010 (b) 2013. (c) 2014. Courtesy Ms. Anwesha Mukherjee, Mr. Dharanedarhan, Mr. Gaurav Murmoo, Students, NIFT.

- (3) *Application of Light* – Creative lighting leads to complete change in the visual perception of the space designed (Figs. 60 and 61).
- (4) *Detailing of craft used* – Meticulously executed intricate detailing of the craft can recreate traditional spaces Fig. 62.

SWOT Analysis

Strength

Craft materials are largely sustainable and renewable in nature, Hence the materials and prototypes can be conveniently adapted to different uses when the present spatial arrangement undergoes change. e.g., a daily use metal Pot can easily become an element of the structure. Similarly, a craft object like a bell can be put to use in a lampshade.



(a)



(b)

Fig. 47 (a) Location of Barisha Club (courtesy Google Maps). (b) Direction of Geometric transformation (Courtesy Ms. Jayati Mukherjee, Assoc. Prof., NIFT).



(a)



(b)

Fig. 48 Barisha Club in (a) 2010. (b) 2016.



(a)



(b)

Fig. 49 (a) Location of Ballygunge Cultural Association (courtesy Google Map). (b) Direction of Geometric transformation (Courtesy Ms. Jayati Mukherjee, Assoc. Prof., NIFT).

Weakness

Craft products and materials mostly come with a short life or with susceptibility to wear and tear. In order to emerge as an alternative material in public spaces which would remain exposed to external environment as well as handling by different people, In order to make it sustain, the materials need to be relooked into or its application reinvented using latest technology.

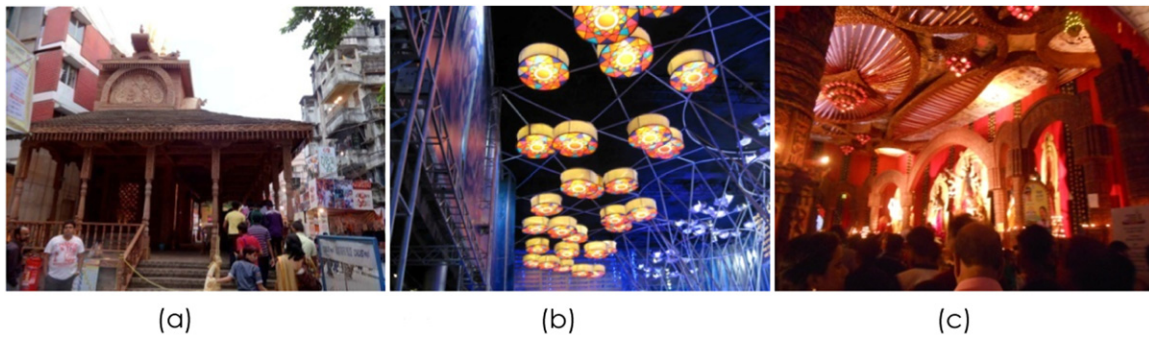


Fig. 50 Ballygunge Cultural Association in (a) 2013. (b) 2014. (c) 2016. Courtesy Ms. Anwesha Mukherjee, Student, NIFT.



(a)



(b)

Fig. 51 (a) Location of Shibmandir (courtesy Google Maps). (b) Direction of Geometric transformation. Courtesy Ms. Jayati Mukherjee, Assoc. Prof., NIFT).



Fig. 52 Shibmandir in (a) 2010. (b) 2012. (c) 2013. (d) 2016.

Opportunity

Using crafts in public spaces open up a vast avenue for revival of the crafts as it comes as an expression of a highly creative form in an urban domain allowing the urbanite to patronise the craft and help it come back. Not only does the craft product improve the aesthetics of the space but also gives it a newer dimension breaking the monotony of a staid urban space otherwise so formal in its character. Crafts, by virtue of their details, colours, features add dynamism to the space.

Threat

Lack of practice has led to a dearth of skilled hands who can actually produce highly creative end products and scarcity of experts on the physical and behavioural properties of a material used in a craft, which was inherent to the master craftsmen who would pass on the knowledge and skill as inheritance. This leads to development of prototypes which are either mixed or created with more commonly available materials. These would lack the finesse and uniqueness of the original craft, having visual similarity, resulting in an inferior imitation.

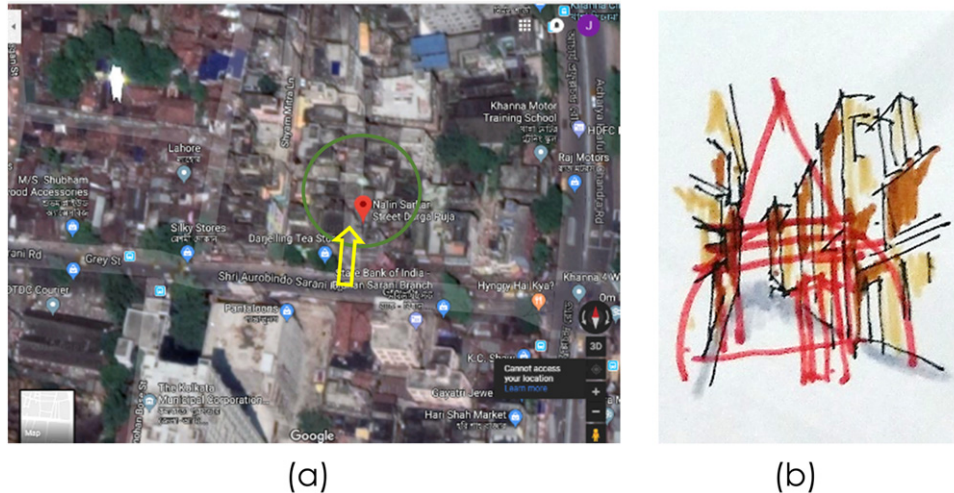


Fig. 53 (a) Location of Nalini Sarkar Street (courtesy Google Maps). (b) Direction of Geometric transformation (Courtesy Ms. Jayati Mukherjee, Assoc. Prof., NIFT).



Fig. 54 Nalini Sarkar Street in (a) 2010. (b) 2013. (c) 2014. (d) 2017. Courtesy Dr. Bishnupriya Basak, CU, Kolkata.

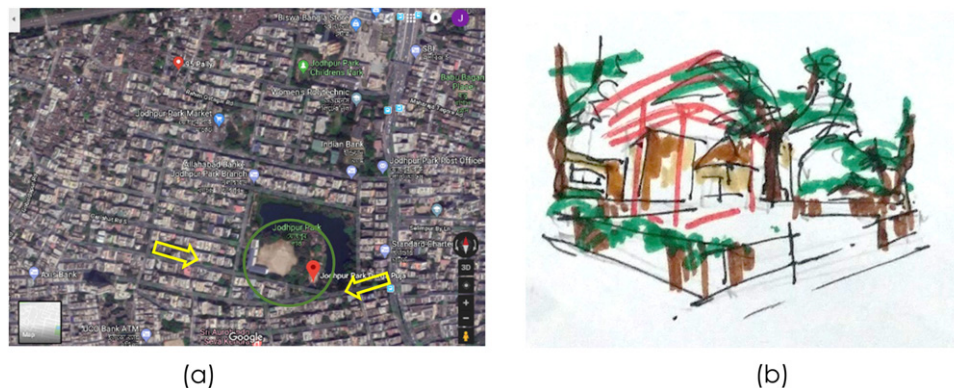


Fig. 55 (a) Location of Jodhpur Park (courtesy Google Map). (b) Direction of Geometric transformation (Courtesy Ms. Jayati Mukherjee, Assoc. Prof., NIFT).

Impact Analysis of Use of Crafts and Materials

Contemporary spaces use new age materials which are industrial products and are diametrically opposite in character to traditional materials. The materials bear the stamp of their production and are impersonal and mechanical in the perception they create. The scale of these spaces are very different from traditional spaces too. Thus, the perception of urban spaces are formal, strictly geometric, somewhat rigid and largely impersonal except maybe for private and personal spaces like residence etc. It has a



Fig. 56 Jodhpur Park in (a) 2012. (b) 2013. (c) 2015. (d) 2017. Courtesy Ms. Anwesha Mukherjee, Student, NIFT.



Fig. 57 Monumental scale. Arnab Paul & Rupayan Biswas, Alumni, NIFT.



Fig. 58 Human scale. Courtesy Dr. Bishnupriya Basak, CU, Kolkata.



Fig. 59 Adjoining building facades painted, coloured and crafted according to the theme. Courtesy Dr. Bishnupriya Basak, CU, Kolkata.

universal identity not exclusive to any region or culture. The scale used is often monumental as these spaces are for public use. Verticality overrules horizontal spread due to dearth of land available vis-à-vis use (Harlan, 1986).

Traditional crafts, by their origin, have an innate rustic or rural characteristic which may not work well with urban or contemporary aesthetics. But the traditional materials and crafts are more environment friendly and the visual perception to use in



Fig. 60 Transformation through light effect – Day and night. Courtesy Dr. Bishnupriya Basak, CU, Kolkata; Courtesy Ms. Anushka de Choudhury, Psychologist, Kolkata.

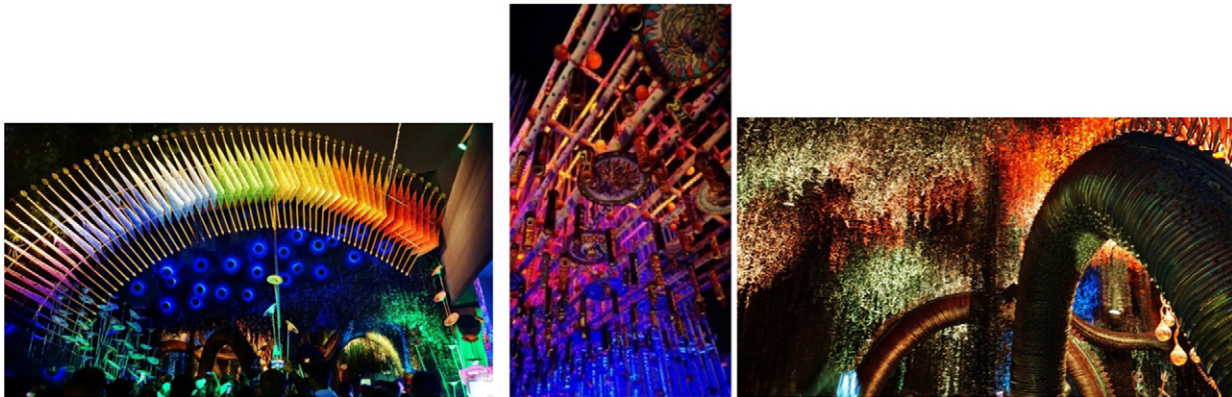


Fig. 61 Creative lighting effect on materials and crafts. Courtesy Ms. Anushka de Choudhury, Psychologist, Kolkata.



Fig. 62 Traditional detailing created with new materials. Courtesy Mr. Arnab Paul & Mr. Rupayan Biswas, Alumni, NIFT.

spaces were developed over time possibly through trial and error to achieve the best possible result. The scale of these objects are more human and easy to relate to.

The use of these crafts in the Durga Puja activities show that they can

- (1) Transform an otherwise mundane impersonal space into a vibrant personal one leading to community involvement.
- (2) Induce identity to spaces, bringing in a human scale to formal areas too.
- (3) Increase entropy of the space drastically which leads to initiating positive interaction and action so necessary in a busy urban life.

Some examples of this Entropy can be seen as below where crafts play the role of creating the vibrancy inherent to it (**Fig. 63**).

Future Implications/Directions

The study based exercises reveal a very interesting direction in the application of crafts. The traditional aesthetics of design is retained as that is the flavour and uniqueness of the craft.

Materials

Introducing the craft in a different place would fail for deficit of raw material. But the cases above reveals a mix of prototypes generated with new age materials along with traditional ones. The new materials introduced have greater sustainability and are worked with the same finesse to produce the form (Figs. 64 and 65).

Design

Considering the sensibility of a contemporary world, the design of the prototypes are creatively evolved into a composition of forms merging the crafts with visual character as is expected in traditional designs. The same detailing with its exquisiteness is available in the end product (Figs. 66 and 67).

Technique

In the absence of skill set owing to decadence in practice, newer technologies can be introduced to generate similar effects and also can lead to greater production due to time saving (Figs. 68 and 69).

New directions

In order to appeal to the generation of youth who are less aware of crafts as materials with their tremendous scope of application, newer methodology is required to adapt them to the aesthetics of crafts and materials (Fig. 70).

The analysis of transformation of the geometry of the urban public space reveals that this could be a major initiative to introducing crafts in urban spaces, both personal and public. Crafts can be introduced not as a cosmetic treatment but as a complete makeover of both exterior and interior spaces. It can initiate revival of the traditional prototyping with interventions in time oriented designs, adopting new materials and technology-bringing back material in a space having greater sustainability, environment friendly solutions, and allowing recycling.

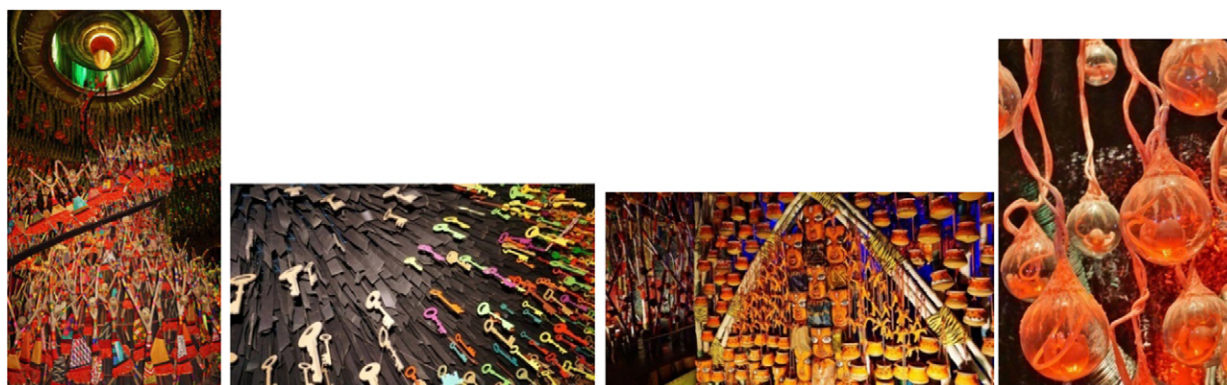


Fig. 63 Vibrancy in space by use of Entropy of crafted elements. Courtesy Ms. Anushka de Choudhury, Psychologist, Kolkata; Courtesy Ms. Anwesh Mukherjee, Student, NIFT.

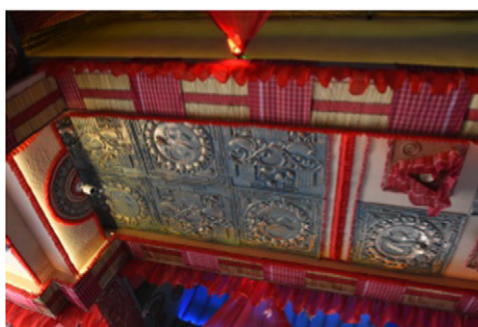


Fig. 64 Mix media use in unconventional manner. Courtesy Ms. Jayati Mukherjee, Assoc. Prof., NIFT.



Fig. 65 Different application of craft. Courtesy Ms. Jayati Mukherjee, Assoc. Prof., NIFT.



Fig. 66 Contemporary design with craft. Courtesy Dr. Bishnupriya Basak, CU, Kolkata.



Fig. 67 Traditional art in new compositions. Courtesy Ms. Anushka de Choudhury, Psychologist, Kolkata.

Sustainability of Materials in Temporary Space Making

Use of materials in Durga Puja Pandals of Kolkata are of temporary nature. Assembly and dismantling of materials happen over a few days only. While the sourcing and assembly is meticulously worked out with adequate time to execute the details and to ensure the final aesthetics of the space created, the dismantling is done in haste and leaves behind a residue of leftover waste



Fig. 68 Laser technology for intricacy. Courtesy Ms. Anwesha Mukherjee, Mr. Dharanedarhan, Mr. Gaurav Murmoo, Students, NIFT.



Fig. 69 Processing of raw material with technology. Courtesy Ms. Jayati Mukherjee, Assoc. Prof., NIFT.

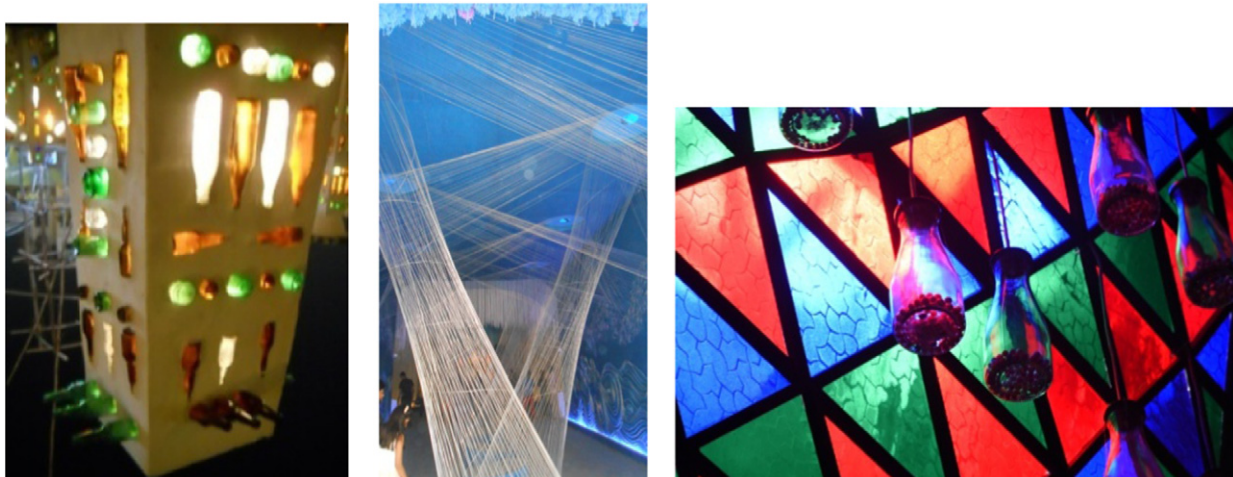


Fig. 70 Use of new materials and recycling for contemporary spaces. Courtesy Ms. Jayati Mukherjee, Assoc. Prof., NIFT.

materials. While major stock of materials are either reused or recycled, the craft materials are largely reused as decorations or sold after the event, while the waste materials are left over and require to be removed as garbage.

The primary materials and their different applications as used in a pandal are listed below –

(1) Bamboo – Available locally, biodegradable

<i>Application</i>	<i>After use</i>
Structure	Reused
Decorative crafts	Reused/sold

(2) Cane – Generally sourced, biodegradable

<i>Application</i>	<i>After use</i>
Decorative crafts	Reused/resale as craft

(3) Wood – Available locally, biodegradable

<i>Application</i>	<i>After use</i>
Partitions	Reused/reconstructed in furniture
Structure	Reused in construction, furniture
Woodcraft	Reused/sold

(4) Fabric – Different types that include cotton, silk, jute and polyester, generally biodegradable

<i>Application</i>	<i>After use</i>
Covering/sheath	Reused/recycled
Decorative designs/prints	Reused

(5) Yarn – Coir, Jute, cotton, silk, biodegradable

<i>Application</i>	<i>After use</i>
In structure	Reused
Decoration/crafts	Reused/sold

(6) Paper – Various types, biodegradable

<i>Application</i>	<i>After use</i>
Panels/partitions	Reused
Decorative designs/artwork	Reused/sold
Crafted items	Reused/sold / recycled

(7) Plastic – In both soft and hard form, non-biodegradable

<i>Application</i>	<i>After use</i>
Acrylic sheets as panels	Reused
As Flex sheets for graphics/	Reused/recycled
Thin sheets as fabric, decorative designs	Reused by pavement dwellers
Crafted decorations	Reused
Small available items such as cups, plates, spoons etc.	Recycled/waste

(8) Thermocol – As sheets, blocks, products, non-biodegradable

<i>Application</i>	<i>After use</i>
Panels/partitions	Reused/waste
Decorations, small items	Recycled/waste

(9) Metal – As sheets, wires, pipes films, some are non-biodegradable

<i>Application</i>	<i>After use</i>
Panels/partitions	Reused
Decorations and crafts	Recycled/waste
Layering of objects	Waste

(10) Clay – As pulp or granular form, biodegradable

<i>Application</i>	<i>After use</i>
Surface design	Waste
Sculpting and crafts	Recycled/waste

(11) Plaster of Paris – As pulp or granular form, semi-biodegradable

<i>Application</i>	<i>After use</i>
Panels/skins	Recycled
Sculpting and crafts	Recycled/waste

(12) Terracota – As solid products, biodegradable

<i>Application</i>	<i>After use</i>
Panels/units	Reused/sold
Decorations and crafts	Recycled/sold

(13) Natural fibres/articles – Sholapith, reeds/grass, shell, coconut shell, seeds dry flowers – Biodegradable

<i>Application</i>	<i>After use</i>
Crafts and decorations	Recycled/sold
Panels/units	

(14) Glass – Sheets/units, semi-biodegradable

<i>Application</i>	<i>After use</i>
Panels	Reused/sold
Products/crafts	Recycled/sold

(15) Paint – Natural dyes or Emulsion, acrylic, synthetic enamel – toxic, non-biodegradable

<i>Application</i>	<i>After use</i>
Natural dyes on crafts	Recycled waste
Industrial paint finishes	Non-recycled waste

The above tables clearly illustrate that in consideration of sustainability, the natural materials and crafts are way above industrially produced materials. The craft materials are generally completely biodegradable or otherwise reused as products or similar purposes, or sold as a craft product owing to exquisite craftsmanship, or recycled into mix-media products. This helps sustain the crafted products and materials for a much longer duration, eventually reducing depletion of resources of Earth, continuing to exist in diverse forms over longer duration, during While the industry produced raw materials continue to be responsible for enhancing the carbon footprint on the Earth. While, on the other hand, materials produced by industrial systems continue to add to the non biodegradable mass of waste products. This justifies the use of crafts and natural materials in temporary structures, like Pandals, even more, and the same may be emulated for permanent spatial structures and buildings or built spaces, leading to reduction in piling of man-made waste generated by the building industry.

Materials as above, used in these temporary spaces, can be broadly classified into the following domains –

- (1) Natural/Man-made.
- (2) Reusable/Non-reusable.
- (3) Bio-degradable Waste/Non-biodegradable Waste.

The materials listed in above tables may be interpreted graphically as –

SL. NO.	MATERIAL	NATURAL	MAN-MADE	REUSABLE	NON-REUSABLE	BIODEGRADABLE WASTE	NON-BIODEGRADABLE WASTE
1	BAMBOO						
2	WOOD						
3	CANE						
4	FABRIC						
5	YARN						
6	PAPER						
7	PLASTIC						
8	THERMOCOL						
9	METAL						
10	CLAY						
11	P.O.P.						
12	TERRACOTA						
13	NATURAL FIBRE/ ITEMS						
14	GLASS						
15	PAINT						

It clearly shows how sustainable natural materials are w.r.t. their properties. Crafts, being born out of natural materials, thus play a vital role towards sustainable design and reducing environmental degradation.

Conclusion

“The purpose – where I start – is the idea of use. It is not recycling, it’s reuse” – Issey Miyake

Design in the context of contemporary urban space need to be relevant to the needs of a developing country like India and be resource saving and employment generative. And it must befit the physical and social needs of the people- expressing respect towards sensibilities, comfort, tastes and sustenance. Realisation of design through local materials and skills naturally imbibes all the factors leading to a successful product or experience that can be replicated and remains accepted by the community in concern. Handicrafts, having been a component of the daily life, is tested over time and is innovation from the roots of a culture, besides being a means of livelihood for generations. Incorporating crafts and materials into public spaces and activities in a diversified contemporary way can bring vibrancy into the spaces, build sense of association related to the perception in its aesthetics, and show new directions for traditional employment using newer technology in hand.

The building materials domain can be relooked into for being inclusive on crafts and materials, resulting in creating unique spaces with an identity of its own which brings back traditional practices and social actions. In an era when the world emphasises the need for going back to the roots, it is important to review the implication of this as it transforms space, and space is to be interpreted and put to use with multi-dimensionality. Considering the youth of the society, who form the majority of population and live in today, creating awareness would lead to sustenance of crafts and infuse new life into these age old professions. It will help revive the crafts as alternative materials for creating interesting visual spaces- rich in its vibrancy and with dynamics that is inherent and an essential expression - the unique identity which arises only from crafts. The experimental experiences in the Theme Pujas of Kolkata definitely indicates the possibility.

Acknowledgement

The authors are grateful to the huge inventory of original pictures and resources collected from:
 Ms Anwesha Mukherjee, Mr. Dharanedarhan & Mr Gaurav Murmoo, students, NIFT Kolkata.
 Mr. Arnab Paul & Mr Rupayan Biswas, Alumni, NIFT Kolkata.

Ms Anushka De Choudhury, Psychologist, Kolkata.
 Dr. Bishnupriya Basak, Professor-CU, Kolkata.
 Prof. Rupkatha Mukherjee, BKG College, Kolkata.
 Mr. Diptarag Bhattacharya, COO, Amway, Gurugram.
 Ar. Kalyan Kumar Mukherjee, Prof. & Principal Om Dayal College of Architecture, Kolkata.
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 All remaining photographs and sketches by author Ms Jayati Mukherjee.

See also: Life Cycle Assessment Methods and Procedures and Their Role in Measuring the Sustainability Component of a Construction Technology

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Understanding High Performance Buildings: The Link Between Occupant Knowledge of Passive Design Systems, Corresponding Behaviors, Occupant Comfort and Environmental Satisfaction

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What is a High Performance Building?

Buildings are designed and operated to function for a purpose. The purpose may be vary and hence design and operational parameters also vary from one building to other. By way of example, commercial office buildings and residential buildings have very different function and purpose. While a high performing office building shall be designed and operated to provide high level of occupant comfort with lower energy and other resource consumption, residential buildings have more diverse requirements in terms of personal needs and variation of space type within the residence. A high performance building shall be designed to perform at high level of all functional parameters. It shall provide optimum level of comfort at minimum energy cost and consumption. For purpose of this article, *we are limiting the discussion to energy and comfort only, though water and waste minimization, recycle and reuse, materiality of a building are equally important for delivering a high performance building.*

Optimised energy consumption, with desirable thermal, visual and acoustic conditions to meet occupant comfort, good quality of air and other indoor environmental parameters all contribute to high performing buildings and occupant well-being and productivity. High performance buildings need to be operated as per design, and hence occupant knowledge of systems and maintenance and monitoring holds key to maintaining high performance through life cycle of the building. To define high performance buildings let us first define key design strategies and approaches that support such buildings.

The energy consumption in a building can be reduced through a multipronged approach. The key steps are:

- Reduction in energy demand
- Use of on site sources and sinks and use of passive systems
- Maximise system efficiency

Reduction in energy demand is a function of architectural design, optimising needs and use of onsite sources and sinks. The building skin or envelope plays a dominant role in this effort. The building envelope protects its occupants from heat of sun, rains, and provide a comfortable environment for work and leisure. Use of space conditioning systems to keep occupants comfortable and use of lighting systems to provide visual comfort is a necessity in most buildings. High performance buildings aim to reduce these requirements and thus reducing the intended energy use, without impacting comfort. Reduction in energy demand entails adoption of design measures to reduce space conditioning, lighting and service water heating loads. The first step to reduce energy demand is to design for the macro and micro climate of the site by adoption of suitable bio-climatic design principles. As suggested by the name itself, bio-climate design varies from one climate zone to other. For example, India has six climatic zones ranging from extreme cold conditions in cold desert of Leh, Ladakh to extreme hot and dry conditions in Rajasthan. A building in a cold climatic zone has to adopt measures to harness the sun to maximum extent by adoption of measures like maximum exposure to south, windows to capture heat, dark colored surfaces, high thermal mass and insulation to retain the captured warmth of the sun, or use of design elements such as trombe wall, sun spaces etc. On the other hand, a building designed for a hot climate would have measures to reduce solar gain like, smaller window sizes, shaded walls, minimum exposure to west and east, external wall and roof insulation or use of design elements like solar chimneys, wind towers, etc to maximise ventilation (**Fig. 1**).

Use of onsite sources and sinks offers wide opportunities for energy savings in a building. Site microclimate is an important aspect that makes building designs in the same climatic zone, distinct from one another. Each building site would have distinct topography, vegetation, wind flow pattern, solar and daylight access- and the design response should be able to address the site requirement. Thus two buildings located in the same climatic zone may have different design features due to varying microclimate. For example in an unconditioned building, design and placement of window according to site wind regime can reduce energy requirement for mechanical ventilation.

Take the example of the office building *Sangath* (**Majumdar, 2001**) of the renowned Pritzker prize winning architect from India Shri BV Doshi. An architectural studio, it is designed to naturally manage the forces of nature. There are spatial, constructional and landscape responses to combat the vagaries of nature in the hot dry climate. For Ahmedabad with summer temperature reaching up to 45°C, sun is very intense and the natural comfort conditions can be achieved by protecting spaces from heat and glare. It is the sun rather than breeze that becomes critical.

The design responses to the same are as follows:

- Subterranean spaces
- Storage walls



Fig. 1 Large south facing windows for solar gain in cold climate of Leh Complex, India.



Fig. 2 Sangath, Ahmedabad, India.

- Vaulted form of the roof
- Sandwiched construction of vault (the vaulted roof is of locally made clay fuses over the concrete slab which provide less-conductive layer; the top finish of china mosaic glazed tiles further enhances insulation property by being white and glossy to reflect sun and being of clay to retard heat transmission; Indirect/Diffused Light; North-glazing)
- Micro-climate through vegetation (Lawn and vegetation cover all around create favourable micro-climate by absorbing solar radiation and providing cooler passage of air through humidity)

These features and many more have ensured excellent climate control within in terms of keeping inside cool and increasing time lag for heat transfer. There are about 8°C temperature difference between interior and exterior of the roof skin temperatures. The time-lag is nearly six hours (Fig. 2).

Passive systems provide thermal and visual comfort by using natural energy sources and sinks, e.g., solar radiation, outside air, sky, wet surfaces, vegetation, and internal gains. Energy flows in these systems are by natural means such as radiation, conduction, and convection with minimal or no use of mechanical means. The solar passive systems vary from one climate to the other. Knowledge of passive systems by occupants is important to enable appropriate operation of the system and derive benefits in terms of energy savings. Let us take the example of Trombe Walls used as a passive walling system to capture solar energy in a thermal mass during daytime and use the stored energy as a source of space heating at night. The Trombe walls are usually vented to avoid excessive heat build up and allow for convective flow of heating energy into the space. However, if the vents are left open at nighttime, the convective currents shall allow cold air to move to the spaces indoors, thus causing thermal discomfort.

Passive systems or combination of passive and active systems have conventionally been able to reduce energy consumption. These systems, once applied need to be well understood by occupants so as to derive benefits of their application. For example,

Daylighting is effective provided it is devoid of glare and occupant knowledge of same is necessary to take advantage of daylight. Some commonly used passive concepts that help reduce energy use in buildings are:

- Proper orientation of buildings (in the northern hemisphere, the most desirable orientation would be to have the facades and fenestrations facing south and north with minimum exposure to east and west);
- Proper placing and designing of windows and their sizes (windows should be optimally designed for daylighting and high percentage of glazed surfaces should be avoided in hot climates);
- Suitable design of louvres/sunshades; proper provision of natural light inside the buildings to reduce the initial and recurring cost of providing artificial lighting systems;
- Insulation, provision of thermal mass, reflective surfaces to reflect radiation etc.

Building energy codes and standards provide recommended envelope and system efficiency parameters for design of energy efficient and high performance buildings. Ashrae 90.1 2010 or later editions provide standards for minimum energy performance in buildings and is followed as an international best practice. Local equivalencies with national building energy codes can be established and followed for design of high (energy) performance buildings e.g., India has its own Building energy code, ECBC 2017 that applies to commercial buildings.

Maximising system efficiency offers further opportunity for energy savings. Use of efficient lighting, air conditioning and service water heating systems can reduce energy use in a building by 30%–40%.

Designing High Performing Buildings: The Key Components

The above section defines the key principles of designing and implementing a high performance building. However, the first principle to achieve objective of a high performance building is to have a coordinated and integrated team that will deliver the same. Integrative design is the first principle to high performance building wherein performance goals are to be set by building users and owners. The goal setting on performance is followed by an integrative approach to deliver the design goals. However, a building should be operated as designed to realise the benefits of a high performance design. Hence the bridge between design and operation is crucial to ensure a building remains high performance throughout its life cycle. The following diagram summarises the steps to achieve and maintain high performing buildings (Fig. 3).

In addition to setting performance metric at overall energy consumption level, performance and/or design metric may also be defined at a component level of building envelope (e.g., thermal transmittance values for walling, roofing, glazing and solar heat gain coefficient of glazing), and at system level for electrical, lighting and HVAC systems. For each system there could be performance metric and design metric at component level or at whole system level.

The following diagram provides a summary of performance parameters that holistically contribute to higher performance as far as energy utilization is concerned (Figs. 4 and 5).

Setting Design and Operational Goals for High Performance Buildings

The first step to high performance buildings is to set design and operational goals. Performance metric in high performance buildings is a combination of metric for:

- Energy (connected load and consumption)
- Water (consumption/capita and source apportionment to fresh water, recycled and reused water and quality of water)
- Waste (reduce waste generation and reuse/renew/recycle waste)
- Comfort (thermal, visual, acoustic)
- Air quality

In this article we have focussed only on energy and associated comfort parameters. Water and waste optimisation and performance is not in scope of this article.

Defining Energy Performance in High Performance Buildings

Energy performance is usually defined by unit of energy consumed in terms of kWh per unit area of space (sqm) over a given period of time, usually over a year. The lower the consumption, the better the environmental impact of the building. Energy consumption in a building varies largely from one to another and is determined by climate, geography, cultural context, economic level, level of technologically advanced systems incorporated, individual behavior and use. There has been an increasing push towards lowering energy intensity in building energy use through passive design, technological advancements in systems design and renewable energy integration in buildings. Highly energy efficient residential and commercial buildings have a total energy intensity of 50–100 kWh/sq m of floor area/year, compared to a typical value of 200–400 kWh/sq m/year (GEA, 2012: Global Energy Assessment: Towards a Sustainable Future, Cambridge University Press, and IIASA, Austria). High performance calls for

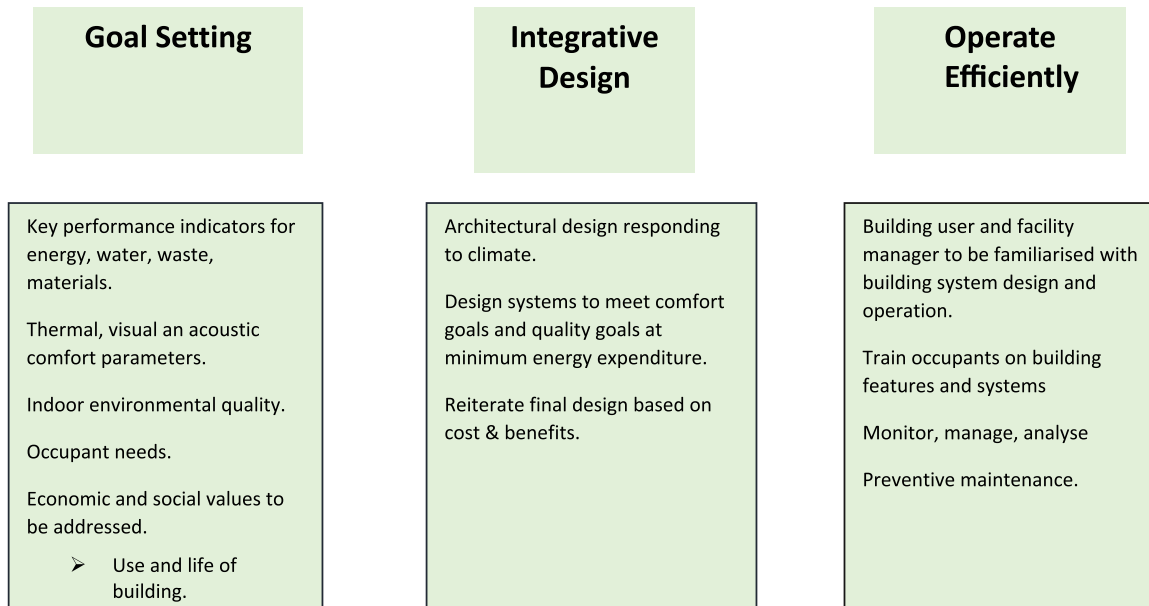


Fig. 3 Steps to a high performance building.

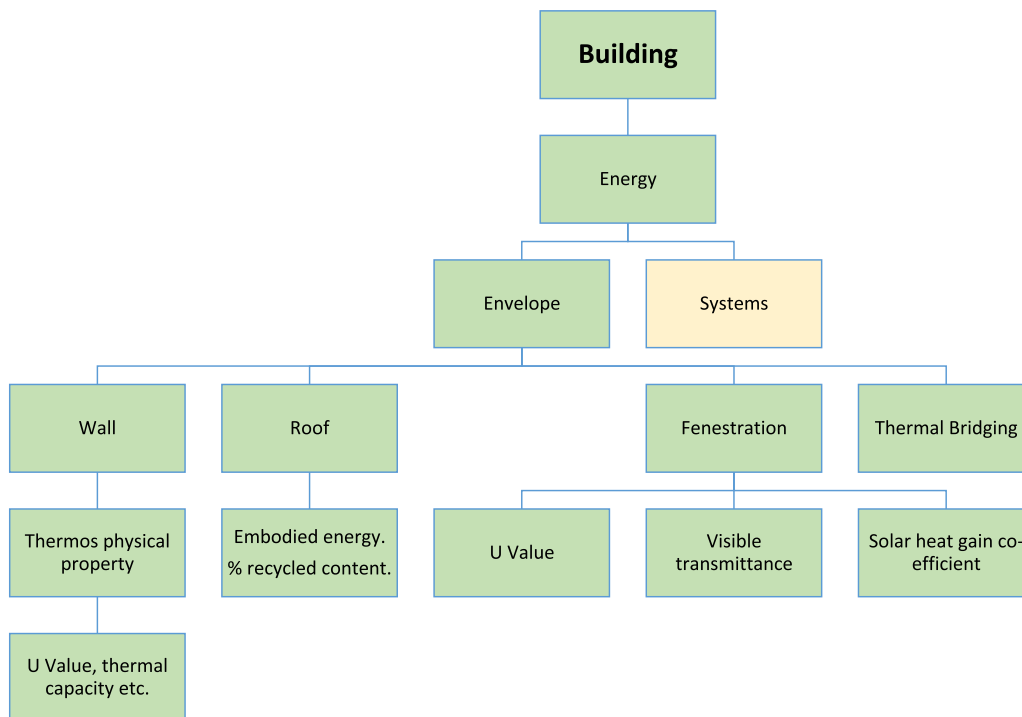


Fig. 4 Some key building components that have a role in high energy performance design.

moving towards a net zero regime in energy use, which essentially requires the consumption to be offset by on site/off site renewable energy. Annual average solar irradiance ranges from 160 W/sq m in middle latitudes to 250 W/sq m in sunniest regions. The potential of generating renewable energy through use of solar will depend of available shadow free area on roof or other suitable surfaces, and thus net zero energy consumption in a building is highly subjective of the location, size and use of the building, other than buildings that have access to off- site generation of RE. U.S Green Building Council (USGBC) has announced Net zero certification for LEED certified projects wherein exemplary projects with any one of the following: net zero carbon emissions, net zero energy use, net zero water use or net zero waste can aim to be Net zero certified.

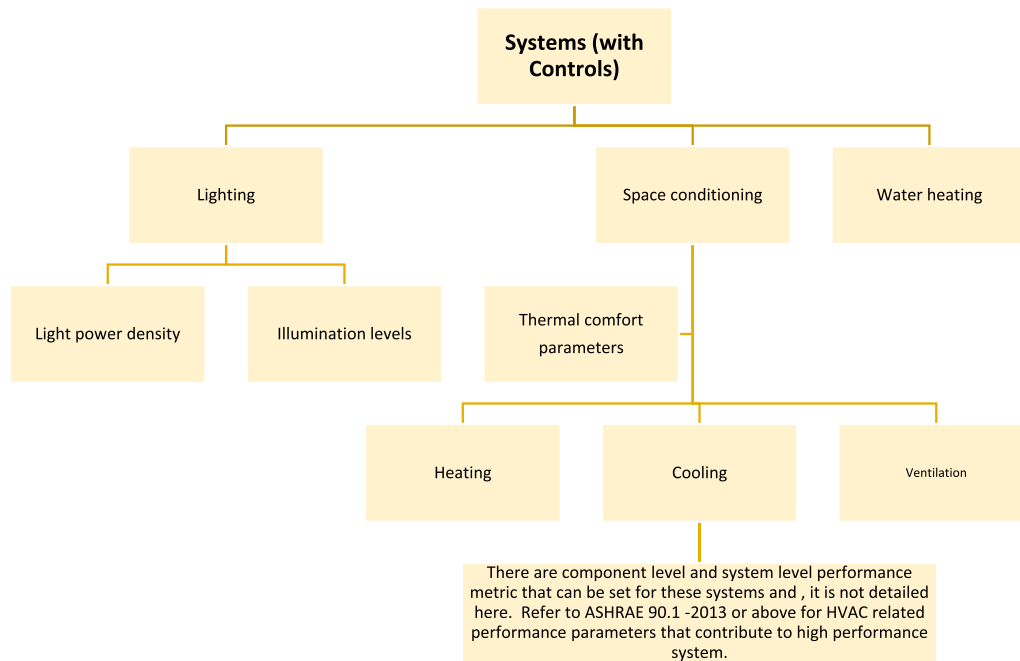


Fig. 5 Key systems that contribute to high energy performance design.

There is a deep co-relation between metric set for Indoor environmental conditions such as level of desirable thermal and visual comfort and metric set for energy consumption. Usually it is inversely correlated. For example an office building designed in hot climate with lower set of temperature e.g., 22°C will have higher energy consumption than if the same space was designed with adaptive comfort. Let us review a few parameters for setting comfort related performance benchmarks for high performance buildings.

Thermal Comfort (U.S. Green Building Council, 2013)

Thermal comfort in a space greatly impacts health and productivity of occupants. It is a cumulative impact of surface temperature, air temperature, humidity, air movement metabolic rate and clothing. Modifying one or more of these factors can greatly influence occupants' comfort perception. ASHRAE 55-2013 or higher is widely followed as a reference standard for setting thermal comfort goals in a space. Other commonly followed standards are ISO 7730 or CEN standard EN 15252, latest version. Thermal comfort is also a personal requirement and varies across individuals. Occupants who are able to modify their thermal environment through thermal controls shall perceive more comfort. Thus a high performance building allows occupants to regulate comfort, thermal and visual through use of effective control strategies to regulate comfort.

Following steps should be adopted to for effective thermal environment in a high performance building:-

- (1) Establish thermal comfort goals. The designer and owner should set building wise and space wise goals for indoor conditions and variations.
- (2) Select space conditioning system to meet the thermal comfort goal. The space conditioning type should be selected based on thermal comfort goals. Natural, mechanical or mixed mode are three common types of space conditioning. Design of natural or mixed mode strategies require careful design considerations of external climate and corresponding indoor conditions that is desirable. However, natural and mixed mode buildings can offer higher level of energy savings through careful planning.
- (3) Select comfort controls. Choose thermal comfort controls based on project type, space function and occupant needs. Thermostat, ceiling fan, adjustable indoor floor diffusers, operable windows are some comfort controls.
- (4) Select thermal Comfort Standard. Select the thermal comfort standard that is suited for the project.
- (5) Commissioning as per design is a crucial step so that the building performs as designed. Performance monitoring for both comfort and energy use is necessary for high performance buildings. Occupant comfort also depends on operation of the building as designed e.g., if a building is designed to benefit from natural ventilation during a certain time of the day by opening the windows, the occupant should have knowledge about it (Fig. 6).



Fig. 6 Convective wall for ventilation.

TERI Bangalore, Office Building

TERI Bangalore – office building is a unique one with solar energy and daylighting used generously to reduce energy consumption. The entrance to the building is on the northern side. The office block is towards the east, and the guesthouse is on the quieter, western end. Traversing the office space you encounter a series of naturally ventilated, and comfortable working spaces, brightly lit using daylight. Energy expense is saved by reducing the energy consumed in lighting. Instead of relying completely on artificial lighting, skylights have been built to allow natural daylight in. Intelligent systems switch between conventional lighting systems and daylighting to maintain visual comfort.

- Behind the building runs a foul-smelling open drain. This was a challenge but an innovative solution was evolved – the use of convection currents to divert smelly air away from the building. This was done by constructing an absorptive double wall along the periphery, with the outer wall made of black stone. When the sun heats the air in the 200 mm gap between the walls, the air rises, setting up a circulation there as well as in the building behind it. Small vents at the top of the wall serve as an outlet for this heated air, providing natural ventilation within the building and also insulation from the sun's heat.
- TERI's building has exploited the sun as an abundant source of sustainable energy. Solar water-heating systems provide hot water to all utilities.

This building is a remarkable exhibition of sensitivity to the environment, sustainable energy use, and modern design, a combination worthy of duplication in today's world where resources are limited. However, the occupants need to be sensitised on how the building functions to give comfort. If the vents for air movement are closed, the ventilation system won't function. Similarly, the daylight shelves and glazing systems need be maintained and cleaned for daylight access. Glare control also had to be put in place to avoid discomfort glare during specific times of the day.

Daylight, Electric Light and Circadian Rhythm (Delos Living LLC, 2016)

Access to daylight has great human health benefits as it reinforces our circadian rhythm. Daylight in buildings helps save on electricity consumption in lighting systems. Glare from daylight should be avoided. Daylight can be designed for and measured using tools. Spatial daylight autonomy (percentage of floor space where a minimum, light level e.g., 250–300 lux) can be met completely for some proportion (say 70% of regular operating hours by natural light) and annual sunlight exposure (ASE: Percentage of space in which light level from direct sun alone exceeds a pre-defined threshold (such as 1000 lux) for some quantity of hours (such as 250 h in a year)). These two indices can be used to ensure that a space is adequately daylight and yet there is limit on inappropriately high levels of sunlight. As per WELL Building Standard V1.0 spatial daylight autonomy (SDA 300, 50%) is required to be achieved for at least 55% of regularly occupied space. In other words, at least 55% of space receives at least 300 lux of sunlight for at least 50% of operating hours each year. LEED v4 provides incremental thresholds for 55%–90% of spaces achieving SDA (300, 50%). ASE (1000, 250) which means that no more than 10% of the area can receive more than 1000 lux for 250 h each year is common for both the rating systems. The SDA and ASE can be analysed using computer simulation tools and followed up by daylight measurements on site.

Good daylighting design has to follow the steps as below:

- (1) Set the design goals. Daylight design goals should be set for the project. The spaces should be organized in a way to have maximum daylight in regularly occupied spaces that benefit from daylight e.g., workstations in offices, patient room in healthcare facilities benefit from daylight and should be placed in periphery of buildings. Spaces such as auditoriums, audio-visual rooms etc that do not benefit from daylight integration could be placed in areas that do not have daylight access.
- (2) Building design and massing. Building siting and massing has great impact on daylighting. Thinner building footprint has better daylight integration possibility. Orientation and shading are two key strategies for daylighting. Consider incorporating both vertical fenestrations in form of windows/clerestoreys or glazing systems and horizontal systems such as atria/skylights for daylight integration. Courtyard spaces light wells are techniques for daylighting in deep office spaces.
- (3) Control glare through shading and controls. Daylight can only be effectively used, if it is glare free. Glare control devices are in form of window blinds, shades, curtains, moveable exterior louvers, screens. Typically occupant should be able to control use of glare control devices (Fig. 7).

Take the example of LEED Platinum YKK building in Tokyo Japan

The YKK building, situated in the thick urban setting of Chiyoda-ku Tokyo, is a LEED Platinum Core and Shell building. The façade is very interesting and aesthetically pleasing. However an intelligent façade design ensures favourable daylighting without glare. A sun screen provides sun protection but allows daylight to penetrate through clear double glazing. Specially designed “bottom up” blinds can be pulled down in case of glare, while also allowing daylight to filter.

Overall lighting comfort is important to ensure that a building functions to maintain uniform lighting.

Good electric lighting design is an important aspect of high performance building. Maintaining lighting standards for illumination with minimum energy expenditure with adequate controls help save energy but enables visual comfort.

In addition to providing visual comfort and ability to see objects, Light drives the circadian system that regulates physiological rhythms throughout the body's tissues and organs affecting hormone levels and the sleep-wake cycle. Circadian rhythms is largely regulated by light which the body responds to in a way facilitated by intrinsically photosensitive retinal ganglion cells (ipRGCs): the eyes' non-image forming photoreceptors. Through ipRGCs, high frequency and high intensity light promote alertness, while the absence of this stimulus signals the body to prepare for sleep. The biological effects of light on humans can be measured in Equivalent Melanopic Lux (EML), a proposed alternate metric by the WELL Building standard that is weighted to the ipRGCs instead of to the cones, which is the case with traditional illumination level measured by Lux level.

Thus occupant visual comfort is a combination of illumination level to suit function of the space, lack of glare, ability to see objects in true color, light to boost circadian rhythm, and other parameters such as brightness, contrast etc. All these should be achievable at minimum energy expenditure by switching to efficient sources such as light emitting diodes etc and a mix of controls. Choice of luminaires attributes significantly to proper lighting distribution and glare control.

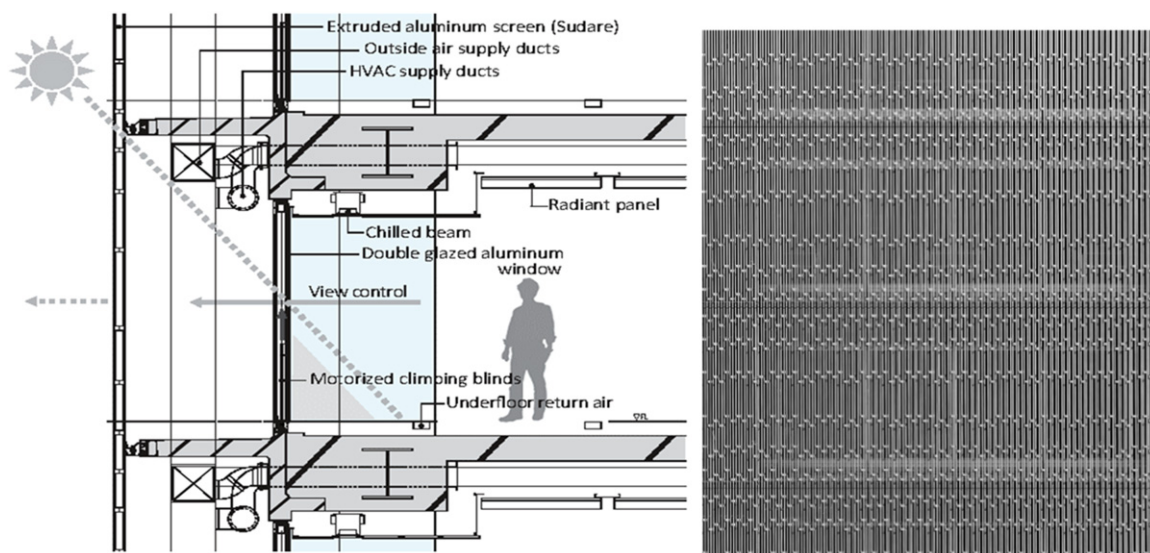


Fig. 7 Cross section of YKK building, Tokyo demonstrating innovative daylight strategies.

Indoor Air Quality

Incidence of fatigue, dizziness and loss of productivity is a common phenomenon in many offices not designed to maintain desirable air quality. Emissions from materials/furniture and furnishings including finishes, paints, varnishes, adhesive and sealants etc in form of Volatile organic compounds (VOCs) are one of the main causes of Indoor air pollution. Other common causes of bad IAQ are increased CO₂ levels due to poor ventilation, particulate matter, tobacco smoke or pollutants such as carbon monoxide (CO), ozone. The outdoor air quality in vicinity of spaces have a direct co-relation with indoor air quality. Bad indoor air has significant impact on health and wellness of occupants of a space. VOCs, combustion by-products such as CO, air borne particulate matter are known to trigger nausea, headaches, asthma, respiratory irritation and allergies. Acceptable limits of pollutants as per international standards for some common indoor air pollutants are:

- Formaldehyde levels less than 27 ppb.
- Total volatile organic compounds less than 500 µg/m³.
- Carbon monoxide less than 9 ppm.
- PM_{2.5} less than 15 µg/m³.
- PM₁₀ less than 50 µg/m³.
- Ozone less than 51 ppb.
- Radon less than 4 pCi/L in the lowest occupied level of the project.
- CO₂ less than 800 ppm.

Further, smoking should be completely banned indoors. The average life expectancy of a smoker is 10 years less than a non-smoker. In addition to nicotine, cigarettes contain about 600 ingredients that form over 7000 compounds when burned, of which at least 69 are known to be carcinogenic. Second hand smoke exposes non-smokers to the same toxins, increasing the number of people subject to health risks from smoking.

A high performance can devise several strategies to have controlled IAQ. Some options are as follows:

- Demand controlled ventilation to maintain level CO₂ level within limit. Design of ventilation system in a mechanically or naturally ventilated building should be done using Ashrae 62.1 standard, latest version or international equivalent.
- Filtration of outdoor air as well as return air in air handling units to remove particulate matter of multiple sizes. Finding out sources of contamination is another critical aspect of good IAQ design. Building nearer to traffic emission sources need to be more cognizant of NO_x CO, ozone as possible pollutants in addition to particulate matter and Volatile Organic Compounds (VOCs). The particulate matter concentration and its fineness distribution is also key to choice of filtration systems. For example installation of very high efficiency filters such as MERV 13 in isolation many not be appropriate in regions with high levels of coarse particles. Multi level filtration is necessary in such situation where a pre-filtration is applied to remove coarse particle followed by higher efficiency filters. Activated carbon filters are also recommended to remove VOCs. In buildings with air-conditioning, it is recommended to employ ultraviolet lamps (using a wavelength of 254 nm so as not to generate ozone) on the cooling coils and drain pans of the mechanical system supplies, to prevent mold growth. The filter guide to particulate matter is illustrated in figure below (Fig. 8):
- Select furniture, finishes, paints, adhesives etc with no VOCs. Testing and certification to international standards is very important. Please refer to LEEDv 4.1 and WELL Building Standard for international standards that should be referred.
- *Use of plants indoors for better air quality:* Certain common indoor plants (Areca Palm, Rubber plant etc.) provides a natural way of removing toxic agents such as benzene, formaldehyde and trichloroethylene from the air, helping neutralize the effects of sick building syndrome. However, it may be noted that indoor plants can hardly be beneficial for controlling particulate matter (PM 2.5 and 10) and need for filtration media is essential for removing particulates (Figs. 9 and 10).

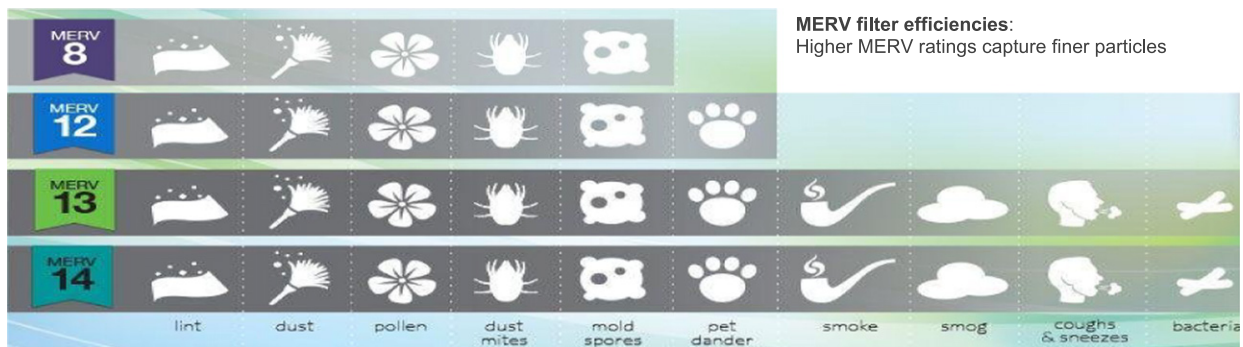


Fig. 8 Filtration efficiency.



Fig. 9 Yliopistonrinne, Tampere, Finland, LEED C&S, Gold: Use of living wall for better indoor air quality.

Case Study: Paharpur Business Centre (PBC), New Delhi

Paharpur Business Centre (PBC), (see "Relevant Website section") is India's first retrofit USGBC LEED Platinum certified green office building in heart of New, Delhi India is located in one of the most polluted places in Delhi; It is currently operating at an average annual electricity consumption of $<17 \text{ Wh/m}^2/\text{h}$. The $\sim 5000 \text{ m}^2$ building is filled with >7000 natural green plants grown, both in special soil and hydroponics and grows its own fresh air. The building, located in an area with high levels of outdoor air pollution has a very good air quality, thanks to extensive air filtration strategies deployed and use of plants for air quality enhancements. PBC has a hybrid air filtration system that includes mechanical equipments and air-filtration plants, grown in Hydroponics. It has a pre-treatment air plant and the building is kept at a positive pressure in order to avoid ingress of outside polluted air.

This unit consists of various components including a Heat Exchanger to pre cool the air without adding humidity to it. The air further passes through Microvee and HEPA filters. Electrostatic filter is used to remove particles from the air by using highly charged electrodes that ionizes the air. In air purification system, activated carbon filters are used in conjunction with HEPA filters to trap allergens and impurities like ozone, dust, lint, mold spores, smoke, benzene and other VOCs. This cooled air goes to greenhouse, which has patented planters with special plants, grown in hydroponics to reduce bacteria and fungus, VOC's and CO_2 in the air. The building is kept at a positive pressure in order to avoid ingress of outside polluted air.

Indoor Air Quality at PBC conforms to:

Temperature: $22 \pm 1^\circ\text{C}$ in winters and $25 \pm 1^\circ\text{C}$ in summers.

RH $70\% \pm 10\%$

PM $1 < 11 \mu\text{g/m}^3$

PM $2.5 < \sim 15 \mu\text{g/m}^3$

PM $10 < 50 \mu\text{g/m}^3$

Sox, $< 40 \mu\text{g/m}^3$

Nox $< 40 \mu\text{g/m}^3$

Ozone $< 50 \text{ ppb}$

TVOC's $< 500 \mu\text{g/m}^3$

$\text{CO}_2 < 350 \text{ ppm}$ above ambient

$\text{CO} < 2 \text{ ppm}$

$\text{CH}_2\text{O} < 30 \mu\text{g/m}^3$

Microbial Count $< 50 \text{ CFU/m}^3$

Compared to other buildings, there is a reduction at PBC, in the incidence of

- Eye Irritation by 52%
- Respiratory Symptoms by 34%
- Headaches by 24%
- Lung Impairment and Asthma by 12%.



Fig. 10 Greenhouse in Paharpur business centre.

While design interventions can significantly influence quality of indoor air, it is equally important to have occupant knowledge of the systems and ability to monitor and maintain. Filtration needs to be regularly checked, filters need to be cleaned or replaced, as needed. Outdoor air should be monitored and controlled as per demand of indoor spaces. It is a very regular finding in many offices, that the outdoor air system is often shut down to reduce energy consumption. This can have serious health impact and lead to sick building syndrome. It is advisable to have regular monitoring and display of common indoor air pollutants to enable taking corrective steps.

Global green building rating systems such as LEED (Leadership in Energy and Environmental Building Design) provides adequate guidance to design and maintenance of high performance buildings.

Conclusions

A High performance building, thus evolves through a careful design process and has to be maintained at high level of performance through occupant knowledge of systems, monitoring of performance parameters and by taking adequate corrective actions, if it fails to perform. Such buildings also, can be designed and maintained to improve on performance over time, by taking suitable retrofit actions. High performance buildings need to be carefully designed by setting performance goals that could be set at a whole building level or at component or system level. Performance goals are varied that can comprise energy consumption per unit area or per occupant, thermal, visual or acoustic comfort provided and maintained, indoor air quality maintained etc. Achievement of high performance is not only a design goal but a long term goal over life of building. Thus operation and maintenance plays a significant role to ensure this. LEED rating system provides guidance on designing and maintaining high performance buildings.

See also: Use of Lime Mortar and Post-Occupancy Thermal Performance Analysis of Buildings

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Further Reading

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Relevant Website

www.pbcnet.com
Paharpur Business Centre
Eco friendly and environmentally certified.

Use of Lime Mortar and Post-Occupancy Thermal Performance Analysis of Buildings

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What is Lime?

Lime is a dehydrated and calcined mineral comprised of Calcium and Magnesium oxides and hydroxides. In the raw form, it is extracted from 'Limestone' (CaCO_3), which is a naturally occurring sedimentary rock and is found in abundance throughout the world. Geologically, limestones are 100–500 million years old and were formed out of compressed calcareous sea remains. Today, it is mined from quarries and is pulverised before being sent to the kilns to be burnt at temperatures ranging from 700 to 900°C to remove the impurities, moisture and excess carbonic content in the form CO_2 . The highly hydrophilic and caustic burnt product, Calcium Oxide (CaO), when mixed with water undergoes an exothermic reaction to yield an alkaline mixture known as 'slaked lime' – Ca(OH)_2 . Slaked lime is adhesive in nature and is generally mixed with multiple aggregates to prepare plasters or mortars, which, with prolonged exposure to ambient air and the sun, undergo carbonation to re-establish itself in its carbonate form. This process, as indicated in Fig. 1, holds true when the raw limestone is pure in nature, i.e., it contains more than 95% of CaCO_3 . The slaked lime yielded after processing pure limestone is called as 'non-hydraulic lime'.

Limestone, in abundance is not found in its pure form. The impure limestone generally contain oxides of Silica, Aluminium, and Iron. However, depending on the geological history of the land, these compounds largely vary, and so does the adhesive nature of the plasters/mortars formed with this 'hydraulic lime'. Vicat, in his early works in the 19th century quoted on the 'Cementation Index' of hydraulic and non-hydraulic limes, which governs the hydraulicity of any lime substrate (Vicat, 2014). Depending on the concentration of the active clay component (impurity), limes are characterised as (Non Hydraulic Lime-n) NHL₂, NHL_{3.5}, NHL₅ etc.; the numbers in suffix govern multiple physical characters of the substrate. For example: the porosity and resultant water permeability of limes decreases as the number in suffix increases; i.e., pure NHL has the highest water permeability, while NHL₅ has the lowest.

Physical Properties

Rangarajan comments on the porous nature of lime, which allows the façade to breathe and remediate the problem of moulds. In addition to its hygroscopic characteristics, lime has a lower embodied energy in comparison to the popular building fabrics like cement (Reddy and Jagadish, 2003). Edwards, in his thesis on 'Properties of hydraulic and non-hydraulic limes for use in construction' has performed experiments to bring out the physical properties of limes. He used Fen-X lime mortar blocks made as per the British standards and cured them under controlled environments (Edwards, 2005). The Table 1 compares the compressive strength of air and water cured Fen-X lime mortar mixed with coarse sand in the lime:sand ratios of 1:1, 1:2, and 1:3 for 1, 2, 4, and 8 weeks of duration.

Fen-X, being a natural hydraulic lime, had the capacity to cure under water too (Constructo, n.d.). It can be seen from the compressive strength measurements, the curing was quicker in air for 1:1 mixture of sand and lime for a prolonged period. However, the 1:2 and 1:3 mixtures for the 'water' case were found to be more durable. Had the substrate been non-hydraulic, the

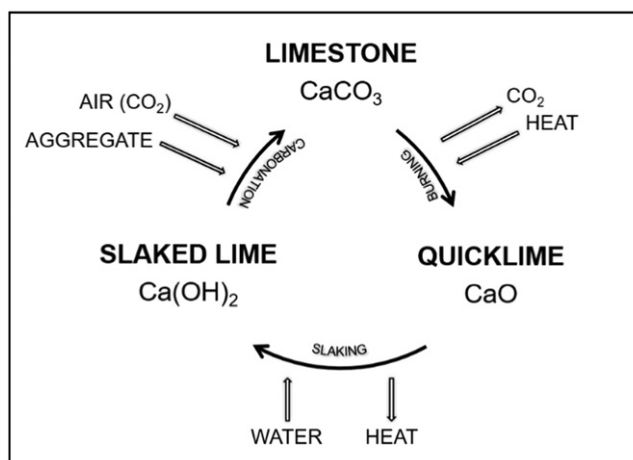
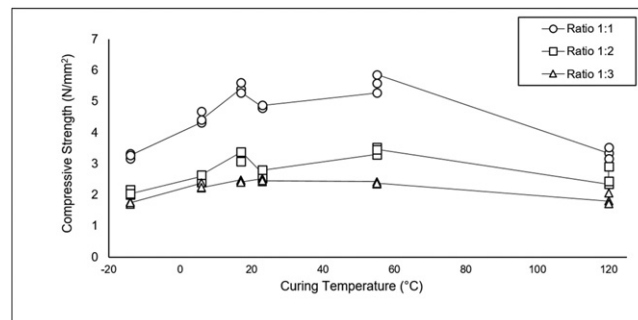


Fig. 1 The lime cycle.

Table 1 Compressive strength of hydraulic lime mortar blocks, mixed with coarse sand in ratios 1:1, 1:2, 1:3, and cured in air and water for 1, 2, 4, and 8 weeks

Weeks	Compressive Strength (N/mm ²)					
	Air Cured (Lime:Sand)			Water Cured (Lime:Sand)		
	1:1	1:2	1:3	1:1	1:2	1:3
1	1.98	1.95	1.66	2.36	1.71	1.30
1	2.10	2.00	1.65	2.25	1.58	1.16
1	2.15	2.12	1.57	2.28	1.64	1.17
2	3.74	2.20	1.37	3.04	2.18	1.70
2	3.51	2.04	1.36	3.14	1.99	1.60
2	3.41	2.06	1.37	2.98	2.05	1.63
4	4.39	1.97	1.17	4.06	2.90	1.98
4	4.19	2.05	1.05	4.20	2.92	1.79
4	4.21	2.08	1.04	4.14	2.79	1.98
8	5.94	2.17	1.14	5.29	3.52	2.57
8	6.11	2.27	1.17	5.61	13.54	2.32
8	6.04	2.19	1.17	4.95	3.18	2.33

Note: Edwards, A.J., 2005. Properties of hydraulic and non-hydraulic limes for use in construction. Doctoral Dissertation, Edinburgh Napier University.

**Fig. 2** Variation of compressive strength with curing temperature for 1:1, 1:2, and 1:3 ratio mortars of lime and sand. Reproduced from Edwards, A.J., 2005. Properties of hydraulic and non-hydraulic limes for use in construction. Doctoral Dissertation, Edinburgh Napier University.

mortar under water would not have hardened at all. In addition to the ambient state, the curing temperature of air also plays a major role in the hardening of the lime. **Fig. 2** below, based on the tabulations by Edwards, shows the variation of compressive strength of lime mortar blocks of 1:1, 1:2, and 1:3 ratio of lime and sand, cured at temperatures ranging from -14 to 120°C (Edwards, 2005). The blocks with 1:1 ratio of sand and lime were found to be the strongest when cured at 55°C , while sub-zero atmospheric temperatures yielded low strength. Therefore, a lime structure made out of same materials in northern Europe will be weaker than one made in central Africa.

The ability to absorb water is one of the most unique characteristics of lime mortar and plaster. The porous nature of solidified lime contributes to the reduction of ambient humidity. Raw limestone has a porosity percentage varying between 2% and 8%, while the pore size ranges between 10 and 100 nm (Atlas, 1981). The extent of porosity of the final hardened product depends on the lime sintering temperature. High temperature leads to emission of CO_2 and consequently leads to shrinkage of the crystal structure. This causes the creation of new interstitial gaps and widening of the existent ones to serve as ideal spots for water molecules to be adsorbed. The porosity of a regular air dried lime mortar is 30% with a 14% water absorption - both of these percentages decrease with the fraction of sand (Edwards, 2005).

Lime in Daily Life

The inception of usage of lime by humans happened about 10,000 years ago (Carran *et al.*, 2012). Its glimpses can be found throughout the history - be it the 7000 year old remains of Jordan valley, the 3000 year old Harappan colonies, or the 2000 year old roman Pantheon, all incorporate lime in one or the other form (Ellis, 2001; Rao, 1979; Muench, 2017). **Fig. 3** shows the white lime plastered walls of the Padmanabhapuram palace in Tamil Nadu, India. The palace was constructed around 1601 CE and includes multiple independent structures for different functions - the centre of the complex includes a four-storeyed mansion for the royal residence.

As discussed in the section above, the ripening of lime mortar and plaster is optimised at relatively high ambient temperatures; its hygroscopic nature allows the absorption of excessive moisture, while the white colour adds to the albedo to regulate the



Fig. 3 Lime plastered walls under traditional tiled roofing in the Padmanabhapuram palace, Tamil Nadu.

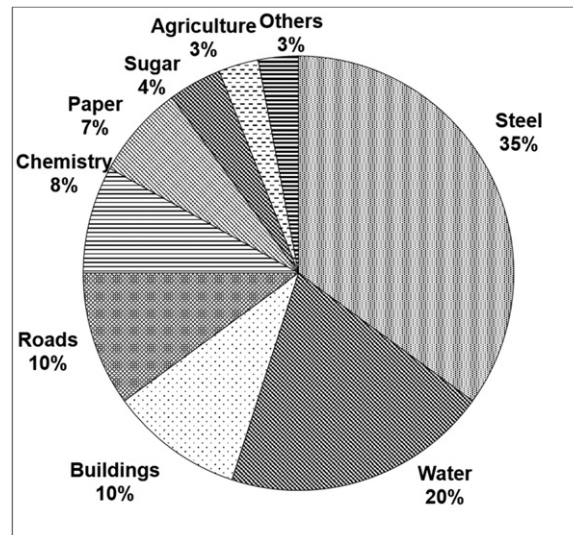


Fig. 4 Usage of lime across industries. Reproduced from Atlas, S., 1981. Process Engineering of Metals and Ceramics. Characterisation of Limestone and Lime. Düsseldorf, Germany: Verlag Stahleisen MBH. 28. Available at: http://www.ltv.ovgu.de/ltv_media/Downloads/Lehre/Vorlesungen/Process+Engineering+of+Metals+and+Ceramics/Chapter+5+Characterisation+of+limestone+and+lime.pdf.

indoor temperatures. Free lime present in the building plaster absorbs low amounts of CO₂ for a prolonged period, and helps keep the indoor environment quality in check (Anon2). The possibility of producing lime at a small scale, and in a varied proportion with multiple aggregates makes it a great binder. Because of being partly water soluble due to the presence of compounds like gypsum, the remediation of cracks is easier in lime – water carries the soluble molecules from healthier portions of the plaster into the cracks and crevices to ultimately dry and solidify into a new chunk of plaster (Rangarajan). These and more are the reasons why lime has been widely used across civilisations and ages for constructing particular building elements or the entire structures (Kapoor and Gujral, 2017).

In the present scenario, buildings utilise only 10% of the total lime used by humans. Other industries such as steel, and water purification utilise a major portion of it as shown in the figure below (Fig. 4).

Buildings in Lime

Buildings consume about 40% of the total global energy (Pérez-Lombard *et al.*, 2008). The tropical climates incur huge cooling loads and have the opportunity of incorporating passive design strategies for a lower carbon footprint. The applicability of lime as a building fabric is highest in the ‘warm and humid’ climate zone defined as per the Indian ECBC (Energy Conservation Building Code) and NBC (National Building Code) – in these climates, the white exteriors reflect light and reduce façade temperatures, while the porous nature moderates the indoor relative humidity (Energy Conservation Building Code, 2017; National Building Code of India, 2005). This helps reduce the need for energy intensive HVAC systems and ultimately results in enhanced sustainability. In order to understand the thermal behavior of buildings incorporating lime plaster and mortar, two occupied buildings – Language Lab (LL) and Mukuduvidu Residence (MR), located in the international township of Auroville, Tamil Nadu, were studied for air/surface temperatures and relative humidity through permanent data loggers and hand-held instruments for the hottest portion of the year.



Fig. 5 Buildings under study: (a) North façade of LL. (b) Central courtyard in LL. (c) North Façade of MR. (d) Indoor view under the vault. (e) Window detail in the dome.

Buildings Under Study

Language Lab (shown in [Fig. 5\(a\)](#)) is a distinctive centre known for teaching languages through its guided study programmes and practicing the Tomatis therapy for cognitive development and psychological wellbeing ([Anon3](#)). The building had a constructed area of 930 m² per floor and came under the category of ‘educational buildings’ as per the Indian NBC. The function of the building required the indoors to be moderated from the ambient heat and provide a mellow backdrop for the therapy rooms. During peak hours of group classes, there were around 50 occupants in the building. All the interior surfaces of the structure were plastered in fine *kadukkai* infused lime on the inside and a coarse lime on the exterior. The slabs of the two floors, including the roof, were made up of reinforced concrete – the floors were covered in polished stone, while the rooftop surface was plastered in white lime. The 27 m², pebble filled central courtyard (as shown in [Fig. 5\(b\)](#)) provided daylight to the indoors while helping maintain a constant wind circulation. The building was occupied and functional during the measurement period, however, multiple sustainability-enhancing elements like cooling towers and solar water heaters were still under construction.

Mukuduvidu (shown in [Fig. 5\(c\)](#)) was a residential building as per the Indian NBC and housed 2–3 occupants throughout the year. The building extensively utilized lime as a mortar and plaster. However, unlike conventional modern lime structures, it used domes and vaults as the architectural form ([Fig. 5\(d and e\)](#)). The two identical domes were 4.8 m in diameter and had an external surface area of 36 m² each, while the lime plastered surface above the vault had a surface area of ~90 m². The domes and the vault is made entirely out of country fired bricks and lime mortar, while the structure of the building also utilized granite slabs and exposed concrete. Located amidst the thickets of bamboo, deciduous trees, and a naturally maintained pond, the building was designed to moderate the indoor thermal environment. It incorporated the tandem of structural and functional sustainability by using optimal size and construction strategies ([Doctor-Pingel et al., 2014](#)). The study for this case focused on contrasting the thermal properties of domes versus vaults made in lime. Interior and exterior surface temperatures for the two domes and vault, as well as air temperature in the spaces under the domes and vault were monitored.

[Fig. 6\(a and b\)](#) show the plan of the buildings with the zones under study. The windows/voids in the buildings, highlighted in yellow allowed efficient air ingress and kept the indoors cool. During the period of study of LL (June 2018) and MR (May 2014), the most prominent wind direction was due South-West.

Local Additives to Lime

LL and MR used lime mortar and plaster made with a fermented mixture of crushed *Terminalia chebula* or ‘Kadukkai’ seeds and jaggery water throughout the building. The mixture of these two components made the plaster water resistant and added

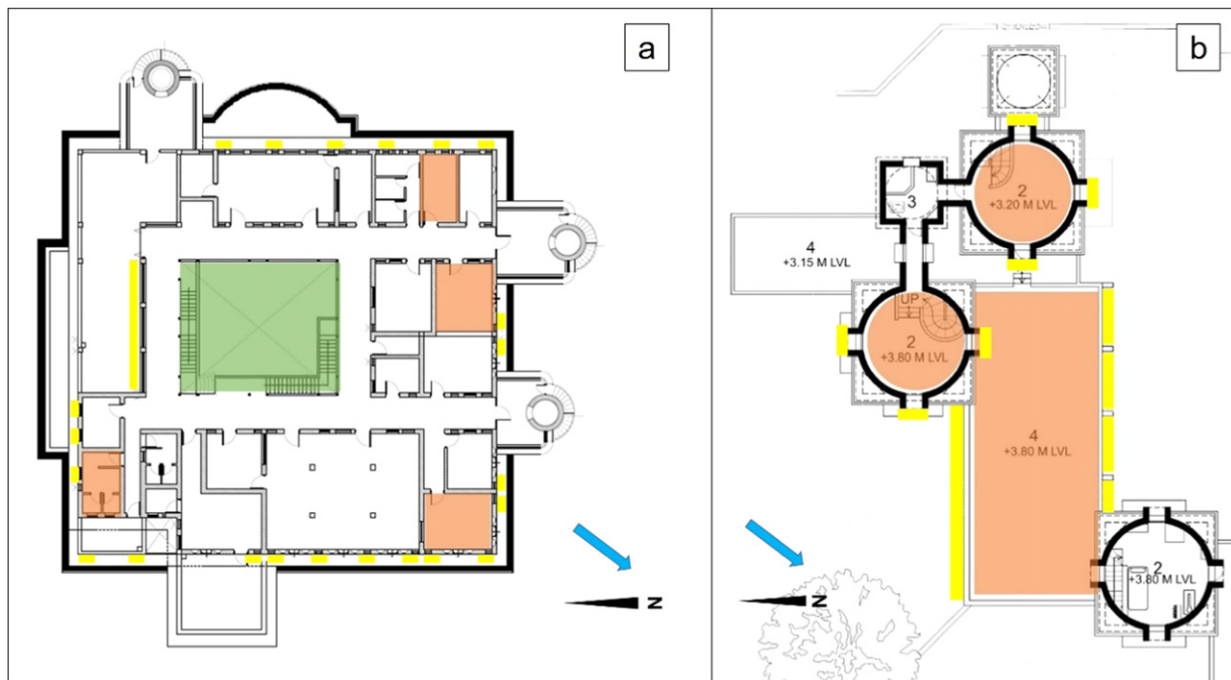


Fig. 6 (a) Plan of LL. (b) MR with the zones under study highlighted in red. The open courtyard in LL is highlighted in green; the blue arrows indicate the prominent seasonal wind direction while the openings/windows are highlighted in yellow.

a beige tinge to the natural colour, while preserving the elemental cool characteristics of lime. Before being mixed in a ratio of 9:10 (Kadukkai: jaggery) with 300–400 litres of unchlorinated water, the Kadukkai seeds were ground coarsely. The Kadukkai, jaggery and water mixture was fermented for two days before being mixed with lime. This mixture was allowed to rest for two weeks in sealed containers. Thereafter, the mixture was used to prepare the plaster with one part lime per three parts sand. The plaster was applied in two coats – the first, coarse coat was allowed to dry for a day before the application of the final coat with a higher amount of fermented water mixture for a smoother finish. The occupants preferred the beige tone of Kadukkai infused lime in LL, while the occupants preferred white indoors and painted the surfaces in white lime in MR. Emayan, in his work on compressive strength of lime mortar with jaggery and Kadukkai admixtures found out that the compressive strength of lime mortar prepared as per the aforementioned method yielded a compressive strength of 1–2.24 N/mm² for a two-week curing period (Emayan and Rahuman, 2015). In addition to this admixture, traditional Indian construction practices have been using edibles like curd, gram, and plant based substrates as additives in lime mortar since centuries, as can be seen in Table 2 (Thirumalini and Sekar, 2013). Attempts have also been made to use potato starch to improve the viscosity and workability of lime based mortars (Izaguirre *et al.*, 2010).

Instrumentation and Data Logging

In order to study the indoor parameters of the two buildings, research questions concerning the behavior of various building elements were formulated and strategic logger placement positions were identified. Fig. 7 shows the types of loggers and hand-held equipment used for the analysis as per the following site-specific research questions:

Case 1: LL

- (1) What were the internal and external surface temperatures of the East, West, North, and South facades throughout the day?
- (2) What was the difference between the roof surface and the ceiling surface temperatures for the hottest hours of the day?
- (3) How did the indoor air temperatures and relative humidity vary across various occupied zones?

Case 2: MR

- (1) What were the internal and external surface temperatures for the two domes and vault throughout the day?
- (2) How did the surface temperature vary with height for the domes?
- (3) How did the indoor air temperature and relative humidity vary for the occupied spaces under the domes and vault?

The measurements across the two buildings involved long-term logging with the help of HOBO loggers as shown in Fig. 7(a). Three kinds of loggers (types B, C and D) were used as per the requirements. Logger B (U12-013) measured air temperature and RH through

Table 2 Usage of traditional organic additives in lime mortar in India

Additives	Purpose
Curd	Finishing
Black Split Gram	Plastering
Jute Fibre	Bonding
Plant Gum	Retarding
Raw Sugar	Bonding
Straw	Crack Prevention
Glue	Bonding
Jaggery	Hardening

Note: Thirumalini, P., Sekar, S.K., 2013. Review on herbs used as admixture in lime mortar used in ancient structures. Indian Journal of Applied Research 3 (8), 295–298.

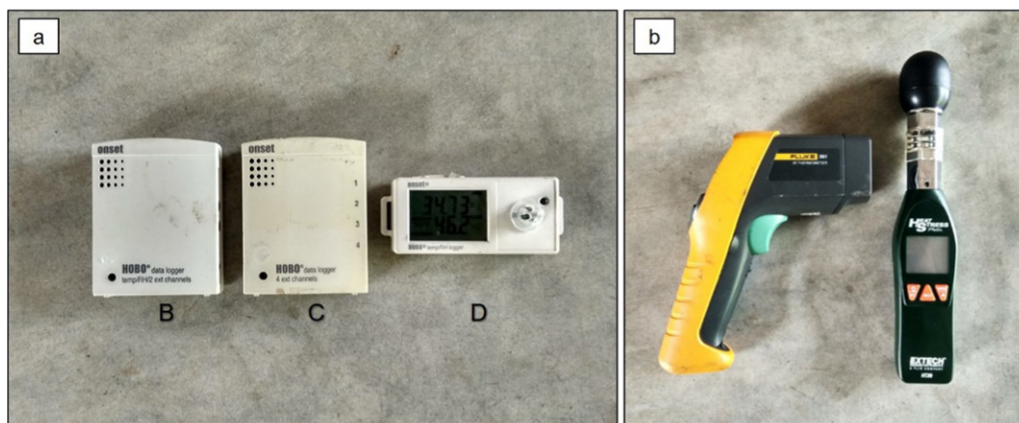


Fig. 7 Instrumentation equipment: (a) Type B, C, and D long-term HOBO loggers. (b) Hand-held Fluke 561 IR Thermometer and EXTECH HT30 Globe Thermometer.

inbuilt sensors and had the provision of two external sensor connections, which in our case were used for surface temperature measurement. Logger C (U12-006) did not have any in-built sensor and was used to measure surface temperature through its four external channels, whereas Logger D (UX100-011) was used to measure air temperature and RH through the built in sensors.

Hand-held equipment, as shown in Fig. 7(b), were used to gather instantaneous readings of the same parameters as measured by the long-term loggers. Instantaneous air and surface temperatures with RH were measured on a sporadic basis and compared against the long-term readings. A comparison between the typical hand-held and long-term readings for LL is given in Appendix A.

The two buildings were placed with multiple type B, C, and D loggers at strategic locations to measure the surface and air temperatures. The locations of logger placement, with the photos of the loggers on site are shown in Figs. 8 and 9.

The data from these loggers was collected after a monitoring of two weeks (6 June 2018–22 June 2018) for LL, and one month (1 May 2014–31 May 2014) for MR as a part of two independent studies. During the monitoring period, the loggers were inspected for loose connections, battery status, and quality of readings. For analysis, the readings were hourly averaged and compared on a case-by-case basis.

Results and Discussion

Language Lab (LL)

The surface temperature sensors installed on the four leading lime plastered walls logged the internal and external surface temperature readings. As shown in Fig. 10(a) - the walls were 640 mm thick and were made out of fired bricks with a lime mortar and Kadukkai-lime plaster on either sides. The exterior side had a coarse plaster finish (35 mm thick) while the interior side had a finer plaster layer (25 mm thick). The wall included a 115 mm air cavity to increase the thermal resistance.

The temperatures across these two surfaces varied with the sun's position throughout the day – the gradual incidence of sun was evident in the early hours on the exterior temperatures of the eastern façade, while as the noon passed, the temperature plateaued

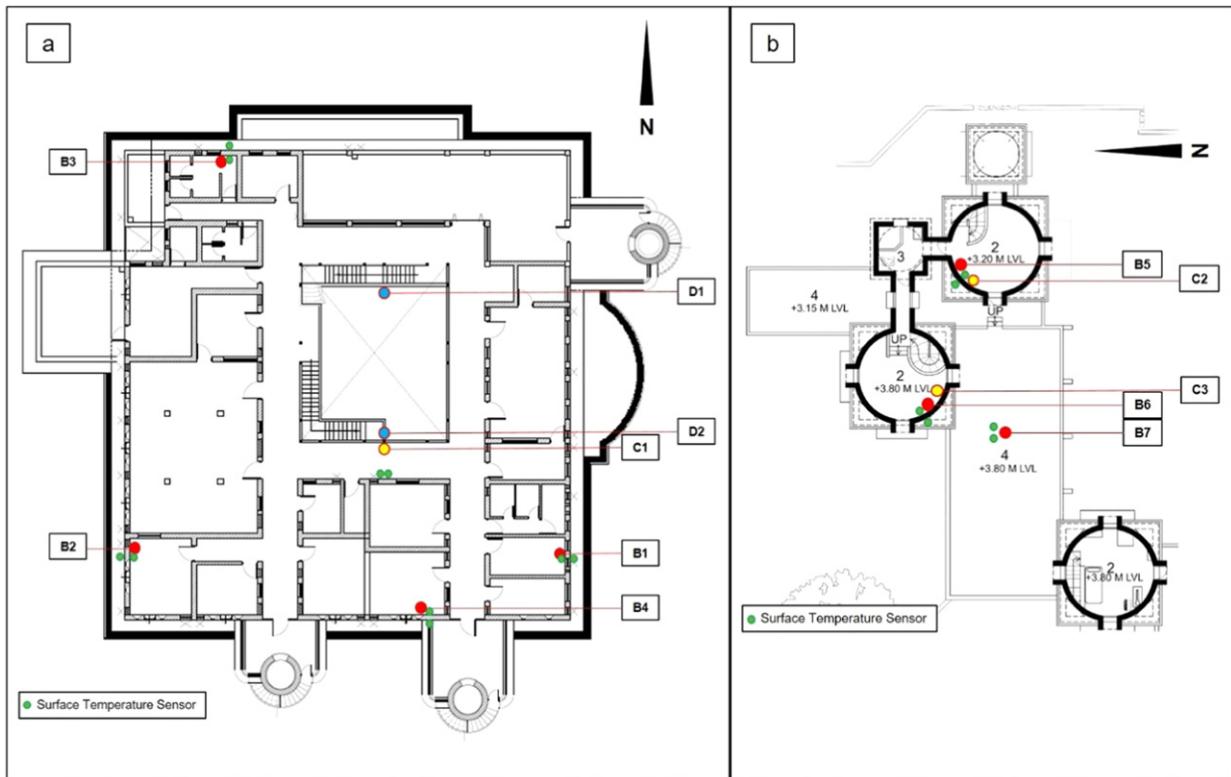


Fig. 8 Position of loggers and sensors in: (a) LL. (b) MR.

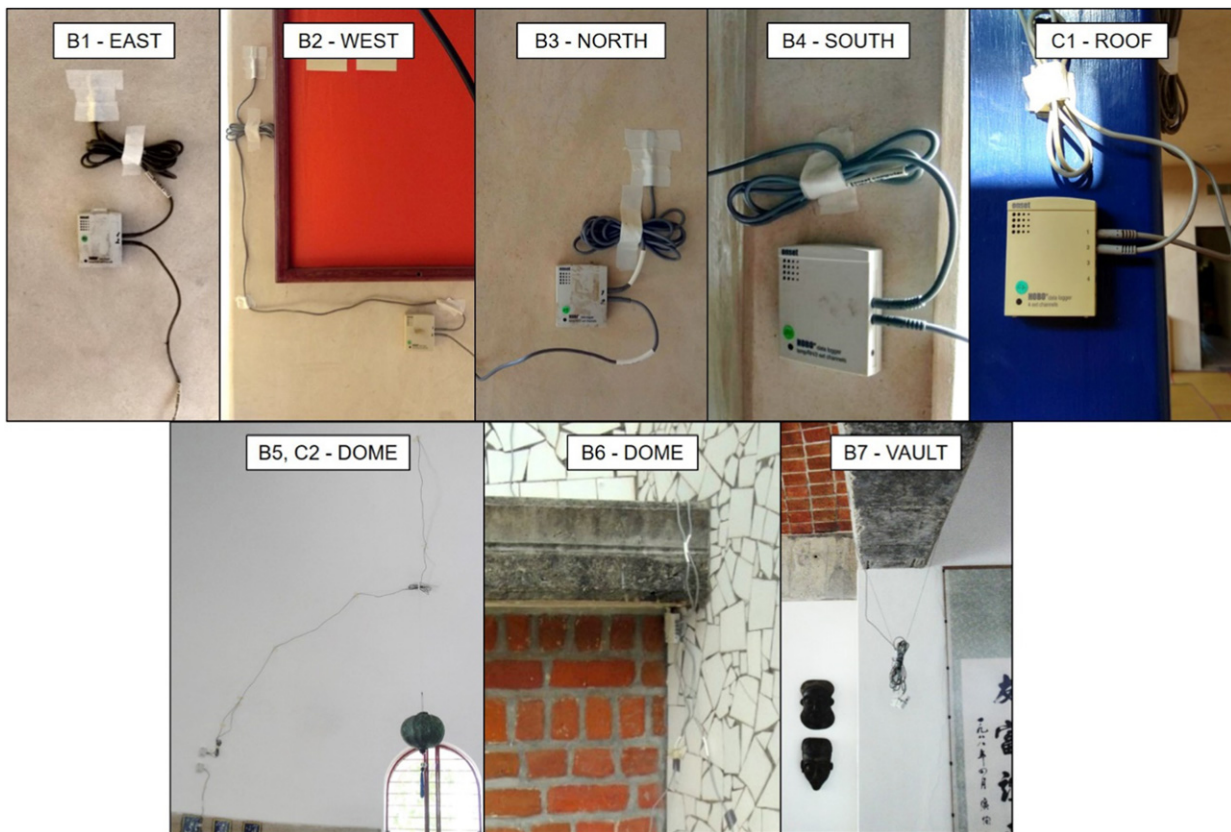


Fig. 9 Loggers placed in LL (B1, B2, B3, B4 and C1) and MR (B5, B6, B7 and C2).

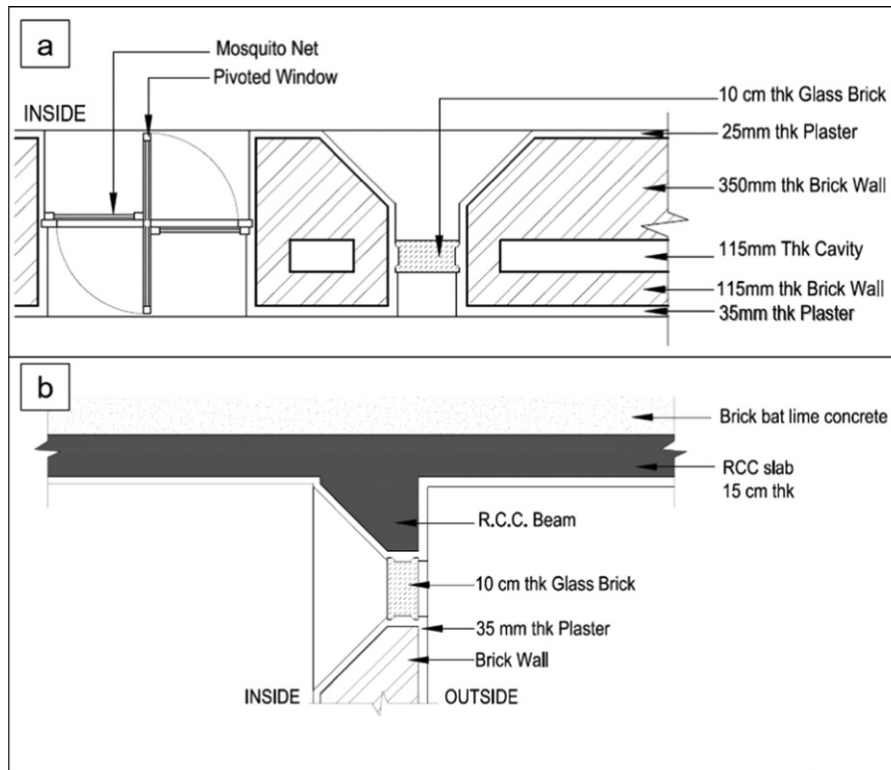


Fig. 10 Cross section of: (a) wall. (b) roof in Language Lab.

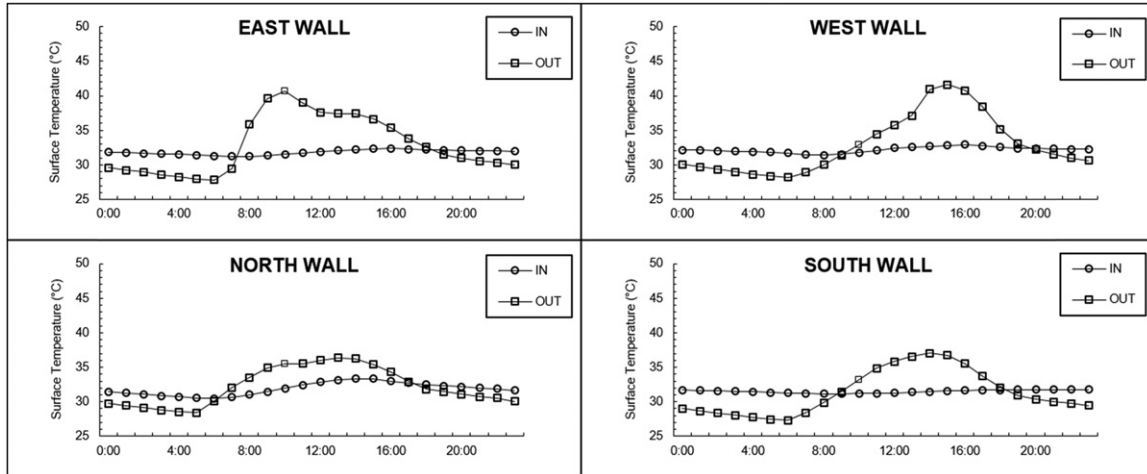


Fig. 11 Hourly averaged surface temperatures for the four leading lime plastered facades.

until the late evening. This was when the sun struck the western façade and elevated its exterior temperature to 1° lesser than the exterior of the eastern façade (41.62°C). As shown in [Fig. 11](#), the west wall was found to be warmer than the east wall in terms of peak temperature. This was because the low ambient temperatures during the night and early morning allowed the east wall to cool down to as low as 27.8°C , which required a higher amount of heat to be brought to an elevated temperature. However, the warmer ambient air and diffused component of solar radiation brought the west wall in the range of $35\text{--}37^\circ\text{C}$ during the late morning hours, even before direct solar radiation struck it. The highest exterior surface temperature of the north and south walls remained at 36.4°C and 37.0°C respectively as at no point of time did the direct sunlight fall on the wall. The indoors surface temperatures across each of the walls were moderated in the range of $30.5\text{--}33.3^\circ\text{C}$ with diurnal fluctuations of 1.2° , 1.5° , 2.8° , and 0.6°C for East, West, North, and South walls respectively. The thermal time lag – time difference between the outdoor and indoor maximum temperatures – was found to be 6 h for the east and south walls, while the west and north walls had a minimal time lag

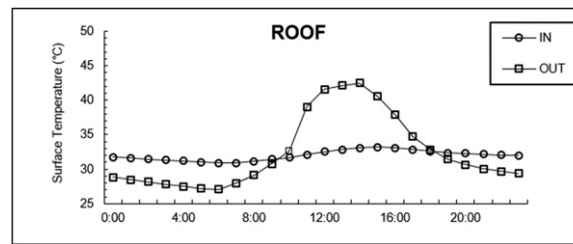


Fig. 12 Hourly averaged surface temperature for the lime plastered roof.

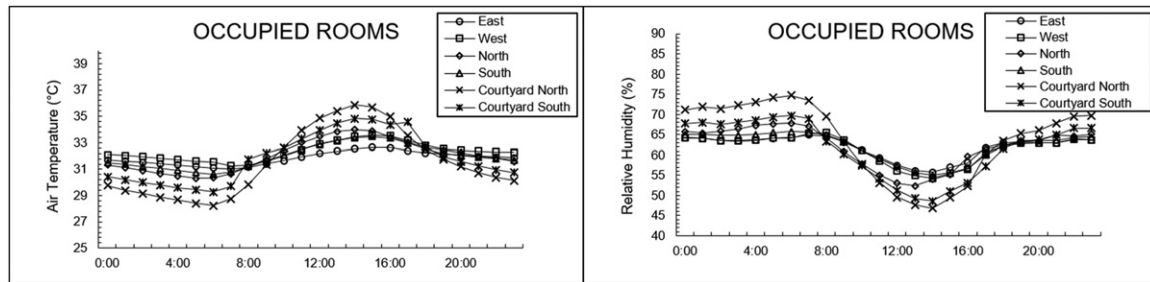


Fig. 13 Hourly averaged air temperatures for occupied rooms and the central courtyard.

of 1 h each. The east and south zones under study were unoccupied for most of the time during the period of study and did not have their windows open for cross ventilation to influence the indoor temperatures. While the western zone experienced constant occupancy with open windows and the operation of a ceiling fan, in addition to the northern zone being ventilated by two continuously open windows – this enhanced the convective exchange with the ambient air and resulted in temperatures higher than the interior surfaces on the east and south.

The roof, as shown in Fig. 10(b) was made out of reinforced concrete (150 mm), a layer of brick bat lime concrete (50 mm) and lime plaster on either sides (similar thickness to wall). Fig. 12 shows the hourly averaged surface temperatures for the internal and external surfaces of the roof. The white lime plastered exterior surface went as high as 43.5°C during the period of study while the internal ceiling surface was moderated at 33.1°C for the hottest hour, creating a thermal difference of 10.4°C. The thermal time lag between the exterior and interior was of 2 h – which is low, considering the high thermal mass and reflectivity of the white lime plaster. The possible explanation for this can be that the ceiling surface under study was exposed to the courtyard zone, which experienced conditions similar to the outdoor environment. The air temperature of courtyard would have affected the ceiling temperature and overshadowed the insulating characteristics of the roof.

Fig. 13 shows the hourly averaged air temperature and relative humidity trends for the four occupied zones and the courtyard. The parameters across the courtyard were closest to the outdoor parameters for it was exposed to the ambience and was open from all four directions at the top. The northern part of courtyard was closest to the fenestration, thus experienced a higher diurnal variation of 7.7°C and 27.9% RH in comparison to 5.6°C and 21.1% RH of the southern part. The studied rooms were warmer and less humid than the courtyard during the non-daylight hours, while the opposite was true during the daylight hours. The air temperature of the rooms was moderated in the range of 30.3–34.0°C, with the northern room being the warmest for the aforementioned reason concerning surface temperatures. There was a fluctuation of 1.7°, 2.3°, 3.7° and 2.8°C for the east, west, north and south rooms respectively, while the RH varied with 9.2%, 11.2%, 15.5%, and 10.7% for the respective rooms.

Mukuduvidu Residence (MR)

The two domes and vault studied for this case, as shown in Fig. 14, were dominantly made out of kiln fired brick and lime. The first dome had a glass cover (open at the sides) at the top to restrict rain, while the second dome had a wind-operated mechanical ventilator. Additionally, both the domes had openable windows as indicated in Fig. 6(b). The vault had mosquito-mesh covered openings right under the arches on either sides to allow natural ventilation. The reflective white exterior surfaces of the domes and the vault were studied for surface temperatures at various heights and the thermal trends are shown in Fig. 15.

The three heights H1, H2, and H3 correspond to 84, 271, and 317 cm from the floor level for the case of domes. The interior and exterior surface temperatures in the two domes increased with the height. However, the magnitude of peak temperatures varied considerably. For the hottest hour of the day, the exterior surface temperatures for dome 1 and 2 at the

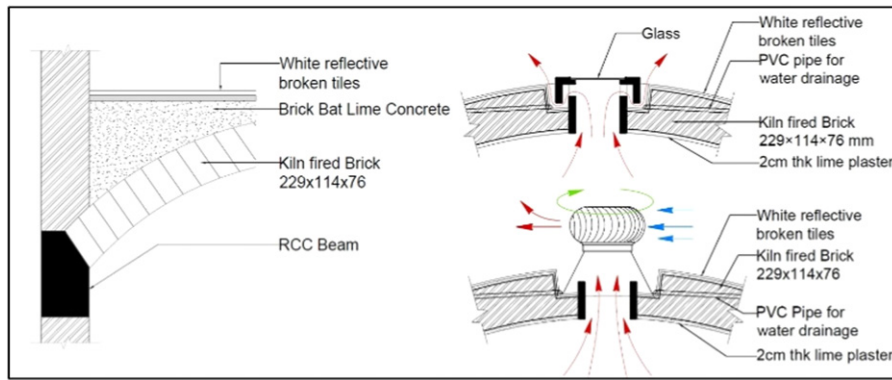


Fig. 14 Section of the two domes and the vault in Mukuduvidu.

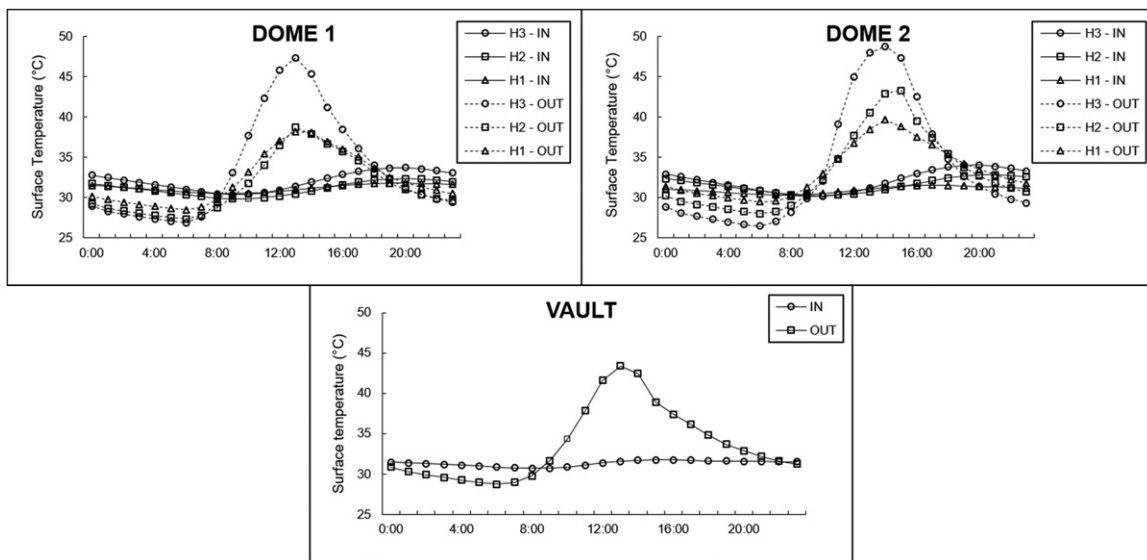


Fig. 15 Hourly averaged interior and exterior surface temperatures for the two domes and vault.

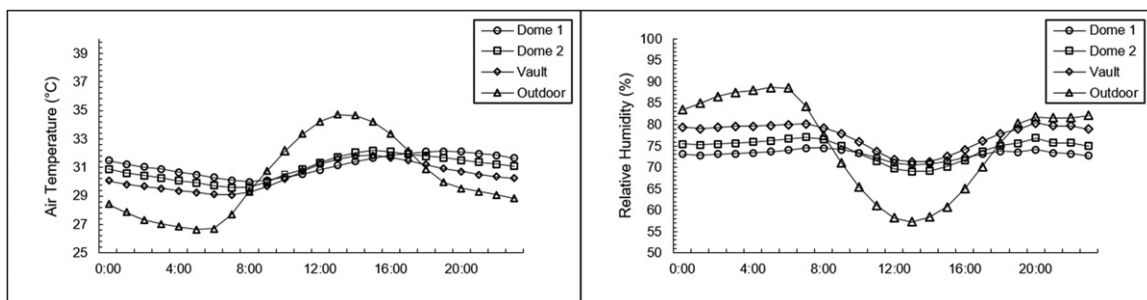


Fig. 16 Hourly averaged air temperature and relative humidity for the zones under the domes and vault.

three height levels were 38.2°, 38.7°, 47.3°C and 39.6°, 43.3°, 48.7°C respectively, while the interior surface temperatures were at 31.8°, 32.4°, 33.7°C and 31.5°, 32.8°, 34.0°C respectively. There existed a thermal time lag of 6 and 5 h at the highest levels for domes 1 and 2 respectively. The exterior surface temperature across the vault was lower than that of the domes by 5.3°C, while the vault ceiling temperature remained between 30.7 and 31.8°C throughout the day with a minimal thermal time lag of 2 h.

Fig. 16 shows the variation of hourly averaged air temperature and RH of the zones under the two domes and the vault. The outdoor air temperature and RH varied in the range of 26.6–34.7°C and 57.3%–88.7%. The highest temperature across the zones

under domes was 32.1°C and 32.2°C, with the lower limits being 30.0°C and 29.6°C respectively. The vault zone had a better ventilation and resulted in a temperature range of 29.1–31.8°C. The efficient ventilation for the case of vault was also reflected in the time lag for air temperatures. The air in zone under the domes had a time lag of 6 and 3 h with respect to the ambient air, while the vault had a time lag of 2 h. The air in the domes was at lower RH levels in comparison to the domes. For the coldest hour of the day, the zones under the domes had 73.7% and 76.3% RH, in comparison to 79.8% RH of the vault zone.

Conclusion

This article discussed the merits of using lime as a building fabric, its physical properties as per existing literature and its performance in moderating temperatures across built structures. Some of the benefits of using lime are:

- Abundant availability throughout the globe.
- Simplistic processes (burning, slaking, & carbonation) and involvement of non-toxic chemicals.
- Recyclability.
- Comparable physical properties to cement-based fabrics.
- Freedom of choice of aggregates.
- Ability to cure under water (for the case of hydraulic lime).
- Progressive increase in strength over time.
- Porosity of the cured surface (helps regulate humidity).
- Easy remediation of cracks and defects in comparison to conventional building fabrics.
- Possibility of mixing various natural substrates for enhanced properties.
- Moderate to high optimum curing temperatures (adept for warmer tropical regions).
- Natural white colour with high reflectivity.
- Possibility of downscaling the production as per need, etc.

In addition to the aforementioned points, use of lime as a building fabric proves to be thermally optimal for the buildings in the warm-humid climatic zones. The study of thermal parameters across the various 'Kadukkai'-lime plastered surfaces and occupied zones for Language Lab (LL) and Mukuduvidu Residence (MR) in the warm-humid tropical climate of Auroville, India yielded notable findings. In LL, the exterior temperatures for the east and west façades were higher than the north and south façades by 10.7%, while the internal surfaces of the façades, at an average, were cooler than the exterior surfaces by 16.8%. The air temperatures of the directional occupied zones were found to be cooler than the naturally ventilated courtyard by 4.2% during the hottest hour of the day – however, due to the lack of outdoor temperature readings, one cannot make a conclusive statement about the air temperature in this case. For MR, the exterior surface of the vault was cooler than the domes by 10.8%, while the interiors of the vault were cooler by 6.5%. The highest point of exterior surface temperature measurement (H1) was warmer than the lowest point (H3) by 18.7% for the two domes. The air temperatures in the zone under the vault was cooler than the zones under the domes by 1.3% for the hottest hour of the day, while the same was cooler by 3.1% for the coldest hour of the day. The domes performed better in terms of thermal time lag, while vault was able to maintain a higher temperature difference. The domes were also able to reduce the relative humidity levels by 7.3% in comparison to the vault. The extent of ventilation for the two building forms played a major role in defining the thermal variables in the respective zones.

Despite the existent research, there exists a wide scope of research on a wide variety of limes and their usage in structures throughout the world. The abundant knowledge must be documented from the traditional artisans, who have been meticulously perfecting the art of building in lime since generations to identify the best-possible solutions to the modern building needs and support the sustainable building fabric called lime.

Acknowledgement

We thank Tapas and Mita, from the Language Lab for facilitating a smooth study. We also thank the CBERD project team from Auroville Centre for Scientific Research and Studio Naqshbandi for the study of Mukuduvidu Residence.

For Mukuduvidu Residence: the U.S. Department of Energy (DOE) and the Department of Science and Technology (DST), Government of India (GOI) provided joint funding for work under the U.S.–India Partnership to Advance Clean Energy Research (PACE-R) program's "U.S.–India Joint Centre for Building Energy Research and Development" (CBERD) project. The Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Building Technology, State and Community Programmes, of the U.S. DOE under Contract No. DE-AC02-05CH11231 supported the U.S. CBERD activity. The DST, GOI, administered by Indo-U.S. Science and Technology Forum, supported the Indian CBERD activity.

Appendix A

Comparison of hand-held and long-term logger readings for Language Lab

<i>Hand-held</i>			<i>Long-term</i>	
<i>Zone</i>	<i>Timestamp</i>	<i>Temp. (°C)</i>	<i>Timestamp</i>	<i>Temp. (°C)</i>
East Surface IN	06-06-2018 13:16	32.0	06-06-2018 13:00	31.9
			06-06-2018 14:00	31.9
East Surface OUT	06-06-2018 13:25	37.3	06-06-2018 13:00	38.5
			06-06-2018 14:00	36.6
West Surface IN	06-06-2018 13:18	32.9	06-06-2018 13:00	32.8
			06-06-2018 14:00	32.6
West Surface OUT	06-06-2018 13:26	43.8	06-06-2018 13:00	38.2
			06-06-2018 14:00	50.2
North Surface IN	06-06-2018 13:19	33.2	06-06-2018 13:00	33.2
			06-06-2018 14:00	32.9
North Surface OUT	06-06-2018 13:29	36.2	06-06-2018 13:00	37.2
			06-06-2018 14:00	35.6
South Surface IN	06-06-2018 13:22	31.7	06-06-2018 13:00	31.2
			06-06-2018 14:00	31.2
South Surface OUT	06-06-2018 13:30	36.4	06-06-2018 13:00	36.6
			06-06-2018 14:00	36.0
Roof Surface IN	06-06-2018 13:31	32.8	06-06-2018 13:00	32.7
			06-06-2018 14:00	32.4
Roof Surface OUT	06-06-2018 13:34	42.3	06-06-2018 13:00	44.9
			06-06-2018 14:00	42.7
East Room Air	06-06-2018 13:37	32.1	06-06-2018 13:00	32.3
			06-06-2018 14:00	32.2
West Room Air	06-06-2018 13:39	33.2	06-06-2018 13:00	33.4
			06-06-2018 14:00	33.0
North Room Air	06-06-2018 13:40	33.9	06-06-2018 13:00	34.0
			06-06-2018 14:00	33.4
South Room Air	06-06-2018 13:42	31.2	06-06-2018 13:00	31.8
			06-06-2018 14:00	32.0
Courtyard North Air	06-06-2018 13:44	34.9	06-06-2018 13:00	36.3
			06-06-2018 14:00	34.4
Courtyard South Air	06-06-2018 13:45	34.2	06-06-2018 13:00	35.0
			06-06-2018 14:00	34.0

See also: Understanding High Performance Buildings: The Link Between Occupant Knowledge of Passive Design Systems, Corresponding Behaviors, Occupant Comfort and Environmental Satisfaction

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Use of Steel as a Sustainable Concept

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Introduction

Today we love to talk about Sustainability as if this one word will transform the way we think about development. Development is a pattern that replaces nature, disturbing the ecological balance with a race for rapid urbanization and in the process implementing project after project. This results in widening inequity and leaving behind a trail of devastation. Sustainability is thus a misnomer – it fluidly changes its meanings, values with a change in context and position.

Human actions can be influenced by business, politics, scientific discoveries, technological advancements or social activism. All these manmade interventions get transformed and manifested with the support of architects, designers, planners and project managers – through the act of building and creating. However, one cannot deny the inherent value of being responsible in our actions to ensure the welfare of planet earth and consider possibilities for a sustainable future. Sustainability thus becomes a concept that relies heavily on making responsible choices for planning, design and construction.

Let us begin by critically examining the pattern of development around us. In the last decade, there has been major transformations in the way the built form is conceived, designed and built, the aspirations have changed, mobility has increased many folds, different building typologies have emerged and public life, institutions have evolved or transformed to match.

We are a global civilization now and we have achieved the capability to dictate life and its associated patterns. To an extent we can even decide on the direction and future course our lives take. In this freedom and increased capacity there is a sense of supreme power and therein lie the danger. With great power comes great responsibility. And if we just take a pause at this stage and introspect, we may realize that our current approach to growth and development also foregrounds areas of grave concern.

We are growing and developing at an uncontrolled SPEED and in the process our ECOLOGY is imbalanced and threatened. We pollute our ENVIRONMENT, and our ENERGY DEMAND is continuously on the rise. Our activities destroy natural and cultural HERITAGE and create ever increasing INEQUITY in our socio-economic sectors. Most of these changes are irreversible and would likely pose major challenges for development in the future.

At this critical juncture, we, the decision makers, designers and planners need to relook at our available options and choose RESPONSIBLY for possible rectification, remedial measures and holistically sensitive approaches of our present development trajectory. As a probable direction we intend to look at Steel as an IDEA that advocates for our sustainable future.

Steel and Civilization – A Connect

With the advent of the Iron Age, mankind started developing tools and equipment. This knowledge gave humans a notion of power – for the first time they learned ways to tame and manipulate nature. From the nomadic life of being hunter-gatherers, humans became settlers. Agriculture, domestication of animals gave rise to concept of Land, Property and Settlement. Slowly an organized way of life was initiated. At the same time, there were conflicts around gaining control of prosperous land, leading to aggression. With war came weapons – the means of destruction as well as possibilities of construction. This pattern evolved and consolidated into a pattern of development where the seat of power was protected in walled cities, surrounded by trade and commercial establishments, and then agricultural land. Broadly this system was propagated through feudalism subsequent influenced patterns of human civilization (Figs. 1–3).

Around 1760, the Industrial Revolution was initiated in Great Britain when the production by hand gave way to machines for large-scale production. This embracement of technical advancement for progress brought about massive improvements in the Iron Industry and increased knowledge of production and processing.

The Industrial revolution in the late sixteenth century was successful in liberating the human civilization from mediaeval practices. The history of the modern steel industry began in 1850 and thereafter Steel has been a basic component of the world's industrial economy. Earlier, large metal structures were made of wrought iron or cast iron produced around Sheffield in Britain. During this period steel was comparatively an expensive proposition. This situation changed with the bulk production of steel, as a result of Henry Bessemer's process. Steel thus produced was cheap and readily available. With the development of iron foundries mankind managed to create improved equipment, tools and machines. Motivated by these, there was a surge in engineering. A new business class, the bourgeois entrepreneurs and financial institutions emerged – providing the required thrust for development and economic growth at an ever-increasing pace. This led to an increase in the need for raw materials – minerals, cotton, etc. to be collected at strategic centralized locations from different regions, often from areas spanning the globe. This also led to the opening up and exploration of new markets that were difficult to access. The discovery of the Steam engine and its implementation spearheaded this process of transportation. It helped in the extraction of natural ores, generation of power and developed major transportation systems like the Railways and global Shipping to facilitate transportation of bulk goods as well as mass



Fig. 1 'Celia' by Barcelona based Sculptor Jordi Díez Fernández in Steel that pays tribute to human emotions and strength.

transportation. Geographical boundaries were thus broken, and remote locations were connected. In a way, this can be seen for the genesis of the concept of Colonization itself, which creating a new sense and understanding of Economy.

The vast railway network comprised of new lines, bridges, viaducts, warehouses, terminals, stations etc. (Fig. 4). The shipping network comprised of ports, jetties, bulk material handling facilities. These new forms of buildings and infrastructure permanently altered the urban landscape. The introduction of factories and mechanization ushered in a new way of life – from feudalism to capitalism. In this new age, there were new economic concepts – capital and production became buzzwords. Trade and commerce flourished. New choices were continuously being made. The flourishing of industries such as the textile industry, building construction, shipping lines, steel production, heavy engineering, automobile industry etc. created huge job opportunities, concentrating the demand for labor and production in huge sprawling cities. This completely changed the prevalent lifestyles. The per capita income and GDP has grown considerably. More opportunities were created for people at large to spend on housing, travel, shopping or for leisure.

Socially, it transformed the way human engagement was thought of. People now talked about collaboration, mass production, and standardization. With an increased empowerment of a larger number of individuals, society started breaking free of the shackles of imperialism and started moving towards democracy. Industry, Trade and Commerce, Construction defined the modern perception of Life – created capitalists and the working class.

This also resulted in the creation of new building typologies – factories, offices, docks, warehouses, stations and terminals. They created a demand for large public spaces – the markets, plazas, auction houses, theatres, auditoriums, assembly in addition to large scale infrastructural projects – railways, bridges, aqueducts, viaducts, jetties, power plants, turbines etc. Concept of marketing the products, machineries and various brands started to emerge at this point. The great exhibition at Crystal Palace in UK showed the world an appropriate way to construct large spaces and in a very short time. A revolution in construction industry has started, with steel at the center of it all. It was at this juncture that Gustavo Eiffel created the icon of industrialization in the form of the Eiffel Tower in the Paris industrial exposition. The Statue of Liberty was also built and transported to New York (Figs. 5 and 6).

Today, there is steel in every bit of our lives. So much is its importance that the growth index of a country has increasingly been equated in terms of the per capita steel consumption.

Steel was not only restricted to the industrial sphere but found expression even in the socio-cultural sphere of human existence. Classical painters found new subjects in these newly built factories, market places, and in the exploration of the lives of common people. They explored the newly manifested dimensions of democracy, power and liberation. The languages and the images transformed (Figs. 7–9).

Slowly, skyscrapers started to dominate the urban skyline. The construction industry became heavily dependent on the steel industry. The techniques started to evolve. There was an advent of pre-engineered components, cables, tensile structures – all of which further pushed the envelope and expanded the horizons of the booming construction industry. People began to push the limits of their creative boundaries, drawing inspiration from traditional wisdom, nature and other sources at will. Connections and detailing became supremely important. Gradually, varieties of steel forms began to emerge, reaching out and working to support other building materials like, wood, stone and concrete. The interesting aspect of steel being a manmade element was that it offered immense flexibility and adaptability to meet various testing conditions and rise up to new challenges (Figs. 10 and 11).

Concerns (Existing Development Pattern)

In a deeper investigation of sustainability, the author focuses on the sustainable aspects of the manmade physical interventions and their impact on the larger ecosystem. He also raises the question of owning responsibility for such decisions and acts. These translate into a series of questions.

the Crystal Palace

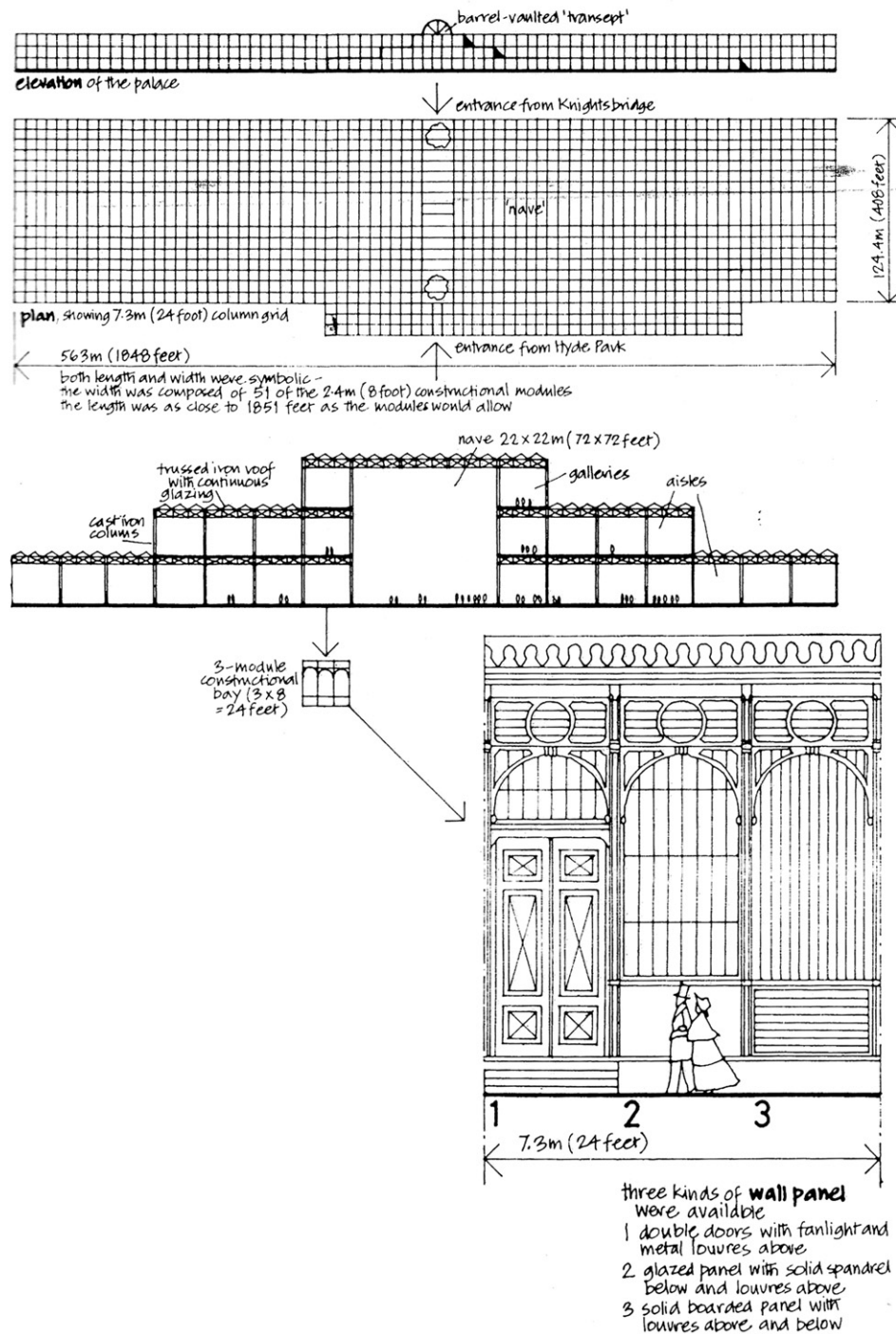


Fig. 2 Drawings of The Crystal Palace, 1851 London.

Are we moving in the right direction?

Is our approach Holistic?

What kind of parameters and considerations do we use while making these choices?

Are our actions reversible, or rectifiable?

What kind of liabilities we are creating for future generations?

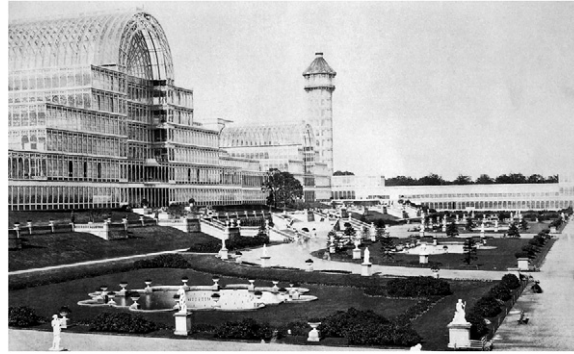


Fig. 3 The Crystal Palace, 1951 London.

These questions are difficult to answer, and disturbing. Yet, we must address these critically and impartially.

To understand that we must relook at the present development trends in the built environment as it is here that most of our actions are physically manifested and contested.

Urbanization

Globally there has been an advocacy for rapid urbanization. In India we are looking ahead, and we estimate that 70% of the total population will be housed in urban areas by the year 2020. At present, we have approximately 35% of the population in the urban areas. Logically an increase in urbanization would help to extend a better quality of life and create more economic opportunities in a sustainable (!) manner. Logically, this must be done through a surge in development of housing (appropriate!), create more jobs (what kind!), provide for adequate infrastructure (practical, maintainable, and upgradable), mass transport options (cheap, eco-friendly, convenient), waste management provisions (recyclable, sensitive!), communication (smart, user friendly), social infrastructure (inclusive, culture sensitive), etc. All these have to be integrated within the existing situation or through the creation of new greenfield projects. These projects look to transform inner-city areas with existing informal slums, convert high-value agriculture land in the periphery of existing urban areas, or convert wastelands, vulnerable wetlands or defunct industrial lands. All of these need to be accomplished at a great speed. This urgency triggers a chain reaction of destruction, new construction, accumulation of construction and demolition waste. We need new forms of Housing – and consequently there is a prevalence of socially isolated gated communities with multi-story blocks fragmenting the cultural fabric of the city. There is a growth of large workspaces with global footprints that occupy very large floor spaces dedicated to different time zones. With the high construction cost, these new developments in the city has been selective and has negated a large section of urban population. These groups have been forced to seek informal arrangements for housing, jobs and access to adequate infrastructure. But the development trends continue in an exclusive way. India today is thinking and planning for 100 new *smart cities* – places where urban development is inherently exclusionary.

Land and Built-up area – is a prerequisite to any kind of development. Buildable land is a scarce resource and is continuously shrinking at an alarming rate. However, major development projects are carried out through two main trajectories.

The first one is commonly known as Green field Development or New Development. Through this process, new land is built on to gradually bring marginal areas into the domain of Urban Development. Most of these lands are agricultural lands. In this process, large amounts of areas have been converted into built areas – displacing nature, local population, changing the demography and the socio-economic structure. The concept of land value has also changed from the value of production to its real-estate value. There has also been a shift in the way we build today. The structure has to be strong to support tall heights and large spans. Time has become an essential component of construction. In addition, the structure must be less environmentally disruptive as well as cost effective.

There is another kind of development, commonly called Brownfield Development. This encompasses approaches to building such as renewal, redevelopment, resettlement, rehabilitation, retrofitting or densification of existing built areas. These is an approach that is a practical solution that emerges from concerns of paucity of land for new development. However, it might also give rise to construction and demolition wastes at a massive scale.

In short, development has created an increased level of pollution, adversely impacting the quality of livable environment.

How can one tackle such a mammoth issue?

The Way Forward

To mitigate the existing destructive, environmentally damaging and inequitable trajectories of development, we are also forced to think of new patterns and approaches to development. This has to be underpinned by alternative construction techniques that are flexible,

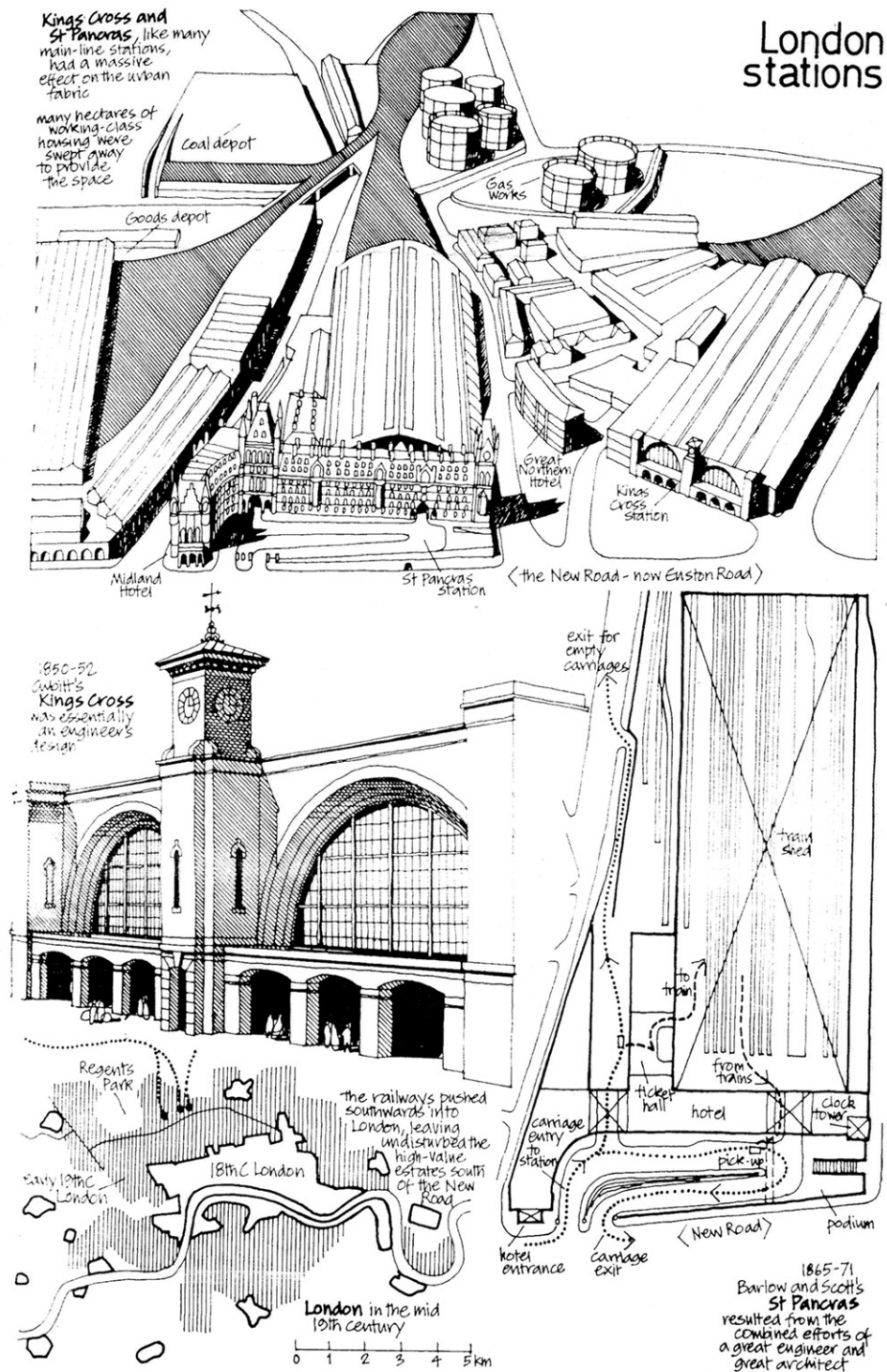


Fig. 4 London Stations, Part of the new transport network.

recyclable, adaptable, up-scalable and versatile. These alternative construction systems should look for the versatility of materials, systems of connections, structural options and their response to other natural or manmade materials. One has to look at the wider ecosystem of construction and implementation and come up with responsible choices amongst the available alternative.

The above discussions help us to understand the interconnections of the development of human civilization to the development of science and technology for identifying the key features of the construction alternatives that we adopt.



Fig. 5 The Galleria Vittorio Emanuele II in Milan 1865–67 is an excellent example of a large public space constructed using new technology.



Fig. 6 Built using beaten copper sheets over a hollow iron structure, The Statue of Liberty with a height of 46.5 m was built by Gustave Eiffel in 1870–1880s.

The appropriate material for future development thus needs to be **RELIABLE** – it must be durable and provide adequate strength for their designed purpose, with required toughness and ductility so that the necessary profiles and forms can be designed and developed in an efficient and effective manner.

To be able to meet the myriad demands of construction and implementation needs the material must be **VERSATILE** and **ADAPTIVE** enough to be transformed into various components, shapes and forms without losing its structural integrity. The material must also be adaptive enough to be used to support and extend the capabilities of other conventional and unconventional construction materials, thereby furthering new possibilities.

REUSABILITY and **RECYCLABILITY** are the other necessary attributes that such a material and its various components must have – to minimize detrimental effects on the environment.

The earlier sections detail how steel has been an integral part of and has supported in its various forms the development of human civilization itself. At this juncture of human development, with the current technology, **STEEL** can be thought of as a unique material that can be made to behave responsibly in its various forms and be the supportive technology for guiding the human race towards development that leads to a **SUSTAINABLE FUTURE**.

The potentials of Steel as key to development of a nation is of paramount importance. Fast growing nations such as India acknowledge the fact, such as in the Annual Report 2017–18 by Ministry of Steel, Government of India. It reports that:

India is currently the world's 3rd largest producer of crude steel and is expected to become the 2nd largest producer of crude steel in the world soon.

India is also the largest producer of direct reduced iron (DRI) or sponge iron in the world. The country is also the 3rd largest consumer of finished steel (83.5 million tons in 2016) in the world, preceded by China (681.0 million tons in 2016) and the USA (91.6 million tons in 2016) The steel sector contributes to over 2% of the country's GDP and employs around 25 lakhs employed in steel/allied sectors (source: world steel association).

Steel – A Responsible Material

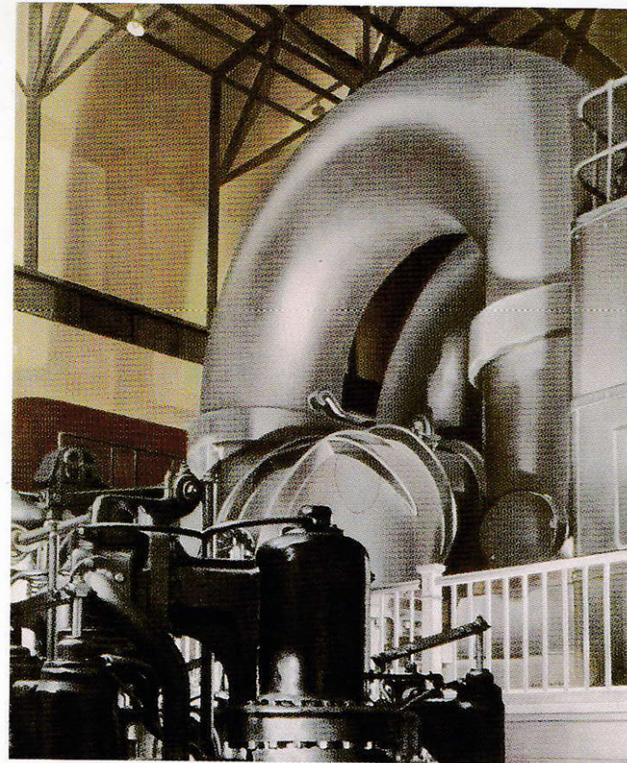
To understand Steel in its true perspective, it is essential to go through the following timeline.

<i>Year</i>	<i>Event type</i>	<i>Details</i>	<i>Present day country/region</i>
4000 BCE	Production	First evidence of use of iron.	Turkey
2000 BCE		Iron production begins in Anatolia. The earliest known steel is about 4000 years old and was excavated in Turkey.	
10th century BCE	Consumption	Iron working is introduced to Greece in the late 10th century BC.	Greece
6th century BCE	Facility	Blast furnaces are developed in China.	China
6th century BCE	Technology	Wootz steel is developed in India. Craftsmen in the southern part of the country use crucibles to smelt wrought iron with charcoal to produce 'wootz' steel.	India
500 BCE	Technology	The technology of iron making reaches the western limits of Europe.	Europe
400 BCE	Technology	The technology of iron making reaches China.	China
300 BCE	Technology	Wootz steel making technique develops in India and Sri Lanka. The technique spreads across the Arabian peninsula.	India, Sri Lanka
300 BCE–1700 CE	Technology	Era of the legendary Damascus Steel.	Near East
206 BCE–25 CE	Technology	The Chinese during the Han dynasty can already produce heat-treated steel.	China
2nd century BCE	Production	Early examples of high-quality steel are produced in China.	China
402 CE	Product	The Iron Pillar of Delhi is erected at around that time. It is the oldest surviving example of rust-resistant steel.	India
1100–1300	Technology	Wootz steel comes to the attention of Europeans in the form of Damascus swords, which are extremely strong, shatter-resistant and can be sharpened to a fine blade.	
12th century	Production	By the 12th century, Sri Lanka is the world's largest supplier of crucible steel.	Sri Lanka
1702		Coke is first used to smelt iron ore on a mass scale, replacing wood and charcoal which start becoming increasingly scarce.	
1712	Product	English inventor Thomas Newcomen builds the first commercially successful steam engine.	United Kingdom
1751	Production	Crucible steel is produced. English manufacturer Benjamin Huntsman develops techniques for production of high quality steel, when he establishes a steelworks at Sheffield, England, where the steel is made by melting blister steel in clay crucibles at a temperature of 1500–1600°C (2700–2900°F), using coke as a fuel.	United Kingdom
1783	Product	English ironmaster Henry Cort invents the steel roller for steel production.	United Kingdom
1784	Technology	English ironmaster Henry Cort develops puddling furnaces, which would be used by ironmakers to transform cast pig iron into a low-carbon content wrought iron.	United Kingdom
1794	Technology	Welsh inventor and ironmaster Phillip Vaughan patents the design for the ball bearing to support the axle of a carriage.	United Kingdom
1856	Technology	English inventor Henry Bessemer develops an effective way to use oxygen to reduce the carbon content in iron. The Bessemer converter (so called because it converts iron into steel) blows air through molten pig iron, which removes its carbon, making it more malleable. The interaction of oxygen and carbon generates a heat which increases the temperature of molten iron, allowing steelmakers to avoid using additional fuel. The process developed by Bessemer becomes a major breakthrough, giving birth to the modern steel industry.	United Kingdom
1860	Production	There are 3400 puddling furnaces in Britain producing a total of 1.6 million tons of wrought iron per year, about half the world's production.	United Kingdom
1860	Production	Crucible steel starts being produced in Pittsburgh, Pennsylvania, using a charge of wrought iron and pig iron.	United States
1860s	Technology	German engineer Karl Wilhelm Siemens further enhances steel production through his creation of the open hearth process, which produces steel from pig iron in large shallow furnaces.	
1860s		Following the American Civil War, the United States' steel production grows with astonishing speed, led by Scottish-American industrialist, Andrew Carnegie.	United States
1868	Technology	British metallurgist Robert Forester Mushet invents tungsten steel.	
1872	Technology	Englishmen John T. Woods and John Clark file for patent of an acid and weather resistant iron alloy containing 30%–35% chromium and 2% tungsten, effectively the first ever patent on what would now be considered a stainless steel.	United Kingdom

1875	Scientific development	Henri Aimé Brustlein from France details the importance of low carbon content in successfully making stainless steel. Brustlein points out that in order to create an alloy with a high percentage of chromium, the carbon content must remain below around 0.15%.	France
1876	Technology	English inventor Sidney Gilchrist Thomas develops a solution to the phosphorus content (a deleterious impurity that makes steel brittle) by adding a chemically basic flux – limestone – to the Bessemer process. The limestone would draw phosphorus from the pig iron into the slag, allowing the unwanted element to be removed.	United Kingdom
1883	Product	The Brooklyn Bridge – the first steel suspension bridge, is inaugurated in New York City.	United States
1885	Product	The Home Insurance Building – the first steel skyscraper, is completed in Chicago.	United States
1895	Technology	German chemist Hans Goldschmidt develops the aluminothermic reduction process for producing carbon-free chromium, thus prompting a major boost in the development of stainless steels.	
1904	Scientific development	French metallurgist Léon Guillet undertakes extensive research on many iron-chromium alloys.	
1907	Technology	The first commercial electric arc furnace (EAF) is established in the United States. Today, almost all stainless steel is produced using the EAF method.	United States
1908	Scientific development	Frederik Becket of the Electro Metallurgical Company at Niagara Falls, New York develops a low-carbon ferrochromium produced by reducing the chromium oxide with silicon instead of aluminium. Over 80% of the world's ferro chrome today is utilized in the production of stainless steel.	United States
1909–1912	Scientific development	Eduard Maurer and Benno Strauss at Krupp laboratories develop high-chromium nickel steels.	Germany
1911		Germans P. Monnartz and W. Borchers discover the correlation between chromium content and corrosion resistance, stating that there is a significant boost in corrosion resistance when at least 10.5% chromium was present. The pair also publishes detailed works on the effects of molybdenum on corrosion resistance.	
1911	Scientific development	American metallurgist Elwood Haynes experiments with high-chromium steels to determine the effect of chromium on corrosion resistance, hardness, elasticity, and cutting qualities. In the same year, Christian Dantsizen of General Electric Research Laboratory also begins experimenting with high-chromium steels for possible commercial development.	United States
1912	Scientific development	English metallurgist Harry Brearley, working in the Brown-Firth research laboratory in Sheffield, England, discovers a martensitic stainless steel while attempting to develop an erosion-resistant alloy for military applications. In 1913 Brearley melts the first commercial chromium steel as a stainless steel for cutlery blades. Harry Brearley is credited with the invention of stainless steel.	United Kingdom
1913	Scientific development	English researcher Harry Brearley creates a steel with 12.8% chromium and 0.24% carbon, argued to be the first ever stainless steel.	United Kingdom
1914	Scientific development	Ludlum Steel Co. metallurgist P.A.E. Armstrong discovers chromium-silicon steels, when a small electric furnace is accidentally contaminated due to some silicon reduced from the asbestos cover on the electrode.	United States
1917	Scientific development	Charles Morris Johnson of the Crucible Steel Company, begins investigating chromium-nickel-silicon steels, which are later patented under the name Rezial.	United States
1919	Technology	American metallurgist Elwood Haynes obtains a patent on martensitic stainless steel.	United States
1919–1923	Product	Cutlery in Sheffield, England start regular production of stainless steel cutlery, surgical scalpels and tools. Early stainless tableware such as dishes and bowls also start to appear at this time.	United Kingdom
1929	Technology	Luxembourgish metallurgist William Justin Kroll discovers precipitation-hardening stainless steel.	
1930	Technology	Avesta Ironworks from Sweden produces duplex stainless steel for the first time, with the microstructure of the alloy consisting of both ferrite and austenite.	Sweden
1930	Technology	The Chrysler building is completed in New York City. It is the first to feature stainless steel roof cladding, which still shines like on its first day.	United States
1935	Technology	Sinks made of 18-8 stainless steel begin to be installed in new houses, instead of porcelain-enamelled cast iron sinks.	

1950	Technology	Basic oxygen steelmaking (BOS) is introduced, limiting impurities and even processing old scrap metal into steel, lowering wastage and increasing efficiency. The BOS process would make the Bessemer Process and other steelmaking processes that developed alongside obsolete. These days, BOS accounts for the majority of steelmaking processes in the industrialized world.	
1960s	Technology	A method to separate oxygen from nitrogen on an industrial scale is developed in the decade. This would allow for major advances in the development of basic oxygen furnaces.	
1989	Technology	Ferritic stainless steel is first used as a large-scale roofing material.	
2001	Technology	The last open-hearth furnace in China closes.	China
2006	Production	China becomes the biggest stainless-steel producer in the world.	China

Note: Selected from Sanchez, S., 2019, Wikipedia. Retrieved from time lines is sarice: https://timelines.issarice.com/wiki/Timeline_of_steel (accessed 19.01.19).



▲ **Steam Turbine** Charles Sheeler *The geometrical shapes of urban and industrial scenes, meticulously depicted by Sheeler and other Precisionists, echo elements of Cubism and Abstract art as well as the more obvious influences of photography and commercial illustration.* 1939, oil on canvas, 56 x 45.7cm, Butler Institute of American Art, Youngstown, Ohio, US

Fig. 7 A painting by Charles Sheeler illustrates changing subjects and landscapes.

The above time line clearly establishes the evolution of Steel as a structural material and also highlights other consumer use and application vis a vis stages of civilization. However, this paper would like to restrict itself to very basics of the Material Steel in relationship to the construction industry. The chronological timeline of Steel clarifies the understanding of steel as a manmade invention – a designed material that has evolved according to the need of the society to suit various purpose and designed intention. The previous sections of this paper have further elaborated on the subsequent widespread use of steel that has been supported by and has supported the development of human civilization itself.

The properties of steel result from its chemical composition and methods of manufacturing. Depending on the intended use case and existing product standards – steel can be designed to have a varying range of yield-strength, ductility, malleability, toughness and weldability.



Fig. 8 A painting by J.M.W. Turner illustrates the industrial landscape.



Fig. 9 The central atrium of the Lloyds Building, London.

While this immensely increases the varieties, forms and usability of steel – this makes the production process highly specialised and energy intensive. This means that steel in its various forms has a relatively high value of embodied energy compared to other natural materials.

The high embodied energy necessitates an awareness that while steel gives us unparalleled freedom, this freedom comes with an added responsibility to rationalise its use. This means that there needs to be creative, out-of-the-box approaches that maximise its longevity, its use and its overall efficiency – keeping in mind that only then can the material justify its high initial energy liability. The following section discusses the possibilities and potential advantages of steel.

Reliability

Most of our conventional construction materials have a limited range of strength and apart from Timber, most are usually weak in tensile strength. Natural materials that are commonly used for structural supports are Stones, Bricks, etc. They are very

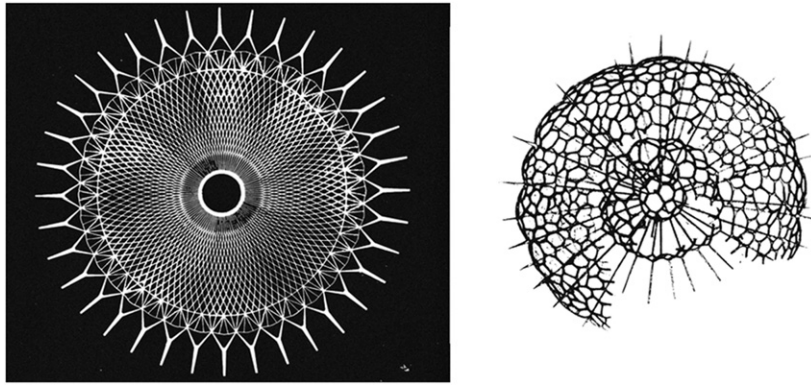


Fig. 10 Structures inspired by learnings from nature.

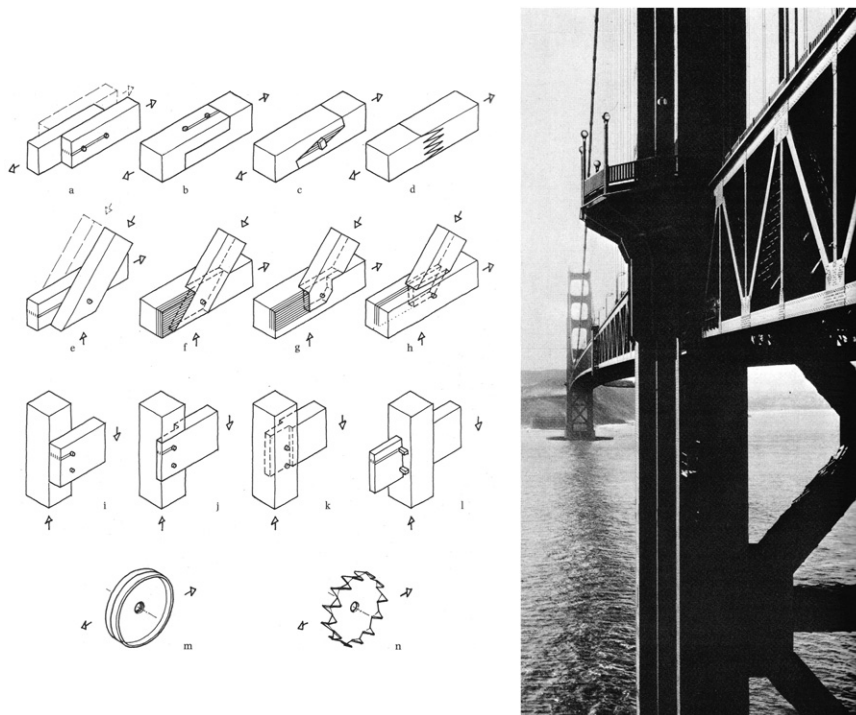


Fig. 11 Structures inspired by learnings from joineries in other materials.

good in compression and thereby provide stability. However; in most structure systems there is the issue of transferring the superimposed load through the horizontal members – slabs, beams etc. to the vertical supports. Stones and bricks can also bridge spans to a limited extent, but they prove to be impractical as the dead load of the structure also increases. Therefore, in ancient times timber has been used to extensively as horizontal connections. Later, innovations in the fabrication process has made it possible to create trusses. This has allowed for accommodation of larger spans using relatively lesser quantity of materials.

We have been extremely resourceful and have managed to use innovative modes of spanning through arches, domes and vaults, or materials such as bamboo or timber. However, slowly their design limitations have come to the foreground, particularly in the present context where we need large uninterrupted spans. Simultaneously there has been an increasing need for taller and taller buildings with an ever-increasing vertical load that are impractical to design by using traditional construction materials.

Steel in its various forms have helped us find solutions and respond to this need, and therefore has been intensely propagated as a designed constructional material for supporting very large spans and for intense loading. Steel has the maximum strength to weight ratio and therefore provides a wide range of choice. It also helps to expand the structural capability of natural materials. Reinforced concrete is another manmade construction material, which gains inherent strength due to incorporated steel members. The ability to explore and support various structural systems has made Steel one of the most RELIABLE materials. The Eiffel tower



Fig. 12 The Eiffel Tower, Paris.

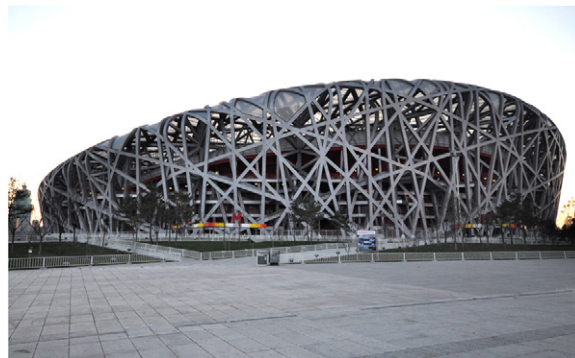


Fig. 13 The Nest Olympic Stadium, Beijing.

in Paris ([Fig. 12](#)), The New London Bridge designed by Fosters or the Nest Olympic stadium in Beijing ([Fig. 13](#)) is a testimony of its reliability.

Versatility and Adaptability

The strength of a material is manifested through various types of structural design options, construction technology and processes of implementation. These are widely varied in Steel. Depending on the type of requirements, steel has a range of forms and types that suit various design implications. They are:

- As-rolled steel,
- Normalized steel,
- Normalized-rolled steel,
- Thermo mechanically rolled (TMR) steel,
- Quenched and tempered (Q&T) steel.

In response to the special needs for enhanced durability, health and fire requirements etc. special steel of appropriate grade has been presently developed making it more environmentally responsible.

Versatility and adaptability of a structural material plays a very important role in the design of innovative, explorative structural systems that are efficient, cost effective and practical in a given context and can be implemented within an acceptable time frame.

Beside large-span structures there is also the added complexities associated with vertical structural typologies such as requirements of high wind pressure, seismic factors, structural fatigue etc. These complicated structural issues can only be mitigated through intelligent choices of structural systems where they perform as groups of smaller components that are connected, joined to provide a strong, reliable, adaptable structural matrix. In this system the final strength is derived through an efficient distribution and dispersal of loads incorporating a complex system of components, nodes and connections. Various such construction systems have been evolved utilizing steel for very large span structures like bridges, aqueducts, viaducts etc. such as systems of steel girders, cable-stays. Other systems such as space frames, geodesic domes or tensile structure have evolved for spanning large exhibition spaces and pavilions. Special forms and shapes have been conceived for multistoried buildings and skyscrapers. These innovations are often inspired from natural forms and

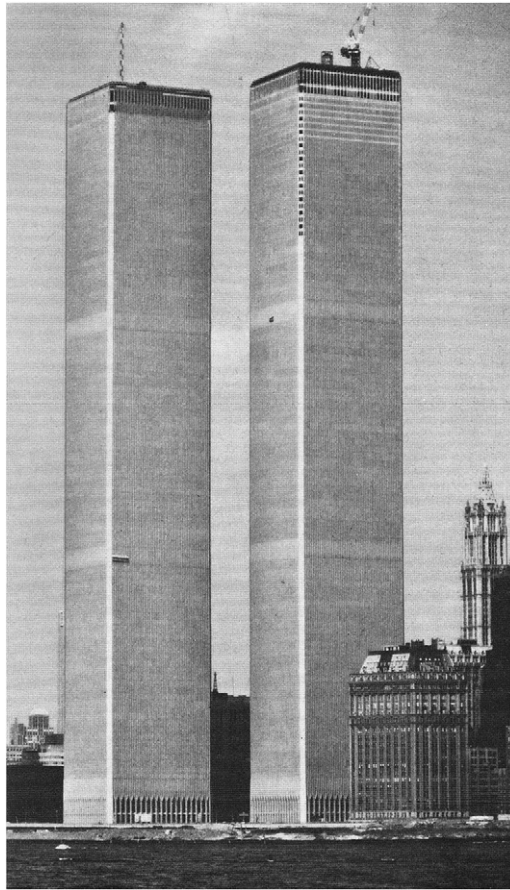


Fig. 14 The World Trade Centre, New York.



Fig. 15 30 St. Mary Axe Building, London.

their structural networks. Such inspiring forms and their development can be seen in the evolution of the World trade Center ([Fig. 14](#)), Chrysler Building, John Hancock center and the 30 St Mary Axe Building ([Fig. 15](#)).

Reusability and Recyclability

The best extent of adaptability of Steel is realized when it can be combined to extend the capability of traditional construction methods and enhance its life cycle, as well as innovate new construction methods like reinforced concrete, pre-stressed and post-tensioned concrete etc. This adaptability is the main reason that steel has become the key material choice in all forms of

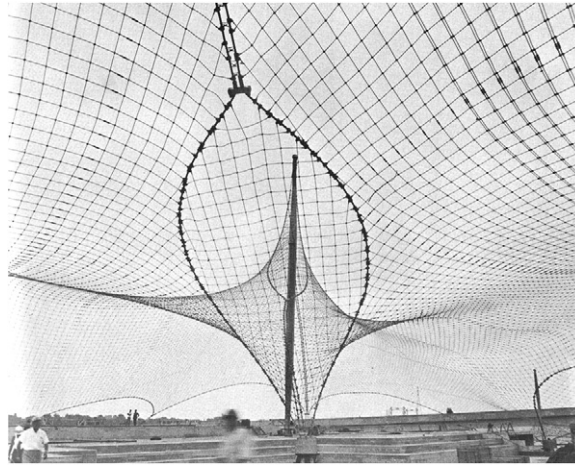


Fig. 16 Using a steel structure with tensile components for a lightweight large span structure.

construction that builds on and strengthens existing assets – such as in the retrofitting of old buildings, infrastructures, etc. The use of steel can extend the life cycle of these assets, thereby rationalizing energy demand and minimizing waste generation.

Steel components are very durable and maintainable. Steel construction has numerous components assembled in a designed manner to systematically distribute the forces through these components, connections and joints. This makes it possible to dismantle the entire system and reuse a large number of the parts. Effectively this means that steel has an extended life cycle. The high degree of reusability also means that construction and demolition waste generated is vastly less. Even if some components cannot be reused as is, or are scraps, they can again be melted and recycled to form other components. It has been estimated that the entire framework of a residential house can be built from the recycled scraps of just eight recycled cars.

Construction Advantage

Construction today needs speed and transportability to meet the demands of ever-increasing urbanization. Steel construction has the highest ratio of strength versus weight, and essentially lighter footprint than conventional construction. Thus, it has a lesser impact on ecology and is less disruptive. Steel – in its entire life cycle has comparatively lesser embodied energy and is thus a GREEN OPTION (Fig. 16).

Steel construction is essentially fabricating pre-engineered components into a designed order for required strength, durability and purpose. Therefore, it involves detailed planning right from design, processing, fabrication and final installation. Components in this system have to be manufactured to meet specified norms, standards and be of required shape, size, and strength to a high degree of accuracy. This necessitates better and more efficient quality control mechanisms for timely production along with all required accessories that adhere to best practices norms. The components are fabricated, transported to designated sites and assembled as per engineering drawings. This process also ensures the extent of construction work on site, creating minimum disturbance to the local context and its surrounding areas. This reduces construction pollution and therefore becomes a SMART CHOICE.

Conclusion

Physical designers, planners, urban designers and the decision makers have to make a responsible choice in holistic ways that balances the needs of development with those of ecology, environment, energy, cost and local socio- cultural contexts. Therefore, the materiality of construction also needs to be assessed and evaluated for its sustainability quotient. Historically, this article has elaborated on how technological advancements in steel have happened concurrently with various stages of development, construction methodology and implementation. Its continued practice has been a responsible choice. Today, new consciousness and awareness of development concerns have made the design and planning process more restrictive. Steel as a flexible, adaptive material with a wide range of mechanical properties, chemical composition and innovative fabrication processes provides us an avenue that combined with the wisdom of being responsible can chart out a path for sustainable future development.

See also: Using Construction and Demolition Waste Materials as Construction Materials for a New Building

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Using Construction and Demolition Waste Materials as Construction Materials for a New Building

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Introduction

Global Construction 2030, a new report prepared by Global Construction Perspectives and Oxford Economics, sponsored by PwC forecasts that the volume of construction output will grow by 85% to \$15.5 trillion worldwide by 2030, with majorly three countries i.e., China, US and India, leading the way and will account for 57% of all global growth. Cities are changing its volumetric profiles throughout the world and India is of no exception. Burgeoning population is creating pressures in cities which in turn compelling the city skylines to have a drastic change in all aspects like land use pattern, height profile, density, socio-economic context etc. The single family houses are converting into multi-family gated communities. The load bearing, low-rise structures are changing into high-rise frame structures which are continuously forcing our cities and neighborhoods to hold this change. This change is giving rise to a huge amount of demolition and construction waste. The primary reasons towards the increase of Demolition and Construction Waste are: (1) Redevelopment, renovation and repair of old building stock, bridges, large scale projects; (2) New development for better economic growth; (3) Debris arising out of some kind of natural or man-made disasters like earthquake, cyclone, floods and fire etc. Higher densities in brownfield areas of cities not only demand for more and more construction materials but also generating a huge quantum of waste on a daily basis. Policy makers are framing rules to incorporate solar panels to buildings in order to facilitate sustainable development. The estimated lifespan of a solar panel is 25–30 years whereas the market is mostly captured by cheap Chinese make panels which never ensure a longer life. In a recent survey, the International Renewable Energy Agency estimated that there were already 250,000 metric tons of solar panel waste worldwide and that this number would grow to 78 million by 2050.

Waste materials have been a great concern for Environmental pollution. Government systems in all countries are spending lot of energy and money in handling the waste further adding pollution to the environment. Illegal dumping of these waste materials into waterbodies, water channels further aggravates the situation. On the other hand, demand and supply of construction materials are also matters of concern. Researchers and Designers are trying to think about the solutions about how to use the waste materials as alternative building material.

In India, the construction industry has attained a steep growth in the recent decades due to the increasing population and growing demand for infrastructure, industry and commerce. The demand for new construction results in demolition of existing structures/built forms. The production of waste materials due to demolition of structures ([Fig. 1](#)) becomes a burden to the management. In addition to this, a huge amount of construction waste is also there. There is an urgent need of management of Construction and Demolition (C and D) waste which is very distinct from Municipal Solid waste. The matter being relatively a new issue in the country, there is hardly any proper database regarding the quantity of waste generation occurs in India. There is nil regulatory framework nor any strict enforcement. *Environmental issues such as increase in the flood levels due to the illegal dumping of construction and demolition waste into the rivers, resource depletion, shortage of landfill and illegal dumping on hill slopes are evident in the metro cities* ([Mullick, 2014](#)). This paper intends to find out the present status



Fig. 1 Waste generated due to demolition of structure.

of Government intervention in handling waste in the country, to identify probable waste materials which can be used as construction materials and their possible ways of use in the production of new stock of buildings.

Components of C and D Waste

C and D (Construction and Demolition) waste is defined in slightly different ways by different countries. For the purpose of this study, the definition used by the Ministry of Environment and Forests, Government of India is being adopted. As per the Notification S.O. 908(E) dated the 25th September 2000 issued by MoEF, the (D and C) “*demolition and construction waste*” means wastes from building materials debris and rubble resulting from construction, re-modeling, repair and demolition operation. In most cases ‘Construction and Demolition’ waste are coupled together but there are differences between demolition and construction waste. Waste may be categorized into two groups: (1) Construction waste (2) Demolition waste.

Construction Waste

Construction waste is newer, cleaner and easy to segregate and recyclable. Construction waste tend to be more homogenous. The materials which are observed and estimated as part of the construction waste component are listed in the [Table 1](#) (See “Relevant Websites section”).

Demolition Waste

The demolition waste materials tend to be mixed with a variety of materials, and difficult to separate and recover. Further categorization is also possible but for this study it is being restricted to only broad demolition waste category. The materials which are observed and estimated as part of the demolition waste component are listed in [Table 2](#) (See “Relevant Websites section”).

Quantifying the Total C and D Waste Generation in India

There is no general agreement regarding the total volume of construction and Demolition waste generated annually in India till date. TIFAC calculation for waste from the construction industry accounting for 25% of solid waste or 12–15 million tonnes per annum. The data in TIFAC study report in 2001 found to be quite an underestimated amount by several researchers time to time.

Table 1 Construction waste component

<i>Component</i>	<i>Material description</i>
Excavated earth	Earth accumulated due to excavation work for foundation
Wood	New wood which may includes plywood, chipwood, shavings and sawdust
Masonry	Inert materials like brick, concrete, rock, and dirt, etc
Metal	Metallic materials consisting metal studs, reinforcement bars, beams, pipes, paint containers etc
Plastic	Plastic materials including PVC pipes, doors, insulation material, plastic sheet, paint containers etc
Cardboard	Cardboard boxes, box board, various packing material, etc
Glass	Very less quantity if broken
Others	Any other material which is not included into the list mentioned above

Table 2 Demolition waste component

<i>Component</i>	<i>Material description</i>
Excavated earth	Earth mixed with foundation material
Wood	Weathered wood typically painted and attached to some other materials
Masonry	Inert materials like brick, concrete, rock, and dirt, etc mixed with other materials
Metal	Metallic materials consisting metal studs, beams, pipes, paint containers etc
Plastic	Plastic materials including PVC pipes, doors, insulation material, plastic sheet, paint containers etc
Paper	Cardboard boxes, various packing material, etc
Glass	mostly broken mixed with painted ones and in fixed condition alongwith doors/windows
Asbestos	Torn off shingles
Rubber	
Others	Any other material which is not included into the list mentioned above

Table 3 Generation of C and D waste by different cities in India

City	Population	Annual C and D generation (Million tonnes/annum)
Mumbai	12,442,373	0.75
Delhi	16,787,941	1.38
Bengaluru	8,443,675	0.26
Chennai	6,500,000	0.75
Kolkata	4,496,694	0.48
Jaipur	3,471,847	0.06
Patna	2,514,590	0.08
Ahmedabad	6,063,047	0.21
Bhopal	1,917,051	0.02
Coimbatore	2,618,940	0.03

Table 4 Generation of C and D waste by other countries

Country	Income based country classification (World bank)	Population	Million tonnes/year	Year
Australia	(HIC)	24,125,848	19	2014
United States	(HIC)	322,179,605	534	2014
UK	(HIC)	65,788,574	66.2	2016
Germany	(HIC)	81,914,672	223	2005
China	(HIC)	1,403,500,365	200	2005
Japan	(HIC)	127,748,513	77	2012
South Korea	(HIC)	50,791,919	61.7	2013
India	(LMI)	1,324,171,354	100	2018

Source: Data collected from various internet sites.

In 2010, MoEF mentioned about the annual C and D waste as 10–12 million tonnes. The Central Pollution Control Board announced it as 12 million tonnes in 2011 whereas in 2017 the estimate reached to 25–30 million tonnes. Another survey conducted for 10 cities in the year 2015 by GIZ and DA also reinforced the fact that the TIFAC estimate was significantly low (**Table 3**) (MoHUA-NITI Aayog, 2018). The document 'Utilization of Recycled Produce of Construction and Demolition Waste: A Ready Reckoner' prepared by BMTPC, MOHUA in 2018 shows that around 100 million tonnes seems to be the approximate generation per annum throughout the country. The data is based on 2011 census with existing housing stock of 110,139,853 in urban areas and 220,695,914 in rural areas coupled with rate of renovation and new construction of 5.75 billion sq. m. area during the period 2005–2012. Thus it is a fact that there is a gross uncertainty in assessing the total quantum of C and D waste generation either per month or annually.

Table 4 shows that excepting India, all other countries fall into the 'High Income' category whereas India only falls into 'Lower Middle Income' category. US, China and India having higher population figure display a very varied account regarding C and D waste generation.

The calculation of C and D waste generation in case of new construction will be very different from an old construction waste generation. It is also dependent on the volume and nature of construction also. It will vary in case of *pucca*, semi-*pucca* and *kucca* construction. However, according to the thumb rule calculation by TIFAC, a new construction generates 40–60 kg of C and D waste per sqm. India must have generated an average of 576 million tonnes of C and D waste in 2013 itself. It was also mentioned that the C and D waste generation due to demolition and repair/renovation of older stock would be 10 times more than the generation from new construction. CSE report estimation shows that the total C and D waste generated by buildings alone in 2013 amounts to 626 million tonnes, 52 times higher than official estimate. This figure will again go up if the C and D waste generation from bridges, road construction is further added. In 2015, whereas CSE estimated a figure of 531 million tonnes per year using McKinsey & Company's report. All published documents mentions about the gross discrepancy regarding the data towards the total C and D waste generation in the country which is without any scientific base and thus there is no denying the fact that there is an urgent need to have a realistic figure and proper estimation in this regard in order to derive a clear roadmap about the actual stock in future.

Composition of the C and D Waste

As per the C and D waste management toolkit document prepared by CPCB, MoEF, MoHUA and NPC in 2017, in India, it is estimated that the amount of C and D waste generated due to different activities in the following manner:

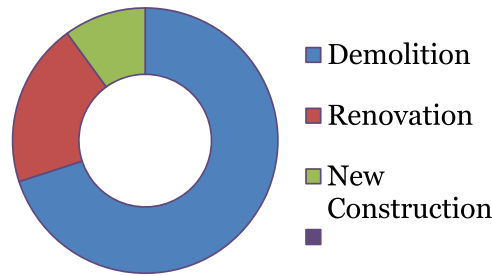


Fig. 2 Percentage distribution of C and D waste generation.

Table 5 Typical Composition of C and D waste in India

Material	TIFAC (%)	MCD (%)	ILFS (%)
Soil, Sand and Gravel	36	43	31.5
Brick and Masonry	31		
Concrete	23	35	–
Metals	5	–	0.4
Bitumen	2	–	–
Wood	2	2	1.5
Others	1	1	7.6

Source: Available at: www.irjet.net.

- An average generation of 500 kg and 300 kg per sqm on account of pucca and semi-pucca building respectively.
- Waste generation during construction around 40–60 kg per sqm.
- During repair/renovation work, it is around 40–50 kg per sqm.

This assumption is almost in tune with the TIFAC data. Waste generation during repair/renovation construction would be much higher depending on the quantum of work and type of construction. However, it is found that this figure is being used in all the documents for the purpose of calculation of waste generation. According to Danish Environmental Protection Agency (DEPA), 2003, 30% of the total solid waste generated was from C and D waste. Of this 70%–75% waste generated was from demolition activity, 20%–25% from renovation and remaining 5%–10% from new building developments (**Fig. 2**). It is very difficult to categorise the composition of the C and D waste especially from demolition waste. However, TIFAC, MCD and ILFS have identified some of the materials broadly as follows in **Table 5**.

The composition of the collected C and D waste is an important data with respect to the creation of databank regarding the stock of raw materials required for construction purpose. NGT has recently issued an order against all sand mining activity being carried out across the country without environmental clearance which means the availability of sand has become scarce now. The same problem lies with the availability of brick also. On the other hand “India needs to build 31,000 new houses a day over the next 15-years to meet the needs of its rapidly growing and urbanising population” a report says. “The demand for aggregates in 2007 has seen an increase by five%, to over 21 billion tones, the largest being in developing countries like example India”. (Study by Asian Institute of Technology (AIT), Thailand for some Asian countries included India, report released in May 2008). The regular flow of raw materials in the construction sector will help to regulate the steady supply of the burgeoning demand of housing stock. Recycling, Reusing the C and D waste might fill up the gap. Thus the generation of C and D waste should not be looked as a burden, rather should be utilized as a facilitating raw material resource in construction sector. At the same time, the actual calculation of the C and D waste generation should be made simultaneously without any further delay.

Policies and Framework in India

Standards and Certification

Any alternative material intended to be used for construction purpose needs to be approved by an authorized agency. A list of approved material which can be used for various purpose of construction is mentioned in various codes and standards. The National Building Code of India (2016) allows for the use of recycled aggregates in certain applications and also mentions in **Box 1** as follows:

Box 1 National Building Code (NBC-CED 46) of India 2016: Part 11 of NBC 2016 'Approach to Sustainability' (article 11), states that:

Recycled Coarse Aggregate may be used in concrete for bulk fills, bank protection, base/fill of drainage structures, pavements, sidewalks, kerbs and gutters, etc.

Up to 30% of natural crushed coarse aggregate can be replaced by the recycled concrete aggregate.

This percentage can be increased up to 50% for pavements and other areas which are under pure compression specific to the standards and practices pertaining to construction of roads.

The Indian Roads Congress (IRC) has issued 'IRC-121:2017 Guidelines for Use of C and D Waste in Road Sector' mentioning about the kind and proportion of materials from recycled C and D waste which can be safely used for specific road construction/repair applications.

Guidelines and Advisories

The constitution of India has provisions for the protection and improvement of the environment. The Environment (Protection) Act, 1986 defines environment as *"environment includes water, air and land and the interrelationship which exists among and between air, water and land and human beings, other living creatures, plants, micro-organism and property"*. In 1986, Environmental Protection Act (29 of 1986), Section 6 and 25 mentions briefly about 'other wastes' and 'recycling'. C and D waste finds a brief mention in Schedule III of the Municipal Solid Waste (Management and Handling) Rules, 2000 and the "Manual on Municipal Solid Waste Management" of the MoUD, 2000 has a article on C and D waste which lays down basic guideline on its handling. Municipal Corporation of Greater Mumbai has notified Construction and Demolition and Desilting Waste (Management and Disposal) Rules 2006. National Environmental Policy in 2006 prepared by MoEF, there are few mentions about waste handling vide Sections 4 and 5.4. The Working Committee (2010) on Municipal Solid Waste Management recommended that this issue may be addressed specifically with due focus and attention.

In 2012, the Ministry of Urban Development (MoUD), vide its Notification dated June 28, 2012 directed all states to set up environment friendly CDW recycling facilities in all cities/towns with population of over 1 million. The MoUD report, 'Technical Aspects of Processing and Treatment of Municipal Solid Waste', under Swachh Bharat Mission also recognized the need for CDW Management.

Central Public Works Department's (CPWD) introduced 'Guidelines for Sustainable Habitats' in the year 2014 wherein a set of 'Guidelines on re-use of recycled C and D waste' was included. The Draft Solid Waste Management Rules, 2015 published by MoEF&CC vide GSR 452(E) dated 3rd June 2015 had a separate article on C and D waste. Subsequently, the draft rules culminated into C and D Waste Management Rules, 2016 issued by MoEF&CC vide notification no. GSR 317(E) dated 29th March 2016.

In 2016 BMTPC prepared the 'Guidelines for Utilization of Construction and Demolition Waste in Construction of Dwelling Units and Related Infrastructure in Housing Schemes of the Government' and highlighted the considerable shortage of conventional and traditional building materials in India based on high demand for building materials by 2021–2022.

The Ministry of Housing and Urban Affairs (MoHUA), vide a letter dated March 23, 2016 circulated a notification by CPWD on mandatory use of recycled portions of C and D waste in construction activities, if the same is available within 100 km of the construction site.

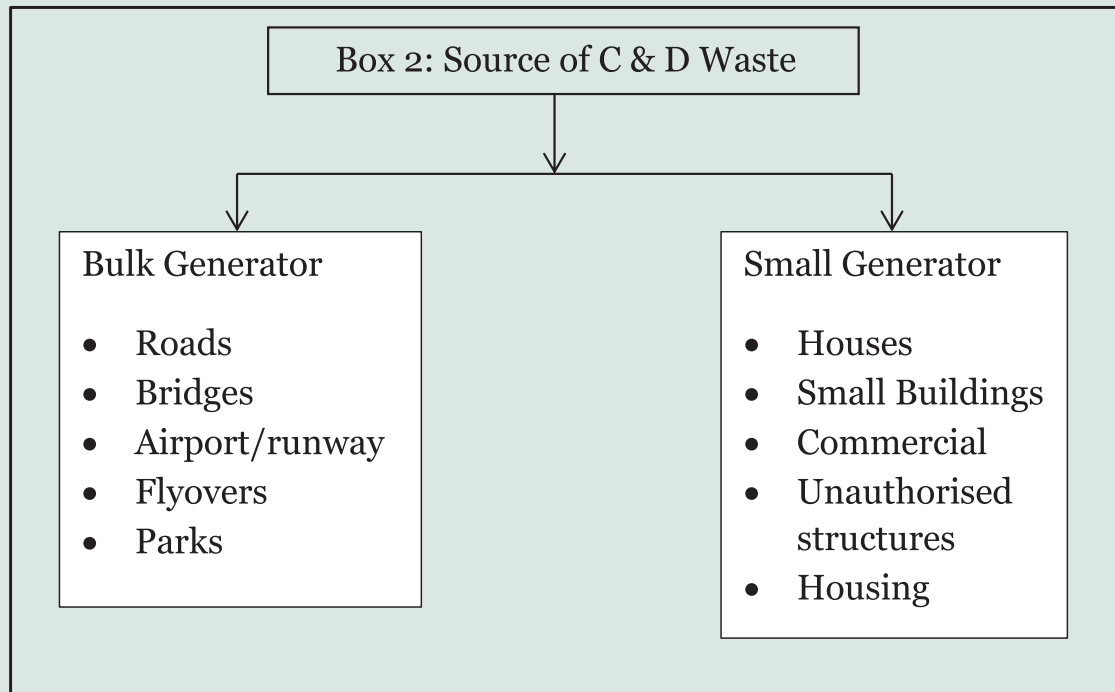
Delhi PWD issued an advisory to all Delhi Government Departments in 2015, mandating a minimum of 2% and 10% use of recycled C and D waste products in building construction and road works respectively. The advisory was reissued by the Delhi PWD in 2018. Use of Construction and Demolition waste 20%–100% is allowed in construction. IS-383 standard code revised. Bureau of Indian Standards (BIS) has issued 3rd amendment to IS-383:2016 "Coarse and fine aggregate for concrete" to include fine and coarse aggregate produced by processing of C and D waste. India Road Congress (IRC) has issued IRC-121:2017 Guidelines for use of C and D waste roads sector.

Source of C and D Waste Generation

As per C and D Waste Rule 3 (j) "waste generator" means any person or association of persons or institution, residential and commercial establishments including Indian Railways, Airport, Port and Harbor and Defense establishments who undertakes construction of or demolition of any civil structure which generate construction and demolition waste. In general, broadly two types of C and D waste generators are considered namely (1) Bulk Generator and (2) Small Generator which is shown in Box 2.

As per C and D Waste Rule, Waste generators who generate more than 20 tons per day OR 300 tons per project in a month are considered as Bulk Generators and they shall segregate waste into 5 streams namely (1) Concrete (2) Soil (3) Steel (4) Wood and plastics (5) Bricks and mortar. Construction sources again consists of two broad areas which are (1) infrastructure development sector and (2) the real estate housing sector. Infrastructure Development Sector includes roads, bridges, airport/runways and any

Box 2



Primary Source: Job Thomas, Wilson P. M “Construction Waste Management in India

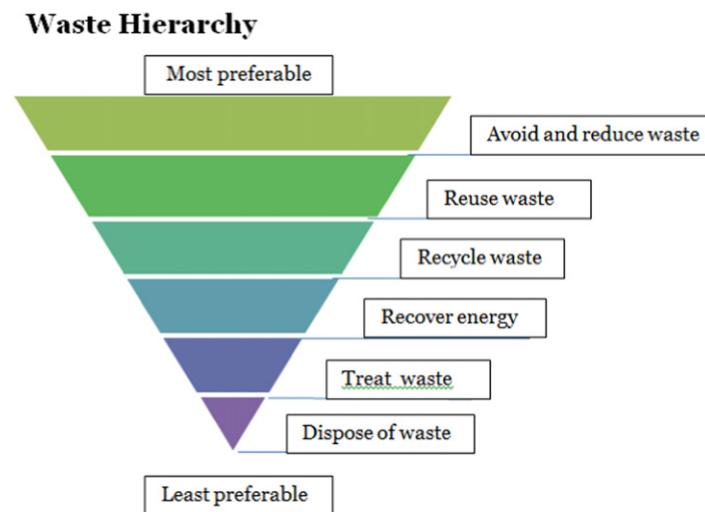
Table 6 Origin and causes of construction waste

Origin of waste	Causes of waste
Contractual	• Errors in contract Document • Contract document incomplete at commencement of construction
Design	• Design changes • Design and construction detail errors • Unclear unsuitable specifications • Poor coordination and communication (late information, last minute client requirements, slow drawing revision and distribution)
Procurement	• Ordering errors (ordering items not in compliance with specification) • Over allowances (i.e., difficulties to order small quantities) • Supplier errors
Transportation	• Damage during transportation • Insufficient protection during unloading • Inefficient methods of unloading
On-site management and planning	• Lack of on-site waste management plans • Improper planning for required quantities • Lack of on-site material control • Lack of supervision
Material storage	• Inappropriate site storage space leading to damage or deterioration • Improper storing methods • Materials stored far away from point of application
Material handling	• Material supplied in loose form • On-site transportation methods from storage to the point of application • Inadequate material handling
Site operation	• Accidents due to negligence • Equipment malfunction • Poor craftsmanship • Time pressure
Residual	• Waste from application processes (i.e., over preparation of mortar) • Packaging
Other	• Weather • Vandalism

Table 7 Components of C and D waste

Major component	Minor component
Cement concrete	Conduits
Bricks	GI pipes/Iron pipes/plastic pipes
Cement plaster	Electrical wires/conduits/fittings
Steel from RCC	Panels
Wooden doors & windows	Asbestos and contaminated soil
Aluminum windows & doors	Glass
PVC doors & windows	Plastic carry bags, sachets of tobacco and other plastics, clothes, cement bags, gunny bags, thermocol, etc.
MS grill, window frames	Trees, plants
Roofing support system	
Rubble	
Timber, etc.	
Stones & Clay (soil from excavation)	

Primary source: Toolkit for C and D waste management 2016.

**Fig. 3** Waste hierarchy. Source: Waste Management Association of Australia.

activity related to the development of infrastructure whereas real estate sector includes the mass housing, shopping malls, healthcare, etc.

Among so many reasons behind the generation of C and D waste, six major causes of waste are design, procurement, materials handling, operation, residual, and other. A recent research that covered C and D waste generation indicated that 33% of on-site waste is due to architects' failure to implement waste reduction measures during design stage. According to Dajadian and Koch, a list of origin and cause of construction waste is mentioned below in [Table 6](#).

According to [Dajadian and Koch \(2014\)](#); Origin and causes of construction waste.

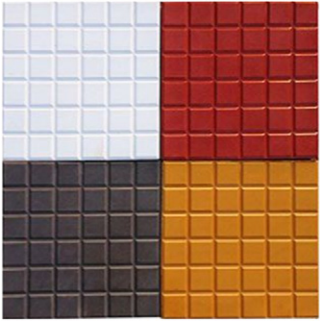
Components of C and D Waste

C and D waste has been classified into two major components as per the Toolkit for C and D waste management 2016 as shown in [Table 7](#).

Waste Handling Options

Across the globe, the waste management sector follows a generally accepted hierarchy. The concept of 4R referring to Reduce, Reuse, Recycle and Recover particularly in the context of production and consumption is very familiar today in most of the developed countries. Re-use and recycling of some materials and resources are becoming industry standard practice ([Fig. 3](#)).

Table 8 Recycled materials and possible applicability

Sl. No.	Product name	Sample image	Probable uses
1.	Ready mix concrete		Can be used in all types of construction work
2.	Hollow bricks		Can be used in any type of building construction
3.	Pavement blocks		● Parking pavements ● Pedestrian pathways ● Passageway
1.	Tiles		
1.	Checkered		Can be used in ● Lobby area ● Footpaths ● Entrance ● Stair-cases of public buildings ● Passages of auditoria and storage godowns
2.	Brick		● Can be used as a cladding material for façade ● In interiors

(Continued)

Table 8 Continued

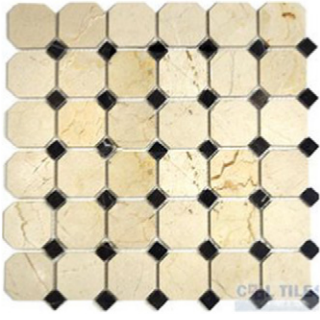
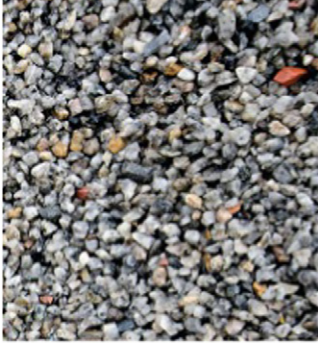
Sl. No.	Product name	Sample image	Probable uses
3.	Dumble		Can be used in ● Footpath ● Outdoor pavement
4.	Wall		Wall Cladding both in ● Interior ● Exterior
5.	Interlocking		Can be used in ● Footpath ● Outdoor pavement
6.	Tech tile		Covering roofs, floors, walls, or other objects such as tabletops
7.	Kerb stones		Used at raised pavements, sidewalks and footpaths

Table 8 Continued

Sl. No.	Product name	Sample image	Probable uses
II	Raw material		
1.	Granular sub base (GSB)		Are used usually as crushed stone, crushed slag or concrete, or slate
2.	Manufactured sand		Manufactured sand have been regularly used to make quality concrete
3.	Aggregates 5–10 mm		Used as base material under foundations, roads, and railroads
4.	Aggregates 10–20 mm		Can be manufactured as per customer requirements
5.	Loose soil/excavated soil		For land filling purpose

(Continued)

Table 8 Continued

Sl. No.	Product name	Sample image	Probable uses
6.	Jali		Can be used in a similar manner as other kind of 'Jali' products available in the market
7.	Drain cover		Can be used in a similar manner
8.	Boundary wall		Various other design options can be made

Primary source: Toolkit for C and D waste management 2016.

Waste Reduction

Waste reduction is the most preferable option of waste management. Every effort should be made towards reduction of waste at the generating points through careful design, construction practices and management. It will bring two-fold benefits in mitigating greenhouse gas emissions. Firstly it will help to avoid the emissions associated with the product manufacturing process and secondly the direct emission involved with the conventional waste management activities.

Waste Reuse

Reusing the C and D waste can save huge amount of natural resources and also can reduce carbon footprint. Disposal of C and D waste into landfills would also be minimized.

Waste Recycling

The principal factors for recycling of Construction and Demolition waste in the building industry are growing concern for environmental protection, conservation of natural aggregate resources, shortage of land for waste disposal, and increasing cost of waste treatment. The reuse of recycled materials derived from construction and demolition waste is growing all over the world.

Table 9 Energy intensities with the recycling process of different building materials

Building materials	Recycled content (%)	Production energy unit for recycle process (MJ/kg)
Aluminum	81	108.6
Asphalt	30	7.32
Concrete	30	0.805
Glass	100	11.9
Reinforcing bar	100	21.6
Stainless steel	100	11
Galvanized steel	100	32.75

Note: Ng, W.Y., Chau, C.K., 2015. New Life of the Building Materials – Recycle, Reuse and Recovery. ICAE.

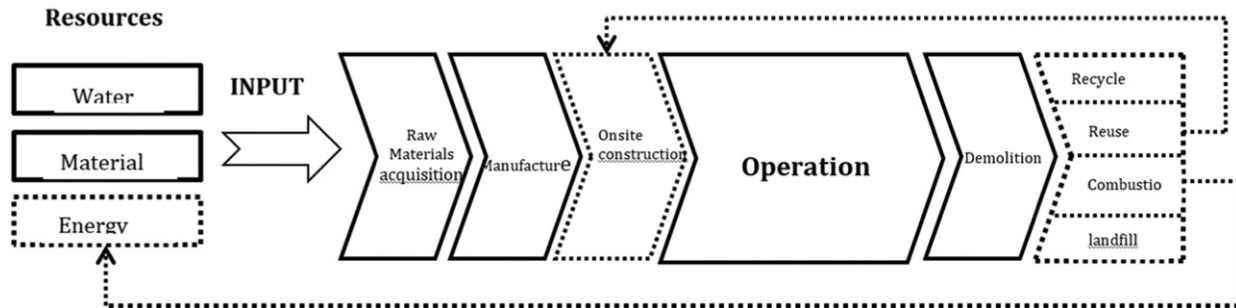


Fig. 4 The life cycle stages and boundary. Source: Ng, W.Y., Chau, C.K., 2015. New Life of the Building Materials – Recycle, Reuse and Recovery. ICAE.



Fig. 5 Fencing done with the waste sheet left over after the laser cutting of metal components. Source: Pushing the boundaries: Fence materials and design. Available at: <https://renew.org.au/>.

Recovery

The recovery of waste and the use of recovered materials should be encouraged widely in order to conserve natural resources. Waste must be recovered without endangering human health and without the use of processes or methods likely to harm the environment. Recovery operation generally implies a prior treatment of the waste.

Recycled C and D Waste Products and its Applications

Construction accounts for 65% of the total investment in infrastructure. Investment in construction accounts for nearly 9% of India's Gross Domestic Product (GDP). This sector is likely to have a steep increase because of Government of India's recent initiative in allowing 100% Foreign Direct Investment in Real Estate Sector. Thus the demand for building materials will increase undoubtedly. Some of the products and possible applications are shown in Table 8.



Fig. 6 Wrought iron fences. Source: Pushing the boundaries: Fence materials and design. Available at: <https://renew.org.au/>.



Fig. 7 Rock Garden, Chandigarh.

Energy Implications

Life cycle assessment (LCA) of buildings is to be carried out properly to evaluate the impacts of buildings on the environment in coming days. Within this framework, Life Cycle Energy Analysis (LCEA) needs to be applied to evaluate all energy uses by a building over its life cycle which mainly consists of manufacturing phase, operation phase and demolition phase. During the calculation process, the optimization of energy use in each and every component and activities will be required. The present day casual practices would be replaced by a more professional quantifiable approach through which all stakeholders involved in the construction process of a building would remain aware about the energy balance in a building (Fig. 4). Thus, the careful selection of building materials out of the whole reserve either natural, manufactured or recycled will make a big difference in retaining a sustainable environment (Table 9).

Some Case Examples

Mara Ripani of Village Dreaming talked about some possible ways of using recycled plastic and wood-plastic composites, metal, stone and living plants. Fencing or boundary wall designs could be made using steel sheet, aluminum or cast iron (Fig. 5).

These materials are non-renewable but very much recyclable. It is a known fact that air-dried sawn hardwood has a very low embodied energy cost of 0.5 MJ/kg, compared to galvanized steel 38.0 MJ/kg and aluminum 170.0 MJ/kg. A metal fence will outlast a longer time compared to any natural material and also a greater mass of natural material would be required to get a similar strength of metal fencing (Fig. 6).



Fig. 8 Collage House, Mumbai-India. *Source:* Available at: <https://www.facebook.com/spsarch>.

The Rock Garden in Chandigarh, India was designed in the year 1957 using natural and recycled or waste materials (**Fig. 7**).

According to S+PS Architects in Arch Daily, this house has a facade made from the doors and windows of homes that were demolished in the city. The project has made use of other recycled materials, including 100-year-old salvaged stone columns, flooring made from the beams of old houses, fabric waste and waste slivers of cut stone (**Fig. 8**).

Conclusion

The construction industry is one of the most polluting in the globe and people always try to hide the debris and filthy waste from sight. The economic and environmental benefits to be gained from C and D waste reduction and recycling are enormous, and it will benefit both the environment and the construction industry in terms of cost savings. Architects, Engineers and designers can take this as a challenge and turn this waste into valuable resources for using it into the construction again in an innovative way. New architectural ideas and design techniques would enrich various possibilities and enhance further scope in this sector. The C and D debris if properly managed can become a major source of construction material.

See also: Use of Steel as a Sustainable Concept

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Use of recycled aggregates in concrete – A paradigm shift.

Advanced Polymeric Coatings and Their Applications: Green Tribology

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Introduction

Recent advances in polymer engineering, such as new emergency materials and new coating technologies enable broader applications of polymeric coatings. Three types of functional coatings, namely tribological coatings, hydrophobic coatings and self-healing coatings have been widely investigated, and summarized in this article.

Tribology has emerged as a field that contributes to the development and implementation of materials that are sustainable, from an energy and environmental point of view. Sustainable materials from the point of view of green tribology are those materials that can diminish friction and wear of interacting surfaces, minimize heat dissipation, and thus lower pollution. Through the development of self-lubricating materials, wear can be minimized and contribute to a greener environment by increasing the life cycle of sliding materials (tribopairs), causing a positive impact in environmental degradation, by decreasing the waste and recyclability cycle (Sasaki, 2010; Anand *et al.*, 2017). Environmentally friendly tribomaterials in the form of self-lubricating advanced polymeric coatings contribute to a greener environment by reduction or complete elimination of liquid lubricants at the sliding interfaces, thus reducing emissions, and in turn less pollution to the atmosphere.

High bearing polymer coatings based on PEEK, PTFE, ATSP and their blends have emerged as a cost-effective solution for friction and wear problems of sliding interfaces that must operate in the absence of lubricant. Experimental results show that the friction coefficient (COF) at a polymer/metal interface is governed by solid lubrication in the form of third bodies, even at values lower than those found in metal/metal interfaces in the boundary and mixed lubrication regimes (Demas and Polycarpou, 2008; Nunez *et al.*, 2010; Akram *et al.*, 2013), thus contributing to a greener environment (less power consumption). In addition, these advanced polymeric coatings have been applied in aggressive tribological applications, such as cryogenic conditions, and in space applications, where materials have to be able to withstand sliding under non-traditional conditions, making their design challenging (Gao *et al.*, 2018). The purpose of this book chapter is to provide an insight of the recent trends in the design of advanced high bearing blended polymer coatings, as viable candidate solutions for aggressive tribological applications in demanding contemporary industries, and their contribution to a greener environment.

Superhydrophobic coatings exhibit low surface energy, and when water rests or slides on the surface, it absorbs dust and together slide off the surface: this phenomenon is called self-cleaning. The self-cleaning property can save cost for cleaning, when superhydrophobic coatings are applied on surfaces such as solar panels and windows. In addition, superhydrophobic coatings can enhance anticorrosion properties by separating water in contact with metal substrates. When coatings are in service, they are prone to damage due to their thin section: once damage occurs, the coatings will lose their functionality such as anticorrosion. Thus, by applying self-healing coatings that can repair themselves is attractive; by self-healing, the coatings will have a longer service life and there is no need to re-apply them when they experience damage.

Polymer Coating Deposition Techniques for Advanced Tribological Applications

Polymer coating deposition on a wide variety of engineering substrates has gained significant attention. Coatings are tailored to provide specific characteristics, such as wear, corrosion, chemical and weathering resistance, to improve thermal conductivity, to provide electrical insulation, and in the case of some polymers, to provide solid lubrication and low friction. Thermal spray (TS) and cold dynamic spray or simply cold spray (CS) are the main techniques employed to coat polymers onto substrates.

Among the main advantages of TS are: (a) the feasibility to coat large components of complex geometries, (b) the use of powder as raw material (eliminating the use of solvents), and (c) the possibility of the technique being applied in the field, to coat and/or repair a component. Depending on the physical principle employed for deposition, TS techniques can be subcategorized as shown in Fig. 1. For instance, in TS, deposited polymer material in powder form adheres to the substrate by a high velocity and high temperature thermal jet produced by electrical or chemical energy. This energy is used to heat, melt, and spray the molten material introduced in the flame through a nozzle, before impacting the target surface. Once the particles impact the substrate, they solidify and form the coating by superposition (Petrovicova and Schadler, 2002).

In CS the amount of energy (electric or calorific) required to accelerate the particles to the substrate is lower, compared to TS. In fact, the name CS refers to the range of temperatures employed during the flow of the gas through the nozzle, which can vary from -100 to 100°C (Raletz *et al.*, 2006). In CS, due to the relatively low temperature process, which is usually lower compared to the melting point of the powder, the adhesion forces between the deposited powder and substrate, along with the cohesion forces between the powder particles in the solid state, make this process remarkable. In fact, due to the low temperature and the absence of oxidation, the final coatings produced by CS not only have lower residual stresses and porosity, but higher bond strength, compared to TS techniques (Champagne and Helfrich, 2014). Unlike TS, CS can be performed at standard pressure, temperature, and humidity, simplifying the operating conditions.

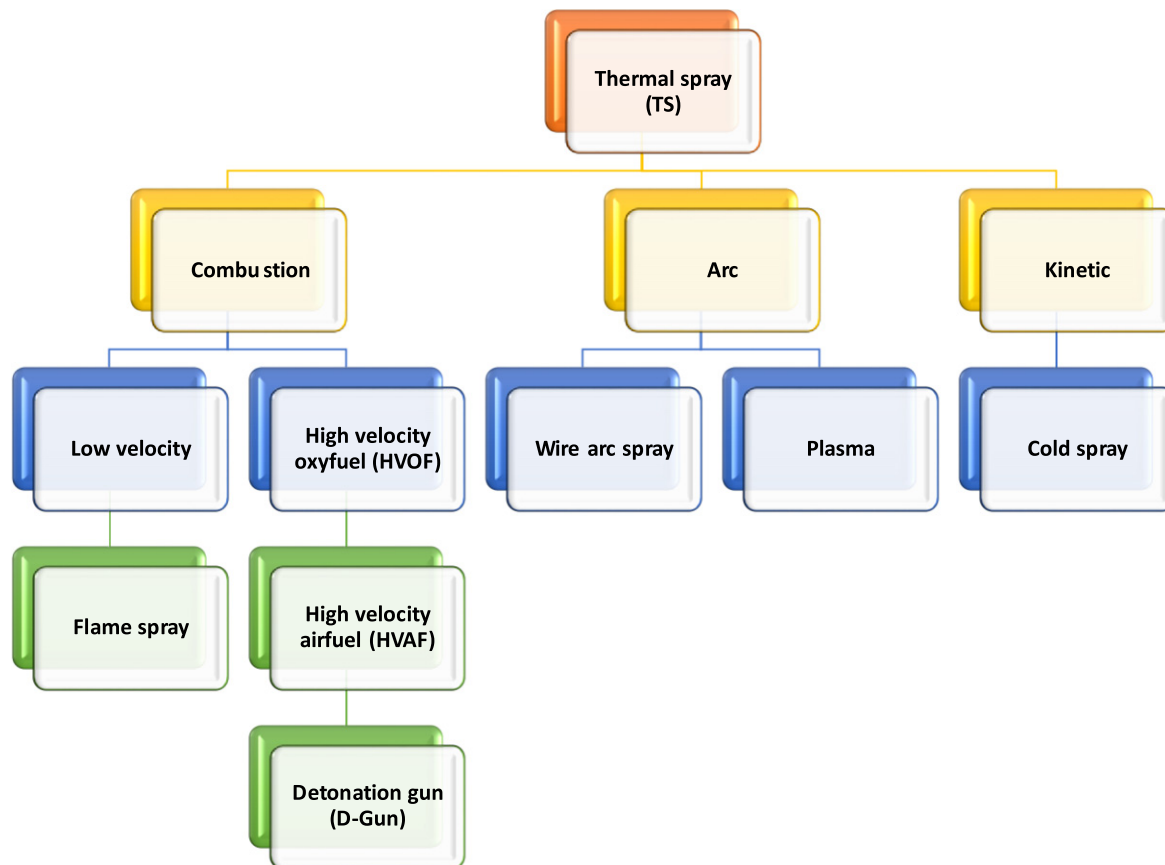


Fig. 1 Thermal spray deposition techniques and subcategories. Modified from Wen, C., 2015. Surface Coating and Modification of Metallic Biomaterials. Woodhead Publishing.

According to **Fig. 1**, TS deposition methods for polymer coatings are classified depending on the energy source employed to accelerate the powder particles towards the substrate. As shown in **Fig. 1**, powder flame spray, arc wire, plasma, high velocity oxyfuel (HVOF), and CS are considered the most popular TS polymer coating deposition techniques, where the final coating thickness ranges from tenths of micrometers to several millimeters (Bach *et al.*, 2006).

Fig. 2(a) shows a schematic of the wire flame spray, where a concentric wire material is driven and reacts with an oxygen-fuel rich gas flame. As a result, the material is melted and sprayed towards the substrate to be coated. Similarly, in powder flame spray, the wire is replaced by a polymer powder which reacts with the flame and reaches the substrate to form the coating. Plasma is another TS process that can be used for the deposition of polymer coatings. As shown in **Fig. 2(b)**, an arc of high frequency develops between a cathode (usually tungsten) and anode, ionizing the gas flowing through the electrodes (for instance He, N₂, H₂). As a result of this process, the temperature of the plasma can reach up to approximately 25,000°C and is used to melt the powder material and accelerate it towards the substrate (Davis, 2001).

Surface preparation is one of the key aspects to avoid delamination of the coating to the substrate. This process is usually performed by roughening the substrate by using grit blasting, which increases the surface roughness. As a result, the exposed surface of the substrate is activated by an increase in free surface energy which improves the bonding between the impacting polymer particles and the substrate (Fender, 1996; Vyawahare, 2006). In CS, powder polymer particles reach and bond to the substrate in solid state by the acceleration of the gas that passes through a convergent-divergent nozzle (Assadi *et al.*, 2011).

Different types of polymers for advanced tribological applications can be applied using the aforementioned techniques. These polymers are classified on a pyramid, based on their mechanical properties, operating temperatures and cost (see **Fig. 3**) (Friedrich, 2018). On top of the pyramid shown in **Fig. 3**, polymers such as Polyetheretherketone (PEEK), Polyimides (PI), Polyamide-imide (PAI), Polytetrafluoroethylene (PTFE) and aromatic thermosetting copolyester (ATSP) (Frich *et al.*, 1996; Frich and Economy, 1997; Zhang, 2008; Lan *et al.*, 2016) are designed for tribological problems, and are commercialized as powders, where their size ranges from 10 to 180 µm (Berretta *et al.*, 2014).

As shown in **Fig. 4**, polymer powder can be obtained using cryogenic mechanical grinding. Tribological studies of high performance thermoplastic polymer coatings, show that flame spray, HVOF, plasma, electrostatic deposition and CS are the most popular techniques to deposit a variety of high-performance polymers (HPPs). For instance, through annealing treatment and holding time of the substrate, it was shown that PEEK coatings deposited on Al substrates by flame spraying showed higher crystallinity. Thus, higher hardness and wear

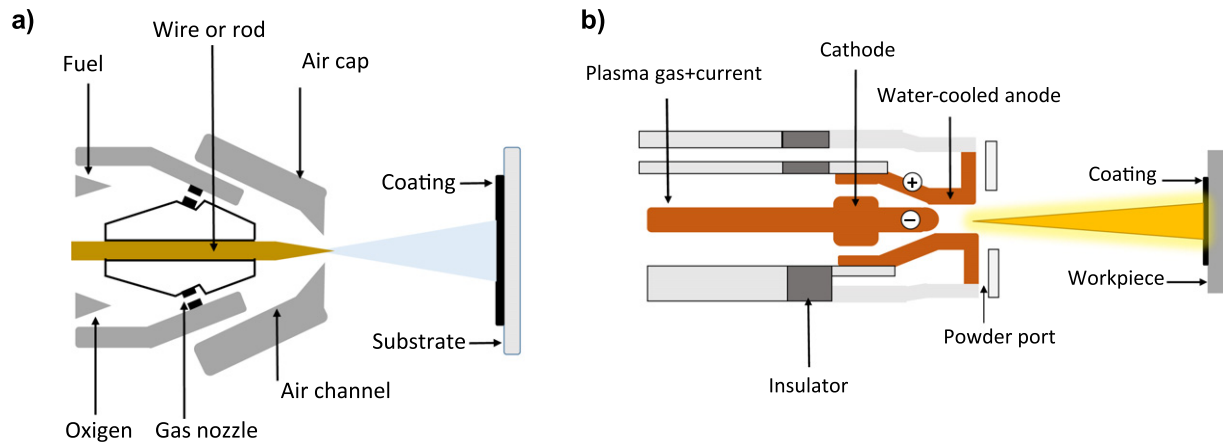


Fig. 2 Thermal spray deposition techniques: (a) Wire flame spray, (b) plasma spray. Modified from Davis, J.R., 2001. Introduction to thermal spray processing. In: Handbook of Thermal Spray Technology, 3–13. ASM International and Thermal Spray Society.

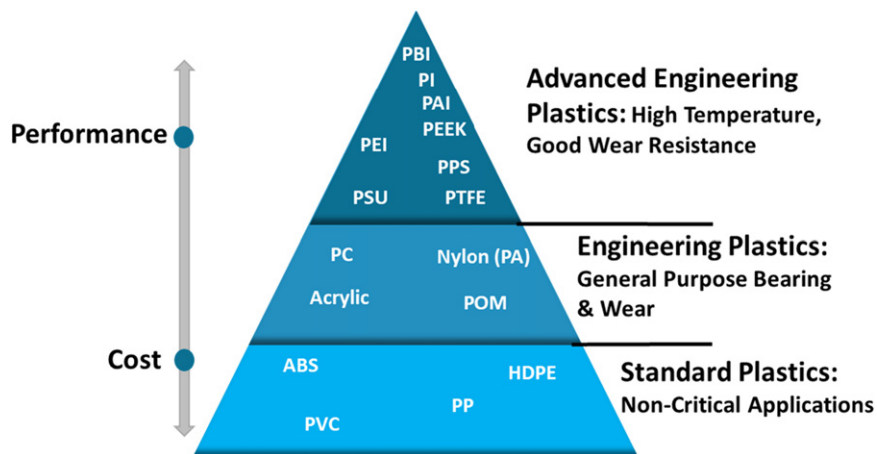


Fig. 3 Polymer pyramid listing high performance polymers used in TS processes organized from amorphous to crystalline. Modified from Friedrich, K., 2018. Polymer composites for tribological applications. Advanced Industrial and Engineering Polymer Research 1, 3–39.

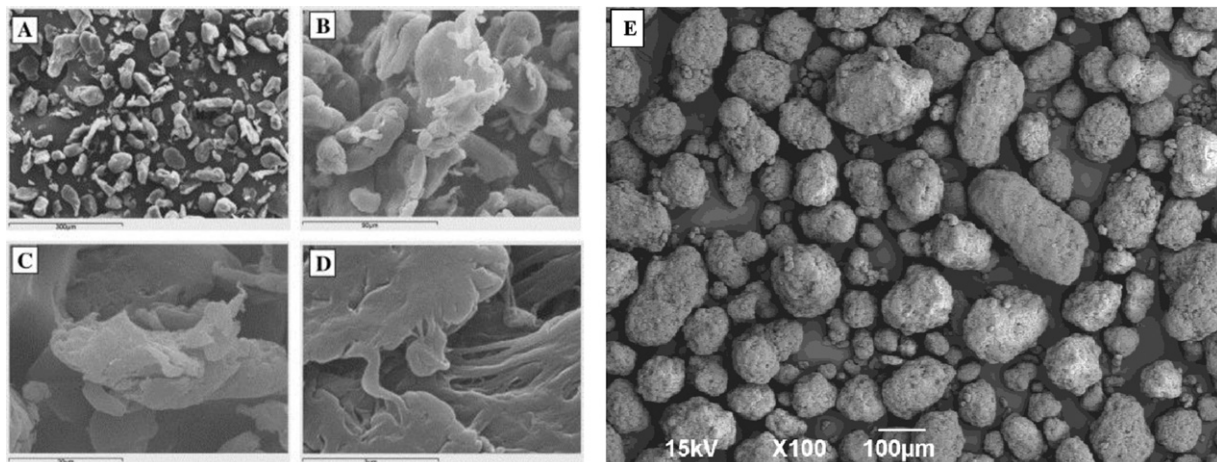


Fig. 4 SEM microscopy images of PEEK powder (A–D), and (E) polymer powder of Ultra high molecular weight polyethylene (UHMWPE). Modified from Berretta, S., Ghita, O., Evans, K.E., 2014. Morphology of polymeric powders in Laser Sintering (LS): From polyamide to new PEEK powders. European Polymer Journal 59, 218–229.

resistance, compared to those treated with lower annealing temperature (Zhang *et al.*, 2006b). Other studies, also show the benefits of substrate pretreatment by Nd:YAG (*neodymium-doped yttrium aluminum garnet*) and CO₂ infrared lasers; these treatments provide advantages compared to conventional grit blasting, especially for brittle materials. Laser surface pretreatment has the advantage of delivering a significant amount of power on a small area of the work piece, without compromising the bulk properties of the substrate. These pretreatments, also reduce the heating time (compared to flame and induction heating) of the substrate, and improve the mechanical properties of the final coatings (Zhang *et al.*, 2006a). It was proven that treatment with CO₂ laser improved densification of the PEEK coating, leading to less porosity and higher mechanical properties, compared to Nd:YAG laser treatment.

Polymer coating deposition is also carried out using electrostatic spraying, where the polymer powder is electrostatically charged under low current (in the μA range) and voltage (30–90 kV) and applied onto the electrically grounded substrate. There is abundant literature related to tribological studies of HPPs deposited using electrostatic deposition. These studies were mainly focused on deposition of blended PEEK, PI, PTFE, and ATSP polymer powders deposited onto substrates such as gray cast iron, Al390-T6, sintered iron, and Mn-Si brass, which are found in different air-conditioning and refrigeration components, as well as electrical submersible pumps (ESPs) (Shaffer and Rogers, 2007; Demas and Polycarpou, 2008; Dascalescu *et al.*, 2009; Nunez *et al.*, 2010; Nunez *et al.*, 2011; Yeo and Polycarpou, 2012; Lan *et al.*, 2017; Lan *et al.*, 2018; Lan and Polycarpou, 2018; Nunez *et al.*, 2019). Deposition of the aforementioned HPPs as coatings through electrostatic deposition, and tailored for tribological applications has proven to be effective and inexpensive, compared to other techniques. However, deposition techniques, such as CS spray eliminate the curing process, required in the electrostatic technique.

Fig. 5 shows typical cross-sectional images of different polymer coatings obtained by electrostatic deposition. It can be seen that the typical thickness of the coatings is of the order of tenths of microns (Nunez *et al.*, 2011). The list of polymers that can be sprayed onto different substrates using different TS techniques is listed in reference (Petrovicova and Schadler, 2002). There are other techniques such as spin coating and dip coating that can be used for the deposition of uniform thin polymer films (from few nanometers to few micrometers) on different substrate materials, and are used in different sectors, such as the semiconductor and biomedical industries. However, coatings developed using these techniques are not specifically designed to address tribological issues (Danglad-Flores *et al.*, 2018).

Tribology of Polymer Coatings Under Extreme Working Conditions

Increasing demand of advanced materials that can withstand extreme operating conditions in several industries, has called the attention of the polymer industry for the development of composites and blends that can perform well under difficult or extreme working conditions. For instance, spacecrafts and satellites are exposed to cosmic rays, impact of debris from spacecraft and

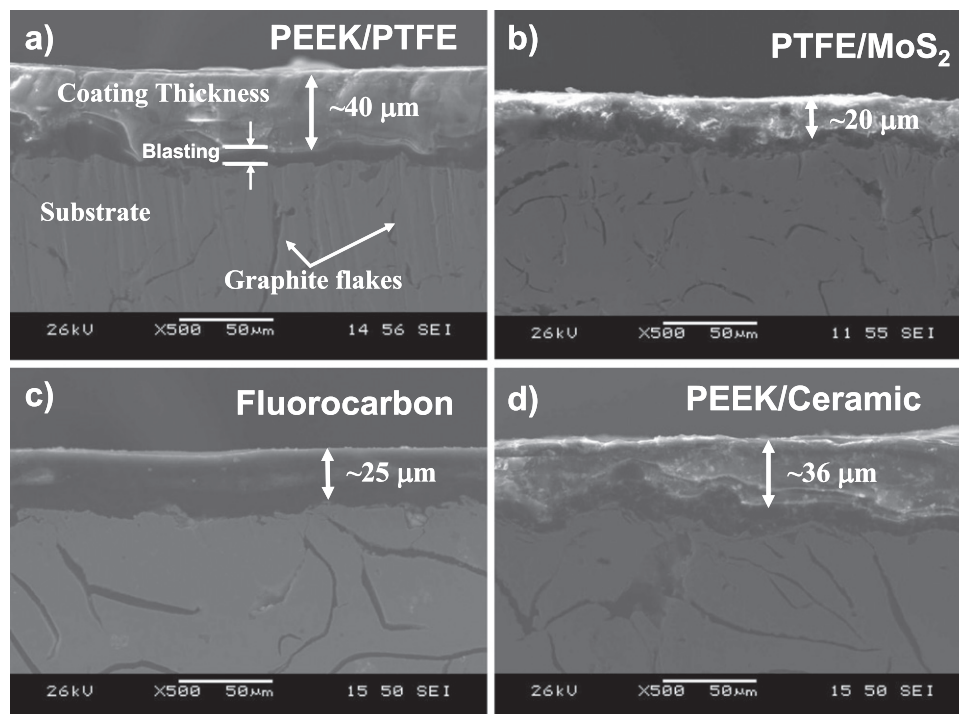


Fig. 5 Cross sectional SEM images of typical HPP coatings: (a) PEEK/PTFE, (b) PTFE/MoS₂, (c) Fluorocarbon, (d) PEEK/Ceramic deposited on gray cast iron by electrostatic deposition. Modified from Nunez, E.E., Yeo, S.M., Polychronopoulou, K., Polycarpou, A.A., 2011. Tribological study of high bearing blended polymer-based coatings for air-conditioning and refrigeration compressors, *Surface and Coatings Technology* 205 (8–9), 2994–3005.

meteoroids, ultra violet radiation, vacuum, microgravity, thermal cycling, and cryogenic conditions, which make the design and selection of materials for these applications challenging (Pippin, 2003; Kondyurina *et al.*, 2006; Wang *et al.*, 2016; Gao *et al.*, 2018). In the air-conditioning and refrigeration industry there has been interest in oil-less compressors, mainly due to the negative thermodynamic effect from the liquid lubricant/refrigerant mixture in the refrigeration cycle. The mixture not only decreases the thermodynamic efficiency, but under boundary/mixed lubrication conditions, it can affect the properties of the lubricant causing scuffing on the sliding components (Demas *et al.*, 2005; Cannaday and Polycarpou, 2006; Nunez *et al.*, 2008; Akram *et al.*, 2014).

Another industry where harsh operating conditions cause tribological issues, is the oil and gas industry. In this regard in ESPs, high bearing loads and high temperature can cause failure of the lubricant film in the hydrodynamic bearings, causing a transition from hydrodynamic to boundary and mixed lubrication regimes. As a consequence, interactions of the asperities of the pad bearings might cause seizure, leading to scuffing at the bearing contact interface (Wang, 1997; Lan *et al.*, 2017). As stated above, advanced thermoplastic polymers can be used to coat different substrates in the tenths of micrometer thickness. One of the main advantages of high bearing blended polymer coatings, is not only the fact that they can provide solid lubrication in the form of third bodies under unlubricated conditions (in the absence of liquid lubricant), but also the fact that they provide a low cost/efficiency ratio (Yeo and Polycarpou, 2012, 2013).

We have been broadly studying the tribological performance of high bearing load blended polymer coatings based on PEEK, PTFE, and ATSP for different industrial applications; Testing instruments include specialized custom-made tribometers, which are capable to carry out tests at high normal loads (up to 5000 N), high temperatures (from 120 up to 1000°C) and high pressures up to 13.8 MPa (Dascalescu *et al.*, 2009). In the air-conditioning and refrigeration industry the studies have been focused on the replacement of sliding components. Namely, Al390-T6, Mn-Si brass, which are used in automotive swash plate compressors, and gray cast iron, and sintered iron, commonly found in scroll and piston compressors, respectively (Yeo *et al.*, 2010).

Three different commercially available PTFE-based coatings deposited onto gray cast iron disks (Dura-Bar G2); namely, DuPont® 958-303, DuPont® 958-414 and Whitford Xylan® 1052, all of them with thickness of approximately 20–30 µm (see Fig. 6), were tested against 52100 steel, under unlubricated conditions (Demas and Polycarpou, 2008). The first two coatings were PTFE/pyrrolidone based, while the latter was PTFE/MoS₂. These coatings were tested under reciprocating motion ($\pm 30^\circ$ at a frequency of 4.5 Hz) to simulate the contact of the wrist pin and the piston in a piston-type compressor. Under aggressive loading conditions (460 MPa Hertzian line contact pressure), the experimental results show that scuffing at the interface was retarded due to the action of third bodies coming from the wear debris. This debris was kept trapped at the contact interface and retarded scuffing by the action of solid lubrication. This was proved after running experiments at 2, 5, 10, and 60 min, where it was shown that most of the wear took place during the running-in transient period, by comparing wear depth contact profilometry measurements against the thickness of the coatings, being in all cases around 20–30 µm (see Fig. 6). These results proved that advanced polymer coatings could potentially be applied in situations of high contact stresses under unlubricated conditions, being a relatively cheaper solution compared to hard diamond-like carbon (DLC) coatings (Grill, 1993; Donnet and Erdemir, 2004).

Studies were performed to understand the feasibility of applying the aforementioned coatings on Al390-T6, gray cast iron, and sintered iron substrates (Yeo *et al.*, 2010). It was proved through X-ray Photoelectron Spectroscopy (XPS), that Al390-T6 was

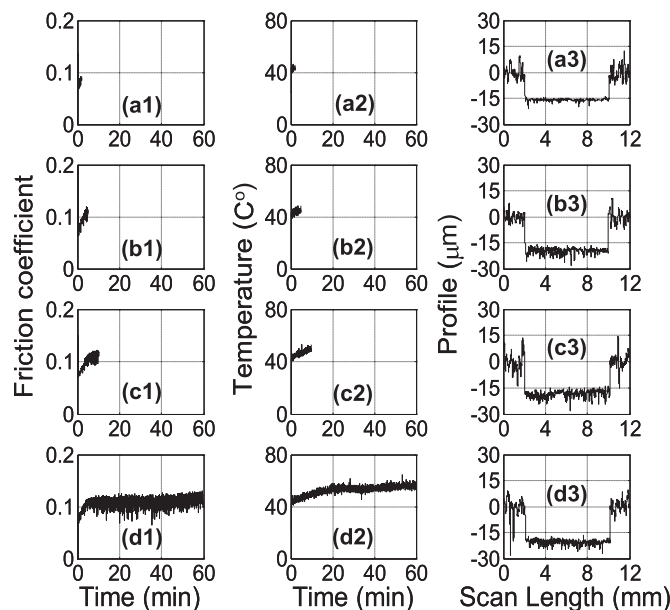


Fig. 6 Friction coefficient, near contact temperature and profilometric measurements for experiments performed at 2 (a1–a3), 5 (b1–b3), 10 (c1–c3) and 60 (d1–d3) mins for DuPont® 958-303 in CO₂ atmosphere at 445 N. Modified from Demas, N.G., Polycarpou, A.A., 2008. Tribological performance of PTFE-based coatings for air-conditioning compressors. *Surface and Coatings Technology* 203 (3–4), 307–316.

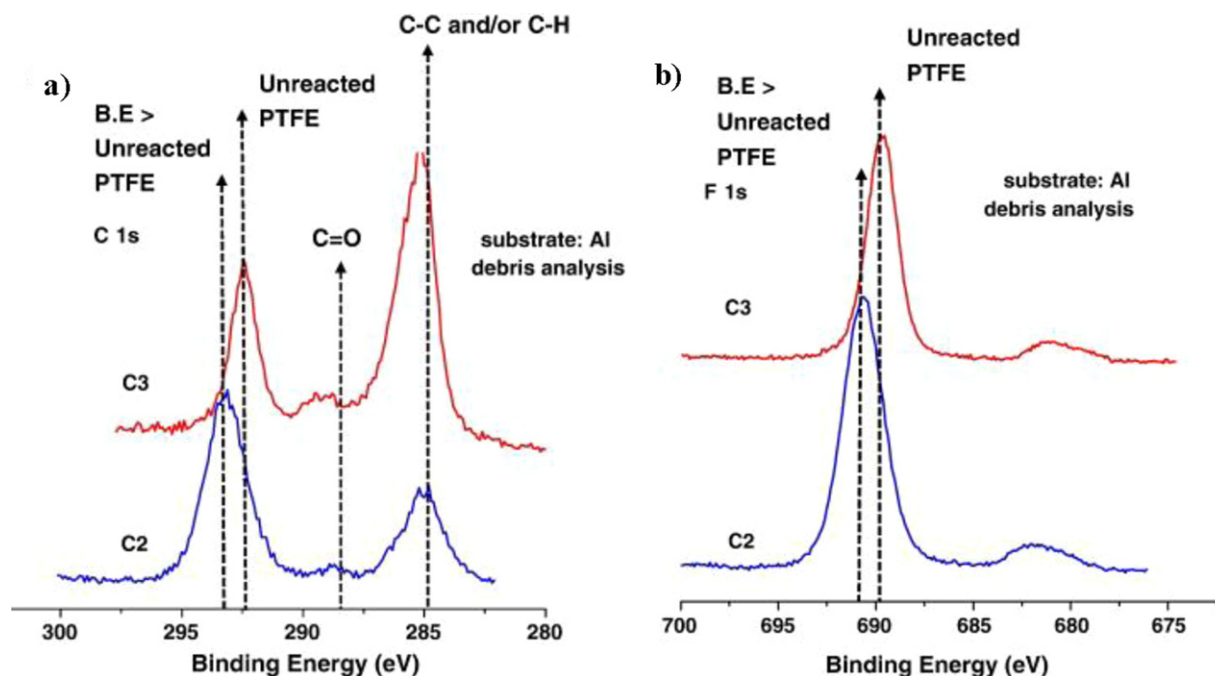


Fig. 7 Analysis of the wear debris after tribotesting of AISI 52100 steel pins against Al390-T6 coated with DuPont[®] 958-414 (coating C2) and Whitford Xylan[®] 1052 (coating C3) by XPS core level spectra (a) C1s; (b) F1s. Modified from Dascalescu, D., Polychronopoulou, K., Polycarpou, A., 2009. The significance of tribochemistry on the performance of PTFE-based coatings in CO₂ refrigerant environment. *Surface and Coatings Technology* 204 (3), 319–329.

Table 1 List of different commercial polymer coatings and engineering substrates

Coating material	Vendor	Substrate material compatibility				Thickness (μm)
		Al390-T6	Gray cast iron	Sintered iron	Chrome copper C182000	
PEEK/PTFE	Southwest Impreglon	Good	Excellent	Excellent	Excellent	30–40
PTFE/MoS ₂ (Fluorolon [®] 325)	Southwest Impreglon	Good	Excellent	Excellent	–	20–30
Fluocarbon (Impreglon [®] 218)	Southwest Impreglon	Poor	–	–	–	20–30
PTFE/Pyrrolidone-1 (DuPont [®] 958–303)	DuPont [®]	Poor	Excellent	Excellent	–	20–30
PTFE/Pyrrolidone-2 (DuPont [®] 958–414)	DuPont [®]	Poor	Excellent	Excellent	–	20–25
PTFE/MoS ₂ (Whitford Xylan [®] 10–52)	Whitford [®]	Excellent	–	Excellent	–	15–20
ATSP/PTFE	ATSP Innovations	–	Excellent	Excellent	Excellent	20–30

difficult to coat and that PTFE/MoS₂ was the only polymer material capable to adhere onto this substrate, and also the only one which did not suffer severe scuffing (Dascalescu *et al.*, 2009). It can be seen in the XPS spectra of Fig. 7(a), that fragmentation of PTFE enabled its interaction with the Al390-T6 substrate. As a result, this chemical interaction improved the adhesion of PTFE to the substrate, based on the C-species peaks at 292 eV, related to PTFE (which is found as a peak in the F1s core level spectra analysis (Fig. 7(b))). It was proven that under unlubricated sliding conditions, these coatings provide solid lubrication through their ability to form transfer films, making them an attractive solution to replace metal tribopairs in oil-less engineering applications (Ovaert and Cheng, 1991; Bahadur, 2000; Nunez and Polycarpou, 2015).

Feasibility of deposition of these commercial coatings onto different engineering substrates is summarized in Table 1. Micromechanical properties of these coatings were also obtained using a TI-950 TriboIndenter (Yeo and Polycarpou, 2013). The elastic modulus and hardness as a function of contact depth is shown in Fig. 8. It can be seen that all coatings show consistent values of reduced elastic modulus (E_r) and hardness (H) at shallow contact depths (1.5–2.0 μm), except for the case of the PEEK/PTFE coating, with its behavior is attributed to significant pile-up. Fig. 9 shows the wear rates of the same coatings under both oscillatory and unidirectional sliding conditions. It can be observed that there are higher wear rates and COF values under oscillatory conditions, compared to unidirectional sliding, for the same polymer coating. This can be explained by the fact that temperature at the sliding interface is governed by the sliding speed and normal load, which is higher under unidirectional sliding, compared to small amplitude oscillatory sliding. It is expected that under high temperature, adhesion and material transfer will be

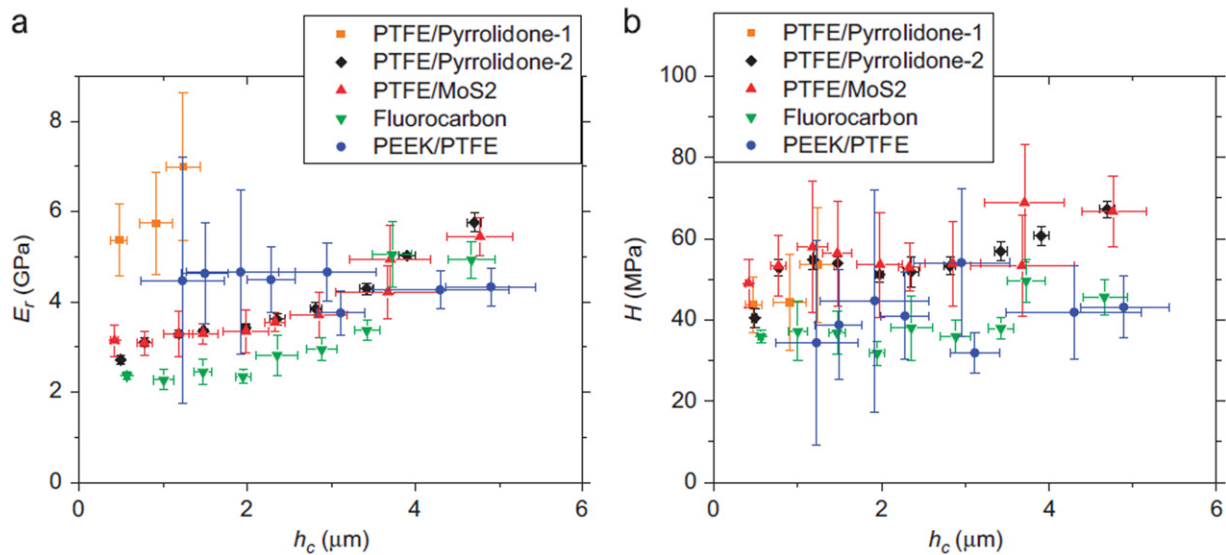


Fig. 8 (a) Reduced elastic modulus and (b) Hardness vs contact depth for five different commercial polymer coatings. Modified from Yeo, S.M., Polycarpou, A.A., 2013. Micromechanical properties of polymeric coatings. *Tribology International* 60, 198–208.

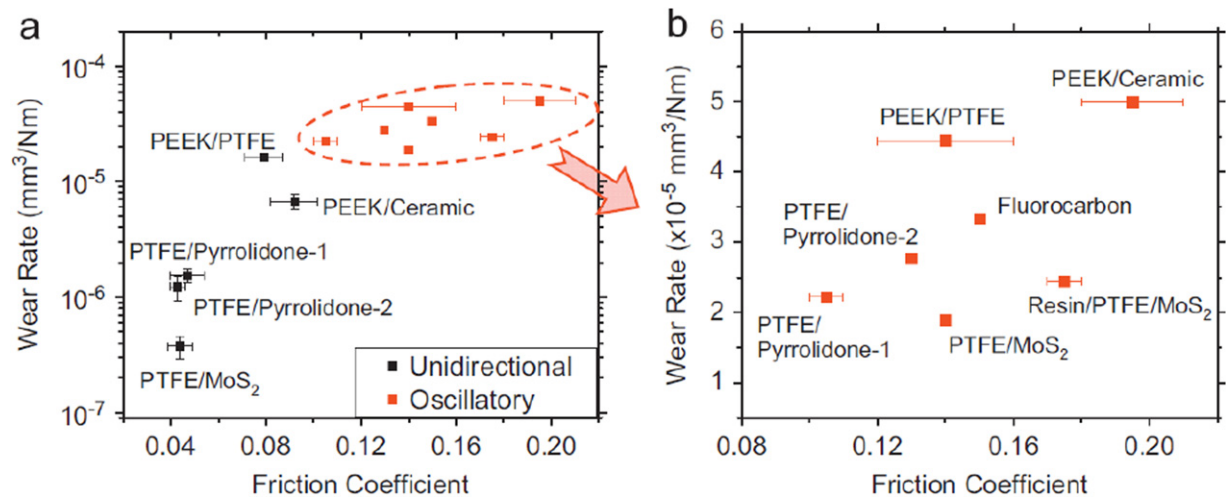


Fig. 9 Friction coefficient vs. wear rate of different PEEK and PTFE blended polymer coatings in CO_2 (22°C and 0.17 MPa) environment at 445 N normal load under both; unidirectional and dry-oscillatory conditions. Modified from Yeo, S.M., Andreas, A.P., 2012. Tribological performance of PTFE-and PEEK-based coatings under oil-less compressor conditions. *Wear* 296, 1–2, 638–647.

enhanced due to higher adhesion which ends up in lower wear rates. Also, under oscillatory conditions, material has to be replenished due to the back and forth sliding motion, decreasing material transfer efficiency (Yeo and Polycarpou, 2014).

Studies on the performance of polymer coatings designed for tilting pad bearings in ESPs have also been performed. C182000 chrome-copper disks were coated by electrostatic deposition with ATSP/PTFE (Zonyl® MP1100) blends (Lan *et al.*, 2017). ATSP-based coatings were compared to PEEK-based coatings (1704 PEEK/PTFE) deposited on the same substrate by an authorized vendor (see Table 1), and both tested against AISI 4130 steel and C932000 bronze cylindrical pins. The experiments were carried out under hydrodynamic lubrication in an abrasive three body (silica) sand (2 wt% silica sand #140) and ISO 46 mineral oil to simulate the conditions of the contaminated lubricated system. The experiments were performed at a nominal contact pressure of 6 MPa with a duration of 30, 80, and 120 min at a sliding speed of 1.9 m/s. It was shown that friction coefficient was lower for PEEK/PTFE coating, compared to ATSP, due to the lower initial roughness of the PEEK/PTFE. Wear rates were lower in case of ATSP tested with smaller sand size, compared to the case of larger #140 sand. This behavior was attributed to the interaction of smaller sand particles at the contact interface when compared to larger size particles (Myshkin *et al.*, 2005). Overall, considering the three different materials tested, ATSP exhibited the lowest wear rate followed by C18200 (chrome-copper), and PEEK/PTFE.

The tribological performance of polymer coatings under cryogenic conditions is of great importance for some industries. For instance, the advent of liquid hydrogen (LH_2) to power rockets and engines poses new challenges in the research of materials that can withstand harsh conditions at very low temperature (Friedrich *et al.*, 2009). The behavior of PTFE at cryogenic temperatures was studied at two different temperatures; namely room temperature (RT) and 77K. It was shown that wear debris of PTFE at RT was governed by creep and shear stresses due to plowing; however, at -196°C abrasion is the main wear mechanisms and wear rate decreases due to an increase in surface hardness (Michael *et al.*, 1991). Tribological performance of ATSP and PEEK based coatings deposited on gray cast iron and tested at -40°C , -100°C and -160°C using a specialized tribometer at normal loads of 5 and 10 N was investigated. No measurable wear was obtained after testing of ATSP and PEEK, and the COF was higher in the PEEK material tested at different cryogenic experimental temperatures. Also, after testing, cracks were observed on the wear tracks and they were related to the elastic modulus of the polymer coatings, where a more ductile PEEK was easier to plastically deform resulting in less microscopic cracks, compared to ATSP.

Hydrophobic Coatings and Their Applications

When a water droplet contacts with a rough solid surface, a contact angle (CA) forms, which is the angle that forms with the vertex located at the three-phase (liquid–vapor–solid) common point: one arm is the liquid–solid interface and the other arm is the liquid–vapor interface, as shown in Fig. 10. When the CA is smaller than 90° , as shown in Fig. 10(a), the solid surface is a hydrophilic surface, which means the solid surface has high surface energy and is able to attract water and wet the surface. Fig. 10(b) shows a hydrophobic surface that has a CA larger than 90° ; the hydrophobic surface has a low surface energy and repels water and resists wetting. When the CA is larger than 150° , the surface is called superhydrophobic surface. The CAs denoted in Fig. 10(a) and (b) are in static condition; once the droplet is in dynamic condition, the contact angle is in a range between receding contact angle (θ_r) and advancing contact angle (θ_a), as shown in Fig. 10(c) on a tilting surface. The contact angle hysteresis (CAH) is equal to the advancing contact angle (θ_a) minus the receding contact angle (θ_r). When the adhesion between the solid and liquid is low, the CAH is small, and vice versa. Thus, the CAH is an important parameter characterizing adhesion, wetting, and energy dissipation during droplet flow (Nosonovsky and Ramachandran, 2015).

The lotus leaf is well-known for its superhydrophobic and self-cleaning property. Fig. 11 shows three different magnifications of SEM images of a lotus leaf surface. Fig. 11(a) with the lowest magnification shows the surface microstructure, which is formed by papillose epidermal cells. After zoom in, a fluffy structure covering the micro-size cell is revealed, as in Fig. 11(b). With further zoom in, the fluffy structure is revealed and shows nano epicuticular wax tubules, as in Fig. 11(c) (Koch *et al.*, 2009). Surfaces with non-polar or less polar material have low surface energy, and such materials include hydrocarbon components of epicuticular waxes. For the lotus leaf, with the nano epicuticular wax tubules as in Fig. 11(c), air is enclosed in the nano structure and forms an

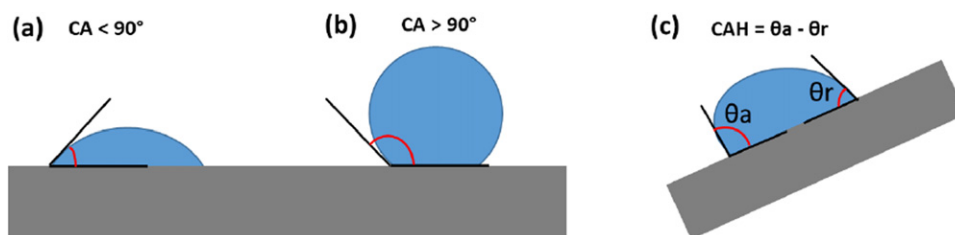


Fig. 10 Presentation of contact angles: (a) Hydrophilic surface, contact angle (CA) $< 90^\circ$, (b) hydrophobic surface, $\text{CA} > 90^\circ$, (c) on a tilting surface, contact angle hysteresis (CAH) = advancing contact angle (θ_a) – receding contact angle (θ_r).

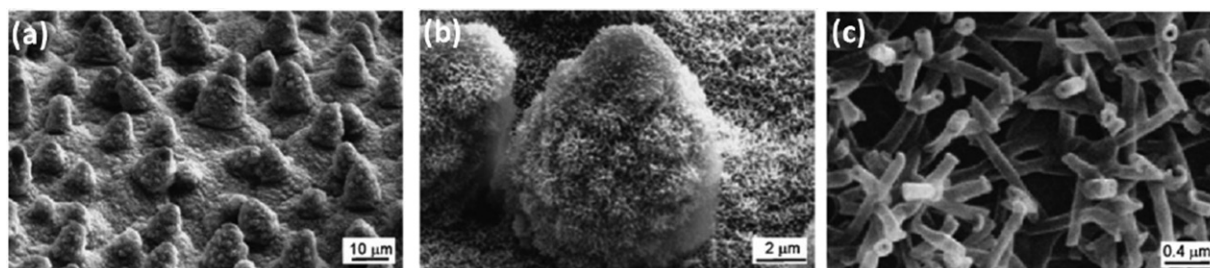


Fig. 11 SEM micrographs with three magnifications on Lotus leaf surface, which consists of a microstructure formed by papillose epidermal cells covered with epicuticular wax tubules on the surface, which create nanostructures. Modified from Koch, K., Bhushan, B., Jung, Y.C., Barthlott, W., 2009. Fabrication of artificial Lotus leaves and significance of hierarchical structure for superhydrophobicity and low adhesion. *Soft Matter* 5 (7), 1386–1393.

air nano tubule composite surface. This composite surface results in low surface energy by increasing the water/air interface and decreasing the solid/water interface.

With large CA, the water is hard to wet the surface and the water droplet forms a near spherical geometry (Barthlott and Neinhuis, 1997). Dirt particles resting on the lotus leaf are usually larger than the surface microstructures, which means that the real solid-solid contact area is small and the adhesion force is also small. Thus, the particle material is more readily wetted by water compared to the epicuticular wax. When the particles encounter the rolling water droplet, the particles are ready to be absorbed by the water droplet and be detached and removed from the lotus leaf (Barthlott and Neinhuis, 1997). Inspired by the micro/nano structure of lotus leaf, artificial coatings have been developed to possess functions such as self-cleaning (Nine *et al.*, 2015; Fenero *et al.*, 2017; Selim *et al.*, 2017; Xiao *et al.*, 2017; Selim *et al.*, 2018b), enhanced antifouling (Selim *et al.*, 2017; Selim *et al.*, 2018a,b), fluid drag reduction (Dong *et al.*, 2013; Srinivasan *et al.*, 2015), and deicing (Arianpour *et al.*, 2016; Nazhipkyzy *et al.*, 2016; Nine *et al.*, 2017). A common method to produce artificial hydrophobic coatings is to use polymers as a binding agent and add different micro/nano particle materials to form the micro/nano structured surfaces (Nine *et al.*, 2015; Fenero *et al.*, 2017; Selim *et al.*, 2017; Xiao *et al.*, 2017; Selim *et al.*, 2018b).

For self-cleaning, the CA should be large, the CAH should be small, and the surface should be formed by a non-polar material. In addition, the hydrophobic coating should have good abrasion/scratch resistance to ensure good durability (Nine *et al.*, 2015), and antistatic capability to dissipate static electricity (as static electricity is prone to absorb small dirt particles (Fenero *et al.*, 2017)). To maintain superhydrophobicity, the key is to maintain the micro/nanostructure, and this could be accomplished using a high wear resistance material, or by wear of the surface layer, but exposing new nanostructure underneath. Nine *et al.* (2005) designed graphene-based superhydrophobic composite coatings with robust mechanical strength, and their tests showed that superhydrophobicity was retained even after sandpaper abrasion and crosscut scratching. In another study, by using a high scratch resistance oxide La_2O_3 , Xiao *et al.* (2017) synthesized coatings that maintained their nanostructure and superhydrophobicity after 80 cycles of sand abrasive sliding. Another terminology worth mentioning is omniphobicity, which describes a surface that has repellent property for both polar and non-polar liquids (such as water, oil, methanol, octane, crude oil and blood), enabling the so called “full self-cleaning” characteristics (Tuteja *et al.*, 2008; Wong *et al.*, 2011; Fenero *et al.*, 2017). These omniphobic surfaces could be used for biomedical fluid handling, fuel transport, self-cleaning windows and optical devices (Wong *et al.*, 2011).

After immersion in seawater, ships will have biofouling on their hulls, thus will increase the fluid drag and fuel consumption (Selim *et al.*, 2018b). Fouling release agents such as Ag nanoparticles, copper and/or booster biocides are commonly used in antifouling paints. When antifouling paints are produced into hydrophobic surfaces, the antifouling performance can be effectively enhanced by inhibiting fouling adhesion and the self-cleaning properties (Selim *et al.*, 2017; Selim *et al.*, 2018a,b). In addition, as water can easily move on hydrophobic surfaces, it can decrease the shear force between the water and the surface (Srinivasan *et al.*, 2015). Dong *et al.* (2013) studied the drag difference between a normal surface and a hydrodynamic surface, and they found that the superhydrophobic surface with static CA of 159.7° could reduce the drag force up to 49.1%, compared with the normal surface. Thus, applying antifouling coatings with hydrophobic surfaces would have combined benefits of enhanced antifouling and hydrodynamic drag reduction.

Another useful application for hydrophobic coatings is for deicing. Ice formed on a surface is due to surface adhesion that retains the water droplets. Hydrophobic surfaces can repel water and have low adhesion, and this can delay the formation of ice and ease the mechanical ice removal (Nazhipkyzy *et al.*, 2016). In addition, for self-induced deicing on a surface, ice removal usually starts when solid-ice melts into water at the interface; while water is super slick on the hydrophobic surface, thus enabling excellent deicing performance (Nine *et al.*, 2017).

Self-Healing Coatings and Their Applications

Polymer coatings are attractive due to their cost effective and excellent performance in different applications. However, when used in actual environments, such as for solar panel protection, the polymer coatings could be eroded or scratched by the high speed abrasive sand particles in the wind (Humood *et al.*, 2017). In addition, the coatings may suffer from decomposition under sunlight (Mozumder *et al.*, 2019). When coatings on solar panels suffer from such damages, transmittance and wettability will decline. Therefore, expensive and inconvenient interval renovations of the coatings is necessary (Mozumder *et al.*, 2019). Inspired by natural plants, such as the lotus leaf that can repair its surface superhydrophobicity, even after damage by regrow of epicuticular wax tubules on the surface (Neinhuis *et al.*, 2001), researchers have shown interest on coatings with self-healing capability, which would be cost-effective and efficient in actual applications (Mozumder *et al.*, 2019). Specifically, anticorrosion has been one of most attractive applications for self-healing coatings (Cho *et al.*, 2009; Samadzadeh *et al.*, 2010; Yabuki and Okumura, 2012; Schreiner *et al.*, 2017; Guo *et al.*, 2018; Njoku *et al.*, 2018).

Maintaining the functions of the coating is the main goal of self-healing, and there are mainly two different methods, namely physical and chemical methods, to achieve this goal. Physical self-healing does not involve any chemical reactions. For example, Wong *et al.* (2011) designed an omniphobic liquid film by using the nano/microstructured substrates to lock in place the infused lubricating fluid: Because the liquid surface is intrinsically smooth and defect-free, the surrounding liquid can immediately wick into the scratched area and the surface is self-healed. In another example, Golovin *et al.* fabricated a superhydrophobic coating that can maintain its hydrophobicity by expositing new micro structures after abrasion. In addition, the coating can regain its surface texture by immersing in heat even after 150 MPa pressure compression (Golovin *et al.*, 2017). In the third example, Yabuki, *et al.* mixed a

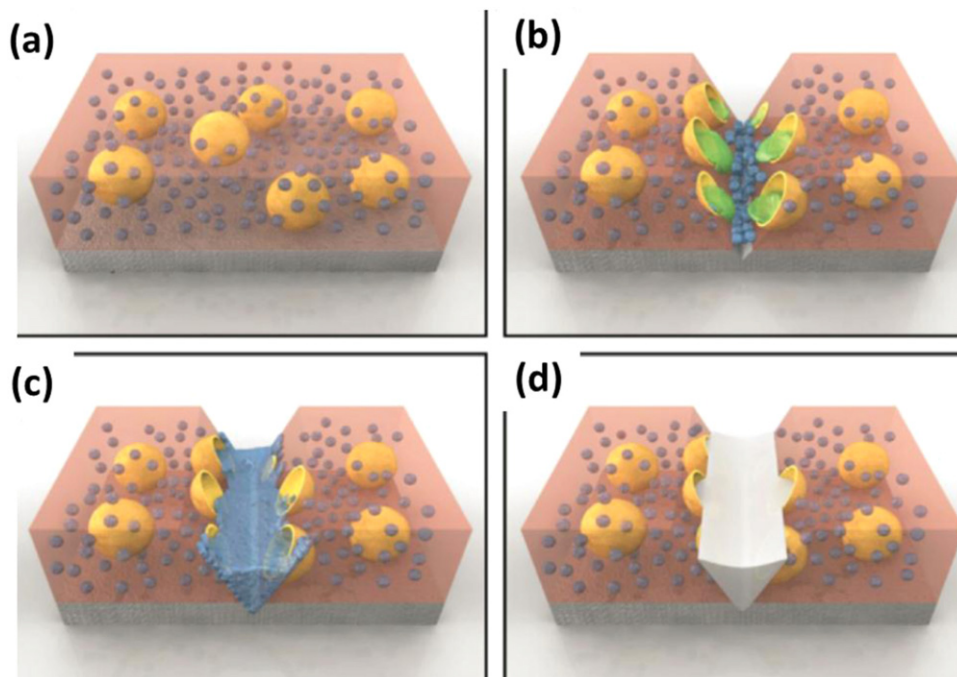


Fig. 12 Schematic of self-healing process, (a) Self-healing coating containing microencapsulated catalyst (yellow) and phase-separated healing agent droplets (blue) in the coating, (b) Damage to the coating layer releases catalyst (green) and healing agent (blue). (c) Mixing of healing agent and catalyst in the damaged region, (d) Damage healed by cross-linked PDMS, protecting the substrate from the environment. Modified from Cho, S.H., White, S.R., Braun, P.V., 2009. Self-healing polymer coatings. *Advanced Materials* 21 (6), 645–649.

superabsorbent polymer (SAP) additive in the vinyl-ester polymer to coat on a metal substrate for corrosion protection. After scratch damage, the SAP in the composite coating could absorb water and the swelled SAP can prevent the diffusion of dissolved oxygen to reach the metal substrate and thus inhibits corrosion (Yabuki and Okumura, 2012; Yabuki *et al.*, 2018).

Compared to physical self-healing, chemical self-healing is more active. Cho *et al.* used a self-healing chemistry based on di-*n*-butyltin dilaurate catalyzed polycondensation of polydimethylsiloxane (PDMS) and polydiethoxysiloxane (PDES). As shown in Fig. 12(a), the dimethyldiethoxysilane (DMDNT) catalyst is microencapsulated and the PDMS-based healing agent (a mixture of 96 vol% HOPDMS and 4 vol% PDES) is distributed evenly as droplets on the coating outside of the microencapsulates. When the coating is damaged by scratch, as in Fig. 12(b), the microencapsulates will break, the catalyst can flow to the scratch and contact with the healing agent. Once the catalyst mixes with the healing agent, as in Fig. 12(c), they will react with each other and heal the scratch and protect the substrate from the environment (Fig. 12(d)). In the same study, Cho *et al.* produced another self-healing coating by encapsulation of both the catalyst and the healing agent, which provided better corrosion protection, compared with the one shown in Fig. 12(a).

There are different chemistries that can be used for self-healing coatings. Lu *et al.* showed that fabrication of composite material coatings with a healing agent could be a promising strategy which was effective, low-cost and easily scalable (Zhai *et al.*, 2018; Zhou *et al.*, 2018). According to Hillewaere and Du Prez (2015), to achieve better healing efficiency, the self-healing chemistry needs to be accommodated with the coating matrix: for siloxane and azide-alkyne chemistry, they work well only in PDMS and polyisobutylene (PIB) matrix. To get a better mixture and cover over the damaged area, reducing the viscosity of the healing chemistry by adding a solvent improves the recovery. There are many different ways to produce the microcapsules for healing chemistry (Park and Braun, 2010; Najjar *et al.*, 2018; Njoku *et al.*, 2018; Zhang *et al.*, 2018). For example, Zhang *et al.* (2018) produced Poly(urea-formaldehyde)-epoxy ester microcapsules through a two-step process in an oil-in-water emulsion: a shell pre-polymer solution was formed in the first step; in the second step, the epoxy was added in the solution and then agitated to an emulsion status, then by changing the temperature and PH, the pre-polymer will consolidate on the surface of the ester droplets and form the ester microcapsules.

In another work, Park and Braun (2010) applied a coaxial electrospinning method to form the capsule for self-healing chemistry and this is a purely physical approach to form the core/sheath structure. As shown in Fig. 13(a) depicting the schematic for the coaxial electrospinning system, two viscous liquids, namely the shell polymer and healing agents (two-part healing agent system), are feed through the inner and outer capillaries, respectively. By controlling the feeding liquids and other operational conditions, the healing agents can be encapsulated in the beads along with polymer nanofibers, as shown in Fig. 13(b) of the randomly orientated core-shell bead-on-string morphology, with two different healing agents in the bead and string shell. After the deposition of the electrospun fiber mat, a UV curing resin was sup-cast on the fiber mat and then cured as self-healing coating. Fig. 13(c) shows the control and self-healing coating samples after initial scratch and aging in corrosion environments, which clearly prove the effectiveness of the healing performance (Park and Braun, 2010).

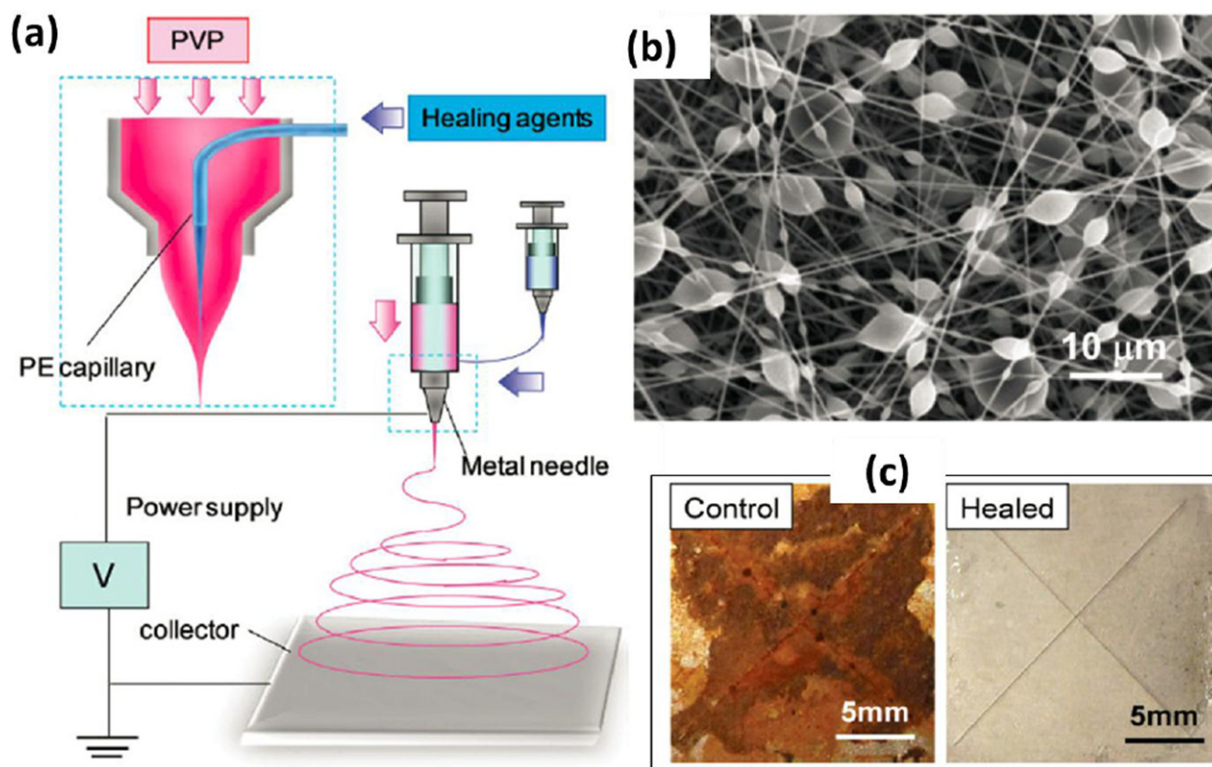


Fig. 13 Coaxial electrospinning of self-healing coating system, (a) the coaxial electrospinneret and fiber spinning process, (b) SEM image of as-spun core-shell bead-on-string morphology, (c) Photographs of control and self-healing coating samples that were stored under ambient conditions for 2 months after 5 days salt water immersion. Modified from Park, J.H., Braun, P.V., 2010. Coaxial electrospinning of self-healing coatings. *Advanced Materials* 22 (4), 496–499.

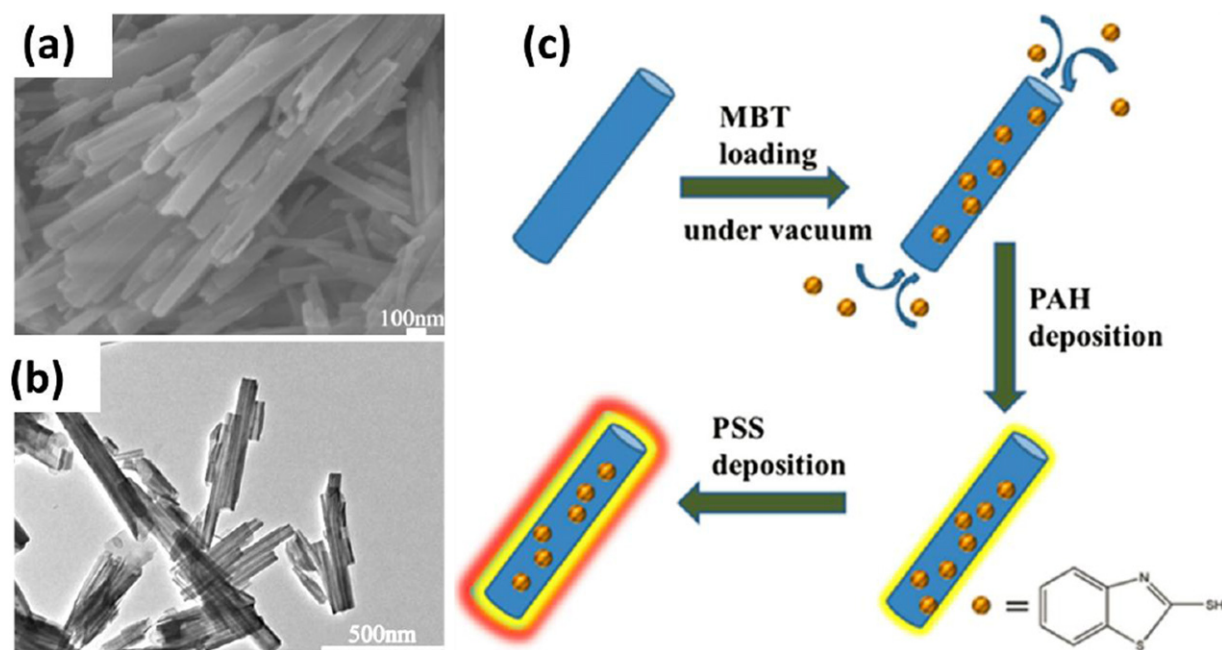


Fig. 14 HNT Nanocontainer for anticorrosion agent, (a) SEM image of HNT, (b) TEM image of HNT, (c) Process of loading and coating of HNT. Modified from Dong, C., Zhang, M., Xiang, T., *et al.*, 2018. Novel self-healing anticorrosion coating based on L-valine and MBT-loaded halloysite nanotubes. *Journal of Materials Science* 53 (10), 7793–7808.

The above mentioned chemical self-healing methods are based on repairing the coating by chemical reaction of the healing agents and forming a new layer on the damaged area. Rather than using the healing agents' reaction, another chemical self-healing method is the continually releasing of functional chemicals, such as anticorrosion agents, in the damaged area where no protection can be supplied by the physical coating coverage. To extend the service life after damage, the functional chemicals need to be released gradually from the carriers, such as halloysite nanotubes (HNT) (Zahidah *et al.*, 2017), cellulose nanofibers (Yabuki *et al.*, 2016) and polymer core-shell nanocontainers (Li *et al.*, 2014). HNT material is abundantly available in nature and it can significantly extend the release time of an anticorrosion agent in water (Zahidah *et al.*, 2017). As shown in Fig. 14(a) and (b) of the HNT morphology, the anticorrosion agent is able to stay in the hollow nanotubes. Fig. 14(c) shows the loading and coating process for HNT.

Under vacuum, the mixture of HNT and the anticorrosion agent was stirred and thus the agent was loaded in the nanotubes. In the next two steps, the loaded HNT was coated with double polyelectrolyte, namely Poly(allylaminehydrochloride) (PAH) and poly(styrene sulfonate) (PSS), respectively. When used in coating applications, the PAH and PSS films can form porous structures and then gradually release the anticorrosion agent from HNT to protect the metal substrate (Dong *et al.*, 2018). Rather than load the anticorrosion agent in side hollow nanotubes, Yabuki *et al.* coated corrosion inhibitors on the surface of the cellulose nanofibers, then the coated nanofibers were mixed with a base polymer and then deposited on the metal surface (Yabuki *et al.*, 2014; Yabuki *et al.*, 2016). When scratch occurs, the corrosion inhibitor is gradually released along the nanofibers pathway, thus protecting the substrate (Yabuki *et al.*, 2014). In addition, by changing the PH value of the coating, the release speed of corrosion inhibitor can be controlled (Yabuki *et al.*, 2016).

Conclusions

In this article, different advanced polymeric coatings and their applications were reviewed, and the following conclusions could be drawn:

- (1) High bearing blended polymer coatings based on PEEK, PTFE, and ATSP materials show promising tribological behavior under aggressive contact conditions. Even in the absent of liquid lubrication, in applications such as air-conditioning and refrigeration compressors, electrical submersible pumps, and under cryogenic conditions, they proved their suitability to withstand demanding contact and sliding conditions at the interface, while maintaining friction and wear at acceptable levels;
- (2) One of the key aspects in the performance of high bearing blended polymer coatings is their ability to provide self-lubricity at the contact interface, by trapping wear debris or third bodies at the contact interface. Keeping these third bodies is what avoids/retards scuffing adhesive phenomena under stringent sliding conditions;
- (3) Electrostatic deposition is one of the most cost/effective methods to coat metallic engineering substrates with polymer coatings. Compared to techniques such as thermal spray, electrostatically deposited coatings proved to perform well under aggressive conditions; and
- (4) Both superhydrophobic and self-healing coatings using special chemistry and structure are used to fulfil their desired properties. Both coatings are using green technologies that can reduce labor cost and reduce environmental impact to maintain the coatings' functionality. Superhydrophobic coatings are more attractive for self-cleaning applications and self-healing coatings are more attractive for anticorrosion applications.

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Application of Life Cycle Assessment for Sustainability Evaluation of Transportation Fuels

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Nomenclature

AHP	Analytical hierarchical process	MAVT	Multi attribute theory
CNG	Compressed natural gas	MCDA	Multi criteria decision analysis
EIOLCA	Economic input output life cycle assessment	ODP	Ozone depletion potential
ELCA	Environmental Life cycle assessment	PHEV	Plug in hybrid electric vehicle
EV	Electric vehicle	PM	Particulate matter
FCV	Fuel cell vehicle	POCP	Photo chemical oxidation potential
FU	Functional unit	PROSUITE	Prospective sustainability assessment of technologies
GDP	Gross domestic product	SDG	Sustainable development goal
GHG	Greenhouse gas	SETAC	Society of environmental toxicity and chemistry
GWP	Global warming potential	SHDB	Social hotspot database
ILCD	International life cycle data	SLCA	Social life cycle assessment
ISO	International standard organization	TBL	Triple bottom line
LCA	Life cycle assessment	TCO	Total cost of ownership
LCC	Life cycle cost	UNEP	United nations environmental program
LCI	Life cycle inventory	VKT	Vehicle kilometre
LCSA	Life cycle sustainability assessment		

Introduction

An ever-increasing growth in economic development, associated products, and services is resulting in improved living standards. These developments, accompanied by massive population growth are increasing the demand for World's non-renewable resources. The transport sector alone consumes more than half of the global oil production. The number of vehicles is expected to increase to 1.7 billion in 2035 which is almost two times more than what is currently being used (IEA, 2012). This scenario can cause a severe scarcity of non-renewable fossil fuels in the near future that may lead the modern economy to experience an enormous challenge to tackle the energy security and associated socio-economic challenges. This may also create barrier to sustainable developments that are necessary to meet the current demands without hampering the ability of the next generations to fulfil their needs. Automobiles are also considered as the major emitters of toxic gases that cause lung diseases, cancers and respiratory problems. Alternative fuels are not only considered to mitigate environmental burden but also to enhance the energy security, create jobs locally and improve income level of particular region (Macombe *et al.*, 2013). Given these economic, social and environmental significances, there is an urgent need to look into alternative transport fuels.

Implementation of renewable energy alternatives and possible energy efficiency and energy conservation strategies are the key pathways to address future sustainable energy challenges. However, the environmental, economic and social implications need to be assessed before implementing any such initiatives which is known as 'triple bottom line' or TBL analysis (Hall, 2011). The LCSA approach evaluates TBL objectives effectively over the life cycle of a product/service (Santoyo-Castelazo and Azapagic, 2014). Under the guidelines of United Nation Environmental Programme (UNEP) and the Society of Environmental Toxicity and Chemistry (SETAC), LCSA comprises of ELCA, LCC and SLCA under the identical system boundaries (UNEP, 2011).

Fig. 1 shows the standard framework that is used to assess the environmental impact of a product or service. It comprises of four stages including goal and scope definition, life cycle inventory, impact assessment and interpretation of results. The first step is to define the goal and scope of the study including the number of stages, processes and the type of inputs and outputs involved. A functional unit is needed to work out the amount of inputs and outputs for developing the life cycle inventory. Once the inventory has been developed, the relevant impact assessment methods are employed to estimate the impacts. Finally, the results are analysed to identify the hotspots, and recommendations are made for improvement in the interpretation phase of the study. The SLCA and LCC can then be conducted using the same system boundary.

The literature shows that a wide range of studies have been conducted on ELCA and LCC of different products and services, whereas the SLCA appears to be a relatively emerging area of attention of researchers. This research reviews the existing literature on alternatives fuels for road vehicles, discuss the methodological aspects and procedures. The study also highlights the lessons learnt, and identifies the avenues for future research. Most of the research on the sustainability aspects of alternative fuels mainly consider the employment of ELCA to assess fuels like bio-liquid fuels, electric vehicles and hydrogen fuel cell (Carneiro *et al.*, 2017; Hawkins *et al.*, 2012; Larson, 2006; McManus *et al.*, 2015; Nordelöf *et al.*, 2014; Shonnard *et al.*, 2015). The purpose of this review,

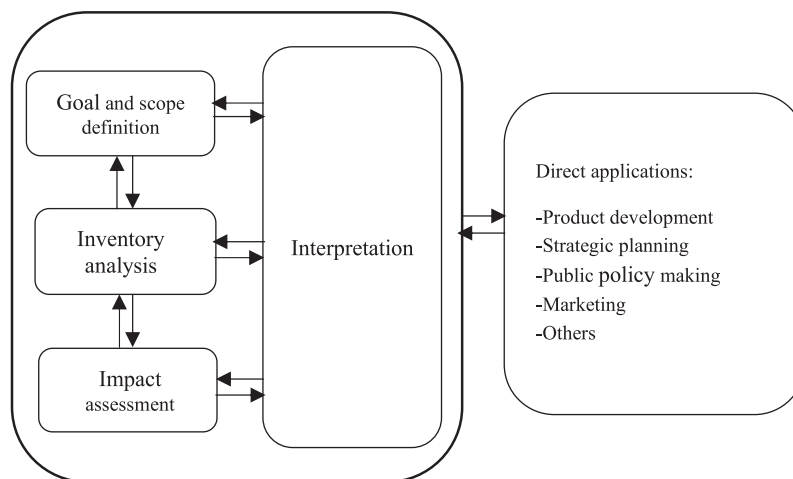


Fig. 1 Four steps of life cycle assessments. Reproduced from ISO14040, 2006. Environmental management – life cycle assessment – principles and framework ISO.

however, is to study the potential for incorporating all the three elements of sustainability, including ELCA, SLCA, and LCC with particular emphasis on sustainable transportation fuel assessment.

Inclusion of Literature and Review Approach

Seventy seven case studies those were published in the last five years pertaining to LCA of alternative transport fuels are selected from different geographical locations to present the state of the art of the application of LCA for environmental, economic and social sustainability analyses. Following Denham *et al.* (2015), the literature of life cycle analysis of alternative transport fuels has been obtained through keywords from various scientific publishers such as Elsevier Science Direct, Springerlink, Wiley Interscience and Emerald Insight. Key words used for literature searching were: “Alternative fuels”, “Sustainability assessment”, ‘Life cycle assessment’, “Environmental life cycle assessment”; “Life cycle costing”, “Social life cycle assessment” and “Life cycle sustainability assessment”.

Once articles have been gathered, they have been classified to facilitate the reviewing process. The distribution of different types of LCA articles shows that the majority of the studies (62%) only performed environmental life cycle analysis (Fig. 2), and nineteen studies (25%) are comparatively recent and considered ELCA and LCC analyses together. About 50% of these were published over the last 2 years and mainly dealt with an emerging concept of life cycle management (LCM) for assessing alternative fuels. LCM mainly assesses the economic and environmental objectives of sustainable production and consumption of products and services utilizing life cycle thinking approach (Jensen and Remmen, 2006) (e.g., Light Emitting Diode lamps not only reduces energy consumption and environment degradation but also offers long-term economic benefits). Social LCA as well as the integration of triple bottom-line objectives into sustainability assessment are still in infancy. A limited number of articles presented the integration of triple bottom line objectives (5%), but the indicators of these studies have not been adequately developed to measure the TBL pillars. Most of these studies did not consider full life cycle of fuel (For example, all stakeholders throughout the supply chain were not considered in the SLCA and for ELCA and LCC of fuels). As of now, mainly biodiesels, ethanol, CNG, electricity and hydrogen fuel cells have been widely considered as alternative fuel options for road vehicles and so the literature on these fuels have been reviewed.

Except case studies, review articles related to LCA of alternative transport fuels have also been reviewed to know the extent of review performed. Other than refereed journal articles, various reports, books and guidelines on LCA such as LCA hand book, ISO guide line for LCA, UNEP-SETAC LCA guideline and ILCD (international life cycle data) hand book have also been reviewed. Similar sustainability assessment articles on other products and services that were published in journals and conference proceedings and other refereed and credible documents have also been reviewed for comparative analysis, learning experiences and supporting statements in order to find out the research gaps in transportation fuels research. In a nut shell, the review covers all the triple bottom line assessment tools including ELCA, LCC and SLCA for assessing sustainability of alternative transportation fuels to determine the gap of existing research that can assist in the development of sustainable alternative fuel scenarios.

Environmental Life Cycle Assessments (ELCA)

Environmental life cycle analysis is a well-established technique to analyse a product from its cradle to grave and to reveal the hotspots so that more sustainable products/services can be designed. Whilst the first formal guideline of LCA was initially devised by the SETAC in 1993, ISO14040 (2006) and ISO 14044 (2006) published the comprehensive LCA principles and requirements

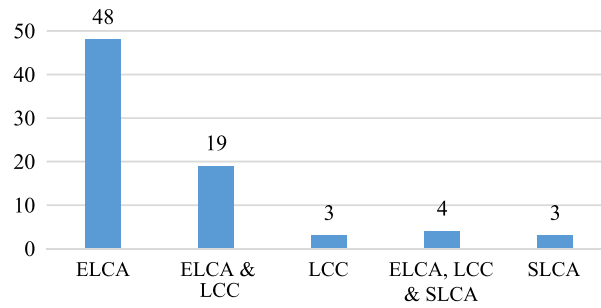


Fig. 2 Number of articles from different LCA.

which were internationally accepted due to their systematic assessment procedure. Besides, life cycle assessment handbook (Curran, 2012) and ILCD hand book published by European Commission are two other established documents for LCA practitioners to maintain quality and consistency in LCA analysis.

The review found two types of ELCA such as Attributional LCA and Consequential LCA, where the former considers the direct impact linked to fuel in its pathway and has been employed by most of the studies whereas relatively less number of studies considered the latter types which considers indirect effects (e.g., environmental consequences associated with the displacement of existing market items due to introduction of a new product or services) as well as direct. Each of these ELCA can either be process based or economic input output LCA (EIOLCA). Quite limited number of authors (4% among the reviewed articles) considered the EIOLCA as this method is based on only a particular economy and number of indicators to assess a product is not sufficient as well (EIOLCA, 2017). Process based LCA, however, considers direct environmental impacts from input output flows from the production stages of any products and which is usually employed by LCA practitioner around the world.

Though LCA is a well-established technique, but outcome of LCA in some cases was uncertain due to different types of assumptions and data variability. Selection of functional unit (FU), system boundary, allocation strategies, emission databases and impact assessment methods have a great influence on LCA outcomes (Hunkeler, 2014). Selection of an appropriate FU, for example, is quite crucial as all the inputs and outputs for LCA analysis are based on this unit (i.e. if vehicle kilometre or VKT is the functional unit then all the inputs and output for LCA analysis will be based on per vehicle kilometre) and different FUs would produce different results (Reap *et al.*, 2008). This FU is often dependent on client's choice and research questions. Among the selected 71 LCA articles on transportation fuel LCAs, VKT (46%) was the most preferred functional unit, followed by energy content in fuel (MJ, 21%) and the amount of biofuel production (litres, 19%). Few articles (7%), however, did not mention FU explicitly as their data was based on a particular software database and showed either percentage of energy consumption and greenhouse gas (GHG) emission compared to fossil fuel or matrix based study. It is, however, required by the ISO guideline that FU should be consistent and clear within the scope of the study to fulfill the desired objectives. Selection of FU and goal of the study determines the system boundary for a particular product which defines the processes or steps those are required for inclusion in the LCA analysis. Reason for choosing or avoiding any processes are also required to be mentioned clearly so that the results of one study are comparable to the other similar studies. Consideration of different life cycle boundaries for ELCA of alternative fuels are presented in Table 1. Among the reviewed articles only 25% have been found to incorporate vehicle life cycle into the fuel LCA (well to wheel approach) to assess the environmental impacts of fuels. A significant number of studies (35%) considered fuel production only (i.e. upstream stages) in order to capture the hydro-geological variation in fuel production and use in different geographical locations (e.g., emissions and farming practices for biofuel crop production varies with soil and climate) (Tabatabaie and Murthy, 2017). ELCA results vary with system boundaries, and therefore, it is important to consider the same boundary for a comparative analysis of alternative fuels.

Co-product allocation has been found to be necessary to define within a system boundary when there are more than one outputs from a single input. Most of the biofuel production systems have a number of by-products, which have economic value and therefore, the environmental burden in these cases need to be shared by both products and by-products. ELCA results sometimes can vary up to 200% only due to the use different allocation methods (Zhao *et al.*, 2016). Surprisingly, allocation methods were not reported in a number of articles (i.e. 31% of the reviewed articles) while they dealt with both products and by-products (e.g., the animal feed was produced as by-product in liquid biofuel production). It is recommended by ISO that the co-product allocation can be avoided by using either subdivision (division of one process into two more sub processes and collection of the input-output data from an appropriate sub process as conducted) or system expansion (expansion of product systems to include the additional functions related to the co-products). When possible, different allocation methods (e.g., mass, energy and economic allocation) could be employed for comparisons among the results. Finally, LCA practitioners need to think critically for the appropriate allocation method for a particular situation as there is no consensus to use exact allocation methods for LCA till now.

The choice of appropriate impact assessment method has been observed as an important criteria for conducting LCA analysis, as LCA results sometimes vary quite significantly due to the different impact assessment methods and also using different databases. For example, there are no common agreement between the software companies about the emission factors in terms of biogenic carbon dioxide emissions (Fan *et al.*, 2012). The use of different emission factors by different software would give

Table 1 System boundaries considered in ELCA

<i>System boundary</i>	<i>Number of studies</i>
Fuel production + Use in vehicle + Vehicle life cycle	25%
Fuel production + Use in vehicle	30%
Only fuel production	35%
Use in vehicle + Vehicle life cycle	5%
Not mention clearly	5%

different environmental performances for the same product (i.e. fuel in this case) or services (i.e. electricity from alternative fuel). It was thus proposed that local databases are generated for software to reflect the local situation. For example, the emission factor for electricity in Denmark would be different to Australia due to differences in the energy mix. There are some countries that have their well-established databases such as European database, National Renewable Energy Laboratory: US life cycle database, Australian LCI database etc. Besides, different countries should have their own impact assessment methods as the impacts caused in Australia would not be the same as North America or Europe.

Due to these reasons discussed above, it is quite challenging to compare LCA results among themselves. Despite these inherent issues, LCA can make researchers critical thinkers and can potentially act as a decision making tool where there is a range of variabilities associated with the production of products such as biofuels. For example, biodiesel is a renewable energy but it does not mean that it can always be environmentally friendly as it depends on where the feedstock of biodiesel was grown and what was used for producing these fuels. [Tabatabaie and Murthy \(2017\)](#), for instance, showed that global warming potential (GWP) emission for 1 MJ of camellia biodiesel in four locations in northwest USA were varied from 44.33 ± 7 g CO₂-eq to $78.88 \pm 4\%$ g CO₂-eq due to the different production practices, use of different agro chemicals and local weather variations. Among the environmental impact categories, it has been found that GWP was one of the most commonly evaluated indicators for fuel LCAs, because there is an urgent need for choosing alternative fuel(s) in order to reduce the GHG emission from the combustion of fossil fuels ([Shonnard et al., 2015](#)). GWP is actually a measure of how much global warming can be caused over a given period by a given mass of chemical relative to similar mass of carbon dioxide ([Demirel, 2014](#)). All the activities related to alternative fuel production have its own GWP due to the production of GHG emissions. [Biswas et al. \(2011\)](#), for example, showed that the total GWP of canola based biodiesel was 1.1 to 2.1 times lower than conventional diesel.

Variation in global warming potential (GWP) were found to be more significant when land use change was considered during the calculation of LCA due to the lack of methodological standards and practical difficulties on assessment of land use change ([Carneiro et al., 2017](#)). As shown in the [Fig. 3](#), significant difference of results has been observed even for a certain feedstock within a particular country.

Variation of results were also observed for electric vehicle (EV) and fuel cell vehicle (FCV) even in a different states within country due to the variation in electricity mix ([Requia et al., 2017](#)). ELCA has potentially been used for designing an environmentally friendly product first by identifying the 'hotspots' and then by incorporating an environmental mitigation strategy to treat this hotspot. As like previous example, electricity has been identified as an input of the electric vehicle causing the significant impact. Therefore, EV and FCV will be considered as a zero or low carbon vehicles if they are powered by renewable energy sources like wind and solar. ELCA studies also confirm that biodiesel and ethanol are not completely emission free unless the emissions from pre farm (i.e. input or fertilizer production) and on-farm stages (i.e. emissions from soil) are considerably reduced. [Daylan and Ciliz \(2016\)](#), for example, found that ethanol could reduce GWP from 4.3% to 47% but increase the eutrophication, photochemical oxidation potential (POCP) and acidification in one km driving compare to conventional gasoline. Similarly, [González-García et al. \(2013\)](#) in Spain found that biodiesel from rapeseed could reduce 74% GWP and 44% ozone depletion potential (ODP) but increase acidification (59%), eutrophication (214%) and photochemical smog (119%). Sustainable production of bio-liquid fuels with renewable sources, however, can outperform fossil fuels from every aspect, where soil emissions from urea application is low ([González-García et al., 2013](#)).

Though a significant number of studies have already been accomplished on ELCA but still there is a potential research gap in regional basis as LCA results of one place cannot be replicated in other places due to the region specific condition and variability of data ([Tabatabaie and Murthy, 2017](#)). The difference in geographical locations, electricity mix and the climatic condition can cause huge variabilities of results. Countries like USA, Australia and Canada cannot also use the result of one state for the biofuels produced in another state due to these reasons. [Requia et al. \(2017\)](#), for example, studied that life cycle CO₂ emission of plug in hybrid electric vehicle (PHEV) in different cities in Canada ([Fig. 4](#)) were different due to the different electricity mixes and the differences associated with the consumption of different percentage of electricity and liquid fuel during the fuel life cycle. [Fig. 4](#) also shows that the life cycle CO₂ emission varied more than 100% in different cities even within the country and so analysis should be done regionally utilising local databases in order to achieve quality LCA outputs. There are no internationally recognised consensus on the use of impact assessment methods, functional units and impact categories ([Hunkeler, 2014](#)). An agreement at an international level and interactions between the practitioners are some important considerations to overcome these limitations. Besides, both base case and other possible scenario analysis should be done so that readers and policy makers can obtain a wide spectrum of ideas to implement. A range of possible region specific impact categories should also be chosen to justify the goal and scope and if required more than one impact assessment method can be chosen to assess the impact categories ([Cavalett et al., 2013](#)). Region wise databases, best practice guideline (e.g., Australian best practice guideline for life cycle impact assessment) for a particular region are also essential for more informed choices.

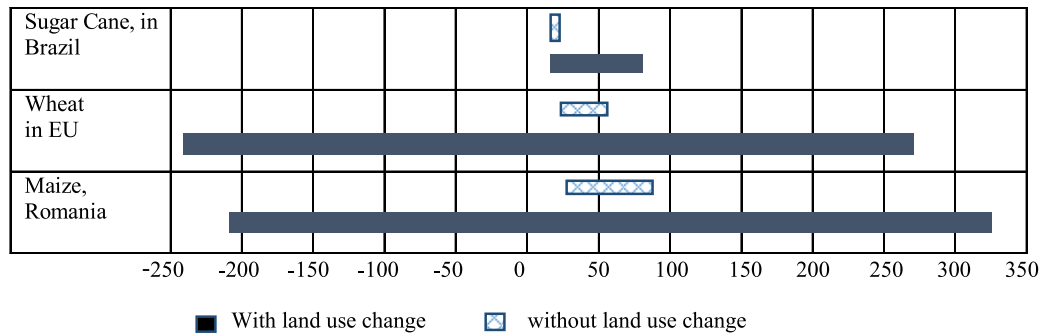


Fig. 3 GWP (g CO₂ eq/MJ) of ethanol production at three different locations. Reproduced from Carneiro, M.L.N.M., Pradelle, F., Braga, S.L., *et al.*, 2017. Potential of biofuels from algae: Comparison with fossil fuels, ethanol and biodiesel in Europe and Brazil through life cycle assessment (LCA). *Renewable and Sustainable Energy Reviews* 73, 632–653.

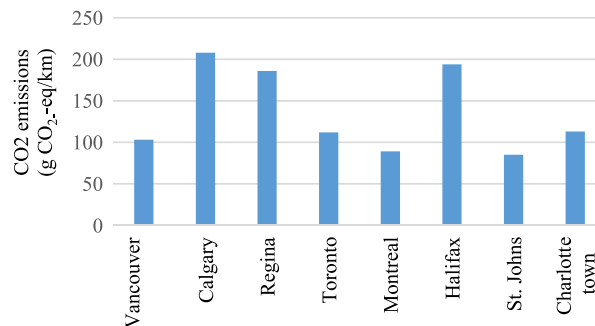


Fig. 4 Life cycle CO₂ emissions of PHEV in different cities in Canada-adapted from. Reproduced from Requia, W.J., Adams, M.D., Arain, A., Koutrakis, P., Ferguson, M., 2017. Carbon dioxide emissions of plug-in hybrid electric vehicles: A life-cycle analysis in eight Canadian cities. *Renewable and Sustainable Energy Reviews* 78, 1390–1396.

Life Cycle Cost Analysis (LCC)

Life cycle cost analysis is quite necessary to know the exact cost associated with a particular product or service over its whole life cycle. The LCC for alternative transport fuels have been performed by the combination of fuel cost and life cycle cost of vehicle as only fuel cost does not reflect the overall economic performance (Sharma and Strezov, 2017). Total life cycle cost, cost/km of vehicle, total cost of ownership (TCO) are the major indicators calculated under LCC where initial cost of vehicle; fuel cost over the life of vehicle; operation and maintenance cost and end of life cost of vehicle were normally considered.

Similar to ELCA impacts, there are also significant amount of variation in findings for LCC in the literature which is obviously due to the difference in underlying assumptions and considerations in different studies. In most of the cases, authors found that the cost of alternative fuel vehicle were higher than the conventional vehicle. In Australia for example, it has been estimated that the TCO of hybrid diesel-electric bus was around 10% higher than the conventional diesel. It has also been expressed that the market penetration of hybrid and hydrogen technology is significantly low compared to conventional diesel fuel and it would be comparable only if diesel price increases substantially (Ally and Pryor, 2016). Similarly, Lajunen and Lipman (2016) in USA found that EV was not cost effective due to the high cost of battery and this is the same for FCV due to expensive hydrogen production and storage systems. Zhou *et al.* (2017) in Canada also came up with almost similar results. Whilst E 10 (10% ethanol with 90% petrol) and B 10 (10% biodiesel and 90% diesel) are successfully implemented in all over the world, though high cost of biofuel production and unfavourable government policies (e.g., subsidized fossil fuel and no subsidy on biofuel) in some countries hinders its cost-competitiveness. Mu *et al.* (2017) also revealed that the cost of biodiesel production from algae would be around 15–20 USD per gallon which was much higher than diesel due to diseconomy of scale.

In contrast to these findings, in a recent study in Florida, USA reveals that the electric trucks have been found to outperform all other existing trucks due to their lower maintenance and repairing cost (Sen *et al.*, 2017). It also has been documented that the use of E 85 instead of petrol could reduce 23% of the life cycle cost in Turkey according to the fuel price of 2009 because of the existence of government subsidy and lower production cost of ethanol in Turkey (Daylan and Ciliz, 2016). Almost similar findings have been revealed by Luo *et al.* (2009) in Brazil. Also Campbell *et al.* (2011) found that biodiesel from algae could be cost competitive with the high rate of production, government subsidy and minimum use of resources (electricity can be produced from the algal by-product and instead of fresh water, salt or waste water, can be used).

Like ELCA, a significant research gap still exists in LCC in terms of regional variation perspective as agriculture, production and transportation cost of fuel are different in different regions. Even cost of petrol and diesel are subsidized in many countries. A systematic regional based LCC study can identify the hotspots and formulate policy instrumentation for reducing the cost. [Ally and Pryor \(2016\)](#), for example, conducted LCC of hydrogen fuel cell vehicle (HFCV) in Western Australian region and summarized that a large scale water electrolysis plant using excess off peak electricity could offer economically feasible option for the HFCV in the state. Besides, cost of relative powertrain along with their maintenance and repairing costs have to be considered in the calculation of life cycle cost of fuels to determine the actual impact but that was not the case in most of the studies due to consideration of biofuel production stages only. Moreover, consideration of inflation and discount rates, government subsidies and proper scenario analysis by considering future cases are essential for proper policy formulations. Moreover, indirect associated cost like environmental emission cost, cost of health impact can be included with LCC in future to address the market failure of these externalities.

Social LCA (SLCA)

Potential social impacts of products or services over their life cycle that are linked to the various stakeholders are considered under SLCA. This is a relatively new LCA guideline that was introduced by United Nation Environmental Programme (UNEP) and Society of Environmental Toxicity and chemistry (SETAC) in 2009 and then further expanded in 2011 ([UNEP, 2009, 2011](#)). Like E-LCA, it also consists of 4 steps for conducting social impact assessment, including goal and scope, life cycle inventory, impact assessment and interpretation of results. However, some modifications and adaptations for SLCA are required as SLCA works with attributes of information or characteristics of a process which cannot be expressed as a unit process. The additional information related to stakeholders (e.g., for worker stakeholders: fair salary, working environment, health and safety etc.) collected for SLCA other than ELCA and LCC, however, provides useful information for enhanced sustainability. Thirty one sub-indicators under five types of stakeholders (workers, local community, society, consumers and value chain actors) and six impact categories (Human rights, working condition, health and safety, cultural heritage, governance, socio economic repercussion) are suggested by the UNEP. As suggested by the UNEP-SETAC, these indicators can be reshaped, refined and varied according to the requirements of a particular region for socio-economic and cultural differences. A similar framework of SLCA was published by the European Commission of Joint Research Centre in 2016. It recommends the use of Sustainable Development Goal (SDG) initiatives for social indicators. Out of 17 SDG indicators in which 8 are directly linked with the social perspectives ([Sala et al., 2015b](#)).

Since the concept of SLCA is relatively newer than ELCA and LCC, there are quite limited research has been conducted on the SLCA (only 4% among the reviewed articles) of alternative fuels in the literature. However, few interesting studies have been carried out in this area as [Manik et al. \(2013\)](#) has converted the qualitative values of social parameters for quantitative analysis for the social sustainability assessment for palm biodiesel production in Jambi province, Indonesia. Twenty-four indicators were developed by the authors based on the UNEP-SETAC guidelines and literature reviews. Social sustainability gaps were calculated based on different stakeholder's perception and expectation on indicators. Finally, these gaps were multiplied with the weight of each criteria to obtain the final scores for social sustainability performance and lower gap would thus offer better sustainability. It has been found that alternative fuel can augment regional development by creating new jobs and by improving the income level but comprehensive social issues over the life cycle of a fuel are needed to be assessed ([Macombe et al., 2013](#)). In the previous case studied by [Manik et al.](#) for example, revealed that palm biodiesel production in Jambi province in Indonesia was socially sustainable from the human rights, governance and socio-economic repercussion perspectives but from working condition (gap: - 1.60; due to mainly terribly low salary) and cultural heritage (gap: - 4.25) perspectives due to conversion of the massive rain forest to palm plantation field resulting displacement of several indigenous and ethnic people which required government attention. [Ekener-Petersen et al. \(2014\)](#) also conducted a social screening of few traditional and alternative fuels based on social hotspot database (SHDB) indicators developed by the New Earth, USA. SHDB mainly consists of 22 social themes under five social categories and each theme has certain number of indicators. All indicators are ranked according to their risk level (i.e. very high risk, high risk, medium risk and low risk) for a certain sector of a particular country. Indicators and qualitative data used for the database were mostly based on World Bank and International Labour Organization (ILO). Major limitation for this database is that it can only be applicable to macro-level study utilizing national database and therefore, there is a need for the development of a region as well as product specific databases. Hybridized method by combining process base LCA and Social LCA to assess the ethanol bio-refineries in Brazil has also been documented by the [Souza et al. \(2018\)](#). Though this holistic approach assisted to conduct comprehensive social sustainability but study considered only workers as stakeholders. Other than transportation fuels, SLCA has also been performed in different sectors using different level of scales (e.g., 1 to 7, 1 to 5, - 2 to + 2 etc.) for data collection followed by MCDA techniques. The selection of impact categories and indicators were the most challenging part for SLCA due to the region specific condition. As of now social LCA are still suffering from lack of actual tools, data and assessment methods ([Petti et al., 2018](#)).

Since SLCA's indicators are based on the local stakeholders' interest, local knowledge and impact categories and expert opinion, the impacts of SLCA vary with regions. There is also a challenge associated with data collection to develop proper indicators for a specific region before conducting SLCA. Size, growth and structure of population, literacy rate, poverty level, natural resources, expenditure on fuel and food, habit of communication and transportation all these factors have influence on social perception and indicators. Indicators, in this regard, should be chosen based on region specific conditions and then refinement of indicators can

be done based on expert opinions. Whilst indicators were selected based on the different internationally agreed guidelines and literature reviews, these indicators do not represent all life cycle stages of a fuel i.e. all stakeholders were not considered in the analysis (Wang *et al.*, 2017). In addition, in the previous studies, the scenario analysis involving different possible cases in the context of a particular region with SLCA were missing which was quite important to allow improved decision formulation based on the different outcomes. Due to these associated challenges, it is still difficult to conduct SLCA properly. However, it is being considered as an indispensable component of TBL sustainability assessment when using a holistic life cycle assessment approach.

Life Cycle Sustainability Assessment (LCSA)

In order to evaluate TBL sustainability, a product should be evaluated from social, economic and environmental objectives. LCA concept can be applied to develop a holistic sustainability assessment toolbox provided newly emerged SLCA tool can be combined with ELCA and LCC tools. LCSA can actually offer a guideline for sustainable consumption and production of goods and services. UNEP-SETAC guideline discussed the concept of LCSA in 2011 which was the evaluation of positive and negative environmental, economic and social impacts of a product/service throughout its life cycle. Different purposes of ELCA, LCC and SLCA have to be described conspicuously under the goal and scope of LCSA (UNEP, 2011). There has to be identical system boundaries for all three components of LCSA and reason of excluding or including any stages have to be justified based on the goal and scope. Impacts for ELCA and LCC could be ascertained on the basis of functional unit like per unit basis but for SLCA no comparable impact assessment steps are required due to the qualitative nature of data. The UNEP-SETAC report also suggested to conduct more researches on LCSA in the different parts of the world to make the LCSA as operational and trusted decision making tools.

Except, UNEP-SETAC guideline, Kloepffer (2008) also provided two concepts of life cycle sustainable assessments. First one was to conduct ELCA, LCC and SLCA separately with identical system boundaries and then to combine together as shown in Eq. 1. The other one was to conduct new LCA which would have one LCI model for all three components (Eq. 2).

$$LCSA = ELCA + LCC + SLCA \quad (1)$$

$$LCSA = 'LCA \text{ new}' \text{ (Including LCC and SLCA as additional impact categories in Life Cycle Impact Assessment)} \quad (2)$$

The author believed that in future ISO 14040 and ISO 14044 could be revised to accommodate option 2. They also expressed that problem with the data availability, selection of indicators was the main challenge of SLCA which needed to overcome. However, it was advised that sustainability had to be established in national, regional, global and even in community level and because of that there were no alternative to investigate further. Similarly, Guinee *et al.* (2010) believed that LCSA would be the future of LCA which would cover the people, planet and prosperity. Like Walter Kloepffer, they have also discussed a conceptual framework by combining process based ELCA with SLCA and LCC for the same system boundary. Three levels of study according to the objectives namely economy wide (i.e. country/region), Meso level (i.e. community or organization) and product (i.e. fuel in this case) level were mentioned in the frameworks. In this regard, Sala *et al.* (2013) suggested that LCSA should be developed with better sustainability which also should include the approach of integrating analytical and descriptive approaches. Zamagni *et al.* (2013) had also expressed that feasibility and testing of LCSA has been accomplished but there should be more practical frameworks with the real case studies in different territories across the world to make the LCSA operational.

There are fairly limited research on LCA which takes into account all three pillars of sustainability of vehicle fuels as economic and social pillars are usually ignored or inadequately conducted. Osorio-Tejada *et al.* (2017) for instance, employed Analytical Hierarchical Process (AHP) method of MCDA technique based on various indicators from three perspective of sustainability to evaluate the biodiesel and LNG as a transport fuel in Spain. Though the comprehensive study was conducted by the authors but selected only three indicators from each pillars of sustainability (Environment: GHG emissions, NO_x and PM, Noise; Economic: Initial and maintenance costs, Reliability, Legislation; Social: Employment, Social benefits, Social acceptability) which were not enough and were also not from different life cycle stages of fuel. For example, important environmental indicators like eutrophication, acidification, ODP and Photo chemical Oxidation potential (POCP) which were found to increase with alternative fuels in many cases were not included in the study. Similarly, aggregated life cycle cost which is termed as LCC is not included as economic indicators as well. Even for social analysis, fuel production stages were not included in the analysis and most importantly authors did not choose the sustainability indicators based on the regional perspective rather depended on global indicators based on a review article published by (Wang *et al.*, 2009). Another study by Onat *et al.* (2016) in USA, evaluated traditional conventional IC engine, hybrid, plug-in hybrid, and battery electric vehicles by considering dynamic modeling. To build the relationship among the indicators, authors used a loop diagram by establishing the relations among the indicators. Though authors introduced a new approach but like previous study as mentioned above, only seven indicators (GHG emission, PM, POCP, Vehicle ownership cost, Contribution to GDP, Employment generation and Human health) were chosen for the TBL assessments. Moreover, the authors agreed that this model and analysis were only in USA but they may not be applicable to other economy. To conduct an LCSA, EIOLCA model and combination of EIOLCA model with process based LCA were also employed (Onat *et al.*, 2014) but as mentioned earlier EIOLCA is not particularly suitable for product level as its calculation are based on the transactions of a particular economy.

Table 2 Summary of LCSA literature

<i>Reference</i>	<i>Sector/product</i>	<i>Basis of indicator selection</i>	<i>Integration method of TBL indicators</i>	<i>Decision context of sustainability</i>
Akber <i>et al.</i> (2017)	Electricity generation	Environmental indicators: CML impact assessment method; LCC and SLCA indicators: literature survey	MAVT, MCDA technique; equal weights for all sustainability indicators	0–1 scale; the higher the score, the better the sustainability
Li <i>et al.</i> (2017b)	Photovoltaic application	Review based article and stakeholders opinion	No integrated single score result	0–100 scale; the lower the score, the better the sustainability
Osorio-Tejada <i>et al.</i> (2017)	Alternative fuel	Review based article	AHP, MCDA technique; Weighting based on the related stakeholders interest	0–1 scale; the higher the score, the better the sustainability
Onat <i>et al.</i> (2016)	Alternative fuel vehicle	Review based article	No integrated single score result; established mutual cause-and-effect relationships between indicators	All indicators are compared with base case scenario
Atilgan and Azapagic (2016)	Electricity generation	Environmental indicators: CML impact assessment method; LCC and SLCA indicators: literature survey	MAVT, MCDA technique; equal weights for all sustainability indicators; scenario analysis by using different weighting	The higher the score, the better the sustainability
Onat <i>et al.</i> (2014)	Alternative fuel vehicle	EIOLCA method	7 indicators are presented in a radar chart to compare alternative fuels	0–1 scale; the lower the score, the better the sustainability
Martínez-Blanco <i>et al.</i> (2014)	Fertilizer production	Environmental indicators: based on previously published environmental indicators; LCC indicators: aggregated life cycle cost; Social indicators: SHDB database	No integrated single score result. Indicators are discussed separately based on the functional unit	ELCA and LCC conducted for per ton of fertilized tomato; SLCA included risk categories (i.e. low, medium, high and very high)
Li <i>et al.</i> (2017a)	Grid connected photovoltaic	Environmental indicators: CML2001; LCC and SLCA indicators: Literature survey and stakeholders opinion	Equal weights for all indicators; a likert scale (1–3) was provided for indicator assessment, where 1 stands for the best performance	All scores are added to obtain a single sustainability score; where lower score mean better sustainability
Keller <i>et al.</i> (2015)	Biorefinery	Based on previous literature	No integrated single score result	Indicators are divided into advantageous (+), neutral (0), disadvantageous (–) categories after setting up a benchmark
Luu and Halog (2016)	Rice husk based bioelectricity	By using PROSUITE (prospective sustainability assessment of technologies) framework	Weighting was accomplished based on the PROSUITE model; only 5 endpoint impacts are weighted for single score result	weighted sum results and overall ranking are presented based on the impact assessment results

Table 3 Benefits and challenges of LCSA

Benefits	Challenges
- Using LCSA, the complex information of environmental, economic and social information are presented in a simplified and structured form (Keller <i>et al.</i>, 2015; Luu and Halog, 2016; Sala <i>et al.</i>, 2013) - LCSA can help achieve balance between sustainability pillars by providing comprehensive picture throughout the product life cycle (Keller <i>et al.</i>, 2015) - LCSA supports organization to implement their strategy effectively by knowing their products/services impacts (UNEP, 2011) - Especially, product development strategies can be designed by knowing weaknesses of three pillars of sustainability throughout the product life cycle (Gencturk <i>et al.</i>, 2016). - LCSA supports decision makers/policy makers to make a decision for selection of sustainable technologies (Buchert <i>et al.</i>, 2015) - Consumers can select/identify environmentally friendly, socially responsible and cost efficient product through the LCSA initiative (UNEP, 2011) - Sustainable production, consumption and new labelling initiative can be implemented by using the LCSA results (UNEP, 2011)	- Lack of data and method especially for SLCA (Akber <i>et al.</i>, 2017; Keller <i>et al.</i>, 2015) - Unavailability of sufficient number of practical case studies (Martínez-Blanco <i>et al.</i>, 2014) and limitation of understanding of three pillars of sustainability (Zamagni <i>et al.</i>, 2013) - There are no established consensus in the weighting steps among the different sustainability indicators (Akber <i>et al.</i>, 2017) - Current LCSA frameworks can not accommodate proper scenario and sensitivity analysis properly from the aspect of TBL sustainability required for life cycle based study (Guinée, 2016) - There is a challenge to adopt SLCA indicators for a particular region as there is no appropriate consensus (Martínez-Blanco <i>et al.</i>, 2014; Petti <i>et al.</i>, 2018) - Limitation of method for integration of TBL sustainability indicators (Nguyen <i>et al.</i>, 2017; Sala <i>et al.</i>, 2013) - Perspective of different stakeholders throughout the life cycle of a product are yet not fully covered by the current LCC and SLCA studies under LCSA (Zamagni <i>et al.</i>, 2013)

There are some effort being made to conduct sustainability by considering all the three aspects of sustainability for other sectors as well as for the energy sector (Akber *et al.*, 2017), fertilizer production (Martínez-Blanco *et al.*, 2014), bio-refinery (Keller *et al.*, 2015), heat pump (Huang and Mauerhofer, 2016) and solar photovoltaic application (Li *et al.*, 2017a). Some recent case studies of LCSA with indicator selection procedure, method of TBL indicators integration and sustainability assessment procedure are presented in Table 2. Most of these studies relied on MCDA techniques by choosing relevant indicators for three pillars or objectives of sustainability and a scoring method that used a Likert scale was used in most of these LCSA studies. Though the authors in some of these cases conducted a comprehensive study but life cycle approaches and guidelines such as different stages of LCA, FU, system boundaries were not explicitly discussed and used in most of this studies. Besides, as discussed for Osorio-Tejada *et al.* study, there is a similar limitation regarding sustainability indicators. Akber *et al.* for example, conducted a detail LCSA pertaining to Pakistan electricity sector and followed the life cycle guidelines and approaches but only 4 socio-political indicators (direct employment, total employment, imported fossil fuel avoided and diversity of fuel mix) were selected for their study which did not include the association of stakeholders such as consumers, workers, local community and value chain actors. As the weighting of indicators are based on expert opinion, MCDA techniques can yield different results for different studies.

The benefits and challenges of LCSA conducted to date are summarized in the Table 3. Sensitivity analysis and robustness are the two key significant techniques of LCA that are needed to be incorporated into LCSA to conduct a real life cycle assessment involving interconnections and interdependencies between three pillars of sustainability (Clímaco and Valle, 2016). As discussed earlier, most of the previous LCSA studies did not consider the whole life cycle of a product (especially all stakeholders were not covered during SLCA as mentioned in the SLCA section and as mentioned in the ELCA section only 25% ELCA studies considered both fuel and vehicle life cycle) which was required to have the actual outcomes of TBL assessments. Besides, limited numbers of indicators were chosen for country or economy level assessment which did not actually reflect the region specific conditions as every region has its unique socio-economic political and climatic conditions. Current LCSA frameworks are not robust enough to analyse the actual results of LCA, LCC and SLCA simultaneously and could not demonstrate the interdependencies between three pillars of sustainability. Moreover, there exists several challenges of SLCA like uncertainties of results and data quality which entirely depends on human perspectives and experts' opinion. Therefore, holistic LCSA frameworks with practical case studies are required around the world for comprehensive TBL sustainability assessment.

Lessons Learned and Future Research Directions

It is evident in the above mentioned studies that there is a research gap within life cycle assessment from the perspective of TBL sustainability assessment of alternative transport fuel. More holistic frameworks and practical case studies should be required to conduct the LCSA, which will reflect all three aspects of sustainability as well as follow the guidelines of LCA adequately. Both fuel cycle and vehicle cycles or any associated change in the vehicles due to use of alternative fuels need to be considered within the system boundary to examine the whole life cycle impacts. Best practice LCA guide line for a particular country or region should be adopted to alleviate the dissimilarities of assessment procedures among the LCA practitioner. It was observed that authors quite often selected sustainability indicators from previous literatures and internationally agreed guidelines which literally did not reflect the actual scenario of particular regions. Due to these reasons, selection of triple bottom line indicators and impact assessment should be in line with the best practice guideline of a particular country/region and should reflect the scenarios of the region.

Possible scenario analysis will also be required to cover the future cases. Required number of impact categories and indicators should be devised based on a region/country as it changes with location and places. As of now, mostly MCDA techniques were used to integrate triple bottom line impacts of ELCA, LCC and SLCA. More novel methods and techniques are needed to assess sustainability hotspots of fuels which are capable of handling both qualitative and quantitative outcomes. Moreover, it is necessary to develop threshold values for sustainability assessments for each alternative fuels for a particular region for sustainability assessment (Sala *et al.*, 2015a). The threshold values for environmental, economic or social score of a particular fuel in fact represent the best or sustainable practice (Lim and Biswas, 2017). Based on the review, it is also found that there is a need to conduct LCA regionally to obtain a better sustainability outcome as LCA result of one region cannot be used in another region due to the data variability. Therefore, more region wise LCA should be conducted for informed decision making processes.

Conclusion

The study has provided a comprehensive review of the existing research in the field of environmental, social and economic analysis and life cycle assessment of alternative fuels for road vehicles. On the basis of the lesson learnt through LCA, LCC and SLCA, the gaps have been identified for future research. There is a need for a holistic framework for life cycle sustainability assessments to evaluate a transportation fuel from triple bottom line objectives. To make the LCSA results more acceptable, assessment should be conducted with the local data mainly because of local policies, socio-economic factors and region specific geographical and climatic variations. This is also because of the differences in regions/countries' underlying assumptions, considerations and life cycle assessment methods. It is suggested from the review that there should be region or country wise databases and best practice guidelines for LCA, which can alleviate many issues and dissimilarities for the LCA practitioners. The findings of the review of the literature on alternative fuels have opened new avenues for future research in this area of life cycle sustainability assessment.

Acknowledgement

This research project is supported by the 'Australian Government Research Training Program Scholarship' which paved the way to produce this publication.

See also: A Comparative Life Cycle Assessment for Utilising Laminated Veneer Bamboo as a Primary Structural Material in High-Rise Residential Buildings

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Biochar Production From Biomass Waste-Derived Material

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Introduction

Biochar is a porous carbonaceous solid material with a high degree of aromatization and strong antidecomposition ability that is produced by the thermal decomposition of biomass from plant or animal waste under oxygen free or limited oxygen conditions (Pandey *et al.*, 2015). It has received much attention during the last few years for its potential applications in various agronomic and industrial sectors. Biochars have a tremendous range of physical and chemical properties (Gul *et al.*, 2015), which greatly affect their wide applications. Recent evidences suggest that the feedstock and the method by which the biochar is produced has a significant impact on biochar characteristics, including concentrations of elemental constituents, density, porosity, and pH, which collectively impact the suitability of the biochar for various applications. In agriculture, it is used to upgrade the soil quality (Aller *et al.*, 2017; Werner *et al.*, 2018). It slows down the rate of decomposition of nutrients from the soil and hence, enhances the soil quality. In different industries, it is used in waste treatment (Ahmad *et al.*, 2014; Oliveira *et al.*, 2017; Uchimiya *et al.*, 2013) to remove organic contaminants, heavy metals and different kinds of dyes and pigments from textile industries. In power generation, biochar can be used as a fuel because biochar contains a high carbon percentage in it. Biomass has been found to be a very potential source of renewable energy (Tripathi *et al.*, 2016) materials and chemicals.

The main sources of biomass, as a raw material, include agricultural residues, algal biomass, forest residues, manures, activated sludge, energy crops, digestate etc. Biomass may be converted into high-value products using a number of physical, thermochemical and biochemical processes. Biochar is produced by thermochemical conversions, such as pyrolysis, gasification, torrefaction, and hydrothermal carbonization of carbonaceous biomass at high temperature (300–900°C) and under O₂-limiting conditions (Lehmann *et al.*, 2011). The physical, chemical and mechanical properties of biochars depend on the feedstock type and pyrolysis operating conditions (Jafri *et al.*, 2018). The selection of a specific type of feedstock is to a great extent determined by the availability of this material in the region where the biochar is likely to be produced, as this reduces the cost of transport while decreasing the carbon footprint of the biochar technology. Production of the biochar from the biomass does not only depend upon the technique which is employed to produce but it is also a function of the process parameters involved in the production also. Studies on the biomass pyrolysis in the recent past have revealed that the production of the biochar depends upon several factors such as type of biomass, moisture content, and particle size, reaction conditions (reaction temperature, reaction time, heating rate) and surrounding environment (carrier gas type, flow rate of carrier gas) and other factors (catalyst, reactor type).

The main objective of this article is to show the potential of waste biomass for production of biochar which is a valuable material with tremendous applications. This article exhaustively describes the possible raw materials for biochar production, biochar production processes, the properties of biochar, followed by biochar applications and final conclusion is presented.

Raw Materials for Biochar Production

Biochar is produced from a wide range of raw materials, and it has a porous structure and negative surface functional groups. Biomass with varying contents of hemicellulose, cellulose, and lignin may yield biochars with distinctive physicochemical properties. The main sources of raw material for biochar production include: biomass, municipal waste, field residues, and animal waste. These raw materials can be lignocellulosic and non-lignocellulosic biomasses. Lignocellulosic biomass (Mary *et al.*, 2016) are abundant bioresource of plant and animal parts including agro-industrial residues, forest-industrial residues, energy crops, municipal solid waste, and others. The widespread non-lignocellulosic biomass wastes include sewage sludge, manure, algae, animal hair, and bone, etc. are with severe challenges for value-added disposal and utilization, because of their complex and various components. Li and Jiang have presented a review on non-lignocellulosic biomass characteristics, thermochemical behaviors of main components (e.g., C, O, N, P, and metals), characterization methods, conversion process, and the main applications of non-lignocellulosic biochar (Li and Jiang, 2017). Compared with lignocellulosic biomass, the non-lignocellulosic biomass has a greater threat for the ecological environment because of its higher contents of heavy metals and heteroatom like nitrogen, phosphorus, sulfur (Agrafioti *et al.*, 2013). The heavy metals in non-lignocellulosic biomass can be dissolved in a water system, leading to water pollution and accumulation in the food chains (Wang *et al.*, 2016). Cellulose, hemicellulose and lignin compositions of such biomass feedstock are depicted in Table 1.

Biochar Production Processes

Biomass can be converted to renewable fuels through biochemical and thermochemical conversion processes. The important biochemical conversion processes include anaerobic/aerobic digestion, fermentation, and enzymatic or acid hydrolysis. In

Table 1 Lignocellulosic composition (wt%) of certain biomass resources

	<i>DPR</i>	<i>DPL</i>	<i>EFB</i>	<i>DPG</i>	<i>PP</i>	<i>CL</i>	<i>OP</i>	<i>HW</i>	<i>SW</i>	<i>LG</i>
Cellulose	40.40	34.87	38.44	22.22	45	40	54.1	45–50	35–40	38
Hemicellulose	33.08	19.84	24.65	20.44	41	50	49	20–25	20–25	26–29
Lignin	12.49	14.03	25.08	16.01	3	8	12	20–25	27–30	15–19

biochemical conversion, biomass molecules are broken down into smaller molecules by bacteria or enzymes. This process is much slower than the thermochemical conversion process but does not require much external energy. In the anaerobic digestion, bacteria take oxygen from the biomass itself instead of atmospheric oxygen. The products of anaerobic digestion are biogas (a mixture of methane, carbon dioxide) and solid digestate. Only 5%–10% of the feed into the digester is digested by the anaerobic bacteria. The digestate consists of remaining indigestible material. Aerobic digestion, commonly known as composting, takes place in the presence of oxygen. It uses different types of microorganisms that access oxygen from the air, producing carbon dioxide, heat and solid residue (compost). In fermentation, starch is converted into sugars using acids or enzymes. Then sugar is converted into ethanol or other chemicals with the help of yeast. The fermentation of lignocellulosic feedstock requires additional pretreatment (hydrolysis) to breakdown the cellulose and hemicellulose into simple sugars. Hydrolysis can be achieved by the use of acids, enzymes or hydrothermally (Basu, 2013). The lignin is not converted and is left for thermochemical conversion. Biochar is not a product of biochemical conversion, as a result, biochemical conversion methods are of no importance in the production of biochar. Major thermochemical technologies for biochar production include slow and fast pyrolysis, gasification, torrefaction, and hydrothermal carbonization. Biochar yield greatly depends on the adaption of pyrolysis type. Slow pyrolysis performed at longer residence time and at a moderate temperature (350–550°C) in absence of O₂ results in higher yield of biochar (30%) than the fast pyrolysis (12%) or gasification (10%).

Thermochemical Conversion Processes

There are many types of thermochemical conversion processes through which biomass is converted to solid, liquid and gaseous products. Thermochemical conversion processes use high temperature to breakdown the bonds of organic matter, including combustion, gasification, and pyrolysis (Lehmann and Joseph, 2009). Combustion is simply a burning of biomass in air. Chemically it is high temperature exothermic oxidation of biomass in the presence of oxygen to form carbon dioxide (CO₂) and water vapor (H₂O), hot flue gas. Char (contains some organic carbon) and ash (typically includes inorganic oxides and carbonates) are the solid byproducts of combustion. Combustion temperatures are usually in the range of 700–1400°C. Combustion is not a preferred method of biochar production as it converts most of the carbon in the biomass into CO₂. Gasification is performed at temperatures greater than 800°C under reduced oxygen atmosphere to avoid complete combustion (Basu, 2013). Gasifiers are designed to produce gaseous products of incomplete combustion comprising carbon monoxide (CO), hydrogen (H₂) together with CO₂, nitrogen (N₂) and moisture (H₂O). Gasification is also a poor choice for biochar production as it converts most of the carbon in the biomass into CO and CO₂.

Pyrolysis Process

Pyrolysis is a thermal decomposition process that takes place in the absence of oxygen to convert biomass into three distinct product fractions: solid residue (biochar), condensable vapors resulting liquid product fraction (bio-oil) and non-condensable gaseous products. Once oxygen is removed, combustion cannot occur instead pyrolysis happens. Pyrolysis temperatures are usually between 300 and 700°C. Pyrolysis is the most promising technique to convert biomass into biochar and bio-oil. Lower pyrolysis temperatures and longer residence times tend to produce more biochar. High temperatures and longer residence times increase the production of gas. Moderate temperatures and short residence times tend to produce more liquids (Bridgwater, 2012).

There are different pyrolysis processes including torrefaction, slow (conventional) pyrolysis, intermediate pyrolysis, fast pyrolysis, flash pyrolysis, microwave pyrolysis, and hydrothermal carbonization. Various operating conditions are used in these processes, for example, residence time can vary from less than 1 second to hours, heating rate can vary from less than 1°C/s to more than 1000°C/s and temperature can vary in the range from 300 to 700°C or higher. As each type of pyrolysis produces different proportions of the three types of products (biochar, bio-oil, and gas), careful selection of the pyrolysis process is important to obtain the final desired product. The primary conversion of biomass during the pyrolysis process can be described by three pathways; char formation, depolymerization, and fragmentation (Collard and Blin, 2014). Char formation is generally favored by intra- and intermolecular rearrangement reactions resulting higher thermal stability of the residue. This pathway is characterized by the formation of benzene rings and the combination of these rings into an aromatic polycyclic structure. These rearrangement reactions are generally accompanied by the release of water or non-condensable gas (devolatilization). Depolymerization is characterized by breaking of polymer bonds, followed by stabilization reactions to produce monomer, dimer and trimer units. These volatile molecules are condensable at ambient conditions and found in liquid fraction. Fragmentation consists

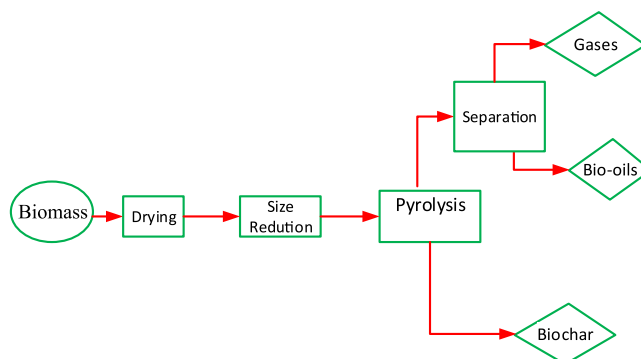


Fig. 1 Conceptual pyrolysis process.

Table 2 Operating conditions of various pyrolysis processes and their product fractions (bio-oil, biochar, and gas)

Mode	Condition	Liquid (bio-oil)	Solid (biochar)	Gas (syngas)	Heating rate
Fast pyrolysis	Moderate temperature (425–600°C), Short vapor residence time (< 2 s)	75% (25% water)	12%	13%	10–1000°C/s
Intermediate pyrolysis	Low to moderate temperature (450–550°C), Moderate hot vapor residence time (10–20 s)	50% (50% water)	25%	25%	1–10°C/s
Slow pyrolysis	Low to moderate temperature (300–550°C), Long residence time (hours to days)	30% (70% water)	35%	35%	1–0.8°C/s
Gasification	High temperature (> 800°C) Long vapor residence time	5% tar (55 water)	10%	85%	
Torrefaction	(450–550°C), (< 2 h)	20%	75%	5%	< 1°C/s
Hydrothermal Carbonization	(< 200°C), (1–16 h)				< 1°C/s
Flash Pyrolysis	(750–1000°C), (0.5 s)				> 1000°C/s
Microwave-Assisted Pyrolysis	(400–800°C),				

the breaking of polymer bonds and even monomer bonds result in the formation of non-condensable gasses and a range of organic vapors which are condensable at ambient conditions (Collard and Blin, 2014).

The gas and vapor products of primary conversion are unstable under pyrolysis temperatures and, with sufficient residence time, can undergo secondary reactions such as cracking or recombination reactions. Cracking reactions consist the breaking of volatile compounds into lower MW (molecular weight) molecules. Recombination consists the combination of volatile compounds into higher MW molecules, which may not be volatile under pyrolysis temperatures. Recombination reactions also result in the formation of secondary char. Primary char can act as a catalyst to the secondary reactions (Collard and Blin, 2014).

As a result of high heating rates and short residence times, fast pyrolysis tends to yield higher proportions of oils. In contrast, slow pyrolysis tends to yield higher proportions of biochars because of slow heating rates and longer residence times. The occurrence of primary and secondary reactions in thermal decomposition of biomass highlight the fundamental difference between fast pyrolysis and slow pyrolysis.

Pyrolysis requires relatively dry feedstock (usually moisture content <30 wt%, but moisture contents of ~10 wt% are preferred), and grinded to different particle sizes based on the type of pyrolysis. A general scheme of a pyrolysis process is represented in Fig. 1.

Feedstock with high moisture contents consumes more energy to account for increasing heat of vaporization during the heating of biomass towards the pyrolysis temperature. Additionally, the gases and vapors produced in pyrolysis using a high moisture feedstock are diluted with steam and have a lower calorific value. Wet biomass, typically with 70 wt% or more water can be converted using hydrothermal carbonization processes. The common processes include slow and fast pyrolysis, and the most successful approach for high-yield biochar production is via slow pyrolysis as directed in Table 2.

Torrefaction process

Torrefaction, a mild form of pyrolysis, involves heating the feedstock to temperatures of 200–300°C at slow heating rates (less than 1°C/s) in the absence of air under atmospheric pressure conditions. Torrefaction removes water as well as superfluous volatiles and partly decomposes the biopolymers (cellulose, hemicelluloses, and lignin) by giving off organic volatiles. It tends to yield higher proportions of solid (torrefied biomass) in addition to liquid and non-condensable gaseous products. As specified by the EBC (2012), the molar oxygen to carbon (O/C) ratio of biochar should be less than 0.4. But torrefied biomass tends to have higher

oxygen to carbon O/C) ratio than the ECB specification of biochar. Therefore, torrefied biomass cannot be referred to biochar. Torrefied biomass has physicochemical properties in-between that of raw biomass and biochar. Torrefaction is a pre-treatment method that is used primarily for moisture removal and densification of biomass, which will reduce the cost of transportation and increase the heating value of biomass. Torrefaction also increases the hydrophobicity, grindability and reduces the biodegradability compared to the untreated biomass feedstock. Torrefied biomass can be stored long-term without degradation. A typical mass yield from torrefaction is 70%–80% and energy yield is 80%–90%.

Slow pyrolysis process

The slow pyrolysis is characterized by moderate temperatures (300–550°C), slow heating rates (0.1–0.8°C/s) and longer residence time (5–30 min or even 25–35 h) (Roy and Dias, 2017). Slow pyrolysis aims at maximizing the yield of biochar by promoting secondary reactions, which is achieved by longer vapor residence times. The biochar produced in slow pyrolysis consists of both primary and secondary char. The slow heating rate with moderate pyrolysis temperatures also promotes the production of biochar. Biochar yield depends on the feedstock properties and pyrolysis conditions such as processing temperature, heating rate and pyrolysis environment (Roy and Dias, 2017). Biomass containing more minerals yields less biochar. The overall slow pyrolysis process can generally be exothermic due to the extensive occurrence of secondary reactions. Slow pyrolysis can accept a wide range of particle sizes (5–50 mm).

Intermediate pyrolysis process

In intermediate pyrolysis, the reaction is faster than slow pyrolysis but slower than fast pyrolysis. It occurs in the temperature range of 450–550°C, at higher heating rate than slow pyrolysis with residence time ranging from 10 to 30 s and produces less biochar than slow pyrolysis process (Bridgwater, 2012; Pandey *et al.*, 2015). Intermediate pyrolysis occurs at controlled heating rates thus inhibiting the formation of high molecular weight tars and yielding products (biochar, bio-oil, and gases) with different product qualities. In intermediate pyrolysis, the biomass particles sizes and shapes are less critical than in fast pyrolysis. It can process a wider variety of biomass, larger particles up to pellets and chips and also material with a water content of up to 40% (Pandey *et al.*, 2015).

Fast pyrolysis process

The fast pyrolysis typically involves high temperatures, high heating rates (10–1000°C/s) and short residence times (0.5–2 s) (Roy and Dias, 2017). Fast pyrolysis prevents secondary reactions from taking place by having short vapor residence times (rapid removal and quenching of the condensable vapors) and by maintaining high biomass heating rates thereby maximizing the yield of condensable vapors (bio-oil). The distribution of products (bio-oil, biochar, and gasses) depends on the biomass composition and rate and duration of heating. If bio-oil is the product of interest, the optimum pyrolysis temperature range is 425–600°C with the peak temperature below 650°C. However, the peak temperature can be up to 1000°C, if the production of gas is of primary interest (Basu, 2013).

A finely ground biomass feed (usually < 1 mm) is required to achieve very high heat transfer rates and thereby very high heating rates which reduce the mass and heat transfer limitations. The biochar yield in fast pyrolysis is generally low as only primary char is being produced. The overall fast pyrolysis process is highly endothermic due to the absence of secondary reactions. Fast pyrolysis prefers biomass with low moisture content (< 10 wt%) in order to minimize the water in the product bio-oil. Low moisture content also facilitates grinding the feed to give sufficiently small particles to ensure rapid heating and fast pyrolysis (Bridgwater, 2012).

Flash pyrolysis process

Flash pyrolysis also aims to maximize the yield of liquid. It is characterized by high temperatures, higher heating rates (> 1000°C/s) and shorter residence times (< 0.5 s). The main product distributions of flash pyrolysis are similar to that of fast pyrolysis. It occurs in the temperature range of 800–1000°C (Pandey *et al.*, 2015). Very fine particles of biomass feed (< 0.2 mm) is usually required.

Hydrothermal carbonization process

Most biomass materials are wet and have moisture contents range up to 95 wt%. Biomass with more than 30 wt% moisture content requires drying prior to pyrolysis. Hydrothermal carbonization (HTC) involves the application of heat and pressure to convert biomass in the presence of water into carbonaceous biofuel. It is a promising technique to convert the wet biomass into biofuels by omitting the energy-intensive drying process. Water plays an active role as a solvent and reactant. When biomass feedstock in water is heated at low temperatures (< 200°C) in a sealed vessel at autogenous pressure, mostly solids (called hydrochar) are formed in a process known as hydrothermal carbonization (HTC). At higher temperatures (between 200 and 350°C), hydrothermal liquefaction (HTL) takes place and the biomass feedstock is mostly converted into a liquid product (bio-oil). Near and above the critical point of water (374°C and 22.1 MPa), hydrothermal gasification (HTG) takes place and the biomass is mostly converted into a mixture of non-condensable gases (H₂, CO, CH₄, and CO₂). Hydrochar has higher H/C ratios than biochar specifications.

Microwave assisted pyrolysis process

In conventional heating, heat is transferred to the material surface (by convection, conduction, and radiation) and subsequently from the surface to the interior of the material by conduction as a result of temperature gradients. On the other hand, microwave

Table 3 Merits and demerits of various pyrolysis processes

Pyrolysis type	Merits	Demerits
Torrefaction	Higher proportions of solid yield (torrefied biomass)	Torrefied biomass have higher O/C ratio than biochar specification
Slow pyrolysis	Maximum yield of biochar. Can accept a wide range of particle sizes	
Intermediate pyrolysis	Can process a wide range of particle sizes and also material with a water content of up to 40 wt%	Produce less biochar than slow pyrolysis
Fast pyrolysis	Higher yield of bio-oil	Biochar yield is generally low. Finely ground biomass feed (usually < 1 mm) is required. Prefer biomass with low moisture content (< 10 wt%)
Flash pyrolysis	Maximum yield of bio-oil	Very fine particles of biomass feed (< 0.2 mm) is usually required
Hydrothermal carbonization	Can convert the wet biomass into biofuels. Drying is not required	Produce solid product (hydrochar) having higher H/C ratio than biochar specification
Microwave-assisted pyrolysis	Uniform heating throughout, rapid heating rate, volumetric and selective heating	Require electricity which is an expensive high quality-energy

energy is delivered directly into materials within an electromagnetic field. The electromagnetic field enters the material and generates thermal energy throughout the penetration depth by dielectric heating through interaction with polarizable dipoles present in the material and heat the material from inside. Microwave heating requires a material with a high dielectric constant. The dielectric constant is a measure of the ability of a material to absorb microwave energy. Biomass has a relatively low dielectric constant. As a result, microwave pyrolysis requires catalyst as well as microwave absorbers to improve the heating. The presence of water in biomass may increase the heating rate of microwave pyrolysis, due to the high dielectric constant of water in comparison with biomass (Yu *et al.*, 2017). Microwave-assisted pyrolysis usually operates in the temperature range at 400–800°C.

Some of the advantages of microwave-assisted pyrolysis over conventional pyrolysis include uniform heating throughout, rapid heating rate, volumetric and selective heating. Microwave heating provides ease of operation by instant on/off control and improves the yield and quality of the products. It reduces the formation of hazardous product and minimizes pollutants emission, making the technique environmentally friendly (Yu *et al.*, 2017). The other advantages include high heating efficiency as heating is in situ, ability to handle wet biomass without drying and ability to pyrolyse large biomass particles. The disadvantage of microwave assisted pyrolysis is that it requires electricity which is an expensive high-quality energy compared to the heat generated by the combustion of pyrolysis gases and vapors in conventional pyrolysis.

The merits demerits of the pyrolysis processes are summarized in the following table (Table 3).

Biochar Quality

The European Biochar Certificate (EBC, 2012) define biochar as a “heterogeneous substance rich in aromatic carbon and minerals. It is produced by pyrolysis of sustainably-obtained biomass under controlled conditions with clean technology and is used for any purpose that does not involve its rapid mineralization to carbon dioxide and may eventually become a soil amendment”. This definition differentiates biochar from other forms of carbonaceous materials such as char, charcoal. The sources of biomass for the production of biochar need to be renewable and sustainable. The intended end use of biochar is soil management and C (carbon) sequestration.

The major component of plant biomass is cellular lignocellulosic material, which is the non-starch fibrous part of the plant materials. The three major constituents of lignocellulosic biomass are cellulose, hemicellulose, and lignin (Basu, 2013). The main constituent of plant cell wall is cellulose, which provides structural support. The second and third most abundant polymers in lignocellulosic biomass are hemicellulose and lignin, respectively. These three forms of polymers are responsible for most of the physical and chemical property modification during the pyrolysis process. The mechanisms of pyrolysis of these polymers are chemically different from biomass species to species. Cellulose and hemicellulose decompose over a narrower temperature range whereas lignin degrades over a wider temperature range compared to cellulose and hemicellulose. Some other compounds present in biomass include inorganic compounds and organic extractives. The inorganic compounds constitute less than 10% by weight of biomass, forms ash in the pyrolysis process. Organic extractives of biomass refer to the nonstructural components that can be extracted by polar or nonpolar solvents. These include fats, waxes, proteins, terpenes, simple sugars, gums, resins, starches, alkaloids, phenolics, pectins, glycosides, mucilages, saponins, and essential oils. Also, biomass has a substantial quantity of free and bound water.

The biochar properties will depend on the feedstock material characteristics and pyrolysis conditions used for the production of biochar. The main parameter that determines the degree of devolatilisation of the biomass is the pyrolysis temperature. Water, both free and bound, is the first constituent removed in heating of biomass to temperatures up to 160°C. Thermal decomposition of biomass begins with devolatilisation/decomposition of extractives at temperatures < 220°C. Hemicellulose is the least stable polymer and break down first at temperatures of 220–315°C. Cellulose has a high degree of polymerization and exhibits

higher thermal stability. It decomposes in the temperature range 315–400°C. Lignin is the most difficult component to pyrolyse which decompose in a wide temperature range from 160 to 900°C (Yang *et al.*, 2007).

Commonly measured quality parameters of biochar include carbon content, bulk density, carbon stability, volatile compound content, surface area, nutrient content, heavy metals, pH value, water and ash content, PAH, water holding capacity, porosity, elemental composition (carbon, hydrogen nitrogen and oxygen), cation exchange capacity and electrical conductivity (EBC, 2012; Song and Guo, 2012). The quality of biochar varies with the feedstock type and pyrolysis process. Pyrolysis parameters such as heating rate, residence time and final temperature greatly influence the biochar quality. Pyrolysis temperature plays an important role in biochar properties such as elemental composition, particle size, specific surface area, pore size distribution, thermal capacity, and electrical conductivity.

Depending on the application of biochar, some quality parameters are more important than others. In crop production, the important quality parameters of biochar include pH, volatile compound content, ash content, water holding capacity, bulk density, pore volume and specific surface area (Song and Guo, 2012). Carbon stability is a critical quality parameter in carbon sequestration and soil fertility enhancement. The other important quality parameters in soil fertility enhancement include surface area and nutrient content. One of the most important characterization parameters of biochar is the molar hydrogen to carbon (H/C) ratio, it is an indicator of the degree of carbonization and the stability of biochar. The value of H/C ratios greater than 0.7 indicate a low biochar quality and pyrolysis deficiencies. Molar oxygen to carbon (O/C) ratio is also relevant for characterizing biochar and differentiating it from other carbonization products (EBC, 2012). The value of O/C ratio greater than 0.4 indicates a lower biochar stability.

The molar H/C and O/C ratios of lignocellulosic biomass are approximately 1.5 and 0.7, respectively. During pyrolysis, the biomass undergoes devolatilization and the solid portion gets enriched in carbon. The H and O are preferably removed over C and the H/C and O/C ratios tend to decrease as biomass undergo its transformation into biochar. The H/C and O/C ratios are used to assess the degree of aromaticity and maturation (Lehmann and Joseph, 2009).

Properties of Biochar

Characterization of biochar for proximate and ultimate analysis reveals the different biochar properties. Important physico-chemical properties include porosity, surface area and pH which all have an effect on its application to soil. Biochar is made up of elements such as carbon, hydrogen, sulfur, oxygen, nitrogen as well as minerals in the ash fraction. The properties of biochar will thus vary depending upon the production conditions and the nature of the feedstock used. For example, during the thermal oxidation of biomass to produce biochar, the inherent carbon is lost in the forms of CO₂, CO, CH₄, and various hydrocarbons. Also, there are cracking and devolatilization creating bigger pore holes inside the biochar if produced at higher temperatures. Elemental compositions of biochars from different biomass resources are shown in Table 4.

Thus, a biochar with desirable properties can be deduced from both its proximate and ultimate analysis. The lower the O/C and H/C ratios, the higher is the loss of oxygen and hydrogen during the combustion process (Nsamba *et al.*, 2015) producing a product richer in higher elemental carbon. The International Biochar Initiative (IBI) recommends a maximum value of 0.7 for the molar H/C ratio (Mary *et al.*, 2016; Nsamba *et al.*, 2015) to distinguish biochar from biomass that has not been or only somewhat thermochemically altered. Thus suitable working conditions and technologies must be selected in order to produce a biochar of high quality. The pH of biochar from different biomass is around 10 and the microscopic surface structure of biochars ranges from around 3 m²/g for rice husk biochar to around 500 m²/g for biochar from wood (Kan *et al.*, 2016).

Biochar Applications

Biochar is widely used for generation of heat and power, and an addition to soils, in which it serves as a fertilizer and carbon sequestration agent, it also used as an adsorbent for many pollutants from different processing sectors. The application of biochar has been shown to improve soil physical properties, especially in soils with bad soil structure or high bulk density. Biochar is also used as a catalyst (Lee *et al.*, 2017) and support of a catalyst. It can also be used as a filter medium and adsorbent for waste treatment to different industrial effluents.

Table 4 Elemental analysis of biochar produced from some typical biomass

	SC	Euc	SWS	DPR	DPL	EFP	DPG	PP	CL	OP
Ash (%)	9.86	3.60	58.53	5.50	11.58	4.20	2.40			
pH	7.18	5.92	4.85							
C (%)	53.96	64.94	22.67	39.95	43.14	43.49	43.65	39.32	31.80	40.43
H (%)	1.83	3.12	1.31	7.19	7.49	7.51	7.59	4.75	3.20	4.83
N (%)	1.24	0.56	3.04	0.16	0.20	0.19	0.16	2.40	4.01	1.56
O (%)	42.98	31.39	72.99	52.70	52.70	52.73	52.74	53.30	59.40	52.90

Note: Mary, G.S., Sugumaran, P., Niveditha, S., Ramalakshmi, B., Ravichandran, P., Seshadri, S., 2016. Production, characterization and evaluation of biochar from pod (Pisum sativum), leaf (Brassica oleracea) and peel (Citrus sinensis) wastes. International Journal of Recycling of Organic Waste in Agriculture 5 (1), 43–53.

Environmental Applications of Biochar

Biochar, a low-cost carbonaceous material, is emerging as an economical substitute to the activated carbon to remove diverse organic contaminants such as agrochemicals, antibiotics, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, volatile organic compounds and aromatic dyes, and a series of inorganic contaminants (e.g., heavy metals, ammonia, nitrate, phosphate, sulfide etc.) from aqueous, gaseous and/or solid phases.

Biochar has wider environmental applications due to its distinctive characteristics, e.g., high adsorption capacity, high specific surface area, microporosity, and ion exchange capacity. Such variability and predominance of a specific reaction are controlled by specific physicochemical properties of the biochar, which is attributed to feedstock types and pyrolysis conditions used during its production. These two factors greatly change the physicochemical properties such as surface area, polarity, atomic ratio, pH, elemental composition, thus overall surface property of the biochar (Ahmad *et al.*, 2014; Uchimiya *et al.*, 2013). These variations in biochar characteristics have significant implications on its suitability and efficacy in remediation of targeted pollutants.

Applications of biochar in soil not only remediate the pollutants from the soil but also improve the soil properties. Biochar improves physical (e.g., water holding capacity, O₂ content and moisture level), chemical (e.g., pollutants immobilization and carbon sequestration), and biological (e.g., microbial abundance, diversity, and activity) properties of the soils (Gul *et al.*, 2015). These biochar characteristics eventually contribute to soil carbon sequestration, greenhouse gases emission reduction, and therefore contribute to an overall improvement in soil health.

Biochar as Adsorbent

Environmental application of biochar is one of the primary applications of biochar. In addition to being used as soil conditioner and carbon sequestration reagent, biochar has attracted much attention in wastewater treatment field. Recent literatures show biochar as a highly efficient, environmentally friendly, and low-cost adsorbent. Biochar characteristic plays a critical role in contaminant removal, which is often governed by pyrolysis temperature and feedstock type. For example, fully carbonized biochar produced at a higher pyrolysis temperature (> 500°C) has more affinity for organic pollutants due to high surface area, microporosity, hydrophobicity, carbon-to-nitrogen (C/N) ratio, pH, and low dissolved organics. On the other hand, partly carbonized biochar produced at a lower pyrolysis temperature (< 500°C) contains a higher content of dissolved organic carbon and O-bearing functional groups, relatively low porosity and C/N ratio, hence more appropriate for removal of inorganic pollutants. Regarding feedstock types, biochar derived from woody biomass and crop residues has higher surface area compared to that of the solid municipal wastes and animal manure-derived biochars. Other factors such as biochar pH (resulting from pyrolysis condition), biochar residence time, biochar application rate and contaminant type also affect the removal efficiency of biochar. There have been significant research efforts to examine the application of biochar for removal of various industrial organic and inorganic pollutants (Lehmann *et al.*, 2011; Oliveira *et al.*, 2017) depicted in Table 5.

Biochar as Catalyst

Biochar's unique chemical structure with a large surface area and tailored surface functional groups can be easily prepared by activation or functionalization and shows great potential to be used as a versatile catalyst or catalyst support in many chemical processes. Biochar can be easily separated from catalysts by oxidation to recover precious metals. Therefore, the application of biochar as catalyst will not only enhance its utilization but also promote the development of a variety of catalysts. Biochar used in the synthesis of carbon-encapsulated iron nanoparticles, and its catalytic activity on the conversion of synthesis gas to liquid hydrocarbons was evaluated. It was found that the CO conversion was about 95% and the selectivity of liquid hydrocarbon was as high as 68%. Similarly, biochar activated with KOH and sulfonated using fuming H₂SO₄, give a high activity on the transesterification for biodiesel production (Xiong *et al.*, 2017).

Table 5 Removal of organic pollutants by biochar derived from different feedstocks and pyrolysis temperatures

Chemicals	Examples
Organic pollutants include agrochemicals	Pesticides, herbicides, fungicide, insecticides include carbofuran, chlorpyrifos, atrazine, simazine, pyrimethanil etc., Phenol, Deisopropylatrazine
Antibiotics or drugs	e.g., sulfamethazine, sulfamethoxazole, tylosine, acetaminophen, ibuprofen, tetracycline etc., Acetaminophen, Ibuprofen, Naproxen, Sulfamethazine,
Industrial chemicals including polycyclic aromatic hydrocarbons	e.g., naphthalene, phenanthrene, pyrene, anthracene, polychlorinated biphenyl, m-dinitrobenzene, catechol, p-nitrotoluene etc.
Volatile organic compounds (VOCs)	e.g., trichloroethylene, benzene, furan, butanol, hexane etc
Cationic aromatic dyes	e.g., rhodanine, brilliant-blue, methyl-violet, methyleneblue etc.
Aromatic cationic dyes	Methylene blue, Methyl violet,
Polycyclic aromatic hydrocarbons	N-nitrosodi-methylamine, Naphthalene, Naphthenic acids, Nonylphenol, Phenanthrene
Miscellaneous pollutants	Furans (Furfural, HMF) inorganic pollutants (e.g., Pb ²⁺ , Cu ²⁺ , Cd ²⁺ , Zn ²⁺ , Hg ²⁺ and Ni ²⁺ , H ₂ S, NH ₃ , NH ₄ ⁺ , NO ₃ ⁻ , Cr ₃ ⁺ , Sb ₃ ⁺)

Catalysts have played a crucial role in developing technologies to convert not only conventional carbonaceous feedstocks (e.g., coal, natural gas, and petroleum) but also renewable feedstocks (e.g., biomass) into value-added products such as fuels and chemicals. The global catalyst market is estimated to be about \$34.3 billion by 2024 (The Global Catalyst Market, 2018), more than 35% of the global GDP was associated with catalytic technologies, and 95% of industrial products were estimated to be produced via catalytic processes. Given that biochar is a highly porous and carbon-rich material, biochar is a promising alternative to replace conventional solid carbon-based catalysts with some known demerits (e.g., expensiveness and environmentally unfriendliness). Various modification can be made for the biochar via acid/base treatment or carbonization to improve its physicochemical properties making it an excellent candidate for catalytic applications. Waste biomass has been increasingly targeted as a renewable feedstock for the production of fuels and more recently platform chemicals,

Biochar as Animal Feed

In addition to the use of biochar to improve soils and to sequester carbon, it can also be used as animal feed and other animal husbandry applications. Recent research results (Carlson and Hawkins, 2018) have shown that the addition of biochar to animal feed may have the potential to offer a number of invaluable benefits: improved digestion, increased immunity, reduced chronic botulism, increased feed, and energy efficiency, increased growth rates, reduced methane production.

Conclusion

The article covers the description of biomass waste-derived material, known as biochar and its physicochemical properties along with its proximate analysis. The potential biomass wastes that can be used for biochar production are presented. Various production routes of biochar have been discussed. Among those, pyrolysis, torrefaction, slow pyrolysis, intermediate pyrolysis, fast pyrolysis, flash pyrolysis, hydrothermal carbonization, and microwave assisted pyrolysis are discussed with their operating conditions and specifications. Biochars have a tremendous range of physical and chemical properties, which greatly affect their wide applications. The physical, chemical and mechanical properties of biochars depend on the feedstock type and pyrolysis operating conditions. The feedstock and the method by which the biochar is produced has a significant impact on biochar characteristics, including concentrations of elemental constituents, density, porosity, and pH, which collectively impact the ability of the biochar for various applications. Slow pyrolysis process is the most suitable process for biochar production. The most common areas of application of biochar are also presented especially in the removal of organic contaminants and heavy metals from waste effluents. The main applications of the biochar are as an adsorbent, as a catalyst and catalyst support. The quality of biochar for various applications are discussed along with different quality parameters.

See also: Large Biomass Burners for Fuel Switch in Existing Fossil Fuel Based Plants. The Nexus Between Biomass – Footprint and Sustainable Development

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Biocompatible Thermoplastic Composite Blended With HAp and CS for 3D Printing

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Introduction

Poly-lactic-acid (PLA) is one of the thermoplastic polymer classes which have turned into a “material of decision” in bio-medical applications or biomedical surgery’s for its capacity to satisfy difficult needs that normally incorporate some special features like: bio-compatibility, bio-degradability, mechanical quality and process ability. In spite of the upsides of unadulterated PLA in a more extensive range of utilizations, it is constrained by its hydrophobicity, with slow bio-degradability and low impact toughness. The bio-degradable polymers have upper hand in polymer field, because of its versatility. PLA is industrially accessible bio-based polymer utilized as a part of an assortment of utilizations because of its high quality modulus and bio-degradability (Conn *et al.*, 1995). It is a thermo-plastic polymer having a place with the α -hydroxy acidic group. The polymer is then blended by coordinate poly-condensation of lactic corrosive utilizing an appropriate impetus (Södergård and Stolt, 2002; Chanfreau *et al.*, 2010; Omay and Guvenilir, 2013). Because of the nearness of two stereo isomers of lactic corrosive, PLA can be integrated as PDLA, PLLA or PDLLA. The two unadulterated homo-polymers and a variety of PDLLA polymers with changing proportions exhibit a scope of thermal, mechanical, internal as well as external properties (Zeng *et al.*, 2015; Zhang and Wang, 2008). PLA has poor tensile properties, low utilization temperature and a comparatively little window for process-ability. The vast majority of the monetarily accessible PLA involves for the most part of PLLA and very less amount of PDLA was mixed to expand the preparing window by instigating liquefying point misery. That causes a significant abatement in crystallinity (Garlotta, 2001). The chitosan (CS) and PLA have got the consideration by researchers as bio-degradable and bio-compatible materials (Zheng and Cui, 2010; Meng *et al.*, 2010; Bi *et al.*, 2011). The CS needs to be dissolved in weaken acidic arrangement, and as a framework/scaffolds material. CS decays gradually, and can’t coordinate with recovery of tissues. Additionally, CS’s mechanical properties are somewhat poor (Chen *et al.*, 2006; Lin and Yeh, 2010; Lee *et al.*, 2010; Fan *et al.*, 2010). These properties confine CS’s significantly for more extensive application in tissue designing. PLA polymers are the most broadly utilized manufactured bio-degradable macro-molecule, with matchless properties and process capacity. In addition, PLA’s degradation rate is customizable. In this manner, CS and PLA can be seen as complimentary in their qualities as tissue building materials. CS can counterbalance the acidic degradation produced by PLA, while, CS’s mechanical properties could be enhanced (Rasal *et al.*, 2010). Bone comprises of 69% (by weight) calcium phosphate, 21% (by weight) collagen, 9% (by weight) water and 1% (by weight) different constituents. It has a composite nature, which is developed of predominantly fired HAp and polymer with a complex various leveled micro-structure exceptionally hard to mimic which gives a large portion of the better mechanical properties than bone. Table 1 shows required mechanical properties of compact bone.

The current advancements in simulated bone territory incorporate earthenware production (ceramics), which are bio-insert substances, for example, alumina and zirconia, resorbable as a tri (calcium phosphate), and bio-active materials such as HAp. Different phases of calcium phosphate ceramics are used depending upon whether a resorbable or bio-active material is required. Numerous applications in hard tissue were chronicled before. A portion of the illustrations are swaps for teeth, hips, ligament and tendons and regeneration for periodontal sickness, maxilla facial remaking, enlargement and adjustment of the jaw bone, spinal combination and bone repair after tumour medical procedure. The tissue connection/bonding with

Table 1 Required mechanical properties of compact bone

Properties	Direction of test	
	Parallel	Normal
Young’s modulus	17.0–18.9 GPa	11.5 GPa
Bending strength	160 MPa	–
Tensile strength	124–174 MPa	49 MPa
Shear strength	54 MPa	–
Compressive strength	170–193 MPa	133 MPa
Yield compressive strain	0.010	0.011
Ultimate tensile strain	0.014–0.031	0.007
Yield tensile strain	0.007	0.004

Note: Pillai, C.K., Paulm, W., Sharma, C.P., 2009. Chitin and chitosan polymers: Chemistry, solubility and fiber formation. Progress in Polymer Science 34 (7), 641–78.

earthenware production (ceramics) and delicate tissues other than the hard tissue can be seen utilizing bio-active ceramics (Liou and Chen, 2002; Dorozhkin, 2009a; Zhang and Zhang, 2001; Kwon *et al.*, 2003). Bio-materials, for example CS, HAp, beta-tricalcium phosphate have noteworthy applications for bone substitution. Their applications incorporate, for instance, prostheses for substitution, materials covering or support in parts of the implants/scaffolds. The most widely recognized bio-material utilized as a part of the previous decades in hard tissue recovery is HAp, since it is the major inorganic compound in mammalian hard tissue and is profoundly perceived and utilized for its bio-compatibility, not costly and plentiful. It has been fused into a wide assortment of bio-medical gadgets including dental inserts, bio-degradable scaffolds, and different sorts of orthopedic embeds in various parts of the skeleton. (Fujita *et al.*, 2003; Kwon *et al.*, 2003; Dorozhkin, 2009b; Combes and Rey, 2010; Zhang and Zhang, 2001). HAp has been broadly utilized because of its compound likeness to bone and great bio similarity in the physiological ecological and a similarity with synthetic and characteristic polymers as poly-saccharides and additionally proteins making a useful bio-material for therapeutic and bio-medical application. HAp stimulates osteo conduction and can be coordinated into bone without inciting an insusceptible response. The basic arrangement of HAp is straightforwardly related with the organic reaction of inserts, affected by variables, for example, size and morphology of the particles inside the manufactured platform, and has been basic in permitting osteo conduction and bone development into the scaffolds permeable while additionally permitting the exchange of supplements through the scaffolds (Muzzarelli, 2011; Muzzarelli and Muzzarelli, 2002; Dorozhkin, 2009b; Pramanik *et al.*, 2009; Wilson and Hull, 2008). The challenge of hard tissue engineering is to develop a suitable bone scaffold with sufficient porosity and mechanical strength to allow cell adhesion, migration, growth and proliferation resulting in good integration with surrounding tissues. The quantity of materials has been utilized for bone tissue engineering including natural polymers, bio-glass and ceramics as like HAp. Surface with a positive charge elevates cell grip because of its negative charge; it can artificially bond with decidedly charged poly-saccharides as well as HAp with negative charge like proteins or potentially another calcium phosphate, for example, – tenocyclidine (TCP), shaping a more grounded platform material (Chen *et al.*, 2006; Dorozhkin, 2009a; Swetha *et al.*, 2010; Muzzarelli, 2011).

In this article, an effort has been made to develop the 3D scaffolds/implants on FDM by using in-house developed bio-compatible/bio-degradable feedstock filament (FDM wire) comprising of PLA, CS and HAp as a case study. Initially five input parameters (namely: material composition, rotational speed, barrel temperature, HAp particle size, and applied load) were judiciously selected for fabrication of FDM input wire. The wires having better flowability and suitable mechanical and dimensional properties have been used on the FDM machine.

Properties of PLA Mixed With Polymers/Composites

In spite of being a material with high quality and modulus, PLA needs application in mechanically requesting conditions because of low effect durability, fragile nature and low break elongation. Table 2 lists the different properties (thermal, mechanical and tensile) of the PLA (Mark, 1999).

In the meantime, PLA mix with different polymers with less strength can improve the polymers modulus and its rigidity with mediocre properties. Subsequently, PLA is regularly mixed with different polymers to upgrade thermo-mechanical properties for both polymeric materials (PLA and other). The alteration of thermal behavior in PLA blends is dictated by the extent of miscibility of the constituent polymers. Polymer mixes can be custom fitted by changing the polymer arrangement to accomplish a blend of mechanical and thermal properties as required for particular applications. The impact of liquefy mixing PLA and PMMA to locate a solitary T_g for the mixes subsequent to warming them to 250°C out of a DSC crucible, with an intermediary to those for individual polymers and effect of durability like the perfect polymer in which they were rich (Anakabe *et al.*, 2015). Jing *et al.* (2015) concluded the impact of handling temperature on the last T_g of the mix since they watched that the mixes prepared at 215°C portrayed double T_g changes because of polymer immiscibility beneath the UCST of 230°C. In another investigation, mixing PLA with thermo-plastic poly-urethane (TPU) upgraded sturdiness and break elongation of PLA, granted by TPU. They additionally noticed that mix with 80% PLA (by weight) has shape memory behavior, which the authors ascribe to the crystalline locales of PLA, causing maintenance of shape by going about as cross-linking focuses in the mixing/blending. Poly ϵ -capro-lactone (PCL) has additionally been describe to build the break elongation and thermal steadiness for PLA in a mix, joined by an abatement in the rigidity and modulus contrasted with flawless PLA because of the lower estimations of these properties in PCL (Ferri *et al.*, 2016; Yang *et al.*, 2015). The addition of PCL also changes the failure properties of the

Table 2 Thermal, mechanical and tensile properties of PLA polymers

Crystallinity	Semi crystalline, 0%–37%, Amorphous
Young's Modulus	1.2–3 GPa
Melting Temperature (T_m)	145–186°C
Glass transition Temperature (T_g)	50–64°C
Elongation at break	2%–6%
Tensile Strength	28–50 MPa

Note: Mark, J.E., 1999. Poly (lactic acid), In: Mark, J.E. (Ed.) Polymer Data Handbook. New York: Oxford University Press, pp. 627–633.

blend from brittle, as in case of pure PLA, to ductile. As specified before, PLA is mixed with pure polymers with lower mechanical strength for improvement of their different properties (such as tensile and thermal). Starch/PLA mixture have been reported where PLA improve the mechanical and tensile properties of the mixture (Shirai *et al.*, 2013b; Preechawong *et al.*, 2005; Shirai *et al.*, 2013a; Wootthikanokkhan *et al.*, 2012). PLA-PCL mixtures, shows improvement in mechanical and tensile properties, break elongation, Young's modulus and hardness with an increment of PLA quantity from 60% to 80% (Zhao and Zhao, 2016). Blended PLA with soya protein results in to increase in tensile properties, which is further improved by the mixing of poly-2-ethyl-2-oxazoline as a compatibilizing agent (Zhang *et al.*, 2006).

Mechanical Properties of Hard Tissues, Soft Tissues, Metallic/Ceramic/Polymeric Biomaterials

Figs. 1–5 showed mechanical properties of hard tissues, soft tissues, metallic biomaterials, ceramic biomaterials and polymeric biomaterials.

In polymer small amount of compatibilizers are mixed/blends to expand the internal bond between polymers, which thusly enhances the different properties of composition of polymeric materials. It exhibit a nitty gritty survey utilization/applications of compatibilization in the mixes of bio-degradable polymers (Imre and Pukánszky, 2013; Yu *et al.*, 2011). The utilization of different compatibilizers has been investigated to enhance the PLA properties mixes with different polymers, which the creators credit to starch going about as a nucleating operator for PLA.

Subsequently the interfaces between two polymers are made strides. In light of the coveted application, polymers are regularly subjected to plasticization to make the material more adaptable. Plasticizers actuate a lessening in T_g , rigidity and arrangement thickness of the polymer, yet increment its extension, affect strength and process ability (Wypych, 2012). In literature review it has been reported that for improvement/enhancement of polymers properties only PLA was mixed with plasticizers polymer and the

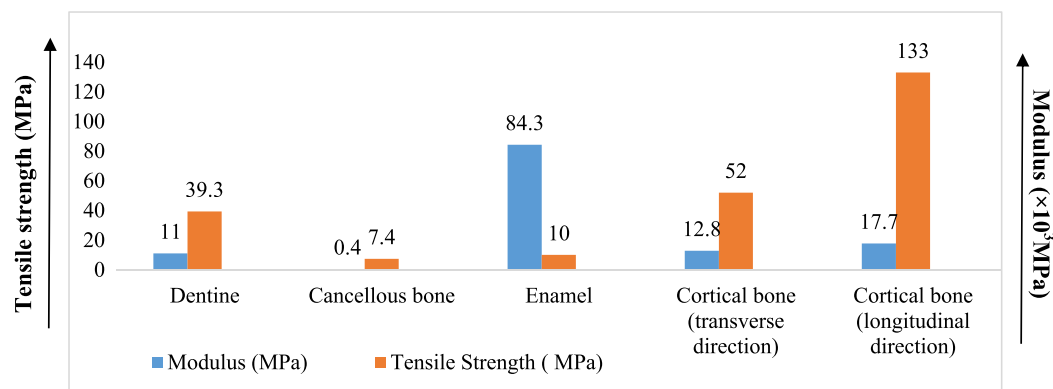


Fig. 1 Mechanical properties of hard tissues. Reproduced from Zhang, J., Jiang, L., Zhu, L., Jane, J.L., Mungara, P., 2006. Morphology and properties of soy protein and polylactide blends. *Biomacromolecules* 7 (5), 1551–1561.

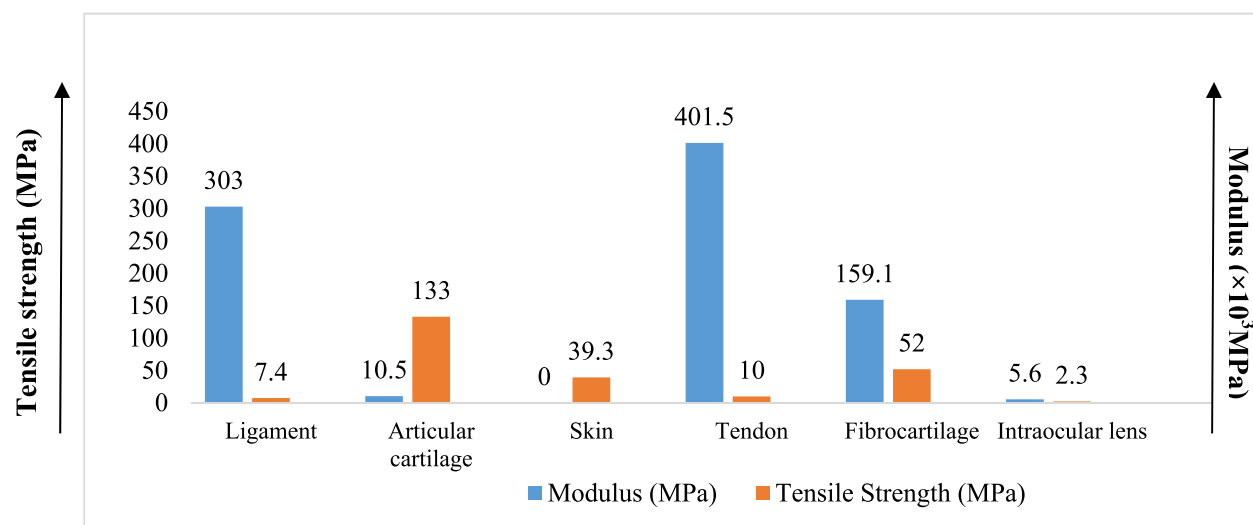


Fig. 2 Mechanical properties of soft tissues. Reproduced from Zhang, J., Jiang, L., Zhu, L., Jane, J.L., Mungara, P., 2006. Morphology and properties of soy protein and polylactide blends. *Biomacromolecules* 7 (5), 1551–1561.

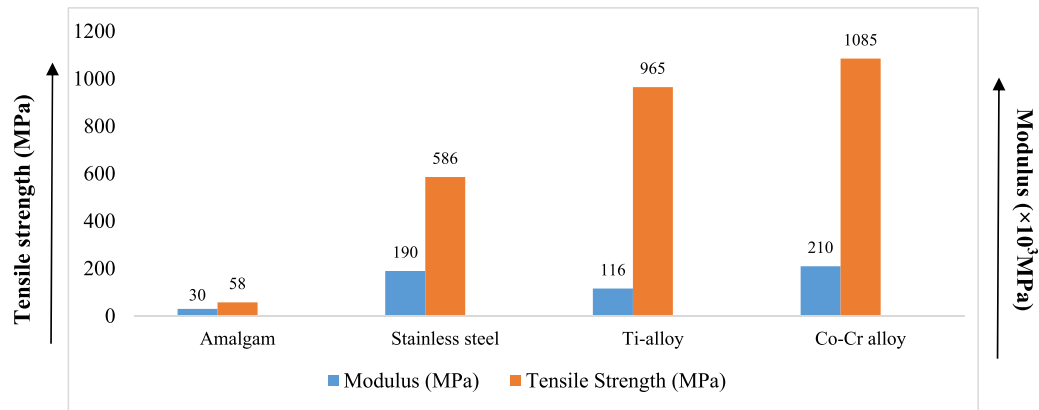


Fig. 3 Mechanical properties of metallic biomaterials. Reproduced from Zhang, J., Jiang, L., Zhu, L., Jane, J.L., Mungara, P., 2006. Morphology and properties of soy protein and polylactide blends. *Biomacromolecules* 7 (5), 1551–1561.

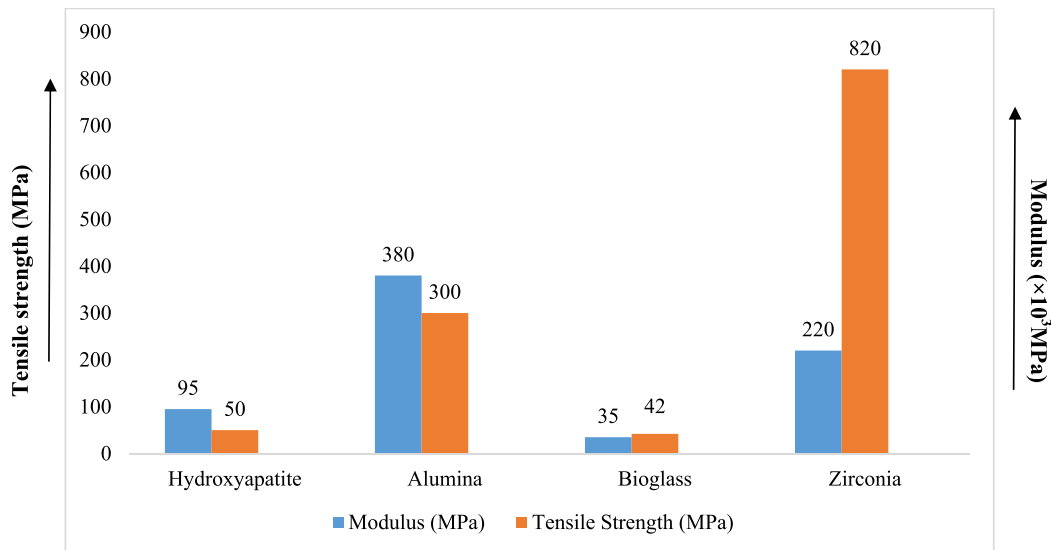


Fig. 4 Mechanical properties of ceramic biomaterials. Reproduced from Zhang, J., Jiang, L., Zhu, L., Jane, J.L., Mungara, P., 2006. Morphology and properties of soy protein and polylactide blends. *Biomacromolecules* 7 (5), 1551–1561.

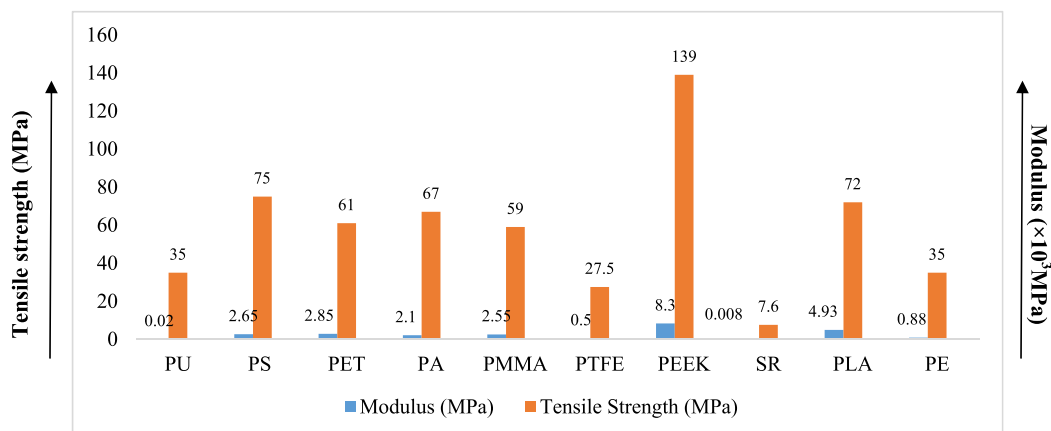


Fig. 5 Mechanical properties of polymeric biomaterials. Reproduced from Zhang, J., Jiang, L., Zhu, L., Jane, J.L., Mungara, P., 2006. Morphology and properties of soy protein and polylactide blends. *Biomacromolecules* 7 (5), 1551–1561. *Note:* PU, polyurethane, PS, polystyrene, PET, polyethylene terephthalate, PA, polyamide, PMMA, polymethyl Methacrylate, PTFE, polytetrafluoro ethylene, PEEK, polyether ether ketone, SR, synthetic rubber, PLA, polylactic acid, PE, polyethylene.

presentation of plasticizers in mixes of PLA with different polymers, either to make them more process able or to additionally enhance properties. It was also reported that for improvement/enhancements of PLA adaptability and different properties (mechanical and tensile) PEG and PEG subordinates or co-polymers are main plasticizers (Sungsanit *et al.*, 2012; Park *et al.*, 2012; Zubrowska *et al.*, 2015; Jia *et al.*, 2009).

As observed from Fig. 5 different thermoplastics have wide range of modulus and tensile strength, so one can select a particular or combination of thermoplastics (based upon compatibility) for tailor made applications.

Bio-Degradability of PLA

The reported literature highlights numerous applications of PLA, including biomedical, compostable bundling (because of its bio-degradable nature). Mixed PLA with different polymers creates another debasement profile that relies upon the measure of every polymer in the mix and also mixes morphology. The degradation rate of scaffolds results of every polymer continue as before as parent polymers, however the rate and level of debasement of the mix is managed by its structure and morphology. In this way, the debasement profile of a mix can be tuned by modifying its creation and handling conditions to suit the requirements of various applications. The bio-degradation of mixes is in simulated compost conditions for 70 days of PLA with TPU at increased temperature of 58°C (Jaso *et al.*, 2015). They found that rate of decaying of PLA mixes is managed by the polymer. They report that the mixes rich in TPU demonstrate quick introductory decaying took after by a level stage, like flawless TPU, which experienced quick beginning debasement, took after by a moderate debasement and just 30% mineralization toward the finish of 70 days. Conversely, the mixes rich in PLA display an underlying slack in debasement, yet accomplish a higher level of decaying toward the end. This is like unadulterated PLA, which begins to degrade following 20 days and is totally debased before 70 days' over. The authors noted that morphology assumes a vital part in the decaying procedure in which co-constant mixes degrading at a higher rate at first contrasted with those with globular morphology.

Notwithstanding mix synthesis and stage scattering, facilitate thermal handling of mixes and the presentation of added substances can dramatically affect the rate of decaying of a mix. Enzymatic decaying of PLA/PBST mixes in Tris HCl support with Proteinase K (Malwela and Ray, 2015). They report an improved decaying rate of the mix contrasted with the individual polymers because of stage isolated morphology of the mix, inferable from immiscibility of PLA and PBST. Strengthening the PLA/PBST films at 70°C decelerates the decaying rate because of the expanded crystallinity of the PBST stage and is additionally diminished by option of nano-clay fillers which upgrades the crystallinity of PBST. Debasement is much more drastically decelerated when the movies are strengthened at 120°C and soon there-after the crystallinity of the PLA stage is improved. This is additionally articulated by the option of nano-clay. Decaying of PLA under anatomical conditions for bio-medical applications is all around prove and has been widely announced and assessed (Saini *et al.*, 2016; Shasteen and Choy, 2011; Tsuji, 2005). An essential plan thought to accomplish ideal execution in-vivo for the finished result is to keep up the debasement of PLA mixes inside the anatomical imperatives, while tuning the decaying profile for particular biomedical applications, similar to tranquilize conveyance and platforms. Tuning the mix piece changes the rate of decayed, as well as adjusts the example to enable the material to degrade in an unpredictable manner. This can be especially useful to configuration discharge profiles for medicate conveyance applications and compatibilize scaffolds/implants decaying to tissue recuperation in tissue building or implants/transplant applications (Vieira *et al.*, 2015; Cai *et al.*, 2002; Kim *et al.*, 2005). PLA mixes with at least one polymer or co-polymers can yield complex degradation designs, which may not be conceivable on account of co-polymers alone, as PLGA, which, in spite of having a digressed decaying profile from source polymers, experience a foreordained decaying profile. For example, Zhu *et al.* (2015) built up a tissue designing platform utilizing a mix of PLA, PEG and a PLA-PEG co-polymer which demonstrate an underlying quick misfortune in reenacted physiological conditions, trailed by a moderate degradation at-least 100 h. This is speedier than the degradation for a flawless PLA platform indicating altogether slower degradation at-least 200 h. The creators likewise contrasted the degradation design with a PLA/PEG double which demonstrates an underlying quick degradation rate because of PEG disintegration took after by the degrading rate like pure PLA. Antimicrobial films fabricated from chitosan/starch/PLA mix by film extrusion utilizing a TSE. Starch gives hydro-philicity to the mix to encourage dissemination of water and starting burst arrival of chitosan, while the moderate degradation rate of PLA keeps up maintained discharge over a more extended time (Bie *et al.*, 2013). Another way to deal with plan bio-degradable films of PLA mixes with thermo-plastic starch and PBAT utilizing blown-film extrusion process. PLA, in these mixes, adds to the improvement of the modulus, quality and hindrance properties of the films, however it diminishes transparency and tensile properties as-like break elongation at more weight percentage (Shirai *et al.*, 2013b).

Fabrication of Bio-Compatible 3D Printed Scaffolds – A Case Study

This case study was conducted in manufacturing research lab (Production Engineering) at Guru Nanak Dev Engineering College, Ludhiana, India (Singh and Ranjan, 2017). An effort has been made to build 3D scaffolds on FDM by using in-house developed bio-compatible FDM wire (Ø 1.50–1.75 mm) by mixing of PVC, PP, and HAp. During pilot experimentation, an effort has been made to prepare the feed stock filament of biocompatible grade of PVC and PP in the ratio of 70:30 (by weight). The first step was to check the possibility of preparation of feed stock filament of PVC and PP, which is reinforced with HAp with varying

input parameters. Taking random selection of different composition/proportions of polymer materials, the best parametric condition or range of parametric condition was established for TSE. Table 3 shows list of input parameters and their levels for the experimental study.

Based upon Tables 3 and 4 shows the control log of experimentation based upon Taguchi L18 orthogonal array (O.A). After successful runs as per Table 4 output as peak Load and Young's Modulus have been recorded while tensile testing on universal testing machine.

As observed from Table 4, experimentation run No. 09 has the maximum value of peak load, as well as Young's Modulus in which parametric conditions are a combination of materials, are 96X + 4 at 50 rpm and the temperature was 200°C with the HAp grain size is 53 µm with a load applied as 20 kg. Further in experimentation run No. 13 was minimum value of peak load as well as Young's modulus in which the parametric conditions are combination of materials are 92X + 8 at 40 rpm and temperature was 190°C with 150 µm of HAp grain size and load applied was 10 kg.

After establishing mechanical properties the finally prepared feed stock filament at best settings were investigated for thermal properties on differential scanning calorimetry (DSC) setup. The sample filament wire prepared for experiment run 9 and 13 were subjected to DSC analysis. For thermal analysis METTLER TOLEDO, Model DSC3, Swiss make with (SW 14.00) software was used in N₂ gas environment. Figs. 6 and 7 shows the thermal analysis of feed stock filament run 9 (with better mechanical properties) and run 13 (with poor mechanical properties) respectively. As shown in Fig. 6, for thermal analysis 2 heating-cooling cycles are involved. In first cycle, initially heat the sample with comparison to reference from 30°C to 220°C at the rate of 10 K/min, after that in the presence of N₂ gas (flow rate is 50.0 ml/min) cooling process is done in which matter was cooled from 220°C to 30°C at the rate of 10 K/min. After that in the second cycle, same process was repeated. The maximum temperature is taken 220°C because of the material was burnt near 230°C and lower temperature is generally taken as near to room temperature. Fig. 7 shows thermal analysis of sample wire run-13. While comparing Figs. 6 and 7 it has been observed that melting point temperature (T_m) of run-9 was 160.29°C and for run-13 was 156.61°C and solidification temperature at 116.45°C in the first case and 114.63°C in second

Table 3 Parameter selected for experimentation

A	B	C	D	E
Composition of materials (in weight percentage) (Polymer + HAp)	Rotational speed (rpm)	Temperature (°C)	Grain size of HAp (µm)	Load (Kg)
96X + 4	30	180	53	10
92X + 8	40	190	106	15
–	50	200	150	20

Note: Singh, R., Ranjan, N., 2017. Experimental investigations for preparation of biocompatible feedstock filament of fused deposition modeling (FDM) using twin screw extrusion process. Journal of Thermoplastic Composite Materials, p. 0892705717738297. doi:10.1177/0892705717738297.

Note: X-70% of PVC and 30% of PP.

Table 4 Control Log of experimentation

S No.	A	B	C	D	E	Peak Load (N)	Young's Modulus (N/m ²)
	Composition of materials (Polymer + HAp)	Rotational speed (rpm)	Temperature (°C)	Grain size of HAp (µm)	Load (Kg)		
1	96X + 4	30	180	53	10	23.00	198.68
2	96X + 4	30	190	106	15	22.16	187.54
3	96X + 4	30	200	150	20	20.50	160.37
4	96X + 4	40	180	53	15	18.60	145.21
5	96X + 4	40	190	106	20	15.20	131.42
6	96X + 4	40	200	150	10	23.50	202.88
7	96X + 4	50	180	106	10	23.52	211.29
8	96X + 4	50	190	150	15	21.28	187.94
9	96X + 4	50	200	53	20	26.52	223.27
10	92X + 8	30	180	150	20	17.10	135.55
11	92X + 8	30	190	53	10	19.87	157.59
12	92X + 8	30	200	106	15	18.60	146.38
13	92X + 8	40	180	106	20	11.70	90.21
14	92X + 8	40	190	150	10	15.98	121.21
15	92X + 8	40	200	53	15	14.20	111.37
16	92X + 8	50	180	150	15	17.10	136.57
17	92X + 8	50	190	53	20	16.10	128.64
18	92X + 8	50	200	106	10	20.12	161.37

case. Further it should be noted that the heat capacity (which is difference of heat input and released) for sample prepared at run-9 has dramatically increased after second repetition of heating-cooling cycle as compared to sample prepared at run-13, which justifies the use of parametric settings suggested for run-9 (as per Table 3).

The SEM analysis was conducted on the fractured surfaces of the samples (feed-stock filament of FDM wire). The micro-photographs suggest that the feed-stock filament have uniformly fibrous and open porous structure (see Fig. 8), which are sufficiently good for growth of cells and are suitable in bio-medical application. The porous structure of an implant provides channels for bone ingrowth. Porous materials have been introduced to obtain biological fixation and improve longevity of

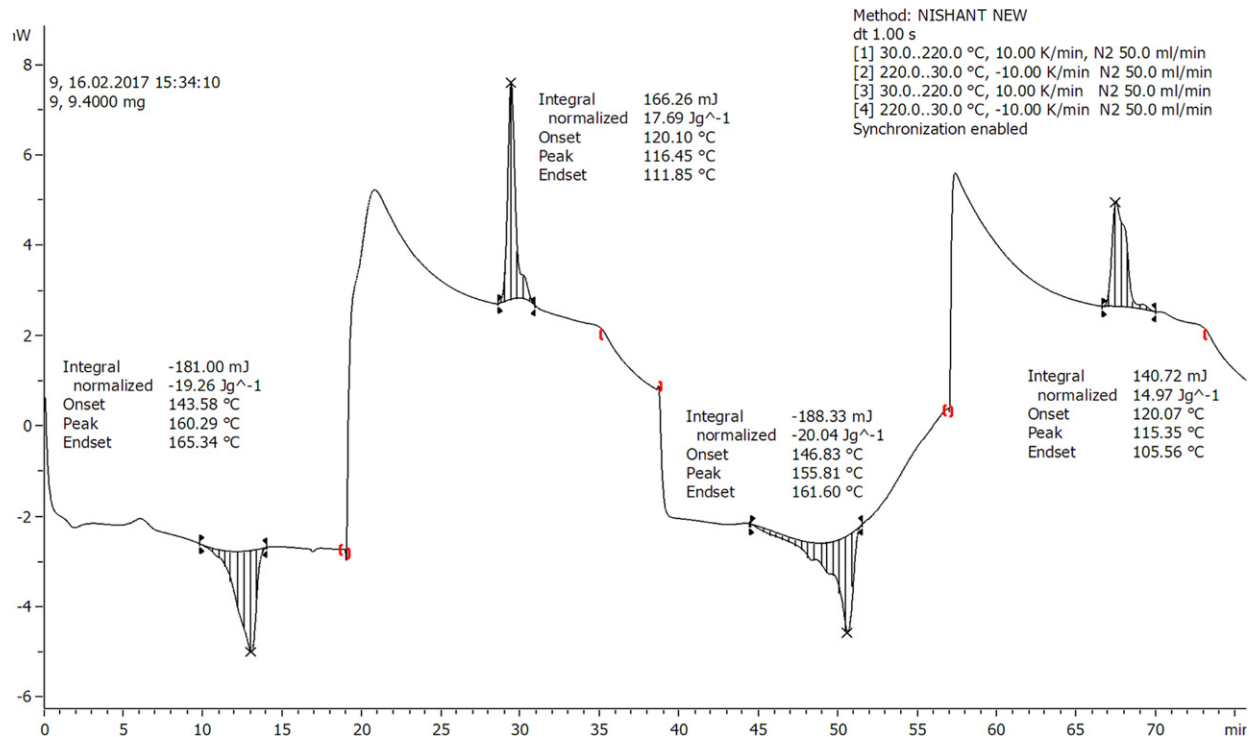


Fig. 6 Thermograph of best feed stock filament according to mechanical properties (as per Table 4, run-9).

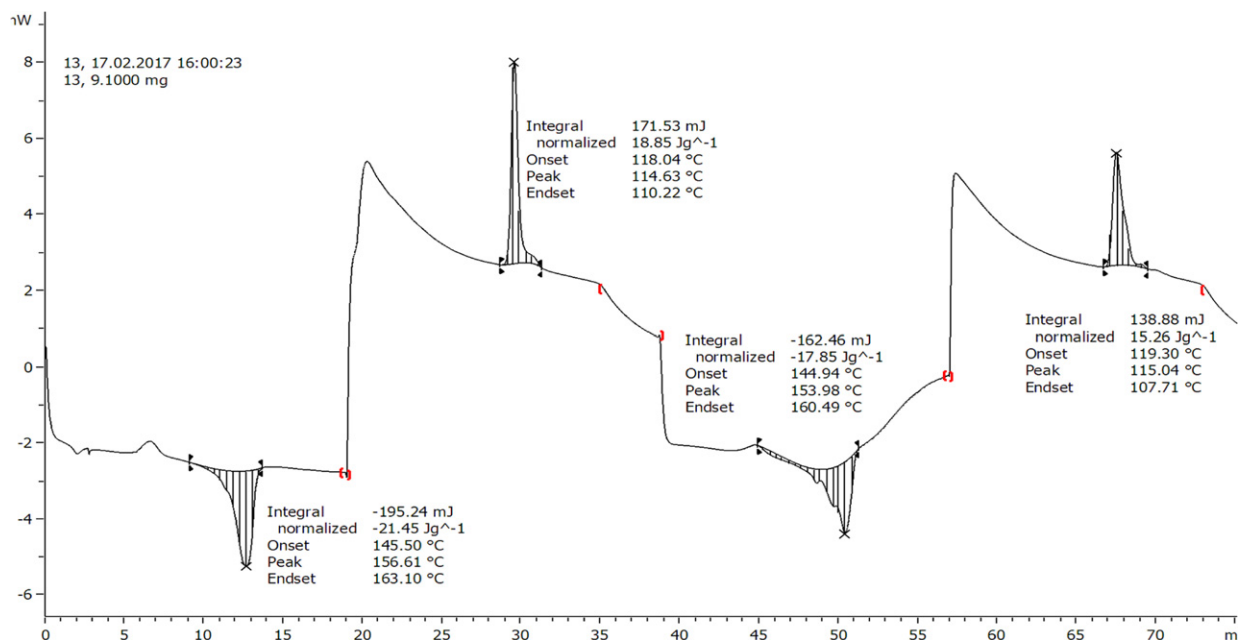


Fig. 7 Thermograph of poorest feedstock filament according to mechanical properties (as per Table 4, run-13).

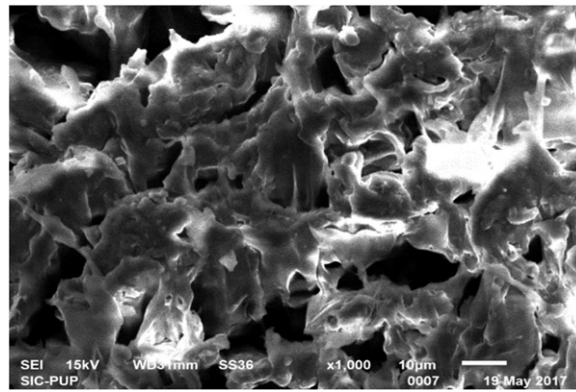


Fig. 8 Microphotographs of the biocompatible feed stock filament taken on SEM.

orthopedic implants. Due to several clinically important disadvantages of dense biomaterials (metallic/polymeric), such as a high value of elasticity modulus, the fabrication of porous structures by powder metallurgy, foaming technologies, as well as AM methods have been widely developed in the last decades to overcome the limitations. In addition, porosity enhances the biological interlock between implant and bone.

Conclusions

In this article a case study for 3D printing of bio-compatible thermoplastic blended with HAp and CS has been presented. The composite based feed stock filament for FDM has been successfully prepared by using TSE. Following are the conclusions from this study:

- The biocompatible polymeric composites comprising of PVC-PP-HAp were prepared successfully with TSE in form of feed stock filament. The filament so prepared is ready to be used on commercial FDM setup without any change in any hardware/software of the system.
- For better understanding mechanical and thermal properties of PVC, PP with HAp reinforcement thermal analysis has been reported. It has been observed that polymeric composite material with composition/proportion as 96% polymer matrix (comprising of 70% of PVC and 30% of PP) and filler (HAp) as 4% (with grain size 53 μm) at 200°C processing temperature and rotational speed of 50 rpm with load applied of 20 kg on TSE are the best parametric conditions observed in this case study (from thermal stability and mechanical properties view point).
- Based upon SEM analysis it has been ascertained that the specimens/functional prototype prepared are structurally good and suitable for repair/regeneration of bone/fractured bone because the internal structure of the sample is fibrous, open and porous.

Acknowledgment

The authors are highly thankful to DST (SERB, Science and Engineering Research Board), Government of India, File. No. SERB/F/3572/2015–2016 and Institution of Engineers (India), File No. R.6/2/DR/2017–18/RDDR2017010 for financial support.

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Characterization and Interface of Natural and Synthetic Hybrid Composites

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Introduction

The trend of renewed interest in natural materials has increased tremendously as researchers and scientists have focused on utilizing the natural materials for replacing the existing synthetic materials. The reason behind this phenomenon is due to ecological concern; the recyclability and environmental safety are becoming crucial for the introduction of new materials and products. Currently, researchers are moving towards combining natural and synthetic material. This is due to the fact that utilization of natural fiber based lignocellulose can be considered as interesting. Natural fibers such as kenaf, jute flax, hemp, oil empty fruit bunch (EFB), sisal, and sugar palm have shown economic and ecological advantages over synthetic fibers. The inferior properties of natural fiber such as physical, mechanical, and thermal properties have motivated a number of industrial sectors especially in the automotive sector to use these fibers as potential candidates in environmentally safe products.

Natural fibers could replace synthetic fibers in various applications. They are renewable, abundant, cheap, recyclable, and biodegradable, and have lower density and are less environmentally harmful compared with synthetic fiber. Nevertheless, the challenges of using these natural fibers, such as high water uptake and low mechanical properties as compared with synthetic fiber, limit its applications. To overcome this problem, many researchers have approached surface modification of fiber (Masudul Hassan and Wagner, 2016). Based on the studies shown, the treatment of fiber diminishes the water uptake and leads to high mechanical properties. Moreover, some researchers have studied the combination of synthetic and natural fiber to improve the performance of the composites. In this paper, the previous research on hybrid composites properties and method to improve the interfacial control between the fiber and matrix through experimental and morphology is discussed.

Hybrid Composites

The incorporation of natural fibers such as kenaf, sisal, jute, flax, and sugar palm fiber with synthetic fiber has gained increasing applications in many areas of technology and engineering. Hybridization of natural fiber with stronger and more corrosion resistant synthetic fiber such as carbon fiber can also enhance the stiffness, strength, as well as moisture resistant properties of the hybrid composites. Hybrid composites that contain two or more types of different fibers could complement what is lacking in the other properties. As a consequence, a balance in the performance of the hybrid composites could be achieved.

Mechanical Properties of Hybrid Thermoplastic Composites

It is well known that the composite properties highly depend on the individual reinforcements like the type of fiber, fiber architecture, and chemical composition of fiber, type of matrix, and fiber–matrix adhesion. Studies on the hybrid thermoplastic composites were carried out with both the natural fiber and synthetic fibers in the short and randomly oriented form (SFRP) and long fiber and mat form as preregs (LFRP).

Short and randomly oriented form composites

The SFRP composite consists of short and randomly oriented fiber reinforcements within the thermoplastic matrix. The chopped fibers are usually taken in a fixed proportion and mixed with thermoplastic resin (in the form of pellets) in a melt mixer to obtain the fiber/matrix mixture. The fiber/matrix mixture gets collected as chunks at the end of the mixing process. These can be used directly or further crushed into small pieces and fabricated using different techniques like hot press molding, pultrusion, and injection molding to form the composite.

Works on the SFRP composites were easy to find and have been studied widely by researchers with different fibers and various thermoplastic resins. This is due to their simplicity in production, cost saving in terms of fabric production, and reduced wastage of fiber due to their use in smaller size as microfibers or powder form. The most commonly identifiable hybrid composite with the short fibers constitutes two or more different fibers within a single matrix.

Increasing the overall fiber loading of jute/coir (mixed in a constant proportion at 1:1 ratio) in polypropylene (PP) matrix resulted in lower tensile strength, superior stiffness, flexural strength and modulus, and impact strength as shown in Fig. 1. Further variants were obtained by mixing jute/coir in different ratio or proportions such as 25:75, 50:50, and 75:25 in terms of fiber weight % while the overall fiber loading and matrix weight% were kept constant. Significant variation in strength and modulus were achieved as shown in Fig. 1 as a result of varying the individual fiber loading in the overall fiber loading (Siddika *et al.*, 2014).

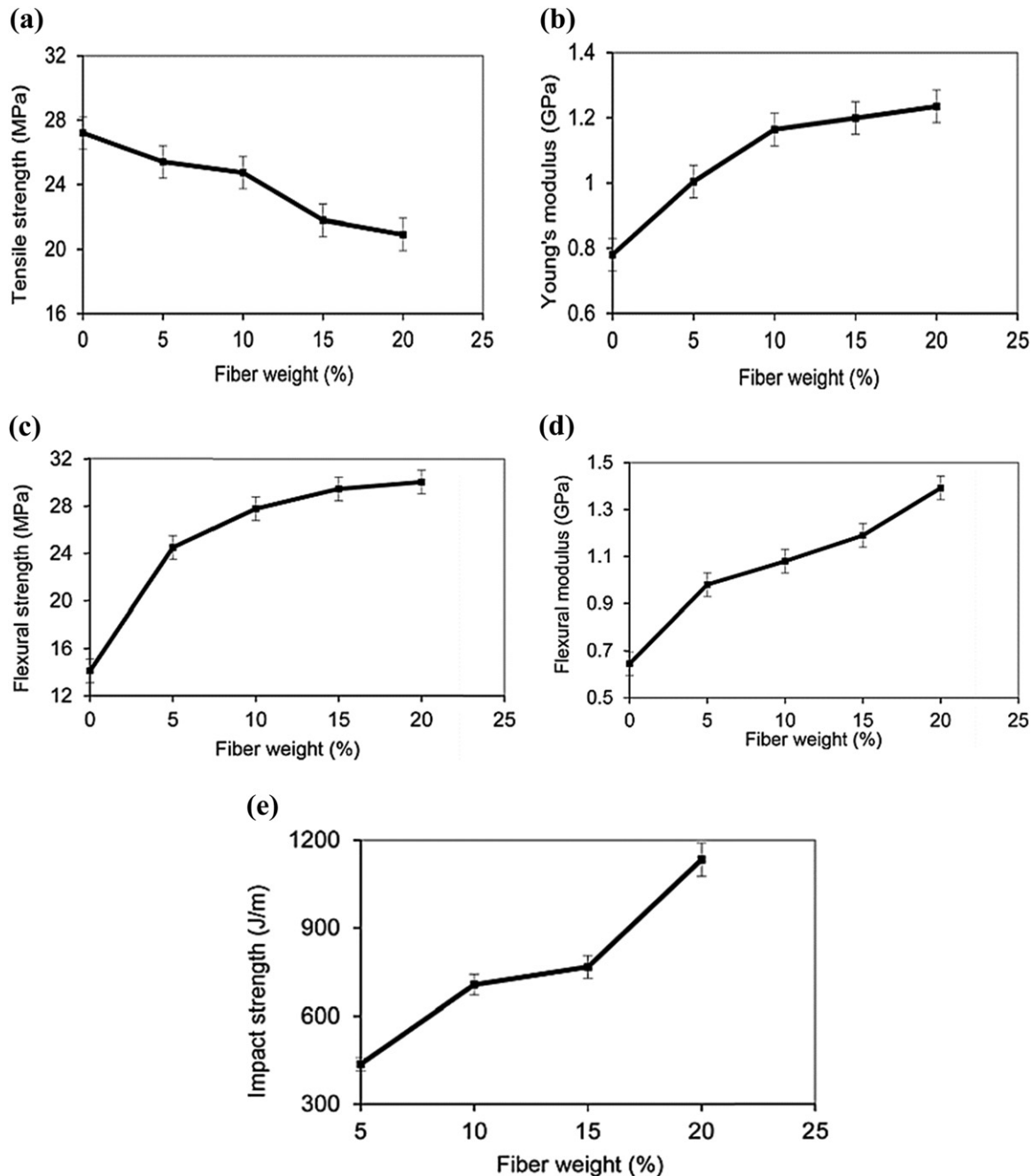


Fig. 1 Mechanical properties of jute/coir reinforced polypropylene composites. (a) Tensile strength, (b) tensile modulus, (c) flexural strength, (d) flexural modulus, (e) impact strength. Reproduced from Siddika, S., Mansura, F., Hasan, M., Hassan, A., 2014. Effect of reinforcement and chemical treatment of fiber on the properties of jute-coir fiber reinforced hybrid polypropylene composites. *Fibers and Polymers* 15 (5), 1023–1028.

Similar variation in tensile, flexural, and impact strength due to the increment of overall fiber loading of hybrid sisal/banana fibers in poly(lactic) acid (PLA) matrix was reported by [Ranjan et al. \(2013\)](#). The composites with higher fiber loading exhibited a drop in strength. According to the authors ([Ranjan et al., 2013](#)), the weak interfacial adhesion between the natural fibers and PLA matrix as evident from the micrographs of the fractured specimen (refer to [Fig. 2](#)) was the primary reason for the lower strength of the hybrid composites.

[Arifuzzaman Khan et al. \(2013\)](#) highlighted that the mechanical properties of the banana/coir/Low density poly ethylene (LDPE) composite can be modified by increasing coir content in the fiber loading. Their results showed that optimum strength and modulus under the different mechanical loads occurred at different weight% (refer to [Fig. 3](#)). For instance, 15% coir fiber weight displayed best impact strength for the hybrid composites while 10% fiber weight showed best strength and modulus under the tensile and flexural load. Similar inferences on improvement in the impact strength were highlighted by [Pérez-Fonseca et al. \(2014\)](#)

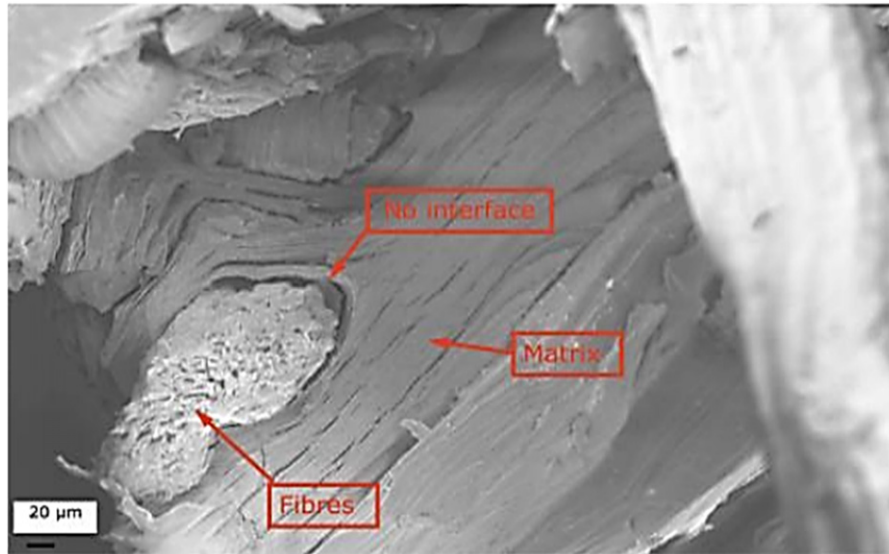


Fig. 2 Image of untreated of sisal/banana hybrid composites. Reproduced from Ranjan, R., Bajpai, P.K., Tyagi, R.K., 2013. Mechanical characterization of banana/sisal fibre reinforced PLA hybrid composites for structural application, *Engineering International* 1 (1), 39–48.

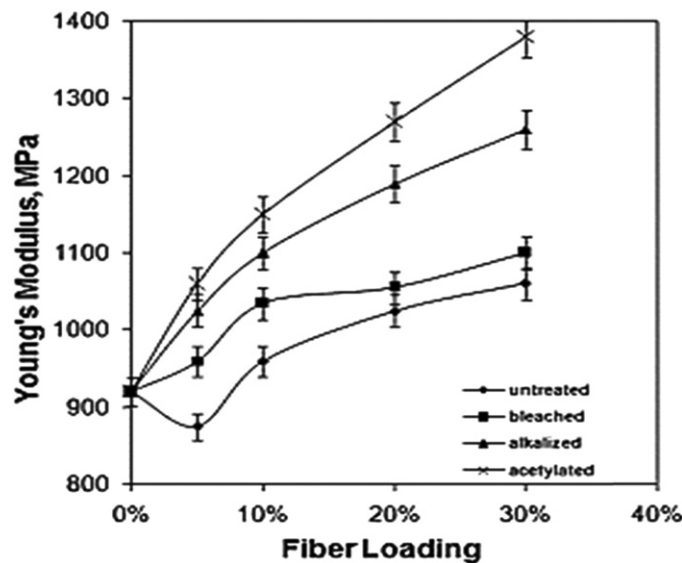


Fig. 3 Young's modulus of untreated and treated banana/coir/Low density poly ethylene composites. Reproduced from Arifuzzaman Khan, G.M., Alam Shams, M.S., Kabir, M.R., *et al.*, 2013. Influence of chemical treatment on the properties of banana stem fiber and banana stem fiber/coir hybrid fiber reinforced maleic anhydride grafted polypropylene/low-density polyethylene composites. *Journal of Applied Polymer Science* 128 (2), 1020–1029.

on increasing coir content on the agave/coir/polyethylene hybrid composites (Pérez-Fonseca *et al.*, 2016). The general theory behind the superior impact strength for hybrid composites on increasing the coir content is due to the following reasons (1) higher amount of energy required to cause fiber pull-out and breakage at larger fiber loading and (2) lignocellulosic contents and elongation at break% of the individual fibers. On the other hand, difficulty in maintaining homogenous fiber dispersion at higher fiber loading, which causes agglomeration regions within the composite was responsible for lower strength and modulus at higher fiber loading (Kakou *et al.*, 2015). These sites act as stress concentration regions on the application of load due to the higher fiber-fiber interaction. This, in turn, leads to crack initiation followed by the final failure (Hassan *et al.*, 2011).

The main drawback of using natural fibers is their inferior strength, hydrophilic nature due to the presence of lignocellulosic contents, and weak interfacial adhesion with the hydrophobic matrix. Efforts have been taken by researchers to improve the performance of hybrid composites with the natural fibers through the following ways:

- Introducing synthetic reinforcements
- Fiber treatments
- Introducing fillers or coupling agents like maleic anhydrides (MA)

Synthetic reinforcements

Ground glass and carbon fibers from the fabric were individually used as reinforcements with sisal and their fiber weight was varied in the ratios of 25:75, 50:50, and 75:25 in the PP matrix. Best mechanical properties were achieved with sisal:glass and sisal:carbon at 25:75 ratio and further increase of the sisal content only led to drop in the strength and modulus. Nearly equivalent performance under the tensile, flexural, and impact loads achieved by composite at 50:50 ratio by sisal:glass highlights that dependency on the less environment-friendly synthetic fibers can be substituted by the natural fibers (Aslan *et al.*, 2018). Ashori *et al.* (2014) introduced 10% and 15% fiber weight glass fibers in the overall 50% fiber loading of bagasse/PP and corn stalk/PP composites. Maximum strength and modulus was observed with 10% while further increase of glass fiber weight to 15% resulted in lower mechanical properties than the former. This behavior at higher fiber loading was caused by the agglomeration of glass fibers leading to lower mechanical properties. On the other hand, corn stalk/glass fibers/PP was able to perform better under mechanical loads than the former due to the higher fiber aspect ratio (fiber length/width) compared with bagasse fibers. This implies that the higher fiber aspect ratio enabled better stress transfer between the fiber and matrix, thereby imparting superior mechanical properties.

Fiber treatments

One of the important reasons for lower mechanical properties of the hybrid composites reinforced with natural fibers is their poor wettability with the hydrophobic matrix. The smoother surface of the natural fiber was modified by subjecting the fiber to different chemical treatments. The commonly used chemical treatments include mercerization with alkali, bleaching, silane, acetylation, etc. The mechanism responsible for improved fiber–matrix adhesion is unique to each chemical treatment. Alkali treatment of the fiber creates rougher fiber surface and leads to fibrillation due to the removal of hemicellulose, lignin, pectin, waxes, and other impurities. The rougher surface and fibrillation permits better mechanical interlocking with the matrix (Chandrasekar *et al.*, 2017). In case of acetylation, presence of $-\text{CH}_3$ groups in the treated fiber enables better wetting with the matrix while bleaching facilitates fibrillation in the fiber surface due to the removal of hemicellulose and lignin (Arifuzzaman Khan *et al.*, 2013).

Atiqah *et al.* (2017) showed that tensile, flexural, and impact properties of the sugar palm/glass/polyurethane composite can be improved by using the 6 wt% sodium hydroxide (NaOH), 2 wt% silane and combined NaOH–silane treated sugar palm fibers. The highest improvement in properties was observed for the combined treatment. This is due to the fact that NaOH treatment creates rough fiber surface while the silane treatment creates silanol groups, which bond with the hydroxyl group of the fiber and lead to stronger fiber–matrix interface (Goriparthi *et al.*, 2012). However, the fiber treatments have limitations too. The improvement in mechanical properties was dependent on the fiber treatment conditions like chemical concentration and immersion time. Jute/coir/PP composites demonstrated better strength and modulus when reinforced with 5% NaOH treated fibers while inferior strength and modulus at 10% NaOH for the same immersion time. The inferior behavior at greater chemical concentration is due to higher degree of fibrillation caused by the excess removal of hemicellulose, lignin, etc. (Siddika *et al.*, 2014). In this case, fibers become brittle, weaker, and ineffective in stress transfer causing premature failure at lower loads. Another advantage of using treated fibers in the composite is their reduced water uptake and moderate loss in strength and stiffness after moisture absorption. Wood flour/wheat husk/PP hybrid composite with NaOH and benzoyl chloride treated fibers was conditioned in the water bath at room temperature for 192 h. The conditioned composites showed lower drop in strength and modulus than the composites with untreated fibers (Upadhyaya *et al.*, 2012).

Fillers

Fillers are additives added in a small quantity to the matrix for enhancing the mechanical properties of the composite. Similar to fiber treatments, the filler concentration and dispersion within the matrix governs the improvement in the properties. From the literature, it was found that MA was the most frequently used filler in the thermoplastic composites. Other than enhancing the mechanical properties, MA was also effective in restricting the water uptake and preventing composite degradation as reflected by the reduced loss in strength and modulus in comparison to the composites without fillers from their research (Pérez-Fonseca *et al.*, 2016). Fillers like aluminum hydroxide, magnesium hydroxide, hydrotalcite, and calcium sulfate dihydrate have superior thermal insulation properties and can be added to the composite to be used for the high temperature applications and materials requiring flammability resistance (Pearce, 2012).

Short and Randomly Oriented Form Composites With Thermoplastic Blends

The variants in the hybrid composites with two or more fibers in a single matrix seen in the previous section were found to have limitations such as weaker fiber–matrix compatibility, fiber agglomeration due to poor fiber dispersion at higher fiber loading and difference in the fiber aspect ratio influencing the mechanical properties. To avoid these problems, hybrid composites with two different thermoplastic blends reinforced with single fiber were proposed and their properties were explored. Table 1 represents some of the thermoplastic blend combinations used by researchers in their research.

Tensile strength was found to decrease with the increase in fiber content of the polyvinyl chloride/thermoplastic polyurethane/kenaf hybrid composite while the impact strength and modulus showed increasing trend with the fiber loading (El-Shekeil *et al.*, 2014). Teixeira *et al.* (2012) studied the influence of cassava starch content (thermoplastic starch (TPS)) in cassava bagasse/PLA/TPS with constant fiber loading. Their results indicate that tensile strength and modulus decrease with the increase in TPS content. According to

Table 1 Hybrid composites based on the thermoplastic blends from the previous studies

Composite	Fabrication method	Resin weight	Fiber weight	References
PVC/TPU/Kenaf (PVC:TPU::1:4 ratio)	Compression molding	60%–80%	20%–40%	El-Shekeil <i>et al.</i> (2014)
PP/PLA/eucalyptus wood flour	Compression molding	2% MAPP 83% PP/PLA blend	15%	Darie <i>et al.</i> (2013)
HDPE/SBR/Flax/SEBS-g-MA	Injection molding	0%–30%	0%–30%	Kakroodi <i>et al.</i> (2012)

Abbreviations: HDPE, high density poly ethylene; MAPP, maleic anhydride grafted polypropylene; PLA, poly(lactic) acid; PP, polypropylene; PVC, polyvinyl chloride; SBR, styrene butadiene rubber; SEBS-g-MA, maleic anhydride grafted styrene-ethylene/butylene-styrene; TPU, thermoplastic polyurethane.

Darie *et al.* (2013) using the modified eucalyptus wood flour with the toluene-2,4-diisocyanate in the PP/maleic anhydride grafted polypropylene/PLA blend resulted in superior tensile strength, stiffness, and impact strength. Hybrid composite with the treated fibers showed greater resistance to accelerated weathering conditions as displayed by moderate loss in strength and stiffness in comparison to the hybrid composite with the untreated fibers. Kakroodi *et al.* (2012) fabricated the flax/high density poly ethylene/styrene butadiene rubber (SBR) with and without the styrene and ethylene/butylene with styrene content of 30% and 2% MA (maleic anhydride grafted styrene-ethylene/butylene-styrene). Optimum strength and modulus was achieved for the hybrid composite having 15 wt% of both the flax and SBR. Use of coupling agent helped the hybrid composites to have superior properties over the composites without coupling agent. Similar improvements in the tensile strength and modulus were reported by Majid *et al.* (2010) on the use of PE-g-MA coupling with the kenaf/LDPE/thermoplastic sago starch composite.

The SFRP composites are less desirable for high-performance applications. This is where the LFRP composites are preferred over the SFRP composite due to their high strength and stiffness characteristic. LFRP composites are also said to have higher impact strength due to their fiber structure, which requires higher energy to cause failure in the form of fiber pull-out after the impact (Dan-Mallam *et al.*, 2014).

Long Fiber and Mat Form as Prepregs Composites

LFRP composite are basically made of prepregs. Initially, the thermoplastic pellets were melted under temperature and pressure in a mold into thin sheets or films. Then, the sheets are placed on top and bottom of the fabric followed by pressing or melting with the temperature and pressure to form the prepregs. Two or more layers of such prepreg with different fabric reinforcements can be cured to form the LFRP composite. The advantages of using LFRP include superior mechanical properties due to the use of long fibers or fabric form.

Karaduman *et al.* (2015) studied the effect of stacking sequence of woven flax (W) and nonwoven jute (N) in PP matrix fabricated by the hot press molding. The hybrid composite WNNW with woven flax on the outer layer and jute as inner core displayed higher strength and modulus while the NWWN configuration exhibited maximum impact strength. Incorporation of 10 wt% glass fiber in the jute/PP (twisted yarn and untwisted yarn) yielded improvement in the tensile and flexural properties (Uawongsuwan *et al.*, 2015).

Dan-Mallam *et al.* (2014) fabricated hybrid composite with the kenaf/polyethylene terephthalate fiber based fabric prepreg in the woven interply and interwoven ply configurations. Interwoven hybrid composites outperformed woven interply hybrid composite in terms of the tensile and impact strength while the latter was found to possess greater flexural strength than the former. Polycopalactone (PCL) was blended with the PLA matrix and the PCL/PLA mixture along with unidirectional stitched jute fabric (Goriparthi *et al.*, 2012). Increasing PCL weight% led to improvement in toughness of the hybrid composite on the expense of tensile strength and modulus. Lower tensile properties on increasing the PCL content were attributed to the poor compatibility with the matrix and their inferior stiffness characteristic.

Many researchers have improved the interface adhesion by reducing the moisture absorption properties through fiber modification of the fiber. Nevertheless, to control the interface between fiber and matrix, layering sequence of the fibers is also important. Stacking of the woven fiber in the middle caused high bending stiffness that leads to larger delamination of composites. The method of fabrication and fiber treatment can influence the interfacial adhesion of matrix and fiber.

Mechanical Properties of Thermoset Hybrid Composites

In a thermoset polymer all the molecules are chemically joined by using cross-links, forming a rigid, three-dimensional network structure. As soon as the cross-links are combined during the curing reaction, the thermoset polymer cannot be melted by applying heat. Nevertheless, if the number of cross-links is lower, it could be possible to soften them at higher temperatures.

The main consideration when selecting a matrix is the basic mechanical properties. High tensile modulus, high tensile strength, and high fracture strength are the most desirable properties of the matrix for producing high-performance composites. All these properties influence the compressive strength, intraply cracking, ply delamination, and crack growth of their respective composites. Thermoset polymers (also known as resins) were traditionally used as fiber-reinforced composite matrix material. The starting materials used to polymerize a thermoset polymer are usually liquid chemicals with a low molecular weight and very low viscosity. Fibers are immersed in these chemicals before the polymerization begins. Furthermore, the viscosity of the polymer is lower at the

Table 2 Hybrid composites based on the thermoset blends from previous studies

Type of fiber and reinforcement	Matrix	Specification	References
Chopped PALF/KF	Phenolic	35% PALF/15% KF, 25% PALF/25% KF, and 15% PALF/35% KF	Asim <i>et al.</i> (2018)
Short banana/sisal	Polyester	Banana/sisal/banana, sisal/banana/sisal, bilayer, intimate mix	Idicula <i>et al.</i> (2005)
Cross-plyed jute fibers and banana fiber	Epoxy	100/0, 75/25, 50/50, 25/75, and 0/100	Boopalan <i>et al.</i> (2013)
Kenaf/jute and kenaf/hemp	Epoxy	Woven kenaf/kenaf, woven jute/jute, woven hemp/hemp, interwoven kenaf/jute, and interwoven kenaf/hemp	Maslinda <i>et al.</i> (2017)
Short banana (B)/coconut sheath (C)	Polyester	CBC, CCB, BCB, BBC, and pure fiber composites; overall fiber loading = 50 wt%	Kumar <i>et al.</i> (2016)
Short sisal (S)/coconut sheath (C)	Polyester	CSC, CCS, SCS, SSC, and pure fiber composites; overall fiber loading = 50 wt%	Kumar <i>et al.</i> (2014)
Banana/jute; fiber length 10 mm	Polyester	The fiber volume fractions were 5%, 10%, 15%, 20%, and 25% maintaining the banana/jute volume in 1:1	Adhikari and Gowda (2017)
Oil palm EFB/KF; mat type	Epoxy	EFB and KF were 4:1, 1:1 and 1:4	Hanan <i>et al.</i> (2018)
Jute/hemp/flax; mat type	Epoxy	Jute/epoxy, hemp/epoxy, flax/epoxy, jute/hemp/epoxy, and hemp/flax/epoxy, jute/hemp/flax/epoxy; overall fiber loading 25 wt%	Chaudhary <i>et al.</i> (2018)
E-glass/kevlar/carbon; woven and knitted	Epoxy	14 stacking sequences; overall fiber loading 45 wt%	Ashraf <i>et al.</i> (2017)

Abbreviations: EFB, empty fruit bunch; KF, kenaf fiber; PALF, pineapple leaf fiber.

time of fiber immersion and can easily be wetted between the fibers and the matrix without the help of either high temperature or pressure. Thermoset polymers are highly thermal and chemical resistant. In addition, these polymers show lower creep and stress relaxation compared with the thermoplastic matrix. Hence, the thermoset matrix has been widely used to produce high-performance polymer matrix composites. Some important works on the thermoset based composites were tabulated in [Table 2](#). The thermoset matrix is reinforced by combining various natural fibers (sisal, banana, pineapple leaf, etc.) or by combining more synthetic fiber (glass, kevlar, carbon, etc.) or combining both natural and synthetic fibers. This section focuses the mechanical properties of hybrid composites made by natural–natural, natural–synthetic, and synthetic–synthetic fibers.

Natural–Natural

The influence of fiber loading on mechanical properties of chopped pineapple leaf fiber (PALF) and kenaf fiber (KF)/phenolic (PF) matrix composites was studied by [Asim *et al.* \(2018\)](#). The PALF/PF, KF/PF, and PALF/KF/PF composites were made by hot press molding technique and the fibers were controlled for 50% by weight in all composites. Various types of hybrid combinations were 35% PALF/15% KF, 25% PALF/25% KF, and 15% PALF/35% KF. Their analysis revealed that the addition of KF with PALF improved the mechanical properties. Among the composites, pure KF/PF composites showed the highest tensile and flexural strengths due to the good bonding and better compatibility between KF and PF. According to the fiber bundle theory, strong fiber (KF) can withstand higher loads and it holds the weaker fiber (PALF) and the matrix (PF). Hence the 15% PALF/35% KF exhibited higher tensile strain than the other types of composites. In case of impact properties, fiber content of PALF influenced the property. Hence the pure PALF/PF composites showed the highest value of impact resistance (7.05 kJ/m²) and energy absorption (63%). Among the hybrids, 35% PALF/15% KF composites exhibited the maximum impact properties. It was attributed to the higher aspect ratio and higher amounts of cellulose contents in PALF. Similar tensile and impact results were reported in [Masudul Hassan and Wagner \(2016\)](#), [Siddika *et al.* \(2014\)](#), [Ranjan *et al.* \(2013\)](#) and [Arifuzzaman Khan *et al.* \(2013\)](#).

[Adhikari and Gowda \(2017\)](#) analyzed the mechanical properties of banana/jute hybrid polyester composites fabricated by compression molding technique with controlled fiber volume fractions from 5% to 25% (increased by 5%), maintaining a 1:1 ratio; whereas the fiber length was maintained to 10 mm. Maximum tensile and flexural strengths were reached at 15% volume fraction at 25.21 MPa and 182.34 MPa respectively. But the impact strength was increased with increasing the fiber volume fractions until the maximum fiber volume fractions (until 25 wt%). Their respective impact strength was around 25 J/m.

For plant-based fiber composites, however, there is a limited interaction between hydrophilic fibers and matrix, which is usually hydrophobic. This leads to poor interface bonding that limits mechanical performance and low moisture resistance that affects long-term properties ([Pickering *et al.*, 2016](#)). Insufficient fiber wetting results in interface defects that can act as concentrations of stress ([Chen *et al.*, 2006](#)). It has been shown that fiber wettability affects the toughness, tensile strength, and flexural strength of composites ([Wu and Dzenis, 2006](#)). Chemical treatment can improve fiber wettability and thus improve the interfacial strength. Alkali, acetyl, silane, and maleated anhydride grafted coupling agent are the most popular, but enzyme treatment is becoming increasingly popular with particular environmental friendliness benefits ([Faruk *et al.*, 2014](#)). To improve the mechanical properties of the composites, PALF/KF fibers were silane treated (2% for 3 h) and the composites were analyzed for mechanical properties ([Asim *et al.*, 2017](#)). Due to the chemical treatment, the flexural and impact properties of hybrids were improved and the tensile strength declined when

increasing the fiber content of PALF in comparison to untreated hybrid composites. The treated PALF has effectively improved the mechanical strength such as flexural strength, modulus, impact strength, and energy absorption whereas the KF was helped to improve the tensile properties. The improvements after the silane treatment were attributed to the removal of lignin and hemicellulose from the surface of the fiber. Similar chemical treatments were reported in Maslinda *et al.* (2017), Kumar *et al.* (2014) and Narendar *et al.* (2016).

The properties of the composites are also affected by the so-called fiber architecture. Fiber architecture implies the use of fibers in various forms as unidirectional, woven structures, chopped strand mat, and 3D random arrangement.

Hanan *et al.* (2018) fabricated bilayer hybrid epoxy composites reinforced by oil palm EFB mat and nonwoven KF mat by hot press molding at 120°C. The different weight ratios of oil palm EFB and KF were 4:1, 1:1, and 1:4 and overall fiber loading was maintained 50% by weight in all the composites. Results showed that the tensile strength and the flexural strengths were more influenced by the addition of KF than the addition of oil palm EFB in hybrid composites. Further, the hybrid composites possessed higher tensile strength than the pure fiber composites (oil palm EFB and KF). Hence they concluded that strong fiber could be used as a skin layer for producing higher tensile properties. Further, the pure EFB composites exhibited lower tensile strength and flexural strength. It was attributed to interlaced EFB fiber bundles. According to Jawaid *et al.* (2013) due to the chemical composition of EFB (cellulose, hemicellulose, and lignin) and cell wall architecture, the oil palm composites exhibited higher impact strength. Chaudhary *et al.* (2018) also studied the mechanical properties of jute/hemp/flax hybrid epoxy composites. Amongst the studied configurations, the jute/hemp/flax/epoxy hybrid composites exhibited the highest tensile (58.59 MPa) and impact strength (10.19 kJ/m²). Jute/hemp/epoxy hybrid composites exhibited the highest flexural strength (86.6 MPa). All components, such as fiber and matrix, could act as a single unit against the flexural load, which in turn results from strong interfacial adhesion of the fiber/matrix interphase.

Natural fibers, however, have some disadvantages that limit their actual application, such as larger scatter in their properties, moisture absorption, and lower thermal stability (Di Landro and Lorenzi, 2009). The researchers, therefore, hybridize synthetic fibers with natural fibers to obtain higher strength and modulus.

Natural–Synthetic

Ahmad *et al.* (2018) analyzed the influence of moisture degradation on the mechanical properties of hybrid composites. These composites were fabricated by using different fibers, such as woven hemp (HH), woven PET (PP), and interwoven hemp/PET hybrid (HP). The HP composites exhibited higher tensile and flexural strengths in dry and wet conditions compared with HH and PP. The higher tensile strength of HP composites was due to orientating high strength fiber (hemp) along the fiber loading direction, whereas the flexural strength was found to be higher due to the type of fiber used (hemp or PET) in the warp and weft directions. Similar types of works were reported by Alavudeen *et al.* (2015) for kenaf/banana (mat form) polyester hybrid composites, whereas the mechanical properties were influenced by the direction of warp- and weft-oriented fibers.

Maslinda *et al.* (2017) also studied the effect of water absorption for interwoven kenaf/jute and kenaf/hemp hybrid epoxy composites and made by infusion technique. The different types of composites were woven kenaf/kenaf (KK), woven jute/jute (JJ), woven hemp/hemp (HH), interwoven kenaf/jute (KJ), and interwoven kenaf/hemp (KH). The interlocking structure between the fiber yarns obtained greater stress absorption of the interwoven hybrid composites; hence the interwoven hybrids need a greater load to break. Further, as a result of water absorption (in longer periods) it reduced the strength and modulus of the composites. However, due to a breakdown of the cellulose structure, the failure strain increased with increasing immersion time.

Raffia/glass/epoxy laminated hybrid composites were fabricated by compression molding technique and the effect of NaOH treatment of raffia fibers on flexural and Iosipescu shear properties was studied (Ouarhim *et al.*, 2018). The hybrid samples encompass three layers. The face sheets were fabricated of 1-mm-thick glass fibers, and the core includes treated or untreated raffia fibers of a thickness 2 mm. The proportion of raffia fibers was maintained higher than the glass fibers in all composites. The pure glass fiber composites gave higher flexural modulus (4 GPa) than the hybrid composites due to their intrinsic properties. However, the treated hybrid composites exhibited higher flexural modulus (3.6 GPa) than the untreated hybrid composites (3.4 GPa). The improvement was attributed to (1) the high load was effectively transmitted from fibers to the matrix during the loading conditions and (2) treated fibers allowed a higher amount of resin penetration, which helped to improve the fiber to matrix bonding and also prevented the detachment of fibers from the matrix.

Iosipescu shear test was used to understand the shear behavior of both isotropic and anisotropic solids, including (1) metals, (2) polymers, and (3) randomly fiber oriented composites. The results of Iosipescu shear stresses followed the same pattern as the flexural modulus of composites, in which addition of glass fiber with raffia fiber had the ability to produce higher shear strength (407.7 MPa) than the pure raffia fiber composites (109.4 MPa). As expected the treated hybrid composites exhibited higher shear strength (600.6 MPa) than the untreated hybrid composites (407.7 MPa).

Natural fibers have many advantages over synthetic fibers, such as reduced health risks, biodegradability and positive environmental impacts, etc. However, the natural fibers have several limitations such as lower tensile strength and they begin to degrade when the temperature exceeds 200°C. The degradation will lead to odor, volatile release, decoloration, and mechanical properties deterioration. The synthetic fiber possesses high tensile strength, high chemical resistance, excellent insulation properties, low cost (e.g., glass fiber), etc. Hence, the researchers hybridized by combining synthetic fibers together to produce higher strengths than the

Table 3 Stacking sequence of composites

Sl. No.	Notation used	Layering sequence
1.	WG ₂ /KG ₂ /WG ₂	WG/WG/KG/KG/WG/WG
2.	WK ₂ /KK ₂ /WK ₂	WK/WK/KK/KK/WK/WK
3.	WG ₂ /KK ₂ /WG ₂	WG/WG/KK/KK/WG/WG
4.	WK ₂ /KG ₂ /WK ₂	WK/WK/KG/KG/WG/WG
5.	WG ₂ /KK ₂ /KG ₂ /WG ₂	WG/KK/KK/KG/KG/WG
6.	WK ₂ /KK ₂ /KG ₂ /WK ₂	WK/KK/KK/KG/KG/WK
7.	WG ₂ /KK ₂ /WG ₂	WG/KK/KK/KK/KK/WG
8.	WK ₂ /KG ₂ /WK ₂	WK/KG/KG/KG/KG/WK
9.	WG ₂ /KG ₂ /WG ₂	WG/KG/KG/KG/KG/WG
10.	WK ₂ /KK ₂ /WK ₂	WK/KK/KK/KK/KK/WK
11.	KK ₂ /KG ₂ /KK ₂	KK/KK/KG/KG/KK/KK
12.	KG ₂ /KK ₂ /KG ₂	KG/KG/KK/KK/KG/KG
13.	WK ₂ /WG ₂ /WK ₂	WK/WK/WG/WG/WK/WK
14.	WG ₂ /WK ₂ /WG ₂	WG/WG/WK/WK/WG/WG

Abbreviations: KG, knitted glass; KK, knitted kevlar; WG, woven glass; WK, woven kevlar.

Note: Ashraf, W., Nawab, Y., Umair, M., Shaker, K., Karahan, M., 2017. Investigation of mechanical behavior of woven/knitted hybrid composites. *The Journal of the Textile Institute* 108 (9), 1510–1517.

natural–synthetic fiber composites. Moreover, the hybrid composites with synthetic fibers possess high strength without compromising safety requirements, for instance, aircraft and military applications, space applications, etc., whereas the use of synthetic fiber composites is unavoidable.

Synthetic–Synthetic

Ashraf *et al.* (2017) initially developed glass/kevlar fabrics (both woven and knitted) then fabricated epoxy based hybrid composites by hand lay-up technique; fiber volume fractions were controlled for 45%. Fourteen different types of stacking sequences were formulated to produce the hybrid composites (shown in Table 3). Results revealed that higher impact strength was achieved when increasing the knitted fabric percentage. But the tensile strength was found to be reduced when increasing the percentage of knitted fabric.

Increasing the kevlar fiber, on the other hand, led to an increase in impact strength. But, the tensile strength of hybrid composites was in contrast to the above, whereas the increase in knitted fabric resulted in a decrease in tensile strength. Since the knitted fabric was more crimping and interloping, the tensile strength was reduced.

In another study Bhudolia *et al.* (2018) used three different types of fibers such as E-glass (plain weave), Kevlar (twill weave), and thin carbon noncrimp fabric and fabricated epoxy based hybrid composites as shown in Fig. 4, using resin transfer molding technique.

Results revealed that increasing the high stiffness Kevlar fiber (GK₃C₄)_s resulted to produce higher flexural strength (458.76 MPa) and flexural modulus (31.56 GPa). The peak impact load of hybrid composites was determined by the total number of fabric layers. However, the increase in peak load with the increase in Kevlar fibers and the reduction of E-glass fibers was observed with the same number of fabric layers. Due to its ductile behavior, the absorbed energy was found to depend heavily on the number of glass layers. Severe fiber breakage with the increase of E-glass fibers and the reduction of Kevlar fibers was observed at the bottom of the specimen.

Mechanical Properties of Hybrid Bioresin Composites

Sustainable material systems have become inevitable due to the mounting concerns over environmental pollution. Greenhouse gas emissions, toxicity, and the depletion of petroleum resources are the major concerns of material scientists all over the world (Faruk *et al.*, 2012). In this context, the development of sustainable material systems requires the increased application of existing green materials. The existing class of materials possessing excellent environmental credentials are green composites, where biopolymers derived from bioresources are reinforced with natural fibers or fillers (Dicker *et al.*, 2014). There are several recently published research works based on green composites for different applications such as automotive (Koronis *et al.*, 2013; Oksman *et al.*, 2003), construction (Dittenber and GangaRao, 2012; Karbhari and Seible, 1999), packaging (Kumar *et al.*, 2018; Senthil Muthu Kumar *et al.*, 2018), biomedical (Sivaranjana *et al.*, 2017; Indiradevi *et al.*, 2018), etc. It is to be noted here that the aforesaid biopolymers may lack in certain characteristics like tensile and thermal properties. Hence, it becomes important to enhance the functional properties by reinforcement of fillers or fibers. Recently, natural fibers are gaining more use as reinforcement materials in biobased composites due to their wide availability, low cost, comparable strength with their synthetic counterparts, and more importantly their degradable nature. The natural fibers have relatively complicated structure with rigid cellulose surrounded by soft hemicelluloses and lignin. They are helically wound along the fiber axis, which makes them more stable and requires more load to break them (Rong *et al.*, 2001). This makes the natural fibers a favorable component in the

E-glass	E-glass	E-glass
Kevlar	E-glass	E-glass
Kevlar	Kevlar	E-glass
Kevlar	Kevlar	E-glass
Carbon	Carbon	Kevlar
Kevlar	Kevlar	Carbon
Kevlar	Kevlar	Kevlar
Kevlar	E-glass	E-glass
E-glass	E-glass	E-glass
(GK ₃ C ₄) _s	(G ₂ K ₂ C ₄) _s	E-glass
		E-glass
		(G ₄ KC ₄) _s

Fig. 4 Type of stacking sequences. Reproduced from Bhudolia, S.K., Kam, K.K., Joshi, S.C., 2018. Mechanical and vibration response of insulated hybrid composites. *Journal of Industrial Textiles* 47 (8), 1887–1907.

making of composites. Further, reinforcement of two or more fibers with the polymer matrix leads to the formation of hybrid composites. The main concept in hybrid composites is to bring the advantages of both the fibers to enhance the functional properties of the material for the targeted application. This section focuses mainly on the mechanical properties of hybrid composites with an emphasis on biobased polymers and natural fibers.

As already known, green hybrid composites are a combination of a biopolymer or resin derived from different biological resources and two or more natural fibers reinforced with the resin. There are many biopolymers that exist. And the commonly used biopolymers in composites are PLA, polyhydroxybutyrate, starch, cellulose, and so on. Similarly, there are many natural fibers such as kenaf, bamboo, flax, sisal, hemp, jute, etc. used as reinforcements in composite materials (Shogren *et al.*, 2004; Staiger and Tucker, 2008).

The properties of the composites are mostly influenced by the physical properties of both the matrix and the reinforcing fiber. The physical properties include fiber dimensions, strength, and structure. In this direction, many researchers have worked on the hybridization and studied the effect of hybridization on the mechanical properties (Aji *et al.*, 2013; Idicula *et al.*, 2010). Green hybrid composites were prepared using PLA as matrix and kenaf, bamboo, and coir fibers by Yusoff *et al.* (2016) They prepared three different stacking designs such as bamboo-coir/PLA, kenaf-coir/PLA, and kenaf-bamboo-coir/PLA with constant weight percentages of fiber to matrix and studied their mechanical properties. The kenaf-bamboo-coir/PLA hybrid composites possessed the highest tensile strength and modulus of 187 MPa and 7.5 GPa respectively. The lowest tensile strength of 105 MPa was exhibited by kenaf-coir/PLA hybrid composites, but it produced a tensile modulus of 7.3 GPa, which was slightly less than the kenaf-bamboo-coir/PLA hybrid composites. The toughness of the hybrid composites was found at 0.97 MJ/m³, 3.54 MJ/m³, and 4.45 MJ/m³ for kenaf-coir/PLA, bamboo-coir/PLA, and kenaf-bamboo-coir/PLA respectively. The higher toughness could be attributed to the optimum fraction of fiber in the composites (Nam *et al.*, 2011). The flexural strength of kenaf-bamboo-coir/PLA and bamboo-coir/PLA hybrids was higher than that of the kenaf-coir/PLA hybrid composites. This could be ascribed to the influence of the strong kenaf and bamboo outer layer in the hybrid composites. A strong interaction between the fiber cell wall and the matrix may result in enhanced flexural properties (Almeida *et al.*, 2013). So, they concluded that the bamboo and KFs compensated the lower strength of coir fiber by bearing the tensile load while the coir fiber contributed in the enhanced toughness of the hybrid green composites.

A study on the impact properties of basalt, flax, and green vinyl ester hybrid composites was reported by Živković *et al.* (2017). They tested the impact property of the hybrid composites in wet and dry conditions. They reported similar impact behavior of dry and wet hybrids with very small difference in the values. The values at different impact height of 2, 2.5, and 3 m were 11.01, 15.85, and 22.66 J respectively.

Huda *et al.* (2007) studied the mechanical properties of PLA based hybrid composites with recycled newspaper cellulose fibers (RCNF) and talc. They investigated the effect of varying concentrations of fillers with and without chemical treatment on the mechanical properties. The flexural and impact properties of the PLA/RCNF composites were enhanced with the addition of 10 wt% of silane treated talc. The flexural strength and modulus of the PLA/RCNF before hybridization was found to be 77 MPa and 6.7 GPa respectively, while the hybridized PLA/RCNF with 10 wt% silane treated talc produced 132 MPa and 15.3 GPa. Similarly, they also investigated the same having PP as the polymer matrix. A similar trend was also noticed when using PP/RCNF with 10 wt% of silane

treated talc. There was a 17% improvement in the impact properties of the PP hybrid composites compared with neat PP. The enhanced mechanical properties of PLA or PP hybrid composites were mainly due to the reinforcement of silane treated talc that enhanced the interaction at the polymer/talc interphase.

Another interesting study (Jacob *et al.*, 2004, 2006) investigated the mechanical and stress relaxation of rubber hybrid composites. Natural rubber was reinforced with sisal and oil palm fibers. The level interfacial adhesion between the matrix and the fibers was poor and when stress was applied it resulted in fiber pull-out from the rubber leaving gaping cavities. Hence, a chemical modification was done with 4% NaOH solution. They found that the mechanical properties increased and the rate of relaxation decreased with chemical modification.

Okubo *et al.* (2009) developed hybrid biocomposite with PLA reinforced with microfibrillated cellulose (MFC) and bamboo fiber. They found that the sudden crack growth was arrested due to the interphase between the cellulose and the PLA matrix around the bamboo fiber. This resulted in better tensile properties and further the diffusion of 1 wt% of MFC in PLA matrix drastically improved the strain energy of the bamboo/PLA composite up to 200%.

From these studies, it can be concluded that the mechanical properties of the hybrid composites can be enhanced by increasing the volume fraction of high strength fibers and chemical treatment of natural fibers can play a major role in the improvement of interfacial adhesion between the matrix and the fibers (Nunna *et al.*, 2012). Further, the exploration of biobased or natural fibers as reinforcing agents is found to be plenty compared with the exploration of biobased or natural polymer matrices in the fabrication of hybrid composites. Very few natural polymers are used as matrices in hybrid composites. Hence, the authors feel that there are scopes in the utilization of biopolymers in hybrid green composites, which can be a great innovation in terms of environmental aspects and enhanced properties.

Conclusion

This paper presents the different combinations of reinforcement used in the hybrid composites such as synthetic–natural, synthetic–synthetic, natural–natural and how these affect performance. Generally, the variation of hybrid composites is fabricated to improve the interfacial adhesion between the fiber and matrix of the composites. In this review, the interfacial properties were assessed through the experimental results and morphological analysis. Different types of fiber yield a variation of performance in the composites. Variation matrix systems have different properties that are very sensitive to processing methods such as fiber volume fraction, fiber length, and fiber orientation. Besides, the mechanical properties of hybrid composites not only depend the fabrication types, but also depend on the fiber modification. Fiber modification can enhance the interfacial adhesion between the matrix and fiber. Natural–synthetic can be combined to produce hybrid composite, which takes full advantage of the best properties of the constituents.

Acknowledgment

Authors acknowledge a seed fund research grant (Project No: U-TS-RD-18-10), Institute of Power Engineering, and Uniten R&D Sdn. Bhd., Universiti Tenaga Nasional for the support to publish these project findings.

See also: Historical Development of Hybrid Materials

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Characterization and Phase Diagram of the Tetragonal Tungsten Bronze Type Ferroelectric Compounds $\text{Pb}_{2(1-x)}\text{Gd}_x\text{K}_{1+x}\text{Nb}_5\text{O}_{15}$ for Energy Storage Applications

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Introduction

Tetragonal tungsten bronze (TTB) ferroelectric oxide type compounds constitute one of largest and intensively studied crystalline families (Podlozhenov *et al.*, 2006; Allouche *et al.*, 2016; Castel *et al.*, 2009). The TTB structure is described as a framework of MO_6 (here $\text{M}=\text{Nb}$) octahedra sharing corners, which reveals in c-axis direction three kinds of tunnels with pentagonal (p), square (s) and triangular (t) section (Jamieson *et al.*, 1969; Ravez and Elouadi, 1975; Ikeuchi *et al.*, 2017). The first two sites with coordination numbers 15 and 12 respectively, can be occupied by ions of large size while the third one, with the coordination number 9, can only be occupied by small size ions (Ravez *et al.*, 1972b; Ma *et al.*, 2015). These compounds present a fundamental interest in technology due to their ferroelectric properties, electrical and optical properties. The physical properties (ferroelectric, pyroelectric, ferroelastic, piezoelectric, second harmonic generation and nonlinear optic) can be tuned and controlled through the chemical content in the cationic channels. (Ballman and Brown, 1967; Imai *et al.*, 1997; Neurgaonkar and Cory, 1986; Foulon *et al.*, 1996; Ahamad *et al.*, 2009) Thus, a large variety of phase transitions or diffuse ferroelectric transitions were reported in this family of compounds (El Alaoui Belghiti *et al.*, 2002; Ke *et al.*, 2008).

Their high electro-optic coefficients and strong photorefractive effects make the TTB oxides attractive for technological applications as holographic storages, spatial light modulators, pyroelectric detectors, surface acoustic wave (SAW) devices and beam steering (Imai *et al.*, 1997; Neurgaonkar *et al.*, 1984; Neurgaonkar *et al.*, 1986; Bian and Frejlich, 1995; Lin *et al.*, 2016; Liu *et al.*, 2007). TTB materials crystallize easily and are generally transparent in the visible light (Foulon *et al.*, 1996). They are widely used for nonlinear optics applications because of their stability under an intense laser irradiation (Wei *et al.*, 2014; Zhu *et al.*, 2013). Their large non-linear and piezoelectric coefficients make them excellent materials in electro-optics, optoelectronics and sensor physics (Gagou *et al.*, 2012; Bobbs *et al.*, 1985; Neurgaonkar and Wu, 1987; Adachi *et al.*, 2013; Sakamoto and Yazaki, 2003; Vazquez *et al.*, 1991). For instance, $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$ is used as frequency doubler diode between 790 and 920 nm to generate the second harmonic of a blue-violet laser at room temperature and photorefractive properties (Vazquez *et al.*, 1991; Foulon *et al.*, 1997; Kaigawa *et al.*, 2002; Zhang *et al.*, 1996). In some TTB compounds, the replacement of niobium by tantalum leads to a decreasing of the Curie temperature and relaxor-type ferroelectric behavior (Castel *et al.*, 2009; Lu *et al.*, 1993). The value of curie temperature in TTB compound is associated with the rigidity of the covalent links between the ions located within the oxygen octahedra (transition/alkali metal), the size and the electronic structure of cations in the tunnels and the filling of the triangular sites implying their use in electrochemical applications (Castel *et al.*, 2009; Ma *et al.*, 2015; Han *et al.*, 2016). The structure stability mainly depends on steric parameter (Ravez *et al.*, 1972b; Parida *et al.*, 2013; Hornebecq *et al.*, 2001) and the direction of the spontaneous polarization can be altered depending on the nature of the atom that occupies the tunnels (Ravez *et al.*, 1972a; Pouchard *et al.*, 1975).

The lead-containing TTB compounds generally exhibit a ferroelectric orthorhombic phase with a distortion due to the strong polarizability of Pb^{2+} ions which causes a structural anisotropy (Hornebecq *et al.*, 2001, 1998). The well-known compounds are derived from PbNb_2O_6 which exhibits ferroelectric properties (Ravez and Elouadi, 1975; Labbé *et al.*, 1977). The distortions of the octahedra lead to a shift of the cation from its center and contribute to the increase of the curie temperature (T_C). Above T_C , the thermal agitation is sufficient to allow atom motions in all the directions cancelling the polarization (Vazquez *et al.*, 1991).

Ravez *et al.* (1972a) have studied TTB niobates including the three compounds $\text{BaCaNaNb}_5\text{O}_{15}$, $\text{SrCaKNb}_5\text{O}_{15}$ and $\text{BaCaKNb}_5\text{O}_{15}$ which showed the influence of cationic occupancy. They showed that the Curie temperature increases with the ionic radius of the cations inserted in the (p) and (s) sites. These authors proved that no ion in TTB structure staying in the (t) cavities can occupy the larger sites (p) and (s) and conversely, any cation occupying the sites (p) and (s) can occupy (t) sites. This distinguishes the TTB from perovskite compounds and can be attributed to the greater stability of the perovskite structure

and the anisotropy of the crystal lattice of TTB compounds (Chen *et al.*, 2003). This behavior is supported by the work of Pouchard *et al.* (1975) which evidenced the great decrease of the covalent metal-oxygen bonds occurring when niobium was substituted by tantalum.

Previous study was focussed on compounds of rare earth family $\text{Pb}_{1.6}\text{K}_{1.2}\text{R}_{0.2}\text{Nb}_5\text{O}_{15}$ (PKRN) (Oualla *et al.*, 2003) with various chemical elements, (R=La, Nd, Sm, Eu and Gd) of TTB-type ferroelectrics that were synthesized by solid state reaction and characterized by powder x-ray and dielectric measurements. The transition temperature PKRN was shown to decrease slowly with increasing of the rare earth ion (R) radius (Oualla *et al.*, 2003). Furthermore, room temperature x-ray powder diffraction patterns had been recorded on several compositions (from $x=0.0$ to $x=1.0$) in $\text{Pb}_{2(1-x)}\text{Gd}_x\text{K}_{1+x}\text{Nb}_5\text{O}_{15}$ family and structural analysis versus Gd-content had been performed based on Rietveld method (Rodríguez-Carvajal, 1993). Some of the results of this study were also reported (Gagou *et al.*, 2007; Amira *et al.*, 2010) that showed the existence of three regions versus Gd-content which merits complementary analysis.

Transition lines appeared from orthorhombic symmetry $Cm2m$ (No. 38) in Region I, to another orthorhombic symmetry $Pba2$ (No. 32) in Region-II, that occurred at $x \sim 0.3$ whereas the compounds in Region III ($x > 0.7$) present a tetragonal structure with $P4bm$ (No. 100) symmetry (Amira *et al.*, 2010). These observations are in favor of the tilting of the polarization from 0° (for $x=0$) to 90° (for $x=1$), which means that the polarization tilts from (a, b)-plane in Region I and goes to the c-axis direction when Gd-content increases. However, in Region II, the x-ray diffraction patterns present a series of Bragg peaks which can be indexed in tetragonal or orthorhombic symmetries. In this region, any better results were obtained without assuming a combination of coexistence of two symmetries ($Pab2$ and $P4bm$). Thereafter, when x increases from $x=0.3$ to $x=0.7$ there is a decreasing of the symmetries proportion of $Pab2$, comparatively to $P4bm$ in a coherent way; that allows us to build the intermediate phase. Beyond this range of compositions, pure symmetries were found.

In region II, the material appears to be a mixture of both phases, similar to what was found in numerous ferroelectric compounds (Cao *et al.*, 2010a,b; Shrout, 2002). These two ferroelectric phases are separated by the so-called morphotropic phase boundary (MPB) (Shrout, 2002; Elkechai *et al.*, 1996; Rao and Wang, 2007) which would take place at room temperature around $x=0.45$. If the situation is analogous to what happens in the perovskite family as mentioned by Frantti *et al.* (2009) the mixture of both phases could lead to enhance piezoelectric properties. Because of the steepness of the phase boundary, any small composition inhomogeneity leads to a coexistence state in this region.

Nowadays, in order to miniaturize the physical devices, and with the development of various physical deposition techniques, this family of compounds can be deposited as thin films and as super lattices by pulsed laser deposition (PLD) as it was reported previously by Allouche *et al.* (2016) and Gagou *et al.* (2012). This work follows the earlier work that was published previously (Gagou *et al.*, 2007). Raman spectroscopy study of $\text{Pb}_{2(1-x)}\text{Gd}_x\text{K}_{1+x}\text{Nb}_5\text{O}_{15}$ (PGKN) has been reported on the structural properties of this family that revealed a more ordered structure when Gd-content increases (Amira *et al.*, 2010).

In the present work, we perform a global analysis on the complete T-x phase diagram of this solid solution, by determining the variation of structural symmetry depending on the temperature, for given compositions. The nature of the intermediate phase between rich and low Gd-content compounds at room temperature is also investigated that permits to elucidate the nature of intermediate phase observed during structural changes versus temperature in the composition of $x=1$ as reported recently (Gagou *et al.*, 2014). The influence of the variation of Gd rate from $x=0$ ($\text{Pb}_2\text{KNb}_5\text{O}_{15}$) to $x=1$ (lead free compound $\text{K}_2\text{GdNb}_5\text{O}_{15}$) is studied by means of dielectric measurements, scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and powder x-ray diffraction versus temperature, for the compositions of $x=0.1$, $x=0.4$ and $x=0.9$ which correspond to each region of the determined phase diagram.

The aim this work is to investigate the influence of Gd^{3+} ions occupancy in the (s) and (p) channels, on the TTB structural properties of the present solid solution. Main focused was done on the structural changes at room temperature varying the gadolinium content and then, we highlight the structural changes in all compositions over temperature, based on dielectric measurements.

Experimental

PGKN compounds were prepared by solid state reaction, with three different oxides such as PbO , Gd_2O_3 and Nb_2O_5 and potassium carbonate K_2CO_3 of 99.99% purity from Sigma-Aldrich. The finely crushed mixtures were pre-heated at 650°C during 6 h, and then annealed at 1200°C during 12 h. Each thermal treatment was followed by crushing in order to obtain well homogenized mixtures. Powders were then compacted under a pressure of 200 MPa, to obtain cylindrical pellets with 13 mm diameter and 1 mm thickness. These pellets were sintered during 2 h at 1270°C . The obtained ceramics had a compactness of about 97% considering theoretical versus experimental calculations. All the ceramics were elaborated in the same conditions. Powder x-ray measurements were performed using a Bruker AXES-D8 Advanced Diffractometer with a Cobalt radiation $\lambda_{\text{CoK}\alpha 1} = 1.7889 \text{ \AA}$ and $\lambda_{\text{CoK}\alpha 2} = 1.7928 \text{ \AA}$. A cylindrical furnace allowed collecting x-ray patterns in Debye-Scherrer geometry versus temperature. Scanning electron microscopy measurements were performed using a JEOL JSM-5500 microscope in order to characterize the micro-structure of the samples. DSC measurements were performed using NETZSCH DSC 204 F1 apparatus under argon gas flow. Dielectric measurements were carried out using a Solartron SI-1260 spectrometer in the 10^1 – 10^6 Hz frequency range. Electrodes were deposited by platinum sputtering on the two faces of the ceramic pellets to get capacitor shaped samples. An alternative voltage source of 1 V maximal amplitude was applied on the 0.8 mm thickness samples and the temperature was controlled using a Linkam TS 93 hot stage allowing $\pm 0.1^\circ\text{C}$ temperature stability.

Results and Discussions

Dielectric Measurements

Figs. 1–3 show the variation of real part of dielectric permittivity versus temperature on heating and cooling, for three representative compositions in this family such as $x=0.0$, $x=0.5$ and $x=0.9$. Thermal hysteresis behavior of each real part of permittivity at the measuring frequency of 100 kHz were shown in Figs. 1(a), 2(a) and 3(a) and their frequency dependence are shown in the Figs. 1(b), 2(b) and 3(b), respectively. Higher dielectric dispersion as a function of frequency was observed for weak Gd-content compounds such as for $x=0.0$ (Fig. 1(b)). This dielectric dispersion attenuates progressively toward intermediate Gd-content compounds (Fig. 2(b)) and becomes very weak for the rich Gd-content compounds (Fig. 3(b)). This behavior was attributed to atomic reordering in this system with the gadolinium rate.

It was observed in Fig. 4 that a significant variation of the dielectric anomaly shapes from one region to another. The width of the dielectric permittivity thermal hysteresis increases with Gd-content followed with a slight decrease in rich Gd-content part. This behavior is in favor of a structural change from a second order (without any drastic permittivity jump and small thermal hysteresis) to a first order (with abrupt permittivity jump and large thermal hysteresis) type transition, when Gd-content increases, as observed in Figs. 1(a), 2(a) and 3(a), respectively. We can clearly observe in Fig. 4(c), in the Gd-rich compounds ($x \geq 0.7$), the

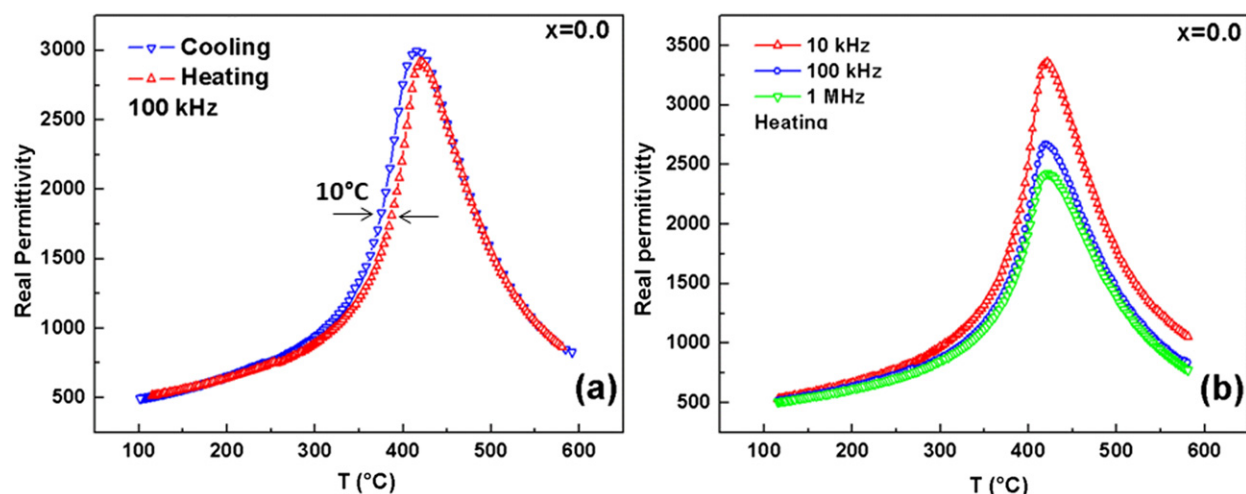


Fig. 1 Dielectric constant versus temperature for (a) $x=0.0$ at 100 kHz on heating and cooling, and (b) evolution of the maximum at several frequencies on heating.

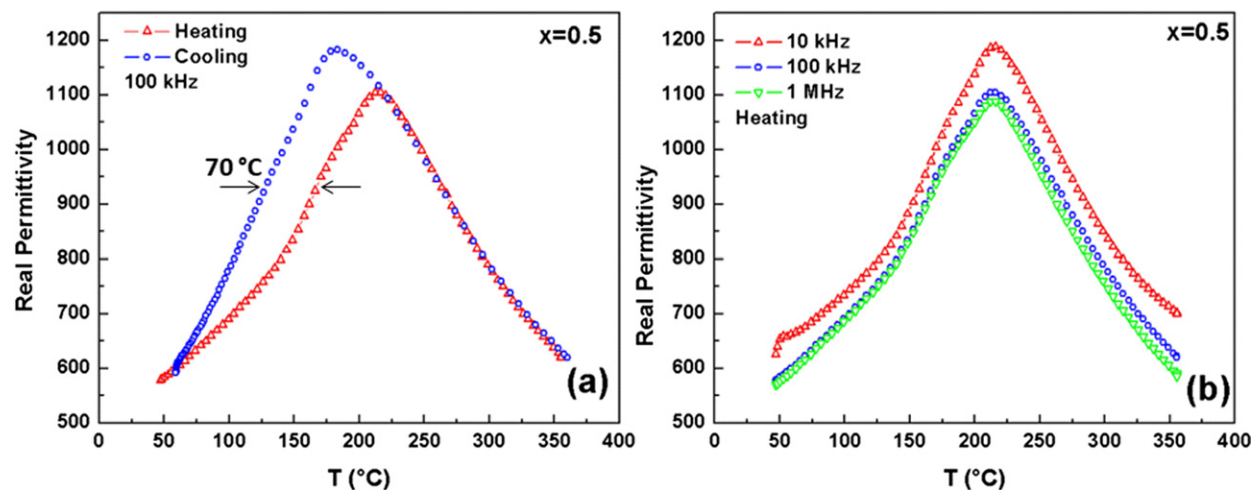


Fig. 2 Dielectric constant versus temperature for (a) $x=0.5$ at 100 kHz on heating and cooling, and (b) evolution of the maximum at several frequencies on heating.

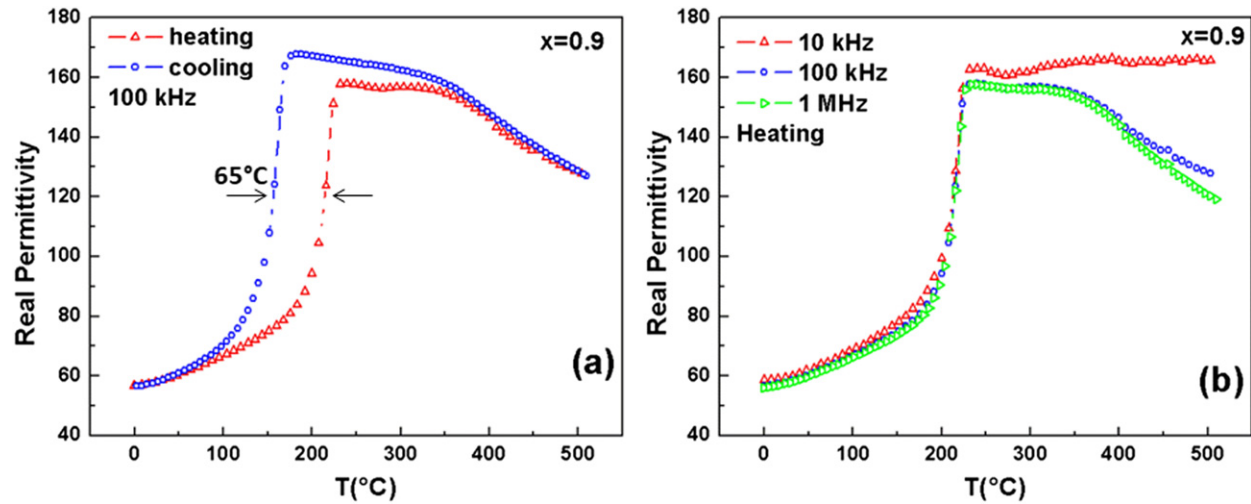


Fig. 3 Dielectric constant versus temperature for (a) $x=0.9$ at 100 kHz on heating and cooling and (b) evolution of the maximum at several frequencies on heating.

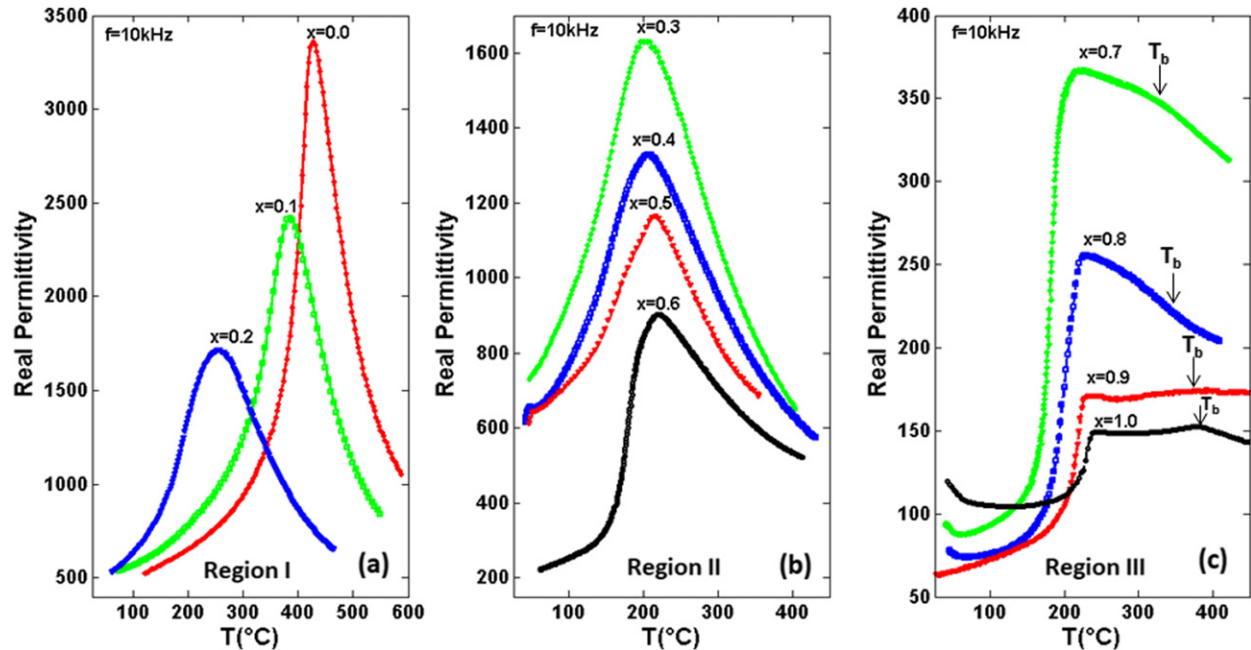


Fig. 4 Dielectric permittivity at $f=10\text{ kHz}$ as a function of temperature on heating, for different compositions: (a) $x=0$ to $x=0.2$ (region I), (b) $x=0.3$ to $x=0.6$ (region II), (c) $x=0.7$ to $x=1$ (region III).

presence of a second anomaly (at T_b) indicating two phase transitions observable on the curve of dielectric permittivity versus temperature. However, only one dielectric anomaly was evidenced for the other compositions (lower Gd-content, with $x < 0.7$). Furthermore, the temperature of the maximum of real permittivity does not present any change with the frequency in the range of 10 Hz to 1 MHz, which indicates the absence of any relaxor behavior in this solid solution. Dielectric measurements show also a decrease of the permittivity maximum value when the Gd-content increases as shown in Fig. 4.

For example, the permittivity value that was about 3400 at $T_C=425^{\circ}\text{C}$ for $x=0.0$ (Fig. 4(a)), decreases to about 1650 for $x=0.3$ at $T_C=204^{\circ}\text{C}$ (Fig. 4(b)) and to about 380 for $x=0.7$ observed at $T_C=230^{\circ}\text{C}$. This is attributed to the decreasing of lead content when the Gd-content x increases. It can be concluded that the high polarizability of Pb^{2+} ion is responsible for the strong ferroelectric behavior in this system, as reported previously by Sciau *et al.* (1993) and Taifi *et al.* (2010).

In Region I (Fig. 1(a)), the curves of real permittivity ($\epsilon_r(T)$) present a thermal hysteresis of about 10°C in the low temperature phase. They are also characterized by a rapid decrease of $T_C(x)$ as shown in Fig. 4(a). The absence of visible jump indicates a

diffuse character of the structural change and a second order type transition when crossing the T_C line in this region. The frequency dispersion behavior (decreasing of the peak magnitude when the frequency increases) that was observed also in Fig. 1(b), Fig. 2(b) and Fig. 3(b) is typical for ceramics and attributed to grain boundaries and grain size effects.

In region II, the behavior is quite different. The curves of $\varepsilon_r(T)$ still present λ -shaped but with a broader peak at T_C and a wider thermal hysteresis (of about 70°C) (see Fig. 2(a)), whereas the frequency dispersion weakens with frequency and $T_C(x)$ is slightly increases, as shown in Fig. 2(b). Such a behavior where an excess of dielectric constant occurs in the region below the dielectric permittivity peak, recalls the situation that happens in potassium dihydrogen phosphate KH_2PO_4 (KDP) that was shown to be dependent on defect concentration (Petrova and Stishov, 2013; Eberhard and Horn, 1975; Sidorkin, 2006) or related to the anisotropy in $\text{K}_{0.4}\text{Li}_{0.6}\text{NbO}_3$ (KLN) (Uitert *et al.*, 1967). In PGKN, this effect could be attributed to the interaction between ferroelectric domain walls and defects. The analogy of these behavior between irradiated KDP and PGKN materials belonging to region II, suggests that a particular situation occurs in this region, with respect to the wall-defect interaction, for instance around 100–150°C for $x=0.5$ (see Fig. 2(a)).

In Region III, the permittivity jump corresponds to a clear first order type transition with larger thermal hysteresis of about 65°C as presented in Fig. 3(a) for the case of the composition $x=0.9$. This first anomaly is followed by a second one T_b above T_C that indicates a second phase change where an hysteresis is observed in a temperature range of about 10°C, observable in Figs. 3(a) and 4(c). This second anomaly occurs without clear permittivity jump, and seems to exhibit a second order type transition character.

Moreover, from the analysis of thermal dielectric permittivity behavior $\varepsilon_r(T)$, we deduced that the temperature corresponding to the real permittivity maxima decreases rapidly in Region I, then increases smoothly in Region II and then increases normally in Region III where we observe a second anomaly that increases rapidly with Gd-content. The temperatures of the second anomalies are denoted T_b in Fig. 4(c).

DSC Measurements

At the same temperature corresponding to dielectric anomalies, DSC measurements show anomalous behavior too. Calorimetric analysis shows some excess of specific heats in this system, in appropriate temperature ranges. DSC measurement results were summarized into three curves corresponding to $x=0.0$, 0.5 and 0.9 and plotted in Fig. 5, where we observe the specific heat flow excess (DSC signal) versus temperature in the three different regions. The composition $x=0.0$ correspond to Region I, $x=0.5$ to Region II and $x=0.9$ to Region III. All curves show corrected values of DSC signal excess, after subtraction of baseline, following a classic procedure.

For the composition $x=0.0$ (Fig. 5(a)) it is clearly observed a broader excess of specific heat around the temperature of the dielectric anomaly ($T_C=425^\circ\text{C}$), that is in favor of a second order type transition highlighted previously by dielectric measurement. The curve corresponding to $x=0.5$ (Fig. 5(b)) shows a λ -shape and symmetrical anomaly at $T_C=216^\circ\text{C}$, in favor of a second order character of the transition. This composition, which corresponds to the coexistence of two phases, presents the weakest excess of specific heat and is in accordance with the temperature position of dielectric permittivity anomaly. However, the curve that corresponds to $x=0.9$ (Fig. 5(c)) shows a full first order type transition exhibited by the clear jump of the DSC signal with the highest excess of specific heat and a typical asymmetry of the peak at the first anomaly, observed at $T_C=226^\circ\text{C}$. This behavior is characteristic of the Region III. As in dielectric response, this anomaly is followed by a second anomaly characterized by a broad signal approximately centered on $T_b=360^\circ\text{C}$ as observed from dielectric measurement. All these observations are in accordance with results obtained in dielectric measurements.

XRD and Raman Spectroscopy Studies

X-ray patterns of the representative compositions of $x=0.1$, $x=0.4$ and $x=0.9$ were recorded as a function of temperature (in the temperature range of 30–600°C). The temperature dependence of lattice parameters a , b and c for each composition are presented in Fig. 6(a–c) respectively. For $x=0.1$ the splitting of a and b lattice parameters in ferroelectric phase shown in Fig. 6(a), occurs at a temperature that coincides with the ferroelectric transition temperature deduced from the dielectric data. This indicates that the structural change occurs between the ferroelectric (orthorhombic) $\text{Cm}2m$ (No. 38) phase at low temperature to the paraelectric, high symmetry tetragonal $P4/mbm$ (No. 127) phase, without evidence of an intermediate phase. For $x=0.4$, in the low temperature phase when $T<60^\circ\text{C}$ the structure is well described by the $Pba2$ (No. 32) space group. We performed also x-ray refinement between 60°C and 120°C. The structure can be refined in the $Pba2$ symmetry as well as in $P4bm$ symmetry. The ferroelectric transition evidenced by the dielectric anomaly is found at the same temperature (see Fig. 4(b)), where ferroelastic splitting at cooling occurred between $P4/mbm$ and $P4bm$ space groups as reported on Fig. 6(b). For the compound with $x=0.90$, all the phases are found to be tetragonal but compatible with different symmetry groups. In the intermediate temperature region ($230^\circ\text{C}<T<360^\circ\text{C}$) this compound exhibits the symmetry group $P4/mbm$ with a doubling of TTB parent unit cell volume, with lattice parameters $a\sqrt{2}$, $a\sqrt{2}$ and c , or in another possible space group $P4nc$ (No. 104) with doubling of c -axis parameter that is also a subgroup of the high symmetry space group ($P4/mbm$).

These behaviors were reported very recently on the compound $\text{GdK}_2\text{Nb}_5\text{O}_{15}$ (with $x=1.0$) (Gagou *et al.*, 2014) where this doubling of c -axis lattice parameter was attributed to an antiferroelectric ordering. At higher temperature ($T>T_b$) the tetragonal structure is stabilized in $P4/mbm$ space group as for all TTB materials. The variation of the lattice parameters versus

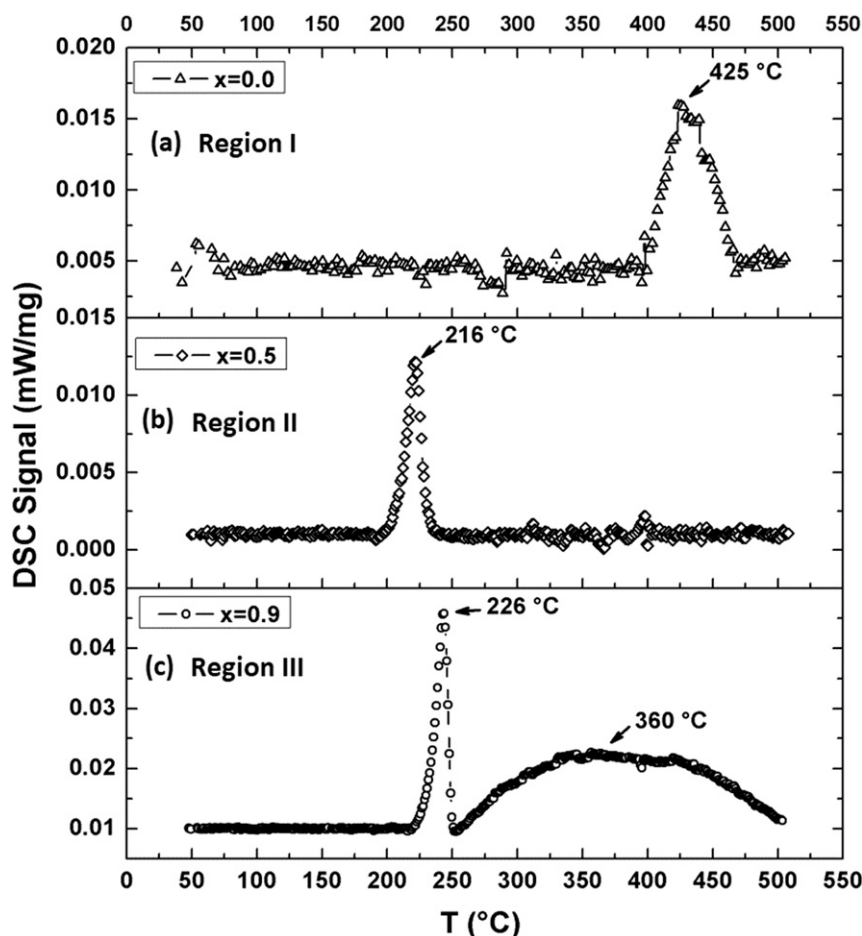


Fig. 5 DSC Signal versus temperature on heating for the three compositions (a) $x=0.0$, (b) $x=0.5$ and (c) $x=0.9$, each Gd-content belonging to Region I, II and III respectively. The DSC signals were corrected by subtracting background obtained by polynomial interpolation and the values correspond to excess of specific heat.

temperature is featured in the Fig. 6(c) as characteristic of compounds in region-III. The $a=b$ parameter increases and the main anomaly was observed on the c parameter at about 230 °C (Fig. 6(c)). The phase transitions between the high temperature tetragonal structure and the low temperature can be described by the loss of the mirror m_z (perpendicular to c -axis) symmetry and the doubling of the c lattice parameter with apparition of the polar axis in $P4bm$ symmetry, when the temperature is lowered.

Fig. 7(a) and (b) show respectively typical x-ray patterns and Raman spectra of the compositions ($x=0$, 0.5 and 0.9), each composition corresponds to Region I, II and III, respectively. The x-axis of these plots are restricted for better understand. The space groups assignment were consistent with, for example, the symmetry change of the indexed line (320) in (tetragonal, Region III) to (321) in (tetragonal, Region II) and its splitting to (510) + (150) in (orthorhombic, Region I), that provide the distortions in (a,b) plane for low Gd-content compounds (rich Pb-content compound), since all the (00ℓ) lines remained unchanged as it can be seen in Fig. 7(a). These analysis were applicable for the indexed line (620) that disappeared in intermediate region before splitting into (840) + (480) in Region I. These results, related to symmetry assignments, were also supported by Raman modes changes with Gd-content in this system, as shown in Fig. 7(b), where a disordered was observed structure from less Gd-content compounds to more and more ordered structure when Gd-content increases.

Relation Between Microstructure and Properties

For better understand of the structural changes and ferroelectric behavior deduced from dielectric measurements it is worth to analyse microstructure effect in this system. For instance, the width of the coexistence region has been connected to the particle size as reported by Mittemeijer and Welzel (2008) and depends on the processing conditions. A spatial variation of composition could also induce some phenomena that were observed, like the wide hysteresis and the diffuse nature of the transitions. To check these points, SEM images have been recorded and shown in Fig. 8. The three compounds: $x=0.1$ (Fig. 8(a)), $x=0.4$ (Fig. 8(b)) and $x=0.9$ (Fig. 8(c)) present typical grain sizes in each image belonging to their related region versus composition. They show a good

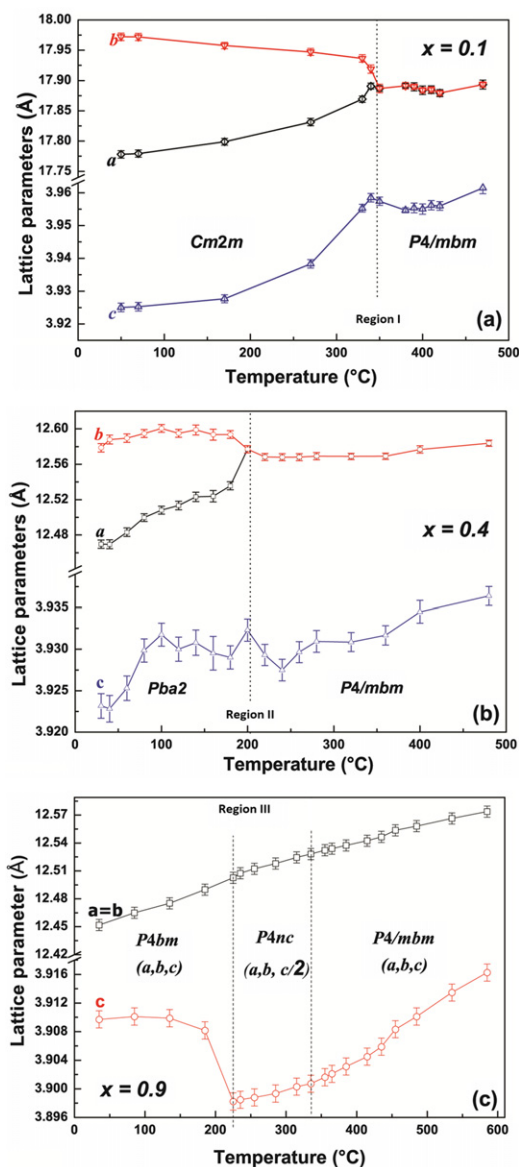


Fig. 6 Unit cell parameters versus temperature for compound with (a) $x=0.1$, (b) $x=0.4$ and (c) $x=0.9$.

crystallization in agreement with the powder x-ray diffraction results which showed narrow lines x-ray patterns, as indicated in Amira *et al.* (2010).

The grain size and the strain analysis of the pseudo-voigt peak shape profile were performed at room temperature using Debye-Scherrer Formula (Welzel and Mittemeijer, 2005). The results of grain size and strain analysis were presented in Figs. 9 and 10, respectively. We can observe the rapid decreasing of the apparent crystallite size with the Gd-content x , followed by a slight decreasing attempting a minimum value in the phases coexistence region II ($0.4 < x < 0.7$).

In the single phase region III ($x > 0.7$), the apparent crystallite size decreases with Gd-content, from micron to sub-micron size (refer to Fig. 8) leading to a more compact ferroelectric compound. Simultaneously, the strain analysis (Fig. 9) indicates a constant and a weak strain (0.2%) up to the composition $x < 0.4$. In the coexistence region ($0.3 < x < 0.7$) the strain increases rapidly for both symmetries and then decreases rapidly with Gd-content to negative values that induce lattice expansion for $x=0.7$. Moreover, for the composition $x > 0.7$ in the $P4bm$ single phase, the mean strain level increases to attempt a level characteristic of the $Pba2$ single phase.

In a nutshell, in this crystalline phase, compounds with $P4bm$ symmetry phase are more plastic and lead to good density ceramics than those in $Pba2$ symmetry phase. This induce high stability and cohesion of chemical elements, since higher strain and mean crystallite-size are more reachable in the $P4bm$ phase ($x > 0.7$) than in the $Pba2$ phase ($x < 0.4$). All these phenomena are obviously connected to the Gd-content in this family, and Gd-rich compounds present the smallest grains. In this system the grain size decreases from about 5 μm (for $x=0.1$) to less than 1 μm for the compound with $x=0.9$.

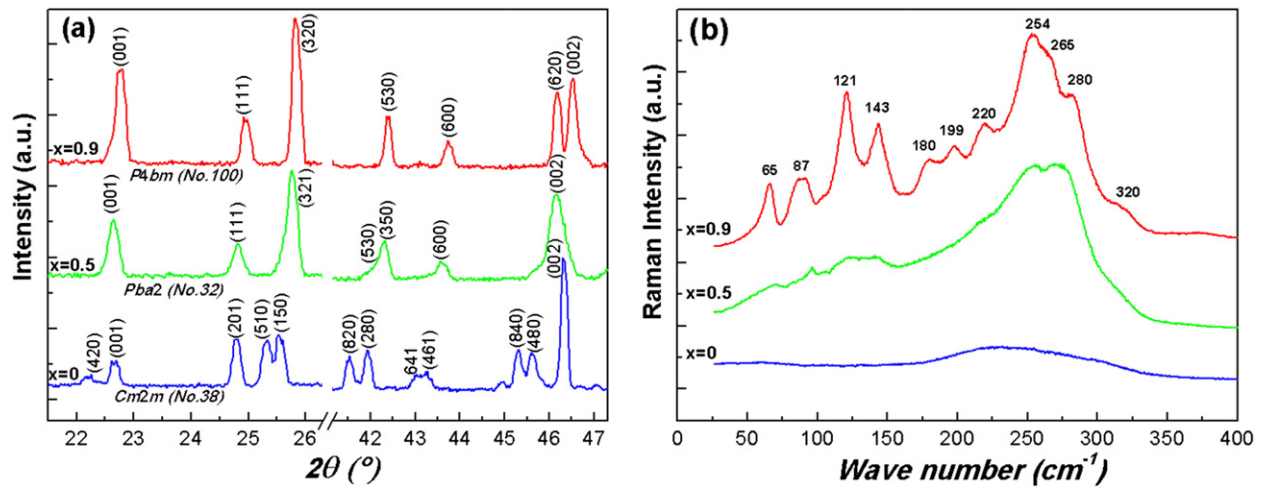


Fig. 7 (a) X-ray patterns of the three composition ($x=0, 0.5$ and 0.9) highlighting structural phase changes in PGKN through the three regions. (b) The symmetry changes were confirmed by Raman spectra recorded on the three compositions.

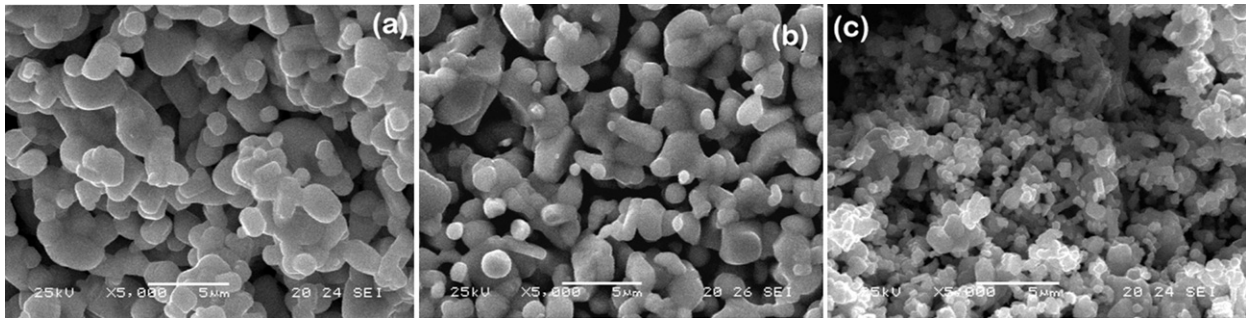


Fig. 8 SEM images showing grain size morphology on ceramics of the three compositions; (a) $x=0.1$, (b) $x=0.4$ and (c) $x=0.9$ selected to be investigated.

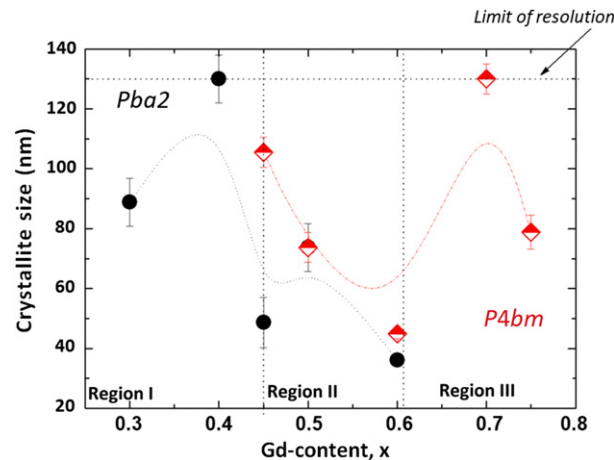


Fig. 9 Evolution of the crystallite size as a function of Gd-content, deduced from powder x-ray diffraction data. (Red diamond symbol corresponds to $P4bm$ symmetry and black solid circle correspond to $Pba2$ symmetry).

Furthermore, compounds with the smaller grains have the sharper jump in the dielectric curves exhibiting a first order type phase transition with the larger dielectric anomalies. The smaller thermal hysteresis were obtained for the compositions having the larger grain sizes (for example, $x=0.1$) in a coherent way.

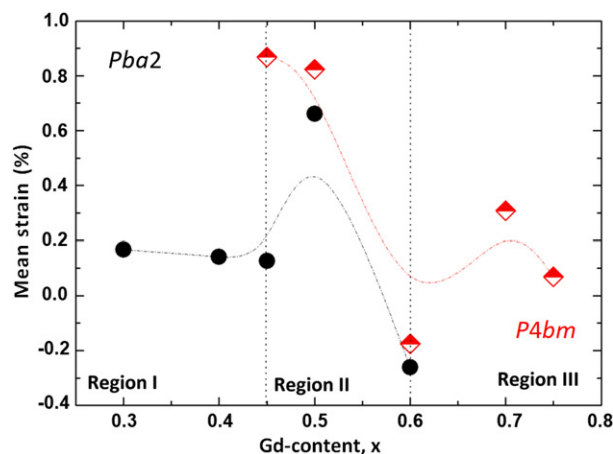


Fig. 10 Evolution of the mean strain as a function of Gd-content, deduced from powder X-ray diffraction data. (Red diamond symbol corresponds to *P4bm* symmetry and black solid circle correspond to *Pba2* symmetry).

Development of Phase Diagram

The data presented above can be summarized in a composition–temperature phase diagram (see Fig. 11), considered as a complete phase diagram in PGKN system, when compared to the previous version proposed in Amira *et al.* (2010). All the temperatures such as T_C and T_b highlighted in the previous analysis, were plotted as a function of the Gd-content in the whole composition, that permits us to build the (x, T) -phase diagram of this family. The results are summarized in Fig. 11 that proposes for the first time the temperature-composition phase diagram, which exhibits interesting phase transition lines and multiple points in this system. The first order transition character for Gd-rich compounds is connected with our previous reported Raman spectroscopy results on this family compound (Amira *et al.*, 2010), while the more ordered structure is observed in this region (Region-III) comparatively to disordered structure in compounds with low Gd content.

In Region I of this phase diagram ($x < 0.3$) the low temperature phase crystallizes in *Cm2m* symmetry group which means the polarization is oriented along the $(010)_o$ orthorhombic 2-fold axis which is perpendicular to the tetragonal $(001)_t$ direction. Ferroelectric properties of both structures are therefore clearly different.

This behavior permits us to conclude that PGKN family compounds exhibit an intermediate region ($0.3 < x < 0.7$) in the composition-temperature phase diagram between low Gd-content compounds (having orthorhombic ferroelectric phase with (a,b) -oriented polarization) and the rich Gd-content compounds (having tetragonal ferroelectric phase like in $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$, with c -axis oriented polarization). In this phase (Region-II), the ferroelectric orthorhombic phase is induced by the ferroelastic distortion in (a,b) -plane and the polarization is related to the niobium atom displacement out of the equatorial plane position inside oxygen octahedra. Such a situation is typical for the traditional lead-containing TTB ferroelectrics like in $\text{Pb}_2\text{KNb}_5\text{O}_{15}$ and $\text{Pb}_{2.05}\text{Na}_{0.90}\text{Nb}_5\text{O}_{15}$ and some perovskite (Ravez and Elouadi, 1975; Sciau *et al.*, 1993; Glazer, 1972).

The symmetry group of this phase, *Pba2*, reveals moreover a spontaneous orthorhombic deformation that can be provided by the specific interaction of ferroelectric and ferroelastic coupling and atom motion through the tunnels along c -axis. Such a situation was observed previously in the TTB-type ferroelectric compound $\text{PbK}_2\text{LiNb}_5\text{O}_{15}$ (Gagou *et al.*, 2004). In *Pba2*, the polarization is oriented along the orthorhombic $(00\ell)_o$ axis, which coincides with the tetragonal $(00\ell)_t$ axis. This structural result is important because it is not possible to pass continuously from the structure with *Cm2m* to that with *Pba2* since the ferroelectric polarization changes its direction from $(110)_o$ to $(001)_t$ (with reference to tetragonal axes).

As a consequence, there should occur a first order transition line between both phases that could terminate in another multiple point in the phase diagram (denoted P_2 in Fig. 11), from which the morphotropic region could start on the right (Region-II). Inhomogeneities in the sample due to the morphotropic region may be at the origin of the special situation regarding interaction between domain walls and defects that was evoked above. In that region, the grain boundaries are expected to be more numerous and their role in the pinning of domain walls may be invoked as the determinant mechanism of domain walls-defects interaction to explain both the excess of dielectric constant on cooling, and the global thermal hysteresis. We expect that the special concentration ($x \sim 0.25$) where the polarization upsets into the basal plane, is a point of special interest in the neighborhood of which the instability of polarization orientation could have interesting physical properties. Moreover, due to the existence of the antiferroelectric symmetry the compositions in this region constitute potential candidates for electrostatic energy storage. PGKN system exhibits the presence of many rich phases symmetries whose determination requires complementary refinements and accurate studies, in particular taking into account the theoretical results of the analysis of rigid unit modes (RUMs) (Smirnov and Saint-Grégoire, 2014) in this crystalline family.

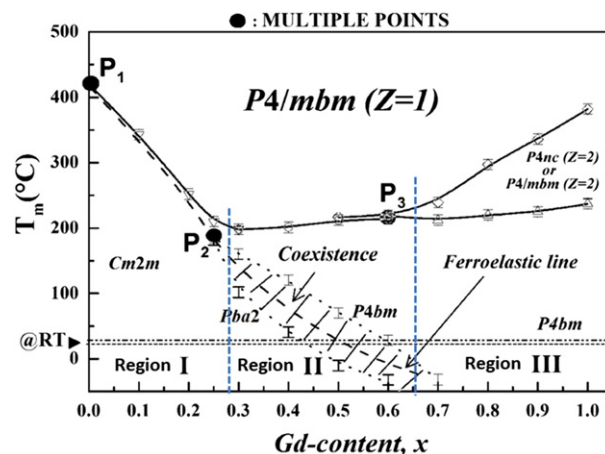


Fig. 11 Composition–Temperature phase diagram of PGKN compounds. Three regions may be distinguished (see text): region I in which phase transition occurs apparently between $P4/mbm$ and $Cm2m$ symmetries. The existence of an intermediate phase cannot be excluded from the data so that a triple point P_1 as shown close to $x=0$ compositions could be present. Region II is characterized by a coexistence zone (dashed region) between $P4bm$ and $Pba2$. There exists then a line between $Cm2m$ and $Pba2$ phases that ends at a multiple point P_2 . Finally, in region III phase transitions occur between tetragonal phases. In that region both transition lines seem to converge to a triple point P_3 that would lie around $x=0.5$ and $T=200^\circ\text{C}$.

Conclusion

TTB compounds containing gadolinium with the general formula $\text{Pb}_{2(1-x)}\text{Gd}_x\text{K}_{1+x}\text{Nb}_5\text{O}_{15}$ (PGKN) have been elaborated by solid state reaction, and have been studied to elucidate their structural electrical and calorimetric behaviors. A new composition–temperature phase diagram was established that appears to be very rich. The results are consistent with the presence of multiple points involving lines between paraelastic–paraelectric–ferroelastic–ferroelectric. Scanning Electron Microscopy shows various morphologies connected with Gd concentration and ferroelectric behaviors connected to grain size and strain analysis. At high temperature, all the compositions are compatible with $P4/mbm$ space group symmetry. At low temperature, three composition regions have been observed in the phase diagram: (i) compounds with a low Gd-content ($0 < x < 0.3$) are compatible with the $Cm2m$ space group, (ii) compounds with a rich Gd-content were refined in the $P4bm$ space group ($0.7 < x < 1$), (iii) compounds with intermediate Gd-content ($0.3 < x < 0.7$) show up a MPB as found in the perovskite family, that can be described as the coexistence of phases with space groups $Pba2$ and $P4bm$. This intermediate phase, that ranges in $0.3 < x < 0.7$, represents a domain where we could expect potential candidates for electrostatic energy storage materials.

Acknowledgement

The work is supported by FP7-IRSES-ROBOCON project which is greatly acknowledged. Authors thank Prof. I. Luk'yanchuk, for his fruitful exchanges about phase changes. Authors also thank the "Program Hubert Curien" (PHC-MAGHREB No. 27958YF and PHC PROTEUS No. 37432UB) for the financial support.

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Conversion of Renewable and Food Wastes Into Useful Products With Environmental Perspectives

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Introduction

A variety of wastes are generated both in the land (forestry, agriculture, food and beverage) and marine sectors (Hettenhaus, 2011; Liu *et al.*, 1997; Pfaffin and Ziegler, 1998; Schiefelbein *et al.*, 1980; Van Luyen and Houn, 1996). Their accumulation on this planet (land and marine) results in several environmental difficulties, health issues, safety hazards, and prevent sustainable development in terms of resource recovery and recycling of waste materials (Taherzadeh and Karimi, 2008). Converting different wastes into value-added (food, feeds, fertilizer and others) products is an effective pathway to reduce environmental harms, and improve economic sustainability of wastes processing. Isolation of natural compounds from wastes generated in the various sectors or their conversion into useful compounds such as food ingredients, bio-fuel, and other value added products by respecting environmental demands is an interesting subjects (Taherzadeh and Karimi, 2008). This recycling approach brings benefits not only to the environments, but also to industries from economical point of view.

A review report for the conversion of different wastes generated from land (food, agriculture, and forestry) and marine sectors, into useful products, provides as a collection and a ready scientific report for investigators, who are involved in both research laboratories and industries. The objectives of this study were: (i) To provide a global information on the wastes generated from different (forestry, agriculture, food, beverage, and marine) sources; (ii) to convert several wastes with the renewable resources into by-products; (iii) to determine the required appropriate (s) conversion into useful components, considering environmental concerns, a gas emission, and a global warming; and (iv) to extract useful components from by-products for different applications.

General Aspects of Renewable and Food Wastes

Land and Marine Renewable Resources Wastes

A large amount of the renewable wastes have been accumulated in the nature (Hettenhaus, 2011; Liu *et al.*, 1997; Pfaffin and Ziegler, 1998; Schiefelbein *et al.*, 1980; Van Luyen and Houn, 1996). Leaves, stems, and stalks are major components of forestry residues (Mishra and Thakur, 2015). Agricultural wastes include leaves, stems, husks (the dry outer covering of various fruits or seeds), woody crops and stalks from different sources such as, corn fiber, corn stover, straw, hulls, peels and hells from cereals (corn, wheat, barely, rice, and sorghum), sugarcane bagasse, and brewer's spent grains (Hettenhaus, 2011; Liu *et al.*, 1997; Mishra and Thakur, 2015; Pfaffin and Ziegler, 1998; Schiefelbein *et al.*, 1980). Crop residues are the main part of agricultural biomass. Corn stover from crop residues and straws (Hettenhaus, 2011; Nelson *et al.*, 2011) from cereal grains (wheat, rice, oat, rye, and barley) are quantitatively the major parts of the residues. Maiorella (1985) reported that "1 kg grains as the main product" was obtained from the original harvested crops. The remained residues "which is straws and can be considered as a by-product" equal to 1–1.5 kg. Industrial processes and residues of agriculture resulted in different wastes including coconut biomass, citrus peels, sawdust, paper pulp, and paper mill sludge (Sadhu *et al.*, 2013). Citrus peel, cooking oil and cashew shell nut liquid were also used as wastes in different countries "China, Morocco, and European (UK, Spain, Greece)" (Lin *et al.*, 2013). Most of marine wastes obtained from crustacean shells (Van Luyen and Houn, 1996). Different wastes obtained from renewable resources were shown in Fig. 1.

Agricultural wastes include high amount of polysaccharides (cellulose, hemicellulose), lignin, and inorganic materials (Ragauskas *et al.*, 2014). Various ingredients of biomass are cellulose, lignin, hemicellulose, proteins, fats and minerals (Sinag *et al.*, 2010). Ligno-cellulose is a complex material comprising two polysaccharides (cellulose and hemicellulose), and a phenolic polymer, lignin, as the major structural component (Howard *et al.*, 2011). They may be combined with small amounts of other components like acetyl groups, minerals and phenolic substituents (Isikgor and Becer, 2015). There are multiple sources of lingo-cellulosic wastes from agriculture and forest residues and industrial agricultural processes (citrus peel, coconut biomass, sawdust, paper pulp, and paper mill sludge) (Hettenhaus, 2011; Liu *et al.*, 1997; Pfaffin and Ziegler, 1998; Sadhu *et al.*, 2013; Schiefelbein *et al.*, 1980). Ligno-cellulosic biomass is a major component of plants (stalks, leaves and roots). Depending on the type of lignocellulosic biomass, these polymers are organized into complex non-uniform three-dimensional structures to different degrees and varying relative compositions. These polymers are closely associated with each other. Basically, cellulose forms a skeleton, which is surrounded by hemicellulose and lignin (Mishra and Thakur, 2015). Lignocellulose has evolved to resist degradation. This is due to the crystallinity of cellulose, hydrophobicity of lignin, and encapsulation of cellulose by the lignin–hemicellulose matrix (Agbor *et al.*, 2011; Barakat *et al.*, 2013). Although the composition of agricultural crop wastes is different, the typical percentages of the dominant chemical composition in corn stover, rice straw, and wheat straw are 35%–50% cellulose, 20%–35% hemicellulose, and 5%–25% lignin (Binod *et al.*, 2010; Lomborg *et al.*, 2010; Weiss *et al.*, 2010). In general, lignocellulosic

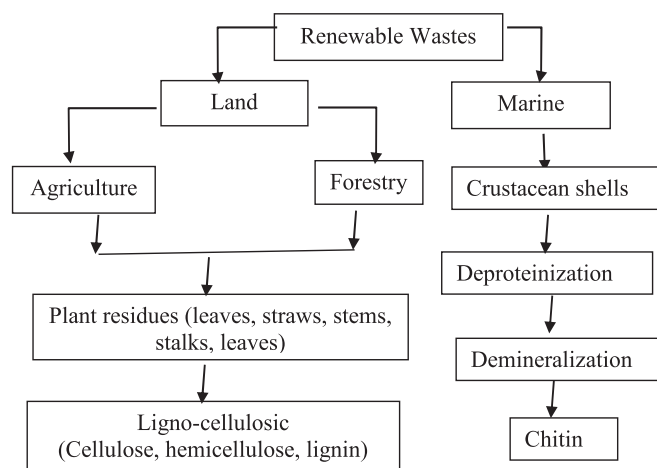


Fig. 1 Major substances derived from land and marine renewable resources.

biomass composed mainly of two carbohydrate polymers cellulose (30%–60%) and hemicelluloses (20%–40%) and an aromatic polymer lignin (10%–25%), which are interlinked to each other in a hetero-matrix. Approximately 90% of dry matter in lignocellulosics consists of cellulose, hemicelluloses and lignin, whereas the rest comprises of ash and extractives (Isikgor and Becer, 2015; Nanda *et al.*, 2014, 2012). The carbohydrate polymers contain different sugar monomers (six and five carbon sugars) and they are tightly bound to lignin. The lingo-cellulosic biomass is abundant, renewable resources on the earth and obtained from forest and agriculture residues (Akhtar *et al.*, 2015; Mishra and Thakur, 2015; Mosier *et al.*, 2005). In the cell wall, cellulose acts as the structural framework, and hemicellulose retains the water for the lingo-cellulosic (lingo-cellulosic) biomass. Lignin plays a role as an adhesive between the various cell wall components. Lignin is also an important component for mechanical support, water transport, and defense against natural invasion (Ragauskas *et al.*, 2014). Cellulose, “the most abundant biopolymer on the earth” is a linear polymer of glucose with β -1, 4-linkages. However, it has crystalline structure and is highly resistant to hydrolysis by both enzymatic and chemical means. Cellulose in secondary cell walls is embedded in a matrix of hemicellulose and lignin with lower amounts of pectin and protein.

Food Wastes

Wastes produced from food industries include: “Dairy products (dilutions of whole milk, separated milk, butter milk, whey, sour milk); brewed and distilled beverages (steeping and pressing of grains; residues from distillation of alcohol, condensate from stillage evaporation); meat and poultry products (stockyards, slaughtering of animals, rendering of bones and fats, residues in condensates, grease and wash water, picking chickens); beet sugars (juicing waters, draining from lime sludge, condensates after evaporator, juice and extracted sugars); cane sugar (spillage from extraction, clarification, evaporation, cooling, and condenser waters); wastes with a high water content such as garbage; and carbohydrate-based (starch, corn, potatoes, and wheat) materials” (Liu *et al.*, 1997; Pfaffin and Ziegler, 1998). Food wastes are sustainable raw materials to produce high value-added products (Lin *et al.*, 2013). Processing of fruits and vegetables (fennels, carrots, citrus, tomatoes) generate high amounts of wastes (Di Donato *et al.*, 2017; Teixeira *et al.*, 2018). These types of wastes are sources of polyphenol compounds.

Environmental Perspectives

It is essential to keep the earth clean for the next generations. Use of carbon-resources materials such as fossil resources (coal, oil, and natural gas), mainly yield in CO₂ emission and increase in pollution, because environmental disorders become more serious (Fomin and Guseev, 2001; Golomb and Fay, 2004; Sudesh and Iwata, 2008). Lignocellulose-based wastes accumulated in large quantities in nature every year resulted in environmental problems (Mishra and Thakur, 2015). Accumulation of forest and agriculture residues and food and beverage wastes without any processing or use of harmful processes such as burning and incineration also yield in environmental problems (CO₂ and heat generation) (Lee and Lin, 2007). Employing food wastes (FWs) for ethanol production yields in global greenhouse gas control, local or regional solid waste and water quality control (Moon *et al.*, 2009). In addition, employing FWs could be a beneficial alternative to conventional incineration and landfill disposals of FWs, which generated second environmental problems such as toxic or greenhouse gas emission, and underground-water contamination by leachates, respectively (Moon *et al.*, 2009). Traditional extraction for the recovery of the value-added materials such as phenolic compounds from vegetable and fruit wastes by toxic (methanol, ethanol, and other organic) solvents may also cause serious environmental problems (Antuono, 2009). In addition, long-term exposure of chemicals such as silica dust have been shown to increase risk of heart disease (McCarthy *et al.*, 2012). The effects of exposing human lung’s sub-mucosal cells to SiO₂ having various sizes (10, 150, and 500 nm),

for 2–24 h *in vitro* have been also studied (McCarthy *et al.*, 2012). The nano-toxicity of 10 nm SiO₂ on the sub-mucosal cells is associated with inflammation. Toxic effects was not observed from amorphous silica with 150 and 500 nm (Kasaai, 2015; McCarthy *et al.*, 2012). Smoke was formed by burning of straws, where it is harmful to people and animals. In addition, remaining all of the stovers and straws in the fields have negative impact on the environment, soil fertility, and its structure as well (Lopez-Bellido *et al.*, 2014; Maiorella, 1985). Various sources of plant-based waste feed stocks as the raw materials have been used for conversion into value-added components. The conversion procedures respecting environmental issues may not have adversely impact to the human food chains (Hossain *et al.*, 2017). In California, there has been much work, with limited success, in trying to develop markets for rice straw as a reactant to its burning (Nelson *et al.*, 2011). In conclusion, it would be an environmental benefit to recover value-added materials from renewable wastes using those procedures, considering environmental concerns, instead of using fossil fuels, and different toxic solvents.

Hazardous chemicals may cause long-term detrimental health effects. There are several types of hazardous chemicals (carcinogens, reproductive and systemic toxins, neurotoxins, immune and dermatologic agents). These compounds may cause physical and/or health risks (Eisler, 2007). Depending on the type of the hazardous involved, chemicals may cause cancer, birth defects, induce genetic damage, cause miscarriage, injury and death from relatively small exposures.

Wastes generated from different resources those can be converted into useful materials by different methods. Three different platforms have been employed for conversion of wastes, biomass or components of biomass into value-added materials as follows: Chemical; physical (thermochemical; supercritical fluid, “SCF”; and supercritical water, “SCW”), and biochemical procedures. Each platform has specific characteristics for the commercial processing, including range of feed-stocks and products, co-products, cost, scale, and stage of technology development (Nelson *et al.*, 2011). Therefore, it has become considerable economic interest to develop processes for effective treatments and employing them for their conversion into useful products (Akhtar *et al.*, 2015). Expressions and their corresponding abbreviations appearing in this manuscript are listed in Table 1.

High degree of crystallinity of cell walls (cellulose and hemicellulose) and their protection by lignin make very difficult for the accessibility of cell wall components by different procedures. The pretreatment would facilitate the accessibility to the cell walls by different methods. All of these methods should make the lignocelluloses available to the different attacks, where crystallinity of cellulose, its accessible surface area and protection by lignin and hemicellulose are the main factors in order to obtain an efficient hydrolysis. In addition, the efficiency and cost of the further processing were improved and reduced, respectively. The pretreatment methods include milling, irradiation, microwave, steam explosion, supercritical CO₂ and its explosion, alkaline hydrolysis, liquid hot-water pretreatment, wet oxidation, diluted- and concentrated-acid hydrolyses, and biological pretreatments (Taherzadeh and Karimi, 2008). Most of pretreatment procedures have diverse advantages, which make them suitable for industrial applications. Pretreatments using dilute acid and hot water are relatively intensive (Eggeman and Elander, 2005), whereas biological pretreatment are extremely slow (Sun and Cheng, 2002). Some technological (energy balance, solvent recycling, corrosion, environmental) should be taken into account in the selected procedures (Taherzadeh and Karimi, 2008).

In order to convert wastes containing carbohydrate polymers into fermentable mono-saccharides effectively, pretreatment must be initially applied on the wastes produced in forestry, agriculture and food to break apart the firm structures of cell wall components. During the last few decades, various approaches have been used as pretreatments for fermentable sugars (Alvira *et al.*, 2011; Gu *et al.*, 2012; Yu *et al.*, 2014; Isikgor and Becer, 2015; Min *et al.*, 2015). Each pre-treatment has shown to have unique advantages

Table 1 Abbreviations appeared in manuscript

Abbreviation	Expression, term
CHG	Greenhouse gas
DSFM	Deproteinized sunflower meal
FW	Food waste
H ⁺	Hydrogen ion or hydronium
HP	High pressure, hot pressurized
HPHT	High pressure high temperature
NFC	Nano-fibrillated cellulose
OH [−]	Hydroxyl ion
OSA	Octenyl succinic anhydride
PLA	Polylactic acid
SBCFE	Sub critical fluid extraction
SBCW	Sub-critical water
SCFE	super-critical fluid extraction
SCF	Supercritical fluid
SCFs	Supercritical fluids
SCW	Super critical water
TOC	Total organic carbon
WRF	White-rot fungi

and disadvantages. Rapidly growing polymer wastes yield in a demand to apply environmentally friendly methods for their conversion. Biodegradable polymers could be derived from renewable resources, e.g., cellulose, starch, chitosan, zein, and poly-lactic acid (PLA) (Ray and Cooney, 2018).

Conversion Methods

Chemical Methods

Lignocellulose can be destructed by chemical means (Taherzadeh and Karimi, 2008). Since the objectives of this study were to choose conversion procedures without any negative impact on environment, thus, dilute and edible acids or dilute bases were used for chemical conversions (Belitz *et al.*, 2009). Concentrated acids or bases and organic solvents have not been used in this study. These materials may cause environmental harms. In the production of chitin, protein and after calcium carbonate components were separated from crustacean shells. Separation of proteins (deproteinization) is performed by their treating with a diluted aqueous NaOH, and calcium carbonate component of shells (demineralization) is separated by dissolving in a dilute HCl at ambient temperature, while the solution is stirring continuously. The demineralization and deproteinization are repeated to remove all inorganic components and proteins in the crustacean shells. Proteins, calcium chloride, and carotenoid pigments are side products obtained from isolation of chitin (Van Luyen and Hough, 1996). Chitin is not soluble in most common organic solvents. Deacetylation of chitin, or introduction of alkyl chains, hydroxyl or carboxyl groups into chitin results in an improvement in its solubility, which promotes processing, and thereby widening its practical applications (Van Luyen and Hough, 1996). Lignocellulose can be also destructed by chemical means (Taherzadeh and Karimi, 2008).

Biochemical Method

Biochemical technology refers to molecular transformations using enzymes and micro-organisms. It is often accompanied with energy efficiency and product specificity (Nelson *et al.*, 2011). Biochemical processing, sometimes refers to the conversion of C6 and C5 sugars or carbohydrates derived from biomass through fermentation process to biofuel and bio-based chemical products. The conversion of the major component of natural renewable resources into ethanol is given in Fig. 2.

Micro-organisms play active roles in degradation of biological wastes. Anaerobic digestion involves different sets of micro-organisms with highly specialized metabolic activities. Different biochemical procedures result in almost complete degradation of organic materials present in the wastes. The diversity and distribution of the micro-origins are of critical importance to the stability and performance of the reactants (Schauer-Gimenez *et al.*, 2010). A group of filamentous fungi (white-rot fungi, WRF) are able to break down lignin (the most resistant component of plant cell walls to degradation process) into CO₂ (Joy *et al.*, 2016). Pretreatment (delignification) plays a critical role in enzymatic hydrolysis of forestry and agricultural wastes by different enzymes to achieve glucose and xylose. In the pretreatment procedure, enzymes can depolymerize cell walls (cellulose and hemicellulose) into

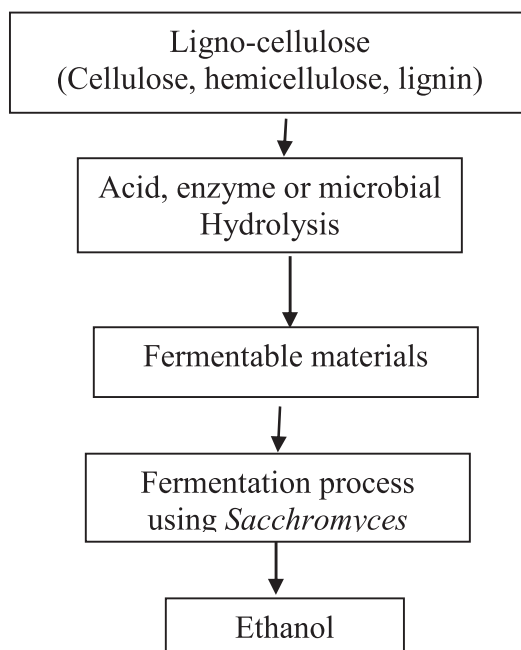


Fig. 2 Conversion of the major components of renewable resources into ethanol.

monomeric sugars. A pre-treatment for oil and fat industrial waste products (de-proteinized sunflower meal, DSFM), was proposed as an effectiveness procedure for their microbial conversion and based on the principles of green chemistry. Three factors such as amount of wastes per unit of the desired product, the amount of hazardous substances used in the pretreatment process, and process efficiency are involved in the proposed method (Makarova *et al.*, 2017). The proposed method was based on the experimental data obtained by chemical hydrolysis and pre-treatment process of DSFM comprising both chemical and enzymatic hydrolysis. The optimal DSFM pretreatment conditions were selected based on the calculated amounts of the process efficiency (Makarova *et al.*, 2017). Lignocellulose can be destructed by enzymes or micro-organisms as a preferred environmental friendly method in comparison with chemical or physical procedures (Taherzadeh and Karimi, 2008). Polysaccharides (cellulose and hemicellulose) can be also destructed by enzymes or micro-organisms into simple sugars, organic acids, acetone and glycerol (Joy *et al.*, 2016; Tomme *et al.*, 1995). Many micro-organisms are able to degrade cellulose and hemicellulose, while micro-organisms have consumed them as carbon and energy sources (Joy *et al.*, 2016).

Food waste (FW) is recognized as an environmental pollutant. However, it is as a valuable substrate containing large amounts of organic materials (soluble sugars, starch, cellulose, proteins, amino acids, fats, oils), and inorganic acids. A comparison evaluation of glucose yields of the FW broth pretreated with amyloglucosidase, carbohydrazase, and a mixture of both enzymes revealed that a higher glucose yield was obtained, when the enzyme mixture was used (0.46 g g^{-1} of dry FW), in comparison with only amylo-glucosidase (0.41 g g^{-1} of dry FW) or carbohydrazase (0.35 g g^{-1} of dry FW) was used. A high ethanol yield (0.23 g g^{-1} of dry FW) was obtained after 15 h of fermentation by *Saccharomyces Cerevisiae* (a species of yeast). The FW broth was hydrolyzed by the enzyme mixture. The yield was estimated to be nearly equivalent to the ethanol yields of lignocellulose biomasses (Moon *et al.*, 2009). Ethanol yield (expressed as ratio of the amount of ethanol produced to the amount of the mass of dry FW) depends on the original of wastes (FW, household waste, starchy biomass, i.e., molasses, sugar cane, corn, wheat, rice, rye, barley, and potato, lignocellulose biomass, i.e., bagasse, corn stover, wheat straw, aspen, willow, and spruce) (Moon *et al.*, 2009; Nakamura and Sawada, 2003; Thomsen *et al.*, 2003). The ethanol fermentation depends on the salt concentration (Hirasawa *et al.*, 2006; Moon *et al.*, 2009). The use of FW for ethanol production by enzymatic hydrolysis and ethanol fermentation by *Saccharomyces cerevisiae* suggests a promising practical approach to prevent environmental pollution (Moon *et al.*, 2009).

Rice straw was converted into nano-fibrillated cellulose (NFC) by a combined procedure of physicochemical pre-treatment and successively enzymatic hydrolysis. The NFC, is characterized by a long and distinct fibrillated cellulose, with a wide of 30–200 nm, exhibiting excellent water retention capacity ($20 \text{ g water g}^{-1}$), and swelling capacity (105 mL g^{-1}) (Yan *et al.*, 2018). Hydrophobic groups (octenyl succinic anhydride, OSA) were grafted onto the surface of NFC to prepare an innovative OSA–NFC as a dietary fiber with enhanced health benefits (such as bile acids, cholesterol, nitrite ion, and oil or fat adsorption) to increase adsorption capacity for oil *in vitro* ($17.8 \text{ g oil g}^{-1}$ fat adsorption after digestion model) and *in vivo* (almost $500 \text{ mg fat g}^{-1}$ feces of rats). OSA–NFC was used as a high-quality dietary fiber with a strong ability to absorb oil to help regulate body weight, representing an innovative way of transforming biomass into value-added products (Yan *et al.*, 2018).

Composting technology

Composting is the biological decomposition of organic materials under controlled aerobic conditions (Epstein, 2001). It can involve both procedures with mesophilic and thermo philic temperatures (Epstein, 2001). Over 80 microorganisms have been identified in composting (Epstein, 1997). The ultimate goal in composting is to produce a humus-like material, which is an excellent soil conditioner and can be used for numerous horticultural and agricultural applications (Epstein, 2001). Physico-chemical properties (moisture content, water retention, infiltration and permeability of water, structure, cation exchange capacity) of soils were improved using materials obtained from composting (Epstein, 2001). In other words, the composting materials can be used as a soil conditioner. The materials listed below are some of the feed-stocks that have been composted (Epstein, 2001): (i) Materials obtained from leaves; (ii) food wastes generated at homes, restaurants and food industries during different processes; (iii) coated papers and cardboards; and (iv) biodegradable polymers such as biodegradable plastic bags (Epstein, 2001). Some of them have been used in food packaging.

Many factors affected the composting process as follows: (i) Oxygen; (ii) moisture; (iii) temperature; (iv) concentration of H^+ or pH; (v) nutrients mainly carbon, nitrogen, and phosphorus; (vi) particle size and surface area; and (vii) chemical and physical nature of the feedstock materials (Epstein, 2001). The rate and extent of microbial decomposition of organic compounds, and biodegradation of polymers/plastics depend on the above-mentioned factors (Epstein, 2001). The efficiency of biodegradation is dependent upon the feedstock, the system, and maximizing the microbial system (Epstein, 2001). Composting provides an alternative method for managing agricultural, forestry, and food wastes. Description on different methods of composting and resulting products are out of the objects of this study. A review article on various composting methods, their applications, the advantages and disadvantages of composting in food processing industries have been found elsewhere (Schaub and Leonard, 1996).

Biofuel production

Fuels as energy sources for engines can be produced by fossil or agricultural resources (Golomb and Fay, 2004; Hettenhaus, 2011; Taherzadeh and Karimi, 2008). Due to different reasons and disadvantages of fossil fuels, biofuels were replaced (Taherzadeh and Karimi, 2008). Various sources of plant-based waste feed stocks as the raw materials have been used for the bio-ethanol production (Hossain *et al.*, 2017). Most of ethanol production is fermented using hexose sugars present in cane syrup and corn (Lin and Tanaka, 2006). The following components of renewable biomass have been used to produce fuel products (ethanol and

biodiesel, fatty acid methyl ester, FAME): (i) Cellulosic materials (cellulose or lignocellulose); (ii) starch feed-stocks (from corn). Starch (other than corn) from crop residues (iii) sucrose feed-stocks (sugarcane or sugar beet); (iv) triglycerides feed-stocks (oilseeds); (v) vegetative waste materials; (vi) foods and yard wastes (Kramer and Belanger, 2011). Biofuels mainly ethanol produced from corn starch, and cellulosic materials (Hettenhaus 2011; Taherzadeh and Karimi, 2008). The FW is a promising substrate for ethanol production via enzymatic hydrolysis and batch ethanol fermentation (Moon *et al.*, 2009). Japanese policy has shifted toward cellulosic feed-stocks (Bacovsky *et al.*, 2009; Procentese *et al.*, 2016; Zhao *et al.*, 2012). The target of displacing 10% of the domestic consumption of fossil fuels by around 2030, is based on the abundant unused biomass resources in Japan, mainly crop and forestry residues. Japan was one of the first countries to process wood for ethanol production (Tang *et al.*, 2006). In Brazil, petroleum-based fuels are considered as an alternative to biofuels. Brazil continues to pursue a balanced approach between the development of fossil and bio-fuels with consideration for environmental impact, feedstock production, food supply, and national security (Kramer and Belanger, 2011). Over the last two decades, wheat straw has been used for the development of cellulosic ethanol. Iogen is one of the world's largest companies in developing, designing, and scaling-up cellulosic biofuel technology (see "Relevant Websites section"). This company transforms cellulosic biofuels into reliable and cost-effective fuels for today's cars and trucks. Iogen's cellulosic biofuels technology incorporates all of the necessary steps required to convert a wide variety of cellulosic feed-stocks into ethanol and other biofuels. Iogen (see "Relevant Websites section") is used wheat straw as a major raw material. The company is planning its first commercial facility in Saskatchewan (Canada) that will utilize cereal straw feed stocks (Nelson *et al.*, 2011).

There are four steps for the conversion of biomass to ethanol: (1) Pre-treatment to remove lignin and hemicellulose; (2) enzymatic hydrolysis of cellulosic wastes to sugars (3) fermentation for ethanol production; and (4) purification of ethanol and other products (Miyamoto, 1997). The pre-treatment step has a positive impact on the amount and type of enzymes that are required for hydrolysis of cellulosic wastes to sugars (Howard *et al.*, 2011). Pretreatment is a well-investigated process for ethanol production from lingo-cellulosic materials (Taherzadeh and Karimi, 2008). Several pretreatment procedures have been presented for lignocelluloses and waste materials in order to improve ethanol or biogas production. All these methods should make the lignocelluloses available to the enzymatic attack.

Conventional fermentation (yeast fermentation), have been selected as an economical procedure for conversion of waste biomass-into-bioethanol. This is because, the "key fermenting agent" yeast, is readily available in local and international markets. It is more cost-effective in comparison with other fermentation agents. Furthermore, yeasts are natural materials having fermentation capability and no chemical hazardous wastes are produced. Ligno-cellulosic wastes were also converted into biological compounds using different types of yeasts and fermentation processes (Hossain *et al.*, 2017).

Fermentation processes were employed to produce ethanol from can juice, sugarcane molasses (Kramer and Belanger, 2011), and cellulosic agricultural wastes (straw obtained from wheat, rice, barley, rye, corn and cobs). Pre-treatment was used to increase efficiency of enzymatic saccharification followed by alcohol fermentation, and to increase the accessibility of cellulose to cellulases (Huang *et al.*, 2017). The sugars are then converted into ethanol by the yeast fermentation. As the second-generation of biofuels, ethanol derived from lingo-cellulosic feed-stocks eliminates the food-fuel issue associated with sugar/starch feed-stocks and has also been shown to have a much more favorable net energy balance and lifecycle GHG reduction than corn (starch-based) ethanol. Within the "biochemical platform" other research is also developing new bacterial organisms and genetically modified yeasts were used to convert both C6 and C5 sugars to other biofuel and chemical products, with perhaps the most advanced efforts directed to produce butanol, an important industrial chemical and possible second-generation biofuel (Nelson *et al.*, 2011).

Physical Methods

Thermal degradation

A thermal treatment is defined as a treatment of a compound in a device, when the temperature is elevated as the primary means to change the composition or characters (chemically, physically, and biologically) of the compound. The major reduction in molecular weight occurred initially in thermal heating of polysaccharides (Belitz *et al.*, 2009; Fennema, 1996). No change in molecular size was observed after further heating. Incineration research for solid waste destruction has been fairly minimal the mid-1970s. The basic principle of solid waste incineration is similar to that of conventional fossil fuel combustion (Lee and Lin, 2007). Combustion or incineration is a very complicated subject.

Thermal degradation of polymers is associated with a series of chemical reactions via chain scission. The chain scission is usually followed by multistep free-radical mechanisms (initiation, propagation, and termination) (Ray and Cooney, 2018). Thermal degradation of polymeric materials generally implies the associated changes at inert atmospheric conditions. Under normal atmospheric conditions, oxygen plays a crucial role in the degradation process. The decomposition of biopolymers is accelerated by the presence of oxygen (Ray and Cooney, 2018). Lignocellulose can be destructed by heat (Taherzadeh and Karimi, 2008). Decomposition of most biodegradable polymers starts at an early stage, followed by a multistep degradation. In the presence of air, the glass transition temperature (T_g) (it is the critical temperature that separates glassy behavior from rubbery behavior. Many amorphous solids, including natural polymers and biopolymers, exhibit glass transition temperatures), profiles of these polymers look quite similar to that obtained in an inert atmosphere, except the primary degradation starts at comparatively a lower temperature (Cowie and Arrichi, 2007).

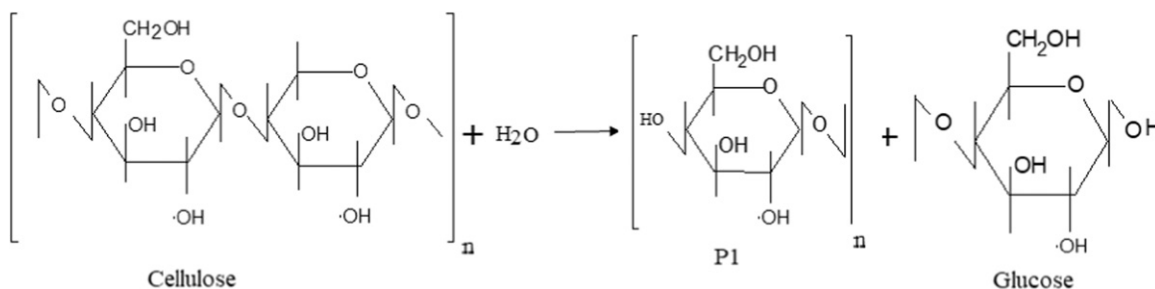


Fig. 3 Hydrolysis of cellulose.

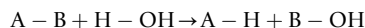
Hot pressurized method

Hot pressurized fluids

A possible alternative to hydro-distillation or solvent extraction could be represented by the use of sub- or super-critical fluid extraction (SBCFE or SCFE) technique. It is based on the utilization of a fluid at sub- or super-critical conditions (Antuono, 2009). For instance, supercritical carbon dioxide has been used for decaffeination of coffee (Zosei, 1978). High pressure (HP), induced different changes (inactivation of microorganisms or enzymes, denaturation of proteins, and conversion of raw materials into useful components). These changes correlate with the food safety, and the food quality (Claeys *et al.*, 2003).

Hot pressurized water, near critical water and sub-critical water

Water is used in food industries as a safe and a non-toxic medium. Under different pressure and temperature conditions, it plays an essential role in producing value-added products from wastes generated in the land or marine. Hot pressurized water has a high reactivity. Hydrolytic reaction is a common process that occurs in water under high pressure-high temperature (HPHT) conditions. Raw materials (A-B) is hydrolyzed by water according to the following reaction (Brunner, 2009a,b):



The above equation shows a chemical reaction (a chemical reaction is a rearrangement of reactants to create different substances as products). The illustrated equation is a generation form of a hydrolysis reaction, where water (H-OH) is a reactant and another reactant (A-B) can be a component of a waste (from example, cellulose) as shown in Fig. 3:

The products of the above reaction are glucose and P1. The P1 has a similar structure of cellulose and its size is smaller than that of the original cellulose. The reaction can be continued with the product P1 as a reactant in a similar fashion as the above-mentioned (BeMiller, 1967; Kasaai *et al.*, 2013; Lazar *et al.*, 1989; Timell, 1964; Zaikov, 1975).

Water under HPHT with a low viscosity and a high diffusivity enhances reaction rates. Hydrolytic reactions occurred in the medium of hot pressurized water are often accompanied with thermal reactions (pyrolysis). The higher the temperature, the greater is the extent of thermal reactions. Either H^+ or OH^- ions generated from water under different temperature and pressure conditions play as a reactant role for fragmentation of biopolymers. The availability of protons increases by dissolving CO_2 in water (Brunner, 2009a,b). The reactions result in smaller macromolecules, oligomers and monomers. Large macromolecules of biopolymers may not be useful as much as the fragmented samples (smaller macromolecules, oligomers and monomers). The fragments containing large amounts of accessible nutritional components can be used as foods for humans. Abundant polysaccharides (such as cellulose and starch) or materials containing proteins can be hydrolyzed, under HPHT conditions and converted into smaller macromolecules, oligomers and monomers (mono-saccharides and amino acids). Under HPHT conditions "concentration of H^+ and OH^- as well as the ion product for water" increases. Change in concentration of H^+ or OH^- influences the results of acid or base hydrolysis (Arai *et al.*, 2001). Using hot pressurized water, polysaccharides, lipids and proteins have been extracted or decomposed. Polysaccharides (starch, cellulose, hemicelluloses, chitin, chitosan, etc.), and materials containing proteins (mainly from animal tissues: Skin, hair, feathers), can be transformed into smaller macromolecules, oligomers and monomers (mono-saccharides or amino acids) under HP conditions (Brunner, 2009a,b; Kasaai *et al.*, 2003; Knez *et al.*, 2018; Lamoolpha *et al.*, 2006). Hydrolysis of polysaccharides and proteins under hot pressurized water resulted in glucose and amino acids, respectively. Glucose and amino acids particularly essential amino acids are food components (Belitz *et al.*, 2009; Berg *et al.*, 2002; Brunner, 2009a,b).

Supercritical water

Under supercritical conditions, water acts as a medium or a reactant, and oxygen as an oxidizing agent. Under these conditions, water exhibits gas-like diffusion along with a high liquid-like collision rate, and the oxidation process takes place in a homogeneous mixture (Brunner, 2009a,b).

Cellulose has been completely converted into smaller molecules under SCW conditions at 400°C. Most of products obtained from cellulose decomposition were glucose, fructose, and oligomers of glucose (cellubiose, cellotriose, cellotetraose, cellopentaose and cellohexasose). Hydrolysis of cellulose under SCW conditions is a promising technology (Arai *et al.*, 2001). Under SCW conditions, combination of extraction and decomposition of polysaccharides, proteins and lipids can be occurred (Arai *et al.*, 2001; Brunner, 2009a,b). Higher efficiency, environmental more safety, and superior quality are the major advantages of extraction by SCF over the conventional extraction. Near critical and SCW have been used to enhance extraction affinity of value-added compounds

(proteins, amino acids, essential oils, oils, fatty acids, carbohydrates, and phenolic compounds) from natural sources (Knez *et al.*, 2018). Production of proteins and amino acids is strongly influenced by temperature (Lamoolpha *et al.*, 2006). Degradation of biomass under sub critical water (SBCW) or SCW cannot be easily described by well-defined single reaction steps, due to the complex degradation pathways of the products (Sinag *et al.*, 2010).

Oxidation procedure of wastes under SCW conditions is an alternative procedure to treat different wastes with a high water content like garbage. Materials from groups of vegetables, meats and fishes were easily oxidized under SCW conditions (Jin *et al.*, 1999). Fatty meats “particularly beef suet” were most difficult to decompose among different components of garbage (Jin *et al.*, 2001). Treatments of carrot and beef suet under SCW conditions were carried out in a bath reactor system with H_2O_2 as an oxidant at a temperature between 400 and 450°C and reaction times from 10 s to 10 min. The results showed that the oxidative decomposition of carrots and beef suet proceeded rapidly and a high total organic carbon (TOC) decomposition of up to 97.5% was obtained at 420°C within 3 min, for carrots and at 450°C within 5 min for beef suet, when there was a sufficient supply of oxygen. The oxidation reaction on carrot and beef suet might be separated into a fast reaction at the early stage and a slow reaction at the latter stage (Jin *et al.*, 2001). The SCW is a good medium for an oxidation process, because oxygen and many organic substances are soluble in the SCW (Brunner, 2009a,b; Franck, 2000). Organic wastes are decomposed or oxidized under SCW conditions in the presence of oxygen (air) (Savage, 2009). Food ingredients with desirable sizes have been produced by fragmentation of large macromolecules using SCW. Water under above-mentioned conditions are not only reaction medium, but also is a reactant. Thus, water as a reactant leads to hydrolysis of reactants, leading to rapid degradation of complex biomass structure such as hydrolysis of cellulose to sugars (Sinag *et al.*, 2010). Global kinetics analysis is described that the early stage is an oxidative reaction of beef suet could be considered as the first-order reaction with respect to the concentration of organic carbon. Polysaccharides “major components of carrot” are initially hydrolyzed to glucose, and then, glucose is being oxidized. Triglycerides “the major components of beef suet” have been initially hydrolyzed to glycerol and carboxylic acids, followed by oxidative decomposition of the further products through consecutive reactions have been occurred.

Comparison of Various Methods of Conversion

Advantages and disadvantages of several methods are given in Table 2. A comparison evaluation of various methods of the conversion in terms of their effects on the conversion procedures (extraction, hydrolysis, decomposition, de polymerization), and from the standpoint of ease of preparation of the useful products, enables one to conclude as follows: (i) Various renewable (agricultural, forestry, beverage, food) macromolecules are decomposed by a variety of enzymes, and micro-organisms into smaller than that of the original ones; (ii) polysaccharides are degraded by acids or enzymes and yielded in a mixture of low molecular weight polysaccharides, oligosaccharides and mono-saccharides (Belitz *et al.*, 2009; Fennema, 1996); (iii) biochemical methods have advantageous over physical and chemical (acid hydrolysis) methods, because they are easy to perform at ambient temperature. These methods can be easily be controlled, due to their low reaction rates. The enzymes and micro-organisms are naturally exist in soils or commercially available with a low price. However, the efficiency of natural enzymes and micro-organisms are significantly lower than that of the commercial ones with a high purity; (iv) physical methods have advantageous over chemical methods, because they do not need chemical reagents, but the equipment for the physical processes are expensive. The incineration procedure (as a traditional, thermal, and a decomposition procedure) is an efficient one, however it is not an environmentally suitable approach. In addition, several useful organic compounds destroyed and may be converted into hazardous compounds; and (v) chemical methods are advantageous over enzymatic and physical methods due to the low cost of chemical reagents and relatively good and reasonable efficiency. However, use of diluted acids or bases as a hydrolytic reactant has a practical limit of conversion. In conclusion, depending on the procedure used and the reaction conditions employed, a variety of products can be obtained (Lee and Lin, 2007; Lin *et al.*, 2013).

Table 2 Comparison of different conversion procedures for wastes derived from land (agriculture, forestry, food, beverage) and marine sectors

Method/procedure	Advantages/performances	Disadvantages/limitations
Chemical	Does not need special apparatus; easy to perform, low cost for the chemical reagents; generally the efficiency of conversion is good. However, the efficiency and reaction rate depend on the concentration of chemical reagent and temperature of the reaction	Needs chemicals; generate hazardous wastes; negative impact on the environment
Biochemical (Enzymatic)	The efficiency depends on the purity of enzymes; better control of the process; natural enzymes and microbes are available in soils	Commercial enzymes with a high purity are expensive
Physical (hot pressurized water, SBCW, SCW)	Does not need chemicals; short time is needed to process, environmentally are safe	High amounts of energy are needed; high technology is required
Physical (Thermal)	Does not need chemical reagent	A part of energy/heat is lost; the conversion products oxidized by oxygen (air); negative impact on the environment

Table 3 Conversion procedures for different types of wastes, by products and their applications

Source of wastes	Type of wastes	Conversion process	By products	Applications	Remarks
Agriculture and forestry	Leaves	Size reduction physically (by mill); mix the powdered leaves with soils	Organic soils	Fertilizers for soils and plants	Leaves mainly contain organic compounds
Agriculture and forestry	Leaves and Peels	Extraction	Phenolic compounds, antioxidants, vitamins	As food additives, antioxidants, vitamins	Leaves from different sources contain different value-added components
Agriculture	Rice straw	Separation of silica from rice straw (digestion with NaOH solution and followed by an acidification step)	Silica,	Silica as a filler for coatings and packaging's	Rice straw contains sufficient amount of silica
Agriculture	Straws from cereal grains (wheat, rice, oat, rye, and barley),	Enzymatic hydrolysis; fermentation	Sugars (glucose, xylose)	As by products for foods; as raw materials for bio-fuels (ethanol).	Straws can be used as animal bedding, feeds,/ fodder, basket-making
Agriculture, forestry, and food	Straws, wastes containing starches or lingo-cellulosic biomass from different crops food, and yard resources	Hydrolysis, and fermentation	Biofuels (ethanol, propanol, butanol)	As energy source for engines;	Starch-based biomass is major components of crop and some plant wastes Ligno-cellulosic biomass is, renewable resources on the Earth and obtained from forest and agriculture residues

Value-Added Materials From Different Wastes

Different naturally occurring and food wastes can be used for production of value-added components as follow: (i) C6 and C5 sugars (glucose and xylose). These sugars are monomer units of carbohydrate polymers (Belitz *et al.*, 2009; Jager and Büchs, 2012); (ii) biofuels (mainly ethanol), organic acids, and food additives (Mishra and Thakur, 2015); (iii) leaves may be converted into smaller sizes. The smaller sizes of leaves can be mixed with normal soil and produced organic soils. The organic soils may be used to fertilize the normal soils for various plants. Plant leaves like dark green leafy vegetables “are rich sources of phenolic compounds, and lipid-soluble antioxidants”. Alpha-tocopherol (vitamin E) and beta-carotene (precursor to vitamin A) were derived from leaves. Their recovery from plant leaves could provide a valuable source of natural vitamins. Alpha-tocopherol was recognized as the main antioxidant compound derived from leaf extracts of 15 plant species (Booth, 1963; Mukhopadhyay, 2000). Tocopherol content could be enriched by hexane extraction up to 4.7% (Booth, 1963; Mukhopadhyay, 2000); (iv) corn stover, straw and leaves are major components of forest and agriculture residues. Corn stover and straw may be discarded in the farming fields to degrade in the nature, burning to generate energy as heat, or may be used as a cattle feed (Lopez-Bellido *et al.*, 2014; Maiorella, 1985); (v) straw, an agricultural by-product (the dry stalks of cereal plants), obtained from the harvested crops, after the grain and chaff have been removed. Straw makes up about half of the yield of cereal crops (wheat, rice, barley, oat, rye). It has many applications “including fuel, livestock bedding and fodder, and basket-making” (Hettenhaus, 2011). The straw of rice is rich in silica content. Silica obtained from the straws has been used as a filler to make composite, construction, and packaging materials (Nelson, *et al.*, 2011). Wheat straw has been used for animal bedding, fodder, and feeds (Nelson, *et al.*, 2011); (vi) plant and food wastes are the most common ones, in which their applications are progressing (Schauer-Gimenez *et al.*, 2010). The extracts materials from citrus wastes (leaves and peels) were efficient materials for the stability against oxidative reactions of the Kraft Papers. The kraft paper treated by citrus wastes can be used for food coatings and food packaging to protect foods from moisture and oxygen deteriorations and to extend their shelf-life (Kasaai and Moosavi, 2017). Oxygen and water barrier properties and antioxidant activity of the treated papers were improved; and (vii) in some cases, the heat generated by incineration can be used to generate electric power. The different wastes were also employed to convert energy such as heat and electricity, for instance, residual sugarcane bagasse was used to generate electricity in Brazil (Gopale and Kammen, 2009). The waste materials are converted into “ash, flue gas and heat” by incineration process. The ash is mostly made of inorganic compounds and may take the form of “solid lumps or flue gas” (Lee and Lin, 2007). Conversion procedures for different types of wastes into “by products and their applications” are presented in Table 3.

Conclusions

The following conclusions are drawn: (1) Wastes generated in the land (forestry, agriculture, beverages, and food), marine, and food sectors are initially described; (2) several substances potentially present in the wastes can be converted into useful

components by pretreatment and further major processing as follows; (i) chemical; (ii) physical (thermal, super-critical fluids, supercritical water); and (iii) biochemical (enzymes, and microorganisms). This study mainly focused on the procedures with environmental perspectives. Biochemical (hot pressurized water, SBCW and SCW) procedures represent as safe and green ones; (3) some useful products obtained from different wastes are "different components of sugars in particular (glucose and xylose), polyphenols as antioxidants and oxygen scavengers, beta-carotene (precursor to vitamin A), alpha-tocopherol (vitamin E), biofuels (ethanol), soil and plant fertilizers, and silica from straws for coatings and packaging composite materials applications" and (4) the final products can be used as foods, feeds, fertilizers of soils and plants, fillers, or animal beds. The value-added products can be also employed for other commercial applications as well.

Future Perspectives

Applications of desirable methods as well as emerging processing with environmental perspectives to convert renewable wastes into value-added components offer a good opportunity to avoid further destruction and pollutions of this planet. To protect this planet for the next generations, all of governments from different countries, commodity groups, manufacturers, research groups, consumers, and in general, human beings must follow a desirable direction for conversion of various wastes into value-added products.

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Energy Storage Device From Polymeric Waste Based Nano-Composite by 3D Printing

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Introduction

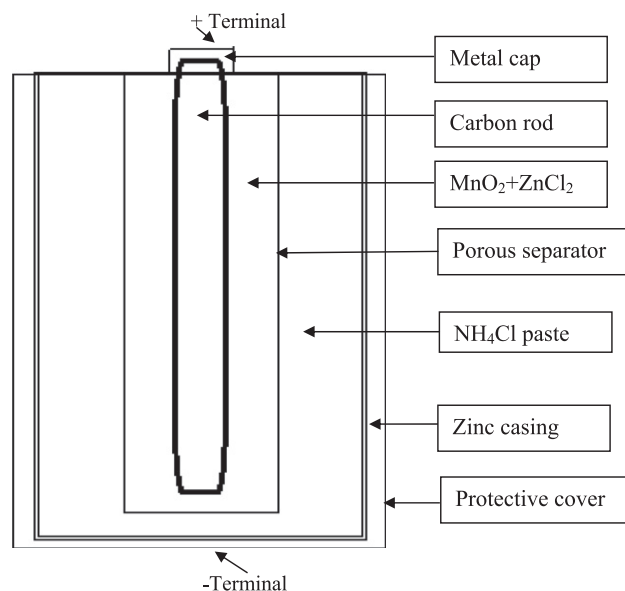
3D printing, a disruptive manufacturing technology, has emerged as an innovative approach to fabricating electrochemical energy storage (EES) devices from nanoscale to macroscale, providing great opportunities to accurately control device geometry (e.g., dimension, porosity, and morphology) and structure with enhanced specific energy and power densities. Moreover, the “additive” manufacturing nature of 3D printing provides excellent controllability of the electrode thickness with much simplified process in a cost-effective manner. With the unique spatial and temporal material manipulation capability, 3D printing can integrate multiple nano-materials in the same print, and multi-functional EES devices (including functional gradient devices) can be fabricated (Shaheen *et al.*, 2005; Sun *et al.*, 2014). The direct material deposition characteristics of these two processes enable them to print on a variety of flat substrates, even a conformal one, well suiting them to applications such as wearable devices and on-chip integrations. Fused deposition modelling (FDM) is one of the efficient process among 3D printing techniques which have the potential to print recycled plastic solid waste as per tailor made applications (Kumar *et al.*, 2017a,b, 2018; Singh *et al.*, 2016, 2018a,b,c). It has been reported that modified two-step in-situ reduced method is used to synthesize reduced graphene oxide (r-GO) (whose electrical conductivity can reach up to 600 Scm^{-1}) which can be easily blended mechanically/ chemically in thermoplastic materials. Some studies have reported that polylactic acid (PLA) and r-GO was mixed by melt blending. These types of reinforcements in plastic solid waste can be used for addressing the waste management issues. The 3D print-used composites filaments with the diameter of 1.75 mm are usually fabricated through melt extrusion. The orientation of r-GO occurs during the extrusion process, which contributing to increase the conductivity of the filaments. The composite also exhibit superior mechanical properties like elastic modulus, ultimate tensile strength may be because of meta material formation (Leigh *et al.*, 2012; Guo *et al.*, 2013; Molina *et al.*, 2014). The printed 2D and 3D flexible circuits have strong interface bonding force between the layers. The filaments from 3D printer can replace the copper wire because of the high conductivity. This arbitrary 3D graphene-based structure printing technique may open a new prospect in electronic and energy storage fields. To create the micro battery, a custom-built 3D printer extrudes special inks through a nozzle narrower than a human hair. Those inks solidify to create the battery's anode (red) and cathode (purple), layer by layer. A case then encloses the electrodes and the electrolyte solution added to create a working micro battery. The inks contain nano-particles of a lithium metal oxide compound that give the anode the proper electrical properties. The printer deposits the inks onto the teeth of two gold combs, creating a tightly interlaced stack of anodes and cathodes (Gross *et al.*, 2014; Tekinalp *et al.*, 2014). After this the researchers packaged the electrodes into a tiny container and filled it with an electrolyte solution to complete the battery (Leigh *et al.*, 2012; Guo *et al.*, 2013; Molina *et al.*, 2014). Organic semiconductor based photovoltaic devices offers the possibility of manufacturing low cost photovoltaic technology that can be 3D printed by roll to roll printing techniques. Existing organic photovoltaic devices are currently limited to solar power conversion efficiencies of 3%–5% (Shaheen *et al.*, 2005).

Graphene is two dimensional materials which has extraordinary material characteristics like: high Young's modulus, ability to thermally and electrically superconductive (high mobility of charge and electron), surface insulating behavior and large aspect ratio for prototype fabrication. Graphite is a low cost raw source for extraction of graphene (Kumar *et al.*, 2017b). Graphene generally extracted via different methods of processing like; chemical vapour deposition (CVD), micromechanical exfoliation, and ball milling etc. (Su *et al.*, 2011; Calderon-Ayala *et al.*, 2017). FDM process as a 3D printing technique with feedstock prepared on twin screw extrusion process can be one of the best alternative for production of electrically conducting nano-porous polymeric composite materials for energy conversion and storage (Kumar *et al.*, 2018). Mechanical properties of FDM fabricated parts are highly dominated by their filament processing. The mechanical sustainability of the fabricated parts are dependent upon the nature of processing of the initial component (grinding, extrusion etc.). Barrel temperature, rotational speed and torque are some of the input variable during the filament processing which largely affects the mechanical sustainability of the FDM fabricated parts (Singh *et al.*, 2017a,b,c,d, 2018d). FDM is one of the economical ways for 3D printing of thermoplastic composite with nano-particles (with use of extrusion process) for development of energy conversion and storage devices. The 3D printed parts may be used in 4D applications as because non conducting thermoplastics have been made conducting with reinforcement of nano particles.

In this work a frame work has been proposed for FDM process based printing of electro chemical storage device from polymeric waste based nano-composite. The proposed methodology will lead to waste management (especially plastic solid waste) for sustainable manufacturing. This will reduce the cost of formation of dry cell which can be easily. The proposed process is cost effective since the material used in making cell as energy storage device is industrial waste (available in abundance) and can be used number of times. Hence it is highly commercially viable. Table 1 shows the merits and demerits of commercial and 3D printed ESD.

Table 1 Merits and de-merits of commercial and 3D printed ESD

<i>Conventional ESD</i>	<i>3D printed ESD</i>
(1) The commercial ESD (mainly commercial dry cell) comprises of different zones/sections of chemicals/salts for initiating a chemical reaction (for converting chemical energy in to electrical energy), which is being put in different forms like powder/paste/slurry in a zinc container resulting into compact structure (2) The advantage with conventional ESD is that since the chemicals/salts are in direct contact with each other, the chemical reaction is relatively fast and one can get high potential difference value	(1) Whereas the 3D printed ESD is directly printable in form of different layers which are assembled in series to provide required potential difference. Since different zones are printed and assembled the final structure is not that compact (2) Where as in 3D printed ESD the chemicals/salts are blended in thermoplastics, so the chemical reaction is little slow and one needs to add catalyst for initiating the chemical reaction But the advantage of 3D printed ESD is: (i) Design flexibility, that means any contour/shape of ESD can be printed (ii) No specific container for putting the chemicals/salts is required. (iii) As the 3D printed ESD are acting as container for chemicals/salts itself additional shell covering is required (iv) The 3D printed ESD are more thermally stable under extreme environment conditions (both hot and cold)

**Fig. 1** Construction of dry cell.

Conventional Dry Cell and Proposed Modification

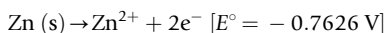
Existing Dry Cell and its Construction

The concept of a dry cell was invented by French scientist G. Leclanche in 1868. As this cell is free from any liquid for its chemical reactions, so it is termed as dry cell. **Fig. 1** shows the basic construction of a dry cell which is composed of number of successive layers for the internal terminal known as carbon rod (positive electrode) to external terminal known as zinc terminal (negative electrode).

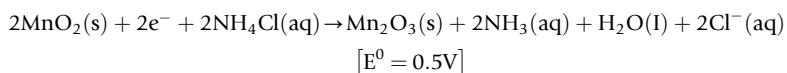
The carbon rod is placed in centre of the dry cell which is being covered by crushed coke and MnO_2 and bagged in the canvas material. The mixture of both is act as the de-polarizer. This de-polarizer material is providing the resistance to hydrogen bubble formation during chemical reactions. The de-polarizer is actions to take the electron during discharge and is basically an oxidizing agent. The paste of ammonium chloride and zinc chloride is act a electrolytic material to support the chemical reactions for energy formation. The electrolytic mixture is covered by saw dust and pitch compound to provide the ventilation to the electrolyte during chemical reactions. Every portion of the battery device has chemical reactions occurring in it. While a reduction reaction occurs at the carbon electrode, oxidation occurs at the zinc casing, which is the anode.

In Zinc-carbon dry cell, the carbon rod acts as cathode, whereas zinc acts as anode. The dry cell results in flow of electron as an oxidation reaction at zinc terminal whereas reduction reaction as carbon rod terminal

The zinc terminal is get oxidized by following oxidation half reaction;



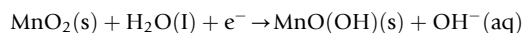
At cathode, the MnO_2 is get reduced by following reduction reaction;



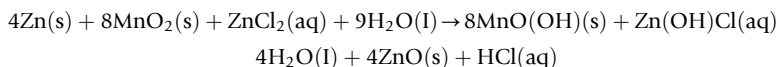
Overall reactions are represented as;



Here, one need to know that zinc chloride is another replacement of ammonium chloride, when ammonium chloride is replaced by zinc chloride then the cathode reactions can be followed as;



Then the overall reaction is processed as;



Unlike a wet cell, a dry cell can operate in any orientation without spillage, (as it contains no free liquid). The wet cells are in fragile glass containers with lead rods hanging from the open top and needs careful handling. A common dry cell produces the electromotive force of about 1.5V. Overall capacity of the dry cell is dependent upon the side reactions and active chemical content. Commonly Zn-C cells have small shelf life as Zn is attacked by NH_4Cl . The Zn container becomes thinner as the cell is used, as because Zn metal is oxidized to Zn^{+2} . When the Zn covering thins enough, ZnCl begins to leak out of the battery. The Zn casing in the dry cell gets thinner even when the cell is not being used, because NH_3Cl inside the battery reacts with the Zn.

Construction of New Dry Cell by 3D Printing

In this study, before printing a dry cell a filament can be developed by mixing different chemical/salts (nano scaled) used in conventional dry cell with acrylonitrile butadiene styrene (ABS)/or other commercially available polymeric waste by using twin screw extruder. After preparation of feedstock filament, it was fed into commercial FDM system (without change in any hardware/software of the system) which print a dry cell layer by layer. As a result, a complete dry cell is printed from a single work station (see Fig. 2).

Fig. 3 shows process flow chart for 3D printing of dry cell.

The reinforcement of chemical/salt with recycled ABS (collected from industrial waste) starts with different proportion/composition, which was poured in to melt flow index machine (as per ASTM D1238) to ensure fluidity/flow ability properties of

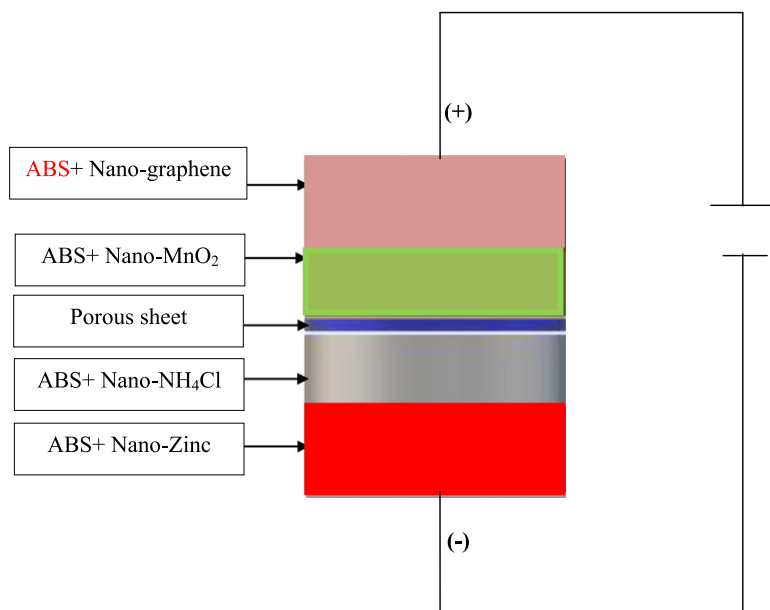


Fig. 2 Various zones of 3D printed dry cell.

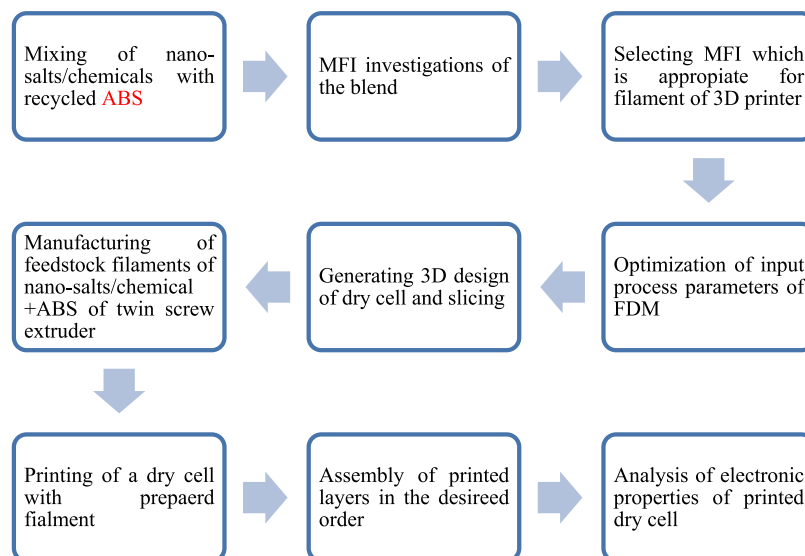


Fig. 3 Flow chart for 3D printing of dry cell.

different reinforcement in polymer matrix. The experimental investigations were performed to set range of all proportions/compositions, so that their MFI values for different type of reinforcements remain close to each other. It has been observed in pilot experimentation that selected recycled ABS with MFI of 2.5 g/10 min resulted into MFI of 2.0–2.3 g/10 min with various reinforcement: (i) ABS + 50% Zn powder, (ii) ABS + 40% nano scaled NH_4Cl , (iii) ABS + 50% nano scaled MnO_2 , (iv) ABS + 10% nano scaled graphene. Due to modified range of MFI for all reinforced materials there is no requirement to change the parameters of FDM while printing of dry cell.

Performance Properties of Graphene Reinforced ABS Waste Composite

There are two basic methods available for mixing of graphene into polymer matrix: mechanical mixing and chemical mixing. The mechanical mixing is the process of mixing graphene into polymer matrix by using twin extrusion process in which granules of polymer matrix mixed with graphene through the compound screws of twin screw extrusion. In chemical mixing, granules of polymer and graphene are being treated under dissolution of chemical (As ABS is being dissolve in acetone solution) During pilot experimentation electrical and thermal conductivities of graphene reinforced ABS (prepared with chemical/mechanical means) were observed. It has been reported that chemical mixing of graphene reinforced ABS polymer matrix resulted in maximum electrical and thermal conductivities for ABS: graphene ratio of 75:25 at 100% infill density. So it is ascertained that mixing of graphene into polymer matrix largely influences the electrical and thermal characteristics.

Graphene is an extraordinary material that is now days used largely to produced nano-porous materials. Graphene also has inherent material characteristics like: excellent thermal and electrical conductivities, high mechanical strength and etc. In the proposed method of 3D printing for development of energy conversion unit a thermoplastic matrix used as main material. As ABS is having excellent moulding stability so this can be selected as for fabrication of conducting as well as non-conducting layers. ABS is a non-conducting material, but when reinforced with nano-sized graphene into its matrix the excellent thermal as well as electrical conductivities can be achieved. [Kumar et al. \(2017b\)](#) outlined that thermal as well as electrical conductivities of recycled ABS polymer matrix can be modified by reinforcement of graphene powder (See [Figs. 4\(a\)](#) and [\(b\)](#)).

Methodology for Electrochemical Dry Cell From Polymeric Waste

Initially the (chemical or mechanical) blend of nano sized reinforcement in ABS matrix in form of pallets was prepared. Pallets of blended nano sized reinforced ABS polymer was processed into the melt flow index (MFI) tester for ensuring the flowability in g/10 min of the blend as per ASTM D 1238 standard. The MFI value in g/10 min is selected based upon the FDM settings so that there is no need of change any hardware/software during printing for different types of reinforcement selected. If the MFI of different blended materials falls in the acceptable/similar range then the printing is performed smoothly. After establishing MFI of various blends, selected composition/blends are further processed on twin screw extrusion machine to prepare the feedstock

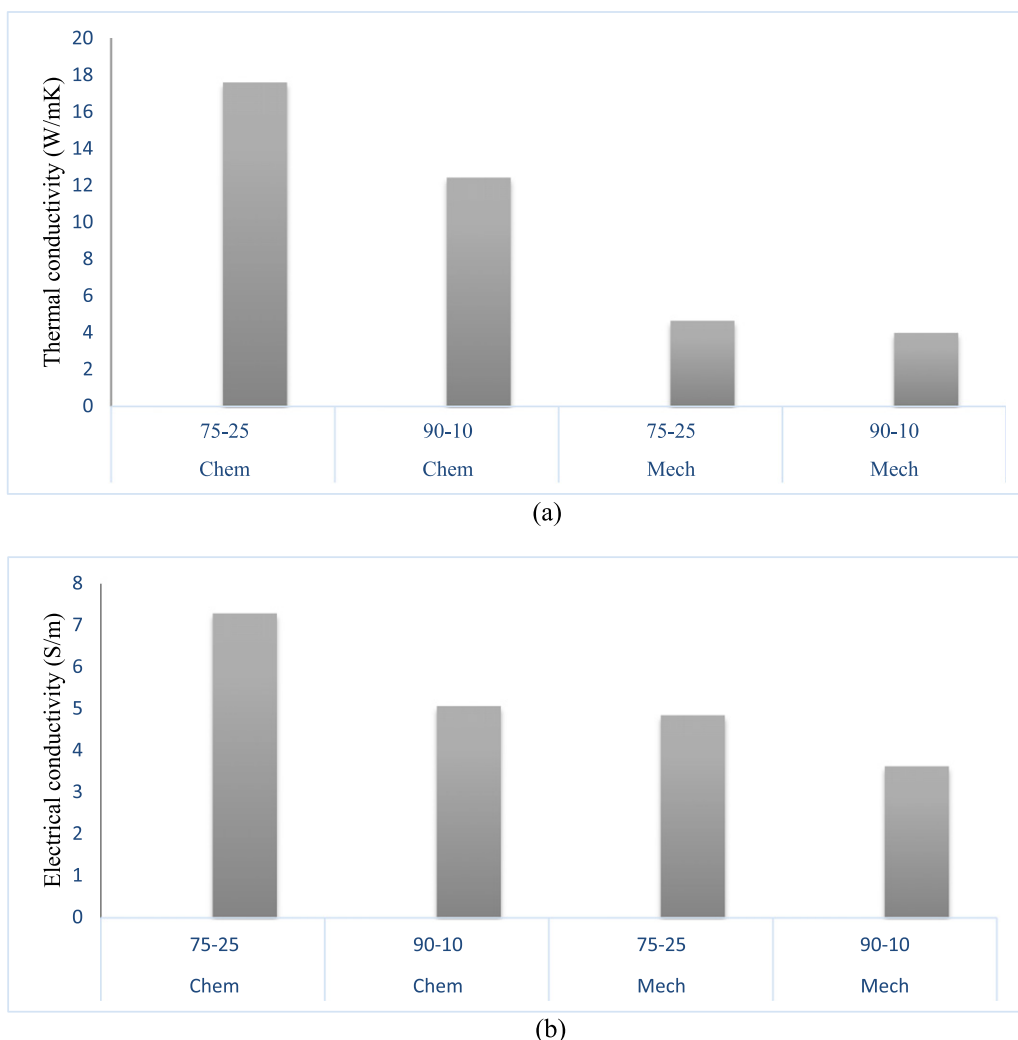


Fig. 4 (a) Thermal conductivity of graphene reinforced recycled ABS. (b) Electrical conductivity of graphene reinforced recycled ABS. Reproduced from Kumar, R., Singh, R., Hui, D., Feo, L., Fraternali, F., 2017b. Graphene as biomedical sensing element: State of art review and potential engineering applications. *Composites Part B Engineering* 134, 193–206.

Note: 75–25 and 90–10 is the proportion of ABS-Graphene in weight percentage. It has been observed that chemically processed blend of ABS-Graphene at 75–25 weight proportion is better from thermal and electrical conductivity view point.

filaments of 1.75 mm diameter. The design software is used to generate the required layers and design of the dry cell component. Finally at optimized input process variable settings, component of the dry cell are printed and assembled in a fashion given in Fig. 2. Further for investigation of performance of dry cell, output voltage, thermal analysis by differential scanning calorimetry (DSC) and mechanical properties needs to be ascertained.

In order to ascertain the stability of recycled ABS reinforced materials; at extreme temperature variations (in which ESD can work) the thermal condition of different zones has been monitored with DSC. For thermal analysis METTLER TOLEDO, Model DSC3, Swiss make with STAR^e (SW 14.00) software (as per ASTM E794–06(2012)) was used in air environment. Figs. 5(a) and 5(b) shows the DSC based thermograph for ABS: MnO₂ as 50:50 (curve 1), ABS: graphite fixed as 60:40 (curve 2) and ABS: ZnCl₂ + NH₄Cl as 60:40 (curve 3).

As observed from Fig. 5a, in two repeated heating cooling cycles, the T_g is above 95°C. Hence it can be ascertained that all the four zones of ESD can be successfully operated up to this temperature range. Further as observed from Fig. 5b the heat absorbed/released per unit g for all three different reinforcements (see curve 1, 2 and 3) is almost same, which signifies the stability of this material for high temperature application (around 95–100°C).

Cost Analysis

It should be noted that the recycled ABS is available at the cost of 1–2 US\$/Kg. The nano size MnO₂, NH₄Cl, graphene, ZnCl₂ is available commercially at the cost of 500 US\$/Kg. After blending of different reinforcements in ABS, out of 1 Kg material around

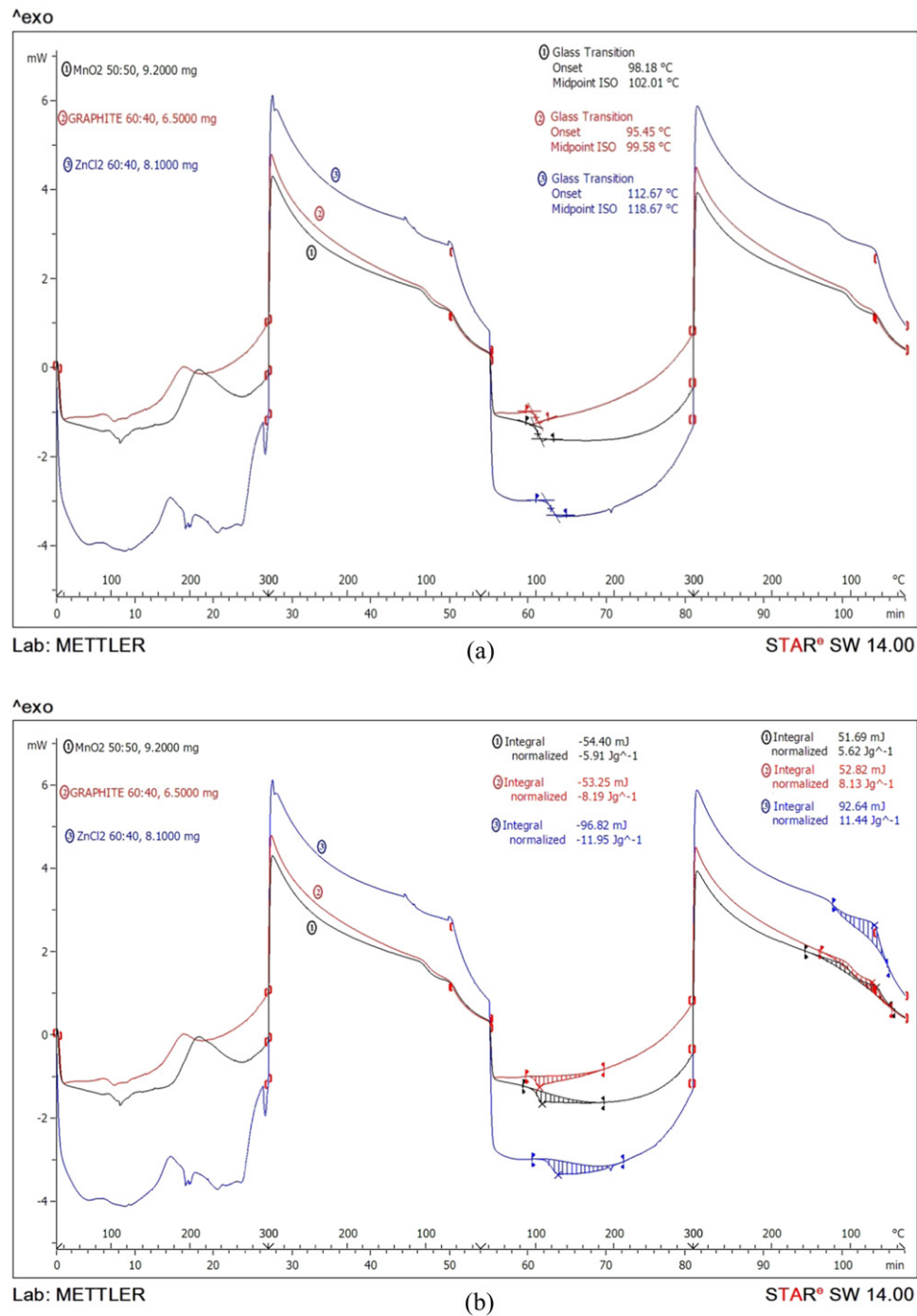


Fig. 5 (a) DSC graphs for glass transition temperature (T_g) of different reinforcement in ABS. (b) DSC graphs for energy absorbed/ released per unit g of different reinforcement in recycled ABS.

5000 pieces of dry cell can be printed. Hence the material cost per cell is estimated as 0.1 US\$, which is comparable to the cost of commercially available dry cell.

Following are some of the important features of the proposed dry cell as ESD in the context of modification of conventional technologies:

- Reduction in the manufacturing cost as major part comes from waste plastics.
- Increased safety while chemical reaction, as the traditional cell starts leaking after some time.
- Waste material management becomes easy as we know the dimensions of material printed at different ends.
- This cell can be used several times by changing the eroded material.

- Material can be used by recycling by its waste contents separately.
- The dry cell printed is more stable under extreme temperature conditions (both hot and cold).
- The user can have the control of changing the potential difference by changing the number of layers while printing.

Summary

Following are the observations from the present study:

The 3D printing of ESD by reinforcement of nano sized particles in recycled ABS is possible through FDM. For ensuring the flow ability of electrolyte salts and nano-composite (namely: MnO_2 , NH_4Cl , ZnCl_2 , Graphene, Zn etc.) reinforcement in waste/recycled ABS, ASTM D1238 is useful in deciding reinforcement proportions. This actually helps in 3D printing of nano sized reinforced particles without change in any hardware or software of the system. The DSC analysis of the different compositions/proportions ensures the thermal stability of dry cell under different temperature conditions. Overall the proposed methodology for 3D printing of ESD can lead to green cost effective solution.

Acknowledgement

The authors are highly thankful to manufacturing research lab (GNDEC, Ludhiana) and DST (GOI) for providing financial/technical assistance to carry out the research work.

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Green and Healthy Alkaline Materials

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Introduction

Green materials means, making healthy, safe and sustainable choices, especially in the way our bodies use energy, water, food intake, and also selecting engineering materials with improved properties and performance. These natural materials are local, renewable, and crucial to maintaining a sustainable healthy and safety life style. Our bodies need the green natural materials such as water, carbohydrates, proteins, amino acids, fat, vitamins, minerals, omega-3 fatty acids etc., to survive a healthy life without sickness and/or diseases. And our environment needs engineering materials that have a positive impact on the surrounding structures to survive a safely life without damages and disasters.

In this article we are concerning human health and to emphasize on how people can make the right diet choice and to avoid food that may have a negative impact on our body which is relevant to everyone. And also concerning human safety by emphasizing on how people can make the right choice of engineering materials to avoid damages and disasters.

Food is an integral component of life and human existence. Since the beginning of time humans have had to eat and to build to survive (Joyce *et al.*, 2013). Resources of food and engineering materials were green, natural, and abundant. The population growth in last several decades has made the need for sustainable production and processing technologies of materials, more important for the increasing number of humans.

The controversial here, is the processed food green, healthy, and advisable to be consumed by humans? To answer this question we need intensive investigation and testing. The challenge here is to convince them to live a green and healthy life by consuming green and sustainable materials.

The food that we choose to eat can have a direct impact on our ability to enjoy a healthy life, and the diet plays a major role in promoting a good health and it may have a long-term effects.

Is all foods we daily consume, green and healthy? This depends on the impact of a specific food whether positive or negative. The food that turns the medium of our bodies into alkaline has a positive impact and it is considered green and healthy food. On the other hand, that turns the medium acidic has a negative impact and considered unhealthy. Therefore, we should have a well control on our daily food intake by eating more alkaline and less acidic, or in other words, to alkalinize our food intake by following a good and healthy diet system. The question here is, why alkaline diet?

The alkaline diet is also known as the acid-alkaline diet or alkaline ash diet. Its premise is that our diet can alter the pH (power of hydrogen or potential of hydrogen) value or the measurement of acidity or alkalinity of our bodies. The conversion of food into energy (the metabolism process) involves a chemical reaction that breaks down a solid mass and releasing energy. When the food we eat burns, an ash residue is left behind known as metabolic waste which can directly affect our bodies' acidity. If we eat foods that leave acidic ash, it makes the blood more acidic and the body became vulnerable to illness and disease. Alkaline ash makes the blood more alkaline and considered protective and improve health (Joe, 2018). We are advised to alkalinize the diet by choosing the right variety of food. Finally we would say that life on earth depends on appropriate pH levels in and around living organisms and cells. Human life requires a tightly controlled pH level in the serum of about 7.4 (a slightly alkaline range of 7.35–7.45) to survive (Gerry, 2012).

The effect of acidity on engineering materials that is in direct contacts such as acid rain and the dry deposition of acidic particles contribute to the corrosion of metals such as iron bronze, and the deterioration of pents and stones such as marbles and limestone. These effects are seriously reduce the value of buildings, bridges, cultural objects such as statues, monuments and tombstones and cars.

What is pH?

pH is a number indicating the acidity or alkalinity of the blood or any other solution. It indicates the acidity and alkalinity by measuring the hydrogen ion concentration $[H^+]$ in the blood. If pH is lower than 7, the blood is more acidic, and if higher than 7 the blood is more alkaline. Blood is neutral when pH is exactly 7. The pH is notionally defined for any medium as the decimal logarithm of the reciprocal of the hydrogen ion activity $(a)_{H^+}$, in the medium as shown in Eq. (1) below:

$$pH = -\log_{10}(a)_{H^+} = \log_{10} 1/(a)_{H^+} \quad (1)$$

It is only for very dilute solutions that the pH can be directly related to proton concentration C_{H^+} as shown in Eq. (2) below (Karastogianni *et al.*, 2016):

$$pH = -\log_{10} C_{H^+} \quad (2)$$

pH is a measurable parameter, to measure it, there are two methods, the first one is by using an electronic device called a pH meter as shown in Fig. 1 below

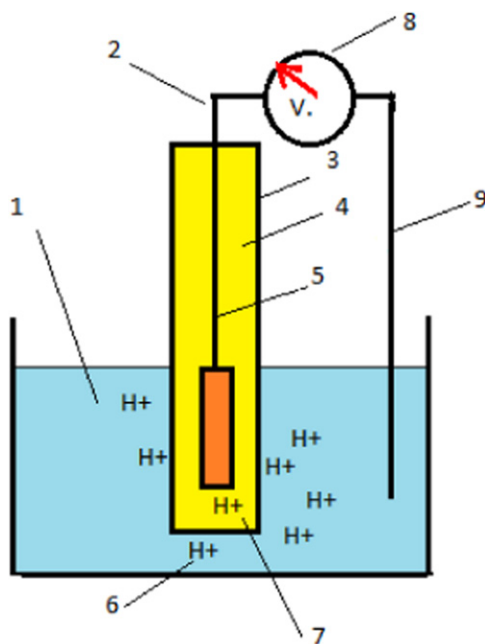


Fig. 1 pH meter.

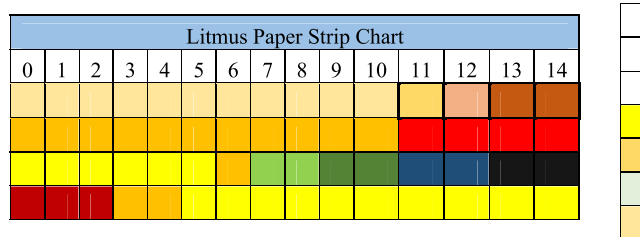


Fig. 2 Litmus paper strips chart and litmus paper strip.

The key parts of the pH meter are:

- (1) Solution being tested.
- (2) Glass electrode.
- (3) Thin layer of silica glass.
- (4) Potassium chloride solution.
- (5) Internal electrode.
- (6) Hydrogen ions.
- (7) Voltmeter converts the potential difference into a pH reading.
- (8) Reference electrode.

The second method is by a accrued estimate of pH in laboratories can also be performed by pH indicators called litmus paper strips for everyday use at home as well which allow the measurement of pH colorimetrically, through color changes. **Fig. 2** shows the litmus paper strips chart.

These indicators are dye-infused paper strips, which are dipped into the solutions and then removed for comparison against a color-pH key (*Karastogianni et al., 2016*), as in the chart of **Fig. 2**.

Basically, the litmus paper turns a slightly different color in solutions between pH 1 and 14 and, by comparing the paper to a color chart, we can read off the acidity or alkalinity without worrying how many hydrogen ions there are.

We can measure the pH of our body at home on daily bases by dipping the litmus paper into the saliva or urine. We should do that in the morning before eat or drink anything. When removed from the saliva or urine, match u p the color of the litmus paper with the color chart. It takes us 20–30 s. This determination of pH helps to balance our acid/alkaline diet.

Material Science and Materials Engineering

Materials science is an interdisciplinary field of science and engineering studying the relationship between the structures of materials and their properties and performance. Whereas materials engineering involves selecting materials, improving their properties and performance, lowering the manufacturing costs, developing new processing methods, and increasing their durability and utility. Basically, materials are the starting point of any project. The effect of acidity on engineering materials that is in direct contacts such as acid rain and the dry deposition of acidic particles contribute to the corrosion of metals such as iron bronze, and the deterioration of pents and stones such as marbles and limestone. These effects are seriously reduce the value of buildings, bridges, cultural objects such as statues, monuments and tombstones and cars.

An experimental study of chemical degradation effects on the mechanical behavior of sandstone in which the sandstone samples were immersed in acid solutions with different pH values to undergo chemical degradation. It is found that the chemical degradation induced the of elastic modules and compression failure strength. In addition to that, the creep deformation rate is enhanced by the chemical degradation (Wang *et al.*, 2016).

Another study on the effects of temperature (10, 20, 30) °C and pH level (1, 2, 0.5) of H₂SO₄ on the properties of concrete. In this study corrosion caused by H₂SO₄ attacks the concrete, resulting in significant economic losses and environmental problems. This research demonstrates a high correlation between the pH level or the Acidity of the solution and the rate of corrosion with respect to time (Mahmoodian and Alani, 2017). Accordingly, Engineering materials particularly the construction materials are exposed to Acidity and high pH level through acid rain and environmental humidity that creates many problems.

Most of the engineering materials come into direct contact with other materials and react chemically to each other that affect the materials properties such as corrosion resistance, Acidity, alkalinity, and many others. Corrosion is a chemical attack on a metal by its surroundings medium such as air, acid, bases, salt solution and so on. Due to the corrosion, metal starts getting converted into an oxide and the strength and life of the materials are reduced.

To decide whether the engineering materials are acetic or alkane, we should look at their pH value which varies from 0 to 14. Materials with pH of 7 are neutral and those of pH below 7 are considered acetic and materials with pH greater than 7 are called alkane.

This information is very important because the value of pH indicates how the materials are reacting with others to be taken into account during application.

Acid/Alkaline Balance

Feeling healthy and energized needs the body to achieve a perfect balance between alkaline and acidic foods. If we eat a modern diet, the balance in our food choices will be flipped to opposite of what our body needs. To test the body balance, the blood pH should be measured. Ideally, the blood pH is between 7.35 and 7.45 which is slightly alkaline. Keeping alkaline blood pH is crucial for healthier life, because acidic blood prevents oxygen from reaching cells, which stops cells from functioning properly and hence, the body unable to producing energy and it will drastically impair metabolic processes in the body (Waugh and Grant, 2007).

A diet containing plenty of animal proteins and deficient in vegetables and fruits may cause low-grade metabolic acidosis which has adverse health consequences, which may be especially true as we age (Hietavala *et al.*, 2015).

The acid – alkaline balance is a condition in which the ratio of carbonic acid to bicarbonate in the blood is maintained at equilibrium state. Although, the hydrogen concentrations of the blood and body fluids may be slightly altered, due to serious disturbances of metabolism or in the functioning of the body organs. All foods may be classified chemically as:

- (1) Acid forming foods (all kinds of meats, fish, shellfish, and eggs), while cereals and breadstuffs show a moderate acidity.
- (2) Alkaline/base forming foods (most of the fruits and vegetables), while milk and cream show a slight alkalinity. The citrus fruits contain acid radicals, but once metabolized in the body, it become potentially alkaline.
- (3) Neutral foods (pure fats, sugars, starches, and foods free of minerals) (Tobey, 1936).

Alkaline Diet

The alkaline diet is based on the idea that, replacing acid-forming foods and increasing alkaline-forming foods, can improve health. Proponents of this diet claim that it can help diseases like cancer (Joe, 2018). This diet can alter the pH of our body, and balanced the pH after which we notice increase in energy levels, better digestion, and easier fat loss, less pain from inflammation, better mental focus and better moods plus, a healthier and more active life (Gerry, 2012). Alkaline diet can help us lose weight and avoid problems like arthritis and cancer. The theory is that some foods, like meat, wheat, refined sugar, and processed foods, cause our body to produce acid, which is bad for us. So, according to the science behind this diet, eating specific foods that make our body alkaline can protect those conditions.

Using the revolutionary alkaline lifestyle provides an easy-to-follow diet that does not limit the food we can eat. Eating alkaline rich foods steering clear of acid-forming processed foods, creates harmony within the body, reduces the strain on the body's digestive system, boosts the immune system, increases energy, and maintaining blood sugar levels (Victoria, 2013).

Table 1 pH values of food products

<i>Foods and drinks items</i> <i>Fruits</i>	<i>~ pH level</i>	<i>Foods and drinks items</i> <i>Vegetables</i>	<i>~ pH level</i>	<i>Foods and drinks items</i> <i>Others</i>	<i>~ pH level</i>
Apples	3.85	Artichokes	5.75	Tofu (soybean curd)	7.2
Apricot	4.05	Asparagus	6.35	Lemon juice	2.3
Bananas	4.85	Avocados	6.43	Apple juice	3.68
Blue plums	3.1	Baby corn	5.2	Tomatoes, juice	4.35
Blueberries	3.2	Beans	6.1	Tomatoes, paste	4.1
Figs	5.5	Beets	5.95	Tomatoes, puree	4.39
Grapefruits	3.4	Beets	5.95	Vinegar	2.9
Grapes	3.35	Broccoli	6.6	Maple syrup	5.15
Limes	2.4	Cabbage	6.0	Jam, fruit	4.0
Mangoes, ripe	5.9	Carrots	5.95	Jellies, fruit	3.25
Melon, honey dew	6.34	Cauliflower	5.6	Ketchup	3.9
Oranges	4.0	Celery	5.85	Butter	6.25
Papaya	5.6	Radishes	5.95	Honey	3.9
peaches	3.7	Corn	6.7	Corn starch	5.5
Pears	4.0	Cucumbers	5.45	Molasses	5.25
Pineapples	3.6	Eggplant	4.9	Corn syrup	5
Pomegranates	3.1	Leeks	5.84	Sugar	5.5
Prunes	3.8	Mushrooms	6.35	Flour	6.15
Watermelon	5.39	Okra	6.1		
Olives	5.6	Onions	4.8		
Pumpkin	5.25	Potatoes	5.65		
Tomatoes	4.6	Spinach	6.15		

In the ordinary mixed diet, the acid and alkaline forming elements will be reasonably well balanced. However, a majority of alkaline foods is desirable, because normal blood is mildly alkaline, with a hydrogen ion concentration (pH) averaging 7.35 (Tobey, 1936).

Acidic Foods

We should be aware how acid and alkaline materials/foods interact with the body before deciding to avoid acidic foods and follow alkaline diet if the acidic foods are harmful to health. When foods metabolized in the body through a chemical processes, leaves behind a chemical residue known as ash. This ash can be either acid-forming or alkaline-forming, when interact with the body fluids. According to the hypothesis, foods containing acid-forming substances lower the pH level of the blood which should be balanced by alkaline materials particularly calcium leaching from the bones. So consuming acid-forming foods for quite some time increases the bone loss of calcium, thereby increasing the risk of osteoporosis. However, alkaline foods are counteracting the effect of excess acid in the body (Charlotte, 2018).

A pH of 0 indicates high level of acidity, a pH of 7 is neutral (neither acidic nor alkaline), and a pH of 14 is the most alkaline. Each type of food has some advantages and disadvantages, all depend on our diet, health, needs (children, teenagers, and pregnant women, all need proteins, vitamins, and calcium), or on our preferred test.

Foods that add high acidity to the body (pH 4.6 or lower) which must be limited or avoided include; grains, sugar, some dairy products, fish, processed foods, all types of meats, fresh and processed, sweetened beverages, and high protein foods. Too much acidity can also increase the risk for cancer, liver problems, and heart diseases. It is advisable to limit the following foods since they affect the acid-alkaline balance or the health in negative ways. These are Corn oil

- (1) Sweeteners (sugar, molasses, maple syrup, processed honey, and aspartame).
- (2) Salt.
- (3) Condiments (mayonnaise, soy sauce, and vinegar).
- (4) Hard and processed cheeses.
- (5) Grains (corn, rice, and wheat).
- (6) Coffee (Zohra and Erica, 2018).

Alkaline Water

If we want to determine the acidity or alkalinity of foods and drinks, measuring the pH values is the solution. The pH values ranges from 0 to 14. The distilled water is neutral and having a pH of 7. When minerals added to the water, it may slightly change its pH value. Any substance below pH 7 is considered acidic and that above pH 7 is considered alkaline. Alkaline water also called

Table 2 Foods' degree of acidity/alkalinity

<i>High Acid</i>	<i>Medium Acid</i>	<i>Low Acid</i>	<i>Food items</i>	<i>Low Alkaline</i>	<i>Medium Alkaline</i>	<i>High Alkaline</i>
Canned and dried fruit	Apple Mango Grapefruit Peach Orange Pear Pineapple	Green banana Plum Date Pomegranate Watermelon	Fruits	Yellow banana Avocado	Kiwi Pear Blueberry Cherry	Lemon Lime
Chocolate	Canned Vegetables	Sweet potato Cooked veg Pickles Kidney bean	Vegetables	Okra Squash Celery Lettuce Beet	Carrot Olive Tomato Corn Cabbage	Asparagus Spinach Broccoli Garlic Kale Sprouts Hemp heart
Roasted nuts	Cashew Peanut	Brazil nut Flaxseed Pecan Walnut	Nuts and seeds	Chestnut	Almond Sesame seed	
White bread Chips Pastries	Barley Oat bran	Whole grain bread	Grains	Quinoa Millet	Wild rice	
Sausage Canned; tuna, Beef Processed cheese	Chicken liver Turkey Oyster	Venison Fish	Meat			
		Yogurt	Eggs and dairy	Whey Soy milk/ chees		
Cotton seeds Palm Soft drinks Grapefruit juice Coffee	Goat cheese Goat milk Sunflower		Oils	Canola	Flaxseed coconut	Olive
	Wine Beer Liquor	Grapeseed Green tea Soy milk Rice milk Almond milk	Beverages	Ginger tea		Herbal tea
	White/brown sugar Molasses	Fructose	Sweeteners	Raw honey Raw sugar	Maple syrup Stevia	
Mustard seed	Yellow mustard White pepper	Vanilla Vinegar	Herbs and spices	Horseradish Nutmeg	Garlic powder Cayenne Fenugreek	Turmeric Basil Cumin Coriander

alkaline ionized water intake may exert positive effects on body weight improvement and cause elevation of metabolic activity. Water produced from minerals such as magnesium and calcium, has high pH level and rich with hydrogen ions. This functional water is introduced as a therapeutic strategy for health promotion, disease prevention, antidiabetic and antioxidant ([Massimiliano et al., 2016](#)).

Alkaline water typically has a pH of 8–9. However, pH alone is not enough to import substantial alkalinity to water. Alkaline water must also contain alkaline minerals and negative oxidation reduction potential (ORP). ORP is the ability of water to act as antioxidant. The more negative the ORP value, the more antioxidizing it is ([Rena and Rachel, 2018](#)).

According to research findings by Mayo Clinic, regular water is best for most people. However, alkaline water with a pH 8.8 may help deactivate pepsin, the main digestive enzyme in the stomach that causes acid reflux and it may have benefits for people who have high blood pressure, diabetes, and high cholesterol. On the other hand, the soft drinks, which are obviously acidic, have very positive ORPs leading to many health problems. Meanwhile, alkalized waters have highly negative ORPs ([Katherine, 2016](#)).

pH Values of Food Products

Table 1 shows the approximate pH values for some selected food products, in which variation exists due to growing conditions and methods of processing. The list in the table includes fruits, vegetables, juices, and other stuff ([Zohra and Erica, 2018](#)).

Acid/Alkaline Foods Chart

To rejuvenate health and make someone look or feel younger, fresher, and livelier we should focus seriously on the information provided in [Tables 1](#) and [2](#), that shows a list of some selected foods we used to eat on daily bases and apply them in our everyday life. In addition to that, one should drink plenty amount of alkaline water based on the weight. Each kilogram of body mass needs ± 300 ml of alkaline water or any other available type of water (mineral or ordinary) to ensure that the body is at its healthiest condition and the pH is at a perfect balance. We can chose our favorite foods fitted into this acid and alkaline food chart, provided that, we keep a perfect balance of acidity and alkalinity for healthy lifestyle ([Yuri, 2016](#)).

Recommendations

Numbers of recommendations, that said to help reduce certain health conditions, such as high blood pressure, heart disease, and other serious diseases. These are:

I recommend and encourage the following;

- (1) A regular pH testing of the urine or/and saliva to monitor the pH level of the body to control your diet system and achieve a green, healthy, and sustainable lifestyle.
- (2) Drinking alkaline waters with pH slightly above 7.
- (3) Mix acid and alkaline diet for normal individuals.
- (4) Alkaline diet for certain individuals with health problems.
- (5) Avoid or stop taking sugar “forever” and replace it with natural honey or stevia. Since sugar is the main food for cancer cells.
- (6) If you suspect you have problems with acidity, you can make changes to your diet system to help improve symptoms.
- (7) Remember that fruit juices are acidic too. So, you should use a straw when drinking fruit juices. This keeps the acidity of the juice from coming in direct contact with your teeth.
- (8) Drink plenty of waters. The amount of water needed every day is based on the weight. For each kilogram of weight, you need minimum of 300 ml of water, or until the color of urine is same as the color of water (colorless).
- (9) Increase alkaline foods and reduce acidic foods as much as possible to control the effects of acidity the stomach and other organs.
- (10) Keep the engineering materials away from acidity sources to avoid oxidation that may collapse the metal structures.

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Heat Affected Zone Morphology of TIG Torch Welded HSLA Steel in Presence of Ti and V Microalloying Elements

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Introduction

Nowadays, the high strength low alloy steels (HSLA) became indispensable alloys as these steels have unique properties, such as high strength, excellent toughness, and good weldability and can efficiently be welded by all types of fusion welding methods. It is used in different applications like the oil and gas transmission lines, manufacture of large ships, pressure vessels, offshore oil drilling platforms, building construction, bridges, and storage tanks (Ragu Nathan *et al.*, 2015). The microstructure constituent and mechanical properties of the welded joint of HSLA steel are the main factors deciding the welding quality. Characterization and evaluation of the properties of the welding areas are necessary to know their behavior as the alterations occurred after the welding process. However, these steels create a harder heat affected zone (HAZ) due to non-uniform heating and cooling in weld metal and base metal, which is susceptible to cold crack and the residual stresses formed in weldments cause detrimental in the material properties (Alipooramirabad *et al.*, 2017; Musa *et al.*, 2015; Show *et al.*, 2010). The local brittle zones (LBZs) and local hard/soft zones are often observed in HAZ. The formation of an LBZ depends on the microstructure in the coarse grain region. Brittle microstructures include large prior austenite grain size, upper bainite, and high-carbon martensite islands. This heterogeneity has remarkable effects in toughness and strength of HAZ and any degradation in the properties occurring in welding and joining of HSLA steel in-service conditions which may leads to a severe failure at an unexpected time (Han *et al.*, 2018). The existence of local brittle zones (LBZs) is one of the most important fractures controlling parameters in respect to metallurgical effects observed in HAZ. For HSLA steels the general tendency in HAZ is:

- The coarse-grained HAZ (CGHAZ) mostly deteriorates toughness.
- The constituent of Martensite-Austenite (M-A) can be large in CGHAZ.
- Microcracks initiate in M-A structures or between M-A, and the matrix structure.

Additionally, the welding process is a critical stage in the manufacturing of structural parts and the microstructure and mechanical properties of the welded joints must be appropriate in order to guarantee the durability and reliability of the components (Baptista *et al.*, 2011). Therefore, it is necessary to find a solution to this problem associated with the welding operation that greatly affects the main properties of these alloys and restrict their uses. Many efforts have been made to eliminate the welding defects concentrated in the welding areas especially HAZ, but no definite or complete solution was found from the previous research works through different heat treatment processes and post-welding heat treatment (PWHT).

The excellent mechanical strength and toughness can be achieved in HSLA steel weld metals by the formation of acicular ferrite microstructure. This can be achieved from the microalloying elements due to intermetallic compounds formed through thermal cycling at the interface between the inclusion and the matrix (Beidokhti *et al.*, 2009). The microalloying elements such as vanadium and titanium contribute extra strength through the formation of carbides and nitrides, acting directly to strengthen the steel by precipitation, or indirectly by mechanisms leading to a refinement of the ferrite grain size (Han *et al.*, 2018; Musa *et al.*, 2017). The addition of titanium to the welds changed the nature of inclusions from the Mn-base inclusions to the Ti-base ones. The precipitated titanium carbonitrides can act as beneficial hydrogen traps and delay cracking in hydrogen sulfide environments. Vanadium is used to interfere with the austenite grain growth at peak temperatures results in fine grain, therefore, achieves good toughness and strength (Beidokhti *et al.*, 2009; Li *et al.*, 2018). Therefore, the objective of this work was to study the effect of microalloying elements such as titanium (Ti) and vanadium (V) powder additions on the hardness and the morphology of the HAZ formed during TIG torch welding process of X65-HSLA steel material.

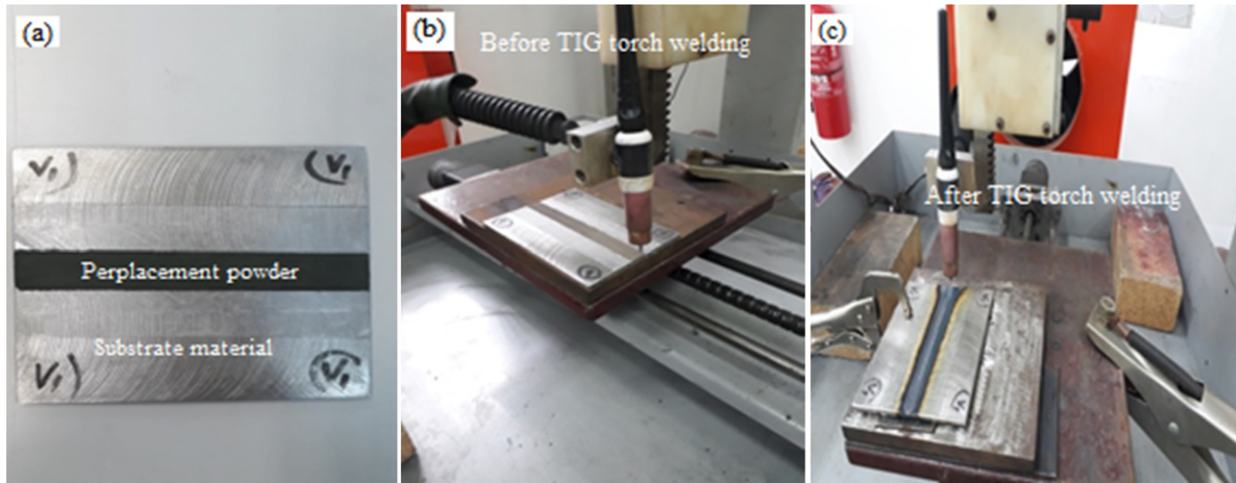
Experimental Method

The HSLA steel utilized in the present work, designated as API X-65 was imported from China in the form of plates with a chemical composition containing 0.08% C and 10 mm in thickness which was used as a substrate material for this investigation and the chemical composition of the HSLA steel is presented in Table 1.

The specimens with the dimensions of 120 mm × 50 mm × 5 mm were cut out from the plate by using CNC machine. The samples surface was rubbed off with SiC paper and degreased using acetone. The 45 μm sizes of Ti and V particles of 99.97% purity were used as preplacement for TIG torch melting and the amount was 1 mg per mm² area of the specimen surface. The Ti and V powders were first made into a pasty mass by mixing using a predetermined amount of organic PVA (polyvinyl acetate) binder, distilled water, and alcohol and then placed on the substrate surfaces (Adeleke and Maleque, 2014). The preplaced specimen was then dried in an oven at 60°C for 1 h to remove moisture. A Miller-Telwin 165 TIG torch source was used for melting purposes. The direct current electrode negative (DCEN) mode and a 3.2 mm diameter tungsten electrode were used in pure argon

Table 1 Chemical composition (wt%) of the API-X65 steel

C	Si	Mn	S	P	Al	V	Nb	Ti	Cr	Cu	Fe	C _{eq} ^a
0.08	0.17	1.41	0.014	0.0017	0.032	0.022	0.019	0.015	0.024	0.011	Bal.	0.38

^aC_{eq}: Carbon equivalent.**Fig. 1** Shows the (a) preplaced specimen with powder; (b) and (c) specimen before and after TIG torch welding.

atmosphere with a gas flow rate of 20 L/min to prevent excessive oxidation. The arc was produced using a different heat input (E) which was calculated with the formula: $E = \eta IV / (v)$, where V is the welding voltage, I is the welding current, (v) is the welding speed and η is the efficiency of heat absorption, which is given as 48% for TIG torch melting (Dieter Radaj, 1992; Easterling, 2013). The cooling time from 800°C to 500°C ($\Delta t_{8/5}$) is widely used to represent the cooling rate index during welding which was adopted in this investigation. It is approximately proportional to the net heat input and can be calculated in terms of equation ($\Delta t_{8/5} = 5 \eta E$) for the welding of HSLA steel plates (Dong *et al.*, 2014; Grong and Matlock, 1986). The melting of the preplaced powder layer was done under the torch at a constant electrode traverse speed of 1 mm/s. The optimum parameters of the TIG torch technique were generated by applying a current of 70 A to 100 A with interval 10 A, and the voltage of 25–40 V with interval 5 V (Maleque *et al.*, 2015). The preplaced specimens with powder before and after welding along with TIG torch welding setup are shown in Fig. 1.

The characterizations of melted microalloying elements addition in HSLA steel were investigated using microhardness testing machine, optical microscope equipped with a digital camera, and JSM 5600 scanning electron microscope (SEM) to characterize the microstructure and the morphology of constituent of HAZ. Microstructural characterization of the HAZ was performed in transverse cuts from the welds. Standard metallographic procedures were followed to obtain polished samples after TIG torch welding by grinding with different grades of silicon carbide papers and polishing with diamond suspensions. Specimens were etched with a solution of Nital diluted 2% to reveal the different regions of the welds and its microstructure. The microhardness was measured at a distance between measurements 200 μ m by using Wilson Wolpert Vickers microhardness tester with a 500-gf load and 10 s dwelling time using a diamond indenter to make an indentation which is measured and converted to a hardness value. An average of three readings was used.

Results & Discussion

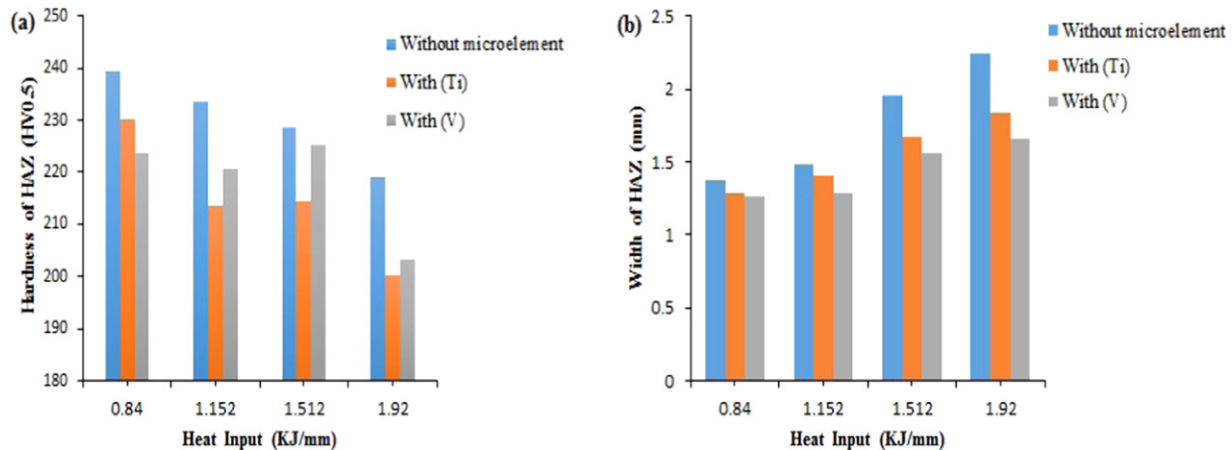
The morphology of welding tracks with and without Ti and V powder at different heat inputs were visually inspected and their surfaces were seen to be free from any cracks or any discernible defects. These additions of microalloying elements were investigated by a variety of techniques to characterize their effects on the morphology of HAZ of X65-HSLA steel. The successful application of this steel depends on the degree of deterioration of the parent metal during welding.

The Effect of Heat Input on Hardness and the Width of HAZ

Hardness is one of the most important critical factors indicating the quality of the welding and its performance in service. From Table 2 the hardness of HAZ of welded X65 HSLA steel showed a remarkable change.

Table 2 The effect of heat input on hardness and width of welded API-X65 steel HAZ

Sample no.	Current (A)	Voltage (V)	Heat input (E) (J/mm)	Cooling rate ($\Delta t_{8/5}$) (sec)	Hardness of HAZ (Hv _{0.5})			Width of HAZ (mm)		
					Without powder	With (Ti)	With (V)	Without powder	With (Ti)	With (V)
1	70	25	840	2.02	249.3	230.2	223.5	1.37	1.28	1.26
2	80	30	1152	2.76	243.6	213.4	220.5	1.48	1.41	1.29
3	90	35	1512	3.63	218.5	214.5	225.2	1.96	1.67	1.56
4	100	40	1920	4.61	209.0	200.2	203.3	2.24	1.84	1.66

**Fig. 2** The effect of heat input on: (a) Hardness of HAZ and (b) Width of HAZ of welded X-65 HSLA steel.

In general, the hardness values of the HAZ region decrease with the increase in heat input. Under the low heat input condition (heat input of 480 J/mm); the hardness value in the HAZ is higher than that in the base metal (The hardness of the as-received base metal is 165 HV). The highest hardness value (249.30 HV) achieved in the CGHAZ where the heat input was lower, due to the formation of lath martensite largely in the CGHAZ. The CGHAZ is considered as the local brittle zone in HAZ.

Both Ti and V microalloying elements additions to the welding region exhibited a decrease in hardness of HAZ with an increase in heat input during welding in this HSLA steel as shown in Fig. 2(a). The hardness of modified welding samples varies from 230.20 HV to 200.23 HV and from 225.25 HV to 203.32 HV for Ti and V samples respectively. These variations attributed to the formation of hard phase and grains of the welded sample. Although the minimum hardness values are in the range of 200.23–203.32 HV, for both Ti and V added HAZ samples but they do not vary significantly, rather closer to the value of the base metal taking into account that all hardness values are within the scope of the acceptance criterion of HAZ and base metal.

The effect of heat input on the hardness lies in the influence of heat input on the microstructure in HAZ. Fig. 2(a) shows that the lower welding heat input which corresponds the higher cooling rate leads to the formation of martensite and increases the microhardness of the HAZ and weld as shown in Fig. 3. Also, as the welding heat input increased, the cooling rate became slower and martensite disappeared gradually with the formation of bainite. So the average hardness of HAZ was decreased from 249.30 HV to 209 HV with the increase of welding heat input, due to the microstructure transformation from martensite to bainite (Dong *et al.*, 2014).

The width of HAZ as shown in Table 2 was influenced by the welding parameters, the wider HAZ width is undesirable and it does not provide any benefit to the welding joint. When different welding heat inputs were used, the HSLA steel base metal near the fusion line experienced different thermal cycles, and different microstructures were formed in HAZ (Wang *et al.*, 2012). When the welding heat input was only 480 J/mm, the cooling time ($\Delta t_{8/5}$) was about 2.02 s, and this fast cooling rate easily produced brittle and hard phases in HAZ. The width of the HAZ and its components greatly increases from 1.37 to 2.24 mm with increasing heat input from 480 J/mm to 1920 J/mm when the cooling rate was about 4.61 s. However, when the microalloying elements Ti and V were added to the welding samples of this steel, the width of HAZ reduced remarkably. The width of HAZ at lower heat input (480 J/mm) decreased by 0.9 mm and 0.11 mm for the modified welded samples with Ti and V respectively as shown in Fig. 2(b). Whereas, at higher heat input (1920 J/mm) the reduction in width of HAZ of modified welded samples were 0.4 mm and 0.6 mm respectively. As shown in Fig. 2(b), both elements have a significant influence on the shape and the width of HAZ with a slight variation between them. The two V and Ti promote carbonitride (C, N) precipitation hardening. They have the ability to limit austenite grain growth due to the undissolved V-Ti (C, N) during the thermal cycle welding (Guillal *et al.*, 2018). This gives rise to grain refinement and limits the coarsening of M-A brittle phase, during intercritical reheating. The minimizing of the risks and failures resulting from the critical welding area especially in HAZ is the main function of these additions.

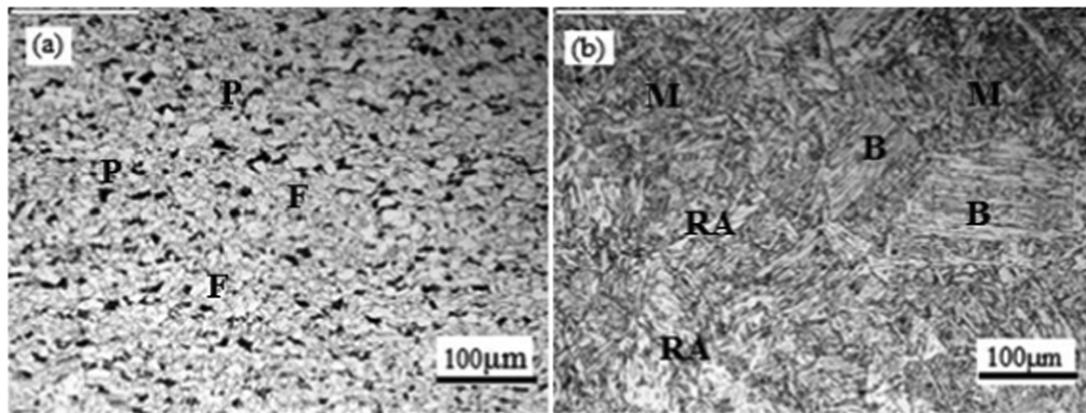


Fig. 3 The microstructures of (a) base metal and (b) the heat affected zones of welded X-65 HSLA steel.

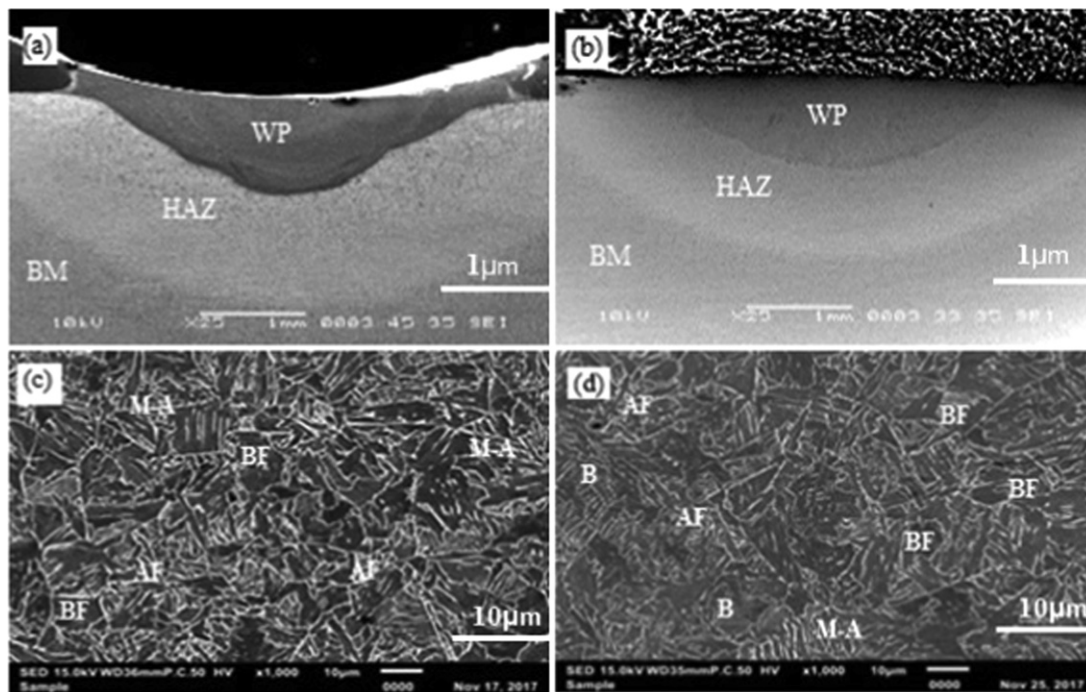


Fig. 4 SEM micrographs of welded X-65 HSLA steel showing: macrostructure of welding zones of modified samples with (a) Ti and (b) V; and microstructure of HAZ of modified samples with (c) Ti and (d) V.

The Effect of Heat Input on the Microstructure of HAZ

After welding the HSLA steel, the HAZ microstructure in the vicinity of the boundary of the welded joint is coarse-grained with the formation of martensite and bainite and, consequently, the hardness exceeds the hardness of the parent metal (Pirinen *et al.*, 2016). The microstructure of welded steels processed at a relatively higher cooling rate contained pearlite and acicular ferrite in addition to the primary ferrite-pearlite constituents. However, at the lower cooling rate, it reveals a microstructure composed of martensite, bainite, pearlite and polygonal ferrite. Fig. 3 reveals that the microstructures of base metal and the heat affected zones of welded HSLA steel. It can be seen that the micro structure of HSLA steel base metal is typically composed of predominantly polygonal ferrite (white) and pearlite which consisted of carbides (black).

While the microstructure of HAZ was typical martensite structure having obvious lath martensite boundary (M), lath bainite (B), retained austenite (RA), and various ferrites (F) with different morphologies could be observed in HAZ of HSLA steel joints (Lan *et al.*, 2012). The mechanical properties and microstructure of the weld metal (WM) and heat affected zone (HAZ) deteriorates due to the increase of welding heat input which increases the peak temperature and decreases the cooling rate. Moreover, the higher heat input promotes austenite grain coarsening and the formation of a higher fraction of large and thin shaped

martensite-austenite (M–A) constituents in the CGHAZ, which leads to properties deterioration (Musa *et al.*, 2018). Practically, it is not always acceptable to increase the welding heat input to increase productivity. Fig. 4 shows the macro and microstructure of the modified welded X-65 HSLA steel samples with titanium and vanadium microalloying elements.

When the microalloying elements of Ti and V were added to the welding tracks, the welding pool and HAZ microstructures were changed due to the effect of these elements as shown in Fig. 4(a) and (b). Melted Ti in welded HSLA steel, usually refines the microstructure by forming stable Ti-rich particles Ti(C, N) as shown in Fig. 4(c). These increased Ti inclusions leads to an increased number of nucleation sites for AF, and performs alteration in the microstructure from allotriomorphic ferrite to acicular ferrite (AF), and refines ferrite grain size (Han *et al.*, 2018). Additionally, a fine and homogeneous distribution of Ti-rich carbonitrides precipitates Ti(C, N) can constrict austenite grain coarsening during austenitization and contribute to grain size refinement when austenite transforms at low temperature. The titanium may precipitate nitrides (TiN) to prevent the grain growth during austenitizing at high temperature (Fletcher *et al.*, 2011; Yan *et al.*, 2006), and it may also precipitate carbonitrides Ti(C, N) or carbides in deformed austenite to retard the recrystallization and growth of austenite during cooling, which is beneficial to grain refinement and enhances the strength of steels greatly (Xia *et al.*, 2017).

The effect of vanadium microalloying addition on the transformation of HAZ microstructures was observed. The microstructure of HAZ of modified HSLA samples with V powder in Fig. 4(d) revealed that the grains became smaller than the grains of normal welded samples. This is due to the addition of these microelements which improves structural and mechanical properties of the welded zones. It can be said that vanadium micro addition plays a very important role in the refinement of ferrite, by enhancing ferrite grain boundary nucleation at early transformation stages and intragranular nucleation later on (Hernandez *et al.*, 2005).

The above mentioned results confirm that microalloying with vanadium and titanium significantly slows down the austenite to ferrite transformation. This is beneficial for pinning of austenite grains and since longer time is available, it enhances ferrite nucleation at prior austenite grain boundaries mainly by V(C, N) or Ti(C, N) precipitates and particles.

Conclusion

In this paper, the effect of microalloying additives (Ti & V) on HAZ of X-65 HSLA steel after TIG torch welding was investigated. It was found that these enhanced the hardness and the microstructure properties of HAZ of high strength low alloy steels. The decrease in the hardness of the HAZ was observed before and after the addition of the two elements with increasing heat input. The discrepancy between the hardness reading after the addition of Ti and V was attributed to the position of the indentation, the grain size and the phases formed.

When the microalloying elements of Ti and V were added to the welding samples of this steel, the width of HAZ reduced remarkably which provided thinner HAZ layer and overall better quality of welding. Both elements have a significant influence on the shape and the width of HAZ with a slight variation between them. Their effects are reflected in minimizing the risks resulting from the critical welding area (HAZ).

On the other hand, the addition of these microalloying elements during the welding process led to the formation of carbonitrides of Ti and V(C, N) in the form of precipitations during the thermal cycle welding. These gave rise to pinning of austenite grains and enhance ferrite nucleation at prior austenite grain boundaries, resulting in a grain refinement and limiting the coarsening of M–A brittle phase in HAZ.

Acknowledgments

The authors would like to acknowledge the Department of Manufacturing & Materials Engineering of International Islamic University Malaysia for the support to carry out this work.

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Historical Development of Hybrid Materials

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Introduction

Hybrid material sourced from nature has existed for billions of years. Nature developed hybrid organic–inorganic materials with exceptional fracture resistance and structural capabilities with complex design (Wegst *et al.*, 2015). Examples of hybrid organic–inorganic materials in nature include bone and narge. Hybrid materials are defined as the combination of organic and inorganic materials, where the range of the hybrid composite is from a few nanometers to tens of nanometers (Mammeri *et al.*, 2005). The organic and inorganic materials result in different properties. The combination of the organic and inorganic components in the formation of hybrid materials is limitless (Kickelbick, 2007). Thus, a new combination can lead to a new type of hybrid materials.

The organic materials are recyclable, cheaper, sustainable, and easy to process (Liu, 2014). Meanwhile, the inorganic materials are excellent in terms of dielectric constant, thermal stability, and high charge mobility (Krasia-Christoforou, 2015). Examples of natural organic–inorganic materials are mollusc shells, crustaceans, and bone, including human bones (Zhu and Yuan, 2015). Manmade hybrid materials have been produced since ancient times. The discovery of Maya blue, which is an intercalated organic pigment in clay minerals, proves the use of hybrid material in the past (Gómez-Romero and Sanchez, 2005). Maya blue is unique due to its resistance to solvent and aging, as well as acid.

Nevertheless, the rapid development of hybrid materials for scientific and industrial purposes has taken place since the early 1940s (Zhu and Yuan, 2015), as shown in Fig. 1. In the 1950s, the intercalation of organic units inside clay and inorganic lamellar compounds was discovered. The term “hybrid composite” was only coined in the mid-1980s. The hybrid materials become a hot topic in the 1990s. From 1980 to 1995, the sol–gel chemistry was established to produce products with different structure, morphologies, and physical properties.

Hybrid materials are defined as the mixture of two moieties on the molecular scale (Saravanan *et al.*, 2018; Tanasa and Zanoaga, 2012). Besides, hybrid materials are often referred to as the component that is formed via in situ process. Based on the International Union of Pure and Applied Chemistry, hybrid materials are defined as the materials made up of the mixture of inorganic components, organic components, or the combination of both. Organic material offers structural flexibility, convenient processing, semiconducting potential, tunable electronic properties, photoconductivity, and efficient luminescence (Haddad and Lichtenhan, 1996; Noh *et al.*, 2013). On the other hand, the inorganic material provides magnetic and electric properties, as well as thermal and mechanical stability (Arkenbout, 2010; Polyakov *et al.*, 2011). The combination to form hybrid material does not take place in normal conditions, but it occurs on the nanometric scale. The resulting hybrid material acquires new properties, which are determined by chemical and individual components, structure, and interface of the different components (Gu *et al.*, 2017). Therefore, hybrid materials offer many possibilities in terms of properties because they can be created by altering the individual components, volumetric content, morphology, size, and arrangement (Ashby, 2005).

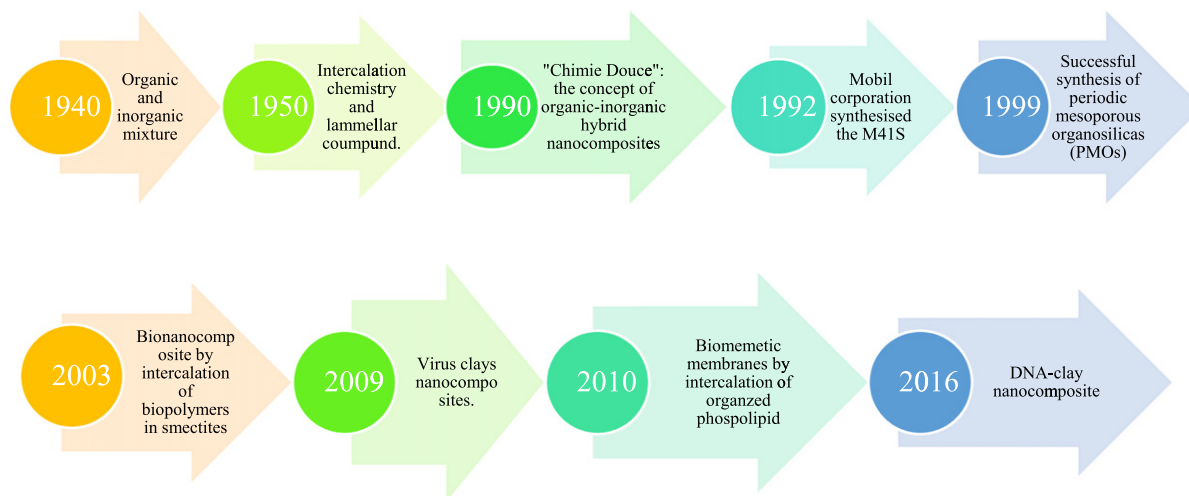


Fig. 1 Rapid development of hybrid materials from the early 1940s to 2016.

The hybrid material systems are divided into homogeneous and heterogeneous systems. The detailed explanation of hybrids material is described via the possible molecular interaction between organic and inorganic species (Mir *et al.*, 2018). In general, hybrid materials are classified into two categories, namely class I and class II, as follows:

- Class I refers to the weaker interactions consisting of van der Waals and hydrogen bonding.
- Class II refers to strong molecular interactions such as covalent, ionic, ionocovalent, and coordinative bonding.

To date, hybrid materials provide many opportunities and challenges, so that the development of hybrid materials is still ongoing. Therefore, this review will cover hybrid material development in terms of development history, synthesis, and properties of hybrid materials.

Synthetization Methods of Hybrid Material

Fundamentals

In this context, hybrid materials are defined as the combination of organic and inorganic materials. The advantage of hybrid materials is that they can combine the different properties of organic and inorganic components. The range of the hybrid composite is from a few nanometers to tens of nanometers (Mammeri *et al.*, 2005). According to the Materials Science Society of Japan (1993), hybrid materials are categorized into four sections: Composite, nanocomposite, hybrid, and nanohybrid. Fig. 2 shows the hybrid material classification is based on the size range.

Organic components can extend the range of matrices available for synthetic chemistry. Organic materials can help in modifying mechanical properties, thus enabling the production of films and fibers, by the casting of various geometric structures for integrated optics to control the network porosity and connectivity and adjust the hydrophilic–hydrophobic balance. Organic components also contribute to physical or chemical properties including electrical or optical characteristics, electrochemical behavior, and chemical or biochemical reactivity. There are two approaches in the hybrid material preparation (Tanasa and Zanoaga, 2012):

- (1) The preformed building blocks react with each other to form a final hybrid material where the precursors maintain their original integrity;
- (2) One or two structural units are formed from the precursors that are transformed into a network structure.

The hybrid materials are prepared using methods as follows (Gómez-Romero and Sanchez, 2005):

- Copolymerization of functional organosilanes, macromonomers, and metal alkoxides
- The encapsulation of organic components within sol–gel derived silica or metallic oxides
- The organic functionalization of nanofillers, nanoclays, or other lamellar structure compounds

Materials

The materials often used to produce hybrid materials are polymers and metals. Polymer helps to integrate the benefit of both materials. The metal component provides the rigidity while the polymer keeps the metal shape intact and offers many functions, besides having damping characteristic. The advantages of polymer and metal are summarized in Table 1, while Table 2 tabulated the properties of hybrid material organic (polymer) and inorganic (transition metal oxides) components.

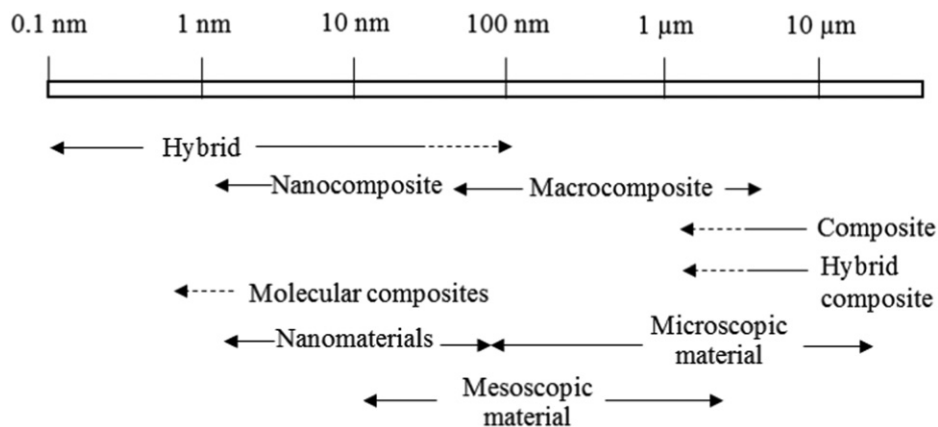


Fig. 2 The range of size of the composite materials. Reproduced from Materials Science Society of Japan, 1993. Molecular Hybridization and Hybrid Materials, Composite System in Materials. Shokabo Publishing Co., 336–343.

Table 1 Advantages of the polymer and metal hybrid material

<i>Polymer</i>	<i>Metal</i>
For esthetics and style	Structural properties
Global cohesion of all the components	Impermeability
Damping	Electrical conductivity
Thermal and electrical insulation	

Note: Kickelbick, G., 2007. Introduction to hybrid materials. Hybrid Materials: Synthesis, Characterization, Applications. John Wiley & Sons, 1–46.

Table 2 The properties of hybrid material organic (polymer) and inorganic (transition metal oxides, TMO) components

<i>Properties</i>	<i>Organic (polymers) component</i>	<i>Inorganic (SiO₂, TMO) component</i>
Nature of bonds	Covalent [C – C], van der Waals, H bonding	Ionic or ionocovalent [M – O] bonding
Glass Transition Temperature (T _g)	Low (–120°C to 200°C)	High (200°C to 1500°C)
Thermal stability	Low (<350°C to 450°C)	High (>> 100°C)
Relative density	0.9–1.2	2.0–4.0
Refractive index	1.2–1.6	1.15–2.7
Mechanical properties	Elasticity Plasticity Rubbery (depending on temperature)	Hardness Strength Fragility
Hydrophobicity	Hydrophilic	Hydrophilic
Permeability	Hydrophobic ± permeable to gases	Low permeability to gases
Electronic properties	Insulation to conductive properties Redox properties	Insulation to semiconductor properties SiO ₂ /TMO redox properties TMO magnetic properties
Processing	High (molding, casting, film formation, viscosity control)	Low for powders High for sol–gel coating

Note: Sanchez, C., Julián, B., Belleville, P., Popall, M., 2005. Applications of hybrid organic–inorganic nanocomposites. Journal of Materials Chemistry 15, 3559–3592.

Processing Methods

To achieve a balance of organic and inorganic between properties, there are many approaches in the combination of organic and inorganic materials. This includes blending process, sol–gel method, emulsion polymerization and photopolymerization, electrocrystallization, hydrothermal wet chemistry and coordination approaches, intercalation, microwave-assisted and electrochemical synthesis, as well as block copolymer-mediated synthesis (Krasia-Christoforou, 2015). Each approach has its own advantages and disadvantages. Table 3 summarizes the advantages and disadvantages of each hybrid material preparation approach.

Properties of Hybrid Materials

Hybrid materials demonstrate better properties than their individual counterparts, where the inorganic components play a role to enhance the mechanical and thermal stability, modulate the refractive index (RI or *n*), provide an accessible and interconnected porous network for sensing or catalysis, or contribute magnetic, electronic, redox, electrochemical, or chemical properties (Azadmanjiri *et al.*, 2018).

There are different combinations of organic and inorganic components in hybrid materials. The hybrid material properties vary, depending on the material (organic/inorganic), structure, and different component interface. As shown in Table 4, the optimum combination can enhance mechanical strength and thermosensitivity, improve thermal and chemical stability, and regulate optical, anticorrosive, magnetic, electrical, and thermal properties as well as fire retardancy. The hybrid material properties were characterized through UV-visible spectroscopy, scanning electron microscopy, and transmission electron microscopy (Ogoshi and Chujo, 2005).

Physical Properties of Hybrid Materials

The hybrid of organic–inorganic materials often has porous crystalline structure (Loy and Shea, 1995). The porous structure contributes to adsorbent properties. Most of the hybrid materials also have unique structure, making them an excellent catalyst for chemical reactions. Besides, hybrid materials have exceptional optical property. Often, they have passive optical properties that do not change by environmental excitation, or active optical properties such as photochromic and electrochromic materials (Kickelbick, 2007).

Mechanical Properties of Hybrid Materials

To predict the mechanical properties of hybrid materials is still a challenge in materials science (Gon *et al.*, 2017). Nevertheless, hybrid materials have exceptional fracture resistance and structural capabilities through extrinsic toughening that protects any

Table 3 Advantages and disadvantages of the hybrid material synthetization methods

<i>Synthetization method</i>	<i>Definition</i>	<i>Advantages</i>	<i>Disadvantages</i>	<i>Refs.</i>
Building block approach	Partially keep their molecular integrity throughout the material formation	The building blocks can be designed in such a way to give the best performance in the material formation	N/A	Kickelbick (2007)
In situ formation	Contrary to the building block approach the in situ formation of the hybrid materials is based on the chemical transformation of the precursors used throughout materials' preparation	Simple, commercially available molecules are applied and the internal structure of the final material is determined by the composition of these precursors but also by the reaction conditions	N/A	Kickelbick (2007)
The sol-gel process	Wet-chemical technique which is to disperse the materials (discrete, colloidal) in a liquid to bring it back in a solid form	- The most applied method - Produce an excellent homogeneity due to the mixing at high molecular level - Required less energy consumption as no need to reach the melting temperature	- Difficult to avoid the residual porosity and oh group - Preferential precipitation of a particular oxide during the sol formation - High initial cost	Ogoshi and Chujo (2005)
In situ approach	Contrary to the building block approach the in situ formation of the hybrid materials is based on the chemical transformation of the precursors used throughout material preparation	Provides stabilization to the metal nanoparticles by the organic soft material and advantageously precludes the use of external reducing or capping agents in many instances	N/A	Ehtisham <i>et al.</i> (2016), Divya <i>et al.</i> (2016)
Electrocrystallization	Process that occurs at the electrode/solution interface that leads to the formation of a solid phase at the electrode surface	- Produces large, good-quality single crystals - The reaction selectivity, the product formation, the phase purity, the kinetics of reaction and the nice crystal growth	- It requires the need of high-purity starting materials in contrast to other techniques - The formation of the product is affected by several parameters like, current, potential, solvent, supporting electrolyte, and also by the operating temperature	Zhang <i>et al.</i> (2014)
Hydrothermal method	Includes the various crystallizing techniques from high-temperature aqueous solution at high vapor pressures (T above 100°C and p above 1 atm)	- Simplicity, it lost cost, it energy saving, it better nucleation control - Pollution-free	- This technique needs expensive autoclaves, and a longer reaction time - Reproducibility is poor, especially when aiming to achieve identical crystal	Finn and Zubietta (2001)
Wet chemistry approach	Variety of simple or classical techniques that involve direct experimentation with liquids	- Simple and inexpensive starting materials, almost no damage occurs during the process; quite easy manipulation - Less time consuming	Poorly controllable especially with small amount of starting materials	Azadmanjiri <i>et al.</i> (2018)

Table 4 The properties of hybrid materials

<i>Organic</i>	<i>Inorganic</i>	<i>Condition</i>	<i>Key properties</i>	<i>Refs.</i>
Chitosan	Tetraethoxysilane/ vinyltriethoxysilane	N/A	Improve tensile and elongation with better thermostability and thermal decomposition	Kickelbick (2007)
Polymerized poly (methyl methacrylate)	Zinc oxide	Polymerization	Flexible design, high transparency, Ion barrier performance	Demir <i>et al.</i> (2006)
	Titanium oxide	Polymerization	Flexible design of particle size and photocatalytic activity	Ling <i>et al.</i> (2006)
Carbon nanotube	Polyaniline	In situ emulsion polymerization	Increase conductivity properties	Deng <i>et al.</i> (2002)

crack from the applied loads (Wegst *et al.*, 2015). The mechanical properties of hybrid materials are influenced by the ratio of organic and inorganic composition. Imbalance in the ratio will affect the viscous–elastic behavior or elastic–plastic characteristic. Besides that, the properties of the hybrid material also depend on the interface between organic and inorganic materials (Munch *et al.*, 2008).

The tensile or compression test is conducted to determine the elastic properties of the hybrid materials. The high content of the inorganic composition, typically more than 15% is good for elastic modulus (Gon *et al.*, 2017). This is because the hybrid materials become more brittle once filler increases. However, when the inorganic composition is less than 15%, there is no change in the elastic behavior. The inorganic component causes the material to become brittle due to high porosity.

Besides, high inorganic content in hybrid materials affects fracture toughness. The composition and size of the inorganic materials determine the hybrid material mechanical behavior. In fact, fracture toughness is influenced by the type of inorganic components, which often consist of metal oxides of Si, Ti, Zn, and Al. Another mechanical property is hardness, which is determined from indentation test. Hardness is associated with wear resistance. The hardness of hybrid materials is influenced by the component morphology during the synthesis.

Optical Properties

The inorganic–organic composites are also versatile in terms of their optical properties. Researchers are actively investigating the optical properties of the hybrid composite to achieve the following objectives (Munch *et al.*, 2008; Lebeau *et al.*, 1999):

- (1) Adjustability of RI over a wide range
- (2) Light transmittance over a wide range
- (3) Lighter weight compared with the inorganic optical materials
- (4) Better heat resistance and stability compared with the organic materials
- (5) Better flexibility compared with the inorganic optical materials

Based on the previous literature (Mahmood and Azarian, 2017), the outstanding optical properties of the inorganic–organic materials have been addressed by researchers. Unlike other composite materials, the inorganic–organic hybrid materials possess a high degree of transparency due to the dispersion of the different components on the material and the smaller structural unit compared with the wavelength of light (Kickelbick, 2014). As reported in one study performed by Mahmood and Azarian (2017) the hybrid composite of epoxidized natural rubber/zirconia (ENR-50/zirconia) demonstrated excellent optical transparency in the visible light range. The transparency of the hybrid materials was influenced by particles. At the high particle concentration level, the particle agglomeration triggered increased light scattering, which induced lower transparency and higher turbidity. On the other hand, the density of the particles strongly influenced the light scattered within the hybrid materials.

The optical properties of hybrid material are often characterized through the RI. Currently, the development of the high refractive hybrid composite is rapidly ongoing due to motivation to achieve perfect balance with mechanical properties and thermal properties RI is defined as the ratio between the velocity of light in a vacuum to its velocity in a specified medium. Normally the organic materials have a RI in a range of 1.3–1.7; meanwhile the inorganic material can have RI below 1 or 3 (Kim and Park, 2016). Through a combination between organic and inorganic materials, the different RI can be modified based on the desired application. The RI of the materials can be relatee molar volume (V_m) and polarizability d to $\text{th}(\alpha)$ of the materials. As shown in the previous research work (Lü and Yang, 2009), the hybrid materials can be tuned to different RI through implementing different heat treatment, type of metal alkoxides, and the weight or volume fraction of inorganic content. Table 5 shows the summary of the RI of the hybrid inorganic–organic materials.

Hybrid Material Applications

The combination of organic and inorganic components has the potential to replace the traditional materials. The development of hybrid material synthetic methods has improved their mechanical properties on the macroscopic scale. Nowadays, researchers focus on hybrid materials with advanced mechanical properties for transportation industry, such as vehicle structure (Gutfleisch *et al.*, 2011; Darder *et al.*, 2007). The process technology and modular construction of hybrid materials highlight their strengths in several applications. Due to the improvement in terms of mechanical and physical properties, hybrid materials are used for many applications such as coating, nanocomposite, medicinal, optical, and electronic domains, which will be discussed later.

Coating Applications

Surface coating is crucial to protect products against environmental and harsh conditions such as multiple loading, corrosion, and abrasion. The coating components in general are mixed into coating formulation, which is applied to a substrate. There are two commonly used coatings methods, namely liquid coating and powder coating. The liquid coating is made based on organic solvent, water, or both, in which solvents are used to dissolve the organic components, control viscosity as required, and control the film formation (Grosso, 2011). Meanwhile, there are two types of powder coating, thermosets and thermoplastics, which are

Table 5 The summary of the refractive index (RI or *n*) of the hybrid inorganic–organic materials

Type of materials	Thickness (μm)	RI	Wavelength (nm)	Refs.
ENR	150	1.472	–	Mahmood and Azarian (2017)
ENR-10% zirconia		1.482		
ENR-30% zirconia		1.495		
ENR-50% zirconia		1.513		
MPEOU-SiO ₂ -GeO ₂	1.73	1.507	632.8	Motakef <i>et al.</i> (1994)
MPEOU-SiO ₂ -ZrO ₂	1.97	1.562		
MPEOU-SiO ₂ -TiO ₂	2.89	1.571		
MPEOU-SiO ₂ -PbO	2.30	1.622		
MPEOU-SiO ₂ -Ta ₂ O ₅	2.06	1.631		
MPEOU-SiO ₂ -ZnO	2.11	1.495		
poly (Ti–O–Si precursor-co-OPPEA)	2.59	1.83	633	Ma <i>et al.</i> (2016)
Organically modified silane (ORMOSIL)-SiO ₂	–	1.52–1.61	633	Que <i>et al.</i> (2000)

Table 6 The summary of polymeric binder in hybrid coatings

Category/Method	Polymeric binder		Coating methods	
	Organic-based solvents	Water-based	Liquid coating	Powder coating
Type	Acrylic	Vinyl acetate	Thiolene	Polyamide
	Vinylidene Fluorides	Vinylidene Fluorides	Polyurethane	Polyurethane
	Phenolic	Acrylic	Polyester	Polyester
	Epoxide	Epoxide	Epoxide	Epoxide
	Polyester	Alkyd	Acrylic	Acrylic
	Polyurethane	Polyurethane	Vinyl ether	Phenolic
	Alkyd	Styrene-Butadiene	Bismaleimide	Epoxide/polyester hybrid

Note: KICKELBICK, G., 2007. Introduction to hybrid materials. Hybrid Materials: Synthesis, Characterization, Applications. John Wiley & Sons, 1–46.

used with common polymers such as polyurethane, polyester-epoxy (hybrid material), epoxy, and acrylics. In terms of hybrid coating, both thermosetting and thermoplastic systems are used (Clemens and Clemens, 2005). Interestingly, the most common functional group is ester, which is in the form of drying oils, alkyds, vinyl acetate, polyesters, and acrylics (Jones *et al.*, 2017). The most common organic binders are polyurethanes, acrylics, and alkyds. Polymeric binders are used in multiple media such as water and organic solvents. The types of media for liquid coating and powder coating are described in Table 6.

In recent decades, organic and inorganic coatings have gained attention as the new functional material (Zareba-Grodz *et al.*, 2004). In general, hybrid material is formed through hydrolysis and condensation of modified silicates with conventional alkoxide precursor (Williams *et al.*, 2001). The characteristics of hybrid coating may lead to complaints in the future regarding its effectiveness to protect any surfaces from natural conditions, as demonstrated by Kachurina *et al.* (2002) on the corrosion resistance performance of multilayer ormosil/conversion coating on 2024-T3 aluminum alloys. Besides, Chou *et al.* (2003) investigated the corrosion resistance behavior of sol–gel derived thin films deposited on stainless material using potentiodynamic polarization curve analysis. Researchers have explored the use of silane-based treatment to protect aluminum (Kachurina *et al.*, 2002; Chou *et al.*, 2003), aluminum alloys (van Ooij, 1998), iron (Subramanian and van Ooij, 1998), and steel (Sundararajan and van Ooij, 2000) from corrosion. In addition, the application of hybrid coating with wood antibacterial properties (Donath *et al.*, 2004), as well as fire, chemical, physical, and water resistance (Wang *et al.*, 2011; Trepte and Böttcher, 2000) was investigated. There is also interest in hybrid coating with embedded metal oxide nanoparticles to protect wooden products from fiber, humidity, and sunlight (Wang *et al.*, 2011). Table 7 summarizes the coating application of hybrid materials, including its method, material, equipment, and purpose.

Nanocomposite Development

Nanocomposites are a new class of composites that are prepared by mixing the inorganic particles into melt polymer at the nanometer stage. The types of nanocomposites depend on the dimension of the dispersed particles in nanometer range. The first type is characterized by one dimension, which is present in the form of nanometer sheets with hundreds to thousands nanometer long. The second type is characterized by two dimensions in the nanometer scale; for instance, carbon nanotubes (Jorio *et al.*, 2007), cellulose whiskers (Oksman *et al.*, 2006). The third type is in three dimensions, which involve isodimensional nanoparticles such as spherical silica nanoparticles (Yang *et al.*, 2004). Nanocomposites have at least one dimension in nanometer scale, which is in the range of 1–100 nm. Moreover, the nanocomposites of conducting polymers and inorganic particles are used to prepare electroactive materials (Cómez-Romero *et al.*, 2003). For example, a polythiophene composite and platinum particles

Table 7 The summary of the coating application technique of hybrid materials

<i>Technique</i>	<i>Materials</i>	<i>Equipment</i>	<i>Purpose</i>	<i>Refs.</i>
Dip coating	Vinyl acetic acid/zirconium n-propoxide	Environmental scanning electron microscopy	Wood protection	Girardi <i>et al.</i> (2014)
In situ	Polyurethanefattyamide/silica	IRPrestige-21, IRAffinity-1, FTIR-8400S, Optical microscopy	Corrosion protection	Ahmad <i>et al.</i> (2012)
Sol-gel process	Polyesters/tetraethoxysilane	Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis, TENCOR-P10 Surface Profiler	Protective coating	Frings <i>et al.</i> (1998)
In situ	Polyvinyl chloride/ZnO	FTIR, X-ray diffraction patterns, field emission scanning electron microscopy and transmission electron microscopy	Corrosion resistance	Olad and Nosrati (2013)
Sol-gel process	Polyfunctional sol-gel precursor/oligomers	UV irradiation, QUV-A irradiation	Outdoor application	Liu <i>et al.</i> (2005), Hofacker <i>et al.</i> (2002)

Table 8 The summary of the applications of nanocomposite hybrid materials

<i>Materials</i>	<i>Key properties</i>	<i>Application</i>	<i>Refs.</i>
The core integrity of inorganic nanobuilding blocks	Vectorial chemistry, hybrid networks, chemical strategies	Nanoparticles	Sanchez <i>et al.</i> (2001)
Polymer-layered silicate nanocomposites	High thermal stability, gas barrier properties, and good flame retardancy	Future application	Alexandre and Dubois (2000)
Plant oil/clay nanocomposites	Flexible property	Renewable resources	Uyama <i>et al.</i> (2003)
Polyaniline/organoclay nanocomposite and EPDM rubber	High conductivity, good mechanical properties	Antistatic coating/ electromagnetic shielding	Soto-Oviedo <i>et al.</i> (2006)
The molecular hybrids PAni/H ₄ SiW ₁₂ O ₄₀	Better energy-storage performance	Solid-state electrochemical capacitor cells	Cuentas-Gallegos <i>et al.</i> (2005)

Abbreviation: EPDM: ethylene propylene diene monomers.

are used as the oxygen-reducing electrode in the fuel cell application (Bashyam and Zelenay, 2011). Table 8 presents the applications of nanocomposite hybrid material.

Medical Applications

In recent years, hybrid materials have gained attention in the research of biomaterials, which focus on hybrid material medical applications, that involve inherent degradability, cytotoxicity, and biocompatibility (Yu *et al.*, 2010; Jiang *et al.*, 2015). Vallet-Regí *et al.* (2011) demonstrated that the incorporation of osteostain peptide into SBA-16 materials reduces tissue encapsulation, which significantly improves local bone induction and develops potential formulation for clinical applications. Fig. 3 shows the schematic representation of organic-inorganic hybrid materials in biomaterials science. In addition, an excellent alternative that leads to higher control of silica leaching under in vitro physiological conditions was reported, by using different methods such as the incorporation of heteroatom into silica framework (García *et al.*, 2009).

Therefore, hybrid materials are significant in the production of bioceramics, which are utilized in medical applications. For example, stimuli-responsive drug delivery system is used as the local carrier, which is synthesized using charged ionic interaction between carboxylic-modified mesoporous silica and polyelectrolyte solution (Yang *et al.*, 2005). Also, hybrid materials are useful in cell targeting. Rosenholm *et al.* (2008) have investigated the use of mesoporous silica nanoparticles functionalized with hyperbranched poly(wedges) in cell targeting, either to assist in drug delivery or cancer cell imaging. Moreover, implant material is compatible in terms of mechanical properties and biological properties, to be applied to damaged or wounded organs. It is adequate to depend on fundamental of biomaterials and hybrids of biomedical applications. Table 9 shows some hybrid material medical applications, including the materials, key properties, and future application.

Optical Applications

Due to high transparency and mechanical flexibility of inorganic/organic hybrid materials, they have potential in optical applications. The development of synthetic strategies at the atomic and nanometer scale with enhanced properties is required. Materials for optoelectronic devices need higher thermal stability and better compatibility, to be used in semiconductor devices. The transparent

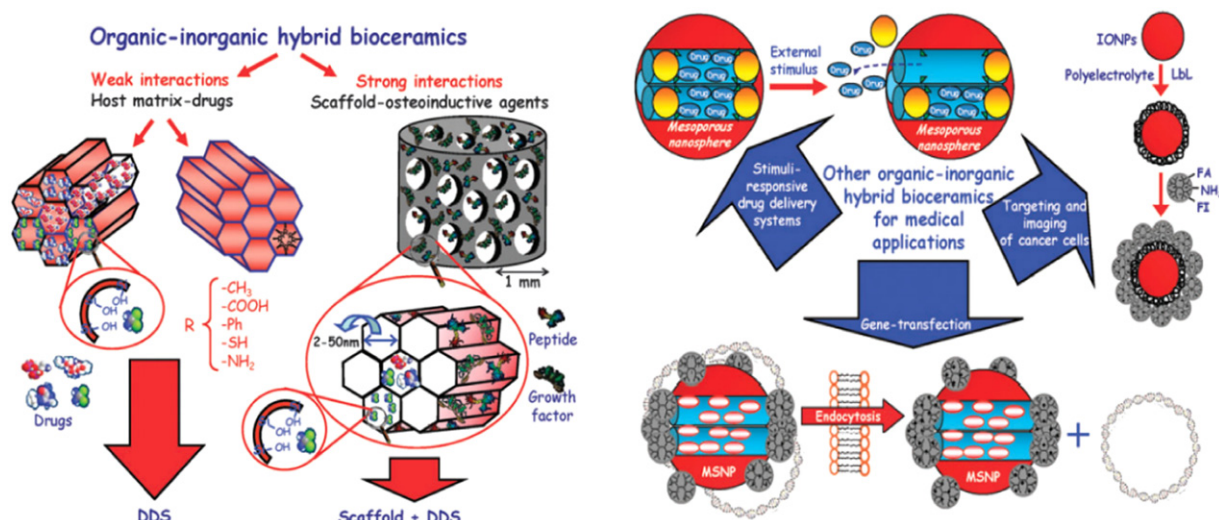


Fig. 3 Schematic representation of organic-inorganic hybrid materials used in medical applications: (a) bioceramics; (b) diverse as drug reservoirs. Reproduced from Vallet-Regí, M., Colilla, M., González, B., 2011. Medical applications of organic-inorganic hybrid materials within the field of silica-based bioceramics. *Chemical Society Reviews* 40, 596–607.

Table 9 A summary of hybrid material in medical applications

Materials	Key properties	Application	Refs.
hybrid cathodes ($\text{Ag}_2\text{V}_4\text{O}_{11}/\text{CF}_x$)	High power and energy density, high stability and reliability	Power implantable device, primary batteries, e.g., ICDs	Chen <i>et al.</i> (2006)
Nanodiamonds and hydrophilic poly	Bone scaffold mineralization and ossification properties	Biomedical structural application	Aversa <i>et al.</i> (2016)
Functionalized C_{60} fullerene-silica hybrid nanometer-sized material	Water-soluble	Optical devices, chemical sensor, catalysis in medical fields	Patwardhan <i>et al.</i> (2002)
Hybrid antimicrobial enzyme/silver nanoparticle	Biocidal properties	Medical instruments	Eby <i>et al.</i> (2009)
Two-photon induced polymerization (Ormocer)	Multilayered artificial tissues	Medical microdevices, such as microneedles, tissue engineering scaffolds	Doraiswamy <i>et al.</i> (2006)

Abbreviation: ICDs, implantable cardioverter defibrillators.

Table 10 A summary of hybrid material optical applications

Materials	Key properties	Application	Refs.
Hybrid semiconductor nanomaterials	Optical properties and functionalities	Energy conversion, sensing, electronics, photonics, and biomedicine	Li and Zhang (2009)
A covalently bonded gold nanoparticle/polylysine (AuNP-PLL)	Reverse saturable absorption, free-carrier absorption, electromagnetic interaction	Miniaturized electronic devices, catalysis, sensors, data storage	Sun <i>et al.</i> (2005)
Inorganic/organic hybrid polymer with silicate-based	High transparency, solvent less, high curability, high thermal stability	Versatile application	Nawata (2013)
Oleic acid-modified LaF_3/Er , Yb nanocrystals	Excellent dispersibility, strong emission	Amplification application	Wang <i>et al.</i> (2007)
Porphyrin and fullerene covalently functionalized graphene hybrid material	Enhance nonlinear optical response	Photonic and optoelectronic devices	Liu <i>et al.</i> (2009)

inorganic glasses and organic polymers have improved over the years. The physical and chemical properties of hybrid material can be functionalized according to its use, such as in waveguides and microoptical devices (Houbertz *et al.*, 2003). The example of hybrid material optical applications are waveguide materials (Zhang and Fallahi, 2005), photodetectors (Wang *et al.*, 2010), and nonlinear optical materials (Innocenzi and Lebeau, 2005). Hybrid materials also have potential in the making of LEDs and photovoltaics, in which the market for the products is large (Kim *et al.*, 2010). Table 10 summarizes the hybrid material optical applications.

Table 11 A summary of electronic applications of hybrid material

Materials	Key properties	Application	Refs.
CuInSe ₂ nanocrystals	High sensitivity and stability	Photodetectors	Wang <i>et al.</i> (2010)
Graphene/free-standing nanofibrillar PEDOT/P (VDF-HFP) nanohybrid	Improved contact surface, high sensitivity, piezo-resistivity	Sensitive electronic skin application	Park and Jang (2015)
Transition metal oxide/polymer	Excellent electrochemical and thermal stability, high electrocatalytic activity	Electrocatalytic application	Rajesh <i>et al.</i> (2005)
Zinc oxide nanoparticle /polystyrene	High stability, high conductivity	Electronic application	Verbakel <i>et al.</i> (2006)
Nanocrystalline zinc oxide nanoparticle (nc-ZnO)/regioregular poly (P3HT)	High solar-energy conversion efficiency	Solar energy application	Beek <i>et al.</i> (2006)

Electronic Applications

There use of hybrid materials in electronics industry has increased, due to the development in integrated circuit performance. Hybrid materials are installed in electronic devices, which are resistant to high temperature using without compromising the device performance. Electrochemically active hybrid materials have several advantages. For instance, hybrid materials offer stability like solid materials but possess liquid properties at the same time. Hybrid materials can integrate the electrical conductivity of solid materials and ionic conductivity of liquid materials, which is useful for electronic devices that provide low-k dielectrics (Liu *et al.*, 2001). The silicon-derived hybrid material is significant in electronic devices (Hartmann-Thompson, 2011). Table 11 presents several electronic applications of hybrid material.

Conclusion

Hybrid materials have served many purposes in the advancement of modern technologies. Even though many studies were performed on hybrid materials, the reported properties and characteristics are still insufficient. This is because hybrid material properties and behavior are influenced by synthetic methods, so that even a small alteration can make a difference. However, the issues in hybrid material synthesis must be solved so that many parties can leverage the hybrid material technology. To refine the production of hybrid materials, further studies should be conducted to improve the physical and mechanical properties. The research in regard to hybrid materials should be carried out to overcome the obstacles in various applications. Yet, the effect of high inorganic composition in the different environmental conditions (such as temperature) remains the same.

Due to the hybrid materials' modular composition, many components are now suitable to be involved in hybrid material organic/inorganic combination. Therefore, there is no limit in the future applications.

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Interface Study of SiC_p/6061Al Composite

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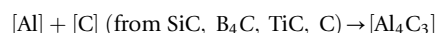
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Introduction

The interface reaction during processing of SiC_p/6061Al composite play a major role in determining the mechanical properties and performance in service (Maleque *et al.*, 2017). Aluminium matrix composite (AMC) possesses potential for the development of lightweight materials where efficiency and improved performance is needed (Adebisi *et al.*, 2014; Wang *et al.*, 2018). Moreover, the mechanical properties is strongly influenced by the microstructure of the processed aluminium composite considering the interface reaction between the matrix and reinforcement phase. The nature of phases present is dependent on the chemistry and interface mechanism which controls the efficiency of load transfer between the matrix and reinforcement (Adebisi *et al.*, 2016a,b). Aluminium composite can be processed using various techniques which include both liquid (centrifugal, squeeze, stir casting) and solid state (powder metallurgy, diffusion bonding) conditions (Narasimha *et al.*, 2013). The stir casting process is commonly employed due to its simple and cost effective advantage. With this technique, there is possibility of a strong interfacial reaction to take place between the matrix and reinforcement phase owing to the prolonged contact during processing. Studies have shown that Al alloy reinforced with various carbide such as SiC, TiC, B₄C or graphite either in form of fiber or particulates results in the formation of Al₄C₃ (alumina carbide) at the interface as presented in the equation:



This formation of Al₄C₃ is detrimental to the development of aluminium composite and also degrades the mechanical properties of the composite (Liu *et al.*, 2015). The degree and extent to the resultant interface reaction depends on a variety of factors which include, processing technique, matrix phase alloying elements, nature of surface treatment and thermal treatment on the composite. In order to limit Al₄C₃ formation during liquid state processing of SiC_p/6061Al composite, three main methods may be adopted;

- (1) Modification of the matrix alloy by addition of Si to the aluminium matrix in order to hinder the interface reaction.
- (2) Pre-oxidation/surface treatment of the reinforcement phase.
- (3) Optimization of process parameters in order to control and limit the extent of interfacial reaction.

Studies conducted by through theoretical calculations (Lee *et al.*, 1998), quantitative modeling (Wang *et al.*, 2015) and experimental data (Sozhamannan and Prabu, 2010) have estimated the equilibrium Si content required to prevent the formation of Al₄C₃ considering the variations in Al and Si as well as other compounds present. Moreover, determining the optimum process condition such as stirring speed, time (Adebisi *et al.*, 2016a,b) and process conditions (Adebisi *et al.*, 2017, 2016a,b; Sozhamannan *et al.*, 2012) has also shown considerable tendency in limiting the formation of Al₄C₃. Besides, the surface modification technique incorporates different procedure which has been experimented by researchers (Lee *et al.*, 2000; Urena *et al.*, 2004).

However, this study aims to investigate the interface nature and reaction products considering the oxidation treatment of the SiC_p reinforcement at high temperature on SiC_p/Al6061 composite. The interface study was characterized using the scanning electron microscope (SEM) and X-ray diffraction (XRD) facilities.

Experimental Procedure

Oxidation Treatment of SiC Particle

The reinforcement used in this study is SiC_p with an average size of 40 μm. The SiC_p is prepared through oxidation treatment in a miniature particle preheating furnace attached to the aluminium stir casting furnace with a heating capacity of 1500°C as shown in Fig. 1. Oxidation treatment of the SiC_p improves the casting processability by means of chemical interface control. The oxidation of the SiC_p is carried out at 1200°C for 2 h in order to initiate surface oxidation. This process is expected to catalyze the formation of SiO₂ layer on the surface of the SiC_p. Moreover, the layer thickness increases with temperature and time to a certain range (Kim and Lee, 2006).

Composite Processing

In this study, AA6061 aluminium alloy is used as the matrix material and silicon carbide particles (SiC_p) as the reinforcement phase material. Table 1 shows the properties of the matrix and reinforcement materials.

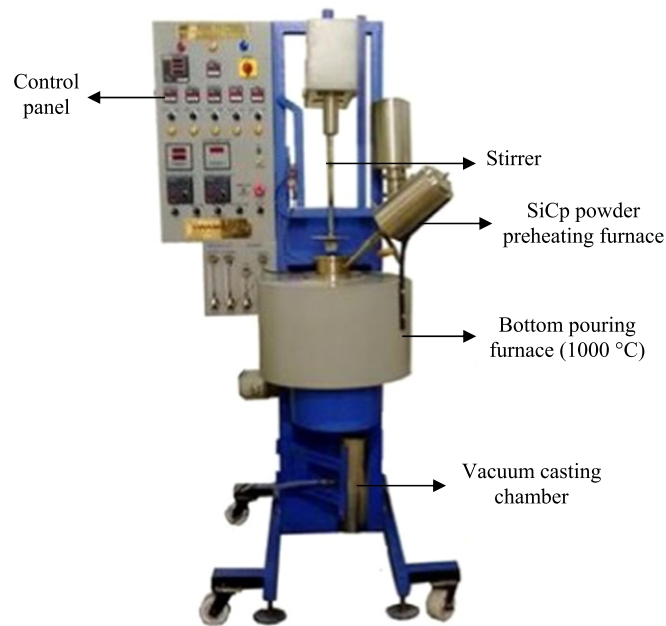


Fig. 1 Bottom pouring stir casting furnace (Swamp Equip, India).

Table 1 Properties of matrix (AA6061) and reinforcing (SiC_p) phase

Property	Unit	Al (6061)	SiC _p
Density	g/cm ³	2.7	3.22
Melting point	°C	660	2973
Coefficient of thermal expansion	μm/m°C	23.4	4
Thermal conductivity	W/m K	166	126
Young's modulus	GPa	70	410

Note: Veeresh, K.G., Rao, C., Selvaraj, N., 2012. Studies on mechanical and dry sliding wear of Al6061–SiC composites. *Composites Part B: Engineering* 43 (3), 1185–1191.

The composite was developed using an electric resistance induction stir casting set up incorporated with a preheating furnace, vacuum chamber, stainless steel stirrer and attached die cavity as shown in [Fig. 1](#). The melting furnace for Al alloy matrix has a heating capacity of 1000°C. The temperature value is determined with a K-type thermocouple for sensing the temperature during the melting process until the desired temperature is attained on the indicator. After melting of the aluminium alloy, dross formation is extracted from the melt surface with a coated skimmer which has been preheated. Moreover, before the incorporation of the prepared (oxidation treated) SiC_p, 1 wt% magnesium was added in the aluminium melt to improve the wettability between the matrix and reinforcement phase. Subsequently, the injection of treated SiC_p was slowly added to the aluminium melt within an average of one (1) min as the stirrer (stainless steel) is gradually lowered into the furnace in order to perform stirring and pouring. The die steel is heated to 500°C for 1 h and then positioned in a vacuum chamber of 350 mmHg before pouring take place. Throughout this process, the composite melt is monitored to be in a molten state.

Metallography and Microstructural Preparation

The surface of the developed SiC_p/6061Al composite is prepared using the ASTM Standard E8-11 ([ASTM E3-11, 2017](#)) as a guide. The grinding is conducted using a four station hand grinder with various stages of Presi abrasive papers ranging from P240 to P1000 (coarse to fine size). Each of the grinding stage removes the scratches from the previous coarse paper and this is achieved by orienting the sample perpendicular to the previous scratch position. Between each grade, the SiC_p/6061Al composite is washed thoroughly to prevent contamination from the previous grinding surface. All through the process, wet grinding is applied to avoid possible side effects due to heating. The grinder also incorporates a flushing action for loose particles to flow from the grinding surface.

The polishing process is conducted using Presi Mecapol P260 machine with a Ø200 mm adhesive polishing cloth on the wheel disc. The polishing cloth has an abrasive size of less than 1 μm and an alumina micropolisher of 0.3 μm is used with a rotation rate of 150–200 rpm. Moderate polishing pressure is applied on the composite as the disc is rotating and this process takes about 3–5 min.

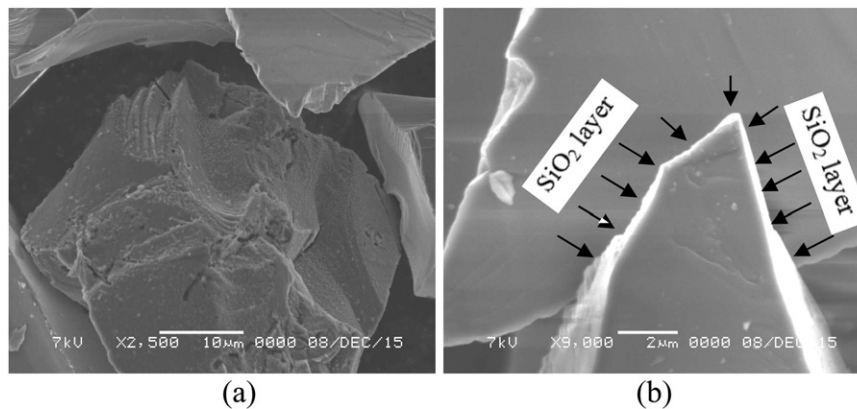


Fig. 2 SEM micrographs of SiC_p: (a) As received-untreated (b) oxidized at 1200°C showing a relatively smooth surface of the oxide layer.

The composite is washed thoroughly with warm soapy water; followed by alcohol to prevent contamination. Finally, minimum polishing pressure is applied and within a short period a mirror like and free from scratches is achieved.

In order to obtain a clear and satisfactory surface examination a proper metallography procedure is required. This process minimizes the number of irregularities on the prepared SiC_p/6061Al composite surface. Chemical etching is achieved through the use of Keller's agent, in order to ensure that all phases present are clearly identified when viewed under the microscope. JEOL, JSM 5600 scanning electron microscope (SEM) is used to characterize the layer formation on the SiC_p and also the morphologies of the interfacial reaction products. Phase identification is conducted with Shimadzu 600 XRD diffractometer.

Results and Discussion

Effect of Oxidation Treatment on SiC_p

The silicon carbide particle (SiC_p) is heat treated to 1200°C for 2 h before incorporation into the aluminium melt. Particle pre heating removes impurities on the SiC_p surface and also alters the surface composition due to formation of silicon dioxide (SiO₂) layer. Observations on the surface morphologies of the as received and heat treated (oxidized) SiC_p were conducted using the scanning electron microscope (SEM). **Fig. 2(a)** and **(b)** show the micrographs of the as received and oxidized SiC_p respectively.

The oxidized SiC_p shows a relatively smooth surface due to the uniform formation of the silica layer. The layer formation is visible at the edges of the SiC_p with a whitish blurred surface which indicates the presence of the silica layer as indicated with the arrows on the high magnification view in **Fig. 2(b)**. Moreover, the SiO₂ also serves as a source of Si which is used to suppress and prohibit the formation of Al₄C₃ (Kim and Lee, 2006).

The phase analysis in **Fig. 3** shows the SiC particle surface experiences the formation of SiO₂ layer when compared to the as received SiC_p. The phases show the presence of SiO₂ diffraction peaks at 2θ for 28.4°, 33.5°, 38° and 41.2°.

Interfacial Reaction Products of Al-SiC_p Composite

The exposure of SiC_p to high temperature environment mainly above 900°C, influences the weight gain on the particles due to reaction with oxygen which forms a thin layer of SiO₂ on the surface of SiC as shown in **Fig. 4**. The oxidation of SiC_p at elevated temperature removes contaminants, impurities, and absorbs moisture from the particle surface. This helps to form a clean and uniform protective layer of SiO₂ as shown in **Figs. 3** and **4**.

The reaction taking place during the oxidation process is effective in prohibiting a direct contact between the SiC_p and Al matrix alloy due to the formation of SiO₂. This process proceeds according to the following reactions in **Eqs. (1)–(3)**:



In spite of which reaction that may proceed, one mole of SiC will oxidize completely into one mole of SiO₂ as presented in the equations. SiO₂ is purposely introduced as a form of surface coating on SiC_p to enhance the wetting property between the SiC_p and the Al, and to serve as a barrier to limit SiC_p from being attacked by molten Al so that the reaction in **Eq. (4)** is restricted (Kindl *et al.*, 1992):



When the reaction of aluminium and oxidized SiC_p occur, the contact gives rise to interface reactions. These reactions takes place considering the Al alloy, SiC_p, SiO₂ and Mg present. In order to examine the morphology of the interfacial reaction products on the oxidized

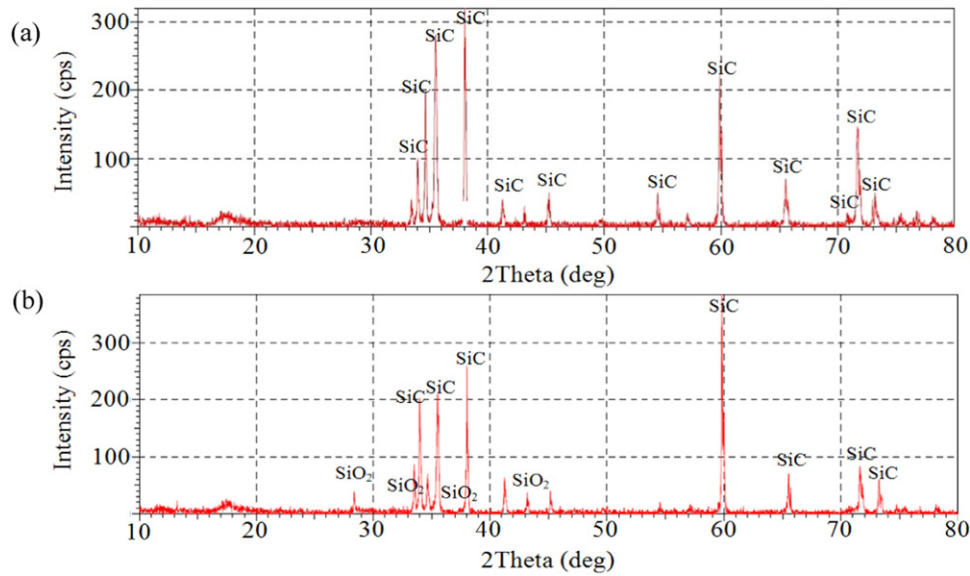


Fig. 3 XRD phase analysis of SiC_p: (a) As received and (b) oxidized at 1200°C for 2 h.

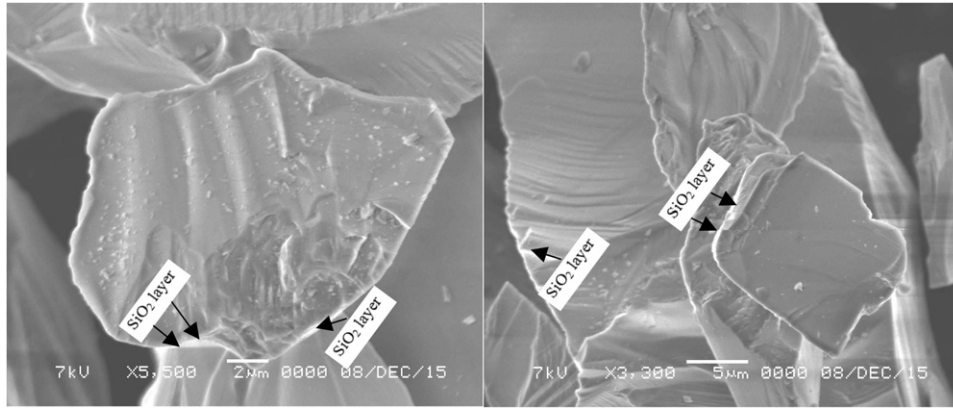


Fig. 4 SEM micrograph of oxidized SiC_p with thin layer formation of SiO₂.

surface of the SiC_p after reacting with aluminium melt, the SiC_p from as cast composite is evaluated and the SEM micrograph is shown in Fig. 5. Though, the Al 6061 alloy has Mg as one of the constituent element, but an additional 1 wt% Mg is added in order to enhance the reactive wettability. This element produces reaction products with SiO₂ layer on the SiC_p surface during composite processing. When Al is alloyed with Mg and Si as constituent elements, Mg₂Si (magnesium silicide) precipitates by the reaction in Eq. (5) (Shi *et al.*, 2001):



In addition, there is a possibility of Mg attacking the SiO₂ directly to form Mg₂Si according to the following reaction in Eq. (6):



The formation of MgAl₂O₄ was found in presence of Mg and SiO₂ (Shi *et al.*, 2001; Ren *et al.*, 2008) as shown in Eq. (7) and also presented in Figs. 5 and 6.



In this present study, there is no evidence of reaction in Eqs. (5) and (6), because Mg₂Si have not been detected as shown in the XRD phase analysis in Fig. 6. Since the contact reaction of Al with SiO₂ film layer is much higher than that of Mg in Al, Al reacts with SiO₂ as shown in Eq. (8). Thus, the formation of MgAl₂O₄ is more acceptable to take place base on reactions in equations 4.9 to 4.10 as presented;



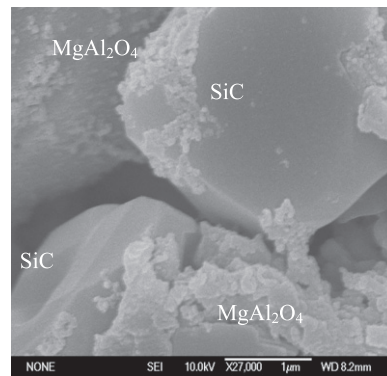


Fig. 5 SEM micrographs showing the growth of MgAl₂O₄ in Al-SiC_p.

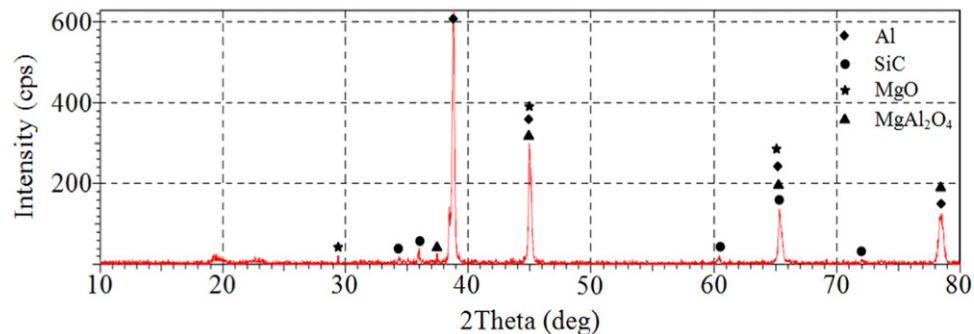


Fig. 6 XRD phase analysis of Al-SiC_p without alumina carbide formation.

The free energy of formation per mole of O₂, of MgO is the lowest, followed by that of Al₂O₃ and SiO₂ (Shi *et al.*, 2001). The change in free energy due to reaction in Eq. (10) is also negative (Shi *et al.*, 2001), which implies that MgO and Al₂O₃ react to form MgAl₂O₄. The mechanism of improvement in wettability on alloying of Al with Mg in the Al-SiC_p composites, involves the reduction of surface tension of molten Al by removal or modification of the oxide skin as suggested by earlier authors (Rohatgi *et al.*, 1986; Cappleman *et al.*, 1985). The presence of the MgO and MgAl₂O₄ phases at the interfaces creates a diffusion barrier which inhibits and restricts the formation of Al₄C₃ due to the reaction of Al and SiC_p as shown in the XRD phase analysis in Fig. 6.

Conclusions

The following conclusions were achieved from this study;

- (1) The successful formation of SiO₂ layer was achieved as a result of oxidizing the reinforcement phase (SiC_p) for a period of 2 h at 1200°C.
- (2) The successful use of reinforcement coating (SiO₂) through oxidation of SiC_p and addition of 1 wt% Mg to influence the formation of stable catalyst compound known as MgAl₂O₄ to enhance the interfacial bond strength and improve wettability between the Al alloy melt and SiC_p.
- (3) The reaction product shows that the presence of Mg at the reactive boundary of the interface coupled with the formation of SiO₂ on the surface of SiC_p confirms the presence of MgAl₂O₄ and MgO due to the reaction synthesis between Al alloy and SiC_p.
- (4) The combination of MgO and MgAl₂O₄ phases at the interfaces creates a diffusion barrier which inhibits and restricts the reaction between Al and SiC_p to form Al₄C₃.

Acknowledgement

The authors acknowledge the support of the International Islamic University Malaysia (IIUM) for the financial support to conduct this research work and Ahmadu Bello University (ABU), Zaria for their staff support.

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Further Reading

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Life Cycle Assessment in Buildings: An Overview of Methodological Approach

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Introduction

Buildings impact significantly on the environment and the construction of buildings consume approximately 50% of raw materials, 71% of electricity, 16% of water usage and produce 40% of waste disposed of to the landfills (Oduyemi *et al.*, 2017). In addition buildings are responsible for emissions and wastes of 18% and 50% respectively caused by raw material exploitation and building operation (Kibert, 2016). Building is a complex product that has a long lifespan. Buildings play an important role in maintaining the well-being of the humankind and the environment which has escalated due to the emergent of building-related health issues.

Buildings offer the most significant potential for mitigating environmental impacts and much attention has been given to improving their efficiency and performance (Hong *et al.*, 2015; Giesekam *et al.*, 2016). Operating efficiency has been the main focus of studies as this is the stage that most of the energy is consumed and most of the wastes are generated in a building's lifecycle. With the advancement of technologies and shifting to the use of renewable energy in the improvement of operating efficiency, more attention has now been given to the upstream flows of energy and emissions embodied in materials (de Wolf *et al.*, 2016).

Life cycle assessment (LCA) is a well-developed tool to assess the environmental performance of materials, products, systems or even the whole building through quantifying the resource consumption and waste generation from the upstream flow of raw material extraction, manufacture, transport, construction and use, and the downstream flow of end-of-life (EOL) deconstruction and disposal (Ding, 2014). The LCA study allows the impact of discrete systems and materials to be weighted against each other so that environmentally friendly materials can be produced and used for the design and construction of buildings. The use of LCA to assess the environmental performance of materials and buildings has increased dramatically over the last decades.

The main objectives of the chapter are to overview the methodological approach of LCA and its uses in the construction industry. This chapter begins with an overview of the LCA methodology, its definition and the International Standards Organization framework, followed by the types and models. This chapter also presents the structure of an LCA approach in the assessment of buildings in the four lifecycle phases of product, construction, use and EOL, and followed by an examination of LCA studies of materials and buildings from the literature. The chapter concludes with a discussion on the limitations of LCA studies in materials and buildings.

An Overview of LCA

The Development

The concept of LCA was originated in 1969 when the Midwest Research Institute in the US conducted the very first LCA study for the Coca-Cola to compare the differences between using plastic and glass bottles (Baumann and Tillman, 2004; De Benedetto and Klemeš, 2008). The reasons for the development of LCA were the problems with rising waste accumulation and the acknowledgment of limited resources and energy supply issues (Klopffer and Grahl, 2014). LCA received more attention from the beginning of the 1990s due to the accelerated deterioration of the environment (Baumann and Tillman, 2004). LCA was initially used for assessing performance impact of a particular product on the environment but it has now expanded to include the assessment of government policy and incorporated as part of the product design process (Kohler and Moffatt, 2003).

LCA is a systematic framework that focuses on dealing with the inflows and outflows and offers a methodology for assessing the environmental impacts spanning from the extraction of raw materials to the eventual disposal (Klopffer, 2006). Lei *et al.* (2003) describe LCA as a quantitative method used to assess the environmental burdens of particular products. Kohler *et al.* (2010) further describe the use of LCA is a paradigm shift in the evaluation of products and services in buildings.

The principal functions of LCA are therefore included quantifying and evaluating the environmental performance of products, processes or systems so that decision-makers can optimize their selections among alternatives. Additionally, it helps to identify potential improvements that can be made to lessening the overall impacts at specific stages in a lifecycle perspective (Wei *et al.*, 2008; Ahn *et al.*, 2010). All the processes of a particular product or service that compose a product system make up its lifecycle and can, therefore, be compared to other product systems that perform an equivalent function.

The Overview

LCA is well regarded as a useful and important assessment tool to sustain manufacturers, suppliers, consumers, policy-makers, and building stakeholders in making decisions about the environmental performance of products and buildings (Jeswani *et al.*, 2010). The Society of Environmental Toxicology and Chemistry (SETAC) has defined LCA as a quantitative method used to assess the

environmental burdens of particular products, processes or systems over their entire lifecycle (Klöpper, 2006; Chau *et al.*, 2015). According to Taygun and Balanli (2007), the use of LCA aims at assisting in:

- Conserving natural resources.
- Preventing environmental pollution.
- Supporting environmental parity.
- Preserving diverse sustainable ecosystems.
- Developing environmental legislation.
- Developing environmental execution evaluation in environmental management systems.
- Providing the manufacture of environmentally friendly building products.
- Decreasing the environmental impacts and health risks in building operation and maintenance.

In the building sector, the improved environmental performance of buildings is the main driving force for saving resources and reducing emissions. An environmental assessment is the evaluation of the environmental effects and from that, possible reduced impacts to the environment may be identified and developed. LCA is used to calculate the quantities of resources demanded and waste produced per functional unit (Rebitzer *et al.*, 2004). LCA has now been extensively used in the building industry in four main areas of evaluating manufacturing processes, developing product labels, comparing materials and methods, and analyzing whole buildings (Simonen, 2014).

International Standards Organization (ISO)

In the early 1990s, there were concerns over LCA results being inappropriately used and claimed by product manufacturers with regards to the environmental benefits of their products for marketing purposes (Curran, 2008). In addition, there were pressures from environmental organizations to standardize the LCA methodology and guidelines on an international level. SETAC initiated to develop a definition for LCA and developed a standardized methodology for LCA studies which has led to the development of the ISO 14040 series (Ekvall, 2002; Curran, 2008).

The standardized methodology for LCA studies was first published by the International Standards Organization (ISO) as part of the ISO 14040 series in 1997. ISO 14040 series provides a standardized method of tracking, reporting, compiling and evaluating inputs, outputs and the potential environmental impacts of a product, process or system throughout the lifecycle. (ISO, 2006a,b). The introduction of these international standards was seen as a milestone for LCA practice, although they are not entirely suited to every methodological choice in LCA. However, Ekvall (2002) states that even though the introduction of the ISO 14040 series was a huge milestone for LCA, the guidelines and principles as outlined in the standards are not in unison with every methodological choice in LCA. As the standard is a generic framework, it allows analysts to use the standards and produce virtually any LCA results. Ekvall (2002) goes on to state that since LCA methodology is continuously evolving, the content of the standard becomes outdated relatively quickly. Therefore for the international standards for LCA to be useful, it is imperative that the standards be updated by the ISO to encompass new ideas that are continually incorporated into the guidelines as state-of-the-art development.

Since the initial release of the ISO 14040 series, it was revised in 2006 (ISO, 2006a,b). The LCA framework has been developed through the ISO 14040 series to include:

- ISO 14040 - Environmental Management: Life Cycle Assessment - Principles and Framework.
- ISO 14041 - Environmental Management: Life Cycle Assessment - Goal and Scope Definition and Inventory Analysis.
- ISO 14042 - Environmental Management: Life Cycle Assessment - Life Cycle Impact Assessment.
- ISO 14043 - Environmental Management: Life Cycle Assessment - Life Cycle Interpretation.
- ISO 14044 - Environment Management: Life Cycle Assessment - Requirements and Guidelines.

ISO 14040 and 14044 have been internationally adopted for more regional specific standards/guidelines to facilitate a more transparent communication for improving the environmental performance of building and to enhance sustainable practices in the construction industry. The regional specific standards/guidelines include the development of the EN 15804 and 15978 standards by the CEN TC 350 in Europe to provide a methodological framework and definition of stages. Similar in the UK, the PAS 2050 was developed in 2008 to provide guidelines for the assessment of lifecycle GHG emissions of products. Internationally, the development of the GHG Protocol Product Standard in 2011 provides requirements for measuring, managing and reporting on GHG emissions (Simonen, 2014; Soust-Verdaguer *et al.*, 2016).

LCA Framework and Methodology

LCA Framework

Early studies of LCA were carried out by specialists for private companies at the discretion of individual practices to suit their own needs (Baumann and Tillman, 2004). With the standardization of the LCA methodology, the ISO has considered as a clear framework that LCA practitioners can follow when conducting an LCA study (Finkbeiner, 2014). In according to the ISO 14040 series the principal objectives of LCA are:

- To measure and appraise the environmental impact of products, processes or systems.
- To support decision making of environmentally friendly products, processes or systems.
- To identify potential improvements to improve the performance of products, processes or systems which may lead to the modification or redesigning to reduce the overall environmental impacts.

The ISO 14040 series outline that the LCA framework includes four phases of goal and scope definition, inventory analysis, lifecycle impact assessment, and interpretation as presented in Table 1. Therefore it is principally essential to define the goal and scope of performing an LCA carefully at the very beginning.

When the LCA framework is applied to undertake environmental impact analysis of buildings it can be done in the following scopes and as presented in Fig. 1:

- Individual building materials or products, e.g., cement, concrete, vinyl flooring.
- Individual building elements, e.g., substructure, reinforced concrete external walls.
- One or several stages in a building lifecycle, e.g., building material production stage, construction on-site, operating phase.
- Whole building analysis, e.g., full lifecycle study.

The arrows in Fig. 1 indicate the interaction within and between the phases that are required to ensure that goals, scope, methods and results are consistent, complete and relevant. The results of an LCA study varies depending on the goal and scope set

Table 1 The purposes of the four phases of LCA

LCA phase	Purposes
Goal and scope	• Identifying the purpose of the study, the limits and the boundary • Setting up a functional unit for the study • Identifying key processes, material and energy flows for analysis
Inventory analysis	• Collecting data • Analyzing material and energy flow for each stage of the lifecycle • Disassembling the process that constitutes at different stages of the lifecycle • Collecting, quantifying and calculating data of inputs and outputs of the system for the entire lifecycle
Life cycle impact assessment	• Quantifying the demand for resources • Evaluating the likelihood of environmental impacts • Classifying and characterizing inventory data into various impact categories using either midpoint or endpoint approaches
Interpretation	• Interpreting environmental impacts results • Conducting improvement analysis for potential opportunities to reduce impacts • Recommending either system improvements or environmentally preferable product and process selection

Sources: ISO, 2006a. ISO 14040: Environmental management – Life cycle assessment – Principles and framework. Geneva: International Standards Organization. ISO, 2006b. ISO 14044: Environmental management – Life cycle assessment – Requirements and guidelines. Geneva: International Standards Organization.

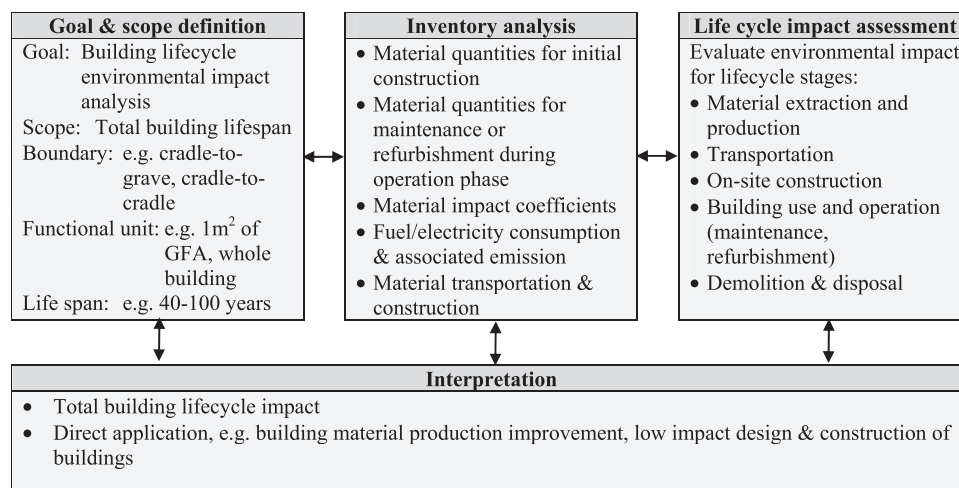


Fig. 1 LCA framework and methodology in the building industry. Rashid, F.A., Yusoff, S., 2015. A review of life cycle assessment method for building industry. Renewable and Sustainable Energy Reviews 45, 244–248. Zhang, W., Tan, S., Lei, Y., Wang, S., 2014. Life cycle assessment of a single-family residential building in Canada: A case study Building Simulation 7, 429–438.

Table 2 Strengths and weaknesses of LCA study

Strengths	Weaknesses
● Provides quantifiable metrics for evaluating environmental impacts ● Results can be used to compare various alternatives or to identify the optimum option ● Impacts can be tracked throughout the supply chain and throughout the lifecycle to provide a more holistic understanding of the environmental impacts of products, processes or systems ● Enable manufacturers and consumers to understand opportunities for improvement and identify where trade-offs occur during the lifecycle ● Minimize the use of unsubstantiated environmental claims such as greener, low impact and so forth	● Require significant resources and time to conduct a detailed study ● Social and economic impacts of sustainability are not included in LCA studies ● Data unavailable for some specific locations and processes being studied ● Much LCA data is proprietary and may only accessible via LCA software ● A full cradle-to-grave LCA study requires the development of scenarios to outline the use and EOL phases which is highly uncertain and actual events such as natural disasters, refurbishments of buildings are difficult to model ● Assume accuracy is a significant flaw in LCA studies as results are often reported as the aggregation of industry average data without in-depth consideration of the variability and uncertainty

Sources: Baumann, H., Tillman, A., 2004. The Hitch Hiker's Guide to LCA. Lund: Studentlitteratur AB. Ding, G.K.C., 2014. Life cycle assessment (LCA) of sustainable building materials: An overview. In: Pacheco-Torgal, F., Cabeza, L.F., Labrincha, J., de Magalhaes, A. (Eds.), *Eco-Efficient Construction and Building Materials, Life Cycle Assessment (LCA), Eco-labelling and Case Studies*. Oxford: Woodhead Publishing, pp. 38–62. Simonen, K., 2014. *Life Cycle Assessment*, Oxon: Routledge.

at the beginning. The accuracy of an LCA study may be jeopardized by the accessibility and availability of relevant data and data quality. Therefore it is important to note that the results generated in an LCA study may be considered as ongoing activities and may contribute to being part of the further study.

LCA study is important in the construction industry as it provides a systematic assessment of impacts by documenting procedures, data sources, boundaries and assumptions to ensure information clarity and facilitate greater comparability of products, processes or systems in buildings. LCA is regarded as a comprehensive methodology for impact assessment but its results may not be easily interpreted if results are overly aggregated. Transparency of processes is important for the validity of an LCA. However, this may discourage many from participating because of the concern over proprietary information. **Table 2** presents the strengths and weaknesses of the LCA study in the construction industry.

Even with the weaknesses and criticisms discussed, LCA study is still important in assisting the construction industry to enhance the goal of sustainability in construction in terms of creating and maintaining a healthy building environment, minimizing consumption of resources, reducing the generation of wastes and emissions to the surrounding environment (Ahn *et al.*, 2010).

Types of LCA

Attributional LCA

Attributional LCA is an approach used to examine the environmental flows to and from a products lifecycle within a chosen system of the functional unit (Finnveden *et al.*, 2009; Simonen, 2014). Attributional LCA specifies information with regards to the impacts of the processes used to produce and dispose of a product (Brander *et al.*, 2008). Brander *et al.* (2008) continue to state that to a large extent attributional LCA methodology was the basis for the formation of the international standard for LCA.

Attributional LCA studies in most cases develop quantitative relationships between input and output within a product. These quantitative relationships allow precise and accurate results to be produced based on the assumption that there will be no impact on the overall changes to the technologically modified environment within the chosen system. Outcomes from the attributional LCA can also be used to compare the direct impacts of different products (Simonen, 2014). Furthermore results from attributional LCA can be used to recognize opportunities for reducing direct impacts at various stages in the product lifecycle. However attributional LCA does not consider any indirect effects within the system boundary. Therefore even though this system boundary issue may be considered as a limitation, but in turn, it denotes that the system boundary of each product in the study will not overlap. It implies that the issue of double counting will not happen as in theory each of the processes of the product merely is added together with the total resulting in the total environmental emissions for the products (Brander *et al.*, 2008).

Consequential LCA

Consequential LCA attempts to model future consequences of changes in the output of a product (Finnveden *et al.*, 2009; Simonen, 2014). It considers effects both inside and outside the product lifecycle. Consequential LCA also models casual relationships that stem from the decision to change the output of a particular product (Brander *et al.*, 2008).

The main difference between attributional and consequential LCA is that attributional LCA focuses on the environmental impacts associated with a product during its lifecycle; whereas consequential LCA focuses on outlining the effects of any changes, i.e., output levels of the lifecycle. According to Ekvall (2002), there are concerns with completeness in the consequential LCA where the full consequences of changes in a lifecycle can never be fully understood and assessed. This is because as the future cannot be easily envisaged, it is not possible to accurately explain the future consequences of changes. Furthermore, as LCAs are principally prone to include large data gaps, adequately forecasting future consequences of changes is very difficult to do accurately. Additionally, there are also concerns about the actual relevance of performing consequential LCAs. Ekvall (2002) states that

decision makers are more concerned with understanding the actual environmental burdens associated with products, processes or systems, than in the knowledge of what potential effects occur as a result of changes in a lifecycle.

LCA Models

There are different LCA models available depending on the type of product, product system and stages of a product's lifecycle. Some LCA models investigate a single product; some are used to investigate the relationships associated with a particular product, process or system; and others are used to compare different products. The main methods used are process-based and input-output models to account for the environmental impact of goods and services and are the foundation for the hybridized methods (Majeau-Bettez *et al.*, 2011).

Process-based model

The process-based LCA analysis method is seen as a conventional approach to LCA (Rowley *et al.*, 2009). It is aimed at the manufacturing process of a product, where all the inputs and outputs for a particular product are itemized. The two main process-based approaches are process flow diagrams and matrix representation of a product (Suh and Huppes, 2005). The process-based method is commonly referred to in the USA as the SETAC-EPA approach due to the large efforts towards its continual development by SETAC and the Environmental Protection Authority (EPA). It is a bottom-up technique that consists of reviewing the required resources and the generation of pollutants from the production processes.

The analysis first determines a system boundary or scope for the study in according to the ISO 14040. Typically this is done by a repetitive process, where an initial system boundary is chosen and then refinements are made through the introduction of new unit processes. This method can also require high resources and labour, making it quite an expensive process due to the large volume of process-specific primary data.

Input-output (IO) model

The input-output (IO) approach was designed to incorporate the economy-wide interdependencies. Wassily Leontief initially developed it in the early 1940s (Rowley *et al.*, 2009). It was not until the 1970s that Leontief proposed using the IO approach to analyzing environmental impacts. Applications of IO analysis started being used in LCA analysis in the early 1990s (Suh and Huppes, 2005). The IO model was developed as an alternative to the process-based model to overcome the limitations of boundary definition and circularity effects that are typically associated with the process-based model. In a process-based analysis, truncation errors continually occurred, because it was not feasible to collect process specific data for the entire economy (Suh and Huppes, 2005). A full system is required to quantify truncation errors and IO analysis has been adopted and used extensively as a method to indirectly estimate the levels of truncated errors that occurred as a result of the process-based LCA analysis (Majeau-Bettez *et al.*, 2011).

The IO analysis is a top-down technique that deals with the economy-wide interdependencies of industries in the national economy through the utilization of sectorial monetary transactions data (Majeau-Bettez *et al.*, 2011). It is essential to account for the movements within the entire supply chain for both direct and indirect activities during the manufacturing of a particular product.

Hybrid models

The hybrid LCA approach has been developed to combine the strengths of process-based and IO analysis into a single model. It is through the amalgamation of these two models into a hybrid model that the limitations associated with these models can be addressed and overcome (Lenzen, 2002). The three main hybrid models are tiered hybrid analysis, IO-based analysis and integrated hybrid analysis (Suh and Nakamura, 2007). IO analysis is a relatively fast approach where the upstream system boundary is most completed, whereas the process-based model, on the other hand, is more accurate to analyze the direct and downstream requirements such as construction, use, maintenance and the EOL of a product.

Advantages and disadvantages of LCA models

The process-based and IO models have both strengths and weaknesses. The development of the hybrid model is more useful for LCI data compilation and it draws on the main advantages of the process-based and IO models (Rowley *et al.*, 2009). It is through the process of linking the process-based and IO models together that hybrid model can draw on the strengths of these two methods. This, in turn, can produce more accurate results and reliability in LCA studies as a whole (Suh and Huppes, 2005). Table 3 summarizes the advantages and disadvantages of the LCA models that are commonly used in the study of environmental impacts.

LCA Studies by Life Cycle Phases of Buildings

A construction project may have various level of environmental impacts at different stages of a building's lifecycle (Malia *et al.*, 2013). Kaatz *et al.* (2006) suggest that a better understanding of building phases and their related activities is fundamental to incorporate sustainability across the different lifecycle stages of a project. Thomson *et al.* (2011) state that the project lifecycle represents an important context as it reflects the consecutive and interlinked stages of the object under consideration. The factors impacting on the sustainability performance of a building may vary according to the project type, scale, location and process. Therefore, when

Table 3 Summary of advantages and disadvantages of LCA models

Models	Advantages	Disadvantages
Process-based	- Can methodically analyze material and energy flows at every stage of the lifecycle - Comparison between products can be made easily - Weaknesses during the manufacturing process can be determined to allow process improvements for future product development assessments - It is also seen as being a more specific approach in comparison to the IO analysis	- Difficult to develop a scope for the study. Large boundary requires substantial collecting and processing of input and output data which is time-consuming and costly. For a small boundary, the environmental impacts throughout the products lifecycle may be jeopardized as various inputs and outputs out of the scope would be failed to account for - The large volume of process-specific data to be collected and analyzed may lead to the study being too expensive and time-consuming to conduct
IO	- It can overcome and address the issues related to system boundary determination and truncation errors in the process-based model - It enables fast screening of LCA of a complex system - It enables the leverage of existing economic data (e.g., annual reports) - It includes comprehensive supply chain inputs beyond what is practical for most process-based model - Publicly available data, reproducible economy-wide results, system and boundary is defined as the entire economy	- Unable to conduct comparative analysis within a sector as data is aggregated by industry - Economic data may be outdated as IO tables are usually published with a time delay for a few years - It is assumed that imported products have the same environmental impacts for products produced locally which may result in large variations in the analysis - The IO tables and databases in different nations may be different due to varying levels of completeness - Maybe more applicable for material production phase but less useful for the cradle-to-grave study - There is a high level of aggregation of products in the IO tables which may make them unsuitable for LCAs - Difficult to identify process improvements, uncertainty and product use.
Hybrid	- Suitable for more extensive and more complex studies. - To address and overcome weaknesses in the process-based and IO models in LCA studies	- The model may require time for collecting a large volume of primary data for the analysis which may turn out to be not all are significant - Requires careful selection between up/downstream to prevent double counting - The interaction between processes is hard to distinguish

Sources: Suh, S., Nakamura, S., 2007. Five years in the area of input-output and hybrid LCA. *International Journal Life Cycle Assessment* 12 (6), pp. 351–352. Rowley, H., Lundie, S., Peters, G., 2009. A hybrid life cycle assessment model for comparison with conventional methodologies in Australia. *International Journal of Life Cycle Assessment* 14, pp. 508–516. Majeau-Bettez, G., Stromman, A.H., Hertwich, E.G., 2011. Evaluation of process and input-output based life cycle inventory data with regard to truncation and aggregation issues. *Environmental Science and Technology* 45, pp. 10170–101707. Simonen, K., 2014. *Life Cycle Assessment*, Oxon: Routledge.

sustainability performance of a construction project is examined, project stages and major activities in each stage must be specified first, so that factors influencing the project's characteristics of each stage can be identified.

Stage divisions of a building's lifecycle have been the focus of some research studies (Thomson *et al.*, 2011; Wu *et al.*, 2012). It is generally summarized that a building lifecycle consists of the extraction and production of raw materials, transportation, construction, operation and final deconstruction at the end of the lifecycle (Wu *et al.*, 2012). Even though different studies can have different goal and scope but lifecycle stages are required to be standardized. An internationally accepted and standardized building lifecycle is presented in the EN 15978 Standard (CEN, 2011). According to the EN 15978 the building lifecycle is divided into four phases as detailed and presented in Fig. 2:

- Product (A1–3) – Raw material supply, transport and manufacturing.
- Construction process (A4–5) – Transport, construction and installation.
- Use (B1–7) – Products in use, maintenance, repair, replacement and refurbishment.
- EOL (C1–4) – Deconstruction/demolition, transport, waste processing, and disposal.

As presented in Fig. 2 the common types of system boundary in LCA or partial LCA include cradle-to-gate, gate-to-gate, cradle-to-grave and cradle-to-cradle. Cradle-to-gate (A1–3) is from the stage of extraction to product completion (excluding distribution) while gate-to-gate (A3) includes only one section of the manufacturing process. The cradle-to-grave (A1–C4) includes the whole lifespan of material from extraction through use and disposal, and cradle-to-cradle involves all the processes from extraction to EOL of a product with the addition of recycling (Puettmann and Wilson, 2005; Mitchell and McFallen, 2008).

Over the years research studies were undertaken to assess the environmental impacts at the various stages of a building's lifecycle. Tables 4 and 5 extract some of the research studies on total energy consumption and global warming potential (GWP) of buildings at various stages in a building's lifecycle in according to the EN 15978 Standard. From the tables most of the LCA studies were breakdown by building stages, except the studies by Zhang *et al.* (2014) and Bawden and Williams (2015) focusing on the total impact only, the study by Serrano and Alvarez (2016) include only part of the use phase and EOL was basically excluded in the study.

The total lifecycle energy consumption in Table 4 demonstrates that the use phase (B1–6) consumes the most energy and followed by the product, construction and EOL. Both the construction and EOL phases consume the least amount of energy in a lifecycle perspective. The total energy consumption of both residential and office buildings in Table 4 varies a great deal. The variations may be due to different system boundary, material manufacturing methods, fuel consumption and so forth.

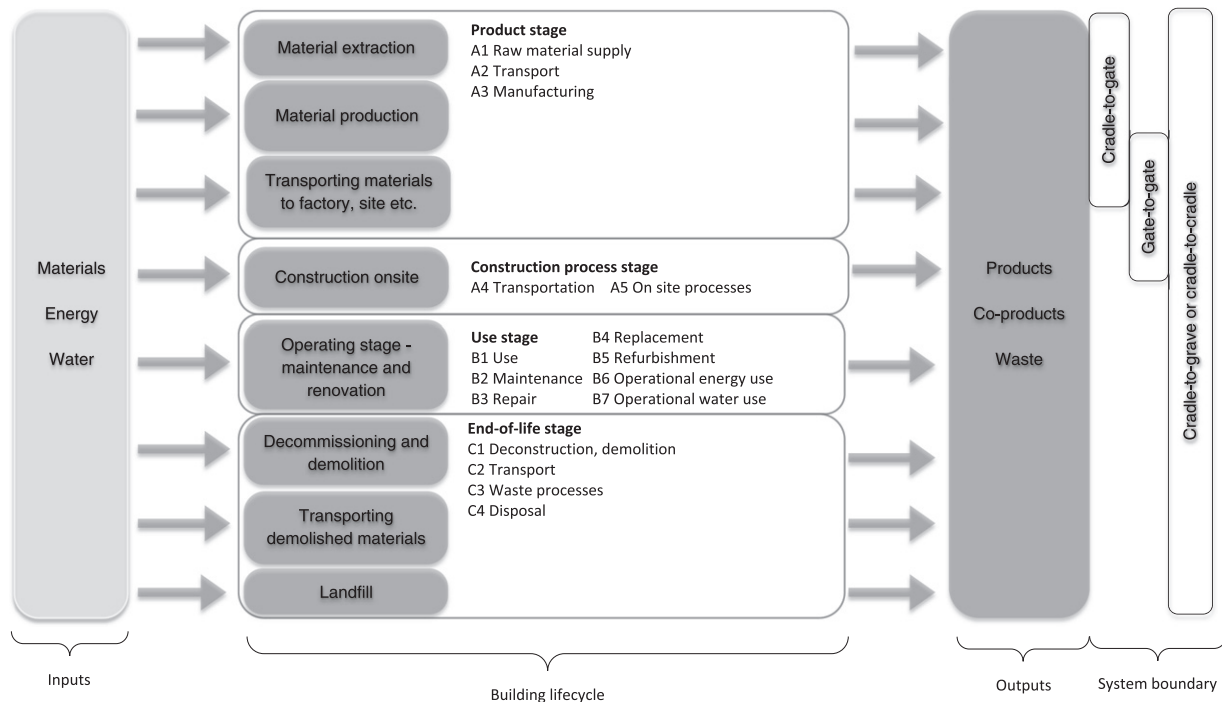


Fig. 2 Building lifecycle and system boundary. Sources: Adapted from ISO, 2006a. ISO 14040: Environmental Management – Life Cycle Assessment – Principles and Framework. Geneva: International Standards Organization. ISO, 2006b. ISO 14044: Environmental Management – Life Cycle Assessment – Requirements and Guidelines. Geneva: International Standards Organization. CEN, 2011. Sustainability of Construction Works – Assessment of Environmental Performance of Buildings – Calculation Method. UK: British Standard Institute.

Similarly, GWP is another impact category that LCA studies are considered. From [Table 5](#) the GWP generated from buildings demonstrates that the use phase generates most of the total GWP and followed by the product, EOL and construction. The GWP of both construction and EOL phases are minimal compared to the other two phases but the EOL phase has a slightly higher impact than the construction phase in the GWP.

Product (A1–3)

This is the first stage of a building's lifecycle and it involves the production of materials that are used in the construction of buildings. There are environmental impacts embedded in the production of the materials used in buildings. [Alcorn \(2003\)](#) states that energy has long been one of the most appropriate indicators of environmental impacts, in particular embodied energy as it denotes the total upstream energy consumption in materials for the construction of buildings. The energy and emissions embodied in materials include extracting raw material from the ground, transporting raw materials to factories and producing building materials. Therefore selecting the appropriate building materials based on the embodied energy and emissions content is crucial for improving the efficiency of buildings.

The energy embodied in building materials is initial embodied energy and in a typical building it ranges from 10% to 60% of the total energy use ([Ramesh et al., 2010](#); [Gustavsson and Joelsson, 2010](#)). The amount of energy and emissions embodied in the production of building materials or components is highly dependent on the type of fuel sources such as oil, diesel, electricity used in the extraction, manufacturing process and the associated quantities involved. ([Chau et al., 2012](#)).

The inventory analysis at this stage involves obtaining data for building materials from the bills of quantities if available. Otherwise, material quantities are estimated from construction drawings or field measurement of work on-site. Therefore it is important to determine the type and quantity of materials used for the building. [Table 4](#) indicates that the energy consumption (MJ/m^2) at the product phase of both residential and office buildings represents around 6%–12% of the total energy consumption. Similarly, the GWP ($\text{kgCO}_2\text{-e}/\text{m}^2$) generation in [Table 5](#) at the product phase is approximately 5%–12% of the total lifecycle emissions.

Construction Process (A4–5)

The construction phase of a building refers to a series of construction activities which include the erection of the structure and installation of building materials or components until buildings are completed. The time taken to construct a building varies according to the size and complexity of the project. A large number of machinery and site personnel are required for the

Table 4 Total energy consumption of buildings by lifecycle stages

Type	Country	Year	Product	Construction	Use	EOL	Total	Product	Construction	Use	EOL	References
			Total energy consumption (MJ/m ²)				%					
Single-storey house	Sweden	2000	60	7	427	2	496	12.1	1.5	86.0	0.4	Adalberth (2000)
Multi-unit apartment	Sweden	2001	65	8	475	2	550	11.8	1.5	86.4	0.4	Adalberth <i>et al.</i> (2001)
Two-storey house	Canada	2014					519					Zhang <i>et al.</i> (2014)
Low rise apartment	US	2015					600					Bawden and Williams (2015)
Medium rise apartment	US	2015					680					Bawden and Williams (2015)
High rise apartment	US	2015					800					Bawden and Williams (2015)
Single-family terraced housing	Spain	2016	16	0.6	244 (B1 & 5)		261	6.1	0.2	93.5		Serrano and Alvarez (2016)
Multi-family housing	Spain	2016	11	0.5	186 (B1 & 5)		198	5.6	0.3	93.9		Serrano and Alvarez (2016)
High rise office	US	2006	141.4	25	1450.9	15	1632	8.7	1.5	88.9	0.9	Junnila <i>et al.</i> (2006)
High rise office	Finland	2006	68.2	21.8	970.5	3.6	1064	6.4	2.0	91.2	0.3	Junnila <i>et al.</i> (2006)
High rise office	China	2012	168.6	19.4	1177.4	3.9	1369	12.3	1.4	86.0	0.3	Wu <i>et al.</i> (2012)

Table 5 Global warming potential (GWP) of buildings by lifecycle stages

Type	Country	Year	Product	Construction	Use	EOL	Total	Product	Construction	Use	EOL	References
			GWP (kg CO ₂ -e/m ²)				%					
Single-storey house	Canada	2014					29					Zhang <i>et al.</i> (2014)
Low rise apartment	US	2015					36					Bawden and Williams (2015)
Medium rise apartment	US	2015					44					Bawden and Williams (2015)
High rise apartment	US	2015					50					Bawden and Williams (2015)
Medium rise apartment (Lightweight)	Australia	2015	5.7	0.7	61.3	1.6	69	8.2	1.0	88.5	2.3	Carre and Crossin (2015)
Medium rise apartment (Typical concrete)	Australia	2015	8.4	0.5	61	0.9	71	11.9	0.7	86.2	1.3	Carre and Crossin (2015)
Semi-detached house	Spain	2016	1.4	0.04	16.9 (B1 & 5)		18	7.6	0.2	92.1		Serrano and Alvarez (2016)
Low rise apartment	Spain	2016	1	0.03	13 (B1 & 5)		14	7.1	0.2	92.7		Serrano and Alvarez (2016)
High rise office	US	2006	9.1	1.8	106.8	0.9	119	7.7	1.5	90.1	0.8	Junnila <i>et al.</i> (2006)
High rise office	Finland	2006	5.9	0.9	53.2	0.3	60	9.8	1.5	88.2	0.5	Junnila <i>et al.</i> (2006)
High rise office	China	2012	14.3	1.8	259	43.5	319	4.5	0.6	81.3	13.7	Wu <i>et al.</i> (2012)

completion of construction projects. The construction stage examines resource consumption, emissions and other environmental impacts about the transportation and construction activities on-site.

The energy and emissions embodied in the construction phase include the use of equipment and transportation of materials and equipment to the site, as well as any supporting processes used on-site. Construction phase contributes a low level of environmental impact compared with the operating stage. Ortiz *et al.* (2009a) state that the construction activities account for approximately 8%–20% of energy consumption in a building's lifecycle but relatively more than the LCA studies in Table 4. The environmental impacts at this stage are relatively small compare to the operating stage of the lifecycle. However, the excessive consumption of energy and generation of emissions during site operation are negative impacts on the environment and the effect is immediate and more intensive due to the shorter period of construction compared with the operating stage (Zhang *et al.*, 2013; Huisingh *et al.*, 2015). In addition construction activities may result in other impacts such contaminating soil, surface and underground water; generating construction and demolition waste; releasing hazardous emissions and odours that may impact on the well-being of the natural and manmade environment (Gangoelle *et al.*, 2009; Ding, 2018).

The transportation of materials to the construction site has some inherent environmental impacts, namely the energy consumption and CO₂ emissions associated with the mode of transportation such as trucks, rails, ships or planes. John *et al.* (2009) state that the contribution of transport of materials to the total lifecycle environmental impacts is approximately 0.3% and 0.5%

respectively for primary energy use and CO₂ emissions which is similar to the LCA studies in Table 5. The use of locally manufactured materials reduces the overall environmental impacts but may not be as significant as the other stages. Transportation data is estimated from the average distances travel from factories or distribution centres to the construction site. Therefore the emission impacts vary with the type and mix of fuel source used in transportation as well as the operation of machinery, equipment and distance from the site.

The quantities at this stage are estimated either from bills of quantities or measurement on-site. The estimation of quantities of materials, components or systems at this phase is important as it relates to the type of machinery and equipment used for construction. The quantity of wastage due to offcuts, mishandling, mistakes in drawings and so forth are also needed to be included in the assessment (Ding, 2018). However, even though the impact may be minimal compared with the operating phase it is still necessary to include in the assessment of environmental impact as part the LCA framework to gain a holistic view of the lifecycle impacts.

In Table 4 the total energy consumption in the construction phase ranges from 1 to 22 MJ/m², representing less than 2% of the total energy consumption. Similarly, the GWP in Table 5 is less than 2 kgCO_{2-e}/m² and about 1% of the total lifecycle GWP. Serrano and Alvarez (2016) studied the impact of two different types of housing topologies on both total lifecycle energy consumption and GWP in Spain. Results reveal that the single-family terraced housing typology consumes nearly 17% more energy and emits 25% more emissions than the multi-family housing typology at the construction stage as multi-family typology allows for more opportunities sharing of common structures and spaces.

Use (B1–7)

The operating phase is the stage where the needs of users are met. During this stage the building is maintained and refurbished throughout its lifecycle to sustain the functional capacity. During this period, the number of repairs, refurbishments and upgrades of building components or services will be required upon demand; while a replacement will replace 100% of a material or component. Replacements may occur several times during the life of the building. All this periodical work will accumulate and require energy to perform and at the same time releasing emissions.

The operating stage of a building entails the energy and emission associated with the cooling, heating, ventilation as well as the lighting, electricity and water supply. There are many variances to the factors affecting a building's operating energy and emissions such as the design of the building, purpose of the building, occupation number, energy source, local climate, building materials type and quality as well as air changes and occupants habits. Ramesh *et al.* (2010) state that the operating stage utilizes approximately 80%–90% of a building's lifecycle energy. Operating energy consumption can either obtained from the analysis of utility bills or use simulation software such as EnergyPlus, AccuRate, ECOTECT to estimate electricity or gas consumption.

The selection and use of materials in building for both the structural elements and interior finishes can influence not only the embodied energy of a building but also the operating energy. Maintenance of a building is required throughout the operating stage and it is where a large variety of building materials that have a lifespan less than that of the building have to be replaced (Ramesh *et al.*, 2010). The actual replacement of materials coupled with the regular maintenance to building components from wear and tear leads to a recurring embodied energy and emissions to occur. Typically the recurring embodied energy and emissions are not associated with buildings structural components as these materials in most cases have a lifespan similar to or longer than that of the building itself. Maintenance and replacement data are difficult to get and highly varies according to the life expectancy of materials, components and systems. Publications such as the study of life expectancy of housing components (NAHB, 2007), the life expectancy of building components (RICS, 2006) and lifecycle costing (AIQS, 2002) are commonly used to study the frequency of maintenance, replacement refurbishment in buildings.

Tables 4 and 5 demonstrate that the use phase consumes the most of energy and generates the most of GWP, approximately 86%–94% and 81%–93% respectively during the building's lifecycle. However, there is no detail information in the studies with regards to whether embodied energy and emission for maintenance and replacement were included in the studies in the tables. Therefore figures in the tables may be higher if the maintenance and replacement of materials or systems are to be allowed for. The study conducted by Carre and Crossin (2015) compared lightweight timber design with the traditional concrete structure for two medium-rise apartment buildings in Australia. Research results indicate that both buildings generate a similar amount of GWP but the product stage of the lightweight construction generates about 32% fewer emissions than the concrete construction. In the study conducted by Serrano and Alvarez (2016) reveals that the multi-family housing typology consumes approximately 23% fewer emissions than the single-family terraced typology.

EOL (C1–4)

Demolition at the end of the building's lifecycle is sometimes inevitable. The most commonly used disposal methods are landfilling, recycling or incineration. The EOL scenarios used are different for different building materials such as landfilling is commonly used for timber while recycling is of steel and concrete (Kellenberger and Love, 2009; John *et al.*, 2009). Incineration is frequently used for timber as wood waste can be burnt for biomass energy.

The EOL phase is important as this is the phase that demolished materials can be recycled to decrease the consumption of energy in the manufacturing of new building materials and reduce to the potential impact on the landfill sites. However, according to Guggemos and Horvath (2005), material recycled, reused or landfilled should not be included in the overall environmental impact assessment of a building for two reasons. Firstly, it is hard to forecast the future value of demolished materials accurately, and whether or not they are appropriate to be reused, recycled or landfilled that they are considered hazardous waste. Secondly, they consider that the recycling of salvaged materials is accounted for in the manufacturing process, and in turn would be accounted for in a future building LCA that uses the recycled materials.

The research conducted by Kellenberger and Love (2009), and John *et al.* (2009) show that landfilled timber has a lower GWP than steel and concrete buildings. Angel and Castle (2007) studied the potential GHG liability of landfill in Australia. It was concluded that there is no future for landfilling wood wastes as they have degradable organic carbon, which decomposes over time and emits GHG when it is landfilled. Therefore future EOL scenarios including incineration with energy recovery (biomass) should start to be adopted more regularly to reduce GHG in the future as every tonne of wood waste disposed into landfill today will be a GHG liability in the future (Angel and Castle, 2007).

The assessment in the impact of EOL phase includes the energy consumed and emission generated by machinery or equipment used during demolition and the average distance of travel by trucks to dispose the waste to the landfill or recycling facilities. From Tables 4 and 5 less than 1% of energy is consumed and about 1%–14% of GWP is emitted during this stage in most of the studies. The study conducted by Wu *et al.* (2012) has the highest EOL impact of GWP, approximately 14% which is much higher than the other two studies of office buildings in the table and from the literature. However there was not enough detail for further examination.

Examples of LCA Studies of Buildings

LCA is a well-developed and useful environmental assessment tool that has been utilized to assess the environmental performance of buildings over their effective life (Bribián *et al.*, 2009). More than 90%–95% of LCA case studies concentrate on assessing environmental impacts within the building sector (Ortiz *et al.*, 2009b). These case studies assist key stakeholders by concentrating on appraising the total environmental impacts and supporting decision-making regarding environmental preferred materials and systems over a building's lifecycle (Chau *et al.*, 2015).

LCA has been used in many studies in the building sector for a complete building or in some studies focusing on the LCA studies of building materials or systems to aid the selection process during the early design stage. Some of these environmental building material studies were based on partial LCAs or cradle-to-gate studies before particular guidelines were introduced to allow for comparative studies based on fixed criteria. Some target one or several stages of the building lifecycle.

Rashid and Yusoff (2015) conducted a review of LCA studies for buildings and summarized that the LCA studies in the construction industry have increased steadily since the 1990s. In another study by Anand and Amor (2017) state that LCA studies have increased more than double in the last five years with 2015 alone about 250 building LCA papers were published. Anand and Amor (2017) continue to state that the LCA studies for buildings have now shifted from focusing from operating phase to a full lifecycle study. Table 6 provides a snapshot of LCA studies from the literature. As also indicated in Table 6 the majority of the LCA studies concentrate on the cradle-to-grave system boundary. The common study period of LCA studies in the table is 50 years lifespan while the functional unit ranges from the whole building assessment to 1 m² of GFA. The total fossil fuel consumption (FFC) and GWP are the two impact categories assessed most of all other impact categories.

The environmental study of building materials or systems are important as results can provide information for the selection of low impact materials or systems to reduce the lifecycle energy consumption and associated impacts. In the table the study by Contarini and Meijer (2015) was to compare several flat roof systems of different materials and thickness of insulations, heat resistance, waterproofing layer and covering layers for an apartment building in the Netherlands. Research results indicate that improving insulation from 2.5 to 5 m² K/W leads to the reductions of the damage scores from about 10%–40%. The outcomes will aid building owners and construction maintenance companies to choose renovation options for flat roofs with the lowest impact on the environment.

Puettmann *et al.* (2010) also documented a cradle-to-gate comparison between hardwood and softwood manufacturing in the US and the result showed that softwood required 50% less energy than hardwood. Kahhat *et al.* (2009) based the LCA framework to analyze the environmental impacts of six different exterior wall systems of a single-storey residential building. Study results indicate that the operating stage of the lifecycle accounts for approximately 94% of total energy consumption. In addition insulated concrete exterior walls consume approximately 700 GJ (5% of total lifecycle energy) than traditional wood frame exterior wall and generate less negative impact to the environment because of the dominance of the use phase in energy consumption. These cradle-to-gate studies are a useful source of data and add to the accuracy of whole building LCA as they continually improve.

LCA studies have also been undertaken to one phase of a building lifecycle which may target for improving the design and construction of buildings. Guggemos and Horvath (2006) analyze the environmental impacts for the construction of structural frame of a university building in California, US. Results reveal that 50% of environmental impacts were related to the use of equipment on-site and the temporary construction materials have the second most significant impact. Bawden and Williams (2015) also conducted research focusing on the operating energy and associated emission for low-rise, medium-rise and high-rise residential buildings in the US. High-rise residential buildings consume the most of energy and associated emissions due to the

Table 6 LCA studies of materials/systems and whole buildings

Type	Country	Year	No of buildings	Functional unit	Boundary	Life span	GFA	Impact categories	References
University building	US	2006	1	Structural frame only	Construction only	50	8760	FFC, GWP	Guggemos and Horvath (2006)
Low rise apartment	US	2015	2	Whole building	Operation only	50	2837	FFC, GWP	Bawden and Williams (2015)
Medium rise apartment	US	2015	4	Whole building	Operation only	50	6045–5580	FFC, GWP	Bawden and Williams (2015)
High rise apartment	US	2015	4	Whole building	Operation only	50	7510–20,135	FFC, GWP	Bawden and Williams (2015)
Single-storey house	NZ	2002	3	Whole building	Cradle-to-gate			FFC	Glover <i>et al.</i> (2002)
Compare softwood & hardwood	US	2010		1 m ³	Cradle-to-gate	50		FFC, GWP	Puettmann <i>et al.</i> (2010)
Multi-family apartment	Netherlands	2015		Roof (300 m ²)	Cradle-to-gate	30		FFC, GWP	Contarini and Meijer (2015)
Single-storey house	Sweden	2000	3	1 m ²	Cradle-to-grave	50	129–136	GWP, AP, EP, POCP	Adalberth (2000)
Multi-unit apartment	Sweden	2001	4	1 m ²	Cradle-to-grave	50	700–1520	GWP, AP, EP, POCP	Adalberth <i>et al.</i> (2001)
Two-storey house	Canada	2014	1	Whole building	Cradle-to-grave	60	236	FFC, GWP, AP, HH, EP, ODP, SP	Zhang <i>et al.</i> (2014)
Single-family terraced housing	Spain	2016		Whole building	Cradle-to-grave	10	20,003	FFC, GWP	Serrano and Alvarez (2016)
Multi-family housing	Spain	2016		Whole building	Cradle-to-grave	10	22,227	FFC, GWP	Serrano and Alvarez (2016)
High rise office	US	2006	1	Whole building	Cradle-to-grave	50	4400	FFC, GWP	Junnilla <i>et al.</i> (2006)
High rise office	Finland	2006	1	Whole building	Cradle-to-grave	50	4400	FFC, GWP	Junnilla <i>et al.</i> (2006)
High rise office	China	2012	1	1 m ²	Cradle-to-grave	50	36,500	FFC, CO ₂	Wu <i>et al.</i> (2012)
Medium rise apartment (Lightweight)	Australia	2015	1	1 m ²	Cradle-to-grave	60	3895	GWP, ODP, AP, EP, POCP, AD	Carre and Crossin (2015)
Medium rise apartment (Typical concrete)	Australia	2015	1	1 m ²	Cradle-to-grave	60	5912	GWP, ODP, AP, EP, POCP, AD	Carre and Crossin (2015)
One to two-storey house	Australia	2018	10	Whole building	Cradle-to-grave	50	124–334	FFC	Thomas and Ding (2018)
Single-storey house	US	2009	6	Exterior wall	Cradle-to-grave	50		FFC, GWP, etc.	Kahhat <i>et al.</i> (2009)
Two-storey house	US	2004	3	Whole building	Cradle-to-grave	50	186	FFC, GWP	Ochoa-Franco (2004)
Office building	US	2005	1	Whole building	Cradle-to-grave	50	4000	FFC, GWP	Guggemos and Horvath (2005)

Note: ODP, ozone depletion potential, EP, eutrophication potential, POCP, photochemical ozone creation potential, AD, abiotic depletion, GWP, global warming potential, FFC, fossil fuel consumption, HH, human health, AP, acidification potential, HT, human toxicity, SP, smog potential.

energy-intensive structural materials to support the loading of the building. The research results indicate a high energy consumption compared to previous studies due to inconsistent system boundary. Thus the explicit definition of functional unit leads to an increase in the contribution of supply chains to building energy lifecycles.

The table also shows that cradle-to-gate is also a commonly used system boundary in LCA studies. Glover *et al.* (2002) compared the impact of wood, steel and concrete when used in three single-storey houses in New Zealand and resulted in the lower embodied energy of 50% for the timber house over the house with concrete floors and steel frames. Other cradle-to-gate studies are mostly undertaken on building materials or components (Kahhat *et al.*, 2009; Puettmann *et al.*, 2010; Contarini and Meijer, 2015).

Besides conducting LCA studies in a single stage, some research works targeted all the stages in a building lifecycle. As stated by Anand and Amor (2017) LCA studies have shifted to focus on full lifecycle studies than a single phase. LCA studies of residential buildings are common ranged from single-storey to multi-unit apartment buildings such as Adalberth (2000), Adalberth *et al.* (2001), and Zhang *et al.* (2014) are some examples that a full building lifecycle was used in the studies. Results indicate that the operating phase consumes most of the energy and other associated emissions and pollutants. Serrano and Alvarez (2016) focus the

study on the impact of the typology of single-family terraced housing with multi-family housing on total energy consumption and emissions on a cradle-to-grave approach and a study period of 10 years. The findings are important for the future planning and design of residential buildings.

Carre and Crossin (2015) compared two medium-rise apartment buildings of lightweight timber design and traditional concrete structure for six impact categories in Australia. Research results reveal that lightweight design with timber and engineered timber construction has less impact compared with traditional concrete structure. The results have provided information for developers and designers to consider timber and engineered timber as structural materials which are not commonly used in Australia. The results were supported by another study by Thomas and Ding (2018) for ten houses of one to two-storey in Australia. The case studies compared engineered timber with traditional brick construction and results suggest that houses built with engineered timber consume less total lifecycle energy.

Ochoa-Franco (2004) uses an input-output approach to evaluate the lifecycle impact of three residential building in the US and found that the operating energy consumption accounts for over 90% of energy use, electricity use, fossil fuel depletion, and human-health impact categories, and for over 50% of global warming effects and air pollution. Guggemos and Horvath (2005) use LCA to compare environmental impacts of steel- and concrete-framed an office building and realize that the operating stage consumes most of the energy. The research also identifies that the impacts at the construction stage are minimal to approximately 0.4%–11% of energy consumption and emissions in the building lifecycle. The maintenance and EOL also account for a small part. Junnila *et al.* (2006) identify similar results in the evaluation of two new office buildings in Europe and the US from material production through construction, use, maintenance and EOL stage. Results reveal that the operating stage accounts for 70% of energy consumption and emissions.

Wu *et al.* (2012) conduct an LCA study of a high-rise office building in China on the energy consumption and associated CO₂ emissions. Similarly, the operating phase consumes most of the energy and generates most of the CO₂ emissions, within which the highest is the heating and cooling system and followed by the concrete and steel in material production. The research has suggested adjusting the set-point temperature in the operation of an office building and increasing the recycle use of concrete and steel as the main objectives in the future design and construction of office buildings in China.

Limitations of LCA Studies in Buildings

LCA has been significantly developed over the years. It is now a useful decision-making tool for appraising the environmental impacts of a building, material or system (Finnveden *et al.*, 2009; Jeswani *et al.*, 2010). However, the applications of LCA are still complicated and challenging to use. There are limits on sustainable knowledge, especially the comprehensive information supported in the assessment of energy, emissions and water consumed in buildings.

The main limitations in regards to performing LCA studies of buildings are having access to up-to-date data. There is a plethora of data for the various material and fuel inputs that go into a building. Around the world there are a large number of gaps in data as there has no accurate lifecycle inventory data available for all materials in buildings. This is particularly serious for developing countries. Therefore LCA studies have relied on using international data or computer programs such as SimPro or GaBi. The international database or computer programs may suffer from regional variations such as different weather conditions, manufacturing processes and fuel sources.

Scheuer *et al.* (2003) and Verbeeck and Hens (2010) point out that the evaluation of buildings is challenging compared to the evaluation of products. Buildings are larger in scale, complicated in installed materials and service functions, and have a long lifespan. However, the lifetime of some components and service systems is shorter than the building and require refurbishment/replacement during the building's lifecycle. An LCA on the environmental impacts can be made when the building is built, upgraded or refurbished. New technologies used to improve the sustainability of buildings enhance over time but the industry's knowledge is commonly left behind. This means that the industry has limited or outdated information on the impacts from the extraction of raw materials for manufacturing building materials, transportation to the site, construction, use, and disposal processes at the EOL stage (Chan *et al.*, 2014; Berardi, 2015).

Challenges associated with LCAs for buildings are that they contain some stages and each of these stages has some variable inputs including material suppliers, manufacturing processes, delivery modes, energy suppliers, maintenance and demolition. In addition to these specific challenges to construction, there are also limitations such as necessary hypotheses, imperfect data, adaptability issues and high costs (Lei *et al.*, 2003). As there are many different LCA models they are each prone to particular challenges so the method should be chosen to suit the particular product or system environment.

Conclusions

Environmental crises such as shortage of natural resources, ozone depletion, emissions of GHG, and climate changes impacting on the living and working environments mean that the building sector has to be improved to meet sustainability requirements. The construction industry plays a vital role in achieving the goal of ecologically sustainable development as buildings have a high impact on the environment. The development of the LCA approach under the ISO 14040/14044 has provided an objective and systematic tool to analyze energy, emissions and resource consumption in the design and construction of buildings. Current

literature of LCA studies of buildings has demonstrated the use phase in a building's lifecycle is the most important stage as this is the stage that consumes most of the energy and generates the most of emissions. However the literature also reveals that the focus of operating stage of a building is now shifted to the upstream material production phase due to the improvement in operating efficiency of buildings. In most of the LCA studies the product phase in a building's lifecycle is the second largest in the consumption of energy and generation of emissions after the operating phase.

The diverse LCA research method with different goals, scopes and boundaries may impact the accuracy and usefulness of LCA results to facilitate direct comparisons of building materials or components and to optimize building design to enhance low impact in the construction industry. In addition LCA study requires a comprehensive data set which may require constant expansion to include new materials and update to reflect on the latest development in the manufacturing processes and construction technologies. LCA study of buildings is challenging as each building is unique and it also involves a vast investment of resources and has a long lifespan. Therefore it is important that the standardization and transparency of LCA framework are adhered to in LCA studies in the construction industry. The implementation of LCA can help designers, practitioners and decision makers to make informed decisions by providing a comprehensive analysis of the environmental performance of materials and buildings.

See also: A Comparative Life Cycle Assessment for Utilising Laminated Veneer Bamboo as a Primary Structural Material in High-Rise Residential Buildings

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Lifecycle Assessment of Building Materials – A Cradle-to-Gate Approach

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Introduction

In recent years the desire to quantify the impact of human activities on the environment has attracted attention around the world, in particular, the activities in the construction of buildings (Takano *et al.*, 2014). The construction of buildings utilizes about 40% of stone, sand and gravel, 25% of timber, 16% of water, and consumes an enormous amount of energy and emits 19% of global greenhouse gases (GHG) annually worldwide (Arena and de Rosa, 2003; IPCC, 2014; Hossain *et al.*, 2017).

In the past, research studies focused on improving operating efficiency as it was regarded as the stage that consumes most of the energy and generates most of the emissions during the building lifecycle. However, energy consumption and emissions due to building operation have been reduced progressively through shifting to the use of renewable energy, and the incorporation of technologies into the design and construction of sustainable buildings (Meggers *et al.*, 2012). The design and production of building materials have now attracted more attention.

To avoid the negative impact on the environment, it is important that the potential impacts of the design and production of building materials are taken into consideration on a lifecycle perspective. The consideration includes the consumption of resources and the damage to the environment caused by the extraction of raw materials, manufacturing and transportation of building materials. Also the recycle content and potential recyclable characteristic of materials should also be considered in the selection process of materials and products for buildings. The durability of the materials and their effect on the entire lifecycle of the building are also important considerations.

Government, industry and research organizations recognize the usefulness of lifecycle assessment (LCA) as a critical tool to identify the potential impacts of materials and products on the environment. The LCA approach is particularly important given the high volume of materials used and the growing importance of environmentally sustainable decisions. For a building, the commonly and traditional used materials are high impacts materials such as concrete, steel, plasterboard. Therefore improving material performance is paramount significant in reducing environmental impacts.

The goal of this article is to review the methodology of LCA of building materials for use in research, policy analysis and building code development. The article begins with a discussion on the importance of materials in a building's lifecycle and the selection criteria, followed by a discussion of the various initiatives and programs related to the evaluation of environmental impacts of materials. This article also reviews the LCA approach in the assessment of environmental impacts of materials on a cradle-to-gate system boundary and includes examples of LCA studies of commonly used building materials. The article ends with a discussion on strategies for reducing environmental load of building materials.

Importance of Sustainable Building Materials

Sustainable development is the foundation of environmentally sustainable practices in the construction industry and within which it provides a framework to develop strategies for buildings to be designed and built by shifting from the use of conventional resources to the use of renewable-based resources. The selection and use of materials in buildings have caused severe environmental impacts associated with the extraction and consumption of raw materials during the entire lifecycle of buildings. In achieving the goal of sustainable development in construction, the production and selection of low impact and environmentally friendly building materials are essential.

With the reduction of operating energy and emissions, the energy and emissions embodied in materials are now attracting more attention in research and development as they are permanent and take immediate effect from when the raw material is extracted and manufactured (de Wolf *et al.*, 2016). Huisinigh *et al.* (2015) state that the emissions embodied in materials in the cradle-to-gate stage account for between 88% and 96% of the total lifecycle emissions. The increased attention on reducing energy and emissions in the material is challenging but can be achieved by shifting to the use of low impact materials and correspondingly changing the perspective people have on these building materials (Meggers *et al.*, 2012).

The impacts of materials have on the environment depend on the length of the lifecycle studied, types of buildings, types of energy used and the related technologies employed within a building. According to Chau *et al.* (2015) conventional commercial buildings are about 10%–27% of the total energy use and carbon emissions with a lifespan of 50 years while residential buildings are about 15%–40%. They go on to state that the building structure is found to have a profound impact of the resources and emissions content due to the vast quantities of materials used in the construction. The percentage tends to become higher with a shorter studied lifespan.

Research studies shown that the material phase has more profound impact than operating phase on zero energy or zero emission buildings. Zero or low energy buildings consume less operating energy in the use phase due to the design and technological advancement (Basbagill *et al.*, 2013). Therefore it increases the importance of energy and emissions embodied in

materials. According to [Chau et al. \(2015\)](#) the energy and emissions embodied in materials of net-zero energy buildings were found to have about 78% of the total in a building's lifecycle. The research further reveals that a passive house with photovoltaic installation was found to be 44% more than its operating energy in a 60 year lifespan and 56% for a 100 year lifespan. [Thiel et al. \(2013\)](#) analyze the environmental impact of a net-zero energy building and found that the most significant environmental impacts were in the structure made from concrete and structural steel. [Haapio and Viitaniemi \(2008\)](#) examine different structural design and material use of 78 single-family houses and results indicate that material production phase has the highest environmental impact for new buildings.

Presently, the construction industry is facing challenges regarding the delivery of sustainable buildings. Significant portions of a building's lifecycle impacts are determined by decisions made in the selection of materials at the early stage of design development. Therefore, choosing materials with low impacts at this stage has the potential to reduce the overall lifecycle impact significantly. For this purpose, it is crucial that both material manufacturers and designers take into account the potential effects and magnitude of the impact of materials on the environment at an early design stage of a building.

An LCA approach is particularly important in this respect as it provides a systematic assessment of the full range of impacts of materials on a lifecycle perspective. The aim of LCA in the first place is to compare the environmental impact of different raw materials and processes that have the same function but have lower impacts. LCA can be used as a decision-making instrument in the design and production of new materials. In choosing materials for buildings, the following criteria are to be taken into account in the design process:

- (1) Materials with recycled content – The use of materials is closely related to the total embodied energy and emission during production processes. The use of materials with recycled content can potentially reduce embodied energy and emissions compared to the manufacturing of using new materials. [Thormark \(2002\)](#) conducts a research study of an energy efficient apartment building in Sweden for a lifespan of 50 years and research results indicate that the recycling potential can reclaim up to 15% of the total energy used.
- (2) Low emission during manufacturing – Emissions are related to the manufacturing process of building materials that may have adverse effects on the environment. This will require the selection and use of building materials with the lowest negative impacts on the environment. Therefore, the environmental performance data of materials from the LCA results and eco-labeling can be useful and important in the selection processes.
- (3) Low energy intensity – Energy is required in the entire supply chain in the production of materials. The production and use of energy affect both the natural and manmade environment through the resulting pollutants and depletion of resources. Therefore the consideration of low energy intensity materials is one of the most important criteria that should be taken into account in the design and construction of buildings.
- (4) Biological content – The biological criterion takes into account the effects of materials on the health and wellbeing of users during the use phase of a building. The knowledge of the risks that old and modern building materials pose to health is essential to ensure the protection of the environment and users.

Initiatives, Certification Systems and Government Regulations for the Assessment of Environmental Performance of Materials

In response to the climate change and environmental degradation, governments and international organizations have developed policies, regulations and standards to reduce impacts of buildings on the environment. The European Union Energy Performance of Building Directive ([Gieseckam et al., 2016](#)) and the Australian National Construction Code Section J ([ABCB, 2010](#)) have been issued to regulate the improvement in the design and construction of building fabric performance for energy efficiency. However, these policies and regulations principally focused on the operating emissions associated with energy consumption for heating and cooling, lighting, and ventilation but have not been extended to the embodied energy and emission associated with the initial production of building materials and products.

The International Organization for Standardisation (ISO) standards is the most important one in providing consistency, transparency and credibility in the assessment, monitoring, reporting and verification of performance for buildings and materials ([ISO, 2006a,b](#)). The ISO 14040/14044 Standards focus on establishing principles and framework and providing requirements and guidelines for the LCA study ([ISO, 2006a,b](#)). The four steps of assessment in the LCA framework have been applied to standardize and quantify the environmental performance of materials ([Finkbeiner, 2014](#)).

In addition to the establishment of the ISO Standards, quantifiable impact such as carbon footprint (CF) and eco-labeling have also been developed as labeling systems to provide environmental performance data of materials and products. These systems are primarily voluntary but can raise awareness about environmental problems and leads to the competition in the material manufacturing industry. CF has been widely used to measure the total amount of GHG emissions of materials and products that both upstream and downstream emissions are accounted for. It is usually expressed in an equivalent value per mass of CO₂ for the GHGs such as N₂O and CH₄ in materials and products ([Basu and Bidanda, 2014](#)).

Eco-labeling for materials has been developed almost in every country now. The purpose of eco-labeling of materials is to promote the supply of materials with lower environmental impacts through verifiable and reliable information and to stimulate manufacturers to improve material performance environmentally. Eco-labeling was initiated by the Global Ecolabelling Network

Table 1 Three types of eco-labeling for materials and products

Type	ISO	Example	Purpose
Type I Third-party ecolabel	14024 (1999)	EU Eco-label, Nordic Swan (Nordic countries), Blue Angel (Germany), Environmental Choice (Australia)	To promote and identify products of the best environmental performance achieved in the market
Type II Self-declared environmental claims	14021 (1999)	In the form of written statements or symbols, e.g., CFC-free, recycled content	To provide environmental performance of products or services
Type III Environmental product declaration (EPD)	14025 (2006)	IBU-EPD Program (Germany)	• To provide independent verification of claims that contain relevant and verifiable LCA information based on the ISO 14040 series of standards • To facilitate environmental comparison between products that perform the same function

Sources: Vigovskaya, A., Aleksandrova, O., Bulgakov, B., 2017. Life cycle assessment (LCA) in building materials industry. MTEC Web of Conferences, 106, 08059, SPbWOSCE-2016 https://www.matec-conferences.org/articles/mateconf/pdf/2017/20/mateconf_spbw2017_08059.pdf. Logon: 15/7/2018.

in 1994 to improve and develop labeling systems of materials and products worldwide. According to the [Global Ecolabelling Network \(2018\)](#), there are more than 463 eco-labeling organizations in 199 countries in over 25 business sectors.

Table 1 summarizes the three types of eco-labeling for materials and products. The three types of eco-labels are developed in according to the ISO standards. Type III eco-label is particularly important as it has to be prepared in according to the rules and requirements of the Product Category Rules which are key part of ISO 14025 to enable transparency and comparability between environmental product declarations ([Vigovskaya et al., 2017](#)). However, the exceedingly supply of eco-labels has abused and misused to claim environmentally friendly materials by manufacturers or suppliers. This is particularly serious for the Type II eco-labels as these labels are developed directly by manufacturers without the certification by a third-party. Some of these labels are based on the LCA approach but this information may not publicly available due to confidentiality ([Basu and Bidanda, 2014](#)).

The use of eco-labeling for the individual material may be informative but is particularly challenging to quantify the environmental impacts of building materials as building materials are functioned together to achieve the stated performance in the design. For example, the effective use of insulation in the building design can result in less energy consumption and better user comfort during the use phase, but its manufacture may involve the release of pollutants ([Basu and Bidanda, 2014](#)). Also building materials require transportation from distribution centres to site that the impact may be significant if sourced from overseas. However, locally harvested raw materials may affect the local ecological systems ([Basu and Bidanda, 2014](#)).

Life Cycle Assessment (LCA) for Building Materials

In the past, environmental studies have focused on the operating stage as this stage represents the majority of energy consumption and emission during a building's lifecycle. However, more attention has now been shifted to the environmental impacts of raw material extracting, manufacturing and transportation ([de Wolf et al., 2016](#)). The assessment of the impact of building materials is similar to an LCA study of a building. The principal objectives of LCA are to quantify and evaluate the environmental performance of materials so that decision-makers can compare and select materials with the least impact on the environment. Additionally, LCA provides a basis for assessing potential improvements in the performance of materials to reduce their overall environmental impacts. This can be done in an overall sense or targeted to improve specific stages during the lifecycle.

Over the years LCA has been used to conduct detail analysis and comparison of the environmental impacts of numerous building materials. [Cole \(1999\)](#) conducts an LCA study on comparing the use of wood, steel and concrete structural assemblies and found that wood has the least impact compared to steel and concrete structure. [Wei et al. \(2008\)](#) use LCA to investigate energy and emissions for different building components while [Goggins et al. \(2010\)](#) investigate to replace Portland cement with blast furnace slag and results indicate a reduction of energy consumption and emissions in the production of concrete. [Mao et al. \(2013\)](#) study the use of industrialized methods of construction and found that prefabrication has lower emissions than traditional methods of construction.

The LCA Framework for Material Assessment

The lifecycle environmental impacts of building materials according to LCA is usually conducted on a 'cradle-to-gate' boundary as indicated in [Fig. 1](#) which presents a building lifecycle stages in according to the CEN 15978 ([CEN, 2011](#)). The LCA study for building materials based on a cradle-to-gate system boundary involves mainly the upstream processes of raw material extraction and associated processing activities ([Hafliger et al., 2017](#)).

Building lifecycle stage															
Product stage			Construction process stage		Use stage							End-of-life stage			
Raw material supply	Transport	Manufacturing	Transport	Construction/Installation	Use	Maintenance	Repair	Replacement	Refurbishment	Operational energy use	Operational water use	De-construction/Demolition	Transport	Waste processing	Disposal
A1	A2	A3	A4	A5	B1	B2	B3	B4	B5	B6	B7	C1	C2	C3	C4

Fig. 1 Lifecycle stage of buildings. *Source:* Adapted from CEN, 2011. Sustainability of Construction Works – Assessment of Environmental Performance of Buildings – Calculation Method. British Standard Institute.

The A1 stage in the CEN 15978 is the raw material supply stage. This stage includes the extraction of raw materials and the associated processing activities from the ground. The A2 stage is the transportation of the extracted raw materials to the factory gate either locally or overseas for the manufacturing of building materials and products. The manufacturing (A3) is the final stage of the Product Stage in a building's lifecycle. This stage involves the manufacturing of raw material into materials and products for buildings.

Energy is required at each stage of the Product Stage. Energy is consumed to operate machinery and equipment for the raw material extraction activities at the A1 stage and the manufacturing processes at the A3 stage. Energy is also required for the transportation (A2 stage) of raw materials and different transportation modes may require different fuel types. The energy consumption at these stages generates a significant amount of energy-related emissions and other pollutants such as dust, noise and contaminants which have a significant impact on the environment (Buyle *et al.*, 2013; Vigovskaya *et al.*, 2017).

LCA study for building materials ends at the production of materials and products at the factory gate and further downstream activities are not part of the cradle-to-gate boundary. Therefore the following stages are outside scope of the LCA study of building materials:

- Construction process stage (A4–5) – Transportation of finished materials and products between manufacturer and building site, and construction activities on-site.
- Use stage (B1–7) – This stage usually refers to the operating and use of buildings. Building materials and products may only be used during repair, replacement or refurbishment during the operating stage of a building.
- End-of-life stage (C1–4) – Similarly, this stage refers to the final stage of a building's lifecycle which may involve eventual demolition and disposal. Some of the salvaged materials may be recycled or reused in the manufacturing process of building materials or components.

The Application of the ISO Standard for the LCA Study of Building Materials

The ISO standard is central to the LCA study of building materials. Fig. 2 illustrates the four steps of the LCA framework and the cradle-to-gate boundary of building material production (shown dotted lines). The four steps are generic for either a whole building LCA study or an LCA study of individual materials. According to the ISO 14040/14044 the LCA framework for material assessment begins with the goal and scope definition. This is the stage that objectives of the study are established so that boundary can be defined and functional unit to be set. For an LCA study of building materials the goal is to determine the environmental impacts from the production of materials and products and the scope of the study focuses on the raw material acquisition, processing and manufacturing.

The second step as indicated in Fig. 2 is related to the development of the lifecycle inventory (LCI) of the material studied. The LCI activities include quantifying the input and output flows of raw materials and energy and analyzing environmental impacts to the production of material in the study. The usefulness of an LCA study is highly dependent upon the accuracy and comprehensiveness of the LCI. Without a reliable and broad LCI, the usefulness of an LCA study may endure and uncertainties may be introduced to the lifecycle impact assessment (LCIA) stage. As illustrated in Fig. 2 the LCI stage of an LCA study of building materials includes identifying and collecting input and output flows in the supply chain of material production. The input flow involves the consumption of raw materials, energy and water. The output flow includes the production of the principal material and the generation of emissions, waste and by-products.

The compilation of data for the LCI can be developed using computer software such as GaBi, SimaPro for product comparison. Commercial and open access databases also exist and provide comprehensive information on environmental impacts of materials and products for developing the LCI. The databases that are commercially available include Ecoinvent or free access such as USDA, openLCA, NEEDS (NEXUS, 2018). However, base the study on different tools and databases may result in different outcomes.

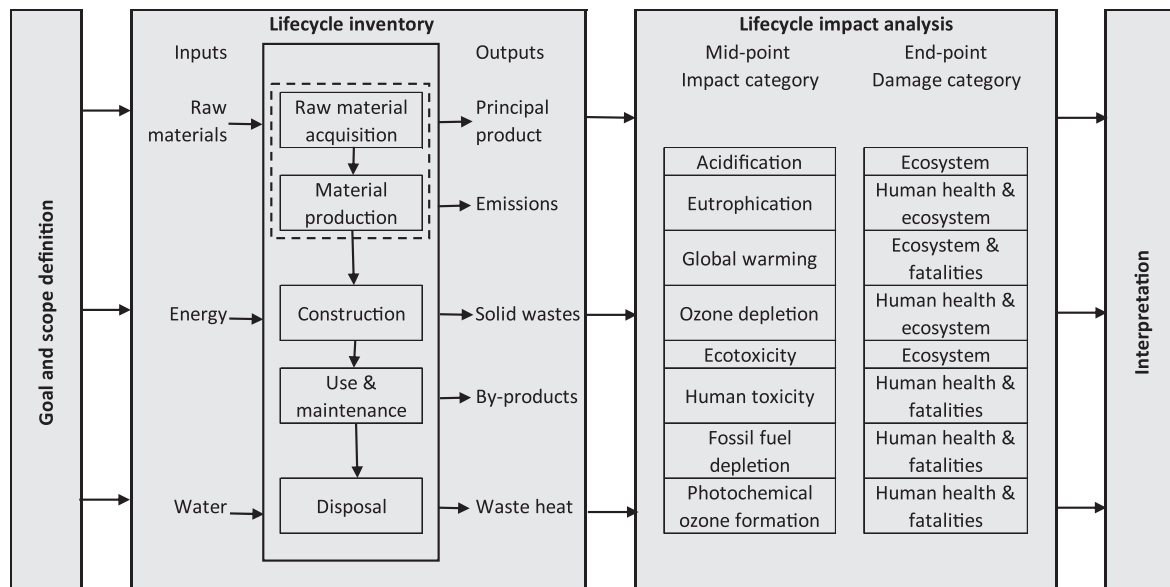


Fig. 2 ISO framework for the LCA study of building materials. *Source:* Reproduced from ISO, 2006a. ISO 14040: Environmental management – Life cycle assessment – Principles and framework. International Standards Organization, Geneva. ISO, 2006b. ISO 14044: Environmental management – Life cycle assessment – Requirements and guidelines. International Standards Organization, Geneva.

Table 2 Selected impact and damage categories in LCA study of building materials

<i>Impact category</i>	<i>Units</i>	<i>Damage category</i>
Acidification potential	kgSO ₂ eq	Ecosystem
Eutrophication potential	kgN eq	Human health & ecosystem
Global warming potential	kgCO ₂ eq	Ecosystem & fatalities
Ozone depletion potential	kgCFC-11 eq	Human health & ecosystem
Ecotoxicity	kgLC ₅₀ eq	Ecosystem
Human toxicity	kgLC ₅₀ eq	Human health & fatalities
Fossil fuel depletion	MJ	Human health & fatalities
Photochemical ozone formation	kgC ₂ H ₄ eq	Human health & fatalities

Source: Adapted from IPCC, 2014. Climate change 2014: Impacts, adaptation, and vulnerability. In: Field, C.B., Barros, V.R., Dokken, D.J. (Eds.), Part A: Global and sectoral aspects. Contribution of Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge: Cambridge University Press.

Takano *et al.* (2014) conduct a research study to examine the numerical and methodological differences of five databases of GHG emission values in the material production phase of five housing projects. Research outcomes reveal that the databases generate different results but show similar trends and the same order of magnitude differences shown by all the databases. Therefore the selection of a database that is relevant to the regional condition and climatic similarity is critical.

The LCIA stage involves the classification and characterization of impacts identified in the LCI stage as illustrated in Fig. 2. The classification of impacts is to sort inventory parameters according to the type of environmental impacts they are contributed to (selected impact categories are included in Table 2), while characterization is to quantify intensity and degree of environmental impacts to each type of impacts such as global warming potential (GWP) is the total of all GHG emissions in materials. Table 2 extracts the common types of impact categories and the associated damage categories in relation to the production of building materials. At the LCIA stage for the LCA study of building materials the impacts are divided into mid-point and end-point category (Fig. 2). At the product stage of building materials the study may focus on all or some the mid-point or end-point impact categories.

The normalization may also be undertaken if impacts are to be standardized or ranked. However, normalization is an option only in according to the ISO 14040/14044. At the end of the assessment, the results are interpreted and conclusions are drawn for product improvement. The improvement can include changing the design and specification of the product to be more energy efficient and fewer emissions on the environment. The LCA results are capable of identifying the key areas for improvement.

Assessing Environmental Impact of Building Materials

Environmental impact (EI) at the product stage takes into account the extraction and consumption of raw materials from the ground and the associated energy in the manufacturing processes and transportation. The process of assessing the EI of individual building materials consists of identifying and collecting input flow of energy use, raw materials and other utilities, and the output flow of product, co-product emissions and waste. The amount and types of inputs used in the production of building materials are assessed according to the total quantity of raw materials needed to fit the functional unit adopted. The calculation of EI of individual building materials requires the quantities per functional unit such as 1 kg of steel, 1 m² of the gross floor area of a building, 1 m³ of concrete. Therefore the calculation of EI of individual building materials is derived by multiplying the quantity of all the raw materials (including wastage) with corresponding EI data in the production of the building material per designated functional unit.

The amount of by-products and emissions associated with the production of building materials and products is highly dependent on the type and efficiency of machinery and equipment used in the extraction and manufacturing process (Chau *et al.*, 2012). The EI computation for energy consumption and emissions is calculated by summing up the duration of machinery and equipment used multiplied by fuel consumption per type and the associated emission coefficient of fuel consumption.

In addition to the energy required to operate machinery and equipment, raw materials are to be transported to the factory gate or finished products to the distribution centres by different modes of transportation. Raw materials transported to factories or distribution centres are delivered via trucks covering the outward trip (usually full load) and return trip (empty). The emissions about transportation are directly related to the efficiency, fuel type, number of truckloads, total distance travel (outward and return trip), fuel consumption and emission coefficient per fuel type (de Wolf *et al.*, 2016). There are various issues of transportation of raw materials that are not extracted locally which are often shipped or by rails from across countries or even from overseas. It is considered that the impact on cross-boundary air qualities and the estimation of EI are much more complicated.

Some Examples of LCA Studies of Building Materials

Cement Material

Cement is commonly used in the construction industry. It is an inorganic and non-metallic substance with hydraulic binding properties, and is used as a bonding agent in building materials. It is used as a component in concrete, mortar, stucco and grout. It is made by heating a mixture of limestone and clay to a temperature of about 1450°C. The product is then grinded to a very fine powder to become cement. During the heating process CO₂ is released from the limestone to produce cement.

The production of cement is an energy intensive process and adversely affects the environment in the form of GHG emissions (Basu and Bidanda, 2014; Hossain *et al.*, 2017). Half of the CO₂ emissions are from the manufacturing process through the combustion of fossil fuel and the rest comes from the calcination of limestone. According to Hossain *et al.* (2017), the production of cement in the world contributes to approximately 5%–10% of the total CO₂ emissions and consumes approximately 12%–15% of total industrial energy use. Overall, for the production of one tonne of Portland cement clinker approximately 0.87 tonne of CO₂ is released into the atmosphere (Hossain *et al.*, 2017). However, this value may vary with the location, technologies used, plant production efficiency, mix of energy sources used and the selection of kiln fuels (Josa *et al.*, 2007).

Fig. 3 summarizes inputs and outputs in the LCA study of the cement production. During the manufacturing process both direct and indirect impacts are considered in the LCA study. The inputs in the production of cement include lime, silica, iron, alumina and small amounts of additives. Approximately 1.6 tonnes of raw materials are needed to produce 1 tonne of cement primarily because of calcination of calcium carbonate, which typically comprises 75%–80% of the raw materials (Huntzinger and Eatmon, 2009). The composition of raw materials varies according to the required properties. The inputs also include the consumption of energy from the combustion of fossil fuels, e.g., coal, gas, oil and renewable energy sources may also be involved in the production processes.

The outputs of the product phase include the production of the cement or clinker. The production processes generate emissions to air, solid waste, waste heat and other by-products. Emissions are generated during the production of cement from the burning process and the diesel trucks. Other emissions include particulate matter from the point and fugitive sources and the combustion gases of CO₂, SO₂, NO_x, carbon monoxide, volatile organic compounds and methane. Solid wastes include cement kiln dust from the production of cement. According to Hossain *et al.* (2017), approximately 1.9 GJ of heat lost per tonne of cement produced. This is heat lost primarily in the kiln and cooler exhaust gases and also by radiation from the kiln shell and other hot surfaces.

The Portland Cement Association initiated to develop LCA-based EPD for three types of cement and they are Portland cement, masonry cement and blended cement (Portland Cement Association, 2016a,b,c). The LCA results are summarized in Table 3. From the table the traditional Portland cement has the most significant impact in all categories and followed by blended and masonry cement. The blended cement is manufactured by mixing Portland cement with mineral admixtures such as fly ash, slag or silica fumes. The masonry cement is mixed with plasticizing materials and other performance-enhancing additions to form mortar for brick, concrete block and stone masonry.

Other LCA studies have also been undertaken to improve the environmental performance of traditional Portland cement. Huntzinger and Eatmon (2009) use LCA to evaluate and compare four cement manufacturing processes on a cradle-to-gate boundary. Research results show that replacing approximately 25% of clinker with natural pozzolans in the

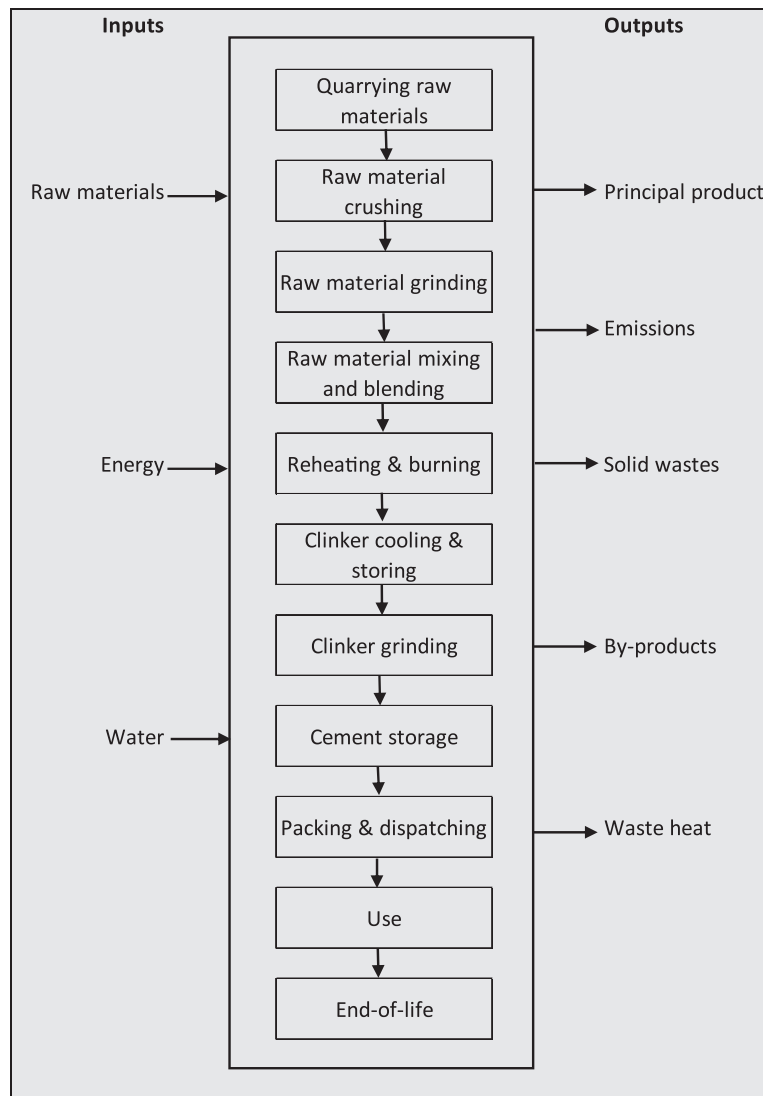


Fig. 3 LCA framework for the production of cement. *Source:* Adapted from Huntzinger, D.H., Eatmon, T.D., 2009. A life-cycle assessment of Portland cement manufacturing: Comparing the traditional process with alternative technologies. *Journal of Cleaner Production* 17, 668–675.

cement manufacturing process has effectively reduced the most substantial environmental impact process (the kiln or pyroprocessing step) by 22%.

Concrete Material

Concrete is a traditional heavy material used widely in buildings. Concrete is commonly used for load-bearing structures which are high in energy intensity and GHG emissions. Concrete is produced by mixing cement with aggregate, sand, water and other admixtures which are then poured into timber mould to form a designed structure. The characteristic and strength of concrete are controlled by the ratio of water to cement and the types of admixtures.

Concrete has a special characteristics to absorb CO_2 from the atmosphere. This is a process of carbonization that CO_2 diffuses back into the concrete and reacts with calcium dihydroxide (H_2CaO_2). The rate of carbonization depends on the CO_2 concentration and humidity in the ambient air. Since carbonization is gas diffusion the process is slower with increasing humidity. It also depends on the density of the concrete (water to cement ratio) and whether the surfaces coated such as painting or wallpaper that may reduce the rate of CO_2 diffusion into the concrete. According to Chau *et al.* (2015), the net CO_2 emission of concrete production after taking into account both calcination and carbonation was estimated to be $0.033 \text{ kgCO}_2/\text{kg}$ concrete.

The inputs and outputs in the LCA study of concrete are presented in Fig. 4. The inputs for the production of concrete require cement, sand, aggregates and admixtures. Cement is required as a bonding agent to bind all the resources together when mixed with water to form

Table 3 Environmental impacts of cement (1 tonne)

Environmental impact	Portland cement	Masonry cement	Blended cement
Global warming potential (100 year) (kgCO ₂ eq)	1040	692	892
Acidification potential (kg SO ₂ eq)	2.45	1.83	2.26
Eutrophication potential (kgN eq)	1.22	0.93	1.11
Ozone depletion potential (kg CFC11 eq)	2.61E-05	2.18E-05	2.48E-05
Primary energy consumption (MJ)	5887	4611	5243
Raw materials (kg)	1428	1259	1243
Fresh water (L)	9700	9330	9240
Waste generated (kg)	9.04	7.76	10.55

Source: Portland Cement Association, 2016a. Environmental product declaration (EPD 033) – Blended hydraulic cement. Skokie: Portland Cement Association. Portland Cement Association, 2016b. Environmental product declaration (EPD 034) – Masonry cement. Skokie: Portland Cement Association. Portland Cement Association, 2016c. Environmental product declaration (EPD 035) – Portland cement. Skokie: Portland Cement Association.

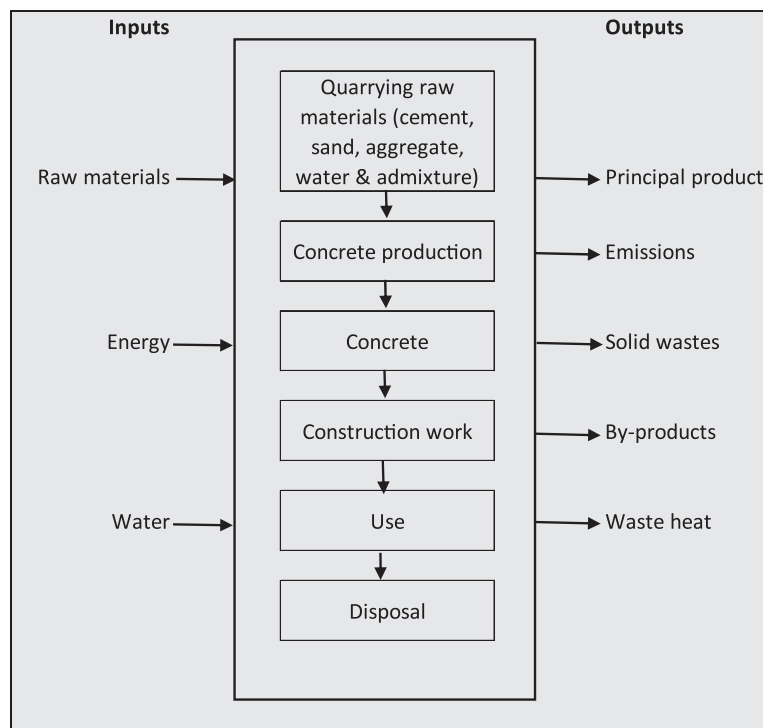


Fig. 4 LCA framework for the production of concrete. Source: Adapted from Chau, C.K., Hui, W.K., Ng, W.Y., Powell, G., 2012. Assessment of CO₂ emissions reduction in high-rise concrete office buildings using different materials use options. Resources, Conservation and Recycling 61, 22–34.

the designed structure in buildings. Sand and aggregates are produced from crushed stone and concrete mix determines the quantities of coarse and fine aggregates. Admixtures such as air entraining, water reducers, accelerators, superplasticizers are widely used in concrete to control the properties and performance but are usually below 1%. Water is needed in the production of concrete which may be affected by the type, location and size of the plant. Water is also used for truck wash out and off the site and the concrete plant.

Energy is used in the concrete plant that includes electricity and fuel used for equipment and heating. Energy is also required for the transportation of materials, e.g., cement, fly ash, aggregates from distribution centres to the concrete plant which can be by road rail or barge using diesel fuel or others.

The outputs at the concrete production stage include generating emissions in the making of coarse and fine aggregates from crushed stone, cement production and the final production of concrete. Emissions also generate from the consumption of diesel fuel by trucks and are calculated from the energy consumption in the same way as in the LCA study of cement in the previous section. Solid wastes are generated during the extraction of raw materials and the manufacturing processes. Waste heat is also produced in the manufacturing process of concrete.

The National Ready Mixed Concrete Association (NRMCA, 2014) developed EPDs for various types of concrete using an LCA approach and results are summarized in Table 4. The table presents the results of cradle-to-gate LCA results for two types of product

Table 4 Environmental impacts of concrete (1 m³)

Environmental impact	281.2 kg/cm ² (27.6 MPa)	562.5 kg/cm ² (55.1 MPa)
Global warming potential (100 year) (kgCO ₂ eq)	432	633
Acidification potential (kg SO ₂ eq)	2.29	3.34
Eutrophication potential (kgN eq)	0.068	0.094
Ozone depletion potential (kg CFC11 eq)	5.61E-06	8.27E-06
Primary energy consumption (MJ)	2646	3678
Raw materials (kg)	2449	2495
Freshwater (m ³)	21.2	17.6
Waste generated (kg)	0.73	0.73

Source: Adapted from National Ready Mixed Concrete Association (NRMCA), 2014. Environmental product declaration (NRMCA EPD: 10005) for concrete. Silver Spring.

Table 5 Percentage distribution of GWP and PEC by product lifecycle stage

Concrete strength	Global warming potential (GWP) (100 years) %			Primary energy demand (PED) %		
	A1	A2	A3	A1	A2	A3
281.2 kg/cm ² (27.6 MPa)	93.7	4.0	2.4	89.3	6.8	4.0
562.5 kg/cm ² (55.1 MPa)	92.7	4.4	3.0	83.9	9.7	6.5

Source: Adapted from National Ready Mixed Concrete Association (NRMCA), 2014. Environmental product declaration (NRMCA EPD: 10005) for concrete. Silver Spring.

mix designs considered within each compressive strength class on 1 m³ of ready-mixed concrete. The LCA results show that the environmental impacts increase to the higher compressive strength of concrete.

Table 5 presents the results in percentage distribution by the three stages of the product phase for the compressive strength of 27.6 MPa and 55.1 MPa. The table shows that the percentage distribution of the raw materials production has the highest in both the global warming potential (GWP) and primary energy demand (PED) which agree with the research undertaken by [Hafliger et al. \(2017\)](#). Overall the upstream materials production accounts for approximately 93%–94% and 84%–90% respectively for GWP and PED associated with the production of ready-mixed concrete. The highest percentage in the A1 stage is due to the manufacture and use of Portland cement which is high in both emission and energy consumption. Materials transportation according to [Vigovskaya et al. \(2017\)](#) and **Table 5** contributes about 4% of the GWP and 7%–10% of primary energy consumption. The manufacturing stage according to [Buyle et al. \(2013\)](#) and **Table 5** contributes the least in both.

Steel Material

Steel is another commonly used material in the construction industry. Steel is combined with concrete to form a reinforced concrete structure for buildings. Steel can also be used as raw materials to make components such as window frames, pipes, machinery and household goods. Steel production is a high energy intensity and GHG emissions. The manufacturing processes of steel involve the extraction of iron ore from the ground which then goes through the melting process in a furnace with oxygen blowing through it to remove impurities and reduce carbon percentage to produce steel. The various industrial processes of iron, coke, sinter and steel production contribute to more than 60% of the total energy-related GHG emissions, of which iron production is the largest (74%) ([Olmez et al., 2016](#)). According to [Quader et al. \(2016\)](#) one tonne of steel manufacturing emits approximately 1.8 tonnes of CO₂.

Improving efficiency in the manufacturing process of steel has been the focus of research and development. Steel has sustainable characteristics which can be recycled entirely and used infinitely. The production of steel can incorporate recycled content and reusing water for cooling purposes. Emissions to the air from the production can also be controlled through better design production technologies. Recycled steel (scrap steel) comes from demolished structures, end-of-life vehicles and machinery. According to [World Steel \(2018a\)](#), it was estimated that 630 million tonnes of scrap steel were recycled in 2017 and of this, approximately 560 million tonnes were used by the global steel industry.

The inputs and outputs in the LCA study of steel are presented in [Fig. 5](#). The inputs in the production of steel include the use of 98% of iron ore, small amount of other elements such as manganese, carbon and coal as the primary energy sources. According to [World Steel \(2018b\)](#), the global steel industry used about 2.1 million tonnes of iron ore, 1.1 million tonnes of metallurgical coal and 560 million tonnes of recycled steel to produce about 1.7 billion tonnes of crude steel in 2017. The steel use is projected to increase by 1.5 times to meet the needs of population growth.

Steel production is energy intensive due to the chemical energy required to reduce iron ore using a carbon-based reducing agent. Iron ore and metallurgical coal are used mainly in the blast furnace process of ironmaking. Typically it takes about 1.6 tonnes of iron ore and around 400 kg of coke to produce one tonne of pig iron ([World Steel, 2018b](#)). Improvements in energy

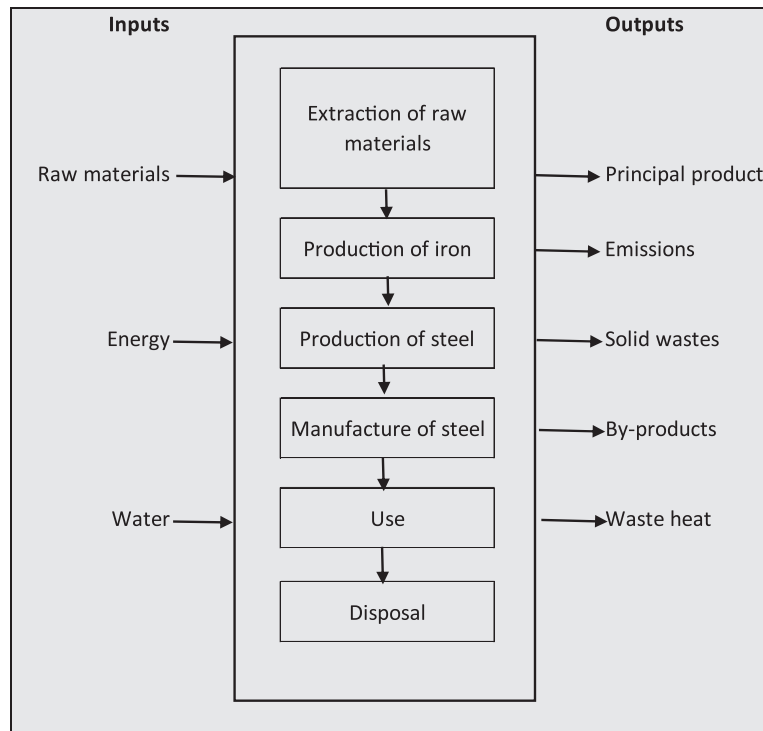


Fig. 5 LCA framework for the production of steel. *Source:* Reproduced from World Steel, 2018b. Life cycle inventory study, World Steel Association, Beijing, China.

efficiency have led to the reduction of about 60% in energy required to produce 1 tonne of crude steel since 1960. The energy efficiency of steelmaking facilities vary depending on production route, type of iron ore and coal used, the steel product mix, operation control technology and material efficiency.

The outputs at the product phase of steel production include the final production of steel but the processes generate various types of emissions, solid wastes, waste heat and other by-products. Similar to the production process of cement and concrete as previously discussed, emissions due to the combustion of fossil fuels in both the manufacturing processes and transportation are also included in the LCA study. The production of steel also generates by-products such as slags, dust and sludge. On average the production of 1 tonne of steel will result in 200–400 kg of by-products. About 90% of the by-products are slags which are solid wastes from the burning processes.

EPDs have been used to provide information on environmental impacts with regards to the production of steel. [Table 6](#) extracts and compares the EPDs for steel production of three different types of steels. The production of hot-dip galvanized steel generates the highest GWP and PDE and followed by hot rolled coil steel. The table also extracts the potential benefits of recycling of the steel at the end-of-life. According to [World Steel \(2018a\)](#), the rate of recycling of steel from the construction industry is approximately 80% which can be recycled as scrap steel in the production of crude steel. From the table hot-dip galvanized steel generates marginally better recycling benefit than the hot-rolled coil steel in both GWP and PED.

Sustainable Building Materials

The design and construction of buildings conventionally focus on using heavy materials such as steel, concrete and masonry but these materials are both high energy intensity and emission content. Therefore over the years research studies focus on using low impact alternative materials, improving technologies and practices to reduce the negative impact of materials on the environment.

Use Low Impact Materials

Construction materials are important for the survival of the industry. However, it is essential that the manufacturing processes of these materials be improved to reduce their impact on the environment. Low impact materials, therefore, play an important role and their selection at an early design stage should be undertaken as it will influence all downstream processes in achieving sustainability in buildings ([Shen et al., 2010](#)). Majority of low impact materials are manufactured from the natural or renewable sources such as timber, straw bale and earth. These materials have low in energy intensity and emissions compared with conventional heavy materials. However, [Giesekam et al. \(2014\)](#) suggest that instead of just replacing conventional materials with

Table 6 Environmental impacts of steel (1 tonne)

Environmental impact	Section		Hot-rolled coil		Hot-dip galvanized	
	Cradle-to-gate	Recycling benefit	Cradle-to-gate	Recycling benefit	Cradle-to-gate	Recycling benefit
Global warming potential (100 year) (kgCO ₂ eq)	1.5	– 0.3	2.2	– 1.2	2.7	– 1.3
Acidification potential (kg SO ₂ eq)	0.0042	– 0.0006	0.0054	– 0.0023	0.0065	– 0.0025
Eutrophication potential (kgN eq)	0.00032	– 0.00005	0.00046	– 0.00017	0.00059	– 0.00018
Photochemical ozone creation potential (kgC ₂ H ₄ eq)	0.00064	– 0.00015	0.00091	– 0.00054	0.00101	– 5.80E-04
Primary energy demand (MJ)	18.3	– 2.8	23.3	– 10.1	29.5	– 10.7

Source: Adapted from World Steel, 2018b. Life cycle inventory study. Beijing: World Steel Association.

natural materials they can be combined to form low impact products such as panelized prefabricated timber and straw bale systems, lime and gypsum to replace convention cement plasters, timber and steel hybrid structures in buildings.

Advancement in the Material Production Technologies

Conventional heavy materials tend to have a long lifespan and require little maintenance and replacement throughout the building lifecycle. However, these materials are both high in energy intensity and emissions that are detrimental to the environment. There are research studies on the improvement of their manufacturing processes to reduce their impacts on the environment. Cement is a mostly used material in the construction of buildings. [Gao et al. \(2015\)](#) state that the production of cement is responsible for about 7% of total CO₂ emission globally. [Ishak and Hashim \(2015\)](#) further state that the clinker production generates about 90% of the CO₂ emissions in the production of cement. Therefore minimizing the need for carbon-intensive cement products is an essential part of reducing the embodied emissions of construction materials ([Giesekam et al., 2014](#); [Gao et al., 2015](#)). The improvement in the production technologies of cement includes recovering waste heat, substituting fossil fuels with renewable energy sources, substituting low carbon cement by cementitious materials such fly ash, silica fume, slag, etc. ([Crossin, 2015](#)). [Gao et al. \(2015\)](#) further state that GHG emissions can be reduced by replacing carbonate-containing materials with non-carbonate materials and changing the clinker ratio in cement production.

Steel is another commonly used and high impact building material. Improvement in the steel production has attracted much attention to reduce the consumption of raw materials and emissions. Improvements include capturing and reusing gas and waste heat, collecting and recycling waste steel to reduce the use of virgin materials, improving the quality of steel products to maximize the lifespan, using energy-saving equipment, and improving the efficiency of energy conversion facilities ([Quader et al., 2016](#)). In the production of concrete solid waste such as use waste glass cullet from waste glass bottles to substitute clinkers can be used to replace virgin materials to produce eco-glass cement. According to [Hossain et al. \(2017\)](#), eco-glass cement has about 16% energy consumption and 17% GHG emission compared to that of traditional Portland cement but comparatively similar strength.

Use Lightweight Building Structures

The design and construction of buildings can be shifted to focus on using lightweight materials ([Meggers et al., 2012](#)). [Meggers et al. \(2012\)](#) go on to state that lightweight building designs can minimize the consumption of raw materials and the structural design of concrete with expanded aggregates can reduce the overall weight as well as improving insulation property of the building. [Giesekam et al. \(2014\)](#) further suggest to use lightweight design in conjunction with structural member optimization to minimize the excessive use of materials but this will require changes in design practices or innovative manufacturing processes. [López-Mesa et al. \(2009\)](#) compare environmental impacts between in-situ and precast concrete floors for two seven-storey residential buildings. Research results indicate that precast concrete floor with a longer span between beams reduces the size of columns and footings and thus reduces the total concrete used in the building which has about 12% lower environmental impact than in-situ concrete.

Use Alternate Fuels

Majority of the energy sources are fossil-based such as oil and coal which are high in emissions. Bio-based and industrial by-products such as waste plastics, scrap tires, wood residues, biomass wastes, wood chips, palm shells, saw dust and so forth can be used as alternative fuel sources in the production of building materials. These waste materials, on the one hand, can be used as fuel to replace fossil fuel, on the other can reduce waste to landfill sites. [Hossain et al. \(2017\)](#) conduct a research study to compare the manufacturing process of four different types of cement. Research results indicate that by replacing 10%–50% of coal with the biofuel produced from locally generated wood wastes, potentially 3%–14% and 6%–29% of total GHG emissions and non-renewable energy consumption can be reduced respectively in the production of one tonne of traditional Portland cement.

Increase Reuse and Recycling of Materials

The construction industry is an industry slow to change. Significant concept changes in the practices of the construction industry to facilitate the reuse and recycling of building materials can be made possible if they can be considered as early as possible in the design development. Such changes could be made to favour the disassembly of the construction materials at the end of their service life and by selecting materials for the recycled sources and assembly, techniques are significant in the reduction of GHG emissions (Bribian *et al.*, 2011). Giesekam *et al.* (2014) state that increased reuse and recycling will require design for disassembly and an increased focus on the end of life project stage during design. Proper early planning in the design and construction of buildings is essential.

Conclusion

Building materials are used for the initial construction of a building and will continue to be consumed during the use phase for maintenance and refurbishment. The production of building materials is both high energy intensity and GHG emissions throughout a building's lifecycle. The building materials while important for the construction industry they are also potentially significant in minimizing environmental loads as materials are used throughout the building lifecycle. To reduce the environmental impact of buildings, it is necessary to design and select materials with low impact to reduce resources consumption and GHG emissions.

This article provides an overview of the importance of building materials and discusses the framework of LCA in the assessment of material on a cradle-to-gate boundary. LCA provides a systematic and transparent framework to generate data to assist the selection of environmentally friendly materials for buildings. Through the LCA analysis, all possible environmental loads of material are ultimately assessed and classified according to their contribution to the environmental impact and damage categories. While LCA can be applied to compare the environmental impact of different materials, it can also be applied to different production processes to determine the stages causing the most significant environmental harm for improvement in a lifecycle perspective.

Over the years significant research and development have been undertaken to improve the manufacturing processes of materials. The common suggestions are substituting high impact resources with more natural and renewable-based materials such as timber, straw bale, and earth in the construction of building materials. Research and development also focus on increasing the use of recycling materials to replace raw materials such as scrap steel, fly ash to produce building materials. Considering to improve the environmental benefits of material it is necessary to encourage more international collaboration and strengthen the policy aspects to promote the principal to reduce, reuse and recycle to reduce the consumption of virgin raw materials.

See also: A Comparative Life Cycle Assessment for Utilising Laminated Veneer Bamboo as a Primary Structural Material in High-Rise Residential Buildings

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Life Cycle Cost Analysis for Green Buildings

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Introduction

Green building implementation is one of the most widely discussed topics of this decade. However, green building implementation is strongly associated with higher costs. There are mixed reviews in the literature regarding the initial cost (Richardson and Lynes, 2007). According to Tatari and Kucukvar (2011), Leadership in Energy and Environmental Design (LEED) registered buildings have to pay a cost premium of 0.66% to obtain a certified status, 2.11% for silver status, 4.41% for gold status, and 6.5% for platinum status. Further, Dwaikat and Ali (2016) illustrated that the maximum reported cost premium of a green building reaches up to 21%. However, these studies focused on the initial cost of the green building.

According to Green Building Council of Australia (2013) Green Star certified buildings use 66% less electricity and 51% less potable water than conventional Australian buildings. According to McGraw Hill Construction (2013), in new green buildings, operation costs decrease by more than 8% over a period of one year, while green retrofits exhibit a decrease of 9%. Similarly, Fowler and Rauch (2006) illustrated that certain green buildings consume approximately 26% less energy and demonstrated 13% lower maintenance costs compared to average commercial buildings. These cost savings throughout the life-cycle are not captured in the initial cost calculations. Therefore, Zhang *et al.* (2018), illustrated that the life-cycle perspective is overlooked in green buildings and therefore, there is an urgent need to provide comprehensive and urgent evidence on life-cycle costs.

Green building implementation has become a requirement in the status quo and therefore, the negative influence of initial cost premiums needs to be eradicated from the green building concept. For that purpose, in the initial decision-making stages there should be a model to look into the life-cycle costs of green buildings considering all the life-cycle savings. According to Zuo *et al.* (2017), the uptake of life-cycle cost in construction is rather slow in the Australian context. Therefore, this research aims to analyse the life-cycle cost for green buildings focusing on specific green building requirements.

Life-Cycle Cost Analysis for Green Building Credits

With the development of green buildings, there was a requirement to evaluate the performance of green buildings. According to the World Green Building Council (2018), many countries have their own green building councils. Most of these countries have their own green building rating tools focusing on various key criteria such as water efficiency, energy efficiency land use and so on. According to Lu *et al.* (2017), to pursue sustainable development, appropriate measurements are critical. Further, Asdrubali *et al.* (2015) identified that there are many green building rating tools that have been developed by many countries, all with the aim of reducing environmental impacts in both, construction and management phases of buildings.

Most green buildings rating tools mainly focus on criteria, such as indoor environmental quality (IEQ), energy, water, and operational waste (Building Construction Authority, 2013; Building Research Establishment Environment Assessment Method, 2014; Green Building Council of Australia, 2015; United States Green Building Council, 2014). Most of the benefits of green buildings such as better human conditions, efficiency in energy and water, life-cycle cost savings, and lower negative impact to the environment are derived through the operational phase, with effective operations of these aspects.

Initially, with the rising interest and demand from policy makers to achieve a sustainable society, there had been an increasing interest in environmental assessments of the built environment, focusing on energy use in buildings, the sick building syndrome, indoor climate, building materials containing hazardous substances, and/or many other aspects (Forsberg and Von Malmberg, 2004). Afterwards, separate environmental indicators were developed, such as energy and water efficiency measurements for the needs of relevant interest groups for building ratings (Haapio and Viitaniemi, 2008). However, these individual benchmarks serve to emphasise the need for a comprehensive rating tool to provide a thorough evaluation of building performance against a broad spectrum of environmental criteria (Ding, 2008). However, the first real attempt to establish comprehensive means of simultaneously assessing a broad range of environmental considerations in buildings was the BREEAM (Building Research Establishment Environment Assessment Method, 2015; Crawley and Aho, 1999) rating tool. There had been many green building rating tools developed by many organisations worldwide ever since.

After an extensive study focusing on 71 green building councils worldwide, Illankoon *et al.* (2017), identified eight widely used green building rating tools representing the five main regions worldwide. These widely used rating tools are: LEED, BREEAM, Green Star from Australia, BEAM (Building Environmental Assessment Method) Plus from Hong Kong, CASBEE from Japan, Green Building Index (GBI) from Malaysia, and the Indian Green Building Council Rating (IGBC) from India. Each of these rating tools has different types of schemes, various ratings, and also various key criteria upon which the building is evaluated. Further, according to Illankoon *et al.* (2017), energy, water, IEQ and material are the widely discussed green building requirements by all these widely used green building rating tools.

After analysing all the credits in Green Star Design and As-Built version 1.1, Illankoon *et al.* (2016), illustrated that out of all the credits with a contribution to life-cycle cost, 3% of the credit points were from management key criteria, 22% were from the energy criteria, 8% came from the IEQ criteria, 12% came from both, material and water criteria, 5% were the emission key criteria, and

1% came from land used and ecology key criteria. Therefore, it is evident that the life-cycle cost contribution is significant in criteria such as energy, IEQ, material and water, which perfectly coincides with the widely assessed criteria among green building rating tools. Therefore, this research study focus on these key criteria for life-cycle cost analysis. Further, Green Star Design and As-Built version 1.1 is identified as the guide for green buildings.

Initially, Green Building Council of Australia had Green legacy tools, and by the end of 2015, all these tools were superseded by a new set of green building rating tools. These tools include four green building rating tools, namely, 'Green Star- Design and As Built', 'Green Star - Interiors', 'Green Star - Communities' and 'Green Star - Performance'. Each of these green building rating tools is applied for different sectors in the built environment. Further, in Green Star there is a scale of 6 stars, starting from one star for minimum practice, and six stars for world leadership. Further, Green Star - Design and As-Built, Interiors, and Communities projects can achieve Green Star certifications of 4–6 Stars. Buildings assessed using the Green Star - Performance rating tool can achieve a Green Star rating from 1 to 6 Stars (Green Building Council of Australia, 2013).

In Green Star Design and As-Built v1.1 tool, there are nine environmental categories, namely, management, IEQ, energy, transport, water, materials, emissions, land use and ecology and innovation. These categories are given credits, and the final score is the sum of all the credit points. Final certification is awarded based on the final score.

Research Methodology for Life-Cycle Cost Calculation and Analysis

According to the Australian National Audit Office (2001), the process of life-cycle costing fundamentally involves assessing costs that arise from an asset over its lifespan, and evaluating alternatives that have an impact on this cost of ownership across the five main phases namely, design, purchase and construction, operations, maintenance, and development and disposal (Australian National Audit Office, 2001).

The life-cycle cost calculation follows the ISO 15686-5:2017, namely, 'Building and construction assets – service life planning – Part 5: Life-cycle costing standard' as a guideline (International Organisation for Standardization ISO, 2017). The net present value (NPV) technique is used to calculate life-cycle costs. Eq. (1) shows the formula for the NPV calculation.

$$NPV(i, N) = \sum_{t=0}^N \frac{R_t}{(1+i)^t} \quad (1)$$

where i denotes the discount rate, t denotes the time of cash flow, R_t denotes the net cash flow, and N is the total number of periods.

The discount rate is established considering the time value of money and the associated risk. The minimum attractive rate of return is commonly used as the discount rate (Dell'Isola and Kirk, 2003). The interest rate on a 25-year treasury bond in Australia is 3.25% per annum (Australian Government, 2016). Furthermore, the return on assets for a non-residential construction firm is approximately 3.30% (Deloitte Access Economics, 2016). Therefore, the discount rate is taken as 3.25% for this calculation. However, this rate changes for each user, because the associated risk differs from person to person. Therefore, in order to calculate the life-cycle cost, a user should identify the associated discount rate. Thus, in the life-cycle cost model, the discount rate is a variable input.

According to International Organisation for Standardization (ISO) (2017), life-cycle costing in construction commences from the planning stage and ends with the disposal stage. Therefore, this study follows a 'gate to grave' analysis on life-cycle costs for green office buildings. The time period for this life-cycle cost calculation is 60 years, as required by the Green Building Council of Australia (2015). Further, all the costs are normalised to one square metre of gross floor area (GFA) of the building.

Externalities and social benefits are not considered in life-cycle costs, as these costs fall under whole-life costing, and not life-cycle costing (International Organisation for Standardization ISO, 2017). In this research study, the construction costs are termed as 'initial cost' because these costs are incurred in the initial stages of the life-cycle, and also include management costs related to construction, as well.

All the costs in this research study are collected from the six main central business districts (CBDs) in Australia, namely, Adelaide, Brisbane, Hobart, Melbourne, Perth, and Sydney. All the prices are excluding Goods and Services Tax (GST) and profit. The initial cost is developed based on first principles using current market prices, and includes all the material, labour, and plant costs.

Maintenance requirements are based on maintenance manuals and guidance from maintenance engineers on specific products and materials. The maintenance requirements are further developed based on the detailed analysis provided by Dell'Isola and Kirk (2003), and Stanford (2010). Apart from maintenance, this study considered replacement of different material, as well. As an example, timber flooring requires replacement in 50 years (Dell'Isola and Kirk, 2003). In such a scenario, the timber flooring is replaced in the fiftieth year of the life-cycle and the cost is discounted to the present value, using Eq. (1).

If maintenance occurs annually over the 60 years lifespan of a building, the annual cost should be discounted 60 times. To avoid excessive calculations, the present value of annuity (PVA) for a period of 60 years is calculated using Eq. (2).

$$PVA = R_m \times \left(\frac{1 - (1+i)^{-N}}{i} \right) \quad (2)$$

where i denotes the discount rate, R_m denotes the annual maintenance cost, and N is the total number of periods.

This research study assumes that the building will be demolished at the end of 60 year period. Further, an additional cost is added for the extra care required during demolition, if a particular item is re-used. The debris is assumed to be transported 15 km away from the site. Disposal of these items occur at the end of the life-cycle. The life-cycle cost calculations include all these related costs and discount them to the present value using Eq. (1).

Sensitivity Analysis of Life-Cycle Cost to the Changes in Discount Rates

The life-cycle cost calculation is based on certain variables. The life-cycle cost fluctuates based on changes in the prices of materials. Therefore, it is also necessary to predict the influence of these uncertain variables in the absence of accurate data by using certain techniques, such as sensitivity analysis (Wong *et al.*, 2010). Therefore, a sensitivity analysis is carried out for the changes in discounting rate for each key each criteria.

IEQ Key Criterion

As the name suggests, IEQ refers to the internal environment quality, or, the quality of the environment within the building, especially focusing on the occupants. According to the Green Building Council of Australia (2015), IEQ key criterion aims to encourage and reward initiatives that enhance the comfort and well-being of occupants. Most of the credits included in this key criterion include all the three cost components of the life-cycle cost.

In the IEQ key criterion, credits such as 'IEQ9.1 Ventilation System Attributes', 'IEQ9.2 Provision of Outdoor Air', 'IEQ14.1 Thermal Comfort' and 'IEQ14.2 Advanced Thermal Comfort' have different options to achieve the credit points, depending on the type of ventilation system in use. As an example, if a building is naturally ventilated, the standards and systems considered for that type of ventilation are completely different from those considered for a building with mechanical ventilation. Therefore, while calculating the life-cycle cost, these two types are calculated separately, and these costs have significant differences in their values. Further, there is a dependency on 'W18B.3 Heat Rejection', whose credit points are awarded when there is no water used for heat rejection. Therefore, a mechanically ventilated system is further divided into two, based on the type of heat rejection method in use. Finally, life-cycle cost calculations are carried out for naturally ventilated systems, mechanically ventilated systems using water for heat rejection, and mechanically ventilated systems using air for heat rejection, separately.

Life-Cycle Cost Calculation for IEQ Credits

Life-cycle cost is calculated for each of the credits in the IEQ criterion. The calculation formulae are presented as follows:

$$\begin{aligned} \text{Life - cycle cost for providing air to the building} \\ = \text{Initial cost for providing outdoor air} + (\text{Annual maintenance}) \times \text{PVa} \\ + \text{NPV for cleaning duct work every 5 years} + \text{NPV for replacing ductwork and other components every 25 years} \\ + \text{NPV of cost of demolition} \end{aligned} \quad (3)$$

$$\begin{aligned} \text{Annual maintenance cost} \\ = \text{Nr of hours per session} \times \text{Nr of Air Conditioning mechanics} \times \text{Hourly rate per Air Conditioning mechanic} \end{aligned} \quad (4)$$

$$\begin{aligned} \text{Life - cycle cost for exhaust air ducts} \\ = \text{Initial cost for providing exhaust air duct} \\ + (\text{Nr of hours for annual maintenance} \times \text{Nr of labourers} \times \text{Hourly labour rate}) \times \text{PV} \\ + \text{NPV for cleaning exhaust ducts every 5 years} + \text{NPV of replacement cost after 30 years} \\ + \text{NPV of cost of demolition} \end{aligned} \quad (5)$$

$$\begin{aligned} \text{Life - cycle cost for acoustic comfort} \\ = \text{Consultancy fee for the acoustic consultant} + \text{Initial cost of sound insulation} \\ + \text{NPV for annual maintenance for every 5 years} \end{aligned} \quad (6)$$

$$\begin{aligned} \text{Life - cycle cost for internal lighting} \\ = \text{Initial cost for light fittings, fixtures and lighting points} + (\text{Annual maintenance} \times \text{PVA}) \\ + \text{Replacement cost of lamps every 3 years} + \text{NPV of annual energy saving} \times 0.26 \\ + \text{NPV of cost of demolition} \end{aligned} \quad (7)$$

$$\begin{aligned} \text{Annual maintenance cost} \\ = [(\text{Nr of hours for annual maintenance} \times \text{Nr of labourers} \times \text{Hourly labour rate}) \\ + (\text{Nr of hours for annual maintenance} \times \text{Nr of electricians} \times \text{Hourly rate for Electrician})] \\ + (\text{Nr of hours for monthly visual inspection and cleaning for lighting fixtures and controls} \\ \times \text{Hourly labour rate} \times 12) \end{aligned} \quad (8)$$

$$\begin{aligned} \text{Life – cycle cost for internal blinds} \\ = \text{Initial cost for internal blinds including fixing} \\ + \text{NPV of maintenance cost every 2 years including replacement if required} + \text{NPV of cost of demolition} \end{aligned} \quad (9)$$

$$\text{Life – cycle cost for paints} = \text{Initial cost for painting} + (\text{Annual maintenance}) \times \text{PVA} + \text{NPV for repainting every 7 years} \quad (10)$$

$$\begin{aligned} \text{Life – cycle cost for carpets} \\ = \text{Initial cost for carpets} + \text{NPV of maintenance cost every 2 years} \\ + \text{NPV of replacement cost every 15 years} + \text{NPV of cost of demolition} \end{aligned} \quad (11)$$

$$\begin{aligned} \text{Life – cycle cost for engineered wood products} \\ = \text{Initial cost for interior doors including fixing} + (\text{Annual maintenance cost}) \times \text{PVA} \\ + \text{NPV for demolition} \end{aligned} \quad (12)$$

$$\begin{aligned} \text{Life – cycle cost for thermal comfort} \\ = \text{Initial cost for HVAC system excluding ductwork} + (\text{Annual maintenance} \times \text{PVA}) \\ + \text{Replacement costs every 3 years} + \text{NPV of annual energy saving} \times 0.43 \times + \text{NPV of cost of demolition} \end{aligned} \quad (13)$$

$$\begin{aligned} \text{Annual maintenance cost} \\ = [(\text{Nr of hours for daily inspections} \times \text{Nr of labourers} \times \text{Hourly labour rate}) \times 365] \\ + (\text{Nr of hours for annual maintenance} \times \text{Nr of Air Conditioning technicians} \\ \times \text{Hourly rate for Air Conditioning technician}) \\ + [(\text{Nr of hours for quarterly maintenance} \times \text{Nr of Air Conditioning technicians} \\ \times \text{Hourly rate for Air Conditioning technician} \times 4)] \end{aligned} \quad (14)$$

By following the given formulae, life-cycle cost can be calculated. An example of the life-cycle cost calculation considering a discount rate 3.25% is given in [Table 1](#).

As per Green Star Design and As-Built version 1.1, a building needs to be evaluated by an acoustic consultant to achieve acoustic comfort credits. Therefore, [Eq. \(6\)](#) included consultancy fees for an acoustic consultant. The cost of demolition is not included separately in [Eq. \(6\)](#). The main reason for this is that sound insulation material will be demolished along with the building structure and allocating separately for demolition of sound insulation is not needed, as the cost is very minimal.

In [Eq. \(7\)](#), 6% of energy savings are allocated to the lighting system, because, according to the [Department of Climate Change and Energy Efficiency \(2012\)](#), in Australian commercial office buildings, the lighting system consumes 26% of the total energy consumption. Therefore, energy savings are also apportioned based on the energy consumption of the building. Similarly, in [Eq. \(13\)](#), only 43% of energy savings are considered due to the proportion of energy consumed by the Heating Ventilation Air Conditioning (HVAC) system [Department of Climate Change and Energy Efficiency \(2012\)](#).

Table 1 An example of life-cycle cost for IEQ credits

Discount rate – 3.25% Ventilation type – Mechanically ventilated using water cooled heat rejection

Credits	Credit point	Life-cycle cost (AUD/m ²)					
		Adelaide	Brisbane	Hobart	Melbourne	Perth	Sydney
IEQ 9.1 Ventilation System Attributes	1	15.41	12.89	12.80	15.41	15.65	15.63
IEQ 9.2 Provision of Outdoor Air – Mechanically Ventilated – Water Cooled system	2	124.21	124.38	124.32	124.66	123.83	124.28
IEQ 9.3 Exhaust or Elimination of Pollutants	1	20.76	17.37	17.25	18.93	21.09	21.06
IEQ 10.1 Internal Noise Levels	1	6.05	5.06	5.02	5.51	6.14	6.13
IEQ 10.2 Reverberation	1	7.50	6.27	6.23	6.84	7.62	7.61
IEQ 10.3 Acoustic Separation	1	8.22	6.88	6.83	7.50	8.35	8.34
IEQ 11.0 Minimum Lighting Comfort	Required	45.70	44.45	44.95	42.46	48.44	45.20
IEQ 11.1 General illuminance and glare Reduction	1	60.93	59.27	59.93	56.61	64.58	60.27
IEQ 11.2 Surface Illuminance	1	64.74	62.97	63.68	60.15	68.62	64.03
IEQ 11.3 Localised Lighting Control	1	76.16	74.09	74.92	70.76	80.73	75.33
IEQ 12.0 Glare reduction	Required	33.49	28.01	27.82	30.53	34.02	33.97
IEQ 12.1 Daylight	2	15.63	13.07	12.98	14.25	15.88	15.85
IEQ 12.2 Views	1	6.70	5.60	5.56	6.11	6.80	6.79
IEQ 13.1 Paints, Adhesives, Sealants and Carpets	1	194.25	177.40	162.54	178.61	189.59	181.66
13.2 Engineered Wood Products	1	28.66	23.97	23.71	26.06	29.03	29.00
IEQ 14.1 Thermal Comfort – Mechanically Ventilated – Water Cooled system	1	155.26	155.48	155.39	155.83	154.79	155.35
IEQ 14.2 Advanced Thermal Comfort – Mechanically – Water Cooled system ventilated	1	124.21	124.38	124.32	124.66	123.83	124.28

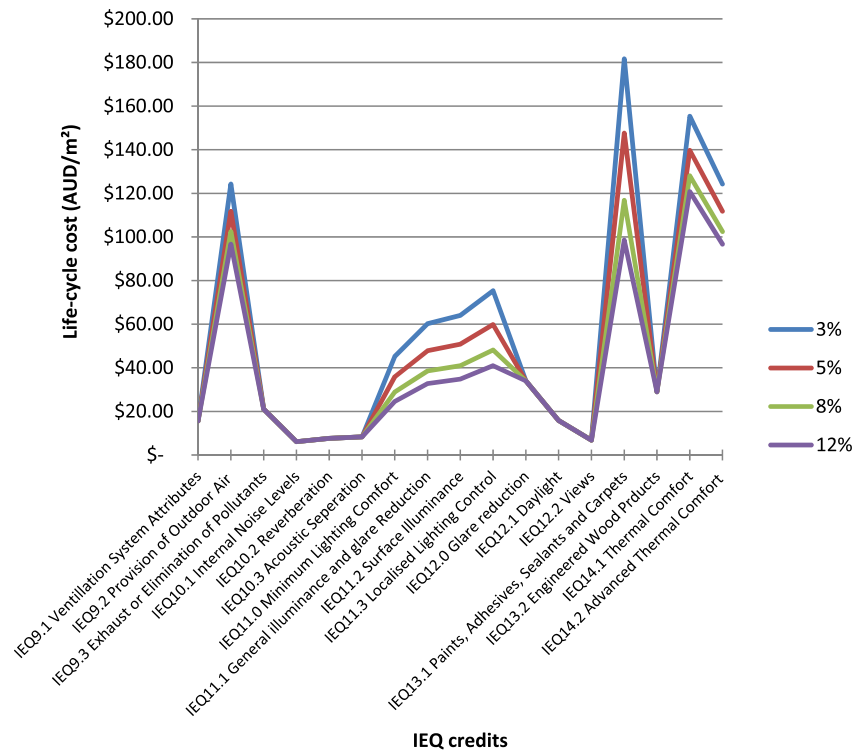


Fig. 1 Sensitivity analysis for IEQ credits at different discount rates.

Sensitivity Analysis for the IEQ Credits

Most of the credits in the IEQ key criterion have significant maintenance costs. Further, certain credits have cost savings throughout the life-cycle of the building. As an example, due to the sufficient light fittings used in the building there are electricity savings. Therefore, this is included in the operational stages of the building. These savings are also reflected in the maintenance, replacement, and other cost components of the life-cycle costs. However, these costs directly depend on the discount rates used in the calculation. Therefore, **Fig. 1** reports the sensitivity analysis of each of these credits, to explain the changes in the discount rate.

Fig. 1 illustrates different life-cycle cost figures for the IEQ credits for an office building located in Sydney with mechanically ventilated air conditioning using water for heat rejection. There are four discount rates used to illustrate the changes in the life-cycle cost (refer **Fig. 1**). There is a reduction in life-cycle cost when the discount rate increases, and this reduction is significant when the contribution of costs during the operational phase is higher in the life-cycle cost calculation. This is significantly evident in credits relating to the lighting system of a building. As an example, credits such as 'IEQ11.0 Minimum Lighting Comfort', 'IEQ11.1 General Illuminance and glare Reduction' and 'IEQ11.2 Surface Illuminance' have significant maintenance, replacement, and other cost proportions. Further, they have considerable costs for electricity throughout the life-cycle of the building. Therefore, with the changes in the discount rates, the changes in the life-cycle cost are significantly evident. However, credits such as 'IEQ10.1 Internal Noise Levels', 'IEQ10.2 Reverberation' and 'IEQ10.3 Acoustic Separation' have minimum costs during the operational phases. Therefore, the maintenance, replacement, and other cost component is at a minimum, and thus, changes to the discount rate are also minimum (refer **Fig. 1**).

The sensitivity of the life-cycle cost to the changes in discount rate is significant in certain IEQ credits. As an example, if 'IEQ12.0 Glare reduction' and 'IEQ11.2 Surface Illuminance' credits are considered when the discount rate is 3%, there is significant difference in the life-cycle costs among these two credits (refer to **Fig. 1**). However, if the discount rate is 12%, there is a slight difference between the two credits (refer to **Fig. 1**). This shows the importance of using the most suited and applicable discount rates to achieve an accurate and consistent life-cycle cost for various requirements. This sensitivity analysis further illustrates that most of the IEQ credits are sensitive to the changes in the discount rate.

Energy Key Criterion

The main aim of the energy key criterion is to reward projects that are designed and constructed to reduce their overall operational energy consumption to below that of a comparable standard-practice building (Green Building Council of Australia, 2015). All the credits in the energy criterion make significant contributions to costs that are incurred during the operational phase of the building. There are five credit elements that have been separately illustrated to achieve 'E15A GHG Emissions Reduction – Prescriptive Pathway'.

These credit elements included building envelopes, glazing, lighting, ventilation and air conditioning, and domestic hot water systems. The building envelope credit focused on roof, floor, and wall insulation, according to the given conditions. There are many options available for these requirements, and considering the optimum solution, focusing on higher thermal resistance and lower life-cycle cost, researchers selected the best material for calculations (Illankoon *et al.*, 2018). Apart from that, glazing, lighting, and air conditioning elements need to fulfil specific requirements. The domestic hot water system needs to be powered by a renewable energy source. Therefore, this credit is bundled with the other credit, namely, 'E16A Prescriptive Pathway: On-site Energy Generation'.

The 'E16A Prescriptive Pathway: On-site Energy Generation' credit requires photovoltaic panels (PV panels) as renewable on-site energy generation sources. Due to the incentives and other benefits given to energy generation through PV panels, there are considerable changes in the life-cycle costs among different CBDs. However, in all the CBDs, there were reported savings in the life-cycle costs (Tam *et al.*, 2017).

Life-Cycle Cost for Energy Credits

Life-cycle cost calculations for energy credits included many formulae as given below.

$$\begin{aligned} \text{Life - cycle cost for building envelope} \\ = \text{Initial cost for building envelope including insulation} + \text{Maintenance cost} \\ + \text{NPV of cost of demolition} \end{aligned} \quad (15)$$

$$\text{Maintenance cost} = \text{NPV of (Nr of hours for maintenance per square meter every 10 years} \times \text{Hourly labour rate)} \quad (16)$$

$$\begin{aligned} \text{Life - cycle cost for glazing} \\ = \text{Initial cost for glazing} \\ + (\text{Nr of hours for annual maintenance} \times \text{Nr of labourers} \times \text{Hourly labour rate}) \times \text{PVA} \\ + \text{NPV of replacement cost} + \text{NPV of cost of demolition} \end{aligned} \quad (17)$$

$$\begin{aligned} \text{Life - cycle cost for domestic hot water (DHW) system} \\ = \text{Initial cost of DHW system} \\ + \text{NPV for maintenance for every 5 years} + \text{NPV for annual energy saving} \\ + \text{NPV of cost of demolition} \end{aligned} \quad (18)$$

$$\begin{aligned} \text{Life - cycle cost for PV panels} \\ = \text{Initial cost for PV panels including fixing} \\ + (\text{Nr of hours of annual maintenance} \times \text{Hourly rate for technicians}) \times \text{PVA} \\ + \text{NPV of cost of demolition} \end{aligned} \quad (19)$$

An example of the life-cycle cost calculation for Sydney considering a discount rate 3.25% is given in Table 2.

According to Green Star there are five options available to achieve 'E15GHG Emissions Reduction'. Further, while using PV panels for on-site energy generation, there are savings on the life-cycle costs.

Sensitivity Analysis for Energy Credits

Similar to the IEQ credits, energy credits also have maintenance, disposal, replacement, and other cost components in the life-cycle cost calculation. Therefore, Fig. 2 illustrates the sensitivity to the life-cycle cost and its impact on the discount rate. The life-cycle costs are for an office building in Sydney and the discount rate changes from 3%, to 5%, to 8%, and to 12%.

Table 2 An example of life-cycle cost for energy credits

Discount rate – 3.25%							
Credits	Credit point	Life-cycle cost (AUD/m ²)					
		Adelaide	Brisbane	Hobart	Melbourne	Perth	Sydney
E15A GHG Emissions Reduction – Building Envelope	1	103.81	114.41	115.85	109.96	119.62	108.68
E15A GHG Emissions Reduction – Glazing	1	146.77	144.37	141.57	141.57	146.77	146.77
E15A GHG Emissions Reduction – Lighting	1	76.16	74.09	74.92	70.76	80.73	75.33
E15A GHG Emissions Reduction – Mechanically Ventilated – Air Cooled System	1	105.27	103.54	104.23	100.78	109.07	104.58
E15A GHG Emissions Reduction – Mechanically Ventilated – Water Cooled System	1	93.16	93.29	93.24	93.50	92.87	93.21
E15A GHG Emissions Reduction – Naturally Ventilated	1	1.46	1.20	1.18	1.30	1.56	1.48
E15A GHG Emissions Reduction – Domestic Hot Water System	1	16.85	17.74	17.38	19.16	14.40	17.21
E16A Prescriptive Pathway: On-site Energy Generation	1	– 18.05	– 15.09	– 14.93	– 16.41	– 18.28	– 18.26

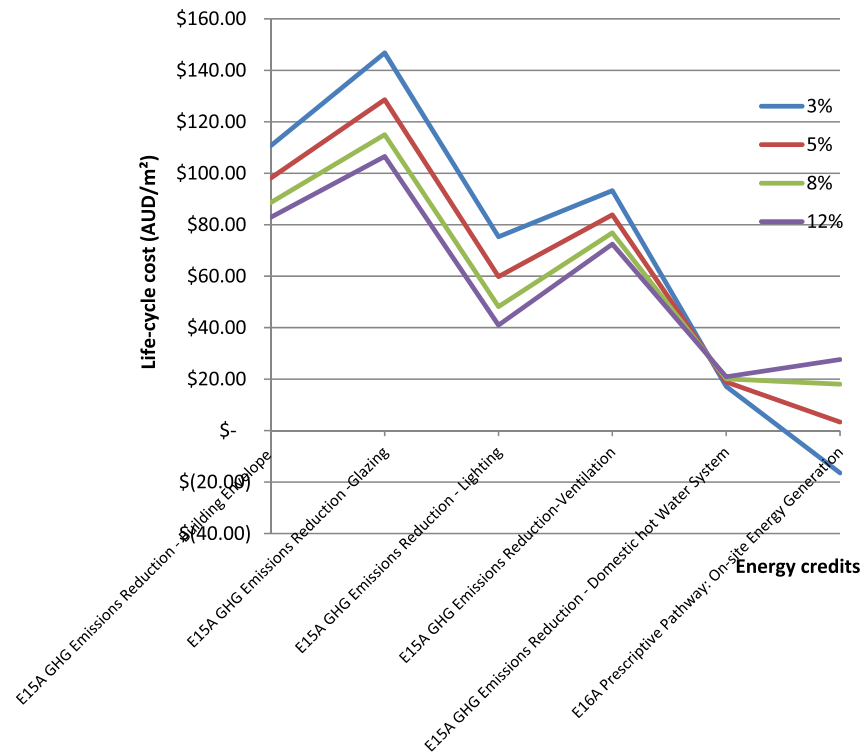


Fig. 2 Sensitivity analysis for energy credits at different discount rates.

According to Fig. 2, there is a major impact on the life-cycle cost, especially for 'E16A Prescriptive Pathway: On-site Energy Generation'. For lower discount rates, there is a cost saving for using the PV panels for energy generation. However, the cost saving is cancelled if the discount rate is higher. Further, a majority of other credits also have substantial impacts on discount rate, and thus, on the life-cycle cost. Therefore, similar to the IEQ criterion, while calculating life-cycle cost, users need to be cautious and input the most suited discount rate to reflect the risk and cost of capital.

Water Key Criterion

By using the prescriptive pathway, the proposed model can achieve up to six credit points through the water key criterion. The main aim of this key criterion is to minimise potable water consumption (Green Building Council of Australia, 2015). To achieve this aim, the users can use water efficient sanitary fixtures, reuse rainwater, avoid using water for heat rejection in HVAC systems, use water efficient landscape irrigation, and so on.

All the credits in water criterion make contributions to all the three types of life-cycle costs. For 'W18B.1 Prescriptive Pathway: Sanitary Fixture Efficiency' credit calculations, all the fixtures are water efficient, and within the required rating levels. Further, while calculating the water costs within the life-cycle of the building, the water savings predicted from using water efficient sanitary fixtures are considered.

Life-Cycle Cost Calculations for Water Credits

While calculating life-cycle costs for 'W18B.2 Prescriptive Pathway: Rainwater Reuse', a 75 kilo-litre water tank is considered. Further, for 'W18B.4 Prescriptive Pathway: Landscape Irrigation' a drip irrigation system is considered. Further, the following formulae were used for calculating the life-cycle cost for water credits.

$$\begin{aligned}
 &\text{Life - cycle cost for sanitary fixtures} \\
 &= \text{Initial cost for sanitary fixtures including fixing} \\
 &\quad + \text{Annual maintenance cost} \times \text{PVA} \\
 &\quad - \text{annual water savings from fixtures} \times \text{PVA} \\
 &\quad + \text{NPV of cost of demolition}
 \end{aligned} \tag{20}$$

Life – cycle cost for rainwater tank

$$\begin{aligned}
 &= \text{Initial cost for rainwater tank} \\
 &+ (\text{Nr of hours for annual cleaning} \\
 &\times \text{Nr of labourers} \times \text{Hourly labour rate}) \\
 &\times \text{PVA} - \text{Annual water savings} \\
 &+ \text{NPV of cost of demolition}
 \end{aligned} \tag{21}$$

Life – cycle cost for drip irrigation system

$$\begin{aligned}
 &= \text{Initial cost of drip irrigation system} \\
 &+ (\text{Annual maintenance cost} \times \text{PVA}) \\
 &+ \text{NPV of cost of demolition}
 \end{aligned} \tag{22}$$

All the sanitary fixtures follow the required water efficiency labelling system (WELS). Therefore, the water savings are based on the saving rates given by WELS. After considering these formulae, the life-cycle cost is calculated and reported in [Table 3](#).

According to [Table 3](#), depending on the type of ventilation system in the building, there are two options available for 'W18B.3 Heat Rejection'. However, once again, using natural ventilation is considered to have lesser life-cycle cost.

Sensitivity Analysis for Water Credits

The credits in the water key criterion have an impact on all the different components of life-cycle costs. Therefore, it is worth identifying the sensitivity of these costs to the discount rate. [Fig. 3](#) below reports the sensitivity of the life-cycle costs to the changes in the discount rate.

In [Fig. 3](#), to achieve 'W18B.3 Prescriptive Pathway: Heat Rejection', a HVAC system using air for heat rejection is used. This system incurs regular maintenance, replacement, and demolition costs. Therefore, there are lots of costs depending on the discount rate. This leads to a drastic change in life-cycle cost as a result of the changes in discount rate. 'W18B.2 Prescriptive Pathway: Rainwater Reuse' and 'W18B.4 Prescriptive Pathway: Landscape Irrigation' credits can be achieved using a minimum life-cycle cost, when compared to the other credits in the water key criterion.

Table 3 An example of life-cycle cost for water credits

Credits	Credit point	Life-cycle cost (AUD/m ²)					
		Adelaide	Brisbane	Hobart	Melbourne	Perth	Sydney
W18B.1 Sanitary Fixture Efficiency	1	84.96	71.06	70.29	77.24	86.04	85.97
W18B.2 Rainwater Reuse	1	2.90	2.42	2.40	2.63	2.94	2.93
W18B.3 Heat Rejection – Naturally Ventilated	2	2.90	1.46	1.16	4.90	9.69	9.63
W18B.3 Heat Rejection – Mechanically Ventilated – Air Cooled System	2	147.38	144.96	145.93	141.09	152.70	146.41
W18B.4 Landscape Irrigation	1	0.62	0.52	0.51	0.56	0.63	0.63
W18B.5 Fire System Test Water	1	42.10	41.60	41.50	41.50	50.90	42.70

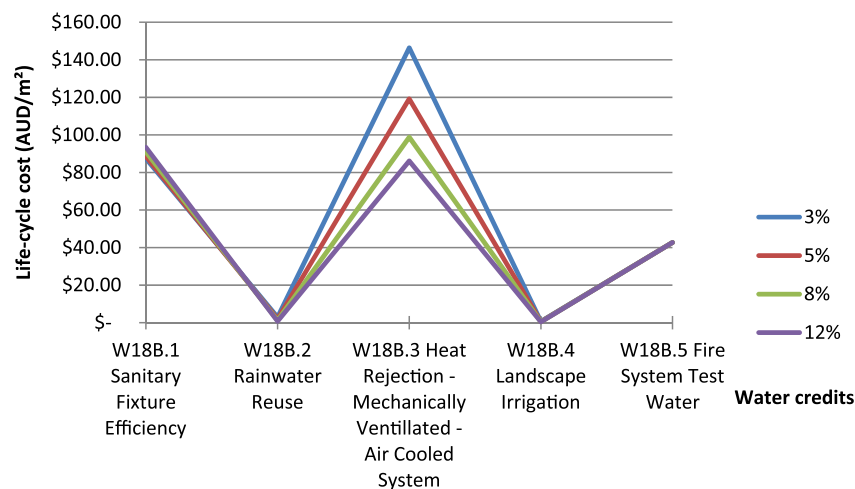


Fig. 3 Sensitivity analysis for water credits at different discount rates.

Table 4 An example of life-cycle cost for material credits

Credits	Credit point	Life-cycle cost (AUD/m ²)					
		Adelaide	Brisbane	Hobart	Melbourne	Perth	Sydney
Mat 19B.1 Life-Cycle Impacts – Concrete	3	246.10	205.83	201.36	223.73	219.21	214.01
Mat 19B.2B Reduced Use of Steel Reinforcement	2	37.85	40.70	37.31	41.00	43.10	51.05
Mat 20.1 Structural reinforcing Steel	1	1.46	1.20	1.18	1.30	1.56	1.48
Mat 20.2 Timber Products	1	21.30	17.81	17.62	19.36	21.57	21.55
Mat 20.3 Permanent, Formwork, Pipes, Flooring, Blinds and Cables	1	1.46	1.20	1.18	1.30	1.56	1.48
Mat 21 Product Transparency and Sustainability	3	4.39	3.59	3.55	3.90	4.68	4.44
Mat 22A Reduction of Construction And Demolition Waste	1	27.29	27.31	14.21	15.61	30.87	−9.95

The sensitivity to the discount rate is significantly displayed in [Fig. 3](#). As an example, if the discount rate is 3%, out of ‘W18B.1 Prescriptive Pathway: Sanitary Fixture Efficiency’ and ‘W18B.3 Prescriptive Pathway: Heat Rejection’, using water efficient sanitary fixtures credit is clearly cheaper, as per the life-cycle cost (refer to [Fig. 3](#)). However, if the discount rate is 12%, ‘W18B.3 Prescriptive Pathway: Heat Rejection’ is slightly cheaper than it was in the previous scenario. Therefore, this scenario illustrates the importance of using the best suited discount rate for life-cycle cost calculations.

Material Key Criterion

As the name suggests, this key criterion focuses on building materials. According to the [Green Building Council of Australia \(2015\)](#), the aim of this key criterion is to address the consumption of resources in a building construction context, by encouraging the selection of lower impact material. The main focus of this key criterion is on material, namely, concrete, steel, timber, and the minimum use of PVC.

According to [Mori and Ellingwood \(1993\)](#), the long-term strength of concrete changes due to maturity. Further environmental stressors may attack the integrity of concrete and/or steel reinforcement in concrete with or independent of operating, environmental, and accidental loads ([Mori and Ellingwood, 1993](#)) causing the strength to degrade over time. Therefore, according to [Illankoon et al. \(2018\)](#), it can be argued that concrete only needs to be maintained due to certain external issues, such as accidental loads and severe environmental conditions. Further, usually in a building, crack formation is mostly due to design failures or technical failures in placing and curing concrete, and other than that, in normal conditions, specific maintenance is not required for concrete ([Illankoon et al., 2018](#)). Therefore, while using supplementary cementitious material (SCM) in concrete for obtaining ‘Mat19B Prescriptive Pathway – Life cycle Impacts’ maintenance and replacement costs are not included. A similar argument can be used for ‘Mat 20.1 Structural Reinforcing Steel’ as well. Since the building is a concrete framed building, for this credit, only reinforcement steel in concrete is considered. Therefore, there will only be an initial cost and a demolition cost, except in extreme conditions, where the structure needs major renovation. As a result, ‘Mat 20.1 Structural Reinforcing Steel’ credit does not include any maintenance, replacement, and other costs.

There are many SCM materials that can be used. However, according to [Illankoon et al. \(2018\)](#) 50% of cement replaced with slag is the optimum solution for SCM replacement. Therefore, this option is used for life-cycle calculation in the proposed model. Further, the regular maintenance costs included in ‘Mat 20.2 Timber Products’ and in ‘Mat 20.3 Permanent, Formwork, Pipes, Flooring, Blinds and Cables’ are at a minimum. As a result of this, the maintenance, replacement, and other costs are minimised in this key criterion. Therefore, the impact on life-cycle cost due to the changes in discount rate is at a minimum. Further, there are no specific formulae used for life-cycle cost calculations in this key criterion. [Table 4](#) reports the life-cycle cost for material credits at a 3.25% discount rate.

Various credits are discussed under the materials key criterion. The life-cycle cost and the credit points vary significantly in this key criterion. ‘Mat19B.1 Life Cycle Impacts – Concrete’ has the highest life-cycle cost, but this credit also achieves three credit points. Further, ‘Mat22A Reduction of Construction and Demolition Waste’ creates significant change in the life-cycle cost depending on the CBD (refer to [Table 4](#)).

Conclusions

This research study focused on analysing the life-cycle costs of various criteria in green buildings focusing on Green Star Design and As-Built v1.1 as a guideline. Initially, life-cycle cost is calculated for various options and afterwards, sensitivity analysis is also carried out.

Discount rate is one of the significant parameters in life-cycle costing. Credits with higher life-cycle cost contribute towards the costs incurred in the operational stage of building, and this is significantly impacted by the discount rate. Based on sensitivity analysis, majority credits in key criteria, such as IEQ and energy, have a significant impact on the discount rate.

Naturally ventilated system has the lowest life-cycle cost due to lower maintenance costs and life-cycle savings associated with natural ventilation. Therefore, more passive solutions, such as using natural ventilation and natural daylight, should be considered in green building implementation.

According to life-cycle cost calculations, natural ventilation and acoustic comfort have lower life-cycle costs in IEQ criterion. Unless there are user constraints, use of PV panels as a renewable energy generating source in green buildings is a lower life-cycle cost option. However, it is interesting to identify whether these options are considered in green building implementation. As an example, natural ventilation is rarely used on certified green buildings. The main reason for this is the lack of information on life-cycle perspectives in the initial decision-making stages. These can be eliminated by using life-cycle cost approach in the initial decision-making stages.

Passive solutions, such as natural ventilation and rainwater re-use in green buildings derive multiple benefits. As an example, if natural ventilation is used credits such as 'W18B.3 Heat Rejection' is directly achievable. Most of the decisions on material selection are carried out in the initial decision making stages. Therefore, life-cycle cost approach must be considered in the initial decision making stages to gain fruitful benefits.

Recommendations

Based on the conclusions, it is evident that certain credits with lower life-cycle costs are eliminated due to higher initial costs during the initial decision-making stages. Therefore, this study clearly signifies the importance of looking into life-cycle cost perspective, while deciding on the green building implementation within the initial decision-making stages.

Discount rate used to calculate the life-cycle cost has significant importance. It directly influences the selections based on life-cycle cost. Therefore, when carrying out life-cycle cost calculations users should be more careful and accurate in deciding the discount rate.

To obtain the credits representing the material criteria, the suppliers also should be selected properly. Specialist contractors providing the HVAC and electrical systems must also be aware of the perceived green building certification. Therefore, in summary, the green building implementation should be a process that involves various professionals attached to various stages of the building's life-cycle. As a result, this study recommends looking into green building implementation as a whole process, integrating all these requirements.

According to the life-cycle cost calculations, passive solutions, such as using natural ventilation, daylight in buildings, and rainwater tanks are always identified as lower life-cycle solutions. However, provisions such as natural ventilation are rarely used in green buildings. Therefore, it is recommended to consider these passive solutions in green building implementation.

Acknowledgement

The authors wish to acknowledge the financial support from the Australian Research Council (ARC), Australian Government (No: DP150101015).

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Nickel Chromium Based Partial Denture Preparation: Conventional vs Additive Manufacturing Techniques

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Introduction

The PD are metal frameworks designed to retain artificial replacement teeth in the oral cavity and smaller version is the fixed partial denture (FPD), also known as a fixed bridge, which can be used if normally healthy teeth are present adjacent to the space where the tooth or teeth have been lost (Eggbeer *et al.*, 2005; Campbell *et al.*, 2017; Block, 2017). Human race is using PD or complete dentures (CD) as early as the 7th century BC. It has been reported that in Italy, PD out of human/animal teeth were fastened with gold bands (Donaldson, 1980). The use of wood based CD has been reported in early 16th century in Japan (Anderson *et al.*, 2004). Pierre Fauchard outlined the fabrication of PD/CD using a frame and teeth sculpted from animal bone in 1728. Further in 1820 'Samuel Stockton' prepared high-quality porcelain PD/CD mounted on 18-carat gold plates (Moriyama and Hasegawa, 1987). Later in 1850s PD/CD were made of vulcanite, (a form of hardened rubber) into which porcelain teeth were set (Rueggeberg, 2002). Further, in 1980s technology was developed to construct PD/CD, which is permanently anchored to the bones in the jaw (Hacking and Khademhosseini, 2009). In the 20th century, thermoplastics were used with conventional methods (McCord, 2009). The PD/CD is fixed or removable replacements for teeth. A CD is made to re-establish both the teeth and the hidden bone when all the teeth are missing in an arch (Mijiritsky and Karas, 2004; Sailer *et al.*, 2007).

The PD is secured to the adjacent teeth by attachment to crowns, or caps, that are affixed to the healthy teeth (Canallatos, 2017). There are two main categories of dentures, the distinction being whether they were used to replace missing teeth on the mandibular arch or on the maxillary arch (Esposito *et al.*, 2009; Carr and Brown, 2010).

Dental implants are the latest tooth-replacement technology (Block, 2017). Modern technology has offered significant advances in the materials used to make artificial teeth and enhanced strategies for pinning them in the mouth (Anusavice *et al.*, 2013). There are many different denture designs available, based upon patient specific needs (Ginsburg *et al.*, 2017; Hunter and Light, 2017). Better design for PD/CD provides more agreeable and effective chewing. However, new dentures known as dental implants are prepared by specialized dentists called denturists (Raskin, 2015). The production of metallic restorations in the dental laboratory has conventionally been carried out by the lost wax casting also called investment casting technique (Pompa *et al.*, 2015; Kalavathi *et al.*, 2016). The PD formed by the traditional method is profoundly relied on the skill and experience of the technician. Its superiority is depended on the accuracy of the technician's final judgment (Noort, 2013). The current fabrication (with CM techniques) of denture, bridges, or crowns requires intensified manual work that undergoes number of steps (Dean, 2015). Most importantly, it does not preserve any quantitative information for future retrieval (Chang *et al.*, 2006).

However, PD can be annoying and problematic, and they often provide patients with only a fraction of the chewing force of natural teeth (Seferli *et al.*, 2014). The first efforts to automate the creation of dental restorations started more than 20 years ago (Sokovic and Kopac, 2006; Bagci, 2009). Advanced imaging and CAD/CAM technologies and their applications in enhancing treatment outcomes in implant dentistry have gained widespread interest (Kattadiyil *et al.*, 2014; Anderson *et al.*, 2014). The process of capturing the shapes of objects through surface data sampling and generating a 3D CAD model is termed as reverse engineering (RE) because the process is the reverse of the normal design and manufacturing sequence (Bi and Wang, 2010; Geng and Bidanda, 2017). The early computer-aided design/computer-aided manufacturing (CAD/CAM) systems were relied exclusively on subtractive methods (Liaw and Guvendiren, 2017). The CAD/CAM systems have many advantages in reducing production and labor cost (Farjood *et al.*, 2017). However, AM strategies have demonstrated fruitful in other dental applications, the absence of appropriate design software has constrained their application in producing PD/CD frameworks (Litjens *et al.*, 2017). AM have been exploited to build complex 3D models in medicine since the 1990s (Huettnier *et al.*, 2018). In recent years, AM progressed rapidly in various fields of dentistry as they have the potential to intimidate known drawbacks of subtractive techniques such as fit problems (Milewski, 2017). AM has recently proposed successful applications in various dental fields, such as fabrication of implant surgical guides, frameworks for fixed and removable partial dentures, wax patterns for the dental prosthesis, zirconia prosthesis and molds for metal castings, and maxillofacial prosthesis and finally, complete dentures (Quadri *et al.*, 2017; Azari and Nikzad, 2009; Torabi *et al.*, 2015). Previous studies have established a valid approach to the computer-aided surveying of digital casts, framework design and the subsequent production of sacrificial patterns by using AM technologies (Eggbeer *et al.*, 2006). Some of the commercially available AM techniques are digital light projection (DLP), jet (PolyJet/ProJet) printing, and direct laser metal sintering (DLMS)/selective laser sintering (SLS), FDM (Masood, 1996; Bilgin *et al.*, 2016; Alharbi *et al.*, 2016).

PD or bridge more often consists of replacement teeth attached to a pink or gum-colored plastic base, which is mainly connected by metal framework that holds the denture in place in the mouth (Brehm, 2018; Caron *et al.*, 2018). PD is used when one or more natural teeth remain in the upper or lower jaw (Groot, 2018). A fixed bridge exchanges one or more teeth by insertion crowns on the teeth on either side of the space and attaching artificial teeth to them (Rubbert and Ellermeier, 2018; Muris and

Kleverlaan, 2018). This “bridge” is then cemented into place. Not only does a PD fill in the spaces created by missing teeth, it prevents other teeth from changing position (Rupp *et al.*, 2018). A precision PD is removable and has internal attachments rather than clasps that attach to the adjacent crowns (Lazareva *et al.*, 2018; Longurova *et al.*, 2018).

There are two types of dentures, removable and complete.

Removable PD: Removable PD are for patients who are missing some of their teeth on a particular arch (Wallace *et al.*, 2018). Fixed PD, also known as “crown and bridge” dentures, are made from crowns that are fitted on the remaining teeth (Campbell *et al.*, 2017). They act as abutments and pontics and are made from materials resembling the missing teeth (Kenna *et al.*, 2015; Schimmel *et al.*, 2015). Fixed bridges are more expensive than removable appliances but are more stable (Armellini and Von Fraunhofer, 2004; Bilt, 2011).

Complete dentures: Complete dentures are worn by patients who are missing all of the teeth in a single arch (i.e., the maxillary (upper) or mandibular (lower) arch) (Jepson *et al.*, 2003; Yagi *et al.*, 2017).

Comparison Between CM and AM

CM and AM both are used to prepare parts of different sizes and complexity. However, in CM route more waste is generated as compared to the AM. This is because of the fact that CM is labor intensive and requires high level of technical skill. AM, on the other hand, is a layer by layer process which leaves relatively less waste material, hence also sometimes, called as near zero waste manufacturing. Further versatility of AM process is of no match with CM, (where there is no or very less control on output parameters in CM and AM delivers the product in high dimensional accuracy with good surface finish without much technical skill). Further there are less chances of metal shrinkage in AM. The whole part is prepared under digitalized environment as it is fully controlled. Fig. 1 shows flow chart for preparation of PD with CM and AM technique.

Conventional Manufacturing (CM) for PD Preparation

According to the 8th edition of The Glossary of Prosthodontics Terms, “impression” is defined as “a negative likeness or copy in reverse of the surface of an object; an imprint of the teeth and adjacent structures for use in dentistry” (The glossary of

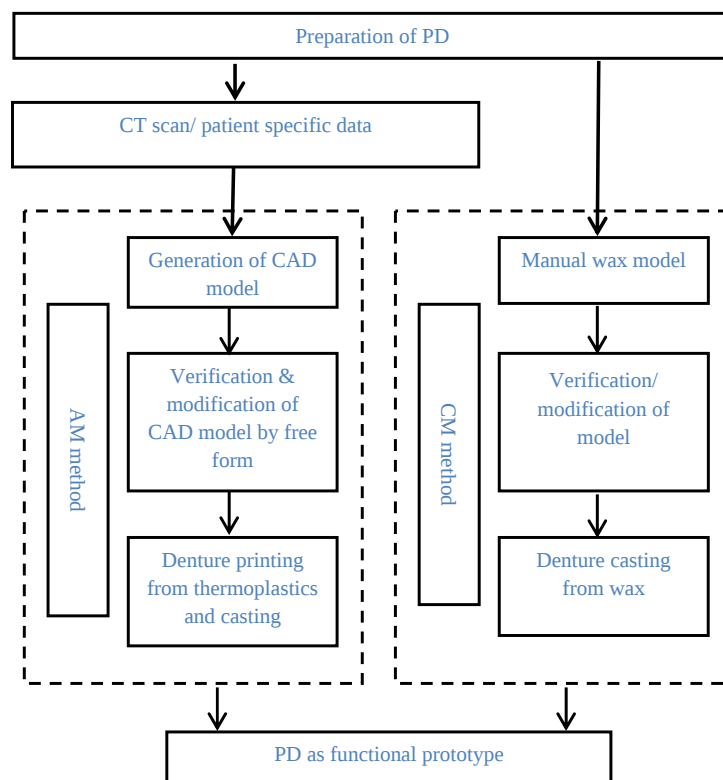


Fig. 1 Flow chart for preparation of PD.

prosthodontic terms, 2005). The exactness of the impression relies upon the impression materials, tray types and techniques (Ender and Mehl, 2013). Each phase in the process introduces human as well as material error (Nedelcu *et al.*, 2017).

There is some variability in impressions and the resulting master casts, depending on the technique and material used by the operator (Lima *et al.*, 2018). The accuracy of master casts has been the subject of numerous research projects, and is dependent on numerous items, including the water/powder ratio, vacuum versus hand mixing and the type of dental stone and its compatibility with impression materials (Menini *et al.*, 2018; Park and Shin, 2018). Fig. 2 shows 3D view of PD.

Steps for Preparation of PD

In this work, dental crown as shown in Fig. 2 has been selected as the benchmark component. This research work has been divided into 12 stages/steps formally from the benchmark to final cast as shown in Fig. 3. First of all, manufacturing process begins with a preliminary impression of the patient's teeth (stage 1). This impression was used to prepare a diagnostic cast. Once an appropriate preliminary cast/impression has been obtained, the final cast (teeth mold) is made from gypsum, a stone-like product (stage 2). For mixing of investment (mixture of siladent powder and water) three different pH value of water (pH-3, pH-7, pH-10) with different powder/water (P/W) ratios by weight (100/12, 100/15, 100/18) has been used (see Table 1). After this preparation of wax pattern and shaping was done manually with conventional method (stage 3). Therefore, tree formation of wax pattern was done prior to filling the investment in the crucible (stage 4). After this, investment was poured in crucible and around the pattern tree (stage 5–7). Investment was baked in Muffle furnace for 1.5 h at 900°C (stage 8–9). The induction casting setup was used for casting of denture with Ni-Cr based alloy (stage 10–11). The final casting of denture fitted on the mold is available after solidification (stage 12).

Optimization of Input Parameters

Table 1 shows input parameters selected for experimentation. All specimens were casted with different input parameters namely P/W ratio (100/12, 100/15, 100/18), second is pH value of water (pH-3, pH-7, pH-10) and Ni% (62%, 65%, 70%) in Ni-Cr alloy for final casting of PD. The dimensional deviation (Δd value) for one critical dimension 10.70 mm is shown in Fig. 2.

Taguchi L9 orthogonal array based design of experiment has been used for PD preparation (Table 2). It has been observed that PD casted at optimum values of P/W ratio 100/12, pH-7 value of water with 65% of Ni in NiCr alloy gives better results for dimensional accuracy as compared to other parts. The measurements of average Δd on castings were measured on the co-ordinate measuring machine (CMM). The average Δd is the difference in drawing dimension and dimension of finally cast component. Three repetitions have been made to reduce the experimental error.

Fig. 4 shows the main effect plot for mean S/N ratio of various factors of CM process. From Fig. 4, lower variation in dimensional accuracy after casting has been observed for specimen casted with P/W ratio of 100/12, pH-7 value of water with 65% of Ni in NiCr alloy.

Based upon Table 2 and Fig. 4, Table 3 shows the analysis of variance (ANOVA) to understand the percentage contribution of input process parameters.

As observed from Table 3, for controlling the dimensional accuracy in CM route, P/W ratio is the most significant factor followed by Ni% where as pH value is least contributing factor.

Additive Manufacturing (AM) for PD Preparation

AM is a 3D printing process that builds up parts layer by layer and differs greatly from CM techniques (Huang *et al.*, 2013). It uses 3D data on the oral situation of the patient as a basis; this is generated using intraoral scanners or by impression or model scans (Lim *et al.*, 2012; Kruth, 1991).



Fig. 2 3D view of PD.

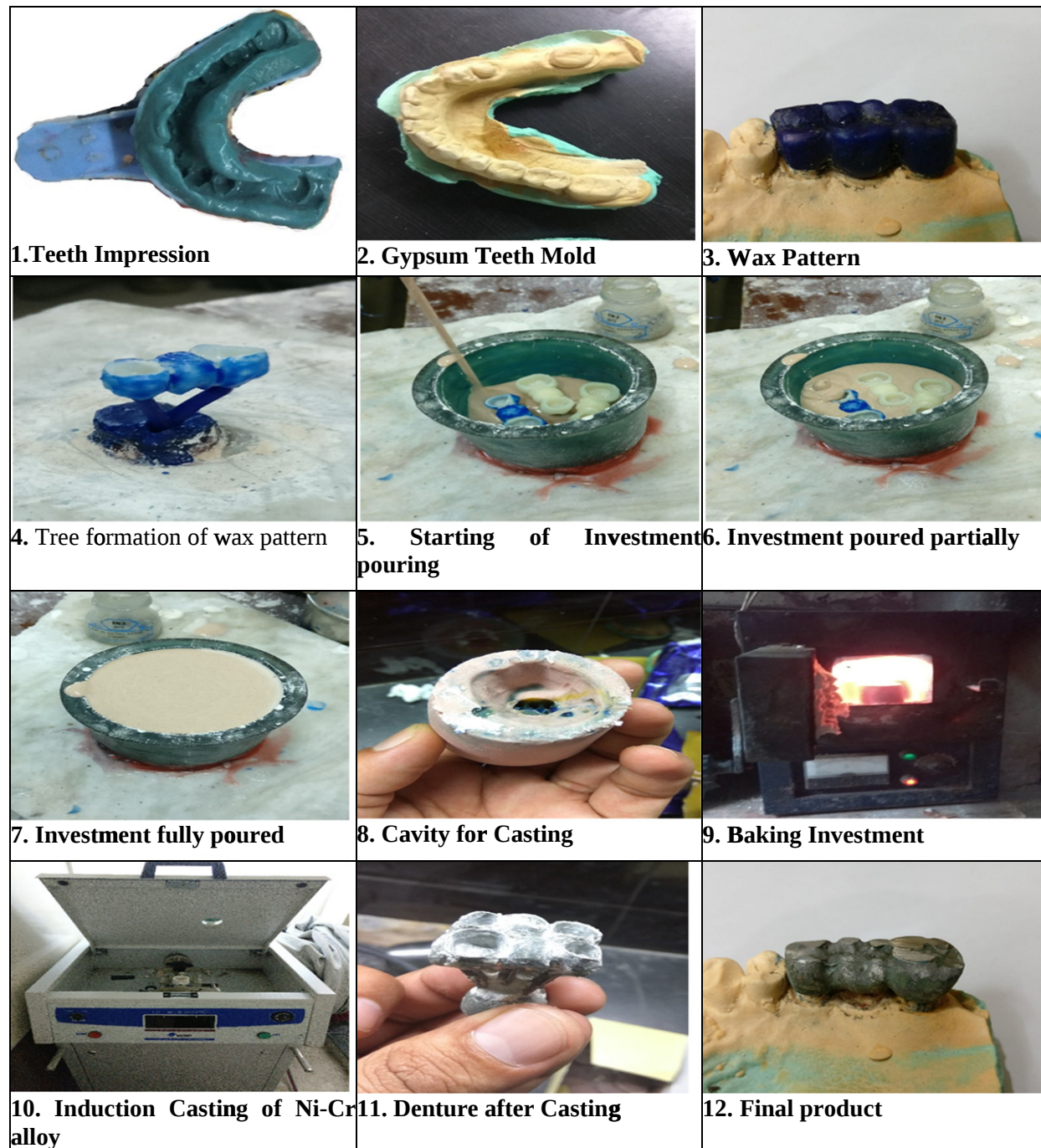


Fig. 3 Steps involved in making partial denture using CM technique.

AM have been exploited to build complex 3D models in medicine since the 1990s (Frazier, 2014; Pham and Gault, 1998). AM has recently proposed successful applications in various dental fields, such as fabrication of implant surgical guides, (Quadri *et al.*, 2017) frameworks for fixed and removable partial dentures, wax patterns for the dental prosthesis, (Thoma *et al.*, 2017) zirconia prosthesis and molds for metal castings, and maxillofacial prosthesis and finally for complete dentures (AlHelal *et al.*, 2017, 2018).

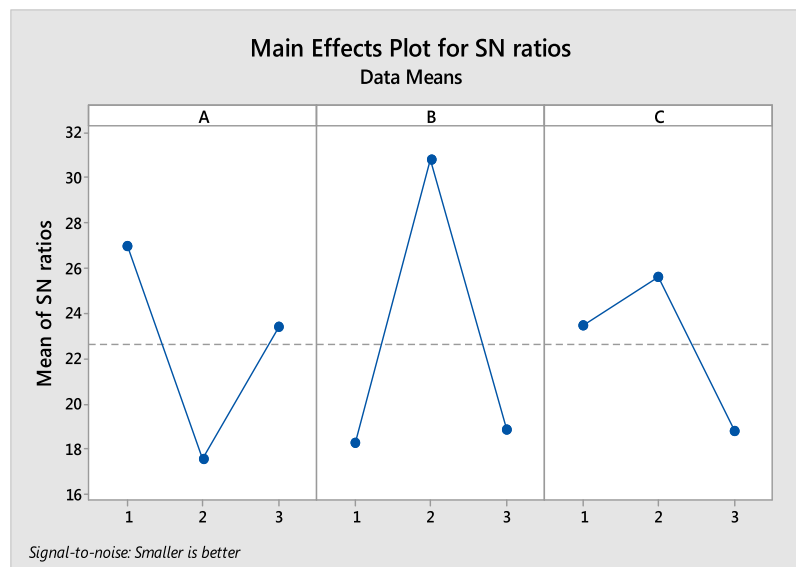
AM techniques, the so-called “generative manufacturing techniques”, show the possibility to overcome the described shortages (Oilo *et al.*, 2018; Grant *et al.*, 2018). The AM simply consists of two phases: virtual phase (modelling and simulating) (Leitz *et al.*, 2018) and physical phase (fabrication) (Ji *et al.*, 2018). Virtual prototyping is development of model by dynamic and interactive simulation. The course of forming the physical model is formation of 3D physical model by CAD (Lu *et al.*, 2018; Maddox *et al.*, 2018).

Table 1 Input parameters for preparation of PD (with CM and AM)

Input parameters Factor	Symbol	Levels		
P/W ratio (g/ml)	A	1	2	3
pH value of water	B	100/12	100/15	100/18
Ni-Cr alloy (%)	C	pH-3	pH-7	pH-10
		Ni 62	Ni 65	Ni 70
		Ni 62%	Ni 65%	Ni 70%
		Cr 25.6%	Cr 22.5%	Cr 13%
		Si 0.47%	Mo 9.5%	Si 4%
		Co 0.31%		Cu 13%
		Mn 0.03%		
		Mo 11.06%		

Table 2 Observations for PD casting using CM technique

S. no.	P/W ratio	pH value of water	Ni %	Average Δd (mm)	S/N ratio (dB)
1	100/12	pH-3	62%	0.10	20.00
2	100/12	pH-7	65%	0.01	40.00
3	100/12	pH-10	70%	0.09	20.91
4	100/15	pH-3	65%	0.13	17.72
5	100/15	pH-7	70%	0.12	18.41
6	100/15	pH-10	62%	0.15	16.47
7	100/18	pH-3	70%	0.14	17.07
8	100/18	pH-7	62%	0.02	33.97
9	100/18	pH-10	65%	0.11	19.17

**Fig. 4** Main effects plot for mean S/N ratio.

Fused Deposition Modelling (FDM) Technique

The FDM is an AM technique, which extruded a thermoplastic material in the form of layer by layer through a nozzle and controlled by temperature (Azari and Nikzad, 2009; Bourell *et al.*, 2017; Long *et al.*, 2017). The FDM head extrudes and directs the material in ultra-thin layers onto a fixtureless flat base with precision (Vaezi *et al.*, 2018; Adel *et al.*, 2018). The FDM process starts with importing a standard triangulation language (STL) file of a model into pre-processing software (Upcraft and Fletcher, 2003; Nikzad *et al.*, 2011). After reviewing the path data and generating the tool path, the data is downloaded to the FDM machine (Wang *et al.*, 2017; Singh *et al.*, 2017).

Table 3 S/N response for output parameter based upon ANOVA in CM

Source	Δd (mm)	
	P-value	% contribution
P/W ratio	0.014	52.45
pH value of water	0.048	14.50
Ni %	0.022	32.31
Error		0.5092

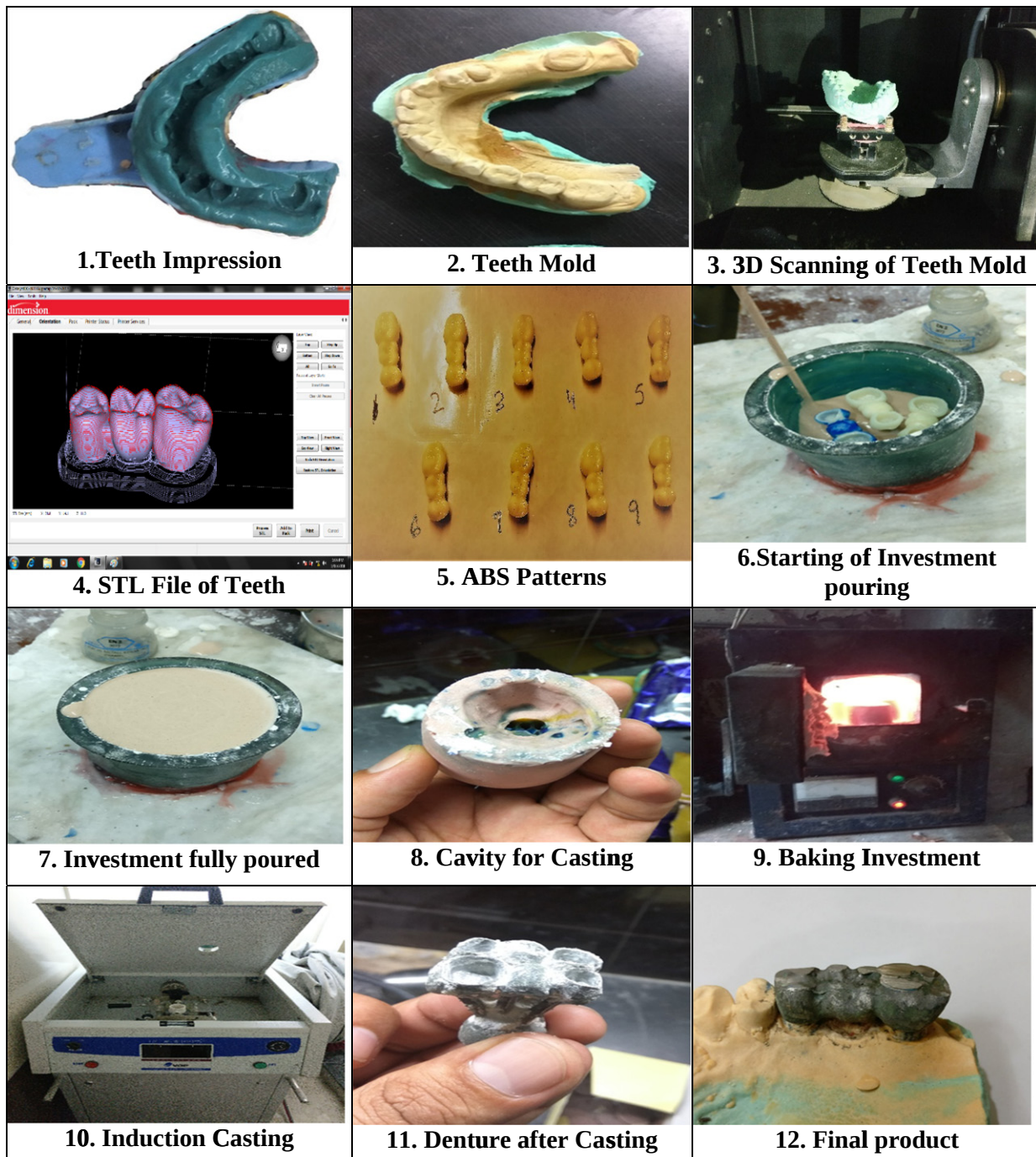
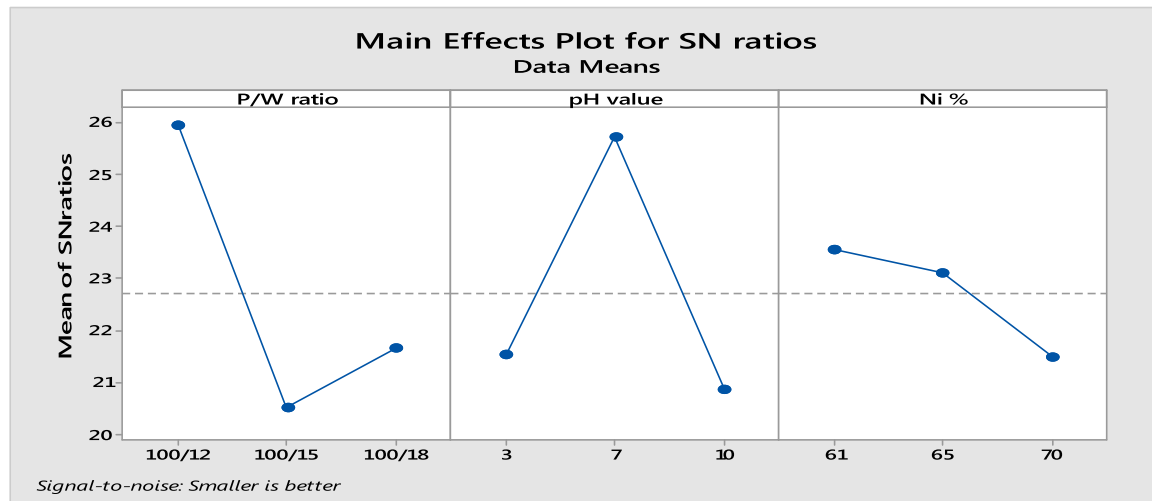
**Fig. 5** Steps involved in making partial denture using AM technique.

Table 4 Observations for PD casting using AM

P/W ratio	pH value of water	Ni %	Dimensional accuracy Δd (mm)= actual cast dimension-drawing dimension	S/N ratio for dimensional accuracy
100/12	pH-3	62%	0.05	26.0206
100/12	pH-7	65%	0.03	29.5424
100/12	pH-10	70%	0.08	22.3079
100/15	pH-3	65%	0.11	19.1721
100/15	pH-7	70%	0.07	22.6940
100/15	pH-10	62%	0.10	19.7152
100/18	pH-3	70%	0.11	19.4394
100/18	pH-7	62%	0.06	24.9334
100/18	pH-10	65%	0.09	20.5993

**Fig. 6** Main effects plot for mean S/N ratio.**Table 5** S/N response for output parameter based upon ANOVA in AM

Source	Δd (mm)	
	P-value	% contribution
P/W ratio	0.031	49.55
pH value of water	0.036	41.68
Ni %	0.179	7.19
Error		1.556

Steps for Preparation of PD

This work has been divided into 12 stages/steps formally from the benchmark to final cast as shown in Fig. 5. First of all, manufacturing process begins with a preliminary impression of the patient's teeth (stage 1). This impression was used to prepare a diagnostic cast. Once an appropriate preliminary cast/impression has been obtained, the final cast (teeth mold) is made from gypsum, a stone-like product (stage 2). For mixing of investment (mixture of siladent powder and water) three different pH value of water was used (pH-3, pH-7, pH-10) with different P/W ratios by weight (100/12, 100/15, 100/18). Then 3D scanning of teeth mold, which is called plaster cast of a patient was digitally scanned with an optical scanner and the captured surface data were imported to 3-D software, which were then used to preprocess the data and design each component of partial denture framework with reference to the scanned digital model. After this operation, the digital model of framework was created, and the data were

saved as standard triangulation language (STL) format for producing a pattern of partial denture with FDM (stage 3–5). Therefore, tree formation of wax pattern was done prior to filling the investment in the crucible. After this investment was poured in crucible and around the pattern tree (stage 6–7). Investment was baked in Muffle furnace for 1.5 h at 900°C (stage 8–9). The induction casting setup was used for casting of denture with Ni-Cr based alloy (stage 10–11). The final casting of denture fitted on the mold is available after solidification (stage 12).

Optimization of Input Parameters

Based upon Table 1, AM route has been followed for preparation of PD (see Table 4). Based upon Table 4, Fig. 6 shows S/N ratio plot for dimensional accuracy (by using minimum the better type case).

As observed from Fig. 6, best settings have been observed for specimen casted with P/W ratio of 100/12, pH-7 value of water with 62% of Ni in Ni-Cr alloy. Further based upon Table 4 and Fig. 6, Table 5 shows percentage contribution of input parameters for Δd via AM route.

As observed from Table 5, for controlling the dimensional accuracy, P/W ratio is the most significant factor. This observation is similar to the case of CM (see Table 3). However the Ni% is least contributing for dimensional accuracy in AM route. This may be because of the high temperature requirement in draining out investment material in AM route. It should be noted that in CM route the de-waxing temperature is in the range of 100–150°C, whereas in AM route this varies from 1050 to 1100°C. The results are in line with the observations made by other investigators (Singh *et al.*, 2017).

Conclusions

In this article detailed procedure for preparation of Ni-Cr based PD by CM and AM technique has been outlined. Two case studies have been presented for CM and AM route for preparation of PD.

- It has been observed that dimensional accuracy required in preparation of PD by both AM and CM lies in acceptable range (as per commercial practice) and best settings for both cases have common with P/W ratio of 100/12, pH-7 value of water. Since CM technique undergoes generous number of steps, hence the procedure takes a long time to finish, whereas, AM technique is more efficient.
- For preparation of PD by CM and AM, P/W ratio is the most significant parameter with percentage contribution of 52.45% and 49.5% respectively. Since the AM route requires high temperature (1050–1100°C) for removal of investment material, the second most significant parameter is pH value with contribution of 41.68%, whereas in CM route the second most significant parameter for dimensional accuracy is Ni%.

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Particulate Composite Protective Coating Using Conventional Melting Approach

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Introduction

The term protective coating or surface engineering means modifying or engineering the surface of material to increase protection against wear and corrosion properties along with other properties. Among the processes employed for protective coating, incorporation of ceramic particles to produce composite protective coating or layer by melting is gaining popularity (Maleque *et al.*, 2017). High energy laser cladding (Zhou *et al.*, 2016; Yang *et al.*, 2016; Qunshuang *et al.*, 2017) and electron beam melting technique (Peng *et al.*, 2011; Lienert *et al.*, 1993) are commonly used for processing such composite protective coating which are reported to significantly increase wear and corrosion resistance of engineering component surfaces. Electron beam welding (EBW) for composite surface coating was developed starting in the late of 1950s. In that method, the electrons are accelerated and kinetic energy is used as the heat input for melting of the substrate material. A negatively-charged cathode filament is heated up to its thermionic emission temperature where electrons are generated. The substrate surface is bombarded with the electron beam at 70% of speed of light. The heat comes from approximately 95% of the electron's kinetic energy. The diameters of the electron beam are between 0.3 and 0.8 mm. Due to its high power density, one of the superior abilities of EBW is the capability of deep melting of the surface layer (Sun and Karppi, 1996).

The composite protective coating of materials can be performed by melting process where high energy source is applied to melt the surface of the substrate together with the reinforcing particles (Sathiya *et al.*, 2009; Lailatul and Maleque, 2017). This resulted in a strong metallurgical bonding upon solidification between the reinforcing particles and the substrate material. The melting process is commonly utilized for ceramic particles for reinforcement due to their superior hardness and thermal stability. In other work, the composite coated layer obtained through laser cladding technique showed low porosity, with homogenous microstructure with proper control of thickness by manipulating the process parameters (Fernández *et al.*, 2014).

The reinforcement can be fed onto the surface of the substrate material using either powder blown, wire feed or pre-place powder surfacing method (Fernández *et al.*, 2014; Folkes, 1994). Powder injection or blown method applied a stream of gas which are usually argon, CO₂ or oxygen to carry the reinforcing powders. The reinforcing powders are delivered using coaxial or lateral feed method. The flow of the carrier gas is maintained properly to have uniform distribution of reinforcement and good quality of melt pool layer. The use of higher gas flow rate in this method can easily decrease the melting temperature of the substrate and hence, less dissolution of particles. On the other hand, the flowability of the reinforcing ceramic particles is reduced with the use of lower gas flow rate and hence, fewer amounts of particles reach the melting area.

Wire feed method is an approach where composite protective coating of metallic materials is performed using filler material. The spool containing filler material is directly fed through a nozzle and onto the substrate. To have a good quality of melt structure, the wire feed used to carry the reinforced particulate material should be free from defects which can affect the flow consistency. When the wire used is bent, the filler material could have deviated from reaching the center of the melt pool. According to Kou (2003), this technique does not waste any filler material compared to the powder injection method. However, some extent of reinforced particles may not reach the center of the melt pool at a certain heat input because of the use of slower wire feed rate. The quality of the melt structure is strongly affected by the wire feed rate. Among the composite surface coating methods, particulate preplacement method is the cheapest, and a simple, flexible way of composite protective coating of metallic alloys with good metallurgical bonding and decent melt pool structure (Maleque *et al.*, 2018). A binder solution such as polyvinyl acetate (PVA) is used to preplace the particulate on the substrate material so that the particulate is not blown away by the shielding gases during the melting process. However, the excessive use of binder could lead to porosity that comes from escaped gas during solidification. The particulate preplacement process is followed by the application of high heat energy to melt the surface layer. Upon solidification, the melted reinforced particle together with the melted surface of the substrate can bond and develop a new microstructure with modified physical, mechanical and tribological properties (Adeleke and Maleque, 2014).

Overall, all the composite protective surfacing techniques mentioned earlier such as powder (particulate) blown or injection method, wire feed method and pre-place particulate method have their own mechanism to supply the reinforcing particulate material onto the surface of the substrate during the melting process. Each of the method has its own sensitive parameters that affect the end quality of the produced melt structure. For instance, powder blown technique heavily relies on the gas flow rate for consistency of the feeding of reinforcing particulates. Generally, pre-place particulate method is beneficial compared to the others because it is the cheapest, simple and flexible way with the ability to produce a good melt microstructure.

However, particulate protective coatings using those techniques have a limited application because of the expensive establishment and precision control of the system. An alternative and novel method was developed using conventional melting (surfacing) technique by TIG torch melting for composite protective coating which is suitable for high temperature application as

well. Requirement for high temperature application includes (Idriss *et al.*, 2017): materials should exhibit high hardness combined with lower wear rate, controlled coefficient of friction, higher level of durability and life-time. Therefore, composite protective surfacing with particulate ceramics for composite protective surface is vital. The main aim of this work is to provide an overview on the composite protective coating of engineering materials by melting technique followed by the evaluation of the influence of TIG parameters on the performance characteristics such as microstructural features, surface integrity and microhardness.

Composite Protective Coating by Melting

Composite protective coating guarantees wear resistance protection while the substrate material maintains the mechanical properties and the component geometry (Maleque *et al.*, 2017). This type of surface is formed by incorporating ceramic particles (such as TiC, SiC, WC etc.) into a molten thin and near surface region of substrate using conventional TIG torch welding technique in order to enhance the wear resistance properties and other mechanical properties which in turn prolong the life of the component or structure. Composite protective coating consists of fusion zone (FZ), heat affected zone (HAZ) and substrate or parent metal (PM) zone as shown in Fig. 1.

The benefits of TIG torch technique are:

- Cheaper in establishment,
- Flexible and simple technique,
- Formed hard layer into a molten thin and near surface region of substrates,
- Good metallurgical bonding between hard particles and substrate material,
- Less processing time,
- Provides good control of heat input.

The features of TIG torch melting compared to the other composite protective coating techniques such as electron beam welding (EBW), laser cladding and thermal spraying are shown in Table 1 in a matrix form.

Materials and Methods

Materials

AISI 4340 low alloy steel plate with the dimension of 100 mm × 40 mm × 20 mm was selected as the parent material which was ground using silicon emery paper and thoroughly cleaned in acetone to remove all the contaminants in a form of oxide layer or grease. The chemical composition of the substrate material is shown in Table 2. Titanium carbide (TiC) particulate (99.8% purity) supplied by Sigma Aldrich was used for composite protective coating. The average size of the titanium carbide particles is 10 µm.

The TiC particulates weighed at the proportion of 1.0 mg/mm² was mixed with organic binder (PVA) and preplaced on the dry substrate surface. The pre-coated substrates were then further cured in an oven to remove any moisture before applying composite protective coating under TIG torch melting technique.

Particulate Composite Protective Coating

In order to develop composite protective coating, surface melting was performed using TIG torch welding. A throated tungsten electrode (2.4 mm Ø) was used to generate a stable arc for the melting at a fixed height of 2 mm from the substrate. The energy density of the TIG torch was controlled by the supply of fixed current (80 A) and four different voltage such as 30 V, 35 V, 45 V and 55 V which corresponds to four different heat inputs of 1152 J/mm, 1344 J/mm, 1728 J/mm and 2112 J/mm respectively with the TiC particle feed rate of 1 mg/mm² to produce single track along the width of the substrate. During the melting process, a stream of pure argon gas (gas flow rate of 20 L/min) was supplied to avoid excessive oxidation of the molten pool. Fig. 2 shows the schematic diagram of TIG torch set-up for composite protective coating development.

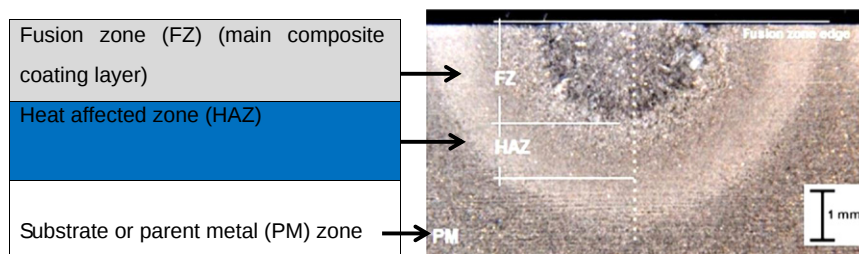


Fig. 1 Composite protective coating layer consists of fusion zone, HAZ and substrate zone.

Table 1 TIG torch protective surface coating compared to the other surface coating techniques

Parameters	Tungsten inert gas welding	Electron beam welding	Laser cladding	Thermal spraying
Working principle	Heat is generated from an electric arc produced between the tungsten electrode and the metal substrate The inert gas used is usually argon and its function is to control the weld environment and thus preventing contamination and oxidation	A beam of electrons is induced and accelerated to have a high amount of kinetic energy The beam of electrons collides with the substrate material and their kinetic energy is transformed into heat, which lead to melting	Laser cladding is a modern technology whereby another material is fused onto the surface of a substrate The laser beam is aimed at the substrate with a selected spot size. The powder coating material is carried by an inert gas through a powder nozzle into the melt pool	Coating material is heated and deposited as individual particles onto the new surface material The sprayed reinforced particles latch onto the substrate surface, they solidify and build up into laminar structure forming the new coating layers
Merits	No flux required due to the use of inert gas shielding, hence, there is no slag or inclusion High surface quality Easy to operate Low installation and maintenance cost Wide range of materials can be used Small flames or sparks leads to less amount of distortion	Perform in vacuum and hence, there is no gas contamination High surface quality even on thicker materials Stable and repeatable process Superior controlled process leads to less distortion and shrinkage	Highly focused heat source, hence, cladding can be placed precisely Full metallurgical bonding with little void and porosity Highly consistence Wide range of materials High energy efficiency	Highest deposition rates up to 15 kg/h Wide range of coating materials Easy to operate Require low input power Can be used on thermally sensitive substrate such as electronic components since less heat is applied on substrate
Demerits	Low deposition rate Small amount of heat sources and hence not suitable for thicker material Slow process	High installation cost due to vacuum set up Size restricted depends on vacuum chamber X-rays generated during the process	Relatively high cost Highly sensitive process Might produce poor quality weld due to random disturbance in the system	Can only be applied on conductive material in certain wire form Large fumes and dust formed, hence there is health and safety issues Higher porosity and oxide levels compared to other methods

Table 2 Composition of the AISI 4340 steel

Element	C	Si	Mn	S	P	Cr	Ni	Mo	Fe
Composition (Wt%)	0.42	0.16	0.65	0.04	0.035	0.75	1.76	0.24	Bal.

Note: Idriss, A.N.M., Maleque, M.A., Yaacob, I.I., *et al.*, 2016. Microstructural aspects of wear behavior of TiC coated low alloy steel. Materials Science and Technology 32 (4), 303–307. (Special Issue).

Coating Characterization

After particulate composite protective coating development, specimens for hardness measurement and morphological characterization were cut along the transverse section of the re-solidified tracks. The cross section specimens were prepared using standard metallographic procedure. The specimen surfaces were then etched with a solution of 2%. The surface topography of the melt pool layers were characterized by scanning electron microscope. The microhardness at a depth of 200 μm from the top surface of the coating was measured using Wilson Wolpert Vickers microhardness tester with a 500-gf load and 10-s dwelling time. The test results were calculated based on the average of three indentations from each specimen.

Results and Discussion

Surface Topography

The surface topography in Fig. 3 shows different formation of rippling marks on the surface of the single melt layers from the energy input of 1152 J/mm to 2112 J/mm. The topography surface in general showed completely free from any crack on the

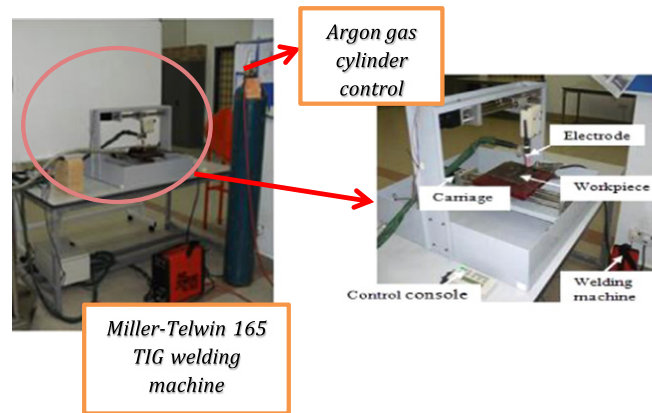


Fig. 2 TIG Torch set-up for composite protective coating.

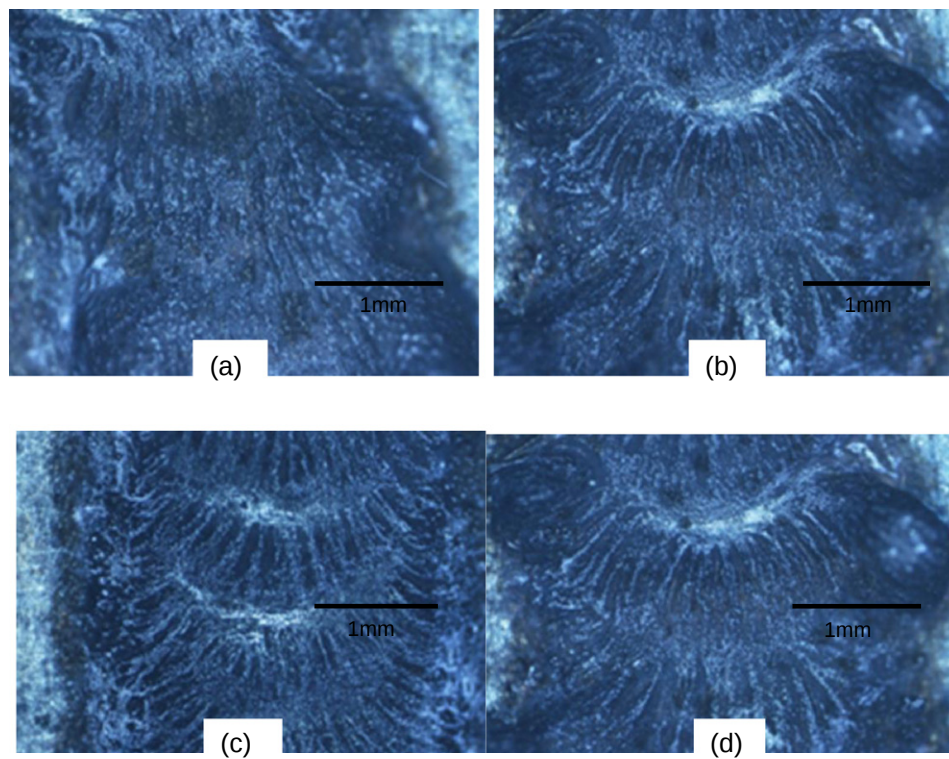


Fig. 3 Effect of energy input on surface topography of TiC particulate protective layer at: (a) 1152 J/mm, (b) 1344 J/mm, (c) 1728 J/mm, (d) 2112 J/mm. TiC particle feed rate, 1 mg/mm²; working distance, 1 mm; and gas flow rate, 20 lit/min.

surface. The protective coating layer resulted in prominent rippling marks that are perpendicular and along the direction of the TIG torch moving path. However, the single layer that is melted at the lowest heat input of 1152 J/mm shown in [Fig. 3\(a\)](#) does not show obvious ripples as observed in for those with higher energy input. The input energy of 1152 J/mm solidified at shortest period of time preventing from enough convection force to turbulence the melt and this might have contributed to the poor rippling marks in both directions which are perpendicular and parallel to the TIG travelling path.

The higher heat input showed almost evenly distributed and consistent rippling marks formation along and perpendicular to TIG travelling direction indicating that most of the input energy contributed to form less viscous melt layer associated with longer solidification time. Rippling marks were also observed by other researchers in the laser and TIG melting technique caused by freezing of the fluid melt ([Mridha et al., 2012](#); [Maleque et al., 2013](#)).

Microstructure

Microstructure of TiC particulate protective coating on low alloy steel substrate at different heat input energy is shown in [Fig. 4](#). The protective layer showed hemispherical in shape due to the Gaussian energy distribution that is high in arc density in the

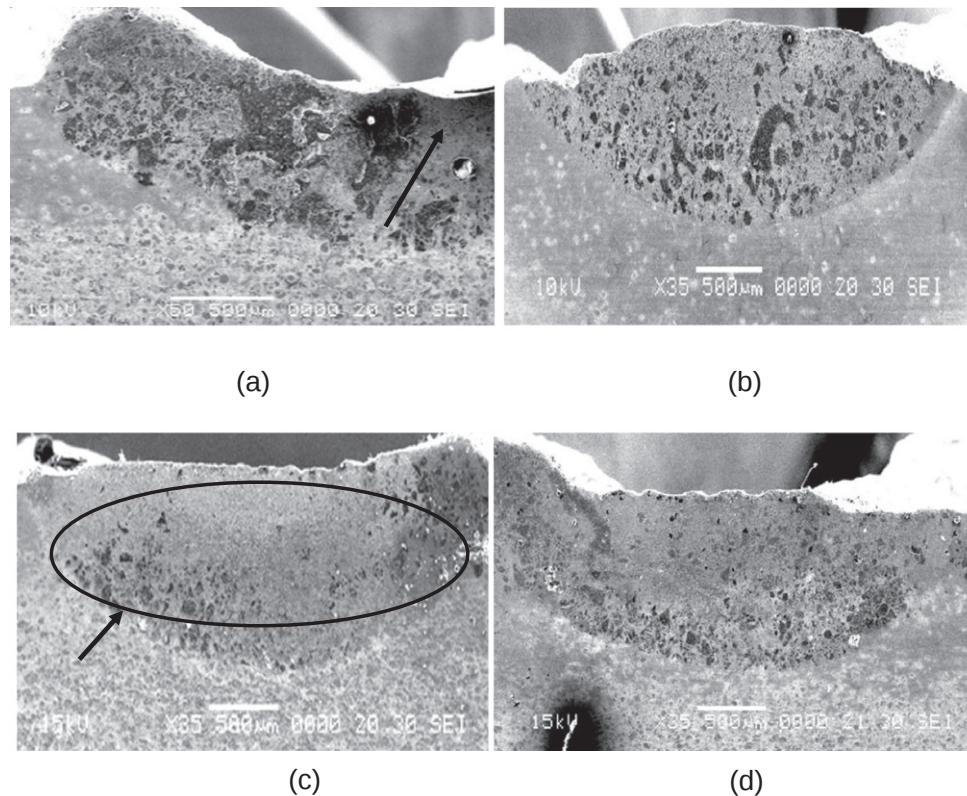


Fig. 4 Microstructure of the protective coating layer at different heat input energy: (a) 1152 J/mm, (b) 1344 J/mm, (c) 1728 J/mm and (d) 2112 J/mm. TiC particle feed rate, 1 mg/mm²; working distance, 1 mm; and gas flow rate, 20 lit/min.

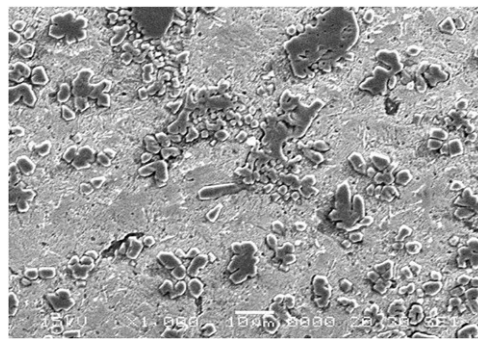


Fig. 5 Flower and globular type of TiC particulate composite protective surface at heat input of 1344 J/mm.

middle of the melt and steadily decreases towards both left and right edges. The lower energy input (1152 J/mm) exhibited less melting pool thus allowing for more TiC particulates to remain un-dissolved particularly at the edge of the melted layer.

The existence of very small area of rich TiC re-precipitated region in the middle of melt in **Fig. 4(a)** suggested that the energy fused just below the arc tip may have generated melting temperature of TiC which is slightly above 3230°C thus sufficiently melting small amount of these particulates. The heat input at 1344 J/mm as in **Fig. 4(b)** exhibited improvement in TiC dissolution where agglomeration is likely to be less than lower heat input. However this energy enlarges the rich TiC re-precipitated region that is located near the arc source together with providing homogeneous distribution of un-dissolved and partially dissolved TiC particulates embedded in the melt layer. Increasing the melting efficiency by increasing heat input to 1728 J/mm and 2112 J/mm (as shown in **Fig. 4(c)** and **(d)**) resulted in dominance of TiC particulates dissolution together with increased melt pool geometry. This is an apparent sign that high in substrate dilution had occurred to help surging the particles along melt waves in the presence of Marangonian convection force.

The cross sectional micrograph of the protective coating under the heat input of 1344 J/mm showed re-precipitation of TiC in globular and flower type of microstructures as shown in **Fig. 5**. The formation of this type of microstructure was also found by other researchers (*Idriss et al., 2017*). Although the energy is considered to be high at the energy input of 1728 J/mm and 2112 J/mm, lower

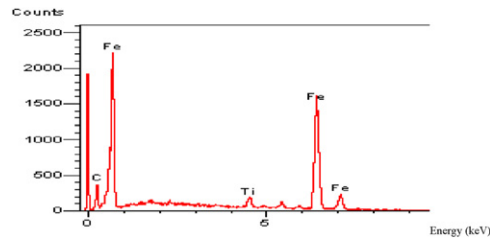


Fig. 6 EDX result of the re-precipitated TiC iron the protective coating surface.

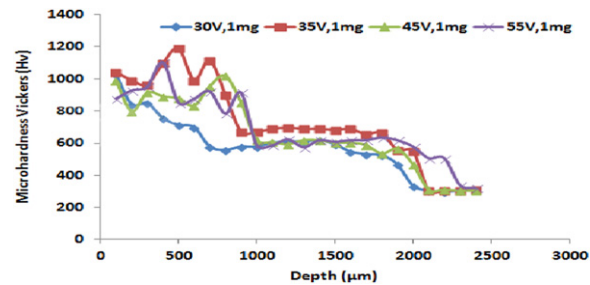


Fig. 7 Microhardness profile of particulate composite protective coating surface of low alloy steel at different heat input energy. TiC particle feed rate, 1 mg/mm²; working distance, 1 mm; and gas flow rate, 20 lit/min.

in TiC agglomeration due to the poor melting efficiency near the substrate remained than those melted with the energy of 1344 J/mm having more in agglomerations. This melt is less viscous on the upper region near the arc source where the energy within this area is sufficient to dissolve the TiC particulates, thus, allows for the re-precipitation of those globular and flower type of TiC microstructures in the presence of longer solidification time.

The EDX results on the re-precipitated TiC microstructure is shown in Fig. 6. The elements of titanium and carbon in Fig. 6 are higher exhibited a little amount of titanium that is observed in the low temperature matrix solution within the re-solidified melt layer at the energy of 1344 J/mm. This is clear evidence that dissolution of TiC happened in the melt layer followed by dissociation of elements into titanium and carbon and the remaining titanium that has not formed TiC remained as solid solution in the matrix.

Microhardness

The microhardness profile of the 1 mg/mm² preplaced particle content on the surface of low alloy steel at different heat input ranging from 1152 J/mm (30 V) to 2112 J/mm (55 V) is presented in Fig. 7. The incorporation of TiC particulates for composite coating layer in general showed improvement in microhardness properties up to 4 times higher than the substrate material. The heat affected zone profile corresponds to the microhardness value ranging from 500 Hv to almost 700 Hv while the substrate at an average of 300 Hv. Melting at different heat inputs showed variation of microhardness values at different depth level which is related to the TiC population, type and amount of substrate dilution from the substrate.

At 30 V power which corresponds to the heat input of 1152 J/mm exhibited gradual decrement from 1000 Hv at the depth of 500 μm to 700 Hv at lower depth level of 1000 μm. This lower energy input showed the lowest microhardness profile on coating layer compared to other heat input. The main reason is the incomplete melting due to the thicker solution that solidify in the presence of defects and poor adhesion or metallurgical bonding of TiC with the lower temperature low alloy steel matrix. Wang *et al.* (2006) also explained that incomplete melting of preplaced particles and cracks are the reason for the reduction of microhardness values. The microhardness trend increasing the depth level acts reversely for 35 V power (energy input of 1344 J/mm) compared to 30 V power (1152 J/mm). Instead of hardness decrement with the increasing depth level, the value is seen to be increased to the lower depth of the melt pool. The microhardness value was more than 1000 Hv at the depth of 400, 500 and 700 μm when measured from the top surface. The main reason of such trend and higher in the hardness value at 35 V power (1344 J/mm) is due to the homogeneous distribution of TiC microstructure consisting of re-precipitated TiC and partial un-dissolved particulates.

The protective coating layer that is produced using the energy input of 1728 J/mm (45 V power) and 2112 J/mm (55 V power) generally showed reduction trend in microhardness along the non-steep hardness profile of the track compared to the lower energy input. The dilution melting of the substrate at 1728 J/mm and 2112 J/mm are coupled with higher dissolution of TiC microstructure that are re-precipitated over larger volume of matrix are the reason for microhardness decrement in the layer. Since TiC has the hardness values at 3000 Hv, incorporation of this particulate promotes the increasing in hardness compared to the substrate material. However, at the depth of 400 μm, the 2112 J/mm heat energy produces microhardness value at 1102 Hv. The 1728 J/mm heat input in TIG melting on the protective coating of alloy steel exhibited the microhardness value at lowest with the value of 800 Hv at 200 μm depth level.

Conclusions

The particulate composite protective coating has been successfully developed on the surface of low alloy steel substrate using conventional TIG torch melting approach. All melted layers exhibited crack free surface together with the cross sectional area which had proven that TiC particulates protective coating via TIG melting endowed superior in adherence compatibility with the AISI 4340 low alloy steel substrate.

In general, rippling marks is an evidence that high dilution of substrate and dissolution of TiC particulates along with more TiC re-precipitation took place beneath the melt surface layer while the dull and undulated ones are indications that undissolved TiC particulates dominated in the embedment of the melt pool. All re-solidified protective coating layer have shown semi hemispherical in shape viewed from the cross sectional side caused by the Gaussian energy distribution from the TIG arc source that depicts greater in arc energy intensity in the middle and gradually depletes as it moves towards the edges. The higher heat input melts more TiC particulates that endowed near to the arc region enriched with re-precipitated TiC that was primarily observed to consist of flower and globular type of microstructures within the matrix. The microstructure contains elements of Ti and C where the evidence can be seen from the EDX result while the matrix showed more in Fe content than the Ti which has been caused by the dissociation of TiC particulates upon melting.

The incorporation of TiC particulates on the surface of the low alloy steel substrate increases hardness properties of the coating layer up to 4 times higher than the substrate that has microhardness value at about 300 Hv. This revealed the potential application of TIG torch melting technique for the composite coatings with the formation of hard composite coating layer in metallic materials especially for high temperature applications.

Acknowledgment

The authors thank the Research Management Center (RMC) of International Islamic University Malaysia for funding this project under Research Matching Grant RMGS 12-007-0020.

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Preparation of Partial Denture With Nano HAp-PLA Composite Under Cryogenic Grinding Environment Using 3D Printing

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Introduction

Today polymers are one of the most important materials in daily life because of their tremendous applications. Some of the applications of polymers are in coating, packaging materials, fabrication of composites, biomedical devices, and electronic devices etc. (Singh *et al.*, 2017, 2018a,b). In last two decades, many researchers are trying to use polymers in the field of biomedical applications. The selection of thermoplastics in biomedical applications is mainly based upon its biocompatibility (Gibson *et al.*, 2015; Gress and Kalafsky, 2015). Biocompatibility term is used to describe the suitability of a polymer for exposure to the body or body fluids. Most of the polymers are commercially sold in the form of granules. For fabricating or manufacturing of biomedical devices, scaffolds, functional prototypes some bioactive and biocompatible materials are required be added (DOE, 2015).

HAp is highly in demand as biocompatible materials for the regeneration and reconstruction of bone tissues (Boisvert and Adelstein, 2015). It has all the characteristic features of biocompatible materials (metals, polymers and composites), such as osteo-conductive, non-immunogenic, bioactive, non-toxic and non-inflammatory properties (Chhaya *et al.*, 2015; Xu *et al.*, 2017). In human body, HAp represents 65%–75% in weight of bone and 88%–92% in weight of enamel. Nano-HAp has a strong capacity to bond with proteins (Huang and Leu, 2014). It has significant effects on dental/dental enamel in terms of regeneration and preventive dentistry and shows good result on the teeth sensitivity (Lyons, 2014). Nano-HAp is used to improve/accelerate the existing/present dental materials as an additive material in the regeneration field. It has been mostly used in maxillofacial and oral surgery because of its some unique properties (such as; non-toxicity, bone reconstruction, strong chemical bond to bone) (Melchels *et al.*, 2012). Nano-HAp is also used as fillers because it repair small cracks and holes present on teeth surface. Calcium HAp is a manufactured material indistinguishable to the substance in teeth and bones (Tumbleston *et al.*, 2015; Venkatesan *et al.*, 2015). It is HAp that gives accelerated growth for damaged bones (Wei and Ma, 2004; Wohlers, 2014). Nano-HAp is a characteristic mineral type of calcium apatite that synthetically looks like the perplexing framework of bone. The nano-HAp is a constituent of bone (around 70%) and is utilized to expand the auxiliary unbending nature of platforms, guaranteeing their appropriateness for bone tissue development methodology (Wu *et al.*, 2014).

The nano-HAp is exceedingly osteo-conductive and displays bone bonding limit, offers a suitable layout structure for bone arrangement, and advances cell working permitting the outflow of bone framing osteo-genic markers (LeGeros, 2002; Venkatesan *et al.*, 2015). The nano-HAp is frequently functionalized with different polymers, for example, PLA, polyetheretherketone (PEEK) and chitosan (CS), to give the mechanical properties required to an embed in the reconstruction and regeneration of bone, tissue (Wei and Ma, 2004; Mangano *et al.*, 2006; Piccirillo *et al.*, 2013).

HAp has attracted more attention in biomedical fields due to its exceptional features such as biocompatibility, bioactivity, osteo-conductivity and osteo-inductivity. HAp has similar structural and chemical resemblance to teeth and bone due to its key inorganic phosphate (Orlovskii *et al.*, 2002; Huang *et al.*, 2011). Bioactivity and biodegradability of HAp generally depend on the Ca/P ratio, crystallinity and phase purity. The appropriate Ca/P ratio for preparation of HAp is 1.67. There are different methods for preparation of nano-HAp including wet chemical, hydrothermal, solid-state reaction, sol-gel and microwave processes. Wet chemical approach possesses several advantages over the other preparation techniques that include low processing temperature, cost-effectiveness, simplicity and production of the highly pure products. Furthermore, this method is able to generate nano-crystalline powders, bulk amorphous nano-particles and thin films. Table 1 shows the chemical composition, and physical properties of PLA and nano HAp used in present study.

The literature review reveals that some studies have been reported on use of PLA, HAp in biomedical applications, but hitherto very less has been reported on use of cryogenic environment while crushing of matrix and reinforcement material (to get uniform dispersion of nano HAp particles in PLA matrix) for preparing partial dentures. In this study detailed procedure for preparation of nano HAp reinforced PLA matrix based partial denture has been outlined by using 3D printing. For experimental analysis, four different proportions of PLA and nano HAp blend have been selected for preparation of biocompatible feedstock filament by using commercial TSE. After selection of best-feedstock filament, based upon MFI, thermal analysis and tensile strength, FDM based 3D printer has been used for printing of partial dentures.

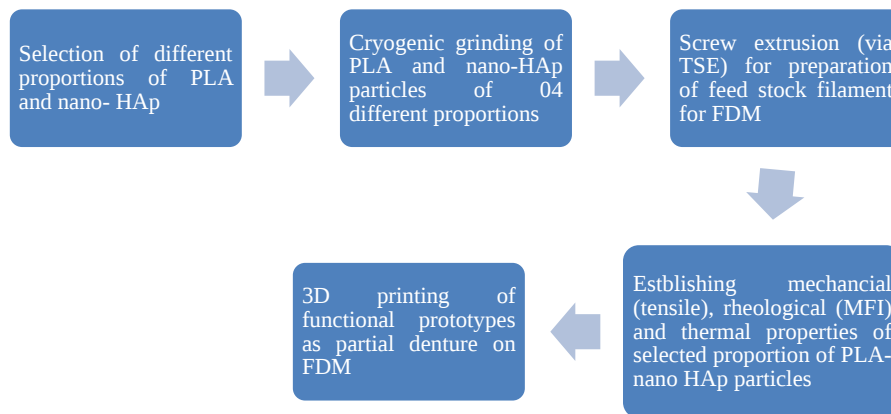
Materials and Methods

Fig. 1 shows process chart for development of partial denture from nano-HAp composite polymer prepared with cryogenic grinding mill.

Table 1 Chemical composition and physical properties of PLA and nano HAp

PLA (Matrix material)		Nano-HAp (Reinforcement)	
Chemical formula	(C ₃ H ₄ O ₂) _n	Chemical formula	Ca ₅ (PO ₄) ₃ (OH)
Density	1.210–1.430 g/cm ³	Density	2–6 g/cm ³
Young's modulus	3.5GPa	Young's Modulus	60–100 GPa
Glass transition temperature	60°C	Glass transition temperature	– 30°C
Melting temperature	162–178°C	Melting temperature	1100°C
Thermal conductivity	0.13 W/mK	Thermal conductivity	10–15 W/mK
Specific heat capacity	1800 J/kgK	Specific heat capacity	653 J/kgK
Applications	Extrusion, injection moulding, spinning for wide range of materials	Applications	Bone grafting, dental prosthetic and repair

Note: PLA procured from Natur-Tec India Pvt. Ltd. (Tamilnadu, India), HAp procured from Intelligent materials Pvt. Ltd. (Dera Bassi, India).

**Fig. 1** Flow chart for printing of partial dentures.

Polymers are commercially available in granules form. For reinforcement of biomedical polymers (granules) with biomedical ceramics (nano-HAp) both should be in powder form for proper mixing. Biocompatible polymers need to be grounded without losing their biomedical properties. For this reason the polymers blended with required reinforcements are grounded at cryogenic temperature (– 50°C to – 196°C). Liquid nitrogen is most commonly used liquid gas in cryogenic grinder due to easy availability. For development of partial denture by 3D printer (open source FDM) initially biocompatible feedstock filaments needs to be prepared with the help of extrusion process. Further in this study for high strength and precise diameter of the feedstock filaments, TSE has been used.

In this article, nano-HAp has been reinforced with biocompatible and biodegradable PLA. For better reinforcement, PLA granules were cryogenically grounded by using commercial setup (Make: RETSCH Cryo-mill, Germany). Initially the PLA granules were processed with Ø25 mm stainless steel ball in 50 ml capacity stainless steel grinding jar for 10 min (5 min precooling and 5 min during grinding) at – 196°C. After that in second stage for less average diameter of PLA granules Ø12 mm stainless steel ball (4 stainless steel ball) in 50 ml capacity stainless steel grinding jar for 10 min (5 min precooling and 5 min during grinding) at – 196°C were used. After grinding of PLA (which was commercially available in granule form), final blend with nano-HAp of different proportion was prepared. Following 04 different proportions/compositions were further investigated: (i) 100% PLA, (ii) 96% PLA-4% HAp, (iii) 94% PLA-6% HAp, (iv) 92% PLA-8% HAp. The blend is further used to fabricate the feedstock filament using TSE at optimized settings. After that for selection of best feedstock filament rheological, tensile and thermal analysis are performed on MFI tester, UTT and DSC respectively. Finally, partial denture of feedstock filament of PLA granules (cryogenically treated) and reinforced with nano-HAp are ready to be used in open source FDM.

Cryogenic Grinding of Biocompatible Polymer (PLA)

Biocompatible grades of PLA are commercially available in granules/rod/sheet/feed stock filament form. **Fig. 2** shows 3D view of Cryo-Mill setup which was attached with liquid nitrogen cylinder. **Fig. 3** shows that 3D view of stainless steel cryogenic grinding jar with capacity of 50 ml. In cryogenic grinding following steps are being followed:

- (1) Charging of vibrating jar (usually up to 1/3rd capacity by volume) and grinding balls as per requirement (see **Table 2**),
- (2) Pre-cooling with flow of liquid nitrogen in vibrating chamber (at frequency of 5 Hz),
- (3) Cryogenic grinding (at frequency of 25–30 Hz) at – 196°C.

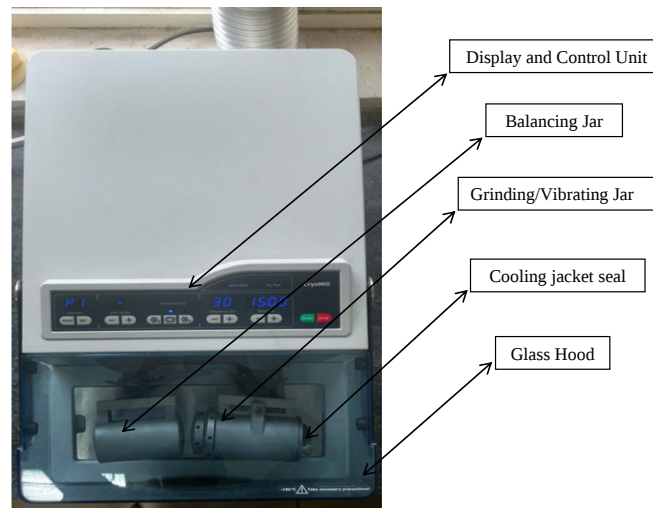


Fig. 2 3D view of Cryo-Mill setup.



Fig. 3 Stainless steel cryo-mill grinding jar (50 ml).

Table 2 Working guidelines for different size of grinding jar

Grinding jar nominal volume (ml)	Sample quantity (ml)	Recommended ball filling (unit)					
		Max. feed size (mm)	Ø 10 mm	Ø 12 mm	Ø 15 mm	Ø 20 mm	Ø 25 mm
25.0	4.0–10.0	6	5–6	2–4	1–2	–	–
35.0	6.0–15.0	6	6–9	4–6	2–3	1	–
50.0	8.0–20.0	8	12–14	6–8	3–4	1	1

Note: Website visited: <https://www.retsch.com>, Operation Manual Retsch® (retrieved on 05 September 2018).

Fig. 4 show the different size of grinding balls of stainless steel (Ø25, Ø20, Ø15 and Ø12) and zirconium (Ø 10). In this study Ø15 stainless steel grinding balls has been used.

Results and Discussion

Fabrication of Nano HAp-PLA Composite Feedstock Filament

For short listing of best proportion of PLA-nano HAp, initially four proportions were selected and subjected to MFI analysis as per the ASTM standard (D 1238-95) (see **Table 3**). All four proportion of PLA-nano HAp reinforced composite were fabricated on TSE, make: HAAKE Mini CTW, Germany. The fixed parametric settings of TSE were: barrel temperature 190°C, 140–150 rpm with 10 kg applied load. After this the composite material was put into the pre-heated barrel of MFI tester. The MFI values for all 04 proportions are also given in **Table 3**.



Fig. 4 Different size of grinding balls stainless steel (Ø 25, Ø 20, Ø 15 and Ø12) and zirconium (Ø 10).

Table 3 Composition of HAp-PLA composite and output result of MFI

S. No.	Compositions/Proportions (by weight) of PLA-nano HAp composite	MFI (g/10 min)
1	PLA 100%	14.83
2	96%PLA-4% nano-HAp	14.02
3	94% PLA-6% nano-HAp	13.05
4	92%PLA-8% nano-HAp	12.28

Table 4 Tensile properties with different proportions of PLA and nano HAp

S. No.	Compositions (PLA-Nano HAp)	Peak load (N)	Break load (N)	Peak elongation (mm)	Break elongation (mm)	Strength at peak (MPa)	Strength at break (MPa)
1	100%–0%	20.70	18.63	2.66	3.99	8.61	7.75
2	96%–4%	18.20	16.38	2.09	3.04	7.57	6.81
3	94%–6%	14.40	12.96	3.04	4.18	5.99	5.39
4	92%–8%	9.60	8.64	1.52	2.01	3.99	3.59

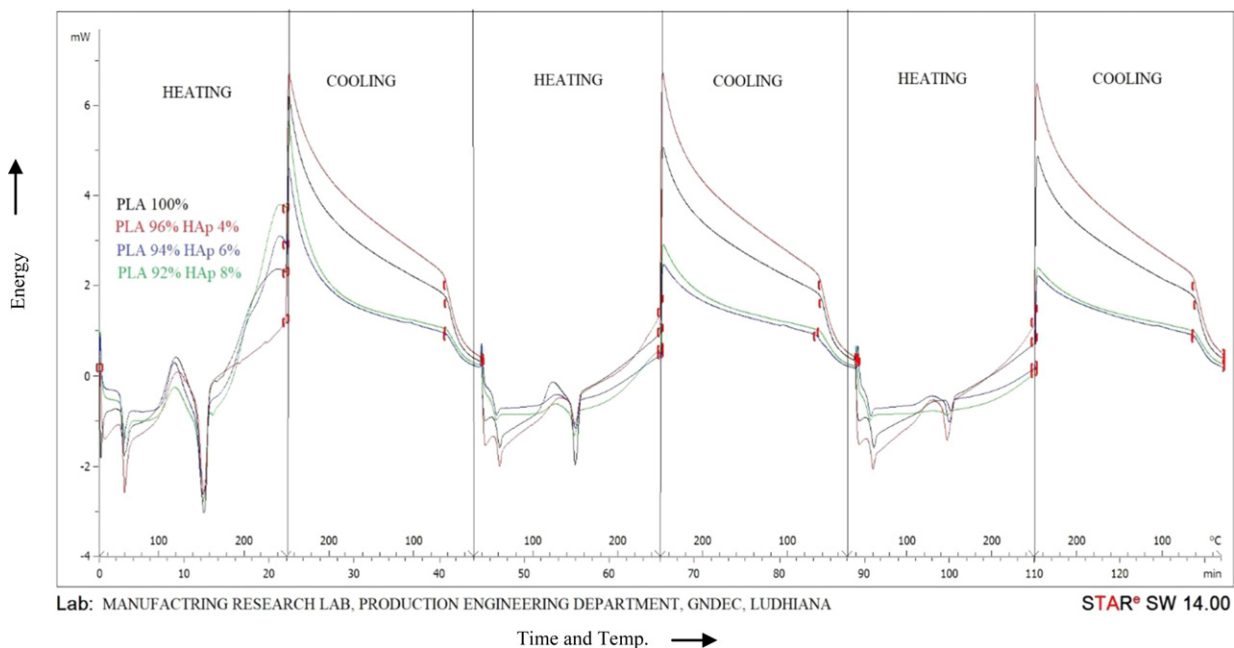
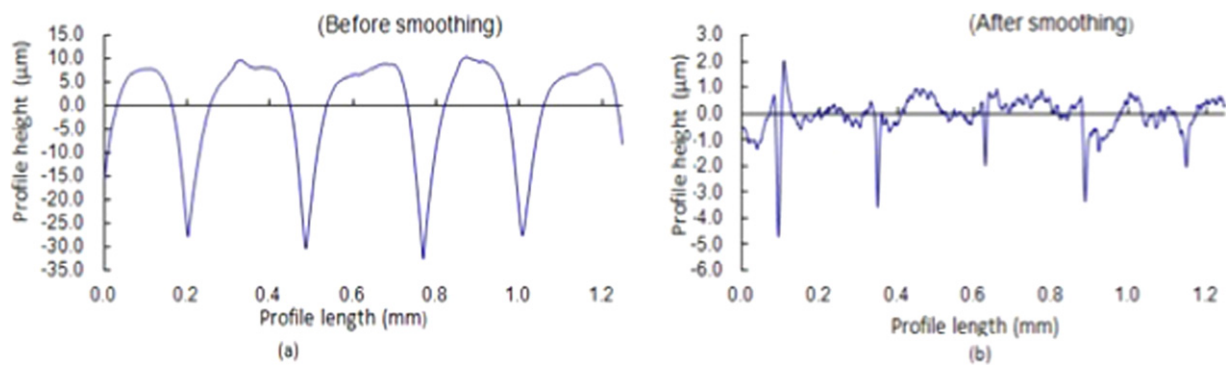


Fig. 5 Thermal analysis curve of PLA-nano HAp composite fee stock filaments.

Table 5 Output value of thermally analysis value of all four feedstock filaments

S. No.	Compositions (Micro PLA-Nano HAp)	1 st heating cycle (°C)		2 nd heating cycle (°C)		3 rd heating cycle (°C)	
		Glass transition temperature	Melting temperature	Glass transition temperature	Melting temperature	Glass transition temperature	Melting temperature
1	100%–0%	56.54	152.71	56.49	149.58	56.43	151.47
2	96%–4%	56.40	152.72	56.29	149.29	55.98	147.27
3	94%–6%	54.97	151.39	53.74	149.62	53.99	149.62
4	92%–8%	56.61	151.72	53.06	148.44	52.81	147.13

**Fig. 6** 3D printed polymeric partial denture.**Fig. 7** Surface roughness profiles of replicas (a) before smoothing (b) after smoothing for 20 s.

Tensile Testing

In this part of experimentation, all four compositions of feedstock filaments were checked from strength point of view (see Table 4).

Based on Table 4, it has been ascertained that all four compositions are having good strength but PLA 96% – nano HAp 4% (see S.no. 2, Table 4) have been selected for further experimentation because it resulted into better mechanical properties than other compositions (see S.no. 3 and 4, Table 4). The mechanical properties for PLA 96% – nano HAp 4% are comparable to virgin PLA. Further as reported in literature nano-HAp reinforcement will result into better biocompatibility as compared to virgin PLA.

Thermal Analysis

In this experimentation part, all four compositions feedstock filament of PLA polymers reinforced with nano HAp ceramics were subjected to thermal analysis. Thermal analysis for all four compositions was carried out by METTLER TOLEDO, Model DSC3; Swiss make with STAR[®] (SW 14.00) software under N₂ gas environment. Fig. 5 and Table 5 show the thermal analysis curve and value of four different biocompatible feedstock filaments.

As observed from Table 5 and Fig. 5 no significant difference in glass transition temperature and melting temperature of all four feedstock filaments was observed. Finally, from all experiments (results of MFI, tensile testing and thermal analysis on DSC) it was

ascertained that for fabrication of feedstock filaments, best materials (PLA polymer granules reinforced with nano HAp) proportions/compositions was selected as 96% PLA – 4% nano HAp (by weight percentage).

The prepared feedstock filaments were used on open source FDM for fabrication of partial denture. For fabrication of partial denture at first stage partial denture CAD file was generated and stored in STL format. Fig. 6 shows that sample of 3D printed partial denture.

The 3D printed partial dentures were observed with micro surface defects (like staircase effect). For minimizing these defects, acetone vapor bath smoothing process was applied on fabricated partial dentures. Acetone was chosen for the smoothing process due to its low cost, low toxicity, and very high diffusion. The interaction of acetone and PLA does not result in a chemical change in the PLA material. Fig. 7 shows surface roughness profile before and after chemical vapor smoothing. The samples exposed for three cycles for 20 s each showed 80%–87% reduction in average surface roughness (Ra).

Conclusions

The present study provides a comprehensive frame work for preparation of partial dentures with biocompatible polymer matrix composite. In this study biocompatible PLA was blended with nano sized HAp particles at cryogenic environment. Based upon mechanical (tensile) and rheological (MFI) properties 96% PLA – 4% HAp was selected for fabrication of feedstock filament for FDM. Finally the surface finish of 3D printed partial denture was improved (from 80% to 87%) with chemical vapor smoothing process.

Acknowledgment

The authors are highly thankful to SERB under AISTDF Secretariat (File no. IMRC/AISTDF/R&D/P-10/2017, Dated 01–02–2018) for financial support.

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Processing of Ceramic Composite Coating via TIG Torch Welding Technique

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Introduction

Surfaces and near-surface regions of engineering components fulfill multiple functions and play important roles in controlling the service life of materials against environmental deterioration caused by wear and corrosion effects (Petrova and Suwattananoni, 2005). Wear is a surface-dependent property and wear resistance characteristics can be improved by appropriately tailoring surface microstructure and/or composition, without affecting the soft, tougher core parts of the bulk material. Until recently, surface modification of ferrous and nonferrous alloy substrates has been achieved using a localized heat treatment methods based on diffusion-controlled hardening processes including carburizing, nitriding, carbonitriding, or chromising. The heat treatment processes have been employed to induce phase transformation (bainite or martensite) in steels, which improve hardness and wear resistant performance characteristics but this occur by sacrificing other properties such as toughness and ductility. In addition, the achievable hard surface layer of 2–3 μm deposited by physical or chemical deposition from a vapor phase techniques (CVD or PVD) are unacceptably thin for modern engineering applications involving abrasive wear and high temperature. These coatings fail by delamination along the coating interface during impact loading (Maleque *et al.*, 2013; Khan, 2007). In this situation, formation of a hard composite layer by the use of surface melting and addition of ceramic particles onto the near-surface region of steel materials have the potential to modify surfaces while retaining the bulk properties of the steel. This process of surface engineering offers a wide range of possibilities to achieve desirable surface characteristics to meet up with the challenges of emerging technologies and applications (Mridha *et al.*, 1988).

Over the years, weld overlay techniques based on laser and electron beam are the possible power sources, which provide a high energy density required for addition of ceramic particles onto melted surfaces. The processes have been successfully used with some ferrous alloys but the components of these energy beams are very complex, expensive and as well require high precision system control and monitoring. Recent attempt has shown that tungsten inert gas (TIG) arc heat source has potential for producing surface composite coating with sufficient engineering thickness. In this treatment, ceramic powder of desirable composition and a thin surface layer of the substrate material are simultaneously melted under TIG torch arc and then allowed to rapidly solidify to generate dense composite coatings, which are metallurgically bonded to the substrate material. In contrast to other techniques, TIG surface welding process is simpler, cost effective, and flexible alternative (Munoz-Escalona *et al.*, 2016; Bello *et al.*, 2016; Ding *et al.*, 2007; Hojjatzadeh *et al.*, 2012).

The aim of the present review is to describe the overview and philosophy of ceramic-based composite coatings and coating technologies. The emergence of tungsten inert gas (TIG) arc welding process as a necessary alternative heat sources for depositing functional composite coatings has also been reviewed in this paper. Brief description of the art of TIG torch arc melting process are given, including the TIG torch coating scheme, fluid phenomenon and process parameter control. The microstructures of TIG modified composite coating system as well as their tribological performances are equally discussed.

Overview of Ceramic Composite Coating Technologies

Ceramic composite coatings generally include hard particles distributed in the near surface layer of metallic matrices. They have advantages in the perspective of properties such as high wear, corrosion resistance and ability to work at high temperature. Due to these potential benefits, varieties of composite coatings are being studied upon and are being developed for use in maintaining wear and controlling friction. Hard coatings have been successfully used particularly to enhance the life of some important alloy substrates (low alloy steel, stainless steel, titanium, magnesium, etc) for various industrial applications as found in automotive, aerospace, machinery and chemical industries (Wang and Zhang, 2014).

The practice of surface coating has a long history of generating metal matrix composite (MMC) coatings or films for providing high surface hardness combined with adequate resistance against wear, corrosion and high temperature effects. The history of hard coating development can be traced back to 1838 when Michael Faraday developed a deposition technique with the existence of vacuum established by Evangelista Torricelli in 1643. This famous technique started to gain attention until when cutting tools coated with TiN was produced in the 1960 in U.S. industry. Unlike developments in bulk materials, many of the advances in surface coating have been motivated by tribological needs of the modern technologies, and this will continue to play a major role in the future. Surface coating route do not only afford surfaces with good tribological properties, but also largely contribute to the conservation of scarce and expensive high-performance materials by concentrating the hardfacing treatment into a surface layer of the substrate (Stachowiak and Barchelor, 2005; Holmberg and Matthews, 1994).

The philosophy in the fabrication of ceramic-based surface composite coatings was due to the natural ability of ceramic phase materials to exhibit rather low friction and low wear under specific conditions such as high loading, speed and temperature. Hard

wear-resistant composite coatings are mostly generated from hard particles of metal carbides such as TiC, SiC, Cr₃C₂, SiC, B₄C, WC and VC (Erdemir, 2001; Holmberg and Matthews, 1994).

Over the years, variants of advanced hard surface coatings methods have been used for depositing a modified layer of both thin and thick coatings in the range of 0.001–20 mm on LAS substrate, depending on the application requirement. These coating techniques include vacuum deposition (e.g., physical vapor deposition (PVD), chemical vapor deposition, CVD), electro-deposition (e.g., electroless, electroplating etc), melting, and alloying deposition processes (e.g., hardfacing by welding, laser cladding, and thermal spraying). Of these techniques, only the surface modification of materials by process of melting and alloying, which uses concentrated heating sources, is suitable for depositing relatively thick functional hard coatings for tribological use. This serves as an advantage over CVD or PVD techniques that can only deposit thin hard coatings of 1–10 µm layer, which seems unsuitable for many applications involving impact-loading condition (Wang and Zhang, 2014; Shipway, 2006).

Ceramic Particles for Composite Coating Reinforcement

A variety of engineering materials can be modified by other expensive bulk processing using alloying, mixing, compositing, and organic coating to achieve adequate resistance to wear, corrosion and friction. Diffusion methods such as nitriding, carburizing, carbonitriding, nitrocarburizing, boriding and aluminizing are also used to harden materials but this process is time consuming and provides limited maximum hardness. However, structural ceramic particles appear to be ideal wear-resistant materials to offer a comprehensive protection against surface wear issues (Bachelor *et al.*, 2002).

Depending on the wear environment and other specific application, wide varieties of ceramic particles are available and can be selected as coating materials on steel substrates to mitigate tribological and corrosion behavior. The common inorganic ceramic compounds used as reinforcing particles in steel matrices include borides (TiB), carbides (TiC, WC, SiC, B₄C, VC), nitrides (TiN, BN), and oxides such as Al₂O₃ and ZrO₂ (Subramanian and Strafford, 1993; Du *et al.*, 2011). These reinforcements are formed mostly from transitional metals and elements of Groups IV and VI in the Periodic Table. Du *et al.* (2011) reported these coating materials have significantly contributed to the development of a series of wear-resistant coating systems. In selecting a coating material, the important material parameters to be considered in achieving better performance are the properties of the coating material, resistance of the coating material to the attack expected, chemical compatibility of the coating and substrate materials and the cost (Subramanian and Strafford, 1993).

Tungsten Inert Arc Torch Welding Technology

Like other surface coating techniques, the use of surface melting and alloying treatment has potential to tailor the intrinsic properties of steel surfaces, while retaining the bulk mechanical properties of the substrate. The application of this thermal hardening method is only possible using the concentrated heating source including high power laser beam, electron beam, thermal flame spray and electric metal arc radiations. Until recently, high energy density beam from laser is widely used to produce thick, high-density ceramic coatings on a range of engineering components to enhance surface properties with superior resistance to tribological phenomena like wear, friction or oxidation resistance (Khan, 2007). The process of laser surface treatment has, therefore, become an important method to produce ceramic hard coating on metallic materials for various tribological uses. However, the applications of laser beam coating techniques for processing such composite layers are limited by many factors such as costly manufacturing procedure, expensive initial investments and precision control of the system (Bello *et al.*, 2016; Hajbagheri *et al.*, 2008). Hence, an alternative heat sources must be considered to generate high energy density that would give more suitable and cost-effective composite coatings.

Recently, another surface coating technology route has emerged based on an electric arc produced by Tungsten Inert Gas (TIG) torch welding. TIG torch welding process originated in the USA in 1930s and was used mainly to facilitate the then rather difficult process of welding aluminum. The process was also known as gas tungsten arc welding (GTAW) and the tungsten arc heat source has shown potential to be used to melt surfaces in a controlled manner for generating composite coating on LAS materials. As shown in Fig. 1, TIG surface coating process utilizes electric arc energy density created between a non-consumable tungsten electrode and the substrate for processing composite layers, which are reported to increase hardness and wear resistance markedly. The adoption of this novel fabrication process is geared towards developing a more simplified and cost effective process of applying hard surface coatings on engineering components such as steels and some nonferrous (Idriss and Mridha, 2012; Hajbagheri *et al.*, 2008).

Fig. 2 further illustrates a typical surface coating scheme based on TIG surface alloying process. In this method, an electric torch with adequate energy density is scanned over a substrate material predeposited with alloy powder of a desirable composition (Fig. 2, section a). A thin surface layer of the substrate absorbs heat energy from traveling TIG torch arc (section b) and become melted at high treatment temperature of the system. As shown in Fig. 2 (sections c and d), rapid mixing of the liquid melt with the preplaced powder occur leading to the formation of the surface melt pool layer from the remelted materials, which sinks towards the substrate by a convective flow to a depth depending on the TIG heat input. Thus, the formation of melt pool begins at the substrate surface through which ceramic particles are introduced to produce composite layer. The occurrence of the intensive mixing in the remelted zone has been attributed to the shear stresses developed in this

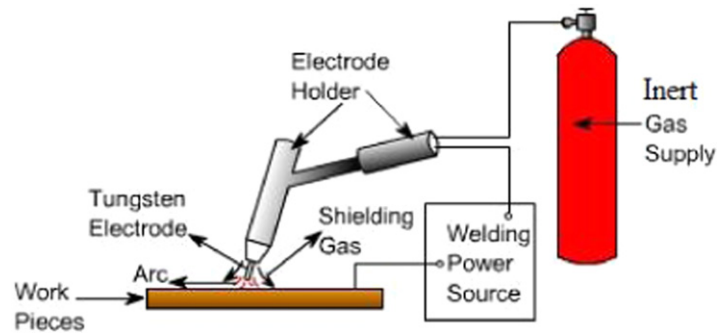


Fig. 1 Schematic diagram of TIG melting process. Available at: <https://nptel.ac.in/courses>.

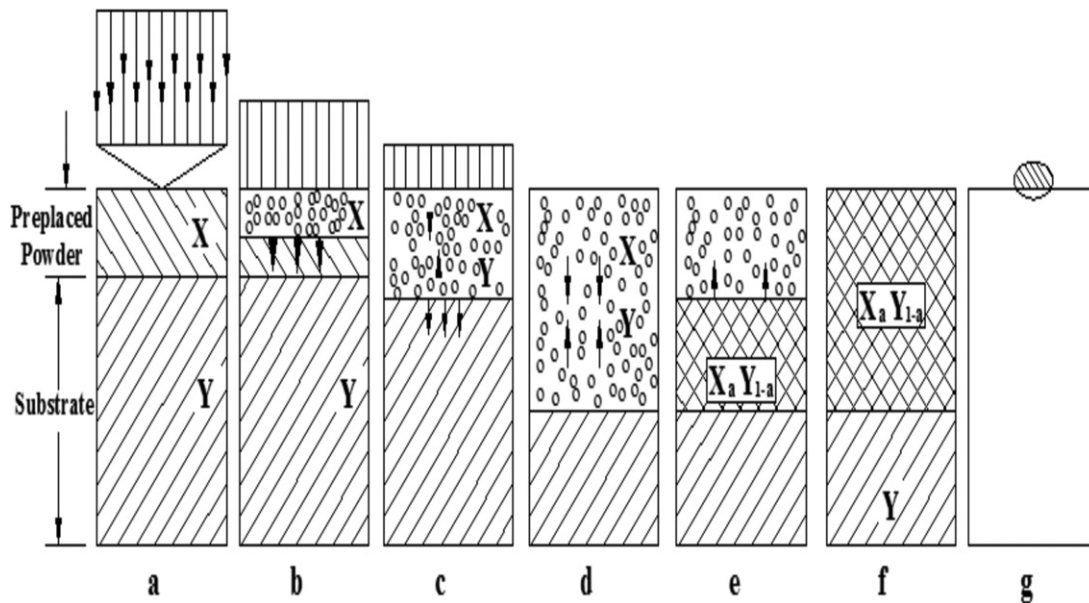


Fig. 2 Schematic diagram showing the various stages involved during the TIG surface melting and cladding process.

region due to the effect of a large thermal distribution gradient between the hot molten metal and the cooler ceramic particles. This process is important as it affects the form of convection flow and the ultimate distribution of the alloying element along the melt pool of the TIG torch modified surfaces (Kuo, 2003). Afterwards, rapid solidification of the remelted layer begins due to the heat dissipation to the cold substrate via the heat affected zone and it thus completes with the formation of dense coating metallurgically bonded to the substrate material (Fig. 2, sections e and f). This rapidly solidified structure obtained by this treatment may contain modified alloy layer of $X_a Y_{1-a}$ (Fig. 2, section f) composition in the steel matrix, which may give rise to new components with high hardness and high resistance against wear, corrosion and temperature. For different applications, TIG welding technique can provide a wide range of possible coating system with single or multi-component, and also of the composite or gradient types. Other advantages offer by TIG coating process lies with its flexibility in operation, economical in time, energy, and material consumption, and low initial capital investments when compared to other conventional processes (Celik *et al.*, 2011).

Fluids Flow Phenomenon in TIG Arc Melting Process

TIG torch welding and alloying process is a relatively new liquid-phase surface treatment technique for metals and alloys in many tribological applications. In this process, the coating efficiency is completely controlled by the microstructure of melt pool and heat affected zone (HAZ). It is well known that the mode of fluid flow field experienced by the melt pool and HAZ during TIG arc melting can alter the microstructure and thus the properties of the coating layer. Therefore, this phenomena fluid flow in the melt pool can significantly influence such factors as the melt pool geometry, the temperature gradients, the heat transfer rates and the resolidified structure. The development of fluid-flow fields in liquid pool is induced by the transporting phenomena from the TIG

electrode arc to the metallic substrate, such as arc current density, heat flux, arc pressure and induced shear stress acting on the weld pool surface (Kuo, 2003; Oreper and Szekely, 1984).

Process Parameters for TIG Welding

Unlike conventional high-energy beam heat sources (such as laser, electron beams and other arc sources), the TIG fusion welding process is a low energy technique that guarantees quality weld surface with minimum defect and production cost. The low-energy TIG melting process is endowed with other attractive features such as flexible power requirement, limited heat inputs, highly autogenous and quite suitable for steel alloys and most reactive metals, such as titanium, zirconium, aluminum and magnesium. Due to these inherent benefits, TIG arc surface melting and alloying is gaining popularity among the current trend in hardfacing (liquid phase surface) treatment of steels via incorporation of ceramic composite powder of desirable composition (Kuo, 2003; Hojjatzadeh *et al.*, 2012).

Many investigations have been conducted using TIG torch as heat sources to achieve composite melted surface layer, which are reported to tailor the structure and properties of steel surfaces against wear and friction. TIG modified surfaces are strongly characterized by the quality of the melt pool. This is because melt pool conditions play a significant role in determining the microstructure and properties of the coated layer. Numerous investigators also observed that the resolidified structures and properties obtained in TIG melted surfaces can be controlled over a wide range by selecting and adjusting desired welding process parameters during the melting process. Among others, TIG welding process is usually controlled by some variables such as arc current, traversing speed, shielding gas flow rate and arc voltage. It is also considered that TIG can be used to deposit coating layer with varying addition of ceramic powder composition and content (Eroglu and Zdemir, 2002; Kuo, 2003; Mridha *et al.*, 2012).

Peng (2012) studied the effect of process variables including current, speed, arc gap and argon gas flow rate on the surface features of surface alloyed carbon steel with TiC particles by using TIG process. The author demonstrated that surface hardness was affected more obviously by the welding speed and welding current than other experimental factors. At a lower speed, the surface hardness was found to decrease with increasing current. Under this condition, both concentration of ferrite and melt dilution content was claimed to increase, which might have contributed to the less dispersion of TiC particles in the melt pool and reason for low hardness development for the treated sample surfaces. It is therefore, noted that the higher the ferrite content due to the dilution from the substrate, the lower the cladding hardness. The surface hardness of the TIG-melted steel seems, however, not to correlate with the arc gap size and the shielding gas flow rate. The author further established that wear resistance and coefficient of friction also depend mainly on the combination of welding current and speed processing conditions, but are independent of electrode arc gap and argon gas flow rate. The wear resistance was measured based on area and depth of wear scar. The study showed that wear scar geometries in the coated samples rapidly increased with increasing current from 120 (A) to 180 (A). This suggests that the lower the scar area, the higher wear resistance. At the lower welding current, wear surfaces of the TiC coating had clean and smooth morphologies in contrast to the severe adhesive wear scar experienced by the untreated carbon steel. The adhesive feature was characterized with microcutting and grooving. Similarly, a lower friction coefficient in this study was obtained under the same optimum condition. A combination of lower welding current and lower welding speed were found, in this study, to be important requirement for the excellent surface wear features observed in TIG alloyed surfaces. This was attributed to the higher hardness of the composite coated surface reducing the asperity contact of the mating materials.

Kuo (2003) reported the influence of welding speed and welding current on the solidification mode of TIG-melted pool in HY-80 steel. Under the same welding speed, the result showed that the melt pool microstructure changes from cellular to dendritic resolidified structures as the welding current increases. The author also observed that the cooling rate increases with increasing speed, under the same applied arc current. It is therefore concluded that the higher welding speed resulted to higher cooling rate and the cells are finer, while the lower speed produced lower cooling rate and coarser resolidified structures.

The effect of shielding gas parameters (types, flow rates and compositions) on the performance of TIG coated and modified surfaces have been studied extensively by many authors (Hojjatzadeh *et al.*, 2012; Wang *et al.*, 2007). The authors proposed that the current density distribution in TIG arc process largely depends on the type of shielding gas. In addition, the authors revealed that among the three shielding environment investigated, argon gas produced the best arc characteristics based on the account of its low ionization potential. The studies demonstrated the effectiveness of using argon gas as the main shielding gas during TIG surface treatment experiments. Shielding gas flow rate is another parameter that also influences the behavior of melt pool structure during TIG arc welding process. The authors also reported an increase in the melt pool bead width and depth as the gas flow rate increases.

Efforts were also made to examine the effects of welding voltage parameter on the surface modification routes with TIG arc heat sources. Mridha *et al.* (2012) investigated the effect of arc voltage on the property behavior of TIG-processed steel alloys. The study revealed that variation in the applied voltage between 30 V and 55 V yielded composite tracks with different microstructural and hardness evolution. Based on the review of the previous studies on TIG surface treatment scheme, it is identified that the structure and performance of TIG-modified surfaces are influenced by multiplicity of key independent parameters ranging from arc welding current, electrode travel speed, welding voltage, polarity, current supply technique (pulsed or continuous), pre-coated powder content, arc length, shielding gas composition and flow rate. The flexibility in controlling these parameters during TIG arc melting process and their corresponding influence on mechanical and tribological performance of engineering remains a new direction for future research in ceramic reinforced composite coatings (Bello *et al.*, 2015; Juang and Tarnag, 2002; Maleque *et al.*, 2013).

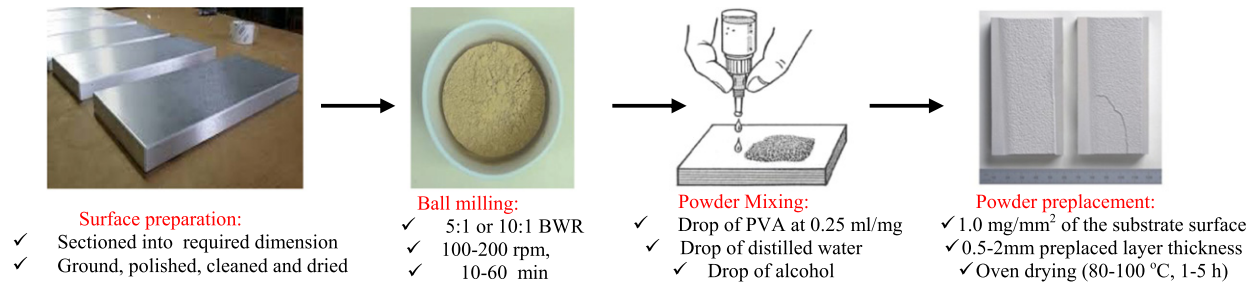


Fig. 3 Schematic flow of powder preplacement process for TIG-based composite coating.

Processing of TIG-Based Ceramic Reinforced Composite Coatings

The feasibility attempt of processing a hard ceramic composite coating by melting engineering alloy surfaces beneath TIG torch arc was initiated by the work of [Mridha et al. \(1988\)](#) and since then many studies have been reported by several researchers on this novel coating technology. TIG surface modification has been used for repairing the worn surface of machine parts and hardfacing of ferrous materials in various industrial applications such as mining, chemical, and petroleum industries. TIG cladding process is usually performed on ferrous alloy (cast-iron, non-alloy carbon steels and alloy steels) and non-ferrous alloy (commercial purity titanium) substrate materials. In TIG-based composite coating, an alloy or a composite layer is usually fused onto the surface of the substrate based on the two-step fabrication process using ceramic powder preplacement and TIG torch melting technique.

Preparation of Ceramic-Powder Preplaced Surfaces

The first step of TIG-based composite coating method is to prepare and place ceramic powder material on the surface of a chosen substrate using powder preplacement process. At first, the surface of the substrate samples is ground and polished to a desired surface roughness using SiC abrasive paper. The polished substrate is then thoroughly degreased in acetone in order to remove any impurities such as grease, dust, and oxide layer from the substrate surface. The ceramic powder is selected based on the requirement of the intended surfaces. The two or more powder material are usually mixed and blended together using a low energy ball-milling machine between 10 and 60 min and ball-to-powder weight ratio (BWR) of 5:1 or 10:1. The powder mixture is weighed at approximate content of 1.0 mg per millimeter square area of the substrate surface. This is mixed with a predetermined amount of organic binder (4% polyvinyl alcohol, PVA), distilled water and alcohol to form a past-like solution or a slurry. Organic binder is used to prevent the powders from blowing away under the flow of shielding gas during TIG glazing operation. The amount of binder used is usually restricted to within the limit of 0.5 ml for 2 mg of powder mixture to prevent excessive pore formation in the resolidified coating layer ([Mridha et al., 1988](#)). The mixed powder paste is dispersed uniformly on the substrate surface with the aid of plastic spatula to form a preplaced layer with desired thickness in the range of 0.5–1.5 mm. The thickness of the preplaced layer is maintained by using the appropriate amount of powder mixture required to cover the surface of the substrate. The approximate thickness of the preplaced layer produced on the substrate surface is measured from the difference in thickness of the substrate before and after the preplacing of powder layer using a Vernier caliper. The preplaced powder surface is then allowed to dry in an oven for 1–5 h at 80–100°C to remove excessive moisture and for ensuring the preplaced powder layer is well adhered to the substrate surface ([Maleque et al., 2018](#); [Munoz-Escalona et al., 2016](#); [Bello et al., 2016](#); [Hojjatzadeh et al., 2012](#); [Wang et al., 2007](#)). A schematic flow of this process is given in [Fig. 3](#).

Surface Melting by TIG Welding

Surface melting of the preplaced substrates is accomplished under the arc torch of TIG welding machine. In this process, the arc generated by the TIG torch welding process, under different conditions, is adapted for the realization of composite coatings by depositing ceramic particles in the melt pool of the substrate. The tungsten inert gas arc process utilizes a localized heat source of an arc created between the tip of a non-consumable tungsten electrode (with varying diameter from 2.4 to 4.8 mm) and the specimen surface as shown in [Fig. 4](#). The arc develops intense heat, approximately 11,000°F (6100°C) which melts a thin surface layer of the base metal to form a molten pool. As depicted in [Fig. 4](#), the TIG heat source or arc is scanned over the preplaced substrate that resulted in melting of the preplaced powder mixture and a thin layer of the substrate underneath the coating layer. The arc is usually controlled by the supply of current (50–110 A) and voltage (10–40 V) to the electrode. The electrode height used is usually maintained between 2 and 3 mm.

During irradiation process, the arc area (weld pool and electrode) is protected from undesirable oxidation by the inert shielding gas such as argon in the range of 10–30 l/min and is channeled through electrode gun. The shielding gas displaces the air, so that the oxygen and nitrogen of the air do not come in contact with the molten metal or the hot tungsten electrode. The preplaced substrate is held stationary under the moving TIG torch at varying electrode-traversing speeds (0.5–3.0 mm/s)

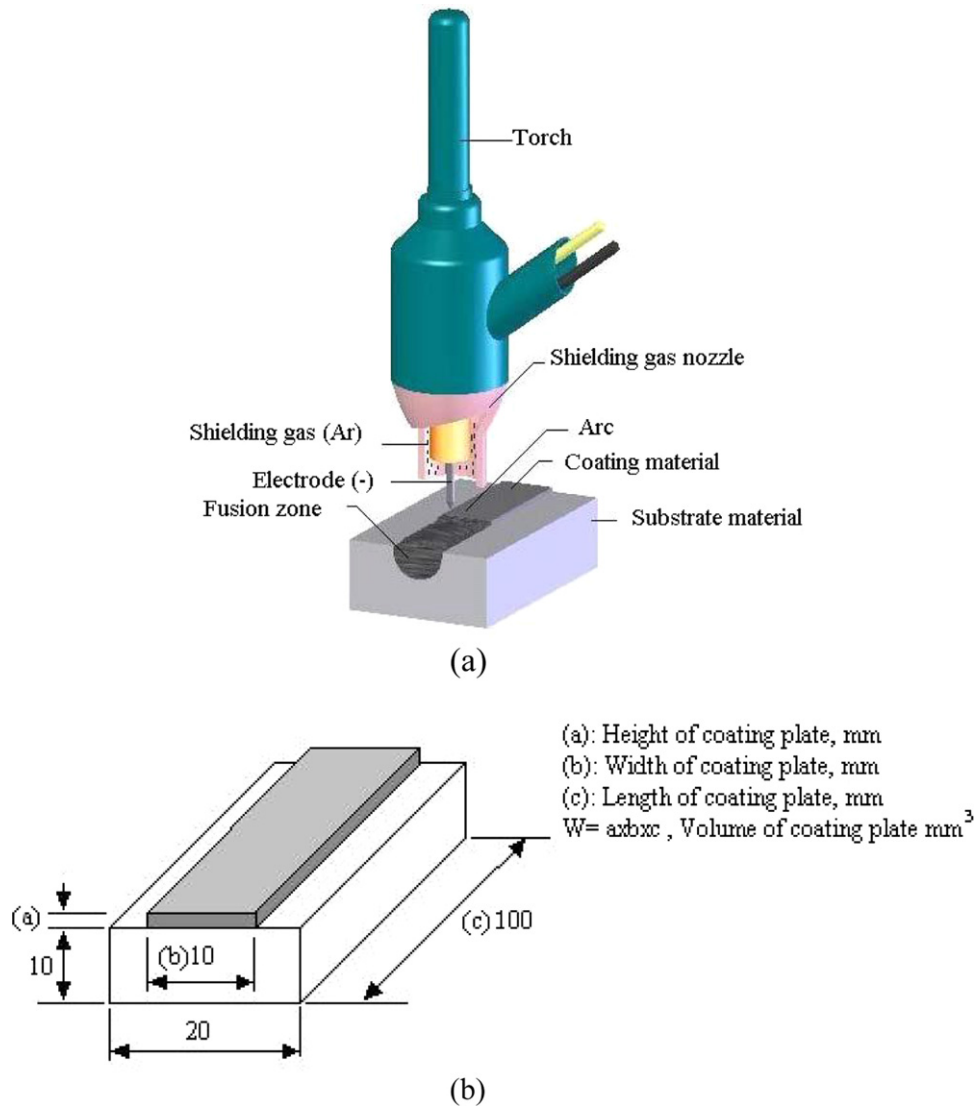


Fig. 4 Schematic representation of surface melting by TIG welding (a) composite coating process and (b) coating specimen. Reproduced from Buytoz, S., Yildirim, M.M., 2010. Microstructure and abrasive wear properties of $M(Cr, Fe)_7C_3$ carbides reinforced high-chromium carbon coating produced by gas tungsten arc welding (GTAW) process. Archives of Foundry Engineering 10, 279–286.

to produce coated tracks along the width of the specimens (Bello *et al.*, 2018; Mridha *et al.*, 2012; Buytoz and Yildirim, 2010; Cheung and Khan, 2003; Eroglu and Zdemir, 2002). The heat input required for the process is calculated using Easterling Eq. (1) (Easterling, 1992):

$$\text{Heat input (J/mm)} = \frac{0.48 \times \text{voltage (V)} \times \text{Current (I)}}{\text{Travel speed mm/min}} \quad (1)$$

Based on the processing conditions, various degrees of heat inputs are generated giving rise to localized heating, melting or evaporation. The application of extremely high power density can increase the melt pool temperature as high as 2000°C to produce high thermal gradients. The microstructure, as well as the composition of the composite coatings depends on the degree of mixing between the molten pool and the ceramic particles. Further, the microstructure of the coating is governed by convection, diffusion, and cooling rates during liquid-to-solid and solid-to-liquid phase transformation. The higher cooling rate produces hard phases and refines the microstructure resulting in solid solution strengthening. Hence, the parameters controlling these mechanisms are of paramount importance to the TIG-based composite coating technology. For the purpose of characterization, both single and multiple coated tracks are produced (Fig. 5). Single tracks are made for the determination of the microstructure and microhardness of TIG modified surfaces. In multiple tracks, series of overlap tracks are clad side by side with an overlap ratio of 25%–50% on the entire surface of the substrate specimen for the tribological test involving friction and wear characterization (Munoz-Escalona *et al.*, 2016; Bello *et al.*, 2016; Hojjatzadeh *et al.*, 2012; Wang *et al.*, 2007; Mridha, 2005).

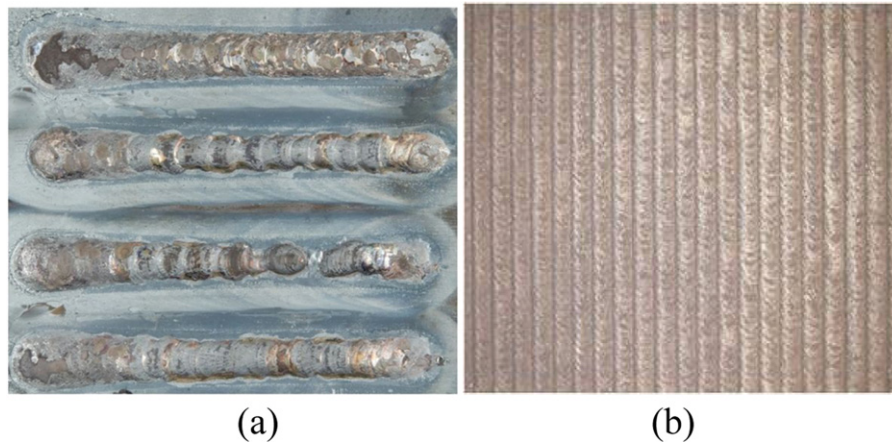


Fig. 5 TIG composite coated tracks (a) single track (b) multiple tracks.

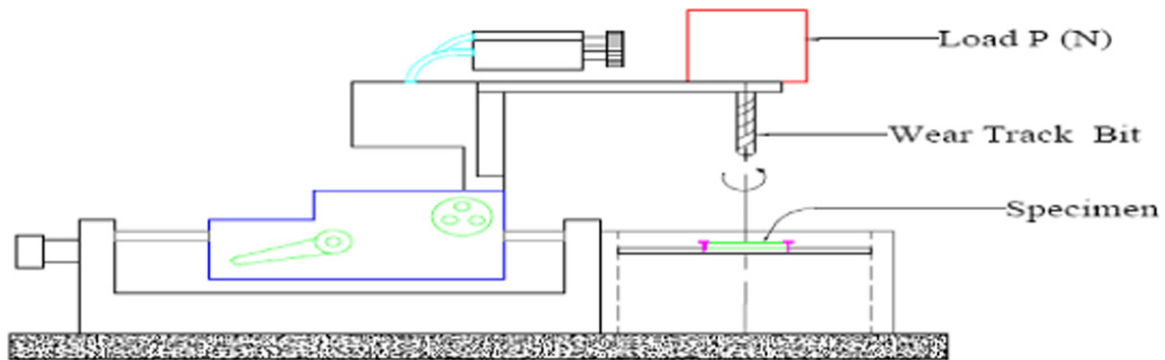


Fig. 6 Schematic diagram of a typical pin-on-disc wear testing machine.

Characterization of TIG-Based Composite Coated Layer

After cladding process, the surface modified specimens are cut at the transverse direction of arc scanning by using wire-EDM or hack saw for microstructural examination and hardness measurement. The cross sectioned specimen are prepared for metallographic examination by grinding on SiC wheels followed by polishing and etched with an appropriate etchant depending on the base material. For example, titanium based substrates are etched with Kroll's reagent (50% HF, 30% H₂O₂ and 20% distilled water by volume) or with a mixture of 20 vol% HF and 80 vol% HNO₃. Most of the steel based specimens are either etched with ferric chloride solution (25 g of FeCl₃, 15 ml of HCl and 100 ml of distilled water) or with a solution of alcohol and 2% nitric acid. The microstructures of the specimens are then observed by scanning electron microscope (SEM), energy dispersive spectra (EDX), X-ray diffraction (XRD) and their spectra analyses are beneficial for microstructure and elemental analysis of the modified surface. Microstructure examinations of the worn surfaces are also evaluated to determine the phases and wear characteristics of the modified surfaces after wear testing. Hardness measurement is performed on the transverse sections of the produced coating surface using a microhardness tester with a Vickers indenter. A varying load (50–500-gf) at a specified dwell time (5–10-s) is used to create indentations along the melt depth of the composite coated specimen, starting from the surface of the melt zone to the base material (Maleque *et al.*, 2018; Buytoz and Yildirim, 2010; Cheung and Khan, 2003; Juang and Tarng, 2002).

Wear tests are performed on TIG modified specimens to determine their tribological properties (wear and friction). Wear experiments are done either at the room or high temperature with pin-on-disc or ball-on-disc type tribometer. This method consists of a static partner, which is held in contact with a rotating disc via a steel pin. The disc and the pin are arranged in such a way that the static partner served as the counterface material while the rotating disc served as the test samples. Fig. 6 shows the schematic illustration of the wear testing apparatus while Fig. 7 shows a typical high-temperature tribometer. The test specimens for the wear experiment are machined from the TIG-based composite coated surface to the standard dimension and are used as the rotating disks for the wear test. Prior to the test, the contacting surfaces of the test samples are ground with SiC paper abrasives followed by cleaning in acetone and drying in hot air to remove any dirt in form grease and debris (Bello *et al.*, 2018; Adeleke and Maleque, 2015; Peng, 2012; Hajbagheri *et al.*, 2008; Mridha, 2005).

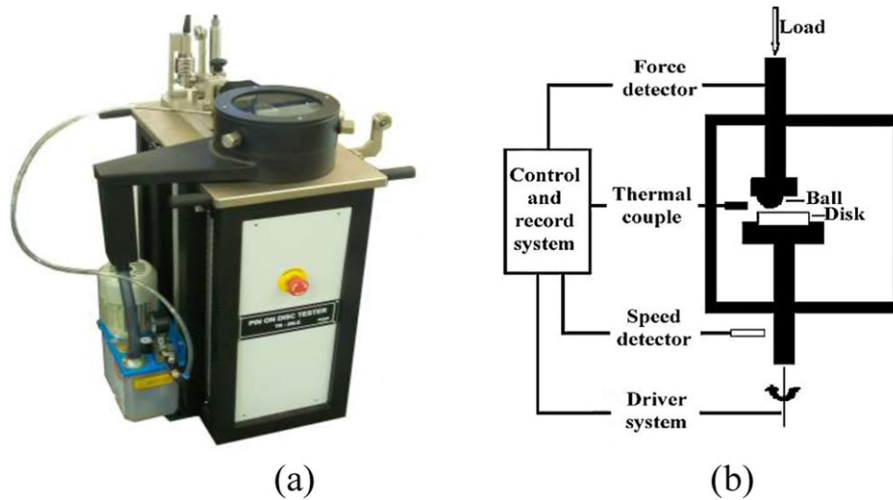


Fig. 7 A typical ball-on-disc apparatus for high-temperature wear testing; (a) TR-20-PHM-CHM-600 DUCOM tribometer and (b) Schematic diagram. Reproduced from (a) Bello, K.A., Maleque, M.A., Adebisi, A.A., Dube, A., 2016. Preparation and characterisation of TIG-alloyed hybrid composite coatings for high-temperature tribological applications. Transactions of the IMF 94 (4), 211–221. (b) Segu, D.Z., Choi, J.H., Kim, S.S., 2012. Sliding wear behavior of Fe-based bulk metallic glass at high temperature. Journal of Mechanical Science and Technology 26 (11), 3565–3570.

The average wear track width is measured with the help of scanning electron microscope and volume loss is obtained using Eq. (2):

$$V = 2\pi R \left\{ r^2 \sin^{-1}(d/2r) - (d/4)\sqrt{4r^2 - d^2} \right\} \quad (2)$$

where R is the wear track radius (mm), d the wear track width (mm) and r is the radius of the pin or ball (mm). Thus, the wear rate (w) is calculated according to the Eq. (3) and expressed as mm^3/Nm :

$$\text{Wear rate} = \frac{\text{wear volume loss}}{\text{sliding distance} \times \text{applied load}} \quad (3)$$

Microstructure and Properties of TIG Processed Composite Coatings

Hardfacing by means of TIG welding method associated with a rapid heating and cooling rate provided a unique opportunity for the non-equilibrium synthesis of materials and produced rapidly solidified fine microstructures with extended solid solution of alloying elements, thus providing remarkable enhancement on corrosion resistance, wear resistance without impairing the bulk properties. Studies conducted on ceramic reinforced composite coatings produced by TIG torch welding method have identified that both the hardness and tribological resistance development are directly related to the melt pool microstructure of the composite coatings (Munoz-Escalona *et al.*, 2016; Hojjatzadeh *et al.*, 2012; Mridha, 2005).

Microstructural Features of the Composite Coatings

Processing of composite coating by TIG torch arc melting results in microstructural evolution with non-equilibrium structures, which are formed under high cooling rates. Hence, the melt structure developed in the ceramic-based coating is related to the extent of melting, solidification process. The cross sections of the re-solidified surface layers are examined by optical and scanning electron microscopy while the elemental, and phase constituents of the coating are determined by energy dispersive spectrograph (EDS) and X-ray diffraction (XRD) analysis. Xinhong *et al.* (2006) realized the application of TIG cladding of AISI 1040 steel with TiC particles reinforced composite coating. Pre-coated FeCrBSi alloy, graphite and ferro-titanium powders on the substrate produced the in situ coating. The authors in their work revealed when the pre-coated thickness of the mixture powder is less than 1.2 mm, the melt tracks were found to be free from gas porosity, inclusions and crack (Fig. 8(a)). Melted tracks gave a smooth rippled surface topography. However, when the thickness of the pre-coated thickness is beyond 2.0 mm, the formation of the tracks became poor, gas porosity and incomplete fusion can be found, as shown in Fig. 8(b).

Bello *et al.* (2018) produced two Fe-based ternary composite coatings by depositing two different powder preplaced mixture (PPM) with nominal percentage compositions of 94Fe4C2Si (PPM1) and 90Fe6C4Si (PPM2) on CP-Ti using TIG cladding process. As shown in Fig. 9, the analysis of the coatings revealed that the microstructure in the melt consists of dendrites of different sizes. At lower powder preplaced mixtures (PPM1, Fig. 9(a)), the dendrite size was larger compared to higher powder

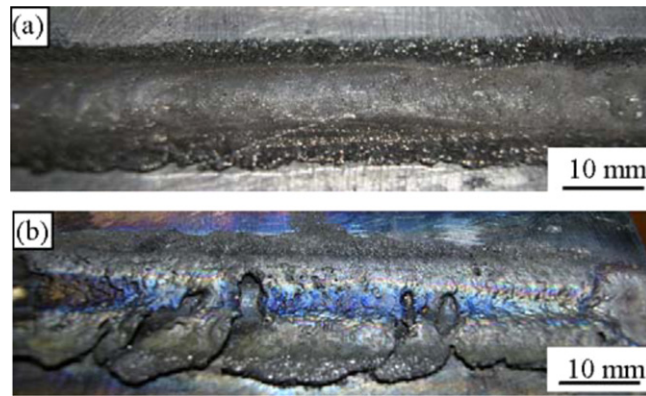


Fig. 8 TIG Melted track produced on the surface of AISI 1040 steel specimen with a pre-coated thickness: (a) 1.2 mm; (b) 2.0 mm. Reproduced from Xinhong, W., Zengda, Z., Sili, S., Shiyao, Q., 2006. Microstructure and wear properties of in situ TiC/FeCrBSi composite coating prepared by gas tungsten arc welding. *Wear* 260, 25–29.

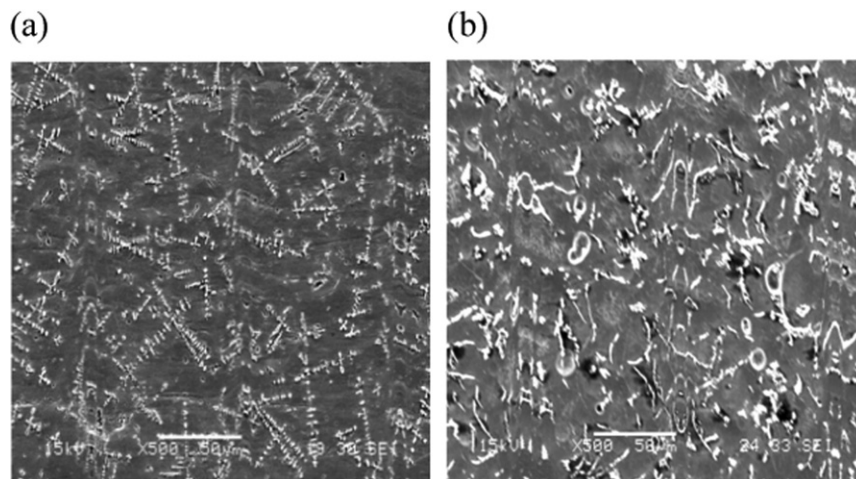


Fig. 9 SEM micrographs of TIG composite coating layers on Cp-Ti: (a) 94Fe4C2Si (PPM1), (b) 90Fe6C4Si (PPM2). Reproduced from Bello, K.A., Adeleke, S.A., Maleque, M.A., Adebisi, A.A., Abdulwahab, M., 2018. Microstructural studies and tribological behavior of Fe-based multicomponent composite coatings deposited by TIG torch melting technique. In: *Proceedings of the Faculty of Engineering International Conference (FEIC) 2018*, pp. 75–86. Nigeria: Nnamdi Azikwe University Awka.

preplaced mixtures (PPM2, [Fig. 9\(b\)](#)). The enlarged dendrites in the PPM1 composite layer track are thought to be associated with higher dissolution of PPM in Ti melt matrix. Also, the amount of carbon is believed to have influenced the growth of dendrites and their concentration in the melt.

Furthermore, the EDX analysis of the dendritic structures in the clad layer revealed that the peaks are mainly from Ti and C ([Fig. 10\(a\)](#)), indicating the in situ formation of TiC in the composite coatings. The high affinity of carbon to titanium is significant to produce such TiC phase. As revealed in [Fig. 10\(b\)](#), the X-ray pattern from the surface of the specimen processed with PPM1 also revealed that the melt structure contains TiC (dendrites), iron carbide and Ti_3SiC_2 (melt matrix).

Microhardness of the Composite Coatings

[Hojjatzadeh et al. \(2012\)](#) have investigated the surface melting of AISI 1045 steel with a preplaced layer of ferro-titanium powder in the presence of a gaseous shield of pure nitrogen, pure argon and via TIG welding process. The results demonstrated that the addition of the gases significantly increased the surface hardness due to the formation of dendrites of TiN and TiC in the composite layer microstructures. [Peng \(2012\)](#) explored the possibility of the formation of TiC-reinforced composite coatings on AISI 1020 carbon steel surfaces by melting of preplaced titanium carbide powder using tungsten inert gas arc process under varying welding parameters. The author showed that precipitated TiC phases formed in the modified layers had substantially improved to over 65 HRB as compared to that of the steel substrate (6.6 HRB). The TiC-reinforced surface also revealed a higher wear resistance and lower coefficient of frictions compared to the substrate material. [Wang et al. \(2007\)](#) reported microhardness improvements by TIG surface alloying of AISI 1045 steel with preplaced powder mixture of graphite, Fe-Ti and Fe-Cr. The study showed that the hardness

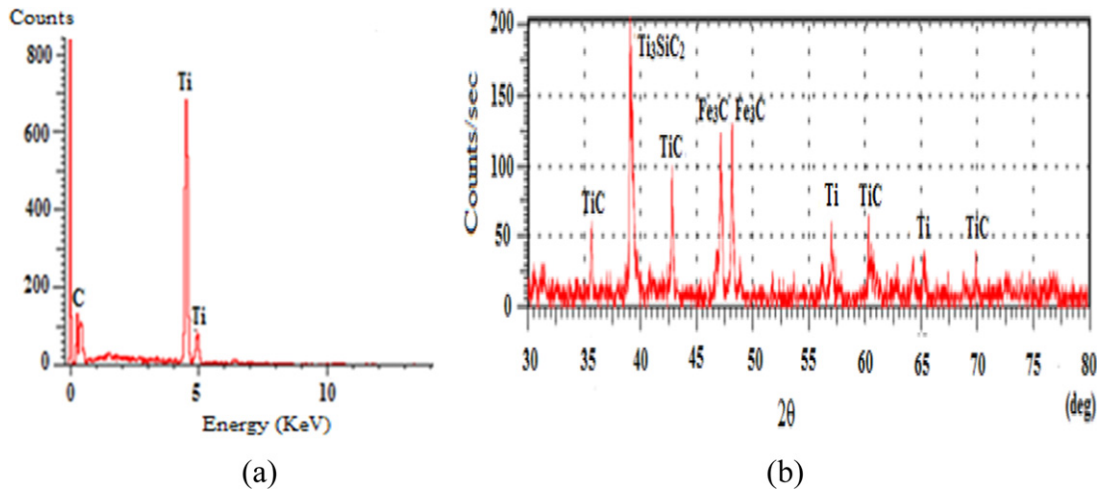


Fig. 10 X-ray analysis of the TIG composite coated specimen (a) EDX of the dendritic structure, and (b) XRD pattern of PPM1 track clad layer.

improvement reduced the wear rate of the TIG alloyed surface to almost four times of that of the untreated material. The authors further demonstrated that the properties of coatings are influenced by the chosen welding variables and thickness of the preplaced powder layer. [Dyuti et al. \(2011\)](#) used TIG heat source to produce intermetallic and nitride claddings on plain carbon steel surfaces with preplaced mixtures of titanium and aluminum powder, under a pure nitrogen-shielding environment. Upon solidification, the authors found that dendritic phases of Ti-Al nitrides and Ti-Al intermetallics were formed in the resolidified layers, which led to an increase in the microhardness of the modified layers by over 4.5 times that of the untreated carbon steels. [Xinhong et al. \(2006\)](#) showed a typical microhardness profile of TIG reinforced composite coated layer of Fe-TiC ([Fig. 11](#)). As shown in the figure, the microhardness of the coating gradually increased with increase of distance from bottom of the coatings. It is noted that there is no sudden transition from the coating to the substrate in the hardness, which indicates an absence of a sharp demarcation in materials properties across the interface.

Tribological Behavior of the Composite Coatings

It is well accepted that the wear and friction characteristics of the composite coating largely govern by the constituent percentage, its microstructure and processing parameters. Hence, it is essential to understand the surface wear characteristics of TIG torch processed coatings. [Elahi et al. \(2012\)](#) compares the variation of the weight losses of the worn surfaces against sliding distance for the as-received and TIG surface coated magnesium alloy. It is observed that the amounts of the weight losses for the untreated substrate and the alloyed layer after 300 m sliding distance are 10.7 mg and 6.1 mg respectively. This indicated that the wear rate of the alloyed sample is almost half of that of the as-received material, which could be attributed to higher hardness of alloyed layer as compared with the hardness of the as-received material. Furthermore, [Buytoz et al. \(2005\)](#) demonstrated that AISI 4340 steel surface treated with WC by using TIG process at high powder feed rate, low process speed and high heat input gave minimum mass loss. [Xinhong et al. \(2006\)](#) in their work revealed that TiC reinforced composite coatings produced by TIG torch melting technique are effective in improving wear resistance and give a much lower increase in wear volume with increasing normal load than that of AISI 1045 steel substrate ([Fig. 12](#)). This is mainly related to the hard carbides of TiC particles. Additionally, amongst the coatings and substrate, the lowest wear volume occurred for the cladding coating with a 1.2 mm thickness of the pre-coated coating and this may be directly attributed to the high hardness achieved with the composite coatings.

[Xinhong et al. \(2006\)](#) further analyzed the SEM micrograph of the worn scar for the TIG modified composite coating with a preplaced TiC layer of 1.2 mm thickness and that of AISI 1045 steel substrate ([Fig. 13](#)). The authors in their work demonstrated that in situ TiC particles reinforced Fe-based composite coating suffered a mild wear with fine scratches, but 1045 steel showed a severe adhesive wear with scale like feature. Due to the hard barriers effect of TiC particles, the scratching was interrupted or the path of scratching was converted. That is in situ synthesis TiC particles reinforced the matrix and protected it from serious abrasion. As a result, the composite coatings possess a much higher resistance to plastic deformation and scratching than that of 1045 steel.

Very recently, [Bello et al. \(2016\)](#) produced TiC/BN and TiC/Ni-P-hBN composite coatings on AISI 4340 steel by TIG cladding process, where BN and Ni-P-hBN act as solid lubricants for high temperature lubrication ([Fig. 14](#)). The wear rates and coefficient were determined for these composite coatings tested at elevated temperature of 600°C ([Fig. 14\(a\)](#)). As shown in the figure, the result of the experiment revealed that the wear resistance of TiC/Ni-P-hBN track layers is over five times higher than that of TiC, or twice that of TiC/hBN coated surfaces.

The authors also demonstrated that the surface coating with TiC reinforcement exhibited coating failure at an early stage of testing (nearly 8 min), which could be related to the poor frictional property of the single-phase coating at elevated temperature. For TiC/hBN hybrid composite coating, the friction coefficient was initially low and quite unstable. It then increased up to 0.62

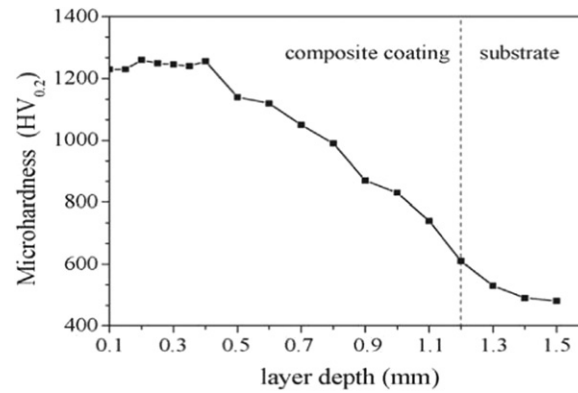


Fig. 11 Variation of microhardness of the TIG surface modified composite layer of Fe-TiC with melt depth. Reproduced from Xinhong, W., Zengda, Z., Sili, S., Shiyao, Q., 2006. Microstructure and wear properties of in situ TiC/FeCrBSi composite coating prepared by gas tungsten arc welding. *Wear* 260, 25–29.

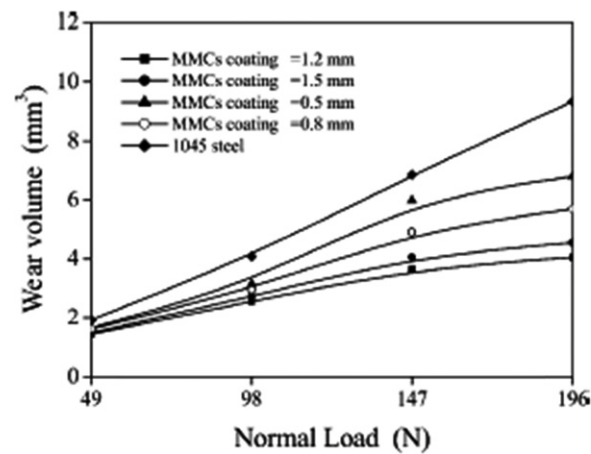


Fig. 12 Wear volume of TiC reinforced composite coatings and 1045 steel. Reproduced from Xinhong, W., Zengda, Z., Sili, S., Shiyao, Q., 2006. Microstructure and wear properties of in situ TiC/FeCrBSi composite coating prepared by gas tungsten arc welding. *Wear* 260, 25–29.

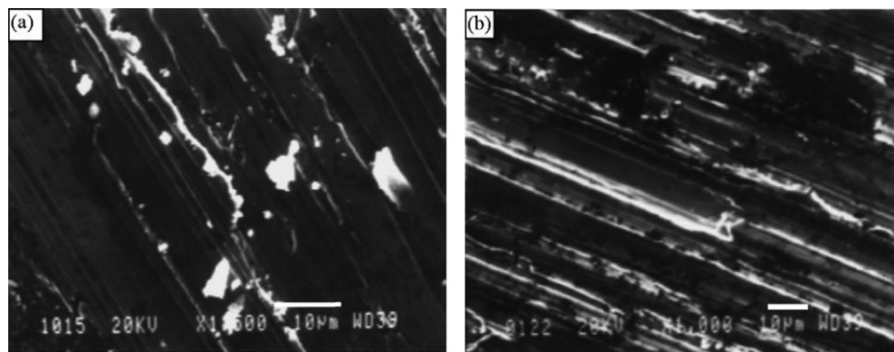


Fig. 13 SEM images worn out surface for: (a) the composite coatings (b) 1045 steel. Reproduced from Xinhong, W., Zengda, Z., Sili, S., Shiyao, Q., 2006. Microstructure and wear properties of in situ TiC/FeCrBSi composite coating prepared by gas tungsten arc welding. *Wear* 260, 25–29.

and remained almost constant throughout the sliding experiment (Fig. 14(b)). The poor frictional control obtained in this class of coating could be attributed to the weak coating strength caused by the presence of non-wettable hBN lubricant powder in the coating architecture. Compared with TiC and TiC/hBN composite coatings, the friction coefficient obtained under the same processing for the TiC/Ni-P-hBN coating exhibited lower and more stable friction throughout the sliding test. It can be seen that

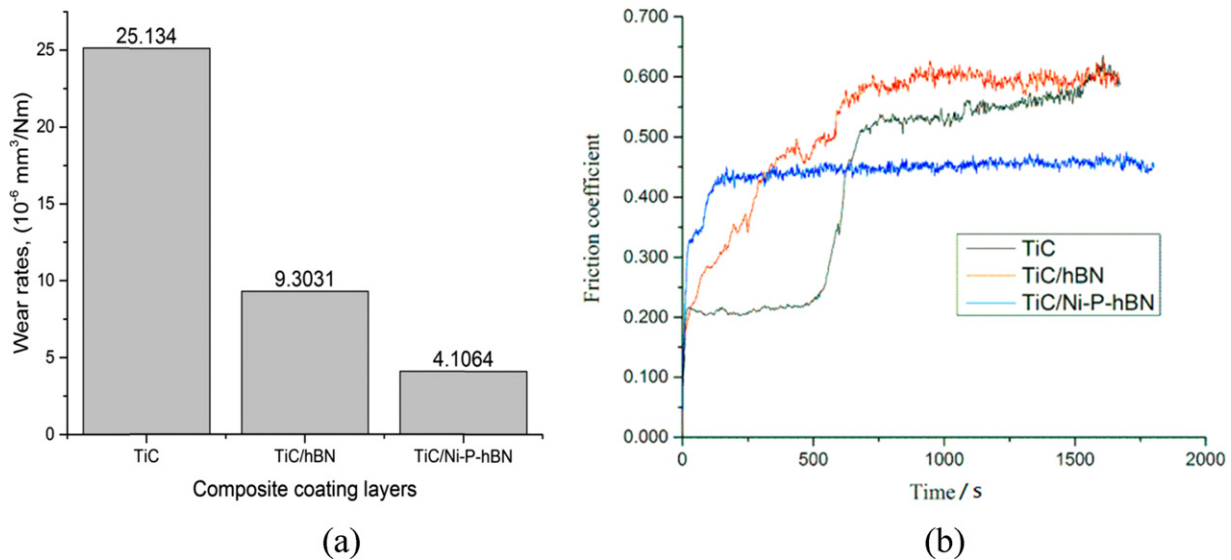


Fig. 14 Variation of tribological behavior for the composite coatings tested at an operating temperature of 600°C (a) wear rate (b) coefficient of friction. Reproduced from Bello, K.A., Maleque, M.A., Adebisi, A.A., Dube, A., 2016. Preparation and characterisation of TIG-alloyed hybrid composite coatings for high-temperature tribological applications. Transactions of the IMF 94 (4), 211–221.

reinforcement of TiC coating with Ni–P–hBN powder is effective in improving frictional behavior and has the lowest coefficient of friction.

Summary and Future Outlook

The present article gives overview of the various surface coatings technologies, which have been evolving over the years. In particular, it outlines newer method of developing ceramic composite coatings on metallic materials via powder preplacement and TIG torch welding process. Although most of the commercially available composite coatings are processed by laser cladding method, the researchers are in constant search for a cost-effective approach, which may offer promising corrosion and wear resistant properties. From this review, TIG arc melting has therefore established its potential to fit in that space and has emerged as a viable replacement to the conventional laser surface treatment due to the complexity and high costs of the laser equipment. This study reveals TIG melting parameter and ceramic composition designs as a key factor in improving composite coating characteristics to give a low wear rate and coefficient of friction values. In future, a thorough study on the new composite coatings added with electroless nickel coatings may offer promising benefits in the development of self-lubricating coatings for tribological applications where components are operating under extreme environment. The authors of this article have developed TiC/Ni-P-hBN hybrid composite coatings with an attractive tribological properties at elevated temperature up to 800°C. With the technological advancement, TIG arc technology could have a bright future for the development of nano-composite coatings and functionally graded coatings using additive manufacturing for advanced tribo-systems in industrial application.

Acknowledgments

The authors would like to thank the Research Management Centre (RMC) of International Islamic University Malaysia for their part in funding this research through project No. RMGS1212-007-0020. One of the authors (K.A. Bello) is equally grateful to Ahmadu Bello University Zaria Nigeria for the Doctoral Tet fund Research support that made this research study possible.

See also: Historical Development of Hybrid Materials

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Removal of Chromium With CNT Coated Activated Carbon for Waste Water Treatment

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Introduction

Since the discovery of carbon nanotubes by Ijama in 1991, a researcher with the Nippon Electric Company (NEC) Laboratory in Tsukuba, Japan (Zhao *et al.*, 2006) has been in the focus of material research due to their unique electronic and mechanical properties in combination with the chemical stability. Carbon nanotubes (CNTs) are nanostructures resulting from revolved graphene planes and have a range of attractive chemical and physical properties. CNTs exist as single (SWNTs), and multi-walled (MWNTs) structures. CNTs theoretically is well known of its high electrical conductivity, very high tensile strength, highly flexibility where it can be bent considerably without damage, very elastic $\sim 18\%$ elongation to failure, high thermal conductivity, low thermal expansion coefficient, good field emission of electrons and high aspect ratio (length to diameter ratio more than 1,000,000) (Dresselhaus *et al.*, 2000; AzoNano, 2005; Danafar *et al.*, 2009).

Hexavalent chromium (Cr^{6+}) is far more mobile than the trivalent (Cr^{3+}) chromium (Selvi *et al.*, 2001). Increased concentrations of these elements in environment prove to be toxic. The main route of chromium excretion in human body is via kidneys into urine, and via bile duct into feces. Irrespective of the manner of intake, Cr^{3+} is absorbed too a far lesser degree than Cr^{6+} . Furthermore, Cr^{6+} is highly toxic when entering through dermal contact and through respiratory tract, respectively. The hexavalent chromium $\text{Cr}(\text{VI})$ poses a threat as a hazardous metal and its removal from aquatic environments through biosorption has gained attention as a viable technology of bioremediation (Al-Homaidan *et al.*, 2018).

Conventional methods have been found to be ineffective, particularly when the metal concentrations have been in the range of 1–10 mg/L. In addition, these techniques produce immense quantities of chemicals. They are also not cheap and impractical to be used widely in low income countries. This study has been emphasized on the application of carbon nanotubes coated by activated carbon (AC) for chromium $\text{Cr}(\text{VI})$ removal from the wastewater. The significance of this study is to have a better understanding in the applications of carbon nanotubes in preserving the environment and also to hold paramount the safety, health and welfare of the society. Furthermore, this study was conducted in order to determine the optimization of the purification process of the aqueous wastewater treatment.

Malaysia is rich in water resources, receiving an annual average of 990 billion m^3 , of which 360 billion m^3 or 36 % returns to the atmosphere as evapo-transpiration, while 566 billion m^3 or 57% appears as surface runoff and the remaining 64 billion m^3 , or 7% goes to recharge groundwater. However, an overall water demand is growing at a rate of 4% annually, and is projected to be about 20 billion m^3 by 2020 (Abdullah, 1999). Quantitatively, this is less than 4% of annual runoff, but due to the variation in rainfall, some regions of high water demand are approaching the limits of readily available water and water stress has become more prevalent over the past few years, culminating in the water crisis affecting some parts of the country in early 1998. In the year 2004, Department of Environment Malaysia (DOE) has recorded 17,991 water pollution point sources in Malaysia comprising mainly sewage treatment plants (8414: 54%), manufacturing industries (8203: 38%), animal farms (904: 5%) and agro-based industries (470: 3%) (Seo *et al.*, 2003).

Furthermore, common pollutants generated by industrial activities are heavy or trace metals such as mercury, arsenic, cadmium, chromium, lead, zinc and copper. Therefore, states with high industrial development (Pulau Pinang, Johor and Perak) have high levels of heavy metal (lead and mercury) contamination (Department of Environment, 2004). The usual concentration of chromium in wastewater in Malaysia is between the ranges of 0.2–0.5 mg/l (Abdullah, 1999). There are several methods which can be used for removal of chromium from wastewater include reduction, precipitation, ion exchange and solvent extraction. However, all of these treatments are said to be high in cost and low feasibility for small scale industries. Therefore, these treatments are not widely practiced. Another method is activated carbon (AC) for the removal of heavy metals from wastewater which is more efficient and widely used technique.

Production of Carbon Nanotubes and its Coating

The production of carbon nanotubes is conducted in two horizontal tubular reactors. The horizontal reactors are a quartz tube of 50 mm in diameter and 1200 mm in length and heated by silicon carbide heating element. The catalyst was fixed at the first reaction chamber while the second reaction chamber was used for the reaction and growth processes. Two types of gases used in this system are hydrogen as a reacting gas and the argon for flushing the air from the system, and both of them were controlled by a flow meter (Chen *et al.*, 2006).

CNT Coated Activated Carbon

For the growth of carbon materials on the surface of the AC, an impregnation process was conducted first. The function of impregnation is to fix the catalyst on the activated carbon at nanoscale level which is then known as nanocatalyst. The method

Table 1 Experimental parameters and its variation

No.	Parameter	Variation		
		Low	Medium	High
1.	Concentration of chromium (mg/L)	0.2	0.35	0.5
2.	Adsorbent dosage (mg/50 mL)	Fixed		
	Normal activated carbon	2	11	20
	Activated carbon coated with carbon nanotubes (Type I)	2	11	20
	Activated carbon coated with carbon nanotubes (Type II)	2	11	20
3.	pH	2	3	4
4.	Time contact (min)	60	150	240
5.	Agitation speed (rpm)	100	150	200

which is used for the growth is wet impregnation where the AC is condensed in the solution. The activated carbon (AC) used for impregnation was pre-washed with nitric acid to remove the inorganic impurities. The AC particle size used is $<50\ \mu\text{m}$. The catalyst salt which has been used in this method is $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ from Aldrich, AR grade. Then, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is dissolved in acetone at a certain amount to reach 1 wt% Ni.

For the wet impregnation, the metal precursor ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was dissolved in 10 ml of acetone and was mixed with the AC support at 25°C under ultrasonic bath for 30 min. The samples were dried at 60°C for 12 h. This step is to create a small Ni catalyst in nanoscale size over the activated carbon as mentioned earlier. After that, the samples were then calcined with O_2 or N_2 at small flow rate in order to change $\text{Ni}(\text{NO}_3)_2$ to NiO and then it has been reduced to Ni by reduction reaction with H_2 before carbon growth in a tubular furnace. The samples are referred Ni/AC-WI. The filamentous carbon was synthesized in tubular quartz reactor at 700°C for 1 h in a mixture of 30 ml/min ethylene and 200 ml/min H_2 flow rate (Chaisitsak *et al.*, 2004).

Adsorption of Chromium

Batch mode adsorption studies has been carried out by taking 50 ml of chromium aqueous solution of the desired concentration (0.2–0.5 mg/l) and desired weight of AC in 100 ml conical flasks. By using the chromium aqueous solution, the optimization of the experimental conditions has been observed. Thus, this is the reason for using chromium aqueous solution instead of wastewater sample. The chromium sample has been prepared by dissolving a known quantity of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in deionized water. The working solutions were prepared by diluting the stock solution with distilled water. Then, the conical flasks were agitated at desired speed using a mechanical shaker. The pH was also adjusted by using 0.1 N sulfuric acid or 0.1 N sodium hydroxide (Yang *et al.*, 2015).

After the desired equilibrate time, the adsorbent and adsorbate have been separated by vacuum filtration and the filtered solution was analyzed by HACH-DR/2400 spectrophotometer with 1,5 diphenyl carbazide at 543 nm. Then, the effects of dosage of AC, the initial concentration of chromium, pH, time contact and the agitation speed have been studied. All of the experiments were carried out in duplicate and mean values have been calculated.

Table 1 showed the experimental parameters and its variation which was used in the batch mode adsorption experiment. The run orders for complete randomized experiment have been determined by using MINITAB fractional factorial design software. Fractional factorial designs are useful in factor screening because they reduce down the number of runs to a manageable size. The runs that are performed are a selected subset or fraction of the full factorial design.

Results and Discussion

The growth mechanism of CNTs concerned decomposition of ethylene molecules into hydrogen and carbon, dissolution of the carbon phase into metal catalyst particles and redeposition of the carbon atoms on the surface of the catalyst. The quality of CNTs was accessed by manipulating the temperature, catalyst type and composition, size of the iron particles and support material. The morphology of filamentous carbon grown was observed by field emission scanning microscopy, FESEM (JEOL JSM-6700F). Platinum coating has been used prior to the FESEM observation. The diameter of the carbon nanotubes has been obtained and the surface of the adsorbents has been observed.

Adsorption Capacity on Cr Removal

The influence of several operational parameters including the dose of adsorbent, agitation speed, initial pH, initial chromium concentration and contact time was investigated for maximum yield and crystallinity of nanotubes. The results were expressed as

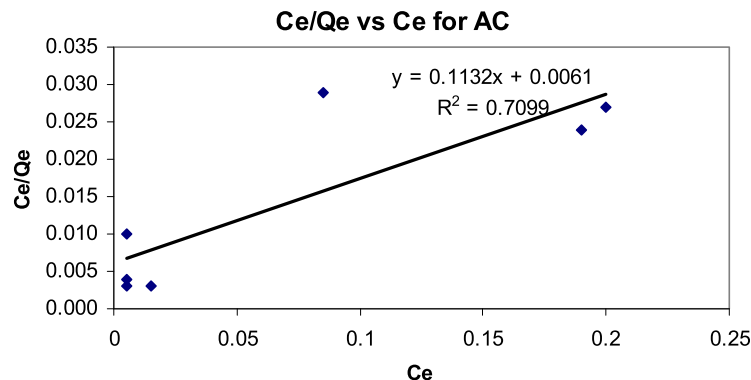


Fig. 1 C_e/Q_e vs. C_e for normal activated carbon.

the adsorption capacity, (mg/g) of the adsorbent on chromium removal which was defined as

$$q_t = \frac{(C_o - C_t)V}{m_s} \quad (1)$$

where:

C_o , and C_t are the Cr(VI) concentrations in mg/L initially and at a given time t , respectively.

V is the volume of the Cr(VI) solution in ml.

m_s is the weight of activated carbon in g.

The removal efficiency (E) of the adsorbent on Cr(VI) ions in solution was calculated using Eq. (2):

$$E(\%) = \left[\frac{(C_o - C_t)}{C_o} \right] \times 100 \quad (2)$$

Adsorption isotherms have been used to determine or examine the relationship between the sorbed (Q_e) and the aqueous concentration (C_e) at equilibrium. In this study, Langmuir and Freundlich equations have been selected since these two sorption isotherms models are most widely used. The Langmuir and Freundlich equations were used to describe the data derived from the adsorption of Cr by each adsorbent over the entire operational parameters range studied. The Langmuir model assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions $S_v + A \leftrightarrow S.A$, where S_v is vacant adsorption site on adsorbent in mole/L adsorbent, A is adsorbate in solution (mole/L Solution), S.A is Adsorbate bound to adsorbent site (mole/m²).

$$\text{At equilibrium } K_{ad} = [S.A]/[S_v][A] \quad (3)$$

Consider total number of sites, S_T , to be fixed: (possible if monolayer coverage is assumed).

$$S_T = [S_v] + [S.A] \text{ (moles/m}^2\text{)} \quad (4)$$

Combining Eqs. (3) and (4)

$$S_T = [S.A]/K_{ad}[A] + [S.A] \quad (5)$$

Solve for $[S.A]$ and use $C_A = [A]$

$$[S.A] = S_T /$$

while, Freundlich model is an empirical equation based on adsorption on a heterogeneous surface (Dow, 1995).

Therefore, from the batch mode experimental data obtained and by using Langmuir equation, the plot of C_e/Q_e versus C_e for each adsorbent has been developed. Figs. 1–3 showed the plot of Langmuir model for normal activated carbon, activated carbon coated with carbon nanotubes (type I) and activated carbon coated with carbon nanotubes (type II) respectively. The slope $\frac{1}{X_m}$ and intercept $\frac{1}{X_m K}$ has been determined from the linearized formed of the Langmuir equation as shown in Table 2. The X_m values obtained from the slope of the graph indicates the constant related to the area occupied by a monolayer of adsorbate which reflecting the adsorption capacity.

For Freundlich model, a plot of $\ln Q_e$ versus $\ln C_e$ which enables the constant $1/n$ and K_f to be determined has been developed and the value for each $1/n$ and K_f is shown in Table 2. Figs. 4–6 showed the plotted graph for normal activated carbon, activated carbon coated with carbon nanotubes (type I) and activated carbon coated with carbon nanotubes (type II) respectively. The K_f value obtained from the Freundlich equations indicates the constant of the relative adsorption capacity of the adsorbent.

All of the figures shown below are the plotted graphs for Langmuir and Freundlich equations for each adsorbent used in the batch mode experiment. The values listed in Table 2 were obtained from these plotted graphs.

Using Langmuir model, it has been noted that activated carbon coated with carbon nanotubes (Type I) has the highest adsorption capacity of 11.574 mg/g followed by activated carbon coated with carbon nanotubes (Type II) and normal activated carbon. It has been calculated that activated carbon coated with carbon nanotubes adsorb 23.7% more compared to normal activated carbon. Similar observation of Freundlich model where activated carbon coated with carbon nanotubes (Type II) has the

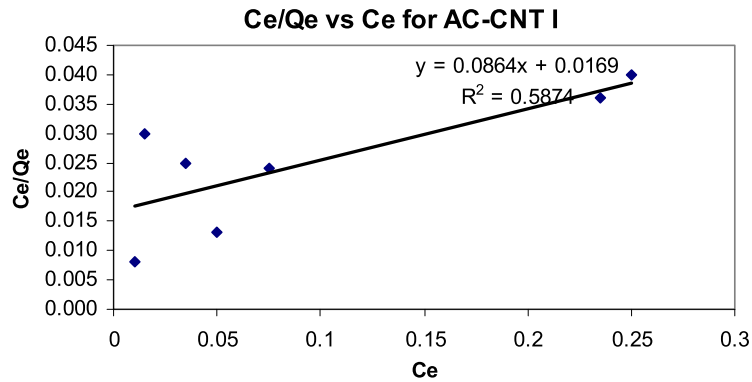


Fig. 2 C_e/Q_e vs. C_e for activated carbon coated with carbon nanotubes (Type I).

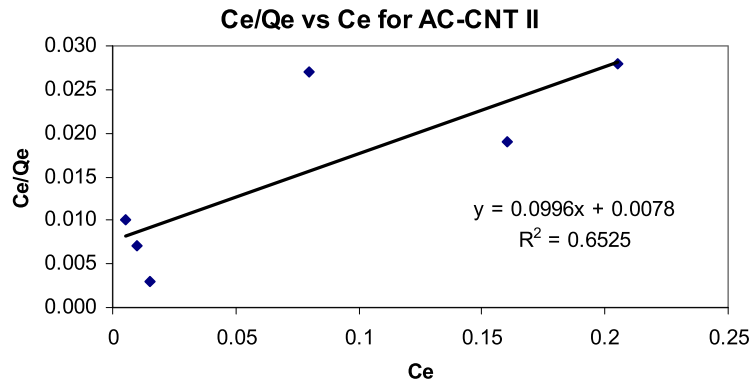


Fig. 3 C_e/Q_e vs. C_e for activated carbon coated with carbon nanotubes (Type II).

Table 2 Isotherms model Constant and correlation coefficients for adsorption of chromium ions from aqueous solution using various adsorbents

Type of adsorbent	Langmuir				Freundlich			
	$\frac{1}{X_m}$	X_m	$\frac{1}{X_m K}$	R^2	$1/n$	$\ln K_f$	K_f	R^2
Normal activated carbon	0.1132	8.834	0.0061	0.7099	0.3361	1.7988	6.0424	0.2088
Activated carbon coated with carbon nanotubes (Type I)	0.0864	11.574	0.0169	0.5874	0.488	1.8793	6.5489	0.253
Activated carbon coated with carbon nanotubes (Type II)	0.0996	10.040	0.0078	0.6525	0.4541	2.1365	8.4697	0.2765

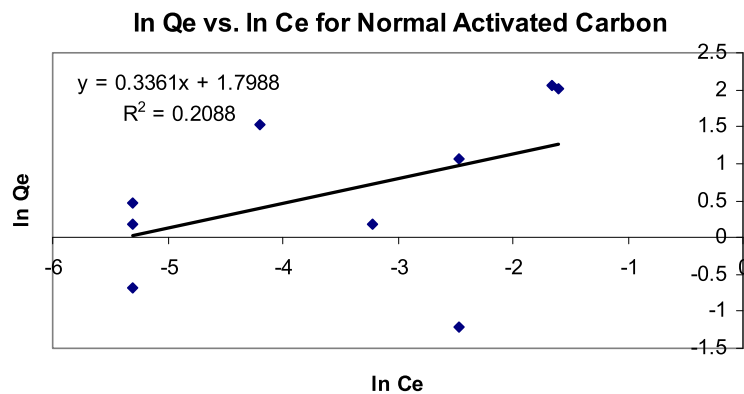


Fig. 4 $\ln Q_e$ vs. $\ln C_e$ for normal activated carbon.

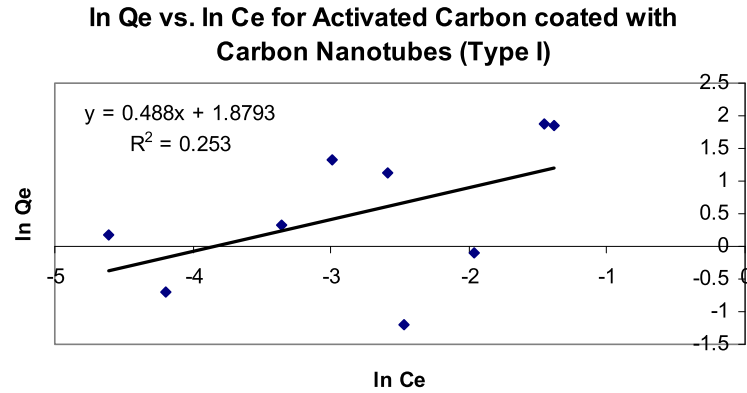


Fig. 5 In Qe vs. In Ce for activated carbon coated with carbon nanotubes (Type I).

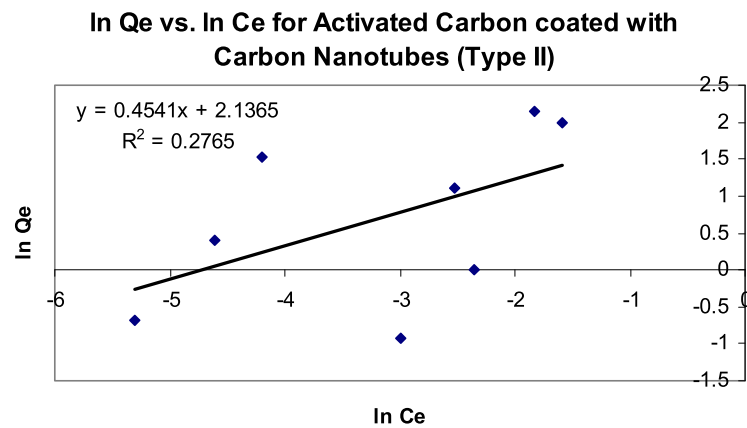


Fig. 6 In Qe vs. In Ce for activated carbon coated with carbon nanotubes (Type II).

highest adsorption capacity of 8.4697 mg/g followed by activated carbon coated with carbon nanotubes (Type I) and normal activated carbon. It is also shows that activated carbon coated with carbon nanotubes has an adsorption capacity of 28.7% more than the normal activated carbon.

Comparison of Langmuir and Freundlich isotherms, Langmuir isotherms have a higher fitting model than Freundlich as the former have higher correlation regression coefficient than the latter as shown in [Table 2](#). Therefore, this indicates the applicability of monolayer coverage of the Cr (VI) on the surface of the adsorbent. This is due to the fact that, activated carbon has a small surface area for metal adsorption ([Nomanbhay and Palanisamy, 2005](#)). Therefore, only monolayer adsorption occurred on its surface.

In conclusion, the usage of activated carbon coated with carbon nanotubes as an adsorbent give a high adsorption capacity compared to normal activated carbon. This is due to the large surface area provided by the carbon nanotubes attached to the activated carbon surfaces. Thus, it increased the ability of the adsorbent to adsorb more chromium ions from the solution. From the adsorption isotherms analysis, it has been found that Langmuir isotherms gives higher correlation on the regression coefficient compared to Freundlich isotherms due to the reasons discussed earlier.

Regression Analysis on Adsorption Capacity

Regression equations for each adsorbent have been developed by using Minitab Release 14 statistical software.

$$\begin{aligned}
 Y = & \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_5 x_5 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{44} x_4^2 + \beta_{55} x_5^2 \\
 & + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{14} x_1 x_4 + \beta_{15} x_1 x_5 + \beta_{23} x_2 x_3 + \beta_{24} x_2 x_4 + \beta_{25} x_2 x_5 + \beta_{34} x_3 x_4 + \beta_{35} x_3 x_5 \\
 & + \beta_{45} x_4 x_5 + \beta_{123} x_1 x_2 x_3 + \beta_{124} x_1 x_2 x_4 + \beta_{125} x_1 x_2 x_5 + \beta_{134} x_1 x_3 x_4 + \beta_{135} x_1 x_3 x_5 + \beta_{234} x_2 x_3 x_4 \\
 & + \beta_{235} x_2 x_3 x_5 + \beta_{345} x_3 x_4 x_5
 \end{aligned} \quad (6)$$

Where Y is the dependent variable which is the adsorption capacity (mg/g), the predicted response; β_0 , intercept; $\beta_1, \beta_2, \beta_3, \beta_4, \beta_5$, linear coefficient; $\beta_{11}, \beta_{22}, \beta_{33}, \beta_{44}, \beta_{55}$, squared coefficients; $\beta_{12}, \beta_{13}, \beta_{14}, \beta_{15}, \beta_{23}, \beta_{24}, \beta_{25}, \beta_{34}, \beta_{35}, \beta_{45}, \beta_{123}, \beta_{124}, \beta_{125},$

Table 3 MINITAB output box regression analysis for normal activated carbon

The regression equation is					
Adsorption Capacity, (mg/g) = 25.3 - 28.5 X1 - 0.0720 X2 - 0.548 X3 - 0.0580 X4					
+ 0.00827 X5 + 0.165 X1X2 + 0.00119 X2X3					
- 0.000019 X2X5					
Predictor	Coef	SE Coef	T	P	
Constant	25.289	4.009	6.31	0.000	
X1	-28.457	7.117	-4.00	0.003	
X2	-0.07196	0.01151	-6.25	0.000	
X3	-0.5476	0.1517	-3.61	0.006	
X4	-0.057969	0.009606	-6.03	0.000	
X5	0.008271	0.003034	2.73	0.023	
X1X2	0.16481	0.03222	5.12	0.001	
X2X3	0.0011892	0.0005337	2.23	0.053	
X2X5	-0.00001927	0.00001067	-1.81	0.104	
S = 0.384236 R-Sq = 99.0% R-Sq(adj) = 98.2%					
Analysis of Variance					
Source	DF	SS	MS	F	P
Regression	8	135.798	16.975	114.98	0.000
Residual Error	9	1.329	0.148		
Total	17	137.127			

β_{134} , β_{135} , β_{234} , β_{235} , β_{345} , interaction coefficients. It is also important to note that, x_1 , x_2 , x_3 , x_4 and x_5 are the independent variables which are known as the initial chromium concentration, adsorbent dosage, pH, time contact and agitation speed respectively.

The results for each regression analysis are shown in the MINITAB Output Box. MINITAB Output **Tables 3** and **4** shows the regression output box developed by MINITAB statistical software package for the regression analysis for normal activated carbon, activated carbon coated with carbon nanotubes (Type I & II) respectively. The print out MINITAB output is produced by following the command path *Stat>Regression* (includes a section labeled 'Analysis of Variance').

Regression analysis for normal activated carbon

The regression analysis for normal activated carbon has been done by analyzing both primary variables and also two factors interaction variables. **Table 3** shows the output obtained from MINITAB.

As a result, the regression equation comprising all the explanatory variables for normal activated carbon analysis is as follows:

Adsorption capacity, (mg/g) = 25.3 - 28.5 Cr Conc. - 0.0720 Adsorbent Dose - 0.548 pH - 0.058 Time Contact + 0.00827 Speed + 0.165 Cr Conc. * Adsorbent Dose + 0.00119 Adsorbent Dose * pH - 0.000019 Adsorbent Dose * Speed

By referring the MINITAB Output Box **Table 3**, the third column "T" and fourth column "P" of the output indicates the test statistics and significant P values respectively. Therefore, the significance of the parameters included can be identified. The larger the magnitude of t-test value and smaller the p-value indicates the high significance of the corresponding coefficient (*Al-Homaidan et al., 2015*). From **Table 3**, t-table with α -value to be 0.025 and degree of freedom equal to 17, the critical value of 't' is 2.1098 has been determined.

From the output, it has been noted that the t-ratios for all parameters are above the t-critical value and small p-values which is less than 0.05, thus all of the parameters are said to be significance to the response variable except for the interaction variable between adsorbent dosage and speed with t-ratio less than the t-critical value and high p-value ($p > 0.05$). From the t-ratios also, it has been identified that adsorbent dosage and contact time are highly significant followed by the interaction variables between initial chromium concentration and pH which also gives a significant value to the response variable.

The coefficient of determination, R^2 has been determined to be 0.99 which means 99% of the variation in adsorption capacity can be explained by the initial chromium concentration, adsorbent dosage, pH, time contact and also speed of mixing. However, the adjusted R^2 obtained is 98.2% of the variation in the adsorption capacity. This adjusted R^2 value is necessary when comparing two or more regression models that predict the same dependent variable but have different numbers of explanatory variables (*Dow, 1995*). By using this adjusted R^2 value, the best model can be identified.

Table 4 MINITAB output box regression analysis for activated carbon coated with carbon nanotubes (Type I)

The regression equation is

$$\begin{aligned}\text{Adsorption Capacity, (mg/g)} = & 28.3 - 33.2 X_1 - 0.0493 X_2 - 0.056 X_3 - 0.0748 X_4 \\ & + 0.00564 X_5 + 0.00059 X_1X_2X_3 + 0.000575 X_1X_2X_4 \\ & - 0.000051 X_1X_2X_5\end{aligned}$$

Predictor	Coef	SE Coef	T	P
Constant	28.268	5.480	5.16	0.001
X1	-33.248	8.588	-3.87	0.004
X2	-0.049320	0.008459	-5.83	0.000
X3	-0.0556	0.1536	-0.36	0.726
X4	-0.07477	0.01476	-5.07	0.001
X5	0.005639	0.003073	1.84	0.100
X1X2X3	0.000590	0.002058	0.29	0.781
X1X2X4	0.0005745	0.0001201	4.78	0.001
X1X2X5	-0.00005069	0.00004116	-1.23	0.249

S = 0.389149 R-Sq = 98.6% R-Sq(adj) = 97.3%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	8	94.269	11.784	77.81	0.000
Residual Error	9	1.363	0.151		
Total	17	95.632			

Regression analysis for activated carbon coated with carbon nanotube (Type I)

The result of regression analysis for activated carbon coated with carbon nanotubes is shown in the MINITAB Output Box [Table 4](#) below. It has been analyzed from both primary and 3 factors interaction variables.

The adsorption analysis has been extracted from regression equation analysis to describe the data is as follows:

Adsorption Capacity, (mg/g) = 28.3 - 33.2 Cr. Conc. - 0.0493 Adsorbent Dose - 0.056 pH - 0.0748 Time Contact + 0.00564 Speed + 0.00059 Cr Conc. * Adsorbent Dose * pH + 0.000575 Cr Conc. * Adsorbent Dose * Time Contact - 0.000051 Cr Conc. * Adsorbent Dose * Speed

From the t-ratios in the MINITAB output box [Table 4](#), shows that there are some of the parameters are highly significant but there are also not significant to the response variable. For an instant, in this study the t-ratios of pH, speed, interaction variables of initial chromium concentration, adsorbent dosage and pH and interaction variables of initial chromium concentration, adsorbent dosage and speed are less than the t-critical value 2.1098 and therefore they are not significant to the adsorption capacity. The observation to the significant P-value stated earlier is greater than 0.05.

Therefore, for this type of adsorbent it has been noted that the parameters which are significant to the adsorption capacity are the initial chromium concentration, adsorbent dosage and also the time contact of the batch mode experiment. However, from the analysis the t-ratio of the adsorbent dosage gives the highest value compared to others which determines that it is highly significant to the response variables. Then the significance levels are followed by the time contact and the initial chromium concentration.

The coefficient of determination which is the square of the coefficient of correlation, R^2 is 98.6% which means that 98.6% of the variation in adsorption capacity can be described for by all explanatory variables and the adjusted R^2 value obtained in this analysis is 97.3%. The values for R^2 and adjusted R^2 obtained from activated carbon coated with carbon nanotubes (Type I) regression analysis are lower than the values of the coefficient of determination obtained from the normal activated carbon analysis.

Regression analysis for activated carbon coated with carbon nanotube (Type II)

The regression output obtained from MINITAB software is shown in the Output Box [Table 5](#) below. The analysis has been done by both primary and 3 factors interactions explanatory variables.

Table 5 MINITAB output box regression analysis for activated carbon coated with carbon nanotubes (Type II)

The regression equation is					
Adsorption Capacity, (mg/g) = 40.3 - 45.5 X1 - 0.0674 X2 - 0.754 X3 - 0.101 X4					
+ 0.00285 X5 + 0.00648 X1X2X3 + 0.000734 X1X2X4					
- 0.000080 X1X2X5					
Predictor	Coef	SE Coef	T	P	
Constant	40.284	4.141	9.73	0.000	
X1	-45.538	6.489	-7.02	0.000	
X2	-0.067370	0.006391	-10.54	0.000	
X3	-0.7542	0.1161	-6.50	0.000	
X4	-0.10126	0.01115	-9.08	0.000	
X5	0.002847	0.002322	1.23	0.251	
X1X2X3	0.006484	0.001555	4.17	0.002	
X1X2X4	0.00073380	0.00009075	8.09	0.000	
X1X2X5	-0.00008038	0.00003110	-2.58	0.029	
S = 0.294038 R-Sq = 99.5% R-Sq(adj) = 99.0%					
Analysis of Variance					
Source	DF	SS	MS	F	P
Regression	8	148.424	18.553	214.59	0.000
Residual Error	9	0.778	0.086		
Total	17	149.202			

The regression equation embracing all the explanatory variables obtained from the regression analysis done by MINITAB is as follows:

Adsorption Capacity (mg/g) = 40.3 - 45.5 Cr Conc. - 0.0674 Adsorbent Dose - 0.754 pH - 0.101 Time Contact + 0.00285 Speed + 0.00648 Cr Conc. * Adsorbent Dose * pH + 0.000734 Cr Conc. * Adsorbent Dose * Time Contact - 0.000080 Cr Conc. * Adsorbent Dose * Speed

By referring the t-ratios obtained from the analysis, it shows that some of the explanatory variables are highly significant and some of the parameters are significant to the response variable. However, the speed of mixing during the experiment is not significance to the adsorption capacity due to the t-ratio and the p-value for this primary variable are 1.23 and 0.251 respectively. The t-ratio is less than t-critical value 2.1098 and the p-value for this parameter are larger than 0.05.

Specifically, the explanatory variables which are highly significant to the adsorption capacity of the adsorbent are the initial chromium concentration, adsorbent dosage, pH, time contact, interactions between initial chromium concentration, adsorbent dosage and pH, interactions between initial chromium concentration, adsorbent dosage and time contact and also interactions between initial chromium concentration, adsorbent dosage and speed of mixing during the experiment.

The coefficient of determination, R^2 obtained from the regression analysis for the activated carbon coated with carbon nanotubes (Type II) is 99.5% which very high compared to other regression model. 99.5% of the variation in adsorption capacity can be accounted for by the explanatory variables. The adjusted R^2 obtained for this regression analysis is 99.0%. The adjusted R^2 value for this regression model is higher than other regression models for different types of adsorbent. Therefore, it can be concluded that this regression model is the best model compared to others due to the adjusted R^2 value.

Effect of Process Variables on Adsorption Capacity

Effect of pH

The pH is also said to be an important parameter for the adsorption of metal ions from aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of adsorbent and the degree of ionization of the adsorbate during the reaction. The removal of chromium by three types of adsorbents with various pH has been studied. The variations of pH used in the experiments are within the range of 2–4. It has been reported that the variation in adsorption capacity in this pH range is largely due to the influence of pH on the adsorption characteristic of the adsorbents used (Nomanbhay and Palanisamy, 2005). This is due to the highly protonated adsorbent surfaces and also the uptake of the free ionic Cr. Therefore, with

Table 6 Effect of pH due to the coefficient of determination, R^2 values for various adsorbents used in the removal of chromium

Adsorbent type	R^2 (%)	Adjusted R^2 (%)
Normal activated carbon	1.0	0.0
Activated carbon coated with carbon nanotubes (Type I)	0.5	0.0
Activated carbon coated with carbon nanotubes (Type II)	0.1	0.0

Table 7 Effect of time contact due to the coefficient of determination, R^2 values for various adsorbents used in the removal of chromium

Adsorbent type	R^2 (%)	Adjusted R^2 (%)
Normal Activated Carbon	8.0	2.2
Activated Carbon coated with Carbon Nanotubes (Type I)	5.6	0.0
Activated Carbon coated with Carbon Nanotubes (Type II)	7.9	2.1

Table 8 Effect of speed due to the coefficient of determination, R^2 values for various adsorbents used in the removal of chromium

Adsorbent type	R^2 (%)	Adjusted R^2 (%)
Normal activated carbon	0.5	0.0
Activated carbon coated with carbon nanotubes (Type I)	0.2	0.0
Activated carbon coated with carbon nanotubes (Type II)	0.0	0.0

increasing pH from 2 to 4 was decrease the degree of protonation of the surface and reduced the adsorption capacity of the chromium. The optimum pH which has been observed during the experiments with 100% Cr(VI) removal is at pH 2.0.

However, from the regression model developed, the value of adjusted R^2 for each adsorbent shown in **Table 6** gives a zero value. Although the values of R^2 is very small, there is no reason to reject the model since it has been clearly stated that pH affects the adsorption capacity as discussed earlier.

Effect of time contact

The variation of time contact in this study is within the range of 60–240 min. Therefore, the effect of this parameter to the adsorption capacity has been observed. It has been reported by (Karthikeyan *et al.*, 1996; Levine *et al.*, 2001) that the removal efficiency of chromium increased with an increased in contact time. From regression analysis also denotes that the time contact during the experiments is highly significance with the adsorption capacity for the three adsorbents used. However, the regression model specifically for the time contact which has been developed by selecting the time contact as the predictor variable gives a small value for both R^2 and adjusted R^2 for each adsorbent as seen in **Table 7**. Despite the small R^2 in this model, it has been clear that the adsorption capacity is dependent on the time contact. Therefore, rejection of this model is not necessary.

Effect of agitation speed

The effect of agitation speed on adsorption capacity of chromium has been studied by varying the speed of agitation from 100 to 200 rpm. It has been said that the percentage of chromium removal increased with increasing agitation speed. From the regression model which has been developed, it is clearly stated that the speed of mixing during the batch adsorption experiment is significant to the removal of chromium using normal activated carbon p-value is less than 0.05 as in **Table 8**. This is due to the fact that, the increase of agitation speed, improves the diffusion of chromium ions towards the surface of the adsorbents. However, it is not significance to the adsorption by using activated carbon coated with carbon nanotubes type I and type II. The regression analysis which has been done specifically for this parameter also shows very small R^2 and adjusted R^2 .

Optimization of Process Variables for Removal of Chromium

As discussed earlier, the batch adsorption experiment which has been done was completely randomized by MINITAB fractional factorial design. The optimum condition has been determined from the tabulated results of adsorption capacity. The adsorption capacity for each experiment has been calculated and has been listed in **Table 9** for the three types of adsorbents which are normal activated carbon, activated carbon coated with carbon nanotubes type I and activated carbon coated with carbon nanotubes type II respectively. The predictive values of the adsorption capacity have been determined from the regression equation obtained. From

Table 9 The parameters condition for optimum adsorption capacity (mg/g) obtained from each adsorbent used

<i>Adsorbent type</i>	<i>Chromium conc. (mg/l)</i>	<i>Adsorbent dosage, m (mg/50ml)</i>	<i>Adsorbent dosage, m (mg/L)</i>	<i>pH</i>	<i>Time contact (min)</i>	<i>Agitation speed (rpm)</i>	<i>Cr remaining, c (mg/L)</i>	<i>Cr removed, x (mg/l)</i>	<i>% Cr removed</i>	<i>Predictive adsorption capacity, (mg/g)</i>	<i>Experimental adsorption capacity, x/m (mg/mg)</i>
Normal activated carbon	0.5	2	40	4	60	200	0.17	0.33	66.0	7.49	8.250
Activated carbon coated with carbon nanotubes (Type I)	0.5	2	40	4	60	200	0.23	0.27	54.0	6.68	6.750
Activated carbon coated with carbon nanotubes (Type II)	0.5	2	40	2	60	100	0.14	0.36	72.0	8.551	9.000

this tabulated results, the optimum conditions for each parameters have been identified and highlighted. The optimum conditions are determined from the highest value of adsorption capacity, (mg/g) of the chromium concentration. The parameters conditions which contributes to the optimum adsorption capacity for each adsorbents used are shown in Table 9.

From the experimental results obtained, the optimum parameters for each adsorbent are dependent on the adsorbent characteristics. The values for each parameter used might be similar and it might vary in order to obtain a maximum adsorption capacity. From Table 9, it has been noted that in order to obtain an optimum value of adsorption capacity, the optimized value for the initial chromium concentration should be 0.5 mg/L with adsorbent dosage of 2 mg in 50 ml solution and it requires 60 min contact time between the adsorbent and the solution for each type of adsorbent studied.

However, the optimized pH for the normal activated carbon and activated carbon coated with carbon nanotubes type I should be at pH 4 which is different to the activated carbon coated with carbon nanotubes type II adsorbent where the optimized pH value for this particular adsorbent should be at pH 2. Furthermore, the agitation speed for activated carbon coated with carbon nanotubes type II is 100 rpm which is also varies with optimized agitation speed obtained for the normal activated carbon and activated carbon coated with carbon nanotubes type I which is said to be 200 rpm. From the tabulated result, the activated carbon coated with carbon nanotubes type II gives the highest value of adsorption capacity with 9.0 mg/g compared to the normal activated carbon and the activated carbon coated with carbon nanotubes type II which are 8.25 and 6.75 mg/g respectively. In conclusion it is clearly confirmed that the activated carbon coated with carbon nanotubes type II gives high adsorption capacity of the chromium concentration within the minimum parameters variation as listed in Table 9.

Conclusion

CNT materials were produced in two horizontal tubular reactors by using different catalyst weights and process temperatures. The formation of dense MWCNT was confirmed through microscopic analysis. The application of carbon nanotubes in removal of chromium from aqueous wastewater have been done in environmental field. In this study, three adsorbents have been used in the study of chromium removal from aqueous wastewater which comprised of normal activated carbon, activated carbon coated with carbon nanotubes type I and II. By comparing these three adsorbents, the efficiency of the adsorption has been determined. There are 5 factors which were said to be contributing the adsorption capacity in the experiment have been studied and the optimized conditions for each parameter have been identified. The initial chromium concentration, adsorbent dose, pH, time contact and the agitation speed are the factors which have been studied. The values for each parameter are completely randomized throughout the designed experiment as discussed earlier. All of the factors used in the adsorption experiment were said to be significance with the adsorption capacity which has been identified from the regression analysis.

Study has been proven that the activated carbon coated with carbon nanotubes as an adsorbent is a good candidate for adsorption of chromium ions and promisingly to be a good candidate for adsorption of other heavy metal ions as well. Hopefully, this study gave an enormous impact on the development of wastewater treatment and the development of nanotechnology applications.

Acknowledgment

This work was supported by International Islamic University Malaysia, Department of Biotechnology Engineering, BERC.

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Residual Stress Analysis for Sustainable Structural Integrity Assessment of an Engineering Component

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List of Symbols

$d(\theta, z)$	Hole diameter before trepanning step
$d'(\theta, z)$	Hole diameter after trepanning step
ν	Poisson's ratio
BU	Bristol University
DH	Deep-hole
DHD	Deep-hole drilling
DHFE	Deep-hole finite element
E	Young's modulus
EPRI	Electric power research institute
FE	Finite element
NKH	Non-linear kinematic hardening

Introduction

Residual stress may be defined as the self-equilibrating internal stress existing in a free body under uniform temperature conditions without any external load or thermal gradient. At equilibrium both the resultant force and the resultant moment of the body are zero. It is most commonly termed as the “residual stress” as it may be “left over” by a previous manufacturing process. Macherauch and Kloos (1986) suggested a classification of residual stress into three groups, as shown in Fig. 1, using the term “homogeneous” to mean “constant in magnitude and direction” as:

- (1) Type I – Macro residual stresses which are homogeneous across several grains of the material and are equilibrated over the body.
- (2) Type II – Nearly homogeneous micro residual stress which are homogeneous only on a part of a grain or one grain and equilibrated over several grains. Such stresses may exist in single-phase materials due to anisotropy in the behavior of each grain or develop in multi-phase materials due to the different properties of different phases.
- (3) Type III – Inhomogeneous micro residual stresses which are inhomogeneous even over sub-microscopic distances inside the body but in equilibrium on small parts of a grain due to the existence of dislocations and other crystalline defects.

One or a superposition of these three categories defines all the residual stress states. However, from an engineering perspective the first category has more importance than the other two since any modification to equilibrium may also modify the external dimensions of the body. Residual stresses arise from a number of sources and can exist in the unprocessed raw material, during manufacturing processes involving material deformation, heat treatment, machining or processing operations which transform the shape or change the properties of a material or can also arise from in-service loading (Withers and Bhadeshia, 2001a).

Welding process commonly generates residual stresses in engineering structures and components which are the key factor in the structural integrity assessment. It is thought that reheat cracking in plant structures is solely driven by the presence of residual stress field (Baikie *et al.*, 1997; Dhooze, 1998; Skelton *et al.*, 2003). Compressive residual stresses can help to restrain crack propagation and enhance fatigue life and therefore, can have a beneficial effect on structural integrity. In contrast, tensile residual stresses in general have an adverse effect on brittle fracture, corrosion properties and fatigue performance. With residual stress levels reaching the material yield strength, the consequence of residual stress effects on structural integrity become substantial. Reliable technique to correctly analyze these residual stresses can help move away from decade old over conservative structural integrity assessment and is a key to an accurate and sustainable structural integrity assessment.

Residual Stress Measurement Methods

Strains rather than stresses are invariably measured by residual stress measurement methods. The measured strains can be used to deduce the residual stresses through a simple elastic relation using the appropriate material elastic constants including the Young's

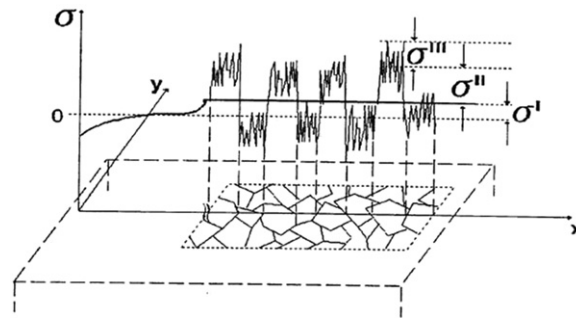


Fig. 1 Classification of residual stresses according to length scales. After Kandil, F.A., Lord, J.D., Fry, A.T., Grant, P.V., 2001. A review of residual stress measurement methods – A Guide to Technique Selection. NPL Report MATC (A) 04.

modulus, E and the Poisson's ratio (ν). A single value of the stress is often quoted instead of its distribution and is assumed to be constant within the measurement volume. When measured residual stresses by different techniques are compared, the sampling volume and the resolution of each measurement method are considered in relation to the type of residual stress being measured (see Fig. 1), in particular if type II and III micro stresses are of interest (Kandil *et al.*, 2001). The concept of the characteristic volume is also considered essential. It is the volume over which a given type of residual stress averages to zero. Most material removal techniques, e.g., the hole drilling method, layer removal method remove large volumes of material over which type II and III stresses average to zero and only the macro residual stresses remain and are measured.

Residual stress measurement methods range from non-destructive technique via semi-destructive to the fully destructive technique. Non-destructive technique includes the diffraction, magnetic and ultrasonic techniques. Semi-destructive techniques where the component is partially damaged and does not compromise its integrity include the incremental center-hole drilling technique and the deep-hole drilling technique. In the destructive technique the component is destroyed completely and includes the Sachs method (Sachs, 1927; Garcia-Granada *et al.*, 2000) and the curvature and the layer removal method (Treuting and Read, 1951; Withers and Bhadeshia, 2001b). Here a description of the mechanical strain relief deep-hole drilling method is reviewed due to its relevance to the present study.

Deep-hole drilling (DHD) method measures residual stresses in thick components. A schematic illustration of the method is provided in Fig. 2. A small reference hole is drilled through the component and the diameter $d(\theta, z)$ of the hole is measured along its depth. A cylindrical column (core) of material concentric to the reference hole is then removed from the component, using a trepanning technique. This causes the stresses in the cylindrical core to relax and change the reference hole diameter and column dimensions. The dimensions of the column and reference hole diameter $d'(\theta, z)$ are re-measured. The dimensional changes caused by removing the material from the bulk of the specimen are then used to calculate the residual stresses.

The method was originally developed by Zhdanov and Gonchar (1978) and Beaney (1978). Zhdanov and Gonchar (1978) measured residual stress in steel welds by drilling 8 mm diameter hole followed by an incremental cutting of a concentric column of metal of 40 mm diameter from the specimen using a hollow drill. By using changes in the axial length during incremental trepanning and measuring the diameter changes in two mutually perpendicular directions at a number of fixed distances along the reference hole they measured the residual stresses in the component.

Beaney's (1978) approach to the measurement procedure was to gun-drill a very smooth and straight hole of diameter 3.175 mm along the direction of a principal stress component and to measure its diameter at three in-plane angles of 0° , 45° and 90° at every 2 mm depth along the reference hole. In his approach, he measured the hole diameter first using strain gauges fixed onto two parallel beams fixed together and drawn along the sidewalls of the hole. By using the strain gauges the changes in diameter were measured due to the trepanning of the core by electro-chemical machining (ECM) process which allows to measure the beam deflection.

A substantial development of the technique has undergone over the past two decades mainly at University of Bristol (Bonner and Smith, 1994; Smith and Bonner, 1996; George *et al.*, 2000; Smith *et al.*, 2000; Hossain *et al.*, 2017) both in the improvement of the method (e.g., using air-probe to measure the hole diameter) and its accuracy. George *et al.* (2002) used small holes to measure stresses in calibration of aluminum and steel samples arising from external applied loading.

The technique was further developed by using smaller hole and smaller core which improved the precision of the measured stresses. Measurements of diametral distortions at higher number of angles, i.e., 18 angular measurements substantially reduced the error associated with the air-probe measurements. Other advancement includes the design of a small-scale portable deep-hole drilling rig (Kingston, 2004; Ficquet, 2007) capable of measuring residual stresses in metal parts of depths in the range of 5–500 mm.

George (2000) used finite element analysis (FEA) to model a pipe under autofrettage and compared the predicted FEA residual stress distribution with the stress distribution measured using deep-hole drilling (DHD) and Sachs methods. By considering removal of elements which defined drilled reference hole and electric discharge machining (EDM) thickness, he further modelled and simulated the deep-hole drilling of the autofrettaged tube. He found that the predicted FEA simulated DHD residual stresses compared well with the stresses measured by the DHD method. In his DHD FEA analysis, he removed the set of elements defining

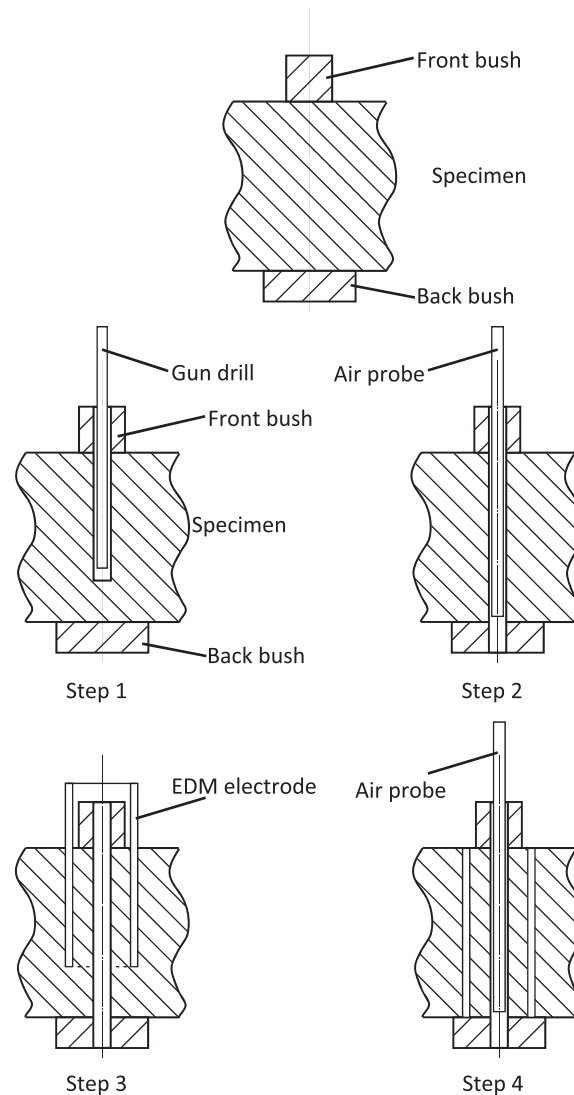


Fig. 2 Schematic of the DHD method: Step 1 – Drilling a reference hole, step 2 – Measuring reference hole diameter, step 3 – Trepanning a core and step 4 – Re-measuring reference hole diameter.

the EDM thickness, i.e., the material which is machined away during the trepanning stage in a single step. However, in practice the trepanning process takes place incrementally so that the removal of elements defining the EDM thickness needs to be carried out incrementally in order to model the trepanning process more realistically.

Residual Stress in Structural Integrity

Residual stresses have influence on the life assessment of engineering structures. Manufacturing process and final fabrication may generate residual stresses. Tensile residual stresses generally have detrimental effect on life of engineering components. The presence of residual stress can solely initiate cracking even in the absence of service loads. When the component enters into service, tensile residual stress combines with service stresses and reduces crack-initiation time and accelerates growth rates of pre-existing or service-induced defects. Welding is a common manufacturing process where residual stresses can reach the level of yield stress. Post-weld heat treatment is usually applied to reduce such stress level. One of the reasons for residual stresses to develop in engineering components is the presence of repair welds. Fabrication defects in castings or welds, or in-service degradation of components which can be treated or improved by applying repair welds and thereby extend the life and economic operation of ageing engineering plant. Repair weld can be applied to a localized shallow excavation using standard weld procedures or to deep excavations covering a significant proportion of the structure. Weld metal failing to fuse completely with the sidewall of the joint lead to sidewall fusion defects. The need to rectify these defects or degraded heat affected zone (HAZ) material typically leads to repairs that are offset from the weld centerline. A survey of weld repair technologies used by electric power research institute (EPRI)

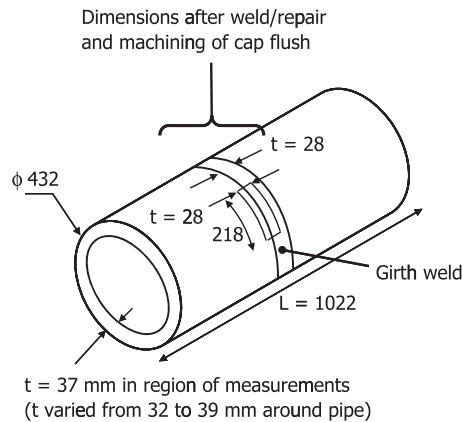


Fig. 3 Arrangement of stainless steel pipe girth weld with repair weld, dimensions in mm. Reproduced from Hossain, S., 2005. Residual stresses under conditions of high triaxiality. PhD Thesis. UK: University of Bristol.

member utilities (Candy *et al.*, 2001) has found that 40% of all repairs to steam chests, piping and headers resulted in subsequent cracking. This was thought to be due to the high level of residual stresses associated with repair process performed without implementing post-weld heat treatment.

Hole drilling (incremental center-hole drilling) and X-ray diffraction techniques are the most widely applied methods to determine the residual stresses in engineering components. However, these methods only provide near surface residual stresses. In order to accurately assess the structural integrity of a component, a good description of the through thickness residual stress distribution along the depth of the component is required. Deep-hole drilling method is a practical means of measuring residual stresses deep into metal parts, e.g., 500 mm deep into steels (Kingston, 2004), whereas the non-destructive neutron diffraction method suffers from limitation in penetrative depth, cost and the availability. Deep-hole drilling residual stress measurements were carried out on a number of 316 H stainless steel mock-up components (George *et al.*, 2002) provided by British Energy Generation Ltd, including information on their fabrication history. Previous studies (Hossain, 2005; Mahmoudi *et al.*, 2009; Hossain *et al.*, 2011a; Zheng *et al.*, 2017) highlighted that the DHD measurement of highly triaxial residual stresses can be problematic due to the redistribution of the stresses during the strain relaxation. A numerical study of the deep-hole drilling process was undertaken to explore how the stress triaxiality and the redistribution influence the deep-hole measurement technique.

Material and Test Specimen

The test specimen consisted of a stainless steel cylindrical pipe girth weld with repair weld. Detail of the fabrication history is available in (Mitsui Babcock Report 316, 2002). Fig. 3 shows the global dimension of the test component. The length included 1022 mm, with outer diameter about 432 mm and wall thickness varying between 32 and 39 mm around the pipe. A 2.4 mm diameter wire tungsten inert gas (TIG) root was used to produce a girth butt weld near the mid-length of the pipe, followed by 16 manual metal arc (MMA) passes with an average girth weld heat input of 2.2 kJ/mm using 2.5, 3.2, 4, and 5 mm diameter electrodes. Further detail of the weld is provided in Hossain *et al.* (2006). By grinding at a location 180°, a repair cavity, 218 mm long at the outer surface of the cylinder, 26 mm deep, 7 mm offset from the girth weld centerline, with sidewall and end run-out angles of 15° and 45° respectively, was excavated. The repair excavation was filled with 14 MMA passes with heat input of 2.1 kJ/mm combining 3.2 mm and 5 mm diameter electrodes. Welding was intentionally carried out in a single direction, in order to maximize the superposition of start and stop effects. The repair cap was ground flush following welding.

The locations of the DHD measurement in the offset repair included Hole 1 which was located at the intersection of the centerline of the girth weld and the mid-length of the repair, and Hole 2 which was located at the intersection of the girth weld centerline and the stop end of the repair (Hossain *et al.*, 2006).

Weld Residual Stress

Fig. 4 shows through-thickness variation of the measured residual stresses at the locations, Hole 1 (mid-length) and Hole 2 (end position). Fig. 4(a) shows the longitudinal component and Fig. 4(b) shows the transverse component of the weld residual stresses. Also shown are the finite element predictions of the weld residual stress distribution. A reasonably good correlation existed between the measured and the prediction particularly for the transverse component of stress (Fig. 4(b)). For the longitudinal stress component (Fig. 4(a)), although similar trend existed, the FEA prediction was much higher in magnitude. For example, the FEA predicted peak longitudinal stress component was almost 300 MPa higher than the measured, giving an error of approximately 50%. In contrast, the error in the measured stresses in steel part is estimated to be ± 30 MPa (George *et al.*, 2002). Thus, the measured result in Fig. 4(a) cannot be acceptable and is further explained below.

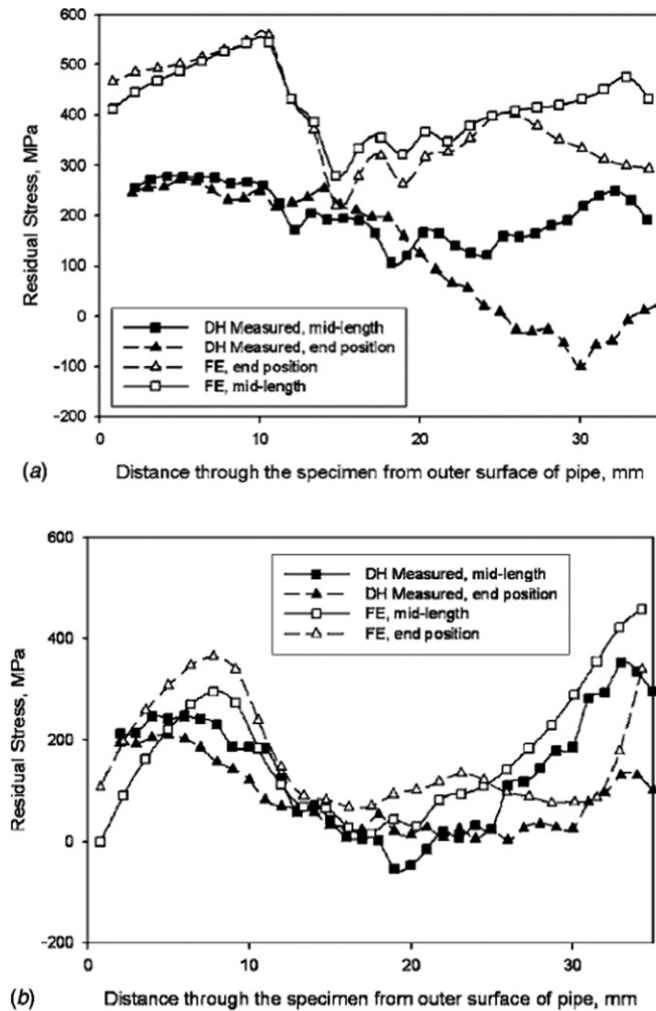


Fig. 4 Measured residual stresses in a 218 mm long, offset, 316 H stainless steel repair weld compared with 3D FEA predictions.

(a) Longitudinal and (b) Transverse. Reproduced from Hossain, S., Truman, C.E., Smith, D.J., Bouchard, P.J., 2006. Measurement of residual stresses in a type 316H stainless steel offset repair in a pipe girth weld. *Journal of Pressure Vessel Technology*, Transactions of the ASME 128 (3), 420–426.

When measuring residual stresses using mechanical strain relief method in components containing highly triaxial residual stress field close to yield extra caution have to be exercised since the introduction of a free surface, created as part of the measurement procedure, can lead to plastic redistribution of the residual stress field. Under normal cases the plastic redistribution is not accounted for in the elastic inversion algorithms of the experimental procedure. The FEA predicted longitudinal residual stress components for both mid-length (Hole 1) and end positions (Hole 2) shown in [Fig. 4\(a\)](#) are substantially high enough for plastic redistribution to occur during the trepanning stage of the deep hole drilling measurement.

Influence of Plastic Redistribution in DHD Procedure

The influence of trepanning step on the DHD measured result was verified by [Hossain et al. \(2011a\)](#). They carried out a FEA simulated DHD procedure on repair welded pipe. The methodology and sequence consisted of four steps. (1) FEA simulation of weld residual stress field conducted by British Energy Generation Ltd (BEGL). (2) The BEGL predicted stresses were mapped onto a mesh which allowed DHD measurement simulation. (3) The FEA DHD measurement simulation was carried out. (4) The FEA simulated DHD reconstructed residual stress distribution was compared with the previously measured stress distribution.

[Fig. 5](#) shows the 3D quarter model (University of Bristol, BU model) of the welded pipe. The overall dimension and the drilling and trepanning regions are shown in [Fig. 5](#) as well. The model constructed with 14,330 quadratic brick elements has two symmetry planes including the XY (1–2) plane and the YZ (2–3) plane. As the repair was offset from the girth weld centerline, the XZ (1–3) symmetry plane did not exist. Although the short repair spans only 218 mm, i.e., covering about 16% of the circumference of the pipe, a fully circumferential repair weld was assumed in the model; the purpose of the FEA study was to investigate the influence of the plastic redistribution in the DHD measurement process on the initial residual stress. Furthermore, by using the British Energy

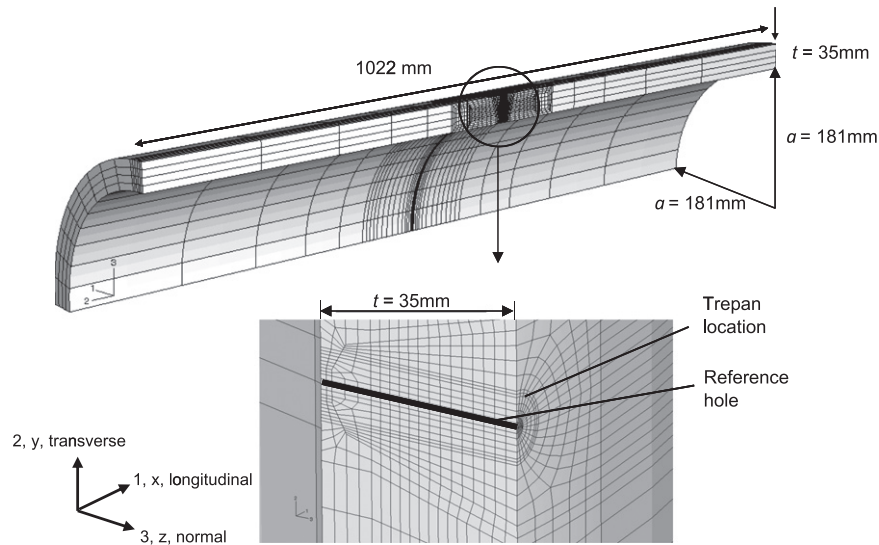


Fig. 5 3D mesh of the repair welded pipe showing overall geometry and the drilling and trepanning regions. Reproduced from Hossain, S., 2005. Residual stresses under conditions of high triaxiality. PhD Thesis. UK: University of Bristol.

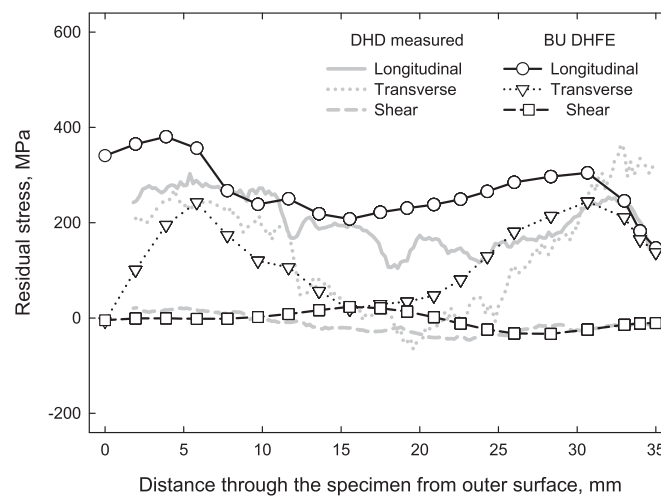


Fig. 6 Comparison of the residual stress distribution at the mid-length of repair weld between the measured and the FEA reconstructed using NKH model. Reproduced from Hossain, S., Goudar, D.M., Truman, C.E., Smith, D.J., 2011a. Simulation and measurement of residual stresses in a Type 316H stainless steel offset repair in a pipe girth weld. Materials Science Forum 681, 492–497.

Generation Limited (BEG) predicted weld residual stress field as initial condition for the BU model the influence of circumferential repair was minimized. Appropriate material model was constructed for parent, girth and repair weld regions, which can be found elsewhere (Hossain *et al.*, 2006).

In addition to the influence of plastic redistribution on the FEA simulated DHD result, the effect of different material hardening models was also studied. Detail of the DHD simulation and the measurement are both provided in Hossain *et al.* (2011a). Fig. 6 shows the main outcome of the study. The DHD measured residual stress distribution at the mid-length (Hole 1) of repair weld (shown in Fig. 4) is compared with the FEA simulated DHD reconstructed residual stress distribution using non-linear kinematic hardening (NKH) model. An excellent correlation exists between the FEA simulated DHD and the DHD measured residual stress distributions as shown in Fig. 6.

FEA Validation of a Modified DHD Method

In the preceding section, results from the DHD FEA simulation highlighted how the DHD process influences the measured residual stresses. In this section, a variation to the standard DHD technique, known as the over-core deep-hole drilling (oDHD) technique

(Hossain *et al.*, 2011b) developed to avoid plasticity issues is validated by utilizing FEA simulation of the technique. The influence of material removal and cutting sequence on the initial residual stress field during the DHD measurement process was explored through a 3D FEA. An FEA predicted weld residual stress field in a 40 mm thick butt-welded pipe was applied as the initial stress condition in a DHD FEA model. Detail of the FEA simulation of the weld residual stress, the standard DHD simulation and the oDHD simulation are provided in Hossain *et al.* (2011b). Fig. 7 shows the schematic of the butt-welded pipe, with outer diameter 369 mm, thickness 40 mm, and length 800 mm. Two SUSF316 stainless steel cylinders of length 400 mm each were circumferentially welded by using alloy 82 weld metal. The DHD measurement and simulation were both carried out through the weld thickness from the outer surface of the pipe.

The DHD reconstructed residual stresses are compared with the initial FEA predicted stresses in Fig. 8. Both the longitudinal and the transverse components of the stresses are shown. Close to the outer surface of the pipe, the longitudinal stresses significantly redistributes. This is attributed to the influence of plasticity during trepanning. A recently developed incremental deep-hole drilling (iDHD) technique (Mahmoudi *et al.*, 2009; Zheng *et al.*, 2017) takes into account the effect of plasticity during trepanning and provides an approximate solution to measurements of near yield residual stresses. The iDHD method has successfully been applied to various components (Hossain *et al.*, 2012; Hosseinzadeh *et al.*, 2009, 2010; Kingston *et al.*, 2010; Mahmoudi *et al.*, 2009b; Mahmoudi *et al.*, 2011; Robinson *et al.*, 2010, 2008; Zheng *et al.*, 2017). However, the iDHD method suffers from a limited spatial resolution.

In contrast, the oDHD technique (Hossain *et al.*, 2011b; Zheng *et al.*, 2017) used in the present analysis significantly improves the spatial resolution. By adding an extra step between steps 2 and 3 in the standard DHD procedure, Fig. 2 where a large core, diameter 40 mm is trepanned ensuring the initial near yield residual stress to redistribute elastically around the reference hole. Hence only elastic unloading occurs during final trepanning step 3. The choice of the over-core size depends on the specimen thickness and the cutting sequence. Zheng *et al.* (2017) studied different over-core trepan diameter to optimize the

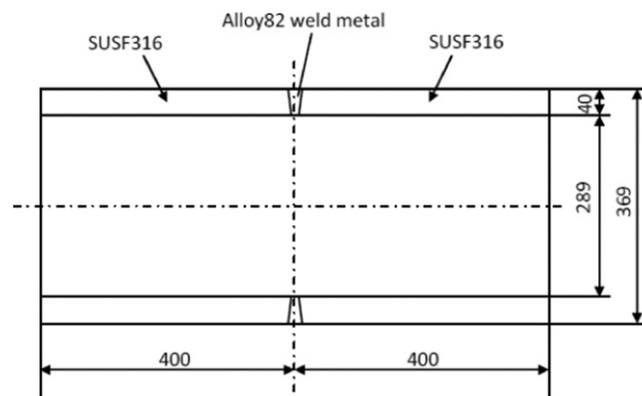


Fig. 7 Schematic of girth-butt welded pipe. All dimensions in mm.

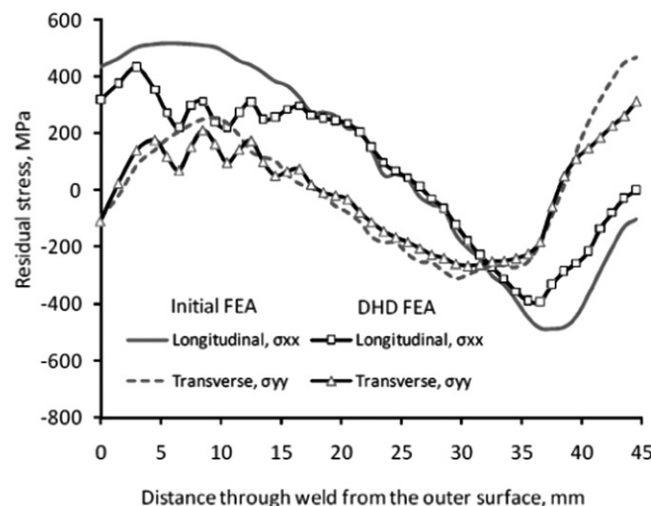


Fig. 8 Comparison of the standard DHD FEA reconstructed and the initial FEA predicted residual stress distribution in the butt-welded pipe. Reproduced from Hossain, S., Kingston, E., Truman, C.E., Smith, D.J., 2011b. Finite element validation of the over-coring deep-hole drilling technique. Applied Mechanics and Materials 70, 291–296.

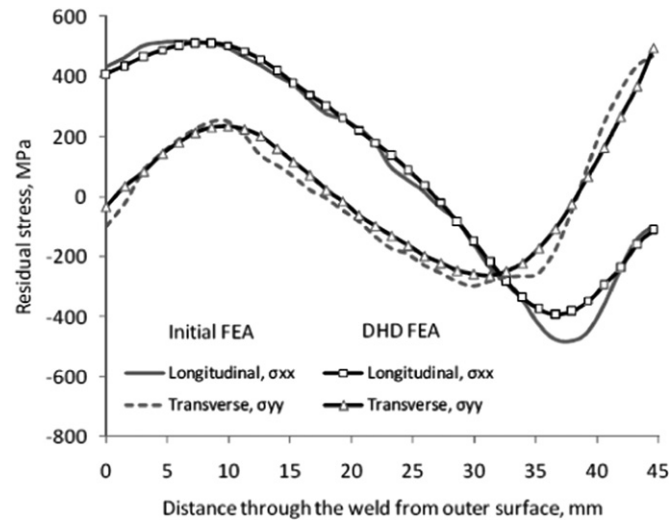


Fig. 9 Comparison of the oDHD FEA reconstructed and the initial FEA predicted residual stress distribution in the butt-welded pipe. Reproduced from Hossain, S., Kingston, E., Truman, C.E., Smith, D.J., 2011b. Finite element validation of the over-coring deep-hole drilling technique. *Applied Mechanics and Materials* 70, 291–296.

trepan size. They found that the over-core size should be larger than both the width and depth of the welding to generate elastic stress relaxation. The size of the over-core diameter can be halved from 40 mm to 20 mm with effectively the same result to keep the destruction to the component at minimum. However, the cutting process may need to be adjusted. Therefore, a thorough FEA simulation of the oDHD procedure conducted prior to a practical measurement can provide an optimum over-core dimension.

An excellent comparison of the oDHD reconstructed residual stress distribution with the initial FEA predicted is shown in **Fig. 9**. The dimension included: Reference hole diameter 1.5 mm, over-core diameter 40 mm, final trepan diameter 15 mm. The excellent correlation between the DHD reconstructed and the initial weld residual stress validated the present oDHD technique. The integrity of the structure nominally depends on the size of the over-core relative to the size of the component structure. The application of a 40 mm diameter over-core which was small enough relative to the size of the butt-welded pipe ensured the oDHD method to remain semi-destructive.

Concluding Remarks

The accuracy in residual stress characterization on the sustainable structural integrity assessment of an engineering component has been highlighted. Two welded pipe samples were considered in the study. The DHD numerical simulation on the welded pipes indicated that the DHD technique works reasonably well for practical components. Measurements of residual stresses were made in practical components using the deep-hole drilling method and were compared with finite element prediction. In general a good correlation existed particularly for the transverse component of the residual stress. The measured distribution was generally lower than the FEA predicted. It is anticipated that a combined hardening model in the FEA study can better represent the initial weld residual stress field.

The study illustrated that a significant influence of the DHD process on the initial longitudinal residual stresses occurred; both the measured and the predicted longitudinal stress component was much higher in magnitude than the transverse component. The FEA reconstructed residual stress distribution did not provide the initial peak tensile stress close to the outer surface of the welded pipes.

The FEA study using a large over-core, diameter 40 mm (oDHD technique) illustrated that the effect of plasticity in the DHD trepanning process can be reduced without affecting the accuracy of the result. Compared to the iDHD technique the oDHD technique is much simpler to apply and can achieve residual stress data of much higher spatial resolution, the same resolution as in the standard DHD technique. The FEA DHD simulation in the butt-welded pipe validated the oDHD technique. Moreover, the study further highlighted the need to exploit an FEA study prior to practical measurements.

Acknowledgement

The authors are grateful for the time provided by the Military Technological College, Sultanate of Oman in order to complete this work.

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Solid Polymer Waste Materials for Repairing of Heritage Composite Structure: An Additive Manufacturing Approach

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FDM and its Utilities for Development of Customized Materials for Maintenance

The whole world has an extraordinary and great past which is preserved in a form of heritage structures and archaeological sites. These historic heritages are the proofs of our golden history which need to be preserved for coming generations to understand its glory. Repair and rehabilitation in some defined ways are used to reconstruct or modify in order to keep their originality to represent. Repair and rehabilitation are mostly performed because of some aspects such as, deterioration due to environmental effects, new functional requirements and damages due to accidents. Epoxy injection, polyurethane injection, stitching cracks and lead flashing are some of the techniques which have been taken into consideration by the engineers for maintenance of structures (Subramaniam, 2016). Under the subject domain 'repair of heritage structures', some studies have been reported on St. Lourdes Church (Tiruchirappalli, India) for its rehabilitations and preservation of exterior surface mortar and steeple cracks. For steeple cracks maintenance, initially cleaning with soap water followed by lime mortar application for plastering has been recommended (Natarajan *et al.*, 2010). It has been reported that leakages and cracks are the mostly observed after degradations of the material used. For better understanding of degradation of material used, a study has been conducted at Nehru memorial college of K.V.G group of institutions at Mangalore, India for repair and rehabilitations of cracks found in walls. At location of cracks plastering was chipped off and V-groove was made by chiseling, water jet cleaning and cracks filling by structural grade repair mortar were performed to solve cracks issues (Pattanaik *et al.*, 2011). AM is the recent progress in the engineering fields which offers to be applicable in industrial production, civil production, aeronautics and medical implants. Additive manufacturing has the potential to be future associated technique in civil engineering field as its produced complex shapes quickly with reduced weight. Composites structures are investigated by their dynamic mechanical capabilities and thermoplastic behavior and parts produced by the additive manufacturing processes can controlled these values (Cannella *et al.*, 2017; Singh *et al.*, 2018b). AM forms the object by successive layers of materials for different application areas. 3D printing has the potential/impact to transform manufacturing supply chain, distribution channel and business model (Singh *et al.*, 2018a,b,c). There are some of the 3D printing technologies which are presently used by the society to apply as specific solutions of assembly, repair/maintenance, rapid tooling, waste management, energy storage and etc. Fused deposition modelling (FDM), stereo lithography (SLA), inkjet printing, selective laser sintering (SLS), digital light manufacturing (DLP), selective laser melting (SLM), electronic beam melting (EBM) and laminated object manufacturing (LOM) are some of the 3D printing techniques which are largely used for printing of functional/non functional prototypes (Kumar *et al.*, 2017a,b, 2018; Singh *et al.*, 2016). There are varieties of screw extrusion processes available for producing feedstock filament for FDM. Single screw extrusion is a conventional process for producing feedstock filament but defects like, tiny pores, blow holes, non-mixing are the major problems associated with this process. Twin screw extrusion has emerged as an advanced technique for producing feedstock filament free from defects. Twin-screw extruder are capable to ensure mixing, shearing, cooling, heating, compressing, transporting, shaping, pumping, etc. with very high level of flexibility. The main advantages of twin-screw extruders (intermeshing co-rotating) are their exceptional mixing capability that gives the remarkable characteristics to extruded products. In the twin-screw extrusion process, the raw materials may be solids (granules, powders & flours), slurries, liquids, and possibly gases (John *et al.*, 2014; Wang *et al.*, 2016a,b). FDM is the melt extrusion process in which robotic device is worked on the CNC programming to control the heating and movement of the filaments. The extruded material through the nozzle head is directed on the print bed and immediately hardened to ensure the part fabrication. To ensure the better dimensional stability of the component formed it is required to process the printing below the melting point of the substrate. Properties of parts produced by the FDM is the function of the filament preparations, extrusion is the basic process which are used for the preparation of feedstock filaments. Extrusion processes are largely used for the production of useful inputs for additive manufacturing techniques. The requirement of these processes is increasingly important from sustainability viewpoints when targeting waste management of thermoplastic materials. Mechanical properties of FDM fabricated parts are highly dominated by their filament processing. The mechanical sustainability of the fabricated parts is dependent on the nature of processing of the initial component (grinding, extrusion etc.). Barrel temperature, rotational speed and torque are some of the input variables during the filament processing which largely affects the mechanical sustainability of the FDM fabricated parts (Singh *et al.*, 2017a,b,c, 2018d; Singh and Kumar, 2017). FDM as 3D printing technique is most economical way of producing 4D thermoplastic composite reinforced with nano-particle using extrusion process for the development of customized material for maintenance of heritages structures.

Proposed Concept for Maintenance of Heritage Structures

The present way of maintenance is based upon traditional practices, which consume lot of time especially when some artistic work is involved. This makes the project cost high and leads to more down time. Some researchers have proposed the use of 3D scanners and 3D printing of mortar etc. for fast maintenance, but hitherto no work has been reported for use of debris of heritage structure itself (for more compatibility) with reinforcement of plastic solid waste through cryogenic grinding followed by extrusion and preparation of feed stock filament for 3D printers. This will significantly improve the processing ability of debris as well as waste management of plastic solid waste. The repaired/modified structures needs to be checked for thermal stability, dynamic mechanical analysis and aesthetic effects. 3D scanning is an important measure of dimensional parameters. A portable 3D scanner can fulfill the requirement of checking exact dimension of damaged parts of heritages. 3D scanner installed with design software then process 3D images into part of damaged filler so that prototypes on 3D printer can be fabricated. The design parts by help of 3D scanner now processed by slicing software to ensure the infill density, printing speed, printing temperature, layer thickness and infill pattern of the part to be prepared on 3D printer. The next step of the proposed methodology is to collect the debris of identified sites, which will be segregated by sieve shaker and then processed with cryogenic milling at -96°C to ensure the enhanced mixing capability with polymeric matrix. In next stage, blend of debris and thermoplastic processed on cryogenic milling is analyzed on melt flow indexing setup and DSC to ensure the flowability and thermal stability of the mixtures. If the thermal stability and melt flow index of matrix are under the acceptable limit then those mixture are processed on the twin screw extruder setup for preparations of feedstock filaments. The feedstock filament of suitable diameter (usually 1.75 mm in commercial FDM setup) will be used as the input material. By following the step discussed above, the customized material for maintenance of heritage structure can be prepared. It should be noted that ultimate characteristic of the feedstock filament will be a result of input process variable applied for processing of material. The next step involved in the present study starts with 3D printing of customized geometry scanned through 3D scanner. Here it should also optimize the input process variable so that fabricated part must attain the uniform material properties. Now the printed part as functional prototype is tested by dynamic mechanical analysis (DMA) setup for ascertaining the storage and loss modulus, SEM, XRD analysis (for ensuring uniform dispersion) and bonding capabilities through FTIR. The destructive testing like; pull out test, impact loading test and tensile test may be performed on the final prototypes to ensure the load bearing capabilities.

The 3D printed parts on FDM can be applied directly on the damaged site in the two different ways. First is use of cement-based adhesive for masonry/construction work and second is use of agricultural waste material for similar work depending upon the age/year of establishment of particular structures. For cement-based masonry/construction sites the debris availability is quite simple and same can be easily blended with polymeric waste after cryogenic treatment and final prototypes (replicas) can be prepared by extrusion and FDM processing. After preparation of replica, the same will be exposed to some chemical environment (like acetone for ABS matrix material) in vapour smoothing station. This will expose the cement powder particles on the outer surface and will provide finished surface up to nano level. The exposed cement particles can have a bonding with other end of the damaged structure with little quantity of water as per regular practices in construction sites. Finally, no post finishing is required as nano level finished structures are available. In the second case for debris other than cement, the same has to be blended with polymeric waste for development of feed stock filament. Here the advantage is that suppose one need 100 g/mm^3 of filler for maintenance of some cavity in the structure and debris available is 10 g/mm^3 . The rest can be filled by thermoplastic which is blended in available debris to make it as 100 g/mm^3 . The finally prepared replica will be pasted on site after post finishing and hence very less time on site will be consumed.

In case of load bearing structures with cyclic loading cases the replicas prepared will be checked for dynamic mechanical analysis so that their storage modulus and loss modulus is computed. As the ratio of storage modulus to loss modulus reflects the ability to absorb shocks under cyclic loading, in case the existing structure stability is questionable the same can be reinforced to improve its storage modulus by increasing the proportion of plastic solid waste. Before applying the plastic solid waste in heritage structure their melt flow characteristics and thermal graphs using differential scanning calorimetry (DSC) will be used to ensure thermal stability under different temperature conditions.

Working Mechanism of Proposed Framework

As per Maxwell's right-hand thumb rule, assume current carrying wire in right hand and thumb's direction denotes the direction of the current flow then direction in which hand is wrapped, represents the direction of magnetic lines of forces. If we take two different parallel current carrying conductors, then two cases emerges: the first case can be emerged as current flow of both conductors is in same direction and second case can be the current flow of both conductors in opposite directions. If the current of two current carrying conductors flows in a same direction then magnetic lines of forces will attract to each other and there will be contraction. Similarly, if the current flows in opposite direction then magnetic lines of forces will repel each other and there will an expansion (which can be noted as the physical quantity).

In the present work, a novel technique for recycling of plastic/polymer waste has been proposed for four dimensional printing applications especially for heritage structures. The idea is to use multi-jet extrusion nozzles of fused deposition modelling setup for printing multi layers of conducting thermoplastic composite (like: graphene reinforced thermoplastics) and non-conducting polymer waste (like ABS, Nylon6). The framework of 4D printing is shown in Fig. 1.

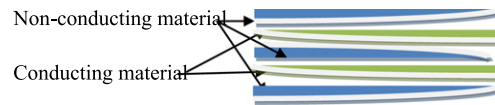


Fig. 1 Framework of 4D printing.

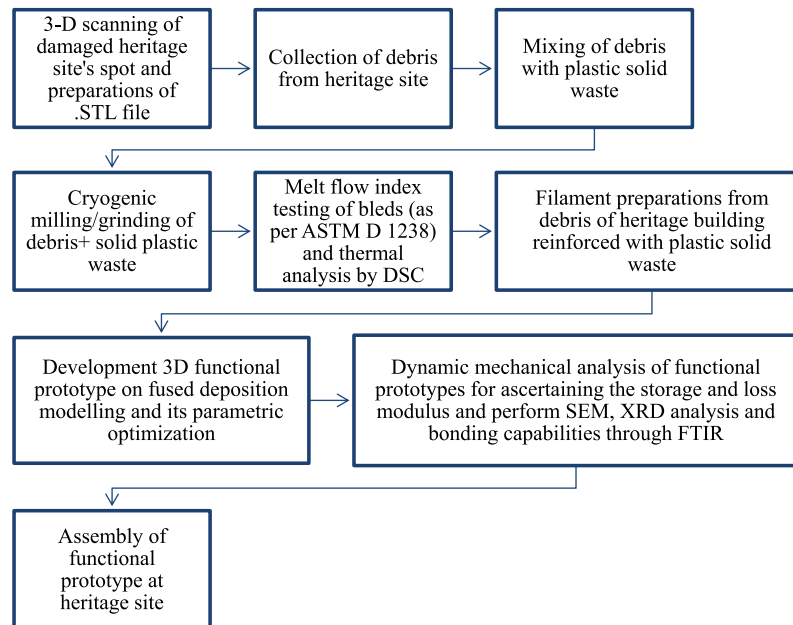


Fig. 2 Methodology for maintenance of heritage structures.

Now if current is passed in same direction between two parallel conductors than by basic principle two conducting wires will generate magnetic field and will attract each other. Similarly when the direction of current between two parallel conductors is reversed they will experience repulsive force. This basic principle has been used to develop new/in-house, 4D printing materials. With this multi material sandwiched component, just by changing the direction of current flow the component will change its thickness, because of change in magnetic field. Finally this helps to fill the cavities emerged in heritage structure (which may be of irregular contour). It should be noted that the flow of current in opposite direction will leads to expansion (as per the space available in the cavity) and one needs to supply the current (quantity) and control the time for flow of current in such a way that it leads to permanent fatigue of thermoplastic material. This will help in self assembly of the polymeric composite into the cavity. As the functional prototypes are prepared off line in some lab environment the down time in maintenance at the heritage site is significantly reduced resulting in cost benefits and waste management of thermoplastics.

Methodology of Proposed Concept

Fig. 2 shows detailed methodology for the development of customized material for maintenance of heritage structures.

Damages in the heritage structures can be of different shapes and size like; flat cylindrical, flat rectangular, conical shapes, trapezoidal, flat triangular etc. **Fig. 3** shows occurrence of common damages in the heritages structures. If the damages geometries are of type 3(a) and 3(b) then the additively manufactured prototypes (of customized material) can act as the filler material for maintenance. But if the damaged section is found to be of **Fig. 3(c)** type (regular/irregular trapezoidal with small inlet) then the problem of material filling might be difficult and it is needed to make an enlargement of that damaged hole to be repaired but enlarging of hole will lead to reduce the strength of that structures.

If the damage of structures is found to be of **Fig. 3(c)** type then the multi-material printing by use of FDM may be one of the best solutions for maintenance. Infield practice, 3D printing of alternating layers of conducting and non-conducting layer of piezoelectric material may be used as filler material on the damaged cavities. Suppose the multi-material printed prototype/replica of cavity consisting of alternative conducting and non-conducting layers are fitted into the cavities as shown in **Fig. 3**, the flow of current in the opposite direction of each layers will repel each layer leading to an expansion of the filler material, resulting into the self assembly.

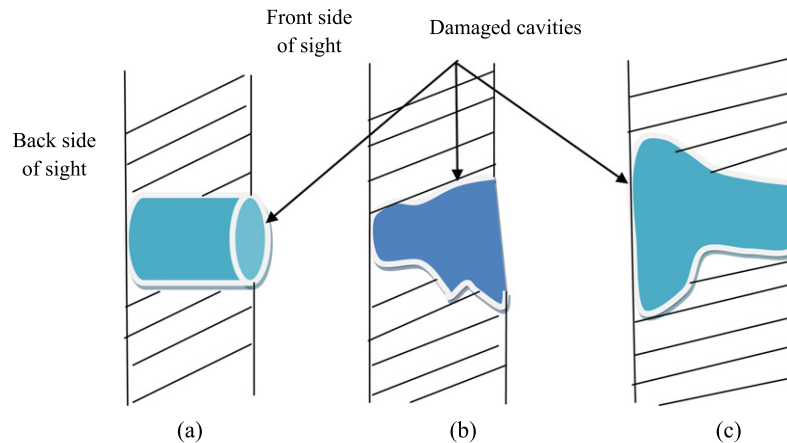


Fig. 3 Common structural damages in heritage structures.



Fig. 4 3D printed polymeric waste component.

Table 1 Mechanical properties of 3D printed multi-material component

Material	Peak load (N)	Peak strength (MPa)	Peak elongation (mm)	Percentage elongation at peak (%)	Young's modulus (MPa)	Yield stress (MPa)
HAP	161.3	8.40	3.04	4	325.00	1.00
AHP	133.9	6.97	2.85	4	72.92	2.73
PAH	149.0	7.76	3.99	5	85.42	0.28

Source: (Courtesy: Manufacturing Research Lab, Dept. of Production Engineering, GNDEC Ludhiana (India), Un-published data).

Polymer Waste Material 3D Printing: A Case Study

Multi-material 3D printing is precursor of present framework which can lead to the preparation of composite structures for maintenance of heritage structures. The alternating layer of conducting and non-conducting layers can be printed easily. In this study, commercial open source FDM setup (Company: Divide by Zero) configured with two nozzle head was selected for multi-material 3D printing. The static parameters for fabrication of composite parts were nozzle diameter of 0.3 mm, filament diameter of 1.75 ± 0.05 mm, layer height 0.27 mm, 3 perimeters (by adjusting 3 top and 3 bottom layers), rectilinear fill pattern, 30 mm/s perimeter speed, travel speed of 130 mm/s, at extrusion temperature of 250°C , bed temperature of 55°C , infill percentage of 100%, and under printing speed of 50 mm/s. The multi-material printing was customized by total 12 layers with 04 layers of each material. The multi-material printing was configured as:

- (1) 04 layers of recycled HIPS on bottom, 04 layers of recycled ABS in middle and 04 layers of recycled PLA on top (HAP),
- (2) 04 layers of recycled ABS on bottom, 04 layers of recycled HIPS in middle and 04 layers of recycled PLA on top (AHP) and
- (3) 04 layers of recycled PLA on bottom, 04 layers of recycled ABS in middle and 04 layers of recycled HIPS on top (PAH).

So, 03 different pieces of varying material as HAP, AHP, PAH have been printed on FDM setup as shown in Fig. 4. It should be noted that HIPS, ABS and PLA selected for printing are primary recycled (commercially available in open market) and can be treated as waste thermoplastics. Here no reinforcement of debris has been made, but by maintaining the debris proportion in thermoplastic matrix based upon rheological properties as per ASTM D1238 for melt flow index and thermal stability, glass transition temperature (analysis based upon DSC) one can easily prepare the feed stock filament for FDM and 3D printing of functional prototypes can be performed.

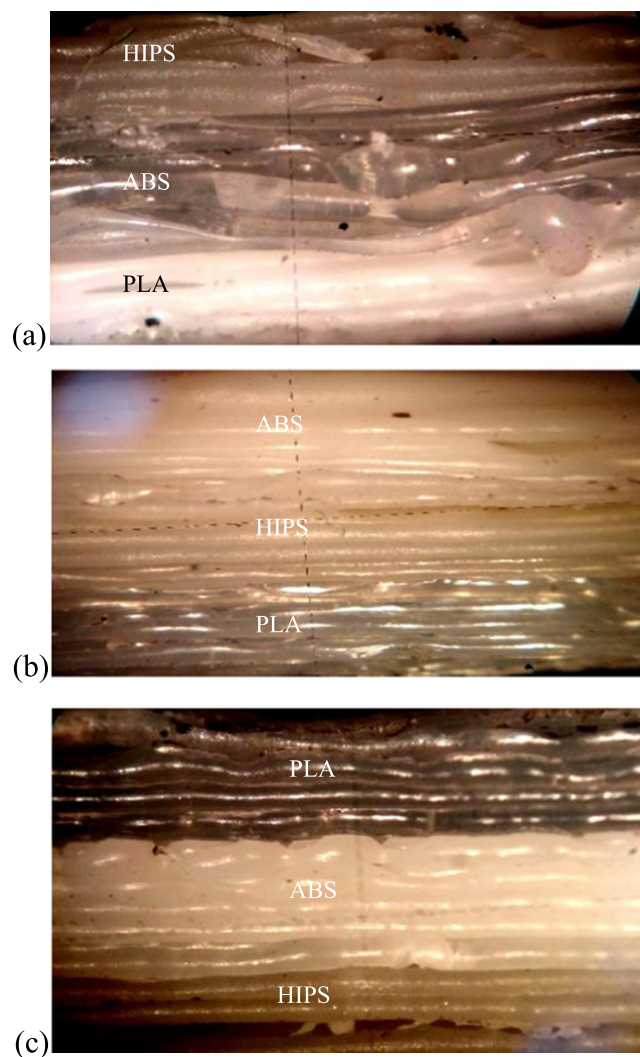


Fig. 5 Micrographs of additively manufactured multi-material components, (a) HAP, (b) AHP, (c) PAH.

It has been observed that 3D printed HAP resulted in the maximum values of peak load, peak strength, peak elongation, percentage peak elongation, Young's modulus and Yield stress (See [Table 1](#)).

[Fig. 5](#) shows micrographs of HAP, AHP and PAH parts (at30X) prepared on FDM (as per [Table 1](#)). Here, it should be noted that mechanical properties of HAP based component has resulted into the maximum tensile strength. This may be because layers of HAP overlapped uniformly to produce stronger joints. Whereas AHP and PAH were observed weaker because their layers are not tightly stacked. Now by selecting materials with alternative conducting and non conducting layers, expansion and contraction of the filler material can be easily controlled for self assembly in the cavity.

Summary

In this article, a frame work for maintenance of heritage structure through AM route has been proposed. The proposed route for development of customized materials for maintenance of damaged structure leads to some interesting features like:

- Reduction in time and cost of maintenance can be achieved by the proposed method for development of customized material for maintenance of heritages structures, as it leads to concept of self assembly.
- The proposed route is the one of the novel way to manage plastic waste into useful constructive prototypes, especially in 4D applications. Any intricate cavity shape can be easily self-assembled with proposed methodology.
- Inhouse developed polymeric material blend with reinforcement of debris recovered from heritage site can be useful for development of maintenance material at low cost.

Acknowledgement

The authors are highly thankful to manufacturing research lab (GNDEC, Ludhiana) for providing financial/technical assistance to carry out the research work.

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Statistical Analysis of Energy Absorption in Aluminum Foam Sandwich Under Impact Testing Using the Taguchi Design

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Introduction

Demand for the use of porous materials in industries is increasing due to the need to reduce the weight of structural parts in most of industries in order to improve market competitiveness. One of the alternatives that have been developed recently was metal foam. Metal foam consist of two types of cell topology which is open-cell and closed-cell foam. The requirement of producing complex parts with advanced material properties and lighter weight are generally needed nowadays especially in structural parts in aerospace, automotive and marine industries. However, foam itself is weak and can not be used alone. therefore, to overcome the problem, researchers had generated a new technology of lightweight material which is Aluminum foam sandwich (AFS). In AFS the metal foam used as a sandwich's core with two sheets as a skin to have interesting properties such as good stiffness and strength to weight ratio, good sound damping, excellent energy absorption and thermal insulation (Styles *et al.*, 2007; Crupi and Montanini, 2007). One of the most encouraging advantages in AFS is the high energy absorption properties. Therefore, the need to understand and investigate the ability of these materials in different applications becomes one of the most important issues. Many researchers investigated the mechanical behavior of the AFS. However, few of them were focused on analyzing the relationship between the skin and core thickness with the ability of energy absorption.

Crupi and Montanini (2007) mentioned that the Aluminum foam sandwich has a lightweight structure with good dissipation of energy under impact and high mechanical strength. By reducing the weight of structural parts, energy consumption can reduce which in turn leading to lessen oil consumption. One of the excellent metal foam that are used by previous researchers in automotive application is Aluminum foam sandwich due to their unique properties such as low density, good energy absorption characteristics. According to Ruan *et al.* (2010), stated that Aluminum foam sandwich panels are good energy absorbers and lightweight which provide wide range of potential applications in automotive industries. Example of the testing methods are compression test, impact test and quasi-static indentation test. All of the testing methods are done by following the standard of ASTM. Shunmugasamy and Mansoor (2018) stated that AFS have been used as energy absorbers, acoustic dampers and weight saving members in automotive and aerospace structures.

Fotsing *et al.* (2016) evaluated the mechanical behavior for composite sandwich structures by performing tensile tests, compressive tests, impact tests and three-point bending tests. The composite sandwich structures are made of honeycomb core and woven carbon epoxy face sheets. All of these tests offer good information about the vibration damping of composite sandwich structures. Srivastava (2012) investigated the impact behavior of composite sandwich structure in order to analyse the energy absorbed and fracture toughness. Izod impact, charpy impact and weight drop test had been performed on the sandwich structures. Glass fiber-reinforced and polyurethane foam were used to prepare the composite sandwich structure.

Damghani and Gonabadi (2017) conducted drop hammer test to investigate the perforation responses of Aluminum foam sandwich by varying the velocities, relative density of Aluminum foams and weights of projectile. The samples were impacted at different energy levels to attain various damage mode levels. Based on the findings, it revealed that by increasing the relative density of Aluminum foam and velocity, the energy absorption of sandwich structure increases.

Meanwhile, Mohammed *et al.* (2014) conducted the low velocity impact test by analyzing the mechanical response of sandwich composites. The most striking result to emerge from this study is that the mechanical behavior of sandwich structure is strongly reliant on the loading rate.

Additionally, Tsuchikura *et al.* (2013) conducted charpy impact test on sandwich composites. Carbon fiber reinforced polymer and acrylonitrile butadiene styrene (ABS) have been used as a core and face sheets for sandwich composite construction. Evaluation of charpy impact test velocity and impact fracture energy had been discussed in this study. The concluded that the new method allows for more efficient beam contact to the inner core and its surface permitting deeper areas in thick laminated composites

Furthermore, Hufenbach *et al.* (2008) performed low-velocity impact which was charpy test on composite structures to observe the impact damage tolerance. Specifically, this study aims to evaluate the factors that give influence to the impact response of composites which are fiber strengths, toughness, thickness of panel, impact velocity and support conditions. The study showed good correlation between experimental and numerical results. Arifin *et al.* (2014) studied the impact behavior of the polymer matrix composites by varying design of the lamination structure. The findings highlighted that selection of reinforcement and matrix types play vital factor for ability to absorb more energy during impact test.

Most of researchers were focusing on determine behavior of closed-cell foam while least of them discuss on open-cell foam. None of them if any have investigate skin to core ratio effect on mechanical behavior of open-cell Aluminum foam sandwich and analyse statically the relationship between the skin and core thickness with the energy absorption ability. Therefore, this present study examines the energy absorption of Aluminum foam sandwich (AFS) with open-cell foam core using Impact testing.

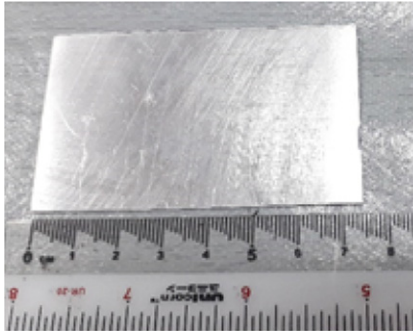
Material Preparation

Aluminum foam sandwich are produced using the following steps:

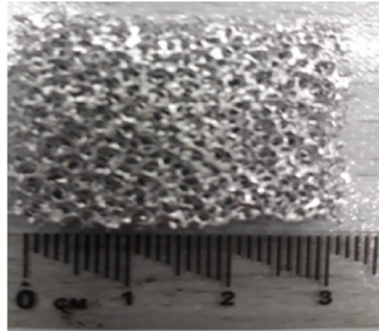
- Aluminum sheet with thickness of 0.4 mm, 0.6 mm, 0.8 mm as shown in Fig. 1(a),
- Aluminum foam with thickness of 3.2 mm, 5.6 mm and 6.35 mm as shown in Fig. 1(b) and,
- Epoxy resin and hardener as shown in Fig. 1(c).

The Aluminum foam was attached together with Aluminum sheets using the epoxy resin with hardener ratio of 2:1 to fabricate Aluminum foam sandwich as shown in Fig. 2.

As in the ASTM standard of C393, the preferable ratio of skin to core ratio is approximately less or equal to 0.10 in order to select the suitable thickness for core and skin which has been followed in this investigation.



a. Aluminium sheet with thickness of 0.4 mm, 0.6 mm, 0.8 mm



b. Aluminium foam with thickness of 3.2 mm, 5.6 mm and 6.35 mm



c. Epoxy resin and hardener

Fig. 1 AFS components for experimental work.

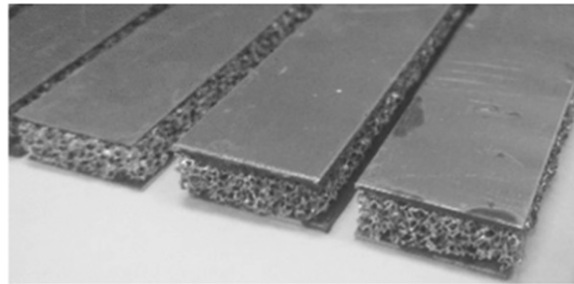


Fig. 2 Aluminum foam sandwich.

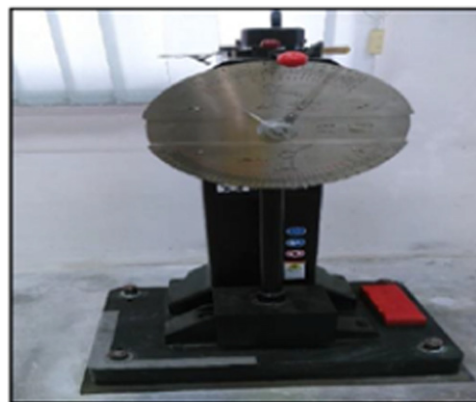


Fig. 3 Charpy impact test machine.

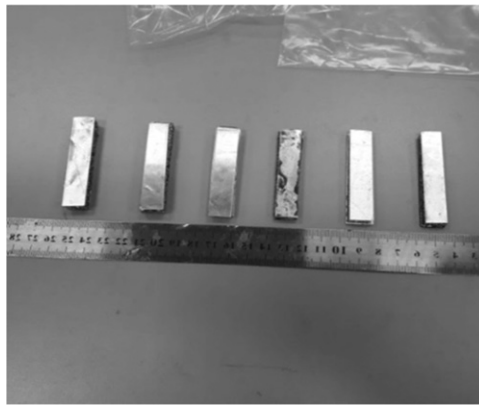


Fig. 4 AFS samples for impact test.

Table 1 Design of experiment

Parameters	L1	L2	L3
Skin thickness, mm	0.6	0.8	1.0
Core thickness, mm	3.2	5.6	6.35

Charpy Impact Test

Charpy impact test were conducted on AFS samples in order to analyse the energy absorbed in breaking the sample that subjected to shock loading according to ASTM standard D4812. During the test, the pendulum is elevated to certain height and allowed to fall while impact velocity is maintained at 3.35 m/s. When the pendulum strikes, it impacts and breaks the sandwich specimens (Srivastava, 2012). Fig. 3 shows the Charpy impact test machine. The specimens for conducting the impact test are shown in Fig. 4. The designation was in rectangular shape with the value of width, 3 mm and length, 64 mm based on ASTM D4812 standard.

Design of Experiment (DOE)

Taguchi design for two independent parameters of core and skin thickness, with three levels has been developed. L^9 orthogonal array have been generated using JMP statistical software (version 11). Levels and main parameters are shown in Table 1. Nine runs of Charpy impact test have been conducted and repeated for three times.

Finally, all of the experimental results are evaluated using Taguchi method by generating the levels and combination input of parameters. Meanwhile, the optimization of the selected parameters is generated using desirability function analysis in order to obtain the maximum responses such as peak force, energy absorbed and impact energy of Aluminum foam sandwich.

Charpy impact test had been conducted with various thickness of Aluminum foam and Aluminum sheet in order to determine the impact behavior of Aluminum foam sandwich. The Charpy impact test was conducted three times for each condition. Nine runs of the test have been performed by varying the thickness of Aluminum foam as core and Aluminum sheet as a skin. Fig. 5 demonstrated the summary of the Charpy impact test for different thickness of Aluminum foam and Aluminum sheet for the three different Runs.

It can be clearly seen that by increasing skin and core thickness, the impact energy of Aluminum foam sandwich increased as well. This current finding is consistent with the previous studies by Ozdemir *et al.* (2015) in which they found that increasing the core and skin thickness eventually increase the impact energy of the sandwich structure. It is apparent from the results that the highest impact energy was 21.67 J for skin thickness of 1.0 mm and core thickness of 6.35 mm.

The current result was in line with the finding of Hufenbach *et al.* (2008) that found by increasing the skin and core thickness, the impact energy of AFS sample increased eventually. Hence, the selected parameters which were skin and core thickness give improvement in terms of good energy absorption by conducting the impact test.

However, the types of failure modes for all tested AFS samples under impact testing are presented in Table 2 by varying the core and skin thickness as selected parameters.

Table 2 shows two main types of failure modes that occurred when AFS sample subjected to impact loading namely skin-core delamination and rupture image is shown in Fig. 6.

The failure mode can result in rupture with different of thickness of core and skin. This may due to different configurations of sandwich structure. The delamination occurs between skin and core layer. This failure was mainly affected by collapse of core cells due to buckling of core itself. The rupture behavior when subjected to impact loading, the core and skin were not fully separated due

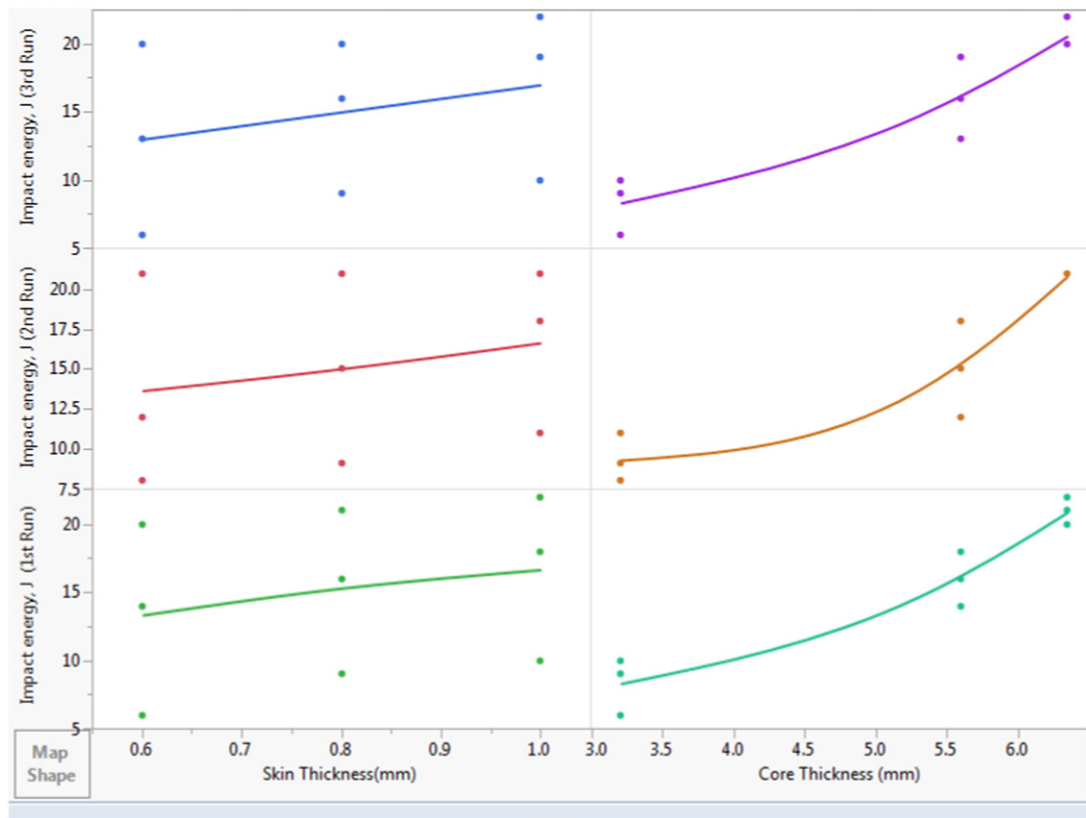


Fig. 5 Summary of Charpy impact test for different thickness of core and skin.

Table 2 Failure modes for each of the AFS samples under impact test

Run	Parameters		Failure modes
	Skin thickness, mm	Core thickness, mm	
1	0.6	3.2	Delamination
2	0.8	3.2	Delamination
3	1.0	3.2	Rupture
4	0.6	5.6	Rupture
5	0.8	5.6	Delamination
6	1.0	5.6	Delamination
7	0.6	6.35	Rupture
8	0.8	6.35	Delamination
9	1.0	6.35	Delamination

to the flexibility of unbroken structure of sandwich itself. The findings of the current study were in line with [Hufenbach et al. \(2008\)](#) which found that rupture mode form the limited damage sizes in skin and core.

Statistical Analysis

The statistical analysis was covered the: summary of fit; analysis of variance (ANOVA); surface profiler and profiler. [Table 3](#) concluded the summary of fit measures.

[Table 3](#) shows high value of R^2 and R^2 adjusted. Moreover they are very close to each other together which mean that the process is almost free from the insignificant terms.

Analysis of variance (ANOVA) has been calculated and concluded in [Table 4](#). The ANOVA and F ratio test was calculated to justify the goodness of fit of model.

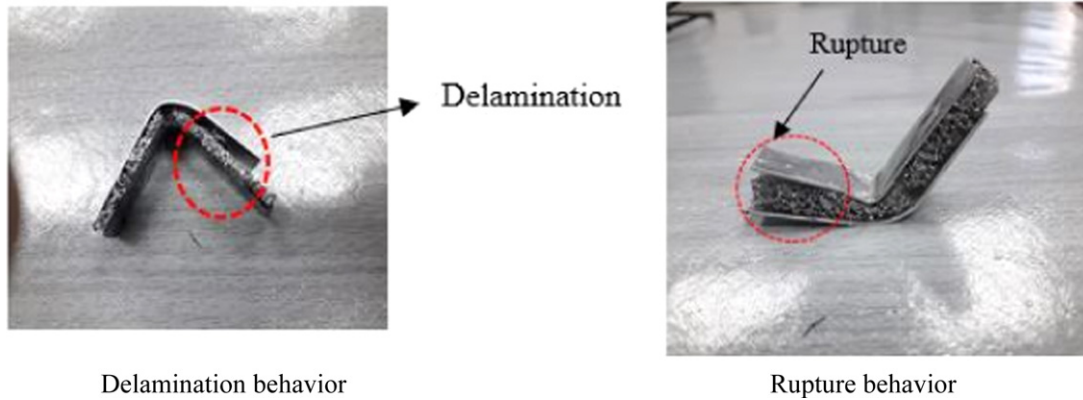


Fig. 6 Failure modes of AFS.

Table 3 The summary of fit

R Square	0.944584
R Square adjusted	0.911334
Root mean square error	1.655643
Mean of response	15.07778
Observations (or Sum Wgts)	9

Table 4 Analysis of Variance (ANOVA)

Source	DF	Sum of squares	Mean square	F Ratio
Model	3	233.61867	77.8729	28.4088
Error	5	13.70578	2.7412	Prob > F
C. Total	8	247.32444		0.0014*

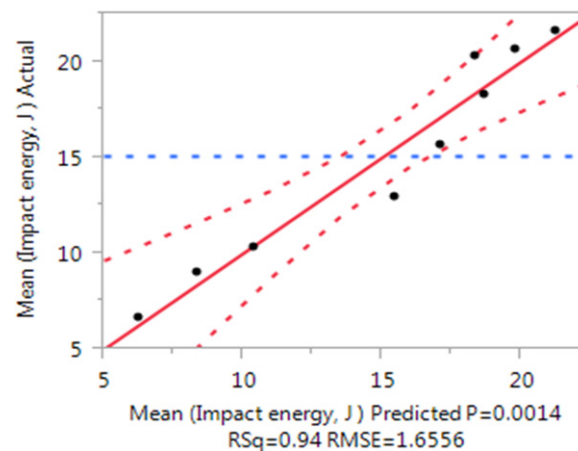


Fig. 7 Actual Data and predicted data.

From **Table 4** it is clearly show that results and the parameters selection with high correlation to the investigated response with the F ratio of 0.0014 which is the ratio of two mean square values and it is less than 5% and means that the level of significant. Finally, to have more understanding for the whole process the relationship between the actual data and the predicted data was extracted and plotted as in **Fig. 7**.

The leverage plots which consists of skin thickness, core thickness and skin thickness*core thickness were developed as shown in **Fig. 8**. The leverage plots showed the unique effect of a term in the model.

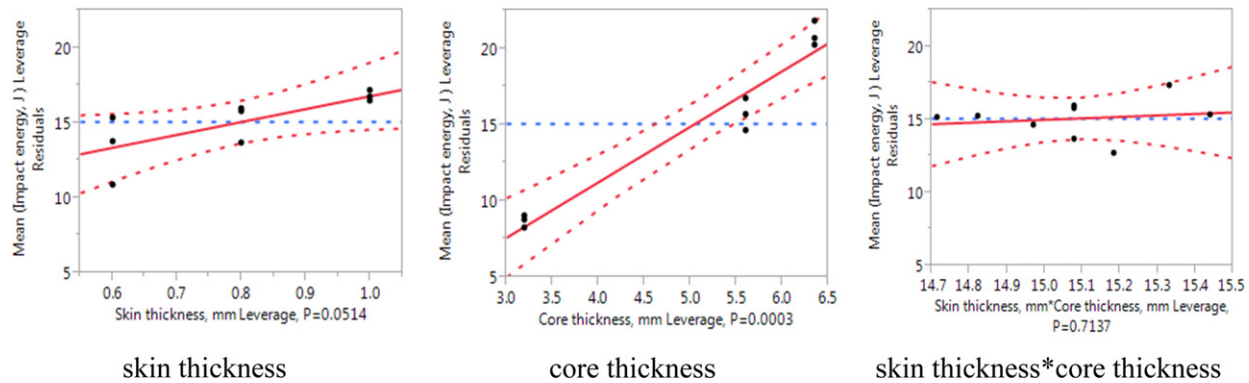


Fig. 8 Leverage plots.

From **Fig. 8**, it can be concluded that the core thickness is the most significant term in the model with the p value of 0.0003.

Conclusion

The following conclusions can be drawn from the present study:

The results showed that the selected parameters have high correlation with the responses of the results with the F ratio of 0.0014 and it is less than 5% hence, the level is significant. However, the core thickness is the most significant term in the model with the p value of 0.0003. Both skin and core thickness have a significant effects when impact on energy absorption. The statistical analysis revealed that the core thickness is more related to energy absorption.

There are two main types of failure mode observed in this investigation when AFS sample subjected to impact loading with skin-core delamination and rupture. Both skin thickness and core thickness have a positive effect on energy absorption in AFS.

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Structural, Thermal, Mechanical and Rheological Properties of Polylactic Acid/Epoxidized Soybean Oil/Organoclay Blends

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Introduction

Plastics are manufactured from non-degradable polymers such as polystyrene, polyethylene and many more, in which their light weight and long-lasting property are causing terrible environmental pollution. To overcome the problem, researchers are exploring on biodegradable materials that can substitute conventional polymers. Among the biodegradable polymers, polylactic acid (PLA) is a biodegradable aliphatic polyester derived from lactic acid, which can be obtained from the fermentation of starchy materials (Mehta *et al.*, 2006). In spite of many attractive properties of PLA, such as biodegradability, high strength and modulus, PLA shows lower flexibility and higher cost, thus limiting the applications of PLA (Rasal *et al.*, 2010).

Epoxidized soybean oil (ESO) is an epoxidized derivative of a mixture of esters of glycerol with various saturated and unsaturated fatty acids. In previous study, ESO has been used as a plasticizer in PLA with 38% increase in elongation at break with 20 parts per hundred (phr) ESO loading (Ali *et al.*, 2009). However, the tensile strength, yield stress and modulus of PLA decreased with addition of plasticizer. It has been reported that addition of plasticizer generally increases the elongation at break but decreases the strength and modulus. Thus, one method that can be used to improve the properties of polymer matrix is by incorporating fillers such as clay (Pluta *et al.*, 2006a; Najafi *et al.*, 2013). Incorporation of clay into PLA exhibited improvement in water vapor barrier and antimicrobial properties (Rhim *et al.*, 2009; Castro-Aguirre *et al.*, 2018).

There are two methods that can be used to disperse the clay in polymer matrices: solution blend and melt blend. In the solution blend method, solvent is used in large amount to dissolve the polymers thus, improving the intercalation of polymer chains and clay platelets (Ozdemir *et al.*, 2016). Whereas, for melt blend method, the layered silicate is mixed with the polymer matrix at the melting temperature of the polymer. This method is mostly used as it is more environmental friendly and polymers can be melt processed. It has been reported that the PLA/clay nanocomposites were prepared by melt blending of PLA with sepiolite and halloysite clays (Russo *et al.*, 2014).

The addition of oligo(ϵ -caprolactone) as compatibilizer has improved the dispersion of silicate layers in nanocomposites (Ray *et al.*, 2002). Enhancement of properties such as crystallization rate (Pluta *et al.*, 2006b), tensile, impact strength, modulus (Najafi *et al.*, 2015), gas permeability, water barrier property (Şengül *et al.*, 2017) and biodegradability (Castro-Aguirre *et al.*, 2018) were observed in PLA/clay nanocomposites. Dispersion of clay is very crucial in obtaining homogeneously dispersed filler in polymer matrix, in which, dispersion of clay in PLA matrix using electric effect was reported by Geun *et al.* (2016).

Thus, this study aimed to prepare PLA blend using ESO as a plasticizer and Cloisite 30B as an organoclay. The PLA/ESO/organoclay nanocomposites were melt mixed with different ratios of organoclay and then investigated the structural, thermal, mechanical and rheological properties of the nanocomposites.

Experimental

Materials

Polylactic was obtained from Cargill-Dow molecular weight (M_w) of 148,000 g/mol, and polydispersity index (PDI) of 1.9, epoxidized soybean oil (ESO) with epoxide content of 6.9 wt% was obtained from Shindongbang Co, Korea. Organoclay, Cloisite 30B was received from Southern Clay Products Inc.

Preparation of PLA/ESO/Organoclay Nanocomposites

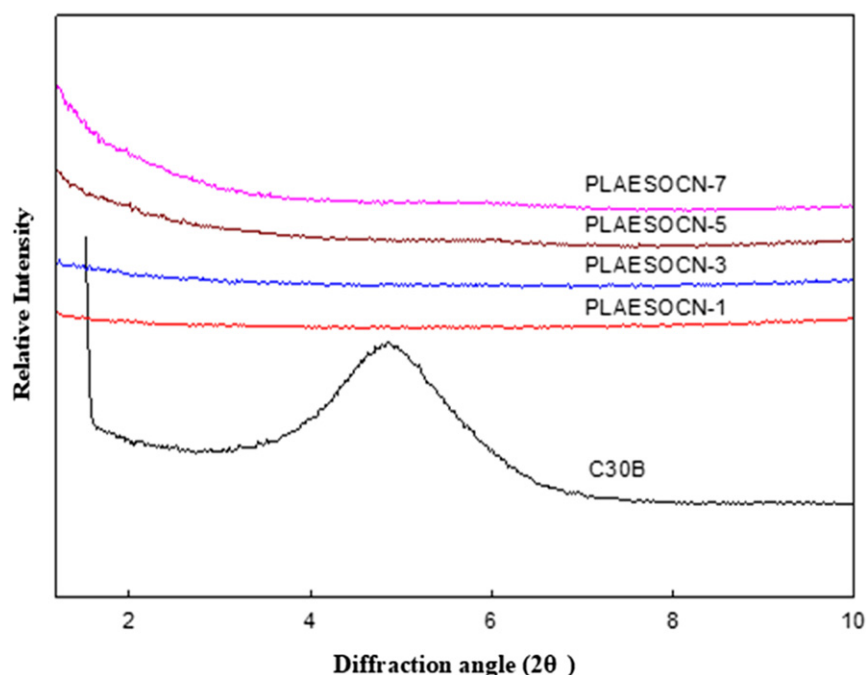
PLA, ESO and Cloisite 30B were dried overnight at 40°C in vacuum. The PLA was melt-blended with 20 parts per hundred (phr) of ESO in a Haake internal mixer at 180°C with a rotor speed of 60 rpm for 10 min. And then Cloisite 30B was added into the internal mixer as ratio mentioned in Table 1 and mixed for another 10 min. The nanocomposites were then molded into 1 mm thickness sheet under a pressure of 44.482 kilonewton (kN) at 180°C for 10 min.

Characterizations

The X-ray diffraction (XRD) patterns were recorded on a Philips, X'pert PRO MRD diffractometer using a CuK α radiation ($\lambda = 1.54 \text{ \AA}$) at voltage of 40 kV and current of 25 mA. The XRD was used to evaluate the dispersibility of the organoclay silicate layers in the PLA matrix. Morphology of the nanocomposites was obtained by transmission electron microscope using LEO-912AB with omega energy filter at

Table 1 Formulation and sample code of PLA/ESO/organoclay nanocomposites (PLAESOCNs)

Sample code	PLA/ESO/Cloisite 30B (phr)
PLAESO	100/20/0
PLAESOCN-1	100/20/1
PLAESOCN-3	100/20/3
PLAESOCN-5	100/20/5
PLAESOCN-7	100/20/7

**Fig. 1** XRD patterns of Cloisite 30B (C30B) and PLA/ESO/Cloisite 30B nanocomposites (PLAESOCNs).

120 kV accelerating voltage. The samples for TEM analysis were all microtomed before the test. TEM was used to observe the dispersion of the organoclay silicate layers in the PLA matrix. Differential scanning calorimetry (DSC) was performed using DSC2010 from TA Instruments. The DSC scans of the samples were run from 0°C to 200°C at the rate of 10°C/min and then kept at 200°C for 5 min to eliminate the previous heat history and subsequently cooled to 0°C at the rate of 10°C/min. The samples were heated again to 200°C at 10°C/min. This second heating process was regarded as melting scan for the analysis. The glass transition temperature (T_g), cold crystallization temperature (T_{cc}), cold crystallization enthalpy (ΔH_{cc}), melting temperature (T_m) and melting enthalpy (ΔH_m) were determined. Temperature at the maximum values were determined as crystallization and melting peaks. Tensile properties were measured using universal testing machine (United Co. STM 10E) at 25°C and with a crosshead speed of 5 mm/min according to ASTM D412 specifications. The tensile test was used to determine the elongation at break, modulus and yield stress. Melt rheological analysis (small amplitude oscillatory shear rheometry) was carried out in a RMS 800 instrument. The dynamic oscillatory shear measurements were conducted at 180°C using a set of 25 mm diameter parallel plates and a sample of 1–2 mm thickness. Preliminary strain sweep test was carried out at frequency of 100 rad/s at 180°C to estimate the linear viscoelastic range of the samples. Afterwards, frequency sweep tests in the linear viscoelastic regime were conducted between 0.1 and 100 rad/s.

Results and Discussion

Structural Properties of the Nanocomposites

The XRD patterns of the Cloisite 30B and PLAESOCN nanocomposites are shown in Fig. 1. The peak corresponding to the basal spacing of the organoclay (C30B) appears at 4.74° (d_{001} spacing is 1.9 nm). As can be observed in Fig. 1, diffraction peaks were not observed in PLA/ESO/organoclay nanocomposites (PLAESOCNs). This implies that silicate layers of organoclay were exfoliated in the PLAESO blend matrix. One possible explanation is that the ESO penetrated into the clay layers and expanding the basal spacing of the layers. This leads

to exfoliation of silicate layers in the nanocomposites. Similar effect of plasticizer was also reported in PLA/clay nanocomposites where exfoliation was dominant compared to non-plasticized PLA/clay nanocomposites (Guralp and Sebnem, 2009).

Dispersion of the clay layers in the polymer matrices of PLAESOCN-5 was confirmed by TEM as illustrated in Fig. 2. Exfoliated (label "C") silicate layers were observed in PLAESOCN-5. The XRD patterns and TEM images confirmed on the delamination of silicate layers in the PLA/ESO/organoclay nanocomposites.

Thermal Properties

The DSC thermograms obtained from second heating scan of PLA/ESO/clay nanocomposites (PLAESOCNs) is shown in Fig. 3. The transition temperatures and enthalpies determined from the thermograms are summarized in Table 2. The glass transition temperature (T_g) of PLAESOCNs increased with the increased of clay content. It increased from 53.7°C for PLAESO to 55.8°C for PLAESOCN-5. The T_{cc} of the PLAESOCNs were also increased with organoclay content. This indicates that organoclay restricts the mobility of polymer chains.

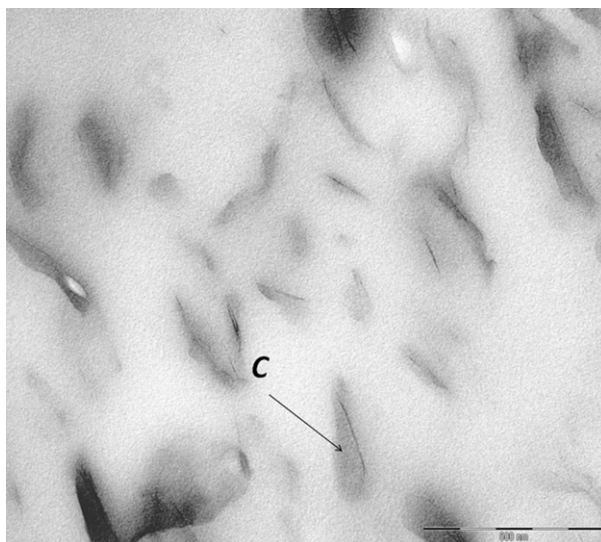


Fig. 2 TEM image of PLAESOCN-5.

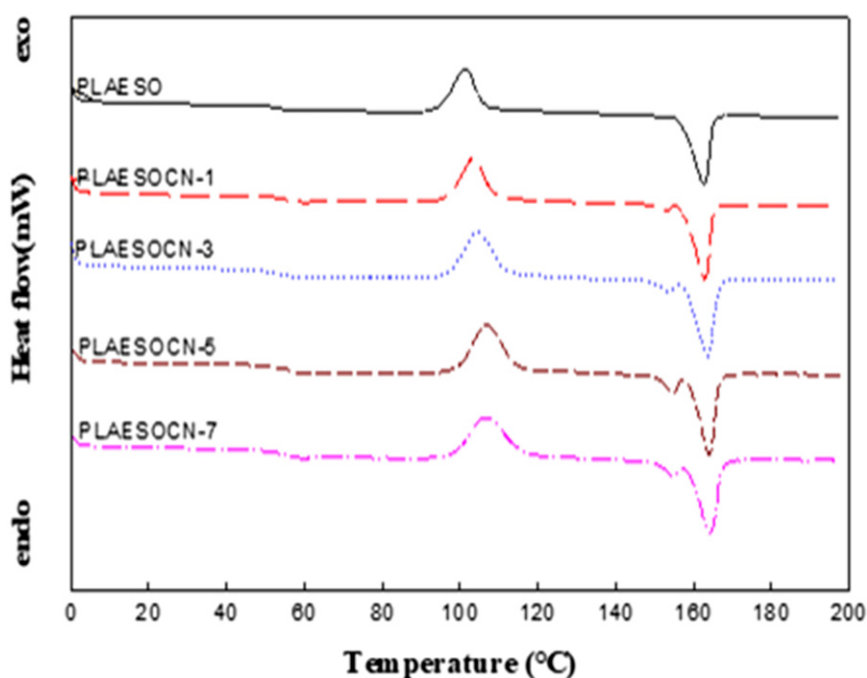
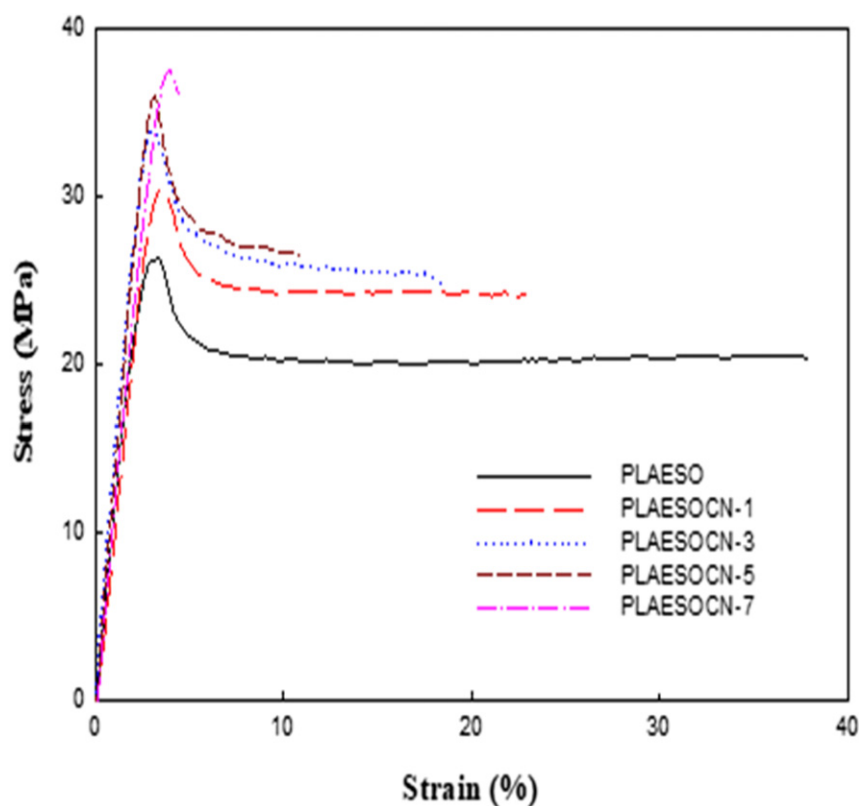


Fig. 3 DSC thermograms of plasticized PLA (PLAESO) and PLA/ESO/Cloisite 30B nanocomposites (PLAESOCNs).

Table 2 Thermal Properties of PLA, PLESO and PLAESOCNs

Sample	T_g (°C)	Cold crystallization		Melting				
		T_{cc} (°C)	ΔH_{cc} (J/g)	T_{m1} (°C)	ΔH_{m1} (J/g)	T_{m2} (°C)	ΔH_{m2} (J/g)	ΔH_{mTotal} (J/g)
PLA	60.4	111.9	39.5	159.5	9.5	166.9	30.2	39.7
PLAESO	53.7	101.2	30.3	151.7	0.2	162.7	31.6	31.8
PLAESOCN-1	54.3	103.3	25.0	152.5	1.4	163.0	24.6	26.0
PLAESOCN-3	54.4	104.6	25.7	153.2	1.9	163.3	24.0	25.9
PLAESOCN-5	55.1	106.4	25.7	154.6	3.5	163.5	22.9	26.4
PLAESOCN-7	55.8	107.1	27.4	154.8	3.5	164.3	24.4	27.9

**Fig. 4** Stress-strain curves of plasticized PLA (PLAESO) and PLA/ESO/Cloisite 30B nanocomposites (PLAESOCNs).

Mechanical Properties

The stress-strain curves for PLAESOCNs is shown in Fig. 4. It was observed that elongation at break of PLAESOCNs decreased with addition of organoclay content into PLAESO blend. Similar observation was also found in the incorporation of clay in PLA/PEG/clay nanocomposites causing decreased in elongation at break (Shibata *et al.*, 2006). Fig. 5 shows the Young's modulus and yield stress of PLAESO and PLAESOCNs. There were significant increases of modulus for PLAESOCNs as compared to PLAESO blend. This is expected when higher aspect ratio and larger surface area of silicate layers organoclays are incorporated into polymer matrix. The yield stress of PLAESOCNs was increased with organoclay content as compared to PLAESO blend. The mechanical analysis showed that the organoclays improved the stiffness and yield stress of the PLA/ESO blend.

Rheological Properties

Preliminary strain sweep tests were performed to estimate the linear viscoelastic range of the PLAESO blend and PLAESOCN-5 nanocomposite. As shown in Fig. 6, the strain sweep measurements were carried out at frequency of 100 rad/s on the PLAESO and PLAESOCN-5 sample. The linear viscoelastic limits extend to a strain of 50% and 6.1% for PLAESO and PLAESOCN-5, respectively. Therefore, the linear viscoelastic properties of PLAESO and PLAESOCNs were conducted at a strain of 5%.

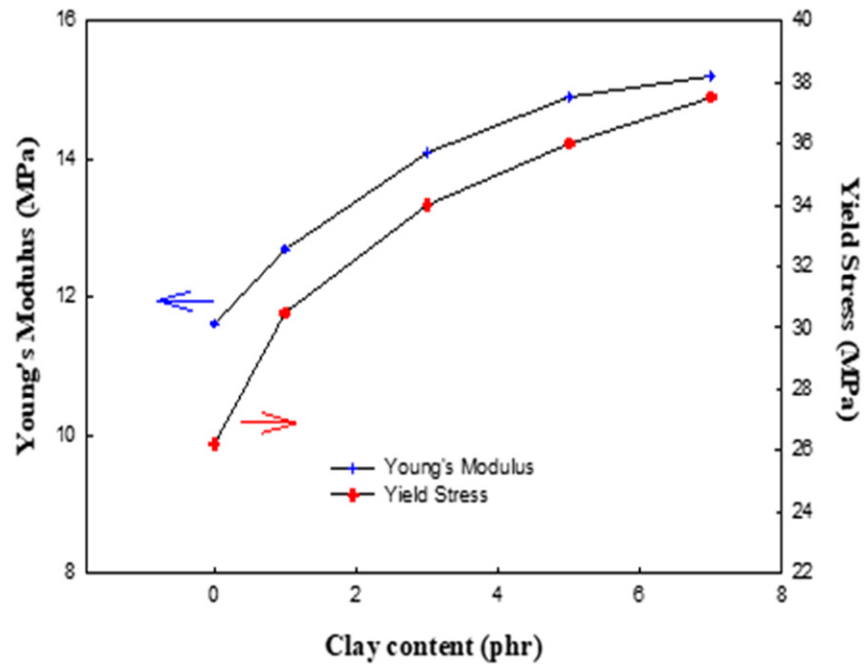


Fig. 5 Young's modulus and yield stress of plasticized PLA (PLAESO) and PLA/ESO/Cloisite 30B nanocomposites (PLAESOCNs).

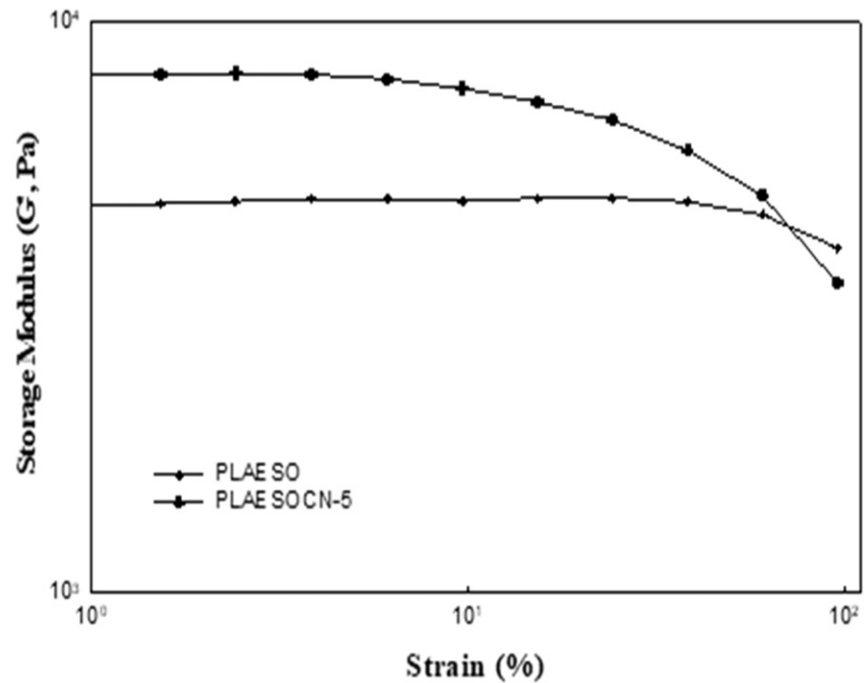


Fig. 6 Storage modulus (melt state) of PLAESO and PLAESOCN-5 as a function of strain amplitude.

As shown in **Fig. 7**, the storage moduli (G'), loss moduli (G'') and complex viscosities (η^*) of PLAESOCNs were higher than those of PLAESO at all frequencies and increase monotonically with the clay content, especially at low frequency (< 10 rad/s). Both moduli of PLAESOCNs showed weak frequency dependence and gradual changes of behavior from liquid-like to solid-like with increasing organoclay content in the PLAESO matrix. The terminal zone slope of PLAESO and PLAESOCNs is shown in **Table 3**. The slope of $G'(\omega)$ and $G''(\omega)$ in the terminal region of the curves of PLAESO matrix is 1.2 and 0.97, respectively, and these values are in range expected for polydisperse polymers (Pluta *et al.*, 2002). On the other hand, the slopes of $G'(\omega)$

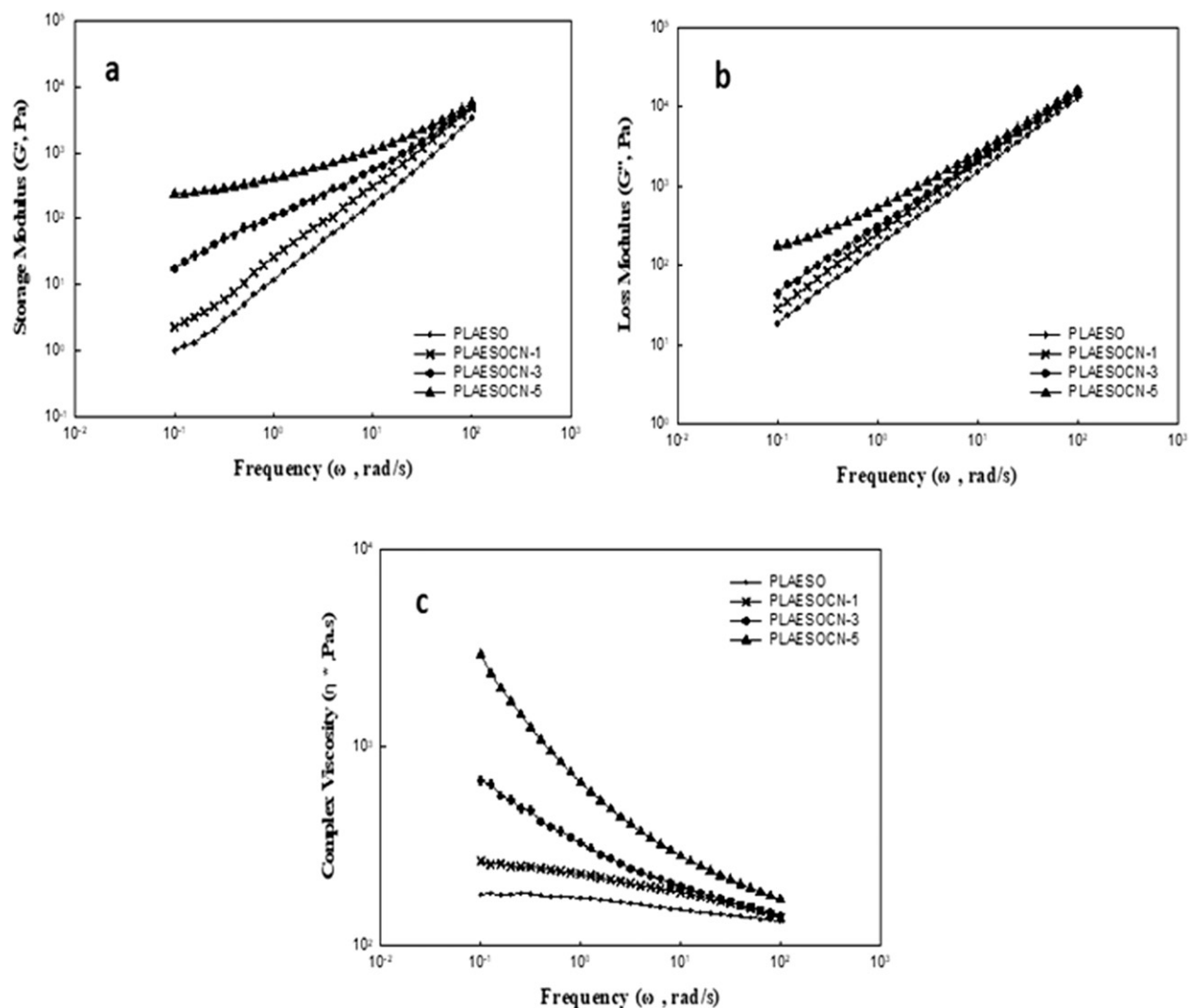


Fig. 7 (a) Storage modulus, (b) Loss modulus and (c) Complex viscosity of PLAESO and PLAESOCNs as a function of frequency.

Table 3 Terminal region slopes of $G'(\omega)$ and $G''(\omega)$ for PLAESO and PLAESOCNs

Samples	slope of $G'(\omega)$	slope of $G''(\omega)$
PLAESO	1.2	0.97
PLAESOCN-1	1.0	0.95
PLAESOCN-3	0.8	0.85
PLAESOCN-5	0.23	0.50

and $G''(\omega)$ were considerably lower for all PLAESOCNs. The differences in slopes may be attributed to difference in extent of exfoliation. A larger extent of exfoliation will lead to more solid-like behavior due to the increased number of particle-polymer interactions.

Conclusion

The PLA/ESO/organoclay nanocomposites were prepared using melt mixing method. XRD patterns showed that silicate clay layers were exfoliated in the nanocomposites and confirmed by TEM. Thermal properties exhibited slight increase in glass transition temperature and cold crystallization temperature of PLA. The mechanical analysis revealed that the organoclays improved the

stiffness and yield stress of the nanocomposites. Rheological studies under dynamic frequency sweep showed that storage modulus at low frequency region of the nanocomposites exhibited solid-like behavior with higher organoclay content. This study showed the enhancement in properties of PLA/ESO/organoclay nanocomposites and its processability in presence of organoclay with different ratios.

Acknowledgement

The author thanked International Islamic University of Malaysia (IIUM) and Kuliyah of Engineering for the support.

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Sustainable Construction Achieved Through Life Cycle Assessment: Methodology, Limitations and the Way Forward

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Introduction

The construction industry is responsible for large consumption rates of natural resources, with demand levels reaching up to 40% of the total materials consumed worldwide (DPTI, 2017). In addition, the construction industry generates large amounts of waste, accounting for 33% of all waste generated in the European Union (European Environment Agency, 2010). The concept of sustainability in construction has always been linked to the quest to reduce impacts of construction operations, particularly environmental ones (Rosen, 2012). Industry professionals and researchers around the world have been attempting to study alternative technologies, materials, and design concepts that are less damaging to the environment, and that can be readily adopted on construction projects.

When considering the minimization of environmental impacts, it is imperative that this is related to the entire life cycle of the project, from the extraction and processing phase of raw materials, to the final disposal of the elements (Akadiri *et al.*, 2012). In this context, different methods of analysis were developed, including the spontaneous or 'Ad Hoc' method (Stamm, 2003) and interaction matrix method (Finucci, 2010). However, one of the most widespread concepts around the world today is the life cycle assessment (LCA) approach, being used in several fields, including the construction sector.

According to United Nations Environment Programme (UNEP), *Life Cycle Thinking* is a way of providing information to stakeholders so that they can make the best decisions regarding the life cycle of products and services, and their impacts based on the triple bottom line of sustainability: social, environmental and economic factors (UNEP, 2013). As stated in the general principles of sustainability in building construction described in ISO 15392, all these three dimensions are necessary in a sustainable assessment (ISO, 2008). However, it is possible to restrict the assessment to an individual dimension, depending on the scope considered in the analysis.

When it comes to environmental studies conducted in the construction industry, difficulties arise due to the high degree of detail required when considering an entire building as a functional unit of analysis. For example, it is important to consider that buildings have a comparatively long life and they often have multiple functions, in addition to the fact that they contain many different components and are normally unique (Bribián *et al.*, 2009). As a result, this research explores the use of LCA in the construction sector, presenting the limitations still existing and elaborating a proposal of how the studies on this theme should be carried out in the future.

This paper is organized as follows: in the next section, the significance of the use of LCA on building projects is highlighted. The section that follows then presents a more detailed explanation of the LCA methodology. Based on the presented methodology, the main challenges of applying LCA to building construction projects are raised. Final concluding remarks are then discussed to outline the path expected to be followed in the future to enhance the sustainability of the construction projects.

LCA Methodology

Significance of LCA in Construction

Several methodologies and initiatives have already been created in the construction sector with the aim of sustainably evaluating buildings and acquiring associated sustainability rating systems and certifications. This includes BREEAM - BRE Environmental Assessment Method (Baldwin, 1998), LEED - Leadership in Energy and Environmental Design (Clevenger, 2008), NABERS - National Australian Building Environment Rating Scheme (Seo *et al.*, 2005), among other examples. Many of the existing certification schemes, however, do not analyze the environmental impacts at each stage of the building's life cycle. That is why the LCA approach has been prominent in research and in the marketplace as a means for combating such shortcomings. LCA is a technique for assessing and quantifying possible environmental impacts throughout the life cycle of a product or process (ISO, 2006a). When applied to a building project, LCA evaluates the building performance and analyzes the potential impacts generated throughout the building's life cycle, along with quantifying materials and construction processes, and their environmental repercussions (de Larriva *et al.*, 2014).

Environmental assessments are often used to assess the impacts associated with manufacturing and maintaining a particular service, product, or system (Karl *et al.*, 2019). But when considering the long lifespan of a building, it is not enough to choose materials and processes that generate few impacts during the manufacturing stage. It is necessary to evaluate the complete life cycle of the building until its demolition (Najjar *et al.*, 2017).

LCA allows the analysis of the environmental impacts permeating all these stages of the building life cycle. In addition, this methodology is already widely disseminated, with several technical standards, computer programs and databases capable of assisting professionals in this work (Anand and Amor, 2017). Using this approach, engineers, architects, and builders can make less environmentally damaging decisions in their construction projects. An overview of LCA is given next.

Overview

The International Standards Organization (ISO) published the most recognized standards of LCA methodology (Khasreen *et al.*, 2009), including ISO 14040 Principles and framework and ISO 14044 Requirements and guidelines.

According to ISO 14040, LCA is the compilation of inputs, outputs and potential environmental impacts of a product system throughout its life cycle (ISO, 2006a). The information generated can be used to improve processes, support public policies and can serve as a basis for decision making. When applying LCA from a building's perspective, the methodology aims to assess the environmental impacts resulting from building materials and building techniques adopted at different stages of the project's life cycle (Figueiredo, 2018).

The most common LCA method is referred to as a 'cradle-to-grave' approach since it encompasses the stages of extraction of raw materials, up to the final disposal of the building components after demolition, where all materials return to nature. LCA also permits demarcating the boundaries of the study in other partial ways, including cradle to gate, gate to gate and gate to grave (ISO, 2006a).

Overall, LCA consists of four main steps: (i) goal and scope definition; (ii) Life Cycle Inventory (LCI) analysis; (iii) Life Cycle Impact Assessment (LCIA); and (iv) Interpretation (ISO, 2006a). These phases are represented in Fig. 1. The first step is intended to guide the subsequent work. Some other definitions need to be specified at this stage: the *Functional Unit*, describes the primary function fulfilled by a product system, and indicates how much of this function is to be considered in the intended LCA study (Guinée, 2002); the *System Boundary*, refers to how far the analysis will be done; the *assumptions and limitations* need to be specified; and finally, the *impact categories* to be used, need to be stated, such as global warming potential (GWP), acidification and energy consumption (Ortiz *et al.*, 2009).

The second step involves the compilation and quantification of inputs and outputs for the *Functional Unit* throughout the life cycle. According to ISO 14044, LCI results are classified into impact categories (ISO, 2006b). These impacts can be evaluated based on midpoints and/or endpoint approaches. A midpoint approach is more related to elementary flows, which specifies the material or energy entering the system that has been drawn from the environment, without previous human transformation, or material or energy leaving the system that is released into the environment without subsequent human transformation (ISO, 2006b). On the other hand, an endpoint approach transmits relevant information about the characterization flows to the decision maker (Ismael, 2018). Midpoint indicators focus on environmental problems, such as global warming or acidification (Gernuks *et al.*, 2007). Endpoint indicators present the impacts of decisions made on human health, biodiversity and resource scarcity. The midpoint is also known as a problem-oriented approach, while the endpoint is designated as a damage-oriented approach (Gernuks *et al.*, 2007).

In the third step of LCA, the LCIA phase aims at understanding and evaluating the magnitude and significance of the potential environmental impacts. According to ISO 14040, LCIA is divided into five stages, of which two are mandatory and three are optional. The Classification and Characterization stages are mandatory, in which the elements of the LCI are attributed to one or more environmental impact categories, with each element then assigned to a value referring to its respective environmental

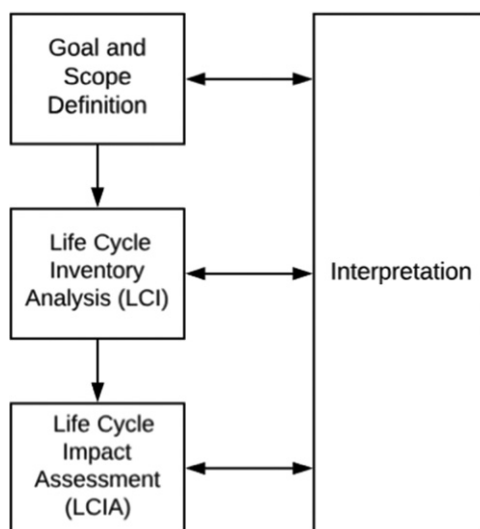


Fig. 1 Life cycle assessment framework. Source: Modified from ISO, 2006a. ISO 14040:2006 – Environmental Management – Life Cycle Assessment – Principles and Framework. doi:10.1136/bmj.332.7550.1107.

damage. The Normalization, Weighting and Aggregation steps in LCIA are optional stages. The results characterized can be normalized to make it possible to observe the most significant impact categories. They can also be weighted, which involves a subjective process where each category of environmental impact is assigned to an importance level. Thus, it is possible to make an aggregation, where the different categories of environmental impact can be aggregated into a single indicator to facilitate decision making.

The interpretation is the last phase of LCA. This step represents a technique for identifying and evaluating all the information from the other phases of the study, in relation to the defined goal and scope. This step is essential for the analysis, because practitioners must formulate conclusions and recommendations considering the uncertainties and lack of consistency in the LCI and LCIA phases. The professionals must analyze if the data quality is enough to achieve the goal of each study.

LCA Applied in Buildings

In the construction sector, LCA is an important tool to assist the assessment of the environmental performance of buildings. To achieve a more sustainable construction industry, it is advisable to use the LCA methodology in the early stages of project design and planning (Najjar *et al.*, 2017). This is because the cost of implementing changes increases as the project evolves, due to the reduction in flexibility of change (PMI, 2017). When performing environmental analyses at an early stage of the project, an opportunity exists to test and compare different types of materials and construction techniques, without this being too costly (Basbagill *et al.*, 2013).

It is important to note that a building is a complex structure, composed of different systems and components. Therefore, the building professional must make a great effort to obtain all the necessary data to perform the analysis. Oftentimes, the studies are not related to an entire building but are limited to individual elements of a building. This is because the size and complexity of a building makes it necessary for professionals to address some limitations in their studies (Lindberg *et al.*, 2004). These more specific studies have great value, but it is still necessary that the building be analyzed as a whole, going through all phases of its life cycle. This is the only way to ensure that construction achieves sustainable standards.

In addition to the importance of considering the whole building, it is ideal to consider all stages of the life cycle of the building. The building life cycle can be divided into eight main stages: (i) extraction of raw materials; (ii) manufacturing; (iii) distribution; (iv) construction; (v) operation; (vi) end-of-life; (vii) disposal; and (viii) recycling. These stages are represented in Fig. 2.

LCA applied to the construction sector has also become a useful tool for developing buildings that consume less resources, such as energy, water and fuel. About half of the world's electricity demand is consumed by the building sector (REN21, 2017). In addition, the construction industry is known to consume a significant amount of water and fuel throughout the project life cycle. When LCA is used to evaluate the energy consumed, all energy input can be accounted for throughout the life cycle, including both embodied energy and operating energy (Cabeza *et al.*, 2014). The same analysis can be done to quantify the consumption of water and fuel. Thus, when applying LCA in a construction project, other types of indicators can be considered in the analysis. It is important to quantify and analyze the consumption of resources, electricity, fuel, water and equipment. For example, to analyze the energy consumption during the operation phase of the building, it is necessary to calculate the energy use for heating, cooling, ventilation, hot water and lighting. Therefore, it is possible to consider the indicators for environmental impacts, known as LCIA impact categories, beyond the indicators for resource use and for other environmental information (EN, 2012).

When considering a building as an object of environmental analysis, it is also important to consider that several types of design decisions can influence the environmental impacts generated. Unlike other products that generate environmental impacts that depend only on the materials used and the manufacturing method employed, other factors need to be considered for building projects. This is because in the implementation of building LCA, it is also necessary to analyze the construction and operation phases, which contain services rather than construction properties (Erlandsson and Borg, 2003). A clear example of this is the location and orientation of the building on the ground. The designer should analyze the best position of the building to make the best use of natural lighting. This factor can drastically decrease the use of electricity over the years. In addition, configuring rooms in such a way to take advantage of natural ventilation can be an assertive decision to reduce the energy consumption produced by cooling systems.

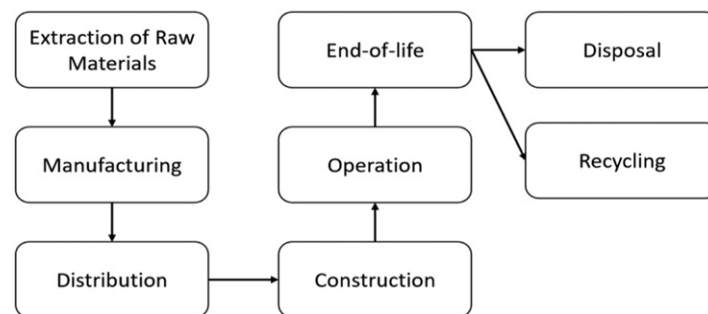


Fig. 2 Life cycle of building projects.

When conducting a building LCA, one should evaluate not only the building, but also the external works attached to this building and temporary works associated with the building's construction. When the purpose of the analysis is the comparison of different alternatives, the definition of the *Functional Unit* is fundamental. In building LCAs, the *Functional Unit* can also be referred to as *Functional Equivalent*. This term refers to the quantified functional requirements and/or technical requirements for a building, to be used as a basis for comparison. The definition forms the basis for transparent and reasonable comparison between different types of buildings, permitting the practitioner to make the comparison qualified with a dimension like per m², per room, etc. (EN, 2012).

Limitations of LCA Application in Building Projects

Due to the great complexity of the buildings, many difficulties can arise during an LCA. It is imperative that professionals consider this complexity when performing a Building LCA. Otherwise, many aspects may be disregarded, and the results may not be representative.

The following will present some limitations present in performing building LCAs. These limitations exist in all types of buildings and should be thought of in all projects. It should be noted that each project is unique and that its particularities must be considered too.

Lifetime of the Buildings

In the construction sector, many LCA studies do not adequately address the actual lifetime of the buildings (Aktas, 2011). When assuming a typical value for the building lifetime, the study does not reflect the particularities of each project. For example, in one research study, the author found that existing service life prediction methods do not incorporate the effects of social factors into the analysis (Aktas, 2011).

Several factors can influence the building's lifetime, such as the materials and components that were used in the construction and the location of the building. In addition, the use of the building also interferes in this data. For example, it has been proven that lifetime of residential and commercial buildings is significantly different (Aktas and Bilec, 2012). This can be explained by the fact that commercial buildings need to be updated more quickly than residential buildings in order to get more economic benefits (Liu et al., 2014). The values need to be determined based on the nature of the construction, purpose, use and environment. One way to determine this value is to consider factors that can influence the lifetime of the building. An existing method, based on ISO 15686-1 (ISO, 2011), uses the following equation:

$$LFe = LFr \times f_A \times f_B \times f_C \times f_D \times f_E \times f_F \times f_G$$

Where:

LFe – Lifetime estimated;

LFr – Reference lifetime;

f_A – Materials quality factor;

f_B – Project quality level factor;

f_C – Execution quality factor;

f_D – Interior environment factor;

f_E – External environment factor;

f_F – Type of use factor;

f_G – Maintenance level factor.

There are already studies that point out the importance of determining with more precision the life span of buildings. One study presents an example of this, performing a statistical analysis that demonstrates that factors such as location, refurbishment, use type and wall material could potentially influence the quantification of the temporal scope of building LCAs (Østergaard et al., 2018).

It is therefore very important that the professional find a way to determine the lifespan of the building effectively. The use of a period of time that does not adequately address the actual lifetime may lead to misleading conclusions at the end of the study (Aktas, 2011).

Dynamic Parameters

The building data is characterized by time-dependent parameters which need to be evaluated (Lindberg et al., 2004). This is another challenge that needs to be addressed when conducting LCA.

The current LCA method considers arbitrarily fixed time horizons and/or steady state conditions (Shimako, 2017). But the concept of dynamic LCA, known by the acronym DLCA, is increasingly widespread among researchers. This concept transforms the LCA into a dynamic perspective, incorporating explicitly the dynamic modeling of processes in the context of temporal and spatial variations (Collinge et al., 2013). There are already several studies on this subject based on the building sector. One of these studies presents a methodology for applying this approach (Negishi et al., 2018). This work lists some dynamic parameters to buildings,

such as energy consumption, the typology of inhabitants and their behavior. These parameters can be variable depending on the economy, culture and climate.

Dynamic LCA can help decision makers improve their understanding of when and in which context potential impacts occur (Fouquet *et al.*, 2015). But certainly, its application is not carried out so easily. There is still much to study on the subject, so that all time-dependent parameters can be considered. Applying this approach requires the practitioner to have a large amount of data. In addition, it becomes necessary to analyze both quantitative and qualitative data at the same time, which can lead to even more uncertainties in the analysis.

Despite the difficulties, it is fundamental that the dynamic nature of projects be taken into account when performing a Building LCA. Considering these dynamic parameters is paramount for more assertive environmental assessments. Ignoring the nature of the data may render the analyses unreliable and nonrepresentative of the reality of the construction project.

Difficulties in Proposing Modifications

To make use of all the potential of the LCA approach on buildings, it is important to compare different materials and resources in the same project in order to choose the more sustainable list of materials in each case. However, making these changes can mean a substantial increase in the work of designers. It is estimated that about 60% of the time is being lost in the early stages of designing construction projects. This is justified by the need to insert repeated information in the model, in order to test the existing alternatives (Najjar *et al.*, 2017). To solve this issue, it is advisable to use a software based on Building Information Modeling (BIM) to create building projects.

For BIM, information is the core of modeling. The three-dimensional model is a real prototype of the building. With this technology, the insertion of all the necessary information associated with the planning of a building is made in a single digital model, allowing, thus, a better management of the whole project (Figueiredo, 2018).

The modeling process is performed parametrically, that is, all elements are represented by parameters that are associated with data. This allows a constant updating of the project, carried out in a dynamic fashion. Besides that, it is important to emphasize that BIM methodology is not limited to the geometric parameters, such as thickness, length and height of objects, present in design or engineering drawings (Jung and Joo, 2011). In fact, the methodology uses a digital model that can be extended for multiple purposes. It is possible, for example, to specify thermal and acoustic properties of the materials used, as well as to consider climatic data of the geographic region. Based on BIM, it is easier to perform simulations in order to critically analyze the building.

The integration of BIM and LCA methodologies in the design phase of the project has great potential in terms of influencing the project (Figueiredo, 2018). With efficient information management, it is possible to design projects that consider environmental aspects. Therefore, it is strongly advised that professionals invest in this integration so that they can consider a large part of the building data.

Uncertainty and Variability

As the time available to develop a building project reduces, it is necessary to also reduce the data collection effort and to make input simplifications and assumptions; this could however result in misleading conclusions (Pannier *et al.*, 2018). Thus, many uncertainties are created and need to be considered in the interpretation of LCA results (Hoxha *et al.*, 2017).

Among other sources of uncertainty, two deserve special attention due to their ability to compromise the reliability of LCA results: poor data quality and the exclusion of site-specific data from the inventory (Ross *et al.*, 2002). There are already computer programs focused on performing LCA in buildings that integrate BIM and LCA methodologies, such as Tally™ (Kieran Timberlake Innovations, 2018) and Impact™ (BRE Group, 2019). Although there are already applications and software for this purpose, they do not present the possibility to perform a Sensitivity Analysis (SA) of the results.

Sensitivity analysis seeks to determine the effect of a variation of a given item on the total impact assessed for that item. Once the professional restricts the data collection, it is necessary to fully understand what consequences will be faced. A sensitivity analysis is essential for the interpretation phase, so that the LCA practitioner can make the best conclusions and recommendations for the project.

The Complexity of Decision Making

The methodologies focused on the life cycle concept allow quantifying various types of impacts. However, the implementation of these techniques increases the complexity of decision making and therefore requires systematic tools and methods (Gaudreault *et al.*, 2009). In this context, Multiple-criteria decision-making (MCDM) and LCA approaches complement each other well.

MCDM is an approach used to aid in the decision-making process, allowing to analyze the problem from different points of view and considering different alternatives. There are many methods in the scientific literature to support strategic decision making, such as mathematical optimization (Hammad *et al.*, 2016, 2018), fuzzy set theory (Onat *et al.*, 2016), and the analytic hierarchy process (Ahmad and Tahar, 2014). Yet there is no method which is known to be the most appropriate as it would depend on the setting in which the project case is considered, along with the information that is available.

It is becoming more recurrent to find studies that use MCDM to contrast between environmental and economic outcomes. A study carried out in 2017 surveyed the existing studies developing or implementing different methods for combining environmental and economic analysis of products, technologies and systems (Miah *et al.*, 2017). This is interesting to understand the progress of using MCDM to integrate life cycle analysis approaches. The authors reported that 30 studies conducted between 1999 and 2016 used MCDM to integrate Life cycle assessment and life cycle cost. Of these, 6 are related to building projects. There were also 32 studies, between 2002 and 2016, in which environmental and economic analysis is taken as an optimization problem. Among these studies, 10 are about buildings.

However, most studies that use MCDM are still focused on comparing financial and social aspects. Much progress still needs to be made in the field on the integration of MCDM and LCA. In order to make a good environmental decision, it is necessary to first choose the importance weights for each impact category considered. This choice is subjective as it will depend on the preferences of the decision maker and therefore can vary from one decision maker to another. This is one of the many challenges that must be addressed, but the study on the integration of these methodologies needs to be encouraged.

Challenges and Way Forward

As previously explained, applying the LCA methodology to building projects is still a major challenge for professionals. A building is composed of several systems and it is necessary to obtain a large number of data for a reliable analysis. As a result, this research explores the possibility of utilizing an integrated platform that combines other methodologies, as shown in Fig. 3. The purpose is not to define a more appropriate method for the analysis of construction projects, but to present a possibility of integration between methodologies that together have the capacity to transform buildings projects into more sustainable ones.

As explained graphically in Fig. 3, the idea is to use the LCA methodology concomitantly with other methodologies to obtain more accurate results. Following the basic principles of LCA, it is advisable for practitioners to perform the following design steps:

- Use statistical analysis to determine more accurately the lifetime of the studied building;
- Adequately evaluate time-dependent parameters based on the concept of dynamic LCA (DLCA);
- Analyze a digital prototype of the building based on BIM, which embeds parameters that generate different simulations;

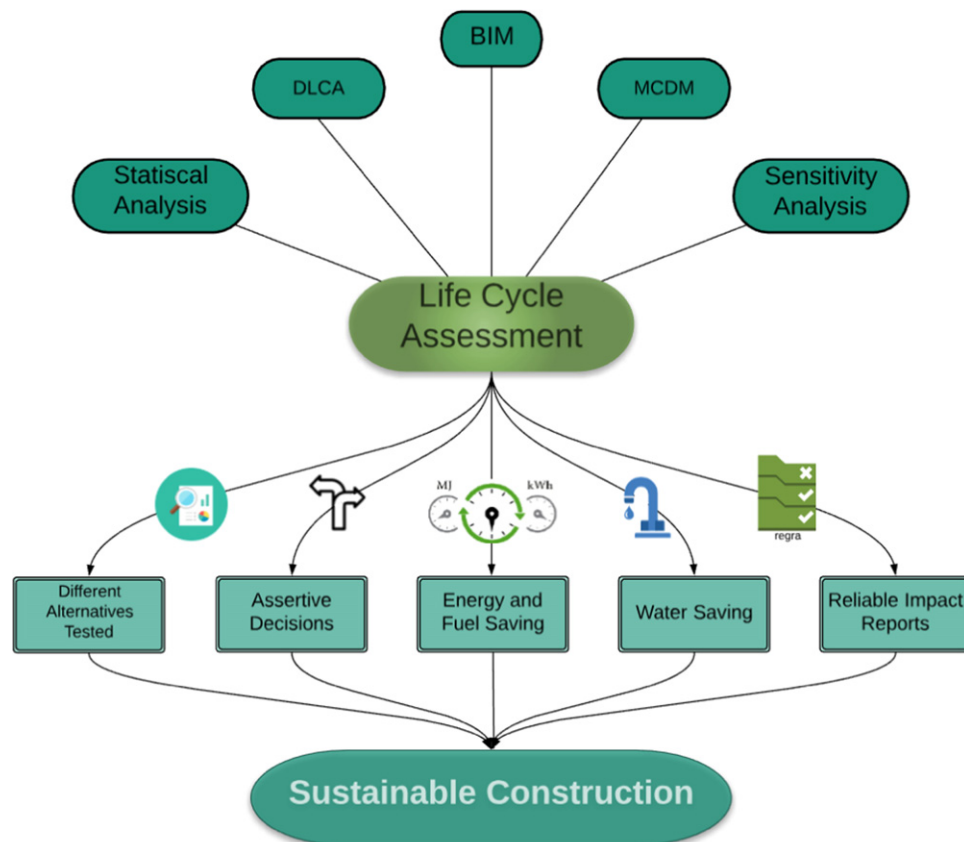


Fig. 3 Integration of methodologies.

- Make use of some MCDM method to aid in the decision making of the project, in order to make the most environmentally conscious choices;
- Conduct a sensitivity analysis to aid in the interpretation of the results obtained.

Thereby, the concept of sustainability in buildings becomes feasible, since the entire life cycle of the building is analyzed in the project planning phase. This allows practitioners to test different alternatives within the building to make more assertive decisions that save energy and water and generate less environmental impacts.

Unfortunately, there is not yet a commercially available platform that gathers all these concepts together, but this development is encouraged by the authors. Such an integration would be a multidisciplinary tool, as it would encompass several areas of knowledge. This requires great knowledge of the team of professionals, as well as requiring more time in the design phase of the construction project. It is thus necessary to encourage research in this area, exploring the use of the proposed framework in real buildings. Finally, it is hoped that the analysis of the social and economic impacts will also be incorporated, so that sustainable construction can be achieved, covering all the main pillars of sustainability.

See also: A Comparative Life Cycle Assessment for Utilising Laminated Veneer Bamboo as a Primary Structural Material in High-Rise Residential Buildings

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Synthesis of High Grade Activated Carbons From Waste Biomass

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Introduction

Activated carbon (AC) is a versatile porous material with the high surface area and high pore volume. It has a wide variety of practical applications such as gas storage (Sheikh *et al.*, 1996; Lozano-Castello *et al.*, 2002; Rahman *et al.*, 2010; Thu *et al.*, 2014), separation (González *et al.*, 2013; Cong *et al.*, 2015), adsorption cooling (Pal *et al.*, 2016, 2017a,b), hydrogen storage (Jordá-Beneyto *et al.*, 2007; Xu *et al.*, 2007), methane storage (Rahman *et al.*, 2010) CO₂ capture (Himeno *et al.*, 2005; Jin *et al.*, 2011; Yu *et al.*, 2015; Kayal and Chakraborty, 2018), and super-capacitor applications (Xing *et al.*, 2006; Wen *et al.*, 2009; Di Biase and Sarkisov, 2013). However, the ACs used in the above applications are expensive and made from non-renewable precursor materials such as coke and petroleum residue (Otowa *et al.*, 1993). On the other hand, there are plenty of renewable precursor sources which can be used for ACs preparation using various techniques. Renewable biomass precursors usually grow through the agricultural activities, and it contains chemical constituents having high carbon content which is beneficial for ACs production. Using biomass as a precursor is termed an environmentally benign approach as it prevents the production of CO₂ and CH₄ during conversion and the byproducts finally enter the natural carbon cycle process. Recently, numerous research works have been reported where ACs are prepared from a different source of waste biomass as it is renewable and cheap (Yang *et al.*, 2010; Hao *et al.*, 2013; Bhatnagar *et al.*, 2015; Mahamad *et al.*, 2015; Jain *et al.*, 2016; Kyzas *et al.*, 2016; Sahoo and Ramgopal, 2016). Danish and Ahmad (2018) reviewed the usage of wood biomass as a sustainable precursor to synthesize ACs where authors cited different agricultural sources for the production of low-cost ACs. Coconut shell-based ACs were prepared using activating agents such as steam, CO₂ and a mixture of steam-CO₂ with microwave heating (Yang *et al.*, 2010). Kyzas *et al.* (2016) explored the use of ACs from waste potato peels using phosphoric acid at different activation temperatures such as 400, 600 and 800°C. The ACs were prepared by Hao *et al.* (2013) from hydrothermally carbonized waste biomass for CO₂ capture from flue gas. Mahamad *et al.* (2015) synthesized ACs from the pineapple waste biomass (leaves, stem, crown) using ZnCl₂ as an activating agent. Nor'Azizi Bin Othman (NOR', 2013) synthesized the ACs from waste palm trunk (WPT) using KOH and steam as an activating agents.

Literature review indicates that biomass is a good choice as precursor materials but the porous properties of the biomass-derived ACs reported so far are not optimized. There is a scope to increase surface area and pore volume if the optimum condition is applied during the carbonization and activation process. Therefore, the aim of this study is to obtain excellent surface area and pore volume contained ACs by optimizing the synthesis process. This article presents the synthesis process of ACs from two kinds of biomass namely waste palm trunk (WPT) and mangrove (M). Some important contributions in this article are:

- Mechanism of activated carbons production from biomass precursors are presented.
- Chemical activation method at different activation conditions is experimentally investigated after carbonization of raw biomass (waste palm trunk and mangrove) to synthesize highly porous ACs.
- Potassium hydroxide (KOH) with different mass ratios is used as an activating agent for chemical activation.
- A series of ACs are prepared from WPT and M by changing the activation conditions.
- Dried, carbonized and activated yield sample are presented at every synthesis condition.
- Surface morphology and elemental composition of synthesized ACs are investigated.

Sample Preparation

Precursor Material

The properties of a precursor material considerably influence the nature of the resulting yield. The chemical nature of the surface oxides and the surface area of the AC are determined by carbonization and activation method whereas the pore size distribution and the pore structure are mostly determined by the nature of the precursor material and the extent of activation (NOR', 2013). In this article, waste palm trunk (WPT) and mangrove (M) are employed as a low cost and renewable precursor materials for the production of ACs that can be used in

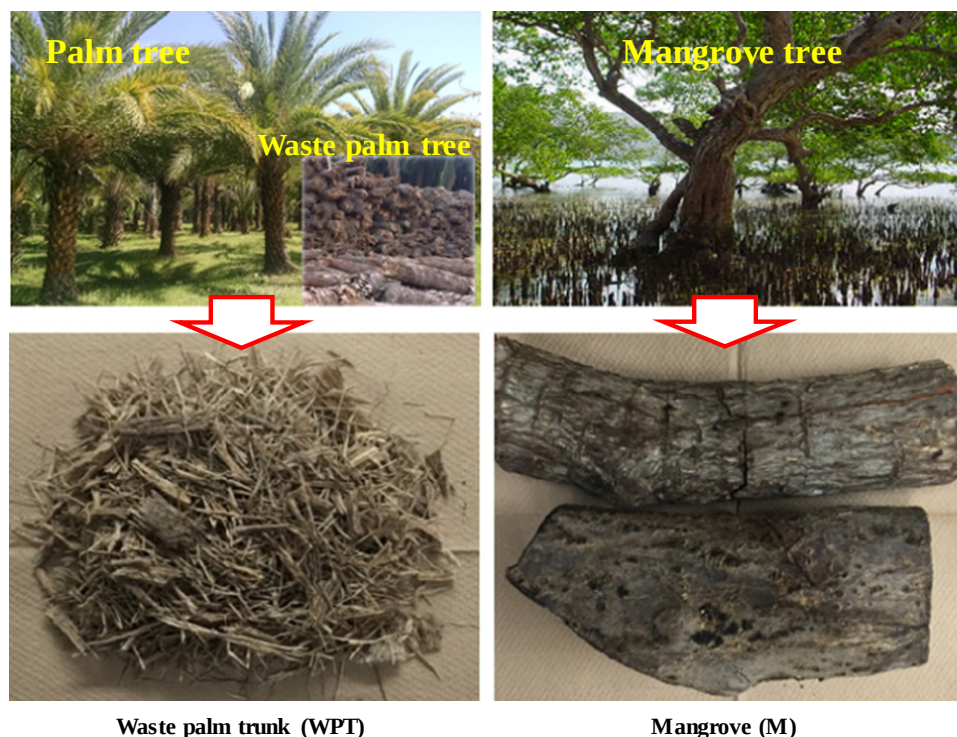


Fig. 1 Pictorial view of two kinds of raw biomass employed for synthesis.

Table 1 Elemental composition of waste palm trunk (WPT) and mangrove (M)

Raw material	Elemental composition [wt%]				Ash [wt%]
	C	H	N	$O_{diff.} [100\% - \sum (C, H, N, Ash)]$	
WPT	44.02	5.75	0.49	48.41	1.33
M	46.70	6.04	0.14	45.98	1.14

various applications such as adsorption heat pump (AHP) systems, CO₂ capture or storage, and energy storage. **Fig. 1** shows the pictorial view of two kinds of biomass that are used as precursors. From the photograph, it can be seen that the WPT and M are structurally different from each other. As a result, both materials may produce different surface area, surface morphology, pore volume, and pore size at different carbonization and activation conditions, as initially expected. Elemental composition of raw samples (WPT and M) are analyzed using a CHN (Carbon, Hydrogen, and Nitrogen) analyzer (MT-5, Yanako, Japan). The assessment of O content ($O_{diff.}$) can be defined by subtracting the sum of the contents of C, H, N, and ash from 100%. The elemental composition of raw WPT and M is shown in **Table 1**. The carbon contents of raw WPT and M are found 44.02% and 46.70%, respectively.

The N₂ adsorption/desorption isotherm and pore size distribution (PSD) of two raw biomasses are shown in **Figs. 2** and **3**, respectively. The N₂ adsorption amount onto both biomasses is low which implies that raw material possesses low surface area and pore volume. However, WPT shows high adsorption capacity of N₂ compared to M. The PSD results show that WPT has a wide range of pore size distribution compared to M. Furthermore, the total pore volume is higher than that of mangrove. The BET report including surface area and pore volume of two raw biomasses are furnished in **Table 2**.

Carbonization of Biomass Precursor

The main purpose of carbonization or pyrolysis is to remove the volatile substances from the biomass in order to convert into a suitable form for activation. It is usually performed in an inert atmosphere. Nitrogen (N₂) is commonly used as an inert gas during the carbonization and activation process because it can repel the gaseous oxygen (O₂) from the pyrolysis chamber. Thus, the burning of the biomass can be avoided. Furthermore, N₂ gas is clean, comfortable to handle, and available at low-cost. During the phase of the carbonization, the carbon content of the product reaches a value of more than 65 per cent and possesses an elementary pore structure. Most of the non-carbon elements, hydrogen, and oxygen are removed in gaseous form during the carbonization process. It consists of four main steps ([Rashidi and Yusup, 2017](#)):

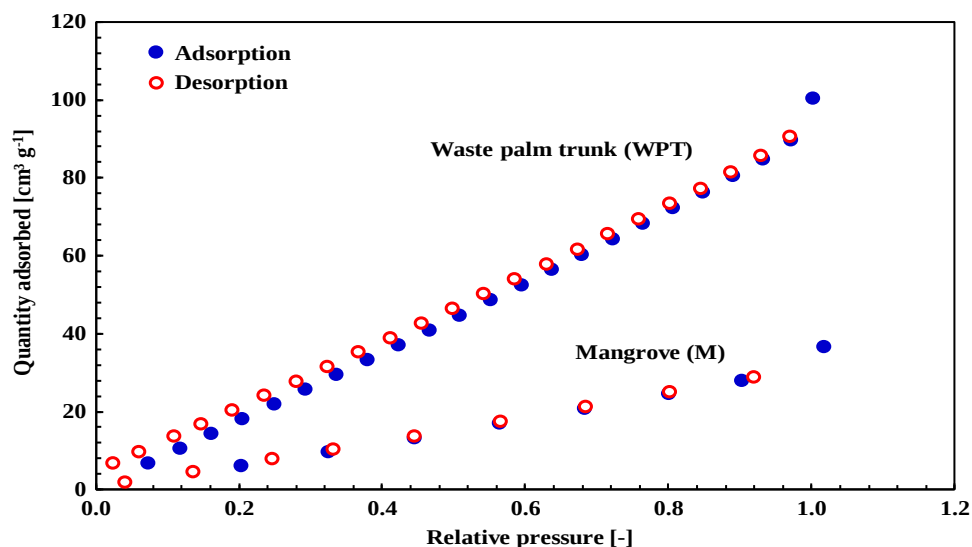


Fig. 2 N_2 adsorption/desorption isotherm of two biomasses, WPT and M.

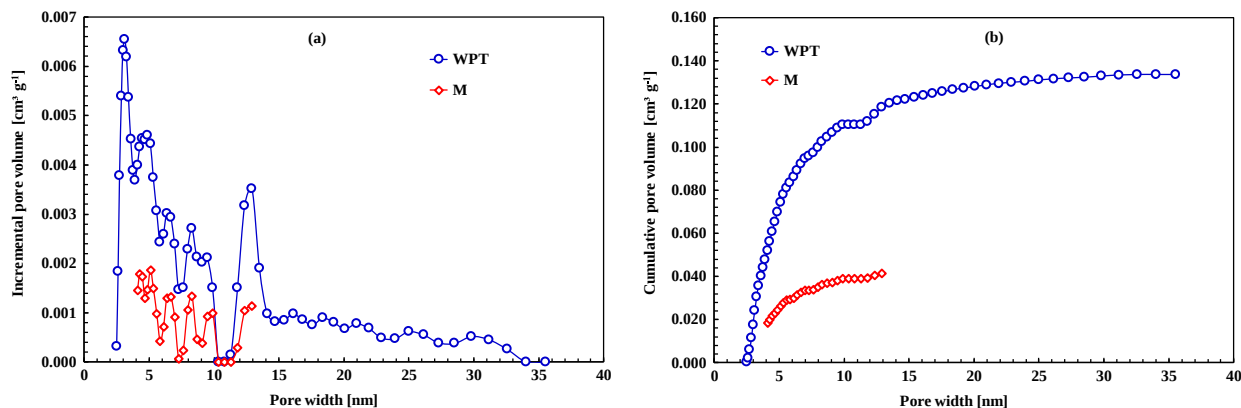


Fig. 3 Pore size distribution of raw WPT and M: (a) incremental; (b) cumulative pore volume.

Table 2 BET report and pore volume of waste palm trunk (WPT) and mangrove (M)

Parameter	WPT	M
BET surface area [$m^2 g^{-1}$]	130 ± 4	43 ± 3
Slope [$g cm^{-3}$]	0.023767 ± 0.000920	0.073269 ± 0.007433
Y-intercept [$g cm^{-3}$]	0.009596 ± 0.000274	0.027351 ± 0.002521
C [dimensionless]	3.476699	3.678805
Q_m [$cm^3 g^{-1}$]	29.9732	9.9383
Correlation coefficient [dimensionless]	0.9940621	0.9948941
Molecular cross-sectional area [nm^2]	0.1620	0.1620
Total pore volume [$cm^3 g^{-1}$]	0.13356	0.04146

Step 1: dehydration process occurs at a temperature lower than $200^\circ C$ in which moisture from the raw material is removed.
 Step 2: at a temperature range of 170 – $270^\circ C$, the biomass starts to decompose while light tar and organic acid are discharged.
 Step 3: the biomass is decomposed, and a significant amount of liquid and gas is released to produce bio-char at temperature 270 – $350^\circ C$.
 Step 4: temperature above $350^\circ C$, an acceleration in carbon content occurs by removing the remaining volatiles.

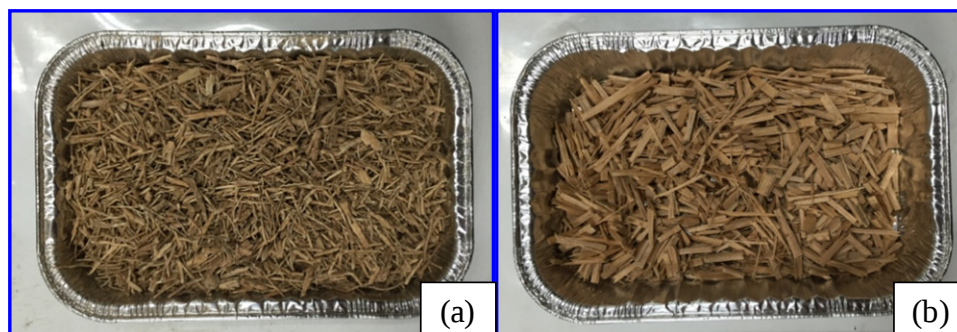


Fig. 4 Crushing and drying samples: (a) WPT and (b) M.

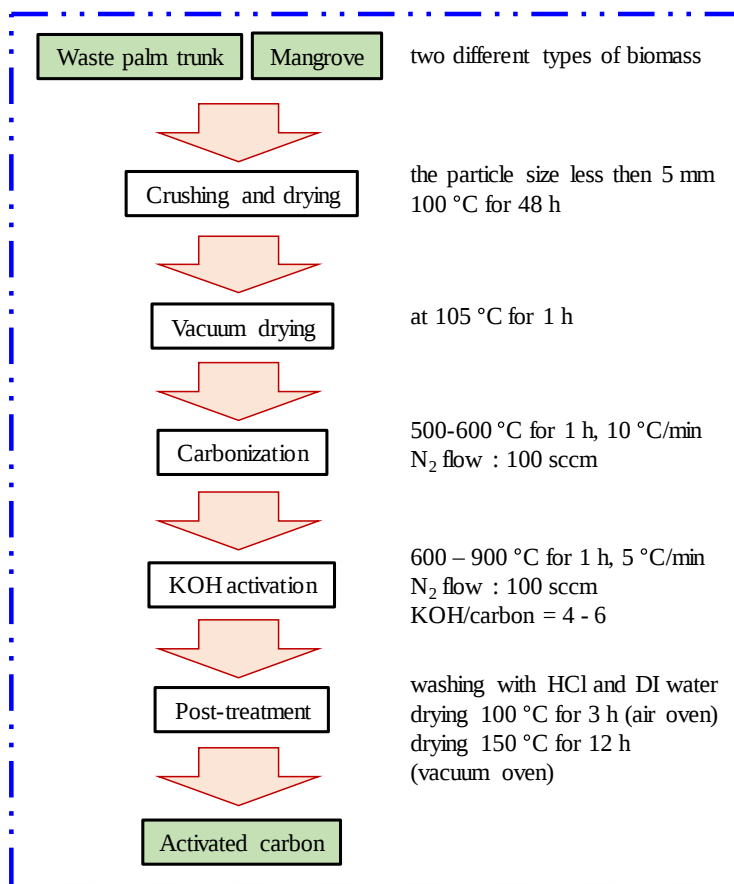


Fig. 5 Preparation steps for biomass-derived ACs. Reproduced from NOR', A.B.O., 2013. Effective utilization of waste palm trunk. Kyushu University. Available at: <http://hdl.handle.net/2324/462781> (accessed 02.04.18).

The precursors are essential to undergo a pre-treatment process before carbonization. According to the literature, pre-treatment procedure includes several phases: (a) washing, (b) drying, and (c) crushing and drying. In this experiment, WPT and M are crushed into a particle size less than 5 mm in order to perform homogeneous drying and carbonization. The crushing samples are then dried in an air dryer at 100°C for 48 h. The vacuum drying at 105°C for 1 h is accomplished after air drying before being used for carbonization. These two drying operations assist for removing water or moisture content from the biomass. The photograph of the crushing and drying of two kinds of biomass is shown in Fig. 4. The carbonization process for both biomasses is carried out at 500 and 600°C at a heating rate 10°C/min with N₂ flow rate 100 cc/min for 1 h. The sample preparation scheme of ACs from biomass is shown in Fig. 5 (NOR', 2013). The carbonization reactor chamber is shown in Fig. 6. The chamber mainly consists of the high-temperature furnace with a temperature controller, stainless steel tube, and N₂ gas tank. The rotameter is used to control the N₂ flow

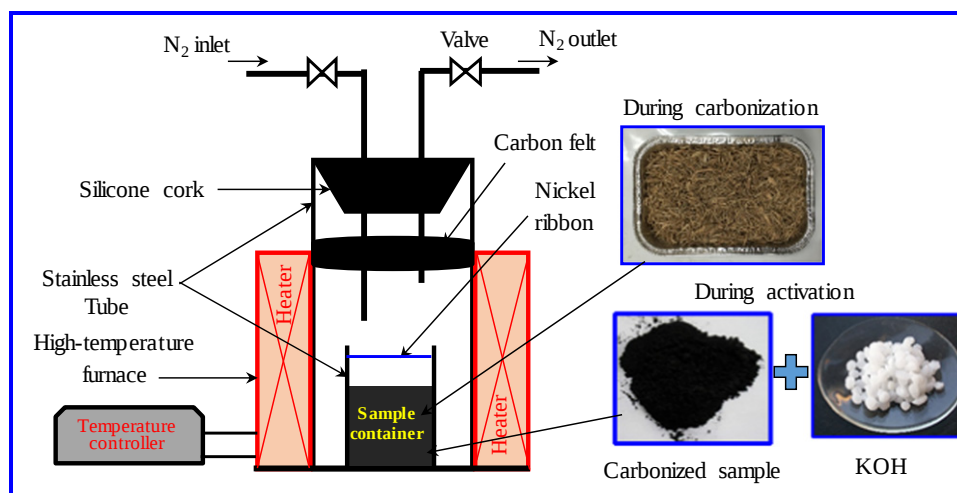


Fig. 6 Schematic diagram of an experimental setup for carbonization and KOH activation process.



Fig. 7 Photograph of carbonized samples: (a) WPT and (b) M.

rate inside the reactor chamber. **Fig. 7** shows the photograph of two carbonized biomass samples. After the heat treatment, biomass-derived carbonized samples are grinded and sieved to mesh size 100 μm for the application to the adsorption heat pump systems.

The resulting carbonized samples have a small adsorption capacity, which is not suitable for adsorption applications. To enhance the adsorption capacity, the activation process is conducted (Section "Activation of Carbonized Biomass Sample") in turn to increase the surface area and pore volume of the ACs.

Activation of Carbonized Biomass Sample

The ACs are mostly prepared using two activation methods: physical activation and chemical activation. Porous properties including surface area and pore structure depend on activation method along with inherent properties of precursor material. Before activation process, carbonized material is required to undergo several stages: (a) drying, (b) grinding, and (c) sieving to preferred size.

Physical activation

In physical activation, the reaction is involved between a carbon atom and the oxidizing gas such as steam, carbon dioxide (CO_2), a binary mixture of CO_2 and nitrogen (N_2), or air at an elevated temperature ranging from 800 to 1100°C. This method can produce ACs with well-developed pore structure. However, the surface area of the prepared ACs is comparatively lower than that of the chemical activation. The physical activation method is considered an inexpensive and environmentally benign process because of the absence of a chemical agent that may create a subsequent disposal problem. However, prolonged activation time together with low carbon yield, and high power consumption are disadvantages of this process (Rashidi and Yusup, 2017). The reaction mechanism for the gas activation of carbon with steam or CO_2 can be characterized by the following several simultaneous/consecutive reactions (Eqs. (1)–(3)). **Fig. 8** shows a schematic drawing of the experimental setup for steam activation. It mainly consists of a high temperature electric furnace, tape heater, N_2 gas, quartz tube, rotameter, valve, water bath for the steam generator, and a cooling bath.

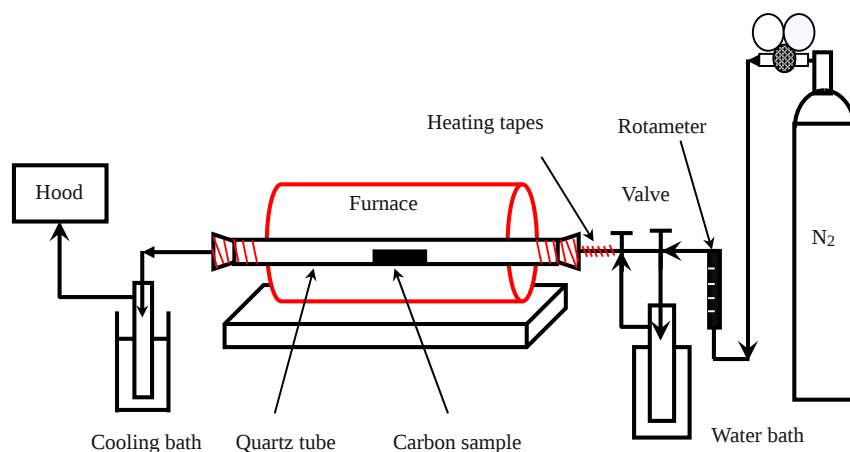


Fig. 8 Schematic drawing of the experimental setup for steam activation.



Chemical activation

The various kinds of activating agents including potassium hydroxide (KOH), sodium hydroxide (NaOH), potassium carbonate (K_2CO_3), phosphoric acid (H_3PO_4), sulfuric acid (H_2SO_4), and zinc chloride ($ZnCl_2$) are usually employed in chemical activation process (Rashidi and Yusup, 2017). Consequently, different chemical agents react differently with the precursors and hence influence the development of porosity, pore structure, and adsorption behavior. This activation is economically feasible compared to physical activation because it requires lower activation temperature, shorter processing time, and gives high carbon yield. However, in this activation process, the sample required washing at the final stage to remove the residual inorganic material which may cause a pollution problem.

In this article, carbonized WPT and M are used as a precursors for preparing ACs by applying chemical activation method. The particle size less than $100 \mu m$ of these two carbonized samples is used for the activation. The activation process is carried out in a nitrogen (N_2) atmosphere which creates an inert atmosphere. The identical activation conditions are applied to both carbonized materials (WPT and M). Fig. 5 represents the processing steps for preparation ACs from raw biomass (NOR, 2013). The chemical activation of various carbon sources using KOH as an activating agent is very promising because of its lower activation temperature and higher yields, and well-defined micropore size distribution and ultrahigh specific surface area up to $3000 m^2 g^{-1}$ of the resulting ACs (Otowa et al., 1993; Tay et al., 2009; Wang and Kaskel, 2012). The same experimental setup (Fig. 6) is used for the preparation of ACs using potassium hydroxide (KOH) as an activating agent. The KOH (purity > 85.0%, Wako Pure Chemical Industries, Ltd.) is selected as an activating agent in the impregnated WPT and M biochar because it is found to be more effective than another chemical agent such as $ZnCl_2$ and H_3PO_4 for creating porosity in ACs. The experimental conditions of temperature, activating agent (KOH), heating rate, holding time, N_2 flow rate are the same for preparation of ACs from both carbonized materials of WPT and M. The chemical activation process using KOH as an activating agent consists of several possible simultaneous/consecutive reactions proposed by several researchers (Otowa et al., 1993; Wang and Kaskel, 2012), which are shown in the following equations.



The chemical reactions presented in the Eqs. (4)–(7) occur at activation temperature lower than $700^\circ C$. A considerable amount of metallic potassium is formed by the reduction of K_2O by carbon and hydrogen when the temperature exceeded $700^\circ C$.

Table 3 Series of AC samples synthesized from WPT and M by changing carbonization and activation conditions

No.	Activating agent	Carbonization temperature [°C]	Activation temperature [°C]	Heating rate [°C/min]	Holding time [h]	KOH to sample ratio	^a Sample naming
1	KOH	500	600	5	1	4:1	WC500A600K4
2			700			4:1	WC500A700K4
3			800			4:1	WC500A800K4
4			900			4:1	WC500A900K4
5			900			6:1	WC500A900K6
6		600	900			6:1	WC600A900K6
1	KOH	500	600	5	1	4:1	MC500A600K4
2			700			4:1	MC500A700K4
3			800			4:1	MC500A800K4
4			900			4:1	MC500A900K4
5			900			6:1	MC500A900K6
6		600	900			6:1	MC600A900K6

^aW: Waste palm trunk (WPT); M: Mangrove; C: Carbonization temperature in °C (for example: C500 means carbonization at 500°C); A: Activation temperature in °C (for example: A600 means activation at 600°C); K4 and K6: 4 and 6 times KOH of carbonized sample.

Table 4 Water content of waste palm trunk (WPT) and mangrove (M)

Sample	Air drying		Vacuum drying		Water content		
	Temperature [°C]	Drying time [h]	Temperature [°C]	Drying time [h]	1st experiment [wt%]	2nd experiment [wt%]	Average [wt%]
WPT	100	48	105	1	8.64	9.32	8.98
M					7.53	7.55	7.54

Based on the above observation, Wang and Kaskel (2012) reported the following three main possible activation mechanisms for KOH activation of carbon.

- (1) Etching the carbon framework by the redox reactions between various potassium compounds with carbon as shown in Eqs. (8), (11), and (12), called chemical activation, are responsible for generating the pore network.
- (2) The formation of H₂O (Eq. (4)) and CO₂ (Eqs. (6) and (9)) in the activation process positively contributes to the further development of the porosity through the gasification of carbon, namely physical activation (Eqs. (5) and (10)).
- (3) The metallic K produced by carbon reduction of K compounds (K₂O and K₂CO₃) as shown in Eqs. (8), (11), and (12), efficiently intercalating into the carbon lattices of the carbon matrix during the activation, results in the expansion of the carbon lattices. After the removal of the intercalated metallic K and other K compounds by the washing of HCl and DI water, the expanded carbon lattices cannot return to their previous nonporous structure, and thus the high microporosity is created.

In this article, the effects of various preparation conditions, including different activation temperatures (600–900°C), the impregnation ratios of KOH/WPT or M biochar (4:1 and 6:1) are studied in order to establish the optimum condition for producing high adsorption ability, large surface area with micropore, and large pore volume of ACs. The activation process can be explained as follows (Pal *et al.*, 2017a): firstly, the weight ratio of KOH/carbonized biomass is set to 4 or 6 and put into the stainless steel container. The KOH and carbonized biomass are then mixed inside the container. After that, the stainless steel container is placed into an electric furnace vertically. The mixture is heat-treated up to 600°C at a heating rate of 5°C/min and maintained at 600°C for 1 h under N₂ flow rate 100 cc/min. After the activation, the remaining KOH and salts formed during the heat treatment are removed by the washing with HCl solution for three times and deionized water once to adjust pH to be about 7. Finally, the collected samples are dried at 100°C for 3 h in an air oven and dried again at 150°C for 12 h in a vacuum oven. A similar procedure is applied to other several activation temperatures. Total 12 samples, six from each type of biomass (WPT and M) are prepared as can be seen in Table 3. The synthesized ACs are then characterized using the investigation of scanning electron microscopy (SEM) image and elemental composition.

Yield of Processed Sample

Yield of Dried Raw Biomass

Table 4 shows the results of water content in raw WPT and M after air drying 100°C for 48 h and vacuum drying at 105°C for 1 h. After completing two consecutive drying processes, it is found that the average water content of WPT and M are 8.98 wt% and 7.54 wt%, respectively. It can be said that water content in WPT is relatively higher than that of M.

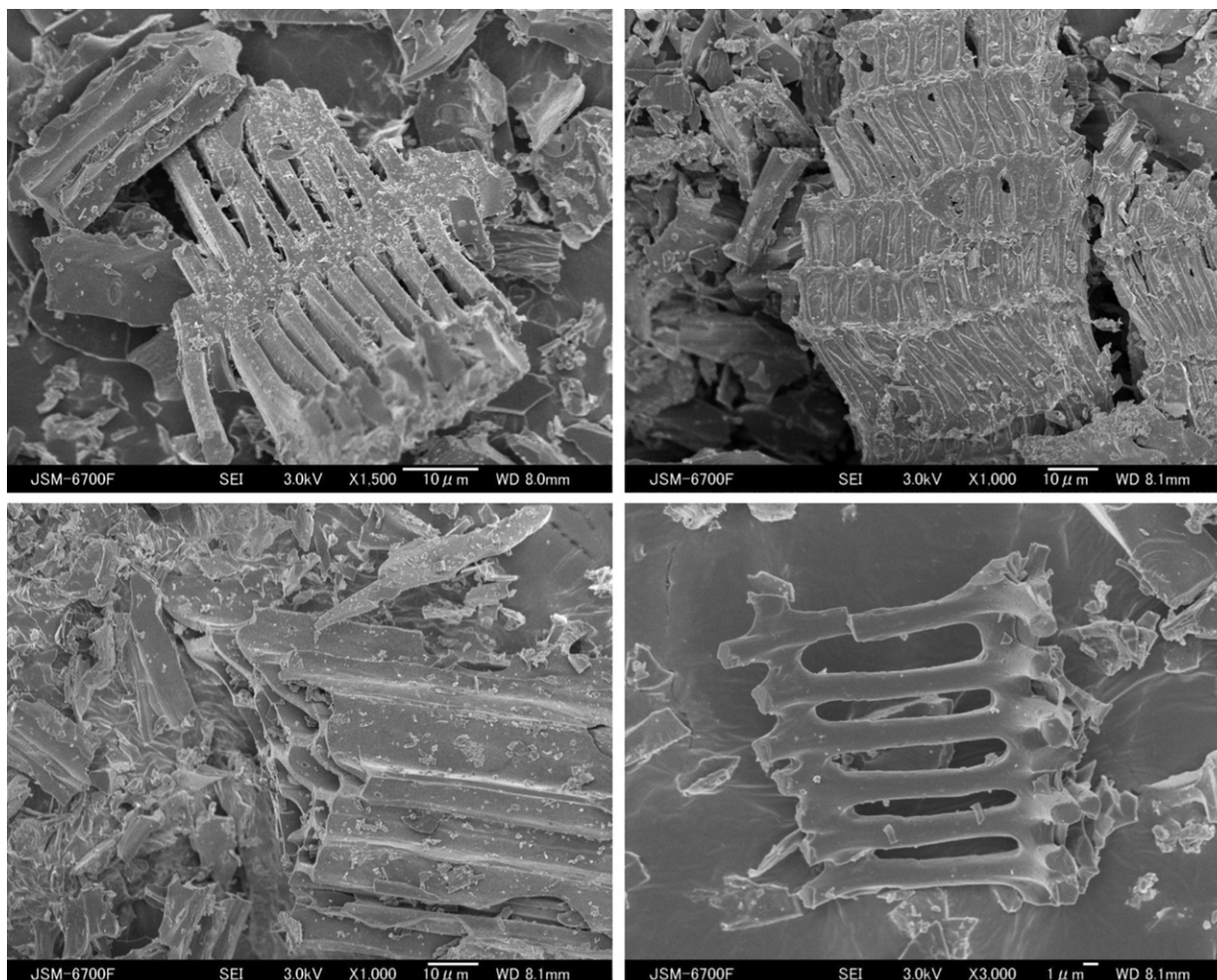
Table 5 Yield of carbonized product of WPT and M at carbonization temperature 500°C

Sample	No. of experiments and yield [wt%]					Temperature [°C]	Heating rate [°C/min]	Holding time [h]	Average yield [wt%]
	1	2	3	4	5				
Carbonized WPT	30.41	30.88	30.71	30.95	30.09	500	10	1	30.61
Carbonized M	31.96	31.94	31.60	31.62	31.36				31.70

Table 6 Yield of activated carbon samples derived from WPT and M

^a Sample	Activation yield [wt%]	^a Sample	Activation yield [wt%]
WC500A600K4	50.17	MC500A600K4	54.61
WC500A700K4	43.04	MC500A700K4	49.84
WC500A800K4	37.87	MC500A800K4	52.46
WC500A900K4	30.99	MC500A900K4	41.03
WC500A900K6	20.54	MC500A900K6	32.14
WC600A900K6	27.27	MC600A900K6	37.54

^aW: Waste palm trunk (WPT); M: Mangrove; C: Carbonization temperature in °C (for example: C500 means carbonization at 500°C); A: Activation temperature in °C (for example: A600 means activation at 600°C); K4 and K6: 4 and 6 times KOH of carbonized sample.


Fig. 9 SEM images of carbonized WPT at 500°C.

Yield of Carbonized Sample

Efficiency of carbonization is expressed in terms of yield production as a percentage of biomass used to produce it. The conversion yield depends on the moisture content of the biomass during carbonization and the carbonization temperature. The yield of carbonized sample derived from the dried WPT and M is shown in Table 5. The carbonization process is carried out at 500 and 600°C at a heating rate of 10°C/min and maintained at 500°C or 600°C for 1 h at N₂ flow rate 100 cc/min. The average yield of carbonized WPT and M for 500°C are 30.61 wt% and 31.70 wt%, respectively. From the results, it can be concluded that M shows a relatively higher yield compared to WPT.

Yield of Activated Carbon Sample

The activation yield of produced ACs derived from carbonized WPT and M is summarized in Table 6. From the results, it can be seen that at low temperature and the low weight ratio of KOH gives higher yield. In the case of WPT-derived ACs, the activation temperature 600°C and four times KOH shows the highest yield, which is about 50.17 wt%. On the other hand, the activation temperature of 900°C and six times weight ratio of KOH produced the lowest yield which is about 20.54 wt%. The M-derived ACs show a similar trend but produces a higher amount of yield. The activation temperature 600°C and four times KOH produced the highest yield, which is 54.61 wt% whereas activation temperature 900°C and six times weight ratio of KOH gives the lowest yield which is about 32.14 wt%. It can be noted that M-derived ACs give higher activation yield compared to the WPT-derived ACs.

Surface Morphology

Figs. 9 and 10 show the scanning electron microscopy (SEM) images of carbonized WPT and M samples at 500°C, respectively. It can be seen that inherently both biomasses possess various kinds of structures. The both WPT and M possess the canal structure,

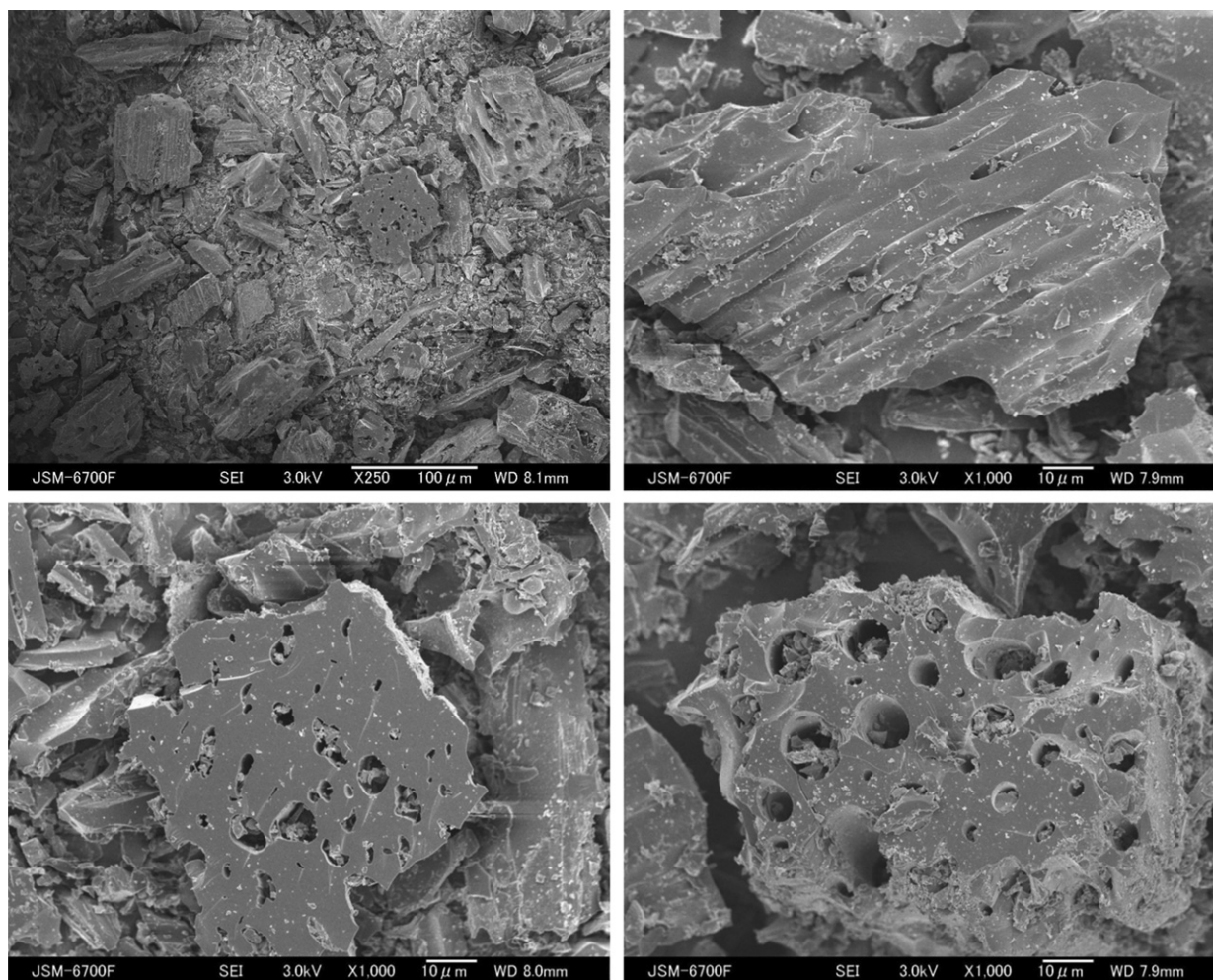


Fig. 10 SEM images of carbonized M at 500°C.

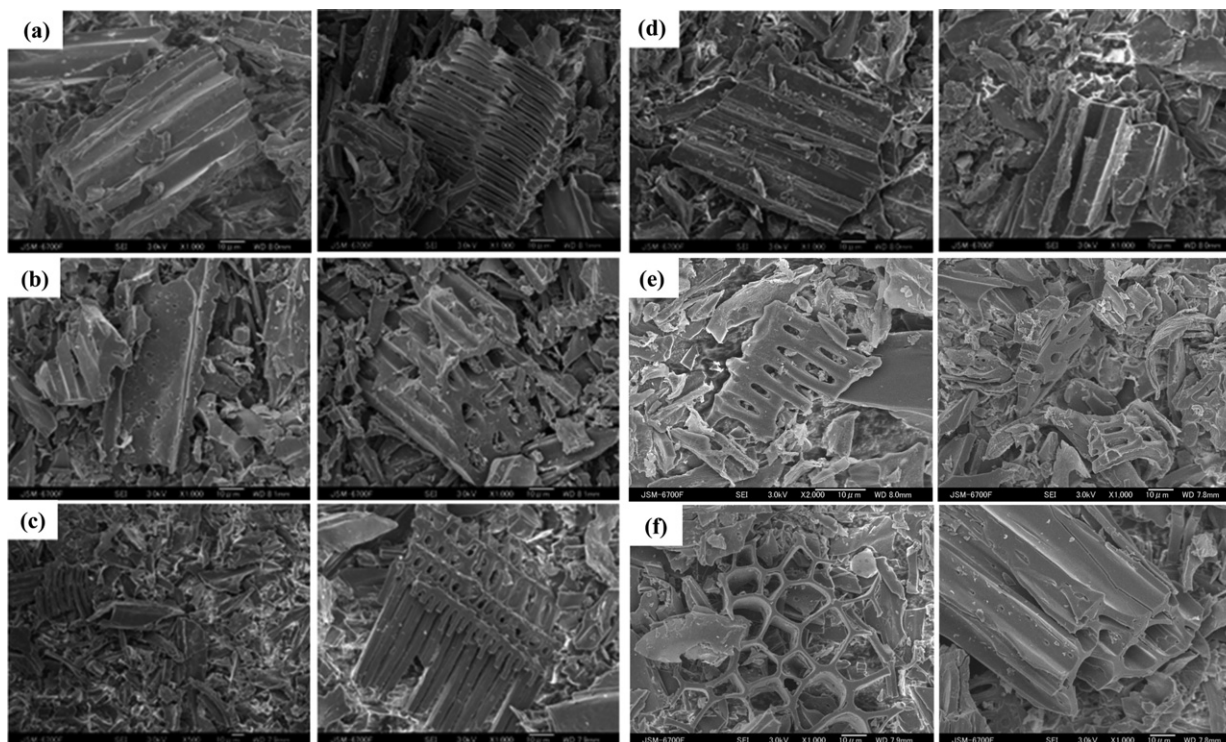


Fig. 11 SEM images of WPT-derived ACs (a) WC500A600K4; (b) WC500A700K4; (c) WC500A800K4; (d) WC500A900K4; (e) WC500A900K6, and (f) WC600A900K6.

which is an excellent texture for ACs production as the activating agent can easily diffuse into the carbon micropores and develop a large surface area and pore volume. During the carbonization, most of the non-carbon elements remove with the basic skeleton of the polymer remaining, which produces biochar retaining the shape of the biomass precursor and formed the initial porosity of the biochar.

The porous structure and chemical nature of ACs depend on the precursor materials, activation methods, and the extent of activation. This is the reason why surface area or pore volume of ACs differ widely from one kind to another. The pore structures of all synthesized AC samples are investigated by scanning electron microscope (SEM). The SEM images reveal the changes in morphology in the AC samples during the activation process. **Figs. 11** and **12** represent the morphology of all WPT and M-derived ACs synthesized from various activation conditions. The synthesized ACs preserve their micro-structural feature even at severe conditions as can be seen from SEM images.

Elemental Composition (CHN) Analysis

The carbonized products are produced from natural starting materials of WPT and M. The elemental composition (Carbon, Hydrogen, and Nitrogen) are analyzed using Yanaco CHN Corder (MT-5) manufactured by Yanagimoto Mfg. Co., Ltd. The CHN analysis method is based on differential thermal conductivity method. A sample of amount 800 μg is used for this experiment. The ultra-micro balance (Mettler Toledo XPR2U) is employed to measure the sample weight and the remaining amount after the experiment. At first, the sample is entirely burned under the flow of He with O_2 gas at a combustion furnace where CuO is filled. So, the sample is converted to CO_2 , H_2O , NOx gases, and others. Among them, NOx gas is reduced to N_2 by Cu at a reduction furnace. The other gases except for H_2O , CO_2 , and N_2 are removed by absorbers in combustion or reduction furnace. H_2O , CO_2 , and N_2 gases are detected by each thermal conductivity detector as counter signals. Finally, they are converted to the content of mass percentage. Typically, a carbonized product comprises high carbon content about 65%–90% which mostly depends on the inherent properties of precursor material. **Table 7** shows the elemental composition of carbonized WPT and M at two different carbonization temperatures, 500 and 600°C. The carbon content increases after the carbonization in both samples. It is observed that the carbon content for 600°C carbonization temperature is higher than that of 500°C for both precursor materials. It is found that the carbonized M sample possesses higher carbon and low ash content compared to the WPT. Actually, the high carbon and low ash content of carbonized materials are suitable for making ACs. The assessment of O content (O_{diff}) can be defined by subtracting the sum of the contents of C, H, N, and ash from 100%.

Table 8 represents the elemental composition of selected ACs to understand the effect of activation condition. It is observed that activation process increases the carbon content and decrease the ash content as expected. The higher activation temperature and KOH

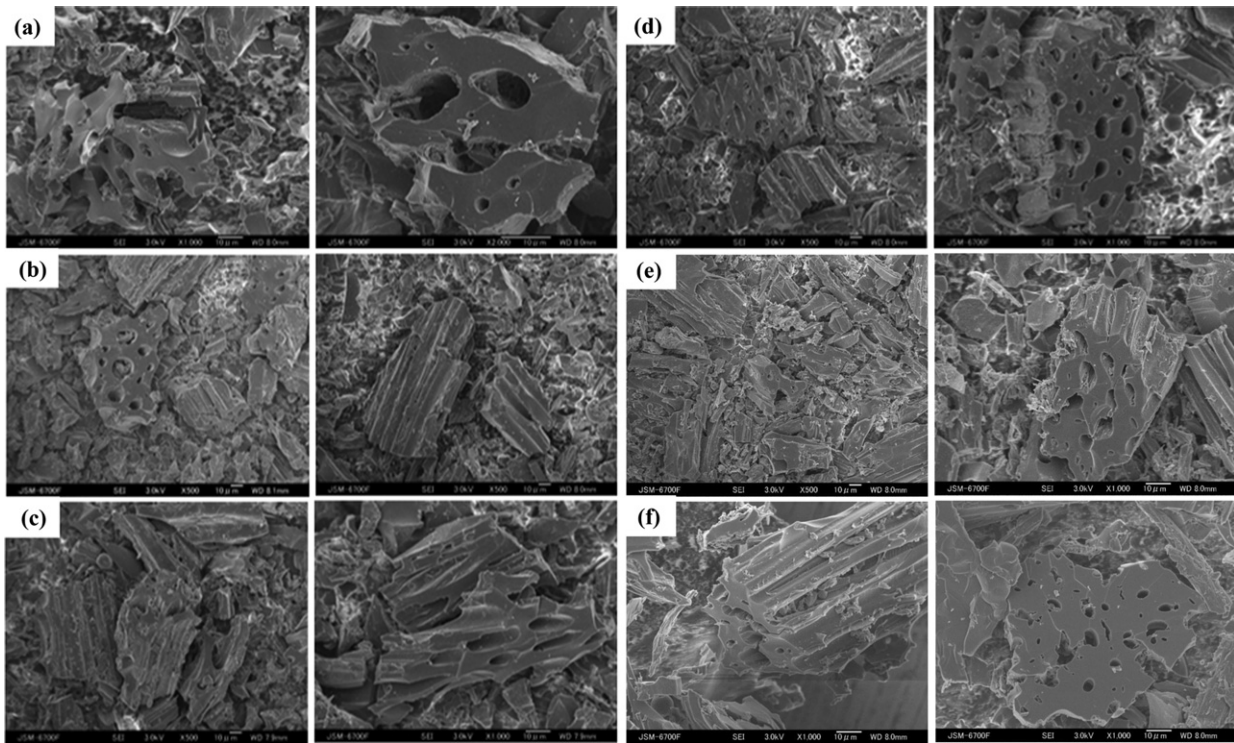


Fig. 12 SEM images of M-derived ACs (a) MC500A600K4; (b) MC500A700K4; (c) MC500A800K4; (d) MC500A900K4; (e) MC500A900K6, and (f) MC600A900K6.

Table 7 Elemental composition of carbonized WPT and M

Sample	Elemental composition [wt%]				Ash [wt%]
	C	H	N	$O_{diff.} [100\% - \sum (C, H, N, Ash)]$	
WPT (C500)	66.59	2.56	0.39	26.14	4.32
WPT (C600)	69.68	1.79	0.39	19.14	9.00
M (C500)	73.85	3.09	0.21	19.91	2.94
M (C600)	79.92	2.22	0.20	14.56	3.10

Table 8 Elemental composition of AC samples derived from WPT and M

Sample	Elemental composition [wt%]				Ash [wt%]
	C	H	N	$O_{diff.} [100\% - \sum (C, H, N, Ash)]$	
WPT (C500A600K4)	79.25	1.27	0.20	18.81	0.47
WPT (C500A900K6)	90.78	0.09	0.12	8.82	0.19
M (C500A600K4)	79.95	1.25	0.10	18.70	Not detectable
M (C500A900K6)	94.28	0.19	0.09	5.44	Not detectable

ratio also increase the carbon content and decrease the ash content. This is true for both sample as can be seen from [Table 8](#). The M-derived ACs show high carbon and no ash content. It is highlighted that carbon content increases to more than 90 wt% and minimizes the ash content after activation for both biomass-derived AC samples which is promising for various gas adsorption applications.

Conclusions

In this article, a series of activated carbons are synthesized from two waste biomasses, namely, waste palm trunk and mangrove. The detail synthesis process is presented which shows that carbonization temperature between 500 and 600°C are optimum to

obtain the ACs with high carbon and yield content. At this temperature almost 100% of all volatile matters and tars remove from the sample. It is found that dried WPT and mangrove give a yield of 30 wt% or more in the carbonization process at temperature 500°C at a heating rate of 10°C/min for 1 h. By KOH activation, biomass-derived ACs produced 20–50 wt% of yield. Particularly, M-derived ACs produced higher yield compared to WPT. It is observed that the carbon content is higher for 600°C carbonization temperature than that of 500°C for both precursor materials. The carbonized M sample possesses higher carbon and low ash content compared to the WPT. The synthesized ACs maintain their micro-structural feature even at high temperature and KOH ratio. The ACs derived from both biomasses contain various types of porous structures. It can be concluded that waste palm trunk and mangrove could be very promising precursors for synthesizing ACs with excellent physical properties. In addition, utilizing biomass as a precursor for synthesizing the ACs is considered as a wise approach since it can avert the production of CH₄ and CO₂. The porous properties, thermal conductivity, gas adsorption capacity are experimentally studied and presented in the next article to manifest its superiority over other ACs. The biomass-derived ACs could be the best choice for various applications including adsorption heat pumps and CO₂ capture or storage.

See also: Thermophysical and Adsorption Characteristics of Waste Biomass-Derived Activated Carbons

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Synthesis, Characterization and Applications of Nano-Structured Sol-Gel Coatings

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Introduction

The relationship between the two words “nano” and “sol-gel” can take several forms, for example nanomaterials can be prepared through a sol-gel process where a variety of shapes can result, allowing the possibility of use in many useful applications (Caruso and Antonietti, 2001). The sol-gel process is a wet-chemical process that used to prepare ceramic nanomaterials. A solution of a metal precursor undergoes hydrolysis or polycondensation reactions to form a colloid or a gel. Then a proper thermal treatment is applied to enhance crystallinity and mechanical properties. Another possible example is the nanocoating, where a sol-gel layer of a nanoscale thickness is prepared on a given substrate (Sepeur and Frenzer, 2014). Coating can enhance the substrate properties by increasing its chemical, thermal, or mechanical stability. Several routes can be used for applying a nanocoating such as plasma-assisted technique, pulsed laser deposition, magnetron sputtering, etc. It is clear that sol-gel layers of nano thickness are not easily prepared and hence, require advanced techniques. The nanocoating definition can also be applied to sol-gel coating with thickness less than 3 μm , containing nanoparticles or nanomoieties. This article focused on the last type and includes the synthesis route of the nanoparticles/sol-gel coatings, characterization techniques, and some of its common applications such as, corrosion protective, scratch-resistant, transparent, catalytic, and bioactive coatings.

Synthesis of Nano-Structured Sol-Gel Coatings

Silica alkoxides are the most frequently used precursors for the inorganic network sol-gel synthesis. Other metal alkoxides, such as titanium, zirconium, aluminum, and zinc alkoxides, can also be added to obtain hybrid coatings with enhanced properties. It was found that Si-M (M is Ti, Zr, Al, or Zn) based hybrid inorganic-organic sol-gel coatings possess better adhesion to substrates, offer enhanced “bridge” effect between inorganic and organic phases (Suriano *et al.*, 2017), and have a pore blocking effect in the coating. The formation of these metal oxides nanoparticles has been noticed upon sol-gel synthesis (Rodric *et al.*, 2016). These nano oxides add more benefits to coating properties and hence diverse its applications. TiO_2 and ZrO_2 have good chemical stability and thermal resistivity making it promising materials for corrosion protection (Ali and Al Ishaibi, 2017; Balaji and Sethuraman, 2016), whereas, TiO_2 is less expensive and exhibits higher efficiency permits its use in semiconductors solar cells (Merazga *et al.*, 2016). Al_2O_3 has lower electron conductivity which is perfect for corrosion protective coatings (Tiwari *et al.*, 2011). ZnO_2 has lower dielectric constant, higher chemical stability, large band gap energy, facilitating its applications in coatings, sensors, solar cells, etc., (Ivanovaa *et al.*, 2018).

Cambon *et al.* (2012) have prepared a hybrid sol-gel coating containing Al_2O_3 by mixing glycidoxypopyl-trimethoxysilane (GPTMS), aluminum tri-*sec*-butoxide, distilled water and propanol with molar of ratio 5:1:1:10. Then the sol is stirred for 2 h at room temperature before being coated on a stainless-steel substrate by dip coating technique. In such a way, both Si and Al precursors are hydrolyzed and condensed simultaneously at a single step to form a sol-gel material containing nano Al-moieties or nano Al_2O_3 . On the other hand, successive and consecutive synthesis steps have been reported by Tiwari *et al.* (2011). At first, the silica sol is prepared by mixing tetraethyl orthosilicate (TEOS) with ethanol and distilled water in a ratio of 4:5.5:90.5 (v/v), and stirring for 10 min. A steel substrate is dip-coated in the silica sol followed by dipping in 0.4 M aluminum oxy-hydroxide solution, calcination at 500°C for 2 h results in a conversion coating layer on the steel substrate. Finally, steel substrate coated with the conversion layer is dipped in Al_2O_3 sol prepared by the hydrolysis and polycondensation of aluminum isopropoxide catalyzed by HNO_3 . Another possible synthetic route is to add a given weight of alumina nanoparticles to the silica sol (Alongi and Malucelli, 2013).

Balaji and Sethuraman (2017) have prepared a hybrid TiO_2 /sol-gel nanocomposite coating by mixing hybrid sol with nano- TiO_2 sol. The hybrid solution is formed by mixing 0.1 M GPTMS and 0.1 M TEOS (3:1) with stirring for 2 h, HCl is added to promote hydrolysis and condensation reactions. While, nano- TiO_2 sol is prepared by mixing 0.1 M titanium (IV) isopropoxide and ethylacetoacetate, as a chelating agent (1:1) and stirring for 15 min. Finally, nano- TiO_2 sol is added into hybrid sol (1:1) with constant stirring. Shanaghi *et al.* (2017) have enhanced the barrier properties against corrosion of silica-titania hybrid coating by silver doping. Ag-doped silica-titania solution has been prepared by using TEOS, butyl orthotitanate, and silver nitrate with 98% ethanol as the solvent, ethylacetoacetate as a chelating agent, and 65% nitric acid as a catalyst to promote hydrolysis and condensation reactions, as shown in Fig. 1.

Hybrid zirconium nanocomposite based sol-gel coatings have been prepared by Balaji and Sethuraman (2016) and doped with thiourea and its derivatives. The hybrid sols were prepared by hydrolysis and condensation of GPTMS, TMOS and tetra-*n*-propoxyzirconium (TPOZ) in acidic solution, followed by the impregnation of thiourea and its derivatives, as shown in Fig. 2.

A mixed zirconia/silica coating can be also prepared by mixing two different solutions, prepared separately due to the different hydrolysis rates of silicon and zirconium alkoxides (Castro *et al.*, 2005; Suriano *et al.*, 2017). The first solution is prepared by mixing TEOS: Ethanol: Water: Hydrochloric acid (1:4.5:3.5:0.07), under stirring for 1 h to permit hydrolysis and condensation of TEOS. The second solution is prepared by mixing TPOZ: Acetic acid: Water (1:5:4) under stirring. The two sols are then mixed and stirred for 1 h to obtain a homogenous solution. In a similar way, Mei *et al.* (2015) have prepared Si-Zr organic/inorganic hybrid sol-gel. Two separated sols, Si sol and Zr sol, are prepared. The Si sol is prepared by mixing GPTMS with ethanol and distilled water with stirring the solution. For Zr sol, TPOZ is mixed with ethyl acetoacetate, and ethanol in a volume ratio of 8:12:3

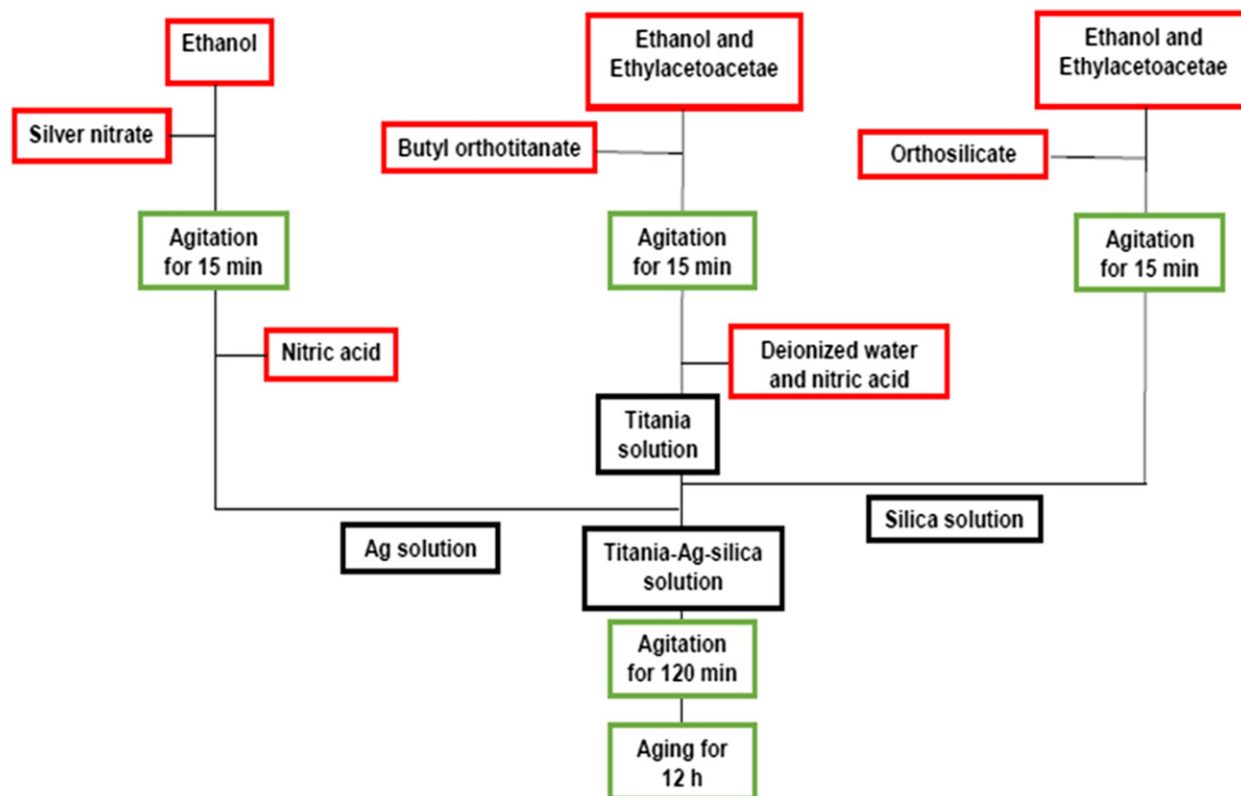


Fig. 1 Schematic presentation of preparation of Ag-doped silica-titania sol-gel material. Reproduced from Shanaghi, A., Nonahal1, H., Chu, P.K., 2017. Effects of Silica and Ag on the electrochemical behavior of titania-based nanocomposite coatings deposited on 2024 aluminum alloy by the sol-gel Method. *Journal of Alloys and Compounds* 739, 92–100.

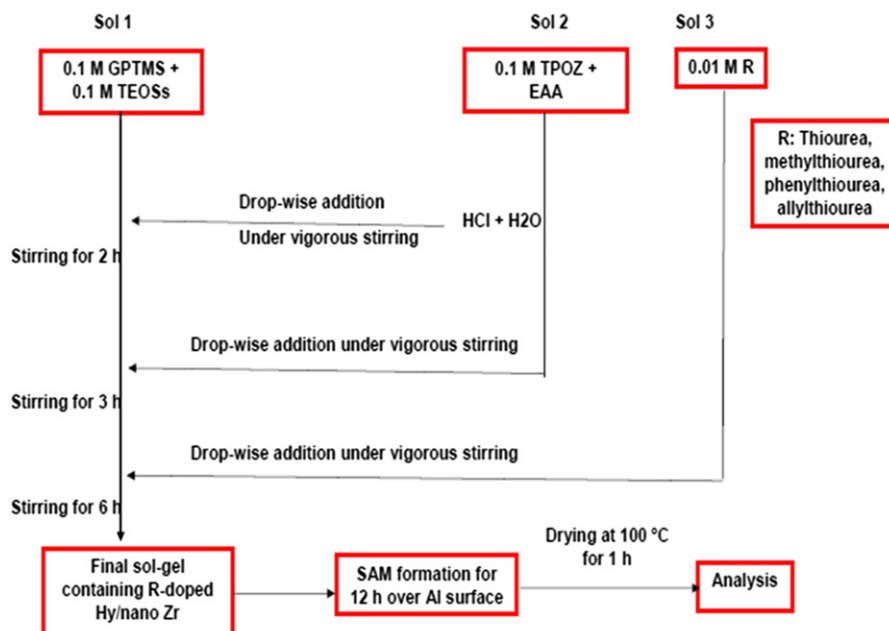


Fig. 2 Schematic presentation of doped hybrid zirconium oxide/sol-gel coatings with thiourea and its derivatives on Al-substrate. Reproduced from Balaji, J., Sethuraman, M.G., 2016. Studies on the effects of thiourea and its derivatives doped – Hybrid/Zirconium nanocomposite based sol-gel coating for the corrosion behavior of aluminum metal. *Progress in Organic Coatings* 99, 463–473.

with stirring. Finally, Zr sol is added into the Si sol with stirring. Rodic *et al.* (2016) have also prepared organic – Inorganic hybrid sol-gel nanocoatings by combining two, alkoxide sols (Sol 1 and Sol 2), separately prepared. Sol 1 is a mixture of TEOS and 3-methacryloxypropyl trimethoxysilane (MAPTMS) hydrolyzed under acid conditions. Sol 2 is a mixture of TPOZ and methacrylic acid. Sol 1 and Sol 2 are then combined to give a final hybrid sol – Gel solution.

ZnO-doped TEOS based sol-gel material is prepared by adding ZnO nanoparticles to TEOS sol-gel (Krupa and Vimala, 2016). The latter can be prepared by mixing TEOS with ethanol, nitric acid, and water to facilitate its hydrolysis and polycondensation.

Characterization of Sol-Gel Nano-Materials

X-Rays diffraction (XRD) analysis can be used to identify the phase composition of hybrid sol-gel coatings. Rodic *et al.* (2016) have performed XRD analysis to TEOS-MAPTMS hybrid sol-gel coatings, deposited on aluminum substrate, modified with different compositions of TPOZ and methacrylic acid, hydrolyzed separately. XRD reflects the appearance of a sole peak of Al_2O_3 at all different modifying compositions due to the interaction of Al-substrate with air. No characteristic peaks are assigned for the sol-gel materials because of its amorphous nature, this limits the use of XRD analysis as a characterization technique of sol-gel materials. Characteristic peaks of ZrO_2 did not appear due to the chelation with methacrylic acid. XRD analysis of TEOS-aluminum isopropoxide based sol-gel coatings deposited on a stainless-steel substrate showed the presence of Fe, $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 phases (Fig. 3(a)). In additions to these phases, SiO_2 , and Al_2O_3 phases appeared (Tiwari *et al.*, 2011). X-Rays photoelectron spectroscopy (XPS) technique has been also carried out to identify the surface composition and surface bonding based on previous XRD analysis results as shown in Fig. 3.

XPS technique has been used to analysis possible chemical states and compositions of surface elements constituting GPTMS-aluminum-tri-*sec*-butoxide based sol-gel, modified with CeO_2 nanoparticles and coated on Al-substrate (Lakshmi *et al.*, 2017). The survey spectra of coating indicate the presence of C, O, Al and Si elements. Individual binding energy scan of each element is also performed. C1s spectrum shows the presence of peaks at 283.9, 284.8, 286.2, 287.6 and 288.9 eV, corresponding to C-Si, C-C or

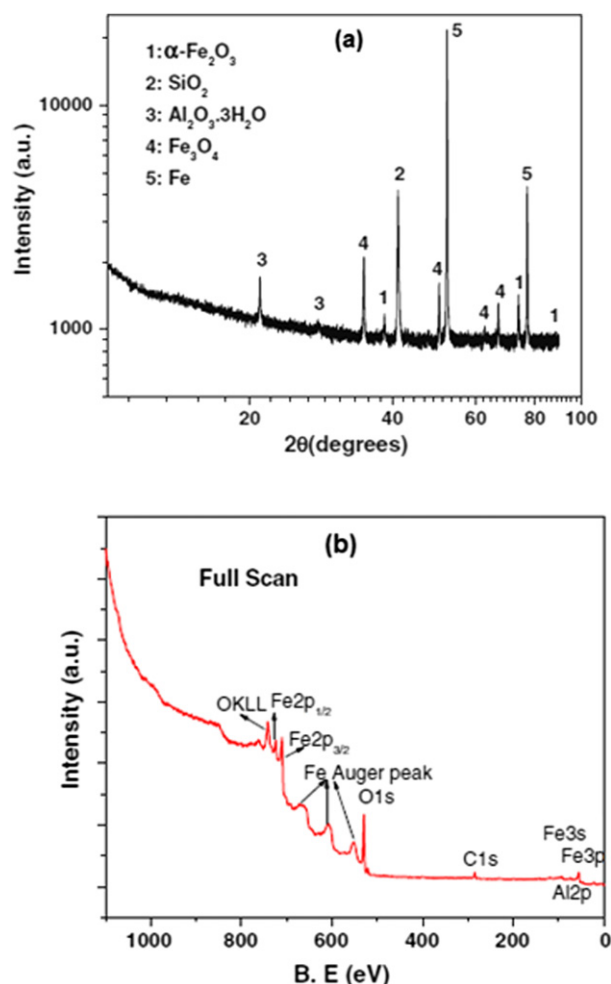


Fig. 3 (a) XRD and (b) XPS of TEOS-aluminum isopropoxide based sol-gel coatings deposited on a stainless-steel substrate. Reproduced from Rodic, P., Mertelj, A., Borovsak, M., *et al.*, 2016. Composition, structure and morphology of hybrid acrylate-based sol – Gel coatings containing Si and Zr composed for protective applications. *Surface and Coatings Technology* 286, 388–396.

C-H, C-O or C-OH, C=O and O-C-O, respectively. High-resolution XPS spectra of O1s show a peak at 530.6 eV assigned for the metal-O-metal bond (Ce-O/Al-O), a peak 532 eV attributed to SiO₂, and a peak at 533.5 eV corresponds to oxygen in the O-H bond, C-O-C, or C-OH groups. Si2p core level spectrum consists of a peak at 100.3 eV, attributed to Si-C bond, the main peak at about 102 eV from the Si-O-Si bonds, and a small peak at 103 eV assigned for SiO₂ network. Al2p spectrum consists of only 1 peak centered at 74.6 eV, corresponding to the Al-O bonds of Al₂O₃ and Al-O-Si bonds.

Fourier-transform infrared (FTIR) spectroscopy can be used to characterize various bonding in sol-gel materials. Balaji and Sethuraman (2017) have used FTIR to identify bonds of hybrid TEOS-GPTMS sol-gel modified with TiO₂ nanoparticles and chitosan. Fig. 4 show FTIR spectra of (a) hybrid sol-gel, (b) sol-gel/nano-TiO₂, (c) chitosan doped-sol-gel/nano-TiO₂ and (d) pure chitosan. The hybrid sol-gel coated aluminum substrate showed a band at 3417 cm⁻¹ assigned for O-H stretching. The band at 1032 cm⁻¹ attributed to Si-O-Si bond, confirming the network formation. The band at 912 cm⁻¹ corresponds to the Al-O-Si bond. Sol-gel/nano TiO₂ spectrum shows the usual bands of sol-gel and additional bands at 926 cm⁻¹ and 735 cm⁻¹, assigned for Si-O-Ti and Ti-O-Ti bonds. This suggested the formation of hybrid network containing nano-titania moieties. Additional chitosan characteristic peaks appear in other spectra, suggesting the successful doping.

Raman spectroscopy has been also carried out to ascertain FTIR results, where a strong band appears at 3022 cm⁻¹ due to O-H stretching, bands at 2924 cm⁻¹ and 814 cm⁻¹ is due to Si-O-Si bond formation and confirms the hydrolysis and condensation of sol-gel. Bands at 1109 cm⁻¹ and 920 cm⁻¹ are due to Si-O-Ti stretching vibration and the band at 814 cm⁻¹ is due to Si-O-Si bond.

The morphology of sol-gel coatings can be studied by scanning electron microscope (SEM) and for nanocoatings, transmission electron microscope is preferred. The surface morphology and energy dispersive X-Rays (EDX) analysis of TEOS-GPTMS based sol-gel/nano ZrO₂ coating has been examined, as shown in Fig. 5 (Balaji and Sethuraman, 2016). SEM photo shows the formation of uniform coating in which ZrO₂ nanoparticles are incorporated into the hybrid sol-gel matrix. The EDX spectrum of hybrid sol-gel/nano ZrO₂ showed peaks of Zr (0.15 keV, 2.02 keV, 2.12 keV), C (0.28 keV), O (0.53 keV) and Si (1.89 keV) which confirms the successful incorporation of nanoparticles into the sol-gel matrix.

Ali and Al lehaibi (2017) have performed TEM for unmodified and modified GPTMS-vinyltrimethoxysilane (VTMS) based sol-gel materials with Ti- and Al-alkoxides, shown in Fig. 6. The unmodified sol-gel has amorphous nature as shown in Fig. 5(a). Crystallinity has been enhanced upon modification and formation of hybrid sol-gel nanocomposites.

The topography and roughness of hybrid TEOS based sol-gel/Al₂O₃ nanocoating have been investigated by Atomic force microscope (AFM), shown in Fig. 7 (Tiwari et al., 2011). AFM image shows a uniform Al₂O₃ coating on sol-gel surface, small dots can be seen in agglomerates like cauliflower of about 300–350 nm diameter. A three-dimensional micrograph (Fig. 7(b)) also shows cluster of particles constituted by nanoparticles of 10–30 nm sizes.

Applications of Nano-Structured Sol-Gel Coatings

Nanosilane-based coatings are innovative coatings of interesting properties that permit its use in many industrial applications. For examples, as scratch-resistant coatings, protective coatings from corrosion, catalytic coatings, bioactive coatings for medical applications, etc. In the following section, a summary of the recent literatures focusing on sol-gel nanocoatings applications are presented in the following section.

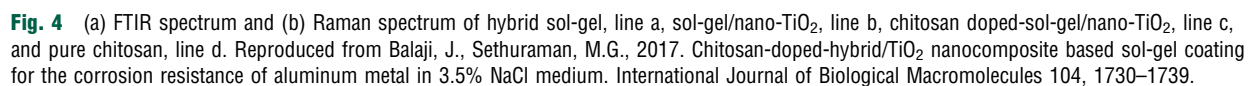
Corrosion Protective Coatings

Enhanced protection ability of GPTMS-VTMS based sol-gel coatings, for zinc corrosion in acidic media, has been presented by Ali and Al lehaibi (2017) through forming nanocomposites with Ti- and Al-alkoxides. The protection efficiency has been estimated by gravimetric, polarization, and electrochemical impedance measurements. It was found that the protection efficiency is enhanced from 69.2% to 96.2 and 95.8% for unmodified, TiO₂, and Al₂O₃/sol-gel nanocoatings, respectively. Lower concentrations of nanoparticles are favored since at high concentrations, galvanic corrosion between nanoparticles and zinc substrate is possible.

A conversion coating is applied on mild steel prior to sol-gel/Al₂O₃ nanocoating to improve the corrosion resistance of mild steel (Tiwari et al., 2011). Fig. 8 shows a comparison between polarization curves of conversion coated and conversion followed by sol-gel/nano-Al₂O₃ coated mild steel in 3.5 wt% NaCl solution. Mild steel coated with the conversion layer showed high corrosion resistance and showed barrier type protection up to ~1.0 V. This is further reduced by ~3 orders of magnitude on subsequent sol-gel/Al₂O₃ nanocoating.

Chitosan doped TEOS-GPTMS hybrid sol-gel/TiO₂ nanocoating is applied successively for corrosion protection of Al-substrate in 3.5% NaCl solution (Balaji and Sethuraman, 2017). Impedance results show that charge-transfer resistance values increased in the order Chitosan doped sol-gel/TiO₂ > sol-gel/TiO₂ > sol-gel > bare Al-substrate, with corresponding coatings protection efficiency values of 94.1, 90.6 and 74.8%, as shown in Fig. 9. The electron-rich oxygen atom attracts the hydrogen in the chitosan leading to the formation of a densely packed adhesive sol-gel coating over Al-substrate.

Silica nanoparticles have been incorporated into TEOS-GPTMS based sol-gel to enhance the corrosion protection ability for mild steel substrate (Mora et al., 2017). Introducing of silica nanoparticles improve the barrier properties of the coating due to cracking prevention and reduced porosity. Further improvement of the corrosion protection is observed by incorporation of functionalized silica nanoparticles compared to unfunctionalized ones. This is possibly due to a dispersion improvement and a stronger interface between the matrix and nanoparticles. Fig. 10 shows the time dependence of the pore resistance for unmodified sol-gel, modified sol-gel with unfunctionalized, and functionalized with silica nanoparticles. The coating with functionalised silica nanoparticles has the highest pore resistance, reflecting the most effective barrier properties of the coating.



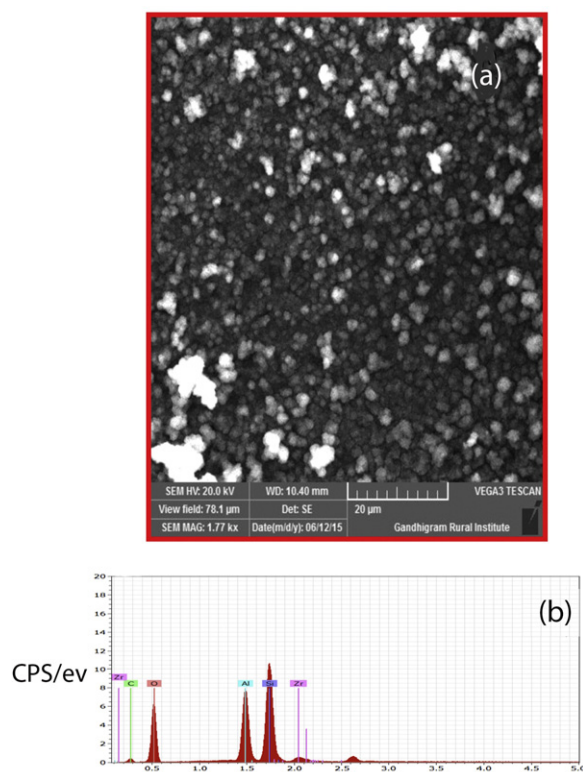


Fig. 5 (a) SEM image and (b) EDX spectrum of hybrid sol-gel/ZrO₂ nanocomposite. Reproduced from Balaji, J., Sethuraman, M.G., 2016. Studies on the effects of thiourea and its derivatives doped – Hybrid/Zirconium nanocomposite based sol-gel coating for the corrosion behavior of aluminum metal. *Progress in Organic Coatings* 99, 463–473.

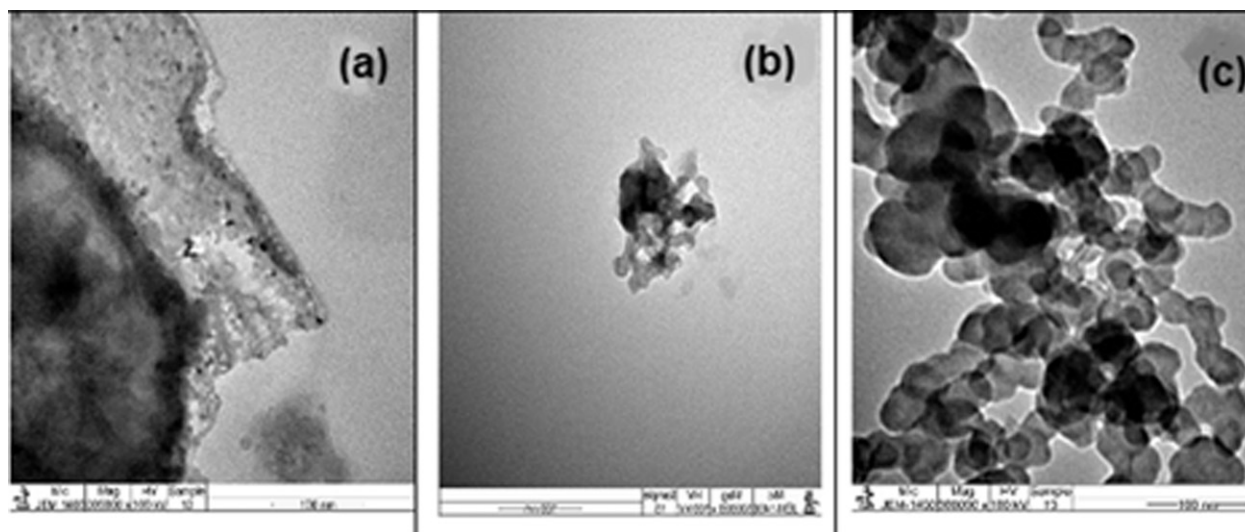


Fig. 6 TEM images of (a) unmodified sol-gel and sol-gel/nanocomposites (b) with TiO₂ addition and (c) with Al₂O₃ addition. Reproduced from Ali, S.M., Al Ishaibi, H.A., 2017. Nano-structured sol-gel coatings as protective films against zinc corrosion in 0.5 m HCl solution. *Journal of Saudi Chemical Society* 21, 473–480.

The effect of nanoparticles composition, nano-ZrO₂, on the formation and ageing of TEOS-MAPTMS based hybrid sol-gel coating is examined (Rodriguez *et al.*, 2016). At higher concentrations of nanoparticles, gelation process is fast, and longer ageing times are not required. The hydrophobicity increases with increasing nanoparticles concentration. Amorphous homogeneous structure

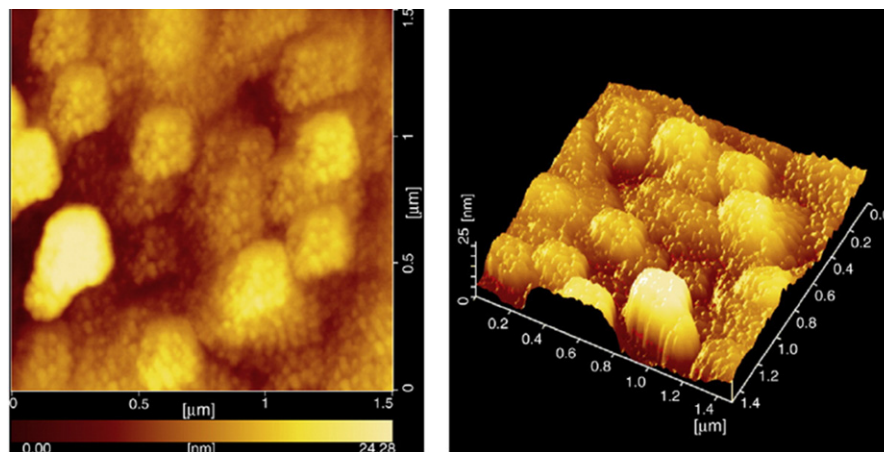


Fig. 7 (a) Two-dimensional and (b) three-dimensional AFM micrographs of sol-gel/ Al_2O_3 nanocoating. Reproduced from Tiwari, S.K., Sahu, R.K., Pramanick, A.K., Singh, R., 2011. Development of conversion coating on mild steel prior to sol-gel nanostructured Al_2O_3 coating for enhancement of corrosion resistance. *Surface And Coatings Technology* 205, 4960–4967.

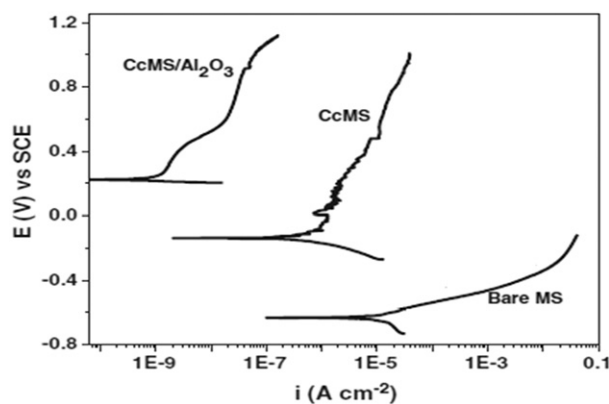


Fig. 8 Polarization curves of bare, conversion coated (Cc), and conversion/sol-gel/ Al_2O_3 nanocoating (CcMS/ Al_2O_3) mild steel (MS) in 3.5 wt% NaCl solution. Reproduced from Tiwari, S.K., Sahu, R.K., Pramanick, A.K., Singh, R., 2011. Development of conversion coating on mild steel prior to sol-gel nanostructured Al_2O_3 coating for enhancement of corrosion resistance. *Surface and Coatings Technology* 205, 4960–4967.

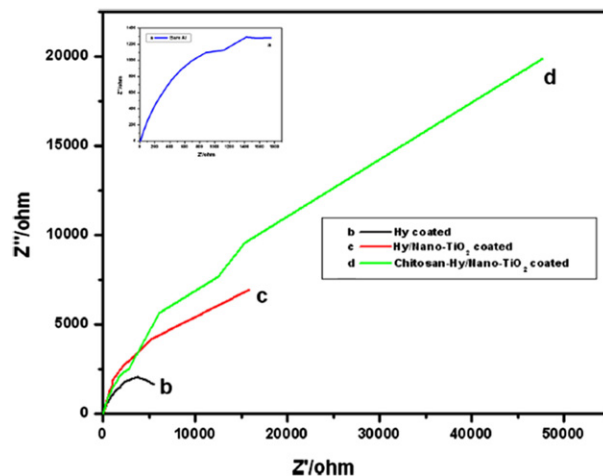


Fig. 9 Nyquist plots for (a) Inset: Bare Al (b) sol-gel coated (c) sol-gel/nano- TiO_2 coated and (d) chitosan doped-sol-gel/nano- TiO_2 coated on Al-substrate in 3.5% NaCl medium. Reoroduced from Balaji, J., Sethuraman, M.G., 2017. Chitosan-Doped-Hybrid/ TiO_2 nanocomposite based sol-gel coating for the corrosion resistance of aluminum metal in 3.5% NaCl medium. *International Journal of Biological Macromolecules* 104, 1730–1739.

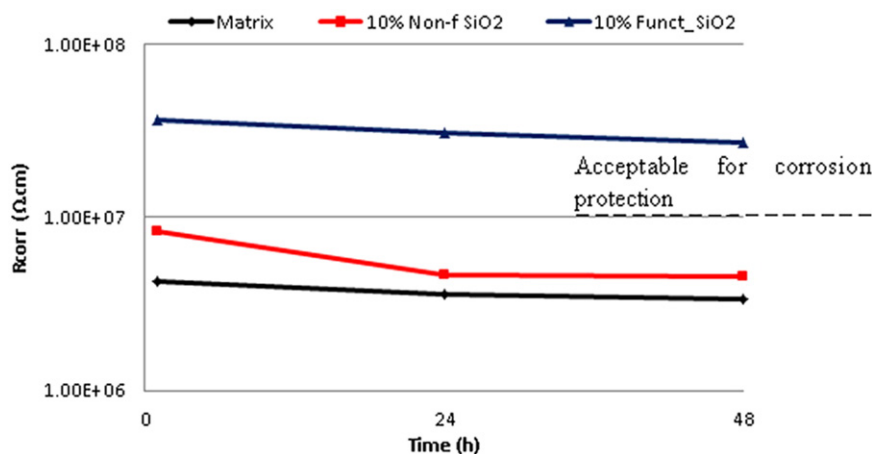


Fig. 10 Time dependence of the pore resistance for unmodified and modified sol-gel with unfunctionalized and functionalized silica nanoparticles. Reproduced from Mora, L.V., Naik, S., Paul, S., *et al.*, 2017. Influence of Silica nanoparticles on corrosion resistance of sol-gel based coatings on mild steel. *Surface and Coatings Technology* 324, 368–375.

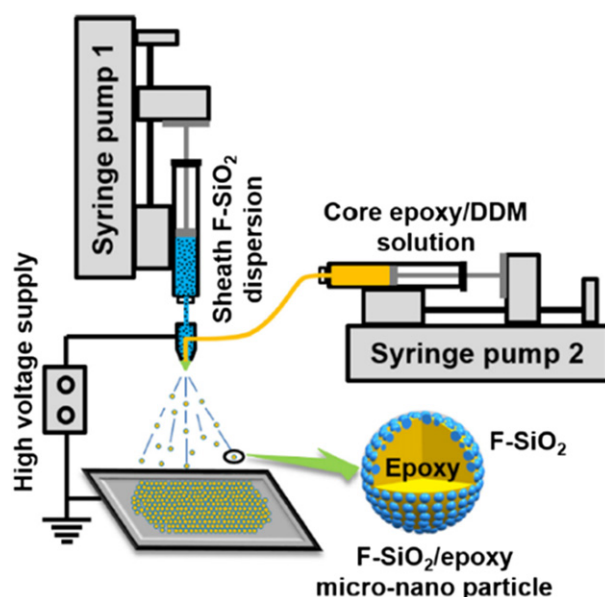


Fig. 11 The coaxial electrospinning process. Reproduced from Li, X., Li, H., Huang, K., *et al.*, 2018. Durable superamphiphobic nano-silica/epoxy composite coating via coaxial electrospinning method. *Applied Surface Science* 436, 283–292.

of low wettability enables to use the hybrid sol-gel/nano-ZrO₂ coating for corrosion protection. Upon coating, the polarization resistance increased up to four orders of magnitude, compared to bare Al-substrate.

Other Applications

Nano-ZrO₂/TEOS based sol-gel combined with chlorotrifluoroethylene-vinyl ether copolymer results in hard, scratch-resistant and transparent coating (Suriano *et al.*, 2017). Durability of the hybrid coating is assessed by water contact angle measurements, pencil and AFM scratch hardness and adhesion tests. Pencil hardness tests confirm the scratch resistance and durability of the hybrid coatings at the macro-scale. AFM indentation and nano scratch tests are used to evaluate the elastic modulus and the dynamic hardness of the hybrid systems, resulting in a high modulus (up to 31 GPa) and high-level scratch hardness (up to 2 GPa). The hybrid coatings exhibit a superior long-term stability and show excellent mechanical strength, high level of hardness and superior integrity after long-term light exposure at low and intermediate zirconia-to-silica ratio. The excellent scratch resistant properties of the hybrid coating permit its applications in automotive field, consumer goods, photovoltaic and optical devices. Nano-fluorinated silica and epoxy composite coating is successfully constructed by the coaxial electrospinning method, as showing in Fig. 11 (Li *et al.*, 2018). Fluorinated nano-silica with uniform nano-size is distributed evenly on the micro epoxy particles, showing a

special micro-nano hierarchical structure. Contact angles measurements in water and ethanediol reached $165 \pm 3^\circ$ and $152 \pm 3^\circ$, respectively, showing a superamphiphobic and good anti-sticking status. Evident reinforcement effect showed improved modulus and hardness in the nano-indentation test. In addition, durability of the superamphiphobic coating was assessed by performing harsh chemical environments immersion and scotch tape test, where the prepared coating can resist damage from strong polar organic solvent and repeated sticky, which can broaden the fields of application.

Conclusion

- Nano-structured sol-gel materials, containing nanoparticles or nanomoieties, can be prepared either by simultaneous hydrolysis and condensation of both Si and metal precursors, or by successive and consecutive synthesis steps.
- XRD structural characterization of sol-gel nanomaterials indicates the amorphous nature of these materials, only characteristic peaks for the nano-oxide appears. The formation of a hybrid network containing nano-metallic moieties is indicated by the appearance of M-O-Si band in FTIR spectra. TEM images show that the crystallinity of sol-gel materials can enhanced upon modification with nanoparticles or nanomoieties.
- Nano-structured sol-gel coatings is applicable to corrosion protective coatings for many metals in different media since nanoparticles improve the barrier properties of the coating due to cracking prevention and reduced porosity and increased hydrophobicity. Lower concentrations of nanoparticles are favored since at high concentrations, galvanic corrosion between nanoparticles and metal substrate is possible.

Acknowledgement

The author is grateful to Cairo University through the General Scientific Research Department.

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Tailor-Made Bioplastics for Environmentally Friendly Food Packaging: A Methodological Approach to a Challenging Problem

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Introduction

The newly developed “instant” coffee capsules machines are progressively imposing on the market, replacing traditional brewing equipments worldwide. Instant coffee machines are fully electric and designed to brew coffee, in both domestic and working environments, with short brewing time, safely and silently. A large variety of coffee blends and other brews can be brewed, thus satisfying a broad range of dissimilar needs of the customers. Nevertheless, “instant” coffee machines rely on plastic or aluminum capsules. Coffee capsules, more than any other consumer items, have negative environmental and social effects. An estimated 10 billion coffee capsules were manufactured each year, producing an astonishing amount of 120,000 tons of plastic waste worldwide to be disposed of 70,000 tons are generated in Europe alone, with the capsules not being recyclable in municipal facilities because they often combine multiple materials ([EU LIFE Project](#)). The coffee capsules are essentially fabricated joining two or more conventional materials like Polyethylene (PE), Aluminum, Ethyl Vinyl Alcohol (EVOH), and Polyethylene Terephthalate (PET). That gives rise to severe environmental concerns: (i) PET and PE are oil-based polymers and their manufacturing process involves about 15,000 tons of non-renewable resource; (ii) PE, PET and aluminum downstream manufacturing represents a significant source of CO₂ emission (i.e., more than 410,000 tons). A potential solution to face the environmental issues related to the manufacturing and landfilling of the coffee capsules lies in the employment of the so-called bio-based materials. Bio-based materials only rely on biological matter. At present, the recourse to fully bio-based materials, certificated compostable or, at least, biodegradable, in the fabrication of coffee capsules and, in general, in food & drug packaging and containers is limited by their often mediocre mechanical, physical and chemical performance. Bio-based materials do not feature satisfactory mechanical strength (above all, toughness and impact resistance), sufficient thermal stability (at 95–97°C for 20 s) and reduced permeability as dictated by the stringent customer requirements (i.e., reduced transmission rate of oxygen and moisture to protect coffee). In contrast, the successful industrialization of fully bio-based, compostable or biodegradable, materials that comply with the strictest technological demands posed by the packaging market, would allow the attainment of impressive environmental benefits: (i) saving 70,000 tons of waste from landfills or incinerators in Europe, assuring biodegradability of the product at end-of-life for billions of coffee capsules; (ii) saving 15,000 tons of oil involved in the current coffee capsules manufacturing process, meaning 100% reduction of the employment of fossil feedstock; saving 405,000 tons of CO₂ equivalent ascribed to PE, PET and aluminum manufacturing process; (iii) saving 20,000 tons of bauxite and others dangerous pollutants involved in aluminum manufacturing process ([EU LIFE Project](#)). The environmental benefits of high performance bio-based materials will be even greater, if the whole European plastic market would be taken into consideration. In fact, 25 million tons of plastic materials are not recyclable today and the introduction on the market of biodegradable/compostable materials could reduce significantly the amount of plastics to landfill each year. This would also lead to an additional saving of 100 Mt of oil that, each year, is employed for the manufacturing of conventional plastics and, in turn, a reduction of 35,000 Mt of CO₂ equivalent emitted in PE and PET manufacturing process.

The methodological approach herein described, was designed to overcome limitations of bioplastic materials during melt processing. Specifically, this work aims at the enhancement of thermal and mechanical properties of PLA based materials, processed by injection molding.

State of Art of the Use of PLA in the Market of Coffee Capsules

The market of coffee capsules is quickly increasing in size and is highly dynamic, with a large number of different technological solutions available. After being used, coffee capsules cannot be easily recycled, as they need to be cleaned from the exhausted coffee before starting any recovery step. They can not be dismissed in the compost, as the plastics, which are commonly used to fabricate them, do not degrade. The introduction of compostable materials in the manufacturing of compostable coffee capsules would allow their simple disposal in the compostable fraction together with the exhausted coffee inside. Yet, the coffee capsules are used in “instant” coffee brewing equipment. They must ensure satisfactory thermal and mechanical properties: (i) compostable according to EU Industrial composability regulations according to the regulation EN13432; (ii) no recourse to nano-materials that can be dangerous for health and environment (no working regulations in EU27); (iii) suitable for food contact according to the Regulation of the European Commission No. 10/2011 on food contact plastic materials and/or safe for humans and environments according to REACH Regulation No 1907/2006 of the European Parliament; (iv) easy to process polymer (extrusion; injection, compression and stretch blow molding; sheet polymer forming; thermoforming; fibres, foams, etc.); (v) tough and thermally stable (min. 100°C for 20 s); (vi) elastic modulus (~4.0 GPa, typical value for as-is PLA-based materials); elongation at break (>> 5.0 %, typical value for as-is PLA-based materials).

In this respect, as it is (neat) PLA resin features appreciable elastic modulus and tensile strength, not far from petroleum-based polymers. Nonetheless, PLA resin is usually brittle, featuring limited thermal resistance, toughness and resiliency. Typical approaches to overcome the drawbacks of the neat PLA resin involve the compounding of PLA by the incorporation of additional materials, like other resins (blending process), mineral fillers and a large variety of additives (nucleating agents, filler dispersants, bonding agents, impact modifiers, lubricants, melt strength enhancers, etc.) (Yu *et al.*, 2006). One of the most common approaches to increase the performance of PLAs is to introduce nano-fillers, including layered silicates, carbon nanotubes, hydroxyapatite, layered titanate, aluminum hydroxide, etc., inside the resin to achieve higher performance. The debate on PLA nano-composites as regards to the safety of nano-materials is ongoing in the scientific community, especially when the final materials are involved in direct food contact. Nano-fillers could migrate inside the food and, if ingested, they could be significantly dangerous for human health. Other routes are, however, promising to improve the properties of PLA polymers. In particular, the properties of PLA can be enhanced by a number of combined actions, which might concur to the establishment of the desired final properties (for example, high thermal stability, good toughness, high dimensional accuracy and stability, etc.). Fine-tuning of morphological structure in the polymers, especially of the crystalline phase can concur to the design of high performance PLA materials, which can comply with the stringent specifications driven from the coffee market. Crystallization of PLA can be achieved by the addition of nucleating agents and careful control of the temperature variations during melt processing. Lastly, reinforcement of the organic matrix with high compatible micro-sized fillers with specific surfaces, establishment of chemical bonding between fillers and matrix in the compounds by organo-silanes, blending with low amount of performant polymers and proper usage of additives can increase further the final properties of the material.

In this respect, many efforts have been made in the past years by Academia to analyze the effect of compounding PLA with other materials. Mathew *et al.* (2005) investigated the mechanical properties of PLA composites containing microcrystalline cellulose, wood flour and wood pulp. Oksman *et al.* (2003) reported that the tensile strength for PLA-flax fibre composites is about 50% better than PP-flax composites, which are used today in many automotive panels. Huda *et al.* (2006) evaluated the mechanical and physical properties of PLA composites containing chopped glass fibre or recycled newspaper cellulose fibre. The study showed that both mechanical and physical properties of the recycled newspaper composite compared favourably with glass fibre reinforced PLA composite, suggesting that these cellulose fibre reinforced composites have the potential to replace glass composites in applications where very high load bearing capabilities are not needed. Shibata *et al.* (2003) evaluated the effect of dispersing abaca fibre (Manila hemp) in several biodegradable polyesters, including PLA. These authors observed a C-mold could increase flexural moduli for poly(butylene succinate) and polycarbonate/PLA blends as the fibre content increased. In contrast, for the PLA-abaca fibre composite, a minimal increase in flexural strength was observed, which is attributed to inherent high flexural strength of neat PLA.

Despite all the research performed up-to now in Academia, a satisfactory PLA-based formulation that can be used in highly demanding applications, such as the fabrication of coffee capsules (but also in many others consumers goods), has not yet been proposed for the market. More recently, Russo *et al.* (2014) investigated the reinforcement of PLA polymers by dispersing micro-talc in the organic matrix, which was found to be extremely beneficial to the final properties of the compound. Barletta *et al.* (2014b) also showed the effect of bonding organo-silane molecules to improve the overall mechanical behavior of organic resins when deposited on inorganic and organic substrates in the form of surface overlaying coatings (Barletta *et al.*, 2014a,b). During some preliminary trials, they showed the satisfactory results achievable, combining the good performance obtainable using talc fillers and organo-silane intermediates to favor bonds among organic and inorganic materials. In particular, they found that pre-treating micro-lamellar talc produced by mechanical exfoliation with 3-aminopropyltriethoxysilane and dispersing it in a neat PLA resin could determine, during lab-scale experiments, an astonishing improvement in the thermal stability and mechanical response of the resulting materials, opening up the route to exploit the PLA in many applications for consumer goods. Adding nucleating agents, impact modifiers and plasticizers to PLA-based materials reinforced with micro-lamellar talc, pre-treated by 3-aminopropyltriethoxysilane, were found to allow the achievement of high performance compounds, potentially suitable for the injection molding process of complex shaped items.

Scope of the Work

In spite of the significant advances in the engineering of PLA-based plastics, bio-derived and biodegradable aliphatic polyesters still suffer from severe hydrolytic degradation mechanisms when melt processed (especially, injection molded) at high temperature and in the presence of oxygen and environmental moisture. During injection molding, the overall performance of the molded items is strictly dependent on the residence time of the bioplastics in the barrel and in the mold. Longer residence time triggers significant degradation mechanisms of the resin that can compromise the final performance of the molded items. Preventing or limiting the onset of the thermal degradation of custom-built Poly Lactic Acid (PLA) formulations during injection molding together with the appropriate strategy to engineer the PLA formulations is therefore the purpose of the present work. In this framework, bioplastics were formulated by reactive compounding extrusion of PLA, PBS, talc, compatibilizing agents and processing additives. The resulting compounds were injection molded to get two kinds of components, flat slabs and cups. Thermo-mechanical performance was evaluated by both static, impact and fracture tests. The results showed that combining wise design of the material formulation and optimizing operational parameters during injection molding can lead to significant progress in the performance of the molded items, opening up great market opportunity for PLA-based materials.

Engineering of the PLA Formulations

The polymers of lactic acid are broadly available on the market, with different molecular weights and D-Isomer content. In the present work, a commercial grade, 3260 HP (Nature Works, Minnetonka, Minnesota) is investigated and a proprietary formulation developed. The 3260 HP grade is characterized by a low content of the D-Isomer and low molecular weight. The low level of the D-Isomer in the polymer allows the following advantages: (i) faster quiescent crystallization speeds (i.e., slower cycle times); (ii) higher levels of crystallinity; (iii) higher stiffness above glass transition temperature; (iv) higher crystalline melting temperatures; (v) higher degrees of stress-induced crystallization at lower strain (or higher temperatures). While the molecular weight of the starting polymeric chain is, instead, important for the final mechanical properties of the material, the choice of a low molecular weight is beneficial for the crystallization speed. A PLA grade with low molecular weight means dealing with chains of enhanced mobility. Higher mobility means better attitude of the polymeric chains to dispose themselves according to tidy orders in the material, thus promoting higher degree of crystallinity quickly. Crystallinity is pivotal in the achievement of high thermal stability. Micro-lamellar talc was chosen as nucleating agent for the 3260 HP PLA-grade. It is small (5–10 microns) but not nano-sized, therefore, suitable for direct food contact. Talc distribution and dispersion inside the PLA matrix was initially achieved by extrusion compounding with a twin-screw co-rotating extruder (Haake PolyLab PW24, Haake, Karlsruhe, Germany), setting the appropriate and proprietary chewing profiles on the screws with a mid-barrel temperature of $\sim 180^{\circ}\text{C}$.

Fig. 1 shows the difference between PLA pellets before and after the addition of the nucleating agent (i.e., micro-lamellar talc produced by mechanical exfoliation and treated with 3-aminopropyltriethoxysilane). When the pre-treated talc is dispersed appropriately inside the material by co-rotating twin-screw extrusion and the appropriate chewing profile of the screws, it favours the crystallization process of the low D-Isomer, low molecular weight PLA grade. The secondary effect of the crystallization is a loss of transparency of the polymer.

Figs. 2 and 3 show the performance of the PLA alone and of the PLA after extrusion compounding with talc as nucleating agent. Both figures report the elastic modulus, mechanical strength, toughness, ductility, impact resistance, heat deflection temperature that were measured during preliminary tests on injection molded flat slabs.

Fig. 2 focuses on the magnitude of the thermo-mechanical properties measured. **Fig. 3** compares them on a normalized 0–100 scale. The flat samples were injection molded (S-2000i/50B, Fanuc LTD, Oshino-mura, Yamanashi, Japan) at a mid-barrel temperature of $\sim 205^{\circ}\text{C}$ in a multi-purpose molds, designed according to the current regulations for each test with a proprietary temperature of the mold walls. The talc as nucleating agent was found to modify significantly the response of the commercial grade PLA. After the addition of the talc, all the vertices of the radar plot (**Fig. 3**) expanded significantly. The mechanical strength of the material increased as well as its toughness, impact resistance and, especially, thermal stability (i.e., heat deflection temperature) that has, surprisingly, doubled. However, this is not uncommon in PLA-based materials. [Wootthikanokkhan et al. \(2013\)](#) reported heat deflection temperature (HDT) of above 120°C for 20 ppf kenaf fibre – PLA composite. Before the addition of the nucleating agent (talc), the thermal stability of the material relied on its amorphous phase only and, thus, on the glass transition temperature of the commercial grade PLA, that is very low (around 52°C). After the addition of the modified nucleating agent (talc), the thermal stability of the material depended on the large crystalline phase formed in it. That allowed the material to be stable well over the temperature of 100°C , as required by the industrial requirements for the plastic coffee capsules. **Fig. 4** reports the improvement in the thermal stability of the commercial PLA grade (3260 HP) after the addition of the talc pre-treated with 3-aminopropyltriethoxysilane and achievement of a sufficient degree of crystallization. After talc addition, the molded items remain flat even after dipping in hot oil at 150°C . The untreated PLA deforms, with a significant warpage of the edges of the molded items.

Despite the improvement in the general mechanical properties of the material observed in **Figs. 2 and 3**, some preliminary tests by injection molding of the coffee capsules with the same material formulation showed that the resulting capsules were still very

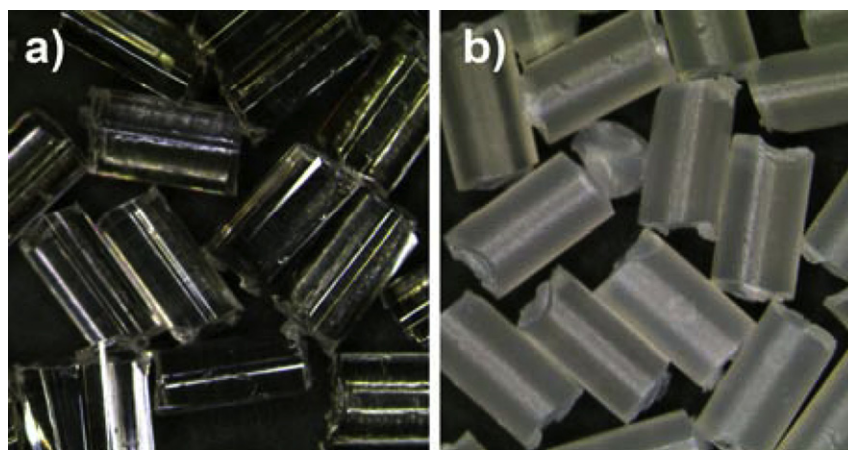


Fig. 1 The pellet achieved by extruding the commercial grade PLA (3260 HP) without nucleating agent (a) and with nucleating agent (b).

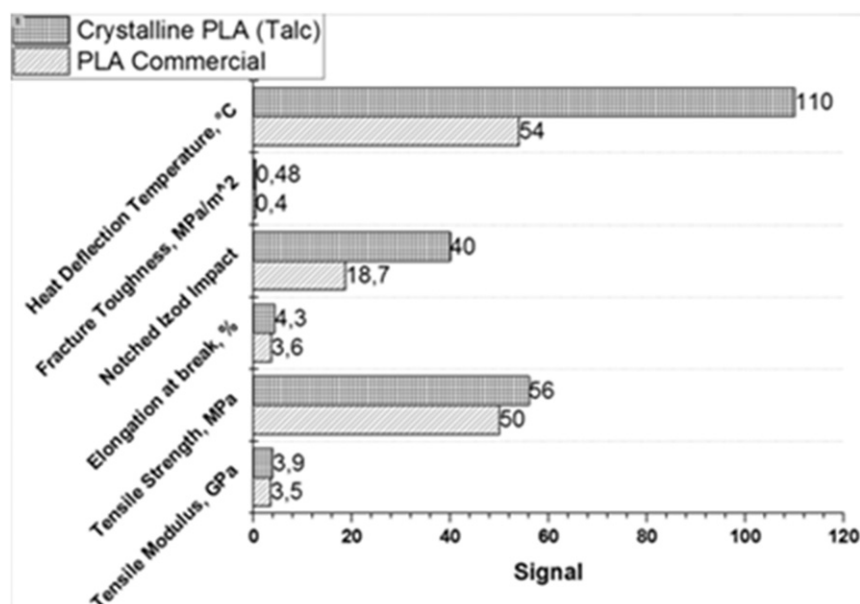


Fig. 2 Summary of the properties (PLA grade 3260 HP and PLA grade 3260 HP + talc).

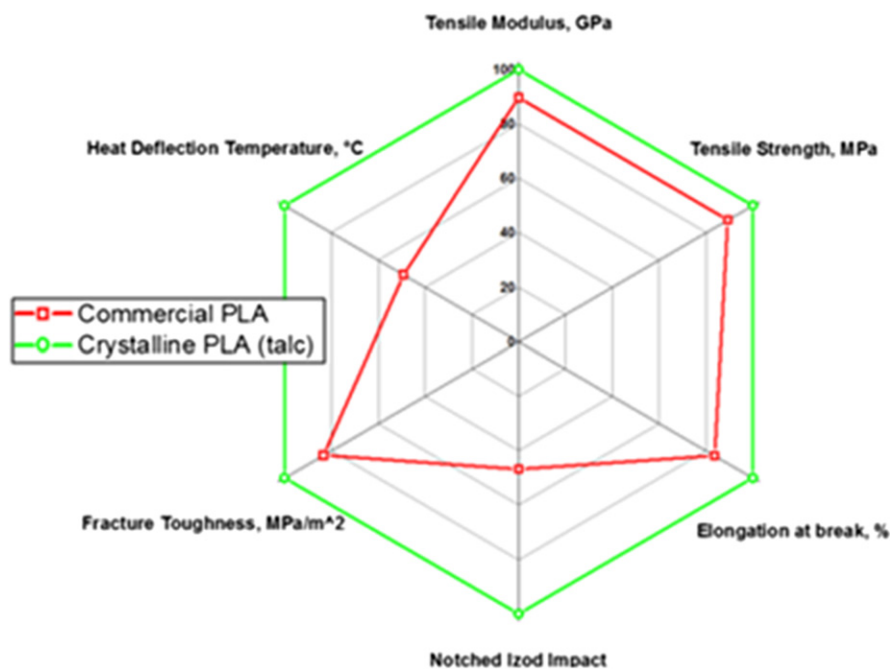


Fig. 3 Radar plot that compares the most important properties of the commercial grade PLA after injection molding in flat samples and the same grade of PLA after compounding with talc and injection molding in flat samples.

brittle, even after the application of very low pressure (Fig. 5). To improve the performance of the molded capsules, distribution and dispersion of the talc pre-treated with 3-aminopropyltriethoxysilane inside the PLA matrix were investigated. Talc is hydrophilic, while PLA is essentially hydrophobic. To compatibilize talc and PLA and improve homogeneity, a custom compatibilizer was introduced. The typical compatibilizers available in the market are acrylate polymers. They are effective to compatibilize talc and PLA, but not compostable as often reported in the literature (Cardoso Arruda *et al.*, 2015).

The compatibilizers herein studied is instead based on a PLA backbone, with both maleate or glycidyl(methacrylate) (i.e., epoxy) reactive groups. The commercial name of compatibilizer involving maleic anhydride (MAH) grafted PLA (PLA-MA) is Scona TPPL 1112 PA(BYK Additives & Instruments, Altana AG, Wesel, Germany), the one involving glycidyl methacrylate (GMA)

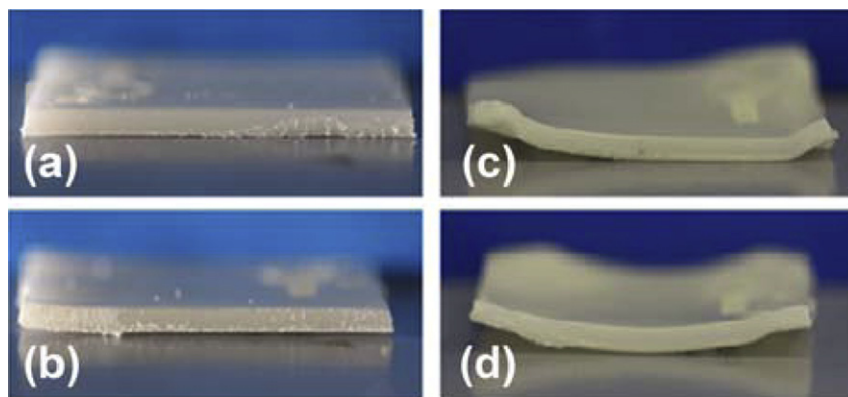


Fig. 4 Different thermal stability of the PLA dipped in hot oil up to 150° before dipping (a, b) and after dipping (c, d) according to the degree of crystallinity: (a, c) low crystallinity; (b, d) high crystallinity.



Fig. 5 Brittleness of a coffee capsules manufactured by the addition of talc in the commercial grade of PLA (3260 HP) through an injection molding pilot plant.

grafted PLA (PLA-GMA) is named Scona TPPL 1214 PA, (BYK Additives & Instruments, Altana AG, Wesel, Germany). They are both compostable and food safe.

The structure of the maleate reactive group is presented in Fig. 6. The compatibilizing agents can be effective to bridge the talc to the PLA promoting the formation of covalent bonds or of simpler physical interactions between the hydroxyl groups on talc and the maleate or epoxy group of the compatibilizers.

The mechanisms are therefore very similar to the ones depicted in (Liu and Zhang, 2011) for conventional acrylate-based compatibilizers. The PLA-based compatibilizing agents were found extremely effective in promoting the distribution and dispersion of the hydrophilic talc pre-treated with 3-aminopropyltriethoxysilane in the largely hydrophobic PLA matrix, improving the overall behavior of the resulting materials. The compatibilizing agents was also extremely effective to promote the chain extension of the commercial grade PLA (NatureWorks LCC, 3260 HP), raising efficiently the average molecular weight of the PLA and preventing the possible negative effects of the hydrolytic degradation of the PLA during the following melt processing. Fig. 7 summarizes the mechanisms of the compatibilizing agents developed and the related chemical reaction routes. Fig. 8 depicts the mechanisms of the chain extensions on PLA. In particular, the compatibilization is achieved by exploiting the reactivity of the terminal hydroxyl groups of the PLA chain that can combine with the functional groups of both the compatibilizing agents.

Figs. 9 and 10 show the performance of the PLA compounds after the addition of the compatibilizing agents, with significant improvements achieved in terms of all the properties under investigation, especially of the heat deflection temperature that can benefit of the better dispersion of the talc up to reach an astonishing 145°C. The talc can act as nucleating agent and promote crystallization of the polymeric chains more effectively. Despite the improvements of the materials, the injection molding tests were not satisfactory yet, as the resulting coffee capsules were still affected by significant brittleness (see the injection-molded capsule shown in Fig. 5). Use of plasticizers or of alternative solutions to improve the toughness and impact resistance of the material was, therefore, studied. In particular, the involvement of a polymer with low glass transition temperature was investigated. This approach is becoming very common in the scientific literature (Liu and Zhang, 2011) and in the technical practice, contrary to the approach that makes use of conventional plasticizers such as phthalates, epoxidized soybean oils or esters citrates (Thummarungsan *et al.*, 2016; Chieng *et al.*, 2014; Harte *et al.*, 2013). The polymers with low glass transition temperature are

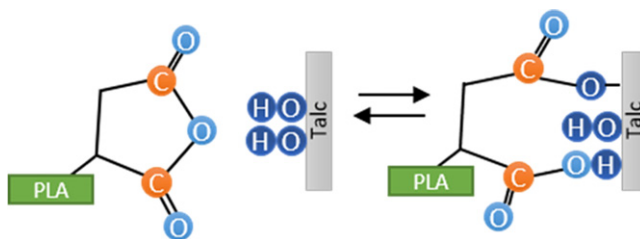


Fig. 6 Action mechanism of the compatibilizing agent based on a PLA backbone and functionalized with maleic anhydride and glycidyl methacrylate groups.

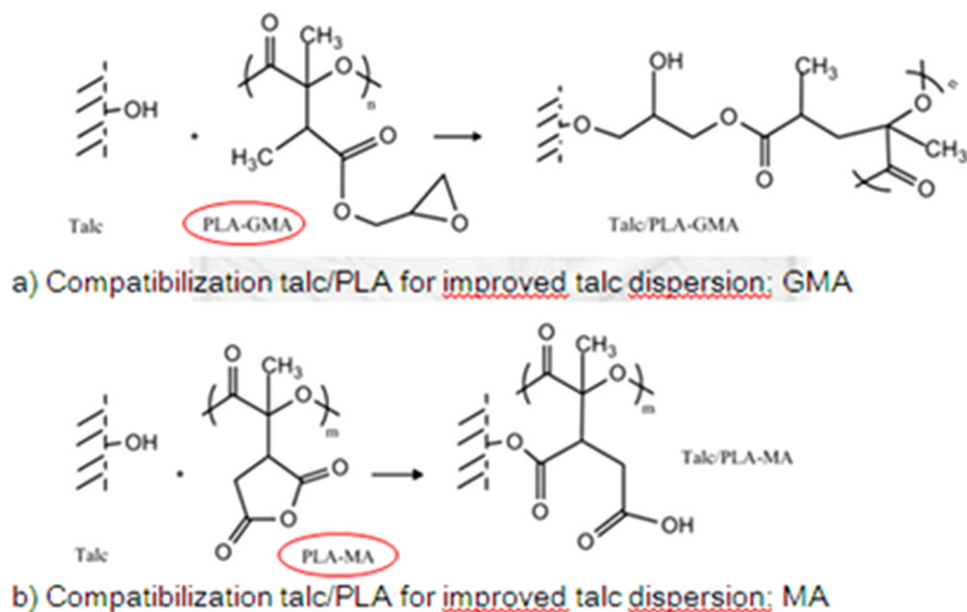


Fig. 7 Compatibilization mechanisms of the compatibilizing agents based on the PLA backbone and endowed with (a) maleate and (b) epoxy functional groups.

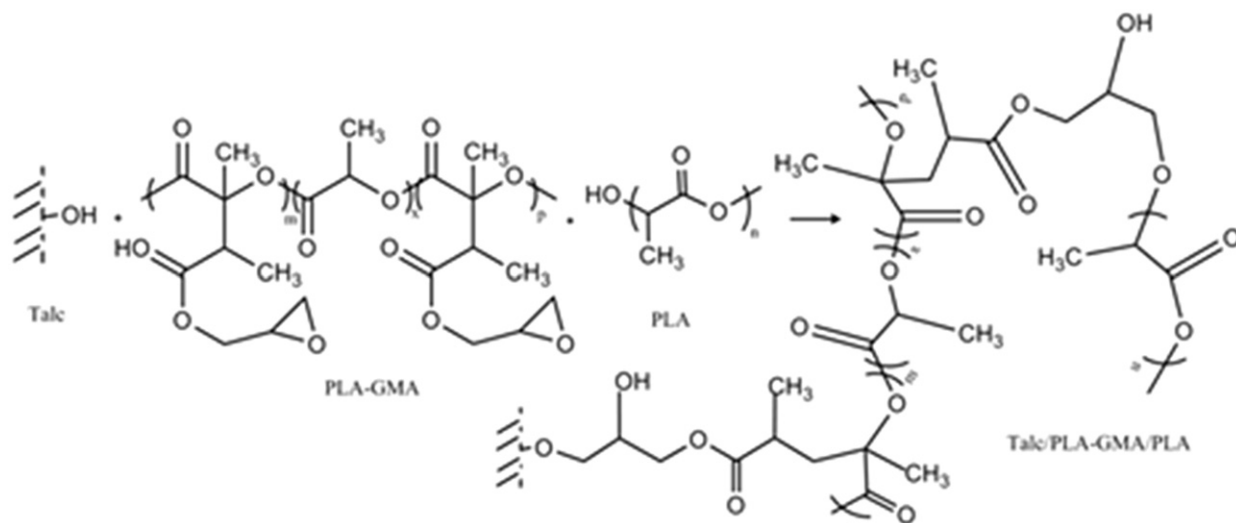


Fig. 8 Chain extension of the PLA with the compatibilizing agent with the epoxy functionality.

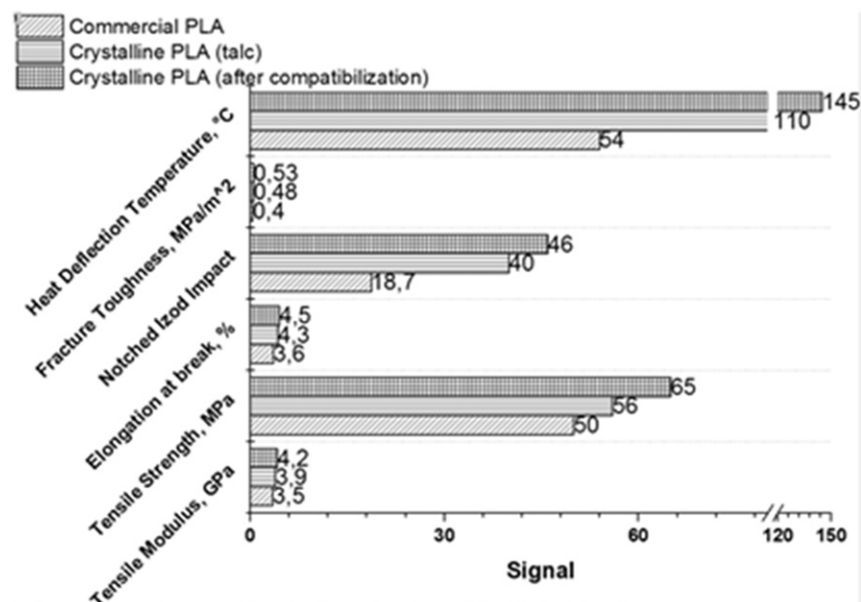


Fig. 9 Summary of the properties (PLA grade 3260; HP PLA grade 3260 HP + talc; PLA grade 3260 HP + talc + compatibilizer).

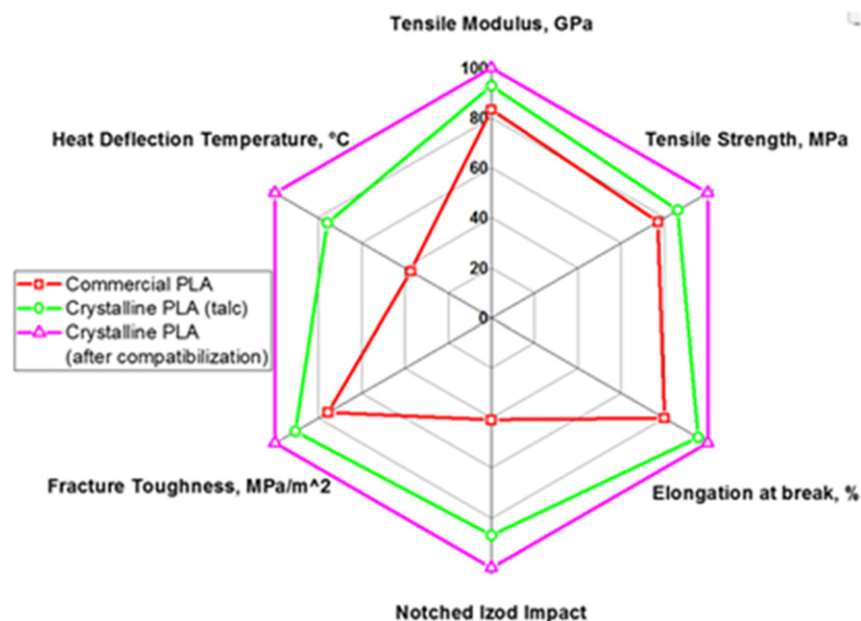


Fig. 10 Radar plot that compares the most important properties of the commercial grade PLA after injection molding in flat samples and the same grade of PLA after compounding with the compatibilizer and injection molding in flat samples.

intended to replace conventional plasticizers in the PLA formulation, creating a so-called secondary polymeric phase in the PLA matrix and exploit its high flexibility already at room temperature. PBS (Bionolle 1020 MD, Showa Denko K.K., Tokyo, Japan) was chosen as material for the formation of the secondary polymeric phase in the PLA compound.

Figs. 11 and **12** show the compatibilization mechanisms to recombine the PLA with the possibly incompatible PBS. Once again, the reactivity of the hydroxyl functionalities of both PBS and PLA were used for compatibilization purposes, using the same compatibilizing agents based on maleate and glycidyl methacrylate groups. PBS and PLA are basically immiscible polymers (Hu *et al.*, 2018), with PBS forming small “droplets” (domains) inside the PLA matrix. Compatibilization means in this case good dispersion and distribution of the PBS domains inside the PLA, with micro-domains homogeneously dispersed and distributed all over the PLA matrix.

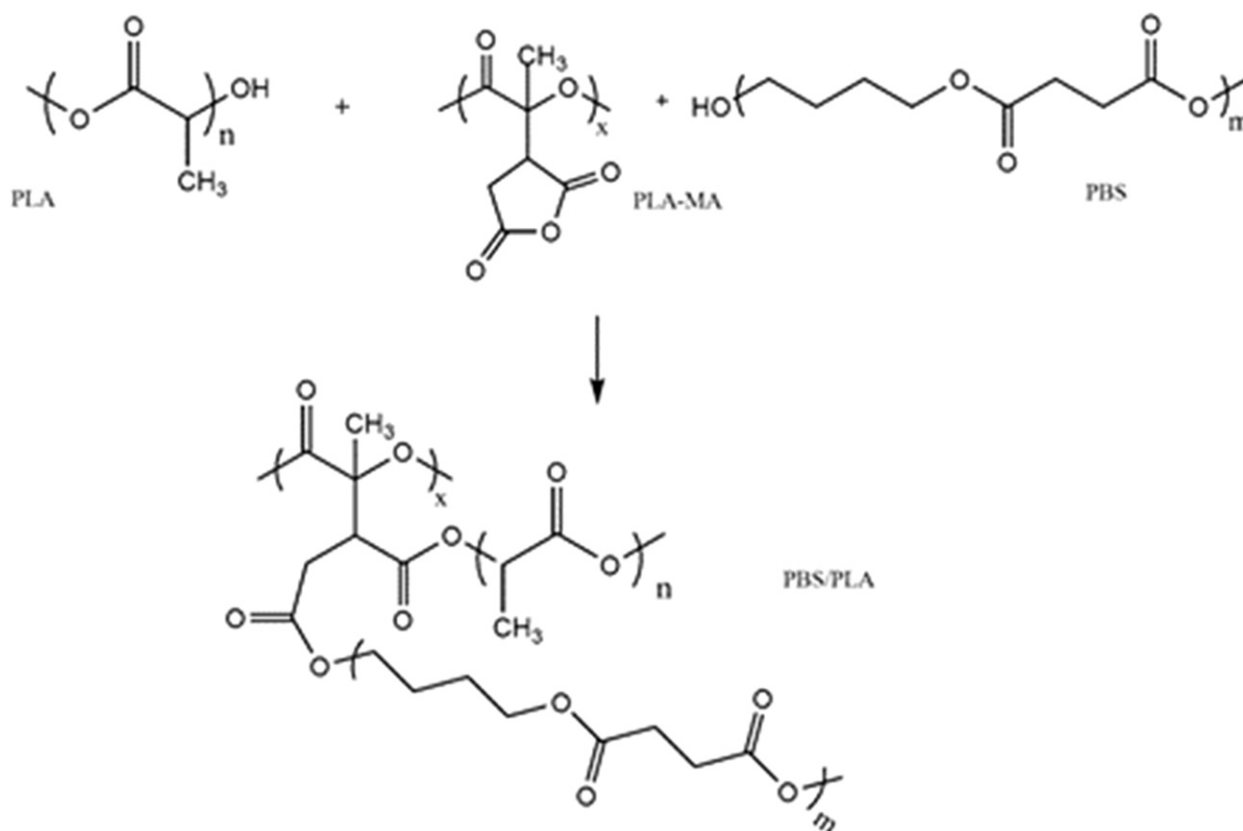


Fig. 11 Compatibilization mechanisms of the PLA with the PBS: the reaction scheme with maleate groups.

Fig. 13 shows the pellets that were produced by the addition of PBS inside the PLA matrix. After the addition of PBS, the materials showed a significant improvement in the global mechanical, physical and chemical performance as evidenced by the radar plot and bar chart of **Figs. 15** and **16**.

Fig. 14 shows that PBS acts as secondary polymeric phase by dispersing and distributing uniformly inside the PLA matrix in the form of small droplets. The good dispersion and distribution of the PBS in the PLA ensure the improvement of the material properties. Specifically, the molded substrates after the dispersion of PBS inside the PLA were found to feature good toughness and strength. Also, the thermal stability of the slabs was extremely good, with peak temperature well over 140°C, specifically 144°C, under a pressure of 5 Mpa (**Fig. 15**).

Figs. 15 and **16** summarize the achieved properties by testing the flat slabs according to the international regulations. Melt blending of PLA with PBS improved toughness, impact resistance and ductility. These materials were then processed by injection molding (process parameters not disclosed) to test them for the manufacturing of coffee capsules. The resulting capsules were ultimately strong and flexible enough for practical purposes.

The capsules also complied with the requirements imposed by the market of brewing equipments. **Fig. 17** shows the capsule manufactured with the compound of PLA, PBS and additives as described before. The whitish color of the capsules symbols the good crystallinity achieved during the injection molding. Similarly, the geometrical details of the capsules were reproduced with great accuracy, leading to a final product of utmost quality.

Injection Molding of Coffee Capsules

Despite the advance in engineering of PLA, injection molding of the capsules is still a troublesome process. The process must be quick to reduce the final cost of the coffee capsules. A whole molding cycle should last not more than 3 or 4 s to be competitive. In addition, the wall temperature of the mold should be very high (> 100°C) to promote a quick crystallization of the PLA in-mold and without any further post-annealing that could increase the overall cost of the process. Nevertheless, if the wall temperature is increased at 100°C, the ejection process of the part from the mold can be troublesome. The PLA blend becomes soft and sticky and ejection could be not correct. **Fig. 18** shows some results about the ejection of the capsules from the mold, varying the wall temperature, with the critical range emphasized. Metal release agents can be, however, added to the compound to improve part ejection even at high wall temperature. A small jet of compressed air in the male mold, right in the middle of the capsule "head"

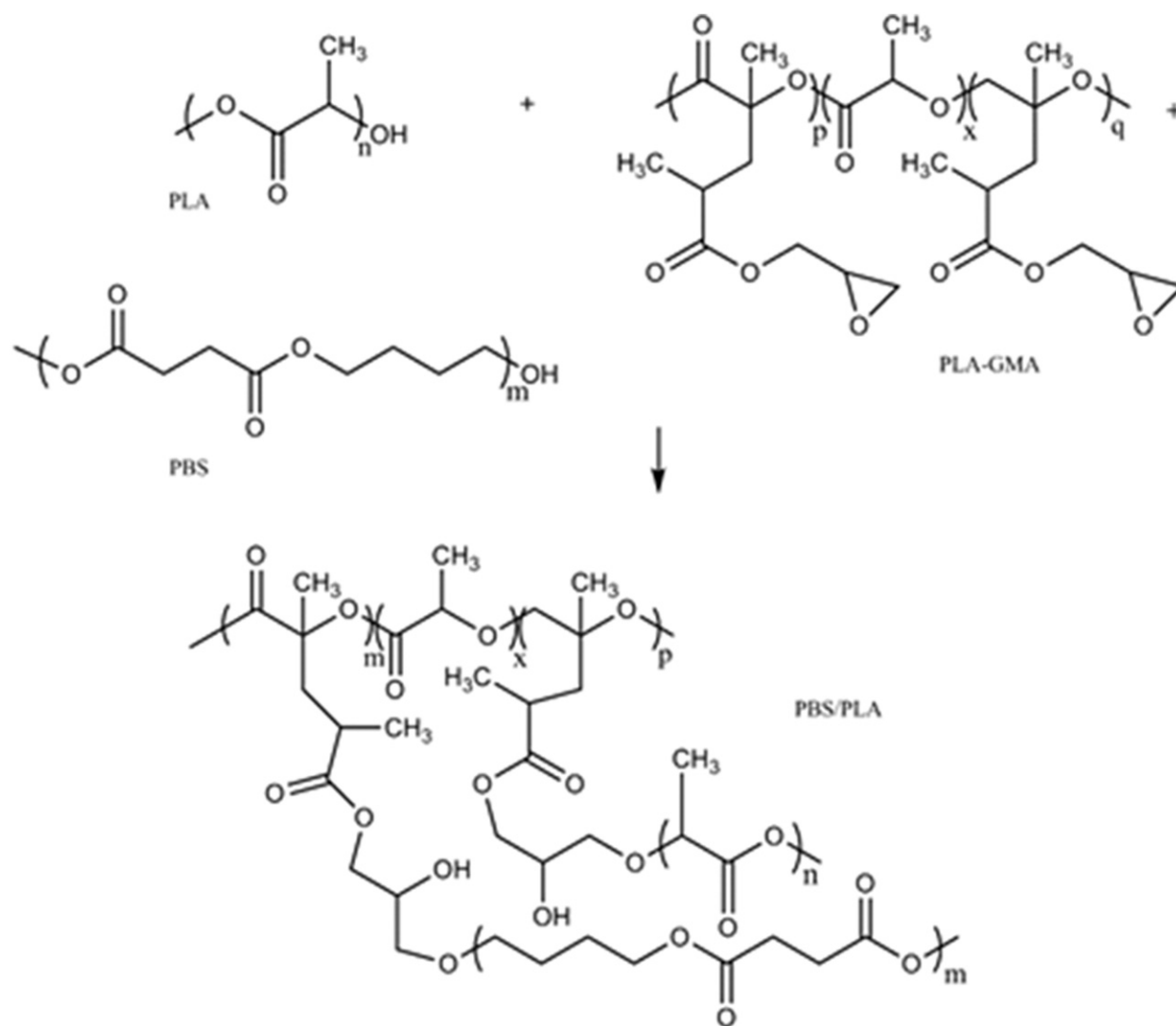


Fig. 12 Compatibilization mechanisms of the PLA with the PBS: the reaction scheme with glycidyl methacrylate groups.

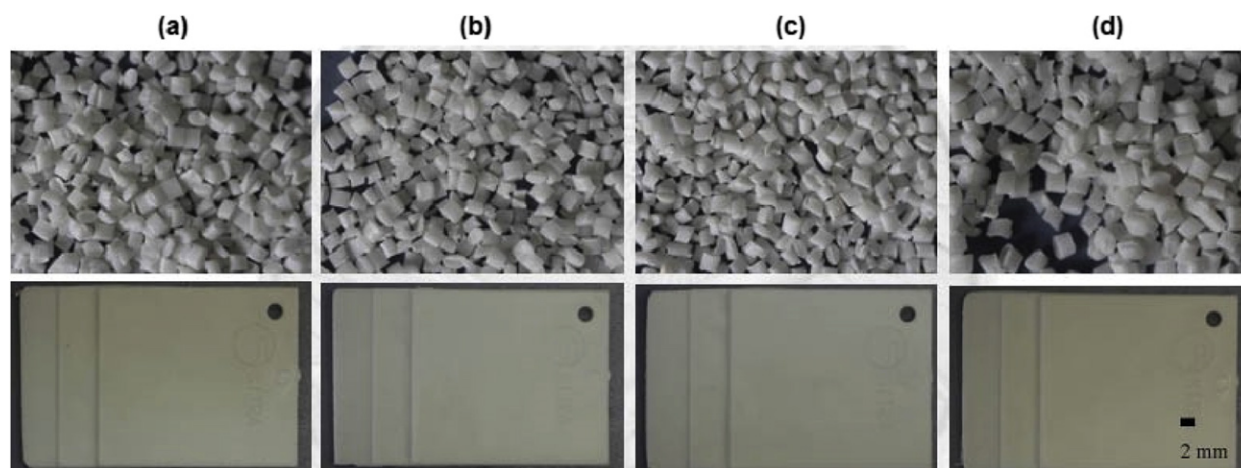


Fig. 13 Pellets produced by blending of PBS and PLA and injection molding of flat samples (a) PLA grade 3260 HP; (b) PLA grade 3260 + talc; (c) PLA grade 3260 HP + talc + compatibilizer; (d) PLA grade 3260 HP + talc + compatibilizer + PBS.

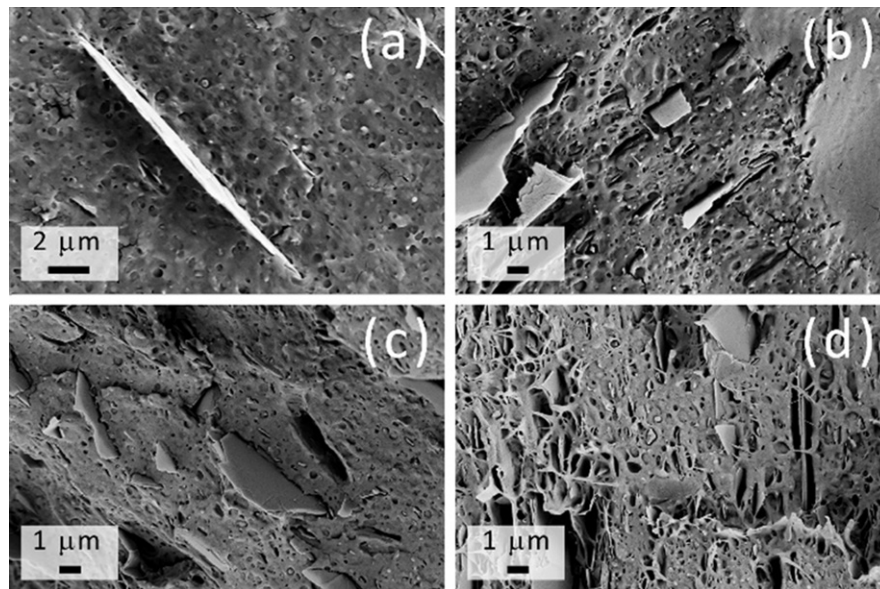


Fig. 14 SEM images show the morphology of talc in the PLA matrix, the distribution of PBS inside the PLA matrix (see the spherical voids that corresponds to the presence of PBS “droplets” before their removal by enzymatic attack with proteinase-k) and the crystalline structure of the polymeric matrix in four test-cases: (a) 2 wt% talc; (b) 5 wt% talc; (c) 15 wt% talc; (d) 30 wt% talc.

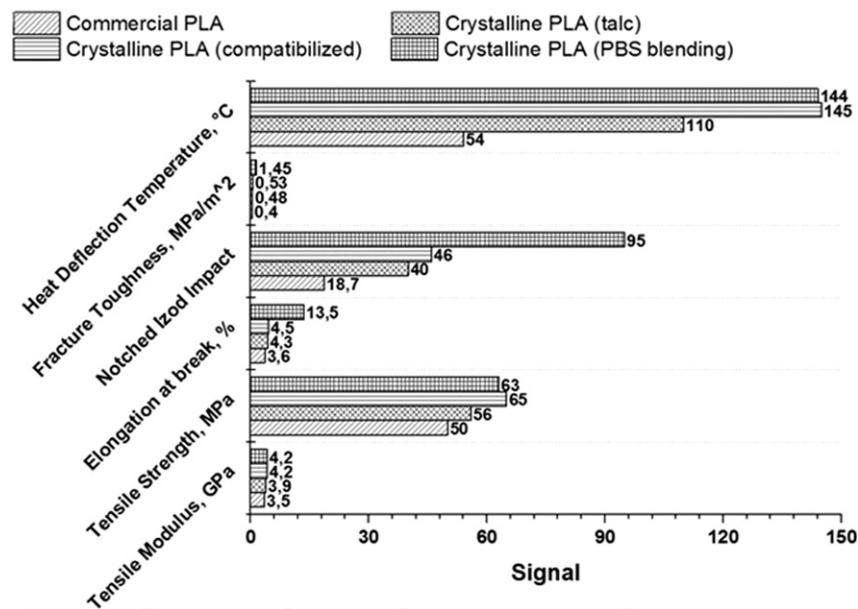


Fig. 15 Overall properties of the injection molded samples achieved by blending PLA and PBS, as copolymer.

can simplify and speed up significantly the extraction of the coffee capsules from the mold. It can, however, have a negative effect on material crystallization as it can promote a faster cooling of the polymer and the resulting block of the crystallization process.

The last issue concerns the hydrolytic degradation of the material when melted inside the chamber. The permanence time of the material in the chamber depends mostly on the ratio between the volume of the chamber of the injection molding equipment (i.e., the melting chamber) and the volume of the cavity inside the mold. In the prototypal equipment used for the preliminary molding tests, the ratio is 80:1. This means that about 80 capsules can be produced by the material contained inside a single spatial volume of the melting chamber. If the cycle time to produce a single capsule is 3 s, the overall maximum residence time of the molten material in the chamber can be 240 s, with an average permanence time of the material of 120 s. If the cycle time increases at 8 s, as sometimes can happen, the overall maximum permanence time of the material inside the chamber is an unacceptable 640 s. This time is extremely long and can bring to severe hydrolytic degradation of the PLA compound. Such

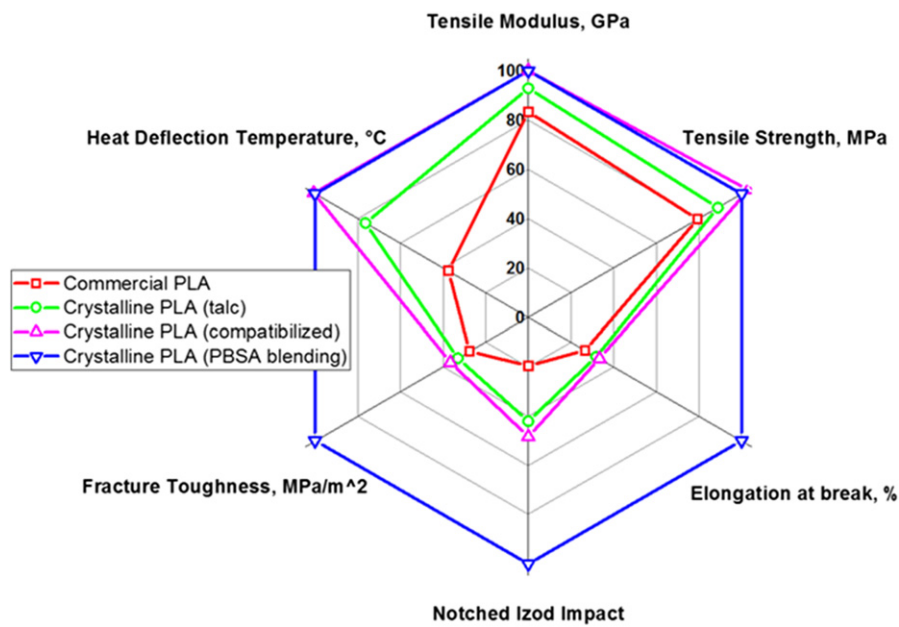


Fig. 16 Radar plot of the injection molded samples achieved by blending PLA and PBS, as copolymer.



Fig. 17 Coffee capsule that was injection molded using a compound of PLA (grade 3260 HP) and PBS (as secondary phase).

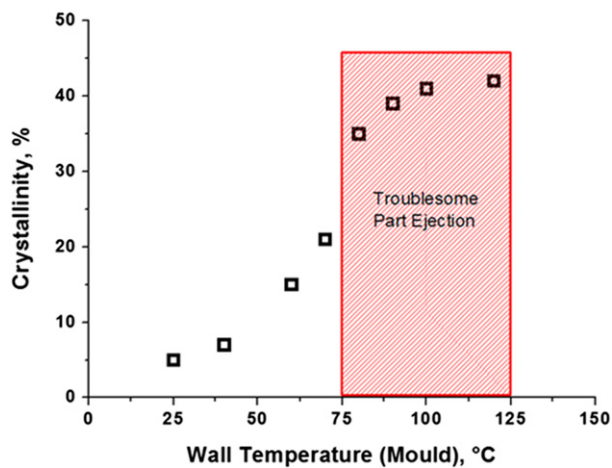


Fig. 18 Part ejection and wall temperature of the mold.

parameter is therefore of great importance in the manufacturing of the industrial devices. This should feature a small chamber to minimize the residence time of the material at high temperature during the injection molding process. Multi-cavity molds simplify significantly this task, reducing the permanence time of the material in the melting chamber of the injection molding equipment, as the molten material can be injected in more cavities of the same mold.

Conclusions

This work presented the results obtained by applying a methodological approach to overcome limitations of bioplastic materials in melt processing applications. The method involves a strategy for the formulation of the compound, in particular the combined effect of a mineral filler, compatibilizers and a copolymer was subsequently evaluated. The components have been compounded by reactive extrusion, which allowed a homogeneous dispersions and distribution of additives as shown by SEM images.

Based on the experimental evidences, the following conclusions can be drawn:

- (1) Addition of talc inside the polymeric blends allows to customize the degree of crystallinity of the materials and, in turn, potentiate the thermal stability of the resulting material;
- (2) Addition of the chain extenders allow to increase the compatibilization between the different polymeric phases, the talc and the polymeric blends as well to compensate the decrease in the molecular weight of the polymer following the thermal processing;
- (3) Addition of the PBS allows to increase toughness of the polymeric blends by the onset of a ductile secondary polymeric phase inside the primary phase based on PLA;
- (4) Injection molding with low cycle time and high wall temperature allow to preserve the features of the polymeric materials, optimizing the crystallization degree and minimizing the occurrence of the thermal degradation.

PLA/PBS blends engineered with talc and chain extenders are extremely promising to manufacture plastic compounds suitable for the fabrication of coffee capsules that are compostable and relying, almost completely, on renewable resources. Furthermore, the proposed methodological approach can be applied in different market segments, allowing to support scientists and practitioners in developing innovative solutions to face the everyday environmental challenges in the field of food packaging.

Acknowledgements

This work is part of the Project co-funded by the European Commission within the LIFE + Programme (2014–2020). Grant agreement no.: LIFE-PLA4COFFEE ENV/IT/000744. The partners of LIFE-PLA4COFFEE ENV/IT/000744 are kindly acknowledged for their continuous support and stimulating insights.

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Thermophysical and Adsorption Characteristics of Waste Biomass-Derived Activated Carbons

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Introduction

To improve the performance of adsorption cooling/heating systems, it is urgent to find new adsorbent with excellent thermophysical properties compared to commercial adsorbents. Higher adsorption capacity and faster kinetics are the keys to develop adsorbent materials. Several adsorbents were studied so far for ethanol and CO₂ adsorption, the promising two refrigerants in heat pump applications. Among them, metal-organic frameworks (MOFs), potassium hydroxide (KOH) activated phenol resin, zeolite and silica gel were extensively investigated (Younes *et al.*, 2017). Considering the ethanol adsorption capacity, KOH treated phenol resin showed maximum capacity (1.98 kg kg⁻¹) followed by MOFs (1.1 kg kg⁻¹), and activated carbon fiber (0.8 kg kg⁻¹). For CO₂ capture, storage and utilization in engineering applications, activated carbons (Fan *et al.*, 2016; Jribi *et al.*, 2017), zeolites (Abdul Kareem *et al.*, 2018), functionalized porous silica gels (Aboudi and Vafaezadeh, 2015), metal-organic frameworks (Fu *et al.*, 2017; Qasem *et al.*, 2017) and covalent organic frameworks (Olajire, 2017) were studied. Among studied adsorbents, activated carbons (ACs) are found very promising due to its attractive surface properties, internal pore structures, low cost and possibility of being produced from renewable biomass precursors (Danish and Ahmad, 2018). Saha *et al.* (2011) reported the maximum CO₂ adsorption capacity onto activated carbon fiber and powder were 1.0 and 1.7 g g⁻¹, respectively. Biloé *et al.* (2002) and Himeno *et al.* (2005) measured equilibrium CO₂ adsorption capacity onto several activated carbons and showed the maximum CO₂ uptake onto Maxsorb was 1.1 cm³ g⁻¹. The maximum CO₂ adsorption capacity for MOF-177 was found 1.47 g g⁻¹ at ambient temperature and 3.5 MPa pressure (Millward and Yaghi, 2005). Fan *et al.* (2016) studied the adsorption cooling cycle using activated carbon/CO₂ pair and achieved the best cooling performance for the pore widths ranging from 7 to 15 Å with higher limiting uptakes or pore volumes.

Literature review indicates that activated carbons are superior adsorbent compared to others in terms of adsorption capacity of ethanol and CO₂. However, still adsorption uptakes of those refrigerants are not in the satisfactory level for wide spread commercialization of the systems. Moreover, the extensive use of ACs is limited due to the production cost and scarcity of good quality precursor materials. Therefore, abundantly available and renewable precursor material can be a good choice for producing high quality ACs. For this purpose, ACs are synthesized from two waste biomass precursors, namely waste palm trunk (WPT) and mangrove (M). The details synthesis procedure including surface morphology and elemental composition are presented in the previous article. This article investigated the porous properties, thermal conductivity, and adsorption characteristics of ethanol and CO₂ onto newly synthesized biomass-derived ACs. Some significant contributions in this article are:

- N₂ adsorption at 77K is measured for estimating surface area, pore volume and pore size distribution.
- Alpha-s (α_s) and non-local density functional theory (NLDFT) are employed to calculate the specific surface area, pore volume, average pore width, and pore size distribution.
- Estimated porous properties are then compared with widely used adsorbents.
- The thermal conductivity of the synthesized ACs is measured.
- Effect of activation conditions on porous properties and thermal conductivity are investigated.
- Equilibrium adsorption performance of ethanol and CO₂ onto synthesized ACs is presented for a wide range of adsorption temperatures and pressures.

Experimental Details

Materials Formulation

The abundantly available and renewable precursor materials, namely waste palm trunk (WPT) and mangrove (M) are employed for synthesizing high grade ACs that can be used in various applications including adsorption heat pump (AHP) systems and CO₂

Table 1 Formulation of synthesized ACs derived from WPT and M

No.	Carbonization temperature [°C]	Activation temperature [°C]	KOH to sample ratio	^a Sample naming
1	500	600	4:1	WC500A600K4
2		700	4:1	WC500A700K4
3		800	4:1	WC500A800K4
4		900	4:1	WC500A900K4
5	600	900	6:1	WC500A900K6
6		900	6:1	WC600A900K6
1	500	600	4:1	MC500A600K4
2		700	4:1	MC500A700K4
3		800	4:1	MC500A800K4
4		900	4:1	MC500A900K4
5	600	900	6:1	MC500A900K6
6		900	6:1	MC600A900K6

^aW: Waste palm trunk (WPT); M: Mangrove; C: Carbonization temperature in °C (for example: C500 means carbonization at 500°C); A: Activation temperature in °C (for example: A600 means activation at 600°C); K4 and K6: 4 and 6 times KOH of carbonized sample.

capture or storage. The properties of raw material, detailed synthesis procedure of ACs, and few fundamental properties of synthesized ACs such as yield, surface morphology, and elemental composition analysis are presented in the previous article entitled as "Synthesis of high grade activated carbons from waste biomass" written by the same authors. Total twelve AC samples (six from each biomass precursor) are synthesized by changing the carbonization and activation conditions. **Table 1** represents the AC samples prepared from WPT and M with sample naming code used in subsequent sections.

Methodology for Thermophysical Properties

N₂ adsorption/desorption isotherms are measured at 77K using volumetric adsorption equipment (Belsorp-Max-S) supplied by BEL Japan Inc., Japan. Before the N₂ adsorption measurement, sample is degassed under vacuum condition at 120°C for several hours for removing unwanted gas and moisture adsorbed on the surface. The sample mass is correctly measured after degassing and around 60 mg mass of each sample is used for this experiment. After that, sample tube is connected to system and performed the leakage test. The system executes the whole experiment automatically by the instruction given in software.

Thermal conductivity measurements are conducted employing C-Therm TCi thermal conductivity analyzer provided by C-Therm Technologies Ltd., Canada. The schematic diagram and experimental details can be found elsewhere (Pal *et al.*, 2017c). Thermal conductivity measurement of all WPT and M-derived AC samples is performed at ambient temperature and pressure conditions. The TCi system employs the modified transient plane source (MTPS) technique for thermal conductivity measurement. The major components of this instrument are (i) one-sided interfacial heat reflectance sensor, (ii) controller unit and (iii) data processing software. The sensor has a central spiral shape heater surrounded by a guard ring. A known constant current is applied to the sensor's spiral heating element which generates a small amount of heat to provide the sample. Approximating a one-dimensional heat flows from the sensor into the tested sample. During the measurement, the sample is heated by approximately 1–3°C. Depending on its thermal properties, the sample absorbs some portion of the heat and the remaining heat causes a temperature rise at the sensor-sample interface. Temperature rise causes the voltage drop on the spiral heated which is measured by the system before and during the measurement. The voltage data are then converted to thermal conductivity value by the data processing software. The temperature increasing rate at the sensor-sample interface is inversely proportional to the thermal conductivity value of the tested sample (Pal *et al.*, 2017c).

Methodology for Adsorption Uptake Measurement

The magnetic suspension adsorption measurement unit of type MSB-VG-S2 for low pressure ethanol vapor adsorption and MSB-GS-100-10M for high pressure CO₂ gas adsorption are employed to measure adsorption capacity for both type of synthesized samples. Both experimental set up are supplied by MicrotracBEL, Japan. **Figs. 1** and **2** show the schematic diagram of ethanol and CO₂ adsorption uptake measurement units, respectively. The adsorption measurement principle for both the instruments is almost similar. However, depending on the measurement pressure, two systems use different types of pressure sensors and the configuration. For low-pressure uptake measurement, three types of absolute pressure gauges (1) 3500 kPa, Keller PAA-35XHTT-35; (2) 133.3 kPa, MKS 628B13TBE1B; and (3) 1.33 kPa, MKS 628B12TBE1B are used in series to measure the ethanol vapor pressure with an accuracy of 0.15%–0.25% of full scale. The temperature of liquid ethanol is measured and maintained precisely by platinum resistance temperature element (100 Ω). However, for

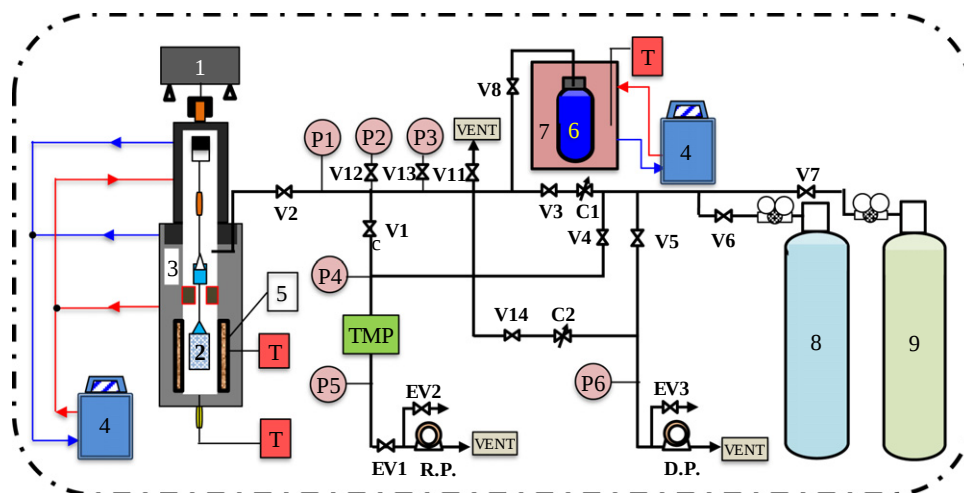


Fig. 1 Schematic diagram of ethanol adsorption uptake measurement unit. Reproduced from Pal, A., Thu, K., Mitra, S., *et al.*, 2017c. Study on biomass derived activated carbons for adsorptive heat pump application. *International Journal of Heat and Mass Transfer* 110, 7–19. (1). Magnetic suspension balance; (2). Sample cell; (3). Circulation oil jacket; (4). Oil bath and circulator; (5). Sheathed heater; (6). Ethanol container; (7). Isothermal oil bath; (8). Helium; (9). Nitrogen; TMP: Turbo-molecular pump; R.P.: Rotary pump; D.P.: Diaphragm pump; T: Thermocouple; P1-P6: Pressure gauges; C1-C2: Control valves; V1-V13: Valves.

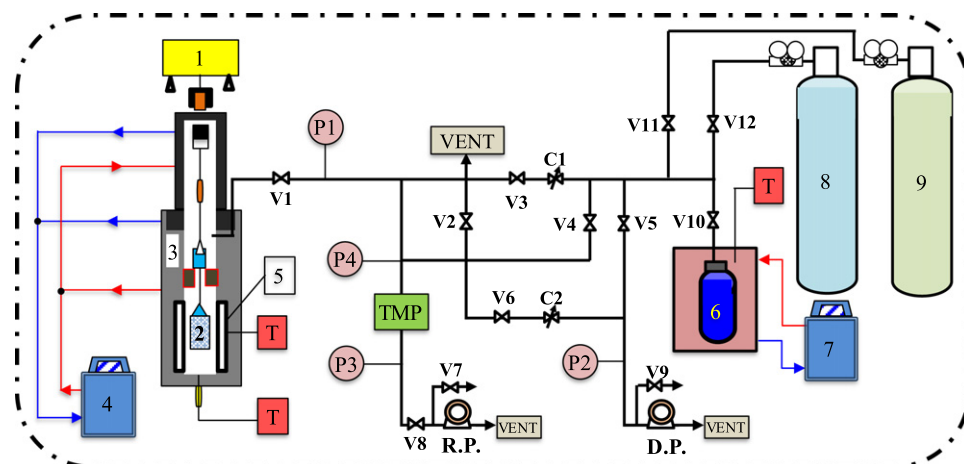


Fig. 2 Schematic diagram of CO₂ adsorption uptake measurement unit. Reproduced from Pal, A., El-Sharkawy, I.I., Saha, B.B., *et al.*, 2016. Experimental investigation of CO₂ adsorption onto a carbon based consolidated composite adsorbent for adsorption cooling application. *Applied Thermal Engineering* 109, 304–311. (1). Magnetic suspension balance; (2). Sample cell; (3). Circulation oil jacket; (4). Isothermal circulation oil bath; (5). Sheathed heater; (6). Refrigerant container; (7). Helium cylinder; (8). Carbon dioxide cylinder; TMP: Turbo-molecular pump; R.P.: Rotary pump; D.P.: Diaphragm pump; T: Thermocouple; P1-P4: Pressure gauges; C1-C2: Control valves; V1-V12: Valves.

high-pressure measurement, one absolute pressure gauge 10,000 kPa, Keller PAA-35X is used to measure the pressure of CO₂ gas with an uncertainty of ± 0.1 of full scale. Excluding the pressure and temperature sensors, the other similar components of both instruments are magnetic suspension balance unit; isothermal circulation oil baths to maintain adsorber and evaporator temperatures; isothermal air bath to avoid condensation through connecting tubes; a series of vacuum pumps including diaphragm, rotary, and turbo-molecular types. Both the system employs nitrogen gas to operate the valves whilst pressurized helium gas is used for checking the leakage as well as to compute the void volume and buoyancy effect. During adsorption measurement, the buoyancy effect is considered automatically by the system. The main feature for both the instruments is that it measures the adsorption amount directly by the magnetic suspension balance unit. The resolution of magnetic suspension balance is $\pm 10 \mu\text{g}$ to record the sample mass. The weight measurement repeatability of the magnetic balance is $\pm 30 \mu\text{g}$ with relative error $\pm 0.002\%$ of the reading.

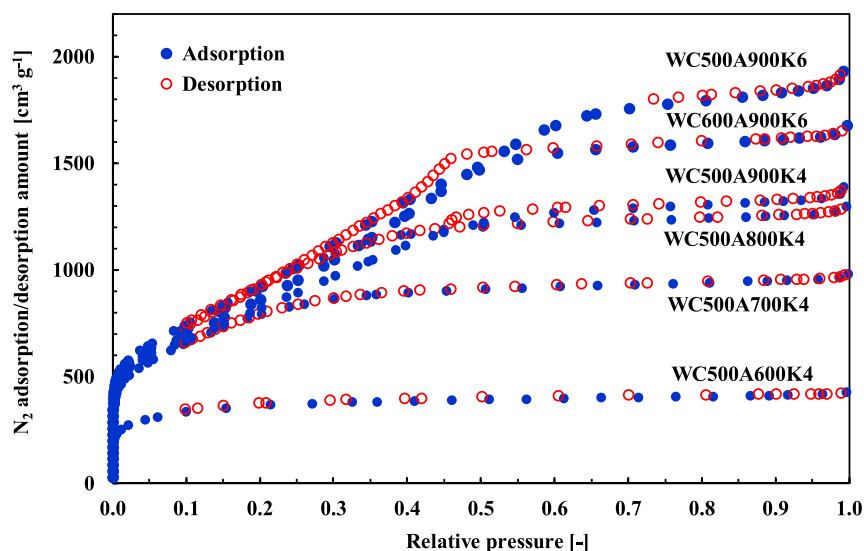


Fig. 3 N_2 adsorption/desorption isotherms of WPT-derived ACs at 77K.

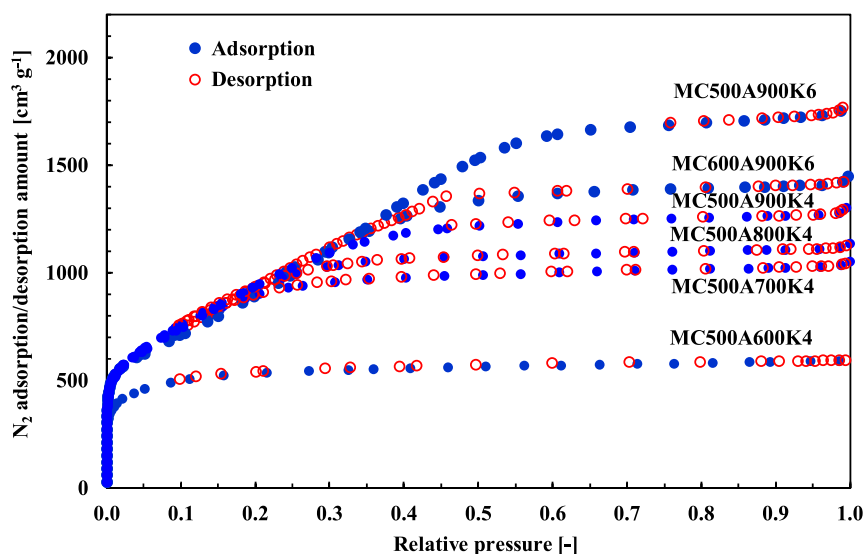


Fig. 4 N_2 adsorption/desorption isotherms of M-derived ACs at 77K.

Porous Properties of Biomass-Derived ACs

Nitrogen (N_2) adsorption is one of the standard procedures to analyze the porous properties of various adsorbent materials, which includes the surface area, pore volume, and pore size. N_2 adsorption/desorption isotherms of WPT and M-derived ACs are shown in Figs. 3 and 4, respectively. A sharp increase in the N_2 adsorption amount at very low relative pressure ($P/P_0 \leq 0.01$) is a characteristic feature of microporous materials, which is observed for all the synthesized AC samples. From the N_2 adsorption and desorption isotherms, it can be seen that biomass-derived ACs possess not only micropores but also some fractions of mesopores. In addition, there is no significant hysteresis in the isotherms. It can be noticed from these figures that N_2 adsorption quantity increases with the increase of the activation temperature and KOH ratio. Total specific surface area, external surface area, total pore volume, micropore volume, and average pore width are evaluated using alpha-s method from N_2 adsorption isotherm.

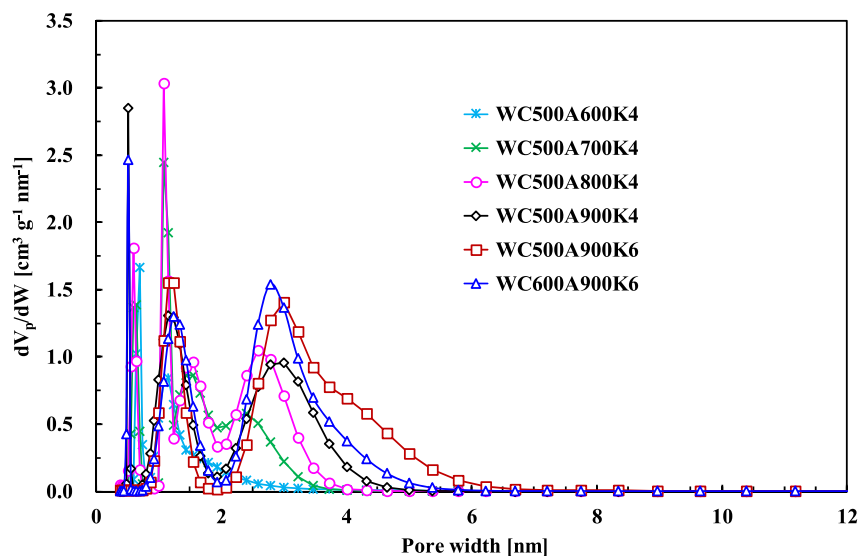


Fig. 5 Pore size distribution of WPT-derived ACs.

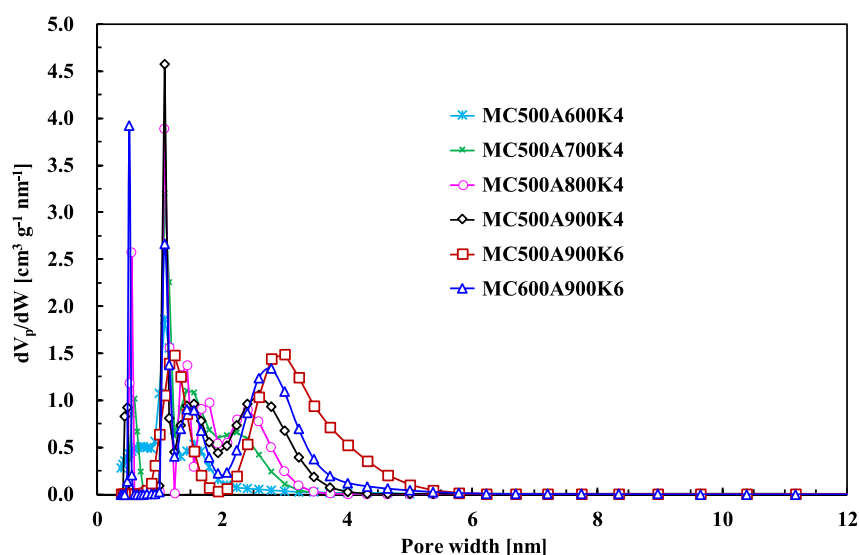


Fig. 6 Pore size distribution of M-derived ACs.

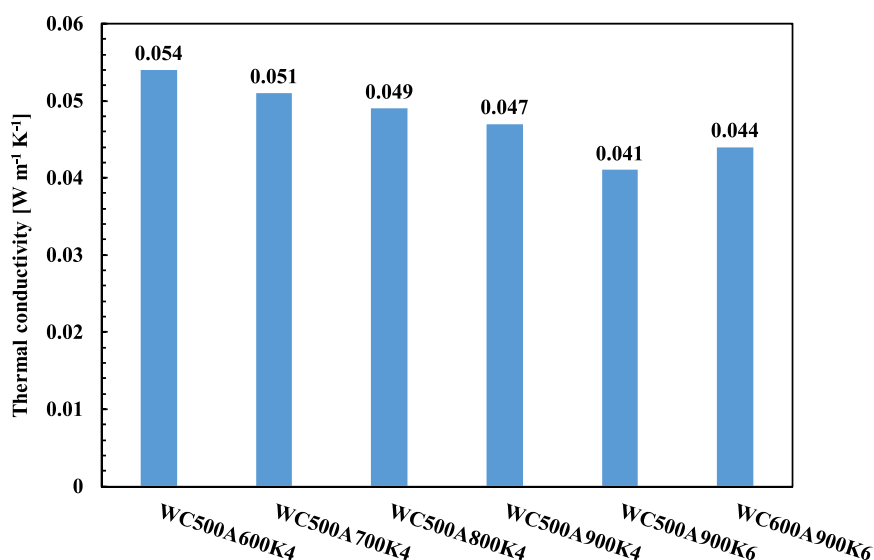
Non-local density functional theory (NLDFT) has been used to estimate pore size distribution. Figs. 5 and 6 show the pore size distribution of WPT and M-derived samples, respectively. The vertical axis represents the differential pore volume with respect to pore width (dV_p/dW) whereas horizontal axis signifies the differential pore width. It can be seen from these figures that pore size distribution changes with the change of activation conditions. Most of the pores are found less than 5 nm in size.

The physical characterization results such as total specific surface area, external surface area, total and micropore volume, and average pore size of all synthesized samples are summarized in Table 2. From the experimental analysis, it is found that carbonization at 500 and 600°C, activation at 900°C, and six times KOH ratio produce highest total surface area and pore volume for both types of biomass-derived ACs. It can be observed that the surface area for both kinds of ACs increases with the increase of activation temperature (Table 2). At activation temperature 600°C, the surface area of WPT-AC is found to be 1402 m² g⁻¹. However, after increasing the activation temperature, it increases to a large value. The surface area is found almost saturated beyond the activation temperature 700°C even though the carbonization temperature and KOH ratio are changed in case of WPT-derived ACs. The maximum surface area is found about 2985 m² g⁻¹ in the case of WPT-derived AC named as WC500A800K4. Similar phenomena is also observed in the case of M-derived ACs as can be seen from Table 2. However, at the condition C500A600K4, the surface area of WPT-derived AC (WC500A600K4) shows very less compared to M-derived AC (MC500A600K4). It is observed that surface area is almost saturated beyond the activation temperature 600°C even though the carbonization

Table 2 Physical properties of synthesized WPT and M-derived ACs

^a Sample	Total surface area [$\text{m}^2 \text{g}^{-1}$]	External surface area [$\text{m}^2 \text{g}^{-1}$]	Micropore volume [$\text{cm}^3 \text{g}^{-1}$]	Total pore volume [$\text{cm}^3 \text{g}^{-1}$]	Average pore width [nm]
WC500A600K4	1402	14.10	0.62	0.65	0.90
WC500A700K4	2583	22.93	1.44	1.48	1.13
WC500A800K4	2985	32.28	1.90	1.96	1.29
WC500A900K4	2771	46.33	1.99	2.07	1.46
WC500A900K6	2848	103.99	2.69	2.87	1.96
WC600A900K6	2927	62.52	2.41	2.51	1.68
MC500A600K4	2131	10.68	0.90	0.91	0.84
MC500A700K4	2878	17.47	1.56	1.60	1.09
MC500A800K4	2919	20.09	1.69	1.72	1.16
MC500A900K4	2925	28.21	1.92	1.97	1.33
MC500A900K6	2911	58.99	2.58	2.68	1.81
MC600A900K6	2924	34.19	2.13	2.18	1.47

^aW: Waste palm trunk (WPT); M: Mangrove; C: Carbonization temperature in $^{\circ}\text{C}$ (for example: C500 means carbonization at 500°C); A: Activation temperature in $^{\circ}\text{C}$ (for example: A600 means activation at 600°C); K4 and K6: 4 and 6 times KOH of carbonized sample.

**Fig. 7** Thermal conductivity results of WPT-derived ACs.

temperature and KOH ratio are changed in case of M-derived ACs. The maximum surface area is found about $2925 \text{ m}^2 \text{g}^{-1}$ in the case of M-derived AC named as MC500A900K4. It is also noticed that at high activation temperature and KOH ratio, surface area for both the samples is nearly the same (Table 2).

The pore volume and average pore size also increase with the increase of activation temperature and KOH ratio for both type of samples. The WPT-derived ACs show higher pore volume and pore size compared to M-derived ACs. The highest pore volume is found to be $2.87 \text{ cm}^3 \text{g}^{-1}$ from WPT whilst $2.68 \text{ cm}^3 \text{g}^{-1}$ from mangrove, these values are the current benchmark. It is highlighted that synthesized biomass-derived ACs show superior porous properties compared to the literature value where the ACs were mostly derived from coal, coke, petroleum residue and different biomass sources (Himeno *et al.*, 2005; El-Sharkawy *et al.*, 2006, 2014; Danish and Ahmad, 2018).

Thermal Conductivity of Biomass-Derived ACs

Figs. 7 and 8 show the thermal conductivity results of WPT and M-derived ACs, respectively. As can be seen from these figures, thermal conductivity slightly decreases with the increase of activation temperature for all kinds of samples because of forming pores

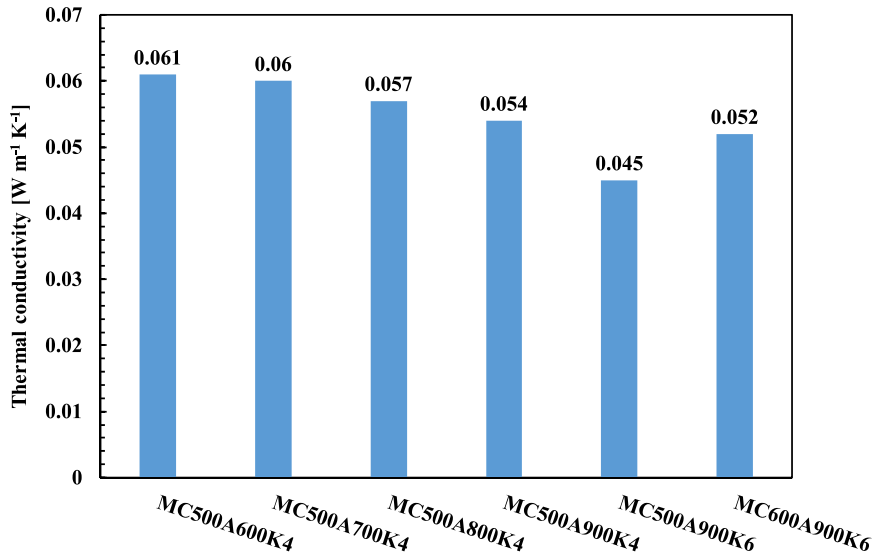


Fig. 8 Thermal conductivity results of M-derived ACs.

into the AC. Large surface area and pore volume reduce the sample density, which might decrease the conductive network. Thermal conductivity values are found in the range of 0.054–0.041 W m⁻¹ K⁻¹ for WPT-derived ACs whilst 0.061–0.045 W m⁻¹ K⁻¹ for M-derived ACs.

Adsorption Performance of Biomass-Derived ACs

Adsorption Isotherm Model

Adsorption characteristic is considered the crucial parameter for designing the AHP systems. The behavior of equilibrium adsorption uptake for a particular refrigerant (adsorbate) entirely depends on adsorbent porous properties. The experimental adsorption uptake for a particular pair is usually correlated with well-known adsorption isotherm models to find the best fitting model. The fittings parameters are usually used to predict the system performance for an adsorbent/adsorbate pair. The commonly used adsorption isotherm models for activated carbon based adsorbents are presented in the following Eqs. (1)–(6).

$$\text{Freundlich: } \frac{W}{W_0} = \left(\frac{P}{P_s} \right)^{1/k} \quad (1)$$

$$\text{Langmuir: } \frac{W}{W_0} = \frac{b_0 e^{\frac{Q_{st}}{RT}} P}{1 + b_0 e^{\frac{Q_{st}}{RT}} P} \quad (2)$$

$$\text{Dubinin – Astakhov (D – A): } W = W_0 \exp \left[- \left(\frac{RT}{E} \ln \left(\frac{P_s}{P} \right) \right)^n \right] \quad (3)$$

$$\text{Dubinin – Radushkevich (D – R): } W = W_0 \exp \left[- \left(\frac{RT}{E} \ln \left(\frac{P_s}{P} \right) \right)^2 \right] \quad (4)$$

$$\text{Tóth: } \frac{W}{W_0} = \frac{b_0 e^{\frac{Q_{st}}{RT}} P}{\left(1 + \left(b_0 e^{\frac{Q_{st}}{RT}} P \right)^h \right)^{1/h}} \quad (5)$$

Dubinin-Astakhov (D-A) for high pressure gas (such as CO₂) adsorption:

$$q = \left(\frac{q_0}{v_m} \right) \exp \left[- \left(\frac{RT}{E} \ln \left(\frac{P_s}{P} \right) \right)^n \right] \quad (6)$$

where W is the equilibrium uptake [g g⁻¹ or kg kg⁻¹], W_o represents the maximum equilibrium uptake [g g⁻¹ or kg kg⁻¹], P is the equilibrium pressure [kPa or MPa], P_s represents the saturated vapor pressure [kPa or MPa], T denotes the adsorption temperature [°C or K], R is the gas constant [J mol⁻¹ K⁻¹], Q_{st} is the isosteric heat of adsorption [kJ mol⁻¹], k is the exponent of Langmuir equation, h is the dimensionless Tóth parameter known as heterogeneity factor, n is the exponent of D-A and modified D-A equations, q denotes volumetric adsorption uptake [cm³ g⁻¹], and q_0 is the maximum volumetric adsorption capacity [cm³ g⁻¹].

The adsorbed phase volume V_m of adsorbate in the Eq. (6) can be calculated using the Eq. (7).

$$V_m = V_t \exp (\alpha^* (T - T_t)) \quad (7)$$

At triple point, the value of parameter V_t of liquid carbon dioxide is 0.84858 cm³ g⁻¹. The thermal expansion α^* of the adsorbed gas is 0.0025 K⁻¹ as suggested by Saha *et al.* (2011), and Himeno *et al.* (2005). In the Eq. (6), the saturation pressure P_s above the critical temperature is calculated by means of pseudo-saturated vapor pressure as given by the Eq. (8).

$$P_s = \left(\frac{T}{T_c} \right)^z P_c \quad (8)$$

where P_c and T_c are the critical pressure [kPa or MPa] and temperature [°C or K] of the high pressure gas, respectively. If the exponent $z = 2$ of the Eq. (8), then the Eq. (6) is called classical D-A. Otherwise ($z \neq 2$), the Eq. (6) is called the modified equation proposed by Amankwah and Schwarz (1995).

Ethanol Adsorption Performance

Ethanol is considered one of the promising refrigerants or working fluids for adsorption cooling applications. In addition, ethanol work as a very good adsorbate for activated carbon (Pal *et al.*, 2017b). Consequently, this article focuses on measuring the adsorption performance of ethanol onto synthesized biomass-derived ACs. To understand the adsorption performance, one sample from each kind of biomass has been chosen, namely WC600A900K6 (WPT-AC) from WPT and MC600A900K6 (M-AC) from mangrove since they possess excellent porous properties. Equilibrium ethanol adsorption uptakes onto WPT-AC and M-AC are measured gravimetrically using magnetic suspension adsorption measurement unit (Rubotherm: MSB-VG-S2) explained in Section "Methodology for Adsorption Uptake Measurement". The details of the experimental procedure for ethanol adsorption can be found elsewhere (Pal *et al.*, 2017c).

Adsorption uptakes of ethanol onto WPT-AC and M-AC are measured at five different temperatures 30, 40, 50, 60, and 70°C with various evaporator pressures. Figs. 9 and 10 represent the measured adsorption uptake data of ethanol onto WPT-AC

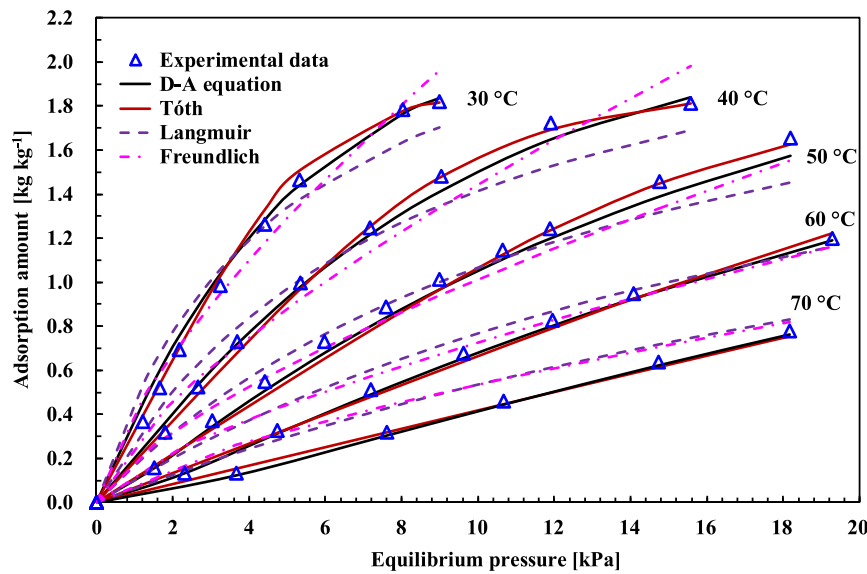


Fig. 9 Adsorption isotherms of ethanol onto WPT-AC (WC600A900K6) (data are fitted with Freundlich, Langmuir model, D-A equation, and Tóth model). Reproduced from Pal, A., Kil, H.-S., Mitra, S., *et al.*, 2017a. Ethanol adsorption uptake and kinetics onto waste palm trunk and mangrove based activated carbons. *Applied Thermal Engineering* 122, 389–397.

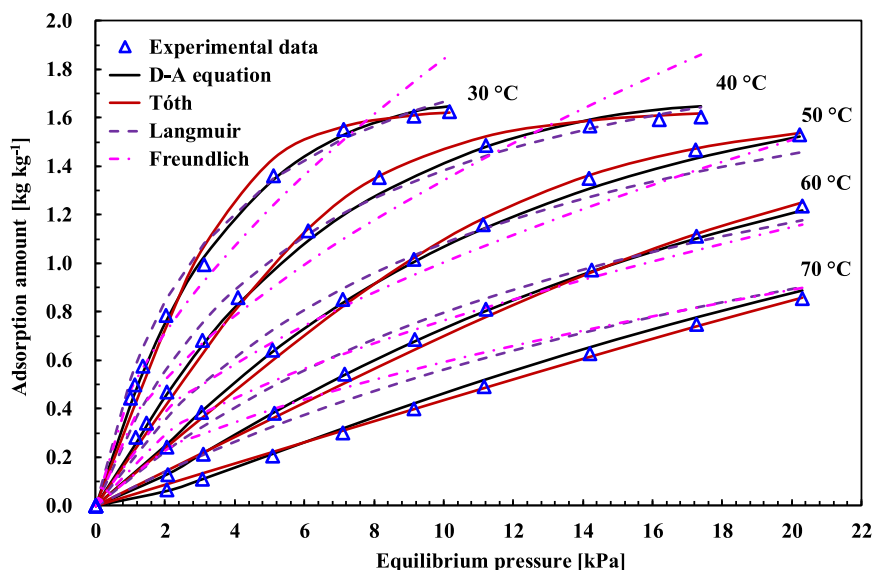


Fig. 10 Adsorption isotherms of ethanol onto M-AC (MC600A900K6) (data are fitted with Freundlich, Langmuir model, D-A equation, and Tóth model). Reproduced from Pal, A., Kil, H.-S., Mitra, S., *et al.*, 2017a. Ethanol adsorption uptake and kinetics onto waste palm trunk and mangrove based activated carbons. *Applied Thermal Engineering* 122, 389–397.

Table 3 Fitting parameters of the studied isotherm models for ethanol adsorption onto WPT-AC and M-AC samples

Model	Fitting parameter	WPT-AC (WC600A900K6)	M-AC (MC600A900K6)
Freundlich	W_0 [kg kg ⁻¹]	2.2	1.9
	k [dimensionless]	1.4	1.7
	RMSD [%]	25.8	52
D-A	W_0 [kg kg ⁻¹]	1.9	1.65
	E [kJ kg ⁻¹]	91.55	105.91
	n [dimensionless]	1.43	1.62
Langmuir	RMSD [%]	5.43	3.40
	W_0 [kg kg ⁻¹]	2.6	2.2
	Q [kJ mol ⁻¹]	45.4	47.66
Tóth	b_0 [kPa ⁻¹]	3.18×10^{-9}	1.91×10^{-9}
	RMSD [%]	19.6	30
	W_0 [kg kg ⁻¹]	1.9	1.65
Tóth	Q [kJ mol ⁻¹]	44.23	46.30
	h [dimensionless]	3.88	3.42
	b_0 [kPa ⁻¹]	4.09×10^{-9}	2.37×10^{-9}
	RMSD [%]	5.13	8.24

Note: Pal, A., Kil, H.-S., Mitra, S., *et al.*, 2017a. Ethanol adsorption uptake and kinetics onto waste palm trunk and mangrove based activated carbons. *Applied Thermal Engineering* 122, 389–397.

(WC600A900K6) and M-AC (MC600A900K6), respectively. The experimental data are fitted with Freundlich, Langmuir, D-A (Dubinin-Astakhov), and Tóth models which are plotted on the same figure. It is found that D-A and Tóth models are fitted well with the experimental data compared to other studied models. The maximum equilibrium ethanol uptake onto WPT-AC is as high as 1.90 kg kg⁻¹ whilst one kg of M-AC can adsorb up to 1.65 kg of ethanol, these are the highest uptake compared to literature reported AC powder or fiber such as Maxsorb III, ACF-20, and ACF-15. The fitting isotherm parameters for all the studied models are presented in Table 3.

CO₂ Adsorption Performance

The CO₂ (R744) is chosen as a refrigerant or working fluid in adsorption cooling/heating applications because it provides numerous benefits including high volumetric capacity and availability. Furthermore, it is a nonflammable, non-toxic refrigerant having zero ODP and zero GWP. In addition, CO₂ also shows good affinity toward the AC. Therefore, many researchers focused on AC/CO₂ pair for adsorption heat pump systems and CO₂ capture or storage.

The magnetic suspension adsorption measurement unit (MSB-GS-100-10M), which is illustrated in Section “Methodology for Adsorption Uptake Measurement”, is used for the measurement of adsorption uptake of CO₂ onto WPT and M-derived ACs. The details of the experimental procedure for CO₂ adsorption measurement can be found elsewhere (Pal *et al.*, 2016; Jribi *et al.*, 2017). Equilibrium adsorption uptakes of CO₂ onto the WC600A900K6 (WPT-AC) and MC600A900K6 (M-AC) are investigated at four different adsorption temperatures namely 30, 40, 50, and 70°C with pressure up to 7 MPa. The plot of experimental data along with isotherm models for WPT-AC/CO₂ and M-AC/CO₂ pairs are presented in Figs. 11 and 12, respectively. The maximum absolute uptakes are found 2.3 cm³ g⁻¹ for WPT-AC/CO₂ and 2.1 cm³ g⁻¹ for M-AC/CO₂ pair, respectively, using a modified D-A model. The isotherm fitting parameters for the studied models for all ACs/CO₂ pairs are summarized in Table 4. It is highlighted that synthesized biomass-derived ACs shows highest adsorption uptake of CO₂ compared to all other ACs such as Maxsorb III, Norit RB3, Norit darco, BPL, A-20, A-10, reported in the literature.

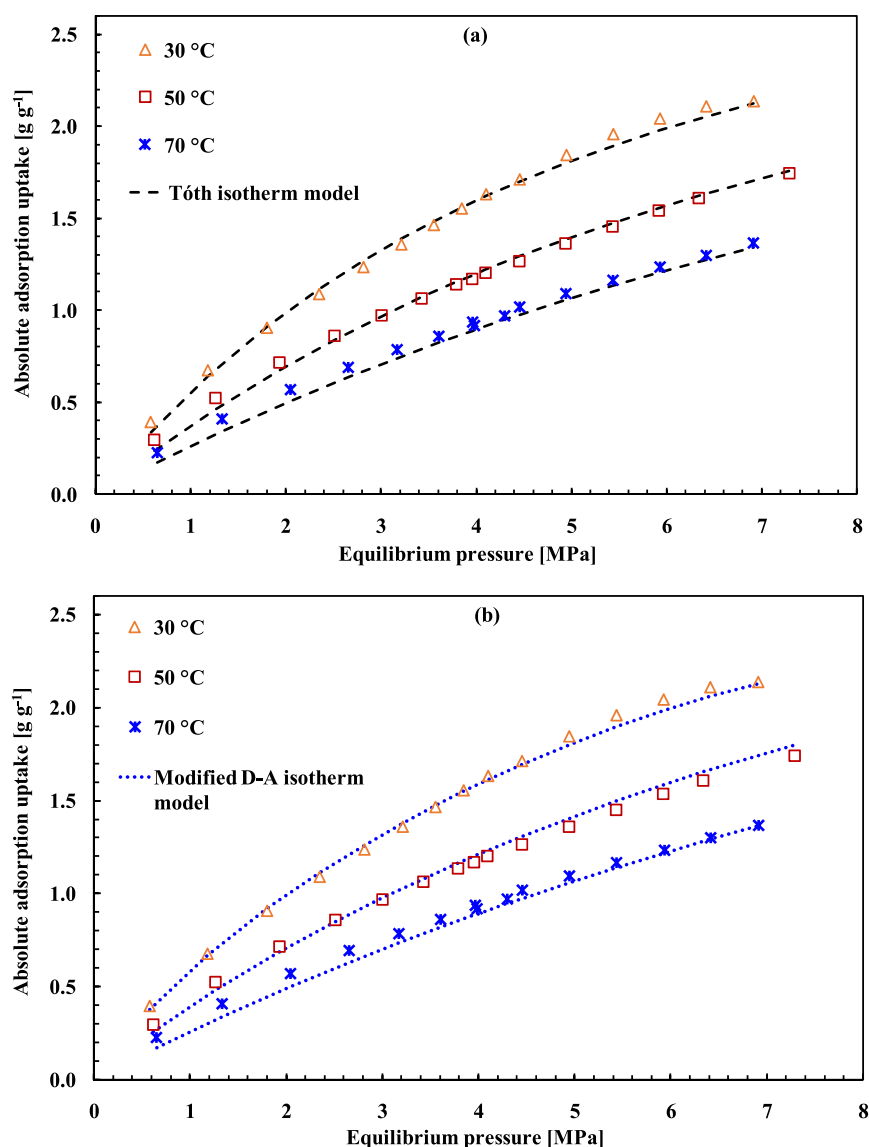


Fig. 11 CO₂ adsorption onto WPT-AC (WC600A900K6) and data are fitted with (a) Tóth model, and (b) modified D-A model.

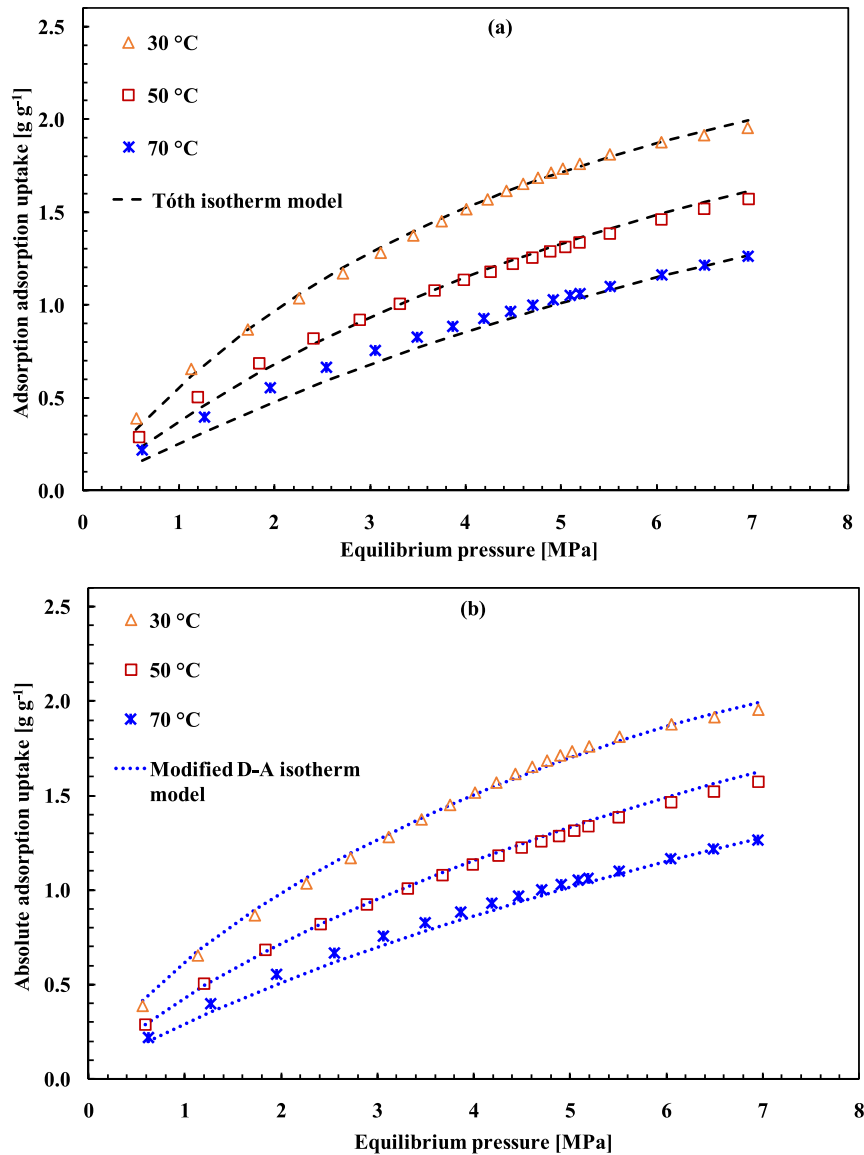


Fig. 12 CO₂ adsorption onto M-AC (MC600A900K6) and data are fitted with (a) Tóth model, and (b) modified D-A model.

Table 4 Fitting parameters of the studied isotherm models for biomass-derived ACs/CO₂ pairs

Model	Fitting parameter	WPT-AC (WC600A900K6)	M-AC (MC600A900K6)
Modified D-A model	q_0 [cm ³ g ⁻¹]	2.2775	2.1321
	E [J mol ⁻¹]	3995.67	4322.67
	k [dimensionless]	4.437	4.749
	n [dimensionless]	1.20	1.15
	RMSD [%]	4.118	2.975
Tóth	W_0 [g g ⁻¹]	3.50	3.20
	Q [J mol ⁻¹]	17,685.23	18,473.66
	h [dimensionless]	1.1743	1.1286
	b_0 [MPa ⁻¹]	1.577×10^{-4}	1.290×10^{-4}
	RMSD [%]	3.967	3.348

Conclusions

In this article, activated carbons are synthesized and found to be excellent porous properties from two waste biomasses, namely, waste palm trunk and mangrove. N_2 adsorption/desorption isotherms show that biomass-derived ACs have a high degree of porosity which is located mainly in micro size of pores. ACs with a surface area between 1402 and 2985 $m^2 g^{-1}$ having pore volume 0.65–2.87 $cm^3 g^{-1}$ are successfully prepared from both type of biomasses. It is worthy to mention that the highest surface area and pore volume of WPT-derived ACs are found to be 2985 $m^2 g^{-1}$ (WC500A800K4) and 2.87 $cm^3 g^{-1}$ (WC500A900K6) and for M-derived ACs it is 2925 $m^2 g^{-1}$ (MC500A900K4) and 2.68 $cm^3 g^{-1}$ (MC500A900K6), respectively. The porous properties achieved in this study are the highest compared to the reported literature data which is a current benchmark. Generally, the increase of the activation temperature and the mass ratio of KOH/carbon can enhance the porosity. However, the micropore is widened when the activation temperature and mass ratio of KOH/carbon is increased. It is found that all the porous properties are saturated at a certain synthesis condition and decreases at higher temperature and KOH ratio. It can be summarized that carbonization at 500 and 600°C, activation at 900°C, and six times KOH ratio produce the highest surface area and a pore volume from both kinds of biomasses. Therefore, WC500A900K6, WC600A900K6, MC500A900K6, and MC600A900K6 can be selected as promising adsorbents among the synthesized ACs for various energy conversion applications. Experimental results show that thermal conductivity values ranging from 0.054 to 0.041 $W m^{-1} K^{-1}$ is for WPT-derived ACs whilst 0.061–0.045 $W m^{-1} K^{-1}$ is for M-derived ACs. The synthesized biomass-derived ACs show highest adsorption uptake of ethanol and CO_2 than that of reported data in the literature. The maximum equilibrium ethanol and CO_2 uptakes onto WPT-AC are found to be as high as 1.90 $kg kg^{-1}$ and 2.3 $cm^3 g^{-1}$, respectively and thus are very promising for energy conversion and storage applications.

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TIG Torch Melting as Surface Engineering Technology

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Introduction

In various engineering applications, the surface properties of engineering components are enhanced using surface modification technology. As a consequence, the interest in surface engineering has risen greatly throughout the past decades. Surface engineering involves the development of a new or modified exterior phase on the substrate material (Chattopadhyay, 2014; Hardell and Prakash, 2010). Through surface engineering, the thin near-surface layer of substrate material is modified while maintaining their core structure and properties (Bello *et al.*, 2016; Dong, 2010; Mridha and Dyuti, 2011).

The surface melting technique also known as cladding which has been widely used as surface engineering technology. The surface melting technology involves of high energy source that is applied to melt the surface of the substrate fed with reinforcing particles (Sathiya *et al.*, 2009). Upon solidification, the reinforcement is strongly bonded with the substrate material. Powder blown, wire feed and pre-place powder are the three methods to feed the reinforcement onto the substrate material prior or during the surface melting technology (Folkes, 1994).

Various surface engineering technologies were introduced by previous researchers through several famous approaches such as tungsten inert gas welding (TIG) (An *et al.*, 2017; Bello *et al.*, 2016; Kumar *et al.*, 2017; Maleque *et al.*, 2017; Sahoo and Masanta, 2017a,b; Saroj *et al.*, 2017a,b), laser cladding (Qunshuang *et al.*, 2017; Yang *et al.*, 2016; Zhou *et al.*, 2016), electron beam welding (EBW) (Lienert *et al.*, 1993; Peng *et al.*, 2011) and thermal spraying (Aussavy *et al.*, 2014; Shibe and Chawla, 2014). Tungsten inert gas welding (TIG) melting technology or also commonly known as gas tungsten arc welding (GTAW) has started to be used during the Second World War. TIG torch technology was designed by Russel Meredith and developed by Linde Company. After several years of development, it was finally modified in 1941 and patent issued in 1942. The heat in TIG melting technology is initiated from an electric arc between the tungsten electrode and substrate material. The melting of substrate surface is protected from contamination using common protective gases such as helium, argon or the mixture of them. The following solidification of the substrate material fed with reinforcement particle produced new intermetallic compound with altered wear and hardness behavior (Maleque *et al.*, 2018; Musa *et al.*, 2018; Mridha *et al.*, 2012a,b).

Another surface melting technology known as electron beam welding (EBW) was developed in 1950s. The kinetic energy of accelerated electrons is used as the heat source for surface melting process in this technique. The generation of high velocity electrons is performed by heating the negative-charged cathode filament up to its thermionic emission temperature. The electron beam with diameter between 0.3 and 0.8 mm hit the base material with velocity up to 70% of the speed of light. Around 95% of the electron's kinetic energy is generated into heat. The power density is up to 10^{10} Wm^{-2} . The superior power density makes EBW capable of deep melting of the substrate surface. This could be an good to fused two metals together, however, surface melting technique does not need such high heat source since the purpose is to modify only the thin near surface layer of the substrate (Sun and Karppi, 1996).

Laser cladding is a recent surface engineering technology where another substance is combined onto the substrate surface for surface modification. Laser cladding is considered as one of the surface melting technology. The fusion of reinforcement particles onto the substrate surface is done using laser as heat source. The method was developed in 1970s and usually used as utility to repair and enhance the surface of engineering parts (Gedda, 2004). The modified layers produce by this method is said to have strong metallic bond, low dilution and less distortion between the reinforcement and the substrate (Huang *et al.*, 2010; Zanzarin *et al.*, 2015). Fernández *et al.* (2014) recommended to control the surface coating thickness by varying the process parameters of laser cladding.

Thermal spraying is a surface engineering technology developed in 1910s to 1920s where the reinforcement materials is melted, sprayed and latched onto the substrate surface. From the same category, a common surface engineering technology known as plasma spraying is developed in 1970s where a high temperature (can exceed 15000K) plasma jet is used to spray refractory materials for examples, oxides and high melting point metals such as molybdenum (Seiji *et al.*, 2008). The deposited reinforcement particles solidify and form laminar structure of the new modified layer (Aussavy *et al.*, 2014; Begg *et al.*, 2016; Seiji *et al.*, 2008; Shibe and Chawla, 2014). The method highly depends on the cleanliness and roughness of the substrate surface. Therefore, surface preparation prior to the surface melting process is very crucial. Furthermore, the grit blasting is usually used on the substrate surface to allow adhesive bonding with the reinforcement. However, grit blasting require more labor and the surface finish for the method is said to be non-consistent (Begg *et al.*, 2016).

Among the surface engineering technology discussed previously, TIG torch surface melting technology is believed as crucial key in the development of the surface modification technology due to its simplicity, flexibility and cheap establishment. The method was used in the world war era by the military on stainless steel, aluminium and magnesium for aircraft components. TIG torch melting now is used in numerous applications in aerospace, automotive, nuclear reactors, ship, civil parts etc. TIG torch technique

can be used not only on the stainless steel, magnesium and aluminium, but also used for other type of alloy steels (low alloy steel, high alloy steel, duplex stainless steel, microalloyed steel etc.), magnesium composite, aluminium composite, titanium and its alloys.

A lots of processing parameters in TIG torch surface melting technology has to be taken into consideration such as the current and voltage applied, welding speed, shielding gas type, composition and flow rates, and powder preplacement rate (Maleque and Afiq, 2018; Bello *et al.*, 2015; Maleque *et al.*, 2015). The varying parameters is optimized to get the best behavior required for demanded applications (Cheniti *et al.*, 2017; Jarial, 2015; Korra and Balasubramanian, 2011; Maleque *et al.*, 2017; Peng, 2012; Srirangan and Paulraj, 2016). Overall, it was found that the methods utilized by previous researchers were beneficial to improve the surface performance of various substrate materials which include their wear, hardness, coefficient of friction and corrosion resistance. The aim of this paper is to review and emphasis the importance of TIG torch melting as surface engineering technology.

Melting Approach in Surface Engineering

Melting route also known as fusion is a technique that utilize high melting heat to form melt layer with metallurgical bonding upon solidification. The use of melting route in surface engineering highly increases when the electric energy was revealed. Fig. 1 shows the evolution of the surface melting route that is rapid began in 18th century. The melting route can be used to fuse the ceramic particles reinforcement and substrate material together and hence modify the thin surface layer for better hardness, friction and wear behavior. The reinforcement used in this melting route is usually ceramic particles since they have high degree of hardness and high thermal stability. Therefore, the superior properties of ceramic particles as reinforcement are beneficial to the surface performance of the metallic substrate.

There are three methods to feed the ceramic reinforcement into the substrate surface in the surface melting process; powder injection or blown, wire feed and powder preplacement method as shown in Figs. 2–4 respectively. For powder injection or blown method, the reinforcement particles are carried using a blow of gas that are commonly argon, CO₂ or oxygen. The reinforcement particles are fed through coaxial or lateral feed method. The stream of carrier gas should be maintained well to produce good quality of surface coating layer with uniform distribution of reinforcement. If the gas flow rate is too high, this might decrease the heat input on the substrate surface and leads to less dissolution of particles. When the gas flow rate is lower, less quantity of reinforcement particles reaches the melted surface.

Surface melting approach in surface engineering also can be conducted using wire feed method as shown in Fig. 3 where the spool containing filler or reinforcement particles are fed through a nozzle onto the substrate surface. The wire feed which is used to transport the reinforcement should have no defects that might disturb the flow consistency and affect the quality of the coating layer. For example, when the wire feed is dented, the reinforcement particles deviates from getting into the centre of the melt layer. The quality of the melted layer also is highly depended on the wire feed rate. For instance, slower wire feed rate causes some amount of the reinforcement unable to reach the centre of the melt layer. According to previous authors, wire feed method does not waste the reinforcement material used as compare to the powder injection method (Kou, 2003; Toyserkani *et al.*, 2005).

Another way to conduct surface melting technique is by introducing powder preplacement method as shown in Fig. 4. Powder preplacement method is the cheapest, simple, flexible way to perform surface modification of metallic materials and able to produce good quality of coating layer with strong metallurgical bonding. Polyvinyl acetate (PVA) solution is used in powder preplacement method as a binder to keep the powder from blown away by shielding gases during melting process. The amount of

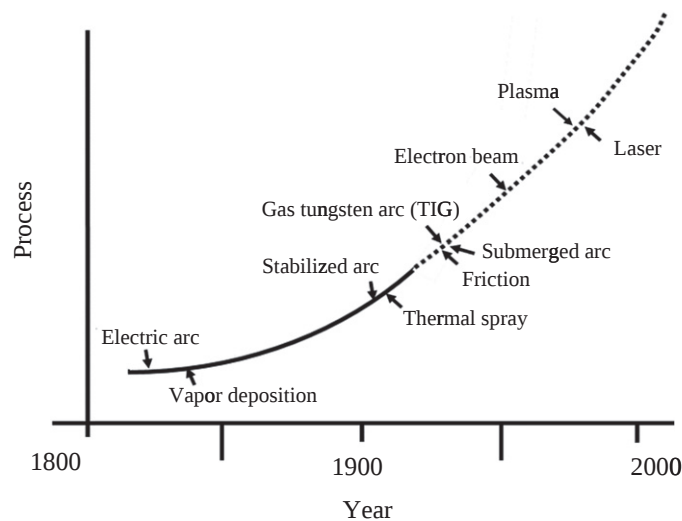


Fig. 1 Development of surface melting process over the years.

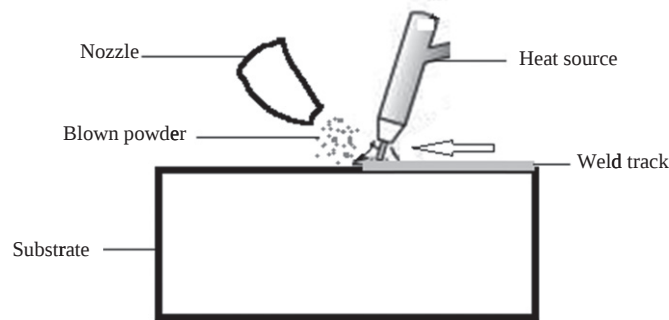


Fig. 2 Powder blown reinforcing method.

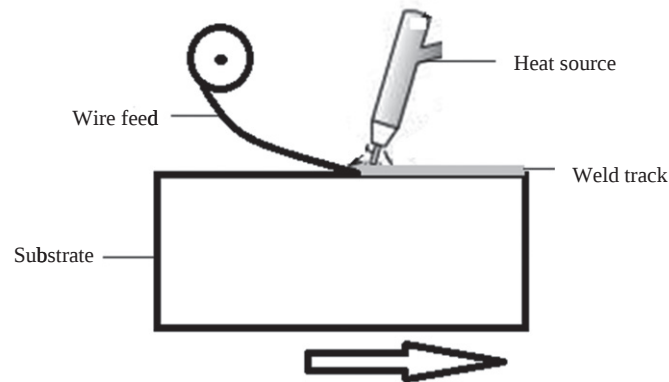


Fig. 3 Wire feed reinforcing method.

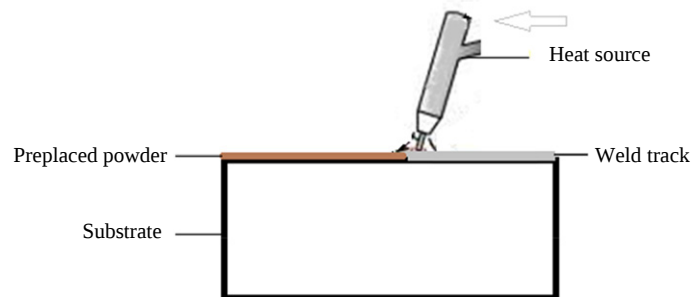


Fig. 4 Powder preplacement reinforcing method.

binder solution is controlled since high amount of binder result in porosity during solidification of the coating layer. High heat input then is applied after the powder preplacement process to melt the reinforcement and substrate surface together. The melted reinforcement and substrate surface forms intermetallic compound upon solidification with new microstructure and altered physical and other properties.

Based on previous discussion, each of the surfacing methods such as powder blown or injection method, wire feed and powder preplacement method have their own mechanism to feed the reinforcement particles onto the substrate surface for surface melting process. The end quality of the coating surface layer is affected by processing parameters which is unique for each of the surfacing method. Overall, powder preplacement process is favorable since it is the cheapest, simple, and flexible and easily controls to produce decent quality of surface melt layer.

TIG torch surface melting technology which utilized powder preplacement process mentioned previously are recently used by various researchers (Adeleke *et al.*, 2015; Maleque and Afq, 2018; Muñoz *et al.*, 2017). The technique uses heat that is generated from an electric arc produced between the tungsten electrode and the metal substrate. Upon melting and solidification of the substrate and ceramic reinforcement, a new intermetallic compound is formed with modified metallographic structure and properties. Argon is commonly used in TIG torch surface melting technology to control the weld environment and thus preventing contamination and oxidation. The advantages of the technique include high surface quality, inexpensive establishment with easy control of the system, low installation and maintenance cost, can be used on a wide range of materials and usually small flames or

sparks is used during melting process which leads to less amount of distortion in the substrate material. However, TIG torch surface melting technology is a slow process, with low deposition rate and it is not suitable for thicker material due to its small amount of heat source (Bello *et al.*, 2015; Lailatul and Maleque, 2017; Maleque and Adeleke, 2013; Musa *et al.*, 2018).

Materials for TIG Torch Surface Melting Technology

TIG torch is most frequently used to weld thin sections of stainless steels and nonferrous metals for instances aluminium, magnesium, nickel and copper (Panigrahi and Sarangi, 2017). Recently, several research works have been conducted on TIG torch surface melting that produces positive results in terms of surface morphology, wear and hardness behavior. (Adeleke and Maleque, 2015; An *et al.*, 2017; Ardeshiri *et al.*, 2017; Ghaffari *et al.*, 2016; Lailatul and Maleque, 2017; Mridha and Baker, 2015a; Muñoz *et al.*, 2017; Stadler *et al.*, 2017).

Alloy steels are the most common reported materials used in TIG torch surface melting technology. Muñoz *et al.* (2017) successfully developed metal matrix composite layer on a microalloyed steel surface by dissociating MAX211 Ti₂AlC particles using a TIG torch technique. Other work using TIG torch surfacing was done by Mridha and Baker (2015a) on low alloy steel surface using titanium carbide (TiC) as reinforcement powder. Stadler *et al.* (2017) study the influence of welding parameters on the weld pool dimensions and shape in a TIG configuration using AISI 304L stainless steel. Bello *et al.* (2016) successfully developed TIG-alloyed hybrid composite coating on AISI 4340 low alloy steel substrate. Lailatul and Maleque (2017) have modified the surface of duplex stainless steel with SiC preplacement using TIG torch cladding.

Mridha and Baker (2015b) also utilized the TIG torch surfacing to examine the corrosion resistance of titanium aluminide coating on pure titanium substrate. The hardness of the surface alloyed layer was found at 400–600 HV_{0.5kgf} which is higher than the substrate hardness (180 HV_{0.5kgf}). The surface alloyed layers also exhibited six times higher oxidation resistance compared to the titanium substrate. Adeleke and Maleque (2015) study the deposition of powder blends of Fe, Si and C on pure titanium Grade 2 by TIG torch surfacing technique to enhance its wear resistance properties. An *et al.* (2017) have performed the TIG torch surfacing on titanium alloy Grade 5 using TiB reinforcement to study the microstructure developed and mechanical performance of the new modified surface. The maximum hardness obtained for the new developed TiB₂/Ti-6Al-4V composite was 800 HV_{0.2kgf} which is 128% higher than the Ti-Al-4V alloy substrate. The coefficient of friction for the new surface of TiB₂/Ti-6Al-4V composite is 0.36 which is also considerably lower than the substrate (0.48). It can be concluded that the TIG torch surface melting is a potential low cost method to improve the surface properties of Ti-6Al-4V alloy.

Surface alloying of A2618 aluminium alloy by Ardeshiri *et al.* (2017) was carried out by pre-placing powder blend of silicon and iron and subsequent TIG process. Surface alloying of AZ31 magnesium alloy was also performed using TIG torch surfacing by Ghaffari *et al.* (2016). The coating reinforcement materials used are the same as previous authors i.e., a mixture of silicon and iron.

Overall, TIG torch surfacing technique can be utilized on almost all metals except zinc and its alloys. This is due to very little difference between the melting and boiling point of zinc and thus could vaporized during TIG welding process. The fumes released are also toxic and hazardous to health (Weman, 2003). However, the surfacing technique is suitable to be used on a wide range of metallic materials including various grades of alloy steels, nonferrous materials such as titanium, aluminium and magnesium and their respective alloys or composite.

Parameters for TIG Torch Surface Melting Technology

Processing parameters are known to have very crucial effect on the quality of the new surface coated layer. Optimization of the melt structure quality often required time and effort. In TIG torch surface melting technology, welding current and voltage, shielding gas flow rate, arc gap and electrode welding speed are known as the main parameters leads to a better surface coated layer. The composition and amount of ceramic particles added also can be varied to control the surface properties required. Some works was done by previous researches on the optimization of the melting process for the surface modification. For example, Bello *et al.* (2015) conducted experimental work on the hardness performance of low alloy steel reinforced with TiC using TIG torch surface melting technology. The effects of welding current and voltage, electrode travelling speed and argon flow rate were analyzed using Taguchi's experimental design. It was found that the welding voltage and electrode travelling speed were more significant parameters than the others as can be seen from Table 1 which shows the Signal to noise (S/N) ratio response analyzed from Minitab software. The significant of the processing parameters depend on the difference between the maximum and minimum delta value. Higher delta value signify higher influence on the respective processing parameters. Hence, from Table 1, it is found that the welding voltage and speed are more crucial in defining the hardness behavior of the low alloy steel.

In similar field, the optimization of TIG torch surface melting was performed on AISI 4340 alloy steel incorporated with TiC particles through Taguchi's design of experiment and analyzed by MINITAB 17 statistical software (Maleque *et al.*, 2017). Similar results obtained where the welding voltage and welding speed are found to be more significant in determining the wear performance of the alloy steel substrate. Another report by Kou (2003) analyzed the effect of welding speed and current on the TIG torch surfacing of HY-80 steel. It was found that the microstructure of the surface melted layer consist of dendritic structure as the applied current is increased with welding speed kept constant. It is also reported that the cooling rate was faster when the welding speed was increased with applied current kept constant. This leads to a finer dendritic structure. Mridha *et al.* (2012a,b) also

Table 1 S/N response table for surface hardness

Levels	Welding current	Welding speed	Welding voltage	Argon flow rate
1	57.13	56.94	57.43	57.20
2	56.88	56.50	56.39	56.69
3	56.77	56.64	56.76	56.80
4	56.69	57.40	56.89	56.81
Delta	0.44	0.9	1.04	0.51
Rank	4	2	1	3

Note: Bello, K., Maleque, M., Ahmad, Z., Mridha, S., 2015. Optimization of hardness behavior of TIG modified ceramic coating using the Taguchi approach. Adv. Mater. Res. 1115, pp. 238–242.

conducted TIG surface melting technology on steel alloys and reported the effect of welding voltage applied. It was observed that when the welding voltage is varied between 30 V and 55 V, the developed microstructure and the hardness of the surface melted layer changed significantly.

Other than that, the effect of shielding gases as processing parameter in TIG surface melting technology have been reported which included the types, gas flow rates and the gas composition (Hojjatzadeh *et al.*, 2012; Vaziri *et al.*, 2012). The type of shielding gas used is found to significantly affect the current density. The common shielding gas used is argon, helium or mixture of them. It is observed that the use of argon leads to stable electric arc and less possibility of ionization. Other several researchers also agreed with the effectiveness of using argon gas as protective gas in TIG torch surface melting (Idriss and Mridha, 2012; Maleque and Sugrib, 2013; Mridha *et al.*, 2012a,b; Wang *et al.*, 2017). Utsumi *et al.* (2001) on the other hand studied the effect of protective gas flow rates on the melted layer dimensions and geometry. It was found that the dimension of the melt pool was larger when higher gas flow rate was used.

Overall, it can be said that TIG torch surface performance characteristics depend on a range of crucial processing parameters from welding voltage and current, electrode travelling speed, current supply technique (pulsed or continuous), preplaced powder content and composition, working distance, shielding gas types, composition and flow rates. Each of the individual without doubt has significant effect on the surface performance of the new modified surface layer. However, welding current, voltage and speed which are basically what made up the heat input, play more crucial role in the optimization of TIG torch surface melting compared to the other processing parameters.

TIG Surface Melting Technology: A Success Story

Carbides, borides and nitrides are the most common reinforcement powders utilized in surface engineering technology. Numerous works were reported on using such reinforcement materials for instances tungsten carbide (WC) (Abioye *et al.*, 2016; Mottaghi and Ahmadian, 2017; Niu *et al.*, 2010; Wang *et al.*, 2018a,b; Zhang *et al.*, 2017), silicon carbide (SiC) (Amirkhanlou and Niroumand, 2012; Cheniti *et al.*, 2017; Khodaei *et al.*, 2018; Moradkhani and Baharvandi, 2018; Ozben *et al.*, 2008), boron carbide (B₄C) (Khan *et al.*, 2018; Li *et al.*, 2018; Moradkhani and Baharvandi, 2017) and a titanium carbide (TiC) (Fattahi *et al.*, 2015; Jin and Plucknett, 2018; Saroj *et al.*, 2017a; Wang *et al.*, 2018a,b). Metal carbides such as TiC, CrC and SiC normally have higher wear resistance, higher degree of hardness, higher melting point and lower coefficient of friction. Another report also mentioned that the transition metal carbides/iron matrix composites are known for their resistance to abrasion, oxidation, and corrosion and they are broadly used in harsh environments in various industries such as mining and mineral processing, cement production, and pulp and paper manufacture (Ye *et al.*, 2015). Based on a numerous research works conducted by authors mentioned earlier, the use of these preplacement of metal carbides on the surfacing of metallic materials enhance their surface performance characteristics. In the following sections, a success stories is presented whereby TIG torch surface melting technology was employed.

Adeleke and Maleque (2015) have been successfully used TIG torch surface melting technology on commercially pure titanium (Cp-Ti). The reinforcement particles used were iron-silicon-carbon powders varied at three different compositions: 97Fe2C1Si (named as PPM1), 94Fe4C2Si (named as PPM2) and 91Fe6C3Si (named as PPM3). The substrate surface was ground first using emery paper to eliminate oxide layer and other contaminant. This ensures proper bonding between the reinforcement powder and substrate during melting process. Then, the reinforcement powder was preplaced on the substrate surface with the same preplacement rate for the three compositions prior to the TIG torch melting process. The current used is 100 A with heat input of 1350 J/mm. The microstructure, hardness and the wear behavior of the TIG torch melted surface modified Cp-Ti were examined.

From the results obtained, it was observed that when PPM2 powder was used, the weld pool was wider and deeper. This is due to thicker carbide formation which lead to more heat released and hence, larger weld pool. Defects were observed on the melt pool when PPM3 powder was used. This is related to the increased in the amount of powder used. The larger quantity of silicon leads to the formation of ferrite microstructure whereas the larger quantity of carbon leads to dendrite structure formation which is observed in PPM2 preplacement track as shown in Fig. 5. From EDX analysis as shown in Fig. 6(a), the dendrites structures exhibited TiC phase. This is due to larger affinity between Ti and C than the Fe and Si element. From Fig. 7(a) it was found that composition of PPM2 on the surface modification of Cp-Ti show highest degree of hardness ~800 HV_{0.5kgf}. This is multiple times

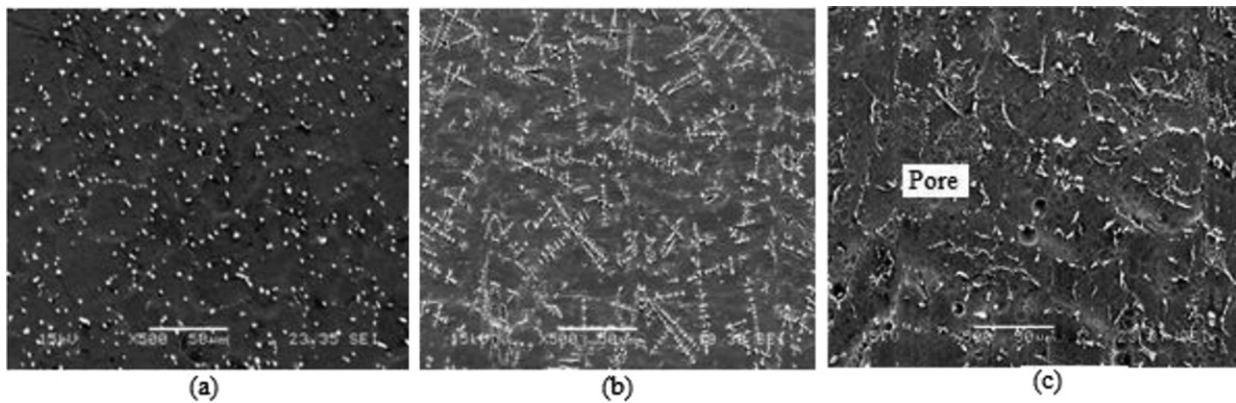


Fig. 5 SEM images of the modified CP-Ti using different composition of reinforcement powder: (a) 97Fe2C1Si (PPM1), (b) 94Fe4C2Si (PPM2) and (c) 91Fe6C3Si (PPM3). Reproduced from Adeleke, S., Maleque, M., Mridha, S., 2015. Thin surface layers of iron-based alloys deposited by TIG hardfacing. *Tribol. Online*. 10, 434–440.

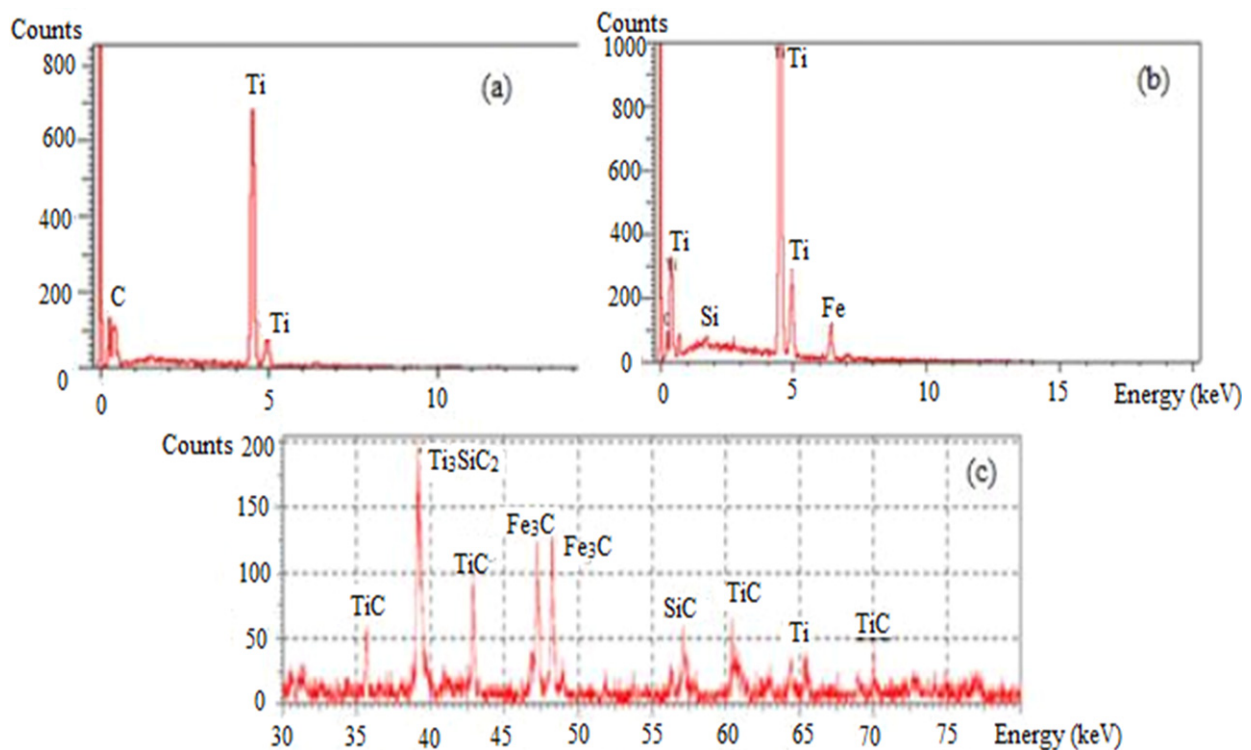


Fig. 6 (a) EDX analysis within the dendrite phase of new developed surface on PPM2 melt track as shown in Fig. 5(b), (b) Elemental analysis after dissolution of Fe, C, Si in Cp-Ti melt matrix and (c) X-ray diffraction pattern of PPM2 melt track at energy input 1350 J/mm. Reproduced from Adeleke, S., Maleque, M., Mridha, S., 2015. Thin surface layers of iron-based alloys deposited by TIG hardfacing. *Tribol. Online*. 10, 434–440.

(4 times) higher than the titanium substrate hardness which is only 200 HV_{0.5kgf}. For the PPM3 weld track, the hardness was recorded at 470 HV_{0.5kgf} which is related to the presence of defects and the unmelted reinforced powders in the weld pool. PPM2 welded track also represents lower wear rate resulting highest wear resistance. This is associated with the larger weld pool area and presence of hard carbides particles. For the PPM3 weld track, the wear resistance is the lowest, as a result from its low degree of hardness. The PPM1, PPM2 and PPM3 powders showed smaller friction of coefficient compared to the titanium substrate as shown in Fig. 7(c). Their coefficients of friction are 0.32, 0.26 and 0.39 respectively. This means that the addition of larger content of the powder composition leads to lower coefficient of friction. Overall, the TIG torch surface melting process was able to improve the hardness of pure titanium substrate up to 3–4 times. The wear, hardness and friction behavior were significantly improved especially when the reinforcement powder of PPM2 was used.

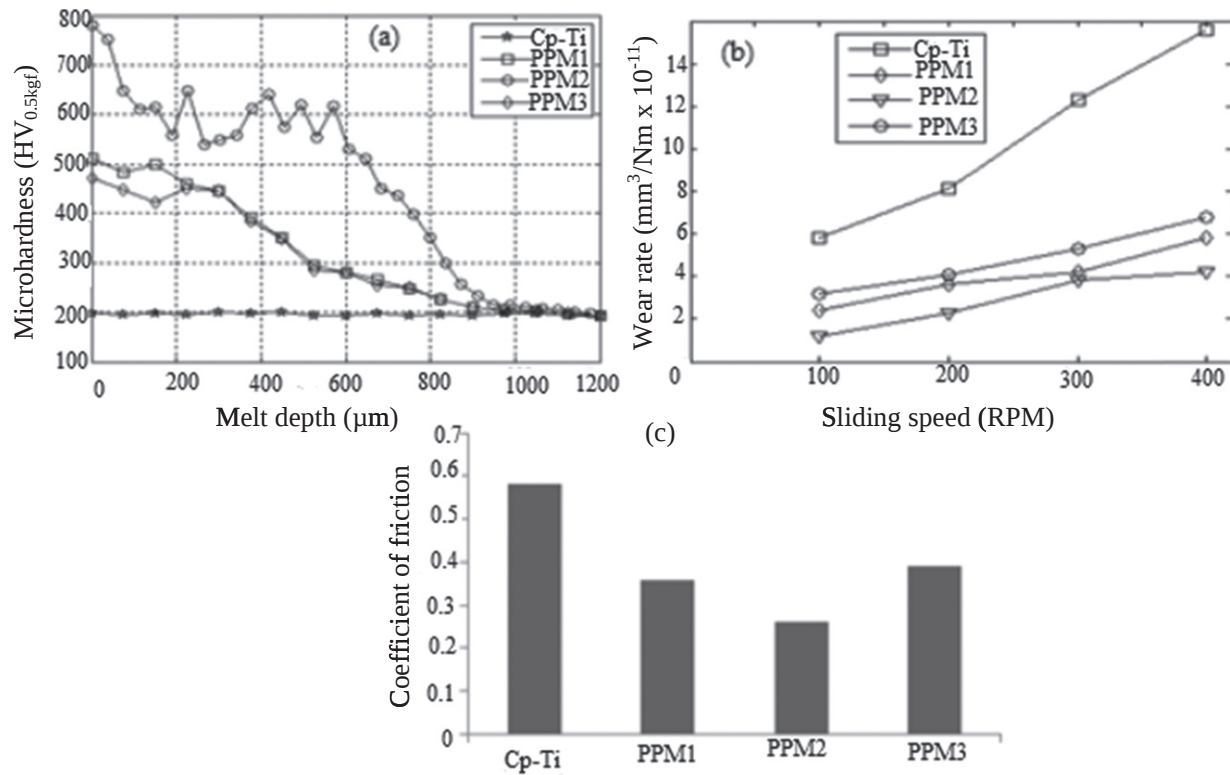


Fig. 7 (a) Microhardness of surface reinforced layer compared to the substrate, (b) Effect of different preplacement powder composition on the wear rate of TIG melted surface modified layer (c) Friction performance of TIG surface reinforced layer with different sliding speed for 30 min, at 200 RPM. Reproduced from Adeleke, S., Maleque, M., Mridha, S., 2015. Thin surface layers of iron-based alloys deposited by TIG hardfacing. *Tribol. Online*. 10, 434–440.

Conclusions

In a conclusion, TIG torch surface melting technology which used powder preplacement method shown to be beneficial in surface modification of engineering parts since it has inexpensive establishment with easy control of the system. It is found that TIG torch surface melting technique can be applied on various metallic materials and give positive results on the surface performance of the surface modified layer. Based on this study, it can be said that the parameters for TIG torch surface melting technology such as welding current, speed and voltage which made up the heat input are the most significant parameters compare to the other processing parameters. Finally, this surface melting technology can produce engineering parts with better wear, erosion and corrosion resistance behavior which can be used for high temperature applications.

Acknowledgement

Special thanks to the Ministry of Higher Education (MOHE) who has funded this research project under Fundamental Research Grant Scheme of FRGS15–203–0444.

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Tribological Interactions of Advanced Polymeric Coatings

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Glossary

Coefficient of friction (COF) The ratio between the generated friction force to the applied normal force.

Tribology The study that deals with the design, friction, wear, and lubrication of interacting surfaces in relative motion as in bearings or gears (Merriam-Webster dictionary).

Introduction

In recent years, the applications of polymers for tribological purposes have been increasing. Understanding the tribological performance of polymers is critical for successful applications. The tribology of polymers is complicated. For example, friction is affected by load, sliding velocity and temperature, and wear can arise from abrasion, adhesion and fatigue (Myshkin *et al.*, 2005). Other environmental conditions such as lubricant, ambient composition, surface roughness, and abrasive particles can also affect the tribological performance (Nunez and Polycarpou, 2011; Lu *et al.*, 2017). Thus, it is hard to predict polymer tribological performance based on simple models, and it is wise to carry out laboratory experimental work which could simulate actual working conditions before deployment in the field. This is the main reason as to why tribology is largely dependent on experimental research, and universal models are non-existent. There are two important aspects that need to take into consideration: (1) Polymers used for tribological applications are typically polymer blends where the additives used tend to strengthen polymers, which are usually referred to as high bearing polymers, or simply polymer blends, and (2) Bulk polymers and polymer blends which could vary from a mm size in thickness to larger sizes suffer from creep and long-term performance. However, polymer blend coatings (of the order of few nanometers to 10s of microns) alleviate bulk polymer issues and take advantage of the strong metal backing/substrate.

Tribology of Polymers

Tribology is the science that deals with friction, wear and lubrication of interacting surfaces in relative motion. The friction force between two solids is usually attributed to adhesion and deformation effects; where the adhesion force involves the shearing between the real contact surfaces and deformation is due to the hard material asperities plowing in the softer material. Due to their low surface energy, low shear strength and low elastic modulus, polymers usually have low COF values. Polymers exhibit viscoelasticity, which is time and temperature dependent mechanical parameters. Specifically, the temperature is the flash temperature at the contact area and this flash temperature is related to normal load, sliding speed and the body temperature of the two contacting parts. Thus, the friction of polymers is largely affected by load, sliding velocity, and temperature (Myshkin *et al.*, 2005).

Wear of polymers and polymer blends are attributed to abrasion, adhesion and fatigue. Abrasive wear on the polymer surface occurs due to the asperities of the counter surface, the contaminant abrasive particles and also from the generated polymeric debris that get squashed between the surfaces and roll or slide on the counter surface; the hardness of the polymer debris could increase in the sliding process as a result of repeated plastic deformation, and then the polymeric debris could act as an abrasive particle itself (Zhang *et al.*, 2006). Adhesive wear is caused by the shearing at the real contact area where the joints break with removal of material due to adhesive forces. Cyclic loads (normal and friction forces) placed on the polymer can cause fatigue of the coating followed by nucleation and propagation of microcracks (Barletta, 2011), resulting in fatigue wear. However, some polymeric coatings show a unique property of generating a thin film/layer on the counter surface that could help better control of wear and friction.

Transfer layers are usually formed on the metal surface when polymers slide against metal, as shown in Fig. 1 (Demas *et al.*, 2008). The film was transferred during unidirectional pin-on-disk experiments using an ATSP/PTFE blend on to gray cast iron counter surface. For this experiment the sliding velocity was 2.4 m s^{-1} and the normal load was 222.4 N. These films could be uniform or patchy depending on, among other factors, the surface roughness of the sliding surfaces (Nunez and Polycarpou, 2015). Transfer films develop because of adhesion and interlocking of the fragments of material into metal asperities. Transfer film affects the wear performance. In this case, transfer film is responsible for the gradual transition from transient progressive wear behavior to steady state wear behavior. Wear occurs initially by the loss of material before a transfer layer is established on to the counter surface and also by the loss of transfer film because of its peeling from the counter surface (Bahadur, 2000). From a qualitative standpoint, sliding conditions such as velocity, load, atmosphere, roughness, and temperature are expected to affect the transfer film formation and destruction. Polycarpou and coworkers found that the surface topography of sliding surfaces and lubrication conditions affect the formation of the transfer layer (Yeo and Polycarpou, 2014).

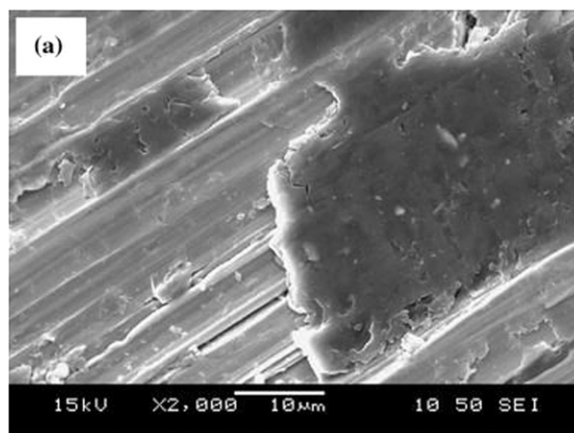


Fig. 1 Scanning Electron Microscopy (SEM) image of transfer layer of ATSP/PTFE blend on the wear track on gray cast iron. Reprinted from Demas, N.G., *et al.*, 2008. Tribological characterization of aromatic thermosetting copolyester-PTFE blends in air conditioning compressor environment. *Tribology Letters* 29 (3), 253–258 with permission from Springer Nature.

Bulk Polymers and Polymer Coatings

In general, polymers can be used in bulk or coating forms in industrial applications. Polymers in bulk form have been widely used, such as the top layer (insert) for thrust tilting pad bearings, washers, and bushings. Usually polymers in pure form (referred to as unfilled polymers) may have high COF values, high wear rate and poor mechanical properties, so they do not satisfy engineering, and in particular bearing application requirements. Thus, researchers have produced composites or blended polymers by adding different fillers and reinforcements in the polymers, improving significantly their mechanical, thermal and tribological properties. For example, in the compressor industry different unfilled and filled polymers in bulk format were investigated as potential compressor bearing materials (Cannaday and Polycarpou, 2005).

However, polymers in bulk form have shortcomings such as low load capability and low dimensional precision, because of low stiffness and high thermal expansion; causing high surface temperature when sliding because thick polymers act as heat insulators; and cold creep. To maintain the bulk polymers' advantages and minimize their drawbacks, thin polymer coatings offer a potential solution. Moreover, thin polymer coatings would have lower cost because of their easy/inexpensive deposition methods and less material needed.

Advanced Polymeric Coatings

In general, coatings can be classified as either “hard” or “soft” coatings and polymer-based coatings belong to the “soft” coating category. The thickness of the polymeric coatings discussed herein is of tens of microns; due to such low thickness, their wear performance is very crucial.

Polymer coatings are widely used as tribological protective coatings, such as erosion/corrosion resistant coatings for automotive applications (Trezona *et al.*, 2000), transparent protective coatings for touch panel screens and optical applications (Masuko *et al.*, 2013), hydrophobic coatings for moisture repellent and dirt resistance (Khanjani *et al.*, 2017), bio-implant materials like artificial joints (Liu *et al.*, 2012), bearing materials for compressor bearings (Akram *et al.*, 2016) or thrust pad bearings (Heshmat *et al.*, 2005). This publication introduces some extreme experimental conditions for advanced bearing grade coatings.

Tribological Applications of Advanced Coatings

Air Conditioning and Refrigeration Compressors

Many types of compressors suffer catastrophic failures due to scuffing of their sliding metallic parts during starved lubrication or dry sliding, where insufficient amount of lubricant is available at the contact. Premature failures of various metallic tribopairs have been shown experimentally (Yoon *et al.*, 2000; Solzak and Polycarpou, 2010). In addition, the inevitable transition to new refrigerants due to environmental concerns, affected the tribological requirements of the sliding surfaces in compressors that are used in air-conditioning and refrigeration applications. Due to polymeric coating's proven performance in similar applications, several studies focused on the tribological performance of PEEK and PTFE blends under compressor-specific operating conditions (Yeo and Polycarpou, 2012). Results indicated COF values generally lower than 0.2 for PEEK and less than 0.15 for PTFE blends. Prevalent wear rates were in the range of 10^{-6} – 10^{-5} mm³ N⁻¹ m⁻¹. The wear mechanisms in polymeric coatings differ significantly compared to their bulk form, which are dominated by mild plowing and delamination. Generation of fine debris due to abrasion

and their role in material transfer to the harder counter surface has been highlighted in several relevant researches. Fig. 2 shows the debris generated due to the abrasion of a polyimide composite sliding against gray cast iron disk. The pin-on-disk configuration was used under unlubricated conditions, and the sliding velocity was 2.4 m s^{-1} and a contact pressure of 7 MPa was applied (Nunez and Polycarpou, 2015).

ATSP both in unfilled (pure) form and in its filled (blended with additives) exhibits superior performance in compressor applications (Zhang *et al.*, 2008). ATSP blended with PTFE (25/75) showed similar COF values compared to other state-of-the-art polymers such as PEEK and outperformed their wear resistance notably when tested in compressor operating conditions (Demas *et al.*, 2008). Fig. 3 depicts the wear and friction performance of some PTFE-based and PEEK-based coatings. PTFE-based coatings exhibited a better tribological performance compared to PEEK-based coatings under both reciprocating and unidirectional operating conditions corresponding to piston type and swash-plate compressors, respectively. Durability tests demonstrated the viability of PTFE/pyrrolidone coatings for oil-less compressors (Yeo and Polycarpou, 2012). A complimentary study conducted on different polymeric coatings under air-conditioning compressor operational conditions proved that ATSP/PTFE coatings outperform the other coatings in both dry and starved lubrication conditions in the presence of environmentally friendly r1234yf refrigerant. It was concluded that surface morphology and chemical composition of the top layers determine the tribological performance of the coatings under starved lubrication conditions (Akram *et al.*, 2016).

The combined effect of lubricant and refrigerant may deteriorate the wear and friction performance of polymeric coatings mainly due to the miscibility of the lubricant and the refrigerant, hindering the formation of effective transfer films, and sweeping away the plastically hardened debris from the contact area (Dascalescu *et al.*, 2009; Akram *et al.*, 2016; Yeo and Polycarpou, 2012).

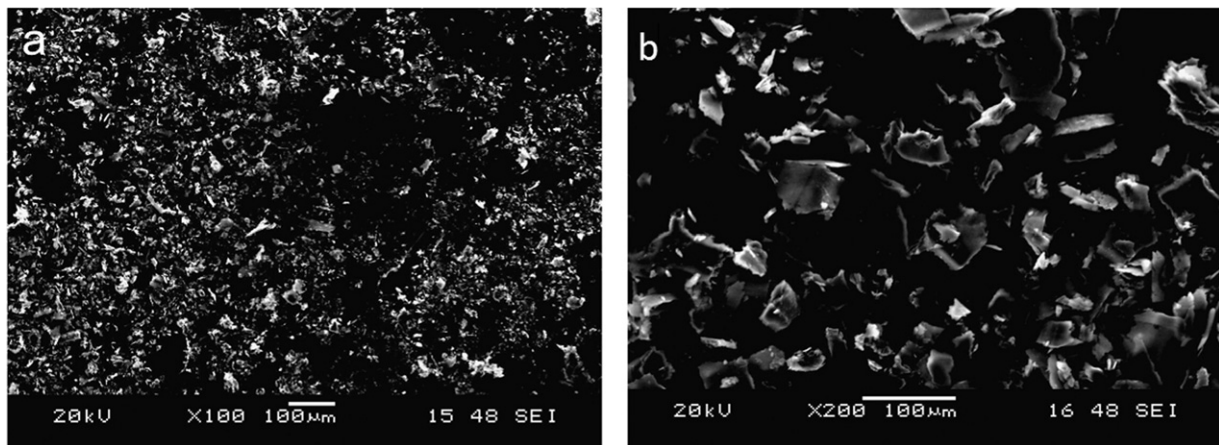


Fig. 2 SEM images of wear debris generated due to abrasion for a polyimide composite pin against gray cast iron disks with (a) rough surface finish (b) smooth surface finish. Reprinted from Nunez, E.E., Polycarpou, A.A., 2015. The effect of surface roughness on the transfer of polymer films under unlubricated testing conditions. Wear 326–327, 74–83 with permission from Elsevier.

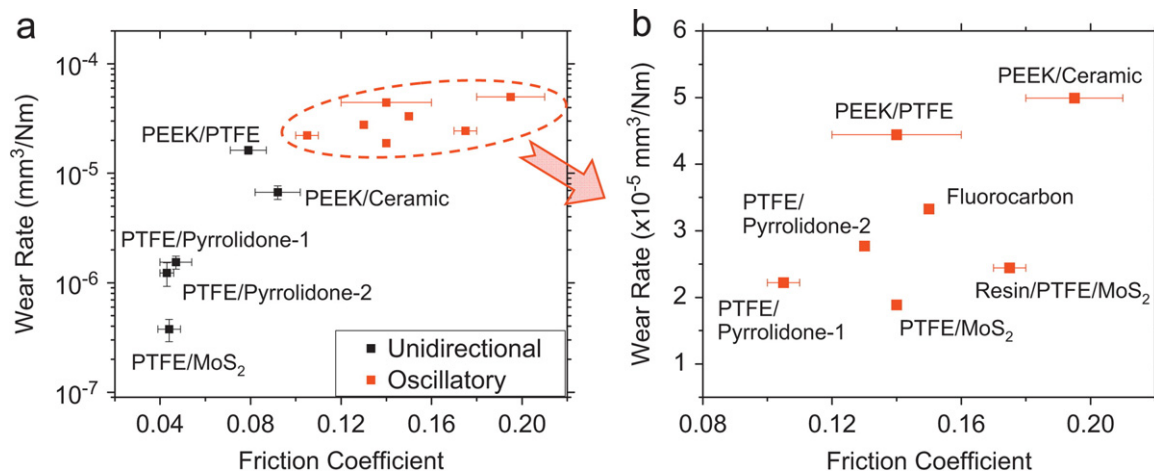


Fig. 3 (a) Friction coefficient vs. wear rate of different polymer-based coatings under both unidirectional and oscillatory testing and (b) zoom-in of only oscillatory testing results. Reprinted from Yeo, S.M., Polycarpou, A.A., 2012. Tribological performance of PTFE- and PEEK-based coatings under oil-less compressor conditions. Wear 296 (1), 638–647 with permission from Springer Nature.

Thrust Bearing Application

Close to 14% of electricity generated worldwide has been via hydro generation whose performance heavily depends on large thrust bearings (Liming *et al.*, 2017). Other applications include electrical submersible pumps (ESPs) used in oil & gas exploration. Due to the high load capacity and capability to operate at higher temperatures and lower film thickness, polymeric pads are viable alternatives for Babbitt, which is a common material for bearing pads in conventional tilting pad bearings (Glavatskih, 2003). Two of the most common polymers used as pad linings are PTFE and PEEK (Wodtke and Wasilczuk, 2016; Simmons *et al.*, 2014). Fig. 4 shows typical PTFE, PEEK, and ATSP lined pads. PTFE exhibits a low run-in friction and integrity of mechanical properties under high loads while PEEK when used as a composite maintains its mechanical properties at high operating temperatures up to 250°C. Other polymeric coatings were also tested for such applications including polyperfluoroalkoxyethylene (PFA) (Mahieux, 2005) and commercial polyimides (Nilsson and Prakash, 2013).

Others (Zhou *et al.*, 2015) tested PEEK lined tilting pad thrust bearings and reported higher load capacity and lower power loss for PEEK lined pads when compared to Babbitt pads. Tilting pads used in the oil & gas industry could also benefit from polymer linings. Lan *et al.* (2016b) showed that ATSP, PEEK and PTFE based coatings exhibit significant enhancement in resistance to scuffing as well as reduced wear when compared to conventional metallic pad materials (Lan *et al.*, 2016b, 2017). Enhancing the mechanical and thermal properties of the polymers using different additives such as carbon nanotubes, fiber glass, and graphene has also been demonstrated (Ye *et al.*, 2016).

Low inherent thermal properties of polymers lead to a drawback in their fitness for applications where high rates of frictional heat are generated. Heat generation due to friction in the pad bearings directly affects the lubrication film. Polymeric pads could act as thermal barriers and hinder the dissipation of generated heat thus affecting film thickness, generated bearing pressure, and maximum temperature. The effect of the thickness of the PTFE pads on the increase of temperature, and reduction in minimum film thickness was shown (Fillon and Glavatskih, 2008). However, such decrease could reduce the energy loss of the bearing (Wasilczuk and Rotta, 2013). Polymer-lined thrust bearings are viable substitutes for conventional White-metal or Babbitt pads and offer higher margin of safety through higher load capacity for the same size. In other words they are better counterparts to satisfy the higher power density of power generator machine requirements because of the smaller size they have compared to conventional pads for the same load capacity (Simmons *et al.*, 1998).

Another front that polymer lining of tilting pads deemed advantageous is water lubricated pads. Tribotesting of unfilled polymers in water lubricated conditions using a pin-on-disk configuration concluded that PTFE coating followed by Ultra-high-molecular-weight polyethylene (UHMWPE) showed the lowest COF respectively, and the abrasive wear mechanism was identified as the prevalent wear mechanism (Golchin *et al.*, 2013). Other studies focused on the possible problems that polymer materials such as PEEK could encounter in water lubricated conditions such as crack propagation and flaking (Xiao *et al.*, 2016).

Polymer Coating for Abrasive Wear Applications

Abrasive wear resistance of thin polymeric coating is also critical for some applications, as the thin coating might be penetrated and wear-out by the hard particles. Abrasive wear relates to cutting or plowing of the surface by harder particles or asperities (Myshkin *et al.*, 2005) and could be in the form of two-body abrasion, three-body abrasion or a combination of the two. Researchers applied different experimental protocols to evaluate abrasive wear resistance. In applications such as tilting pad bearings in ESPs in oil wells, or the drilling string in oil & gas drilling, the working conditions of the contacting surfaces are much more severe, compared to other experimental protocols (Shipway and Ngao, 2003; Harsha, 2011; Unal *et al.*, 2005). Thus, there is a need for aggressive experimental conditions to study the abrasive wear resistance of polymer coatings under such severe conditions/applications.

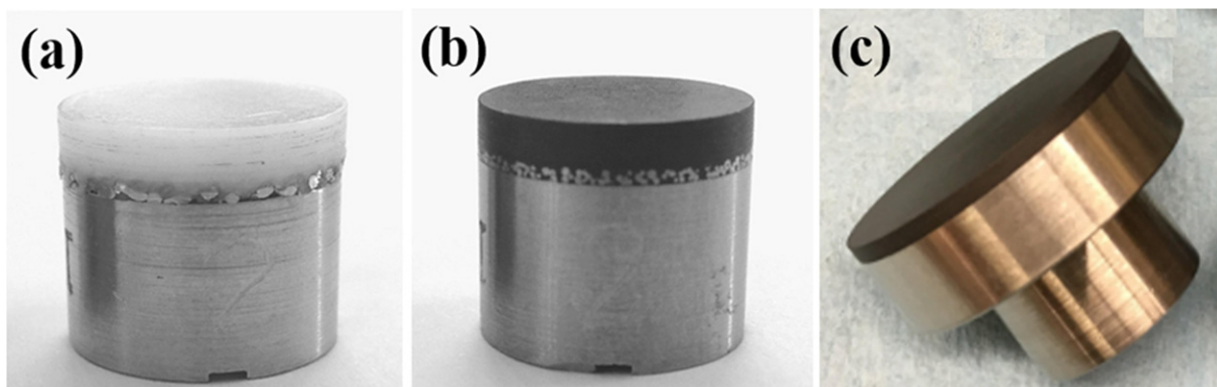


Fig. 4 Bearing pads lined with (a) PTFE blend (b) PEEK blend (diameter of 15 mm and thickness 2–3 mm). Reprinted from Wodtke, M., Wasilczuk, M., 2016. Evaluation of apparent Young's modulus of the composite polymer layers used as sliding surfaces in hydrodynamic thrust bearings. *Tribology International* 97, 244–252, with permission from Elsevier and (c) ATSP composite (diameter of 25 mm and thickness of 1 mm).

In the article of Lan *et al.* (2017), two advanced polymeric coatings (ATSP-based and PEEK-based) were selected and tested under severe sand abrasive conditions. A contaminated lubricant by sand (#140, 2 wt%) was used to simulate severe sand contaminated conditions such as those in ESPs. Under these conditions, ATSP exhibited superior wear resistance (wear rate of $6.1 \times 10^{-7} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$). The abrasive sand worked as a solid lubricant causing a beneficial effect in the PEEK-based coating case, with a decrease in wear rate from $5.8 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ under clean lubrication to $2.1 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ in the presence of sand, albeit significantly higher than ATSP.

The tribological performance of ATSP-based coatings under much more severe abrasive conditions of oil & gas Extended Reach Drilling (ERD) applications (high contact pressure, high concentration of abrasives and high temperatures) has also been studied (Lan and Polycarpou, 2018). By utilizing its long horizontal section, ERD can reach offshore reservoirs from onshore drilling stations. Excessive drag that is generated by the rotational friction of the drill string on the wellbore limits the reach of the ERD technique. This drawback could lead to the reduction of production or the complete shutdown of a well. To reduce friction, ATSP-based coatings were applied on the disks (representing the drilling pipe) and pin-on-disk experiments were carried out. The results showed that the ATSP coatings reduce the COF at different temperatures ($\sim 58\%$ reduction), compared with bare substrate O1 tool steel material (see Fig. 5).

SEM/Energy Dispersive Spectroscopy (EDS) analyses showed that the particles embedded in the coating surfaces (Fig. 6) were solids that came from the drilling fluid, including barite and silica sand. These hard particles were embedded on the coating and could sustain the load and protect the coating from severe wear (Lan and Polycarpou, 2018). Meanwhile, the coating itself worked as a solid lubricant, thus the COF was lower, compared with the bare tool steel, especially at higher temperatures of 175°C .

Extreme Temperature Applications

Thin polymeric coatings are excellent candidates for extreme dry sliding conditions, where oil lubricants and greases are ineffective, such as for space applications. However, cryogenic and elevated temperatures encountered in space applications set a limit for a lot

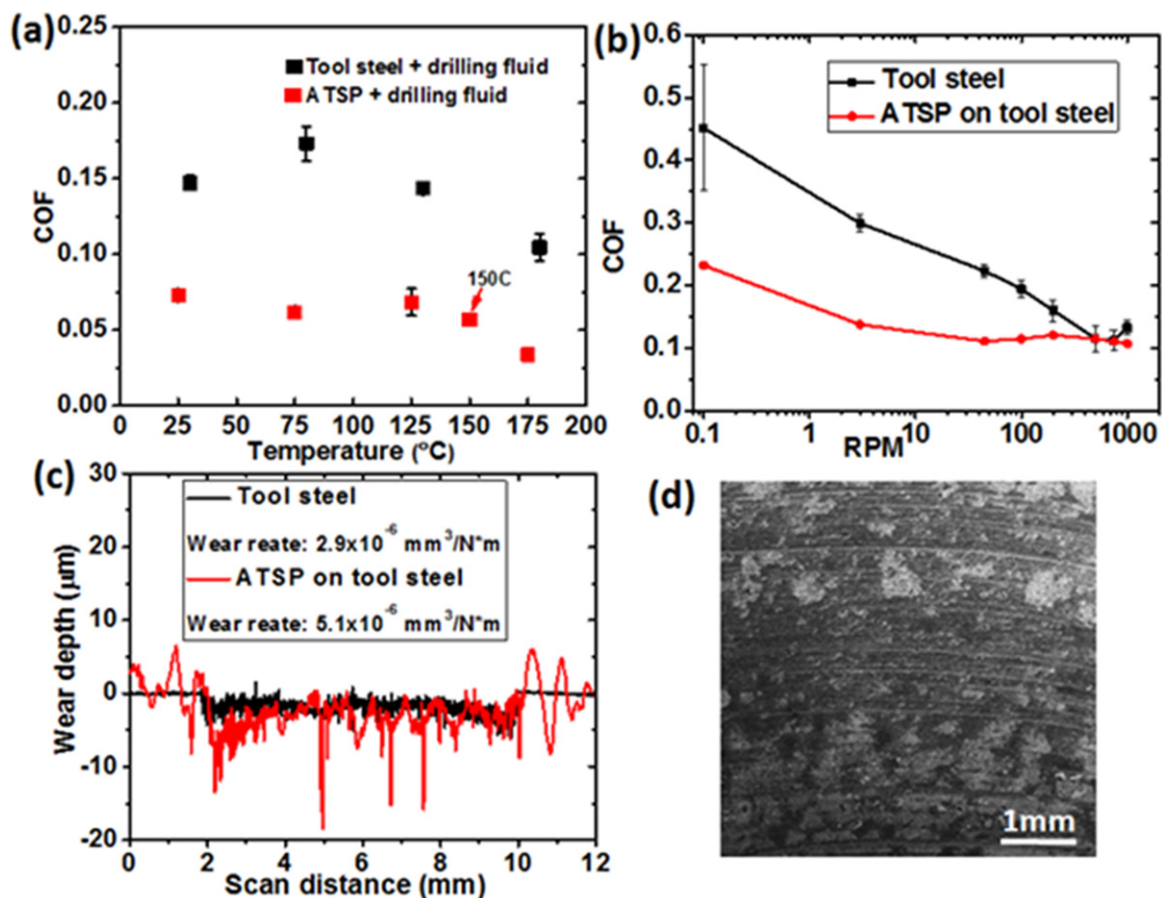


Fig. 5 Tribological results of ATSP-based coatings and bare substrate in drilling fluid. (a) COF vs. temperature, (b) COF vs. speed, (c) wear scan after 1 h experiments at 75°C , (d) SEM of ATSP-based coating after temperature effects study up to 175°C . Reprinted from Lan, P., Polycarpou, A.A., 2018. High temperature and high pressure tribological experiments of advanced polymeric coatings in the presence of drilling mud for oil & gas applications. Tribology International 120, 218–225. with permission from Elsevier.

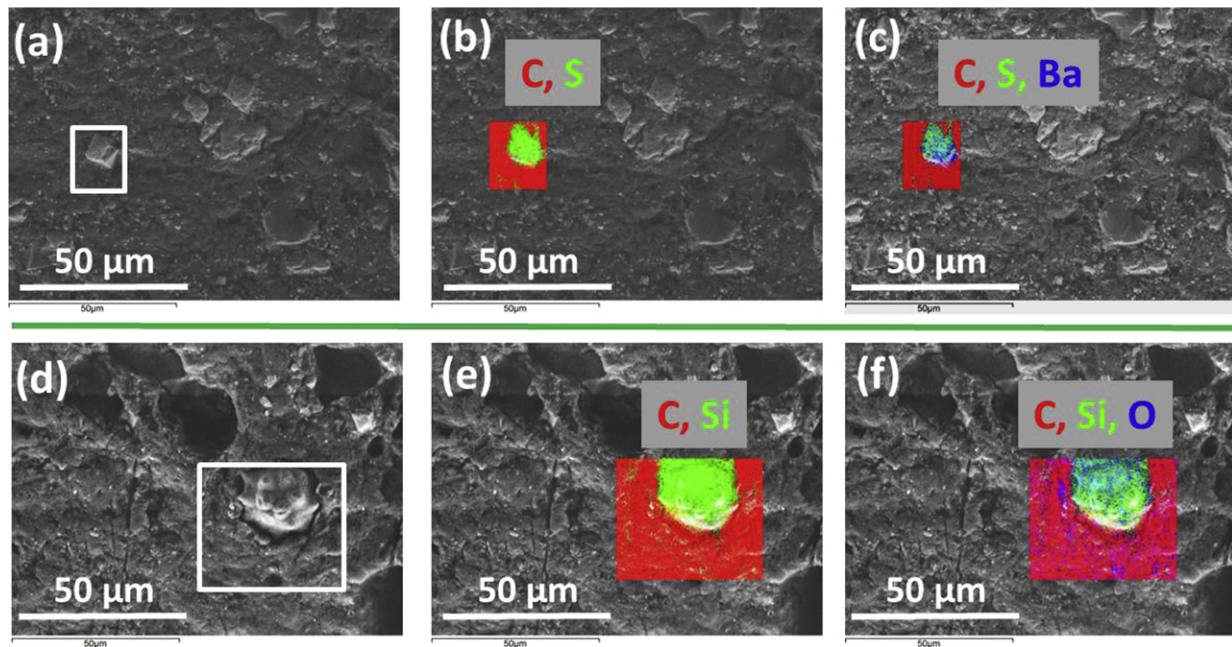


Fig. 6 SEM/EDS of ATSP after 175°C experiments: (a, b, c) particle source of BaSO₄, which is barite particle. (d, e, f) particle source of SiO₂, which is silica sand. Reprinted from Lan, P., Polycarpou, A.A., 2018. High temperature and high pressure tribological experiments of advanced polymeric coatings in the presence of drilling mud for oil & gas applications. *Tribology International* 120, 218–225, with permission from Elsevier.

of polymer materials. **Fig. 7** shows summary results of elevated temperature (23–260°C) dry condition tribological studies of ATSP-based coatings and PEEK-based coatings. ATSP-based coatings exhibited “zero wear” under these experimental conditions, except at 260°C and 10 N normal force for 430 m sliding distance; for PEEK-based coatings, due to the temperature effects on the hardness/flexibility, with increasing of the operating temperature, the abrasive wear became less important and the adhesive wear became more dominant, and at 180°C, the PEEK based coating formed a transfer layer that helped decrease both COF and wear rate (Lan *et al.*, 2016b).

The tribological performance of ATSP-based and PEEK-based coatings under cryogenic conditions, with temperatures as low as –160°C using a ball-on-disk experimental configuration, was also investigated (Lan *et al.*, 2018a). The COF of ATSP-based coatings increased with decreasing temperature, with a peak value at –100°C; similar to the elevated temperature experiments, the COF decreased when the load increased. The PEEK-based coatings showed 68% and 35% higher COF, compared to ATSP-based coatings at –40°C and –160°C, respectively. The experiments also showed that under cryogenic temperatures, both coatings exhibited near zero (immeasurable) wear.

SEM/EDS investigation revealed that the favorable transition (a decrease of COF for ATSP at –160°C with 10 N normal force) is due to the development of a polymer transfer film on the counter surface (see **Fig. 8**). While at low load of 5 N at the same temperature, transfer film did not develop after the same sliding distance, the higher load accelerated the development of the transfer film for the ATSP-based coating that consequently reduced the COF.

Micro/Nanomechanical Behavior of Polymeric Coatings

For tribological contacting/sliding surfaces, generally the top surface layers are the ones that determine the tribological performance in real-life applications. Thus, the measurement of the micro/nanomechanical properties of the top layers of bearing surfaces is critical in understanding their tribological behavior. Nano-indentation is a simple characterization technique to quantify the performance of such polymer surfaces (Yeo and Polycarpou, 2013).

Micro/Nano Indentation Results of Polymer Coatings

The Oliver-Pharr indentation method is a widely-used technique to measure the mechanical properties of materials, including thin films. In micro/nano indentation experiments, a rigid probe is pressed into the sample, and the transducer records the in-situ force and displacement responses. The elastic modulus can be obtained from the slope of the initial portion of the unloading curve and the hardness can be calculated by dividing the maximum indentation load with the contact area (Oliver and Pharr, 1992).

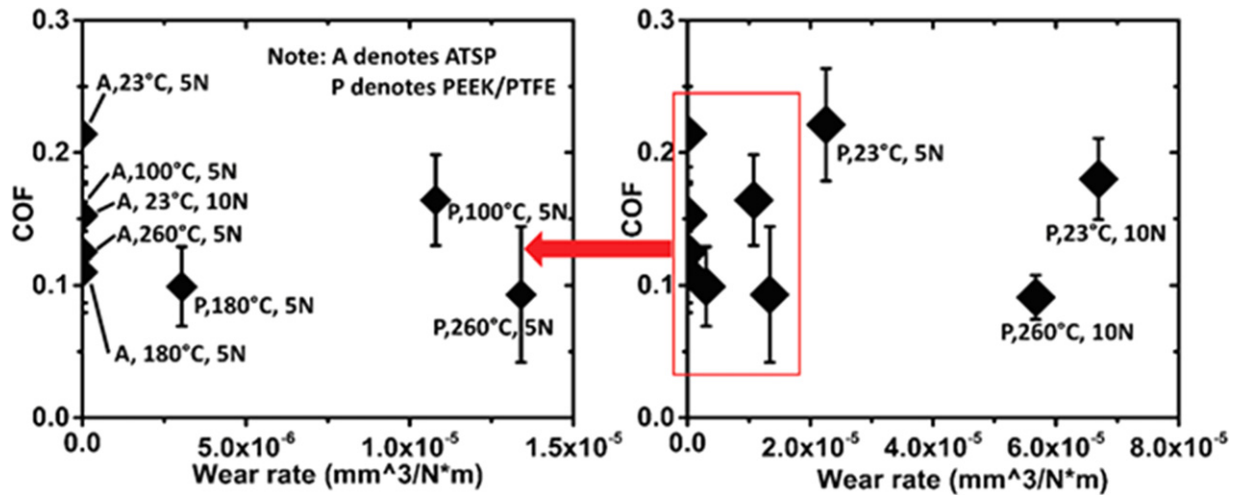


Fig. 7 Summary of ATSP/PTFE and PEEK/PTFE coating results: average COF vs wear rate, showing that ATSP/PTFE exhibits “zero wear” while PEEK/PTFE shows a higher wear rate. Data labels indicate material (ATSP or PEEK), test temperature, and normal load, sliding speed = 0.139 m s^{-1} . Reprinted from Lan, P., Meyer, J.L., Vaezian, B., Polycarpou, A.A., 2016b. Advanced polymeric coatings for tilting pad bearings with application in the oil and gas industry. Wear 354–355, 10–20 with permission from Springer Nature.

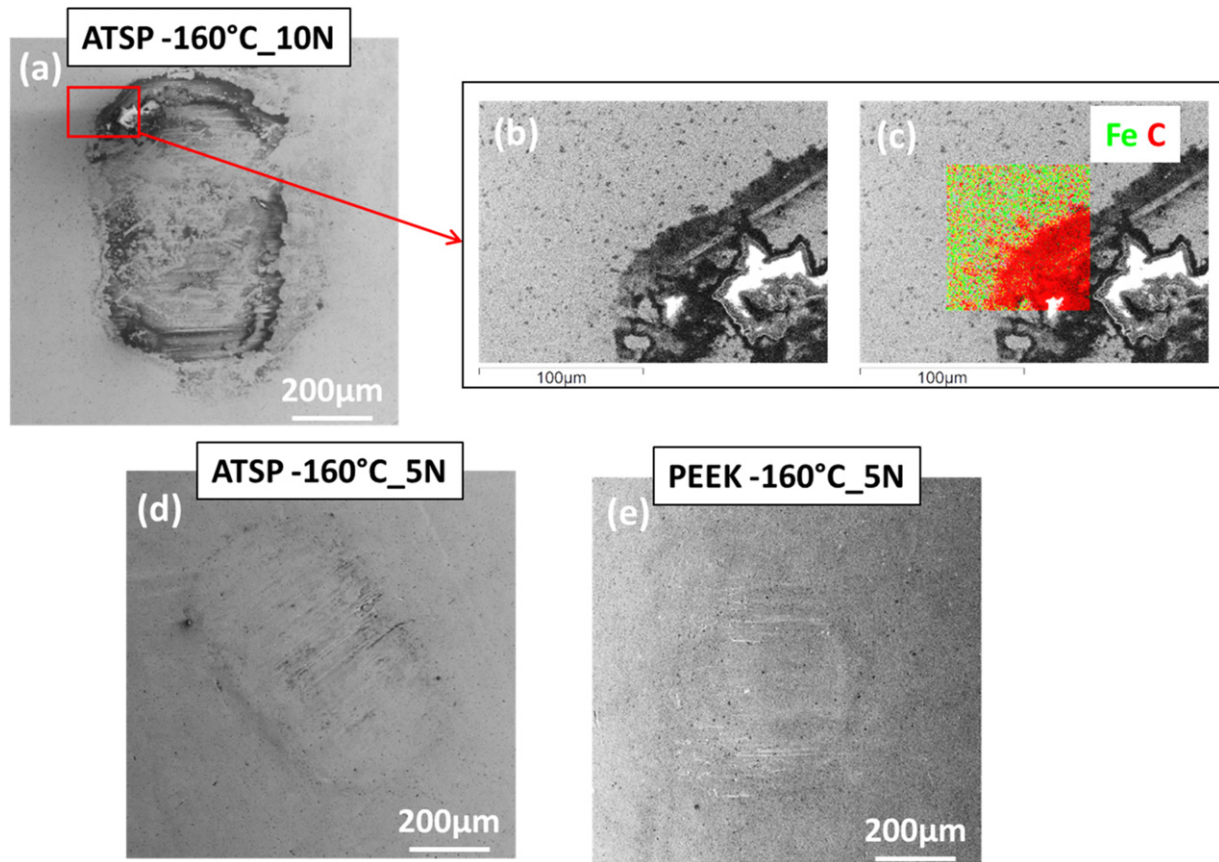


Fig. 8 Wear scar on 316 stainless steel balls after cryogenic -160°C experiments under different conditions: (a) ATSP coating (5 N, 5000 cycles), (b) SEM image of the film transfer from ATSP to the ball (c) EDS analysis of the film transfer showing dominant presence of the carbon (d) ATSP coating (10 N, 5000 cycles), (e) PEEK coating (5 N, 5000 cycles). Reprinted from Lan, P., Gheisari, R., *et al.*, 2018. Tribological performance of aromatic thermosetting polyester (ATSP) coatings under cryogenic conditions. Wear 398–399, 47–55 with permission from Elsevier.

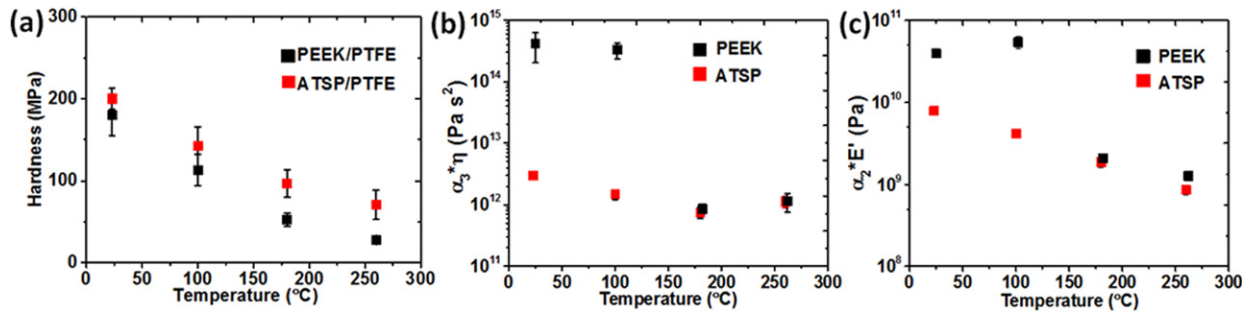


Fig. 9 Results of high temperature nanoindentation of ATSP-based and PEEK-based coatings. (a) hardness vs. temperature, (b) viscous term vs. temperature and (c) elastic modulus term vs. temperature, where α_2 and α_3 are tip geometry related terms. Reprinted from Lan, P., Zhang, Y., *et al.*, 2018b. A phenomenological elevated temperature friction model for viscoelastic polymer coatings based on nanoindentation. *Tribology International* 119, 299–307, with permission from Elsevier.

Yeo and Polycarpou (2013) carried out micromechanical property measurements of different polymeric coatings; the load–unload responses were used to measure the load-bearing properties of the coatings, as well as to extract their elastic modulus and hardness values. The measured micromechanical properties of the various polymeric coatings tested showed that PEEK-based coatings exhibited higher elastic modulus than PTFE-based coatings, while their hardness values showed the opposite trend. Their tribological performance, however, was not directly related to their micromechanical properties, but rather to the coating structural uniformity (Yeo and Polycarpou, 2013). High temperature nanoindentation experiments (Lan *et al.*, 2018a) were conducted at the same elevated temperatures as in macro-scale ball-on-disk tribological experiments (Lan *et al.*, 2016a) at different temperatures (25°C, 100°C, 180°C, and 260°C). The two coatings showed decreasing hardness, elastic modulus and viscosity trends, with increasing temperature, as shown in Fig. 9. The ATSP coatings exhibited higher hardness, compared to the PEEK coatings, which correlated with ATSP's better wear resistance in the ball-on-disk experiments. In addition, to explaining the macro tribological performance, these micro mechanical properties can also be inserted into a friction model and the model showed reasonable COF prediction for the two coatings at higher temperatures, below the glass transition temperature.

Micro-Scratch Results of Polymer Coatings

Micro scratch experiments were conducted by penetrating and moving a diamond tip probe in the top layers (a few microns depth) of a sample and in-situ measurements of the normal and friction forces were recorded. The obtained forces help understand the microtribological behavior of the top layers. Micro-scratch experiments using a diamond conospherical probe with a tip radius of 4.3 μm were performed to further investigate the tribological behavior of ATSP and PEEK coatings (Lan *et al.*, 2017). The load function was a ramp load that applies a linearly increasing normal force, while it is moving laterally for a set distance. During the scratching process, the transducer records the in-situ normal displacement. The recorded normal displacement has both elastic and plastic deformations and is called in-situ displacement. The normal displacement as a function of normal load and the retrace steps provide information for the in-situ and residual depths, respectively. The recovery rate is an important and straightforward parameter to compare materials' resistance to plastic deformation or damage. This parameter is calculated by dividing the elastic recovery with the in-situ scratch depth. It varies from 0 to 1 or 0–100% (percentile scale). The larger the elastic recovery rate, the stronger the material's resistance to plastic deformation. The ATSP and PEEK coatings exhibit elastic recovery rates of 57.3% and 32.7%, respectively. The 24.6% higher elastic recovery rate of the ATSP coating makes it more scratch resistant, compared to PEEK coating.

Conclusion

The increasing usage of advanced polymer coating materials for tribological benefits in different industries were described. The inherent mechanical properties of the polymers were briefly discussed and their effect on their tribological performance was addressed. The application of polymers in bulk format and their advantages were summarized. Some of the state-of-the-art polymer coatings were introduced and their performance in air-conditioning and refrigeration compressors, thrust pad bearings, abrasive conditions, and extreme temperatures were presented and compared. Appropriate characterization techniques to obtain the micro mechanical properties of the thin coatings were discussed. The scope of the present article is to introduce some of the tribological applications of polymeric coatings. Specifically, ATSP, PEEK, and PTFE-based high bearing polymeric coatings are readily available, inexpensive and offer significant tribological advantages over a wide range of applications and conditions.

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Waste Conversion Into Sustainable and Reinforcing Fillers for Rubber Composites

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Introduction

Waste is inevitably produced by agriculture and industry. Increasing population and decreasing available space on earth, require that waste management is sustainable and economic. Landfill is a traditional method of waste disposal, but land contamination and high cost make this method unsustainable. Waste has been combusted to replace petroleum as an energy source but greenhouse gases are vented and ash residuals still remain. Furthermore, not all wastes can be burnt. Recycling and repurposing are ideal waste management strategies, because they can increase waste value and prevent pollution. Low price and abundant supply make wastes attractive for high volume uses, such as alternative fillers for rubber and plastic composites.

Rubber is one of the most important and widely used materials. Although rubber, itself, possesses excellent impact strength and elasticity, rubber still needs to be reinforced by fillers to further improve its mechanical properties for many applications. The properties of rubber composites are highly related to the characteristics of their fillers. Carbon black (CB) and high surface area precipitated silica (PS) are the most commonly used reinforcing fillers in rubber composites (Leblanc, 2002). Both PS and CB have reinforcing effects on rubber composites. As synthetic fillers, CB and PS are expensive and cause environmental problems. Also, U.S. CB supply is facing a shortage because of increasing consumption and environmental concerns, and the shortfall may be as much as 0.2 million tons by 2025 (Moore, 2018). The price of CB has increased steadily for nearly 20 years, in parallel to the producer price index increase from 83.1 in 1990 to 329.8 in 2018 (U.S. Bureau of Labor Statistics, 2018). The high price of CB has a profound effect on rubber product cost. The price of PS faces a similar situation and one of the biggest global silica suppliers, PPG, announced that the price of silica products will increase by up to 6% in 2018 (PPG, 2017). Therefore, manufacturers using PS and CB are interested in their partial or complete replacement by alternative fillers which are low-cost and environmentally friendly (Table 1).

Neither PS nor CB are renewable, but waste-derived fillers with ready availability and low price are easily obtained from agricultural and industrial production facilities. Replacing CB and PS fillers and developing new rubber composites with waste-derived fillers would mitigate carbon emissions. On a production scale, it is likely that waste-derived fillers could be produced much less expensively than PS (\$500-800/ton) or CB (\$720-730/ton) (Bashir and Manusamy, 2015; Jinzhou Hancheng Chemicals Co, 2017; Weifang Longstar Economy And Trading Co, 2017). Furthermore, the new rubber composites may not only match current commercial rubber product properties, but evince new combinations of properties (Barrera and Cornish, 2016a, 2017b). These may open new markets and further increase the value of the wastes used to make the fillers.

Curing behavior and reinforcing effects of fillers are studied to characterize rubber composites and determine their potential usefulness. Usually, scorch and cure time, and minimum and maximum torque are measured to describe the curing behavior. Scorch time is the time during which a rubber compound can be worked at a given temperature without scorching before curing begins and indicates that the material has been partially vulcanized and that its plasticity has been reduced. The rubber material can't be reprocessed after the scorch time. Cure time is the time needed for the rubber to vulcanize sufficiently to reach its optimal properties. Torque indicates the resistance of the sample during curing to shear stress. During vulcanization, the rubber molecules are crosslinked by curing agents, usually sulfur. Crosslink density (the number of rubber diene monomers between the cross-linking points) is used to quantify the degree of vulcanization. Reinforcing effects of waste fillers are measured by their mechanical and dynamic mechanical properties. Tensile strength, elongation at break, modulus and hardness characterize the mechanical properties, whereas storage modulus, loss modulus and $\tan \delta$ in specific temperature or frequency ranges characterize the dynamic mechanical properties.

Silica-Based Fillers in Rubber Composites

Background

Silicon is one of the most abundant elements on the earth. Silicon dioxide, also called silica, is the main residue from the combustion process of thermal power generation, due to its heat stability. Coal is the fossil fuel generally used to generate electricity, and co-produces large amounts of fly ash (FA) (Ren, 2016). The main components of FA are silica (39.7%–51.1%) and metal oxide (41.4%–60.6%) (Blissett and Rowson, 2012). Annually, over 750 million tons of FA is produced in the world (Gwon *et al.*, 2017). Without proper management, FA can cause air pollution by releasing dust into the atmosphere; it is traditionally disposed of by landfill, but expensive landfill fees and massive land occupation encourage utilization of FA

Table 1 Comparison between CB, PS and waste fillers

	CB	PS	Waste fillers
Production	Incomplete combustion of petroleum oil under high temperature (5.7 kg carbon dioxide per kg CB) (Lockwood and Van Niekerk, 1995; Rodat <i>et al.</i> , 2011)	Precipitated reaction of silicates in sulfuric acid (Schlomach and Kind, 2004)	Byproducts from agricultural and industrial productions
Price	High and increased (U.S. Bureau of Labor Statistics, 2018)	High and increased (PPG, 2017)	Low
Reinforcing effect on rubber composites	Improved strength, modulus and abrasion resistance of rubber composites (Kohls and Beaucage, 2002)	Reduced rolling resistance combined with high tear strength and abrasion resistance (Hashim <i>et al.</i> , 1998)	Dependent on filler size, chemical structures and surface morphology

(Blissett and Rowson, 2012). For example, FA has been used in self-compacting concrete, which has good deformability and segregation resistance (Siddique *et al.*, 2016).

Silica based fillers also can be obtained from agricultural byproducts. Rice husk is a byproduct of rice-milling processes. About 28% of rice is husk and 200 million tons of rice husk was produced in 2017 (Lane, 2017). Generally, rice husk is used as fuel to generate power. After combustion, white rice husk ash (WRHA) and black rice husk ash (BRHA) are both produced as residuals. WRHA is produced as the inner part of the rice husk ash (RHA) because of the higher temperature, while BRHA forms the outer layer of RHA (Ishak and Bakar, 1995). WRHA possesses a higher silica fraction (96%) than BRHA (54%), which also contains 44% carbon (Ismail *et al.*, 1999a,b). These RHAs also contain less than 3% metal oxides (Ishak and Bakar, 1995).

Oil palm is the highest yielding oil crop, and its oil is the second most traded vegetable oil in the world after soybean oil (Sumathi *et al.*, 2008). Palm oil production cogenerates a large amount of solid waste, much of which is burnt to generate electricity leaving oil palm ash (OPA). In Malaysia alone, OPA production is 4 million tons/year (Foo and Hameed, 2009). Disposal costs are significant in both developing (\$5/ton) and developed countries (\$50/ton), and so converting OPA into value-added materials is important (Foo and Hameed, 2009). OPA contains similar amounts of silicon dioxide (37%–63.6%) to BRHA, as well as metal oxides (calcium oxide, aluminum oxide, iron oxide, magnesium oxide, sodium oxide and potassium oxide) (21.5%–49.3%) (Foo and Hameed, 2009).

Silica-rich FA, RHA and OPA may have utility as waste-derived fillers in rubber composites as substitutes for precipitated silica.

Curing Behavior

Silica-based fillers affect curing behavior differently depending upon the type of rubber. In general, they significantly retard the vulcanization of rubber composites, because the essential chemical accelerators in the compounds can react with the silica instead of the rubber molecules (Mukhopadhyay and De, 1979; Ismail *et al.*, 1999a,b; Sombatsompop *et al.*, 2004; Raji Vijay *et al.*, 2016). The cure time of natural rubber (NR) from the *para* rubber tree (*Hevea brasiliensis*) (HNR) is independent of FA filler loading (Sombatsompop *et al.*, 2004), while the cure time of styrene butadiene rubber (SBR) is reduced as FA loading increases (Sombatsompop *et al.*, 2004). The scorch and cure times of OPA-filled HNR become faster with increasing OPA content (Ismail and Haw, 2008; Ooi *et al.*, 2013a,b). The faster cure and scorch times occur because the high metal oxide levels (calcium oxide, aluminum oxide and magnesium oxide) in the FA and OPA silica-based fillers act as vulcanization rate accelerators. This does not occur in RHA filled HNR composites (Da Costa *et al.*, 2002) because of their low metal oxide content.

Surface modification with silane coupling agents is generally used to improve the interaction of silica fillers with rubber and so enhance their reinforcement of the composite material (Wang, 1998; Ansarifar *et al.*, 2003). Silane coupling agents have tetrasulfane and ethoxy groups: the tetrasulfane groups react with double bonds on rubber molecules to form –S–C– bonds, while the ethoxy groups react with the silanol groups to form –Si–O– bonds. Since FA has silica as a major component, silane modification can be used to improve its interaction with rubber. However, as silane content increases, the cure and scorch times of FA-filled HNR composites slow (Thongsang and Sombatsompop, 2006). This is believed to be caused by reactions between unsaturated groups, like carbon-carbon double bonds, in HNR and silane's tetrasulfane groups, instead of with the sulfur, limiting the formation of sulfur crosslinked macromolecular structures. In addition, the large size of silane molecules may sterically hinder the reaction between sulfur and HNR molecules (Poh and Ng, 1998). Maleated HNR, when used as a coupling agent, also improves the reinforcement of HNR composites by OPA. Scorch and cure times further slow with increasing coupling agent content, which can be explained by the strong interaction between OPA and rubber by coupling agent (Ismail and Haw, 2008).

The silanol groups on silica form a hydrogen bonded filler network (Wang, 1998), which increases both minimum and maximum torque of PS filled rubber composites. The other silica-based fillers have different effects on the curing behavior. The minimum torque is unaffected but maximum torque increases with increasing FA content in HNR and SBR composites (Sombatsompop *et al.*, 2004). OPA-filled HNR composites have similar torque changes to those in FA composites, which are caused by the reduction of the movement of rubber chains (Ooi *et al.*, 2013a). Both FA and BRHA reduce maximum and

Table 2 The changes of minimum torque and maximum torque of rubber composites with increasing content of silica-based fillers (all values were compared to the unfilled rubber composites)

Filler	Size (μm)	Rubber matrix	Minimum torque	Maximum torque
FA (Sombatsompop <i>et al.</i> , 2004)	50–100	HNR	No change	Increased 0%–200%
PS (Sombatsompop <i>et al.</i> , 2004)	Not mentioned	HNR	Increased 0%–730%	Increased 0%–410%
FA (Sombatsompop <i>et al.</i> , 2004)	50–100	SBR	No change	Increased 0%–100%
PS (Sombatsompop <i>et al.</i> , 2004)	Not mentioned	SBR	Increased 0%–830%	Increased 0%–420%
OPA (Ooi <i>et al.</i> , 2013a)	41	NR	Increased 0%–40%	Increased 0%–10%
WRHA (Da Costa <i>et al.</i> , 2002)	2	NR	Reduced 0%–210%	Increased 0%–30%
BRHA (Da Costa <i>et al.</i> , 2002)	3	NR	Reduced 0%–120%	Increased 0%–20%
PS (Da Costa <i>et al.</i> , 2002)	0.018	NR	Increased 0%–370%	Increased 0%–30%
OPA (Ismail and Haw, 2008)	75	Maleated HNR	Increased 0%–230%	Increased 0%–50%

minimum torque less than PS because of their weaker filler-filler interactions (Da Costa *et al.*, 2002; Sombatsompop *et al.*, 2004). Maleated HNR increases both the minimum and maximum torques of HNR composites with increasing OPA content, because of the increased filler-rubber interaction (Ismail and Haw, 2008) (Table 2).

Reinforcing Effect on Mechanical Properties

Unmodified FA poorly reinforces rubber composites, decreasing the tensile strength, elongation at break and tear strength, compared to unfilled HNR (Sombatsompop *et al.*, 2004). The large FA particle size (50–100 μm) and poor rubber-filler interaction explains the inferior tensile strength, elongation at break, hardness and modulus, compared with PS. At low filler loading of OPA (less than 1 phr) and RHA (less than 30 phr) filled HNR composites, tensile strength and elongation at break increase (Ishak and Bakar, 1995; Ooi *et al.*, 2013b). The increased mechanical properties were explained by the full wetting of the OPA and RHA by the NR matrix (Ooi *et al.*, 2013b). As filler content further increased, the mechanical properties decreased due to poor filler dispersion (Ismail and Haw, 2008; Ooi *et al.*, 2013b). WRHA filled NR composites exhibit higher tensile strength, modulus at 300% strain, elongation at break and tear strength than BRHA, though BRHA has smaller particle size (Ishak and Bakar, 1995). Both WRHA and BRHA filled NR composites have higher tear strength but lower tensile strength, modulus at 300% strain and hardness than CB (Sae-Oui *et al.*, 2002). The inferior reinforcing effect of RHA is caused by the large filler particle size and greater filler agglomeration. OPA filled NR composites have lower hardness and tensile modulus than PS and CB (Ooi *et al.*, 2013a). The high stiffness of CB filled NR composites is due to the small particle size of CB. However, OPA filled NR also exhibits higher tensile strength and elongation at break than PS (Ooi *et al.*, 2013a) (Table 3).

As silane concentration increases, tensile strength, modulus and tear strength of PS filled rubber composites also increase, because the coupling agent increases the rubber-filler interaction (Thongsang and Sombatsompop, 2006). However, the silane treated FA still has weaker rubber-filler interaction than silane treated PS. Tensile strength, modulus at 300% strain, elongation at break, tear strength and hardness reduce, as FA partially or completely replaces PS in HNR composites (Thongsang *et al.*, 2012). Silane-modified RHA-filled HNR still possesses lower tensile strength and modulus than CB and PS filled HNR, which is due to fewer silanol groups on the RHA surface (Sae-Oui *et al.*, 2002). The multifunctional additive (n-fallow-1-3-propanediamine salt) also acts as a coupling agent in RHA-HNR composites, up to 5 phr, increasing tensile strength, modulus at 300% strain and tear strength (Ismail *et al.*, 1999a,b).

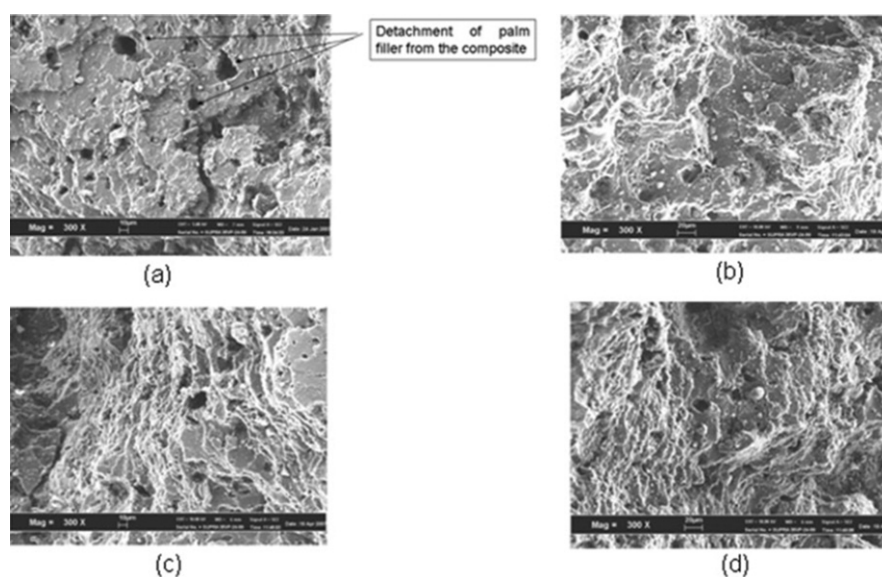
Maleated HNR can form hydrogen bonds with silanol groups on the OPA surface, and is miscible with HNR (Ismail and Haw, 2008). The hydrogen bonds enhance the wettability and attachment of OPA with HNR, increasing elongation at break, modulus, tensile strength and fatigue life (Ismail and Haw, 2008). The improved HNR-OPA interaction also is supported by scanning electron microphotographs of fracture surfaces (Fig. 1).

Nano-sized FA (148 nm), produced by high energy milling, reinforces SBR more than CB, precipitated silica or unmilled FA (60–100 μm) (Paul *et al.*, 2009), and the composites have higher modulus, tensile strength and hardness. The fracture surfaces of scanning electron micrographs and bound rubber evince the uniform dispersion and strong rubber filler interaction of nano-sized FA filled SBR. As FA size reduces from macro (89 μm) to micro (12 μm), modulus at 300% and tensile strength of HNR and GNR composites increase (Barrera and Cornish, 2015, 2016a). However, tensile strength, modulus at 300% strain and elongation at break of HNR and GNR composites decrease with the reduction of FA size from micro (12 μm) to nano (218 nm) (Barrera and Cornish, 2017b). The poor reinforcement by nano FA was explained by increased attraction between FA particles (Fig. 2).

RHA also reinforces thermoplastic elastomers (rubber/plastic composites). As RHA content increases from 0 to 25 phr, tensile strength, elongation at break, tensile modulus and hardness of SBR/linear low-density polyethylene composites increase (Khalf and Ward, 2010). The increased mechanical properties of thermoplastic elastomers are related to enhanced interfacial interaction between the polymer matrix and RHA, caused by the coupling agent, maleic anhydride. RHA also increases the Young's

Table 3 The changes of mechanical properties of rubber composites with increasing content of silica-based fillers (all values were compared to the unfilled rubber composites)

Waste filler	Size (μm)	Rubber matrix	Tensile strength	Elongation at break	Tear strength	Modulus at 300% strain
Unmodified FA (Sombatsompop <i>et al.</i> , 2004)	50–100	NR	Reduced 0%–90%	Reduced 0%–60%	Reduced 0%–60%	Fluctuated, little change
WRHA (Ishak and Bakar, 1995)	5	Epoxidized NR	Increased 0%–110%, then decreased	Increased 0%–20%, then decreased	Increased 0%–30%, then decreased	Increased 0%–100%
BRHA (Ishak and Bakar, 1995)	2	Epoxidized NR	Increased 0%–90%, then decreased	Increased 0%–20%, then decreased	Increased 0%–30%, then decreased	Increased 0%–140%
OPA (Ooi <i>et al.</i> , 2013a)	41	NR	Increased 0%–20%, then decreased	Increased 0%–10%, then decreased	Unknown	Increased 0%–20%

**Fig. 1** SEM microphotographs of the tensile-fractured surface of 30 phr OPA filled SMR L/MANR blends with different weight ratios: (a) 100/0, (b) 5/95, (c) 10/90, and (d) 20/80 (magnification=300 $\times$). From Ismail, H., Haw, F.S., 2008. Effects of palm ash loading and maleated natural rubber as a coupling agent on the properties of palm-ash-filled natural rubber composites. *Journal of Applied Polymer Science* 110 (5), 2867–2876.

modulus but decreases the tensile strength and elongation at break of unfilled epoxidized HNR/thermoplastic polyurethane blends (Pongdong *et al.*, 2016). The enhanced modulus is attributed to hydrodynamic effects and chemical bonds between polar functional groups of RHA and polymer matrix (Table 4).

Cellulose-Based Fillers in Rubber Composites

Background

Natural fibers, such as oil palm fiber (OPF), sisal fiber (SF) coir fiber (CF), and tomato peels (TP), are lightweight, high-modulus, non-toxic materials which absorb carbon dioxide during their growth (Kabir *et al.*, 2012). Natural fiber is a common construction material for roofing and cladding (Frazão *et al.*, 2018), but production is far greater than consumption (Geethamma *et al.*, 2005). Thus, new large scale applications of natural fibers are needed, perhaps including their use as fillers in composites.

Oil production from oil palm in 2006 reached 36.9 million tons (Sumathi *et al.*, 2008), with 31.8 million tons of coproduced OPF (Karina *et al.*, 2008; Shinoj *et al.*, 2011). The main components of OPF are cellulose (42.7%–65.0%) and lignin (13.2%–25.3%) (Shinoj *et al.*, 2011). Sisal is a native plant of Mexico and SF, mainly composed of cellulose (78%) (Frazão *et al.*, 2018), and 4.5 million tons is produced per year (Li *et al.*, 2000). Coconut is an important natural resource for food, cosmetic and charcoal production and coconut processing coproduces 0.75 million tons of CF annually (Rejeesh and Saju, 2017). The main components of CF are cellulose

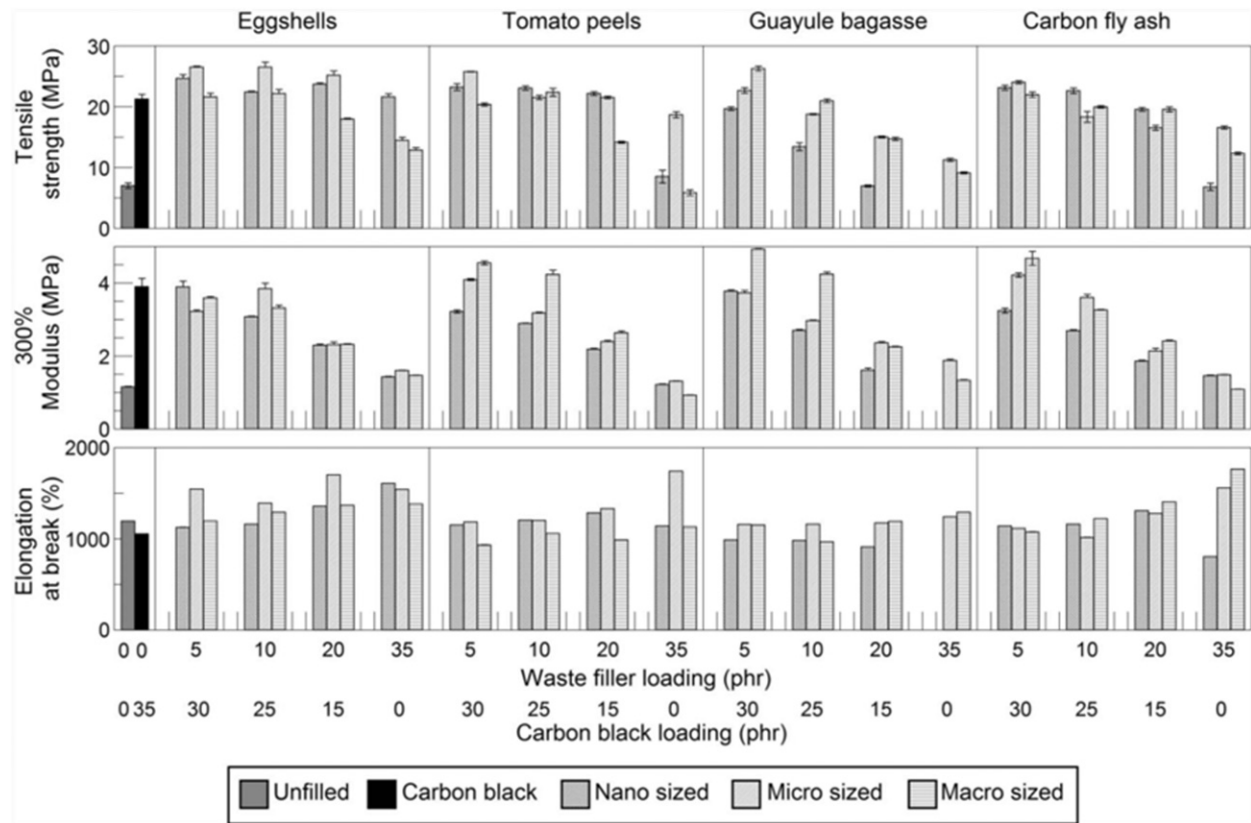


Fig. 2 Mechanical properties of waste fillers (eggshell, tomato peels, guayule bagasse and carbon fly ash) and carbon black filled GNR blends at various filler composition. From Barrera, C.S., Cornish, K., 2017b. Processing and mechanical properties of natural rubber/waste-derived nano filler composites compared to macro and micro filler composites. *Industrial Crops and Products* 107 (May), 217–231.

Table 4 The changes of mechanical properties of thermoplastic composites with increasing content of RHA (all values were compared to the unfilled thermoplastic composites)

Waste filler	Size (μm)	Rubber matrix	Tensile strength	Elongation at break	Tear strength	Modulus at 300% strain
RHA (Khalf and Ward, 2010)	Unknown	SBR/linear low-density polyethylene blends	Increased 0%–170%, then decreased	Increased 0%–60%, then decreased	Unknown	Increased 0%–70%, then decreased
RHA (Pongdong et al., 2016)	4	HNR/thermoplastic polyurethane blends	Decreased 0%–30%	Decreased 0%–90%	Unknown	Increased 0%–20%

(30%–45%) and lignin (30%–45%). TP is an agricultural byproduct from food industry. In the U.S. in 2017, 29 million metric tons of tomatoes were produced with over 100 thousand metric tons of TP coproduced (the peel yield is 7%–10% of tomato weight) (Ayvaz et al., 2016; USDA, 2018).

Curing Behavior

The addition of OPF has no significant effect on the scorch and cure times of HNR composites (Ismail et al., 1997). The maximum and minimum torques increase with increasing OPF loading, because the stiffness of OPF filled HNR composites also increases. The cure time of OPF filled HNR composites increases in a tricomponent coupling system (silica, resorcinol formaldehyde and hexatetramine) due to the enhanced rubber-OPF interaction (Ismail et al., 1997). TP filled HNR and GNR composites have lower crosslink density than CB (Barrera and Cornish, 2016b, 2017b), because CB can form more crosslink structures by physical interaction with the rubber matrix (Fröhlich et al., 2005) than can the other two fillers.

Table 5 The changes of mechanical properties of rubber composites as increasing the content of cellulose-based fillers (all values were compared to the unfilled rubber composites)

Waste filler	Size (μm)	Rubber matrix	Tensile strength	Elongation at break	Tear strength	Tensile modulus
OPF (John <i>et al.</i> , 2008)	150–500	HNR	Reduced 0%–120%	Reduced 0%–20%	Increased 0%–110%	Increased 0%–50%
Sodium hydroxide treated OPF (John <i>et al.</i> , 2008)	150–500	HNR	Reduced 0%–30%	Reduced 0%–50%	Increased 0%–190%	Increased 0%–250%
Silane treated OPF (John <i>et al.</i> , 2008)	150–500	HNR	Reduced 0%–30%	Reduced 0%–50%	Increased 0%–160%	Increased 0%–230%
Hybrid filler of OPF and SF (1:1 mixture by weight) (Jacob <i>et al.</i> , 2004)	OPF: 150–500 SF: 120	HNR	Reduced 0%–50%	Reduced 0%–10%	Increased 0%–100%	Increased 0%–240%
TP (Barrera and Cornish, 2016a)	23	GNR	Increased 0%–160%	Increased 0%–50%	Unknown	Increased 0%–20%
TP (179 μm) (Barrera and Cornish, 2016a)	179	GNR	Reduced 0%–40%	Reduced 0%–10%	Unknown	Reduced 0%–20%
TP (Barrera and Cornish, 2017a)	0.386	GNR	little change	Reduced 0%–40%	little change	Increased 0%–130%

Reinforcing Effect on Mechanical Properties

Tensile strength, elongation at break and tear strength decrease, but modulus and hardness increase, as OPF loading increases in HNR rubber composites (Ismail *et al.*, 1997; John *et al.*, 2008), due to the poor wettability of OPF by the HNR matrix and interruption of strain induced crystallization (John *et al.*, 2008). A hybrid filler of OPF and SF (1:1 mixture by weight) increases tear strength and modulus, but decreases tensile strength and elongation at break compared to unfilled HNR (Jacob *et al.*, 2004). The hybrid fiber has an optimal fiber loading of 30 phr, which maximizes tensile strength, elongation at break and tear strength but is still lower than unfilled HNR. At lower hybrid fiber loading, the distance between fibers is too far to transfer stress from the rubber matrix, which results in load concentration and material failure. Higher hybrid fiber loading contributes to agglomeration of the fibers, which blocks load transfer (Jacob *et al.*, 2004). Reinforcement by OPF and SF also is dependent on fiber length, with best performance at 10 mm OPF and 6 mm SF (Jacob *et al.*, 2004; John *et al.*, 2008). Longer fibers entangle and reduce mechanical properties of composites (Jacob *et al.*, 2004). TP (23 μm) filled GNR has similar tensile strength, hardness and higher elongation at break to CB composites with less than 60% CB replacement (Barrera and Cornish, 2016a, 2017b). The irregularity of TP increases the rubber-filler interaction (Barrera and Cornish, 2016a). In contrast, TP reduces the tensile strength and modulus of HNR composites as CB is replaced (Barrera and Cornish, 2015). The branched structure of HNR may block the load transfer from HNR to TP and explain the poorer reinforcement of TP in this type of rubber (Barrera and Cornish, 2016a). CF is the poorest reinforcing fibrous filler among these different fibers because of its high microfibrillar angle and large diameter (Geethamma *et al.*, 1998) (Table 5).

Modification of cellulose-based fillers can improve their reinforcement effects. Sodium hydroxide (4%–5%) treated fibers in HNR composites improve tensile strength, elongation at break, modulus and hardness more than untreated OPF, SF and CF (Geethamma *et al.*, 1998; John *et al.*, 2008). Alkali treatment breaks fiber bundles and decreases fiber size, which increase the interfacial area between rubber and fiber (Li *et al.*, 2000). Also, the alkali treatment produces voids by reacting with the globular protrusions which exist on the surface of CF enhancing the surface roughness of CF (Geethamma *et al.*, 1998, 2005). Thus, the interfacial area and adhesion between fiber and rubber matrix increases (Geethamma *et al.*, 1998; Li *et al.*, 2000), resulting in more efficient stress transfer from the rubber matrix to the fiber (John *et al.*, 2008). On the other hand, high concentrations of sodium hydroxide (more than 8%) result in OPF degradation and deterioration of mechanical properties of HNR composites (John *et al.*, 2008). Tensile strength of 5% alkali treated CF decreases as CF increases up to 30 phr, then increases (Geethamma *et al.*, 1998). Insufficient stress transfer explains the low tensile strength at lower CF loadings, while high fiber loadings restrain the rubber matrix. Sodium hydroxide-treated CF filled HNR composites exhibit two obvious $\tan \delta$ peaks at low and high temperature, which correspond to the HNR and CF. The loss modulus and $\tan \delta$ increase with increasing CF loading from 0 to 60 phr, because of increased energy dissipation under dynamic conditions (Geethamma *et al.*, 2005). The interfacial area between CF and the rubber matrix becomes larger with more CF loading, which results in more energy dissipation in the HNR composites. The $\tan \delta$ peak of CF filled HNR composites moves towards higher temperature as fiber loading increases, corresponding to a higher glass transition temperature (Geethamma *et al.*, 2005) (Fig. 3).

Silane coupling agent also improves the reinforcing effect of the hybrid filler of OPF and SF, but their performance is still lower than unfilled HNR (John *et al.*, 2008). The silane forms chemical bonds between the rubber matrix and the fibers, as the silane forms silanol groups in the presence of water, which then react with the hydroxyl groups on the surface of the OPF and SF. The functional groups of the silane coupling agent, such as amino group or fluorine, also can form hydrogen bonds with HNR (John *et al.*, 2008).

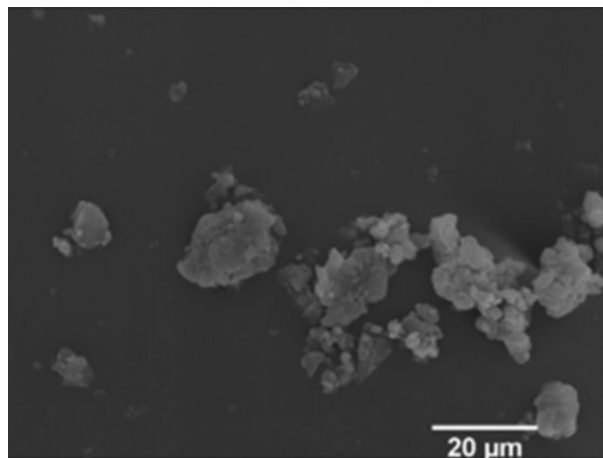


Fig. 3 SEM microphotographs of TP (23 μm). Figure from Barrera, C.S., Cornish, K., 2016a. High performance waste-derived filler/carbon black reinforced guayule natural rubber composites. *Industrial Crops and Products* 86, 132–142.

Physical treatment also significantly affects NR reinforcement by TP (Barrera and Cornish, 2016a, 2017b; Barrera *et al.*, 2018). Tensile strength, modulus at 300% strain and elongation at break of GNR composites increase with decreasing TP particle size from macro-size (179 μm) to micro-size (23 μm) as the TP-GNR interaction increases (Barrera and Cornish, 2016a). However, tensile strength and elongation at break of GNR composites all decline in nano-TP filler (386 nm), due to the increased filler-filler interactions among the polar functional groups on the TP surface (Barrera and Cornish, 2017b).

Calcium Carbonate-Based Fillers in Rubber Composites

Background

Calcium carbonate is a common filler in rubber composites largely as a diluent filler. However, calcium carbonate-based waste fillers, like ES, increase elongation at break and tensile strength, while production cost is reduced (Saeb *et al.*, 2013; Barrera and Cornish, 2017b). Commercial calcium carbonate is produced by mining or chemical precipitation, and both methods are energy intensive, nonrenewable and emit greenhouse gases (Klungsuwan *et al.*, 2013). Thus, calcium carbonate fillers from renewable resources are desired to help establish sustainable rubber composites. Marine products and eggs are two potential sources.

As an important protein source, eggs are consumed globally. The United States produces over 100 billion eggs every year (United States Department of Agriculture, 2017). The average weight of an egg is 60 g, and each egg includes about 11% eggshell (ES) (Tsai *et al.*, 2006). Thus, about 0.7 million tons/yr of ES are produced as food waste in the U.S. ES waste produced by the food processing industry is mainly landfilled, which is neither economic nor eco-friendly (Carvalho *et al.*, 2011; Iyer and Torkelson, 2014). ES fillers, used on a large scale, would reduce the cost and pollution of disposal (Mičicová *et al.*, 2016). The chemical composition of ES is 94% calcium carbonate, 1% calcium phosphate, 1% magnesium carbonate and 4% organic matter (protein fibers and mucin protein) (Tsai *et al.*, 2006). Since calcium carbonate is used as a non-reinforcing diluent filler (as a polymer extender) in rubber products, ES may be an alternative source. In addition, ES have high porosity, developed to support the high gas exchange needed to allow developing chicks to respire efficiently (Wangenstein *et al.*, 1970; Barrera and Cornish, 2015), and this architecture persists in micro ES particles, which increases the interfacial area between ES and rubber.

Cuttlefish is a common food in tropical countries. The skeleton of cuttlefish or cuttlebone is a byproduct from food industry and consists of 91% calcium carbonate and 8% protein and chitin (Poompradub *et al.*, 2008). Cuttlebone particles also may be an alternative filler to calcium carbonate in rubber composites.

Curing Behavior

The alkalinity of calcium carbonate can accelerate the vulcanization process (Baranwal and Stephens, 2001; Klungsuwan *et al.*, 2013; Barrera and Cornish, 2017b). During vulcanization, the maximum torque and crosslink density are enhanced but the scorch and optimum cure times decrease with increasing ES and cuttlebone loading in untreated and epoxidized HNR and SBR composites (Poompradub *et al.*, 2008; Intharapat *et al.*, 2013; Klungsuwan *et al.*, 2013; Barrera and Cornish, 2016a). ES filled rubber composites have higher maximum torque, and shorter scorch and cure optimum times, than commercial calcium carbonate (Intharapat *et al.*, 2013), which is attributed to the accelerating effect of metal oxides and amino acids in ES (Intharapat *et al.*, 2013; Saeb *et al.*, 2013). Also, ES proteins can form hydrogen and covalent bonds with the oxirane rings of epoxidized HNR. Stearic acid coated ES reduces the scorch time of HNR and SBR, but with no significant effect on cure optimum times (Saeb *et al.*, 2013).

Table 6 The changes of mechanical properties of rubber composites as increasing the content of calcium carbonate-based fillers (All values were compared with the unfilled rubber composites)

Waste filler	Size (μm)	Rubber matrix	Tensile strength	Elongation at break	Tear strength	Hardness
ES (Intharapat <i>et al.</i> , 2013)	26	Epoxidized HNR	Reduced 0%–30%	Reduced 0%–20%	Reduced 0%–10%	Increased 0%–20%
ES (Saeb <i>et al.</i> , 2013)	0.349	HNR	Increased 0%–30%	Reduced 0%–10%	Unknown	Unknown
ES (Saeb <i>et al.</i> , 2013)	0.349	SBR	Increased 0%–40%	Increased 0%–25%	Unknown	Unknown
Cuttlebone (Klungsuwan <i>et al.</i> , 2013)	106	HNR	Increased 10%, then reduced 40%	Fluctuated, then reduced 40%	Unknown	Increased 30%

Reinforcing Effect on Mechanical Properties

Tensile strength, elongation at break and tear strength decrease, but hardness increases, with increasing ES content from 0 to 75 phr in epoxidized HNR composites (Intharapat *et al.*, 2013). Tensile and tear strength decline because the continuous phase sustains more stress with increasing filler loading. ES-filled epoxidized HNR has higher tear strength, storage modulus and tensile strength, but lower elongation at break, than when commercial calcium carbonate is used (Intharapat *et al.*, 2013). The higher tensile and tear strength are due to the larger surface area of ES particles and stronger covalent bonds formed by oxirane rings of epoxidized NR and the amines of ES. Hardness is similar in ES and calcium carbonate filled HNR and SBR composites (Saeb *et al.*, 2013). The stearic acid coated ES-filled SBR and NR have maximum tensile strength at 5 phr loading, due to the optimal crosslink density at this filler loading (Saeb *et al.*, 2013). However, elongation at break decreases as ES fraction increases, because of the large particle size in this study (Table 6).

Increasing cuttlebone content in HNR composites increases hardness, brittleness and reduces elongation at break, while maximum tensile strength occurs at 20 phr filler loading (Klungsuwan *et al.*, 2013; Poompradub, 2014). Cuttlebone filled HNR has higher tensile strength than commercial calcium carbonate, because of its different filler morphology, even though the particle size of cuttlebone (106 μm) is much larger than commercial calcium carbonate (1.5 μm) (Klungsuwan *et al.*, 2013). The rod-like cuttlebone has more surface area and a stronger filler-rubber interaction than the spherical, commercial calcium carbonate.

At 35 phr filler total loading (CB and ES), tensile strength and elongation at break of GNR composites are maximal with 5 phr ES (average particle size is 23 μm) and 30 phr CB (Barrera and Cornish, 2016a). Increased rubber-ES interaction formed by the hydrophobic components of ES, and the complex shell micro-architecture, may explain these increased mechanical properties. However, tensile strength and 300% modulus slightly reduce with further increasing ES and decreasing CB content (Barrera and Cornish, 2016a). One explanation is that CB has a very small particle size (108 nm) and a non-polar surface (Baranwal and Stephens, 2001; Barrera *et al.*, 2018), which results in a stronger rubber-filler interaction than ES (Barrera and Cornish, 2016a). However, ES filled HNR exhibits different mechanical properties (Barrera and Cornish, 2015) compared to the GNR composites. The modulus at 300% strain and tensile strength of HNR decrease, as ES fraction increases and CB decreases at constant filler loading (Barrera and Cornish, 2015). The various non-rubber components and different rubber macromolecular structure may explain the different reinforcement ability of ES in the two types of NR composites. HNR has a branched structure mediated by proteins and lipid linkages (GNR is linear), and HNR contains considerably more protein than GNR (Tarachiwin *et al.*, 2005; Sarkawi *et al.*, 2013). The branched structure of HNR may impede the establishment of the filler-filler network and reduce rubber-filler interactions (Barrera and Cornish, 2016a). The particle size also affects the ES reinforcement. Both HNR and GNR are more reinforced by micro-sized ES (23 μm) than by macro-sized ES (241 μm) (Barrera and Cornish, 2015, 2016a). However, as the particle size of ES further decreases to nano size (73 nm), the tensile strength, elongation at break and modulus at 300% of the composites are lower than composites made with micro-sized ES, possibly due to nano-ES aggregation (Barrera and Cornish, 2017b).

Application of Waste-Derived Fillers in Rubber Composites

Rubber composites have a variety of applications, which include tires, mats, seals, shoe soles, toys, and many more (Thongsang *et al.*, 2012) and, as mentioned in section “Silica-Based Fillers in Rubber Composites”, some waste-derived filler rubber composites have comparable, or even superior, performance to commercial fillers and a lower cost. Short fiber filled NR composites can be applied to tires (the chafer strip), sole and cord construction (Nair and Joseph, 2014). Tomato peels, ES and carbon fly ash solely filled guayule NR can be applied as rubber tapes (Barrera and Cornish, 2016a). The performance of tire treads, surgical drainage tubes and seals may also be achieved by a hybrid filler of ES and TP filled GNR composites (Barrera and Cornish, 2016a).

Conclusion

Recent progress in research and development of waste fillers in rubber composites has been reviewed in this article. Most waste-derived fillers have potential application in rubber products with the advantage of low cost. Furthermore, silica, cellulose and calcium carbonate based waste fillers improve the mechanical properties of rubber composites, due to uniform filler dispersion, chemical or physical modifications and strong rubber-filler interaction. However, most of the reported studies are still at laboratory scale. Future work, like economic analysis and product design, are needed to develop and commercialize the eco-friendly and reinforcing waste fillers. Waste-derived fillers are expected to open new markets of sustainable rubber products.

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Waste Printed Circuit Board (WPCB) Recovery Technology: Disassembly and Desoldering Approach

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Introduction

The development of the electronic industry is associated with an increased demand on more precious metals (PMs) and scarce metals (SMs), and increased growth of waste electrical and electronic equipment (WEEE). It is considered to be one of the fastest growing solid waste streams in the world (Sun *et al.*, 2015; Kaya, 2016a). WEEE grows three times faster than the municipal wastes. The final disposal of WEEE is an issue of current worldwide concern. Conventional disposal and incineration methods can pose threats to the whole environment, from the atmospheric to the aquatic and terrestrial compartments. In recent years, recovery of metals from e-waste has become increasingly important due to potential risk of strategic and scarce raw materials and environmental concerns. Half of the e-waste comes from electrical appliances and the rest comes from electronic goods (Kaya, 2016b). In the world, 41.8 Mt e-wastes were produced and 6.5 Mt were formally treated in 2014 (Web 1). In 2016 e-waste amount increased to 44.7 Mt (Web 2). Average e-waste generated per inhabitant was 5.9 kg in 2014 and 6.1 kg in 2016 in the world (Web 1; 2). Proper e-waste management for all countries is necessary; because, e-waste pollutes the ground water, acidifies the soil, generates toxic fume and gas after burning, accumulates fastest in municipal disposal areas and releases carcinogenic substances into the air. E-waste constitutes about 8% of the all municipal waste and contains 40% of Pb and 70% of heavy metals in landfills (Kaya, 2016c).

In order to achieve environmental and metal sustainability in circular economy, green processes need to be developed for the recycling of metals and nonmetals from e-waste (Dodson *et al.*, 2015; Clark *et al.*, 2016; Dodson *et al.*, 2012; Hunt *et al.*, 2015). For example, printed circuit boards (PCBs) are essential components and widely used in different fields such as electric and electronic equipment, information technology (IT), and sensing and control industries (Alippi, 2016; Jin *et al.*, 2016; Hadi *et al.*, 2015; Zeng *et al.*, 2016a,b). WEEE and WPCBs are attractive polymetallic secondary source, referred to as "Urban Mines". WPCBs may contain more than 60 metals, including valuable base metals (BMs) (e.g., Sn, Fe, Cu, Zn, Pb, Al etc.), PMs (Au, Ag etc.), platinum group metals (PGMs) (Pd, Pt, Rh, Ir, Ru etc.), SMs (Te, Ga, Se, Ta and Ge) and hazardous metals (HMs) (e.g., Pb, Hg, Be, Cr⁶⁺, As, Sb, Cd etc.) and hazardous substances (e.g., Brominated flame retardants (BFR), acrylonitrile butadiene styrene (ABS), polyvinyl chloride (PVC) etc.) (Zeng *et al.*, 2017; Chen *et al.*, 2016). Informal recycling of metals from WPCBs, especially in developing countries, has caused serious environmental pollution and human health risks (Yu *et al.*, 2016; Fu *et al.*, 2013; Zeng *et al.*, 2016a,b; Awasthi *et al.*, 2016; Li *et al.*, 2015). Using the "Twelve Principles of Green Chemistry" is the most effective way to solve these issues while at the same time alleviating the shortage of mineral resources (Matus *et al.*, 2012a,b; Sheldon, 2016; O'Connor *et al.*, 2016). Based on the principles of Green Chemistry, many environmentally sound processes have been developed to recover metals from e-waste (Hu *et al.*, 2016; Maât *et al.*, 2016; Singh *et al.*, 2016; Sun *et al.*, 2017; Zeng *et al.*, 2015; Guan *et al.*, 2015). WEEE represents a secondary source of metals that have been mined from natural ore resources, where they are often present at low concentrations. Thus, WEEE recovery for the production of secondary materials needs to be encouraged more now and in the future.

There are four main aims of WPCB/e-waste recovery:

- Take care of hazardous/toxic substances contained in e-waste in an environmentally sound manner while preventing secondary and tertiary emissions.
- Recover valuable raw materials (metals and nonmetals) as effective as possible.
- Create economically and environmentally sustainable businesses (optimize eco-efficiency),
- Consider the social implications and local context of operations (e.g., employment opportunities, available skills and education etc.).

Today in e-waste recovery, material (and metal) centric recycling approach changed to product centric recycling approach.

E-Waste, WPCB and Solder Composition

E-waste, especially a mixture of end-of-life (EoL) electronic products from a variety of sources, is of inherently high complexity in composition, phase and physicochemical properties. WPCBs contain about 40% of metal, 30% of organic resins (plastics) and 30% of ceramics. Bare/unpopulated PCBs represent about 23% of the total WPCBs (Duan *et al.*, 2011). WPCBs

contain many ECs; such as resistors, relays, capacitors, integrated circuits (ICs), chips etc. Therefore, dismantling of ECs from WPCBs is the first and the most important step in recycling chain, which can help to conserve scarce resources, establish the reuse of components and eliminate hazardous materials from the environment (Li *et al.*, 2007). WPCBs include ECs and a bare board, which is a mixture of thermosetting and bromine epoxy resins reinforced with glass fibers and several embedded metals in them. PCBs are essential and common elements of almost all of the electronic systems. PCBs are used to mechanically support and electrically connect ECs using conductive pathways, tracks or signal traces etched from Cu sheets laminated onto a nonconductive substrate. PCBs, which provide interconnection between software and hardware, are found in all EEE. Average PCB amount in e-waste is about 3%–5% and even more in some EEEs, like TV set 7%, computer 19%, mobile phone 21% (Duan *et al.*, 2011). Most recycling approaches practiced can only recover metal contents of PCB scraps to an extent 30% of the total weight. More than 70% of PCB scraps (i.e., nonmetal fraction) cannot be efficiently recycled and recovered and have to be incinerated or landfilled (Li *et al.*, 2004).

WPCBs are in generally scraps, faulty, malfunctioning, redundant and over-capacity products. There are three grades of WPCBs according to values; low, medium and high grades. Hagelüken (2006) used Au content of e-waste for classification. If Au content is less than 50 ppm, it is low grade; if Au content is between 50 and 100 ppm, it is medium grade and if Au content is between 100 and 200 ppm, it is high grade and if Au content is more than 400 ppm, it is very high grade. TV boards (without cathode ray tube (CRTs)), audio scraps, calculators, power supply units, alkaline batteries, Pb-batteries, phone batteries, Ni-Cd batteries, laptop batteries, laminate off cuts, transformers and heat sinks are low grade WEEEs. Pins, keyboards, PWBs, car electronics, lamps, phosphors, CRTs, ICT wastes, PC boards, laptops, handheld-computers, WEEE fines and edge connectors are medium grade and prices change from 1 to 8 Euros kg⁻¹ and ICs, optoelectronic devices, PCB scraps, mobile phones, NdFeB magnets, multi-layer ceramic capacitors (MLCCs), some boards and main frames are high grade WPCBs and prices change from 8 to 25 Euros kg⁻¹. High grade and high value WPCBs are estimated about 15% of total PCBs (Kellner, 2009). Value of WPCBs changes from 1000 to 25,000 Euros per ton according to grade quality.

Table 1 shows representative material compositions of WPCBs by wt% used in 31 previous studies. (Duan *et al.*, 2011; Chancercel *et al.*, 2009; Kaya, 2016a). These materials can be categorized in three groups: organic materials, metals and ceramics. Bare/unpopulated WPCBs without any ECs and solder represent 65%–70% by weight of an average PCB and easy to recycle to obtain Cu, epoxy resin and glass fiber with some Au, Ni and Cu plating on their surfaces. Yang *et al.* (2017) determined WPCBs from desktop and laptop PCs after central processing unit (CPU) and random access memory (RAM) had been removed. Bare PCB is rich in Cu, Sn and Ag and ECs are rich in Cu, Fe, Sn, Ag and Au (Table 2). Recycling of these metals is becoming more and more important in order to counteract the depletion of scarce mineral resources, especially as demand for these metals continues to increase.

The oldest and most common Pb-based solders used in electronics are 63Sn–37Pb. Table 3 shows solder alloys using in PCB packaging. Melting points of solder alloys are low and change between 176 and 228°C which is important for desoldering ECs from WPCBs. The Sn-Pb alloys, particularly those near to the eutectic composition, are used as solders while the main substrate or leads are made of Cu.

History of E-Waste Recovery

In the past few decades, recycling of WEEE by environment-unfriendly, hazardous and crude primitive technologies in China, India and some Africa countries has increased. Massive amount of dumping, acid leaching or open burning of WEEE took place. Resource reutilization and safe disposal of metals from WEEE has a great environmental protection. In the initial stage of WEEE

Table 1 WPCB material composition

Metals (~ 40%)	(%)	Ceramics (~ 30%)	(%)	Plastics (~ 30%)	(%)
Base metals					
Cu	6–27	SiO ₂	15–30	PE	10–16
Fe	1.2–8.0	Al ₂ O ₃	6.0–9.4	PP	4.8
Al	2.0–7.2	Alkali-Earthoxides	6.0	PS	4.8
Sn	1.0–5.6	Titanates-micas	3.0	Epoxy	4.8
Pb	1.0–4.2			PVC	2.4
Ni	0.3–5.4			PTPE	2.4
Zn	0.2–2.2			Nylon	0.9
Sb	0.1–0.4				
Precious metals					
Au (ppm)	9.0–2050				
Ag (ppm)	110–5700				
Pd (ppm)	3.0–4000				
Pt (ppm)	5–40				
Co (ppm)	1–4000				

Table 2 Bare PCB board and ECs compositions

Composition (%)	Bare PCB board	ECs	Total
Sn	10.12	3.20	6.0
Pb	3.20	0.68	1.7
Cu	21.62	13.80	19.9
Fe	0.21	19.49	11.80
Al	1.36	6.91	4.7
Zn	0.056	5.66	3.4
Ni	0.036	0.65	0.4
Cr	0.027	0.53	0.3
Cd (g/t)	0.53	14.45	8.9
Au (g/t)		40.76	24.4
Ag (g/t)	194.91	112.68	145.7

Table 3 Solder alloys using in PCB packaging

Element	Melting point (°C)	Eutectic composition	Melting point of eutectic solder (°C)
Sn	223.0	67Sn33Cd	176
Cd	320.8	63Sn37Pb	183
Pb	327.5	60Sn40Pb	183–190
Zn	419.4	50Sn50Pb	193–215
Ag	960.8	91Sn9Zn	199
Cu	1083.1	96.5Sn3.5Ag	221
Al	660.1	99.3Sn0.7Cu	227
Mg	651.0	99.5Sn0.5Al	228
		98Sn2Mg	200

Note: Reproduced from Kaya, M., 2016b. Recovery of metals from electronic waste by physical and chemical recycling processes Int. J. Chem. Nucl. Mater. Metall. Eng. 10.

recovery, simple and rough recovery processes were widely adopted. Manual dismantling, wet gravity separation (i.e., shaking tables), strong acid leaching etc. were the first crude WEEE recovery processes. These methods have both low recovery rates and damage the human health and environment. At the beginning of 1970s, mechanical separation methods began to be utilized to treat the WEEE (Zhang and Forssberg, 1997). There are international programs combating e-waste problems today. Transboundary movement of hazardous waste has been banned by Basel Convention since 1989. Japan, the EU and OECD countries adopted laws/directives related to e-waste after 2001. European Innovation Partnership (EIP) on raw materials, ERA-MIN roadmap and UNEP resource panel are activities addressing recycling innovation.

Fig. 1 show both physical properties of metals and plastics in WEEE and potential separation method selection for metals recovery from WEEE. Plastics have specific gravities between 0.9 and 2.0 g cm⁻³. Al is the lightest metal in WEEE. Six metals (Cr, Sn, Fe, Ni, Co and Cu) have a specific gravity between 7 and 9 g cm⁻³. Pb, Ag and Pd have specific gravity between 10 and 12 g cm⁻³ and three metals (W, PGMs and Au) have between 19.3 and 21.4 g cm⁻³. Mechanical recycling steps include selectively dismantling, crushing and physical separation methods in which separation criteria's, possible equipment and separation characteristics are summarized in Table 4 along with advantages and disadvantages. Plastics and glass are non-conductor. Five metals (Pb, Cr, Sn, Fe and Pd) have electrical conductance less than 10; three metals (Ni, Co and Al) have between 10 and 40 and three metals (Au, Cu and Ag) have between 40 and 70*10⁶ m⁻¹ Ω⁻¹. Au, Ag, Pb and Cu metals, plastics and glass are diamagnetic; Pd, Sn, Cr and Al are paramagnetic and Fe, Ni and Co are ferromagnetic metals. Based on these data, plastics and Al metal can be separated from other metals by gravity separation; ferromagnetics (Fe, Ni and Co) can be separated from diamagnetics (plastics, glass, Au, Pb, Ag and Cu) by magnetic separation and metals and Al-Cu can be separated from plastics by electrostatic separation methods.

WPCB Reuse and Recovery Systems

PCBs are always mounted with ECs whereby PCBs without ECs are called bare PBC or printed wiring board (PWB). Most of the ECs are functional and usable at the time of disposal/dismantling. Therefore, dismantling ECs from WPCBs is a crucial step from both standpoints of materials recovery and ECs reuse in the WPCBs recovery chain to conserve scarce resources, reuse functioning ECs,

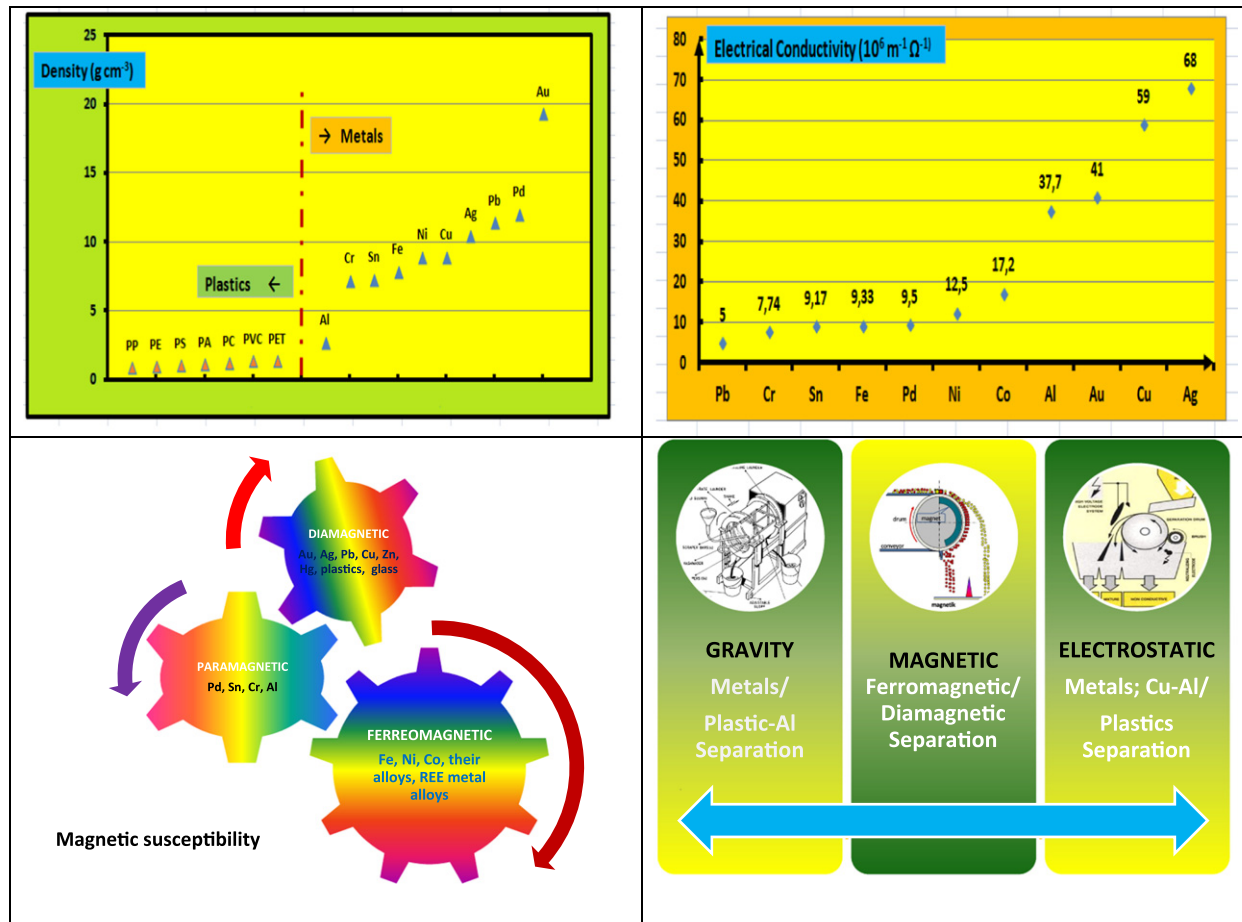


Fig. 1 Physical properties of metals and plastics in WEEE and potential physico-mechanical separation method selection for metal recovery from e-waste.

Table 4 Physico-mechanical separation methods used in WEEE recycling

Separation method	Separation criteria	Separation equipment	Separation character	Advantages/disadvantages
Gravity separation (GS)	Density difference	Air current separation (ACS) Shaking tables, Jigs, Heavy media separation (HMS)	Separates light plastics/glass from heavy metals	Air velocity, particle size, shape and density affect separation
Magnetic separation (MS)	Magnetic susceptibility	Dry magnetic separation (DMS)	Separates ferrous metals from non-ferrous metals (Al, Cu, Au, Ag etc.)	Suitable for separating Fe, steel, Ni, Cr; but, not suitable separating nonferrous metals
Electrostatic separation (ES)	Electrical conductivity/ density	Eddy current separation (ECS)	Separates ferrous and nonferrous materials	Recover nonferrous metallic particles (Al, Cu) from non- metals (plastic, glass)
	Electrical conductivity	Corona electrostatic separation (CES)	At 0.2–1.2 mm, separates metallic particles from nonmetallic particles	Metals/precious metals from plastic/glass

and eliminate potential exposure to hazardous materials. For example, removal and disposal of toxic (mainly in electrolytes), explosive and combustible materials from Al-electrolytic capacitors (AECs) is essential and crucial in WPCB recovery. AEC also contains up to 50 wt% Al and Fe and worth recovering (Zhang and Forssberg, 1997). Current generic material and component recovery methods are typically combination of the following recycling processes. The recycling chain for e-waste is classified into four main subsequent steps:

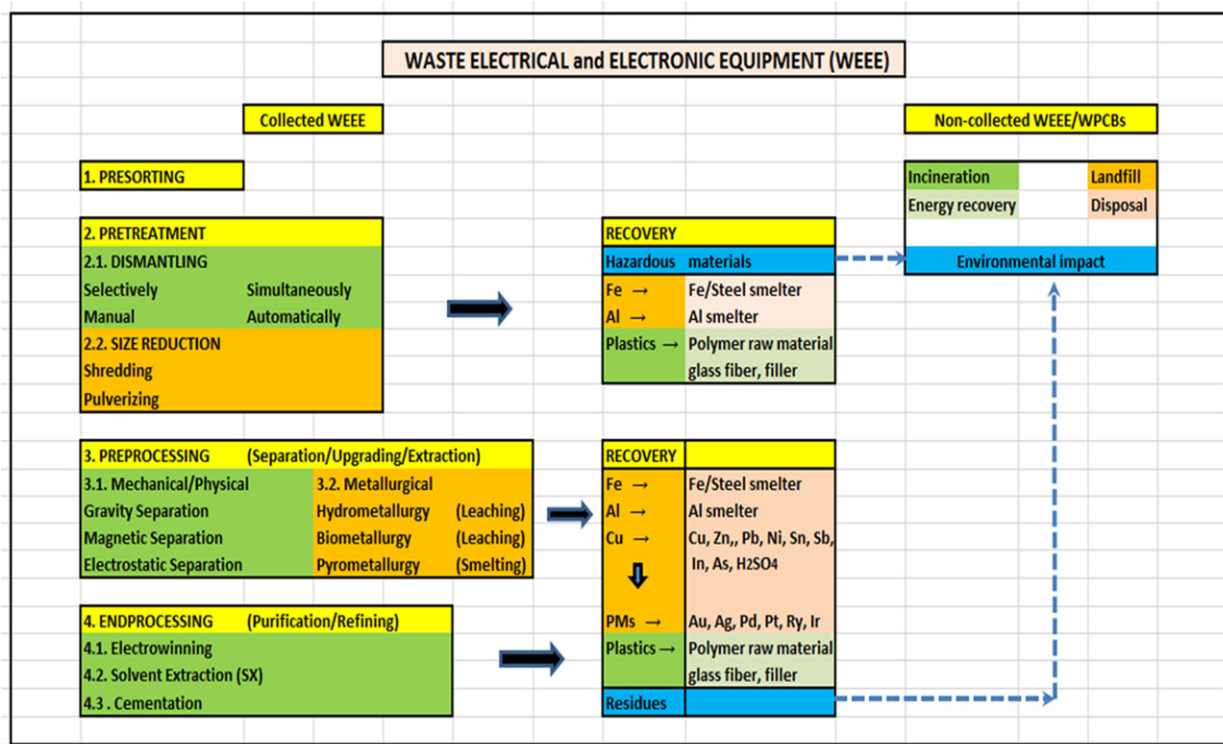


Fig. 2 E-waste recycling chain and end-of-life WEEEs/WPCBs treatment options.

- 1st Step: Collection and presorting,
- 2nd Step: Pretreatment (includes dismantling and size reduction for liberation),
- 3rd Step: Preprocessing (includes separation, upgrading and extraction), and
- 4th Step: End processing (purification and refining) (Fig. 2).

Collection of e-waste is of crucial importance as this determines the amount of material that is actually available for recycling. Many collection programs are in place; but, their efficiency varies from place to place and improvements of collection rates depend on more on social and societal factors than on collection methods. WEEE/WPCBs follow four different treatment options: landfill, incineration, shredding and disassembly. Reuse of some ECs can be achieved with only disassembly. Shredding produces products for recycle, incineration and landfill. WEEE/WPCBs can also be disposed by either incineration or landfilling.

Dismantling/Disassembly

Disassembly process employs to segregate ECs and/or materials that are reusable, identifiable or hazardous in such a manner as to maximize economic return and to minimize environmental pollution, enabling subsequent processes to be performed more efficiently and effectively. Disassembly is the systematic removal of ECs, parts, a group of parts or a subassembly from e-waste. Depollution is the removal of toxic or environmentally harmful components/substances containing Pb; Cr⁺⁶; Hg switches/lamps; CRTs; P coatings; NiCd/NiMH/LiOn and Li polymer batteries; de-gassing; oil; polychlorinated biphenyl (PCB) containing capacitors; inks; toners; coolants/refrigerants; CFCs/HCFs in foam etc. and useful/reusable EC materials. The aim of dismantling process is to liberate the materials and direct them to adequate subsequent pre/end- treatment processes. Hazardous substances have to be removed and stored or treated safely while valuable components/materials (WPCBs, HDs etc.) need to be taken out for reuse or to be directed to efficient recovery processes. Dismantling of ECs on WPCBs is the first and the most important step in a recycling chain which can help to conserve scarce resources, establish the reuse of components and eliminate hazardous materials from environment. Disassembly is the major cost element and time consuming operation in recycling technology. Low processing capacities hinders the application of manual disassembly in large scale industrial processes. The development of automatic disassembly process is vital when considering the amount of WPCBs worldwide. The most valuable part of e-waste (i.e., PCBs) can be removed from the devices by manual dismantling and mechanical treatment or a combination of both. Manual removal of PCBs prior to e-waste shredding will prevent losses of PMs and SMs. Manual dismantling holds a dominant position in pre-treatment of WPCBs and has low investment cost, utilizing simple electrical/pneumatic tools and can be done by people with little or low education after appropriate training. Increasing labor cost and low processing capacities are hindering the application of

manual disassembly in large scale industrial processes. Because the labor cost already become the second largest expenditure of EU WEEE plants. Manual or automated disassembly can be performed either partially (selectively) or completely (simultaneously).

Selective disassembly targets out hazardous or valuable components for special treatment. Selective dismantling is generally performed manually and takes a long time. In simultaneous disassembly, entire ECs are evacuated from WPCBs together. Mixed ECs disassembly is good for time saving. Dismantling is performed semi-automatically/automatically. Automated disassembly provides a cost-effective recycle at minimum labor force on a large scale. Radio frequency identification (RFID) tags are very helpful for recognition of ECs on WPCBs (Kellner, 2009). Table 5 summarizes the comparison of manual and automated/semiautomated dismantling methods for e-waste recycling. Automated dismantling has more advantages and less disadvantages than manual dismantling.

Current WPCB dismantling procedures have restrictions on e-waste recycling due to low efficiency and negative impact on environment and human health (Zeng *et al.*, 2013). Therefore, there is a need to seek an environmental-friendly dismantling process. Manual disassembly and sorting are major cost element and high labor burden within any WEEE recycling methodology. The components reuse oriented selective disassembly technology for WPCBs with wet chemical selective desoldering may prevent also environmental pollution and recover expensive solder (contains Sn + Pb).

Although WPCBs are designed for durability of 500,000 h, the average EoL for ECs is 20,000 h, or less than 5% of its designed lifespan. Hence, many ECs are still functioning and usable at the time of disposal as e-waste. Therefore, disassembling ECs from WPCBs is a first and crucial step in WPCBs recovery chain to conserve scarce resources, and eliminate potential exposure to hazardous materials. ECs are usually divided into two parts: functional and usable ECs which could be reused for new products and repairment; and damaged ECs which could be disposed for metals recovery. Large numbers of researches are being focusing on ECs dismantling from WPCBs (Wang and Xu, 2015), mainly processed in two steps (Fig. 3): (1) remove solder joints between base boards and ECs, including wearing down the solder joints on the back-side of WPCBs by grinders (Lee *et al.*, 2012); dissolving the solder by chemical reagents (Haruta *et al.*, 1991); melting the solder by infrared heaters (IR) (Yokoyama, 1997), electronic heating tubes (Ding *et al.*, 2008; Gao *et al.*, 2008), hot air (Pan *et al.*, 2007; Lee *et al.*, 2012) and hot liquids (Guo, 2007; Zhang *et al.*, 2008; Frank, 2002; Zhao *et al.*, 2009) like molten solder, diesel, paraffinic oil and silicon oil; (2) dislodge ECs from WPCBs, including mechanical sweep (Wang *et al.*, 2013), gas jet (Pan *et al.*, 2007; Lee *et al.*, 2012), and centrifugation (Zhou and Qiu, 2010). However, almost all of these technologies could not be applied for industrialization attributed to their various limits, such as low efficiency and high cost.

Undoubtedly, the metal recovery from WPCBs is necessary to the sustainable development of the electronics industry, and many techniques for WPCB dismantling and metals recycling have been developed for the last two decades. Usually, chemical and heating technologies are used for dismantling ECs from WPCBs (Fig. 4). The former faces to the problems of the selection of suitable chemical reagents and their damage to components, which prevents this application in practice. For dismantling ECs and recovering the solder from WPCBs, thermal treatments – such as IR heating, using an electric heating tube, liquid-medium heating, and solder-bath heating – are most commonly used. All these methods generally operate at about 225–265°C which is 40–50°C higher than solder melting point. Critical temperature to generate toxic fumes of WPCBs is 270–280°C (Duan *et al.*, 2011). Because of this heating temperature, dioxin may form during dismantling (Duan *et al.*, 2011; Wang and Xu, 2015; Lee *et al.*, 2012; Zhou and Qiu, 2010; Park *et al.*, 2015). For example, Zeng *et al.* (2013) used water-soluble ionic liquid as a heating medium to dismantle ECs and recover Sn solder from WPCBs, nearly 90% of the ECs were removed from the WPCBs, at 250°C. Simultaneously, an automatic system for disassembling WPCBs with heated air at $265 \pm 5^\circ\text{C}$ was developed by Wang *et al.* (2016). But more energy was consumed by heating WPCBs above the melting point of Sn solder.

Table 5 Comparison of manual and automated/semiautomated dismantling methods

<i>Manual dismantling</i>	<i>Automated/semiautomated dismantling</i>
Advantages	Advantages
● Low investment cost ● Utilize simple tools ● Low educated workers ● Can be performed selectively/simultaneously ● Small scale	● Time saving ● Cost effective ● Minimum labor force ● Large scale ● Semi/full automatic ● Environmental friendly ● Without dust
Disadvantages	Disadvantages
● Takes long times ● Occupational health and safety problems ● Dust exposure ● Bad smell and black fumes ● High labor force ● Expensive ● Informal, banned process	● High investment cost

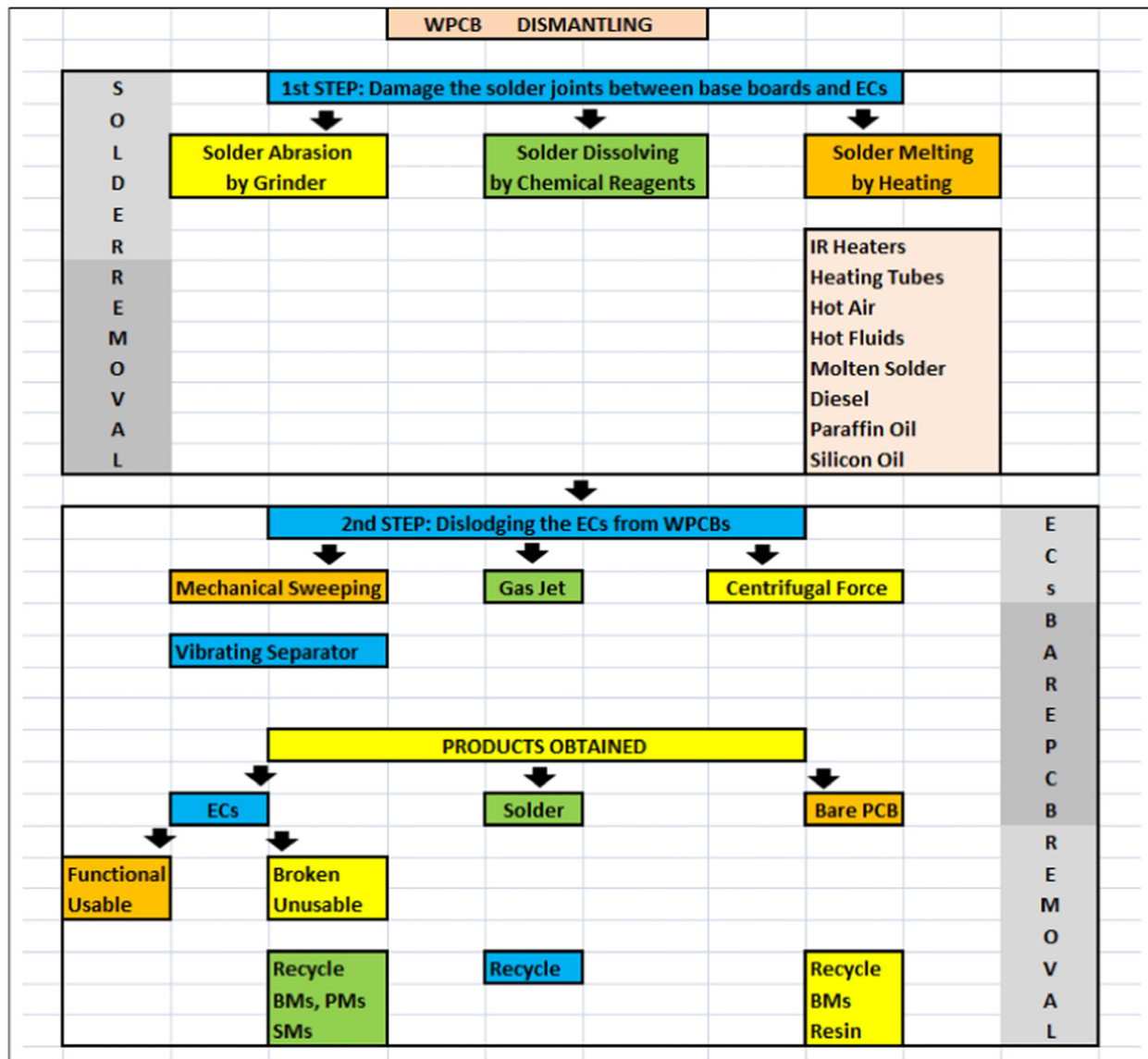


Fig. 3 WPCB dismantling steps.

Recently, a chemical reagent was used to recover Sn solder from WPCBs. [Yang et al. \(2016\)](#) reported that 99% of Sn could be leached with SnCl_4 and HCl at 60–90°C, and the Sn was then recovered from the purified solution by electro deposition. HBF_4 containing H_2O_2 was used to dissolve Sn solder by [Zhang et al. \(2015\)](#), and almost 100% of the solder was dissolved. Recently, [Zhang et al. \(2017\)](#) reported that a leachant containing methanesulfonic acid (MSA) and H_2O_2 can also selectively dissolve the Sn–Pb solder. Although these techniques were conducted at lower temperatures, new chemical reagents (such as SnCl_4 , HCl, HBF_4 and H_2O_2) were consumed.

Desoldering

Desoldering or solder removal is necessary for dismantling ECs from WPCB assemblies. Currently, informal manual selective dismantling uses chisels, hammers and cutting torches to open solder connections and separate various types of metals and components. Cooking on a wood/coal/electric heated plate and melt solder in order to sell the expensive chips and other recovered ECs to acid strippers for further processing is another manual process. Manual informal dismantling has some disadvantages such as a bad smell, black fumes and being a banned process ([Kaya, 2016a,b](#)). There are two different formal desoldering methods: melting solder by heating (thermal treatment) and leaching solder by chemicals (chemical treatment). Leaching easily generates a large amount of waste acid, alkaline liquid, sludge and water, which cause secondary pollution.

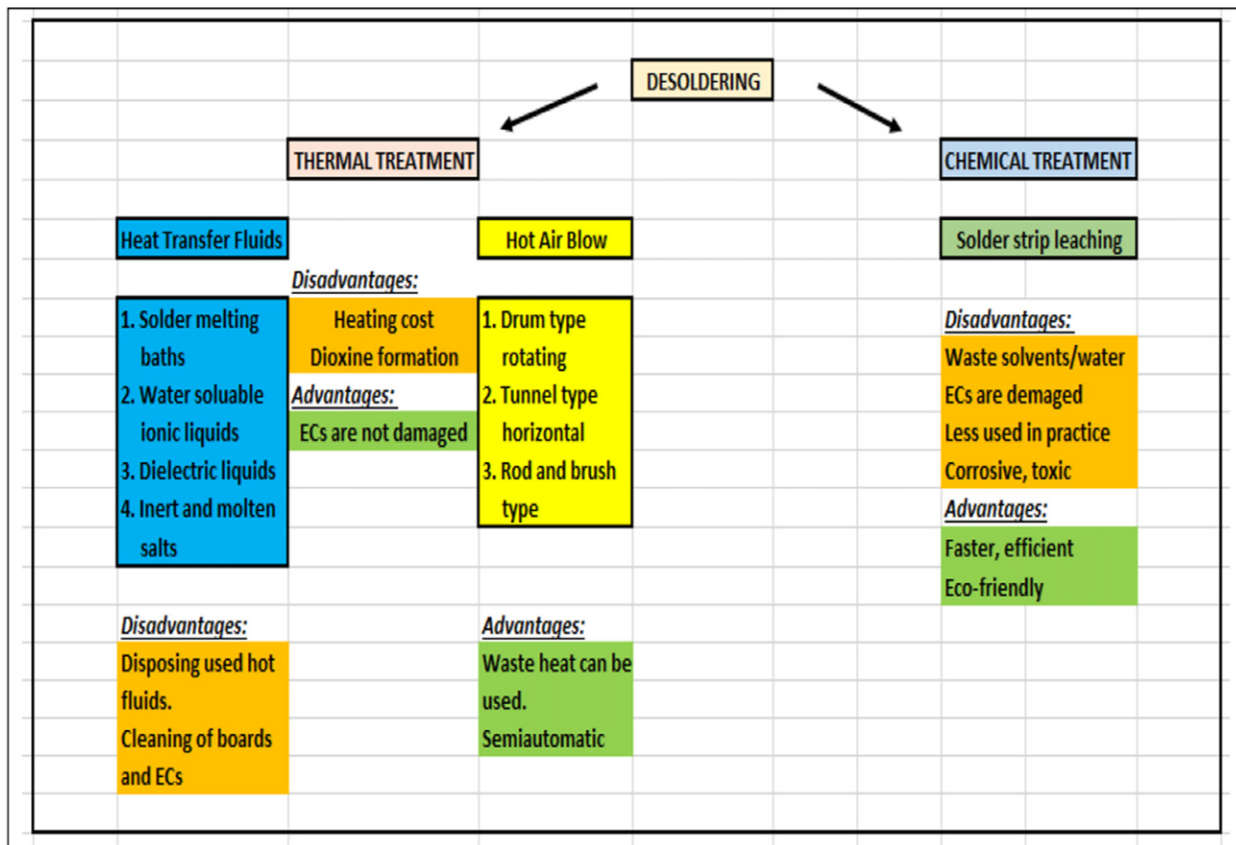


Fig. 4 Thermal and chemical desoldering treatment of WPCBs for disassembly.

Thermal Treatment for Desoldering

In thermal treatment, molten solder baths and different heating elements (i.e., wire/ribbon/strip/tabular resistances made of Nichrome (80/20 NiCr), Kanthal (FeCrAl), Cupronickel (CuNi), ceramic or composite), IR sources, hot air guns, hot air blowers, heat transfer liquids etc. can be used for heating WPCB assemblies for desoldering. Most of the large ECs and surface mount components (SMCs) are dislodged successfully from WPCBs by heating. However, through hole components (THCs) cannot be disassembled although all solder was removed from the WPCBs due to bending of pins under the PCBs and big components with more pins. But, these parts can be removed by a plyer without heating since there is no solder remained on the WPCBs after heating (Wang *et al.*, 2016). Heating method should give minimum damage to the ECs and most of the components should be reused. Heating of WPCBs is performed in a solder melting bath/stove, in a rotating drum dismantling machines, horizontal tunnel furnaces or IR heated lamps (250 W) and brushes. In solder melting baths, electricity is used in heating. When the solder melts, ECs are removed by hitting and shaking the board. Most of the ECs fall from the board. (Fig. 5). Industrial MX-300 melting stoves have a power of 4.0 kW, capacity of 0.4–0.8 tons/h/worker/table and a dimension of 720*500*390 mm (Web 3). One worker works at one tin melting stove table under fume hoods.

Heating with heat transfer liquids (hot fluids)

Bulk heating of WPCBs for desoldering can be achieved in water-soluble ionic liquids, 1-butyl-3-methylimidazolium tetrafluoroborate ((BMIm)BF₄) (Zeng *et al.*, 2013), dielectric liquids, transformer oils, mineral oils, methylphenyl silicon oil and cryogenic liquids (O₂, N₂, H₂, He and Ar). Ninety percent of the ECs were removed from WPCBs at 250°C with water soluble ionic liquids. Inert and stable molten salts (LiCl + KCl (58,2% + 41,8%) and NaOH-KOH eutectic composition (41% NaOH-59% KOH)) can be used as a heat transfer fluid to dissolve glasses, oxides and to destruct plastics present in WPCBs without oxidizing the most of the metals. At 450–470°C range, metal products in either liquid (solder, Zn, Sn, Pb etc.) or solid (Cu, Au, Fe, Pd etc.) form can be recovered. PCB pyrolysis gives 70% solid (metal and glass fiber), 23% oil and about 6% gas product in average (Flandinet *et al.*, 2012; Riedewald and Gallagher, 2015). Disposing the used hot fluid and cleaning of bare boards and components for further processing are disadvantages of using heat transfer fluids. Hot fluids have the disadvantages of generating large quantities of hazardous waste that need to be further disposed and bare boards and components need to be further cleaned (Chen *et al.*, 2013).



Fig. 5 Tin melting baths/stoves layout and operation for ECs dismantling from WPCBs.

Heating with industrial waste heat

Chen *et al.* (2013) used industrial waste heat (i.e., pulsating air jet) to melt solders and separated the ECs from base PCBs. They tested preheat temperatures in increments of 20°C between 80 and 160°C, and incubation times of 1, 2, 4, 6 or 8 min, heating source temperatures ranging from 220 to 300°C in increments of 20°C. The optimum preheat temperature, heating source temperature and incubation time were 120°C, 260°C and 2 min, respectively. The disassembly rate of small SMCs was 40%–50%, and THC and other SMCs were more than 98%. Inlet pressure was 0.5 MPa.

Automatic dismantling machines

WPCB dismantling machines are used to remove the solder and ECs from mixed type WPCB assemblies automatically in e-waste recycling. Thus, labor force is saved and only two people are enough for easy operation. Wang *et al.* (2016) used 245–265°C heating temperature, 2–8 min. incubation time and 6–10 rpm rotating speed for drum type of automated dismantling machine. According to Boks and Tempelman (1998), the main obstacles preventing automatic disassembly of WPCBs from commercially successful are too many different types of products, very small products, general disassembly-unfriendly product design, material logistics problems and control of functioning ECs.

Drum type dismantling machines

The high temperature and abrasion resistant cylindrical drum/barrel is made of steel. This machine works with gas/dust cleaning system or under exhaust hood (Fig. 6). Dismantling machines are safe, reliable and operated easily and have stable performance, high precision and the durability characteristics for WPCB recycling plants. Solder and dismantled ECs without damage are removed in one step by blowing hot air in the drum by a blower. WPCB dismantling machines have automatic temperature control system. Capacities range from 200 to 500 kg h⁻¹, motor power from 2.2 to 3.7 kW and weight from 0.35 to 0.60 tons (Web 4). ECs dismantling rate is claimed as high as 99% without dust in an eco-friendly way. The use of electrical resistances instead of hot air blowers are also possible for heating (Web 5) The off-gas purification with activated carbon is used to avoid hazardous gas discharge to the environment so as to protect workers' health and environment (Wang *et al.*, 2016).

Tunnel type dismantling machines

This system consists of a horizontal solder melting furnace with IR heaters, automated dismantling, dust catching, conveying and panel systems. Higher automation reduces dismantling labor and time. Dust catching prevents dust pollution in the environment. It requires less area in the plant. Dismantling machine technical block flowsheet is given in Fig. 7. From this operation solder, bare PCB assemblies, ECs and dust are collected. Tunnel type dismantling/depopulating machine cross-section details developed in the USA are shown in Fig. 8 (Web 6). 200 kg h⁻¹ capacity dismantling machine has external dimensions (l*w*h) of 8.1*1.6*3.3 m. Total power supply is 15.2 kW and total weight is 1.4 tons. Dust removing efficiency is more than 95% (Web 7).

Rod and brush type disassembly apparatus with IR heater

Park *et al.* (2015) designed and tested automatic rotating rods and sweeping steel brushes type apparatus to dismantle ECs from WPCBs. They used six IR heaters, three rows of rotating six feeding rods and six EC removing steel brushes (Fig. 9). 94% disassembly ratio was obtained at a feeding rate of 0.33 cm s⁻¹ and a heating temperature of 250°C.

Chemical Treatment for Desoldering

Desoldering chemical treatment requires the leaching of Sn and/or Pb to remove ECs on WPCBs. Hydrometallurgical leaching uses various lixiviants/chemicals (such as strong inorganic/weak organic acids, caustic watery solutions, halides etc) to selectively dissolve valuable metals. Chemical leaching is faster and more efficient; however, waste water and waste gas is generated invariably during this process. Hydrometallurgy can be industrially applied to metal recovery for WPCB recycling due to its flexibility, environmental-benign and energy saving features. Its corrosive and poisonous properties require corrosion-proof equipment as well as complicated process operation.

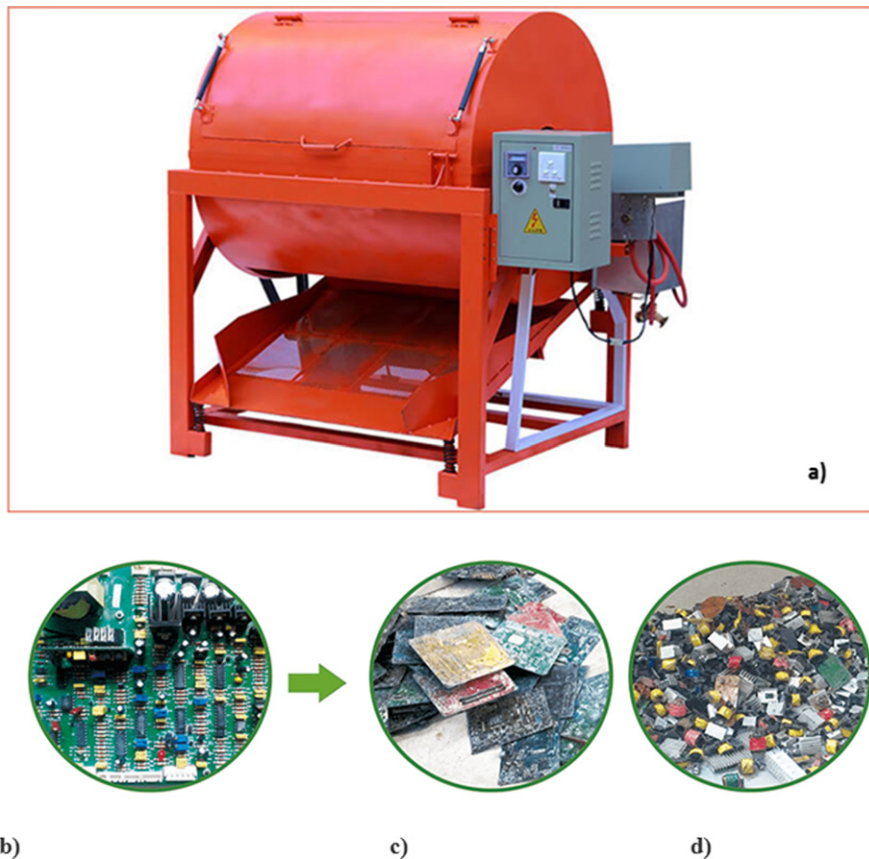


Fig. 6 Automated drum-type WPCB dismantling machine with ECs and solder separating screen (a) along with feed WPCBs (b), bare WPCBs (c) and ECs (d) obtained.

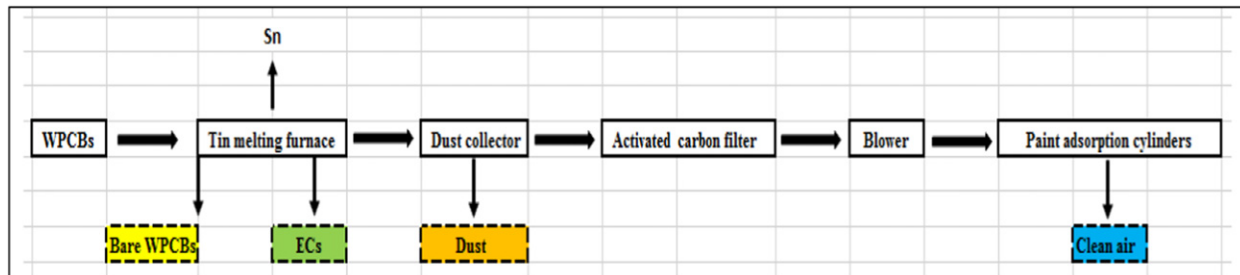


Fig. 7 Tunnel type dismantling machine flowsheet.

Generally, higher lixiviant concentrations and higher temperature enhance leaching rates. A smaller particle size and lower pulp density (solid/liquid (S/L) ratio) are desirable for metal leaching. The particle size can influence the surface area exposed to the leachant. A low S/L ratio indicates that larger volumes of liquid are required. Stirring speed is essentially related to diffusion phenomena, since higher stirring speed usually promotes mass transfer of reactants and reaction products in solution as the diffusion layer at the S/L interface is reduced. Overgrinding should be minimized for economic reasons, since this operation can only be justified to facilitate material handling or for homogenization purposes. Organic acids, which undergo biodegradation and are not evolve toxic gases, are considered as green acids as they are less toxic and corrosive in comparison to inorganic mineral acids.

Solder stripping leach

Several regenerable leaching systems were proposed and tested, e.g., electrogenerated Cl_2 in HCl solution (Kim *et al.*, 2011), $\text{FeSO}_4/\text{H}_2\text{SO}_4$ (Lister *et al.*, 2014), $\text{Fe}_2(\text{SO}_4)_3/\text{H}_2\text{SO}_4$ (Diaz *et al.*, 2016), FeCl_3/HCl (Fogarasi *et al.*, 2013, 2014, 2015), SnCl_4/HCl (for solder stripping) (Jian-guang *et al.*, 2016). Unfortunately, the electrochemical regeneration of chloride based leaching agents

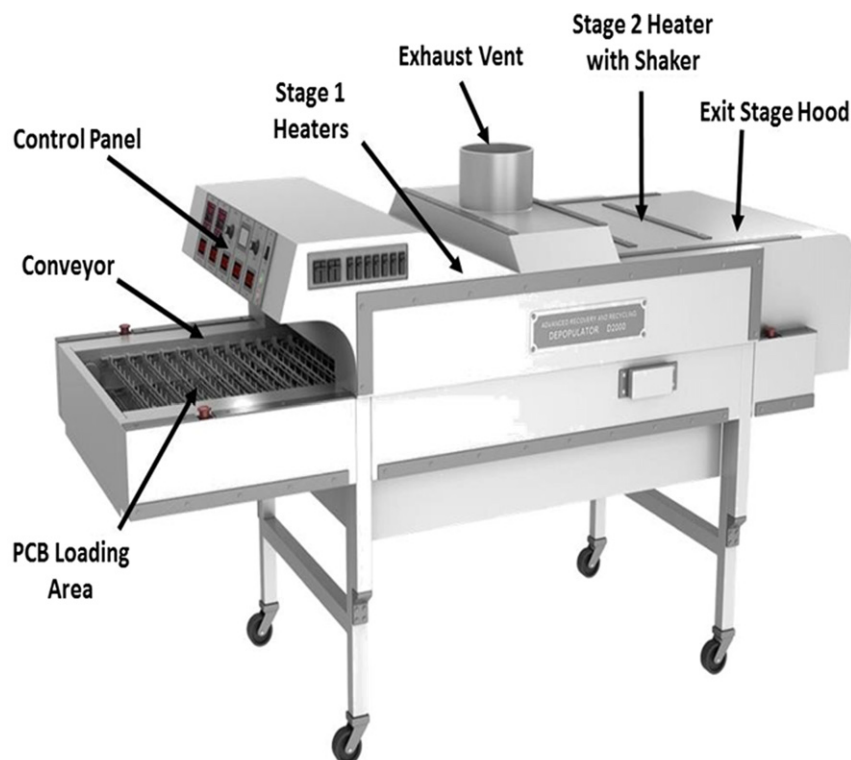


Fig. 8 Schematic view of tunnel type, heated dismantling/depollutor machines.

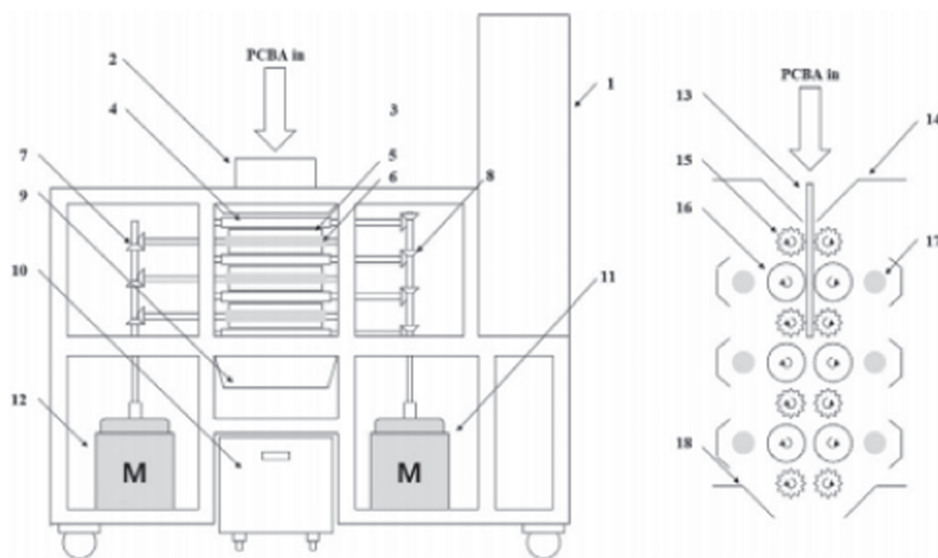


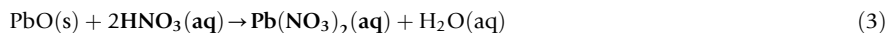
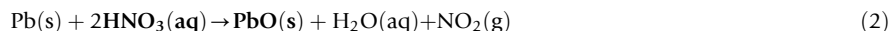
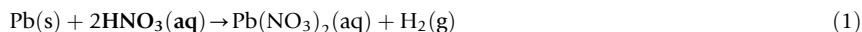
Fig. 9 Rods and brush type ECs disassembly apparatus (on the left); Structure of the disassembly apparatus (on the right).
 1. Control Panel (controllable factors: rotating speed of feeding rod, rotating speed of steel brush, heating temperature), 2. PCBA, 3. Feed hopper, 4. Feeding rod, 5. Steel brush, 6. IR heater, 7, 8. Trapezoidal gear change, 9. Product hopper, 10. Basket, 11, 12. Motors. (right) Detailed diagram of the disassembly modules. 13. PCBA, 14. Feed hopper, 15. Feeding rod, 16. Steel brush, 17. IR heater, 18. Product hopper.

Fig. 9 Rods and brush type ECs disassembly apparatus (on the left); Structure of the disassembly apparatus (on the right).

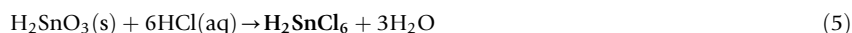
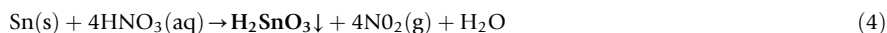
presents the risk of chlorine evolution, requiring well sealed equipment. Also, the presence of sulfate induces a low rate of the solder alloy dissolution if large amounts of Pb are present. The Br_2 based lixivants can be also used, but some authors suggest that these are unattractive due to the high vapor pressure of Br_2 (28 kPa at 35°C) (Zhang *et al.*, 2012). Contrarily, other researchers

indicate that the use of the adequate complexing agents like bromide or organic ammonium per halides can resolve this problem (Mpinga *et al.*, 2015).

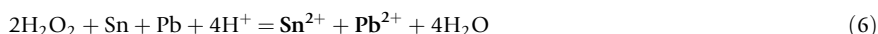
Pb dissolution from solder with HNO_3 oxidizes Pb to PbO which subsequently lead nitrate as given in the following equations:



Sn in solder partially dissolves at low HNO_3 concentrations and form metastannic acid above 4 M HNO_3 concentrations (Mecucci and Scott, 2002). This precipitated metastannic acid dissolves at low HCl concentrations:



Green and strong methanesulfonic acid (MSA) ($\text{CH}_3\text{SO}_3\text{H}$) (pK_a ($-\log K_a$): 1.9 and low molecular weight: 96 g/mol) biodegrade by forming CO_2 and sulfate and leaches solder along with oxidant H_2O_2 (Zhang *et al.*, 2017). Thus, 3.5 M MSA + 0.5 M H_2O_2 aqueous system provides environmental-friendly desoldering separation of Sn-Pb alloy for dismantling ECs from WPCBs. MSA is organic, environment friendly, biodegradable, less toxic, less corrosive acid. It also produces no toxic gas. In MSA- H_2O_2 desoldering leaching, H^+ and CH_3SO_3^- are ionized by MSA and the differences of the standard electrode potential between $\text{H}_2\text{O}_2/\text{Sn}$ (1.912 V) and $\text{H}_2\text{O}_2/\text{Pb}$ (1.902 V) are so close that they can be considered to be stripped down easily from the WPCBs with almost the same ratio at room temperature (Batnasan *et al.*, 2018). Moreover, H_2O_2 is relatively stable in the acidic medium, and its final products environmental-friendly, hardly affecting the recycling of the leachant. Thus, MSA- H_2O_2 aqueous solution system can be regarded as green desoldering separation of Sn-Pb alloy for simultaneous dismantling ECs from WPCBs. In MSA + H_2O_2 aqueous system Sn and Pb leached at room temperature in 45 min. with negligible Cu recovery as per following equations:



Dorneanu (2017) used aqueous bromine-bromide (Br_2/KBr) media for preliminary leaching and dismantling of WPCBs. In this electrochemical recycling system, all metallic parts were removed simultaneous with the lixivants regeneration and the partial electrodeposition of the dissolved metals. For dismantling, specific energy consumption was 0.65 kWh kg^{-1} of treated WPCB. After leaching tests, the remaining undissolved parts (fiberglass boards, ECs, plastics etc.) preserve their original shape and structure, allowing an easier consequent separation/classification and a more efficient recycling.

Size Reduction of WPCBs

The reutilization of WPCB is a focused topic in the field of environment protection and resource recycling. Presently, WPCB is mainly processed using physical, chemical and biological methods or combinations of these approaches. Size reduction is one of the key and crucial processes during pretreatment in recycling. Its importance for chemical and biological methods is that the crushing process must make the surface of the resulting particles appropriate for subsequent contact with the chemical or biological medium. Considering physical methods, particle sizes affect the subsequent process efficiencies, such as separation and leaching. In mechanical separation of metallic components from WEEE is easy to accomplish with a smaller particle size and a narrow size distribution (Cui and Forssberg, 2003; Oggunniyi *et al.*, 2009). During PM leaching, the smaller the particle size (due to higher surface area) the higher the leaching efficiency. But, finer sizes cause more dust generation and environmental pollution.

Kellner (2009) stated that WPCB comminution to -5 mm generated 96%–99% metallic liberation. Duan *et al.* (2009) found that most WPCBs were liberated in the 2–5 mm size. 95% liberation was obtained at -1 mm size for WPCBs. Shredding (fragmenting), crushing, pulverizing, grinding and ball milling are relatively traditional methods for reducing particle size. Recently, the use of cryogenics is being tested and it is believed that it could be used for size reduction in the future due to high cost. In this article, only shredding, pulverizing and delamination are covered in detail. Shredding is a process in which feed material is fragmented, ground, ripped or torn into small pieces. Then, shredded materials are granulated into fine particles (3–20 mm) in pulverizes. Leak tightness of size reduction machines and pipelines must be ensured. Dry crushing generates fugitive odor and dust during crushing. Wet impact crushing to -1 mm is possible. This prevents odor and dust problems and then wet gravity separation using Falcon concentrator can be used for metal recoveries (Duan *et al.*, 2009). Wet impact crushing has the advantages of higher crushing efficiency, less over crushing and no secondary pollution. Water can be recycled in the process only a small amount of fresh water need be supplied. Doddiba *et al.* (2016) proposed an underwater explosion method to disassemble the whole mobile phone units; but, since it is not suitable for industrial practice, it will not be covered here.

Shredders

Shredders are size reducing, crushing and volume reducing machines for e-waste. There are three types of industrial shredders; single-shaft, double-shafts and four-shafts (Fig. 10). Low capacity shredders use one motor and some high capacity shredders have two motors. Shredder machines employ a low speed and high torque mechanism at low noise, energy and dust. They have a wide range of applications because they can shred many different materials. Shredders include cutting chamber, bearings and gears, hexagonal shaft, feed hopper, guard, reducer, cushioned torque arm, drive belt, electric/hydraulic motor (s) and electric panel with PLC control, cabinet and base unit. Different kinds of blades are available for different material shredding to ensure durability and flexibility. Rotary knife thickness, shape, sharpness, design and processing sequence are important for high capacity and long lasting. For industrial shredder applications, blade diameters change from 200 mm up to 800 mm and blade thicknesses range from 20 mm to 80 mm. Thicker blades are used for higher diameter blades. As the blade diameter increases the number of blades increase from 16 to 50. Shredder capacities change from 300 to 40,000 kg h⁻¹ and power consumption from 7.5 to 264 kW (Web 8; 9).

Shredders crush material down to 20 mm. In a single-shaft shredder, the number of rotary blades is between 24 and 57; shaft diameter 220 and 350 mm; rotor length 500–2000 mm, rotating shaft speed 75 and 90 rpm, fixed knife 1 and 2; pressure 6 and 12 MPa; crushing capacity between 250 and 400 kg h⁻¹ and 600–1200 kg h⁻¹; feeding caliber/hopper size (l*w) between 550 and 650 mm and 1280 and 1300 mm; motor power outputs 18.5 and 55 kW; mesh size 20 and 40 mm; weight 3.5 and 9.5 tons and dimensions (l*w*h) 3000*1600*2200 mm and 4500*2500*2800 mm. In double-shaft shredders; the number of rotary blades is between 60 and 150; rotating shaft speed 65 and 87 rpm, fixed knife 4 and 8; blade thickness 30 and 75 mm; crushing capacity 500–2000 kg h⁻¹; feeding caliber (l*w) 700–800 mm and 1650 and 2000 mm; motor power: 18.5*2 and 45*2 kW and weight 4.0 and 9.5 tons. Product size changes from 5 to 20 mm. In four-shaft shredders; the number of main/assistant knife rotary diameter is between 150 and 400 mm; feeding caliber (l*w) 1000–800 mm and 2000–1800 mm; rotating speed 25 rpm; main knife 24 and 64 and main power 11*2 and 45*2 kW. Some companies are producing double story/flat double shaft shredders. Double story shredder and pulverizer on a single chassis are available on the market today. A precrushing shredder is accupulated on the same monoblock body with a pulverizer in some industrial equipment (Web 10).

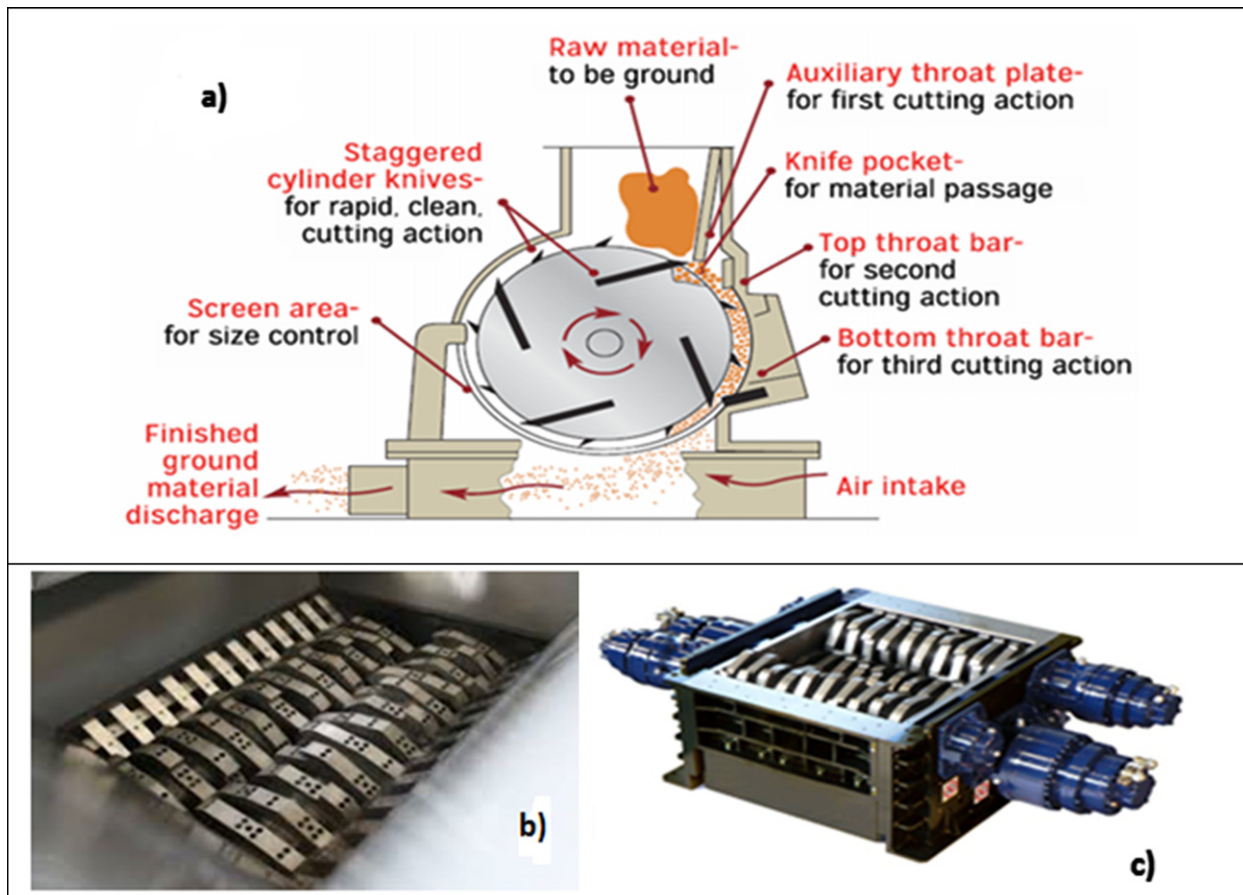


Fig. 10 Industrial scale single-shaft shredder cross-section (a), double-shaft shredder (b) and four-shaft shredder (c) photos.

Hammer Mills (Pulverizers/Granulators)

Granulator machines are designed with high speed, medium inertia, open rotor body for fine grinding, with 2, 3 or 5 hardened steel knives/blades. Granulators can grind material down to 0.185 mm or up to 5 cm in size. Generally resulting particles can vary in size from 3 to 20 mm. Interchangeable qualifying screens with various diameter holes determine the final reduction size. With decibel ratings of less than 65 dB, these units are ideal for placement at individual work stations. Pulverizers may be gravity discharge or pneumatic discharge. Pulverizers are ideal for heavy, hard and abrasive materials. Granulators are sized by the dimensions of the cutting chamber size ($l \times w$), which changes from 20*25 to 40*88 cm. Motor sizes range from 3.7 to 29 kW. Complete systems can include air discharge units or conveyors, and can easily be integrated with existing shredder or grinder systems. Granulators have a smaller footprint than a full sized grinder, but can still handle high volumes of product in the granulation process (Fig. 11) (Web 9). Hammer mills accomplish size reduction by impacting at a rate of typically 7000 rpms and higher (Kellner, 2009).

Hammer mills can be used for grinding scrap Cu wires, WPCBs, metals and plastics. These granulators are used for the sizing of plastics, non-ferrous metals, and heterogeneous materials and enable to reach controlled output size in the recycling process with the use of classifier screens starting from 2 mm diameter. Sizes of the granulators ($l \times w \times h$) change from (1060–1800) * (1700–1800) * (2000) mm; power from 8 to 90 kW and weight from 0.7 to 4.2 tons. Because of the strength and tenacity of WPCB material, much dust and harmful gas could be produced in the process of dry pulverizing at normal temperatures. On the other hand, after very long operation, very high temperatures can develop in the equipment causing melting and jamming of the particles and, hence, reduced efficiency of crushing/pulverizing and environmental pollution too. A way to enhance crushing efficiency and reduce secondary pollution during processing of WPCB is an important problem. One typical method is to cool the WPCB below the embrittlement temperature using liquid nitrogen and then crush it. The high cost of low temperature crushing limits its further industrial application. To achieve high crushing efficiency and to resolve the secondary pollution problems of dust and gas from the crushing process, a wet impacting crusher can be used to perform comminution of WPCB in a water medium (Duan *et al.*, 2009).

Fractionator

The fractionator process technology is a breakthrough or emerging process to recycle metals from e-wastes in a purely mechanical way. The underlying physical principle is to use the different properties of the materials (density, plasticity, ductility etc.) to separate the layers by creating huge accelerations and decelerations. In a fractionator, a composite material (like WPCBs) with heterogeneous composition and size is submitted to a high frequency series of accelerations and decelerations (impacts). The phases of the material react differently due to their heterogeneous densities and plasticities (Web 11). During accelerations (respectively decelerations), the lighter phases tend to go faster (respectively slower), which create shearing forces at the boundaries. Impacts deform the phases in different ways according to their plasticities. The metals, which are ductile, tend to aggregate into compact shapes and the minerals (i.e., fibers) which are brittle be fragmented while the plastics tend to keep their original shape. WPCBs are shredded and granulated to less than 22 mm. During the process, ferrous materials are easily separated by magnetic separation.

Delamination

The series of high frequency impacts are achieved in a fractionator machine which features an annular space between a rotor and a stator equipped with radial tools. Materials are fed from the top and fall by gravity. The high speed rotation of the rotor drives the materials which then impacts with a high frequency the static tools of the stator as shown in Fig. 12 (Web 11).

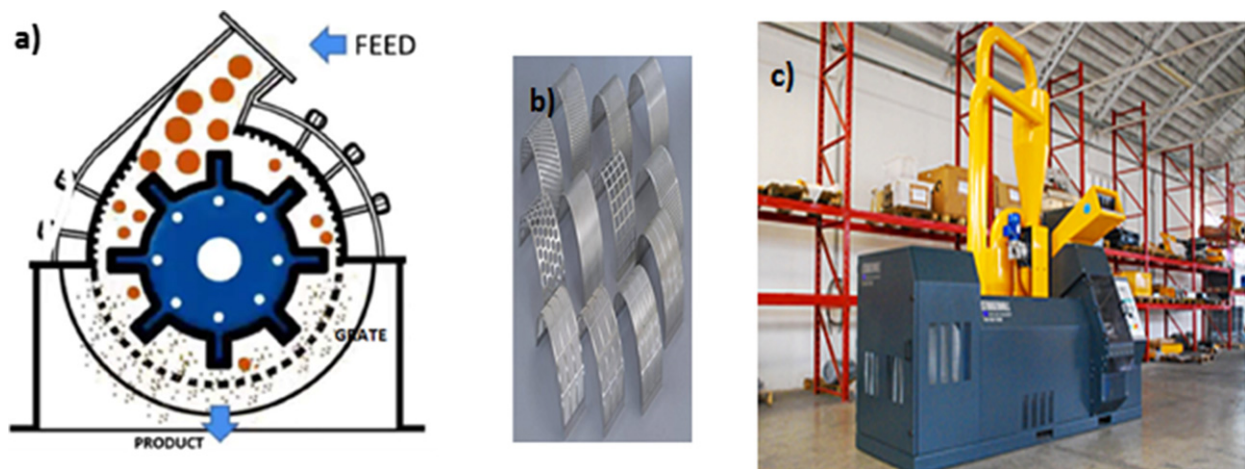


Fig. 11 Hammer mill cross section (a) with detachable screens (b) and industrial scale pulverizer machine along with dust collection cyclone (c).

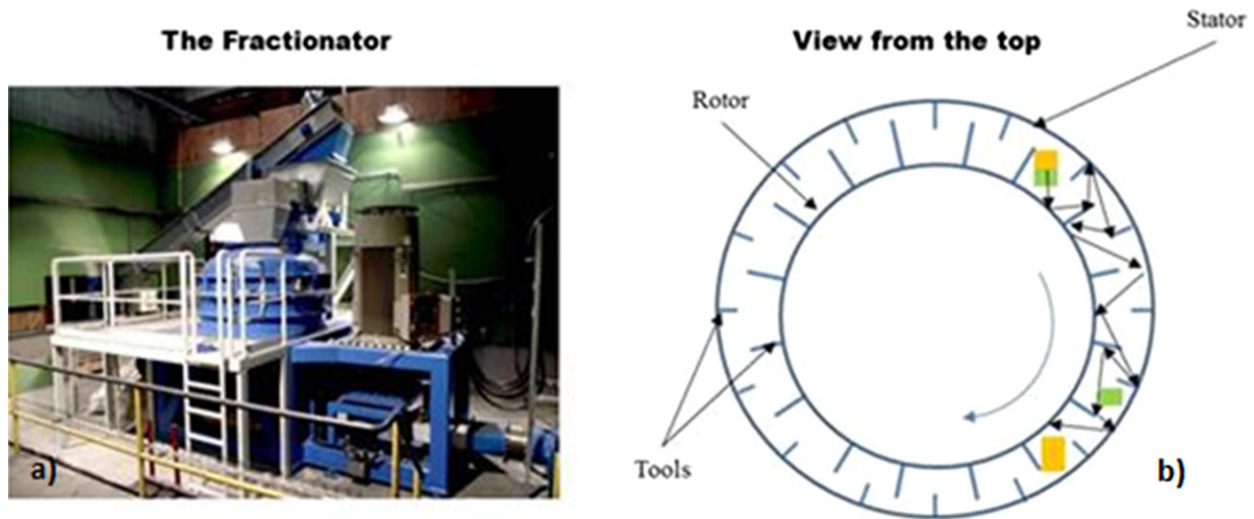


Fig. 12 Industrial size fractionator (a) and cross-sectional view (b).

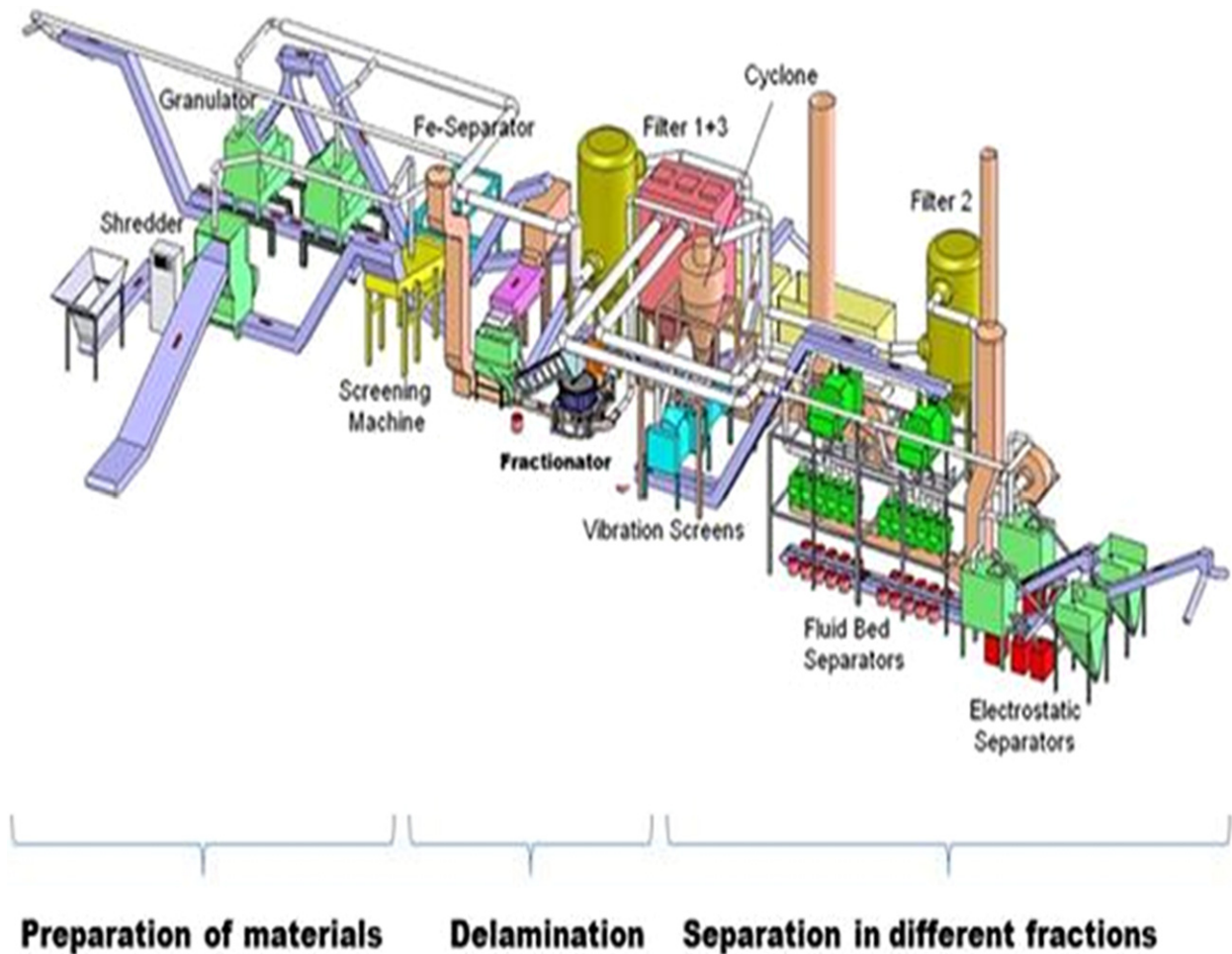


Fig. 13 Mechanical separation with fractionator and fluidized bed separator for delamination.

Fractionation with delamination

At the bottom of the fractionator, metals, plastics, minerals are liberated; but, still need to be separated. The size distribution is much differentiated at the exit of the fractionator. Plastics are found in relatively coarse particle size distributions. Al and Cu metals

are found as very pure granules with sizes between 50 μm and 5 mm. PMs are in the fines sizes. This makes the two stage separation process (by size and density) very efficient. Metals and nonmetals are separated by size. Light (Al) and heavy (Cu) metals are separated by density in a fluidized bed separator (Fig. 13). (Web 11 and 12).

The process generates different output fractions: Several nonmetallic fractions (plastics, resins, fibers, etc.) with sizes, a ferrous fraction, several light metal (typically Al) fractions, several heavy metal (PMs, Cu and Cu alloys, Ni, Pb etc.) fractions and three dust fractions (the 3 stages – Granulator, Fractionator and Separator – are equipped with aspiration systems and filters). This process has been used more than 20 plants built worldwide since 1995 with the previous generation fractionators. Metal recovery rates are claimed to be above 97%, and the output fractions have a high purity. This process is environmentally friendly; due to dry mechanical treatment, low temperature, no gases or fluids and very limited ultimate wastes. This flexible process has a capacity of 3 t h⁻¹ for very wide range of wastes, suitable for very small lots and campaigns. This plant layout has a competitively low capex and opex, high automation with only 2 workers per shift (Web 11 and 12).

Sizing/Classification

Industrial sizing of materials is extensively used, and the types of equipment are many and varied. Screening is generally carried out on relatively coarse material, as the efficiency decreases rapidly with fineness. Fine screens are very fragile, expensive and easily blocked. Screening is generally limited to the material above about 250 μm in size, finer sizing normally being undertaken by classification (Wills, 1988). Industrial screens may be stationary (i.e., grizzly, sieve beld) or moving (i.e., revolving, reciprocating, gyratory, vibrating etc.). Classification is a method of separating mixtures of minerals into two or more products on the basis of the velocity with which the particles fall through a fluid medium. In classification; hydraulic classifiers, hydrosizers, mechanical classifiers, spiral classifiers hydro/air cyclones can be used (Wills, 1988). Round and rectangular deck shaken sieves and drum sifters are used to classify and sort material according to the size. Trommel screens are large-drum shaped devices with a grate-like surface with large openings. Trommels are used to separate very coarse materials from bulk materials such as coarse plastics from finer Al recycled material. Air/water classifiers, cones, rake classifiers or cyclones can also be used for size classification. Cyclones are essentially settling chambers where the effect of gravity has been replaced by centrifugal acceleration.

Conveyor Belts

Belt conveyors transport material between equipment. Conveyor belts in various sizes and configurations with or without cross-belt magnetic separators for removing ferrous fragments from the flowing material stream during a recycling process are used. Industrial conveyor belt length changes between 2.0 and 3.5 m; width between 0.5 and 0.8 m; height between 1.5 and 2.0 m; weight from 120 to 400 kg; roller diameter size from 10 to 17 cm; roller height from 10 to 53 cm and motor power from 0.5 to 1.1 kW.

Filtration Systems

Filtration systems, operating with sleeve filters, offer a full range of solutions for the dedusting of WPCB recycling process improving the air quality and increasing the efficiency of plants. Reliable and robust SM filters can provide air cleaning with control system. Triple dust collector systems (tetra cyclone + air purifying electrostatic precipitator) or pulse dust removal devices are generally used. Dedust system and activated carbon adsorption tower realize no pollution in whole recycling process. Plants are designed with exhaust gas treatment system. In order to avoid exhaust gas and bad smell for the high temperature, plants are equipped with water spray and active carbon absorption system.

Conclusions

The handling of e-waste including combustion in incinerators, disposing in landfill or exporting overseas is no longer permitted due to environmental pollution and global legislations. The problem caused by e-waste increasingly becomes an international issue due to the characteristics of e-waste amount, discarding continuously, high value materials content and most of all pollutants migration. In order to achieve environmental and metal sustainability in circular economy, green processes need to be developed for the recycling of valuable metals and nonmetals from e-waste. WPCBs, which are the core and most valuable part of WEEE due to PM contained, are a dangerous toxic waste; but, at the same time WPCBs are attractive polymetallic secondary source, referred to as "Urban Mines". WPCBs may contain more than 60 metals and some nonmetal substances. Today in e-waste recovery, material (and metal) centric recycling approach changed to product centric eco-efficient recycling approach.

Illegal and crude e-waste recycling techniques (such as dumping, acid leaching or open burning) used in developing countries are not eco-efficient and economical processes today. Current state-of-the art recycling processes are capable of recovering <95% of the in-feed metals. The development of the recovery technologies for WEEE has entered a new stage. The WEEE disposing

technologies have evolved from simple manual disassembly, classification and sorting to high value-added novel utilization technologies (i.e., physico-mechanical separation and pyro/hydrometallurgical processes) after removing the reusable electronic components by thermal and/or chemical desoldering pretreatment. The components reuse oriented selective disassembly technology for WPCBs with wet chemical selective desoldering can both prevent environmental pollution and recover expensive solder (contains Sn + Pb) material along with bare WPCBs which also contain some nonmetals (i.e., resins, and glass-fibers) and some Cu.

A disassembly stage using thermal and/or chemical desoldering is always required to remove both dangerous components and reusable ECs. Disassembly has traditionally been undertaken manually, but newly developed automated systems impact upon future recycling strategies both to maximize cost-effectiveness for low-value component recovery and as an initial stage for recycling approaches to maximize yield of residual intrinsic-material value. Selective dismantling after desoldering, comminution with two step crushing (i.e., shredding to – 20 mm, delamination and/or pulverizing to – 3 mm) and separation are then key points for improving successful further treatments. 95% metal and nonmetal liberation can be achieved at – 1 mm size. Developing new, clean and economical technologies for recycling of complex and heterogeneous WPCBs is significant challenge. A hidden value in the e-waste can be unlocked by both sustainable recovering base/precious/scarc metals and nonmetals from WPCBs. Therefore, processing of the e-waste must optimize recovery of metals and nonmetals, preserve resources, save energy, prevent pollution, generate new jobs, accelerate economy, minimize final waste volume and processing emissions.

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Waste Printed Circuit Board (WPCB) Recycling: Conventional and Emerging Technology Approach

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Introduction

Disposal and incineration of e-waste can pose threats to the whole environment, from the atmospheric to the aquatic and terrestrial compartments. In recent years, recovery of metals and/or nonmetals from e-waste has become increasingly important due to potential risk of strategic and scarce raw materials and environmental concerns. The useful life of electrical and electronic equipment (EEE) has been shortened as a consequence of the advancement in technology and change in consumer patterns. This has resulted in the generation of large quantities of e-waste that needs to be managed properly. The handling of e-waste including combustion in incinerators, disposing in landfill or exporting overseas is no longer permitted due to environmental pollution and global legislations. Additionally, the presence of BMs and PMs makes e-waste/WPCBs recycling attractive economically. The main purpose of this article is to provide a comprehensive review for conventional and emerging WPCB recycling technologies using physico-mechanical treatment and/or pyrometallurgical process solutions for secondary metal recoveries. WPCB recycling contributes to resource efficiency, access to critical raw materials and innovation.

It is clear that mechanical pretreatment, which includes desolder dismantling stage to remove both dangerous components and reusable ECs, and metal-nonmetal liberation, are frequently required with the aim to improve the valuable metal and/or nonmetal recovery rates. Selective manual dismantling is still in operation despite the attempts to proceed by simultaneous automatic dismantling procedures, which however, need more progress to be really effective. Shredding, crushing, pulverizing and physico-mechanical separation are then key points for improving successful further end treatments.

Here, firstly separation of metals from WPCBs using physico-mechanical preprocessing and then pyrometallurgical routes are critically analyzed. Pyrometallurgical routes are widely used in e-waste recovery industries and comparatively economical and eco-efficient if the hazardous emissions are controlled. In this article; the existing industrial WPCB recycling practices, used equipment types, sizes and capacities are also covered. Industrially, different physico-mechanical and/or metallurgical routes are separately and/or successively used to extract valuable metals from e-waste. Both pyrometallurgical and hydrometallurgical processes are commonly employed to recover BMs and PMs. Here, pyrometallurgical route was described and its advantages and disadvantages are outlined. Finally, insights into e-waste recovery in the World context are presented. The challenges and barriers associated with recovery of the BMs and PMs are highlighted.

Eco-efficient recycling of WEEE/WPCBs is very important. This means achieving the environmental and economic balance in recycling. It entails maximizing both the physical recycling of metals (or other materials) and the revenue obtained, while minimizing the associated environmental burden and total cost. An eco-efficient process also considers the “environmental fingerprint” of materials, i.e., how much negative environmental impact can be saved by recycling, for example, a metal instead of producing it “new” by mining. Due to the considerable (environmental) impact of turning PMs from low grade ores into pure metals, a high overall recycling yield of them has not merely economic benefits, but also substantial ecological advantages. E-waste recovery offers a sustainable solution to WPCB in order to extract reusable metal components while eliminating organic matter as well as all toxic gas and emission. The end product is a high-grade nonferrous metal concentrate which can be directly reintroduced into the marketplace.

Conventional and Emerging Recycling Methods

Table 1 shows the classification of traditional and emerging WEEE/WPBC recycling methods. Incineration, mechanical separation (gravity) and open acid leaching are conventional crude recycling methods. Pyrometallurgy, physico-mechanical separation (gravity/magnetic/electrostatic), hydrometallurgy, electro-chemical, vacuum metallurgical, super critical and other novel technologies are advanced new technologies. Here, traditional technologies, physico-mechanical separation and pyrometallurgical methods are covered and compared in detail. In the metal recovery processes, mixed type of WPCBs are typically crushed, ground and smelted without disassembling the ECs (Lee *et al.*, 2012). Disadvantageously, when WPCBs are ground, only the plastic fraction can be effectively liberated from metals. However, this leads to the recovery of only Cu, Au and Ag metals and loss of low concentration rare metals. These rare metals can only be recovered by hydrometallurgical processes. Therefore, it is imperative that ECs are disassembled in order to recover these valuable and scarce metals.

Conventional Methods for WPCB Recycling

Incineration

In this process, different type of mixed WEEE is burned in the blast/shaft furnace to obtain 75%–85% black Cu. Then, oxidized in converter and later reduced in the anode furnace. Impurities are mostly segregated into the vapor phase and are discharged in the

Table 1 Classification of conventional and emerging methods for WPCB recycling

Conventional methods	Advanced methods
● Incineration (i.e., burning in blast furnace) ● Mechanical separation – Wet gravity separation (i.e., shaking tables) – Dry gravity separation (i.e., zigzag 3-way air classifier) ● Acid leaching (solubilization + purification)	● Pyrometallurgical technology (smelting + converting + refining) ● Physico-mechanical separation (Gravity-magnetic-electrostatic) ● Hydrometallurgical processes – Mild extraction technology – Bioleaching – Biosorption ● Electrochemical technology ● Supercritical technology ● Vacuum metallurgical technology (vacuum evaporation/sublimation) ● Other novel technologies (ultrasonical, mechanochemical technologies)

off gas. Anodic Cu can be purified with H_2SO_4 along with Ni, Zn and Fe (Zhang and Xu, 2016). Thermal methods result in the emission of hazardous chemicals to the atmosphere and water due to the degradation of epoxy and volatilization of metals (including Pb, Sn, As and Ga). These processes are also high energy consumer and require expensive exhaust gas purification systems and corrosion resistance equipment (Chen *et al.*, 2015a).

Mechanical Separation

This process comprises shredding and grinding of the whole mixed e-waste, followed by separation and concentration using dry/wet gravity separators. WPCBs are ground only plastic resin fraction can be effectively liberated from metal fraction and toxic gases are evolved due to temperature increase in the mill. Accordingly, mechanical methods do not result in high recovery rates, especially for PMs. With dry mechanical separation processes, the potential loss of PMs may be high due to liberation problem between metals and plastics. E-wastes are managed without proper handling by informal sectors in under-developed and developing countries. Since the informal sectors cannot invest in high-tech equipment and machines, it is important to provide a more economical, yet environmentally friendly mechanical separation solutions to this problem. Therefore, it is important to provide simple physical material recovery procedures, which can be applicable for informal sectors.

Acid Leaching

Generally, acid leaching technology is technically more exact, predictable and controllable in material extraction from resources and has already been applied in WPCB recycling for almost three decades (Kaya, 2016c; Lee *et al.*, 2012; Baba, 1987). Various lixiviates/solvents (such as strong inorganic acids, caustic watery solutions or halides) are used to selectively dissolve and precipitate metals in leaching. Selectivity and effectiveness of valuable metals are always important in leaching process. Traditionally, inorganic mineral acids ($HCl/H_2SO_4/HNO_3/HClO_4$) can be used for extracting BMs (Cu, Pb, Zn etc.). Aqua regia (AR) can also be used for non-selective and aggressive digestion of base (Cu, Pb, Zn) and precious (Ag, Au) metals from WEEE. The corrosivity towards Cu, Fe and brass have been proposed in the following order: $HNO_3 > H_2SO_4 > HCl$ (Samina *et al.*, 2011). The majority of hydrometallurgical routes for processing WPCBs use H_2SO_4 (cheapest and widely used acid) leaching in the presence of H_2O_2 as oxidizing agent, followed by solution refining. The use of HNO_3 and HCl was also studied extensively; but, because of the environmental regulations and corrosive nature of these leaching agents they are as appropriate as the less hazardous H_2SO_4 (Yang *et al.*, 2011). HNO_3 has the maximum environmental impact (Iannicelli-Zubiani *et al.*, 2017). Generally, higher acid concentrations and higher temperatures enhance leaching rates. A smaller particle size and lower pulp density (S/L ratio) are desirable for metal leaching (Gu *et al.*, 2017). Low S/L ratio indicates that larger volumes of liquid are required. Metal recoveries most of the time is higher than 90%. Leaching time changes from 60 to 180 min. Leaching can be accelerated with the use of mixing and supercritical CO_2 (g) with significantly increased power consumption (Calgaro *et al.*, 2015).

Advanced Methods for WPCB Recycling

Pyrometallurgical Metal Recovery Processes

Pyrometallurgical processes for recovering metals from various waste materials have been used during the last two decades. Smelting in furnaces, incineration, combustion and pyrolysis are typical e-waste recycling processes. The high temperature in furnace or smelter is generated via the combustion of fuel or via electrical heating. Technical hardware includes submerged lance

smelters, rotary furnaces, electric arc furnaces etc. In contrast to WPCBs from computers, monitors and TV boards usually contain massive Fe and Al parts (i.e., cooling elements, transformers, frames etc.) and possibly large condensers. It is recommended to remove these massive parts before sending the remaining boards to the integrated smelter and refinery (ISR) for final processing. Benefits of such a removal are twofold: Firstly, Al and Fe parts can be valorized by sending to appropriate endprocessing facilities. Secondly, the WPCBs freed from these massive parts are relatively upgraded in the Cu and PM contents, which will generate better revenues obtained from smelter. Such state-of-the-art smelters and refineries can extract valuable metals and isolate hazardous substances efficiently. Such recycling facilities can close the loop of valuable metals and reduce environmental impact arising from large quantities of e-waste. Currently, e-waste recycling is dominated (about 70%) by pyrometallurgical routes, whereas the steel industry embraces the ferrous fractions for the recovery of Fe, and the secondary Al industry takes the Al fractions. The metal fractions separated during the preprocessing of e-waste are composed of Fe, Al, Cu, Pb and PMs. Since Fe and Al, Cu and Pb are the main constituents of a typical e-waste, it is logical to send e-waste to smelters that accept Cu/Pb scrap. Currently, Cu and Pb smelters work as e-waste recyclers for the recovery of mixed Pb/Sn, Cu and PMs. In these pyrometallurgical processes, e-waste/Cu-Pb scraps are fed into a furnace, whereby metals are collected in a molten bath and oxides form a slag phase. Cu smelting route is more environmentally friendly and cheaper than Pb smelting route (Khaliq *et al.*, 2014).

Both ferrous and nonferrous smelters need to have state-of-the-art off-gas treatment in place to deal with volatile organic compounds (VOCs), dioxins and furans. Paints, labels, plastics and resins contain significant amount of flame retardants. Painted scrap should be delacquered prior to smelting using appropriate technologies. For treatment of WPCBs, it is utmost importance that smelter is equipped with state-of-art-gas treatment equipment, since otherwise dioxins are formed and emitted. Process gases are cooled with energy recovery and cleaned. A number of technologies are available for destruction or capture of dioxins, furans and other gases, such as adiabatic coolers, scrubbers, bag house/electro filters and catalytic decomposition are used in combination for optimum performance (Gu *et al.*, 2017). Formation of dioxins during smelting can be prevented by sufficiently high temperatures and long retention time in the smelter. Excess heat from off-gas can be used in subsequent processes.

Pyrolysis, which belong to pyrometallurgical route, has some obstacles to limit large scale operations at present: (1) the yields of gas and liquid generated are low that indicate economic effect; (2) further separation is essential for mixture of pyrolysis residues and metals; moreover pyrolysis residues generally contain toxic materials, like PBDD/Furans and PCDD/Furans and should be disposed properly; (3) the further process cleaning, which would lead to more complex of the process and facilities, which is required for the metals obtained from the course of pyrolysis (Wang and Xu, 2015).

The WPCBs and small devices are mixed with catalysts, by-products from nonferrous industries or primary ore and directly (without further size reduction) treated in ISR. Organic components are converted to energy during smelting. Mechanical upgrading other than disassembly, grading and shredding for bulk volume reduction prior to smelting is not undertaken due to inherent yield loss, particularly of PMs. This loss may be typically in the order of 10% but may be much higher (Kellner, 2009).

Metals from WPCBs were separated utilizing two steps microwave heating. Firstly, heating WPCBs to a temperature sufficient to combust the organic materials present, and the metals of low melting point (like Sn and Al) are removed simultaneously; secondly, heating the WPCBs to a higher temperature at which glass formers present in the WPCBs begin to vitrify, and then metals with higher melting points could be recovered from the solidified residues or might be removed at their respective melting points which are below the vitrifying temperature. This approach is highly efficient; however, this recycling technology has not been transferred to industry because of its high economic cost (Jones *et al.*, 2002). In the processing, the crushed scraps are burned in a furnace or in a molten bath to remove plastics, and the refractory oxides form a slag phase together with some metal oxides. Further, recovered materials are retreated or purified by using chemical processing. Energy cost is reduced by combustion of plastics and other flammable materials in the feeding. Soare *et al.* (2016) used a laboratory furnace with microwave field in Ar inert atmosphere to melt WPCBs after comminution (0.5–2.0 cm) at 1000–1200°C for 30 min. A complete separation of the metallic fraction from the organic components was achieved. Multi-component metallic alloy was processed through combined hydrometallurgical and electrochemical methods. Microwave melting presents a series of advantages, such as rapid heating cycles saves about 35% energy compared to conventional melting, and improved process control, no direct contact with the heating materials, the possibility of processing various nonferrous metals containing wastes.

Industrial processes for recovering metals from e-waste are based on combined pyrometallurgical, hydrometallurgical and electrometallurgical routes. Fig. 1 shows pyrometallurgical Cu production layout from primary ores and WPCBs. In pyrometallurgical processes, e-waste is blended with other materials and incorporated into primary/secondary smelting processes (e.g., into Cu or Pb smelters) at 1250°C. Cu smelting is the dominating route for e-waste recycling where PMs are collected in Cu matte or black Cu. In the final stage of Cu production, i.e., the electro refining process, pure Cu metal is produced and the PMs are separated into slimes where they are recovered using hydrometallurgical routes. Currently, various industrial processes are used globally for extracting metals from e-waste, including the Umicore Hoboken (Belgium) ISR facility, the Noranda process in Quebec (Xstrata), Rönnskär smelters in Sweden (Boliden), Kosaka's recycling plant in Japan (DOWA), the Kayser recycling system in Austria and the Metallo-Chimique N.V plants operated in Belgium and Spain. SIMS Recycling Solution in Singapore and Roorkee, and Attero Recycling in India are some other important e-waste recyclers.

In pyrometallurgical processing, generally WEEE firstly dismantled, shredded, ground for size reduction and liberation of components and then, smelted in furnaces (i.e., blast furnace, reverberatory furnace, Imperial smelting furnace, Outokumpu flash smelting, Mitsubishi continuous smelting, Isasmelt/Csiromelt, Noranda, CMT/Teniente, Vanyukov (Russia), Bayia (China), plasma arc furnace etc.) to obtain coarse Cu sulfide/metal ingots. Noranda uses 10%–14% WPCBs and 86%–90% Cu concentrate as feed. The two basic and widely applied smelting processes include flash and bath smelting. The next step is converting process in

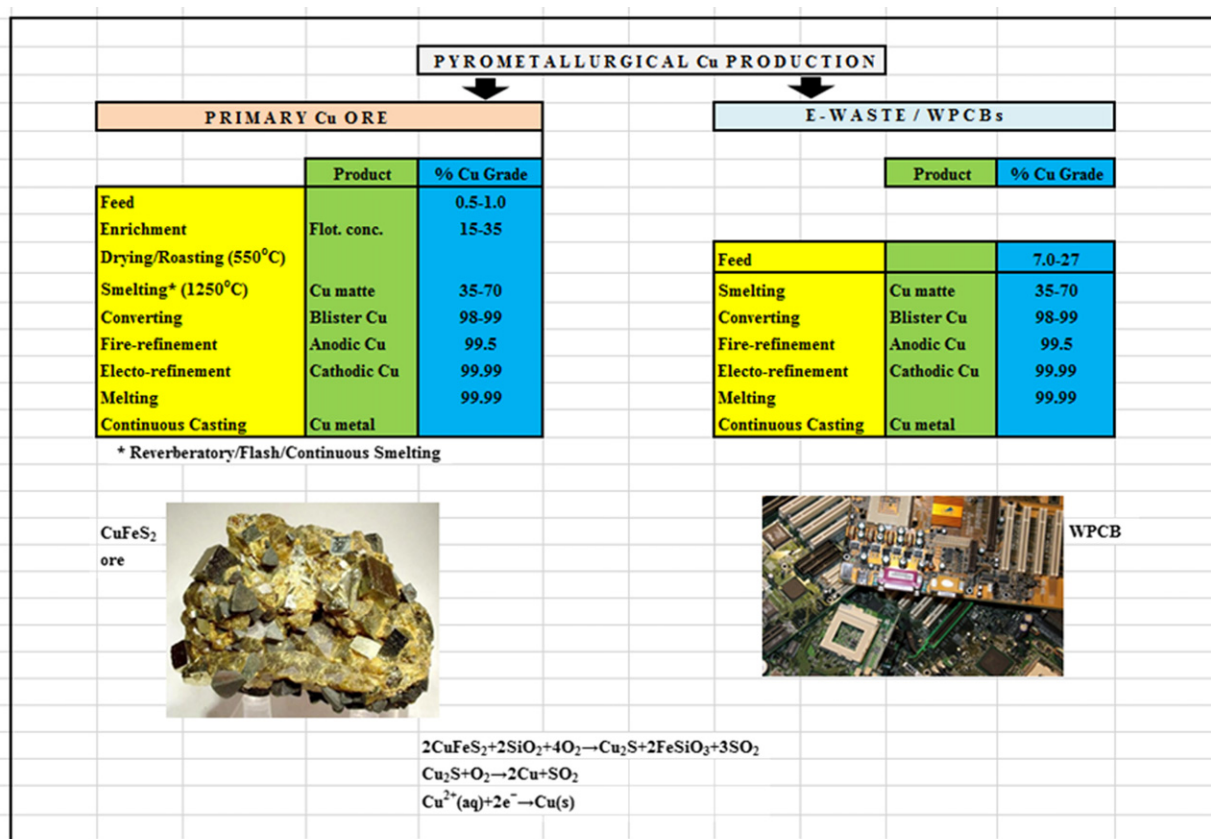


Fig. 1 Pyrometallurgical Cu production layout from primary Cu ore and WPCBs.

Cu converter by blowing hot air from tuyeres in order to obtain molten Cu matte (Cu-Fe-S) (35%–70% Cu). This step oxidizes iron sulfide and convert copper sulfide to metallic blister Cu (about 98.5% Cu). The last step is anodic Cu production in a furnace (99.5% Cu). Anodic Cu is refined by electrolysis to obtain 99.99% Cu ingots and PMs are recovered from anodic mud. **Fig. 2** shows schematic diagrams of Rönnskär smelter for Cu production from both ore concentrate and e-waste. [Zhou and Qiu \(2010\)](#) used 12% NaOH as slag-formation material which promotes the effective separation of metals from slag.

Another application for pyrometallurgical process was the plant of Umicore's ISR, which include Cu smelter, Pb blast furnace and PMs and SMs refineries along with H₂SO₄ plant (**Fig. 3**). Umicore has the world's largest waste recycling facility at Hoboken, Belgium at a feeding capacity of 350,000 t y⁻¹ and annual production capacity of over 50 tons of PGMs, 100 tons of Au and 2400 tons of Ag ([Hagelüken, 2006](#); [Khaliq et al., 2014](#)). Umicore planned to expand its production capacity to 500,000 t y⁻¹ ([Scott, 2014](#)). This process mainly focused on recovery of PMs from WEEE including Ag, Au, Pt, Pd, Rh, Ru and Ir. Its procedures include: firstly, WEEE is pretreated (i.e., dismantling, shredding and physical processing) and then the precious metals operations (PMO) are smelted in an IsaSmelt furnace. Almost all other metals are concentrated in the slag after smelting; thirdly, the slag is further treated at the base metals operations (BMO). The base metals are the byproducts from the PMO which are subjected to electrolytic refining to gain high purity BMs, such as Cu ([Le Ret and Briel, 2011](#); [Tuncuk et al., 2012](#)). At Shanghai Xinjinqiao Environmental Co., Ltd. and Yangzhou Ningde Precious Metal Co., Ltd. in China with the capacity of 5000 t y⁻¹ WPCBs; vacuum metallurgical separation is used to reclaim metals including Cu purification and other metals, such as Pb, Cd, Bi *et al.* separation sequentially (**Fig. 4**) ([Wang and Xu, 2015](#)).

Glass or binder encapsulation, where harmful contents are safely sealed in, to produce low grade construction blocks, is a further emerging thermal process being developed at the expense of resources lost. Vacuum, thermal plasmas and lasers to enhance the thermal treatment are novel research topics being searched ([Kellner, 2009](#)).

Drawbacks of pyrometallurgical processes

Pyrometallurgical routes are generally more economical, eco-efficient and maximize the recovery of PMs, however, they have certain limitations that are summarized here ([Khaliq et al., 2014](#)):

- Recovery of plastics is not possible because plastics replace coke as a reducing agent and fuel as a source of energy;
- Fe and Al recoveries are low, due to the loss of noble metals into the slags, and are not easy as they end up in the slag phase as oxides;

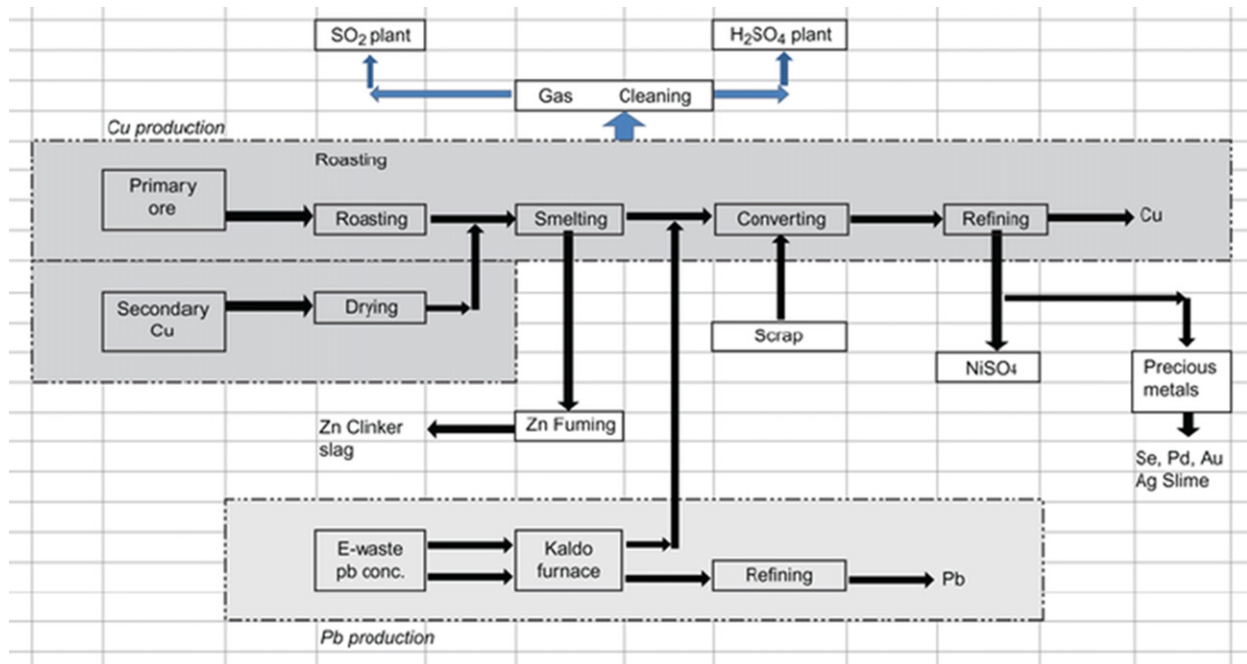


Fig. 2 Boliden's Rönnskär smelter (Skelleftehamn, Sweden) flowsheet for Cu production. Reproduced from Zhang, L., Xu, Z., 2016. A review of current progress of recycling technologies for metals from waste electrical and electronic equipment. *Journal of Cleaner Production* 127, 19–36. doi:10.1016/j.jclepro.2016.04.004.

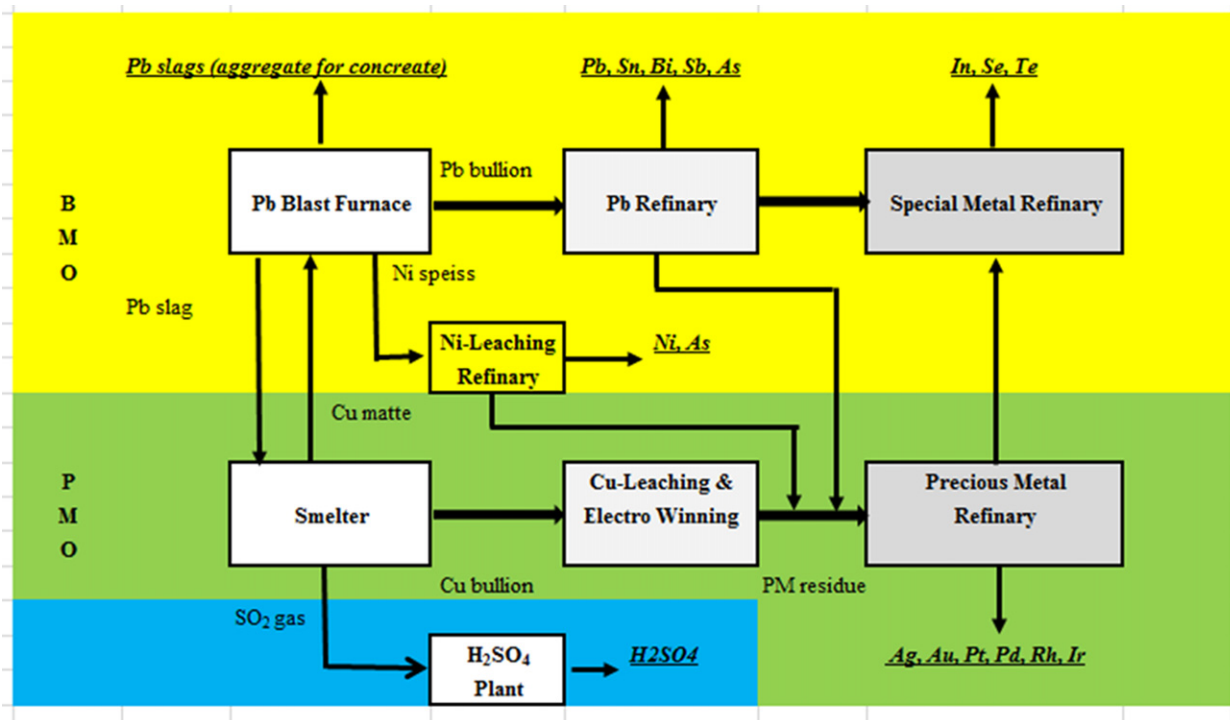


Fig. 3 Umicore Hoboken integrated smelter and refinery flowsheet.

- Hazardous emissions such as dioxins are generated during smelting of feed materials containing halogenated flame retardants. Therefore, special installations are required to minimize environmental pollution;
- A large investment is required for installing integrated e-waste recycling plants that maximize the recovery of valuable metals and also protect the environment by controlling hazardous gas emissions;

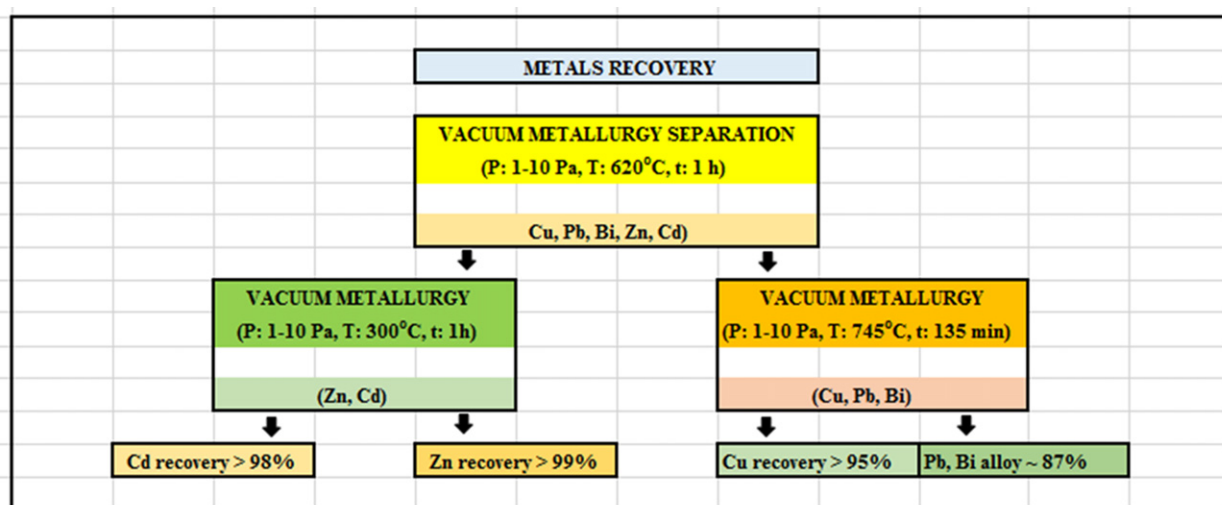


Fig. 4 Vacuum metallurgical separation of WPCBs.

- Instant burning of fine dust of organic materials (e.g., plastics) can occur before reaching the metal bath. In such cases, agglomeration may be required to effectively harness the energy content and also to minimize the health risk posed by fine dust particles;
- Ceramic components in feed material can increase the volume of slag generated in the blast furnaces, which thereby increases the risk of losing PMs from BMs;
- Partial recovery and purity of PMs are achieved by pyrometallurgical routes. Therefore, subsequent hydrometallurgical and electrochemical techniques are necessary to extract pure metals from BMs;
- Handling the process of smelting and refining is challenging due to complex feed materials. The expertise in process handling and the thermodynamics of possible reactions will be difficult.

Hydrometallurgical Metal Recovery Processes

The recycling of BMs and PMs is becoming more and more important, in order to counteract the depletion of scarce mineral resources, especially as the demand for these metals continues to increase. While all of the methods discussed above have proved effective at recovering metals from WPCBs, it is essential to develop more environmentally friendly processes that exhibit better performance in terms of both valuable-metal recycling and hazardous-substance control. These existing processes of recycling WPCBs focus on the recovery of the valuable materials in the WPCBs. Nowadays, physico-mechanical methods, which contain crushing, grinding, electrostatic separation, gravity separation, magnetic separation, density-based separation, etc., are widely employed to separate metals and nonmetals from WPCBs. Then, the nonmetal fraction (NMF) can be directly used as molding filler compound, concrete and modifier. After NMF modification high-value added products (i.e., catalysts, absorbents and filler support) can be produced. The recovered metallic powders may also need further purification before they can be utilized (Gao *et al.*, 2008). Zhu *et al.* (2013) separated WPCB bromine epoxy resin using dimethyl sulfoxide (DMSO) at S/L ratio of 1/7, 145°C for 60 min. Valuable metals and glass fibers are recovered after filtration and DMSO was regenerated.

For metals recycling from WPCBs without ECs, electrostatic separation (Hou *et al.*, 2010; Wu *et al.*, 2008; Li *et al.*, 2008; Li *et al.*, 2007), wet jigging (Sarvar *et al.*, 2015), froth flotation (Sarvar *et al.*, 2015; Estrada-Ruiz *et al.*, 2016), air current separation (Xue and Xu, 2013) etc., have been used to separate metals from nonmetals, pure metals can then be extracted from the mixed metals by vacuum metallurgy (Zhang and Xu, 2014; Zhan *et al.*, 2016; Zhan and Xu, 2011).

Hydrometallurgy (Chen *et al.*, 2015a; Jadhav and Hocheng, 2015; Chen *et al.*, 2015b; Qu and Li, 2014), biohydrometallurgy (Rodrigues *et al.*, 2015; Arshadi and Mousavi, 2015, 2014; Jadhav *et al.*, 2016; Chen *et al.*, 2015c) and supercritical fluid (Liu *et al.*, 2016; Calgaro *et al.*, 2015; Xiu *et al.*, 2015) have also been applied, to leach valuable metals from WPCBs. Valuable metals can be further recovered from leaching solution by adsorption-elution (Neto *et al.*, 2016) electrowinning (Fogarasi *et al.*, 2014, 2015) and so on. Nowadays, the main technologies used for the recovery of valuable metals from WEEE are based on pyrometallurgical and hydrometallurgical processes (Cui and Zhang, 2008). Generally, hydrometallurgical processes are technically more predictable and controllable in material extraction from resources (Cui and Zhang, 2008) and have already been applied in WEEE recycling for almost three decades (Zhang and Xu, 2016; Baba, 1987; Cui and Zhang, 2008; Sheng and Etsell, 2007; Behnamfard *et al.*, 2013). Thus, continued research on the recycling of WPCBs is necessary. Hydrometallurgical process is typically used to purify metallic powders, which are leached in aqueous solvents such as strong acids and alkalines. This is often applied together with other complexing agents, such as oxalic acid, acetic acid, cyanide, halide, thiourea, and thiosulfate. Hydrometallurgical process easily generates a large amount of

waste acid, alkaline liquid and sludge, which cause secondary pollution. Hydrometallurgical processes are less energy and cost demanding than pyrometallurgical treatments, and also applicable in plants with relatively small capacities (Le Ret and Briel, 2011). Biometallurgical technology, which based on microorganisms assisted reactions, has been regarded as a potential major technology breakthrough and has already applied in waste recycling. The leaching process is the initial and the most important step for both hydrometallurgical technology and biometallurgical technology. Pyrometallurgical processes require the heating of WEEE at high temperatures (often greater than 1000°C) to recover valuable metals. These thus represent highly energy-consuming treatments that lead to the production of hazardous gases that must be correctly removed from the air with flue gas cleaning/treatment systems. Recently hybrid technologies have also been applied, which integrate the chemical approach (more efficient) with biological strategies (more eco-compatible), thus taking advantage of the benefits of both chemical and biological leaching (Pant *et al.*, 2012).

Physico-Mechanical Separation Process

Physico-mechanical separation techniques include gravity, magnetic and electrostatic separators together. Simplified process flowsheet for a mixed WEEE metal recovery plant has a manual sorting line to remove batteries, toners/inks, paper and external cables; shredding and manual picking line/band to remove large capacitors, motors and transformers; over band magnetic separation to remove coarse ferrous metals; pulverizing followed by magnetic separation to remove again fine ferrous metals and steels; Eddy current separators (ECS) to separate metallic (Cu and Al) and nonmetallic (plastics, rubbers, glass, wood and stone) and finally Cu rich and Al rich materials can be separated by density separation (Kellner, 2009).

Gravity separation

Gravity separation is based on the specific density differences. Concentration criterion (CC) can be used for gravity separation using the following equation:

$$CC = (\rho_h - \rho_{\text{fluid}}) / (\rho_l - \rho_{\text{fluid}}) \quad (1)$$

where ρ_h : specific gravity of heavy material; ρ_l : specific gravity of light material and ρ_{fluid} : specific gravity of fluid medium (water/air). If $CC > \pm 2.5$, gravity separation is relatively easy until 74 μm . If $2.5 < CC < 1.25$, efficiency of gravity separation decreases. Separation is possible between 149 and 250 μm particle sizes. If $CC < 1.25$ gravity separation can be possible under careful density control conditions.

$$\text{For plastics and Al/glasses, } CC = (2.7 - 1) / (2 - 1) = 1.7 \quad (\text{Gravity separation is possible; but, not easy}) \quad (2)$$

$$\text{For plastics and metals, } CC = (7 - 1) / (2 - 1) = 6.0 \quad (\text{Gravity separation is easy}) \quad (3)$$

$$\text{For Al/glasses and metals, } CC = (7 - 1) / (2.7 - 1) = 3.53 \quad (\text{Gravity separation is easy}) \quad (4)$$

After required liberation, plastics and Al/glasses can easily be separated from metals by gravity separation methods. Plastics and Al/glasses gravity separation can be possible under careful specific gravity control conditions.

Gravity concentration methods separate materials of different specific gravity by their relative movement in water or air. Nonetheless, this separation is not only dependent on the density of the components, but also on their size and shape. Besides gravity one or more of the other forces, like force exerted by the viscous liquids, can serve as the separation medium (Kaya, 2016a). Rectangular riffled air tables can be used for e-waste sorting. By using different heavy liquids (such as tetrabromoethane-TBE (2.97 g cm^{-3}) and acetone, which lowers density and viscosity), the metals can be separated from the plastics or ceramics. Al metal went to the light fraction due to the lower density. Cu was more effectively separated at size 149 μm (Hanafi *et al.*, 2012). Water or airflow tables, heavy media separation and sifting are common gravity separators used in e-waste recycling. Different metal particles can be further separated. For this purpose, the WPCB material is processed on concentrating tables. The shaking tables exploit the difference in the specific gravity and particle size to achieve desired separation. The principle of the air classification technique is based on the suspension of the particles in a flowing air stream and the separation of the particles based on their density difference. Air tables move back and forward shaking at 200–300 rpm. Air tables have an upward tilt. They are equipped with a porous deck, which is inclined and subjected to vibration which causes material in contact with the deck surface to convey up the inclined surface of the deck. Low-pressure air by a blower is forced through the deck to fluidize the dry mixture so that the lighter materials are lifted from the deck surface and allowed to float down the inclination of the deck. The final result, presented at the discharge face of the deck, is a continuous, graduated progression from the least to most dense, smallest to largest, and least to most aerodynamic (Fig. 5). The feed side is lower and concentrate side is higher. Narrow size range feed (0.25–3.2 mm) is introduced to the air table (The riffles are always taller on the feed side of the table, and decrease in height as they progress towards the tailing side of the table). Material is fed perpendicular to the riffles and the high density material remains behind the riffles and low density material flows above and over the riffles. Air tables are used for separation of metallic and plastic components from a feed of $\sim 7 \text{ mm}$ in size after ferromagnetic separation. Recovery rates for Cu, Au and Ag of 76%, 83% and 91%, respectively achieved from low grade WPCB or general e-scrap. Gravity separation techniques which are well-known in the mineral processing industry have found their way into e-waste recycling based on the fact that e-scrap consists essentially of plastics, with a density less than 2.0 g cm^{-3} ; light metal, primarily Al and glass, with a density of 2.7 g cm^{-3} ; and heavy metals, predominantly Cu and ferromagnetics, with a density more than 7 g cm^{-3} . In sink-float separation, both PC and PCB scraps $\sim 50\%$ (weight) of floats which is primarily plastics can be separated out at the specific density of 2.0 g cm^{-3} (Zhang and Forssberg (1997)). Sarvar *et al.* (2015) used a jig for $+0.59$ and 1.68 mm WPCB particles.

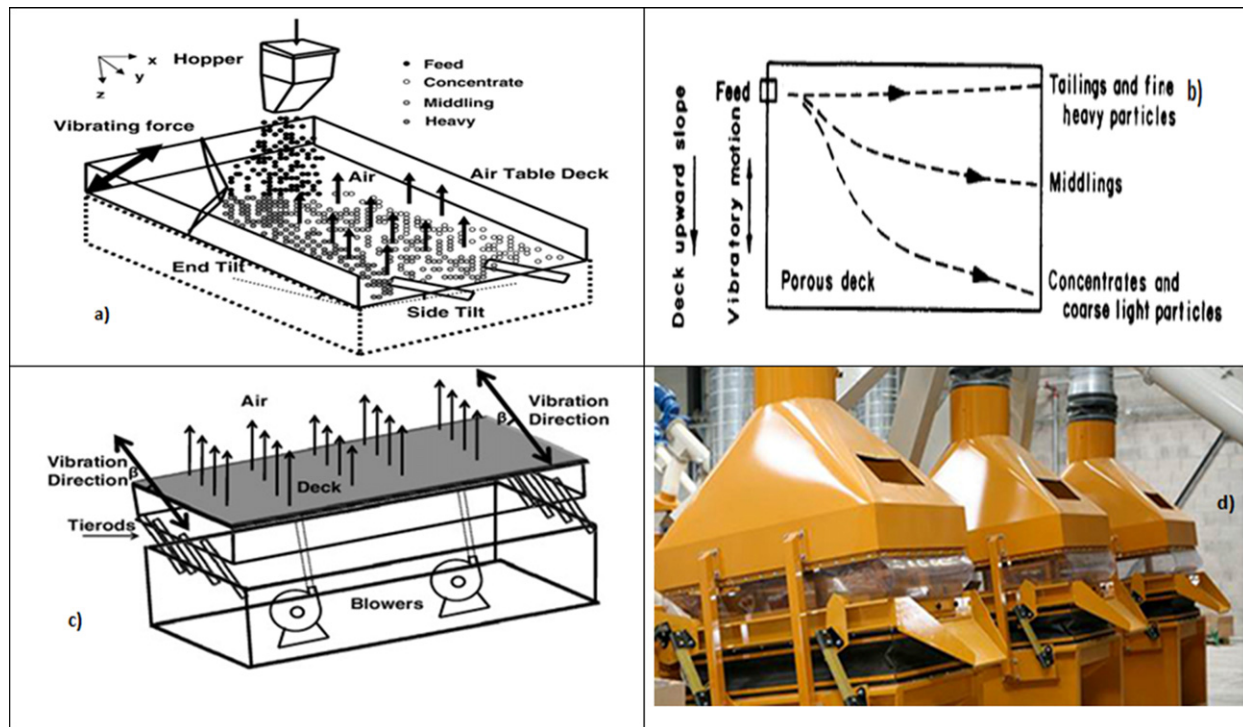


Fig. 5 Gravity separator for e-waste recycling: (a) Dry shaking air table details, (b) schematic material separation, (c) air table working principles, and (d) industrial scale equipment.

Wet gravity separation

In the past, WPCB recycling lines with gravity separating type used widely wet gravity separators (i.e., hydraulic shaking tables, jigs, Falcon centrifugal separator etc.) to obtain only crude Cu metal particles from WPCBs. Metals and nonmetal (i.e., plastic and glass fiber) materials have different densities. If there is a large difference in densities, gravity separation is more economical than electrostatic separation. This process produces huge amount of waste water and residues, which may create serious secondary environmental problems. Other metals and nonmetals cannot be recycled (Huang *et al.*, 2009). Recently zigzag 3-way air classifiers were used for dry separation (pneumatic) to overcome above problems along with magnetic and electrostatic separators. Fig. 6 shows a typical wet gravity separation flowsheet for WPCB recycling. Cu metal can be separated from plastics. Ferrous material is removed after shredding by magnetic separators. Wet separation reduces air and noise pollutions, recycle water and reuse limited resources. Duan *et al.* (2009) used a Falcon SB40 centrifugal separator to recycle metals from WPCBs crushed to less than 1 mm. This separator separates materials by density using up to 300 g acceleration. Industrial scale plants have a capacity of 0.8–1.0 t d⁻¹, power requirement 160 kW, water requirement 20–30 t d⁻¹ and floor space requirement 150 m². Dimensions (l*W*h) are 26.3*6.1*6.4 m. Fe recovery rate is claimed to be 99% and Cu and epoxy resin recovery rates are more than 95% (Web 1). Angle of deck, length and frequency of stroke, splitter positions and riffle heights, feed rate and pulp density (above 40%) significantly affect the separation efficiency.

Dry gravity separation

Dry WPCB recycling equipment with air-separation type is applicable to recycle various waste and bare WPCBs. The mixture of metal and nonmetal materials gained from crushing-pulverizing-classifying of WPCB materials is fed into the material hopper of air separator, then into the separating zone of the separator to separate metal, glass fiber and resin mixtures. Since the separator is connected with a dust removal system, a horizontal air current is formed which moves the materials in horizontal direction. Meanwhile, with the action of the gravity, the materials move downward. Due to the different specific gravity of materials, nonmetal materials such as fine dust and grains with lower gravity are taken away by the dust removal system when the mixture passes the separating plate, leaving the metal materials with larger gravity into finished product recovery zone. Thus, the separation of metal from nonmetal materials is achieved. Zigzag (3-way) air classifiers remove the light part of heterogeneous materials by means of an air flow in counter-current inside a zigzag pipe. They clean residues and separate light parts in WPCB recycling. Fig. 7 shows zigzag air classifier details and dry gravity separation plant picture. Industrial scale plant capacity is about 0.2–0.3 t h⁻¹. Low noise, no need for water, no dust pollution, power and labor savings and no waste and above 95% metal and nonmetal recoveries are main advantages. Floor space requirement (l*w*h) is 7*5*5 m and load weight is more than 10 t. Dust pollution is prevented by two-in-one dust removal device: cyclone collector and pulse bag dust collector (Web 2). Air table techniques can be utilized for the separation of particulate fractions in the 5–10 mm, 2–5 mm and <2 mm ranges, respectively (Kellner, 2009). High

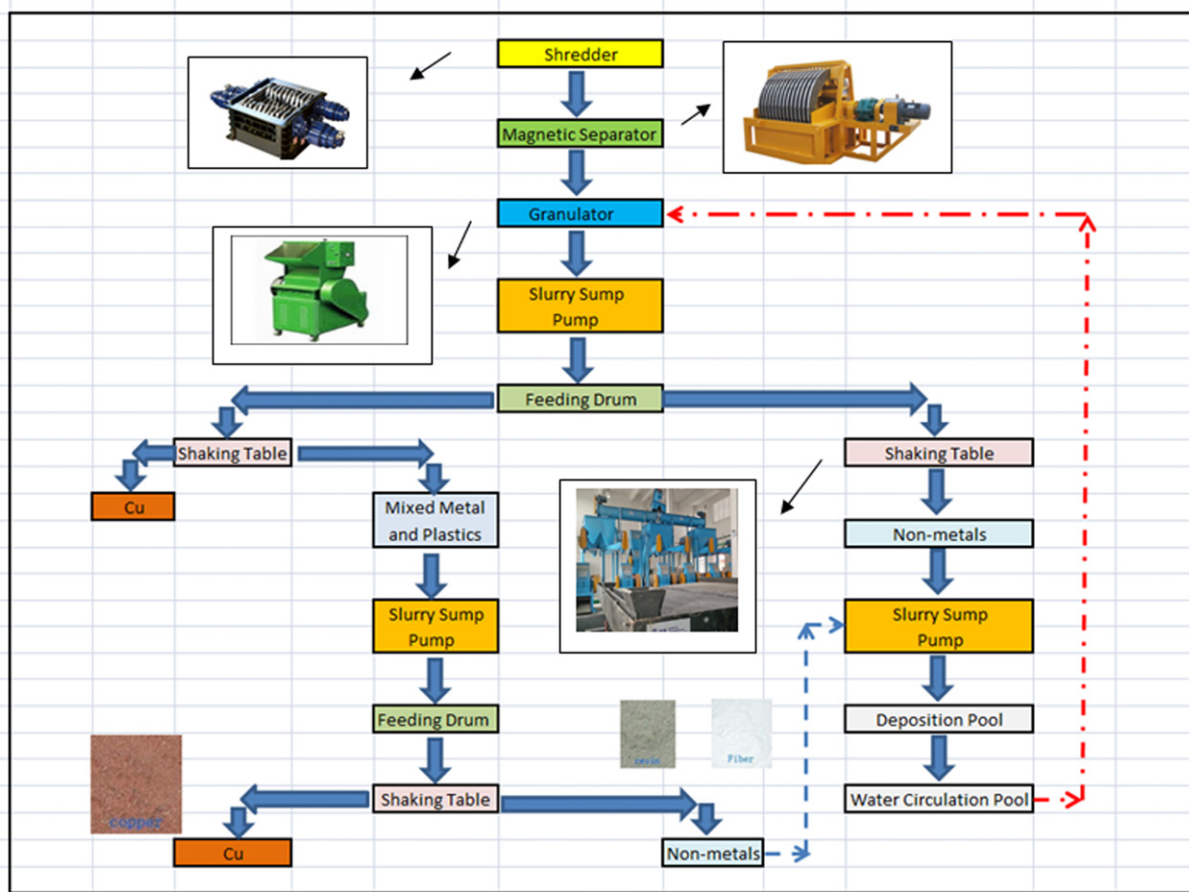


Fig. 6 Flowsheet of wet gravity separation for WPCB recycling.



Fig. 7 Zigzag air classifier: (a) Working principle, (b) pilot plant classificatory, and (c) industrial scale equipment.

selectivity with high upgrading ratio and able to see separation and making adjustments, no need for addition thermal drying are advantages of dry air tables. Low capacity, large floor area requirements, frequent operator attention, checking and adjustment, noisy and dusty, dust control system requirement and feed sizing requirements are the main disadvantages.

Zhang *et al.* (2017) used vibrating gas-solid fluidized bed (VGFB) for recovering residual metals from nonmetallic fraction (Fig. 8). Vibrated fluidized bed column segregates metals, plastic organics and glass fibers at different size classes according to particle size, shape and density at different superficial air flow rates ($0.1\text{--}0.2\text{ m s}^{-1}$), fluidization frequencies ($20\text{--}30\text{ Hz}$) and fluidization times ($120\text{--}150\text{ s}$). Compared with coarse fraction, the segregation of fine particles has a need for lower vibration frequency and superficial air velocity but longer fluidizing time. The metal recoveries of $-1 + 0.5\text{ mm}$, $-0.5 + 0.25\text{ mm}$ and -0.25 mm size fraction are 86.4%, 82.2% and 76.6% respectively, meaning the bad segregation efficiency of VGFB for fine particles.

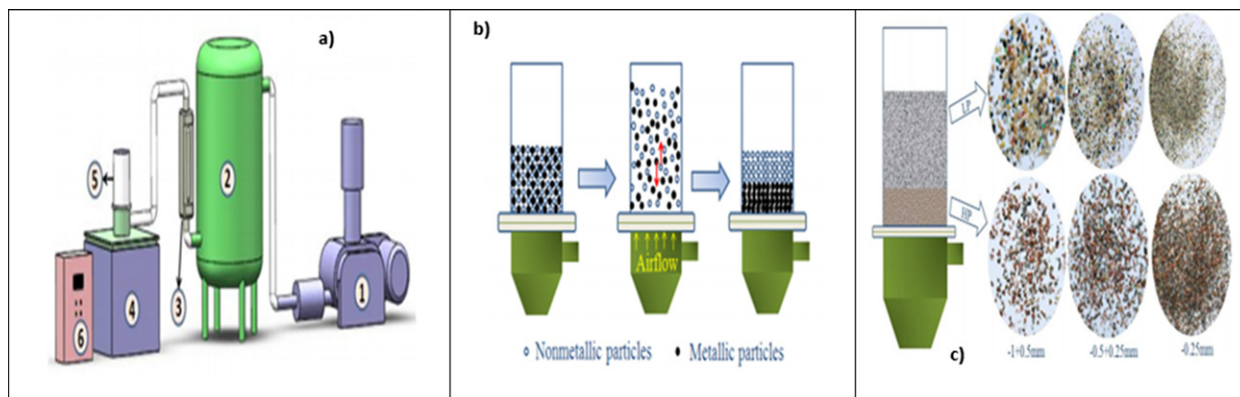


Fig. 8 Segregation process of metallic and nonmetallic particles in a vibrated gas-solid fluidized bed separation system: (a) Illustration of vibrated gas-solid fluidized bed separation system ① roots blower; ② pressure tank; ③ rotameter ④ vibrating table ⑤ gas-solid fluidized vessel; ⑥ control unit, (b) segregation process of metallic and nonmetallic particles, and (c) segregation results for each size fractions. Reproduced from Zhang, G., He, Y., Wang, T., *et al.*, 2017. New technology for recovering residual metals from nonmetallic fractions of waste printed circuit boards. *Waste Management* 64, 228–235. doi:10.1016/j.wasman.2017.03.030.

Dry air tables use a shaking motion similar to that of wet shaking tables, but instead of water, air is used to separate heavy materials. The table deck is covered with porous material and air is blown up through the deck from a chamber underneath. The chamber equalizes the pressure from the compressor and thus ensures an even flow of air over the entire deck surface. Generally, air tables consist of a ripped top deck mounted over a base that contains a compressor. The deck is tilttable and riffles are tapered, much like a wet shaking table. The attached motor powers the system. The dry feed is introduced at one corner of the deck. The deck is shaken laterally and air pressure is regulated to keep lighter materials move down slope along the shortest route. Heavier particles move upslope due to the movement of table. Splitters allow and adjustable middling fraction to be collected (Web 3).

Electrostatic separation

Electrostatic separation (E-sorting) adopts high voltage electrostatic processing principle, separating the conductive metal and nonconductive nonmetal/nonferrous materials according to their conductivity/resistivity differences. Conductors have valence electrons from a sea of electrons between positive ion cores and insulators have valence electrons tightly bounded to nucleus. Ag, Cu, Au, Fe, Al, Mg, Zn, Cd, Ni, Sn, graphite are conductor and ceramic, glass, plexiglas, wood, paper, plastic, teflon, paraffin and resin are nonconductor (insulator/dielectric) components of WPCBs. Conductors have high conductivity and nonconductors do not have conductivity. Electrostatic separation system is the most innovative technology for an efficient final stream granulometric separation in recycling processes. Exploiting the electric fields generated the more conductive fraction (i.e., metallic) can be separated from the lower conductive fraction (for instance paper, plastic, rubber) (Web 4). The charged nonconductors are attracted to an oppositely charged electrode and collected.

A conductive material allows electrons to flow easily across its surface or through its volume. When a conductive material becomes charged, the charge (i.e., the deficiency or excess of electrons) will be uniformly distributed across the surface of the material. If the charged conductive material makes contact with another conductive material, the electrons will transfer between the materials quite easily. If the second conductor is attached to an earth grounding point, the electrons will flow to ground and the excess charge on the conductor will be “neutralized”. A material that prevents or limits the flow of electrons across its surface or through its volume is called an insulator. Insulators have an extremely high electrical resistance. A considerable amount of charge can be generated on the surface of an insulator. Because an insulative material does not readily allow the flow of electrons, both positive and negative charges can reside on insulative surface at the same time, although at different locations. The excess electrons at the negatively charged spot might be sufficient to satisfy the absence of electrons at the positively charged spot. However, electrons cannot easily flow across the insulative material's surface, and both charges may remain in place for a very long time.

The particles may be charged through contact electrification, conductive induction or high tension (ion bombardment). However, triboelectric charging is the most common. High voltage ionization, induction, tribo charger and lifting electrodes can be used around rotating grounded drum. One or more than one electrode series can be employed for charging. Conductor materials are pulled towards positive charging electrode(s). Nonconductors are scraped from the surface of rotating drum with brushes. There are three typical electrical conductivity-based separation techniques: (1) Corona electrostatic separation (CES), (2) Triboelectric separation (TES) and (3) Eddy current separation (ECS) (Kaya, 2016b). The electrostatic separating capability depends on the difference in polarity and the amount of charge acquired by particles to be separated. Induction or Corona charging can successfully separate the mixed particles that have large difference in conductivities. Tribo-electricity or contact charging is useful for charging and separating materials that have similar conductivities. The principle of ECS is that in separation zone gravitational, centrifugal, frictional, and magnetic deflection forces influence the falling particles, but only magnetic force deflects the ferrous particles to a higher degree. To separate ferrous particles, the magnetic deflection force acting on the ferrous

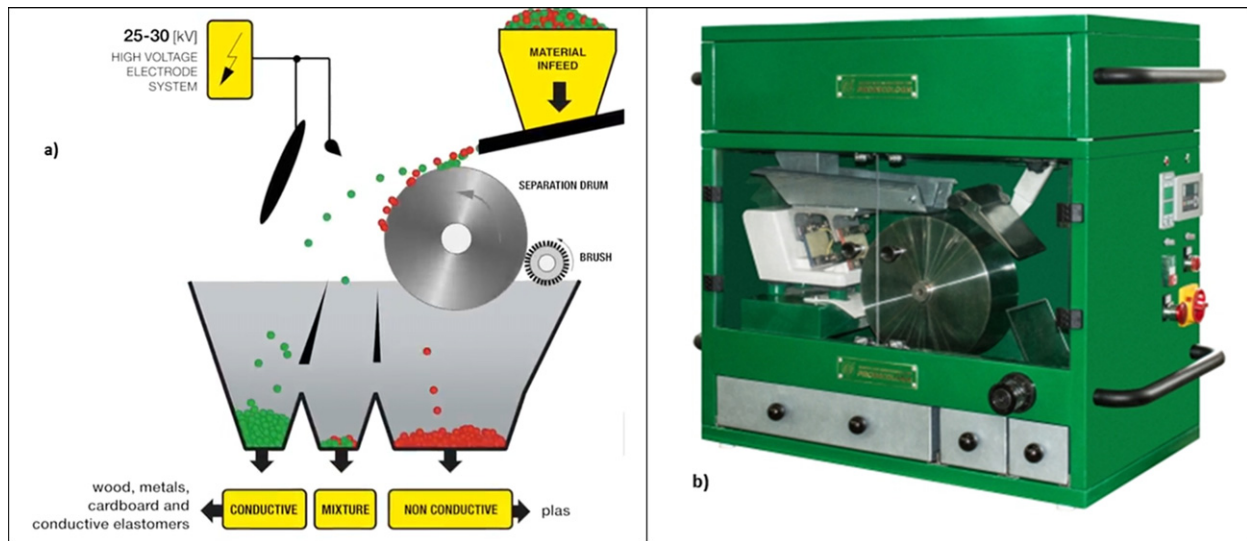


Fig. 9 CES separator: (a) Principle of separation operation, and (b) laboratory scale equipment.

particles has to be greater than all competing forces (Li *et al.*, 2004). Some examples of the use of high voltage electrostatic separators: metal-plastic separators ($8.0 \text{ mm} > d_p > 0.1 \text{ mm}$) and plastic-plastic separators ($2 < d_p < 12 \text{ mm}$) (Web5). They are used for:

- Dry separation (ideal surface moisture $< 0.2 \%$) of light fractions of metals (Cu and Al) from the nonconductor plastic fraction of the recycling operations of cables and electrical wiring at $8.0 \text{ mm} > d_p > 0.1 \text{ mm}$ in size.
- Recovery of light fractions PMs (Au, Ag and Pd) in the recycling of WPCBs, e-scrap and WEEE at $8.0 \text{ mm} > d_p > 0.1 \text{ mm}$ in size.

Corona electrostatic separation

The rotor type Corona-electrostatic separation (CES) method is perhaps the most effective separation technology for the conductive (metallic) and nonconductive (nonmetallic) fractions at present. The method has the advantage of being environmentally friendly, producing no wastewater and no gaseous emissions. In the CES, electrode system, rotor speed, moisture content and particle size have the greatest effect in determining the separation results. CES can be used for recovery of Cu or Al from chopped electrical wires and cables and for the e-sorting, downstream of the WPCB system, separates metals and allows to recover the finer fractions of PMs. The WPCBs with the metallic components removed must be reduced to very small particles, which can be achieved by accelerating them at high speed to impact on a hardened plate. Then, the small particles, typically less than 0.6 mm are passed along a vibratory feeder to a rotating roll to which is applied a high voltage electrostatic field using a Corona and an electrostatic electrode (Lu *et al.*, 2008; Hadi *et al.*, 2015). The nonmetallic particles that become charged and attach to the drum eventually falling off into storage bins; whereas the metallic particles discharge rapidly in the direction of an earthed electrode. Fig. 9 shows the principles of separation operation and laboratory scale CES equipment.

There are two series of CES machines: double-rollers and multi-rollers electrostatic separators. Roller length changes from 1000 to 2000 mm , roller quantity $1-4$, power $1.5-4 \text{ KW}$, speed $20-300 \text{ rpm}$ and outlet motor $0.75-2.2 \text{ kW}$ at a production capacity between 300 and 500 kg h^{-1} . Separation efficiency is as high as 99% . Electrostatic separator features a high precision separation with easy operation and simple maintenance. They cover a small area and easily move. It has been found that particle sizes of $0.6-1.2 \text{ mm}$ are the most suitable size for separation in industrial applications. Therefore, a two-step crushing process (shredder + hammer mill) has been proposed to achieve this particle size. Li *et al.* (2008) found that as the angle of the static electrode reduced and the Corona electrode angle was increased, the separation efficiency was enhanced. It was reported that applied voltage of $20-30 \text{ kV}$, center distance of 21 cm , static electrode radius of 1.9 cm , Corona wire radius of 11.4 cm , static electrode angle of 20° and Corona electrode angle of 60° were the optimum operating parameters influencing the separation efficiency. Considerable work is continuing in this area with particular focus on the electrostatic behavior of the system and the field intensity (Hadi *et al.*, 2015). CES methods are now capable of producing two streams from WPCB comprising a metallic and a nonmetallic portion with little cross-contamination; the method is dry at room temperature and as such is almost zero polluting depending on the quality of the dust extraction system. The residual Cu metal in nonmetallic fraction, which were separated from WPCBs without ECs by using the CES, showed that most of the residual Cu is in fine size range ($7-9 \mu\text{m}$) (Gao *et al.*, 2008).

Industrial scale electrostatic separators (Fig. 10) adopt physical high voltage to separate conductor metals from nonconductor nonmetals with a separation efficiency of $95\%-99\%$ purity. Electrostatic separator power changes from 1.5 to 3 kW , rotational speed from 20 to 300 rpm , static electricity from $50,000$ to $150,000 \text{ volt}$ adjustable (Web 6). Considerable work is continuing in this area with particular focus on the electrostatic behavior of the system and the field intensity.



Fig. 10 Industrial scale electrostatic separators: (a) Single-roll separator, (b) multiple-roll separators, and (c) electrostatic separator with dust collection systems.

Triboelectric separators

Static electricity is defined as an electrical charge caused by an imbalance of electrons on the surface of a material. Electrostatic charge is most commonly created by the contact and separation of two similar or dissimilar materials. Creating electrostatic charge by contact and separation of materials is known as “triboelectric charging”. It involves the transfer of electrons between materials. The atoms of a material with no static charge have an equal number of positive protons in their nucleus and negative electrons orbiting the nucleus. The amount of charge created by triboelectric charging is affected by the area of contact, the speed of separation, relative humidity, and other factors. Once the charge is created on a material, it becomes an “electrostatic” charge. This charge may be transferred from the material, creating an electrostatic discharge event. When the two materials are placed in contact and then separated, negatively charged electrons are transferred from the surface of one material to the surface of the other material. Which material loses electrons and which gains electrons will depend on the nature of the two materials. The material that loses electrons becomes positively charged, while the material that gains electrons is negatively charged.

This imbalance of electrons produces an electric field that can be measured and that can influence other objects at a distance. Electrostatic discharge is defined as the transfer of charge between bodies at different electrical potentials. When two materials contact and separate, the polarity and magnitude of the charge are indicated by the materials’ positions in the triboelectric series. The triboelectric simply lists materials according to their relative triboelectric charging characteristics. When two materials contact and separate, the one nearer the top of the series takes on a positive charge, the other a negative charge. Materials further apart on the table typically generate a higher charge than ones closer together. Triboelectric charging properties of materials found in WPCBs can be seen in [Table 2](#). Some substances have positive and some have negative charging characters. [Fig. 11](#) shows the industrial scale TESs along with separation equipment.

Eddy current separators

An Eddy current separator (ECS) uses a powerful magnetic field to separate nonferrous metals from waste after all ferrous metals have been removed previously by some arrangement of magnets. The device makes use of eddy currents to effect separation. ECSs are not designed to sort ferrous materials, which become hot inside the eddy current field. This can lead to damage of ECS unit belt. ECS is applied to a conveyor belt carrying a thin layer of e-waste. Nonferrous metals are thrown forward from the belt into a product bin, while nonmetals simply fall off the belt due to gravity. ECSs use a rotating drum with permanent/electro magnet. [Fig. 12](#) shows the separation principles of ECS and pilot-scale equipment. It is mainly used for recycling Cu, Al and other nonferrous metals from industrial waste and living garbage waste, can be widely used in garbage disposal, recycling of WEEE, other environmental industry and nonferrous metal materials processing industry. The main criterion to distinguish is the ratio of material conductivity and density values, the higher ratio value is more likely to separate. Typical particulate sizes processed tend to be in the 3–150 mm size range. High frequency ECSs, where the magnetic field changes very rapidly, are needed for separation of smaller particles ([Kellner, 2009](#)).

ECSs produce high frequency alternating magnetic field on magnetic roller; if conductive nonferrous metal goes through the magnetic field, it will produce induced current and this induced current will produce magnetic field opposite with original magnetic field, then the nonferrous (i.e., Al, Cu etc.) metal will fly ahead according its transporting direction by repulsive force of the magnetic field; hence, nonferrous metal is separated from other non-metal material. ECSs are composed of a separator and an electric controlling cabinet. Main body includes separating assembly, motor, frame and cover etc. Separating assembly includes permanent magnet roller (FeBNd), transporting system (includes transporting belt, driving roller and reducer). ECSs have a good separating result for multiple nonferrous metals, strong adaptability, reliable structure, strong adjustable repulsion with high separating efficiency. Magnet roller diameter is generally 300 mm. Magnet roller revolution changes up to 3000 rpm. Belt

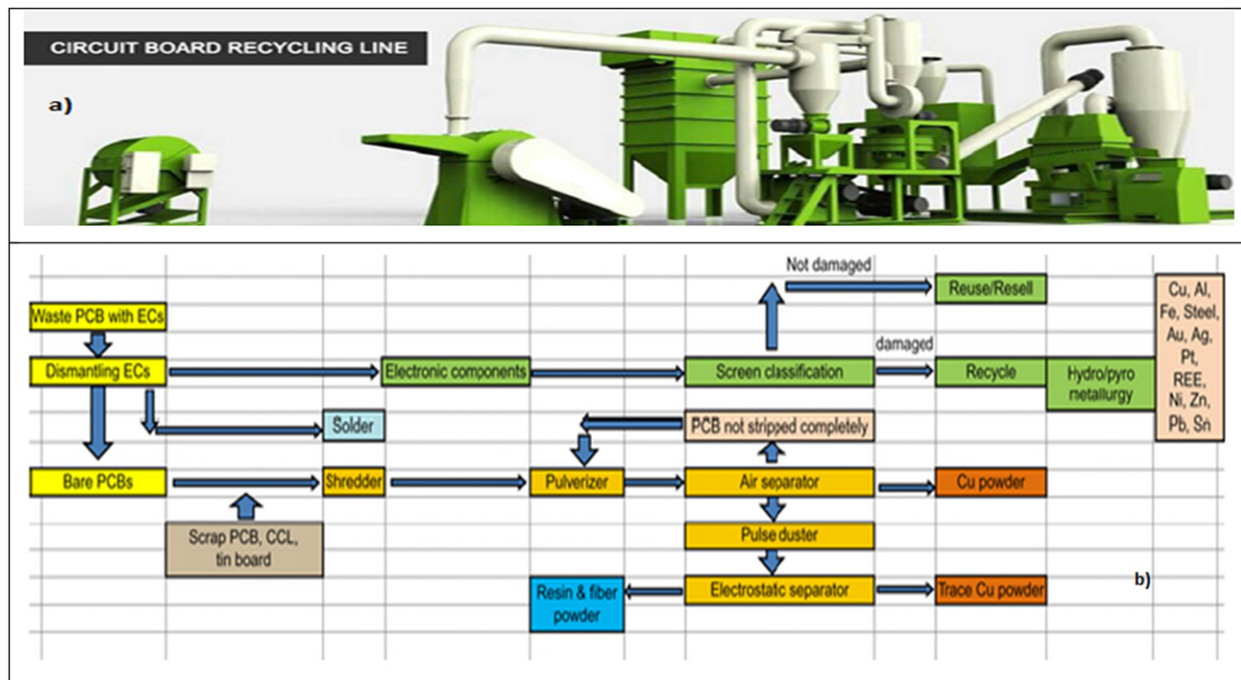


Fig. 13 Physico-mechanical e-waste recycling plant: (a) integrated desoldering disassembly, shredder, pulverizers, air separator and ECS plant layout, and (b) flowsheet for metal (Cu)-nonmetal (resin/glass fiber) products.

Highest capacity plants have one double-shaft shredder, hammer mill, bucket elevator and storage bin; two belt conveyor, specialized crusher, classifier, cyclone, four level cyclone, three-in-one dust catcher, vibrating screen; four electrostatic separator and six bucket elevators. **Fig. 13** shows industrial scale integrated physico-mechanical WPCB recycling plant flowsheet with air separator and ECSs along with feed-product photos obtained.

Magnetic separation

By creating an environment comprising a magnetic force (F_m), a gravitational force (F_g) (determined by particle size and density) and a drag force (F_d) (for wet magnetic separators determined by particle diameter, shape, liquid viscosity and velocity and for dry magnetic separators, determined by particle size, density and air velocity) magnetic particles can be separated from nonmagnetic particles by magnetic separation. Magnetic separators (MS) exploit the difference in magnetic properties between particles. All materials are affected in some way when placed in a magnetic field.

$$\text{Magnetic attraction force (F}_m\text{)} = V * X * H * \text{grad}H \quad (5)$$

Where V: Particle volume (determined by process)

X: Magnetic susceptibility

H: Magnetic field (created by the magnet system design) in mT

Grad H: Magnetic field gradient (created by the magnet system design) in mT

(mT: milli Tesla, 1kGauss = 100 mT = 0.1 T, 1 T = 10,000 Gauss)

Materials are classified into two broad groups according to whether they are attracted or repelled by a magnet. Non/diamagnetics are repelled from, and ferromagnetics/paramagnetics are attracted to a magnet. Ferromagnetic substances are strongly magnetic and have a large and positive magnetism. The magnetic moments in ferromagnetic material are ordered and of the same magnitude in the absence of an applied magnetic field. Paramagnetic substances are weakly magnetic and have a small and positive magnetism. The magnetic moments in a paramagnetic material are disordered in the absence of an applied magnetic field and ordered in the presence of an applied magnetic field. In diamagnetic materials, magnetic field is opposite to the applied field. Magnetisms are small and negative. Nonmagnetic material has zero magnetism. These materials are not attracted towards magnet.

Ferromagnetism is the basic mechanism by which certain materials (such as Fe) form permanent magnets, or is attracted to magnets. Ferromagnetism (including ferrimagnetism) is the strongest type. Ferromagnetic materials can be separated by Low Intensity Magnetic Separator (LIMS) at lower than 2 T magnetic intensity. Paramagnetic materials can be separated by dry or wet High Intensity Magnetic Separators (HIMS) at 10–20 T magnetic intensities. Diamagnetic materials create an induced magnetic field in a direction opposite to an externally applied magnetic field, and are repelled by the applied magnetic field. Non-magnetic substances have little reaction to magnetic fields and show net zero magnetic moment due to random alignment of magnetic field of individual atoms. Strongly magnetic materials can be recovered by a magnetic separator with the use of relatively weak magnetic

induction, up to 0.15 T. Weakly magnetic materials can be recovered by a HIMS generating induction up to 0.8 T with modest values of the gradient of the magnetic field. Induced roll separators, field intensities up to 2.2 T and Permroll separators can be used for coarse and dry materials ($> 75 \mu\text{m}$). Fine materials reduce the separation efficiency due to particle-rotor and particle-particle adhesion/agglomeration. For wet HIMS, Gill and Jones separators are used at a maximum field of 1.4 and 1.5 T, respectively at $-150 \mu\text{m}$ size (Wills, 1988).

Dry LIMs are used for coarse and strongly magnetic substances. Magnetic field gradient in separation zone (approximately 5 cm from drum surface) changes 0.1–0.3 T. Below 0.5 cm, dry separation tends to be replaced by wet methods (wet LIMS). Concurrent and countercurrent drum separators have nonmagnetic drum containing three to six stationary magnets of alternating polarity. Separation depends on pick up principles. Magnetic particles are lifted by magnets and pinned to the drum and are conveyed out of the field. Field intensities up to 0.7 T at the pole surfaces can be used. Coarse particles up to 0.5–6 mm can be tolerated. Drum diameter is 1200 mm and length 600, 1200, 1800, 2400, 3000 and 3600 mm. Concurrent operation is normally used as primary separation (cobber) for large capacities and coarse feeds. Countercurrent operation used as rougher and cleaner for multistage concentration.

Moderately magnetic dry substances on a conveyor/belt can be collected by overhead, cross-belt or disc separators using magnetic field intensities between 0.8 and 1.5 T. Very weakly paramagnetic substances can only be removed if field intensities are greater than 2.0 T. At 5–200 mm size fraction, overhead permanent magnets are used to remove ferromagnetics. Magnetic separators, such as dry low-intensity drum types, are widely used for the recovery of ferromagnetic materials from nonferrous metals (Al and Cu) and other nonmagnetic materials (plastic and glass) at -5 mm in size. The magnetic field may be generated by permanent magnets or electromagnets. There have been many advances in the design and operation of HIMS due mainly to the introduction of rare-earth alloy permanent magnets with the capability of providing high field strengths and gradients. There are some problems associated with this method. One of the major issues is the agglomeration of the particles which results in the attraction of some nonferrous fraction attached to the ferrous fraction (Veit *et al.*, 2005). This will lead to the low efficiency of this method. Through the process of magnetic separation, it is possible to obtain two fractions: Magnetic fraction, which includes Fe, steel, Ni etc. and nonmagnetic fraction, which includes Cu (Yamane *et al.*, 2011). For WEEE, magnetic separation systems utilize ferrite, rear-earth or electromagnets, with high-intensity electromagnet systems being used extensively.

Veit *et al.* (2005) employed a magnetic field of 0.6–0.65 T to separate the ferromagnetic elements, such as Fe and Ni. The chemical concentration of the magnetic fraction was 43% Fe and 15.2% Ni on average. However, there was a considerable amount of Cu impurity in the magnetic fraction as well. Yoo *et al.* (2009) used a two-stage magnetic separation to milled WPCBs. The milled WPCBs of particle size $> 5.0 \text{ mm}$ and the heavy fraction separated from the $< 5.0 \text{ mm}$ WPCBs particles by gravity separation. In the first stage, a low magnetic field of 0.07 T was applied which led to the separation of 83% of Ni and Fe in the magnetic fraction and 92% of Cu in the nonmagnetic fraction. The second magnetic separation stage was conducted at 0.3 T which resulted in a reduction in the grade of the Ni–Fe concentrate and an increase in the Cu concentrate grade. Hanafi *et al.* (2012) had an agglomeration problem of nonmetals which were pulled with ferrous materials.

Conclusions

Conventional processes for WPCB recovery include incineration/combustion, mechanical separation with gravity separation methods and crude acid leaching. Incineration is a traditional process and accepts every e-waste as its (i.e., mixed and without size reduction). Process time is short and heat energy is produced. Incineration is irreversible process and changes the chemical and physical phases very high. Process capacity is large, and product efficiency, recovery rate and purity are low. Selectivity between metals is low. Incineration is environmentally unfriendly and requires expensive gas purification systems. Equipment used should resist to corrosion. From the incineration process, only Cu, Au and Ag metals are recovered from the ashes, and Fe and Al cannot be recovered. WPCBs, which include plastics and some reusable ECs, are burned and lost. Cu can be purified by H_2SO_4 leaching. Au and Ag can be recovered from the Cu electrolysis mud.

Mechanical separation includes size reduction and gravity separation processes. Multi-step crushing/shredding and pulverizing/grinding only liberates low value plastics from metals. Metals are not liberated from each other. Two-step size reduction is generally preferred. Size reduction generates excess heat, toxic gases, noise and dust. There is a significant PM loss in dry separation due to liberation problem. Dry separators must require dust removal system. Wet gravity separation can reduce dust and noise problems; but, it generates waste water matter. Air tables and zigzag 3 way classifiers do not have waste water problem. Wet shaking tables, heavy media separation and jigs produce huge waste water. Recovery rate in gravity separation is as high as 95%. Gravity separation is more economical than electrostatic separation in metal and plastic/Al/glass segregation.

Advanced pyrometallurgical process for WPCB recovery is currently most commonly used process in the industry. Integrated smelters and refineries accept both WPCBs directly without size reduction to reduce PM losses and raw ores. Removing massive Fe and Al parts for valorization and upgrading Cu and PMs is required. Process time is short in pyrometallurgical treatment. However, smelting is energy intensive ($> 1200^\circ\text{C}$) process. Initial investment and energy costs are very high. Plant capacity is large. Product efficiency, recovery, selectivity and purity are low as compared to hydrometallurgical processes. Pyrometallurgical processes are environmentally unfriendly, require expensive gas purification systems for VOCs, dioxins and furans and necessitate corrosion resistant equipment. From an ISR plant, 20 different metals can be recovered along with hydrometallurgical and electro-metallurgical techniques. Glass and plastics are lost and converted to slag, ash and heat energy.

Hydrometallurgical processes are advanced and promising aqueous recovery techniques for metals from WPCBs. They are easy to apply, simple to operate and selective, flexible and stable to use. Higher recovery rates, faster kinetics, easier control, lower temperature requirement, less hazard to environment, low gas emission, low energy consumption, low initial investment cost, higher recovery rates and more predictable results are some of advantages of hydrometallurgy as compared to pyrometallurgy. Reagent recyclability and selective recovery of both all BMs and PMs are important benefits of the hydrometallurgical processes. However, the use of strong and corrosive reagents, long process time, discharged toxic wastes and high cost of recovery are some of the disadvantages of hydrometallurgical process.

Currently, pyrometallurgical WPCB recycling routes are generally used globally (about 70%) with high investment cost, temperature and ecological problems. Smelting process segregates and upgrades PMs into BMs followed by hydrometallurgical and electrometallurgical processing for the recovery of pure BMs and PMs. Comparing with the pyrometallurgical processing, hydrometallurgical method is better, more predictable, and more easily controlled. New promising biological processes are now under development.

Metals and nonmetals/nonferrous materials in WPCB can be dry separated by electrostatic separation. There is no water requirement and no gaseous emission from this process. Environmental friendly electrostatic separation is performed at room temperature with a separation efficiency 95%–99% purity. Dust extraction requirement is only disadvantage of the process. CES separates Cu from plastics and mixed particles that have similar conductivities at a separation efficiency as high as 99% for particle sizes between 0.6 and 1.2 mm. Easy operation, simple maintenance, small area requirement and little cross contamination are some important advantages of this separation process. TES separates two similar or dissimilar materials by contact charging. ECS separates nonferrous metals of Al and Cu from plastics at a particle sizes at 3–150 mm.

Magnetic separators separate magnetic particles from nonmagnetic WPCB particles in dry or wet medium. In dry separation, there is an agglomeration problem. LIMS separates ferromagnetic fraction from Cu, Al and plastics at lower than 2 T magnetic intensity. Dry LIMS are used for coarse particles (0.5–6 mm) and wet LIMS are used for fine particles (< 0.5 mm). HIMS separates paramagnetic materials at 10–20 T magnetic intensity.

Second generation physico-mechanical separation (Gravity + Magnetic + Electrostatic) along with hydrometallurgical treatment approaches offers a cost effective, eco-friendly and more sustainable alternative methodology to smelting. Physico-mechanical WPCB recycling is a promising recovery technology without environmental pollution and with reasonable equipment invests, low energy cost and diversified potential applications of products. However, separation between the metallic and non-metallic fraction from WPCBs has to be enhanced. In the future, author believes that unlocking the hidden value from waste electronic asset/e-waste by Urban Mining will gain more importance in the World.

See also: The Potential of Core-Shell Technique in the Enhancement of Different Derived Calcium Carbonate Wastes in Anticorrosive Paints

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Library of Congress Cataloging-in-Publication Data

A catalog record for this book is available from the Library of Congress

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library

ISBN 978-0-12-813195-4

For information on all publications visit our
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PREFACE

The *Encyclopedia of Renewable and Sustainable Materials* is a novel initiative, launched to cater for researchers, industrial practitioners and environmental conservationists to bring to the fore the issues of renewability, regeneration, recyclability and sustainability of natural material resources for the greater good of the environment, society and renewable resources. With these objectives the project was constituted of 11 sections, led by one Section Editor each. There are about 4,000 printed pages, accommodated in five volumes ranging from 600 to 1000 pages each.

This encyclopedia is the primary reference source for researchers at different levels and stages in their career in academia and industry and those with an interest in environmental protection and sustainability, including re-use and recycling of natural and synthetic materials and regeneration of natural materials. The work encompasses the knowledge and understanding of many experts into a single, comprehensive work of about 370 articles comprising a combination of review articles, case studies and research findings resulting from research and development activities in both industrial and academic domains. The encyclopedia, focuses on how some of these topics bring advantages for a broad range of technologies and environmental protectionists. These include harnessing existing materials both natural and synthetic, their re-usability and regeneration possibilities for the greater good of society and the environment. The aspects of feasibility, conservational objectives and practicability of implementation have been addressed through a number of relevant articles.

As Editors in Chief of this five-volume comprehensive publication, a truly collaborative work, we are greatly indebted to the 11 Section Editors who are internationally renowned experts in their fields, for guiding and selecting the topics for their respective sections which constitute the five volumes, commissioning authors and reviewing the contents so meticulously. Their true dedication to the scientific community and society is reflected in the time and energy they have given to this project. My sincerest thanks are due to all the authors – researchers, environmental protectionists and practitioners who have contributed extensive coverage of literature review as well as recent works of research to this substantial five volume encyclopedia. The excellent insight and specialist knowledge in their respective fields is reflected in the high quality content of this unique work.

Both of us and all the section editors are greatly appreciative of all the hard work undertaken by all concerned to turn this concept of the *Encyclopedia of Renewable and Sustainable Materials* into a publishable work. Our special thanks go to Ruth Rhodes and Michael Nicholls, the Project Manager, along with Kshitija Iyer and the rest of the team at Elsevier who served successively to keep the project on track through friendly nudges in order to ensure timely completion. We are also hugely grateful to other colleagues at Elsevier production unit for the coordination of the proofs.

The extensive research treatment of core ethos of renewability, recyclability and regeneration, supplemented by applied case studies has drawn together many areas of research and we sincerely hope that this work will prove to be of great help to both the young and experienced members of the international research community, academics and industrial practitioners associated with sensible utilization of natural and synthetic materials for many years to come.

Saleem Hashmi and Imtiaz Ahmed Choudhury
Editors in Chief – *Encyclopedia of Renewable and Sustainable Materials*

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Advanced Separation Processes for Recovery of Critical Raw Materials From Renewable and Waste Resources

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Critical Raw Materials (CRM) Recovery – Significance and Impact on Circular Economy

In the present world, raw materials are in greater demand but are becoming ever scarcer. To imply the sign of criticality, knowing that there is a high risk of supply shortage and economic impact, the European Commission formally adopted a list of specific raw materials designated as ‘critical raw materials’ (CRMs) as represented in Fig. 1. Regulatory policies are being implemented to bring down the extraction/mining trend for ultimately extending the lifetime of CRMs. On the other hand, advanced recycling systems are being practiced to promote and establish a core circular economy context by recycling, recovering, and separating CRMs. These recycling approaches are mostly aimed at the recovery of various metals such as palladium, gallium, germanium, copper, which are critical raw materials for the technology sector. There are also a specific group of CRMs including Phosphorus (P), natural phosphate rock and Magnesium (Mg) representing major primary, and secondary resources for industrial applications of high economic value (Loganathan *et al.*, 2017; Yan *et al.*, 2018). Crucially only P and Mg are deemed suitable candidate CRM’s for

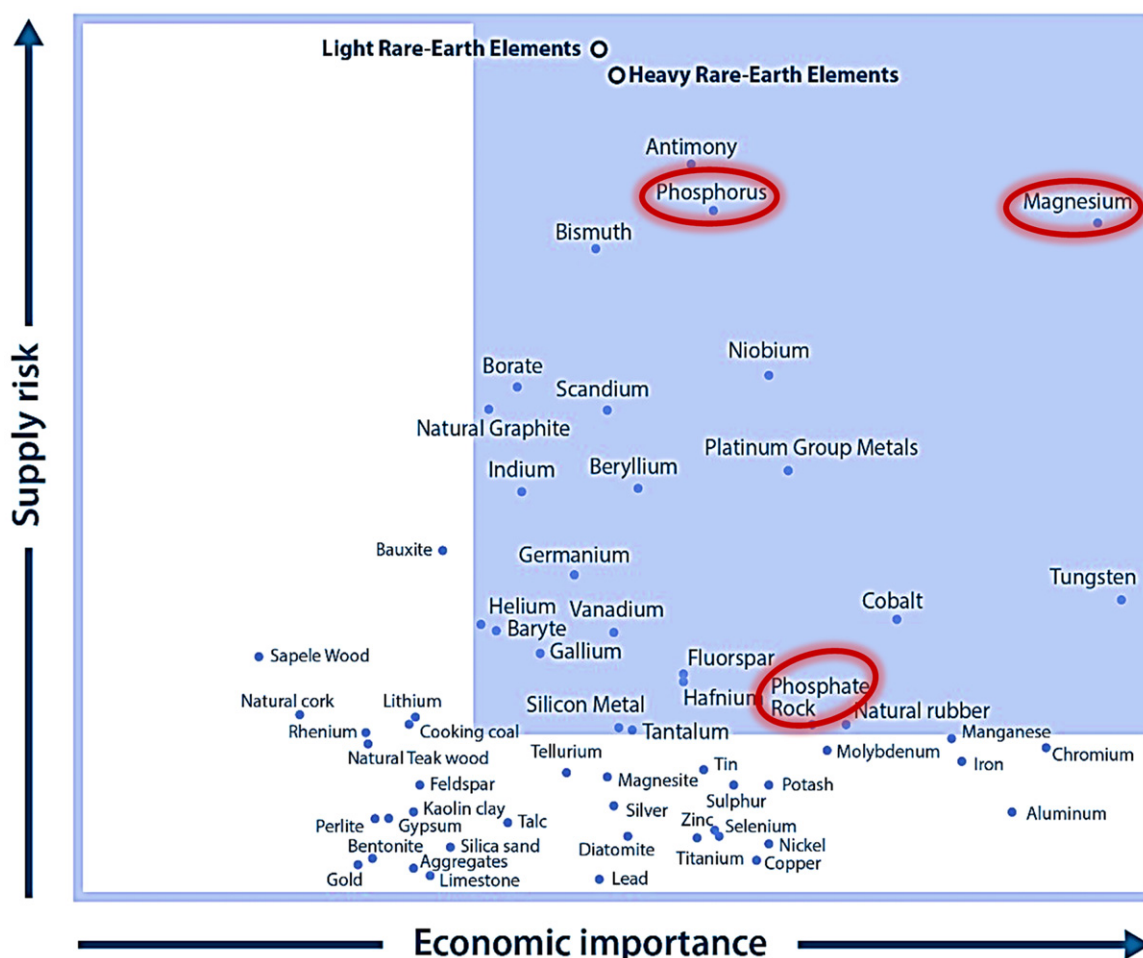


Fig. 1 List of CRMs (shaded blue) among which phosphorus, phosphate rock and magnesium are highlighted for its representation in greater scale of economic importance and supply risk. Courtesy: Study of the review of the list of Critical Raw Materials, 2017.

recovery from waste streams through effective separation and recycling strategies. Further, its supply-demand status and substitutability risks have driven the requisites for resource supplementing technology through effective recovery and recycling strategies.

The core focus of this article is to review the most effective sustainable technologies to recover CRMs. Specifically for P and Mg recovery, it is essential to balance the depletion of its primary reserves, whilst mitigating the disposal issues with a view to remediate industrial brine/waste sludge rich in Mg and P nutrients respectively. Hence, special emphasis has been given to recovering CRMs from waste streams, currently a source of both high potential and environmental, and health concerns. Long-time benefits would be possible by the recovery of P and Mg as a secondary resource to ameliorate the CRMs supply risk in countries deprived of natural mineral reserve. Perhaps, natural lifecycle of phosphate could be balanced by maintaining its sustainable supply to plants while controlling eutrophication, a phenomenon leading to excessive oxygen depletion in water bodies owing to disproportionate phosphate discharge. In a viewpoint to achieve dual advantage of discharging pollutant-free waste sludge and to allow efficient recovery of P/Mg in different forms useful to mankind and environment, robust recycling/recovery strategies are consolidated and discussed in the following sections.

Overview on Conventional Approaches of P and Mg Recovery

As the levels of CRMs in the natural sources are limited, their recovery from non-conventional secondary sources such as end-of-life products and waste generated through industrial activities is essential to meet the global demand. Various conventional methodologies are reported in literature based on physical, chemical and biotechnological principle for the critical raw material recovery for magnesium and phosphorus. General summary on the widely adopted spectrum of methodologies for the P and Mg recovery are discussed in this section.

Since P is an essential component of fertilizer composition, the waste water produced from fertilizer industry is considered as an important secondary source for the recovery of P. Other sources utilised for P recovery include effluent from waste water treatment plants, household activities, municipal waste and industrial organic solid waste. While sea water is considered as a largest source of Mg, exhausted waste brine solutions from industry is also Mg rich.

The widely used methodologies for the recovery of divalent Mg and P mainly involve chemical precipitation, adsorption and membrane separation. Chemical precipitation is considered as a most popular method which involves leaching of Ca/Mg using acidic or alkaline conditions followed by their precipitation by adding metal hydroxide such as calcium hydroxide. The precipitation of P is achieved in the form of struvite (magnesium ammonium salt) and hydroxyapatite. Further, manipulation of Ca/P ratio and calcium phosphate concentration in solution, leads to fast precipitation and recrystallization of phosphate (Vasenko and Qu, 2018). In addition a hybrid methodology involving both oxidation and ultra-sonication assisted pre-treatment, was found to improve P recovery. In recent reports, electrolytic system in combination with ion-exchange membrane was demonstrated where OH^- ions released from water breakdown help in the precipitation of Mg (Sano *et al.*, 2018).

Adsorption methodology is considered a relatively simple process for the recovery of metal ions from aqueous waste. Activated charcoal and metal oxides such as ferric oxide/hydroxide, activated aluminium oxide and lanthanum oxide are well explored for their ability to adsorb metals from aqueous solutions. Ion-exchange resins are also used for metal ion recovery. The use of Anion exchange resin and cation exchange resins was studied for the recovery of P and Mg respectively. Further, application of magnetic ion-exchange (MIEx) resin is demonstrated for the recovery of Mg and P (Kim, 2015; Lehmann *et al.*, 2014). MIEx are adsorptive resins where iron oxide particles, with magnetic properties, are incorporated into a polymeric matrix. MIEx assisted adsorption can be combined with membrane separation, and precipitation methods, to improve the recovery of metal ions. Recently Lanthanum based nanoparticles and nano-composites receiving greater attention for the recovery of Phosphate from aqueous solutions (Wu *et al.*, 2017). Membrane separation is another popular method for the concentration and recovery of metal ions. Microfiltration, ultra-filtration, nanofiltration and dia-filtration have largely been demonstrated for the recovery P and Mg. Further, membrane separation is used in combination with ion-exchange resin and precipitation methodologies to improve the process recovery.

Advanced Technologies for CRM Recovery

Status of Phosphorus

Stimulated by the fact that phosphate rock resources have started depleting, the P recovery from any phosphorus-rich residue has drawn extensive attention to meet the industrial demand for P. The elevated phosphate concentration in wastewater/waste sludge presents significant opportunities for P recovery techniques to be readily integrated into current wastewater treatment infrastructure. Phosphate rock is the major natural source of phosphates used in fertilisers but the P extraction rate far exceeds the regeneration, thus estimating its depletion in the next 40–100 years. In contrast, 90% of the phosphate in wastewater is trapped in the sludge solids and also present as soluble PO_4 in the reject wastewater (> 80% of total P) (Yan *et al.*, 2018). Fig. 2 illustrates the simplified scheme of natural P cycle and its flows and distributions in global food chain. However the challenge remains to directly recover P/ PO_4 from municipal wastewater which redirects the focus to recover P as secondary resources for its significance in various industrial applications (Fig. 3).

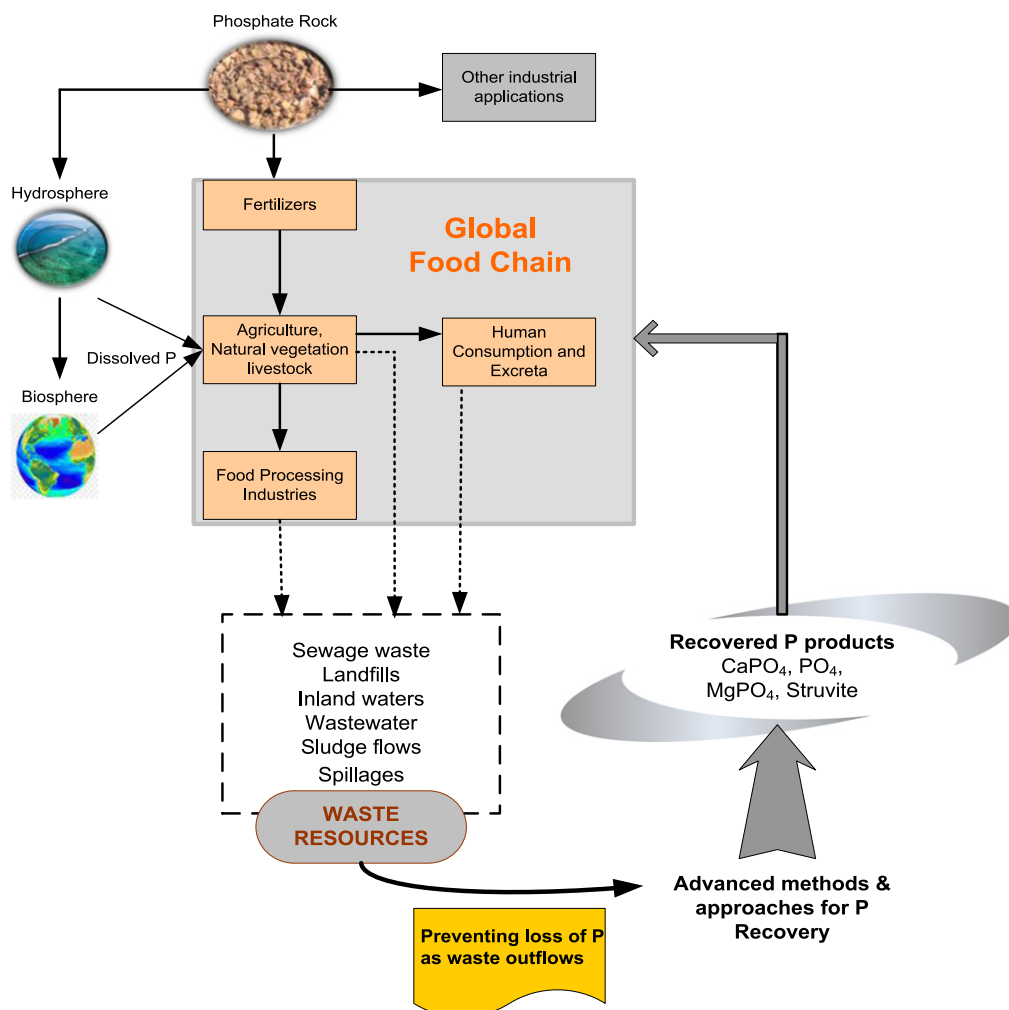


Fig. 2 Scheme illustrating the potential of P recovery in partial closing the loop of global P cycle. Re-drawn with permission from Venkiteshwaran, K., McNamara, P.J., Mayer, B.K., 2018. Meta-analysis of non-reactive phosphorus in water, wastewater, and sludge, and strategies to convert it for enhanced phosphorus removal and recovery. *Science of the Total Environment* 644, 661–674.

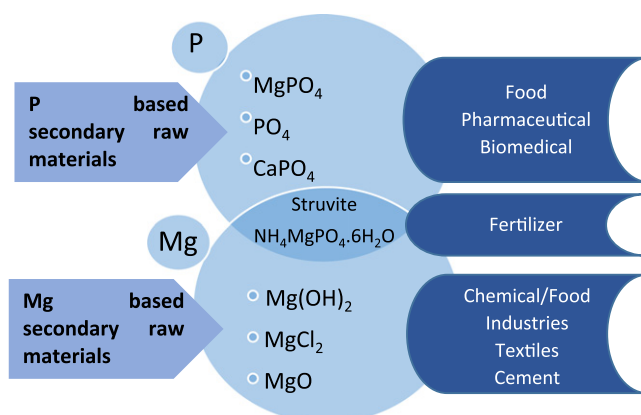


Fig. 3 P and Mg based secondary raw materials its broad applications.

Struvite is one of the widely attracted secondary raw material rich in both P and Mg. It is interesting to note that resources constituting Mg is crucial to maximize the P separation based on either conventional precipitation or novel osmotic membrane separation methods. Calcium phosphate is yet another promising P based raw material, allowing recovery directly from the liquid phase (as dissolved P), which is not otherwise possible using conventional biological based wastewater treatment. If P can be

Table 1 Classification of membrane processes specific to desired mineral recovery

<i>Mg/P based raw materials</i>	<i>Hybrid membrane processes</i>	<i>Sources</i>
CaPO ₄	Nanofiltration-Crystallization Nanofiltration-Membrane Crystallization Microfiltration-Osmotic Membrane Bioreactor-Reverse osmosis	Secondary effluent Activated sludge Municipal wastewater Anaerobic digested sludge Wastewater
P, Mg	Electrodialysis Electrodialysis-Anaerobic Bioreactor	
MgSO ₄	Membrane distillation-crystallization	NF/RO retentate (real time/ simulated)
Struvite	Selectrodialysis-struvite bioreactor Membrane Crystallization	Anaerobic sludge Municipal wastewater
PO ₄	Microfiltration-Forward osmosis membrane bioreactor Electrodialysis-Membrane Bioreactor	Municipal wastewater Phosphorus rich wastewater
MgPO ₄	Combined membrane gas separation	Swine manures
PO ₄ , MgCl ₂	Osmotic Membrane Bioreactor-Membrane distillation	Activated sludge

removed and recovered at the very beginning of the wastewater treatment, then steps related to downstream processing of P-rich sludge could be avoided.

Status of Magnesium

The economic gains obtained by extracting minerals depend mainly on the concentration of minerals and their market price. In this respect, Na, Ca, Mg, K, Li, Sr, Br, B and U are potentially attractive for extraction, provided economically feasible extraction methods can be found to avoid direct land mining. There is a great demand for the group of minerals that can be profitably extracted from seawater, or effluent brine to benefit agriculture, industry, environmental remediation, and medicine. Mg is identified to be one of the key CRMs posing a huge demand, owing to its application in wide spectrum of industries including chemicals, construction materials, aluminium, steel and fertilizers. With magnesite being a prime source for Mg recovery, the growing demand and faster depletion of naturally occurring mines has led to the exploration of other Mg sources including dolomite, forsterite and brucite deposits. Mg and P are rather different class of CRMs that does not fall into the categories of precious metals like gold, silver and palladium; and selected set of critical metals (S-CRMs) like gallium, indium, rare earth elements (REEs), tantalum, and cobalt. Moreover, such different classes of CRMs, except Mg and P, could be readily recovered by recycling the WEEs. The world production of Mg is around 12 million ton per year (2012), but only 14% is produced in EU area. If the Mg recovery from waste brine of European saltworks are highly efficient, then the production from the EU zone could increase by 5% (Nakoa *et al.*, 2016).

Membrane Based Approaches for P and Mg Recovery

Combining P recovery with domestic/industrial wastewater treatment systems

To overcome the limitations related to lower P recovery and high cost required (e.g., the addition of inorganic salts like Mg) for conventional precipitation, it is rather important to focus on advanced separation technologies like membrane processes for improving the P recovery. Research interests on P recovery using forward osmosis, selective electrodialysis, and osmotic membrane bioreactor as an integrated process have recently been increased (Qiu *et al.*, 2016). Table 1 summarizes some of the feasible combination of membrane processes for recovery of P and Mg based raw materials from different waste resources. Thermally driven membrane processes like membrane distillation (MD) and membrane crystallization (MCR) have been widely used for desalination with simultaneous recovery of MgSO₄·7H₂O, owing to its well-controlled and easy tuneable precipitation at low energy requirements, which are difficult to obtain from normal crystallization processes. However, MCR/MD for P recovery is also feasible to produce both solid struvite precipitate, and ammonia rich liquid stream, while also being operated using waste heat to ensure a lean cost process.

In most of the osmotic membrane bioreactors, FO membrane helps to reject P to one side of a collection tank, while the MF/UF membrane permeates it for final recovery of P without the need for any addition of calcium or magnesium ions. Further, other rejected solutes in the FO system are transported into the bioreactor for final extraction using MF, which also enables lowering the salt accumulation in the bioreactor. Electrodialysis (ED) is one of the versatile methods which have had its prime role in heavy metals remediation of pollutant streams including industrial effluents and sewage sludge. Recently studies are investigating ED for direct P recovery, while being integrated with biological reactors to ensure both P availability and to make use of great fertilizer value of final sludge solids. The present challenges of ED including membrane fouling and increased electrical resistance (translating into higher operating/maintenance costs) could be effectively met by combining ED with anaerobic biological process, which stimulates the P release. Ion exchange membranes are known for its synergistic mechanism of membrane separation with selective ion-exchange capacity. Extensive potential of the ED has been utilised to separate phosphate from waste/sewage sludge.

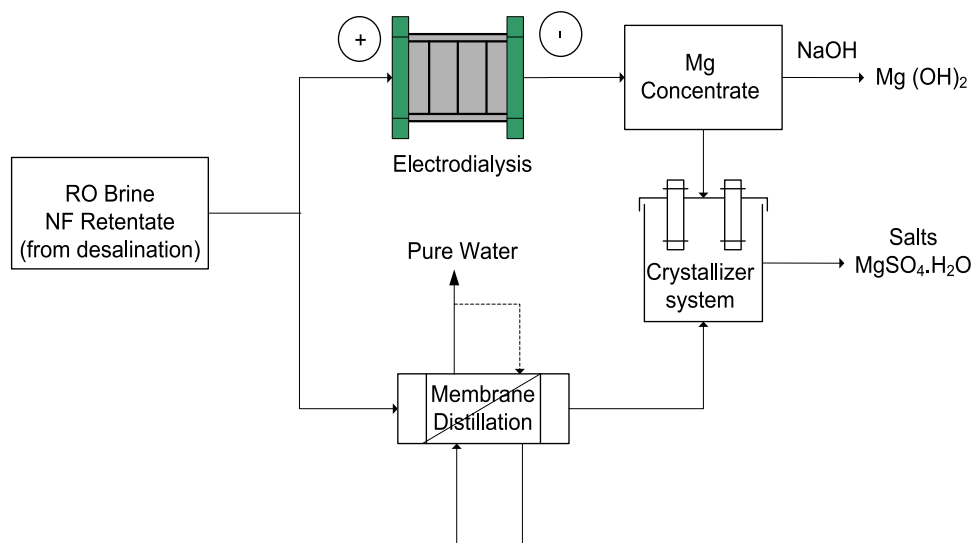


Fig. 4 ED and MDC approaches for combining Mg recovery with desalination.

Combining Mg recovery with desalination systems

In order to maximize the production of Mg, membrane technology is considered a leading viable option, due its established popularity in the field of desalination. Wide spectrum of CRMs are found in sea water, yet commercial scale recovery remains a major barrier due to its low concentrations upon recovery. Whereas, industrially processed effluents are considered as one of the richest sources of inorganic salts/minerals, thus shifting the need for CRMs recovery towards effluents coming from desalination and wastewater treatment units. The paradox in combining minerals recovery with desalination, is that water is both a human necessity, but also a waste product in the mining industry. Likewise the desalination industry have seen their mineral-rich stream as waste, during the production of clean water. By combining these two industries in 'mining from the sea', many synergies can be obtained. The interesting objective of recovering minerals from the sea might actually partly aim to reduce the problem of brine disposal in desalination. Moreover, as an intriguing, positive side effect, it can contribute to the conventional mining industry, thus reducing mineral depletion. Several methods are emerging for mining valuable minerals on both individual and combined basis among which majorly employed methods include solar evaporation, electrodialysis (ED), and membrane distillation (MD)/membrane distillation crystallization (MDC) (Loganathan *et al.*, 2017). Schematic of the process flow diagram employing ED and MD with crystallizer systems for Mg recovery is shown in Fig. 4.

Membrane distillation

Growing research interest in zero liquid discharge (ZLD) technologies have driven the importance of treating RO concentrate, as it is considered as one of the waste resources to recover magnesium salts (Chung *et al.*, 2017). Research studies dealing with the treatment of emerging RO concentrate are to develop cost-effective methods to minimize the potential impacts on the environment. This will also offer alternative strategies to viably extract available salts, and to recover purified water. Several strategies have been adopted for the treatment technologies of RO brines and multiple review papers have also been published in the last decade (Subramani and Jacangelo, 2014; Jensen *et al.*, 2019).

Second major component of RO brine is magnesium and mostly the elements remain in the form of sulphates than carbonates. Major obstacle lies on the presence of calcium, either as CaCO_3 or CaSO_4 , both of which affects the membrane performance due to its poor solubility. Despite having no direct influence of Ca^{2+} present in seawater on Mg recovery, its impact is indirect on the efficiency of struvite recovery due to calcium phosphate formation. However, association of calcium carbonate (CaCO_3) with Mg results on the production of Dolomite ($\text{CaMg}(\text{CO}_3)_2$), which represent one of the primary natural sources of magnesium production.

Membrane crystallization

In a typical reactive crystallization, magnesium salts can be precipitated by means of hydroxyl radicals. Cationic form Mg^{2+} form can further be obtained based on electrodialysis mechanism. In the reactive hybrid process, integration of ion exchange membranes enables the development of Membrane Crystallizer Reactor (MCR) wherein IEMs are in selective contact with the alkaline reagents. In MCR, precipitation reaction occurs between brine and alkaline solution with no direct contact which is in contrast to conventional reactive crystallization. Moreover, indirect contact of IEMs with two different electrolyte solutions reduces the risk of co-precipitation of by-products thus enhancing the recovery efficiency. MCr was applied in an integrated system working on NF and RO brine for the recovery of sodium and magnesium. Introduction of NF is required to separate bivalent and monovalent ions, thus providing that

magnesium can be recovered from the NF retentate and sodium from the RO retentate, since it highlights that MCr can control/tune the polymorph selection, thus increasing the product value and minimizing the post-treatment.

Electrodialysis

In contrast to P, only scarce Mg sources are available from struvite or municipal wastewater, thus driving the need for fractionating Mg^{2+} from seawater. Hence, ED takes its role by combining the standard cation-exchange membranes, and monovalent selective cation-exchange membranes, for selective fractionation of Mg^{2+} from various side-streams rich in divalent ions (not limited to bittern, sea water, brucite, RO brine, and NF retentate). Seawater, containing substantial Mg^{2+} , is regarded as one of the leading potential resources offering the combination of desalination for product water treatment along with Mg^{2+} recovery.

Strategies to Maximize Mg and P Recovery

Integration of Mg and P Recovery Process- Closing the Loop Approaches

An integrated approach of bringing together various membrane processes having lower footprint may be significant to extract one or more valuable minerals, in particular Mg and P from seawater/brine effluent, and sewage wastewater respectively. Struvite, one of the potential secondary raw materials for both soluble P and Mg, can be recovered from wastewater based on various strategies. Membrane technologies employing advanced osmotic membrane reactors (OMR) as a stand-alone process (or integrated with other filtration processes like microfiltration/ultrafiltration) are now viewed as viable options for both P recovery and the production of clean water.

Design of a continuous and closed loop system for the recovery of valuable minerals like P and Mg from waste and renewable resources would be the challenging implementation steps for waste treatment or desalination. Process intensification is gaining more focus to mitigate against the issues related to CRMs depletion, water shortage, global warming, and waste recycling. Membrane processes closely match the current requirements of process intensification, for its energy-efficient separation routes when compared with conventional separation technologies. Membrane separation processes are already recognized as the best available technologies, allowing easy retro-fitting to most of the available processes to contribute to sustainable development.

For instance, current products such as membrane bioreactors (MBRs), primarily use for wastewater treatments, membrane-assisted crystallization, condensation and distillation, are based on the concept of facile redesigning of conventional energy-intensive separation methods. The interesting results achieved with these new technologies could overcome the limitations in recycling strategies. A relatively high P concentration combined with relative low organic matter content can be achieved by stimulating release of P from secondary sludge using volatile fatty acids (VFAs) under anaerobic conditions. Extracting P from the resulting liquid phase of the sludge will result in less fouling of the membranes and subsequently higher efficiency of P extraction.

By judicious selection of the draw solute for the operation of OMR, it is quite feasible to integrate hybrid MF/UF-OMR system into the tertiary wastewater treatment phase, wherein retentate stream of nanofiltration (NF) permeate or reverse osmosis (RO) retentate system containing MgCl_2 helps to enhance ionic strength and precipitation potential for P recovery (Ashley *et al.*, 2016). With pH adjustment greater than 8, P could be precipitated directly recovered from MF permeate without requiring any inorganic salts. With pH adjustment greater than 8, P could be precipitated, directly recovered from MF permeate, without requiring any inorganic salts. The feasibility of using sea water as a draw solute for P recovery using hybrid MF-OMR, followed by separation of Mg by electrodialysis would be gaining greater potential in terms of economics and process integration (Joo and Tansel, 2015). A typical process flowchart illustrating the concept of simultaneous recovery of both P and Mg and the integration potential of sea water RO (SWRO) brine, a concentrated stream of concern from desalination systems being used as a draw solute for operating FO as shown in Fig. 5.

Pre-Treatment Approaches

For integrated process design of advanced technologies for CRM recovery, pre-treatment strategies play a crucial role as most of the CRM recovery is aimed from secondary waste resources/ raw materials. Specifically to recover P and Mg, several methods including acid, alkaline, electrodialytic and ultrasonic, incineration have been studied, yet it is challenging to choose appropriate pre-treatment to best exploit the efficacy of entire recovery system. Despite many methods can significantly accelerate the phosphorus release during the sludge disintegration process, it is indispensable to choose cost-effective and efficient methodology. Most of the conventional stand-alone methods are cost intensive due to high energy inputs and/or substantial chemical requirements which might limit its largescale application. Furthermore, those methods certainly pose negative consequences on environment. Therefore, a cost-effective, efficient and environmentally friendly treatment method to enhance phosphorus release from wastewater is needed. For instance, mineralization of struvite or whey (dairy by-product) is quite complex due to the presence of various inorganic minerals/materials. Herein, implementation of simple and efficient pre-treatment steps could play a major role in removing the valuable minerals which would rather hinder the efficiency of further downstream processing. In lactic acid production process from dairy by-product streams, $\text{Ca}(\text{OH})_2$ precipitation has proven as an efficient pre-treatment step in recovering CaPO_4 while enhancing the production efficiency of lactic acid from whey permeate (O'Brien *et al.*, 2018). Fig. 6 summarizes the series of advanced pre-treatment, intermediate and final steps being adopted to enhance P release from wastewater and Mg recovery from seawater/brine.

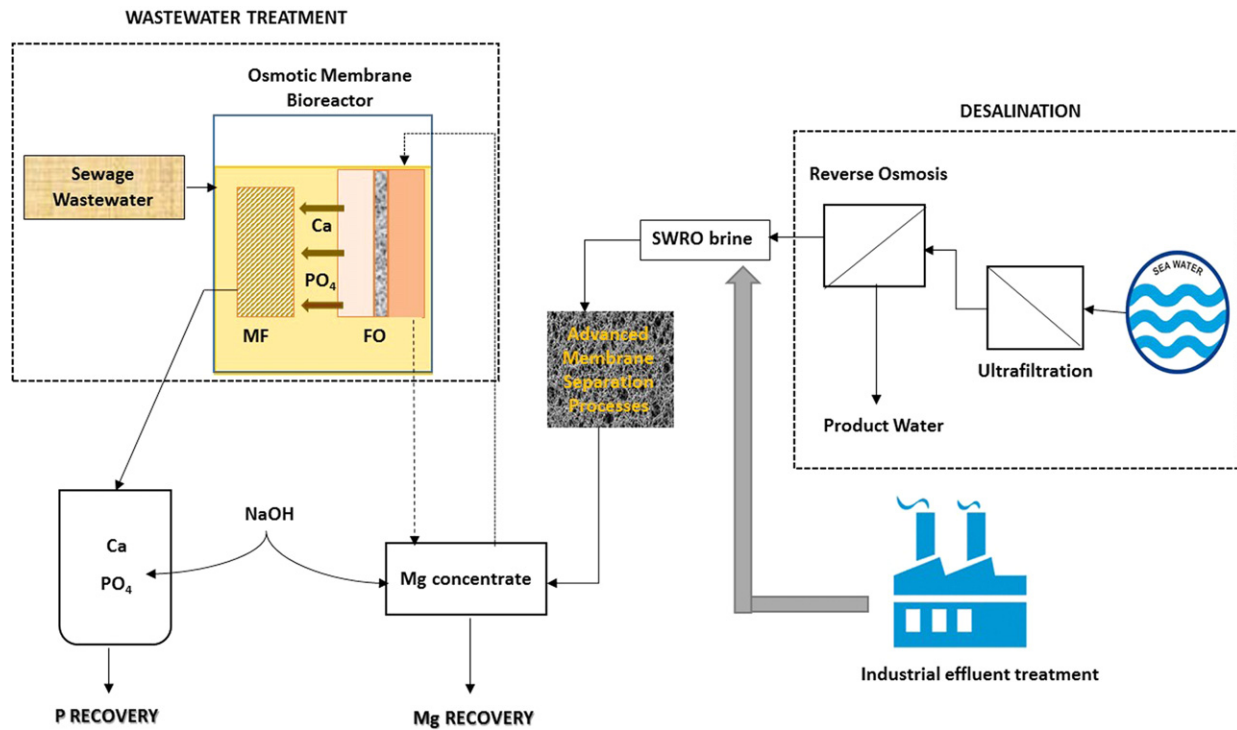


Fig. 5 Process integration of wastewater treatment and desalination systems for simultaneous P and Mg recovery.

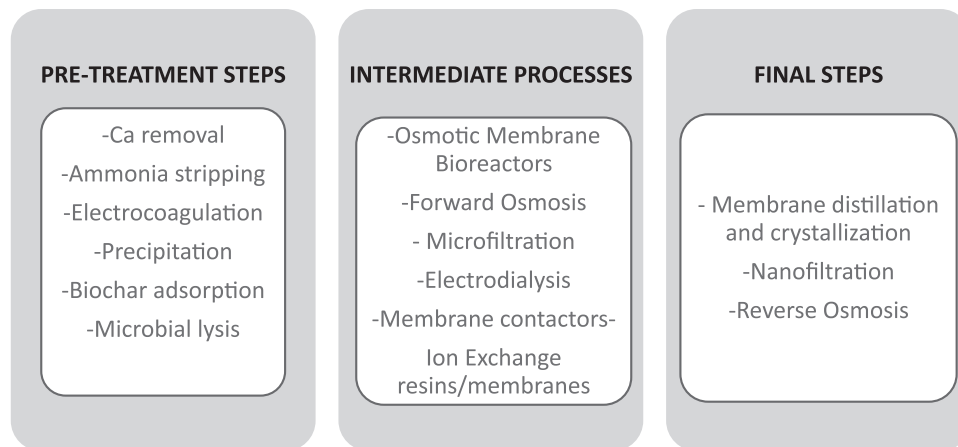


Fig. 6 Summary of advanced pre-treatment, intermediate and final processing steps specific to Mg and P recovery.

Biotechnological Approaches

Phosphorous can be recovered by biotechnological approaches based on two strategies. The first being microbial cell lysis for release of intracellular phosphate accumulated during biological nutrient removal process and the other is to induce the precipitation of phosphorous by influencing the pH conditions of the wastewater through metabolic pathways. In general, wastewater generated by domestic activities contains 5–20 g of phosphorous per cubic metre. The domestic wastewater is mostly treated using activated sludge processes. During the activated sludge process, the phosphates available in the wastewater are taken up by the microbial consortia present in the sludge to meet the metabolic needs of the cell. The excess phosphate taken up by the cell is stored as polyphosphate with in polyphosphate accumulating organisms. These organisms can be enriched by recirculating the activated sludge for accumulation of significant amount of phosphorous (up to 90%) (Wang *et al.*, 2017). Hence, waste activated sludge (WAS), a by-product of biological wastewater treatment process is gaining attention for recovery of phosphate due to its

availability and affordability. However, several challenges are need to be addressed such as low phosphorous release, economics of the entire process etc. Though the substrate is cheaply available, low recovery of phosphorous pose a serious challenge in recovery of phosphorous from sludge.

The first step in recovery of phosphorous from WAS is the release of phosphorous from intracellular and extracellular of the microbial cell. This step is typically done by microbial cell disintegration, yet efficient means of cell disintegration are required to meet the desirability. Various methods such as acid/ alkali hydrolysis, incineration, electro dialysis, ultrasonication have been investigated (Xu *et al.*, 2018). Though these methods can substantially increase the rate of release by disintegrating the cell wall and extra cellular polymeric substances, requirements of huge amounts of chemicals (acid/alkali), energy requirements affects the commercial viability and eco-friendly nature of these processes. Hence, identification of eco-friendly, energy efficient and affordable technologies to promote the recovery of phosphorous from waste activated sludge is need of hour. Few processes such as free ammonia treatment have been investigated for its biocidal activity and its application in sludge disintegration at lower concentrations. In this context, insights into energy efficient technologies need to be developed for enhanced recovery of phosphorous from microbial sludge produced during biological treatment processes.

On the other side, phosphorus can be precipitated/crystallized as hydroxyl apatite via changing the pH conditions and chemical dosing in wastewater (Baur *et al.*, 2008). However, this phenomenon could lead to clogging of the pipes if not properly controlled and can lead to economic loss. Therefore alternate strategies need to be explored for precipitation of phosphorous. Aerobic granular sludge process is one process that could be investigated as economically viable option for phosphorous recovery. The aerobic granular sludge process is recognized as a promising technology for treatment of wastewater at high organic loading rates. In addition to the removal of organics simultaneous nitrification and denitrification, phosphorous accumulation could be achieved. Precipitation of P has also been reported during activated sludge systems, however more insights into the process need to be developed. Calcium phosphate precipitation is a key contribution for P removal during Enhanced Biological Phosphorous Removal Processes (EBPR) and it is believed to increase the efficiency of biological phosphorous removal.

Future Perspectives and Technology Challenges on Sustainability

Globally securing sustainable access to CRMs is of high importance to meet the demands of industrialisation. However, with varying substitutability indices across the CRM spectrum, certain countries hold a monopoly on future, finite supplies. Currently the processing, recycling, reuse and recovery technologies of CRM are very complex, costly, and with very low yields. It is essential that new innovative technologies are implemented to provide efficient and scalable solutions to recover CRMs such as P and Mg from various complex resources. However, the biggest challenge to industry is to scale the innovative recovery technologies to produce commercially viable CRM's in a sustainable manner. A recent report highlighted that the use of CRM's in the EU economy is far from the ideal closed loop, circular economy (Mathieux *et al.*, 2017). That report also suggests a multi-component approach to tackle this global issue:

- (1) The need for a legislative framework governing processes to facilitate the extraction of CRMs from input flows.
- (2) Implement a sustainable policy on product life cycle - recycling, re-use, product lifetime extension, and new business models.
- (3) Ensuring up-to-date data is produced tracking CRM's across the life cycle (e.g., via The Raw Material Information System).

In order make these technologies industrially adoptable, it is essential to integrate traditional recovery processes with novel separation processes, such as membrane based technologies. The main advantage of membrane separation processes is that can offer relatively high yield CRM recovery, at low temperatures which minimises energy consumption. However to overcome other existing limitations of traditional membranes, more advanced membranes such as surface functionalised ion exchange membranes and electrospun membranes may offer a sustainable solution (Saranya *et al.*, 2018). These separation processes can further coupled with pre-treatment and bioremediation processes, resulting in relatively high yield and purity products. Clearly it is of critical importance that new processes that are developed are environmentally friendly with high energy efficiencies to create a global sustainable solution to this immediate issue.

Adoption of integrated process to catalyse a switch in the recycling and production transformation for CRMs and fossil-energy based materials could essentially help in building circular material flows on par with United Nations Sustainability development Goals. Promotion of sustainable technologies for sewage waste management and desalination enable P and Mg recycling respectively to ensure several sustainable aspects, however not limiting to depollution, renewability, demand-supply balance, food/environmental safety, macronutrient balance. It is also worth mentioning that one best solution does not preferably be suited for either P or Mg recovery as the process selection and integration depends on various factors including the geographical context, feed wastewater properties and so on. For example, membrane bioreactor combined with struvite precipitation is effective in terms of biosolids management, energy and P recovery. Further research and monitoring are strongly needed, including into improving organic contaminants removal in biosolids treatment, optimisation of energy recovery, and development and implementation of nutrient recovery processes. While focusing particular methodology for sewage/brine management and P/Mg recycling, the merits of various approaches specific to each stand-alone process must be brought together in the context of zero waste, quality control, transparency and effective product recovery. The European Commission has also estimated that P recycling methods could preferably replace 30% of Europe's P import for producing mineral based fertilizers. In the context of sustainability and renewability of Mg, it is worth considering the findings from a recent publication which highlighted that for every litre of

freshwater output, desalination plants produce approximately 1.5 litre of brine (Jones *et al.*, 2018). On the global level this equates to 142 million cubic meters of hypersaline brine discharged every day, as a magnesium rich waste stream. Unfortunately to date, the high economic costs and energy demands of brine treatment for the recovery of magnesium remains a significant barrier to more widespread application. The role of research and innovation is critical to realise a closed loop solution to this immediate issue, and membrane separation technical developments now offer a viable future path. Indeed, future vision on committing to 'sustainability' and 'zero waste' are focused greatly on CRM recovery from waste to stay well ahead of strict regulations on waste management and circular economy.

Acknowledgements

The authors are thankful for the funding by Science Foundation Ireland (SFI) under AMBER Grant No. SFI/12/RC/2278. Sarat would like to acknowledge financial support from BBI-IA-FLAG-Biobased Industries Innovation Action-Flagship-AgriChemWhey project under grant agreement-744310. Ramesh acknowledges the financial support from SFI under BEACON Grant No: 16/RC/3889.

See also: Bio-Waste Based Nanofiber Materials. Conversion of Renewable and Food Wastes into Useful Products with Environmental Perspectives. Food Waste for Sustainable Packaging Materials. Recycling Approaches, Policies and Regulations on Electronic Waste With Special Focus on India. Recycling of Construction and Demolition Wastes Into Renewable Construction Materials. Recycling of E-Waste. Reuse of Waste Corrugated With Coir Fibers as a Packaging Material. System Optimization for Control of Solid Waste. Toward Reclamation of Fibrous Waste Stream Materials. Waste Conversion Into Sustainable and Reinforcing Fillers for Rubber Composites. Waste Printed Circuit Board (WPCB) Recovery Technology: Disassembly and Desoldering Approach. Waste Resources Recycling in Achieving Economic and Environmental Sustainability: Review on Wood Waste Industry

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Further Reading

Directorate-General for Internal Market, Industry, Entrepreneurship and SMEs (European Commission). Study of the review of the list of Critical Raw Materials. EU Publications. doi:10.2873/398823.

Biochar as Sustainable Reinforcement for Polymer Composites

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Introduction

Polymer composites reinforced with various fibre and particulate materials receive greater interest due to their physicochemical and functional properties, which significantly replace and substitute the traditional metal components in many potential applications with the added advantages of simple manufacturing ability and cost reduction (Pickering *et al.*, 2016; Giannelis, 1996). Various types of thermoset, thermoplastic and elastomeric matrix based composites have been extensively fabricated and explored for a wide range of industrial and consumer products. The increasing usage of polymer composites in various industrial sectors including, the wind energy, aerospace, packaging, construction and automotive lead to their market growth from the US \$ 72.58 billion in 2016 to the US \$ 115.43 billion by 2022, with the compound annual growth rate (CAGR) of 8.13%. Most of the polymer composites exist in the current market consist of petroleum based matrixes, which are nonrenewable and non biodegradable (MarketsandMarkets™). The issues arise during their post consumption disposal, which creates severe environmental impact. The emerging environmental concerns (i) in utilizing the petroleum feedstocks for polymer matrix, (ii) waste generation on their end of life disposal, (iii) greenhouse gas emission during the various stages of their value chain and (iv) the demand for sustainable manufacturing lead the researchers to work aggressively towards the alternate solution. As the result, biopolymers that includes the biodegradable polymers from petroleum feedstock and biodegradable/non- biodegradable polymers from renewable based resources have been invented and explored for various uses (Reddy *et al.*, 2013). In reinforcement perspective, various synthetic fibres such as glass, aramid, nylon, rayon, polyester, and carbon have been extensively explored in polymer composites. Non-renewable source and manufacturing cost of those synthetic fibres created the demand for renewable and cost-competitive substitute for composite fabrication. Thus, more attention has been paid by academic and industrial researchers in formulating new polymer composites containing natural reinforcements of fibres and particulates. Biomass reinforcement in polymer matrix offer, not only the environmental and economic benefits but also reduces the overall weight of the products compared with their glass fibre counterpart. Abundance of renewable resources lead to the effective utilization of various types of biomasses, which includes bio fibres (jute, sisal, cotton, cellulose), biomasses (switchgrass, miscanthus, sawdust), industrial coproducts (lignin, distiller's dried grains with solubles (DDGS), husks, shells) as the reinforcement in composite fabrication. Bio fibres can be classified based on the part of the plant, which includes, bast or stem fibres (jute, mesta, banana etc.), leaf fibres (sisal, pineapple, screw pine etc.) and fruit fibres (cotton, coir, oil palm etc.) (Wambua *et al.*, 2003). However, the biomass reinforcement creates few challenges such as, there moisture absorption behavior, limited thermal stability and poor compatibility with various kinds of polymer matrix, which limit the commercial potential of their composites. In the thermoplastic platform, bio-reinforcement creates the major issue of their thermal degradation during the extrusion process, which hampers the physicochemical performance of composite material due to the poor compatibility between thermally degraded biomass and the polymer matrix. Hence, the bio-reinforcement in engineering plastics is still challenging task as it has higher melt processing temperature ($\sim 220\text{--}300^\circ\text{C}$). Extensive efforts have been made in order to enhance the thermal stability of biomass, which includes water washing, chemical modifications and physical treatments. Recent advancement in that aspect is the thermal stabilization of biomasses, which can be termed as torrefaction, charification, carbonization, and graphitization that deals with the varying temperature and environments. Prior thermal history of biomass creates an enhanced thermal stability during their melt processing and the bio-reinforcement is possible in all the thermoplastics, including engineering plastics such as PET, PBT, PTT, and Nylon. Among the various thermo-stabilized biomasses, biochar receives significant attention in recent years and has been explored for composite applications. Biochar has been reinforced in a wide range of polymers from thermoset, thermoplastic and elastomeric categories. Conversion of biomass into biochar lead to the enhancement of their thermal stability creates new functional groups and reduces the density, which are the essential features for the efficient reinforcement. Increasing importance for the biochar reinforced polymer composite leads to this article, which deals with a brief summary of biochar based polymer composites and their properties. Further, it also discusses the biochar production, properties and their modification strategies for polymer composites along with their other potential applications.

Feedstocks, Process, Properties and Potential Applications of Biochar

Biochar is a carbonaceous solid product obtained from the biomass through the pyrolysis process along with syngas and biooil. The application potential of the biochar is depended on its inherent physicochemical and functional properties, which are influenced by many factors that include the nature of feedstock, type of pyrolysis process and pyrolysis conditions (temperature, heating rate, environment and resident time). Hence, it is necessary to understand the feedstock- process- property co-relationship in order to meet the demand for the specific application.

Feedstock for Biochar Production

Biochar has been produced from various biomass sources, which can be categorized into (i) agro/forestry residues (straw, stover, stalk, bark and wood chips), (ii) marine products (micro/macro algae), (iii) industrial coproducts (lignin, DDGS, hull/husks, oil

cakes, coffee chaff/ground, nut shells, tomato/grape/apple pomace, seeds and fruit peels), (iv) short term woody biomasses and energy crops (willow, poplar, miscanthus and switchgrass) and (v) municipal clean wastes (cardboard sheets and wooden pallets). In some cases, biochar also been produced through the co-pyrolysis of plastic wastes with various biomasses (Sharypov *et al.*, 2002). Most of the feedstocks that used for biochar production are undervalued, which creates various environmental issues on their storage and disposal. In most of the cases, the industries face economic burden due to the expenses for their effective disposal. Traditionally they have been explored as low cost fuel for energy application and creating new products through pyrolysis enhance their economic return and strengthen the waste based economy. Recent advancement in biochar utilization in many areas lead to creating an ever-increasing demand and causes the supply chain related issues, which can be addressed by exploring a diverse range of biomass for biochar production. Also, the biomass diversity and their availability vary region to region, which creates the necessity for biomass integration in char production in order to sustain their related technologies. Apart from the char production, it also helps to prevent the waste generation, reduces the greenhouse gas emission, creates more economic benefits and generates more employment opportunities (Cha *et al.*, 2016; Inyang *et al.*, 2016). Based on the nature of biomass, biochar production technology also varies in order to get more energy and cost efficiency. For intense, the physicochemical properties of the biochar are significantly impacted by the type of process and processing conditions.

Biochar Processing

The three major thermochemical conversion of biomass are the combustion/incineration (decomposition of biomass through complete oxidation), gasification (partial oxidation of biomass to get hydrocarbons), and pyrolysis (degradation of biomass without oxygen or inert atmosphere), which results in bioenergy, biofuels, biochemicals, and other value-added products (Yin, 2012; Motasemi and Afzal, 2013). Among them, pyrolysis has been explored for the production of biochar along with syngas and biooil. In biochar production, the critical factors are the yield and carbon content, which are controlled by the pyrolysis process. Various processes, which includes direct thermal pyrolysis (DTP), microwave assisted pyrolysis (MAP), plasma assisted pyrolysis (PAP) and hydrothermal carbonization (HTC) processes have been extensively used for the biomass pyrolysis/carbonization in order to get pyrolytic products such as syngas, biooil and biochar. The char product obtained from HTC process often called as hydrochar. Direct thermal pyrolysis process can be further classified into following three categories, (i) slow pyrolysis-lower heating rate of the biomass, (ii) fast pyrolysis- higher heating rate of the biomass, (iii) flash pyrolysis - exposure of biomass in heat for very short span of time i.e., few seconds (Goyal *et al.*, 2008). In this process, electric heaters or flame are employed as the source of heat. In order to enhance the carbonization uniformity and efficiency with a reduced duration other energy sources, which are based on microwave irradiation and plasma exposure have been introduced for the pyrolysis of biomass. The microwave is an electromagnetic radiation with the frequency ranging between 0.3 and 300 GHz and most of the laboratory microwave reactors operate at 2.45 GHz frequency (Motasemi and Afzal, 2013). In conventional thermal heating, the heat is transferred from the surface into the core of the material, whereas in microwave heating process the radiation can penetrate the materials and the heat can be produced throughout its volume. Microwave assisted biomass pyrolysis reduces the residence time due to effective heat transfer mechanisms, which leads to effective energy savings (Motasemi and Afzal, 2013). The plasma is consist of a large fraction of ionized gas and generates very high temperatures, which is capable of pyrolyzing the biomass and various organic waste streams. A diverse range of plasma sources are available, which can be effectively utilized for the pyrolysis of various biomasses (Chang, 2001). Plasma pyrolysis also results in the formation of gaseous and liquid hydrocarbons along with solid matter i.e. biochar (Huang and Tang, 2007). Thermal decomposition of biomasses employing the subcritical water is commonly known as hydrous pyrolysis or hydrothermal carbonization (HTC) (Libra *et al.*, 2011). The advantage of HTC process is the effective utilization of wet biomasses to turn into carbonaceous with relatively high yields comparing to the other carbonizing or pyrolysis processes. HTC is a green and sustainable process and a variety of biomasses can be converted into carbonaceous material in water at mild temperatures (Titirici and Antonietti, 2010).

Physics and Chemistry of Biochar

The thermal treatment of biomass alters its original physical and chemical structures through microscopic rearrangement, decomposition, pore formation, and crack generation, which are highly depend upon the chosen biomass and processing conditions (Downie *et al.*, 2009). Physical properties of the biochar that includes, density/porosity (pore volume and pore size distribution), specific surface area, hydrophobicity and water holding capacity, mechanical stability/grindability, electrical/electromagnetic properties, thermal stability/conductivity /heat capacity and agglomeration potential play important role in their application potential (Weber and Quicker, 2018). These properties highly depend on their chemical features, which can be assessed by means of atomic ratios, elemental composition, energy content, fixed carbon and volatile matter, functionality, pH value, ash content and self heating (Weber and Quicker, 2018). The density of the biochar can be correlated with the density of the parent biomass and it was observed that the higher density of the biochar could be obtained by using high density biomass as a feedstock (Byrne and Nagle, 1997). Increasing carbonization temperature increases the surface area up to 800°C. Further, the increment of carbonization temperature ranging between 800°C and 1000°C causes the reduction of surface area, which is due to the pore closing mechanism during the graphitization (Brown *et al.*, 2006). Carbonization process of biomass can improve the carbon content, which increases with increasing carbonization temperature and can be reached to ~90%. Irrespective of feedstock,

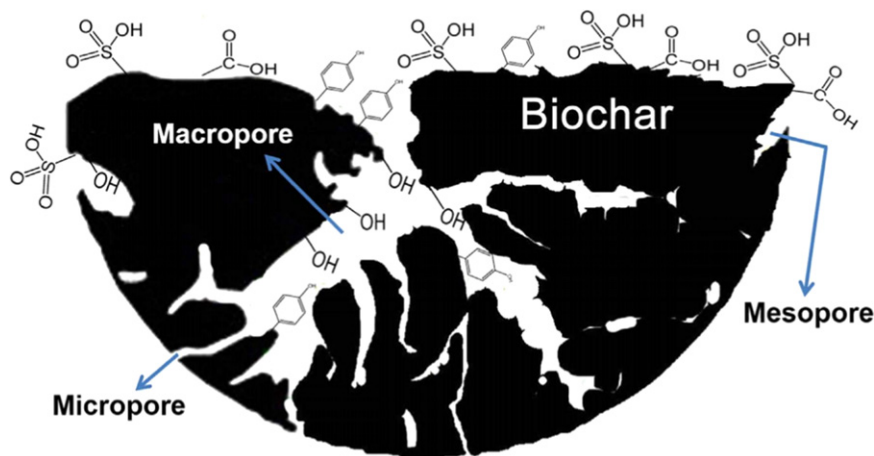


Fig. 1 Schematic representation of the various functional groups and the pore configuration of biochar. Reproduced from Lee, J., Kim, K.-H., Kwon, E.E., 2017. Biochar as a catalyst. *Renewable and Sustainable Energy Reviews* 77, 70–79.

biochar exhibits various functional groups on their surfaces, which includes carboxyl ($-\text{COOH}$) and hydroxyl ($-\text{OH}$) groups (Lee *et al.*, 2017). Fig. 1 shows the schematic representation of various functional groups of biochar and its pore configuration. Increasing pyrolysis/carbonization temperature decreases their surface functionalities. Biomass feedstock is slightly acidic or mildly basic, which exhibited the pH-value varies from 5 to 7.5. Pyrolysis process increases its pH-value, which can be reached 10–12, while the pyrolysis temperature is 500°C and above. The ash content of biochar is mainly dependent on the ash content in the parent biomass. It consists of various metal oxides, which includes SiO_2 , CaO , K_2O , P_2O_5 , Al_2O_3 and MgO (Weber and Quicker, 2018). All the above discussed properties are highly depend on the characteristics of biomass feedstock and the chosen carbonization process as well as their conditions, which can be precisely controlled through appropriate selection of materials and methods to achieve desired product properties. Understanding the process-property co-relationship is the critical aspect of biochar utilization for various applications.

Potential Applications

The unique and diverse physicochemical, morphological, structural and functional properties of the biochar lead them as suitable material for the various potential application. The application platforms of biochar can be classified into two categories such as traditional and technological. Traditional applications of biochar include soil amendment, energy production and carbon sequestration, whereas technological applications deals with catalytic, energy storage/conversion, activated carbon production, and environmental remediation. In addition to that biochar also been explored as the suitable candidate as the reinforcement for the fabrication of polymer composites.

Traditional applications

- (1) **Soil amendment:** The various roles of biochar in soil amendment is the immobilization of contaminant elements, sustained nutrient release, enhance organic carbon of the soil, alteration of pH and efficient water holding capacity (Uchimiya *et al.*, 2010). The biochars contain a wide range of nutrient with highly varying release rates, which impacts the overall soil quality and increases the crop yield significantly (Chan *et al.*, 2008). The biochar addition to the soil also stimulate the growth of soil microorganisms and lead to improved nutrient recycling, which are trapped in biochar (Steinbeiss *et al.*, 2009). It has been found that the biochar addition to the waterlogged paddy soil reduces the greenhouse gas (CH_4 and CO_2) emission (Liu *et al.*, 2011). The inclusion of biochar can effectively influence the soil-forming processes, which is an integrated action (accumulation, transformation, and translocation) of the soil constituents and can modify the soil morphology, pedogenic activity, and productivity (Richter, 2007). Altogether, biochar based soil amendment can be considered as the sustainable solution as it utilizes organic residues to generate biochar.
- (2) **Bio-Energy production:** Using raw biomass as fuel exhibits challenges like its high moisture content, lower energy density and poor grindability, which leads towards higher transportation cost. Converting biomass into biochar overcomes these disadvantages with higher energy density. It was observed that the biochar produced at $\geq 320^{\circ}\text{C}$ exhibits the H/C and O/C ratios as similar as to Collie coal (Abdullah and Wu, 2009). Efficient grinding is possible after the biomasses were converted into biochars leading to the increment of its volumetric energy density. Apart from the elemental carbon content, the ash concentration of biochar is the critical factor, not only in getting more calorific value but also the lifetime of the combustion chamber (Laird *et al.*, 2009). Hence, it's necessary to choose the biomass with less ash content for biochar production towards energy application. For the effective transportation of biochar with our any spillage, it must be pelletized or compacted.

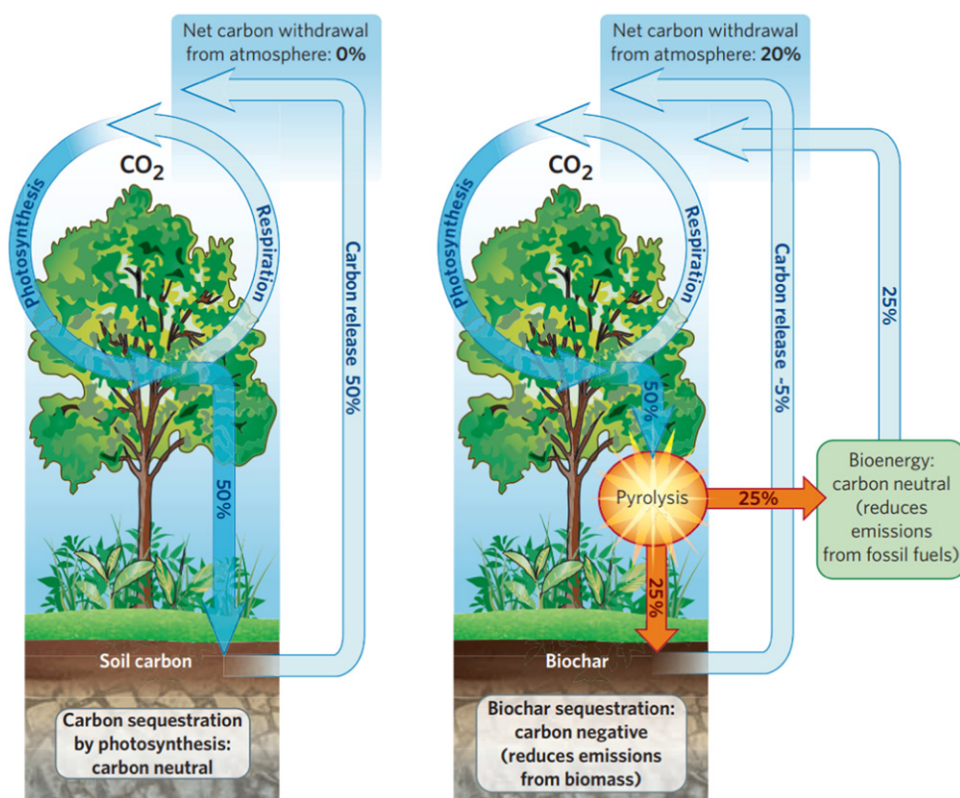


Fig. 2 Schematic for the comparison between carbon and biochar sequestration. Reproduced from Lehmann, J., 2007. A handful of carbon. Nature 447, 143.

Pelletizing ability of the biochar can be increased by reducing the particle size or exploring the any environmental friendly binder (starch, natural gum, and lignin).

- (3) *Carbon sequestration*: The challenging climate change and global warming impacts can be reduced either by avoiding greenhouse gas emission or by eliminating the atmospheric CO_2 through excessive plant growth, which can act as CO_2 sequester (Lehmann, 2007). This kind of sequestration can be further enriched by converting the biomass into biochar through pyrolysis process (heating the plant biomass in oxygen less environment), in which biochar holds twofold higher carbon content comparing to their respective biomass (Baldock and Smernik, 2002). Producing biochar as the by product in pyrolysis industries during bioenergy production lead their relevant sequestration process with carbon-negative impact as shown in Fig. 2. Biochar sequestration can also consider as the robust and simple method as it does not require any scientific and technological advancement.

Technological applications

As the carbonaceous product, biochar receives great attention for various technological applications in order to substitute or replace the existing carbon materials that are obtained from petroleum resources. This will create a fundamental transformation of biochar production from waste management strategy into advanced materials manufacturing.

- (1) *Activated carbon*: The carbon material with high specific surface area and micro sized porosity, which are commonly produced from carbon rich and inorganic less feedstocks. Agro/forestry residues and various industrial by-products have been found as suitable raw materials for activated carbon due to their abundance and cost effectiveness (Ioannidou and Zabaniotou, 2007). Being a carbon rich product biochar can be explored for the production of activated carbon by employing various activation processes, which are based on physical, chemical and radiation platforms. Physical activation of biochar deals with its carbonization at elevated temperature in presence of various oxidizing mediums including CO_2 , steam, air and their mixtures. In the chemical activation process, the char products are finely mixed with the chemical activating agent such as KOH, ZnCl_2 , H_3PO_4 , and K_2CO_3 , followed by their carbonization at higher temperature and acid washing. Along with these, the microwave based activation process also been explored for the effective conversion of biochars into activated carbons. Selectivity of these processes is strictly based on the desired physicochemical and functional properties for specific applications.
- (2) *Catalysis*: Biochar has been extensively explored as the green and versatile catalyst for various applications including chemical synthesis, biodiesel production, tar reduction in pyrolysis process during bio-oil/syngas generation, microbial fuel cell

electrodes, deNO_x applications and pollutant degradation (Cha *et al.*, 2016; Lee *et al.*, 2017; Xiong *et al.*, 2017). Studies reviles that the catalytic performance of the biochar is comparable and even superior than the traditional resin, silica, and carbon-based catalysts (Xiong *et al.*, 2017). Various inherent properties of the biochar such as specific surface area, the assistance of micro/nano pores and their distribution and the –SO₃H site density play vital role in the catalytic performance of biochar. The catalytic activity of the biochar is highly dependent on the nature of biomass, biochar generation method and their conditions, and the pre/post treatments of the biochars (Lee *et al.*, 2017). Post treatments-post activation and oxidative acid treatment of the biochar play significant role in creating new functional groups, which can enhance the catalytic activity (Cha *et al.*, 2016; Anstey *et al.*, 2016). Selection of biomass, pyrolysis process, processing parameters are the key factors to get desired properties for biochar as the suitable catalyst for the specific application.

- (3) *Energy storage and conversion*: Carbon materials including, carbon black, carbon nanotubes, graphene and carbon fibres have been extensively used in energy storage and conversion devices such as batteries and supercapacitors (Zhang and Zhao, 2009). Along with these, biochar also receives increasing importance due to its unique physicochemical properties, surface area, porosity, structural stability during long term cycling performance and diverse morphological features. Pristine and modified forms of biochars have been explored as an anode material for various lithium batteries including lithium-sulfur, lithium oxygen and lithium-selenium (Zhang *et al.*, 2015; Gu *et al.*, 2015; Li *et al.*, 2016). In the electric double layer capacitor (EDLC), biochar products have been explored as the electrode material, which showed improved electrochemical performance (You *et al.*, 2017). Along with these, the biochar based polymer composites fabricated with polyaniline and polypyrrole also explored in fabricating supercapacitors.
- (4) *Environmental remediation*: Carbon materials exhibit excellent performance in various environmental remediation activities, which includes the immobilization of heavy metals, absorption of dyes/organic contaminants, and the removal of odor from water/air (Ahmad *et al.*, 2014). Biochar plays vital role in the above mentioned applications due to its porous structure and higher specific surface area. A wide range of metal impurities (Pb, Ar, Cr, Hg and Cd) (Inyang *et al.*, 2016), organic dyes (methyl orange), and chemical components (dichloro-diphenyl-trichloroethane (DDT), tetracycline (TC) (Liu *et al.*, 2012), polycyclic aromatic hydrocarbons (PAHs) as well as inorganic compounds (nitrate, ammonium, and phosphate) (Yao *et al.*, 2012) have been effectively removed from the aqueous medium by employing biochar. Further the activation process (physical, chemical, and radiation) of biochar enhances its porosity and active surface area, which improves its overall absorption performance. Being cost effective and greener product, biochar can have a great potential for environmental remediation application. The mechanism behind the absorption of inorganic contaminants by biochar is schematically shown in Fig. 3 (Ahmad *et al.*, 2014).

Biochar as Sustainable Filler/Reinforcement in Polymer Composites

Carbon materials including, carbon fibres, carbon black and carbon nanostructures (carbon nanotubes, graphene) have been widely explored as filler/additive/reinforcement for composite fabrication (Coleman *et al.*, 2006; Chand, 2000; Kim *et al.*, 2010; Huang, 2002). Apart from the reinforcing effect, those carbon materials also provided various functional properties that include electrical conductivity, EMI shielding and UV filtration. As a green and sustainable alternative, biochar receives great attention as efficient reinforcement in polymer composites for various matrix systems.

Thermoplastics

The interesting aspect of biochar utilization in composite fabrication is their feedstock diversity, which offers biochar with a wide range of structural, morphological and functional properties. Biochar obtained from various renewable resources were explored as reinforcement for thermoplastic matrix systems employing melt extrusion process. Polypropylene (PP) has been widely explored as the matrix for the fabrication of biochar reinforced composites. The biochars obtained from various bio-feedstocks such as agro/forestry reduces (hardwood (DeVallance *et al.*, 2016), bamboo, date palm tree wastes (Poulose *et al.*, 2018)), perennial grasses (miscanthus (Behazin *et al.*, 2017a)) industrial coproducts (lignin), organic wastes (landfill pine wood (Das *et al.*, 2017), sawdust, sewage sludge, and poultry litter (Das *et al.*, 2016b)) have been extensively explored for composite fabrication. It has been found that the surface area of the biochar play a significant role in the thermal and mechanical properties of composite material (Das *et al.*, 2016a). It has been observed that biochar reinforcement in PP not only enhance the mechanical properties but also improves its thermal stability/insulation properties and water absorption /thickness swelling performances (DeVallance *et al.*, 2016; Das *et al.*, 2016a). In order to enhance the mechanical properties of the biochar reinforced PP composites, researchers also explored the modification of matrix by incorporating an elastomer named poly(octene ethylene) (PEO). Also, the addition of compatibilizer, which enhances the interfacial adhesion between biochar and PP/PEO matrix, which results in the significant improvement of stiffness and toughness (Behazin *et al.*, 2017b). Along with the PP, polyethylene (PE) also been explored as the matrix for the reinforcement of biocarbon (biochar/charcoal) to fabricate biocomposites with the improved physicochemical properties (You and Li, 2014; Chen *et al.*, 2016; Li and Li, 2014). Very few research works also available for the reinforcement of biochar in polyvinyl alcohol (PVA) matrix in order to enhance their performance (Nan *et al.*, 2016; Nan and DeVallance, 2017). It was found that the reinforcement of biochar made of mixed hardwood into PVA matrix leads to having the similar electrical

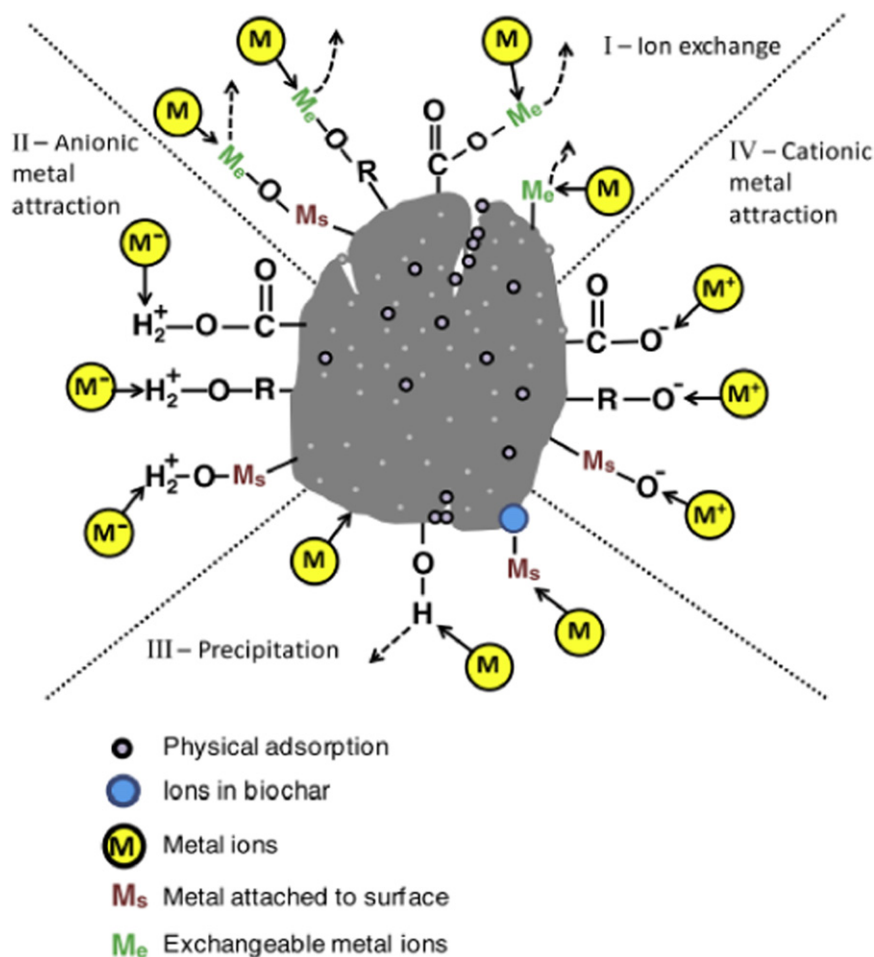


Fig. 3 Schematic of mechanisms of biochar interactions with inorganic contaminants. Reproduced from Ahmad, M., Rajapaksha, A.U., Lim, J.E., et al., 2014. Biochar as a sorbent for contaminant management in soil and water: A review. *Chemosphere* 99, 19–33.

conductivity performance as most of the CNTs and graphene based PVA composites (Nan et al., 2016). The wood-derived biochar reinforced PVA composite was used for the pressure sensor applications (Nan and DeVallance, 2017).

As the demand for biobased polymers increases due to the increasing environmental concern in using PP and PE, the polylactic acid (PLA), which is commonly derived from corn receives greater attention in recent years for various potential uses (Pang et al., 2010). The challenge in PLA based polymer technology is the enhancement of its thermal, mechanical and thermomechanical properties in order to substitute or replace traditional PP based materials that are available in the consumer market. Effective reinforcement is one of the possible ways and hence various synthetic and natural reinforcements have been performed to achieve desired properties. Biochar obtained from bamboo (Ho et al., 2015) and Kudzu biomasses (Salak et al., 2015), also been explored as the renewable reinforcement for PLA. Bamboo biochar /PLA composite showed the improved mechanical properties and compost degradation rate. The thermally treated Kudzu biomass improved the water resistance of obtained PLA biocomposite. Pre-thermal history of biochar exhibits higher thermal stability of biomasses (~500°C), which can be reinforced even in engineering plastics, which exhibit higher melt/processing temperatures. Carbonized biomasses of lignin, miscanthus fibres have been respectively reinforced in the engineering plastics of poly (trimethylene terephthalate) (PTT) and polyamide 6, 10 (nylon) (Myllytie et al., 2015; Ogunsona et al., 2017a). It was observed that the biocarbon obtained at lower temperature (500°C) showed better affinity with nylon matrix and hence improved the impact strength of the composite (Ogunsona et al., 2017b). Fig. 4 schematically shows the affinity of biochar prepared at 900°C and 500°C with nylon matrix. The particle size, size distribution and shape of the biochar play a vital role on the composite properties. Particular with nylon, it was observed that the impact strength was improved with decreasing particle size (Ogunsona et al., 2017a). In another study, it was found that the biochar incorporation into nylon 6 matrix leads to the increment of the melt viscosity of the composite, which can be manipulated by the biochar particle size (Huber et al., 2015).

Apart from the individual polymer matrix, binary and ternary polymer blends also been explored as the matrix for biochar reinforcement. Poly(trimethylene terephthalate) (PTT) and poly(lactic acid) (PLA)PTT-PLA blend matrix was explored by Nagarajan et al. (2016) for the effective reinforcement of miscanthus-based biocarbon. They have investigated the effect of biochar size on the

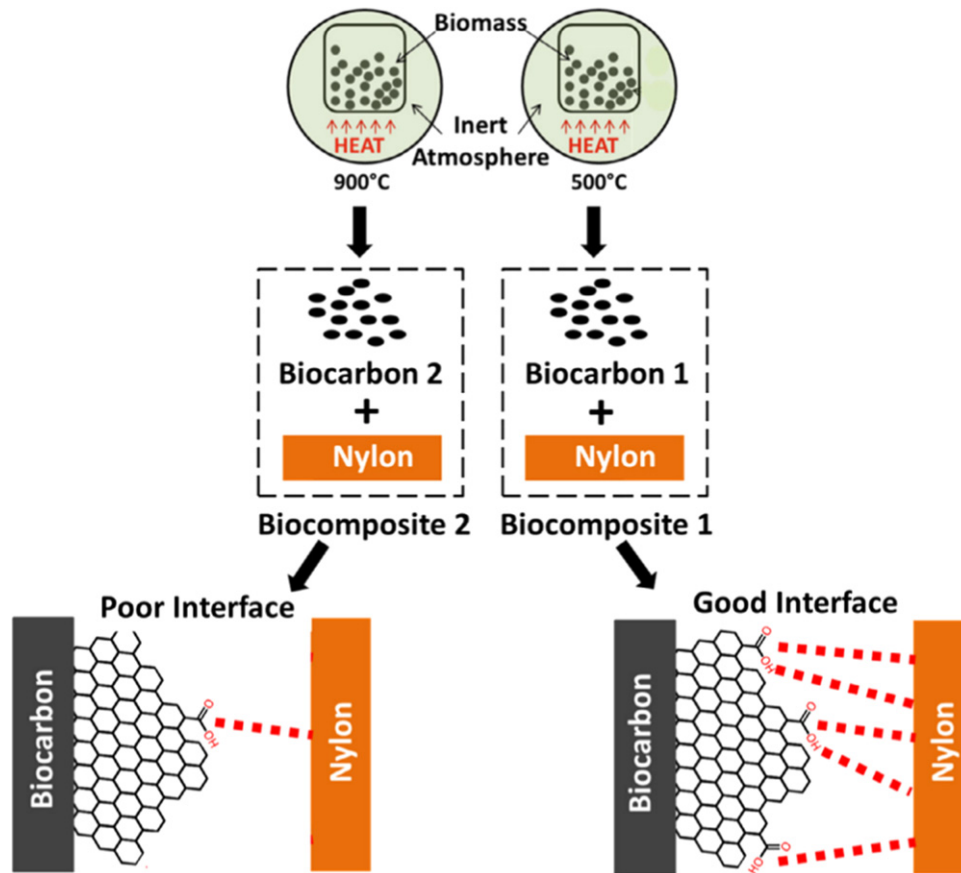


Fig. 4 Schematic representation of the biochar affinity with nylon. Reproduced from Ogunsona, E.O., Misra, M., Mohanty, A.K., 2017. Impact of interfacial adhesion on the microstructure and property variations of biocarbons reinforced nylon 6 biocomposites. *Composites Part A: Applied Science and Manufacturing* 98, 32–44.

performance of composite and found that the increasing particle size slightly decreases their mechanical properties (tensile and impact), which can be improved by manipulating processing conditions (mold temperature) and incorporating chain extender. [Snowdon et al. \(2017\)](#) reported the miscanthus-based biocarbon reinforced ternary blend (Polypropylene/Poly (lactic acid)/Poly (hydroxybutyrate-co-hydroxy valerate)) composite, which showed the reduced tensile and improved flexural/impact properties. Along with the blending the co-injecting molding of biochar reinforced PTT/PBT as a core with polybutylene succinate (PBS) and polybutylene adipate terephthalate (PBAT) skin ([Mohanty et al., 2015](#)). The obtained co-injecting molded composite showed a slight increment in the tensile and flexural modulus. It was suggested that the core made from biochar reinforced PTT/PBT cause the poor tensile and flexural properties and the skin made out of PBS and PBAT lead to having higher impact strengths. [Codou et al. \(2018\)](#) investigated the effect of particle size and morphology of the miscanthus based biochar on the performance employing Maleic anhydride grafted PP (MAPP) compatibilized blend of nylon 6/polypropylene as the matrix (PA6/PP/MAPP). The particle size reduction of biocarbon influences the viscoelastic and thermo-mechanical performance of the fabricated biocomposites. [Fig. 5](#) shows the SEM micrograph of the pristine and ball milled biocarbon (for 4, 12, 18 and 24 h) reinforced PA6/PP/MAPP biocomposites along with the matrix. It was observed that addition of biocarbon inhibited the PP droplet formation (which is observed for the matrix in [Fig. 5\(f\)](#)) and no PP droplets are noticed after the reinforcement of biocarbon ([Codou et al., 2018](#)).

Further, the biochar has also been hybridized with other natural reinforcements such as wood fibre and the resulting hybrid composites exhibit the benefits of both the reinforcements ([Das et al., 2015a](#)). [Das et al. \(2015b\)](#) reported the fabrication of landfill pine wood based biochar and wood reinforced PP composites employing twin screw co-rotating extruder followed by injection molding. Through this work it was identified that the addition of biochar as a hybrid reinforcement along with wood in PP matrix lead to the better mechanical and thermal properties ([Das et al., 2015b](#)). [Andrzejewski et al. \(2018\)](#) reported the fabrication of polycarbonate biocomposites reinforced with the hybrid reinforcement of recycled carbon fibre and biocarbon. The obtained results confirmed the positive impact of biochar hybridization with carbon fibre. The composites made of 10% rCF and 10% biochar as hybrid reinforcement showed 270% improvement in the tensile strength and the 35% enhancement in the modulus with reference to the 20% pure biochar composites. The biochar hybridization will effectively create a new material choice with improved composite performance. [Fig. 6](#). shows the tensile and flexural properties of PC based recycled carbon fibre/biochar hybrid composites ([Andrzejewski et al., 2018](#)).

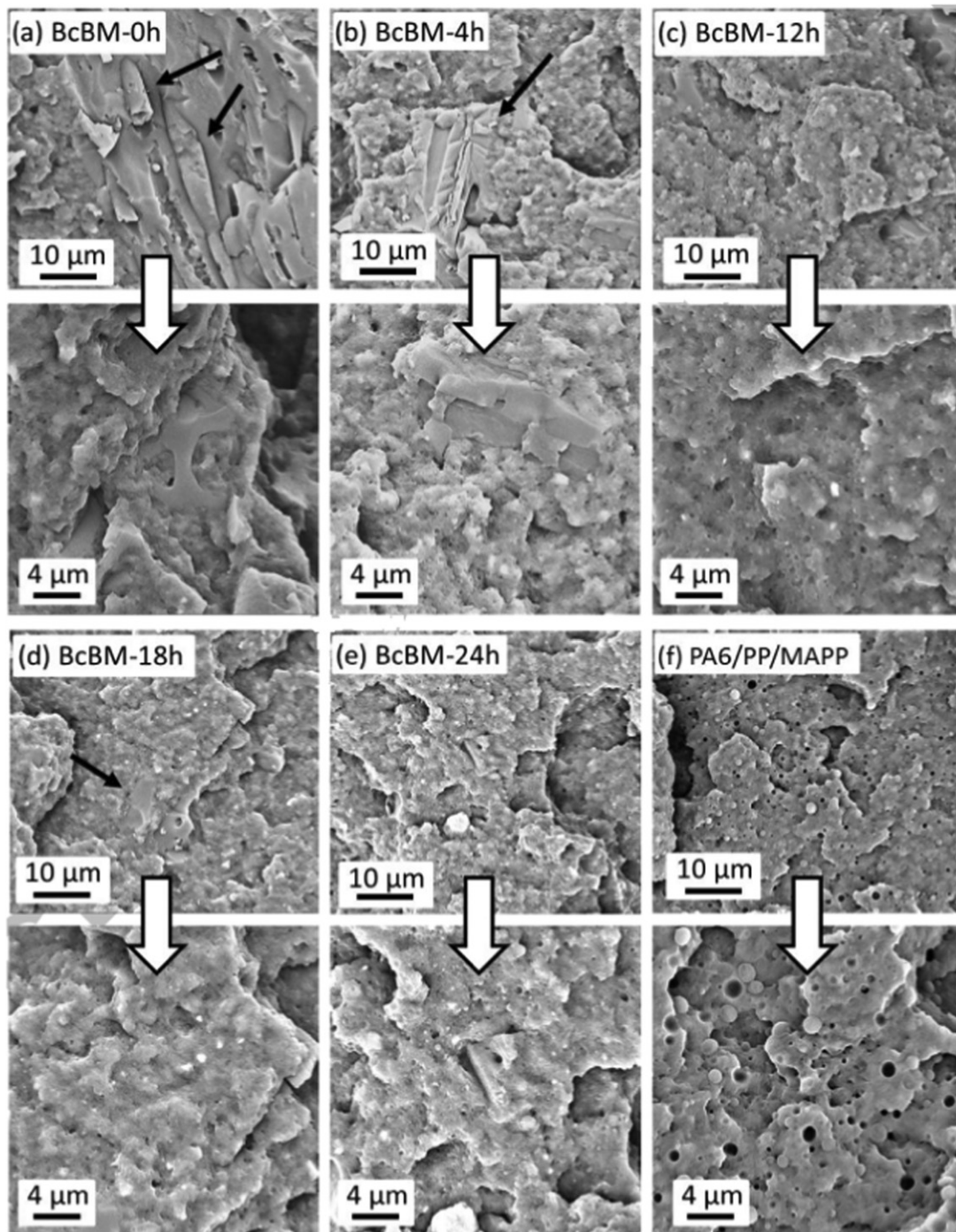


Fig. 5 SEM micrograph of the pristine (a), ball milled biocarbon for 4, 12, 18 and 24 h reinforced PA6/PP/MAPP biocomposites at higher and lower magnification (b-e) and the PA6/PP/MAPP matrix (f). Reproduced from Codou, A., Misra, M., Mohanty, A.K., 2018. Sustainable biocarbon reinforced nylon 6/polypropylene compatibilized blends: Effect of particle size and morphology on performance of the biocomposites. Composites Part A: Applied Science and Manufacturing 112, 1–10.

Thermosets

Thermosets are the polymeric material, which is highly cross-linked and can be cured by employing heat, pressure, and light irradiation. The most common classes of thermosets are phenolic, epoxy, polyurethane and polyester resins, which can be produced from either petroleum or natural resource based monomers (Raquez *et al.*, 2010). Among them, the epoxy resins, which are extensively used in many applications including aerospace, automotive, sports, constructions, and electronics due to their superior mechanical properties, chemical resistance and structural stability. However, the challenging issue for

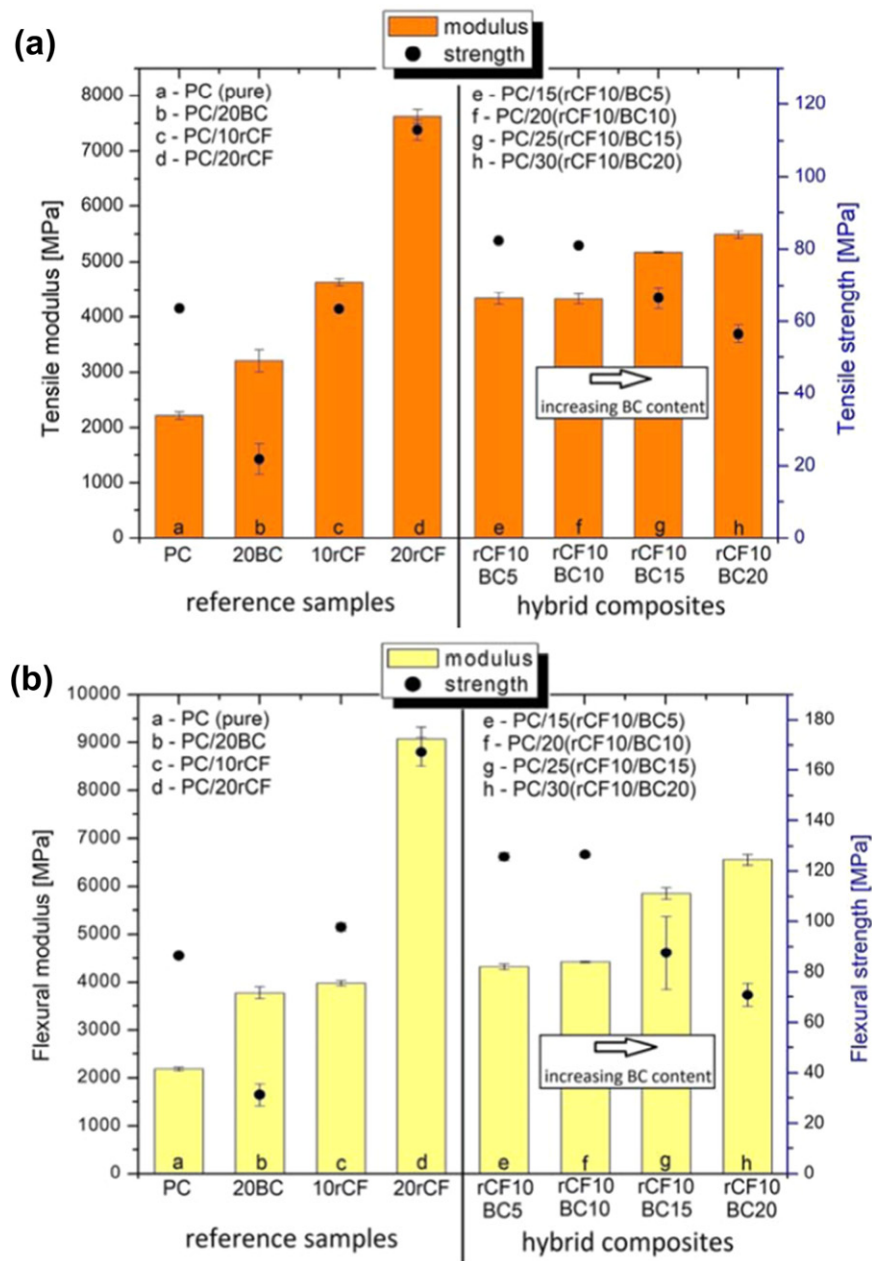


Fig. 6 Tensile and flexural analysis results of PC based recycled carbon fibre/biochar hybrid composites. Reproduced from Andrzejewski, J., Misra, M., Mohanty, A.K., 2018. Polycarbonate biocomposites reinforced with a hybrid filler system of recycled carbon fiber and biocarbon: Preparation and thermomechanical characterization. *Journal of Applied Polymer Science* 135, 46449.

thermoset is their intrinsic brittleness, which can be improved by reinforcing various fibre and particulate materials. Reinforced thermoset composite exhibits the enhanced mechanical properties including the impact strength and hence a wide range of fibrous and particulate materials with natural or synthetic origins have been explored as reinforcement for composite fabrication. The char products of plastic waste, wood shaving and pine cone was explored for the fabrication of epoxy composites with the loading of 5–30 wt% (Ahmetli *et al.*, 2013). Superior tensile properties was observed for the composite reinforced with waste plastic char. The enhanced thermal stability was noticed for the composite made with pine cone char due their shielding effect (Ahmetli *et al.*, 2013). Fig. 7. shows the SEM images of the fracture surface of pure chars of plastic waste (PWC), pine cone (PCC) and wood shavings (WSC) along with the tensile properties of their reinforced epoxy resin composite (d). The biochar derived from china poplar and pine cone has been reinforced with epoxy resin (based on the diglycidyl ether of bisphenol-A) by varying the biochar loading (Oral, 2016). The effect of biochar loading on the elastic properties of epoxy resin/biochar composite was investigated by employing ultrasonic pulse echo overlap (PEO) method. It was observed that the increasing biochar content increases the ultrasonic velocities and effective elastic properties

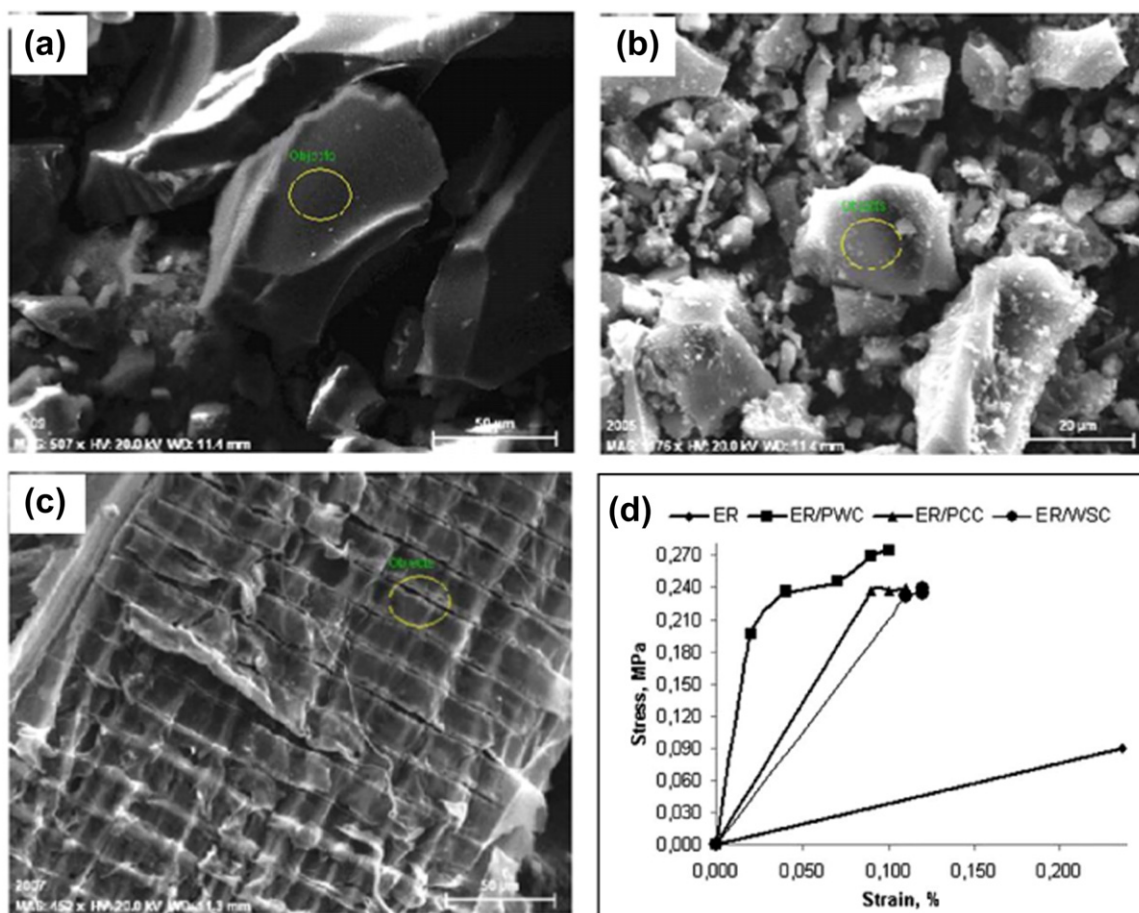


Fig. 7 SEM images of the fracture surface of pure chars of plastic waste (a), pine cone (b) and wood shavings (c) along with the tensile properties of their reinforced epoxy resin composite (d). Reproduced from Ahmetli, G., Kocaman, S., Ozaytekin, I., Bozkurt, P., 2013. Epoxy composites based on inexpensive char filler obtained from plastic waste and natural resources. *Polymer Composites* 34, 500–509.

(Oral, 2016). In another work, the permittivity and conductivity of the pristine and activated biochar reinforced epoxy resin composite were investigated. It was found that the composite made with the activated biochar showed enhanced performance (Giorcelli *et al.*, 2016). The biochar obtained from maple wood biomass by pyrolyzing at the higher temperature of 950°C was reinforced with epoxy resin. Mechanical and electrical behavior of the fabricated epoxy resin/biochar composite was compared to the composites made with the carbon black and multiwall carbon nanotubes reinforcement (Khan *et al.*, 2017). The mechanical properties of the composite material were increased for the 2% of biochar reinforcement and exhibited better performance up to 20%, however, showed inferior properties in the plastic zone (Khan *et al.*, 2017). It was also observed that the tensile behavior of the epoxy resin composites reinforced with 4 wt% of MWCNTs and 20 wt% of biochar (maple wood) are similar (Savi *et al.*, 2017). Along with this, the miscanthus biochar reinforced epoxy resin, poly(furfuryl alcohol) and poly(propylene carbonate) composite also fabricated and the statistical approach was made employing ANOVA to find the correlation between the composition and mechanical properties (Mashouf Roudsari *et al.*, 2017).

Elastomers

Elastomeric materials originated from natural and fossil resources have been extensively used as their pristine and reinforced forms. Increasing the reinforcement of rubber material increases various properties, which includes tensile/tear strength, stiffness, modulus, and rupture energy. A wide range of reinforcements, which belongs to minerals, natural fibres and carbon materials have been explored for the enhancement of elastomeric materials. Among them, carbon black, obtained from the petroleum resources, has been extensively used to fabricate rubber composites due to its desired physicochemical properties. As the demand for sustainable materials that are fabricated from renewable resources and waste streams increases day by day, there is a drive for finding an alternative to carbon black. Being a carbonaceous material with the renewable origin, biochar has found great potential in the fabrication of elastomeric composites as green and sustainable reinforcement. The modified biochar has been effectively reinforced in SBR showed the enhanced tensile properties. Corn stover based biochar was hybridized with corn starch and corn flour for the reinforcement in carboxylated styrene–butadiene as the rubber matrix

(Peterson, 2012). The obtained hybrid rubber composite loaded with 3:1 ratio of cornstarch: biochar showed efficient reinforcing effect, which lead to have better toughness, tensile strength and elongation than the carbon black counterpart (Peterson, 2012). Woody waste feedstock based low ash content biochar was hybridized with carbon black (CB) as filler for styrene-butadiene rubber (Peterson, 2013). At higher loading, carbon black reinforced SBR showed better performance, however at 10% total filler with 25%–50% biochar resulted in composite materials with enhanced mechanical performance compared to those with 100% carbon black filler. The biochar obtained from bricwood, which showed high carbon content (89%) and less ash content (1.8%) was reinforced with styrene-butadiene rubber (SBR) and the obtained composite material showed superior toughness properties (Peterson *et al.*, 2016). Coconut shell based pyrolytic biocarbon also reinforced in styrene-butadiene rubber and their performance of the obtained composite materials was compared with the traditional carbon black based composite (Fan *et al.*, 2017). The obtained results reveal that the carbon black can be partially substituted with coconut shell char due to their favorable performance. It has been found that the birchwood biochar reinforced SBR composite could partially replace the carbon black composite without loss of toughness and tensile strength. The biochar of the dry hardwood obtained from fence-clearing activity was investigated for their surface modification with the heat treated starch in order to enhance the reinforcing effect (Peterson and Kim, 2018).

Modification Strategies of Biochar for Composite Application

Particle size and their distribution of the biochar play important role in their composite fabrication. Many studies found that the reduction of biochar particle size improves the reinforcing effect and enhance the composite performance. This can be achieved by employing various techniques including mechanical grinding ball milling processes. It was reported that the specific surface area of the miscanthus based biochar increased from 148 m²/g to 300 m²/g after the ball milling process for 2 h (Wang *et al.*, 2018). During the reinforcement of ball milled biocarbon with the PP matrix, it was found that the increased milling time increases the impact strength of the composite material.

The surface functionality of biochar is the key factor for the composite application, which influences the biochar-matrix interaction and enhances the load transfer properties. The effective load transfer mechanism play a significant role in improving the mechanical properties of composite materials. Hence the surface modification of biochar is very essential in order to improve overall composite performance. It has been reported that the surface modification of biochar obtained from bamboo biomass with HNO₃ and NaOH solution introduced amino and carbonyl/carboxyl groups respectively (Anstey *et al.*, 2016; Qian *et al.*, 2018). The functionalized biochar showed excellent interaction with PLA matrix and the obtained the PLA/bamboo-char composites result in the enhanced tensile and impact properties.

Conclusions

Biochar materials obtained from various biomasses have been explored as the effective reinforcing materials in composites for the various thermoplastic, thermoset, and elastomeric matrixes. A wide range of biomasses have been converted into biochar and explored as sustainable reinforcement for various polymer systems originated from renewable and petroleum feedstocks. The observed results indicate that the physicochemical and functional properties of the biochar can be precisely tuned by manipulating the various pyrolysis conditions in order to meet the requirement for specific composite. Hybridization of the biochar along with other kinds of reinforcement such as carbon fibres, carbon black and natural fibres exhibited improved composite performance than their individual counterpart. However, the composite technology based on the biochar reinforcement is in its infancy, which needs more advancement to compete with the composite materials that exist in the commercial marketplace. Extensive research effort needs to be devoted to the development of new biochar based composite systems. This will enable the effective product diversification for the possible commercialization of the biochar reinforced composite material.

Acknowledgements

SV acknowledges University Grants Commission (UGC), India for the financial support for this research activity through the Minor Research Project (MRP/UGC-SERO- Proposal No.: 1593).

See also: Bamboo Fiber as Fillers for Polypropylene-Nanoclay via Injection Molding. Biochar Production From Biomass Waste-Derived Material. Renewable Agricultural Fibers as Reinforcing Fillers in Plastics: Mechanical Properties of Kenaf Fiber-Polypropylene Composites. Waste Conversion Into Sustainable and Reinforcing Fillers for Rubber Composites

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Biomass Conversion to Selected Value-Added Chemicals Using Zeolites: A Review

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Introduction

The fossil resources are being utilized by human beings to advance technologically. There is no argument in saying that without fossil resources these advances are not possible in such a short span of time (about 150 years of discovery of these resources). However, this progress has been happening at the expense of rapid depletion of these resources as well as an adverse impact on the environment. Now it is time to think about the alternative, renewable and sustainable resources for generating electricity and synthesizing the fuels and chemicals. We have several such alternative resources such as biomass, solar, geothermal, wind, tidal etc. Among these, the biomass is an abundantly available and more evenly distributed resource in the world through which the solar energy is being stored in the form of chemical energy. Moreover, biomass is the only alternative and renewable resource which contains useful carbon atoms which can be converted to fuels and chemicals relatively easily. It has been suggested that the biomass be used for synthesizing the fuels and chemicals and other alternative resources be used for the generation of electricity. The biomass conversion to value-added chemicals is pursued as a greener, renewable, and sustainable approach to produce fine and pharmaceutical chemicals.

During acid catalyzed hydrolysis and dehydration of carbohydrates, the presence of lignin and inorganic metal salts may deactivate the catalyst. Therefore, it is advisable to remove these parts before processing the carbohydrates to value-added chemicals. Various methods (such as steam and CO₂ explosion, acid, and alkali treatment) have been used to separate the three components (cellulose, hemicellulose and lignin) of the biomass. The major portion of the lignocellulosic biomass is the cellulose (40–60 wt%). However, many pathways use fructose as the starting substrate to produce chemicals and fuels (Saravanamurugan *et al.*, 2017). Therefore, cellulose should first be converted to fructose. Two major steps (cellulose hydrolysis to glucose and glucose isomerization to fructose) in series have to be followed to convert cellulose to fructose. The research on the direct conversion of cellulose or even raw biomass to value-added chemicals is also speeding-up in recent years (Zhang *et al.*, 2017; Li *et al.*, 2016; Badgujar *et al.*, 2019).

The acid hydrolysis of cellulose takes place in three reaction steps: protonation of glycosidic oxygen, cleavage of glycosidic bonds and nucleophilic attack of water (Kang *et al.*, 2018). The cellulose hydrolysis step has been carried out using various catalysts such as acidic, enzymatic. The zeolite catalysts have also been used for this step (Hu *et al.*, 2015). Cellulose and hemicellulose could be depolymerized using hydrolysis reaction over zeolites. Various zeolites and metal encapsulated zeolites have been tested for the reaction (Shrotri *et al.*, 2018). Particularly, dealuminated zeolites showed good activity in hydrolysis reaction (Moreau *et al.*, 2000). Incorporation of hydrophobicity into the zeolites by dealumination also resulted in the better conversion and yields (Buttersack and Laketic, 1995, 1994). The dealuminated Sn-Beta zeolite with balanced Brønsted and Lewis acidity is demonstrated to be highly effective for sucrose (a non-reducing carbohydrate) to fructose conversion with high yields (Saravanamurugan *et al.*, 2017). Various properties of the zeolites such as micropore topology, mesoporosity, and acidity could significantly influence the hydrolysis process (He *et al.*, 2014). The hemicellulose hydrolysis is relatively a milder process as compared to cellulose hydrolysis.

Several studies have been carried out to understand the mechanism of glucose to fructose isomerization by homogeneous catalysis (with metal ions or acids) (Choudhary *et al.*, 2013; Nagorski and Richard, 2001; Pagán-Torres *et al.*, 2012), by enzymes (Toteva *et al.*, 2011) and by base-catalysis (Liu *et al.*, 2014). It has been observed that the base catalyzed reaction follows the proton transfer mechanism whereas the acid catalyzed reaction follows the hydride transfer mechanism. Significant work has been carried out by Davis' group to obtain insights on isomerization of glucose to fructose on hydrophobic, solid Lewis acid catalysts such as Sn-Beta and Ti-Beta (Bermejo-Deval *et al.*, 2012; Bermejo-Deval *et al.*, 2014; Nikolla *et al.*, 2011). It has been identified that the metal centers present in Sn-Beta and Ti-Beta act similar to the metal centers present in metalloenzymes towards this isomerization reaction (Moliner *et al.*, 2010). The authors proposed that the "metal-assisted intramolecular hydride shift" mechanism is responsible for glucose isomerization to fructose on these catalysts (Román-Leshkov *et al.*, 2010).

Zeolites are good catalyst systems for various processes where acid catalysis is involved. However, the microporosity is the major drawback of these materials in biomass processing as the reactants and products involved are bigger in size than the pore sizes of the microporous zeolites. Recently, researchers have demonstrated that hierarchical zeolites containing both micropores and mesopores are highly suitable for the biomass conversion reactions with enhanced activity (Kang *et al.*, 2013; White *et al.*, 2014; Moreno-Recio *et al.*, 2017). Both top-down (Nandiwale *et al.*, 2014a; Yu *et al.*, 2015) and bottom-up (White *et al.*, 2014; Zhu *et al.*, 2014) approaches have been used to synthesize the hierarchical zeolites. The top-down approaches, such as steaming, desilication, and dealumination, are straightforward and cheap. However, these may result in low pore-wall crystallinity which in turn may result in lower catalyst stability. Therefore, the bottom-up approach is more attractive.

The scope of this review is to summarize the recent literature on biomass (and its constituents: cellulose, and hemicellulose) to value-added chemicals using zeolites, zeotype, and functionalized zeolite catalysts. The major focus of this review is on the production of levulinic and lactic acids and their esters.

Carbohydrates to Levulinic Acid and its Esters

The levulinic acid (4-oxopentanoic acid) is a promising platform chemical with applications in several areas such as biofuels, cosmetics, agrochemicals, fragrances (Pileidis and Titirici, 2016). US DoE identified LA as one of the top 12 platform chemicals. The LA contains two functional groups, one is a ketone and the second one is acid. The bi-functionality of LA makes it highly reactive and suitable for transformation to other value-added chemicals (Badgujar *et al.*, 2019). According to the survey by the research and market survey, the LA market projected revenue by the year 2025 is \$ 57.6 million and its compounded annual growth rate is 15.4% (Badgujar *et al.*, 2019). LA could be produced from cellulose as well as from hemicellulose (Li *et al.*, 2019). However, the hemicellulose route involves the formation of furfural alcohol from furfural (by hydrogenation) which requires a metal catalyst and H_2 with moderate pressure. Therefore, conversion of hemicellulose to LA requires a bi-functional catalyst containing both acid and metal sites.

An early work reported the fructose conversion to LA over LZY zeolite catalyst at 140°C (Jow *et al.*, 1987). A maximum LA yield of 43 wt% with very low 5-HMF yield is obtained and is attributed to stronger dehydration ability of Lewis acid sites and the molecular-sieving effect of the LZY zeolite. Using Amberlyst-15, Son *et al.* (2012) reported a LA yield of 52% from fructose at 120°C for 24 h.

Acharjee and Lee (2018) tested a dual solid-acid catalyst (Amberlyst-15 and Sn-Beta) for the conversion of glucose to LA. Due to the availability of both the Lewis and Bronsted acid sites, the dual solid-acid catalyst shows higher yields of LA as compared to Amberlyst-15 alone. The Lewis acid sites available on the Sn-Beta favor the isomerization of glucose to fructose. Kumar *et al.* (2016) synthesized Ga-modified mordenite zeolites by the sonochemical method, used for the glucose conversion to LA and reported an LA yield of 60% in a reaction carried out at 175°C for 6 h. The authors emphasized that the synergism between the Lewis acid sites of Ga^{3+} and the Bronsted acid sites of MOR resulted in higher yields. Ramli and Amin tested a series of Fe/HY catalysts for the production of LA from glucose. The surface area, porosity and amount and type of acid sites are found to have a profound influence on the activity of the catalyst. Catalysts with higher Lewis acid sites are found to form humins and those with relatively high mesoporosity are found to exhibit decent LA yields. 10%Fe/HY exhibited the best performance with LA yields of 62% at 180°C in 180 min (Ramli and Amin, 2015a). The same group reported LA production from oil palm fronds with yields of 17.6% (Ramli and Amin, 2015b). The authors reported a stable operation up to five cycles without any significant Fe leaching. Suacharoen and Tungasmita (2013) reported an LA yield of 38% from glucose over 20% Ru/ZSM-5 catalyst. Yáaini *et al.* (2013) synthesized hybrid catalyst $CrCl_3$ /HY and tested for glucose to LA conversion. With 1:1 ratio of $CrCl_3$:HY, the authors reported an LA yield of 62% at 160°C in 180 min of reaction time.

Dumesic and co-workers used various catalysts (such as zeolites, Amberlyst-70) for the direct conversion of cellulose to LA. Using a mixture of 90% γ -valerolactone (GVL) and 10% water as a solvent, the LA yield over zeolites ZSM-5 and mordenite is 35%, while that over Amberlyst-70 is 69%. However, when pure water is used as a solvent the LA yields are significantly lower (2% over both the zeolites and 19% over Amberlyst-70). Therefore, it is understood that GVL plays a significant role in dissolving the cellulose into the reaction media and thereby enhancing the solid (cellulose) – solid (catalyst) interaction (Alonso *et al.*, 2013). Huber and his group used a two-step process for the conversion of cellulose to LA. In the first step, they have decomposed the cellulose non-catalytically and hydrothermally to the water-soluble LA precursors. In the second step, they converted the water-soluble compounds to LA and formic acid over Amberlyst-70 at 160°C. The maximum yield of LA is reported to be 28% of theoretical (Weingarten *et al.*, 2012b).

Hartono *et al.* (2016) used the corncob as a substrate for the production of LA over acid activated natural zeolite and reported a maximum LA yield of 262.4 mg/g of dried corncob. Yáaini *et al.* (2012) tested 10% $CrCl_3$ /HY for the conversion of empty fruit bunch and Kenaf biomass substrates to LA and reported 15.5 (29.2% theoretical) and 15 wt% (22.7% theoretical) LA yields, respectively. Krisnandi *et al.* (2019) synthesized hierarchical $MnOx$ /ZSM-5 and tested for the conversion of delignified rice husk to LA. The authors reported an LA yield of 16 wt% based on the cellulose weight after delignification.

The activation energies for glucose to 5-HMF and 5-HMF to LA reactions are reported to be 64 and 61 $kJ\ mol^{-1}$, respectively. Whereas, those for the conversion of glucose to humins and 5-HMF to humins are reported to be 76 and 70 $kJ\ mol^{-1}$, respectively (Ramli and Amin, 2016). This might highlight the fact that glucose to LA reaction is relatively more favorable than that of glucose or 5-HMF to humins. Weiqi and Shubin (2017) and Wei and Wu (2018) studied the kinetics over Cr /HZSM-5 and reported the activation energies for glucose dehydration and 5-HMF rehydration reactions to be 69.1 and 54 $kJ\ mol^{-1}$, respectively. From most of the kinetic studies reported in the literature, the activation energy of glucose to humins reaction is higher as compared to that of 5-HMF to humins, with both homogeneous (Weingarten *et al.*, 2012a) and heterogeneous (Ramli and Amin, 2016) catalysts. Moreover, the activation energy of glucose to the 5-HMF reaction is lower as compared to that of glucose to humins reaction. These data clearly indicate that the humins formation is favoured from the 5-HMF rather than from the glucose.

Researchers have explored the possibility of converting the C5 sugars (hemicellulose based) to LA. In a three-step process (xylose $\rightarrow$ furfural $\rightarrow$ furfural alcohol $\rightarrow$ LA), Dumesic and co-workers (Gürbüz *et al.*, 2012) reported an LA yields of up to 70%. However, when HZSM-5 is used as a catalyst the yield of LA is very low (15%). In another publication from the same group, they reported an LA yield of 75% from furfural alcohol (a derivative of xylose) over HZSM-5 with SiO_2/Al_2O_3 ratio 80 (Mellmer *et al.*, 2015). The authors also tested the effect of various solvents and found that a mixture of water and tetrahydrofuran (THF) with a THF:H₂O ratio of 4 gives the highest yield of LA and remains nearly constant with the solvent ration varied from 19 to 2. Sulfuric acid as catalyst showed a lower yield of LA (maximum 56% at THF:H₂O ratio of 19 and decreased with increasing the water content). A similar yield (56%) is obtained over HZSM-5 with a very low solvent ratio of 0.5. The authors attributed the higher yields at lower solvent ratio over HZSM-5 to the constant internal solvent microenvironment, which in turn is due to the hydrophobicity of the zeolite. Jeong *et al.* (2018) reported an LA yield of 43% from xylose over alkali treated HY zeolites.

Chamnankid *et al.* (2014) demonstrated that upon alkali treatment and formation of strong acid sites, the zeolite Y can be used for the direct conversion of xylose to LA with a maximum yield of 30%.

The major application of levulinate esters (LE), such as methyl, ethyl and butyl levulinate, is as a fuel additive (Climent *et al.*, 2014; Démolis *et al.*, 2014). In gasoline, they act as octane number boosters and in diesel they act as fuel extenders. Up to 5% of LE could be blended in conventional diesel fuel (Fernandes *et al.*, 2012). The other applications of LE are in industries such as flavoring, pharmaceutical, and fragrance (Zhang *et al.*, 2018). Research is being carried out to produce LE from various feedstocks such as LA, fructose, glucose.

Earlier studies reported esterification of LA with alcohols to produce LE. Fernandes *et al.* (2012) tested various zeolites (HUSY, HBEA, HMOR, HZSM-5, and HMCM-22) for the esterification of LA to ethyl levulinate (EL). HMCM-22 showed the highest conversion of LA followed by HUSY. The lowest activity is showed by HZSM-5. The data indicate that the topology of the zeolite plays an important role in imparting the activity. The zeolites with larger pores show higher activity owing to their ability to incorporate the large-sized transition states. Bokade and co-workers (Nandiwale *et al.*, 2013; Nandiwale *et al.*, 2014b; Patil *et al.*, 2014) synthesized various zeolite catalysts with varying mesoporosity and tested for LA to LEs conversion. The activity of desilicated H-ZSM-5 is higher as compared to its fresh counterpart. The activity is further increased when dodecatungstophosphoric acid is impregnated on to the desilicated H-ZSM-5 (Nandiwale *et al.*, 2013). The same desilicated H-ZSM-5 when used for LA esterification with different alkyl alcohols, the authors found that the activation energy decreases with the increase of alkyl chain. For example, the activation energy with methanol is 52 kJ mol⁻¹, whereas, that with n-octanol is 17 kJ mol⁻¹. The recyclability of the catalyst is good with only a marginal decrease of activity in six cycles (Nandiwale and Bokade, 2015). Lucas *et al.* (2019) synthesized silicotungstic acid supported on ALSBA-15, tested for LA to EL conversion. The catalyst shows an EL selectivity of 100% at an LA conversion of 87%.

Saravanamurugan and Riisager (2013) tested various zeolites for the direct conversion of carbohydrates to levulinate esters (methyl and ethyl levulinate). The authors observed that H-USY is a highly active zeolite among the tested. Various carbohydrates used in the study resulted in a nearly equal yield of methyl levulinate (50%). In another communication (Saravanamurugan and Riisager, 2012), the same group presented that the catalyst SO₃H-SBA-15 showed an improved ethyl levulinate yields of up to 57% from fructose at 140°C. The authors also showed that the catalyst is more selective to form EL as compared to the other zeolites (H-ZSM-5 and H-MOR) used in the study. The combination of Lewis and Brønsted acid sites (SO₄²⁻/ZrO₂ and Sn-Beta) shows a good yield of methyl levulinate (62%) from glucose at 170°C for 24 h (Jiang *et al.*, 2018). The similar yields have been reported with fructose and sucrose as substrate. The methyl levulinate yield is very low (<3%) over Na/montmorillonite (Mt) (Liu *et al.*, 2017). However, the yields increased significantly up to 60% upon exchanging the Na with metals such as Sn, Al, Cu and In (Liu *et al.*, 2017; Liu *et al.*, 2018).

Tang *et al.* (2018) used catalytic transfer hydrogenation for the conversion furfural to ethyl levulinate over a combination of Lewis and Brønsted acid catalysts (Zr-SBA-15 and ZSM-5). The tandem catalytic reaction produced EL with yields up to 55% in a reaction conducted at 180°C for 16 h.

Carbohydrates to Lactic Acid and its Esters

The lactic acid (LAC) formation from glucose starts with the isomerization of glucose to fructose. The formed fructose converts to glyceraldehyde by retro-aldol condensation. The glyceraldehyde after undergoing a few more reaction steps forms the lactic acid. The retro-aldol condensation and the dehydration (to form 5-hydroxymethylfurfural) reactions compete for acid sites. The Brønsted acid catalysts favor the dehydration reaction. Whereas, the Lewis acid catalysts increases the possibility of retro-aldol condensation occurrence. However, all the Lewis acid catalysts are not favorable for the retro-aldol condensation. For example, even though the H-Beta and H-ZSM-5 possess Lewis acid sites, the lactic acid formation is negligible over these catalysts (Marianou *et al.*, 2018). When Sn is impregnated/ion-exchanged on to these zeolites then lactic acid formation is observed. Effect of acidity of catalyst and the solvents on the production of lactic acid from glucose over Sn/zeolites is reported by Marianou *et al.* (2018).

Xia *et al.* (2018) recently tested a bimetallic catalyst loaded on beta zeolite for the lactic acid production from glucose and observed yield of 52% at a glucose conversion of >99% at 190°C for 2 h under ambient air pressure. The roles of individual metals are found by testing the intermediates as reactants. The lead plays an important role in promoting the isomerization and retro-aldol reactions. Whereas, tin plays a superior role in activating the dehydration of dihydroxyacetone, the hydration of pyruvaldehyde and the isomerization of pyruvic aldehyde hydrate. A clear synergism is observed over the bimetallic catalyst as compared to that over a catalyst containing the individual metals. The same group has utilized 3-aminopropyltrimethoxysilane functionalized Sn-Beta for the sucrose to LAC conversion and reported a 58% yield at complete conversion at 190°C for 4 h. The functionalized catalyst promotes the hydrolysis and suppresses the dehydration (to form 5-HMF) reaction (Kong *et al.*, 2018).

Murillo *et al.* (2014) demonstrated that the Sn-MCM-41 catalysts are highly efficient in converting glucose to methyl lactate (yield 43%) at 160°C for 20 h. From trioses, yield more than 95% could be obtained using Sn-Beta catalyst at very low temperatures of 40°C (Osmundsen *et al.*, 2012). Other catalysts (such as Sn-MCM-41, Sn-MFI, Sn-SBA-15) used in that study showed much lower activities as compared to Sn-Beta. A similar trend is observed with the sucrose as substrate at 160°C. Sn-Beta catalyst showed at least two times the higher yield of methyl lactate as compared to other catalysts. The reason for the lower activity of the Sn-MCM-41 or Sn-SBA-15 catalysts is their inability to promote the hydride shift reaction.

Holm *et al.* (2010) tested various metal (Ti, Zr, and Sn) containing Beta zeolite for the retro-aldol condensation of fructose, glucose and sucrose to alkyl lactates at 160°C for 20 h in methanol. The authors found that the Sn-Beta shows the best activity with a methyl lactate yield of 64% from sucrose. Whereas, over the same catalyst glucose and fructose results in a yield of 44%. The yields of methyl

lactate are lower over Ti-Beta and Zr-Beta catalysts as compared to that over Sn-Beta. The best activity over Sn-Beta catalyst is attributed to the stronger Lewis acid sites present on this catalyst. In the presence of other higher alcohols as solvents results in the formation of the corresponding alkyl lactates and with water as solvent lactic acid is formed, all-be-it, with lower yields. The methyl lactate is not forming at all over Al-Beta and Si-Beta, owing to the absence of Lewis acid sites. Tolborg *et al.* (2015) reported a higher yield (75%) of methyl lactate from sucrose when Sn-Beta is used along with alkali carbonates at 170°C. The authors found that alkali presence is inevitable, as in the absence of alkali the yields are very low (30%). The beneficial effect of alkali presence is also demonstrated with the other stannosilicate materials such as Sn-MCM-41 and Sn-SBA-15. The alkali present in the solution exchanges with the open sites in the stannosilicate materials to form 1,2-intramolecular carbon shift (1,2-CS) sites (Bermejo-Deval *et al.*, 2014).

The catalysts which do not promote the aldose-ketose isomerization would be beneficial for the retro-aldol reaction to produce the alkyl lactate selectively. With this notion and to reduce the reaction temperature, Orazov and Davis (2015) tested a combination of two catalysts for the production of alkyl lactate (or lactic acid) from ketohexoses. The catalysts which promote 1,2-CS (such as molybdenum oxide) and 1,2-intramolecular hydride shift (such as Sn-MFI) reactions are used. The authors demonstrated that the combined catalyst system ($\text{MoO}_3 + \text{Sn-MFI}$) is able to convert fructose to alkyl lactate with yields as high as 75% at a temperature as low as 100°C. However, the effect of substrate concentration is significant. The yield of alkyl lactate decreases significantly from 75% to 21% as the fructose concentration increases from 0.2% to 5%. Use of water instead of alcohol as a solvent also decreases the yield significantly (from 68% to 27%).

Mesoporous methylated stannosilicates are also used for the production of ethyl lactate from dihydroxyacetone (DHA) and reported a selectivity to alkyl lactate of > 99% (Vivian *et al.*, 2018). Yamaguchi *et al.* (2018) used a simple $\gamma\text{-Al}_2\text{O}_3$ catalyst containing both acid and base sites for the conversion of glucose to methyl lactate and observed yield of 34% at 100% glucose conversion at 160°C for 6 h.

Cellulose and raw biomass (Oakwood) have also been used as substrates in the production of methyl lactate (Verma *et al.*, 2017). While the methyl lactate yields from cellulose, glucose, and fructose are in the close range of 58%–67%, the order is as follows: $Y_C < Y_G < Y_F$. However, the yield from Oakwood is much lower (<10%). The high yields from the monomers and cellulose are due to the proper L/B ratio that is maintained by doping Ga onto the Zn/H-Y catalyst. Presence of a small amount of water in the reaction mixture drastically decreases the methyl lactate yield. For example, the methyl lactate yield from cellulose is decreased from 51% to 29% at 280°C when 10% of water is added to the reaction mixture. Adsorption of water onto the Lewis acid sites is cited as the possible reason for the decrease in yield.

The C5 carbohydrates have also been converted to lactic acid/alkyl lactate (Paksung and Matsumura, 2015; Yang *et al.*, 2016; Holm *et al.*, 2012). The hemicellulose monomers (C5 compounds) such as xylose, arabinose, and ribose are converted to methyl lactate over Sn-Beta and found that the xylose resulted in methyl lactate yields of 41%. As compared to C5 carbohydrates, C6 carbohydrates (fructose, glucose, etc.) give higher yields over the same catalyst and under similar reaction conditions (Holm *et al.*, 2012). However, over Zr-SBA-15, Yang *et al.* (2016) reported a similar methyl lactate yield of approximately 40%–44% from both C5 and C6 carbohydrates.

Summary

In summary, the zeolite and zeotype catalysts are highly active and selective for the production of levulinic and lactic acids and their esters. For glucose conversion to levulinic acid and its esters, it is observed that a catalyst containing a combination of Lewis and Brønsted acid sites (e.g., CrCl_3/HY) is highly beneficial in obtaining higher yields. Even the physical mixtures of the catalysts containing Lewis and Brønsted acid sites (e.g., $\text{SO}_4^{2-}/\text{ZrO}_2$ and Sn-Beta) gives impressive results. Kinetic analysis indicates that the humins formation is exclusively from 5-hydroxymethylfurfural. Therefore, catalysts for LA production should be chosen in such a way that the rehydration reaction favors over the condensation of 5-HMF to humins. Solvents and solvent+catalyst combinations also play a significant role in obtaining higher yields of LA/LE.

The catalysts which promote retro-aldol reaction over the aldose-ketose isomerization are beneficial for the production of lactic acid and its esters. The catalysts containing the sites that favor the 1,2-intramolecular carbon shift and 1,2-intramolecular hydride shift reactions demonstrate good yields of lactic acid esters.

See also: Biochar Production From Biomass Waste-Derived Material. Biomass for CO_2 Sequestration. CO_2 Sequestration Using Algal Biomass and its Application as Bio Energy. Co-Firing of Biomass to Reduce CO_2 Emission. Green Energy Fuel From Biomass and Sea Water. Large Biomass Burners for Fuel Switch in Existing Fossil Fuel Based Plants. Renewable Biomass: A Candidate for Mitigating Global Warming. Technology for Producing Briquettes From Wet Biomass. The Nexus Between Biomass – Footprint and Sustainable Development. Thermophysical and Adsorption Characteristics of Waste Biomass-Derived Activated Carbons. Traditional Biomass: A Replacement for Petro-Fuels

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Bio-Nanocomposites for Food Packaging Applications

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Introduction

Worldwide annual plastics manufacturing is appraised to exceed 330 million tons by 2020, growing at a CAGR (Compound Annual Growth Rate) of 5.3% from 2014 to 2020 (Plastics market to reach \$ 654.38 billion by 2020), showing trillions of dollars regarding world economic returns. More than 40% of the plastics are used for packaging, and almost half of them are used for food packaging in the form of films, sheets, bottles, cups, tubs, and trays, etc (Rhim *et al.*, 2013). Petroleum resources are widely employed in manufacturing these polymers, which generate issues regarding both economic and environmental protection. After their beneficial life, it is preferable for the packing materials to biodegrade in a reasonable time without generating environmental problems. Though the synthetic plastic materials have been extensively utilized for the packaging of several kinds of food; they cause severe environmental issues because they are not readily degraded in the environment after use (Rhim *et al.*, 2013). So, there is an increasing trend to utilize environmentally friendly polymers with the aim of substituting non-degradable materials, thus lowering environmental pollution as a result of waste accumulation. To address environmental issues, and simultaneously increase the shelf life and quality of food, decreasing packaging waste has catalyzed the exploration of new bio-based packaging materials like edible and biodegradable films (Desobry and Debeaufort, 2011).

Nanotechnology is considered an essential tool for the improvement of advanced materials. By 2020 it is expected that nanotechnology will influence at least \$3 trillion of the worldwide economy, generating a request for 6 million employers in different production fields (Duncan, 2011). Nanoscience and nanotechnology applications in the agriculture, food sector and food safety are relatively recent compared with their use in cosmetics and personal care products (60%), paints and coatings, catalysts and lubricants, security printing, drug delivery and pharmaceuticals, medical therapeutics and diagnostics, energy production, molecular computing and structural materials (Shankar and Rhim, 2018a; Vasile, 2018). Over \$17.8 billion global investment was made in 2010 for research and development in nanotechnology, and this will grow to \$3 trillion by 2020. Food packaging sector counts for ~50% market value for all nanotechnology-enabled products with an annual growth rate of 11.65%. Through this global tendency, it is predictable that nanotechnology will offer the main drive in the progress of novel packaging applications systems for satisfying consumer's requirements.

Nanotechnology deals with the particle size of less than 100 nm at least in one dimension, and the nanosized particles show unique chemical and physical properties which are meaningfully diverse from the properties of macro-scale materials containing identical materials (Youssef *et al.*, 2013). Nanotechnology is mainly applied to extremely high gas barriers packaging materials with antimicrobial properties and nano-encapsulants for the delivery of aromas, flavors, or nutrients (Rhim *et al.*, 2013).

Bionanocomposites are believed to be one of the potential technologies that can be used to increase the storability of foods and to improve the present packaging technology, helping to ensure the microbial safety and the preservation of food from the influence of external factors (Fig. 1). Although extensive research is being undertaken at industry and academic levels, bionanocomposites in food packaging is still in the developmental phase. For the growth of bionanocomposites in food packaging at an advanced level, it is

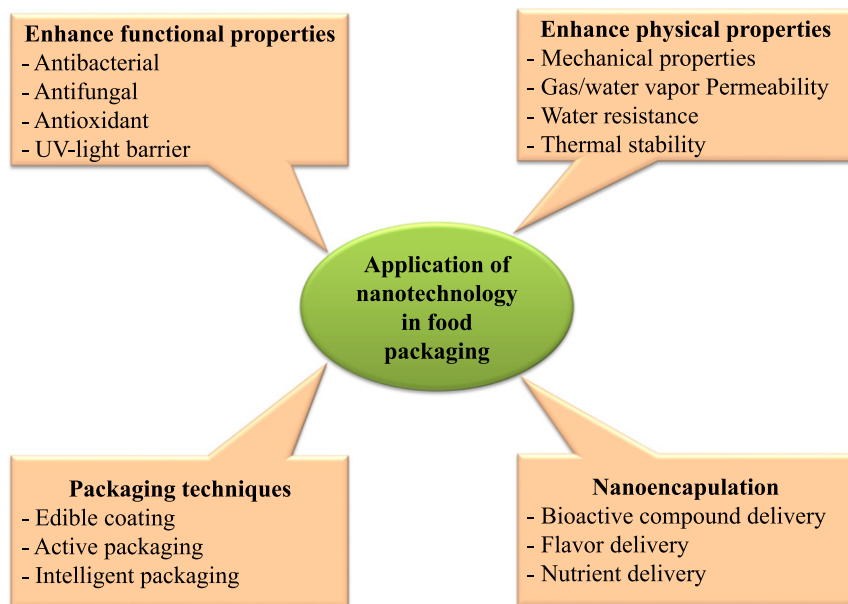


Fig. 1 Application areas of nanotechnology in the food packaging sector.

essential to look at the complete life cycle of the packaging (from raw material extraction and production to usage and administration), integrating and balancing cost, performance, health, and environmental considerations. The multidisciplinary research is required in bionanocomposites-based food packaging area to overcome the barriers like safety, technology, regulation, standardization, trained workforce, and technology transfer to achieve the benefit for commercial products in the global market. Moreover, owing to the enormous growth application potential of bio-nanocomposites in food packaging, the emerging technology will be a hub of new employment opportunities because of degradable and eco-friendly nature (Silvestre *et al.*, 2011). The bio-nanocomposites packaging has great potential as an innovative food packaging technology to maintain the food quality and safety, and to extend the shelf life of the packaged food products. Although promising results were obtained, the road to the successful application of bionanocomposites in food packaging is still long. Considering the points above, this article is focused on the composition, preparation, characterization, and application of bio-nanocomposite materials in the food packaging area.

Composition of Bio-Nanocomposites

Bionanocomposites consist of a biopolymer having nanoparticles or nanofillers dispersed in the biopolymer matrix. These may be of different shapes (e.g., platelets, fibers, spheroids) or size, but at least one of the dimension must be in the range of 1–100 nm. The bio-nanocomposite systems require controlled mixing/compounding, stabilization of the achieved dispersion, the orientation of the dispersed phase, and the compounding strategies.

Biopolymers

Biopolymers are polymeric materials produced from renewable resources such as a plant, animal, and microorganisms. Biopolymers comprise monomeric units that are covalently bonded to form a larger assembly. There are three main classes of biopolymers, classified according to the monomeric units used and the structure of the biopolymer formed: polypeptides, which are short polymers of amino acids; polynucleotides (RNA and DNA), which are long polymers composed of nucleotide monomers; and polysaccharides, which are often linear bonded polymeric carbohydrate structure (Shankar *et al.*, 2016a; Shankar and Rhim, 2016a). Other examples of biopolymers include lignins, rubber, melanin, and suberin. Biopolymers can be categorized into three groups depending on the origin of the biopolymers, which includes natural biopolymers extracted from biomass (e.g., agro-resources), synthetic biopolymers from microbial production or fermentation (e.g., PHA), and synthetic biopolymers conventionally and chemically synthesized from biomass and petroleum products (e.g., PLA, PCL) (Fig. 2). Among the biopolymers, the most common type that has been studied to produce bio-nanocomposite materials for food packaging applications are carbohydrates, proteins, and their derivatives (Nafchi *et al.*, 2013; Shankar *et al.*, 2016b, 2017). Carbohydrate and protein-based polymers and their derivatives are commonly edible. Thus, they are safe as food packaging materials. Studies have shown that these polymers are degradable and could stimulate biodegradability of non-biodegradable materials when mixed them. However, biopolymer-based packaging films have poor mechanical properties which can be improved with additives such as plasticizers and nanofillers (Sorrentino *et al.*, 2007). Some biopolymers studied include cellulose such as cellulose acetate (Bruna *et al.*, 2014), carboxymethyl cellulose (Oun and Rhim, 2015), and hydroxypropyl methylcellulose (George *et al.*, 2014), chitosan (Shankar and Rhim, 2018b), agar (Orsuwan *et al.*, 2016; Shankar and Rhim, 2017; Shankar *et al.*, 2014a), gelatin (Kanmani and Rhim, 2014a; Shankar *et al.*, 2016c, 2014b), gluten (Rafieian *et al.*, 2014), alginate (Shankar *et al.*, 2018; Wang *et al.*, 2017), pectin (Shankar *et al.*, 2016b), synthetic biopolymers

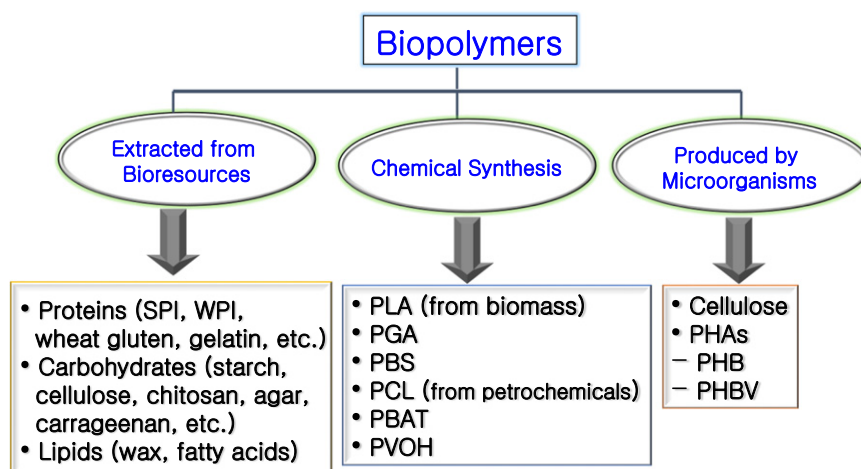


Fig. 2 Classification of polymers based on their origin.

such as polylactide (PLA) (Arfat *et al.*, 2018; Rhim *et al.*, 2006), polyhydroxyalkanoates (Fabra *et al.*, 2016), poly(ϵ -caprolactone) (Yahiaoui *et al.*, 2015), and microbial synthesized polymers such as PBAT (Li *et al.*, 2015; Shankar and Rhim, 2018c). The most common synthetic biopolymer that has been studied is PLA which is produced from lactic acid. PLA can be generated by fermentation of carbohydrates from plant resources such as sugar beet and corn (Sorrentino *et al.*, 2007). The advantages of PLA include biodegradability, and the lifespan of PLA can be tailored accordingly. However, some of the drawbacks of using biopolymers as food packaging materials compared to the conventional non-biodegradable materials, especially those that are petroleum-derived include poor mechanical (e.g., low tensile strength) and barrier properties (e.g., high water vapor permeability). Biopolymers are brittle, have a low heat distortion temperature, and low resistance to prolonged process operations. For instance, the most favorable synthetic biopolymer, PLA, for food packaging exhibits low performance due to a low heat distortion temperature, low resistance to extreme heat and humidity, and low flexibility (Sorrentino *et al.*, 2007). Nevertheless, the advantages of using biopolymers as packaging materials, mainly to cater for societal demands for sustainability and environmental safety, have to lead to many studies directed towards improvement of biopolymers for food packaging applications. Incorporating nanofillers in the biopolymers have been established as a promising route to enhance mechanical and barrier properties of biopolymers.

Nanofillers

Many types of nanosized fillers (less than 100 nm) have been used to enhance the performance of biopolymers. The nanofillers that are commonly studied for food packaging applications can be classified into several types including nanoparticles, nanofibrils, nanocubes, nanoplates, nanorods, and nanotubes. The nanofillers can be basically divided into two major groups: (1) organic nanofillers and (2) inorganic nanofillers. Organic nanofillers include cellulose nanoparticles (Shankar and Rhim, 2016b), cellulose nanowhiskers (Wang *et al.*, 2017), cellulose nanofibrils (Oun and Rhim, 2017a), chitin nanofibrils (Shankar *et al.*, 2015a), chitin nanocrystals (Oun and Rhim, 2017b), starch nanocrystals (Dai *et al.*, 2015), melanin nanoparticles (Roy *et al.*, 2019), keratin nanoparticles (Spiridon *et al.*, 2013), lignin (Shankar *et al.*, 2015b; Shankar and Rhim, 2017), grapefruit seed extract (Shankar and Rhim, 2018c; Wang and Rhim, 2016) etc. Whereas, inorganic nanofillers include silver nanoparticles (Kanmani and Rhim, 2014a; Roy *et al.*, 2019), gold nanoparticles (Shankar *et al.*, 2016c), zinc oxide nanoparticles (Shankar *et al.*, 2014b), copper oxide nanoparticles (Shankar *et al.*, 2014a, 2017), titanium oxide nanoparticles (Zhang *et al.*, 2017), sulfur nanoparticles (Shankar and Rhim, 2018b), graphene oxide nanoparticles (Arfat *et al.*, 2018) etc. Another type of nanofillers includes organic-inorganic hybrid nanofillers (Guo *et al.*, 2016; Oun and Rhim, 2017c) and inorganic-inorganic hybrid nanofillers (Shankar *et al.*, 2016c). Researchers have used different types of fillers and biopolymers to produce bio-nanocomposite materials, and have studied different properties of the resulting bio-nanocomposite materials, making a comparison based on the published literature difficult. For example, (Shankar *et al.*, 2014b) studied the physiochemical properties of antimicrobial composite films made from gelatin and different types of zinc oxide nanoparticles). Rafieian *et al.* (2014) studied the thermomechanical and morphological properties of bio-nanocomposite films made from wheat gluten matrix and cellulose nanofibrils, while Arfat *et al.* (2017) studied the thermo-mechanical, rheological, structural, and

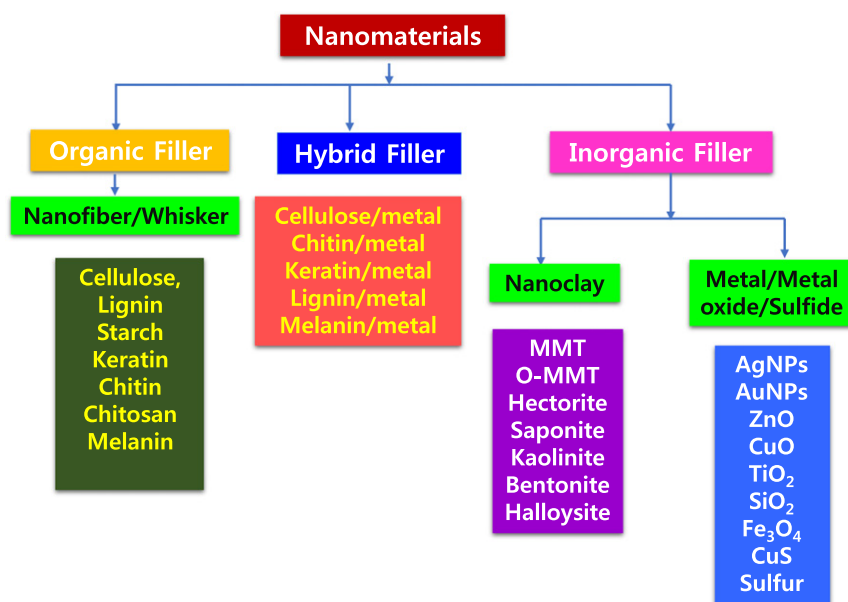


Fig. 3 Various types of nanofillers.

antimicrobial properties of fish skin gelatin films incorporated with silver-copper nanoparticles. Fig. 3 represents some of the nanofillers that can be used for the preparation of nanocomposite films.

Types of Bio-Nanocomposites

The commercial use of biopolymers-based composite films for food packaging is currently limited due to the problems in their performance, processing, and cost (Zhang *et al.*, 2014). At this point, nanotechnological approaches have opened new ways for the utilization of great performance, reduced weight, green nanocomposite materials making them supplant traditional non-biodegradable petroleum-based plastic packaging materials. The inclusion of nanoparticles in biopolymers can enhance their mechanical and barrier properties which are associated with high aspect ratio and high surface area of the nanoparticles (Rhim *et al.*, 2013).

Carbohydrate-Based Bio-Nanocomposites

Agar

Agar is one of the most favorable polysaccharides for developing biodegradable films due to its moderate water resistant property and high mechanical strength (Giménez *et al.*, 2013). Agar is a mixture of agarpectin and agarose, in which the former is a slightly branched and sulfated nongelling polymer and the later is a linear gelling polymer composed of a repeating unit of agarobiose (composed of 1,3-linked-D-galactose and 1,4-linked 3,6-anhydro-L-galactose). Since the most agarpectin fraction is removed during processing, food-grade agar is mainly composed of agarose with a molecular weight of about 120 kDa (Shankar *et al.*, 2014a). Agar has been successfully used to make nanocomposites with cellulose, clay, copper, and silver, nanoparticles and reported that the mechanical properties and water vapor permeability have been improved with the addition of nanofillers (Giménez *et al.*, 2013; Kanmani and Rhim, 2014b; Orsuwan *et al.*, 2016; Shankar *et al.*, 2015b, 2017, 2014a).

Alginate

Alginate is a naturally occurring poly-anionic polysaccharide derived from brown marine algae (Phaeophyceae), and it is commercially extracted from brown seaweed including giant kelp (*Macrocystis pyrifera*, *Ascophyllum nodosum*) and various types of Laminaria species such as *Laminaria hyperborea*, *Laminaria digitata*, and *Laminaria japonica* (Lee and Mooney, 2012). Alginate is made up of a linear block co-polymer of 1, 4-linked β -D-mannuronic and α -L-guluronic residues in varying proportions. As a low-cost, abundantly available, biocompatible and environmentally friendly biopolymer, it has been used in numerous applications in the food and biotechnology industries such as a non-toxic food additive, thickening and gelling agent, and colloidal stabilizer (Carneiro-da-Cunha *et al.*, 2010). Alginate films are highly transparent with high mechanical strength. However, they have a poor water vapor barrier property with low flexibility like other biopolymer-based films. Various types of alginate based nanocomposite films have been prepared using different types of nanofillers such as nanocellulose (Wang *et al.*, 2017), copper oxide nanoparticles (Shankar *et al.*, 2017), zinc oxide nanoparticles (Kanmani and Rhim, 2014b), halloysites (Shankar *et al.*, 2018).

Pectin

Owing to the environmentally friendly nature, good processing ability, and acceptable mechanical and barrier properties, pectin has been used for food packaging and other value-added applications. Pectin is an important component of the cell walls of terrestrial plants that widely used as a functional food ingredient, and about 4–5 g of pectin is consumed daily in the diet (Willats *et al.*, 2006). Pectin is a family of polysaccharides and oligosaccharides with diverse structures (Ridley *et al.*, 2001). Since pectin is rich in galacturonic acid (GalA), the FAO and EU stipulated that pectin must contain at least 65% of GalA. Pectin can form a gel when homogalacturonan is crosslinked to form a three-dimensional crystalline network in which water and solutes are trapped. Gelling properties of pectin are determined by various factors such as the type of pectin, the degree of methyl esterification, the degree of acetylation, temperature, pH, sugar and, calcium (Willats *et al.*, 2006). Various nanofillers have been used to improve the mechanical and functional properties of the pectin-based composite films. Shankar *et al.* (2016b) prepared pectin-based composite films incorporated with *Caesalpinia mimosoides* Lamk extract capped silver nanoparticles. The UV-light barrier, thermal stability, mechanical strength, and water vapor barrier properties of the pectin films significantly increased after incorporation of AgNPs. Also, the pectin/AgNPs nanocomposite films showed strong antibacterial activity against *Escherichia coli* and *Listeria monocytogenes*.

Carrageenan

Carrageenan is a water-soluble sulfated polysaccharide extracted from various species of *Rhodophyta* (red marine algae) and consists of long linear chains of D-galactose and D-anhydrogalactose with anionic sulfate groups (OSO_3^-) (Liu *et al.*, 2015). The excellent film-forming ability of carrageenan promoted its use for the preparation of composite films using carrageenan alone or combined with other biopolymers. Various nanofillers have been used as a reinforcing material to improve the mechanical and functional properties of carrageenan-based nanocomposite films. Shankar *et al.* (2015a) prepared carrageenan-based nanocomposite films reinforced with chitin nanofibrils. The found that the carrageenan/chitin nanofibrils composite films were

smooth and flexible and the chitin nanofibrils were dispersed uniformly in the carrageenan polymer matrix. The tensile strength and modulus of carrageenan film were increased significantly ($p < 0.05$) after chitin nanofibrils reinforcement with up to 5 wt%.

Cellulose

Cellulose nanostructures have been most usually applied as reinforcing phases, but they may also be used as matrices for a variety of materials including films for food packaging applications. Chitosan nanoparticles were incorporated into cellulose films, in which 5% addition of chitosan nanoparticles into cellulose films resulted in 85% inhibition in *Escherichia coli*. Cross-linking of the cellulose films with citric acid reduced water absorbency by 50% the growth of *E. coli* by 3% (Romainor *et al.*, 2014). Ghule *et al.* (2006) proposed a simple approach to produce a nanoparticle-coated antimicrobial paper. They used an ultrasound-assisted approach to coat the cellulose fibers over the paper surface with zinc oxide nanoparticles. The coated paper showed antimicrobial activity against *E. coli* 11,634 (Ghule *et al.*, 2006). A similar study investigated the antimicrobial effect of copper nanoparticles incorporated into chemically modified cotton cellulose fibers (Mary *et al.*, 2009). Siqueira *et al.* (2014) analyzed the antimicrobial effect of silver (Ag) nanoparticles incorporated into carboxymethylcellulose (CMC) films. The Ag-CMC nanocomposite inhibited the growth of a Gram-positive bacteria, *Enterococcus faecalis*, and a Gram-negative bacteria, *E. coli*, at a concentration of 0.1 $\mu\text{g/mL}$ (Siqueira *et al.*, 2014).

Chitosan

Chitosan is a random copolymer obtained from the alkaline deacetylation of chitin, formed by D-glucosamine and N-acetyl-D-glucosamine units, linked by β -1,4-glycosidic linkages. The ratio between the two units is considered as the degree of deacetylation (Bedian *et al.*, 2017; Verlee *et al.*, 2017). When the deacetylation degree of CS reaches about 50%, it becomes soluble in aqueous acidic media (Chang *et al.*, 1997). When chitosan is dissolved in an acidic environment, the amino groups in the chain protonate and the polymer becomes cationic, allowing it to interact with diverse types of molecules, thus turning chitosan into the only cationic marine polysaccharide (Lizardi-Mendoza *et al.*, 2016). This positive charge is thought to be responsible for its antimicrobial activity, via the interaction with the negatively charged cell membranes of microorganisms (Cazón *et al.*, 2017). Chitosan has been extensively studied due to its excellent film formability, antibacterial properties, physical and mechanical properties, biocompatibility and biodegradability (Khokhlova *et al.*, 2012; Munteanu *et al.*, 2014). Chitosan is obtained by alkaline deacetylation of chitin, which is extracted from a variety of crustacean shells, fungal cell walls and other biological materials (Kim *et al.*, 2011). Chitosan, which listed in the generally recognized as safe (GRAS) materials by U.S. Food and Drug Administration in 2001, is used as a food preservative since it is biocompatible and non-toxic for human beings and animals (Friedman and Juneja, 2010). In food industries, chitosan has been used extensively for surface coating of meat and fruit products to reduce food deterioration and water loss, as well as a delay in the ripening of fruits (Aranaz *et al.*, 2009). Chitosan is also known to have antimicrobial activity that inhibits the growth of a wide range of fungi, pathogenic bacteria and spoilage microorganisms (Dutta *et al.*, 2009). Shankar and Rhim (2018b) prepared chitosan-based nanocomposite films reinforced with sulfur nanoparticles and obtained improved properties of nanocomposite films with strong antibacterial activity against *E. coli* and *L. monocytogenes*.

Starch

Oleyaei *et al.* (2016) also used a solvent casting method to prepare ternary potato starch bio-nanocomposite films containing sodium montmorillonite (MMT) and TiO_2 nanoparticles. A 5% MMT addition to starch-based bio-nanocomposite showed a 50% reduction in water vapor permeability. Moreover, those blend nanocomposite films showed an antimicrobial activity against *Listeria monocytogenes* which is a Gram-positive bacterium (Oleyaei *et al.*, 2016). Nearly the same enhancement in water vapor barrier properties and tensile strength was reported with starch-based nanocomposite film incorporated with hydrothermally synthesized zinc oxide nanoparticles (Andiyana and Suyatma, 2016).

Gellan and guar-gum

Gellan is released and extracted from the bacterium *Sphingomonas elodea* (previously named *Pseudomonas elodea*). Gellan gum is a linear anionic heteropolysaccharide having a tetrasaccharide repeating unit comprising of rhamnose, D-glucose and D-glucuronic acid in the ratio of 1:2:1. It has the potential for partial or entire replacement of existent gelling agents (Chaudhary *et al.*, 2013). Mun *et al.* (2015) reported the preparation and characterization of graphene oxide-gellan gum-sodium alginate nanocomposites. The obtained findings revealed that the addition of graphene oxide and sodium alginate drastically improved the tensile strength and Young's modulus of gellan gum. Arfat *et al.* (2017) investigated the potential of guar gum-based nanocomposite films prepared by incorporating silver-copper alloy nanoparticles (Ag-Cu NPs) through solution casting method as an active food packaging material. Tensile test results showed an improvement in mechanical strength. Also, the films showed excellent UV light and oxygen barrier capability. Furthermore, strong antibacterial activity was observed against both Gram-positive and Gram-negative bacteria (Arfat *et al.*, 2017).

Others

Rhim and Wang (2013) prepared a ternary blend bio-hydrogel film by solvent casting method comprised of agar, konjac glucomannan powder, and κ -carrageenan reinforced with nanoclay (Cloisite® 30B). They found that the addition of nanoclay improved the tensile strength of the ternary blend bio-hydrogel film from 62 to 76 MPa and decreased the water vapor

permeability from 1.25×10^{-9} to 1.05×10^{-9} g m⁻¹ s⁻¹ Pa⁻¹. The ternary blend bio-hydrogel films exhibited an enormous increase in the water holding capacity up to 5488%. They applied the developed film for the packaging of green onion and found the potent application of the developed film for the antifog packaging of highly respiring fresh produce like spinach (Rhim and Wang, 2013).

Protein-Based Bio-Nanocomposite

In commercial applications, the following animal-derived proteins used are: casein, whey protein, collagen, egg white and fish myofibrillar protein. The plant-based proteins also under large scale application consideration include soybean protein, zein (corn protein) and wheat gluten. Compared with non-ionic polysaccharide films, protein films, due to their more polar nature and more linear (non-ring) structure and lower free volume offer better oxygen barrier properties and lower water vapor permeability (Arora and Padua, 2010). The transparent films based on whey protein show good oxygen barrier and TiO₂ or ZnO were added to form nanocomposites with improved antimicrobial properties used to fabricate food-grade, biodegradable packaging materials (Sothornvit and Krochta, 2005; Zhou *et al.*, 2009; Shi *et al.*, 2008). Chen and Zhang (2006) and Yu *et al.* (2007) showed that the addition of small amounts (<1 wt%) of TiO₂ nanoparticles significantly increased the tensile properties of whey protein film (from 1.69 to 2.38 MPa). Soy protein nanocomposite films exhibited reduced water vapor permeability, improved elastic modulus and tensile strength compared with the neat polymer. Zein, a biodegradable polymer, is used in the food industry as a coating agent (Liu *et al.*, 2005). It is less water sensitive than other biopolymers but shows high water vapor permeability and low tensile strength when compared with commodity polymers. To ameliorate its inherent brittleness, plasticizers may be used.

Gelatin

Gelatin is a water-soluble protein derived from the partial hydrolysis of the fibrous insoluble protein, collagen. Collagen is a major protein constituent in the bones, cartilages, and skins of animals and fish. Therefore, the properties of the gelatin are greatly influenced by the source, age of the animal, type of collagen, and processing method (Gómez-Guillén *et al.*, 2011). For the production of gelatin, various mammalian sources are used, such as pig skin (46%), bovine hide (29.4%), and pork and cattle bones (23.1%). Nonmammalian sources like fish skin (1.5%) are not significant, but have recently gained momentum as potential alternatives (Gómez-Guillén *et al.*, 2011). However, the rheological properties of gelatin obtained from nonmammalian sources are less stable than those of mammalian sources. Depending on the processing methods, gelatin is classified into two types, i.e., type A gelatin and type B gelatin (Arvanitoyannis, 2002). Type A gelatin is obtained by acid treatment of collagen and it has an isoelectric point of 7–9. However type B gelatin is derived from the alkali treatment of collagen with an isoelectric point of 4–5 (Gómez-Guillén *et al.*, 2011). Initially, the insoluble native collagen is pretreated by heating above 45°C in water to get the soluble gelatin from collagen. Then, the chemical treatment breaks the noncovalent bonds and disrupts three-dimensional structures of the proteins, thus resulting in adequate swelling and solubilization of collagen. The subsequent heat treatment cleaves the hydrogen and covalent bonds and unfolds the triple-helix, resulting in helix-to-coil transition and conversion of collagen to soluble gelatin. The degree of collagen conversion into gelatin is dependent on the pretreatment with warm-water extraction, pH, temperature, and extraction time (Hanani *et al.*, 2014). Gelatin is composed of 50.5% carbon, 25.2% oxygen, 17% nitrogen, and 6.8% hydrogen (Smith, 1921). Gelatin is a mixture of α -chains (one polymer/single chain), β -chains (two α -chains covalently cross-linked), and γ -chains (three α -chains covalently cross-linked) (Papon *et al.*, 2007). Generally, gelatin with a high percentage of α -chain possesses higher gel strength. The amino acid composition of gelatin is characterized by the structure of Ala-Gly-Pro-Arg-Gy-Glu4Hyp-Gly-Pro- (Shankar *et al.*, 2010; Nilesh *et al.*, 2011). Gelatin is a tasteless, odorless substance and is produced in a granulated or powdered form. Gelatin is hygroscopic, but its water absorbing capacity depends on the relative humidity at which it is dried and stored. Extreme pH and high temperature denature the gelatin and change its properties by disrupting three-dimensional structures of gelatin and forming a random coil. Therefore, the processing conditions of gelatin need to be carefully controlled to get a high gelling strength. By exploiting its diverse functional properties, gelatin has been widely used industrially, not only for food packaging materials, but also in various applications such as emulsifiers, cosmetics, photography, foaming agents, hydrogels, and colloid stabilizers (Arora and Padua, 2010; Shankar *et al.*, 2010). In the pharmaceutical industry, gelatin has been exploited for making hard and soft capsules, emulsions, ointments, plasma expanders, and wound dressing materials (Ulubayram *et al.*, 2001; Wang *et al.*, 2012a,b). In the food industry, gelatin is used in food packaging and food coating materials, and also as gelling, stabilization, texturization, and emulsification for bakery, beverages, confectionery, and dairy products (Djagny *et al.*, 2001). Gelatin is a promising protein biopolymer, owing to its remarkable film forming property, biodegradability, abundance, and cost-effectiveness (Farris *et al.*, 2011). Also, the introduction of nanoparticles into gelatin matrices greatly enhances the overall properties, such as the biocompatibility, physical and mechanical properties, and biodegradability of gelatin-nanocomposite films (Duncan, 2011). Also, some of the nanocomposite systems provide extra-functional properties, such as antioxidant and antimicrobial functions. Bionanocomposite films that are fortified with antimicrobial properties especially broaden the application range of the films in food packaging industries. They mitigate the risk of foodborne pathogens outbreak, which subsequently renders supreme food safety and quality, and extends the shelf life of food (Llorens *et al.*, 2012). Numerous metallic or inorganic nanoparticles such as gold, silver, zinc, copper, and clay, in conjunction with gelatin, have been used to improve the functional properties of gelatin. Additionally, gelatin has been used for the preparation of completely biodegradable

bionanocomposite food packaging films. This is done by blending with other organic polymers, such as nanocrystals of cellulose, starch, chitin, and chitosan (Pereda *et al.*, 2011).

Soy protein

Soy protein has attracted great research interest for the development of environmentally friendly protein materials with potentially good properties, such as regeneration, biocompatibility, biodegradability, etc., (Echeverría *et al.*, 2014; Garrido *et al.*, 2013). Soy protein has been widely used in hydrogels, adhesives, plastics, films, coatings and emulsifiers, and it has also been reported as a promising material for biotechnological and biomedical utilization (Zhao *et al.*, 2013). Soy protein is extracted from soybean seeds that are used to obtain soy oil and can be used for food packaging or edible films since it meets food grade standards (Garrido *et al.*, 2013). Soy proteins are composed of a mixture of albumins and globulins, 90% of which are storage proteins with globular structure, consisting mainly in 7S (β -conglycinin) and 11S (glycinin) globulins (Ciannamea *et al.*, 2014; Koshy *et al.*, 2015). Soy protein is commercially available in three different forms from soybean processing plants, namely, soy flour (SF: 54% protein), soy protein concentrate (SPC: 65%–72% protein) and Soy protein isolate (SPI: $\geq 90\%$ protein) (Saenghirunwattana *et al.*, 2014). Soy flour is made by grinding soybeans into a fine powder, which contains about 56% protein and about 34% carbohydrates. Soy protein concentrate, prepared by eluting soluble components from defatted soy flour, contains more than 65% protein and 18% carbohydrates. Soy protein isolate is a highly refined or purified form of soy protein with a minimum protein content of 90% on a moisture-free basis. It is made from defatted soy flour which has had most of the nonprotein components, fats and carbohydrates removed (Kalman, 2014). The protein content of soy protein isolate (SPI) is more than those of other soy protein products, which makes it exhibit a higher film-forming ability. Moreover, SPI also produces softer, more transparent and flexible films compared to those derived from other sources, and they have effective gas barrier properties compared to films prepared from lipids and polysaccharides (Gonzalez and Alvarez Igarzabal, 2014). SPI films do not show satisfactory mechanical properties or water vapor barrier properties in practical applications due to their inherent hydrophilicity. SPI contains 58% polar amino acids that cause hydrophilicity as well as the strong molecular interaction of natural protein; and these properties become poorer under highly humid conditions (Choi *et al.*, 2003). Various methods to enhance the physical properties of protein films have been suggested. Environmental friendly thermoplastic nanocomposites were successfully developed using a colloidal suspension of chitin whiskers (wet basis) as a filler to reinforce SPI plastics by Lu *et al.* (2004). Analysis showed that nanocomposites with lower whisker content exhibit a relatively uniform dispersion in the SPI matrix than those with higher chitin content. Compared to glycerol plasticized SPI sheet, the chitin filled SPI composites exhibited an increase in Young's modulus and tensile strength from 26 to 158 MPa and 3.3–8.4 MPa, with increasing chitin content from 0 to 20 wt%. Wang *et al.* (2006) prepared SPI/cellulose whisker composites using a colloidal suspension of cellulose whiskers from cotton linter pulp and reinforced to SPI polymer matrix. With the addition of 0–30 wt% (wet basis) of cellulose whiskers, strong interactions occurred between the cellulose whiskers and the SPI matrix that resulted in improved mechanical and barrier properties of the nanocomposite films. Also, the inclusion of inorganic nano fillers into the soy protein matrix results in a drastic change in matrix properties which depends on many factors such as nanoparticle size, aspect ratio, surface area, and polymer/filler compatibility. SPI-MMT polymer clay nanocomposites have been prepared using several methods like melt extrusion (Kumar *et al.*, 2010), casting (Echeverría *et al.*, 2014) and solution intercalation (Chen and Zhang, 2006). The nanoclay was shown to become highly exfoliated with positive surface charges on the globulins anchoring into the negatively charged montmorillonite galleries, and good nanoclay dispersion occurred due to electrostatic interactions and hydrogen bonding. Zhao *et al.* (2013) prepared SPI/AgNPs films, that showed considerable antimicrobial activity against both Gram-positive bacteria (*Staphylococcus aureus*) and Gram-negative bacteria (*E. coli*) even when the Ag content was only 0.1%. When the Ag content in the film was larger than 0.5% (w/w), almost all of the bacteria were killed within 2 h. Therefore, the addition of AgNPs was found to have the effect to prevent bacteria growth on the SPI based materials, and thus prolong their useful life. SPI (5.0 g/100 mL) films embedded with nano-TiO₂ (0, 0.5, 1.0, 1.5 and 2.0 g/100 mL) were prepared by solution casting (Wang *et al.*, 2012a,b) and modified by ultrasonic/microwave assisted treatment (UMAT) by Wang *et al.* (2014). Nano-TiO₂ could react with SPI, and these interactions can result in stronger interfacial adhesion between nano-TiO₂ and SPI matrix, which leads to a higher efficiency of the stress transfer from the matrix to the nanoparticles and hence an increase in tensile strength.

Application of Bio-Nanocomposites

Bio-nanocomposite films are used for a variety of active packaging and smart packaging applications, as well as for improving film properties and application of biodegradable packaging materials (Fig. 4).

Antimicrobial Packaging

One of the main reasons for the deterioration of food quality is microbial growth, which leads to discoloration, off-flavor development, textural changes, and the loss of nutritive value, and thus reduces the shelf-life of foods and increases the risk of food-borne illness (Malhotra *et al.*, 2015). Antimicrobial packaging prolongs the lag time of microbial growth and slows the growth rate of microorganisms, extending the shelf life of the food and maintaining the quality and safety of the food (Han, 2000). The antimicrobial packaging film can be brought into direct contact with the food surface to evaporate the antimicrobial agent or deliver it to the food. Many antimicrobial agents such as ethanol, carbon dioxide, silver ions, chlorine dioxide,

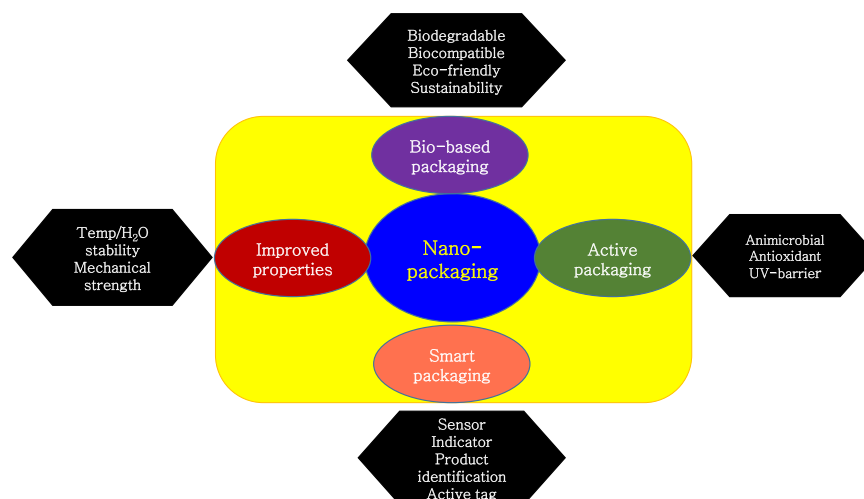


Fig. 4 Multifunctional applications of bio-nanocomposite packaging films.

antibiotics, bacteriocins, organic acids, essential oils, and spices have been tested to inhibit the growth of microorganisms in packaged foods (Jayasena and Jo, 2013; Malhotra *et al.*, 2015), but antimicrobial packaging is commercially limited except silver nanomaterials (Realini and Marcos, 2014). Although an increasing effort has recently been devoted to the development of antimicrobial packaging solutions, there are considerable differences in the ways antimicrobials are used at laboratory-scale and in real-time applications, and, together with regulatory issues and technical constraints, these differences are some of the main factors limiting the commercialization of antimicrobial packaging systems (Realini and Marcos, 2014; Malhotra *et al.*, 2015). To successfully introduce antimicrobial packaging into the market, it is essential to choose a package that is compatible with antimicrobial agents and the environmental conditions facing the particular food. A multidisciplinary approach involving researchers from all fields of biotechnology, particularly microbiology, food technology, engineering, and materials science, will be necessary to create antimicrobials with a promising future in the food packaging industry (Malhotra *et al.*, 2015). Several types of antimicrobial packaging have been commercialized (Ahmed *et al.*, 2017; Fang *et al.*, 2017).

Antioxidant Packaging

High levels of oxygen in food packages can facilitate microbial growth (such as aerobic bacteria, molds, and insects), oxidation of lipids and pigments, and loss of O₂-sensitive nutrients such as vitamins A, C, and E, which lead to changes in flavor (typical of rancidity), color, texture, and nutritive value. These changes can render the product unacceptable for human consumption and may even result in the formation of toxic aldehydes due to the degradation of polyunsaturated fatty acids that have been positively correlated with the prevention of cardiovascular disease (Fang *et al.*, 2017; Realini and Marcos, 2014). Additionally, oxygen has a considerable effect on the respiration rate and ethylene production rate of respiring foodstuffs such as fruits and vegetables (Lopez Rubio *et al.*, 2004). Therefore, the removal of O₂ from the package headspace is crucial to improving the quality and safety of oxygen-sensitive food products, and it has long been a goal of food-packaging scientists. Although vacuum packaging combined with a good oxygen barrier in the packaging film can effectively limit the presence of oxygen, such techniques do not completely remove the oxygen inside the package because O₂ permeates from the exterior through the packaging film, because of residual O₂ at the time of packing, or because of poor sealing (Ahmed *et al.*, 2017). Antioxidants can be directly added to food formulations by using certain processing steps such as spraying, immersion, or mixing, which may cause changes in food quality parameters (color or taste) and may affect consumer acceptance of the product.

Furthermore, such methods may encounter the following limitation: once the active compounds are consumed in the reaction, the protection ceases, and the quality of the food degrades more quickly (Mastromatteo *et al.*, 2010). In these cases, active antioxidant packaging represents an innovative strategy to improve the stability of oxidation-sensitive food products and thus extend their shelf-life by incorporating antioxidant agents in a polymer. Table 1 represents the application of nanocomposites in the packaging of food.

Biodegradability, Renewability, and Sustainability

Biodegradation means fragmentation, loss of mechanical properties or chemical modifications through the action of microorganisms when polymeric materials are exposed to a natural environment (Calmon-Decriaud *et al.*, 1998). Biodegradation is a complex process that finally converts the material into carbon dioxide, water, inorganic compounds, methane and biomass (Lucas *et al.*, 2008). Environmental conditions such as atmospheric pollutants, climate, and humidity, as well as the properties and composition of polymeric materials, are some of the reasons that may interfere on their biodegradability (Lucas *et al.*, 2008).

Table 1 Application of packaging materials

Function	Biopolymer	Nanofiller	Application	Reference
Antimicrobial	Chitosan	ZnO NPs, neem oil	Carrot	Sanuja <i>et al.</i> (2015)
	Gelatin	ZnO nanorods/clove essential oil	Shrimp	Ejaz <i>et al.</i> (2018)
	Cellulose	AgNPs	Fresh-cut melon	Fernandez <i>et al.</i> (2010)
	Pullulan	AgNPs	Turkey deli meat	Khalaf <i>et al.</i> (2013)
	Pullulan	ZnO NPs, essential oils	Meat and poultry products	Morsy <i>et al.</i> (2014)
	Agar	Ag-MMT NPs	Fior di Latte cheese	Incoronato <i>et al.</i> (2011)
	Gelatin	Oregano, rosemary essential oils	Cod smoke sardine	Gomez-Estaca <i>et al.</i> (2007)
	Gelatin	Laurel essential oil	Rainbow trout fillets	Alparslan <i>et al.</i> (2014)
	Chitosan	Grapefruit seed extract	Sliced bread	Tan <i>et al.</i> (2014)
	CMC-Chitosan	ZnO NPs	Bread	Noshirvani <i>et al.</i> (2017)
	Starch	Green tea extract	Beef	Nisa <i>et al.</i> (2015)
	Grain protein	Green, black and oolong tea extracts	Fresh pork	Yang <i>et al.</i> (2016)
	Whey protein	Cinnamon (85%) + Rosemary essential oil (15%)	Pork salami	Ribeiro-Santos <i>et al.</i> (2018)
Antioxidant	Whey protein	Oregano extract	Painho	Catarino <i>et al.</i> (2017)
	Chitosan	Tea polyphenols	Cooked pork sausages	Qin <i>et al.</i> (2013)
	Chitosan	MMT, rosemary and ginger essential oil	Fresh poultry meat	Pires <i>et al.</i> (2018)
	Chitosan	TiO ₂	Tomato	Kaewklin <i>et al.</i> (2018)
	Chitosan			
Ethylene absorber	Chitosan			

Among abiotic conditions, eg: light, mechanical, thermal, and chemical effects also provoke deterioration that deteriorates the polymeric structure preferring the biodegradation process (Eubeler *et al.*, 2010; Shah *et al.*, 2008). Biodegradation of polymer matrices depends mainly on the length of the polymer chain, the complexity of the polymer matrix, and their degree of crystallinity (Pantani and Sorrentino, 2013). Polymer products degrade in a controlled way, such as natural polymers (humus, lignin, rubber) and synthetic polymers (polyolefins) follow the mechanism of oxo-biodegradation (Rydz *et al.*, 2014). During the degradation of oxocarboxylic acid molecules, low molecular weight alcohols, aldehydes, and ketones produced by peroxidation process that is initiated by heat or light, which are the main cause of the loss of mechanical properties of the polymers, followed by bio-assimilation by bacteria, fungi, enzymes resulting in increasing biomass and CO₂. Hydrobiodegradation is a process that yields biodegradable products from cellulose, starch, and polyesters. The aliphatic polyesters are hydrolyzed rapidly in an aqueous medium and biodegrade (Scott and Wiles, 2001). However, cellulose and starch swell in water and then biodegrade. There are hydro-biodegradable aliphatic polyesters such as polylactic acid and poly (hydroxy acid).

The biodegradable polymers must disintegrate in a short time and must be compatible with the composting process. They should not release toxic substances during degradation while maintaining the quality of the compost produced (Scott and Wiles, 2001). Absorption and interaction between the polymers and chemicals may affect the properties of the polymer being investigated. Therefore, it is necessary to evaluate the effectiveness and suitability of biopolymers for storage and food packaging as well as their byproducts during biodegradation.

Future Perspectives and Conclusion

Bionanocomposites represent an inspiring route for creating new and innovative packaging materials. By adding appropriate nanoparticles such as organic, inorganic or organic-inorganic hybrid nanomaterials, it will be probable for fabricating films for packaging have good mechanical, barrier thermal and other functional properties. They can reduce flammability significantly and maintain the transparency of the polymer matrix. Inserted nanomaterials into packaging materials as nano-sensors will alert the customer if food has gone bad. Bionanocomposites are a viable technology for “new” materials for near-future packaging applications, especially for flexible, fire resistance, antimicrobial and transparent barrier packaging films.

In conclusion, the area of bio-nanocomposites as packaging materials still need scientific research and improvement to develop the shelf life, quality and marketability of diverse packaging materials. What can be in the near, design and incorporate multiple desired functionalities? For example antimicrobial, antibiotic, biodegradable, and combine responses to environmental or chemical changes. Moreover, it can be in the not-so-near future, fabricate bioinspired nanostructure polymers nanocomposites. Look at nature’s examples of packaging, skins, structures with specific processes, and imagine if we could make synthetic equivalents.

Acknowledgments

This study was supported by the R&D Convergence Center Support Program of the Ministry of Food, Agriculture, Forestry and Fisheries, Republic of Korea (ARC 710013-03) and Korea Research Fellowship Program through the National Research Foundation of Korea funded by the Ministry of Science, ICT and Future Planning (2016H1D3A1903910).

See also: Biodegradable Packaging. Biodegradable Packaging Materials. Bio-Polymeric Packaging Material for Packaging of Raw Food. Biopolymers in the Synthesis of Different Nanostructures. Bio-Waste Based Nanofiber Materials. Developing Successful Biobased Product: Key Design and Manufacturing Challenges. Jute/Coir/Banana Fiber Reinforced Bio-Composites: Critical Review of Design, Fabrication, Properties and Applications. Processing, Properties and Prospects of Nano-Biocomposites. Recyclability of Packaging Materials for Domestic Applications. Role of Green Polymers in Food Packaging

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Cellulose Nanocrystal as a Prospective Reinforcement for Polymer Matrix Nanocomposites

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Introduction

Cellulose is one of the most abundant natural polymers on the planet earth and renewed continuously through photosynthesis. Building block derived from the renewable resources attracts considerable attention for the design of novel materials and systems. Cellulosic nanomaterials can be regarded as sustainable nano sized materials due to easy availability of source raw materials, renewability, nontoxicity, biodegradability etc. There is a rapid growing trend for the use of nanocellulose as a potential renewable nanomaterial for the development of novel functional materials (Yanamala *et al.*, 2014). Like other types of cellulosic nanomaterials, cellulose nanocrystals (CNC) are nontoxic, sustainable and renewable nanomaterials with high surface area, low density and excellent mechanical properties. Therefore, CNC have emerged as promising green nanofillers for the reinforcement in the range of polymer matrix and improve the properties of nanocomposites (Shin *et al.*, 2017; Mannan *et al.*, 2016).

Composite or nanocomposites are multi-phase materials manufactured by combination of various component materials in order to achieve the functional properties that none of the individual components possesses. In the composite/nanocomposite materials various phases retain their physical identity while bonded together by physical/chemical or combination of physical and chemical means. In a polymer based nanocomposite, polymer is a major phase while nanofillers are minor or reinforcement phase. Some of the well-known nano-reinforcements are nano-titanium dioxide (Anh *et al.*, 2018; Huppmann *et al.*, 2014), silica nanoparticles (Abdollahi *et al.*, 2015; Kang *et al.*, 2018; Tang *et al.*, 2016; Krishnan *et al.*, 2011), nano-clay (Dabbaghianamiri *et al.*, 2017; Zhai *et al.*, 2017; Zhou *et al.*, 2016), various carbon based nano-reinforcement (viz. carbon nanotube (Kausar *et al.*, 2017; Sapalidis *et al.*, 2018), graphene (Ma *et al.*, 2018; Sobolewski *et al.*, 2016; Zhang *et al.*, 2018), carbon nanofiber (Bafekrpour *et al.*, 2013) etc.), cellulose nanocrystal (El Miri *et al.*, 2015; Liu *et al.*, 2015; Vestena *et al.*, 2016) etc. Cellulose nanocrystal is renewable nano reinforcing material and can be used for the fabrication of high performance nanobiocomposites.

Most of the synthetic polymers derived from the petroleum based raw materials are non-degradable in nature. Environmental pollution by nondegradable synthetic polymers is a serious concern now a days, and researchers are looking for completely degradable or partially degradable polymeric products for daily uses. The major concern with the synthetic polymers derived from the petroleum based resource is the disposal as the solid waste disposal continues to be an ever increasing concern in this planet. As the landfills continue to be filled up by the synthetic polymers, there has been a significant demand for the renewable materials or nano-materials based polymer products (Tsai and Wertheim, 2001). Biodegradability of synthetic polymer is an interesting field of research to create polymeric products in order to decompose it into harmless byproducts when discarded. The demand for environmental friendly nano-materials which can be incorporated into the polymer matrix to enhance the degradability will increase (Doke and Garag, 2003). Therefore, the aim of this book article is to provide an overview of cellulose nanocrystal as a prospective renewable nanoreinforcement in the synthetic polymers to enhance the degradability of non-degradable synthetic polymers.

Cellulosic Nanomaterials

Cellulosic nanomaterials are group of renewable nanomaterials of cellulose structure with at least one dimension is less than 100 nm. Various types of cellulosic nanomaterials includes cellulosic nanofibrils, cellulosic nanocrystal and bacterial synthesized nanocellulose (Aitomaki and Oksman, 2014). Bacterial nanocellulose is produced by selective bacteria e.g., *Gluconacetobacter xylinum* (Avila *et al.*, 2014; Kuzmenko *et al.*, 2013). In a controlled environment, selective bacteria produces 3D network of nanofibrils which represents an interesting nano biomaterials for various biomedical applications such as artificial skin, artificial blood vessel, wound dressing, carrier for drug delivery etc (Barud *et al.*, 2016). Cellulosic nanomaterials can be prepared by bottom up and top down approaches. Preparation of cellulose nanofibrils from lignocellulosic biomass by using mechanical method, and preparation of cellulose nanocrystal from lignocellulosic biomass by dissolving amorphous region are top down approaches of nano-cellulose preparation. While, bacterial synthesis of nano-cellulose in a controlled environment is a typical example of bottom up approach for nano-cellulose preparation. Abraham *et al.* (2011) reported a novel process of acid hydrolysis followed by steam explosion for preparation of stable colloid suspension of cellulose nanofibrils (CNF) by using various lignocellulosic raw materials such as banana (pseudo stem), jute (stem) and pineapple leaf fiber. Steam explosion further remove amorphous region of lignin, hemicellulose etc. from inner part of fibers by depolymerization and defibrillation. Steam explosion i.e., high pressure steaming followed by decompression is an effective method for separation of nanofibrils from biomass (Cherian *et al.*, 2010, 2008). Diameter of cellulose nanofibrils is 5–50 nm for the pineapple raw fibers and 15–25 nm when nanofibrils extracted from

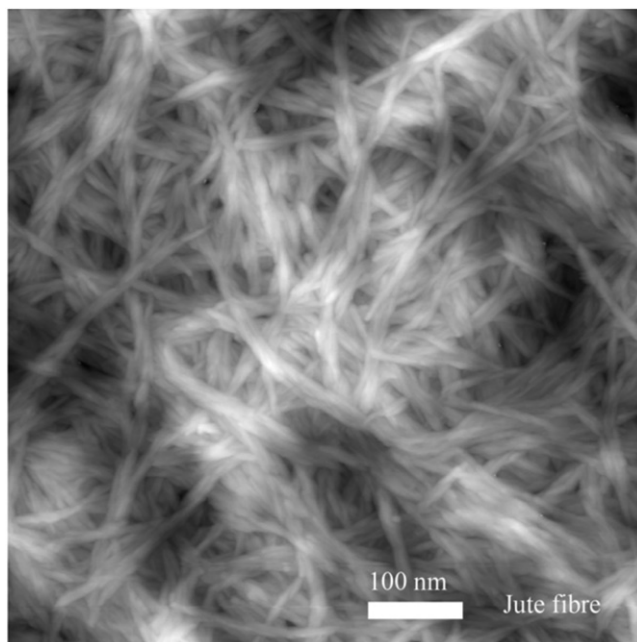


Fig. 1 Scanning probe microscopic (SPM) image of jute nano fibrils dispersion. Reproduced from Abraham, E., Deepa, B., Pothan, L.A., *et al.*, 2011. Extraction of nanocellulose fibrils from lignocellulosic fibers: A novel approach, *Carbohydrate Polymers* 86, 1468–1475, with permission.

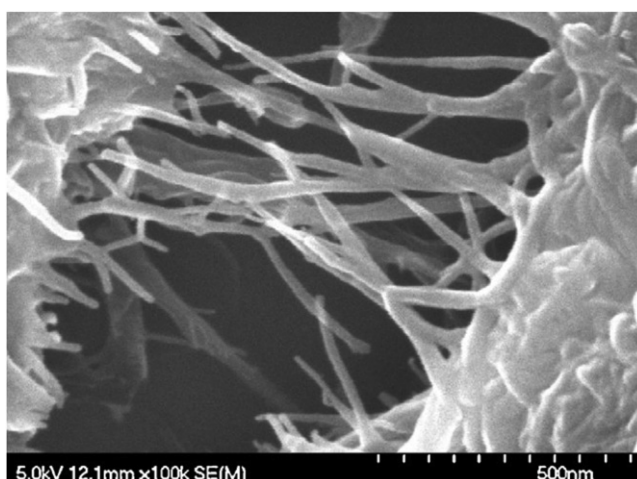


Fig. 2 Scanning electron microscopic image of CNF prepared by 12 passes of high pressure homogenizer. Reproduced from Chun, S.J., Lee, S. Y., Jeong, G.Y., Kim, J.H., 2012. Fabrication of hydrophobic self-assembled monolayers (SAM) on the surface of ultra-strength nanocellulose films, *Journal of Industrial and Engineering Chemistry* 18, 1122–1127, with permission.

the jute ([Fig. 1](#); [Abraham *et al.*, 2011](#)). Cellulose nanofibrils can also be prepared by high pressure homogenizer. [Chun *et al.* \(2012\)](#) reported diameter of CNF from 20 to 50 nm, after 12 passes through high pressure homogeneizer ([Fig. 2](#)). Another form of cellulosic nanomaterial i.e., cellulosic nanocrystal can be prepared by selectively hydrolysis of amorphous region from raw cellulose.

Preparation of Cellulose Nanocrystal

Cellulose nanocrystal can be prepared by following various top down methods. Some of the extracted cellulose nanocrystals from various cellulosic resources with their dimensions are tabulated in [Table 1](#) ([Tabassi *et al.*, 2016](#); [Dhar *et al.*, 2015a](#); [Urena-Benavides](#)

Table 1 Characteristics of cellulose nanocrystals

Source raw material	Process	Dimension of CNC (nm)		Ref.
		Lowest dimension	Length	
Microcrystalline cellulose (MCC)	Acid hydrolysis	61	272	(Tabassi <i>et al.</i> , 2016)
Bamboo (Bambusa balcooa)	Acid hydrolysis	15–20	400–600	(Dhar <i>et al.</i> , 2015a)
Cotton	Sulphuric acid hydrolysis	6.8	130	(Urena-Benavides and Kitchens, 2012)
Microcrystalline cellulose	Sulphuric acid hydrolysis	6.96 ± 0.87	178 ± 55	(Cho and Park, 2011)
Leaves <i>licuri</i>	Sulphuric acid hydrolysis	157 ± 24	5.7 ± 1.6	(Costa <i>et al.</i> , 2014)
Bleached kraft bagasse pulp	Sulphuric acid hydrolysis	7.5–16.6	143.4–202.5	(El-Wakil <i>et al.</i> , 2015)
Raw cellulose	Sulphuric acid hydrolysis	~5	~100	(Jebali <i>et al.</i> , 2015)
Rice straw	Sulphuric acid hydrolysis	Average thickness 4.7 ± 1.3 ; average width 6.4 ± 1.2	143 ± 31	(Jiang and Hsieh, 2014)
Cellulose nanofibers	Sulphuric acid hydrolysis	~7	~370	(Mondragon <i>et al.</i> , 2015)
Mulberry pulp	Sulphuric acid hydrolysis	40–50	200–350	(Reddy and Rhim, 2014)
Cotton linter	Sulphuric acid hydrolysis	~12	~177	(Morais <i>et al.</i> , 2013)

and Kitchens, 2012; Cho and Park, 2011; Costa *et al.*, 2014; El-Wakil *et al.*, 2015; Jebali *et al.*, 2015; Jiang and Hsieh, 2014; Mondragon *et al.*, 2015; Reddy and Rhim, 2014; Morais *et al.*, 2013). Leao *et al.* reported preparation of cellulose nanocrystal from sugarcane bagasse fibers. Prior to nano-cellulose extraction, fibers are pre-treated with sodium hydroxide or sodium chloride. Afterwards, cellulose nanocrystals can be obtained by sulphuric acid hydrolysis. Chemical composition and morphology analysis revealed that obtained cellulose nanocrystal exhibiting hemicellulose and lignin removal, nano dimension of 8–12 nm, high crystallinity and low thermal stability (Leao *et al.*, 2017). Orue *et al.* reported extraction of cellulose nanocrystal from office waste papers. CNCs are extracted by alkali pre-treatment, followed by acid hydrolysis. Concentration of alkali solution influences properties of CNCs. CNC extracted with 2 wt% of NaOH solution treatment and subsequent acid hydrolysis exhibit cellulose I crystalline structure, and around 40% increase of crystallinity index as compared to initial office waste paper. Whereas, CNC extracted with 7.5 wt% of NaOH solution pre-treatment and subsequent acid hydrolysis shows mixture of cellulose I and cellulose II polymorphs. CNC prepared by using higher concentration of NaOH exhibits poor thermal property (Orue *et al.*, 2017). Dungani *et al.* reported cellulose nanocrystal extraction from oil palm fronds (*Elaeis guineensis*). Before acid hydrolysis, materials are pre-treated with sodium hydroxide/anthraquinone followed by total chlorine free bleaching treatment. Bleaching treatment, prior to acid hydrolysis improved crystallinity index and thermal stability of extracted CNC. CNC contain cellulose I polymorph, and mean diameter and average fiber aspect ratio are 7.44 ± 0.17 nm and 16.53 ± 3.52 , respectively, making it suitable as reinforcing filler for polymer nanocomposite (Dungani *et al.*, 2017).

CNC can be extracted from microcrystalline cellulose by acid hydrolysis. Extracted nanocellulose has rod like structure with average diameter of around 7 nm (Fig. 3), aspect ratio approximately 25 and crystallinity of approximately 82% (Cho and Park, 2011). Costa *et al.* (2014) reported cellulose nanocrystal extracted by using sulphuric acid hydrolysis of licuri leaves which is composed of approximately 68% cellulose, 15.9% lignin and 8% hemicellulose. Transmission electron microscopic image revealed both individual as well as agglomerated CNC.

Cellulose Nanocrystal as a Renewable Reinforcement in Polymer Matrix

Cellulose nanocrystal (CNC) with enhanced mechanical and chemical properties, have gained huge interest as potential of nanofiller for reinforcement in polymer matrix composites (Yanamala *et al.*, 2014). Li *et al.* reported poly (butylene succinate) (PBS)/cellulose nanocrystal nanocomposites fabricated by solution coagulation. Solution coagulation shows improvement in dispersion and distribution of CNC in the polymer matrix, which subsequently improved properties of the composites (Li *et al.*, 2017). Rahimi and Otaigbe presented cellulose nanocrystal reinforced polyamide 6 nanocomposite prepared via ring opening polymerization and subsequent melt extrusion. CNC surfaces were modified with aminopropyl triethoxysilane. Surface modified CNC reinforced composites were compared with neat CNC reinforced composites. Surface modification of CNC improves dispersion of nanofillers in the polymer matrix as well as interfacial interaction between matrix phase and reinforcement phase. Improved dispersion and the development of the strong interfacial layer, subsequently improved solid state mechanical properties of nanocomposites (Rahimi and Otaigbe, 2017). Being its nano dimension and existence of enormous hydroxyl groups on its surface, uniform dispersion and distribution of cellulose nanocrystal in polymer matrix is a challenge for polymer scientist (Fig. 4). Dispersion and distribution of cellulose nanocrystal can be improved by surface modification of cellulose nanocrystals by using various functional groups. Dufresne proposes various approaches for chemical surface modification of CNC. Approaches can be categorized into three distinctive groups such as: (i) substitution of hydroxyl groups with small molecules, (ii) polymer “grafting onto” approaches and (iii) polymer “grafting from” approaches (Dufresne, 2013). Orr and Shofner use various processing

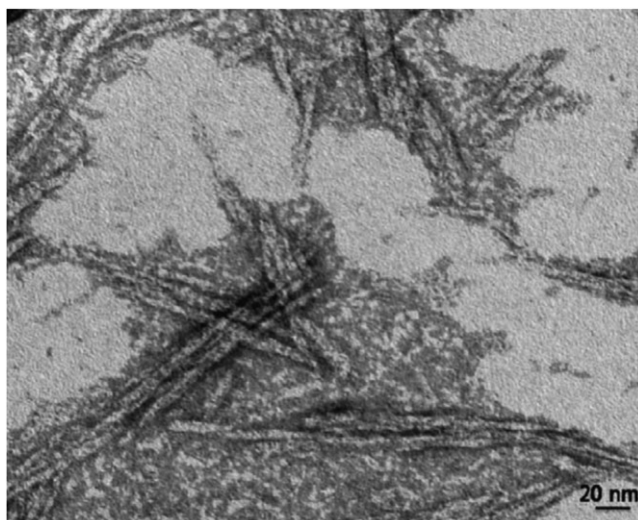


Fig. 3 TEM image of cellulose nanocrystal (CNC) prepared from microcrystalline cellulose by acid hydrolysis. Reproduced from Cho, M.J., Park, B.D., 2011. Tensile and thermal properties of nanocellulose-reinforced poly(vinyl alcohol) nanocomposites, *Journal of Industrial and Engineering Chemistry* 17, 36–40, with permission.

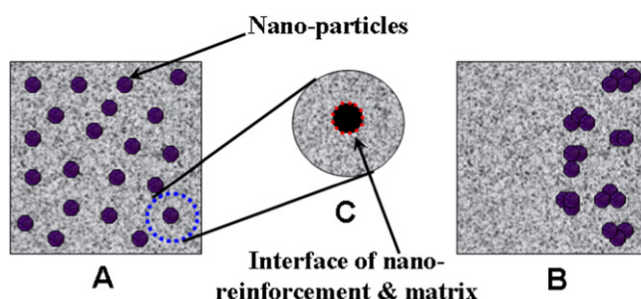


Fig. 4 Schematic showing: (A) good dispersion and distribution of nano-reinforcement; (B) poor dispersion and distribution of nano-reinforcement and (C) interface between nano-reinforcement and matrix phase.

strategies to achieve good dispersion and distribution of cellulose nanocrystal in the polyethylene-co-vinyl alcohol composite. They have proposed three processing strategies viz. melt processing, solution casting and combination of solution casting followed by melt processing technique. Nanocomposites fabricated by using multi-steps process shows better dispersion of cellulose nanocrystal in the polymer matrix (Orr and Shofner, 2017). In order to achieve homogeneous dispersion and distribution of cellulose nanocrystals (CNC) in the polymer matrix, different strategies can be applied as summarized in Fig. 5 (Dufresne, 2013) and detail information can be obtained from the literature (Dufresne, 2012).

Each building block of CNC contains three hydroxyl groups on its surface. Being its polar character, it is quite difficult to disperse the unmodified CNC into nonpolar polymer matrix. Surface grafting is a useful tool for widening applications of CNC. Mannan *et al.* proposed surface modification of CNC with bifunctional organic molecules having terminal vinyl groups that in-situ copolymerized with ethylene using a constrained geometry catalyst. This hybrid materials compatibilize hydrophobic polyolefin phase as well as hydrophilic CNC, which subsequently enhanced dispersion and distribution of CNC in hydrophobic polymer e.g., polyethylene (Mannan *et al.*, 2016). Espino-Perez *et al.* (2016) presents surface grafting of CNC with aromatic surface grafts using widely employed methods: the creation of urethane linkages, silylation and esterification to enhance adsorption of particular molecules. Mariano *et al.* (2017) reported noncovalent surface modification of CNC with poly(L-lactide) (PLLA)-based surfactants in order to improve compatibility between reinforcement phase and poly(lactic acid) of nanocomposites.

Mabrouk *et al.* presented CNC based nanocomposite prepared by using in situ mini-emulsion polymerization of acrylic monomers on CNC in presence of methacryloxypropyl trimethoxysilane (MPMS) as a coupling agent for a stable nanocomposite dispersion. Silane on surface of the polymer particles enhances adsorption of CNC through hydrogen bonding on polymer particles (Fig. 6). Prior to the film formation, during water evaporation, polymer particles come closer together with CNC being

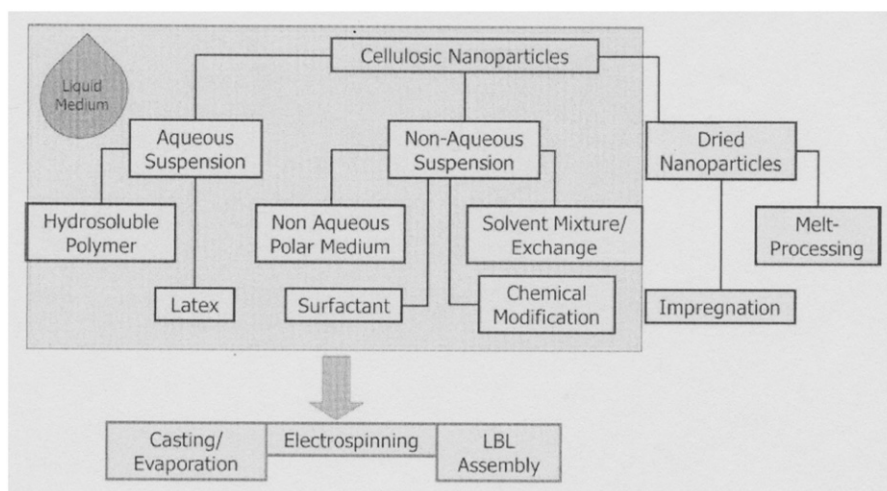


Fig. 5 Schematic showing different strategies for the processing of CNC reinforced polymer nanocomposites. Reproduced from Dufresne, A., 2013. Nanocellulose: A new ageless bionanomaterial, *Materials Today* 16, 220–227, with permission.

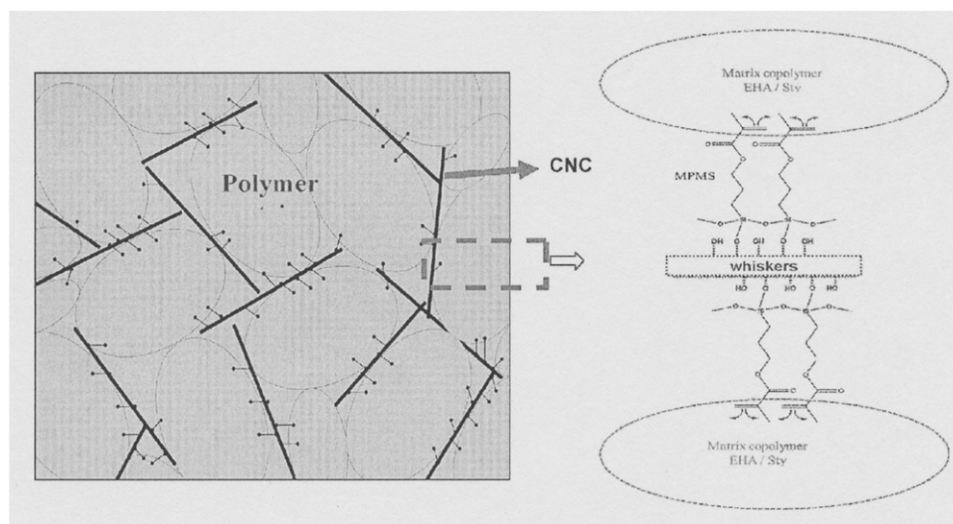


Fig. 6 Schematic representation of CNC entrapment into the polymer matrix of nanocomposite. Reproduced from Mabrouk, A.B., Salon, M.C.B., Magnin, A., Belgacem, M.N., Boufi, S., 2014. Cellulose-based nanocomposites prepared via mini-emulsion polymerization: Understanding the chemistry of the nanocellulose/matrix interface, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 448, 1–8, with permission.

physically adsorbed on their surface turned into chemical linkages by condensation reaction between surface silanol group of MMPS and hydroxyl groups of CNC. The whole processes helps to completely entrap the CNC into polymer matrix of the nanocomposites (Mabrouk *et al.*, 2014).

Properties of Cellulose Nanocrystal Reinforced Polymer Nanocomposites

Reinforcement of cellulose nanocrystal in the polymer matrix is an interesting approach to enhance the performance of polymer matrix by fine tuning of their morphology. Specifically dispersion and distribution of cellulose nanocrystal, and in particular, understanding of contribution of polymer matrix/cellulose nanocrystal interface are keys to design high performance nano bio-composites (Espino-Perez *et al.*, 2018). Depending on dispersion (i.e., individualization of nanofillers) and distribution (i.e., spread of nanofillers throughout the matrix) of cellulose nanocrystal in the polymer matrix, there might be four situations viz. (i) poor dispersion and poor distribution; (ii) poor dispersion and good distribution; (iii) good dispersion and poor distribution; and (iv) good dispersion and good distribution of cellulose nanocrystal in the polymer matrix. Fig. 4 shows schematically poor dispersion and poor distribution, and good dispersion and good distribution of cellulose nanocrystal in the polymer matrix. Apart

from dispersion and distribution of cellulose nanocrystal (CNC), interfacial interaction between CNC and polymer matrix is another key aspect for the improvement of nanocomposite properties. In order to improve the interfacial interaction between CNC and polymer matrix, CNC can be modified by various molecules. Each unit of cellulose nanocrystal contains three hydroxyl groups in its structure, which provides the chemist enormous opportunity for the surface modification of cellulose nanocrystal with various organic molecules. Depending on type selected molecules for the modification, CNC surface could be hydrophobic or hydrophilic, hence, could be reinforced to hydrophobic as well as hydrophilic polymer matrix. Strong interfacial interaction is desired in order to properly utilize the cellulose nanocrystal as reinforcement in the polymer matrix, hence, to improve the mechanical properties of polymer nanocomposites. In case of good interfacial interaction between CNC and polymer matrix, stress transfer from matrix to filler and vice versa will be appropriate, and that will improve mechanical properties of resultant composites. Whereas, in case of poor interfacial interaction, CNC's contribution towards resultant mechanical properties of composites will be minor, as there will be void formation (in case of poor interfacial interaction between polymer matrix and CNC) in the interface of CNC and polymer matrix (Mondal, 2018).

Smyth *et al.* reported improvement of mechanical properties of modified CNC reinforced alginate. CNCs were functionalized with 4-pentenoic acid (PA-g-CNCs) by using a solvent free environmental friendly esterification method. Surface grafting by using PA does not affect physical properties viz. crystallinity and dimensional properties of CNC. Reinforcement of functionalized CNCs has improved dry as well as wet mechanical properties of alginate (Smyth *et al.*, 2018). Shin *et al.* showed improvement of stiffness and energy dissipation of CNC reinforced epoxy composite as compared with neat epoxy material. With 5 wt% of CNC reinforcement in the epoxy matrix, storage and loss moduli in glassy region have been increased by 31 and 57% respectively, while thermal property of nanocomposite remained similar to that of the neat cured epoxy material. In their study, surface modification of CNC with a curing agent (Epikure 3140) exhibit no observable advantage to that of unmodified CNC (Shin *et al.*, 2017). Dhar *et al.* reported around 58% improvement of tensile modulus with 2 wt% loading of CNC in the poly(3-Hydroxybutyrate) matrix. Improvement of mechanical property of CNC reinforced composite is due to the strong interfacial bonding between CNC and poly(3-hydroxybutyrate), which was revealed by the fractured morphology (Dhar *et al.*, 2017). In another study, Dhar *et al.* reported polylactic acid grafted cellulose nanocrystal (PLA-g-CNC) nanocomposite films using dicumyl peroxide as cross-linking agent prepared by single step reactive extrusion process. Presence of chemical cross-linking agent led to efficient transfer of load from CNC to PLA matrix, hence, improved tensile strength by 40% and Young modulus by 490% respectively. The developed composites are thermally recyclable for multiple cycles (Dhar *et al.*, 2016). De France *et al.* reported enhancement of mechanical property of poly (oligoethylene glycol methacrylate) hydrogels by reinforcement of CNC. CNC are uniformly dispersed throughout the hydrogel matrix, and enhances mechanical property of hydrogel. With 5 wt% of CNC in hydrogel matrix, 35 fold increases in storage modulus was observed (De France *et al.*, 2016). Tabassi *et al.* reported CNC reinforced starch green nanocomposites. CNC and thermoplastic starch (TPS) possesses similar polysaccharide structure, hence, provide good interfacial interaction between CNC and starch matrix, and as a result of remarkable improvement of mechanical properties could be observed. With 9 wt% of CNC reinforcement in starch matrix, tensile strength of TPS increased from 3.1 to 11.1 MPa, Young modulus from 237.3 MPa to 4.2 GPa, while, glass transition temperature has been increased from 69.2 to 90.7°C (Tabassi *et al.*, 2016). Chang *et al.* reported CNC reinforced polyacrylonitrile (PAN) fiber prepared by gel spinning. 10 wt% CNC reinforcement can increase tensile modulus and strength from 14.5 to 19.6 GPa and from 624 to 709 MPa, respectively (Chang *et al.*, 2015). Iyer *et al.* reported cellulose nanocrystal reinforced low density polyethylene (LDPE) by using solvent less melt mixing method. Green biocomposite shows 69% increase in Young modulus with 10 wt% reinforcement of CNC as compared with the neat LDPE, while, biocomposite retain their elongation at break (Iyer *et al.*, 2015). Dhar *et al.* presents influence of CNC polymorphs for reinforcement capability and ability to form percolated network. CNC II significantly improved Young modulus of polylactic acid based composite, due to the extensive hydrogen bonding with polymer matrix, leading to the enhancement of mechanical and barrier property of composite films, while, the elongation at break decreases for reinforcement of CNC II as compared with reinforcement of CNC I in the PLA matrix (Dhar *et al.*, 2015b). Lin *et al.* reported acetylated CNC (ACNC) reinforced castor oil based polyurethane nanobiocomposite. With 25 wt% ACNC reinforcement in the polyurethane matrix, tensile strength and Young modulus of nanobiocomposite have been increased from 2.79 to 10.41 MPa and from 0.98 to 42.61 MPa, respectively. Whereas, breaking at elongation increased to maximum, with 10 wt% of ACNC reinforcement in the polyurethane matrix of more than twice than that of the control sample (Lin *et al.*, 2013). Lu and Hsieh reported CNC reinforced poly(acrylic acid) nanofiber spun by electrospinning. The Young modulus and tensile stress of PAA/CNC nanocomposite fibers were significantly improved with increasing CNC concentration in the fiber matrix by up to 35 fold and 16 fold respectively (Lu and Hsieh, 2009).

Optimum concentration of CNC is required for the improvement of mechanical property of nanocomposite. Cho and Park reported that with 3% reinforcement of CNC in poly (vinyl alcohol), storage modulus has been increased up to 74%, while, with 5% of CNC in the PVA matrix, 69% increase of storage modulus was observed due to the interaction of CNC with polymer matrix by hydrogen bonding. However, with 7% of CNC reinforcement in the PVC matrix, the storage modulus decreases (Fig. 7) due to the agglomeration of CNC in the PVC matrix (Cho and Park, 2011). Nicharat *et al.* reported improvement of mechanical property of the CNC reinforced polymer nanocomposite. CNC reinforced thermoplastic polyurethane fabricated by melt mixing shows significant improvement of storage modulus to that of unreinforced polymers. Reinforcement of CNC improves stiffness as well as the shape memory behavior of nanocomposite materials (Nicharat *et al.*, 2017).

Xu *et al.* reported crystallization behavior of CNC and acetylated CNC (aCNC) reinforced polylactide (PLA) nanocomposite. Presence of CNC enhanced melt crystallization rate and degree of crystallinity of PLA nanocomposites. Modified CNC improved

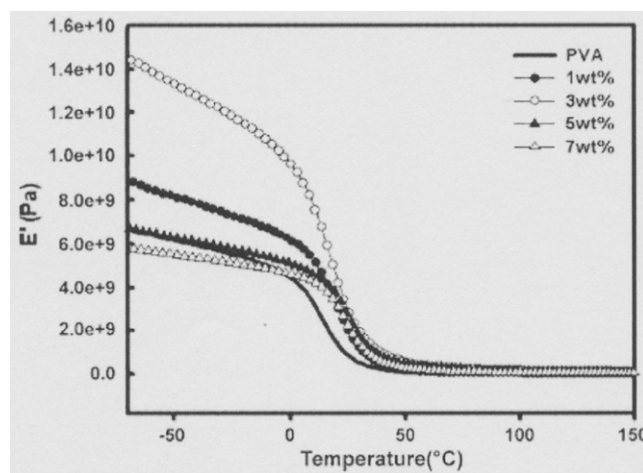


Fig. 7 Storage modulus with respect to the temperature for various CNC reinforced PVA nanocomposites. Reproduced from Cho, M.J., Park, B. D., 2011. Tensile and thermal properties of nanocellulose-reinforced poly(vinyl alcohol) nanocomposites, *Journal of Industrial and Engineering Chemistry* 17, 36–40, with permission.

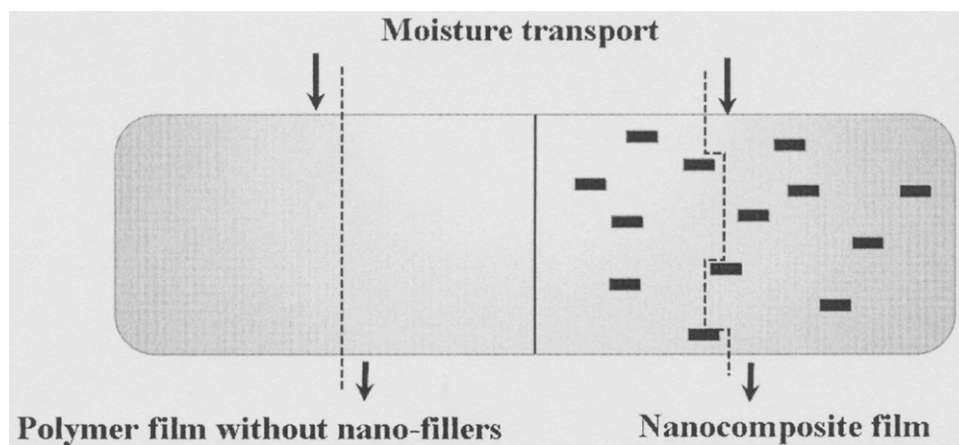


Fig. 8 Schematic representation of barrier property of cellulose nanofiller polymer nanocomposite. Reproduced from Mondal, S., 2018. Review on nanocellulose polymer nanocomposites, *Polymer-Plastics Technology and Engineering* 57 (13), 1377–1391.

melt crystallization and shows dense surface relative to unmodified CNC (Xu *et al.*, 2017). Dense surface can improve barrier property of the nanocomposite. Barrier property of CNC reinforced polymer nanocomposites can be achieved by crystalline nature of CNC and CNC's ability to form percolating network structure with the polymer matrix by strong hydrogen bonding, and all these increases tortuosity path for diffusing mass molecules (Fig. 8). Mass transfer property through dense polymer film would occurred by molecular mechanism i.e., sorption-diffusion-desorption. Decrease of diffusivity would effectively decreases resultant permeability of mass molecules, hence, improved barrier property of the polymer nanocomposite films. Further, with well dispersed and distributed CNC in polymer matrix can reduce the chain mobility of matrix polymer, as a result further decrease of penetrant diffusivity could be achieved (Dufresne, 2013; Mondal, 2018).

Applications of Cellulose Nanocrystal Reinforced Polymer Nanocomposites

Cellulose nanocrystal reinforced polymer film can be used widely for the food packaging. For food packaging and many other applications, barrier properties of film/membrane are important. The purpose of food packaging is to protect food stuffs from external abuses such as physical, chemical, or biological abuses and also preserve the quality of the food contain from the time of manufacturer to the time of consumption (Khan *et al.*, 2014; Nair *et al.*, 2014). Espino-Perez *et al.* reported barrier properties of CNC reinforced polylactide (PLA) nanocomposites with chemically designed interfaces in order to enhance compatibility of constituents and impart mass transport mechanism. Penetrants such as oxygen molecules and cyclohexane are slightly interacting with composite constituents, whereas, water vapor is highly interacting with the CNC, and anisol (an aromatic organic

vapor) is interacting only with designed CNC surfaces. Water vapor causes significant swelling of CNC, and subsequently creates favorable pathways for mass transport, hence, surface grafting of CNC could interfere this phenomena and decreases water transport rate. The specifically designed barrier properties by designing nanocomposite interface could be useful to design CNC reinforced membrane with selective mass transport properties (Espino-Perez *et al.*, 2018).

CNC reinforced chitosan composite can be used to improve ultra violet blocking property of cotton fabric. Composite can be used as efficient and durable UV blocker, and retain the UV blocking property even after 30 times laundering. CNC reinforced chitosan film coating improve mechanical properties, while decreasing the hydrophilicity of modified cotton fabrics (Yang *et al.*, 2018). Yuwawech *et al.* proposed applications of CNC reinforced polyurethane composites for transparent moisture barrier coating for encapsulation of dye sensitized solar cells. Reinforcement of pure and esterified CNC reduces water vapor transmission rate while light transmission values maintained to be above 80%. Mechanical property of polyurethane composite is higher for the esterified CNC reinforced system than the untreated CNC reinforced PU system. Better stability and efficiency of solar cell can be obtained with CNC reinforced PU, which indicates longer lifetime usage (Yuwawech *et al.*, 2017). Liu *et al* reported conductive CNC-polyaniline nanocomposite prepared by in-situ polymerization of aniline HCl onto cellulose nano-whisker. CNC-polyaniline nanocomposite shows improved conductivity as compared with the pure nanocellulose film. Significant improvement of conductivity of nanocomposite film is due to the dense coverage of tiny PANI particles on the surface of CNC. Flexible conductive nanocomposite films could find applications in sensors, batteries, conductive adhesives etc (Liu *et al.*, 2014).

Cellulose Nanocrystal Reinforced Degradable/Partial Degradable Renewable Nanocomposite Materials

Plastic waste disposal become an ever increasing concern in the planet earth, due to non-degradable nature for most of synthetic plastics derived from petroleum based resources (Al-Maaded *et al.*, 2012; Al-Salem *et al.*, 2014; Briassoulis *et al.*, 2014; Gobbi *et al.*, 2017; Mourshed *et al.*, 2017; Quartey *et al.*, 2015; Rigamonti *et al.*, 2014; Subramanian, 2000). Hence, synthetic plastic/polymers are accumulated over time once discarded after use. On the other hand, degradable plastics are degraded by enzymatic action of the microorganism as well as hydrolysis of long polymer chains (Barragan *et al.*, 2016; Chinaglia *et al.*, 2018; Rujnic-Sokele and Pilipovic, 2017; Iwata, 2015; Jiang *et al.*, 2015; Watanabe *et al.*, 2014). Nondegradable synthetic polymers can be partially/ completely degradable by incorporation of renewable reinforcements such as various cellulosic nano-reinforcements. Abraham *et al.* reported biodegradation of natural rubber and nanocellulose based nanocomposites. Biodegradation of nanocellulose reinforced rubber nanocomposites are shown in Fig. 9. Fig. 9 shows that biodegradation of nanocomposites accelerated with the increase of nanocellulose content in the rubber matrix possibly due to the accumulation of microorganism in peripheral

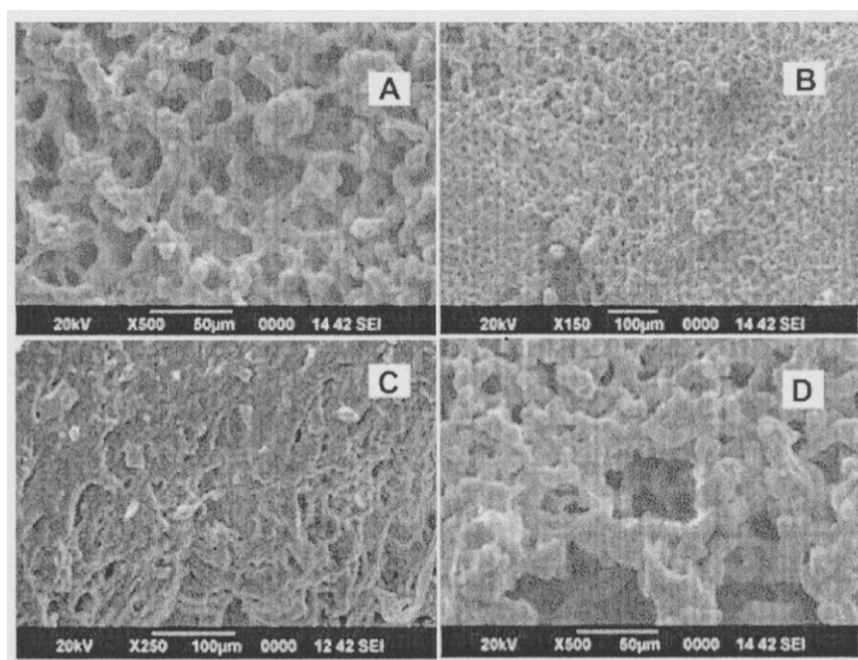


Fig. 9 Scanning electron microscopy (SEM) images of natural rubber (NR)/nanocellulose composite during the final stages of biodegradation. (A) 7.5% non-cross linked composite (B): 10% cross linked composite (C): standard cross linked matrix (without filler). (D): 10% non-cross linked composite. Reproduced from Abraham, E., Elbi, P.A., Deepa, B., *et al.*, 2012. Thomas, X-ray diffraction and biodegradation analysis of green composites of natural rubber/nanocellulose, Polymer Degradation and Stability 97, 2378–2387, with permission.

nanocellulose reinforcements. It is assumed that biodegradation starts from nanocelluloses due to the accumulation of microbes, which subsequently leaves holes and increase surface area for the biodegradation of remaining matrix materials. Each cellulose unit in nanocellulose contains three hydroxyl groups which are active sites for microbes (unless occupied by hydrogen bonding). Their result also shows that non-cross linked composites show a faster biodegradation than their cross linked counterpart. Interconnected network in the crosslinked nanocomposites could hinder the accessibility of microorganism as compared with the noncrosslinked nanocomposites (Abraham *et al.*, 2012).

Cellulose nanocrystal contain enormous hydroxyl functionality on its surface which could attract water molecules as well as microorganisms required for degradation of CNC reinforced nano-biocomposites (Mondal, 2018). Lin *et al.* reported acetylated CNC reinforced poly (lactic acid) matrix based fully biodegradable composite with superior mechanical property and thermal stability. Improvement of mechanical and thermal property of composite is due to the improved dispersion and strong interfacial interaction between reinforcement phase and matrix phase. The performance of ecofriendly nanobiocomposites expand the utilization of CNC derived from renewable resources (Lin *et al.*, 2011). Fig. 10 illustrates, schematically the cellulose nanocrystal reinforced polymer nanocomposite recycling system in nature. Wood pulp can be prepared from tree, afterwards, cellulose nanocrystals can be manufactured by using acid hydrolysis. Thus, CNC is derived as natural renewable resources. Polymer nanocomposites can be composted or land-filled after uses which will decompose into carbon dioxide and water through the action of microorganisms in the ground. Both CO_2 and H_2O are required for photosynthesis of plants.

Conclusion: Challenges of Cellulose Nanocrystal as Reinforcement

Cellulose nanocrystal has abundant resources; therefore, cellulose nanocrystal holds a great promise in a wide verity of applications including reinforcement in the polymer matrix to prepare polymer nano-biocomposites. There is a huge potential for biodegradable polymers and polymer composite/nanocomposite. Therefore, research effort for the optimization of nanocellulose reinforcement in the polymer nanocomposite will be interesting to explore. In this article, author briefly discusses the cellulose nanocrystal as potential reinforcement for polymer matrix composites. However, CNC possesses several challenges as cost effective nano-reinforcement for polymer matrix nanocomposites. These challenges need to be overcome, before we take the cellulose nanocrystal as potential filler for the bulk nanocomposite fabrication and commercialization. At present cost of cellulose nanocrystals are bit higher therefore to reduce cost of cellulose nanocrystal and increase the productivity, novel technically/commercially viable routes for the manufacturing of nanocellulose should be explored. Furthermore, methods to control size of CNC and the reduction of production cost will be interesting research topic as well. Being its nano size, it is very difficult to disperse and distribute cellulose nanocrystal in the polymer matrix. Development of novel processes to improve dispersion and distribution of nanocellulose in the polymer matrix is quite important. In order to overcome the synthetic plastic pollution, more research effort must be paid for cheap and environmental friendly degradable/partially degradable polymer nanocomposites, and cellulose nanocrystal reinforced polymer nanocomposites should be a competitive candidate. More and more research effort must be made for detail study of CNC reinforced polymer nanocomposite to make CNC reinforced nanocomposite a truly renewable one.

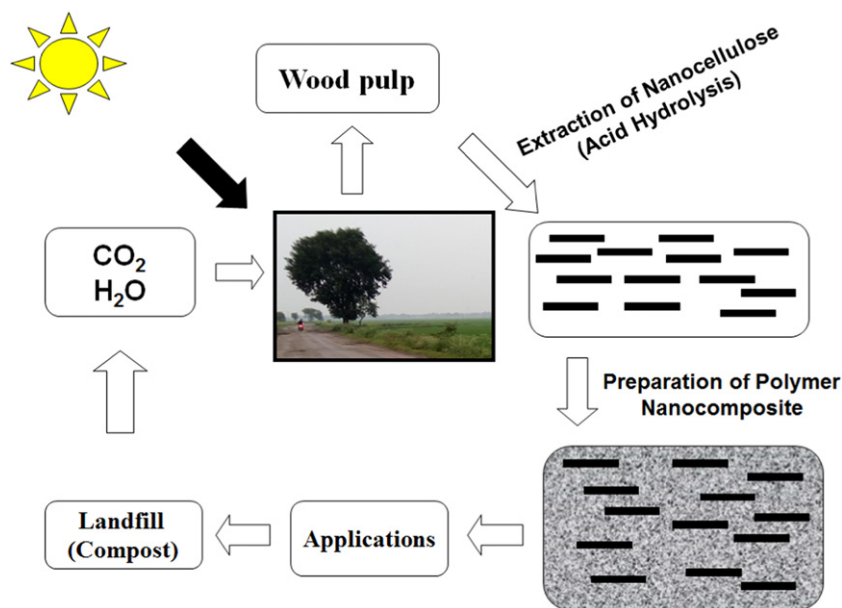


Fig. 10 Schematic showing recycling of renewable nanocellulose reinforced polymer nanocomposite.

See also: Bacterial Cellulose Based Nanocomposites for Electronic and Energy Applications. Biopolymers in the Synthesis of Different Nanostructures. Bio-Waste Based Nanofiber Materials. Green Composites From Sustainable Cellulose Nanofibrils. Nanocellulose Based Aerogels for Varying Engineering Applications. Nano-Porous Materials for Use in Solar Cells and Fuel Cells. Processing, Properties and Prospects of Nano-Biocomposites

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Development and Characterization of Aluminum Hybrid Metal Matrix Composites Used in Automotive Applications

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Introduction

Today, reducing fuel consumption in the automotive industry becomes the main agenda due to the emission to the environment and awareness on environmental sustainability. In order to address these issues, manufacturers are considering few approaches namely aerodynamic or streamlining design, incorporating lightweight materials such as aluminum alloys and composites (Qin *et al.*, 2005; Jiang *et al.*, 2005). Aluminum matrix composite (AMC) is one of the competitive lightweight materials used in automobile and other industries during the last decades. Hypereutectic Al-Si alloys with high Mg content are in fact an in-situ aluminum matrix composite containing a large amount of hard Mg_2Si particles. The Al- Mg_2Si composite has a potential as a material for automobile brake disks because the intermetallic compound of Mg_2Si exhibits high melting temperature, low density, appropriate hardness, low thermal expansion coefficient and reasonably high elastic modulus (Zhang *et al.*, 2000; Jing *et al.*, 2009). Compared to conventional ex-situ processes, in-situ technique produces composites with clear interface, better wettability and more even distribution of reinforcements within the matrix. Besides, in-situ method provides reinforcements which are thermodynamically stable since they are the product of reactions within the molten matrix alloy (Ghandvar *et al.*, 2018). However, the Al- Mg_2Si composite has low temperature brittleness and deficient wear resistance, which limit its application. SiC is also the most commonly used reinforcement phase in aluminum matrix composites (Mahmoud *et al.*, 2008; Sakthivel *et al.*, 2008; Song and He, 2010) due to its excellent properties such as higher melting point, higher hardness, better specific strength, excellent wear resistance good wear resistance compared to aluminum alloy (Lee *et al.*, 2001). The combination of aluminum with reinforcement particles is expected to extend the service life of the structures and also to improve the performance of the structure, especially for operations at elevated temperatures. Stir casting is a simple and cost effective method to fabricate the ex-situ aluminum MMCs compared to other fabrication processes. However, various conventional ex-situ processes of fabricating Al-SiC composites have some of the inherent problems, such as poor wettability of the reinforcement, reaction of matrix-reinforcement interface, and inhomogeneous distribution of SiC particles in the matrix (Madarasz *et al.*, 2011). Wettability in stir casting is the interface relationship between the matrix and the reinforcements. It can be defined as the ability of liquid to cover the solid surface, in this case, the reinforcement particles. In addition, wettability can be considered as measure of interface bonding between the matrix and the reinforcements, since different properties of materials within the composite cause discontinuities within the composite (Dutta and Surappa, 1998). It is suggested to add magnesium to improve wettability between SiC particles and the matrix (Nagarajan *et al.*, 1999). In addition, according to previous studies, the SiO_2 layer on the surface of SiC reacts with the Al matrix and Mg that segregates on the interface to form $MgAl_2O_4$ and Si (Lee *et al.*, 2000, 1999; Shen *et al.*, 2009), which prevents the formation of Al_4C_3 and results in the improvement of wettability of the Al-SiC system. Some previous studies have been conducted on the microstructure evolution of Al-SiCp composites (Dutta and Surappa, 1998; Nagarajan *et al.*, 1999). Nagarajan *et al.* (1999) reported that an increase in SiC volume fraction led to a reduction in the size of eutectic Si and also changed its morphology from needle-like to equiaxed, and that SiC particles were found to have negligible influence on DAS. Dutta and Surappa (1998) studied the solidification behavior of Al/Cu-SiCp composite under multi-directional solidification conditions. It was reported that SiCp promoted grain refinement in the matrix in the absence of convection, and matrix dendrite arm spacing (DAS) was not significantly altered by the presence of SiCp. However, there is limited experimental study on the effects of SiC particle addition on the microstructure and tensile properties of Al- Mg_2Si in-situ composites. Therefore, the aim of present study is to characterize the microstructure and elucidate the tensile properties results of the fabricated hybrid reinforced Al matrix composites through the Mg_2Si in-situ synthesis in melt combined with the SiC ex-situ stir casting at different contents of SiCp. This would improve not only the deficient wear resistance of Al- Mg_2Si composite, but also the machinability of SiC/Al composite.

Experimental Procedure

To prepare Al-20 Mg_2Si -2Cu in-situ composite ingot, commercially ADC12 alloy, magnesium (ingot, >98.0% purity) and aluminum (ingot, >98.0% purity) were used. In order to prepare the hybrid composite Al/(Mg_2Si + SiC), firstly, the SiC particles (>99% purity, 10–30 μm) (Fig. 1) were peroxidized at 800°C for 2 h to obtain a better wettability (Lee *et al.*, 2000, 1999). The mass fractions of SiC particle addition were set at 0 wt%, 5 wt%, 10 wt% and 15 wt%, respectively. Secondly, About 300 g of Al-20 Mg_2Si composite ingot was melted in a graphite crucible in an electric resistance furnace. Then the pre-heated SiC particles were added into the Al-Si-Mg melt at 750°C with a stirring action, in which the stirring condition for the fabrication of Al/(Mg_2Si + SiC) composite was: stirring speed of 500 r/min and stirring time of 15 min. Subsequently, after holding for 15 min, the composite melts were reheated to 720°C, and poured into steel die to produce cylindrical samples with 30 mm thickness.

Parallel to casting of test samples, around 100 g of melt was poured in pre-heated ceramic mold (500°C $\pm$ 15 min) for thermal analysis. The temperature-time data was recorded using an EPAD-TH8-K high-speed data acquisition system linked to a computer

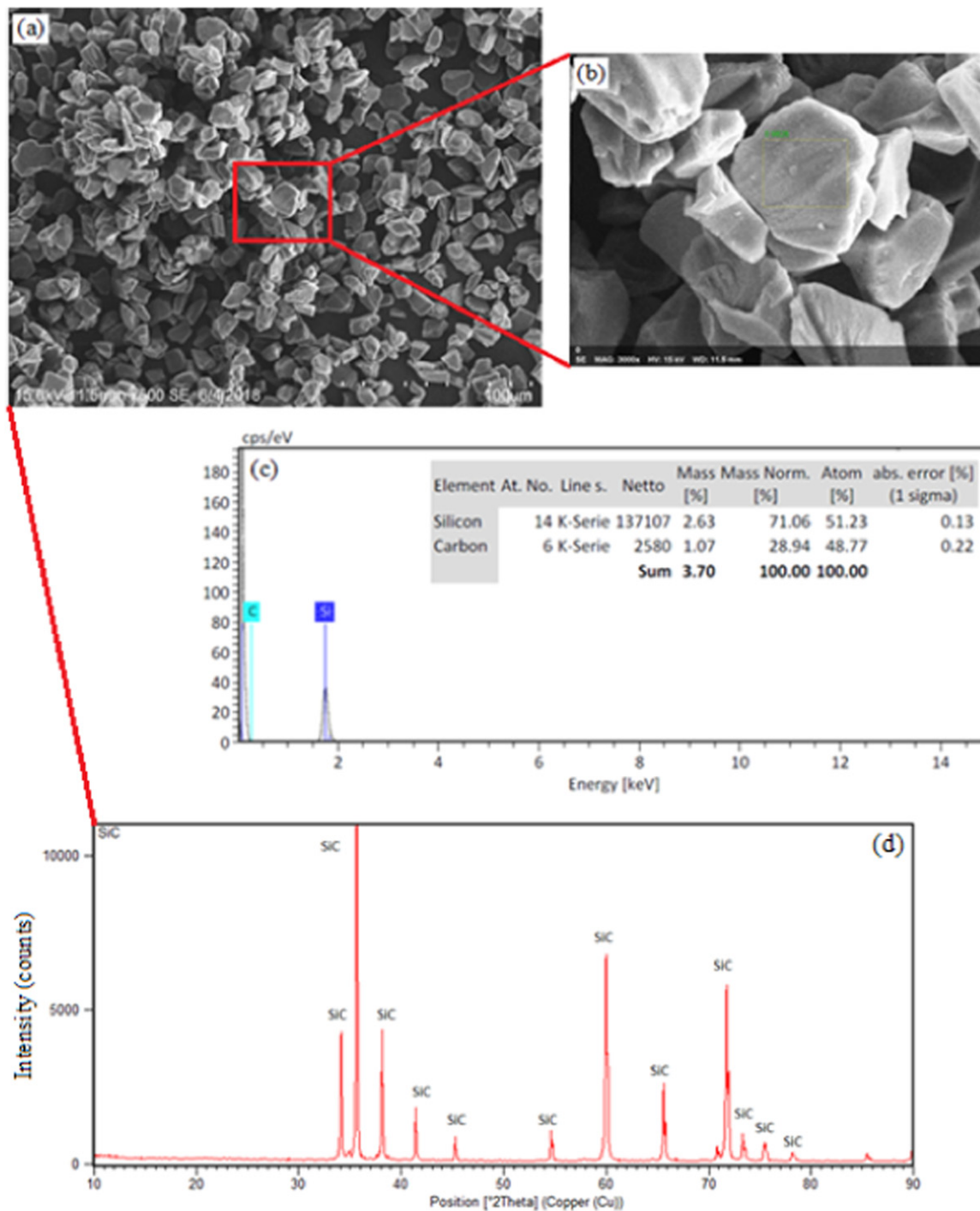


Fig. 1 (a) SEM micrograph of SiC powder used to fabrication of MMCs, (b) high magnified micrograph of SiC particles with corresponding (c) EDS spectra and (d) XRD analysis.

with DEWE Soft 7.5 at a dynamic rate of 100 Hz/ch. FlexPro10 data analysis software was used for smoothing the curves and plotting the cooling curve, first (dT/dt) and second derivative (d^2T/dt^2) curves for the extraction of thermal information.

The flat tensile test bars were produced out of the solidified rods and prepared according to ASTM E8/E8M-13. Tensile tests were carried out using an Instron universal mechanical testing machine (5982), equipped with a strain gauge extensometer, at a constant crosshead speed of 1.0 mm/min at ambient temperature.

Metallographic specimens were prepared through standard routines and examined using optical and SEM microscopy to observe the features of the Mg_2Si phase and SiC particles in the composites. The microstructure characteristics of the specimens were examined with a scanning electron microscopy (Philips XL40); coupled with energy dispersive spectroscopy (EDS), while the

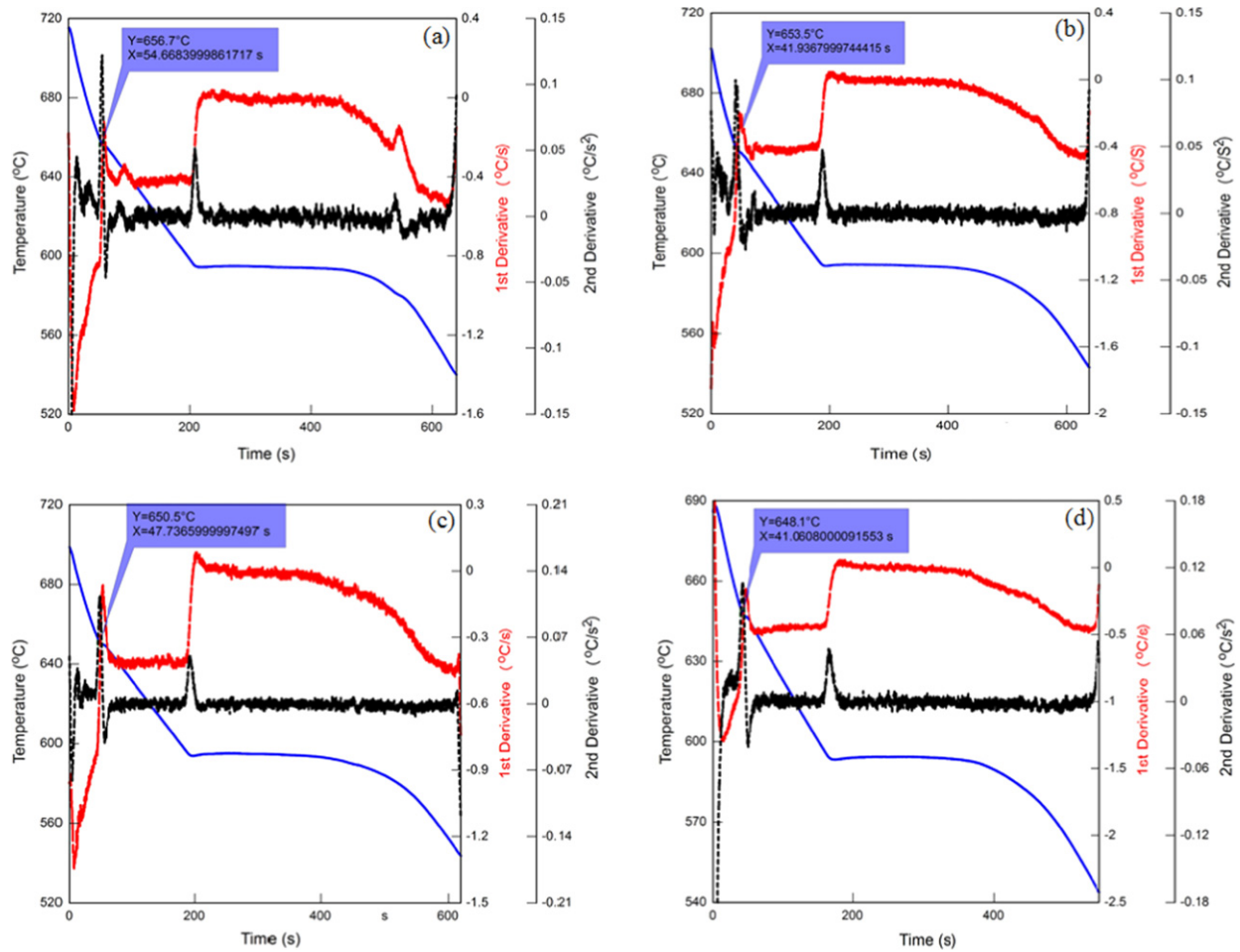


Fig. 2 Cooling curve and corresponding first and second derivative curves of (a) Al-20%Mg₂Si, (b) Al/(Mg₂Si + 5 wt% SiC), (c) Al/(Mg₂Si + 10 wt% SiC) and (d) Al/(Mg₂Si + 15 wt% SiC).

mean size of Mg₂Si particles was analyzed by a quantitative analysis system (i-Solution image analyzer). The phase constituents were analyzed using X-ray diffraction (XRD) (PHILIPS binary diffractometer with Cu- α radiation application).

Results and Discussion

Thermal Analysis

Typical cooling curves and first and second derivative curves of Al-20%Mg₂Si composite without and with different percentages of SiC particles are shown in Fig. 2(a-d). These curves have major importance as they indicate the behavior of the composites during solidification process and the effect of the addition of different concentrations of SiC reinforcement on the nucleation temperature of Mg₂Si phase. When the SiC reinforcement is added to Al-Mg₂Si composite, the nucleation temperature of Mg₂Si decreased especially for high percentages of SiC. As depicted in Fig. 2(a), the nucleation temperature (T_N) of Al-20%Mg₂Si is 656.7°C. With addition of 5, 10 and 15 wt% SiC into Al-20%Mg₂Si the nucleation temperature (T_N) of Mg₂Si decreased to 653.5°C, 650.5°C and 648.1°C as indicated in Fig. 2(b-d) respectively. This may be due to the fact that the addition of reinforcements to the matrix leads to a shift in the phase diagrams. Hence, the changing in the eutectic, eutectoid or peritectic points may occur (Daoud and Abo-Elkhar, 2002).

Microstructure Examination

Fig. 3(a) shows the as-cast microstructure of the Al/(Mg₂Si + 10 wt% SiC) composite. As observed the structure of the composite consists of α -Al as matrix and Mg₂Si and SiCp as the reinforcement particles. Furthermore, the EDS results of Mg₂Si and SiC particles are depicted in Fig. 3(b) as indicative of presence of these compounds in the MMCs.

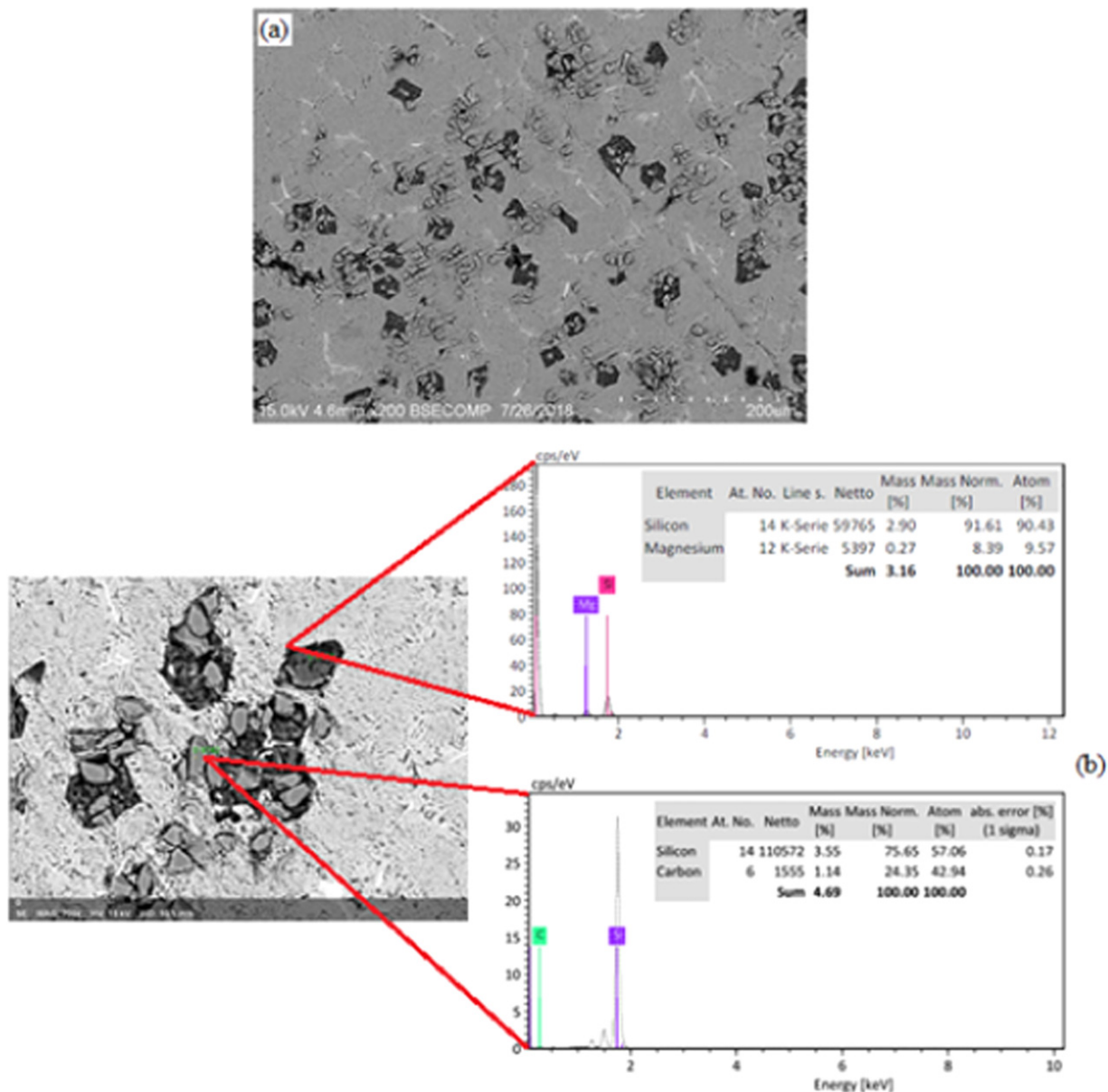


Fig. 3 (a) As-cast microstructure of Al/(Mg₂Si + 10 wt% SiCp), (b) The EDS results of Mg₂Si and SiC reinforcement particles.

Furthermore, Fig. 4 shows the XRD patterns of Al-Mg₂Si and Al/(Mg₂Si + 15 wt% SiCp) hybrid composite. The XRD result in Fig. 4(a) reveals that the constitutions of the Al-Mg₂Si composite consist of Al and Mg₂Si phases. When SiC particles are present in the composites, the constitutions of Al/(Mg₂Si + SiCp) composites contain the aforementioned phases as well as SiC phase (Fig. 4(b)).

Fig. 5 shows the microstructures of Al/(Mg₂Si + SiCp) composites with different SiCp contents. As shown in Fig. 5(a), The Mg₂Si phase is in coarse dendritic shape with an average particle size of 70 μm. From Fig. 5(b) through Fig. 5(d), microstructural changes could be observed. When 5 wt% and 10 wt% SiC particles were added into Al-Mg₂Si composite, the morphologies of Mg₂Si particles in the prepared samples remained polygonal, and the shape was relatively regular and the size decreased to 40 μm and 30 μm, as shown in Fig. 5(b) and Fig. 5(c) respectively. Nevertheless, as shown in Fig. 5(b), the hybrid composite contains 5 wt% SiC contains some porosities in the structure. The existence of porosity is due to entrapment of air during stirring process. With increasing the content of the SiC particles from 10 wt% to 15 wt%, the morphology of Mg₂Si particles was changed to quadrangular with a decrease in size from 30 μm to 20 μm, as shown in Fig. 5(d). It can be concluded that an increase in SiC particle content can lead to grain refinement of Mg₂Si particles. However, as shown in Fig. 5(d) and Fig. 6 although the Mg₂Si particles distributed uniformly in the matrix, with increasing the contents of SiCp to 15 wt%, the agglomeration of SiC particles occurs as shown in Fig. 5(d) (yellow circle) which could decrease the mechanical properties of the composite.

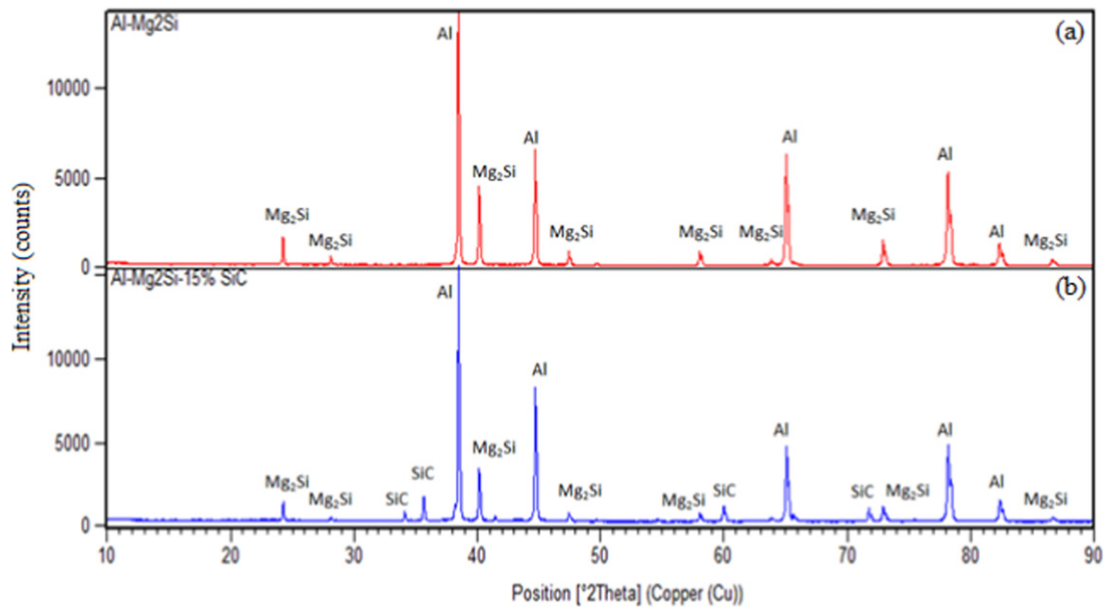


Fig. 4 XRD patterns of Al-20%Mg₂Si composites in (a) base and (b) with 15 wt% SiCp addition.

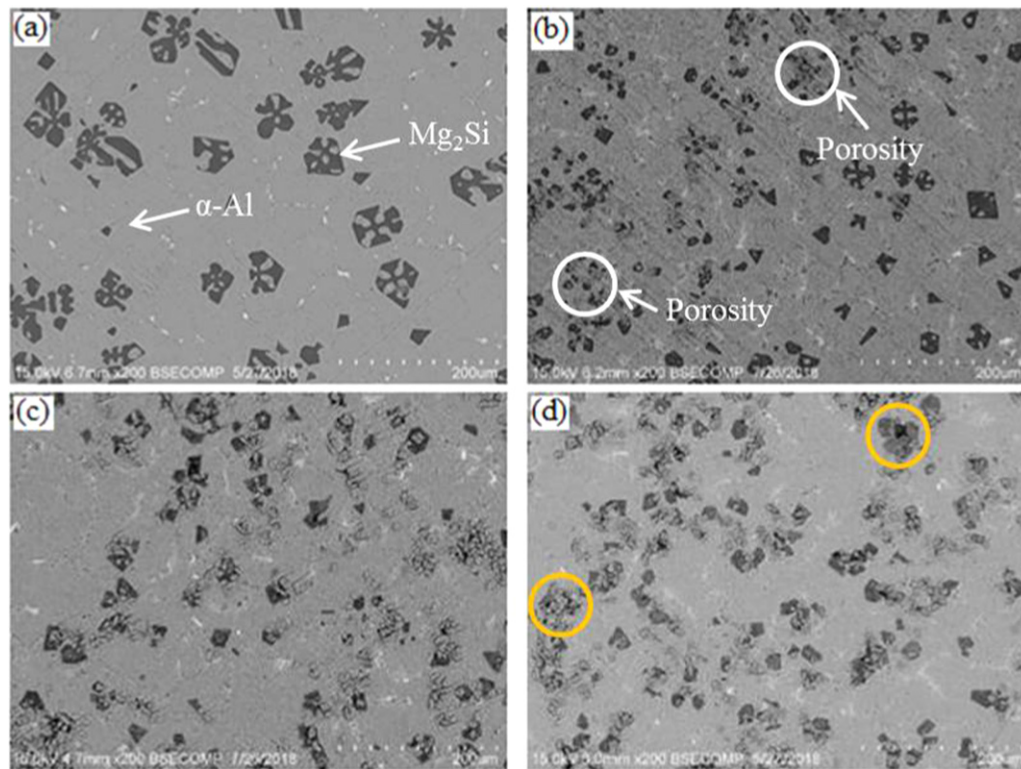


Fig. 5 SEM micrographs of hybrid MMCs with different SiC contents: (a) 0 wt% SiC (b) 5 wt% SiC (c) 10 wt% SiC (d) 15 wt% SiC.

Effect of SiC Particle Addition on Refinement of Mg₂Si Particles

In the Al-Si-Mg melt, the primary Mg₂Si begins to precipitate and grow up with the decreasing of temperature, leading to the gradual decrease of Mg and Si contents. Accordingly, the Al content gradually increases. It is very obvious that the Mg₂Si forms in the melt with a lower content of Mg and Si and a higher content of Al. As a result, there are Al dendrites surrounding the primary Mg₂Si, as shown in Fig. 5(a). When SiC particles were added into the Al-Si-Mg melt, the size and morphology of primary Mg₂Si changed. Guo *et al.* (1997) found that there was enrichment of Mg element at the Al/SiC interface. In the present study, SiC was

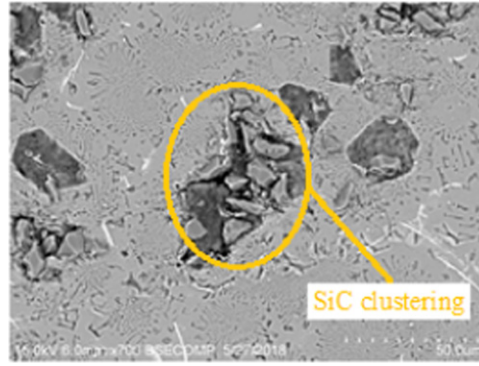


Fig. 6 SEM micrographs of hybrid MMCs with 15 wt% SiCp in higher magnification illustrating the clustering (agglomeration) of SiC particles in the matrix alloy.

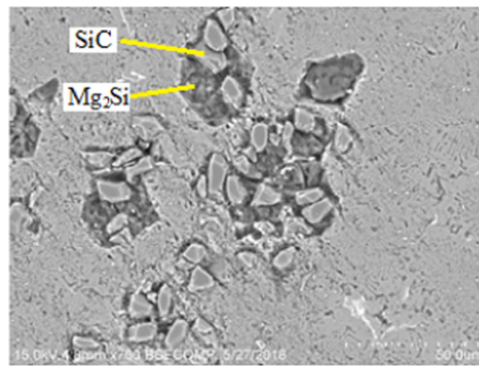


Fig. 7 SEM micrograph of Al/(Mg₂Si + SiC) hybrid composite indicating the heterogeneous nucleation of Mg₂Si on SiC particles.

oxidized in air at 800°C, and the SiC reacted with the oxygen to form a thin layer of SiO₂ on the surface of SiC. Furthermore, the SiO₂ layer reacted with Al and Mg within the matrix alloy, forming MgAl₂O₄ and Si at the expense of the SiO₂ layer, according to the reaction given by Eq. (1) (Lee *et al.*, 2000, 1999).



MgAl₂O₄ crystal formed as a result of this interfacial reaction is face-centered cubic structure with lattice constant of $a = 0.8085 \text{ nm}$ (Chawla and Shen, 2001).

According to the interface lattice mismatch theory, when the atomic arrangement and inter-atomic distance on the surface of solid phase substrate are close to that of newly formed crystal nucleus, the solid-liquid interfacial free energy is very low, and the external solid phase has a very strong capability to serve as site for heterogeneous nucleation Zhang *et al.* (2000) found that the calculation value of planar mismatch δ between [110] MgAl₂O₄ and [010] Mg₂Si is 0.109, namely the interfacial-bonding mode between MgAl₂O₄ and Mg₂Si is semi-coherent, and so MgAl₂O₄ formed at the SiC surface may serve as favorable sites for the heterogeneous nucleation of Mg₂Si phase. As a result, some Mg₂Si particles cling to SiC particles and grow up, and others nucleate independently and grow up in the liquid phase. The morphologies of Mg₂Si and SiC particles in (Mg₂Si + SiCP)/Al composite are shown in Fig. 7. It is obvious that primary Mg₂Si particles cling to SiC particles. Thus, with the increasing of the number of SiC particles, more nucleation sites can be provided for the primary Mg₂Si phase, essentially leading to refinement of grain size. On the other hand, the presence of SiC particles restricts the growth of Mg₂Si due to their mechanical obstruction. In short, it is the factors discussed above that cause refinement of Mg₂Si particles.

Tensile Properties

The ultimate tensile strength and percentage of elongation of the MMCs without and with different percentages of SiC are given in Fig. 8. It is noted that with addition of 5 wt% SiC to Al-20%Mg₂Si, the UTS decreased from 67.61 MPa to 53.58 MPa, similarly, the El (%) decreased from 0.57 to 0.42. Although addition of 5 wt% SiC particles leads to refinement and modification of Mg₂Si particles by decreasing in Mg₂Si size and transformation in the adverse structure of Mg₂Si (dendritic morphology to polygon) (Fig. 5(b)), the presence of porosity in the composites due to gas entrapment during stirring the melt, when compared with the Al-Mg₂Si composite is one of the reasons for lowering the tensile properties of the fabricated hybrid composite. In fact, the increase of pores in the composite would create more sites for crack initiation and hence lowers down the load bearing capacity of the composite. The structures and

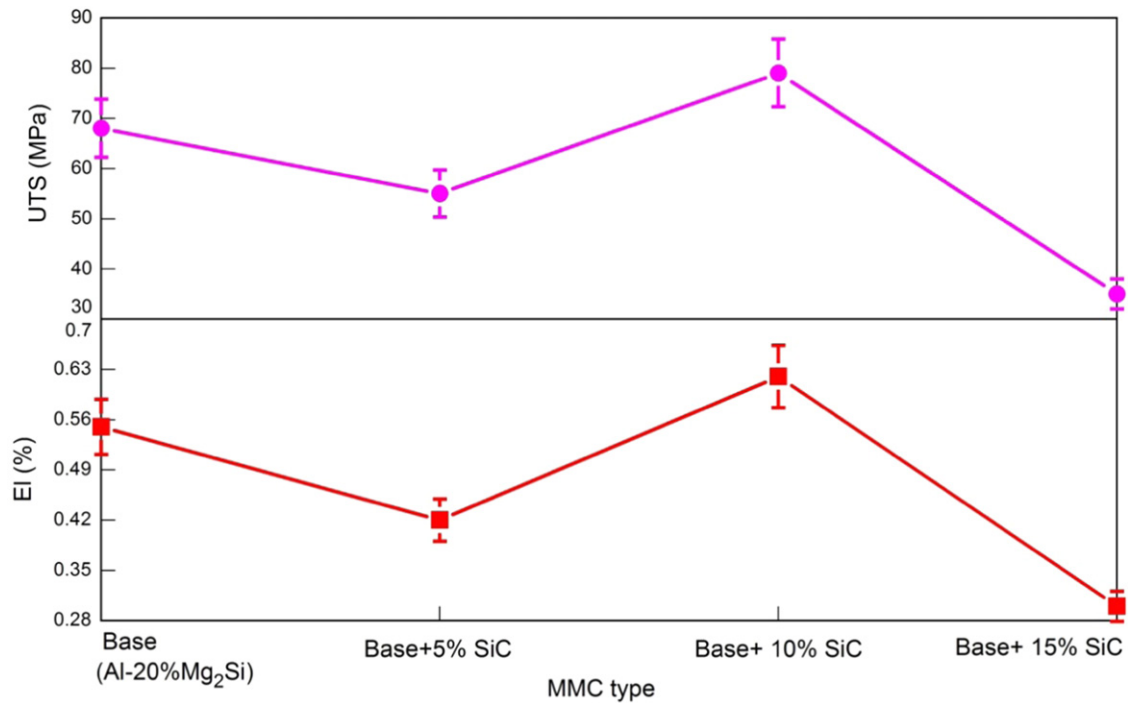


Fig. 8 (a) UTS and (b) El (%) of fabricated MMCs.

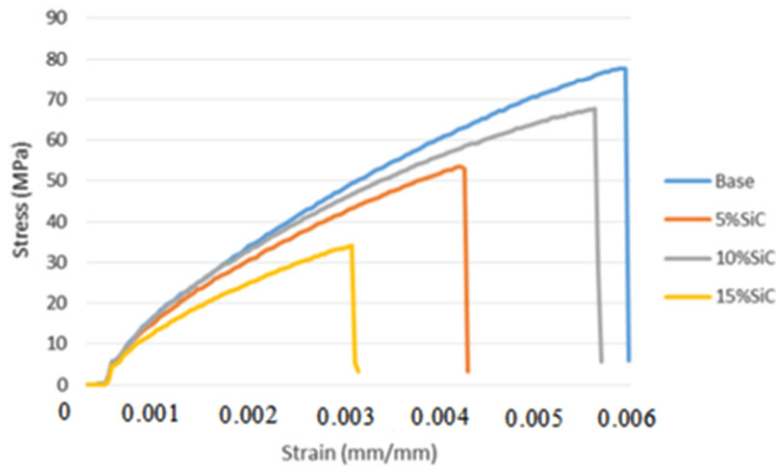


Fig. 9 Engineering stress-strain curve of Al-20%Mg₂Si composite (Base) and hybrid MMCs with different percentages of SiCp.

properties of the interface between the particles and matrix alloys play a significant role in controlling the tensile properties of the composites. However, as observed in Fig. 8, with increasing the SiC content to 10 wt%, the tensile properties increased as the UTS and El (%) of fabricated MMCs increased to 77.45 MPa and 0.6 respectively. The presence of good interfacial bonding and lower content of porosity in the structure of MMC compared to 5 wt% MMC is the reason for improving in the tensile properties of the Al/(Mg₂Si + 10 wt% SiC). In fact, the SiC reinforcements are tend to support the load applied on the matrix through direct strengthening mechanism. The mechanism supports the composite by transferring the applied load from the matrix to the SiC reinforcements through their interface. Hence, good interface between the matrix and the reinforcements is required so that the load can be transferred effectively (Chawla and Shen, 2001). As observed in Fig. 8, the hybrid Al/(Mg₂Si + 15 wt% SiC) with the most refine Mg₂Si particles with quadrangular shape (Fig. 5(d)) compared to other fabricated MMCs shows the lowest tensile properties; the UTS and El (%) of the fabricated composite decreased to 34.11 MPa and 0.3 which can be due to presence of agglomerated SiC in the structure of composite (Figs. 5(d) and 6) which in turn decreased the tensile properties of the MMC.

Fig. 9 shows the stress versus strain curve for the Al-20%Mg₂Si in-situ and hybrid composites with different contents of SiC. The Al-20Mg₂Si in-situ composite (base) exhibits more ductile properties compared to the others. The tensile results demonstrate that

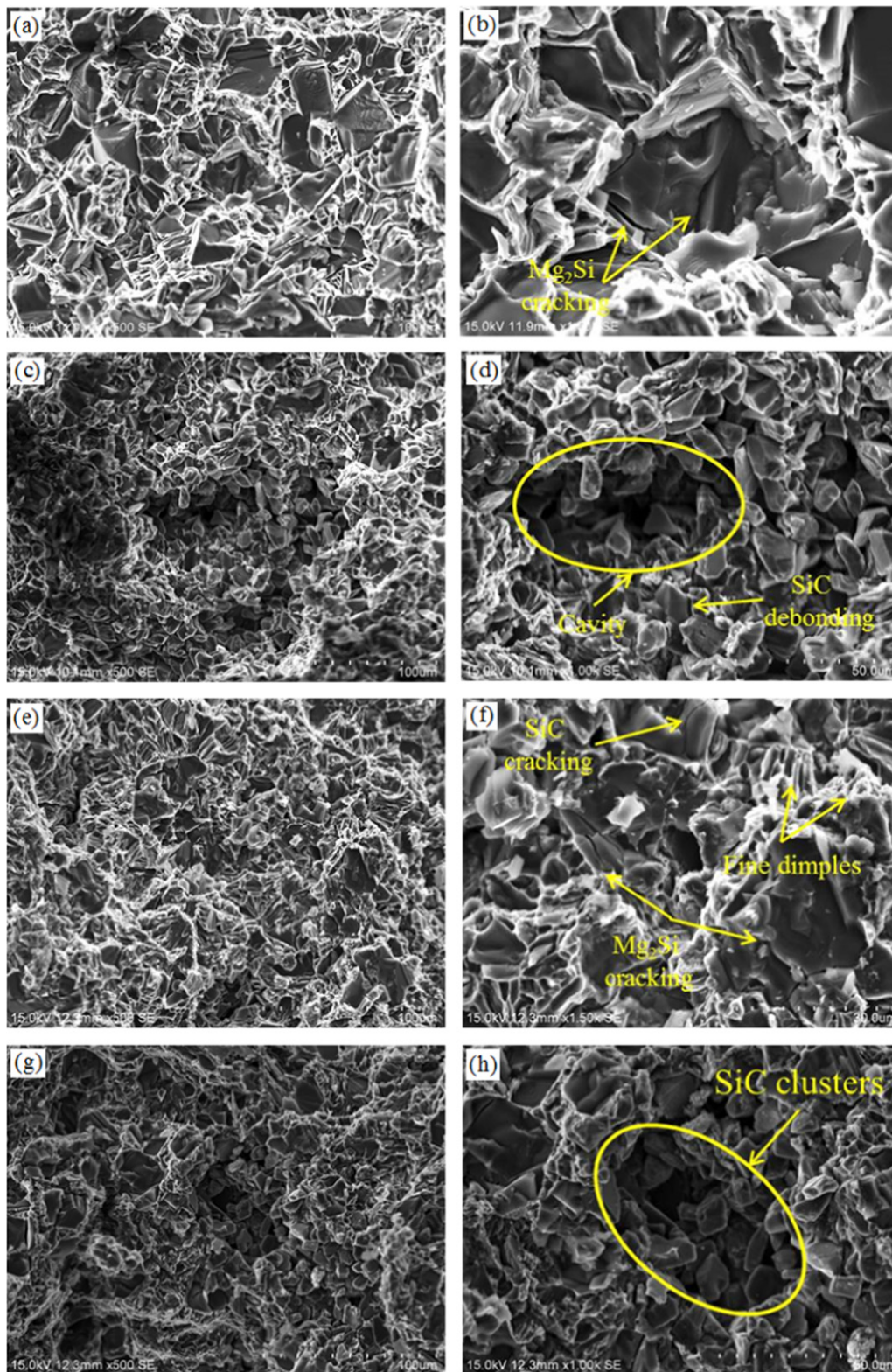


Fig. 10 SEM micrographs of fracture of hybrid MMCs with different SiC contents: (a, b) 0 wt%, (c, d) 5 wt%, (e, f) 10 wt% and (g, h) 15 wt% in low (left) and high (right) magnifications.

the increase in SiC particles transforms the ductile properties to brittle properties. The decreases in the ductility of the hybrid composites may be related to the presence of porosity in the composites, in comparison to that in the Al-Mg₂Si alloy. Porosity can serve as an effective stress concentration site, which promotes crack initiation and results in decreasing the proportion of the composites. In addition, the plastic deformation of the composite may be prevented by the particles and the larger differences in the CTEs between Al alloy and the particles lead to thermal mismatch. The stresses generated due to this thermal mismatch put the particles into compression and the matrix into tension. These residual stresses would probably contribute for the brittle nature of composites (Arsenault, 1984; Taya *et al.*, 1991).

Fractography

Fig. 10(a–h) depicts the SEM fracture surfaces of the MMCs after tensile test with 0, 5, 10 and 15 wt% SiC addition in low (left) and high (right) magnifications. **Fig. 10(a,b)** illustrates a typical surface of the in-situ Al-20Mg₂Si composite with cellular fracture (Lewandowski *et al.*, 1989) as a result of cleavage in fracture planes of coarse Mg₂Si particles. Furthermore, as observed in **Fig. 10(b)**, the fracture occurred in the Mg₂Si particle. It is because in in-situ composite, the stress concentration is easy to localize near the sharp tips of the coarse dendritic Mg₂Si particles; as a result, a sharp crack with a critical length was provided which caused brittle fracture. As shown in **Fig. 10(b)**, these areas are potential sites for nucleation and propagation of micro-cracks through the coarse Mg₂Si directly (due to their intrinsic brittleness) or along the interfaces between matrix and Mg₂Si crystals or eutectic cells which undoubtedly decreased the ductility of the matrix. The fracture surface of Al/(Mg₂Si + 5 wt% SiC) is shown in **Fig. 10(c and d)**. As observed in **Fig. 10(d)**, the particle–matrix interface debonding can be seen in the fracture surfaces of the composite. Cavities formed due to porosity are also observed in the composite fracture surface. It has been reported (Lewandowski *et al.*, 1989) that the fracture of MMCs depends on particle cracking, particle–matrix debonding or grain boundary fracture, which are influenced by the local stress field, the presence of the interface inhomogeneities, structural alterations in the matrix close to the interface or flaws around and inside the particles. Strain localization at the sharp corners of particles may also lead to debonding between the particle and matrix, which is a possible source of the failure of the present composite. The fracture surface of Al/(Mg₂Si + 10 wt% SiC) is depicted in **Fig. 10(e and f)**. Compared to MMC with 5%SiC, this hybrid composite illustrated a better fracture behavior as some dimples are observed on the fracture surface indicating ductile fracture. Furthermore, less voids or porosity are observed on the fractured surface of this MMC due to uniform distribution of the SiC particles in the matrix and good interfacial bonding in the interface of SiC and Al matrix as a result of proper wettability of SiC particle in the matrix alloy. Therefore, the SiC reinforcements can provide better support for the matrix when the stretching load is applied. Particle cracking can be observed in SiC particle in the fracture surface (**Fig. 10(f)**) which indicates good bonding, as the result the highest tensile strength is recorded for this composite (**Fig. 8**). However, the fracture surface of Al/(Mg₂Si + 15 wt% SiC) in **Fig. 10(g, h)** shows clear cleavage on fracture surface of the hybrid composite which is due to improper wettability between SiC and the matrix and hence agglomeration of SiC particles occurred which signifying that particle–matrix interface debonding (**Fig. 10(h)**). Furthermore, the large differences of CTEs between the Al alloy and SiC particles produce large thermal mismatch stresses on cooling from processing temperature to room temperature, which may result in generating microcracks at the interface between the matrix and particles. Consequently, the composite becomes brittle, stress concentration becomes more liable to occur and the ultimate tensile strength and ductility decrease. In summary, it is thought that cracks mainly initiate at particle–matrix interface, propagate through the matrix and link up with other cracks leading to failure of the composites.

Conclusion

By adding SiC particles into Al-Si-Mg melt, Mg₂Si and SiC particles hybrid reinforced Al matrix composites with relatively homogeneous distribution of the reinforcement Mg₂Si and SiC particles can be obtained through Mg₂Si in-situ synthesis in melt combined with SiC ex-situ stir casting. With increasing the content of the SiC particles from 5 wt% to 10 wt%, the morphologies of the primary Mg₂Si particulates in the prepared samples remain polygonal, but the size of the primary phase decreases slightly. However, the morphologies of the primary Mg₂Si particulates change to quadrangular with a decrease in size from 30 µm to 20 µm when the SiC particle addition reaches 15 wt%. In comparison to those of Al-Mg₂Si composite, the Al/(Mg₂Si + 10 wt% SiC) showed the highest tensile properties in term of UTS and El (%), however, Al/(Mg₂Si + 5 wt% SiC) and Al/(Mg₂Si + 15 wt% SiC) depicted low tensile properties due to existence of porosity and agglomeration of SiC particles in the fabricated composites. In Al/(Mg₂Si + 5 wt% SiC) and Al/(Mg₂Si + 15 wt% SiC) produced composites, cracks may initiate at particle–matrix interface and SiC clusters respectively, propagate through the matrix and link up with other cracks, leading to failure of the composites. However, in Al/(Mg₂Si + 10 wt% SiC) fine dimples and particle cracking was observed on the fracture surface indicating suitable interfacial bonding between SiC and matrix.

Acknowledgments

The authors gratefully acknowledge this research project under the Fundamental Research Grant Scheme (FRGS) from the Ministry of Higher Education, vote number 4F945.

See also: Experimental Investigations for Development of Aluminum MMC With Hybrid Reinforcement and Vacuum Moulding. Investigations for Metal Matrix Composites Prepared by Using Waste Polymer-Based Sacrificial Rapid Pattern in Investment Casting. Natural Fiber Composites: Review of Recent Automotive Trends. Recycling and Downstream Processing of Aluminium Alloys for Automotive Applications. Recycling of Flax Fiber Towards Developing Biocomposites for Automotive Application From a Life Cycle Assessment Perspective. Renewable and Sustainable Materials in Automotive Industry. Renewable Metal Working Fluids for Aluminum and Heavy Duty Machining.

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Ensuring Security With Evolutionary Green Computing Solutions for Sustainability of Mission Critical Cyber-Physical Systems

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Introduction

Green computing refers to the efficient use of computers and their resources during their lifetime and in conjunction with minimizing environmental impact (e.g., the reuse of resources to prevent air pollution, water pollution and to reduce electricity consumption, etc.) to maximize economic efficiency and viability. The recent development of green computing offers significant advantages for organizations to outsource their Information and Communication Technology (ICT) infrastructures, including telecommunications.

At the same time, the widespread use of datacenters used to establish green computing environments creates an ever-increasing carbon footprint and draws additional energy consumption thereby raising environmental concerns. Researchers have focused on developing energy management proposals to reduce massive energy consumption from telecommunication networks. One of the growing concerns of green computing is the lack of data security when green vendors store data. To protect data and information, vendors need to deploy additional hardware/software systems to provide sufficient security measures, which increases the demand of energy consumption.

The research and industry focus is on the development of energy-efficient computers and telecommunication infrastructures. In addition, how these developments may vary at a low hardware level to a high software level is of concern. The majority of the research proposals aim at energy efficiency for Cyber-Physical Systems (CPSs). The research suggests there is an unresolved gap in the security aspect of these systems. This article focuses on the development of green computing solutions to enhance security in Mission Critical Cyber-Physical Systems (MC-CPSs), and introduces Seddulbahir as an evolutionary green computing security solution.

The organization of the rest of the article follows: Section “Mission Critical Cyber-Physical Systems (MC-CPSs)” provides an overview on mission critical Cyber Physical Systems and elaborates on the details and main characteristics of these systems. Section “Renewability, Sustainability and Recycling Issues of Green Computing” expands upon green computing solutions for Mission Critical Cyber-Physical Systems. Section “Seddulbahir” introduces the Seddulbahir Firewall-as-a-Service model to enhance a green computing environment. This section also compares the design of this development with the existing systems based on a performance matrix. Section “Conclusion” concludes the study with future recommendations on the usage of outsourced communication security infrastructures.

Mission Critical Cyber-Physical Systems (MC-CPSs)

In recent years, Cyber Physical Systems (CPSs) have become an emerging paradigm for monitoring, controlling, coordinating and managing physical and engineered systems. Examples include an ever-growing number of cyber-connected devices, automated health care systems, smart electricity grids, energy efficient green-clouds and the surveillance of unmanned aerial vehicles (UAVs). CPSs are intelligent systems that are co-engineered to have the ability to interact with a variety of physical components through communication networks (Banerjee *et al.*, 2012). Due to expanding usage and service availability measures, the assemblage of most infrastructures include modern CPS components since cyber-based services have become an inevitable component used in mission critical applications. The typical infrastructure characteristics are fault-tolerant, reliable, safe, and include accessing data in real-time. In addition, their designs survive over time and provide more efficiency, autonomy and reliability compared to manually controlled and loosely coupled systems.

The development of smart and mission critical systems are widespread, and they transfer into our everyday lives. In the health sector, the development of physiological sensors used on humans allows for fast detection of injuries during medical emergencies. In addition, the deployment of such sensors in energy-efficient smart buildings detects the absence of occupants in an area and shuts-down the cooling/heating unit for energy efficiency. The previous are examples of the interaction between our physical environments with embedded systems. A final example of a CPS are UAVs that track, monitor and/or capture an image of a geographic terrain to perform surveillance.

Mission Critical Cyber-Physical Systems (MC-CPSs) are complex integrated systems that entail a group of “systems within systems” (Moholkar, 2014). Such complexity and integration of CPSs may result in different vulnerabilities in terms of safety, security and sustainability. The combination of cyber systems with physical systems within an MC-CPS infrastructure exposes significant inherent vulnerabilities and threats that may raise specific needs and require designers to take certain precautions. A failure of any one system may result in a catastrophic failure of a mission critical infrastructure and service.

For example, a cyber-attack generated against MC-CPSs at a hospital might lead to the untimely delivery of medication to a patient. CPSs that control UAVs or drones have similar vulnerabilities that might lead to the malfunction of UAV control systems/ algorithms and cause UAVs or drones to crash into geographical regions causing a potential loss of civilian lives (Moholkar, 2014).

Maintaining maintenance measures is an important aspect of MC-CPSs since they provide services for extended periods. In addition, resource utilization is another component in maintaining a long operational life. Green energy supported CPSs are more powerful since their lower usage of energy draws from battery or other power sources. The previous advancements result in the increase of a computer/system's life and reduces the cost of operation of a MC-CPS. Furthermore, infrastructure architects carefully address the functionality of MC-CPSs to ensure safety, security and sustainability. Meeting the satisfaction of the previous metrics also depends upon the types of information extracted from the computing unit. Therefore, the design of a secure, safe and sustainable MC-CPS also requires an investigation of the behavioral characterization of the physical environment, which affects the metrics directly.

The violation of security access rules of MC-CPSs and unauthorized access to restricted systems in CPSs of health systems, transportation (air, land, sea, space) infrastructures, water infrastructure systems, gas and smart electricity-grid infrastructures can lead to a loss of CPS security. As a result, there may be significant negative and hazardous impacts in a society, including the loss of privacy, potential physical harm and personal discrimination and/or abuse.

The next section "Renewability, Sustainability and Recycling Issues of Green Computing" elaborates on the renewability, sustainability and recycling issues of green computing. Section "Green Computing Solutions for Mission Critical Cyber-Physical Systems" elaborates on existing solutions and proposals for energy consumption and workload issues and provides insight about existing energy efficient green computing solutions for MC-CPSs. Next, the introduction of Seddulbahir's design by using Artificial Intelligence (AI) also addresses green computing. The section also covers Seddulbahir's performance metrics such as security, safety and sustainability to ensure security of CPSs to prevent cyber-attacks.

Renewability, Sustainability and Recycling Issues of Green Computing

Green computing can lead to a reduction in energy costs for servers, cooling and lighting. Due to advancements in green computing, the IT industry has especially focused on the improvement of power and cooling issues through the development and processing of new electronic equipment. Worldwide organizations spend a considerable amount of effort to achieve major green computing goals for energy-hungry centers.

Addressing the human factor is one of the greatest challenges of green computing goals in IT. The greatest challenge for a society is to understand the goals and objectives of green computing and only then, can the environment be renewed and sustained. To reduce negative environmental issues organizations propose standards to regulate the environmental effects caused by the IT industry. The Organization for Economic Co-operation and Development (OECD) has published a survey of several countries and industry initiatives on green ICT to avoid environmental changes. In Table 1 below is a list of country agencies and organizations that support green computing and adhere to proposed standardizations and compliances (Raza *et al.*, 2012).

Some of the good practices conducted in the international arena are through international standards such as ISO-14000 and the Occupational Safety Standard (OHSAS-18001) on environmental management. The proposed standards focus on risk, the nature of that risk and the required control of measures for protecting an environment. In the area of equipment disposal, there is no control due to a lack of standard policies on the degradation and reuse the technological scrap. In order to maintain the green revolution, government agencies must focus on the implementation of strong guidelines for scavengers and propose practical "disposal training" as a requirement.

Countries and organizations telecommunication infrastructures rely on complex networks. However, proposed green computing solutions should be universal and simple to apply. Therefore, the proposal of policies and regulatory obedience should be compulsory items for the sustainability of green computing. In addition to this, the proposed green computing technologies must address end-user satisfaction, management re-information and the virtualization of server resources. In the recycling context of the

Table 1 Green Regulations Proposed by organizations and countries

<i>Organization/regulation/program</i>	<i>Country</i>
VIA Technologies Regulations	—
Energy Star	United States
Restriction of Hazardous Substances Directive (RoHS) Computing	—
China Energy Conservation Program	China
Energy Conservation Center	Japan
Electronic Product Environmental Assessment Tool (EPEAT)	—
The Confederation of Professional Employees, Tjänstemannens Central-Organization (TCO)	Sweden
ISO Standardizations (14001/14065/14066)	—
Blue Angel	Germany
Manufacturing Resource Planning (MRP II)	Sweden
Climate Savers Computing Initiative	United States

proposed green computing technologies, the proper disposal of electronic scrap and waste, efficient energy usage, thin client solutions and return on investment (ROI) must be targeted (Harmon *et al.*, 2010).

As a result, the most important factor is to increase public awareness of the governmental initiatives through 'awareness campaigns' on extending sustainability, renewability, recycling and the green computing concept.

Green Computing Solutions for Mission Critical Cyber-physical Systems

Researchers have focused on the development of green computing solutions that satisfy some of the expected properties of Mission Critical Cyber-Physical Systems (MC-CPSs). As mentioned earlier, conventional security precautions are not sufficient to protect the vulnerability of MC-CPSs from attackers (Estevez and Wu, 2016). Through access to sensors, an attacker could potentially tamper with a smart data center resulting in an air conditioner overload. One of the solutions proposed by researchers is to model an energy management strategy for MC-CPSs. The main aim is to create a balance between the produced-available power and the power demand of a workload (Ge *et al.*, 2014). A proposed solution named Dynamic Power Balance Strategy (DPBS) coordinates both the workload and the battery usage to ensure the sustainability of energy computing in an energy management system for a specific device.

Researchers have proposed the cooperative differential game model in order to elaborate on the trade-off problem between bandwidth and energy (Fuhong *et al.*, 2014). Earlier, Miao *et al.* (2012) proposed a model based on bandwidth and energy. The research model proposed by Pan *et al.* (2015) aimed to control energy modes of various appliances in order to put them into energy-saving mode in case of an idle state of any device.

Since there are a significant number of equipment used and deployed in a telecommunication operator infrastructure, additional effort addresses the telecommunication sector and the development of energy efficient communication infrastructures and MC-CPSs. The model developed by Lin *et al.* (2011) focused on real-time monitoring for energy consumption and real-time controlling of the energy state at base stations for telecommunication operators to make intelligent decisions based on the environment's current state. A linkage created between the monitoring devices of MC-CPSs and power management systems solved the problem.

Some research exposes the need for energy efficiency of IoT networks and claims that the raise in energy consumption is due to the communication between massive counts of sensors used in IoT networks. In order to achieve energy efficiency for an IoT, Sundar Prasad and Kumar (2012) proposed scheduling an algorithm for the participating IoT nodes to have the ability to decide to be active or not based on the information gathered from its neighbors. Deployment of such algorithms may increase the performance of the nodes, but not the security. Chao *et al.* (2011) have discussed the same matter since security is a concern for the IoT. Later, Chao and Wu (2015) succeeded in the deployment of an algorithm with specific architecture and force for IoT nodes to consume energy only when necessary.

Zhou *et al.* (2016) proposed the deployment of an optimized energy efficient protocol called Enhanced Channel-aware Routing Protocol (ECARP) for underwater operations. The new improvements and optimization of a protocol focused on improved data transmission and improved routing that is targets and explores vast ocean space.

As mentioned above, the proposed green solutions for MC-CPSs by the researchers focuses on specific architectures and/or requires deployment of many nodes to work efficiently in a complex environment. The majority of models predominately focus on energy consumption and energy efficiency, and a lack of security remains as a gap in the field. In order to close this gap, the next section details a green computing solution model for Seddulbahir.

Seddulbahir

Firewall as a Service (FaaS) technologies provide security at a lower cost and with lower maintenance, lower complexity and higher efficiency, which attracts organizations and has become their first choice as a solution. Apart from this, virtualization becomes another opportunity to decrease the cost of hardware and software deployed for an organization's communication infrastructure. However, the research shows that in practice, there is a difficulty in managing and establishing security in a virtualized environment so there is a need for advancements in security tools to monitor, debug and control malicious network traffic was inevitable.

Seddulbahir is a Firewall as a Service security system developed by researchers in Turkey to provide analysis of incoming/outgoing flow of network traffic within the country's MC-CPSs for security measures (Sari, 2018). It was developed and simulated to control a variety of different communication infrastructures in sectors ranging from hospitals to universities. The initial architecture of Seddulbahir, deployed in a Wide Area Network (WAN), monitored, debugged, interfered and controlled malicious network traffic, as illustrated in Fig. 1 below.

Upon further development, the deployment of Seddulbahir in a Virtual Machine (VM) environment in organizations provides integrated enhanced security and energy-efficiency. Companies using a VM environment and wishing to avoid purchasing additional security hardware and software has lowered their deployment and maintenance costs for the entire system security.

As illustrated in Fig. 1 above, the performance metrics of the Seddulbahir system in a WAN indicated success above the expected level (Sari, 2018, 2019). In order to provide services for lower level network architectures, further development and

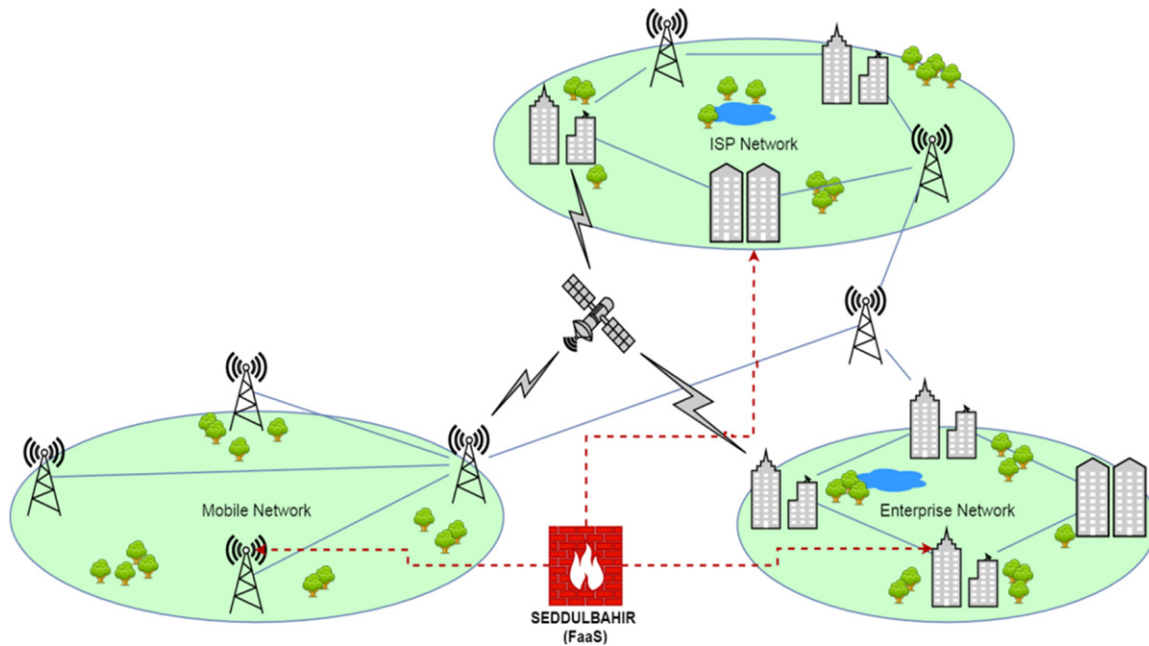


Fig. 1 WAN deployment model of Seddulbahir.

deployment in a bare-metal server that hosts VMware ESXi (formerly ESX) operating systems can provide a stable virtualization environment.

Even though vast amounts of research exists on achieving energy efficiency, there remains a serious gap in the security of MC-CPSs. The widespread deployment of Seddulbahir provides a variety of advantages in terms of energy efficiency, performance, reliability, maintainability, monitoring, control and security.

The deployment of the Seddulbahir firewall system in a network environment can communicate with virtual machines, proxy servers, Windows/Linux Servers (Ubuntu 18.06) and vSphere Server. The ESXi 6.0 operating system is used to provide virtualization services on the bare-metal server. The bare metal server best selected is the IBM x3500 M4 with a configuration of Intel Xeon E5 2620 V2 CPU, 96 GB ECC RAM, 2 TB SSD. The deployment of Seddulbahir requires very basic resources in VM environment. The deployment also requires an Ubuntu 18.06 OS with only 8 GB ECC RAM and with a single core virtualized CPU and 20 GB of storage. The deployment infrastructure model of Seddulbahir on a VM environment is illustrated in [Fig. 2](#) below.

As shown in [Fig. 2](#) above, the VMware systems are installed on a bare-metal IBM X3500 M4 server, which is illustrated as “Source ESX host” in the [Fig. 2](#). In this scenario, the ESXi host provides virtualization on the bare-metal server for 4 interconnected networks, which are VM Campus wing A, B, C and D.

All of the virtual machines hosted in these networks are connected to each other through virtual switches. Each network contains virtual machines, proxy servers, Windows/Linux servers and a Seddulbahir node. The Seddulbahir node acts as an intermediary between the internal and external network flow to monitor the network traffic.

The incoming and outgoing traffic flow is inspected based on the “Rule Engine” of Seddulbahir, which is developed based on the Radial Basis Function (RBF). The rule engine contains set of rules to differentiate malicious/benign traffic and blocks the corresponding flow based on specific features of the incoming package such as flags, ip src, src port, dst port, seq, checksum, ip dst, ttl, ackseq and data. There is the possibility to inspect and differentiate between binary based (e.g., dns) protocols, text-based protocols (e.g., http), packet-based protocols (e.g., ip) and stream-based protocols (e.g.) in the network flow. All of these features eliminate the necessity of different hardware and software deployments. The entire network can be controlled with a deployment of a single appliance of Seddulbahir on the IP address assigned as 172.52.9.56.

The Local Area Networks (LAN) with an IP address that blocks assigned protocols of 10.56.5.1, 10.56.6.1, 10.56.7.1 and 10.56.8.1 are controlled with separate instances of Seddulbahir, and these appliances are dedicated to their networks, which has no interaction with other Seddulbahir appliances.

Since the entire security system is integrated with many modules, the tshark tool is used as a packet capture module. There are a variety of other details related with Seddulbahir and provided by researchers ([Sari, 2018, 2019](#)). The system has a remote connection and access features to provide remote management possibilities. Therefore, the system administrator can access a firewall interface through the web and manage the entire network in a VM environment. The Seddulbahir deployed on the Ubuntu 18.06 server appliance with a dedicated dashboard developed to measure a variety of performance metrics is illustrated in [Fig. 3](#) below.

This dashboard contains different features, menus and sub-menus to provide accessibility monitor and control the entire system security and performance. The developed dashboards illustrate the system performance and the overall power

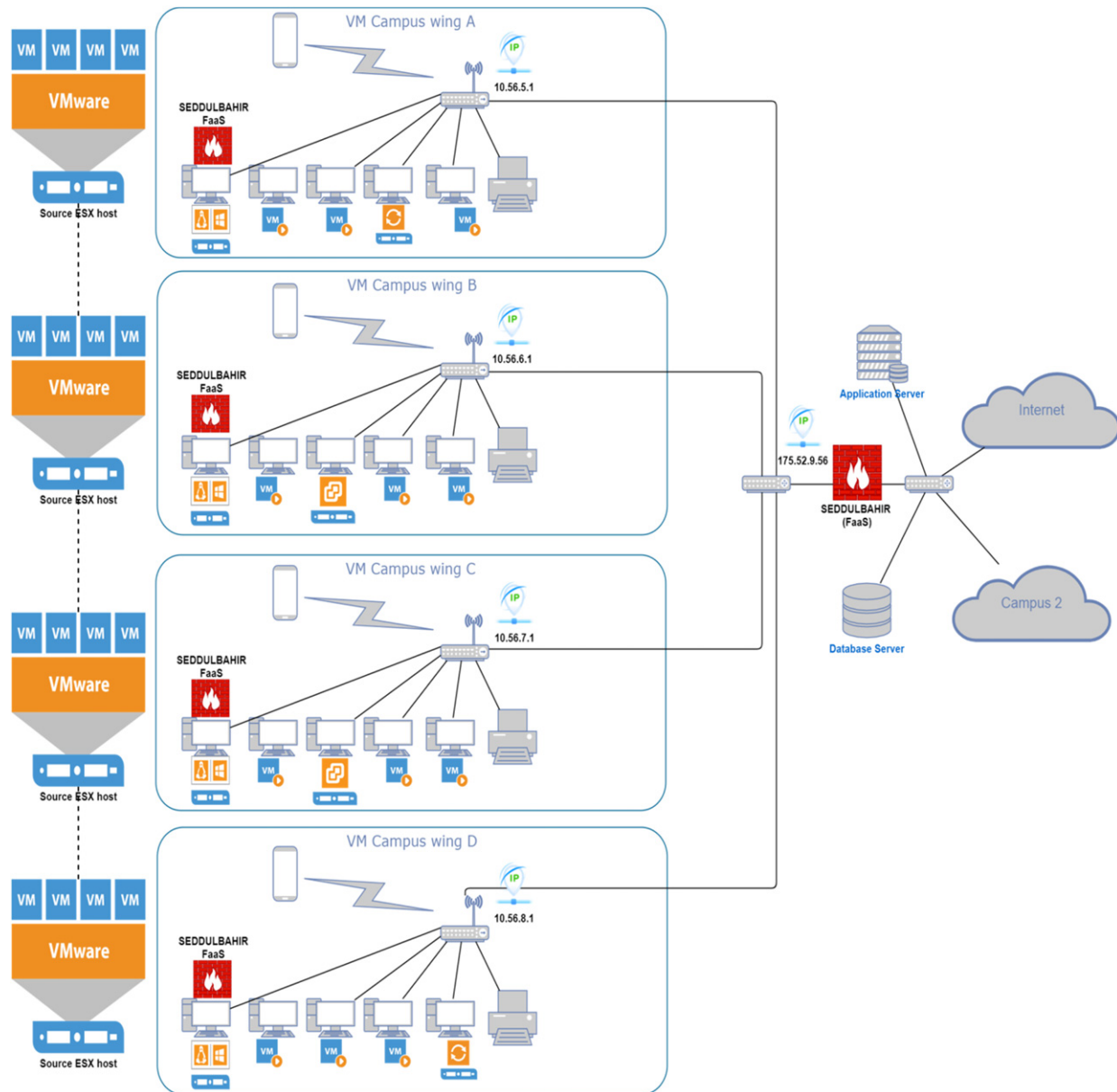


Fig. 2 VM deployment infrastructure of Seddulbahir.

consumption. The load and performance of each system component can be monitored without the need of any additional hardware installations.

- The Dashboard Menu contains: Overview, Traffic Summary, Network Snapshot and System Performance,
- Inventory Elements Menu contains: Devices, Interfaces, IP Groups, Interface Groups,
- Alarms Menu contains: Active Alarms, All Alarms, Events, Create Alert Profile,
- Maps Menu contains: Attack Maps, Google Maps, Zoho Maps,
- Reports Menu contains: Forensics, Protocol Distribution, Attack Report, Consolidated Report,
- Attacks Menu contains: General Attacks, Attacker Profiles, DPI (Deep Packet Inspection),
- Rules Menu contains: Rule Engine, Firewall Rules, Add New Rules,
- Settings Menu contains: System Settings, Basic Settings.

At this point, there are no further details on the system due to limitations and scope of the book. However, there will be further research efforts discussed that will expose the performance results of existing developments in different environments and different layers of networks.

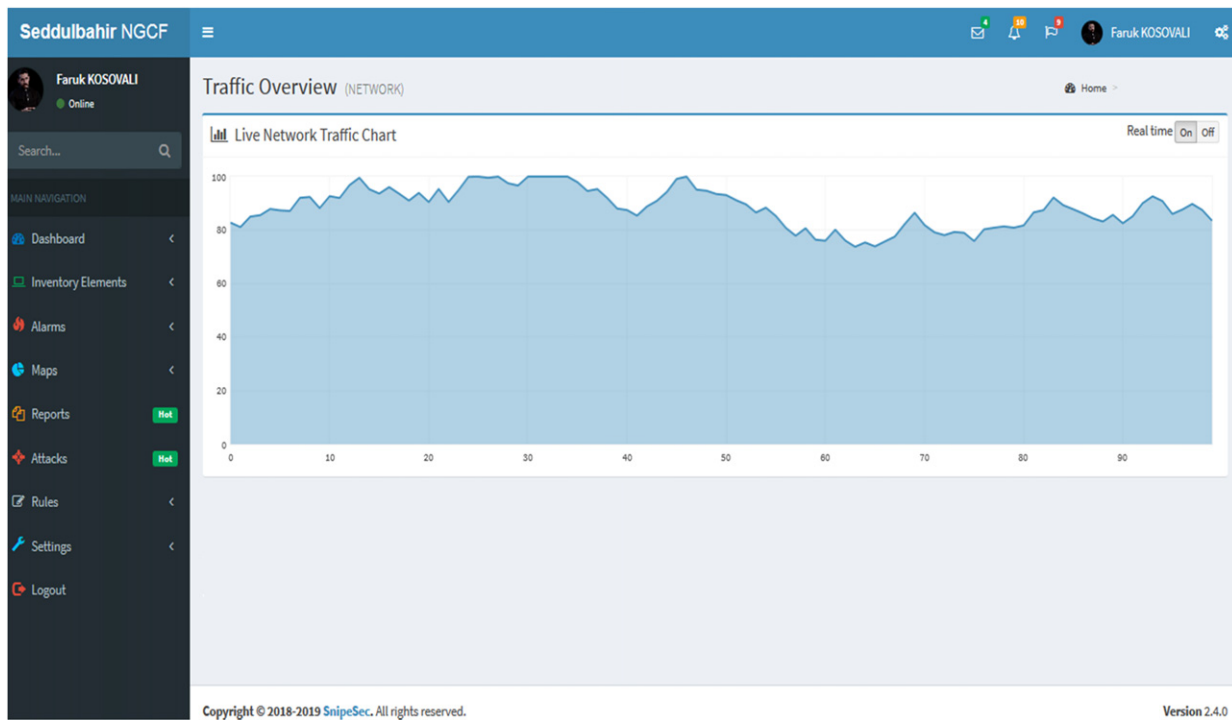


Fig. 3 Dashboard of Seddulbahir.

Conclusion

The rapid growth in the demand of network traffic requires intensive deployment of new hardware/software infrastructures that also address today's global environmental state. Conventional hardware/software infrastructures and bare-metal systems are approaching their capacity and performance limits. Development of security systems must smartly integrate computing, controls, sensing, and networking to transform the joint behavior of elements in an environment-friendly manner while also focusing on sustainability and providing security.

The design of environment-friendly security systems used to enhance green computing and support security, faces many challenges. The design and the development of systems can follow design principles at the deployment level, the traffic routing level, the traffic demand level and the transmission level. To eliminate many challenges, the classification of Seddulbahir as a Next Generation Cyber Firewall (NGCF) can provide lightweight deployment with integrated enhanced security measures that meet at different levels of a communication network.

Deployment of Seddulbahir as a green-security solution or FaaS solution reveals significant advantages. It lowers the amount of workload needed to maintain an infrastructure by lowering the number of IT staff needed to administer/maintain a system, which in turn will increase the efficiency and effectiveness of the business. Additional benefits include an increase in the diversification of job positions by raising the need for data analyst specialists, firewall developers, SOC specialists, and data miners. Finally, there would be a decrease in the cost of energy spent on a system's infrastructure (hardware-software).

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Experimental Investigations for Joining of 3D Printed PEEK Substrates for Biomedical Applications

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Introduction

PEEK has got significant attraction of today's researcher due to its properties like: hot strength, temperature resistivity and good performance in mechanical parameters (Yang *et al.*, 2017; Jin *et al.*, 2017). Virgin PEEK has poor wear resistance but by adding carbon fiber in PEEK these properties can be enhanced. Temperature is also observed as a considerable parameter that can change the wear behavior of PEEK (Lind *et al.*, 2015). Machinability of virgin PEEK is higher as compared to its composite with carbon fiber and glass fiber (GF). The difference of 100 N is observed in cutting of virgin PEEK and PEEK-GF reinforced samples at cutting speed of 50 m/min at feed rate of 0.05 mm/rev (Davim *et al.*, 2010). PEEK polymer shows good fracture resistance as compared to other polymers (Lesiuk *et al.*, 2017). Due to the high strength to weight ratio, PEEK composite is used in clinical dentistry and orthopedic scaffolds. It has been reported that due to lower surface energy and chemical inertness the bonding energy of PEEK composite is low (Tsuka *et al.*, 2017). In case of dynamic loading, coefficient of dynamic friction is found to be directly proportional with load. In case of harsh ambient conditions like high temperature and chemical toxic atmosphere PEEK composite can be used (Zsidai and Kátai, 2016). For the ultrasonic fabrication of PEEK the frequency of 5 MHz is more sensitive for the span of 0.5–10 MHz (Du *et al.*, 2014). The wear rate of PEEK composite is small as well as coefficient of friction in comparison with virgin PEEK (Du *et al.*, 2014). The impact durability of porous PEEK is more as compared to titanium coated PEEK. The surface erosion of porous PEEK is less and no significant change in porosity is observed (Torstrick *et al.*, 2018). The thermal expansion of the PEEK polymer at high temperature create a hindrance in observing wear rate. It was observed during wear test that at starting

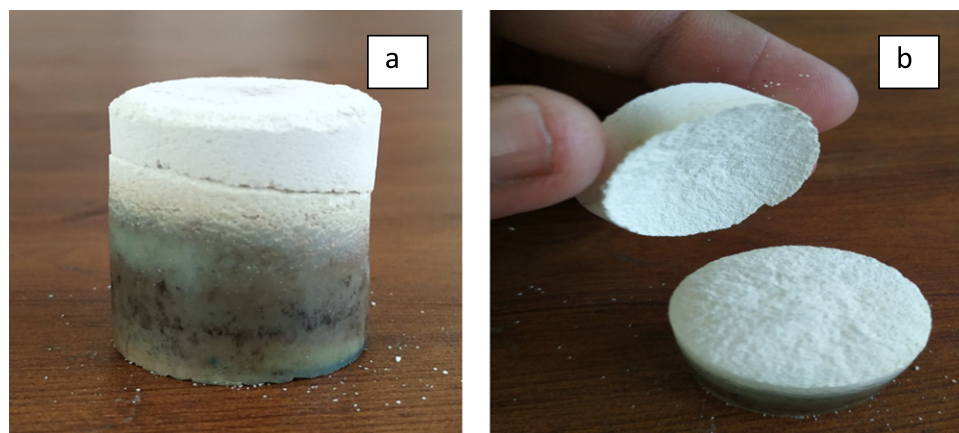


Fig. 1 (a) PEEK sample prepared by hot mounting compression molding machine. (b) Un-bound PEEK powder.



Fig. 2 3D printed PEEK substrates.

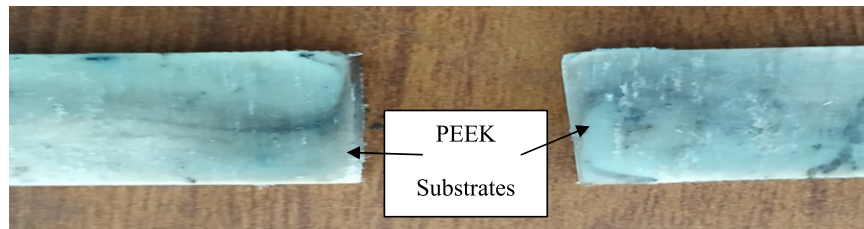


Fig. 3 FDM printed PEEK samples for joining.

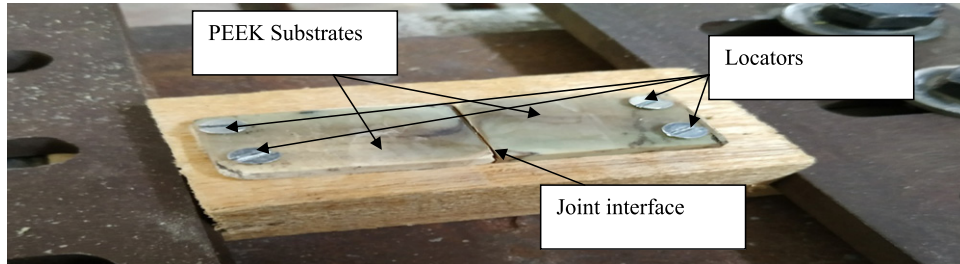


Fig. 4 Friction stir welding fixture.

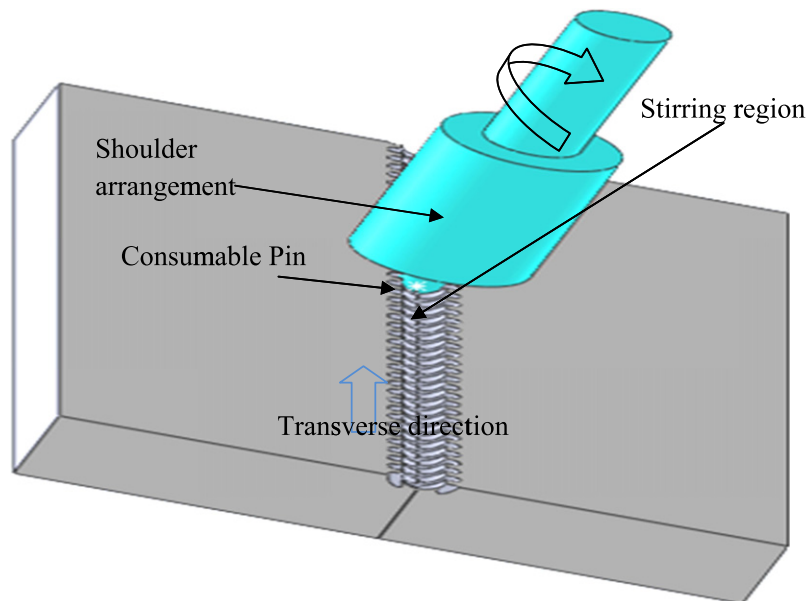


Fig. 5 FSW process for dissimilar thermoplastic joining.

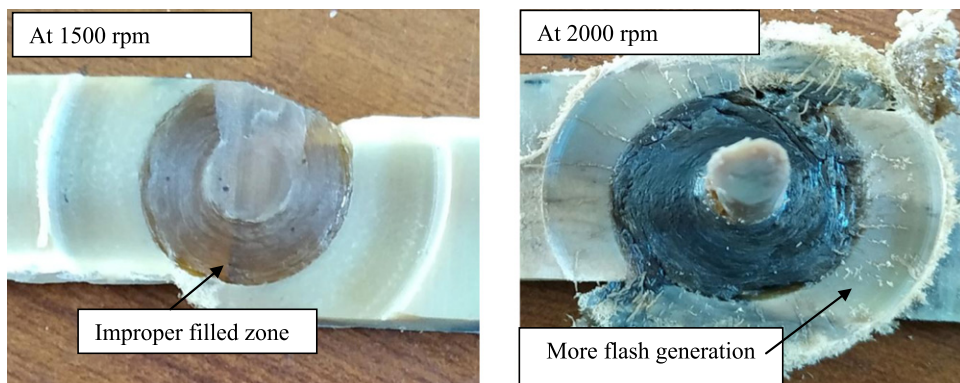


Fig. 6 Friction stir welded PEEK specimens.



Fig. 7 Tensile testing of PEEK joint.

Table 1 Observations for mechanical properties

Sl. No.	Rotational speed	Strength at peak (MPa)	Strength at break (MPa)	% Elongation at peak
1.	2000 rpm	12.9	11.61	10
2.	1500 rpm	11.38	10.24	10

Note: Peak strength of 3D printed PEEK specimen was 50 MPa.

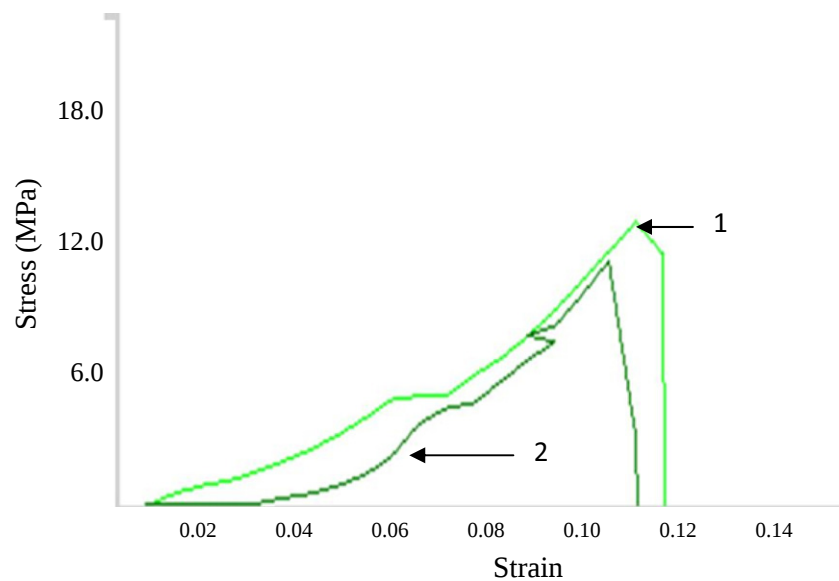


Fig. 8 Stress-strain curve for PEEK joint.

time span the wear increase but after some time it remain constant (Kónya *et al.*, 2005). During solidification of PEEK with carbon fiber reinforcement the fiber acts as a nucleation site. The melting and transition temperature of PEKK is found to be 145°C and 337°C respectively by means of differential scanning calorimetry (DSC) testing (Nguyen and Ishida, 1986). Although today mostly body implants use metals like titanium but its long run embedment can create allergic tissue at the emend portion of body. By the replacement of titanium with PEEK this problem can be solved to the great extent (Ma and Tang, 2014). With the reinforcement of

Table 2 Observed porosity based upon photomicrographs at 100X

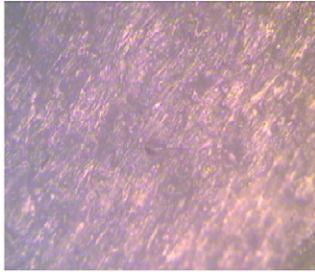
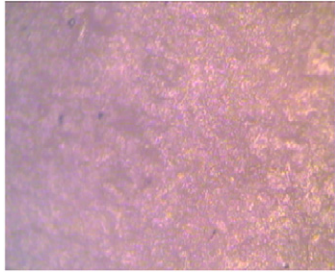
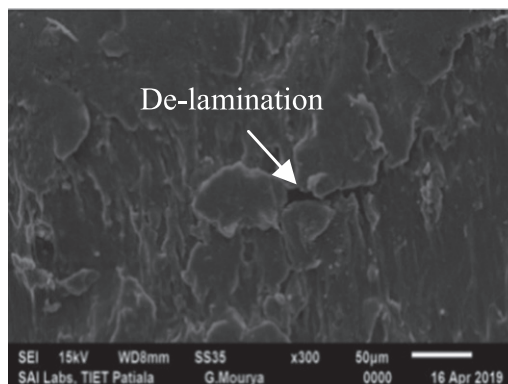
Sample rpm	2000	1500
Porosity level	12.64%	23.61%
Photomicrograph		

Table 3 Observations for Shore D hardness at the joint

Sl. No.	Input rpm	Shore D hardness at the joint	
		Outer weld zone	Inner weld zone
1.	2000	77	64
2.	1500	61	57

Note: Hardness of PEEK sample was 70.5 Shore D.

**Fig. 9** SEM for sample No. 1 (as per Table 1).

silica fibers into the PEEK sample (30% by weight) the mechanical strength is found to be increased 1.5 times to that of virgin PEEK. Further 1.25 times increase in micro hardness was observed for this reinforcement. Proper adhesive bonding was found to be established among the amorphous fiber of silica and PEEK polymer (Monich *et al.*, 2017). The stress shielding effect is observed when the natural bone is replaced by titanium metals due to significant difference (more than 7 times to that of bone) among the strength of materials. Although PEEK Young's modulus is half to that of bone but by means of fiber reinforcement its strength become very close to human bones. This makes it more desirable polymer that can replace metals in orthopedic implants and lowering the stress shielding effect (Najeeb *et al.*, 2016).

Some studies have been reported on 3D printing of PEEK with fused deposition modeling (FDM) based printers (Vaezi *et al.*, 2018; Yu *et al.*, 2018; Stepashkin *et al.*, 2018). But hitherto very little has been reported on joining of PEEK substrates with resistance welding processes like FSW. This is required for special cases when some trauma patient is operated and fixed with PEEK based scaffolds/implants and after the major surgical operation again because of another injury or stress concentration on the scaffold/joint minor surface cracks are observed in follow up sessions by the surgeon (especially while 3D scanning). For maintenance and repair of small cracks, FSW can be performed on line on the patient with hand held rotating mechanism in place of replacement of scaffold/implant from the patient body (as this will be less painful and less time consuming activity). This study reports the investigations for joining of PEEK substrates with PEEK based consumable rapid tooling prepared in pin shape and processed on conventional vertical milling setup as a novel method.

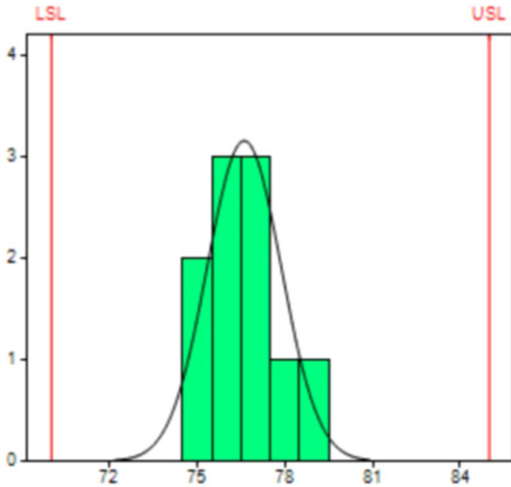
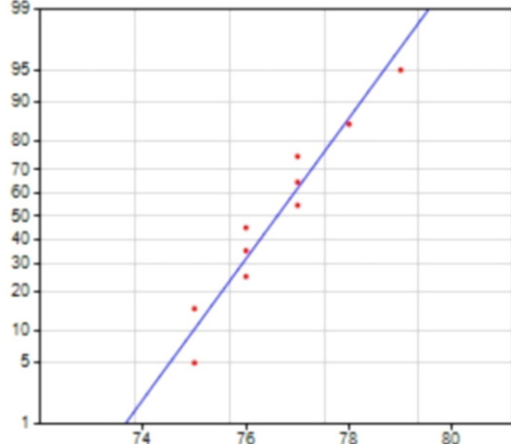
Experimentation

The virgin PEEK polymer of bio-compatible grade was procured from the local market in the form of fine powder. The melt flow index for selected PEEK grade was 3.01 g/10 min as per ASTM D1238. This powder was molded into cylindrical shape disks with the help of hot mounting machine. Hot mounting machine consist of a chamber that is covered by heaters. These heaters heat the

Table 4 Observations for mechanical and morphological properties for joints prepared at 2000 rpm with FSE

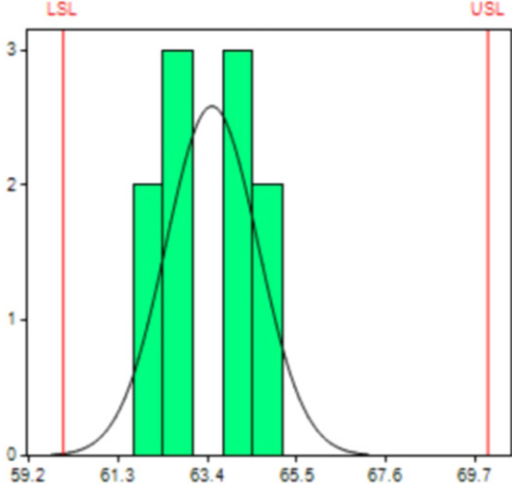
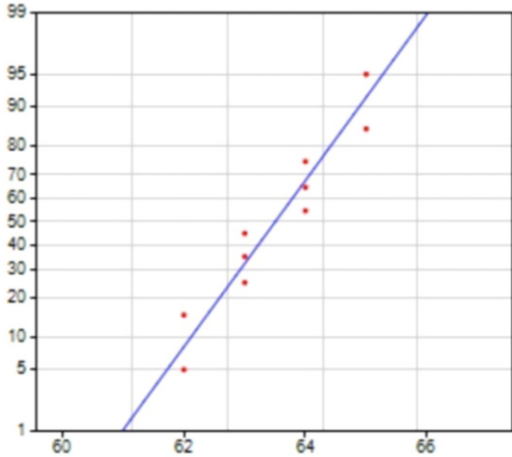
Sl. No.	Shore D hardness at outer weld zone	Shore D hardness at inner weld zone	Porosity (%)	Peak strength (MPa)	Break strength (MPa)
1.	77	64	12.64	12.90	11.61
2.	75	63	12.53	13.30	11.79
3.	77	62	13.20	13.09	11.70
4.	76	64	13.27	12.56	11.80
5.	79	65	12.67	12.37	10.90
6.	77	63	12.78	12.77	10.79
7.	76	64	12.89	12.38	11.54
8.	78	65	13.03	12.87	11.74
9.	75	63	12.34	12.36	11.23
10.	76	62	11.98	13.20	12.01

Table 5 Process capability report for shore D hardness at outer weld zone

Histogram		Capability statistics	
		Readings	10
		Subgroup size	10
		Tolerance range	
		USL	85
		Maximum	79
		LSL	70
		Average (X-Bar)	76.6
		Minimum	75
		Data range	4
		Normality test [$\alpha = 0.05$]	
		AD test	PASSED
		A-Squared	0.35
		p Value	0.394
		Statistic	
		Median	76.5
		Skewness	0.544
		Kurtosis	-0.026
Normal probability plot		Potential capability	Overall capability
		Std. deviation	1.299545
		Cp	1.92
		Pp	1.98
		Cpu	2.15
		Ppu	2.21
		Cpl	1.69
		Ppl	1.74
		Cpk	1.69
		Ppk	1.74
		CR	0.52
		PR	0.51
		Estimated parts per million	
		Based on potential	Based on overall
		PPM < LSL	0.2
		PPM > USL	0
		PPM	0.2
		Based on overall	Based on observed
		PPM < LSL	0.1
		PPM > USL	0
		PPM	0.1

Note: USL: Upper specification limit, LSL: Lower specification limit, PPM: Parts per million.

Table 6 Process capability report for Shore D hardness at inner weld zone

Histogram:		Capability statistics:	
		Readings 10 Subgroup size 10	
		Tolerance range	
		USL 70	Data range
		LSL 60	Maximum 65
		Tolerance 10	Average (X-Bar) 63.5
			Minimum 62
			Data range 3
		Normality test [$\alpha = 0.05$]	
		AD test PASSED	Statistic
		A-Squared 0.407	Median 63.5
		p Value 0.281	Skewness 0
			Kurtosis -1.032
Normal probability plot:		Potential capability	
		Std. deviation 0.974659	Overall capability
		Cp 1.71	Std. deviation 1.080123
		Cpu 2.22	Pp 1.54
		Cpl 1.2	Ppu 2.01
		Cpk 1.2	Ppl 1.08
		CR 0.58	Ppk 1.08
			PR 0.65
		Estimated parts per million	
		Based on potential	Based on overall
		PPM < LSL 164.7	596.9
		PPM > USL 0	0
		PPM 164.7	596.9
			Based on observed
			0
			0
			0

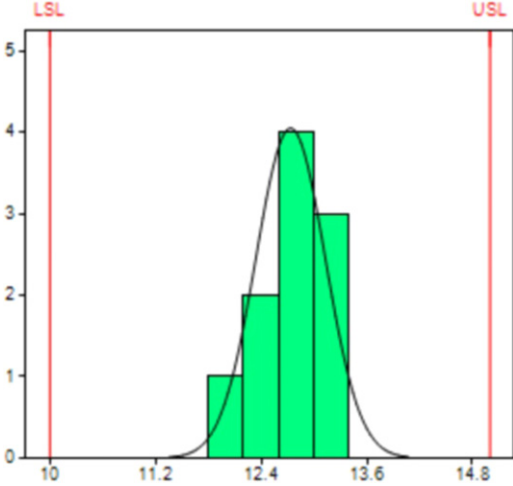
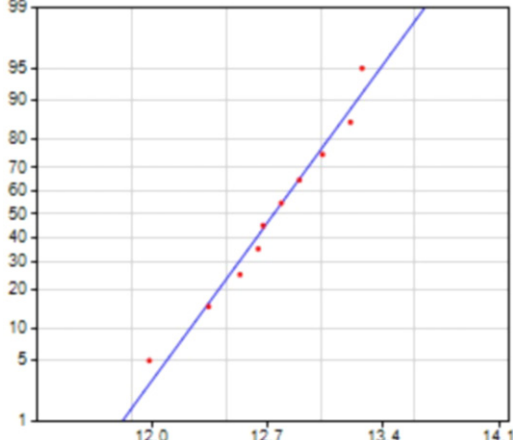
polymer at elevated temperature and ensure the proper bonding between the filled polymers. The PEEK polymer was filled into the chamber and temperature of 415°C was attained at slow heating. It must be ensured that the air bubbles should not entrap inside the chamber that create porous structure inside the final part. To tackle this problem the chamber was put under high compression that also increase the density of the final product. Fig. 1 shows that lower half portion of the polymer was bonded and converted into solid shape but the upper half of the polymer remained un-bonded. This may be due to lower thermal conductivity of the polymer. Due to this limitation there is a constraint for length of the cylinder made in hot mounting machine. On the other hand the polymers like PLA having more thermal conductivity then PEEK can be made in solid form with more length (approximately double). To overcome this problem PEEK powder was first processed on single screw extruder at temperature of 430°C and FDM feed stock filament was prepared at 100 rpm screw speed. The feed stock filament was prepared of diameter 1.75 ± 0.05 mm and was fed to commercial FDM printer (Make: Prusa i3 MK3S kit) with alteration in print head (temperature range up to 430°C). The in-house prepared feed stock filament was fed to FDM setup and functional prototypes were prepared at 50 mm/sec printing speed, with 04 number of perimeter layers, print bed temperature 110°C and travel speed of 120 mm/s with rectilinear fill pattern.

Fig. 2 shows the cylindrical disks printed by commercial FDM based 3D printer.

For investigations of joining capabilities with FSW, two plates of length 30 mm and thickness 4 mm were 3D printed. The consumable pin of diameter 4 mm was also 3D printed with same material. Fig. 3 shows the 3D printed plates made from PEEK material.

Based upon pilot experimentation, to make joint with friction stir welding, the depth of 2 mm was selected which was sufficient to generate frictional heat and make a strong joint in remaining thickness. The welding time of 20 s was selected that is sufficient to develop material flow to fill the joining interface and proper heating of the joint. The rotational speed of the holder was varied in this investigation. Two rotational speeds 1500 rpm and 2000 rpm were selected for the investigation. It has been observed that

Table 7 Process capability report for porosity (%)

Histogram:		Capability statistics:	
		Readings	10
		Subgroup size	10
		Tolerance range	
		USL	15
		LSL	10
		Tolerance	5
		Normality test [$\alpha = 0.05$]	
		AD test	PASSED
		A-Squared	0.152
		p Value	0.938
		Statistic	
		Median	12.725
		Skewness	-0.477
		Kurtosis	0.067
		Data range	13.27
		Average (X-Bar)	12.733
		Minimum	11.98
		Data range	1.29
Normal probability plot:		Potential capability	
		Std. deviation	0.419103
		Cp	1.99
		Cpu	1.8
		Cpl	2.17
		Cpk	1.8
		CR	0.5
		Overall capability	
		Std. deviation	0.393956
		Pp	2.12
		Ppu	1.92
		Ppl	2.31
		Ppk	1.92
		PR	0.47
		Estimated parts per million	
		Based on potential	
		Based on overall	
		Based on observed	
		PPM < LSL	0
		PPM > USL	0
		PPM	0

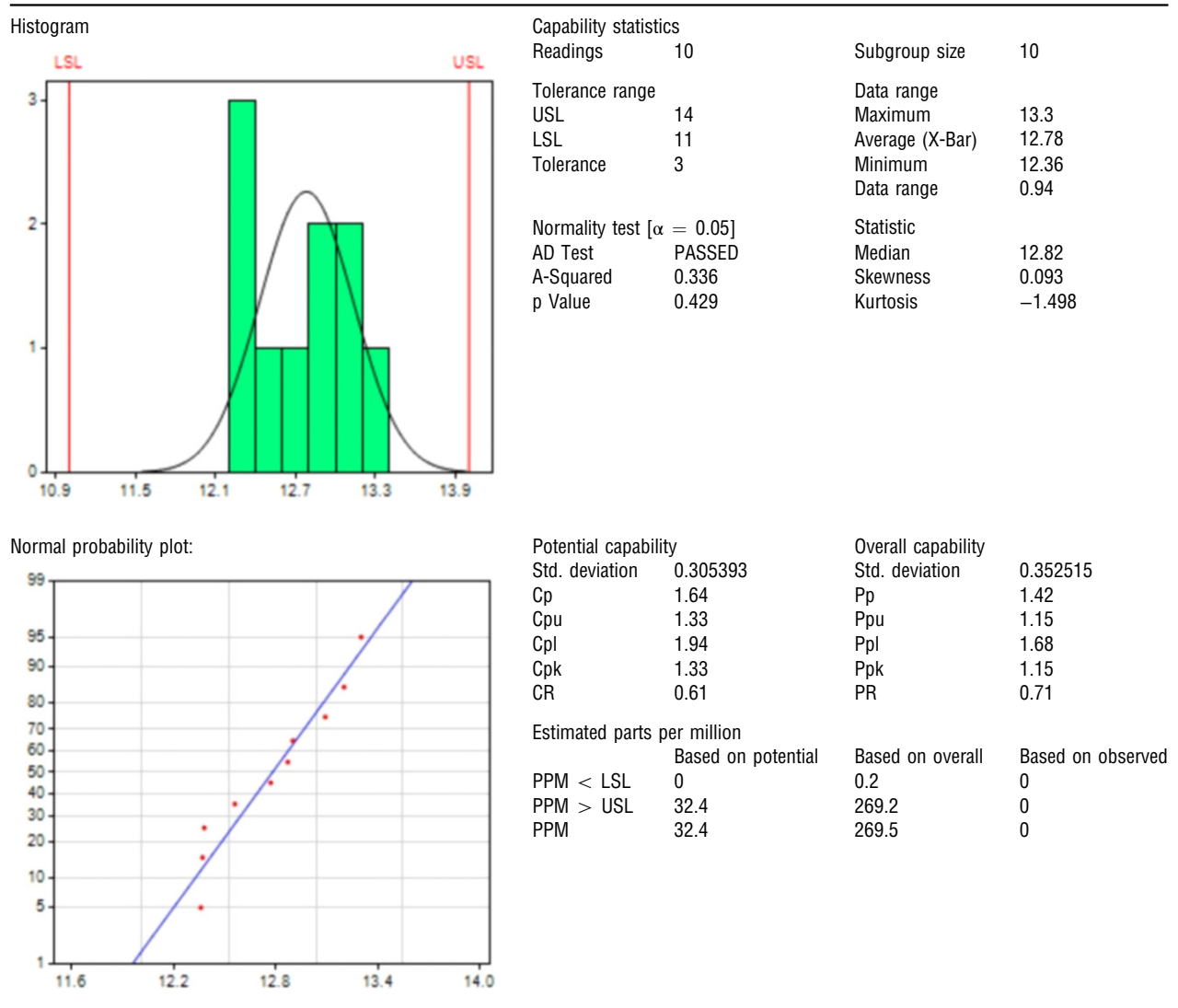
below 1500 rpm joint was not feasible and above 2000 rpm more flash was generated which decrease the strength of the joint. **Fig. 4** shows the fixtures for FSW.

Figs. 5 and **6** respectively shows the schematic of FSW and specimen prepared. As observed from **Fig. 6** joint prepared at 1500 rpm has some unfilled region at the interface as compared to joint prepared at 2000 rpm. From this observation it is clear that at 1500 rpm frictional heat is not sufficient to generate enough flow ability of material from consumable pin (printed as rapid tooling) to the joint interface. On the other hand joint made at 2000 rpm seems to be better due to more bonding at the interface.

Results and Discussion

Fig. 7 shows sample being tested on universal tensile tester as per ASTM D638. **Table 1** shows observations for mechanical properties and typical stress-strain curve for joints prepared by PEEK (**Fig. 8**). Initially extra flash was removed from the joints by grinding.

As observed from **Table 1** the joints made at 2000 rpm shows more strength as compared to 1500 rpm. Both samples show almost same value of strain. The joint prepared at 2000 rpm did not break from the interface which ascertains that the sound joint was formed. **Table 2** shows the porosity data of weld zone for both the samples. The microscopic observation was taken at 100X zoom level. The level of porosity in the sample prepared at 2000 rpm was 12.64% which is approximately half for sample prepare at 1500 rpm (23.61%). Here high porosity may have resulted into weak mechanical properties. Further Shore D hardness was measured at the joint prepared with two different rpm settings (see **Table 3**). The hardness data was taken from outer weld zone and inner weld zone. Three observations are taken and average of all three reading is coated. As observed from **Table 3**, higher rotational speed results into more hardness. This may be due to fact that at higher rpm more frictional heat is generated and

Table 8 Process capability report for peak strength (MPa)

material get more flowing capability to fill the remaining voids at the weld zone that increase the hardness level and decreases the porosity level. It is also observed that hardness level at inner zone is always lower. This is due to the fact that the flowing material is always tried to move outside from the interfacing zone. So more flowing material automatically come towards outer weld zone and results in more hardness.

Fig. 9 shows the SEM of the fractured zone for sample 1 prepared at 2000 rpm. The fracture mechanism seems to be delamination in tensile testing.

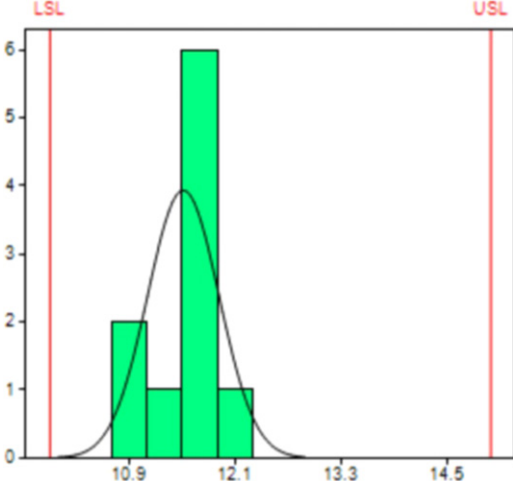
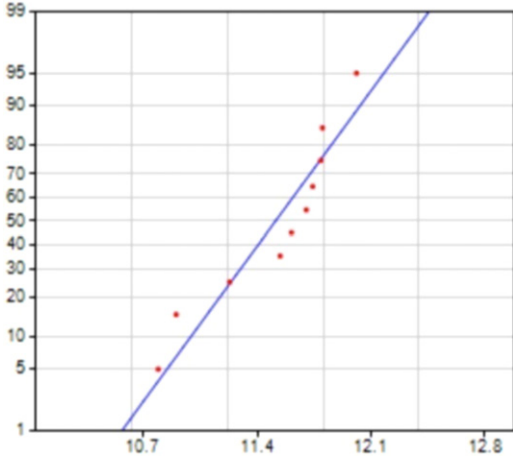
Based upon **Tables 1–3**, 2000 rpm has been selected for joint preparation by FSW. Ten repeated trials were made on 3D printed PEEK substrates. The observations for mechanical and morphological properties are shown in **Table 4**.

Based upon **Table 4**, **Tables 5–9** shows process capability report for (a) Shore D hardness at outer weld zone, (b) Shore D hardness at inner weld zone, (c) Porosity (%), (d) Peak strength (MPa), (e) Break strength (MPa). As observed from **Tables 5–9**, process capability histogram, normal probability plot is well in control and process capability indices Cp and Cpk are ≥ 1 . Hence it is ascertained that the joining process for PEEK with FSW at proposed settings are under statistical control and can be used for batch production.

Futuristic Aspects of PEEK Joining With FSW for Sustainability

The published literature reveals that PEEK has been accepted as useful thermoplastic for bio-medical applications as well as for handling/transportations of low intensity nuclear waste such as gloves used by medical practitioner while chemotherapy (in form of

Table 9 Process capability report for break strength (MPa)

Histogram		Capability statistics	
		Readings	10
		Subgroup size	10
		Tolerance range	
		USL	15
		LSL	10
		Tolerance	5
		Normality test [$\alpha = 0.05$]	
		AD test	PASSED
		A-Squared	0.566
		p Value	0.106
		Statistic	
		Median	11.655
		Skewness	-0.905
		Kurtosis	-0.351
		Data range	12.01
		Average (X-Bar)	11.511
		Minimum	10.79
		Data range	1.22
Normal probability plot		Potential capability	Overall capability
		Std. deviation	0.396361
		Cp	2.1
		Cpu	2.93
		Cpl	1.27
		Cpk	1.27
		CR	0.48
		Std. deviation	0.405694
		Pp	2.05
		Ppu	2.87
		Ppl	1.24
		Ppk	1.24
		PR	0.49
		Estimated parts per million	
		Based on potential	Based on overall
		PPM < LSL	68.9
		PPM > USL	0
		PPM	68.9
		Based on overall	97.9
		Based on observed	0
		Based on overall	0
		Based on observed	0

some containers) (Ajeesh *et al.*, 2015; Miedema and Walker, 2001). Many commercial manufacturers have lunched PEEK containers as a product for these applications. As observed from the mechanical properties achieved in present case study, for maintenance and repair, sealing of charged/filled containers of PEEK (for airtight sealing) the proposed process of FSW can be successfully used. The idea over here is to use PEEK based consumable tool on PEEK substrate in FSW (for minor repair/sealing of the PEEK containers containing nuclear waste for storage applications). This may provide a cost effective, foolproof sealing and repair of PEEK containers as per tailor made requirements leading to better sustainability and repair of existing containers for better re-usability.

Conclusions

The 3D printed PEEK based functional prototypes were successfully joined in the present case study with FSW. Following are the conclusions from the present study:

- (1) The results of study suggest that the joint strength in FSW of 3D printed PEEK was compromised (around 12.9 MPa from 50 MPa of substrate) at the weld zone but the surface hardness observed was of the similar range.
- (2) At outer weld zone even betterment in surface hardness has been observed with controlled porosity level.
- (3) As regards to mechanical and morphological properties, process capability histogram, normal probability plots are well in control and process capability indices Cp and Cpk are ≥ 1 . Hence the joint properties of PEEK with FSW at proposed settings are under statistical control and can be used for batch production.
- (4) Finally the proposed process can be utilized for minor on-line repair of scaffolds/implants in field applications.

Acknowledgment

The authors are highly thankful to SERB under AISTDF Secretariat (File No. IMRC/AISTDF/R&D/P-10/2017, Dated 01-02-2018) for financial support.

See also: 3D Printing of Carbon-Based Conductive Materials for Electrochemical Energy Storage (EES) Application. 3D Printing of Polyether-Ether-Ketone Functional Prototypes for Engineering Applications. A Comprehensive Study for 3D Printing of Rapid Tooling From Reinforced Waste Thermoplastics. Biocompatible Thermoplastic Composite Blended With HAp and CS for 3D Printing. Experimental Investigations for Friction Stir Welded 3D Printed Dissimilar Thermoplastics With Consumable Tool. Joining of 3D Printed Dissimilar Thermoplastics With Consumable Tool Through Friction Stir Spot Welding: A Case Study. Joining of 3D Printed Dissimilar Thermoplastics With Friction Welding: A Case Study. The Effect of CaCO₃ Nanoparticles and Chitosan on the Properties of PLA Based Biomaterials for Biomedical Applications

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Green Composites From Sustainable Cellulose Nanofibrils

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Introduction

The journey of the application of cellulose nanofibrils in green composites has dated back over six decades with progressive achievement on the vital role of nanocellulose NC as an important material in industrialization. The roadmap for the emergence of NC in the creation of new bio-economy has witnessed the application of microcrystalline cellulose in food and cosmetics, pharmaceuticals and basic industrial chemicals. Based on the unique properties of these materials, the global market outlook has projected that the annual turnover of NC could reach 808.29 million dollars by 2022 ([Rajinipriya et al., 2018](#)). Recently, there has been global shift from the utilization of Petroleum based polymers composite due to environmental issues, increases in the price of petrochemicals and thinning accessibility of petrochemical resources ([Zia et al., 2016](#)). Other factors include the non biodegradability of their waste materials after their functional life and consequently poor waste management resulting in green gas emission and environmental pollution as a result of poor waste management ([Otegbulu, 2011](#)). This has drawn the attention of the researchers to the exploration of materials that could be reused, recycled or reduced after use in order to mitigate this ugly development. For over three decades now there has been an increasing demand for products made from renewable and sustainable resources that are biodegradable, non-petroleum based, and carry low environmental, animal/human health, and safety risks ([Woldeyohannes et al., 2016](#)).

Basically green composite are formed by the combination of biodegradable polymers like Polysaccharides (Starch, Cellulose, Chitin), Proteins (Collagen/Gelatin Casein or proteins from legumes) of Polyesters with natural biodegradable resins to form natural fibers recyclable green composites. Cellulose has been the most favourable candidate being the most abundance biopolymer on earth, as well as its derivatives have been widely studied as renewable materials. Cellulose which comprises of a linear polysaccharide made up of β -D-anhydroglucopyranose units is abundantly present in wood, cotton, hemp, and other plant-based materials and serves as the dominant reinforcement material in plant structures ([Chiellini and Morelli, 2011](#)). Cellulosic materials such as wood, hemp, cotton, and linen have been used in the area of pharmaceutical, food, biomedical, paper production and engineering construction ([Sundarraj and Ranganathan, 2018](#)). Apart from plant materials, cellulose has been found in some species such as, invertebrates, fungi, tunicates, bacteria algae, amoeba and fungi ([da Silva et al., 2017](#)). The major functional parameters of nanocelluloses produced from difference sources vary in geometrical dimensions depending on the source of the cellulosic material and the hydrolysis conditions with their functional properties are shown in [Table 1](#).

From [Table 1](#) it is shown that the morphological characteristics of the various fibers are studied with the aid of equipment such as Transmission Electron microscopy (TEM). Others include- Atomic force microscope (AFM) Field Emission Scanning Electron Microscopy (FESEM), Small angle neutron scattering (SANS) and both polarized light scattering and depolarized dynamic light scattering (DLS, DDLS). The abundance of cellulosic materials is pivotal to the level and volume of its consumption in agro-based industries such as craft and textiles; paper and particle boards; wood furniture and particle boards etc ([Laftah and Wan Abdul Rahman, 2016](#)).

Nanocellulose NC

Globally, nanocellulose has been gaining increasing interest in the variety areas of application due their excellent mechanical properties, renewability, biocompatibility, good optical properties and biodegradability. It has been found profound application in the field of material science and engineering for food packaging and construction. [Fig. 1](#) is the summarized scheme of area of utmost application of the green nanocellulose.

Recently polymer industrial researchers have found another breakthrough in the extraction and modification of the wood fibers for nanocellulose with one dimension of the material in the nano range. This cellulosic material has been reported as a promising candidate as biodegradable materials ([Khalil et al., 2017](#); [Owolabi et al., 2017](#); [Abdul Khalil et al., 2018a](#)). Cellulose is an assembly of uniaxially ordered fiber naturally built up in hierarchical structured which can be broken down to cellulose nanofibrils. These nanofibrils are made up of firstly longer reaching to several microns in length semi-crystalline elementary fibrils called cellulose nanofibrils (CNFs), and secondly dimensionally smaller and chemically isolated from CNF called cellulose nanocrystals (CNCs). Their properties are adjudged on the basis of their morphology surface chemistry, crystallinity and aspect ratio. Primarily these nanocellulose materials are stimulated by their methods of extraction route ([Saurabh et al., 2016](#)).

Significant increasing research on nanocellulose and nanocellulose-based materials production have been accomplished over the last few decades as a result of their nanoscale dimensions which make them susceptible to modifications. Results from the

Table 1 Types of cellulose nanofibers and their particle sizes

Sources	Length (nm)	Width (nm)	Detection technique
Bacteria	100–1000	10–50	TEM
	100–1000	5–10 × 30–50	TEM
Cotton	100–150	5–10	TEM
	7–170	~70	TEM
	200–300	8	TEM
	255	15	DDL
	150–210	5–11	AFM
Cotton Linters	100–200	10–20	SEM – FEG
	25–320	6–70	TEM
MCC	35–265	3–48	TEM
	250–270	23	TEM
	~500	10	AFM
Ramie	150–250	6–8	TEM
	50–150	5–10	TEM
Sisal	100–500	3–5	TEM
	150–280	3.5–6.5	TEM
Tunicate		8.8 × 18.2	SANS
	1160	16	DDL
	500–1000	10	TEM
	1000–3000	15–30	TEM
	100–1000	15	TEM
	1073	28	TEM
Valonia	> 1000	10–20	TEM
Soft wood	100–200	3–4	TEM
	100–150	4–5	AFM
Hard Wood	140–150	4–5	AFM

Note: Adapted with permission from Habibi, Y., Lucia, L.A., Rojas, O.J., 2010. Cellulose nanocrystals: Chemistry, self-assembly, and applications. *Chemical Reviews* 110 (6), 3479–3500, Copyright 2014. Reproduced with permission of Copyright © 2010, American Chemical Society.

literatures have shown that these materials have excellent mechanical properties, biodegradability and nontoxicity (Jorfi and Foster, 2015). Nanocellulose can be extracted from various lignocellulosic biomass sources by means of mechanical, chemical, and enzymatic methods or combination of any of the techniques. Based on the preparation technique used and the appearance of nanocellulose, they are divided into three general groups, namely CNFs, BC, and CNCs. Fig. 1 illustrate the relationship between these different kinds of nanocellulose (Vieira *et al.*, 2011).

Nanocellulose fiber production (NCFs) is natural fiber mainly produced from cellulose via mechanical treatment such as grinding or homogenization. Furthermore, they are flexible fibers with diameter ranging between 20 and 50 nm and the fiber length in 500–2000 nm entangled fibrils that contain both amorphous and crystalline cellulose domains (Mishra *et al.*, 2017). On the other hand, CNCs are produced via acid hydrolysis, which is a chemical treatment process. CNCs are whiskers or needle-shaped and are shorter with length in the range of 100–500 nm and diameter in the range of 3–50 nm (Tan *et al.*, 2015; Abdul Khalil *et al.*, 2018b). The size of the isolated CNFs and CNCs depends on the preparation conditions and source of cellulose. Currently, conventional mechanical and chemical treatment processes, which are traditionally used to prepare CNFs and CNCs are still very well known. Other promising production techniques as well as pretreatment processes have also been proposed in order to develop an economically efficient and eco-friendly production route for nanocellulose (Kargarzadeh *et al.*, 2018).

Mechanism of Nanocellulose Reaction

Broad studies on the application of nano-scaled cellulose have been conducted and reported in various field such as: composite, biomedical, automobile, paper industry, packaging, membranes, food or pharmacy, and construction (Trache *et al.*, 2016). The reactivity of the NC is borne out of the presence of three hydroxyl groups in each anhydroglucose unit. These anhydroglucose unit can react partially or fully with chemicals with improve property characterizations. It was reported that the hydroxyl group at the 6th position acts as a primary alcohol, while the 2nd and 3rd positioned hydroxyl behave as secondary alcohol (Lin and Dufresne, 2014) as shown in Fig. 2.

The reactivity of each anhydroglucose moiety in the polysaccharide is a function of the replaceability of the –OH group which is termed degree of substitution DS in the anhydroglucose unit (Mondal, 2017). Each of the unit can only replace a maximum of three resulting in the DS values ranging from 0 to 3. This phenomenon of degree of substitution promotes the reactivity of the anhydroglucose unit through the intramolecular hydrogen bonds. The intramolecular hydrogen bond occurs between the hydrogen borne by the OH group of the C3 carbon and ring oxygen of the adjacent glucose unit (O5). In addition the

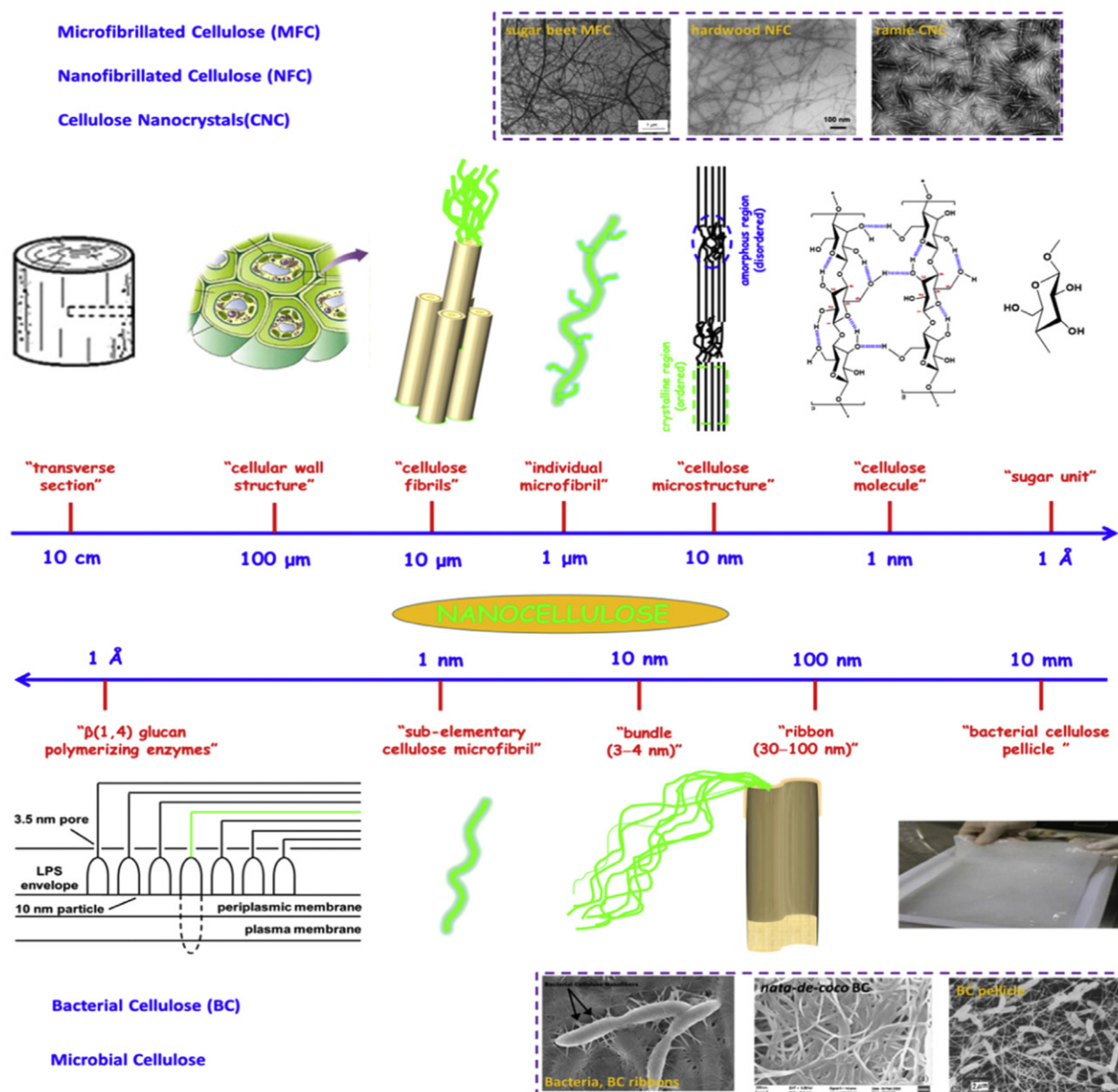


Fig. 1 Relationship between different kinds of nanocelluloses. Adapted with permission from Lin, N., Dufresne, A., 2014. Nanocellulose in biomedicine: Current status and future prospect. *European Polymer Journal* 59, 302–325, Copyright 2014. Reproduced with permission of Elsevier.

intermolecular hydrogen bonds occur between the hydrogen of the OH-6 primary hydroxyl and oxygen in position O3 in a cycle of a neighboring unit, as well as the hydrogen of OH-2 and oxygen in position O6 (De France *et al.*, 2017). The ability of these hydroxyl groups to form hydrogen bonds plays a major role in the formation of fibrillar and semicrystalline packing (Li *et al.*, 2013). Aside the presence of the -OH group, another interesting radical introduced to the surface of the nano sized crystalline particles is the negative sulphide radicals (Xiang *et al.*, 2017). These substances were introduced to the surface of crystalline nano cellulose particle during the sulfuric acid hydrolysis of CNF that leads to the cellulose nanocrystalline CNC synthesis.

Life Cycle Assessment of Green Composite

The term green composites is generally refers to materials prepared by blending biodegradable polymeric substance and other organic or inorganic components. This blending uses conventional plastic processing equipments followed by thermo-molding of the mixture at elevated temperatures to crosslinked the matrix (Van den Heede and De Belie, 2012). As shown in Fig. 3, the philosophy behind the life cycle assessment of green composite is evaluating the synergy of the mutual interaction between green composite manufacture and the environmental reaction.

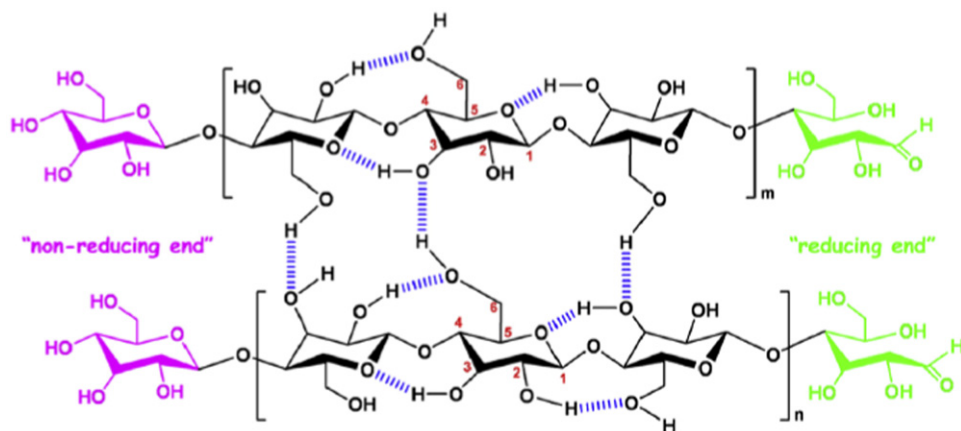


Fig. 2 Schematic representation of the chemical structure and intra-, inter-molecular hydrogen bonds in crystalline cellulose. Adapted with permission from Lin, N., Dufresne, A., 2014. Nanocellulose in biomedicine: Current status and future prospect. *European Polymer Journal* 59, 302–325, Copyright 2014. Reproduced with permission of Elsevier.

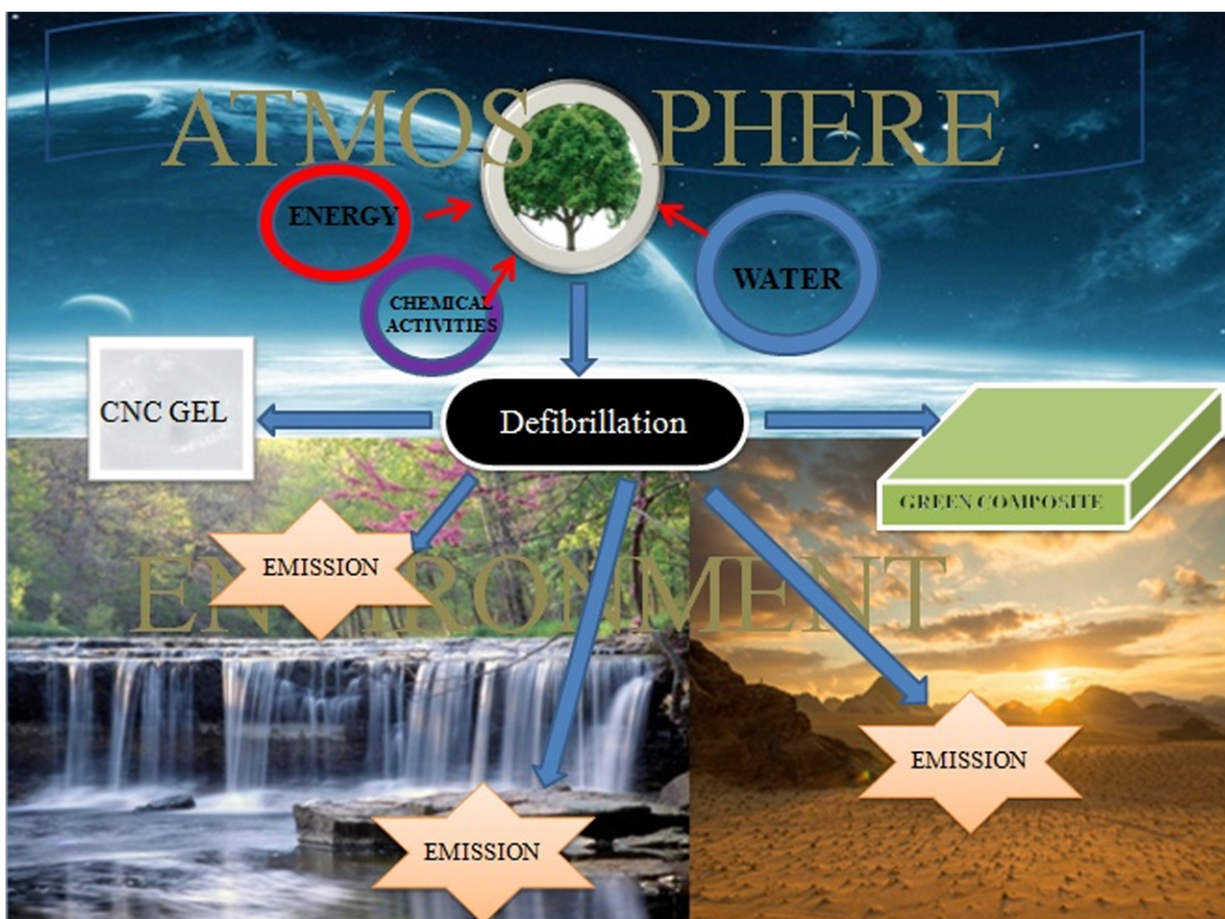


Fig. 3 Life cycle assessment of green composite.

It is pertinent to note that evaluation of ‘green’ nanotechnology is very important especially its impact on the environment requires a full life cycle assessment (Flynn and Traver, 2013). The roadmap to green composite has witnessed the use of natural fibers which is green by the virtue of its biodegradability as reinforcement for plastics, replacing fibers synthetic materials. Life Cycle Assessment (LCA) which was kick started about two decades ago, is now spelled out in the International Organization for Standardization (ISO) 14040 environmental management series standard. The major function of LCA is that, it evaluates every

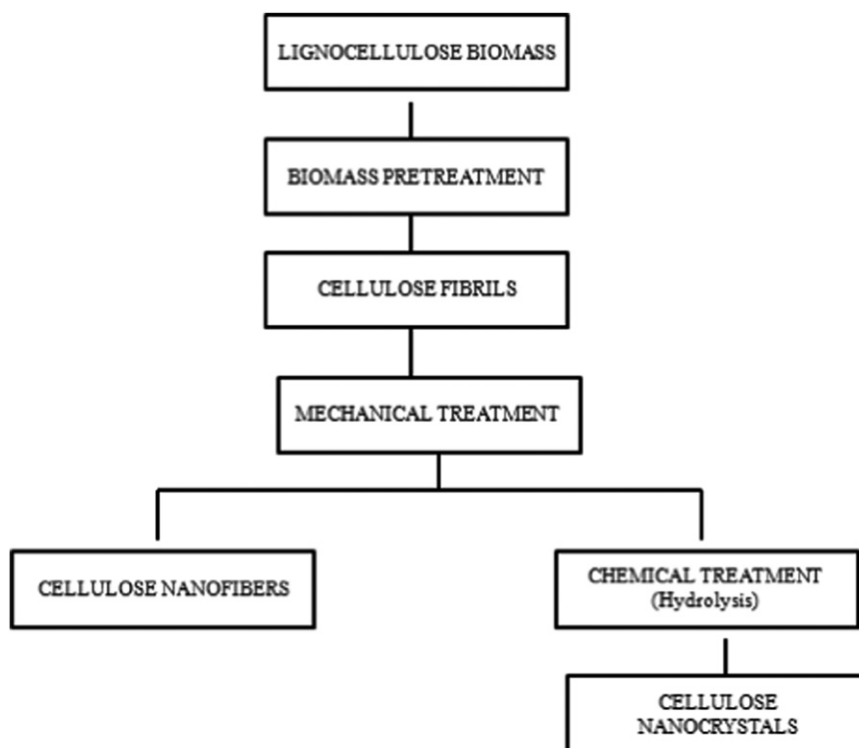


Fig. 4 Summary of the general method of production of nanocellulose.

environmental impact assessment EIA presented by the manufacture with respect to the application and disposal of their product. The operation of the LCA consists of four major steps: (1) goal and scope definition; (2) inventory analysis; (3) impact assessment and (4) interpretation (Liu and Ramirez, 2017). It has been proposed that industries need to show the life cycle benefits of composites which is the focus of LCA. Fig. 4 presents a typical life cycle of polymer nanocomposite.

Biocompatibility and Toxicology

Cellulose is generally considered as biocompatible due to their ability to blend with living tissues in vivo without causing injurious changes, which is an important prerequisite for biomedical materials (Rosamah *et al.*, 2018). Biocompatibility of CNs have made very easily incorporated into a wide range of polymer matrices, which has also made them very useful in biomedical application because they remain in contact with living tissue without causing any cytotoxic or other side effects as revealed by in vivo animal experiments. Despite the non toxicity of nanocellulose materials, it has been reported that excessive inhalation dosage of the material may trigger pulmonary inflammation because of the self-aggregation and bioaccumulation of cellulose material in the body (Jorfi and Foster, 2015). Many literature reports have attested to the cellulose biocompatibility through various studies. Of all the studies conducted, BC is commonly regarded as a material possessing best biocompatibility. Examples of the recent toxicology reports for different types of cellulose materials are summarized in Table 2. The cellulose- biomaterial interaction has been reported largely influenced by the presence of hydrophobic and hydrophilic sphere of influence. Other factors that are crucial to the cellulose biomaterial interaction include surface charge, wettability, surface chemistry and surface topography. Nanocellulose materials are very versatile and very important as biomedical materials due to their biocompatibility and nontoxicity.

Meanwhile their chemical surfaces functionalization with bioactive molecules is important in biomedical applications for improved interactions with the human body.

Isolation of Cellulose Nanofibrils CNFs

Cellulose nanofibers are extracted from lignocelluloses materials like wood, non wood, agricultural residues like wheat straw, soy hulls etc by a chemi-mechanical technique as summarized in Fig. 4, to examine their potential for use as reinforcement fibers in biocomposite applications. The ability of nanofibrillated cellulose in improving the quality of paper and paper products, etc has led to assiduous and potential research on its unexploited potential and potential means of its generation.

Basically, three main processes are identified with CNF production from cellulosic fibers which include (a) mechanical treatments (e.g., Cryocrushing, High-pressure homogenization, High intensity ultrasonication, homogenization, grinding, and

Table 2 Toxicological evaluation of some cellulose-based materials for biomedical applications

Cellulose type	Toxicology experiment	Results
CNC	Acute lethal test	Low toxicity potential
	Multi-trophic assays	Low environmental risk
	Animal experiments with fathead minnow and Zebrafish reproduction tests	
	In vitro rainbow trout hepatocyte assay	
	Respiratory toxicity of aerosolized CNC on the human airway with a co-culture of human monocyte-derived macrophages, dendritic cells and a bronchial epithelial cell line	Low cytotoxicity Somewhat (pro-)inflammatory cytokines
	In vitro gene mutations	No evidence of high toxicity
	In vitro and in vivo chromosomal tests	
	Skin irritation and sensitization tests	
	Animal experiments with rat feeding study (28 d)	
	Cytotoxicity evaluation with L929 cells	Low cytotoxicity at low CNC concentration
CNF	Cytotoxicity evaluation with nine different cell lines	No cytotoxic effects in the concentration range (0–50 lg/mL) and exposure time (48 h)
	Cytotoxicity evaluation with human monocyte and mouse macrophages	No evidence of inflammatory effects or cytotoxicity
	Kinetic luminescent bacteria test for acute environmental toxicity	
	In vitro genotoxicity with enzyme comet assay	No significant DNA damage
	Neurotoxicity and systemic effects with a nematode model	Low or no cytotoxicity
	In vitro pharyngeal aspiration study for pulmonary immunotoxicity and genotoxicity with mice	No DNA and chromosome damage
		Pulmonary inflammation
	Cytotoxicity evaluation with 3T3 fibroblast cells (including the test of cell membrane, cell mitochondrial activity and DNA proliferation)	No toxic phenomena for pure CNF Somewhat cytotoxicity for modified-CNF (with PEI or CTAB surface modification)
	Cytotoxicity evaluation with bovine fibroblasts cells	Low cytotoxicity at low CNF concentration (0.02–100 lg/mL)
	Effects of gene expression in vitro	Reduction of cell viability and affection of the expression of stress- and apoptosis-associated molecular markers at high CNF concentration (2000–5000 lg/mL)
BC	Cytotoxicity evaluation with human dermal fibroblasts	No evidence of cytotoxicity for pure CNF Improved cytocompatibility of EPTMAC-modified CNF
	Cytotoxicity evaluation with osteoblast cells and L929 fibroblast cells	No evidence of cytotoxicity
	Cytotoxicity evaluation with human umbilical vein endothelial cells	
	Animal experiment with C57/Bl6 male mouse	No evidence of toxicity in vitro and in vivo
	In vitro immunoreactivity with human umbilical vein endothelial cells	Non-toxicity and non-immunogenicity
	In vivo intraperitoneal injection study with BALB/c male mice	

Abbreviations: PEI, polyethyleneimine; CTAB, cetyl trimethylammonium bromide; EPTMAC, glycidyltrimethylammonium chloride.

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milling), (b) chemical treatments (e.g., TEMPO oxidation), and (c) combination of chemical and mechanical treatments simple mechanical shear, refining or by a combination of chemimechanical milieu (Shaghaleh *et al.*, 2018). It has been reported in the literature that CNF has been isolated and characterized from variety of lignocelluloses sources using different methods (Kargarzadeh *et al.*, 2018; Shaghaleh *et al.*, 2018; Owolabi *et al.*, 2016). Below is a short appraisal of some of the widely reported preparation protocols for CNF materials.

Cryocrushing

This is a method to produce cellulose nanofibrils through the combine action of rigorous shearing in a refiner prior to high-impact crushing under liquid nitrogen (Chakraborty *et al.*, 2005). The mechanism of this process involves action of high impact forces the fibers frozen under liquid nitrogen followed by high pressure fibrillation. This method of CNF production has successfully been used to prepare CNF from soybean stock (Torregrosa *et al.*, 2016), from wheat straw and soy hull (Alemдар and Sain, 2008). While wang and Sain (Wang *et al.*, 2007) reported the resultant fibers were 50–100 nm in diameter, Alemдар and Sain (2008) reported that the diameter of the extracted nanofiber was in the range of 10–80 nm with length on the order of a few thousand nanometers. The studies characterized the CNF with respect to the physical and thermal properties of the nanofibers with the aim of assessing their feasibility in biocomposite applications.

High-Pressure Homogenization (HPH)

This is a type of CNF production by mechanical means. Large scale production of CNF has been achieved through the use of High-pressure homogenization (HPH) (Wang *et al.*, 2017). This mechanical technique utilizes variety of forces for size reduction of natural cellulose leading to nanoscale cellulose. Most high-pressure homogenizers use a combination of forces – most commonly cavitations and impact, which is homogenizers and microfluidizers (Mishra *et al.*, 2017). The perception of the “homogenization” refers to the ability of producing a homogeneous size distribution of particles in a liquid suspension. Conventionally HPH delivers pressure and flow based on a constant volume method and variable homogenizing valve configurations, which commonly yields very large process pressure variations during each pumping cycle (Owolabi *et al.*, 2017; Orsuwan and Sothornvit, 2018). The higher the pressure, the higher would be the disruption efficiency per pass through the equipment. The resulting particle size is usually large with a broad size distribution. Consequence to intensifier pump and fixed geometry orifice, uniform shear with small particles distributions is achievable by microfluidizer (Tang *et al.*, 2001). Herrick *et al.* (1983) and Saarikoski *et al.* (2015) first reported this mechanical technique of CNF production with homogenizer and large pressure. Consequently Li *et al.* (2014) reported the extraction CNFs from depectinated sugar beet pulp through the combination of chemical treatment with HPH while Chen *et al.* (2014) also reported the CNF production from raw dried cotton fibers. The diameter of the resultant CNFs ranged from several nanometers to 70 nm and it was shown that the crystallinity of the nanofibers increased significantly after treatment.

On the issue of the thermal effect, the majority portion of the mechanical energy applied to any system will eventually be dissipated into the form of heat. HPH usually causes the excessive temperature increase in the processed materials. Although it depends on the setup and what the mechanisms are within the system to mitigate heat buildup. Microfluidized materials will only have moderate temperature increment, which makes it ideal for applications with heat sensitive materials (Jana *et al.*, 2017). Generally this method has been reported as the most expensive method for the nanomaterial isolation.

Refining Process

CNF production with improved functional characteristics has been saddled with a lot of challenges due to the growing demand in the fields of medicine, food and cosmetic and packaging industries. The process involving the passage of cellulose through a gap in between two ridged discs is called grinding process. In this case, cellulose fibers are enforced through two wavy discs one of which is static and the other revolving at about 1500 rpm. Delamination of the cell wall occurred through the process by the high shear forces, resulting in the production of individual nanosized fibers. The extent of fibrillation depends on the distance between the discs, morphology of the disc channels, and number of cellulose fibers that passed through the grinder. It was reported that application of the grinding method on wet wood fiber resulted in 15 nm diameter of CNF (Abe *et al.*, 2007), which give the efficiency the application of this method in nanofiber production. This result was similar to the report of Iwamoto and coworkers (Iwamoto *et al.*, 2005) after the application of the grinding method on cellulosic pulp resulted in CNF of 50–100 nm diameter.

High Intensity Ultrasonication

This is a chemimechanical technique involving the combine chemical pretreatment and high-intensity mechanical ultrasonication (Chen *et al.*, 2011). In this milieu, the introduced cellulose fibers are steadily disintegrated into nanosize due to the impact of ultrasonic waves. The process involves the chemical delignification of the plant fibers by either mild acid hydrolysis, or alkali treatment prior to bleaching process to remove non-cellulosic materials such as hemicelluloses and lignin. Prior to the ultrasonication process, the chemical pretreated cellulose fibers are thoroughly washed and soaked in distilled water (Nurul Fazita *et al.*, 2016).

Steam Explosion Process

This is another process of CNF extraction involving explosive decompression prior to the use of vapor phase short cooking duration at 180–210°C vapor phase cooking for a short duration at a temperature in the range of 180–210°C, followed by explosive decompression and sudden release of pressure (Stelte, 2013). The lignocelluloses biomass to be used for this protocol are subjected to short time pressure in a steam autoclave followed by explosively ejection to the atmospheric pressure leading to rapid breakup of the lignocelluloses material into a fibrous detached solid fibers. On the long run this process results in significant breakdown of the lignocelluloses division dissolution of the lignin structures and the separations of the fiber materials. The application of this technique has been widely reported in the literature. According to the literature, steam explosion process has been used for the extraction of cellulose nanofibers from pineapple leaf fibers (Cherian *et al.*, 2010), banana plant (Deepa *et al.*, 2011), isora fiber (Chirayil *et al.*, 2014) etc.

Electrospinning

Electrospinning is a simple method of NFC production with a solvent or chemical derivatization of cellulose. This method was formulated as a result of the difficulty experienced during direct dissolution of cellulose (Bhardwaj and Kundu, 2010). This nanofiber solution process of production has been adjudged very simple since it uses electrospinning under the action of a high electric field and economical because once the voltage is sufficiently high, a charged stream of matter is ejected following a rather complicated loop. During this process, the solvent evaporates leaving behind randomly oriented nanofibers that accumulate on the collector (Sun *et al.*, 2014). CNFs production

through electrospinning technique has been reported in the literature. According to [Ma et al. \(2014\)](#), cellulose acetate (CA) nanofibers was prepared by the electrospinning technique with an acetone/dimethyl formamide (DMF)/trifluoroethylene (3:1:1) mixture as the solvent. The result showed that the diameter of the produced nanofiber ranged from 200 nm to 1 μ m.

Cellulose Nanocrystals (CNC) Production

CNCs are produced via acid hydrolysis of the nanofibrillated cellulose through chemical treatment process or from naturally occurring cellulose sourced from cotton, variety of wood pulp from different protocols, bacteria cellulose and tunicates. CNCs are whiskers or needle-shaped and are shorter with length in the range of 100–500 nm and diameter in the range of 3–50 nm ([Kallel et al., 2016](#)). The size of the isolated CNCs like the CNFs depends on the preparation conditions and source of cellulose. Besides the conventional mechanical and chemical treatment processes, which are traditionally used to prepare CNFs and CNCs, other promising production techniques as well as pretreatment processes have also been proposed in order to develop an economically efficient and eco-friendly production route for nanocellulose ([Chen et al., 2015](#)). The general method commonly used for the production of cellulose nanocrystal CNC is either hydrochloric or sulfuric acid hydrolysis with heat controlled techniques followed by centrifugation/redispersion and dialysis until neutral pH is obtained. One of the unique characteristics of sulfuric acid hydrolysis is the attachment of negatively charged sulfate half-ester groups onto the surface of the particles, which impose electrostatic repulsion between fibers particles preventing aggregation of the nanocellulose crystals in aqueous suspensions. Additionally, the rod-like shape of CNCs leads to concentration-dependent liquid crystalline self-assembly behavior with near-perfect crystallinity of about 90% ([Reid et al., 2016](#)).

Bacteria Cellulose (BC)

BC is also known as cellulose nanowhiskers (CNW) or bacterial nanocellulose is characterized by high purity, strength, moldability and increased water holding ability. It is produced extracellularly by microorganisms like bacteria of which *G. xylinum* is the most famous of them mainly to form protective envelopes around their cells ([Huang et al., 2014](#)). Unlike the plant sourced nanocellulose, BC is synthesized as pure natural cellulose with average fiber diameter of 20–100 nm and several micrometer lengths. microbial cellulose is more chemically pure, containing no hemicellulose or lignin, has a higher water holding capacity and hydrophilicity, greater tensile strength resulting from a larger amount of polymerization, ultrafine network architecture ([Stumpf et al., 2018](#)). Furthermore, bacterial cellulose can be produced on a variety of substrates and can be grown to virtually any shape due to the high moldability during formation. Additionally, bacterial cellulose has a more crystalline structure compared to plant cellulose and forms characteristic ribbon-like microfibrils. A hallmark of microbial cellulose, these thin microfibrils are significantly smaller than those in plant cellulose, making bacterial cellulose much more porous ([de Oliveira Barud et al., 2016](#)).

Challenges of Nanocellulose Application

Despite the wide acceptability of nanocellulose in various field of manufacturing, nanocellulose in spite of their versatility nanocellulose fibers still show some properties that limit their applications. One of the challenges in the use of nanocellulose is compatibility with the polymer matrix in composite development ([Jorfi and Foster, 2015](#)). This is attributable to the hydrophobic nature of the polymer matrix as against the nanocellulose that are majorly hydrophilic fibers which result in non-uniform dispersion of fibers within the matrix hence poor mechanical properties. In order to have a good blend the projection on the nature of the molecular structure and the proposed interfacial interaction expected between the matrix and the nanocellulose fibers is of great importance in polymer composing. The main aim of green composite development is the enhancement of the mechanical properties which tend to be compromised in some cases. Most biopolymers employed for this purpose like Chitosan ([Serpa et al., 2016](#)), cellulose and gelatin are not readily available hence involves laborious efforts to be extracted. It has been reported that the use of starch nanoparticles tends to compromise the mechanical properties hence lead to the use of plasticizer unlike poly lactic acid (PLA). However, PLA used in green nanocomposite has been reported characteristic thermally low glass transition temperature and weak thermal stability. Green nano composite suffers the problem of dispersion of the biopolymers in the polymer composite ([Ng et al., 2017](#)). In some cases specialized equipment like high sonication is needed to enhance adequate spread of the nanocellulose fillers. The mechanical properties of the green nanocomposite also depend on the fiber orientation which is pretty difficult to achieve with nanoparticles unlike the micro cellulose counter-part. Apart from the above methods at overcoming the challenges of filler/matrix adhesion in green nanocomposite, efforts such as fiber surface modification, addition of compatibilizers and also matrix mercerization have been reported ([Haafiz et al., 2017](#)). To overcome the challenges of compatibility and grafting between fibers and thermoplastic matrices in green composites production, surface treatment by the use of additives is adopted. The common additives used include chemical coupling agents or compatibilizers Maleated polyethylene (MAPE) ([Sundrababu and Griskevicius, 2018](#)), carboxylated polyethylene (CAPE) ([Li et al., 2012](#)), titanium derived mixture (TDM), Maleic anhydride polypropylene (MAPP), ([Benhamou et al., 2015](#)), calendaring, stretching ([Jonoobi et al., 2015](#)), thermo treatment ([Effah et al., 2018](#)), reaction with methanolmelamine, isocyanates, triazine, silane ([Ashik et al., 2017](#)) and mercerization of the matrix ([Liu et al., 2015](#)). Despite all these possibilities, a better understanding of the molecular structure and interfacial

interaction between the matrix and the fibers and the relationship between the structure and property is very important in this area of research (Adeosun *et al.*, 2012).

Recent Advances in Green Nanocomposite Research

Green nanocomposites are gradually gaining wide acceptance in the mainstream of global industrial landscape like biomedical, construction, packaging, and plastics processing. The production of these nanocomposite materials with particles measuring tenths of a nanometer has almost revolutionized the plastics industry with respect to its production and applications (Rosamah *et al.*, 2018). Nanocelluloses which are nano-structured cellulose (CNC or NCC, CNF) have been reported use nanotechnology through hydrogel or aerogel in which the liquid component for the gel has been replaced with a gas for water purification. As a result of their biodegradability, excellent thermal and mechanical properties couple with low density and high aspect ratio, CNCs stand the potential candidate to replace the toxic or non-biodegradable materials mostly in the composite industry. Although one of the main challenges restraining the usage of CNCs in polymer biocomposite is hydrophilicity which is being addressed by altering its surface chemistry to improve its compatibility with hydrophobic matrices. As a result of the excellent properties and eco-friendliness of the nanocellulose it has attracted wide research applications in fields like in the manufacture of green nanocomposite materials, material surface modification, and functional transparent paper. Therefore nanocellulose (CNF, CNC or BC) applications in green nanocomposites have been recently reported as they are better and potential candidate to provide a positive environmental impact and remarkable characteristics. The summary of the recent research efforts in the area of nanocellulose applications is summarized in Table 3.

Table 3 Summary of recent advances in nanocellulose-thermoplastic composites

Nanocellulose type	Polymer component	Manufacturing technique	Applications
CNCs	Methylcellulose	Hydrogel by aqueous dispersion	Thermoreversible and tunable nanocellulose based hydrogels
	Plasticized starch	Solution casting	Transparent materials
	Starch blending	solution casting	Air permeable, resistant, surface, sized paper, food packaging
	PVA	Solution casting	Stretchable photonic devices, conductive materials
	Plasticized PLA	Twin screw extruder	Film blowing, packaging Wound diagnosis/ biosensor scaffolds
	Maleic anhydride grafted PLA	Electrospinning	Bone tissue engineering
	Cellulose esterified with lauroyl chloride	Solution casting and thermopressing	Interface melting
	PC	Matsterbatch melt extrusion process	Optical devices
	PC based polyurethane blend	Solution casting	Smart actuators and sensors
	Ethylene-co-vinyl acetate rubber	Solution mixing and vulcanization	Transparent, rubbery materials
CNFs	PU	Solution casting	High temperature biomedical devices
	Polyethylene glycol	PEG-g-CNF ribbons by stretching hydrogel	Ultra-high tensile strength and modulus for optoelectronic and medical devices
	Amorphous dialcohol cellulose	Oxidation + reduction of CNF	Surface Barrier films
	Polyethylene	Extrusion	High performance cellulose, environmentally friendly HDPE
	Thermoplastic starch	Solution Casting	Evaluation of cotton filler in LDPE
	Maize amylopectin	Solution casting	thermally stable starch
	Polyvinyl amine	Layer by layer	Continuous papermaking
	Polyacrylamide	Solution casting	Self healing polymer films
	PVA	Solution casting	Films with good mechanical, optical thermal and oxygen barrier properties
	Carboxymethyl cellulose	Solution casting	Flexible displays, optical devices, packaging and automobile windows, Food packaging
BC	Poly(butylene adipate-co-terephthalate)	Injection molding	Edible coatings and packaging materials
	Poly(ethylene oxide) based block copolymer	Solution casting	Light-weight and high performance materials for defense, infrastructure and energy
	PMMA	Solution casting	Transparent biocomposites
CNFs, CNCs, BC		Solution casting	Packaging, flexible screens, optically transparent films and light, weight materials for ballistic protection

Note: Adapted with permission from Abitbol, T., Rivkin, A., Cao, Y., *et al.*, 2016. Nanocellulose, a tiny fiber with huge applications. *Current Opinion in Biotechnology* 39, 76–88, Copyright 2014. Reproduced with permission of Elsevier.

Prospect of Green Nanocomposite

The current progressive milestone recorded in the area of green revolution in bio-composite from natural fiber with respect to environmental friendliness, has instigated further research and development of potential application of nanocellulose in green composite. This has heralded a lot of breakthroughs in this design with numerous applications. Irrespective of the reported limitations with respect to the hydrophilicity of the nanocellulose in green nanocomposite research and development and has rendered the attention on the use of petrochemical based composites unappealing due to a few challenges that bother on environmental and community pollution, waste management such as disposal, reusability and recycling problems (Abdul Khalil *et al.*, 2012). **Table 4** gives a summary some of the activities carried out under the green nanocomposite study.

The large concentration of hydroxyl groups on the surface of the nanocellulose enhances their high hydrophilic properties as a result of their enlarged surface area which enables their use as rheology modifiers mainly in paints and personal care products. Preparations of nanocellulose based hydrophobic aerogels produced from various agricultural wastes have been reported, and results showed the great tendency towards their use in water body purification. Apart from the above mentioned, green nanocomposite material is pivotal on some vital properties such as light weight low density and high mechanical properties. Nanocomposites have been used in several applications in automotive industries such as various vehicle types of door handles, door panels, instrument panels, parcel shelves, head rests, roofs, upholstery and engine covers and intake manifolds and timing belt covers. The use of green nanocomposite in impellers and blades for vacuum cleaners, power tool housings, mower hoods and covers for portable electronic equipment such as mobile phones, etc are receiving interesting attentions (Garate *et al.*, 2018). As long as the consumption of these materials continues to increase, there is bound to be new discoveries for the use of green nanocomposite. The intrinsic properties of nanocellulose which include low density with high aspect ratios facilitate the application of Nano Cellulose in green composites for the fabrication of lightweight and high performance materials. Despite the various research reports on potential and progress made in the application of green nano composite especially in the area of improvement of its commercial potential, sustainable environment should be created to compete with petroleum-based plastics, economically. Another area of paramount importance is in the area of providing cheap and affordable technology proficiency to produce the green nano composite. **Fig. 5** summarizes some prospective industrial application of nanocellulose for green nanocomposite.

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They have been widely used as reinforcement filler in the field of nanocomposites with improved barrier and mechanical properties of dry green composites and also enhance biodegradability of the prepared green composite. Various research finding

Table 4 Recent application of biodegradable fillers in green nanocomposite

<i>Green fillers</i>	<i>Application</i>	<i>Reference</i>
Chitosan	Biopolymer – Clay Nanocomposites Based on Chitosan Intercalated in Montmorillonite	(Darder <i>et al.</i> , 2003)
Plant oils	Microcrystalline cellulose: Isolation, characterization and bio-composites application – A review	
Poly(3-hydroxy butyrate)	A first insight on composites of thermoplastic starch and kaolin	(De Carvalho <i>et al.</i> , 2001)
Thermoplastic starch	Preparation and properties of biodegradable thermoplastic starch/clay hybrids	(Park <i>et al.</i> , 2002)
Cellulose	Effect of compatibilizer on nanostructure of the biodegradable cellulose acetate/organoclay nanocomposites	(Park <i>et al.</i> , 2004)
Gelatine	Gelatine/montmorillonite hybrid nanocomposite. I. Preparation and properties	(Zheng <i>et al.</i> , 2002)
Poly(lactide)	Structure and thermal/mechanical properties of poly(lactide)- clay blend	(Ogata <i>et al.</i> , 1997)
Chitosan Cellulose nanofibers	Nanocellulose reinforced chitosan composite films as affected by nanofiller loading and plasticizer content	(Azeredo <i>et al.</i> , 2010)
Cellulose nanofibers	Particle board and oriented strand board prepared with nanocellulose-reinforced adhesive	(Veigel <i>et al.</i> , 2012)
Cellulose nanofibers	Transparent nanocomposites based on cellulose produced by bacteria offer potential innovation in the electronics device industry	(Nogi and Yano, 2008)
Nano crystalline Cellulose	Nanocrystalline cellulose (NCC): A renewable nano-material for polyvinyl acetate (PVA) adhesive	(Kaboorani <i>et al.</i> , 2012)
Cellulose nanofibers	Cellulose-nanofiber-reinforced poly (lactic acid) composites prepared by a water-based approach.	(Wang and Drzal, 2012)

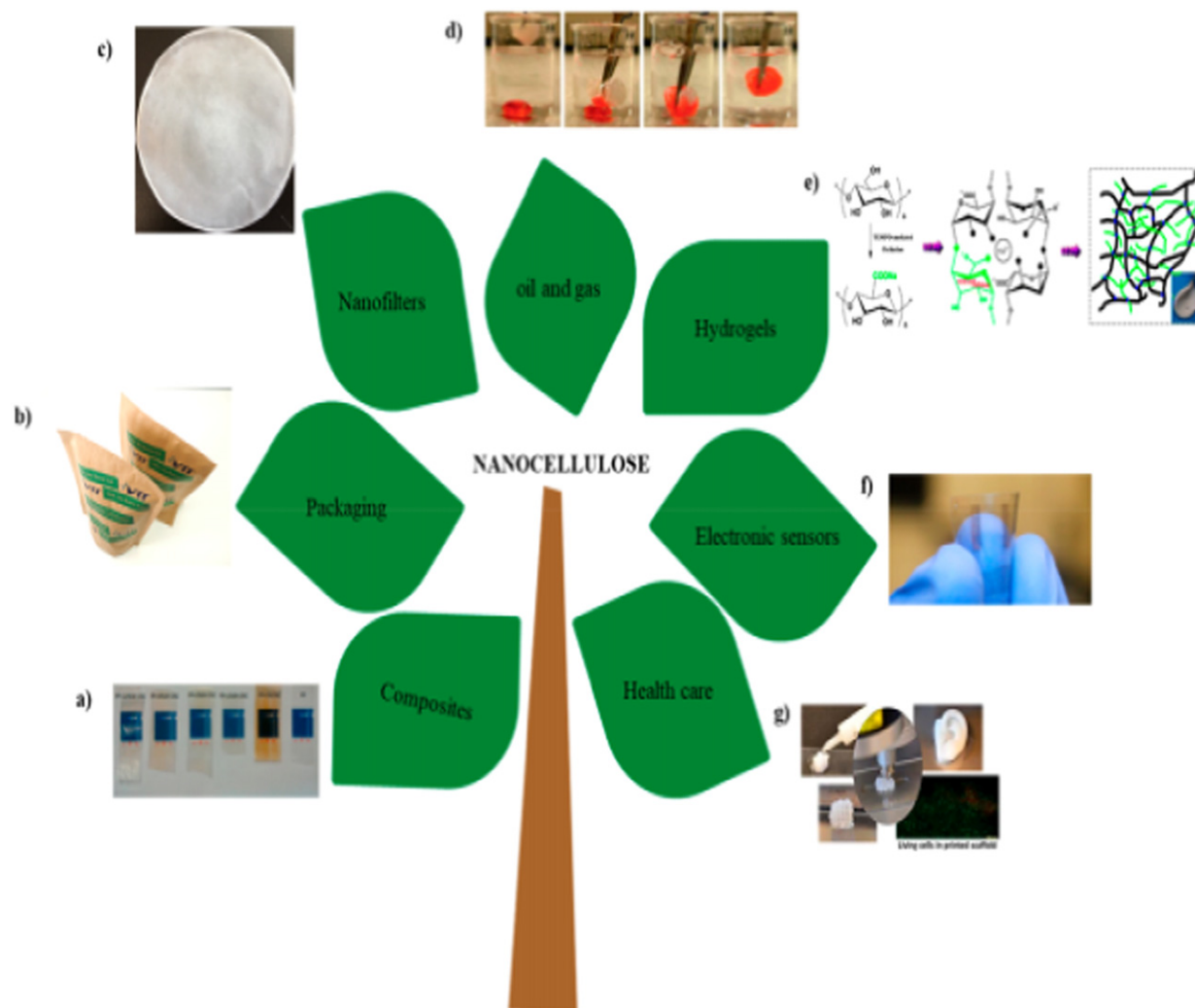


Fig. 5 Multitude of applications of nanocellulose. Adapted with permission from Rajinipriya, M., Nagalakshmaiah, M., Robert, M., Elkoun, S., 2018. Importance of agricultural and industrial waste in the field of nanocellulose and recent industrial developments of wood based nanocellulose: a review. *ACS Sustainable Chemistry and Engineering* 6 (3), 2807–2828, Copyright 2018. Reproduced with permission of Copyright © 2018, American Chemical Society.

have reported the excellent mechanical strength enhancement of the nanocomposite addition in polymer matrix. According to the literature reports, nanocellulose extracted of soyabean gave significant improvement in the mechanical properties when used to reinforce synthetic polymers (Abdul Khalil *et al.*, 2014). When used to reinforce polylactic acid, nanocellulose was discovered to enhance the mechanical properties of the composite formed (Aulin *et al.*, 2013). Green polymers so far used for the preparation of nanocomposites include chitosan (Kumar, 2018).

Conclusions

The recent attention on the use of biodegradable polymer in various industries due to economic and environmental consideration have given rise to the interest in green nanocomposite which has gained wide range of applications in food packaging, fibers, automobile, hydrogels, or aerogel biomedical, transparent films, and agriculture fields. In green composite and sustainable materials, nanocellulosic materials have played significant role based on their fundamental intrinsic properties. Consequently, the previous milestone of achievement on the applications of nanocellulose (CNCs, CNFs, and BC) in various fields of manufacturing has not been exhaustively researched based on sources and applications. They are considered better replacements for petroleum-based products in terms of ecology and economical issues. There are still possibilities of more discoveries based on the abundance of the array of sources which may no longer be of concern but the cost of production. It is obvious that there is abundant window of opportunities for unraveling the potentials in nanocellulose as potential candidate for solving more problems in the industries

and assist researchers in tackling more imminent challenges in the field. Plant sourced nanocellulose has been shown to have unique characteristics such as high crystallinity, aspect ratio, Young's moduli, and tensile strengths, which originate from the properties of natural wood cellulose microfibrils. The ubiquitous cellulose with unique flexible properties to replace the synthetic and petrol chemical materials is of particular interest for the future application.

See also: Bacterial Cellulose Based Nanocomposites for Electronic and Energy Applications. Cellulose Nanocrystal as a Prospective Reinforcement for Polymer Matrix Nanocomposites. Eco Friendly Flocculants: Synthesis, Characterization and Applications. Green and Sustainable Manufacturing of Metallic, Ceramic and Composite Materials. Green Manufacturing: Progress and Future Prospect. Nanocellulose Based Aerogels for Varying Engineering Applications. Palm Oil Fuel Ash: Innovative Potential Applications as Sustainable Materials in Concrete

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Kenaf Fiber Reinforced Composite in the Automotive Industry

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Part 1 – Background

Historical Usage of Kenaf

Kenaf (*Hibiscus cannabinus* L., Malvaceae) is a warm season yearly fiber crop closely associated with cotton (*Gossypium hirsutum* L., Malvaceae) and okra (*Abelmoschus esculentus* L., Malvaceae), which can be grown effectively in a big part of the field. The commercial use of kenaf continues to diversify from its historical usage as a cordage crop (rope, string, and sackcloth) to its various new applications, including paper products, construction materials, absorbents, and livestock feed.

Kenaf has been utilized as a cordage crop to create twine, rope, and sackcloth for more than six centuries (Dempsey, 1975). Kenaf was first trained and utilized in Northern Africa. India has delivered and utilized kenaf throughout the previous 200 years, while Russia began creating a war in 1902 and introduced the product to China in 1935. In the United States, kenaf research and creation started amid World War II to supply cordage material for the war effort (Wilson, 1965). The war did not just intrude on the remote fiber supplies from nations like the Philippines. However, the US inclusion in the war had additionally expanded the utilization of these strands by the US. It was resolved that kenaf was a reasonable harvest for US use, so an experiment was initiated to augment US kenaf yields. Subsequently, researchers successfully grew high-yielding anthracnose-safe cultivars, instituting social practices and gathering apparatus that expanded the fiber yields (Nieschlag, 1960; Wilson, 1965; White *et al.*, 1970). At that point during the 1950s and mid-1960s, as USDA specialists were assessing different plant species to satisfy future fiber requests in the US, it was resolved that kenaf was a superb cellulose fiber hotspot for an expansive scope of paper items (newsprint, bond paper, and layered liner board). It was additionally confirmed that pulping kenaf required less vitality and concoction contributions for preparing than standard wood sources (Chark, 1962). Later, innovative work during the 1990s showed the plant's appropriateness for use in building materials (particle sheets of different densities, thickness, with flame and insect resistance), adsorbents, materials, animal feed, and filaments in new and reused plastics (infused, shaped, and expelled) (Webber and Bledsoe, 1993) (Fig. 1).

Harvesting and Processing

The assessment of strategies for harvesting kenaf keeps on being a critical part in commercialization. The harvesting technique relies on the production area, the gear accessibility, processing strategy, and utilization of the final product.

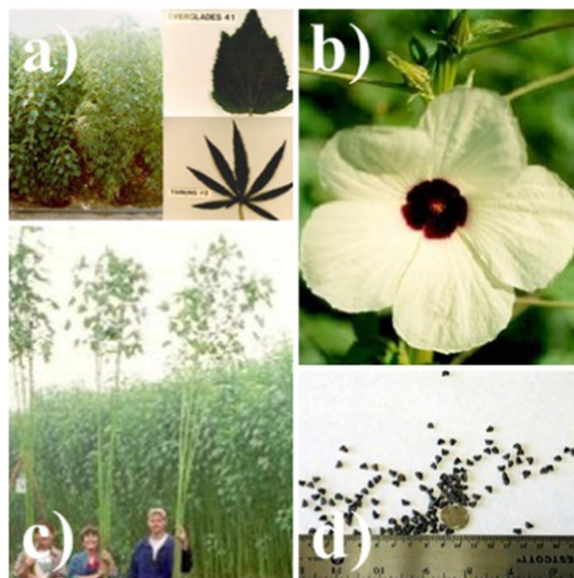


Fig. 1 Plant components. (a) Leaves and plants of kenaf. (b) Kenaf flower. (c) Kenaf stalks at harvest, 150 days after planting. (d) Kenaf seed. From Webber III, C.L., Bledsoe, V.K., Bledsoe, R.E., 2002. Kenaf harvesting and processing. In: Janick, J., Whipkey, A. (Eds.), Trends in New Crops and New Uses, vol. 9. Alexandria, VA: ASHS Press, pp. 340–347.

Harvesting

Hand harvesting and retting for cordage fiber

Over the last 6000 years, since its first domestication, kenaf has systematically been hand-harvested to be used as a cordage crop (rope, twine, and sackcloth) (Dempsey, 1975). The bast strands, settled within the kenaf bark, are the supply for these cordage products. Once hand-harvested, the tall, cylindrical-shaped stalks were cut at or close to ground level with an arched blade or knife. The hand-harvested plants were then ready for the retting method. Retting is a method that sometimes involves moisture with bacteria or chemicals, to get rid of the unwanted bark material from the kenaf fiber strands among the bark. Kenaf was retted by natural processes that use primarily aerobic (air loving) bacteria, unlike water-retting of flax that is carried primarily by an anaerobic bacteria and varied fungi. The entire stalk kenaf (bark and core still attached), or solely the bark parts, are tied in bundles and placed in pond canals, or slow-moving streams to permit the bacteria to digest the material around the bark's fiber strands (bast fibers).

The plant material status before retting influences the water-retting potency for kenaf. Removing the higher, nonfibrous portion of the plant before the retting method will increase the retting rate by decreasing the quantity of leaf and material to be digestible. Whether or not the higher portion of the plant is removed, the setting method will be redoubled if the plants are allowed to dry for 24–48 h after harvesting to enhance defoliation. Removal of the bark from the stalk conjointly makes the retting method more economical. Once drying has occurred, the bark will adhere more aggressively to the stalk core and bast fibers will also be more difficult to separate from the nonfibrous material in the bark. In addition, drying the bark while either attached to or separated from the stalk will impede the water-retting process. Though the natural water-retting (bacterial) method remains to be used throughout several parts of the world, newer chemical retting processes were studied, developed, and enforced to supply fibers of superior chemical and physical uniformity (Dempsey, 1975; Ramaswamy, 1999). The analysis determined that hand-stripped green bark ribbons and automatically separated bark material could be effective with chemicals retted by using 7% and 1% sodium hydroxide, respectively, to produce decent textile quality fibers from kenaf.

Processing

Early processing methods and equipment will be dependent on several factors, such as the assembly location, equipment accessibility, the economic variables concerned, and the available industrial markets. One of the primary process selections is whether the whole stalk, either as an unmodified stalk or as a chopped stalk, will be separated into its bast and fiber components or left unseparated for use as a combined fiber source. Many existing industrial kenaf facilities automatically separate the two fiber elements by totally different ways with distinct process efficiencies, employing a variety of equipment with variable rates of outturn, leading to variable degree of fiber separations. Every separation system conjointly has distinctive economic ramifications that support its integrated production, harvesting, processing, and utilization systems. One methodology of fiber separation adapts unused machine facilities that are scattered throughout the southern region of the United States to process the kenaf fibers. The improved equipment and facilities give outstanding machinery for separating the kenaf core material from the bast fibers, exactly like the strategy used by the cotton gin method to separate oilseed from the cotton fibers. Since the amount of active machine facilities is decreasing with the decline in cotton production, unused gin facilities are obtainable for changing to kenaf separation facilities.

Kenaf Fiber in Technical Applications: Market and Trends

Kenaf (*H. cannabinus* L.) is a plant very similar to jute, and in production statistics, it is usually confused with jute. Moreover, another example of the polysemic use of the word *hemp*, kenaf is usually called “ambary hemp.” According to world production of kenaf and allied fibers was around 340,000 t in 2007/08, down from 430,000 t in 2002/03. The largest 2007/08 producers were India (140,000t), followed by China (87,000t) and Thailand (36,000t), and in all three countries, kenaf is on the decline. According to news reports, kenaf may experience a renaissance nevertheless, specifically in technical applications (Adnan, 2010; Shimbun, 2003), as there is a selected downside with jute for an exposed use, for instance within automotive interiors, which makes kenaf a perfect substitute. To make the jute fibers more elastic and softer, which improves the carding and spinning process, they are usually pretreated with a mineral oil-based so-called jute batching oil, which has a lot of potential for migration, ends up with an oily or fishy smell, and was reported to be carcinogenic (Mehrotra et al., 1988).

Part 2 – Kenaf Fiber Composites in The Automotive Industry

Recently, natural fibers have become more attractive in the automotive industry as an alternative reinforcement for glass fiber reinforced plastics. Furthermore, natural fiber components in the automotive industry can provide many advantages as compared with conventional fibers, such as reduction of weight and price, recyclability, renewability, and eco-efficiency. Therefore, the employment of natural fibers within the automotive industry has shown progressively rigorous environmental criteria (Hassan et al., 2017). Besides, amongst classified bast fibers, such as flax, hemp, jute, ramie, and kenaf, kenaf fiber is seen as a potential natural fiber with sturdy mechanical properties. Kenaf fiber had been explored to enhance desired mechanical properties as automotive structural elements.

Automotive production rate has improved and it has been predicted that 76 million cars will be produced annually by 2020. For that purpose, utilization of biocomposites will lead to major reduction in the weight of vehicles and emissions. And yet, it is estimated that a 25% reduction in automobile weight would correspondingly save 250 million barrels of crude oil (Ranjan *et al.*, 2013). Because of this significance, the automotive industry is meeting these challenges by improving recyclability of recently created and manufactured bio-based products that use domestic natural resources, particularly for the body of cars to achieve weight reduction (Alves *et al.*, 2011; Chen *et al.*, 2005; Jeyanthi *et al.*, 2012). For example, natural fiber composites with thermoplastic and thermoset matrices were embraced by European automobile manufacturers and suppliers for door panels, seat backs, headliners, package trays, dashboards, and interior elements (Holbery and Houston, 2006). Natural fiber reinforced composites are primarily used as low-cost materials that have been utilized in applications like automotive interior linings (Fiore *et al.*, 2015).

Natural fibers have gained revived interest, particularly as a glass fiber substitute in the automotive industry (Mohanty *et al.*, 2005). Commonly, natural fibers may be classified into animal, plant, and mineral sources. Among the three kinds of classification, the natural plant fiber has a lot of potential. According to the plant class, the fibers are extracted, such as bast, leaf, seed, wood, fruit, and straw. Among these, bast fibers have low density and better mechanical properties, thus the opportunity for reinforcements in lightweight composite for automotive parts (Salit, 2014). Bast fibers are derived from flax, hemp, jute, ramie, and kenaf. They provide automobile part reinforcement, owing to such drivers as reductions in weight, cost, and eco-friendliness (Holbery and Houston, 2006). Once an eco-design is taken into account, environmental data with mechanical behavior is progressively being requested too.

A significant current advancement in this field has been the presence of biocomposites, which combine good mechanical performance and low environmental impact (Le Duigou *et al.*, 2014). Due to the attention on environmentally friendly material, natural fiber reinforced polymer composites have increased excellent attention and interest among material scientists and engineers for their mechanical properties and potential contributions (Azwa *et al.*, 2013). They are renewable, cheap, totally or partly recyclable, and biodegradable. They are materials with highly specific strength and modulus, low prices, recyclable, and effortlessly obtainable in some countries (Azlan and David, 2011). Amongst the stated fibers, kenaf (*H. cannabinus* L. family Malvaceae) is one of the strong and stiff agro-based fibers and has adequate potential to reinforce polymers.

Due to the light weight of kenaf fiber composites, the fuel consumption and emission are improved, particularly in the automotive industry. Table 1 shows the dimensions of kenaf fibers for the outer part (bast fiber) and the inner part (core fiber). Each element showed improved mechanical properties even with a different dimension. Comparing with different kinds of plant fiber, kenaf fiber has more potential because both parts of kenaf, bast and core, give good mechanical performance. It is different with other fibers, where only the outer part gives good performance and some fibers only have an inner part that can be used. Considering these advantages, kenaf tends to be grown as another potential natural fiber that can be a substitute for glass fiber within the automotive industry.

Table 2 displays the comparative properties of density, strength, modulus, and elongation at break between kenaf fiber and glass fiber. Glass fiber presents a dominant value for each property, and is widely applied in automotive components. However, kenaf fiber has some advantages over glass fiber in terms of cost, density, renewability, recyclability, abrasiveness, and biodegradability. Improvement in composite properties depends on the fiber-matrix interface, and this contributes to transfer stress from the matrix to the fiber.

Table 1 Fiber dimensions of kenaf fiber

Properties	Bast fiber	Core fiber
Length (mm)	2.32	0.74
Diameter (μm)	21.9 ± 4.6	22.2 ± 4.5
Lumen diameter (μm)	11.9 ± 3.4	13.2 ± 3.6
Cell wall thickness (μm)	4.2 ± 0.8	4.3 ± 0.7

Source: Hassan, F., Zulkifli, R., Ghazali, M.J., Azhari, C.H., 2017. Kenaf fiber composite in automotive industry: An overview. *International Journal on Advanced Science, Engineering and Information Technology* 7 (1), 315–321.

Table 2 Comparison properties of kenaf and glass fiber

Properties	Kenaf fiber	Glass fiber
Density (g/cm^3)	1.4	2.5
Strength (MPa)	284–800	2000–3000
Modulus (GPa)	21–60	70
Elongation at break (%)	1.6	2.5

Source: Jeyanthi, S., Jeevamalar, J., Jancirani, J., 2012. Influence of natural fibers in recycling of thermoplastics for automotive components. In: *Proceedings of the International Conference on Advances in Engineering, Science and Management (ICAESM)*, pp. 211–214. Institute of Electrical and Electronics Engineers.

The use of natural fiber reinforcement in the automotive industry proves that it is viable in a number of automotive components. Currently, flax, sisal, and hemp are processed into door protective covering, seatback linings, and floor panels (Holbery and Houston, 2006). Prior to this, proper material selection of natural fibers and careful design ought to be carried out so as to attain a better impact behavior, particularly for core structures like the bumper beam for absorbing energy in a crash (Jeyanthi *et al.*, 2012). Numerous recognized compositions of kenaf fiber with matrix and some additives can meet the automotive industry's needs for interior and exterior components as long as they are for nonstructural and semistructural applications. From Table 3, twisted kenaf fiber (Jeyanthi *et al.*, 2012) presented the performance of beams improved with hybrid kenaf/glass reinforced material. This proved that it could be employed in automotive structural components. A twisted kenaf hybrid material could be improved by optimizing the structural parameters, such as thickness, beam curvature, and strengthening ribs. Their applications in automotive components are as bumper beams and front-end modules.

Furthermore, it is a fact that "going green" does not have to cost more. Kenaf-based auto components do not solely prove to be superior with product performance but are also saving auto companies money. Natural fiber-reinforced plastics, vegetable oil-based polyols and polyamides, bio-based polyesters, and thermoplastic elastomers are some of the bio-based materials incorporated in numerous vehicles. A DEFRA report from 2012 projected the expansion rates for biofibers in automotive components at 54% per annum. European automakers have, within the last decade, welcomed biofiber reinforced polymer composites for door panels, seat backs, package trays, dashboards, and trunk liners. In recent years, biofiber composites have become widely acceptable in North America, where virtually 1.5 million vehicles are comprised of applications for biofibers such as kenaf, jute, flax, hemp, and sisal in combination with thermoplastic polymers, such as polypropylene and polyester. The employment of kenaf is anticipated to offset 800,000 pounds of oil-based resin per year in North America alone. The employment of this eco-friendly material reduces the weight of the door bolsters by 25%. Weight savings translate into fuel savings for drivers (Fig. 2).

Besides that, the international automotive industries have been under pressure due to environmental problems, where various regulations were introduced for the sake of environmental protection. One of the problems is recycling automotive interior elements, which has become tough because most petrol-based polymer materials are mixed with composite structures. Current disposal approaches for these auto interior elements are either garbage dumps or burning, both causing environmental concerns (Yan *et al.*, 2005). Due to environmental problems, the replacement with biodegradable material like natural fiber

Table 3 Kenaf fiber composition

Composition	Findings
Twisted kenaf fiber LFRT (TKLFRT) and LFRT	Performance of beams increased
Kenaf with PFA poly(furfuryl alcohol) bio-resin	Good damping behavior
Kenaf and ramie nonwoven fiber with binder: PVA and acrylic copolymer	Enhance the performance of composite thermal and mechanical properties
Kenaf with PLA	Good esthetics and strength

Source: Jeyanthi, S., Jeevamalar, J., Jancirani, J., 2012. Influence of natural fibers in recycling of thermoplastics for automotive components. In: Proceedings of the International Conference on Advances in Engineering, Science and Management (ICAESM), pp. 211–214. Institute of Electrical and Electronics Engineers.



Fig. 2 (a) Toyota Gohsei kenaf insert molding, (b) kenaf used in the door of the new BMWi3, (c) kenaf used in Mercedes door trim, (d) hemp and kenaf materials contribute to BMW's i3's natural looking interior. From Ecotech Alliance, 2014. The Automotive Industry. Retrieved 1 December 2018, from <http://www.ecotechalliance.com/>.

reinforced composite is more preferable. At present, the use of natural fiber reinforced plastics for interior parts can be classified as low. Kenaf bast fiber is recognized to have the potential as a reinforcing fiber in plastic composites. This is often due to its superior toughness and high aspect ratio as compared to other fibers (Akil *et al.*, 2011). The utilization of kenaf fibers reinforced plastics for interior parts requires major technical attention before it is accepted as a substitute for the existing material. Most interior elements need a high standard of mechanical performance, however, it is difficult to find an ideal material that can fulfill the requirements (Nick *et al.*, 2002).

Overall, to enhance the mechanical performance of kenaf fibers as reinforcement material, it is essential to alter them into more stable materials. Among natural polymer composite for long fiber is two-dimensional (2D) woven preform, comprising two yarns, a warp yarn in the vertical direction and weft yarn in the horizontal direction that are interwoven together. The advantages of 2D woven preform are good dimensional stability in warp and weft direction, high yarn packing density, high out-of-place strength, low shear rigidity and good formability (Song *et al.*, 2012). To obtain the best-woven preform for the reinforcement in composite, consideration must be given to the strength, stiffness, and lightweight material.

Recycling and Renewability Issues of Kenaf Reinforced Composites in the Automotive Industry

Waste management is an emerging issue all over the world. This is because of the large amount of waste that is being generated daily and the impact of such waste is hazardous to the environment and living beings. With the rapidly increasing volume of vehicles, there is a parallel need to increase waste management initiatives by governments across the world and also on modern facilities for reuse and recycling of waste materials. The automobile is a major material consumer. Increasing production of vehicles is the key driver for the growth of the automobile market. The production of automobiles results in the generation of waste materials, which are recycled by many manufacturers as it helps to resolve supply shortage during the manufacturing process. The average vehicle is a mix of materials: Steel body frame, glass windows, rubber, lead batteries, and copper wires (House *et al.*, 2011). Steel is one of the most important materials in automobiles because of its toughness, durability, and malleability, but it remains very heavy, and for this reason, manufacturers have been trimming down its use. Composite materials are extending the horizons of designers in all branches of engineering. Eco-friendly biocomposites from plant-derived fiber are one of the novel materials in this era, not only as a solution to the growing environmental threat but also as a solution to the uncertainty of the petroleum supply (Mohanty *et al.*, 2000). Kenaf fiber (renewable material) reinforced nonbiodegradable polymer-based composites are gaining market demand in light of increasingly strict environmental regulations, and have thus attracted much industrial attention. Kenaf reinforced composites manage to overcome the challenge in replacing conventional glass-reinforced plastics with parts that exhibit structural and functional stability during storage and use, yet are susceptible to microbial and environmental degradation upon disposal, with no adverse environmental impact (Mohanty *et al.*, 2002). Since kenaf reinforced composites are derived from renewable resources, material costs can be markedly reduced with their large-scale usage. Their unique balance of properties would open up new market development opportunities for various biocomposites in the 21st century "green materials" world.

Future Prospects of Kenaf Fiber in the Automotive Industry

Kenaf fiber provides a lot of benefits to both the automotive industry and environment, such as minimized dependency towards nonrenewable energy/material sources, lower pollutant emissions, lower greenhouse gas emissions (Begum and Islam, 2013), increased energy recovery, end of life biodegradability of components (Akil *et al.*, 2011), reduced fuel consumption, and reduced weight of vehicles. Even though the advantages of kenaf fiber give specific benefits to the environment, all these properties should be supported by a quantitative analysis. In this aspect, Joshia *et al.* stated three comparative life cycle assessment studies to assess the overall environmental performance. This research led to specific applications, and analysis in the study showed that natural fiber composites are environmentally suited to replace the conventional fiber composites on most midpoint indicators. Drivers of superior environmental performance are expressed from the comparative analyses below (Begum and Islam, 2013):

- Less environmental impact from natural fiber production as compared with glass fiber production.
- Substitution of the matrix (synthetic polymer) by a higher content of natural fiber in the composite.
- Improvement of fuel efficiency and less used phase emissions due to weight reduction.
- Energy and carbon credits from the end of life incineration of natural fibers.

Reinforced plastics based on natural, primarily plant-derived substances show the promise of providing this and may become one of the material revolutions of this century. The automotive industry is one of the industries that need the "green" composites the most so as to produce vehicles with less weight and fuel efficiency. Faced with the pressure to produce fuel efficient and low polluting vehicles, the industry has utilized fiber reinforced plastic composites to make lighter products. However, fabricating the composites is energy intensive and polluting, while the durability of conventional composites is often seen as an advantage. Glass, carbon, and aramid fiber reinforced polyester, epoxy, and other similar resins are difficult to recycle and hard to dispose of, and so will remain on Earth for hundreds to thousands of years.

Conclusion

Based on the evaluation, biocomposites manufactured from kenaf fibers have received continual acceptance by industries around the world, even though it has not been rapid. Kenaf biocomposites have a promising potential to substitute petrol-based composites like glass-fiber composite as they have comparable mechanical and physical properties to the latter. In some countries, biocomposite technology is relatively new; however, it has a bright future to grow through constant research and development as well as ingenious commercialization strategy. Approaching manufacturers and helping them to implement good biocomposites production process to attain high-quality biocomposites is crucial. To ensure a continuous supply of high-quality kenaf fibers to meet the rising demand of kenaf biocomposites, the upstream is also required to practice better kenaf plantation procedures. Both upstream and downstream need to work together meticulously to ensure persistent development and acceptance of kenaf fiber-based biocomposites in various applications.

See also: Kenaf Fiber Based Bio-Composites: Processing, Characterization and Potential Applications. Natural Fiber Composites: Review of Recent Automotive Trends. Recycling of Flax Fiber Towards Developing Biocomposites for Automotive Application From a Life Cycle Assessment Perspective. Renewable Agricultural Fibers as Reinforcing Fillers in Plastics: Mechanical Properties of Kenaf Fiber-Polypropylene Composites. Renewable and Sustainable Materials in Automotive Industry. Renewable Biofuels and Their By-Products for Automotive Applications

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Lignin: A Renewable Raw Material

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Introduction

The name *lignin* is derived from the Latin term *lignum*, which means wood (Calvo-Flores *et al.*, 2015). It was introduced by the Swiss botanist A. P. Candolle (1778–1884) in 1819 (Jouanin and Lapierre, 2012). Under the name *lignin* we can find a group of plant-derived polymers with diverse structures (Huang *et al.*, 2019).

Lignin plays a multifunctional role in plants: It has a structural function giving rigidity and hardness to plant tissues. In addition, lignin plays an important biological function, because it forms an effective defensive barrier against insects and fungi attacks, allowing the efficient transport of water in the vascular tissues and it prevents the absorption of water by other plant components as polysaccharides in plant cell walls (Huang *et al.*, 2019; Liu *et al.*, 2018).

Lignin is the second most abundant organic substance in plants, and constitutes 30% of the nonfossil organic carbon in nature, and it is the natural raw material with the highest content of aromatic moieties (Huang *et al.*, 2019).

Chemically, lignin is a randomly cross-linked, aquiral polymer, formed mainly by three units with a phenolic core, known as monolignols. Monolignols are joined to some carbohydrate moieties to form an amorphous structure (Calvo-Flores and Dobado, 2010).

The three basic monolignol constituents of lignin are p-Coumaryl alcohol, Coniferyl alcohol, and Sinapyl alcohol abbreviated as M1_H, M1_G, and M1_S, respectively (Fig. 1). The three basic monolignols have a common origin: The phenylalanine molecule. The three major phenolic structures are present in the polymer and they form p-Hydroxyphenyl (H), Guaiacyl (G), and Sinapyl (S) residues. In addition, other less abundant monolignols have been detected in the polymer (Li and Chapple, 2010).

Free monolignols in plants are not abundant, but rather exist as glycosylated derivatives of the former monolignols, which can be transported in the plant and stored in lignifying tissues. Glycosylated derivatives of monolignols are synthesized in plants by an enzymatic process between glucose-uridine diphosphate molecule and the corresponding monolignol (Calvo-Flores and Dobado, 2010; Wang *et al.*, 2013b). The polymerization process in plants is known as lignification (Wang *et al.*, 2013b).

It is very important to point out that there is not a unique lignin in nature. There are remarkable structural differences depending on the plant species (Liu *et al.*, 2018).

In addition, in the paper industry, as a result of pulping process, a family of by-products called lignin are obtained every year (Gratzl and Chen, 1999; Zhong and Nie, 2018).

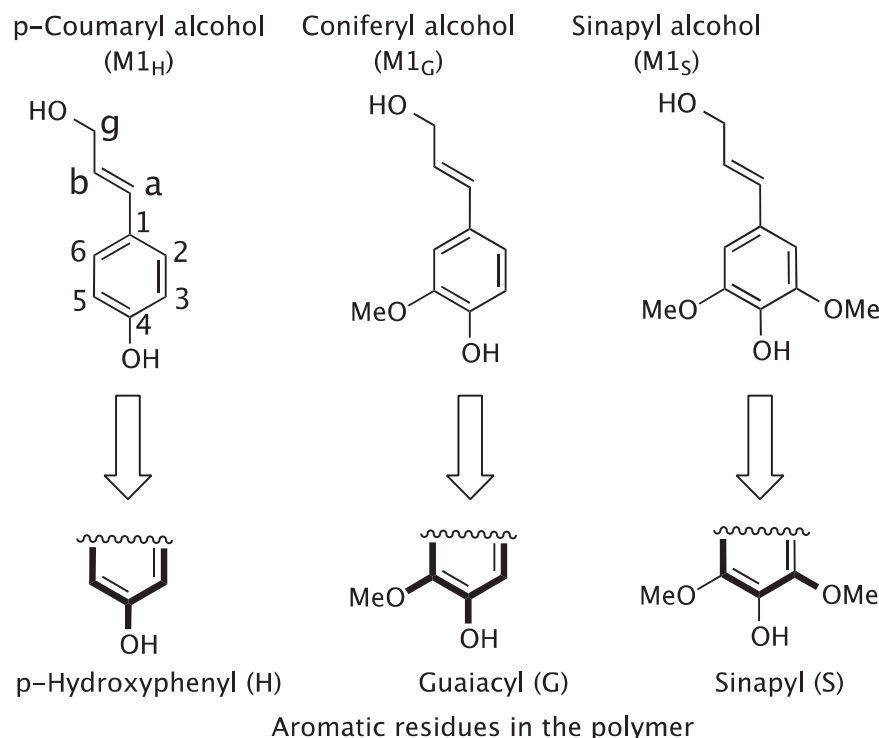


Fig. 1 Monolignols and aromatic residues in lignin.

Table 1 Proportions of monolignols in wood and herbaceous plants

Type	<i>p</i> -Coumarin alcohol	Coniferyl alcohol	Sinapyl alcohol
Softwood	<5%	>95%	0%
Hardwood	0%–8%	25%–50%	45%–75%
Herbaceous plants	5%–55%	35%–80%	20%–25%

Because of the structural diversity of lignin, it would be more precise to talk about lignins as a family of randomized polymers formed in plants and as a by-product of the paper industry with different functional groups depending on the pulping processes and the reactions that take place in such procedures.

Natural occur lignins (native lignins) can be classified according to two criteria: Plant taxonomy and the rate of basic phenolic units (Barros *et al.*, 2015; Espiñeira *et al.*, 2010). Considering the first criteria, lignins can be divided in three categories (Zhou *et al.*, 2016):

- (1) Angiosperm lignins (hardwood plants)
- (2) Gymnosperm lignins (softwood plants)
- (3) Grass lignins (herbaceous plants)

This classification has shown many exceptions; for this reason a more robust criteria has been developed on the basis of the abundance of the basic phenolic moieties in the polymer (Espiñeira *et al.*, 2010; Hatfield and Vermerris, 2001):

- (1) Type-G
- (2) Type-G-S
- (3) Type-H-G-S
- (4) Type-H-G

In case of softwood and hardwood, lignin is preferentially type-G and type-G-S respectively. For herbaceous plants lignin is basically type-H-G-S. However, proportions of monolignols are variable in every group, and very dependent on the species (Patil *et al.*, 2016) (Table 1).

The diversity of lignins arise from two facts: The different types and proportions of monolignols in the polymer and the different ways that monolignol linkages are produced, which lead to several C–C and C–O.

Monolignols play the role of building blocks but they are joined with several types of linkages. In consequence, different C–O and C–C bonds may be formed between monomers.

Fig. 2 shows some C–O and C–C bonds between monomers.

- (1) Monolignols represented on the right are noted with primes (')
- (2) The carbon atoms linked to another carbon chain are named with number 1
- (3) Carbons of side chains are named with α , β , and γ , starting with the closest atom to the aromatic ring

According to this nomenclature only eight types of bond arrangement show significance:

- (1) β - β' , β -1' and 5-5' for carbon–carbon bonds
- (2) β -O-4, α -O-4', and 4-O-5' for carbon–oxygen bonds
- (3) β -5'/ α -O-4', β - β' / α -O- γ' for carbon–carbon and carbon–oxygen bonds

Several phenylpropane type linkages have been described for carbon–oxygen and carbon–carbon bonds.

According to this data, some structural models for native lignin have been developed for softwood lignin (Neish, 1968; Glasser *et al.*, 1976; Adler, 1977) and for hardwood lignin (Nimz, 1974). In all cases such models must be considered as approximate because of the diversity of methods for taking information and structural data of the fragments.

Physical and Chemical Properties of Lignins

As any other biopolymer, lignin has been studied through the years to determine their properties and their structure. The main reports about their physical and chemical properties are related to:

- (1) Molecular weight
- (2) Dispersity index
- (3) Solubility
- (4) Thermal properties

Molecular Weight

Molecular weight (Lapierre, 1999; Vanholme *et al.*, 2010; Dong and Liu, 2012) is one of the more common parameters used for the characterization of lignin. This is a key property for the description of native lignins, but even in the present, still remains under

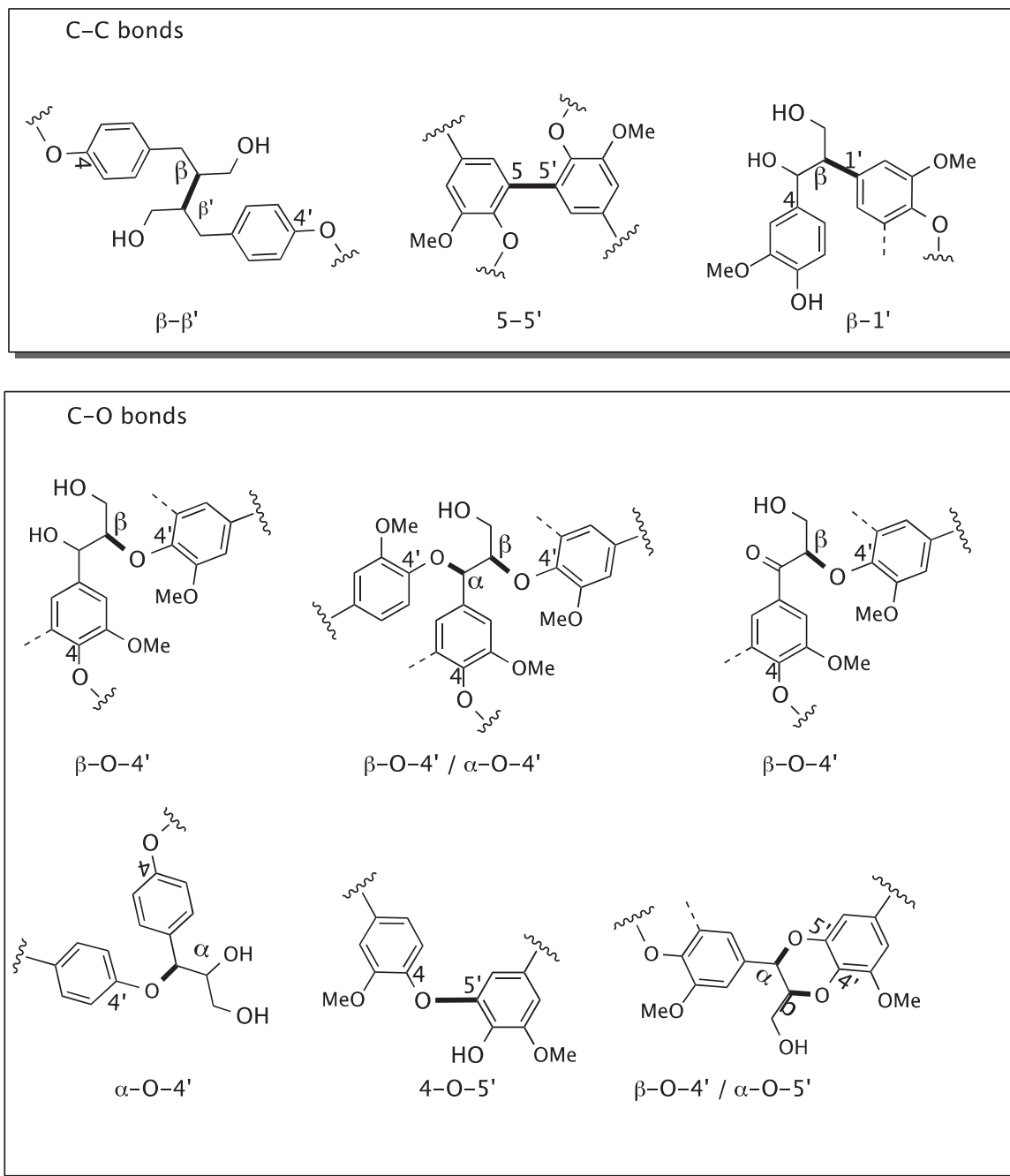


Fig. 2 Bonds formed between monomers. (top) C—C bonds, (bottom) C—O bonds.

debate because of the diversity of lignins in herbaceous plants and trees and the difficulty of sample preparation. Despite all these difficulties researchers agree in a M_w of isolated lignin in a 10^3 – 10^5 range depending on the plant species and the isolation and measuring methods. For softwood, values of M_w is greater than $2 \cdot 10^4$ and lower values for hardwood.

Dispersity Index

The dispersity index is a parameter used for the description of polymers to measure the molecular weight distribution expressed as $D_m = M_w/M_n$, when M_w is the weight-average molar mass, or molecular weight, and M_n is the number-average molar mass (Jones, 2010). Experimental data agree with the idea that soluble lignins and their derivatives show a remarkable dispersity with values that may vary from 2.5–3.0 to over 10–11, depending on the lignin origin (Brauns, 1962).

Solubility

From the first studies of lignin, solubility has been shown to be a key aspect for lignin handling (Maurer and Fengel, 1992). Native lignins obtained directly from biomass are insoluble in water and in most common organic solvents. To solubilize lignin, modifications must be performed to provide such goal. Generally it is necessary to carry out a pretreatment of lignin. In 1956 Björkman developed a technique for spruce wood that dissolves more than 50% of the lignin residue with a mixture of water-dioxane, if milled thoroughly (Björkman, 1954). Other pretreatments are based on thermal procedures, with proper solvents mixtures. Most of these procedures assume a partial degradation of native lignin into lower molecular weight fragments.

Thermal Properties

As any other polymer, lignin can be characterized by some parameters as T_g (glass transition temperature). Glass transition temperature is a parameter used for amorphous or semicrystalline polymers when they transform from a glassy state to a viscous and rubbery state. For this data, a range of values is obtained. T_g values for lignins (Irvine, 1985) from about 200°C to 500°C have been found (Laborie *et al.*, 2004).

About the Structure of Lignin

Despite the fact that lignin has been studied for decades, the understanding of such polymer has not been a simple task. The first attempts to unravel its structure were done in 1875 by Bente (1875). Those preliminary experiments showed for lignin a nature constituted by aromatic units. Other important step was when in the last decade of the 19th century Benedikt and Bamberger (1891) demonstrated that methoxy groups were an essential component of lignin. Along the years, many scientists have developed studies for the characterization of lignins, including spectroscopic methods, which have contributed to the development of “logic” models of lignin structure.

The first idea that can be extracted from such studies is the great structural diversity of lignins. Lignin is a key component of plants, and because of the vegetal kingdom’s biodiversity, lignin shows structural differences depending on the origin. There is not a unique technology capable to isolate lignin from nature or from other sources such as the paper industry. This is a real task for the valorization of lignin as a renewable raw material.

Basic Data for Determination of Lignin Structure

(1) Elemental analysis and empirical formulae

As with any other organic molecule, the elemental analysis of lignin has been carried out (Brauns and Brauns, 1960). Many researchers the last century determined the elemental composition of a variety of lignins. Some conclusions can be obtained (Huang *et al.*, 2019):

- (a) In native lignins only carbon, hydrogen, and oxygen can be found.
- (b) Average of these three elements varies depending on the source and the isolation method. Composition of lignins can be described in terms of structural units of nine atom carbons (C9).

According to experimental data, in case of milled wood lignin (MWL) for typical softwood and hardwood, the formulae are $C_9H_{8.3}O_{2.7}(OCH_3)_{0.97}$ and $C_9H_{8.7}O_{2.9}(OCH_3)_{1.58}$, respectively (Forss, 1966). It is important to remark that in such expressions, methoxy groups are highlighted because they contribute for differentiating monomer units in soft and hard woods (Sjostrom, 2013).

(2) Molecular weight determination

Molecular weight is a basic value that has been used in chemistry for characterization of any molecule, and lignin is not an exception. Despite the long time since the first studies were made, the molecular weight for lignin is still under debate, and values are not universally accepted for the same reasons that have been discussed before: The diversity of the starting material and the different methods for sampling isolation and analysis.

Four parameters are used as an approach for the concept:

- (a) Mole fraction
- (b) Weight fraction
- (c) M_n (number-average molar mass)
- (d) M_w (mass average molar mass)

In all cases, a key problem, as in any other property in lignin, is related to solubility of samples of lignins in organic solvents because almost always, an insoluble fraction remains in sample preparation, which disturbs the final results.

Common techniques used for such determinations are gel-permeation chromatography, light scattering, vapor-pressure osmometry, or ultrafiltration.

(3) Determination of functional groups in lignin

Despite the structural complexity of lignin, the analysis of native lignins has shown a relatively limited number of functional groups:

- (a) Methoxy groups (Freudenberg *et al.*, 1929)
- (b) Hydroxyl groups (phenolic and aliphatic) (Tiainen *et al.*, 1999)
- (c) Carbonyl groups (Li *et al.*, 2015)
- (d) Carboxyl groups (Lin and Dence, 2012)

The first results were obtained based on classical analytical methods:

- (1) The earlier studies of native lignin showed the presence of methoxy groups attached to aromatic moieties. The reactions used for such purpose were based on reactivity of lignin refluxing with HI to give methyl iodide, which was detected when it was treated with a solution of silver nitrate to give a solid silver iodine (Patil *et al.*, 1967). The same process may be positive when ethoxy groups are present. The percentage of methoxy groups depends on the origin of lignin and the method used for lignin isolation.
- (2) Hydroxyl groups attached to aromatic rings has been detected, for example, by acetylation of lignin followed of aminolysis. In case of aliphatic hydroxyl groups the average is calculated comparing total -OH groups detected with phenolic hydroxyl groups (Patil *et al.*, 1967; Serrano *et al.*, 2018).
- (3) The presence of carboxyl groups was detected by reaction of lignin with phloroglucinol and concentrated hydrochloric and UV spectroscopy (Speer, 1987).
- (4) Carbonyl groups in lignin have been determined chemically by calcium acetate method based on ion-exchange resin (Lin and Dence, 2012).

Characterization of Lignin by Spectroscopic Methods

Spectroscopic methods are the most reliable techniques for determining the structures of chemical substances and have carried out in the last decades an unstoppable development even for the more complex molecules as polysaccharides and proteins. Lignin has also been studied intensively by spectroscopic methods (Stark *et al.*, 2016), which has clarified many aspects of its structure, giving rise to much more precise models than those obtained exclusively by chemical methods (Sjostrom, 2013; Stark *et al.*, 2016).

Fourier-transform infrared spectroscopy (FTIR) spectroscopy, Raman spectroscopy, ultraviolet, and especially nuclear magnetic resonance of protons and carbon have been the main techniques used for structural elucidation on lignins.

FTIR spectroscopy may be used on native lignin in solid state (Faix, 1986). Very small quantities are required. Specific absorptions of the functional groups may be detected. They agree with previous results obtained with chemical tests, but information on connectivity of the fragments and moieties remains confused with this spectroscopy technique. Something parallel occurs with Raman spectroscopy or UV spectroscopy. The presence of functional groups and atom groupings can be detected, but a more approximative idea of the real structure of lignin is not possible.

The study of nuclear magnetic resonance (Chen and Robert, 1988) of protons and carbon of native lignin and fragments has contributed to give a more precise idea of lignin structure despite the fact that most chemical shifts for protons are observed in a rather limited range and the low abundance of ^{13}C nucleus that suppose long acquisition times for sample analysis.

Even with such limitations, very useful information about lignin structure may be obtained as a real ratio of monolignols in polymer and their connectivity.

Models of Lignin

Hardwood models

There is not a unique model that can properly describe hardwood lignin. Many studies have shown significant variations in lignin, such as syringylpropane/guaiacylpropane ratio (*S/G* ratio), arylglycerol- β -aryl ether (β -O-4), degree of condensation, and elemental and methoxyl contents, depending on the hardwood species (Santos *et al.*, 2012; Hori and Meshitsuka, 1999; Shimizu *et al.*, 2012). These structural variations among species appear to be correlated to the factor syringyl/guaiacyl ratio. A new method to predict the *S/G* ratio of total lignin in wood was developed, using a calibration line established by the syringaldehyde/vanillin (*S/V*) ratio (nitrobenzene oxidation) and the *S/G* ratio (^{13}C NMR) of MWL.

Fig. 3 shows a schematic representation of lignin for hardwood species according to literature data. Some characteristic functional groups are highlighted.

Softwood models

Structural models for softwood lignin have been proposed mainly based on degradation products of native lignin (Sakakibara, 1980). As for hardwood lignin models, there is not a single model. Structural analysis of degradation products of softwood lignins obtained for several methods (for example by hydrolysis with dioxane/water and catalytic hydrogenolysis) may be performed. More than 20 different fragments obtained by this way, have shown a good concordance with the various analytical data obtained so far in the lignin chemistry. A model of softwood lignin is given in Fig. 4.

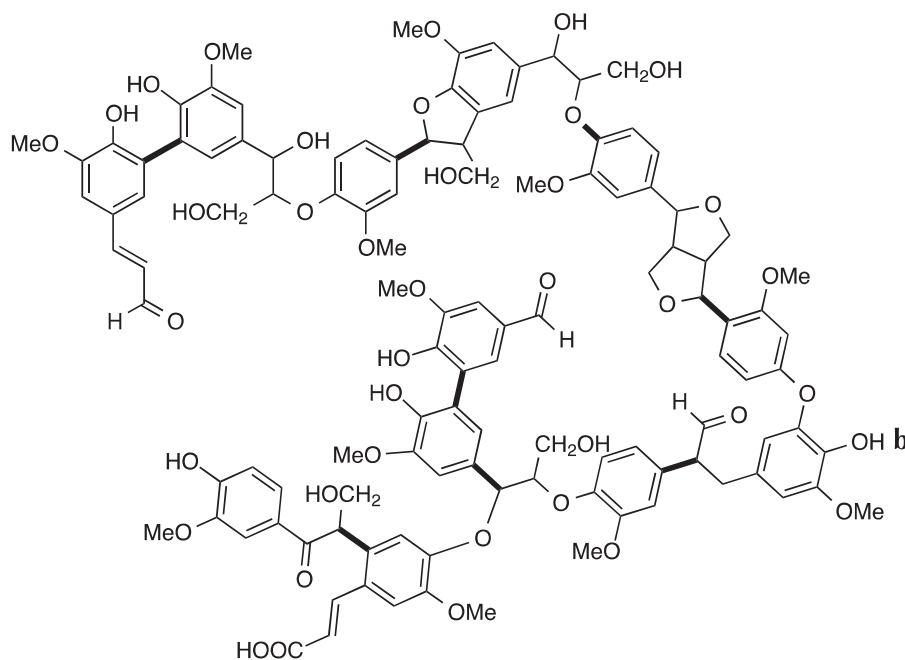


Fig. 3 Lignin for hardwood species.

Herbaceous plants models

Straw lignins of herbaceous crops (Dalimova and Abduazimov, 1994; Karmanov *et al.*, 2014) are structurally different from those of softwood or hardwoods lignins (Buranov and Mazza, 2008). They possess characteristic alkali solubility because of the availability of alkali-labile ester bonds between hydroxycinnamic acids and hemicelluloses (arabinoxylans) in lignin/phenolics-carbohydrate complexes (see Fig. 5). In addition their monomeric composition contains all three H, G, and S subunits with the H subunit up to 15% in rice straw, whereas hard and soft wood lignins contain mainly G and S subunits (except for compression wood which contains H and G units). In this regard, the lignin in flax sheaves is more similar to hardwood lignin as it contains G (75%) and S (25%) subunits.

Commercial Lignins

The so-called commercial lignins are those obtained in the paper industry, and those that can be isolated from plants. Most of them are obtained from the paper industry (Calvo-Flores and Dobado, 2010).

In the paper industry, the goal is to obtain cellulose as pure as possible for paper manufacture by the pulping process. In this procedure lignin and hemicellulose are dissolved from the lignocellulosic biomass to isolate cellulose, and the remaining lignin as a by-product must be separated. Every year a huge amount of such lignins are produced around the world (Constant *et al.*, 2016). A characteristic of such lignins is that they are chemically modified if compared with native lignin, depending on the chemicals used for pulping.

Five main groups can be described.

- (1) Kraft lignin
- (2) Sulfite lignin
- (3) Soda lignin
- (4) Organosolv lignin
- (5) Steam-exploded lignin

- (1) Kraft lignin

One of the more popular pulping processes is kraft pulping, covering greater than 80% of the pulping capacity of the paper industry (Hu *et al.*, 2018). It was developed in Germany in 1879. This method cleaves the β -O-4 linkages between the C9 units in lignin using sulfides in an alkaline environment with temperatures up to 170°C (Chakar and Ragauskas, 2004). With such pulping method, the native polymer is fragmented into lower molecular mass units. A hypothetical model of kraft lignin is given in Fig. 6 but the structure of kraft lignin is still under revision, and some relatively recent papers can be found in literature (Crestini *et al.*, 2017; Mattsson *et al.*, 2017).

Kraft lignin is produced at a rate of 40 million tons per year (Crestini *et al.*, 2017).

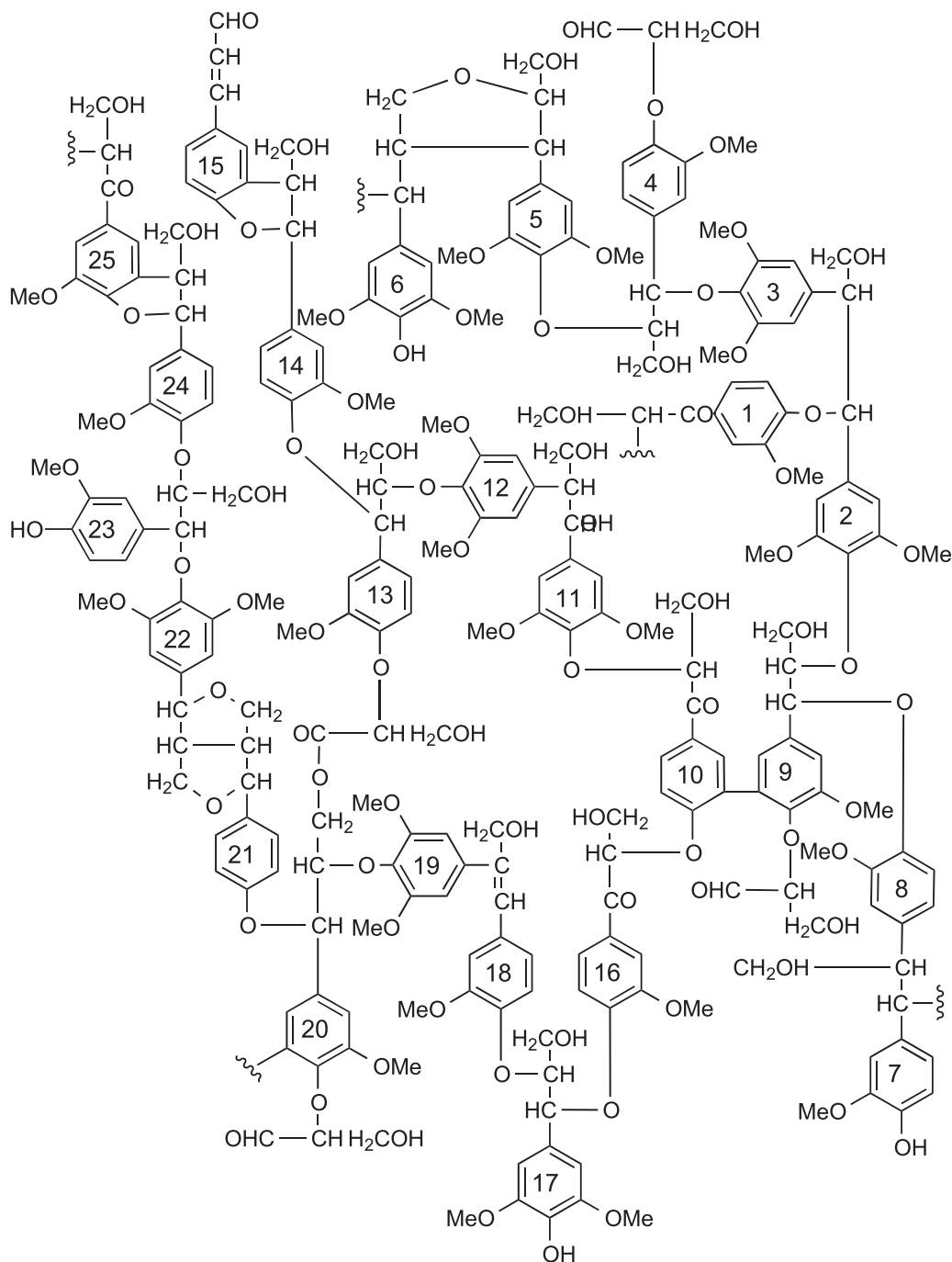


Fig. 4 Lignin for softwood species.

(2) Sulfite lignin

The acid sulfite pulping process was first developed in Germany in 1840. Lignin is dissolved by treatment with SO_3^{2-} salts or HSO_3^- in case of acidic environment, at a range of temperatures from 50°C to 160°C (Ahlm and Brauns, 1939; Gellerstedt *et al.*, 1975).

Ether bonds are broken and modified lignin is formed with $-\text{SO}_3\text{H}$ groups linked to lignin (Ahlm and Brauns, 1939). The higher number of such groups produce a higher water solubility and lignin can be separated from cellulose by washing out, but with a higher molecular weight fragments than kraft lignin (Table 2).

The sulfite lignin residue, once water is removed, has the commercial name of lignosulfonate, with an estimated production in a rate 8–10 million tons per year (Crestini *et al.*, 2017; Li and Ouyang, 2012). Structure of sulfite lignin is given in Fig. 7.

Soda pulping process used to be used for pulping of nonwood materials, such as straw, sugarcane bagasse, flax, etc., that are digested with aqueous solutions of sodium hydroxide at temperatures of 160°C or lower (Chakar and Ragauskas, 2004). The

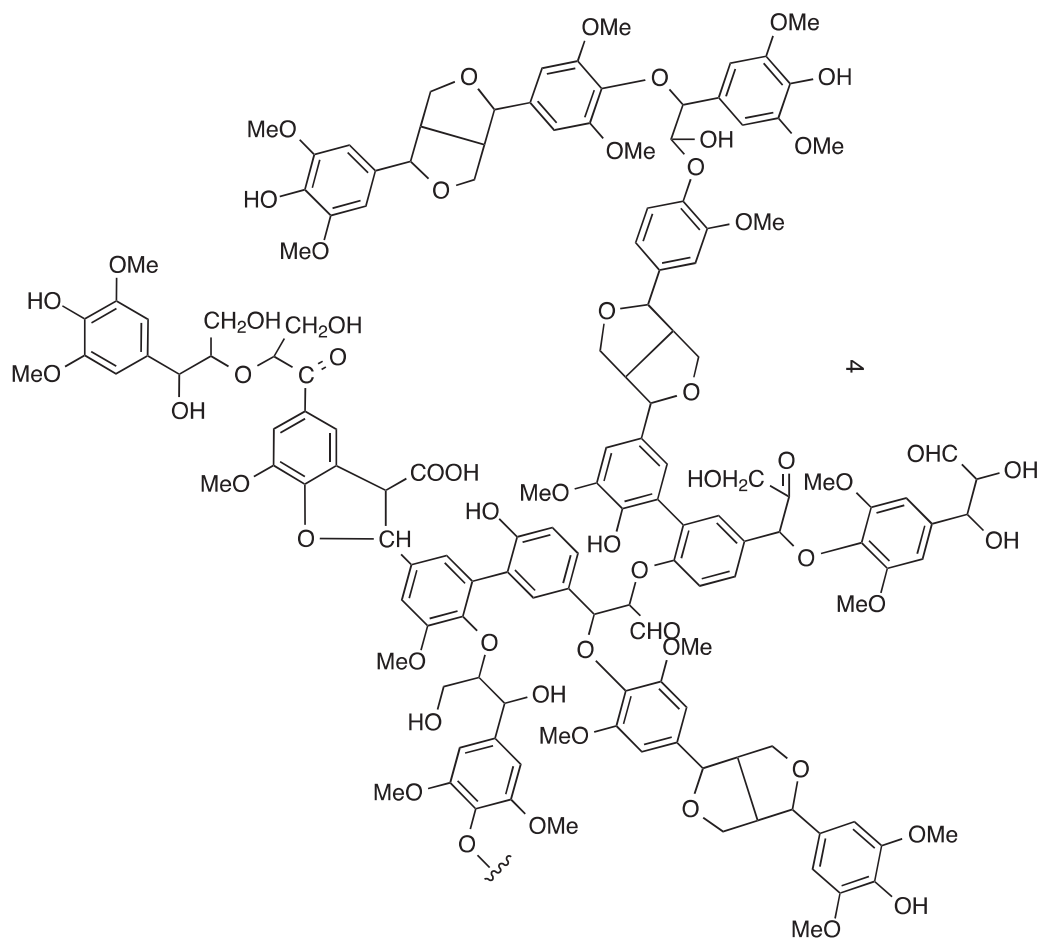


Fig. 5 Alkali-labile ester bonds between hydroxycinnamic acids and hemicelluloses (arabinoxylans) in lignin/phenolics-carbohydrate complexes.

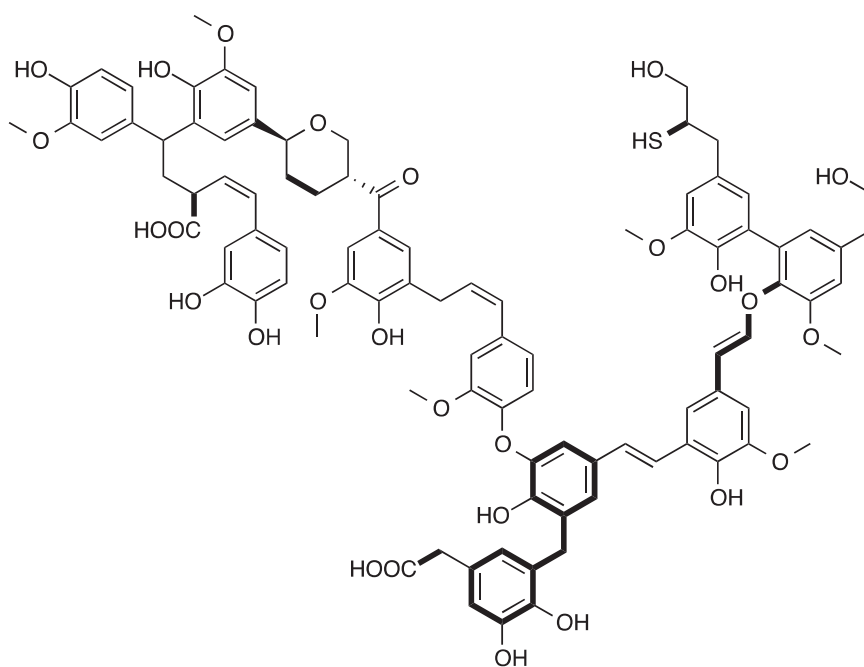
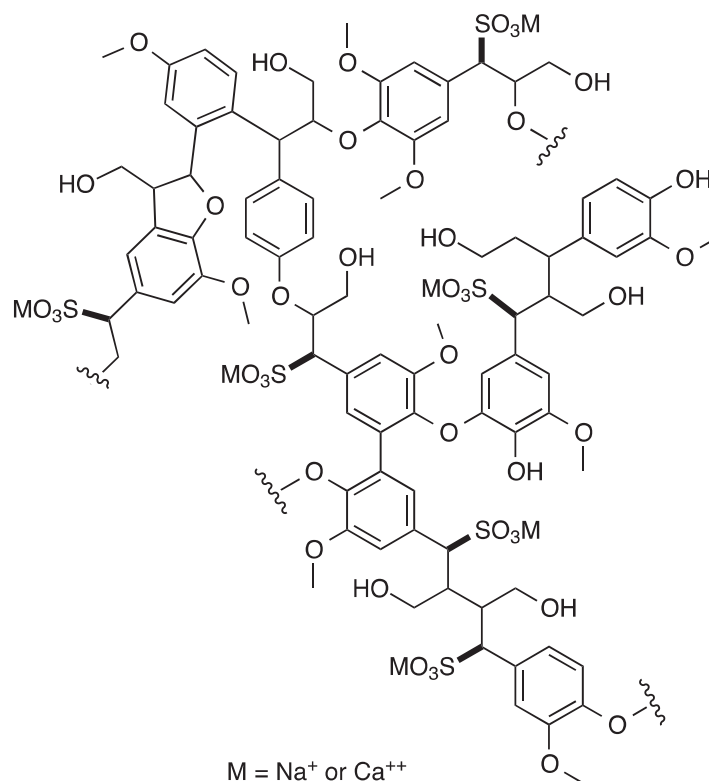


Fig. 6 Hypothetical model of kraft lignin.

Table 2 Sulfite processes

Process	Chemicals	pH range	Temperature range (°C)
Bisulfite	HSO_3^-	3–5	150–175
Neutral sulfite	$\text{HSO}_3^-/\text{SO}_3^{2-}$	6–57	150–175
Acid sulfite	$\text{SO}_2/\text{HSO}_3^-$	1–2	125–145
Alkaline sulfite/anthraquinone	Na_2SO_3	9–13	50–175

**Fig. 7** Structure of sulphite lignin.

procedure is known from 1853. There are some similarities between soda pulping and the kraft process as cleavage of lignin-carbohydrate linkages and depolymerization of the lignin and its recondensation take place. Lignin depolymerization occurs principally by the cleavage of aryl ether bonds, first in phenolic units and in a later phase of delignification in nonphenolic units. The generation of free phenolic groups in such reactions results in lignin fragments that are soluble in the alkaline environment, but insoluble in pure water. Soda lignins are significantly different from liginosulfonates, which shows lower molecular weight. Soda lignin is sulfur free and is obtained with low levels of sugar and ash contaminants.

(3) Organosolv lignins

Organosolv lignins are a group of lignins obtained by direct extraction from biomass of the polymer with organic solvents (Lindner and Wegener, 1988). Most organic solvents are used together with water and some chemicals are added to improve the yield of the process at high temperature and/or pressure (Table 2). Once the solvent treatment is performed lignin is isolated by precipitation in acidic media. All lignins isolated by such procedure are sulfur free and show a structure more similar to native lignin.

Several procedures have been described in literature. Alcohols are the most widely used solvents. Lignins extracted by such methods, use to be nominated according to the experimental process. Table 3 summarizes some of the most popular procedures that have been described. However, only Alcell and Organocell lignins are commercially available.

(4) Steam-exploded lignin

This type of lignin is obtained when wood is treated with steam at high temperature/pressure (Nonaka *et al.*, 2013; Grāvis *et al.*, 2010), and then a sudden decompression is applied in the presence of some chemicals. In these conditions a partial hydrolysis of lignin occurs, and a water-insoluble lignin is obtained with a low level of impurities. The polymer shows a slight

Table 3 Organosolv lignins and procedures

<i>Organosolv lignin type</i>	<i>Solvent/catalyst system</i>
Alcell	Ethanol/water
Organocell (Lindner and Wegener, 1988)	Pulping with methanol, followed of NaOH and anthraquinone in methanol
Acetosolv	Acetic acid/Chlorhydric acid
Acetocell	Acetic acid/water
Formacell (Lindner and Wegener, 1988)	Acetic acid/ Formic acid/Water

reduced molecular mass because partial acid hydrolysis reactions take place under these conditions. This procedure is often combined with enzymatic hydrolysis to obtain carbohydrates for fermentation reactions.

Applications of Lignins

As mentioned above, lignin is the second most abundant biopolymer in nature, and the natural substance with a greater presence of aromatic moieties. In fact it is the largest source of aromatic substances without considering the oil.

Many researchers and industrialists have coined the sentence “with lignin you can do anything but money” (Graichen *et al.*, 2017). This sentence supposes a quite realistic approach to the current picture on lignin. The chemical industry is mainly based on oil as source of raw material. Despite the horizon of a world without oil, it has been delayed for a few years due to more efficient oil extraction methods, so the obtention of raw materials from renewable sources is a necessary goal to develop a more sustainable economy, with a better CO₂ balance and ready for a future based only in renewable sources (Graichen *et al.*, 2017; Langeveld *et al.*, 2012).

Lignin as a renewable raw material from biomass with two sources:

- (1) By-product of paper industry
- (2) Direct extraction from plants

The main source of lignin is the paper industry, which produces huge amounts of chemically modified lignin as a by-product. As it has been described before, depending on the method to separate cellulose from biomass in pulping, several types of commercial lignins are obtained.

In the last decades there has been progress on the valorization of lignin, but considering the enormous quantities of lignin that the paper industry produces every year, and the potentiality of this raw material as a source of fine chemicals, especially aromatic compounds, the results are still modest for obtaining commercially valuable products. Two main directions can be considered for lignin valorization:

- (1) The use of lignin keeping the polymeric structure with chemical modifications of the material or not
- (2) Valorization of lignin by depolymerization reactions to give simple aromatic molecules

Applications of Unmodified Lignins

Combustion

Lignins obtained from the paper industry are the more available group of these polymers.

The major application of lignins in the paper industry is as fuel in the same factory to obtain energy. Black liquor is the spent liquor formed in the kraft process. Pulpwood is transformed into paper pulp by removing mainly lignin, hemicellulose, and other extractable materials, which are separated from cellulose fibers. When it is used in the sulfite process the spent liquor is usually called brown liquor, but other terms such as red liquor, thick liquor, or sulfite liquor are also used for this pulping technology. It is assumed that approximately seven mass units of black liquor are produced in the manufacture of one mass unit of pulp (Biermann, 1993). Water is removed from black liquor and the solid is burned. Another more efficient option than the conventional recovery boiler for power production (Speight, 2014) is to carry out gasification, which has the potential to achieve higher overall energy efficiency (Yu *et al.*, 2018).

In this field, lignin is used as additive for biomass heating as binder of pellets, artificial fire logs, and other wood derivatives. The introduction of lignin in these materials are very convenient because it is able to improve fuel properties.

Direct applications

Lignin is a nontoxic polymer and a quite inert substance when interacting with living organisms. This behavior and some properties such as natural antioxidant (Yu *et al.*, 2018; Mahmood *et al.*, 2018), free radical scavenger (Pan *et al.*, 2006), or its capacity to link to cations, have meant that lignin may be used in the preparation of commercial products for agriculture (García *et al.*, 1996), livestock (Baurhoo *et al.*, 2008), or in medicine to protect against the development of different diseases (Vinardell and Mitjans, 2017).

For example, kraft lignin or steam-exploded lignin has shown antioxidant activity in human red blood cells, and water-solubilized lignin derivatives present antiviral activity in vitro, and some other lignin derivatives have shown antibiotic properties, and even anticarcinogenic activity. Based on these properties, some applications are under development (Larrañeta *et al.*, 2018).

Some sulfur-free lignins such as commercial Alcell lignins, have exhibited prebiotic effects in monogastric animals (Baurhoo *et al.*, 2008). The addition of this kind of lignins to animal feed may improve the growth of beneficial bacteria and morphological structures in the intestines.

On the other hand, lignin fragments have shown bactericidal properties so that they may help control intestinal pathogens in livestock products and lignin-based biopolymers have antioxidant capacity (Mahmood *et al.*, 2018). However, much research is still required to determine optimum lignin dosages for livestock and the potential effects on the environment.

Related to human health and illness (Vinardell and Mitjans, 2017), some tests to reduce the genotoxicity in drugs and side effects on patients have been carried out and in case of lignin dietary fiber (Lábaj *et al.*, 2003), it has shown to be important in absorbing bile acid and thereby influences lipid metabolism (Eastwood and Girdwood, 1968).

Technical Applications

Lignin sulfonates are probably the most abundant lignin derivative. They have shown some interesting applications as low cost binders in coal briquettes (Saranchuk *et al.*, 1995), ceramics (Somiya *et al.*, 2003), mineral dusts or wood derivatives as boards or plywood (Pizzi, 1989). Because they are not hazardous, they have been used as eco friendly binders for furniture and other wood products (Grāvītis *et al.*, 2010), but probably the more extended use is as moisture-retention agents and dust suppressors in public works, unpaved roads, airports, sports facilities, or racing circuits. Added to soil, dust particles remain in the ground without entering the atmosphere (Gargulak and Lebo, 1999).

Lignin sulfonates are used as additives in concrete mixtures (Mullick, 1996) because they prevent lumping and settling of unsolved particles in suspension. Other applications of lignin sulfonates can be found in leather tanning factories (Suparno *et al.*, 2004), ceramics (Cerrutti *et al.*, 2012), and gypsum-board manufacture (Northey, 2002). On the other hand, lignin sulfonates are able to stabilize emulsions (Gharehkhani *et al.*, 2018) of immiscible liquids making them highly resistant to breakdown, for example asphalt emulsions (Gharehkhani *et al.*, 2018; McIntosh, 1952), pesticide formulations (Wilkins, 1983), wax emulsions, pigments, and dyes (Wilkins, 1983; Rojas *et al.*, 2007).

Lignin sulfonates present a remarkable affinity for some metal ions because of their polar groups with chelating properties (Ge and Li, 2018). Used low concentrations (ppm-scale) may prevent scaling in hot and cooling waters or remove toxic metals from waters (Crist *et al.*, 2005). Several commercial derivatives are used as micronutrient transporters or as cleaning and decontaminating agents in water and soils (Wise, 2000).

Lignin as a Copolymer Component

The incorporation of lignin in the diverse formulations of synthetic polymers has been investigated for decades to modify the properties of some polymers and to improve environmental behavior of some formulations. Despite the efforts, practical results in this field are still limited and modest.

Two approaches have been developed in this field. First is to use lignin without chemical modification within the polymer. The second approach involves the chemical transformation of lignin to improve the reactivity, before the incorporation into the polymer.

Formulations without chemical modification of lignin

Because of its phenolic nature, it is not difficult to use lignin in polymer chemistry; for example in phenol-formaldehyde resins (Siddiqui *et al.*, 2017). Such resins are widely used in technical and industrial applications (Siddiqui *et al.*, 2017; Pye, 2008) as adhesives for plywood (Wang *et al.*, 2018), chipboard, medium-density fiberboard, and oriented strand board (Inamuddin, 2016), in the manufacturing of mineral wool, abrasives, refractory and friction materials, and rubber products. The classical method for the synthesis of such resins consists to polymerize mixtures of phenol and formaldehyde in acidic or basic media. Depending on proportions and the conditions the so-called resol (Tkachuk *et al.*, 1971) and novolac (Chaplan, 2014) polymers are obtained for acid or basic reactions, respectively.

Acetosolv, organosolv, or hydrolyzed lignins have been used instead of pure phenol (Tachon *et al.*, 2016) in phenolic resins to produce modified polymers. Such materials exhibit satisfactory properties with good curing characteristics. In binders, about 50% of Kraft lignin or lignosulfonate lignin can be added instead of phenol to phenol-formaldehyde resins without substantially modifying the final product properties. The substitution of phenols by lignins (Tachon *et al.*, 2016) is not only environmentally friendly but also less expensive than other binders used in the wood-composite industry (El Mansouri *et al.*, 2018). Some physical and mechanical properties are modified, for example, in novolac-type resins, the addition of lignin leads to polymeric systems with increased rigidity. Lignin has been used in formulations of polyolefins polymers, polyesters, acrylamide, or polyurethanes, in some cases as an additive, and as macromonomer in others.

For example, the addition of 30% of dry lignin powder to high-density polyethylene (Sameni *et al.*, 2018), low-density polyethylene (Lüftl and Visakh, 2016), or polypropylene (PP) (Morandim-Giannetti *et al.*, 2012) can modify the mechanical and

technical properties of polymeric materials. Lignin has been shown to be a stabilizer against the photo-oxidative degradation of common polymers such as polyolefins (Mikulášová *et al.*, 2001). However, polymers as PP or polyethylene are materials that are highly resistant to biodegradation. This is a serious environmental problem, because of the massive use of such polymers together with the great deficiencies about recycling these polymers.

Lignin-based thermoplastic copolyesters can be synthesized by using Kraft lignin (Guo *et al.*, 1992; Guo and Gandini, 1991) as a macromonomer to form a high-molecular-weight polymer. Kraft lignin is polymerized with sebacoyl chloride (decanedioyl dichloride) in the presence of triethylamine in N,N-dimethylacetamide (DMAc) (Hori and Meshitsuka, 1999; Binh *et al.*, 2009). The resulting polymer is an eco friendly material that exhibits good thermal stability up to 200°C.

Precured polyurethanes can be synthesized by the reaction of Kraft lignins (Yoshida *et al.*, 1987), or organosolv lignins (Yoshida *et al.*, 1987; Hatakeyama, 2002) polyols such polyethylene glycol or polypropylene glycol and methylene diphenyl isocyanate and a plasticizer. Rigid polyurethane sheets and foams can be prepared by this procedure.

German researchers Pfister and Nägele have obtained promising results, from the Fraunhofer Institute for Chemical Technology. They have developed a new thermoplastic material, named ARBOFORM (Nägele *et al.*, 2002). This new bioplastic material is made by mixing specific types of low-content sulfur lignins with natural fibers from several plants and natural additives such as wax. Sulfur-free lignins are usually water-soluble, so they are unsuitable for manufacturing certain objects such as toys or household items. With the aid of additives, the bioplastic can be modified in such a way that it survives contact with water and saliva undamaged. This material is a plastic granulate that can be melted and injection-molded, so it can be applied with conventional plastic-processing machines in just the same way as a petrochemical thermoplastic material (Nedelcu *et al.*, 2014). The final product resembles highly polished wood, or may have a more matte finish and look like the plastic used in most household items, and it is highly recyclable.

Polymeric formulations with chemical modification of lignin

The aromatic moieties of lignin, theoretically, may be subjected to a wide range of reactions as alkylation, dealkylation, oxyalkylation, amination, carboxylation, acylation, halogenation, nitration, hydrogenolysis, methylation, oxidation and reduction, sulfomethylation, sulfonation, silylation, phosphorylation, and nitroxide formation (Loh and Kai, 2018; Podschun *et al.*, 2015). Such modifications have mainly been used to improve dissolution of lignin into organic solvents and to determine the functional groups of lignin but they may be useful in the synthesis of copolymers with modified lignins.

One problem of lignin in polymer chemistry is that phenolic hydroxyl groups remains hindered into the lignin matrix, therefore, the reactivity of phenolic groups remains quite low if compared with phenol, to be incorporated in other polymeric materials properly. Some of these reactions provide a higher reactivity because the functional groups play a role of spacer.

Epoxy resins are well-known polymers with many applications. Most epoxy and phenoxy resins use epichlorohydrin as a major raw material to induce polymerization. Epichlorohydrin reacts with molecules such as bisphenol-A to yield polymers (van de Pas and Torr, 2017). Modified lignin can be added as a cross-linker material in phenol-formaldehyde resins, to give several resins (Nada *et al.*, 2003) and adhesives (Danielson and Simonson, 1998), but in most cases, lignin must be activated introducing more reaction sites towards formaldehyde. Lignin is modified by phenolization and/or demethylation. Phenolization increases the number of phenol units in lignin by reaction of lignin with phenol and demethylation increases the number of free OH groups in lignin by treatment with some chemicals, for example, molten pyridinium chloride. Both, additional phenol moieties and demethylation can be incorporated into the lignin structure by the reaction of lignosulfonate with phenol in sulfuric acid media. Two reactions take place in such conditions: Some new phenolic units are introduced into the lignin matrix and some lignin is hydrolyzed to give diphenolic moieties (Fig. 7).

On the other hand, an alternative strategy that has stirred growing interest is the use of pyrolytic lignin as a renewable resin from pyrolysis of biomass, due to the high yield of pyrolytic lignin and its easy assimilation into phenol formaldehyde formulations. Most of these pyrolytic lignins appear to be oligomeric alkylated phenolic units probably linked by CC bonds.

High-Value Products From Lignin

The higher task related to lignin is to use it as a true source for the preparation of high value materials, especially chemicals.

The first level for lignin valorization may be through thermal transformations. As most biomass or related substances, lignin can be transformed by gasification into syngas (Soomro *et al.*, 2018), mixtures of hydrogen and carbon monoxide. Syngas is per se a fuel used in combined cycle power plants and a valuable starting material for the synthesis of many chemicals. The coal and natural gas industries have used syngas for decades and this technology is well established, but lignin gasifiers based on lignin are still in an early stage of development.

However, the major challenge related to lignin is to obtain low molecular mass aromatic compounds as a real alternative to the petrochemical industry. The potentiality of this area is enormous, but the practical results are still modest. Every year a remarkable amount of work on this field is published (Hu *et al.*, 2018; Das *et al.*, 2018; Abad-Fernández *et al.*, 2019; Ragauskas and Yoo, 2019; Sun *et al.*, 2018).

To obtain high value molecules from lignin it is necessary to carry out an effective depolymerization of the polymer by thermochemical or chemical transformation processes.

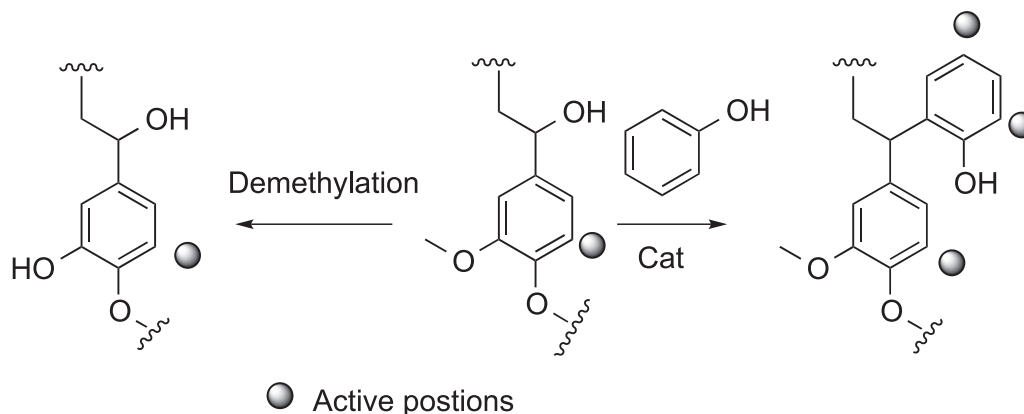


Fig. 8 Oxidation reaction with a copper catalyst for lignin obtention.

The goal for such transformations is to obtain benzene toluene xylenes aromatics, as they are known in the petrochemical industry mixtures of benzene, toluene, and the o-, m- and p-xylene isomers, and other substances as cresols (o-, m- and p-isomers), catechol, resorcinol, benzoquinones, vanillin, or guaiacol. The state of the art remains at a very basic level, because the practical application of these techniques is still very modest.

Depolymerization of lignin may be produced by

- (1) Thermolysis: Pyrolysis of lignin by a rapid heating at elevated temperatures to give the so-called bio-oil, gas, and a solid residue (ash or char). Catalysts are often used in this procedure (Fan *et al.*, 2017).
- (2) Hydrogenolysis: Similar to the previous procedure but in presence of hydrogen as reducing agent (Cao *et al.*, 2018).
- (3) Hydrothermal hydrolysis: Lignin is converted into liquid mixtures when treated with water, which is used as hydrogen source, together with other chemicals (Ma *et al.*, 2014).
- (4) Depolymerization in acid media (Wang *et al.*, 2013a).
- (5) Depolymerization in base media (Pandey and Kim, 2011).
- (6) Oxidative depolymerization: Treatment with oxidants as chlorine, oxone, hydrogen peroxide, or peroxy acids (Wang *et al.*, 2013a; Lange *et al.*, 2013).

Vanillin

Vanillin is one of the more used food additives and flavoring agents in cosmetic and other household products (Taylor and Linforth, 2009). The natural sources of vanillin are insufficient for the industry requirements, and it may be synthesized from benzene, following several routes with conventional reactions on aromatics.

However, vanillin can be obtained from lignin. In fact, spontaneous decomposition of lignin produces vanillin. This is in part the cause of the typical odor of old books. The residual lignin of paper decomposes through the years giving the characteristic aroma of old books.

Vanillin has been produced by several companies from lignin (Fache *et al.*, 2015), but using lignin as raw material for vanillin synthesis is quite limited. Borregard is one of the world's leading suppliers of vanillin from lignin, based on the biorefinery concept. According to company reports, from 1000 kg of wood 3 kg of lignin may be obtained. The key step for lignin obtention is an oxidation reaction with a copper catalyst, which is recycled (Fig. 8).

Active Carbon and Carbon Fibers

Lignin is a good starting material for active carbon preparation. Activated carbons are used widely, as absorbents in removing a wide variety of both organic and inorganic substances, for example pollutants or impurities from liquid or gaseous phases because they form a very porous structure with a large internal surface area. Lignin may be used for that, because it is easily available and is inexpensive. The general method involves the pyrolysis of lignin under inert atmosphere to obtain a char that must be activated, by physical methods with the treatment of a gas as CO₂ or water vapor, or chemically by treatment, by impregnation with chemicals such as H₃PO₄, KOH, or NaOH (Hayashi *et al.*, 2000). Depending on the activating agent and other variables as activation time and temperature several surface areas and micropore volume can be obtained (Shendrik *et al.*, 2007; Suhas *et al.*, 2007). Such activated carbons have been tested, for example for treating gaseous streams (Song *et al.*, 2017) or as part of electric supercapacitors (Hayashi *et al.*, 2000; Hu and Hsieh, 2017).

Carbon fibers (CF) are materials composed of fibers with diameters from 50 to 10 μm, mainly conformed by carbon atoms that show low density, high flexibility and resistance, low weight, low thermal expansion coefficient, and are stable at

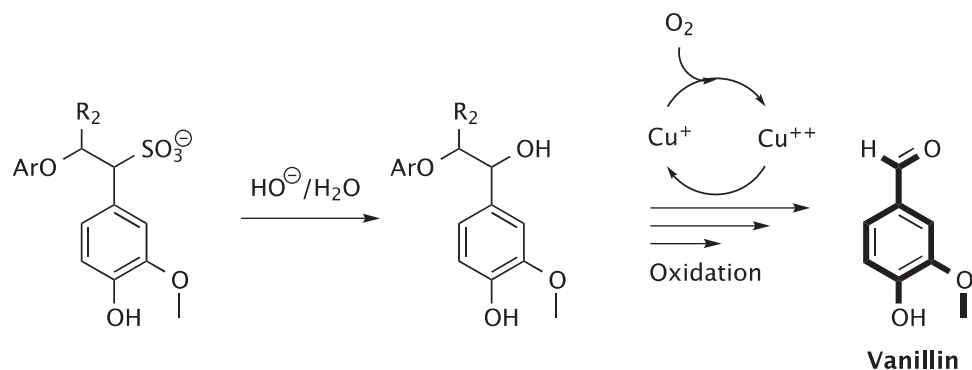


Fig. 9 Lignin transformation into selective chemicals.

high-temperatures values. These materials are focused on high technology sector, where the large-scale use of CF is driven by maximum performance and not by cost factors (Chung and Chung, 2012). Many researchers have considered lignin-based CF as an alternative (Yue *et al.*, 2017), comparing the process to current precursors (Yue *et al.*, 2017; Kadla *et al.*, 2002). Organosolv lignins and Kraft lignins have been tested as affordable precursors for the synthesis of CF. Lignin-based CF procedures are less energy intensive and emit around 22% less CO₂-equivalent greenhouse gas emission than conventional Polyacrylonitrile-based carbon fiber. Despite several challenges that must be overcome, lignin-based CF can be produced nowadays under limited mechanical properties, but enough to attend to some industrial branches. This has great potential for market insertion, emerging as a material with high technological impact, economically attractive, and environmentally sustainable (Souto *et al.*, 2018).

Nanoparticles From Lignin

Nanoparticles are materials having size ranges from 1 to 100 nm that have attracted the scientific community for their potentiality in diverse fields, such as catalysis, imaging, drugs delivery, energy-based research, or environmental applications. They can be classified many ways based on their properties, shapes, or sizes (Jeevanandam *et al.*, 2018). They can be synthesized both from organic or inorganic sources.

To valorize lignin, researchers have focused on using lignin as a renewable source to obtain nanoparticles (LNPs).

Some recent examples can be found in literature, indicating that recently LNPs have been obtained from several types of lignin using castor oil, ethylene glycol, or water as reaction media, and the resulting nanoparticles evaluated as anticorrosion agents (Rahman *et al.*, 2018). Kraft lignin is able to form stable and spherical nanoparticles enzymatically, in a nonmalodorous colloidal dispersion in water or organic solvent becoming an attractive bionanomaterial for many industrial applications (Mattinen *et al.*, 2018). But probably, one of the most promising fields related to LNPs applications is their use as carriers for drug delivery (Yiamsawas *et al.*, 2017). Lignin is a biocompatible and nontoxic material that can play an important rule in this area (Mattinen *et al.*, 2018; Figueiredo *et al.*, 2017; Dai *et al.*, 2017).

Conclusions

Lignin is the second most abundant organic substance in plants, and constitutes 30% of the nonfossil organic carbon in nature, and it is the natural raw material with the greatest content of aromatic moieties. The structure of native lignin is complex and diverse, depending on the plant species. But the major source of lignin is the paper industry, which through the pulping processes separates lignin from cellulose, and diverse lignin types are commercially available.

Despite the enormous amounts of lignin produced every year, the use of lignin as raw material for obtaining high value substances and consumer goods is still at a very basic stage in development. For the next few years, and with a world without oil on the horizon, the basic and applied research on lignin is a great challenge for researchers and industries. Probably the most important task for next few years will be the development of efficient and selective catalysts for lignin transformation into aromatic chemicals with reasonable yields for the petrochemical industry and a better use of lignin (Fig. 9).

See also: A Review of the Value-Added Chemicals and Materials From Bio-Based Lignin Feedstocks. An Overview on the Development of Natural Renewable Materials for Textile Applications. Bamboo: The Emerging Renewable Material for Sustainable Construction. Conversion of Renewable and Food Wastes into Useful Products with Environmental Perspectives. Opportunities With Renewable Jute Fiber Composites to Reduce Eco-Impact of Nonrenewable Polymers. Properties and End-of-Life of Polymers From Renewable Resources. Renewable Biomass: A Candidate for Mitigating Global Warming

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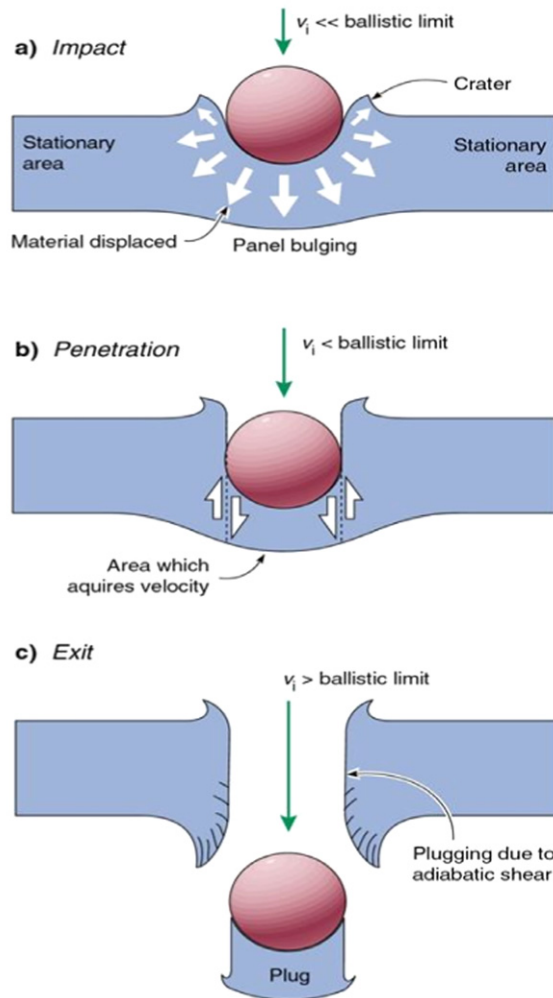


Fig. 2 Low velocity impact failure mechanisms. Reproduced from Yungwirth, C.J., Connor, J.O., Zakraysek, A., Deshpande, V.S., Wadley, H.N.G., 2011. Explorations of hybrid sandwich panel concepts for projectile impact mitigation. *J. Am. Ceram. Soc.* 94, S62–S75, doi: 10.1111/j.1551-2916.2011.04501.x.

applications. LVIs of homogenous basalt and glass fibre polymer composites are compared. Epoxy resin and the vacuum-assisted resin transfer moulding (VARTM) method were used to fabricate the composites. BFRP has superior LVI performance to CFRP due to its higher stiffness (Shishevan *et al.*, 2017).

Similarly, recycled carbon fibre composites were compared with treated recycled carbon fibre and virgin carbon fibre composites. Virgin carbon fibre composites showed an enhancement in damage protection, higher residual strength and angle of shear failure during impact. The damaged specimen was examined with an ultrasonic C scan, photography, and SEM. The fibre orientation is chosen to improve the property of the composites (Shi *et al.*, 2014).

The fibre orientation also influences the parameters in the polymer composites. Basalt fibre polyester composites were manufactured with three different fibre orientations. Among these, three 0° laminated composites showed better LVI results than the plain woven and cross ply laminates (Gideon *et al.*, 2014). Recently, researchers have focused on fibre metal laminates as an alternative, in order to enhance the LVI of the composite by adding metal layers into the polymer composites. Sharma *et al.* (2018) prepared Fibre Metal Laminate (FML) composites with glass fibre using the hand-layup technique followed by vacuum bagging. The specimens were fabricated with different layering thickness and it was concluded that the FML with 0.6 mm thickness and 90° orientations showed minor levels of cracking and deformation at the maximum force. For woven glass fibre reinforced composites manufactured with varying volume fractions using vacuum bagging techniques, the results showed that a volume fraction of 43%–44% gave a better impact resistance.

The damage resistance and post-impact of non-woven flax epoxy composites was studied by Habibia *et al.* (2018). With the help of c scan inspection, the damage mechanism was analysed. The damage was induced due to matrix cracking and delamination. An auxetic warp-knitted spacer fabric structure has outstanding mechanical properties, shear-resistance, cushioning property and energy absorbing abilities. Chang *et al.* (2017) used the same to study the impact resistance and energy

absorption capability under LVI. The negative value of Poisson's ratio means that it has a better energy absorption capability and impact resistance.

A cylindrically shaped object was also tested by [Khan et al. \(2016\)](#). They used filament wound glass fibre reinforced vinylester and epoxy-based pipe composites with a thickness of 6 mm and an internal diameter of 150 mm. A single bounce LVI tester was used with a spherical head steel impactor. During the elastic deformations, there was no gross damage, and at peak load there was damage initiation and propagation was observed. It was concluded that Glass Fibre Reinforced/Epoxy (GFRE) pipes required more energy to initiate damage than did Glass Fibre Reinforced/Vinylester (GFRV) pipes.

By varying the thickness of the composites, [Caminero et al. \(2017\)](#) investigated the damage resistance of CFRP epoxy composites to measure the influence on composite thickness and stacking sequences. C scan and micrographs were used to measure the failure mechanisms. It was observed that the damage resistance decreased with increasing impact energy and the thicker laminates absorbed less energy. Using a variety of fibres for the development of LVI for the studies, changing the matrix materials also influenced the LVI.

Flax fibre reinforced composites with different types of matrix, namely epoxy and Anhydride grafted Polypropylene (MAPP), have been used. From the results, it can be understood that the selection of two different matrixes highly influences the absorbed energy and the damage area, and the flax-MAPP composite was found to be 50% higher compared to the flax-epoxy composites. The orientation of the fibre has a limited contribution in the damage of the composites. The ductile nature of the thermoplastic matrix resulted in a decreased impact damage area, by between 38% and 59% ([Bensadoun et al., 2017](#)).

[Li et al. \(2017\)](#) investigated the LVI of GFRP composites with the energy ranging from 16.75 to 67 J. The damage analysis and failure mode of the composites were analysed for different levels. Numerical analysis was also carried out to confirm the experimental results in terms of load-time and central deflection-time curves.

Concerning the recyclability aspect, for the fully thermoplastic plastic composites, both the reinforcement and the matrix were made in polypropylene, as prepared by [Boria et al. \(2017\)](#). The polypropylene composites were subjected to LVI testing under different impact loading conditions. The composites showed a ductile performance and developed extended plasticity without a crack tip, and damage causes in the composites were due to yarn sliding, delamination and fibre fracture.

[Martins et al. \(2018\)](#) studied the tufting of woven carbon fibre composites and the impact on LVI and compression after impact. The density and the angle of tufting were varied to attain better results. The tufting of the fibre was performed in two different ways: transverse tufting and angular tufting. It was revealed that transverse tufting gives better results than angular and non-tufted composites, and an increase in the tufting density resulted in a decrease of the damaged area by 4 times and the ultimate compressive strength improved. Further extending the performance of the composites, [Ravandi et al. \(2017\)](#) investigated the effect of a stitched and unstitched woven flax/epoxy composite and LVI, with perforated and non-perforated damage. Flax yarn stitched composites reduced the intra-laminar fracture toughness of the flax fibre composite by 16%, but for the cotton yarn stitched composites the value was 5%.

[Mingmin et al. \(2016\)](#) investigated the LVI of 3 different alumina/epoxy/metal laminated composites with epoxy resin, with Al foil, Cu foil, and steel mesh as the metal interlayer. Different energy levels were used for the different composites, such as 5 J and 5.5 J for the A/A composites, 10, 15, and 19 J for the A/Al Composites, 19, 22, and 25 J for the A/Cu composites and 19, 25, and 30 J for the A/S composites. A/A has poor impact resistance and was penetrated at the lowest energy levels. An A/S composite has the best impact resistance, followed by the A/Cu and A/Al composites.

[Razali et al. \(2014\)](#) experimentally investigated the LVI of two types of glass fibres, namely C glass and G glass fibre, and the fabricated glass fibre epoxy composites were analysed with varying impact energies. It was concluded that the C glass fibre composites absorbed more energy than the G glass fibre composites. A comparison was made between Basalt fibre and glass fibre reinforced Bisphenol-A epoxy based vinylester matrix composites, as prepared by [Sfarra et al. \(2013\)](#) using resin transfer moulding techniques. NDT techniques, e.g., Square Pulse Thermography (SPT), were used to inspect the specimens. It was observed that the impact damage resistance of the basalt fibre composite was superior to that of the glass fibre composite. At higher impact energies, delamination in the glass fibre composites and fibre breakage in the basalt fibre composites are the predominant failures in the composites. These suggest that hybrids of basalt/glass fibre composites can overcome the delamination and fibre breakage in the composites. They also suggest that varying the stacking sequence of the basalt/glass fibre composites is a good way forward.

[Whisler and Kim \(2012\)](#) examined the influence of impact radius on the LVI of glass/epoxy composites. Three types of hardened hemispherical steel impactor were used (radii of 12.7, 50.8, and 152.4 mm). It was observed that the larger radius impactor required more energy to produce damage in the composites. An impactor of radius 152.4 mm required 1.7–4.8 times more energy to initiate damage compared to the 12.7 mm radius impactor. The thicker composites were affected less than the thinner composites by increasing the tip radius due to the contact area of the impactor.

The stitching of the fibre is a new and promising area to strengthen the fibre further. [Bilisik and Yolacan \(2014\)](#) developed 2D stitched glass fibre composites to study the effect of stitching the fibres. They developed the following composites: 1–4 directional hands stitched, 1–4 directional machines stitched and unstitched polyester composites. It was observed that the front and back face area damage of the 2D multi-stitched composites was smaller than for the 2D unstitched composites. When the stitching density increased and the stitching direction increased, the front and back area damage decreased.

[Hadi and Khaleel \(2015\)](#) studied the effect of LVI on a composite plate with and without holes. Experimental work included the manufacturing of an E-glass fibre reinforced polyester composite plate. It was concluded that the presence of holes decreases

the natural frequencies of the composite plate, and absorbed energies and impact force, while the displacement of the composite plate was increased by increasing the number and diameters of the holes.

Naik *et al.* (2000) and Naik and Meduri (2001) investigated the LVI of plain weave glass fibre reinforced epoxy composites with varying levels of impact energies. It was found that the damage tolerance was superior for the low mass and higher velocity combinations when compared to the high mass and low velocity combinations. Reghunath *et al.* (2015) studied the impact resistance of glass fibre composites with different volume fractions of glass fibre and carried out at different impact velocities. This revealed that 43% of the glass fibre composites showed better impact resistance than other composites.

Effect of Temperature on LVI

Composite materials are widely used in the aerospace and space engineering fields in many structural components. Such materials should be surveyed in different environmental conditions, *e.g.*, temperature, pressure etc. For that purpose, Khashaba and Othman (2017) examined the damage resistance of a woven CFRP epoxy composite in varying temperatures, *e.g.*, room temperature, 50°C and 75°C. Compression after impact is also taken into consideration to measure the residual strength. At a higher temperature (75°C), there is no penetration due to the softening of the plasticization of the epoxy matrix. Debonding was observed at the fibre and matrix interface, and also increases in the interfacial stress concentration of the re-solidified matrix were observed. Similarly, Dhakal *et al.* (2014) explored the influence of temperature on the LVI of jute fibre reinforced UP composites. They conducted testing at 30, 50, and 75°C with impact velocities of 1.5 and 2 m/s. The results showed that the jute fibre composites had a maximum load carrying capacity at 30°C.

Consequently, during the bending tests (flexural strength after impact (FAI)), when increasing the testing temperature, there is an extensive reduction in the FAI. A woven-ply carbon fibre reinforced polyphenylene sulfide (CF/PPS) composite was subjected to high temperatures of 95°C and 125°C. A hot pressing technique was used to fabricate the composites with a thickness of 3.72 mm and impact energies of 5, 15, 25 and 35 J. Varying the temperature of the composites highly influenced the impact response, with plastic deformation of the matrix and a coupling effect in the resin rich area and the fibre bridging mechanism (Wang *et al.*, 2018).

Similarly, carbon fibre nanocomposites were studied by Kara *et al.* (2018) at temperature conditions of 23°C, 0°C, – 50°C, – 100°C, – 196°C with an impact energy of 15 J. Multi-walled carbon nanotubes were added into the epoxy composites. At lower temperature, the damage on the composites increased for all the specimens. Moreover, addition of nanoparticles resulted in a higher contact force for the same temperature and there was less damage in the specimens.

Foam Composites Effect on LVI

Foam is the most common form of core material in polymer composites, and has better static and dynamic mechanical properties. Foam is derived from various polymers. Bi-material structures were made from a PLA lattice structure and polyurethane (PU) foam by Koa *et al.* (2018). It was concluded that the flexible foam gave a more positive impact energy absorption than the rigid foams, with a maximum energy absorption of 23% and the proper selection of foam, which enhanced the impact energy of the composites. Likewise, Caliskan and Kemal Apalak (2017) experimentally studied a specimen involving an expanded polystyrene foam core reinforced by an aluminium face sheet using LVI testing and adhesive bonding techniques. LVI testing of foam composites is based on the foam, the foam density and the plate thickness. The lowest permanent deflection and contact force was observed in the highest foam core density and thicker foam core. The energy absorption capacity was increased by increasing the foam core thickness and density. PVC foam has been used as a core material in sandwich composites with epoxy and a polypropylene matrix. Due to the densification of the core material, the response of the structure was changed by increasing the impact energy. Also, the bending stiffness of the thermoplastic composites was lower than that of the thermoset composites, which makes thermoset composites more rigid and stable (Dogan and Arkan, 2017). Woven natural silk/epoxy sandwich composites were prepared by the hand-layup technique and drop weight impact testing was conducted at 32 J. The woven natural silk fibre foam epoxy composites showed better energy absorption than the other sandwich composites prepared. Woven natural silk fibre epoxy core-mat composites possessed enhanced load bearing capacity over the other sandwich composites prepared (Ude *et al.*, 2013).

Bahkoglu *et al.* (2018) investigated the compression after impact behaviour of wooden composites reinforced with pinewood and ashwood as intermediate layers. The composites were manufactured using the VARTM method with 15 and 25 mm thick PVC foams. The energy levels used in this study were 30 J and 60 J, with conical and hemispherical impactors. The pinewood and ashwood intermediate layers increased the residual compression after impact strength and decreased the impact damage depth.

Nano-Composites Effect on LVI

Nano-particle inclusion in the polymer composites enhanced the property of the materials. Many researchers infuse different nano-particles in polymer matrix composites to gain the advantages of the nano-particle. Sonication is the best way to disperse the nano-particle into the polymer matrix to achieve the uniform distribution of the nano-particles. Nanomer organically modified montmorillonite nanoclay was dispersed into an epoxy matrix in a wt% ranging from 1% to 3%. This modified epoxy matrix was

used to fabricate a 15-layer plain weave carbon fibre composite using VARTM. The LVI response was tested for three energy levels. The infusion of nanoclay into the composites reduced the damage due to the increased stiffness and damage resistance (Hosur *et al.*, 2007).

Castellanos *et al.* (2017) investigated the enhancement of the LVI strength of ZnO nano-wires on dry woven carbon fabric layers. To protect against damage in the layered composites, ZnO nano-wire was added into the interlaminar regions. These composites were fabricated with 16 layers of dry fabric with a vinyl ester matrix by the VARTM process. The ZnO nano-wire reinforced composites exhibited lower damage when compared to those without ZnO nano-wire. Also, it was observed that there was an increase in the impact peak load and a reduction in the deflection between cases with and without nano-wire reinforcements. The functionalised multi-wall carbon nanotube (MWCNT) material was added in different weight percentages, *e.g.*, 0.5%, 1% and 1.5%, into the woven carbon fibre composites to increase the impact strength of the composites. The addition of 1.5% MWCNT resulted in a 50% increase in energy absorption and damage size (Soliman *et al.*, 2012).

Carbon nanofillers are other promising fillers for enhancing a material's properties. A carbon nanofiller has been infused into GFRP polyester matrix composites using VARTM in the range of 0.1–0.3 wt%. With the inclusion of the carbon nanofiller in the polyester composites, there was a decrease in the absorbed energy. The wt% of 0.2 carbon nanofillers gave the highest peak load and the lowest energy absorptions compared to conventional composites. The lowest energy absorption was due to delamination, matrix cracking, fibre fracture or pull-out, fibre-matrix debonding and back-face fibre fracture followed by penetration. For all the cases at 30 J, there was clear penetration. However, the addition of nanofillers reduced the delamination in the composites (Tita *et al.*, 2008). To improve the LVI characterization of the composites, a nanoclay and graphene were added into Kevlar fibre-reinforced Epoxy (KE) composites by Rahmana *et al.* (2018). The fillers were added up to 10 wt% with 16 ply KE composites. It was found that the nanoclay (NC) is more effective than graphene (G) for impact resistance and the absorption of impact energy. Also, an NC composite has a better preventing capability than G composites with regards to penetration.

Fibre Metal Laminate Composites – Effect on LVI

The cost effectiveness of the composite structure is increased when using aluminium alloy in fibre reinforced composites. But there are disadvantages with these materials, *e.g.*, the fatigue of the aluminium alloy, and the poor impact and residual strength of carbon fibre composites. Combining these two materials to make hybrid composites can overcome the disadvantages of the materials (Vogelansang and Vlot, 2000; Sinmazçelik *et al.*, 2011). The influence of the carbon fibre orientation in aluminium metal laminates was studied with varying carbon fibre arrangements in the form of Al/(04)/Al, Al/(02,902)/Al, Al/(0902,0)/Al, Al/(0,90,0,90)/Al and Al/(0,±45,90)/Al (subscript 2 – 2 layers, 4 – 4 layers). The energy absorption of the composite was calculated as in Eq. (1) (ASTM D7136/D7136M-15, 2015):

$$E = \frac{m(v_i^2 - v^2)}{2} + mg\delta \quad (1)$$

where,

δ – Indenter displacement (m),

v_i – Initial velocity of the impactor body (m/s),

v – Final velocity (m/s),

m – Mass of the indenter (kg),

g – Gravitational acceleration, 9.81 m/s².

It was observed that the fibre orientation and changing the number of interfaces had no obvious influence on the shape and size of the delamination in carbon aluminium metal laminate composites, and fibre failure was dominant in AlC composites under impact. A crack at the bottom aluminium layer propagated in a perpendicular manner to the direction of the carbon fibre of the adjacent layers (Jakubczak *et al.*, 2017). Similarly, Ferrante *et al.* (2016) studied the LVI of basalt aluminium metal laminate composites with two different impactors: hemispherical and an ogival. It was confirmed that the cause of the damage was delamination between the basalt layers and the aluminium foils.

Glass-reinforced aluminium laminate (GLARE) is the popular hybrid composite in aerospace structure applications. A GLARE composite was fabricated with Nylon 6, 6 nanofibre non-woven mats by the electro-spinning technique and interleaved between aluminium sheets and glass fibre. The Nylon 6, 6 nanofibres showed lower debonding length and reduced the outer damage area by 62% (Zarei *et al.*, 2017). In the same way, two types of FML composite were prepared by Sadighi *et al.* (2017): 3 layers of aluminium alloy sheet with one core glass fibre and epoxy prepreg and another composite, 3 layers of aluminium alloy sheet with two core glass fibre and epoxy prepreg. LVI testing was conducted with the successive impacts which reduced energy levels. Visual inspection and the ultrasonic C-scan method were used to examine the damage, and the damage caused due to the visible damage without internal and external damage, visible internal damage and external damage. It was concluded that the damage propagation by the consecutive impact energy was negligible.

Low Velocity Impact on Hybrid Composites

Hybrid composites are materials fabricated with two or more constituents to gain the advantages of each of the constituents in the final materials. By making hybrid composites, one can reduce the cost of the materials and increase their strength, as well as making environmentally friendly materials. Many researchers are studying hybrid composites to obtain materials with better properties. Accordingly, Hosur *et al.* (2005) studied the low-velocity impact response of 4 different woven hybrid composites. The hybrid composites were fabricated by vacuum assisted resin moulding using carbon and glass fabric with epoxy resin. It was concluded that there was a considerable improvement in hybrid composites over the carbon/epoxy composites.

3D angle-interlocked Kevlar/basalt reinforced polypropylene composites were prepared by Bandaru *et al.* (2016). Three types of composites was manufactured, namely Kevlar 3D, Basalt 3D and Hybrid 3D, using the vacuum-assisted compression moulding method to manufacture the composites. The energy level for all the composites was set as 120 J. The 3D hybrid composites with basalt yarns for warp reinforcement and Kevlar yarns for weft and binders absorbed 7.67%–48.49% more energy than the 3D homogeneous Kevlar and basalt composites.

To take advantage of the high strength fibres, a hybrid of glass/carbon fibre reinforced epoxy composite was prepared. Eight layers of E-glass fibre and carbon plain weave ($0^\circ/90^\circ$) fibre were stacked in different sequences. The LVI of the hybrid composites was analysed for different energy levels. Carbon fibre as the top and bottom layer helped to reduce the damage size and the deflection of the composites. Thermo-graphical imaging is a kind of non-destructive evaluation which is also used to identify the damage occurring on composites (Hung *et al.*, 2018). Basalt/Kevlar fibre hybrid polypropylene composites were made by the alternative stacking of basalt and Kevlar in each 4 layer, Kevlar layers on the front face and basalt 4 layers on the back face of the composites. The hybridization and stacking sequences increased the impact performance of the composites. The alternative arrangement of the Kevlar and basalt fibre composites absorbed more energy than the remaining composites fabricated (Bandaru *et al.*, 2016). Again, a carbon fibre hybrid with aramid epoxy composite was manufactured using the resin transfer moulding process. A hemispherical impactor was used with a diameter of 12.7 mm at 26.8 J. The results showed that carbon fibre as an impact surface has better performance than other composites. Given the average damage area of the composites, the carbon fibre in the impactor surface performed better than the aramid fibre in the impactor surface (Ying *et al.*, 2016). Hea *et al.* (2018) investigated the impact and post-impact flexural strength of carbon fibre reinforced sandwich hybrid composites. A corrugated core aluminium sheet was used to fabricate the sandwich composites using the hot pressing moulding method. In sandwich composites, the top face plays an important role in the composites; the top face does not suffer a lot at lower impact energy and delamination occurred due to matrix cracking. At higher impact energy, the top face was penetrated completely and failure occurred due to fibre fracture and matrix cracking. The post-impact flexural strength and the residual flexural strength depend on the impact energy and the impact location.

The LVI of shape memory alloy (SMA) hybrid composites was characterised by Rim *et al.* (2011). SMA embedded with conventional composite and non-SMA (graphite/epoxy prepreg composites) composites have been investigated.

The incident impact energy (e) is calculated as follows (Rim *et al.*, 2011):

$$e = mgh \quad (2)$$

where

e = the incident impact energy,

m = the mass of the impactor, and

g = the acceleration due to gravity,

h = the height of the impactor.

It was confirmed that embedding SMA with conventional composites increased the impact energy absorption. Wang *et al.* (2008) investigated the influence of the fibre orientation in 3D woven hybrid composites on the LVI properties; aramid (Kevlar[®] 129), basalt fibres and epoxy resin were used to fabricate the interply hybrid composites. The specific energy absorption of the interply hybrid composites was shown to be higher in the warp and weft directions of the composites than in the intraply hybrid composites due to the layer by layer fracture mode.

The LVI behaviour of basalt/nylon intraply laminate hybrid composites was investigated experimentally. A composite plate was fabricated with different warp and weft fabrics. Varying energy levels were used with a hemispherical impactor. It was observed that the impact resistance of the hybrid composites was extensively affected by the addition of the nylon and basalt fibre content (Dehkordi *et al.*, 2010).

Basalt/glass fibre hybrid composites were fabricated by RTM techniques by varying the stacking sequences in the form of BG-HS (7 layers of glass fibre – core, and 3 layers of basalt fibre – skin), BG-HI (basalt fibre stacked alternatively) and mono-composites of basalt and glass fibre composites. Both the hybrid composites performed better than the mono-composites, and basalt as skin and glass as core performed better than the intercalated BG-HI. Basalt fibre composites showed better energy absorption than glass and BGHS composites (Sarasini *et al.*, 2013). To study the damage resistance of the glass and jute fibre hybrid composites, the specimen was fabricated using the hand-layup technique under light pressure at room temperature. The results revealed that the jute laminates have better impact energy absorption than the hybrid composites. But the damage resistance capability is less than that of the hybrid composites (Ahmed *et al.*, 2007).

Thorssona *et al.* (2018) investigated the behaviour of laminated composites on low velocity edge on impact and the compression after impact of the composites. Different impact energies and impact angles of 0° and 45° and NDT techniques were used.

Table 1 LVI of different hybrid composites, energy level, and impactor used

Reference	Composite materials	Energy level	Impactor
(Sharmaa <i>et al.</i> , 2018)	FML – Glass Aluminium composites	20, 30, 45, 60 and 75 J	16 mm dia Hemispherical
(Chen <i>et al.</i> , 2017)	Flax fibre epoxy composites	4, 6, 8, 10, 12 and 14 J	12.7 mm dia Hemispherical, Conical
(Chang <i>et al.</i> , 2017)	Auxetic warp-knitted spacer fabric	3–12 J	12.5 mm dia Hemisphere
(Kaoa <i>et al.</i> , 2018)	Foam, PLA and PU	–	10 mm dia Cylinder
(Khan <i>et al.</i> , 2016)	Glass Epoxy composite	6, 30, 70 and 100 J	12.7 mm dia
(Reghunath <i>et al.</i> , 2015)	Glass vinyl ester composites	12, 35, 80 and 110 J	Spherical head steel
	Glass fibre composites	2 m/s, 2.5 m/s and 3 m/s	10 mm radius
(Rahmana <i>et al.</i> , 2018)	Kevlar Nanoclay	At 32 J	Hemispherical head 15.9 mm
(Ansaria <i>et al.</i> , 2017)	Kevlar Graphene composites	5–50 m/s	Hemispherical
	Glass fibre composites		19 mm dia Cylindrical blunt steel
(Ferrante <i>et al.</i> , 2016)	Fibre metal laminates	30, 45, 60, 5, 120 J	Hemispherical – 20 mm dia
(Caminero <i>et al.</i> , 2017)	Basalt/ Aluminium foil	3, 5 m/s	Ovial – 12 mm tip
	Carbon/glass hybrid composites		Hemispherical 6 mm radius
(Bienias <i>et al.</i> , 2016)	Aluminium / glass laminates	10, 25 J	Hemispherical 12.7 mm
(Elias <i>et al.</i> , 2017)	3D woven carbon fibre yarn embedded in epoxy composites	60, 100, 150, 220 J	Hemispherical 40 mm dia
(Boria <i>et al.</i> , 2017)	Polypropylene composites both reinforcement and matrix	57, 144, 342 J	Hemispherical 20 mm dia
(Zarei <i>et al.</i> , 2017)	GLARE, Aluminium glass epoxy, Nylon 6,6 composites	6, 12, 18, 32 J	Hemispherical 12.7 mm
(Balkoglu <i>et al.</i> , 2018)	Pinewood, ashwood Wooden composites as intermediate layer	30, 60 J	● 78° peak angle, tip 3 mm conical ● Hemispherical, 12.7 mm dia
(Wang <i>et al.</i> , 2018)	Carbon polyphenylene	5, 15, 25, 35 J	Hemispherical 12.7 mm dia
(Ravandi <i>et al.</i> , 2017)	Flax/epoxy stitched composites	19.6 J – non perforation 44.6 J – full perforation	Hemispherical 12.7 mm dia
(Dogan and Arian, 2017)	Glass/epoxy Glass/polypropylene PVC foam sandwich composites	25, 50, 75, 100, 125 J	Hemispherical
(Hung <i>et al.</i> , 2018)	Glass/carbon hybrid epoxy composite with different stacking sequence	6, 8, 10 J	12.7 mm dia Hemispherical
(Dhakal <i>et al.</i> , 2018)	Flax unsaturated polyester composites	25, 27, 29 J	16 mm dia Hemispherical
(Bandaru <i>et al.</i> , 2017)	Kevlar/basalt hybrid polypropylene composites	25, 50, 75 J	19.8 mm dia Hemispherical
(Razali <i>et al.</i> , 2014)	Types of glass fibre epoxy composites	14, 28, 42, 56 J	12.7 mm dia Hemispherical
(Dehkordi <i>et al.</i> , 2010)	Basalt/Nylon woven fabric composites	15, 30, 45 J	10 mm dia Hemispherical
(Sfarra <i>et al.</i> , 2013)	Basalt fibre composites Glass fibre composites	7.5, 15, 22.5 J	12.7 mm dia Hemispherical
(Soliman <i>et al.</i> , 2012)	Carbon epoxy MWCNT composites	15, 24, 30, 60, 120 J	12.7 mm dia Hemispherical
(Sarasini <i>et al.</i> , 2013)	Basalt/glass hybrid composites	5, 12.5, 25 J	12.7 mm dia Hemispherical
(Whisler and Kim, 2012)	Glass/epoxy composites	5, 10, 15, 15, 20, 25, 30, 35, 40 J	12.7 mm dia Hemispherical 12.7 mm dia 50.8 mm dia 152.4 mm dia

The impact angle of 0° showed a highly localised event, but for the 45° impact angle, there was a considerable global deformation through bending. The impact damage at 0° angles was shown to be more significant than at 45° angles. In the case of the delamination of the composites, for 0° angles of the tested composites, it was clearly visible but for 45° it was hidden from the naked eye. The materials used, the energy level applied and the impactor used are presented in [Table 1](#).

Numerical Studies of Low Velocity Impact

Numerical modeling is a useful tool for analyzing engineering problems and gives approximate results to reality. Numerical modeling can reduce the number of trials needed for the experimental work, which reduces the cost. Likewise, many researchers are doing their modeling using software as well as a theoretical approach. [Tita et al. \(2008\)](#) performed a failure analysis of carbon epoxy composites using numerical and experimental approaches. It was concluded experimentally that the stacking sequence and the energy level are the influencing parameters. Many failure mechanisms were found, *e.g.*, fibre rupture, matrix cracking and delamination.

Honeycomb structures were prepared with a carbon epoxy sandwich composite by [Chen et al. \(2017\)](#). The study obtained experimental data which was compared with the numerical results, and both were in good agreement. [Tiea et al. \(2018\)](#) investigated experimentally and numerically patch-repaired CFRP laminates of different shapes (circle, square, rhombus, hexagon and octagon patches) and sizes placed on a single side of the parent laminate plates. The damage mechanism and the failure prediction of the composites were obtained using numerical methods. From the results, the circle patch leads to a better repair performance than other combinations in terms of the energy absorption and delamination area. A new type of numerical prediction has been implemented by [Salveti et al. \(2018\)](#). The performance of Olsson's analytical model was matched with the experimental values. The volume fraction and the incidental impact energy of the glass fibre reinforced polyamide composites were analysed. The impactor velocity has significant effects on the impact response and the contact force ([Mars et al., 2018](#)).

The FEA model has been developed for glass fibre composites using ANSYS/AUTODY hydro code. The rebound velocity of the projectile increased with the incidence velocity until penetration started, and it was also found that increasing the projectile velocity meant that the energy absorption of the composites also increased ([Ansaria et al., 2017](#)).

LVI and compression after impact have been investigated numerically by [Soto et al. \(2018\)](#) with special attention being paid to computational efficiency. Numerical study demonstrated that delamination and fibre breakage are the predominant failures in the composites. [Topac et al. \(2017\)](#) examined the LVI of CFRP composites experimentally and numerically. The damage mechanism was studied using high-speed camera imaging and the experimental value was compared with the numerical value. [Long et al. \(2015\)](#) predicted the delamination of composites with 2 types of stacking order, and the ultrasonic C-scan was used to identify the delamination area.

Again, FEM was used for carbon and glass fibre interply hybrid composites with varying impact velocities of 3 m/s, 5 m/s and 7 m/s. The experimental output illustrated that the hybrid composite at mass ratio of 37.63 absorbed more energy than the pure composites and the results are in good agreement ([Yang et al., 2015](#)). [Bienias et al. \(2016\)](#) studied the LVI of aluminium glass fibre laminates using both experimental and numerical approaches. Composites plates were fabricated with a thickness of 1.5–3.5 mm using the autoclave process. The LVI analysis was done at room temperature with impact energies of 10 J and 25 J. The damage to the composites includes the delamination taking place in the composite interlayer and on the metal composite interface, and cracking in the composites and in the lower layers of the metal.

[Kathiresan and Manisekar \(2017\)](#) studied the LVI of glass fibre reinforced polymer composites with varying orientations, *e.g.*, random, woven [0/90] and angle-ply [$\pm 60^\circ$]. Using glass fibre, conical frusta shaped composites were fabricated with a semi-apical angle of 15° – 24° . The FEA model was also used, using ABAQUS software to calculate the collapse behaviour and energy-absorption characteristics of GFRP with similar experimental conditions. 3D carbon fibre epoxy composites were prepared with 11.5 mm thickness. The damaged area and the residual depth of the impacted composites plates were analysed ([Elias et al., 2017](#)).

[Pach et al. \(2017\)](#) experimentally and numerically analysed the ballistic resistance of Carbide, steel and Al_2O_3 with 10 layers of Aramid fibre reinforced styrene-butadiene-styrene (SBS) copolymer hybrid composite shields. The experimental and numerical values are compared. They suggested that in order to improve the weft and warp threads of the aramid fibre, the moulding parameters need to change.

Jute-epoxy, rubber, and jute-epoxy-rubber sandwich composites' ballistic impact have been analysed for the different thicknesses and velocities. It was shown that there was a considerable amount of energy absorption in the rubber composites compared to the jute fibre epoxy composites. The damage area of the composites shows the ductile nature for rubber composites and the brittle nature for jute epoxy composites ([Sangamesha and Kulkarni, 2018](#)).

[Pashmforoush et al. \(2018\)](#) performed an optimization of the stacking sequence of carbon epoxy composites in multi-directional laminated composites under LVI to perform damage analysis experimentally and numerically. The composites were cured in various conditions, *i.e.*, in a vacuum with an autoclave pressure of 0.103 MPa, heated at $5^\circ\text{C}/\text{min}$ to 105°C for 60 min and cooling was performed at $50^\circ\text{C}/\text{min}$ to 65°C . The results showed that the stacking sequences of [90/90/90/0]s and [0/90/90/0]s had the minimum damage under compression, [45/_60/60/45]s and [60/90/0/_45]s had the minimum fibre damage under tension [45/_60/0/90]s and [45/_60/60/45]s had the minimum matrix damage under compression and [45/_45/45/_45]s and [0/90/90/0]s had the minimum matrix damage under tension. [Table 2](#) represents the numerical approach used to analyse the LVI of the composites.

Flax fibre reinforced unsaturated polyester composites were studied with three energy levels nearer to the perforation using a hemispherical steel impactor. LS DYNA was used to study LVI. Both the maximum load and the energy absorption were reduced extensively post-impact ([Dogan and Arikan, 2017](#)). Aramid fibre reinforced polymer composites were prepared with varying geometries, *i.e.*, cylinder, ellipse and sphere. The elliptical sample has the highest energy absorption capability, which was due to

Table 2 Numerical approach used for LVI

<i>Ref.</i>	<i>Material</i>	<i>Numerical model used</i>
(Tita <i>et al.</i> , 2008)	Carbon epoxy composites	Hill's model User material subroutine ABAQUS
(Chen <i>et al.</i> , 2017)	Carbon epoxy honeycomb structure	Continuum damage mechanics (CDM) Cohesive zone method (CZM) ABAQUS
(Tiea <i>et al.</i> , 2018)	Patch repaired CFRP	Continuum damage mechanics (CDM) Cohesive zone method (CZM) ABAQUS
(Salvetti <i>et al.</i> , 2018) (Mars <i>et al.</i> , 2018)	CFRP Glass fibre polyamide composites	Olsson model User defined material subroutine (UMAT) ABAQUS
(Ansaria <i>et al.</i> , 2017) (Soto <i>et al.</i> , 2018)	GFRP Fabric thin ply laminates	ANSYS / AUTODYN, hydro code Cohesive zone method (CZM) Continuum finite element model ABAQUS
(Topac <i>et al.</i> , 2017)	CFRP unidirectional laminates	Continuum damage mechanics (CDM) User written VUMAT subroutine
(Long <i>et al.</i> , 2015) (Yang <i>et al.</i> , 2015)	Carbon epoxy composites Carbon/glass fibre interply hybrid composites	Hashin damage criteria Subroutine VUMAT ABAQUS
(Bienias <i>et al.</i> , 2016) (Kathiresan and Manisekar, 2017)	Aluminium glass laminates Glass fibre epoxy conical frusta	VUMAT Hashin's criteria ABAQUS
(Elias <i>et al.</i> , 2017)	Carbon fibre yarn 3D composites	Onera damage model for polymer matrix composites (ODM-PMC) Continuum damage model Subroutine VUMAT
(Pashmforoush <i>et al.</i> , 2018)	Carbon fibre epoxy composites Different stacking sequence	
(Bandaru <i>et al.</i> , 2017)	Aramid fibre polyester composites Varying geometrical shapes	LSDYNA
(Balkumar <i>et al.</i> , 2016) (Zhang <i>et al.</i> , 2016)	Aluminium based Aramid, glass and carbon metal laminates Unidirectional carbon epoxy honeycomb sandwich panel	ABAQUS VUMAT Hashin's failure theory ABAQUS

the effective stress transfer and maximum energy absorption capacity; the difference was 17% between the elliptical and cylindrical geometries (Ayten *et al.*, 2016). Glass fibre FML composites were studied by Balkumar *et al.* (2016) numerically. They used Design of Experiments (DOE) for the different data set and numerically the results were compared with the already available literature.

Zhang *et al.* (2015) investigated the LVI and compression after impact of honeycomb sandwich composite panels experimentally and numerically. The honeycomb sandwich panel was fabricated with different face sheet thicknesses. The C scan inspection technique was used to inspect and analyse the damage in the composites and it was observed that thin face sheet thickness sandwich composites had less damage area than the thick face sheet thickness sandwich composites. The compressive damage and shear damage are addressed by testing the three point bending test for the honeycomb damage model.

Recyclability of Fibre Reinforced Polymer Composites

Day by day the applications of fibre reinforced polymer composites increased involved in many industrial applications, automobiles, sports etc. since used polymer more possibility for environmental issues. Another side there is a biggest challenge in recycling these wastes. These wastes can be recycle using different techniques like Mechanical recycling, Pyrolysis, Fluidized-bed process, Micro-wave assisted pyrolysis, Solvolysis etc. it was seen that glass fibre polymer composites the mechanical recycling is most suitable (Oliveux *et al.*, 2015). Pyrolysis recycling is most suitable process for carbon fibre composites. Liu *et al.* (2017) reviewed the research papers and found that there is lack of composites recycling workshop and lack of optimization mathematical model to predict the parameters which are influencing the environmental issues. Recycling required the suitable method, work-force, and research plan optimization operations. Asmatulu *et al.* (2014) reviewed the structural composites recycling is important aspects since most of the industries are using composites for structural applications. Ribeiro *et al.* (2016) reviewed the different recycling techniques and advised that the recycling concept need to be improved.

Conclusion

This review has focused on single fibre composites, hybrid composites and metal laminate composites and their low velocity impact properties. The low velocity impact analysis was concerned with the development of new materials for structural applications in the automobile and aerospace industries. Different aspects of the parameters are taken into account for the betterment of LVI in terms of the fibre, matrix, fillers, metal laminates, nano-particles, energy levels, failure, mechanisms, and numerical approach etc. This review concludes with the following:

- (1) Proper selection of the fibre can produce enrichment of the LVI. High strength synthetic fibre is always a better choice for the ballistic nature of the applications. The failures of the single fibre composites are due to the fibre breakage, delamination and matrix fracture.
- (2) Aluminium metal laminate composites are a promising alternative to high strength fibre. In metal laminate composites, interfacial bonding is the key issue, meaning that delamination is the predominant failure mode in composites.
- (3) Nano-particle reinforcement in a polymer composite helps to improve the low velocity impact strength.
- (4) From an environmental perspective, reducing the usage of synthetic fibres in composites means that many researchers have focused on hybrids of natural–synthetic fibres. The stacking sequence and volume fraction of the constituent material enhance the material's properties.
- (5) The numerical approach is an alternative tool to performing the LVI analysis of the composites. Finite element methods are commonly used, and for simulation ABAQUS explicit and ANSYS is used. Almost all of the researchers checked their numerical results with the experimental values.
- (6) For recyclability aspect of polymer composites essential to establish the standard method to recycle the composite waste properly.

Acknowledgements

This work was supported by the Universiti Putra Malaysia under the research grant UPM/GP-IPS 9490602. Special thanks to the Aerospace Manufacturing Research Centre (AMRC), Universiti Putra Malaysia, and also to the Laboratory of Biocomposite Technology, Institute of Tropical Forestry and Forest Products (INTROP)-HiCOE, Universiti Putra Malaysia.

See also: Characterization and Interface of Natural and Synthetic Hybrid Composites. Development and Characterization of Aluminum Hybrid Metal Matrix Composites Used in Automotive Applications. Experimental Investigations for Development of Aluminum MMC With Hybrid Reinforcement and Vacuum Moulding. Historical Development of Hybrid Materials. Investigations for Rapid Tooling Prepared With Waste Polymer-Based Hybrid Filament. Subtractive Versus Hybrid Manufacturing

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Mechanical Properties, Sealability, and Recyclability of Elastomeric Materials in Petroleum Industry

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Introduction

The ongoing efforts of engineers and scientist in materials and their processing results in development of new material types and/or an improvement in the properties or processing of existing materials. The natural desire for improvement and/or the need to fulfill a task always leads to emergence of new materials or process improvement with an aim to better the performance of an existing system or build a totally new system. As is the process, new materials bring new challenges for the entire spectrum, that is, from basic morphology, characterization, manufacturing, sustainability, recycling until disposal. All of these create new opportunities for design, manufacturing, fabrication, assembly, maintenance, etc. as well as expose the limitations of new developments posing new challenges for research and development. Such an interrelated process is highly instrumental in the development of host of manmade materials (materials that do not exist in nature and are developed by manipulating one or more materials) including the development and application of elastomers. According to ISO (1382:1996), elastomers are *high molar mass material which when deformed at room temperature reverts quickly to nearly original size and form when the load causing the deformation has been removed*. The term elastomer originates from two terms, *elastic*, meaning the ability of a material to return to its original shape upon load removal, and *-mer* from polymer, which means parts. It consists of chains of units and each unit is called a “mer.” Each chain consists of large number of “mers.” These “mers” are linked or polymerized together to construct the elastomer. Each “mer” is usually made of carbon, hydrogen, oxygen, and/or silicon. These are amorphous polymers existing above their glass transition temperature, so that considerable segmental motion is possible. The molecular structure of elastomer consists of *mer* chains, which are cross-linked with each other. Elastomers are derived from many sources but only natural rubber is extracted from the rubber tree (organic production). All other types of elastomers are composed of a wide variety of minerals, which are subjected to polymerization process, the linking together of molecules to create the properties and texture commonly associated with rubber, before it can be used commercially.

Fundamentally, an elastomer is a rubber like polymer, which is both viscous and elastic by nature. In other words, the elastomers have low Young's modulus of elasticity and high strain at fracture/break as compared with other materials. Under application of forces, elastomers conform to large deformation by breaking of intermolecular but without the breaking of covalent bonds of the compound, primarily made of five major elements, that is, carbon, oxygen, nitrogen, silicon, and hydrogen. All elastomers are affected when exposed to different types of fluids. Swelling occurs due to absorption of appropriate fluid, resulting in a volume increase. The degree of swelling depends on the type of base elastomer and the type of fluid that is exposed to base elastomer. It can be as low as negligible and as high as a few hundred percent. When the degree of swelling is substantial, it is termed as a swellable elastomer, else it is known as inert elastomer. In short, a swelling elastomer is a viscoelastic material that swells when placed in certain fluids. The swelling fluid can be fresh water, water with different percent salinity, oil of various grades, a mixture of oil and water, acid, and gas. Water swelling elastomers consist of a base elastomer mixed with hydrophilic filler or swell in water themselves such as hydrophilic polyurethanes.

The application of elastomer spans a wide spectrum including but not limited to automotive, steel, renewable energies, oil and gas, material handling, mining, etc. Recent innovative use of elastomers in defense applications opened another research avenue (Wood, 2018). The self-healing effect of an elastomer due to the local heating helped in closing the fracture surface (Varley and Zwaag, 2010). Thermoplastic elastomer is used in many medical devices due to their recyclability, sterilizability, low level of extractable compounds, and cost effectiveness. The elastomer has successfully found a wide range of applications in the oil and gas industry such as seals due to its high elasticity characteristics, zonal isolation under normal and HP/HT (high pressure/high temperature) conditions, assistance in improving well yield, belts for transmission system, flexible hoses, expansion joints, personal protective apparatus, etc. (Falco, 2000). The use of them as dampers has also made significant inroads in multitude of applications particularly in offshore platform structures. However, the use of swellable elastomer as sealant in nontypical environments, which exist in surface and subsurface conditions, has attracted the attention of the oil and gas industry. The importance of these rubbers can be judged from the fact that global revenues are forecast to rise to US\$56 billion in 2020 (Ceresana Market Research, 2013).

Elastomers in Petroleum Industry

For years, the conventional or multiple casing string technology has been used in the petroleum industry to drill oil and gas wells. The conventional drilling requires current section of the pipe to go through the previous pipe section, which continues until the target depth is achieved. This means that with each section, there will be a reduction in pipe diameter compared with the previous one, which results in loss of internal diameter from the surface to the total depth. These diameter reductions are typically large, for example, a surface hole of 36-in. diameter results in 4-in. diameter at the final depth of the well. These so-called telescopic wells

limit the reachable depth and hence prevent accessibility to deeper reservoirs. The limits imposed by loss of inner diameter on exploration and production of hydrocarbons are not only a mere inconvenience but also results in loss of reservoirs. The development of solid expandable technology (Filippov *et al.*, 1999) enabled the industry to design and build slim wells by significantly reducing the loss of reservoirs as well as premature abandonment of wells due to the unrepairable damages (Pervez *et al.*, 2008, 2007; Seibi *et al.*, 2009; Blasingame and Cales, 2003).

However, with every new development new problems surface. As the well becomes deeper, the seepage of fluids from fractures in the formation and flow of waters in specific zones or the reservoir itself causes many problems in the wells. In particular, when a well experiences aging, unwanted fluids start flowing through the perforations in the pipe. In fractured carbonate reservoirs, the problem arises in cementing due to heavy losses in the circulation material, adjacent to reservoir zones that are subjected to different development scheme such as water flood, gas/oil gravity drainage, and steam or polymer injection, which are critically needed for isolation of undesirable zones (Kleverlaan *et al.*, 2005). Besides all these, water influx causes many difficulties for reaching deep and faraway targets in drilling process and affects the stability of the hole (i.e., creating unstable formations) since it makes the formation over or under pressurized conditions.

All these problems, when combined, result in reduction of oil production, as water seeps inside the production pipe. The resulting effect is more production of water as compared with the hydrocarbon. The energy required to lift this undesired water, separating it from oil/water mixture and later disposal of the separated water adds cost of produced water disposal, treatment against corrosion, and complying with environmental regulations. At times, it has resulted in shutdown of a well due to high ratio of undesired water to hydrocarbon ratio.

Zonal Isolation

The phenomena of shutting of fractured reservoirs producing unwanted fluids or repairing a damaged well pipe fall are the most demanding challenges faced by hydrocarbon producers. Zonal isolation refers to the condition or situation with which the fluid in one permeable zone can be kept separable from those fluids of another zones. The main functions of zonal isolation systems are to shut off water in the permeable zone and divide the well in segments. This segmentation enables for corrective action after water or other fluids break through in one of the segments. Technologies have been developed to design the sheath in an oil/gas well to effectively isolate problematic zones or repair damaged wells using cement slurry, mechanical packers, or swellable elastomers. There are various conventional and new methods for zonal isolation. A brief description of these methods follows in subsequent sections.

Cement liners

Oil well cement is used for zonal isolation and inflow control. The cement is used to seal the annulus between the pipe and the formation wall to prevent mixing between various fluid layers and the migration of gases. However, a series of disadvantages is involved in using cement. Namely, cement shrinks on its setting or environment; it becomes brittle after hardening, and it has unpredictable setting times, thus it can put tools or even the entire well at high risk. Besides that, repairing of a failed cement job is extremely difficult and costly. Cement seals off all zones containing oil and subsequently needs perforation. Fig. 1 shows the consequence of poor cementing, that is, perforations.

External casing packers

External casing packers (ECPs) are considered as one of the mechanical isolation methods. They are short rubber packers inflated by cement as shown in Fig. 2. ECPs work by inflating them during the installation process. For long-term applications, it requires

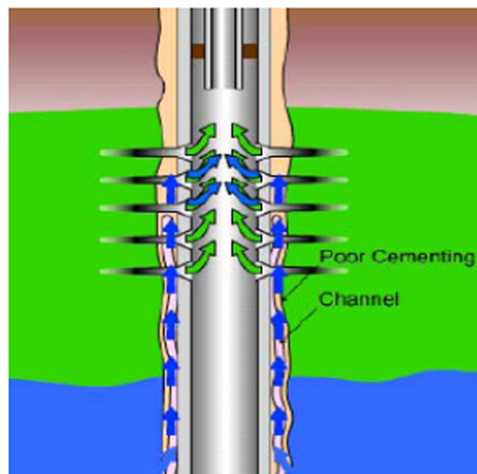


Fig. 1 Wellbore schematic with consequence of poor cementing. Reproduced from Laws, M.S., Fraser, J.E., Soek, H.F., Carter, N., 2006. PDO's proactive approach to solving a zonal isolation challenge in Harweel HP wells using swell packers. In: Proceedings of the IADC/SPE Asia Pacific Drilling Technology Conference and Exhibition, SPE 100361. Bangkok, Thailand, 13–15 November 2006.

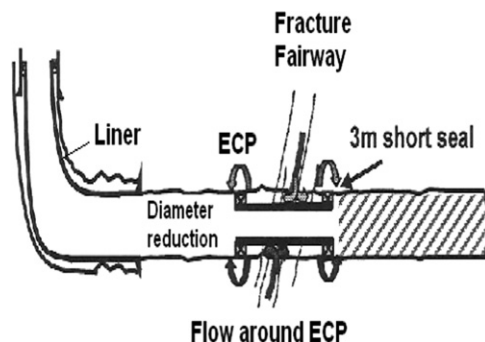


Fig. 2 Use of ECP to shut off fractured carbonate reservoir. Reproduced from Marketz, F., van Noort, R.H.J., Baaijens, M.N., 2004. Expandable tubular completion for carbonate reservoirs. In: Proceedings of the 11th Abu Dhabi International Petroleum Exhibition and Conference, SPE 88736. Abu Dhabi, UAE, 10–13 October 2004.

cement inflation to minimize adverse effects on the packers. If the wells have high deviation or turn to horizontal wells then installation process becomes very complex due to cement inflation. When external casing packers are used for sealing in a permeable formation, some fluids will bypass the rubber element through the pores in the formation. This adversely affects the effectiveness of the packers. In addition, use of ECPs reduces the diameter of the borehole, and the installation involves pumping cement; consequently a cleanout trip is needed (Coronado *et al.*, 2002).

Chemical shutoff

In simple words, chemical shutoff means to shut off zones with gel, where gels and polymer can be placed deeper into the formation (Welling *et al.*, 2007). However, it is also a costly method and in some cases not considered as an efficient way to achieve perfect zonal isolation.

Swellable elastomers

The flexibility in adjusting the material properties (Young's modulus and the compressibility) of swellable elastomers under different temperature, pressure, and working fluids helped to enhance the effectiveness of zonal isolation. During the last two decades, field data showed stress corrosion cracking failures of oilfield pipes and completion-tool equipment. Studies have been done in the laboratory to understand the interaction of heavy brines with commonly used metallurgical alloys in service tools, work string materials, and others. It was found that amine compounds destroy elastomer seals in heavy brine at elevated temperature. Silverman *et al.* (2003) conducted tests for North Sea wells and found that NBR packing and FKM O-ring seals rapidly lose their elongation at break (embrittlement). Elastomer seals made of FEPM Aflas seals remained flexible and elastic in this harsh environment. A comparison between various types of packers is shown in Table 1.

Swell Fix has developed a series of products called a Zonal inflow profiler (ZIP) system, which is one of the new technologies in oil well fields that has helped in solving many resolved problems. The ZIP system has various six combinations, that is, I-ZIP, E-ZIP, X-ZIP, S-ZIP, C-ZIP, and G-ZIP, all of which are based on same work principle (Vliegthart, 2008). ZIP systems have many advantages:

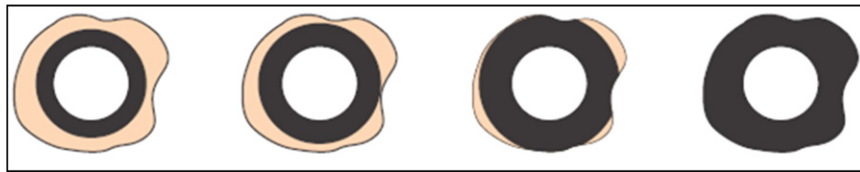
- (1) they provide immediate fracture shutoff,
- (2) they incur less operating cost,
- (3) they have a quick response (less oil loss),
- (4) they make it possible to log and see the flow from each section,
- (5) they have a self-activating mechanism and maintain zones out of water.

Swellable Packers

Swellable packers are made of elastomers that are elastic materials, and significantly swell when exposed to various types of fluids such as saline water, oil, acid, or gas. The two commonly used types are water-swellable or oil-swellable elastomers. Typically, a water-swellable elastomer works on the principle of diffusion and osmosis, and operates in temperature range of 50–90°C. While the oil-swellable elastomers works on the principle of diffusion with a temperature range of 80–130°C. When a wellbore fluid comes in contact with the elastomer, swelling starts due to the process of absorption. Because of absorption, the rubber molecules stretch from low to very high volume. This swelling effect can cause a 600% increase in its volume and over 100% change in its original thickness. Fig. 3 shows an elastomer before and after swell, which clearly demonstrates manifold increase in its volume. The challenge is to obtain a high swell ratio with a good pressure sealing capability. The elastomer swelling rate depends on wellbore pressure, temperature, and fluid composition present in the wellbore.

Table 1 Comparison between three zonal isolation techniques

Comparison parameters	Isolation type		
	Cement liners	ECPs	Swellable elastomers
Sealing effectiveness	Good	Low	Good
Reliability	Good	Below average	Good
Cost	High	Average	Low

**Fig. 3** Original and swelled elastomer in saline water.**Fig. 4** Swellable elastomer seal swell to fill the shape of the wellbore.

The main characteristics of swellable elastomers are as follows:

- (1) Throughout the swelling process, the elastomer absorbs swelling fluids from its environment. Therefore, to enable the elastomer to develop pressure and swell completely on the borehole wall, sufficient swelling fluid should be there.
- (2) In low viscosity oil and higher temperature, oil-swellable elastomers swell further and faster. However, if the oil has high viscosity the swelling process becomes very slow.
- (3) It is not possible to fully preswell the elastomer in lighter oil and then maintain this swell in heavier oil.
- (4) In low salinity water and higher temperature, water-elastomers swell further and faster.
- (5) It is not possible to fully preswell the elastomer in less-saline water and then maintain this swell in a more-saline environment.
- (6) In a mixture of oil and water environment, water-swelling elastomers will only react with water and swell as if they were only submersed in water. On the other hand, oil swelling elastomers will only react with oil and swell accordingly.

One of the excellent characteristics of elastomer seals is their ability to fill any wellbore shape or cavity, pits, scratches and deform easily around asperities as shown in [Fig. 4](#). Thus, to ensure effective sealing, the elastomer seal must maintain a contact pressure greater than the fluid pressure in the formation. For water flood wells a combination of swelling and nonswelling elastomer seals have been used to ensure a compromise between maximum seal coverage, provide the capability to perforate between no swelling seals and protect swelling seals with abrasion-resistant and corrosion resistant rubber while running in the hole ([Marketz et al., 2006](#)).

To attain effective swelling using swellable elastomers, it is necessary to have:

- (1) Correct elastomer composition depending on borehole fluid and operating temperature,
- (2) Supply sufficient swelling fluid,
- (3) Proper seal length to prevent any leakage in permeable formations,

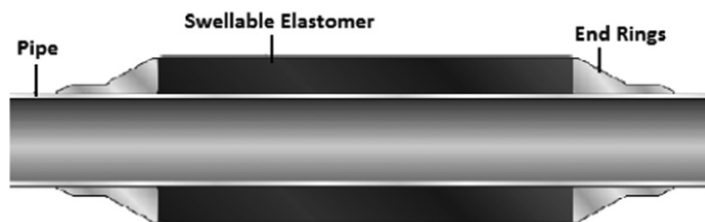


Fig. 5 A typical swellable packer for oil-well applications.

- (4) Seal of adequate thickness,
- (5) Correct depth where elastomer seal need to be placed, and
- (6) Sufficient swelling time to allow installation.

In oil and gas wells, swell packer technology consists of standard oilfield pipes with vulcanized elastomers of various lengths spaced at constant or variable interval as shown in Fig. 5. Once the swell packer comes in contact with formation or borehole fluids, the elastomer element swells to form an effective annular seal through thermodynamic absorption process.

The major advantages of the swellable packer are that they eliminate the need for any extra running or setup and have no moving parts. In addition, they swell nicely o fill all the asperities around that place to form a complete seal. The condition of having adequate time to swell can only be considered as a negative aspect of this process. Therefore, it is important to provide enough time to complete the sealing before the section is used for its intended purpose. However, this problem nowadays tends to be fixed; since new types of swelling elastomer are designed to swell as short as a day or even few hours. Another critical factor to be considered is that getting the placement of the packer wrong can obviously have harmful results to the well. Thus, accurate placement of the packer in an appropriate environment is essential to ensure successful outcome.

Characterization of Swellable Elastomers

Performance estimation of swellable elastomers requires material data along with the geometrical parameters, end conditions, operating parameters and constraints, if any. Hence, comprehensive information is needed regarding the response of material under different operating conditions. Since, the application focus is downhole sealing, therefore material data is required for various salinity, temperature, swelling fluid, etc. Different experiments were designed and implemented for characterization of swellable elastomer and their performance evaluation when used as seals in downhole applications. Standard procedures are available to conduct these tests on rubber materials, which are also carefully followed to obtain consistent results. The objective is to follow ASTM standard as much as possible. The tests include hardness, tensile, compression, and swelling behavior. Test temperatures and salinity conditions were selected to imitate actual well conditions in different oil wells. Three different geometries of elastomer samples are used for characterization.

- *Rings*: These samples are used to obtain the modulus of elasticity of the elastomer by measuring their fracture strength and strain in addition to their cross-sectional area and flattened length.
- *Plates*: These samples are used to obtain the swelling amount of the elastomer over several weeks. The swelling is determined by measuring the volume of the plates every week using graduated cylinder and dimensions and comparing it with the initial volume.
- *Disks*: These samples are used to obtain the hardness of the elastomer every week in addition to the change in volume.

These samples, as shown in Fig. 6, are cut from fresh/unused elastomers. A total of 16 jars are used to hold three types of samples (plate, disc, and ring) under one temperature and one salinity condition. Out of these 16 jars, three jars used to hold three plate samples with one plate in each jar, five jars used to hold disk sample with three disks in each jar, and seven jars used to hold ring samples containing five rings in each jar. The process is repeated for various combinations of temperature and salinity. The selected temperatures are 25/30, 50/80, and 97 °C. The water salinity considered for the tests are 0.5%, 12%, and 25%. All samples at 30°C are kept in laboratory room environment. Four ovens are used to hold samples at 50°C, 80°C, and 97°C. Two small ovens are allocated for 50°C temperature, while one big oven is allocated for 80°C and 97°C temperatures. The following paragraphs describe each test type and associated equipment used for conducting the test.

Tensile Test

The objective of the tensile test is to determine the force required to break the specimen along with the stretch or elongation to the breaking point. Such test data is needed to specify the material type as quality control check of materials, and in designing components or systems to withstand given applied force. Since the elastomer is exposed to different temperature and salinity, it also helps to understand and quantify the chemical and thermal exposure effects on itself. Due to the swelling character of the elastomer, the tensile properties will also change with respect to the time over the entire swelling period. To accommodate this,



Fig. 6 Test sample geometries for elastomer characterization.

Table 2 Tensile test data for HNBR elastomer at 25°C and salinities of 0.6%, 12%, and 25%

Week #	25°C, 0.6%			25°C, 12%			25°C, 25%		
	Modulus (E)	Fracture stress (Pa)	Fracture strain (ε%)	Modulus (E)	Fracture stress (Pa)	Fracture strain (ε%)	Elastic modulus (E)	Fracture stress (Pa)	Fracture strain (ε%)
1	38,159.67	497,285.00	180%	14,369.00	23,831.00	197.27%	48,546.33	787,126	211.47%
2	35,219.33	267,698.12	146%	35,273.00	447,818.57	184.80%	44,864.00	674,515.36	214.60%
3	25,903.50	231,721.06	133%	35,819.33	364,345.33	152.87%	44,176.00	495,112.44	207.60%
4	33,215.00	267,295.09	112%	35,168.33	290,543.25	163.47%	41,419.67	568,650.43	178.53%
5	26,834.00	164,805.28	128%	33,357.67	311,546.39	144.47%	39,630.33	296,996.49	196.07%
6	29,527.00	229,114.88	124%	36,911.67	383,315.01	158.87%	39,929.00	534,934.33	199.80%
7	28,281.67	211,331.80	120%	33,199.33	380,363.33	167.87%	40,514.67	508,812.34	187.23%
8	34,992.33	249,933.46	117%	32,738.33	349,678.78	157.93%	36,158.33	445,540.46	185.60%
9	27,222.00	175,144.40	120%	32,180.67	300,099.57	139.53%	40,374.33	494,906.77	174.80%
10	32,582.00	223,417.65	113%	36,497.00	347,028.13	147.93%	38,036.67	446,766.77	179.73%
11	32,524.00	216,408.00	113%	36,863.00	364,745.00	153.60%	41,141.00	481,522	179.20%
12	32,466.33	209,400.33	112%	37,230.33	382,463.97	159.33%	44,244.00	516,279.82	178.73%
13	30,414.00	221,769.00	132%	35,750.00	378,730.00	166.50%	43,298.00	505,053	181.00%
14	28,949.33	234,139.15	153%	34,270.33	374,998.24	174.20%	42,353.33	493,827.04	183.37%

samples placed in specific environment are picked at regular time interval, such as one per week, and tests were conducted according ASTM standard D412-06a (ASTM D412-06a, 2007). Tests data are then used to obtain Young's modulus of elasticity, ultimate tensile strength, fracture strength and percent elongation (or percent reduction in area), and other tensile properties. Ring samples are used for this test. The apparatus used are typical universal testing machine and extensometer. Tables 1–4 show the results of 14 weeks' test for Young's modulus of elasticity (E), fracture stress (σ_f), and strain (ϵ) at fracture. The results show a variable nature of increase and decrease in the values of E , σ_f , and ϵ for different combinations of temperature and salinity. Separate tests were conducted to obtain stress versus strain diagram of the elastomer at room temperature as shown in Fig. 7. The stress-strain curve is almost linear, which implies that swelling elastomers (because of their peculiar cross-linking and special filler materials) do not behave like normal rubbers that generally exhibit a nonlinear tensile behavior. The average determined values are $E=14.4$ MPa, $S_{ut}=36.5$ MPa and % elongation = 265%.

Hardness Test

The resistance to penetration in an elastomer is measured through hardness. A durometer is used to measure the elastomer's resistance to penetration without any puncture on its surface based on ASTM standard ASTM D2240 (ASTM D2240-05, 2007). A blunt indenter point was pressed onto the elastomer surface against the action of a spring and readings were recorded based on the A scale as used for soft materials. Every week a swelled sample is taken out of the jar and three measurements of hardness are made at different positions on the sample at least 6 mm apart.

The average of three readings is taken for each sample and the process is repeated for 10 weeks for combinations of temperature and salinities. Figs. 8–11 show the variation in hardness over a period of 10 weeks at temperature of 25°C, 50°C, 80°C, and 97°C. From the figures, one can notice that the hardness is maximum at room temperature and it decreases with time for all salinities. However, the maximum hardness occurred when the salinity is high, that is, 25% and it remained so all along the weeks of the test. It decreases as the concentration of solution decreases, which is true due to the fact that diffusion of salt particles will fill the void in the polymer chain resulting in an increase of its resistance to penetration.

Table 3 Tensile test data for HNBR elastomer at 50°C and salinities of 0.6%, 12%, and 25%

Week #	50°C, 0.6%			50°C, 12%			50°C, 25%		
	Modulus (E)	Fracture stress (Pa)	Fracture strain (ε%)	Modulus (E)	Fracture stress (Pa)	Fracture strain (ε%)	Modulus (E)	Fracture stress (Pa)	Fracture strain (ε%)
1	99,938.00	239,415.00	111.10%	14,771.00	144,342.00	140.57%	43,373.00	483,917.00	160.60%
2	33,903.33	212,972.99	109.13%	37,177.00	353,099.38	149.20%	39,269.00	444,988.73	177.93%
3	35,458.33	219,281.25	104.67%	40,759.67	365,555.33	149.10%	45,426.00	539,695.56	180.40%
4	36,864.00	199,518.87	95.63%	39,461.00	386,853.04	150.43%	43,553.33	529,506.91	180.83%
5	35,232.33	173,440.73	108.93%	36,224.33	283,757.33	153.73%	40,673.00	480,687.24	191.63%
6	36,022.67	183,879.50	104.27%	44,866.33	437,121.66	156.03%	38,116.00	339,760.75	179.40%
7	34,698.00	114,410.10	94.00%	39,716.33	403,651.74	156.33%	43,446.00	500,737.28	180.00%
8	38,299.67	216,427.83	105.77%	45,489.33	456,383.81	157.57%	43,027.33	454,153.96	170.33%
9	41,101.33	226,979.14	97.90%	38,545.67	338,597.67	137.13%	40,016.33	462,383.07	173.43%
10	34,198.66	200,691.76	108.93%	41,891.67	398,713.62	150.73%	48,313.00	526,049.86	177.97%
11	37,060.00	204,326.00	104.68%	45,156.00	437,265.00	155.40%	47,516.00	513,081.00	176.40%
12	39,920.33	207,961.74	100.43%	48,421.00	475,817.60	160.10%	46,720.33	500,113.12	174.83%
13	34,464.00	204,088.00	116.42%	42,769.50	425,204.00	162.66%	45,452.50	535,727.00	179.30%
14	29,009.00	200,214.09	132.40%	37,118.00	392,591.40	165.33%	44,185.67	571,341.60	183.77%

Table 4 Tensile test data for HNBR elastomer at 80°C and salinities of 0.6%, 12%, and 25%

Week #	80°C, 0.6%			80°C, 12%			80°C, 25%		
	Modulus (E)	Fracture stress (Pa)	Fracture strain (ε%)	Modulus (E)	Fracture stress (Pa)	Fracture strain (ε%)	Modulus (E)	Fracture stress (Pa)	Fracture strain (ε%)
1	30,520.00	213,542.00	110.67%	14,016.67	147,916.00	156.23%	51,823.67	621,871.00	171.83%
2	37,697.67	191,611.42	102.53%	41,696.67	398,684.98	157.27%	46,482.67	544,238.39	188.87%
3	42,856.67	240,262.37	105.53%	47,316.33	422,294.41	143.70%	55,593.67	524,657.09	173.47%
4	43,645.33	138,292.43	95.63%	43,583.33	386,144.55	160.13%	45,632.67	542,639.05	159.30%
5	41,578.00	178,335.24	102.60%	60,845.33	556,946.42	142.53%	51,779.67	558,638.21	185.30%
6	41,696.67	175,540.97	101.30%	42,650.33	338,460.84	152.73%	45,440.00	502,428.81	180.47%
7	42,716.00	203,834.49	102.33%	46,029.33	376,510.94	145.23%	45,426.67	453,517.81	166.07%
8	37,594.67	163,955.38	96.47%	49,909.33	455,440.67	153.43%	43,654.67	464,496.01	174.63%
9	43,739.00	169,896.85	87.37%	44,620.33	442,152.17	162.10%	44,857.67	484,364.30	173.00%
10	39,370.00	168,085.51	96.27%	51,200.33	424,778.07	146.17%	52,420.00	546,614.48	171.57%
11	38,436.50	189,897.00	102.90%	53,772.50	464,730.00	151.62%	52,172.50	519,838.00	162.77%
12	37,503.00	211,710.61	109.53%	56,345.33	504,682.05	157.07%	51,925.33	493,061.51	153.97%
13	37,778.00	205,929.00	108.10%	52,398.50	490,245.00	151.65%	49,519.66	442,569.00	141.94%
14	38,053.67	200,148.91	106.67%	48,452.67	475,808.43	146.23%	47,114.00	392,078.62	129.90%

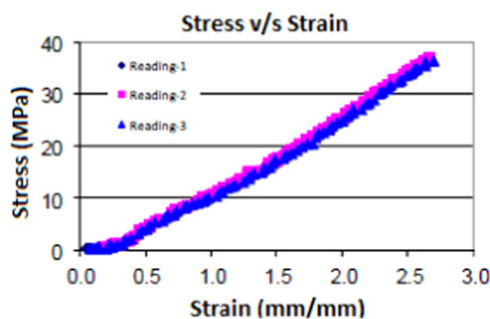
What happens to the hardness of an elastomer as it swells can be of significance in determining seal stability after prolonged exposure. Fig. 12 summarizes the change in hardness for disk samples as they swell in salt solutions of various low level concentrations (0.5%–5%). Hardness of the original elastomer samples (before swelling) on the Shore-A scale was around 60. It is interesting to observe that within a day or two of swelling, hardness drastically dropped down to 10–12, 8–9, 6, 5, and 1–2 for solutions of 0.5%, 1%, 1.5%, 3%, and 5% salt concentrations. What happens to seals formed by these very soft swollen elastomers if subjected to high-pressure differentials can be quite interesting.

Swelling Test

As mentioned in previous sections, swelling in elastomers happens due to the diffusion of salt particles, which results in volume increase as well as change on its thickness. The change in volume and thickness is a function of swelling material, temperature, pressure, swelling fluid and solution concentrations, if any. Free swell test is done using disk samples of 11.2 in./28.4 mm diameter and 0.5 in./12.7 mm thickness, and constrained swelling tests are done using plate samples, that is, elastomer of 6 mm thickness mounted on 50 mm × 50 mm steel plates. To keep track of any fast swell during early days, measurements were taken daily exactly at 24-h intervals for the first 10 days, and then on alternate days until 24 days. Volume measurements were done by in-house constructed graduated beaker-cylinder arrangement. Thickness measurements (average of three readings) were carried out using digital Vernier caliper. After measurements, samples were put back into the respective solutions. Readings were the average of three measurements. Considering the application for field conditions at ambient temperature and around 1–2% brine

Table 5 Tensile test data for HNBR elastomer at 97°C and salinities of 0.6%, 12%, and 25%

Week #	97°C, 0.6%			97°C, 12%			97°C, 25%		
	Modulus (E)	Fracture stress (Pa)	Fracture strain (%)	Modulus (E)	Fracture stress (Pa)	Fracture strain (%)	Modulus (E)	Fracture stress (Pa)	Fracture strain (%)
1	38,727.67	171,477.00	90.63%	14,941.33	144,135.00	149.73%	50,435.67	569,357.00	167.87%
2	43,315.00	194,961.55	102.87%	42,692.00	383,044.10	158.07%	55,363.67	521,499.78	168.20%
3	38,325.67	159,453.32	87.50%	44,517.67	421,100.11	147.30%	51,763.67	534,076.78	162.07%
4	40,078.67	164,839.15	97.57%	48,756.67	416,178.57	155.27%	47,721.33	471,802.60	161.13%
5	43,433.00	171,051.69	100.03%	44,270.00	384,223.88	142.10%	44,369.67	273,522.97	143.70%
6	42,680.67	168,938.49	102.37%	44,652.67	343,640.38	160.70%	50,684.67	440,035.55	170.43%
7	37,786.00	154,902.05	99.97%	46,639.33	398,970.92	146.09%	50,482.00	510,442.69	167.37%
8	41,010.00	164,629.99	99.63%	42,258.33	363,146.30	151.53%	43,651.67	432,848.21	172.17%
9	37,698.33	148,806.02	95.80%	41,877.00	368,008.82	152.83%	51,909.00	498,338.53	164.80%
10	38,474.00	147,386.56	97.40%	44,922.00	384,226.09	152.27%	50,601.00	495,845.31	169.23%
11	38,679.50	146,276.00	95.80%	44,669.00	377,494.00	152.30%	52,661.80	493,614.00	162.27%
12	38,885.00	145,167.72	94.20%	44,416.00	370,761.31	152.33%	54,722.67	491,383.28	155.30%
13	37,349.50	152,776.00	97.65%	47,513.00	456,209.00	157.80%	53,566.67	510,720.00	151.75%
14	35,814.00	160,386.15	101.10%	50,610.67	541,658.21	163.27%	52,410.67	512,057.60	148.20%

**Fig. 7** Stress-strain curve for HNBR elastomer at room temperature.

concentration, a thorough test scheme is selected for room temperature and five different concentrations, that is, 0.5%, 1%, 1.5%, 3%, and 5%.

Fig. 13 plots the change in volume of disk samples against number of days of swelling in solutions of different salt concentrations. As can be observed, swelling quickly attains a high value during the first 7–10 days (380% in 0.5% solution, 310% in 1% solution, 250% in 1.5% solution, 190% in 3% solution, and 150% in 5% solution) and then increases rather slowly. The maximum volume swelling observed in 0.5%, 1%, 1.5%, 3%, and 5% solutions after a 23-day period is 430%, 350%, 280%, 250%, and 230% respectively.

Fig. 14 summarizes the volume change against time behavior of plate samples. As observed for disks, plate samples also show a rapid increase in swelling during the first 10 days, and then the amount of swelling slows down (170% in 0.5% solution, 125% in 1.5% solution, 80% in 3% solution, and 55% in 5% solution). Only two plates completed swelling periods of over 20 days: 220% swelling in 0.5% solution, and 150% swelling in 1.5% solution. Therefore, disk samples show far more swelling than plate samples; disks are free to swell on all sides while plates are constrained from one side (elastomer glued onto the plate).

Volume change is a good indicator of swelling of the sample. However, when an elastomer is mounted on a pipe (in a cased hole, for example), sealing between the pipe and the casing is actually achieved through swelling in the thickness (radial) direction. It is therefore very important to observe thickness change with swelling time. **Fig. 15** plots the change in thickness of disk samples against number of days of swelling in solutions of different salt concentrations. As can be observed, thickness swelling quickly attains a high value during the first 7–10 days (90% in 0.5% solution, 80% in 1% solution, 70% in 1.5% solution, 60% in 3% solution, and 50% in 5% solution) and then increases rather slowly. The maximum thickness swelling observed in 0.5%, 1%, 1.5%, 3%, and 5% solutions after a 23-day period is 110%, 90%, 85%, 70%, and 65% respectively. **Fig. 16** summarizes the thickness change against time behavior of plate samples. As observed for disks, plate samples also show a rapid increase in thickness swelling during the first 10 days (80% in 0.5% solution, 60% in 1.5% solution, 45% in 3% solution, and 38% in 5% solution), then the amount of swelling slows down. Only two plates completed swelling periods of over 20 days: 95% swelling in 0.5% solution, and 80% swelling in 1.5% solution.

Note that disk samples again show more swelling than plate samples. As mentioned earlier, thickness change gives swelling in only the radial direction, while volume change represents swelling in all six directions. That is why volume-swelling figures are far higher than thickness swelling values. For instance, maximum volume swelling for disk and plate samples was 430% and 220%

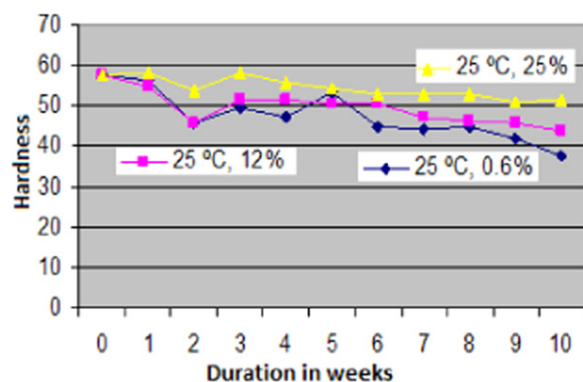


Fig. 8 Variation in hardness over 10 weeks for HNBR elastomer at 25°C.

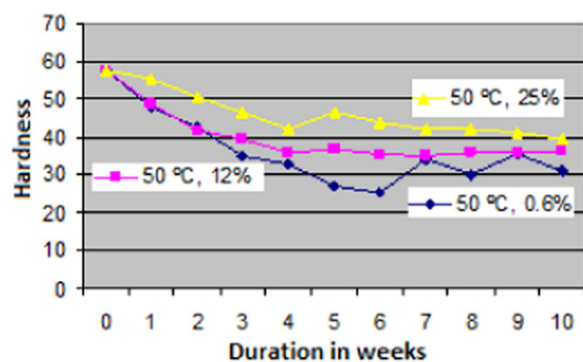


Fig. 9 Variation in hardness over 10 weeks for HNBR elastomer at 50°C.

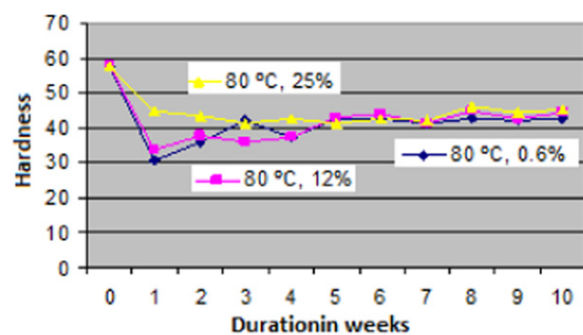


Fig. 10 Variation in hardness over 10 weeks for HNBR elastomer at 80°C.

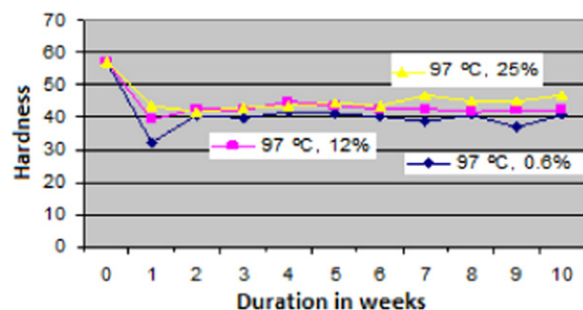


Fig. 11 Variation in hardness over 10 weeks for HNBR elastomer at 97°C.

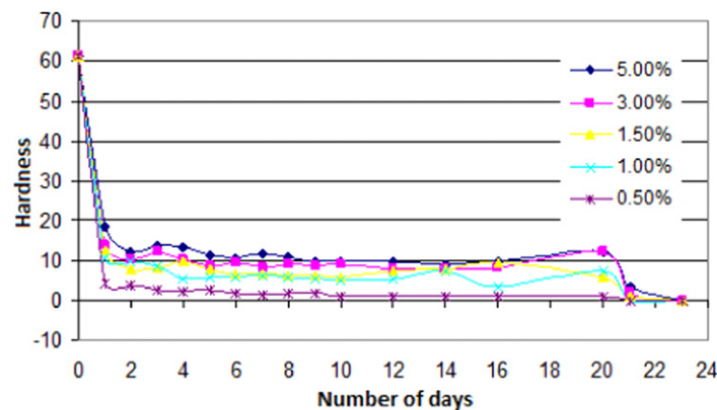


Fig. 12 Hardness change of disk samples at different salinities.

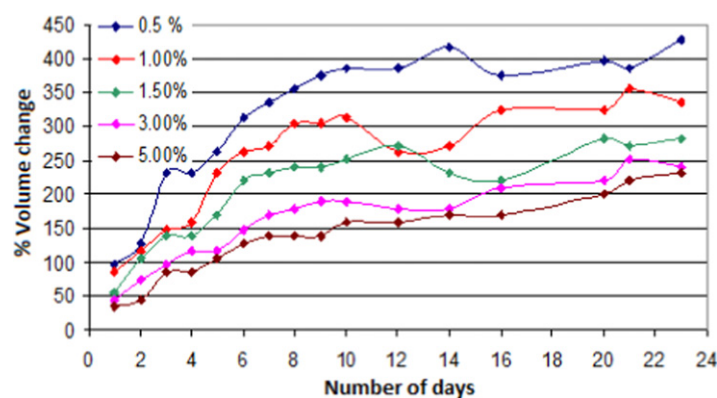


Fig. 13 Volume swelling of disk samples in different salt solutions.

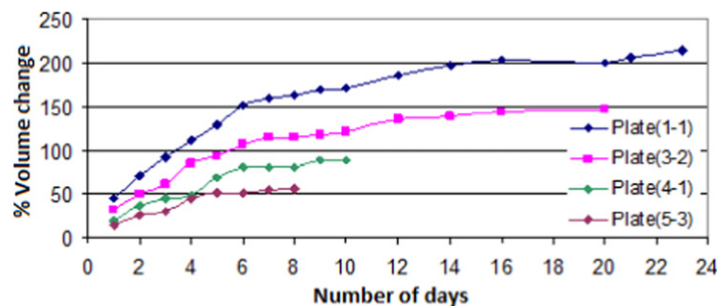


Fig. 14 Volume swelling of plate samples in different salt solutions.

when exposed to 0.5% salt solution for 23 days, while maximum thickness swelling for disk and plate samples under the same conditions was only 110% and 95%, respectively.

Compression-Set Test

Compression-set tests were conducted on fresh EPDM elastomers and when kept in saline water for a period of 22 and 70 h. Test standard ASTM D395 method B is followed (ASTM D395-03, 2007). Compression set is defined as the ratio of change in original and final thickness to the change in thickness due to 25% compression as per standard. Fig. 17 shows the variation in % compression-set at three temperatures and 0.6% salinity. Disk samples were put in an in-house built test set-up to measure compression set. Samples were compressed and held in the fixture for the duration as specified in the standard. Upon removal from the fixture, samples were kept at room temperature for 30 min before taking the final measurement to determine the resultant compression (Pervez et al., 2012). It was found that the compression set rises sharply with an increase in temperature. This increase is more dominant when the exposure time is changed from 22 h to 70 h. Hence, when an elastomer is compressed for

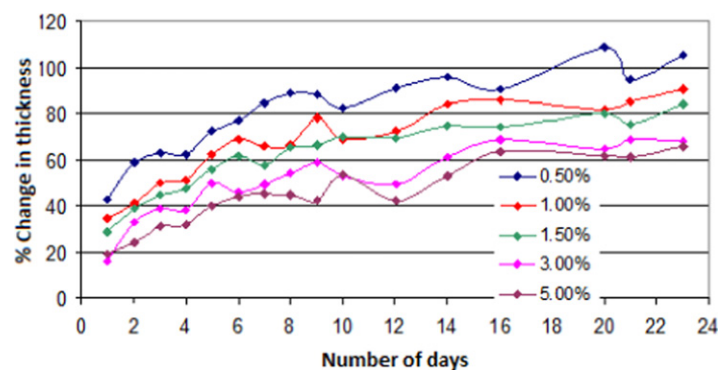


Fig. 15 Thickness swelling of disk samples in different salt solutions.

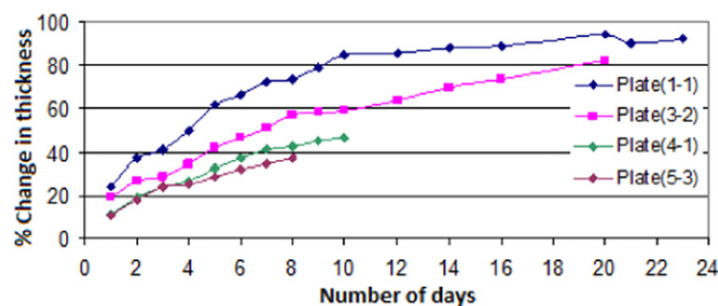


Fig. 16 Thickness swelling of plate samples in different salt solutions.

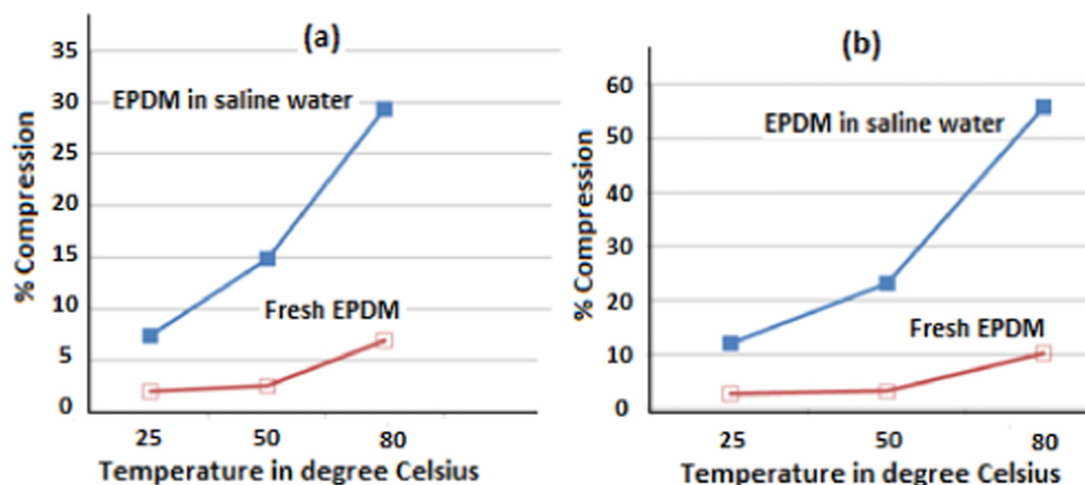


Fig. 17 Variation in % compression for duration of (a) 22 h and (b) 70 h.

a longer time and/or higher temperature, the permanent deformation set in would be larger. Furthermore, the compression-set values are higher in elastomer exposed to saline water compared with the fresh ones. This happens due to the loss of material elasticity resulting from settling in of salt particles within the polymer chain.

Swellable Elastomers With Expandable Tubulars

Sufficient literatures have already been published on solid expandable tubular and its importance. Here we look at the prospect of using swellable elastomers with expandable tubular to develop an effective seal. The characteristics of an elastomer are an important element in seal design considering the surrounding factors. It is a standard practice that each oilfield wellbore operation requires its own design criteria. The fluctuation in pressure and temperature in different production wellbores sets one of the many

specifications required for designing a viable solution for the seal to work in the targeted zone. These specifications have either direct or indirect influence on the design. The constraints include operating factors inside the wellbore (direct), specifications requirements for material selection and storage conditions (indirect), and the use of the elastomer material and strength data.

Composition of fluids inside the well

Various fluid types are produced in the well. These mainly include water and hydrocarbons (oil or gas). This part is important to be stated, as one needs to know what fluid will be in contact with the elastomer seal. The current problem looks into the issue of water shutoff operations in wellbores. Thus, water is the primary fluid and one must know its chemical and characteristics such as the percentage of salinity, viscosity, etc.

Wellbore temperature and pressure working ranges

The target is to get the widest suitable working temperature and pressure ranges, which act inside the wellbore at specified depth. By knowing these ranges, one can set the design parameters for the seal to withstand such variations within the specified ranges and to accommodate short-term fluctuations outside the ranges. The ideal wellbore operating range is considered here between a maximum temperatures of 80°C to a minimum of 45°C and between a maximum pressure differences of 70 bars to a minimum of 20 bars.

Applied static and dynamic loads on the seal

Due to pressure variance inside the wellbore, as depth increases, the elastomer seal would experience higher magnitudes of loads. When the tubular, around which the swelling elastomer is held, is in motion towards inside the wellbore, dynamic loads are to be distributed around the seal. Thus, the transient dynamic load will originate from the moving component while installation. Similarly, when the tubular is on hold, static loads act on the elastomer based on the wellbore pressure.

Regularity of shutdown cycles and temperature/pressure changes during shutdown

It is important to know how often well shutdowns are attempted, as these operations may lead to changes within the specified ranges of temperature and pressure surrounding the swelling elastomer. To avoid failure of the seal, one has to set a limit on which the elastomer can endure the shutdown.

Storage conditions

A vital issue of the specification process addresses the question of storage conditions and lifetime, which involves the preuse phase of the elastomer. These include an optimal temperature range set by the manufacturers for storing the swelling elastomer. Humidity must be kept normal inside the storage area. High or even very low temperatures cannot be accepted as a storage condition. These may lead to elastomer degradation, making it not suitable for use. To reduce amount of dirt or dust particulates contacting the surface of the elastomer, normally black polythene bags are used to cover the seal. It also helps to block exposure to sunlight. Storing the elastomer in well-shadowed place away from sunlight is necessary, as it prevents the UV rays from penetrating through the elastomer, which if they do, will harden the material. The use of polythene bags is another solution for protecting the seal against these harmful rays. Adding additives to the elastomer, such as UV light absorbers, may minimize the amount of the rays absorbed. It is also important to assure that the elastomer seals on tubulars do not experience unnecessary external loads. These external loads, if prolonged, may deteriorate the elastomer, causing a plastic deformation to the shape and size of the seal. Fig. 18 shows a solid expandable tubular with cascade of seals around it, ready to be used in an oil well.

A finite element model is developed to simulate the sealing behavior of the seal on a tubular as shown in Fig. 18. The well bore diameter is 155.575 mm, tubular outer diameter=114.3 mm, tubular length=11.6 m, length of each elastomer seal segment=200 mm, seal thickness=17–19 mm, space between seals=200 mm, and seals can swell up to 175.26 mm outer diameter. The objective is to have an effective sealing against formations/casing. In other words, this elastomer seals must be able to develop a contact differential pressure greater than the pressure resulting from the well (liquid pressure) against the seal, $\Delta P_{\text{elastomer}} > \Delta P_{\text{well}}$, as shown in Fig. 19. This target, $\Delta P_{\text{elastomer}} > \Delta P_{\text{well}}$, will be achieved if the elastomer seal is compressed in such a way that internal pressure developed in the seal exceeds the differential pressure. In fact, the swellable seal expands to certain limit depending on available space for swell. Further swelling results in compression of the seal. This will result in a development of pressure within the seal. EPDM is the selected material for swelling the elastomer seal. A comprehensive review of its material properties is provided by Boyce and Arruda (2000). Table 6 shows the yield stress versus plastic strain for the tubular material and Table 7 describes properties for all.

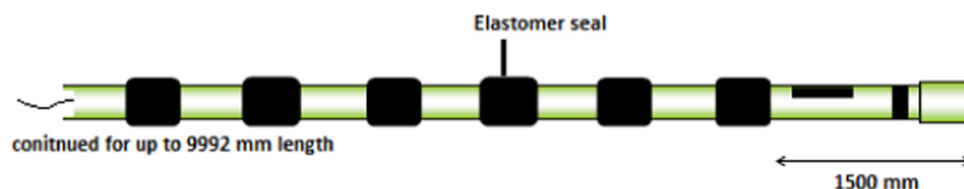


Fig. 18 Solid expandable tubular with swellable elastomer seal.

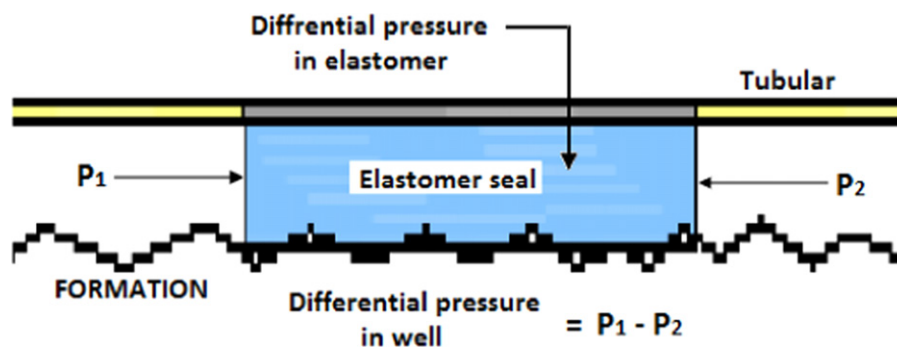


Fig. 19 Differential pressures developed by the elastomer seal.

Table 6 Tubular material data used in finite element simulation

Yield stress	Plastic strain
595.0	0.0000
645.0	0.0081
695.0	0.0247
745.0	0.0573
795.0	0.1189
845.0	0.2306
895.0	0.4264
945.0	0.7593

Table 7 Input material data used in finite element model

Material type	Material behavior	Input data
Elastomer	Hyperelastic	Uniaxial experimental test data input as nominal stress and nominal strain of the elastomer (Tables 2–5), Poisson's ratio: 0.4–0.495, Arruda–Boyce model in ABAQUS is used to model the material.
Formation	Elastoplastic	Elastic: Young's modulus = 1.9995×10^6 N/mm ² , $\nu = 0.1$, Mohr coulomb plasticity: friction angle = 18°, dilation angle = 15°, cohesion yield stress = 7.51555 MPa, absolute plastic strain = 0.
Tubular	Elastoplastic	API grade L-80 steel, density = 7800 kg/m ³ , elastic: Young's modulus = 2.1×10^{11} Pa, $\nu = 0.3$, plastic: material test data input for yield stress and plastic strain (Table 7).

To create the model and to perform the finite element simulation, the following assumptions have been made:

- (1) There is a perfect bonding between the elastomer seal and tubular.
- (2) Elastomer is a hyper elastic material.
- (3) The simulation is carried out under steady state condition.
- (4) Dynamic effects are negligible.
- (5) The geometry of the model and the loading are considered as axisymmetric elements.
- (6) Formation is modeled as an elastic/plastic material.

In finite element simulation, initially, the maximum swelled thickness of the elastomer seal is considered as a reference point, assuming that the elastomer had expanded to its maximum thickness based on the experimental test data obtained in the laboratory. A uniform load is applied across the tubular length, which is in contact with the elastomer. The forces will cause the seal to compress between the surrounding boundaries, namely the formation and the tubular once it comes in contact with the formation. This will result in forming a normal distribution of contact pressures against the formation across the seal length. The process of seal compression continues until the desired compression of the seal is attained. This compressed thickness represents the magnitude of true swelling of elastomeric seal, once it starts to swell, under different salinity and temperature.

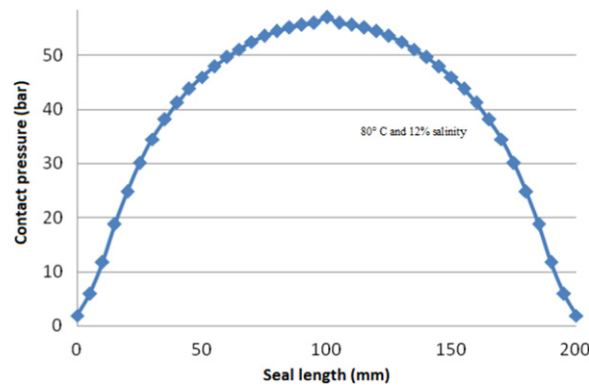


Fig. 20 Variation in contact pressure along the seal.

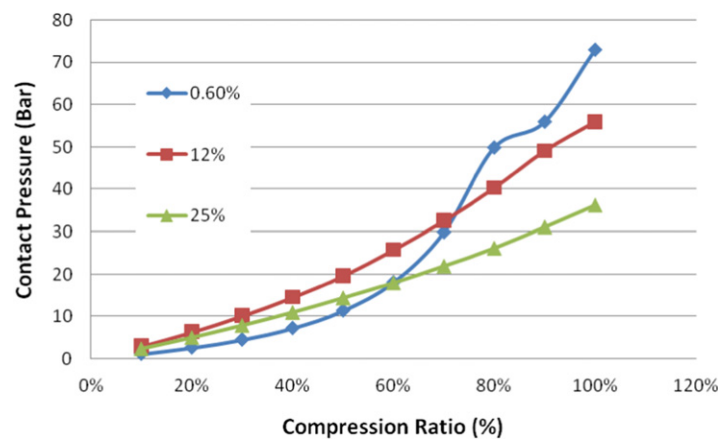


Fig. 21 Contact pressure against compression ratio at 80°C.

The pressure distribution along the elastomer seal is shown in [Fig. 20](#), which shows that the contact pressure reaches a maximum value at the center of the seal whereas it tends to drop off as it moves towards the ends of the seal. This is as expected since at ends the seal has the freedom to bend and deform perpendicular to the load direction. This bending at the unconstrained seal end will provide relief in contact pressure developed between the seal and formation. The effects of temperature (80°C) on the developed contact pressure have been studied by considering three different values of salt concentrations as shown in [Fig. 21](#). Simulations are done for other temperatures for which the results are not shown but the discussion includes all. In all cases of salinity, the contact pressure increases with an increase in temperature up to 80°C. At temperature higher than 80°C, the contact pressure sharply decreases for 0.6 saline solution. However, for 12% and 25% saline solutions the contact pressure keeps increasing beyond 80°C, with more increase in higher salinity solution. For low salinity, when the elastomer seal is exposed to very high temperatures the rate of diffusion of liquids increases and chemical degradation will accelerate. Therefore, the swelling will be more, that is, higher temperature generate much higher swelling, consequently the elastomer seal will be accompanied by a loss in strength and related properties.

The elastomer becomes so soft and chemical degradation might occur which eventually causes a weakness on the elastomer resulting in a reduction of the elastomer capability to withstand high pressure and rupturing can occur very quickly at low loads. On the other hand, for high salinity solution, the salt particles find a place in the polymer chain due to its swelling and results in maintaining the material rigidity at high temperature. This may be one of the reasons that can justify the increase in seal contact pressure for high salinity solution at high temperatures. Therefore, at high temperature and high saline solutions an increase in elastomer thickness due to swelling has a positive impact in its ability to maintain better seal pressure and reduces the probabilities to have fractures or sudden failures. Ultimately, contact pressure values tend to be close to each other at higher temperatures; a large amount of swelling makes the elastomer softer so that hardness does not change much under different concentrations and this means less variation in tensile properties and so the contact pressure.

[Fig. 22](#) shows a comparison between the three different water salinities at a temperature of 50°C, which is an illustrative representation of four simulations run for different temperatures. [Fig. 23](#) shows the resulting contact pressure against salt concentration for different temperatures. Three different salt concentrations have been studied (0.6%, 12%, and 25%) to investigate the effect of water salinity on the contact pressure while temperature is kept constant each time (25, 50, 80, and 97°C); the results obtained are also tabulated in [Table 8](#).

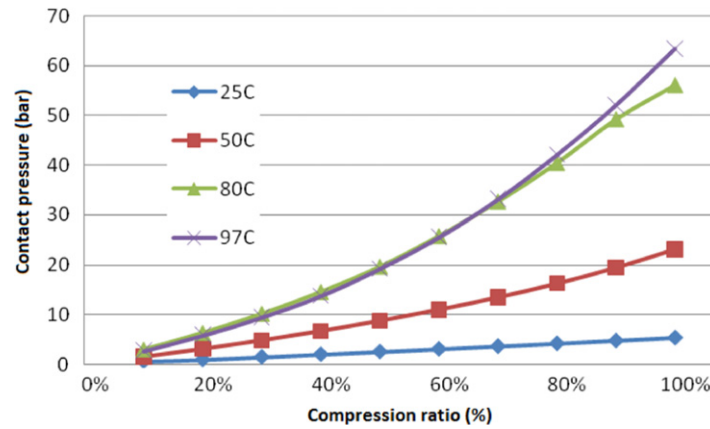


Fig. 22 Contact pressure against compression ratio at 80°C.

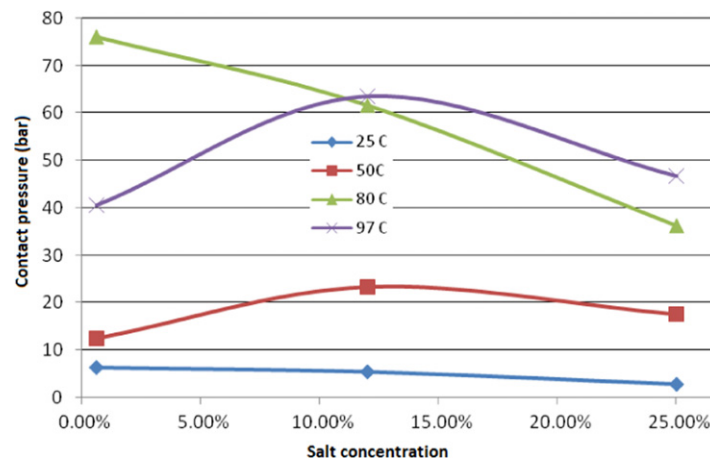


Fig. 23 Variation in contact pressure for different salt concentrations.

At temperatures of 25°C and 80°C, the seal pressure obtained from analysis shows that as the water salinity increases the seal pressure decreases. This was expected since as the salt concentration becomes higher in the solution there will be less swelling on the elastomer and lower swelling in most cases yields lower contact pressure. Although it is known that lower swelling in the elastomer yields higher hardness and better tensile properties of the elastomer, hence the contact pressure is supposed to be higher. However, to certain limit of temperature, for example, 25–80°C, which means certain limit of swelling thickness the elastomer tensile properties can still tolerate the change on the elastomer seal thickness (no significant weakening occur on the structure of the elastomer) and provide the desired contact pressure.

Conversely, fluctuation behavior of the contact pressure takes places at temperature of 50°C. The seal pressure follows fluctuation in tensile properties of the elastomer at this particular temperature. In reality, this result is valid only if we consider that the hardness of the elastomer increases as the salinity of the water increases since the swelling thickness will lower and the tensile properties will increase. Thus, the elastomer seal with low swelling thickness can give high contact pressure.

This result, actually, contradicts with the previous conclusion drawn for the 25°C and 80°C cases. More elastomer material tests need to be done to find out the reasons for these contradictory behaviors. It is also possible to consider this case as an anomalous condition and one can clarify this fact since the tests results show that the tensile properties for swelling elastomers do not always follow the expected trends for usual rubbers. Tensile properties exhibit a fluctuating behavior as there is a two-way transport of brine (from the solution into the elastomer, and from the elastomer into the solution), which causes changes in salt content and cross-link structure inside the elastomer. Thus, this may have a direct effect on the fluctuation, which makes the elastomer behave in an unpredictable way.

At 97°C, also there are fluctuations in the values of seal pressure. This can be realized by observing the behavior of the material tensile property data set that the developed pressure becomes higher as the water salinity increased to about 12% even though the swelling decreases. The reason behind that is as pointed out earlier; at very high temperatures when there is a large amount of swelling, the elastomer loss its hardness and tend to be very soft thereby it loses its ability to achieve a high contact pressure. The drop in pressure at 25% salinity was expected, since definitely when the swelling thickness becomes very small the pressure sealing capabilities will decrease.

Table 8 Values of contact pressure obtained from finite element simulations

Salinity	Contact pressure (bar)			
	25°C	50°C	80°C	97°C
0.6%	6.3	12.4	72	40.5
12%	5.4	23.3	57	63.5
25%	2.8	17.5	36.3	46.67

Renewability of Elastomeric Materials

One of the major questions posed by environmentalists over the use of elastomers is how quickly the elastomers are manufactured and how fast they can be recycled or degrade naturally within an acceptable time frame, or be replenished within a time frame of 10 years or less. Garvin defines renewable materials as those that can be manufactured or generated quickly enough to keep pace with how fast they are used up (Garvin, 2000). Fundamentally, renewable materials are organic and contain carbon. Gelder (2000) points out that renewable materials will have three basic characteristics, that is, they sequester carbon, they burn, and they are biodegradable. It is possible to develop new products with new functionalities by synthesizing atoms and molecules, which would otherwise will not be possible or difficult to achieve in nonrenewable materials.

The elastomers used in the oil and gas industry are selected based on the requirements of flexibility, processability, mechanical and chemical resistance, diffusion, absorption and osmosis, and functionality at medium to high ranges of temperatures and pressures. It has already been explained that in the majority of downhole applications these elastomers are used in vulcanized form. The global consumption of vulcanized elastomers is about 17.2 million tons/year, out of which 40% comes from natural rubber mainly for the aerospace industry. Hence, it is important to think about what to do with these vulcanized elastomers after their productive use in the field. The process of elastomer recovery is difficult, but there are plenty of reasons to work on its recovery or effective disposal, such as material cost reduction, material and mechanical property enhancement, alternate uses of the waste elastomers, and improved process efficiency. If one looks at the entire life cycle of the elastomer from the inception of material to product design and manufacturing, use, recycle, and final disposal, it can be easily classified in three tiers:

Tier 1: Design and develop material and final products,

Tier 2: Recycle to either recover energy or reuse for further product development,

Tier 3: Final disposal.

Legislative restrictions and financial constraints guided by the environmental problems necessitate the demand for research and development of economic and ecological recycling of elastomer (tier 2) or final disposal (tier 3). There are three alternatives for recycling of elastomers (Hanhi *et al.*, 2015). These are:

- (1) Use in another physical form without any further processing, for example, tires are widely used in making pavements by cutting into fine pieces and mixing with cement slurry, sound barriers, polymer mortars, and concretes. This falls in the category of physical reuse. The physical use of the material in granular form is another way of recycling. The use of rubber scrap is very useful in particular manufacturing processes such extrusion, calendaring, molding, and mold flow applications.
- (2) Reclaim material via a proper chemical process. It leads to a different cadre of the same material either with reduced or enhanced properties. The thermal recovery process such as pyrolysis and combustion is also used for reclaiming of elastomeric materials for material reuse.

Another form of recovery is to incinerate the material and recover energy from it. This type of recycling is questionable based on its impact on the environment, complete transformation of material from solid to ash, and the amount of energy generated through this incineration process. Therefore, out of the three recycling methods, the energy recovery method is least effective in terms of economic and environmental aspects, while reuse, either product or material, has the maximum economic and environmental attractiveness.

CERMAT has developed a cost effective method to recycle elastomer, which was a multinational European project focused on developing complete recycling processes for rubber and polyurethane waste, resulting in mass production of recycled low cost elastomeric composites with good noise and vibration damping capabilities. The recycled elastomers were used again in manufacturing chain at low cost. As a result, the companies adopting it became very competitive or remained competitive in the market for the long run. The research work included complete cycle assessment of six different recycling processes including their environmental impact assessment. The recycled elastomeric material obtained through these six cycles showed similar or slightly lower chemical and material properties, which indicates its potential to enter the market with new or similar products.

A closer look at use of swellable elastomers in oil and gas wells reveals that in the majority of applications, the used materials are not recovered to the surface either due to its full deterioration in corrosive environment, particularly the sulfur corrosion, or difficulty in bringing those materials to the surface. Unsuccessful deployment of vulcanized elastomer on pipe/tubulars results in immediate pull out of the pipe to the surface. These elastomers are kept as is for a few days, devulcanized, and processed again to manufacture for lower grade application such as to reduce salinity, etc.

See also: Challenges and Developments of Rubber Materials as Vibration Isolator. Rubber Scrap as Reinforced Material in the Production of Environmentally Friendly Brake Lining. Waste Conversion Into Sustainable and Reinforcing Fillers for Rubber Composites

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Relevant Website

<https://www.iso.org/standarad/2185.html>

ISO 2185:1972 – Muscovite mica blocks, thins and films – Visual classification.

Microbial Production of Polyhydroxyalkanoates From Plant Oils: Renewability and Biodegradability

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Introduction

The use of petroleum-based plastic materials has contributed to serious environmental problems and is a hot topic discussed globally. The world is currently unable to cope with the environmental degradation arising from existing chain processes associated with the irresponsible use of plastics by global consumers. Global plastic production reached 322 million tonnes in 2015 alone (Gear *et al.*, 2018), and most of these plastics are non-biodegradable, ending their useful lives in landfill sites and the natural environment. For these reasons, the concept of Sustainable Development Goals (SDGs) proposed by the United Nations (UN) has quickly gained worldwide support for its drive toward a healthy and sustainable global economy. Its goal is to solve environmental problems at the most fundamental level and increase consumer responsibility by managing consumption and production.

There have been extensive efforts to develop and use biodegradable polymers such as polyhydroxyalkanoates (PHAs) as alternatives to fossil-derived materials for a wide range of applications (Huschner *et al.*, 2015; Prados and Maicas, 2016). Biodegradable polymers are naturally synthesized by bacteria and offer advantages over conventional plastics such as polypropylene. The ability of PHAs to be degraded naturally in diverse conditions is one of the most commercially attractive aspects that differentiates them from conventional plastics. PHAs are completely degradable under natural conditions and do not liberate toxic compounds. Carbon dioxide and water are the products of PHAs degradation under aerobic conditions, whereas methane is generated in the absence of oxygen. In this regard, PHA production is carbon neutral because the generated carbon dioxide is returned to the environment (Fig. 1).

The rapid development of commercial biotechnology enables plastic production from bio-based renewable resources. In the last few decades, improvements to PHA-producing bacterial strains has been achieved by optimizing the genetic pathway and upregulating the metabolic flux (Budde *et al.*, 2011b; Tappel *et al.*, 2012). Moreover, recent advances in synthetic biology have contributed to higher PHA yields, particularly in synthesizing next-generation biopolymers (Hiroe *et al.*, 2016; Scheel *et al.*, 2016). For example, the use of recombinant microorganisms in the fermentation process facilitates effective PHA production. Of equal importance is the carbon-containing substrate, and the choice of substrate affects the reliability and economics of the fermentation process, especially in large-scale production. Sugars such as glucose, xylose, and fructose are commonly used as a starting raw materials in PHA production (Hiroe *et al.*, 2016; Mizuno *et al.*, 2018). Nevertheless, the fermentation processes developed using sugars have high production costs because of the cost of the raw materials, which accounts for 45% of the total production cost (Kourmentza *et al.*, 2017).

Taking into account the costly raw materials, alternative feedstocks derived from agricultural activities such as glycerol, fatty acids, and plant oils are favorable for the industrialization of PHA production (Koller *et al.*, 2005; Riedel *et al.*, 2014). Among these, plant oils are seen as valuable agricultural commodities and could serve as an effective carbon source for PHA production. The well-known plant oils include canola oil, corn oil, olive oil, palm oil, soybean oil, and sunflower oil. Plant oils are extracted from the plants through cold pressing and the highest oil content is commonly found in the seed. Among all plant oils, palm oil (PO) is seen as an attractive commodity and contributes significantly to the global oil and fat supply. Palm oil plantations are experiencing rapid expansion throughout Southeast Asia, which is the world's largest producer of plant oils. In 2012 alone, the

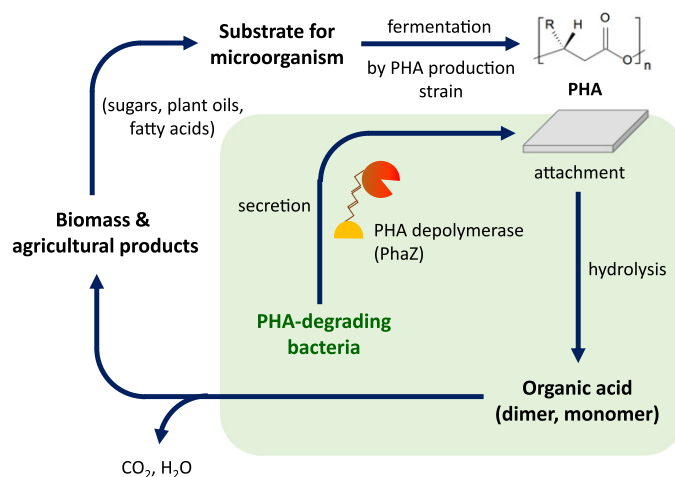


Fig. 1 Bioproduction of PHA and its biodegradation steps in the natural environment.

palm oil production reached about 55 million tonnes, accounting for over 30% of global plant oil production (Oosterveer, 2015). Growing demand for palm oil is driving the market, particularly because of its use in food processing and the increasing demand for biofuel feedstocks (Mekhilef *et al.*, 2011) and bioenergy (Umar *et al.*, 2013).

There is keen interest in using plant oils in the industrial production of bio-based products, more specifically in PHA synthesis, because of the early use of palm oil as the research model (Majid *et al.*, 1994). Plant oils have greater carbon content than other carbon sources such as glucose, making them as excellent raw materials for high-yield PHA production. Theoretically, the PHA yield obtained by using plant oil as a carbon source is twice that obtained from sugar (i.e., up to one gram of PHA per gram of plant oil). For example, a low PHA yield is obtained when using glucose: 0.3–0.4 g-poly(3-hydroxybutyrate) (PHB)/g-glucose (Akiyama *et al.*, 1992) whereas a high PHA yield is obtained when utilizing plant oil: 0.84 g-PHB/g-palm oil (Budde *et al.*, 2011a). In a different study utilizing soy bean oil as a substrate for culturing *Ralstonia eutropha*, a high PHA yield also was reported: 0.76 g-PHB/g-soybean oil (Kahar *et al.*, 2004). These reports show the potential of plant oils to be used as sustainable resources for efficient PHA production. Further development and extensive research will promote the use of sustainable resources and may eventually reduce the PHA production cost, allowing bio-based plastics to flourish in diverse applications.

Polyhydroxyalkanoates: A Family of Natural Polyesters

Polyhydroxyalkanoates are a family of natural polyesters synthesized by bacteria from renewable resources in the presence of excess carbon and stress-triggering conditions. When bacteria are grown in such environments, water-insoluble inclusion bodies are accumulated and conserved as an energy resource. These energy storage molecules are broken down under carbon starvation conditions by intracellular PHA depolymerases as a mechanism for bacterial survival. The native PHA producing microorganisms are *Aeromonas* sp., *Bacillus megaterium*, *Cupriavidus necator*, *Pseudomonas putida*, and halophiles such as *Halomonas* sp. However, most proof of concept studies have focused on *E. coli* (Kahar *et al.*, 2004; Tappel *et al.*, 2012) or *P. putida* (Ouyang *et al.*, 2007), which are well understood and whose genetic manipulation is well studied. There are two types of PHA depending on the carbon numbers of their monomeric constituents: short-chain length (scl) PHA with 3–5 carbons and the medium-chain length (mcl) PHA containing 6–14 carbons. The general structure of PHA (shown in Fig. 1) contains carbon, hydrogen, and oxygen, with each monomer having a side chain group, R (Fig. 2). Examples of scl-PHAs include poly(3-hydroxybutyrate), PHB; poly(4-hydroxybutyrate), P4HB; and poly(3-hydroxyvalerate), PHV; or the copolymer; poly(3-hydroxybutyrate-co-3-hydroxyvalerate), PHBV. Examples of mcl-PHAs are poly(3-hydroxyhexanoate), PHHx; poly(3-hydroxyoctanoate), PHO; poly(3-hydroxydecanoate), PHD; and poly(3-hydroxydodecanoate), PHDD; or copolymers like poly(3-hydroxyhexanoate-co-3-hydroxyoctanoate), P(3HHx-co-3HO); poly(3-hydroxydecanoate-co-3-hydroxydodecanoate), P(3HD-co-3HDD); as well as copolymers incorporating both scl and mcl monomers; such as poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) PHBHHx. The mentioned PHAs have relevant thermo-plastic properties and have attracted huge commercial interest. Currently, the available PHAs differ greatly in their thermal and mechanical properties. For instance, the hydrophobicity, melting temperature, glass transition temperature, and crystallinity of the PHAs depend entirely on their monomer composition.

PHB was the first PHA to be discovered in 1926 by the French scientist Maurice Lemoigne. It was found as intracellular granules produced by the bacterium *B. megaterium*. Since then, PHB has been the most extensively studied and characterized polymer in the PHA family, and up to 80 wt% of the cell dry weight can be accumulated when grown with a suitable carbon source (Ng *et al.*, 2010; Park and Kim, 2011). PHB possesses several interesting features, such as water insolubility, low oxygen permeability, and optical purity. It is regarded as a highly crystalline polymer because of its stereoregularity. Given its high crystallinity, this causes PHB to become very stiff and brittle, which eventually results in poor mechanical properties. The mechanical properties of isotactic PHB are as follows: Young's modulus, 3.5 GPa; tensile strength, 40 MPa; and elongation at break, 6%. Compared to petroleum-based plastic such as polypropylene, PHB has a higher tensile strength and Young's modulus. The elongation at break of PHB is just 6%, which is extremely low compared to polypropylene (PP) (400%); thus, PHB easily breaks even at low strain. In addition,

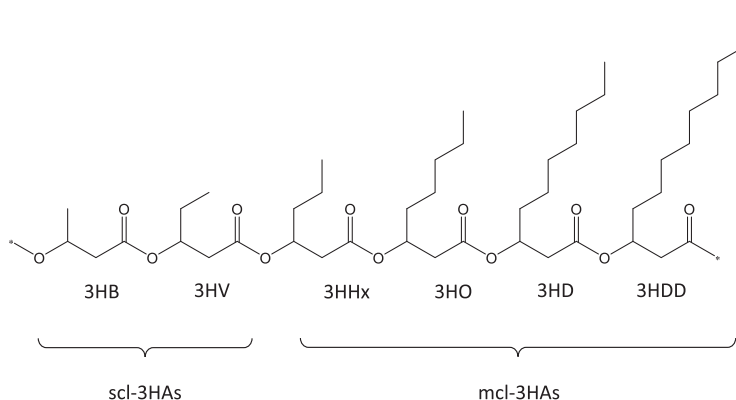


Fig. 2 Short-chain length and even-number medium-chain length PHA monomers.

PHB has a melting temperature of 177°C, which is close to its thermal decomposition temperature. At this temperature, the molecular weight of PHB decreases significantly, resulting in difficulties for conventional melt processing. These limitations limit the commercial value of PHB, and, thus, its properties require significant improvement.

The physical and mechanical properties of PHB could be enhanced by increasing the molecular weight. The long polymer chains in high-molecular-weight PHB polymers have greater chain entanglement, making them much stronger and highly resistant towards degradation (Kabe *et al.*, 2012). The ultrahigh-molecular-weight PHB (UHMW-PHB) has been reported to have a tensile strength of up to 3.88 MPa after processing the PHB fiber by annealing and drawing methods (Aoyagi *et al.*, 2003). In another study, bacterial PHB fibers with up to 1.3 GPa tensile strength were successfully produced through combination of cold-drawing and two-step-drawing methods (Iwata *et al.*, 2004).

Another frequently used technique to improve the properties of PHB is copolymerization with other monomers. PHBV is an important scl-PHA copolymer and can be produced via fermentation by co-feeding bacterial cultures with propionic acid as a precursor for 3HV incorporation. PHBV copolymers with a broader range of 3HV content between 6.5 and 40 mol% have been acquired by growing the *Burkholderia sacchari* IPT 189 strain via two-stage cultivation (Rocha *et al.*, 2008). In the first stage, cells are allowed to grow with sucrose, followed by the addition of propionic acid at a low concentration during the PHA accumulation stage. Developments to feeding methods were reported by Shang and co-workers. They employed sequential and simultaneous feeding for the growth of a recombinant *R. eutropha* strain with glucose and valerate. This strain was capable of producing a high 3HV unit fraction of 62.7 mol% (Shang *et al.*, 2008). The incorporation of 3HV slightly improved the mechanical properties of PHB, although there were still many inherent disadvantages such as a low crystallization rate, low nucleation density, large-size spherulites, and secondary crystallization. Because of the lower glass transition temperature of PHBV, the crystallization rate usually remains low, which limits the development of PHBV. Processed PHBV copolymer tends to be sticky during melt extrusion and remains soft even after long cooling times. The addition of nucleating agents may provide a solution to these complexities. They are added to bacterial polyesters to improve the crystallization rate by increasing the nucleation density and reducing the spherulite size. Among the available nucleating agents, boron nitride has been shown to have a significant nucleating effect on the crystallization rate of PHBV. A few studies have reported the effects of boron nitride on polymer crystallization (Kai *et al.*, 2005). Additionally, it was found that reinforced boron nitride PHBV nanocomposites prepared by melt processing have higher thermal stability and improved gas barrier properties (Ten *et al.*, 2010). PHBV can also form blends with other copolyesters, polylactide (PLA), thermoplastic starch, and natural rubbers (Zhang *et al.*, 2014). PHBV has dual properties that combine the mechanical properties of polyethylene (PE) such as elasticity, flexibility, stiffness, and toughness with the chemical properties of biopolyesters (degradability and biocompatibility). These features make them attractive PHAs for consumer applications, notably in the biomedical field.

Another promising copolymer with attractive features is PHBHHx. This polymer comprises scl and mcl-monomers and has unique characteristics. The incorporation of mcl-monomers to the PHB chains makes the copolymer highly elastic and reduces the crystallinity compared to that of neat PHB. The 3HHx monomer fraction greatly contributes to the polymer properties. The alteration to produce PHBHHx with diverse 3HHx content has been extensively studied by growing recombinant bacteria in a medium containing plant oils as a carbon source. One study reported that PHBHHx containing up to 32 mol% 3HHx was produced and improvements were observed in the mechanical properties (Doi *et al.*, 1995). The P(3HB-co-32 mol% 3HHx) polymer has comparable stiffness to low-density polyethylene (LDPE) and high elongation at break of 856%. This remarkable flexibility makes PHBHHx an excellent biomaterial for medical implants and drug delivery systems.

Nevertheless, the existing methods of PHA production presents some difficulties, such as high input cost, low productivity, and lack of process development, which are drawbacks for broader application. In the subsequent section, the use of renewable and inexpensive carbon sources for PHA production is described in detail, focusing, in particular, on the applications of plant oil and fatty acids as feedstocks.

Plant Oils: A Potential Feedstock for PHA Bioproduction

Plant oils and their derivatives represent a renewable resource that has high potential as a chemical feedstock for the bioproduction of new polymers with a variety of structures and functions. They have been extensively utilized for the production of diverse types of PHAs incorporating scl or mcl or scl-mcl monomers. The synthesis of PHA from plant oils has been the subject of green material research for a long time (Table 1). Akiyama first demonstrated the application of corn oil that is rich with polyunsaturated fatty acid for the production of the PHB homopolymer (Akiyama *et al.*, 1992). New strains of *Alcaligenes* sp. were grown in single-stage batch culture by feeding with 3 g/L corn oil. The dry cell mass reached 2.8 g/L with a PHB content of up to 39 wt% after culturing for just 48 h. Other studies have also reported the use of corn oil for PHB and PHBHHx production using *A. eutrophus* H16 and *A. eutrophus* PHB⁴/pJRDEE32d13, respectively (Fukui and Doi, 1998). These strains grew well and accumulated higher PHA content after being subjected to nitrogen-limiting conditions. Relatively large quantities on a dry cell basis were achieved in both cultures (3.6 g/L dry cell), demonstrating the effectiveness and huge potential of corn oil as a carbon source for PHA production.

Moreover, palm-oil-based products have been extensively used to produce various type of PHAs. Palm kernel oil (PKO) is the oil derived from the kernel of the fruit of the oil palm, *Elaeis guineensis*. It is rich in saturated fats, comprising a mixture of medium and long chain fatty acids (Yun *et al.*, 2003). Initially, Tan and co-workers conducted a feasibility assessment of saponified palm kernel oil (SPKO) for growing *P. putida* cultures (Tan *et al.*, 1997). The strategy employed two-stage cultivation for enhanced cell growth in the first 20 h, followed by PHA accumulation in the later stages. The dry cell mass of the harvested biomass reached a maximum of 6.8 g/L with 1.0% w/v SPKO supplementation. The produced PHA accounted for 27 wt% of the dry cell mass and comprised seven

Table 1 Bioproduction of PHAs from various types of plant oils

Carbon source	Strain	PHAs	Growing conditions	Dry cell wt. (g/L)	Polymer content (wt%)	Reference
Corn oil	<i>Alcaligenes</i> sp. AK201	PHB	Cells were grown in a mineral medium with 3.0 g/L corn oil added.	2.8	39	Akiyama <i>et al.</i> (1992)
	<i>Alcaligenes eutrophus</i> H16	PHB	Cells were grown in a nitrogen-limited medium containing 1% (v/v) corn oil.	3.6	81	Fukui and Doi (1998)
	<i>Alcaligenes eutrophus</i> PHB ⁺ 4/pJRDEE32d13	PHBHHx		3.6	77	
Palm kernel oil (PKO)	<i>Pseudomonas putida</i> PGA1	MCL-PHAs	Cells were cultured in the growth medium for 20 h and transferred to the nitrogen-limited medium containing saponified palm kernel oil (SPKO) at 1.0% w/v for PHA production.	6.8	27	Tan <i>et al.</i> (1997)
	<i>Ralstonia eutropha</i> PHB ⁺ 4 recombinant	PHBHHx	Cells were grown in a nitrogen free medium and 5 g/L PKO was added as a carbon source.	4.3	87	Loo <i>et al.</i> (2005)
	<i>Cupriavidus necator</i> PHB ⁺ 4 recombinant	P(3HB-co-3HV-co-3HHx)	Cells were grown in a mineral medium containing 5 g/L PKO and 10 g/L of valerate was fed at 36 h.	7.9	79	Bhubalan <i>et al.</i> (2008)
	<i>Cupriavidus necator</i> H16	PHB	Cells were grown in a nitrogen-limited medium with 5 g/L PKO added.	5.6	77	Lee <i>et al.</i> (2008)
		PHBV	5 g/L of propionate was added to the medium containing 5 g/L PKO and maintaining the C/N ratio at 42 by adding NH ₄ Cl.	7.5	90	
Soybean oil (SBO)	<i>Ralstonia eutropha</i> PHB ⁺ 4 recombinant	P(3HB-co-3HA)	Cells were grown in a mineral salt medium supplemented with 20 g/L SBO.	1.6	57	Tsuge <i>et al.</i> (2009)
	<i>Cupriavidus necator</i> H16	PHBHHx	Cells were grown in a nitrogen-limited mineral salts medium containing 1% (v/v) SBO.	5.2	89	Mifune <i>et al.</i> (2010)
Jatropha oil	<i>Cupriavidus necator</i> H16	PHB	Cells were grown with jatropha oil (12.5 g/L) as a carbon source and urea (0.54 mM) as a nitrogen source.	13.1	87	Ng <i>et al.</i> (2010)
		PHBV	Cells were grown with jatropha oil as a main carbon source (5.19 g/L) with valerate (4.32 g/L) addition as a 3HV precursor.	6.7	76	Ng <i>et al.</i> (2011)
	<i>Cupriavidus necator</i> PHB ⁺ 4/pBBREE32d13	PHBHHx	Cells were grown with jatropha oil at 10 g/L as a sole of carbon source.	8.7	75	
Canola oil	<i>Cupriavidus necator</i> H16/pMRC03	P(3HB-co-3HV-co-3HHx-co-3HO)	Cells were grown with fructose at 10 g in the growth stage (18 h) and then shifted to the PHA production stage by the addition of canola oil (5% v/v).	6.2	96	Valdés <i>et al.</i> (2018)

different mcl-monomers with 3HO as the predominant component. In more recent studies, a recombinant *R. eutropha* strain was demonstrated for the production of PHBHHx with higher PHA content in a nitrogen free medium (Loo *et al.*, 2005). However, the low molar fraction of 3HHx (5 mol%) acquired under all conditions is unfavorable and less attractive for commercial use. Later, the *C. necator* PHB4 with PHA synthase from *A. caviae* was used to biosynthesize P(3HB-co-3HV-co-3HHx) terpolymers from PKO (Bhubalan *et al.*, 2008). The highest cell growth and PHA accumulation was acquired using PKO (5 g/L) with sodium valerate (10 g/L) addition after 36 h of cultivation. In a separate study, the wild *C. necator* H16 strain was investigated for the production of P(3HB) and P(3HB-co-3HV) (Lee *et al.*, 2008). Palm kernel oil was added to a nutrient-rich medium at 5 g/L for the production of both PHAs. A mixture of 5 g/L PKO and 5 g/L propionate in the presence of ammonium chloride allowed the synthesis of a high content of the P(3HB-co-3HV) copolymer, up to 90 wt% of the dry cell mass. They found also that the 3HV monomer was incorporated to a much higher extent than those copolymers produced from mixtures of plant oils and valerate used as a 3HV precursor. Thus, the use of palm oil seems to be favorable because of its suitability for supporting various bacteria, as well as its ability to produce a high dry cell mass. This opens up the possibility for reproducible PHA production with different functionalities.

Another relevant plant oil is soybean oil (SBO), which is widely used for effective PHA production. PHA synthase from *Pseudomonas* sp 61-3 (PhaC_{1Ps}) can synthesize the P(3HB-co-3HA) copolymer using *R. eutropha* as a host strain (Tsuge *et al.*, 2009). The recombinant *R. eutropha* grew in a mineral salt medium supplemented with SBO at 20 g/L. Various mutations in the PhaC1 genes were performed and screened for their ability to grow and produce P(3HB-co-3HA) using soybean oil as a carbon source. There were up to 20 mutants exhibiting high PHA production of over 30 wt% and a maximum 57 wt% of dry cell mass. In addition, the use of the *C. necator* H16 strain expressing PHA synthase from *A. caviae* showed good growth ability and superior PHA accumulation, up to 89 wt% of the dry cell mass (Mifune *et al.*, 2010). Despite this, there has been a lack of improvement in the physical properties of the acquired PHBHHx because of the small 3HHx fraction in the polymer chain. Further strategies have, thus, been implemented to incorporate more 3HHx units that will make the resulting polymers more suitable for wider use. In the same study, the 3HHx monomer fraction was enhanced to 9.9 mol% by introducing a mutant PhaC_{Ac} enzyme, PhaC_{Ac} (NSDG), and deleting PhaC_n to depress the supply of 3HB monomer. The cell growth was slightly reduced although the significant incorporation of 3HHx was observed.

Because the use of plant oils competes with food production, non-edible jatropha oil has been suggested as a suitable feedstock for efficient PHA production. Wild-type *C. necator* H16 was used by Ng and co-workers for the production of PHB and PHBV (Ng *et al.*, 2010). The PHB production and cell growth were increased on increasing the jatropha oil dose to 12.5 g/L, indicating its non-toxicity at high concentrations. Under optimal conditions, the culture produced 13.1 g/L dry cell mass and accumulated 87 wt% PHB with supplementation of ammonia (0.54 g/L) as the nitrogen source. The production of PHBV containing as high as 42 mol% 3HV has been achieved by using the similar strain as in the previous PHB production process (Ng *et al.*, 2011). Increasing the sodium valerate concentration gradually increased the 3HV fraction, but this simultaneously decreased the cell growth. This is partly due to the addition of sodium valerate in the initial stage, which somehow has an inhibitory effect on the cells, which cannot tolerate the higher precursor concentration. As the total carbon from jatropha oil and precursor used was set at 9.51 g/L, the cell growth and PHA content were achieved at 6.7 g/L and 76 wt%, respectively. In addition, the production of PHBHHx from jatropha oil as the sole carbon source was demonstrated by using *C. necator* PHB4/pBBREE32d13 expressing the *A. caviae* PHA synthase. Feeding with 10 g/L of jatropha oil produced a dry cell mass and PHA contents 6.7 g/L and 84 wt%, respectively. However, the recombinant strain was only able to incorporate 3 mol% of 3HHx in the copolyester chain.

Another plant oil that holds great potential for PHA production is canola oil. Canola oil is extracted from the canola variety of rapeseed, which is derived from diverse rapeseed cultivars. In a recent study, canola oil has been used as a non-expensive substrate for PHA production (Valdés *et al.*, 2018). The strategy employed two-stage cultivation by growing the recombinant cells first in a medium containing fructose, followed by PHA accumulation by adding canola oil after 18 h. The recombinant *C. necator* H16 expressing heterologous PhaC2 synthase from *P. putida* CA-3 has been used for the production of scl-mcl PHA copolymers. The incorporation of scl-mcl-PHA monomers implies that the overexpressed synthase has a broad substrate specificity. The strategy enhanced the accumulation of intracellular polymer effectively. After cultivation for 30 h, the PHA concentration in the *C. necator* H16 (pMRC03) reached up to 96 wt% of the dry cell mass, which is high for PHA production.

The results presented here show that plant oils are highly promising substrates for the production of diverse PHAs. Despite the improvement in the PHA content obtained at the small scale, the establishment of high-cell-density cultivation is necessary for feasible large-scale processes.

Using fermentation, many strategies can be applied to achieve high biomass production, and fed-batch feeding is one such way. In fed-batch feeding, the substrate is added depending on the cellular response. The simplest method, pH-stat control, is widely used in lab-scale studies because an increase in the pH of the culture indicates the depletion of the available carbon source. Fed-batch *E. coli* using pH-stat control has proven effective for obtaining high density cell cultivation. Many research works have reported the high-cell-density culture obtained by the fermentation process using plant oils as a feedstock for larger scale PHA production (Table 2). The utilization of soybean oil was found to be highly feasible and effective for PHB production. Using wild-type *R. eutropha* H16 and the PHB4/pJRDEE32d13 mutant strain, both cultures grew well in a mineral salt medium (MSM) containing soybean oil in the presence of ammonium chloride (Kahar *et al.*, 2004). Fed-batch cultivation is key to maintaining the optimum carbon and nitrogen concentration for achieving high cell growth and PHA accumulation. This strategy successfully produced dry cells in 118–126 g/L yield with 71–76 wt% PHA. Using the same carbon source, another study reported PHB homopolymer production using *R. eutropha* KCTC 2662 grown in batch and fed-batch culture (Park and Kim, 2011). The supplementation of soybean oil three times at an initial concentration (20 g/L) by fed-batch culturing at 18 and 50 h increased the

Table 2 Strategies to produce PHAs from plant oils in high-cell-density cultivations

Carbon source	PHAs	Strategies	Dry cell wt. (g/L)	Polymer content (wt%)	Reference
Soy bean oil (SBO)	PHB	<i>R. eutropha</i> KCTC 2662 was grown in batch culture containing 20 g/L SBO and fed-batch culture with 20 g/L SBO added three times.	15–32	78–83	Park and Kim (2011)
		<i>C. necator</i> DSM 545 was grown in a mineral medium with 40 g/L SBO. Pulsed feeding of SBO was carried out when the residual SBO concentration reached 5 g/L.	83	81	da Cruz Pradella <i>et al.</i> (2012)
	PHBHHx	<i>R. eutropha</i> TT013ΔfadB1 was grown by feeding with SBO continuously and stepwise feeding of NH ₄ Cl. Phosphorus-limitation was applied to induce PHA production.	52.2 ^a	65.7	Insomphun <i>et al.</i> (2014)
	PHB and PHBHHx	<i>R. eutropha</i> H16 and PHB ⁺ 4/pJRDEE32d13 were grown in mineral salt medium, and SBO was added by fed-batch feeding (20 g/L) to the culture without nitrogen limitation.	118–138	71–76	Kahar <i>et al.</i> (2004)
Corn oil	MCL-PHAs	<i>P. putida</i> KT2442 was grown by the fed-batch method in mineral medium containing hydrolyzed corn oil. Then, 15 g/L was added to the medium when the corn oil was exhausted.	103–109	27.1–28.5	Shang <i>et al.</i> (2008)
Palm oil (PO)	PHBHHx	<i>R. eutropha</i> Re2058/pCB113 was grown by the fed-batch method with, initially, 20 g/L PO, and nitrogen sources (urea or ammonia) were added to increase PHA production.	98–139	70–74	Riedel <i>et al.</i> (2012)
Palm kernel oil (PKO)	PHB	<i>C. necator</i> H16 was grown with PKO as the sole carbon source by intermittent feeding.	160	72	Sato <i>et al.</i> (2013)
	PHBHHx	<i>C. necator</i> strains CNPJN and CNPCN expressing <i>phaC</i> _{Ac} NSDG were grown with PKO in fed-batch fermentation.	111–165	60.8–76.4	Sato <i>et al.</i> (2015)
		<i>C. necator</i> ASBK was grown in mineral medium with butyrate added as a 3-hydroxyhexanoate precursor. The butyrate/PKO ratios (wt./wt.) were 16.7/83.3 and 23.1/76.9.	170–175	76.5–78.6	
		<i>C. necator</i> strains with upregulated <i>PhaJ4</i> genes were grown in modified basal medium. Stepwise fed-batch processing was employed at 5 g/h and then increased to 10 g/h after 24 h.	215 ^b	81 ^{b,c}	

^aThe dry cell weight was calculated from the polymer content and PHA concentration.^bAll strains were produced with almost the same dry cell weight and polymer production.^cPolymer content was calculated from the dry cell weight and PHA concentration.

dry cell mass twofold, but the PHA content was slightly reduced. Although the dry cell mass was much lower, the PHB yield was 0.82 g/g-soybean oil consumed, which is higher than the previously reported by Kahar *et al.* (2004), which were 0.72–0.76 g/g-soybean oil used. In another study, the high-cell-density fed-batch culture of *C. necator* DSM 545 was reported for PHB production (da Cruz Pradella *et al.*, 2012). The culture produced up to 83 g/L biomass concentration with 81 mol% PHA achieved with SBO (40 g/L initial concentration) and subjected to an unlimited carbon source. The PHB yield calculated from utilized SBO showed very high values of 0.85 g/g-soybean oil compared to those previously reported. Using a similar carbon source as above, *R. eutropha* TT013ΔfadB1 has been tested for the production of PHBHHx by deleting the key genes involved in fatty acid β -oxidation (Insomphun *et al.*, 2014). The deletion of β -oxidation gene clusters on chromosome 1 (*fadB1*) significantly improved the 3HHx incorporation (with 15.7 mol% after 96 h cultivation) with fewer effects on cell growth and PHA production. The culture was continuously fed with SBO at 20 g/L by pulsed addition along with the stepwise feeding of NH_4Cl . During the cultivation, phosphorus-limitation was applied to induce the PHA production. It was demonstrated that the defective β -oxidation strain was able to produce the PHBHHx copolymer with a high 3HHx fraction, although the 3HHx fraction detected in PHA was much higher (23.6 mol%) in the early stages of cultivation.

Another common feeding strategy applied for achieving a high-cell-density culture is using a dissolved oxygen (DO)-stat feedback control. This is employed when the dissolved oxygen concentration (DOC) shows a more sensitive response than the pH when the substrate concentration is depleted, especially in the PHA accumulating phase of the fermentation process. DO-stat control has been used to control the feeding rate of corn oil hydrolysate in a fed-batch culture of *P. putida* with phosphate limitation for mcl-PHA production (Shang *et al.*, 2008). When the hydrolyzed corn oil (mainly consisting of linoleic acid and oleic acid) became depleted in the medium, the carbon source was automatically added so that the concentration of corn oil increased to about 15 g/L. This approach was able to produce a dry cell mass and mcl-PHAs contents of up to 109 g/L and 28.5 wt%, respectively. The produced mcl-PHAs predominantly contained 3HO, 3HD, and unsaturated monomers in the copolyester chain.

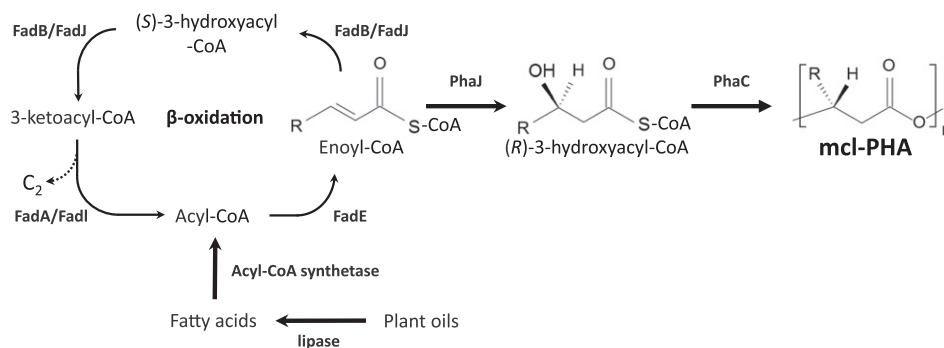
Strategies such as supplementing cultures with nitrogen during fermentation have been used to produce a high concentration of PHBHHx in fed-batch fermentations (Riedel *et al.*, 2012). Palm oil (PO), which served as the sole carbon source, was directly utilized from the pure stock, and ammonia and urea were supplied as the nitrogen sources. As a result, the maximum cell growth was achieved, yielding 139 g/L, and up to 74 wt% PHA was accumulated on the basis of the total biomass with urea supplementation. The previously prepared *R. eutropha* Re2058/pCB113 strain used in this work also able to grow in the antibiotic free medium. The addition system present in the newly constructed strain was robust in high-cell-density cultures and showed high plasmid maintenance. Thus, this method may serve as an alternative way for retaining the plasmid without antibiotics, thus significantly reducing the cost of the fermentation process.

Other than PO, PKO is also an excellent carbon source for high-cell-density cultivation. Sato and colleagues tested the PHB homopolymer production from PKO using *C. necator* H16 (Sato *et al.*, 2013). The wild-type strain produced 160 g/L dry cell mass with a PHA content accounting for 72 wt% of the dried cell mass. Additionally, the other two *C. necator* strains, CNPJN and CNPCN, expressing *pha*_{CAC} NSDG were also grown with PKO in fed-batch fermentation for producing PHBHHx. The CNPJN culture only produced dry cell and PHA contents of 111 g/L and 60.8 wt%, respectively. Meanwhile the CNPCN culture resulted in up to 165 g/L dry cell mass with 76.4 mol% PHA. The low yield obtained from CNPJN culture is because the CNPJN strain had low plasmid stability caused by the loss of pJRD215NSDG plasmid in high-cell-density culture. On the other hand, the pCUP3NSDG introduced in the CNPCN strain is highly stable and has proven useful for large-scale PHA production. Unfortunately, the 3HHx fraction obtained was very low and did not provide any advantages for consumer applications. In a more recent study, other groups have continued to produce the same copolymer, targeting an increase in the 3HHx fraction (Sato *et al.*, 2015). The first approach involved replacing the native *phaC1* gene located on the chromosomal DNA of *C. necator* H16 by the mutant synthase of *pha*_{CAC} NSDG from *A. caviae*. Subsequently, they also introduced the β -ketothiolase encoded by the *bktB* gene in the PHA-producing strain (regarded as *C. necator* ASBK) to enhance the formation of the 3HHx intermediate and (R)-3HH-CoA was added along with butyrate to the culture medium as a co-substrate. The upregulated *bkt* gene introduced to the *C. necator* ASBK strain successfully yielded a 3HHx fraction of 13 mol% with supplementation in a butyrate to PKO ratio of 23.1/76.9. The strategy was also capable producing as high as 175 g/L dry cell mass with 78.6 mol% PHA. Moreover, the stepwise fed-batch process was initially carried out with 5 g/h of PKO, which was subsequently increased to 10 g/h after 24 h, and this successfully produced a dry cell mass of more than 200 g/L (Arikawa and Matsumoto, 2016). Thus, a highly effective process for cell growth with a high PHA content can be achieved by using a high-cell-density fed-batch culture. Nonetheless, controlling the 3HHx composition remains a significant challenge, especially on a commercial scale when using recombinant strains. In addition, there are difficulties in controlling the 3HHx fraction, which may vary according to the bioreactor size and culture conditions such as the aeration and feeding of the carbon sources.

Fluorescent and non-fluorescent pseudomonads are well known and can also accumulate mcl-PHA when grown on suitable fatty acids. Recently, several strains of pseudomonads such as *P. entomophila* and *P. putida* have been reported in the literature to have this ability (Table 3). Additionally, they are highly tolerant towards high fatty acid feeding concentrations. Because effective carbon feeding is required, the precursor fatty acid was added twice to the *P. putida* KT2442 culture (each 5 g/L) at 12 and 24 h after growth in a nutrient-rich medium (Wang *et al.*, 2011). An exogenous supply of fatty acids serves as an energy source for bacterial growth and provide intermediates for mcl-PHA biosynthesis, which directly involves the degradation of fatty acids via the β -oxidation pathway. Fatty acids enter the β -oxidation pathway in the form of acetyl-CoA and released two carbon units in each degradation cycle (Fig. 3). Two key enzymes, FadA and FadB, are involved in the last two steps of the β -oxidation pathway. To produce mcl-PHAs effectively, the carbon flux must be channeled directly to the PHA biosynthetic pathway by deleting these two enzymes, which will weaken the β -oxidation pathway. The mutant strain *P. putida* KTOY06 with a defective

Table 3 Bioproduction of mcl-PHAs from fatty acids by pseudomonads

Strain	Fatty acid feeding	PHAs	Dry cell wt. (g/L)	Polymer content (wt %)	Reference
<i>P. putida</i> KTOY06	Sodium dodecanoate (C12) at 12 g/L	mcl-PHA (40.9% 3HDD)	5.31	84.3	Ouyang <i>et al.</i> (2007)
	Sodium decanoate (C10) at 12 g/L	mcl-PHA (47.8% 3HD)	8.84	76.1	
<i>P. putida</i> KTMQ01	Lauric acid (C10) at 12 g/L	mcl-PHA (55.3% 3HO)	2.75	30	Cai <i>et al.</i> (2009)
	Decanoate acid (C10) at 12 g/L	mcl-PHA (58.2% 3HO)	1.69	26.6	
	Sodium octanoate (C8) at 10 g/L	mcl-PHA (83.4% 3HO)	4.02	86.4	Liu <i>et al.</i> (2011)
<i>P. putida</i> KTOY08	Single tetradecanoic acid (C14) addition at 4 g/L	mcl-PHA (93.1% 3HTD)	1.36	54.3	
	Single dodecanoic acid (C12) addition at 6 g/L	mcl-PHA (34.6% 3HO) (32.4% 3HD) (28.3% HDD)	1.56	19.8	Wang <i>et al.</i> (2011)
<i>P. putida</i> KT2442	Decanoic acid (C10) at 2 g/L twice	mcl-PHA (71.8% 3HD)	1.44	36.7	
	Octanoate (C8) added twice at 5 g/L	mcl-PHA (81.0% 3HO)	4.64	28.9	Chung <i>et al.</i> (2011)
<i>P. entomophila</i> L48	Dodecanoate acid (C12) at 12 g/L	mcl-PHA (44.5% 3HO)	7.80	50.4	
<i>P. entomophila</i> LAC26	Dodecanoate acid (C12) at 12 g/L	mcl-PHA (98.8% 3HDD)	2.70	90.9	
<i>P. entomophila</i> LAC03	Dodecanoate acid (C12) at 12 g/L	mcl-PHA (41.0% 3HD)	9.90	51.9	

**Fig. 3** Biosynthesis of mcl-PHA from plant oils via the β -oxidation pathway. PhaJ; (R)-specific enoyl-CoA hydratase, PhaC; PHA synthase, FadE; acyl-CoA dehydrogenase, FadB; 3-hydroxyacyl-CoA dehydrogenase, FadA; 3-ketoacyl-CoA thiolase, FadJ/FadI; homolog of FadB/FadA.

β -oxidation pathway produced higher 3HD and 3HDD fractions when grown with sodium decanoate and sodium dodecanoate, respectively (Ouyang *et al.*, 2007). Despite this, the deletion of *fadB* and *fadA* genes from the chromosomal DNA was not effective in slowing the β -oxidation. In addition, another strategy demonstrated the use of a *P. putida* KTMQ01 mutant strain with a deletion in PHA polymerase (*phaZ*) (Cai *et al.*, 2009). By removing the bacterial PHA degradation mechanism, the synthesis of higher fraction of the mcl-PHA dominant unit has been achieved. Morphological analysis revealed that the deletion of PHA depolymerases resulted in the PHA granules becoming larger, explaining why the PHA content reached 86.4 wt% of cell mass. Further, a double mutant of the *P. putida* KTOY08 strain derived from *P. putida* KT2442 was grown in various fatty acids (Liu *et al.*, 2011). There were some irregularities observed in the dominant monomers with different added fatty acids. The feeding of tetradecanoic acid to the double mutant culture for example produced mcl-PHA with a high 3-hydroxytetradecanoate (3HTD) fraction of 93.1 mol%. In contrast, dodecanoic acid supplementation resulted in mcl-PHA with the most abundant monomer fractions, and 3HO was the dominant monomer. The engineered metabolic pathways have proven to be beneficial tools for improving mcl-PHA production in *P. putida*. Similarly, β -oxidation blockage was introduced in *P. entomophila* L48 (Chung *et al.*, 2011). The resulting *P. entomophila* LAC26 with *FadA* and *FadB* deletion accumulated over 90 wt% mcl-PHA composed of 99 mol % 3HDD. However, the dry cell mass was greatly reduced because of the growth retardation caused by defective β -oxidation. However, the *P. entomophila* LAC03 strain with *fadB2x* and *fadAx* deletion produced the same PHA yield as same as the wild-type (*P. entomophila* L48), indicating that mutation did not affect the β -oxidation and high cell growth was observed.

There has been an increase in the production of homopolymer mcl-PHAs in the last decade (Table 4). These studies were driven by the resemblance of many structurally related substrates required for mcl-PHA homopolymer biosynthesis, mainly fatty acids. Hence, it is possible to fine-tune the composition of the mcl-PHAs to obtain significant improvements in the thermal and mechanical

Table 4 Microbial production of homopolymer and near homopolymer mcl-PHAs from fatty acids

Strain	Fatty acid	mcl-PHA homopolymer/near homopolymer ^a	3HA fraction (mol%)	Dry cell wt. (g/L)	Polymer content (wt%)	Reference
<i>P. putida</i> KTQQ18	Decanoate (C10)	PHD	100	1.43	10.6	Liu <i>et al.</i> (2011)
<i>P. putida</i> KTHH03	Heptanoate (C7)	PHHp	100	5.32	68.9	Wang <i>et al.</i> (2011)
	Hexanoate (C6)	PHHx	100	3.56	21.2	
<i>E. coli</i> CAG18496	Decanoate (C10)	PHD	99.6	0.54	26.5	Sato <i>et al.</i> (2012)
	Nonanoate (C9)	PHN	99.4	0.60	21.3	
	Octanoate (C8)	PHO	99.1	0.58	21.1	
	Heptanoate (C7)	PHHp	100	0.69	19.0	
	Hexanoate (C6)	PHHx	100	0.42	11.1	
<i>E. coli</i> LSBJ	Dodecanoate (C12)	PHDD	100	1.03	28.6	Tappel <i>et al.</i> (2012)
	10-Undecenoate (C11)	PHUn	100	1.07	41.0	
	Decanoate (C10)	PHD	100	1.03	25.7	
	Octanoate (C8)	PHO	100	0.86	47.3	
<i>E. coli</i> RSC02	Dodecanoate (C12)	PHDD	Near 100	1.11	29.3	Scheel <i>et al.</i> (2016)
	Decanoate (C10)	PHD		1.49	40.4	
	Octanoate (C8)	PHO		1.03	54.1	
	Heptanoate (C7)	PHHp		1.02	30.2	
	Hexanoate (C6)	PHHx		1.06	27.3	
<i>E. coli</i> LSBJ	Dodecanoate (C12)	PHDD	98.8	3.64	11.6	Hiroe <i>et al.</i> (2016)
	Decanoate (C10)	PHD	99.6	4.72	28.7	
<i>P. entomophila</i> LAC23	Tetradecanoate (C14)	PHTD	97.4	1.50	27.8	Wang <i>et al.</i> (2017)
	Tridecanoate (C13)	PHTriD	99.7	1.60	68.1	
	Dodecanoate (C12)	PHDD	98.5	2.60	93.8	
	Undecanoate (C11)	PHU	99.0	2.40	86.3	
	Decanoate (C10)	PHD	99.6	3.00	68.1	
	Nonanoate (C9)	PHN	Near 100	5.10	26.3	

^aPHHx, poly(3-hydroxyhexanoate); PHHp, poly(3-hydroxyheptanoate); PHO, poly(3-hydroxyoctanoate); PHN, poly(3-hydroxynonanoate); PHD, poly(3-hydroxydecanoate); PHUn, poly(3-hydroxy-10-undecenoate); PHU, poly(3-hydroxyundecanoate); PHDD, poly(3-hydroxydodecanoate); PHTriD, poly(3-hydroxytridecanoate); PHTD, poly(3-hydroxytetradecanoate).

properties. Mutant *P. putida* KTQQ18 was constructed from the previous *P. putida* KTOY08 strain but with an additional deletion in the *fadB* gene, which encodes the β -oxidation complex subunit alpha, and the *phaG* gene, which encodes the 3-hydroxyacyl-CoA-acyl carrier protein transferase (Liu *et al.*, 2011). The resulting strain was able to synthesize PHD homopolymers in the presence of decanoate, yielding 10.6 mol% PHA. In addition, the *P. putida* KTHH03 mutant with a knockout in the *phaG* gene and other β -oxidation-related genes likewise enabled the production of mcl-PHA homopolymers from hexanoate and heptanoate (Wang *et al.*, 2011). Poly(3-hydroxyheptanoate) (PHHp) homopolymer production was as high as 68.9 wt% at 5.32 g/L dry cell mass. However, the production of the PHHx homopolymer was low, and only 21.2 mol% of dry cell mass was achieved. In the same manner, the production of mcl-PHAs from fatty acids in recombinant *E. coli* CAG18496 was achieved by utilizing the *fadB* mutant strain as the host and expressing heterologous biosynthetic enzymes from *P. putida* and *P. aeruginosa* (Sato *et al.*, 2012). The heterologous production system produced mcl-PHAs homopolymers and, to a lesser extent, near homopolymers. The PHA production was over 20 wt% when cells were grown on 2-alkenoic acids with acyl chain lengths from C8 to C10, whereas PHA was inadequately accumulated in the presence of the shorter chain 2-alkenoic acid. Furthermore, the production of mcl-PHA homopolymers from recombinant *E. coli* LSBJ with the elimination of *fadB* and its homolog, *fadJ*, genes from the β -oxidation pathway was studied, where fatty acids were used as the sole carbon source (Tappel *et al.*, 2012). The defective β -oxidation resulted an accumulation of enoyl-CoA intermediates, which were then converted to the corresponding mcl-PHAs by heterologous expression of (R)-specific enoyl-CoA hydratase (PhaJ4) and a broad specificity PHA synthase [PhaC1 (STQK)] from the plasmid DNA. The recombinant *E. coli* production system offers a wider range of mcl-PHAs than the previous work reported in *P. putida*. However, the cell production and PHA yields acquired are much lower than the *Pseudomonas* system developed by Wang and co-workers, suggesting the low intolerance of *E. coli* towards the high concentrations of the fatty acids supplied. To overcome the drawbacks of low PHA yield, Scheel and associates prepared an *arcA*-deleted strain to inhibit the expression of genes involved in β -oxidation along with a *fadR* (the regulatory protein that represses the genes for the β -oxidation pathway and activates unsaturated fatty acid synthesis) mutation (Scheel *et al.*, 2016). Removal of the *arcA* transcriptional regulator in the *E. coli* LSBJ strain had a significant effect on the inhibitive expression of β -oxidation-related genes. The resulting *E. coli* RSC02 strain had improved metabolic flux through the fatty acid

Table 5 Thermal and mechanical properties of mcl-PHAs

Strains	PHA	Melting temperature, T_m (°C)	Glass transition temperature, T_g (°C)	Tensile strength (MPa)	Young modulus (MPa)	Elongation at break (%)	Reference
<i>P. putida</i> KTQQ20	PHD (100% 3HD)	72	−37	12	20	313	Liu <i>et al.</i> (2011)
	PHDD (84% 3HDD)	78	−32	5	103	88	
<i>P. putida</i> KT2442	PHN (70% 3HN)	46	−45	6.6	1.5	1327	Jiang <i>et al.</i> (2012)
	PHN (95% 3HN)	63	−48	15.7	11.3	1317	
	PHO (88% 3HO)	54	−40	9.6	3.4	1384	
	PHO (94% 3HO)	58	−	11.7	4.7	1267	
<i>E. coli</i> LSBJ	PHDD (74% 3HDD)	76	n.d.	10	114	225	Hiroe <i>et al.</i> (2016)
	PHDD (85% 3HDD)	77	n.d.	10	156	161	
	PHDD (99% 3HDD)	82	n.d.	11	180	270	
	PHD (99% 3HD)	70	−46	8	118	226	

catabolic pathway, which eventually increased PHA accumulation. Although PHA production was enhanced, a key challenge related to this fatty acid biosynthetic pathway is in achieving high cell production as well, a crucial factor for an effective production system. Continuing with the previous use of the *E. coli* LSBJ strain, further improvements in PHA production were carried out by the supplementation of sugars as co-carbon sources, which is necessary to promote the production of biomass (Hiroe *et al.*, 2016). Cells were initially grown with glucose supplied at 10 g/L to allow high cell biomass production; then, fatty acids (2 g/L) were added after 6 h to induce PHA production. The two-stage culture strategy achieved up to 3.64 and 4.72 g/L dry cell masses for PHDD and PHHD production, respectively. On the other hand, PHA production remained moderate, and further process development is required to increase the PHA yield. In a more recent study, *P. entomophila* LAC23 (deletion in *fadB*, *fadA*, and *PSEEN 0664* genes) has been demonstrated for producing mcl-PHA with chain lengths from C7 to C14. The highest PHA yield was obtained with 12 g/L sodium decanoate and accumulated over 90 wt% PHA consisting of 99.6 mol% 3HD.

Table 5 presents the thermal and mechanical properties of mcl-PHAs produced by *E. coli* and *P. putida* strains. The dominant mcl-PHA monomers play an important role in enhancing the tensile strength and Young's modulus in PHO and poly(3-hydroxy-nonyanoate) PHN (Jiang *et al.*, 2012). Furthermore, the melting temperature, Young's modulus, and elongation at break of the PHDD homopolymer from *E. coli* were, of course, not only higher than those conventional mcl-PHA but also the copolymer itself (Hiroe *et al.*, 2016). This demonstrates the flexibility of the mcl-PHA homopolymers, which could be used as stretchable films. The naturally synthesized mcl-PHA copolymers from pseudomonads are soft but sticky and, thus, difficult to process; however, the homopolymer polyesters are hard elastomers and, thus, have advantages for melt processing. Because mcl-PHA homopolymers are superior to the copolymers, they have a versatile range of thermal and mechanical properties that are desirable for many applications.

Challenges, Future Outlook, and Concluding Remarks

In a challenging global scenario with unstable fossil fuel prices and increasing serious environmental problems, PHA is certainly a promising polymeric material that demands further attention. The exorbitant price of pure chemical feedstocks and use of antibiotics are two major factors increasing the cost of large-scale PHA production. Although many innovative strategies for PHA production have been demonstrated, these methods are still inapplicable for industrial use. Therefore, the use of plant oils as an alternative carbon source is expected to reduce the production costs in more reasonable way. Plant oils and their derivative products are renewable resources, guaranteeing availability for the effective production of PHA. It is expected that the demand for plant oil products will continue to increase as a result of the development of green polymers. Hence, worldwide participation is encouraged to establish an effective supply chain and to increase the output of plant oils to ensure continuous and efficient PHA production at the industrial scale. In addition, the use of plant oils is not driven by the cost and yield alone but also provides versatility for the development of various PHA with broad applications.

From the small- to pilot-scale, PHA production has been demonstrated with the use of recombinant microorganisms in culture suspensions. Nevertheless, there are still several issues related to the PHA-producing strain itself, where plasmid instability may occur in high-cell-density cultures. Additionally, the complexity of the fermentation process such as aeration, substrate feeding rate, inhibition, and stress response, as well as polymer extraction, may also influence the properties of the PHA. More work should be carried out on process development to improve process efficiency further to increase the competitiveness of PHA plastics. An integrated solution for highly efficient and productive strains capable of utilizing cost-effective substrates with an optimized fermentation process will certainly lead to the use of PHA as a sustainable material in the near future.

This review has summarized the recent trends in PHA production from plant oils as a way for diversifying PHAs for broader applications. The strategies involve the genetic modification of microorganisms combined with the use of plant oils to provide a unique type of PHA that cannot be synthesized naturally. The mcl-PHA homopolymers, which are structurally related to the corresponding fatty acids, having similar chain lengths, are novel materials with outstanding properties. In the future, further improvements in the processability and applicability of PHAs for consumer use could increase their use in biodegradable plastics,

food packaging, toiletries, and other consumable products. The sustainability of PHA and its promising applications apply not only to the consumer plastics industry but also biomedical industries.

See also: Analyzing Biodiesel Production From Cooking Oil. Natural Oils as Green Lubricants in Forming Processes. Natural Oils as Green Lubricants in Machining Processes. Palm Oil Fuel Ash: Innovative Potential Applications as Sustainable Materials in Concrete. Renewable Energy Production From Environmental Hazardous Palm Oil Mill Waste Materials: A Review. Structural, Thermal, Mechanical and Rheological Properties of Polylactic Acid/Epoxidized Soybean Oil/Organoclay Blends. Synthesis of Multiwalled Carbon Nanotubes (MWCNTs) From Waste Cooking Oil Catalyzed by Mill-Scale Waste for Development of Microstrip Patch Antenna (MPA). Vegetable Oil-Based Polymeric Materials: Synthesis, Properties, and Applications

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Natural Fiber Reinforced Composites in the Context of Biodegradability: A Review

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Introduction

The evolution of materials started in 10,000 BCE when the wood and stones were used as tools and weapons. The relative importance of the ceramics, composites, polymers and metals as a function of time and their evolution are presented in Fig. 1. The use of materials begins in Stone Age around 10,000 BCE, when humans began using bone, clay, animal skin, shells, fibers and feathers for making jewelry, weapons, tools and shelter. At the end of the Stone Age metals, polymers, composites and ceramics were used to create the ornaments and tool. The first extraction and use of copper and bronze are roughly estimated between 4000 BCE and 1000 BCE is called the Bronze Age. During this time the use of copper had become very apparent due to their superior properties which allow shaping these materials to any required shape. The period from 1000 BCE to 1620 CE is called the Iron Age. In the year 1620, development of cast iron technology has established the dominance of metals in industries and then the evolution of steels, alloy steels, lightweight and superalloys took place during the 1800–1940 (Ashby, 1987). During this time materials like rubber, glass, cement, refractory materials and glues were also used in many applications but the relative importance for these materials was less as because of the dominance of metals. After the World War II between 1940 and 1945, the major transition has taken place in the development of new materials – lightweight with high strength titanium and zirconium alloys has given new hopes to aerospace, energy and civil construction industries. Also, the development of new metallic alloys and demand for steel and cast iron are fallen down from 1960. After 1970, there is a drastic change in the development of alloy materials like dual phase steels, microalloyed steel, superalloys are seen in the market.

On another hand, the development and demand for polymers, composites and ceramics were growing rapidly from the 1970s. The attractive features of composite materials like lightweight, high specific strength, stronger, harder, stiffer, flexibility in design and ease of tailoring the required properties calls for research attention. The development of new composites and their use still has higher market potential and is projected to increase in future years. Today composite materials have taken 60%–70% of the market due to their superior characteristics as mentioned above. The following section gives an insight on composites, classifications and role of natural composites.

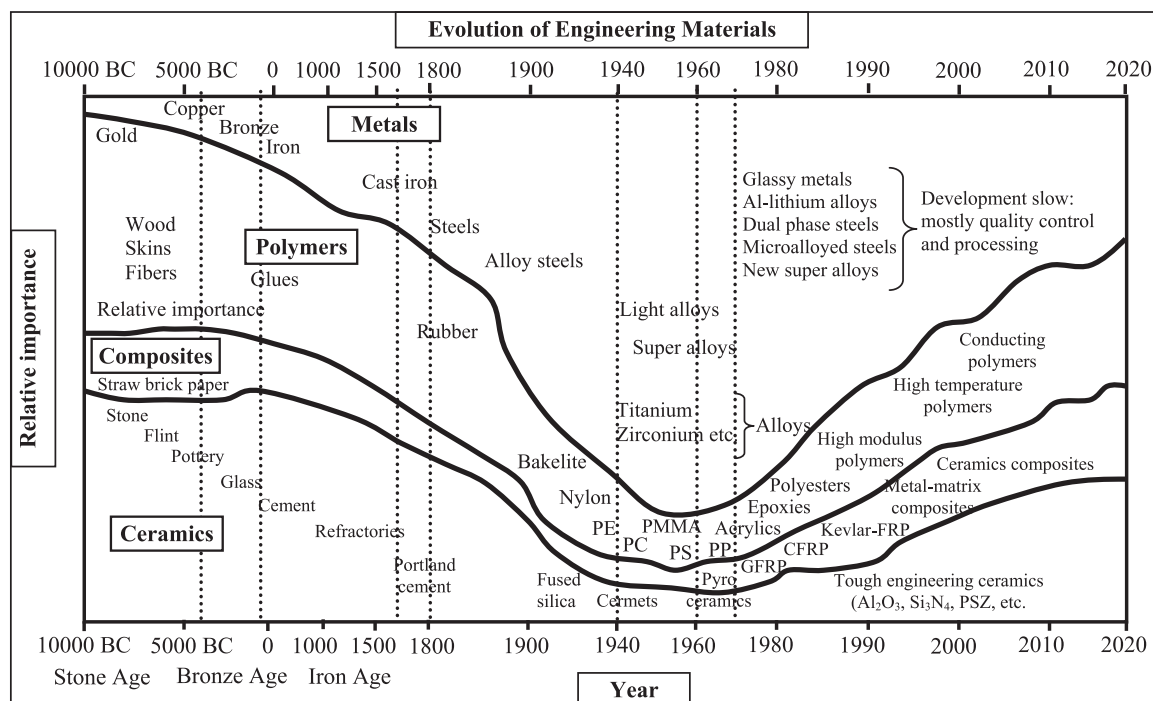


Fig. 1 Schematic of relative importance of the metals, polymers, composites and ceramics as a function of time. Modified from Ashby, M.F., 1987. Technology of the 1990s: Advanced materials and predictive design. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 322 (1567), 393–407. doi:10.1098/rsta.1987.0059.

Composite Materials and Classifications

Composite materials are a new class of engineering materials made from two or more constituent's materials that remain separate and distinct on the macroscopic level while forming a single component. Which performs better than those of the individual constituents used independently (Anandjiwala and Blouw, 2007). In contrast to alloy, each material retains its inherent characteristics such as physical, chemical and mechanical properties. It consists of a matrix phase as a continuous phase and the reinforcing phase as a discontinuous phase.

Composites are mainly classified based on the matrix phase such as metal (known as metal matrix composite – MMCs), polymer (known as polymer matrix composites – PMCs) and ceramic (known as ceramic matrix composite – CMCs). Similarly, composites are classified based on reinforced phase such as particulate (known as particulate composites), fiber (known as fiber composites) and structural (Known as structural composites) as detailed in Fig. 2. Detailed constituents of these composites are listed in Table 1.

The constituent materials are selected based on properties requirements for the applications and cost of the materials. Metal matrix, polymer matrix, ceramic matrix and fiber composites are commonly used in most of the industrial, automotive, aerospace, sports and space applications. Although tremendous development in the field of composite materials there has been always in search of new materials which can perform better at affordable costs compared to previous materials and also the developed materials should be biodegradable. The biodegradability of the materials is very important in the current scenario to overcome the problem associated with disposal and most of these materials take more time to decompose. Table 2 shows the life span of various materials that takes to decompose as the time lapses. Natural fibers and related components will takes less than a year to decompose compare to other materials.

At present most of the industries are switching to biodegradable materials due to

- Growing interest in reducing the environmental impact of polymers or non-biodegradable composites due to increased awareness of eco-friendliness (Satyanarayana et al., 2009; Bajpai et al., 2017).
- Finite petroleum resources, decreasing pressures for the dependence on petroleum products with an increasing interest in maximizing the use of renewable materials.
- The availability of improved data on the properties and morphologies of natural materials such as lignocellulosic fibers, through modern instruments at different levels, and a hence better understanding of their structure-property correlations (Satyanarayana et al., 2009).

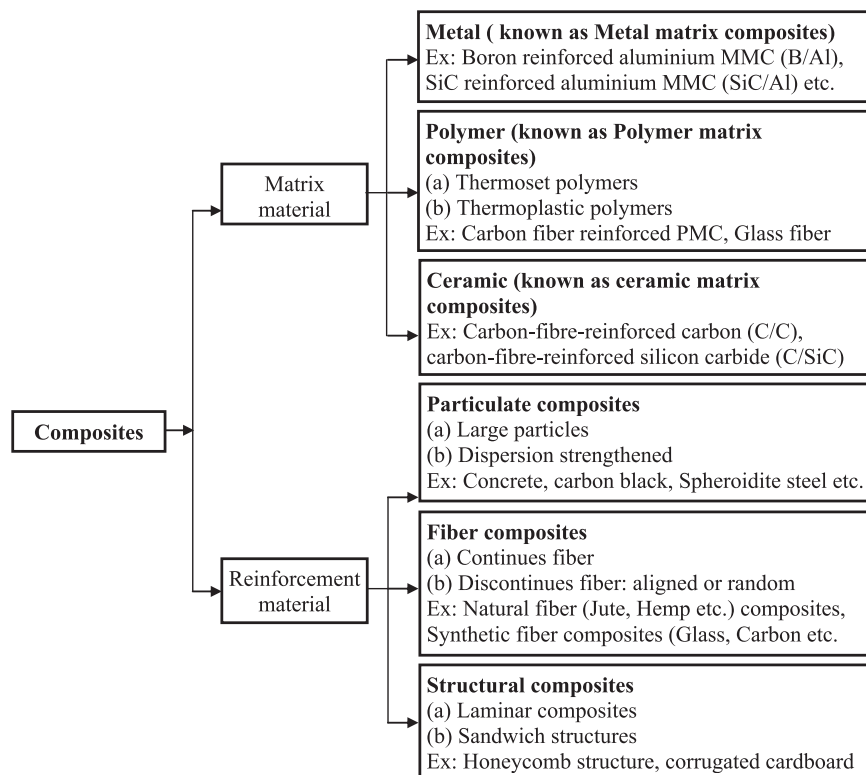


Fig. 2 Classifications of composite materials.

Table 1 Constituents of different composites and their applications

Sl. No.	Composites	Applications
1	<i>Metal matrix composites</i> Matrix: Aluminum, magnesium, titanium, cobalt, copper etc. Reinforcements: Boron carbide, silicon carbide, alumina, graphite, titanium carbide	Engine cylinder sleeves, piston-recess walls, bearings, brake discs, heat-sinks in electronics, bicycles frames etc.
2	<i>Polymer matrix composites</i> Matrix: Thermoset polymers: Epoxy, polyester, phenolics etc. Thermoplastic polymers: polycarbonate, polyvinyl chloride, nylon, polystyrene, polyethylene etc. Reinforcements: Glass, carbon, aramid fibers etc.	Boat bodies, load-bearing aerospace structures like wings, tennis racquets, bulletproof jacket, canoes, kayaks, automotive parts etc.
3	<i>Ceramic matrix composites</i> Matrix: Silicon carbide, Boron carbide, Alumina oxide Reinforcements: Silicon carbide fibers, alumina fibers, carbon fibers etc.	Heat shield in space vehicles, cutting tool inserts, dies, pressure vessels, jet engines, gas turbines, turbine blades, brake disk etc.
4	<i>Particulate composites</i> Matrix: Cement, elastomeric polymer, epoxy etc. Reinforcements: Aggregates (sand and gravel), ceramics particles, glasses and metal particles, carbon nanotubes etc.	Concrete, sand and water, wood particle board, tire etc.
5	<i>Fiber composites</i> Matrix: Epoxy, phenolic, polyester, vinyl ester etc. Reinforcements: Chopped or continues glass fibers, carbon fibers, hemp fibers, jute fiber, aluminum, aluminum oxide, aluminum silica etc.	Bulletproof vests, landscaping timbers, park benches, window and door frames, indoor furniture
6	<i>Structural composites</i> Matrix: Plastic matrix, face sheet of metals Reinforcements: Metal sheets, cotton, paper, woven glass fibers, foamed polymers, synthetic rubbers, inorganic cement, balsa wood etc.	Roofs, floors, walls of buildings, and in aircraft for wings, fuselage and tailplane skins

Table 2 Life span of material decomposition

Material	Time to degrade in the environment
1. Glass and tires	Uncertain time
2. Plastic	450 years
3. Aluminum can	200–500 years
4. Tin can, Rubber boot sole	50–80 years
5. Painted wood	13 years
6. Natural Composites	
a) Wool stocking	1 year
b) Bamboo stick	1–3 years
c) Cotton, Banana peel, Orange peel,	1–5 months
d) PolyCaprolactone - Grafting - Maleic Anhydride /starch, PolyCaprolactone - starch	2 months
e) Waste Gelatin / Polyvinyl Alcohol, Waste Gelatin / Sugar Cane Bagasse, Conventional copy paper	1 month

Note: Satyanarayana, K.G., Arizaga, G.G.C., Wypych, F., 2009. Biodegradable composites based on lignocellulosic fibers-An overview. Progress in Polymer Science 34 (9), 982–1021. doi:10.1016/j.progpolymsci.2008.12.002.

These factors have greatly increased the understanding and development of new materials such as biocomposites in which the natural fibers are reinforced in natural resins or thermoset/thermoplastic resin. The following Section “Natural Fiber Reinforced Composites” provides an overview of different aspects of natural fiber composites.

Natural Fiber Reinforced Composites

Natural fiber reinforced composites contain reinforcement phase as natural fiber itself they are abundant, renewable, biodegradable, low-density compared with other synthetic materials (Joseph *et al.*, 1999; Akil *et al.*, 2011; Chaudhary *et al.*, 2018b). Some of the commonly used natural fibers are as a reinforcement are rice husk (Wei and Meyer, 2016), henequen (Herrera-Franco and Valadez-González, 2005), banana (Oksman *et al.*, 2009), pineapple, abaca (Cai *et al.*, 2016) sugar cane, birch fibers (Mejri *et al.*, 2018), oil palm, hemp (Dayo *et al.*, 2017), jute (Basak *et al.*, 2018; Chaudhary *et al.*, 2018a,b), sisal (Giridhar *et al.*, 1986; Li *et al.*, 2016; Bajpai *et al.*, 2017), flax (Andersons *et al.*, 2005; Arbelaziz *et al.*, 2006), curaua fibers (Monteiro *et al.*, 2015), Sour-weed (Patel *et al.*, 2018), betel nut (Merajul Haque and Hasan, 2016) etc. The reinforcement is

mixed with the matrix phase – natural resins, thermoset and thermoplastic polymers (Alves *et al.*, 2010) which acts as a binder to form the composites. Natural resin includes wheat starch, corn starch, potato starch, biodegradable polyester, polyacids etc., (Satyanarayana *et al.*, 2009) thermoset polymers include epoxy, polyester, phenolics etc., and thermoplastic polymers include polycarbonate, polyvinyl chloride, nylon, polystyrene, polyethylene etc. (Alves *et al.*, 2010; Ku *et al.*, 2011; Sahari and Sapuan, 2012; Mitra, 2014; Dayo *et al.*, 2017).

Major factors to be considered when the natural fiber is used as reinforcement are thermal stability of fibers, fiber volume fraction, fiber size, orientation, texture, wettability, moisture content and humidity (Yallew, 2015). The biodegradability of plant fibers can contribute to a healthy ecosystem while their low cost and high performance fulfill the economic interest of the industry. When natural fiber-reinforced plastics are subjected, at the end of their life cycle, to combustion process or landfill, the released amount of CO₂ of the fibers is neutral with respect to the assimilated amount during their growth (Wambua *et al.*, 2003; Thakur, 2013; Merajul Haque and Hasan, 2016). Synthetic fibers such as glass, carbon and aramid reinforced with polymer matrix materials provide advantages of high stiffness and strength to weight ratio in many applications as compared to conventional construction materials. In spite of these advantages, researchers are trying to develop natural composites as because the widespread use of synthetic fiber-reinforced polymer composite has a tendency to decline because of their high-initial costs. Another major drawback is the production of synthetic composites requires a large quantum of energy and quality of environment suffered because of the pollution generated during the production and recycling of these synthetic materials. Natural fibers are classified into three groups plant fibers, animal fibers and mineral fibers. Fig. 3 shows the classifications of natural fibers.

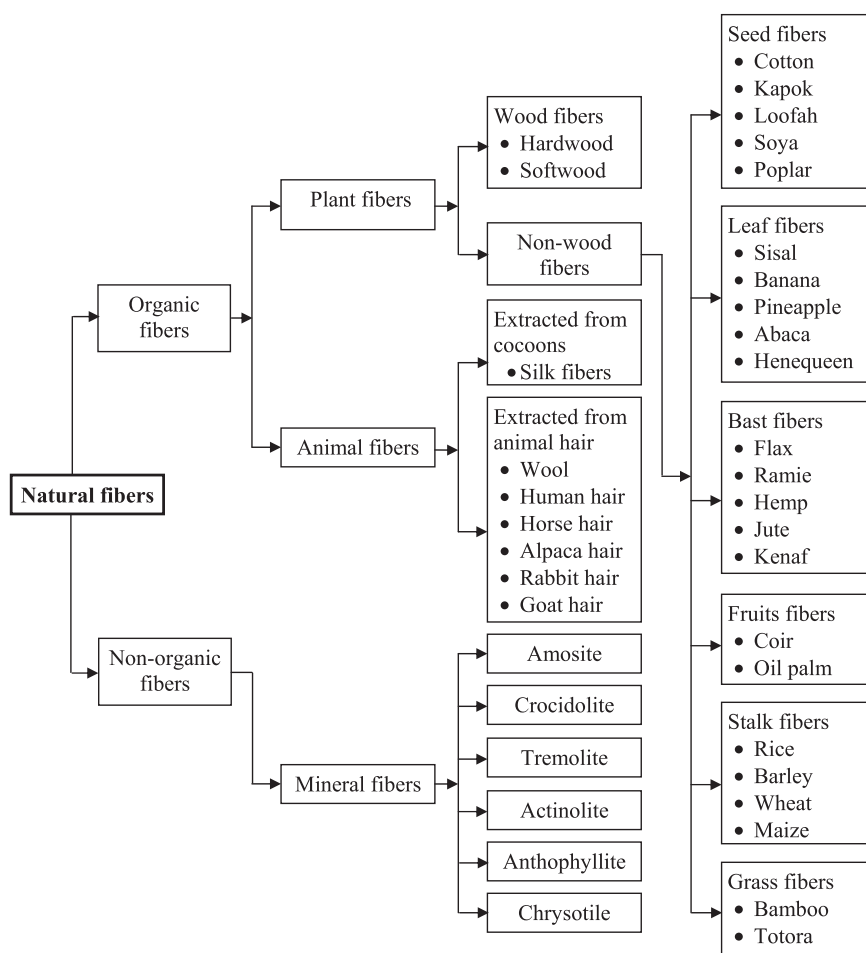


Fig. 3 Classifications of natural fibers. Modified from Mohanty, A.K., Misra, M., Drzal, T., 2005. Natural Fibers, Biopolymers, and Biocomposites, first ed. CRC Press, Taylor and Francis group. Riedel, U., Nickel, J., 2005. Applications of Natural Fiber Composites for Constructive Parts in Aerospace, Automobiles, and Other Areas. Weinheim: Biopolymers Online, Wiley-VCH Verlag GmbH & Co. KGaA. doi:10.1002/3527600035.bpola001. Akil, H.M., Omar, M.F., Mazuki, A.A.M., *et al.*, 2011. Kenaf fiber reinforced composites: A review. Materials and Design 32 (8–9), 4107–4121. doi:10.1016/j.matdes.2011.04.008. Pandey, J.K., Nagarajan, V., Mohanty, A.K., Misra, M., 2015. Commercial potential and competitiveness of natural fiber composites. Biocomposites: Design and Mechanical Performance, 1–15. doi:10.1016/B978-1-78242-373-7.00001-9. Hiremath, A., Sridhar, T., 2018. Use of bio-fibers in various practical applications. Reference Module in Materials Science and Materials Engineering, 1–5. doi:10.1016/B978-0-12-803581-8.11116-6.

Plant-based fibers are also known as cellulose fibers which contain mainly cellulose and lignin. Plants, agricultural waste, agro-industrial residues and vegetal substances are major sources of these fibers (Yao *et al.*, 2008). These fibers are further divided into wood fibers and nonwood fibers. Further non wood fibers are categorized as seeds fibers which are extracted from dried seeds of the plant, leaf fibers extracted from leaf, bast fibers extracted from inner bark of a trees, fruits fibers extracted from dried fruits (Joseph *et al.*, 1999), stalk fibers taken from the stalk of a plant and grass fibers. Photographic view of some of the commonly used plant's fibers is shown in Fig. 4(a). Chemical compositions, type of processing techniques, dimensions of the fibers, place of growth and time of harvest are some of the important factors influence the final properties of the natural fibers. Plant-based fibers are commonly used in automotive interior design, construction industries, aerospace interior parts and sports equipment. Largest producers of natural fibers and productions rate are also presented in Table 3. These fibers are reinforced in the natural resin, thermoset and thermoplastic matrix materials to achieve the required shape of the end products and strength.

Animal fibers are another alternative to replace the synthetic fibers which are generally comprised of proteins, examples mohair, wool, silk, alpaca, angora (Cheung *et al.*, 2009). These fibers are generally divided into two categories such as fibers extracted from cocoons – silk fibers and the fibers taken from hairs of animals or hairy mammals. Some of the examples for animal hairs used to manufacture natural composites are sheep's wool, human hair, goat hair, rabbit hair, alpaca hair and horse hair. Feathers and feather fibers collected from birds also reported in the by researchers. Table 4 shows the properties and chemical composition of the different natural fibers. Photographic views of some of the commonly used animal fibers are shown in Fig. 4(b).

Mineral fibers are a third class of natural fibers which are naturally occurring fiber or slightly modified fiber procured from minerals comes from the asbestos group. Some of the mineral fibers are amosite, crocidolite, tremolite, actinolite, anthophyllite, chrysolite. Fig. 4(c) shows the photographic view of some of the commonly used mineral fibers.

There are plenty of research papers are available on natural fiber reinforced composites in which some of the selected literature are listed in Table 5 which gives information on reinforcement and matrix materials used to manufacture the natural fiber composites and important characteristics drawn based on the different test conducted by researchers.

Manufacturing Techniques

Some of the commonly used manufacturing techniques are:

- (1) Hand layup technique
- (2) Compression molding technique
- (3) Vacuum-assisted resin transfer molding technique
- (4) Injection molding technique
- (5) Pultrusion technique

Hand Layup Technique

Hand layup technique (Harish *et al.*, 2009; Kumar *et al.*, 2011; Junior *et al.*, 2010; Ashok Kumar *et al.*, 2010; El-Tayeb, 2008) is most commonly used method for manufacturing the biocomposites from small to the large scale shown in Fig. 5. It is the simplest molding technique and most economical method which can be applied to a wide verity of products. In this process initially, gel coating is applied on the prepared mold surface for ease of removal of composites from the mold. After the gel curing natural fiber mats are manually placed inside the mold and thin coat of the resin is applied on the mats manually. Hand roller is used to distribute the resin equally over the mat by wetting the reinforcing fiber completely and also to remove the entrapped air. This procedure will be carried out until it reaches the required thickness.

A similar method is also used to develop the particulate composites in which reinforcing long fibers chopped into short fibers and mixed with natural or synthetic resin then which will be poured into prepared size and shape of the mold. After the sufficient amount of time is given for curing composite is removed from the mold for further processing. The main limitation with this process is delamination of fibers if the resin is not applied properly and time consumption for curing.

Compression Molding Technique

Compression molding (Wambua *et al.*, 2003; Kumar *et al.*, 2011; Bakare *et al.*, 2010; Dayo *et al.*, 2017) is a high volume and high-pressure technique used to fabricate the high strength composite materials. This method has the ability to produce large and complex shapes and it is economical compared resin transfer molding and injection molding. In this process, the composite can be produced with unidirectional mats, bi-directional fabrics, randomly oriented composites or chopped strands. Application of heat and pressure is used in this method. Fig. 6 shows the schematic of the compression molding technique. In which charge (stacking laminates or chopped fibers with resin) is placed inside the mold cavity which of the required shape of the component. The upper part of the mold is closed and pressure is applied to force the premixed charge to take shape of the mold cavity.

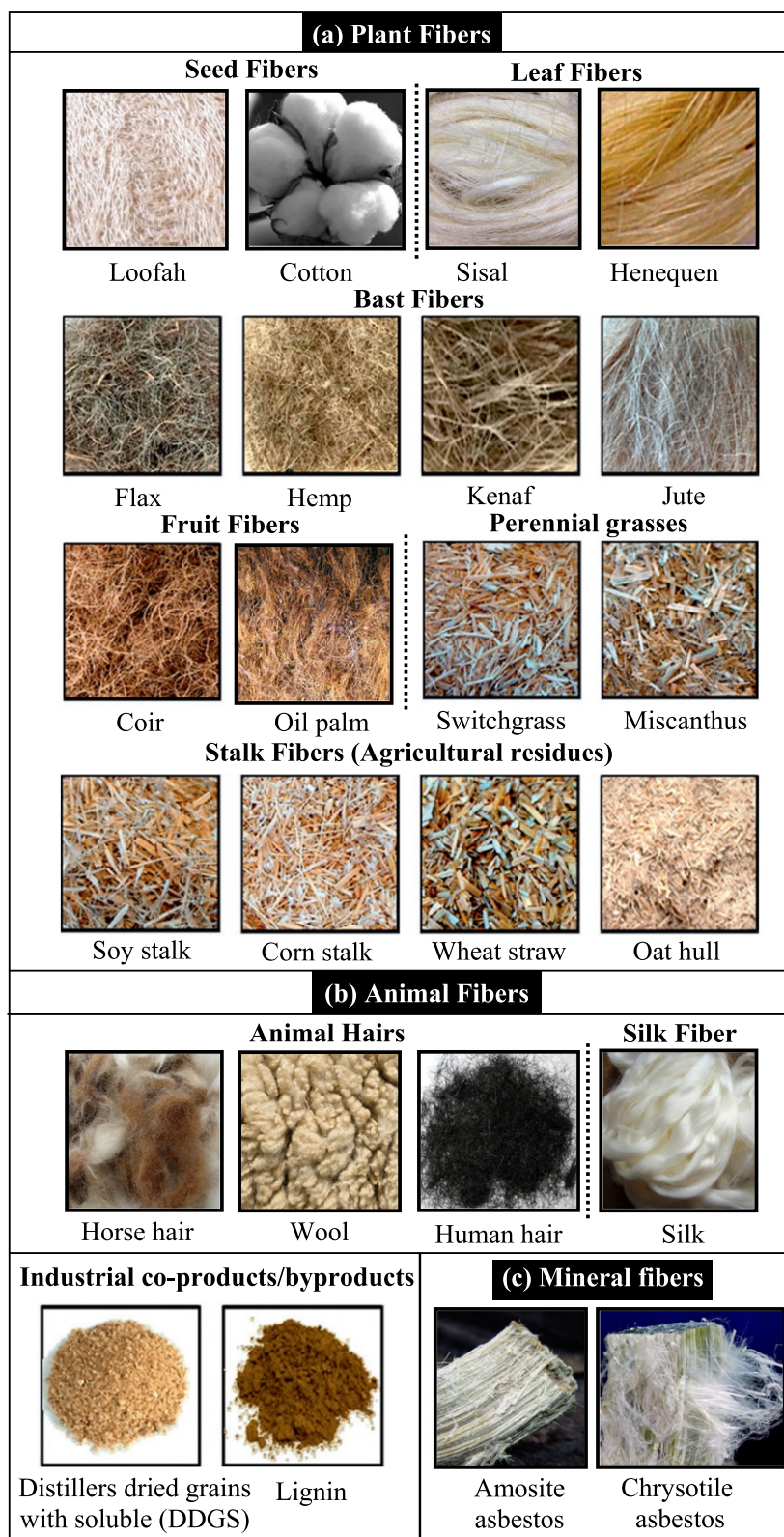


Fig. 4 Photographic view of some of the commonly used natural fibers. Modified from Pandey, J.K., Nagarajan, V., Mohanty, A.K., Misra, M., 2015. Commercial potential and competitiveness of natural fiber composites. *Biocomposites: Design and Mechanical Performance*, 1–15. doi:10.1016/B978-1-78242-373-7.00001-9. Cheung, H., Ho, M., Lau, K., Cardona, F., Hui, D., 2009. Natural fibre-reinforced composites for bioengineering and environmental engineering applications. *Composites Part B: Engineering* 40 (7), 655–663. doi:10.1016/j.compositesb.2009.04.014. <http://www.silken-soaps.com/silk-in-skin-care-products.htm>. <https://www.bkb.co.za/wool-outlook-for-2018/>. <https://slipstreamfiberarts.wordpress.com/2010/03/15/spinning-horsehair/>. https://www.flickr.com/photos/asbestos_pix/5542483226. https://www.flickr.com/photos/asbestos_pix/7152870569.

Table 3 Natural fibers production and countries of origin

Type of fiber	Fibers extracted from	Countries of origin	World production (10 ³ ton)
Flax	Bast	Canada, France, Belgium, Spain	830
Hemp		China, France, Philippines, Poland, Spain	214
Jute		India, Egypt, Guyana, Jamaica, Ghana, Malawi, Sudan, Tanzania, Brazil, China, Bangladesh	2300
Kenaf	Leaf	India, Bangladesh, USA, Iraq, Tanzania, Jamaica, South Africa, Cuba, Togo, Thailand	970
Ramie		China, Brazil, Philippines, India	100
Abaca		Philippines, Ecuador, Costa Rica, Colombia	70
Curaua		Brazil, Venezuela, Guyana, Columbia	> 1
Pineapple		Philippines, Thailand, Indonesia	74
Sisal		Brazil, East Africa, Haiti, Venezuela, Antigua, Kenya, Tanzania, India	378
Coir		India, Sri Lanka, Philippines, Malaysia, Brazil	100
Cotton	Seed	China, India, USA	25,000
Oil Palm		Malaysia, Indonesia	40
Bagasse		Brazil, India, China	75,000
Bamboo		India, China, Indonesia	30,000

Note: Adekomaya, O., Jamiru, T., Sadiku, R., Huan, Z., 2016. A review on the sustainability of natural fiber in matrix reinforcement – A practical perspective. *Journal of Reinforced Plastics and Composites* 35 (1), 3–7. doi:10.1177/0731684415611974. Antov, P., Savov, V., Neykov, N., 2017. Utilization of agricultural waste and wood industry residues. *International Journal – Wood, Design and Technology* 6 (1), 64–71. Majeed, K., Jawaid, M., Hassan, A., et al., 2013. Potential materials for food packaging from nanoclay/natural fibres filled hybrid composites. *Materials and Design* 46, 391–410. doi:10.1016/j.matdes.2012.10.044.

Table 4 Properties of natural fibers

Fiber type	Density (g/cm ³)	Length (mm)	Diameter (μm)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongtn at break (%)	Cellulose (wt%)	Hemi-cellulose (wt%)	Lignin (wt %)	Pectin (wt%)	Waxes (wt%)
E-glass	2.5–2.59	–	<17	2000–3500	70–76	1.8–4.8	–	–	–	–	–
Abaca	1.5	–	–	400–980	6.2–20	1.0–10	56–63	20–25	7–13	1	3
Alfa	0.89	–	–	35	22	5.8	45.4	38.5	14.9	–	2
Bagasse	1.25	10–300	10–34	222–290	17–27.1	1.1	32–55.2	16.8	19–25.3	–	–
Bamboo	0.6–1.1	1.5–4	25–40	140–800	11–32	2.5–3.7	26–65	30	5–31	–	–
Banana	1.35	300–900	12–30	500	12	1.5–9	63–67.6	10–19	5	–	–
Coconut	–	–	100–450	131–175	4–13	–	36–43	0.15–0.25	41–45	3–4	–
Coir	1.15–1.46	20–150	10–460	95–230	2.8–6	15–51.4	32–43.8	0.15–20	40–45	3–4	–
Corncob	–	–	–	–	–	–	26.1	45.9	11.3	–	–
Cotton	1.5–1.6	10–60	10–45	287–800	5.5–12.6	3–10	82.7–90	5.7	<2	0–1	0.6
Curaua	1.4	35	7–10	87–1150	11.8–96	1.3–4.9	70.7–73.6	9.9	7.5–11.1	–	–
Flax	1.4–1.5	5–900	12–600	343–2000	27.6–103	1.2–3.3	62–72	18.6–20.6	2–5	2.3	1.5–1.7
Hemp	1.4–1.5	5–55	25–500	270–900	23.5–90	1–3.5	68–74.4	15–22.4	3.7–10	0.9	0.8
Henequen	1.2	–	–	430–570	10.1–16.3	3.7–5.9	60–77.6	4–28	8–13.1	–	0.5
Isora	1.2–1.3	–	–	500–600	–	5–6	74	–	23	–	1.09
Jute	1.3–1.49	1.5–120	20–200	320–800	8–78	1–1.8	59–71.5	13.6–20.4	11.8–13	0.2–0.4	0.5
Kenaf	1.4	–	–	223–930	14.5–53	1.5–2.7	31–72	20.3–21.5	8–19	3–5	–
Nettle	–	–	–	650	38	1.7	86	10	–	–	4
Oil palm	–	0.89–0.99	19.1–25	–	–	–	65.0	–	19.0	–	–
EFB	–	–	–	–	–	–	–	–	–	–	–
Oil palm fronds	–	1.52–1.59	19.7	–	–	–	56.03	27.51	20.48	–	–
Olive husk	–	–	–	–	–	–	40.56	18.10	23.43	–	–
Piassava	1.4	–	–	134–143	1.07–4.59	7.8–21.9	28.6	25.8	45	–	–
PALF	0.8–1.6	900–1500	20–80	180–1627	1.44–82.5	1.6–14.5	70–83	–	5–12.7	–	–
Ramie	1.0–1.55	900–1200	20–80	400–1000	24.5–128	1.2–4.0	68.6–85	13–16.7	0.5–0.7	1.9	0.3
Rice husk	–	–	–	–	–	–	25–35	18–21	26–31	–	–
Rice straw	–	–	–	–	–	–	59.1	18.4	5.3	–	–
Sisal	1.33–1.5	900	8–200	363–700	9.0–38	2.0–7.0	60–78	10.0–14.2	8.0–14	10.0	2.0
Soy hulls	–	–	–	–	–	–	56.4	12.5	18.0	–	–
Wheat straw	–	–	–	–	–	–	43.2	34.1	22.0	–	–

Table 4 Continued

Fiber type	Density (g/cm ³)	Length (mm)	Diameter (μm)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongtn at break (%)	Cellulose (wt%)	Hemi-cellulose (wt%)	Lignin (wt %)	Pectin (wt%)	Waxes (wt%)
Eucalyptus wood	—	—	—	—	—	—	37.6	32.9	19.1	—	—
Hardwood	—	3.3	33	—	—	—	31–64	25–40	14–34	—	—
Softwood	—	1.0	20	—	—	—	30–60	20–30	21–37	—	—
Sugarcane bagasse	—	103–126	1200–2700	170–290	15–19	—	32%–50%	19%–25%	25%–32%	—	—
Wool	—	—	—	120–174	2.3–3.4	25–35	—	—	—	—	—
Spider silk	—	—	—	875–972	11–13	17–18	—	—	—	—	—
Bombyx silk	—	1.33	—	208.45	6.10	19.55	—	—	—	—	—

Note: Dittenber, D.B., GangaRao, H.V.S., 2012. Critical review of recent publications on use of natural composites in infrastructure. *Composites Part A: Applied Science and Manufacturing* 43 (8), 1419–1429. doi:10.1016/j.compositesa.2011.11.019. Li, X., Tabil, L. G., Panigrahi, S., 2007. Chemical treatments of natural fiber for use in natural fiber-reinforced composites: A review. *Journal of Polymers and the Environment* 15 (1), 25–33. doi:10.1007/s10924-006-0042-3. El-Tayeb, N.S.M., 2008. A study on the potential of sugarcane fibers/polyester composite for tribological applications. *Wear* 265 (1–2), 223–235. doi: 10.1016/j.wear.2007.10.006. Akil, H.M., Omar, M.F., Mazuki, A.A.M., et al., 2011. Kenaf fiber reinforced composites: A review. *Materials and Design* 32 (8–9), 4107–4121. doi:10.1016/j.matdes.2011.04.008. Majeed, K., Jawaid, M., Hassan, A., et al., 2013. Potential materials for food packaging from nanoclay/natural fibres filled hybrid composites. *Materials and Design* 46, 391–410. doi:10.1016/j.matdes.2012.10.044. Saba, N., Tahir, P., Jawaid, M., 2014. A review on potentiality of nano filler/natural fiber filled polymer hybrid composites. *Polymers* 6 (8), 2247–2273. doi:10.3390/polym6082247. Sanjay, M.R., Madhu, P., Jawaid, M., et al., 2018. Characterization and properties of natural fiber polymer composites: A comprehensive review. *Journal of Cleaner Production* 172, 566–581. doi:10.1016/j.jclepro.2017.10.101.

Table 5 Literatures on natural fiber reinforced biodegradable composites

References	Reinforcement	Matrix	Processing Method	Properties	Major findings
Wambua et al. (2003)	(a) Sisal: 40% (b) Kenaf: 30%, 40%, 50% (c) Hemp: 40% (d) Jute: 40% (e) Coir: 40%	Polypropylene	Compression molding using a film stacking method at 180°C for 2 min at 5 bar pressure	● Tensile strength ● Flexural strength ● Impact strength	● Coir composites showed the lowest mechanical properties and hemp composites showed the highest mechanical properties. ● Coir composites displayed higher impact strength than jute and kenaf composites.
Fung et al. (2003)	Sisal fiber yarns: 10%	Polypropylene	Injection molding with two temperature profile: Low temperature (LT): High temperature (HT)	● Thermal gravimetric analysis (TGA) ● Tensile strength	● Incorporation of 10 wt% of sisal fibers increases Young's modulus by about 150%, and the tensile strength of about 10%. ● The reinforcement efficiency for LT specimens is slightly higher than the HT samples.
Anuar and Zuraidda (2011)	Kenaf fiber: 20%	1. Thermoplastic natural rubber 2. Polypropylene/ethylene–propylene–diene–monomer	Double melt blending method using Haake internal mixer	● Tensile strength ● Flexural strength ● Impact strength	● Kenaf fiber has greatly enhanced the impact strength for both types of composite.
Harish et al. (2009)	Coir fiber	Epoxy – CY205	Hand lay-up technique	● Tensile strength ● Flexural strength ● Impact strength ● Fractography	● Coir/epoxy composites exhibit the tensile strength 17.86 MPa, flexural strength 31.08 MPa and impact strength of 11.49 kJ/m².
Kumar et al. (2011)	(a) Sansevieria cylindrica, (b) Waste silk, (c) Jute, (d) Drumstick	Polyester resin	Hand lay-up technique with compression molding	● Tensile strength ● Flexural strength ● Dielectric properties	● Tensile and flexural properties increase with fiber volume fraction. ● The dielectric strength of Sansevieria cylindrica fiber composites increase with an increase in volume fraction of fiber and which is not observed in many of the natural fiber composites.

(Continued)

Table 5 Continued

References	Reinforcement	Matrix	Processing Method	Properties	Major findings
Junior <i>et al.</i> (2010)	Coir fiber	Polyester resin	Hand lay-up technique (Molding and pouring)	● Tensile strength ● Fractography	● Continuous coir fibers incorporated into polyester matrix composites do not improve the tensile strength and the stiffness. ● The weak interface between the coir fiber and the polyester matrix, which allows cracks to be nucleated and propagate along the fibers/matrix interface.
Bakare <i>et al.</i> (2010)	Sisal fiber: 10%, 20%, 25% and 30%	Rubber seed oil-based polyurethane	Closed mold method	● Spectroscopy analysis ● Fourier Transform Infrared (FTIR) spectroscopy analysis ● Thermal Gravimetric Analysis (TGA) ● Water absorption behavior	● The strength of the composites increases with fiber loading. ● The tensile and flexural strength and a flexural modulus of the bio-composites vary between 57 and 119 MPa, 69–103 MPa and 2.28–3.25 GPa, respectively which are greater than un-reinforced rubber seed oil-based polyurethane. ● The loss in tensile strength is observed at 25% and 30% fiber loading after composite immersed in water for 30 days.
Ashok Kumar <i>et al.</i> (2010)	Sisal fiber and glass fiber hybrid	Epoxy resin	Hand lay-up followed by post-curing at 70°C for 1 h	● Hardness ● Impact strength ● Frictional coefficient ● Chemical resistance	● The fiber length of 2 cm hybrid composites exhibits better properties compared to 1 cm and 3 cm fiber length.
Ramesh <i>et al.</i> (2010)	Black Cotton soil with Coir fiber - 0.5%–3% (by weight of soil) with aspect ratio of 20, 40, 60, 80, 100 and 120 + Lime	–	Simple compacting process	● Compaction test ● Moisture absorption ● Compression strength	● Addition of randomly distributed coir fiber in black cotton soil increases strain and sample shows ductile properties. ● Addition of lime to black cotton soil increases the strength but samples show brittle properties.
Yuanjian and Isaac (2007)	Hemp fiber mat	Polyester resin	Hand lay-up method and curing with the application of low pressure (40 kPa) and high pressure (2 MPa)	● Tensile strength ● Low-velocity impact strength ● Fatigue test	● Composite of non-woven hemp fiber mat reinforced polyester cured at low pressure shown poor mechanical properties. ● In order to achieve better mechanical properties composites should be cured at high pressure to accommodate high fiber fraction.
Oksman <i>et al.</i> (2009)	(a) Sisal (b) Banana (c) Jute (d) Enzyme retted flax fibers (Fiber fraction: 20 wt%–45 wt%)	Polypropylene (PP)	Long fiberthermoplastics (LFT) processing method – LFT extrusion	● Flexural strength ● Izod and Charpy test ● Morphological study	● When adhesion between the reinforcement fibers and matrix is poor, the high fiber l/d ratio, high microfibrillar angle, high fiber properties, have limited impact on the mechanical performance of the composites.
Lee <i>et al.</i> (2009b)	(a) Kenaf (b) Jute (Fiber fraction: 10%, 20%, 30%, 40%, 50%, and 70 wt%)	Polypropylene (PP)	Carding process	● Tensile strength ● Flexural strength ● Fiber Volume Fraction, ● Void Content and Surface Morphology	● Kenaf fiber reinforced polypropylene composites have an optimum nominal fiber fraction of 30% ● Jute fiber reinforced composites have an optimum fiber fraction of 40% by weight at which the tensile and flexural modulus are the highest, while the reduction in strength is minimal.

Table 5 Continued

References	Reinforcement	Matrix	Processing Method	Properties	Major findings
Bledzki <i>et al.</i> (2007)	(a) Abaca fibers (b) Jute fibers (c) Flax fibers	Polypropylene (PP)	Mixer-injection molding	● Tensile strength ● Flexural strength ● Charpy test (Impact) ● Odour measurement ● Morphology	● Composite with 40% abaca fiber loading shown better mechanical properties. ● Abaca-PP composites shown better damping characteristics. ● Jute-PP and flax-PP composites discharged less odorous gas than abaca-PP composites.
Lee <i>et al.</i> (2009a)	Kenaf fiber: Weight fractions 10%, 30%, 50%, 70%	Poly lactic acid (PLA)	Carding process	● Flexural strength ● Dimensional stability and water absorption ● Dynamic mechanical analysis (DMA) ● Differential scanning calorimetry (DSC) ● Thermogravimetric analysis (TGA)	● Formulation of 50% kenaf and 50% PLA fibers represents an optimal formulation which may prove useful in a variety of applications. ● These materials can be successfully utilized to manufacture automotive headliners.
Angelov <i>et al.</i> (2007)	Flax fibers	Polypropylene (PP)	Pultrusion	● Flexural strength ● Impact strength	● The composites developed by pultrusion process exhibit satisfactory mechanical performance, similar to those of the composite manufactured by compression molding.
El-Tayeb (2008)	Sugarcane fibers	Unsaturated polyester	Hand-lay-up and open mold techniques	● Tribological properties	● Sugarcane fiber reinforced polyester ● SCRPP composite offers a good degree of wear resistance and friction coefficient comparable to glass fiber reinforced polyester GRP when sliding against stainless steel. ● Wear rate decreases with increasing the fiber length from 1 to 5 mm and then increased at 10 mm fiber length, indicating that there exists a critical fiber length (close to 5 mm) at which the wear rate was a minimum.
Chin and Yousif (2009)	Kenaf fibers	Epoxy resin	Direct mixing and pouring in a mold with application of Vacuum	● Pull-out test ● Tribological properties	● Fiber orientation had a pronounce influence on the frictional and wear performance of the composite.
Azwa and Yousif (2013)	Kenaf fibers	Epoxy resin	Direct mixing and pouring in a mold with application of Vacuum	● Thermogravimetric analysis	● Addition of fibers into the epoxy composites improves the thermal stability of the composites. ● Kenaf fiber/epoxy composites will suffer a great reduction of its mechanical properties at 150°C temperature.
Arib <i>et al.</i> (2006)	Pineapple leaf fiber	Polypropylene (PP)	Carver press a machine with a temperature and pressure control	● Tensile strength ● Flexural strength	● Tensile and flexural properties increased as the fiber volume fraction increased ● Flexural properties are lower compared to previous work may be due to lower values of flexural properties may be attributed to fiber to-fiber interaction, voids and dispersion problems.

(Continued)

Table 5 Continued

References	Reinforcement	Matrix	Processing Method	Properties	Major findings
Arrakhiz <i>et al.</i> (2012)	Coir fiber treated with Alkali, Ether, Silane	High-density polyethylene (HDPE)	Compounding and casting	● Chemical analysis ● Tensile properties ● Torsion properties	● Chemical treated coir fiber composites shown better mechanical properties compared to untreated.
Alavudeen <i>et al.</i> (2015)	Banana/kenaf fiber hybrid	Unsaturated polyester	Hand lay-up technique followed by post-cured in an oven at 50°C for an hour	● Tensile strength ● Flexural strength ● Impact strength ● Fractography	● Tensile, flexural and impact strengths of the woven hybrid composite of banana/kenaf fibers are superior to those of the individual fibers. ● Fractography studies indicate better fiber-matrix adhesion exists in the hybrid composite due to the interlocking of fibers.
Boopalan <i>et al.</i> (2013)	Jute and Banana fiber hybrid	Epoxy resin	Hand-lay-up technique followed by a light compression molding technique	● Tensile strength ● Flexural strength ● Impact strength ● Thermogravimetric analysis (TGA) and heat deflection temperature analysis (HDT).	● Mechanical properties such as tensile strength, flexural strength and impact strength are found to be maximum for 50/50 weight ratio of jute and banana fiber reinforced epoxy hybrid composites ● Moisture absorption study of hybrid composite shows the minimum moisture uptake is by 50:50 hybrid composites.
Codispoti <i>et al.</i> (2015)	(a) Jute fibers (b) Flax fibers (c) Sisal fibers (d) Hemp fibers	Epoxy resin, Polyester	Wet lay-up technique and vacuum infusion process	● Tensile properties	● Wet lay-up is, most probably, the easier and faster. ● Flax fibers are the most suitable natural fibers to manufacture composite materials for strengthening existing structures, both in terms of strength and stiffness.
Gunti <i>et al.</i> (2018)	(a) Jute fibers (b) Sisal fibers (c) Elephant gras	Poly lactic acid (PLA)	Vertical injection molding technique	● Tensile strength ● Flexural strength ● Impact strength ● Water absorption study ● Thermal degradation study	● Mechanical properties increased initially after 20% fiber loading properties decreased. ● Water absorption for all composites increased gently during the first 24 h and then leveled-off. ● Degradation was high at untreated fiber composites.
Anand <i>et al.</i> (2018)	(a) Jute fiber (b) Kenaf fiber (c) Jute/Kenaf hybrid	Epoxy resi	Hand-lay-up technique	● Tensile strength ● Compressive strength ● Flexural strength ● Impact strength ● Moisture absorption study ● Morphology study	● Mechanical properties of treated hybrid fiber reinforced epoxy composites show excellent figures than other conventional fiber reinforced polymeric materials. ● Rougher surface and increased effective surface area of the chemically treated fibers facilitated better interaction between the fiber and matrix.
Chaudhary <i>et al.</i> (2018a)	(a) Jute fiber (b) Hemp fiber (c) Flax fiber (d) Jute/Hemp/ Flax/ hybrid	Epoxy resin	Hand-lay-up technique	● Hardness ● Tensile strength ● Flexural strength ● Impact strength ● Morphology study	● Hybrid composites such as Jute/Hemp/ Flax/Epoxy shown better properties due to the combined properties of four materials and improved bonding.

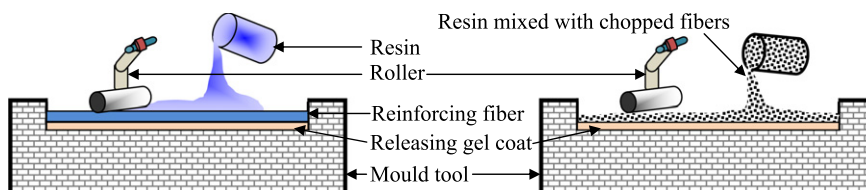


Fig. 5 Schematic diagram of Hand layup technique. Modified from http://www.composites.ugent.be/home_made_composites/organizing_your_composite_workshop.html. McIlhagger, A., Archer, E., McIlhagger, R., 2014. Manufacturing processes for composite materials and components for aerospace applications. *Polymer Composites in the Aerospace Industry*, 53–75. doi:10.1016/B978-0-85709-523-7.00003-7.

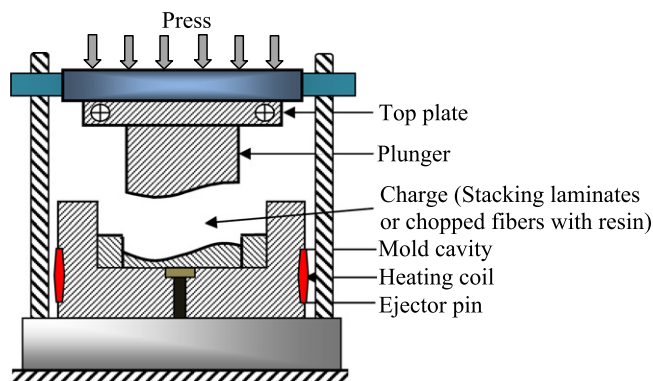


Fig. 6 Schematic diagram of compression molding technique. Modified from Wang, R.-M., Zheng, S.-R., Zhen, Y.-P., 2011. Forming technology of polymer matrix composites, *Polymer Matrix Composites and Technology*, Woodhead Publishing, 253–548. doi:10.1533/9780857092229.2.253.

With application of force and heating the charge it is allowed to cure for some time and after cooling using ejector pin final component is removed from the mold cavity. Extra material is trimmed from the final component to achieve the final shape. This method can be used to produce precision components with a large scale. When it is used to produce natural composite operating temperature should be maintained based on the decomposition temperature of fibers used to produce the components.

Vacuum Assisted Resin Transfer Molding Technique

It is low pressure and low-temperature technique in which liquid thermo-set resin is transferred inside the mold consists of fiber mats. **Fig. 7** shows the vacuum assisted resin transfer molding technique (Sanjay *et al.*, 2018). This method is gained popularity because of the capability of manufacturing a high-performance structure with a large scale. In this process, a vacuum bag is used to apply pressure on the mats and to distribute the resin uniformly.

Natural fiber mats are placed inside the mold and peel ply is placed on the stacked fiber mats. Two tubes are connected to the mold at the two ends to pump and to transfer the liquid resin inside the mold through the fibers using the pump. The extra resin is removed at the other end of the mold. The components are removed from the mold after it allowed for sufficient time for curing. In this process, the resin can be transferred directly from the top of the reinforced stacks or from the side based on the size and shape of the component.

Injection Molding Technique

Researchers and industries are successful in using injection molding (Fung *et al.*, 2003; Lee *et al.*, 2009a,b) technique shown in **Fig. 8** to manufacture the natural fiber composites. In this process raw materials are in the form of pellets, granules or powder is fed inside the barrel from the hopper. Further, it is conveyed along the barrel where it is heated with the application of heaters placed in the barrels and sheared with the application of movement of the screw. The pellets fed from hopper remains dry throughout the process and resin melts and mixes with the fiber pellets. The molten composite is further compacted and injected to the mold cavity through the nozzle with the application of the screw movement.

This process consists (a) feed zone (b) compacting zone and (c) metering zone. Electric motor with gear arrangements is used to drive the screw and based on the requirement single screw and multi screws are used to achieve the better compacting. After curing, the components are removed from the mold for further processing. The main advantage of this method is, near to net shape can be achieved with good surface finish and dimensional accuracy. Limitations are high capital investment and more time

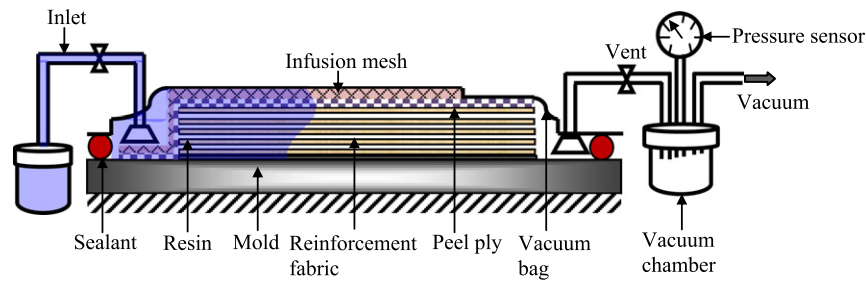


Fig. 7 Schematic diagram of Vacuum assisted resin transfer molding technique. Modified from Wang, R.-M., Zheng, S.-R., Zhen, Y.-P., 2011. Forming technology of polymer matrix composites, *Polymer Matrix Composites and Technology*, Woodhead Publishing, 253–548. doi:10.1533/9780857092229.2.253. McIlhagger, A., Archer, E., McIlhagger, R., 2014. Manufacturing processes for composite materials and components for aerospace applications. *Polymer Composites in the Aerospace Industry*, 53–75. doi:10.1016/B978-0-85709-523-7.00003-7.

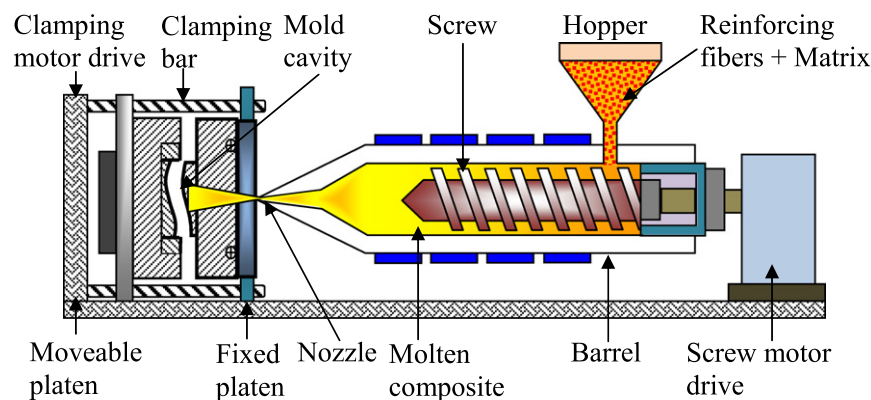


Fig. 8 Schematic diagram of injection molding technique. Modified from <http://www.daviesmolding.com/Pages/Resources/Engineering-Specifications/Plastic-Molding/Injection-Compression-Molding.aspx>. <https://www.custompartnet.com/wu/InjectionMolding>. Sarasini, F., Puglia, D., Kenny, J.M., Santulli, C., 2019. Injection moulding of plant fibre composites. In: Bafekrpour, E. (Ed.) *Advanced Composite Materials: Properties and Applications*. Berlin, Boston: De Gruyter. Liu, S.-J., 2012. Injection molding in polymer matrix composites. *Manufacturing Techniques for Polymer Matrix Composites (PMCs)*, Woodhead publishing series in composites science and engineering, Woodhead Publishing, 15–46. doi:10.1533/9780857096258.1.13.

is required to design and develop the molds. The major challenge in this process is: maintaining the barrel temperature which is equivalent to the decomposition temperature of the natural fibers.

Pultrusion Technique

The pultrusion technique (Angelov *et al.*, 2007; Sanjay *et al.*, 2018) is a method reported in the literature, which is feasible to use for manufacturing the natural fiber composites as shown in Fig. 9. It is a continuous manufacturing process used to manufacture a fixed type of profiles based on the required shape of the composite with any length. In this process a continuous fiber from the roving is pulled and processed through the resin bath where the melted resin is infused with the fibers and shaped to the required profile. Further, it is cooled to the normal temperature at the cooling chamber and cut using cut off saw to the required length. This process is also used to manufacture the pellets which are used in the injection molding process. A major challenge associated with this process is controlling the viscosity of the resin bath which helps in wetting of fibers easily and also controlling the temperature to prevent the fibers from thermal degradation.

ASTM Standards for Testing

Literature shows there have been numerous characterization techniques are used to evaluate the properties such as tensile, compression, flexural, shear, fracture toughness, fatigue, impact, physical and chemical properties of the natural fiber reinforced polymer and laminated composites. The varying degrees of standardization methods are used in industries as well as by

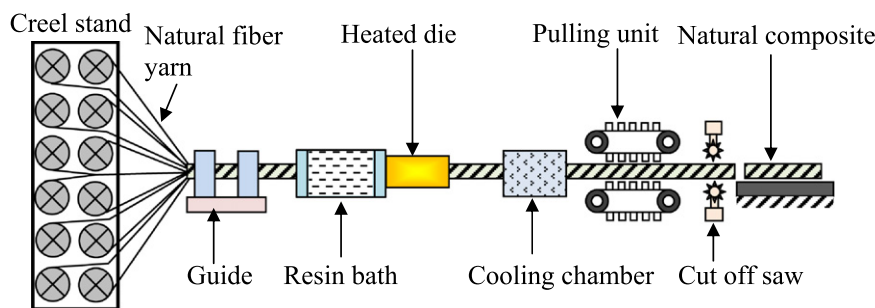


Fig. 9 Schematic diagram of pultrusion technique. Modified from McIlhagger, A., Archer, E., McIlhagger, R., 2014. Manufacturing processes for composite materials and components for aerospace applications. *Polymer Composites in the Aerospace Industry*, 53–75. doi:10.1016/B978-0-85709-523-7.00003-7. Wang, R.-M., Zheng, S.-R., Zhen, Y.-P., 2011. Forming technology of polymer matrix composites, *Polymer Matrix Composites and Technology*, Woodhead Publishing, 253–548. doi:10.1533/9780857092229.2.253.

Table 6 Standard test methods for testing composite materials

Designation	Description
ASTM C393/C393M	Test method for shear properties of sandwich constructions by beam flexure
ASTM D256	Test methods for determining the Izod impact resistance of plastics
ASTM D638	Test method for tensile properties of plastics
ASTM D695	Test method for compressive properties of rigid plastics
ASTM D790	Test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials
ASTM D2344/D2344M	Test method for short-beam strength of polymer matrix composite materials and their laminates
ASTM D3039/D3039M	Test method for tensile properties of polymer matrix composite materials
ASTM D3410/D3410M	Test method for compressive properties of polymer matrix composite materials with unsupported gage section by shear loading
ASTM D3479/D3479M	Test method for tension-tension fatigue of polymer matrix composite materials
ASTM D3518/D3518M	Test method for in-plane shear response of polymer matrix composite materials by tensile test of a $\pm 45^\circ$ laminate
ASTM D3846	Test method for in-plane shear strength of reinforced plastics
ASTM D4255/D4255M	Test method for in-plane shear properties of polymer matrix composite materials by the rail shear method
ASTM D5379/D5379M	Test method for shear properties of composite materials by the v-notched beam method
ASTM D5467/D5467M	Test method for compressive properties of unidirectional polymer matrix composite materials using a sandwich beam
ASTM D5528	Test method for mode I interlaminar fracture toughness of unidirectional fiber-reinforced polymer matrix composites
ASTM D6415/D6415M	Test method for measuring the curved beam strength of a fiber-reinforced polymer-matrix composite
ASTM D7264/D7264M	Test method for flexural properties of polymer matrix composite materials
ISO 527	Plastics – determination of tensile properties

Note: ASTM D4762-18, 2018. Standard Guide for Testing Polymer Matrix Composite Materials. West Conshohocken, PA: ASTM International, www.astm.org. Fung, K.L., Xinga, X.S., Li, R.K.Y., Tjong, S.C., Mai, Y.-W., 2003. An investigation on the processing of sisal fibre reinforced polypropylene composites. *Composites Science and Technology* 63 (9), 1255–1258. doi:10.1016/S0266-3538(03)00095-2. Wambua, P., Ivens, J., Verpoest, I., 2003. Natural fibres: can they replace glass in fibre reinforced plastics *Composites Science and Technology* 63 (9), 1259–1264. doi:10.1016/S0266-3538(03)00096-4. Anuar, H., Zuraida, A., 2011. Improvement in mechanical properties of reinforced thermoplastic elastomer composite with kenaf bast fibre. *Composites Part B: Engineering* 42 (3), 462–465. doi:10.1016/j.compositesb.2010.12.013.

researchers based on the requirements. Some of the standards used to evaluate the basic properties of the composites are listed in Table 6 and most of the standards are selected from American Society for Testing and Materials (ASTM).

Applications

Natural fiber reinforced composites currently occupied many sectors due to its superior qualities such as low density, biodegradable and recyclable, acceptable specific strength, ease of availability, reduced tool wear during the molding process, better acoustic properties, low cost and easy of processing. Fig. 10 shows the history of the application of composites includes various materials used with the time frame. The use of natural composites started 3000 years ago where clay and mud reinforced by straw fibers to build the walls in the construction of huts. The first successful use of natural fiber composites was attempted in 1939 where flax is mixed with a phenolic matrix to manufacture fuselage skins. Hemp is used to manufacturing a prototype composite car by Henry Ford in 1942. Presently it is occupied many sectors by replacing synthetic fiber composites mainly to reduce the cost and to overcome disposal problem associated with other materials (Sanjay *et al.*, 2018).

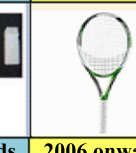
Applications	Clay/mud reinforced composites	Fuselage skins of spitfires	Prototype composite car by Henry Ford	Body of trabant car in Germany	Number of automotive applications	E&E: Cases of cellular phones	Sporting goods	Roof top wind turbine blades
Materials								
Time Frame	In Egypt clay/mud reinforced by straw to build walls	Shortage of aluminium in England, led to use natural fiber		First production car built from natural fiber composites				
	3000 year ago	1939	1942	1950-1990	2000 onwards	2004 onwards	2006 onwards	2014

Fig. 10 History of the application of composites includes various materials used with time frame. Modified from <https://www.yumpu.com/en/document/read/30864428/opportunities-in-natural-fiber-composites-lucintel>.

Automotive and construction industries are using natural fiber composites in large scale (Mohanty *et al.*, 2005). This section highlights some of the important applications of the natural fiber composites in

- (a) Automotive industry
- (b) Construction industry
- (c) Sports industry
- (d) Miscellaneous Products

Automotive Industry

Ever since the major transition took place in the development of new lightweight and economical biodegradable composite materials automotive sectors are the major consumers. Natural fiber reinforced composites are commonly used in door panels, seat back, interior decoration, body panel etc. (Fung *et al.*, 2003; Mohanty *et al.*, 2005; Cheung *et al.*, 2009; Sanjay *et al.*, 2018; Zaidi *et al.*, 2018). Table 7 shows some of the natural fiber composites used in automotive industries.

Construction Industry

The construction industry constitutes the second largest sector to employ natural materials in a wide range of products. Wood flour, flax, rice husk and bagasse fibers are extensively used in light structural walls, insulation materials, floor and wall coverings, window frames, geotextiles and thatch roofing. The key drives for using natural fibers in construction industry are low life-cycle cost, low and easy maintenance, eco-friendly, easily available and friendly government regulations (Mohanty *et al.*, 2005). Natural fibers are also used as reinforcements with cement for building materials.

Sports Industry

Sports industries also major consumers of natural fibers. Some of the recent developments in manufacturing sports equipment using natural fiber composites are: flax fibers are used to manufacture tennis racket, bicycle frames, fork and seat post in medium size due to its superior anti-vibration characteristics. Hemp fibers are also used in the manufacturing of snowboarding. Carrot fibers are used to manufacture fishing rods (Suddell, 2008).

Miscellaneous Products

Manufacturing industries applications such as grinding wheel discs with 1 million units being produced each year under the trade name Plantex, in this instance hemp and polypropylene (PP) are being used to create the backing plates for these industrial products. Cosmetic packaging is an area also seeing the adoption of natural fibers. In the USA, a lipstick casing made from Flax fibers and PP which has been on sale for 4 years selling 4 million units per year. Funeral Urns made from natural fibers and PLA which after a limited time will naturally decompose leaving no physical residue behind. Key events such as the 2008 Olympics

Table 7 Natural fiber composites applications in the automotive industry

<i>Manufacturer</i>	<i>Model</i>	<i>Application</i>
Audi	A2, A3, A4, A4 Avant, A6, A8, Roadstar, Coupe	Boot-liner, spare tire-lining, side and back door panel, seat back, and hat rack
BMW	3, 5 and 7 series and other Pilot	Seat back, headliner panel, boot-lining, door panels, noise insulation panels, and molded foot well linings
Citroen	C5	Interior door paneling
Daimler Chrysler	A, C, E, and S class, EvoBus (exterior)	Pillar cover panel, door panels, car windshield/car dashboard, and business table
Fiat	Punto, Brava, Marea, Alfa Romeo 146, 156, 159	Door panel
Ford	Mondeo CD 162, Focus	Floor trays, door inserts, door panels, B-pillar, and boot-liner
General Motors	Cadillac De Ville, Chevrolet Trail Blazer	Seat backs, cargo area floor mat
Honda	Pilot	Cargo area
Lotus	Eco Elise (July 2008)	Body panels, spoiler, seats, and interior carpets
Mercedes Benz	C, S, E, and A classes	Door panels (flax/sisal/wood fibers with epoxy resin/UP matrix), glove box (cotton fibers/wood molded, flax/sisal), instrument panel support, insulation (cotton fiber), molding rod/apertures, seat backrest panel (cotton fiber), trunk panel (cotton with PP/PET fibers), and seat surface/backrest (coconut fiber/natural rubber)
	Trucks	Internal engine cover, engine insulation, sun visor, interior insulation, bumper, wheel box, and roof cover
Mitsubishi		Cargo area floor, door panels, and instrumental panel
Opel	Vectra, Astra, Zafira	Door panels, pillar cover panel, head-liner panel, and instrumental panel
Peugeot	406	Front and rear door panels, seat backs, and parcel shelf
Renault	Clio, Twingo	Rear parcel shelf
Rover	2000 and others	Rear storage shelf/panel, and insulations
Saab	9S	Door panels
Seat	—	Door panels, Seat backs
Saturn	L300	Package trays and door panel
Toyota	ES3	Pillar garnish and other interior parts
Toyota	Raum, Brevis, Harrier, Celsior,	Floor mats, spare tire cover, door panels, and seat backs
VAUXHALL	Corsa, Astra, Vectra, Zafira	Headliner panel, interior door panels, pillar cover panel, and instrument panel
Volkswagen	Passat Variant, Golf, A4, Bora	Seat back, door panel, boot-lid finish panel, and boot-liner
Volvo	V70, C70	Seat padding, natural foams, and cargo floor tray

Note: Mohammed, L., Ansari, M.N.M., Pua, G., Jawaid, M., Islam, M.S., 2015. A review on natural fiber reinforced polymer composite and its applications. *International Journal of Polymer Science*, 1–15. doi:10.1155/2015/243947. Suddell, B.C., 2008. Industrial fibres: Recent and current developments. In: *Proceedings of the Symposium on Natural Fibres*, Rosemaund, 56, pp. 71–83. Faruk, O., Bledzki, A.K., Fink, H., Sain, M., 2014. Progress report on natural fiber reinforced composites. *Macromolecular Materials and Engineering* 299 (1), 9–26. doi:10.1002/mame.201300008.

hosted by China and held in Beijing (predominantly) presented an ideal opportunity to utilize natural materials on a global stage. This event alone used 80,000 tonnes of natural fibers, mainly in the construction of buildings (Suddell, 2008).

Advantages and Limitations

Some of the advantages of natural fiber composites are (Anandjiwala and Blouw, 2007; Pandey *et al.*, 2015):

- Low specific weight, which results in higher specific strength and stiffness than glass. This is a benefit especially in parts designed for bending stiffness.
- It is a renewable resource and the production requires little energy.
- Producibile with low investment at a low cost, which makes the material an interesting product for low-wage countries.
- Friendly processing, no wear of tooling, no skin irritation.
- Thermal recycling is possible, where glass causes problems in combustion furnaces.
- Good acoustic insulating properties.

Some of the limitations of natural fibers are (Anandjiwala and Blouw, 2007; Pandey *et al.*, 2015):

- Lower impact strength.
- No control over property, depending on unpredictable influences such as weather.
- Moisture absorption, which causes swelling of the fibers.
- Restricted maximum processing temperature.

- Lower durability, fiber treatments can improve this considerably.
- Lower thermal resistance.
- Price can fluctuate based on harvest results or agricultural politics.

Research Challenges

In spite of the wide range of applications of natural fiber reinforced composites in automotive, constructions, sports and some of the miscellaneous products these composites still exhibits significant challenges in full-scale utilization and their advancement. Some of the major challenges are low mechanical properties, poor moisture resistance, low fire resistance, variability in the quality of the fibers and difficulties in manufacturing. Another major issue associated with the development of natural fiber reinforced composites is adhesion between fiber and matrix which has a great impact on delamination. The manufacturer should have a good knowledge of properties of fiber such as wetting, adhesion properties and weight fraction of fiber-matrix materials to avoid delamination issues. Machining of these composites also challenging because fiber pullouts and delaminations are the common problems observed by researchers during the machining. These materials also pose challenges to material scientists particularly with the acceptance criteria for being their performance and cost, despite the renewability and recyclability of the matrix and the reinforcements used (Satyanarayana *et al.*, 2009).

Conclusions

Natural fiber reinforced composites offers several advantages such as biodegradability, eco-friendly, abundant, renewable, low-density and many more. These are potential materials to replace the synthetic fiber reinforced composites. This article presents major findings reported in the literature on the study conducted on a different aspect of natural fiber reinforced composites. Standards used for testing materials, manufacturing techniques available and potential use of natural fiber reinforced composites in a different field are described in this article. Some of the major conclusions drawn from this study are:

- Natural fiber reinforced composites are the best solution to meet the growing interest in reducing the environmental impact of synthetic fiber reinforced composites.
- Natural fibers are classified based on the source from where fibers are extracted and grouped under plant fibers, animal fiber and mineral fibers.
- Some of the commonly used manufacturing techniques of natural fiber reinforced composites are hand layup technique, a compression molding technique, vacuum-assisted resin transfer molding technique, injection molding technique and pultrusion technique.
- Major factors to be considered during the manufacturing of natural fiber reinforced composites are fiber/matrix selection, composition, fiber size, shape, fiber treatments and post-curing.
- Hybridization of multiple natural fibers reinforced with matrix has been recognized as the best possible solution to meet the different category of the customers.

See also: Biodegradable Packaging. Biodegradable Packaging Materials. Kenaf Fiber Reinforced Composite in the Automotive Industry. Natural Fiber and Synthetic Fiber Composites: Comparison of Properties, Performance, Cost and Environmental Benefits. Natural Fiber Composites: Review of Recent Automotive Trends

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Polymer Blends and Composites From Renewable Resources

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Introduction

Research about renewable polymers have been carried out for centuries. However, the interest of utilizing this material through various types of blend and composites had become increasingly thriving since the limitation of crude oil and more concern about the greener material that is environmentally friendly. With more technology in microstructure elucidation, it is possible to apprehend more knowledge regarding the relationship of properties and structure. Nevertheless, more efforts are needed to achieve better properties of the renewable polymer blend and composites, and at the same time troubleshooting the shortcomings of this new material. In order to do that, basic understanding was needed with regard to the types of renewable materials, the structures, the properties and the potential application. There are three types of renewable polymers that have been used as the matrix, which are natural polymers, synthetic polymer (natural monomers) and fermentation of microbial's polymers (Yu *et al.*, 2006). Hence, the manufacturing route for bio polymer also follows these three categories. The bio-based polymer manufacturing route is displayed as Fig. 1 (Okan *et al.*, 2019). In this article, more explanation shall be made based on these three categories of renewable polymer matrix.

Blends and composites obtained from renewable resources usually quoted as green composites. Typically green composites were friendly to the environment and becoming an alternative to polymers made from petroleum and traditional composites. To reduce the fossil oil depletion, renewable resources like vegetable oils, carbohydrates and proteins have been utilized as biopolymer matrices. Hence, this biocomposites have increased the possibility for sustainable and 'biodegradable', and meet the criteria of 'green materials' (Jadhav *et al.*, 2019). Currently, green material, environmentally friendly material, sustainable material and eco-efficiency, are some of the terms that directing the advancement of the succeeding group of new materials, products, and processes. Materials made from renewable resources (agricultural/biomass) such as biocompatible/biodegradable polymers could dominate the future by replacing the petroleum feedstock. Besides utilizing renewable resources as the matrix, it can be also exploited as the fiber reinforcement to strengthen the matrix. For instance, natural/bio fiber reinforcement is developing as a feasible alternative to reinforcement made from glass fiber. It can be applied in automotive industries, domestic utilities and several building structures. Such natural/biofibers line bamboo, sisal, banana/pineapple leaves, kenaf, hemp, flax and jute, with various types of matrix made from polymer matrices, either renewable or not, have been studied extensively by many researchers (Mohanty *et al.*, 2002).

Bio-based polymers not only replace existing polymers in a number of applications, nonetheless also provide new combinations of properties for new applications. For bio-based polymers like PLA and PHA, additives are being developed to improve their performance, by blending with other polymers or making new copolymers (Shivam, 2016). Many researchers are attempting to create different products by utilizing natural fibers as reinforcing agents. Hence, it is important to draw out the issues related to

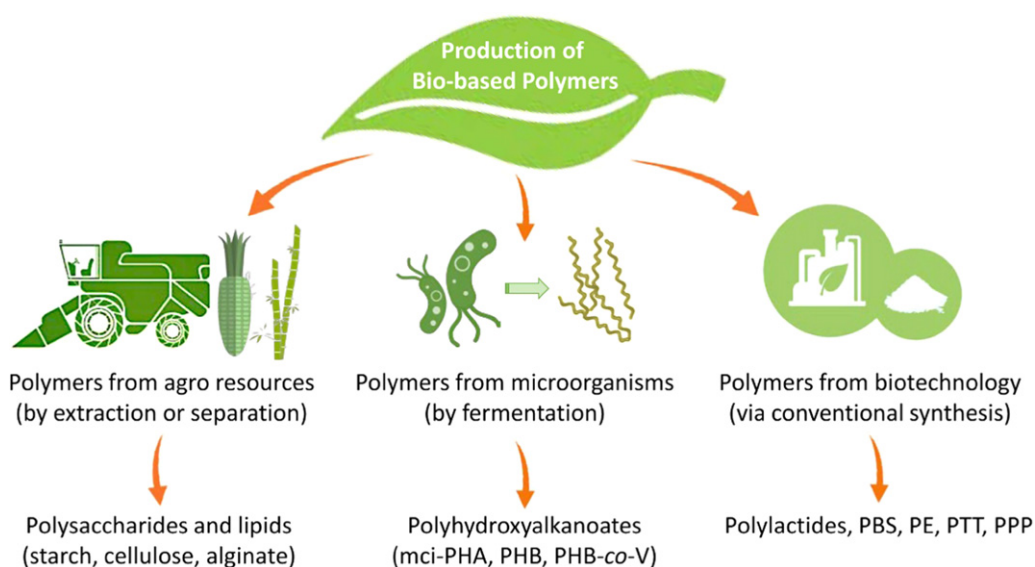


Fig. 1 Bio-based polymer manufacturing route. Credit to: Okan, M., Aydin, H.M., Barsbay, M., 2019. Current approaches to waste polymer utilization and minimization: A review. *Journal of Chemical Technology & Biotechnology* 94 (1), 8–21.

the processing of natural fibers and their green composite has been tended to. The types of fibers utilized as a part of composites, surface modifications and processing techniques of these green composites were some of the important issues that need to be studied among researchers. Based on previous findings, it is presumed that the natural fibers are the potential replacement option for unadulterated manufactured fibers and the utilizations of these fiber composites will increase in the future (Ramesh and Deepa, 2019). Henceforth, the compilation of previous research related to this topic will be the essence of this article for future reference and guidelines.

Natural Polymer

The first type of renewable polymer which is going to be discussed is natural polymer. This material, mostly are hydrophilic, due to the existence of either hydroxyl or polar groups. Differently, most of synthetic polymer is sensitive to moisture (hydrophobic). Therefore, combining these two materials will be fascinating, whereby a wide range of biodegradable material could be obtained, since modern technology could utilize the knowledge of compatibilizer usage and reactive extrusion could improve the adhesion of this combination (Yu *et al.*, 2006).

There are many extensive kinds of renewable resources' derived of polymer that could be used in many different ways. The usage of some of these materials are not being optimized. It can be grouped into several classes according to their chemical properties or physical structure. Fig. 2 shows the classification of natural polymers (Kaplan, 1998; Gross and Scholz, 2001).

Based on the natural polymer native setting, it can develop certain functions that can be utilized for engineering applications. Generally, natural polymer was used as adhesives, coatings, gels, foams and films. To quote one example, the protein could become a catalyst and a structural material. Polysaccharides can be functional as wastewater adsorbents, energy utilization and drug loaded particles. As for lipid, it can be used as energy stores, structure of cell membranes, signaling and cosmetics. Another example is starch that had been applied in corrugated board adhesives, papermaking and textiles. However, there are certain drawbacks of this material. The disadvantages of this material typically related to their dominant hydrophilic character, such as rapid degradation rate with weaker mechanical properties at watery condition (Kaplan, 1998).

To overcome this problem, the idea of blending the natural polymer with synthetic polymer had come across the researchers. The technology of blending and extrusion could assist this process, whereby most of the aim is to combine two or more materials with cautions not to alter the properties radically, nonetheless obtaining several better properties and provide the solution of the drawbacks (Kaplan, 1998). However the job is not that easy. Failures could happen when the outcomes were not satisfying. For instance, back in the 1970s and 1980s, several types of polyolefin have been blended with starch to evaluate their performances. Unfortunately, the produced blend was not environmentally friendly since it cannot be decomposed through natural resources. Hence it could contaminate the land by polluting the earth. Herein, the gain of using natural polymer was absent (Yu *et al.*, 2006). However, there are more successful findings about the blend of natural polymers. Several examples like chitosan, elastin, natural fibroin, silk, chitin and keratin have been deliberate as a component of blends and composite from renewable resources. Table 1 shows the blending of natural polymers with their applications or advantages (Sionkowska, 2011).

The potential application that could be obtained from the blend of natural polymer and synthetic polymer was heavily depended on the processing factors. For instance, the age of the tissue will influence the solubility of collagen (Miyahara *et al.*, 1982). As for collagen, it could be blended with synthetic polymer in a solvent. It could be applied in biomedical field as films and sponges. A good quality of hydrogels also could be produced by blending the collagen with other hydrophilic polymers (Wang *et al.*, 2011). A research about the blend of collagen–chitosan hydrogel for endothelial differentiation and angiogenesis had

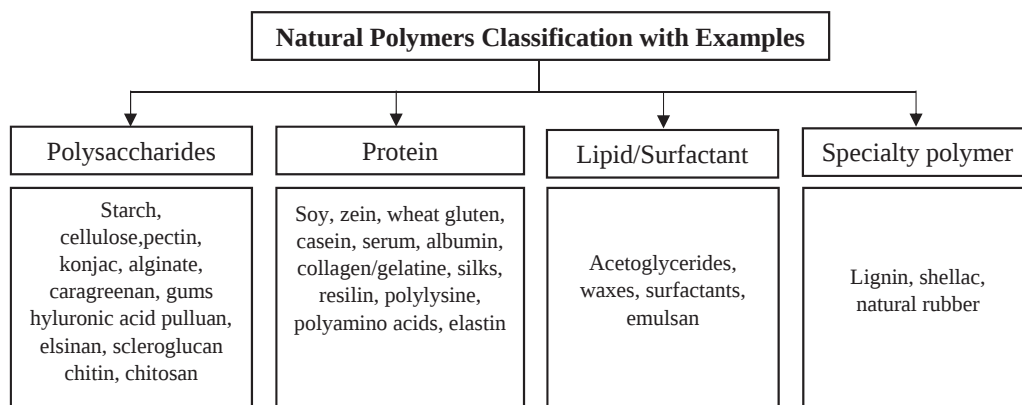


Fig. 2 Classification of natural polymers. Credit to: Kaplan, D.L., 1998. Biopolymers From Renewable Resources: Macromolecular Systems-materials Approach. Springer-Verlag Berlin Heidelberg. Gross, R.A., Scholz, C., 2001. Biopolymers From Polysaccharides and Agropoteins. American Chemical Society.

Table 1 Blends of natural polymers and their applications/advantages

Blends	Application/Advantages
Chitosan/poly (vinyl alcohol)/poly (ethylene oxide) and poly (vinyl pyrrolidone)	Oral gingival delivery systems
Chitosan/poly(vinyl alcohol)	Superior in other properties compared to chitosan, Used in drug delivery systems
Chitosan/poly (vinyl pyrrolidone)	Sterilization, drug release system and release profile of a drug
Elastin hydrolysates and collagen	Increase of biocompatibility, elasticity, less sensitive to ultraviolet irradiation
Natural fibroin/synthetic polymers	Scaffolding, cost reduction, mimicking the structure and/or function of the native extracellular matrix, biosensors
Silk fibroin/Nylon-6	Thermal stability
Silk fibroin/wool keratose	Nanofiber preparation, heavy metal ion adsorbent
Silk/polyurethane	Elastic biofibers, smooth surface, dense structure, and considerably higher strength
Chitin/silk fibroin	Biomimetic nanostructured scaffolds
Chitosan/silk fibroin/methoxy poly(ethylene glycol)- <i>b</i> -poly(DL-lactide)	Film strength increment and a decrease in film flexibility and wettability
Keratin/chitosan	Adjustment of mechanical properties. Strong, flexible film. Supported fibroblast attachment and proliferation

Note: Sionkowska, A., 2011. Current research on the blends of natural and synthetic polymers as new biomaterials. *Progress in Polymer Science* 36 (9), 1254–1276.

proven it can be used as biodegradable polymeric scaffolds (Deng *et al.*, 2010). Furthermore, the findings of electro spun collagen–chitosan– thermoplastic polyurethane nano fibrous scaffolds could be widely used in medical applications (Huang *et al.*, 2011).

The most important notes that need to be monitored closely was the solubility of the polymeric components in a common solvent. One of the common solvent that had been used was water, because most of the natural polymer could be solvable in water. Not only act as a solvent, the water could also become a dispersion medium and plasticizer if the preparation of numerous natural polymer blends and composites (Matveev *et al.*, 2000). For example, proteins and polysaccharides structure–property relationships was developed based on their interaction with water and with each other in a water medium. In order to illustrate the role of water in these materials, researchers should carry out certain analysis of the glass transition temperature and thermal profile (Yu *et al.*, 2006).

To quote one example, in term of the application of natural polymers blends and composite, some researchers have established the findings in utilizing this material for drug delivery devices. The drug delivery process has been embedded in the research about experimental design optimization and biodegradation behavior of poly (vinyl alcohol)-collagen hydrolysates (Alexy *et al.*, 2003) and microcapsules formed by polyelectrolyte copolymer and modified collagen have been successfully performed (Quek *et al.*, 2004). These drugs were released by diffusion through the polymer barrier, by erosion of the polymer material, or as a result of the combination of both. According to the results, the delivery system design obtained from the exploitation of this renewable polymers was flexible enough as compared with the non-biodegradable polymeric matrices. In this system, which have been predetermined rate and duration, it was found that the bioactive substances were released as they degrade to the desired area with an effective dose (Sionkowska, 2011).

Synthetic Polymers

Monomers from natural resources could be used to produce synthetic polymers. This progress had provided potential upgrades to produce polymers from renewable resources. One of the famous examples of this material was poly (lactic acid). Another name of this material is polylactide. This thermoplastic aliphatic polyester is biodegradable and bioactive. Poly(lactic acid) is made from renewable resources, which is agricultural products such as sugarcane, chips, cassava roots, and corn starch. Through the fermentation of these agricultural resources, the controlled depolymerization of lactic acid could produce the lactide in a cyclic dimer. This technology was not new, but the blends of this material with other material have lots of potential. Not only it can be used as biodegradable material, poly (lactic acid) also has very low or no toxicity and high mechanical performance, as compare with other domestic polymers (Yu *et al.*, 2006).

Conversely, the disadvantage of this material is the thermal stability. It is generally not sufficiently high enough for poly (lactic acid) to substitute certain commercial polymer applications. Hence, more investigations have been executed towards many types of poly (lactic acid) blends and composites, in order to overcome the thermal stability (Yu *et al.*, 2006). For instance, a review had been made about several researches towards the stereocomplex formation, which was made from enantiomeric poly (lactic acid)-PLA, poly (L-lactic acid)-PLLA and poly (D-lactide)-PDLA. The blend of these materials was proposed because of the strong interaction between PLLA and PDLA chains. It was found that the PLLA/PDLA blend has a higher hydrolysis resistance, as compared with pure PLLA and PDLA, even when it was amorphously made. The X-ray diffractometry and differential scanning calorimetry results also elucidated that all initially amorphous poly (lactic acid) films remained amorphous, even after autocatalytic hydrolysis for 16 months for PDLA film and 24 months for PLLA/PDLA non-blended films

and PLLA/PDLA (1/1) blended film. Correspondingly, after the hydrolysis process was completed in 24 months, the detected melting peaks were attributed to those of homo and stereocomplex crystallites. However, this condition was not happening through the autocatalytic hydrolysis. Therefore, based on the results, the enhancement of thermal stability for PLLA/PDLA blend could be achieved through melt enantiomeric polymer blending, and this condition is better than pristine PLLA and PDLA. Further research also have been carried out toward film of PLLA and PDLA and their equimolar enantiomeric blend (PLLA/PDLA). The analysis of the effects of enantiomeric polymer blending (isothermally and non-isothermally under nitrogen gas) towards the thermal stability and degradation of the prepared films. The investigation was carried out by using thermogravimetric, and the results show that the blend had augmented the thermal stability of the PLLA/PDLA films (Yu *et al.*, 2006).

It is important to control the PLA hydrolytic degradability. Hence, more researches have been conducted to clarify the effects of various components in the PLA blend systems. For instance, a research had been performed to accelerate the degradation of PLA by using poly (aspartic acid-*co*-lactide) or PAL. According to the findings, as the amphiphilic copolymer, which was attained from aspartic acid and lactide, PAL had provided several benefits through the blend with PLA, which are (Shinoda *et al.*, 2003):

- (1) PAL could form a homogeneous mixture when added together with PLA.
- (2) The films made from PAL/PLA is homogeneous without weakening the characteristic of PLA.
- (3) The PLA transparency shall be remained.
- (4) The blend can performed as antistatic agents by adding with poly (sodium aspartate-colactide).
- (5) The degradation rate of PLA in water, soil and compost can be boosted.
- (6) Hydrolysis resistant.
- (7) Long shelf life.
- (8) As for the usage of polybutylene succinate and polycaprolactone, it could raise the rate of the non-enzymatic as the additive component.
- (9) Enhanced the PLA's thermal stability.

Besides that, this research also clarified the usage of poly DL-lactic acid (PDLLA) could accelerate the degradation of the blend, because of its amorphous structure. Consequently, it is possible to control the degradation time of PLLA/PDLLA blends, by applying different blending ratios of PLLA and PDLLA (Shinoda *et al.*, 2003).

The extension of this research have been made to find out more details about the preparation and characterization of biodegradable PLA polymeric blends. For instance, a group of researchers has prepared several blends of biodegradable PLLA and PDLLA. These blends were made by dipping the blend into dichloromethane solution with different ratios. The additional component was added to these blends, which are copolymer of ethylene oxide and propylene oxide as the surfactant. Based on the findings, the differential scanning calorimetry (DSC) shows that PLLA/PDLLA blends had two T_g values for the blend without the surfactant, but when the surfactant was added, a linear shift of the single T_g as a function of composition was appeared. It was noted also that the blend with lower percentages of PLLA had creating lower glass transition temperatures. This shows that better miscibility had been attained. As for the second analysis, the dynamical mechanical analysis (DMA) findings showed a high elastic modulus and elongation for 40/60 PLLA/PDLLA blends without the surfactant, and by adding 2% surfactant. As for another formulation with 50/50 PLLA/PDLLA, the addition of 2% surfactant into the blend had resulting the highest elastic modulus, yield strength and break strength. At the end of the research, the addition of PDLLA and surfactant towards PLLA via solution blending could bring much benefit in term of toughness and biocompatible for medical use, such as in dental and orthopedic (Chen *et al.*, 2003). Similar outcome also have been achieved, in term of the crystallinity, the glass transition behavior, the tensile modulus and the biodegradability of the blends of polylactides with high and low L-isomeric ratios of the lactate units (Urayama *et al.*, 2002).

Polymers From Microbial Fermentation

As for the third group of renewable polymer, this material was prepared through the fermentation of microbial. For instance, poly (hydroxyalkanoate)s or normally known as PHA, had been preferred to be scrutinized among new material researchers. PHA was made from a variety of micro-organisms that are molded as naturally occurring storage polyesters. The key criteria for this material to be included in the renewable polymer was the truly biodegradable and highly biocompatible properties which were obtained from the bacterially synthesized PHA. According to a review that had been made, it can say that over 90 different types of PHA blend consisting of numerous types of monomers have been attested and the affection towards this material had been snowballing.

Several bacterial species like Actinobacillus, Azotobacter, Agrobacterium, Rhodobacter and Sphaerotilus have been under focus for their ability of converting organic waste to bacterial PHA. For industrial production of biocompatible poly (3-hydroxybutyrate) (PHB), some bacterial species like Bacillus spp., Pseudomonas spp., Aeromonas spp., Cupriavidus spp. have been extensively used for their potential to produce PHB. Since the production of bio-plastic is expensive many techniques have been adopted for large scale production. But, to obtain PHB in large amount the selection of proper strains of bacteria, capable of producing or accumulating PHB is necessary (Shivam, 2016). For examples, several types of copolymer could be obtained through biosynthesis and characterization of hydroxybutyrate(HB) with 3-hydroxyvalerate(3HV), 3-hydroxypropionate (3HP), 3-hydroxyhexanoate (3HH) and 4-hydroxybutyrate (4HB) (Yu *et al.*, 2006).

The PHB and its copolymers with 3-hydroxyvalerate (PHBV) were also have been documented specimens of PHA group, whereby these materials have promoted several gains in term of biodegradability and biocompatibility over other thermoplastics with valuable mechanical properties as well. Unfortunately, the factor of cost and performances need to be monitored closely through exploring the suitable polymer to be blended with. For instance, the miscibility, morphology, mechanical behavior and other prominent characteristics of several blends and composites of PHB and PHBV with a few polyethers, polyesters, polyvinylacrylates and polysaccharides have been investigated with a wide range of properties emerges in term of crystallinity, glass transition and melting temperatures. Another imperative key that needs to be studied more was the microstructure of the blends, which could be obtained thermodynamically and kinetically. These factors were vital in directing the mechanical and the biodegradation behaviors of the blends. What is more, certain attentions need to be focused in order to elucidate the miscibility behavior differences of the blends, such as the nature of the “driving force” of the miscibility (Avella *et al.*, 2000).

Further evaluation had been made towards PHB–PHV copolymer biodegradable composites, by incorporating two particulate bioactive ceramics, which were hydroxyapatite (HA) and tricalcium phosphate (TCP), to yield new biomaterials for possible medical applications. The origin materials could be obtained easily, and could be characterized preceding to composite manufacture. It was reported that up to 30 vol% of the bio ceramics could be acquired through the recognized method made towards HA/PHB–PHV and TCP/PHB–PHV composites. Numbers of experiments utilizing tools such as thermogravimetric analysis, scanning electron microscopy, differential scanning calorimetry and dynamic mechanical analysis have been executed. Based on the results, the intended compositions of composites had been achieved and bio ceramic particles were well distributed in the polymer. With the addition of bio ceramics, lower degradation temperature was obtained and affecting the melting temperature of PHB–PHV composites. Varies type of PHB–PHV’s crystallinity was also observed according to the existence of HA or TCP particles. The increment of the storage modulus and loss modulus was paralleled by adding more and more HA or TCP content. The high stiffness could be achieved through the highest percentage of bio ceramics. In order to induce the formation of bone-like apatite, the enhanced ability of these composites have been obtained through preliminary in vitro experiments (Chen and Wang, 2002).

As one of other research, a study had been established by utilizing the diazotrophic bacteria of Azotobacter and Rhizobium genus, to produce the composite of PHB and PHBV with different molecular weight at different conditions - in vitro and in vivo. The development of numerous medical applications, such as surgical meshes, screws and plates for bone fixation, periodontal membranes, and wound dressing were also being studied. A demonstration of implanted animal tissue upon the PHB films and medical devices also had been achieved (Bonartsev *et al.*, 2007).

There are promising trend in the modern technology which have intensively made several progress through the exceptional properties of PHB and its copolymers, such as (Holmes, 1985):

- Optical active property of PHB.
- Utilization of PHB as an intravenous or oral carbon supply, with numerous of clinical benefits over glucose drip.
- Piezoelectric properties comparable to natural bone. A composite of PHB can be used to make a bone fracture fixation plate with akin characteristic of natural bone. This composite also promotes bone healing and growth. Moreover, it is biodegradable and unnecessary to be removed since it can resolve to the body.
- Controlling drug release in medical use. It can also be used as surgical pads, wound dressings and lubricant for surgeons’ gloves in fine powder form.
- With the aid of advanced equipment it can be utilized as a vascular graft or blood vessel, composed of very fine fibers, arranged to form a water impermeable tube of suitable internal diameter.

Application and Future Recommendations

Some of the recent advances had been achieved for conductive polymer composites from renewable resources, with a number of potential applications. Various filling contents and matrix polymers have been developed to give renewable polymer composites better electrical and thermal conductivity properties (Huang *et al.*, 2019).

More application of biopolymer had been discovered, such as the development of flame retardant (FR) additives from these materials. Most of the FRs prepared are problematic due to their negative impacts on human health and the environment. Furthermore, their preparations are neither green nor sustainable since they require typical organic, synthetic processes that rely on fossil fuels. Because of this, the need to develop more sustainable and non-toxic options is vital. Many research groups have turned their attention to preparing new bio-based FR additives for synthetic polymers (Hobbs, 2019).

More application in the automotive industry had been conducted with more studies towards the usage of biomaterials. Because of their low weight, these materials improve the efficiency of the automobile in terms of lower fuel consumption. Most of the major automotive industries are successfully employing natural fiber composites for the development of different automobile parts. Hence, a study of the crashworthiness and the use of these composites for the development of the interiors and exteriors of automobiles had become the interest among researchers recently (Verma and Senal, 2019).

Another opportunity for biocomposites application is to be used as automotive interior parts. The world automotive industry of interior parts is continuously optimizes the price/quality relation to gain competitiveness in the market. Nowadays, the importance of biodegradable polymers or polymers from renewable sources and the utilization of natural vegetal fibers to reinforce the polymers are increasing. These types of polymers and composite materials associated with the life cycle analysis are

gaining popularity and making a turning point in the automotive industry. A research had been conducted about the development of a novel green composite by the use of biopolymer poly (lactic acid) and natural-based cellulosic fibers in automotive interiors. As the results suggest, the incorporation of 20% fiber improves the thermal behavior of the composite without compromising the mechanical behavior of interior door trims (Loureiro and Esteves, 2019).

Renewability, Recyclability and Sustainability

In terms of recycling, the waste management system for composite from renewable resources are still in studies. Some of the international bodies, such as ICS-UNIDO had worked an activity about environmentally degradable plastics. Standardization, availability of renewable and non-renewable resources for production of environmentally degradable plastics, integration of policies and regulations relevant to waste management, life cycle approach and eco-design of product were identified as key issues in this material promotion and large scale application (Miertus and Ren, 2002).

Polymer recycling is being considered as one of the most widely accepted remedies to the threat of growing amounts of plastic waste by both the public and scientists. In practice, recycling is associated with many difficulties, such as problems related to separation, sorting and cleaning operations, lack of fiscal subsidies, instability of selective garbage separation programs, high transport and electricity costs, etc. Some novel approaches such as application in carbon capture or the synthesis of carbon nanostructures from the plastic waste are among the new process technologies of recycling. From traditional and promising polymer waste utilization approaches, there are needs for sustainable methods to reduce impacts of plastic waste on the environment. Fig. 3 shows some promising and eco-friendly plastic management approach. The same issue faced with polymer made from renewable resources (Okan *et al.*, 2019). Hence, more studies were needed to improve the waste management of this material.

In renewability and recycling, a study of thermal ageing behavior could be beneficial. Investigation of the ageing effect on biocomposites would supplement current knowledge and may help in encouraging their use in real life applications. Based on a research, an investigation had been carried out to determine the variation in various properties of bagasse fibers reinforced PLA biocomposites during accelerated thermal ageing. The study revealed that the PLA structure had deformed in biocomposites, at lower temperatures than their glass transition temperature, when subject to prolonged duration. Therefore, the study provides a comprehensive understanding of the thermal ageing of biocomposites and its effect on various properties (Lila *et al.*, 2019). Another recent application of bio polymer is the eco-friendly membrane with highest conductivity. This application contributes good cycling properties and possesses higher value of cationic transference number when compared with other electrolyte samples. A lithium ion conducting battery constructed using the highly conducting polymer membrane sample is used to light up the red LED (Perumal *et al.*, 2019).

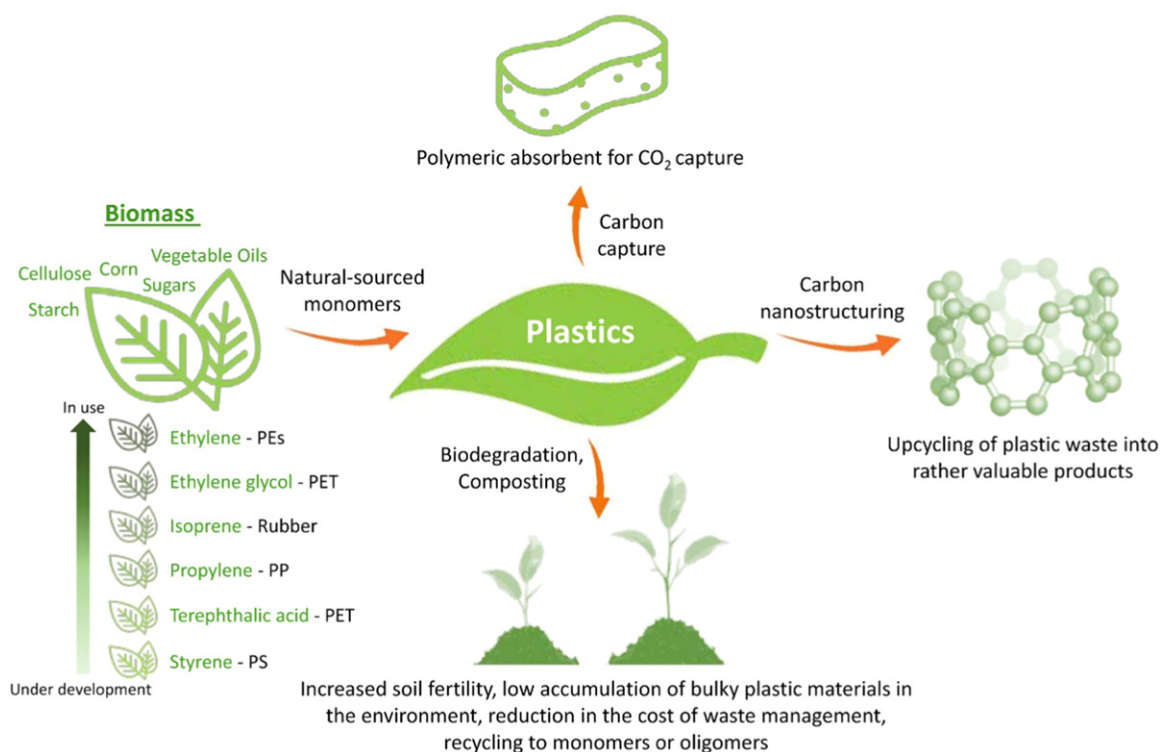


Fig. 3 Promising and eco-friendly plastic management approaches. Credit to: Okan, M., Aydin, H.M., Barsbay, M., 2019. Current approaches to waste polymer utilization and minimization: A review. *Journal of Chemical Technology & Biotechnology* 94 (1), 8–21.

Another method to recycle bio polymer is by applying the composite coagulant. For example, to attain an efficient composite coagulant with less environmental risks, a novel inorganic/natural polymer composite polyaluminum ferric chloride-starch graft copolymer with acrylamide and dimethyl diallyl ammonium chloride (PAFC-Starch-g-p[AM-DMDAAC]) was prepared, and applied for textile wastewater treatment. The results showed that PAFC-Starch-g-p(AM-DMDAAC) exhibited higher and more stable dye removal efficiencies than other prepared composite coagulants. For synthetic textile wastewater treatment, these composites could reduce the chemical dosage by more than 50% compared with conventional coagulation-flocculation process. Hence, it can be concluded that PAFC-Starch-g-p(AM-DMDAAC) is an eco-friendly composite coagulant with excellent performances and broad utilization range, showing promising application prospects (Zhou *et al.*, 2019).

Conclusion

As for the summary, findings from previous research that are related to the progress of renewable resources that have been exploited in polymer blends and composites. The detail explanation has been prepared based on the three categories of renewable polymers. The prominence on potential applications could inspire more research and inquiries about this special material, since it was cheaper, ecofriendly, biodegradable, and is widely used as a substitute for existing polymer from crude oils. Henceforward, the compilation of previous research related to polymer blends and composites from renewable resources had been delivered as the outcomes of this article, with the additional prospect for future direction and references.

See also: Biopolymer-Based Composites for Medical Applications. Biopolymers in the Synthesis of Different Nanostructures. Cellulose Nanocrystal as a Prospective Reinforcement for Polymer Matrix Nanocomposites. Energy Storage Device From Polymeric Waste Based Nano-Composite by 3D Printing. Investigations for Metal Matrix Composites Prepared by Using Waste Polymer-Based Sacrificial Rapid Pattern in Investment Casting. Investigations for Rapid Tooling Prepared With Waste Polymer-Based Hybrid Filament. Opportunities With Renewable Jute Fiber Composites to Reduce Eco-Impact of Nonrenewable Polymers. Solid Polymer Waste Materials for Repairing of Heritage Composite Structure: An Additive Manufacturing Approach. Sustainable and Environment Friendly Power Sources for Long Duration Environment Monitoring

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Polysaccharide Based Rubber Nanocomposites

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Introduction

Rubber refers to an elastomeric compound that consist of various monomeric units which form polymer and are heat cured. Rubber correctly refers to the natural gum produced from the sap of the Hevea tree (Visakh *et al.*, 2012). Usually they found in the form of colloidal emulsion in a milky white fluid which is called latex. The Hevea tree originated from Brazil which was introduced to Sri Lanka, Malaysia, Singapore and some surrounding countries where soil suited for its growth (Junian *et al.*, 2015).

Natural rubber (NR) is considered as one of the principal elastomeric unit which is widely utilized in different industries (Abdelmouleh *et al.*, 2007). In this present period, *Hevea Brasiliensis* is the only natural source for production of commercial rubber known as NR has proved as the best producer, accepting the highest productivity of the plants with magnificent physical properties of the rubber product (Junian *et al.*, 2015). The oldest known rubber is the polymer of high molecular weight isoprene unit (2-methyl-1, 3-butadiene) (Visakh *et al.*, 2012). Natural rubber latex generally contains about 4%–5% non-rubber constituent consisting carbohydrate, protein, lipids while synthetic rubber is manufactured from petrochemical by products. Another type of rubber is vulcanized rubber, which is prepared by vulcanization process. In the vulcanization process the long chains present in the rubber molecule undergo crosslinking, as a result the weak, soft, plastic material loss these properties and gain the strong elasticity property having high deformability and a great mechanical property. The vulcanization of rubber leads to loss the thickness of rubber and become more resistance towards light, heat and aging process (Visakh *et al.*, 2012).

NR exhibit some favourable properties that leads to its use in very large extent in heavy duty truck, defence industry, aerospace and medical fields (Malas *et al.*, 2014). Other industries which include packaging products such as tapes, films NR is used (Bras *et al.*, 2010). Butadiene Rubber (BR)/styrene butadiene rubber (SBR) blends are used in passenger car radial (PCR) tire compounds. Das *et al.* has done dispersion of multiwalled carbon nanotube (MWCNT) in the SBR/BR blends successfully without any damage of their unique properties and also observed the unproved mechanical properties in comparison of unfilled rubber. Still NR lacks some properties for its utilization in the rubber industries. Due to the unsaturated backbone NR decayed by thermal attacks and ozone (Junian *et al.*, 2015). Another property of NR like low strength become soft in warm weather and brittle in cold lead to limit its use (Visakh *et al.*, 2012). To overcome the limitation many researchers, work on the NR to enhance its property. A study has observed on the remarkable improvement of the storage tensile modulus on filler addition (Bras *et al.*, 2010). Due to the renewable character, biodegradable property, low density, high specific resistance related with certain properties of nanoparticle, the use of reinforcing agent taken from natural source produced a good advantage (Pasquini *et al.*, 2010). Rajisha *et al.* have studied about on the preparation of excellent nanofiller (prepared from nanocrystals). For NR latex and that possess the potential to replace the conventional polymer composite and nanocomposite (Rajisha *et al.*, 2014). Angellier *et al.* has described the improvement in relaxed storage modulus of various weight% with respect to different temperature, filler content in a NR matrix. Dufresene and Caville also have reported about the great reinforcing effect of starch nanocrystals especially at temperature when more than glass transition temperature (T_g) of the matrix (Le Corre *et al.*, 2010). This reinforcing effect can be increased on addition of the filler amount and also on the reduction of particle size (Angellier *et al.*, 2005). Bras *et al.* (2010) has reported that on addition of polysaccharide (starch) to polyethylene lead to the faster disintegration and this mechanism could be utilized also in case of NR to increase its biodegradability faster in presence of polysaccharide (cellulose whisker). For many authors the result of addition of nanofillers is an increase in the tensile strength and also the elastic modulus of the composite together.

The literature regarding the designing of the materials towards imitating the NR with similar characterization and properties is plenty. The materials like polyurethane, silicon etc., have the behaviour of NR. However, the natural and synthetic rubber have the limitation in properties like mechanical behaviour, biodegradability, gas permission and acid base resistance those are challenge for present researchers to overcome these properties. When polysaccharides are incorporated in rubber it gives an interactive compatible composite for enhancement in various properties because polysaccharides are functional biopolymers, those have strong interaction with the functional group of the rubber. Hence, the choice of polysaccharides as incorporating material has greater objective for improvement of important properties of rubber.

Although numerous numbers of articles are reported the literature related to different polysaccharide based rubber composite, however a concise report summarizing all different polysaccharide incorporated rubber composite is scanty in literature. Present article involves the summary related to the reinforcement of polysaccharide such as starch, cellulose, chitosan and dextran.

Types of Polysaccharide Reinforced Rubber

Starch

Starch is the superabundant material found in nature. The occurrence of starch are mainly in stalks, plant roots, staple crops like rice, wheat, corn, potato, tapioca and also from crop seed. Primarily starch produced as flour like white powder after its extraction

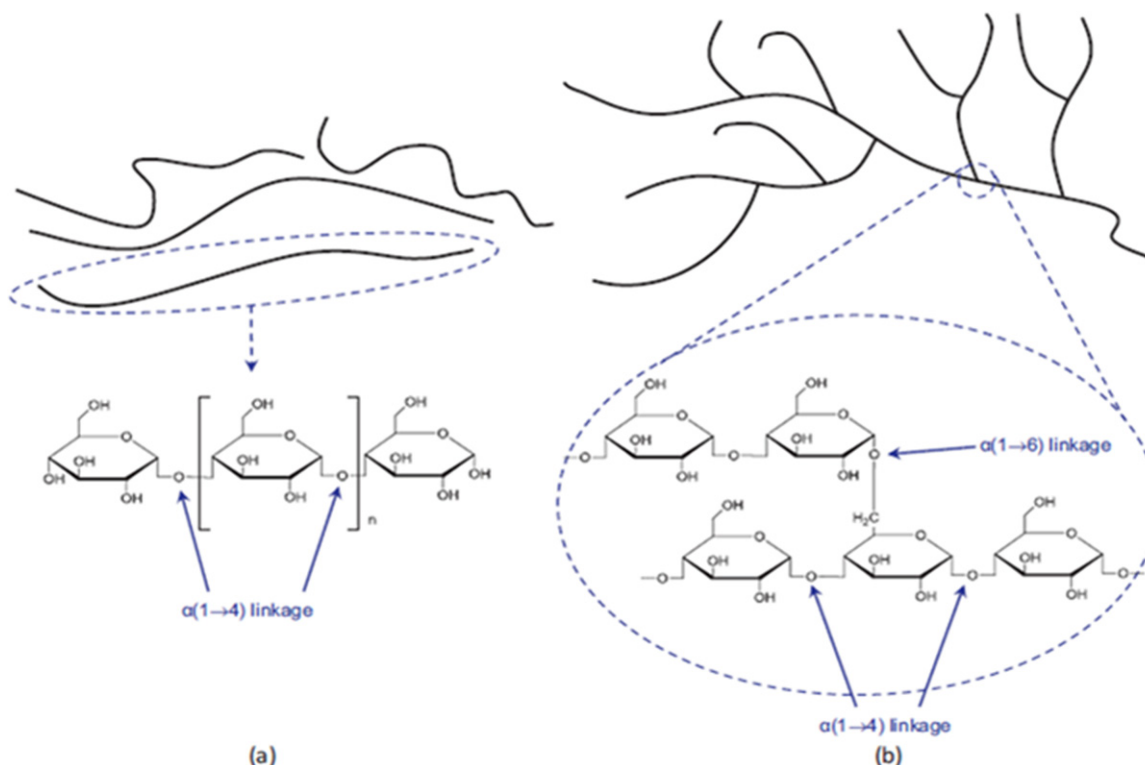


Fig. 1 Chemical structure of amylose (a) and amylopectin (b). Reproduced with permission from Xie, F., Pollet, E., Halley, P.J., Averous, L., 2013. Starch-based nano-biocomposites. *Progress in Polymer Science* 38, 1590–1628.

from plants and this powder form is insoluble in cold water. It is a biodegradable, natural, renewable agro polymer which produced by many plants (Le Corre *et al.*, 2010; Tang and Alavi, 2011; Savadekar and Mhaske, 2012; Du *et al.*, 2019; Peres *et al.*, 2016). The starch granules consist of two types of glucosidic macromolecules generally. One is (i) branched amylopectin (ii) essentially linear amylose (Shen *et al.*, 2016). The amylose of starch is defined as a linear branch of α -D glucopyranose linked by (1–4) α -D-glycoside bonds. Amylopectin linked through a high molecular weight consisting of relatively short branches of α -D-(1-4) glucopyranose linking linear chain of α (1→6) linkage (Xie *et al.*, 2013; Paoribut *et al.*, 2015; Ali *et al.*, 2011). The chemical structure of amylose and amylopectin are represented in the Fig. 1 (Xie *et al.*, 2013).

Angellier *et al.* has reviewed about the waxy maize starch nanocrystals which exhibit all the properties to use as reinforcing filler for NR and considered as one of the principle elastomeric unit used in industries (Du *et al.*, 2019). Rajisha *et al.* (2014) has studied a new reinforcing filler for NR prepared from potato starch nanocrystals and this can have creditable contribution towards the development of new green composite and reported that it can be a better replacement carbon black (CB) due to its tremendous strengthening effect like elastic behaviour, stiffness.

Synthesis of starch nanocrystals

In the recent research, starch nanoparticle gain the attention of researchers in number of works which are increasing exponentially for the development of bio composites. A few scientists have studied about the synthesis of microcrystalline starch and starch nanocrystals using acid hydrolysis. The literature (Rajisha *et al.*, 2014) describes the reinforcing effect of starch nanocrystals prepared from potato. The nanocrystals were synthesized by acid hydrolysis with sulphuric acid (H_2SO_4). In the first step of preparation of nanocrystals 36 g of starch granules from potato has taken and 25ml of H_2SO_4 (36 N) mixed for 5 days and remain at 40°C with constant stirring of 100 rpm speed. The aqueous suspension obtained undergoes centrifugation and ultrasonic treatment. Finally, the solid fraction (3.4 wt% weight concentration) of aqueous suspension has obtained. Xu *et al.* (2010) have reported the preparation of corn starch nanocrystals and acetylated starch nanocrystals; the literature also follows the acid hydrolysis method for preparation of nanocrystals.

Properties of starch

Thermal property

Thermogravimetric analysis (TGA) of polymeric material gives a brief knowledge about the thermal stability and polymer composite (Pan *et al.*, 2014; Wu *et al.*, 2018; Senna *et al.*, 2012). Duy *et al.* has studied the thermal property of NR and composites prepared by different method (Duy *et al.*, 2012; Wu *et al.*, 2009). Fig. 2 gives a brief explanation about the TG curves of NR gum vulcanizate, NR/cassava starch (10 phr) composite has prepared by direct blending and also for composite prepared by coagulation and Table 1 outline the summary of thermal degradation from the TGA curve of the composite and NR. The literature has said about no thermal degradation

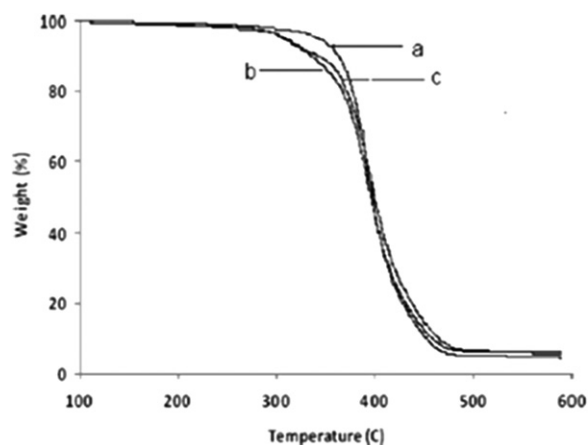


Fig. 2 TG curve of NR and composites (a) NR; (b) cassava starch (10 phr)/NR composites prepared by direct blending; (c) cassava starch (10 phr)/NR composites prepared by co-coagulation. Reproduced with permission from Duy, N.Q., Rashid, A.A., Ismail, H., 2012. Effects of filler loading and different preparation methods on properties of cassava starch/natural rubber composites. *Polymer-Plastic Technology and Engineering* 51, 940–944.

Table 1 Thermal degradation of NR gum vulcanization, cassava starch/NR composites with different methods of preparation

Sample	$T_{-5\%}$ ($^{\circ}\text{C}$)	$T_{-50\%}$ ($^{\circ}\text{C}$)
NR	343	397
Cassava starch (10 phr)/NR composite prepared by direct blending	310	386
Cassava starch (10 phr)/NR composite prepared by coagulation	318	399

Note: Reproduced with permission from Duy, N.Q., Rashid, A.A., Ismail, H., 2012. Effects of filler loading and different preparation methods on properties of cassava starch/natural rubber composites. *Polymer-Plastic Technology and Engineering* 51, 940–944.

below 300°C. In between 300 and 450°C all thermal degradation has shown and presence of polyisoprene chain increases the degradation. Although the NR gum vulcanizate at 300°C but maximum decomposition occurs at 450°C while in case of cassava starch if stabilised up to 275°C and at 375°C the maximum decomposition takes place. Thus it leads to failure of thermal stability of composite.

Biodegradable properties

In this literature (Pichaiyut *et al.*, 2016), the increase in biodegradability of rubber on addition of starch has reported by the soil burial test. The amylopectin of starch is more easily undergo broken down by microorganisms than amylose along with hydrolysis rate also higher than amylose and this leads to degradation of starch structure (Pang *et al.*, 2013). The biodegradation test of composite was held by estimating the weight loss percentage of neat rubber and three ternary blends such as unmodified NR (RSS#3), epoxidized NR with 25 mol% epoxides (ENR-25) and 50 mol% epoxides (ENR-50) after 2–6 months buried in soil.

The Fig. 3 gave a brief study about weight loss of neat rubber i.e., RSS#3, ENR25, ENR50, linear low density polyethylene (LLDPE), TPS and the ternary blends of RSS#3/LLDPE/TPS, ENR-50/LLDPE/TPS, ENR-25/LLDPE/TPS. It has been seen that there is 8.73 and 54.05 wt% loss in neat TPS in 2 and 6 months respectively and also show that TPS degrade faster than that of other neat polymers and ternary blends, while LLDPE lost 0.02 and 0.09 wt% in 2 and 6 months respectively which is a very little in amount. The ternary blend of NR/LLDPE/TPS show highest weight loss than that of ternary blend with ENR-25 and ENR-50. This is due to the stronger interfacial interaction. Azura *et al.* have studied effect of sago starch on soil decomposition of NR via enzymatic cleavage and oxidation of poly isoprene backbone as the more feasible biodegradation of starch component in comparison to poly isoprene backbone (Afq and Azura, 2013).

Cellulose

In the present era cellulose is considered as the most abundant renewable biopolymer produced from biomass (Lavoine *et al.*, 2012). Annually the production rate of cellulose has estimated 7.5×10^{10} tons. Wide distribution in higher plants-woods, 50% of which are cellulose content and these are the most important raw source of cellulose. The cellulose also can derive from several marine animals, annual crops and lesser degree in fungi, algae, bacteria (Brinchi *et al.*, 2013). For the preparation of green rubber composite, cellulose has taken the attention of researchers towards itself due to its renewable, low density, low energy consumption, biodegradability, environmental friendliness, and low cost, easy processing properties (Roy and Potiyaraj, 2018). Cellulose is a homo polysaccharide consists of β -D-glucopyranose units. These units are linked together by β -1–4 linkages. Each

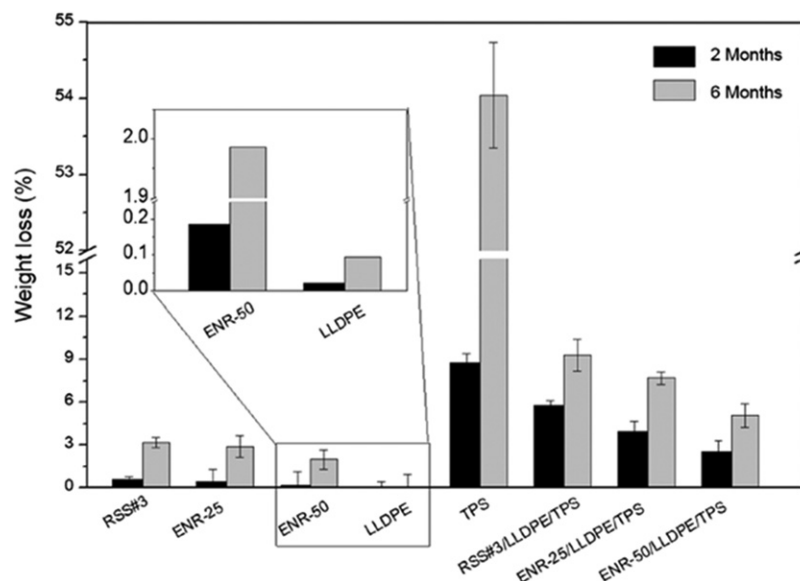


Fig. 3 Weight loss of neat rubbers and 50/40/10 ternary blends after burial in soil for 2 and 6 months. Reproduced with permission from Pichaiyut, S., Wisunthorn, S., Thongpet, C., Nakason, C., 2016. Novel ternary blends of natural rubber/linear low density polyethylene/thermoplastic starch: Influence of epoxide level of epoxidized natural rubber on blend properties. Iranian Polymer Journal 25, 711–723.

monomer of cellulose has 3 hydroxyl groups and those groups possess ability to form H-bond and this ability play an important role governing the physical properties of cellulose (Brinchi *et al.*, 2013). Bras *et al.* (2010) has reported about the incorporation of cellulose whiskers into NR, thus the green composite obtained have high thermo mechanical, biodegradable properties and the composite also show resistance to water vapour permeability. Pasquini *et al.* (2010) have obtained report on significant report of storage modulus of composite when cellulose whisker (filler) added to NR.

Synthesis of cellulose nanocrystals

Generally, the 3 hydroxyl group present in polysaccharide nanocrystals impart possibility of various reactions (Prusty *et al.*, 2017). Lam *et al.* (2012) have reported about chemical modification nano crystalline cellulose (NCC) with the help of present hydrolysis groups in the glucose units and reviewed about different application of NCC as a result of chemical modification. Some of the chemical modification of hydroxyl group of NCC is shown in Fig. 4.

The fabrication of CNCs via acid hydrolysis of cotton linter and utilizing it as a reinforcement material for nitrile rubber (NBR) has reported by Cao *et al.* (2013) In this literature small pieces of cotton seed linter pulp has mixed with aqueous solution of sulphuric acid (250 ml, 64 wt%) followed by 2 h of vigorous stirring at 60°C. The suspension thus obtained has washed with water by the help of centrifugation and the suspension undergone purification in terms of dialysis against deionized water to achieve the neutral pH of suspension. As a result, a stable suspension of CNCs has formed after concentrating by evaporation process. The suspension obtained contains 5.0 wt% solid. Finally, it has stored in the refrigerator.

Synthesis of hydrophilic bacteria cellulose whiskers (BCWs) as a result of acid hydrolysis of BC particles was demonstrated by Chen *et al.* (2018) and form nanocomposite with carboxylated acrylonitrile butadiene rubber (XNBR). The literature emphasized on the XNBR/BCW nanocomposite as an attractive candidate for the new type of stimuli responsive material. Johar *et al.* (2012) have reported about the fabrication of CNCs from rice husk. This paper involves preparation of CNCs by three steps as alkali treatment, bleaching process and acid hydrolysis respectively. Bras *et al.* (2010) in this study have demonstrated the preparation of CW from biogases pulp and focussed on the significant improvement of tensile strength and due to addition of CW and also the improvement in young's modulus which is represented in Fig. 5.

The CNCs synthesized by literature (Chuayjuljit *et al.*, 2009) and the method involves the preparation of CNCs by sulphuric acid (H₂SO₄) hydrolysis. At first 2 g of pulp has taken and added with 100 ml of 55 wt% H₂SO₄ at 50°C and followed by mechanical stirring at 300 rpm for 1.5 h. Thus the hydrolysed suspension form has diluted with the help of ice cubes so the reaction stops and then undergoes centrifugation (to wash) and dialysis (to achieve neutrality). The CNC suspension undergoes ultrasonic treatment about 10 min for completion. Finally by freeze drying process the CNC powder has collected.

Properties

Mechanical property

The mechanical loss factor ($\tan\delta$) and the log of the storage modulus i.e., $\log(E'/\text{Pa})$ of NR films reinforced with different wt% (0,2,5,7) CWs which are extracted from cassava biogases following 2 produces (CW₂₀ & CW₄₀) as a function of temperature are explained in Figs. 6 and 7. The storage modulus of unfilled NR gives a constant graph at 1 GPa on increasing the temperature. At

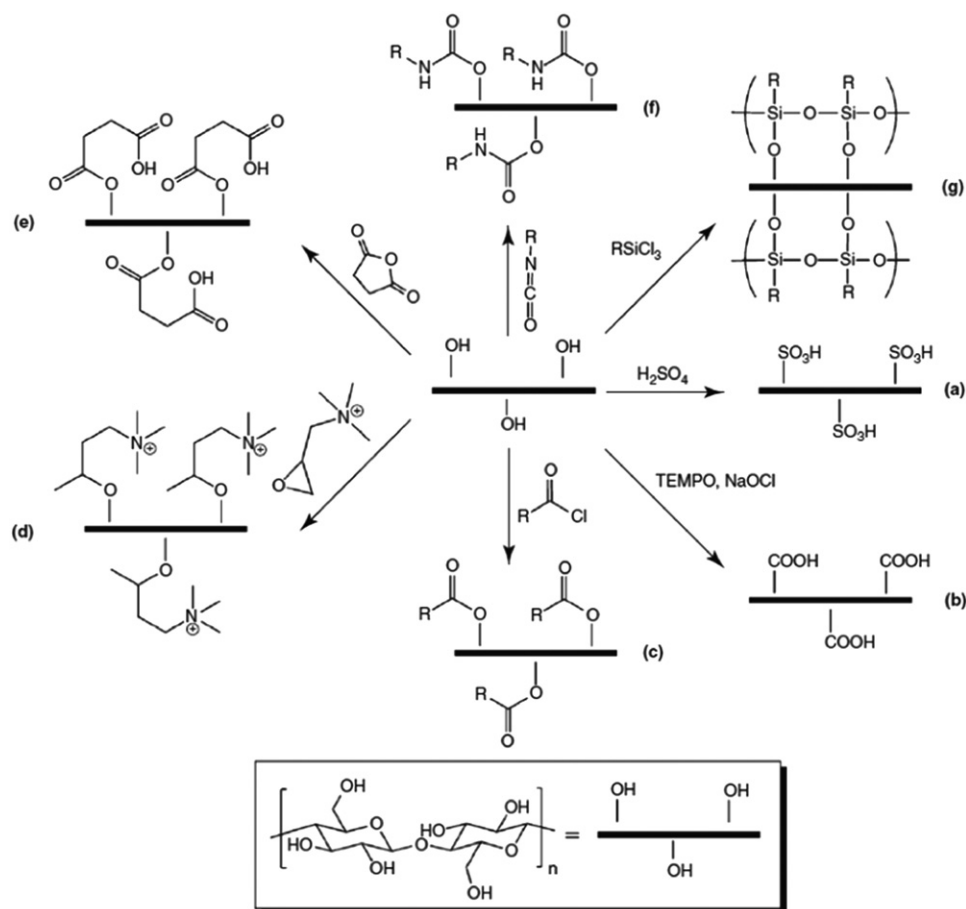


Fig. 4 Some possible routes for chemical modification of NCC (clockwise from right) (a) sulfonation (b) oxidation by TEMPO (c) ester linkages via acid chlorides (d) cationization via epoxides (e) ester linkage via acid anhydrides (f) urethane linkages via isocyanates and (g) silylation. Reproduced with permission from Lam, E., Male, K.B., Chong, J.H., Leung, A.C.W., Luong, J.H.T., 2012. Applications of functionalized and nanoparticle-modified nanocrystalline cellulose. *Trends in Biotechnology* 30, 283–290.

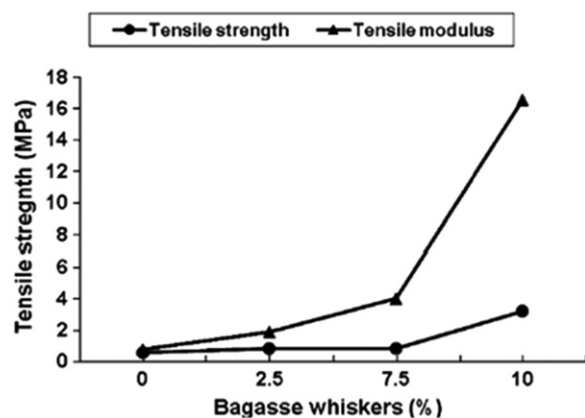


Fig. 5 Tensile strength and modulus of rubber/ cellulose whiskers nanocomposites film as a function of composition. Reproduced with permission from Bras, J., Hassan, M.L., Bruzesse, C., *et al.*, 2010. Mechanical, barrier and biodegradability properties of bagasse cellulose whiskers reinforced natural rubber nanocomposites. *Industrial Crops and Product* 32, 627–633.

–60°C a sharp decrease in the glass rubber transition is reported. The rubbery modulus has decreased slightly till 1 MPa & at 1 MPa it remains almost constant in the neat matrix or else the mechanical loss factor is observed around –55°C, which evidenced the relaxation process also it is seen that on addition of CW the magnitude of $\tan\delta$ peak decreases (Fig. 6). The rubbery relaxed modulus value and main relaxation processes temperature value (T_α) has reported in Table 2.

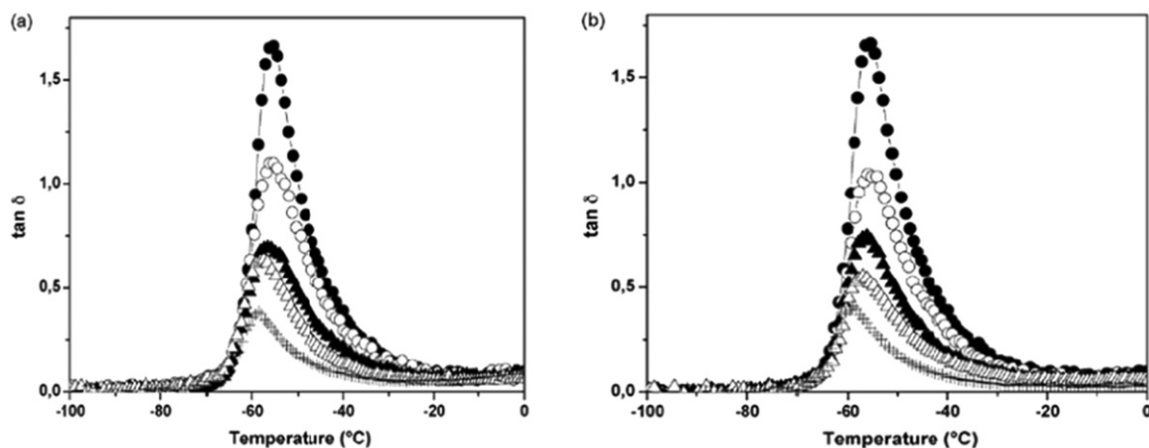


Fig. 6 Evolution of the loss angle $\tan \delta$ as a function of temperature at 1 Hz for NR films reinforced with 0(●), 2(○), 5(▲), 7(△) and 10 wt%(+) cellulose whiskers obtained according to hydrolysis condition CW₂₀(a) and CW₄₀(b). Reproduced with permission from Pasquini, D., de Morais Teixeira, E., da Silva Curvelo, A.A., Belgacem, M.N., Dufresne, A., 2010. Extraction of cellulose whiskers from cassava bagasse and their applications as reinforcing agent in natural rubber. *Industrial Crops and Products* 32, 486–490.

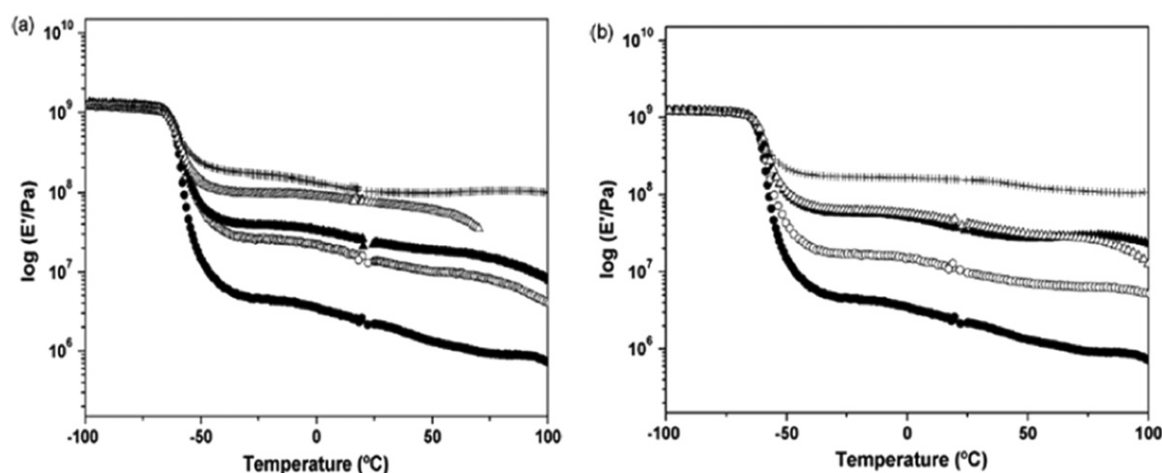


Fig. 7 Evolution of the logarithm of storage modulus as a function of temperature at 1 Hz for NR films reinforced with 0(●), 2(○), 5(▲), 7(△) and 10 wt%(+) cellulose whiskers obtained according to hydrolysis condition CW₂₀ (a) and CW₄₀ (b). Reproduced with permission from Pasquini, D., de Morais Teixeira, E., da Silva Curvelo, A.A., Belgacem, M.N., Dufresne, A., 2010. Extraction of cellulose whiskers from cassava bagasse and their applications as reinforcing agent in natural rubber. *Industrial Crops and Products* 32, 486–490.

On addition of cellulosic nanoparticles an insignificant increase in T_g while a significant increased rubbery modulus and increased reinforcing effect has observed. [Pasquini et al. \(2010\)](#) have found the relative modulus of the nanocomposite around 46 for CW₂₀ and 70 for CW₄₀ respectively. The storage modulus remains constant and it is mainly due to the restriction of molecular motion to vibration and also to the short range molecular motion at glassy state ([Visakh et al., 2012](#)).

Thermal properties

The TGA and differential thermo gravimetric (DTG) plots of NR/CW composites ([Visakh et al., 2012](#)) are reported in [Fig. 8 \(a\)](#) and [\(b\)](#) respectively. TGA estimates the weight change of the material on heating in presence of air. At lower temperature when rubber compound heated firstly the evaporation of volatile components mostly moisture took place & further heating cause degradation of polymer part this lead to weight loss as shown in curve. The plot- 8(a) gave information about TGA analysis of NR and NR/CW nanocomposite having 2.5, 5 & 10 wt% of whisker content. For NR the beginning of degradation takes place around 260°C and undergo a constant shift to 273, 276, 278°C for the nanocomposite having 2.5, 5, 10 wt% CNWs respectively with increase cellulose nanowhiskers (CNW) concentration to 10 wt% the first degradation peak of NR increased from 275°C to about 350°C ([Fig. 8\(b\)](#)). When the cellulose whisker added to the composite it has been observed that the thermal stability along with de composition temperature increases at different stages ([Fig. 8\(b\)](#)).

Table 2 Main relaxation temperature (T_{α}) and storage tensile modulus (E') estimated at 25°C for NR nanocomposite samples

Hydrolysis time (min)	Whisker content (%)	T_{α} (°C)	E' (25°C) (MPa)
20	0	-55.4	2.2
	2	-56.2	13.7
	5	-56.6	23.0
	7	-57.5	73.8
40	10	-58.6	102.2
	2	-55.9	9.8
	5	-56.1	33.4
	7	-56.9	41.1
	10	-58.9	153.9

Note: Reproduced with permission from Pasquini, D., de Moraes Teixeira, E., da Silva Curvelo, A.A., Belgacem, M.N., Dufresne, A., 2010. Extraction of cellulose whiskers from cassava bagasse and their applications as reinforcing agent in natural rubber. *Industrial Crops and Products* 32, 486–490.

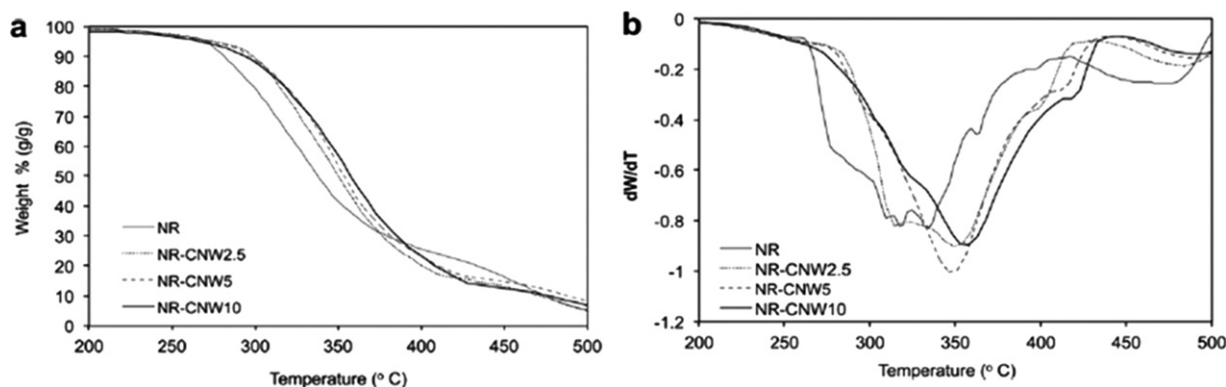


Fig. 8 TGA and DTG plots of neat NR and cellulose whiskers/NR nanocomposites showing the degradation behaviour. Reproduced with permission from Visakh, P.M., Thomas, S., Oksman, K., Mathew, A.P., 2012. Crosslinked natural rubber nanocomposites reinforced with cellulose whiskers isolated from bamboo waste: Processing and mechanical/thermal properties. *Composites Part A: Applied Science and Manufacturing* 43, 735–741.

Biodegradation property

Generally, NR undergoes degradation by nature in a slow process. [Bras et al. \(2010\)](#) studied about the increase in degradation speed of NR on addition to CWs as biodegradable nanocomposite plays an important role in the area of packaging materials. The biodegradable property of the samples was done by buried the sample in soil ([Chuayjuljit et al., 2009](#)). The result of biodegradation analysis of rubber on reinforcement of CW is depicted in [Fig. 9](#).

The graph said about the difference in weight loss in between neat rubber and cellulose containing nanocomposite. The neat NR undergoes 19% weight loss while NR with 7.5 & 12.5 wt% of CWs undergo 62 & 71% weight loss respectively after 4 weeks. Presence of cellulose component in the nanocomposite leads to increase in porosity, loss of the integrity, void formation of the rubber matrix which result quicker disintegration of nanocomposites having CWs than neat rubber matrix ([Yang et al., 2014](#)).

Chitosan

Chitosan is a bio decomposable and biocompatible polymer with a vast structural possibility for its modification (chemically and mechanically) to generate unique functions and properties in biomedical and other fields ([Mao et al., 2010](#); [Nagpal et al., 2010](#); [Prabaharan, 2014](#); [Shukla et al., 2013](#)). The primary $-NH_2$ present in chitosan structure is very useful in case of pharmaceutical application than other natural polymers. The glycosidic bond present in chitosan structure is unstable in acidic medium thus it can be hydrolysed under acidic environment which cause the decrease in viscosity and molecular weight ([Shukla et al., 2013](#); [Arya et al., 2007](#)).

[Nagpal et al.](#) have studied various properties of chitosan which makes the biopolymer has a very shining future in pharmaceutical nanotechnology area. Due to the absorption enhancing effect of chitosan it did improvement of the drug bioavailability & its nano size helps to facilitate the drug delivery through the cell membrane ([Nagpal et al., 2010](#)). The various properties of chitosan depend on the degree of deacetylation, molecular weight & viscosity. Chitosan having low degree of deacetylation are reported as the active absorption enhancer of both high & low molecular weight. Due to better stability of chitosan nanoparticle

they offer many advantages (Prusty *et al.*, 2017; Arya *et al.*, 2007). Many applications of chitosan nanoparticle has studied by scientists like in case of parental drug delivery, non-viral gene delivery, brain targeting, vaccine delivery, insulin delivery, electro deposition, stability improvement, pre-oral administration, mucosal drug delivery, ocular drug delivery, controlled drug delivery, tissue engineering, & increase of antioxidant, biosensors, food packaging, membrane & medicine (Shukla *et al.*, 2013; Arya *et al.*, 2007; Jayakumara *et al.*, 2010).

Preparation of chitosan nanocrystals

Among many synthetic and natural polymers available chitosan is broadly studied in case of preparing both micro and nano particles for drug encapsulation (Arya *et al.*, 2007). Although, $-NH_2$, $-OH$ group present in chitosan structure primarily provides basis of interaction with other molecules & polymers. Modification of chitosan such as nitration, alkylation, thiolation, azylation and some other modification is shown in Fig. 10 (Shukla *et al.*, 2013).

Different method has been put forward to synthesize chitosan macro/nano particles such as precipitation, evaporation, ionic gelation, spray drying, electro spraying (Arya *et al.*, 2007). Other method of preparation of chitosan nanoparticles extensively have studied by Nagpal *et al.* (2010) which include micro emulsion, emulsification-cross linking, polyelectrolyte complex, solvent

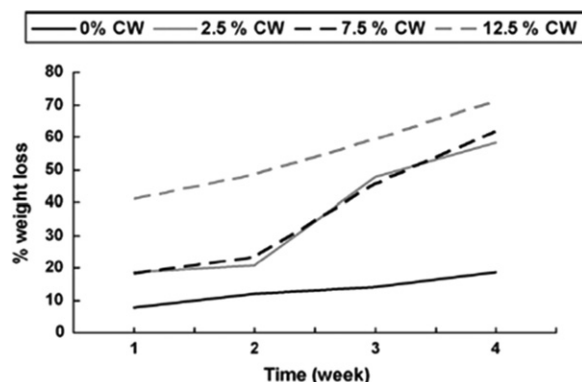


Fig. 9 Bio-disintegration of rubber/cellulose whiskers (CW) nanocomposites in soil for up to 4 weeks. Reproduced with permission from Bras, J., Hassan, M.L., Bruzesse, C., *et al.*, 2010. Mechanical, barrier and biodegradability properties of bagasse cellulose whiskers reinforced natural rubber nanocomposites. *Industrial Crops and Product* 32, 627–633.

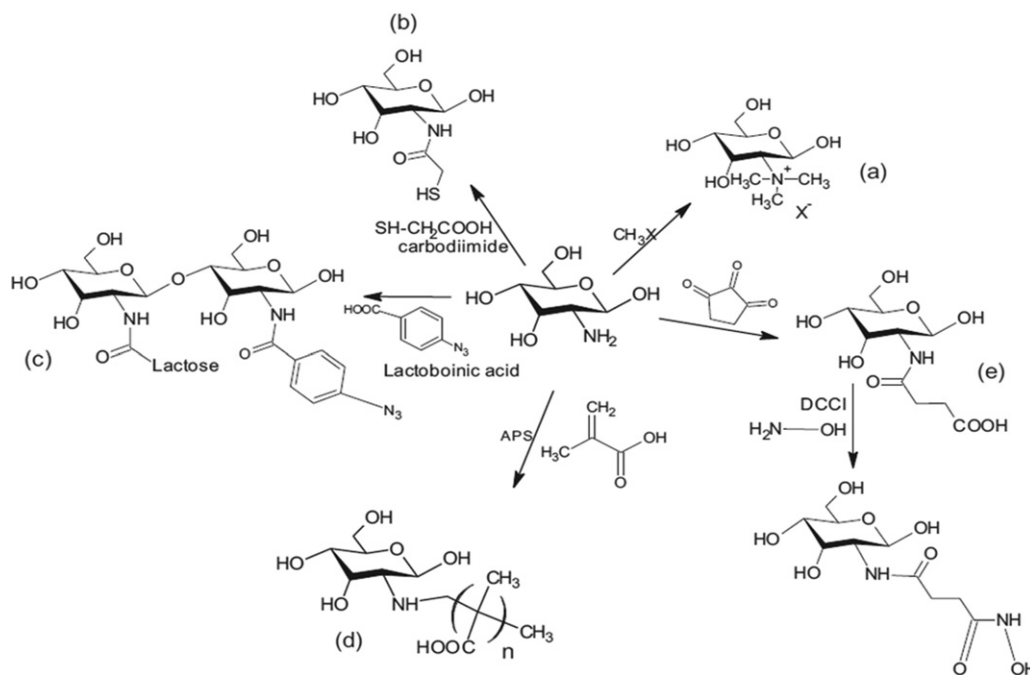


Fig. 10 Chemical modification of chitosan for different application (a) methylation; (b) thiolation; (c) azylation; (d) co-polymerisation; (e) N-succinylation. Reproduced with permission from Shukla, S.K., Mishra, A.K., Arotiba, O.A., Mamba, B.B., 2013. Chitosan-based nanomaterials: A state-of-the-art review. *International Journal of Biological Macromolecule* 59, 46–58.

evaporation methods, complex coacervation. Saharan *et al.* (2013) have demonstrated the chitosan nanoparticles preparation by doing modification of ionic gelation method of chitosan with tripolyphosphate (TPP) anions. In this method chitosan taken has dissolved in 1% acetic acid (0.1% level) & then placed in a magnetic stirrer for overnight stirring at 200 rpm followed by filtration through poly vinyl dine difluoride membrane syringe filler with 0.22 μm pore size. After that chitosan undergo crosslinking with TPP anion at equal volume in a magnetic stirrer and the stirring process was done at 700 rpm. The resulted mixture has placed to centrifugation for 10 min thus the re-suspension of pellet was took place and finally undergo ultra-sonication. 3 times repeatedly this process of centrifugation followed by ultra-sonication was done and thus the formed precipitate was stored at 4°C. The chitosan microsphere preparation by ion induction & chemical crosslinking has reported by Ming-zhe *et al.* (2017).

Properties

Tensile properties

The tensile property of NR & its vulcanizes depends on crosslinking density (Rubentharen *et al.*, 2015), degree of crystallization and degree of filler addition (Ming-zhe *et al.*, 2017). The effect of different amount of chitosan (CTS) content on the tensile property of chitosan epoxidized natural rubber (CTS-t-ENR) biocomposites is represented in the Fig. 11. The tensile strength of CTS-t-ENR increases up to 5 phr & thereafter a decrease in tensile strength noticed due to the strong interpretation of polymer-filler. CTS-t-ENR blend having 2.5 & 5 phr chitosan content show uniform dispersion in ENR matrix but at 10 phr tensile property decreased as CTS undergo aggregation causing agglomeration in the ENR matrix. As the literature said when filler amount overcome the critical value the aggregation develop which lead to break down of the new material along with reduction of the properties (Rubentharen *et al.*, 2015). Fig. 12 represented the percentage elongation break with chitosan loading up to 2.5 phr homogeneous filler formation became tougher & thus there is matrix-filler interaction become poor. As the chitosan content increases the overall modulus also increases this could be viewed from the Fig. 13. Thus it could be drawn out chitosan provide a better strengthening effect to the rubber.

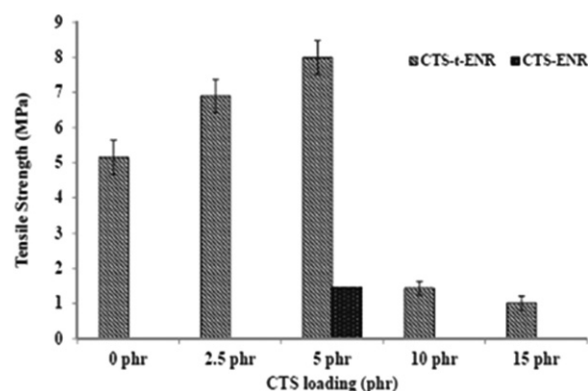


Fig. 11 Tensile strength of (i) CTS-t-ENR (with CTS loading of 0, 2.5, 5, 10 and 15 phr) and (ii) 5 phr CTS-t-ENR. Reproduced with permission from Raju, G., Haris, M.R.H.M., 2016. Preparation and characterization of acidified chitosan immobilized in epoxidized natural rubber. Polymer Testing 53, 1–6.

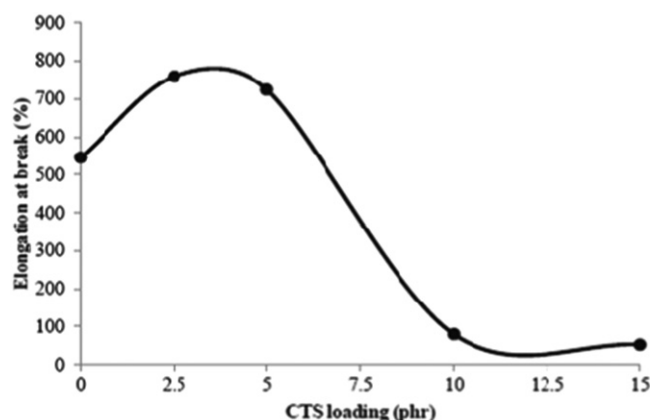


Fig. 12 Effect of CTS loading on the elongation at break of the CTS-t-ENR. Reproduced with permission from Raju, G., Haris, M.R.H.M., 2016. Preparation and characterization of acidified chitosan immobilized in epoxidized natural rubber. Polymer Testing 53, 1–6.

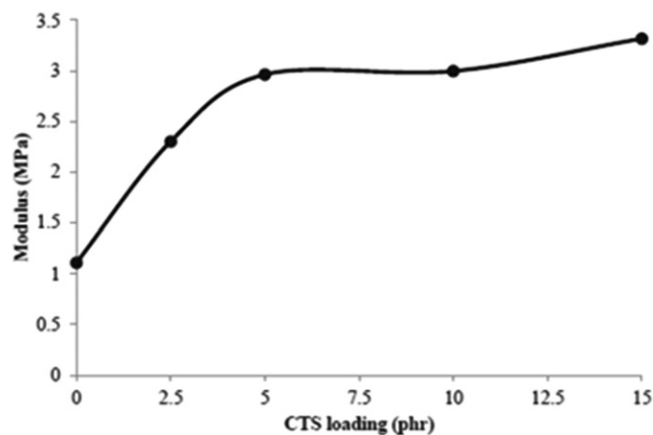


Fig. 13 Effect of CTS loading on the modulus of the CTS-t-ENR. Reproduced with permission from Raju, G., Haris, M.R.H.M., 2016. Preparation and characterization of acidified chitosan immobilized in epoxidized natural rubber. *Polymer Testing* 53, 1–6.

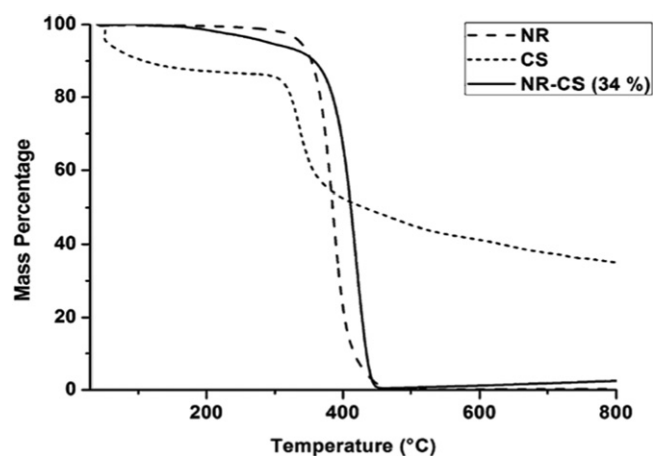


Fig. 14 TGA curves of NR, CS and NR-CS (34%). Reproduced with permission from Venkatanarasimhan, S., Dhamodharan, R., 2015. A new route to polymeric materials derived from chitosan and natural rubber. *Polymer Bulletin* 72, 2311–2330.

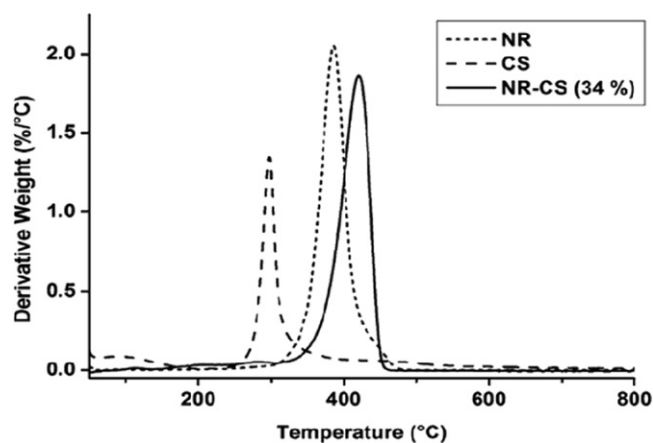


Fig. 15 Derivative thermogravimetric curves of NR, CS and NR-CS (34%). Reproduced with permission from Venkatanarasimhan, S., Dhamodharan, R., 2015. A new route to polymeric materials derived from chitosan and natural rubber. *Polymer Bulletin* 72, 2311–2330.

Table 3 Degradation temperatures and char at 900°C

Sample	Onset degradation temperature(°C)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	Residual product at 900°C
NR	385	352	410	0.5
Chitosan	305	150	365	34
NR-CS(34%)	420	357	413	3

Note: Reproduced with permission from Venkatanarasimhan, S., Dhamodharan, R., 2015. A new route to polymeric materials derived from chitosan and natural rubber. Polymer Bulletin 72, 2311–2330.

Table 4 Preparation, characterization, and properties of different polysaccharide based rubber nanocomposites

SL no.	Rubber types	Polysaccharide	Process adopt	Techniques used for characterization	Properties studied	Reference
1	NR	Starch	Mechanical mixing	TGA, SEM	Thermal, mechanical, hardness, viscosity, morphology	(Senna <i>et al.</i> , 2012)
2	NR	Starch	Mechanical mixing	FTIR, SEM	Mechanical, Structural, Morphology, mass loss, Water uptake, cross-linking density	(Manaila <i>et al.</i> , 2018)
3	NR	Porous starch	Mechanical mixing	SEM, Rotational viscosity test	Morphology, money viscosity, rheology	(Du <i>et al.</i> , 2019)
4	NR	Cassava Starch	Blending and coagulation	XRD, SEM, TGA	Morphology, mechanical, Thermal,	(Duy <i>et al.</i> , 2012)
5	NR	Porous starch	Blending	SEM, TGA	Morphology, thermal stability, swelling, Mechanical	(Pan <i>et al.</i> , 2014)
6	NR	Starch	Blending, Mechanical stirring, Coagulation	TGA, XPS, SEM, FTIR	Morphology, thermal stability, cross linking density, rheology, dynamic mechanical analysis, mechanical	(Wu <i>et al.</i> , 2018)
7	NR	Starch xanthenes	Mechanical mixing	(RPA), (DSC), (ODR), (MDR)	Vulcanization kinetics	(Luo <i>et al.</i> , 2013)
8	SBR	Starch	Mechanical mixing followed by coagulation	SEM, Dynamic Mechanical Thermal Analysis (DMTA)	Mechanical, viscoelasticity, Morphology	(Wu <i>et al.</i> , 2009)
9	BUNA-N	Cellulose	Acid hydrolysis	SEM, TGA, DMA, RPA	Mechanical, morphology, Structural, thermal stability, dynamic viscoelasticity	(Chen <i>et al.</i> , 2018)
10	XNBR	Bacterial cellulose	Latex blending	TEM, AFM, SEM, XRD, FTIR, DMA	Tensile storage modulus, Water uptake behaviour, Water stimuli-responsive, structure, morphology	(Johar <i>et al.</i> , 2012)
11	NR latex	Cellulose	Coagulant Dipping	FTIR, SEM	Mechanical, morphology	(Harahap <i>et al.</i> , 2018)
12	Liquid Epoxidized NR (LENR)	Cellulose	Mechanical mixing	FESEM, TEM	Morphology, mechanical	(Kargarzadeh <i>et al.</i> , 2018)
13	Synthetic rubber	Cellulose	Mechanical mixing	TGA, DMA, DSC, FESEM	Mechanical, thermal, dynamic, morphology, impact	(Ketabchi <i>et al.</i> , 2017)
14	NR	Cellulose	Mechanical mixing	TEM, SEM, TGA	Mechanical, thermal, Morphology, physical	(Phiriyawirut <i>et al.</i> , 2010)
15	NR	Cellulose	Mechanical mixing	TGA, FESEM, DTG, FTIR	Mechanical, thermal, cross-linking density, solvent uptake, cure	(Prusty <i>et al.</i> , 2017)
16	NR	Bacterial cellulose	Mixing followed by evaporation	AFM, TEM, SEM, XRD, FTIR, DMA	Morphology, dynamic mechanical, water uptake, water responsive behaviour, structure, tensile storage modulus	(Yin <i>et al.</i> , 2018)
17	NR	Chitosan	Mechanical mixing	FTIR, SEM, TGA, DSC, particle size analysis	Morphology, thermal, structural, mechanical, antibacterial, hydrophilic	(Ming-zhe <i>et al.</i> , 2017)
18	NR	Chitosan	Casting		Swelling, thermal, mechanical	(Paoribut <i>et al.</i> , 2015)
19	NR	Chitosan	Mechanical mixing	FTIR, FESEM, TGA	Thermal stability, mechanical, morphology	(Raju and Haris, 2016)
20	NR	Chitosan	In situ	UV, NMR, FTIR, TGA, DSC, SEM, XRD	Mechanical, thermal	(Venkatanarasimhan and Dhamodharan, 2015)

Thermal property

Thermal decomposition analysis is meant to evaluate the thermal stability of NR/chitosan (CS) blends (Venkatanarasimhan and Dhamodharan, 2015). Figs. 14 and 15 are the TGA & DTG curve of NR, CS, NR/CS blend, NR/CS (34%). The degradation temperature at 10% & 50% along with the residual char amount at 900°C was described in Table 3. In comparison with NR CS possess poor thermal stability and the literature also said that CS initiated at about 305°C, where the NR have higher thermal stability than CS and its decomposition initiating at 385°C. Also there was significant mass loss of NR-CS (34%) graft copolymer commences above 420°C (Table 3). This degradation temperature of the NR/CS (34%) is extremely higher than that of CS and also upgraded by 35°C that of the NR. The TGA & DTG studies validate about the grafting reaction of CS on the NR matrix raises the thermal stability of both NR & CS.

Degradation Properties

Undoubtedly NR has huge limitation of very low degradation property. So addition of polysaccharide helps to increase the degradability of NR. The test was done by taking samples of high ammonia concentration latex (HA) without filler; chitosan filled HA, fresh latex (FL) without filler. Chitosan filled FL and shrimp shell filler with NR. The entire matrix prepared with 20 wt% of filler. Then by taking an acrylic box the test was done. The NR without filler on the surface of soil & the underground sample found still sticky after the degradation test, this result indicate chitosan impart degradation effect on the NR/chitosan composite on the surface of soil. The polysaccharide based rubber nanocomposites can be prepared by various reported methods such as mechanical mixing, *in situ*, blending, latex blending, coagulation, acid hydrolysis and dipping techniques. Preparation, characterization, and properties of different polysaccharide based rubber nanocomposites have been reported elsewhere. These are summarized as Table 4.

Conclusion

Rubber nanocomposites are a new class of elastomeric materials with a future promise of potential applications as high-performance materials. These articles are mainly focused on the preparation of different polysaccharide based nanostructures like starch nanocrystals, cellulose nanowhiskers and chitosan nanocrystals and their successful reinforcements to the natural rubber towards the development of biodegradability along with improved mechanical, thermal, rheological and anti-bacterial behaviors. It is noticed that the biodegradable properties of rubber is achieved by dispersion of different kind of polysaccharide based nanostructures like starch nanocrystals, cellulose nanowhiskers and chitosan nanocrystals without much compromise with other properties. The main scope of the present article relevant to the equal distribution of different polysaccharide based nanostructures like starch nanocrystals, cellulose nanowhiskers and chitosan nanocrystals and improving the strong interfacial adhesion between starch nanocrystals, cellulose nanowhiskers and chitosan nanocrystals and rubber. As natural rubber is obtained from renewable resource so it is not economic than different polysaccharide based nanostructures like starch nanocrystals, cellulose nanowhiskers and chitosan nanocrystals. So nanocomposites of natural rubber and different polysaccharide based nanostructures like starch nanocrystals, cellulose nanowhiskers and chitosan nanocrystals will become emerging future materials.

See also: Bacterial Cellulose Based Nanocomposites for Electronic and Energy Applications. Bio-Nanocomposites for Food Packaging Applications. Effect on Compounding Process in Natural Rubber for Sustainable Suspension Materials. Polysaccharide-Based Flocculants for Industrial Effluents. Rubber Scrap as Reinforced Material in the Production of Environmentally Friendly Brake Lining. Waste Conversion Into Sustainable and Reinforcing Fillers for Rubber Composites

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The Potential of Environmental-Friendly Biopolymers as an Alternative to Conventional Petroleum-Based Polymers

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Introduction

Polymers have become one of the most important class of materials nowadays because of their fascinating properties and ease of manufacturing. Thermoplastics can also be recycled which make them environment-friendly. However, the source of most plastics up-to-date is the petroleum industry. It is understood that fossil fuels are the main reason for CO₂ emissions (Liddle and Sadorsky, 2017) and hence efforts are made to find other sources of polymers. Unfortunately, it is difficult to replace polymers with metals or ceramics due to many reasons. One of the reasons is that polymers can be processed at relatively low temperatures compared to metals, which induces less energy requirements and hence relatively much less infrastructure for manufacturing. One of the toughest polymers is polycarbonate which can easily be processed at around 250°C. In contrast, the processing temperature of aluminum is about 610°C for the sintering process only without even reaching to the melting point (Issa *et al.*, 2017). Another interesting feature of polymers is their viscoelastic response which is important for damping and sealing applications.

Since polymers are an important class of material for today's applications, searching for an environmental-friendly alternative of petroleum-based polymers becomes a necessity due to the adverse effects of utilizing fossil fuels on our environment. Petroleum-based polymers are characterized with excellent thermal stability and mechanical properties compared to bio/bio-based polymers. For example, the glass transition temperature of polylactic acid (PLA), which is a biopolymer derived from renewable resources such as corn starch, tapioca roots, chips or starch, or sugarcane, is around 56°C, while the softening temperature is about 105°C for acrylonitrile butadiene styrene (ABS), which is one of the most commonly used thermoplastic petroleum-based polymers. Nevertheless, biopolymers are the safest choice for bio-applications due to their biocompatibility and acceptable thermal range. Luo and Hu (2017) reviewed variety of works on biopolymer-based nanoscale nutrient delivery systems to avoid any side effects or toxicity and to maximize their effectiveness to boost bioavailability of encapsulated nutrients. Biopolymers can also be used for structural application if being fabricated either as porous structures or part of a composite material. The applicability of biopolymer-based composites in developing construction materials for architecture designs was proven by Dahy (2017). For thermal applications such as solar thermal collectors, biopolymers have shown the potential to replace aluminum and copper as absorber materials (Klein *et al.*, 2017).

Two case studies are presented in this article to illustrate the potential of two biopolymers for structural applications and damping attenuation, namely, polylactic acid (PLA) which is a biopolymer and green high density polyethylene (GHPE) which is a bio-based polymer. The green high density polyethylene is made by consuming CO₂ from the atmosphere. The first case study presents the development of functionally graded porous structures made of polylactic acid and their potential as light weight but strong porous materials. The second case study, presents a bio-composite made of green high density polyethylene blended with waste rubber and thermally activated microspheres for the application of impact absorption. Both studies proved the potential of bio/bio-based polymers and composites for structural and damping applications, and hence, potentially, may replace conventional petroleum-based polymers.

Material Structures of Biopolymers for Enhanced Strength and Damping

As mentioned earlier in the article that biopolymers have the limitation of less mechanical strength and low thermal stability compared to the petroleum-based polymers. This statement is true for raw materials, but biopolymers can be fabricated in specific structures that can enhance the mechanical properties. Fabrication of such structures, as will be discussed later, may also contribute to alleviate the thermal instability issue to some extent. Certainly, if petroleum based polymers are fabricated in these specific structures, they will outperform biopolymers, but the objective here is to develop biopolymeric structures that can replace the current petroleum-based polymeric products in the market and not competing with the strength. Three structures are believed to explore the potential of biopolymers as structural components, namely, hierarchical structures, functionally graded porous structures, and multiphase green composites with thermally activated microspheres. Combination of the three classes of material structures is capable of producing superior materials for a variety of engineering applications like structural design and impact absorption. This article will take particularly these two applications as examples where biopolymers can be tailored for high performance.

Hierarchical structures can be used for tailoring the properties and monitoring failure at multiple length scales, which are especially prominent in applications like impact attenuation. Additionally, functionally grading the material results in continuous spatial-temporal variation in the microstructural properties. This eliminates the presence of interfacial weakness due to discontinuous boundaries. The properties of functionally graded polymeric based hierarchical structures can be tailored from nano-scale all the way up to the microstructural level using thermo-mechanical and chemical processing methods. Due to the

visco-elastic/plastic nature of polymers in general, biopolymeric material structures can be manufactured with appreciable energy absorption capability using intrinsic and extrinsic mechanisms while providing energy dissipation to reduce shock during impact, for example. Specifically, besides tailoring of the material properties, advantage will be taken of the spatial-temporal state of the system. As a result, failure propagation will be resisted not only by the intrinsic properties (e.g., visco-plastic dissipation) but also by extrinsic factors like controlling crack propagation pathway and strain energy absorption through increase of internal degrees of freedom (e.g., buckling or rotation of internal cell walls in the case of porous structures).

Nature Inspiration of Material Structures

Development of high performance hierarchical structures may come from the designs existing in nature itself. Widespread examples include the clubs of mantis shrimps, nacre-like structure in sea shells, and bone. A characteristic feature in all these structures is high stiffness but also high deformation at large stresses. Stiffness and toughness of a material are normally exclusive properties. The reason is that stiffer materials have lower ability to flow and relax internal stress. As a result, when the internal stresses at high stress point like crack tips exceed failure strength, the material fails with very little resistance. On the other hand, materials which have the ability to flow and relax stresses usually display poor stiffness and lower absolute strengths. The exception is high density materials like metals which may display high stiffness and toughness due to the larger number of molecules or bonds per unit volume. However, in many cases, it is undesirable to use high density materials due to power and efficiency limitations.

Intrinsically, it is difficult to find high strength, toughness, and low density all in one material. For obtaining the most optimal combination of these characteristics, extrinsic reinforcement systems must be employed. For high toughness, rupture of molecular bonds should be minimized and frictional flow between molecules should be promoted. But as discussed, too much flow can also result in reduction of stiffness. For obtaining the optimal balance, it is possible to have an extrinsically reinforced system which does not allow sliding at low stress but promotes sliding at high stresses to minimize cleavage of the material (Fig. 1). An example of a flawless incorporation of such system design can be found in sea shells. These are nacre like structures which are made up of three dimensional brick and mortar layout. The bricks here are composed of hard hydroxyapatite substances of sub-micrometers in dimension. The mortar is made of soft organic materials which act as a high strength glue to hold the bricks together. In addition to this, mineral bridges and nanoscale-asperities exist between the bricks. At low stress, these bricks support most of the load and hence the structure has a high stiffness response. At higher stresses, instead of the bricks cleaving apart, the interface dissipates energy across many length scales – from molecular level viscous sliding of the organic glue to breaking of nano- and micro-scale asperities and bridges. These nacre-like structures have been used as inspiration for the development of synthetic lightweight ceramic structures with toughness on the order of some aluminum alloys. Another example is bone, which is functionally graded foam with a solid outer shell and a soft inner core. Multiple dissipation mechanisms from nanoscale sliding of crystals to crack bridging results in bone displaying greater ductility than steel despite being composed of very brittle hydroxyapatite molecules. It is such intrinsic and extrinsic reinforcement mechanisms which results in effective properties of hierarchical materials far above the individual components.

Why Polymers?

Polymers are simply assemblies of chains composed of various side groups along carbon-carbon backbone bonds. The backbone bonds composed of carbon linkages are extremely stiff. During deformation upon application of load, strain energy is stored in both the bond stretching and chain sliding. Due to the large amount of frictional sliding between molecules (chains), polymers usually display low specific modulus as compared to other classes of materials (ceramics or metals). However, they also display higher specific toughness or impact resistance than most other material classes. Because of their low density, polymers usually display low strength on a per-unit volume basis. In order to effectively utilize the inherent benefits of polymers for impact

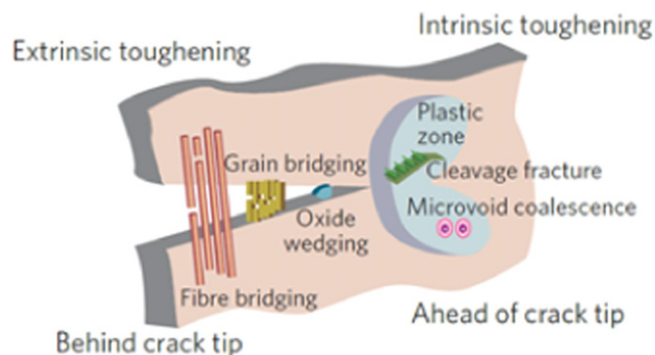


Fig. 1 Healthy human cortical bone resists fracture through complementary intrinsic and extrinsic contributions. Reproduced from Wegst, U.G.K., Bai, H., Saiz, E., Tomsia, A.P., Ritchie, R.O., 2014. Bioinspired structural materials, *Nature Materials* 14, 23.

resistance while maintaining strength and stiffness, it may be necessary to extrinsically reinforce polymers with the addition of filler materials. These fillers may be polymer-based or from other classes of materials. Numerous studies have shown the potential of filler reinforcement to improve properties of the resulting polymer based composites beyond the individual components as a result of hierarchical reinforcement mechanisms. Nano-polymer composites are also another class of composites with high interest. In these composites, one of the phases is in the nanometer dimensions. This results in multi-scale reinforcement mechanisms acting to retard crack propagation and improve toughness.

Functionally Graded Porous Composites

Continuous fiber reinforced composites have been used as an alternative to high strength metals in order to reduce weight and improve the specific load bearing capacity. They are primarily composed of mats of aligned fibers impregnated with a resin adhesive to bond and facilitate load transfer between adjacent fibers. The high degree of alignment and aspect ratio of the fibers permit utilization of a large portion of the fiber's inherent strength and stiffness. Aligned carbon fiber-epoxy composites for replacement of metal structural components have been of interest in the defense aviation and recently, commercial aviation sectors. While these composites provide very high strength and weight reduction, they are low in impact resistance due to the relatively brittle nature of both epoxy and carbon fibers. Of high interest in research is the development of bio-inspired intrinsic and extrinsic dissipation mechanisms in composites such that the overall strength is suitably maintained while significantly improving impact resistance.

Introducing porous structures can significantly reduce the weight further and potentially improve the toughness of polymers by increasing the complexity of failure or crack propagation. Additionally, the thin walls of foams can increase localized plane stress condition at the cell walls which acts to improve the toughness. The increased internal rotational and translation degrees of freedom of the foam cells also act to retard crack-propagation. These extrinsic reinforcing mechanisms in foams result in higher specific properties than the fully solid counterparts. The properties of foams are entirely dependent on its microstructure which has two main characteristic features – the cell size and the void fraction both of which can be controlled dependently or independently depending on the processing route.

Functionally graded structures have the potential to combine the benefits of all the above mentioned material systems in a continuous spatial-temporal variation that is advantageous in critical loading conditions. This has the benefit of eliminating discontinuous boundaries in a graded material. Discontinuous boundaries in conventional composites weaken the effect of hierarchical reinforcement. An example is functionally graded foams which can have properties superior to honeycombs. In a functionally graded foam, the porosity (void fraction) from the outside layer (solid) to the inside layer (foam) is continuously varied. In contrast, honeycomb structures often display sharp and discontinuous interfaces between the outside skin and the inside hollow core which creates natural sites of weaknesses.

Recyclability and Reproduction of Virgin Biopolymers

At the end of biopolymeric products, the goal is to close the loop and recycling the product to be reused whether as a secondary raw material or reproduce the virgin biopolymer by polymerization from the recycled monomers. The recycling can be broadly classified to mechanical recycling, organic recycling or composting, and chemical recycling or feedstock recovery. In mechanical recycling, the molecular structure of the precursor biopolymer is not broken but rather re-processed to new products through conventional techniques. However, the molecular chain is broken in the case of composting to biomass in addition to water and CO₂ or to the basic monomeric building block of the precursor biopolymer as in the case of chemical recycling.

For mechanical recycling, bio-based polymers and biopolymers can be recycled as most conventional thermoplastics but it need to be recycled in separate streams for each material type. The recycling stream for a specific type of conventional plastics (e.g., Polyethylene (PE) or Polyethylene terephthalate (PET)) can be used to recycle their counterparts of the bio-based alternatives like bio-PE and bio-PET. [Fig. 2\(a\)](#), ([European Bioplastics e.V, 2017a](#)) shows the general steps for typical mechanical recycling. In this type of recycling, the bio/bio-base-polymer is recycled into a new (secondary) raw material without altering the basic molecular structure of the precursor polymer. The bio-wastes are collected and segregated according to the material type through some techniques such as near infrared spectroscopy (NIR), laser or x-ray beside other techniques. After cleaning and grinding the bio-waste, it is recovered to new products by conventional processing techniques through direct melting or pelletizing at first before further processing.

Organic recycling or composting is another route for sustainability of biopolymers where biodegradation takes place under certain aerobic conditions within a specific period of time. Microbes, like bacteria or fungi and their enzymes, are able to digest the chain structure of compostable bio/bio-based-polymers as a source of nutrition. The speed of biodegradation depends on the temperature, humidity, and the number and types of microbes. The typical range of temperature for an industrial composting process is 50–70°C. All those requirements are given in industrial composting facilities to convert compostable plastic products into CO₂, water and biomass ([European Bioplastics e.V, 2017b](#)).

In chemical recycling, ([The Bioplastics Guide, 2016](#)) biopolymers cannot only be melted and used as granules again in a new application, but they can also be broken down into its starting chemical building block, the monomers. The monomers are used as the feed to the polymerization process to synthesize virgin biopolymer. For example, Lactic acid can be recovered from PLA and

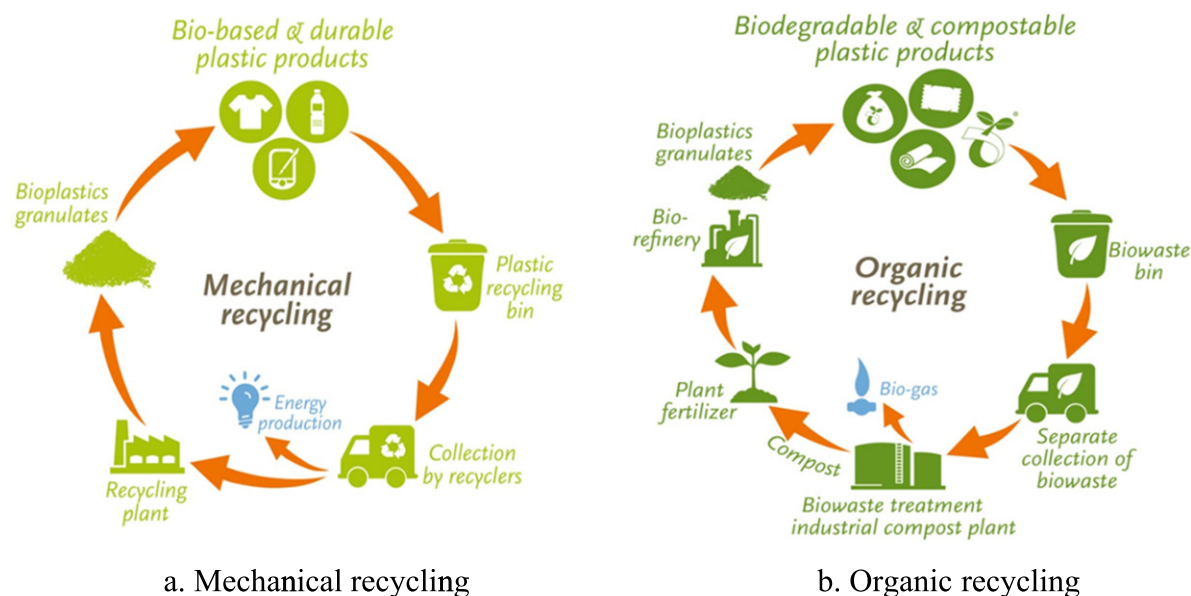


Fig. 2 Recycling processes for biopolymers. Reproduced from (a) European Bioplastics e.V., 2017a. Recycling. Available at: <https://www.european-bioplastics.org/news/publications/>. (b) European Bioplastics e.V., 2017b. Composting. Available at: <https://www.european-bioplastics.org/news/publications/>.

can be again used to make PLA resin. The exciting fact about chemical recycling is that same polymer from different products can be recycled all together to produce the precursor monomer. This process has the advantage of producing virgin polymers in addition to the cost reduction. Chemical recycling seems to be the future trend in polymers recycling with ongoing research efforts.

Case Study 1: Functionally Graded Porous Structures of PLA for General Structural Applications

Fabrication techniques of porous materials, in general, include but not limited to solvent particulate leaching (Shastri *et al.*, 2000; Harris *et al.*, 1998), gas foaming (Harris *et al.*, 1998; Nadella *et al.*, 2005; Zhou *et al.*, 2011), co-continuous melt blending (Yuan and Favis, 2005, 2004; Yao *et al.*, 2009; Pötschke and Paul, 2003; Singh *et al.*, 2004; Zhang *et al.*, 2010), and rapid prototyping (Landers and Mülhaupt, 2000; Ang *et al.*, 2002; Hoque *et al.*, 2005). However, the combination of those techniques lead to more control of the pores growth (Nadella *et al.*, 2005; Zhang *et al.*, 2010), and better mechanical properties (Harris *et al.*, 1998). Nadella *et al.* (2005), fabricated a closed-cell functionally graded PLA by annealing gas foamed samples with a temperature gradient rather than quenching in a bath of uniform temperature. The process of fabricating FG PLA porous structures in this case study is adopted from the work of Nadella *et al.* (2005) on constrained foaming. Details of the fabrication process can be referred to previous work of the author (Jahwari and Naguib, 2016) but will be summarized here.

Hydraulic compression mold was used at 185°C and 3 tons pressure to make the plate-like samples of PLA. The samples were then placed in a pressurized chamber of carbon dioxide (CO₂) at 400 psi for 48 h. CO₂ is the physical foaming agent in this process. The pressure and time of saturation are being selected based on previous experience with PLA to assure enough quantity of the physical blowing agent being dissolved. Skin layer can be formed if the samples left at atmospheric pressure for some time (desorption) after the 48 h of pressurizing in CO₂. However, the samples in this case study were annealed between two hot platens at different temperatures without desorption immediately after the pressure is released. The higher temperature is denoted as T_H and the lower temperature by T_L in the remaining of the text. The minimum of platens temperature is the glass transition point of PLA (56°C). This causes a gradual distribution in pores' sizes and density because of the induced thermal gradient. The pores grow bigger in size from the platen of lower temperature to the platen of higher temperature.

The functionally graded PLA had been fabricated successfully with a gradually changing porosity as shown in Fig. 3. The microstructure is observed to be of three main zones starting with large pores at the side of higher temperature (zone 1), then having a transition region with pores' sizes shifting to smaller pores (zone 2), then a sudden drop of porosity with pores distributed in islands-like structure but with much smaller pores than zones 1 and 2 (zone 3). The SEM images shown in Fig. 3 are for T_H = 130°C, T_L = 80°C and 5 min annealing. Zone 3 dominated 77% of the sample thickness. The remaining 23% of the thickness was for zones 1 and 2 combined.

The relaxation modulus as shown in Fig. 4 was obtained experimentally from the relaxation test for solid PLA, homogeneous porous PLA, and the 130–80°C functionally graded PLA (Fig. 3). Functionally graded PLA shows higher values for the relaxation modulus compared to the homogeneous porous PLA plates which is due to the gradient of pores distribution. The drop in relaxation modulus for the FG PLA is 8.44% only while it is 46.72% for the homogeneous case compared to the solid PLA sample.

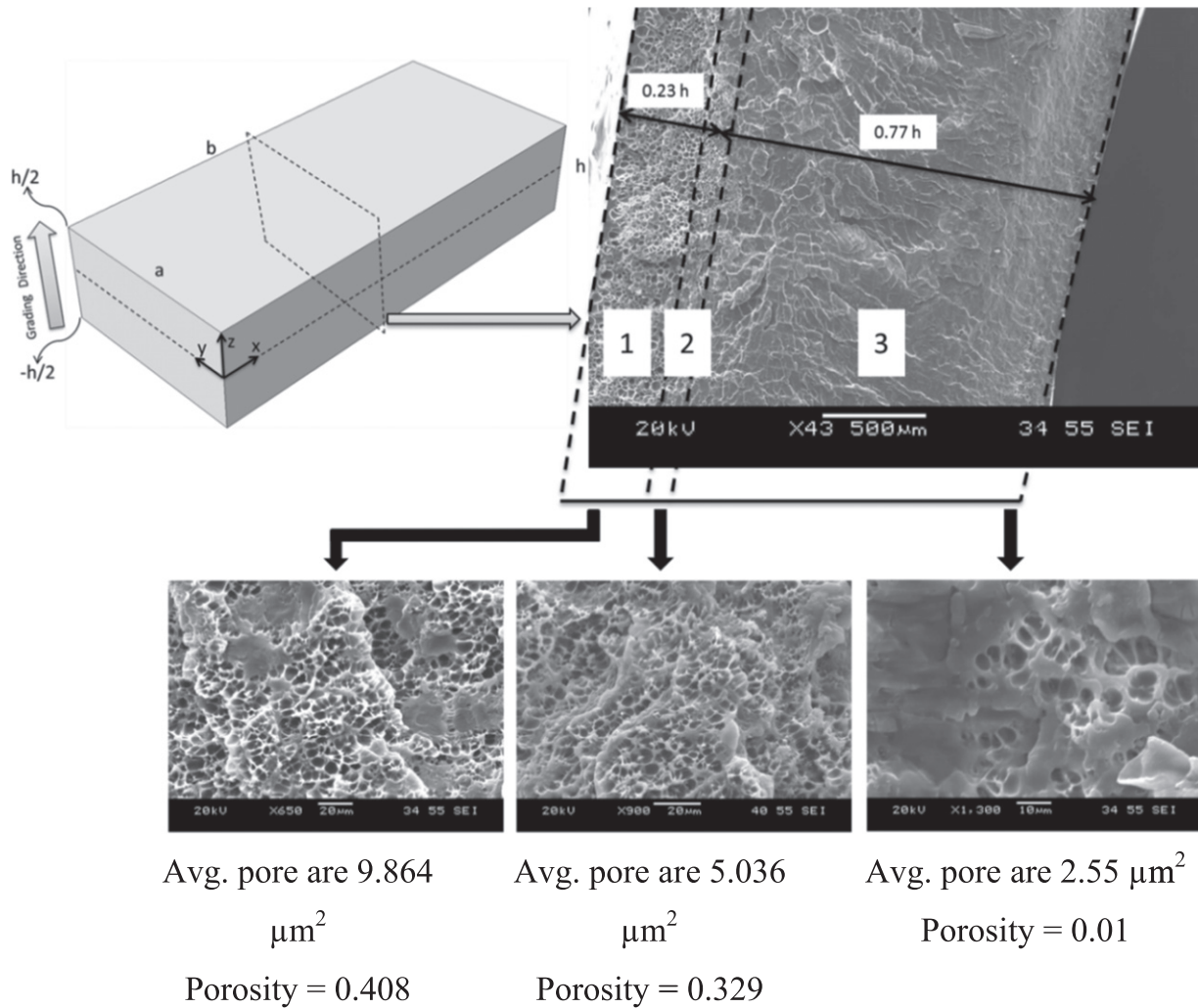


Fig. 3 Functionally graded PLA for $T_H=130^\circ\text{C}$, $T_L=80^\circ\text{C}$, and 5 min annealing (porosity = area of all pores/total area). Reproduced from Jahwari, F.A., Naguib, H.E., 2016. Analysis and homogenization of functionally graded viscoelastic porous structures with a higher order plate theory and statistical based model of cellular distribution, *Applied Mathematical Modeling* 40, 2190–2205.

The density of solid PLA is 1.24 g/cm^3 but it is measured to be 0.9052 g/cm^3 for the FG PLA. The drop in density for the FG PLA is 27% while the drop in relaxation modulus is 8.44% only. However, for the homogeneous porous PLA, the density drop is 29.063% only compared to 46.72% drop in the modulus. This is a clear evidence to show the potential of FG porous biopolymers as light weight but strong structures that can find a wide range of applications in many industries like automotive and aerospace load bearing members.

Case Study 2: Bio-Composites Made of Green HDPE for Impact Attenuation

In this case study, composites of Green High Density Polyethylene (GHDPE) and Ground Tire Rubber (GTR) were fabricated by using compression molding technique. Thermally activated microspheres were used as the mean to introduce a porous structure in the composite. The samples were made to test the impact absorption of the bio-composites according to ASTM D5420–10 by dropping a mass of 3.63 Kg (8 lb) from height of 0.635 m (25 in.). The experimental set up shown in Fig. 5 was developed to measure the residual impact load at the receiver side rather than at the impacted surface as done conventionally. The purpose of this setup is to pay more attention to the impact force transmitted across the material towards the receiver. The material is then designed to minimize the transferred force while keeping reasonable level of deformation. Fig. 5(b) shows a sample of the force output. There is a peak of the force at the time of impact which is considered as the transferred load to the receiver.

A strike-face (the face of the material structure which faces the striker) made of polyurethane and 5% silicon carbide was used to protect the porous structure from damage by the striker during impact. The polyurethane/silicon carbide sheet was attached to all the samples in order to compare the effect of GTR to porous structure in terms of energy absorption. The difference in

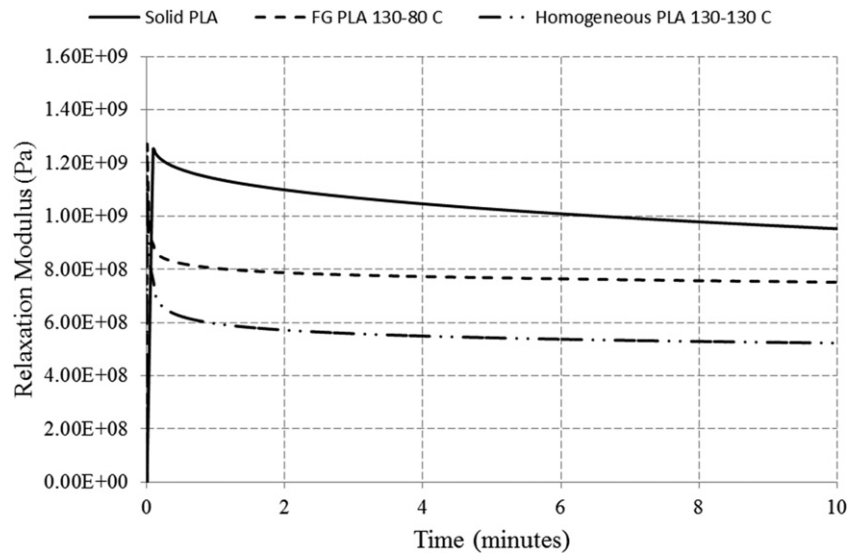


Fig. 4 Relaxation modulus of the solid, homogeneous and 130–80°C FG porous PLA. Reproduced from Jahwari, F.A., Naguib, H.E., 2016. Analysis and homogenization of functionally graded viscoelastic porous structures with a higher order plate theory and statistical based model of cellular distribution, *Applied Mathematical Modeling* 40, 2190–2205.

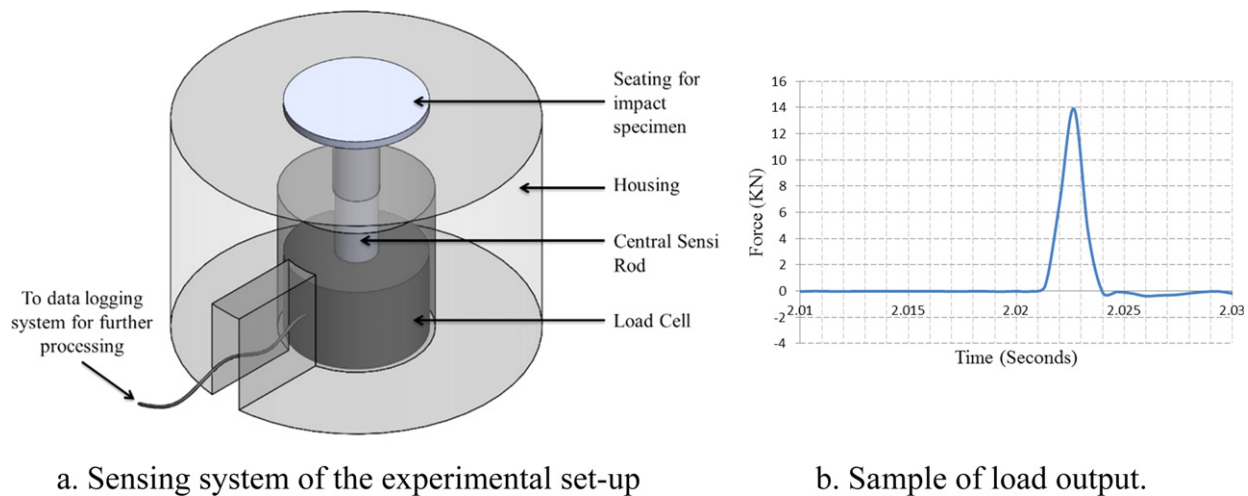


Fig. 5 Experimental set-up for impact testing and sample load output. Reproduced from Jahwari, F.A., 2016. Development and Modeling of Functionally Graded Porous Structures and Composites (PhD), Canada: Department of Mechanical and Industrial Engineering, University of Toronto.

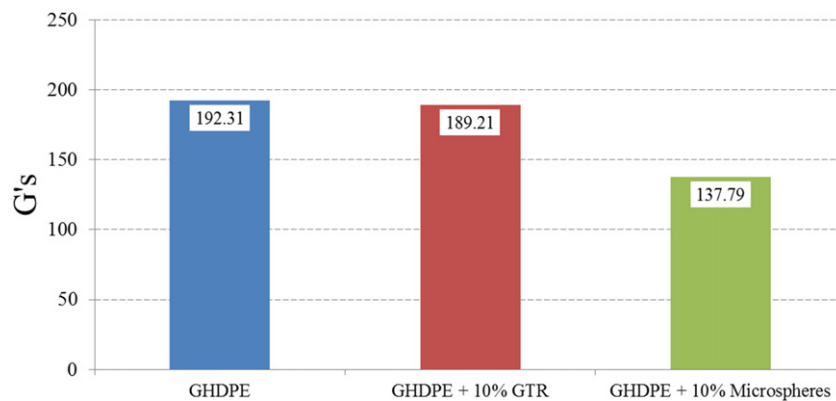


Fig. 6 Transferred acceleration from impact of rubber and porous base polymeric systems. Reproduced from Jahwari, F.A., 2016. Development and Modeling of Functionally Graded Porous Structures and Composites (PhD), Canada: Department of Mechanical and Industrial Engineering, University of Toronto.

transferred G's (the ratio between the transferred impact load and striker mass) between pure GHDPE and the corresponding composite with 10% GTR was negligible as can be seen in Fig. 6. This could be due to the strike-face that is a rubber-like material which hindered the effect of rubber particles. In contrast, the porous structure with 10% microspheres loading reduced the transferred acceleration by about 28% even with the strike-face. In a functionally graded porous structure, the strike-face can be integrated as part of the system which eliminates the possibility of delamination as well as ease of processing. This result proves the potential of bio-composites to be used for impact absorption and possibly replace the petroleum-base dampers. GTR is waste tires rubber which cannot be recycled and hence is harmful to the environment. The bio-composite developed in this case study, re-used GTR as a damping filler in a new composite material, which can have a wide range of applications in energy absorption systems.

See also: Biopolymer-Based Composites for Medical Applications. Bio-Polymeric Packaging Material for Packaging of Raw Food. Biopolymers in the Synthesis of Different Nanostructures. Manufacturing of Biodegradable Poly Lactic Acid (PLA): Green Alternatives to Petroleum Derived Plastics

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3D Printing of Polyether-Ether-Ketone Functional Prototypes for Engineering Applications

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Introduction

Polyether-ether-ketone (PEEK) has certain matchless advantages like its superb biocompatibility, markedly lower weight compared with conventional implant materials, lower tendency to absorb water, excellent mechanical properties, and thermal stability up to 400°C. By utilizing the advantages of additive manufacturing, it is possible to produce an implant according to patient specific contours and needs (Haleem and Javaid, 2019). PEEK has been sulfonated to serve the purpose of drug delivery. But sulfonated PEEK has compromised cytocompatibility, probably due to dispersion of sulfonic compounds in near vicinity. Also sulfonated PEEK shows lower rate of cell proliferation when compared against normal PEEK (Brum *et al.*, 2019). When smooth PEEK is compared against porous PEEK and titanium coated PEEK, then it is found that osseointegration results are superior for porous PEEK (Torstrick *et al.*, 2018). It has been reported that when PEEK is reinforced with short fibers of carbon and glass, that is, short carbon fiber-PEEK and short glass fiber (SGF)-PEEK, it is found that compressive strength comes out to be more for composites than neat PEEK. The failure mode in both types of composite is debonding of matrix–fiber interface. The fibers seem to have been pulled out of the matrix. If SGF-PEEK specimens are made one time by extrusion and another time by injection molding, it is found that extruded specimens possess lower value of toughness than injected ones (Chen *et al.*, 2019). Some studies suggested that if PEEK is coated with pure magnesium, a rise in antibacterial action has been observed (Yu *et al.*, 2018).

Fused deposition modeling (FDM) has marked its presence in the competitive manufacturing technologies owing to its relatively lower costs, versatility in hardware configuration, and capability to process a variety of materials. On reinforcing carbon nanotubes in PEEK, no sufficient impact on mechanical behavior is realized (Berretta *et al.*, 2017). During FDM of PEEK, it is found that diameter of the extruded filament depends upon the melt pressure and surface morphology of the extruded filament is also a function of melt pressure. It is observed that a defect-free surface tends to be produced when melt pressure is appropriately high (Geng *et al.*, 2019). In FDM, when raster angle is 0° and 90° while printing in horizontal (H) direction and when raster angle is 90° while printing in vertical (V) direction, it is observed that the best performance in fracture, tensile, and flexural tests comes out for H0°, then for H90°, and finally for V90° (Arif *et al.*, 2018). When carbon fibers are reinforced in PEEK (CF-PEEK), it is observed that there occurs a drop in density of printed composite material owing to presence of porosity and imperfections among adjacent layers (when taken in comparison against cast counterparts). The cast specimen shows relatively higher thermal conductivity and diffusivity when taken in comparison with the printed composite. Taking the advantage of FDM, anisotropy in thermal characteristics can be obtained according to user specific needs. But this is not possible in cast counterparts (Stepashkin *et al.*, 2018). The reported literature outlined that most of the work done so far has been focused to analyze the mechanical behavior from standard test specimens only and little has been done to test end-use products. When the question of optimization arises, studies take into account only the process parameters. Instead, optimization should comprise of all the factors including polymer type, 3-D printer type, along with process parameters. The mechanical performance can be boosted by employing a negative raster-raster air-gap. While extensive research has been done on certain process parameters, parameters like bed temperature and nozzle temperature have not been properly investigated (Popescu *et al.*, 2018). When annealing is performed on the PEEK printed specimens, it becomes clear that no marked effect is produced in the properties (Tseng *et al.*, 2018). If a coating of nanoparticles of silver is applied onto PEEK, it becomes clear that rate of cell proliferation and antibacterial activity is appreciably good (Deng *et al.*, 2017). PEEK finds applications in dental prosthesis, bone substitution, interbody spinal fusion, treatment of skull bone, and regenerative medicine. Some studies reported the investigations of tensile strength in PEEK-hydroxyapatite composite report an improvement in tensile strength (Yang *et al.*, 2017; Vaezi *et al.*, 2018; Singh *et al.*, 2019). In recent reported studies 3D printing of PEEK was performed with high-end commercial printers. But hitherto very little has been reported on the use of low cost FDM setup with small alteration in print head hardware for printing PEEK based functional prototypes. The functional prototypes prepared were subjected to mechanical, rheological, and thermal stability investigations to ensure their stability in various engineering applications.

Methodology

Fig. 1 shows the methodology for 3D printing of PEEK on low cost FDM setup. The PEEK thermoplastic granules were procured from local market and processed at 430°C temperature on single screw extruder to prepare a feed stock filament of diameter 1.75 ± 0.05 mm. The in-house prepared feed stock filament of PEEK was fed to the FDM printer. In this study a PRUSA printer (Prusa i3 MK3S kit) with alteration in print head (temperature range up to 430°C) was used.

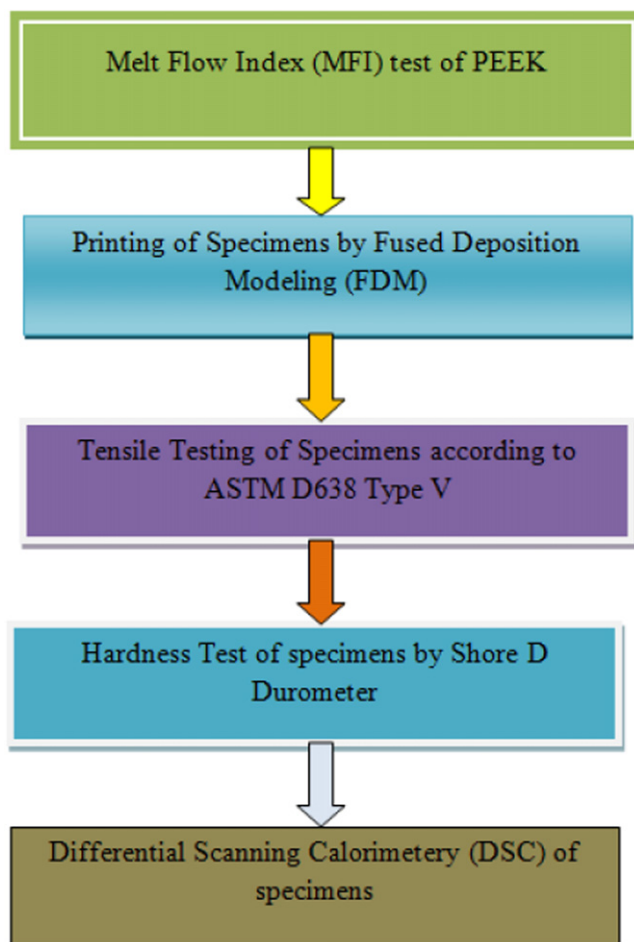


Fig. 1 Methodology for 3D printed polyether-ether-ketone functional prototypes.



Fig. 2 Melt flow index tester.

Experimentation

Melt Flow Index

PEEK has been tested for melt flow index (MFI) using ASTM D1238 standard. A load of 2.16 kg was applied at a temperature of 400°C to determine the flow rate. **Fig. 2** shows the pictorial views of MFI testing. Three repetitions were made to calculate the MFI, which comes out to be 3.01 g/10 min. The evaluation of MFI as basic rheological property was required to ascertain the flow of

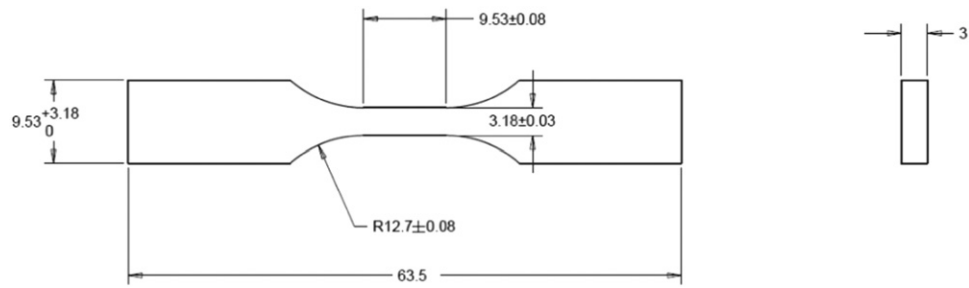


Fig. 3 ASTM D638 Type V specimen (All dimensions in mm).

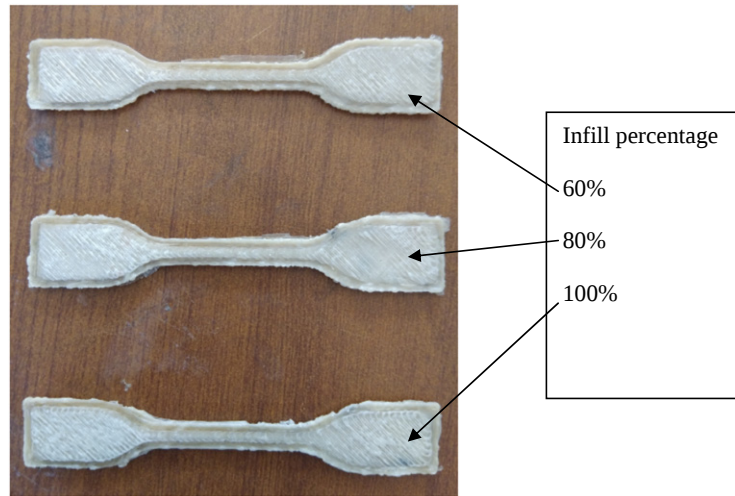


Fig. 4 Specimens printed by fused deposition modeling.

Table 1 Effect of infill percentage on peak strength

Sample no.	Infill density (percentage)	Peak strength (MPa)
1	60	51.3
2	80	68.8
3	100	70.2

extrudate from commercial FDM setup. Since most of commercial FDM setups are designed for thermoplastic with MFI of 2–2.5 g/10 min and work in the range of 250–300°C, to run the PEEK feed stock filament, the print head temperature needs to be increased.

After establishing MFI for the selected PEEK granules, feed stock filament was prepared on a single screw extruder. The in-house prepared feed stock filament was fed to FDM setup and functional prototypes were prepared at 50 mm/s printing speed, with 04 number of perimeter layers, print bed temperature 110°C, and travel speed of 120 mm/s with rectilinear fill pattern. The functional prototypes were prepared as per ASTM D638 type V standard (see Fig. 3).

Tensile Testing

Fig. 4 shows 3D printed tensile samples as per ASTM D638 Type V.

For understanding the effect of infill density expressed as infill percentage three specimens were printed with different infill density and subjected to tensile testing for evaluation of peak strength. Table 1 shows effect of infill percentage on peak strength.

As observed from Table 1, as the infill percentage is increased, tensile strength is improved. The typical values of tensile strength for PEEK in literature for injection molded samples have been found to be about 90 MPa. But here, for 3D printed samples



Fig. 5 Fractured tensile test specimen.

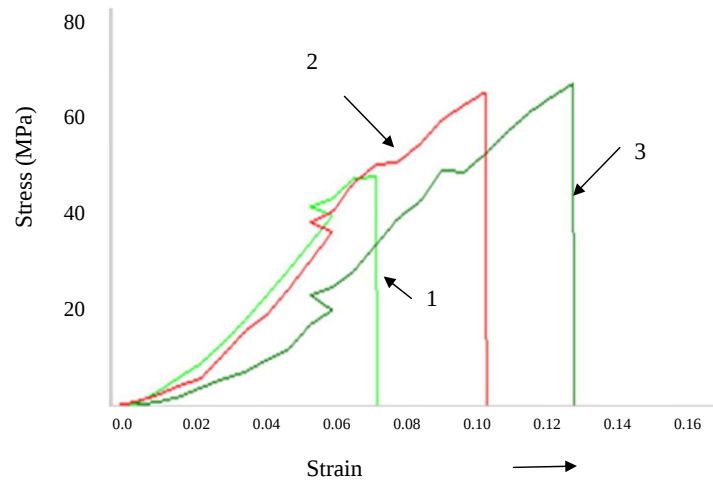


Fig. 6 Stress–strain diagram for 3D printed samples.

Table 2 Observations for Shore D hardness

Sample no.	Shore D hardness
1	70.5
2	74.0
3	80.0

Table 3 Observations for peak strength and Shore D hardness

S. no.	Peak strength (MPa)	Shore D hardness
1	70.26	80.26
2	70.27	80.27
3	70.28	80.28
4	70.24	80.24
5	70.24	80.24
6	70.23	80.23

observed value of peak strength has shown a dip, which may be due to porosity/air gap between subsequent layers during the printing process. **Figs. 5** and **6** respectively show the sample after tensile testing and stress–strain diagram for printed samples as per **Table 1**.

Hardness Test

The 3D printed specimens as per **Table 1** were tested for hardness on Shore D Durometer (see **Table 2**).

As observed from **Table 2** maximum hardness was observed for sample 3 with 100% infill density, which is obvious as more density will result in more rigidly stacked layers.

Based upon observations in **Tables 1** and **2** sample no. 3 was considered better. Now to understand whether the process is under statistical control, 06 PEEK samples were printed with 100% infill density, 50 mm/s printing speed, with 04 number of

Table 4 Observations for peak strength for 06 repetitions

Run no.	Observations for peak strength (MPa)	Average	Over average/below average (OA/BA) w.r.t. mean	Above (A) or below (B) the previous reading
1	70.26	70.25	OA	–
2	70.27	70.25	OA	A
3	70.28	70.25	OA	A
4	70.24	70.25	BA	B
5	70.24	70.25	BA	–
6	70.23	70.25	BA	B
Average	70.25		E(run) = Change from OA to BA = 1	Change from A to B = 1

Table 5 Observations for Shore D hardness for 06 repetitions

Run no.	Observation	Average	Over average/below average (OA/BA) w.r.t. mean	Above (A) or below (B) the previous reading
1	80.24	80.25	BA	–
2	80.24	80.25	BA	–
3	80.23	80.25	BA	B
4	80.26	80.25	OA	A
5	80.27	80.25	OA	A
6	80.28	80.25	OA	A
Average	80.25		E(run) = Change from BA to OA = 1	Change from B to A = 1

perimeter layers, print bed temperature 110°C, and travel speed of 120 mm/s with rectilinear fill pattern. The observations for peak strength and Shore D hardness is given in **Table 3**.

Based upon **Table 3**, **Table 4** and **Table 5** respectively show statistical analysis for 06 repeated observations with respect to (w.r.t) mean value.

In the present study, the sample size of the observations as well as the number of samples was small, so the X-bar and R-chart could not been drawn.

Calculating standard normal deviate (Z) for OA and BA:

Expected number of above and below runs, $E(\text{run}) = 1 + N/2 = 4$

And standard deviation, $\sigma_{AB} = \sqrt{(N - 1)/4} = 1.118$

So, $Z_{OABA} = (1 - E(\text{run})_{OABA})/\sigma_{OABA} = -2.68$

$|Z_{OABA}| = 2.68$

Further, calculating 'Z' for A and B:

Expected number of up and down runs, $E(\text{run}) = (-1 + 2N)/3 = 3.666$

$\Sigma_{AB} = \sqrt{(-29 + 16N)/90} = 0.8628$

And, $Z_{AB} = (-E(\text{run})_{AB} + 1)/\sigma_{AB}$
 $= -3.091$

$|Z_{AB}| = 3.091$

For calculating Z critical, [NORMSINV (- $\alpha/2$)+1] formula of Microsoft Excel has been used by assuming a marginal error (α) as 0.05.

$$\text{So, } Z_{\text{critical}} = 1.959963$$

It has been found that $|Z_{OABA}|$ and $|Z_{AB}|$ both have greater value than Z_{critical} , which highlights the presence of random-free pattern. In the present work, the cumulative probability (P_i) plot was drawn with the help of following rule:

$$\text{Cumulative Probability, } P_i = (-0.5 + \text{Sr.No.})/N$$

Where "N" is the total number of observations and "Sr. No." is serial number of observation in ascending order.

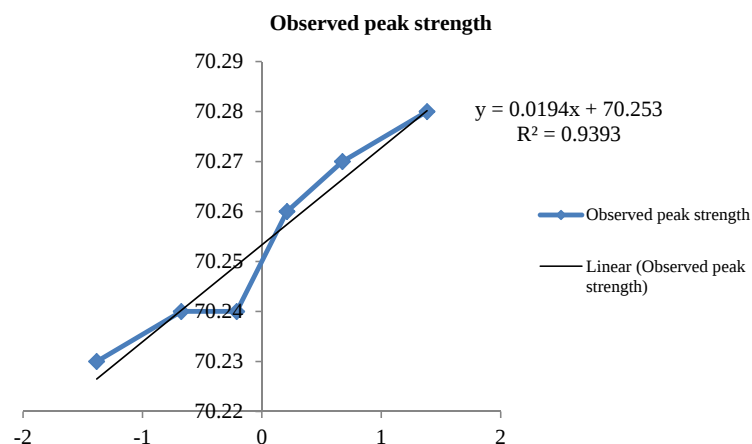
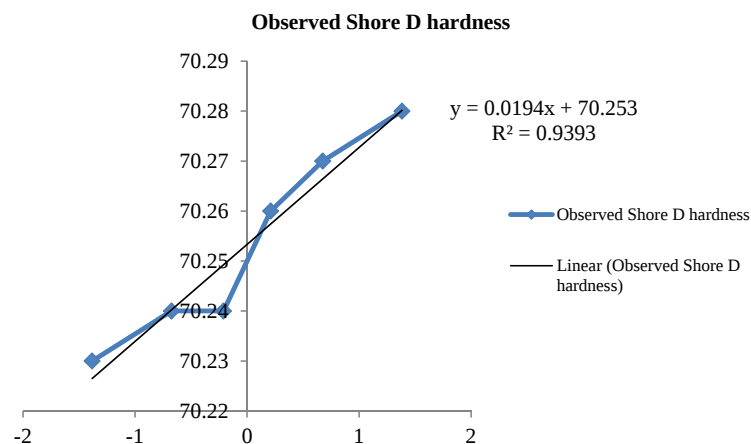
Standard normal deviate (Z):

$$Z = (-\mu + X_i)/\sigma$$

As "Z" follows normal distribution with (mean (μ) = 0 and standard deviation (σ) = 1) hence the equation obtained presently follows normal probability curve. For the calculation of "Z," [NORMINV(P_i)] formula of Microsoft Excel has been used. The observed values, P_i , and Z (in ascending order) are given in **Table 6**. Based upon **Table 6**, **Figs. 7** and **8** shows the best fitted curve for normal distribution of data (peak strength and shore D hardness).

Table 6 Observed value, P_i and Z

<i>S. no.</i>	<i>Observed value (peak strength)</i>	<i>Observed value (Shore D hardness)</i>	P_i	Z
1	70.23	80.23	0.083	−1.38299
2	70.24	80.24	0.25	−0.67449
3	70.24	80.24	0.416	−0.21043
4	70.26	80.26	0.583	0.21043
5	70.27	80.27	0.75	0.67449
6	70.28	80.28	0.916	1.38299

**Fig. 7** Best fitted curve for normally distributed data (peak strength).**Fig. 8** Best fitted curve for normally distributed data (shore D harness).

From the above statistical tests, it has been observed that a nonrandom pattern has been followed by the aforesaid data. Further the data follows normal probability curve as desired hence there is a high probability for this process to be statistically controlled in case of batch and medium production runs.

Differential Scanning Calorimetry

Finally sample 3 (as per Table 1), with better mechanical strength and hardness, was subjected to differential scanning calorimetry (DSC) analysis for thermal stability. Exothermic and endothermic heating/cooling rate was 10°C/min with N₂ gas supply of 50 ml/min. Fig. 9 shows the DSC graph for sample no. 3. As observed from Fig. 9, in two repetitive heating/cooling cycles the melting peak was observed at around 338.04–339.71°C and solidification peak 277.57–281.08°C. Similarly the change in normalized heat input was insignificant (i.e., from 24.88 J/g to 24.77 J/g). This justifies the thermal stability of the selected 3D printed samples for use as biomedical scaffolds/implants.

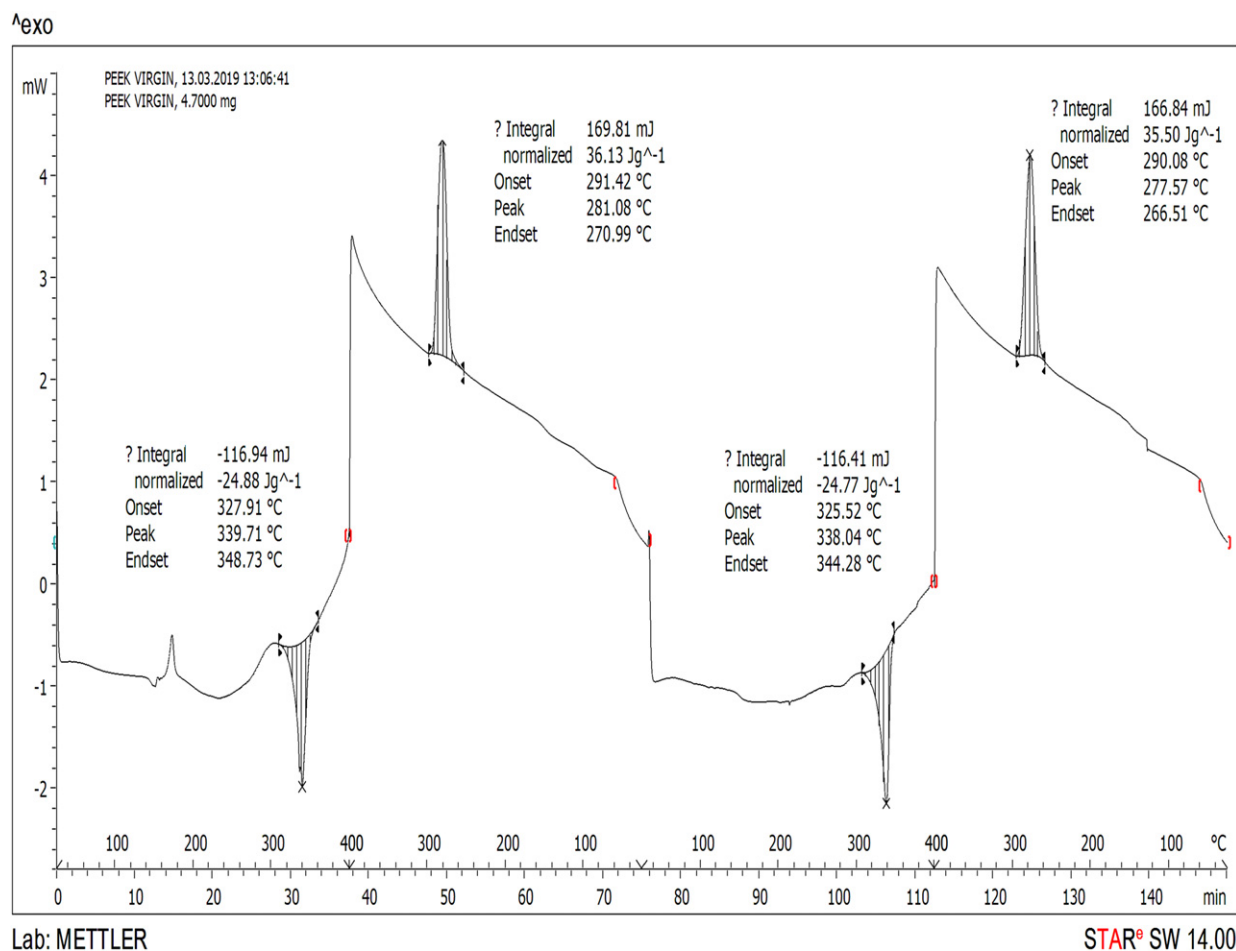


Fig. 9 Differential scanning calorimetry of 3D printed polyether-ether-ketone sample no. 3.

3D Printing of PEEK for Sustainability

The PEEK based composite materials are a novel invention and the application of such materials for handling nuclear waste is in their beginning phase. Some studies have been reported for use of PEEK polymers for suitable resistance to radiations (Kulshreshtha and Vasile, 2002). The resistance to radiations and high temperatures still precludes this polymer based composite from uses inside the core of fission or fusion reactors. But this material has some applications within the nuclear industry and space industry, at least where the radiation fields are moderate or low. The use of 3D printed PEEK based containers for radioactive waste storage applications needs to be explored. Whatever is the type of radiation (charged or neutral particle, or electromagnetic radiation of enough energy) its effect always results in excitation and ionization of the polymer chain. Polymers are usually electrical insulators; if they are subjected to high dose-rate irradiation, the number of free electrons may reduce significantly their resistivity, but this is only a transient effect. If charged particles are used, electric charges may accumulate in organic insulators and seismic loads, making this material very useful for the present day nuclear waste disposal chamber (Tavlet and Ilie, 1999). The 3D printed PEEK based waste container can be crucial components in conducting a defensible safety assessment.

Summary

The 3D printing of PEEK based functional prototypes was successfully performed in the present case study with small alteration in print head hardware of a commercial FDM setup. The functional prototypes prepared were subjected to mechanical, rheological, and thermal stability investigations. The result of this study suggests that 3D printed PEEK functional prototypes are thermal stable. The MFI 3.01 g/10 min is acceptable for successful printing on any commercial FDM printer with small iteration in print head. Finally peak strength of 70.2 MPa and surface hardness of 80 Shore D was obtained for 3D printed functional prototypes, which are acceptable for biomedical scaffolds/implants. The results of the

study suggest that data for peak strength and shore D hardness follows normal probability curve, hence there is high probability for this process to be statistically controlled.

Acknowledgment

The authors are highly thankful to SERB under AISTDF Seretariat (File No. IMRC/AISTDF/R&D/P-10/2017, Dated 01-02-2018) for financial support.

See also: 3D Printing of Carbon-Based Conductive Materials for Electrochemical Energy Storage (EES) Application. A Comprehensive Study for 3D Printing of Rapid Tooling From Reinforced Waste Thermoplastics. Biocompatible Thermoplastic Composite Blended With HAp and CS for 3D Printing. Experimental Investigations for Friction Stir Welded 3D Printed Dissimilar Thermoplastics With Consumable Tool. Experimental Investigations for Joining of 3D Printed PEEK Substrates for Biomedical Applications. Joining of 3D Printed Dissimilar Thermoplastics With Consumable Tool Through Friction Stir Spot Welding: A Case Study. Joining of 3D Printed Dissimilar Thermoplastics With Friction Welding: A Case Study. The Effect of CaCO₃ Nanoparticles and Chitosan on the Properties of PLA Based Biomaterials for Biomedical Applications

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Recyclability of Natural Fiber-Filled Thermoplastic Composites

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Introduction

The use of natural fiber composites has been becoming popular since the end of the 20th century. One of the main reasons is the environmental awareness. Besides, many researchers reported the advantages of the natural fiber composites as compared to the conventional composites in some areas, including acceptable specific properties, biodegradability, energy recovery, CO₂ balance, and recyclability properties. Those advantages lead to the growing demand in a lot of industries, including automotive, building, and construction (Faruk *et al.*, 2014).

Many authors mentioned the environmental issues to describe the advantages of natural fiber composites in comparison with conventional composites, such as glass and carbon fiber reinforced polymers (GFRP and CFRP). It is related to the properties of a natural fiber, such as biodegradable and CO₂ balance (Bledzki and Gassan, 1999; Braga *et al.*, 2017; Maciel *et al.*, 2018; Monteiro *et al.*, 2009; Shahinur and Hasan, 2019). However, the environmentally friendliness of a natural fiber composite becomes questionable when the natural fiber is incorporated in a synthetic polymeric matrix due to ecological threat from the polymer. It is well known that the synthetic polymers are resistant to biodegradation. The volume of polymeric waste has been accumulated in the environment and creating a serious problem (Fakhrul and Islam, 2013). Hence, recyclability of the composites must be considered.

Another question is then raised when a natural fiber is incorporating into a thermoplastic polymer. In theory, a close-loop recycle of most thermoplastics is possible when it is not contaminated with other materials (Hopewell *et al.*, 2009). The possibility is then questioned when the thermoplastic is “contaminated” with a natural fiber. In this chapter, reports related to the recyclability of natural fiber-filled thermoplastic composites and its recycling processes are reviewed. For better understanding, the discussion is begun with the waste management strategies and recycling processes of the composites in general, followed by the recycling process of thermoplastic composites and the natural fiber-filled thermoplastic composites.

Waste Management Strategies

There are five broad waste management strategies, also called as waste hierarchy, namely prevention, preparing for reuse, recycling, recovery, and disposal (Rybicka *et al.*, 2016). Table 1 shows the stages of management hierarchy, starting from the most desirable one (Defra, 2011).

Prevention or waste minimization offers the highest economic and environmental benefit by increasing the efficiency of the material usage and minimizing the waste at the first place. One of the efforts is developing a manufacturing process which results in minimizing the production waste (Conroy *et al.*, 2006). Preparing for re-use, including refurbishing and repairing parts, is also a desirable option. However, not all the products can be reused. Hence, in regards with composite materials, most of the researcher focus on the recycling technologies to convert the unused materials into another valuable products (Correia *et al.*, 2011; Rybicka *et al.*, 2016). Some efforts fall into recycling stage in the waste management hierarchy but some others fall into reuse and energy recovery (Rybicka *et al.*, 2016). Hence, practically, recycling process of a composite covers three stages in the waste management hierarchy, including preparing for re-use, recycling, and other recovery.

Recycling Processes of Composites

Developments in composite recycling is highly related with developments in thermoset composites recycling. However, some of them can be modified to recycle thermoplastic composites. Research in this area is divided into three eras (Overcash *et al.*, 2017). The

Table 1 The waste management hierarchy

Stages	Includes
Prevention	Waste minimization, using minimum volume of material in design and manufacturing, longer product life-time, reuse, avoiding the using of hazardous materials
Preparing for re-use	Refurbishing and repairing parts
Recycling	Converting waste into a new product
Other recovery	Any activities recovering energy, backfilling operations
Disposal	Landfilling and combustion without energy recovery

Note: Defra, 2011. Government Review of Waste Policy in England 2011. London: Department for Environment, Food and Rural Affairs. Rybicka, J., Tiwari, A., Leeke, G.A., 2016. Technology readiness level assessment of composites recycling technologies, J. Clean. Prod. 112, 1001–1012. doi:10.1016/j.jclepro.2015.08.104.

first era is in the years of 1980–2006, when the efforts focus on recovering fibers and resin from composite. The second era is in the years of 2009–2012, when researchers find a way to incorporate recovered fibers into a new thermoset resin, following by the third era (2012–2016) when the development turned into retaining the original fiber/resin properties and make a new composite.

Recycling processes are carried out in various techniques. They are divided into at least three processing, namely mechanical, thermal, and chemical processing (Asmatulu *et al.*, 2014; Feraboli *et al.*, 2012). In mechanical processing, a composite part is crushed through a series of mills producing various particle sizes ranging from 5 μm to 10 mm. Product of the recycle process, named as recyclate, is still a mixture of the fiber and matrix. The recyclates can be used as a filler in another composite, which is not a structural composite, as a replacement of calcium carbonate. This filler may reduce the density of the replaced materials. Moreover, there is a potential use of fibrous recyclates as reinforcement (Asmatulu *et al.*, 2014; Pickering, 2006), despite higher energy is needed to improve the quality of a recyclate (Shuaib and Mativenga, 2016).

Thermal processing is commonly used to separate fibers from a thermoset matrix. It requires external heating to transform the phase of the matrix into liquid or gas and hence separating the fibers from the polymer (Asmatulu *et al.*, 2014; Conroy *et al.*, 2006; Pickering, 2006). Due to the difference in decomposition temperature among elements in a composite, the thermal process is also used for separating the components of a composite. As an example, when the temperature of glass fiber reinforced composite is increased, the matrix will firstly decompose and leave the glass fibers and other inorganic parts as a residue, due to higher decomposition temperature. The thermal processing includes combustion, pyrolysis, and fluidized-bed processes (Asmatulu *et al.*, 2014; Oliveux *et al.*, 2015).

Combustion process of thermosetting polymer matrix composite produces a source of heat which can be converted into various energy, including electricity and mechanical energy, due to a high calorific value of the thermosetting polymer (Asmatulu *et al.*, 2014). Hence, when a thermosetting resin is burned, the composite converts into energy and a residue contained fibers and other inorganic materials. The residue can then be used as a reinforcement or filler in a new composite as well as other purposes. The burning process may also be carried out in a cement kiln. In this process, the heat released from the matrix is used for the cement production. At the same time, the glass silica is used as a filler in the cement. As a result, it reduces the overall cost (Asmatulu *et al.*, 2014; Pickering, 2006).

Fluidized-bed is a bed of silica sand which is fluidized with a hot air stream. It heats up a composite rapidly and volatilized the organic part of the composite, leaving the inorganic parts as a solid particulate. The process is then completed with Pickering's process to separate fibers from fillers. Furthermore, the organic part or the resin is degraded by transferring it to a secondary combustion chamber at a temperature of about 1000°C. The degradation produces a clean flue gas. Hence, the process produces fibers and fillers, that can be reused in a new composite manufacturing or other applications, and a clean flue gas that can be used as a source of heat or energy (Asmatulu *et al.*, 2014; Oliveux *et al.*, 2015; Pickering, 2006; Pickering *et al.*, 2000; Zheng *et al.*, 2009).

Pyrolysis is a thermal decomposition of materials at a high temperature in the absence of oxygen. This process at 300–800°C allows the recovery of long fibers under the controlled temperature and time (Blazsó, 2009; Yang *et al.*, 2012). Mainly, this process aims to obtain the recycled fiber in a good condition to be reused in other applications (Yang *et al.*, 2012). Since the beginning of 21st century, microwave-assisted pyrolysis has also been developed. It offers very fast thermal transfer by heating the materials in its core (Oliveux *et al.*, 2015).

Chemical recycling process is an effort to dissolve the solid composite into different liquid products (Asmatulu *et al.*, 2014). The process is often called solvolysis and classified based on the solvent used. The classification namely hydrolysis, glycolysis, and acid digestion, which are carried in the solution of water, glycols, and acid, respectively (Yang *et al.*, 2012). There are many researchers reported the experiments on chemical recycling process with various solvents under various temperature and pressure (Bai *et al.*, 2010; Liu *et al.*, 2012; Piñero-Hernanz *et al.*, 2008). However, only few of them successfully reached the industrial-scale (Oliveux *et al.*, 2015).

Recycling Processes of Thermoplastic Composites

Recycling method of thermoplastic composites includes mechanical, thermal and chemical recycling (Oliveux *et al.*, 2015; Yang *et al.*, 2012). Among the processes, remelting and remolding process, or often called as direct re-processing, is more studied for scrap processing. This process offers no separation process of fiber and matrix but results (Yang *et al.*, 2012).

Schinner *et al.* (1996) studied two approaches in recycling carbon-fiber-reinforced thermoplastic composites. The first approach is grinding the composites and using the grinding fractions in injection or press molding compounds. The other approach is reforming process without grinding. Both approaches show minimum changes in the material properties, indicating a good recyclability of the thermoplastic composite. Moreover, Steenkamer and Sullivan (1998) reported a similar result for a cyclic thermoplastic composite material, which was recycled by grinding, followed by compounding, and injection molding. Physical and thermal properties of the recycled cyclic thermoplastic materials are comparable to those of a commercially available thermoplastic composite, with an exception in the elongation.

Li and Englund (2011) reported a close-loop recycling of the thermoplastic composite is possible under a proper process parameter. The particle size of mechanical refined scraps affects the mechanical properties of a recycled thermoplastic composites. The finer scraps resulted in the higher mechanical properties. Furthermore, a recent study on the recycling of thermoplastic reported that a chemical process, namely dissolution, allows a recovery of both fiber and matrix while maintaining their stiffness and strength (Cousins *et al.*, 2019; Liu *et al.*, 2018).

Recycling Processes of Natural Fiber-Filled Thermoplastic Composites

Despite the increase in research on natural fiber-filled thermoplastic composites, only few of them focused on its recycling and recyclability. Morán *et al.* (2007) extruded a flax fibers-reinforced polypropylene (PP) at multiply cycles and reported that the

process resulted in thermo-mechanical degradation. The recycled product performed higher modulus but lower in strength. The product, however, can be used for industrial application when a compatibilizer is incorporated.

Meanwhile, Sanetuntikul (2008) reported that the mixture of wood plastic composite (WPC) scrap and WPC fresh-feed at a ratio of 30:70 can be recycled up to five cycles without significant effect to the thermal and mechanical properties of WPC.

Furthermore, Twite-kabamba *et al.* (2010) recycled a birch fiber/low density polyethylene up to ten cycles of extrusion. It was found that the extrusion process increased the polymer crystallinity and decreased the zero-shear viscosity. At the same time, the fiber length and diameter also decreased.

Recently, recyclability studies were also carried out on oak wood flour (WF) filled HDPE (Bhattacharjee and Bajwa, 2018) and sugarcane bagasse (SB) filled PP (Lila *et al.*, 2018). After recycling process, the strength, stiffness, and crystallinity of WF/HDPE decreased while the strain and thermal stability increased. Meanwhile, the tensile properties, hardness, and crystallinity of SB/PP increased after recycling without significant.

The various results reported in regard with the recycling of natural fiber-filled composites indicating that there are many factors affects to the recyclability of the composite. The different properties of the recyclates are obtained in consequence of the raw material, processing, and environmental effects (Winandy *et al.*, 2004).

Summary

In general, among so many composite recycling processes, the most feasible recycling process for the thermoplastic composites is to reproduce with or without scrapping. A close-loop recycle of natural fiber-filled thermoplastics is possible due to the properties of thermoplastic. The close-loop recycling of thermoplastic has been widely practiced in industries. An addition of the natural fiber, however, make it more complicated. The properties of the fiber, including physical and chemical properties, play an important role in recyclability of the composite. The most issue discussed in many reports is the fiber degradation during processing, due to thermal and shear stress. In the end, there are a huge area of research need to be explored in regards with the recyclability of natural fiber-filled thermoplastic composites. The development continues.

See also: A Comprehensive Study for 3D Printing of Rapid Tooling From Reinforced Waste Thermoplastics. Biocompatible Thermoplastic Composite Blended With HAp and CS for 3D Printing. Experimental Investigations for Friction Stir Welded 3D Printed Dissimilar Thermoplastics With Consumable Tool. Influential Parameters on Formation of PEMs on Recycled Fibers: A Review. Joining of 3D Printed Dissimilar Thermoplastics With Nonconsumable Tool Through Friction Stir Welding: A Case Study. Polymer-Recycling of Bulk Plastics. Recycling of Plastics for Low Cost Construction

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Renewability of Polymer-Based Thin Films for Packaging

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Overview

A brief summary of the history of food packaging (Risch, 2009) shows that the development of materials has impacted the food industry. Before 7000 BCE, ceramics and glass were used for packaging. In the 1900s, the catalytic effect of the military's need for nonperishable packaged food led to the use of synthetic polymers for packaging. Throughout that entire period to now, the ingenuity of humans has made an impact on the environment. Risch (2009) makes a brief note on efforts towards sustainability in the summary of her paper. Certainly not being harmful to the environment or depleting natural resources (i.e., sustainability) would be desirable. The reality is that nearly all of the thin films currently used for packaging comes from a non-renewable resource, fossil fuels (van den Oever *et al.*, 2017; Hodges, 2018).

Hodges (2018) describes the current global status of the cost of crude oil and the production of polymers from crude oil. He notes that in 2016, 46% of poly(ethylene) (linear low density poly(ethylene) (LLDPE), low density poly(ethylene) (LDPE), and high density poly(ethylene) (HDPE)) was used for flexible packaging; 22% of poly(propylene) (PP) was used for flexible packaging. This represents nearly 58 million tons of these materials. Hodges discusses the uncertainties in the global market with respect to crude oil and polymer production from the crude oil. Significantly, he describes the change to manufacturing sustainable materials; his current prediction is that sustainable materials will be manufactured from non-renewable polymer-based materials. He notes that the cost of manufacturing packaging from renewable resources is not competitive with the production of packaging from recycled non-renewable polymer-based materials.

Pollution caused by non-sustainable plastics is a major concern (Kershaw, 2015; WWF; North and Halden, 2013; Bradley, 2017) that has generated a variety of views. The initial concern about the larger, visible pieces of non-sustainable plastics has evolved to a concern about microplastics (Rochman, 2018). Additionally, the focus of research on microplastics has moved from materials in the oceans to materials in fresh water, soils, and the air. In other words, the concern has literally become global (Rochman, 2018). A multi-year study of plastic debris in the eastern Pacific Ocean, combined with data from other sources, gave a clear picture of the concentration of the debris in a particular region of the ocean (Law *et al.*, 2014). Over an 11-year period (2001–2012), annual cruises occurred where samples were collected systematically from the eastern part of the Pacific Ocean. An estimate of more than 21×10^3 tons of floating microplastic was derived from this study. The observed concentration of the plastic in the northeast region of the Pacific Ocean was consistent with models based on the currents of the ocean. Law *et al.* (2014) are careful to note the challenge of obtaining useful data on the trends in accumulation of plastics in the ocean. For example, they attempt to include the effect of wind data into the conclusions from their data set but note that this wind data is not always available. Regardless, their results clearly provide a basis for understanding the magnitude of the accumulation of plastic waste in the ocean.

Data on the transport of plastics from rivers to oceans (Schmidt *et al.*, 2017) was interpreted to estimate that between 0.4 and 4×10^6 tons per year are so transported. As expected, calculations on the concentration of plastic waste in rivers relative to the concentration of plastic waste in oceans showed that the river concentration is greater than the ocean concentration by a factor of 40–50 times. The information for the this paper (Schmidt *et al.*, 2017) paper came from ten peer-reviewed publications and three non-peer-reviewed publications. These overviews on ocean data (Law *et al.*, 2014) and rivers (Schmidt *et al.*, 2017) are valuable resources on this environmental concern. Very recently, the American Chemistry Council reported actions taken at the June 2018 G7 meeting in Canada indicating the global concern for this issue (Killenger, 2018). Obviously, removing the non-renewable plastic waste from our oceans is one issue; developing a renewable resource solution to packaging is equally important.

Renewability

Renewability refers to materials that can be replaced by new growth. In that sense, natural polymers such as polysaccharides are renewable. They are obtained from various natural sources. Unfortunately, without modification, polysaccharides cannot be a replacement for polymers from fossil fuels that are used to produce thin films that are used for packaging. The permeabilities to oxygen, carbon dioxide, and water vapor of low density poly(ethylene) (LDPE), as well as the mechanical properties of films prepared from LDPE, are superior to the properties of polymeric thin films prepared from renewable materials. A thin film made from starch, for example, will have a high water vapor sensitivity and will also have poor mechanical properties. These differences will be presented in this article.

Considerable research has been published on polymeric thin films from renewable resources. A number of recent reviews provide an indication of the magnitude and importance of the work on this subject (van den Oever *et al.*, 2017; Cazon *et al.*, 2017; Wang *et al.*, 2018b; Madhumitha *et al.*, 2018; Schneiderman and Hillmyer, 2017; Hu, 2014; Nagarajan *et al.*, 2016; Shah *et al.*, 2015). Although business projections predict an increase in the production of polymeric thin films from renewable resources (van den Oever *et al.*, 2017), the contribution of these films to the total production is predicted to remain small in the near future.

Competing strongly with the development of polymeric thin films from renewable resources is the development of thin films through recycling of fossil fuel-based polymers (Hodges, 2018; Neufeld *et al.*, 2016). Improvement in both cost and properties for renewable resource polymeric thin films is necessary if these films are to be competitive with polymeric thin films obtained from non-renewable fossil fuels. However, the cost factor will not be the focus of this article. Instead the focus will be on the properties of the polymeric thin films. These properties will be presented for neat renewable materials and for modified renewable materials. These properties for the renewable materials will be compared to those of commonly used packaging thin films synthesized from fossil fuels. The physical, thermal, and mechanical properties will be discussed. Just as the properties of synthetic polymers can be modified by mode of synthesis, modest changes in functionality, addition of nanomaterials, various degrees of crosslinking, etc., so can natural polymers such as polysaccharides be modified in order to improve properties for particular applications. It is from this point of view that this article will be presented.

This article is not intended to be a complete review; it is intended to be a presentation of recent work done in the area of improving the properties of polymeric thin films from renewable resources for the application of packaging. While it is hoped that there will be a “magic bullet”, or at least hint of a pathway towards potential “magic bullets”, that will inspire production of thin films for packaging that come from renewable resources, it is also hoped that the readers of this article will be inspired to continue the effort to develop polymeric thin films from renewable sources.

Non-Modified Biopolymer Films

This section will discuss films from renewable sources that have been processed but are essentially the renewable material. Later in this article, modified biopolymer films will be discussed.

Polysaccharides

Polysaccharides include starch, cellulose, chitin, and hemicellulose. Considerable work has been done historically on the modification of these materials in order to improve their properties for particular applications while still retaining their ability to biodegrade without environmental damage (Narayan, 1994; Roman, 2010; Halley *et al.*, 2008; Hansen and Plackett, 2008). More recently, this topic has been reviewed towards the goal of providing a summary of what is currently being done, as well as the strengths and weaknesses of the current research (Wang *et al.*, 2018b; Rajinipriya *et al.*, 2018).

Starch

There are various types of starches from natural sources (potato, wheat, rice, corn, etc.); the differences depend largely on the amylose and amylopectin content of the starch. Films prepared from starch generally have low oxygen permeability and low water vapor permeability (Liu, 2008). These barrier properties, of course, makes starch films good candidates to compete with films from fossil fuels. However, starch films are brittle and can have tensile strengths as low as 1 MPa (Liu, 2008). Interestingly, the incorporation of plasticizers into the starch base gives films not only with improved mechanical properties but also with improved barrier properties (Liu, 2008; Combrzynski *et al.*, 2013; Shah *et al.*, 2015). Other modifications of starch to give that result in improved films for packaging will be discussed in the section of this article on modified biomaterials. Some properties of starch films are shown in Table 1.

Cellulose

A review of cellulose nanomaterials (CNMs) (Wang *et al.*, 2018b) provides detailed information on cellulose films, CNM coatings, and CNM nanocomposites. The information on films will be discussed in this section. The section on modified biopolymers will discuss the coatings and nanocomposites using CNMs. The intent of the review (Wang *et al.*, 2018b) is to provide a common connection among the various reports on CNMs, particularly the CNMs used for food packaging. The authors note the importance and difficulty of knowing where a particular CNM falls in the spectrum of possible dimensions. The review provides specific dimensions for cellulose microfibrils (CMFs), cellulose nanofibrils (CNFs), and cellulose nanocrystals (CNCs) while noting that many reports do not use these designations; hence production methods were used to distinguish CNMs.

Moisture absorption by CNMs is a complex phenomenon; two major considerations are morphology of the CNM and surface functionality. Water vapor permeability measurements allow a ranking of films with respect to this quality. An understanding of this ranking is more challenging. Even so, the best results located by Wang *et al.* (2018b) for this measurement, based on various sources using similar procedures, are shown in Table 1. Similarly, oxygen permeability is an important measurement for the comparison of various films that are used or have the potential for being used as a packaging material (Table 1). The CNM with high ranking values for both water and oxygen permeability is indicated. While there were other CNMs that performed well in one or the other or both categories, the range of values for water permeability and oxygen permeability were from 10.63×10^{-15} to 321.9×10^{-15} and 2.14×10^{-21} to 184.4×10^{-21} kg m/m² s Pa, respectively. For comparison, values for films derived from common petrochemicals are also given. For these non-renewable films, polyvinylidene chloride (PVdC) gave the best values in both water and oxygen permeability.

Table 1 Properties of non-modified biopolymer films

Film	Permeability ($\text{kg mm}^{-2} \text{s}^{-1} \text{Pa}^{-1}$)			Mechanical properties			Reference
	Oxygen	Carbon dioxide	Water vapor	Tensile strength, MPa	Elongation at break, %	Modulus, MPa	
CNM: CMFs, refined and ground	3.7×10^{-21} to 4.6×10^{-21}		10.6×10^{-15}				Wang <i>et al.</i> (2018b)
CNFs, carboxylated, Ca^{+2}	0.33×10^{-21}						Wang <i>et al.</i> (2018b)
Chitosan	12×10^{-21} to 9895×10^{-21}		107×10^{-15}				Wang <i>et al.</i> (2018b)
PLA				59.48	4.94	2670	Meekum and Khiansanoi (2018)
PLA (two bound sheets)	2.51×10^{-15}		8.21×10^{-15}				Goh <i>et al.</i> (2016)
PLA	2.0×10^{-17} to 2.8×10^{-17a}	1.8×10^{-17}	18×10^{-15}				Auras <i>et al.</i> (2004)
PHB					5		Bugnicourt <i>et al.</i> (2014)
P3HBHV				25	~ 15	1200	Bugnicourt <i>et al.</i> (2014)
CNF non-crosslinked, dry				~ 40			Sharma and Deng (2016)
Starch, 27% amylose; no plasticizer	2.00×10^{-20}		1.22×10^{-14} to 3.47×10^{-14}				Liu (2008)
Starch, amorphous				7.30	33.40	73.10	Ali <i>et al.</i> (2018)
Hemicellulose	1.98×10^{-21}			55	2.7	2735	da Cunha Goncalves (2011)
PE	5.4×10^{-17} to 21.4×10^{-17}		27×10^{-17}				Wang <i>et al.</i> (2018b)
PP	5.4×10^{-17} to 10.7×10^{-17}		8×10^{-17} to 23×10^{-17}				Wang <i>et al.</i> (2018b)
PP					400		Bugnicourt <i>et al.</i> (2014)
PET	107×10^{-21} to 535×10^{-21}		0.5×10^{-16} to 9.2×10^{-16}				Wang <i>et al.</i> (2018b)
PVdC	1.1×10^{-21} to 32×10^{-21}		2.0×10^{-16}				Wang <i>et al.</i> (2018b)
PS	—	1.6×10^{-16}	6.7×10^{-15}				Auras <i>et al.</i> (2004)
PET	—	1.7×10^{-17}	1.1×10^{-15}				Auras <i>et al.</i> (2004)
LDPE				8.43	91.28	140	Meekum and Khiansanoi (2018)

^aData is for PLAs that are 94% and 98% L-lactide, respectively.

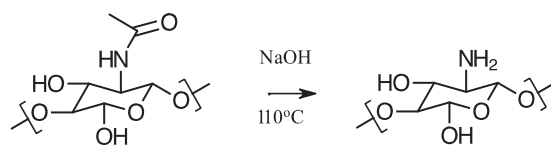


Fig. 1 Chemical conversion of chitin to chitosan.

Surface functionality change as subtle as the counter ion for a carboxylate of a CNM was reported to play an important role in the oxygen permeability ([Table 1](#)). The aluminum and calcium cations gave the best results for this parameter. The authors ([Wang et al., 2018b](#)) do not give the water permeability for these salts, although they did note that moisture increases their oxygen permeability values.

Efforts to produce a soluble cellulose system have been considerable ([Xu et al., 2018](#)). These authors have synthesized and analyzed an ionic liquid/cellulose system that dissolves cellulose at 25°C and from which cellulose can be easily regenerated. Success in this arena would be invaluable in the development of thin films for packaging from abundantly available cellulose.

Chitin/chitosan

After cellulose, chitin is the second most available biopolymer. Since chitin is a very insoluble material, it is generally transformed to its more soluble derivative chitosan. Chitosan is prepared by the deacetylation of chitin. This can be done by various versions of chemical syntheses ([Fig. 1](#)) ([Hadi, 2013](#); [Long, 2013](#); [de Queiroz Antonino et al., 2017](#)). A variety of other approaches is discussed by [Liu et al. \(2017\)](#); these include the use of (1) an enzymatic catalyst rather than a highly concentrated aqueous sodium hydroxide solution, (2) microwave radiation to provide the energy source for the reaction in aqueous sodium hydroxide, (3) autoclaving and γ irradiation of the chitin/aqueous sodium hydroxide solution, and (4) ionic liquids and heat as the medium for the deacetylation. These methods are critiqued by [Liu et al. \(2017\)](#) as related to cost and/or environmental factors. These authors present an approach using glycerol and somewhat lower concentrations of sodium hydroxide to react with the insoluble chitin. Additionally, they present a method to recover most of the glycerol/sodium hydroxide reaction medium for reuse.

Pure chitosan is used as a packaging film. A review specifically devoted to pure chitosan and its derivatives and their potential for food packaging applications ([Wang et al., 2018a](#)) provides a summary of current efforts in this area. As a polycation, pure chitosan is noted for its antimicrobial activity. Its oxygen barrier properties and its mechanical properties are good ([Wang et al., 2018b](#)), although they do not match the films from fossil fuels that are currently in use. The water barrier properties of pure chitosan, as expected, are poor. There are simply too many sites for hydrogen bonding of water and chitosan. Some of the properties of pure chitosan are given in [Table 1](#). From this data, it is evident that pure chitosan will not become competitive as a thin film for food packaging. However, since chitin is such a dominant natural resource and since the production of chitosan from chitin is so well established, it is clear that there should be considerable effort towards the production of chitosan derivatives for this application. The most current work in this area will be discussed later in the article.

[McDonnell et al. \(2016\)](#) modeled a chitosan/chitin system. The system had fifteen monomer unit chains; five were chitin and ten were chitosan, representing 66% deacetylation. Twenty percent of the chitosan molecules were protonated. The relative humidity range for the molecular dynamics study was 15%–95%. Molecular oxygen was introduced so as to give random trajectories. This computational effort is quite detailed both in terms of the work itself and in terms of analyzing other literature efforts related to their work. The oxygen permeability predicted from the first level of calculations showed oxygen to be more permeable at low relative humidity; this was the opposite to experimentally reported results. Adjustment of their calculations gave results with the correct trend but still not in agreement with experimental values at low relative humidity. Based on the literature and on their work, the authors infer that the presence of isolated aqueous domains in the chitin/chitosan polymer chain would lower oxygen permeability. Future ab initio calculations are suggested by the authors to provide a more accurate model to predict oxygen permeability for the chitin/chitosan system.

Hemicellulose

The composition of hemicellulose varies with feedstock ([Hansen and Plackett, 2008](#)). This is a significant difference in comparison with polymers made from monomers derived from fossil fuel feedstock. While the fossil fuel feedstocks vary, refining produces very specific monomers that are used to prepare specific polymers.

The oxygen permeability and mechanical properties of hemicellulose thin films make hemicellulose a very good candidate for packaging ([Table 1](#)) ([da Cunha Gonçalves, 2011](#)). However, the biggest challenge for the use of hemicellulose as a thin film for packaging is the moisture vapor permeability of its thin film. There has been success in the chemical modification of hemicellulose thin films. Acetylation using acetic anhydride ([Fig. 2](#)) is a classic example of a modification that decreases moisture permeability. Somewhat more recently ([Hartman, 2006](#)), benzylation was shown to significantly decrease moisture vapor permeability while still maintaining acceptable oxygen permeability and mechanical properties. More recent modifications of hemicellulose films are discussed in the modified biomaterials section.

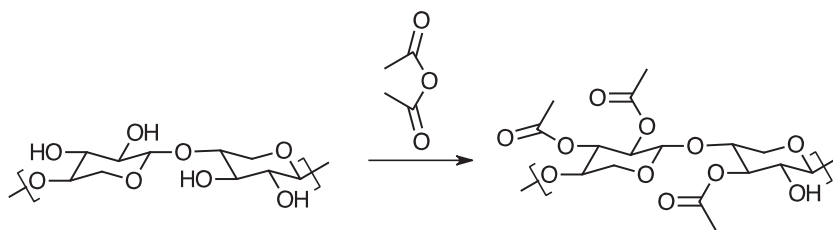


Fig. 2 Acetylation of hemicellulose.

Table 2 Comparison of glass transition, melting point, and percent crystallinity for PLA, PS, and PET

Polymer/property	PLA ^a	PS	PET
T _g , °C	66.1; 71.4	100	80
T _m , °C	140.8; 163.4	NA	245
Crystallinity, %	25; 40	NA	38

^aData is for PLAs that are 94% and 98% L-lactide, respectively.

Note: Auras, R., Harte, B., Selke, S., 2004. An overview of polylactides as packaging materials. *Macromolecular Bioscience* 4, 835–864.

Films From Biomonomers

Poly(lactic acid) (PLA)

The potential of poly(lactic acid) (PLA, the polymer from lactic acid (2-hydroxypropanoic acid)) as a renewable material is well established (Auras *et al.*, 2004). The biomass corn can be converted to lactic acid, which is then converted to PLA. Molecular weights of more than 100,000 daltons have been produced from lactic acid. The chiral center of lactic acid provides the basis for variations in the PLAs that can be synthesized. High molecular weight and amorphous PLA has a T_g of 58°C and decomposes between 215 and 285°C. Semi-crystalline PLA has a T_g between 58 and 70°C, a melting point range from 130 and 207°C, and decomposes between 215 and 285°C.

Auras *et al.* (2004) draw a comparison among PLA, poly(styrene) (PS), and poly(ethylene terephthalate) (PET) (Table 2). This comparison certainly shows that PLA is comparable to these synthetic polymers. They also note that the surface tension values for PLA are comparable to those of PS and PET; these values are somewhat higher than those for poly(ethylene) (PE) and poly(propylene) (PP). While moisture absorption by PLA is higher than that for PS and PET, this absorption has no significant effect on the T_g for PLA.

The limitations of “pure” PLA as a packaging material become obvious when processing is considered. There is only a 12°C window for processing in order to avoid degradation of the polymer (Auras *et al.*, 2004). The thermal stability of PLA is similar to that of poly(vinyl chloride) (PVC); PLA is less thermally stable than PS, PET, PE, and PP. The mechanical properties of PLA are similar to those of PS; the mechanical properties of PLA and PET are less similar. A useful property for PLA is its insolubility in water. In comparison to PS and PET, PLA has comparable properties as a barrier to carbon dioxide (Table 1); the oxygen permeabilities for PS and PET are similar to that for PLA; additionally, the water vapor permeability coefficient for PLA is similar to those for PS and PET (Table 1).

In addition to PLA originating from a renewable resource, PLA is degradable. The initial degradation occurs by hydrolysis of the ester linkage of the polymer. Finally, the lower molecular weight products from the hydrolysis are degraded further by microorganisms. Originating from a renewable resource and then degrading in the environment are clear advantages for the use of PLA in packaging. Recent efforts to modify PLA by creating blends or copolymers, or by the addition of materials to create composites is the current focus and will be discussed in another section of this article.

Films From Bacterial Biosynthesis

Poly(hydroxyalkanoates) (PHA)

In order to improve the economic competitiveness of polyhydroxyalkanoates (PHAs) as packaging films, various methods to obtain PHA were compared systematically. PHA is produced naturally. The most common method to extract PHA from biomass has been dichloromethane extraction. In this work (Gutt *et al.*, 2016), seven methods to extract poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (P3HBHV) from *C. nectar* biomass were compared. The extraction methods were: (1) solvent extraction with dichloromethane; (2) polycarbonate; (3) ionic liquids; (4) enzymatic lysis; (5) sonication; (6) bead milling; and (7) use of surfactants. Also, a combination of mechanical disruption and surfactants was examined. The goal was to obtain high purity P3HBHV in high yield by a process that could be recommended for industrial scale-up. Initial experiments showed the surfactant

approach (sodium dodecyl sulfate (SDS), 6 h at 90°C) gave the highest purity P3HBHV. This approach was combined with mechanical bead milling (2 min at 500 rpm) in order to optimize the processing time and hence cost. Additionally, distilled water was used for the final purification of the P3HBHV, instead of methanol. Modeling was used to optimize the protocol for the selected surfactant/bead milling method. Considered in the modeling were the weight of the biomass, the time and pH for the bead milling, and the concentration and treatment time for the surfactant. The final protocol resulting from this approach (buffer pH 2.6, milling time of 2 min at 500 rpm, surfactant concentration of 5%, and 30 min surfactant treatment time), followed by one or two distilled water washes, gave purity (92% and 94%, respectively) and yield results for P3HBHV comparable to those obtained by the traditional dichloromethane extraction method. Characterization showed trace impurities in this new approach that were ascribed to proteins and polysaccharides from the biomass cell wall and metal from the milling beads.

Poly(3-hydroxybutyrate), the most studied of the PHAs, has properties sensitive to storage time. For example, the tensile strength of PHB stored for 30 days at 50% RH is approximately 47 MPa. After approximately 60 days under the same conditions, the tensile strength reduces to approximately 34 MPa. The slope of the stress/strain curve remains the same (Bugnicourt *et al.*, 2014). Introducing valeric acid into the structure to give P3HBHV increase the elongation to break to approximately 15%; the tensile strength and modulus are 25 MPa and 1.2 GPa (Table 1). In other words the mechanical properties of the butyric acid/valeric acid copolymer (P3HBHV) are similar to those of PHB. The implication here is that in order for PHB or copolymers of PHB to be useful in packaging applications, blends or other components will need to be incorporated into these systems. Generally this is true for PHAs.

Modifications of Biopolymer Films

Attempts have been made to modify biopolymers using nanomaterials. Dispersing these very small particles in the polymer matrix can have the effect of improving barrier properties by simply making the path through the film more tortuous. The dispersion of nanoparticles in the biopolymer matrix can also improve certain mechanical properties. Other approaches have included blends of biopolymers (with or without nanoparticles), and minimal crosslinking. The number of empirical approaches may be limitless, but those reported are generally limited by systematic rationales. The possibility of developing models for the modified biopolymer films is an approach that could streamline the development of packaging films from renewable sources. This section of the article discusses some recently reported possibilities.

Polysaccharides

Starch

Ali *et al.* (2018) examined the effect of cellulose crystals and starch crystals on the properties of corn starch films. The films were made from corn starch alone and from 2%, 5%, 7%, and 10% cellulose or starch crystals in the corn starch. There were subtle but no remarkable differences between the cellulose crystal/starch (CX/S) composite and the starch crystal/starch (SX/S) composite. Of particular note is that the crystal/starch composites improved protection against UV radiation. The tensile strength, elongations at break, and modulus were affected by the addition of the crystals (Table 3); however, the changes were relatively small. It should also be noted that all the materials used in these experiments are acceptable as food ingredients.

In order to improve the water absorption and strength properties of starch films, Aqlil *et al.* (2017) examined a biocomposite composed of a starch/lignin matrix and a graphene oxide reinforcement. The lignin was extracted from sugar cane bagasse. The graphene oxide (GO) was synthesized from natural graphite. The composite film was cast from a sonicated aqueous/glycerol solution of starch and lignin (5:1 weight ratio, respectively) to which 0.3, 0.5, and 0.7 wt% GO (based on the dry starch and lignin) were added. Control films of starch and of starch/lignin were also prepared. The designations for the starch, starch/lignin, and GO-containing starch/lignin films were ST, ST/L, and ST/L-x, where x represents the percent GO in the film.

FTIR spectra of ST, ST/L, and the ST/L-x films showed systematic shifts in the starch C-O absorptions at 1152 cm⁻¹, 1077 cm⁻¹, and 1008 cm⁻¹ to 1134 cm⁻¹, 1062 cm⁻¹, and 999 cm⁻¹ for ST/L-0.7 that were interpreted to indicate a significant interaction between starch and GO. Thermal gravimetric analysis indicated that incorporation of GO into the starch/lignin system decreased the amount of water absorbed and increased slightly the thermal stability of the system. The measured moisture uptake of the films, following a slight variation of ASTM E104, for ST, ST/L, ST/L-0.3, ST/L-0.5, and ST/L-0.7 were 12.36%, 9.2%, 5.71%, 5.16%, and 5.15%, respectively. The ST/L-0.7 film had a significantly lesser water swelling than the other films. The water vapor permeability of the starch control and the ST/L-0.3 and ST/L-0.7 films are shown in Table 3. Clearly the GO is playing a role in improving the water absorption of starch films. Additionally, Aqlil *et al.* (2017) determined that the introduction of GO into the starch/lignin system appears to promote resistance to the hydrolytic degradation of these films.

The mechanical properties of the starch control and of the ST/L-0.7 film are shown in Table 3. These properties were measured for all the films; clear trends were shown: the tensile strength regularly increased from the starch control to the ST/L-0.7 film; the elongation at break decreased from the starch control to the ST/L-0.7 film; and the modulus increased from the starch control to ST/L-0.7. The addition of GO had improved the mechanical properties of the starch film. It should be noted though, for application purposes, that the addition of lignin and of increasing amounts of GO resulted in a corresponding decrease in the transparency of the films.

Cellulose

In a study where cellulose is the reinforcement and a natural rubber is the matrix (Sun *et al.*, 2018), a composite has been prepared that is potentially useful as a packaging film. The natural rubber used as the matrix, *Eucommia ulmoides*, is predominantly

Table 3 Properties of modified biopolymer films

Film	Permeability ($\text{kg mm}^{-2} \text{s}^{-1} \text{Pa}^{-1}$)			Mechanical properties			Reference
	Oxygen,	Carbon dioxide	Water vapor	Tensile strength, MPa	Elongation at break, %	Modulus, MPa	
PLA/silicone (with talc)				46.77	2.76	4030	Meekum and Khiansanoi (2018)
PLA/PBAT (with NA)				12–24	150–250		Mallegni <i>et al.</i> (2018)
PLA/PBS (with NA)				14–20	200–260		Mallegni <i>et al.</i> (2018)
PLA-GO	0.71×10^{-16}		3.37×10^{-15}				Goh <i>et al.</i> (2016)
PLA-rGO	0.26×10^{-16}		1.01×10^{-15}				Goh <i>et al.</i> (2016)
s-PLA-5CMC				57.3	24		Gupta and Katiyar (2017)
s-PLA				29.2	1.9		Gupta and Katiyar (2017)
Rubber control			2.1×10^{-16}	8.1	135.2	97.3	Sun <i>et al.</i> (2018)
4%NCC/rubber composite			1.6×10^{-16}	15.7	378.8	120.7	Sun <i>et al.</i> (2018)
8%NCC/rubber composite			2.0×10^{-16}	5.7	114.4	55.4	Sun <i>et al.</i> (2018)
Starch, neat, control				7.30	33.40	73.10	Ali <i>et al.</i> (2018)
10% SX/S composite				8.88	28.63	88.20	Ali <i>et al.</i> (2018)
10% CX/S composite				8.10	28.30	98.10	Ali <i>et al.</i> (2018)
ST, control			3.17×10^{-6}	3.7	13.68	32.0	Aqil <i>et al.</i> (2017)
ST/L-0.3			1.07×10^{-6}				Aqil <i>et al.</i> (2017)
ST/L-0.7			1.04×10^{-6}	5	9.07	60.23	Aqil <i>et al.</i> (2017)
CNF crosslinked by PAE, dry				~105			Sharma and Deng (2016)
CNF crosslinked by PAE, wet				~32			Sharma and Deng (2016)
PLA	1.65×10^{-16}			40.85	8.88	542	Pal and Katiyar (2016)
PLA/OLLA-g-CH, 1%	1.00×10^{-16}			40.26	9.17	490	Pal and Katiyar (2016)
PLA/OLLA-g-CH, 3%	0.382×10^{-16}			33.73	17.43	402	Pal and Katiyar (2016)
PLA/OLLA-g-CH, 5%	0.302×10^{-16}			33.33	34.3	298	Pal and Katiyar (2016)
Chitosan				44.14	21.83	324	Pal and Katiyar (2016)
Chitosan/sodium phytate, stripping film			4.59×10^{-21} to 9.56×10^{-21}	32.44			Yang <i>et al.</i> (2018)
Chitosan/sodium phytate, casting film			12.5×10^{-21} to 44.8×10^{-21}	49.21	25.1	3646.68	Yang <i>et al.</i> (2018)
PHB/PCL			2.62×10^{-14}	6.29	3.03	817	Correa <i>et al.</i> (2017)
PHB/PCL/Clo 10A			1.05×10^{-14}	7.49	0.91	1035	Correa <i>et al.</i> (2017)
PHB/PCL/Clo 30B			1.26×10^{-14}	7.06	0.72	1226	Correa <i>et al.</i> (2017)
S-24 ^b				6	40		Akkus (2015)
S-24 A90 30 ^b				13	23		Akkus (2015)
30-Gly-120 ^b				0.7	7.5	17.3	Akkus (2015)
30-Gly-120-A60 ^b				31	35.3	1470	Akkus (2015)

^aThe water vapor permeability values for 1 – ST, control; 2 – ST/L-0.3; and 3 – ST/L-0.7 represent a trend but are probably incorrect by a factor of 10^{-9} .

^bS-24 = hemicellulose obtain by 24% KOH extraction of corn cobs (not desalted); S-24 A90 30 = acetylated hemicellulose obtained from S-24, reacted at 90°C for 30 min; 30-Gly-120 = desalted hemicellulose extruded at 120°C with 30% glycerol content; 30-Gly-120-A60 = 30-Gly-120 acetylated for 60 min (at 120°C).

trans-1,4-polyisoprene. Films were prepared by casting dispersions of 2%, 4%, 6%, and 8%, w/w, nanocrystalline cellulose (NCC) in a petroleum ether solution of the natural rubber; a control film (0% NCC) was also prepared. The introduction of NCC into the natural rubber enhanced the crystallinity of the rubber, as shown by the X-ray diffraction patterns of the samples. This indicated some level of interaction between the NCC and the rubber. However, NCC had little effect on the T_g and T_m of the nanocomposites. Two percent NCC decreased the T_g from -65.9°C (control) to -66.5°C . The higher concentrations of NCC did not cause any further significant change in the T_g . The T_m for the control, 51.2°C , was decreased to 50.3°C , 50.2°C , 49.2°C , and 50.7°C for the NCC concentrations of 2%, 4%, 6%, and 8%, respectively. The contact angle decreased from 90.5° for the control to 89.8° , 87.8° , 86.7° , and 76.9° for the NCC concentrations of 2%, 4%, 6%, and 8% respectively. The water vapor permeability (Table 3) reduced from $2.14 \times 10^{-16} \text{ kg m}^2/\text{sPa}$ for the control to $1.61 \times 10^{-16} \text{ kg m}^2/\text{sPa}$ for the 4% NCC/rubber composite; however, for the 8% NCC/rubber composite, the water vapor permeability was $2.03 \times 10^{-16} \text{ kg m}^2/\text{sPa}$. In terms of water vapor permeability, the 4% NCC/rubber composite is the most promising for application as a packaging material. The mechanical properties of the control, the 4% NCC/rubber composite, and the 8% NCC/rubber composite (Table 3) also favor the 4% NCC/rubber composite. However, the T_g and T_m properties would limit its use to low temperatures.

Through the use of a polyamidoamine-epichlorohydrin (PAE) (Kymene) crosslinking agent, improved films from cellulose nanofibrils (CNF) were made (Sharma and Deng, 2016). The barrier properties and mechanical properties of the CNF films degrade in humid environments. A minimal amount of the crosslinking agent was used (one percent based on the dry weight of the CNF) in order to obtain a material that would presumably still be biodegradable. In processing the CNF film, conditions were used that not only crosslinked the CNF with the PAE, but also allowed for crosslinking of the PAE molecules with themselves (Siqueira, 2012; Sharma and Deng, 2016).

The water vapor permeability of the crosslinked CNF improved considerably in comparison with the CNF that was not crosslinked (Table 3). This result was also reflected in the contact angle measurements for these materials, 110.5° and 50.2°, respectively, for the crosslinked CNF and the uncrosslinked CNF. Mechanical testing was performed on dry and wet crosslinked and non-crosslinked CNF samples. The wet samples were soaked in water for 30 min prior to testing. For both dry samples and for the wet crosslinked sample, the tensile stress at break is distinct (Table 3). However, the wet, non-crosslinked sample shows a non-linear pattern interpreted as tearing apart of fibrils whose connectivity has been weakened by absorption of water molecules between the fibrils. From the pattern of the stress-strain curves for the four samples and from SEM images of the fracture surfaces, Sharma and Deng (2016) rationalize that the PAE crosslinking serves to initially protect the cellulose fibers from breaking; once the strain has caused breaking of the PAE connectivity, then the cellulose fibers break.

Chitin/chitosan

Yang *et al.* (2018) addressed two of the poor properties of chitosan films, their water permeability and their mechanical properties. Using 90% deacetylated chitosan and the sodium salt of phytic acid, they used two approaches to prepare thin films. In one, which they called the “stripping-film technique”, they added a solution of sodium phytate onto a solution of chitosan. A film formed at the interface of the two solutions; the film was removed and dried and the process was repeated with a fresh sodium phytate solution. The second approach was called the “casting-film technique” and involved adding successive layers of chitosan and sodium phytate solutions to give a ten-layer film. Obviously, the second approach gave a thicker film (70–130 µm) than the first approach (9–26 µm). Various properties of the two types of films were examined. The water vapor permeabilities measured for both films were much lower than those for chitosan (Table 3). The best observed mechanical properties are given in Table 3. There were variations observed related to the concentrations of the solutions. Both the water vapor permeability and mechanical properties show that these films are good candidates for food packaging films. The films are reasonably transparent and both components of the films are safe to use for this application and are renewable materials.

A combination of molecular dynamic calculations and experimental measurement of mechanical properties was performed for chitosan matrices with various degrees of deacetylation that were reinforced with functionalized carbon nanotubes (CNTs); the CNT functional groups were the amine (-NH₂) or carboxylic (-COOH) groups (Aztatzi-Pluma *et al.*, 2016). Additionally, the authors examined calculations were the amide and amine functionalities on the chitin/chitosan polymer chain was varied. The calculations indicated that the strongest interaction occurred between the 50% deacetylated chitosan and the amine functionalized CNT. The experimental measurements showed a similar result; the Young's modulus for a film prepared from 54% deacetylated chitosan reinforced with an amine functionalized multiwall CNT gave the largest Young's modulus (approximately 3225 MPa). The Young's modulus for the carboxylic functionalized multiwall CNT in the 54% deacetylated chitosan was somewhat lower (3175 MPa). However, the Young's moduli for two other deacetylated chitosans (64% and 76% deacetylated) were consistently higher for the systems reinforced with amine functionalized multiwall CNTs.

Hemicellulose

Akkus (2015) explored a number of approaches towards improving the properties of hemicellulose films for packaging. Samples of hemicellulose were obtained by extraction of corn cob using an aqueous solution of potassium hydroxide. These samples were treated variously (desalted or not desalted; desalted with glycerol added; desalted with poly(vinyl alcohol) added). The purified hemicellulose was extruded at 90°C or 120°C to give 5 mm × 0.5 mm (width × thickness) “strips”. Some of the films were heat treated and some were acetylated. The properties of the various “strips” of hemicellulose and modified hemicellulose were determined. The most promising modified hemicellulose “strips” were: (1) Acetylated hemicellulose prepared from a not desalted precursor (i.e., the hemicellulose contained potassium acetate) and (2) acetylated desalted hemicellulose where the “strips” had been processed with glycerol. The mechanical properties of both types of modified hemicellulose “strips” are shown in Table 3. For both types, their water solubilities were very significantly less than that for the unmodified hemicellulose precursors. In the experiments with blends of desalted hemicellulose and poly(vinyl alcohol) (PVA), neat or acetylated, no advantage was shown for this system with respect to decreasing the water solubility of the hemicellulose. Nevertheless, Akkus' work (Akkus, 2015) provides a basis for the use of hemicellulose as a thin film packaging material.

Films From Biomonomers

Poly(lactic acid) (PLA)

In an attempt to improve the toughness of PLA and maintain transparency, blends of PLA and silicone were examined (Meekum and Khiansanoi, 2018). The intended application was frozen food packaging. The other additives in the experiment were 3-aminopropyltriethoxysilane (for crosslinking), a plasticizer (a polyester polyol), and talc. For 700 g of PLA, the amount of

silicone was varied from 0 to 12 parts per hundred (phr); one phr silane and 1 phr plasticizer were used in all the experiments to produce extruded strands. The strands were pelletized. A portion of the pellets were crosslinked by heating the pellets at 65°C and 100% RH for 12 h. The non-crosslinked and crosslinked systems were then processed into films.

Impact strengths of the PLA/silicone films were tested at room temperature and at approximately -98°C . Also tested were low density poly(ethylene) (LDPE) and neat PLA. At room temperature and for the unnotched specimens at the sub-zero temperature, the performance of LDPE was far better than that of the PLA/silicone films. However, for the notched samples, the crosslinked specimen with 8 phr silicone performed best. Specifically, at -98°C , the impact strength of the 8 phr crosslinked sample and LDPE were 8.32 kJ/m² and 3.62 kJ/m², respectively.

In order to improve the film forming process, Meekum and Khiansanoi (2018) experimented with various amounts of talc incorporated into the 8 phr crosslinked sample. They were able to produce acceptably reproducible, relatively transparent films. An optimal value of 40 phr talc was determined based on the ease of forming a film and relatively good tensile properties and impact strength values even though the addition of talc did decrease the impact strength for the notched specimen at -98°C . LDPE had a comparable impact strength to the talc-containing sample, but LDPE had better film forming properties.

In a different approach towards improving film from PLA, Mallegni *et al.* (2018) melt mixed PLA with either poly(butylene succinate) (PBS) or poly(butylene adipate-co-terephthalate) (PBAT) in the presence of an epoxy ring-containing plasticizer (polypropylene glycol diglycidyl ether). Additionally, the blends contained varying amounts of a nucleating agent (NA) (the potassium salt of dimethyl 5-sulfoisophthalate). The NA enhanced the rigidity of the blend sufficiently so that suitable pellets could be prepared.

The mechanical properties of the films with plasticizer and NA are shown in Table 3. Values obtained for pellets of PLA with or without the plasticizer and with no NA gave values similar to those shown for the Mallegni *et al.* (2018) films (Table 3). While there are challenges in preparing films from the PLA blends with PBAT or PBS and with the NA, the mechanical properties of these films are reasonably similar to the values for LDPE (Tables 1 and 3). Mallegni *et al.* (2018) also performed the Trouser tear test on the PLA/PBAT and PLA/PBS films. The results for the Trouser tear strength were 8250 N/m and 5700 N/m for the PLA/PBAT and PLA/PBS film, respectively. This compares well with the value for PP (5560 N/m); however, these results are quite less than the Trouser tear strength for LDPE (55,560 N/m).

In another clever approach (Goh *et al.*, 2016), graphene oxide (GO) and reduced graphene oxide (rGO) sheets were prepared and placed between two overlapping PLA films. To prevent delamination, the processing involved a binder and hot pressing to connect the PLA and the graphene materials. These systems (PLA-GO and PLA-rGO) and a control (PLA alone processed as were the graphene materials) were well characterized by scanning electron and atomic force microscopies (SEM and AFM), Raman and attenuated total reflection FT-IR (ATR) spectroscopies, X-ray diffraction (XRD), rheometry, and mechanical testing. From this, the differences in the GO and rGO sheets were established. Specifically, the reduction from GO to rGO gave a reduced material with sheets that stacked more closely than its precursor. This is obviously because of the reduction of the oxygen in GO. The data for oxygen and water permeability show the effect of this molecular change (Tables 1 and 3). The PLA sandwich containing rGO provided the best barrier to oxygen and water among the three samples examined. The permeability values obtained are comparable to others reported (Tables 1 and 3).

Goh *et al.* (2016) simulated the shelf life got PLA-rGO, PLA-GO, and the control. Their model was based on the oxygen permeation rate and the rate of oxidation of the packaged material (edible oil and potato chips). From the permeability data, clearly PLA-rGO had the best shelf life. Comparisons were not made with other packaging films. The authors also noted the PLA-GO was translucent and PLA-rGO was opaque; they noted that further work was needed to improve the transparency of PLA-GO and PLA-rGO if these materials were to be generally used for packaging.

Gupta and Katiyar (2017) reviewed previous work on stereocomplexation of PLA to produce a film with enhanced thermal, barrier, and mechanical properties. In their work, they grafted cellulose microcrystals (CMCs) to the D-enantiomer of lactic acid; CMCs were used to initiate the polymerization of D-lactide to PLA. The percent of CMC used for the polymerization was varied (1%, 5%, and 10% CMC). The biocomposite material was prepared by melt mixing equal amounts of the CMC-grafted D-isomer PLA and ungrafted L-isomer PLA. The resulting products were labeled as s-PLA-0.5%CMC, s-PLA-2.5%CMC, and s-PLA-5%CMC; the control was labeled as s-PLA.

DSC analysis resulted in the data shown in Table 4. s-PLA additionally showed endotherms at 151.8°C and 179.3°C, interpreted as due to melting of homocrystals of the two enantiomeric PLA systems. The biocomposite of these polymers without the influence of the grafted CMC is the melting endotherm at 211.1°C. Clearly the grafted system promotes the formation of the biocomposite. FTIR and X-ray diffraction results corroborate the DSC results in terms of structural changes upon grafting CMC to PLA. Examination of barrier properties gave further indications of the effect of the grafting. The oxygen permeability for s-PLA-5CMC was 25% less than that of the control (Table 3). For four different temperatures (15°C, 23°C, 35°C, and 45°C), the oxygen permeability decreased as the percent of CMC grafted to PLA increased. Interestingly, the water vapor barrier property showed significant improvement for s-PLA-2.5CMC compared to the control, s-PLA; however, there was only slight improvement for s-PLA-5CMC compared to s-PLA. The authors (Gupta and Katiyar, 2017) rationalized that the increase of CMC in the structure probably provided a denser structure to prevent water molecules from passing through the film, but also provided a larger hydrophilic area. The tensile strength of the grafted PLA biocomposite s-PLA-5CMC was significantly greater than the control s-PLA (Table 3). The percentage elongation at break also increased for the biocomposite relative to the control (Table 3). There is a remarkable difference in the percent elongation at break for s-PLA-0.5CMC relative to the control: 36% and 1.9%, respectively. For s-PLA-2.5CMC and s-PLA-5CMC, the percent elongation at break decreases to approximately 24% each. One rationale for this

Table 4 Thermal analysis of biocomposites from interaction of PLA L-isomer and CMC grafted to PLA D-isomer

Polymer	T_m , °C	ΔH_m , J/g
s-PLA	211.1	34.8
s-PLA-0.5CMC	209.1	48.2
s-PLA-2.5CMC	209.8	49.4
s-PLA-5CMC	208	15.2

observation is the even distribution of CMC provided by the grafting of CMC to PLA. SEM and AFM data corroborate this rationale.

A unique PLA film was prepared by incorporating a reinforcement prepared from chitosan and lactic acid (Pal and Katiyar, 2016). Seventy percent deacetylated chitosan and lactic acid were reacted by microwave heating at 110°C for thirty minutes under a nitrogen atmosphere. The resulting nanoparticles (OLLA-g-CH, oligomeric lactic acid grafted to chitosan) were characterized. FTIR analysis showed a new absorption at 1539 cm^{-1} interpreted as due to a primary bond between a chitosan amine group and a the carboxylic group of lactic acid; additionally, the X-ray and TGA data for OLLA-g-CH in comparison to appropriate chitosan and PLA controls supported the conclusion that a compound with lactic acid grafted to chitosan had been prepared. The OLLA-g-CH nanoparticles were incorporated into a PLA matrix at three different concentrations (1%, 3%, and 5%) and the films prepared from this composite (PLA/OLLA-g-CH, 1%, 3%, and 5%) were studied.

The PLA/OLLA-g-CH film study included determination of mechanical properties and of oxygen permeability (Table 3). Most notable among the mechanical properties is the increase in the percent elongation of the films as the percent of PLLA-g-CH is increased. Although the tensile strength of the composite films decreased as the percent OLLA-g-CH increased, the composite with five percent OLLA-g-CH showed promising mechanical properties as a packaging material. Additionally, the oxygen permeability decreased as the percent of OLLA-g-CH in the composite increased (Table 3); the oxygen permeabilities of PLA and of PLA/OLLA-g-CH, 5% are $1.65 \times 10^{-16} \text{ kg m/m}^2 \text{ s Pa}$ and $0.302 \times 10^{-16} \text{ kg m/m}^2 \text{ s Pa}$, respectively. The rationale for the improvement in oxygen permeability is interpreted as an interaction between PLA and the chitosan backbone of OLLA-g-CH giving a barrier network in the polymer system (Pal and Katiyar, 2016). The water vapor transmission rate (WVTR) determined for PLA and the PLA/OLLA-g-CH composites showed an increase as the percent OLLA-g-CH in the composite increased. Imagining the composite as a sea of PLA (the matrix; $M_n = 15 \times 10^4 \text{ Da}$ and $M_w = 20 \times 10^4 \text{ Daltons}$) containing nanoparticles that appear to be a chitosan head with a PLA tail ($M_n = 1.4 \times 10^3 \text{ Daltons}$ and $M_w = 3.0 \times 10^3 \text{ Daltons}$), the hydrophilic chitosan head most likely contributes to the WVTR for these systems. Even so, the TGA results (Pal and Katiyar, 2016) show far less water absorbed by the composite films than by the chitosan film.

Films From Bacterial Biosynthesis

Poly(hydroxyalkanoates) (PHA)

A nanocomposite of a PHA has been examined as a support for nisin, an antibacterial peptide. Specifically, poly(3-hydroxybutyrate)/polycaprolactone (PHB/PCL) (a blend) films reinforced with organoclays were studied (Correa et al., 2017). PHB is a renewable material. PCL is synthesized from the ring opening polymerization of caprolactone, which is synthesized industrially from cyclohexanone and peracetic acid; even so, PCL is biodegradable. Hence the PHB/PCL blend is a good candidate for an environmentally friendly material.

The barrier and mechanical properties of films of the blend and of the nanocomposites of the blend were determined (Table 3). As expected, the nanocomposite films (PHB/PCL/Clo 10A and PHB/PCL/Clo 30B) had improved water vapor permeability compared to that of PHB/PCL; the tensile strengths of the nanocomposites were greater than that of the blend. Although all three nisin-activated materials were effective against a meat-spoiling bacterium, the three samples were equally effective with no significant differences measured. The authors conclude that all three materials are potential candidates for meat packaging films.

Conclusions

Although this article is not a review, a clear observation that was apparent from the preparation of the article is that the effort to explore renewable thin films is global. While the quality of the work reported may be variable, the various approaches to find replacements for non-renewable films from fossil fuels provide a significant view of what is possible. Among the notable approaches are (1) the use of cellulose crystals and starch crystals in corn starch that provided significant improvement in UV protection (Ali et al., 2018); (2) a starch/lignin blend with a graphene oxide reinforcement that improved water vapor permeability and resistance to hydrolytic degradation and gave good mechanical properties (Aqlil et al., 2017); (3) the melt mixing of PLA with either PBS or PBAT, and other additive, that gave films with properties similar to those of LDPE (Mallegni et al., 2018); (4) the synthesis of a PLA-chitosan nanoparticle for dispersion in a PLA matrix to give films with good mechanical and oxygen

permeability properties (Pal and Katiyar, 2016); (5) the preparation of films for low temperature applications from cellulose crystals in a rubber matrix (Sun *et al.*, 2018) and from a crosslinked PLA/silicone blend (Meekum and Khiansanoi, 2018); (6) the sandwiching of a reduced graphene sheet between two PLA films to give films with improved oxygen and water vapor barrier properties (Goh *et al.*, 2016); and (7) the comparison and molecular dynamic calculations with experimental data on the mechanical properties of chitosan/nano-reinforced systems (Aztatzi-Pluma *et al.*, 2016).

In a glimpse of the future, it would be ideal if all commonly used materials could be prepared from renewable resources. Films used for packaging food is an example where the replacement of non-renewable and non-biodegradable films by renewable and biodegradable films will have a significant effect on the environment. The nature of packaging materials has evolved over time. As recently as the 1960s, multi-layer films, produced to protect food products were first made; these films were largely polymers synthesized from fossil fuels. Since the 1960s, the development of these films allowed for creative approaches to producing films that could protect against oxygen, moisture, carbon dioxide, ultraviolet light, etc., in order to protect packaged food. The manufacture of thin films for packaging from renewable resources could be another transformative step in the history of packaging. Assuming the desirability to use renewable and/or biodegradable materials in the production of packaging films, if there is an application and if the production cost is reasonably competitive, then this new class of packaging films will become part of this evolutionary pattern. Hopefully this article can assist in this development.

See also: Biodegradable Packaging. Biodegradable Packaging Materials. Bio-Polymeric Packaging Material for Packaging of Raw Food. Recyclability of Packaging Materials for Domestic Applications. Role of Green Polymers in Food Packaging. Tailor-Made Bioplastics for Environmentally Friendly Food Packaging: A Methodological Approach to a Challenging Problem

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Renewable Agricultural Fibers as Reinforcing Fillers in Plastics: Mechanical Properties of Kenaf Fiber-Polypropylene Composites

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Introduction

Renewable resources have created more demand and opportunities, to reduce problems such as pollution, climate change and resource reduction. More research had been developed to utilize these resources, for various types of application. For example, a renewable resource such as natural fibers could be used for insulation materials in structures, patch and orchard utensils, recycled packaging, makeups, and nutrition productions too (Ramesh, 2016).

One of the methods to use these renewable resources, such as the lignocellulosic fibers and wood/agricultural wastes is to use this material as fillers and reinforcing fibers in polymer matrix (Akil *et al.*, 2011). However, several issues need to be considered before blending these materials together, such as the preparation method, the appropriate and accurate ratio of reinforcement have been reported, with improved filler/matrix interaction, quality of dispersion of the reinforcement particles and the interfacial interaction between the matrix and the reinforcement (Utracki, 2004).

According to several previous reviews, it was stated that the progress of renewable agricultural is rapidly growing, because this material can be used over and over again, and the resources are able to be replaced naturally, with minimum impact to the environment. Above all fibers from natural resources, kenaf had been chosen by several researchers over the past few years, because it potentials in term of availability, market demand, preparation procedures and the fiber's exceptional properties. Since sustainability and green material was preferred nowadays, using kenaf fiber as the reinforcing fillers for plastic composites will motivate scientists and manufacturing engineers, as this article provides the extension of previous review to address more important notes for future references (Akil *et al.*, 2011).

In this article, mechanical properties of kenaf fiber-polypropylene composite has been elaborated. As for mechanical and physical testing, which are normally performed towards composite materials, standard tests such as high-force tension (tensile), compression, impact, flexural, shear, rheology, and fatigue are known. Interestingly, the physical testing includes density, void content, water absorption, hardness, and scratch resistance. Currently, polymer and polymer composite tests have been standardized by a number of organizations by leading manufacturers and research institution, such as ASTM, ISO, CEN and other standards (Saba *et al.*, 2019).

Utilization of Kenaf

Kenaf is an annual plant originating from West Africa, growing to 1.5–3.5 m tall with a woody core. The stem's diameter is 1–2 cm and they are often, but not always, branched. The fruit is a capsule 2 cm in diameter, containing several seeds. The stem contains a bast fiber portion comprising 26%–35% (by dry weight). The average length of the fiber is 2.5 mm (Pari *et al.*, 2014). Kenaf shows robust mechanical properties. In recent years, two main reasons have contributed to the very high interest in kenaf cultivation. Kenaf has ability to absorb nitrogen and phosphorus within the soil. Kenaf also able to accumulate carbon dioxide at a significantly higher rate (Aji *et al.*, 2009). India and China are the most important producers of kenaf (Carus *et al.*, 2014). Kenaf is mainly grown in China and Indonesia, and can be grown for various applications. The crop has traditionally been used to produce fiber and food. The fibers can be used to make cordage, rope, burlap cloth, and fishnets because of its rot and mildew resistance. Besides these traditional applications, there are also a number of new uses, such as paper pulp, building materials, biocomposites, bedding material, oil absorbents, etc. Recently it has also come to be considered an important medicinal crop, as its seed oil able to cure certain health disorders and help in controlling blood pressure and cholesterol (Monti and Alexopoulou, 2013).

Kenaf fibers are used as reinforcement or filler in polymer composite materials, which are used increasingly in the automotive industries. Kenaf fiber composites are used in automotive applications, mainly because of its light weight and end-of-life properties (Monti and Alexopoulou, 2013). The growing demand for kenaf in the automotive industry stems mostly from the explicit wishes of some OEMs. In this context the following considerations arise (Carus *et al.*, 2014):

- Non-woven producers are reporting high fiber losses during the processing of kenaf fibers.
- Water retting is practiced to obtain the desired fiber qualities. However, water retting implies negative ecological effects (biochemical oxygen demand of the retting water) and negative social impacts (mostly working conditions and wages) in the fiber producing countries, e.g., Bangladesh, India and Indonesia.
- Nevertheless, the quality of water-retted kenaf fibers make them especially interesting for the automotive industry, since they allow for very thin laminations on composites, which are desirable for the design and weight reasons.
- It is not easy to distinguish kenaf fibers from jute fibers, so customers cannot always be certain that their bale labelled "kenaf" does not contain any jute. In the textile process chain, jute is treated with batching oil to make the fibers easier to process. Due to fogging problems, fibers treated with batching oil are not acceptable in the automotive industry. Though if jute fibers that are free of batching oil are used, there is no fogging and they can be processed just as well as kenaf, sometimes even better.

Natural fibers are relatively easy to obtain at a high yield and high specific surface area and can be treated chemically to compete with synthetic fibers. Hence, to study the mechanical properties of fiber-reinforced polymers, certain issues associated with the fiber-matrix condition needs to be solved first. A number of factors such as the matrix and fiber selection, fiber dispersion and orientation, and pretreatment of fibers can be used to tailor the mechanical properties of the fiber-reinforced polymer. The influence of fracture toughness, the compressive response and failure characteristics of natural and synthetic fibers have been analyzed and reviewed by several researchers. It was found that the hydrophilic nature of fibers leads to reduce the compatibility of the fiber with hydrophobic polymers, which has a negative effect on fracture toughness (Ghalia and Abdelrasoul, 2019). To quote one example, the performance of ultra-high molecular weight polyethylene/high density polyethylene-reinforced kenaf composites had been analyzed in terms of tensile, flexural (three-point bending) and an impact test (Charpy). The tensile results of these samples are significantly higher (20%) than pure blend resin. However, the flexural and Charpy strengths showed the drawback results, whereby the performance of composite is reduced (Mokhtar *et al.*, 2013).

As for the potential of kenaf, some researcher have recommended kenaf as the additional fillers that could improve the engineering behavior of sand-clay mixtures. The reinforcement of structural elements and construction materials using natural fibers have gained popularity among researchers and industries due to environmental concerns and financial problems of synthetic fibers. The contribution of natural fibers as soil reinforcement elements enhances the shear strength properties as the stresses in the soil mobilize tensile resistance in the fibers. Based on the results, the addition of a certain amount of kenaf fiber to the sand-clay mixture enhances the mixture ductility, improves the shear strength parameters, and ultimately makes it an appropriate candidate to be used in construction projects such as pavement layers, slope protection, embankment, and building foundation (EsmaeilpourShirvani *et al.*, 2019).

Kenaf Fibers–Polypropylene Composites

Kenaf was originated from *Hibiscus Cannabinus L* family *Malvacea*, a cellulosic source which could be harvested after sowing the seeds within a three month period, with capability to nurture under various condition of weather. The average height of this plant is 3 meters and above, with the base diameter of 3–5 cm. Several characteristics could be gained from kenaf fiber, with a few advantages as compared with common plants such as (Akil *et al.*, 2011):

- (1) Light-weight and cost-effective.
- (2) Remarkable papermaking features.
- (3) Requires much less energy compared to synthetic fibers.
- (4) A good rotation crop for maize, groundnuts, with capability to enrich the land.
- (5) The ability to absorb nitrogen and phosphorus.
- (6) Significantly higher carbon dioxide absorption rate.
- (7) Higher photosynthesis rate as compare with typical plants.

By integrating this plant for value added outcomes, kenaf had become the preferred crops, as compared with wood that was typically used in pulp and paper industries. Hence, kenaf could reduce or eliminate the forest destruction. However, recent progress had stated that the usage of kenaf in paper production is still very limited. One of the reasons is the suitable part of kenaf that for paper is a bast fiber, which only consist of 35% of kenaf structure, whereas 65% underutilized part of kenaf is the core. Therefore, more attempts had been made towards utilizing kenaf, such as preparing the kenaf as woven and non-woven textiles. Besides that, a number of research had discovered the potential of kenaf as a reinforcing fiber in thermoplastic composites, based on the findings that shows the composite had the superior toughness and high aspect ratio in comparison to other fibers (Akil *et al.*, 2011).

As mentioned before, researchers have discovered the possible use of kenaf as an alternative reinforcement material. One of the examples is by incorporating kenaf fiber into the polypropylene matrix. First of all, practically kenaf fibers offer a low cost-massive volume of resources, similar with polypropylene. Polypropylene (PP) is a thermoplastic commodity polymer from the group of polyolefins, used in diverse applications. It is produced through chain-growth polymerization of the propylene monomer, partially crystalline and non-polar. Based on a review, the mixture of kenaf and polypropylene is good in improving certain features of the polypropylene. The mechanical properties of kenaf fiber-polypropylene composite is equivalent to certain properties of materials, such as glass fiber polypropylene. Diverse range of structural and non-structural, industrial products could be prepared from this material. However, some drawbacks have been reported whereby kenaf fiber-polypropylene composite absorb more water and low notched impact strength. To overcome the high water absorption problem, thorough consideration has to be made before using these composites as water's absorber. As for lower resistance towards impact can be solved by using impact-modified polypropylene copolymers and flexible maleated copolymers, although the modulus and tensile strength could be compromised. The most interesting part in the effect of higher fiber volume fractions. Some of the findings have stated an interesting point to note that the agro based composites are better, compared to those of the inorganic-filled systems. This finding is important since the cost of material could be reduced, as well as the energy usage, instead of producing the high energy utilizing glass fibers or mined inorganic. Other issues that need to be controlled is the dispersion and adhesion between the nonpolar polypropylene matrix and the polar lignocellulosic fibers. These are the critical factors that need to be controlled, so that it is easy to determent the properties of the composite. More study had been carried out towards the usage of functionalized additives to improve the dispersion and the interaction between cellulose-based fibers and polyolefins, such as maleic anhydride grafted polypropylene (Sanadi *et al.*, 1995).

Preparation and Treatment

The preparation kenaf fiber-polypropylene composite was very important, since it shall provide better results and properties. For instance, the usage of high shear mixing technique from the thermokinetic mixer could produce better fiber attrition. Higher strengths could be obtained if alternate processing techniques are developed to reduce the amount of fiber attrition, and to get better fiber dispersion (Sanadi *et al.*, 1995).

Most of the research used compression molding as the preparation technique for kenaf fiber-polypropylene composite. As for an example, a research had use compression molding to fabricate kenaf fiber-polypropylene composite sheets. A thermoformed composite promotes more potential applications, and equivalent to current synthetic composites. The preparation of these sheets needs to be optimized, so that it could produce a good outcome. The compression molding process was executed by applying kenaf fibers with layered sifting polypropylene in a form of micro fine powder. Based on the findings, the tensile and flexural strength of kenaf fiber-polypropylene composite is comparable 40% by weight with polypropylene composite that used hemp and flax as their fibers, and higher when equated to polypropylene-coir and sisal composite. Furthermore, kenaf fiber-polypropylene composite also provide higher modulus per cost and specific modulus than sisal, coir, hemp, flax and E-glass. This condition can be achieved by controlling the temperature of the die and preform. The temperature should be elevated so that the cooling and tearing during forming could be avoided (Zampaloni *et al.*, 2007).

Researchers work also finds that controlling and optimizing the processing conditions/techniques have the remarkable consequence of the mechanical properties of fiber reinforced composites (Saba *et al.*, 2015). For instance, a research performed the optimization of processing conditions towards the long kenaf fiber-polypropylene composite. The compression molding machine was chosen to prepare the product, with the arrangement of component as displayed in Fig. 1. It was found that the tensile and impact strength was affected by the processing conditions, whereby better results could be obtained through the optimal setting. The setting was optimized, as the temperature of 230°C and a barrel speed of 16 Hz (Bernard *et al.*, 2011).

More research had been carried out towards the mechanical characterizations of kenaf fiber polypropylene composite, by using non-woven materials, with optimum processing condition. Fig. 2 shows the fiber images of the non-woven kenaf and polypropylene. The optimum condition was 230°C for temperature and 60 s for compression time. The results found that linear elastic behavior within valid strain range of 0%–0.5% of uniaxial tensile test and 0%–1% of flexural test. The open-hole test shows that the strength-reducing effect of stress concentration is mitigated greatly by the ductile-like behavior of kenaf fiber-polypropylene composite. Besides that, these composites also sensitive to strain rates (Hao *et al.*, 2012).

Based on a review made towards the factors that affecting the mechanical properties of kenaf fiber-polypropylene composite, one of the factors was the pretreatment process during the fabrication of this material. Before combining the kenaf fiber in the polypropylene matrix, a pretreatment is a necessity since it improves the properties of mechanical and tensile, by promoting good adhesion or interfacial linkage between fiber and matrix. The improved adhesion was obtained because the surface of kenaf fiber was cleaned and modified chemically. Moreover the moisture absorption process is reduced with the expansion of surface unevenness. Other pretreatment process which is typically available in industry also can be performed towards these fibers, as displayed in Fig. 3. Other than that, coupling agent also can be used to improve the interface linkage of fiber/matrix (Saba *et al.*, 2015). To quote an example, some researchers had performed an alkali-silane treatment towards short fiber non-woven kenaf fiber that's used polypropylene as their matrix. The responses of the treatment were tensile and flexural strength. According to the findings, the tensile and flexural strength were getting better. Based on the scanning electron microscopy observation, best result was obtained from the good interfacial bonding of fiber/matrix. The highlight of this research is the optimum concentration of sodium hydroxide (NaOH) was 6%, and 30% by mass of kenaf in this composite are comparable to glass fiber composites (Asumani *et al.*, 2012).

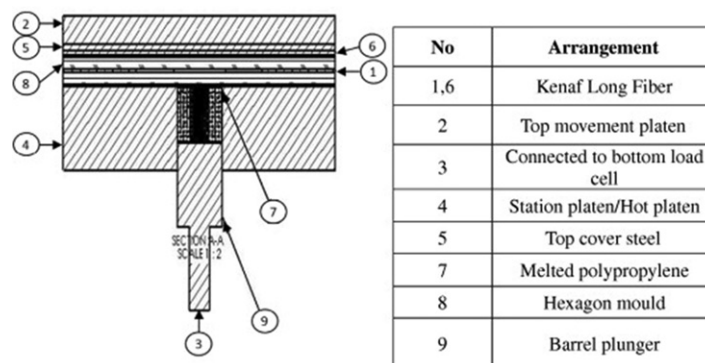


Fig. 1 Compression molding machine component arrangement for long kenaf fiber-polypropylene composite. Credit to: Bernard, M., Khalina, A., Ali, A., *et al.*, 2011. The effect of processing parameters on the mechanical properties of kenaf fiber plastic composite. Materials & Design 32 (2), 1039–1043.

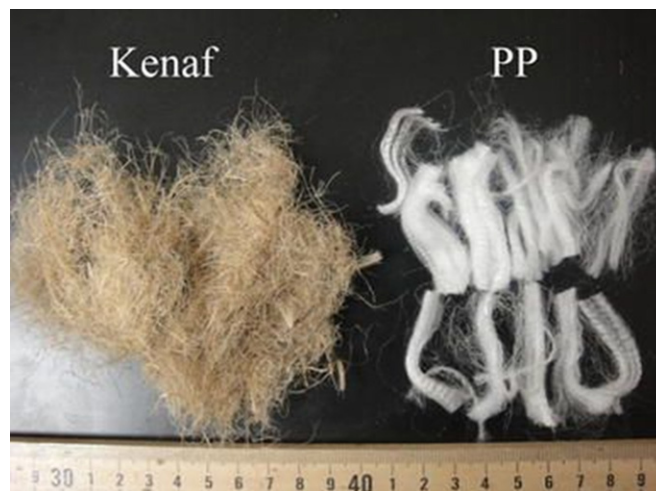


Fig. 2 Fiber images of the non-woven kenaf and polypropylene. Credit to: Hao, A., Zhao, H., Jiang, W., Yuan, L., Chen, J.Y., 2012. Mechanical properties of kenaf/polypropylene nonwoven composites. *Journal of Polymers and the Environment* 20 (4), 959–966.

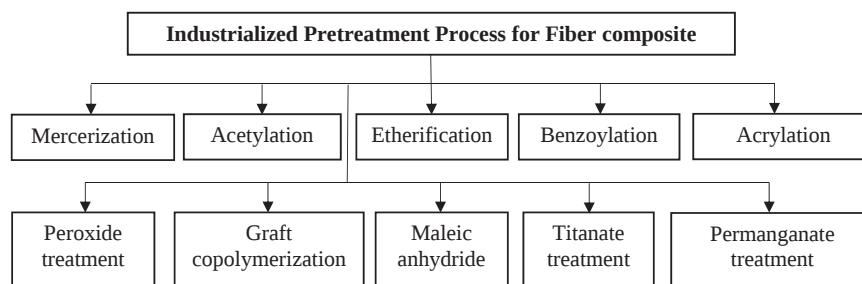


Fig. 3 Industrialized pretreatment process for fiber. Credit to: Saba, N., Jawaid, M., Sultan, M.T.H., 2019. An overview of mechanical and physical testing of composite materials. In: *Mechanical and Physical Testing of Biocomposites, Fiber-Reinforced Composites and Hybrid Composites*. Woodhead Publishing, pp. 1–12.

More study had been carried about the utilization of coupling agent to improve the surface properties of kenaf fiber-polypropylene composite. In this research, the type of coupling agent that was used was a protein extracted from corn, typically known as zein. Based on the results, the zein coating of nonwovens kenaf was enhancing the flexural, viscoelastic properties, storage modulus and stiffness in composites. A slight decrease of thermal stability was also found in the chemical modification of kenaf nonwovens (John *et al.*, 2010). As for another example, a research had discovered that the alkali treatment combined with three-aminopropyltriethoxysilane treatment for kenaf fibers had improved the tensile and flexural properties. The properties are considerably better than those obtained from either alkali or silane treatment alone (Akil *et al.*, 2015). However, certain precautions need to be noted as awareness, such as (Ramesh, 2016):

- Chloride in clean water that was used in retting process during fiber extraction could cause fiber structure's damage, thus weakened the mechanical properties.
- There is no difference in term of fiber tensile strength, between natural pond, artificial pond with natural water and river water, if these waters were used in the retting process for initial treatment.
- If the NaOH solution was selected, it is not recommended to use more than 8%, because it can cause the fiber damage, lots of wrinkles, smaller diameter and brittle.

Some of the researchers had prepared and characterized short kenaf fiber-based biocomposites reinforced with multi-walled carbon nanotubes. The specimens were produced by melt blending process in an internal mixer. Based on the results, The optimum in mechanical strengths was detected at 1 wt% multiwall carbon nanotubes (MWCNTs) and the values of the different weight loss temperatures and second decomposition peak temperatures increased after incorporation of MWCNTs due to the barrier effect of the MWCNTs. Morphological study, which characterized using scanning electron microscopy (SEM) technique verified that a good and homogeneous distribution of MWCNTs through the biocomposites. However, some aggregates were revealed at higher MWCNT content (Yaghoobi and Fereidoon, 2019).

The Fiber Content's Effects

Beside pretreatment, the amount of fibers or fiber contents also affecting the mechanical properties of this material. Besides that, the fiber size and the aspect ratio also need to be monitored, because high ratio will transfer the stress efficiently in the matrix (Saba *et al.*, 2015). According to a review, at this moment, 60% by weight of kenaf fiber content was the maximum amount that is allowed to reinforce the kenaf fiber-polypropylene composite. More research and innovations were needed to increase the kenaf fiber content for commercial use, whereby close monitoring was required to maintain the sufficient properties of the composites. For instance, an innovative approach had been performed, by adding a special process to compound 85 wt% of kenaf fiber in polypropylene matrix. The results show that the composite had produced good modulus of rupture (MOR)- flexural strength and a modulus of elasticity (MOE)- flexural stiffness which was equivalent to common fiberboards (Sanadi *et al.*, 2002).

Another example of research that studies the effect of different fiber content was carried out by using dynamic mechanical analysis. Two types of formulation were prepared for kenaf fiber-polypropylene composite with different fiber content. As compared to original resin, it was found that the mechanical loss factor (damping) was decreased. In the other hand, the storage and loss moduli were increased, proving that the kenaf had efficiently reinforced the polypropylene matrix. More than that, there are shifting in the terms of glass transition towards the lower temperature, and the increase of temperature intensity also occurred (Tajvidi *et al.*, 2006). Additional study also had proven that kenaf fiber in powder form, with different loading, had provided adequate reinforcement to increase the strength of the polypropylene. However, this research promotes the use of coupling agent, to achieve better fiber/matrix interfacial bonding (Zampaloni *et al.*, 2007).

Morphology and Mechanical Properties

Several reviews have been made towards the morphology and mechanical properties of kenaf fiber/polypropylene composites. As for morphology studies, a research had presented the thermograms of wide endothermic of differential scanning calorimetry, demonstrating the existence of moisture. The content of moisture needs to be reduced or eliminated because it can weaken the mechanical properties. Other than moisture, the crystallization also needs to be monitored because it can affect the recrystallization, melting and spherulitic architecture. The thermograms also indicated a shift in melting temperature towards the lower temperature, nevertheless increases in enthalpy values. When the onset of recrystallization increased, the added fibers changed the crystallization by providing nucleation sites for the polymer. It is important to control the length of fiber, because more fiber tips will affect the nucleation. The fiber also influences the rate of crystallization and surface roughness, whereby the viscosity of the composites could be modified. As for the findings from the scanning electron microscope micrograph, it was displayed that the main failure factors of these composite structures were influenced by the fiber pull out and breakage (Ramesh, 2016).

In terms of mechanical properties, kenaf fiber-polypropylene composite had better properties as compare with typical fiber-polypropylene composites. For instance, the flexural and tensile modulus for 50% by weight of kenaf fiber-polypropylene are better than glass fiber-polypropylene and mica fiber polypropylene. More comparison had been made towards other types of fillers such as calcium carbonate, newspaper fibers, and talc. It was found that 40% by weight of kenaf fiber-polypropylene are much more superior to these fillers (Akhtar *et al.*, 2016). However, several factors need to be deliberated before obtaining the benefits of mechanical properties from kenaf fiber-polypropylene composite. The factors were displayed in Fig. 4 (Ramesh, 2016).

The specific properties of the natural fiber composites were in some cases better than glass fiber. Hence, the natural fiber composites have a potential to replace glass in many applications that do not require high load bearing capabilities. The relationship between tensile modulus of the kenaf composites with fiber weight fraction is demonstrated in Fig. 5. The results show an increase in the tensile modulus with increasing fiber weight fraction. Additionally, the effect of fiber weight fraction on the impact strength is indicated in Fig. 5. A moderate increase in impact strength is seen between 30 and 40% fiber weight fraction and a sharp increase from 40% to 50% fiber weight fraction. A larger serrated fracture surface was noted at 50% fiber weight fraction compared to the case at 30% fiber weight fraction of the composites, where the fracture surface was more or less flat. The serrated failure mode absorbs more energy than a sharp fracture. The failure mechanism was mainly by fiber pull out due to the weak interface strength between the fibers and the matrix (Wambua *et al.*, 2003).

More study had been conducted towards the development of thermoplastic elastomer composite reinforced with 20 vol% kenaf fiber. Two types of impact modifier were blended with polypropylene namely; thermoplastic natural rubber (TPNR) and polypropylene/ethylene-propylene-diene-monomer (PP/EPDM). It was found that the tensile strength for TPNR is about 12%

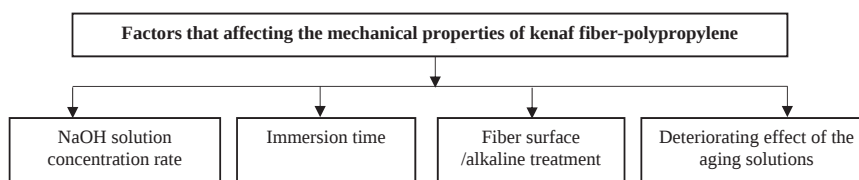


Fig. 4 Factors that affecting the mechanical properties of kenaf fiber-polypropylene composite. Credit to: Ramesh, M., 2016. Kenaf (Hibiscus cannabinus L.) fiber based bio-materials: A review on processing and properties. Progress in Materials Science 78, pp. 1–92.

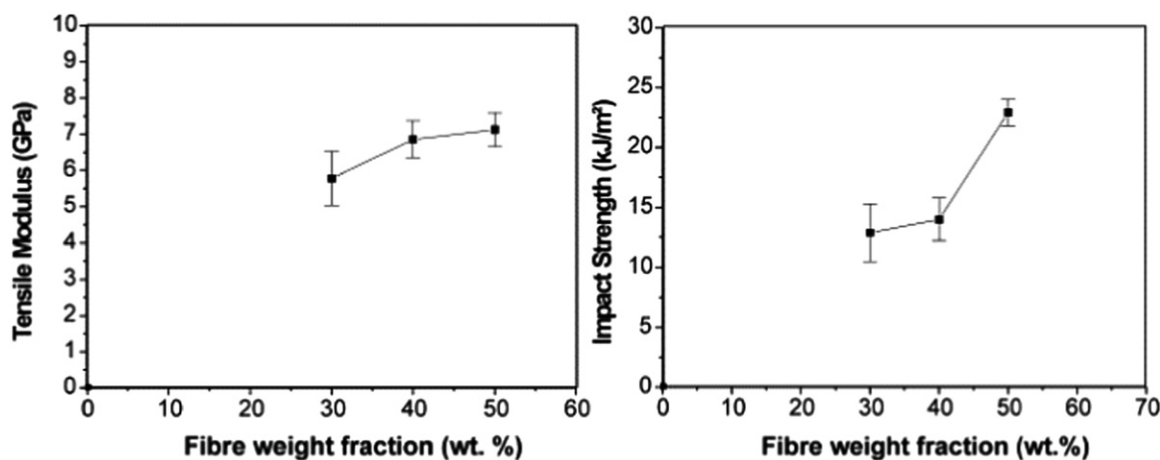


Fig. 5 Effect of fiber weight fraction on the tensile modulus and impact strength (Charpy) of kenaf fiber reinforced polypropylene composites. Credit to: Wambua, P., Ivens, J., Verpoest, I., 2003. Natural fibers: Can they replace glass in fiber reinforced plastics? *Composites science and technology* 63 (9), 1259–1264.

Table 1 Summary of kenaf fiber-polypropylene properties

No	Properties	Details
1.	Strength and modulus	● Tensile strength increase. ● Small improvement in flexural strength. ● The tensile modulus improved by adding more fibers. ● Higher modulus for composites (uncoupled).
2.	Failure strain and tensile energy of absorption	● More fibers could reduce the failure strain, due to the restriction towards molecules mobility. ● The addition of fibers also reducing the tensile energy absorption, whereby the energy absorbed was leveled off at 35 volume percentages of fiber.
3.	Impact properties	● Regardless the sample was notched or unnotched, the impact properties of this material were subjected to standard test and fiber content. ● For instance, at 45% of the fiber, the impact strength was improved. ● More fiber would create the stress concentration region that needs less energy to crack. Hence, the interfacial bonding of fiber/matrix has to be monitored.

Note: Sanadi, A.R., Caulfield, D.F., Jacobson, R.E., Rowell, R.M., 1995. Renewable agricultural fibers as reinforcing fillers in plastics: Mechanical properties of kenaf fiber-polypropylene composites. *Industrial & Engineering Chemistry Research* 34 (5), pp. 1889–1896.

higher than the PP/EPDM matrix. The present of kenaf fiber and maleic anhydride grafted polypropylene (MAPP) however, has significantly increased the tensile strength of the PP/EPDM composite by approximately 81%, while only 55% increment attained in TPNR–Kenaf fiber–MAPP as compared to unreinforced TPNR. Apart from that, flexural properties and impact strength are greatly improved for kenaf fiber composite (treated). This shows that kenaf fiber has imparted its tensile strength to the PP/EPDM system with good interaction provided by the compatibilizer agent. Scanning electron micrographs (SEMs) revealed that the improvement achieved in mechanical properties was due to the interaction between both matrix systems and kenaf fiber (Anuar and Zuraida, 2011).

As for another example of research, a lightweight laminate composite made from kenaf fiber/polypropylene was fabricated. The results show that the flexural modulus increased with increasing number of kenaf layers and heating time. The research also concluded that by using the optimized kenaf weight fraction, a maximum flexural modulus of the composite specimen shall decreased with the decrease of the bulk density (Shibata *et al.*, 2006). **Table 1** shows the summary of mechanical properties that could be obtained from kenaf fiber-polypropylene composite (Sanadi *et al.*, 1995).

Renewability, Recyclability and Sustainability

The awareness towards the environmental issues such as global warming, emission of toxic pollutants and contaminants in the sea, air and on land, destruction of biodiversity and the needs to meet the sustainable development goals, has stimulated interest in the development of recyclable and eco-friendly single polymer composites. The comparison had been made to the heterogeneous composites, fully recyclable and therefore providing economic and environmental advantages. An increasing trend is the use of natural fiber reinforced composites as low-cost composites with low density and high specific properties, non-abrasive and

biodegradable. The major challenge in the fabrication of single polymer composites is the small melting temperature difference between the fiber and the matrix, and in the case of natural fibers, the incompatibility of the fibers with the matrix, and the poor resistance to moisture (Abdullah *et al.*, 2019). When natural fibers are closely compared to inorganic fibers, it presents some well-known advantages such as lower density and cost; are less abrasive to the processing equipment, easy to modify the fiber surface, and its relative non abrasiveness. Furthermore, they are recyclable, easily available in most countries, harmless, biodegradable and renewable. (Li *et al.*, 2008). So, the renewability of kenaf fiber-polypropylene composites was typically associated with the renewability of kenaf as natural fiber.

Environmental concerns have attracted researchers to recycle composite materials and thermoplastics due to the desire not to waste materials and reduce disposal of scraps that may eventually pollute the environment. Hence, more studies associated with kenaf recycling had been carried out, such as the effect of recycling on the mechanical properties of kenaf fiber/polyethylene terephthalate reinforced polyoxymethylene hybrid composites. The result shows that the tensile strength after second recycling process is lower compared to the virgin hybrid composite. The impact strength also dropped to 4.3 J cm^{-1} as against 10.5 J cm^{-1} for the virgin hybrid composite. In the other hand, there was a significant increase in flexural modulus compared to the virgin hybrid composite. The results of thermal degradation showed about 80% weight loss for kenaf fiber between 300°C and 350°C . This condition happened because of the degradation of cellulose and hemicellulose content of the fiber. The percentage water absorption of the recycled composite dropped by 80% compared to the virgin hybrid composite (Dan-mallam *et al.*, 2014).

Some of the researchers try to blend the kenaf fibers with recycled plastics or low-cost polyethylene in form of post-consumer film wastes and shrink wraps. Manufacturing tests were conducted at the U.S. Forest Products Laboratory, showed that kenaf stems can be used as filler in virgin plastics to yield impact properties, similar to wood-filled composites. However, the deficiency of the kenaf-based composites was the low tensile strength which suggests that they should not be utilized in systems requiring high tensile property. Recyclable and environmental-friendly products could be produced from kenaf fibers with potential used in industries like the container and the automotive industry (Chow *et al.*, 1998). Another project that used recycled polypropylene (rPP)/recycled polyamide 6 (rPA6) reinforced with kenaf had been conducted, whereby the composites thermal properties, processing behavior and morphological study were investigated. Based on the findings, instead of the decrement in impact properties, other mechanical properties were improved when the compositions of kenaf were increased. However, it was difficult to process the high composition kenaf by using the typical injection molding machine as the melt flow index values increased. Scanning electron microscopy (SEM) micrographs showed an improvement in the dispersion of kenaf in the matrix when kenaf compositions were increased. The overall results showed the best composition of kenaf was at 30 wt% (Arsad *et al.*, 2013). The recycling frequency also had been studied, whereby the properties of polypropylene-based composites reinforced with kenaf fibers were investigated with respect to their recyclability. As for the results, the recycling processes do not induce very significant changes in flexural strength and thermal stability of the composites. In particular, polypropylene-based composites reinforced with kenaf fibers are less sensitive to reprocessing cycles as compared with polypropylene-based composites reinforced with rice hulls (Srebrenkoska *et al.*, 2008). More than that, the recycled polypropylene kenaf composites also can be utilized for inflammability and biodegradability of biocomposites improvement. The example of materials formulations content that could be used as a fire retardant were recycled polypropylene, modified acrylic acid, reinforcement kenaf fiber, the mixture of magnesium hydroxide and aluminum hydroxide, without or with boric acid (Suharty *et al.*, 2014).

More research had utilized the recycled polypropylene reinforced with kenaf fiber. These composite comes with the improved interfacial adhesion between fiber and recycled polypropylene (RPP) matrix. The improvement was carried out by performing fiber surface modification through ultrasound treatment. Maleic anhydride grafted polypropylene (MAPP) was used as a coupling agent. The composites were examined by mechanical test, melt flow indexing test, scanning electron microscopy, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). Water uptake analysis and accelerated weathering test were also carried out to find the suitability of the composites in outdoor application. Among the raw fiber contents ranging 10–50 wt% in the composites, the maximum tensile strength was observed at 40 wt% fiber loading without using MAPP. Treated fiber based composite with MAPP promotes the maximum of tensile, which is 57% higher than that of untreated composite. TGA and DSC analyses exhibit an enhancement of thermal stability for composite with MAPP. Incorporation of MAPP in the composites shows higher activation energy, suggesting improved interfacial bonding between fibers and matrix (Islam *et al.*, 2013). This research was continued by characterizing the laccase-treated kenaf fiber reinforced recycled polypropylene composites. Raw and laccase-treated kenaf fiber was used individually to reinforce RPP using extrusion and injection molding. Laccase was used to modify the surface of the fiber to improve the compatibility between fiber and matrix. Enzyme concentration and soaking time were considered as the treatment parameters. Based on the findings, the optimum fiber loading of 40% gave the highest tensile properties. Tensile strength improved due to coupling agent by 37%, whereas treatment of fiber did the same by 40%. Flexural, impact, and thermal properties of the composites and crystallinity of the matrix were improved due to treatment. Morphological images of the composites showed better adhesion, and moisture absorption was reduced by 37% due to treatment and use of coupling agent (Islam *et al.*, 2013).

In terms of sustainability, the carbon footprint of kenaf can be used as the guide. A system had been studied by adopting from cradle to grave concept of kenaf fiber production. The cultivation and fiber processing are anticipated to take place in India and Bangladesh. Transportation to the harbor in Hamburg, Germany, happens via ship and continues with lorry to the factory gate of the nonwoven producer in Germany. Typically kenaf is cut and water retted like jute. After retting, the fibers are manually extracted from the stems, then washed and sun dried. These activities are done manually by farmers, but not all agricultural and

decortication steps are done manually: some field applications involve tractors. Lastly, the dried fibers is delivered in rough fiber bundles to the so-called “fine-opening-processing” site, where they are refined and cut into the desired length for selling to the non-woven producer. These finishing steps are done with machines. Regarding the kenaf scenario, the fertilization is the main contributor to kenaf’s carbon footprint. The carbon footprint of the kenaf fiber scenario is 767 kg CO₂-eq/tons of kenaf fiber. In contrast to hemp and flax, kenaf plants are generally cultivated manually, but sometimes small tractors are also used for this kind of work. Because of manual field operations, emissions stemming from this process are quite small. On the other hand, emissions from transporting the kenaf from Asia to Europe have to be taken into account as well (Barth and Carus, 2015). According to (ISCC, 2013), it states a seventh principle, which deals with the designation of greenhouse gas emissions and which needs to be applied for the production of biomass. Hence, the development and utilization of kenaf fiber with polypropylene should consider the listed principles in order to achieve the suitability goals. The principles are:

- (1) Biomass shall not be produced on land with high biodiversity value or high carbon stock. High conservation areas shall be protected.
- (2) Biomass shall be produced in an environmentally responsible way. This includes the protection of soil, water and air and the application of Good Agricultural Practices.
- (3) Safe working conditions through training and education, use of protective clothing and proper and timely assistance in the event of accidents.
- (4) Biomass production shall not violate human rights, labor rights or land rights. It shall promote responsible labor conditions and workers’ health, safety and welfare and shall be based on responsible community relations.
- (5) Biomass production shall take place in compliance with all applicable regional and national laws and shall follow relevant international treaties.
- (6) Good management practices shall be implemented.
- (7) Calculation and verification of greenhouse gas emissions must be provided by the biomass producer.

Industrial Applications and Developments for the Future

Most of the applications were proposed based on the kenaf fiber-polypropylene composite mechanical properties. However, other properties could bring more applications. For instance, based on a review, the sound insulation test had been carried out towards these composites. It was verified that there are relationship between mechanical properties and acoustical behavior. This verification was described by the panel resonance theory, indicating that the classic panel resonance theory. Other than that, the utilization of kenaf fiber-polypropylene composite also have some benefits in terms of the thermal behavior. For instance, the test of heat deflection temperature or heat distortion temperature had produced a higher heat deflection characteristic than pristine polypropylene. A wear test also had been conducted, with the results shows that the fiber orientation, applied load and sliding velocity have a significant effect on the wear properties of kenaf fiber reinforced composite laminates. The wear mechanisms of the composite were also predominated by micro-cracks and debonding in the fibrous regions and deformation in the resinous regions. Hereafter, any product associated to wear and tear should take this substance into deliberation. Even though kenaf fiber-polypropylene composite had many potential and applications, precaution was needed to ensure the reliability of the product to be maintained. For instance, the exposure of the kenaf fiber reinforced composites to environmental conditions such as distilled water, sea water and rain water may result a decrement of fracture toughness. However, this condition relies on the content of the fiber, fiber orientation, area of exposed surface, and permeability of fiber, void content and the hydrophilicity of the individual component (Ramesh, 2016).

Another potential application of kenaf fiber that can be considered is to use kenaf as a bulletproof vest. A research had stated some findings about the tensile and flexural characteristics and high-velocity impact properties of a new composite material aimed to replace the current insert plate for existing available bulletproof vests or body armor. In this design, materials used are a kenaf, and x-ray film. Results showed that the designs enabled the material to absorb some impact energy because it was able to bounce back bullets shot (Azmi *et al.*, 2019).

Natural fibers have recently become attractive to the automotive industry as an alternative reinforcement for glass fiber reinforced thermoplastics. The best way to increase the fuel efficiency without sacrificing safety is to employ fiber reinforced composite materials in the body of the cars so that weight reduction can be achieved. A research has focused on partially eco-friendly hybrid long fiber reinforced thermoplastics with natural kenaf fiber to enhance the desired mechanical properties for car bumper beams as automotive structural components. The comparison had been made with a typical bumper beam material made from long fiber reinforced thermoplastics (LFRT). The results indicate that some mechanical properties such as tensile strength, young’s modulus, flexural strength and flexural modulus are more advantages to LFRT, the new material also must improve the ability to absorb more impact load and increase the protection of the front car component (Jeyanthi and Rani, 2012).

Another potential of kenaf fiber reinforced composites is to be used as electronic products. Some researchers have developed high-performance biomass-based plastics that consist of polylactic acid (PLA) and kenaf fiber, which fixates CO₂ efficiently. Adding this fiber to PLA greatly increases its heat resistance (distortion temperature under load) and modulus and also enhances its crystallization, so the ease of molding this material is improved. Eliminating the short particles from the kenaf fiber improves its effect on the impact strength. Furthermore, adding a flexibilizer (a copolymer of lactic acid and aliphatic polyester) to the

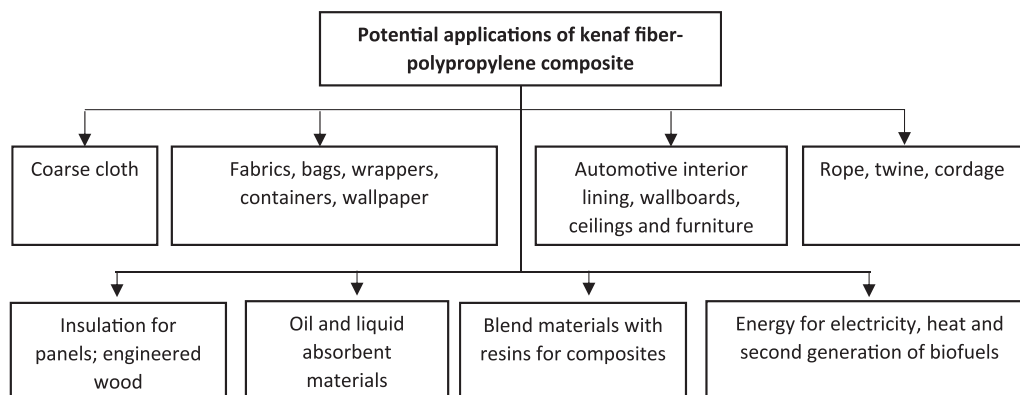


Fig. 6 Potential application of kenaf fiber-polypropylene composite. Note: Ramesh, M., 2016. Kenaf (*Hibiscus cannabinus* L.) fiber based bio-materials: A review on processing and properties. *Progress in Materials Science* 78, pp. 1–92.

composites improves their strength. These composites (PLA/kenaf fiber and PLA/kenaf fiber/flexibilizer) show good practical characteristics of housing materials of electronic products in comparison with petroleum-based plastics used in housing such as glass-fiber-reinforced acrylonitrile-butadiene-styrene (ABS) resin (Serizawa *et al.*, 2006).

Kenaf composite also can be used as insulation boards. An eco-profile of the kenaf-fiber thermal insulation board has been defined and, on the basis of a life-cycle approach, the energy and environmental benefits and drawbacks associated with its use in residential buildings have been assessed. The kenaf-fiber based products become widely the less impacting ones if different disposal scenarios are adopted. Finally the energy saving during the building operating time results largely higher than the global energy consumption related to the kenaf insulation board life-cycle. This confirms the large energy and environmental advantages related to the employment of insulating materials (Ardente *et al.*, 2008). Based on the benefits that were obtained by combining kenaf fiber with polypropylene, industries are willing to invest their capital in producing several products, made from kenaf fiber-polypropylene composite. Some of possible application of kenaf fiber-polypropylene composite are displayed in Fig. 6 (Ramesh, 2016).

Research about biocomposites had created remarkable achievements to replace conventional non-biodegradable petroleum-based materials. Bio-based materials could provide solutions for petroleum shortage and waste management problems. The specific focus has been given to wood-derived polymers (lignin, hemicelluloses, and cellulose) for production of bio nanocomposites. Large-scale productions of bio-macro/micro/nanocomposites at pilot/industrial scale and various fundamental and technical challenges in production (both in lab and pilot scale) have been given priority for further development (Nagalakshmaiah *et al.*, 2019). As for future development, kenaf fiber reinforced composite has a good prospect to be utilized in various manufacturing processes that have never been associated with other natural fibers before, such as pultrusion and filament winding. According to the previous review, the use of kenaf fiber reinforced composite in building and construction, is highly possible due to two main factors, which are low in cost and lightweight material (Thiruchitrabalam *et al.*, 2012). Moreover, recent development had concentrated more towards sustainable materials and manufacturing, whereby more focus and research had aimed towards renewable and biodegradable resources. Kenaf, also comes in the several forms and shape, also can be planted in different region will inspire the researcher to study the effects and propose more applications in wider aspects of industries. By solving the ecological issues, the massive usage of kenaf fiber may reduce pollutions towards atmospheric and water, showing it has a brighter future as compare to other industrialized fibers. However, treatment of effluents, disposal of waste and packing material and recycling issues will also require enormous capital outlays motivate the usage of these composites (Ramesh, 2016).

In the Industrial Revolution 4.0 (IR4.0) era, some of the key content of future technology is related to the Internet of Things (IoT), Cyber Physical System (CPS), Information and communications technology (ICT), Enterprise Architecture (EA), and Enterprise Integration (EI) (Lu, 2017). Hence, these technologies can be supported through computer modeling and simulation. Future development of research related to composites, modeling and simulation also had become the trend among researchers. For instance, a paper introduces a numerical model of kenaf composites, made from the unsaturated polyester matrix reinforced with unidirectional kenaf fiber. Two different dynamic failure models, both the ductility and shear failure models were described in the matrix. Hashin's failure criterion was used for the fiber to predict the mechanical behaviors of the kenaf composite under distinct high strain rate loading. It was found that the developed meso-scale model is found to be effective in providing detailed information regarding the deformation and stress distribution of the kenaf composites to obtain a better understanding of the mechanical response of the constituent materials under different loading conditions (Seman *et al.*, 2019). More research had been carried out about the input for computer simulation, such as a research about the inverse method for identifying the material properties of a kenaf reinforced composite test model. An initial finite element model of the composite test model is developed and normal modes analysis is carried out to calculate the modal parameters of the initial finite element model. It was found that the identified material properties are well matched with that of previously published papers in terms of the reduction in total errors (Peter *et al.*, 2019).

Conclusion

Explorations on kenaf fiber reinforced composite have created more influence among researchers due to the ecological factor, as well as the cost and the properties gained from this composite. This article had provide summaries in term of why kenaf fiber and polypropylene were chosen to be combine, the preparations and treatments needed, the effect of fiber content, the morphology and mechanical properties, and the renewability, recyclability and sustainability of kenaf fiber reinforced polypropylene. At the end the list of application and future development of this advanced material. As for the conclusion, kenaf could be a good alternative fiber to be used with polypropylene, with more and more applications and prospect for impending progress.

See also: Bamboo Fiber as Fillers for Polypropylene-Nanoclay via Injection Molding. Bio-Waste Based Nanofiber Materials. Influential Parameters on Formation of PEMs on Recycled Fibers: A Review. Kenaf Fiber Based Bio-Composites: Processing, Characterization and Potential Applications. Kenaf Fiber Reinforced Composite in the Automotive Industry. Natural Fiber and Synthetic Fiber Composites: Comparison of Properties, Performance, Cost and Environmental Benefits. Natural Fiber Composites: Review of Recent Automotive Trends. Natural Fiber Reinforced Composites in the Context of Biodegradability: A Review. Recyclability of Natural Fiber-Filled Thermoplastic Composites. Reuse of Waste Corrugated With Coir Fibers as a Packaging Material. The Utilization of Vegetable Fibers in Cementitious Materials. Use of Bio-Fibers in Various Practical Applications

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Renewable Metal Working Fluids for Aluminum and Heavy Duty Machining

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Introduction

Lubrication and cooling are the most important functions of a fluid applied during a metal cutting operation. However, the type and degree of lubrication and the degree of cooling required for a particular metal removal process depend on various factors which include the type of operation, the properties of the cutting tool and workpiece material, and the speed, feed, and depth of cut selected. Conventional machining processes are associated with heat generation, tool wear, energy consumption, surface and subsurface defects of the workpiece including surface roughness, residual stresses etc. All these problems can be checked by providing proper lubrication to the machining zone during the machining process. The cutting fluid reduces coefficient of friction at the chip-tool interface as well as at the tool-workpiece interface. This in-turn results in reduction of resultant force by diminishing frictional forces at the two interfaces. At the same time, it also helps in removal of chips during machining and cooling down the cutting zone effectively. The most common and conventional method of the application of lubricant during machining is flooded lubrication technique in which the lubricant is allowed to impinge on the cutting zone in abundance. Flooded lubrication technique is associated with various economic and environmental issues. Abundant usage of lubricant increases manufacturing cost and causes dermatological and respiratory syndromes to the machinists. A large amount of fluid used in this technique is generally mixed with biocides to make it reusable. Biocides are detrimental to the environment. Disposing of cutting fluid is also a great ecological concern if it is non-biodegradable. That is why governmental rules are becoming stricter towards the use and disposal of cutting fluids. The best and ideal alternative is to perform dry machining where no harmful cutting fluid is used. However, dry machining is not feasible in most of the cases, especially in Al and heavy-duty machining. Another alternative is to use environmentally safe renewable cutting fluids. Nevertheless, the problem is that they can be used only after mixing with various additives. The additives are mixed in these oils to make them suitable for the use as cutting fluids. Several blends of such cutting fluids are available in the market. Initially, the share of such lubricants was very low in the worldwide lubricant market, but now, the growth is anticipated at a very high rate annually. There has been increased interest in the development of metal working fluids that can be derived from renewable resources. The most common renewable base oils used for the development of cutting fluid are synthesized esters received from a triglyceride of vegetable oil (e.g., rapeseed oil, palm oil) or animal fat. Renewable base oil, either natural or synthesized, required additives and the formation methodology as transesterification, hydrogenation etc. used to tailor the properties. These are to be carefully considered for the formation of a renewable metal working fluid.

Renewable Metal Working Fluids

Traditional non-renewable lubricants can be effectively replaced by the cutting fluids produced through renewable base stocks. In the modern era, industries are adopting measures for sustainable development by reducing the dependency on non-renewable natural resources. Therefore, the demand for renewable metal working fluids is increasing day by day because they are generally non-toxic, environment-friendly and readily biodegradable in nature along with having good lubricating properties. In some cases, renewable metal working fluids, having high affinity to the mating surfaces during machining, show better lubricating properties than that of the petroleum-based oils. These oils can be used as base oils in lubricants because they generally remain liquid at room temperature as well as they contain at least one ester as a functional group. Chemical properties of the base oil affect its successful application in machining process. Adsorption property of the oil makes it able to adsorb onto frictional surface and prevent their contact during machining processes. This property depends on interaction of functional groups of the oil with the surfaces. Properties which allow a lubricant to act as metal cutting fluid include its non-toxicity, biodegradability, high viscosity index, good lubricity (Mahadi *et al.*, 2017) and its ability to form a boundary lubricant through penetration into the mating surfaces during machining. By adding suitable additives, properties of a natural oil acting as base oil can be altered to make it suitable for acting as a lubricant in machining processes. There are three important factors on which the performance of a lubricant depends namely, base oil, additives and formulation methodology as shown in Fig. 1 below. Low thermo-oxidative stability is a major issue encountered during the use of renewable natural oils in metal cutting applications. Their stability can be improved either through esterification/transesterification process for modification of the carboxyl group or through the methods like selective hydrogenation, dimerization/oligomerization, formation of C–C and C–O bonds, metathesis or oxidation used for modifications of the fatty acid chain (Shashidhara and Jayaram, 2010).

Additives

Renewable oils, either natural or synthesized, cannot be used in their purest form (without additives) as metal cutting fluids because they lack various essential features. Performance of the oil is improved with the addition of proper additives in appropriate proportions. Additives affect the properties of tribofilms or boundary lubrication film significantly. This surface protection

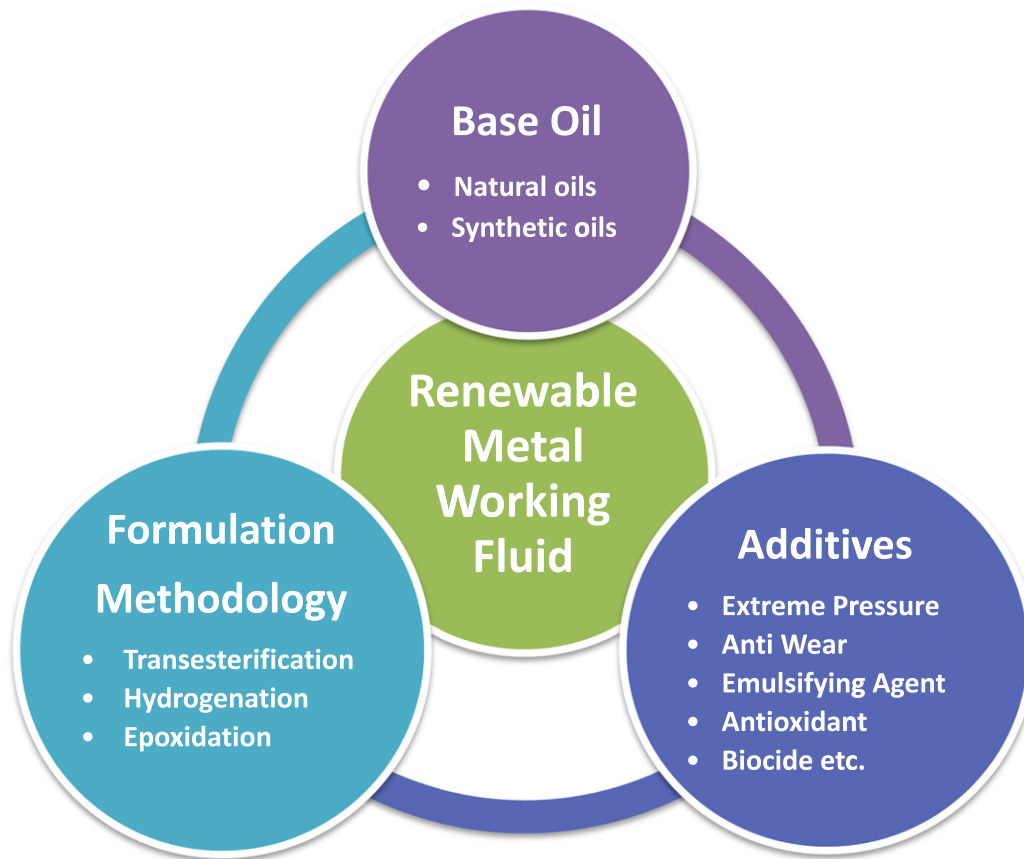


Fig. 1 Formation of renewable metal working fluids.

film is developed between the mating surfaces by chemical changes on the surfaces, which are influenced by these additives. Anti-wear additives (AW), extreme pressure additives (EP), anti-oxidants (AO), emulsifying agents (EA), and biocides are the most commonly used additives.

Primary function of EP and AW additives is to protect the metal surface during rubbing. These additives react thermo-chemically with the heated metal surface and produce a protective film of easily sheared layers of sulphides, chlorides or phosphides. These layers are sheared off first during machining protecting the tool and machined surface. Some of the examples of AW additives are zinc dialkyldithiophosphates (ZDDP), S-[2-(acetamido) thiazol-1-yl] dialkyl dithiocarbamates, Palm oil methyl ester (POME), Dibutyl 3,5-di-*t*-butyl-hydroxy benzylphosphate (DBP) etc. The additives form polar head of the molecular layers, which are closely packed and arranged in a proper order to form the lubricating film. Extreme Pressure (EP) additives form layers of sulphides, chlorides or phosphates of iron through tribochemical reactions and protect the mating surfaces in EP conditions. Zinc-Dialkyl-Dithio-Phosphate (ZDDP) acts as EP additive. Butylated hydroxyl anisole (BHA), Butylated hydroxyl toluene (BHT), Mon-*tert*-butyl-hydroquinone (TBHQ), propyl gallate (PG) are those additives that act as chain-breaking antioxidants. Zincdithiophosphates (DTP), Dithiocarbamates (DTC) are the examples of peroxide decomposer antioxidants (Choudhury and Muaz, 2018). Environmentally safe nanoparticles, like TiO₂, CuO and ZnO are reportedly giving good results comparable to the conventional EP additives (Zainal *et al.*, 2018). Emulsifying agent (EA) is also an important additive for such applications. EA is mixed to develop stable renewable oil-in-water emulsion. Polyoxyethylene (20) sorbitan monopalmitate, polyoxyethylene (40) sorbitan tetraoleate, polyoxyethylene (20) sorbitan monostearate, Ethoxylated oleic acid ester are some common non-ionic EA. Biocides and anti-corrosive agents are to be added as additives according to the requirement. Ethanolamine is a good example of anti-corrosive agent as it helps in stabilizing the emulsion too. Biocides generally belong to family of triazine derivative (triclosan). They restrict the growth of bacteria and fungus in most of the renewable oils. Selection of the additives should be made intelligently and only those additives should be added which are necessary for a particular application (Choudhury and Muaz, 2018).

Properties of Renewable Metal Working Fluids (MWF)

Renewable MWF are now becoming the most important alternatives to traditional petroleum-based fluids because of their inherent qualities like possibility to achieve tailor-made properties, no toxicity, and excellent biodegradation. Organic compounds

containing ester linkage have good lubricating properties. An ester is a product of chemical reaction between alcohol and fatty acid. Presence of organic groups coming from alcohol and organic acid and the ester linkage of high bond energy incorporates excellent properties to the oil, including good response to additives. Various biopolymers, glycerol and gelatin were also tested in the application of metal working fluids. Renewable oils demonstrated similar or in some cases better machining performance than that of the conventional mineral oils. In some basic properties, most of the renewable oils are superior to mineral oils. As far as their application in machining is concerned, the most important property is the lubricity of the renewable oil. Boundary lubrication is the dominant lubrication mechanism in the vegetable oils because of high polarity of the base oil due to which strong interaction occurs between the fluid and the mating surfaces during machining. Presence of polar charge and oxygen containing functional group in the oils make these oils able to produce thick and stable lubricating layers on the interfaces (Choudhury and Muaz, 2018). Polar charge present in fatty acids of the oil draws the molecules of oil towards the metallic surfaces. These molecules do not flow out easily from the interacting surfaces. Oxygen-containing functional groups present in these oils also have an affinity towards metallic surfaces. The most basic component of a vegetable oil is a glycerol molecule. Triacylglycerides (triglycerides) are glycerol molecules consisting of three long-chain fatty acids. Hydroxyl groups are attached to the fatty acids through ester linkages. Long chains of fatty acids are polar in nature, which make them able to provide lubricant films of high strength. This film interacts strongly with metallic surfaces and reduces both friction and wear.

Renewable oils, in various aspects perform better than mineral oils because the viscosity, flash point, biodegradability and lubricity of renewable oils are higher while toxicity, friction and wear characteristics are lower than that of the mineral oils (Zainal *et al.*, 2018). High viscosity indices of vegetable oils make them applicable for a wide range of temperature by maintaining thick lubricating film even at high temperatures. In the purest form, renewable oils generally are more viscous than mineral oils. In most of the metal cutting applications, high viscosity is favorable because it provides a stable layer over the mating surfaces. However, the viscosity depends on temperature, pressure and film formation. Higher flash points of vegetable-based lubricants made them safer than mineral oils. Antiwear properties of these oils are also better than mineral oils as they can easily produce protective film over the contacting surfaces (Chandrakar and Suhane, 2014). However, these oils are inferior to mineral oils in terms of oxidation stability, thermal stability, corrosion protection etc. but can be modified by blending with suitable additives.

Classification of Renewable Metal Working Fluids

Renewable metal working fluids can be broadly classified as water-based or oil based fluids as shown in Fig. 2 below. Water based fluids can be further divided into emulsions and solutions. Emulsions can be produced through synthesized renewable oils or through natural vegetable oils after blending the oils with suitable emulsifiers. A large number of different vegetable oils namely, palm, coconut, olive, soy, neem, sunflower, castor, jojoba etc. can be used for the production of emulsions. These oils do not dissolve in the water but only get dispersed homogeneously producing emulsions. Water-based solution can be produced by using materials synthesized from renewable base fluids. Examples include glycerin and cellulose. Oil-based renewable metal working fluids can also be produced by using vegetable natural oil or by using synthesized esters. These esters are extracted from renewable resources that may be floral or faunal. In all the oils discussed so far, the base oil is extracted from a renewable resource and then it is modified as per the machining requirements. Compositions of the cutting fluids vary with the requirements. As an example, composition of emulsions required for light to heavy duty machining is illustrated in Table 1 below.

Selection of Cutting Fluid

Considerable efforts are necessarily to be made when selecting a right metal working fluid for machining practice. Choice of a cutting fluid is based on various factors including the properties of workpiece material, the type of machining operation, required output responses like tool life, surface finish, desired tolerance etc., along with economic and environmental concerns (Kelly and Cotterell, 2002). In the 1960s, the most important criterion was the price per gallon of the oil because it was believed that this have no significant influence on the manufacturing processes. In modern days, serious attention is generally paid towards selection of a proper fluid according to the requirements. Following criteria must be considered for selecting a suitable cutting fluid for a particular application:

- Lubricating and cooling ability.
- Operator safety.
- Renewability of the resources.
- Ease of disposal or recyclability.
- Low cost.

The most important criterion is the ability of the fluid to improve the machinability by generating desired shape, size, finish and accuracy on work material and extending the tool life. Next is the compatibility of the fluid in terms of its applicability to a wide range of work materials, anti-corrosion properties, resistance to microorganism growth and long life. Similarly, the fluid should be safe for operators' health and for the surrounding environment. In a nut shell, cheapest fluid must be selected based on

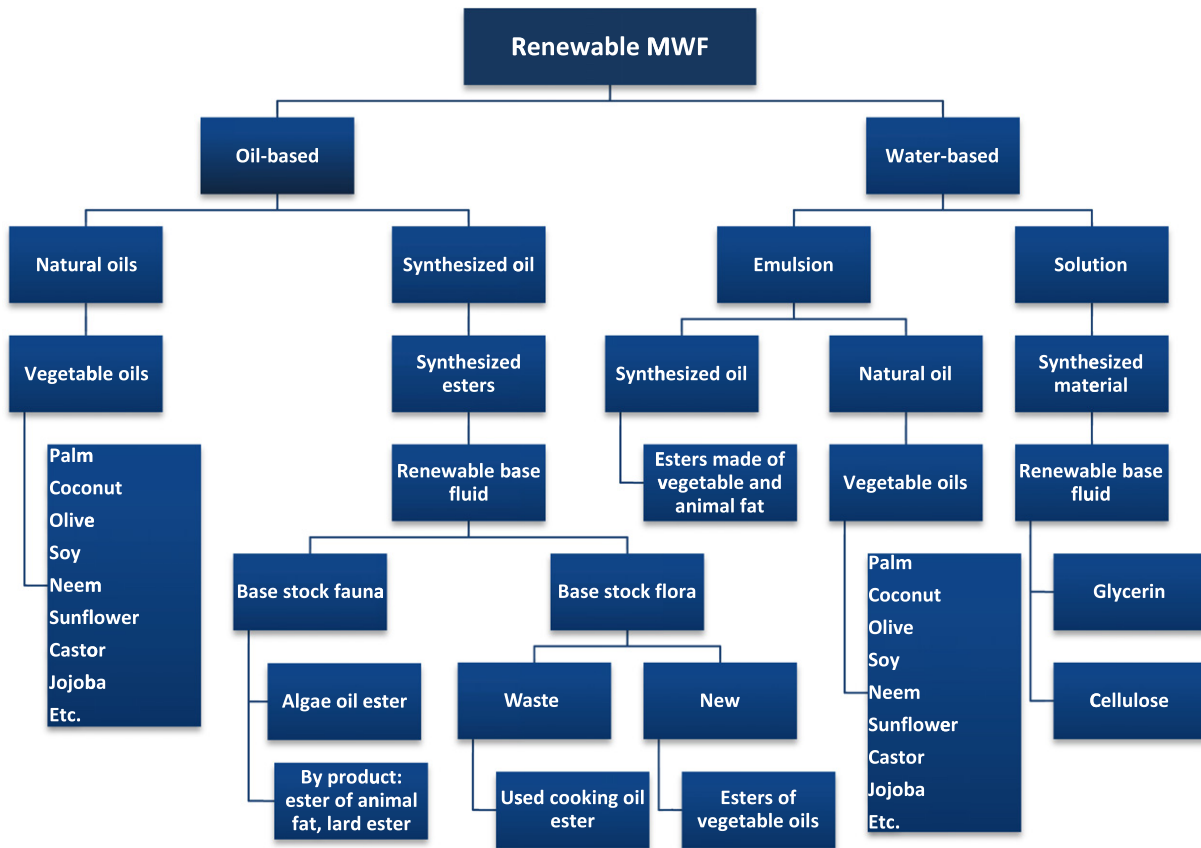


Fig. 2 Classification of renewable metal working fluid. Reproduced from Brinksmeier, E., Meyer, D., Huesmann-Cordes, A.G., Herrmann, C., 2015. Metalworking fluids – Mechanisms and performance. CIRP Annals – Manufacturing Technology 64 (2), 605–628. doi:10.1016/j.cirp.2015.05.003.

Table 1 Composition of cutting fluids (in wt.%) for different types of machining

	Base oil	Emulsifier	EP additives	Other additives
Light duty machining	83	15	0	2
Medium duty machining	70	15	10	5
Heavy duty machining	30	20	40	10

Note: Stephenson, D.A., Agapiou, J.S., 2016. Metal Cutting Theory and Practice. third ed. Boca Raton: CRC Press, Taylor and Francis Group.

operator safety, kindness to the machine, ease of disposal, the ability to perform the needed cutting (Sluhan, 1994). Different cutting fluids show a variety of diverse properties: some fluids provide only good cooling effect, some provide only good lubrication while some are good enough in demonstrating both of the two properties simultaneously. Economic issues related to the cutting fluids like the cost of recycling the fluid, the cost of fluid disposal are also to be considered. Moreover, environmental issues are becoming more important day by day. Nowadays, sustainable development is becoming the necessity where resources should be utilized keeping in mind the needs of the future generation. Sustainable development of manufacturing industries can be achieved through a modern manufacturing strategy known as green manufacturing by reducing the resource consumption, waste production, and pollution through proper design of product or process (Dixit *et al.*, 2012). Use of conventional metal working fluids can be effectively replaced with the fluids produced by utilizing renewable resources. Cutting fluids based on vegetable oils are the best alternatives to the conventional ones as they are non-toxic, environment-friendly and readily biodegradable in nature along with having good lubricating properties. As far as the properties of workpiece materials are concerned, the required properties of the cutting fluids vary widely. Cutting fluid used for machining a ductile material like Al should possess good cooling capacity while for a hard and difficult-to-cut material highly viscous fluids with good lubricating properties are required. Emulsifiable oils which are more advantageous than straight or compounded cutting oils in various aspects can be used for most heavy duty applications (El Baradie, 1996).

Application of Renewable MWF for Machining of Al

Ordinary cutting fluids used for machining of steels are not feasibly applicable for the machining of Aluminum and its alloys. Cutting fluids are to be modified to make them suitable for this special case. Therefore, special attention should be paid towards selection of the best suited fluid by considering following three important points (Kelly and Cotterell, 2002):

1. Rapid thermal expansion

Coefficient of thermal expansion of Al is very high as compared to iron and steel. During machining, when temperature of the workpiece increases, undesirably it expands rapidly in all directions. Therefore, cutting fluids with high heat dissipating ability are desirable.

2. Formation of hard Aluminum oxides

Temperature of the workpiece increases during machining. When heated metal is exposed to the oxygen, very hard Aluminum oxide films are developed. These films are responsible for reduction of tool life and deterioration of machined surface. Therefore, such cutting fluids are required, which have the ability to suppress the formation of Aluminum oxides.

3. Adhesive nature

Presence of significant amount of Silicon in an Al alloy makes it sticky in heated condition. As a result chip welding and built-up edge formation is promoted which is detrimental to the tool life and machined surface. Particular additives should be mixed with the lubricant to cope up with this problem.

Among all the three problems associated with the cutting of Aluminum, adhesion is the most detrimental. Adhesion is basically dependent on the presence of Si in an Al-alloy. As Al alloys are lightweight, they are used in large volumes in automotive industry to make the vehicles fuel-efficient. The automotive parts like engine and gear box are generally manufactured through casting operation. Ability of the Si to improve the castability and to make the final product more abrasive resistant made its addition into the alloy inevitable for complex castings (Coelho *et al.*, 1995). However, as far as machining of the cast parts are concerned, it shows detrimental effects by making the material adhesive. It is very important to consider its presence before starting work on it. Some researchers investigated the application of natural oils using MQL during machining of especially this type of Al-alloy. Although, MQL is emerging as an environment-friendly and promising technique for the application of metal cutting fluids, it has not been selected for the machining of Al alloys extensively (Filipovic and Stephenson, 2007). As compared to conventional machining, machining of Al through MQL is cheaper, environmentally safe by reducing the aerosol particles, and produces dry chips since the applied lubricant is fully burnt out at the machining zone. Itoigawa *et al.* (2006) investigated the effects of natural oil mixed with water and applied through MQL to the Aluminum silicon alloy (AlSi5), which is not easily machinable. Natural oil develops a boundary film on the tool face. This film is very weak and therefore it can only be beneficial in light cutting operation. It neither can restrict the adhesion of the work material to the tool nor provide good friction. Water mixed with oil plays an important role in MQL application to the Al-alloy. Water helps in providing proper lubrication by improving chemisorption and by sustaining film strength by cooling down the oil (Itoigawa *et al.*, 2006).

Davoodi and Tazehkandi (2014) applied vegetable oil while machining Aluminum alloy 5083 and tried to provide optimum cutting parameters that can be used to eliminate the usage of lubricant completely. However, the details about the oil used are not provided by the authors.

Sreejith (2008) investigated the effect of dry, flooded and MQL conditions on the machining of 6061 Al-alloy which has Mg and Si as major alloying elements. It was observed that the work material adhered to the tool at all faces and in all machining conditions. The adhesion was dependent on the amount of applied lubricant. However, adhered amount was lowest during flooded lubrication while highest during dry cutting. MQL reduced the adhesion as compared to dry cutting. The author suggested that it could further be reduced in the case of MQL by improving the tool geometry. Similar trend was found for cutting forces also and it was suggested that cutting fluid constituents should be investigated for further reduction of forces in MQL application. Surface roughness was observed to be reduced with the application of cutting fluid. Economic and environmental benefits associated with MQL make this technique more acceptable for machining (Sreejith, 2008).

Jatropha-based soluble cutting oil, a renewable metal working fluid, exhibits satisfactory performance during the machining of 7050-T7451 Aluminum alloy. Its performance was compared with other oils like canola (vegetable oil), semi synthetic (mineral oil), and synthetic (Jatropha ester) oils. The Al-alloy, having composition of 6.2% Zn–2.3% Cu–2.2% Mg and 0.2% Zr, is commonly used for the production of the components of aeronautical structures. The presence of esters, unsaturated aliphatic hydrocarbons (double-linkage), polycyclic/mono-replaceable aromatic hydrocarbons, CH₂ of long chain and linkages N–H along with sulphur (0.63694%) make them suitable for machining of Al-alloy. Absence or insignificant presence of phosphorous, chlorine and nitrosamines make the oil environmentally safe. The addition of extreme pressure (EP) additive containing Sulphur is necessary for an oil to act as good lubricant. However, its content should be below the allowed limit (<4%) set by ASTM D874. Significant reduction in cutting force and increment in tool life was observed when Jatropha based oil was applied. Very low cutting forces were observed. The fluid showed much better lubricating ability as compared to other oils like canola (vegetable oil), semi synthetic (mineral oil) or synthetic (Jatropha ester) oils by increasing the tool life tested at various feed rates. Foam generated by Jatropha based fluid was at the acceptably low level as compared to the canola-based oil. The renewable metal working fluids that have clusters of nitrogen and hydrogen (N–H) as in Jatropha vegetable-based oil are more suitable for machining of Al-alloy as compared to the fluids containing clusters of alcohol and CH₂ as in canola vegetable-based oil (Bork *et al.*, 2014).

The renewable metal working fluids should not be relied upon solely for the machining of Al-alloys, especially the alloys with high Silicon content. Other factors responsible for improving the machinability should also be considered simultaneously. For example, during reaming of an Al-alloy (AlSi12), acceptable results were obtained when the fluid consisting of fatty alcohol was applied through minimum quantity lubrication technique and the tool with PVD coating was used (Lugscheider *et al.*, 1997).

Application of MWF for Heavy Duty Machining

Heavy-duty machining demands cutting fluids capable of providing heavy-duty lubrication and high cooling. Moreover, as the fluids are to be impinged at high pressure and flow rates, they must have low foaming characteristics. Creep-feed grinding and hard turning are the examples of heavy-duty machining that requires such type of cutting fluids, which have the combination of all the three properties (Sluhan, 1994). Heavy-duty machining operations require cutting fluids that exhibit very good lubricating property along with cooling ability at heavy loads. Emulsions exhibit both lubricity as well as cooling ability due to the presence of soluble oil and water respectively (Muaz and Choudhury, 2019). However, the oil film strength or hydrodynamic lubrication potential is reduced due to the presence of water. Therefore, in order to make emulsions suitable for heavy-duty applications, lubricant additives are added. Boundary lubricants such as lard oil, esters, amides, soaps, and rapeseed oil can be used as boundary lubricants. Similarly, chlorinated, sulfurized, and phosphorus-based extreme-pressure additives are necessarily be added to improve the load carrying capacity (Childers, 2006). Renewable metal working fluids like vegetable oils cannot perform satisfactorily in their original form. However, their properties can be improved by blending the base oil with suitable additives. EP soluble oils, commonly known as heavy-duty soluble oils, are the best alternatives as they can satisfy both the requirements in most of the cases. Conventional EP soluble oils can be replaced effectively by renewable metal working fluids by modifying vegetable oils base blended with EP additives in large amount (about 40% by weight). EP additives improve the load carrying performance of the base oil. Most of the EP additives contain chlorine, sulphur or phosphorus.

Cooling capability of renewable metal working fluid can be enhanced by blending emulsifiers into the base oil. Emulsifiers make it possible to form an oil-in-water emulsion containing a dispersion of oil droplets in a continuous phase of water. Chlorinated paraffins or sulfurized fat emulsifiers are utilized for producing heavy-duty soluble oils (El Baradie, 1996). As the cooling ability of the fluid is to be enhanced significantly for heavy-duty applications, about 20% by weight of emulsifiers are to be blended with 30% of the base oil as shown in Table 1. For low speed heavy-duty machining operations such as threading, broaching, tapping gear hobbing, etc. such oils are required that can chemically react with machining surface at high machining pressures and temperatures (Shokrani *et al.*, 2012).

Avila and Abrao (2001) performed rough turning of hardened AISI 4340 steel (49 HRC) at a depth of cut of 2 mm by mixed alumina ($\text{Al}_2\text{O}_3 + \text{TiC}$) tool. Three cutting fluids, namely fluid A (emulsion without mineral oil), fluid B (synthetic) and fluid C (emulsion containing mineral oil) were applied and compared with dry cutting. Fluid A does not contain any mineral oil but contains some grease into it. For the heavy-duty machining, fluid A containing no mineral oil provided best results while fluid B containing mineral oil exhibits worst results as far as tool life was concerned (Avila and Abrao, 2001).

Some patented renewable metal working fluids are available in the market that are suitable for heavy duty machining of most ferrous alloys. These fluids can be applied during stamping, drawing, milling, turning, drilling, grinding, honing, broaching, thread cutting, and tapping operations. Examples of such fluids include Bio-HeavyTM S Cut which is formulated by highly viscous agricultural vegetable oils, high oleic base stocks (HOBS), blended with active sulphur extreme pressure additives. The fluid provides wetting and oiliness of tool, extreme pressure and antiwear properties with additional load carrying capacity.

In some severe heavy-duty machining conditions, if a lubricant fails to penetrate the machining zone, application of the cutting fluid with compressed gas is also an alternate method.

Future Trends

Heavy-duty applications demand high concentration of additives that are generally not good for environment. Environmentally benign alternate additives, like nanoparticles, are to be explored and their use to be established for the machining operations.

Rigorous multi-objective optimization of the parameters of the renewable metal working fluids must be performed for selecting and implementing the best-suited fluids to a particular machining process on the shop floor.

Emulsifying agents are also not recommended to be used in the fluids because these elements are hazardous to human health and detrimental to the environment. Research must be carried out in the direction of exploring the possibilities of emulsion development without mixing emulsifying agents. A very little work has been reported in this direction e.g., ultrasonic atomization, but must be explored further for renewable MWF.

Conclusion

Renewable metal working fluids have shown great ability to work satisfactorily in Al as well as in heavy-duty machining applications. Dependency on non-renewable resources can be reduced by replacing the mineral oils with renewable oils in production

of metal working fluids. A cutting fluid capable of performing well in a particular application should be selected judiciously based on the requirements and the properties of the fluids. The fluid properties can be tailored according to the requirement.

See also: Application of Nanofluids for Radiator Cooling. Natural Oils as Green Lubricants in Forming Processes. Natural Oils as Green Lubricants in Machining Processes. Sustainable Cutting Fluids: Thermal, Rheological, Biodegradation, Anti-Corrosion, Storage Stability Studies and its Machining Performance. Sustainable Machining with Self-Lubricating Coated Mechanical Micro-Textured Cutting Tools

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Sustainability Issues in Bioplastics

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Introduction

The dawn of proliferating production and consumption of products has brought along with it increased exploitation of natural resources and waste generation, which conspicuously reflects an increase in the rate of damage done to the environment. Apart from rapid depletion of fossil fuels, development has left behind pollution, deforestation, loss of biodiversity and climate change. A considerable contribution to environmental damage is inflicted by the global stock of plastics. While the utility and production of plastics outclasses most other material systems, the exhaustive investment of fossil resources for their synthesis and the aftermath associated with their disposal has rendered these multiutility materials subject to comprehensive environmental scrutiny. In the first ever global analysis of commercial plastics, [Geyer et al. \(2017\)](#) estimated a total production of 8300 million metric tons (MT) of virgin plastics by 2017, and generation of plastic waste amounting to 6300 million MT by 2015. Of the plastic waste, it was estimated that 9% was recycled, 12% incinerated and a perturbing 79% was accumulated in landfills and other dumping sites such as oceans. Following this, 12,000 million MT of plastic waste is expected to stockpile in natural sites by 2050. In 2015, [Jambeck et al. \(2015\)](#) calculated that out of 275 million MT of plastic wastes generated in 192 tropical countries in 2010, 4.8–12.7 million MT eventually found its way into the ocean. While this might not appear significant compared to the aforementioned global statistics, such annual influx of plastic debris has the potential to devastate the marine ecosystems.

Sought as a solution to the environmental crisis effectuated by commercial fossil-based plastics, bioplastics incorporate plastics developed from renewable resources as well as those which are biodegradable. While biodegradability is an indispensable requirement for any eco-friendly plastic, those obtained from renewable feedstock do not always meet it ([Fig. 1](#)). Biobased plastics such as Nylon 11 derived from 11-aminoundecanoic acid present in castor oil and polyethylene synthesized from bioethanol present in sugarcane and corn for instance are not biodegradable ([Deanin, 1978](#); [Tokiwa et al., 2009](#); [Kuo et al., 2006](#)). Likewise, it is also not necessary for a biodegradable plastic to have biobased origins. Essentially biodegradation of any plastic is a complex phenomenon depending on its molecular weight, hydrophobicity, and the nature of additives present in the matrix and has been addressed in detail later in this text. Thus, bioplastic is a general term associated with any plastic that has at least one eco-friendly facet.

It is necessary for the ensuing discussions that the term sustainable development is not misapprehended. It accounts for evolution that answers to the requirements of the industry and the economy without inflicting damage upon the environment. For instance, an extremely eco-friendly material with inferior properties that do not allow it to settle into industrial applications is not sustainable. Naturally, no material or process can be perfect with respect to this idea of development. However, the closer they get to it, the more they are preferred. Any material affects the environment in several stages throughout its life span. While finding potential renewable materials for development of plastics and compostability of existing commercial plastics have been meticulously investigated and discussed in literature, the other aspects of the life-cycle of a plastic such as requirement and discharge of toxic effluents and energy influx during the extraction of raw materials, production of plastic and disposal must also be scrutinized to assess the overall impact on the environment. It is further imperative to consider these factors because the damage done to the environment is not limited to waste accumulation and depletion of fossil reserves, rather pollution, global warming and depletion of biodiversity are also pressing concerns. Along these lines, considering biobased or biodegradable plastics as the goal of sustainable development is biased and flawed. A perfect bioplastic, while catering to the industrial requirements it is designed for, must therefore cast the minimum deleterious impact on the environment through its entire life-cycle.

A comprehensive analysis of the sustainability concerns associated with the existing bioplastics is crucial for identification of research gaps and subsequent development of methods for eliminating them. In this article, the possible detrimental impacts of bioplastics on the environment and the established sustainability concerns associated with these have been delineated. The most common commercial bioplastics were analyzed with respect to their life-cycle, and product-based case studies were provided.

Quantification of Sustainability

Consider the life cycle of a plastic product ([Fig. 2](#)). The consumption of fossil fuels is not limited to extraction of raw materials, rather the energy consumed at each stage of the life cycle is either directly or indirectly derived from fossil resources. Moreover, release of emissions and effluents as well as consumption of water also occurs at each stage. The overall environmental impact of a bioplastic must depend on total resources (fossil, water and land) consumed, the total emissions and effluents released into the environment as well as the toxicity of these. In a theoretical statistical analysis, minute components of the product life cycle such as

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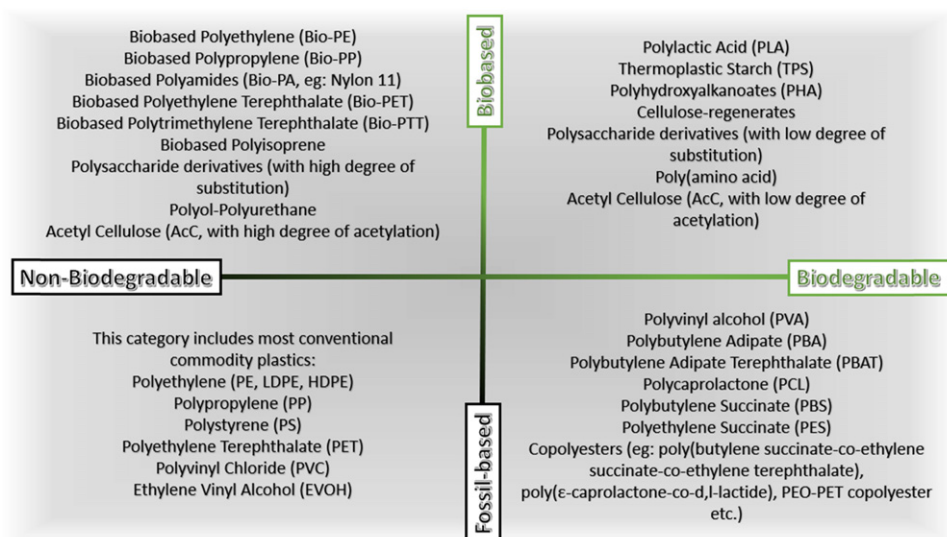


Fig. 1 The different categories of bioplastics represented by the first, second and fourth quadrants Reproduced from Tokiwa, Y., Calabia, B., Ugwu, C., Aiba, S., 2009. Biodegradability of plastics. *International Journal of Molecular Sciences* 10 (9), 3722–3742; Rujnić-Sokele, M., Pilipović, A., 2017. Challenges and opportunities of biodegradable plastics: A mini review. *Waste Management & Research* 35 (2), 132–140; Ach, A., 1993. Biodegradable plastics based on cellulose acetate. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry* 30 (9–10), 733–740; Iwata, T., 2015. Biodegradable and bio-based polymers: Future prospects of eco-friendly plastics. *Angewandte Chemie International Edition* 54 (11), 3210–3215; Deng, L.M., Wang, Y.Z., Yang, K.K., *et al.*, 2004. A new biodegradable copolyester poly (butylene succinate-co-ethylene succinate-co-ethylene terephthalate). *Acta Materialia* 52 (20), 5871–5878; Zhao, X.Y., Wang, M.Z., Xing, A., Xiao, J.J., Xie, J., 2014. Design and synthesis of biodegradable copolyester poly (ϵ -caprolactone-co-d, l-lactide) with four pendent functional groups. *Polymer Engineering & Science* 54 (9), 2170–2176; Chen, Y., Tan, L., Chen, L., Yang, Y., Wang, X., 2008. Study on biodegradable aromatic/aliphatic copolyesters. *Brazilian Journal of Chemical Engineering* 25 (2), 321–335.

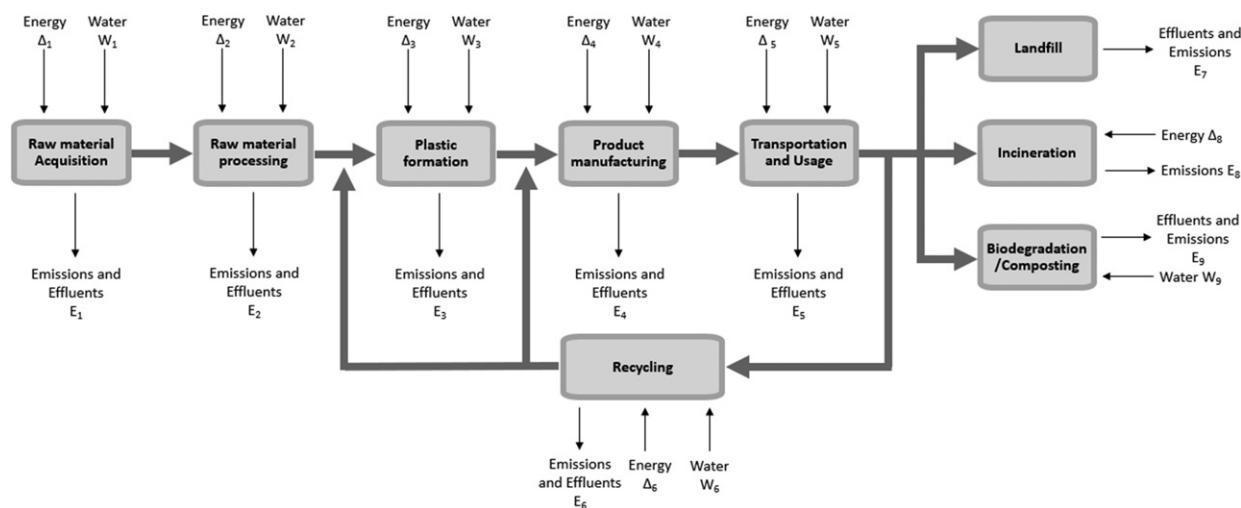


Fig. 2 Block diagram representing the life cycle of a plastic product.

the amount of water used in irrigation of the crops which yield the monomer for the plastic are difficult to include, since a broad analysis taking into account all such components of the study requires collection and analysis of an enormous amount of data. The small environmental impacts associated with all such components of the life cycle cumulatively generate a significant environmental impact. Thus, in order to develop a complete picture, databases as well as pre-defined standardized mathematical approaches are required to obtain reliable and relevant conclusions. For this reason several sustainability measurement methods have been developed. The most common methods, which assign quantitative indexes to the sustainability potential of bioplastics and therefore make the associated environmental impacts easy to visualize have been discussed as follows.

Sustainability Metrics

Over years of environmental concerns, several methods and approaches have been developed to quantify the potential of processes and products for sustainable development. One such approach is the evaluation of “Ecological Footprint” developed by Wackernagel and Rees (1998), which is an approximation of the ecological capacity necessary to support a population or economy based on statistics of consumption of natural resources and waste generation by a pre-defined unit. Subsequently comparisons are made to juxtapose the required ecological capital with the available natural capital to evaluate the gap between the unit functions and sustainability. Along similar lines the World Business Council for Sustainable development (WBCSD) has developed approaches to amalgamate general business practises with sustainability and advocates accelerated transition to an ecologically stable world (Sandberg *et al.*, 2010; Lehn, 1998; World Business Council for Sustainable Development WBCSD, 2001). Other common approaches include Circles of Sustainability (James, 2014), Environmental Sustainability Index (ESI) (Esty *et al.*, 2005), Environmental Impact Assessment (EIA) and Life Cycle Sustainability Assessment (LCSA). The latter two approaches have been used specifically for analysis of products and manufacturing methodologies, especially in plastics, and have henceforth been described.

Environmental impact assessment (EIA)

Environmental impact assessment constitutes one of the oldest tools for evaluation of the environmental footprint of a process, project, material, policy or product. While several similar procedures have existed for years, the most standard and widely accepted EIA process emerged from the US National Environmental Policy Act 1969 (NEPA), and has been expansively used for identification, prediction and mitigation of ecological damage associated with development propositions. It is performed in sequential stages including screening, scoping, baseline data collection, impact prediction, impact assessment, mitigation, formulation of Environmental Impact Statement (EIS), subsequent review and follow-up. While EIA forms an effective utility for analysis of potential damage by plastic processing methodologies such as plastic injection molding (Pun *et al.*, 2003), and lays the framework for finding alternative approaches, there are numerous limitations associated with the formal and informal review generated post EIA, along with the dispute on fulfillment of its objectives specified in NEPA (Petts, 2009). The approach has received criticism for its limited scope and effect on the final decisions associated with proposals (Jay *et al.*, 2007). For such reasons, it is not preferred for the smaller, more specific domains.

Life cycle sustainability assessment (LCSA)

LCSA constitutes a comprehensive sustainability assessment, involving a thoroughgoing analysis of environmental, economic and socio-economic impacts of a product throughout its life cycle (Fig 3):

The concept of using the three assessment techniques i.e., LCA, LCC and S-LCA together was first proposed by Kloeppfer (2008) and is now endorsed by United Nations Environment Program (UNEP) and several other international organizations working towards sustainable development. Since sustainable development is an amalgamation of environmental, social and economic viability in development, simultaneous assessment of all the aspects of the unit under consideration are important. For example, an eco-friendly product that is either very expensive or does not meet the requirements of the social backdrop will not broadly supplant its less eco-friendly alternative.



Fig. 3 The concept of sustainable development.

Life cycle assessment (LCA)

Life Cycle Assessment is the most broadly accepted method for quantifying the environmental impacts associated with products. The need for LCA stems from the requirement to consider the entire spectrum of environmental impacts that are connected to the life cycle of any entity, which is not only lacking in other assessment routes, but also provides an all-encompassing assessment which generates the overall perspective necessary to compare between alternatives and select the eco-friendliest option. LCA is performed either by considering the complete life cycle which includes the extraction and processing of raw materials, manufacturing, transportation and distribution, use reuse and maintenance, recycling and final disposal, in which case it is called a cradle to grave assessment, or by evaluating only the part of life cycle involving production. The latter is called cradle to gate assessment and is usually used mostly by firms producing the product. The input and output of energy and materials at each stage of product life is considered and analyzed. Thereafter, indices are provided to estimate quantitatively the overall damage fostered in various aspects, each of which represents a facet of pressing environmental concerns. A life cycle study can either be focused on assessment of an individual product or utilize the collected data to compare between two products or processes, in which case it referred to as comparative LCA. In accordance with the international standards accepted for LCA (ISO 14040 and ISO 14044), it is performed in four steps: goal and scope definition, life cycle inventory, life cycle impact assessment and interpretation. These have been described briefly as follows:

- (1) *Goal and Scope Definition*: A life cycle study is typically application specific and requires a framework for distinguishing and filtrating relevant data from the countless data elements available. For quantification, data must be limited to a functional unit and the circumference of the aspects related with the product or process to be considered must be established. Thus, in this step, the following factors are defined to build the framework for the subsequent study:
 - (a) The requirement and purpose of the study (or the 'Goal') is defined, which makes the overall study concise and compendious.
 - (b) System boundaries, such as technical and geographic limits on the subject as well time frame of analysis are specified. The systems to be analyzed in the study are also delimited.
 - (c) Reference function (or Functional unit), which provides the baseline for calculation of input and output variables through the life and the ensuing quantification of associated impact. For example, in a study of polyethylene bags, a functional unit could be 100 bags manufactured in a particular region.
 - (d) The various assumptions associated with the study are demarcated, along with a description of the groups the study will be addressed to (following the earlier example, the study could be addressed to academic, technical, and marketing personnel, along with general public or legislative bodies).
 - (e) The standardized methods implemented in the study, and the specific impacts to be addressed in the study, along with the weight assigned to each specific impact studied is defined.
 - (f) If the study is intended for public and academic reference, it is necessary to specify the need of a peer review.
- (2) *Life Cycle Impact Assessment*: This step involves collection, description and verification of relevant data, which includes emission and resource consumption values, along with intermediate chemicals and other unit processes which are likely to yield an environmental impact. Data acquired can be of two types, based on its origin:
 - (a) Primary data includes data acquired directly from its source, such as in annual government or company reports, interviews and other official articles. This data is considered more relevant and reliable from a scientific perspective.
 - (b) Secondary data is acquired from commercial and public LCA databases such as Ecoinvent and European Life Cycle Database, and from previous published LCA studies. A very common approach towards contemporary life cycle studies is use of LCA software database, of which two very broadly used softwares include SimaPro (PRé Sustainability) and GaBi (Thinkstep). A few other LCA softwares such as OpenLCA (GreenDelta) and Umberto (Ifu Hamburg) are also used.

Based on the choice of processes to be included in the study, the product system is modeled and fed the amassed data. The step produces a Life Cycle Inventory (LCI), which contains organized information related to the various input and output processes between the product system and the environment.

- (3) *Life Cycle Impact Assessment (LCIA)*: In this step, the raw data accumulated in LCI is used to evaluate the quantified contribution of the product or process in consideration on impact categories, which represent environmental issues of concern such as global warming, eutrophication, fossil depletion etc. It is concluded in five stages: Selection, classification, characterization, normalization and grouping. Relevant impact categories are chosen based on the assumptions taken, the goal and scope of the study, as well as based on the environmental impacts that need to be studied in reference to the subject. Post characterization, the impact categories are normalized and assigned weights based on which environmental aspect is considered more critical with respect to the application being studied.
- (4) *Interpretation*: This step involves analysis of the LCIA results to provide meaningful and comprehensible conclusions. Sensitivity and uncertainty analysis are performed to check the reliability of the results of the study, based on which, it is inferred whether the goal and scope of the study have been met.

Life cycle costing (LCC)

Life Cycle Costing (LCC) is an important economic evaluation employed in the selection of alternatives that impact both pending and future costs. It combines and thereafter assess the costs related to the product over the span of its life i.e., production, use,

reuse, maintenance and disposal (Andrews, 2009). It is driven by the fact that the purchase price of the product does not reflect the complete picture of all the costs that are caused by the product and thus takes into account all costs occurring during a product's life cycle irrespective of the party bearing them. Conventional LCC has existed since a long time but is quite different from the concept of environmental LCC. It is performed to back the policy making process in the financial division to predict the preliminary investment and subsidiary monetary flows on maintenance, disposal, etc., (Spierling *et al.*, 2018). The focus of conventional LCC is on net savings, benefits or savings-to-investment ratio (Kloepffer, 2008). Moreover, since the conventional LCC lacks compatibility with LCA (Herrmann, 2009), therefore the LCI of both LCC and LCA are kept same and the boundary conditions are kept equivalent so as to ensure the compatibility between two in order to carry out a meaningful analysis. In case of biobased plastics, conventional LCC can be of interest especially when it comes to new production equipment.

Social life cycle assessment (S-LCA)

This technique is a collection of chronological procedures very similar to LCA which allow evaluation of the social impacts of a product through its life-cycle. Analogous to how LCC establishes the economic feasibility of a product or process, SLCA discusses the social feasibility based on the evaluated social impacts. It is based on the ISO 14040 framework and is related to assessment of impacts that directly affect the stakeholders, the social circle the product or process is addressed to and provided by.

Drawbacks

LCA constitutes one of the very few methods available for identification, quantification and analysis of sustainability issues associated with bioplastics. It is therefore very necessary that the results obtained at the end of an LCA study are inclusive of all the

$$LCSA = LCA + LCC + SLCA$$

possible environmental impacts of the bioplastic under consideration. However, in most LCA studies conducted, only few impact categories are considered, due to which they fail to provide a wholesome picture. There are two very discernible reasons behind this: the LCA methodology is complicated, which makes it difficult to analyze a plastic's potential for each impact category and the requirement of an enormous amount of data to ensure fair and accurate results in a study. Uncertainty in data is a major drawback of the LCA method, due to which most LCA studies rely on assumptions, which may or may not materialize in all real-life situations. The case study on sandwich composite panels discussed later exemplifies how unavailability of relevant data mandates assumptions which might make the data unreliable or case-specific. Thus, a requirement for improvement in the quality as well as the quantity of data available on databases is felt.

Another major drawback in LCA is the lack of standardization. For instance, if two bioplastics, each of which has been studied via LCA individually need to be compared, the previous studies cannot be used to draw comparison, since it is unlikely that the studies will be based on the same functional unit, or will have the same system boundaries. For any application specific analysis, a fresh LCA study is required. This makes comprehensive evaluation of bioplastics a resource-intensive process, which is a potential reason behind the lack of sufficient LCA studies. Due to the structure of LCA method, the results obtained are usually influenced by the nature of assumptions and the application, and thus cannot be generalized.

Biodegradability

While the global bioplastic production capacity is expected to wax from 2.05 million MT in 2017 to 2.44 million MT in 2022, biobased non-biodegradable plastics such as biobased polyethylene, biobased polyethylene terephthalate, and biobased polyamide currently constitute 56% (1.2 million MT) of global biobased production capacity (European Bioplastics, 2017). The precipitous rise in the aggregate Municipal Solid Wastes (MSW) due to plastics has compelled many governments to impose legislation to stem the plastic waste generation. Driven by such crucial requirement for waste management, and since it is the eco-friendliest solution to the end of life for plastics, biodegradability has been studied extensively and mandates special emphasis with respect to sustainability concerns. Composting is a special case of biodegradation. While biodegradation refers to the process of decomposition of plastic to CO₂, H₂O, CH₄ or elemental carbon, which can occur in soil or water in the presence of relevant enzymes, composting refers to biodegradation in an environment of decaying organic matter. Thus, every compostable plastic is biodegradable, however biodegradable plastics may or may not be compostable. For a plastic to be compostable, the following criterion should be met, in reference to the nature of its degradation (Rujnić-Sokele and Pilipović, 2017):

- The product must be composed of a minimum of 50% organic matter and should not contain heavy metal content beyond a certain allowable limit.
- The product must disintegrate to particles not visible to naked eye (< 2 mm in diameter) within 12 weeks and must biodegrade by at least 90% within 6 months in controlled composting conditions.
- Upon degradation, the plastic should not release toxins or materials which cast a detrimental effect upon the ecosystem of soil i.e., the residual compost should be non-toxic in nature (Fig. 4).

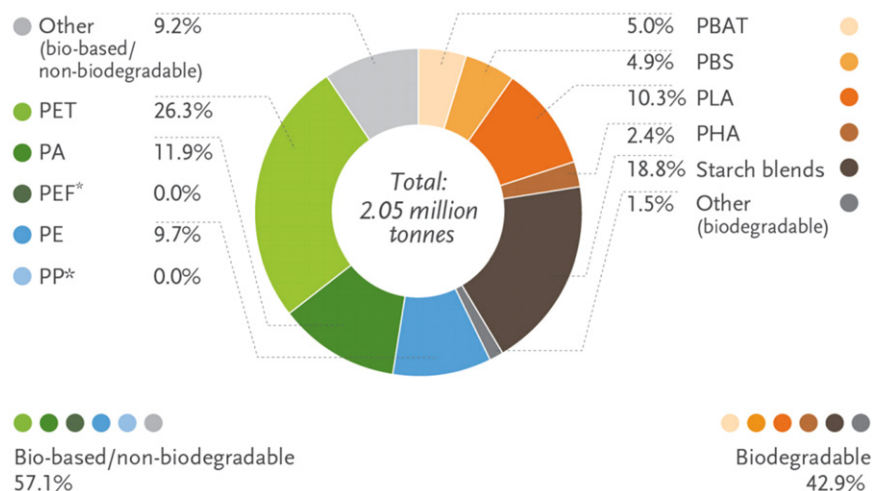


Fig. 4 Global production capacities of bioplastics in 2017. Adopted from European Bioplastics, 2017 Bioplastics: Facts and figures. Berlin. Available at: <https://www.european-bioplastics.org/market/>.

In general, fragmentation of plastics in natural environments such as soil and marine follows exceedingly slow kinetics and is projected to take centuries to exhibit any significant corrosion. Following decades of development in this sphere, the natural degradation procedures available now for plastics are not limited to soil composting under readily available environments. Rather several combinations of microorganisms and tailored environments for catalysing their activity, man-made enzymes and materials to effect deterioration etc. have been formulated. Developed bioplastics with augmented rate of natural degradation are now broadly used for manufacturing medical implants, carrier and waste bags, disposable cutlery, flexible films as well as rigid containers and bottles, diapers, tyres, mulch films and multitudinous other commonplace commodities (Rujnić-Sokele and Pilipović, 2017). Although there are sustainability concerns associated with degradable plastics, biodegradation still has the potential to develop into a solution to several environmental concerns. In order to develop biodegradable plastics with few to no concomitant sustainability issues, it is essential to understand the mechanism and methodologies of biodegradation.

Routes to Environmental Degradation of Plastics

Environmental degradation of plastics is a combination of several degradation mechanisms functioning simultaneously and consecutively. Prior to molecular degradation, corrosion and subsequent weakening of material is essential, which is contributed by a combination of mechanical, chemical, thermal and other abiotic factors operative in the outdoor environment. Usually these factors initiate and sometimes accelerate the degradation process.

Degradation by microbial communities

Polymeric materials have been shown to degrade in several natural and specifically defined artificial environments in the presence of microorganisms. However, soil is the most suitable environment for biodegradation, owing to the diversity of microbial communities that exist therein due to factors favouring survival. The microorganisms capable of degrading specific plastics are many and the nature and extent of degradation is also defined by ambient temperature and availability of free oxygen (Nishide *et al.*, 1999). Suyama *et al.* identified and isolated 39 morphologically different species of soil bacteria that could degrade poly(β -hydroxyalkanoate), poly(ϵ -caprolactone), poly(hexamethylene carbonate), and poly(tetramethylene succinate) (Suyama *et al.*, 1998). Biodegradation by microorganisms is a complex process, which follows three distinctive steps. An elaborate discussion of these has been provided by Lucas *et al.* (2008), and the stages have been very briefly summarized as follows:

Biodeterioration

It is a surface-level degradation which alters the physical, mechanical and chemical properties of the plastic and prepares it for ensuing break-down. This kind of degradation is usually an outcome of a combination biotic and aforementioned abiotic factors. From the perspective of microbial activity, there are several biotic mechanisms associated with this stage:

- Microorganisms secrete a complex amalgam of polysaccharides, proteins and similar polymeric substances, which allows them to adhere to the surface of the plastic. This material not only protects the microbes against unfavorable conditions, but also weakens the plastic in general by percolating through the pores in the plastic and converting them to cracks.
- The extracellular polymers secreted by microbes provide a medium for exchanges between hydrophilic and hydrophobic phases. This allows for easy permeation of bacterium into the plastic. It is also estimated that such secretions favor accumulation of atmospheric pollutants and provides favorable conditions to growth of microorganisms, which in turn accelerates the deterioration process.

- In thermoplastics, biodeterioration can either effect the bulk or the surface of the plastic. Bulk deterioration is usually dominated by abiotic factors such as ambient radiation and eroding compounds such as acid, bases, radicals etc. This naturally depends on the chemical characteristics of the plastic such as solubility and chemical resistance. Bulk deterioration results in disintegration of large chunks of plastic and cleavage of bonds, which effects reduction in the molecular mass. Surface deterioration is governed by enzymes secreted by microorganisms, which only cause loss of material and do not affect the plastic on a molecular level. Enzymes are not capable of producing bulk deterioration due to their inability to penetrate the polymer matrix, which is also why polymer molecules stay intact in surface deterioration.
- Certain species of bacterium, such as chemolithotrophic bacteria secrete inorganic acids and elements such as sulfur, hydrogen sulfide, ammonia and nitrates as sources of ions, electrons and energy. Likewise, chemoorganotrophic bacteria produce organic acids such as oxalic acid, fumaric acid etc. Such secretions can either react with and subsequently corrode the plastic or release cations which form stable organometallic complexes, thereby oxidizing the plastic. While each microbial community utilizes different secretions and mechanisms for biodeterioration, enzymatic action mostly only affects the surfaces exposed to them.

Biofragmentation

Cell membranes are impermeable to polymer molecules because of their large structure. Thus, prior to ingestion of molecules, they are fragmented to constituting monomers and oligomers. Akin to biotic biodeterioration, microbes employ different mechanisms for cleavage of bonds in polymer ranging from secretion of enzymes which reduce the activation energy of molecules and make them susceptible to chemical reactions causing bond rupture to generation of free radicals. The chemical aspects of the process are diverse and hence have not been covered in this text.

Assimilation

It occurs inside the cell and can be conveniently considered as the last catabolic stage of plastic digestion. The end products of biofragmentation are transported inside the microbial cell by membrane carriers and are subjected to catabolism. Disintegration of molecules into atoms yields the necessary nutrients required for the cell and produces Adenosine Triphosphate (ATP), which provides the energy for cellular metabolism and reproduction. Although some monomer and oligomer molecules obtained post fragmentation cannot permeate the cell membrane, they undergo bio-transformation reactions and subsequently assimilate inside the cell.

Factors Affecting Biodegradability of Plastics

During natural degradation of plastics, ambient conditions such as temperature, the amount of moisture, light and oxygen present as well as the pH of the soil or compost effect the rate and extent of degradation (Emadian *et al.*, 2017). Some of these abiotic factors and their contribution in biodegradation have been discussed in Table 1. Since biodegradation involves chemical interactions between the plastic and microbial interface at every step, the molecular characteristics of plastics have a significant impact on the viability and kinetics of enzymatic reactions, which in turn influence the rate and potential for biodegradation. Certain modifications in the composition, such as including additives containing high concentration of soluble sugar might enhance the biodegradability of the plastic (Emadian *et al.*, 2017). Thus, in order to design bioplastics with high biodegradability, it is necessary to have a comprehensive understanding of the factors that affect biodegradability. Andradý (2007) discussed the various factors which have been shown to affect biodegradability of synthetic and biobased plastics. Molecular characteristics which more prominently effect biodegradability have been summarized as follows:

Molecular weight

Molecular weight of a polymer molecule is a function of chain length and degree of polymerization, both of which have been shown to affect biodegradability. Earlier studies conducted on polyethylene established that biodegradation becomes negligible above a molecular weight of 4000 (Jen-hou, 1961). Later a more direct relationship was established in evaluation of degradation of polycaprolactone films of different molecular weights using the mold *P. Pullans* by Fields *et al.* (1974). The behavior of polycaprolactone was evidently similar to polyethylene, in that the degradation became negligible above a molecular weight of 15,000. A very sharp decline in the weight of plastic film recovered after 3 weeks in mold inoculated medium was observed in grades with molecular weight increasing from 1000 to 5000, post which it was concluded that degradation was directly proportional to low molecular weight.

Rivard *et al.* (1995) studied the effect of ester group chain length and the degree of substitution on anaerobic microbial digestion of starch esters including acetate, propionate, butyrate, valerate and hexanoate groups. A sigmoidal decrease in biodegradability of starch esters was observed upon increasing the chain length as well as degree of acetylation. It was also concluded that for maintaining a high biodegradation potential, with an increase in chain length, the degree of substitution should be decreased, which was generalized for natural polymers.

Chemical structure

The enzymes released by microorganisms react with the relevant functional groups to cause cleavage of polymer bonds. Generally, a plastic is acted upon by a colony of different microorganisms, each of which release different enzymes which collectively

Table 1 Types and mechanisms for abiotic degradation of plastics

Degradation type	Mechanism
Catalytic degradation	Catalysts such as zeolites, non-zeolites, platinum-cobalt and platinum molybdenum supported by SiO ₂ , transition metal catalysts supported by Al ₂ O ₃ etc., which are present or artificially added in the soil or other degradation environments are helpful in initiation or propagation of degradation. These catalysts reduce the temperature required for degradation, improve the quality of residues left post-degradation and increase selectivity for the product under consideration. In the initiation step, carbon-carbon bonds are cleaved to form free radical, which then leads to a chain propagation, where the hydrocarbon free radicals are converted to lower hydrocarbons. Thereafter disproportionation or recombination of free radicals then terminates the propagation step.
Ozone-induced degradation	Traces of ozone present in the atmosphere are known to increase the rate of polymer ageing. Ozone attacks the unsaturation present in the plastic and forms an ozone-olefin adduct known as primary ozonoid, which subsequently cleaves into carbonyl oxide and carbonyl compounds. The electron deficient carbonyl oxide is subsequently attacked by oxy-anion.
Mechanochemical degradation	This occurs due to existing mechanical stress, or due to exposure to ultrasonic radiation. The mechanical stress or the ultrasonic radiation (if the polymer is present as a solution) causes breakage of polymer chains into free radicals. These free radicals are generated by tearing of polymer chains, which generates fragments of chain carrying the free radical, thereby reducing the molecular weight. If oxygen is present in the degradation environment, then the free radicals are converted to peroxy radicals. This further leads to chain propagation. However, it must be noted that the cleavage discussed in this degradation occurs only in the amorphous regions present in between the crystalline regions.
Photo-oxidative degradation	Near UV radiation (290–400 nm) are responsible for degradation of plastics exposed to sunlight. The plastic undergoes loss of mechanical properties, yellowing and changes in molecular weight. At any given ambient condition, the rate of degradation increases with the incoming flux of solar radiation. The plastic absorbs UV light, which generates free radicals. In the propagation step, hydroperoxide radicals are generated, which cause backbone degradation, followed by beta scission. The backbone degradation follows either the Norrish Type I or the Norrish Type II mechanism. Subsequently in the termination step, the free radicals combine to form inert products.
Thermal degradation	While photo-oxidative degradation affects only the surface of the plastic, thermal degradation affects the bulk of the plastic. Usually either of Chain-end degradation or Random degradation mechanisms follow the application of heat, resulting cleavage of polymer chains: Chain-end mechanism initiates at terminal monomer unit in the chain and the monomers are stripped off the polymer chain one by one. In random degradation mechanism, the polymer randomly tears into two smaller molecules. Usually, both the reactions contribute in chain initiation step. However, the chain propagation step follows chain-end mechanism. The termination step follows either radical disproportionation or radical coupling reaction.

Note: Based on Singh, B., Sharma, N., 2008. Mechanistic implications of plastic degradation. *Polymer Degradation and Stability* 93 (3), 561–584

complete the many enzymatic steps involved in the degradation. A complex chemical structure with a large number of similar functional groups must require high stoichiometric amounts of enzymes, and those with many different functional groups must require many different enzymes for reaction and subsequent cleavage. Therefore, plastics with complex chemical structures usually form poor substrates for biodegradation (Andrady, 2007). This was experimentally observed in the biodegradation of dialdehyde starch and dialdehyde inulin (Van der Zee *et al.*, 1995). A higher degree of oxidation in both the polymers resulted in a lower rate of degradation. It was also observed that the oxidized grades of starch and inulin adopted different molecular conformations, which further altered their susceptibility to microbial attack.

Interaction with water

Microbial degradation involves enzymatic interaction on the plastic-microbial interface. The enzymes released by microorganisms sometimes require water a solvent medium. A hydrophobic plastic might restrict microbial growth on its surface (Fig. 5), which is manifested in higher biodegradability exhibited by water soluble polymers such as polyethers, PAA (polyacrylic acid), and PVA (polyvinyl alcohol) when compared with the water-insoluble polymers (Andrady, 2007). Likewise, in a study investigating the biodegradation of polyethylene (Karlsson *et al.*, 1988), which is hydrophobic in nature, it was observed that using a surfactant along with polyethylene enhanced its biodegradability. It was thus concluded that hydrophilic polymers exhibit increased accessibility for microorganisms. Presence of functional groups such as carbonyl can also increase the accessibility, and hence the biodegradability of the plastic (Andrady, 2007; Karlsson *et al.*, 1988).

Crystallinity

Crystallinity is known to hinder microbial degradation of plastics. A study conducted on the biodegradation of Polycaprolactone (Benedict *et al.*, 1983) suggested that crystallinity inhibited the fungal degradation of the plastic. In an analysis of degradation of Polycaprolactone by Cook *et al.* (1981), it was observed that the bacteria exhibited preferential degradation of amorphous plastic. In another study on the biodegradation of Poly(3-hydroxybutyrate) (Nishida and Tokiwa, 1993), it was similarly observed that occurrence of crystallinity suppressed biodegradation in PHB samples. The bacteria used in the inoculum preferentially colonization in and degraded the amorphous sites created in samples, whereas the crystalline sheets were left undegraded. This could be

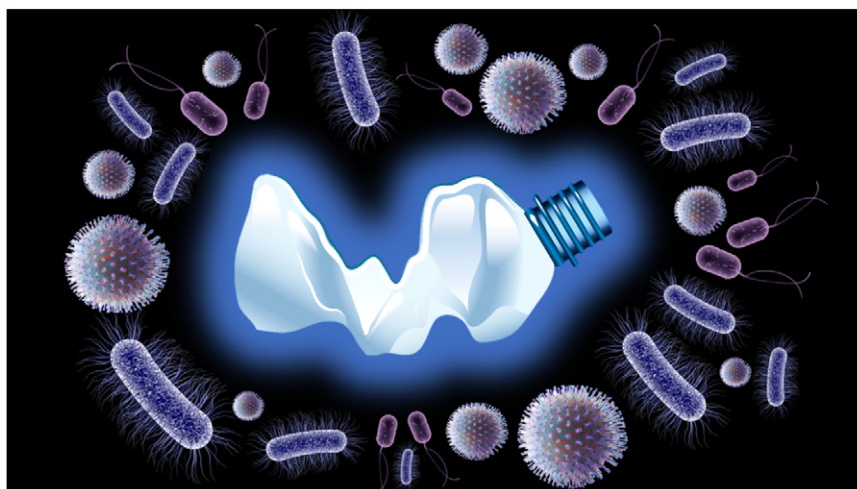


Fig. 5 Bacterial interaction with hydrophobic polymers.

due to easy penetration of microbial enzymes in the less ordered amorphous plastic, which allows for homogenous enzymatic action. Since the microorganism itself feeds on the plastic being degraded, higher degradation in an amorphous plastic must release sufficient energy for more organisms to feed on and thus becomes a preferential colonization site. This in turn further increases the enzymatic action in the region and must increase the rate of degradation, much like a chain reaction (Nishida and Tokiwa, 1993).

General Concerns: Biodegradable Plastics and Biodegradability

Driven by the most common misconceptions about biodegradable plastics, which roughly equate the biodegradability of plastics to that of general organic matter, they are frequently sought as a solution to the problem of plastic littering and landfills. In reality however, biodegradable plastics degrade in very specific conditions, and these conditions must be provided as the end of life scenario in order to reap the advantage of biodegradability at all. For example, PLA is highly biodegradable in soil and compost, but is almost non-biodegradable, when placed in a marine environment (Haider *et al.*, 2019). In such a situation, PLA that ends up in the oceans forms marine debris. Most studies evaluate the biodegradability, or develop plastics degrading in laboratory conditions, which do not materialize in the direct environment that the plastic is expected to encounter. Even if it then degrades in its natural environment as well, the rate of degradation is usually very different from what is determined in the laboratory (Haider *et al.*, 2019). Thus, a perfectly biodegradable plastic is no better than a synthetic commodity plastic, so long as it is not provided the degradation environment in which it degrades post usage.

Biodegradability of plastics has been exhaustively studied in literature and methods for enhancing the degradation of fundamentally non-biodegradable plastics by addition of materials, such as in oxo-degradation have also been developed. Despite this the data published cannot be used for comparing two biodegradable plastics, unless they have been evaluated together in a single study in the same test conditions. Even in a case where two biodegradable plastic are evaluated and compared together, the results are specific to the test conditions and cannot be generalized to other environments (Andrady, 2007). Biodegradable plastics are also difficult to recycle. Upon mixing with the recyclable waste, they tend to act as contaminants and are difficult to isolate from the recycling stream (Kubowicz and Booth, 2017). These and several other factors raise the question of which out of recycling and biodegradation is the eco-friendlier alternative. These and other sustainability concerns associated with biodegradable plastics have been discussed as follows.

Ecotoxicity concerns in biodegradable plastics

Although the definition of biodegradation entails reduction of plastic to CO_2 , H_2O and any free form of carbon, in most plastics with enhanced biodegradability, other by-products are also released. Ecologically, it is fundamentally necessary that any such released chemical is not harmful to the ambient biome. A study conducted on brackets made of polyoxymethylene (POM), which a useful engineering polymer concluded that the primary degradation products released include Formaldehyde (Kusy and Whitley, 2005). Phytotoxicity tests on the rate of germination of radish seeds and Cytotoxicity tests on human epithelial cells using by-products usually released in hydrolysis of polyester revealed toxicity. It was also observed that aromatic compounds are more harmful than the aliphatic by-products (Kim *et al.*, 2001). Even polyurethane sheets have been demonstrated to release MDA (4,4-diamino diphenyl methane), into an activated vermiculite environment (Degli-Innocenti *et al.*, 2001). While certain plastics such as aliphatic-aromatic polyester Ecoflex® have been tested to degrade completely leaving behind no toxic residue (Witt *et al.*, 2001), there is huge number of commercial partially or fully biodegradable plastics which have not been evaluated with respect to the nature of degradation by-products.

Where the rapid biodegradation of any plastic material would solve the problem of plastic waste accumulation, release of toxins during degradation introduces the question of whether in case of mass utilization and disposal of such a plastic, the release of the same toxin in bulk into the environment will create a bigger problem than waste generation. Ecotoxicological concerns therefore form a viable part of the big picture which needs to be analyzed before a plastic walks the markets as a potential biodegradable plastic.

Oxo-biodegradability

Oxo-biodegradability is the accelerated environmental degradation induced by incorporation of certain additives to the non-biodegradable polymer matrix. This especially inspired interest in enhanced degradation of petroleum-based plastics such as Polyethylene (PE) and other polyolefins (Chiellini *et al.*, 2006; Vogt and Kleppe, 2009). The additives involved in this method, known as prodegradants are metallic salts of carboxylic acids and dithiocarbamates, utilizing transition metals such as Cobalt, Manganese, Copper, Iron, Nickel, Vanadium and others. These salts catalyse the breakdown of molecular chains, especially when the polymer is subjected to heat, which results in embrittlement and subsequent fragmentation of the plastic. Usually, along with prodegradants, antioxidants are also added in the plastic to avoid initiation of degradation while the plastic is serving its life.

Scott (1995) discussed the involvement of peroxide groups and free radicals in the cleavage of polymer chains in the presence of heat and oxygen, which the initiative step in biodegradation (biodeterioration). Presence of transition metals triggers a redox reaction with peroxides which yield rapid formation of free radicals. The molecular bonds are further severed by these free radicals. It has however been realized over years that rapid fragmentation through oxo-biodegradation produces micron size particles called microplastics, beyond which prodegradants can cause no further fragmentation. These microplastics are still resistant to complete biodegradation and persist in the environment for long intervals of time (Kubowicz and Booth, 2017). Microplastics have several detrimental impacts on the environment, especially concerning accumulation in marine ecosystem, wherein they collect hydrophobic pollutants and upon ingestion by fauna, pose the potential threat of transferring additives and pollutants to the marine food cycle (Cole *et al.*, 2011). Despite misleading advertisements portraying oxo-biodegradable plastics in the light of fully biodegradable plastics, this is conspicuously not true. However there still exist multitudinous debates and deliberations on whether the concept in general can be utilized for the greater good in plastic waste management.

Recycling versus biodegradation: Which is greener?

Plastic waste management has not been dealt with the responsibility and awareness that it deserves as a potential environmental concern. In 2010, the gross plastic waste generated in the United States alone amounted to 31.04 million tons, which is roughly 12.4% of the total waste generated (U.S. Environmental Protection Agency, 2011). In 2015, the generated plastic waste increased to 34.5 million tons (U.S. Environmental Protection Agency, 2018). Over years, these figures have become further worse, which is concerning given that most of this plastic ends up either in landfills or in water bodies as marine debris. In proportion to the severity of this, several plastic recycling technologies have evolved and have been discussed in literature (Burillo *et al.*, 2002; Pickering, 2006; Garcia and Robertson, 2017; Ragaert *et al.*, 2017). In broad practise, the recovery of a plastic is achieved through either mechanical or chemical recycling. Mechanical recycling is constituted by collection, sorting, grinding and washing of plastics, of which any sequence of steps can be used based on the material characteristics of the plastic. While mechanical recycling does not affect the molecular composition of a plastic, in chemical recycling the plastic is depolymerized into smaller molecules, which are subsequently polymerized to form the recycled plastic. Since recycling has had ample time to advance through continuous research, it is very well-developed and ready to be implemented in most cases. Naturally, efficiently performed recycling must serve as a solution to excessive plastic waste accumulation while simultaneously reducing the fossil fuel requirements for plastic manufacture. A study performed by Chen *et al.* (2011) simulated the implementation of Japanese plastic recycling and energy recovery technologies in Shenyang, China, where out of the 3 million tons MSW generated, roughly 71% waste was left in landfills in 2008. It was observed that when implemented, the recycling models reduced the Greenhouse Gas (GHG) emissions by 1.66 kgCO₂e/kg-plastic and fossil fuel consumption by 0.77 kgce/kg-plastic. Mechanical recycling was also observed to have the maximum potential for reducing environmental impacts. This study gives a perspective of the amount of environmental gain that can be achieved by implementation of advanced recycling methodologies globally. However, while recycling thus represents a promising and viable solution for the plastic waste crisis in general, the global statistics for plastic recovery and recycling are disappointing and thwart the hope of recycling saving the day. In 2012, only 9% of the plastic waste was recycled in the United States, leaving 32 million tons of plastic waste in the national waste stream. The same year, in Europe, 38% of post-consumer plastic was estimated to have ended up in landfills. The figures are worse for the other parts of the world (Gourmelon, 2015).

There are many reasons behind the poor implementation of recycling. For recycling individual petroleum plastics, they need to be separated from the general plastic garbage. Thus, plastic waste requires sorting and separation before recycling is initiated, which is very labor intensive and requires a significant input of resources. Most plastic waste which comes from the food and packaging industry is contaminated post disposal and requires cleaning before it is recycled (Kuruppalil, 2011). Even if the resources required for establishment of recycling facilities for different commodity plastics are neglected, the continuous resource input required for sorting, separating and pre-cleaning the plastic waste is high and this could make recycling unworkable for weaker economies. Although this problem can be solved by labeling the plastic composition on the product and expecting assortment of plastics during disposal, it is highly unreasonable to expect 100% responsibility from consumers.

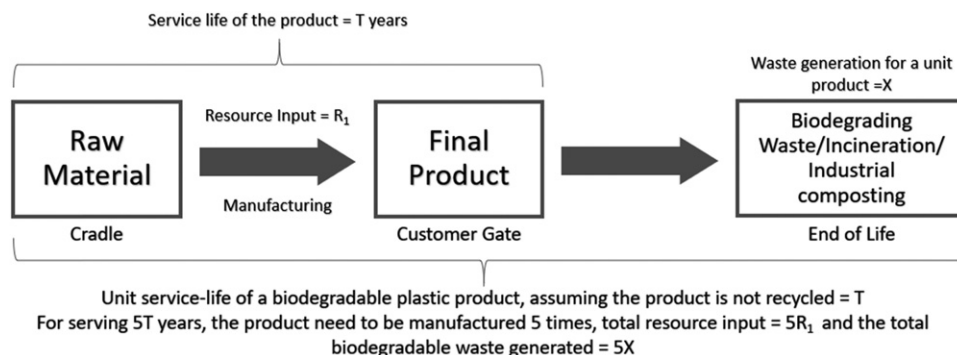


Fig. 6 Case 1 – Hypothetical biodegradable plastic.

Against this backdrop, biodegradable plastics have surfaced as another solution for the plastic waste crisis. While it might seem like biodegradable plastics offer an easy use and throw routine, it has been discussed earlier that most biodegradable plastics disintegrate only in very specific environments. It must thus be observed that a plastic that degrades well in an industrial composting facility, when thrown in a landfill in the natural environment is just as good as a non-biodegradable plastic that adds to the litter. In fact, a study performed in Los Angeles observed that providing young individuals with biodegradable plastics for usage increased the general littering behavior, since in accordance with the general misconception associated with biodegradable plastics, consumers generally feel discharged from the responsibility of disposing waste off properly (United Nations Environment Program, 2016). Thus, biodegradable plastics have an environmental gain to offer only when they are disposed in predefined ways, such that they reach their respective degradation environments. Notably, 100% responsibility from the consumer is required in disposing off biodegradable plastics as well, in which case it cannot be established that it is a better end of life scenario for a plastic when compared with recycling. Moreover, since the known biodegradable plastics are few, in order to meet the performance requirements of a broad range of products, usually blending or copolymerization is required. However, blending of biodegradable and non-biodegradable plastics is not recommended since upon exposure to the necessary conditions, the biodegradable component in the blend disintegrates, leaving behind small particles of the non-biodegradable component (Tokiwa *et al.*, 2009; Iwata, 2015). These small plastic fragments are difficult to manage and subsequently scatter in the environment causing plastic pollution. Copolymerization with a non-biodegradable plastic on the other hand may or may not yield a biodegradable product at the end (Álvarez-Chávez *et al.*, 2012). Therefore, there is a lack of flexibility in easy modification of biodegradable plastics for obtaining tailor-made properties for specific applications.

There are multitudinous other environmental concerns associated with biodegradable plastics. It was determined by Detzel *et al.* (2012) that unlike decaying of organic matter, biodegradation of plastics does not benefit the quality or structure of soil. In addition to this, upon degradation in landfills, biodegradable plastics release considerable quantities of methane and carbon dioxide and thus contribute to global warming. If it is hypothetically assumed that all commodity plastics are replaced with biodegradable plastics, the logical estimation of greenhouse gas emissions will be petrifying. It is thus required to simultaneously capture the evolving methane and CO_2 , which can be further used for biogas production. However, it must be realized that establishing facilities for capturing greenhouse gases from a large quantity of decaying plastic, such as industrial composting units will require investment of resources, akin to recycling.

Conclusively, which out of a recyclable and a biodegradable plastic will have minimum environmental impact is subject to a comprehensive analysis of several factors involved. It is thus required to mathematically compare between these for identifying the eco-friendlier alternative with respect to the application being considered. There are several nuances associated with plastic waste management, since it depends on factors such as public awareness and responsibility towards it, government initiative and the extent to which corporate firms are willing to invest into recycling or expensive biodegradable plastics. These factors cannot be taken into account in any statistical analysis to compare between recycling and biodegradation. Thus, to obtain a perspective of why such an analysis is needed in the first place, a hypothetical ideal scenario has been discussed.

Consider two hypothetical plastics: a biodegradable plastic which is not recycled after its service life (Fig. 6), and a non-biodegradable highly recyclable plastic (Fig. 7), both developed for a particular product which serves an average life of T-year. Such an example is chosen because cases of products made out of biodegradable plastics, recycled multiple times in their life-span are rare. If the parameters are evaluated with respect to a unit product, to serve for 5T-year, the biodegradable product must be manufacture 5 times. If the amount of resources required for manufacturing one product is R_1 and the amount of waste generated per product is X, this will require $5R_1$ resources (Energy, water, land etc.) and generate 5X degradable waste. In the case of the non-biodegradable, highly recyclable plastic, it can be manufactured once and reused for 4 times before being disposed of. This will require $R_2 + 4R_3$ amount of resources and generate X amount of non-biodegradable waste.

In between the two cases, which is a greener alternative is cannot be predicted without considering the specific application and the regional parameters. However, which out of X amount of non-biodegradable waste and 5X amount of biodegradable waste is favorable in reference to the application and the ecosystem it directly affects can be decided. Likewise, which out of $5R_1$ and

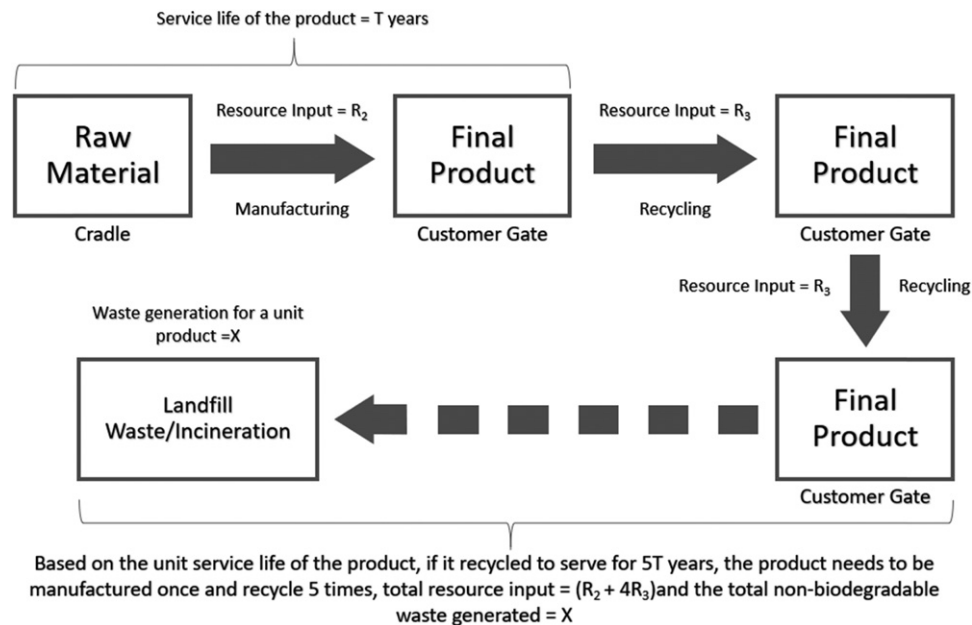


Fig. 7 Case 2 – Hypothetical non-biodegradable, highly recyclable plastic.

$(R_2 + 4R_3)$ is more, and by how much, must determine which out of recycling and biodegradation consumes more fossil fuels, and how much consumption is affordable from an environmental perspective. It is known that biodegradable plastics are in general more expensive when compared with conventional commodity plastics (United Nations Environment Program, 2016), therefore an analysis must be done to evaluate the cost involved in the two cases, as well as the technical and social feasibility of each. Thus, these and such questions must be asked and relevant analyzes must be performed to evaluate the greener alternative between recyclable and biodegradable plastics.

An example of such an analysis is the life cycle assessment performed by De Andrade *et al.* (2016) which compares the environmental impact produced by three end of life scenarios for PLA: mechanical recycling, chemical recycling and biodegradation. The reference flow for this study was 1 kg of residual PLA and three impact categories were considered, namely climate change, human toxicity and fossil depletion. It was observed that composting exhibited maximum potential for detrimental impact in all the three categories, which was significantly higher than both mechanical and chemical recycling. The impact of composting was unusually high because in the case of composting, the plastic must be manufactured again by means of the energy intensive traditional processing for every time the plastic was recycled from residual PLA. Mechanical recycling exhibits the lowest environmental impacts in all the three categories, however an associated disadvantage with mechanical recycling is that the resulting product has inferior polymer properties (Piemonte *et al.*, 2013; Żenkiewicz *et al.*, 2009). This loss of properties is not observed in chemical recycling, since repolymerization is involved, however it exhibits higher environmental impacts, since energy is invested in the chemical reactions involved.

Sustainability Assessment of Biobased Plastics

Biobased plastics are developed from monomers found in renewable resources. These materials not only serve to limit the requirement of fossil fuels for development of plastics, but also exploit the atmospheric carbon and solar energy for manufacturing the monomers through natural processes. Momani (2009) maintains that if all the existing plastics would be replaced with biobased plastics, while assuming that the energy consumed in cultivation and manufacturing of plastic products is derived from renewable resources, it would save approximately 3.49 million barrels of fossil fuel per day – which is approximately 4% of the global fossil fuel usage. Some biobased plastics such as biobased PET allow for utilization of agricultural and forestry wastes, which are otherwise mostly burnt. However, against the backdrop of depleting fossil reserves, whilst the idea of biobased plastics thus presents an attractive solution, academics have been questioning the potential of biobased plastics as more sustainable alternatives. In his contribution on green plastics, Mülhaupt (2013) asserted that the actual carbon cycle followed by biobased plastics is in fact very different from the closed carbon cycle (Fig. 8) that ideal green plastics are assumed to mimic.

There are several aspects to consider before a biobased plastic can be deemed fit to replace a conventional synthetic plastic. It is not clear whether the biobased plastics developed so far are capable of emitting less carbon than their fossil-based alternatives, since the overall carbon footprint is determined by processing as well. Moreover, since the very concept of sustainability potential rests on environmental, economic as well as social impact of a material, it is necessary for any plastic, whether or not derived from

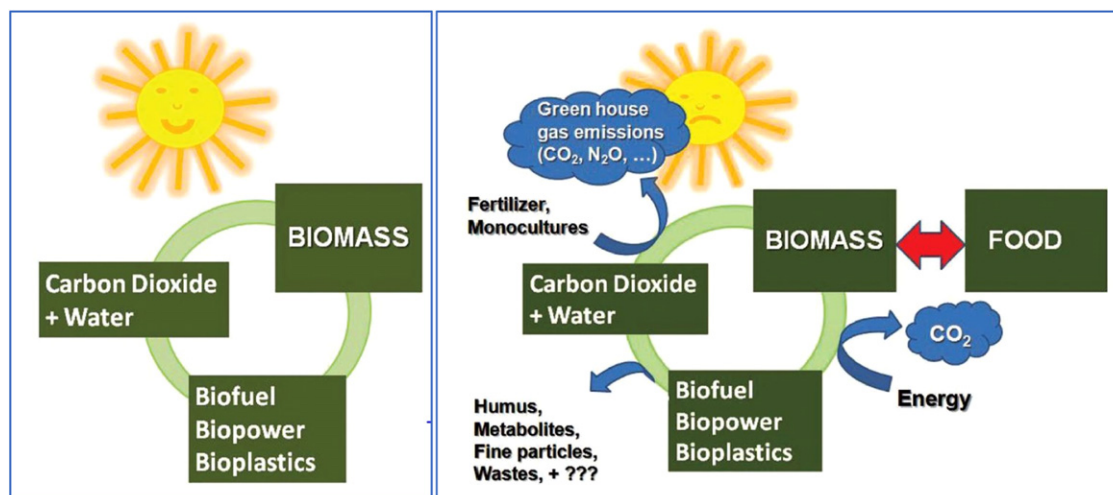


Fig. 8 The closed carbon cycle (left), The actual carbon cycle followed by bioplastics (right). Adopted from Mülhaupt, R., 2013. Green polymer chemistry and bio-based plastics: dreams and reality. *Macromolecular Chemistry and Physics* 214 (2), 159–174.

renewable resources to be favorable with respect to all the three criteria. For example, a biobased plastic that exhibits poor thermomechanical performance, or one that is too expensive will fail to find its designated place in the industry.

Renewable Plastic $\neq$ Sustainable Plastic

General Concerns Related to Biobased Plastics

Environmental concerns

In general, the evolution of society has left behind adverse effects on several aspects of the environment. The process of sustainable development is thus complicated, since where initiatives such as biobased plastics aim to ameliorate a particular environmental problem (in this case, rapid depletion of fossil reserves), there is a possibility that these might serve to exacerbate a few other environmental problems. If the complete picture of the contemporary scenario of global development and the concomitant deleterious environmental impacts is considered, one reaches the conclusion that it is necessary to solve all these environmental problems: solving any one, and making another worse might not be a wise choice in reference to the many-sided damage that has been done to the environment. The International Life Cycle Data system (ILCD) implemented in LCA studies identifies 12 impact categories at the mid-point level (European Commission-Joint Research Center, 2010), a detailed classification for which has been provided in Fig. 9. It must be noted that fossil fuel depletion presents just one of the many potential damaging impacts of a product or process, that require immediate attention. A hypothetical biobased plastic which allows for maximum conservation of fossil reserves, but unfavorably affects any four out of the 12 impact categories might not be a very desirable material.

Another important aspect to consider is the market layout of biobased plastics, which has although exhibited rapid growth in the past decade, yet most biobased plastics are produced in very small quantities when compared with commercial fossil-based plastics. According to a report published in 2017 (Degnan, 2015), biobased plastics constitute merely 1% of the global plastic production and require only 0.02% of the available arable land for the cultivation necessary to support the entire production. This leads one to think about the amount of arable land that will be required, should the biobased plastics supplant the entire global production of plastics. Land is a limited resource as well, albeit not as limited as fossil-fuels. Mass production of biobased plastics to match the global production quantity of synthetic plastics will require an excess of arable land as well as exhaustive farming on available land. Since land is also required for cultivation of food produce, it might lead to several major crises which have been discussed as follows:

- Changes in utilization of land reflect on the economy as well as on the global environment (Turner *et al.*, 2007). The present state of global widespread hunger and rising food demands have created pressure on the existing land resources, such that the available cultivable land itself is expanding, and the need for efficient utilization of available land to meet the food demand is felt (Fischer *et al.*, 2012). Approximately 11% of the total land available is utilized for production of crops to meet the food requirements, which is slightly more than one third the portion of land that can be potentially used for cultivation (Bruinsma, 2017). It is however estimated that to feed an expected population of 9 billion people by 2050, the land used for food production must be increased by nearly 70% (Fischer *et al.*, 2012). It has further been established that climate change is expected to adversely affect food security across the world (Schmidhuber and Tubiello, 2007). Thus, the state of food crisis, along with the excessive global competition for cultivable land leaves very little room for allocating a major section of land for cultivation of feedstock for production of biobased plastics. Mass production and commercialization of biobased plastics will inevitably lead to competition with food production, in which case the latter will obviously earn preference.

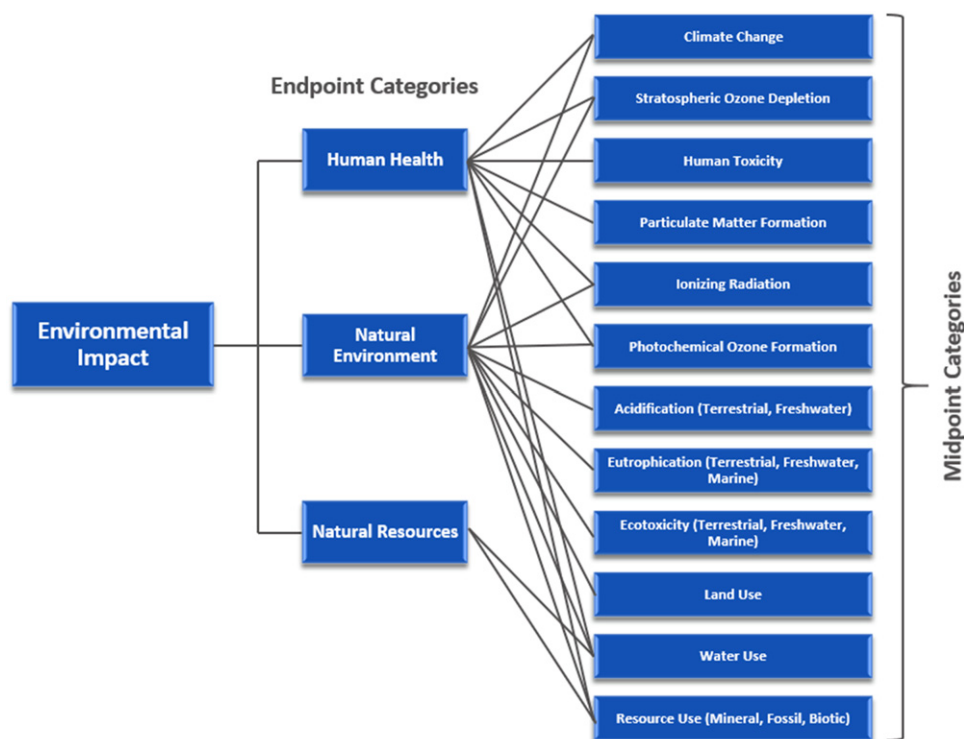


Fig. 9 The classification of impact categories in accordance with ILCD. Redrawn from ILCD European Commission-Joint Research Center, 2010. Institute for Environment and Sustainability: International Life Cycle Data System (ILCD) Handbook – Framework and Requirements for Life Cycle Impact Assessment Models and Indicators. first ed. Ispra. European Commission, Joint Research Center, Institute for Environment and Sustainability. Available at: <https://eplca.jrc.ec.europa.eu/uploads/ILCD-Handbook-LCIA-Framework-Requirements-ONLINE-March-2010-ISBN-fin-v1.0-EN.pdf>.

- If the competition with food production must be dodged, it will require generation of arable land other than that being used, or is expected to be used in the future for cultivation of food. Requirement of more arable land will result in deforestation and grassland conversion for farming. It is well known that agriculture is one of the major causes of deforestation (Grau *et al.*, 2005; Benhin, 2006; Pimentel *et al.*, 1986), which in turn is followed by a host of problems such as rapid increase in atmospheric greenhouse gases, soil erosion, flooding, desertification etc. and constitutes one of the most major contributors to global climate change. Likewise, conversion of any natural ecosystem to an agricultural ecosystem is known to leave a detrimental impact on the existing water resources as well (Scanlon *et al.*, 2007). Considering these aspects, it appears that generation of excess land to support a completely biobased plastic driven industry might cost much more than its primary purpose to conserve fossil reserves.
- While the scarcity of land puts pressure on the available land for generation of more biobased plastic per unit land available, a prominent issue with enhancing the productivity of cultivable land is that it comes at a cost. This cost is either defrayed in terms of excessive use of fertilizer, pesticides and fungicides, Genetically Modified Organisms (GMOs), growth hormones and antibiotics, each of which has its individual detrimental impact on the quality of soil and the natural microbial ecosystem of the soil (Jaisankar *et al.*, 2018; Savci, 2012; Kumar *et al.*, 2005), or in the form of the extra expenditure invested in organic farming. While utilizing organic resources to enhance soil productivity is a viable solution to the problem of soil deterioration through the inorganic chemical usually used by farmers, the quantity of organic resources available is very limited and this reflects in the cost of the produce as well, due to which the organic bioplastic might exceed the financial capacity of most people. In both the cases, the feedstock grown for bioplastics suffers a major setback, which might affect its sustainability potential.
- In the discussion of plastics which must be grown in farms, it is necessary to understand the perspective of the farmer as well. Since biobased plastics are expensive, for commercial benefit, the farmer could prefer cultivation of plastics over cultivation of food. This will lead to scarcity of food, especially in countries where the entire population is barely fed. In order to maximize the profit, the farmer might be lured into practising unhealthy agricultural methods such as crop monoculture. Such practises deplete the natural quality of soil, which in the long run is not only detrimental for the environment, but also in general for the farmer. Mass production of plastics will thus require strict legislation, which optimizes the farmer's profit, prevents competition of plastics and food, generates sufficient raw material to sustain the biobased plastic industry and sufficient revenue to sustain the bioeconomy. By visualizing a bioeconomy that involves mass production of all the biobased plastics, it can be understood that it will be very delicate. In fact, such a bioeconomy which holistically replaces all commodity plastics with bioplastics

would be resting on the edge of a knife, and it will require enormous efforts and resources to keep it generally stable. Any bias towards either the environmental, social or economic scenario would not only cripple its stability, but would also leave behind impacts which will be hard to recover from.

- It is expected that mass production of biobased plastics will exhaustively employ Genetically modified microorganisms (GMO), Genetically modified crops and transgenic plants in cultivation (U.S. Environmental Protection Agency, 2011). *Álvarez-Chávez et al. (2012)* states that for improving the properties of starch and for maximizing production, the GMOs used in the cultivation of PLA and starch are an 'unknown health hazard'. This is because the effect of hybridization and genetic modification of plants and organisms on the environment and other species is not known. There is a possibility of human health hazards such as toxicity of the new gene developed, alteration of metabolic pathways and allergic reactions. While these have undisputed agricultural benefits, these have multitudinous possible environmental impacts (*Hails, 2000; Snow et al., 2005*), because of which these genetically modified organisms and crops are heavily debated on and generally discouraged.

While this discussion concludes in establishing that the available land resource is a crucial factor in analyzing the socio-economic feasibility and overall environmental impact of any plant feedstock-based plastic, which includes most of the known biobased plastics, due to challenges in the contemporary sustainability measurement methods (as discussed earlier), this aspect remains beyond comprehensive analysis. Although it is mentioned as an impact category, it is usually not included in the analysis in Life Cycle Assessment studies (*Finkbeiner et al., 2014*). In fact, there is no agreement on a standard method to assess the impact of a biobased plastic on land use, and any method that is validated may be applied (*Spierling et al., 2018*). For this reason, the many sustainability concerns that surround it, such as destruction of biodiversity, depletion of water resource, deforestation and consequent increase in greenhouse gas emissions, loss of ecosystems and climate change are also not thoroughly evaluated. Thus, it is difficult to assess even the overall environmental impact a biobased plastic is expected to have when it is mass produced.

Although there are concepts such as sustainable agriculture (*Altieri, 2018*), however mass production of biobased plastics will require aggressive cultivation to meet the global plastic needs. To what extent this can be managed with the available state of the art technology without inflicting significant damage upon the environment in terms of depletion of land resource is the question that we need to ask, based on which the scientific community must bend its course to develop alternative solutions and prospective technologies to solve the problem from either ends. In nutshell, the battle to save fossil reserves must not lead to another battle for either saving another limited resource, or recovering any other significant environmental damage.

It further becomes obvious from this perspective that most concerns associated with biobased plastics remain beyond observation because they are not mass produced like synthetic plastics. The issues discussed above and many such conditions, which might present a potential threat to the ecosystem can be analyzed only by hypothetically simulating the mass production as well as commercialization of a certain biobased plastic. This condition is in all aspects equivalent to an iceberg structure, an analogy in reference to which has been presented in *Fig. 10*. It is therefore necessary to consider a biobased plastic in this light, before the economy invests resources into it.



Fig. 10 Iceberg analogy – A comparison between the current and the prospective mass production scenarios of biobased plastics.

A study conducted on 7 fossil based plastics, 4 biobased plastics along with 1 plastic based on both fossil fuels and biomass by [Tabone et al. \(2010\)](#) delineated the alignment of the green design principles such as the “12 principals of green chemistry” and the “12 principles of green engineering” with the environmental impacts of the 12 aforementioned plastics found using Life Cycle Assessment. It was observed that when broadly correlated, adherence to green design principles yielded reduction in environmental impacts. However, when the environmental impacts of the individual plastics are observed in the same study, it can be distinguished that both the grades of Polylactic acid used, namely PLA-G (obtained by a general process) and PLA-NW (obtained from Nature-Works LLC) exhibited significantly negative impact on eutrophication and ozone depletion. Likewise, the general grade Polyhydroxyalkanoate obtained from corn grain (PHA-G) exhibited significantly negative impact on acidification and ozone depletion. It was also shown to not have a very significant contribution in conservation of fossil reserves. Simultaneously, the PVC grade obtained from fossil fuel feedstock exhibited superior potential for conservation of fossil resources than the biobased plastic PHA-G. While this study provides examples of bioplastics that consume less fossil fuels, yet contribute significant damage to the environment in other impact categories, it also verifies that it is not necessary for a biobased plastic to save the amount of fossil fuels it is intended to save. This must happen because the total consumption of fossil fuels in the entire life cycle of a plastic takes into consideration both the amount of fossil fuels invested in obtaining the raw material for plastic as well as that utilized in processing, since the energy used for commercial processing is chiefly derived from fossil-based feedstock. It must however be observed that although this study gives a perspective of the sustainability concerns associated with biobased plastics, yet it constitutes only a portion of the complete picture. This is because it neither includes the impact on land resources, and the environmental problems that follow it, nor does it consider a hypothetical mass production and commercialization scenario in which the concerned biobased plastics are as bulk-produced as the concerned fossil-based plastics.

Economic concerns

Biobased plastics constitute a relatively recent development when compared with the conventional synthetic plastics. Thus, the cost of research and development associated with biobased plastics, as well as the additional cost of production ([Thakur et al., 2018](#)) makes them more expensive than fossil-based plastics per unit weight ([Van den Oever et al., 2017](#)). Furthermore, the currently low price of oil makes conventional plastics cheaper, and the corresponding biobased plastics appear more expensive. Studies have also shown that consumers are unwilling to pay an extra amount for an eco-friendlier option and tend to incline towards synthetic plastics because of the difference in price. This however is not the case with companies ([Degnan, 2015](#)). Over the past decade, more companies have adopted a sustainability-oriented approach and switched to biobased plastics, due to which their market-price has undergone a slow decline. Also, the market price of petroleum is expected to rise in the future due to an impending deficit, the high price of biobased plastics might balance the increasing price of petroleum-based plastics. However, due to rapid progress in the development of non-conventional oil recovery processes from shale gas, it is expected that there might be an intermittent stage where fossil fuels will be available at much cheaper prices before the aforesaid rise in price commences ([Iwata, 2015](#)).

That we might witness a situation where the fossil-based and biobased plastics are equally expensive and consumers might thus shift their preference towards the more ecological alternative is a possibility in the distant future. The present situation calls for an assessment of each individual biobased plastic in reference to its life cycle, such that the factors responsible for the excessive cost can be identified and attempts can be made to develop alternative processes or technology that could provide a solution. Unfortunately, Life Cycle Costing studies have been conducted only on biofuels. Bioplastics have not been subjected to such analyzes, and thus the economic aspect of biobased plastics, which is a significant factor in determining whether the plastic will find a place in the market as well as in establishing its sustainability potential needs comprehensive study in the future. It is also necessary to distinguish between the Life Cycle Costing analysis done on biobased plastics on the basis of region, since it will depend on the local prices of petroleum and its products, which change drastically between countries.

Most governments have initiated subsidies to promote biofuels over the conventional non-renewable fuels. However, in the case of biobased plastics, such support from the government is received only in the Research and Development sector ([Philp, 2015](#)). Although the immediate solution could be governments providing similar support for expanding the usage of biobased plastics despite the high price, the relevance of this approach in the long run must be questioned. After a certain span of time, once the subsidies are withdrawn, the bioplastic market might collapse. Thus, providing subsidies serves as merely a temporary solution ([Carus et al., 2011](#)). In the long run, it is required to develop biobased plastics that settle smoothly into the economy, which can be achieved only by an in-depth analysis of where the contemporary biobased plastics are going wrong.

Individual Analysis of Common Biobased Plastics

Polylactic Acid (PLA)

PLA is a biobased and biodegradable plastic, which has been widely implemented in the packaging industry. It also finds application in textile industry, paper-coating and disposable service-ware ([Yates and Barlow, 2013](#)). The basic raw material for PLA is starch, which can be obtained from corn, sugarcane, sugar-beet, rice, sweet potato, wheat, cassava etc ([Vink et al., 2003](#)). Enzymatic hydrolysis of starch yields dextrose, which is subsequently fermented to obtain Lactic acid. Lactic acid then undergoes

either direct condensation polymerization or ring opening polymerization to produce PLA (Vink *et al.*, 2003). The mechanical properties of PLA are better than Polystyrene and comparable to Polyethylene Terephthalate, which makes it an ideal industrial replacement for both (Yates and Barlow, 2013). Due to its numerous existing and prospective applications and material characteristics, PLA is a promising bioplastic and consequently several life cycle studies have focused on evaluating the environmental impacts that PLA is expected to have in its life cycle. Three primary case studies and their results have been discussed as follows:

- (1) In a cradle to gate life cycle assessment performed by Groot and Borén (2010), the environmental impacts of sugarcane based PDLA (Poly-D-lactic acid, developed from D-lactide) and PLLA (Poly-L-lactic acid, developed from L-lactide) were evaluated and compared with standard petroleum-based commodity plastics, polypropylene, polystyrene and PET, LDPE and HDPE. The functional unit for this study was 1 tonne of plastic at the factory gate in Thailand. It was observed that in comparison with all the fossil-based plastics, non-renewable energy consumption, GHG emissions and material resource usage was less for PLA. However, PLA exhibited higher potential for acidification, eutrophication, farmland usage and photochemical ozone creation.
- (2) A life cycle study performed by Vink *et al.* (2003) investigated the sustainability of the corn based PLA, manufactured and marketed by NatureWorks®. Two grades of PLA were considered for evaluation, PLA1, the general grade and PLA B/WP, an environmentally superior grade which utilized wind power, energy saved from crop residues from corn and other and process optimization. The two bioplastics were compared with Nylon 66, Nylon 6, Polycarbonate (PC), High Impact Polystyrene (HIPS), cellophane, General Purpose Polystyrene (GPPS), LDPE, PET (Solid State Polymerization – bottle grade), PET (Amorphous – fiber and film grade) and polypropylene. Both the bioplastics exhibit less gross fossil resource consumption when compared with the other synthetic plastics. However, between the two grades, the gross fossil energy use in the processing decreased from 54.1 MJ/kg in PLA1 to 7.4 MJ/kg in PLA B/WP, which evidences the superiority of PLA B/WP. Interestingly, while all the fossil-based plastics exhibit detrimental impact in terms GHG emissions, the PLA B/WP grade has a positive impact on GHG emissions, since it utilizes renewable power during the entire cradle to gate life. In terms of water use, PLA 1 and PLA B/WP perform equivalent to the plastics that exhibit the lowest impact.

It was however observed by Yates and Barlow (2013) that the two aforementioned studies draw comparisons between PLA and other synthetic plastics on the basis of weight, which is not appropriate because different material properties needed for specific applications might require different mass of the plastics, since the material characteristics of plastics vary significantly. It is thus required that LCA studies consider the specific application and its performance requirements to draw an unbiased comparison. The study discussed henceforth evaluates and compares the bioplastics taking the reference of a unit product:

- (3) A cradle to consumer gate LCA study performed by Suwanmanee *et al.* (2013) compared polystyrene, corn based PLA and cassava starch based PLA/starch blends. The functional unit is 10,000 units of thermoform boxes and the impact categories considered include global warming potential, photochemical ozone formation and acidification potential. This study revealed that the polystyrene thermoform boxes, in the overall assessment of environmental impacts performed better than both PLA and PLA/starch blends. Amongst the several cases considered, each encompassing different manufacturing methodologies used for plastic production in Thailand and a few other assumptions, a hypothetical case in which Land Use Change (LUC) was not included in the evaluation and both the bioplastics were manufactured by Thai Integrated Gasification Combined Cycle (TIGCC) is especially interesting. In this case both the bioplastics exhibited the lowest environmental impacts amongst all the considered cases, however even in this case the overall normalized impact of PLA and PLA/starch blends was 1.59 and 1.09 times that of polystyrene respectively. Although the performance of PLA was poor in this study, it must be realized that this study does not include the end of life scenario. Since PLA and starch are both biodegradable, the effect of greenhouse gases released at the end of life, which results in an approximate carbon neutrality has not been included here.

Nevertheless, since the first cradle to gate study compared between PS and PLA and arrived at totally different conclusions, this study provides a perspective of the how the sustainability issues associated with bioplastics surface in a product unit based comparison. It also demonstrates how a slight difference in assumptions might lead to biased results.

Biobased Polyethylene (Bio PE)

Biobased polyethylene or Bio-PE is a biobased non-biodegradable plastic manufactured by polymerization of the ethylene obtained by intramolecular dehydration of bioethanol. Bioethanol used for bio-PE production is usually derived from either sugar-beet or starch, which can be obtained from wood, wheat, maize, corn etc. In contrast to this, ethylene obtained from steam cracking of naphtha, heavy oil, ethane and propane is used for manufacturing fossil-based PE. Interestingly, the level of contaminants present in both the aforementioned biobased and fossil-based ethylene grades is same (Kikuchi *et al.*, 2013). Thus, the resulting material properties and characteristics of bio-PE and fossil-PE are equivalent, which is not usually observed in biobased counterparts of synthetic plastics. It also implies that only the equipment used for manufacturing ethylene requires substitution, should a firm invest in replacing fossil-based PE with biobased PE.

A life cycle study performed by Kikuchi *et al.* (2013) compared the GHG emissions resulting from bio-HDPE and fossil-based HDPE. Since the molding of product, use and waste collection are identical for PE and bio-PE, these stages of the life cycle have not been included in the system studied in this LCA. Incineration has been chosen as the end of life scenario and its effect has been

included in the evaluation of GHG emissions since this study assumes carbon neutrality in the biobased plastic. The effect of CO₂ thus evolved in the incineration of bio-PE is negated. The functional unit for this study is 1 kg of HDPE in Japan. It was observed that all the considered scenarios bio-PE exhibited fairly less potential for GHG emissions when compared with synthetic PE. This is due to the utilization of bagasse and energy generated during production of bioethanol, the negative effect of which is considered on the GHG potential of bio-PE. Moreover, cracking of naphtha is extremely energy intensive and contributes more than twice the amount of GHG emissions than dehydration of bioethanol.

Another study performed by [Bos et al. \(2012\)](#) evaluated and compared the Non-Renewable Energy Use (NERU) potential of LDPE, bio-LDPE and PLA. The functional unit for the LCA was 1 metric tonne of product. This study evaluates grades of bio-PE developed from wheat, maize, sugar-beet, sugarcane as well as miscanthus. It was observed that all the grades of bio-PE exhibited significantly lower non-renewable energy requirement than synthetic PE in accordance with today's agricultural practises. It must however be noted that wheat and sugar-beet require maximum and minimum arable land respectively, which must affect their individual potential for other impact categories. Since the amount of arable land is limited resource and it varies between the plastics evaluated, this study introduces the idea of NERU avoided per unit hectare of land, which in this study is maximum for sugarcane-based PE. This idea is of relevance to future studies, since it optimizes the results obtained in two different but very prominent impact categories to identify the most suitable bioplastic, and such approaches can be actively used in LCA in situations where more than one impact category is sensitive. Although these results favor bio-PE, this study reveals that the NERU avoided per unit hectare of land in PLA is significantly higher than bio-PE because cultivation for a fixed quantity of plastic requires nearly 3 times as much land in each grade of bio-PE than PLA, which implies that land resource consumption might arise as an issue in mass production of bio-PE.

LCA studies are further required to evaluate the potential of bio-PE for other environmental impact categories. However, given that bio-PE does not lack in properties and produces lower environmental impacts than synthetic PE, it still emerges a promising bioplastic. Since PE is one of the most exhaustively used plastics, supplanting it with bio-PE will conserve a large amount fossil resource, however since bio-PE is itself non-biodegradable, it will hardly be a solution for the plastic waste generation. Therefore, options such PLA, which are biobased and biodegradable must also be simultaneously considered.

Product Based Case-Studies

Sandwich Composite Panel

A comparative cradle to gate Life Cycle Assessment study was conducted by [La Rosa et al. \(2014\)](#) to evaluate the environmental impacts of a sandwiched composite structure based on a partially biobased epoxy relative to that based on a fossil-based epoxy. Super Sap 100 (Resin) and Super Sap 1000 (Hardener), a material system with approximately 50% biobased content was reinforced with hemp fiber to develop the outer-skin, which was sandwiched with a panel made of granulated cork to develop the eco-sandwich panels. The traditional sandwich panel was developed from a Polyurethane based epoxy, Prime 20LV which was reinforced with glass fiber to develop the outer skin, with a core panel made out of Polyurethane foam. The chosen functional unit for this study was a block of the eco-sandwich panel of specified dimensions, however for the purpose of a fair comparison between two structures intended for the same application, the thermal insulation property of both the panels was made equal by varying the thickness of the insulating material used in the traditional sandwich panel (PU foam).

Based on the production inventory of granulated cork panels, the heat for required for boiling the raw cork as well binding of cork was obtained from burning of cork dust, in order to minimize the electricity used in the process, since electricity is obtained from fossil-energy. The water used in the process was obtained from a well and it was recycled several times to further minimize the environmental impact. Abiotic depletion was thus minimized for this study, however the same cannot be assumed for all industrial processes. A comparison was subsequently drawn between the two plastics, the two fibers used for reinforcement as well as the overall structure, however for the purpose of this discussion, only the comparison between the plastics is considered and analyzed.

In comparison with the petroleum-based epoxy, the biobased epoxy exhibited significantly reduced potential for abiotic depletion and moderately reduced potential for acidification, global warming, cumulative energy demand, ozone layer depletion, and freshwater aquatic ecotoxicity. However, the biobased plastic simultaneously exhibited a moderately increased potential for eutrophication and human toxicity along with an eight-fold increase in the terrestrial ecotoxicity potential. Although terrestrial ecotoxicity has a critical effect on ecosystems, the study concludes that the biomass-based plastic used in this analysis has an overall reduced carbon footprint and does not compete with food sources. It must however be observed that the relative importance of the different impact categories changes with geographical and local ecological parameters. For example, in a region where the terrestrial ecosystem is damaged or sustains a very delicate balance, the increased terrestrial ecotoxicity might present a very significant threat, and thus the relevance of this biobased plastic could be negated in this particular region. Apart from this, the ozone depletion potential for the partially biobased plastic Super 100/1000 is calculated to be zero, which is a very surprising result considering the fact that the petroleum-based plastic used in the study (LV20 Epoxy) exhibits negative impact on ozone depletion and that there is approximately 50% petroleum-based content in this partially biobased plastic as well.

The most limiting aspect of this study is that due lack of availability of primary data for both Super Sap 100/1000 and LV20 Epoxy system in LCA databases, comparison was made by assuming a standard petroleum-based epoxy in place of the used

epoxies in both the developed sandwich composite panels. In this reference, the results obtained in this study might change drastically if the original data for both the epoxy systems is used in place of the assumed standard commercial epoxy. However, this study still provides a perspective of the sustainability potential that can be achieved in biobased plastics and that a complete mathematical evaluation might unearth hidden detrimental impacts on the environment which the bioplastics can have. Considering that this study was conducted in 2014, another concern that surfaces is that the contemporary LCA databases are deficient in the data necessary for a much-needed critical analysis of all bioplastics. A possible reason for this is that many local LCA studies which are conducted to evaluate the region-specific impacts of bioplastics cannot be generalized. Thus, the produced data uncertainty, a major drawback of the LCA method reduces the legitimacy of many studies conducted under similar assumptions. It is therefore necessary to take relevant steps for enriching and updating the existing databases.

Water Bottles

The global statistics for plastic consumption in the form of water bottles are alarming. In 2007, United States alone produced two million plastic bottles every 5 min (Palliser, 2010). Since most plastic bottles around the world are made from Polyethylene Terephthalate (PET), which is a fossil-based plastic, this quantity of production implies significant consumption of oil. In 2006, to meet the demand for plastic bottles in the packaged drinks industry, approximately 17 million barrels of oil were used (Palliser, 2010). It is reasonable to assume that since PET is highly recyclable, most of the waste generated from plastic bottles must be recycled to reduce the amount of fossil fuel needed in making fresh batches of bottles, however in reality only 20%–30% of plastic bottles are recycled (Palliser, 2010). It has thus been very necessary to find biobased alternatives to solve this problem. So far, biobased PET and PLA have surfaced as suitable alternatives, and the industry is willing to adopt them on a large scale. In fact, the Coca-Cola company, which is one of the largest manufacturers of bottled beverages introduced 30% biobased Dasani water bottles in 2009. This company has been further planning to replace the fossil based plastic bottles with 100% biobased PET bottles (Chen *et al.*, 2016). On the other hand, due to lower fossil fuel consumption in its manufacturing as well as its biodegradability, PLA is being studied as a prospective biobased plastic for bottle production (Papong *et al.*, 2014; Gironi and Piemonte, 2011). In this section, three conducted Life Cycle Assessment studies have been discussed which evaluate the sustainability issues that might be associated with these two alternative biobased plastics in reference to water bottle production.

Fossil-based PET versus 100% biobased PET

This comparative cradle to gate LCA study performed by Chen *et al.* (2016) focuses on evaluating the sustainability potential of a biobased PET bottle relative to that of a fossil-based PET bottle. It is interesting that the processing of both the fossil-based and biobased grades of PET differs only in the origin of raw materials. Polyethylene Terephthalate is manufactured by polymerizing a mixture of 30% Ethylene Glycol and 70% purified Terephthalic Acid (PTA). In the case of fossil-based PET, Ethylene Glycol is obtained by hydration and oxidation of ethylene, which is extracted from natural gas and Paraxylene extracted from Xylene mixture in petroleum is oxidized to obtain PTA. On the other hand, for manufacturing biobased PET, the ethylene obtained from bioethanol is hydrated and oxidized to obtain Ethylene Glycol and Isobutanol extracted from biomass is subjected to pre-treatment, enzymatic hydrolysis and fermentation to obtain Paraxylene, which is further oxidized to obtain PTA. The processing steps following the production of Ethylene Glycol and PTA include polymerization into amorphous grade PET granulate, which are then processed into bottle grade granulate by solid state polycondensation. These bottle grade granulate are then converted to bottles via injection blow molding. These steps are the same for both fossil-based PET and biobased PET, and consequently the nature of both plastics is the same. The usage and the end of life scenario is thus the same for either and does not need evaluation in the Life Cycle study.

The functional unit for this study is 1kg of PET bottle. Corn, switchgrass, wheat straw and fossil feedstock were used to manufacture 4 different grades of Ethylene Glycol, while forest residue, corn stover and fossil feedstock were used as raw material for 3 grades of PTA. Thus, 12 grades of PET, from a combination of each grade of EG and PTA were produced and analyzed. Out of all the developed grades of PET, the grades which utilized PTA generated from forest residue exhibited overall lowest environmental impact when compared with those that utilized PTA developed from corn stover and fossil resources. Considering the results obtained for all the 12 grades together, it was concluded that extraction of biomass feedstock and pre-processing to obtain Isobutanol in the case of fully and partially biobased grades produced much more emissions than processing of fossil-based feedstock. This is because a significantly large amount of energy is spent in agricultural operations and subsequent manufacturing of immediate chemical products. The global warming potential of the forest residue-based PET grades was 27% and 21% lower than that of corn stover and fossil-based PET grades. The group of PET grades that utilized corn stover PTA had the maximum potential for acidification, whereas the fossil-based PET grades had minimum acidification potential.

In this study, it has been assumed that the biobased feedstock has been obtained by collecting the forest residue, which is otherwise not fit for trading and is burnt. This process is known as slash pile burning and is a major contributor of emissions due to incomplete combustion of biomass. The negative impact of slash pile burning, which was avoided by exploiting the concerned biomass in production of biobased PET grades has been subtracted from the overall environmental impact observed in the PET grades. It is observed that if the effect of avoiding slash pile burning and other similar impacts were ignored, the biobased PET grades would perform poorly in the LCA study. Moreover, uncertainty in the impacts due to

Isobutanol production and slash pile burning have rendered a significant influence on the final environmental impact obtained at the end of the study.

Since a large range of PET grades from fully biobased to fully fossil-based were analyzed in this study, mixed results were obtained in general. However, in several aspects, the fossil-based grades were observed to have lower environmental impacts than the biobased grades. It is certain that biobased grades save a certain amount of fossil fuel due to their origin, however the subsequent processing and its impacts largely govern the overall environmental impact. Thus, this study clearly demonstrates that just being biobased does not qualify a plastic as the more sustainable option.

Fossil-based PET versus PLA

This comparative cradle to grave LCA study performed by [Papong et al. \(2014\)](#) considers and evaluates the potential of PLA as suitable alternative for water bottles relative to the fossil-based PET. Lactides can be conveniently mass produced by fermentation of biomass-based substances containing carbohydrates such as starch. Thus, for an application like plastic bottles, which requires production in bulk quantity to meet the global needs, PLA might be able to provide for the mass production. It is also well known in literature that PLA consumes lower fossil energy as compared to Polypropylene, Polystyrene, and fossil-based PET ([Madival et al., 2009](#); [Vink et al., 2007](#); [Uihlein et al., 2008](#)). For these reasons, a PLA grade developed from Cassava starch was chosen for this comparative analysis. The functional unit for this study is 1000 units of 250 ml bottles.

The global warming potential as well as the total consumption of fossil energy for PLA was found to be less than PET. In fact, when compared with PLA derived from corn, the cassava starch-based PLA exhibited lower fossil consumption, since despite use of inorganic fertilizers and pesticides, the yield of corn is usually less. However, PLA evidences significantly approximately 5 times the impact in eutrophication and moderately higher impact in acidification than fossil-based PET. This study also evaluates the performance of PLA while assuming that energy conservation methods such combined heating and power generation systems are adopted for an eco-friendlier processing of PLA. Despite this, the calculated eutrophication potential for PLA is more than twice that of PET, which clearly indicates that eutrophication might be a serious implication of PLA processing. It must therefore be observed, that in PLA processing, additional measures be opted to counterbalance the eutrophication effect that a PLA plant is expected to produce.

As discussed earlier, PET is manufactured by polymerizing Ethylene Glycol and purified Phthalic Acid. This process is extremely emission intensive, and consequently PET exhibits more than 8 times the potential for human toxicity than PLA. For the end of life case, four scenarios are considered and analyzed for the produced environmental impacts: Landfill, incineration, recycling and composting. It is concluded that for PLA, incineration is the eco-friendliest alternative, followed by recycling and composting. As far as recycling is concerned, PLA is blended with other polymers for most of its applications, which makes recycling expensive and technically complicated, in comparison to which PET is very easy to recycle. Although in conclusion this study favors PLA, this conclusion is based mostly on the Greenhouse Gas emissions observed in both cases. In reality many more fundamental aspects need consideration such as which impact category requires the most attention for particular applications, as suggested by [Gironi and Piemonte \(2011\)](#) in another comparative LCA between the same systems i.e., PLA and fossil-based PET.

This study calculates the environmental impacts of PLA derived from corn in comparison with PET. The cradle to gate analysis establishes that while PLA conserves fossil resources, it causes substantial damage to the ecosystem quality and human health. Considering the weightage assigned to macro-impact categories by the LCA Suisse group (40% ecosystem quality, 40% human health and 20% resources), both PLA and PET perform equally. In the cradle to grave analysis, PLA fares better than PET when recycling is assumed to be the end of life scenario, however apart from the above-mentioned nuances associated with the recycling of PLA, it also depends on plastic waste sorting systems, which are not very well developed and practiced, which makes recycling of PLA further difficult.

Diapers

Diapers have been subject to meticulous evaluation since these not only directly affect the sanitation and health of children, but are also a potential consumer of fossil resources and a source of significant waste generation, owing to the rise in global population which leads to increase in the demand for diaper. LCA studies conducted on reusable cloth diapers have revealed that raw material production and manufacturing require attention with respect to the environmental aspects. For disposable diapers however, the same studies assign maximum importance to the end of life scenario ([Aumonier and Collins, 2005](#)). Although composting appears to be the most suitable method for getting rid of used wet diapers, presence of non-biodegradable plastics and components in disposable diapers prevents complete biodegradation. Several eco-friendlier alternatives to the conventional disposable diaper have been developed and numerous analyzes have been performed to understand the sustainability potential of the various types of diapers available today. One such study established that 'glue-less' diapers are both 7%–170% eco-friendlier and 11% cheaper than the conventional product ([Mendoza et al., 2019](#)). It is however necessary to take into consideration that since diaper has a critical effect on child health, it is not possible to convince a majority of consumers to switch to an option that is widely socially accepted and trusted. Any new development thus also requires a study to evaluate and establish the effect and compatibility of the used plastics with the skin as well as an in-depth S-LCA study to determine whether it is social acceptance can displace the conventional diaper.

A cradle to gate LCA study performed by [Mirabella et al. \(2013\)](#) considers disposable diapers manufactured and marketed by WIP S.p.A., in which the plastics used in a conventional diaper are replaced with biobased and biodegradable plastics. The

disposable diaper consists of three layers made of Polypropylene (PP), Polyethylene (PE), Superabsorbent Polymer (SAP) along with an Acquisition and Distribution Layer (ADL). The eco-friendly diaper analyzed in this study includes replacement of Polypropylene with Polylactic acid (PLA), SAP with fluff made of organic Totally Chlorine Free (TCF) pulp certified by PEFC (Program for the Endorsement of Forest Certification), Polyethylene with Mater-Bi® and the ADL is made out of 50% PP and 50% PLA. The functional unit for this LCA is one diaper. Since the data for composting supply chain is not available on databases, the end of life scenarios for the WIP S.p.A diapers could not be analyzed.

The environmental effect in reference to 18 impact categories is investigated. It is observed that out of the four layers of the diaper as well as the transportation and packaging processes, the TCF pulp contributes the maximum detrimental impact in 7 out of 18 categories. Amongst the 7 impact categories it contributes more than 60% impact in agricultural and urban land occupation, natural land transformation, water depletion. Although the replacement of SAP with TCF pulp leaves behind a very small quantity of SAP in the eco-friendly diaper, it is still the second most major contributor to the environmental impacts overall, which implies that SAP replacement is indeed environmentally a very smart choice. While PLA shows extremely promising results in the potential for ozone depletion, human toxicity, ionizing radiation, marine ecotoxicity, fresh water eutrophication and agricultural land consumption, it exhibits detrimental impact on fossil resource consumption, terrestrial ecotoxicity and particulate matter formation. It is to be noted that a biobased plastic, PLA contributes approximately 30% of the total fossil resource consumption amongst all the components, including transportation and packaging. Amongst all the bioplastics employed in the diaper, the contribution of Mater Bi is not more than 15% in any impact category, and thus it presents a very promising bioplastic for this application.

When a comparison was drawn with the LCA results of the conventional disposable diaper, the eco-friendly diaper surprisingly performed better only in 7 out of the 18 impact categories. It was also observed that the bioplastic-based diaper has more severe environmental impact in categories related to land resource consumption and transformation, eutrophication and water depletion. Upon normalizing the results of all the impact categories, both the diapers overall exhibited significant potential for human toxicity, marine ecotoxicity, freshwater eutrophication and natural land transformation. However, when the normalized results of the eco-friendly diaper were compared with the conventional diaper, the former performed better in 3 out of the 4 aforementioned categories. It is therefore concluded that since the eco-friendly diaper fares better than the conventional diaper in most of the categories in which any kind of diaper is expected to yield maximum detrimental impact, it solves its purpose of reducing environmental impact and must be preferred.

Notably, if the land resource consumption was not studied along with the other impact categories, the effect of the diaper on water depletion could have been less since a large quantity of water resource is invested in irrigation. Considering the performance of the bioplastic-based diaper in all the categories together, there is a possibility that the results for this eco-friendly diaper would have been very promising if the land resource consumption was not evaluated, since its performance declines significantly only in this and its related categories. In this light, the other LCA studies which do not include evaluation of the land resource category and conclude in the favor of the bioplastic appear incomplete and biased. It is evidenced in this study that land resource consumption has a drastic impact on the overall sustainability potential, and it is possible that upon evaluation, this impact category would alter the results of other LCA studies as well.

Future Outlook

A future that enjoys harmony between the environment and the human population can only be realized by means of sustainable development, the goal of which is to strike a balance between environmental, social and economic impacts of a process. This balance is delicate because compromising with any of these three pillars might not seem like a significant damage but will eventually add up to the situation where sustainable development will not be feasible anymore. In this light the most ideal material system for sustainable development should be one that optimizes environmental impacts, economic feasibility and social acceptance. The question of whether the contemporary bioplastics in any way come close to such a material system still needs to be answered. Due to the shortcomings of LCA studies performed on bioplastics and lack of S-LCA and LCC studies, it is impossible to see the complete picture. What can be concluded from LCA studies are fragments of the overall evaluation that cannot be extrapolated to concrete conclusions. However, an analysis of the performed sustainability measurements establishes that the bioplastics do have detrimental environmental impacts, which remain beyond sight unless they are explicitly evaluated.

Even if the solution is sought in bioplastics and the forthcoming century must witness supplanting synthetic commodity plastics, the realized and unrealized environmental, social and economic impacts associated with unit products will cumulatively produce enormous impacts during mass production. Several sustainability issues associated with biobased plastics which can be identified only by visualizing a hypothetical mass production scenario such as competition with food production, mass depletion of land and water resources and cost uncertainty have been evaluated in the previous discussions. Therefore, the discussed hypothetical simulation of mass production for each individual bioplastic which is aimed at any industrial application will provide a foresight of such impedances to sustainable development and hence is indispensable. However, since the available sustainability measurement methods provide no such tools, it is necessary at this stage to develop mathematic methodologies focusing on this. The end of life scenario has an equally significant contribution in environmental and economic impacts. An analysis for identifying the ideal end of life scenario out of recycling, biodegradation and incineration, an example of which has been discussed, is required.

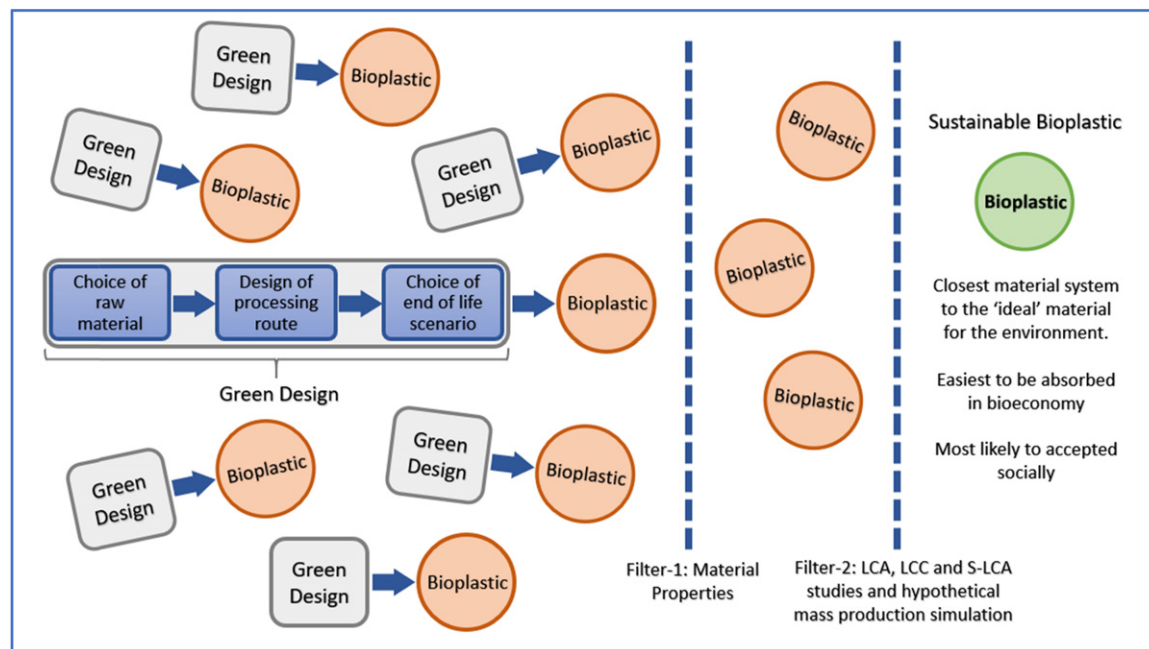


Fig. 11 Design of a sustainable bioplastic.

It is therefore very necessary at this stage that the discrepancies associated with sustainability measurement are eliminated and the sustainability potential of bioplastics is holistically evaluated. Although, the discussed bioplastics in this contribution exhibited detrimental environmental impacts and several social and economic concerns were associated with their mass production, it does not imply that these cannot develop into ideal material systems. For the purpose of designing a bioplastic, the general guideline to be followed is given by the 12 principles of green engineering. However, these are generalized concepts which give little insight into the protocol or strategy for developing of a sustainable bioplastic. This leaves bioplastic material design a process with no definite ends.

What can be done?

- The purpose for designing a bioplastic must initiate from the requirement of replacing a specific synthetic plastic used in a particular product. Since environmental, social and economic conditions vary regionally, the general goal of the design must be to develop a sustainable bioplastic that satisfies the balance needed for sustainable development in reference to regional production and commercialization of the bioplastic. For this, the availability and abundance of local land and water resources must be identified, such that cultivation of the crop which yield the raw material for the bioplastic can be initiated without restricting the production of food and other crops. The choice of raw material must minimize the environmental impacts such as soil depletion, which its production is expected to produce. For example, a plastic crop which can be cultivated in crop-polyculture with food crops, where each crop symbiotically replenishes the nutrients the other crop depletes can be a good place to start. The cultivation of plastic crop must be analyzed for other such possible environmental impacts.
- Once the raw material is identified, the regional environmental and economic conditions must be analyzed to assign weightage to the different environmental impacts possible. Subsequently a processing route must be designed such that it yields minimum to no environmental impacts in categories which cannot be damaged any further. It is essential that the cost of the developed product is such that it can be commercialized easily. Processes such as pre-consumer recycling, biodegradation and incineration must be implemented to aid the sustainability potential of the product being designed.
- The end of life scenarios possible must be evaluated, while taking into consideration the environmental and social impacts of these, the regional awareness and responsibility of consumers towards waste management as well as the available government incentives for implementing the concerned waste management option. For example, biodegradation may not be a suitable solution for a region, from where the waste usually finds its way into the marine environment, unless an industrial composting facility is established and the it is ensured that the plastic waste reaches it upon disposal.
- Thereafter, the developed bioplastics must be filtered for the options which offer the required properties. The bioplastics which do not pass this filter can then be considered for other applications, for which their properties are suitable.
- Once the product life cycle has been designed, all the filtered bioplastics must undergo comprehensive LCA, LCC and S-LCA studies, which holistically evaluate all the impact categories and yield an unbiased wholesome picture. This step will identify the environmental and other impacts which were left unrealized in the design of the life cycle. These impacts must then be addressed by modifying the design of the processing route, or the choice of raw materials etc.

- For the remaining bioplastics, each of which has the relevant set of material properties and is environmentally, socially and economically suitable for regional commercialization, a hypothetical mass production must be simulated to identify the hidden sustainability issues which surface only in mass production. The bioplastic which passes this filter is the ideal sustainable material system for implementation in the desired application and subsequent commercial use (Fig. 11).

Several such protocols can be developed based on the requirements and factors, which are specific to either the region, the application or the plastics. However, it is essential that the protocol holistically evaluates the bioplastic and the implemented bioplastic is stable environmentally, commercially and socially.

Summary

In this article, the evaluated and possible sustainability issues associated with biobased and biodegradable plastics have been discussed. The drawbacks associated with LCA which prevent an unqualified assessment of bioplastics have been highlighted. Since bioplastics constitute both biobased and biodegradable plastics, both of these and the sustainability issues associated with them have been analyzed. Biodegradability and recycling have been compared for identification of the eco-friendlier end of life scenario and the need for simulating hypothetical mass production to foresee the sustainability concerns associated with bioplastics has been emphasized. Assessment of individual bioplastics and three product-based case studies have been discussed to provide an insight into the sustainability issues of existing bioplastics.

Acknowledgments

The authors wish to acknowledge the financial support by Robert Patrick Jenkins Professorship, and the Dean's Faculty Fellow Professorship.

See also: Evaluating the Sustainability Performance of Building Systems and Technologies for Mainstreaming Sustainable Social Housing in India. Renewability and Sustainability: Current Status and Future Prospects. Renewable Agricultural Fibers as Reinforcing Fillers in Plastics: Mechanical Properties of Kenaf Fiber-Polypropylene Composites. Sustainability and Recycling of Bamboo for Engineering Applications. Tailor-Made Bioplastics for Environmentally Friendly Food Packaging: A Methodological Approach to a Challenging Problem

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Sustainable Future Alternative: (Bio)degradable Polymers for the Environment

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Introduction

Commonly used traditional polymeric materials such as high or low density polyethylene (HDPE or LDPE), polypropylene (PP), poly(ethylene terephthalate) (PET), polystyrene (PS) or poly(vinyl chloride) (PVC) have good resistance to water, gases, temperature and chemicals. They also have high mechanical strength, transparency, low mass and low price, as well as, ease dyeing. Moreover there is a lack of interaction between them and the product with which they stay in contact with. These materials have a negative impact on the environment, therefore the use of polymers with a minimal carbon footprint should become widespread. Due to environmental issues, more attention is being paid to renewable resource-based plastics. Furthermore, degradable or biodegradable polymers attract a lot of consideration in view of the current interest not only in sustainable development but also in recycling, environmental protection, and healthcare. From the sustainability perspective, (bio)degradable polymers are considered to be safe for the environment and to represent an interesting and fairly versatile alternative to conventional polymers. There is also increasing demand for (bio)degradable polymers that have been designed as materials for multi-faceted applications with a specific lifetime. Currently, there are challenges related to the design of materials that are stable in use, and at the same time susceptible to microbial attack during organic recycling.

According to the polymers origin or origin of the raw material needed to obtain them, (bio)degradable polymers can be classified as follows: natural polymers (biopolymers), polymers from renewable resources (of biological origin), and those from non-renewable/fossil resources such as oil, natural gas and coal (synthetic polymers) (Table 1).

Polymers from renewable resources differ from natural polymers by the fact that the synthesis is purposely initiated and caused either by microorganisms or by chemical means. The biopolymer is specifically “a polymer formed by living organisms; man-made polymer is not a biopolymer”. According to the terminology of the International Union of Pure and Applied Chemistry (IUPAC), a degradable polymer is “a polymer in which macromolecules are able to undergo chain scissions, resulting in a decrease of molar mass.” Biodegradation is “caused by enzymatic process resulting from the action of cells”, but *in vivo* degradation resulting “only from hydrolysis by the water present in tissues and organs” must be defined as hydrolytic degradation. An *in vitro* abiotic degradation by isolated enzymes is “a degradation caused by the catalytic action of enzymes” and is not considered as biodegradation. The fact that a polymer is from renewable raw materials is “composed or derived in whole or in part of biological products issued from the biomass” does not mean that the material is biodegradable. Biodegradation is an enzymatically catalyzed hydrolysis of the ester, amide, or urethane polymer bonds in the process of surface erosion; because enzymes do not penetrate deep into the polymer matrix, this leads to water-soluble oligomers metabolized by microbial cells. In the cases of high-molar-mass polymers, the first degradation step is conventional hydrolysis, which is not catalyzed by enzymes, and the depolymerization intermediates are finally metabolized by microorganisms (Rydz *et al.*, 2015a,b, 2018).

Environmentally-Friendly Polymers

Natural Polymers

Due to their natural origin, all naturally occurring polymers are biodegradable, since, for any polymerase activity that leads to a natural polymer, there is depolymerase that can catalyze the degradation of this natural polymer to maintain the balance of nature. The advantageous properties of natural polymers are their bioactivity, antimicrobial and antioxidant properties, renewable origin, relatively low cost, high prevalence, and the fact that they have no negative impact on the environment.

The essential polysaccharides used in material applications are cellulose and starch. These polymers are classified by their monosaccharide components and their ring size (furanose or pyranose), their absolute configuration (*D*- or *L*-), the sequences and linkages between them, the anomeric configuration of linkages, as well as any other substituents present in the molecule. Starch is a hydrocolloid that contains two types of polymers: amylose (20%–30%) and amylopectin (70%–80%) with *D*-glucopyranoside repeating units. This polymer is found in corn, potato, wheat, rice, barley, oat, and soy in the form of granules of different shapes and sizes from 0.5 to 175 μm . Starch, depending on the source, has different proportions of amylose and amylopectin. It has very favorable physical properties, such as high barrier properties (low gas and water permeability), transparency, ability to give the desired color and good rheological properties. Cellulose a polysaccharide and one of the most commonly occurring natural polymers is found in all plant materials, some amoebae, sea animals, bacteria, and fungi. Cellulose consists of very long macromolecular chains of one repeating unit: cellobiose. This polymer's molecules have hydrophilic nature, poor solubility characteristics, and highly crystalline structure. Moreover, cellulose is infusible and insoluble in all organic solvents. Chitosan is other linear polysaccharide consisting of β -(1 $\rightarrow$ 4)-linked 2-amino-2-deoxy-*D*-glucose (*D*-glucosamine) and 2-acetamido-2-deoxy-*D*-glucose (*N*-acetyl-*D*-glucosamine) units.

Table 1 Classification of (bio)degradable polymers

Polymer group	(Bio)degradable representatives
Natural polymers (biopolymers)	● Polysaccharides: cellulose, starch, chitin and chitosan, alginate, hyaluronic acid; ● Poly(amino acid)s: poly(γ-glutamic acid), poly(ϵ-L-lysine), cyanophycin; ● Peptides, proteins: whey protein, soy protein, zein, casein, wheat gluten, gelatin.
Polymers from renewable resources (artificial biopolymers)	● Polymers with microbiological origin (biotechnological polymers): polyhydroxyalkanoates (PHA)s, microbial cellulose; ● Polymers from renewable monomers (from bioderived monomers): polylactide or poly(lactic acid) (PLA), polyglycolide or poly(glycolic acid) (PGA), poly(butylene succinate) (PBS)^a, poly(butylene adipate-co-terephthalate) (PBAT)^a.
Polymers from non-renewable resources (non-natural/man-made polymers)	● Aliphatic polyesters: poly(ϵ-caprolactone) (PCL), poly(3-hydroxybutyrate) (PHB), poly(butylene succinate); ● Aliphatic-aromatic copolyesters: poly(butylene adipate-co-terephthalate); ● Poly(amino acid)s; ● Polycarbonates; ● Polyanhydrides.

^aBiobased currently in development.

Chitosan is obtained by partial alkaline *N*-deacetylation of chitin. Chitin is a component of shells of crabs, shrimp, crawfish, and insects. Depending on the preparation method, the degree of deacetylation (the ratio *D*-glucosamine to *N*-acetyl-*D*-glucosamine) may range from 30% to 100%. The composition of the polymer affects the crystallinity, surface energy, and degradation rate of chitosan. Due to the fact that chitosan has a rigid and compact crystalline structure and strong intra- and intermolecular hydrogen bonding it is insoluble in water and alkaline media. This polymer has antimicrobial activity and can, therefore, be used to extend the shelf life of food and as a component of biodegradable edible films for food. Hyaluronic acid is a high-molar-mass, linear polysaccharide classified as glycosaminoglycan, consisting of the repeating disaccharide units. Hyaluronic acid is present in all organisms. The highest concentration of this polymer is found in soft connective tissue. The traditional method of obtaining hyaluronic acid was extraction from rooster combs and bovine vitreous humour. This polymer offers many unique advantages as a building block for biomaterials. Hyaluronic acid is used commercially as an aid in ophthalmic surgery.

Poly(amino acid)s consist of amino acids linked through amide bonds. These polymers are characterized by biocompatibility, bioabsorbability, and adequate mechanical properties. Some of the most important α -amino acids containing polymers are poly (aspartic acid), poly(L-lysine) and poly(L-glutamic acid). Proteins are thermoplastic heteropolymers built from different polar and non-polar α -amino acids. Amino acids can form intermolecular linkages that result in different interactions. This offers a wide possibility of chemical functionalities and functional properties. Fibrous proteins, such as silk, wool and collagen are neither soluble nor fusible and must be used in their natural form for those reasons. Collagen is the elementary protein component of animal connective tissues. Collagen contains various polypeptides built from mostly glycine, hydroxyproline, proline and lysine. The flexibility of the polymer depends on the glycine content. More flexibility is obtained by an increase of the content of glycine. Due to their unique biological properties collagen is used in biomedical applications. Zein is a protein mixture varying in molecular size and solubility, classified as a prolamin. This mixture contains 44%–79% of the endosperm protein depending on the variety of corn and separation method. Zein has both hydrophobic and hydrophilic properties and due to its poor mechanical properties it is mainly used as a protective, impermeable coating, due to its good gas barrier, biodegradation and biocompatibility properties. Soy protein is another widely known protein that is isolated from soybean and are processed into high protein commercial products such as soy flour and soy concentrates by dehulling and defatting processes, are processed into high protein commercial products such as soy flour and soy concentrates (Ulery *et al.*, 2011; Kunduru *et al.*, 2016).

Polymers From Renewable Resources

Considering renewable resources for the production of polymeric materials, two different directions can be adopted. The first is the direct conversion of renewable resources into the final polymer. In the second, the monomer or other substrates are obtained from renewable resources and next are transformed directly or via few, chemical stages into final polymer. Polyesters with microbiological origins, such as polyhydroxyalkanoates illustrate the first direction. Polylactide, an aliphatic (bio)degradable and a biocompatible thermoplastic polyester, is an example of the second direction of the production of polymeric materials from renewable resources.

Polyhydroxyalkanoates are a family of natural biodegradable polyesters produced by genetically modified plants or microorganisms, as their reserve material (Fig. 1).

The assimilated coal is biochemically processed into the monomer (the appropriate hydroxyalkanoate), which polymerizes in the presence of PHA synthase (PhaC) enzyme. Obtained PHA are storage inside the cell in the form of sub-micron inclusion bodies. Under normal conditions the amount of polymer in the bacteria cell is in the range from 1% to 30% of their dry mass, but when the fermentation conditions are controlled some bacteria can accumulate PHA up to 90%.

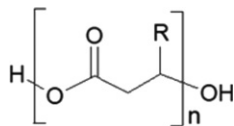


Fig. 1 General molecular formula of PHAs, where R is H for poly(3-hydroxypropionate) (PHP), CH₃ for poly(3-hydroxybutyrate) (PHB), C₂H₅ for poly(3-hydroxyvalerate) (PHV), C₃H₇ for poly(3-hydroxyhexanoate) (PHHx), C₅H₁₁ for poly(3-hydroxyoctanoate) (PHO), C₇H₁₅ for poly(3-hydroxydecanoate) (PHD).

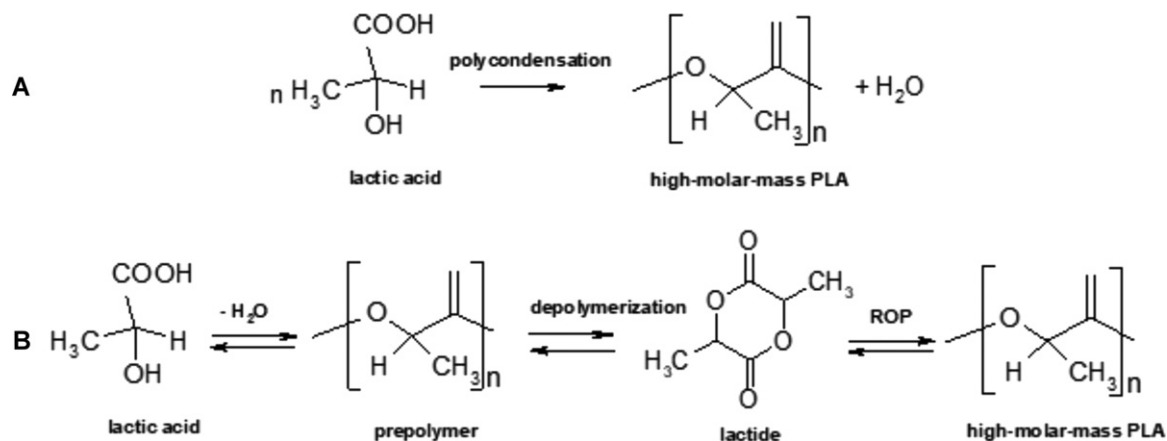


Fig. 2 Methods to obtain PLA.

The microorganisms are the main source of PHA, because of their ease of obtaining from the cell by the solvent extraction method. Under *in vivo* conditions the polymer is in an amorphous state, but after extraction it takes a crystalline form. Molar mass of polymer depends on microorganism type and the fermentation conditions. PHAs show non-toxicity and biocompatibility while retaining the properties of classic plastics. They are characterized by good barrier properties. The water vapor permeability of PHA materials is lower compared to other (bio)degradable materials (e.g., PLA). Poly[(*R*)-3-hydroxybutyrate] (nPHB) is the best-known polyester from PHA group, it is a brittle, crystalline (up to 80%) and thermoplastic linear homopolymer. Unfortunately, this polymer is susceptible to the thermal degradation in the range of its melting temperature (T_m) because T_m is close to the decomposition temperature, which hinders its processing and thus limits its applications. nPHB is obtained by enzymatic polymerization of (*R*)-3-hydroxybutyric acid with coenzyme A. Control of fermentation conditions and the type of carbon source leads to obtaining different copolymers, such as poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P3HB4HB) or poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), which are an alternative to non-biodegradable plastics. The introduction of (*R*)-3-hydroxyvaleric acid into the polymer chain during the microbial fermentation results in a PHBV copolymer with a lower degree of crystallinity. PHBV can be processed by traditional methods at a temperature lower than the polymer decomposition temperature. The PHA properties can be modeled by controlling the fermentation conditions and providing a suitable carbon source. Mechanical properties of PHA depends on the type of substituent group present and a variety of polymers, from rigid to brittle may be obtained. Blending of different PHAs increase their application range, hence the reason why PHA copolymers seems to be an interesting alternative in the production of biodegradable materials (Rydz *et al.*, 2015a,b).

Poly(lactide) is the most popular synthetic (bio)degradable polymer obtained from renewable raw materials. PLA is biocompatible thermoplastic, with possibility to process it in a large-scale commercial processing equipment by conventional methods and can replace classic thermoplastics. PLA has a high modulus and tensile strength, it also is resistance to UV radiation and fats, has good barrier properties of flavor and odor, good printability and processability, however, is brittle and degrades easily as temperature rises. PLA is obtained in two ways: direct polycondensation of lactic acid (Fig. 2(A)) or ring-opening polymerization (ROP) of lactic acid cyclic dimer, known as lactide (Fig. 2(B)). The lactic acid used is obtained from the fermentation of raw materials derived from renewable resources such as starch, cellulose or simple sugars (glucose, dextrose, maltose, sucrose).

ROP leads to high-molar-mass polymer with good mechanical properties. In the direct condensation, materials of low to intermediate molar mass are obtained because a solvent is used and a higher reaction time is required. The properties of PLA depend from the molar mass and stereochemical composition of the repeat units and their distribution along the polyester chain. Homochiral PLA (poly(*L*-lactide) (PLLA) or poly(*D*-lactide) (PDLA)) is isotactic stereoregular polymer with glass transition temperature (T_g) in the range of 55°C to 65°C. PLLA and PDLA are the semicrystalline polymers while the poly(*D,L*-lactide) (PDLLA) is more amorphous. Therefore, the products made of PLA have a very wide range of mechanical properties from soft, flexible plastics to rigid durable products. However, it is not suitable for some applications, so the physical properties of this material can be

improved either by blending with other polymers or with copolymerization. The biocompatibility and non-toxicity of PLA and its degradation products made this polymer a very interesting material for medical applications. The important role in its practical application plays the PLA crystallinity. Devices made of semicrystalline PLA are characterized with good mechanical strength and found application e.g., in packaging industry. The blends (physical mixtures of at least two structurally different polymers) of PLA with poly(ethylene oxide), poly(ethylene glycol), PCL, poly(vinyl acetate), nPHB, cellulose acetate, PBS and poly(hexamethylene succinate) as well as the plasticizers such as oligolactide, glycerol, low-molar-mass triacetin and citrates are also used (Nowak and Pająk, 2010).

Polymers From Fossil Resources

Man-made synthetic biodegradable polymers have more advantages than natural polymers because, they can be tailored to give a wider range of properties and can be transformed into a degradable material for specific applications. Generally, they are biologically inert, have more predictable properties, and the source of raw materials used to obtain such polymers is more readily available. The most commonly used synthetic polymers from non-renewable sources are poly[(*R,S*)-3-hydroxybutyrate] [(*R,S*)-PHB], poly[(1,4-butylene adipate-*co*-1,4-butylene terephthalate)], poly(butylene succinate) and its copolymers: poly(1,4-butylene succinate-*co*-1,4-butylene adipate) (PBSA) and poly(1,4-butylene succinate-*co*-1,4-butylene terephthalate) (PBST) as well as poly(ϵ -caprolactone).

A synthetic analog of aliphatic biopolyester, nPHB – (*R,S*)-PHB – is considered as a suitable modifier for (bio)degradable polymers, such as the highly crystalline PHAs of bacterial origin or the brittle PLA. PHBs and their block and graft copolymers can be obtained by direct copolymerization of the corresponding epoxides with carbon monoxide or anionic ring-opening polymerization of (*R,S*)- β -butyrolactone in the presence of the anionic initiators activated by macrocyclic ligands, such as crown ethers or cryptands. (*R,S*)-PHB is used for the physical or chemical modification of natural polymers by blending or by block or random copolymer synthesis. The blends of (*R,S*)-PHB with natural PHBV (containing 10 mol% of 3-hydroxyvaleric units) are compatible within the range of the tested compositions: 10%–50% of the (*R,S*)-PHB content. The PHBV copolymers with lactide, ϵ -caprolactone, β -lactones and higher lactones, as well as with poly(methyl methacrylate), poly(vinyl alcohol), poly(ethylene glycol) or polysaccharides are obtained by polymerization occurring in the presence of a macroinitiator or copolymerization of macromonomer. The copolymers obtained have a different chain structure: statistical, grafted, block (from diblock to multiblock) and different architecture: linear, comb and star. Anionic polymerization of at least two monomers with similar reactivity allows obtaining polymers with a statistical distribution of these two types of constitutional units in the polymer chain.

PBAT is an aliphatic-aromatic copolyester obtained from terephthalic acid or dimethyl terephthalate, adipic acid and 1,4-butylene glycol. Preparation and biodegradation studies of aliphatic-aromatic copolyesters, especially PBAT, have enabled the implementation on an industrial scale production of a compostable plastic called Ecoflex[®] produced by BASF Germany. PBAT is a flexible material with functional properties allowing its widespread use. The PBAT copolyesters combine the good functionality of aromatic polyesters with the biodegradability of aliphatic polyesters and can also be used in the form of a blend with other polyesters. The change of PBAT properties can be obtained by blending it with e.g., maleic anhydride or PHBV. The blends of PBAT with PLA and thermoplastic starch, have properties similar to polypropylene. Poly(butylene succinate) is produced from ethylene glycol or 1,2-ethylenediol, 1,4-butanediol and succinic acid. Its mechanical properties are comparable with PP and LDPE. The properties and biodegradability of PBS depends on amounts and type of glycols or diols and diacids used during production. Addition of adipic acid gives the PBSA copolymer. Increasing in the susceptibility to microbial attacks of poly(tetramethylene succinate) (PTMS) is achieved by introducing the carbonate into its crystal structure.

PCL is a synthetic, linear aliphatic polyester produced by the ring-opening polymerization of ϵ -caprolactone. It shows good biodegradability and susceptibility to hydrolytic degradation. However, due to the low flow temperature (around 60°C) its processing is much more difficult (Rydz *et al.*, 2015b, 2018).

Global Carbon Life Cycle and Principles Concerning Sustainability

The carbon cycle is a biogeochemical cycle through which carbon is converted between the earth's different types of coal reservoirs in the biosphere, pedosphere, geosphere, hydrosphere and the atmosphere. The earth's atmosphere contains carbon primarily in the form of carbon dioxide (CO₂) and, although CO₂ levels in the atmosphere are not constant, it is the fifth most abundant gas therein.

Polymers are carbon-based materials and, in the ecosystem, carbon is part of the biological life cycle; it is therefore vital that carbon-based polymeric materials are sustainably adapted to the natural carbon cycle. The traditional petrochemical-based polymers produced by cracking feedstocks from raw materials, such as natural gas and crude oil, are known for the difficulties in managing them sustainably and ecologically, due to the lack of degradation. Therefore, the conversion rate of non-renewable resources (petroleum-based polymer materials) into CO₂ is in total imbalance with the rate at which they are consumed and renewed (Fig. 3). In this way, carbon is not managed sustainably and ecologically: it is either locked up in landfills due to lack of degradation and practical recycling procedures of plastics or released as CO₂ into the environment through the incineration of

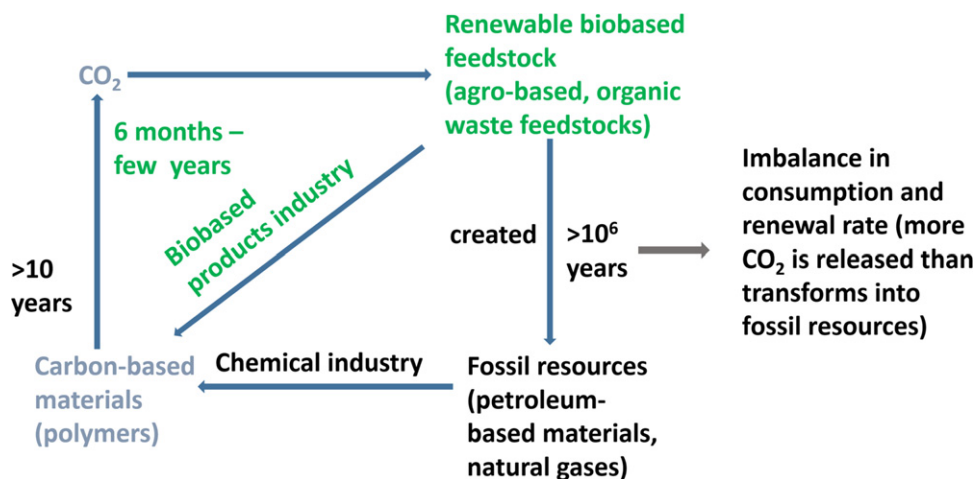


Fig. 3 Global carbon life cycle.

plastics, rather than its transformation back into carbon resources. The latter is also outpacing nature's CO₂ recycling capability through photosynthesis, causing a significant increase in the global CO₂ level.

Significant advances have been made in the development of several ecofriendly materials with low environmental impact. These can be obtained from different types of carbon-based feedstock including agricultural products, such as corn or soybeans, and from other sources like algae or food waste. The development of environmentally friendly materials and the sustainable production of polymers from renewable feedstock is vital for our declining natural resources and therefore ecofriendly polymers are becoming increasingly important from the sustainability point of view. Biomass provides a path for renewable sources of both carbon-based energy and polymer ecomaterials. Using annually renewable crop resources or biomass as raw material for polymer production, the rate at which CO₂ is renewed equals its consumption, which is naturally sustainable. Also, the use of synthetic (bio)degradable materials does not involve long-term deficits, and their resources are renewed in a short time. Biobased polymers are characterized not only by their origin from renewable sources but also by the following: easy disposal, recycling, the reuse of waste, biodegradation or composting and the fact that they are health-safe. The impact on human health is reduced, along with a reduction in pollution and material use as well as the creation of energy efficiency.

Carbon footprint (CF) and life cycle assessments (LCA) of polymer materials are methods used to quantify the sustainability of plastics and their global carbon life cycle. Carbon footprint is a term that had a wide appeal and has been driven mainly by people outside the research community, partly because the term gives a much easier way to calculate and grasp the concept of carbon emissions. But it also takes only one factor into account and therefore oversimplifies the notion of CO₂ emission. In the life cycle assessment, however, the discussions also include many other factors such as the quantification of methane losses, condensation trails, ozone formation, and cirrus clouds, and many other technicalities. Life cycle assessment is a much more robust way of highlighting the full environmental impact of a process, product or activity from cradle to grave, or cradle to gate, depending on what stage of the investigation is the focus of interest. According to the International Organization for Standardization (ISO), there are several key steps in performing and implementing LCA. That is, the environmental impact of all phases of the product's life are assessed (inputs and outputs), from raw material extraction, manufacturing, distribution, storage, usage, recycling, reuse and disposal. LCA is a good measure of the environmental performance of the selected product and creates a holistic picture, which avoids solving one environmental issue but creating a new one in the process. Multiple substances can be assessed separately or simultaneously to better understand their contribution to various environmental problems. A well-implemented LCA contributes to important knowledge which not only enables producers to identify more sustainable methods of production, use and disposal of the polymer, but can also give an opportunity for further environmental adjustments as needed. The problem with LCA is the complexity of the process involved and the time it takes to identify and quantify all the material and energy flows related to the product, process or activity. Additionally, it is difficult to get hold of reliable data and it is also complicated to establish which flows provide the cause of any environmental impact.

The LCA databases used to quantify the environmental sustainability of biobased and/or biodegradable polymers. For example, poly[(R)-3-hydroxybutyrate] is compared to the petroleum-based polypropylene and polyethylene. Despite several controversial issues related to the nPHB production, such as the high energy demands, the LCA of this polymer shows that it is much more environmentally friendly than polyolefins. The study, however, did not consider the effects of polymer disposal and it was anticipated that the incineration of polyolefins will add a further burden while giving nPHB additional benefits. This is a very common procedure for many LCA studies, and it is due to the scarcity of the end of life data. Although a lot of factors must be considered when comparing biobased polymers with traditional petroleum-based polymers, the differences between the biobased polymers are not that significant. The energy demand for feedstocks production and lack of composting facilities, as most plastics end up in a landfill, are some of the common issues hampering the full benefit of biobased polymers. The current understanding

of biopolymer distribution in waste streams is also insufficient and is hence the reason why the resultant cradle to grave life cycle environmental impacts remain ambiguous.

Problems such as the lack of dedicated waste collection systems and recycling methods are also regarded as barriers to sustainability. High energy demands, lack of extensive end-of-life (EOL) data, and also those of high material and water requirements from the farming and production processes, give a greater environmental burden and contribute negatively to the overall LCA outcome. Just because certain plastics are produced to be environmentally friendly, does not mean that they can be dumped into a landfill and become biodegradable under unfavorable conditions. It must be created a safe and sustainable way to facilitate the speedy degradation of biobased polymers and return them back to the carbon cycle in a sustainable manner (Harding *et al.*, 2007; Hottle and Bilecand Landis, 2013; Kyulavska *et al.*, 2018).

Applications of Environmentally-Friendly Polymers

For each polymer application, understanding which materials are optimal for their purpose allows for the exact selection of the right polymer material. In recent year's research and development above new materials including (bio)degradable plastics with well-defined properties, from both service and environmental point of view, has shown continuous progress.

Medical, Pharmaceutical and the Dental Sector Applications

The fact that (bio)degradable polymers are readily absorbed by the human body drives both the scope of application and the extent to which they are used in medicine and dentistry. Some of the examples of their usage include assorted medical and dental devices or their components, surgical sutures, (bio)degradable components used in the repair of ligaments. These polymers also found a wide application in the manufacturing of tools used during a variety of surgical procedures as well as for the making of devices that are permanently implanted. The accessibility of coated or time-released drugs requires the availability of carefully chosen and formulated polymers that will allow for a uniform release of predetermined doses on medication over time. (Bio)degradable polymers, such as PGA, PLA, poly(glycolide-co-lactide) (PLGA), poly(*p*-dioxanone), poly(glycolide-co-trimethylene carbonate) and PCL are used as materials for surgical sutures or resorbable implants, stiffening dressings and controlled drug delivery systems. In dental procedures, the (bio)degradable polymers are used as void filler following tooth extraction (porous polymer particles can be packed into the cavity to promote quicker healing) and a (bio)degradable film that can be positioned to prevent epithelial migration following periodontal surgery. There is expanding need in the field of orthopedics for joint replacements, items used in the repair of fractures, bone fillers and bone cement, as well as artificial orthopedic constructs used to replace parts that sustained irreparable damage. PGA, PLA and its copolymers, PHA and PCL are particularly desirable for orthopedic devices due to their excellent biocompatibility and the possibilities to adjust physical properties and degradation properties to a specific application. Implants are being developed using biopolymers such as collagen, elastin, hyaluronic acid, chitosan, silk, and starch. The synthetic and natural polymers have been combined with nano-hydroxyapatite (nano-HAP) or tricalcium phosphate (TCP) which allows for the design of implants that have bone-like compositions. A different example of the application of these polymers is the production of composites that simulates bone tissue growth. (Bio)degradable polyesters can also be used as a coating on a medical device or as a completely (bio)degradable devices such as anastomosis rings and tissue staples, ligating clips, tissue engineering scaffolds vascular grafts and stents.

Packaging Sector and Food-Services Sector Applications

Delivery of food products to the point of sale or to the consumer requires a large and varied amount of packaging product, each designed to serve its unique purpose. The function of packaging is threefold: the material from which it is made must be approved for direct contact with food, the design of packaging must protect its contents from external contamination, and also must serve to protect it from loss of flavor. Additional requirements address transportation and storage requirements. Starch is readily available in large volumes and at relatively low cost. It has also attractive physical properties, low permeability of gases and water (barrier), transparency or ability to impart desired color (optical), which makes it one of the best candidates for biodegradable food packaging. Thermoplastic starch is used for food wrappings and cups, plates and other food containers. Because starch has poor mechanical properties and poor resistance moisture which place limits on it uses this polymer can be blended with various polymers such as PLA, PCL or PVA. The polymer/starch blend can be used in the production of flexible and rigid films, allowing for thermoforming into rigid injection molded packaging trays and for coating of paper and cardboard (direct contact with food). Another polymer used for packaging material is cellulose and its derivatives, like cellulose acetate. It is extensively used in the packaging of fresh products and baked goods. Chitosan can be blended with PCL, protein such as zein, gluten, soy protein or whey protein. PLA is a proper candidate as green food packaging material, due to its high molar mass, easy processing by thermoforming, and (bio)degradability. PLA is finding practical application in the production of beverage bottles, transparent rigid containers, bags (also from PBAT), jars, food containers, disposable cups, coating for all types of packaging and film packaging foams. Materials based on PLA and PHBV have shown effective application for the production of thermoformed containers for food packaging. PHAs such as PHB and its copolymers: PHBV, poly(hydroxybutyrate-co-hydroxyhexanoate) (PHBHx), poly

(hydroxybutyrate-*co*-hydroxyoctanoate) (PHBO), poly(hydroxybutyrate-*co*-hydroxyoctadecanoate) (PHBOd) and P3HB4HB can be used in packaging for deep drawing foods such as bottles, disposable cups, laminated foils and fast food.

Agriculture and Horticulture Applications

Recent trends in the agricultural application include the use of natural and synthetic (bio)degradable polymers such as agar, starch, pectins, alginates, chitin, lignin, cellulose and its derivatives, PLA and PCL to replace traditional plastics. Soil retention sheeting, agricultural foils, seed or fertilizer tapes and binding materials, threads, clips, staples, bags containing fertilizer, envelopes of ensilage and trays of seeds, plant pots are being replaced by (bio)degradable equivalents and disposable items so that the used (bio)degradable materials does not have to be removed after use. Natural polymers along with synthetic (bio)degradable polymers such as PLA or PCL can be used as carriers in controlled release systems of pesticides, herbicides, nutrients, fertilizers, pheromones to repel insects. The active agent can either be dissolved, dispersed or encapsulated by the polymer matrix or coating, or is a part of the macromolecular backbone or pendent side chain. PBAT can be used as greenhouse tunnels and mulching foils.

Automotive and Transportation Sectors Including Aerospace Applications

Current objectives of the automotive industry are to reduce fuel consumption and CO₂ emission. One way to accomplish this is to reduce vehicle mass. This offers an opportunity to expand biobased and (bio)degradable polymer applications suitable for the automobile construction. (Bio)degradable polyesters can be used in automotive manufactures as coatings for interiors or exteriors, thermoplastic elastomers, fiber reinforced thermosetting, shape memory and self-healing items, piezoresistive components for interior trims prototypes and for strain gauges for vibration monitoring. One of the most commonly used materials is composites. Those materials have good mechanical properties and the relative facility of combining them with other materials. In the automotive industry, biobased polymer composites, but only those that can be recycled, could be used in structural parts of the vehicle's body such as door handles, dashboard fascia, panels, floor trim, scooter frames, secondary paneling or interiors and underbonet. About 50% of all interior components, including safety subsystems, door and seat assemblies in commercial vehicles are made of plastics. Starch-based polymers are used as an additive in the manufacturing of tires. Starch reduces the resistance to the movement, the consumption of fuel, and reduces fine greenhouse gas emissions. Industrial sectors, such as construction, automotive and transportation sectors including aviation and aerospace use additive manufacturing as an integral tool in the design process. Three-dimensional (3D) printing technology allows us to build concept cars and aircraft, but it also allows for the rapid printing of components using experimental material and compares them with traditionally made parts.

Building and Construction Sector Applications

Unlike the automotive industry, the building construction is striving to reduce its CO₂ footprint and emissions. Ecofriendly buildings are intended to provide a healthier place to live and work. Such materials include laminated wood plastic components, polymer compositions (polyesters with jute fibers or fiber-reinforced polymers). Biobased and/or (bio)degradable plastics can be used as molds for truss joints, high thermal insulation rigid foams, new mortars or concretes, piezoresistive strain gauges for monitoring mechanical deformations of structures. PLA-based composites could be used as internal window profiles or, with the addition of aluminum hypophosphite, can provide flame retarding properties to some construction materials. The application of the composites determines their classification: structural (bridges, and roof components), and non-structural (windows, exterior components, composite panes, door frames).

Consumer Goods Applications

This category of goods includes a very large number of items ranging from domestic implements to recreational sports items, toys, and consumables. A new generation of adhesives, paints, engine lubricants, and construction materials, as well as golf tees and fishing hooks, is made of (bio)degradable polymer materials. Toothbrush handles and adhesive tape backing include chemically modified plant cellulose. Traditional materials used in the manufacturing of coffee capsules, which are used in large numbers, are replaced with starch-based materials, or with (bio)degradable polyesters. A (bio)degradable material used in 3D printing made from non-genetically modified maize corn starch is used to produce clothes using 3D printing method. Additionally, testing is underway to use it in the manufacture of toys. Cups, plates, bowls and shoes can also be made using this material. (Bio)degradable material from a marine shell is used to make Lego blocks, plastic balls, model toys, pens and art knives.

Electric and Electronic Sector Applications

Composites based on hollow keratin fibers and chemically modified soybean oil find applications in electronics as new low dielectric constant material. Other electronic devices that use (bio)degradable polymer-based materials include capacitors, communication devices, loudspeakers with advanced functionalities and paper-based displays made from wood lignocellulose microfibers-based polymers or batteries for microelectromechanical systems. Electroconductive plastics were developed to

manufacture electronics from sustainable sources. This is accomplished by spinning of different nanofibers individually or by hybridizing with other materials and incorporating them with suitable biobased polymers which can produce nanocomposites as possible superior structural components (lighter than their micro counterparts). These materials find application in a variety of electrical, optical and biomedical items such as components of various functional devices. Ecofriendly materials can be used in vacuum cleaners, as housing for power tools, and for portable electronic equipment including cellular phones. Electronic industry is also using (bio)degradable materials such as PLA/CORDENKA® composites. PLA can also be functionalized with various additives. PLA and kenaf are used as composites in electronic applications such as compact disks or computer cases. PLA can be enhanced by special technology to achieve properties such as conductivity, significant improvement in thermal stability or mechanical properties and are suitable for 3D printing technology, giving almost unlimited possibilities in the production of ready-to-use (bio)degradable polymer-based electronic materials (Rydz *et al.*, 2018; Włodarczyk *et al.*, 2018).

Three-dimensional Processing of (Bio)degradable Materials

The additive manufacturing (AM) is a type of manufacturing technology that produces 3D objects and this has received considerable attention in recent years. The process creates a 3D object in which materials are joined layer upon layer, while the structure is usually designed and processed under 3D computer modeling software.

There are different types of methods or 3D printers available today and they differ both in the way the successive layers are deposited as well as in the materials that can be used. Some of the most common are digital light processing (DLP), fused deposition modeling (FDM), stereolithography (SL), selective laser sintering (SLS), selective laser melting (SLM), laminated object manufacturing (LOM) and PolyJet technology. However, it seems that SLS and FDM are attracting growing interest since they produce high durability complex parts and allow for the quick identification of any design issues. The 3D technology is in rapid development and it has moved from being used as a tool to create and verify prototypes to becoming a powerful method of manufacturing final products from a myriad of different materials, such as metals, paper, liquid, wax, powder, wood and different types of polymers. Polymers are by far the most utilized material and there is a growing number of polymers currently used for 3D printing technology such as polyamides or polyesters.

Both naturally occurring and synthetic polymers are used for 3D printing filaments and each one has its own advantages and limitations. Naturally occurring polymers like collagen, chitin, gelatin, chondroitin, chitosan and various types of alginate can be used for tissue and organ engineering as well as diagnostic platforms. However, polymers such as polyamides, PCL, PLA, PGA, PLGA and different types of polymer blends offer unlimited opportunities for various medical purposes. This include both tissue engineering and drug delivery systems as they offer rather more possibility of tailoring the chemistry to the specific requirements, such as a specific end group, molar mass, polymer composition and biocompatibility. For the polymer industry, this is a manufacturing technology that has enormous potential and it is predicted that the adoption of 3D manufacturing will continue to expand in the future. Furthermore, the prospect for biomedical applications of 3D printing is the most interesting area (Rydz *et al.*, 2015a; Włodarczyk *et al.*, 2018).

Factors Affecting the Rate of (Bio)degradation Processes

There are many factors that have an influence on the (bio)degradation process of (bio)degradable materials, which are not only concerning the polymer itself but also exposure conditions. From the point of view of polymer, the molar mass, type of functional groups, crystallinity, type of additives, pretreatment of material and surface to volume ratio play an important role in its (bio) degradation. Polymers are rather resistant to the microbial attack, as long as their molar mass remains high. Hydrolysis or photodegradation can cause a decrease of molar mass until the level that microorganisms are able to utilize it. The enzymes have easier access to the polymer chain in the amorphous regions, where the less-ordered packing occurs. Higher crystallite edge surface in the polymer leads to higher degradation rate, because this rate is dependent on the availability of substrate. Increasing of the surface to volume ratio in the polymer also increases the availability of substrate and hence the degradation rate. The influences of the polymer additives on the degradation progress depend mainly on the type and the amount of it (Chandra and Rustgi, 1998; Rydz *et al.*, 2017).

If the polymer is suitable for organic recycling the rate of its (bio)degradation depends on the composting conditions. Aerobic decomposition of organic matter by the microorganisms is an important process in any ecosystem. This biological process occurs naturally anywhere where the organic matter has contact with air and humidity. The composting process mimics and intensifies the processes occurring in nature by creating optimal conditions. The rate and course of composting are influenced by the type and amount of microorganisms, temperature, pH, the presence of oxygen, humidity and carbon to nitrogen ratio (C/N). In the compost plenty of microorganisms are active. At the beginning of the composting process, the bacteria colonize the wastes. When the compost starts to dry the fungi begin to dominate. During the first composting phase the temperature rise is caused by mesophilic organism's action. When the temperature reaches at 45°C the thermophilic organisms continue the process, raising the temperature of the material to 65°C or higher. This phase is very important for the quality of the compost as the heat kills pathogens and deactivates weed seeds. Also, the high temperature phase of composting can accelerate the degradation progress of (bio)degradable polymers. When the high energy sources start to end, the cooling and maturation phase begins. Too high and too

low pH is toxic for microorganisms, it causes the change of ionization state of amino and carboxyl groups of proteins. If pH drops below 6 the microorganisms are dying and the decomposition of organic matter runs slower. pH above 9 causes the release of nitrogen to the atmosphere in the form of ammonia. Hence the nitrogen is not available for microorganisms. Optimal humidity for the composting process is in the range of 45%–60%. Exceeding of the 65% value promotes the formation of anaerobic zones, while achieving the value below 40% the nutrients become difficult to access for microorganisms. The main of (bio)degradable polymers are based on synthetic polyesters or modified biopolymers that are susceptible to enzymatic and/or hydrolytic degradation. The higher the moisture contents, the more quickly the degradation of moisture sensitive polymers occurs. However, the balance from the technological point of view must be preserved. In order to maintain optimal humidity of the compost among others the aeration of waste is used. This technique is also necessary to obtain the optimal temperature. Proper amount of oxygen causes the correct biological activity of microorganisms. The microorganisms which are responsible for composting process needs to receive the nutrients in the form available to them. The right concentration and proportions of the necessary elements must be ensured. To the most important ingredients needed for the proper functioning of microorganism belongs: carbon (C), nitrogen (N), phosphate (P) and potassium (K). Carbon is the energy source for microorganisms and nitrogen determines their speed of growth. C/N ratio of organic matter is an important factor that determines decomposition by the microbial. Composting occurs most efficiently when the C/N ratio is between 25:1 and 35:1 (Jędrzak, 2008; Rydz *et al.*, 2017).

Polyesters (Bio)degradation Studies under Laboratory and Real Conditions

Research on novel polymeric materials and their susceptibility to degradation are nowadays very important from both scientific and technological points of view. Advanced polymer materials are under consideration for new applications e.g., as superconductors, engineering materials and (bio)degradable packaging materials. (Bio)degradable materials are regarded to be essential also in medical and biological usages and therefore there are very important for human beings. Developing such polymeric materials for many applications is therefore of great importance. Products made from (bio)degradable polymers after using are susceptible to organic recycling, which reduces the environmental impact of polymer waste and allows for the rational utilization of these materials under composting conditions in accordance with new trends in the management of this type of waste. However, the efficient use requires basic research necessary to determine the relationship between the structure of such materials (including the topology of the macromolecules), properties and degradation mechanism. Prediction studies are needed in the area of advanced polymer materials particularly (bio)degradable polymers in order to increase efficiency and to define and minimize the potential failure of novel polymeric products before and after specific use. Due to the wide spectrum of potential applications of (bio)degradable polymers in medicine, in the field of compostable polymer packages (especially of long shelf life products such as cosmetics or household chemicals) as well as in agrichemical formulations degradation studies in different environments provide basic knowledge and a valuable service by increasing understanding and helping prevent future problems. Such innovative approach may help to design novel polymeric materials and to avoid the failures of existing ones. Therefore, it is so important to determine the degradation conditions during virtual testing of (bio)degradable polymer materials for the intended applications. Materials for specific applications must not only perform specific functions but also must meet acceptable standards of safety during use and exhibit chemical and physical stability. The complete replacement of conventional plastics with environmentally friendly polymers is impossible to achieve without recognizing and assessing the possible risks. In the case of (bio)degradable polymeric material, it should be chosen so as to minimize the impact of environmental conditions leading to (bio)degradation during usage. Therefore, modeling and simulation of degradation allows the prediction of the behavior of a complex polymer system during their use and disposal based on the comprehensive characterization of degradation pathways.

Thermo-, photo-, radio-, oxo- and mechanical degradations are important degradation mechanisms considering aging and the pre-programmed lifetime of particular polymeric materials. Photochemical degradation is initiated by the action of visible or ultraviolet light in the presence of chromophore groups (absorb light). These reactions can occur in the main chain and in the side groups. Mechanical degradation occurs under the influence of stress and takes place primarily in areas of material weakness (aggregates of small-molecule polymer fractions, inclusions of foreign bodies, end of chains, residual monomer, solvent, etc.). The atmospheric degradation proceeds according to mechanisms of oxidation (thermooxidation) and photooxidation (photo-degradation). During the oxidation molecules with a low molar mass are formed and groups containing oxygen are appeared along the polymer chain or on its ends. Thermooxidation takes place in the entire volume of the polymer and occurs at an increased temperature and in the presence of oxygen. Photooxidation occurs under the influence of UV radiation, mainly on the polymer surface. Photooxidation causes the breakdown of the chains into free radicals. Atmospheric degradation leads to the changes in the chemical structure of the polymer (branching, crosslinking), reduction in the molar mass (chain cracking), damage (cracking, scratches), which leads to changes in the physical properties of the materials.

The susceptibility of polymers and polymeric materials to (bio)degradation depends primarily on their chemical structure. For this reason, the origin of polymers, whether they are obtained from renewable (biomass) or non-renewable (fossil) resources, does not refer to the biodegradation. But the combination of biodegradation with the use of renewable resources for the production of bioplastics is a unique opportunity to adapt their life cycle to the natural cycle of matter. (Bio)degradable polymer evaluation studies for the final products for long-term applications involves virtual tests under different environmental conditions, including biodegradation under laboratory conditions (disintegration/biodegradability tests), pot degradation experiment, degradation under industrial composting conditions (static composting open-air pile, KNEER container system, BIODEGMA system) and

weathering test (the degradation of materials under natural atmospheric conditions). Often, under laboratory conditions, the reference degradation tests are carried out, parallel to real-world tests. During those tests, degradation products (collected during degradation) can be investigated and their structure or interactions between the polymeric material and the product with which it stays in contact can be determined. Under industrial composting conditions neither the collection process nor the compatibility test is practically a viable option. The behavior of polymeric material in nature and its factors impact (sunlight, rain, wind) on the samples tested should also be determined. The weathering tests are carried out in placing the sample on sloping shelves oriented to the sun. In the northern hemisphere, these stands are at an angle of 45° to the south, and in the south it is at a 45° angle to the north. This setting guarantees the full use of the whole spectrum of solar radiation. To achieve the maximum level of degradation, high temperature and humidity are also necessary, which can be achieved in tropical areas. Florida possesses all these features and therefore it is the global standard for natural aging methods. Generally, the biodegradation under natural conditions is more complicated process compared to degradation in controlled conditions and requires a complex and comparative procedure. Biodegradation studies under the industrial composting conditions can be referred to biological tests conducted *in vivo*, because they reflect the real conditions prevailing during organic recycling. Biodegradation carried out under laboratory composting conditions using a Micro-Oxymax respirometer, is in this case a reference to *in vitro* tests. During the biodegradation process under aerobic conditions, the material decomposes that leading to the formation of CO₂, water and solid residue – biomass. Thus, an evaluation of the progress of this process can be the measurement of released CO₂ or consumed oxygen (O₂), using the experimental technique such as of titrimetric analysis, gas chromatography or the automatically system – respirometer Micro-Oxymax. During incubation in the respirometer, the amount of released CO₂ from samples tested is monitored as a function of time. Obtained the cumulative value of CO₂ is used to determine the degree of biodegradation of studied materials. The degree of biodegradation (*B*) is calculated as the ratio of measured in the test amount of evolved CO₂ to the theoretical amount of CO₂ (*Th*_{CO₂} that can be produced by total oxidation of the tested material):

$$B = (m_{\text{CO}_2\text{test}} - m_{\text{CO}_2\text{blank}}) / Th_{\text{CO}_2} \times 100\%$$

where: *m*_{CO₂test} and *m*_{CO₂blank} are the amount of CO₂ [mg] evolved from tested material and blank inoculum, respectively.

The assessment of soil and compost quality, in which the biodegradable materials are incubated, is carried out on the basis of phytotoxicity tests in accordance with the guidelines contained in the Guide for Organization for Economic Cooperation and Development, OECD 208; EN 13432: 2000, by the method based on the comparing of the ability to grow of selected terrestrial plants in standard conditions with growth of plants on the tested soil and/or compost (pot experiment). The average values of fresh and dry matter of plants that grew on soil and/or compost after the degradation of the samples tested should be similar to those of control plants. Similarly, the growing percentage of the examined plants within each species examined should be similar to the control samples. As a result, this visual assessment of plant damage should confirm the lack of harmful effects of the samples examined on tested environments. The European Norm EN13432 that recommended composting as a method of organic recycling post-consumer, biodegradable polymeric materials waste including also test scheme and the procedure to assess the compostability. The organic recycling is recommended for waste susceptible for biodegradation and fragmentation during biological treatment, without an adverse effect on the composting process, and a negative impact on the quality of the compost obtained. In contrast to bacterial polyesters such as polyhydroxyalkanoates, which directly undergo biodegradation by many microorganisms present in the environment, the high-molar-mass PLA is colonized by relatively few microorganisms and more often takes place the water-catalyzed hydrolysis of those material. But generally, for (bio)degradable polymers the first step of biodegradation under natural and laboratory conditions is a chemical hydrolysis (mainly by random chain scission) which leads to the reduction of molar mass. In the next step, called mineralization the oligomers formed are bioassimilated by microorganisms as an energy source. The final result of biodegradation under natural conditions (composting process) is compost, where water and CO₂ are emitted into the atmosphere. The material can be qualified for organic recycling if it meets the following criteria: (i) for the process of industrial composting, lasting a maximum of 6 months, at least 90% of the material transformation into CO₂ is required, (ii) under anaerobic conditions during the 2 months of testing the degree of degradation (determined based on the separated biogas) should be 50%. If there is such a possibility, then biodegradation tests should be performed for packaging in the final form (pilot scale study). This allows specifying possible negative effects associated with the biodegradation process during the recycling of large quantities of the final products waste.

Although environmentally friendly polymers have gained much attention as possible substitutes for conventional plastics, the factors that influence their sustainability are often difficult to examine. Before the widespread use of any novel (bio)degradable/renewable polymer is advocated the full environmental impact (ecobalance) must be assessed. Moreover, the polymer material can interact with the product in which it stays in contact with such as food, cosmetics or the human body. These interactions can lead to changes in the product as well in the polymeric material structure and should be studied in detail. For this purpose, research in the field of safety engineering is carried out, checking the behavior of polymeric material/product systems in simulated and natural conditions. Obtaining basic knowledge about these interactions will allow better targeting of innovative applications of advanced polymeric materials and avoiding problems when using final products (e.g., cosmetics or food packaging and implants). End-products made of (bio)degradable polymers when subjected to the composting process will be (bio)degradable, and if they get into the environment in an uncontrolled way, they will undergo environmental and atmospheric degradation under the influence of the factors there (Musiol *et al.*, 2018).

See also: Biodegradable Packaging. Biodegradable Packaging Materials. Manufacturing of Biodegradable Poly Lactic Acid (PLA): Green Alternatives to Petroleum Derived Plastics. Natural Fiber Reinforced Composites in the Context of Biodegradability: A Review

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Valorization of Olive Biomass Fly Ash for Production Eco Friendly Ceramic Bricks

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Introduction

The increase in population worldwide and technological advances aimed new consumption habits which have led to the accelerated growth of large amounts of wastes. Currently, the amount of waste of all types generated worldwide is 1.3 billion ton/year, with a prospect for 2025 increasing to 2.2 billion tons per year ([Al-Fakih et al., 2019](#)). As a consequence, there is growing interest looking for new ways where these can be minimized or even used as a resource for added value. The recycling of by-products generated during industrial processes should be a priority action.

Wastes and by-products have great potential for its incorporation in the construction sector as raw material contributing to the called Circular Economy with lower production cost and more environmentally friendly. Ashes generated during the biomass combustion process are one of these by-products.

Currently, there is a growing interest in the valuation and recycling of waste and by-products throughout the world. The maximum reuse of any waste or by-product generated during an industrial process must have now a priority character. Among the most feasible alternatives at industrial level is the incorporation of these by-products as raw material in the manufacture of construction materials. Something that can contribute to reduce the risk of depletion of raw materials used by this industry, as well as to the called Circular Economy. In this way it is intended to make these industrial processes more sustainable and eco-friendly.

The most interesting wastes to be use as raw materials are the ashes of organic or biomass origin. It is due to their great generation, since at a global level, the increase that the use of biomass has had in recent years, as alternative energy source to those of fossil origin, has been spectacular.

In recent years, biomass energy has increased its use as alternative energy source. The conversion of biomass waste into energy can reduce their environmental impact. Several European directives such as 2009/28/EC of the European Parliament and of the Council ([European Parliament, 2009](#)) promote policies for the use of energy from renewable sources to reduce the net flow of greenhouse gases (CO₂) to the atmosphere ([Eliche-Quesada et al., 2017b](#)). However, it should also be noted that although this process of combustion of biomass in general is quite beneficial environmentally, also has some problems such as low combustion efficiency, high humidity and a high price of transport to the combustion site ([Batidzirai et al., 2013](#)).

In the world, large quantities of waste of agricultural origin are produced. Only in Europe, the amount of waste generated by agriculture is 250 million ton/year ([Setti and Ansaloni, 2005](#)). The waste to energy conversion processes for energy generation can have good economic and market potential. Biomass energy is an alternative source of energy compared to traditional sources of fossil such as coal and oil.

The large amounts of ash produced in biomass combustion process are an economic and environmental problem due to the high cost of storage, and management in landfills ([Chaunsali et al., 2018](#)).

When biomass is used as fuel to obtain electric and thermal energy, two types of ash are produced: bottom ash and fly ash ([Eliche-Quesada et al., 2017a](#)). Bottom ash constitute the unburned fraction produced on the boiler grate and in the primary combustion chamber and fly ash are carried with the flue gas and collected in cyclones and emissions control equipment (filters). The amount of bottom and fly and biomass ashes generated is about 480 million tons per year ([Modolo et al., 2014](#); [Vassilev et al., 2013](#)).

To close the circle and propose a Circular Economy, the use of biomass ash is proposed as a raw material to manufacture new materials, specifically for the construction sector.

Biomass ashes have been traditionally used as fertilizer ([Maschowski et al., 2016](#)). In recent years, the number of studies carried out for its reuse as raw material in construction materials has been important. Due to its proven pozzolanic activity, biomass ash is applied in the development of alkaline activated materials or geopolymers ([Peys et al., 2016](#); [Bonet-Martínez et al., 2018](#)), the manufacture of cement ([Yin et al., 2018](#)), concrete ([Lessar et al., 2017](#)), mortar ([Tosti et al., 2019](#)) or ceramic bricks ([Pérez-Villarejo et al., 2012](#); [Fernández-Pereira et al., 2011](#); [Cultrone and Sebastián, 2009](#)), and even as filler aggregate for bituminous mixtures ([Melotti et al., 2013](#)) and in general as binder raw material ([Chaunsali et al., 2018](#); [Hinojosa et al., 2014](#)).

The olive tree is one of the largest sources of biomass in Spain. Olive cultivation has a long tradition in the Mediterranean basin but also in other areas, such as South Africa, some areas of central Chile, California and southeastern Australia. At a global level, in 2016, the area dedicated to the cultivation of olive trees is almost 11,425 million hectares ([Vilar and Pereira, 2016/2017](#)), which indicates the economic importance for the world economy as well as the large amount of biomass waste generated by the processing necessary for the final transformation into olive oil.

Table 1 XRF composition of raw materials

Oxide content (wt%)	Clay	Olive biomass fly ash
SiO ₂	54.40	11.70
Al ₂ O ₃	12.36	2.51
Fe ₂ O ₃	4.58	1.26
CaO	8.76	10.20
MgO	2.46	3.03
MnO	0.03	—
K ₂ O	3.37	42.66
TiO ₂	0.60	0.11
P ₂ O ₅	0.11	2.97
SO ₃	0.68	3.60
ZnO	0.03	—
SrO	0.03	0.04
ZrO ₂	0.03	—
Cl	—	2.26
LOI	12.51	18.54

One of the great challenges that need to be addressed in terms of the valorization of olive biomass ashes is the great variability with respect to the types of plants used for incineration. It is also very seasonal, and this variability has a decisive influence on the chemical composition from the ashes. The chemical composition can also be affected by the transformations suffered in the combustion process at various temperatures to which they are subjected (Vassilev *et al.*, 2010). The mixture of burned biomass can also vary the composition of its ashes depending on the combustion technology used in different incineration plants. Chemically, olive biomass ash is basically composed of mineral oxides such as silica (SiO₂), alumina (Al₂O₃), calcium oxide (CaO) and carbon (C), which are also rich in potassium and unburned organic matter (Alburquerque *et al.*, 2004).

Ceramic materials, both for the mineralogical composition of the natural raw materials used for their shaping and the new minerals formed after their sintering-firing process, have a wide range of chemical and mineralogical composition. For this reason bricks can tolerate presence of different types of waste (Barbieri *et al.*, 2013). In this way part of the clayey raw Materials can be replaced by others that are currently considered industrial wastes. Although various studies have been made of the addition of biomass ash from different sources to building materials, few studies have been carried out using fly ash from the combustion of by-products of olive biomass (de la Casa and Castro, 2014; Eliche-Quesada and Leite-Costa, 2016).

On the other hand, construction sector consumes enormous quantities of raw materials, mainly clays. This new approach, where different percentages of raw materials are substituted by agro-industrial waste, can contribute to sustainability and prevent the depletion of natural resources.

In addition to this, it is noteworthy that the introduction of this type of waste decreases the thermal conductivity of the final material, thus it affects to energy savings. This fact is a key issue for the sustainability for the construction Materials.

This study aims to advance and deepen the recyclability of industrial waste by using it as a component to manufacture construction ceramic materials. Thus, fly ash was used from the combustion of the olive pomace, (a by-product of the olive oil production) as clay substitute raw material in the manufacture of ceramic bricks. The aim is to deepen in the characterization of the olive biomass fly ash (pomace) studying how different additions of waste (10–30 wt%) to clay pastes, as well as the firing temperature (900°C or 1000°C) modify the technological brick properties.

Materials and Methods

The raw materials used for this study were clay and fly ash from biomass of the olive grove (OBFA). The clay comes from Bailén quarries (Jaén, Spain), an industrial core for the manufacture of ceramic bricks, and the biomass ashes from the energy generation power plant of La Loma S.A., located in Villanueva del Arzobispo (Jaén, Spain).

Raw materials were characterized to know their mineralogical composition by means of X-ray diffraction (XRD) and its chemical composition by X-ray fluorescence (XRF). The characteristics of the equipment were the following: an X'Pert Pro MPD X-ray diffractometer from PANalytical and a Philips equipment model PW-2440.

Once the raw materials were characterized, clay and ashes were used to manufacture ceramic bricks with dimensions of 60 × 30 × 10 cm. 8 batches of 10 ceramic pieces each one were formed in a mold to be able to carry out all the technological tests proposed in the study, in which the percentage of ash was changed, replacing pure clay, 0 wt%, 10 wt%, 20 wt% and 30 wt%, and these percentages were made in duplicate in order to study two firing temperatures, 900°C and 1000°C. The batches were named 9C and 1C for the control bricks and the rest of batches with ashes added were named with 1 or 9 OBFAXX, being 1 or 9 the sintering temperatures and XX 10, 20 and 30 the content in weight% of olive biomass fly ash.

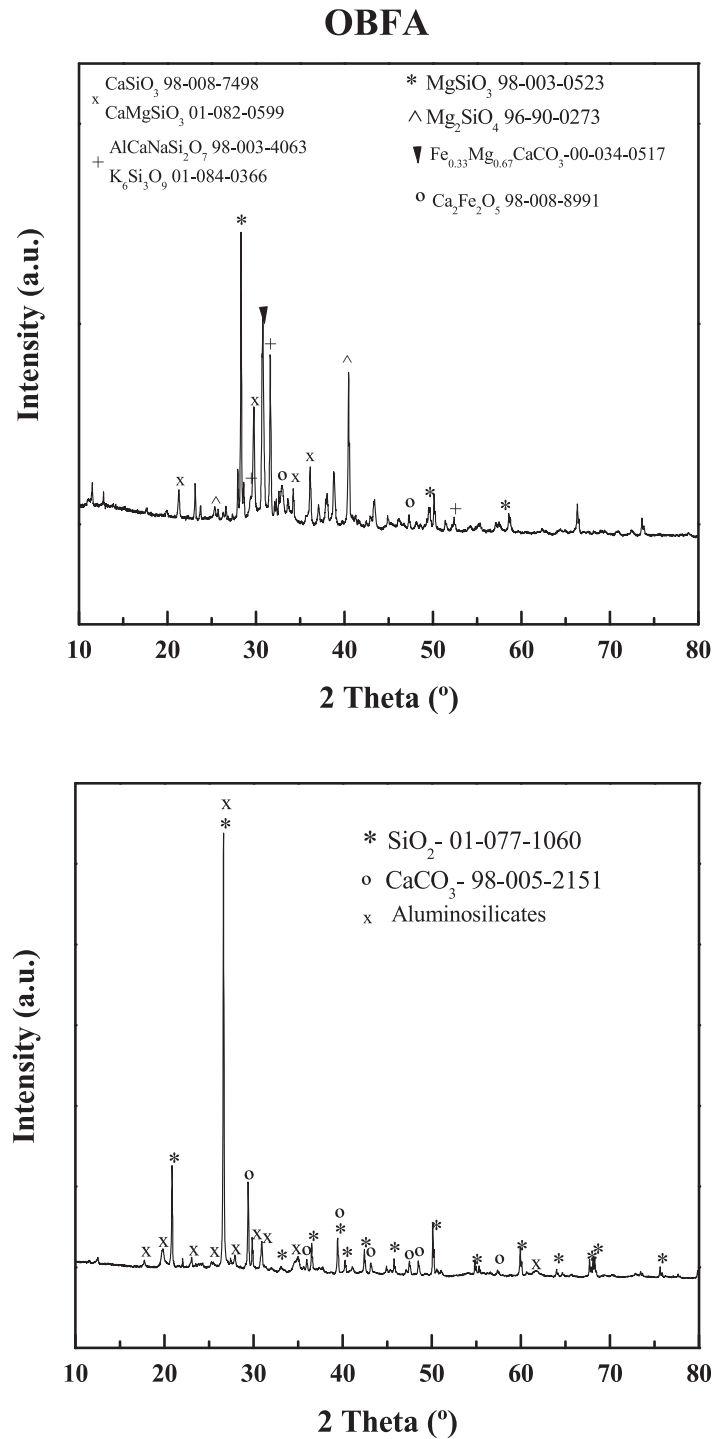


Fig. 1 XRD of olive biomass fly ash and clay.

Once the bricks were formed, and then characterized to determine their technological properties. The suction test was carried out according to the UNE-EN 772-11 standard (Spanish standard UNE-EN 772-11, 2011) and the absorption test with ASTM C373 standard (ASTM C373, 1994). For the measurement of the linear shrinkage, a calliper (accuracy of ± 0.01 mm) was used to determine the length of the ceramic samples before and after the firing process (ASTM C326, 1997).

Bulk density was calculated using the Archimedes method (ASTM C373, 1994). The tests of compressive strength were carried out according to the standard UNE-EN 772-1 (Spanish standard UNE EN 772-1, 2011) in a laboratory press MTS 810 Material Testing Systems. Prior to the breakage of the ceramic samples, the average surface of the two faces was calculated and the maximum load

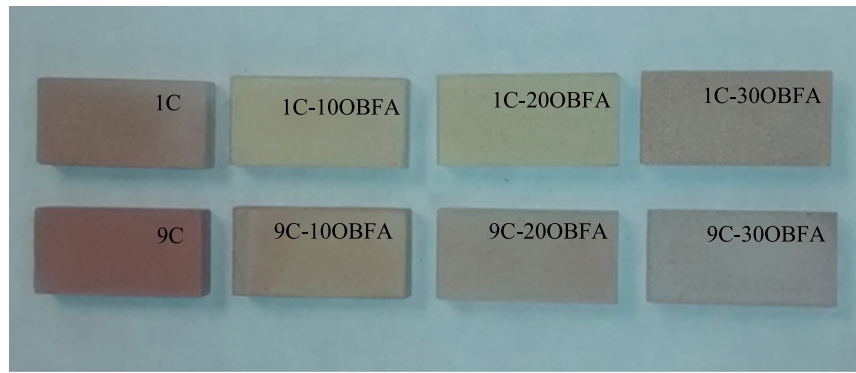


Fig. 2 Pictures of control bricks and bricks containing (10–30 wt%) olive biomass fly ash fired at 900 and 1000°C.

Table 2 Linear shrinkage, loss on ignition and bulk density of clay bricks containing different proportions of olive biomass fly ash and sintered at 900 and 1000°C

	Waste content (wt%)	Sintering temperature (°C)	Linear shrinkage (%)	Loss on ignition (wt%)	Bulk density (kg/m ³)
9C	0	900	-0.518 ± 0.10	9.24 ± 0.09	1839 ± 4
9CFA10	10	900	-0.898 ± 0.072	12.54 ± 0.15	1781 ± 18
9CFA20	20	900	-1.622 ± 0.110	13.81 ± 0.15	1709 ± 8
9CFA30	30	900	-2.056 ± 0.108	14.62 ± 0.23	1635 ± 12
1C	0	1000	-0.379 ± 0.055	12.10 ± 0.29	1865 ± 5
1CFA10	10	1000	-0.774 ± 0.092	13.18 ± 0.10	1806 ± 9
1CFA20	20	1000	-1.290 ± 0.078	14.63 ± 0.10	1731 ± 6
1CFA30	30	1000	-1.805 ± 0.060	16.64 ± 0.38	1633 ± 10

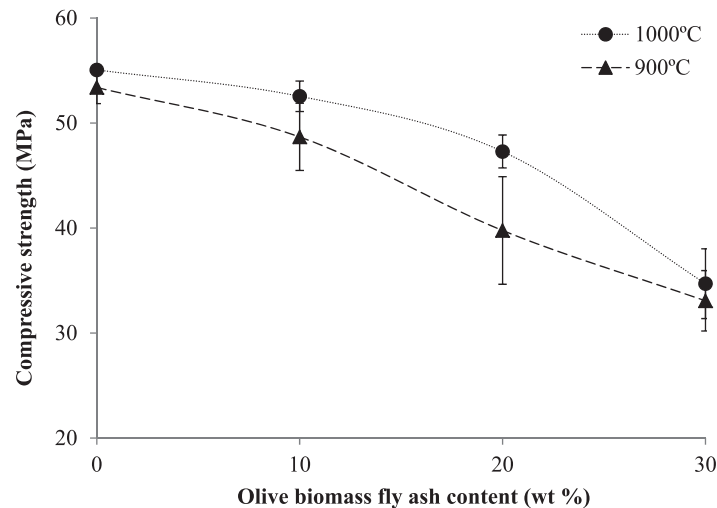


Fig. 3 Average values of compressive strength as a function of the percentage of olive biomass fly ash content.

reached between the average surfaces was divided and expressed with an accuracy of 0.1 MPa. Thermal conductivity of the bricks fired at 1000°C has been evaluated with a C-ThermTCi Analyzer with a universal sensor from Mathis Instruments Ltd.

Finally, the microstructure of the samples, once firing were studied using a High-Resolution Scanning Electron Microscope (HR-SEM) JEOL model SM 840, equipped with a device for measuring X-ray spectroscopy of dispersive energies (EDS) at 20 kV. In order to perform the EDS analysis on the samples, they were deposited with a carbon layer using a JEOL ion sputtering device, model JFC 1100.

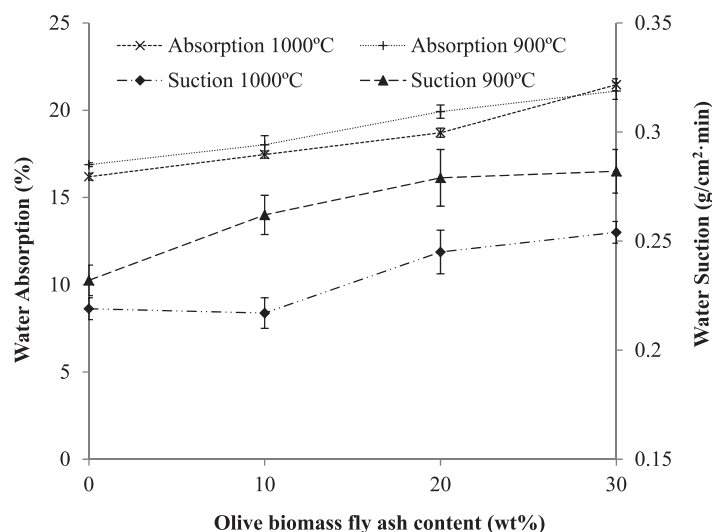


Fig. 4 Water absorption and suction of ceramic bricks as a function of the olive biomass fly ash content at the two firing temperatures evaluated, 900 and 1000°C.

Results and Discussion

Raw Materials Characterization

Table 1 shows the values of the chemical composition, expressed in oxide form found in the raw materials by means of XRF. Clay has a chemical composition common to clays used in the manufacture of ceramic bricks with a preponderance of minerals rich in silica and alumina. Clay also has high values of calcium oxides in their composition, due to the presence of calcium carbonates (calcite). Regarding the chemical composition of olive biomass fly ash are rich mainly in potassium because it is the main component of pomace used as fuel. It has significant amounts exceeding 10 wt% of silica and calcium oxide, with amounts greater than 2% in SO_3 , MgO , P_2O_5 and Al_2O_3 . The high content of flux oxides, such as K_2O and oxides of auxiliary fluxes, such as CaO and MgO in the waste, fluxing facilitates firing at a lower temperature and introduces necessary elements for the formation of new phases.

Loss of ignition loss at 950°C of both the clay and the olive biomass fly ash may be due to a high content of organic matter (2.3 and 4.7 wt%), and mainly of carbonates (7.4 and 31.2 wt%) as well as the decomposition of inorganic compounds, such as SO_3 (0.7 and 1.3 wt%).

As regards the mineralogical composition of the clay (**Fig. 1**), associated minerals (quartz and calcite) and clay minerals as aluminosilicates are identified.

In the X-ray diffraction diagram of olive biomass fly ash (**Fig. 1**) it can be observed that there are hardly any crystalline potassium species. Considering that according to the data of XRF (**Table 1**) almost 43 wt% of the ash is composed of potassium oxide, it could indicate that potassium is forming part of amorphous species that are highly reactive and that will react with clay to form new mineralogical species to be sintered, acting mainly as fluxes and decisively influencing the porosity of the pieces. The crystalline mineralogical species observed in the XRD pattern are quite diverse, such as calcium silicates (CaSiO_3), magnesium (MgSiO_3 and Mg_2SiO_4) and calcium-magnesium (CaMgSiO_3), aluminum and potassium ($\text{K}_6\text{Si}_3\text{O}_9$), as well as species containing elements such as iron ($\text{Ca}_2\text{Fe}_2\text{O}_5$).

Characterization of Clay-Olive Biomass Fly Ash Bricks

During the firing process the dimensions and color variations take place in the bricks containing olive biomass fly ash. As can be seen in **Fig. 2**, bricks change color both by adding different amounts of ashes and with the firing temperature, having a more yellowish color at firing temperatures of 1000°C. In the bricks no defects were observed as cracks, the defect known as black heart due to incomplete combustion of organic matter or efflorescences after the firing process. Different technological properties of the fly ash bricks of olive and clay biomass compared to the control brick (containing only clay) were studied.

The linear shrinkage of the bricks reflects the expansion/contraction behavior during the thermal firing treatment. In **Table 2** it can be seen that the linear shrinkage of the control bricks fired at 900 and 1000°C was -0.52% and -0.38% , respectively. The addition of increasing amounts of biomass fly ash produces an increase in linear shrinkage. Therefore, the control samples, such as the samples containing olive biomass fly ash, expand slightly during the firing process. This expansion could be due to the gases released during the firing process due to combustion of the organic matter and the decomposition of the carbonates contained both in the clay and in the residue (fly ash).

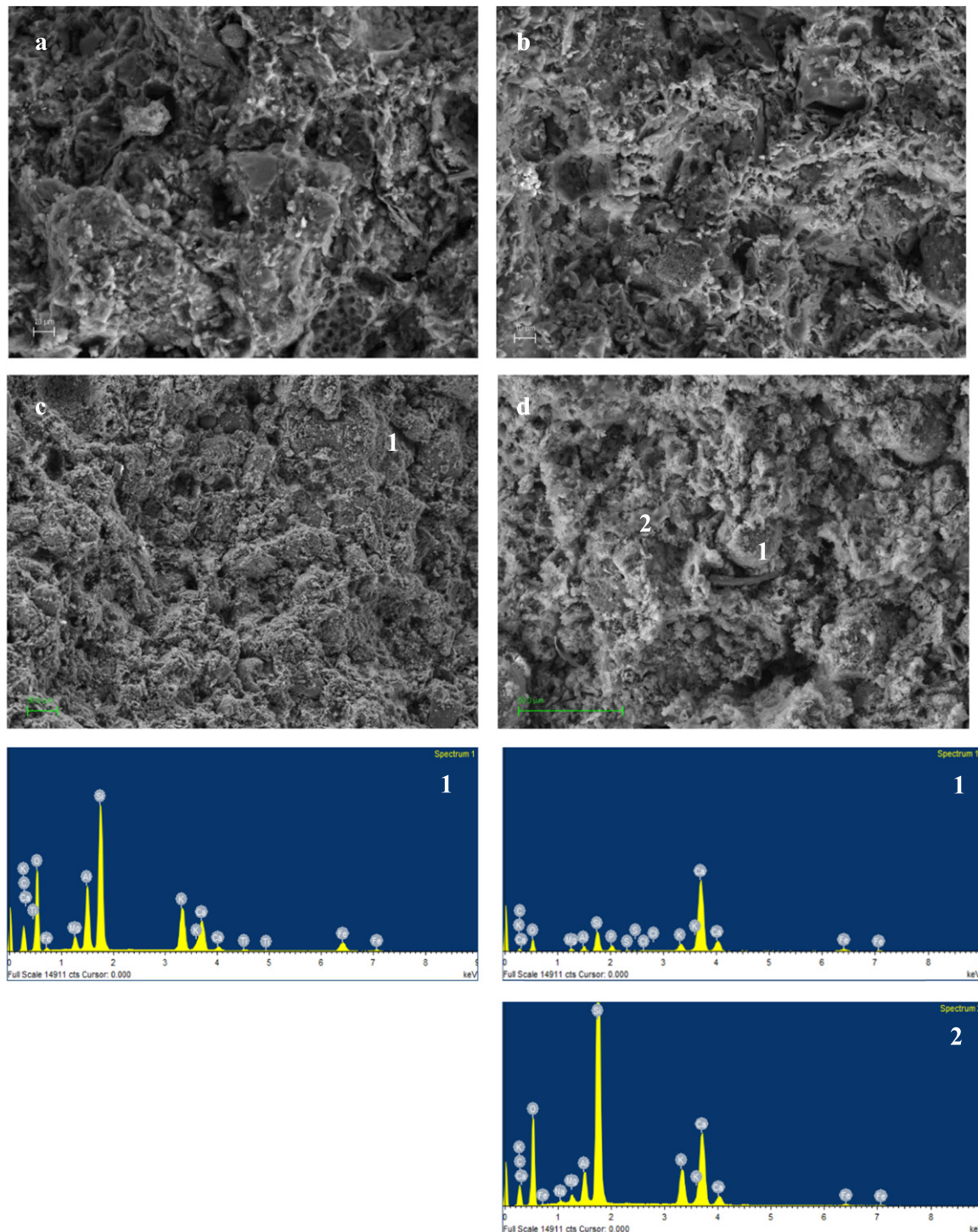


Fig. 5 SEM micrography and EDS analysis of ceramic samples: (a) Clay at 900°C, (b) clay at 1000°C, (c) 9CFA10, (d) 9CFA30, (e) 1CFA10, and (f) 1CFA30.

Clay control bricks have the lowest loss on ignition when firing at 900 and 1000°C (9.2% and 13.2%, respectively). The addition of fly ash increased the loss of ignition to greater addition of waste and higher sintering temperature. The increase observed in the weight loss on ignition could be due to the greater amount of organic matter and the higher content of carbonates present in the olive biomass fly ash.

Fig. 3 shows the variation of the compressive strength of the ceramic samples manufactured as a function of the percentage by weight of fly ash added to the clay at the firing of 900 and 1000°C. The mechanical strength depends on the

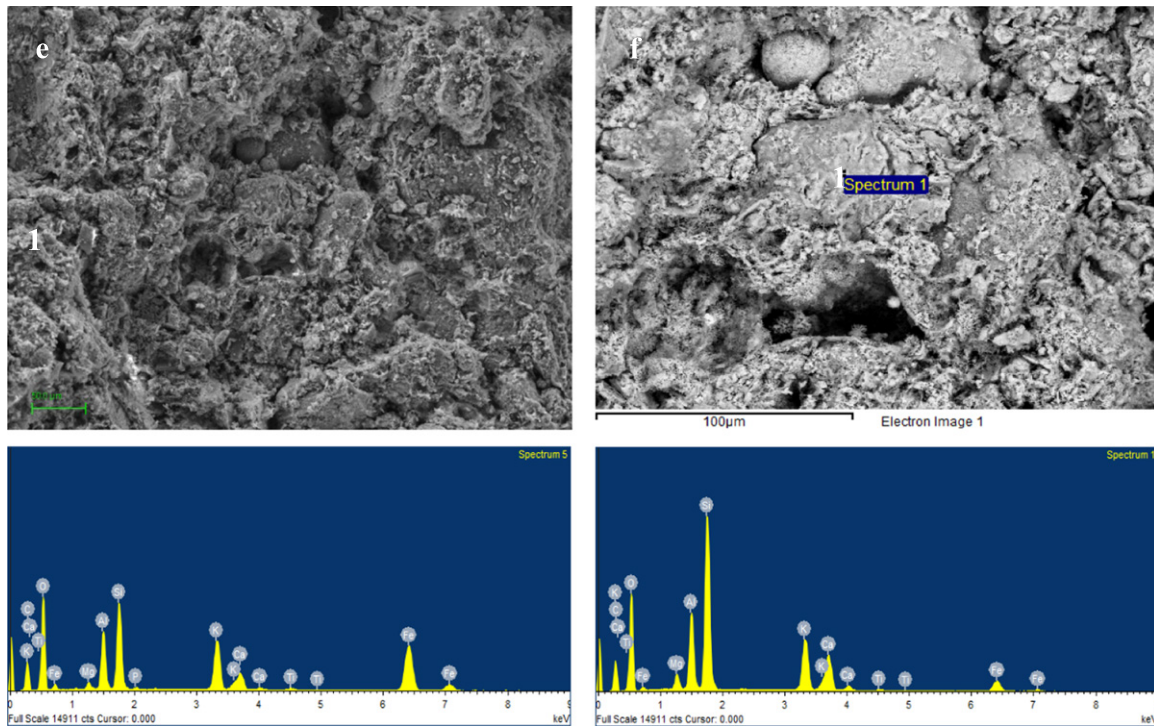


Fig. 5 Continued

microstructure of the pieces, such as porosity, microcracks and also on the phase changes produced during the firing process (Vieira *et al.*, 2005). The substitution of clay by ashes produces a decrease in the compressive strength at both firing temperatures. This loss in the mechanical properties as increasing amounts of fly ash residue in the samples could be due to the increase in porosity, as indicated by the decrease in bulk density (Table 2). Pores and other imperfections act as concentrators of tensions, decreasing the resistance to compressive strength. As for the influence of the firing temperature, an increase in the mechanical resistance of the ceramic bricks firing at 1000°C is observed due to the greater degree of densification achieved. Ceramic bricks fired at 1000°C present higher apparent density values. The densification is achieved by the viscous flow of a sufficient amount of liquid phase to fill the spaces occupied by the pores between the solid grains, due to the tensile forces of the surface. During cooling, the molten phase solidifies and the vitreous matrix favors the formation of a more resistant and dense structure (Eliche-Quesada *et al.*, 2017b). The compressive strength value for pure clay samples at 900°C is 53.39 MPa and from this value, increasing the ash replacing percentage, the values of mechanical resistance are gradually decreasing, reaching the minimum value, 33.07 MPa for a 30 wt% substitution, which means a fall of almost 40%. For the case of pieces fired at 1000°C, the reduction from 55.06 MPa for pure clay to the minimum value, those pieces containing 30 wt% ash, 34.70 MPa, which means a drop of 37%. This lower fall of the mechanical strength values indicates that the degree of sintering and therefore of densification, reached for the pieces at 1000°C is higher than those of 900°C. On the other hand, the development of crystalline phases at higher temperatures could lead to the production of products with greater mechanical resistance, such as tridymite, the intermediate temperature phase of silica. According to the regulations applicable to ceramic construction bricks (Annex, 2008), the values reached by ceramic bricks must be at least 9.8 MPa. So all the series obtained in this study meet this requirement.

In Fig. 4, water absorption and water suction of the firing samples fired at 900 and 1000°C respectively can be observed. The water absorption is related to the open porosity developed during the firing process. It decreases with increasing sintering temperature from 900 to 1000°C, likewise increases in both series as the fly ash increases. The decrease in the water absorption with the firing temperature has been observed previously by other authors (Lessar *et al.*, 2017). This decrease is related to the formation of a greater quantity of vitreous phase at a higher firing temperature, obtaining a denser microstructure that closes the pores and their interconnections. As pointed by Romero *et al.* (2008), the generation of liquid or amorphous phase causes the particles to approach each other and generates a smaller volume of pores. Consequently the porosity must decrease. Another aspect to take into account is the presence of fluxing agents such as potassium, magnesium, sodium and calcium. According to the chemical composition of the fly ash (Table 1), the sum of flux oxides and auxiliary flux oxides in the ash is almost 56%. So increasing its content in the clay the structure should be denser, with less open porosity. However, the observed effect is opposite, since there is an increase in water absorption and a decrease in bulk density. This could be due to the fact that at both sintering temperatures, the viscosity of the liquid phase allows the decomposition of the gas phases. The waste, fly ash, presents a higher

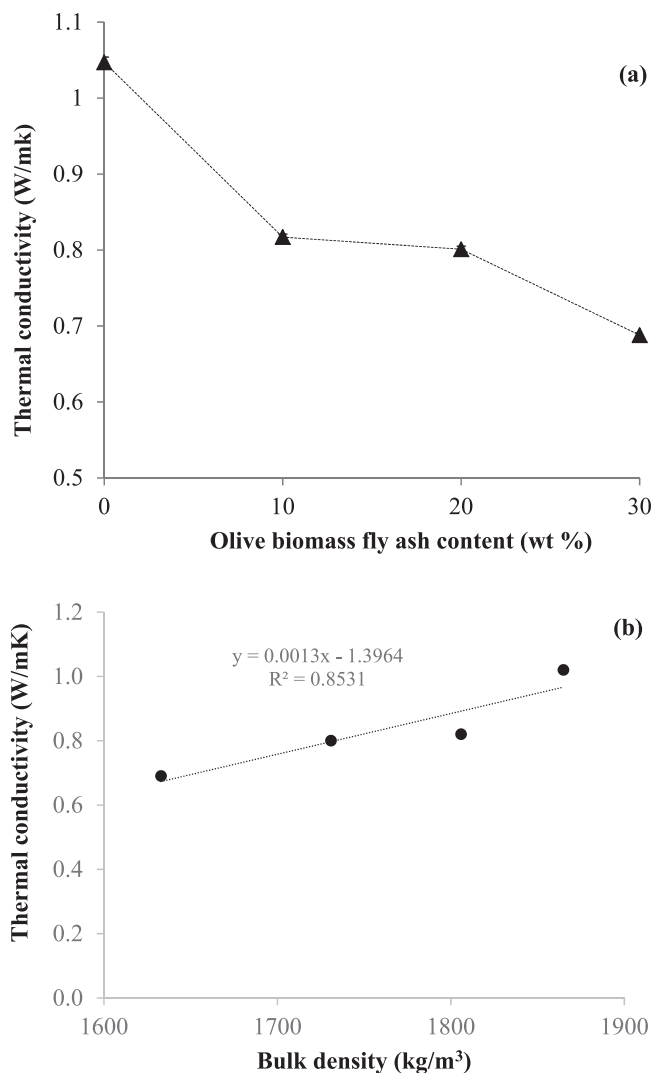


Fig. 6 (a) Thermal conductivity of the bricks fired at 1000°C and (b) Relationship between the thermal conductivity and the bulk density of the ceramic pieces.

content in organic matter and, especially, of calcite greater than in the clay, generating CO_2 during the firing process that remains trapped, generating porosity in the pieces.

The suction of water is related to the interconnected surface porosity and its value depends on the union of the brick and mortar and the water retention of the mortar. Low water suction values are preferred. This would indicate that the brick does not absorb a large amount of water. It leaves enough mortar for the mortar to harden at a speed that allows the correct adhesion of the bricks with the mortar. As can be seen in Fig. 5, the water suction for the control bricks fired at 900 and 1000°C was 0.23 and 0.22 g/cm² min respectively. The water suction is slightly increased when larger amounts of waste fly ash are added. This increase is being more pronounced in the bricks fired at 900°C. Thus the water suction increases from 0.26 to 0.28 g/cm² min with the addition of 10 and 30 wt% of OBFA in the bricks fired at 900°C and from 0.22 to 0.25 g/cm² min for the bricks fired at 1000°C. The increase in water suction could be due to an increase in interconnected surface porosity at higher fly ash content and lower sintering temperature due to pore growth, both in number and size, caused by the largest amount of organic matter and carbonates in the waste. The regulations applicable to this test mark the maximum admissible value for ceramic pieces 0.45 g/cm² min. None of the ceramic clay bricks containing waste exceed the limit value. However, when presenting values higher than 0.15 g/cm² min, the bricks should be moistened before they are placed to achieve an adequate bond between the brick and the mortar.

The microstructure and porosity of the control bricks and bricks containing olive biomass fly ash after the firing process were studied by SEM-EDS. Fig. 5 shows some details of the fracture surface of different ceramic pieces studied, control pieces and pieces containing 10 and 30 wt% of OBFA fired at 900 and 1000°C. In the micrographs a morphological and compositional heterogeneity of the samples as well as the present porosity can be appreciated. It is known that the morphology of the pores influences the mechanical properties exhibited by the materials. In this context pores with angled shape act as stress concentrators, thus

reducing their mechanical resistance. Concerning the influence of firing temperature, a greater concentration of angular pores can be observed in the samples fired at 900°C. However, as the firing temperature increases up to 1000°C sintering increases and it is promoted that a greater proportion of liquid phase is formed. This effect generates greater closed porosity and modifying the shape of the pores, observing more rounded pores.

In relation to the influence of the residue content, it is observed at the two firing temperatures, a low degree of densification, lower at lower firing temperature. It is obvious the presence of open porosity, the higher is the higher is the incorporation of residue. Open porosity is largely responsible for the decrease in compressive strength as the percentage of ash replaced by clay increases. Some areas were analyzed by EDS microanalysis, showing that there are zones with the presence of the typical minerals of the ceramic materials, such as aluminosilicates. It is confirmed by the presence of some cations, for instance Ca, Mg, K and Fe (Fig. 5(c-f)), which agrees with the elemental analysis found by XRF (Table 1) and the mineralogy by XRD (Fig. 1). The micro-analysis also shows areas where the presence of fly ash added, as in Fig. 5(d and f) where there is a strong presence of K and Ca. These components are identified coming from the ashes.

The thermal conductivity of the bricks fired at 1000°C has been determined. Thermal conductivity is an important property, since an increase in the thermal insulation of bricks can lead to significant energy savings in buildings. The thermal conductivity of the control bricks was 1.05 W/mK (Fig. 6(a)) reducing the value of thermal conductivity to 0.82, 0.80 and 0.69 W/mK with the addition of 10, 20 and 30 wt% of olive biomass fly ash. This value indicates that the incorporation of 10, 20 and 30 wt% of ashes produces a decrease of 21.9%, 23.8% and 34.3%, respectively. So, the use of bricks incorporating fly ash as structural elements in the building would produce significant energy savings. A linear relationship between thermal conductivity and the bulk density of the fired ceramic pieces at 1000°C has been found (Fig. 6(b)). The regression analysis shows a coefficient of $R = 0.8531$.

Conclusions

This study has demonstrated the feasibility of using fly ash from olive groves as a substitute for raw material for the manufacture of ceramic bricks, with similar characteristics in quality to those made with pure clay, which served as control for the study. Ceramic bricks were produced by adding percentages of ash substitution between 0 and 30 wt% and fired at two different temperatures: 900 and 1000°C. The following conclusions of this study can be established, as follows:

Compressive strength of the ceramic brick decreased with increasing replacement of clay by fly ash. This occurs due to the increased porosity generated in the pieces during firing, as indicated by the decrease in bulk density. Ceramic bricks fired at 1000°C present bulk density values higher than 900°C and therefore better mechanical performances. On the other hand water suction is slightly increased when larger amounts of olive biomass fly ash are added.

From the microstructural point of view, the morphology of the pores influences the mechanical properties exhibited by the materials. Pores with an angular shape act as tension concentrators, thus reducing their mechanical resistance. The fired samples at 1000°C had a lower concentration of angular pores of this type than those of 900°C. It can be concluded that also at 1000°C the samples had a greater proportion of liquid phase, generating greater closed porosity, increasing the bulk density and increasing the mechanical resistance.

Finally, the thermal conductivity of the control bricks was 1.05 W/mK and the samples with 30 wt% of fly ash fired at 1000°C showed a 34.3% reduction, which would produce an important energy saving in the studied samples.

Acknowledgments

This work has been funded by the Project "Valuation of various types of ash for the obtaining of new sustainable ceramic materials" (UJA2014/06/13), Own Plan University of Jaén, sponsored by Caja Rural of Jaén. The authors thank to the company "Energía de la Loma S.A." for supplying the ashes. Technical and human support provided by CICT of Universidad de Jaén (UJA, MINECO, Junta de Andalucía, FEDER) is gratefully acknowledged.

See also: Biochar Production From Biomass Waste-Derived Material. Co-Firing of Biomass to Reduce CO₂ Emission. Large Biomass Burners for Fuel Switch in Existing Fossil Fuel Based Plants. Renewable Biomass: A Candidate for Mitigating Global Warming. Synthesis of High Grade Activated Carbons From Waste Biomass. Technology for Producing Briquettes From Wet Biomass. The Nexus Between Biomass – Footprint and Sustainable Development. Traditional Biomass: A Replacement for Petro-Fuels

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Vegetable Oil-Based Polymeric Materials: Synthesis, Properties, and Applications

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Introduction

Crude oil has been the source of chemicals often used as monomers to form commercial polymers for many decades. Since 1907, when the first synthetic polymer (Bakelite) was prepared by Leo Baekeland, great advancements have been made in the polymer field. In spite of its widespread use, the finite nature of crude oil poses a fundamental challenge for its continuous use. It has become obvious that mankind needs alternative resources to attain a sustainable lifestyle in industrialized countries (Rudolph, 2018). In that context, vegetable oils offer a renewable feedstock that can be used as a substitute of petroleum-based chemicals in various applications, including transportation fuels and polymers.

Vegetable oils are easily extracted from plants, hence their abundance and renewable nature. Different plants naturally produce different oils, with a different chemical structure and different properties. Therefore, a great variety of materials can be prepared from vegetable oils. Despite the great variability found in vegetable oils from different plants, the vegetable oil produced by any given plant species is very consistent, making vegetable oils a very reliable renewable resource for the preparation of polymers. In this text, the term “vegetable oil” is used in reference to triglycerides. Triglyceride oils have been heavily investigated as the source of various monomers for the preparation of bio-based polymers. Bio-based polymers are defined as any type of polymeric substance produced from renewable resources of biological origin. Fig. 1 presents the structure of a triglyceride, as well as other molecules directly derived from it.

The use of renewable resources in replacement of petroleum is justified by the need of reducing carbon footprint. Indeed, when a renewable raw material, such as vegetable oils, is employed in the fabrication of plant-based biopolymers, a neutral carbon footprint is achieved since the plants harness carbon from the atmosphere in the form of CO₂ in order to produce the oils, which are then converted into polymers and composites. This contrasts with the free “generation” of carbon when petroleum-based monomers are used instead.

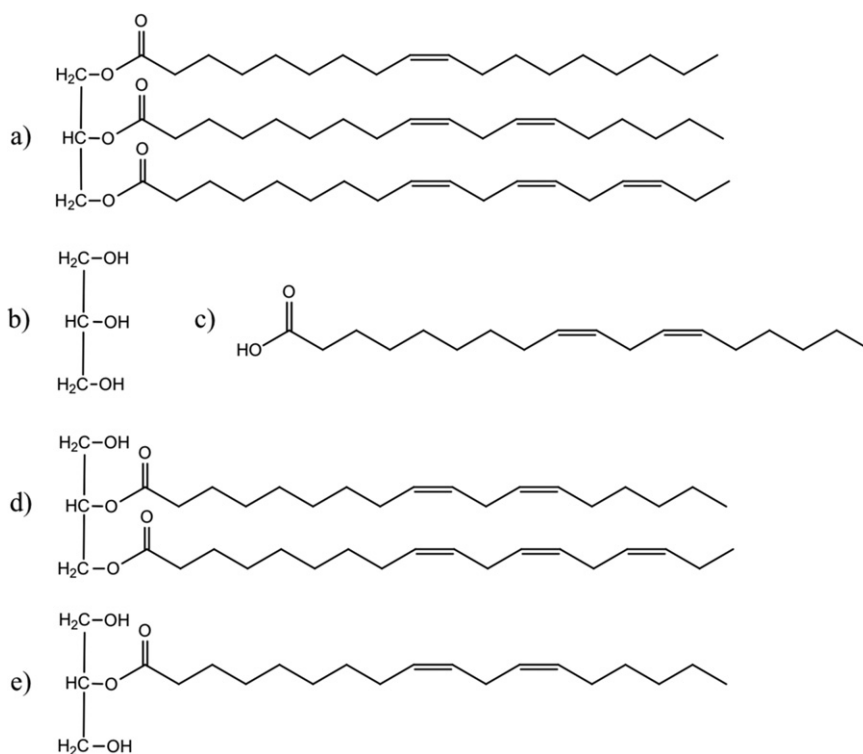


Fig. 1 Chemical structure of (a) soybean oil triglyceride, (b) glycerol, (c) linoleic acid, an example of a fatty acid, (d) soybean oil half ester, (e) soybean oil monoglyceride.

In this text, the major classes of vegetable oil-based polymers are discussed. Emphasis is given to polyolefins from unmodified oils, polyurethanes, and polymers from maleated oils and half-esters. Other approaches, such as the ring-opening of caprolactones, olefin metathesis, and polyester resins are also briefly covered. The reinforcement of these systems with natural and inorganic materials to generate bio-based composites of relevant properties is systematically addressed before concluding with a perspective of current commercial applications of vegetable oil-based polymers and composites.

Vegetable Oil-Based Polymers

Polyolefins

Within the last decade, various vegetable oil-based co-polymers with a range of thermal and mechanical properties were prepared from the free radical or the cationic co-polymerization of triglycerides with reactive petroleum-based comonomers. In such systems, the carbon-carbon double bonds constitute reactive sites, which can be enhanced when they are conjugated (Fig. 2; Xia *et al.*, 2013).

The low reactivity of regular vegetable oils towards free radical or cationic polymerizations limit their direct use (without chemical modification) for the preparation of bio-based polymers. Drying oils have been historically used in paints and coatings. The spontaneous auto-oxidation of such oils under air leads to a crosslinked polymer network with interesting properties. Following a similar approach, co-polymers containing vegetable oils can be prepared by free radical polymerization. For example, 30–65 wt% of unmodified linseed oil has been free radically co-polymerized with styrene (ST), and divinylbenzene (DVB) to form thermosetting polymers with mechanical properties that vary depending on the oil content. Along the same lines, 30–70 wt% of unmodified tung oil was copolymerized with ST and DVB in the absence of free radical initiators to yield materials ranging from elastomers to rigid polymers, with glass transition temperatures (T_g) of -2 to 116°C and crosslink densities of 1.0×10^3 – 2.5×10^4 mol/m³. The monomer mixture was simply heated at 85 – 160°C . It was found that the addition of catalytic amounts of Co, Ca, and Zr salts increases the thermal polymerization rate and results in thermosets with improved properties (Xia *et al.*, 2013). Indeed, tung oil consists of 84% of α -eleostearic acid (a naturally conjugated fatty acid), totaling an average of 9.0 carbon-carbon double bonds per triglyceride, and making tung oil readily polymerizable under mild conditions.

Conjugated triglycerides are more reactive towards free radical polymerization than non-conjugated triglycerides. Therefore, conjugated oils are most commonly used for the preparation of vegetable oil-based polymers. The conjugation of carbon-carbon double bonds in triglycerides can be easily accomplished with the use of a rhodium catalyst (Quirino and Larock, 2012a). Translucent thermosets have been prepared from the bulk free radical polymerization of 30–75 wt% of conjugated linseed oil (CLO), acrylonitrile (AN), and DVB. The thermal, physical, and mechanical properties of these materials decrease with increases in the vegetable oil content. Also, the percentage of unreacted oil in the final polymer ranges from 4 wt% to 39 wt% and is directly dependent on the amount of oil employed. Several other conjugated oils have been used for the preparation of bio-based polymers using a similar approach, however when an oil that is less reactive than TUN is used, a microphase separation is typically obtained (Xia *et al.*, 2013).

Vegetable oil-based thermosetting materials can also be obtained via cationic polymerization of triglycerides in the presence of other reactive co-monomers. Similarly to the free radical polymerization, strong materials with room temperature storage modulus of ~ 2 GPa can be obtained by the cationic copolymerization of 50–55 wt% of TUN with DVB. Blends of TUN and other oils with a lower degree of unsaturation, such as soybean oil (SOY), can be used to achieve desired polymerization rates. Poor miscibility between the oil and the cationic initiator (BF_3) results in micro-phase separation with distinctly different crosslink densities in different parts of the bulk copolymer. Modification of BF_3 with less reactive oils helps to ensure formation of more homogeneous vegetable oil-based polymers. Other oils used for cationic polymerization include regular and conjugated corn oils, olive, peanut, sesame, canola, grapeseed, sunflower, safflower, walnut, and linseed oils. The cationic polymerization of soybean oil with 4-vinylphenyl boronic acid or 4-trimethylsilylstyrene afforded boron- or silicon-containing thermosets with flame retardant properties. Also, uniform bio-based cationic polymers have been obtained from the copolymerization of Dilulin and ML189 (pericyclic products of linseed oil and cyclopentadiene) with dicyclopentadiene (Xia *et al.*, 2013).

More recently, less common oils have been used as monomers for the preparation of bio-based polymers. For example, the oil extracted from the seeds of *Vernonia galamensis* was directly polymerized using fluorosulfonic acid as a catalyst. The resulting polymer ranged from a viscous oil to an insoluble resin, depending on the amount of catalyst used (Biswas *et al.*, 2014). A variety of plant oils were also polymerized using triazolidinedione, yielding polymers with gel times in the 2–8 min range (Türünç, 2015). Along the same lines, the oil of the *Ricinodendron heudelotii* plant was also photopolymerized with and without a photoinitiator under UV radiation (Assanvo *et al.*, 2015).

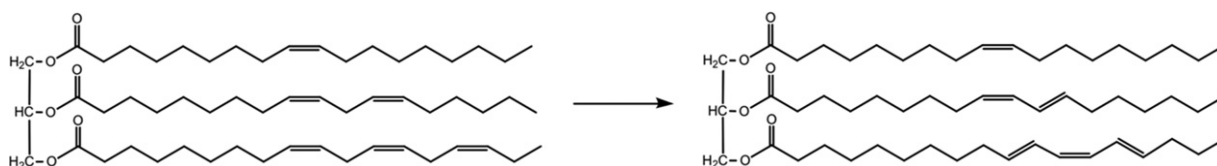


Fig. 2 Simplified reaction scheme showing the conjugation of carbon-carbon double bonds in soybean oil.

Polyurethanes (PUs)

Due to its natural hydroxyl groups, castor oil has been widely used in the synthesis of vegetable oil-based polyurethanes. Indeed, castor oil (**Fig. 3**) is formed of approximately 90% of ricinoleic acid. Thermosetting PUs with good thermo-mechanical and swelling properties have been obtained from the reaction of castor oil with diisocyanates, such as toluene diisocyanate, isophorone diisocyanate, and hexamethylene diisocyanate. Other approaches involve blending castor oil and poly(ethylene glycol) during the synthesis of PUs. Such materials have shown potential for use as biomedical implants and for tissue engineering (Xia *et al.*, 2013).

The carbon-carbon double bonds in other vegetable oils can be converted into hydroxyl groups, therefore providing a great variety of renewable polyols for the preparation of bio-based PUs. Following that approach, PUs with different crosslink densities have been prepared from rapeseed, palm, canola, soybean, sunflower, corn, and linseed oils. Soybean oil-based polyols with hydroxyl numbers ranging from 82 mg KOH/g to 225 mg KOH/g have been used in the preparation of PUs ranging from brittle to rubbery. In the preparation of polyols from epoxidized vegetable oils, different nucleophiles, such as lactic acid, diethylene glycol, hexamethylene glycol, methanol, glycerol, and 1,2-propanediol can be used to carry-out the ring-opening reaction (**Fig. 4**; Xia *et al.*, 2013).

A polyol from carbonated soybean oil (**Fig. 5**) has been obtained by a ring-opening reaction with ethanolamine. This polyol was condensed with polyisocyanates to generate thermal and electrical insulating PUs. Another approach towards vegetable oil-based polyols consists in the hydroformylation of carbon-carbon double bonds, resulting in aldehydes that can be subsequently reduced to primary alcohols. These polyols have been reacted with MDI to obtain polyurethane thermosets with different crosslink densities. The ozonolysis of canola oil has led to polyols used for the preparation of PUs with 1,7-heptamethylene diisocyanate (Xia *et al.*, 2013).

Waterborne anionic polyurethane dispersions (PUDs) have been prepared by dispersing a PU formed from the reaction of soybean oil polyol and isophorone diisocyanate with deprotonated dimethylolpropionic acid (DMPA). The Young's modulus of corresponding dry films ranged from 8 to 720 MPa, while the tensile strength ranged from 4.2 to 21.5 MPa, and the elongation at break varied from 16% to 280%. In a similar approach, cationic PUDs were obtained simply by replacing DMPA with protonated

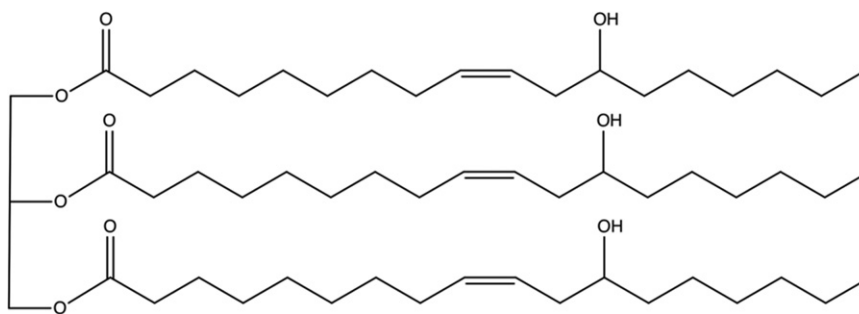


Fig. 3 Chemical structure of castor oil.

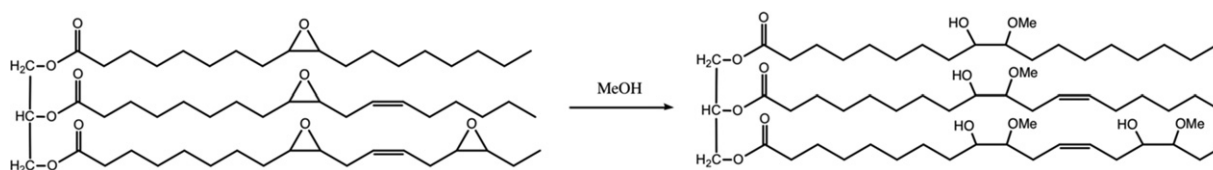


Fig. 4 Simplified reaction scheme of the ring-opening of epoxidized soybean oil with methanol.

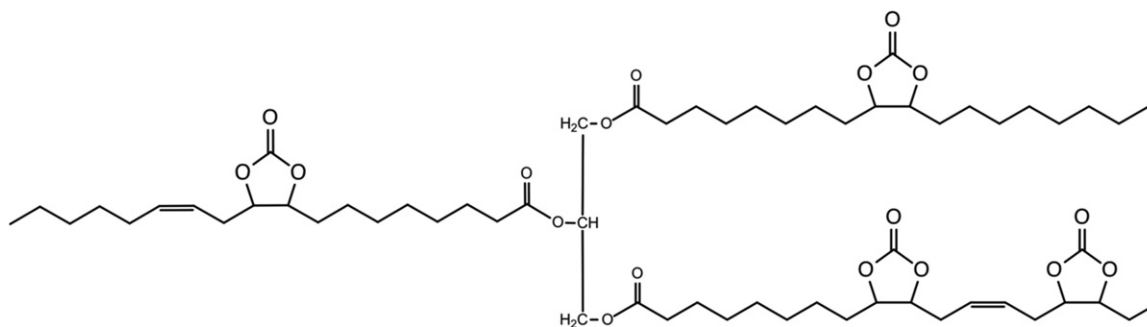


Fig. 5 Chemical structure of carbonated soybean oil.

N-methyl diethanol amine (MDEA). PU-silica nanocomposite dispersions were prepared by grafting silica nanoparticles to the PU chains, resulting in an overall improvement of thermal and mechanical properties (Xia *et al.*, 2013).

Alternative vegetable oils, such as jatropha oil, were recently used for the preparation of polyols through epoxidation followed by oxirane ring-opening. The polyol obtained was reacted with isophorone diisocyanate and DMPA to form an aqueous polyurethane dispersion (Saalah *et al.*, 2017). In a differently approach, non-isocyanate PUs can be prepared from cyclic carbonates derived from glycerol, which forms the backbone of triglyceride oils. Glycerol can be easily converted into glycerol carbonate. A variety of cyclic carbonates have been prepared from glycerol and subsequently reacted with a range of amines to yield polyhydroxyurethanes through ring-opening polymerization (Johns *et al.*, 2016).

Acrylated/Maleated Oils and Half Esters

The carbon-carbon double bonds in unsaturated vegetable oils can be chemically modified for the incorporation of acrylates. Acrylated epoxidized soybean oil (AESO) has been copolymerized with ST, resulting in structural thermosetting materials. Likewise, acrylated epoxidized methyl oleate has been prepared by the same method and used in the preparation of a bio-based polymer by free radical emulsion polymerization. An alternate route for the preparation of acrylated triglycerides consists in the oxidation of unsaturated vegetable oils with singlet oxygen to form hydroperoxides, which can then be converted into secondary allylic alcohols, followed by further reduction of residual carbon-carbon double bonds. These alcohols can be easily functionalized with acrylate groups, which serve as monomers for free radical polymerization, resulting in materials with similar properties to those of AESO-based materials. Maleated epoxidized soybean oil (MAESO) is obtained by the reaction of AESO with maleic anhydride (MA). When MAESO is copolymerized with ST, higher crosslink densities, T_g 's, and storage moduli than the corresponding AESO-based polymers are obtained (Xia *et al.*, 2013).

Besides modification of the carbon-carbon double bonds, chemical changes involving the ester groups of vegetable oils is another viable method for the preparation of triglyceride-based polymers. A series of rigid thermosetting polymers with T_g of 135°C and storage modulus of 0.92 GPa at 35°C have been prepared via bulk copolymerization of soybean oil monoglyceride (SOMG – Fig. 1) maleates with ST. An increase in the properties of the SOMG maleate-ST polymers has been observed when neopentyl glycol and bisphenol A were added to SOMG prior to the reaction with MA. The same methodology has been applied to linseed, and castor oils, with improved properties (Xia *et al.*, 2013). On a different approach, tung oil was used to synthesize a co-ester containing acrylates and maleates. This co-ester was copolymerized with ST to produce a rigid material with a tensile strength of 36.3 MPa and a Young's modulus of 1.70 GPa (Liu *et al.*, 2016).

Other Approaches

In previous sections, polyurethanes, polyolefins, maleated oils and half esters synthesis methods and properties were discussed. In this section, ring-opening metathesis polymerization (ROMP), acyclic diene metathesis (ADMET) polymerization, mechanisms involving polyesters such as condensation polymerization, polyamides, and other commonly utilized polymerization methods will be discussed. Olefin metathesis methods originate back to the 1960s and has hence forth paved the way for the currently utilized, highly reactive, metal alkylidene catalysts. These carbene complexes of transition metals are reactive enough to interact with most functional groups, while maintaining stability when exposed to air or moisture. These catalysts are crucial in the following two polymerization mechanisms, ROMP and ADMET.

Monomers applicable for ROMP mechanisms are strained, unsaturated cyclic hydrocarbons such as norbornene groups (Fig. 6). These strained rings are catalyzed with a ruthenium carbene catalyst to break the carbon-carbon double bonds. Castor oil, a vegetable oil containing approximately 85%–90% ricinoleic acid, polymerized with bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride, produces a functionalized bicyclic castor oil derivative (BCO). The BCO derivative and cyclooctene can be co-polymerized to yield a co-polymer with elastomeric properties. BCO, as do other vegetable oil derivatives, exhibit high viscous characteristics due to their low glass transition temperatures (T_g 's) (Henna and Larock, 2007). Which inherently creates a co-polymer weight percentage threshold for the polymerization to materialize. As expected, there is a direct correlation between the percentage of unreacted triglycerides and the thermal stability in the final polymer.

The majority of reactions involving vegetable oils occur at the ester group due to its inherent reactivity (Armylisasa *et al.*, 2017). Acyclic Diene Metathesis (ADMET) is a derivative of cross-metathesis in which dienes produce linear polymers by step-growth kinetics, with the production of ethylene as a by-product. Since ADMET is a reversible process is, ethylene must be removed to

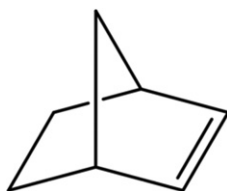


Fig. 6 Chemical structure of norbornene.

favor polymerization. One significant application of this versatile polymerization mechanism is in the production of dendrimers. Recently, di(trimethylolpropane)tetra-acrylate and dipentaerythritol hexa-acrylate core units, and a fatty acid-derived 10-undecenyl acrylate monomer were prepared for post-polymerization via a base-catalyzed Thiol–Michael addition to create a hyper-branched dendrimer (Unverferth and Meier, 2014). Additionally, under this mechanism, bio-based polymers ranging from tacky oils to elastomeric materials have been polymerized utilizing Grubbs 1st generation catalyst and soybean oil. Furthermore, undec-10-enyl undec-10-enoate, vinyl dienes derived from plant oils, generated highly crosslinked block co-polymers under ADEMT conditions. These co-polymers can easily be manipulated to suit multiple applications by simply altering the amount of monomer and chain stopper used in the synthesis (Murawski and Quirino, 2018).

Internal carbon–carbon double bonds, and ester groups are pivotal in the activation of many polymerization reactions. In regards to condensation polymerization, the reaction does not respond to internal carbon–carbon double bonds, such as free radical or ionic polymerization. Instead, the ester bond is broken to yield glycerol and the respective fatty acids. Although, the unsaturations in vegetable oils are often converted into polyols prior to polymerization. Condensation polymerization is commonly used in the preparation of polyesters and polyamides from vegetable oils. There are several successful methods for the synthesis of polyesters from vegetable oils, such as transesterification, acylation, condensation of dicarboxylic acids and anhydrides, and ring-opening of lactones. Nahar seed oil was reacted with glycerol under alcoholysis conditions to produce polyols, which then underwent esterification with acid anhydrides. These newly formed polyester resins were found to have a high resistance to harsh solutions such as dilute, strong acids, and aqueous NaCl solutions, making these polymers optimal for coating applications. Soybean oil with maleate grafted residues allow vegetable oil derivatives to polymerize with polyols and yield crosslinked thermosets. These thermosets have a wide spectrum of applications, highly dependent on the polyol and oil utilized in the polymerization reaction. Similar materials prepared from castor oil have resulted in flexible thermosets with low T_g s and comparable mechanical properties to that of commercially available polyurethanes. Despite an observable decreased hardness in comparison to their petrochemical analogues, these bio-polymers could be used as efficient sealants on account of their increased elasticity (Murawski and Quirino, 2018).

Polyamides are formed from the condensation of diamines and dicarboxylic acids, with water as a by-product. In fact, polyesteramides have been synthesized by curing ethylenediamine tetra acetic acid (EDTA) with linseed oil, poly(styrene-*co*-maleic anhydride) at ambient temperature for applications in coatings based on its decomposition resistance and physico-mechanical properties. A castor oil amide derivative (N,N'-bis(2-hydroxyethyl) anhydride) was subjected to condensation polymerization with diethanolamine to produce a hyper-branched polyesteramide with promise for applications as surface coatings. Long chain polyesters and polyamide vegetable oil derivatives have been the center of recent attention and have been suggested as suitable bio-based replacements for polyethylene. Many advantageous qualities arise from these polymers such as increased hydrophobicity, as well as increased structural stability (Zhang *et al.*, 2017). Block co-polymers were also synthesized by the polymerization of soybean oil-based dicarboxylic acids, diamines and amino acid monomers. As expected, the type of amino acid monomers utilized in the polymerization reaction determined the chain structure and crystallinity of the cured polyamide co-polymer (Murawski and Quirino, 2018).

Composites

The polymers mentioned in Section “Vegetable Oil-Based Polymers” have been reinforced with natural fibers and inorganic materials to generate a series of bio-based composites suitable for structural applications. For example, cationic copolymers of corn oil, ST, and DVB have been successfully reinforced with up to 45 wt% of glass fibers, resulting in significant improvements in Young’s modulus and tensile strength. The use of conjugated corn oil in replacement of regular corn oil results in a material with overall improved properties. Likewise, soybean oil-based cationic polymers have been reinforced with up to 50 wt% of glass fibers, leading to significant increases in Young’s modulus and tensile strength. Glass fibers were also used as reinforcement in ROMP copolymers of dicyclopentadiene (DCPD) and dilulin, resulting in a significant increase in Young’s modulus (Quirino *et al.*, 2014).

Another reinforcement studied for the preparation of vegetable oil-based composites is montmorillonite. Indeed, cationic thermosetting copolymers from conjugated soybean oil showed intercalated and exfoliated clay morphology for loadings of 1–2 wt%. Similarly, montmorillonite was used as a reinforcement in corn oil-based composites, resulting in an improvement in mechanical properties. In that system, optimum properties were obtained for clay loadings of 2–3 wt% (Quirino *et al.*, 2014).

Bio-based composites with a biorenewable content of up to 95 wt% have been prepared by reinforcing vegetable oil-based thermosetting resins with corn stover, wheat straw (Quirino *et al.*, 2014), spent germ (Pfister *et al.*, 2008), soybean hulls (Quirino and Larock, 2009), rice hulls (Quirino and Larock, 2011), wood flour (Quirino *et al.*, 2012b), oat hulls (Quirino *et al.*, 2012a), and sugar cane bagasse (Quirino and Larock, 2012b). In these composites, the polymerization had to be carried-out through a free radical process because the ligno-cellulosic fillers rapidly quench strong Lewis acids typically used for cationic polymerization. During compression molding, the presence of ligno-cellulosic filler particles minimize shrinkage of the resin, limiting the formation of micro-cracks (Quirino *et al.*, 2014). In order to improve mechanical properties, recent studies of natural filler-reinforced composites suggest that MA (Quirino *et al.*, 2012b), and asolectin are good filler-resin compatibilizers (Johns *et al.*, 2015).

Spent germ of different particle sizes was used to reinforce a tung oil (TUN)-based resin, resulting in an increase in storage modulus. The incorporation of shorter particles and higher DVB content also resulted in an overall improvement of the material’s properties. When the filler load was increased from 40 wt% to 60 wt%, agglomeration and formation of micro-voids in the

Table 1 Maximum mechanical properties obtained for selected vegetable oil-based resins and composites

<i>Oil</i>	<i>Reinforcement</i>	<i>Modulus (GPa)</i>	<i>Strength (MPa)</i>	<i>Reference</i>
Corn oil		0.05 ^a	4.6 ^a	Quirino and Kessler (2015)
Corn oil	Glass fibers	0.90 ^a	5.9 ^a	Quirino <i>et al.</i> (2014)
Conjugated corn oil	–	0.07 ^a	7.0 ^a	Quirino and Kessler (2015)
Conjugated corn oil	Glass fibers	1.00 ^a	8.3 ^a	Quirino <i>et al.</i> (2014)
Soybean oil	–	0.05 ^a	2.5 ^a	Quirino and Kessler (2015)
Soybean oil	Glass fibers	2.70 ^a	76.0 ^a	Quirino <i>et al.</i> (2014)
Conjugated soybean oil	–	0.23 ^a	11.5 ^a	Li and Larock (2001)
Conjugated soybean oil	Soybean hulls	0.80 ^a	2.5 ^a	Quirino and Larock (2009)
Tung oil	–	1.10 ^b	144.0 ^b	Li and Larock (2003)
Tung oil	Spent germ	0.87 ^a	12.4 ^a	Pfister <i>et al.</i> (2008)
Linseed oil	–	0.10 ^a	5.6 ^a	Quirino and Kessler (2015)
Linseed oil	Glass fibers	1.5 ^a	145.0 ^a	Quirino <i>et al.</i> (2014)

^aTensile.^bCompression.

composite caused an overall decrease in mechanical properties. It was also found that residual corn oil from the spent germ acted as a plasticizer in the composite. Removing the oil prior to impregnation of the fillers resulted in better mechanical properties (Pfister *et al.*, 2008). In a conjugated soybean oil-based free radical resin reinforced with soybean hulls, when BMA or DVB were substituted with dicyclopentadiene, the mechanical properties were compromised. The different reactivities of the comonomers used to form the matrix resulted in a micro phase-separation (Quirino and Larock, 2009).

When using rice hulls as reinforcement, it was observed that composites prepared with conjugated linseed oil exhibited better overall properties than those prepared from conjugated soybean oil due to the higher degree of unsaturation of the former (Quirino and Larock, 2011). A thorough study on the effects of different natural oils and different natural fillers on the properties of cationic composites was also carried out. Cationic resins made from conjugated soybean, linseed, and corn oils were reinforced with corn stover, wheat straw, and switch grass. Among the fillers evaluated, wheat straw afforded the most promising composites (Quirino *et al.*, 2014). Recently, resins produced from epoxidized acrylated sunflower seed oil copolymerized with ST in the presence of boron trifluoride were reinforced with short fibers of Alfa plant. It was found that 7.5 wt% of Alfa fibers treated with 5% NaOH produced sunflower seed oil composites with best mechanical properties (Kadem *et al.*, 2018). In another study, epoxidized soybean oil reacted with acrylic acid, then with maleic anhydride, was blended with 33 wt% ST. Cetyltrimethylammonium bromide-modified bentonite was added to the resin via compression molding. After testing, soybean oil-based composites with 3 wt% of modified bentonite exhibited the best mechanical properties (Mandal *et al.*, 2018). **Table 1** presents a comparison of the maximum mechanical properties obtained for some selected vegetable oil-based unreinforced resins and composites prepared from the same oils.

Conclusions

In an effort to cover the main advancements in the synthesis, properties, and applications of vegetable oil-based polymeric materials in a concise way, this text covered various types of bio-based resins, including those from polyolefins, polyurethanes, acrylated/maleated oils and half-esters, along with some other relevant approaches. All of these systems have been reinforced with inorganic materials and natural fibers to generate vegetable oil-based composites exhibiting promising properties.

Public pressure and government-driven initiatives pushing for more sustainable commercial practices have incentivized companies to seek ways to reduce their impact on global ecosystems. As the majority of plastics in current commercial use are non-biodegradable and/or from non-renewable origins, reducing the impact of plastics on the environment presents a potential approach. One of the main alternatives for the preparation of polymers with a lower environmental impact is the use of vegetable oils as a building block. Indeed, vegetable oils are widely available natural resources that have been a subject of great interest in polymer research over the past few decades. With the market for bioplastics expected to increase in the foreseeable future, it is important to understand the role that vegetable oil-based polymer applications play in that context.

It is worth noting that, in many cases, the positive environmental impact of polymeric materials prepared from renewable resources is more related to their sustainable nature than to biodegradability and recyclability aspects. In fact, there are very few studies on the biodegradability of the systems presented here. From a chemistry stand point, the highly crosslinked systems typically prepared from unsaturated vegetable oils represent a recycling challenge. Some new recycling approaches are currently under investigation, but no concrete progress has been reported to date. The breakdown of biocomposites can be facilitated by swelling and water absorption of the natural fibers commonly used as reinforcement, but the biodegradation of the polymer

matrix hasn't been extensively investigated. When considering sustainability aspects, however, the use of biorenewable building blocks, such as vegetable oils, promotes a better balanced carbon cycle, since the carbon source of the renewable monomers is ultimately atmospheric CO₂ captured by plants during photosynthesis and eventually incorporated into vegetable oils. Therefore, the use of biorenewable monomers results in a virtually neutral carbon footprint, as opposed to polymers derived from petroleum, which in net terms, introduce more C into the carbon cycle.

The use of vegetable oils has been encouraged in efforts to address the concerns that have arisen from the increased manufacturing and disposal of petroleum-based plastics. Vegetable oil polymers are becoming more commonly used to produce plastic applications such as packaging, hot-melt adhesives, coating applications, inks, among other diverse uses. The current investigation of new methods for the production of tires has seen the use of vegetable oil-based polymers as a potential alternative. The use of vegetable oils in paint coatings represents an advancement in the replacement of petroleum-based chemicals previously used.

Research into the reinforcement of composites from these materials has investigated the use of natural fibers to provide properties that render them more suitable for commercial use. In view of these current trends, vegetable oil polymers seem to show promise for future development; and while these materials show the potential to have a lower environmental impact than petroleum-based products, more information is still required to achieve a full understanding of their entire cost, from both economic and environmental standpoints.

See also: Bio-Based Materials in Sportswear Applications. Biopolymer-Based Composites for Medical Applications. Bio-Polymeric Packaging Material for Packaging of Raw Food. Biopolymers in the Synthesis of Different Nanostructures. Developing Successful Biobased Product: Key Design and Manufacturing Challenges. Edible Films and Coatings for Fruits and Vegetables. Natural Oils as Green Lubricants in Forming Processes. Natural Oils as Green Lubricants in Machining Processes. Valorization of Marble Waste in Cement-Based Materials

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The Suddenly Surging Business of Recycled Plastic Puffer Jackets.

Worldwide Research Trends in the Recycling of Materials

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Nomenclature

Al₂O₃ Alumina

CO₂ Carbon dioxide

HDPE High-density polyethylene

JCR Journal Citation Reports

LDPE Low-density polyethylene

PP Polypropylene

RHA Rice husk ash

SJR SCImago Journal Rank

SNIP Source Normalized Impact per Paper

TH index Thematic H Index

WoS Web of Science

Introduction

Recycling is an activity that has been carried out in the biosphere as an inseparable part of biological processes since the beginning of time (Sidiq *et al.*, 2010; Botetzagias *et al.*, 2015). A leaf that falls, a tree that burns, or an animal that dies and, in general, all the events that happen in nature, end up becoming part of the biochemical, physical, or geological processes maintaining the balance and sustainability of ecosystems.

As humankind has become independent from the biological processes of the biosphere, it has increased its capacity to transform the environment, introducing new and differentiated systems and elements as a result of that capacity for transformation acquired over millions of years of evolution.

Metallurgy, agriculture, animal husbandry, the development of cities, the manufacture of textiles, the discovery of paper, and many other milestones in the history of humanity have introduced elements processed through techniques and “artificial” methods that are not easy to integrate into the natural cycles of the biosphere.

Today, cities and their surrounding activities generate thousands of tons of waste that, without recycling, ends up in landfills (Zaman and Lehmann, 2011). Recycling involves the reuse of different types of items and objects that would otherwise be discarded, contributing to a larger amount of waste and ultimately continuously damaging the planet, making it an act of vital importance to society. Recycling refers to an act by which an object that has already been used is carried through a renewal process rather than being discarded. Experts in the field consider that almost all the elements that surround us can be recycled or reused in different situations, although some of them, because they are extremely toxic, cannot be conserved (Westkämper and Warnecke, 2010).

The current model of production and management of resources, goods, and services seeks to promote consumption in the short term and this pushes the planet into an unsustainable situation. The concept of sustainability includes the circular economy, which proposes that waste produced by industry, municipalities, services, etc., can be valued and transformed into new materials (Geissdoerfer *et al.*, 2017). Thus, the circular economy is presented as a system of resource utilization where the reduction of elements is a priority: Minimize production to the minimum indispensable, and when it is necessary to make use of the product, and finally, for elements that cannot return to the environment due to their properties, it is necessary to bet on recycling. In short, the main premise of circular economy is that waste becomes a resource (Macarthur, 2013; Files, 2015).

Price, in 1963, defined science as that which is published in scientific journals and the scientist as the person who has collaborated by writing in one of those journals (Furner, 2003). As scientific research becomes increasingly global, interdisciplinary, and collaborative, it is necessary to understand the state of art of a given discipline starting with a bibliometric study, which offers a worldwide view of the state of art and the study of its evolution allows for the analysis of changing trends in that particular scientific field (Kurtz and Bollen, 2012).

The bibliometric study and the use of its indicators are essential scientific instruments because they provide an accurate quantification of knowledge in a given scientific field and its compilation in bibliographical databases. Bibliometric studies undoubtedly facilitate the understanding of research activities in a specific scientific field, regardless of the objections that can and should be made. However, it must be noted that, in general, bibliometric analyses are valid in those areas in which scientific literature is an essential result of research. The aim of this article will therefore be to provide an overview of scientific publications in the field of recycling, with a special focus on the category of materials.

Data

The coexistence of two large scientific databases, Scopus and WoS, raises the question of the stability of the statistics obtained by one or the other sources of information. Several studies have measured the overlap between databases and the impact of using

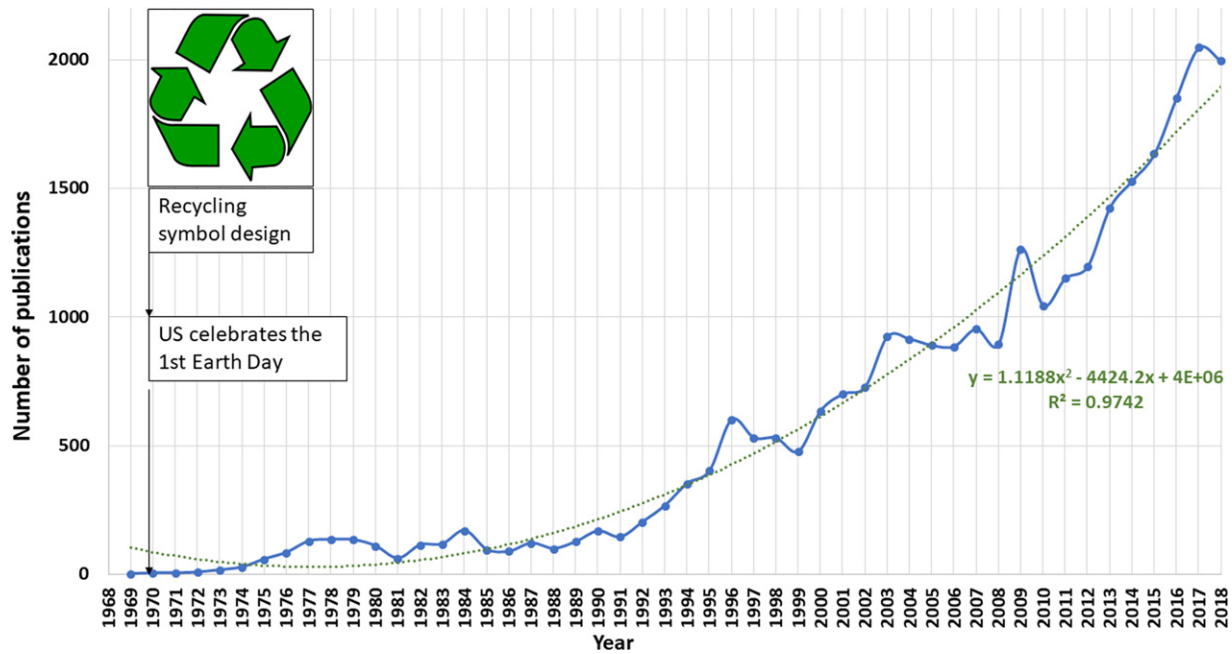


Fig. 1 Trend over time.

different data sources for specific research fields on bibliometric indicators, demonstrating a larger number of journals indexed by Scopus compared with WoS (Mongeon and Paul-Hus, 2016); regarding the overlap, 84% of the WoS titles are also indexed in Scopus, while only 54% of the Scopus titles are indexed in WoS (Gavel and Iselid, 2008). For example, some studies related to citations in the papers conclude that each database covered 90% of the citations in the other database when the citation period is limited to Scopus citation coverage, from 1996 onward (Bosman *et al.*, 2006). The use of the Scopus database for bibliometric studies is fully extended in different fields such as education (Diem and Wolter, 2013), energy (Manzano-Agugliaro *et al.*, 2013), medicine (Garrido-Cardenas *et al.*, 2018a,b), or environment (Brimblecombe and Grossi, 2009).

One of the world's largest databases of scientific literature is Elsevier's Scopus, which contains approximately 18,000 titles from more than 5000 international publishers, including coverage of 16,500 peer-reviewed journals in the areas of science, technology, medicine, and social sciences, including the arts and humanities. For this reason, Scopus was selected for this work.

The Scopus database has been consulted with the following search string: TITLE-ABS-KEY ("recycling") AND (LIMIT-TO (SUBJAREA, "MATE")), of which more than 28,000 results have been obtained in the period between 1969 and 2018.

Results

Trend Over Time and Types of Publications

Fig. 1 shows the evolution in time of the recycling works published in the category of materials. It is observed that since the recycling symbol was designed in 1970, and the United States celebrated the first Earth Day, the trend has been upward, but especially since 1990, reaching a local maximum point in 2010, where the trend of growth has been constant, reaching more than 2000 publications a year from 2017.

With regard to the type of publication (Fig. 2), it can be seen that 74% are articles, while 17% are conference papers. When the research topic is very novel, the percentage of conference paper is higher than the percentage of articles, and when it is a consolidated topic the percentage of books is more representative, around 10%. This indicates that the subject of recycling in the category of materials is a topic of growing research, but that it is not yet fully mature, as the percentage of books is still quite low.

Subjects From Worldwide Publications

The categories in which the research is distributed are relevant because it can be seen which areas are working on the issue of recycling materials. Fig. 3 shows the distribution by subject category to which the Scopus database has assigned them. It can be seen that it is dominated by the engineering category with 34%, followed by three other categories of similar size, around 15%: chemistry, physics and astronomy, and chemical engineering. These first four categories account for about 80% of the scientific production of recycling in matters of materials. If we add to this the categories of energy and environmental sciences, it reaches 90%. Then, there are a whole series of categories, which we could qualify as minor because they are about 1%, showing the

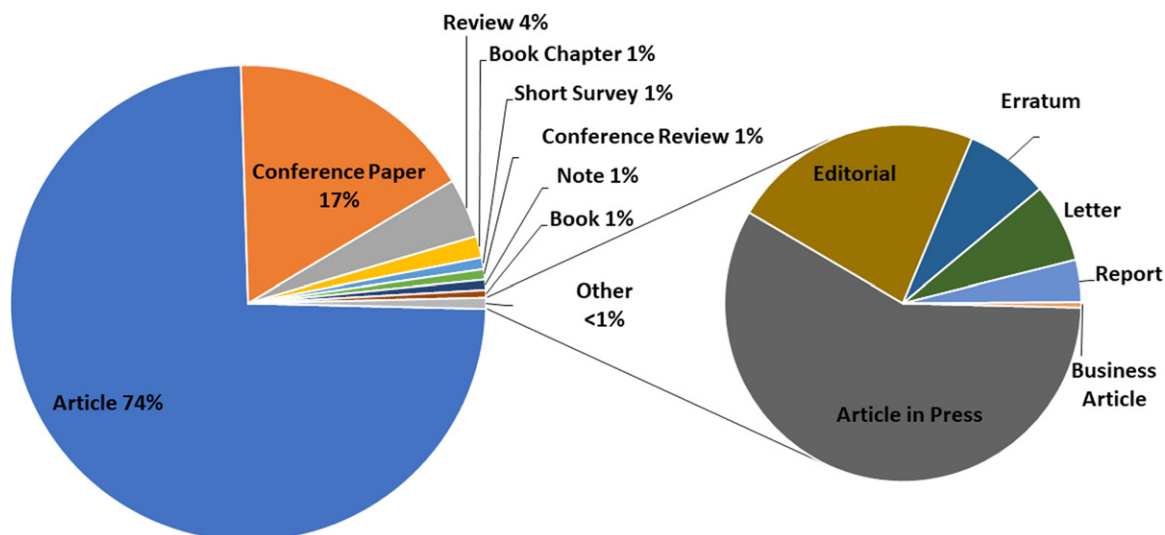


Fig. 2 Distribution of publications type.

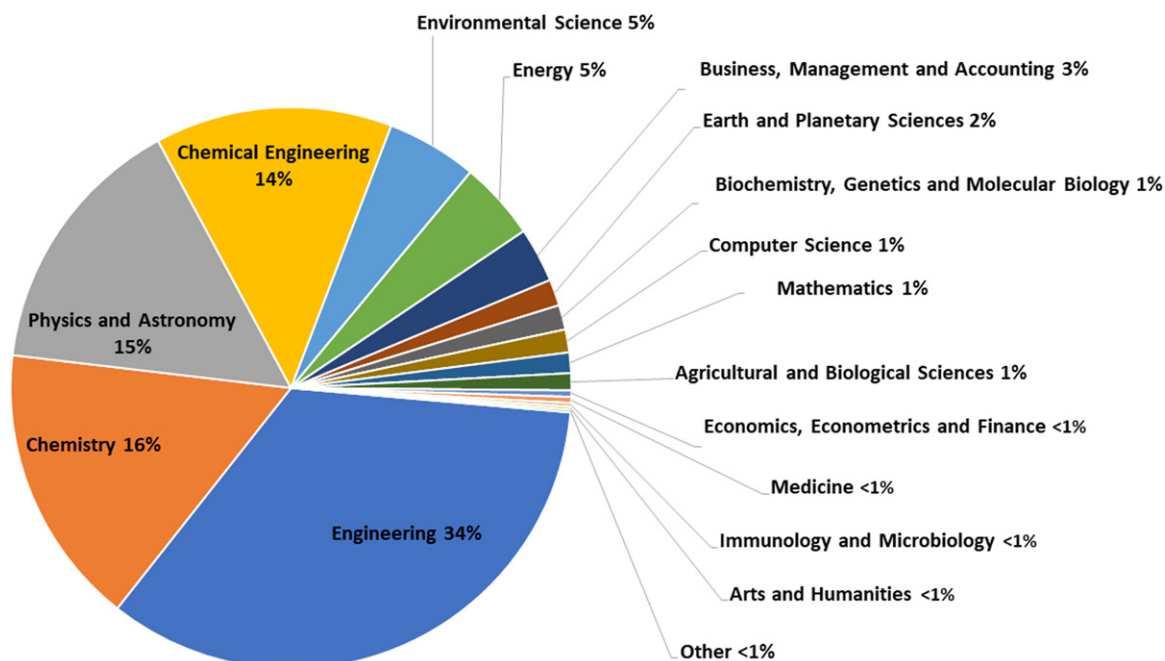


Fig. 3 Distribution of subject category.

importance of the subject as it is addressed from many points of view: Business, management and accounting; earth and planetary sciences; biochemistry, genetics and molecular biology; computer science; mathematics; agricultural and biological sciences; economics, econometrics and finance; medicine; immunology and microbiology; arts and humanities; and others.

Journals and Proceedings Metric Analysis

One of the most important elements of a bibliometric study is the publication media in which the works object of the study is published. This offers a relative importance of the field under study, compared with other similar studies. The assessment of scientific journals with bibliometric indicators has been largely driven by the impact factor since the 1970s. The journal impact factor is defined as all citations to the journal in the current JCR year to items published in the previous two years, divided by the total number of scholarly items (these comprise articles, reviews, and proceedings papers) published in the journal in the previous two years. On the other hand, Elsevier has decided to include in Scopus among other indicators the CiteScore. CiteScore metrics are part of the Scopus basket of journal metrics that includes SNIP, SJR, citation and document

Table 1 Main journals and their metrics

Journal/meeting	%	N	Impact factor (2017)	Citescore	Highest percentile/category	TH index	Citations (C)	C/N
Construction and Building Materials	3.83	1072	3.485	4.22	96% civil and structural engineering	74	11,604	10.82
Journal of Nuclear Materials	2.46	688	2.447	2.51	86% nuclear energy and engineering	48	7827	11.38
Journal of Applied Polymer Science	2.39	669	1.901	1.87	73% polymers and plastics	46	7879	11.78
Desalination	1.93	539	6.603	6.41	98% water science and technology	61	12,224	22.68
TMS Annual Meeting	1.41	394	–	0.12	14% metals and alloys	11	607	1.54
Materials Science Forum	1.29	362	–	0.3	22% general materials science	13	908	2.51
Key Engineering Materials	1.27	356	–	0.29	21% general materials science	10	610	1.71
Iop Conference Series Materials, Science and Engineering	1.09	305	–	0.49	42% 157/270 general engineering	12	221	0.72
Journal of Materials in Civil Engineering	1.03	289	1.763	1.94	81% building and construction	44	5022	17.38
Polymer Degradation and Stability	1.02	285	3.193	3.59	91% mechanics of materials	52	5830	20.46

counts, and percentage cited. The integration of these metrics into Scopus provides insights into the citation impact of more than 22,220 titles. CiteScore is the number of citations received by a journal in one year to documents published in the three previous years, divided by the number of documents indexed in Scopus published in those same three years. The two main strengths of this index are as follows:

- (1) Three years is the best choice for a wide-ranging database, as it includes a representative proportion of citations from all disciplines, while reflecting relatively recent data. Especially if compared with the two years of the impact factor (IF) or the five years of impact factor (5-year journal Impact Factor), both of the JCR (Journal Citation Reports).
- (2) All document types are included in both the numerator and denominator, making it difficult to manipulate the calculation of this indicator.

Table 1 shows the main media where recycling topics are published in the category of materials. The top 10 sources by number of publications have been taken into account. The relative percentage of publications has been calculated for the search terms, observing a great dispersion, since it by no means reaches 5% of the total of the publications. The leading journal in this ranking is *Construction and Building Materials* with 3.83%, followed by *Journal of Nuclear Materials* with 2.46%, and, in third place, *Journal of Applied Polymer Science* with 2.39%. It can be seen that journals rank very well in their specific categories, all of them being in the first quartile, that is, above 75% of the category in which they are indexed. These categories are civil and structural engineering, nuclear energy and engineering, polymers and plastics, water science and technology, building and construction, and mechanics of materials. It is also remarkable that journals do not repeat any category, although apparently the titles of the journals may seem the opposite. However, in the meetings some appear in the same category (general materials science).

Another indicator that has been calculated in this section is the TH-index. The H-index is used as an indicator of a certain author or journal, and is calculated by counting the number of publications for which an author has been cited by other authors at least that same number of times. So, the TH-index is calculated by counting the number of publications for which journal manuscripts have been cited by other manuscripts at least that same number of times. This ranking of TH-index is led by the journals *Construction and Building Materials* (74), *Desalination* (61), and *Polymer Degradation and Stability* (52).

Finally, the average citations of the articles published in the subject (C/N) of recycling in the category of materials have been calculated. This ranking is no longer necessarily led by the journals that publish more on the subject such as *Desalination* (22.68), but is followed by others such as *Polymer Degradation and Stability* (20.46), and *Journal of Materials in Civil Engineering* (17.38), which are not the most productive in this field.

Countries, Affiliations, and Their Main Topics

The main countries that publish materials on recycling are shown in **Fig. 4**. It can be seen that this ranking is led by countries with more than 3000 publications, including the United States and China, followed by Japan with more than 2000. With more than 1000 publications are, in fourth place, Germany, fifth, United Kingdom, and sixth, India. And with more than 800 publications highlighted in order of importance: South Korea, France, Spain, Italy, and Brazil. In general it is observed in **Fig. 5** that the great areas of the world that do not investigate in this field are the African countries, Central America, and the central zone of Asia. Perhaps this can be attributed to less industrialized geographical areas.

If this analysis is made taking into account the institutions (**Fig. 5**), it is observed that this ranking is led by Chinese institutions, with three of them among the top five, specifically the first place occupied by the Ministry of Education China, second place Chinese Academy of Sciences, and fifth place University of Science and Technology Beijing. It can also be observed how among this

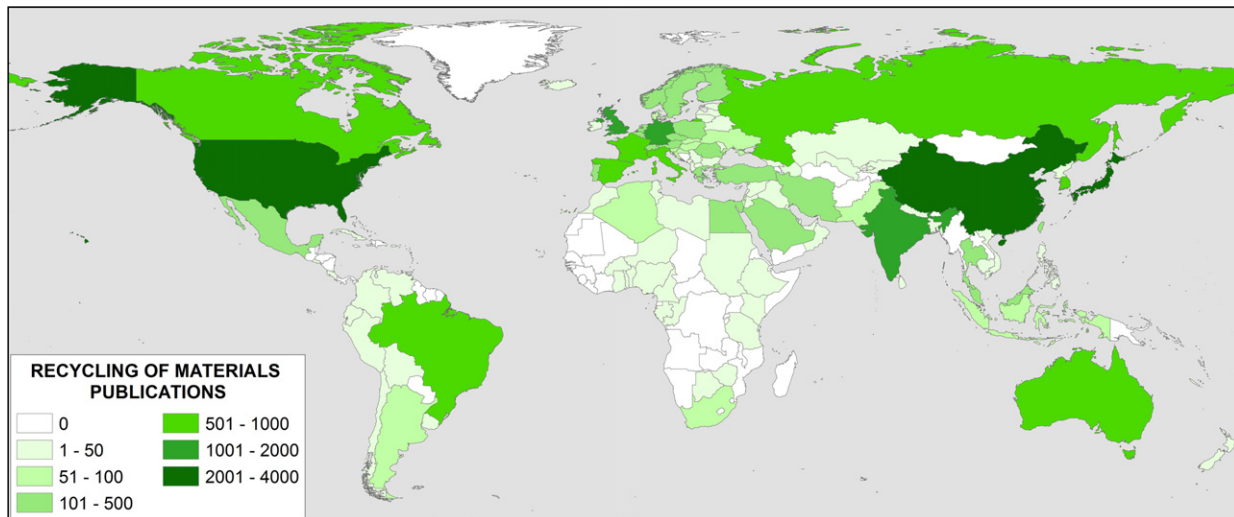


Fig. 4 Worldwide distribution of the publications.

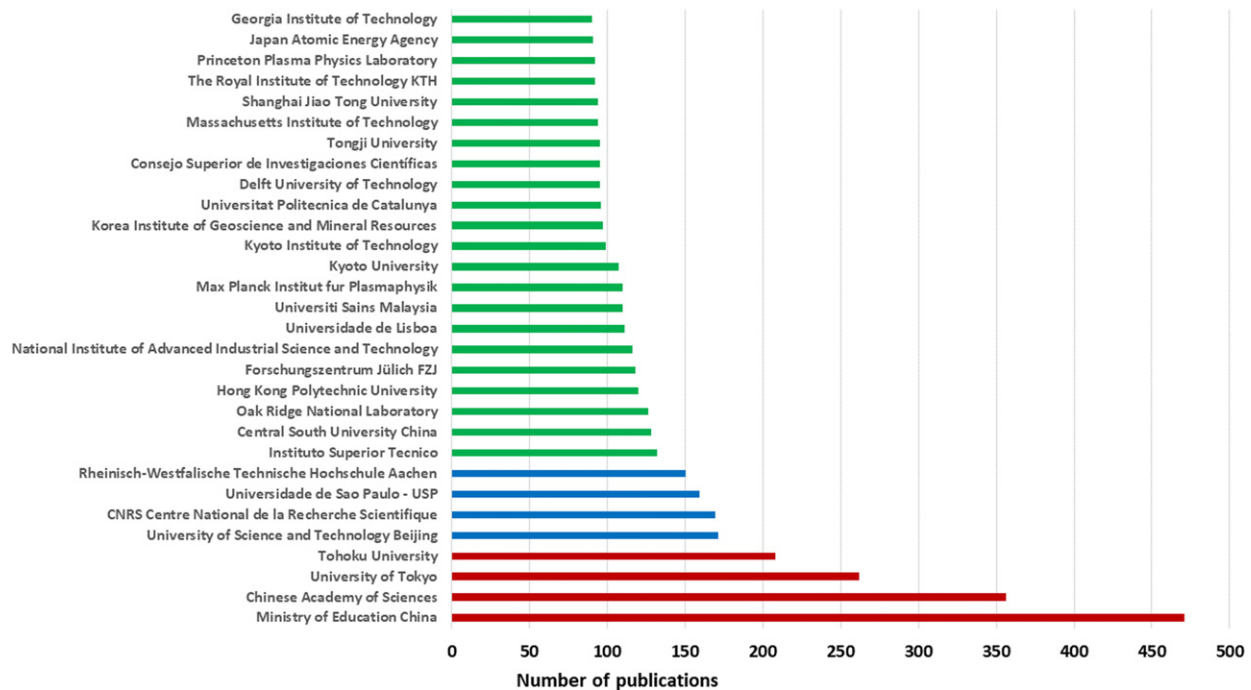


Fig. 5 Main institutions.

top 5 are two Japanese institutions: In third and fourth place, with the University of Tokyo and the Tohoku University. It is noteworthy, given the ranking of countries, that the first institution in the United States, Oak Ridge National Laboratory, is ranked 11th in the ranking of institutions, with no more in the top 20. This suggests that the United States, despite being a world leader in this field, does not have any institution strongly focused on this field, and this research is spread among the set of research institutions in this country.

The first German institution, the Rheinisch-Westfälische Technische Hochschule Aachen, occupy the 8th place in this ranking of institutions, and the Forschungszentrum Jülich FZJ, the 13th place, the latter being one of the largest interdisciplinary research centers in Europe. The first UK institution, The Royal Institute of Technology KTH, ranks 27th. For South Korea, Korea Institute of Geoscience and Mineral Resources in position 20; for France, CNRS Centre National de la Recherche Scientifique in position 6; for Spain, Universitat Politècnica de Catalunya in position 21; for Italy, Consiglio Nazionale delle Ricerche in position 31 and Brazil, Universidade de São Paulo (USP) in position 7.

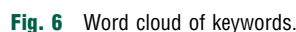


Table 2 Main keywords

Keyword	N	%
Mechanical properties	2076	2.72
Concretes	1341	1.75
Scanning electron microscopy	1296	1.69
Tensile strength	1212	1.58
Aggregates	1166	1.52
Water recycling	1164	1.52
Compressive strength	1112	1.45
Concrete aggregates	1065	1.39
Fibers	979	1.28
Polymers	944	1.23
Environmental impact	851	1.11
Aluminum	820	1.07
Scrap metal reprocessing	811	1.06
Slags	784	1.02
Sustainable development	760	0.99
Environmental protection	730	0.95
Polypropylenes	729	0.95
Polyethylene terephthalates	718	0.94
Degradation	697	0.91
Composite materials	690	0.90
Wastewater treatment	687	0.90
X-ray diffraction	678	0.88
Catalysis	661	0.86

Keywords From Worldwide Publications

Keywords are ideas and topics that define the research content. In addition, keywords are blocks of text that help search engines identify the topics of the research. If the keywords of all the articles studied are analyzed, and with them a cloud of words is made (Fig. 6), one can have a visual idea of the content of the global research. Of course, search terms, *recycling* and *materials*, appear in it at a larger size, but it also highlights everything that is important: Water, plastic, metals, paper, waste, aluminum, etc. Apart from a quantitative idea of the topic, a table has been elaborated with the frequency that these keywords appear in the analyzed works (Table 2). Thus it is observed that *mechanical properties* is the keyword that dominates although below are other very related as *tensile strength* or *compressive strength*. The concretes appear in an outstanding second place, but they also have quite a few variants such as *concrete aggregates* or *aggregates*.

Water recycling, as expected, also appears very prominently, although there are quite number of variants within the keywords used: *Wastewater*, *wastewater reclamation*, *wastewater treatment*, *water*, *water absorption*, or *water treatment*. Fibers play a leading role in the recycling of materials such as glass fibers (Zhou and Qiu, 2010; Zheng *et al.*, 2009) and carbon-fiber (Schinner *et al.*, 1996; Liu *et al.*, 2004; Morin *et al.*, 2012).

With regard to the techniques used, scanning electron microscopy is observed as very outstanding and to a lesser extent X-ray diffraction, thermogravimetric analysis, transmission electron microscopy, and chemical analysis.

Polymers are other materials frequently studied, and although there are many types of synthetic polymers such as nylon, Bakelite, or polyethylene, it is the latter that has an important role in the subject of recycling, as it is one of the most common plastics due to its low price, and simplicity in its manufacture. Within the highlighted keywords are *polypropylenes* or *polyethylene terephthalates*. The PPs are recycled as thermoplastic elastomers (Ismail and Suryadiansyah, 2002). On the other hand, quite a few lines of research propose to use the polyethylene terephthalates as an additive to concrete, given its mechanical properties (Jo *et al.*, 2006; Choi *et al.*, 2009).

Clusters Analysis Based on Keywords

If the relationship between the articles cited among them referring to the subject of recycling in the category of materials is represented, Fig. 7 is obtained. Ten clusters have been obtained, of which the first eight are representative because they have more than 1% of the publications.

Table 3 shows the first 5 keywords of each cluster, which has allowed its classification. The largest cluster is for plastics with 35% of publications, followed by the concrete cluster with just over 18% of publications. In third place is the rubbers cluster with almost 12%. It is followed in fourth and fifth place by the aluminum and blast furnace clusters, with more than 9% each. In sixth and seventh place are the batteries (7.7%) and paper (4.2%) clusters. The last significant cluster is wastewater, with 3.5%.

Regarding the grouping within the general subject of recycling (Fig. 7), it is observed how the two most compact clusters are plastics and concrete. The rubbers cluster is quite close to both but is very integrated with the plastics, as expected. The other clusters are more dispersed, but the wastewater theme draws attention, which is clearly isolated from the rest and seems to be linked only to the plastics theme. The blast furnace, although it dominates the topic of the recycling of gases, is close to the rubbers. It is also remarkable how far away is the recycling of paper from water, because as it will be seen they have quite a lot in common, unless it is a specific recycling of water for this type of industry.

The critical public debate on natural resource conservation and recycling has led to a renewed interest in biomaterials, leading to research into renewable raw materials (Mohanty *et al.*, 2000). The elimination of traditional composite material structures, generally made of glass, carbon reinforced with epoxy, unsaturated polyester, or phenolics, is considered essential for global sustainability. So, in the first cluster, is found the recycling of polymers or waste products based on low-density polyethylene, HDPE, or PP using chemical recycling methods such as pyrolysis or dissolution/precipitation (Achilias *et al.*, 2007). In this type

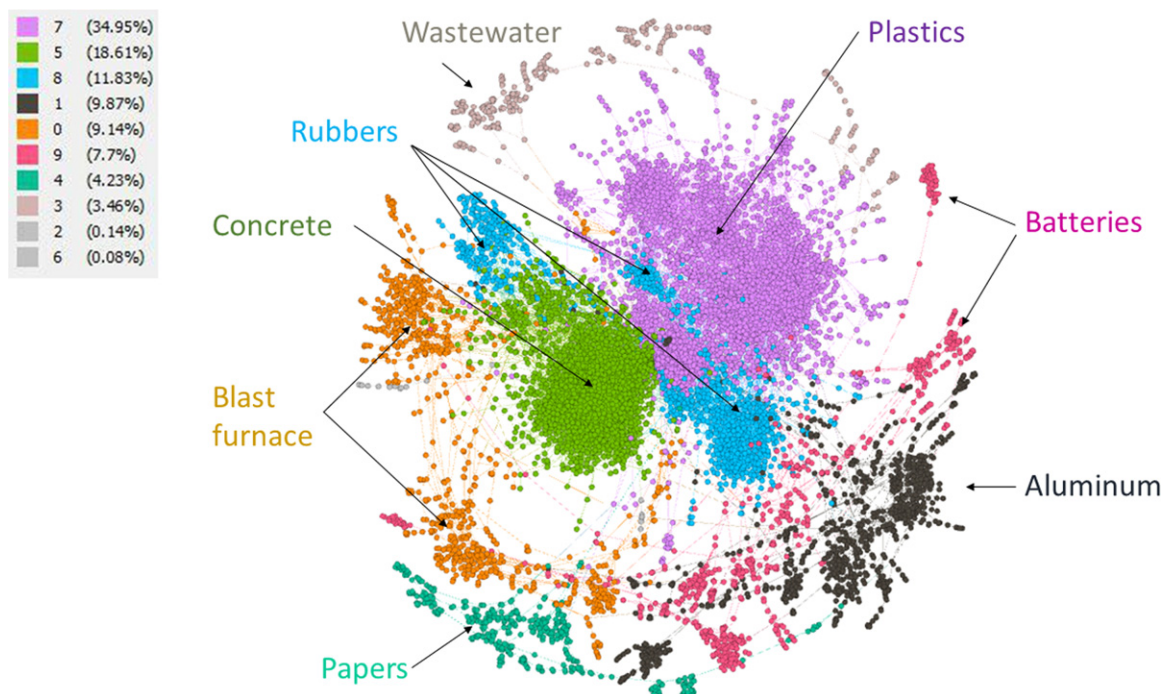


Fig. 7 Community detection of worldwide research on material recycling: Clusters.

Table 3 Cluster analysis

Cluster	%	Name	Keyword				
			1	2	3	4	5
7	34.95	Plastics	Mechanical properties	Composites	Degradation	Polypropylene	Chemical recycling
5	18.61	Concrete	Recycled aggregate	Durability	Concrete	Mechanical properties	Rice husk ash
8	11.83	Rubbers	Mechanical properties	Devulcanization	Rubber	Polyurethane	Glycolysis
1	9.87	Aluminum	Aluminum	Life cycle assessment	Accumulation	Impurity	Magnesium
0	9.14	Blast furnace	Blast furnace	Coke	Oxygen blast furnace	Top gas recycling	Zinc
9	7.7	Batteries	Leaching	Hydrometallurgy	Cobalt	Permanent magnets	Silicon
4	4.23	Paper	Deinking	Flotation	Reclaimed fibers	Paper recycling	Pulp properties
3	3.46	Wastewater	Reverse osmosis	Nanofiltration	Membrane bioreactor	Water reuse	Photocatalysis

of work there is an enormous amount of research dealing with the study of mechanical properties (Arbelaz et al., 2005) such as rigidity (Bourmaud and Baley, 2009), but also rheology or calorimetric properties (Bourmaud and Baley, 2007).

The second cluster is focused on concrete. Most of the world's total production of solid waste comes from construction and demolition waste (Rao et al., 2007). Construction waste materials typically go to landfill, where concrete waste accounts for approximately 50% of it (Tam, 2008). One of the most widespread methods of recycling concrete waste is the generation of recycled aggregates (Tabsh and Abdelfatah, 2009). What is striking about this study is the frequent occurrence of the term RHA. However, it is something that has been studied for a long time, above all as a replacement for cement to make concrete, especially as a binder material (Bui et al., 2005; Givi et al., 2010). For example, RHA has a positive effect on the concrete compressive strength at early ages (Rodríguez De Sensale, 2006).

The third cluster is focused on rubber. An average car tire can travel about 30,000 km over its lifetime before it needs to be replaced. So, nearly 1 billion rubber tires are thrown away each year. If they are not recycled, they end up in landfills. As an example, in Sulabiya (Kuwait) is the world's biggest tire graveyard. Since 2006 EU rules have banned the disposal of tires in landfill sites. Rubber residues are among the most difficult materials to recycle as they do not dissolve or melt. The recycling of rubber can be achieved by size reduction and production of powders (Fang et al., 2002), devulcanization (Green, 2007), reclaiming (Gaustad et al., 2012) and recovery of chemicals (Shinzato and Hypolito, 2005) and energy (Rabah, 2003).

The fourth cluster is focused on aluminum recycling. Aluminum is the most abundant metal in the Earth's crust, accounting for approximately 8% of the weight of the Earth's solid surface (International Aluminum Institute, 2009). The highest concentration of aluminum oxide is found in bauxite ore, but despite being very abundant it is also one of the most expensive metals to obtain. Pure aluminum is obtained by extracting alumina from bauxite. The great cost of this process is the energy required for its production, as each ton of aluminum requires more than 15 MWh of energy, which means a cost of 25%–40% of the final price of aluminum and hence aluminum is one of the most expensive metals to obtain. In fact, Iceland is becoming one of the largest producers of aluminum, and that which has no bauxite ore, but what it does is "sell" its energy from its geothermal power stations and five large hydroelectric reservoirs that collect water from glaciers, using part of this energy in the transformation of bauxite into aluminum, as this energy cannot be stored. Note that energy in Iceland is 30% cheaper than in the United States. This same circumstance is happening with the United Arab Emirates in the production of aluminum. The most widely accepted industrial method for producing alumina from bauxite is based on the dissolution of bauxite with soda, then by different decanting, separation, and calcination processes; thus alumina (Al_2O_3) is obtained. Alumina is electrolyzed by the Hall–Héroult process to finally obtain aluminum. Thus, 1.9 kg of alumina produces 1 kg of pure aluminum.

From an environmental point of view, obtaining aluminum is a highly polluting process, both in the extraction of bauxite, and in the subsequent processes commented on in the conversion of bauxite to aluminum. Thus, its recycling is a major issue, as well as the high cost of this material and the serious environmental consequences. Used aluminum arrives mainly through two channels: Domestic waste (e.g., used beverage cans) and industrial waste (e.g., electricity cables, lithographic sheets, vehicle scrapping, or construction demolition).

The cluster obtained shows that they appear as keywords *accumulation* and *impurity*. This is because the accumulation of impurities in these recycled material streams may provide a significant compositional barrier to the recycling goals (Gaustad et al., 2012). The keyword *magnesium* linked to aluminum recycling is due to aluminum–magnesium alloys (Shinzato and Hypolito, 2005). For example, in 2003 the existing recycling system was updated by introducing the elimination of coating paint and the reduction of magnesium losses during the melting process of used beverage cans (Rabah, 2003). Today, approximately 30% of the aluminum used is provided by recycling plants (International Aluminum Institute, 2009).

Iron and steel alloys remain the key materials in the automotive, construction, marine, and many other industries due to their strength, hardness, versatility, and low cost. The fifth cluster obtained is related to blast furnace and top gas recycling. One of the central functions of the blast furnace is iron making. For example, iron ores with lower iron content such as taconite are first processed to concentrate the iron level and drive off volatile impurities. This process uses coke. A specialized type of coal, called hard coal, is used to make coke, a porous form of carbon. Coke is a reductant, or a chemical, that can reduce iron oxide to iron metal. One of the main goals of this process is minimizing CO_2 emission; this is top gas recycling (Murai et al., 2008). It should be

noted that CO₂ has many uses such as carbonated beverages, protective atmosphere packaging, electronics, oil extraction, chemical industry, inertization metals, pulp and paper, environmental testing, iron and steel industry, welding, food transport, or water treatment. Unlike other gases, air separation is not the main source of carbon dioxide. The cheapest way to produce carbon dioxide is to recover it as a subproduct from the production processes of other factories or from natural wells.

Cluster 6 is about batteries. Battery recycling can be a great opportunity for the development of the world economy and the preservation of the environment. Batteries' main component, lead, is almost 100% recyclable and can be used endlessly in the manufacture of new batteries, without the need for new raw materials and their extraction from natural reserves. In addition, batteries made from recycled material have the same quality and offer the same performance as their equivalents made from new raw materials. In this cluster there are keywords linked to lead research such as leaching or cobalt. Above all, the used lithium-ion batteries have cobalt and lithium as cathodic active materials (Lee and Rhee, 2003). Research is focused on finding environmentally friendly leaching processes (Li *et al.*, 2010).

The advantages of paper recycling are well-known (cluster 7), for example, the amount of forest cut is reduced, the need to plant monocultures of conifers and eucalyptus trees is reduced, water consumption is reduced by 85%, energy consumption is reduced by 65%, polluting effluents are reduced by 35%, or landfill space is reduced. The fact that it is cluster number 7 in terms of the importance of the research carried out does not mean that it is less important, but that it is a well-known process and the associated technology is fully mature, despite which research in this field continues. One of the most studied problems in this field is deinking. As an example, Europe's pulp and paper industry produces 11 million tonnes of waste annually, 70% of which comes from the production of deinked recycled paper (Monte *et al.*, 2009). So, paper machines and bleaching plants generate a huge amount of effluents in this industrial process (Ochoa de Alda, 2008); the World Bank recommended wastewater reduction including the recycling of wastewater with simultaneous recovery of fibers.

Finally, there is the recycling or treatment of water for reuse, cluster 8. In this cluster there are five main lines that are currently being researched in this field: Reverse osmosis, nanofiltration, membrane bioreactor, water reuse, and photocatalysis.

See also: An Overview of the Global Ship Recycling Industry. Nuclear Electricity – Renewability, Losses and Recycling. Polymer-Recycling of Bulk Plastics. Prospect of Recycling of Plastic Product to Minimize Environmental Pollution. Recycling and Downstream Processing of Aluminium Alloys for Automotive Applications. Recycling Approaches, Policies and Regulations on Electronic Waste With Special Focus on India. Recycling of Agricultural Waste for Wastewater Treatment. Recycling of Construction and Demolition Wastes Into Renewable Construction Materials. Recycling of E-Waste. Recycling of Plastics for Low Cost Construction. Sustainability and Recycling of Bamboo for Engineering Applications. Treatment and Recycling of Domestic and Industrial Wastewater. Waste Resources Recycling in Achieving Economic and Environmental Sustainability: Review on Wood Waste Industry

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Augmented Reality and Occupational Safety

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Introduction

Placing the worker in a safety-management context is very important due to current practices in the working environment that ensure uninterrupted functioning of the everyday job routine. Exposure to risks, caused by unsecure handling, can lead to hazardous situations that often result in injuries and delays in finishing technological processes. Therefore, safety measures have to be appreciated by strictly following the rules prescribed for each particular task by occupational safety experts. Although protection measures are precisely defined, there is a need to ensure and further improve their application in the industrial environment.

The advent of information technologies, accompanied by new hardware solutions such as smart mobile devices, enables a quick and precise display of safety instructions in the workplace. Consequently, they can be efficiently used in improving occupational safety conditions, especially in the industrial environment.

The emerging augmented reality (AR) technologies, coupled with ubiquitous mobile devices, can be used as an interface between the working environment and the worker, since they enable the presentation of relevant safety information in a distinct and intuitive way at a particular work location. In this way, the worker will be precisely informed about the security measures which need to be implemented prior to performing the concrete task assigned. Therefore, providing virtual safety information combined with a real space image during realization of daily tasks can help in reducing the error rate.

Application of Augmented Reality in Industry

The application of AR in industry is a field of study with rapidly increasing interest (Navab, 2004; Fite-Georgel, 2011; Blanco-Novoa *et al.*, 2018; Jetter *et al.*, 2018). AR as a significant aid during the daily work process is described in (Gimeno *et al.*, 2013; Re *et al.*, 2016; Benbelkacem *et al.*, 2013; Wang *et al.*, 2014b). This kind of research focuses on fields such as maintenance and repair that are a part of various complex industrial systems where the worker gets predefined virtual information during everyday routine work (Zhu *et al.*, 2014; Koch *et al.*, 2014; Henderson and Feiner, 2011; Scurati *et al.*, 2018; Palmarini *et al.*, 2018). Also, there are research papers discussing manufacturing (Yew *et al.*, 2016; Uva *et al.*, 2018) and assembling (Wang *et al.*, 2016) of complex systems by using AR to improve the efficiency of implementing the related procedures. Systems based on AR presented in the relevant literature also address problems in industry fields such as collaboration (Wang *et al.*, 2014a; Zhou *et al.*, 2011), management (Espíndola *et al.*, 2013), and product design (Park and Moon, 2013; Arroyave-Tobón *et al.*, 2015) with the main goal of improving communication between worker groups gathered on the same industrial project.

Training systems are a special field of application of AR (De Crescenzo *et al.*, 2011; Watanuki and Hou, 2010; Borsci *et al.*, 2015; Yim and Seong, 2010), usually represented as virtual guidance. This provides a more complete and easier way to perceive and understand information compared to the usual approaches based on classical printed manuals.

Different types of hardware aids are proposed for resolving particular tasks by using AR technology. By pointing the camera of a mobile device such as a smartphone and tablet towards a predefined spot, while walking in an industrial environment, the worker can get job instructions (Webel *et al.*, 2013; Schall *et al.*, 2013). While scanning the industry space, one or both hands are occupied and the worker has to watch each instruction before he can perform any action. This can be viewed as a drawback of that approach. Therefore, Head Mounted (HMD) or Head Worn Devices (HWD) such as smart glasses and smart helmets are recommended instead of mobile devices (Syberfeldt *et al.*, 2017). By using such a device, assistive information is projected on the glass atop the worker's head during work. Reduced field of view is often considered as a limiting factor in the widespread use of these devices. An alternative could be found in projection systems which combine the image of the real world with computer generated multimedia content on a suitably positioned big screen or directly on the work surface (Fiorentino *et al.*, 2014; Di Donato *et al.*, 2015).

Occupational Safety in Industry and Augmented Reality

An emerging field of potential research in computing concerns the application of augmented reality technology in improving occupational safety. Combination of industrial safety and AR is used to help workers realize tasks with a necessary simultaneous protection against hazards and risks in the industrial workplace (Grabowski *et al.*, 2018; Velosa *et al.*, 2018).

It has been observed by many experts in the area that in industry, workers often neglect security signals and then end up in a risky situation while performing task. On the other hand, traditional methods for issuing security signals are not efficient enough. These methods are often static and tend to interfere with other workers by giving a warning signal to more than just the intended recipient. Augmented reality technology can be used to improve the release of security signals. In (Dzwiarek and Luczak, 2008) the

issuance of security signals was defined through smart glasses in combination with AR technology. It turned out that the warning elements displayed should be as simple and easy to recognize as possible.

The work (Kim *et al.*, 2016b) presents a study in which experts from several different industries have been interviewed to define the current state and future development of the AR HWD system for industry needs. It turned out that only a well-executed combination of AR and HWD systems can contribute both to improving safety and health at work and to the successful execution of work tasks. Also, certain limitations of AR HWD systems are mentioned, as well as recommendations for the development of potential applications through this technology.

The construction industry is a very complex environment in which workers are exposed to risk of injury at work (Li *et al.*, 2018). Most accidents are caused by the human factor; therefore, new methods of protection should be explored. Usually prevention of accidents is done by educating workers, but pedagogical methods of occupational safety are mainly theoretical without much practice in the field. Therefore, a system for improving occupational safety with the help of virtual and augmented reality technologies has been described in Le *et al.* (2015). The system is implemented on mobile devices and consists of a user interface, content editing part and a database. An evaluation of the developed prototype has shown that such a system can significantly improve learning about error identification and application of security procedures. In this system, the time required for the creation of educational scenarios has been pointed out as a disadvantage.

Another study involving the construction industry where augmented reality technology is used for safety improvement is presented in Talmaki *et al.* (2010). Due to the complexity of installations that are located below ground, which require changes, careful excavation in exact places is necessary. This necessitates careful work at these exact locations without much room for mismatches. Augmented reality technology is used to display data from a geospatial database in the form of a 3D model and in this way provide the precise position of the installations during excavation. The simulation of excavations is realized inside an excavator cabin where a monitor displays the data about the installations in the field by using a combination of AR technology and a GPS system.

Natural catastrophes lead to damage of urban areas after which it is necessary to analyze the consequences. In order to evaluate building damage and safety, a system (Kim *et al.*, 2016a) has been proposed to assist security risk assessment. The system is designed to use AR technology on mobile devices to compare the situation before and after the disaster. Based on insight into the current and previous state, an expert for risk assessment is able to quickly determine the degree of damage and the security level for the use of that facility.

Incidents in nuclear installations cause long-term consequences and adversely affect environment. In such situations, human evacuation is a primary goal where modern technology such as AR can be helpful. The integration of the geographic information system and augmented reality technology that facilitates the evacuation of people is presented in Tsai *et al.* (2012). Using this mobile system, shelters can be reached faster, and the evacuation of people performed efficiently. An improvement of this system is shown in Tsai and Yau (2013). Indoor orientation has been introduced, as well as the integration of 3D models that help the evacuation. Two additional mechanisms are also integrated: (1) An alarm which converts text into sound that is activated in the vicinity of the shelter for more accurate guidance, and (2) an SMS service, to help in case of problems during the evacuation. An experimental evaluation shown that the improved system is a better solution.

Occupational Safety Framework for Industry Purposes

AR technologies enable the development of an occupational safety framework tailored for different industrial environments and various circumstances in which hazardous situations can occur. As an example, we will present such a framework derived from an analysis of injuries which occur during the daily work process in an industry environment (Fig. 1). It can be observed that the causes of injuries are either inadequate training in the case of less qualified workers, monotony of the job and excessive self-confidence of high qualified workers due to which they often tend to skip some of safety procedures. Therefore, an augmented reality system is realized with the intention of providing occupational safety (OS) instructions and work and maintenance (WM) instructions during job execution in an industry environment (Tatić and Tešić, 2017). The system in Tatić and Tešić (2017) is realized as a client server application where the client part is realized as a mobile application.

The model of the system is based on an analysis of technological process in a thermal power plant. Each task in the technological process is divided into OS instructions defined by a safety officer and WM instructions issued by a technology officer. The information provided to the worker depends on his qualification level, so that less qualified workers get a detailed set of working and safety instructions, while highly qualified workers get a reduced set of WM instructions. Each worker gets the same set of OS instructions and is required to confirm their implementation.

Determination of the task content is done upon the authorization from the mobile device. Task data such as safety and work instructions are stored in a database and linked to the multimedia content in a Multimedia repository. Communication between the mobile device and database application is realized by the REST service on the server side.

Upon successful registration, data are transferred on the client side by a Communication module that is responsible for communication with the server. Data are stored in the Task module that regulates issuing of current and saved information about the implemented OS and WM instructions. After each occupational safety instruction, the next work and maintenance instruction is projected on the screen of the mobile device.

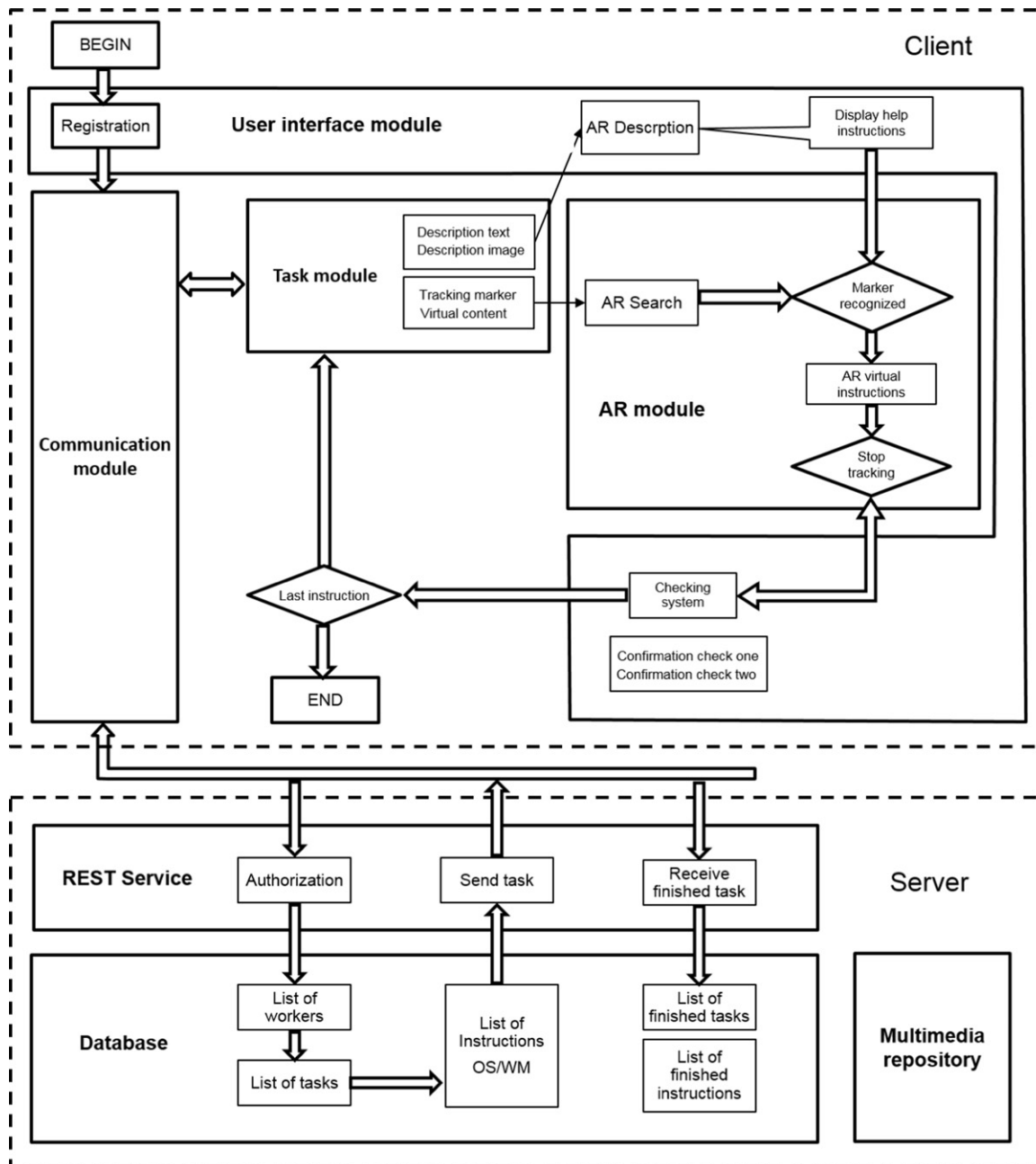


Fig. 1 Occupational safety framework based on augmented reality.

The user interface module navigates the user to find the exact spot in the concrete work environment and scan it with his mobile device. At the same time, the AR module responsible for visualization of OS and WM instructions is activated. Upon scanning, elements of the User interface module are removed from the screen and the AR instructions are shown during the tracking.

The worker is obliged to watch and perform the given instructions. A single instruction is active at a time and only one location can be tracked. When the worker stops tracking, the checking system is projected. The worker must pass verification that the current instruction is finished in order to get the next instruction. A double check procedure is realized to prevent unintended confirmation. After confirmation of the current occupational safety instruction, the next working instruction is issued. The data about each finished instruction are stored in the database for further analysis and control of the entire technological processes over an extended period of time.

Conclusion

As can be seen from a literature review, the augmented reality is an attractive research field for industrial applications. Due to the continuous advent of mobile hardware this technology become widely applicable in different areas of industry. Special attention is devoted to the usage of AR in occupational safety where some concrete application have been already shown. We present an occupational safety framework based on augmented reality aimed at preventing risk and injuries by issuing work and occupational safety instructions directly at the workplace.

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Barriers and Benefits Towards Sustainability Driven Business Models

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Introduction

Debate on sustainable development in manufacturing and business dates back to mid-twentieth century, which rose into prominence with growing environmental concerns. Over time, the concept of sustainability has been tagged with the various operations of industry, business, and society, which became a part of ethical governance. Sustainability and efficiency in business domain are considered as socio-political ethical parameters to measure the public performance of businesses today. However, the concept of sustainability in business still remains obscure and theoretical as not much efforts have been put in implementing sustainability plans in business through public-private partnership. Generating social awareness and civic consciousness, about eco-friendly responsibilities and consumption patterns under the broad framework of green consumerism, has yet to taken to the heights of industrialization. Though sustainability in business has been achieved to a large extent through social and workplace engagements in developed economies, the benefits of sustainability in business is yet to be realized fully in the emerging markets. Sustainable development in business can achieve its potential by integrating stakeholders into the planning and measurement systems of business enterprises. The terms of reference for sustainability in business need to be made obligatory by the governing authorities and articulated by the business leaders at the level of their organizations.

Innovating sustainable business model is about creating superior customer- and firm value by involving stakeholders and market players such as supply chain and packaging partners. Sustainable business model of a company addresses societal and environmental needs in through integrated business operations. For example, the Finnish oil refiner Neste uses sustainable and renewable raw materials for its fuels, and produces premium quality traffic-fuels that generate 90% less emissions than conventional fuels. Neste provides environmental training across all its sites and ensures that the palm oil it uses is certified by the 'Roundtable on Sustainable Palm Oil'. Sustainability enables business strategy to grow in the company in general and as an integral part of its corporate responsibility plans in particular. In industrial products manufacturing companies alike Neste, safety management and practices, and increasing the use of waste and residues in the production of renewable products are administered as topical strategic focus areas. These areas require sharing of competence and cooperation across inter- and intra-organizational infrastructures (Bocken *et al.*, 2019).

Business models in manufacturing companies require a purposive design to deliver desired sustainability impacts in the society and industry. 'Ecosystems' of different business models are specific to the purpose and the corporate goals of the companies. Some companies that grow with social innovation objectives have a greater number of qualitative designs encompassing social needs, stakeholder education, user value generation, and bridging the corporate social responsibilities. Social sustainability manifests itself in corporate culture, organizational behavior, and functional practices of companies. Some aspects of socially sustainable culture demonstrated by European companies can be well correlated with their corporate reputation and financial success. The success-driven social sustainability dimensions of corporate culture include sustainability strategy and leadership, mission, communication and learning, social care and work life, and loyalty and identification. In addition to other indicators related to measure the business performance of a company, the above mentioned indicators are taken into consideration for a company to be classified as financially successful. Thus, companies and stakeholders intending to manage social sustainability proactively need to undertake participatory projects with key partners and stakeholders on cultural change and development initiatives towards sustainability (Schönborn *et al.*, 2019).

In order to create and measure the impact of sustainable business models on environment, society, economy and other key stakeholders; collaborative and longitudinal approaches over phased project timeline work better. Hence, a systemic form of sustainable business model can be developed to ensure clarity in propositions and constructs, and make geo-demographic expansion possible. Sustainable business models are spread longitudinally, so they are bound to face unforeseen risks which need to be managed in association with the stakeholders. However, companies must engage in mapping the performance of pilot business-experimentation models. Such performance maps of business sustainability models help companies combine economic, environmental and social components of sustainability, and integrate the concept of social and stakeholder thresholds into the logic composite index of corporate sustainability. Benefits could be associated with the concepts of carrying capacity, safe minimum standards and critical capital (Nikolaou *et al.*, 2019).

This article discusses the process of designing and management of sustainability-driven business models in manufacturing and services companies. It contributes to research on sustainable innovation, design, and experimentation of business model. It argues the need for understanding ecosystems of different business models and integrating them on social and cultural foundations of the society. It also guides managers how to develop business model innovations to achieve the sustainability performance.

Literature Review

Companies have become social assets than just profit-making business bodies today. Companies increasingly emphasize on corporate social responsibility, governance on sustainability, and public-private participation for business-society wellbeing to

cater to social and environmental needs. Exploring strategic orientations towards the interface between business and society in order to influence organizations' sustainability performance has become a major challenge in the twenty-first century, as global community have gone critical on wider business-society nexus (Nijhof *et al.*, 2019). Business plans related to corporate sustainability have built a social sentiment across industries, which encourages companies to solve ecological, social, and economic problems. Such efforts require more resources, greater commitment, and higher stakeholder participation towards developing new products, new processes, or new organizational designs (Hahn *et al.*, 2017). The need of the hour is to develop robust strategic orientations with right stewardship to link business with society, and to draw an impact of business model innovations on sustainability performance and dynamic managerial capability.

Most manufacturing companies are revising their business models in accordance with the shifts in societal-, stakeholder-, and regulatory requirements. Business model innovation has emerged as a key advantage for companies to augment financial- and sustainability performance. Emerging companies acquire capability to move into new business models rapidly and successfully by exploring involvement of stakeholders in creating mutual values. Cognitive dimensions (knowledge, emotions, and self-image congruence) and corporate resources (budgetary allocations, collaborative business models, stakeholders) are important determinants to achieve sustainable competitive advantage for companies (Geissdoerfer *et al.*, 2018). However, using new technologies in sustainability programs is often difficult for companies, as there remains a wide gap between the diffusion and adaptation of technology under various social and cultural conditions. Technological advances towards sustainability are incremental and many companies find it difficult to meet their sustainability targets. Innovation in business models help to align social and stakeholder benefits, and revenue stream management to leverage sustainable solutions (Rashid *et al.*, 2013).

Business model innovations tend to yield higher returns than product or process innovations (Lindgardt *et al.*, 2009), while sustainable business models might deliver value added community benefits. Such business models not only add societal and stakeholder values, but also help in exploring business diversification with sustainable growth. Bio-mimicry companies aiming at industrial and community products have gained high growth and performance over time and expanded geo-demographically with several co-creation opportunities. Bio-mimicry driven business models in construction industries have helped companies to grow sustainable. The construction industry has significant and adverse impacts on the environment such as pollution, high-energy consumptions, amongst others (Oguntona and Aigbavboa, 2017).

Successful businesses in manufacturing and service sectors tend to understand the challenges and opportunities linked to business transition towards sustainability in a society today. They disseminate awareness in the society on sustainable products and services on environment and green consumption perspectives. Companies are able to innovate sustainability-linked business design in context of their focus on corporate social responsibility and build business models that are functional in this context (Franca *et al.*, 2017). For example, Nestlé links its business models with the sustainability projects on improving environmental performance focusing on water conservation, reducing food loss and waste, organic cultivation of coffee and food grains, and managing climate change effects at local levels. Large companies develop a strategic sustainability framework within the business model canvas. However, during this process, the business case of sustainability is often not understood profoundly by the companies as the scope of vision and system of business planning are inadequately managed. Business model innovations in a company thus aim at achieving sustainability impact on society and stakeholders by improving the organizational competence to bring people together into systematic public-private ventures. However, such corporate efforts are slow and complex (Birkie, 2018).

Companies with focus on sustainability-linked business development plans can be successful in the long term by creating value for both stakeholders and society through a holistic approach. This approach is defined as Creating Shared Value (CSV), which serves as the fundamental guiding principle for consumer-centric companies. Through CSV, sustainable development can be easily integrated into business activities. Such business models with sustainability focus is increasingly attracting long-term investors and involving unrelenting stakeholder participation. CSV brings business and society together by generating values for the local livelihood economy, global economic concerns, and value for society. Sustainability-linked business model innovations span beyond ecological and environmental protection perspectives, and cater to foods and nutrition, health, and social wellness dimensions. These extended objectives of sustainability-linked business model innovations serve as value added solutions towards creating a better civilization on the planet by improving the quality of life and human participation. Under such business models, partnerships between government, people, and companies are formed to create shared value, which functions as institutional frameworks for the development of sustainable agricultural production, rural non-farm industries, renewable energy, water, and silviculture (Senevirathna, 2018). Rural development programs for farmers offer commercial differentiation to consumers in developing countries. These programs are the responsible stewardships on managing sustainable natural resources like land fertility and water conservation; and help in reducing production costs and securing supplies for agri-business companies.

Successful business model innovation embedding objectives of sustainability attract global investors, funding from international organizations, and political and technological support for effective implementation of sustainability projects. Long-term investors can ensure companies to employ adequate capital and human resources for carrying out corporate social responsibility (CSR) projects, which maximizes stakeholder value. These investors increase the value to stakeholders of CSR activities not through higher cash flow, but through lower cash-flow risk with effective implementation of the sustainability projects. CSR engagements of companies, with local impact on communities and stakeholders, are the key performance indicators used to measure the sustainability projects. The wider social impact on stakeholders, quality-of-life index, and environment protection objectives is the main driver that explains higher stakeholder value and operating performance of business model innovations with focus on sustainability (Byun and Oh, 2018).

In sustainability-driven business model innovations, transport ecosystems are more critical than other services domains as the transport systems contribute to the greater environmental degradations than natural resources. Carbon emissions, partial pollution, and air quality deterioration are widely caused by the unregulated transport services. In order to reduce the transportation-related environmental degradation and to improve sustainability in the transport services industry, the shared 'logistics business-model innovation' has geared-up global concerns. This new economic model has been supported by technology that gives companies, people, and other players in transport services industry an opportunity to share and monetize the excess capacity of their assets comprising vehicles, houses, parking spaces, *etc.* It is an innovative initiative aimed at wider effects on sustainability. However, potential effects of this model are difficult to quantify, but it has been ventured that this new economic relationship would yield greater efficiency to businesses across the world, especially in the supply chain and city logistics processes. Application of the shared economy model to logistics brings up concepts of logistics sharing capacity. Logistics sharing capacity assumes the access and sharing of operational capabilities, either by pooling transportation services, by vehicle capacity sharing, sharing warehousing or infrastructure sharing, and leads to improved environmental sustainability in the region (Melo *et al.*, 2019).

The transformative business sustainability (TBS) model has emerged as an innovative model of stakeholders and sources in sustainable business practices, which helps companies in building an interface with stakeholders, and exchanging plans of resource residuals. TBS model of sustainable development complements and emphasizes the importance of commitment to far-reaching goals through corporate leadership in critically manifested areas of strategic priority such as energy, water, soil conservation, air quality control, organic farming, and managing non-biodegradable waste. Such transformation business models purposively respond to current and future environmental regulation and social needs involving stakeholders and all market players. In recent developments, efforts aimed towards business sustainability and application of sustainable business practices have expanded beyond corporate initiatives, which involve interfaces and interactions between stakeholders, market players, and sources (Wagner and Svensson, 2014).

Although business models of any type, whether innovative or transformative, deliver desired impact on sustainability; few tools that assist in sustainable business modeling need to be categorically identified by the companies to measure their impact on society, stakeholders, key partners, and targeted resources (land, water, energy, environment *etc.*). New businesses intending to create sustainability-linked business models focus on balanced social, environmental and economic value. A value-mapping tool thus need to be developed for each sustainability project to help companies create value propositions. A multifaceted value-measuring tool supports sustainable business modeling on three forms of value (captured value; disguised value either missed, destroyed or wasted; and opportunity) and four major stakeholder groups including environment, society, customer, and network players (Bocken *et al.*, 2013).

Business model innovation for sustainability, therefore, can be defined as innovation that creates significant impacts for the environment and society through changes planned by an organization to create value-network among stakeholders, market players, and companies. Business model archetypes embed one or more sustainable development projects as goals of the company for creating and delivering social values. Minimum viable archetype models for sustainability focus on value proposition in products- or services-deliveries designed to provide maximum possible usable life, and on providing environmental and social sustainability. Most consumer-centric companies are offering consumer education on the use of the sustainable products and services to add long-term economic gains (Birkie, 2018).

Business Model Innovation

Business model innovation (BMI) with focus on sustainability is beyond simple discovery of new mode of value proposition, value capture and value creation, as the process involves stakeholders to explore social and environmental needs in association with the companies. Business-to-consumer companies give priority to resolve environmental effects of their products and services on the society for innovating their business models. BMI allows the entrepreneurial firms operating at local level, also to reconfigure the value creation mechanisms and increase the performance (Desyllas and Sako, 2013).

Cognitive process of business model on sustainability is widely influenced by social and economic needs. The business model for recycling of polyethylene terephthalate bottles has different social and geo-demographic dimensions. Ecologically minded constructors in developing countries have decided to try to address the issue of low-cost and atmospherically-controlled housing by repurposing plastic bottles as a construction material. Plastic bottles have been used to build not only houses, but also water wells, raised bed gardens, and garden sheds. Beverage manufacturing companies have also come-up with similar theme to address in their social sustainability projects (Twumasi and Oppong, 2017). In a socio-commercial innovation, 'pickup and drop' business model for sharing services within the circular economy, developed by automobile rental companies, became iconic as it meets the sustainability concerns in developed countries like the USA. Business models for sustainability have been proved to increase economic performance, and collaborative product recovery management in many African countries. These models are used to develop business strategies for people and companies with long-term socio-commercial objectives to sustain in the market. Sustainable business development models integrate three bottom line concepts: protecting environment, and improving economic and social performance (Ray and Mondal, 2017).

Business model innovation with focus on sustainability has the philosophy of giving more for fewer returns, unlike investing in business for profit. It is a featured concept of effective altruism adapted by companies to grow in the society. Corporate social responsibility has a latent sense of altruism, which is exhibited more apparently in the community than other socio-economic

services projects. Altruistic trend in companies show pro-social goals regardless of whether reputational incentives or returns on social investment are present (Simpson and Willer, 2008). Reciprocity is an underlying driver of social sustainability, which tends to bridge the gap between business and society. The principles of reciprocity build social sustainability by increasing trust and cooperation among people in the society, and stakeholders and employees of the company. From a difference perspective, organizational and societal social sustainability are mutually reinforcing in the long-run, and they stay discrete over time and space. Such connectivity between the sustainability concerns of society and business explains a complex relationship (Roca-Puig, 2019). However, quick reciprocity in sustainability based business models is a far cry.

Business model innovation embedding sustainability projects broadly moves through four stages: conceptualization, determining key indicators, drafting business model innovation, and sustainable consumption. The canvas of business model innovation is exhibited in Fig. 1, which illustrates that corporate goals for working on sustainability projects should be profoundly connected with the society and stakeholders. Sustainability projects are commonly long-term projects and need longitudinal evaluations. Therefore, adequate allocation of resources (capital, human resources, and technology) is one of the critical requirements in business model innovations. Though businesses are increasingly adopting sustainability, the environment continues to decline. One the most critical reasons of failure of sustainability projects is their inability to integrate micro and macro perspectives of sustainability. Corporate sustainability and environmental management can be determined as macro factors, while corporate social responsibility and sustainability development are micro aspects, as they are need based and involve community. Thus, corporate social responsibility and sustainability development should be addressed together by companies over and above a simple business case (Landrum, 2018).

Companies need to explore opportunities for sustainable social development and value perceptions in order to connect stakeholders and business models. Sustainable social development has widespread issues, and its outreach has both latitudinal (geo-demographic or spatial) and longitudinal (over time or temporal) effects (Hervani et al., 2017). Sustainable social development is a blend of social and environmental goals. Therefore, pursuing social goals is generally associated with higher environmental impacts; though interactions differ across geo-demographic segments and depend on specific target-oriented goals. Although efforts by high- and low-income groups are needed in developing and implementing sustainable social development projects, companies need to reinforce the social needs and encourage participation also by involving non-governmental organizations. Given the importance of both social and environmental sustainability, the sustainable development goals laid by United Nations need to be clearly understood by companies to develop business model innovations (Scherer et al., 2018).

There are several ways to link sustainable social development with the corporate business models, as shown in Fig. 1. It ranges from environmental conservation projects to reduce the depletion of natural resources. Consumer centric companies are engaged in sustainable agriculture, developing green by-products emerging from ecological conservation projects. In developing countries, sericulture (silk farming using silkworms), worm farming (role of earthworms in soil fertility and soil structure), and apiculture (beekeeping and extraction of honey and natural paraffin) have risen into prominence as an outgrowth of silviculture and sustainable farming projects. Stakeholders contribute significantly in developing sustainability projects with the companies, and in carrying out the implementation of projects at the field level. Accordingly, stakeholders collaborate, co-create, and co-manage

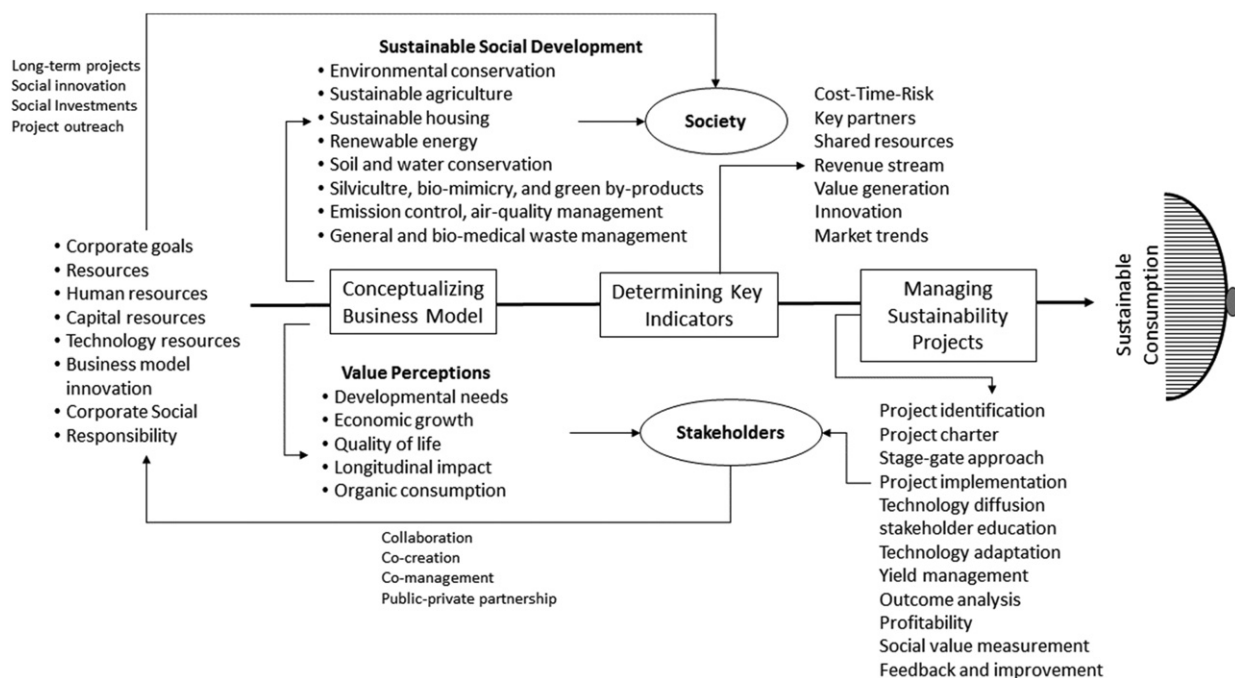


Fig. 1 Business models with focus on sustainability. Source: Author.

sustainability projects. Value perceptions of sustainability projects integrated into business model innovations are closely associated with the development needs, economic growth, and quality-of-life improvement of society in general and stakeholders of the company in particular. Sustainable social development projects have spanned over long time and their measurable impact is longitudinal.

The key indicators in developing business model innovation with focus on sustainability are largely profit- and market oriented. Companies grow with profit-making concerns, and cannot ever serve as non-governmental organizations or non-profit institutions. Companies look for return on investment made in sustainable social development projects sooner or later. Therefore, integrating sustainable social development projects into business model(s) is the only option for the companies. As the sustainability projects are embedded in the business models of companies, all elements on the business-modeling canvas need to be considered. Among the elements of canvas, measuring cost-time-risk (CTR factors), key partners, possible shared resources, predetermined revenue stream and its management, social value generation, investment on social-innovation, and analyzing market trends make significant contributions.

Business model innovation should clearly explain the implementation process of sustainability projects by clear project identification; developing a comprehensive project charter involving the stakeholders; and stage-gate process map demonstrating the spread of stages in the project and list of quality checks as gate for each stage in the project lifetime. Most companies invest in technology to drive sustainability projects. This task has two major challenges of technology diffusion and stakeholder education. Commonly, there exists a wide gap between technology diffusion and creating technology awareness, which causes low response among stakeholders on adapting to new technology. Technologies can be improved in a dyadic manner, both as 'learning-by-doing', and adapting the technology to local conditions. However, advanced technology has potentially greater returns on capital investment, and to 'learning-by-doing' to stimulate stakeholders for its adaptation (Lahiri *et al.*, 2018). Sustainability projects often deliver delayed outcome as the gestation period of such projects are prolonged. However, companies invest time and resources to achieve sustainable effects. For example, landscape designing in public places or common properties is a labor-intensive sustainability approach to landscape management. Projects must ensure to impart systemic knowledge on the sustainability benefits, and drive collaborative action between stakeholders and project owners (company). Collaborative design projects facilitate implementation of complex sustainability projects like community landscaping and biofuels management (Lucia *et al.*, 2018).

Marketing Sustainability Projects

Sustainability is a social concept, and sustainable products like green energy, organic products, and environmental services are social products. Linking sustainability to business models poses major challenge to companies on marketing of such social products, as they are off-stream, trigger voluntary consumption, and need to be backed thorough consumer education. Therefore, sustainability is broadly tagged with social marketing perspectives and challenges. Sustainability business models invariably incorporate marketing plans, which is referred as social, green, and critical sustainable marketing. Social sustainable marketing follows the logic of demand-driven marketing management and undertakes the responsibility for sustainable development outside the firm. Green sustainable marketing projects are initially oriented towards consumer education and develop proactive marketing strategies within existing institutional structures in the long run. Such marketing strategy guides sustainable development in the firm. Critical sustainable marketing aims for reassessment of assumptions of the existing market systems, which prevents social sustainability and green consumption behavior. Companies can achieve success in marketing of sustainable products and services by carrying out extensive sustainable development in society and industry (van Dam, 2017).

A new commercial reality in today's global marketplace is the rapid shift in consumer behavior due to the emergence of dynamic disruption of innovation and technology in consumer products on a previously unimagined scale of magnitude. Environmental sustainability and consumption of green products has driven the world towards converging openness, transparency, and commonality. However, most consumer-centric companies have shifted their strategy emphasis from sustainability to customization by reorienting marketing strategies on hedonic, functional, reliable, and utilitarian values; and low prices. They benefit from enormous economies of scale in production, distribution, marketing, and management. The growing concept of circular economy has given further boost to companies to adapt to the public-private policies of marketing sustainability driven products. Combining sustainable consumption with the circular economy concept could reduce the incidence of resource scarcity and climate change by reducing resource use and increasing cycling of products. To achieve sustainable consumption in a circular economy, production and consumption practices need to shift to sustainable measures. Business models can potentially influence both practices as they define how a company conducts business and shapes the company-consumer relationship (Tunn *et al.*, 2019).

Corporate consciousness on marketing of sustainable products has emerged in the early decade of twenty-first century by generating awareness among consumers. Such efforts have made a major impact on transforming the regional markets in setting vogue, cultural values, and social validity for multidimensional growth of companies. However, growing trends in consumption of eco-friendly, green, and organic products, due to social media effects and experiential marketing, have appeared to be strong catalytic elements in drifting consumer behavior. Growth of sustainability projects converging business-to-business, business-to-consumers, and consumer-to-consumer business models has been the most successful design of ecofriendly companies such as IKEA, Unilever, Panasonic, and IBM. However, some firms in a niche have also evolved organizational designs that signal a new way of resolving challenges within the sustainability-linked business models. For example, a South Korean organic food products company uncovers three consumption practices, which include investing in prolonged wellbeing, expressing sustainability values,

and building self-esteem and social status among consumers. A critical examination of consumer behavior on sustainable products reveals that they are close to modern luxury fashion consumption (Chung *et al.*, 2016).

Opportunities for sustainability-linked businesses through global to local markets are expanding due to the increasing consumer awareness, which is introducing radical shifts in consumption pattern and value perceptions of environmentally sustainable products. The fast-growing markets for sustainable products today have expanded from food portfolios to natural pharmaceutical products, and organic cosmetics to organic clothing due to changing perceived value, sustainability commitment, uniqueness, acquisition from known sources, and lifestyle changes. Ecolabel criteria mainly focus on ecological considerations in production. The connection between ecolabels and clothing designers is expanding rapidly in the developed economies. Many companies look to ecolabelling schemes as the means to set performance criteria and to demonstrate progress to customers (Clancy *et al.*, 2015).

Marketing of environmentally sustainable product suffers from INVUCA, which constitutes investment risks, new products and services management, market vulnerability, behavioral uncertainties of consumers, decision complexities, and ambiguity in marketing strategies. Conventionally, companies have adapted to sustainability-linked business models with a mindset of exploring opportunities to sell their products and services in the global markets. Such companies make cold calls on environmental issues; though they raise public or government funds for sustainable social development projects. However, most companies build their businesses by harnessing the best markets and consumer segments across geo-demographic territories with sharp external focus. Fig. 2 illustrates the cognitive map of consumer perceptions and factors determining consumption pattern for sustainable products.

Fig. 2 explains that companies need to understand consumers and markets simultaneously before setting sustainable products for launch. Cognitive determinants comprise perceptual values and social interface, which act as pull and push factors respectively for consumers to develop consumption preferences for sustainable products over time. Consumers derive perceptual values through 4As, which include awareness about sustainable products, availability within the proximity of consumers, affordability in the context of price and total cost to customers, and scope of adaptability of green products. In addition, perceived use value of consumes, based on perceived benefits, determines the cognitive pull factors. Corporate social responsibility projects implemented by food products companies, to educate consumers on the effect of sustainable and organic products on health and family wellness, have significantly increased consumer demand for these products. The social interfaces in reference to creating peer influence and community awareness, driven by effective corporate-social leadership and motivation, serve as push factors to develop consumption behavior towards sustainable products. Preferences of sustainable products sets a consumption pattern affected by the cognitive influence, linear process of knowledge, attitude and behavior, experience sharing by disseminating user generated contents, and self-image congruence.

Sustainable consumption pattern needed to support marketing strategies can be developed as an outgrowth of social innovation, involving non-governmental organizations in consumer education and production process. Companies intending to develop 'design to sustainability' business model can effectively create consumption eco-systems in the society. The consumption eco-systems guide companies to reinforce their business models in the existing and new markets through high corporate thrust and semiotics to enhance consumer outreach for sustainable products. Such backward linkage would help in building green supply-chain, retaining, and consumption options. In order to make this process effective, governments propose economic policies on sustainable consumption and eco-label certifications, help in creating consumer trust on sustainable products, and reinforce consumer preference towards their consumption. Following the above discussed process, companies can develop markets for sustainable products, and integrate marketing strategy into the business model innovation charter.

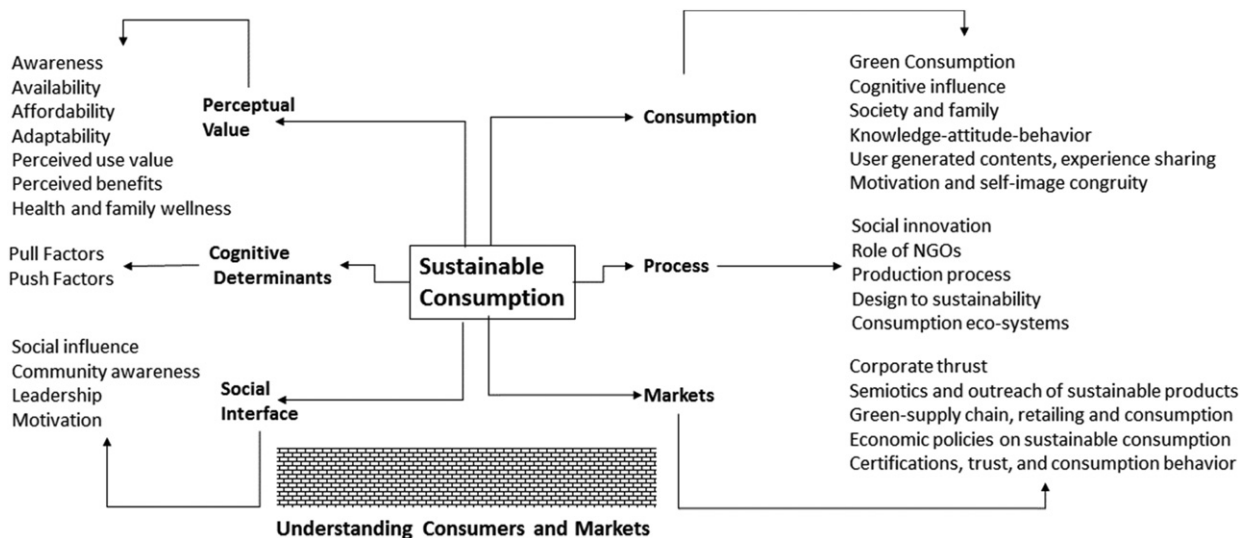


Fig. 2 Factors determining consumption pattern for sustainable products. Source: Author.

Rapidly growing technology-based companies harness the resources and ideas by crowdsourcing and analyzing industry attractiveness to achieve a large global footprint quickly. Moreover, operational complexity in the contemporary business environment is about the trade-offs between the social costs and corporate benefits. Therefore, managers need to find the optimal global footprint for their organization (Kerr, 2016). Customer, the end user, is the ultimate target for sustainable social products towards building aggressive and defensive strategies in business. The competing firms try to attract customers by various means to polarize business, and earn confidence in the market place. It is necessary for successful business companies to look for a place of business, which provides them more location advantage, and holds the customers for their goods and services. Business cordoning, or securing trade boundaries, is an essential decision to be taken for building competitive strategies to attack rivals across regions. Even a small business company can compete globally with firms of all sizes through the internet. In managing sustainable products marketing, the institutional and political patronage provides long-term support to the companies. Winning in product, channel and factor market place, in many instances, may not last long in building relationships with the customers. Many business firms have found themselves outmaneuvered in various functional aspects of business by the adept actions of rivals in the institutional arena (Rajagopal, 2016).

Social values are built on cultural dimensions and ethnicity. Egalitarianism and embeddedness of consumers in the society affect the business environment. Thus, companies develop social welfare policies as corporate social responsibilities, and build consumer values. Moreover, social values affect that individual ideological orientation on consumer attitudes towards industry, government policies, and consumer behavior (Arikan and Bloom, 2014). Technology shows significant positive impact on economic growth, while both human capital and technology are important determinants of growth in developing countries and emerging markets. Therefore, improvement of the educational sector, and more funding for research and development among developing countries are prominent considerations to monitor and measure business growth. Such conditions encourage innovations needed to facilitate sustained economic growth (Adelakun, 2011).

Companies invest enormous resources in consumer education to develop brand knowledge, product perceptions, and purchase intentions, using effective advertising, communications, and informal learning on the social media and community platforms. Consumer today buy solutions, not products *per se*. Therefore, consumer centric companies employ resources on consumer research periodically to understand and refresh the consumer needs and preferences. Accordingly, companies offer marketing solutions to consumer with competitive advantage to encourage acquisition and retention of profitable customers. A company in a competitive marketplace manages customers individually, demonstrating how its products or services help in solving problems of buyers and develop higher perceived value. Brand awareness, quality referrals, and sharing of brand experience reap enormous benefits in developing individual relationships with customers. To achieve these goals, companies must become aware of the different types of benefits they offer and convey their value to the appropriate executives in the customer company. Loyal customers display behaviors in a predictable manner, from growing the relationship and providing word-of-mouth endorsements to help company in acquiring new customers (Narayandas, 2005). Consumer behavior is governed by the following synchronized linear cognitive-materialistic-utilitarian relationship among other attributes:

- Knowledge, perception, attitude, and behavior
- Awareness, attributes, affordability, and adaptability
- Validity, value, venue, and vogue
- Engagement, explorative, emotions, and consumption experience

Most consumer centric companies tend to develop positive relationships with consumers to create sustainable buying behavior and perceived values. Consumer centric companies motivate consumers to use new products, perceive their use value, analyze value for money, develop consumption experience, and change their behavior. However, consumers often fail to develop sustainable consumption behavior as companies over-promise and under-deliver product values in the competitive marketplace. In addition, consumers irrationally conceive the product attractiveness, and overestimate their benefits, which causes dissatisfaction and withdrawal behavior of consumers. This leads to a serious behavioral dichotomy among consumers. However, companies can overcome this disconnect by mapping the easy sells, probable failures, complex growth, and co-created consumption experiences. Marketing strategies under each product category has a different ratio of product improvement and consumer value metrics. As companies realize an appropriate fit of products into this strategy grid, they can manage to streamline the consumer behavior, and reduce behavioral inconsistency among consumers. Accordingly, companies can encourage consumers to experiment new products, make improvements in the products to converge product-value with self-congruity of consumers, and reduce the impact of substitute products in the marketplace. Companies can also make their products compatible with substitutable goods by developing brand loyalty, and generating effective psychodynamics among consumer communities (Gourville, 2006).

Consumers commonly tend to generate comprehensive awareness on innovative attributes of products by measuring technology, product life cycle, and their complementarity with other products and services. Most consumers also realign their buying behavior in reference to their self-learned concepts developed out of their previous consumption experience. Consumers update knowledge about the attributes of competitive products. As a result, they learn about value additions, competitive benefits, price and promotions, and serviceability of products to develop purchase intentions. Buying decisions are largely affected by affordability of products in view of consumers' purchasing power. However, most consumer products companies and retailers attract consumers by offering credit support to enhance their purchasing power. Consumer cooperative stores, and delivery of products through public distribution system also augment the purchasing power of consumers. Consumer awareness about brands, analysis

of brand attributes, and their purchasing power required to buy them develop need-based or referred motivations. Such motivations help consumers in adapting to the brands. The quality of referrals, peer experience, and shared decisions also motivate consumers to use sustainable products and adapt them to the social value and lifestyle.

Summing-Up

Sustainable development is a multidisciplinary concept, which combines various fields of knowledge and action including economics, social justice, environmental science and management, business management, politics and global-local laws. It is a debatable domain to argue in real life and real time dimensions on what is required in the society, who are accountable to support the society, and how can the society-industry balance be maintained. Sustainability today has become an outgrowth of social innovation to deliver quality products and services towards sustainable consumption, environment protection, optimization of natural resources, and improving quality of life. As innovation is a key driver for sustainability; the industry players, social representatives, stakeholders, and government agencies are actively involved in diffusing innovation and technology in the society. Therefore, sustainable development is a persistent concern between the society and industry that requires people's action and stringent regulatory requirements from governments. Working on sustainable social development is a continuous process, and project trajectories are the paths, which fortify the development process through learning the behaving of stakeholders and society. It is a crucial element for holistically implementing the sustainable development through local-global innovations. This approach leads to exploring reverse innovation opportunities in social sustainable development (Silvestre and Țircă, 2019).

Society and governments have also looked to business corporations to support social sustainable development, as corporations have more resources than the other entities. Thus, they have always stood as engines for economic and social development. However, companies need to be more proactive in balancing their drive with social equity and environmental protection, though the corporate social responsibility and social sustainability projects discretely contribute to their profit. Besides sustainable production in the agricultural and industrial sectors, achieving sustainable development goals depends also on bolstering the performance of service sector, and improving access to specific services in developing countries. The level of economic development; openness to services trade, and social investment is positively related to financial, information communication technology, and transport services. Appropriate convergence of the macro development factor with micro indicators (stakeholder behavior) in services sector also contributes in achieving the sustainable development goals. Reducing the restrictiveness of services trade policies can enhance performance of the service sector, as openness in services marketing is positively correlated with indicators of sustainable development goals (Fiorini and Hoekman, 2018). However, sustainability concept in business has received mixed reactions due to the latent barriers and benefit that often raise questions on continued investment on sustainable social development. The common barriers and benefits in carrying out sustainability projects are exhibited in Table 1.

Sustainable development as a concept of societal development encompasses some problems that need to be addressed carefully. It can be viewed from the Table 1, that common barriers to implementing sustainability projects are conflict of interest,

Table 1 Barriers and benefits in implementing of sustainability projects

Process	Accountability	Barriers	Benefits
State planned projects	Partially of companies and government	● Project charter and administration ● Resource flow and performance audit ● Transparency in decisions ● Stakeholder engagement	● Long span of projects ● Corporate involvement ● Understanding social dimensions and stakeholder perceptions
Company owned projects	Social-cultural teams within company	● Large volume of financial and human resources ● Non-profitability and longitudinal projects ● Monitoring of sustainability projects	● Creating stakeholder value ● Compliance with government rules ● Tax benefits ● Building corporate image in society
Co-created projects	Public-private partnership	● Lack of clarity of goals ● Public commitment and task management ● Social conflicts and litigations ● Local politics and interventions ● Difficult in monitoring and evaluation of projects due to conflict of interest	● Low pressure on business operations ● Democratic decisions ● Use of voluntary manpower ● Public interest in social development
International alliance projects	Triangular accountability-government, international agency, and company	● Convergence of goals from international to local development concerns ● Operational difficulties due to local laws ● Financial controls and capital workflow ● Commitment, bureaucratic interventions, and goal realization ● Socio-political ideological disruptions	● Availability of funds ● Predetermined goals and project charter ● Clarity of tasks and operations ● Systematic monitoring and evaluation ● Rewards and recognition

Source: Author.

commitment, political intervention, and bureaucratization, irrespective of the ownership of the project (government, companies, public, or international agencies). However, there are prolonged benefits from sustainability project to society, but business companies always feel the pinch of high investment for marginal benefits in the long term. The barriers in sustainable development categorically relate to political, financial, and technological limitations. Besides, social and individual lifestyle patterns reduce environmental impact, sustainability concerns, and green economy benefits. Social accountability of sustainability project is one of the major challenges to governments and business houses. It can be stated that implementing sustainability projects is no longer based on goodwill of individuals, but has emerged as responsibility of the entire generation (Mikulcic *et al.*, 2019).

Contribution of sustainable development to corporate sustainability is bi-dimensional. Firstly, it helps leave the areas that companies should focus on: environmental, social, and economic performance towards their commitment to the society at large; and secondly, it provides a business-blended societal goal to work with ecological, social, and economic sustainability projects. However, sustainable development by itself does not provide necessary arguments for why companies should care about these issues. Those arguments come from corporate social responsibility and stakeholder theory. Over the years, there has been intense debate on when stakeholder pressures are effective in driving firms to contribute to sustainable development. Reviewing the institutional theory and slack resources theory, it may be stated that country-level sustainability performance interacts with low- or idle resources in shaping corporate responsiveness to stakeholder pressures (Xiao *et al.*, 2018).

Social institutions play significant role in nurturing cultural heritage which is reflected in individual behavior. Such institutions include family, education, and political structures; and the media affect the ways in which people relate to one another, organize their activities to live in harmony with one another, teach acceptable behavior to succeeding generations, and govern themselves. The status of gender in society, family, social classes, group behavior, and age groups; and how societies define decency and civility; are interpreted differently within every culture. Social institutions are the systems of regulatory norms and rules in pursuit of predetermined goals within the ultimate common value system of a community. An international marketer should evaluate the psychographic and demographic profiles of consumers that indicate the target market of urban and ethnic groups. The firm may choose to provide the marketing communication to the target segments close to their lifestyle (Rajagopal and Zlatev, 2017).

Technological changes are the main impetus behind exploring new opportunities for sustainability and social development advancements. The extent of such change may be explained from hybrid technologies to the appropriate and intermediate technologies. Strategic choices have wide-ranging ripple effects in the organization that determine the key success factors and growth performance or otherwise. Some companies make right strategic choices by improving the implementation process of sustainability projects and reaping long-term advantages. These companies are guided by shared strategic vision, and are driven by responsive attitude towards the sustainability requirements. They emphasize the continuous strive to satisfy the stakeholders. A strategic vision in sustainability may be understood as the guiding theme that explains the nature of business and the future social relations with the industry and governments in general. Such intentions on taking forward the sustainability projects depend on collective analysis of the environment that determines the need for new developments or diversifications. The vision should be commissioned on a concrete understanding of the business and the ability to foresee the impact of market forces on sustainable social development and growth of business. This vision motivates the organization for collaborative business planning and implementation of sustainability projects. Powerful visions are also the statements of intent that create an obsession with winning the socio-commercial goals of the business organizations.

See also: Green Energy Fuel From Biomass and Sea Water. Low Carbon Economy for Sustainable Development. Renewability Assessment of a Production System. Sustainable Biodiesel Production. Sustainable Production and Consumption – Business Perspective. Toyota Production System – Monitoring Construction Work Progress With Lean Principles

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Biodegradable and Recyclable Packaging Materials: A Step Towards a Greener Future

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Introduction

Packaging a science, workmanship and technology used to ensure the item with appropriation, convey nutritional data and present the item to buyer (Ojha, 2015; Meena *et al.*, 2017). Different materials are used for packaging in combination with more than one material in the form of metals, glass, wood, paper or pulp, plastic or composite (Kumar and Gupta, 2012). Most of them are enter in the municipal waste streams at the end of their service life (Gale, 2002). Major segment of packaging in India and around the world, are flexible packaging and laminates that is composed of different synthetic plastic. The wide usage of plastic packaging has caused concerns about environmental problem in the world (Green and Tonjes, 2014).

Plastic packaging materials include (polypropylene), polyester (PET), polyethylene, polystyrene and other petroleum-based polymers. Although, a large part of plastic is recyclable in most of the countries. Technically, consumed plastic packaging waste is rarely recycled due to technical and economic constraints. About 1 million tons of plastic wastes are produced annually in China, but about 20% of it is recycled (He and Nie, 2011). A foremost proportion of used plastic remaining waste which is either deposited mainly in landfills or contributes to litter on our roadsides (Gomez and Michel, 2013). The continuous use of synthetic plastic in the form of wastes is raising the general global concerns and makes a bad impact on the environment. These problems arise due to limitations of satisfactory landfill, burning of packaging waste that leads to generation of toxic air pollution.

Biodegradable polymers are specific type of polymer that breaks down through the action of naturally occurring micro-organisms, such as bacteria and fungi, over a period of time result in natural by products such as gases (CO₂ and N₂), water, biomass and inorganic salts. A few biodegradable materials, for example, starch, cellulose, chitosan and so on are utilized for bundling purposes (Table 1). The new and current pattern is to utilize of various biopolymers, for example, starch-PLA mixes; starch-PCL mixes and so forth which are semi-manufactured in nature (Meena *et al.*, 2017).

Classification of Biodegradable Polymer

Natural Biopolymer

Starch-based plastics

The main source of biodegradable plastics is storage of cereals, legumes and tubers, polysaccharide i.e., starch which is a renewable and widely available raw material. A challenge for the development of starch materials is the brittle nature of blends with high concentrations of starch. Plasticizers like glycerol, other low-molecular weight polyhydroxy compounds, polyether and urea are added in blends to overcoming the brittleness of starch for achieving full biodegradability in blends. Plasticizers having property to lowers the water activity thereby limiting microbial growth. Thermoplastic starch (TPS) can be formed by application of thermal

Table 1 Raw materials for biodegradable packaging material

Raw material	Origin	Advantages	Disadvantages
Chitosan	Chitin derivative	Antimicrobial and antifungal activity Good mechanical properties Low oxygen and CO ₂ permeability	High water sensitivity
Zein	Maize protein	Good film forming properties Good tensile and moisture properties Antimicrobial and antifungal activity Good mechanical properties Low oxygen and CO ₂ permeability	More brittle which can be overcome by using plasticizers
Gluten	Wheat derivative	Low cost Good oxygen barrier Good film forming property	High sensitivity to moisture Brittle
Whey protein isolate	Cheese derivative	Good oxygen and aroma barrier	Moderate moisture barrier

and mechanical energy and addition of plasticizers which is used as substitute for polystyrene (PS). When starch is modified to form films that provide adequate mechanical properties of high percentage elongation, tensile and flexural strength, it works as effective packaging material. Starch is modified through either plasticization blending with other materials, genetic or chemical modification or combinations of different approaches. These starch-based thermoplastic materials such as, polyethylene vinyl alcohol or polyvinyl alcohol, polycaprolactone have found wider industrial applications ranging from extrusion applications, injection moulding, blow moulding, film blowing and foaming (Mensitieri *et al.*, 2011).

Cellulose and derivatives

Cellulose is the most richly occurring natural polymer on earth and is an almost linear polymer of anhydroglucose. Due to its hydrophilic nature, insolubility and crystalline structure, its use is very difficult but is a cheap raw material. To prepare cellulose or cellophane film, cellulose is dissolved in an aggressive, toxic mixture of sodium hydroxide and carbon disulphide ("Xanthation") and then recast into sulphuric acid. The produced cellophane is very hydrophilic and moisture sensitive, but it has good mechanical properties. To improve barrier properties Cellophane is often coated with nitrocellulose wax or PVdC (poly vinylidene chloride) and in such form it is used for packaging of baked goods, processed meat, cheese and candies. Commercially a number of cellulose derivatives are produced, mostly carboxymethyl cellulose, methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose and cellulose acetate. Cellulose acetate is widely used in food packaging (baked goods and fresh produce). These are processed by laminating, injection or extrusion moulding and exhibit good film forming properties.

Proteins

Proteins can be divided into two categories one is proteins from plant origin (e.g., gluten, soy, pea and potato) and another included proteins from animal origin (e.g., casein, whey, collagen and keratin). The major drawback of all protein-based plastics, apart from keratin, is their sensitivity towards relative humidity. Blending or lamination with other biobased materials may overcome this challenge with lower sensitivity towards humidity.

- *Casein*

Casein is a milk-derived protein. It is easily processable due to its random coil structure. Materials can be made with mechanical performance varying from stiff and brittle to flexible and tough performance, upon processing of material with suitable plasticizers at temperatures of 80–100°C. Casein melts are highly stretchable making them suitable for film blowing. In general, casein films have an opaque appearance. Casein materials are not soluble in water but they show approximately 50% weight gain after 24 h of immersion. Casein is used as a thermoset plastic for buttons and for bottle labelling.

- *Keratin*

Keratin is cheapest protein. It can be obtained from extraction of waste streams such as hair, nails and feathers. Because of its structure and a high content of cysteine groups its processing is difficult. Fully biodegradable, water insoluble plastic is obtained after processing.

Synthetic Biodegradable Polymer

Synthetic biodegradable polymers are the synthetic ones with hydrolytically unstable linkage in backbone. This is accomplished by utilization of functional groups (for example esters, amides, anhydrides and ortho-esters). Their application in field of packaging is most suitable. For the most part aliphatic polyesters are the dominants of this category.

Aliphatic polyesters

Aliphatic polyesters are most widely studied class of biodegradable polymers, due to their important diversity and its versatility. Basically two routes i.e., polycondensation and ring opening polymerization guiding to the development of synthetic polyesters. Polycondensation of bifunctional monomers specially yields low molecular weight polymers. Ring opening polymerization is favoured when high molecular weight polymers are needed. Most of the biodegradable polyesters are manufactured by means of ring opening polymerization of six or seven member lactones. The aliphatic polyesters are biodegradable in nature because of their hydrolysable ester bonds and approximately all aliphatic compounds are the high molecular weight biodegradable compounds.

- *Poly (glycolic acid) (PGA)*

PGA is an aliphatic polyester. It is crystalline, with a crystallinity of 45%–55% and consequently isn't dissolvable in most organic solvents. It has a high melting point 220–225°C and a glass change temperature of 35–40°C. It is prepared by ring opening polymerization of a cyclic lactone, glycolide. It has amazing mechanical properties. PGA has significant advantage of degradability through simple hydrolysis of the ester backbone in aqueous environment. The polymer is known to lose its strength in 1–2 months when hydrolysed and losses mass within 6–12 months.

- *Poly (lactic acid) (PLA)*

PLA It is a translucent aliphatic polyester prepared entirely from various natural sources found in great abundance like tapioca, corn, sugar beets wheat and etc. It is prepared by repeating units of lactide. It is a semi-crystalline polymer. The level of crystallinity is around 35%–40%. It is a recyclable thermoplastic as the structure doesn't frame crosslink (Yang, 2014). PLA is degraded by simple hydrolysis of the ester bond and does not require the bonding of compounds to catalyze its hydrolysis (Singh *et al.*, 2011). Different routes are used to obtain PLA. PLA, a thermoplastic polymer having high-quality, high-modulus and a hard polymer whose hardness is like acrylic plastic, is not solvent in water and it is totally degraded under compost conditions. It can be made from annual renewable resources so that the industrial packaging area or bio-compatible/bio-absorbable medical devices can provide articles for use in the market (Rasal *et al.*, 2010; Singh *et al.*, 2011). It is effectively prepared on standard plastics hardware to yield shaped parts, film, or filaments. PLA can accomplish excellent mechanical properties if high molecular weight PLA is used as compare to low or medium molecular weight. PLA polymers are materials that have high potential for packaging applications and generate a lot of interest in the packaging industry for its properties and earth-friendly biodegradability. PLA are resistance to oil-based products, seal ability at lower temperatures, and can act as flavour or odour barriers for foodstuffs. Lactic acid, the monomer of PLA may easily be produced by fermentation of carbohydrate feedstock. Carbohydrate feedstock may be agricultural products such as maize, wheat or alternatively may consist of waste products from agriculture or the food industry, such as molasses, whey, green juice, etc. PLA works as a packaging material it is depend on the ratio between the two optical isomers of the lactic acid monomer. When 100% L-PLA monomers are used it results in very high crystallinity and melting point, whereas 90/10% D/L copolymers result in polymerizable melt above its T_g and thus fulfils the requirements of bulk packaging by facilitating it's processing. The first biobased polymer is PLA and it can be shaped into injection moulded objects, films and coatings (Rasal *et al.*, 2010). PLA replaces high-density polyethylene, low-density polyethylene (LDPE) and polyethylene terephthalate.

- *Poly(lactide-co-glycolide) (PLGA)*

L-lactide and DL-lactide have been utilized for copolymerization with glycolic acid monomers (G). The different proportions of Poly (lactide-co-glycolide) have been commercially prepared. A copolymer with a monomer ratio of

25L: 75G monomer ratios – Amorphous polymer

80L: 20G monomer ratios – semi-crystalline.

- *Polyhydroxyalkanoate (PHA)*

PHA are normal, thermoplastic, aliphatic biogenic polyesters that can be naturally cumulated in microbial societies and they vary in their properties relying upon their chemical composition (homo-or copolyester, contained hydroxyl unsaturated fats).

Properties of PHA:

- Water insoluble and relatively resistant to hydrolytic degradation.
- Poor acid and base resistant but good ultra-violet resistance.
- Soluble in chloroform and other chlorinated hydrocarbons.
- Biocompatible thus suitable for medical applications.
- Sinks in water, facilitating its anaerobic biodegradation in sediments.
- Non-toxic.
- Less 'sticky' than traditional polymers when melted.

PHA is a carbon-neutral and important polymer that are bacterial polymer that could be created from numerous renewable carbon sources by microorganisms usually under unbalanced growth conditions, making it a sustainable and environmental-friendly material. At present, there is no competitive cost compared to fossil products.

Encouraging and intensifying research work on PHA is expected to increase its economic viability in the future. Because of mechanical properties of PHAs, they are suitable for substitutions of petro-chemically obtained plastics (polyethylene, polypropylene and so forth.), however as opposed to these item plastics PHA through natural microbiological mineralization, are totally degradable to carbon dioxide and water.

- *Poly-3-hydroxybutyrate (PHB)*

PHB is aliphatic polyester of D (-)-3-hydroxybutyric acid is one of the biodegradable PHA. In 1925 Lemoigne first discovered hydroxyacid (a linear polyester) in bacteria. It is cumulated in intracellular granules by a wide variety of Gram-positive and Gram negative organisms under condition of neutral supplement limitations other than the carbon source. Mostly microscopic organisms like *Alkaignes eutrophus* is utilized for production in which it act as a storage material. A nature of PHB is a linear, semi crystalline and has relatively high glass transition and melting temperatures, are not good features for packaging applications. That's why PHB is synthesized with various co-polymers such as poly-(3-hydroxyvalerate) (HV) leading to a decrease of the glass transitions and melting temperatures to improve flexibility. Current utilizations of PHB-based polymers or composites include the packaging industry, medicine, pharmacy, agriculture, food industry. The characteristics of biodegradability and biocompatibility enable PHAs to be focused in competitive special market sectors. Both PHB homopolymer and PHBV copolyester have been

getting commercial enthusiasm as a promising possibility for the large scale generation of biodegradable and biocompatible thermoplastics.

Properties of PHB:

- Eco-friendly, biodegradable
- Decompose into water and CO₂ by microorganisms
- They are composed of chain of 14 monomeric units.
- Usually molecular weight varies from 2 to 3 × 10³ kDa.
- A good substitute for synthetic plastic.
- Produced from non-replenishing sources.

This basic human friendly polymer has a place with an huge class of biopolymers by PHA and surely understood for their physico-compound properties as normal polymers. Their properties look like synthetic plastic, although the most attractive property of them is production and degradation which is contradictory to synthetic plastic.

● *Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)*

Among PHA class, the main biodegradable microbial polymer studied is a copolymer of hydroxybutyrate and hydroxyvalerate (HV). It can be produced by adding propionic acid to nutrient feedstock supplied to bacteria. Mixed carbon source is also used. PHBV is potential environment-friendly substitute for traditional plastics. Many groups have been reported about the structure, mechanical properties and biodegradability of PHBV as biodegradable plastics (Wang, 2005). PHBV is a highly crystalline polymer with a melting point of 108°C and glass transition temperature to the range from −5 to 20°C. The pure copolymer is also brittle and brittle less than PHB. Elongation at break is lower than 15% and elastic modulus is 1.2 GPa. The properties of copolymer can be modified by changing the hydroxyvalerate unit content:

- Melting point of the copolymer as well as the glass transition temperature and the crystallinity decreases as the hydroxyvalerate unit content increases.
- The impact strength increases and the tensile strength decreases with an increase of the HV units. Some of the properties of the PHBV range span convert polypropylene in to polyethylene. But PHBV properties can also be enhanced by adding normal polymer additives such as natural plasticizers, fillers, colorants, etc.

PHBV's have biodegradability, apparent biocompatibility are obtain from renewable resources and the main keys of their wide applications. Primary application areas in which these features connect with some market needs are:

- (1) Disposable personal hygiene: PHBV can be used as the sole structural material or as part of a degradable composite;
- (2) Packaging: PHBV could be used for films, blow moulded bottles, and as a coating on paper
- (3) Medical: Potential in reconstructive surgery and controlled in release fields due to PHBV's biocompatibility coupled with its slow hydrolytic degradation.

● *Polycaprolactone (PCL)*

PCL is obtained from crude oil and biodegradable thermoplastic polymer which is synthetic biodegradable polyester. It has a good resistance to water, oil, solvent and chlorine. Nature of PCL is hydrophobic, semi crystalline polymer and having a glass transition temperature (T_g) of −60°C. Its melting point between 59 and 64°C, dictated by the crystalline nature of PCL which enables the easy formability at relatively low temperatures. A semi-crystalline straight polymer is acquired from ring opening polymerization of ε-caprolactone in presence of tin relatively cheap cyclic compound. The number normal atomic weight of PCL tests fluctuate from 3000 to 90,000 g/mol and can be evaluated by the molecular weight. PCL crystallinity indirectly relies upon the molecular weight i.e., increment in molecular weight tends to decrease in crystallinity.

PCL is a semi-rigid material has a modulus in the scope of low-thickness polyethylene and high density polyethylene, a low elasticity of 23 MPa and has a high extension to break (more than 700 at room temperature). Several copolymers with lactide or glycolide have been developed to improve the degradation rate. PCL has an extensive variety of utilization zone, for example, packaging, therapeutic embed, and controlled drug delivery system framework, so the crystallization and the morphologic properties of PCL are essential. Crystallization is a important procedure due to the last properties of any polymer can be determined by the super structural and small scale space morphology and by large crystallinity. Added substances can be utilized to control the crystallization properties of PCL. Enzyme and fungi can easily biodegrade PCL. Hence, to improve the properties of the native polymer several co-polymeric systems containing PCL have been investigated due to the rapid degradation rate of PCL. Co-polymers of εcaprolactone with DL lactide have yielded materials having high rate of degradation (Alp et al., 2011).

Natural-Synthetic Polymer Blend

This category mainly consists of blends of aliphatic polyester with starch. Due to various disadvantages starch is unsuitable for many applications. These include brittleness in the absence of suitable plasticizers, hydrophilic nature of starch and poor water resistance, deterioration of mechanical properties upon exposure to environmental conditions like humidity, soft and weak nature of starch in the presence of plasticizers. Most of the synthetic polymers are hydrophobic and thermodynamically immiscible with

hydrophilic starch, thus mixing result in phase incompatibility and poor mechanical properties. Ideally, starch and the second polymer should be covalently bonded through existing functional groups or by introduction of new functional groups. One means to improve the characteristics of starch films is through the preparation of composites or blends with other materials such as fibres, nano clays or biodegradable polymers. Studies on starch/polyester blends have focused on the incorporation of starch in the polyester matrix to reduce production costs and maintain the biodegradability.

Starch and poly(vinyl alcohol) (PVA)

PVA is a synthetic polymer which is non-toxic, flexible, and biodegradable and dissolves in water. PVA shows outstanding mechanical and barrier properties and good biocompatibility with high thermal stability. It is also well-matched with starch. The physical properties of PVA, such as resistance, water solubility, thermal characteristics and gas permeability vary with the degree of crystallinity which is highly dependent on the degree of hydrolysis and average molecular weight of the polymer. PVA can be mixed with starch. A soil bacteria *pseudomonas can* completely degrade PVA but under the presence of plasticizer glycerol degradation of pure PVA is very slow. It is the largest synthetic water-soluble material formed in the world and biodegradable in nature and it is compatible to get easily blend with starch. Thus, starch/PVA blends is the most popular biodegradable polymer but it still lacks in mechanical strength and is hydrophilic in nature. The blend with 70% PVA and 30% starch shows the best mechanical strength. Upon addition of nano-filler the mechanical strength has increased significantly in all the samples. Sample with 70% starch shows maximum increase in strength compared to the unfilled sample (Sadhu, 2014).

Starch and PLA

Starch is rich in plants, for example, maize, wheat, potato, rice, and pea, and in this way it is easy and promptly available. Physical treatment of native starch, i.e., disruption of its granular structure, generates thermoplastic starch (TPS), which unfortunately has poor mechanical properties and are inappropriate for use as a polymer matrix. Therefore, it is predominantly used as cheap filler for biodegradable polymers. On the other hand, PLA (produced from the chemical treatment of native starch and sugar) is naturally biodegradable and compostable. PLA has excellent mechanical properties and can be processed using normal equipment and also makes it a promising bio-friendly replacement for many other petrol-based plastics.

Starch-polycaprolactone (PCL) blend

Aliphatic polyesters commonly have good processivity, thermal stability, excellent mechanical properties, good water resistance, and biodegradable thermoplastic polymers with dimensional stability. For achieving the better quality of the blends the compatibility between the natural polymer and the aluminium polyester should be increased and there has been a considerable progress in this regard. Among all biodegradable polymeric materials that are nowadays commercially available, blends based on destructured starch and hydrophobic synthetic polymers, like aliphatic polyesters, have received increasing industrial attention for using as commodity plastics. PCL is biodegradable synthetic polymer. PCL is usually modified by blending with resins or the type of starch used in the polymer blend significantly contributes to the blend resulting in properties for getting better processing and mechanical properties.

Starch-PHB blend and starch-PHBV blend

It was shown that poly (hydroxaclanateate) can make a mixture with polymers in which contain a proper functional group i.e., capable of hydrogen bonding or donor sensor interaction. The properties of mixing films with different ratios of starch are similar. For all samples the glass transition temperature is obtained which are semi-crystalline. A PHB/starch ratio of 70/30 (% wt/wt) has optimum tensile strength. In this particular case a beneficial cost reduction and improved mechanical properties as compared to pure PBB are occurred.

Biodegradable Versus Conventional Packaging Material

Biodegradable material are those material which can be easily decomposed by natural agents like water, oxygen, sun light, microorganisms, etc. These natural agents facilitate the decomposition by breaking the complex organic forms to simpler units. The decomposed matter ultimately mixes or returns back to the soil and thus the soil is once again nourished with various nutrients and minerals. Food waste like vegetable and fruit peels, dead plants and animals, chicken, egg shells, paper materials, garden waste etc., are comes under biodegradable substance. There are many biodegradable and recyclable packaging material alternatives available. These include:

- *Paper and cardboard* – Paper and cardboard is reusable, recyclable and biodegradable. There are a number of advantages in making of this type of product and its packaging and they are readily available. Many packaging manufacturing companies offer an environmental friendly option which has been created using a high proportion of recycled paper.
- *Corn starch* – Items made from corn starch are biodegradable and are ideal for items which have a limited use such as takeaway food. They are good options for all types of food packaging and also make good packaging 'peanuts' to protect and support items when sent through the post. Corn starch packaging biodegrades and has a limited negative impact on the environment.

- *Bubble wrap* – Bubble wrap is widely used as a packaging material. Environmental friendly alternatives include bubble wrap made from recycled polythene and bubble wrap which is completely degradable.
- *Bio-based foam* – Starch-based foam is used as packaging material because of its biodegradability the low costs and low density. Starch can be processed in different ways to make products containing certain properties similar to petroleum-based plastics. The main technical challenges with starch bio-foam have low elasticity, high hardness and high water absorption. To improve strength and water resistance, researchers have added coating with mineral fillers, wood fibre, resin, or wax to starch materials. Cellulose fibres can be used as additives in starch matrix to increase the strength properties such as tensile strength, stress performance, and toughness. In addition these fibres' or natural latex can produce synergistic effects to further improve the functional properties of bio-foam.

Conventional materials are those materials which cannot be broken down or decomposed by natural agents. These substances composed of plastic materials, metal scraps, aluminium cans and bottles, hazardous chemicals etc. It is reported that these things are practically immune to the natural processes and as a result cannot be fed upon or broken down even after thousands of years. Thus, these waste rather than returning back, contribute to solid waste which is very hazardous for the environment. The ever increasing load of non-biodegradable trash is a growing concern all over the world. That's why several countries are looking for eco-friendly alternatives that can minimize the threat on several land and aquatic life forms.

Biodegradable substances on breaking up are converted into simple organic matter and are thus assimilated in the soil and thus become a part of the carbon cycle of the atmosphere. In contrast, conventional substances are resistant to the environmental factors and never decompose and instead contribute to majority of the solid waste. Biodegradable substances can be decompose within a few days or months, whereas non- biodegradable items can take thousands of years or cannot be broken and as it remains in their original form. The costs of bioplastic polymers are generally still much higher than that of their traditional plastic counterparts (Tharanathan, 2003). Bioplastic polymers are hoping to become more valuable in the form of commodity material when an important mass is achieved.

Biodegradable plastics have easily degradable linkages like anhydride, orthoester, esters. Due to the presence of these linkages the molecular weight of the plastic drops down to 1000's from lakhs as a result of degradation. Microorganisms are capable of assimilating these low molecular weight organic materials whose molecular weight is less than 10,000 (approx) and release CO₂, H₂O, CH₄ as metabolic products on other hand non-biodegradable do not contain easily degradable linkages. Their main groups are hydrocarbon groups, amine groups, ester members with hindering groups to prevent easy degradation. So they stay on land without degrading for years. However, when these plastics degrade to molecular weight range of 1000s they will also be assimilated by biological agents as the case of biodegradable plastics. Biodegradable waste is used to produce energy manure, compost and biogas whereas conventional waste can be separated and recycled but the process is very expensive.

Need of Biodegradable Packaging Material

The different applications of Biodegradable material are listed in Table 2. Use of biodegradable material is necessary because of following reasons:

- Many environmental problems resulting from the uncontrolled disposal of plastic wastes can reduce by using biodegradable plastics. They are mainly suitable to recycling alongside organic wastes, as long as the plastics are 'compostable'.
- Biodegradable plastics are used to substitute conventional plastics that produce environmental problems either during use or at their end-of-life. Typical examples are indecently disposed of shopping bags, which can be harmful for sea life, or when conventional plastics packaging becomes contaminated by food, so making it more difficult to recycle.

Table 2 Current application of biopolymers

Packaging application	Biopolymer packaging material	Company
Potato chips	PLA bags	PepsiCo's Frito-lay
Yoghurt	PLA jars	Stonyfield (Danone)
Bread	Paper bags with PLA window	Delhaize (retailer)
Fresh cut fruits and vegetables	Rigid PLA trays and packs	Asda (retailer)
Coffee and tea	Cardboard cups coated with PLA	KLM
Beverages	PLA cups	Mosburger (Japan)
Fresh salads	PLA bowls	McDonald's
Organic tomatoes	Corn-based packaging	Iper supermarkets (Italy) CoopItalia
Milk chocolates	Cornstarch trays	Cadbury Schwepps
Sweets	Metalized cellulose film	Thomton
Organic pasta	Cellulose-based packaging	Birkel
Kiwi	Bio-based trays wrapped with cellulose film	Wal-Mart
Potato chips	Metalized cellulose film	Boulder Canyon

- Compostable plastic bags are also useful in the separate collection of food wastes from households and businesses. These bags can be fully embedded in composting (i.e., material recycling) processes, without causing any negative effect on the compost produced.
- The use of biodegradable products is not the only solution to landfill problems or to the world's environmental issues. However, it should be looked at as a part of the solution along with measures such as reducing consumption, reusing products and recycling.

Disadvantage of Conventional Plastic

- Every year about 100,000 animals such as dolphins, turtle's whales, penguins are killed due to plastic bags. Plastic bags ingested by many animals instead of food, and therefore die and the ingested plastic bag remains intact even after the death and decomposition of the animal. So, it lies around in the landscape where another victim may ingest.
- Conventional plastic contaminate beaches and oceans garbage has been discarded into the oceans for as long as humans have sailed the seven seas or lived on seashores or near waterways flowing into the sea. Use of plastic has increased drastically as a result a huge quantity of nearly indestructible, lightweight material floating in the oceans and ultimately deposited on beaches worldwide.
- Items made from Styrofoam and non-biodegradable plastic wind up in landfills by the ton every year. These products take centuries to degrade and when they do, they can leave toxic residue behind.
- Some of the constituents of plastic such as benzene are known to cause cancer. Plastic resins themselves are flammable and have contributed considerably to several accidents worldwide.

Biodegradation of Polymers

There is a change in polymer properties – tensile strength, colour, size, etc., – in the effect of one or more environmental factors such as heat, light or chemicals of polymer or polymer based product. These changes are usually unwanted such as it reduces the molecular weight of the polymer for changes in the use of products, cracking and depolymerisations, or more rarely desirable, in biodegradation or deliberately lowering the molecular weight of a polymer for recycling. These changes in properties are often called “aging”. Such changes in a finished product are to be stopped or delayed. However degradation may be useful for recycling/ recycling polymer waste to avoid or decrease the environmental pollution. Degradation can be intentionally induced to assist in determining structure. Polymeric molecules are very large (on molecular scale), and unique and useful properties are primarily the result of their size. Any loss in the length of the chain reduces the tensile strength and is the primary cause of premature cracking. Surgeries are most common in India. Mainly metal plates are reserved as the supporting material but now it is replaced by biodegradable polymer materials.

Biodegradation of polymers involves following steps:

- (1) Attachment of the microorganism to the surface of the polymer.
- (2) Growth of the microorganism, using the polymer as a carbon source.
- (3) Ultimate degradation of the polymer.

Normal soil bacteria and water are generally required which adds to the appeal of microbial reduced plastics. Polymers that are based on naturally grown ingredients (like starch or flex fibre) are susceptible to degradation by microorganisms. In the case of materials where starch is used as an additive for conventional plastic matrix and polymer is attacked by microorganisms when it comes in contact with soil or water. Microbes digest starch and leaving behind a porous, spongelic structure with a high interfacial area and less structural strength. When the starch component is minimal, the polymer matrix starts to degrade with enzymatic attack. Each reaction result occurs in the scission of the molecule which helps in gradually reducing the weight of the matrix until the whole material is digested. Another approach to microbial degradation of biopolymers involves growing of microorganisms for the specific purpose of digesting polymer materials. This is more intensive process that ultimately takes more costs and avoid the use of renewable resources as biopolymer feed stocks. The underlying microorganisms are designed to target and break down petroleum-based plastics. Even though this method decreases the volume of waste it does not aid in the preservation of non-renewable resources. Photodegradable polymer undergoes degradation from the action of sunlight. In many cases, polymers are photo chemically attacked, and break up into small pieces. After this the microbial degradation should be to achieve the actual biodegradation. Polyolefin (a type of petroleum based conventional plastic) polymers are considered to be the most susceptible for photodegradation The proposed approaches for further developing photodegradable biopolymers include incorporating additives that speed up photochemical reactions (e.g., benzophenone), modifying the composition of the polymers to include more UV absorbing groups (e.g., carbonyl), and synthesizing new polymers with light sensitive groups.

An application for biodegradable polymers which experience both microbial and photodegradation is in the utilization of disposable mulches and crop frost covers.

The suitable microorganisms are helpfully found in waste water treatment plants. Procter and Gamble has built up an item like Depart, named Nodax PBHB. Nodax is an antacid absorbable; implying that introduction to a solution with a high pH causes a quick basic breakdown of the material. Biopolymer materials which disintegrate upon exposure to aqueous solutions are advantageous for the disposal and transport of biohazards and medical waste (Kumar *et al.*, 2011).

Successful Examples of Commercial Packaging Products Made of Natural Cellulose Fibres

In recent years, different companies launched several fibre-based to replace traditional plastic packaging. These products not only have excellent functionality, but also maintain the underlying benefits associated with natural fibre which also includes biodegradability. Trayforma boards are used for food packaging from Stora Enso (Storaenso, 2017). They can be modified to different designs suitable for various applications. For example, the Trayforma boards used in making of bowls and plates which are made up of top layer (Kraft pulp), middle layer (Kraft pulp + CTMP), bottom layer (Kraft pulp); customer-designed coating may also be applied. Boards can be used as a basic packaging material for heating in a microwave or conventional oven. Södra has launched a bio-composite (Durapulp®), a mixture of cellulose pulp and the biopolymer polylactic acid (Södra, 2016). The bio-composite is suitable for many industrial applications such as moulding, air-laid, sheet or board, for packing food and consumer goods. VTT is developing fibre foam technology (VTT Technical Research Centre of Finland, 2017). The chief raw materials are wood fibre (virgin or recycled), while nanofibrated cellulose can be used to increase specific properties.

Carlsberg has developed Green Fibre Bottle products that can be used for beer (Didone *et al.*, 2017). Paper bottles are prepared by moulding and free of internal liner, and fully biodegradable. Using different bio-based coatings on paper substrate and 100% bio-based stand-up pouches with oxygen, grease and mineral oil barrier properties which is based on the enzymatic fibrillation of cellulose (HefCell) technology developed by VTT (Eagle, 2017). Recently the food service industries have switched to

Table 3 Several patents for biodegradable packaging

Patent	Description	Publication (Year)	References
A biodegradable bio-compostable bio-digestible plastic	Investigation propose a biodegradable bio-compostable bio-digestible plastic and a process for preparation thereof which improves polymer biodegradability/biocompatibility/biodigestion without the loss of physical strength, structural characteristics and also being recyclable in the main recycling stream should the opportunity arise without affecting the stream.	EP 3,162,841 A1 (2017)	(Ravi, 2017)
Biodegradable plastics, method for production thereof and use thereof	Investigation provide a plastic composition which is biodegradable and which does not discharge contaminants during incineration and to provide a plastic composition which does not leave plastic fragments after degrading.	US 9,637,608 B2 (2017)	(Rosen, 2017)
Biodegradable plastic from non-edible natural polymer	Provide a natural biodegradable polymer and its method of production and disclose a non-edible starch based biodegradable plastic composition.	WO 2017/056102 A1 (2017)	(Bali, 2017)
Biobased rubber modifiers for polymer blends	Described polymer blend compositions of polyvinyl chloride (PVC) or polymethylmethacrylate (PMMA) or polyoxymethylene (POM) with polyhydroxy alkanoates (PHAs) that have improved properties including but not limited to improved processability, impact strength, tear resistance, and toughness.	US 9,475,930 B2 (2016)	(Weinlein and Kann, 2016)
Bioplastics	Investigate biodegradable materials based on flours and polymers eg., starch and their thermomechanical processing.	EP 2,432,830 B1 (2013)	(Tangelder <i>et al.</i> , 2013)
Biodegradable disposable labwares for use in laboratories	Invention provide laboratory disposable Supplies which can be degraded in nature without causing environmental contamination while having superior chemical and physical properties for quality products and good processing characteristics applicable to injection/blow moulding.	US2012/0009103 A1 (2012)	(Liu, 2012)
Biodegradable plastic based on fruit waste powder mixture	Invention focus on biodegradable plastics having enhanced rate of biodegradability due to the presence of powdered fruit waste, such as skin and seeds from rambutan, banana, jackfruit and other tropical fruits.	WO2012/078021 (2012)	(Ismail and Aziah, 2012)
Biodegradable cleaner	A cleaning composition is provided in which each of the components of the composition is biodegradable, eliminating the need for the extensive disposal procedures required when discarding prior art cleaning compositions.	US 7,799,145 B2 (2010)	(Thompson, 2010)

biodegradable products made from vegetable and sugar substances such as sugarcane easily in the soil. Since they are made of naturally occurring materials, these products are easily broken into the soil.

Future Prospective for Biodegradable Packaging Materials

Biodegradable polymers are a piece of the bigger plastics market. In Table 3 different patents regarding biodegradable packaging are listed. Food packaging, dishes and cutlery constitute a major market for the product because these materials can be composted with the food waste without sorting, which is a enormous benefit to the waste management effort and to reducing food waste and packaging disposal in landfills. Increasing legislation and consumer pressure are also encouraging retailers and manufacturers to explore these biodegradable products and materials. In the bio-based biodegradable plastic market, there is approximately 66% of the packaging industry which is more than the others. It is expected that with the highest increase in Europe in 2020, the growth of bio-based plastic is high, followed by the United States, then South America and then Asia. Increasing urbanization and the total consumption of packaged products will increase in the expected dramatic increase of Indian middle class from 50 million to 583 million by 2025. The Indian retail market is the fifth largest retail destination globally and it has been ranked second in the most attractive emerging market for investment. Furthermore this the foreign direct investment in multi-brand retail will fuel the packaging industry in the coming years.

Conclusion

There are an unlimited number of such areas where biodegradable polymer material can be used. Environmental friendly polymers are required in areas of agriculture, automotive, medicine, and packaging. Each industry is able to create its own ideal material because the level of biodegradation may be tailored to specific needs. Biodegradable polymers will play a vital role in the packaging sector in future. Natural cellulose fibre's are bio-based materials that are suitable for packaging applications with good biodegradability and recyclability. Although they should be selected and processed according to the requirement of packaging products, keeping in mind the environmental, social and economic sustainability. When cellulose fibre's are used in starch-based foams, it can provide excellent mechanical, vibration and impact cushioning properties. Biodegradable bio plastics are most reasonable for organic waste treatment through industrial or domestic composting and potentially are subject to further demonstration in the anaerobic digestive system. They should ideally be separated at the household level from other, non-biodegradable materials and collects with organic waste, including food waste. The total quantities of waste sent to landfill are reduced and the composts generated can be used as valuable soil improvers by using these biological treatment methods. Bioplastic polymers have great potential to contribute to material recovery and reduction of landfill and use of renewable resources. Effective infrastructure for strict control of mass public awareness and certification, collection, separation and composting of these materials will be important for achieving these benefits in full.

See also: Biodegradable Packaging. Biodegradable Packaging Materials. Sustainable Future Alternative: (Bio)degradable Polymers for the Environment

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Circular Economy in the Built Environment: Designing, Deconstructing, and Leasing Reusable Products

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Introduction

The prevalent linear economy model, in which material components are fabricated, built, demolished, and dumped, is not sustainable due to material resource scarcity, energy consumption, emissions, generation of solid waste, and ever-increasing population growth and demand trends. In contrast, the circular economy (CE) model has emerged as a sustainable and alternative approach in which material components are fabricated, built, disassembled, and reused. The CE model aims at increasing material resource and energy efficiency, minimizing waste, and promoting low-carbon footprint. To achieve these goals, the CE model proposes the design of durable components that can be disassembled and reused multiple times in a closed-loop cycle.

The CE model has been inspired by core disciplines in sustainability science, most notably industrial ecology and cradle-to-cradle design. According to [Korhonen et al. \(2018\)](#), the main CE contributions to the body of knowledge are a shift towards sustainable production and consumption culture, the relevance of material durability, and the intertwine between shared economy and sustainable production. In the literature, a diversity of CE definitions exists. The Ellen MacArthur Foundation (EMF) has defined CE as an economy “that is restorative and regenerative by design and aims to keep products, components, and materials at their highest utility and value at all times, distinguishing between technical and biological cycles” ([EMF, 2015](#)). [Geissdoerfer et al. \(2017\)](#) attempted to conceptualize CE as “a regenerative system in which resource input and waste, emission, and energy leakage are minimized by slowing, closing, and narrowing material and energy loops. Such regenerative system can be achieved through long-lasting design, maintenance, repair, reuse, remanufacturing, refurbishing, and recycling”. Following the analysis of 114 definitions, [Kirchherr et al. \(2017\)](#) added that CE aims at accomplishing sustainable development and is enabled by innovative business models and responsible consumers. Even though applicable to any sector, the potential economic, environmental, and social benefits of the CE model can be maximized when implemented in economic sectors with massive material resource consumption, such as design and construction, an activity that result in the built environment that surrounds us.

Indeed, the construction activity represents a leading industry sector that accounted for 12.4% of the gross world product (GWP) in 2014, with such contribution to the global economy estimated to increase to 15% by 2030 ([Global Construction Perspectives and Oxford Economics, 2015](#)). The construction sector is a significant contributor to material resource and energy consumption, and solid waste generation. Construction includes the design and construction of what is commonly referred as the built environment (i.e., buildings, facilities, infrastructures, etc.) but has failed to devise strategies that prevent the demolition and corresponding generation of solid waste once a building, facility, or infrastructure reaches the end its service life. It has been pointed out that current material resource use rates in construction paired with global population growth and consumption trends will result in the scarcity of certain materials, such as steel and copper, which are prevalent in the built environment. However, steel and copper are highly durable materials, which implies that an opportunity for their reuse exists. It is important to clarify that the CE concept of reuse means the reuse of the product or component as is or through refurbishment or remanufacturing but without recycling. Recycling is the process of converting used or waste products into new products, and often requires the consumption of large amounts of water, energy, and the corresponding generation of greenhouse gas emissions. Thus, recycling does contribute to the conservation of raw materials but results in a higher environmental impact than the reuse or remanufacturing (inclusive of refurbishment) of previously-manufactured products. In addition, recycling can encumber highly inefficient steps. For example, it has been documented the shipping of scraps (i.e., recyclable materials) overseas just because of lower production costs. In such case, transportation generated greenhouse emissions and energy consumption that defeated the purpose of recycling from an environmental perspective. As such, the CE model observes recycling as an alternative only when reuse or remanufacturing are not viable ([Stahel, 2016](#)).

Designing products or components with an aim for them to be dismantled and reused is a core competency in the CE approach ([EMF, 2013](#)). Such a design practice is known as design for disassembly (DfD). In the built environment, DfD is also referred as *design for deconstruction* and enables the future disassembly (or deconstruction) of the built assembly with the ultimate goal to facilitate the reuse of their components or products. Complementarily, product-service systems (PSS) enable the collaborative consumption of products and services and thus represents an innovative relationship between supplier and user: selling function instead of volume. PSS focus on extending the services associated with a product complement the CE model with services such as leasing or sharing of products (as opposed to purchasing), in which the reuse of products is an inherent condition. In such PSS approaches, manufacturers are responsible for the maintenance of products, which enables reverse logistics (or take-back), repair, remanufacturing, and reuse. PSS offers building and facility owners highly efficient and sustainable alternatives to services without the burden of ownership and its high investment costs and corresponding depreciation.

Overall, the global problem of resource scarcity demands thinking beyond incremental changes in the linear economy. It demands a holistic, effective, and radical departure that effectively extends the life of construction components and products over

multiple uses. In response to such challenge, the simultaneous use of CE, DfD, and PSS in the built environment is often regarded as a synergistic combination that promises to promote closed-loop cycles while meeting customer and environmental needs in a cost-effective manner.

Circular Economy in the Built Environment

In their cited publication “Towards Circular Economy”, EMF identified construction and demolition (C&D) as a noteworthy opportunity for the implementation of CE. According to EMF, only between 20% and 30% of the C&D waste is recycled or reused, mostly because of the lack of focus on design for disassembly and reuse, which results in a “significant loss of valuable materials for the system” (EMF, 2013). EMF highlighted the central role of design in a shift towards CE:

“At its core, a circular economy aims to ‘design out’ waste. Waste does not exist—products are designed and optimized for a cycle of disassembly and reuse. These tight component and product cycles define the circular economy and set it apart from disposal and even recycling where large amounts of embedded energy and labor are lost” (EMF, 2013, p. 7)

According to Stahel (2016), designing products for reuse must become the norm, and the prefabrication of components and their modularization can be leveraged for that purpose. In modular design and construction, the building is produced in similar “modules” that are built off-site and put together on-site. The process of assembling prefabricated modules in turn offers an opportunity for designing such modules so they can be easily assembled and disassembled and reused in the future. Stahel (2016) claimed that the lack of education about CE and the corresponding fear of the unknown have also prevented its adoption, such that “as a holistic concept, [CE] collides with the silo structures of academia, companies, and administrations”. Urbinati *et al.* (2017) reviewed ongoing CE efforts in 86 companies from various sectors and locations around the world. Only 5 of those companies operated within the built environment. Within those, the authors found that the adoption of CE currently depends on the owner’s commitment and not so much on other factors such as company size, location, or market sector.

Fig. 1 illustrates key factors that, when combined, are prone to create the ideal conditions to promote the adoption of CE. Examples of top-down initiatives include offering market incentives for salvaged materials, increasing landfill fees to increase waste diversion and reuse, implementing take-back policies such as extended producer responsibility, offering credits for CE initiatives in green building rating systems, implementing tax incentives to reduce carbon emissions, and promoting education efforts. Examples of bottom-up initiatives include enhancing product durability, leveraging complementary strategies (such as DfD, PSS, prefabrication and modularization), increasing design collaboration among project stakeholders (e.g., owner, designer, contractor, trade partners) and between them and supply chain actors with advanced design technologies (e.g., Building Information Modeling [BIM]), leveraging tracking technologies such as radio frequency identification (RFID), and exploring CE initiatives within corporate sustainability efforts. Among those, this article focuses on the bottom-up strategies of DfD, reuse, and PSS.

Fig. 2 illustrates the difference between the linear economy and the CE model in the built environment. The linear economy model begins with the extraction of raw materials (e.g., mining, logging). These materials are then manufactured into products and

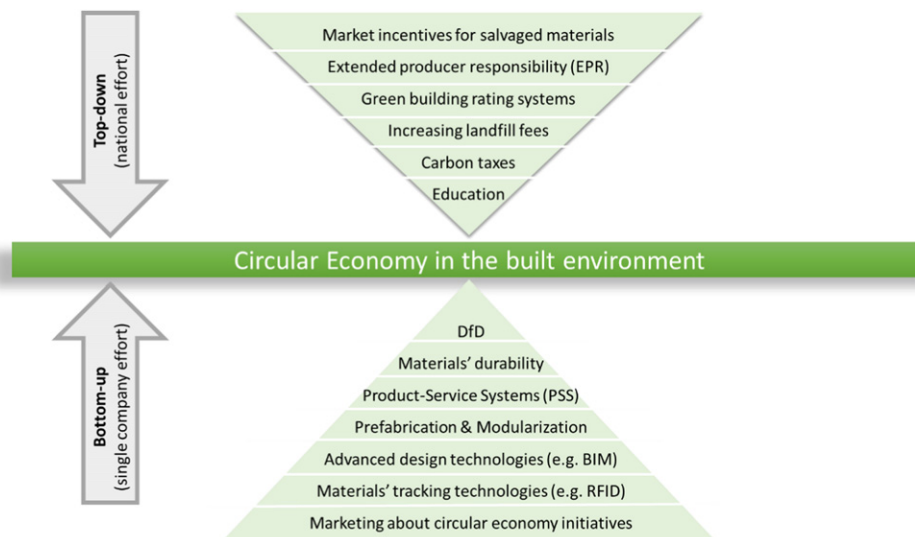


Fig. 1 CE implementation factors in the built environment. Reproduced from Cruz Rios, F., 2018. Beyond Recycling: Design for Disassembly, Reuse, and the Circular Economy in the Built Environment (PhD thesis). Tempe, Arizona: Arizona State University. Lieder, M., Rashid, A., 2016. Towards circular economy implementation: A comprehensive review in context of manufacturing industry. *Journal of Cleaner Production* 115, 36–51. doi:10.1016/j.jclepro.2015.12.042.

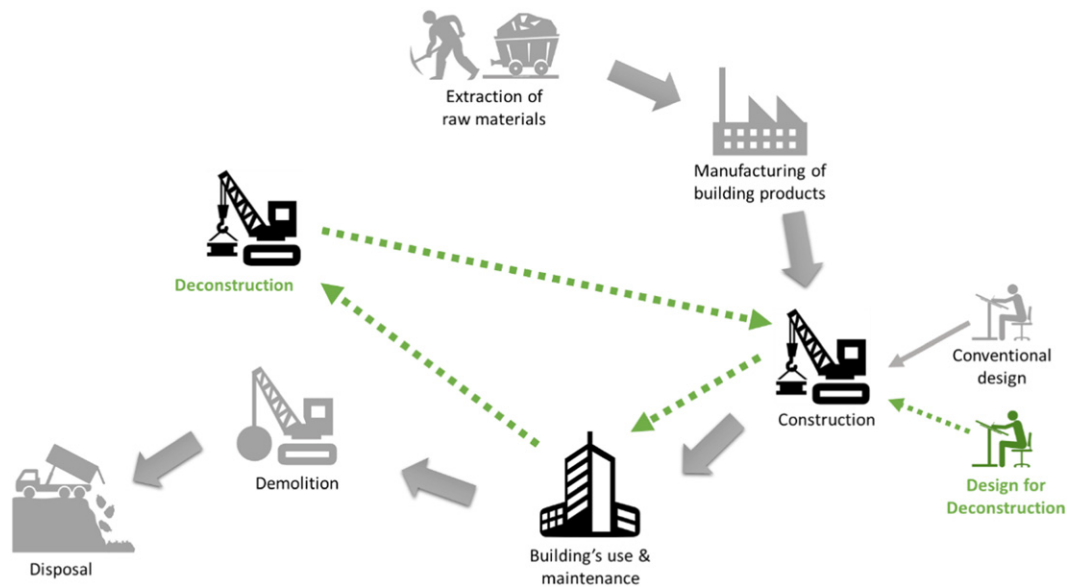


Fig. 2 CE and DfD in the built environment.

components, like a steel beam, glazing, insulation, or engineered wood members. Such products and components are eventually installed by contractors in their final position as informed by designers (represented in Fig. 2 as “conventional design”). Once construction is completed, the building, facility, or infrastructure is ready to be operated and maintained, usually for a few decades, until it is demolished. Then, a small portion of the components is salvaged (before demolition) and recycled, while a majority of the components are simply dumped into landfills.

Conversely, the CE model (represented by green arrows in Fig. 2) proposes the disassembly of the building, facility, or infrastructure components by means of a deconstruction process so that they can be reused. Thus, CE proposes a closed-loop cycle that reduces the need for extraction and manufacturing of raw materials into building products. In the CE model, both construction and deconstruction are informed by DfD so that components are fabricated and assembled while facilitating future renovations and deconstruction. Such a closed-loop cycle reduces the extraction of raw materials, embodied energy, carbon emissions, and material/products costs.

Key DfD principles include to (1) properly document “materials and methods” for deconstruction; (2) design of accessible connections that ease dismantling (e.g., designing with bolted, screwed, or nailed connections as opposed to chemical or welded connections); (3) design for production and assembly techniques that facilitate deconstruction, e.g., prefabrication and/or modularization; (4) sort non-recyclable, non-reusable, and non-disposal items, such as those in mechanical, electrical, and plumbing (MEP) systems; (5) standardize components, assemblies, and dimensions; and (6) design according to labor practices, productivity, and safety regulations (Guy and Ciarimboli, 2007).

Despite the potential benefits of DfD, there are a few more than two dozen buildings that have been designed for disassembly. Perhaps the most notable example is the Bullitt Center, in Seattle, known as the greenest commercial building in the world. The Bullitt Center was designed by Miller Hull architects for the Bullitt Foundation with the goal to create a resilient building that would last 300-year. By using DfD strategies like mechanical joints, durable materials and a façade independent of the building structure, the architects have designed for adaptability against future changes in scope or functionality and natural disasters. Dennis Hayes, the president of the Bullitt Foundation, has explained that in the aftermath of a natural disaster the damaged parts would be easily disassembled and replaced. Despite this notorious example, the implementation of the CE model will remain scarce in the built environment as long as CE-prone strategies such as DfD remain anecdotal.

Challenges to CE Implementation in the Built Environment

The challenges to implementing the CE model can be divided into two major groups: barriers against reusing components and barriers against designing for disassembly. The barriers related to the reuse of components include quality, demand, consumer preferences, and knowledge. First, uncertainty about the quantity and quality of used products and components exists. For example, assume a client who needs twenty doors in like-new condition, but the varying quality and uncertain quantity from unreliable-perceived sellers of salvaged components becomes a disincentive for the client who may opt for the investment in new doors -despite higher costs. As DfD facilitates deconstruction and creates new market opportunities, the development of large storage yards is proposed as a partial solution for a stable supply (Environmental Protection Agency, 2008). Also, the regulation of salvaged materials is observed as a potential positive factor in disclosing product/component quality to the final client. Second, the

low demand for salvaged materials is another major barrier against CE. Components are subject to damage during deconstruction, and damages can likely prevent reuse. Such deconstruction issue could eventually be minimized through appropriate deconstruction planning and training. Third, a negative consumer perception about salvaged components exists. Salvaged components are perceived as being inferior in quality compared to virgin materials and components, both aesthetically and for safety reasons (Environmental Protection Agency, 2008).

Finally, there is a lack of research on components reuse and its environmental impact. Research on environmental impacts has focused on the operational phase of the building's or facility's life-cycle. That is because most of the environmental impacts related to the built environment used to be caused by the energy consumption for lighting and heating, ventilating, and air conditioning. In response to that, highly energy-efficient equipment and technologies were developed. As a result, the energy use during the operational phase is much lower than before. Indeed, the building's energy consumption can be entirely offset by renewable energy systems (the so-called NetZero energy buildings). High-efficient buildings with lower or zero energy consumption imply that the other phases of the building's life cycle (e.g., extraction and manufacturing of raw materials, demolition, disposal of solid waste) have a much larger impact than before, and thus mechanisms to reduce their environmental impacts should be investigated. DfD eventually offers the opportunity to reduce such environmental impacts associated with both resource consumption and solid waste generation.

However, there are several reasons why DfD strategies are scarce in the current design practice, such as: architects have little knowledge about DfD; owners have no liability for the building/facility/infrastructure end-of-life; most green building rating systems do not value DfD; and, planning for deconstruction may stretch the project's initial schedule and budget. In addition, DfD guides and manuals list a set of design principles to be followed, and although some of them are feasible in today's practices (modularization and prefabrication), others involve major changes in the way design and construction stakeholders operate (e.g., providing standard and permanent identification of materials chemistry).

In order to drive such change, the reader wants to understand the two reasons why owners (or clients) engage in sustainable concepts through the design of a building or facility: it either makes financial sense, or the client believes that it is "the right thing to do". The former driver represents the *sophisticated* clients and the latter driver represents the *transformational* clients. Obviously, many owners do not fit in either group and consequently have little or no interest in sustainable design. The designer's role, in turn, is to listen to the client and align the goals with those of the design firm. If the designer is aware of DfD and willing to make the effort to plan for future reuse, he or she will need to engage the client. Sophisticated clients want to understand how DfD will increase their ROI, and transformational clients want to understand why DfD is a better choice for the environment.

That a large majority of designers are not aware of DfD or its basic concepts further complicates its adoption. For example, designers often do not understand the difference between reusing and recycling. Similarly, designers aware of DfD express conflicting views about what DfD means in terms of resiliency. Architects often associate the ability to disassemble a building to temporary construction, such as temporary structures or expo pavilions. Some even regard DfD and resiliency as opposites, that is, they think that a "permanent" building or facility does not lend to disassembly. On the contrary, designers with DfD experience note that disassembly actually *enables* resiliency (Cruz Rios, 2018). Designers express that DfD results in a flexible and mutable design that can adapt to future changes in structure, envelope, roofing, or interiors (e.g., partitions).

Finally, the complex design and construction process becomes another prominent barrier against DfD. Each design and construction effort has a unique combination of requirements, codes and regulations, construction methods, schedule, budget, project team, or contractual clauses, among several other factors. Fitting the innovative CE model results in an increased complexity to an already intricate design and construction process. Such increased complexity further prevents DfD adoption.

Overall, the shift towards CE in the construction industry demands research, resources, education, and time. It requires holistic changes in design, business models, supply chain relationships, and codes and regulations. The PSS approach, however, can contribute to activating the implementation of the CE model in the built environment.

Product-Service Systems (PSS): The Future Driver for CE Adoption?

The challenging adoption of the CE model can benefit from the more certain implementation of innovative PPS approaches. The need to improve resource productivity led to the idea of "dematerialization", that is, the reduction of material flows in production and consumption (Mont, 2002). A dematerialized economy is a service-oriented economy, where the consumer values the utilization of the product rather than the product per se. "Functional economy" is another term for a service-based economy, where the manufacturers focus on the provision and performance of services (Mont, 2002). For example, the consumer buys solar power instead of solar panels. Thus, the provider installs and rents (or leases) solar panels for a customer that benefits from solar power without investing in the purchase of solar panels. The objective of a functional economy is to "create the highest possible use value for the longest possible time while consuming as few material resources and energy as possible" (Mont, 2002).

A PSS has been defined as "a marketable set of products and services capable of jointly fulfilling a user's need" (Goedkoop et al., 1999). PSS has been popular among researchers from the mid-1990s (Tukker, 2015) and is perceived inherent to a functional economy. In theory, PSS are designed to be competitive, satisfy customer's needs, and create less environmental impacts than a product-based business approach. PSS tend to close material loops, reduce consumption, and increase resource productivity (Mont, 2002). It also brings benefits to manufacturers, such as adding value to products and increasing their competitiveness, improving relationships with customers and customer's loyalty (because the manufacturer and customer connect through the

product's and/or service's life-cycle), and giving manufacturers an early advantage by anticipating future take-back legislations (Mont, 2002). In a successful PSS, the extended involvement of the manufacturer throughout the product's and/or service's life-cycle enables not only take-back and reuse but also refurbishment, remanufacturing, and product durability as a result of timely maintenance and repairs.

Michelini *et al.* (2017) investigated whether or not researchers agree that PSS increase resource-efficiency and can support the CE model. The authors found very few efforts that connect PSS with CE but noted that the novelty of the topic in the literature. The authors concluded that "PSS have tangible contributions to CE only when the customer pays for the provision of a service instead of the product's ownership". That way, when the service is over, the producer takes back the product, and either leases it to another customer or uses its components to remanufacture the product for a different service (Michelini *et al.*, 2017).

PSS have the potential to create not only environmental and economic benefits but also socio-ethical ones. For instance, leasing high-quality, technically-advanced products can ease the access to such options among low-income populations by minimizing or eventually eliminating initial costs (Vezzoli *et al.*, 2015). Low-income customers can have access to renewable energy by leasing solar panels instead of buying them. Such PSS approach eliminates the burden of the initial investment and enables a reduced power bill whenever energy savings overcome leasing costs.

Case studies have documented how PSS can be implemented in the built environment, for instance, through the Sustainable Product Development Network (SusProNet) project funded by the European Union (Tukker and Tischner, 2006). SusProNet tested many PSS implementations, including those for the construction sector, like the service of recovering and reselling materials and components from demolition or energy conservation systems in residential homes. In the latter approach, the service provider paid the monthly energy bills of homeowners and supplied energy-saving building products. The authors suggested other construction-related PSS concepts in which the supplier provides a "dry environment" to a house instead of selling a roof. The roof is designed by the supplier, who is responsible for maintenance and take-back services.

Another documented application of PSS is the lease and reuse of building components. For example, technology-intensive or expensive components can be leased to owners (such as a university, commercial building, or multi-family apartment complex). Examples of components suitable to be leased include, among many others, perforated copper panels (often used as exterior cladding protection), curtain walls, interior partitions, equipment (such as heating or cooling units), or modularized roof assemblies.

At the time the PSS concept was created, there were three main uncertainties associated with its implementation: (1) the readiness of companies to adopt PSS, (2) the readiness of customers to accept PSS, and (3) the environmental implications related to PSS (Mont, 2002). However, new technology advances can provide the structure required for PSS to happen, such as the creation of new networks (e.g., research networks, information-sharing networks, and industrial symbiosis networks). Recent technologies and tools such as Radio Frequency Identification (RFID), Internet of Things (IoT), Building Information Modeling (BIM), and big data analytics may have an important role in boosting PSS business models (and consequently CE). For example, Ness *et al.* (2015) proposed using RFID coupled with BIM to enable tracking and reuse of steel structural components through their life-cycle. The authors argued that this approach could create "a platform for the company to provide a 'steel service', retaining ownership of the steel over its lifetime, licensing its use by customers in appropriate locations and circumstances, and providing it as part of a PSS, with some similarities to leasing and renting" (Ness *et al.*, 2015).

Besides emerging technologies, policy actions can accelerate the implementation of PSS in the built environment. Such actions can be indirect (e.g., carbon taxes, extended producer responsibility, eco-labeling) or direct (e.g., green public procurement focused on PSS, incentives, support of PSS pilot projects). Policies and regulations can be local, regional, national, or international, and some of them are already being proposed and implemented in European countries.

See also: Reducing Waste in Circular Economy. The Circular Economy: Additive Manufacturing and Impacts for Materials Processing

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Corporate Social Responsibility in Supply Chains

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Introduction

In the recent years, the term triple bottom line (TBL) has gained increased importance in the business world. As also endorsed at the World Summit on Sustainable Development (WSSD), in 2002, under the aegis of United Nations, this concept broadens the focus of an organization from simply the financial bottom line to also include social and environmental concerns. Accordingly, the triple bottom line performance of an organization is collectively considered an indicator of its corporate social responsibility (CSR), economic value and environmental impacts. It is increasingly being realized that the scope and scale of human generated activities continues to put enormous pressure on the natural environment, society, firms, citizens at large and governments. Thus, all such stakeholders have become immensely concerned about the well-being of society and the environment (Tate *et al.*, 2010).

In such a context, the role of supply chains has assumed renewed interest. A supply chain is defined as comprising of all entities involved in fulfilling a customer order (Chopra and Meindl, 2007). The chain is often visualized as consisting of people, organizations and resources which are involved in movement of goods or service from the supplier to customer. A schematic view of a supply chain is depicted in Fig. 1. As shown in the figure, a typical supply chain comprises of several entities starting from the raw material suppliers to the sub-assembly vendors, to manufacturer, wholesaler, retailer, and eventually, for end consumption by the consumer. If we consider the manufacturer as the focal entity in this supply chain, then we can readily classify the various players in the supply chain into two categories – upstream and downstream players.

Much of the supply chain research in the areas of corporate social responsibility (CSR) and sustainability has been confined to a standalone fashion, with relative less appreciation of the interrelationships amongst varied areas such as environment, diversity, human rights, philanthropy, safety, etc. (Carter and Liane Easton, 2011). This state of affairs is found in practice too, when supply chain managers often initiate and manage projects in a standalone fashion, without a clear, holistic, and more strategic understanding of the organization's overall CSR or sustainability position (Carter, 2005). Going beyond these concerns, it is our assertion in this paper, that to get a more holistic and integrative view of the central concept of CSR, as applicable to supply chains, organizations need to take into consideration CSR related efforts of their upstream and downstream players. Such an integrative or holistic overview of CSR indexes would be beneficial to all supply chain players and various stakeholders of the organization at large.

While there are several measurement indicators of CSR practices, which have been discussed in literature, it is evident that (i) there are no common set of metrics for measuring CSR performance of an organization, and (ii) there is no integrative or holistic overview of CSR indexes which is applicable to an entire supply chain. Yet, past literature provides substantive guidance regarding the beneficial effect that the CSR effort of an organization has on its supply chain partners (Carter and Jennings, 2002). Thus, the prime objective of this paper is to posit, based on the extant literature, a general, holistic and integrative overview of CSR indicators in supply chains. Such a set of indicators would be helpful for future researchers as a reference framework to develop further studies in this area of important concern to supply chain managers and researchers.

The rest of this paper is organized as follows. The next section provides a basic foundation of the concept of CSR in an organization. Section "CSR in Supply Chain" provides a basic understanding of the notion of CSR in supply chains. In Section "CSR Imperatives for Supply Chains", we discuss the CSR imperatives for a supply chain. Section "CSR Indicators" provides a broad overview of CSR

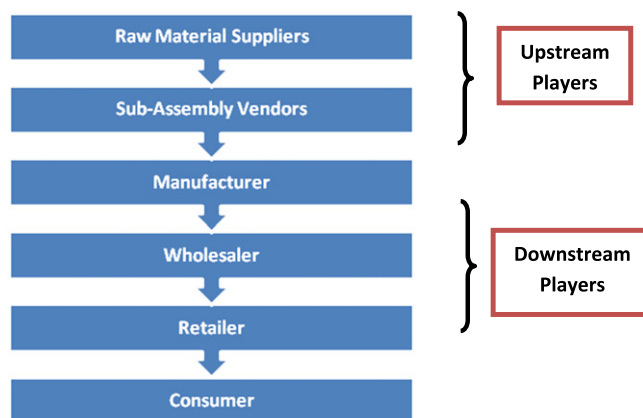


Fig. 1 A schematic view of a supply chain.

indicators in supply chain. The next section provides a select group of case studies in a representative industry sector, namely, the textile sector. We conclude in the last section with implications for researchers, managers, and practitioners.

CSR in Organizations

Bowen (1952) first introduced the concept of CSR and stated that organizations, while implementing strategies, should consider society's values. Later, towards the end of 1970s, CSR was redefined in the context of stakeholder theory. Carroll (1979) defines CSR as social responsibility of business encompassing economic, legal, ethical and discretionary (later termed as philanthropic) responsibilities towards the society. Visser (2011) defines CSR in business as creating shared value in society through economic development, good governance, stakeholder responsiveness and environmental improvement. The four responsibilities as stated in Carroll's definition of CSR have been described through varied approaches.

Economic Dimension

In accordance with the minimalist 'economic' approach, CSR has been defined as meeting shareholders' interests through profit generation (Friedman, 1970). According to 'shared value' approach, CSR refers to meeting both business and community interests (Porter and Kramer, 2006). 'Corporate citizenship' approach aligns CSR to social, economic and environmental needs of the society with no or limited benefit to organization (Waddock, 2008). Economic responsibilities of CSR refer to company discharging economic responsibilities towards the society including sustaining viable business model (Carroll, 2016).

Ethical Dimension

Ethical responsibilities of CSR refer to company behaving as per societal and ethical norms by not only complying with legal norms but also following evolving ethical norms (Garriga and Melé, 2004). In accordance with 'stakeholder theory', CSR refers to sustainability and human rights considering stakeholder's perspective. As per 'triple bottom line' approach, ethical responsibilities refer to maximizing economic, social and environmental contributions of the company (Dahlsrud, 2008; Pesmatzoglou *et al.*, 2014).

Legal Dimension

Legal responsibilities refer to companies abiding by state and national laws and following outlined industry standards (Cramer, 2005; Michell and McManus, 2013). Legislative responsibilities of CSR refer to establishing legal ground-rules under which organizations operate and follow minimum standards of set practices (Carroll, 2016).

Philanthropic Dimension

Philanthropic responsibilities of CSR refer to contributing human, monetary and physical resources to the society (Baden, 2016; Carroll, 2016). Philanthropic activities comprise myriad of activities such as giving monetary and service donations and volunteerism by both management and employees for providing service to the community.

These four responsibilities are embodied into classical model of CSR 'Pyramid of Responsibilities' showcased as non-mutually exclusive obligations of managers (Refer Fig. 2). Though Carroll's Pyramid has become an established CSR concept, it was critiqued as it fails to explain the interactional effect of different responsibilities on one another (Visser, 2006; Geva, 2008) and also because the pyramid model was made in reference to developed countries, thus limiting its usage in developing and underdeveloped economies (Visser, 2006).

Visser (2006) developed a CSR model based on Carroll's pyramid to improve the reliability of the model in developing countries. He rearranged the responsibilities in the Carroll's pyramid model (1999). According to the model, economic responsibility receives utmost priority while philanthropic responsibility receives the second highest priority, followed by legal responsibility and ethical responsibility (Refer Fig. 3).

These models are useful as they bring a broad understanding of the CSR concept and describe the CSR theoretical construct though the scope of various responsibilities in the pyramid model that has evolved over the time.

CSR in Supply Chain

CSR has continuously evolved in practice over the years but its application in supply chain has surfaced in the last two decades. A closely related concept of CSR in supply chain management is sustainability. Elkington (1997) defines sustainability as the concept ensuring that our actions today do not limit the economic, social and environmental options to be transferred to the future generations. For example, Adidas addresses sustainability issues right from supplier



Fig. 2 Pyramid of responsibilities. *Source:* Adapted from Carroll, A.B., 1991. The pyramid of corporate social responsibility: Toward the moral management of organizational stakeholders. *Business Horizons* 34 (4), 39–48.

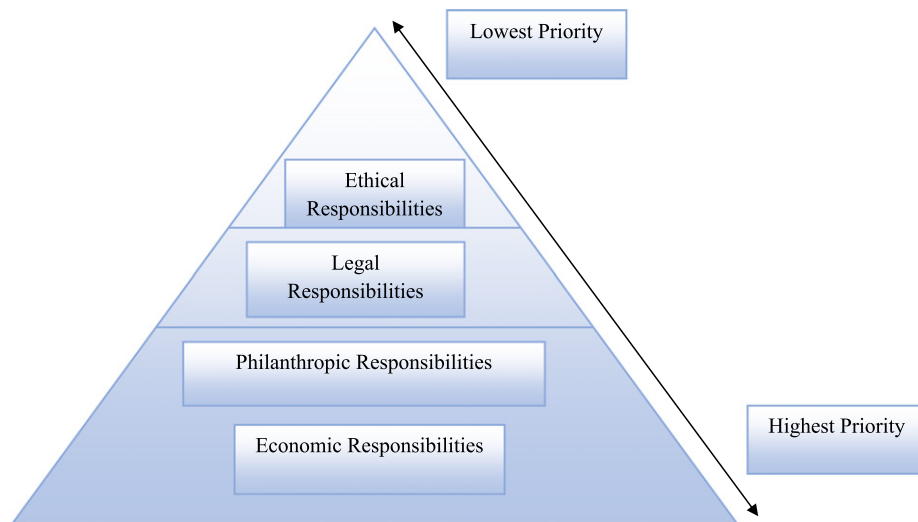


Fig. 3 Drivers for CSR pyramid model for developing countries. *Source:* Adapted from Visser, W., 2006. Revisiting carroll's CSR pyramid: An African perspective. In: Huniche, M., Rahbek, E.P. (Eds.), *Corporate Citizenship in Developing Countries New Partnership Perspectives*. Copenhagen: Copenhagen Business School Press, 29–56.

management to effective product design and environmentally friendly packaging. With vertical integration of manufacturing companies operating nationally to contract-based manufacturing across national borders, CSR concept has broadened from individual company's domain to entire supply chain. Moreover, increased pressure by stakeholders especially on multinational companies to implement CSR practices across the supply chain has made it critical for these companies to be responsible for environment and labor practices of not only their own production facilities, but also of their supply chain partners.

Firms can have a two-pronged approach to implement CSR practices along the supply chain: (a) Complying with the CSR standards, and (b) Capacity building. A firm should comply with the established CSR standards, as well as set standards for stakeholders throughout the supply chain and ensure that the stakeholders comply with these standards through strict monitoring process encompassing audits, physical inspection, etc. Capacity building on the other hand, should aim at enhancing their stakeholders' social and environmental responsibilities by closely working with them, focusing on continuous improvement and conducting random audits (Martela, 2005). For example, Pfizer (Pfizer is a multinational pharmaceutical company with headquarters in New York, US) continuously works with its upstream supply chain players to reduce ingredient costs and, at the same time, maintains the highest quality and safety standards; and reserves the right for random audits and site inspections.

CSR Imperatives for Supply Chains

Socially responsible practices should be implemented throughout the supply chain from procurement of raw materials till delivery of the products to the end consumer. For example, Wells Fargo (Wells Fargo is a multinational bank and financial services company headquartered in the U.S. (see “Relevant Websites section”)) is concerned with the social issues of all the communities in which the organization’s entire supply chain operates. We now discuss CSR imperatives for different stages of supply chain.

Procurement

CSR in procurement can be defined as purchasing in accordance with the CSR principles (Maignan *et al.*, 2002). If a company complies with social and environmental standards in the procurement processes, CSR concept can be spread to the suppliers. For example, Walmart has strict supplier agreement under which it demands EHS (Environmental Health and Safety) standards in supplier’s operations; the right to conduct supplier factory EHS audits without prior information; and the supplier’s adherence to Walmart’s requirements in terms of quality, logistics and customer service. CSR practices in procurement also include purchase of recycled and recyclable materials (Zhu *et al.*, 2007), prioritizing suppliers who invest more in environmentally friendly technologies and materials. Companies can also provide training and development of suppliers on the company policy regarding CSR issues.

Production

CSR in production comprise effective product design considering CSR principles (Sarkis, 2003), environment-friendly production process, reduced disposal, prevention of work accidents, improved working conditions, etc. In addition to this, identifying the reuse of the materials at any stage of product life cycle and using it in production and recycling it for the betterment of the society is also a prevalent CSR practice (Büyükoğkan and Vardaloğlu, 2008). Thus, social responsibility can take place both in forward and reverse supply chain management activities. Reverse supply chain management is defined as set of processes and activities which help retrieve end of life or end of use products from customers, for further reuse, repair or resale (Guide and Van Wassenhove, 2002). Reverse supply chain also includes functions such as transportation, product collection and testing, warehousing, inventory management etc. It not only gives economic advantage to the organization by reduction in production costs, but also gives competitive advantage by portraying green image of the organization in the society.

Packaging

CSR in packaging includes use of non-hazardous materials in packaging to protect products. It also includes use of recycled material and consumption of less energy and low waste production in the process (James *et al.*, 2005). Small packaging size and innovative package design for better resource usage is also an important CSR practice in packaging.

Logistics and Transportation

The concept of CSR in logistics and transportation emerged during 1990s and includes giving opportunities to local transportation companies, reduced traffic congestion, implementing safety mechanism in transportation and automation of loading and unloading. Substituting the use of information technology for transportation is also an evolving CSR practice in logistics and transportation (Feitelson, 2002).

Storage and Warehousing

Social responsibility in warehousing commences right from selection of an appropriate location considering relevant environmental and social parameters. Companies storing hazardous materials, such as, chemicals, should take special measure for environment safety. Necessary safety measures for securing worker’s health and safety is also an important CSR imperative (Ciliberti *et al.*, 2008).

CSR Indicators

In 1990s, database methods were used for measuring CSR activities. The Kinder Lydenberg, and Domini (KLD) (see “Relevant Websites section”) evaluates companies based on nine dimensions: the environment, military contracting, employee relations, community involvement, product safety, quality programs, excessive compensation of executives, diversity and nuclear power. Another database measure that was extensively used was CSID (see “Relevant Websites section”), which calculates the sum of the average of a firm’s strength and weakness focusing on seven dimensions: community, employee relations, environment, diversity, product and business practices, international operations and corporate governance. The limitation of these databases

is restricted use of these to certain countries only. Besides these databases, various researches in literature have proposed one or more of the following CSR measurement approaches (i) pollution indices (Igalens and Gond, 2005) (ii) organizational reputation indicators (Igalens and Gond, 2005; Turker, 2009) (iii) perceptual measures derived from surveys (Igalens and Gond, 2005; Maignan and Ferrell, 2000) (iv) content analysis of annual reports (Igalens and Gond, 2005; Turker, 2009) (v) data produced by research organizations (Igalens and Gond, 2005), and (vi) single- and multiple-issue indicators (Maignan and Ferrell, 2000; Turker, 2009).

The major limitation of pollution control indicator is its unidimensionality. In reputational measures, the sample is usually business students, corporate staffers or experts that evaluate a given number of organizations mentioned in the questionnaire. This limits the number of organizations rated because usually the respondents cannot rate more than 20–30 companies at a time. A similar limitation exists in surveys also. In content analysis of annual reports and organization's publications, the CSR score is derived from the percentage of lines, words, or pages in reports related to corporate social activities. Since the method relies totally on self-disclosure of information in company reports, the analysis may not be considered fully reliable. Regarding the multiple indicators approach, there is no agreement regarding appropriate number and type of indicators used worldwide. Some of the widely used measures include: The Jantzi Social Index (see "Relevant Websites section") measures performance of Canadian companies in social areas such as aboriginal relations, community involvement, corporate governance, employee relations, the environment and human rights and introduces more than 200 indicators, the JSE SRI Index (see "Relevant Websites section") includes 71 indexes which further consists upto 9 sub-indicators and the Dow Jones Sustainability Index (DJSI) (see "Relevant Websites section") comprise over 48 indicators and proposes both general and sector-specific indicators to include the specific challenges and trends of each sector.

Jantzi Social Index does not include companies involved in production of nuclear power, manufacture of tobacco products and weapons. DJSI does not include sectors involved in alcohol and tobacco production and gambling. JSE SRI Index takes into account all types of sectors in the measurement procedure. There are more indexes used in different countries with the limitation of its usage in particular types of economies or countries only. Thus, it can be said that there is no universal agreement regarding usage of indexes. Moreover, most of the measures suggested above comprise CSR indicators in context of the organization's domain with very less or no focus on the organization's upstream and downstream players. Thus, the present paper suggests holistic and integrative set of CSR indicators for the organization's supply chain.

In this regard, a series of studies conducted in understanding responsible businesses in an emerging economy like India, hold important lessons for developing CSR indicators in supply chains. Interchangeability of CSR and sustainability definitions, lead to four broad categories of measurement, namely- Sustainability, Governance, Disclosure and Stakeholder Management (see "Relevant Websites section") (Also refer Majumdar *et al.*, 2015).

The Sustainability category comprises of environmental and social dimensions. Within these, the environmental dimension includes, waste, water, energy and emissions management. It also includes, incorporation of biodiversity objectives, environmental compliance and environmental management systems in firms and supply chains. The social dimension includes employment, occupation health and safety, labor relations, training and education, non-discrimination, diversity and opportunity, community involvement, customer and worker health and safety.

A summary of the composite index discussed in the section below, is provided in Table 1.

Sustainability

Environmental dimensions

Water as an indicator relates to groundwater usage, percentage of water used versus received, marine water protection, water abstraction etc. Energy indicator includes energy efficiency of entities in the supply chain, energy usage in production processes, percentage of renewable energy used etc. Waste indicator includes hazardous emissions, recyclability of wastes, toxic chemicals discharge, landfill waste, amount of waste being incinerated etc. Emissions include CO₂ emissions, other greenhouse gas emissions. Measures of biodiversity include protective measures of forestland, habitat protection, wildlife protection, land usage etc. Lastly, environmental management systems and compliance include adherence to ISO14001 measures, implementation of environmental management systems, and audits in supply chains.

Social dimensions

Social indicators in training and development category include demonstrated responsibility of senior management for training and development, training and development programs for organization's employees, annual budget for training, hours spent on training, developing and carrying out training programme for suppliers, procedures for assessment of training and development effectiveness of supplier's training. Occupational health and safety include physical and psychological working conditions in compliance with rules and regulations of national and international standards, compliance with industry health and safety rules and regulations, details of appropriate policies and procedures of implementation of employee health and safety measures, coverage of certified health and safety systems, screening of suppliers based on health and safety procedures implemented, number of random inspections at suppliers premises and warehouses for checking physical and psychological working conditions, number of random inspections at suppliers premises and warehouses for checking health and safety systems implementation etc.

Table 1 Composite CSR Index

<i>Index</i>			
<i>Sustainability</i>	<i>Governance</i>	<i>Disclosure</i>	<i>Stakeholder Management</i>
Environmental Objectives:	Top management overview of CSR and sustainability initiatives.	Report activities and disseminate information through financial and non-financial measures.	Inclusive business and supply chain considering diverse objectives of customers, suppliers, employees and communities.
Waste	Managerial accountability of responsible business measurement and reporting.	Adherence to reporting standards such as Global Reporting Initiative (GRI) standards.	
Water			
Energy	Availability of formal CSR and sustainability policies.		
Emissions			
Biodiversity	Adherence to international standards on CSR activities and reporting.	Participation in international projects such as Carbon Disclosure Project (CDP).	
Environmental Compliance			
Environmental Management Systems	Existence of management systems to continuously benchmark firm and supply chain performance against international standards.		
Social Objectives:			
Employment, Occupation health and safety			
Labour relations, Training and education			
Non-discrimination, diversity and opportunity, Community involvement, Customer and Worker health and safety			

Diversity and opportunity category include establishing procedures and mechanisms for providing equal opportunity to all employees, number of women in lower, middle and senior level management, number of people with disabilities employed, value statements of the organization making diversity a core value, established procedures and mechanisms for monitoring all suppliers, number of diverse suppliers of various geographic regions, collaborations and partnerships with industry groups to increase the diversity of supply chain. Community involvement includes annual monetary donations for community upliftment, gifts in kind, payroll schemes, etc., details of the community projects supported, organization's policy on community participation in administration and management, level of community participation in administration and management and decision making. Customer and worker health and safety includes procedures in place to ensure safe storage of products under appropriate conditions, packaging to protect product from deterioration, appropriate labeling on product packaging indicating contents, procedure to use and store the product, compliance with product safety regulations, number of product recalls, use of information technology for supplier management, tools and techniques employed for traceability of the flow of raw materials, parts for assembly and finished goods, assessment of supplier systems to consistently deliver products that meet certain safety and quality standards and so on.

Governance

Governance includes top management overview of CSR and sustainability initiatives, managerial accountability of responsible business measurement and reporting, availability of formal CSR and sustainability policies, adherence to international standards on CSR activities and reporting, existence of management systems to continuously benchmark firm and supply chain performance against international standards (Majumdar *et al.*, 2015).

Disclosure

Disclosure relates to the ability to report activities and disseminate information through financial and non-financial measures (some of the measures have been discussed in the previous paragraphs), adherence to reporting standards such as Global Reporting Initiative (GRI) standards, participation in international projects.

Stakeholder Management

Lastly, stakeholder management includes ability to have an inclusive business and supply chain considering diverse objectives of customers, suppliers, employees and communities (some of the measures related to multiple stakeholders have been discussed earlier). Including these multiple and often diverging stakeholder centric views to design and implement supply chains is considered in stakeholder management category.

In what follows, we discuss various cases of firms which have attempted to incorporate CSR initiatives in their supply chains.

Case Studies in CSR Initiatives

Corporate social responsibility, or CSR, has assumed great importance for the textile industry in recent times. One of the chief reasons for this renewed importance is the linkage of this industry with the fashion industry, which has realized the need to be more sustainable in future. Another reason is the multiplicity of the stakeholders in this industry, such as, consumers, suppliers, manufacturers, designers, retailers, unorganized boutiques, employees, governments, regulators, export-import regimes, trade blocks, non-governmental organization, society, media, public relation groups, etc. It is clear that such multiplicity of stakeholders, and their complex interactions, put enormous pressure on the textile businesses to act and appear socially responsible. Additionally, it is crucial for the textile industry that implementation of environmentally and socially sustainable policies are spread across the entire production chain.

Corporate social responsibility efforts greatly benefit the companies in this sector by enhancing brand recognition, recognition, global reputation, and even, employee morale on a global scale and greater opportunities to attract better and more qualified staff. However, it can also be quite challenging for the organizations in this industry because of the global nature of their supply chains. Such challenges include different tariff zones and diversity of cultures. Thus, most organizations in this industry tend to focus on short-term profit gains rather than long-term sustainable efforts like CSR (see “Relevant Websites section”).

In the sub-sections below, we briefly highlight CSR efforts of some of the salient organizations in the textile industry.

Zara

Inditex, the parent company of the famous brand Zara, has aligned itself with the seventeen Sustainable Development Goals (SDG) of the United Nations, and its targeted themes of people, prosperity, peace, planet and partnerships. Its recycling initiative, aptly called Closing the Loop, encourages customers to deposit their used garments in the retail stores for an incentive. An explicitly stated goal of Inditex is that, by 2020, they will not need to direct any material from their headquarters, distribution channel partners, or factories to the landfills. The company also uses the Greenhouse Gas Protocols for the measurement and reporting of carbon emissions, which guides their goals of the reduction targets. The company also has plans to reduce their water footprints through a master plan. It lays great emphasis to ethics, which involves setting criteria for wage rates, employee empowerment, supply chain transparency code of conduct. For instance, Inditex has instituted a complete ban on child labor, or bonded labor. It has a strong animal welfare policy which puts a strict ban on fur, angora or the products tested on animals.

Some salient actionable pointers of the Zara’s CSR policy are listed below:

- A Teaming programme, through which its employees can donate a fixed amount of their salaries to initiatives of social organization like Red Cross and Oxfam
- Profit-sharing plan for employee’s benefit
- Participation in community service projects
- Implementation of newer and better health and safety standards for clothing, footwear, accessories, cosmetics or food-based products.
- Implementation of EPGO programs (Educate People, Generate Opportunities), which invests in education and training for employment of vulnerable groups, such as displaced or refugees
- Instituting an honorary award “Inditex Chair Professors Funding” for outstanding research scholars from Emerging Markets Institute

Patagonia

Patagonia, a California, U.S.-based company, which specializes in outdoor apparel, has taken a rather unconventional route for CSR activities. Sustainability and caring for the environment are the key to the core values of the company, and drives its vision and missions. Patagonia has been donating a huge amount of money to the nonprofit and environmental groups since its inception. Additionally, it has a number of social ventures, and a countless number of volunteer hours by its employees.

Some key indicators of the Patagonia’s CSR efforts are listed below (Zurn, 2017):

- Membership of The Planet (an alliance of businesses), through which Patagonia gives 1% of its sales to the preservation and restoration of the natural environment.
- Donations to nonprofits through an Employee Charity Match programme
- Employee volunteer hours
- Establishment of FootPrint Chronicles, an interactive newsletter and map, which provides a complete picture of its supply chain
- Publication of Environmental and Social Initiative Report, and an online database which gives the breakdown of grants, campaigns, events, sustainability and fair trade efforts, materials selection, etc.
- Patagonia effectively uses social media and online communities to create awareness on ethical issues like #ProtectBearsEars
- In collaboration with their suppliers, production of organic cotton certified by the Global Organic Textile Standard (GOTS)
- Effective recycling programs for polyester, nylon, and wool, thus rejecting fast fashion by creating high-quality, and long-lasting products. Patagonia even attempts to discourage customers from purchasing too many of their products.
- Good labor policies with a view of payment of minimum wages, transparency, and worker empowerment.

- An effective Supplier Code of Conduct, with provisions for tracing and auditing the entire supply chain across vendors and sub-contractors.
- Strong animal welfare policies, with no use of angora, leather or fur; and encouraging used of recycled wool and down feather, accredited by the Global Traceable Down Standards
- Common Threads Initiative, which promises recycling and repairing free of charge.

Levi's

For a number of years, Levi's brand name has been synonymous with the counterculture and effortless style. However, such brand positioning and a mammoth global production scale has not prevented the denim giant Levi's to heed serious thought to the growing importance of CSR concepts, and relatedly, to ethics and sustainability. The company realizes that the decisions taken in this regard by itself, a manufacturing giant with its marquee products of blue denim, will have far-reaching consequences in this industry. Indeed, the Levi's 1991 document, titled 'Terms of Engagement,' which reflects a code of conduct reference for ensuring ethics in the production through its supply chain, is claimed to be a landmark and has exhorted several apparel companies to develop a similar reference document for their organizations.

Some salient pointers of the Levi's CSR efforts are illustrated below (see "Relevant Websites section"):

- A product life cycle analysis of Levi's demonstrated that, for the, Stonewash Jeans, one of its marquee products, a significant proportion of the climate effect and the consumption of water resources occurred during the crucial phase of consumer care. Levi's took a vital cue from this research result and has tried to shift the attitude of consumers from fast-fashion consumption to treat Levi's jeans as a long-term investment.
- Levi's is highly committed to the production of denim under sustainability norms, and have tried to significantly reduce their water use, under its Water<Less™ programme. It is also a prominent participant of the Better Cotton Initiative.
- Levi's has set up stiff reduction targets for greenhouse gas and electricity consumption.
- In 2012, Greenpeace organization launched an aggressive campaign, labeled 'Toxic Threads', against Levi's for the water pollution caused by the company in Mexico. Levi's constructively responded to the issue and vowed and took action for the reduction of the hazardous chemicals used in the dyeing and treatment of their apparels.
- Levi's has a good record in human rights and worker welfare.
- Levi's traces and audits its entire supply chain on key CSR parameters over an extended period.
- Levi's does not use fur, angora, shearling, karakul or other exotic animal skin or hair. Their Animal Welfare Policy ensures that the processes of all supply chain partners are traceable and transparent to ensure animals welfare. Levi's sources its wool raw material from the certified non-mulesed sheep.

Conclusion

Stakeholder expectations from firms and supply chains have led to evolution of responsible businesses in several cases. In particular, CSR has evolved from a voluntary initiative to a strategic decision for firms with organizations increasingly looking to incorporate CSR in their boardroom decisions. However, measurement and reporting of CSR is still evolving with different CSR indexes being used. In this study, we provide a holistic overview of CSR indexes while integrating sustainability dimensions with CSR.

For several organizations, CSR remains a voluntary initiative. However, for many firms, owing to changes in government policies, CSR has become a mandatory activity. Further, pressure from other stakeholders such as consumers, non-governmental organizations, media, communities etc., have also made it difficult for firms to work in silos without integrating environmental and social objectives. Geographically spread supply chains have the potential to cause significant negative impact on environment and communities, if not monitored. A supply chain centric view in this regard, helps firms work with other partners in the supply chains beyond the boundaries of their own organization.

In this context, the paper discusses several objectives that can be integrated in CSR measures of supply chains. The paper addresses the difficulties that firms face in reporting CSR activities, specially the non-financial measures. The paper also illustrates the incorporation of CSR activities in supply chains through various case studies.

There are several directions for future research that emerge out of this discussion. There is a scope of empirically validating the CSR measures and analyzing the reporting practices of global firms. Further, analytical models to understand the economics of CSR effect on firms and supply chains could also provide several insights. Studying the impact of CSR policy changes on industry sectors is another area in which further research can be conducted.

See also: Sustainability Indicators in Supply Chains. Sustainable Supply Chain Management in Developed vs. Emerging Economies: Evidence From the UK and China's Manufacturing Industry

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- <https://textileconsult.wordpress.com/2018/01/29/why-is-corporate-social-responsibility-so-vital-for-textile-sustainability/>
Why is corporate social responsibility so vital for textile sustainability.

Cradle-to-Cradle Versus Consumer Preferences in the Fashion Industry

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Introduction

Sustainability is not a new phenomenon, but rather has been discussed since the 1980s when the Brundtland Commission (WCED, 1987) formulated one of the most iconic definitions of the term highlighting that the needs of the current generation should be met without compromising opportunities to meet future generations' needs. Although heavily criticized and debated, this definition remains to date the most cited in the literature and provides an initial insight into key priorities. The report indicates that industries and consumers should change their current practices to become more sustainable, thereby providing an outline of what sustainability is. This implies that the Brundtland Commission's report (WCED, 1987) leaves room for interpretations to be made by key stakeholders in the industry and consumers as to how they can contribute to a more "sustainable" world and what they deem fit to change. Sustainability to date remains a key topic, and, particularly within the fashion industry, has become a buzzword, as societal and environmental issues are increasingly emerging through negative media headlines.

Sustainability is a key driver for innovation that encourages out-of-the-box thinking and avant-garde behavior by finding new solutions and possibilities to produce and create products/services that the current generation may need without exploiting the social, environmental, or economic environment. Thus, it is guaranteeing a future for generations to come. A key issue in the 21st century is waste, with unwanted garments being discarded in landfill – in the UK this equates to 300,000 t annually (WRAP, 2017). Although this number has significantly decreased since 2012, when 350,000 t of garments were binned, this still raises concerns, especially since "industry, innovation, and infrastructure" and "responsible consumption and production" are two of the 17 top priorities to be addressed by the United Nations (UN, 2018). To put this into further perspective, garments that are simply binned in the household waste account for 5.7% of solid waste in landfill, a figure that is rather substantial and could be dramatically reduced in the future (Weber, 2015).

A current challenge faced in the 21st century is the fact that "we think of materials in a 'human timeframe,' when actually they can relate to materials which in some cases took millions of years to form (and will take hundreds of years to decompose). We need longer term thinking" (Goldsworthy cited in Gould (2015)). A majority of materials take longer to decompose than a human lifetime (if at all). This implies that waste products remain for our future generations to deal with. This is an issue that does not fit with the Brundtland Commission's vision of a sustainable future. Although there are fashion companies that are more forward thinking, such as the Swiss manufacturer Freitag, who has developed a fully biodegradable pair of jeans, the fashion industry as a whole needs to considerably change, as current business models are unsustainable. Thus, this article focuses on cradle-to-cradle versus consumer preferences in the fashion industry, providing key definitions and valuable insights into the topic area of the circular economy.

Cradle-to-Cradle

Cradle-to-cradle is a design principle that sees waste as a new resource and thus works on the basis of designing for a circular approach that reloops materials. This implies that products are designed in a way that make it more cost effective to recycle them rather than purchasing new materials and thus, create less waste (McDonough and Braungart, 2002). The cradle-to-cradle design principles fall within the circular economy. The latter is defined as "looking beyond the current take-make-waste extractive industrial model [...] and] is based on three principles: (1) design out of waste and pollution; (2) keep products and materials in use; (3) regenerate natural systems" (Ellen McArthur Foundation, 2017). The origins and implications of cradle-to-cradle are further explored in the following.

The majority of current industry practices adhere to a linear economic model that is based on transforming raw materials into a product then distributing the product to the consumer until it reaches the end of its "useful" life. To explain, it is a one-way approach that is not necessarily concerned with reducing environmental and societal impacts. Rather it is solely focused on creating products that are one-off items that enter the supply chain as raw materials and exit as postconsumer waste products. The circular economy challenges this system's thinking approach by moving away from the linear economic model towards one that is regenerative in nature and based on closed loop systems (Niinimäki, 2017). As such, the circular economy provides an opportunity for manufactures and suppliers to rethink their current practices by strategically planning how their products/services can be reused. The RSA Action and Research Centre (Royal Society for the encouragement of Arts, Manufacturers and Commerce (RSA Action and Research Centre, 2016)) identifies four possibilities of fostering the relooping process, by designing for (1) longevity, (2) leasing or service, (3) reuse in manufacture, and (4) material recovery.

The origins of the circular economy can be found in the cradle-to-cradle principle developed by McDonough and Braungart (2002). Cradle-to-cradle takes three core aspects from nature in that everything can be used as a resource; this indicates that waste materials can

be utilized as raw materials for another product and relooped into the system. As such, products can either enter the biological cycle or the technical cycle.

Biological Cycle

The biological cycle implies that products are created with design in mind, indicating that anything can be designed to decompose into soil at the end of the life cycle. Although biodegradability or the biological cycle could be seen as an ideal option, as no waste would be produced with fabrics and/or fibers dissolving into a natural product (soil), there are various challenges associated with the biological cycle. To explain, some argue that it is not possible to have fibers and textiles biodegrade safely. Firstly, textiles need certain conditions to biodegrade, which are usually not found within nature. Secondly, the majority of garments are cultured and treated with chemicals that, in a state of biodegradation, would filter into the natural environment and could cause harmful damage (Niinimäki, 2013). As such, it is questionable whether the biological cycle can be regarded as an option of relooping, especially within the fashion industry. Whilst biodegradability could overcome a current challenge of textile waste in landfill, more research would need to be done to explore how to hinder the harmful substances with which materials are treated, to enter the natural environment. To explain, a question that needs to be addressed is what the better option entails – reusing recycled materials or virgin materials, by assessing their impact on the natural environment through, for example life cycle assessment of energy use, recyclability of the end product, and overall use of chemicals.

A further challenge in relooping textiles and fibers concerns the composition of our garments. The majority of garments currently in the market are made from mixed materials, such as natural and synthetic fibers. A majority of these cannot be recycled as these fibers cannot be separated/split into their original components. Moreover some recycling processes are simply too costly to be introduced as mainstream practices, which implies that it would be cheaper for manufacturers to use virgin materials, rather than to reloop textiles.

Technical Cycle

The technical cycle on the other hand repurposes and reuses high quality materials for new products. The technical cycle of relooping textiles and garments could be seen as the best option within the fashion and textiles industry. To explain, harmful chemicals are not released into the natural environment, but rather fibers are broken down and reused without contamination (McDonough and Braungart, 2002). Yet, a key challenge here is the current fast fashion model, which is dominating the industry. The fast fashion model is based on, as indicated in the name, fast stock turnover at an increasingly low cost, which also affects the quality of the raw material used (Rutter *et al.*, 2017). It can be argued that consumers have been educated to develop a fashion appetite that almost forces industry players to cut corners to supply cheap garments (Sharma and Hall, 2010). However, this has both environmental and social implications whilst simultaneously decreasing the quality of the products. The latter has a knock on effect for the industry, as the cradle-to-cradle process is reliant on good quality raw materials to be looped back into the supply chain and reused for new products. As such, if the quality of garments is decreasing then the quality of the raw material may not be up to standard, and thus, cannot be reused in the relooping process.

Cradle-to-Cradle Barriers

The cradle-to-cradle approach provides a foundation for the circular economy, which challenges the current system's thinking approach of linearity, by encouraging the industry to consider designing products for circularity. Yet, as indicated in the previous sections there are key barriers garment manufactures face, which are linked to both the biological and the technical cycle. Although the 21st century has seen an increase in technology and new innovations, they (technology, innovations) still lack the ability to split mixed fibers into individual components and hinder chemicals used in the dyeing process to be released in the natural environment. Furthermore, with businesses focusing on a quantity over quality approach, raw materials cannot be relooped (Niinimäki, 2013, 2017). More research needs to focus on the feasibility of the cradle-to-cradle approach especially within the fashion industry and explore viable options to move forward to a more sustainable future.

Consumer Preferences

When considering introducing a cradle-to-cradle approach, organizations must firstly consider their customer's preferences. Customer preferences indicate the level of demand for their products, and indirectly determine whether this is a feasible business option. Customer preferences are especially vital within the fashion industry, as fashion is much more than simply clothes that follow trends. Garments showcase our personality by representing which social groupings (e.g., hipster, punk, Goth, upper class) we belong to and by highlighting a desire to be unique and creative. Fashion visualizes our identity to the outside world and makes a statement about who we are, how we see ourselves, and who we want to be in the future (aspiration) (Myzelev, 2013). Clothing is used as a vehicle of self-presentation whereby an individual can defend, maintain, and create multiple identities in an attempt to align oneself with perceived social norms. Social norms are unwritten rules of behavior that are considered to be acceptable by society and/or groups

within (McNeill, 2017). Unsurprisingly clothing consumption in a postmodern world is a crucial element in the construction of identity and the self and vitally important for individuals (Niinimäki, 2010; Tiggemann and Andrew, 2012).

From a marketing perspective, consumer preference refers to the likelihood of an individual purchasing one product over another. This is based on subjective value indicators that are dependent on an individual's personal taste, cultural influencers, their education, and reference groups. The latter aspect is linked to the theoretical concepts of self-esteem and self-concern, as individuals seek to be part of an "in group" to satisfy their needs of belonging to a specific "in group" (e.g., reference group) (Millan and Mittal, 2017). Self-esteem is defined as an individual's evaluation of themselves, which can either be positive or negative, and thus determines their own worth, value, and importance. As such, consumer preference is influenced by how a product, in this case a garment and/or accessory, makes them feel about themselves. Today's society is driven by hyper consumerism and an "I want this now and cheap" phenomenon, often referred to as fast fashion. As such it may be challenging for organizations to break consumer habits of wanting to purchase new items at an increasingly rapid speed. Although garments and textiles, especially in the technical cycle, are "new" they could be perceived to be produced from postconsumer waste, and as such have a negative connotation. Similarly, the self-concept is defined as the totality of a person's thoughts, feelings, and attitudes towards oneself (Goldsmith *et al.*, 1999). Rosa *et al.* (2006) found that consumers seek to affirm their self-concept through the use of apparel. Thus, to increase the saleability of sustainable garments, they must appeal to a consumer's self-concept and boost their self-esteem. The notion of acting responsibly is not the sole driver when buying clothes, which further highlights that there is an attitude-behavior gap of people wanting to do something versus actually acting upon it. Self-esteem and self-concept are linked to self-concern, which focuses on the individual's desire to either keep up or achieve a desirable standing within their social group and/or society, and thus gain respect from others (Henninger *et al.*, 2017; Millan and Mittal, 2017). This suggests that if consumer's peers start acting more socially responsible and are shopping more sustainably, then they are likely to follow suit. Hence, making sustainable purchases has the potential to act as a status enhancer, as individuals may want to be seen as being more "green" and making a conscious choice of consuming in a more environmentally friendly or socially responsible manner. This idea does seem to be having some effect, as one-fifth of consumers now say that they prioritize sustainability when shopping for clothes (Drapers, 2018). Furthermore, this sentiment has been capitalized on by certain brands by becoming 100% fur and leather-free and/or creating animal rights campaigns for sustainable consumption. Examples of companies are Stella McCartney, Ralph Lauren, Calvin Klein, and Tommy Hilfiger. This highlights that there is a shift within the industry that clearly aligns with the goals set by the United Nations. With major brands jumping on this bandwagon, the idea of making sustainable and/or ethical clothing "cool" is a concept that is not so far removed anymore. As such, it can further push the cradle-to-cradle paradigm to not only be a viable option in the future, but also to be the best option in terms of business model development. Consumers have the ability to make or break a business, by changing their own practices and demanding a different way of production organizations can be almost "forced" into changing their current business models.

Yet, the attitude-behavior gap remains to be a significant challenge when it comes to purchasing sustainable garments. Despite a positive intention to purchase more sustainably, the appetite for fast fashion is thriving. Online fast fashion retailers such as Boohoo.com and Prettylittlething.com record a continued year-on-year sales increase. These companies have moved from a fast fashion paradigm to a hyper fashion one, implying that stock turnover has been reduced to a one-week turnover (Geoghegan, 2018). Furthermore, the lack of availability of sustainable products or the perception that sustainable garments are not trendy or fashionable enough may be reasons for not purchasing them. This further increases the attitude-behavior gap. For some consumers, ethical purchases will only take place if there is no perceived real or imagined cost, in terms of added price or loss of quality. Currently there is still a perception that products, especially garments that are more "sustainable" come at a higher cost, and thus, may no longer be affordable (Rutter *et al.*, 2017). While concern for the environment and society at large are key drivers for making ethical purchasing decisions, egoistic motivations such as value for money, image, or well being have an even bigger influence on purchasing decisions. This makes it difficult to justify a high price for ethical garments (Jägel *et al.*, 2012). In line with this, there appears to be a general lack of consumer awareness around sustainability issues in the fashion industry. Consumers are unaware of the difference that engaging in ethical behavior could make, in terms of an environmental and social impact (Shen *et al.*, 2012). This implies that more needs to be done by educators and marketers to decrease the attitude-behavior gap and educate consumers about the impact the fashion industry has on the environment and society as a result of hyper fast fashion production and consumption.

What is apparent from the previous discussion is that marketing and especially marketing communications are vital in influencing consumer preferences, through appealing to a consumer's self-esteem and self-concept. The way that organizations broadcast their messages on the circular economy needs to be clear and coherent to create customer buy-in that can foster a decrease in the attitude-behavior gap and fully capitalize on the United Nations' sustainable consumption and production goals through, ideally, a cradle-to-cradle business model (Niinimäki, 2010; Henninger, 2015). Yet, whilst customer preferences may be an indicator for customer demand there are other aspects that can further influence an individual's choice, such as availability, pricing, and associated value.

Conclusion

Although this article might be seen to set out a bleak backdrop on current practices in the fashion industry, by highlighting that a cradle-to-cradle approach may not necessarily be feasible, especially as it faces challenges through the attitude-behavior gap, there are positive outcomes that can be observed.

Despite negative media, the fashion industry is changing, with one of the biggest changes being that we can now observe the normalization of sustainability across the industry. Organizations within the fashion industry are increasingly adopting and developing sustainable policies that align with the United Nations' goal of "sustainable production and consumption," whilst furthermore setting "sustainable" performance indicators, such as using sustainable raw materials and/or recycled fibers or design for longevity, and other mandates. All of these aspects can be linked to a cradle-to-cradle design process and more specifically the circular economy. Although challenges remain with current practices that can be observed within the fashion industry, they clearly highlight a step into the right direction and promote an optimistic outlook for the industry as a whole.

The article highlights that more needs to be done to educate and inform consumers about the consequences of their consumption decisions on the natural and social environment. This could help to further reduce the attitude-behavior gap that remains in the current society. As such, the role of marketing communications is important to influence consumer preferences (specifically the self-concept and self-esteem) and purchase decisions. Communication needs to come from different angles and different media, as fashion consumers gain their information from a variety of sources (e.g., communication channels). Thus, fashion retailers and specifically fast fashion retailers should clearly communicate their sustainable practices and approaches to a more responsible production processes. Consumers need to understand what the real benefits are of sustainable products, to make an informed decision, and how they can get access to them. The overall offering of sustainable fashion products needs to increase for consumers to be able to make a choice. Sustainable brands, especially those aligning with the cradle-to-cradle model should not be perceived as being niche and expensive, but rather as the best option.

Social media has become a very influential communication channel that allows users to broadcast messages within real time to a truly global audience. Different social media platforms (e.g., Facebook, Twitter, Instagram) have been used to facilitate dialogic communication between different stakeholders and to popularize sustainable fashion on a wider scale. Examples that can be brought forward are the Campaign for Clean Clothes, which actively promotes sustainable fashion practices, as well as the nonprofit organization Labour Behind the Label, which manifests for more accountability and transparency within the fashion and textiles industry, thereby calling on organizations and consumers alike (Rutter *et al.*, 2017). Currently fashion brands are not fully capitalizing on the communication channels available to them, which indicates that they need to provide more information within their advertising and promote the benefits of sustainable fashion and the cradle-to-cradle approach for consumers to make better ethical judgments (Rutter *et al.*, 2017). Having clear marketing communications based on transparency has the potential to not only influence but also change consumers' preferences. To reiterate this further, some campaigns do have a strong effect on the promotion of cradle-to-cradle and circular economy practices. Fashion Revolution has contributed to give visibility and increase awareness about movements and initiatives related to a more responsible and conscious approach to fashion, demanding responsibility from retailers and consumers.

See also: Lifecycle Assessment of Building Materials – A Cradle-to-Gate Approach

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Eco-Innovation Options in Food Processing

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Introduction

The challenge for developing a “green production-oriented economy” relies on the definition of sustainable production and consumption patterns, which can enlarge the current approach oriented to the greening of single production as opposed to the creation of a comprehensive sustainable production system. The food we grow, harvest, process, distribute, trade, and consume plays a vital role in the connection between people, planet, and prosperity (UN, 2016). Since food production and consumption are considered two primary sources of environmental impacts, eco-innovations addressing the food system are crucial to sustainability. International resolutions widely highlight the necessity of a more sustainable approach to production and consumption patterns as an essential element to promote sustainable daily life activities (see, for instance, UN SDGs) (UN, 2015). Ensuring sustainable human development means being able to feed a planet with increasing population, decoupling the socio-economic development from the environmental impacts (UN, 2015).

Food supply chains are increasingly associated with environmental impacts while showing both positive and negative socio-economic implications. An increasing global population, with associated increasing in food and energy consumption, an evolution in consumers’ needs, and changes in consumption models pose serious challenges to sustainable production and consumption of food. Life cycle thinking (LCT) and in particular life cycle assessment (LCA) are powerful analysis methods that scientist leverage in their quest for solutions to major food-related global challenges.

In fact, as impacts occur along the food supply chain (agriculture, manufacturing, distribution, retail, consumption, and end of life) (Notarnicola *et al.*, 2017), the LCA method can support the identification of eco-innovations and the comparison of options with a plausible impact on those innovations. Hence, industrial ecology approaches, LCT and LCA are increasingly considered in order to re-think current production and consumption patterns (Sala *et al.*, 2013), especially in support of a transition towards a bio and circular economy. This life cycle perspective reflects the widespread of sustainability science as a solution-oriented discipline that requires the integration of methodologies towards concrete and positive actions. In 2017, a collection of studies on food impact assessment and possible solutions has highlighted that nutrient recovery, resource efficiency, enhanced food waste management, better governance and cooperation among the actors along the entire supply chain are at the heart of the environmental sustainability and innovation of food systems (Sala *et al.*, 2017).

The introduction and adoption of green technologies are regarded as the most cost-effective path to reduce environmental pressure without compromising economic competitiveness, even though quantitative empirical findings on the effectiveness of green technologies in improving environmental performance are scarce (Costantini *et al.*, 2017). However, acting on technological aspects is not enough, and social aspects (from consumer behavior shifts to engagement of stakeholders along the food chain) are also crucial.

Recent theories evolving from the so-called “sustainable transition” towards “substantial system changes” (Dentoni *et al.*, 2017) suggest that in order to accelerate such a transformative turn, change agents or stakeholders should seek coherence among actors co-creating knowledge, mutually supporting interventions, intervening at technological, organizational, and behavioral levels, and enforcing changes. Trends of innovation in the food industry are deeply affected by cultural heritage, habits, and institutional contexts (Savino *et al.*, 2018).

This article presents a state-of-the-art review of eco-innovations in the food chain and discusses a structured approach for their identification and the evaluation of their environmental benefits. LCA is a reference method for the identification of eco-innovation needs and the comparison of eco-innovation options. Indeed, LCA can be applied for defining solutions to major food-related global challenges and specifically for the identification of eco-innovations, their impact across all the stages in the food supply chain, and the comparison of options for food supply chain optimization. Eco-innovation is often implemented in the assessment of environmental gains and possible trade-offs. Eco-innovations include technological improvement, behavioral changes, and the assessment of potential changes in eco-innovations under different environmental conditions (e.g., climate change).

Identification of Eco-Innovations

The use of LCA is crucial to assess the sustainability of the food sector and food supply chains. LCA may be complemented with more site-specific methods (e.g., to address the intrinsic variability of food systems at any stage from agriculture to food manufacturing stages) or with a study encompassing categories of impact usually not covered by LCA (e.g., impacts of invasive species, or of genetically modified organisms). In a comprehensive study, the assessment of a basket of food products (with more than 30 products) unveiled the environmental impacts associated with the consumption of food in the European Union within 16 impact categories and for all life cycle stages (Notarnicola *et al.*, 2017 and related updates, such as Castellani *et al.*, 2017a). This study used a bottom-up approach, based on the selection of representative food products and related life cycle inventories. The method defined a baseline scenario modeled in consideration of the statistics on food consumption by the average European citizen. Such baseline scenario was leveraged as a reference in the evaluation of potential improvements from eco-innovation and behavioral changes.

The majority of studies in the literature highlight the high contribution of all the life cycle stages of the food production chain to Greenhouse Gases (GHGs) emissions. Such contribution is due mainly to the emissions in the agricultural stage and in the end of life, e.g., from landfill (food wastes in landfills emit large amounts of methane – which results in a high global warming potential – and carbon dioxide), and the use of energy during production (from agriculture – including land use change – to processing, manufacturing, transportation, storage, refrigeration, distribution, retail, and consumption) leading to climate change impacts. However, more comprehensive studies inclusive of diverse impact categories beyond climate change (such as ecotoxicity, eutrophication, or land use) are being published. In these studies, climate change, land use, water use, ecotoxicity, eutrophication, and acidification appear as leading impact categories. Recurrently cited impacts associated to the above-mentioned impact categories include the alteration of biogeochemical cycles of N and P – e.g., used as fertilizers in agriculture –, loss of soil quality due to land use, and loss of biodiversity due to land transformation for food and feed cultivation, loss of biodiversity due to the use of pesticide, and water consumption by agriculture and food manufacturing.

Regarding life cycle stages, agriculture usually contributes more than 70% of the overall environmental impacts, followed by end of life, which generates eutrophication impacts due to the human metabolism of food (i.e., wastewater treatment), and industrial processing, especially for what concerns energy-related emissions and water depletion. Assessing the relative importance of consumed food products, those related to animal husbandry and related feedings, such as beef, pork and poultry meat, and dairy products result in a higher impact.

Indeed, specific food sectors generate higher environmental impacts than others. Beef, butter, and cheese generate higher environmental burdens, primarily related to their carbon footprint and material intensity. On the contrary, vegetables, cereal products, potatoes and fruit such as apples, when consumed in their season, generate much lower impacts. These higher environmental burdens are confirmed by meta-analyses that have collected large bodies of LCA studies to draw general conclusions on the hierarchy of impacts across different food categories. On GHGs emissions, these studies reach similar conclusions in identifying animal-based products (and in particular beef meat) as those responsible for the largest emissions while fruit, vegetables, and grains result in the lowest impacts. Within the livestock sector, feed production is a relevant source of impact.

Very often eco-innovations are associated with the food processing or product itself but do not consider packaging (e.g., for a beverage bottled in glass), even though packaging often becomes the factor leading to major environmental impacts.

Most of the studies in the literature address the environmental assessment of single products, but only a few studies adopt a consumption-oriented approach that assesses the impact of food supply chains in large geographical areas. However, studies at both meso- and macro-scales are fundamental in providing decision makers with data for an informed transition to sustainable production and consumption patterns, and to decouple environmental impacts from responses to societal needs while ensuring economic growth.

At the macro scale, environmental impacts associated with consumption have traditionally relied on a ‘top-down’ approach by using the sectorial economic information of input-output tables. The macro-scale approach often calculates physical material flows of economic sectors and then supplements such information with environmental data in order to assess the sustainability of product groups.

The food loss and waste happening throughout the whole food supply chain, from agriculture to food consumption of households, represents a hotspot that cross-cuts products, life cycle stages, and impact categories, and thus demands specific interventions both at technological and behavioral levels.

Eco-Innovations in the Food System

Possible solutions for reducing impacts of the whole food sector or of specific product groups should strategically address the eco-innovations in the literature and in consideration of product groups, life cycle stages, and impact categories. Ideally, eco-innovations should act at different levels, such as, for example: selection of raw materials; technological improvements in manufacturing; optimization of storage, logistics, and distribution; and, consumer behavior. For each stage in the life cycle of a food system, keywords and key concepts are used to guide eco-innovation. See Fig. 1.

Initially, based on the extensive assessment conducted by [Castellani et al. \(2017a\)](#), by [Proctor \(2018\)](#), and -specifically for food processing- by [Chemat et al. \(2017\)](#), potential improvements were identified for this article through the review of existing technological eco-innovation options and existing trends towards sustainable consumption behaviors. The studies resulted in a list of areas of improvement, some of them related to specific food products, others cross-cutting among different products. The documents reviewed about eco-innovation in the food sector were scientific papers and technical reports. The eco-innovations follow.

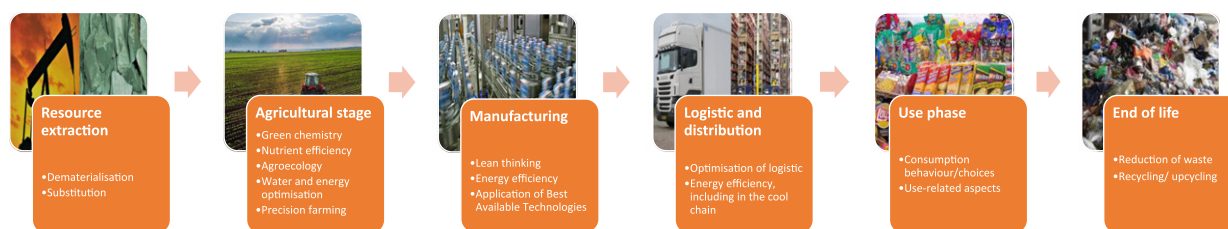


Fig. 1 Illustration of the main concepts and principles underpinning ecoinnovation in the food system and supply chain.

Resource Extraction

Regarding the resources needed as input in the food system, two general principles are applied to enhance sustainability: Dematerialization regarding resource efficiency (doing more with less), and substitution of the most impacting resources with less impacting ones. Regarding the input in the food system, fossil resources are needed in almost all food life cycle stages but should be systematically reduced. Moreover, the food system heavily relies on mineral resources (e.g., phosphate for fertilizer production) that bring pressure on mineral resource availability. This is indicating the clear priority to be given to nutrient recovery.

Agriculture

Eco-innovation in the agricultural stage focuses on the application of green chemistry principles, nutrient efficiency, implementation of agro-ecological solutions, and resource efficiency (e.g., water and energy optimization). In agricultural activities, the hotspot of nutrients losses can be addressed both at the input stage and at the output stage. Several agronomic measures allow reducing nutrients input to crops, including the avoidance of oversupply, whereas several other technical solutions allow recovering nutrients at the end of life, e.g., from the industrial or household stage (e.g., from wastewater treatment plants). Moreover, in the post-harvest stage, several techniques are available to improve the storage of food and prevent food waste, especially for fruits and vegetables. Regarding animal-based products, the innovations aim at the optimization of feed production and the amount of feed needed per animal (e.g., improving the efficiency of feed) as well as the recovery of food waste as a source of animal feed. In general, the protection of animal welfare is also an element to be considered for the overall sustainability of meat production. Better manure management is another path to reduce emissions from manure storage and processing, e.g., by storing it on covered floors to reduce leakages or to recover it via anaerobic fermentation in order to produce biogas. Finally, animal breeding practices (especially for pigs and poultry) can reduce environmental impacts (e.g., through energy and water saving measures applied to animal housings) as well as improved nutritional strategies to reduce ammonia emissions. Concerning the hotspot of human toxicity related to metal emissions, there is the possibility to reduce the amount of metals (especially Cu and Zn) supplied to e.g. pigs through the feed.

Agro-ecological solutions are those related to a more ecological approach to agriculture, e.g., via organic or integrated agricultural practices, aiming at design and management of agroecosystems that are both productive and natural resource conserving. These solutions imply that: Crops rotate so that on-site resources can be efficiently used; chemical pesticides, synthetic fertilizers, antibiotics and other chemical compounds are reduced or banned; genetically modified organisms (GMOs) are banned or used with extreme caution; on-site resources are leveraged, such as manure for fertilizer or feed produced on the farm; and, disease-resistant plant and animal species adapted to the local environment are leveraged.

Regarding marine and aquaculture fish products, eco-innovations focus on solutions that aim at fish being sustainably caught and grown, including energy and resource efficiency and reduction of by-catch.

In the last 25 years, there has been a growth of green chemistry solutions (namely those that utilize preferably bio-based raw materials, eliminate waste, and avoid the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products) (Sheldon, 2017). Applying green chemistry in the food system entails the use of less hazardous chemical synthesis, safer chemicals, solvents, and auxiliaries. Thus, green chemistry affects e.g. the selection of pesticides in the agricultural phase and the use of solvents in food manufacturing.

Finally, increasing energy efficiency primarily in the form of indirect energy used for fertilizers, pesticides, and irrigation remains a crucial objective. Efficient fertilizer production technologies and avoidance of unnecessary fertilizers through adequately designed cultivation practices (e.g., precision farming) complement each other and play a major role in decreasing indirect energy inputs to agriculture. In this sense, considerable experience and data exist for organic farming no-tillage and integrated farming, which is designed to minimize energy and material inputs. An analysis of these aspects has been conducted in Europe and shows a decoupling of yield from resource inputs over time (Monforti-Ferrario *et al.*, 2015).

Food Processing and Manufacturing

“Green Food Processing” is a novel concept that aims at meeting the challenges of the 21st century and protect both the environment and consumers. Moreover, the application of lean thinking (Vlachos, 2015) is a promising way to address ecoefficiency and economic efficiency in food manufacturing. Lean thinking is a set of principles, philosophies and business processes that enable the elimination of waste and add value to customers, basically simultaneously eliminating waste (in its broader sense, everything that is not needed) and improving customer satisfaction. Notwithstanding specific energy ‘costs’ cannot be avoided, such as in chilling, freezing, or cooking, many process improvements can lead to substantial savings. In general, the most relevant solutions for the processing stage relate to the implementation of energy and water saving measures. These two factors show the highest improvement potential as identified by several Best Available Technologies Reference (BREF) documents, which for the food sector focus on food, drink and milk industries, and slaughterhouses (European Commission, Joint Research Centre, 2018).

In the study “Energy use in the EU food sector: State of play and opportunities for improvement” by Monforti-Ferrario *et al.* (2015) a detailed analysis on energy use in the European food sector was performed and areas of improvement were identified. Key processes that can be improved are cooling and freezing which in Europe accounts for about 30% of electricity consumption in the food industry. In general, the so-called “top 10 energy saving tips” in the industrial sector can be applied to the food industry. As such, possible measures span from high-efficiency motors and increased use of combined heat and power (CHP) to intelligent and

efficient lighting, or appliances' voltage optimization, all of which should be integrated into a comprehensive energy management system for a factory/industry. Moreover, the food processing industry is also exploring the possibility of recovering the energy contained in food residues on site, through biogas production or in dedicated combined heat and power plants.

Besides, most of the equipments in the food industry is sanitized (cleaned and disinfected) daily, in some cases several times per day, thus requiring the consumption of water, energy, and chemicals. For example, the European LIFE+ project "ECOD-HYBAT" demonstrated that a proper eco-design criterion can reduce the consumption of water, energy and chemical cleaning and disinfection agents in food processing companies, as well as the environmental cost of sanitation processes.

Logistics

Logistics and distribution systems, including refrigerated transport of food, can be a relevant source of impacts on resource consumption, climate change, and ozone depletion (due to refrigerants used in refrigerated transport and refrigerated storage units). A general indication is to promote the consumption of locally produced food - in their growing season- or to reduce the transportation distance. For refrigerated transport, efficient refrigeration units (e.g., switching off when not needed) can become a decisive contributing factor too. Thus, the optimization of procurement strategies plays a pivotal role in reducing food waste and improving the overall sustainability of the retail system.

Packaging

The reduction of packaging mass per unit of product has been a well-known key factor for reducing the environmental impacts. Recently, the issue of increasing the use of easy-to-recycle and bio-based materials has become a hotspot. However, alternatives should be carefully assessed because of possible trade-offs between the potentially increased environmental impact of packaging and the need for reducing food waste.

Consumption Phase

Eco-innovations in the use phase are mainly related to consumer choice and behavior. For example, since meat and dairy products production chains have higher environmental impacts, several studies model the possible environmental impact reduction through dietary shifts (e.g., comparing the environmental impact of different dietary protein choices). Besides, the consumption of ready-made products has been globally increasing. The preparation of ready-made meals and ready-made products (such as fresh-cut vegetables) is an activity that produces additional impacts if compared to less-processed food. Therefore, the reduced consumption of ready-made products can bring environmental benefits. However, impacts associated with meals prepared at home also exist, and due to the efficiency of mass production, a ready-made meal can be (or can become through technological improvements) more sustainable. Several improvements are proposed for catering services, especially in regards to sustainability strategies in the purchase of food, the type of cooking option, the selection of cutlery and dishes (e.g. avoiding single-use items).

End of Life and Food Waste

Food loss and waste are increasing worldwide due to a number of different production and consumption drivers. The increasing food demand provides new market opportunities in the agro-farming sector, such as the reduction of impacts and the maximization of resource recovery. Solutions to food waste are numerous and include waste prevention strategies, industrial symbiosis at the processing stage (Mirabella *et al.*, 2014), recovery of waste at the end of life (e.g., to produce animal feed), and avoiding the landfilling of organic waste. Assessing food systems with LCA includes assessment of the end of life phase, namely the food waste generated in the different life cycle stages, and the potential for resource efficiency regarding recovery of materials and energy from food waste. The identification of eco-innovations related to food waste requires several steps: (i) The systematic accounting of food loss generated along the stages of the food supply chain; (ii) the modeling of waste treatments according to the specific characteristics of food, and (iii) the modeling of multi-functionality. Corrado *et al.* (2017) proposed an approach with the goal to improve food waste modeling. Moreover, the use of unavoidable food waste or food by-products as input for added value bio-based materials to be used in pharmaceuticals, nutraceutical (Mirabella *et al.*, 2014), becomes a source for reducing impacts and promoting a circular bioeconomy.

Eco-Innovation Analysis With LCA

Identification of eco-innovations is not enough, as there is a need of verifying the magnitude of the benefits and the existence of possible trade-offs. This benefit analysis is needed to: Avoid that an expected benefit in an impact category poses a burden on another category; avoid that reducing impact in a life cycle stage implies additional burden in another stage; and, validate that the innovation leads to an overall benefit. The assessment of potential benefits in LCA results from the analysis of a baseline scenario and its contrast against additional scenarios representative of all life cycle stages and factor variances. This analysis is often complemented with optimization functions, namely prioritization of interventions based on benefit maximization (e.g., an environmental and economic optimization of food prevention actions, see by Cristobal *et al.*, 2018).

Conclusion

Eco-innovations are pivotal towards more sustainable food supply chains and entail technological, organizational, and behavioral aspects. Eco-innovation analyses should focus on the identification of critical impact hotspots and should be assessed with holistic LCA approaches that encompass all the life cycle stages from the extraction of raw materials to the end of life. The assessment of potential benefits in LCA results from the analysis of a baseline scenario and its contrast against additional scenarios representative of all life cycle stages and factor variances. This article presented an overview of possible areas of eco-innovations with a life cycle perspective. Core eco-innovations were identified in resource extraction, agriculture, processing and manufacturing, logistics, packaging, consumption, and end of life. The complexity of the challenges in the food system requires enhancing the cross-pollination among difference science domains (such as environmental, technological, social, and economic ones) that are required to support the definition and the implementation of eco-innovations. The implementation of an eco-innovation requires the life cycle modeling in order to validate its potential benefits, to assess the magnitude of such benefits, and to unveil possible trade-offs.

See also: Conversion of Renewable and Food Wastes into Useful Products With Environmental Perspectives. Food Residue, Loss and Waste as Animal Feed. Food Waste for Sustainable Packaging Materials. Local Food and Healthy Eating for Wholesome Life: Some Policy Considerations. Sustainable Technologies in Agriculture Sector: Ensuring Green Food Production for Resource Conservation. Upcycling Fresh Food Items in Retail Operations

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Edible Films and Coatings for Fruits and Vegetables

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Introduction

Fruits, vegetables and other food products are preserved or stored since the beginning of human civilization. With technological developments the way of storage and preservation of food products including fresh fruits and vegetables also changed and modernized. The techniques such as chemical fungicides, modified atmosphere packaging (MAP), controlled atmosphere packaging/storage (CAP/CAS) and plastic films are being used for post-harvest management of fruits and vegetables since many decades (Mario *et al.*, 2010). Though these technologies are dominating the sector of post harvest management and storage of fruits and vegetables but still they produce lots of limitations like- growth of tolerant pathogens, fungicide residual hazards, anaerobiosis, improper ripening and off-flavor development but failed to increase the shelf life up to maximum desirable level. Further, these techniques are not universally applicable for all perishable fruits and vegetables. So, an urgent need of an alternative technique such as edible coating with active functional materials like – antioxidants and antimicrobials etc., was realized to inhibit the rapid quality degradation of food products including horticultural crops without significant risk to environment and health hazards.

Application of edible films and coatings in food products including fresh fruits and vegetables seems new, but its basic technology is an age-old practice. Wax coatings have been applied to reduce dehydration of citrus fruits in China since 12th centuries (Guilbert and Biquet, 1986). Use of coating in meats to thwart shrinkage has been in practice since at least 16th century, where meat cuts were coated with lipids (Kester and Fennema, 1986a,b). Yuba, which is a proteic edible film obtained from the skin of boiled soybean milk, was conventionally used in Asia to enhance the exterior and preservation of various food products since the 15th century (Gennadios *et al.*, 1993). Later in the last century, the preservation of meat and other perishable food products by coating them with gelatin was recommended (Contreras-Medellin and Labuza, 1981). In the 19th century, sucrose was initially applied as an edible coating on dry fruits and nuts to prevent oxidative rancidity during storage. The more important application of edible films and coatings extensively started particularly since the 1930s with the use of an emulsion made of waxes spread on fruits to improve their appearance (shininess, color, softening), onset of mealiness, carriage of fungicides, and to better control their ripening and to delay the dehydration. Over the last 40 years, extensive researches on the optimization of formulation, methods of application, and characterization of edible films and coatings have been carried out and reported in both scientific and patent literature.

Many types of material used for enrobing (i.e., wrapping or coating) various food to extend shelf life of the product that may be eaten together with the coated food. Both edible films and coatings are similar in composition but basic difference among them is edible coating remain adhered with the surface of the product, whereas edible films do not adhere with the product rather it fulfills the utility of wrapping or packaging purposes. Edible coatings and films are generally produced from renewable natural and biodegradable polymeric materials such as polysaccharides, proteins, lipids, or the combination of these components (composite and conglomerate coating/film). For the past decade, research on edible films and coatings in foods is driven due to the high demand of consumers for longer shelf-life and better quality of fresh foods as well as of environmentally and health friendly packaging (Debeaufort *et al.*, 1998; Tharanathan, 2003; Cha and Chinnan, 2004; Siracusa *et al.*, 2008).

It is being observed that coatings and films with single basic material possess several limitations. To overcome the drawbacks of single component edible films and coatings, a concept of combining the unique features of different individual coating materials in desired combination has been developed in the name of composite coatings and films. It is constructed either by making successive layers of different film forming material, or in the form of a single layer film from emulsion, suspension or dispersion in the immiscible layers at a time, or by making solution of different materials in the same solvent and subsequent formation of film or coating. In this direction, edible coatings made with chitosan and yam starch demonstrated significant antimicrobial activity when used in the coating of carrots (Durango *et al.*, 2006), strawberries (Mali and Grossmann, 2003), mango etc (Vargas *et al.*, 2006) and raspberries, as well as in table grapes inoculated with *B. cinerea* (Romanazzi *et al.*, 2002).

Further, functional and active edible coatings and films are also being developed by introducing certain materials like- antioxidant, antimicrobial and nutraceuticals into the coating or film which prevents the growth of micro organisms, reduce oxidative degradation and also enhance the nutritive value of the packaged food (Bifani *et al.*, 2006; Lin and Zhao, 2007; Vargas *et al.*, 2008). Reported that different functional materials including nanomaterials in edible coatings can increase the desired functionalities of packaging materials extending the shelf life of the coated produce. The extract of natural herbs can also be incorporated inside the molecular orientation of the edible polymeric base of edible coatings and films (Paul, 2018). Edible films and coatings with tea extracts, different edible oils etc are already applied successfully to extend the shelf life and retention of quality attributes. In edible films and coatings these additives demonstrated prolonged and controlled efficacy due to their immobilization inside the polymeric chains. These extracts are also eliminate the application of hazardous chemical substances and are expected to contribute positively in the search of green and natural materials.

In addition to the natural extracts, various active, smart and intelligent functional additives are also being incorporated into edible films and coatings to achieve certain goals. It is demonstrated by various researchers that appropriate incorporation of

certain engineered substances including nanomaterials in edible films and coatings substantially enhance the required functionalities of the film or coating by controlling microbial, enzymatic, biochemical reactions of the internal environment. Their incorporation can also impart in low oxygen availability, controlled release of carbon dioxide and excellent mechanical and barrier properties. Though in present days, scientists are interestingly creating a domain for novel application of nanotechnology in various fields of food processing keeping in mind about their probable risks and safety issues, but till now very little research has been done in the area of edible nano-packaging for foods especially fruits and vegetables. Observing and analyzing each and every dimension of developments of edible films and coatings author expects that improved edible films and coatings with various active materials including natural extracts, their nanomaterials and safer synthetic nanomaterials will dominate among the existing technologies for preservation and primary packaging of fruits, vegetables and various other food products.

Edible Films and Coatings

Any type of material used for enrobing (i.e., wrapping or coating) various food to extend shelf life of the product and/or value addition that may be eaten together with food with or without further removal is considered as edible film or coating. Both edible film and coatings are similar in composition but basic difference among them is edible coating remain adhered with the surface of the product, whereas edible film do not adhere with the product rather it fulfills the utility of wrapping or packaging purposes. Edible films and coatings have been applied on meat, poultry, seafood, fruits, vegetables, grains, candies, heterogeneous and complex foods, or fresh, cured, freeze, and processed foods. An ideal coating is defined as one that can extend storage life of fresh fruits or vegetables without causing anaerobiosis and reduces decay without affecting the quality of the coated fruits or vegetables (Ghaouth *et al.*, 1992). When edible coating or film contains any functional or active material (antioxidant, antimicrobial or nutrients etc.) then it is termed as functional edible coating or film, which seems to have tremendous scope for value addition and storage. Improvement of the technology in this domain is of great importance for the present day food and packaging scientists. For the past 10 years, research on edible coatings in foods is driven due to the high demand of consumers for longer shelf-life and better quality of fresh foods as well as of environmentally and health friendly packaging (Debeaufort *et al.*, 1998; Tharanathan, 2003; Cha and Chinnan, 2004; Siracusa *et al.*, 2008). Indeed, edible coatings can be used as a vehicle for incorporating natural or chemical antimicrobial agents, antioxidants, enzymes or functional ingredients such as probiotics, minerals and vitamins (Bifani *et al.*, 2006; Lin and Zhao, 2007; Vargas *et al.*, 2008).

Edible coatings provide replacement and/or fortification of natural layers to prevent moisture losses, while selectively allowing for controlled exchange of important gases, such as oxygen, carbon dioxide, and ethylene, which are involved in normal respiration processes and ripening of fruits and vegetables. A coating can also provide surface sterility and prevent loss of other important components.

The principal reason of fruit and vegetable spoilage are gas exchanges (respiration and transpiration) during ripening and storage, and/or microbial growth, particularly molds and rots. In addition, changes in gas transition leads to various other equally important detrimental characteristics. These include loss or change of flavor and aroma, esthetically unacceptable appearance and changes in texture (Paul, 2018).

The main advantage of edible coatings over traditional synthetics is that they can be consumed with the products and are environmentally safe. The coatings are produced exclusively from renewable and edible ingredients and therefore are anticipated to degrade more readily than polymeric materials. Edible coatings can enhance the organoleptic properties of coated foods provided they contain various components (flavorings, colorings, sweeteners). Their use based on natural polymers and food grade additives has been constantly increasing in the food industries, including fruits and vegetables. The coatings/films can be produced with a variety of natural products such as polysaccharides, proteins and lipids, with the addition of plasticizers and surfactants. The functionality and performance of edible coatings mainly depend on their barrier, mechanical and optical properties, which in turn depend on coatings composition and manufacturing process. The choice of an edible coating mainly depends on the specific characteristics of the food product that requires protection and its storage conditions.

The new generation of edible coating is being especially designed to increase their functionalities by incorporating natural or chemical antimicrobial agents, antioxidants, enzymes or functional ingredients such as probiotics, minerals and vitamins (Bifani *et al.*, 2006; Vargas *et al.*, 2008). Antimicrobial and antioxidant coatings have advantages over direct applications of the antimicrobial or antioxidant agents because they can be designed to slow down the diffusion of the active compounds from the surface of the coating. Edible coating can enhance the nutritional value of foods by carrying basic nutrients and/or nutraceuticals in its matrix. The sensory quality of coated products can be also improved if flavor and pigment compounds are added in the matrix. Incorporation of antimicrobial agents such as benzoic acid, sorbic acid, propionic acid, lactic acid, nisin, and lysozyme in coating have shown retarded surface growth of bacteria, yeasts, and molds on a wide range of products, including various fruits and vegetables. Various antimicrobial edible films have been developed to minimize growth of spoilage and pathogenic microorganisms. The effect of coatings on fruits and vegetables depends greatly on temperature, alkalinity, thickness and type of coating, and the variety as well as maturity/ripening stage of the fruits and vegetables (Park *et al.*, 1994). Various types of polysaccharide-based (cellulose, chitosan, alginate, starch, pectin, and dextrin), protein-based (wheat gluten, collagen, corn zein, soy, casein, and whey protein), lipid-based (waxes, acylglycerols, and fatty acids) edible films, as well as their composites are already developed and at present these are a commercial reality. Wide ranges of functional agents are being successfully incorporated into such

coatings during manufacture and several are yet to explore to enhance the safety and shelf life of fresh and ready-to-eat foods including fruits and vegetables.

Edible Coating Materials

Hydrocolloids (i.e., Proteins and Carbohydrates) and Lipids are the base matrix materials that generally being used for the production of edible films and coatings. Combinations of different materials at various ratio in the form of composite films or coatings are the improved type with higher functionality to address the limitations of the individual one (Li and Barth, 1998; Park *et al.*, 1994; Guilbert *et al.*, 1996a,b; Mahmoud and Savello, 1992).

Hydrocolloid materials

Hydrocolloids are hydrophilic polymers that generally contain many hydroxyl (-OH) groups. Now-a-days they are widely used as the base material for film-forming solution to execute and control the texture, flavor, color and shelf-life of foods (Williams and Phillips, 2000). They are fully or partially soluble in water and are used principally to increase the viscosity with or without the external application of heat to the continuous phase of the film forming solution i.e., as gelling agent or thickener (Baldwin *et al.*, 1995; Kester and Fennema, 1986a,b). They also possess the stabilization property to prevent the separation of emulsion (if the coating or film contains oil-in-water or water-in-oil components) due to an increase in viscosity of the aqueous phase. The kinetic motion of the oil droplets is reduced, resulting in a lower rate of flocculation and coalescence in the film.

Polysaccharide based films and coatings

Polysaccharide films and coatings are principally made from starch, pectin, cellulose (Li and Barth, 1998), chitosan (Zhang and Quantick, 1998, 1997; Ghaouth *et al.*, 1991, 1992; Jiang and Li, 2001; Cheah *et al.*, 1997; Li and Yu, 2000) and alginate etc. Due to their ability to form gel, thickening quality, viscosity and adhesiveness during the application of coating, as well as their efficacy to impart hardness, crispiness and compactness to the final product, they are extensively utilized in the practical field. Because of the makeup of the polymer chains, these coatings exhibit excellent gas permeability properties, resulting in desired modified atmospheres that enhance the shelf-life of the product, especially fresh products like – fruits and vegetables, without creating anaerobic conditions (Baldwin *et al.*, 1995). Additionally, polysaccharide films and coatings can be used to extend the shelf-life of various foods by preventing dehydration, controlling oil and aroma transmission, oxidative rancidity and surface browning but their hydrophilic nature makes them poor barriers for water vapor. The primary advantages of polysaccharide films or coatings are their structural stability and ability to slow down oxygen transmission due to their tightly packed, ordered hydrogen bonded network and low solubility. As a general rule coatings or films which do not provide protection against water transmission often have desirable properties in preventing oxygen transmission and vice versa (Banker, 1966). These coatings may retard ripening and increase shelf life of coated fruits and vegetables, especially climacteric fruits without creating severe anaerobiosis (Arvanitoyannis and Gorris, 1999).

Protein based films and coatings

Corn zein, wheat gluten, milk proteins, whey proteins, soy proteins and gelatin are being extensively studied for their film and coating forming ability, their features and functional efficacy in terms of quality retention and shelf life of coated products. Protein based films and coatings exhibit better resistance to gas transmission and mechanical and structural properties than polysaccharides. As like polysaccharide films, protein based films also possess excellent oxygen, aroma, and oil barrier properties. But, it also shows poor water vapor barrier property due to their hydrophilic nature (Baldwin and Baker, 2002). Like other films and coatings, properties of protein based films and coatings also directly depend upon type, composition and application/formation process of the coating and/or film (Sothornvit and Krochta, 2000, 2001; Sothornvit *et al.*, 2002; Cho and Rhee, 2002; Wan *et al.*, 2005).

Lipid based films and coatings

Lipid substances are utilized as protective coating to improve the gloss and most importantly to prevent moisture transmission, due to its hydrophobicity. Moisture transmission rate decreases with the increase in hydrophobic phase. Lipids offer limited oxygen barrier properties due to the presence of microscopic pores and elevated solubility and diffusivity. Lipid films or coatings are usually opaque, lack structural rigidity, mechanical strength and relatively inflexible (Guilbert *et al.*, 1996a,b). Due to their low polarity, films from lipid become thicker and brittle and thus they must be combined with different film forming hydrocolloids or their derivatives to provide mechanical and structural strength (Debeaufort *et al.*, 1993). Several lipid materials including paraffin wax, bee wax, acetoglyceride, shellac resins etc are extensively used to provide edible surface coating to retain the quality attributes of various fruits, vegetables and other food products during storage (Figs. 1 and 2).

Composite films

To overcome the drawbacks of single component edible films and coatings, a concept of combining the unique features of different individual coating materials in desired combination has been developed in the name of composite coating. It is constructed either by making successive layers of different film forming material, or in the form of emulsion, suspension or

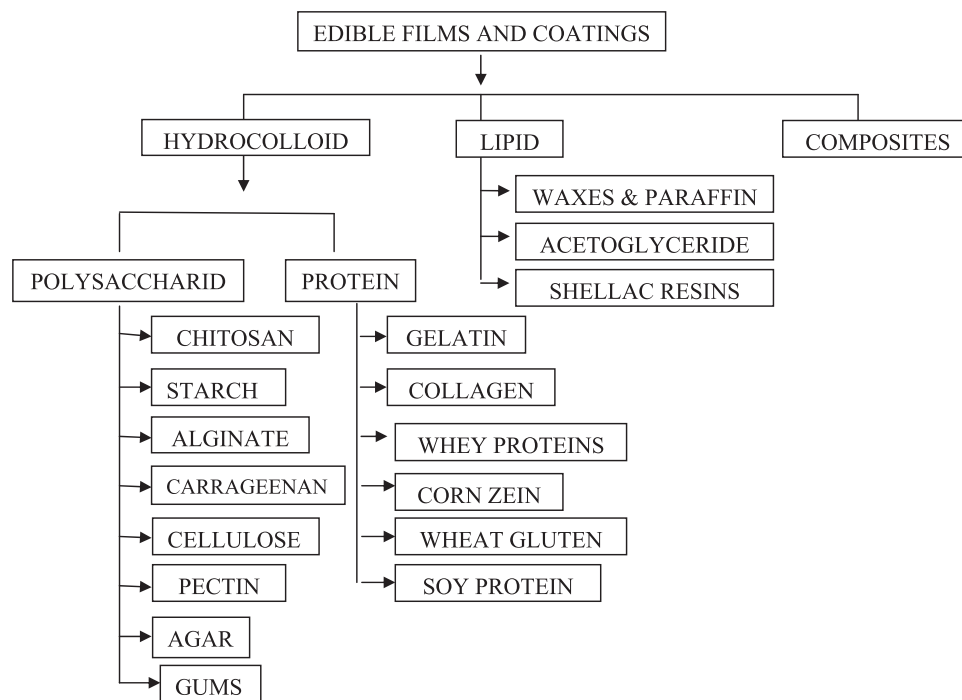


Fig. 1 Classification of edible films and coatings based on generally used material.

dispersion in the immiscible layers at a time, or by making solution of different materials in the same solvent and subsequent film or coating application. Improvement of mechanical, structural and permeation properties of the film or coating is the main motto of producing composite films. Extensive work has been carried out by the researchers exploring various improved properties by combining different proportions of methyl cellulose and fatty acid (Kamper and Fennema, 1984), lipid and hydroxypropyl methyl cellulose (Hagenmaier and Shaw, 1990), methyl cellulose and lipid (Greener and Fennema, 1989), methyl cellulose and fatty acid (Sapru and Labuza, 1994), casein and lipids (Avena-Bustillos and Krochta, 1993), gelatin and soluble starch, hydroxypropyl starch and gelatin (Arvanitoyannis *et al.*, 1998), corn zein and corn starch (Ryu *et al.*, 2002), gelatin and fatty acid (Bertana *et al.*, 2005), soy protein isolate and polylactic acid (Rhim *et al.*, 2007) to maximize the quality retention and extension of shelf-life of the coated items.

Methods for Film and Coatings Formation

Formation and/or processing techniques differ between edible film and coating. Edible coatings are mostly applied on the surface of the material by dipping, brushing and spraying of the coating solution depending upon the feasibility, whereas, like thermoplastic polymeric structures solvent casting, extrusion, spinning etc. are the mostly used techniques of present day for edible film formation and processing. In food industry, coating by spraying is the conventional method generally used when the coating forming solution is not very viscous. Indeed, highly viscous solution cannot be or very easily sprayed and brushing also can't coat a material in a homogeneous and uniform way. Thus only dipping techniques can be applied giving high thickness to the coating with uniformity. The adhesiveness of the coating on the surface of the food product mainly depends on its specific nature, i.e., on its affinity, but little depends on the coating technique used. Affinity depends on the physical nature and on the number of interactions or bondings between coating and support surface. So, the use of substances like-emulsifiers makes possible the sticking of a hydrophobic coating on a hydrophilic food surface (Gontard and Guilbert, 1994). On the other hand, coating thickness depends essentially on the application technique and on the viscosity of the formulation (Fellows, 1990).

Formation of effective and quality edible coating requires several sophisticated steps and optimized judgment. The basic process of present day as standardized by this author (Paul, 2018) for the development of a new edible coating on a product is explained in the following outline:

- (1) Preparation of coating formulations by taking a range of independent variables and varying their concentration in the formulation.
- (2) Designing of experiments by using appropriate statistical method like- Central Composite Rotatable Design (CCRD), Completely Randomised Block Design (CRBD) based on number of variables and set of run.

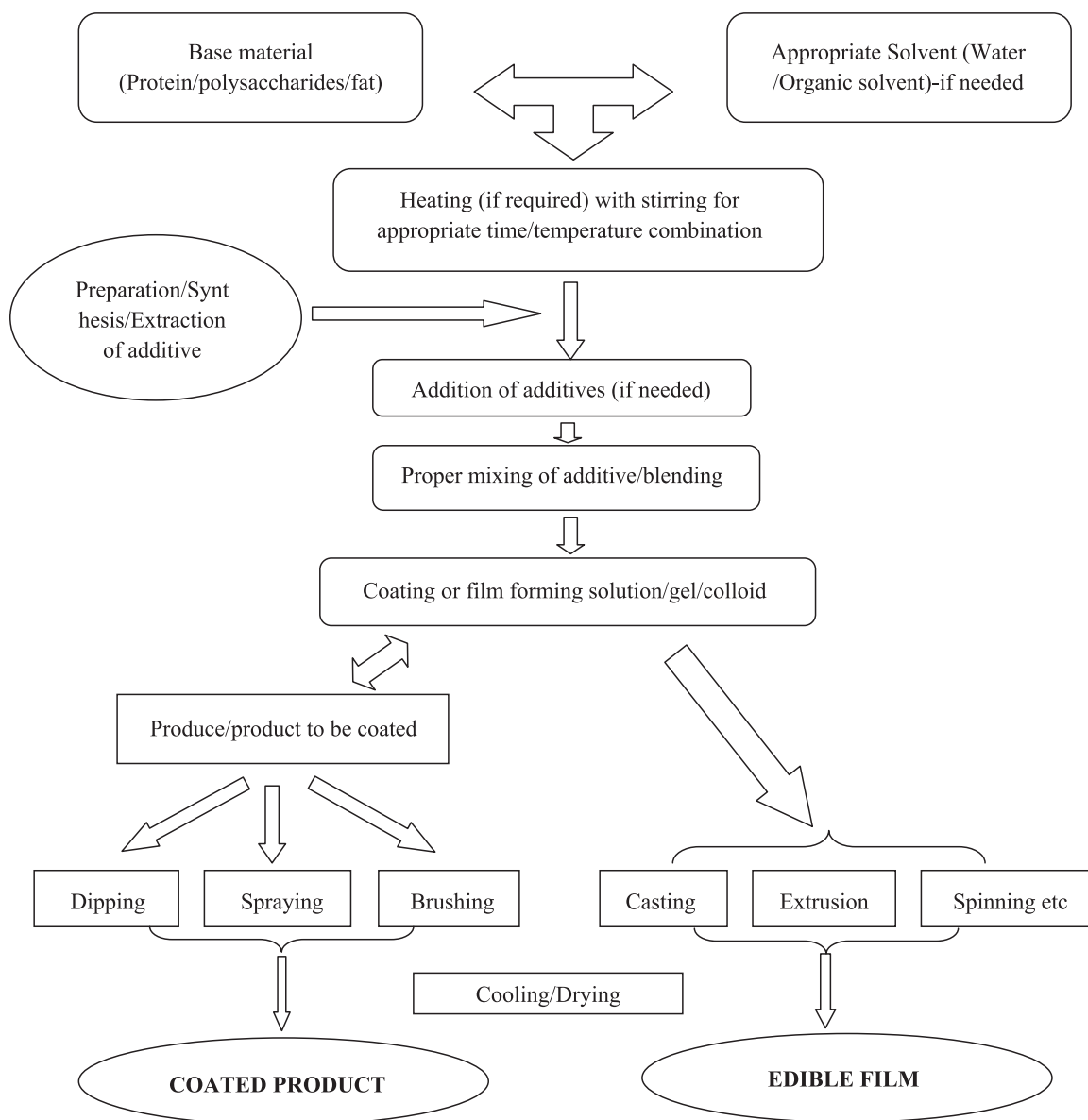


Fig. 2 General flow diagram of application/production of edible coating and film.

- (3) Model fitting and soft computing optimization of the composition of coating formulation among the set of formulations based on the experimental results of coating attributes and product characteristics.
- (4) Impregnation of additives at a range of concentration into the optimum coating formulation (if desired).
- (5) Application of coating by modern coater (may be separately developed and optimized based on the product type) at standardised thickness throughout the process.
- (6) Storage analysis of the coated product and determination of minimum but most effective concentration of additives by statistical tools in terms of retention of quality attributes and extension of shelf life.
- (7) Compilation and recommendation of final process and formulation by model validation with experimental data.

Now a day's dipping is a common method for applying coatings on fruits and vegetables (Vargas *et al.*, 2008). The coating is made by dipping in a coating solution with standardized properties such as density, viscosity and surface tension, as well as keeping time and food withdrawal speed from the coating solution (Cisneros-Zevallos and Krochta, 2003). These properties have direct effect on the final coating thickness and thus different theoretical approaches can be used to estimate film thickness from coating solution properties (Snoeijer *et al.*, 2008). Generally the food is dipped into the film-forming solutions between 5 and 30 s and suitable coatings are obtained with remarkable utility (Vargas *et al.*, 2006; Ayranci and Tunç, 1997). Direct application of antimicrobial agents onto food surfaces by dipping has proven to be less effective as there is loss of activity because of leaching onto the food, enzymatic activity, and reaction with other food components and therefore embedding the active materials into

coating base can show higher efficacy limiting the problems. The application of edible coating to minimally processed fruits is not easy because it is difficult to obtain a good adhesion of the coating to the hydrophilic surface of the cut fruit. A solution to solve this problem could be a multilayer composite technique: the layer-by-layer electro deposition where two or more layers of material with nanometer dimensions are physically or chemically bonded to each other (Vargas *et al.*, 2008; Weiss *et al.*, 2006).

In case of edible film production, the process up to the preparation of coating or film forming solution/gel/colloid is same like the process of edible coating (till step (iv) of the outline) as described in previous paragraph. Appropriate film forming method should be selected depending upon the properties of base material, prepared formulation, product to be packaged and requirement of any special features in the produced film. Techniques used for the producing of flexible plastic films can also be used for edible and biodegradable films (Lindstrom *et al.*, 1992; Fellows, 1990). These techniques can be extrusion or co-extrusion for multilayer films, solvent casting, spinning, lamination, and roll-drying for the solvent removal of the polymer formulation. After the film processing it should be dried carefully and produced films are used for packaging purposes.

Properties of Edible Films and Coatings

Thickness

Thickness of edible films and coatings is an important parameter since it directly affects the biological properties and shelf life of the coated food by interfering permeability, transparency etc. The effectiveness of edible films and coatings for protection of food depends primarily on controlling the spreading of the coating solutions, which affect the thickness of the film and thus leading to its affect into porosity, transparency, gas and water vapor permeability etc.

Mechanical properties

Tensile strength, Young's modulus and elongation at break are the most important key parameters to study the mechanical properties of edible film, whereas for edible coating these properties are not directly determined. Still, these properties are indirectly associated with various other properties of edible coating that significantly affect the product quality. Researchers have determined these parameters from the stress-strain curves according to the norm of the American Society for Testing and Materials (ASTM). These properties of films are very important for their application as a packaging material. These properties indicate the strength, elasticity and protect-ability of the film.

Barrier properties

Protecting features of edible films or coatings against the permeation of gases, water vapor, oil, aroma compounds and light are very important key factors for maintaining the quality of the products during storage and extension of the shelf-life, which determine the efficacy of the film or coating. Chemical composition and structure of the film/coating-forming polymers, composition of film/coating solution, interactions between the sorbent and solvent, processing and drying parameters, the characteristics of the product, and the storage conditions are mainly responsible for the barrier properties of the film or coating (Paul *et al.*, 2015, 2018; Paul, 2018).

Optical properties

Optical properties are characteristics of surfaces which are detected by human vision affecting some crucial aspects including esthetic properties of food quality. Gloss, transparency and color are the main optical properties of edible coatings and films. The internal and surface film microstructure together plays an important role in overall optical properties of the film and coated product. Indeed, the intensity of light reflected by the coated food is determined both by the light directly reflected at the interface between air and the coated food surface, which is responsible for the gloss of the product (specular reflection) and by both the light re-emitted out of the surface in all directions after penetrating into the coating of the food and scattering internally (indirect reflection) depending upon the transparency of the coating. Specular reflection is related to the gloss of the coating or film. The gloss and indirectly specular reflection property of edible coatings as well as film is affected by coating microstructure in particular, by the type and level of surfactant, the distribution and the size, particle diameter of dispersed phase, relative humidity, storage time and the surface roughness (Nikolova *et al.*, 2005; Villalobos *et al.*, 2005). The transparency of films was measured through the surface reflectance spectra in a spectrophotometer, which is inversely proportional to the absorbance at a particular wavelength (Das *et al.*, 2013; Paul *et al.*, 2015).

Thermodynamic parameters associated to sorption phenomenon

The interactions of between the sorbant and solvent can define the efficiency of the edible film and coating to control the gas permeability and therefore also controls the respiration and ripening of fresh fruits and vegetables, as well as the stability of the coated food. The relationship between the total moisture content and the water activity (A_w), over a range of values, at constant temperature, yields the sorption isotherm when expressed graphically. When obtained at different temperatures, the energy associated to moisture interactions at low water vapor pressures can be estimated. Various mathematical models have been developed to describe sorption isotherms, which are also used to standardize the edible films and coatings to achieve better efficacy (Sabeti *et al.*, 2015).

Advantages of Edible Films and Coatings

Edible coatings and films are used to improve food appearance and conservation due to their various advantages over usual synthetic packaging materials. These are produced from both animal and agricultural products, hence possess environment-friendly, biodegradable and eatable nature. Edible packaging also reduces the wastage of packaging materials in compared to synthetic packaging (Petersen, *et al.*, 1999; Park *et al.*, 1994; Sothornvit and Krochta, 2000). They act as barriers to moisture, oxygen and other gases during processing, handling, and storage (Li and Barth, 1998; Avena-Bustillos *et al.*, 1994a,b), and not only retard food deterioration but also enhance its safety due to either their natural biocidal activity or the incorporation of antimicrobial compounds, that also leads to the advancement of the concept of active packaging (Appendini and Hotchkiss, 2002; Cha and Chinnan, 2004). Thus, the use of an edible coatings and films, such as chitosan and yam starch were found to be a viable alternative for controlling microbial growth in minimally processed carrots (Durango *et al.*, 2006), strawberries (Mali and Grossmann, 2003), and raspberries (Han *et al.*, 2004), as well as in table grapes inoculated with *B. cinerea* (Romanazzi *et al.*, 2002).

Advantages of edible films and coatings also include, improved retention of moisture, firmness, color, acids, sugars, and flavor components, reduced weight loss, reduction of storage decay, improved consumer appeal and extended shelf-life (Park *et al.*, 1994; Sothornvit and Krochta, 2000; Davis and Hofmann, 1973; Avena-Bustillos *et al.*, 1994a,b, 1997; Baldwin *et al.*, 1995).

Edible films and coatings have also found to retard respiration rates (Banks, 1984), reduce ethylene production (Banks, 1984; Baldwin *et al.*, 1995), reduce metabolism and oxidation rates (Li and Barth, 1998), hinder solute movement (Li and Barth, 1998), retard loss of chlorophyll and other coloring compounds thus retaining the color (Banks, 1984), seal in flavor volatiles, carry additives that could contribute in their specific functionality (Baldwin *et al.*, 1995).

Thus the major benefits of edible films and coating are that they can be consumed along with food, can provide additional nutrients, may enhance sensory characteristics and may include quality enhancing antimicrobials and antioxidants and also extension of shelf-life as well as preservation of product quality during storage (Guilbert *et al.*, 1996a,b).

Limitations and Ongoing Improvement Strategies

Even though some edible coatings and films have been successfully applied to fresh produce and substantial scopes are seen to address several technological problems but some correctable limitations are also observed which may further reduce limitations in terms of quality aspects of the product and food safety. Modification of internal atmospheres by the use of edible coatings can increase disorders associated with high carbon dioxide or low oxygen concentration leading to anaerobiosis (Smith *et al.*, 1987). It was observed that tomatoes coated with 5–66 μm zein film produced alcohol and off-flavors internally which were attributable to an internal gas composition with too low in oxygen and too high in carbon dioxide (Park *et al.*, 1994). It was also found the development of alcoholic flavors in apple and pear due to inhibition of normal respiration rate leading to anaerobic fermentation on sufficient wax coating. Increased core flush incidence was also observed along with some other different advantages in apple when coated with sucrose fatty acid ester (Momen *et al.*, 1997). Sometimes, micro organisms can also get favorable condition for their growth in edible coating or film that may leads to the mass scale spoilage of the product. Another existing disadvantage of these techniques is the loss of quality of the edible coatings and films since there is no control over the shape, size and size distribution of the dispersed elements (e.g., additives, ingredients, etc.) in the support structure matrix. Another disadvantage of these techniques is that the thickness of the films is generally not constant and difficult to control.

To overcome these problems so many strategies are being adopted and some can still be adopted after thorough research in the aspect of analysis, value improvement and optimization. The effects of edible coatings on internal gas composition and their interactions on quality parameters must be determined for coated fresh produce. For example, color change, rate of ripening, firmness, ethanol fermentation, decay-ratio, and weight loss are very important quality parameters of fruits and vegetable in terms of storage and shelf life (Ninja *et al.*, 2017; Paul, 2018). Also, if a coating is too thick, detrimental effects can result due to an internal oxygen concentration below a desirable level and an associated increased carbon dioxide concentration above a critical tolerable level. Such a condition leads to anaerobic fermentation and off flavor formation. In this regard, it is proposed that these issues can be addressed by: (a) developing several edible coatings with suitable structural additives like- plasticizer with different concentrations and combinations and optimizing the independent parameters with respect to the dependant, (b) incorporation of functional materials like antimicrobial, antioxidants (e.g., natural, permitted chemicals or suitable nano materials etc.) in different concentration into the optimized concentration and analyzing its effects after coating, (c) measuring volatile components and gas permeation properties of selected coatings, (c) measuring diffusion properties of skin and flesh of selected fruits, (d) predicting internal gas compositions for the fruits coated with edible films with respect to the coating period, and (e) observing coating effects on the quality changes of the coated products with respect to the coating period.

Functional Additives and Other Strategies to Improve Edible Films and Coatings

Improvement of mechanical and functional properties of edible films and coatings is done by adding certain additional substances like – plasticizer, oils, natural active materials, antioxidants, antimicrobials, nutrients, colorants, vitamins, probiotics etc., into the coating solution, which may be termed as additives. However, plasticizers are the main and commonly essential additives used in films and coatings. Antioxidant and antimicrobial agents can play remarkable role in extension of shelf life by preventing oxidation by limiting oxygen availability and microbial degradation respectively. Other functional additives may have

preservative, nutritional or esthetic value to the coated product. Various natural functional extracts and phytochemicals as well as green nanomaterials with tremendous functionalities have become the most important zone of interest among the global scientists to combine them with edible coatings and films. These materials have no or very minimum hazards to environment and may also add some nutritional and nutraceutical benefits to the consumers. The ability of edible films to retard moisture, oxygen, aroma and solute transport may be improved by introducing additives such as antioxidants, antimicrobials, colorants, flavors, fortifying nutrients and spices in film formulation (Pranoto *et al.*, 2005).

Plasticizers

These are small molecular-weight compounds that can be added mainly in an edible film or coating solution to improve the flexibility and mechanical properties of the film matrix. As a general rule, the addition of a plasticizer increases the permeability of a film or coating. Plasticizer combines with the main component of the film, moving the component's chains apart, and thus reduces rigidity of the structure (Guilbert and Biquet, 1996). Without plasticizers, most films and coatings are brittle, and it is difficult to form a homogenous film. The effectiveness of a plasticizer depends upon three things: size, shape and compatibility with the matrix (Sothornvit and Krochta, 2001). Plasticizer also attracts water molecules around it, which reduces intermolecular interactions of the main component (Ke and Sun, 2001). Plasticizers normally generate a homogenous mixture without phase-separation. There are two types of plasticization: internal and external. Internal plasticizers chemically modify a polymer chain through addition of substituent groups attached via covalent bonds. Internal plasticizers create steric hindrance between the polymer chains, leading to increased free volume and improved flexibility. External plasticizers solvate and lubricate the polymer chains, lowering the glass transition temperature of the base polymer and also increasing the free volume. The most effective plasticizer is, of course, water. The state of the plasticizer under normal storage conditions may also affect its permeability and flexibility. Solid plasticizers may have an "anti-plasticizing" effect, and decrease matrix flexibility, while improving permeability (Dangaran and Krochta, 2007). In traditional polymer-plasticizer systems, anti-plasticization occurs when a plasticized system is harder and less flexible than the pure polymer at a temperature below the glass transition or T_g (Chang *et al.*, 2000; Morara *et al.*, 2002).

The most commonly used plasticizers for polysaccharide films are glycerol, sorbitol and polyethylene glycol (Sothornvit and Krochta, 2005; Mali and Grossmann, 2003). Disaccharides such as sucrose and monosaccharides (e.g., fructose, glucose, and mannose) have been investigated as their potentiality as plasticizer and found to be exhibiting films with lower WVP compared to those containing polyols as plasticizers (Zhang and Han, 2006; Olivas and Barbosa-Cánovas, 2008). Fatty acids have also been used as plasticizers in edible films and coatings, though they are not very common. A mixture of starch and alginate to form edible film has been studied to improve the mechanical properties of film. The mesquite gum forms films with excellent water vapor barrier properties when small amounts of lipids are added in their formulation. Addition of plasticizer such as glycerin in gluten films is very useful to improve film flexibility (Gennadios *et al.*, 1994). However, increasing film flexibility by increasing sorbitol content reduces film strength, elasticity and water vapor barrier properties (Contard *et al.*, 1993). Tensile strength of gluten films can be improved by using a cross-linking agent such as glutaraldehyde, or heat curing at 80°C (Gennadios and Weller, 1992; Koelsch and Labuza, 1992).

Antimicrobial and antioxidant agents

Antimicrobial and antioxidant coatings have advantages over their direct applications because they can be designed to slow down the diffusion of the active compounds from the surface of the coated food. The use of active or functional edible films and coatings in food protection and preservation has recently increased since they offer several advantages over synthetic materials, such as being biodegradable and eco-friendly (Tharanathan, 2003; Ponce *et al.*, 2008).

Antimicrobial agents: The antimicrobial coatings and films are rapidly developing technologies that are being employed for controlling the microbiological decay of perishable food products (Del Nobile *et al.*, 2008). Common chemical antimicrobial agents used in food systems, such as benzoic acid, propionic acid, sodium benzoate, sorbic acid, and potassium sorbate etc may be incorporated into edible films and coatings to inhibit the outgrowth of both bacterial and fungal cells. In fact, the antimicrobial compounds, when establish contact with food, inhibit the growth of microorganisms present in the surface (Appendini and Hotchkiss, 2002). These films could prolong the shelf-life and ensure the safety of foods by acting as a hindrance for growth of pathogenic and spoilage microorganisms due to their lag-phase extension and/or their growth rate reduction. However, due to the health concerns of consumers related to chemical preservatives, the demand for natural substances has spurred the search for natural bio-preservatives in edible films-forming preparations. The most frequently used bio-preservatives as antimicrobial are lysozyme and nisin. These biopreservatives are shown bactericidal effect on Gram (+ve) bacteria but they can also become effective on Gram (-ve) bacteria if they are combined with chelating agents such as ethylene diamine tetraacetic acid (EDTA). Common other bio-preservatives that may be used in edible films and coatings are other bacteriocins, such as lactacin and pediocin and antimicrobial enzymes, such as chitinase and glucose oxidase. Natural antimicrobial compounds have also been incorporated into protein or polysaccharide-based matrices: rosemary, and garlic essential oils, lemon grass, cinnamon oil etc at different concentrations.

Antioxidants: Incorporation of antioxidants in edible films-forming preparations to increase product shelf life by protecting foods against oxidative rancidity, degradation, and discoloration has become very popular. Most antimicrobial compounds also have antioxidant properties. Natural antioxidants such as phenolic compounds (such as carvacrol, camphor, eugenol, linalool and thymol), vitamins E and C in place of synthetic antioxidants are extensively used in edible films. Essential oils and various extracts exhibit a wide range of biological effects, including antioxidant and antimicrobial properties.

Essential oils

Consumers have been continuously moving towards the food products with NO or LESS chemicals. So, the searches for natural substances which can act as alternative active and functional materials are in peak. Essential oils are one of the search outputs those are aromatic, natural antioxidant, and antimicrobials obtained from plant sources. They consist of a mixture of various natural functional compounds, such as terpenoids, phenolic acids, terpenes, and various other aromatic and aliphatic compounds, but their exact composition varies based on their source. The presence of essential oils can extend the shelf life of food products by limiting microbial growth and preventing lipid oxidation (Tongnuanchan *et al.*, 2013; Perdonés *et al.*, 2014).

However, some of their properties like- strong aroma, risk of toxic effect, and alteration of organoleptic properties of the food – have restricted their application in direct food preservation. However, a strategy is being developed to solve this problem by incorporating essential oils into edible films and coatings. It is possible to reduce the required doses by immobilizing them into the polymeric matrix, which limits their volatilization, controls their leaching, and preserves the quality and maintain the safety of fresh and fresh-cut fruits and vegetables (Sánchez-gonzález *et al.*, 2011; Bonilla *et al.*, 2013; Ruiz-Navajas *et al.*, 2013).

Tongnuanchan *et al.* (2013) studied the antioxidant properties of the edible film made by fish skin gelatin incorporated with essential oils of ginger, turmeric, and plai, where they showed higher antioxidant activity than the control film. Perdonés *et al.* (2014) reported that chitosan films containing cinnamon leaf oil also exhibit higher antioxidant activity. Ruiz-Navajas *et al.* (2013) also developed chitosan films introducing *Thymus piperella* oil presented higher antioxidant activity than edible films containing *Thymus moroderi* essential oil. The antioxidant activity hence depends upon the nature of essential oils and the structural features of the molecules, mainly the reactivity of the hydroxyl groups of the compounds. Concentration, temperature, light, physical state of the system, substrate type, and microcomponents acting as pro-oxidants or synergism also impact the antioxidant activity. Ponce *et al.* (2008) reported that butternut squash containing chitosan coatings incorporated with oleoresins improves the antioxidative protection of the fresh-cut squash, limiting the browning process without adversely affecting their organoleptic acceptability. However, the addition of antioxidants to films not necessarily always improves the antioxidant efficacy. Indeed, Atarés *et al.* (2010) reported that incorporation of Cinnamon oil and ginger oils with sodium caseinate films does not enhance antioxidant effect as compared with the control film without essential oils, even though cinnamon oil alone show high antioxidant property. In addition to their high antioxidant property, essential oils can also strengthen the water barrier properties of the film because they display the hydrophobic nature of lipids (Atarés *et al.*, 2010; Kaliana *et al.*, 2014).

Extracts

Chemically synthesized antioxidants have raised some safety concerns and various regulatory agencies have already restricted their use as food additives, so researchers have focused on films incorporated with antioxidants from various natural extracts (Murcia and Martínez-tomé, 2001; De'nobili *et al.*, 2013; Ninja *et al.*, 2017; Paul, 2018). These extracts also contribute to nutritional and quality features without affecting the food product integrity (Guilbert *et al.*, 1996a,b).

Extracts like tea extracts (Das *et al.*, 2013; Li *et al.*, 2014), ginseng extract (Norajit *et al.*, 2010), fruit and vegetables extracts (Akhtar *et al.*, 2012; Supapvanich *et al.*, 2012), and tulsi extracts (Ninja *et al.*, 2017) possess tremendous antioxidant activity, can reduce lipid oxidation, and enhance the quality and storage life of various food systems. The antioxidant effect of these extracts results primarily due to phenolic compounds and their antagonistic, synergistic, and additive effects (Krochta and Mulder-Johnson, 1997). However, despite their excellent scavenging effect and ability to protect the food products, they are still less effective than synthetic antioxidants.

Several studies on antioxidant and functional extracts that also confer color to edible films have been published (Gómez-estaca *et al.*, 2009a,b; Norajit *et al.*, 2010; Akhtar *et al.*, 2012; Li *et al.*, 2014). In addition, it has been well established that extracts exhibit coloring and antioxidant properties that enables effective control against photo-oxidation by reduced light transmission, especially ultra violet radiation (Norajit *et al.*, 2010; Li *et al.*, 2014). Hence, in the same way that natural extracts were successfully incorporated into edible coatings and films. Their use in edible films and coatings in fruits and vegetables could maintain food quality and also extend the shelf life. However, light exposure may degrade the active compound during storage and deteriorate optical properties like luminosity or chroma. Nevertheless, several scientists including the author of this article have shown that this technology can better control weight loss, color, nutrient loss and respiration rates, allowing for longer shelf life as compared with control samples (Pastor *et al.*, 2011; Das *et al.*, 2013; Kaliana *et al.*, 2014; Ninja *et al.*, 2017; Paul *et al.*, 2018; Paul, 2018).

Nanomaterials

Incorporation of nanomaterials into other base materials exhibit modifications in the properties of the materials and impart novel properties to the materials. In order to achieve these modifications in films and coatings, a proper interaction between the polymeric base and the nanofiller is desired (Lagaron and Lopez-Rubio, 2011).

Impregnation of the filler into the polymeric matrix can be achieved using in situ polymerization (dissolution of the nanoparticles in the monomer solution before polymerization), solvent intercalation (use of a solvent to increase the affinity between the nanoparticles and the polymer) and melt intercalation (addition of particles during the preparation of formulation for extrusion) (Chivrac *et al.*, 2009). When the affinity between the nanoparticles and the polymer is low, the nanoparticle or nanoclay interlayer does not expand and the nanostructures or clay tactoids remain as such in the polymeric base. In this way, no true nanocomposite can be formed. When the affinity between the nanostructure and the polymer is moderate, the polymer can partly penetrate the clay interlayer, leading to an intercalated structure, which is still a layered structure. When the affinity is high, an

exfoliated structure is formed by dispersion of the nanostructures into the polymeric base (Arora and Padua, 2010; Chivrac *et al.*, 2009; Paul, 2018). Since a high surface-to-volume ratio has the enhanced effect on the attributes of the developed polymer, the exfoliated structure is the ultimate goal.

Various chemical modifications on nanostructure surface in order, such as cationic exchange, use of block copolymers adsorption, ionomers, and organosilane grafting, are sometimes necessary to make the surface more hydrophobic leading to intercalation/exfoliation in the polymer matrix. Modification of the polymer can also lead to a more homogeneous dispersion (Chivrac *et al.*, 2009; Arora and Padua, 2010; Silvestre *et al.*, 2011).

Other strategies

Another way to enhance the performance of edible packaging is by chemical and/or physical modification of the polymers. Modification can impart a positive effect on mechanical properties and water vapor permeability of the produced film. It can also be used as a tool to enhance compatibility between two polymers or even polymers and additives. Towards this objective, mainly starch from different sources has been modified to improve their hydrophobicity, making them more compatible with hydrophobic functional additives and other polymers or food surfaces.

Oxygen permeability and hydrophobicity of microfibrillar cellulose (MFC) films was found to be improved by acetylation with acetic anhydride. Film thicknesses from 42 to 47 μm lead to oxygen permeability values required for MAP application (Rodionova *et al.*, 2011). Flexible starch films with water resistant properties can be produced by heating gelatinized starch with lithium chloride in an anhydrous suspension in the presence of an organic solvent (Fang *et al.*, 2005).

Cross-linking of cellulose acetate with tri-sodium tri-meta phosphate led to materials with higher tensile strength, lower water absorption and slower degradation kinetics (Demirgöz *et al.*, 2000). Crosslinked starches are more hydrophobic because it has additional carbon chains than native starches. This causes better compatibility of the starch with other polymers or additives (Kim and Lee, 2002).

According to Gennadios *et al.* (1993), water vapor permeability and oxygen barrier properties of a wheat gluten film can be improved by partial substitution of the wheat gluten with hydrolyzed keratin, probably due to bonding between the two proteins. Better water vapor resistance property was also demonstrated by soaking wheat gluten film in CaCl_2 solution and then in distilled water or in a neutral solution. This treatment process also showed enhanced tensile strength and is probably due to cross-linking of Ca^{2+} in the film structure and protein insolubility of wheat gluten at a pH equal to the isoelectric point. Further, Rhim *et al.* (1999) demonstrated that irradiation with ultra violet light on wheat gluten based film increases the tensile strength by 20%, suggesting a probable cross-linking within the film composition.

Regulatory Status

At global level, proper regulation for edible films and coatings, especially their additives and their quantum to be used is lacking. However, some countries have introduced few points in their own food safety regulations to keep the application of edible films and coatings within the safety limits. European Directive and USA regulations consider edible films and coatings as food ingredients, food products, food additives food packaging materials or food contact substances (ED European Parliament and Council Directive No95/2EC, 1995).

In Europe, the substances that can be incorporated into edible coating formulations are mainly considered as food additives and are listed in the list of food additives for general purposes, although acacia, pectins, karaya gums, polysorbates, beeswax, fatty acids, and lecithin are mentioned specifically for applications in edible films and coating (ED European Parliament and Council Directive No95/2EC, 1995). In any case, the use of these film or coating forming ingredients is allowed, provided that the "quantum satis" principle is observed. This Directive was complemented by the introduction of specific purity criteria for food additives.

In most of the countries, chemical substances used as antimicrobials are regarded as food additives, only if the primary purpose of the substances is to extend the shelf life. Another important domain of concern within regulatory status is the presence of allergens. Many edible films and coatings are made with the substances that could cause allergic reactions among certain individuals. Several edible films and coatings are also made from whey protein, casein, gluten, soy protein and peanut protein (Rojas-Graü *et al.*, 2009). So, the presence of a known allergen in edible packaging of food including fruits and vegetables must also be clearly labeled.

Further, edible films and coatings are meant for the purpose of its direct consumption, hence proper regulations for the compositions of edible films and coatings should be formulated and each and every ingredient should be properly labeled. Looking into the research outputs provided by various researchers, uses of organic, inorganic or biological nanomaterials are also being emphasized by business communities. Safety of consumption of nanomaterials and other chemically modified substances could not be assured till date. However, business communities may also adopt fraudulent means to incorporate potentially harmful substances through the gaps within the regulations. As the application of edible films and coatings are increasing continuously, therefore the regulatory authorities of every country should take the matter seriously into their notice and frame a proper regulation so that the goodness of the technology can be adopted eliminating any immediate or future safety issues among the consumers.

Future Trends

Edible films and coatings are very promising technologies for the future improvement in post harvest management, storage and packaging of fruits and vegetables. Indeed, they could be used where petroleum based packaging cannot be used, like – they can separate several compartments within a single food products if needed. Edible packagings can also be fabricated and utilized as *intelligent packagings* because they can be both active, selective and also be incorporated with smart features for infinite potential use.

A new generation of edible coatings for climacteric and perishable fruits and vegetables is under development, with the aim of allowing the incorporation and/or controlled release of functional compounds using micro-level and nanotechnological solutions such as nanoencapsulation and multilayered coatings, thus enhancing their viability and stability. Alginate is the most widely used biopolymer for encapsulation, but materials from different other biological sources can also be used. Enzymes, antioxidants, antimicrobials, colorants, flavors, probiotic, prebiotic, essential oils (omega-3-fatty acids) are among the most applied functional substances in encapsulations.

Nowadays, nanotechnologies are being used to enhance the nutritional aspects of food by means of nanosized additives and nutrients and nanolevel delivery systems for functional compounds. The concept of nanocomposites further brought a stimulating route for creating new and innovative materials, also with natural polymers. Coating foods with nanolaminates involves entirely either food-grade ingredients (proteins, polysaccharides, lipids) or could also include various functional materials such as anti-microbials, antioxidants, antibrowning agents, enzymes, colorants and flavorings. Further, the electrodeposition technique has also demonstrated potential that could be used to coat highly hydrophilic food including fruits and vegetables surfaces such as fresh-cut fruits and vegetables.

Consumer demands are driving the global scientists to search for alternatives to synthetic packaging materials with cost effectiveness. However, it is observed that the cost of edible films and coatings is many folds higher than those of polyethylene or polypropylene film. However, their cost is not major hurdle to their development because quantities used are very low, and till now they are especially applied for very specific goals in value-added food products. Thus, the concept of edible polymers and that of synthetic materials should be used synergistically for the development of new scope and utility, new biodegradable and edible materials, and new environment friendly approaches with the primary objective of proper post harvest storage, packaging and transportation of agricultural and horticultural produce and also shelf life extension of fresh and processed food products.

See also: Biodegradable Packaging Materials. Bio-Nanocomposites for Food Packaging Applications. Food Waste for Sustainable Packaging Materials. Role of Green Polymers in Food Packaging. Tailor-Made Bioplastics for Environmentally Friendly Food Packaging: A Methodological Approach to a Challenging Problem

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Energy Efficiency Improvement Opportunities in the Global Industrial Sector

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Introduction

In 2016, the global industrial sector consumed 144 EJ final energy, which corresponded to 36% of global final energy consumption (based on IEA, 2018a). The International Energy Agency (IEA, 2018b) projects that without any further actions, by 2040, industrial energy use will increase to 206 EJ (or by 43%). Improved energy efficiency can limit industrial energy use and is considered as one of the most cost-effective ways of reducing greenhouse gas emissions (Ryan and Campbell, 2012). Although in the past decades the adoption of energy efficiency measures reduced industrial energy intensity, increased energy demand due to increased industrial production, has offset any energy gains from improved efficiency. With increasing industrial productivity, industrial energy use and associated greenhouse gas emissions are expected to grow further, increasing the importance of energy savings.

In this article we will first give an overview of past developments of energy use and greenhouse gas emissions in industries, where we look at trends in sectors and countries (Section “Energy Use and Greenhouse Gas Emissions in Industries”). In Section “Energy Efficiency Measures” we focus on four major energy consuming sectors (chemicals, iron and steel, cement and aluminum) and describe the main energy consuming processes and energy saving opportunities. Finally, conclusions are given in Section “Conclusions”.

Energy Use and Greenhouse Gas Emissions in Industries

Fig. 1 shows a breakdown of global energy use in industries by sector, based on IEA (2018c). The chemical sector (including petrochemicals) is the biggest sector and is responsible for 26% of industrial energy use in 2016. This sector is followed by the iron and steel sector, which accounts for 19% and non-metallic minerals and oil refineries which both consume 9% of industrial energy

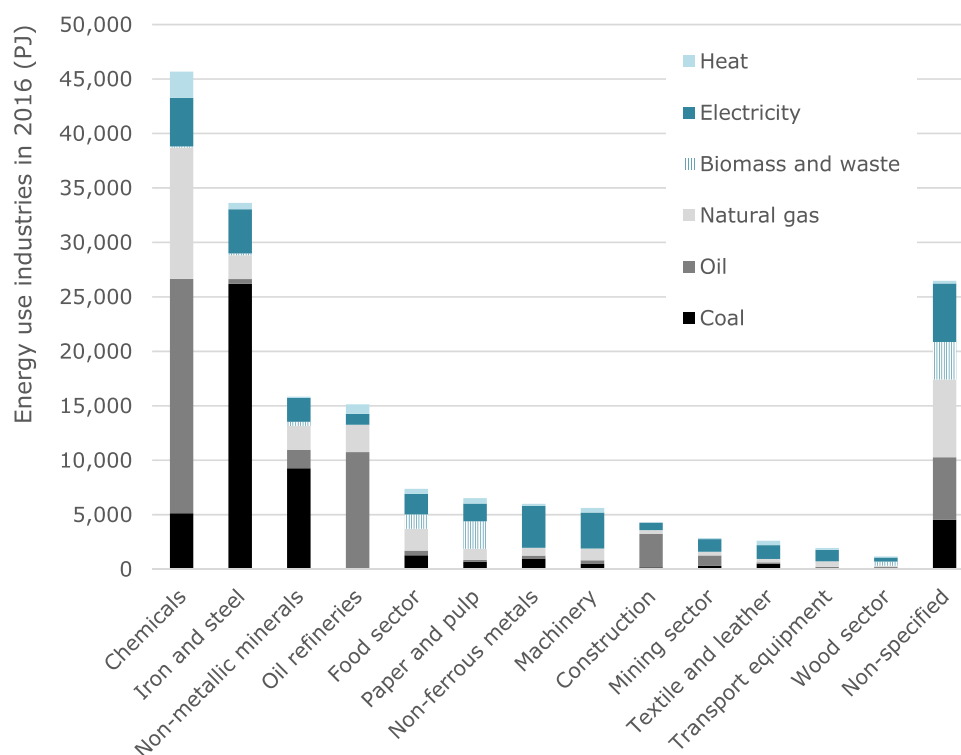


Fig. 1 Global energy use in industries in 2016 (PJ). Based on data from IEA, 2018c. Extended World Energy Balances Database. 2018 ed. Paris: International Energy Agency (IEA).

use. Energy use in non-metallic minerals is mainly related to cement production, which accounts for 70%–80% of the sectors energy use (Kermeli *et al.*, 2019).

Out of the energy carriers, coal is most often used in industries with 28%, followed by oil (26%), natural gas (19%) and electricity (18%). Renewable energy use, excepting biomass, is negligible so far. Coal is mainly used in the iron and steel sector (78% of total coal use in industries) and non-metallic minerals (19%), followed by chemicals (10%). Natural gas is more spread over all sectors, with its main use in chemicals (37%). Oil use is mostly occurring in chemicals (47%) and oil refining (24% of total oil use). Electricity use is also widely spread but highly consuming sectors are chemicals (14%), iron and steel (13%) and non-ferrous metals (12%). The energy use in the non-ferrous metals sector is for about 70% related to aluminum production (Kermeli *et al.*, 2015).

If we add up all sectors the total energy use in industries amounted to 174 EJ in 2016, which is 30% of total primary energy use worldwide (576 EJ). This includes:

- (1) 144 EJ final energy use; of which 30 EJ is non-energy use (consisting for 26 EJ of feedstocks in petrochemicals),
- (2) 14 EJ of energy use and transformation losses in coke ovens and blast furnaces and
- (3) 15 EJ of energy use in oil refineries.

Indirect energy use from electricity consumption that is not produced on site is not included.

Fig. 2 shows the development of energy use in industries over time in the period 1990–2016 (based on IEA, 2018c). In this period an increase is visible of 56%, from 111 EJ to 174 EJ, mainly occurring in the 2000s. The share of iron and steel in this period increases from 15% to 19% and of chemicals from 22% to 26%. Also the non-metallic minerals sector shows an increase from 6% to 9%. Meanwhile the other sectors remain more or less constant, while the category “non-specified industries” (which is part of “others” in Fig. 2) decreases from 25% to 15%.

Fig. 3 shows the development of industrial energy use by country. Here it is quite visible that a large share of the increase in industries in the 2000s is related to growth in China. Excluding China, industries grow from 99 EJ in 1990 to 119 EJ in 2016 (increase of 20%). In China industries grow from 12 EJ to 55 EJ (+360%), increasing its share in global industrial energy demand from 11% in 1990 to 32% in 2016. Other fast growing countries are India (from 3.5 EJ to 10.8 EJ), South Korea (1.3–5.3 EJ), Saudi Arabia (0.8–3.2 EJ), Iran (1.0–3.2 EJ) and Brazil (2.3–4.0 EJ). The EU-28 is one of the regions with a decrease from 22 EJ in 1990 to 18 EJ in 2016. Also Russia (13 to 12 EJ), Japan (7.3 to 6.1 EJ) and the United States (20.3 to 19.7 EJ) show a decrease.

CO₂ emissions from energy use in industries (including oil refineries and non-energy use) amounted to 9.7 Gtonne CO₂ in 2016 (based on data from Fig. 1 and typical emission factors of 94 g CO₂/MJ for coal, 73 g CO₂/MJ for oil and 56 g CO₂/MJ for natural gas (IPCC, 2006)). Including indirect CO₂ emissions by electricity consumption adds 4.8 Gtonne CO₂ in 2016 (based on Fig. 1 and a global average emission intensity for power generation of 532 g CO₂/kWh in 2016 (based on IEA, 2018b)). Finally, industrial process emissions add another 3.2 Gtonne CO_{2eq} in 2014 (ClimateWatch, 2019). These emissions are for more than half related to process emissions from cement production, which were 1.7 Gtonne CO_{2eq} in 2012 (Janssens-Maenhout *et al.*, 2017). Together it means that total industry is responsible for about 35% of global GHG emissions, which were 50 Gtonne in 2014 (ClimateWatch, 2019).

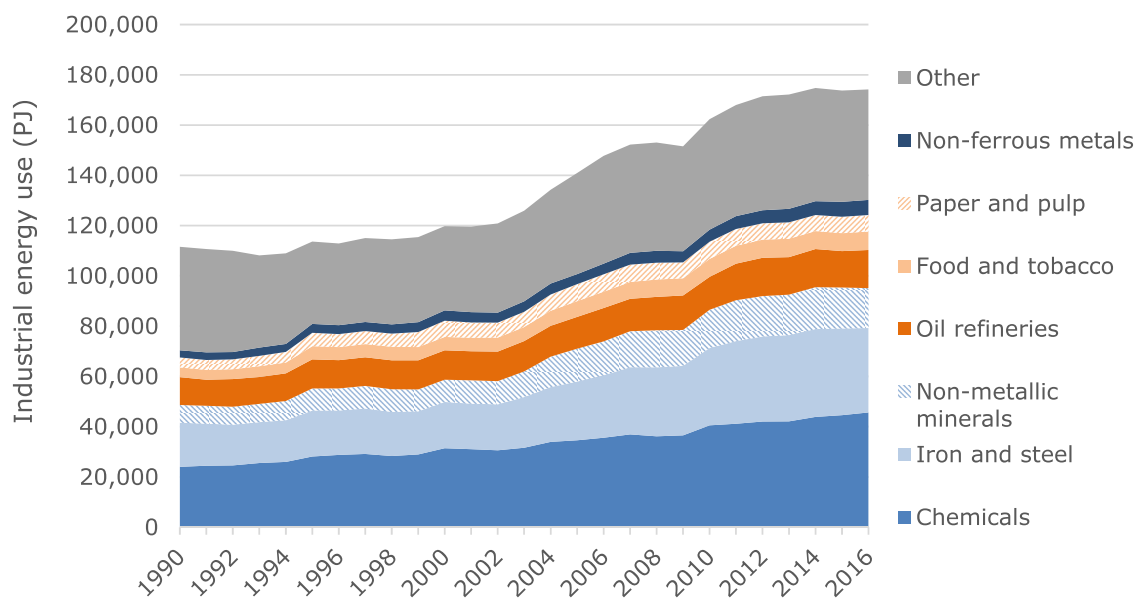


Fig. 2 Global industrial energy use per sector. Based on data from IEA, 2018c. Extended World Energy Balances Database. 2018 ed. Paris: International Energy Agency (IEA).

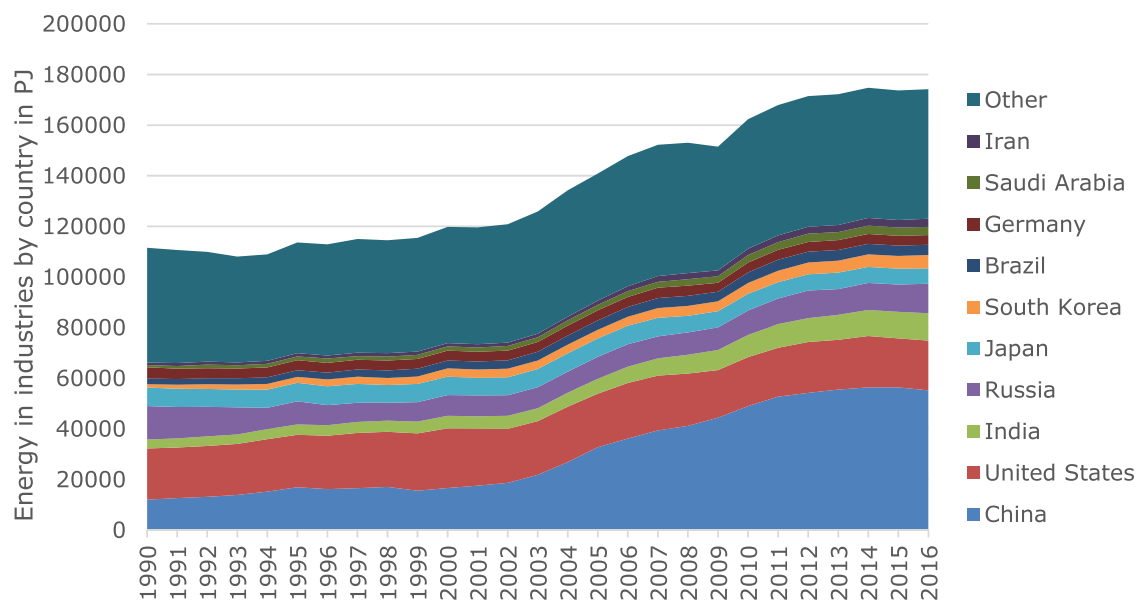


Fig. 3 Energy use in industries by country. Based on data from IEA, 2018c. Extended World Energy Balances Database. 2018 ed. Paris: International Energy Agency (IEA).

Energy Efficiency Measures

In this section we will discuss main energy saving options in the main industrial sectors which are chemicals, iron and steel and cement. Also we include aluminum production, which is the biggest electricity consuming sector, after chemicals and iron and steel.

Chemicals

The chemical industry produces many different chemical products (e.g., ammonia, caustic soda and ethylene) and is by far the largest industrial energy user. The global energy demand of the chemical industry is 19 EJ excluding feedstock and 46 EJ including feedstock, accounting for about 26% of the total industrial energy demand in 2016 (IEA, 2018a). While the chemical industry produces thousands of chemicals, only a few chemicals consume most of the energy. These are the production of light olefins (ethylene and propylene), BTX aromatics (benzene, toluene and xylenes), ammonia and methanol, which account for 73% of the total energy use of the chemical industry (IEA, 2017). Improving the energy efficiency in the energy-intensive processes is key to reduce overall energy consumption in the chemical industry worldwide.

One of the main energy consuming processes is steam cracking of hydrocarbon feedstocks, which is used in the petrochemical industry to produce ethylene and propylene and BTX aromatics. These products are further processed into polymers, solvents and resins. Steam cracking results in a large variety of products with varying energy intensities and accounts for about 20% of the final energy use (excl. feedstocks and electricity in the chemical and petrochemical industry (IEA, 2009a)). Saygin *et al.* (2011) estimate that by implementing best practice technology the average world energy intensity of 16.9 GJ/tonne High Value Chemicals (HVCs) (including ethylene, propylene, benzene, butadiene, acetylene and hydrogen) could decrease by 26% (excl. feedstocks). When implementing best available technology an improvement of 37% was estimated to be possible (Kermeli *et al.*, 2014).

The manufacture of ammonia and methanol accounts for about 32% of the energy consumed in the chemical and petrochemical sector (IEA, 2017). Ammonia is mainly used as a feedstock in fertilizer production. Saygin *et al.* (2011) estimate a global fuel savings potential for ammonia production, when implementing best practice technology, of 31% (excl. feedstock and electricity use).

Methanol is used mainly as antifreeze, solvent and fuel. The majority of methanol production (80%) is natural gas-based with the remainder, mainly taking place in China, being coal-based (Kermeli *et al.*, 2014). The world average energy use in methanol production is estimated at 10.9 GJ/tonne (excl. feedstock and electricity) (Saygin *et al.*, 2011). The worldwide adoption of best practice technology (8.5 GJ/tonne), would result in a 22% decrease of the energy intensity.

Chlorine production is the main electricity consuming process in the chemical industry (Graus *et al.*, 2011). The most efficient production process for chlorine production is the membrane process which consumes 2600 kWh/tonne chlorine, which is already close to the most efficient technology considered feasible (IEA, 2008). As a comparison to commonly used mercury process has an energy intensity of around 4000–4500 kWh/tonne chlorine (Kermeli *et al.*, 2014), but is being phased out in many countries.

Table 1 gives an overview of the main energy efficiency technologies that can be implemented in the chemical industry with their main characteristics.

Table 1 List of energy efficiency technologies applied in the chemical industry

<i>Sector</i>	<i>Energy efficiency technology</i>	<i>Investment (€/tonne chemical)</i>	<i>Energy savings (%)</i>	<i>Source</i>
Ammonia	Adiabatic pre-reformer	17.7	7.5	Boulamanti and Moya Rivera (2017) and Kermeli <i>et al.</i> (2017)
	Heat exchange autothermal reforming	25.2	6	Boulamanti and Moya Rivera (2017) and Kermeli <i>et al.</i> (2017)
	Advanced conventional processes	31.5	10	Boulamanti and Moya Rivera (2017) and Kermeli <i>et al.</i> (2017)
	Reduced primary reforming and increased process air	29.4	5	Boulamanti and Moya Rivera (2017)
	Preheat mixed feed and efficient gas turbine	14.5	16.6	Boulamanti and Moya Rivera (2017)
	Advanced process control	6	2.3	Boulamanti and Moya Rivera (2017), Kermeli <i>et al.</i> (2017) and Yue <i>et al.</i> (2018)
	Low pressure ammonia synthesis catalysts		3.9	Boulamanti and Moya Rivera (2017) and Kermeli <i>et al.</i> (2017)
	Using hydrogen from water electrolysis	176	66.3	Boulamanti and Moya Rivera (2017)
	Improved the reforming section	37	13.3	Boulamanti and Moya Rivera (2017)
	Multi-nozzle opposed coal water slurry gasification	110	15	Yue <i>et al.</i> (2018)
	New reforming membranes ^a	348.1	17	Boulamanti and Moya Rivera (2017)
	Solid state ammonia synthesis ^a	241.1	66.3	Boulamanti and Moya Rivera (2017)
	Short contact time catalytic partial oxidation ^a	1670	11	Boulamanti and Moya Rivera (2017)
	Used new membranes for CO ₂ removal ^a		<5	Boulamanti and Moya Rivera (2017)
Light olefins	Decoking activities		<5	Boulamanti and Moya Rivera (2017)
	Advanced furnace materials such as selective radiant coils and ceramic-coated tubes	2.1	10	Boulamanti and Moya Rivera (2017)
	Improving compression and separation section (ICSS) – Advanced distillation columns	0.8	1.5	Boulamanti and Moya Rivera (2017)
	ICSS – Mechanical vapor recompression	0.6	5	Boulamanti and Moya Rivera (2017)
	Adsorption heat pump ^a	10.8	12	Boulamanti and Moya Rivera (2017)
	ICSS – Membranes ^a	18.4	8	Boulamanti and Moya Rivera (2017)
	Olefin production via methanol ^a		5	Boulamanti and Moya Rivera (2017)
	Energy integration – reformat based process	9.5	25 electricity and 20 thermal	Boulamanti and Moya Rivera (2017)
	Energy integration – pygas based process	9.5	9 thermal	Boulamanti and Moya Rivera (2017)
Hydrogen and methanol	Air preheat	6.8	5	Boulamanti and Moya Rivera (2017)
	Minimal steam: carbon ratio and associated measures		<5	Boulamanti and Moya Rivera (2017)
	Hydrogen from electrolysis	2211.7	35	Boulamanti and Moya Rivera (2017)
	Membrane methane reforming ^a	1978.0	20	Boulamanti and Moya Rivera (2017)
	Short contact time catalytic partial oxidation ^a	695.3	15	Boulamanti and Moya Rivera (2017)
Soda ash	Integrated design and operation	40	44.6 electricity and 17.6 thermal	Boulamanti and Moya Rivera (2017)
	Vertical shaft kiln for the production of concentrated CO ₂ gas and reactive lime	16	2.7	Boulamanti and Moya Rivera (2017)
Chlor-alkali	Conversion of mercury to membrane cell plants	426.2	28.4 electricity	Boulamanti and Moya Rivera (2017)
	Conversion of asbestos diaphragm to membrane cell plants	367	7 electricity and 70.5 steam	Boulamanti and Moya Rivera (2017)
	Asbestos-free diaphragms	10	4.4 electricity	Boulamanti and Moya Rivera (2017)
	High performance bipolar membrane cells	21	13.6 electricity	Boulamanti and Moya Rivera (2017) and Yue <i>et al.</i> (2018)
	High performance electrodes and coatings		3–4	Boulamanti and Moya Rivera (2017)
	Recovered hydrogen as a chemical reagent or fuel		<5	Boulamanti and Moya Rivera (2017)
	Oxygen depolarized cathodes ^a	89	15	Boulamanti and Moya Rivera (2017) and Yue <i>et al.</i> (2018)
	Four-stage caustic evaporator in membrane plants ^a		20	Boulamanti and Moya Rivera (2017)

Table 1 Continued

<i>Sector</i>	<i>Energy efficiency technology</i>	<i>Investment (€/tonne chemical)</i>	<i>Energy savings (%)</i>	<i>Source</i>
Ethylene oxide & ethylene glycols PVC	Shell OMEGA process	244.4	20	Boulamanti and Moya Rivera (2017)
	Pigging system	101,568 (for 100 m pipeline)	19 electricity	Boulamanti and Moya Rivera (2017)
	High pressure distillation for calcium carbide-based PVC	1	24 electricity	Yue <i>et al.</i> (2018)
Ethylbenzene & styrene	Advanced control and optimization	6.1	5	Boulamanti and Moya Rivera (2017)
	Exelus styrene monomer process ^a	184.1	40	Boulamanti and Moya Rivera (2017)
Calcium carbide ^b	Advanced kilns such as vocarse shaft kiln, double shell shaft kiln and maerz PFR shaft kiln	37	13	Yue <i>et al.</i> (2018)
	Transforming semi-covered furnace to closed furnace (exclude the utilization of tail gas)	33	5 electricity	Yue <i>et al.</i> (2018)
	Direct current electric arc furnace	42	10 electricity	Yue <i>et al.</i> (2018)
	New conductive copper contact shoe for closed furnace	43	4 electricity	Yue <i>et al.</i> (2018)
	40.5 MVA closed furnace	50	18	Yue <i>et al.</i> (2018)
	63 MVA closed furnace	101	25	Yue <i>et al.</i> (2018)
	Low-voltage dynamic reactive power compensation	12	4.5 electricity	Yue <i>et al.</i> (2018)
	Combination electrodes	12	5.4 electricity	Yue <i>et al.</i> (2018)
	Comprehensive compensation of short-supply network	27	7	Yue <i>et al.</i> (2018)
	Electricity saving expert system for electric arc furnace	6	3 electricity	Yue <i>et al.</i> (2018)
	Automatic control system for materials feeding and batching	12	4 electricity	Yue <i>et al.</i> (2018)
	Waste heat of flue gas for power generation	33	11 electricity	Yue <i>et al.</i> (2018)

^aUncommercialized technology.^bThe technologies used in calcium carbide are mainly based on China because China represents around 95% of global production and consumption of calcium carbide (SEC: 3400 kWh/t-calcium carbide).

Energy efficiency improvement through the use of best practice technologies can reach around 17% for the chemical industry. Higher potentials can be realized through process integration (4%), Combined Heat and Power (CHP) generation (10%) and recycling and energy recovery (1%) (Saygin *et al.*, 2011). From the regional perspective, IEA indicate that China has the largest potential to improve energy efficiency in the chemical industry, accounting for 40% of global energy savings potential (IEA, 2013).

At the end of the useful life of plastics, it is possible to save energy by recycling (mechanically or as feedstock) and energy recovery. Mechanical recycling is by far the most widely used approach worldwide. The main alternatives to recycling are incineration (with and without energy recovery) and landfilling. Globally, less than 10% of the total plastic waste is recycled. In Europe and Japan, the share of recovered plastic waste (by mechanical recycling and energy recovery) is higher than global average. Around 20% of the plastic waste is mechanically recycled and 30% is combusted with energy recovery in Europe. The remaining 50% is unrecovered (disposed by landfilling or incinerated without energy recovery). In Japan the share of recovered waste is higher than in Europe (60% in comparison to 50%) (Saygin *et al.*, 2011).

As seen in Section "Energy Use and Greenhouse Gas Emissions in Industries", China is one of the main energy consuming countries in terms of industrial energy use, being responsible for 32% in 2016. This is reflected in China's chemical industry which shows a strong growth since 2000, with an annual growth rate of 9%, for main chemicals (Yue *et al.*, 2018). As the largest chemical market worldwide, China represents around 1/3 of the global chemicals production. In particular, China is the largest producer and consumer of ammonia, caustic soda, polyvinyl chloride and calcium carbide. Energy consumption of China's chemical industry increased with the growth of chemicals output from 4.1 EJ in 2000 to 14.4 EJ in 2015, accounting for 11% of China's total energy demand. The final energy consumption mix of China's chemical industry shows that electricity has increasingly become the dominant energy source, amounting to 30% in 2015. The growing energy consumption of the chemical industry has resulted in enormous emissions of air pollutants and GHGs. Energy-related CO₂ emissions of China's chemical industry account for 3.7% of global total in 2015, with 1220 Mt CO₂, which nearly doubled since 2005. As a key emitter of air pollutants, China's chemical industry emitted 2254 kt of SO₂, 1512 kt of NO_x and 808 kt of PM in 2015, contributing 12%, 8%, and 5% to the national emissions, respectively (Yue *et al.*, 2018).

Cement

In 2014, the cement industry consumed 10.6 EJ of energy (7% of industrial energy use). Due to the high level of process emissions, cement production comprises the second largest industrial emitter, following the iron and steel industry, accounting for 27% (2.2 GtCO₂ in 2014) of industrial emissions and 6% of global CO₂ emissions (IEA, 2017).

Main processes in cement manufacturing are raw material preparation, clinker production (limestone calcination) and cement grinding; with clinker production being the most energy intensive step (Worrell and Galitsky, 2008). Clinker is produced by burning a mixture of mainly limestone, silicon oxides, aluminum oxides and iron oxides in a kiln. Based on the moisture content of raw materials, clinker production can take place in a wet, dry, semi-dry or semi-wet kiln. The dry process has lower energy requirements due to lower evaporation needs.

The adoption of more energy efficient technologies and the decrease of the clinker content in cement can significantly reduce the energy use in cement manufacturing.

The thermal energy use for clinker production in the different world regions ranges between 3.1 and 5.0 GJ/tonne clinker (see Fig. 4). It differs mainly due to the kiln technology type used and the level of energy efficiency (Kermeli *et al.*, 2019). The lowest energy consumption is observed in India where cement capacity increased significantly in recent years. The highest is in CIS which still relies heavily on the wet process. Dry kilns equipped with a precalciner and several preheater stages (5–6 stages), are currently considered best available technology, and can have under optimal conditions a fuel consumption of about 2.9–3.3 GJ/tonne clinker (EIPPCB, 2010). The theoretical minimum energy requirements are about 1.65–1.8 GJ/tonne (WBCSD/CSI-ECRA, 2009). The difference in energy use between typical kilns and the theoretical energy occurs mainly due to heat losses. The energy use in state-of-the-art dry kilns is not expected to significantly decrease in the future (IEA, 2009a).

In the cement industry, electricity is mainly used for the preparation of raw materials, fuels and additives, and for cement grinding. Current state-of-the-art techniques use roller presses and vertical roller mills for grinding. The energy requirements mainly depend on raw material hardness, moisture content and the type and amount of additives used. Fig. 5 shows the electricity use for cement making in different world regions. In 2012, electricity use ranged between 81 and 126 kWh/tonne cement. The lowest electricity use is observed in India and the highest in the North America and CIS. The implementation of best practice technology can decrease electricity use to about 70 kWh/tonne cement.

Table 2 shows main energy efficiency measures for clinker making for dry process cement plants, including fuel savings, electricity savings and payback period.

Additional energy savings can be obtained by reducing the clinker content in cement. Portland cement has a clinker to cement ratio of 95%–100% (the remaining part is gypsum). Substituting a part of clinker with other materials with similar properties (hydraulic and/or pozzolanic) reduces the clinker content in cement lowering the demand for clinker. Reducing clinker production by 1 tonne will roughly reduce CO₂ emissions by the same amount. Cements that contain clinker substituting materials in considerable quantities are known as blended cements. These materials are either interground with clinker in the final step of cement making or are ground and dried separately before being mixed with clinker. Clinker can be substituted by industrial by-products such as coal fly ash, blast furnace slag or pozzolanic materials (e.g., volcanic material). The relative importance of additive use can be expressed by the clinker to cement ratio. Fig. 6 shows the clinker content in cement for different world region. The average clinker to cement ratio is estimated at 70% (Kermeli *et al.*, 2014).

Iron and Steel

Steel is a widely used material in modern society, which has been linked to the development of steel end use sectors, e.g., building and infrastructure, manufacturing, and transport systems. The iron and steel industry is one of the world's

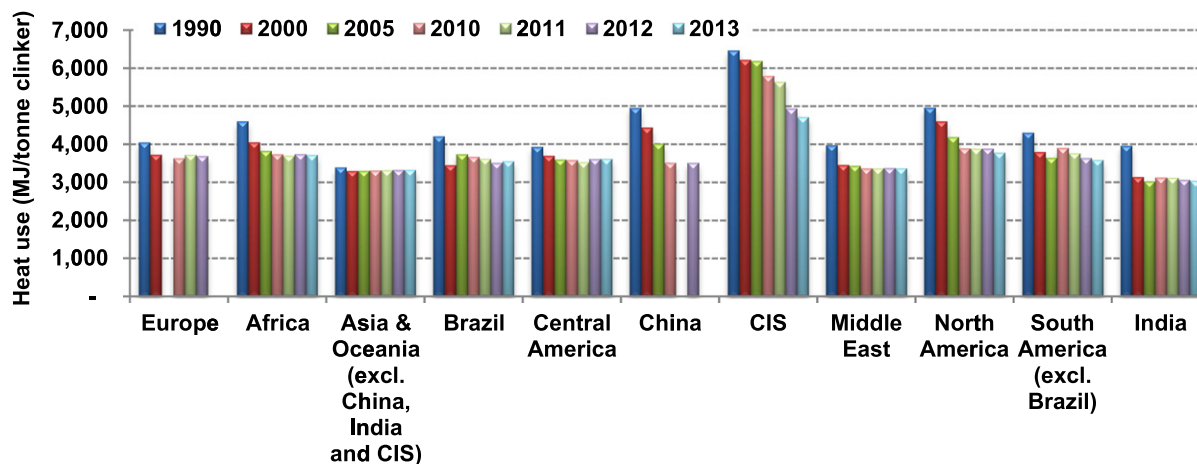


Fig. 4 Heat consumption for clinker making per world region (excluding heat loss for drying). Reproduced from Kermeli, K., Edelenbosch, O.Y., Crijns-Graus, W., *et al.*, 2019. The Scope for Better Industry Representation in Long-Term Energy Models: Modeling the Cement Industry.

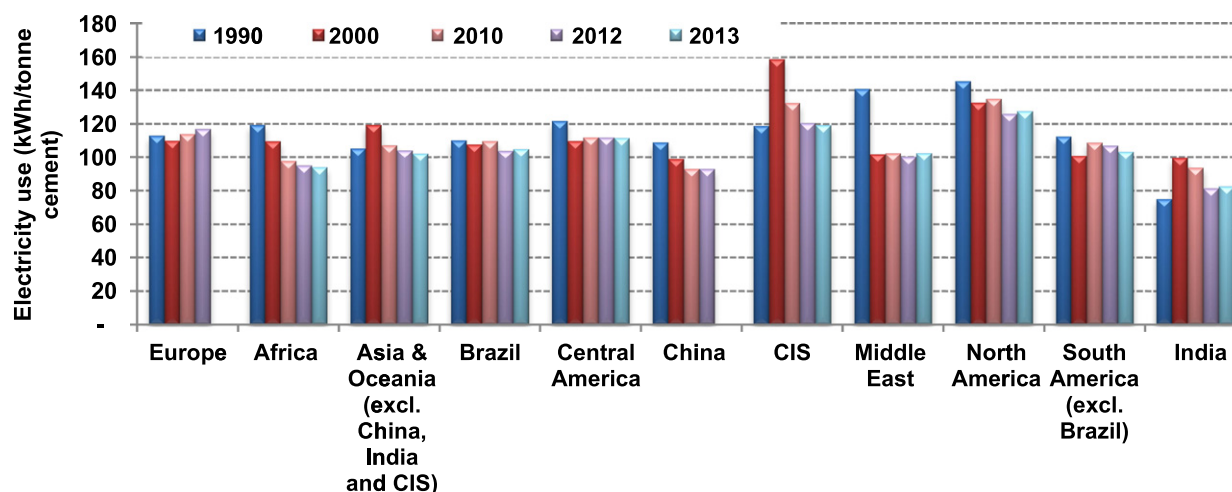


Fig. 5 Average electricity consumption for cement making per world region. Reproduced from Kermeli, K., Edelenbosch, O.Y., Crijns-Graus, W., *et al.*, 2019. The Scope for Better Industry Representation in Long-Term Energy Models: Modeling the Cement Industry.

Table 2 Energy efficiency measures for clinker making – dry process plants

Energy efficiency measure	Specific fuel savings (GJ/tonne clinker) ^a	Specific electricity savings (kWh/tonne clinker) ^a	Estimated payback period (years) ^b
Energy management and control systems	0.1–0.2	0–4.9	<2
Kiln combustion system improvements	0.1–0.4	–	1.0–5.0
Mineralized clinker	0.0–0.2	0 to –1.0	N/A
Indirect firing	0.2	0 to –0.6	>10
Oxygen enrichment	0.0–0.2	(–)9 to (–)32	N/A
Mixing air technology (PH kilns)	0.20	(–) 0.03	2
Seal replacement	0.02	–	<1
Kiln shell heat loss reduction	0.1–0.6	–	<1
Preheater shell heat loss reduction	0.02	–	6
Refractories	0.06	–	4
Conversion to grate cooler	0.3	(–)3.00 to (–)6.00	>18
Optimize grate cooler	0.05–0.16	0.0 to (–)2.0	2.00–7.00
Low-pressure drop Suspension preheaters	–	0.6–4.4	>10
Heat recovery for power generation	–	20.0	2.00–14.00
Conversion of long dry to preheater	0.7–1.6	–	10
Increase preheater stages (from 5 to 6)	0.1	–	>7
Addition of precalciner or upgrade	0.2–0.7	–	>10
Conversion of long dry kiln to preheater precalciner	0.84–1.11	–	>10

^aNegative values for electricity saving indicate that although the application of this measure saves fuel, it will increase electricity consumption. However, the total primary energy savings of these measures is positive.

^bThe estimated energy and expenditure savings and payback periods are averages for indication, based on the average performance of the U.S. cement industry (e.g., clinker to cement ratio). The actual savings and payback period may vary by project based on the specific conditions in the individual plant.

Note: Worrell, E., Kermeli, K., Galitsky, C., 2013. Energy Efficiency Improvement and Cost Saving Opportunities for Cement Making. United States Environmental Protection Agency (U.S. EPA).

largest energy consumer and therefore a major contributor to global anthropogenic CO₂ emissions, accounting for 9% of global energy use and 4%–7% global anthropogenic CO₂ emissions (Pauliuk *et al.*, 2013). In the period 1960–2018, the historical steel production has risen fivefold. In 2018, China is the largest steel producer, accounting for 51.3% of the global total, followed by the European Union, India, USA, and Japan (World Steel Association, 2019). Many studies indicate that global steel demand is expected to more than double by 2050, depending on the industrialization in developing regions (Ruijven *et al.*, 2016).

Manufacturing steel can be divided into the following processes; raw material preparation (including coke making, iron ore extraction and sinter/pellets making), iron making, steel making, casting, rolling, forming and coating, and fabrication. Currently, two manufacturing routes have been widely used in crude steel production. The integrated route is based on iron ore and

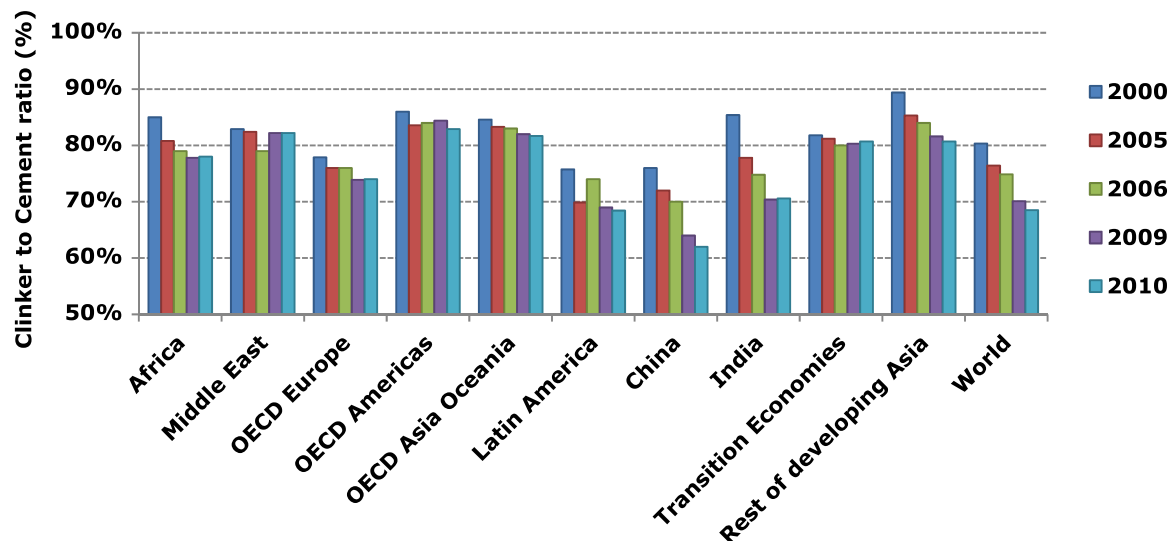


Fig. 6 Clinker content in cement in the different world regions. Reproduced from Kermeli, K., Edelenbosch, O.Y., Crijns-Graus, W., *et al.*, 2019. The Scope for Better Industry Representation in Long-Term Energy Models: Modeling the Cement Industry.

limestone and consists of coke ovens, sinter/pellets plants, blast furnaces (BF) and Basic Oxygen Furnaces (BOF) or an open-hearth furnace (OHF), while the recycling route uses scrap as main material in electric arc furnaces. For integrated steel-making, around 70% of energy is consumed in the blast furnaces, followed by sintering and coke making (Zhang *et al.*, 2014). For the recycling route, scrap is mainly coming from casting, forming and other fabrication processes in steel making and after use (Cullen *et al.*, 2012). The energy consumed in the recycling route is about 20% of the energy used for integrated steel making from iron ore, because using scrap offsets the demand for energy and natural resources in the iron making process (Kermeli *et al.*, 2014). In 2016, 74% of global crude steel production was produced by the integrated route while 25.5% came from electric arc furnaces. There are two relatively new manufacturing routes, namely direct-reduced iron (DRI) and smelting reduction, which currently together account for less than 1% of global steel production. The key advantage of these routes is that 20%–25% of CO₂ can be avoided, compared to the integrated route (Pardo *et al.*, 2012).

Specific energy consumption and the associated CO₂ emissions per ton of steel production differ widely across countries, due to the difference of production route applied, plant size, level of waste heat recovery, quality of iron ore, and operation efficiency of the plants (IEA, 2012b; Worrell and Carreon, 2017). Since 1960, the energy intensity in the global iron and steel industry improved significantly and decreased by 60%. There are still large opportunities to improve energy efficiency though. Overall, the implementation of best available technology (BAT) could save 9%–18% of energy use (Worrell and Carreon, 2017). Table 3 lists the current best available technologies for energy-efficiency improvement in the iron and steel industry. The energy savings potential varies per country. Take China as an example, cogeneration by heat recovery, coke dry quenching (CDQ) and coal moisture control (CMC), injection of pulverized coal in BF are the most important measures to save energy and together can reduce energy use by 50% in the integrated steel making route. For the recycling route, scrap preheating and process control could contribute to one third of energy saving (Zhang *et al.*, 2014). Milford *et al.* (2013) estimate that energy efficiency alone is not enough to limit CO₂ emissions in the iron and steel sector, which would only decrease up to 20% of emissions by 2050, compared to a business-as-usual scenario. Therefore, material efficiency improvement is another key opportunity to reduce energy use and consequently lower CO₂ emissions. Strategies to improve material efficiency include reducing demand for the service, optimizing the weight of products, reducing yield losses, increasing product lifespans and recycling of end-of-life scrap (Allwood *et al.*, 2013). With the growing concern for climate change and ambitions to lower global temperature increase to well below 2°C, deeper decarbonization of the steel industry is needed, e.g., by using Hydrogen (H₂) or electricity to replace coke in the blast furnaces or the adoption of carbon capture and storage (CCS) and carbon capture and usage (CCU).

Aluminum

The primary aluminum industry is one of the top electricity consuming industries and is responsible for about 8% of global electricity consumption in industries (Kermeli *et al.*, 2014). The production of primary aluminum is a multi-stage process. Initially, bauxite ore is resolved/digested and refined into alumina in the Bayer process. Alumina is then transformed into aluminum in an electrolytic cell with the Hall-Héroult process. Molten aluminum is cast into ingots which are transferred and further processed in aluminum foundries. The most energy intensive processes in primary aluminum production are alumina refining and aluminum smelting, responsible for 27% and 70% of energy use, respectively. Anode production is responsible for about 2%, while aluminum casting for about 1.4% of the energy use (IAI, 2013a).

Table 3 Main energy efficiency measures

Process	Measures	Fuel saving (GJ/ton)	Electricity saving (GJ/ton) ^a	Capital cost (2005 \$/ton)
Sintering	Small pellet sintering technology	0.26	0.00	2.06
	Low temperature sintering	0.26	0.00	2.95
	Improved charging method	0.10	0.00	1.07
	Increasing bed depth	0.10	0.00	0.00
	Heat recovery from sinter cooler	0.40	0.00	2.93
Coke making	Use of waste fuel in sinter plant	0.16	0.00	0.21
	Pressure Shift-Absorbing Technique in H ₂ unit	0.05	0.00	0.00
	Programmed heating in coke oven	0.16	0.00	0.21
	Variable speed drive on coke oven gas compressors	0.01	0.00	0.32
	Coal moisture control	0.33	0.00	5.97
Iron making	Coke dry quenching (CDQ)	0.81	0.00	12.58
	Moisture Removing Blowing Technique in BF	0.23	0.00	1.86
	Dry Bag Dedusting System of Blast Furnace Gas	0.01	0.00	0.11
	Injection of pulverized coal in BF	0.64	0.00	4.99
	Injection of natural gas in BF	0.32	0.00	4.81
	Injection of oil in BF	0.48	0.00	9.10
	Injection of plastic waste in BF	0.16	0.00	4.99
	Injection of coke oven gas in BF	0.32	0.05	4.81
	Top-pressure recovery turbines (TRT)	0.21	0.00	2.40
	Cogeneration with untapped coke oven gas, blast furnace gas, and basic oxygen furnace-gas	0.23	0.00	2.61
Steel Making_BOF	Recovery of blast furnace gas	0.09	0.00	1.16
	Improved hot blast stove control	0.32	0.00	0.32
	Improved blast furnace control	0.32	0.00	0.53
	Integrated casting and rolling (Strip casting)	0.73	0.00	6.34
	Recovery of BOF and sensible heat	0.56	0.00	23.51
Steel Making_EAF	Variable speed drive on ventilation fans	0.00	0.00	0.21
	Efficient Ladle preheating	0.02	0.00	0.06
	vacuum degassing from liquid iron	0.10	0.00	0.37
	wet and heat recovery of slag	0.09	0.00	0.55
	Scrap preheating	0.36	0.00	4.26
	Adjustable speed drives (ASDs) on flue gas fans	0.00	0.05	2.14
	Oxy-fuel burners/lancing	0.00	0.05	1.38
	Improving process control in EAF	0.24	0.09	1.28
	Direct current (DC) arc furnace	0.00	0.03	0.40
	Bottom stirring/gas injection	0.00	0.01	0.07
Casting, rooling and finishing	Flameless oxyfuel burners	0.64	−0.02	2.67
	Insulation of reheat furnaces	0.16	0.00	8.00
	Hot charging	0.48	0.00	16.03
	Process control in hot rolling	0.30	0.00	0.75
	Waste heat recovery from cooling water	0.03	0.00	0.85
	Continuous annealing	0.16	−0.02	287.67
	Reduced steam use in the acid pickling line	0.24	0.01	2.88
	Preventative maintenance in integrated steel mills	0.32	0.02	0.01
	Heat recovery on the annealing line	0.24	0.01	2.88
	Recuperative or regenerative burner	0.56	0.00	2.66
	Low temperature rolling technology	0.13	0.00	1.08
	Endless Hot Rolling of Steel Sheets	0.36	0.00	6.73
	Multislit Rolling Technique on the Bar Rolling	0.15	0.00	1.22
	Energy monitoring and management systems	0.08	0.01	0.16

^aNegative values for electricity saving indicates that although the application of this measure saves fuel, it will increase electricity consumption. However, the total primary energy savings of these measures is positive.

Note: Based on Hasanbeigi, A., Morrow, W., Sathaye, J., Masanet, E., Xu, T., 2013a. A bottom-up model to estimate the energy efficiency improvement and CO₂ emission reduction potentials in the Chinese iron and steel industry. *Energy* 50, 315–325. doi:10.1016/j.energy.2012.10.062. Hasanbeigi, A., Price, L., Arens, M., 2013b. Emerging Energy-Efficiency and Carbon Dioxide Emissions-Reduction Technologies for the Iron and Steel Industry. Lawrence Berkeley National Laboratory (Available at: <http://china.lbl.gov/sites/all/files/6106e-steel-tech.pdf>). Worrell, E., Blinde, P., Neelis, M., Blomen, E., Masanet, E., 2010. Energy Efficiency Improvement and Cost Saving Opportunities for the U.S. Iron and Steel Industry. Lawrence Berkeley National Laboratory. IIP, 2013. The Institute for Industrial Productivity: Iron and Steel, Technology and Resources. Available at: <http://www.iiedt.iipnetwork.org/content/iron-and-steel>. Mao, X., Zeng, A., Liu, S., Hu, T., Youkai, S., 2012. Assessment of SO₂, NO_x, and CO₂ co-control effects by technological reduction measures in iron & steel industry. *Acta Scientiae Circumstantiae* 32, 1253–1260. Xu, T.T., 2011. Development of Bottom-Up Representation of Industrial Energy Efficiency Technologies in Integrated Assessment Models for the Iron and Steel Sector. Lawrence Berkeley National Laboratory. Available at: <http://escholarship.org/uc/item/8n82s7j3>. Dai, Y., Xiong, H., 2013. Roadmap Study on Achieving Technical Energy Conservation Potential in China's Industrial Sector by 2020. China Science and Technology Press.

The typical energy use for alumina refining with the Bayer process is 12 GJ/tonne (Henrickson, 2010). China and Russia due to their poor quality bauxite reserves have used alternative processes to produce alumina; the Combined Bayer-Sinter and the Sinter processes with typical energy consumptions of 26 and 38 GJ/tonne alumina, respectively (Li *et al.*, 2008; Smith, 2008). Other processes that have been only recently widely used in China are the Flotation-Bayer and the Lime-Bayer processes (Gu and Wu, 2012). If China and Russia would use good quality bauxite and adopt the more energy efficient Bayer process, the energy consumption would significantly decrease. In 2009, the world average energy use for alumina refining, excluding China, is estimated at 12.5 GJ/tonne alumina. Energy efficient alumina refineries (Bayer process) can have an energy use of 8–11 GJ/tonne (Wischnewski *et al.*, 2011; Worrell *et al.* 2008; Henrickson, 2010) while the theoretical minimum energy requirement is 0.24 GJ/tonne (BCS, 2007).

As mentioned, the production of primary aluminum from alumina (aluminum smelting) is the most energy intensive step in primary aluminum production. Aluminum is produced by passing a direct current through a bath with alumina dissolved in a molten cryolite electrode. The electricity intensity in the various world regions ranged between 13.5 and 15.6 MWh/tonne aluminum in 2014 (IEA, 2017). The theoretical minimum energy requirement for electrolysis is 6.0 MWh/tonne (IEA, 2009a) while best practice is 13.5 MWh per tonne (IEA, 2017).

The primary aluminum industry is a large energy consumer and also a major greenhouse gas (GHG) emitter, as next to the emitted greenhouse gas emissions during fuel combustion and electricity generation, perfluorocarbons (PFCs) are emitted. PFCs are gases with a high global warming potential (GWP), ranging from 6500 times for tetrafluoromethane (C_2F_4) and 9200 times for hexafluoromethane (C_2F_6) the GWP of carbon dioxide (CO_2) (IPCC, 2006). In 2007, the primary aluminum industry emitted a total of about 400 Mt CO_2 -equivalent of GHGs (including indirect CO_2 emissions from electricity consumption and process emissions from aluminum smelting); equivalent to about 1% of global greenhouse gas emissions (IEA, 2009b). In the same year, IAI estimates global PFC emissions from aluminum smelting at about 29 Mt CO_2 -eq (IAI, 2013b).

Tables 4 and 5 show main measures for energy efficiency improvement for alumina refining and smelting, respectively. Besides these measures cogeneration of heat and power can be implemented in alumina refineries which could lead to 15% energy savings (Moya Rivera *et al.*, 2015). Furthermore waste energy from smelter off gases could be recovered (3–5 GJ/tonne aluminum accessible heat) (Moya Rivera *et al.*, 2015). The adoption of this technology depends on the proximity of heat demand in the surroundings of the smelter. Few currently available technologies can reduce the energy use in aluminum smelters. Innovative technologies such as wetted cathodes and inert anodes, although promising, are still being developed.

Aluminum can also be produced from scrap, in the secondary production route. Only 5% of the energy needed to produce primary aluminum is required to produce aluminum from scrap (IEA, 2012a). Around 30.5 Mtonnes of aluminum scrap was used in 2017 globally, which contributed to around 32% of aluminum production (World Aluminum, 2019). Out of the total scrap, 12.5 Mtonne consists of new scrap (e.g., from casting) and 18 Mtonne is from end-of life scrap. Total end-of-life scrap is estimate to be 25 Mtonne, implying that absolute scrap use can be increased up to 23% by higher recycling rates, thereby increasing the share of scrap used up to 39%. Aluminum products can be recycled repeatedly; cans, aluminum foil, and automotive components can be melted down to make

Table 4 Energy efficiency improvements for alumina refining

Measures	Electricity savings (kWh/tonne alumina)	Fuel savings (GJ/tonne alumina)	Investment costs (\$/tonne alumina)
Sweetening	N/A	0.9	8
Tube digestion + indirect heating	–	4.4	36–97
High rate thickeners – HT Plants	N/A	0.2	6
High rate thickeners – LT Plants	N/A	0.15	6
Seed filtration – HT Plants	N/A	0.9	14
Seed filtration – LT Plants	N/A	0.7	14
Inter-stage cooling – HT Plants	N/A	0.4	5
Inter-stage cooling – LT Plants	N/A	0.35	5
Direct cooling – HT Plants	N/A	0.3	4
Direct cooling – LT Plants	N/A	0.2	4
Kiln retrofit	–	1.4	43
Optimized cyclone operation	3	0.2	0.1
“Hydrate-by-pass” system	–	0.1	3.3
Improved waste heat recovery	–	0.1	6.5
Advanced process control	14	0.6	3.0
Combined Bayer-Sinter→ Bayer-flotation	N/A	10.4	160
Sinter→ Bayer-flotation	N/A	22.0	230
Combined Bayer-Sinter→ Bayer	N/A	16.0	100
Sinter→ Bayer	N/A	27.0	170
Bayer-flotation, Lime-Bayer→ Bayer	N/A	5.0	20

Note: Kermeli, K., Ter Weer, P.H., Crijns-Graus, W., Worrell, E., 2015. Energy efficiency improvement and GHG abatement in the global production of primary aluminium. *Energy Efficiency* 8 (4), 629–666.

Table 5 Energy efficiency improvements for aluminum smelting, anode production and ingot casting

<i>Measures</i>	<i>Electricity savings (MWh/tonne aluminum)</i>	<i>Fuel savings (GJ/tonne aluminum)</i>	<i>Investment cost (\$/tonne aluminum)</i>
VSS → Point fed pre baked	2.8	–	2600
HSS → Point fed pre baked	2.8	–	2600
SWPB → Point fed pre baked	0.8	–	620
CWPB → Point fed pre baked	1.7	–	260
Optimize cell operation	2.0	–	240–410
Optimum combustion air flow	–	0.2–0.8	2.2–3.0
Efficient operation of burners	–	0.2–0.3	1.6–2.0
Furnace pressure control	–	0.2–0.3	1.4–1.8
Furnace insulation	–	0.1–0.2	0.4–0.6
Waste heat recovery	–	0.3–1.0	8–12
Sensor and control systems	–	0.2–0.3	0.2–1.0
Optimized motor system operation	0.1	–	7

Note: Kermeli, K., Ter Weer, P.H., Crijns-Graus, W., Worrell, E., 2015. Energy efficiency improvement and GHG abatement in the global production of primary aluminium. *Energy Efficiency* 8 (4), 629–666.

again similar products. The share of secondary aluminum production cannot be increased infinitely, as product quality is affected by the use of scrap as a feedstock. Certain high quality products will still require the use of new aluminum.

Conclusions

The industrial sector is a major energy consumer, responsible for 36% of the global final energy consumption and about 35% of global greenhouse gas emissions. Main energy consuming sectors are chemicals, iron and steel and cement.

The implementation of best available technologies can lead to reduced energy use and greenhouse gas emissions. Energy savings depend on the current level of efficiency, sector and production characteristics, but are typically in the range of 20%–40%.

In the coming twenty years industrial energy use is expected to increase by about 40%. This means that in light of 2° scenarios, besides energy-efficiency measures, other measures are needed to reduce greenhouse gas emissions. Crucial in this regard is material efficiency in a broad sense, including limiting material use by product design, re-use of materials, recycling of materials and substitution of materials. For longer term and further greenhouse gas emission reduction, measures such as carbon capture and storage are needed or fossil fuel substitution by hydrogen or electricity (produced from renewable energy) and biomass.

See also: Challenges of Employing Renewable Energy for Reducing Greenhouse Gases (GHGs) and Carbon Footprint. Clean Energy Technologies: Hydrogen Power and Fuel Cells. CO₂ Sequestration Using Algal Biomass and its Application as Bio Energy. Green Energy Fuel From Biomass and Sea Water. Renewable Energy Production From Environmental Hazardous Palm Oil Mill Waste Materials: A Review. Use of Clean, Renewable and Alternative Energies in Mitigation of Greenhouse Gases. Utilizing the Greenhouse Effect as a Source to Produce Renewable Energy. Water Resource Management for Renewable and Sustainable Hydro Energy in Turkey

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Environmental Impact Subtracting Versus Additive Manufacturing

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Introduction

The term *manufacture* originated from two Latin words: *Manus* ("hand") and *factus* ("make"). The Oxford English Dictionary defines *manufacture* as "to make or produce goods in large quantities, using machinery." In other words manufacturing means to create and add value to the product. This can also be understood as the conversion of materials input into goods and services (Ford and Despeisse, 2016). The various sustainability issues in manufacturing are energy consumption, waste generation, water usage, and the environmental impacts during the production phase and also for manufactured parts in service (Sreenivasan *et al.*, 2010). Moreover, cleaner production and environmental sustainability are necessary to prevent the depletion of environmental resources during manufacturing (Le Bourhis *et al.*, 2014).

The article begins with an overview of manufacturing processes (Fig. 1), followed by a review of previous studies on environmental issues of subtractive and additive manufacturing processes. The primary cause of industrial hazards is the fundamental workings of conventional additive manufacturing processes (such as welding, casting, forging, and heat treatment), which involve heating of metal to high temperature to join or reshape the material for the production of the desired goods. Subtractive manufacturing techniques also contribute to environmental pollution and various sources will be discussed in later section. This article also explores examples from current practice.

Additive Manufacturing Processes

As the name signifies, additive manufacturing means addition of material during the part building process. It includes various joining (assembly) processes and rapid prototyping processes (regenerative processes). Further, assembly processes encapsulate welding and fastening. The most significant risks of welding and microwelding operations in industry are the environmental hazards produced, knowingly or unknowingly. This releases heavy metal particles and metal oxides into ambient air, which increases environmental pollution. As the basic principle is the application of heat and pressure to join two metals, the heating process tends to melt the metal for short duration at specified locations. This leads to release of toxic gases and metal fumes of variable composition, which depends upon base metal or alloy and material welding. During complex vaporization, condensation, and oxidation processes, various hazardous gases such as carbon dioxide, carbon monoxide, nitrogen oxides, sulfur dioxide, and ozone are released into the environment. Moreover, it is estimated that about 90%–95% of metal fumes are produced from heating of filler metal and flux coating of filler metal. These metal fumes consist of various components in gaseous and solid state at the macro, micro, and nanoscale.

It is estimated that about five tonnes of fumes are emitted by the welding industry annually if an average 0.5% of metals are released in air during metal joining process. In spite of automation, 3 million people are presently involved directly or indirectly in this profession, who are knowingly or unknowingly subjected to these environmental hazards.

The testing of samples collected from tin–lead microwelding site revealed fast evolution of nanoparticles (5.6–560 nm), which is representative of nucleation mode as demonstrated by Avino *et al.* (2015). Moreover, they found that pollution caused by copper–aluminum soldering was 20 times higher than tin–lead micro welding.

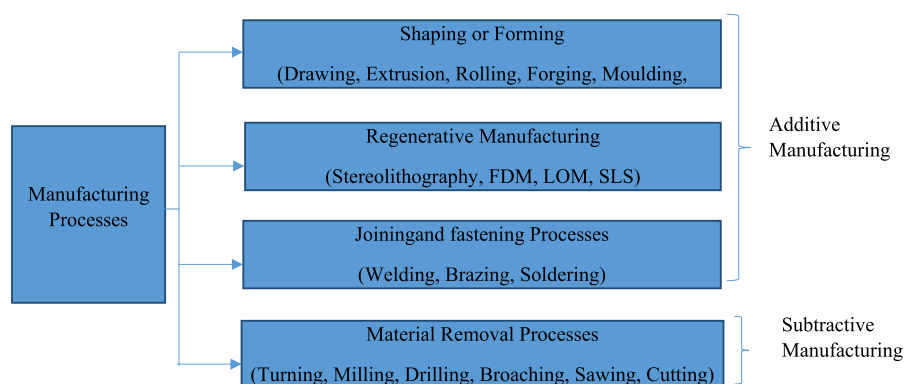


Fig. 1 Classification of manufacturing process.

Table 1 Concentration of particulate matter in welding industries

Industry type	Particle concentration ($\mu\text{g}/\text{m}^3$)			
	Outdoor PM_{10}	Indoor PM_{10}	Outdoor PM_5	Indoor PM_5
Small A	474.1 $\pm$ 71.3	540.9 $\pm$ 69.1	5.82 $\pm$ 2.76	9.13 $\pm$ 3.40
Small B	448.8 $\pm$ 120.4	520.2 $\pm$ 63.3	8.11 $\pm$ 4.19	13.44 $\pm$ 4.26
Medium A	523.7 $\pm$ 31.7	581.0 $\pm$ 41	12.20 $\pm$ 4.03	21.64 $\pm$ 9.05
Medium B	580.9 $\pm$ 54	578.1 $\pm$ 45	16.04 $\pm$ 5.01	30.30 $\pm$ 6.37
Large	650.7 $\pm$ 69.6	679.0 $\pm$ 59.5	23.13 $\pm$ 9.40	38.60 $\pm$ 12.70

Note: Pervez, S., Mathew, J., Sharma, R., 2005. Investigation of personal-indoor-outdoor particulate relationships in welding workshops. *Journal of Scientific and Industrial Research* 64, 454–458.

Table 2 Concentration of hazardous gases and total dust during welding operation

	Concentration of gases and metals (mg/m^3)								
	SO_2	CO	CO_2	Mn	P	Al	Ni	Ca	Cr
Metal cored wire	2.09	181	3590	16.86	–	1.809	0.1741	0.717	0.0785
Self-shielded wire	2.62	17.2	5760	2.574	2.376	8.564	0.0742	0.4356	0.00495

Note: Popović, O., Prokić-Cvetković, R., Burzić, M., Lukić, U., Beljić, B., 2014. Fume and gas emission during arc welding: Hazards and recommendation. *Renewable and Sustainable Energy Reviews* 37, 509–516.

Similarly, [Pervez et al. \(2005\)](#) collected data from small, medium, and large scale Indian industries, which extensively performed welding operations to investigate adverse effects on environmental air. The concentration of particulate matter less than $10\text{ }\mu\text{m}$ (PM_{10}) and five micron (PM_5) was found beyond permissible limits as per Indian standards. Moreover, it was found that PM_{10} concentration was 1.5 times and PM_5 was 2 times greater in indoor as compared with outdoor locations ([Table 1](#)).

[Popović et al. \(2014\)](#) measured concentration of various gases and metal fumes involved in ambient air at indoor conditions using metal cored and self-shielded wire during arc welding operation ([Table 2](#)). It was found that the quantity of few harmful gases and toxic metal fumes was higher than permissible limits, which must be controlled to prevent environmental hazards.

In steel and iron manufacturing industries, many pollutants are involved during various stages of metal processing. During different metallurgical processes performed on iron ores, poisonous gases such as carbon monoxide, sulfur dioxide, and other heavy metals such as manganese, lead, nickel, arsenic, cadmium, and chromium are released in ambient air, which deteriorates the overall air quality.

In foundry industries, the major pollutants are released during pattern making, sand preparation, molding, mold drying, ladle heating, pouring and mold cooling, knockout, fettling, and heat treatment processes. Moreover, during pouring operations in the casting industry, the metal fumes, gases, vapors, and smoke are produced in excess amount.

In a comprehensive study on airborne particles emitted in cast iron foundries conducted by [Moroni et al. \(2014\)](#), the bulk chemical approach was used for characterization of aerosol samples; see [Table 3](#). The testing of air samples under scanning electron microscopy, transmission electron microscopy, and energy dispersive x-ray spectroscopy revealed excess amount of carcinogenic agents such as quartz and other heavy metals. The quartz was found above permissible limits at sand making and molding sites of industry. At shaking out locations, carbonaceous material consisting of irregular chains of carbon with size up to $1\text{ }\mu\text{m}$ was found. Moreover, concentration of heavy metals such as zinc, lead, manganese, and iron was found near the melting zone.

[Rafiei et al. \(2009\)](#) tested air quality on two production lines of the steel manufacturing industry in Iran and found higher levels of respirable particulate matter (3.09 and $3.78\text{ mg}/\text{m}^3$) in ambient air as compared with permissible limits ($3\text{ mg}/\text{m}^3$). Moreover, health tests showed that workers exposed to this environment were under higher risk of cardiovascular, pulmonary, and psychological diseases. Similarly, [Chohan and Bilga \(2011\)](#) found higher concentration of suspended particulate matter ($175\text{ }\mu\text{g}/\text{m}^3$) in small scale steel manufacturing industries in India. There was a significant impact of exposure conditions on workers' pulmonary functions as compared with control group workers who were unexposed.

In addition to casting, steel making, and welding operations, there are many other conventional manufacturing processes that significantly contribute to environmental pollution. For instance, heating of metals at higher temperature for heat treatment suspends micro-sized metal fumes in the air. In addition to this, various waste chemicals used in heat treatment result in water pollution in case of inadequate disposal facilities.

In addition to adverse effect on air quality, the excessive heat and noise released by conventional manufacturing units is a matter of grave concern. There are a plethora of production processes such as pressing, blanking, punching, molding, grinding, forging, fettling, trimming, and barreling creating both intermittent and impulsive noise. Prolonged exposure to loud noises (above 88 dB) may lead to cardiovascular disease, high stress, high blood pressure, and headache. The high-intensity noise may

Table 3 Mass concentration of samples at different locations in two foundries

Foundry	Location	Mass concentration (mg/m ³)
1	Melting	0.60
1	Molding	0.77
1	Sand making	2.72
1	Shakeout	0.70
1	Cleaning	1.22
1	Core making	0.28
2	Shakeout	0.74
2	Core making	0.18
2	Molding	0.48
2	Melting	0.60
2	Sand making	0.72

Note: Moroni, B., Viti, C., Cappelletti, D., 2014. Exposure vs toxicity levels of airborne quartz, metal and carbon particles in cast iron foundries. *Journal of Exposure Science and Environmental Epidemiology* 24 (1), 42.

cause even permanent or temporary hearing loss/deafness and central nervous system disorders. Singh *et al.* (2010) found that noise levels in a foundry in India were than the permissible limits (90 dB). The noise levels at drop forging and grinding locations may increase up to 135 dB, which is highly hazardous for those workers who don't use personal protective equipment.

In the casting, forging, and steel making processes, the second most prominent environmental hazard is excessive heat evolved during various activities. The workers engaged in these tasks are more highly prone to heat stress, heavy sweating, and daily tiredness. Chohan and Bilga (2011) reported high heat concentration near steel furnace with dry bulb temperature more than 37°C whereas the permissible temperature level for working conditions recommended by OSHA is 27.80°C. Singh *et al.* (2010) measured wet bulb temperature at casting unit ranging from 32.17°C to 37.31°C and in forging unit ranging from 33.47°C to 38.03°C in an Indian working environment. In casting and forging industries, the major source of heat is induction and oil fired furnace and heat treatment.

Many developed nations have minimized the use of these aforementioned additive manufacturing techniques (welding and casting) owing to enormous environmental hazards. This led to a shift toward regenerative manufacturing processes commonly known as rapid prototyping or 3D printing. The distinction of rapid prototyping processes (such as selective laser melting, selective laser sintering, electron beam melting, fused deposition modeling, and stereolithography) is due to their good environmental characteristics (Sreenivasan *et al.*, 2010). By utilizing only the amount of material required for the product, rapid prototyping methods have the potential to limit the life cycle material mass and energy consumed as compared with subtractive manufacturing techniques. This can be achieved by eliminating scrap and the pollution enablers. Although it is costly, it can be considered as an innovative mode of part production (Kafara *et al.*, 2017). Le Bourhis *et al.* (2014) formulated a predictive model of consumption and integrated it into the design process, which evaluated the product's environmental impact during manufacturing. The model optimization can also be carried out by keeping environmental issues in view. However, environmental issues can also be compensated by enhancing the functionality of additive manufacturing manufactured parts (Kellens *et al.*, 2017).

Subtractive Manufacturing Processes

Subtractive manufacturing is basically a process of removing materials through chip formation using a sharp cutting tool by the application of mechanical energy using cutting fluid to maintain the temperature at the cutting zone. Some of the common subtractive manufacturing process are milling, turning, drilling, grinding, broaching, and sawing. Apart from these traditional manufacturing processes, a multitude of nonconventional processes have been developed over the last three decades to overcome the limitations of the former. These nontraditional subtractive manufacturing techniques have a tendency to machine a material with greater hardness and complex shapes with comparatively higher accuracy and lower cost. Interestingly, these advanced techniques have higher initial cost but they have played a major role in area of micromachining as a smaller amount of material is removed from the workpiece. Chemical machining, electrodischarge machining, and laser beam machining are some of the advanced subtractive techniques.

In subtractive manufacturing processes, a plethora of solid, liquid, and gaseous wastes can be identified, which have a significant impact on environment and occupational health (Fig. 2). Furthermore, noise and vibrations, fire and explosions, and other accident-related factors arising from these processes also pose grave danger to the environment.

Metal dust, in the form of fine particles with size ranging from submicrons to a few nanometers, is produced when material is particularly machined in dry conditions or inadequate lubricating conditions. Metal dust is also produced from friction between the cutting tool and work material, and rubbing of different machine components with each other. In the grinding process, for example, fine dust is produced from both the wheel and machined parts. As beryllium, silicon, chromium, zinc, nickel, and cobalt

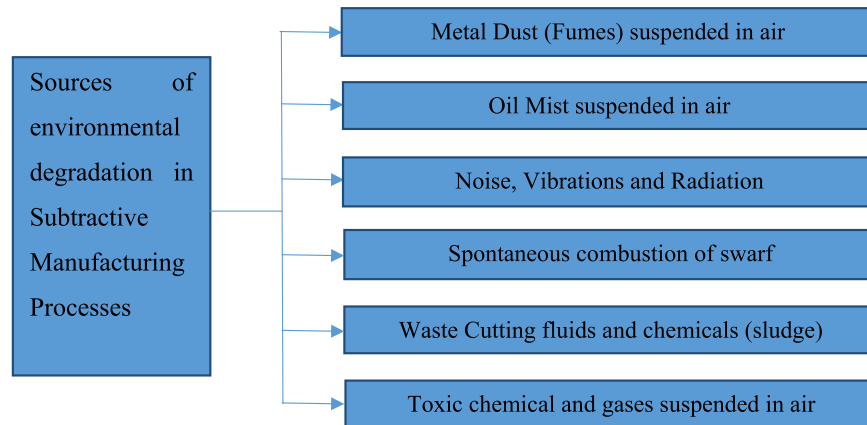


Fig. 2 Sources of environmental degradation in subtractive manufacturing processes.

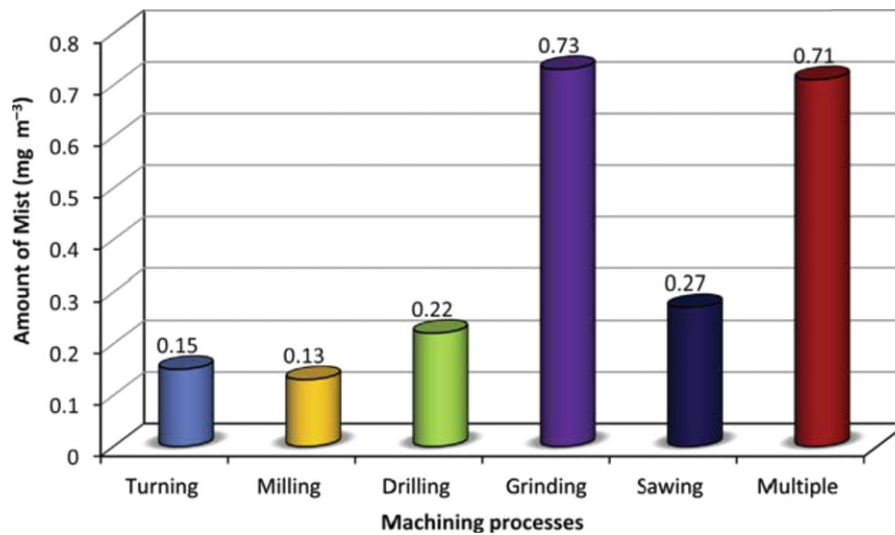


Fig. 3 Mist concentration during different subtractive processes. Reproduced from Simpson, A.T., Stear, M., Groves, J.A., *et al.*, 2003. Occupational exposure to metalworking fluid mist and sump fluid contaminants. *Annals of Occupational Hygiene* 47 (1), 17–30.

Table 4 Machining liquids and chemicals used in advanced subtractive process

Sl. no.	Manufacturing process	Materials/liquids/chemicals used	Environmental threats
1	Chemical machining	FeCl ₃ , CuCl ₂ , and alkaline etchants	Hafnium suspended in air, disposed waste chemicals
2	Electrochemical machining	Sodium chloride, sodium nitrate	Hydrogen gas, mists, chromate, nitrate and ammonia suspended in air, disposed waste chemicals
3	Electrodischarge machining	Dielectric fluids	Polycyclic aromatic hydrocarbons, benzene, carbon monoxide, nitrous oxide, ozone and aerosols
4	Laser beam machining		Metal fumes, aerosols and radiation, noise
5	Electron beam machining		Metal fumes
6	Ultrasonic machining	B ₄ C, Al ₂ O ₃ and SiC abrasive slurry	Electromagnetic radiation, high frequency noise and abrasive slurry
7	Abrasive jet machining	Abrasives	Abrasive and metal fumes

dust is suspended in the air, it causes adverse pulmonary health effects such as asthma and lung cancer in addition to having harmful impact on eyes and skin.

Liquid droplets in size ranging from 0.01 to 100 μm that are suspended in air during various subtractive processes such as turning, milling, drilling, and grinding are called mist. In wet machining, mist is mainly aerosol suspended in air, causing serious health risks to workers and adding to environmental degradation. Even in minimum quantity lubrication, the mist is prominent due to high pressure air–oil mixture impinging on tools and work material. Volatile hydrocarbons present in cutting fluid are suspended in air due to vaporization and atomization due to heat generated by cutting tools and high mechanical energy used in machining.

A survey in the manufacturing industry indicated that drilling, sawing, and grinding pose higher health risks due to mist formation as compared with turning and milling operations (Fig. 3).

Cutting fluid mists, if inhaled for longer durations, can potentially harm lung functions and cause chronic bronchitis, asthma, and pneumonitis in addition to esophagus, stomach, pancreas, colon, prostate, and rectum cancers. Furthermore, the chips and swarf are the main solid wastes, which are initially hot and may injure workers' skin and eyes. In some instances, swarf may consist of fine iron powder that can burn spontaneously due to rapid oxidation caused by air contact.

Machining noise is a major source of noise pollution in the manufacturing industries, which adds to environmental degradation as exposure to noise level more than 85 dB for an 8-h shift is not acceptable in an industrial environment. A survey shows that subtractive manufacturing industries contribute to 41% of occupational hearing loss cases out of total noise-related cases in Europe.

Apart from traditional processes, several advanced subtractive manufacturing techniques significantly contribute to environmental degradation. In spite of being efficient and accurate machining process, these manufacturing techniques such as chemical machining and electrochemical machining extensively use chemicals that are suspended in indoor air. Moreover, cutting of hard materials takes place at high temperature, which increases concentration of metal fumes, oxides, and aerosols as compared with traditional manufacturing processes. Table 4 illustrates various environmental hazards related to different subtractive manufacturing techniques. Apart from air pollution, plenty of industries dispose of sludge containing heavy metals and chemicals in rivers and lakes, which leads to destruction of flora, fauna, and marine life. Several advanced manufacturing techniques include laser beam, electron beam, and ultrasonic machining.

Outcomes and Future Scope

Although the shift to bulk industrialization and mass production has a positive impact on populations, the adverse effect on the environment caused by manufacturing processes cannot be neglected. There is a tremendous amount of air pollutants evolved during conventional additive manufacturing processes (welding and casting) but their overall contribution is less due to limited use by developed nations. The last two decades have experienced a significant change in the manufacturing industry by introduction of regenerative (additive) manufacturing processes, which are able to reduce environmental degradation. These additive manufacturing techniques such as fused deposition modeling, stereolithography, selective laser sintering, and laminated object manufacturing are however, economical for part production and thus, the need and scope of subtractive manufacturing techniques cannot be ignored especially in the case of mass production. Thus, there is an urgent need for further innovation and research in the environmental aspect of these subtractive manufacturing processes, as in the present scenario, they are a major source of environmental pollution due to the large volume of products produced worldwide.

See also: Recent Advancement and Challenges of Additive Manufacturing Geospatial Images Solution Integration. Renewability Assessment of a Production System. Subtractive Versus Hybrid Manufacturing

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Further Reading

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Food Residue, Loss and Waste as Animal Feed

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Introduction

In 2011–2013, world production of food averaged 9.7 billion tonnes (metric tons, FAO Food Balance Statistics) which included alcoholic beverages, cereal grains, dairy products, eggs, fruits, ground nuts, fish and marine products, meats, oil seeds, pulses, root crops, spices, tea, coffee, cocoa, sweeteners, and vegetables. About 49.5% of world food production, 4.8 billion tonnes, was available to consumers. Of the 4.8 billion tonnes of food available for consumption, consumers threw out 1.3–1.6 billion tonnes as food waste (Gustavsson *et al.*, 2011). Some food waste was inedible, but the majority of waste (about 80%) was edible portions. The result is that of food produced only about 35% was consumed by humans. A majority of wasted food was disposed as municipal solid waste to landfills. The consequence is that as the organic food waste decomposes, it contributes about 5% to total CO₂ equivalent emissions and nutrient leachate of N and P, contributing to water pollution (Kaza *et al.*, 2018). Reducing food waste is a first step in to improve sustainability of food production for future generations (Giroto *et al.*, 2015). However, the food system will inevitably produce organic waste, which needs to be more effectively utilized than disposal as MSW. One such use would be to capture food waste as animal feed.

A significant amount of food and food residues are used as animal feed. About 12.8% of food produced over the period from 2011 to 2013 was used directly as animal feed; primarily cereal grains, which are 80% of the food used for animal feed. Twenty two percent (22.2%) of food produced is processed for production of juices and jellies, preserved products, prepared meals, and distilled beverages. Although food processing produces value added products for human consumption, it also produces residues which are largely inedible or not preferred by consumers. The majority of these residues, 95%, are used as animal feed. In addition, some grocery products removed for expired shelf life are collected and combined with food residues as animal feed. Food waste would extend the volume and complement these food losses if included in animal feed, and could reduce the amount of cereal grains diverted to animal feed, extending human food supplies. Projections of world population are that it will increase to 9.7 billion people by 2050, which will necessitate an increase in world food production of 43%. Reducing food waste could significantly contribute to the increase in food availability, whereas utilizing food waste as animal feed could significantly contribute to more efficient food production needed to meet increasing human food needs (Zu Ermgassen *et al.*, 2016).

Globally, it has been recognized that it is critical to reduce food waste and to improve the capture of unconsumed food products to other useful purposes than disposal in landfills (see “Relevant Websites section”). A hierarchy of food loss and waste use has been proposed. First, food waste and losses should be reduced, directly increasing food availability. Secondly, food waste and food residues should be collected and used for animal feed. Thirdly, food waste and food residues not used for animal feed should be composted, and lastly used in anaerobic digestion for energy production (Giroto *et al.*, 2015; Papargyropoulou *et al.*, 2014; Food Waste Reduction Alliance, 2013).

Food Supply Chain and Food Loss and Food Waste

For a detailed discussion of losses and waste the reader is referred to papers by Giroto *et al.* (2015), Hebrok and Boks (2017), Papargyropoulou *et al.* (2014), and Priefer *et al.* (2016). In brief, food reaches consumers through a food supply chain or system (Papargyropoulou *et al.*, 2014). Production begins in the agriculture sector at the farm and is harvested and transported from the farm either to processors and manufacturers or directly to markets. Processors and manufacturers distribute food to retailers, institutions, and restaurants, which provide the final food produced to consumers. The chain can be summarized as producers, intermediaries, and end users. Inefficiencies along all components of the chain result in organic waste (Priefer *et al.*, 2016). Disposal of the waste and the capability to capture waste into animal feed differs along each segment of the food supply system. As food moves from producer to end user, more of the waste ends up as MSW.

Gustavsson *et al.* (2011) partitioned lost food into food loss and food waste. Food loss represented a decrease in edible food mass prior to the end user, whereas food waste was loss of edible components at the end of the food supply chain (Gustavsson *et al.*, 2011). Papargyropoulou *et al.* (2014) suggested that food diverted to animal feed should be included as food loss, as this has a direct impact on reducing food supply to humans. For this paper, food diverted to animal feed will be included in the discussion of food utilized in animal feeding in addition to food loss and waste.

Losses and waste along the food supply chain may be classified into four main streams: food consumable by humans diverted to animal feed (primarily cereals), food residues that result from food processing, food losses that occur due to spillage, spoilage, and transport losses, and food waste that end users dispose. Food diverted into animal feed is primarily cereal grains, which could be used directly by humans. Corn is the primary cereal diverted to animal feed. Food residues result from food processing and manufacturing which lead to by-products not preferable or not consumable by humans. These are residues of cereal, vegetable, and fruit processing such as seeds, hulls, pulp, pomace, and discarded whole fruits and vegetables considered unacceptable for markets. The meat and fish industry produce food residues of condemned and rejected carcasses, blood, offal, and trimmings.

The brewing and distillery industries produce residues of cereal fermentation for alcohol production. The oil industries produce plant meal residues after oil extraction. Many of these residues are used as animal feed.

Food losses represent inefficiencies in infrastructure along the supply chain once food leaves the farm. Spills, spoilage, transport losses result from poor refrigeration and storage at collection points. Losses in transport are due to poor collection vehicles. These losses are difficult to collect unless directly from the manufacturing facility. Losses from processors and manufacturers have a greater opportunity to be collected and used for alternative purposes, thus MSW disposal tends to be low for losses from this sector (BSR, 2013). In addition, processors and manufacturers have significant income from the sale of food residues as animal feeds.

Losses from retailers, restaurants, institutions, and markets present difficulties in collection due to high moisture content, rapid aerobic deterioration, low daily volumes, and spatial distribution of end users. Household food waste presents more problems in collection and handling than waste from retailers and markets. Volume of collection can be significant at grocery stores and markets making collection more efficient. Due to technological collection problems from households, food waste at the consumer end of the food chain results in MSW disposal. In the US, 21% of food waste ends up in landfills. The major challenge at the consumer sector is collection of food waste so it can be diverted to alternative uses such as animal feed. In addition, food waste is high in moisture content and nutrients which result in rapid spoilage, necessitating frequent collection.

Food waste is estimated at 1.3–1.6 billion tonnes annually (Gustavsson *et al.*, 2011). Food used as animal feed is estimated at 1.25 billion tonnes by the FAO (FAO STATS, Food Balance Statistical Summary). Residues of food processing vary by sector for fruit, vegetable, meat, meat, brewing and distilling, and dairy. However estimates from various industries are that residues are 20%–40% of raw food inputs after product production. This would result in 0.40–0.86 billion tonnes of food residues used for animal feed. The animal feed available from these three streams would provide 2.9–3.4 billion tonnes annually.

The Animal Feed Industry

Alltech surveyed the world feed industry in 2013 (All About Feed, 2014). There were 26,240 feed mills in the world producing 963 million tonnes (1062 million US tons) of animal feed. The number one producer of animal feed was China at 189 million tonnes (208 million US tons) from 9500 feed mills, followed by the US with 169 million tonnes (186 million US tons) of animal feed from 5236 feed mills. World-wide, poultry feed is the number one product at 444 million tonnes (489 million US tons) (Table 1). Swine are the second largest feed consumer at 243 million tonnes (268 million US tons) followed by all ruminants at 196 million tonnes (216 million US tons) (Table 1).

Feed produced by feed mills is a dry product, containing 10% or less of moisture. The residues referred to above, 2.9–3.4 billion tonnes, from food waste, food used for feed and food processing residues, contain a significant amount of moisture, except for cereal grains used as animal feed. The equivalent dry tonnage of these residues is more likely to supply 1.6–1.7 billion tonnes of dry animal feed. In addition, feed from feed mills is not the only source of feed for livestock. Forages, pasture grasses, and crops grown on farms supply a substantial amount of feed for livestock in the world. Food waste as animal feed would supplement animal feed sources and not entirely replace all animal feeds.

The major products used in animal feed are summarized in Table 2 based on a paper by Capper *et al.* (2013). Forage crops comprise a major component of herbivore (primarily ruminants) feedstuffs and are not consumed by humans. Other feed items are co-products or waste products of the food processing industries and have variable value as human food sources. Cereal grains are the major food group used in animal feeds which could be consumed by humans.

The utilization of food used in animal feed based on estimates by the Food Agriculture Organization is in Table 3 for the year 2011 (see “Relevant Websites section”). Overall, 13.6% of world food production was used in animal feeds in 2011 (Table 3). Cereal grains comprise the largest component of animal feeds with 34.9% of production going into animal feed,

Table 1 World feed production as reported by Alltech in 2014 for the situation in 2013

Rank	Animal group/Item	Million tonnes	Number
1	Poultry	444.0	
2	Swine	243.0	
3	Ruminants	195.0	
4	Aquaculture	34.4	
5	Pets	20.7	
6	Equine	12.4	
	Total feed mills		26,240
1	China	189	9500
2	US	169	5236
3	Brazil	67	1237

Note: All About Feed, 2014. Alltech Global Feed Survey, 2014. Available at: www.Alltech.com.

Table 2 Examples of feeds commonly used within U.S. livestock production systems^a

Feed source	Examples	Human edible?
Forage crops	Pasture grasses, alfalfa, clovers, hays, silages (grass or crop based)	No
Cereals	Corn, wheat, barley, millet, sorghum, triticale, oats	Yes
Plant proteins	Soybean (meal and hulls), cottonseed (whole and meal) safflower meal, canola meal, peanut meal	Partially
Vegetable oils	Soybean, canola, corn, sunflower oils	Yes
Grain by-products	Distillers grains (wet and dry), corn gluten, wheat bran, straw, crop residues	No
Vegetable by-products	Apple pomace, citrus pulp, almond hulls, pea silages	No
	Waste fruit/vegetables	Partially
Food industry by-products	Bakery waste, cannery waste, restaurant waste, oils, expired candy, potato chips, bakery products, greases	Partially
Sugar industry by-products	Molasses (cane, beet, citrus), beet pulp	Partially
Animal by-products	Meat and bone meal, tallow, feather meal, bloodmeal, poultry litter	Partially
Dairy by-products	Milk, whey products, casein	Partially
Marine by-products	Fish and seafood meal and oils, algae	Partially

^aCapper *et al.* (2013).**Table 3** Major food groups used in animal feeds^a

Food group	Production	Animal feed	% of production	% of food used for animal feed
	Metric tonnes	Metric tonnes		
Cereals	2,345,593	818,837	34.910	64.898
Sugar crops	2,092,347	51,699	2.471	4.097
Vegetables	1,087,523	52,565	4.833	4.166
Starchy roots	798,181	177,246	22.206	14.048
Milk	739,114	78,962	10.683	6.258
Fruits	629,014	5547	0.882	0.440
Oilcrops	550,924	35,565	6.456	2.819
Meat	296,615	74	0.025	0.006
Sugar	205,114	434	0.212	0.034
Vegetable oils	159,184	773	0.486	0.061
Fish, seafood	149,496	23,443	15.681	1.858
Eggs	70,684	73	0.103	0.006
Pulses	68,336	13,243	19.379	1.050
Animal fats	36,480	2065	5.661	0.164
Aquatic products	23,127	159	0.688	0.013
Stimulants	18,398	12	0.065	0.001
Offals	18,151	1041	5.735	0.083
Totals	9,288,281	1,261,738	13.584	100.000

^aFAO Stats (accessed October 2014). Available at: <http://faostat.fao.org/>.Note: FAO, 2011. Food Balance Sheets. Food and Agriculture Organization. Available at: <http://faostat.fao.org/site/368/default.aspx#ancor> (accessed August 2018).

representing almost 65% of animal feeds (**Table 3**). Starchy roots (22.2% of production) and pulses (19.4% of production) were the next largest contributors to animal feed based on production totals. Slightly over 15% (**Table 2**, 15.7%) of fish and seafood production was used for animal feed, but it comprised only 1.86% (**Table 2**) of total animal feeds. Milk and milk products were a significant contributor at 6.26% of animal feeds and 10.68% of total production (**Table 2**). Oil crops, such as soybeans, cottonseeds, and rape seed, contributed 6.46% of total production to animal feed, but were only 2.82% of animal feed (**Table 3**). The data suggest that only reducing cereal grains in animal feeds would have a significant benefit to human food supply. If all cereal grains were diverted from animal feed, it would increase human food supply about 1 billion metric tonnes, about 50% of the needed increase in food supply by 2050.

Table 4 looks more closely at the use of cereals and other animal products in animal feeds. Of cereals used for animal feed, maize was 59.25% of all cereals (**Table 4**). Wheat (17.35% of cereals used in animal feeds, **Table 4**) and barley (10.92% of cereals in animal feeds, **Table 4**) were the next major cereals used in animal feeds. A little over half of maize production (54.75%, **Table 4**) was used for animal feed, whereas 69.3% of oat production and 71.5% of other cereals were used for animal feed, but these cereals were less than 4% of all cereals used as animal feeds. The cereal grains barley (67.294%) and oats (69.285%) were primarily used for animal feed (**Table 4**) but their total contribution to animal feed was only 10.92% and 1.89%, respectively (**Table 4**). Cassava, followed by potatoes and sweet potatoes were the most common starchy roots used as animal feed (**Table 4**). Of oil seeds, soybeans and cottonseeds were the major co-products used in animal feeds (**Table 4**).

Table 4 Utilization of agricultural products for animal feed

<i>Item</i>	<i>World production (Metric tonnes)</i>	<i>Feed Use (Metric tonnes)</i>	<i>% of total production</i>	<i>Feed (Tonnes)</i>	<i>% of Feed</i>
All Cereals	2,345,593	818,837	34.909	818,837	100.000
Rye	13,029	4845	37.186		0.592
Oats	22,318	15,463	69.285		1.888
Cereals, other	25,494	18,236	71.531		2.227
Millet	27,137	4134	15.234		0.505
Sorghum	58,093	26,697	45.956		3.260
Barley	132,894	89,430	67.294		10.922
Rice (Milled)	481,177	32,838	6.825		4.010
Wheat	699,350	142,039	20.310		17.346
Maize	886,101	485,155	54.752		59.249
Starchy Roots	798,181	177,246	22.206	177,246	100.000
Cassava	246,120	77,662	31.555		43.816
Potatoes	374,425	49,702	13.274		28.041
Sweet potatoes	103,174	40,899	39.641		23.075
Yams	56,677	8235	14.530		4.646
Roots, other	17,785	748	4.206		0.422
Sugar Crops	2,092,347	51,699	2.471	51,699	100.000
Sugar cane	1,814,267	34,772	1.917		67.259
Sugar beet	278,080	16,927	6.087		32.741
Sugar and Sweeteners	205,114	434	0.212	434	100.000
Sugar	8671	320	3.690		73.733
Sugar Raw	170,669	78	0.046		17.972
Sweeteners	24,196	36	0.149		8.295
Honey	1578	0	0.000		0.000
Pulses	68,336	13,243	19.379	13,243	100.000
Beans	22,926	2753	12.008		20.788
Peas	9739	3330	34.192		25.145
Pulses Other	35,671	7160	20.072		54.066
Oilcrops	550,924	35,565	6.456	35,565	100.000
Soyabeans	261,892	13,404	5.118		37.689
Groundnuts	28,168	2	0.007		0.006
Sunflower seed	40,785	2659	6.520		7.476
Rape and Mustard seed	63,269	5165	8.164		14.523
Cottonseed	48,814	12,199	24.991		34.301
Coconuts/Copra	57,194	46	0.080		0.129
Sesame seed	4667	3	0.064		0.008
Palm kernels	13,433	0	0.000		0.000
Olives	20,417	0	0.000		0.000
Oilcrops, other	12,285	2087	16.988		5.868
Vegetable Oils	159,184	773	0.486	773	100.000
Soyabean Oil	41,915	22	0.052		2.846
Groundnut Oil	5703	0	0.000		0.000
Sunflower Oil	13,354	0	0.000		0.000
Rape and Mustard Oil	22,908	750	3.274		97.025
Cottonseed Oil	5194	0	0.000		0.000
Palmkernel Oil	6020	0	0.000		0.000
Palm Oil	48,543	0	0.000		0.000
Coconut Oil	3109	0	0.000		0.000
Sesameseed Oil	1073	0	0.000		0.000
Olive Oil	3620	0	0.000		0.000
Ricebran Oil	1084	0	0.000		0.000
Maize Germ Oil	2325	0	0.000		0.000
Oilcrops Oil Other	4336	1	0.023		0.129
Vegetables	1087,523	52,565	4.833	52,565	100.000
Tomatoes and products	158,055	1751	1.108		3.331
Onions	84,907	82	0.097		0.156
Vegetables, Other	844,561	50,732	6.007		96.513

Table 4 Continued

<i>Item</i>	<i>World production (Metric tonnes)</i>	<i>Feed Use (Metric tonnes)</i>	<i>% of total production</i>	<i>Feed (Tonnes)</i>	<i>% of Feed</i>
Fruits-	629,014	5547	0.882	5547	100.000
Oranges, and Mandarines	95,569	10	0.010		0.180
Lemons, Limes and products	15,155	0	0.000		0.000
Grapefruit and products	7773	0	0.000		0.000
Citrus, Other	12,610	0	0.000		0.000
Bananas	102,172	1543	1.510		27.817
Plantains	35,898	2917	8.126		52.587
Apples and products	76,108	633	0.832		11.412
Pineapples and products	21,429	0	0.000		0.000
Dates	6922	333	4.811		6.003
Grapes and products	69,979	0	0.000		0.000
Fruits, Other	185,399	111	0.060		2.001
Stimulants	18,398	12	0.065	12	100.000
Coffee	8299	0	0.000		0.000
Cocoa Beans	4691	12	0.256		100.000
Tea incl mate	5408	0	0.000		0.000
Meat	296,615	74	0.025	74	100.000
Bovine Meat	66,359	8	0.012		10.811
Mutton and Goat	13,518	17	0.126		22.973
Pig meat	107,893	0	0.000		0.000
Poultry Meat	102,466	0	0.000		0.000
Meat, Other	6379	49	0.768		66.216
Offals	18,151	1041	5.735	1041	100.000
Animal fats	36,480	2065	5.661	2065	100.000
Butter, and Ghee	9404	4	0.043		0.194
Cream	3327	0	0.000		0.000
Fats, Raw	22,710	1592	7.010		77.094
Fish, Body Oil	1022	462	45.205		22.373
Fish, Liver Oil	17	7	41.176		0.339
Eggs	70,684	73	0.103	73	100.000
Milk	739,114	78,962	10.683	78,962	100.000
Fish, seafood	149,496	23,443	15.681	23,443	100.000
Freshwater Fish	50,546	585	1.157		2.495
Demersal Fish	20,761	1168	5.626		4.982
Pelagic Fish	34,088	19,908	58.402		84.921
Marine Fish	10,855	1439	13.257		6.138
Crustaceans	11,869	174	1.466		0.742
Cephalopods	3850	151	3.922		0.644
Molluscs, Other	17,527	18	0.103		0.077
Aquatic Products	23,127	159	0.688	159	100.000
Meat, Aquatic Mammals	0	0	0.000		0.000
Aquatic Animals Other	1351	0	0.000		0.000
Aquatic Plants	21,776	159	0.730		100.000

Note: FAO, 2011. Food Balance Sheets. Food and Agriculture Organization. Available at: <http://faostat.fao.org/site/368/default.aspx#ancor> (accessed August 2018).

For vegetables, fruits, and meat small percentages of total production was used in animal feed (Table 4). These amounts would represent cull products that were excluded from processing or sale from retail markets. Very little of food production of vegetables, fruits, and meat were used as animal feed. Animal feed from these products typically is from co-products of food processing and not direct diversion of these foods to animal feed.

Table 5 presents the utilization of by-products from food processing and cereal grains used for animal feeds in the US in 2012 (NASS publication). Consistent with the FAO data, cereal grains are the major item used as animal feed with food processing residues comprising 25.8% of livestock feeds. The majority of co-products used as animal feed are from the vegetable oil industries from the processing of oil seeds, producing oil seed meals, which typically are high protein feeds (Table 5). However these estimates do not include vegetable, citrus, bakery, candy, chip and other food waste which comes from retailers and juice and vegetable processors.

Table 5 United States department of agriculture statistics for products used in animal feeds in 2012

<i>Feed group by-products</i>	<i>Utilization (Metric tonnes)</i>	<i>Cereals grains</i>	<i>Utilization (Metric tonnes), (US)</i>
Oilseed meals		Cereals	
Soy bean meal	27,487,698	Corn	116,845,395
Cottonseed meal	2,290,641	Sorghum	1,360,777
Linseed meal	178,715	Oats and Barley	2,630,836
Peanut meal	86,183	Wheat	5,352,390
Sunflower meal	326,587	Rye	90,718
Animal Proteins			
Tankage and Meat Meal	2,131,884		
Fish Meal	181,437		
Dried Milk	226,796		
Mill Products			
Wheat Mill Feeds	5,805,982		
Gluten feeds and meal	4,603,963		
Rice Mill Feeds	521,631		
Alfalfa Meal	NA		
Totals			
By-products	43,841,517	Cereals	126,280,116
By-products used as a percent of total animal feeds, %	25.8		

Source: National Agriculture Statistical Services Publication 2012.

Co-Products of Processing Industries

Data from [Crawshaw \(2001\)](#), [Macgregor \(1989\)](#), and the [National Research Council \(2001\)](#) is summarized in [Table 6](#) for co-product feeds typically used in ruminant and swine diets. As Crawshaw has pointed out, the production of feed grade co-products inevitably increases as higher standards are imposed on foods for human consumption. Thus, we may expect feeds from these co-products to increase in production as more rigid standards are applied based on appearance, uniformity in size, absence of defects, and lower contamination thresholds in human food regulations. Presented in table six are values for dry matter (DM), crude protein (CP), neutral detergent fiber (NDF), starch, fat, ash, and metabolizable energy for ruminants (ME, MJ/kg, (Mjoules/kg)) ([Table 6](#)). For comparison, fine ground corn has an energy value of 14.4 MJ/kg on a DM basis whereas alfalfa hay has a value of 7.8 MJ/kg. Most co-products have an energy value slightly lower than ground corn, unless they have a significant fat content, but have a higher energy value than most forages. However, as seen [Table 6](#), many co-products have low DM content and, unless excessive water is removed, present a problem in transport and storage due to low aerobic stability. Removal of water is necessary to economically transport co-products to farms or feed mills which may be located at some distance from the processing plant. In addition a dry product is necessary to improve stability and handling.

Co-products from processing industries are an important source of revenue and comprise the greatest food waste source for animal feed. Processing plants provide a large volume of residues at a defined location, improving the efficiency of collection. However, residues of processing have a high moisture content and may be located some distance from farms that may use the product. This facilitates collection, but challenges distribution. Removing moisture adds to handling and processing costs, increasing the cost of the co-product. Co-products in [Table 6](#) include items such as pomace or pulp from the canning and juice industries, secondary products of the ethanol, spirits, brewing or oil industries, expired bakery, vegetable, and candy products, and residues of the rendering industry. Most of these items would only be partially consumable by humans, but would not be preferred food items. Livestock industries provide a valuable resource for disposal of these items as opposed to municipal disposal or incineration. Livestock convert typically poor quality residues into high quality animal protein for human consumption.

Food Waste From Retail, Restaurant, and Household Sectors

The reader is referred to a paper by [Dou et al. \(2018\)](#) for a comprehensive review of the feasibility and challenges of feeding food waste to livestock. Historically swine have been the preferred animal for food waste feeding ([Dou et al., 2018](#); [Salemdeeb et al., 2017b](#)). Swine are omnivores and can handle diverse feed inputs. However, fish, poultry, pets, and ruminants may also be fed food waste, but with limitations on total quantity in the diet. In 1995 the National Animal Health Monitoring Service ([USDA, 1995](#)) estimated that 3.9% of hog farms in the US were feeding food waste based on a sample of 418 operations in 1995.

In 2012 NAHMS sampled small hog farms (< 100 hogs/farm, 534 farms sampled) for feeding practices. On hog farms with 50–99 hogs (460 farms sampled), 12.0% were feeding table-food waste, whereas on farms with 1–49 hogs (79 farms sampled),

Table 6 Major co-products of food processing used as animal feed^{a,b}

Industry	Product	DM %	CP	NDF	Starch	Fat	Ash	ME MJ/kg
Almond Nuts	Almond hulls	91	4.2	28–42	6	3.5	7.6	10.4
Apple Processing	Cider Apple Pomace	20–28	6.7	43–56	2–7	2.3–3.2	2.3	9–12
	Culinary Apple Pomace	19	4.5	34	NR	NR	3.0	11
	Apple Pomace	21	7.6	42–52	4	4.8	2.2	11
Bakery Products	Bread	65/90	14.0	–	70–73	3.0	2.8	14
	Cake	68–87	5–14.7	–	18–32	6–35	NR	14–19
	Cookie meal	90–94	5–10	–	21–76	10–25	4.5	15–17
	Breakfast cereal	90–93	9–13	–	49–62	1–2.5	2.5	13.5
	Bakery Waste	91	12.1	7.0	51	11.0	4.4	14
Malting, Brewing and Vinegar	Malt powder	88–95	6–17	12–71	NR	1.5–4.5	2–11	8–13
	Malt screenings	88	10–13	16–21	NR	3.8	2.6	13
	Malt culms	92–96	20–32	48.4	3–19	2.9	5.7	11.1
	Malt residue pellets	90	23	48	15.8	2.5	6.2	11.5
	Brewers' grains	18–25	19–31	50–64	2–8	8.5–11	3.5–9	11–12.5
	Mash filter grains	24–30	20–25	49–57	4–11	9–12	4.8	12–12.7
	Vinegar grains	21.5	21.7	50–59	7–13	8.6–13	4.2	11.7–13
	Malt extract grains	21–27	21–24	43–57	6–18	7.5–10	4.6	11.9–13
	Black grains	27.4	21–29	45–55	6–11	6–8	3–17	9–10.7
	Grains pressings	9	38	17	23	7.9	3	NR
	Brewer's yeast	12–16	36–50	3–10	2–20	2.5–4.5	6–10	13.5
	Beer	5.5–9.5	4–7				9–16	NR
	Vinegar still bottoms	67.4	33.1	0.1	2	0.15	10.8	14
	Liquid malt extract	76–78	6.4	0	0	0	1.6	NR
	Brewer's grains wet	20	26	42	10.3	5	4.8	10.5
Citrus/Tropical Fruit	Citrus pulp	17–24	6.8–9.7	19–26	0.1–8.8	1.1–3.7	4.3	13.6
	Orange pulp	17–24	7.9	20.8	2.5–21	1.1–3.5	3.9	13.6
	Lemon pulp	16–19	6.8	28.7	5.0	1	5.0	13.0
	Citrus molasses	71	5.8	0.0	NR	0.3	6.6	11.3
	Fruit salad	8.7–9.5	11–13	33	11.5	5.2	5.3–10.7	11.0
	Citrus pulp pellets	90	6.9	23	2	14.4	6.8	12.7
Candy	Candy Products	97	8.5	10.9	15	24.4	NR	15
Corn (Maize)	Screenings	87	9.2	16	72	3	0.6	13.7
	Corn steep liquor	45–50	40–45	0	2–5	0.1–2	9–22	11.5–13
	Corn gluten feed	86–91	20–25	33–45	9–28	3–7	4–10	11.3–14
	Corn gluten meal	89	66	7.5	15.5	6	2	14.5
	Corn germ meal	88	25–26	37	23	3.4	3	13.6
	Corn cannery waste	22	8.6	53.2	NR	5.2	NR	10.5
	Corn steep liquor dry	94	33	19	1	1.3	NR	12.5
Cottonseed	Whole cotton seeds	93	23	44	5	20	4.8	15.1
	Cotton seed hulls	91	4.1	85	15	2.4	2.80	6.5
Distillery co-products	Draff	20–26	20–23	60–66	0–5	9–13	3.5	11
	Pot ale syrup	30–50	34–38	0.6	1.3	2–3	9.5–10.5	15.6
	Supergrains	25	29	53–64	5	9–12	2.5	14.1
	Evaporated wash	27	31	38–51	7	6–9	2.8	13.6
	Distillers' malt	90	27	42	2.5	7.5–9	6	12.6
	Distillers' wheat	90	32	23–46	4.5	6–7.5	5.3	13.3
	Distillers' corn	90	29	23–51	2.5	10–11.5	4.5	14.9
	Distillers' w/ solubles	92	29.3	12	12	8–14.5	4.8	13.8
Potato co-products	Potato feed	10–14	17	22.1	36.6	1.6	9.3	11.7
	Potato feed permeate	9–13	18.5	11	43	1	10.0	12.6
	Potato feed solids	11–15	17	33	30	2	10	10.4
	Abraded peel	7	11.4	32–52	24–38	2.6	8.4	8.5–11
	Potato skin	10.6	18.4	70.1	4.2	3.9	6.6	5.5

(Continued)

Table 6 Continued

Industry	Product	DM %	CP	NDF	Starch	Fat	Ash	ME MJ/kg
% DM								
	Off-cuts potatoes	21.1	7.6	10	75.3	0.9	3.2	13.3
	Potato slice	17.4	9.3	25.5	60.1	1.9	6.1	11.1
	Peel and trim	32.4	6	18.5	66.9	3.77	10.5	12.6
	Potato mash	21.8	8.1	7.4	69	1.4	3	13.5
	Potato flake	90.9	8.5	5.4	78.9	1	4.5	13.4
	Potato chips	34	6.9	5.8	65.3	10–20	3.2	14.8–16
	Fries	39.9	6	14.1	42.9	20.3	3.7	16.4
	Hash browns	38.6	7.1	10.8	52.9	18.8	6.2	16.1
	Potato starch	60	1	0.7	97.7	0.2	0.3	13.9
	Potatoes	23	9.5	6	71.7	0.40	4.80	13.2
	Potato by-prod. meal	93.6	10.7	12.1	62	5.9	4	15.1
Milk Products	Whey	5–7	13–15	0	0	1	10	13.5
	Whey concentrate	30–50	12.4	0	0	1.4	7.4	13.5
	Whey permeate	18,25,45	3.8	0	0	0.2	11	11.6
	Delactosed whey	38–45	24	0	0	1.2	16	11.2
Sugar Beet co-products	Tails	9–15	7.5	NR	NR	0.3	7–25	10–11.5
	Dried molasses feed	88	11	32.1	6.5	0.4	8.8	12.5
	Beet pulp	21–30	10	52.4	0.4	0.7	8.2	12.5–13
	Beet molasses	74–78	10–14	trace	0	trace	11	10.3–12
	Beet Pulp dry	91	14.70	41.60	9	1	12.20	11.7
Wheat co-products	Wheat bran	88.8	17	44	22	4.5	5.80	10.8
	Wheat millrun	89	18	40.8	33	4.6	2	11.4
	Wheat midds	89	18.4	38	19	5	6.5	12.5
	Wheat shorts	89	15	25	36	3.5	2	12.9
	Wheat red dog	88	20.1	27	37	4.1	3.7	13.3
Hard nuts	Wheat germ	91	25	15	13	7	2	15.1
	Pistachio culls	90	11.4	53.3	NR	25.4	NR	10.1
	Peanut skins	90	14	34	22	20	6	9.9
Oil meals	Peanut hulls	90	15	45	28	2	6	8.7
	Soybean meal	90	55	10	2	3	6.7	13.9
	Canola meal	90	36	30	14.3	5.7	7.3	10.6
	Cottonseed meal	92	42	30	1.7	6.1	6.9	11.1
	Linseed meal	90	32	31.4	13.1	3.5	6.5	10.1
	Peanut meal	92	52	14	11	1.6	7.8	13.2
	Safflower meal	91	27.3	51	4.4	1.4	5.3	6.4
Animal Products	Sunflower meal	93	49	35	4.8	3.3	8	9.0
	Blood meal	90	93	0	0	2	2.4	14.6
	Feather meal	93	88	0	0	10	1.9	11.94
	Fish meal	90	68	0	0	9	19	12.5
	Meat meal	94	58	0	0	12	23	10.2
	Meat and bone meal	95	50	0	0	12	30	9.0

^aFrom [Crawshaw \(2001\)](#).^bFrom [Macgregor \(1989\)](#).

23.6% were feeding table-food waste. Table-food waste was not listed as a feed component on large swine farms (> 100 hogs/farm), despite feeding a variety of food processing by-product feeds. Small hog farms feeding table-waste is historical; hogs were often kept on family farms to utilize household food waste. This practice is still common on small hog farms throughout the world. However, the hog industry has intensified into larger units with more mechanized feeding systems, which dictates that feeds need to be dry and handled in bulk. Commercial feed sources composed of cereal grains, oil seed meals, and byproduct feeds are more easily handled in these systems and dominate feed supply. Westendorf (reported in [Dou et al., 2018](#)) observed that fewer swine farms were feeding food waste in New Jersey in 1994 than in 1964, 36 farms versus 250 swine farms, respectively. Commercial mills need to utilize feeds which can be easily handled in bulk, stored in bins and combined in mixers, which necessitates using dry feeds. In addition, feed efficiency (feed to gain) and time to slaughter are critical components of efficiency on large swine operations. Large swine operations are under pressure to utilize cost effective feeds which are consistent in nutrient

content and quality. Cereal grains and food residue by-products provide dry, consistent feed ingredients. Whereas food waste is wet and variable in nutrient content and difficult to handle.

Feeding of food waste from retailers, restaurants, institutions, and households presents challenges in collection, processing, distribution, safety, and acceptance by consumer and producer. Currently, other than in South Korea, Japan, Taiwan, and Thailand (Zu Ermgassen *et al.*, 2016), little food waste is used in animal feed. Worldwide only 4%–5% of food waste is used in animal feed due to difficulties of collection, risk of disease, and variation in nutrient content. Collection presents difficulties from residential households without central collection points. Variation in household food inputs into waste creates variation in nutrient content. High moisture content increases risk of spoilage. Meat residues in food waste are a risk for viral, bacterial, and nematode diseases for livestock consuming unprocessed waste. To reduce the risk of disease, some have recommended only utilizing fruit and vegetable waste as the sole source of animal feed, but these waste products are low in protein content which would limit inclusion rates and eliminate substantial amounts of food waste from re-feeding (San Martin *et al.*, 2016). Collection, nutrient variation, moisture content, and disease risk must be controlled to utilize food waste as a viable animal feed.

To utilize food waste efficiently as a livestock feed requires handling capabilities either at feed mills or directly on farms and methods to control disease and reduce moisture. Although swine are the most common livestock fed food waste, food waste may be fed to fish, pets, poultry and ruminants as long as appropriate inclusion rates in rations are followed. On dairy farms, waste with a high moisture content, such as brewer's grains and fruit and vegetable waste, can be handled more readily than on swine and poultry farms, as commodities can be stored in bulk in open trenches and incorporated into total mixed rations without drying using a feed mixer wagon. Since total mixed rations on dairy farms typically are about 50% dry matter, the high moisture content in food waste is not a problem as long as inclusion rates are limited to a maximal inclusion rate of about 20%. The challenge on dairy farms is to utilize food waste at a sufficient rate that spoilage of stored product is minimized. This often requires small volumes of product be delivered frequently, about once a week, and at volumes that can be fed out within a week. Therefore, sources of wet food waste need to be located in close proximity to the farm utilizing the waste.

Beef farms also can utilize wet food waste or wet by-products such as wet distiller's grains or brewer's grains. Similar issues apply, as high moisture feeds can limit feed intake if they are too high a proportion in the total ration. Wet feeds spoil rapidly if not used at a sufficiently rapid rate. Wet food waste can be ensiled to improve storage, but fermentation takes time to achieve a low enough pH to stabilize the material. Extremely wet material creates seepage during the ensiling, and needs to be collected to prevent environmental spillage.

Disease Risks Feeding Food Waste

A detriment to feeding food waste from end consumers to ruminants is contamination with ruminant meat, which is prohibited due to disease risk of Bovine Spongiform Encephalopathy. Bovine Spongiform Encephalopathy, (BSE) is a neurologic prion disease of cattle, which was spread in the United Kingdom through feeding meat, brain and spinal cord residues to cattle. Not only was this a risk to cattle, but humans consuming meat produced from cattle consuming meat meal were at risk for developing a variant of Creutzfeldt-Jakob disease (CJD), a rapidly progressive, invariably fatal neurodegenerative disorder related to BSE. Therefore, household waste, restaurant, and institution plate waste are not acceptable as ruminant livestock feed due to ruminant meat contamination.

In addition to BSE, animal products pose a significant feed safety risk due to viral and bacterial contamination for all livestock consuming food waste. Animal products may harbor food born bacteria, such as *Salmonella*, *E. Coli*, *Listeria*, and *Corynebacteria* spp. Contamination with viruses such as Foot and Mouth Disease, African Swine Fever, and Swine Vesicular Disease and parasites such as *Trichinella* pose significant risks when feeding food waste with meat products.

Due to disease risk, the European Union has banned feeding food waste to livestock. Disease outbreaks in the United Kingdom (UK) associated with food waste feeding are fresh in people's minds (Luyckx, 2018). In 2001, Foot and Mouth Disease occurred due to a swine farm illegally feeding poorly processed food waste, which led to significant livestock condemnation to eradicate the virus. Thousands of livestock were destroyed to stop the outbreak and eradicate the virus from the UK. Total costs were estimated at £8 million British pounds (Luyckx, 2018). Feeding ruminant meat meal to cattle lead to outbreaks of BSE between 1986 and 2001 in the UK, with cases of variant CJD in humans linked to consuming infected beef. Due to the long incubation period of BSE in cattle, infected cows could go to market with no obvious signs of infection. Meat from infected but normal appearing cattle became a source of variant CJD disease in humans. Thousands of cattle in Britain were slaughtered and rendered to remove the risk of eating contaminated beef by humans.

To control disease risk requires strict regulations and oversight (Dou *et al.*, 2018). The most common approach is to heat food waste to inactivate bacteria and viruses (Zu Ermgassen *et al.*, 2016). In the US, feed mills must be licensed to process food waste for animal feed and have facilities to heat food waste to 100°C for at least 30 min (US Swine Health Protection Act, 1980). Heating may be either steam injection or direct fire cooking, with continuous agitation of the waste to ensure uniform heating. There are only 2722 licensed facilities in the US. These facilities produce 266,104 tonnes (293,330 US tons) of swine feed, which is only 0.6% of all swine feed sold in the US.

South Korea and Japan have implemented control programs which cook food waste to prevent disease. Pasteurization of food waste destroys pathogens and allows safe feeding. Food wastes are treated for three minutes at 80°C, or 30 min at 70°C, enough to deactivate viruses such as foot-and-mouth. Since the introduction of these regulated systems, no disease outbreaks have been associated with swill feeding in these countries (Zu Ermgassen, 2016; Luyckx, 2018). The ban on feeding food waste in the EU may

need to be re-evaluated for future sustainability. Licensing feed facilities and regulation to ensure pasteurization of food waste can be employed to ensure food safety with waste that includes meat scraps.

Some have recommended using only plant based food waste in animal feeds to reduce disease risk. However, fruit, vegetable, and cereal products may also pose a health risk when used in animals feeds. Plant by-products may be a source of mold toxins, bacterial toxins, and other contaminants. Mold toxins may be produced prior to harvest or post-harvest if grains are not properly stored at appropriate moisture content. Typically moisture content below 20% will protect most grains from post-harvest mold growth. Pre-harvest fungal invasion of the grain may occur from insect damage, drought conditions and other stresses to the plant in the field. Mycotoxin(s) may be present in the grain at harvest from conditions in the field which encourage spore invasion and growth within the grain head. Threshold levels of mycotoxin concentration in grains make it illegal to use these grains in human foods and in animal feeds. Bacterial contamination is possible when moisture content is above 30% in grains and food waste. Bacterial growth under aerobic conditions causes spoilage and loss of nutrient content and is a significant problem in utilizing high moisture food residues. High moisture content and anaerobic conditions can lead to growth of *Clostridia botulinum* and botulism toxin contamination of food wastes.

Bacteria, bacterial and mold toxins, viruses and parasites are not the only health risk when feeding food waste and residues. Food waste may contain residues of heavy metals and pesticides. Pesticide residues may be high due to inclusion of peels and rejected fruits in waste. Heavy metals may be increased due to contamination from collection vessels. San Martin *et al.* (2016) tested for residues of metals and pesticides (and mycotoxins) and found contamination risk was low in fruit-vegetable waste and fish waste. However, Garcia *et al.* (2005) found lead and cadmium at high concentrations in restaurant and household food waste, which means surveillance of potential toxic materials needs to be in place. Monitoring of toxic content of mold toxins, pesticides, and heavy metals should be a best management practice in food waste feeding systems. In addition to prevent spoilage prior to processing, collection needs to be timely and containers cleaned between loads. This creates logistic problems when collecting household food waste. San Martin *et al.* (2016) proposed a series of technologies be in place to safely use food waste as animal feed. These include consistent feed evaluation and testing, processing to reduce moisture and prevent disease, and incorporation in diets to achieve a consistent feed product for consistent production of meat quality.

Variation in Nutrient Content in Food Waste

Moisture content may be 70%–80% in food waste, which makes them extremely unstable at ambient temperatures. The high moisture content necessitates frequent collection and safe storage conditions. San Martin *et al.* (2016) observed that fruit and vegetable waste was acceptable over several days collection when stored in bins at markets despite the high moisture content. In addition to high moisture content which can decrease stability over time, household and restaurant food waste may contain a significant concentration of fat, which may be prone to rancidity if not stored appropriately.

Although food waste has nutrient values acceptable for livestock feeding, variation in moisture content, protein, fat and minerals make it challenging to achieve comparable growth rates when included in swine diets. Wet food waste fed as the sole source of feed in swine diets limits feed intake and slows rates of gain (Westendorf and Myer, 2004). In addition, feeding food waste as the sole source can have a negative impact on meat quality due to high polyunsaturated fatty acid and salt content (Choe *et al.*, 2017). Limiting the amount of food waste included in total diets can achieve consistent meat quality and rates of gain. Márquez and Ramos (2007) found no negative effects on organoleptic quality when food waste from fruit and fish shops was included in finishing diets at 17% of total diet and nutrient content was comparable to control diets. Zu Ermgassen *et al.* (2016) in a summary of published feeding trials found no negative impacts on meat quality when diets were appropriately formulated to meet nutrient requirements.

However, Zu Ermgassen *et al.* (2016) reported that inclusion of 50% food waste in pig diets would reduce growth rates by 13%. To offset the slower growth rates, the cost of feeding food waste in swine diets would need to reduce feed costs to compensate for the longer days on feed. Food waste feed sources are 40%–60% lower in price compared with conventional feeds used in swine diets in Japan (Zu Ermgassen *et al.*, 2016). Average conventional feed price was 58.87 yen/kg compared with 25.32 yen/kg for dry food waste and 25.53 yen/kg for liquid food waste (Zu Ermgassen *et al.*, 2016). However, the cost of the total diet will depend on the amount of food waste blended into the total feed offered. It requires about 328–340 kg of feed to finish a hog over a 6 month period using conventional feeds. If including food waste increases time to finish by 13%, which will increase total feed consumed, then the lower cost of the diet including food waste would need to offset the higher feed volume and longer time to finish. At Japanese feed prices, food waste would need to be at least 23% of the feed to be economically attractive in swine finishing rations. However, total societal benefits and risks should be considered in assessing the utility of using food waste in feeds fed to animals.

The reduction in growth rates in swine fed food waste occurs for two reasons. The first is the high moisture content which can depress feed intake (Westendorf and Myer, 2004). The second is the variation in nutrient content (Garcia *et al.*, 2005; Westendorf *et al.*, 1999; Westendorf and Myer, 2004). The variation in nutrient content in food waste has been demonstrated in multiple studies (Dou *et al.*, 2018; Esteban *et al.*, 2007; Garcia *et al.*, 2005; San Martin *et al.*, 2016; Salemddeb *et al.*, 2017a; Westendorf and Myer, 2004; Westendorf *et al.*, 1999). The variation in crude protein content of food waste compared with variation in soybean meal and corn and other common by-products serves as an example of the challenge in using food waste in livestock rations. Soybean meal and corn have a coefficient of variation (CV) of protein content of 1.3% and 9.0%, respectively whereas household food waste is reported to have a CV for protein content of 24.4%, 27.4%, and 29.4%. Drying household waste does not reduce the variation in protein content. Institutional food waste (CV of CP from 20% to 57%) and restaurant waste (CV of CP from 23.3% to 37.5%) were as variable as household waste.

Even fruit and vegetable waste had a CV for protein content of 31%. Along with CP variation, concentration of other nutrients also vary, such as fat, fiber, ash and carbohydrate content. This makes it challenging to maintain a consistent nutrient content in the final diet delivered to the farm without rapid analysis of nutrient content in the collected food waste.

Variation in protein and other nutrients occurs due varying proportions of food inputs (varying fruits, vegetables, cereals, pulses, and meat), cooking practices (grilling, roasting, frying), and seasoning (salt and other spices). Food waste will vary in nutrient content due to differences in household food preferences and from restaurants and institutions as meals vary throughout the week. Furthermore, food waste from supermarkets, farm markets, restaurants, and households will vary in nutrient content due to variation in commodities in the waste. [Hebrok and Boks \(2017\)](#) reported that fruits, vegetables, bread and bakery products were the most wasted food in households, but dairy and meat sources were also common. Household food waste contains products with high carbohydrate content and low protein content (fruits, vegetables, breads and bakery products) along with variable amounts of products that are high in protein and fat content, but low in carbohydrate content (meat and milk). Mixing food waste with other feed commodities can be utilized to minimize variation in nutrient content, but this requires rapid analysis of nutrient content and storage facilities to separate and re-blend waste products to achieve consistent nutrient values. Rapid analysis of nutrient content in food waste using near infrared spectroscopy can allow for more precise incorporation of food waste into animal feed to achieve a consistent final product.

Due to high moisture content and its negative effects on feed intake in livestock, food waste is best utilized after dehydration ([San Martin et al., 2016](#)). Removing moisture aids in handling food waste. Dried food waste can be mixed with other feeds to improve the consistency of nutrient content. It is more cost effective to truck dry feed to farms than wet feeds, especially over long distances. In addition [Esteban et al. \(2007\)](#) observed that heating fruit-vegetable waste and fish waste improved digestibility as long as temperatures were $<105^{\circ}\text{C}$. If heating is excessive digestibility is reduced due to formation of carbohydrate and protein complexes. Dehydrating food waste can inflate costs to utilize food waste in livestock feeds, therefore there is a trade off in utility of handling with higher cost of processing ([Salemdeeb et al., 2017b](#)). Wet food waste is best used when collected near the farm and directly transported to the farm. Urban centers can more strategically collect food waste centrally, dry, grind and combine with other feeds to transport across greater distances to livestock facilities or feed mills.

Value in Feeding Food Waste to Livestock

Re-feeding food waste to animals is the preferred method of disposal after reduction and diversion to food banks, compared with composting and anaerobic digestion ([Salemdeeb et al., 2017b](#)). Composting and anaerobic digestion are commonly used to prevent disposal in landfills, particularly in the EU which bans livestock feeding ([Salemdeeb et al., 2017a](#)). Which method provides better overall environmental benefits was examined by [Salemdeeb et al. \(2017a,b\)](#). They performed a life cycle analysis for wet food waste feeding, dry food waste feeding, composting, and anaerobic digestion. Wet food waste feeding provided the greatest benefit to the environment, with dry feeding a close second. Benefits were realized because food waste replaced significant amounts of conventional feeds. They estimated that 20% of EU pork production could be supported by incorporating food waste into swine diets. One tonne of wet food waste could replace 109.5 kg of dry feed in swine diets. Similarly, [Zu Ermgassen \(2016\)](#) estimated that feeding food waste in the EU would reduce the land needed to support pig production by 1.8 million hectares. Feeding food waste frees up available land for food production for human consumption. Even with drying food waste, increasing local cost and associated emissions, the benefits in reducing conventional feed inputs create a global benefit in reducing the environmental foot print of livestock feeding.

To encourage use in animal feed, government subsidies and regulated programs may be needed to induce food waste feeding. [Priefer et al. \(2016\)](#), although not directly describing animal feeding, discusses incentives and regulations governments may need to employ to encourage diversion of food waste from MSW to animal feed, or other more sustainable uses. South Korea has implemented a policy of consumer separation of house hold waste into three categories: food waste, recyclable waste, and other waste, which has significantly reduced organic MSW. Consumers pay for food waste disposal and are fined if they are in noncompliance ([Priefer et al., 2016](#)). Policies in Japan and South Korea have resulted in significant amounts of food waste going to animal feed. In Japan 52.5% of food waste from manufacturing, retail, and catering industries is used in animal feed ("Ecofeed"; [Dou et al., 2018](#); [Zu Ermgassen et al., 2016](#)). Ecofeed comprises 5.8% of all concentrate fed (2014 data) on pig, poultry and ruminant farms in Japan ([Zu Ermgassen et al., 2016](#)). No household food waste is included in Japan re-feeding, but South Korea incorporates household waste in animal feed. Due to concerted government effort, 42.5% of all food waste is recycled as animal feed ([Dou et al., 2018](#); [Zu Ermgassen et al., 2016](#)). Government regulation, tight oversight, and continuous monitoring in Japan and South Korea demonstrate food waste can successfully be utilized in livestock diets.

The Food Waste Reduction Alliance (FWRA) in the US was formed in 2011 under the auspices of the Grocery Manufacturers Association (GMA), the Food Marketing Institute (FMI), and the National Restaurant Association (NRA) (see "Relevant Websites section") The alliance includes more than 30 manufacturing, retailing and foodservice companies and expert partners from the anti-hunger community and waste management sectors (see "Relevant Websites section"). The FWRA commissioned BSR to conduct and analyze a survey they designed to assess food waste among food manufacturers, retailers, and wholesalers ([BSR, 2013, 2014](#)). Two surveys were completed, Tier I and Tier II.

In the FWRA surveys food waste from the manufacturing sector was 20.09 million tonnes (44.3 billion US lb.); only 1.09 million tonnes (2.4 billion US lb.) was disposed in MSW. The majority of food waste was diverted to animal feed, 13.88 million tonnes (30.6 billion US lb.). Next greatest diversion from land-fills was land application at 3.81 million tonnes (8.4 billion US lb.).

Only 0.32 million tonnes (0.7 billion lb.) of manufacturing food waste was donated for food consumption. A survey of the retail sector estimated food waste was 1.72 million tonnes (3.8 billion US lb.) of which 0.77 million tonnes (1.7 billion US lb.) was deposited as MSW. Only 0.24 million tonnes (0.53 billion US lb.) was recovered as animal feed from the retail/wholesale sector, but 0.72 million tonnes (1.59 billion US lb.) was used for food donation and composting from this sector (Tier 1 and Tier II BSR survey, 2013). Restaurant respondents donated or recycled 15.7% of food waste, largely recycled cooking oil (BSR, 2014). However, 84.3% of restaurant waste went to landfills with an annual food waste of about 14,969 tonnes (33 million US lb.) (BSR, 2014). The consumer sector, households, grocery stores, restaurants, and cafeterias contribute the major amount of food waste to MSW in the US (and in Europe, (WRAP)). This is the major sector to focus on to reduce landfill disposal of food waste.

Conclusion

Food waste can be used as a significant source of animal feed and can be a reasonable energy or fiber source and replace cereal grains to a variable extent in animal diets. Food processing waste is easier to incorporate into animal feed due to concentrated points of collection and processing to remove water. Restaurant and retail food waste are more difficult to include in animal feed due to dispersed points of collection, and higher animal food content, which requires special processing to be used in animal feeds. High moisture content increases transportation and handling costs. Aerobic spoilage is a higher risk with high moisture content. High moisture content can limit feed intake. Variable content of sources of waste products incorporated into food waste can cause significant variation in nutrient content which limits extent of inclusion in animal diets. However, inclusion of food waste in livestock diets could displace food consumable by humans that is currently fed to livestock, primarily cereals. This would have benefits environmentally, socially, and economically in total human food supply.

See also: Conversion of Renewable and Food Wastes into Useful Products With Environmental Perspectives. Food Waste for Sustainable Packaging Materials. Upcycling Fresh Food Items in Retail Operations

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FWRA – Food Waste Reduction Alliance – Reduce Waste – Reuse.
- <http://www.fao.org/faostat>
Faostat.fao.org.

Impact of Environmental Initiatives on Environmental Performances: Evidence From the UK Manufacturing Sector

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Introduction

Being sustainable is one of the key objectives of business today. Pressure from various stakeholders such as customers, suppliers, employees, institutional investors, or policy makers has been made to adopt sustainability initiatives a priority for business. However, often firms are skeptical on how to approach sustainability, what could be the best combination of initiatives that each firm should adopt based on their own circumstances, or how this could affect their environmental footprints. The findings of previous research to such questions are often ambiguous and contradictory. For example, one stream of research suggests that environmental initiatives have positive influence on firm performance both financially and environmentally. Such studies suggest a “win-win” argument and show that the benefits of any such initiative is larger than its cost (e.g., [Porter and van der Linde, 1995](#); [Montabon et al., 2007](#)). On the other hand, another stream of studies shows that any environmental initiatives can lead to uncertainties in the operations of an organization, generate unforeseen costs, and not all firms are capable of adopting a proactive green strategy as any such initiatives is contingent on certain firm characteristics such as its environmental commitment or resource capabilities (e.g., [Aragon-Correa et al., 2003](#); [Berrone and Gomez-Mejia, 2009](#)). Therefore, managers are often unsure about how to approach and adopt environmental initiatives within their organization, should they adopt a leadership role or a “wait and watch” strategy towards their environmental responsibilities, and how any such initiative leads to enhanced environmental performance.

The UK, being an advanced and developed nation, must take responsibility towards leading the environmental initiatives among the other industrialized nations. However, the data tell a different story. A recent study shows that the UK is the 8th largest emitter of greenhouse gas, and that each person in the UK population consumes energy twice the global average ([London Climate Change Migration, 2018](#)). There are several reasons why the UK is not able to fulfill its leadership role to tackle environmental challenges. Extant research shows that the UK manufacturing industry responds to environmental demands in an economically driven, reactive fashion with concern for bottom-line rather than any strategic objectives to achieve competitive advantage. For example, early studies in environmental research in the UK context shows short-term dividends drive environmental strategies for UK firms and many such firms adopt environmental initiatives to comply with the regulations and avoid penalty ([Ghobadian et al., 1995](#); [Strachan et al., 1997](#)). Even recent research shows that UK manufacturers adopt short-term pollution control views with a focus on cost saving rather than a long-term environmental strategy ([Dahlmann et al., 2008](#); [Nath and Ramanathan, 2016](#)). However, as environmental regulations have a significant impact on manufacturers, UK firms need to have strategic thinking on how to respond to such regulations. Thus, it becomes imperative to investigate how the UK manufacturing industry at present views and adopts environmental initiatives; and how long-term environmental performances play a dominant role in their business strategies. In this study, we address these issues in two stages: (1) identify and measure the relationship between various environmental initiatives and performances, and (2) explore how UK manufacturers can develop their long-term sustainability strategies based on such association.

The structure of the paper is as follows. The next section discusses the background theory and constructs of the conceptual framework. We then discuss the methodological framework. The last section discusses the results and implications of this study.

Conceptual Framework

Environmental Initiatives

An organization's environmental initiatives are characterized by its motivation, sensitivity, and response towards changes in the environment ([Dahlmann et al., 2008](#)). An organization adopts such initiatives to respond to three interrelated pressures. First is the economic pressure, such as the potential cost savings that might arise from tackling resource inefficiency. Second is the stakeholder pressure, which includes everything from regulations through to shareholder resolutions and customer demand. Third, is the strategic pressure, which involves the desire for the firm to position it as being environmentally conscious.

Environmental management literature broadly classifies environmental initiatives as strategic and tactical ([Montabon et al., 2007](#); [Nath and Ramanathan, 2016](#)). Strategic environmental initiatives involve coordinated planning, and implementation of controls established by top managers. It involves practices such as long-term environmental plans, and integration of environmental policies with business objectives. Tactical environmental initiatives, on the other hand, involve internally focused environmental management exercise that pertains to shop floor practices. It involves initiatives related to structural changes in operational systems such as change in plant capacity, production equipment, and production technology to contain waste in production process.

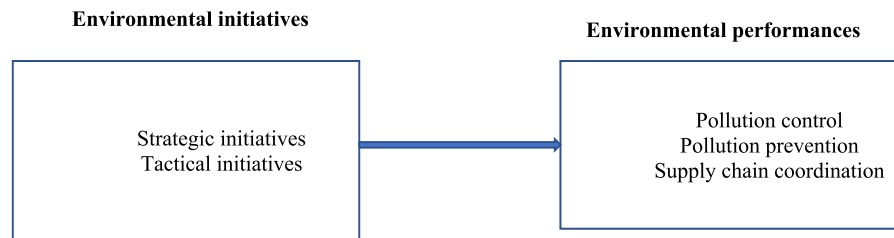


Fig. 1 Conceptual framework for investigation of relationship between environmental initiatives and environmental performances.

Environmental Performance

Environmental management literature broadly classifies environmental performance into three categories: Pollution control, pollution prevention, and supply chain coordination (Berrone and Gomez-Mejia, 2009; Montabon *et al.*, 2007; Nath and Ramanathan, 2016). Pollution control refers to end-of-pipe technology that captures, treats, and disposes of waste at the end of production process. Pollution control is a short-term compliance strategy that relies on pollution abatement. Such hazard control technology is often an environmental objective for firms that do not have resources to implement new environmental technologies. Pollution prevention, on the other hand, aims to minimize pollution at various stages of the production process and requires structural investments in product and process redesign (Klassen and Whybark, 1999). Pollution prevention is often the environmental objective for firms with superior resource base as it offers a unique competitive advantage. Supply chain coordination involves how a manufacturer works with its suppliers and contractors together to achieve a common environmental goal.

Environmental Initiatives and Environmental Performance

Exploring the role of environmental initiatives on environmental performance is not straightforward. For instance, Darnall *et al.* (2005) draw on the resource-based view of the firm and suggest that the adoption of environmental management systems might be with the genuine intention of improving environmental performance (and thus business performance). Alternatively, they reason, espoused environmental concern may be little more than a symbolic gesture to appease various pressure groups (for instance, stakeholders such as employees, shareholders, and so on). Such practice might also be undertaken with a view to preempting future environmental regulation or might be part of a strategic need to be “seen to be green,” thus wooing environmentally conscious consumers. The phenomenon of “green washing” where a firm makes unsubstantiated environmental claims is widely practiced in industry.

Environmental studies in the UK context also report such conclusions. For example, Dahlmann *et al.* (2008) find that the motivation for environmental concern amongst firms in the UK is chiefly economic, rather than regulatory or strategic or as a response to various stakeholder pressures (this finding is in line with that of earlier UK surveys such as Ghobadian *et al.*, 1995; Strachan *et al.*, 1997). In such cases, it seems that there is little reason to suppose that the mere fact of environmental rhetoric from top management in a company will be a guarantor of genuine improvements in environmental performance. Nath and Ramanathan (2016) in their study observe that UK manufacturers focus on tactical initiatives to achieve short-term pollution control objectives. However, when there is significant pressure from external market stakeholders such as customers and suppliers, such firms go beyond the “compliance” goals and adopt strategic environmental initiatives to achieve long-term pollution prevention objectives.

Thus, the motivation for this study is to establish whether the adoption of environmental management strategies and supposed environmental concern do in fact lead to improved environmental performances. Fig. 1 illustrates the conceptual framework for the study.

Methodology

Data Collection

Sustainability researchers have used a variety of approaches to collect data for their studies. For instance, a large number of studies use objective databases such as Toxic Release Inventory (TRI, 1988) or use subjective approaches like managerial surveys or case studies. However, such approaches have their own drawbacks. For example, objective databases on environmental initiatives and performance are not available widely in the public domain in many countries. Often such databases are incomplete or not authentic due to the lack of stringent policy controls. Self-reported surveys or case studies also suffer from drawbacks as respondents can either underreport an undesirable environmental behavior or even overreport certain environmental initiatives to maintain social desirability bias. To overcome such issues, we adopted a novel method of content analysis of the annual and environmental reports that are available publicly and are duly audited from the corporate websites. Content analysis is a systematic tool to analyze a piece of text to investigate if certain words or concepts are within the text (Nath and Ramanathan, 2016).

Table 1 Firms used in this study

<i>SIC Code 28 (11 companies) Fabricated metal products except machinery and equipment</i>	<i>SIC Code 29 (10 companies) Machinery and Equipment not elsewhere classified</i>	<i>SIC Code 30 (11 companies) Office machinery and computers</i>	<i>SIC Code 31 (9 companies) Electrical Machinery and Apparatus</i>
Foster Wheeler Hill and Smith Severfield-Rowe Mabey Holding William Hare Group Ideal Boilers Tomkins Wolseley Plc C-Rh Engineering Serco Group Plc Rexam Plc	Rolls Royce Perkins Spirax Sarco TI Automotive Weir Valves & Co Linde Material Invensys Plc Smith's Group Plc Hanson Limited Agco International	Xerox Ricoh Hewlett Packard IBM National Semiconductor Fujitsu Jabil Circuits Kenn Truss Astec International Altera European RM Plc	Chloride Siemens (UK) Alstom Ltd Converteam Schneider ABB Limited Ultra Electronics Halma Public Ltd Prysmian Cables
<i>SIC Code 32 (9 companies) Radio, Television and Communication equipment and apparatus</i>	<i>SIC Code 33 (8 companies) Medical Precision and Communication equipment and apparatus</i>	<i>SIC Code 34 (10 companies) Motor vehicles, Trailers and Semi-trailers</i>	<i>SIC Code 35 (7 companies) Other Transport Equipment</i>
TT Electronics E2V Technologies Thales group UK AVX Online CSR Plc Wolfson Micro Cambridge Silicone Orange Retail Raytheon System	Consort Medical Huntleigh Health Key med Ltd Gyrus Group Meggitt Plc Spectris Plc SSL International Phoenix Healthcare	Vauxhall Motors Peugeot Ford Bentley Nissan Honda Toyota Iveco Limited Leyland Trucks Senior Plc	BAE Systems VT Group Cobham Plc Smith's Group Plc Marshall Aerospace Melrose Plc Airbus UK

The study hired three trained researchers who collected the electronic reports from corporate websites, searched for a list of keywords or key phrases, read around the area where such keywords/phrases are mentioned, and subjectively evaluated the involvement of the firms based on their environmental initiatives and performances. We developed the list of keywords/phrases based on an extensive literature review (based on Klassen and Whybark, 1999; Montabon *et al.*, 2007; Nath and Ramanathan, 2016). Each item was measured using a 5-point Likert scale (1 = strongly disagree, 5 = strongly agree) and used a time lag of one year between the reports that were used to evaluate the environmental initiatives and to measure performances. This is necessary as the effects of any environmental initiatives on performances are not instant. Based on the data availability, the final sample consisted of 76 top UK manufacturing firms (based on their revenue figures) from 8 different sectors (SIC 28–35). Table 1 shows a brief summary of the companies studied.

Analysis Methodology

The analysis involved two stages. In the first stage, we used exploratory factor analysis to identify appropriate constructs and organize the content analysis data. In the second stage, we used canonical correlation analysis (CCA) to identify the relationships between the latent constructs. CCA measures the interrelationship between a linear combination of independent variables (called the independent variate) and a linear combination of dependent variables (called the dependent variate). CCA chooses the weights for the linear combinations to maximize the correlation between the independent and dependent variates. Since the objective of this study is to understand the relationship between multiple independent environmental initiatives variables (strategic and tactical) and multiple dependent environmental performances variables (pollution control, pollution prevention, and supply chain coordination), CCA is the appropriate tool (see Hair *et al.*, 1998 for an excellent primer on CCA).

Results

Stage 1: Factor Analysis

Principal component analysis with varimax orthogonal rotation on the list of 34 environmental measures shows that the items are loaded on five factors explaining 76.35% of the variance (see Table 2 for the list of items under each construct and the items that are deleted due to poor or multiple loading on more than one construct). The five-factor structure corroborates the conceptual framework of this study.

Table 2 Principal component analysis of the scale items

Item (based on Klassen and Whybark (1999), Montabon et al. (2007) and Nath and Ramanathan (2016))	Mean (SD)	Strategic initiatives (Cronbach's alpha $\alpha = 0.92$)	Tactical initiatives ($\alpha = 0.89$)	Pollution control ($\alpha = 0.84$)	Pollution prevention ($\alpha = 0.96$)	Supply chain coordination ($\alpha = 0.87$)
Reward for environmental project	2.42 (1.75)	0.691				
Integration with long-term business strategy	2.36 (1.78)	0.717				
Explicit definition of environmental policies	2.55 (1.86)	0.754				
Environmental mission statement	2.39 (1.78)	0.717				
Strategic alliances for environmental projects	2.13 (1.61)	0.704				
Employee environmental training ^a	2.26 (1.72)	–				
Market surveillance for environmental issues ^a	3.0 (1.26)	–				
Cross-functional cooperation for environmental improvements ^a	2.65 (1.85)	–				
Money spent on environmental initiatives ^a	2.47 (1.82)	–				
Environmental audits	3.05 (1.93)		0.593			
Environmental participation such as ISO 14001, EMAS	3.0 (1.78)		0.566			
Environmental risk analysis	2.44 (1.80)		0.650			
Environmental management system	3.18 (1.82)		0.648			
Dedicated environmental department	2.96 (1.80)		0.521			
Continuous improvement in environmental standards	2.97 (1.80)		0.657			
Eco-efficient design ^a	2.71 (1.83)		–			
Environmental design targets ^a	2.36 (1.79)		–			
Remanufacturing a product where some parts are recovered or replaced	1.80 (1.47)			0.818		
Substitution: Replace a material with another environment friendly material	2.13 (1.67)			0.604		
Consume waste	2.13 (1.70)			0.700		
Creating market for waste product ^a	2.13 (1.70)			–		
Environmental certifications ^a	2.28 (1.71)			–		
Recyclable packaging	3.89 (1.61)				0.930	
Waste reduction (proactive)	4.0 (1.51)				0.921	
Waste reduction (reactive)	4.0 (1.51)				0.921	
Energy conservation	3.86 (1.61)				0.859	
Product development and innovation	2.68 (1.87)				–	
Resource consumption ^a	3.15 (1.92)				–	
Recycling performance ^a	3.21 (1.80)				–	
Supply chain management	3.26 (1.79)					0.790
Early supplier involvement	2.82 (1.85)					0.754
Environmental standard for supplier	2.55 (1.81)					0.683
Environmental audit for supplier ^a	2.32 (1.69)					–
Spreading risk to third party ^a	3.0 (1.46)					–

^aItem dropped because of low loadings or loading on two constructs.

Note: Total explained variation 76.35% with varimax orthogonal rotation.

Factor 1 involves long-term strategic initiatives to tackle environmental issues. It explains how a UK manufacturer has a planned approach to control environmental factors embedded in its business strategies.

Factor 2 involves the short-term tactical initiatives adopted by companies to develop, assess, and implement an environmental management system across the organization to tackle issues related to the natural environment.

Factor 3 reflects the pollution control aspect in environmental performance. A manufacturer uses such operational capabilities to reduce resource consumption, replace hazardous materials in the manufacturing process with greener substitutes, and recycle waste.

Factor 4 represents pollution prevention strategies for organizations. This involves practices leading to waste reduction through both proactive measures like pollution prevention, elimination of waste before production, and reactive measures like having specialized waste treatment facilities.

Factor 5 reflects supply chain coordination, which involves conformance by suppliers and contractors to environmental standards as specified by the manufacturer. This involves setting up environmental standards for suppliers and taking decisions on raw material sourcing using environmental criteria.

Table 3 Canonical correlations and loadings (estimation sample)

	<i>First canonical function</i>	<i>Second canonical function</i>
Canonical correlations	0.87	0.34
Bartlett test of residual correlations (Chi-square, df, <i>p</i> -value)	55.92, 6, 0.00	4.67, 2, 0.09
Canonical loading of independent variables		
Strategic environmental initiatives	0.93	−0.38
Tactical environmental initiatives	0.96	0.28
Redundancy indices	0.67	0.01
Canonical loading of dependent variables		
Pollution control	0.94	−0.16
Pollution prevention	0.60	0.75
Supply chain coordination	0.84	0.03
Redundancy indices	0.49	0.02

Note: Stewart–Love redundancy index for overall analysis is 0.51.

Stage 2: Canonical Correlation Analysis

Hair *et al.* (1998) suggests use of split-sample technique to test the validity of CCA results. Thus, in this study, we divided the sample size of 76 randomly into estimation sample (with size 41) and validation sample (with size 35). The results from both the samples are similar, therefore we report the results based on the combined sample.

Table 3 describes the results of the CCA. Magnitudes of canonical correlation coefficients as well as the redundancy indices for each pair of the linear composites of the variables measure the strength of association between each set of independent and dependent variables. Canonical correlation indicates the strength of relationship between the linear composites of independent and dependent variables, while redundancy index gives the variance in canonical variates (Hair *et al.*, 1998). For both the canonical functions, the canonical correlation coefficients are 0.87 and 0.34. The first canonical function is significant at 0.05 levels using Bartlett's chi-square test. However, the second function is insignificant. Therefore, we ignore the second function for predictive purposes and for drawing managerial implications from the results. For the first canonical function, the redundancy index for the independent variables is 0.67, which indicates that independent variables explain 67% of the variation in the three dependent variables. Similarly, environmental performance items explain 49% of the variance in the environmental initiative constructs. Thus, the choices of independent–dependent variables are significantly interrelated. The Stewart–Love canonical redundancy index for the overall analysis is 0.51, which is analogous to *R* squared statistic in multiple regressions (Hair *et al.*, 1998).

Canonical loadings measure the simple correlation between the variables and their respective canonical variates. As suggested by Hair *et al.* (1998), we interpret these canonical loadings to indicate the strength of relationships between the sets of dependent variables and independent variables in this study. For the first canonical function, in the independent variate, both variables have loading of more than 0.9. This suggests that both the organizational strategic and tactical initiatives highly represent the organization's environmental efforts. For the dependent variables (environmental performances), the canonical loadings for pollution control and supply chain coordination are very high. This indicates that environmental initiatives greatly influence these two outcome variables. The canonical loading for pollution prevention is 0.6, which exceeds the 0.30 level as suggested by Lambert and Durand (1975) as the minimum acceptable loading value. However, this indicates that pollution prevention (the strategic outcome) does not play a significant role (in comparison to the other performance constructs) on firm environmental policy. The positive loadings for all the five constructs signify a strong positive impact of the environmental initiatives on environmental performances.

Discussions, Contributions, and Conclusion

Our study has thus provided an interesting view of the relationship between environmental initiatives and environmental performance. While it agrees with previous similar studies in that there is statistically strong association between the two, our study provides more interesting insights to extend the results of these previous studies. We do this by distinguishing three distinct measures of environmental performance: Pollution control, pollution prevention, and supply chain coordination. Of the three, pollution prevention seems to be less well associated with environmental initiatives compared with the other two (pollution control and supply chain coordination). It has to be noted that the literature has highlighted the distinction between pollution control and pollution prevention. While the former involves short-term view in managing environmental performance, the latter involves a longer-term view (Klassen and Whybark, 1999; Nath and Ramanathan, 2016). Thus, our study shows that there is less support in UK manufacturing firms in taking longer-term view on environmental performance, and that these firms tend to take shorter term view when it comes to improving environmental performance using various environmental initiatives.

Contribution

This study contributes both to environmental management literature and to understand the environmental approaches adopted by the UK-based manufacturing firms. Earlier studies in environmental management literature (e.g., Montabon *et al.*, 2007; Berrone and Gomez-Mejia, 2009) often provide a contradicting and inconclusive association between environmental initiatives adopted by firms and their environmental performances. Based on a content analysis approach and in a multisector manufacturing setting, this study empirically demonstrates that environmental initiatives (strategic and tactical) have positive but varying levels of influence on the three environmental performance constructs (pollution prevention, pollution control, and supply chain coordination). This study thus empirically verifies the ambiguity (positive as well as negative) in relationships between environmental initiatives and performance stated in extant research and supports the “win-win” hypothesis (Porter and van der Linde, 1995).

The study also finds that UK manufacturing firms adopt environmental initiatives both to attain economic (short-term) or strategic (long-term) goals but the focus has been more on the short-term, compliance based, and reactive objectives rather than the long-term, proactive strategic ones. Thus, the study provides evidence to UK policy makers to design better legislation or added incentives to ensure UK firms adopt pollution prevention rather than pollution control environmental strategies.

Implications

The findings of this study conclude that the commitment of top management in the UK manufacturing firms in devising appropriate environmental initiatives trickles down to generate expected results in terms of environmental performances. All the canonical loadings are high; loadings for the two independent variables exceed 0.9 while loadings for dependent variables are also high except for pollution prevention. The loading is moderate (0.60) for pollution prevention indicating that top management’s environmental commitment may not have resulted in a long-term realization of waste control targets. This finding is not surprising as UK manufacturers are more concerned about rise in energy prices, landfill taxes; cost of dealing with hazardous wastes, thus a current immediacy of benefits is of primary concern to them. This is consistent with the findings of previous studies (like Dahlmann *et al.*, 2008; Ghobadian *et al.*, 1995) which characterize British firms as adopting short-term, risk avoidance attitudes towards environmental initiatives with cost reduction as primary motive. The most important managerial implication of our results is that it provides evidence in the UK context that operational level environmental targets can be realized with adequate strategic support and environmental management plans from the top management. However, the motivation to achieve the environmental targets is still economics driven. Given the growing importance of conformity to environmental regulations, and the changing landscape to incentives to comply with environment (like carbon trading programs), UK policy makers need to offer the right package of incentives to manufacturing firms to make them more environmentally proactive.

See also: Advanced Vehicle Systems and Technologies: Economic and Environmental Implications. Environmental Analysis Waste Management Model. Environmental Assessment of Green Buildings. Is the Production of Biofuels Environmentally Sustainable?. Modeling of Information System for Air Waste Management. Modeling of Information System for Liquid Waste Management. Modeling of Information System for Nuclear Waste Management. Modeling of Information System for Solid Waste Management. Plant-Microbe Interaction: An Ecofriendly Approach for the Remediation of Metal Contaminated Environments

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Life-Cycle Impact of Concrete With Recycled Materials

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Introduction

The circular economy is the evolution of the linear business model in which products are manufactured from raw materials, then abandoned in landfills at the end of their useful life (Tecco *et al.*, 2016). In the circular business idea, product design is developed with the aim to repair, reuse or recycle the products at the end of their life cycle (World Economic Forum Mining & Metals Industry Partnership in collaboration with Accenture, 2014). The model is based on the idea of minimizing waste and their amount. In recent years, the construction sector has been the focus of the scientific community in terms of circular economy and emission reduction: construction and demolition waste (C&DW) accounts for 34.7% of total waste production in Europe as reported by Eurostat (see “Relevant Website section”). Thus, the interest of the policy makers and the scientific community to reduce the impact deriving from this waste stream is evident. In this regard, the European directive 2008/98/EC indicates that 70% of waste must be recycled by 2020. Currently, the best way to recycle construction and demolition waste is the production of recycled aggregates, to be mixed to concrete in order to build new structures (Colangelo *et al.*, 2015, 2017). Construction and demolition waste also represent a problem from the social point of view. It is clear if we think about the quantity of rubble as a result of disasters such as earthquakes, the impact of a quarry near urban areas or the volume occupied in landfills by inert materials, which forces to increase the storage space available in landfill, often going to affect the well-being of the community. In literature, there is a debate on the actual advantage of using recycled aggregates (Colangelo *et al.*, 2016; Colangelo and Cioffi, 2017). It arises from the need to use a greater quantity of cement, compared to a mixture containing only sand and gravel (natural aggregates), in order to ensure the same performance in terms of mechanical properties. The problem linked to cement is the fact that its production involves the emission of large quantities of CO₂. Mixtures with recycled aggregates have generally a lower density that allows to use a lower quantity of steel in the load-bearing structure of a building to guarantee the properties required by the legislation (World Steel Association, 2015). Regarding CO₂ emissions due to the production of cement, there is a debate in literature about a possible replacement of the traditional binder with a geopolymer, in order to reduce the global warming (Petrillo *et al.*, 2016; Turk *et al.*, 2015; Coppola *et al.*, 2018). It is clear that in achieving a circular economy model within the building sector, an approach that looks after the problem in its entirety is fundamental, analyzing all the possible advantages and disadvantages. This is fundamental in order to avoid that the achievement of the “zero waste” scenario requires a high price to pay: on one hand eliminating the production of natural aggregates, on the other hand increasing the production of cement. The most appropriate methodology to analyze the goodness of the recycling process for construction and demolition waste is the LCA. Using this approach, that takes into account all the phases of a building’s life cycle, it is possible to highlight the critical phases on which it is necessary to intervene to reduce environmental impacts.

In this study, the impacts related to the production of recycled aggregates for structural purposes is analyzed, considering different quantities of steel and cement depending on the use of recycled or natural aggregates within the mixture. In addition, the study investigates the sustainability of the mixture made with geopolymer binder in substitution of cement.

The aim of the present work is to contribute to the current indications given by the 2008/98/EC regulation on the recycling process of aggregates, as well as indicating possible ways to be followed in the near future. Unlike the papers found in literature, the impacts deriving from the production of the steel necessary for concrete reinforcement have also been taken into account. Furthermore, interesting considerations can be drawn about examined geopolymer mixtures.

The rest of the article is organized as follows: in Section “Overview on Life Cycle Approach of C&DW” materials and methods are described; Section “Materials and Methods” summarizes the main results of the environmental analysis; Section “Mixtures” discusses the mixtures prepared while the Section “Results” deals with the outcomes of the study. Finally, in Section “Conclusion” the main contribution of the work and future developments are analyzed.

Overview on Life Cycle Approach of C&DW

Since the 90s, many studies, have used the life cycle approach to analyze the impacts related to the production and use of concrete, as well as the reuse of demolition materials. These showed how the evolution of the C&DW study, using the LCA methodology, went hand in hand with the evolution of the reference legislation. Among these works, ten were taken as a reference for developing this study. The aforementioned studies are summarized in Table 1 that shows the object of the study, which ranges from the production of recycled aggregates to the production of the concrete mixture, the methods for defining the boundaries of the system and the functional unit adopted by the authors, in order to approve the best practices in the sector studies.

Table 1 State of art

Authors	Object of the study	Functional unit	Stages of LCA/system boundaries	Materials compared	D.B. and Methods
Blengini and Garbarino, 2010	LCA of C&DW recycling chain in the administrative territory of Provincia di Torino in Northern Italy	1 tonne of collected and recycled C&DW	● Unloading, moving and uploading CDW in transfer stations; ● CDW recycling, including the treatment of the extraneous fractions separated from the inert mineral fraction (i.e., recycling of ferrous metals and landfilling of unrecoverable residues); ● CDW disposal; ● natural aggregates (NAs) avoided production; ● primary steel avoided production; ● transportation of CDW to plants, ● transportations of RAs from recycling plants to concrete plant ● transportation of NAs from quarries to concrete plant	Fixed and mobile recycling plant; 3 types of recycled aggregates quality	● Literature and database of provincia di Torino, Interview with operators, distances retrieved from a GIS model; ● Impact 2002+, Ecoindicator 99
Borghi <i>et al.</i> (2018)	LCA of C&DW recycling chain in Lombardy, Italy	1 tonne of non-hazardous CDW mixture managed in 2014	● Unloading, moving and uploading CDW in transfer stations; ● CDW recycling, including the treatment of the extraneous fractions separated from the inert mineral fraction (i.e., recycling of ferrous metals and landfilling of unrecoverable residues); ● CDW disposal; ● natural aggregates (NAs) avoided production; ● primary steel avoided production; ● transportation of CDW to plants, ● transportations of RAs from recycling plants to final users ● transportation of NAs from quarries to final users	Fixed and mobile recycling plant; 3 types of recycled aggregates quality	● Primary data for recycling plants (visited) ● Literature and ecoinvent for recycling of steel and landfilling of inert
Estanqueiro <i>et al.</i> (2018)	Comparative LCA of natural aggregates and recycled aggregates from fixed and mobile plant	1 tonne of coarse aggregates ready to be used in concrete production, including the transportation to site of the corresponding quantity of ready-mixed concrete	● Raw material extraction and transport to concrete plant ● RA production and transport to concrete plant ● Concrete transport to construction site	3 scenarios: For fixed and mobile plant and for traditional	● Site-specific primary data ● Ecoindicator 99, CML Baseline and cumulative energy demand
Vossberg <i>et al.</i> (2014)	Comparative LCA of natural aggregates and recycled aggregates from fixed and mobile plant	1 tonne of collected and recycled aggregates	● CDW recycling, ● CDW disposal; ● transportation of CDW to plants, ● transportations of RAs from recycling plants to final users ● transportation of NAs from quarries to final users	3 scenario: Landfilling + natural aggregates Recycling with fixed plant Recycling with mobile plant	● Interviews, ecoinvent database ● IPCC 2007

(Continued)

Table 1 Continued

<i>Authors</i>	<i>Object of the study</i>	<i>Functional unit</i>	<i>Stages of LCA/system boundaries</i>	<i>Materials compared</i>	<i>D.B. and Methods</i>
Marinkovic <i>et al.</i> (2010)	Comparative LCA of natural aggregates and recycled aggregates concretes	1 m ³ of concrete	● Raw material extraction and transport to concrete plant ● Cement production and transport to concrete plant ● RA production and transport to concrete plant ● Concrete production ● Concrete transport to construction site ● Demolition	3 Natural aggregates concrete mixtures 3 Recycled aggregates concrete mixtures River sand as fine aggregates in all 6 mixtures	● Primary data from their previous work, database ● CML
Tošić <i>et al.</i> (2015)	LCA and VIKOR analysis in order to choose the best recycled aggregates percentage and transport scenario in Serbia	1 m ³ of concrete	● Raw material extraction and transport to concrete plant ● Cement production and transport to concrete plant ● Admixtures ● RA production and transport to concrete plant ● Concrete production	4 concrete mixtures (40 MPa) 2 recycled 2 traditional (one with river fine aggregate, one with crushed fine aggregate)	● Primary data and database ● CML
Colangelo <i>et al.</i> (2018)	LCA of concrete production using recycled materials	1 m ³ of concrete (30 MPa)	● Raw material extraction and transport to concrete plant ● Cement production and transport to concrete plant ● Admixtures ● RA production and transport to concrete plant ● Concrete production ● Concrete transport to final users	Concrete with recycled aggregates (from C&DW) Concrete with marble sludge Concrete with cement kiln dust	● Literature, Sima pro database, LCI from Italian Technical Economic Association of Concrete (ATECAP), literature review ● Eco-indicator 99 ● Companies and literature ● CML and Cumulative Energy Demand
Braga <i>et al.</i> (2017)	Comparative LCA of natural aggregates and recycled aggregates concretes	1 m ³ of concrete	● Raw material extraction and transport to concrete plant ● Cement production and transport to concrete plant ● Admixtures ● RA production and transport to concrete plant ● Concrete production	216 concrete mixes from 24 references	● Ecoindicator 99 and Ecological Scarcity 2006; also GWP and ADP
Knoeri <i>et al.</i> (2013)	Comparative LCA of natural aggregates and recycled aggregates concretes	1 m ³ of concrete	● Demolition; ● Cement production ● Additive production ● CDW recycling, including the treatment of the extraneous fractions separated from the inert mineral fraction (i.e., recycling of ferrous metals and landfilling of unrecoverable residues); ● CDW disposal; ● primary steel avoided production; ● transportation of CDW to plants, ● transportations of RAs from recycling plants to concrete plant ● transportation of NAs from quarries to concrete plant	12 recycled concrete (RC) mixtures with two different cement types and compared it with corresponding conventional concretes (CC) for three structural applications	● Ecoinvent, literature (distances) ● Ecoindicator 99 and Ecological Scarcity 2006; also GWP and ADP
Marinkovic <i>et al.</i> (2008)	LCA of NAC in Serbia	1 m ³ of concrete	● Raw material extraction and transport to concrete plant ● Cement production and transport to concrete plant ● Concrete production ● Concrete transport to construction site ● Demolition	Traditional concrete with river aggregate SAS fine aggregate	● Primary data, databases

In this work impact linked to the construction of the reinforced concrete structure of a building, with different types of concrete is analyzed: with recycled aggregates and natural aggregates. To make the analysis complete, impact of the construction of the aforementioned building with geopolymer concrete mixtures is assessed.

Materials and Methods

Goal and Scope

In this work a *from cradle to grave* approach has been used, i.e., the life cycle of the concrete mixture is taken into consideration starting from the extraction of raw materials up to the demolition, considering that our case study is about a building. Eight concrete mixtures were prepared with recycled and natural aggregates (with an amount of recycled aggregates ranging from 0% to 100%) and using both a traditional and a geopolymer binder. The SimaPro software was used according to ISO 14040-44 standards.

Functional Unit

In literature, we face with different types of functional units that are chosen with respect to the specific study. From [Table 1](#), it is clear how to move from one unit to another depending on the focus of the study. In the papers by Borghi and Blengini ([Blengini and Garbarino, 2010](#)) focused on the processes to which C&DW is subjected, one tonne of C&DW is certainly suitable for highlighting the criticality of the issue. Studies whose purpose to focus on the impact deriving from the production of aggregates, identify the functional unit as the tonne of aggregate produced. Again, as can be seen from [Table 1](#), it is possible to find LCA analyzes that take into account the use of aggregates in the production of concrete. They tend to take as a functional unit a cubic meter of concrete, often defining a particular class of mechanical resistance.

In this work the functional unit is represented by a cubic meter of reinforced concrete with mechanical resistance of 30 MPa: in this way in addition to taking into account the use of raw materials needed to the production of the building material, is also highlighted the contribution of steel to the sustainability of a building.

System Boundaries

The waste from construction and demolition, after the selective demolition, travel by road to the recycling plant, where they are treated; the secondary raw materials, output of the waste treatment plant, are then sent to the concrete mixing plant. The natural aggregates are transported from the quarries to the concrete mixing plant where concrete is produced and then sent to the construction site.

The impacts related to the construction, use and maintenance phase of the functional unit in a building have not been taken into account. This hypothesis is supported by numerous studies in the literature and it is assumed that the impacts are the same for all the mixtures analyzed. The analysis of the life cycle sees the demolition of the building as the final point; the steel of the demolished structure is sent to the recycling process and 15% of the inert materials is landfilled, following the hypothesis defined by [Colangelo et al. \(2018\)](#). Regarding to the remaining 85% of inert material, the process to which it is subjected has not been specified; this following the idea that in about sixty years, when the building will be subjected to partial or total demolition, the techniques of recovery could be reasonably changed.

The distances considered are the following:

- 30 km traveled by C&DW from the demolition site to the selected recycling plant.
- 20 km covered by recycled aggregates from the treatment plant to the concrete plant.
- 30 km from the cement production plant to the concrete mixing plant.
- 30 km from the sand and gravel quarries to the concrete mixing plant.
- 40 km from the concrete plant to the construction site.
- 300 km traveled by steel for the building's reinforcement. This is the approximately the distance that separates the steelworks of Taranto from a hypothetical construction site in the province of Naples.

In the case of geopolymer concrete production, the activities that lead to its production are very similar to those of mixtures with traditional binder except the production of the binder.

The distances considered are the following:

- 30 km traveled by C&DW from the demolition site to the selected recycling plant.
- 20 km covered by recycled aggregates from the treatment plant to the concrete plant.
- 100 km is the distance between the chemical plants that produce the precursors of the geopolymer and the concrete mixing plant.
- 30 km between the sand and gravel quarries to the concrete mixing plant.
- 40 km is the distance traveled by the concrete from the concrete plant to the construction site.
- 300 km are traveled by steel for the building's reinforcement and for the transport of the blast furnace slag from the steelworks to the concrete mixing plant.

Life Cycle Inventory

Data collection was carried out drawing on the numerous studies in the literature or, alternatively, using the data present in the eco-invent database. As an example below, we briefly elaborate some of them

- For the gravel natural aggregate, the ecoprofile is represented by the entry “Gravel, market for gravel, round {RoW} (RoW means for Rest of the World, while GLO means Global. They both represent activities which are considered to be an average valid for all countries in the world. They were chosen whenever specific data for the South of Italy could not be found)” in the ecoinvent 3 database.
- For recycled aggregates, the study by [Borghi et al. \(2018\)](#) has been considered. This study, supported by the administration of Lombardy region, has as its object the LCA of the current chain of disposal of demolition waste in Lombardy. [Borghi et al. \(2018\)](#) have quantified the consumption of electricity and fuel of fixed and mobile plants for the production of recycled aggregates. For the former has been estimated an electricity consumption of 1.74 kWh/t of recycled aggregate produced; 0.38 litres of diesel are used to produce one tonne of secondary raw material, and 0.03 kg of steel is used in the production of one tonne of recycled aggregate from a fixed plant.
- For the transportation, it was assumed that the materials travel on road, so the impact connected to the transported tonnes/km was assessed by referring to the item “Transport, freight, lorry 16–32 metric tonne”, EURO5 {GLO} | market for | Alloc Def, S “in the ecoinvent 3 database”.
- Electric energy; the data present in ecoinvent 3 have been used, in particular has been considered the medium voltage electricity produced in the Italian market.
- Also, data on the demolition of a building have been obtained from the study. In particular, 89.59 MJ of energy deriving from the combustion of diesel are needed to demolish 1 m³ of concrete.

Life Cycle Impact Assessment

In this work, the IMPACT 2002+ evaluation method was used to assess the impacts related to the production of concrete. The results of the characterization phase were interpreted.

Mixtures

In the present study, eight blends were analyzed. The four mixtures of concrete with recycled and natural aggregates are those suggested in the study.

Table 2 shows the composition and characteristics of these first 4 mixtures:

- Mixture with cement as binder and 0% recycled aggregates.
- Mixture with cement as binder and 25% recycled aggregates.
- Mixture with cement as binder and 50% recycled aggregates.
- Mixture with cement as binder and 100% recycled aggregates.

In **Table 3**, instead, the compositions and characteristics of the geopolymer mixtures under examination, prepared in the laboratory of the University of Naples “Parthenope”, are shown:

- Mixture with geopolymer binder and 0% recycled aggregates.
- Mixture with geopolymer binder and 25% recycled aggregates.
- Mixture with geopolymer binder and 50% recycled aggregates.
- Mixture with geopolymer binder and 100% recycled aggregates.

The amount of steel constituting the reinforcement was assumed to be 120 kg/m³ of concrete.

Results

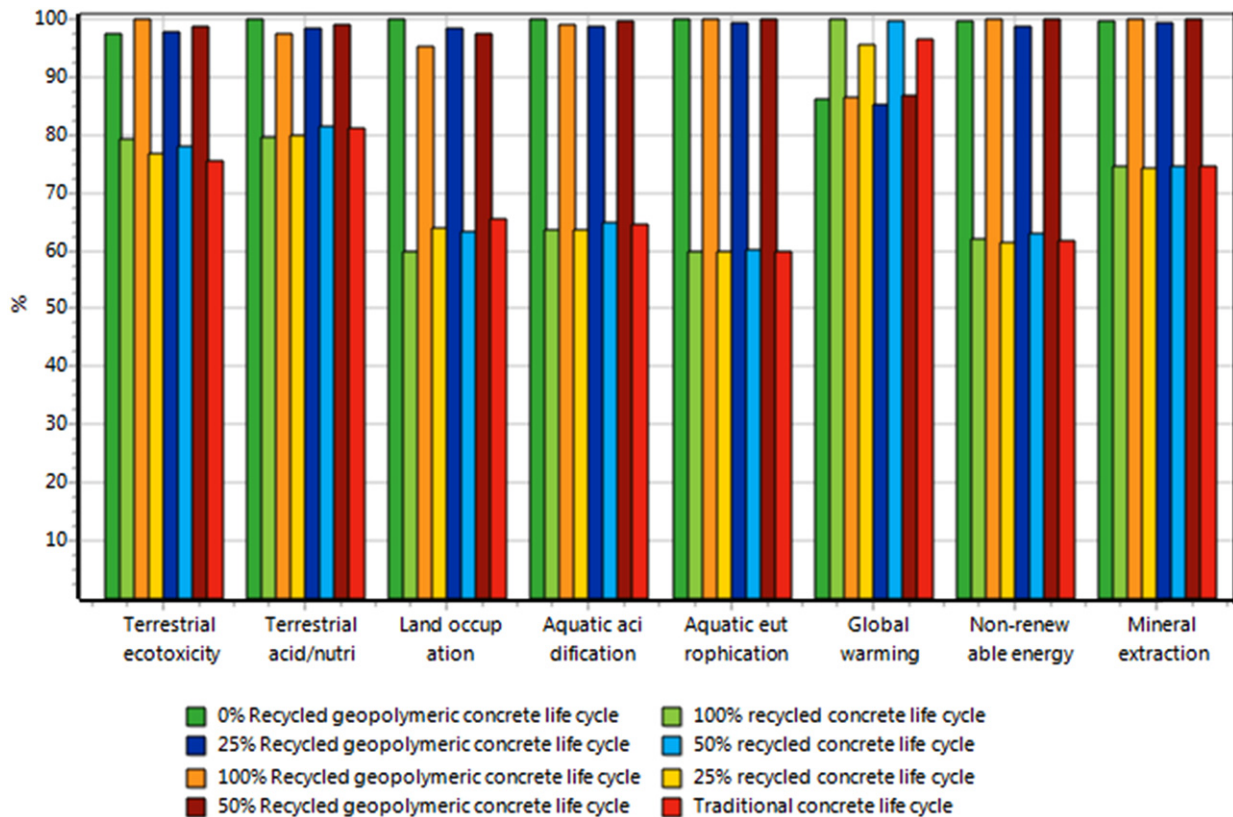
The obtained results show a small improvement of the environmental profile as the percentage of aggregates increases; thus supporting the circular economy. In **Fig. 1** it is possible, in particular, to see the values assumed by the impact indicators after the

Table 2 Mix proportioning of concrete mixtures with Portland cement (wt%)

	<i>Traditional concrete</i>	<i>25% R.A. concrete</i>	<i>50% R.A. concrete</i>	<i>100% R.A. concrete</i>
Cement	12.31	12.49	13.43	14.17
Water	6.77	6.87	6.97	6.84
Recycled aggregate	0	11.08	22.64	47.44
Sand	31.39	31.86	31.22	28.86
Gravel	49.53	37.69	25.73	0

Table 3 Mix proportioning of geopolymer mixtures (wt%)

	GGBFS0%Rec	GGBFS25%	GGBFS50%	GGBFS100%
Ground granulated blast furnace slag GGBFS	14.62	14.73	15.45	16.86
Sand	30.79	31.02	31.63	32.27
Natural aggregate	45.87	35.40	21.59	0
Recycled aggregate	0	10.06	22.36	41.73
NaOH solution	2.82	2.84	2.90	2.96
Na ₂ SiO ₃ solution	5.90	5.95	6.06	6.91


Fig. 1 Characterization, comparison among 8 mixtures using IMPACT 2002+.

characterization phase. It is shown, for each impact category, with the value 100% the most impactful mixture, the other mixtures assume values between 0 and 100 by comparison with the higher one. From these first data it is possible to understand which categories are important to analyze in order to identify solutions that make the production of concrete more sustainable, as well as to identify areas where there is a large inequality between one solution and another one. Results seem to discourage the production of the geopolymer mixture.

Discussion

Thanks to the results of the present study it is possible to give an answer to the questions that have moved the research, as well as to identify possible future developments. The use of recycled aggregates is always preferable compared to the traditional solution: the use of a circular economy model represents an efficient strategy for the construction and demolition waste sector. It would be interesting to analyze the impact deriving from the use of recycled aggregates from a mobile plant in order to evaluate the potential advantage in logistical and social terms. Other categories, such as "Mineral Extraction", are mainly influenced by the materials constituting the steel rebars. In this study a fixed amount of steel was considered for each mixture, it would be interesting to quantify the impacts after the calculation of the effective quantity of steel needed in each mixture.

Conclusion

The problems related to the increase in construction and demolition waste, together with the desire to reduce the impacts deriving from the construction sector, have pushed this study to find a strategy to reduce the environmental impacts. After a careful literature analysis aimed at identifying the best practices of the LCA applied to the construction sector, it was decided to analyze the results of the characterization phase for each impact category. It was therefore possible to identify the best scenario to investigate, as well as to evaluate the effective validity of the application of the circular economy concept in the construction sector suggested by the European Directive 2008/98/EC. With the assumptions made in the present study, the solution consisting in concrete with 25% of recycled aggregates is the best in most of the selected environmental impact categories of the method IMPACT 2002+. Furthermore, all solutions with recycled aggregates are not more impacting than those having exclusively gravel in the mix design. Therefore, the recycling of concrete for the production of secondary raw materials is perfectly in line with the dictates of an efficient circular economy. Excluding the recycling, steel accounts for about 15% in two of the main categories of the IMPACT 2002+ method and about 30% in the “Respiratory Inorganics” category. Other categories, such as “Mineral Extraction”, are predominantly influenced by the material constituting the steel rebars. The values can change considerably applying one impact evaluation method rather than another. In this regard, efficiency could be increased generating a greater number of facilities of the “chain” that allows to obtain the concrete available at the construction site. It would be interesting to study what would happen in case of production of recycled aggregates of sufficient quality in a mobile plant, followed by a reuse on site; it would be also interesting to examine an already developed context where the distances to travel are shorter. As regards the possibility of using geopolymers, these represent an already valid alternative with regard to the reduction of “global warming”; however, the big impact in the other categories, connected to the production of sodium silicate and sodium hydroxide, represent an obstacle to their employment. The weak point of this study is represented by the absence of primary data: databases and data in literature have been used. The above perspectives indicate the importance of studying in detail the production process of geopolymer precursors in order to identify the critical issues: a possible reduction of the environmental load connected to the production of sodium silicate and sodium hydroxide would increase the employment of third-generation cements.

See also: A Review on Utilization of Electronic Waste Plastics for Use Within Asphaltic Concrete Materials: Development, Opportunities and Challenges for Successful Implementation. Recycled Ceramics in Concrete. Recycled Concrete. Sustainable Production of High Performance Concrete

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Further Reading

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Waste statistics – Statistics Explained – European Commission.

Local Food and Healthy Eating for Wholesome Life: Some Policy Considerations

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Introduction

Wholesome life is a way to live in a manner that makes one feel whole and fulfilled every moment of one's life. The word *wholesome* is a condition, and in the present context, means the whole, sound, and perfect health of a person. Wholesome people are healthy, not only in body but also in mind and in spirit. According to the Bhagavadgita, the *gunas* (the primary qualities or modes of nature) are three in number: *Sattva*, *rajas*, and *tamas*. They exist in all, including humans, in various degrees of concentration and combination. They also exist in all objects and natural products. Hence, even the food that we eat is important if we want to cultivate good behavior. Food choices must be conducive to the cultivation of *sattva*, since *sattva* improves the vigor and the brilliance of the mind and the body. We are, however, ignorant of the fact that the food we eat plays a huge role in our ability to keep our physical, mental, emotional, psychological health, and overall well-being in balance.

Kuhnlein *et al.* (2009) rightly emphasize on dimensions of nature and culture that define a food system contributing to the whole health picture of the individual and the community, not only physical health but also the emotional, mental and spiritual aspects of health, healing and protection from disease. Kuhnlein *et al.* (2009) further assert that "indigenous people never separated food from medicine, depending upon which part of the plant is used, the season of the year and physiological condition of the person using the crop, the same plant can be consumed as food or medicine." Further sustainability of the environment happened to be one of the critical issues in the food acquisition and consumption of indigenous communities the world over (Demi, 2016).

Sadhguru Jaggi Vasudev, a yogi, a profound mystic, a visionary humanitarian, a prominent spiritual leader and author, and founder of the Isha Foundation, a nonprofit organization that offers Yoga programs around the world and involved in social outreach, education, and environmental initiatives, also asserts that the type of food we eat has a huge impact on our body. He says that "in yogic system there is a physical body and a mental body. There is an intelligence and memory running right across the body. People generally think the brain is everything just because it handles the thought process. And because of this separation of body and mind, a large number of people in the West are taking antidepressants at some point in their life."

Mental health is a major concern worldwide and India is not far behind in sharing this. If we evaluate developments in the field of mental health, the pace appears to be slow (Srivastava *et al.*, 2016). Dr. Brock Chisholm, the first Director-General of the World Health Organization, in 1954, had presciently declared that "without mental health there can be no true physical health" (Kolappa *et al.*, 2013). More than 75 years later, the scenario has not changed substantially. About 14% of the global burden of disease is attributed to neuropsychiatric disorders. The burden of mental disorders is likely to have been underestimated because of inadequate appreciation of the interplay between mental illness and other health disorders (Prince *et al.*, 2007). There remain considerable issues of priority-setting based on the burden of health problems and of addressing inequalities in relation to determinants and solutions for health problems.

We all are familiar with the age-old saying "you are what you eat" but are often ignorant of this profound notion in applying it to our life. It is an accepted fact that some foods are good and some are bad for us but beyond this level of understanding we do not know the deeper meaning of food we eat. As we eat habitually and not intentionally or consciously, we have become so disconnected from the natural world that we do not know what this food is doing in our body beyond the momentary taste sensation in the mouth.

It is common knowledge that all animals, except human beings, living in their natural environment are not overweight or suffer from any chronic illness as a result of their diet, as they have natural intelligence that drives their food choices and they know what to eat. We, therefore, need to change our food system because the solution for health is not necessarily healthcare, it is actually our food system. Addressing both together, that is, creating a mindful nation and changing the food system, is the answer.

We all are aware that modern life, in this technological age, is very stressful as many things are competing for our attention and we are living in a constant state of excitement. Meditation has been advocated as one way to find stillness and quieten the mind but it has been quite challenging to many of us. The food we eat has been considered to play an important role in our ability to reach that meditative state. Our nervous system and brain never allow us to transcend our body when certain nutrients are not present, or when we are in a state of *nutritional stress*.

Our bodies contain similar nutrients to the food we eat. Therefore, depending on what kind of food we are consuming and the contents of that food, we are affecting our nutrient levels and overall, our health. On average, the human body is 6% minerals, carbohydrates, and other nutrients; 16% fat; 16% protein; and 62% water. Of course these percentages vary for every individual person depending on diet and lifestyle.

As mentioned above, it is important to eat a wide variety of foods from the five food groups to ensure that we are consuming all the different nutrients that our body needs. Eating one type of food may supply us with excess of a particular nutrient, but our body will be lacking other vital nutrients only obtainable from different foods. We often don't think about the nutritional content

of our food, but need to do some research and find out what we're really putting in our body when we eat certain foods. "When it comes to food, ask the body with what kind of food it is really happy. Try different foods and see how your body feels after eating the food. If your body feels very agile, energetic and nice, that means the body is happy. If the body feels lethargic and needs to be pumped up with caffeine or nicotine to stay awake, the body is not happy" asserts Sadhguru. Awareness of the contents of our consumption is the first step in moving towards a healthier diet and therefore, a healthier body. If we eat large quantities of high-sugar foods, we can continuously tax our system and eventually cause problems that can affect our health forever, such as type 2 diabetes. It is important to make a habit of healthy eating. The more often we eat healthy, the easier it will be and the more we will start to enjoy healthy food over unhealthy food.

Although food is something that we need to sustain us physically, there's a spirituality to food that is being increasingly acknowledged by consumers. "To be healthy in mind, body and spirit, it's essential to be spiritually connected to the food we eat and to relish the experience of eating," said Heidi Demars, an organizer with the Bisman Food Co-op and 2013 Bush Fellow. "Understanding how to eat is just as important – sometimes even more so – as what to eat." For Peter Bolland, humanities department chair and professor of philosophy and humanities at the School of Social Science, Business, and Humanities at Southwestern College in Chula Vista, California, all food is sacrifice, because all food is gained by death.

Demars noted that issues with obesity in the United States, which have increased since the 1990s, also have made many consumers connect with food in a more meaningful way and seek healthier choices. As consumers, Demars said the biggest question is how we can be more mindful of where our food is coming from and the people that produce it. This also means considering the long-term consequences that might occur to our current food system.

In the present communication, therefore, some policy considerations based on the outcomes of a few exploratory case studies on local food system and culture conducted recently by the author (Bisht, 2018; Bisht *et al.*, 2017, 2018a,b) in the Uttarakhand Hills are outlined. The Uttarakhand Hills are primarily an agriculture-based society with a rich native food culture and traditions. Traditional farming landscapes and local farming communities provide us the opportunity to showcase how indigenous food sovereignty and food systems can contribute for overall health, well-being, and wholesome life of native communities. There has been an enhanced emphasis globally now on indigenous food sovereignty. The enhanced production and consumption of native food is being emphasized so that the poor have adequate access to good quality healthy food for a nutritionally adequate diet. This includes not only food rich in energy but also micronutrients, that is, the vitamins and minerals and other trace elements necessary for normal growth and development. The author's case studies' outcomes and similar studies on traditional food systems and indigenous food sovereignty documented elsewhere have been discussed here in context of policy considerations for overall health and well-being of the native communities. It is expected that this communication can serve as a guide to our planners and policy makers designing appropriate food, nutrition, and health related policies at the state, regional, national, and global levels for health care and overall well-being of the native communities.

Representative Agro-Ecologies of Uttarakhand Hills of India and the State of Household Nutrition and Health

Of the total geographical area of Uttarakhand State, about 86% is hills where subsistence agriculture is practiced, which directly or indirectly sustains about 50% of the population of the state. On the other hand, there is 14% plains area where improved agriculture is practiced and most of the food grains are produced here. Farming communities in hilly areas of Uttarakhand State traditionally grow diverse crops as polyculture. Most of these native crops and their traditional landraces/farmers' varieties form the "functional foods" to hill farming communities with nutraceutical properties and high nutritional value. Further, about 70%–80% of the population is still directly or indirectly engaged in agriculture and allied sectors.

The traditional hill agriculture is highly knowledge-based and farmer-led innovations are predominantly practiced. All farmer-led innovations are socioeconomic and are not of a technical nature. Uttarakhand also has a rich food culture and tradition. Three representative farming agro-ecologies in Uttarakhand Hills as outlined by Bisht *et al.* (2018a,b) include:

- (1) Small-scale crop-livestock mixed-farming systems representing about 70% cropped area under rain-fed farming. The farming situations could be characterized by high household food production and dietary diversity. In the mixed crop-livestock farming system of the hills, there still exists a dynamic relationship among Common Property Resources (CPRs), native crops, and livestock. The livestock substantially contributes to household cash income whereas the surplus crop produce, if any, is sold locally and contributes very little to the household cash economy. The farming communities largely rely on plant-based vegetarian food. The wild plant resources also form an important component of the household dietary diversity.
- (2) High elevation mountainous areas adjoining Tibet with a mix of nomadic pastoralism, some arable land, and wild harvesting including foraging and trading of medicinal herbs. Sheep and goat are the herded livestock. Level of household food production and dietary diversity is moderate. This system is representative of about 10% of the farming areas in hills of Uttarakhand. Livestock grazing is practiced throughout the mountain valleys, although at rates significantly lower since the Indo-China conflict of 1962. Largely because the loss of trade with Tibet, demand for livestock and agriculture products as well as other professions linked to trade and agriculture including wool crafting and freight shepherding has dropped considerably but still contributes a lot to the rural economy. Consumption of meat is relatively high. Additionally, the wild harvested food resources such as *Jambu* or *Faran*, *gandharini*, *kala* or *bhotia jeera*, etc., are contributing immensely to the household cash economy.

- (3) A few interspersed river valleys where improved agriculture under assured irrigation is practiced and rice-wheat or rice-potato is the predominant cropping pattern. Household food production and dietary diversity is very low. The livestock herding particularly rearing of goats is minimal with limited contribution of livestock to overall cash income of the households. The river valleys represent about 10% of the cropped area in Uttarakhand Hills. In the river valleys, there is greater contribution of agriculture produce to the household economy.

A comparative study of household production and dietary diversity of the different farming situations was carried out during 2016 from 20 niche sites representing the above stated three agro-ecologies of the Uttarakhand Hills. Greater household production and dietary diversity were recorded in traditional rain-fed, small-scale crop-livestock mixed-farming systems followed by mountainous valleys with nomadic pastoralists, and least in river valleys with improved agriculture (Bisht *et al.*, 2018a,b).

A nutrition transition was clearly evident in farming agro-ecologies of river valleys with the emergence of cash crop economies and impact of globalization in recent years. Enhanced use of improved crop varieties from formal seed system, synthetic fertilizers, and pesticides is commonly seen in these farming systems. About 70%–80% of the cropped area is planted with a few improved cultivars of rice, wheat, and potato bred by public and private sector institutions. The produce of improved cultivars is generally sold in markets for cash income. Relatively reduced access to indigenous food resources and increased access to energy dense foods are creating an “obesogenic” environment in river valley areas.

In spite of nutrition transition trends in many other parts of Uttarakhand, it is widely acknowledged that in the representative target regions rich in crop and livestock diversity and use of wild harvested foods, the food traditions are still prevailing in the life of rural households to a greater extent. This is indeed heartening that the traditional food habits are still playing a great role in contemporary food habits of the target communities; therefore, the possibility of reversing the trends in favor of dietary diversification from dietary simplification looks promising. It was found that the root cause of both malnutrition and overnutrition/obesity is inadequate or improper nutrients. Consumption of an appropriate portion of food rich in essential nutrients can eliminate both pandemics.

In a comparative study of the connection between household production and the food local communities consume, and the physical, emotional, and mental health of the three representative farming agro-ecologies of Uttarakhand Hills, a clear linkage could be established. The high production and dietary diversity of traditional farming areas with small-scale crop-livestock mixed farming recorded the least incidence of food-based noncommunicable diseases like hypertension, type 2 diabetes, certain cancers, and everything from Attention Deficit Disorder to bipolar diseases, and to depression. A critical analysis of the food choices of the native communities in such farming situations indicates that they largely depend on a plant-based vegetarian diet. The wild plant resources also form an important component of their dietary diversity (Bisht *et al.*, 2017, 2018a,b). The wild plant resources, generally consumed in live form, make the communities physically and mentally agile and active.

Such farming agro-ecologies, therefore, need to be protected and a food-based approach made a primary healthcare policy in such farming agro-ecologies at the state, regional, and national levels (Bisht, 2018). Further, the cash crop economies in hill farming need to be discouraged as they will lead to enhanced malnutrition and outmigration of the rural youth.

Policy Considerations for Traditional Farming Communities for Their Food, Nutrition, Livelihood Security, and Overall Well-Being

The exploratory study of the author on household production and dietary diversity of different representative farming situations in Uttarakhand State clearly indicated that high production and dietary diversity is linked with better community health and nutrition (Bisht *et al.*, 2018a). Further, the traditional farming innovations are sustainable in terms of food production and spirituality in food systems is deeply integrated. The following policy interventions for overall well-being of traditional hill farming communities may, therefore, be considered:

- *Initiatives and research interventions for a diverse production system*

It has been emphasized that better and balanced nutrition in the human diet depends not only on growing a diversity of crops but also on the diversity within the crops (Mouille *et al.*, 2010). The micronutrient superiority of landrace cultivars complemented with wild food resources in traditional hill farming has been revealed by our case study findings (Bisht *et al.*, 2017, 2018b). Past researches, for example, have shown substantial intervarietal differences, for example, for beta-carotene in sweet-potato cultivars and the pro-vitamin A carotenoid of banana cultivars (Burlingame *et al.*, 2009; Litaladio *et al.*, 2010). The protein content of rice cultivars has also been reported to range from 5% to 13% (Burlingame *et al.*, 2009; Kennedy and Burlingame, 2003). Intake of one variety rather than another can be the difference between micronutrient deficiency and micronutrient adequacy in traditional farming. The micronutrient superiority of some lesser-known cultivars and wild varieties over others has been confirmed by certain recent researches (Heywood, 2013; Bharucha and Pretty, 2010). Unfortunately, we lack detailed information about such diversity within most crops at the cultivar level and the role it plays in nutrition because of the general neglect by researchers/professionals (Burlingame *et al.*, 2009) and much of the evidence is anecdotal.

Coates *et al.* (2007) suggest that dietary diversity can be used as a proxy indicator for nutrient adequacy. Adequate human nutrition thus involves regular intake of a wide range of nutrients, some of which must be consumed on a frequent basis, even if in small quantities. We believe that the trend in nutrition transition can be slowed down and certain approaches are needed to move

the nutrition transition in a more positive direction. Suggested public health promotion strategies, policies, and intervention approaches, as outlined by Smith (2013) include (1) holistic integrated food and nutrition interventions, (2) addressing under- and overnutrition simultaneously, (3) involving communities in planning interventions using a bottom-up rather than top-down approach, and (4) focusing on diversification of diets rather than a reliance on fortified foods and supplementation where possible.

We therefore need more diversity deployed in any production systems rather than uniformity and monoculture as advocated by corporate agriculture.

- *Documenting the indigenous knowledge and innovations*

Kuhnlein *et al.* (2009) argued that “Indigenous peoples’ food systems contain treasures of knowledge from long-evolved cultures and patterns of living in local ecosystems.” Therefore, traditional food systems need to be documented so that policy makers know what is at stake by ruining an ecosystem, not only for the native peoples living there, but also for everyone. Our study clearly indicated that malnutrition is not the result of food scarcity but foods poor in essential nutrients. Although the problem of diminished food sovereignty and food insecurity is one that affects all people, not just indigenous communities, indigenous peoples are uniquely situated to offer solutions. Armed with ancient traditional knowledge and a deep connection to their lands, indigenous communities, and particularly indigenous women are developing projects and building networks to revitalize local food capacity and strengthen food sovereignty.

The native food culture of Uttarakhand Hills can be discussed here in greater detail based on local IK in the context of food, viz. spirituality, food security, harvesting regulations/restrictions, and reliance on locally available material as outlined by Bisht *et al.* (2018a,b). The predominantly crop-livestock small-scale mixed-farming systems of Uttarakhand Hills encourage farmer households to consume more traditional crops instead of animal flesh, except for the nomadic pastoralists of high mountainous regions who depend relatively more on animal products. In indigenous animal husbandry of Uttarakhand Hills, the livestock are mainly fed with crop by-products while substantive food is mainly reserved for human consumption. Such systems save humans from competing with livestock for food and ensuring food sufficiency. In contrast, industrial agriculture contributes to creating food insecurity through the use of whole grains and cereals as key components of animal feed (Demi, 2016). The transformation of US diets from high-calorie crop products to low-calorie meat, for example, has greater environmental consequences (Albritton, 2012), with meat production contributing disproportionately to greenhouse gas emissions (Carlsson-Kanyama and Gonzalez, 2009; United Nations Environmental Programme, 2012). Further, feeding farm animals on crop by-products and forage ensures production of lean meat that helps reduce fat-related complications and diseases (Bernard *et al.*, 2006, 2009; Demi, 2016).

In traditional hill farming, use of local readily available materials, for example, use of forest litter, animal waste, farmyard manure, etc., and avoidance of synthetic fertilizers, except in river valleys where modern agricultural practices are followed, ensure that safe organic foods are produced for human consumption. These practices intend to help improve human health and preserve the environment for future generations. Indigenous diets worldwide are varied, suited to local environments, and can counter malnutrition and disease. For many indigenous communities, their food systems are complex, self-sufficient, and deliver a very broad-based, nutritionally diverse diet. But the disruption of traditional lifestyles due to environmental degradation, and the introduction of processed foods, refined fats and oils, and simple carbohydrates, contributes to worsening health in indigenous populations and a decline in the production of nutrient-rich foodstuffs that could benefit all communities.

The indigenous knowledge and innovations, therefore, need to be properly documented and used to bring sustainability in production systems.

- *State support to indigenous food sovereignty movements and promoting community-supported agriculture*

The development of sustainable agriculture will require a more radical transformation of agriculture, one guided by the notion that ecological change in agriculture cannot be promoted without comparable changes in the social, political, cultural, and economic arenas that help determine agriculture. The organized peasant and indigenous-based agrarian movements – such as the international peasant movement La Vía Campesina and Brazil’s Landless Peasant Movement – have long advocated for genuine agrarian reforms to access and control land, water, and biodiversity that are of central importance for communities to meet growing food demands.

Moving toward a more socially just, economically viable, and environmentally sound agriculture will be the result of the coordinated action of emerging social movements in the rural sector in alliance with civil society organizations that are committed to supporting the goals of these farmers’ movements. As a result of constant political pressure from organized farmers and others, politicians will, it is hoped, become more responsive to developing policies that will enhance food sovereignty, preserve the natural resource base, and ensure social equity and economic agricultural viability.

Within the larger society in which they live, despite the wealth of knowledge rural indigenous people have of their local environment and food system, they often face vulnerabilities derived from extreme poverty, discrimination, and marginalization. It has been rightly argued that the emerging concept of food sovereignty emphasizes farmers’ access to land, seeds, and water while focusing on local autonomy, local markets, local production–consumption cycles, energy and technological sovereignty, and community level farmer-to-farmer networks (Altieri, 2009). The case study on household production and dietary diversity is expected to set the stage for the future research to demonstrate how these local foods contribute to food security, nutrition, and health. Our long-term objectives will be to address scientific issues, public health, and policy, with the

goal of influencing local, national, and international policies for environmental protection of indigenous peoples' land and food resources. In this way, communities can be encouraged to strengthen their use of local food and sustain knowledge of their local food systems for essential contributions to cultural protection, well-being, and health. Local biodiversity should be recognized as a significant contribution to a sustainable agriculture–food–nutrition strategy alongside other nutrition–agriculture interventions (Heywood, 2013).

Local biodiversity and ecosystem services play an essential role in the lives of communities throughout the developing world, by providing a social safety net for food, medicine, fiber, fuel wood, etc., that can act as a route out of poverty and a source of income generation and can prevent people from falling further into poverty or in extreme cases as an emergency lifeline through the provision of “famine food” (Roe *et al.*, 2010). It can also play a major part in addressing issues of malnutrition (Heywood, 2013).

It has also been rightly argued by those concerned with the global food sovereignty movement that it is the small-scale farmers that actually have control of the food system, of information, and of food culture as against the social perception in the Northern Hemisphere that the large food chains feed society (Patel, 2009). Facing this, in the entire world, and especially in the Northern Hemisphere of the United States, Canada, Europe, impressive associations of critical consumers, and producers are being developed. In France, for example, there are 3000 producer–consumer associations. In Canada and the United States, where there is a common problem of reduced numbers of farmers, there is an enormous demand from citizens to have control over what they eat, how it is produced, and who produces it. They are demanding a new type, a new model of farmer, one that isn't trained in a productivist model (Patel, 2009).

It is believed that one of the effects of producer–consumer associations is to support the new farmers, who are increasingly coming from urban areas. In Europe, for example, many farming men and women now make a living based on local markets. They have a much better chance of survival than those farmers who depend on the transnationals for their inputs and sales. This is a very clear reality. To overcome this, urban social movements must come together with rural movements to develop a new type of agriculture and training that dignifies the profession, to excite young people (Patel, 2009).

Food sovereignty advocates rightly argue that the antipoverty approach runs the risk of reducing the issue of hunger and malnutrition to a humanitarian problem for rich countries to solve, a position that is highly contested by countries and societies that have long depended on agriculture for the livelihood (Mazhar *et al.*, 2007). Wittman *et al.* (2010) defined food sovereignty as the right of nations and people to have control over their own food systems, including their own markets, production modes, food cultures, and environments. Food sovereignty works with the concept of self-sufficiency in food production, democracy, and diversity. Lack of appreciation of these complex issues explains in part the rising cases of chronic diseases such as obesity and hypertension associated with overeating in the midst of food insecurity (Martin, 2012).

We therefore need community-supported biodynamic agriculture so that the problem of malnutrition is addressed by making available fresh and healthy food at the consumer's doorsteps.

- *Promoting wild food resources as component of dietary diversity*

Dependence of local communities of Uttarakhand Hills on diverse plant resources including wild food resources ensures that the plant species are protected, and in this way an effective mechanism of sustainability that indigenous communities can employ to maintain a cosmic balance with the ecosystem could be duly showcased by a recent case study research (Bisht *et al.*, 2017, 2018a,b).

Use of wild plant food resources in traditional farming as a component of dietary diversity, therefore, needs to be encouraged and wild habitats and CPRs duly protected through enabling policy support.

- *Participatory approaches and cross-sectoral collaboration and advocacy agenda for food-based approach towards community nutrition and health*

To achieve sustainable reductions in undernutrition and other forms of malnutrition, national policies and programs must be complemented by effective community-based actions. A key dimension of this strategy is enabling households to maximize food security and nutrition with existing household resources, while also striving to increase such resources. This requires a process of effectively mobilizing communities and shifting from a centralized to a more decentralized approach, with wider participation on the part of the community. A number of activities that address problems of household food insecurity and the various forms of malnutrition are being undertaken by FAO in both urban and rural areas. An important focus is community empowerment, with appropriate support from various governmental agencies and civil society institutions. At the community level, targeted and coordinated efforts focusing on improving household food security, fostering people's participation and empowering women and marginal groups are needed to address local food and nutrition problems.

Progress in promoting and implementing food-based strategies to achieve sustainable improvements in micronutrient status has generally been slow. These strategies focus on improving access to and availability and consumption of vitamin- and mineral-rich foods. Benefits of such food-based strategies include not only improved intakes of specific nutrients but also improved overall diet and health status. Since 1985, FAO has participated actively in defining and implementing programs to reduce micronutrient malnutrition. FAO strongly supports the promotion of the production and consumption of micronutrient-rich foods as the sustainable solution to micronutrient deficiency problems. This activity clearly falls within the Organization's mandate and overall strategy, which emphasizes the relationship between nutrition and agriculture to ensure food security and to improve the health and nutritional status of all populations.

Agricultural biodiversity is important for food and nutritional security. It also acts as a safeguard against hunger, a source of nutrients for improved dietary diversity and quality, and strengthening local food systems and environmental sustainability.

A recent compilation by Fanzo *et al.* (2013) explores the current state of knowledge on the role of agricultural biodiversity in improving nutrition and food security. The book explores current strategies for improving nutrition and diets and identifies key research and implementation gaps that need to be addressed to successfully promote better use of agricultural biodiversity for rural and urban populations, and societies in transition.

One of the world's greatest challenges is to secure sufficient and healthy food for all, and to do so in an environmentally sustainable manner. While the complexity and underlying determinants of undernutrition have been well-understood for decades, the scaling of food and nutrition system approaches that combine sustainable agriculture aimed at improved diet diversity and livelihoods have been limited in their development and implementation. However, an integrated system approach to reduce hidden hunger could potentially serve as a sustainable opportunity.

Uttarakhand State has limited political commitment to nutrition-sensitive agriculture. With the current emphasis on nutrition, a window of opportunity exists to promote nutrition-sensitive cross-sectoral strategies. However, efforts to communicate nutrition-sensitive agriculture and food systems as the system approach that encompasses all underlying causes of malnutrition in their interrelatedness and complexity along the whole value chain must be significantly increased (Balz *et al.*, 2015). Such an understanding is especially needed for a sustainable development goal concerning nutrition such as eradicating malnutrition in all its forms through sustainable food systems. Nutrition-sensitive agriculture seems to be more of a term than a concept. To promote nutrition-sensitive agriculture, a systemic approach and true cross-sector collaboration are needed (Balz *et al.*, 2015).

Research strategies designed to codeliver economic, environmental, and health goals will need to draw on interdisciplinary collaborations to define priority research questions. They should include a range of environmental indicators and not just greenhouse gas emissions and they need to take into account differences in impacts (partly due to different production systems) between countries (Gill *et al.*, 2015). Food-based solutions to hunger, malnutrition, and poverty are of global concern and must be addressed if food and nutrition security is to be achieved in a sustainable manner (Thompson and Amoroso, 2014).

The rising cases of chronic illness such as cardiovascular diseases, diabetes, and certain cancers among native and urban communities across the globe have been attributed to moving away from traditional foods rich in fiber, fruits, vegetables, and leafy greens to foods high in fat, sugars, and salt (Bjerregaard, 2010; Delormier *et al.*, 2009). Nestle (2007) asserted that different cultures understand their relation to food differently. Whereas the goal of food and eating within many indigenous communities is a means of expressing culture, upholding traditions, and strengthening cultural knowledge about the world (Willow, 2005), the goal of conventional nutritional science research reduces foods to its biochemical properties and categorizes it according to chemical compounds (Lupton, 1996; Scrinis, 2012; Warde, 1997).

The small-scale ecological farming methods are the key to ensuring resilience to climate change in Himalayan agro-ecologies. They are based on enhancing diversity, thereby increasing options to respond to climate instability. There is a need to support these traditional systems to feed local communities and at the same time address the traditional food-based approach of community nutrition and health. A proactive alliance, collaboratively creating a research and advocacy agenda in support of agrobiodiversity and the revival of diverse local food systems and landscapes, will be needed between indigenous peoples, local communities, and their key allies within the broader framework of indigenous food sovereignty. There is a need to reassess existing food and nutrition-related health and agriculture policy and develop cross-sectoral implementation strategies on food security, nutrition, and health. Further, there is need of continuous policy advocacy activities to educate functionaries across different sectors. Developing food composition databases is vital for effective advocacy tools and critical for cross-sectoral policy and program development (Bisht, 2018).

The general ignorance of nature and use of nutrient-rich indigenous and traditional food resources over the years has resulted in these foods being left out of most nutritional strategies put in place to address food security and nutrition problems of the population. Beside research-oriented activities, advocacy is an important thrust area of local institutional collaboration. There is a strong need to enhance the knowledge base of policy and decision makers at the local, regional, and national level across agriculture, food, and public health sectors on traditional food and nutrition. Continuous policy advocacy activities in the form of workshops, round-table discussions, stakeholders' meetings, etc., need to be organized to educate various functionaries across different sectors. There is also a need to reassess existing food and nutrition-related health and agriculture policy at local, regional, and national levels, harmonize such policies, and develop cross-sectoral implementation strategies that would positively impact on food security, nutrition, and health of the native communities.

There is lack of credible data and information on the compositional attributes of traditional food resources, which has greatly hampered efforts to inform and educate the population on the nutritional and healthful attributes of these foods. Developing the food composition database will be vital for effective advocacy tools and critical for policy and program development across agriculture, food, nutrition, and health sectors.

- *Enhanced market access and value chain development for traditional food resources*

Traditional varieties of different crops not only have different genetic attributes than modern varieties, they also have several consumption characteristics such as taste, aroma, cooking quality, nutrition, etc. In part for this reason – and in part, by virtue of commitments to environmental values – there is scope for development of local and distant markets in which traditional varieties command a price premium. Labeling systems can assist in creating such markets (Mann, 2004; Bisht, 2018; Bisht *et al.*, 2014, 2018a).

Again, this could not only provide direct rewards to growers, but also help to raise public consciousness of the importance of diversity and the need for public policies to sustain it.

Further, enhanced marketability and making them easily available in local markets through proper processing/packaging can add value to local food resources and increase their value in household food choices and family diets. Markets can play an important role in mainstreaming local foods in household diets and integration on nutritional contribution of traditional food resources to the well-being of the rural poor in the region.

In many instances it may be difficult to secure stable markets for raw agricultural products. This is particularly the case for crops requiring processing before they can be used. In these cases it may be possible to enhance the benefits to farmers of local varieties by processing them for particular markets. Increasing benefits to farmers through processing is one of the more costly and time consuming options available to enhance on-farm conservation. Detailed economic research and sample pilot studies are usually necessary to establish whether an initiative can be profitable and sustainable. Processing plants may be capital-intensive. Moreover, developing an industry to supply an agricultural product is likely to require government permission and regulation. One advantage to this approach is that interventions to increase benefits to farmers through processing can provide a sustainable mechanism for economic development and (after an initial outlay) may require only minimal monitoring and maintenance.

Ragi, finger millet or *madua*; rice; local black-seeded soybean, *bhat*; *gahat* or horse gram, etc., from traditional hill farming areas have a greater potential for value chain development and other marketing interventions.

- *Integrating local nutrient-rich food in midday meal program in line with lessons learned from Brazilian experience on school feeding programs*

In line with the success of Brazil's school feeding program, the traditional and healthier eating habits of Uttarakhand Hills can also be rescued. Several local crops offer more fiber, more vitamin B, and complex carbohydrates. Through policy advocacy activities, the school students should be made familiar and comfortable with what they are eating.

Further, like the Brazilian program, a substantial amount of Ministry of Human Resource Development budget can be diverted to small holder farmers for local purchasing of native healthy food to school feeding programs (midday meal scheme). In Brazil, 40% of food served to students is from local farmers and processors. The Brazilian experience has proved that small agriculture can produce good quality processed products – the kind of value-added products that can make farming more profitable. The small farms were capable of producing quality and good, dignified products that could positively contribute to the Brazilian school feeding program.

(Is any country, in general, and traditional farming areas like Uttarakhand Hills, in particular, ready for the change?)

- *Policies that encourage part-time farming*

One should recognize that farming need not be an all-or-nothing occupational choice. In an exploratory study from traditional crop-livestock small-scale farming areas, it was revealed that a small fraction of households (10%) earn their livelihoods entirely from farming, about 50% households earn most of their cash income from farming, and 40% households derive most of their cash income from nonfarm sources. The expansion of nonfarm employment at the community level will never eliminate farming.

Traditional agriculture in Uttarakhand Hills is highly labor-intensive and often does not provide full-time employment year-round to the labor force involved. Women comprise about 50% of the family labor force involved in agricultural operations, and the village youth, the rural labor force, is often not predominantly engaged in agriculture. Many youths also see traditional agriculture as an activity not worth the effort. It used to be family labor mainly involved in agriculture operations in the past. Outmigration of family labor in search of off-farm jobs to urban areas now is adversely affecting agriculture in the region. Policies that help to generate part-time, off-farm employment opportunities at the community level in rural areas can, therefore, help sustain small farms. So can policies that promote agriculture-friendly tourism, thereby internalizing another positive externality often generated by small-farm landscapes including the scenic beauty of Uttarakhand Hills. In supporting small farms, such policies could help to sustain agricultural biodiversity, especially if accompanied by other policies that recognize and reward the social value of its in situ conservation.

The off-farm job opportunities at the community level can be weaving, milling, food processing, eco-tourism, etc. Mahatma Gandhi National Rural Employment Guarantee Act of India, as a concept, has been a welcome initiative in this direction though there is a need to address problems in its proper implementation.

- *Awards and intellectual property rights (IPR) protection of farmer-led innovations*

The Protection of Plant Varieties and Farmers' Rights Authority (PPV&FRA) of India has instituted several awards in form of cash prizes, viz. Plant Genome Savior Community Award, and Plant Genome Savior "Farmer Reward" and "Farmer Recognition" to communities and the farmers engaged in the conservation of genetic resources of crop landraces and wild relatives of crop plants and their improvement through selection and preservation and the material so selected and preserved has been used as donors of gene in varieties registrable under the PPV&FR Act, 2001. Similar awards have also been instituted by the National Biodiversity Authority and State Biodiversity Boards for biodiversity conservation.

Another important step would be to promote noneconomic rewards for the conservation of agricultural biodiversity in annual fairs at the community level to farmer households. Such recognition not only makes farmers feel good; it also helps to create public awareness of the need for policies to provide economic rewards. Documentation and facilitating on-the-spot registration of farmer's varieties will help address IPR protection and enhanced exchange of local diversity. As farmers of the

region often have limited economic incentives in cultivating local landraces, native crop biodiversity can be recognized as a significant contribution to a sustainable agriculture–food–nutrition strategy alongside improvements in agricultural productivity and other nutrition–agriculture interventions.

Conclusion

Food choices must be conducive for improving the vigor and the brilliance of our mind and the body. The food we eat plays a huge role in our ability to keep our physical, mental, emotional, psychological health, and overall well-being in balance. Traditional diets are considered a delicious roadmap to healthy eating. Rather than relying on highly processed foods that are stripped of their nutrients, traditional diets celebrate the abundance of the earth's offerings, highlighting seasonal and regional produce, hearty recipes, and the pleasures of the table. Today, people are more disconnected with how food is grown and cooked than ever before. Excess salt, sugar, and saturated fats added to foods have been linked with rising public health problems, and changing food habits have distanced us from our bodies' natural hunger and fullness cues.

Traditional food systems play a significant role in maintaining the well-being and health of native communities. The traditional food choices include enhanced consumption of fruits, vegetables, and whole grains. By embracing traditional diets we can rediscover the joy in eating, as traditional diets are a delicious and pleasant way of enjoying healthy food for the rest of our lives. It has been reported that the deterrent of traditional foods to Western diets has caused a rise in obesity, cardiovascular disease, diabetes, and other health issues have increased in the last decade because of the availability of unhealthy foods. These are the risks of globalization when it comes to health and diets. It damages and shifts the developmental, cultural, and behavioral norms of its society. It changes food preferences.

Changing food patterns can damage the good health of the society. There is, therefore, a need to reassess existing food and nutrition-related health and agriculture policy, and develop cross-sectoral implementation strategies on food security, nutrition, and health. Further, there is need of continuous policy advocacy activities to educate functionaries across different sectors.

See also: Conversion of Renewable and Food Wastes into Useful Products With Environmental Perspectives. Upcycling Fresh Food Items in Retail Operations

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Local Skills for Moveable Factories

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Introduction

Moveable factories are a leapfrog technology. As mobile telephony and finance leapfrog over fixed infrastructure in telecommunications and banking, so mobile factories leapfrog over fixed industrial infrastructure in manufacturing. Lack of local production skills is no barrier to rapid deployment of moveable factories. This is because local skills for moveable factories can be instructed in a few days through on-the-job training. Rapid training is facilitated by engineering uncertainty out of production operations to be carried out with moveable factories.

Moveable Factories

The technical feasibility of production operations without industrial infrastructure is increased by the diversity and sophistication of manufacturing machines that are becoming small and light enough to fit into trucks, trailers, carry cases, etc. Operational practicality is increased by capability of moveable factories to carry their own energy generating equipment, such as solar panels, across rough terrain. Economic viability is increased by reduction in capital investment costs from not having to construct factory buildings, and reduction in variable operating costs through not having to operate factory buildings. Although manufacturing may still involve the consumption of some non-renewable resources, these improvements to feasibility, practicality and viability bring concomitant opportunities for increased ecological sustainability. For example, building smaller lighter manufacturing machines involves less consumption of non-renewable raw materials; the use of mobile renewable energy generation reduces expansion of fixed power grids deploying non-renewable energy sources; and reduced construction of factory buildings further reduces consumption of non-renewable materials. At the same time, moveable factories open up new opportunities for increasing social sustainability by providing production employment for local people (Fox, 2015).

Local Skills for Moveable Factories

Local skills for moveable factories are not dependent upon medieval skill training practices, such as long apprenticeships, or 19th Century practices, such as construction of fixed training centers in buildings. Rather, local skills for moveable factories can be instructed in a few days of on-the-job training: provided uncertainty is engineered out of production operations with moveable factories. This involves engineering production processes to be capable processes (Figs. 1 and 2). In other words, engineering production processes so they conform to the production specification within upper and lower specification limits. The fulfillment of end-user expectations depends upon production processes being capable from conversion of raw materials through to the final product (Oakland, 2007). Having set upper and lower specification limits, further refinement of production processes can be achieved by reducing situated entropy. In particular, where work is right-first-time, there is zero situated entropy. In other words, the expenditure of energy is focused upon productive work: rather than energy being dissipated in unproductive iterations of trial and error. Consider, for example, self-assembly furniture kits. Information is provided by the furniture kit components themselves that can only be put together one way.

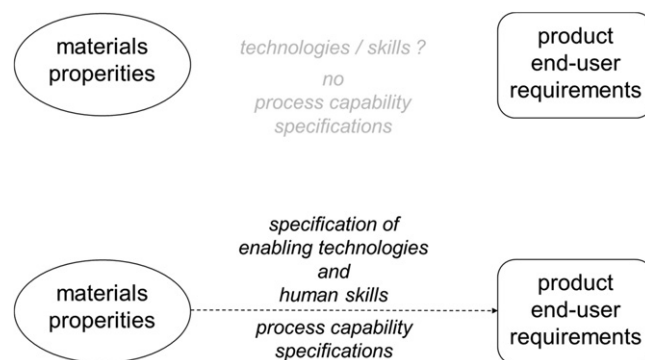


Fig. 1 Process capability specifications define technologies and skills.

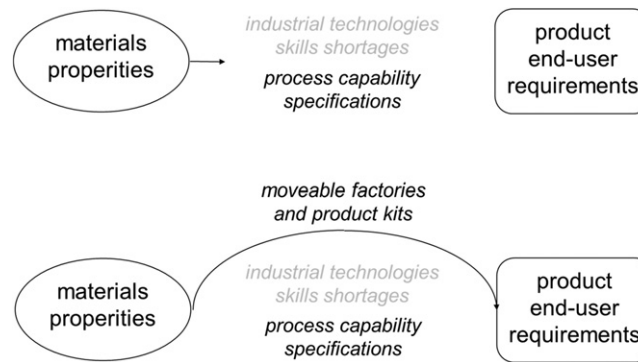


Fig. 2 Moveable factories together with product kits leapfrog over skill shortages.

Information is provided by the hand tools that will only fit connecting bolts etc., in one way. Information is provided by visual instructions that can only be read in one way. Where there is only one way that something can be done in a particular situation, there is zero situated entropy. Where there is zero situated entropy, there are no skill shortages where the work is situated. By contrast, the more ways there are of doing something, the higher the situated entropy and the larger the skills shortage (Fox and Kotelba, 2018).

Conclusions

Throughout the world, there are large regions of unmet demand and unemployed people. This pernicious combination leads to social unrest, rural exodus, over urbanization, and mass migrations. The persistent failure to address this global challenge is rooted in the fixation of policy makers on extending 19th Century industrialization and rooting the training of skills in medieval practices such as apprenticeships that last many years. Moveable factories leapfrog over lack of industrial infrastructure and lack of local production skills. By providing on-the-job training, moveable factories becoming moveable training factories as well as moveable production factories.

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Mining Industry

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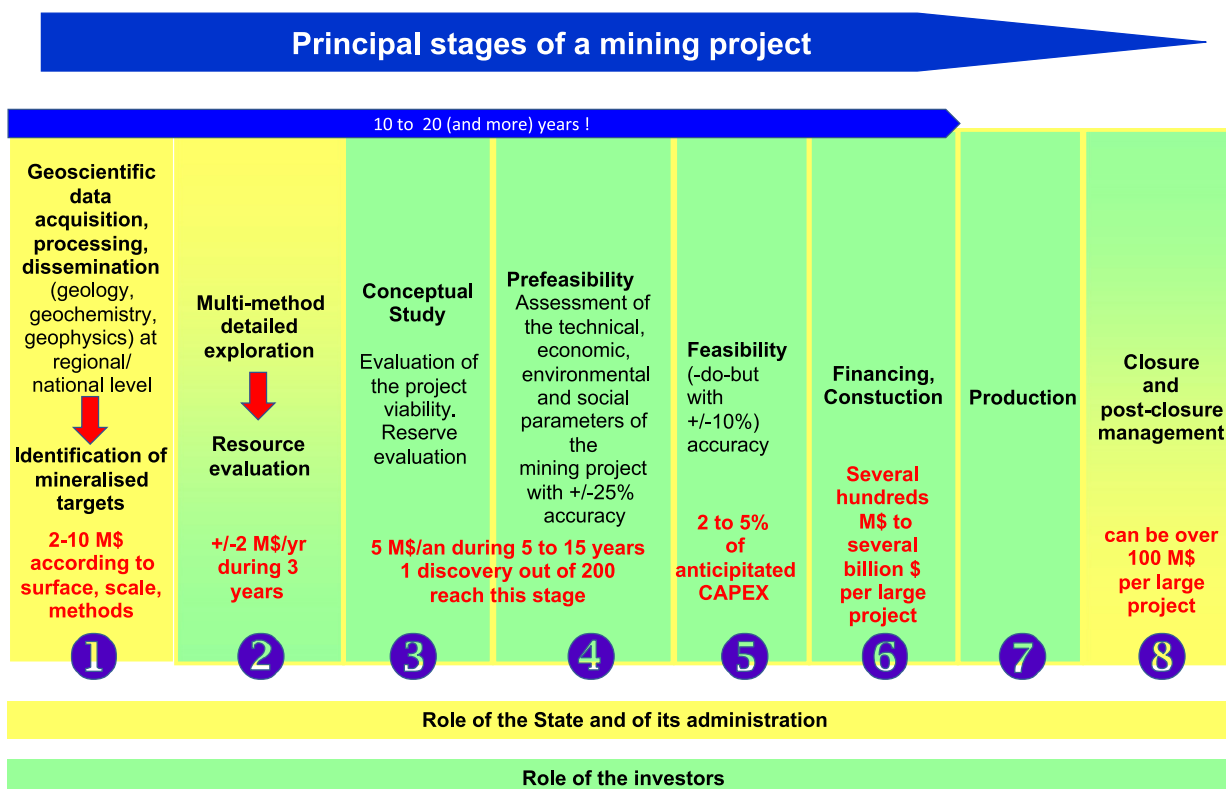
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Introduction to the Global Mining Industry

Together with agriculture and cattle rearing, mining, the process of extracting minerals from nature to turn them into the ever-growing range of products and services that humans nowadays rely on, is one of the oldest human industries. Nowadays, this industry comprises a myriad of very diverse activities of any scale, from artisanal (frequently informal) activities (Data and knowledge on this specific part of the global mining activities, of major social importance in a number of developing countries is provided by website present in “Relevant Websites section” and not further discussed here, as it has a limited role in the global production of minerals and metals, except for tantalum), to large scale highly capitalistic and complex industrial operations. It produces the minerals and metals needed by the infrastructure and many of the goods and services we, as humans, rely on. Almost every person living on Earth is depending on mining activities, however to different degrees of intensity ([International Resource Panel, 2011, 2019](#)), as the minerals and metals use of a country depends on its economic development level.

Modern industrial mining comprises all the very diverse activities ([Fig. 1](#)) that are needed to:

- Find (‘explore’) mineral concentrations of potential economic value (stage 1 and 2 in [Fig. 1](#)).
- Develop new mining projects through the assessment of the economic, environmental and social feasibility of their exploitation (stages 3 through 6 in [Fig. 1](#)).
- Mine these concentrations, to extract their economically valuable part (stage 7 in [Fig. 1](#)).
- Process the extracted material(s) in order to obtain marketable products meeting well-defined specifications (part of stage 7 in [Fig. 1](#)). Processing can involve several distinct steps. In the case of metals production, it mostly requires the production of a concentrate of the metal bearing mineral(s) contained in the natural metal bearing mineral assemblages known as ores. The valuable metal content of ores is extremely variable: while Brazilian or Australian iron ores commonly contain over 60% Fe, Chilean copper ores contain only about 0.6% copper, in average, and gold ores frequently contain less than 1 gram per ton.



Data shown in red, is indicative

Fig. 1 Simplified outline of the principal stages of an industrial-scale mining project. Figures in red are estimates of the average investment needed for industrial scale mining projects, based on Canadian mining projects.

- Close mining and related operations at their end-of-life and transfer back land that was leased for mining operations to its original owners or the state. Mine closure includes the decommissioning of the existing installations and, in principle, environmental restoration in order to avoid negative post-mining impacts (stage 8 in [Fig. 1](#)).

The mining industry has many specificities that differentiate it from other industries:

- The location of mines is determined by geology. This makes mines immovable assets.
- The importance of the framework conditions that attract or deter investment in specific jurisdictions, such as the quality of the geological database, the stability of the taxation and of the regulatory framework. Every year a report by the Canadian Fraser Institute ([Stedman and Green, 2018](#)) evaluates these framework conditions for a large number of jurisdictions.
- Minerals and metals are commodities. The price of one ton of copper is the same whether it comes from a Chilean, an US or a Polish mine. Mining companies have little or no influence on minerals and metals prices. These reflect demand and supply balances that are very difficult to forecast as they depend on multiple factors with complex feedback loops. These factors include speculative anticipations, technology shifts that can impact on both the demand or supply side, the development of recycling, of substitution or public policies ([Wellmer and Hagelüken, 2015](#)). Due to the commodity nature of minerals and metals also means that companies operating according higher sustainability standards than their competitors can't sell their products at higher prices than their competitors operating according to lower standards.
- The cost of mineral exploration and of the different stages necessary up to the demonstration of the economic and, nowadays, environmental and social feasibility of a project. In case of large-scale projects this can require tens of millions \$US without any certitude to ever recover this investment from a profitable mining operation.
- The risky capital expenditure needed to commission a new industrial-scale mine. A Global Data Energy survey of 483 mining projects worldwide, either in construction or predicted to enter the construction stage by 2020 ("see Relevant Websites section", (accessed 22.12.18)), shows that the average initial capital expenditure of these projects is 524 M \$US per mine, with wide fluctuations around this average. The capital expenditure varies a lot from project to project, reflecting the specificity of each mining project such as:
 - Differing production capacities;
 - Varying degrees of vertical integration (some projects have their own smelter/refinery while many only have ore processing plants);
 - Technical complexity and infrastructure requirements (some places on Earth have no energy and water supplying infrastructure).

For the largest and most complex projects the initial capital expenditure needed to build the mine and its auxiliary facilities can exceed 10 billion \$US.

- The average lead time from the initial discovery of a mineral concentration of potential economic interest and the commissioning of the related mine ranges from one to several decades. Project lead times depends on the economic attractiveness of the individual projects, the framework conditions existing in the different jurisdictions, the complexity of individual projects and their initial capital expenditure requirements. This lead time tends to get longer and longer in a number of jurisdictions as authorities impose that multiple detailed studies be completed and reviewed before granting the mining permit. These studies may include environmental and social baseline and impact assessments, environmental management and mine closure plans. prior to the delivery of the mining lease and mining permit that a company will need to obtain prior of building a new mine.
- The range of risks that may impact on mining projects at any of their stages (2 through 7 in [Fig. 1](#)) is wide. These include political instability, changes in applicable legal and taxation conditions, difficulties in obtaining the social license to operate, downturns in minerals and metals prices to name but a few risk factors typical of mining activities.

[Fig. 1](#) represents the main stages of mining projects from the initial geological surveys needed to locate potentially mineralized areas until mine closure, with an indication in \$US of the average investment required to finance each stage. No figure is given for the "production stage" as, under normal circumstances this stage generates revenue, whereby a part of it will be used to finance the capital expenditure that may be needed during mine life, for instance to finance an extension of the operations. The yellow background color shows where the role of States is predominant, through their public institutions (Geological survey, Department of Mines, Environmental Agency ...) promoting and regulating the development of mining activities. The green background highlights the stages where the role of investors, which can be private or public, is preminent.

More information on above stages can be found in specialized literature (see "Further Reading" at the end of this article) and websites such as the Canadian Queen's University Mine Design Wiki (see "Relevant Websites section").

While in China, the State directly or indirectly controls the mining industry via, for instance, regional banks, elsewhere minerals and metals industry activities are rarely vertically integrated in a single company. Exploration and the development of new projects the exceptions are essentially carried out by junior exploration companies ([Schodde, 2017](#), states that in the Western world junior companies make 70% of all the discoveries). Many of them listed on the Canadian (Toronto) or Australian (Sidney) stock markets. In its latest annual report on global mineral exploration, [S&P Global Market Intelligence \(2019\)](#), one of the leading consultancies specialized in minerals and metals related intelligence, states that over 3000 such companies are active worldwide. Larger mining companies, mostly transnational companies having the expertise and the resources needed to manage complex industrial projects, frequently take over advanced (Projects at the prefeasibility or feasibility stage. For a detailed overview of the design stages of new mining projects see for instance: website provided in "Relevant Websites section") projects to raise the capital needed for their

commissioning and then to operate the resulting mine and its related installations. Metallurgy and the related metal refining activities, where needed, are quite frequently run by different companies than mining operations. Taking the iron value chain as an example, the list of the world ten largest steelmakers (see “Relevant Websites section”) and of the ten largest iron ore producers (see “Relevant Websites section”) have only one company in common.

Most minerals and metals are produced by large transnational companies, with the exception of sand and gravel, ornamental and precious stone or tantalum, which are widely produced by smaller scale companies, and in the case of tantalum from the Democratic Republic of Congo or Rwanda, artisanal mines. In 2017, the 10 largest iron ore miners produced 53% of the world production, the top ten aluminum metal producers had an output of 56% of the global production, for copper this ratio was 47% and for nickel it was 64.

Except for the production of construction minerals and of dimension stone which is very widespread across the world, mining is concentrated in a rather limited number of countries. According to data from Reichl *et al.* (2018) (Fig. 2) only 16 countries contributed by value to 1%, or more, of the total world production. Nowadays, China is the world largest producer of 40 different minerals metals, including aluminum, cement and steel. On the basis of their per capita income level as defined by the World Bank (see “Relevant Websites section”), 4 out of the 16 countries listed are high income countries, and 9 of them are upper middle-income countries. Many of these countries developed their economic wealth due to a long history of mining and derived industrial and economic development.

Historically, up to the end of the 20th Century, the largest companies active in mining or metallurgy/refining had their history and headquarters rooted in a few countries with an ancient mining and/or metallurgical history and advanced financial services, mainly Australia, Brazil, Canada, the United Kingdom and the United States. Since the beginning of the current millennium large Chinese companies, as well as some Indian companies, appear among the world leading mining and metallurgical companies, in line with the rapid development of East Asia as the current economic powerhouse. In as little as three decades (1988–2017) China became the world largest producer of 40 minerals and metals (Schodde, 2018), reflecting the government’s strategy to foster economic dominance of some markets of major importance to the global economy such as consumer electronics, electric cars, information and communication technologies, solar panels, windmills.

Several public free-of-charge sources provide minerals and metals production statistics and, for some, much broader information about the global mining industry:

- The United States Geological Survey (see “Relevant Websites section”) provides production statistics, in some cases back to 1900, global reserves data, annual average minerals and metals prices, as well as annual reviews of the global industry organized per single minerals and metals or per individual countries and additional analysis.
- The British Geological Survey (see “Relevant Websites section”) provides production statistics, as well as additional analysis.
- World Mining Data (see “Relevant Websites section”), provides production statistics as well as country level estimates of the values of their productions.
- The Indian Bureau of Mines: in addition to information and data on India’s minerals and metals industry and trade it also provides global production data as well as some country level information (see “Relevant Websites section”).

In addition, various national authorities, such as Geological Surveys, provide national data and information in their respective national languages.

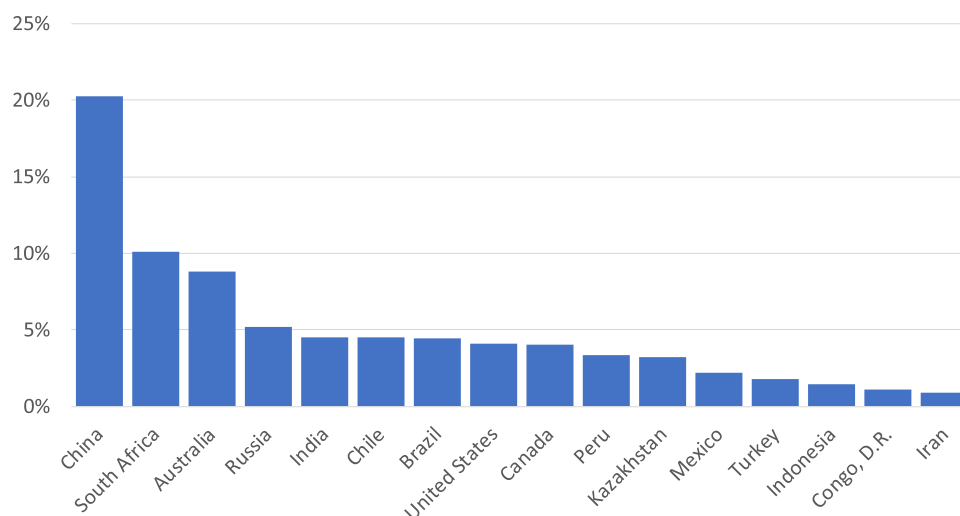


Fig. 2 World largest minerals and/or metals producing countries, ranked by their 2016 production value of non-energy minerals and metals, expressed in % of the world production value (approx. 745 billion \$US), not including the value of construction materials production (clay, cement, dimension stone, gravel, sand). Reproduced from Reichl, C., Schatz, M., Zsack, G., 2018. World Mining Data 2018 – Statistical Handbook. Austrian Ministry for Sustainability and Tourism. p. 263. <http://www.wmc.org.pl/sites/default/files/WMD2018.pdf>.

Mining Industry Segmentation

The mining industry comprises a number of main segments, defined according to the marketable products produced:

- Construction minerals: bulk or processed materials (*e.g.*, cement, clay, concrete, dimension stone, sand and gravel).
- Metals (including iron and ferro-alloys, non-ferrous and precious metals).
- Industrial minerals and derived products (*e.g.*, bentonite, gypsum, potash, phosphoric acid obtained from phosphate, sulfur).
- Precious and semi-precious minerals (*e.g.*, amethyst, emerald, diamond, ruby, tourmaline, sapphire).
- Energy resources (coal, lignite, peat, oil, gas, thorium, uranium).

As know-how, technologies and markets differ, most companies tend to specialize in only one of these segments, or even in the production of just one mineral or metal.

While this segmentation is widely used to document and describe the global mining industry, there is no global consensus about the segmentation of this industry, and different terms are used, for instance “minor metals”, a widely used term lacking a solid, reliable definition. These are supposed to be metals produced in small quantities, mostly as by-products of “main” or “carrier” metals, that are not traded via one of the specialized metals trading Exchanges (London Metal Exchange, Shanghai Futures Exchanges, New York Mercantile Exchange). There are some minor metals that hardly fit to this definition, for instance manganese, whose annual production (16 Mt in 2017 according to the USGS) is larger than the production of lead (4.7 Mt) or zinc (12.6 Mt), both traded on above mentioned exchanges. Manganese also is not recovered as a by-product.

It took the 1997 6 bn \$ fraud known as the Bre-X scandal, to trigger the development of a series of national resources and reserves reporting standards, providing data traceability and much improved transparency of exploration projects, up to the completed feasibility study. The Bre-X scandal happened in absence of a clear, enforced, regulatory framework on resources and reserves reporting by exploration companies: a junior company could lure unsuspecting investors towards the development of an allegedly major gold discovery on the island of Borneo (Indonesia), that finally proved to be a hoax.

The most widely known standards are the Canadian National Instrument NI 43-101 and the Australian JORC Code. The development of the international coordination of the various standards is the scope of CRIRSCO (Committee for Mineral Reserves International Reporting Standards) (ICMM, 2013). The UN Economic Commission for Europe (UNECE) develops the United Nations Framework Classification for Resources (UNFC) (UNECE, 2009) as a voluntary international resources and reserves reporting framework. The development of a global consensus on the definitions of the terms used in relation with the mining industry remains a field where progress is needed.

Mining, One of the Oldest Human Industries and One of the Most Modern Ones

The two oldest currently known underground mining activities were for flintstone, used for the production of tools and to light fires, at Nazlet Sabaha in Egypt, dated 40,000 years BCE, and for iron oxide at the Lion Cavern in the Ngwenya Mountains of western Eswatini (formerly Swaziland), also dated about 40,000 years BCE (see “Relevant Websites section”). The red colored iron oxide was probably used after crushing and grinding for body adornment and rock art. The production of stone tools started much earlier, some 3.3 million years BCE, even predating the appearance of the genus *Homo* by more than a million years (Harmand *et al.*, 2015). For more than 3 million years our ancestors use of the mineral realm was limited to the ever more sophisticated use of stone.

In the long human history, the use of metals only developed quite recently during the period from 7000–4000 years BCE, in a vast region covering parts of Mesopotamia (nowadays parts of Iran, Iraq, Syria and Turkey), Cyprus and Bulgaria to the West. Gold and, more rarely copper, naturally existing in their pure metallic form were the first metals used to produce artifacts. The extraction of copper from its natural mineral assemblages, named ore, through simple metallurgical processes appears to have developed during the same time. As arsenic is not unfrequently present in copper ores, some hard alloy of arsenious copper could be obtained that served to produce the first metallic plowshares, a major step in the development of Mesopotamia as a cradle of civilization. It also served to produce military hardware such as lances, daggers and arrow heads, an early illustration of the dual use of many technologies.

During Antiquity mining and metallurgical activities became locally very important economic activities. The Laurion silver mines located about 60 km East of Athens were critical to the cultural might of Athens, the Las Medullas gold mining and the Rio Tinto lead, silver and gold mines (both nowadays located in Spain) or the tin mining in Cornwall (nowadays in the United Kingdom) were major sources of wealth in support of the development of the Roman Empire. The long-distance trade of small amounts of minerals and metals also started well before the current era: the trade of oxhide copper ingots around the Mediterranean basin is documented about 1600 BCE (Rice Jones, 2007), amber from the Baltic coastline was discovered in Egyptian graves dated about 1400 BCE and glass beads of Egyptian origin, dating from the same period were discovered in Denmark (Varberg *et al.*, 2015).

Table 1 compares the estimated annual production of metals produced at the times of Emperor Augustus Roman Empire (27 BCE–476 CE) with their annual production in 2016, showing the massive production development that happened since these ancient times. Despite these early developments the production of minerals remained very limited up to the 20th century. It took

Table 1 Comparison the estimated average annual metals production rate at the times of the Roman Empire with their 2016 production at mine level (metric tonnes of metals contained in the ore)

Metal	Roman Empire, Augustus Reign (27 BCE–14 CE)		2016 mine production	
	Annual production estimate (in metric tonnes)	Source	Annual production (in metric tonnes)	Source
Silver	200	Varberg <i>et al.</i> (2015)	27,000	United States Geological Survey (2018)
Copper	15,000	De Callatay (2006)	19,400,000	United States Geological Survey (2018)
Iron/pig Iron	82,500	De Callatay (2006)	1,150,000,000	United States Geological Survey (2018)
Lead	80,000	De Callatay (2006)	4,820,000	United States Geological Survey (2018)
Gold	6	Varberg <i>et al.</i> (2015)	3100	United States Geological Survey (2018)

the many major discoveries made in engineering, in physics and in chemistry as well as the development of modern project management practices, particularly throughout the 19th and 20th centuries, to make modern mining and metallurgy possible. Before this industrial revolution mining techniques remained for centuries those described in [Al Hamdani's \(about 940\)](#) and [Agricolae \(1556\)](#) classical text books on mining and metallurgy.

Some of the landmark innovations that led to development of the modern mining industry are Newcomen's steam machine (1712), commercial electricity production (1870), dynamite (1866), ore minerals concentration by flotation (1886), and the numerous metallurgical and refining processes still used nowadays to produce aluminum (Bayer process for the production of alumina, 1888; Hall-Heroult process for the production of aluminum, 1886), steel (Bessemer process for the production of steel, 1856), copper (Outokumpu's flash smelting process, 1947). The continuous development of information and communication technologies that was triggered by the discoveries of the transistor (1947) and of the integrated circuit (1959) has also much contributed to the development of mining, ore processing and metallurgical technologies.

The development of ever larger bulk carrying ships after World War II, with the largest current vessels (the Brazilian Valemax vessels, Vale being a Brazilian iron ore producer) having a capacity of 400,000 t deadweight, was a major driver of the global trade of minerals and metals observed after World War II. While in 1950, Australia and Brazil respectively produced 2.4 and 1.9 Mt iron ore ([Melcher and Forbes, 1950](#)), in 2017 they respectively produced 880 and 440 Mt (A respective production rise of about 37,000% and 23,000%). The production of both countries is widely exported, essentially to China.

Innovations, as well the development of the mastery of large-scale industrial mass production during the first part of this century and around World War II (WWII) led to the massive development of the minerals and metals production recorded since the end of WWII ([Fig. 3](#)). While, within the 1927–2016 period (90 years) the human population rose by a factor of 275%, from 2 to 7.5 bn people, the cumulated tonnage of the minerals and metals represented grew by a factor of nearly 3200%. This highlights the massive development of material intensity happened since the 1950s, essentially in developed countries, leading to the development of large per capita stocks in society, with large differences between developed and developing countries ([International Resource Panel, 2011](#)).

After World War II, several European countries, as well as Australia, Canada, Japan, New Zealand, South Korea and the USA witnessed rapid economic growth, fueled by the need for reconstruction and rising living standards driving a rapid rise of the demand for minerals and metals until the two successive energy shocks of 1973 and 1979. Afterwards, their growth continued but at a reduced rate, as the demand for new infrastructure reduced and consumer goods became more resource efficient. A new, intense, demand for minerals and metals developed from 2002 onwards, due to the extremely rapid development of the Chinese economy. The 2008 economic crisis only temporarily reduced the demand for ever more minerals and metals.

The technologies, and the related skills, equipment and capital investment, needed nowadays by the mining industry are extremely diverse. They range from simple manual digging of galleries with basic tools such as digger's spikes, shovels, hammers, chisels widely used in informal artisanal mining up to advanced heavy and complex machinery that are increasingly embedding sensors, and complex functions such as 3D modeling of ore deposits and mine planning, preventive maintenance, real-time process and cost control or remote wireless/automated operation of mine or haulage equipment.

[Fig. 4](#) shows the development of the world production from 1927 to 2016, expressed in metric tonnes, of the same metals and minerals shown than those shown in [Fig. 3](#). This time the 1927 production is expressed as a basis level of 100, common to all selected minerals and metals. It shows that in just ninety years the production of aluminum grew by a factor of over 250 times the 1927 production, that the production of cement, chrome and nickel grew by factors in the 60–70 range, while copper, iron, manganese, phosphate, potash and zinc productions grew by factors comprised between 8 and 25.

The continued growth of the demand for minerals and metals observed since WWII is likely to continue over the coming decades ([Christmann, 2018](#); [Elshkaki *et al.*, 2018](#)), driven by demographic growth, the rapid development of the global middle-middle class ([Kharas, 2017](#)) and the continued urbanization of the world population ([United Nations, 2018](#)). The transition towards the use of low-carbon energy production to combat climate change will further stimulate the demand for several minerals and metals such as aluminum, cement and concrete, copper, steel and some rarer metals needed, to build wind and solar energy based production, storage and transportation capacities. The deployment of electric vehicles needed to improve urban air quality

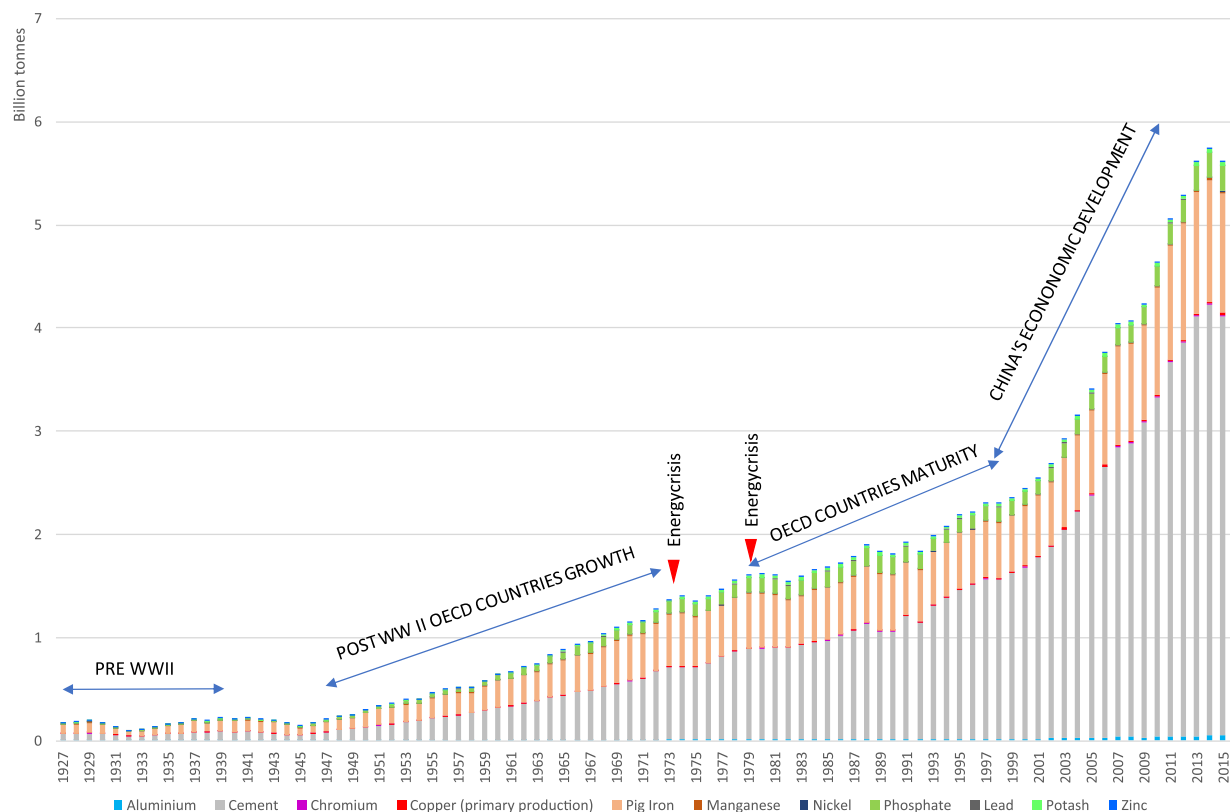


Fig. 3 Production from 1927 to 2016, in billion metric tonnes, of a selection of widely used minerals and metals. Data from Kelly, T.D., Matos, G.R., 2018. Historical statistics for mineral and material commodities in the United States. United States Geological Survey. Data Series 140 Reston, Virginia, USA. Available at: <http://minerals.usgs.gov/minerals/pubs/historical-statistics/> for all data points, except for the 2012–2016 chromium production, taken from Reichl, C., Schatz, M., Zsack, G., 2018. World Mining Data 2018 – Statistical Handbook. Austrian Ministry for Sustainability and Tourism. p. 263. <http://www.wmc.org.pl/sites/default/files/WMD2018.pdf>, and for the other 2016 production data from U.S. Geological Survey, 2018. Mineral commodity summaries 2018. U.S. Geological Survey, p. 200. Available at: [doi:10.3133/70194932](https://doi.org/10.3133/70194932).

and the growing use of desalinated sea water to supply water to regions where surface and/or groundwater are scarce will also contribute to stimulate the future demand for more minerals and metals (Arrobas *et al.*, 2017; International Energy Agency, 2015; Moss *et al.*, 2013; OECD, 2018).

Sustainability Challenges: The Need for a Global Mineral Resources Governance Based on a Sustainable Development License to Operate (SDLO)

Despite the progress in minerals and metals recycling, recycling rates of many metals remain very low (Fig. 5, International Resource Panel, 2011) for a wide range of metals, especially the rarer ones used in small quantities in electric appliances, electronics, car or aircraft construction. In many of these end-uses they are difficult to economically recycle (International Resource Panel, 2013a) as products have not been conceived in view of the end-of-life recycling of the minerals and metals they contain, or because the prices of primary minerals or metals are too low and recycling technologies too complex to make them economically profitable. Another limit to recycling is the long use phase of some metals in a context of a continuing exponential growth of the demand: aluminum, copper and steel based products can have use phases of many decades, meaning that even if 100% of the corresponding stock would be recycled at the end-of-life of these products (rails, electric generation and transmission infrastructure, built infrastructure, aircraft ...) the recycled flow would only partly meet the demand.

The production of minerals and metals has important environmental impacts, both at their production sites, and globally through global greenhouse gas (GHG) emissions and, in some cases mercury emissions (International Resource Panel, 2013b; Kesler and Simon, 2015; United Nations Environment, 2013). These impacts are extremely variable, depending on the nature of the minerals or ore mined, on the processes used for mining, mineral processing and metallurgy/refining in the case of the production of metals. Impacts also depend on the energy sources used, coal being the most problematic, as well as on local environmental factors, on the governance of the operating companies, on the quality of the applicable local regulatory framework and of its effective implementation.

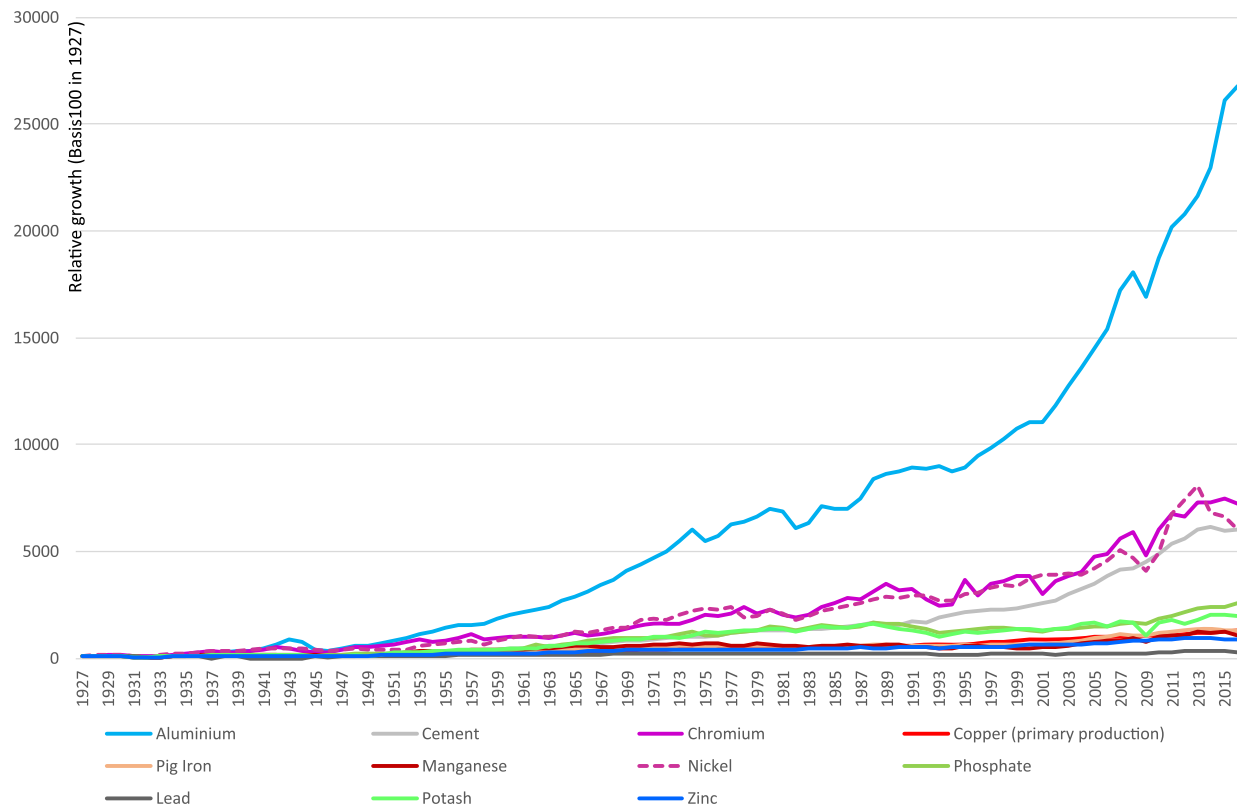


Fig. 4 Production growth of the same selection of minerals and metals than in Fig. 3, over the 1927–2016 period. Basis 100 in 1927 common to all minerals and metals. Data from Kelly, T.D., Matos, G.R., 2018. Historical statistics for mineral and material commodities in the United States. United States Geological Survey Data Series. 140 Reston, Virginia, USA. Available at: <http://minerals.usgs.gov/minerals/pubs/historical-statistics/> for all data points, except for the 2012–2016 chromium production, taken from Reichl, C., Schatz, M., Zsack, G., 2018. World Mining Data 2018 – Statistical Handbook. Austrian Ministry for Sustainability and Tourism. p. 263. <http://www.wmc.org.pl/sites/default/files/WMD2018.pdf>, and for the other 2016 production data from U.S. Geological Survey, 2018. Mineral commodity summaries 2018: U.S. Geological Survey, p. 200. Available at: [doi:10.3133/70194932](https://doi.org/10.3133/70194932).

In addition of a mineral resource, the production of minerals and metals requires different inputs, essentially energy (as electrical power, fuels and explosives), water and a wide range of chemicals that may be needed for mineral processing, metallurgy and refining. The OECD (2018) estimates that the production of the most common metals (aluminum, copper, iron, lead, manganese, nickel and zinc) is the cause of 7% of the current GHG emissions, while concrete is the cause of an additional 9%. By 2060 they could respectively represent 9% and 12% of the global GHG emissions. In Chile, the world largest copper producer (about 28% of the 2017 world copper production) it took an average of 94,000 litres of water per ton of copper produced. Water can be an extremely scarce resource in very dry regions, such as the northern part of Chile where most of the very large mines are located.

Emissions of GHG and of other gases such as sulfur and nitrogen oxides, vaporized metals or particulate matter can all happen during the production of minerals. The production of minerals and metals can also generate enormous amounts of residual solid waste, especially of ore processing tailings, a sand like material that is the uneconomic part of the original ore after the recovery of the valuable minerals. In addition to chemical residues, tailings can contain residual metal bearing minerals either because processes used to recover these minerals never have a 100% efficiency or because these metals are in minerals that were not considered as economic to recover. From there metallic ions may be leached out and form chemical compounds that can be harmful to humans and/or the environment. The issues can be particularly problematic in the case of low grade ores that contain a range of by-products metals that remain in tailings or metallurgical slag. In this context copper and gold ores can be of particular concern. Gold ores generally have grades of only a few grams gold per ton, meaning that 99.99% of the extracted ore will become tailings. In the case of Chilean copper ore, the average grade is about 0.6% Cu, meaning that 99.4% of the extracted ore will become tailings. In both cases these tailings may contain arsenic, cadmium, lead, mercury selenium and tellurium which can migrate into the environment.

The impacts of past mining activities can last for centuries after the closure of a given mine. The migration of harmful chemical compounds into surface or groundwater, soil contamination, wind dissemination of contaminated dust, and/or land subsidence due to the collapse of underground cavities resulting from mining activities can be cause of long-lasting harm. These impacts can be aggravated by local natural conditions such as important seismic and/or volcanic activity and/or landslides. The mitigation of

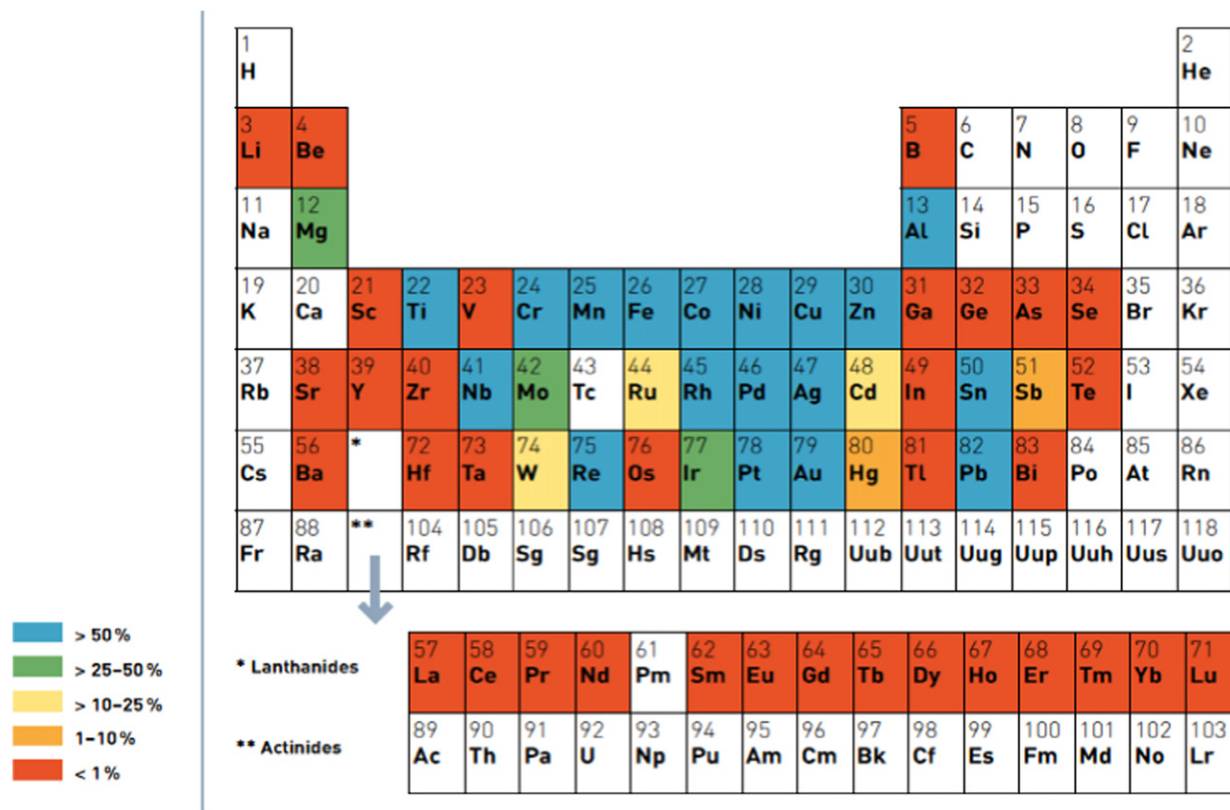


Fig. 5 Recycling rates of 60 elements, mostly metals, from end-of-life products. Source: International Resource Panel (IRP), 2011. Recycling rates of metals – A status report (it is its Fig. 4). A report of the working group on the global metal flows to the UNEP international resource panel. In: Graedel, T.E., Allwood, J., Birat, J.-P., *et al.* (Eds.), UNEP. Nairobi, Kenya. http://www.unep.org/resourcepanel/Portals/24102/PDFs/Metals_Recycling_Rates_110412-1.pdf.

these impacts and the clean-up of derelict mining sites can be very costly to generations of taxpayers that did not benefit from the past mining activities (Indian and Northern Affairs Canada, 2010; Lysyk, 2015). It is only since some years that the cost of future mine closure and of site remediation are integrated in the feasibility studies and properly provisioned for by some companies.

Raising awareness of populations about the potential impacts of mining activities can lead to conflicts that, in the worst case, have a high human toll (Hammond, 2012) or simply ruin an investment, such as the recent Minas Congas conflict in Peru. New mining projects are confronted with a rising opposition to new large-scale mining projects and with the demand of various government for ever more detailed environmental impact assessments. At the same time the demand for minerals is growing and, in total contradiction, the ever growing part of the richer part of the world population demands more and more minerals and metals.

Despite its impacts, the mining industry is vital to humankind and it contributes in many ways to the United Nations Sustainable Development Goals (UN SDGs) (Columbia Center on Sustainable Investment, 2016).

To further strengthen the positive linkages between the minerals and metals industry and the UN SDGs requires:

- A strong, publicly verifiable, indicators based, commitment of individual companies to these goals.
- Market recognition of good corporate practice.
- Effective regulatory frameworks, including for international trade, enshrining sustainable environmental and social conditions.

Meeting the challenges of the 21st century requires the definition of a Sustainable Development License to Operate, based on:

- The recognition and verifiable involvement by mining companies and governments of populations living in the vicinity of future mining, ore processing and/or metallurgical projects. Local populations are an important stakeholder that needs to be associated to the design and planning of new projects from their early stage (exploration). Local populations need to be convinced about the sustainable benefits that will result for them from the project, and how the ecosystemic services they depend on for their livelihoods will be protected.
- Transparency and publicity of projects from their earliest planning stages (stages 2–5 in Fig. 1). In this context the Canadian regulatory obligation, known as National instrument NI 43-101 (Canadian Institute of Mining, Metallurgy and Petroleum, 2016), that makes it compulsory for any company listed on a Canadian stock market to report and publicly disclose its exploration and mine planning activities in a specified format, should be considered as good practice.

- Allocation of mining permits on the basis of public feasibility studies. For larger projects and/or projects liable to generate significant environmental and/or social impacts, the feasibility study needs to comprise environmental and social baseline studies and impact assessments, auditable environmental management strategies and plans, a social development plan, provisions for an annual sustainability reporting, a mine closure and a post closure monitoring and management plan with the guarantees necessary for their financing by the future mining activities;
- Quadruple (economic, environmental, governance and social) public sustainability reporting of producing mines, ore processing and metallurgical/ refining facilities with production above a given threshold or liable to produce significant impacts. The current best practice in this respect is reporting using the mines and metals industry reporting standards developed by the [Global Reporting Initiative \(2013\)](#) and the ISO 26000 standard.

These regulatory obligations need to be adjusted for smaller projects and those that have demonstrably limited environmental and social impacts.

However regulatory frameworks, and especially the public capacity to effectively implement them, remain weak in some countries due to a number of factors ([World Bank, 2017](#)) with regulatory frameworks not properly integrating sustainable development issues and/or institutions such as Geological Surveys, Mining Directorates and Environmental Departments not being properly supported, in terms of budgetary, human and technical resources to properly develop and enforce pro-sustainable development regulatory frameworks.

In addition, as stated by [Ali et al. \(2017\)](#) "*International environmental policy is currently missing the resource dimension for meeting both ecological and development targets.*". Unfortunately, instead of working on the development of the sustainability based global playing field, based on the SDLO, with transparency and quadruple bottom-line accountability, there is a growing trend towards resource nationalism. China, as the world largest producer of 40 minerals and metals, needs to play a leading role in fostering the transparency and the quadruple bottomline accountability of the global mines and metals industry, including for their operations outside of China. So far its efforts remain very modest.

The issues ahead call for much more international cooperation, to set up the needed global governance framework needed to address them. The creation of an International Mineral Raw Materials Agency based on the model used to develop the International Energy Agency (See "Relevant Websites section") could be an important step in the right direction. From a sustainability perspective there would also be much scope for a decommodification of minerals and metals, whereby economic incentives should be given to minerals and metals produced by companies offering verifiable high-level sustainability performance.

See also: Green Mining of Rare Earth Elements (REE) to Diminish Greenhouse Gas (GHG) Footprint

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Plant-Microbe Interaction: An Ecofriendly Approach for the Remediation of Metal Contaminated Environments

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Introduction

Heavy metal contamination has become a serious problem for all over the world due to indiscriminate use of anthropogenic activities. Heavy metals include a heterogeneous group of elements having relatively high density ($< 5 \text{ g/cm}^3$) and atomic weight. Heavy metals naturally exist in the earth, but their concentration is continuously increases due to rapid industrial and human activities (Nagajyoti *et al.*, 2010). Heavy metals are non-degradable due to their complex chemical composition and thus persist into the environment for years and years.

Industrial activities such as smelting, tanning and mining, pulping, dyeing, food processing, electroplating, chemical manufacturing are the major point sources for the metal contamination into the environment. These all industries are highly water consuming industries i.e., these are using a huge amount of water for their processing and after processing them, also release water as in the form of effluent or wastewater (Mishra and Bharagava, 2016; Dixit *et al.*, 2015). The wastewater released from such industries containing a rich amount of pollutant both organic and inorganic and metals. Most of the metal ions such as mercury, cadmium, chromium, lead, and nickel are highly toxic in nature and tend to accumulate in living organisms causing carcinogenic, genotoxic, mutagenic and teratogenic disabilities (Yadav *et al.*, 2017). Heavy metals are become an issue of public health concern about environmental contamination and pollution. Thus, it is very essential to remove or reduce heavy metal contamination from the environment in order to protect the ecological balance of between aquatic and terrestrial ecosystems. According to World health Organization (WHO) every year 15,000 metric tons of cadmium is added to oceans.

The negative effects of metal pollution on the environment and human health, becomes an issue of serious matter of concern, which needs an alternative methods for excavation and incineration for the clean-up of metal contaminated sites resulted in the emergent of advanced and environment friendly applications of bioremediation practices.

Rhizoremediation is one of the best, widely accepted, cost effective bioremediation technique that subsequently focus on the application of rhizospheric microorganism and interaction with plant under stresses environment (Hryniewicz and Baum, 2011). Under metal contaminated environment, the application of rhizospheric microorganisms can enormous, since they are able to increase the tolerance level of plants against higher concentrations of toxic metals, enhances plant growth and accelerated the accumulation and biodegradation of toxic metals and other pollutants to in a more efficient way. Hence, here in this article, we will discuss the burning problem of heavy metal pollution originating from increased industrialization and urbanization and its management practices by using metal and microbes interactions in an ecofriendly manner.

Metal Contamination in Environment & its Sources

There are two main routes of heavy metals into the environment the first one is natural weathering of parent rock material and second through anthropogenic activities. Natural sources include paedogenesis and weathering of minerals, volcanic activities, and erosion. Whereas, anthropogenic sources includes various industrial and domestic activities such as smelting, electroplating, tanning, mining, use of chemical fertilizers and pesticides in agricultural practices, paints, pigments and dyes in textile and food processing industries (Gadd, 2010). Regular practices of mining procedures from coal mines for the extraction of metals such as Cd, As, Fe, Cr, Pb etc., are mainly responsible for the direct contamination of these metals into the nearby soil areas. Paint and electroplating based industries contributes for the Pb and Cd contamination into the environment. Tanning industries are the biggest source of Cr contamination because of its chrome tanning process using chromium salts (Bharagava and Mishra, 2018).

The widespread use of chemical fertilizers in agricultural practices for crop yielding donates substantial amounts of various toxic metals like Mo, Fe, Zn, Ni and Pb to the soil in the form of macro and micronutrient elements. However, these metals play an essential role in the metabolic and enzymatic processes of plant growth and soil fertility, but their excess concentration in soil results in toxic detrimental effect on plants soil and on humans as well (Reeves and Baker, 2000). The untreated wastewater and sludge emanating from such industries is the major source of metal pollution in water bodies and land areas. Once the metals enters into the water or soil systems above their permissible limit, becomes toxic in nature and are able to cause serious various complications in human, plants, animals as well as in aquatic and terrestrial biota (Zhang *et al.*, 2011). The heavy metals become a

major threat to the soil and water systems because of their extensive use and demand in industrial sectors. The heavy metals released from industrial activities, possess harmful effects which directly affect the biodiversity of any ecosystem (Arao *et al.*, 2010).

Toxicity of Metals in Environment & Living Beings

Metals play a vital role as a catalyst, co-factor and or in associated form in enzymatic and non-enzymatic reactions in biological processes of any living organism. However, their higher dose could be lethal for any living being and ecosystem as well. Many heavy metals such as calcium, cobalt, nickel, copper, iron, potassium, magnesium, sodium, zinc are essential and required in a trace amount as micronutrients and therefore are called “trace metals” or “trace element” (Wuana and Okieimen, 2011). Trace metals actively take part in redox-processes and enzymatic processes for proper functioning of metabolic reactions. Some metals like aluminum, silver, lead, and mercury have no defined role in biological systems so they are known as non-essential metals and these may be considered potentially more toxic than trace metals.

However, the higher concentration of both essential and non-essential heavy metal is extremely toxic and lethal for humans, animals and plants as well. As, which is predominantly used as coloring in textiles, is conspicuously lethal, causing cancer and numerous other health disorders like skin damage, and circulatory problems (Scragg, 2006; Yadav *et al.*, 2017). Cd is ranked as the sixth most toxic metal which severely affects metabolic rate of Ca^{+2} ion resulting in low muscle power, bone fractures, cartilage disorders, kidney damage (ATSDR, 2008). It also causes indirect oxidative stress and nutrient deficiency in plants too by inhibiting enzymatic reaction (Irfan *et al.*, 2013; Giaginis *et al.*, 2006). Pb is highly toxic and hazardous metal, when enters into the human body causes infertility and memory dysfunction. It prominently plays a role in the severe Pb-poisoning in infants and young children, which leads to even death also by altering cell signaling, protein folding and inhibitory effects on di and monovalent cations (Monterroso *et al.*, 2003; Flora *et al.*, 2007). Pb toxicity in plants results in membrane damage, disruption of photosynthetic cycle and production of reactive oxygen species (ROS), has detrimental effect on plant (Najeeb *et al.*, 2014).

Hg is a well-known hazardous and exceedingly poisonous, causing neurotoxicity, gastrointestinal toxicity and nephrotoxicity. It also results in protein damaging, cellular dysfunction, lipid peroxidation and accumulation of neurotoxic molecules (Tchounwou *et al.*, 2003; Patrick, 2002). Chromium is well reported extremely toxic, priority pollutant, designated as “Human carcinogen” metal by International Association of Research Cancer (IARC, 1990). Cr toxicity leading to severe health implications like; nasal irritation, lung carcinoma, hearing impairment, causes mutations and genotoxic abnormalities (Stern, 2010; Mishra and Bhargava, 2016). It severely affects soil fertility and plant growth by the destruction of microbial diversity. Ni, Zn and Cu play an important role as a catalyst in various metabolic reactions in humans and plants as well, however, its excess concentration beyond the required amount makes them toxic and leads to disruptions of enzymatic reactions and metabolic processes (Nagajyoti *et al.*, 2010). Thus, the continuous entrance of metals through anthropogenic or natural sources into the various fractions of environments, results into severe toxicological effects on humans and plants as well, beyond exceeding concentration of their permissible limits.

Remediation Approaches

The increasing concentration of heavy metals into the environment is a drastic challenging problem which ultimately affects all the life forms present on earth in a direct way or sometimes indirect way. There are various remediation technologies that have been used for the removal and reduction of toxic heavy metals from contaminated areas. Removal of heavy metals from the environment is very essential for safe and healthy environment. Some useful remediation technologies are summarized as below:

Conventional

The conventional treatment approaches that involve various physical and chemical practices like chemical precipitation, ion exchange, electrochemical treatment technologies. But, all these methods have significant disadvantage of incomplete removal, high energy requirements, costly maintenance, and production of secondary pollutants and generation of enormous amount of toxic sludge (Chandra *et al.*, 2011). Metal remediation can be achieved by physical excavation and transport of polluted soil to landfills. Apart from the risk of metal dispersal during transport of contaminated sites, makes these methods more time consuming and expensive. Scarcity of landfills is also a big problem for the disposal of metal contaminated wastes. Therefore, the application of conventional approaches is not very reliable and suitable for the remediation of metal contaminated sites.

Bioremediation

Bioremediation is an ecofriendly cleaner technology for the remediation of organic, inorganic and metal pollutants present into the environment in safe and healthy way (Saratale *et al.*, 2007; Bhosale *et al.*, 2006). This technology uses biological systems, plants, animals including microorganisms. Past few decades, the use conventional treatment technologies for the clean-up of various contaminants from environmental matrices creating an indirect pollution problem for the living beings and environment by the generation of secondary pollutants and sludge (Chandra *et al.*, 2011).

Thus, conventional technologies are not very reliable and safe from environmental perspective. Bioremediation is a multidisciplinary approach; it involves both in-situ as well as ex-situ method of treatment for any kind of contaminants. Microbes are best suited for bioremediation technology because of their vast adaptability in any environment. Microbes are easily adapted and grow in extreme environmental and nutritional conditions. The microorganism can be utilized in bioremediation practices in several ways such as:

- (1) *Biostimulation*: This process enhances the activity of indigenous microbes with the addition of adequate amounts of nutrients, water and oxygen into the soil. Application of different rate limiting nutrients and electron acceptors such as carbon, nitrogen and phosphorus are required for the modification of existing environment and facilitate the metabolic activities and growth of native bacterial population for the effective bioremediation. The main advantage of this application is that bioremediation process carries out by indigenous microbes that are well suited and spatially distributed in the contaminated environment (Simpanen *et al.*, 2016).
- (2) *Bioaugmentation*: It is the practice of addition of microbial culture to the soil and water subsurface to speed up the process of biodegradation. Microbes that are isolated from site of pollution are able for the degradation or transformation of pollutants, but sometimes this process is very and inefficient. So the introduction of exogenous varieties of microbes can improve the remediation process (Anjaneyulu *et al.*, 2005).
- (3) *Bioventing*: It is one of the promising new technologies, which boost-up the natural in-situ biodegradation of any aerobically degradable compounds in soil by providing oxygen to existing soil microorganisms. It mainly stimulates aerobic biodegradation with the help of delivering pure oxygen into the unsaturated zone through gas injection or extraction wells installed into the soil (Brown *et al.*, 2017).

Rhizoremediation

Rhizoremediation is a specific process of phytoremediation which shows the keen relationship between rhizospheric microorganism and plant root zone for the degradation and detoxification of heavy metals and other toxic pollutants (Thijs and Vangronsveld, 2015). Microbes can form a close relationship with the root region of plant including its root tissue system, root surface known as “**rhizoplane**” and in the soil particles attached to root region known as “**rhizosphere**” (Gaskins *et al.*, 1984). A variety of microorganisms can be found in the rhizosphere micro-habitat but, the highest proportion of microorganism which inhabit the rhizosphere are bacteria and fungi. Among bacterial population, *Pseudomonads* are well reported for their dominating space in the rhizosphere. These bacteria live in the root region of plants in metal contaminated soils by developing survival strategies like: resistance to metal either by sequester/bioaccumulate or biosorption process into the cell. Rhizospheric microbes are also able to transform toxic metal state to non-toxic or less toxic by enzymatic detoxification mechanism or by exo-polysaccharide production (Kamaludeen and Ramasamy, 2008). Root associated bacteria and fungi interact with plant improves plants growth as well fertility of soil.

Role of Rhizospheric Microorganisms in Plants Growth and Remediation of Metal Contaminated Sites

Plant Growth Promoting Rhizobacteria (PGPRs)

PGPRs play an important role in the rhizospheric microbial community. These microbes can directly increase the bioremediation process by altering the metal availability through the production of various phytohormones, changing pH, discharge of chelator etc. Mostly PGPRs endorse plant growth directly by enabling resource procurement as or by diminishing the inhibitory effects of several pathogens on plant growth in the form of bio-control agent (Glick, 2012). *Pseudomonas*, *Bacillus*, *Brevibacillus* are well known to promote growth and yield in different hyper accumulator plants and used in rhizoremediation of metal contaminated environments. PGPRs also act as biocontrol agents, which do not necessarily inhibit pathogens but increase plant growth through the improved cycling of nutrients and minerals such as nitrogen, phosphates and other nutrients (Ryan *et al.*, 2008). Most of the phosphorus and potassium available in the soil is in the insoluble form and cannot be utilized by plants. Phosphate solubilizing rhizobacterial strains have ability to solubilize insoluble phosphorus with the production of organic acids and enhance minerals availability to plants (Meena *et al.*, 2014; Gusain *et al.*, 2015). There are two common types of PGPRs associations are found in the rhizosphere zone are: (a) Extracellular plant growth promoting rhizobacteria (ePGPR) and (b) Intracellular plant growth promoting rhizobacteria (iPGPR) on the basis of their interaction with root cells of host plant (Bhattacharyya and Jha, 2012; Glick, 2012). Metal resistant PGPRs strains are capable to tolerate high concentration of toxic metals and possess efficient uptake and accumulation of heavy metals and therefore can be effectively used in metal contaminated environments.

When PGPR are introduced to a contaminated site, they increased the potential for plants that grow there to sequester heavy metals and recycle nutrients, maintain soil structure, detoxify chemicals and control diseases and pests. PGPR also decreases metal toxicity by developing mechanisms of biotransformation, biosorption, bioaccumulation, and biomineralization. In this multi-component system, the plants in turn provide the microorganisms with various essential root exudates such as free amino acids, proteins, carbohydrates, alcohols, vitamins and hormones, which are important sources of their nutrition. The rhizosphere has high concentrations of root exuded nutrients and attracts more bacteria than does bulk soil.

These bacteria of the rhizosphere, facilitate plant growth by increasing nutrient uptake availability, produce phytohormones like indole 3-acetic acid (IAA) and provides protection to the plants against pathogenic attacks by bio control and antagonistic activities (Ahemad, 2012). PGPRs can remediate the contaminated environment by affecting plant growth

through direct and indirect mechanism includes siderophore production, phosphate solubilization and production of 1-aminocyclopropane-1-carboxylate (ACC) deaminase and other plant growth, which provide resistance to plants against higher concentration of toxic metals and helps in the detoxification, bioaccumulation and transformation of toxic metals into less toxic or non-toxic states (Bhattacharyya and Jha, 2012; Glick, 2012).

Mycorrhiza

Rhizoremediation through the application of mycorrhizal fungi is a viable approach for the decontamination of polluted environments in a natural way. This not only helps in the biodegradation of soil contaminants but, also stimulates the soil fertility and microbial diversity by increasing nutrients uptake ability of plant (Chibuikwe, 2013). Heavy metals like Cd, Zn, Pb, Cr and As adversely affects soil properties by reducing microbial diversity and nitrogen fixation ability. "Mycorrhiza" is the symbiotic relationship between the fungal species and roots of vascular plants. Mycorrhizal fungi help in improving plant growth by increasing surface area of the plant's roots which enhances its nutrient and water uptake ability from soil. It increases the bioavailability of nutrients especially phosphorus and nitrogen, reduces environmental stress related with low level of water and increasing the resistance to pathogenic microorganisms by stimulating phyto-hormones (Merkl *et al.*, 2005; Kohler *et al.*, 2007).

Mycorrhizal fungi can protect plants from abiotic (e.g., increased heavy metal concentrations) and biotic (e.g., soil-borne pathogens) stress through enhanced nutrient supply. It actually acts as filters for plants that prevent the entrance of toxic metals by the use of their mycelium. However, plants in reverse provide nutrients substances like carbohydrates for the survival and growth of fungal cells. Mycorrhizae can only be found in plant roots hence they can also be called as modified form of rhizoremediation that explores the beneficial effects of mycorrhizal fungi.

There are mainly two common types of mycorrhizal associations are seen in plants: ecto-mycorrhizae (EM) and Arbuscular mycorrhizae (AM). Among which, Arbuscular mycorrhizae (AM), has been recently proved to remove toxic pollutants and enhanced rate of rhizoremediation by improving soil structure and plant tolerance to toxic metals and organic and inorganic pollutants (Chibuikwe, 2013). AM can alleviate root exudation process which also helps to improve rhizospheric microbial activity and remove pollutants by plants uptake and accumulation.

Metal-Microbe Interaction

Microorganism especially bacteria are believed to be the most diverse organism on earth which are ubiquitous and can survive in any extreme or inadequate conditions. They are able to evolved different tolerance mechanisms under stress condition for their survival. Moreover, in response to direct exposure to metal pollution, microorganisms have developed metal tolerance mechanisms under metal polluted environments. Microorganisms play an important role and in the remediation of metal contaminated soil and wastewaters. Microorganisms offer an ecofriendly and cost effective approach for the removal of toxic metal pollutant with considerable operation flexibility. Microorganisms are capable to degrade or reduce a wide range of pollutants including organic, inorganic and metals (Lloyd and Lovley, 2001). However, metals cannot be purely degraded or destroyed by microorganisms, but, they can influence metals mobility in the environment by altering or transforming their chemical and physical states (Eccles, 1999). Continuous discharge of industrial wastes, have resulted in the accumulation of high concentration of toxic metals into the environment. It has been well reported that microorganism especially bacteria capable to reduce metals from their highly toxic state into less toxic or non-toxic state by developing a variety of resistance mechanisms (Silver, 1992). Bacteria possess various types of heavy metal resistance mechanism including cellular accumulation, biosorption, intracellular and extracellular sequestration, plasmid resistance and enzymatic reduction or detoxification (Maier *et al.*, 2009). Microbial interaction with metals is highly advantageous in bioleaching, bioventing, bio-transformation of complete or partial mineralization of metal contaminated sites (Ehrlich, 1997).

Microbes have significantly affected the bioavailability and mobility of metals into the environment. Microorganisms secrete a variety of inorganic metabolic products of carbonate, sulfide, phosphate ions to form precipitated complex with toxic metals ions by the process of non-enzymatic detoxification. Microorganisms have evolved metal tolerance due to their direct or indirect exposure to toxic metals (Bopp *et al.*, 1983). The continuous interactions between metals and microbial cells increase the adaptability to survive in metal contaminated environment. In response to metal resistance into the environment, microbes have evolved indigenous mechanism of metal resistance and detoxification. However, various ways of interactions between metal and microbial cells are presented in Fig. 1. Microbial cells can immobilize toxic metals via cellular sequestration and accumulation. Toxic metal cations such as Cr^{+6} , Cu^{+2} , Pb^{+2} , As^{+3} and Hg^{+2} cope with negatively charged groups carboxyl, phosphoryl and hydroxyl of bacterial cell wall through adsorption and retained by mineral nucleation (Wase and Forster, 1997).

Metals Stress Tolerance Mechanism of Rhizospheric Microbial Community

Rhizospheric microorganisms deserve special attention for the remediation of metal contaminated environments, as they not only being useful for the remediation purpose but, they also have the advantage to promote the growth of plant in such metal contaminated environment by developing different kinds of metal resistant strategies. The most common mechanisms includes synthesis of metal-chelating siderophores, production of phytohormones, secretion of EPS, and biosurfactant production, helps in the removal of toxic metals and promoting plant growth and development. There are following some mechanism by which rhizospheric microbial community survive under metal stressed environments.

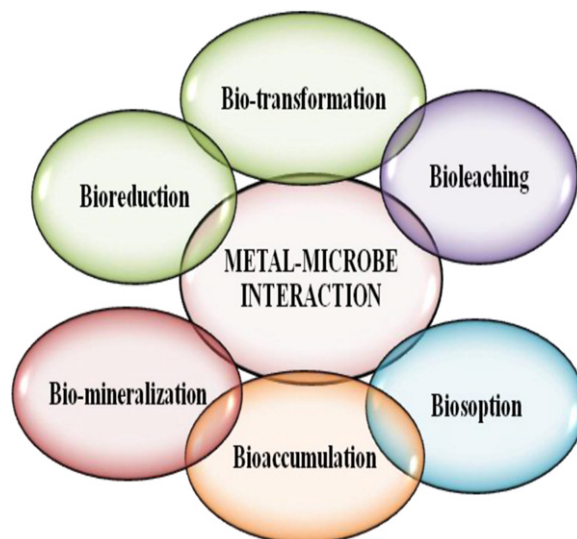


Fig. 1 Various ways of metal-microbe interaction.

By Exopolymer Binding

To survive under metal contaminated environment many bacterial strains secrete certain extracellular exo-polymeric substances (EPS) that are highly slimy in nature and help to reduce the bioavailability of heavy metals. These exo-polymeric substances are made up of polysaccharaides, nucleic acids, carbohydrates and fatty acids. These EPSs plays an essential role in binding of heavy metals and provide protection to microbial cell to abiotic and biotic stress conditions of desiccation, phagocytosis and parasitism (Gonzalez *et al.*, 2010; Kazy *et al.*, 2002). Since, metals are positively charged and bind with negatively charged functional groups are greatly influenced by changing pH of the stressed environment. Bioremediation of metals through EPS results in immobilization and hindrance the entry of metals into the microbial cell (Maier *et al.*, 2009). Nocelli *et al.* (2016) reported that Wild and mutant types strain of *S. meliloti* are able to produce to EPS I and EPS II under higher concentration of Hg (II) and As (III) and EPS producing mutants strains were found more sensitive to these metals. Rhizobacterial strains belong to genera *Mesorhizobium*, *Sinorhizobium*, *Bradyrhizobium*, and *Rhizobium* are widely reported for the production EPS and Biofilm formation in metal contaminated environment (Rinaudi and Giordano, 2010). EPSs provides protection to the bacterial cell in metal contaminated environment by the precipitation of metallic cations, or by binding to metal ions as reported in *Bradyrhizobium* and *Rhizobium*, respectively (Corzo *et al.*, 1994; Foster *et al.*, 2000).

By Siderophore Complexation

The production of siderophore by the rhizospheric microorganisms is an important feature which helps in the acquirement of heavy metals by metal chelating properties. Siderophores are normally low molecular organic chelating substances produced by bacteria and fungi, have the ability to form complexes with metal ions, and helps in sequestration of iron under low iron conditions (Neilands, 1995). Under metal (Cd, Zn, Al, Pb) stressed environment, siderophore production is induced by *Pseudomonas* and *Rhizobium* spp. to form steady complexes with these heavy metals and increase soluble metal concentration and alleviated the metal stress (Ganesan, 2008). Siderophore production enhanced plant growth by increasing protein content and chlorophyll content and decreases the heavy metal accumulation (Burd *et al.*, 2000). Rhizospheric bacteria increase the iron uptake ability of plant roots, from the complex ligand siderophore compound that are produced by them to increase the growth and development of plant and remediate metal contaminated environment (Rashmi *et al.*, 2013). Heavy metals, damages cellular membrane and disrupt the functioning of ferric reductase, and hence reduces iron uptake and result in iron deficiency in plants as chlorosis. Bacterial siderophores preclude iron deficiency and helps in the production of growth hormones under metal pollution conditions. It enhances auxin synthesis in the presence of Al, Cd, Cu, and Ni by chelating them and decreases metal contamination and promote plant growth (Seneviratne and Vithanage, 2015).

By Biosurfactant Complexation

The toxicity of heavy metals is depended largely on their solubility and bioavailability. Most of the metals can form complexes with soil particles. This lack of bioavailability often lowers removal efficiency (Johnson *et al.*, 2005). Rhizospheric bacteria use different strategies to promote the bioavailability of toxic metal compounds with the excretion of biosurfactant. Biosurfactants are amphiphilic molecules that form spherical or lamellar micelle concentration exceeds a critical micelle concentration that is specific for each compound.

Hydrophobic contaminants become solubilized in the hydrophobic cores of the micelles, which increases the transfer of the compound from a solid to water phase where it becomes more accessible to bacteria (Segura *et al.*, 2009).

Rhamnolipids has been reported as one of major biosurfactant produced by bacteria under metal stressed environment which increases the biodegradation rate of pollutant (Mulligan, 2005; Cui *et al.*, 2008). The selection and application of rhizobacteria, which stimulate the bioavailability of metal is therefore of great interest in the context of metal remediation. Currently, bio-surfactant complexation have been investigated for their ability to bind with heavy metals like Cd, Pb, Zn, Cr and As to form complex compounds with increasing solubility that is non-toxic to the cell.

Economic Importance

Rhizoremediation can be successfully used for the restoration of contaminating sites by the right selection of plant cultivar with potential rhizobacterial strain on field trials. The proper inoculation of efficient rhizobacterial strain enhances hyper accumulation ability of plant for commercial phytomining. Rhizoremediation do not needs expensive treatment maintenance and chemical reagents, which make it an ecofriendly and economically suitable technology for the safer use in the progression of environment and farmers to reduce the use of chemical and expensive remedial practice for the removal of toxic pollutants.

Conclusion

Rhizoremediation is a becoming a popular sustainable practice in forestry and agricultural management for the remediation of various pollutants and contaminants. This technology is largely useful in metal contaminated soil areas with nutrients deficient conditions. It involves the use of cheap renewable resources like PGPRs and Mycorrhizal fungi making it more profitable than other remedial technologies as it can be used as fertilizer and prevents the use of pesticides naturally. Thus it is more convenient, environmental friendly and economically profitable approaches instead of other conventional practices.

Acknowledgment

Authors are highly grateful to the University Grant Commission (UGC) Government of India (GOI), New Delhi for UGC NON-NET fellowship to Miss Sandhya Mishra. The financial support received from "Science and Engineering Research Board" (SERB), Department of Science & Technology (DST), Government of India (GOI), New Delhi, India, as "Major Research Project" (Grant No.: EEQ/2017/000407) is also dully acknowledged.

See also: Advanced Vehicle Systems and Technologies: Economic and Environmental Implications. Environmental Analysis Waste Management Model. Environmental Assessment of Green Buildings. Impact of Environmental Initiatives on Environmental Performances: Evidence From the UK Manufacturing Sector. Is the Production of Biofuels Environmentally Sustainable?. Modeling of Information System for Air Waste Management. Modeling of Information System for Liquid Waste Management. Modeling of Information System for Nuclear Waste Management. Modeling of Information System for Solid Waste Management

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The Potential Role of Re-Distributed Manufacturing in Improving Industrial Sustainability

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Introduction

Mass manufacturing was a central part of the industrial revolution, and up to the later part of the 20th century much of manufacturing production was carried out within urban areas – in fact manufacturing businesses financed much of the building of cities in developed regions (Schmenner, 2009). Mass manufacturing has largely disappeared from city centers in industrialized nations, having been moved to lower-cost global regions or dedicated manufacturing plants typically on city outskirts – as, for example, German automotive plants are. Manufacturing production in developed global regions is now largely restricted to niche consumer goods; high-value products including pharmaceuticals, vehicles and specialist high-tech artefacts; perishable goods such as food and medical supplies; and low-value bulky goods such as steelwork for construction, building parts and materials.

Manufacturing organizations carry out many types of activities, including: (i) technology and materials research, (ii) product design and development, (iii) supply chain management, (iv) production (fabrication), (v) sales and distribution logistics, (vi) in-life service, (vii) product remanufacturing (the reprocessing of parts in used products or the replacement of components in a used product, which bring products to a like-new condition (Atasu *et al.*, 2008)), (viii) product refurbishment or reconditioning (product is returned to satisfactory working condition by replacing or repairing major components that have malfunctioned or are close to failure, product is as good as new (Leino *et al.*, 2016)), (ix) product repair (specified product faults are corrected, product can be less than new (Leino *et al.*, 2016)), and (x) product take-back (collection of used products and their recovery or proper disposal (Klausner and Hendrickson, 2000)).

Re-distributed manufacturing (RDM) has been defined as “technology, systems and strategies that change the economics and organization of manufacturing, particularly with regard to location and scale” (Pearson *et al.*, 2013). Out of all the activities associated with manufacturing listed in the previous paragraph, RDM is focused mostly on production, repair, refurbishment, and remanufacturing. The main idea behind RDM is that physical manufacturing activities can be transferred from large-scale, centralized facilities to small-scale facilities located closer to customers. A second definition of RDM, which takes into account its wider implications, is that it is the localization of the production of manufactured artefacts which has the potential to benefit economy, society and environment, and to improve supply chain resilience (Freeman *et al.*, 2017).

The RDM agenda is based on several enabling and driving trends:

- The growing availability of new types of technologies and materials that can be used in fabrication, repair and remanufacturing (e.g., 3D printing). New technologies can allow small-scale production of products that would otherwise be made in large production plants (requiring large capital investment), and they can enable production and repair costs to be reduced through gains in production efficiency (e.g., with automation) – meaning manufacturing in high-cost regions becomes cost-competitive.
- The growth of the digital economy, which enables improvements and cost reductions in the non-production part of manufacturing activities, especially in customer interactions, business to business collaboration, and distribution and take-back logistics. Digital technologies can support collaboration with other companies even if located remotely; and allow access to individual and business customers all around the world.
- The growing number of new types of sustainable business models, enabled by the digital economy, which can work at varying scales and especially for small to medium enterprises (SMEs). New business models, especially “local to local” or “local to global”, can allow flexibility in how products are made, sold and serviced; allow companies to adopt a more circular use of materials, and improve their sustainability (Bocken *et al.*, 2016). These business models are especially beneficial for emerging industries and supporting increased innovation in manufacturing processes (Srai *et al.*, 2016).
- The RDM agenda is also being driven by the increasing demand for customization or personalization of products and services, and the increasing enhanced participation of designers, producers, and end-users across the manufacturing value chain (Srai *et al.*, 2016).

Classification

A dominant trend in the past few decades has been the off-shoring (transfer) of manufacturing production to low-cost regions, by manufacturers based in high cost regions. For many reasons, including higher than expected costs and supply chain risks, more recently the strategy of re-shoring is being adopted by many manufacturers (moving some of all of their production back to the country in which the company is based (Moradlou and Backhouse, 2016)). Drivers for re-shoring include: the narrowing of differentials in labor costs between global regions; higher transport costs; greater need to be close to target markets; product quality concerns; advantages of co-location of design, R&D and production; and changing energy costs (Foresight, 2013).

RDM aligns well with the drivers for re-shoring, especially in being able to locate production closer to customers, co-locate R&D and production, and making use of the increasingly reduced differences in labor costs between global regions. Where best-shoring or right-shoring is the chosen strategy (in which the optimum balance of production on-shore versus off-shore is derived from careful analysis of determining factors (Fox, 2015)), use of RDM could allow the proportion that is re-shored to be increased. RDM could also support on-shoring (the setting up of completely new manufacturing organizations and facilities in higher-cost regions (Fox, 2015)). Although on-shoring is not exactly RDM, since there is no *re*-distribution, the approach could be applicable and provide similar types of benefits.

RDM is similar but different to the following classifications of the organization of manufacturing:

- Decentralized manufacturing, in which large centralized manufacturing plants are replaced with numerous smaller manufacturing units, providing benefits in reduced delivery times and transportation costs, and increased agility (Mourtzis and Doukas, 2012). Manufacturing can be spread over distributed production structures such as replicable, scalable, reconfigurable, or changeable (smart) model factories (Matt *et al.*, 2015). Decentralized manufacturing differs from RDM in that no assumptions are made about re-shoring or on-shoring, or novel technologies that enable small scale production, or industrial sustainability improvements.
- Distributed manufacturing refers to the geographical distribution of the production of one organization, or the distribution of manufacturing within a dispersed production network of autonomous agents (Rauch *et al.*, 2016). Distributed manufacturing differs from RDM in that there are no assumptions about production being close to customers or happening in smaller production units, or in using new production technologies.
- Agile manufacturing is an approach to manufacturing with key characteristics that include: highly customized products; an ability to mobilize core competencies; responsiveness to social and environmental issues; synthesis of diverse technologies; responsiveness to change and uncertainty (Yusuf *et al.*, 1999). Agile manufacturing differs from RDM in that there are no assumptions about offshoring or reshoring, location in relation to customers, small scale production, or use of new technologies; it is similar to RDM in its focus on responsiveness and customized products.

Technologies Used in RDM

A wide range of technologies can be used in RDM. Following is a list of example technologies; this is by no means a comprehensive list, and in fact new technologies are in development all the time that could be useful in RDM, but it represents the most important ones to RDM at the time of writing.

- (1) Additive layer manufacturing technologies, such as 3D printing, are techniques with which complex geometries can be produced directly from digital designs “through the sequential solidification of layers of material” (Li *et al.*, 2016). Additive layer technologies can be used to create prototypes and to do small scale production; their flexibility allows the optimization of design for lean production; their use can improve resource efficiency and allow more flexibility in production (Huang *et al.*, 2013). Their suitability for small-scale and customizable production makes them a key technology for RDM.
- (2) Laser additive technologies are particularly suitable for the repair, refurbishment and remanufacturing of used products, an important potential benefit of RDM. Example applications include gas turbine blade repair, mould and die repair in the tooling industry, reconditioning of crankshafts, and refurbishment and repair of structural components in the aerospace industry (Leino *et al.*, 2016). Additive manufacturing can be used to carry out maintenance, repair and overhaul of specialist equipment parts such as adding laser cladding to high-volume aerospace, automotive, marine, or rail components, where excessive wear has occurred (Wits *et al.*, 2016).
- (3) Digitally controlled cutting tools such as laser cutters can be used to improve a wide variety of types of production, including traditional small-scale production and prototyping. For example, a producer of leather goods combines traditional leather making skills with computer-aided cutting machines, new splitting and buffing machines and other facilities to improve efficiency and keep producing their products on-site (Thomas Ware leather goods: see “Relevant Websites section”).
- (4) Automation and robotics are envisaged as part of the concept of Industry 4.0 – “highly developed automation and digitization processes...the use of electronics and information technologies (IT) in manufacturing and services” (Lu, 2017). This approach may better suit large scale production due to its high set up costs; however, automation and robotics can also be used to reduce costs and improve efficiency in smaller scale facilities. For example, a UK company manufacturing plastic hangers for retail display of footwear was able to re-shore five manufacturing jobs through a program of production efficiency improvements including automation of assembly processes (*Bristol jobs boost as plastics manufacturer Phineas Group brings production home*: see “Relevant Websites section”).
- (5) Big data, the gathering and analysis of a wide range of manufacturing, product and customer data, is being used by some consumer goods companies to support consumer-inclusive co-creation practices. The analytics provided by data science helps companies to define customer motivation and identify opportunities for co-innovation and co-production between producer and customer – leading to more adoption of RDM business models (Zaki *et al.*, 2017).
- (6) Digital fabrication is the ability to send product designs digitally across the world (Gershenfeld, 2012) and make products locally, rather than making products centrally and shipping them to different locations. This fits with the idea of RDM in bringing production closer to customers and small-scale production and prototyping with innovative production technologies.

- (7) New composite materials that incorporate recycled waste can improve product sustainability. For example, polymers from carpet waste are being combined with other raw materials and used to make products in a molding process (Wang, 2010); wood wool composite boards are being used for building insulation, and natural fibers are being added to bio-composites (Mohanty *et al.*, 2002). New technologies allow composite materials to be made in small batches with locally available materials, further improving sustainability. For example, a small company in the UK is making furniture from composite material that incorporates locally available waste wool (Solid Wool furniture: see “Relevant Websites section”).
- (8) Makerspaces are community workshops that allow visitors to develop new product prototypes and experiment with materials and product designs, including digital fabrication. Makerspaces could play a vital role in evolving sustainable design and manufacturing practices, and in overcoming some of the challenges of increasing RDM, including: (i) Scalability (maturing from prototyping to batch production, supply chain management issues, developing knowledge of production management, identifying and developing means to access local markets); (ii) Context (developing routes to local integration, methods to access and manage local material supplies); (iii) Collaborations (meeting the need for collaborations with other producers) (Prendeville *et al.*, 2016).

Applications of RDM

Responsive RDM has been envisaged as forming a part of the future production landscape, with more urban manufacturing and responsive “reconfigurable units integrated with the fluid requirements of their supply chain partners” (Foresight, 2013). Little data exists on how much RDM has affected manufacturing sectors to date, but it is likely that only a very small percentage of total manufacturing production has been redistributed. The use of additive layer technologies, one of the more common technologies used in RDM, is estimated to account for less than half a percent of global manufacturing value (Li *et al.*, 2016). Some re-shoring of manufacturing in developed regions is happening in transportation goods, computers and electronics, fabricated metal products, machinery, plastics and rubber, appliances and electrical equipment, furniture, ceramics, and textiles. Low volume products, for example automotive and aerospace parts, appliances and construction equipment in which labor accounts for a minor proportion of total costs, are considered to be the most suitable for re-shoring (Foresight, 2013).

RDM is not suitable for all types of manufacturing. For many cheap consumer goods, like toothbrushes, the benefits of centralized production in terms of economies of scale currently outweigh the potential benefits of RDM. However, general moves towards production that is smaller scale, distributed and more localised have been seen in how manufacturing is organised; in future it is predicted that large scale production will no longer be globalized by default, and regionalisation or even localization will occur in many sectors (Livesey and Thompson, 2013). There are several practical factors influencing the trend towards adopting smaller scale, dispersed manufacturing options: improved industrial sustainability, the democratizing effect on participation in industrial systems at a socio-economic level, the incentive to make supply networks more adaptive and responsive; the ability to increase product variety while reducing inventory size (Srai *et al.*, 2016).

There are several types of potential applications of RDM.

- RDM can occur in existing sectors where some combination of automation, robotics and different types of efficiency improvements such as Lean Manufacturing is able to reduce the cost of production enough to make re-shoring or localizing production economically viable. There may not be any particular innovation in product design; the innovation comes in how products are made and in finding potential for remanufacturing or repair.
- RDM can be used by companies providing on-demand supply of bespoke, high-value and technically innovative products; these are often customized to individual customers. Examples include medical devices and implants, pharmaceuticals (Roscoe and Blome, 2016), and parts for high-tech and specialist industries such as aerospace and the defense industry (Busachi *et al.*, 2017). This could be done by SMEs supplying large enterprises or by large enterprises replacing some of the products sourced from supply chains with in-house on-demand fabrication.
- RDM can be the basis for the growth of companies specializing in repair, remanufacturing, refurbishment, and reconditioning of products – which could be the original equipment manufacturer or smaller companies that only do this type of work. RDM can change the economics of such processes since innovative technologies allow them to be done on a wider variety of products and they can be done closer to customers – reducing wait times, simplifying take-back logistics, and reducing shipping costs (Wits *et al.*, 2016).
- RDM fits with the niche product market, where the location of production is part of the selling point of the product, or products are highly specialized but not necessarily high-tech. The niche aspect allows higher sales prices and therefore justifies the higher production costs in high-cost regions. This is not strictly re-distributed manufacturing, since it includes production that was never centralized or offshored, but it prevents even more centralization and job losses and the expenses of re-distributing manufacturing at a later date. Niche manufacturing contributes to the local economy through local jobs, local taxes, retaining local expertise in product making and product design, and other local economic activities such as tourism. Examples include regional food specialties (e.g., whisky from Scotland), products made in niche industries with a local history (e.g., Cameron Balloons (Cameron Balloons: see “Relevant Websites section”)), and traditional local making skills combined with new digital tools.

In terms of which types of enterprises could apply RDM, this will vary by size of company, the type of goods or services, the business model, and the location of customers. Companies may produce goods locally for local sale (e.g., food products, spare

Table 1 Types of manufacturing enterprises and their potential for using redistributed manufacturing (RDM) in improving organizational sustainability and industrial sustainability. Scoring is as follows: 1 = low, 2 = medium, 3 = high. B2B = “business to business”; SME = small to medium enterprise; LE = large enterprise

Type of enterprise	Examples from the UK	Where and to whom enterprises sell	Drivers for RDM	Future RDM Potential and Drivers			
				Susceptible to technology disruption	new products and growth	new jobs, especially semi-skilled	sustainability and resilience
Sole trader makers	Violin makers, tailors, jewelry makers	Direct to customers in the area and via internet	Improve access to customers, reduce production costs	1	2	1	2
Product based SMEs, niche producers	Cameron Balloons, Solid Wool Furniture	Customers & retailers, in the area & export	Localism, local production	1	2	1	2
SME high tech makers/designers	Local suppliers to large high-tech companies	Mostly B2B, in the area and export	Competition, staying in manufacturing cluster	3	3	2	3
Low tech makers	Print shops, steel fabrication, joinery	Mostly B2B, mostly local to local	New types of jobs	1	1	2	3
Product based LEs	Few existing companies but future potential	Mostly to retailers, in the area and export	Competition with global manufacturers & mass customization	2	2	1	2
SME food production	Fresh food, dried foods, specialty drinks, etc.	Mostly in the area, some global distribution	Local branding, exports	2	1	2	3
High tech LEs	Aerospace, defense, pharmaceuticals	Almost all export, global	Global competition	3	2	2	1

parts for local industries), or produce goods locally for national or international sales (e.g., bespoke jewelry sold over the internet, customized medical devices shipped overseas). SMEs could especially benefit from the RDM model, increasing the ability to customize solutions for their customers while minimizing environmental impacts by locating technology, people and materials close to markets (Ball and Jolly, 2015). RDM could help established companies deal with the threat of technology disruption – technology innovations that are “disruptive to both producers and consumers and...a result of supply push processes originated by entrepreneurs rather than incumbent firms” (Albors-Garrigós and Hervás-Oliver, 2013).

Table 1 outlines different types of enterprises and the potential for them to benefit from RDM in different ways.

Industrial Sustainability

Rauch *et al.* (2015) identify four key elements in industrial sustainability: economy (cost of energy and materials), ecology (rate of use of resources), social (workplace welfare, skill levels), and political-institutional (public funding for sustainable manufacturing); the authors find that while the concept of distributed manufacturing systems could play a major role in improving industrial sustainability, it cannot be applied within every industrial sector and for every product. Potential sustainability benefits of RDM include: reduced shipping distance between production location and customers (saving energy and emissions from transport), improved material efficiency of production (saving materials), improved opportunities for remanufacturing and repair that extend usable lifetime of products and parts, new uses for locally available materials that would otherwise have been wasted or which would no longer be cost-effective to use (including natural materials such as leather), and the use of new composite sustainable materials in innovative product design.

Kohtala (2015) conceptualized the future distributed production landscape as consisting of: bespoke fabrication, personal fabrication, mass customization and mass fabrication – each with its own potential environmental benefits and concerns; however, the author states that there is no certainty that distributed production will lead to a new and clearly cleaner manufacturing paradigm. Additive layer manufacturing in particular can enable improved sustainability within the processes of “product and

process redesign; material input processing; make-to-order component and product processing; and closing the loop” (Ford and Despeisse, 2015).

In theory, products made through RDM might be expected to be less environmentally impactful than products that arrive through a long supply chain, especially if made “local for local”, yet there are several open issues that remain to be addressed:

- There needs to be sufficient and appropriate environmental regulation for RDM, and this is more difficult to implement when production is small-scale and distributed, especially for enforcement of regulations; furthermore, ensuring compliance with regulation is more difficult for smaller companies where having in-house expertise may not be affordable.
- There is a lack of evidence on whether RDM processes are more or less energy and material efficient than mass manufacturing (Huang *et al.*, 2013); material efficiency depends upon the product design, its material construction, and its lifetime of use.
- Some technologies used in RDM, such as 3D printing, produce products that are not recyclable or repairable. Polymer feedstocks used in 3D printing are made from fossil fuels, and the production of powder metals involve vacuum and inert gas processes which may have significant environmental impacts (see “Relevant Websites section”).
- Customized products may not be as reusable as mass produced products since they are not made for universal applications and may not be designed for disassembly at end of life.
- Re-shoring of manufacturing would also re-shore some of the negative environmental impacts in the country to which manufacturing has been transferred: energy use and associated greenhouse gas emissions (depending on carbon content of energy used), consumption of raw materials (including increased imported materials), consumption of water, creation of waste, and increased freight on transport networks. This may or may not lead to a net increase in environmental impacts, depending on aspects such as level of mechanization and automation and the types of energy and materials used, but environmental accounting should keep track of this.

Economic Benefits of RDM

RDM has been described as epitomizing an on-demand economy, with a growing number of local manufactories helping to reconfigure and redefine product markets and supply chains, invoking new decentralized business models (Pearson *et al.*, 2013). Those manufacturing companies that apply resiliency and business sustainability models – for example, Six Sigma, quality management, lean, fit manufacture, knowledge management, etc. – generally achieve better business sustainability (Thomas *et al.*, 2016) (where the term “business sustainability” indicates that businesses are able to stay afloat indefinitely). However, even these efficiency improvements may not be enough to achieve business sustainability in a fast-changing globalized business environment, especially where there is constant threat of disruptive technological change. Organizations must also be flexible and agile, such as through establishing collaborative supply chain relationships based on transparency of key information (Christopher and Peck, 2008), and evaluating the use of advanced manufacturing technologies in a way that goes beyond standard economic criteria (Mohanty and Deshmukh, 1999).

RDM has the potential to improve flexibility and agility for individual companies, and to provide secondary benefits to local economies, including: new workforce skills and manufacturing specialties that improve the competitiveness of the local economies of cities and regions, new semi-skilled jobs especially in communities that have been left behind by deindustrialization, and the application of traditional making skills in a novel way to ensure their longevity and the survival of local cultural heritage.

The Future for RDM

As indicated in Table 1, there is likely to be some potential for RDM in all sectors. A summary of three studies into RDM follows, as examples of how RDM can align with the particular needs of product types.

In the consumer goods sector there is potential for RDM to support a circular economy when combined with “digital intelligence” (the ability to understand and interact with digital information, and to arrange, manipulate, and display it (Adams, 2016)). More understanding of where value is captured and delivered will be essential for identifying the significant opportunities that exist (Moreno and Chamley, 2016). A case study (the Shoe Lab) developed a model of implementation of RDM for sports shoes, which includes: (i) customer 3D scanning of their feet at home; (ii) customer use of virtual reality technology to customize the shoe design on-line; (iii) the choice to pay outright or subscribe; (iv) “smart” shoes embedded with sensors that can track location, performance data and shoe condition; (v) shoes 3D printed to the customized design, with manufacture (and re-manufacture/ upgrade of components) taking place close to customers; (vi) Shoe brand can forge data-driven relationships with users via digital intelligence, enabled through new business models (Keely *et al.*, 2016).

In the healthcare sector, RDM has the potential to change how products are delivered, transforming the manufacture of medical devices, pharmaceuticals, biopharmaceuticals and regenerative medicinal products (Phillips *et al.*, 2018). In fact, the top three fastest growing segments for additive layer manufacturing are medical and dental diagnostics and treatment, and medical prosthetic devices including dental implants (Li, Myant and Wu, 2016). Key challenges to realizing the potential in healthcare products include: regulatory standards, the need for new training patterns, social and human factors, and new supporting organizational structures and commercial arrangements. In the long term, strong investment will be needed to enable RDM platform systems to deliver medical products rapidly,

at an affordable cost, and in a more sustainable manner than existing modes of production (Phillips *et al.*, 2018). Roscoe and Blome (2016) identified several niche applications in which RDM could be applied within pharmaceutical supply chains: “additive manufacturing could be used to create compound products such as infusion bags...in radio pharmacy radioactive drugs could be created at the hospital for immediate patient use...late stage dispensing using additive manufacturing technology could cut down on the waste currently generated from de-blistering” (Roscoe and Blome, 2016).

Srai *et al.* (2016) examined cross-sectoral issues related to RDM in emerging industries, identifying the nature of industrial innovations and the different types of advantages they provide, across six sectors: defense aerospace, maritime, built environment, industrial biotechnology, photovoltaics, and last mile logistics. The authors found that from a RDM perspective, (i) smaller scale and dispersed production options can improve industrial sustainability and democratize participation within industrial systems at a socio-economic level; (ii) RDM systems can drive more adaptive and responsive supply networks, supporting increased product variety while inventories are reduced; (iii) new e-Commerce models featuring digitalized supply chains can support “rapid replenishment and decoupled distribution channels, with drop-points located closer to end-users” (Srai *et al.*, 2016).

There are some practical considerations for the adoption of RDM in different regions and industries.

RDM activities will require some of the same supportive conditions that enabled mass manufacturing to thrive in the past – including a diverse manufacturing sector, high-tech manufacturing clusters, investment in new skills and technology innovation, local ownership of companies and industrial leadership, and investment in building and maintaining civil infrastructure that can host manufacturing. However, in many countries the importance of manufacturing to the economy is significantly lower than in the past, and it is uncertain how well RDM aligns with the goals of local, regional and national governments.

While RDM has been proposed as a way to bring back some of the semi-skilled manufacturing jobs that have been lost, so far most of the new jobs associated with RDM appear to be for highly skilled personnel. The contribution of RDM to reducing inequality has up to now been small, and even less than traditional manufacturing. In fact, there might be job losses for SMEs if large companies start to fabricate their own parts instead of buying in parts from suppliers. To create more semi-skilled jobs might require new business models and new types of public sector support. RDM business development, especially for SMEs, needs to be supported by local enterprise promotion of manufacturing clusters, academic and government support for technology innovation, ensuring companies can get space such as through planning zones that allow manufacturing, and skills training for the use of new technologies. Ensuring that products can be reliably shipped to customers, both local and global, is also key for business success, and with RDM rural transport links may become more critical.

Many of the services that manufacturing uses are supplied through infrastructure, and innovation in infrastructure can even stimulate innovation in manufacturing (Luger *et al.*, 2013). However, in developed regions many urban and suburban areas are now dominated by housing, retail outlets, distribution centers, and the services sector, and some developing regions are following this pattern. Competition for physical space will only become more intense in future due to the trend for urbanization, increasing prosperity in developing regions, and increasing population. Although RDM is small scale, it still requires some physical space, and cash strapped start-ups require spaces with cheap rents where manufacturing is allowed; rural and city governments should ensure that some affordable space remains for RDM and that its growth is not prevented through urban gentrification.

Strong growth in RDM would start to reverse the previous decade’s dominant trend for offshoring and centralizing production, opening up a wide range of potential benefits for startups, small to large manufacturing companies, companies dealing with technology disruption, traditional and sole trader makers, and local economies in general.

Funding

The research behind this book article was carried out at the University of Bristol, UK, as part of the network project Redistributed Manufacturing for the Resilient, Sustainable City (RDMIRSC), funded by the UK’s Engineering and Physical Sciences Research Council, grant EP/M01777X/1. The authors would like to sincerely thank all the participants in the RDMIRSC network.

See also: Worldwide Research Trends in the Recycling of Materials

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Recycled Concrete

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Introduction

Concrete is the second most consumed material on Earth, after water. It is estimated that roughly 25 billion tons of concrete are manufactured globally each year (World Business Council for Sustainable Development, 2015). As the highest used construction material and the most widely used manmade material on Earth, concrete makes up a considerable portion of the world's waste. Concrete consists of cement, coarse and fine aggregate, and water primarily, together with other additives and supplementary materials. When a building constructed with concrete reaches the end of its life, it is demolished resulting in construction and demolition (C&D) waste. Concrete waste is part of the C&D waste stream, with other materials such as brick, wood, plastics, and other mixed waste. C&D stream is considered the single largest waste stream in the world, accounting for 30%–40% of the world's waste volume. Typically, demolition activity accounts for less than 10% of total C&D activity, yet demolition waste accounts for about 50% of the total C&D waste stream (Tam, 2008).

Construction and Demolition Waste

The extent of C&D waste stream as a part of the total waste generated differs within a large range among countries. Even among developed countries such as Japan (16%), the United States (29%), Australia (42%), and the UK (>50%) there are significant variations (Hiete *et al.*, 2011). Also per capita waste generation figures of different countries vary; as an example Norway with 0.2 tons per capita, Australia with 0.88 tons per capita, and the UK with 2 tons per capita, approximately (Tam *et al.*, 2008). Additionally, the extent of concrete waste in the C&D waste stream could also differ and these variations are due to different economic activities, differences in building tradition and materials, the maturity and current phase of the construction industry, and differences in data collection with inclusion and exclusion of specific streams such as earth excavations (Hiete *et al.*, 2011). An example would be that houses constructed mainly with wood in countries having four distinctive seasons would consume less concrete, whereas countries building more permanent structures traditionally (e.g., Asian countries) would consume more concrete. Therefore, when the C&D waste is recycled, the amount of recycled concrete in the stream will depend heavily on the construction industry practice.

Considering the C&D waste stream, concrete waste results from:

- (1) Construction waste: The residual concrete remaining in ready-mix concrete bowsers once the pouring is done, overordered concrete (wet concrete) or hardened concrete removed from structures at construction stage (dry hardened concrete).
- (2) Demolition waste: Concrete waste mixed with other rubble (such as bricks, asphalt, roof tiles, wood etc.) resulting from demolition of a structure.

For the purpose of this article, we consider the recycled concrete resulting from concrete waste from demolition waste as the main source, as it represents the majority of concrete waste. Recovery of wet concrete resulting from construction processes is not discussed in this article.

Concrete in Construction and Demolition Waste

Concrete waste in the C&D stream is either separated before and/or after recycling. The large concrete chunks could be separated from demolition waste prior to recycling and after recycling other embedded waste such as reinforced steel needs to be removed. The amount of concrete waste in the C&D waste stream is considered close to 50% in some studies (Tam *et al.*, 2009), while a few other studies report that it could be as high as 70%–85% (Nicolas *et al.*, 2008).

Recycled Concrete Production

Concrete waste is a two-phase material at a broad level: Coarse aggregate, which is used to provide volumetric stability to the original concrete and dried mortar, which acts as a binder of aggregates. The mortar phase typically consist of fine aggregates (sand) and hardened, hydrated cement slurry.

Once a construction containing concrete is demolished, some of the concrete waste may be mixed with other demolition waste, while some would remain intact and hence some would qualify for recycling and the rest would reach landfills. Recycled concrete can either be produced at the demolition site using a mobile recycling facility or can be transported to a fixed recycling facility, where it would be recycled. The resulting product from the recycling operation, which is typically a crushing operation, is referred to as crushed concrete or recycled segregation concrete.



Fig. 1 Construction and demolition waste sorting and steel reinforcement removal. Reproduced from MilBank, 2018. Waste Recycling, MilBank.

On-Site Concrete Waste

Some of the concrete waste resulting from demolition is often mixed with other materials such as, plastic, brick, steel etc., and some will remain unmixed as large concrete pieces, gravel, or fines.

If the demolished construction has contained reinforced concrete in its structure, the concrete waste would have steel reinforcement, binding the waste concrete together. To recycle concrete, some of this steel reinforcement is removed at the demolition site, to make the large concrete pieces transportable to a recycling facility. This process is illustrated in [Fig. 1](#).

The Recycling Process

In general, separation of concrete waste and crushing of concrete waste is referred to as concrete recycling, however, there could be variations to this process as discussed in this section.

Goals of the recycling process

The goals of the recycling process will largely depend on its destined use. Mainly, there are two different types of goals that the recycling process aims to achieve, based on the final properties of the recycled concrete. This would lead to use of two different categories of technologies as discussed by [Doshio \(2008\)](#). These are:

- (1) Achieve complete refinement, so that the coarse aggregate portion of the concrete will have equivalent properties to natural aggregate (NA) used to make the primary concrete.
Technologies used to achieve this goal fall under the broad category of “aggregate refinement method.” Complete refinement is achieved via completely removing the residual mortar attached to the concrete and separating out the fine portion of cement mortar in the recycled concrete. To achieve this, it is not usually sufficient to use crushing processes where the concrete waste is broken down to small particles. Chemical processes, such as heat treatment or other means such as scrubbing would be required, making the recycling operation energy intensive and costly in comparison. However, the main advantage is that the two main volumetric components, namely the aggregate and the mortar component would be fully phase separated at the end of a recycling process following aggregate refinement.
- (2) Achieve a coarse aggregate containing residual mortar in its surface, referred to as recycled concrete aggregate (RCA) and some fine aggregate with fine mortar.
Technologies employing the above are often referred to in research as aggregate replacement methods. This is achieved via crushing of the recycled concrete using an impact crushing process to reduce the particle size and then using another mechanical process (such as sieving or airlifting) to separate the coarse aggregate portion and the fine portion of the resultant material. The objective of the recycling process is to reduce the influence of mortar on the coarse RCA; however, the process does not intend to achieve complete refinement. Therefore, these technologies employed achieve a resultant material stream with partial refinement of the coarse aggregate with residual mortar on its surface and a fine recycled concrete aggregate (FRCA) portion. The subsequent processes using the coarse aggregate portion would need to take into account that the coarse recycled concrete would contain residual mortar and deal with it accordingly.

Recycling process

At a recycling facility, typically concrete waste undergoes manual and mechanical sorting (manual separation of large items and magnetic separation of steel reinforcement), impact crushing, and size separation through sieving. If there are oversized particles or

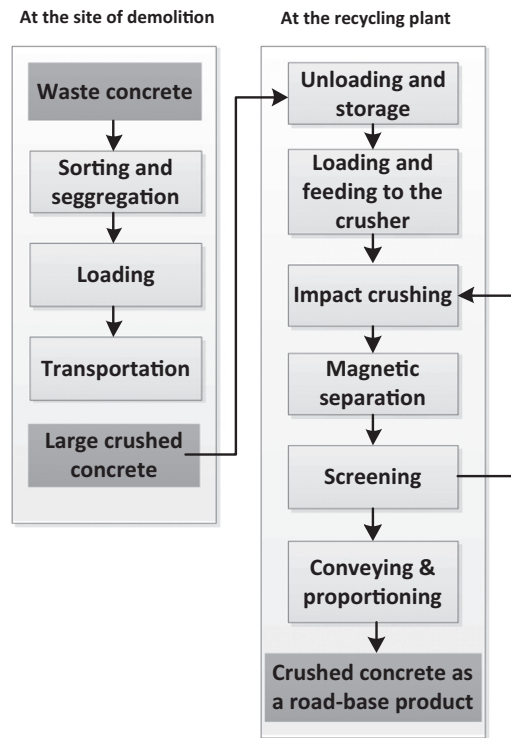


Fig. 2 Process steps of concrete waste processing to produce Recycled concrete aggregate.

contamination discovered during the sieving process, they are dealt with separately. The oversized particles would be diverted back to the impact crushing process, while contamination is separated through a technology such as airlifting. This is illustrated in Fig. 2.

Recycling technologies – To achieve partial refinement

The above process is sufficient to achieve partial refinement of the output product. The output, referred to as recycled concrete, therefore would consist of:

- (1) Coarse RCA – Typically above 5 mm in size, and with some residual mortar on the surface, typically 55%–73% of recycled concrete.
- (2) Fine RCA – Typically less than 5 mm in size, mixed with coarse RCA, typically 27%–45% of recycled concrete.

Recycled concrete containing these two materials is usually used as a road-base material or a filler material. The differing sizes of the two constituent materials do not pose a limitation in this application. However, as recycled concrete replaces a low-value use, this is generally regarded as a downcycled option.

Recycling technologies – To achieve full refinement

In addition to employing a typical crushing process, to achieve a level of refinement similar to that of NA, several technologies can be used. The main methods that are used at industrial scale include (1) heated scrubbing, (2) mechanical scrubbing (using eccentric rotor or a screw mill), and (3) wet scrubbing (Doshio, 2008). These methods are specifically used in Japan as the Japanese standards recognize high quality RCA as being similar in quality to NA used in concrete. The above methods use heat or mechanical scrubbing (dry – against each other or wet – using water) as a technique to embrittle the residual mortar attached to the aggregate. These processes that are used to achieve full refinement are presented in Figs. 3–6.

Some other methods trialed in laboratory and pilot scale to achieve refinement of the recycled aggregates include (1) nitric acid dissolution method, (2) presoaking method, (3) microwave heating method, (4) ultrasonic treatment method, and (5) surface modification methods (Behera *et al.*, 2014). The purpose of all these methods is to achieve low fracture energy in disintegrating mortar in concrete, ease the liberation of aggregate by improved surface conditions or weakening the mortar phase, and to remove the adhered mortar without losing the integrity of the original aggregate.

Properties of Recycled Concrete

This section will discuss the properties of recycled concrete that has achieved partial refinement, as that is the most generally available form of recycled concrete. Countries such as Japan have standards recognizing fully refined coarse RCA as equivalent to

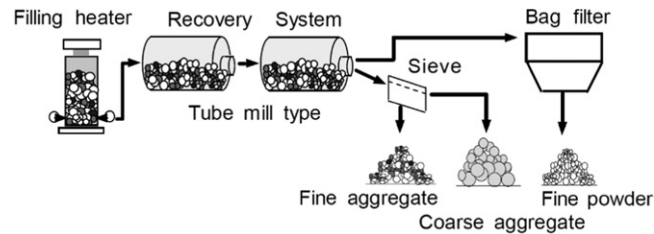


Fig. 3 Operation of a heating grinder. Reproduced from Tomosawa, F., Noguchi, T., Tamura, M., 2005. The way concrete recycling should be. *Journal of Advanced Concrete Technology* 3, 3–16.

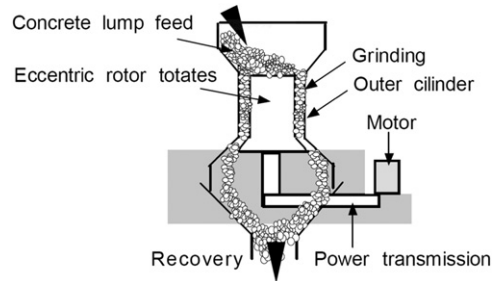


Fig. 4 Operation of an eccentric rotor-type mechanical grinder. Reproduced from Tomosawa, F., Noguchi, T., Tamura, M., 2005. The way concrete recycling should be. *Journal of Advanced Concrete Technology* 3, 3–16.

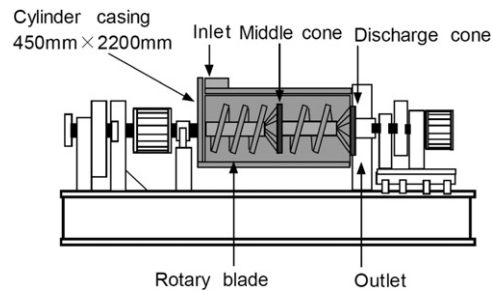


Fig. 5 Operation of a screw mill. Reproduced from Tomosawa, F., Noguchi, T., Tamura, M., 2005. The way concrete recycling should be. *Journal of Advanced Concrete Technology* 3, 3–16.

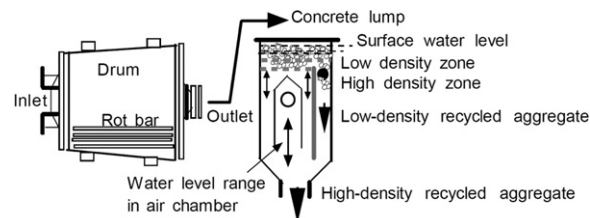


Fig. 6 Operation of a wet scrubber/levigator. Reproduced from Tomosawa, F., Noguchi, T., Tamura, M., 2005. The way concrete recycling should be. *Journal of Advanced Concrete Technology* 3, 3–16.

NA, however, in most other countries, the refinement is carried out partially. The output from recycling when partial refinement is achieved, would consist of a coarse aggregate containing residual mortar on its surface mainly (>5 mm) and a fine aggregate crushed into fine particles (typically less than 5 mm). Due to the differing sizes and constituents, these two materials in the recycled concrete stream differ in properties significantly. Most of the coarse portion would consist of rock/aggregate with mortar content amounting to 15%–30% by weight, while the fine portion would have cement mortar particles and fine aggregate coated with cement mortar. This article discusses the properties of the mixed stream and each of the two constituent material streams.



Fig. 7 Mixed recycled concrete.

Mixed Recycled Concrete

As the mixed recycled concrete has two distinctively different materials mixed together, their proportion would determine the properties of the mixed material stream. [Fig. 7](#) shows an image of mixed recycled concrete.

Properties of mixed recycled concrete

Mixed recycled aggregate from a typical crushing process would contain 55%–73% of coarse recycled aggregate, 25%–47% of fine recycled aggregate, and 0%–2% of other contaminants.

Applications of mixed recycled concrete

As a mixed material, mixed recycled concrete can be used for a more generic purpose, where the specific properties of the constituents do not affect the application significantly. Therefore, this mixed recycled concrete is used as a filler material, mostly to cover road bases. As a road-base material, recycled concrete replaces gravel and rock and is used as a filler. While this application makes the recycling process very simple and less costly, it is considered as a downcycling option. The simplicity to the recycling process comes from the fact that the coarse and fine recycled concrete does not need to be separated and the material can contain a high degree of impurities and still be considered acceptable for the application.

Coarse Recycled Concrete Aggregate

The separated out coarse recycled concrete has a high representation of the coarse NA used to manufacture concrete.

Properties of coarse recycled concrete

Physical properties

The main difference that is physically observable between coarse RCA and NA is the presence of residual mortar originating from the parent concrete, which recycled concrete was originally a part of. It is observed that the old adhered mortar present on the aggregate makes the coarse RCA particles (1) less dense, (2) inhomogeneous, and (3) porous ([Poon et al., 2004](#)). The density of coarse recycled concrete may vary from 2200 to 2400 kg/m³ compared with the density of NA, which is observed to be approximately 2600–2650 kg/m³ ([Poon et al., 2004](#)). The reason for the difference in density is attributed to the porosity of the aggregate, which results in a lighter structure and higher water absorption.

The dimensional and surface characteristics of recycled concrete contribute to higher water absorption, in addition to the porosity resulting from residual mortar.

Comparison of surface texture, which measures the degree to which the particle surfaces are polished, dull, smooth, or rough, depends on the hardness, grain size, and the pore characteristics suggesting that coarse recycled concrete has a weak surface with microcracks compared with the surface of NA ([Tam and Tam, 2007](#)). The texture of recycled concrete is observed to be rough and consist of a granular texture due to adhered mortar, which contributes to higher water demand ([Etxeberria et al., 2007](#)).

Coarse recycled concrete is considered to have a heterogeneous distribution of attached mortar, with larger particles carrying less of mortar compared with their size. Therefore, coarse recycled aggregate with larger particle sizes tend to be less water absorptive compared with smaller particles.

Roundness, which measures the relative sharpness or angularity of the edges and corners of a particle, is largely controlled by the strength and abrasion resistance of the parent material ([Neville, 2011](#)). Coarse recycled concrete is observed to be more angular compared with round-shaped natural coarse aggregate and hence demands more water ([Behera et al., 2014](#)).

While some researchers argue that the presence of residual mortar makes the aggregate surface weak and brings inferiority to any material that contains it, some argue that having residual mortar can be viewed as a complementary inclusion, especially when it is used as an aggregate replacing NA in concrete. This is because RCA brings additional mortar to the new concrete.

Mechanical properties

As a composite material with multiple phases, the properties of the recycled concrete are affected by (1) the characteristics of the aggregate, (2) the bond between the aggregate and the mortar, and (3) the characteristics of the mortar. Therefore, the mechanical properties are discussed considering the above three phases.

(1) Characteristics of the aggregate

The toughness of the aggregate is an important parameter and it is indicated by the impact value and the crushing value. Research has highlighted the importance of evaluating the strength characteristics of coarse recycled concrete, especially when it is used as a constituent material in concrete and correlation is observed between the aggregate crushing value and the strength of the aggregate. This is due to the fact that the adjustments required for the mortar mix may not be necessary if the aggregate has considerable strength (Butler *et al.*, 2013). The concretes produced with varying quality and hence strength of coarse RCA have found to have different tensile strength, modulus of elasticity, and energy at rupture, despite the adjustments in the concrete mix to have the same compressive strength (Butler *et al.*, 2013).

The surface texture and shape of the aggregate affects the strength of concrete by contributing to differing levels of bond with the mortar (Neville, 2011). Generally, a rougher texture of the aggregates results in a larger adhesive force between the particles and the cement matrix; whereas larger surface area of angular aggregate allows a larger adhesive force to be developed. The flexural strength of concrete is observed to be more affected by the texture and shape of the aggregate than the compressive strength. While the physical properties of aggregate have some influence on the strength of concrete, the effect due to the mechanical strength of the aggregate is quite significant (Neville, 2011).

(2) Bond between the aggregate and the mortar

The interlocking of the aggregate and the old mortar occur due to the surface roughness of the aggregate. The retention of residual mortar following the crushing operation is identified to be higher when the bond between the aggregate and the parent concrete is stronger (Behera *et al.*, 2014). It is identified that the strength of the aggregate and the compressive strength of the parent concrete would influence the modulus of rupture of the concrete due to the strength of the bond formed between the aggregate and the old mortar (Butler *et al.*, 2013).

(3) Characteristics of the mortar

The strength of the cement mortar attached to the recycled concrete has been observed to affect its strength directly as it is a significant proportion of the material. It is identified that the amount of residual mortar in RCA depends on the initial mortar content, the mechanical properties of the initial mortar, and the mechanical quality of the transition zone at the interface between the initial aggregate and the cement mortar (Belin *et al.*, 2013). Therefore, if the recycled concrete is used as a constituent material in concrete, it is advisable to study the source and characteristics of the parent concrete, both in terms of aggregate quality and mortar quality.

Applications of coarse recycled concrete

As a road-based material (in mixed form)

Currently, coarse recycled aggregate (sizes > 5 mm) is mostly used as a road-base material. As a filler for road-bases, coarse recycled aggregate is used as a part of the mixed recycled concrete stream. Using it in the mixed form, replacing natural rock as filler, is considered a downcycling option. On the other hand, when used as filler, the material remains mixed with the natural gravel or rock on the original surface being filled. The environmental risks associated with having recycled concrete mixed together with natural soil and rock in a submerged condition at ground level or underground, such as leaching, are to be explored yet and are being studied.

As a constituent material in concrete

Use of RCA substituting the NA in structural concrete is a preferred upcycled solution, as it has multiple advantages. Firstly, the resource value of the material is recovered and secondly, the material can be circulated in a closed loop. Thirdly, extraction of NA can be avoided, conserving natural, nonrenewable resources.

Coarse aggregates typically amount to 60%–75% of the volume of concrete, and their properties greatly affect the durability and structural performance of concrete (Behera *et al.*, 2014). Therefore in considering to replace the coarse aggregate portion of concrete with an alternative material such as recycled aggregate, it is important to consider the basic functions performed by aggregates in concrete. Aggregates, when used in concrete, (1) act as an economical filler in the concrete, (2) bring volume stability to concrete, and (3) bring durability properties to concrete (Neville, 2011) and any material replacing is expected to perform these functions.

When coarse recycled aggregate is used as a constituent material in concrete, it replaces NA fully or partially. If the aggregate is recycled employing a refinement methodology and the resultant coarse aggregate is similar to NA without the presence of residual mortar on the surface, the level of replacement of NA is high. However, if the aggregate is recycled using a typical crushing process, the residual mortar present on the surface of the aggregate makes it different to NA, so the manufacturing method or ingredients of



Fig. 8 Cross-section of a low-strength (30 MPa) concrete cylinder made with recycled concrete.

the new concrete needs to be modified to account for the difference in the properties of the aggregate. The identified ways to account for this change are (1) use of modified methods to prepare the coarse recycled concrete as a constituent material in concrete, (2) use of modified mix design methods to prepare the mortar phase of new concrete, and (3) use of modified ready-mix concrete manufacturing methods in producing concrete.

Several countries have developed guidelines for using coarse recycled concrete in concrete. Countries such as Japan have provided several options to use RCA based on their level of refinement, whereas other countries who deal with partially refined RCA have used several strategies to account for the changes that could come with using an alternative material in concrete. Considering the fact that recycled concrete could pose risks on the new concrete produced, the guidelines depicting the use of RCA often limit its use by imposing limits on the rate of replacement in concrete applications, limits on the types of applications (e.g., nonstructural applications), and limits on the level of strength categories it can be used for (e.g., low-strength applications). There are guidelines and standards developed across the world enabling grading of the recycled concrete and then diverting to recommended practices. [Fig. 8](#) shows a cross section of a low-strength (30 MPa) concrete made with coarse RCA, with some aggregate particles showing residual mortar.

Fine Recycled Concrete Aggregate

Fine recycled concrete is typically the portion that is less than 5 mm after the impact crushing process of concrete waste. This consists of fine hydrated cement particles in the crushed old mortar and fine aggregates in the old mortar.

Properties of fine recycled concrete

Similar to the coarse RCA particles, the fine RCA particles will also have the original fine aggregate with residual mortar attached to it, in addition to its containment of hydrated cement fines. It is observed that the residual mortar content attached to the original aggregate particle is heterogeneous based on its size. The amount of mortar attached to the fine fraction (33%–55%) was greater than that attached to the coarse fraction (23%–44%) as observed by [de Juan and Gutiérrez \(2009\)](#). Therefore, the amount of mortar and cement in the fine RCA stream tends to be higher than that in the coarse aggregate stream.

Applications of fine recycled concrete

There are several applications for fine recycled concrete identified in research. They are:

- (1) Use of FRCA replacing fine aggregate in concrete

Inclusion of fine RCA replacing fine NA has been studied by several researchers. While some researchers state that this is a complementary addition to the concrete if water absorption could be managed using appropriate quality control methods ([Dosho, 2007](#)), there are arguments against the replacement of fine aggregate with fine RCA mainly quoting the reduction of compressive strength ([Yang et al., 2008](#)).

It is argued that use of FRCA up to 30% does not affect the compressive strength of concrete ([Evangelista and de Brito, 2007](#)) and experimental investigations have suggested the strong possibility of the use of FRCA in concrete to yield high performance, even exhibiting behaviors similar to high-performance concrete ([Evangelista and de Brito, 2013](#); [Evangelista et al., 2015](#)).

- (2) Use of FRCA in precast concrete products

Another possible application for fine RCA is to use them in precast concrete products manufacturing, following a wet grinding process [Dosho \(2008\)](#).

- (3) Use of FRCA in clinker manufacturing

Inclusion of a large amount of hydrated cement provides the ability for fine RCA to be used in clinker manufacturing, which is a process step in cement manufacturing. Fine RCA can be used as an additive and it has been observed that adding such improved the burnability of the cement raw meal without negatively affecting the cement clinker properties ([Galbenis and Tsimas, 2006](#)).

Challenges and Opportunities – Recycled Concrete

Challenges in Using Recycled Concrete

Some of the main challenges in using recycled concrete in up cycled options, such as its use as a constituent material in concrete include complexities that could arise due to receipt of material from different origins, including different demolition sites and from construction applications using different materials. In addition to that, the use of material from demolition waste poses challenges due to contamination. Therefore, in diverting recycled concrete to an upcycled solution where producing a waste-derived, homogeneous material is a requirement, the following poses challenges considering the quality of the source material.

- (1) Differing compositions due to inclusion of aggregates and mortars coming from several sources and hence the differences in type and strength of the constituents
- (2) Uncertainty in the variability of critical parameters such as the strength
- (3) Unpredictability of contamination present in the materials

To overcome some of the challenges, tracking and control of the source concrete data are recommended as a proactive measure, and establishing a sound quality control system encompassing the entire supply chain is also required.

Opportunities for Using Recycled Concrete

In considering the solutions available to recover the maximum resource value of recycled concrete and divert it to an upcycled solution, use of recycled concrete in structural concrete seems to be the ideal option. This option enables recirculation of concrete waste in a closed loop and helps conservation of NA extracted for producing concrete.

To facilitate this, there are a number of explorations and advancements happening in research, which facilitates product and process developments to produce concrete, referred to as RCA, which resembles concrete made with NA and have equivalent properties. Most of the current advancements happening are in material characterization and improvement of the performance of the material considering production of recycled aggregate concrete RAC. The microscale studies of the material consider improvements to the interfacial transition zones formed between the coarse aggregate and residual mortar surfaces with the new mortar.

These advancements include:

- (1) Aggregate preparation methods

There are advanced methods considered for preparing the RCA such as presoaking the aggregate and coating the aggregate with pozzolanic materials. Presoaking is expected to saturate the particle, whereas fine pozzolanic materials is observed to act as a microfiller in filling pores, thereby making the aggregate particle stronger.

- (2) Design of mortar mixes in manufacturing RAC

Considering concrete as a multiphase material with coarse NA and mortar, replacement of one material, which constitutes a single phase, with another material, affects the integrated properties of the composite material. Therefore, redesign of the other phase, which is the mortar phase, is required to obtain the same properties of the original composite material.

The techniques adopted in mix design gathered from various researches include:

- (a) Addition of mineral (fly ash and slag) admixture and chemical admixture (plasticizer and super plasticizer) to counteract higher water absorption associated with RCA.
 - (b) Addition of cement and supplementary cementitious material to strengthen the mortar phase of the concrete.
 - (c) Design for higher strength and decrease water to cement ratio to account for higher variation associated with RCA.
- (3) New mixing methods to produce RAC

Tam and Tam (2007) suggested to adopt a two-stage mixing approach to produce RAC of improved quality, with a strengthened interfacial transition zone formed between the fresh mortar and the RCA. This mixing approach has also been observed to overcome the typical problems resulting from high water absorption and high porosity of RCA. A novel triple mixing process method was developed by Kong *et al.* (2010), where a surface coating is applied using pozzolanic materials to further improve the microstructure of the interfacial transition zones formed in the RAC.

Concluding Remarks

Concrete as the second most consumed material on Earth contributes to the equally large waste material stream – C&D waste. Concrete waste is either included in the construction waste stream as process waste or the demolition waste stream, as end-of-life products of a construction. Recycled concrete produced after separating out the concrete waste portion of C&D waste is mostly used as a road-base material nowadays. The main constituents of recycled concrete – the coarse aggregate, the fine aggregate and cement/mortar fines have immense potential to be used as a constituent material of concrete and in other products and forms that provide better value to the recovered material. While recycled concrete, being a waste material, poses challenges concerning homogeneity and inconsistencies to be used in concrete and other traditional products, the product design, characterization, as

well as processing technologies have been evolving in the last couple of years, enabling improved product performance. The destination researchers intend to reach is to allow possibilities for concrete to run in a closed-loop as a construction material, allowing iterative production, recycling, and reuse, and the journey to that destination has already commenced.

See also: A Review on Utilization of Electronic Waste Plastics for Use Within Asphaltic Concrete Materials: Development, Opportunities and Challenges for Successful Implementation. Life-Cycle Impact of Concrete With Recycled Materials. Recycled Ceramics in Concrete. Sustainable Production of High Performance Concrete

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Reducing Waste in Circular Economy

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Introduction

The global population has crossed 7 billion by 2018 and is expected to go beyond 9 billion by 2050 (Maassen and Altamirano, 2017). There is a rapid pace of urbanization which is creating a significant stress on the society and environment related to noise, air, water and soil pollution and increasing amount of solid and e-waste. The linear model of mass production and consumption is breaching the sustainability limits of the globe and taking the world closer to ecological disaster (Esposito *et al.*, 2015). Going by the current production and consumption patterns, people living on this earth will require two planet equivalents of natural resources to meet their consumption need by 2030. This demand will increase to three planet equivalent of natural resources by 2050. There is a need to make a shift from “take-make-waste” oriented linear economy towards “reduce-recycle-reuse” driven circular economy (CE) (Hower, 2016). Though in a state of infancy, there is an increasing realization among the global economies and companies towards adoption of sustainable products and consumption patterns. Going by the current rate of consumption and increasing disposable incomes, material consumption is expected to triple by 2025 (Bhutani and Arya, 2017). This calls for a paradigm shift from ‘produce-consume-dispose’ led linear economy to ‘reduce-recover-reuse-recycle-redesign-remanufacture’ led circular economy. During COP21 (2015 Paris Climate Conference), Karmenu Vella, European Union (EU) Commissioner for Environment, Maritime Affairs, and Fisheries stressed upon the role of CE in tackling climate change (Tse *et al.*, 2016). He highlighted how EU invested Euro 650 million for tackling the ecological imbalance and waste pile-up. Setting up a CE value chain is necessary to improve the overall production and consumption patterns. According to C40 Deadline 2020 research (see “Relevant Websites section”), it is required to reduce the carbon emissions from an average of 5 tons carbon-dioxide (CO₂) per capita to 3 tons CO₂ per capita by 2030 (EMF, 2018). CE is defined as the systemic focus on elimination of waste by adopting the recycling, reuse and repair paradigms (Bordoloi, 2016). CE is more about a new way of thinking towards a sustainable and cleaner tomorrow. It is not only about conservation of resources and restoration of ecological balance. It is rather an orientation towards “cradle to cradle” economy, which will lead to better growth and socio-economic equality for the people across countries (Esposito *et al.*, 2015). CE has moved beyond the humble origins of recycling and repair to widespread adoption in terms of sustainable value chains and business models. During 1990–2020, CE has moved up on the maturity curve beyond the focus on resource efficiency and sustainable production towards sustainable consumption. Both production and consumption patterns need to be addressed to drive the change on this planet. The idea behind circularity is to look at the conceptualization and value-chain of the products in terms durability, reuse and repair. Also, circularity stresses upon the optimal utilization of resources. For example, individual owned cars remain parked more than 80% of the time and the commercial space has an average utilization of only 40% of the time in Europe (Plastrick and Cleveland, 2018). One need to look at shared economy models to enhance the utilization of resources. According to noted researchers, waste has a significant value within but remains a waste as long as we consider it to be a waste (Himmelfab and O’Dea, 2015). As world is becoming inter-connected, geographic boundaries are fading away, global marketplace is taking shape with suppliers and consumers coming closer than ever (Hoekstra, 2018). This has created a situation where both suppliers and buyers need to recognize, align and work towards a cleaner tomorrow.

This article exemplifies how nations, cities, companies, and individuals can make a significant contribution in reducing waste by adopting CE practices. The article proceeds as follows. The first section defines CE. The second section highlights the need for making a shift from linear economy to CE. This is followed by a section explaining the challenges in going circular. The fourth section talks about business model typologies. The fifth section highlights the examples regarding adoption of CE approach by companies and nations. Finally, there is a conclusion section to summarize the role of CE in reducing waste.

What is Circular Economy?

According to Ellen MacArthur Foundation, CE is one that is restorative and regenerative by design and is all about an upstream solution that focuses on enhancing the natural capital, preserving the natural resources, and minimizing the waste generation (Shareable, 2018). The core defining element of CE is the “restorative use” of resources (Geisendorf and Pietrulla, 2018). CE stresses upon the active use and extended life-cycle of products, materials and resources in the economy as well as minimizing waste generation (see “Relevant Websites section”). CE is an intersection of economic and environmental aspects which marks a shift away from the linear economy. CE is gaining traction as a meaningful alternative to make a transition from continuous growth in production and consumption towards resource efficiency and ecological balance (Ghisellini *et al.*, 2016). CE involves steps for cleaner production orientation at company level, higher responsibility and awareness among producers and consumers, use of renewable sources, and push for recycling, reuse and repair oriented business models. CE focuses on creating an ecosystem which is restorative and regenerative by design. This implies setting up a value chain in which materials flow in a “closed loop” system rather than following a linear use and throw approach. Adoption of a CE approach yields benefits for the business and

environment in terms of lower costs, less waste and sustainable ecological balance. CE is looked upon differently by different people from implementation perspective. Ellen MacArthur Foundation (EMF) defines CE as an approach linked to resource efficiency, closed-loop supply chain, reverse logistics, low-waste production, industrial ecology, longer product life, and disruptive business models (Geisendorf and Pietrulla, 2018). According to research recommendations, adoption of CE approach can reduce the consumption of new materials upto 30% by 2035 and 50% by 2050 (Esposito *et al.*, 2015).

Why Need for Transition From Linear to Circular Economy?

The moot question today is that what we are going to leave for the future generations. Will they be able to sustain and survive considering the rapid environmental degradation and exploitation of resources? Are we going to create a better world for tomorrow or not? Certainly not, if we take into consideration the over consumption of resources, linear use and throw mind-set, consumption led marketing, ecological imbalance, and cities becoming garbage dumps. Everybody from government to companies to individuals needs to make a transition from linear consumption orientation to circular approach to create a better tomorrow (Goyal *et al.*, 2016). Refer to Figs. 1 and 2 for a comparative view of Linear Economy and Circular Economy.

According to World Bank estimates, cities globally produce 1.3 billion tons of solid waste annually. This is expected to reach 2.5 billion tons by 2025 (Shareable, 2018). Around 46 million tons (41.8 million metric tons) of electronic waste (e-waste) was produced in 2014 having an intrinsic material value of around USD 52 billion (Hoff, 2015). The e-waste volume is expected to reach beyond 60 million tons by 2020. USA and China contributed one-third of this e-waste in 2014 (Hoff, 2015). Major proportion of the consumables is getting into landfills every year due to lack of incentives for recycling, under-developed policy framework, dis-aggregated recycling setup, inefficient reuse and non-focused repair ecosystem. For example, India produced around 62 million tons of municipal solid waste (MSW) in 2016 with more than 81% of the same going to landfill sites rather than getting processed. India, being an extensive coal-use economy will have more than 225 million tons of fly ash by 2032 (Bordoloi, 2016). Till 2016, India was able to use only 38% of its fly ash in other activities like cement manufacturing, brick manufacturing, etc. India had more than 8.5 million end-of-life vehicles on the road generating huge amount of environmental pollution (Bordoloi, 2016). The number of end-of-life vehicles is expected to reach 22 million by 2022.

Adoption of CE approach can yield tremendous socio-economic and environmental gains for the countries. For example, one ton of recycled paper saves approximately 17 trees, 2.5 barrels of oil, 4100 kWh of electricity, 4 cubic meter of landfill and 31,780 litres of water over production of virgin paper from wood (Bhutani and Arya, 2017). One ton of recycled steel scrap saves 1.2 tons of iron ore, 0.7 tons of coal, 0.5 tons of limestone, 287 litres of fuel oil, and 2.3 cubic meters of landfill (Bhutani and Arya, 2017). According to a study by the University of Oklahoma, recycled steel reduces 97% mining waste, saves 75% of energy, cuts back 86% of air pollution and 76% on water pollution (Bhutani and Arya, 2017). Similarly, recycling of aluminum cans or replacing those with glass containers leads to significant reduction in waste going into land-fills.

Transitioning to a CE is a mandatory action needed to restore the social, economic and ecological balance (Hoekstra, 2018). At the same time, this is needed to safeguard the planet for the future generation. As per the current production and consumption trends in lineal economy, resources on this planet will not be enough to feed the people beyond 2050. Following are the major risks of continuing with a linear approach to design, manufacturing and disposal. *First*, linear use and throw approach has resulted in huge ecological imbalance - land, soil, air, and water. This has a cumulative effect on the physical and socio-economic well-being of the people. *Second*, more than 80% of the raw materials used in design and manufacturing of product offerings end up in landfill sites sooner or later thereby leading to growing volumes of waste going into landfills and creating ecological imbalance. *Third*, use and throw mind-set creates a scarcity of raw materials resulting in demand-supply gaps and cost overheads for the manufacturers and consumers. *Fourth*, linear consumption and discard approach forces the companies to focus on volumes driven value chain without any means of recycling or reuse. This restricts the scope for innovation in traditional companies leading to

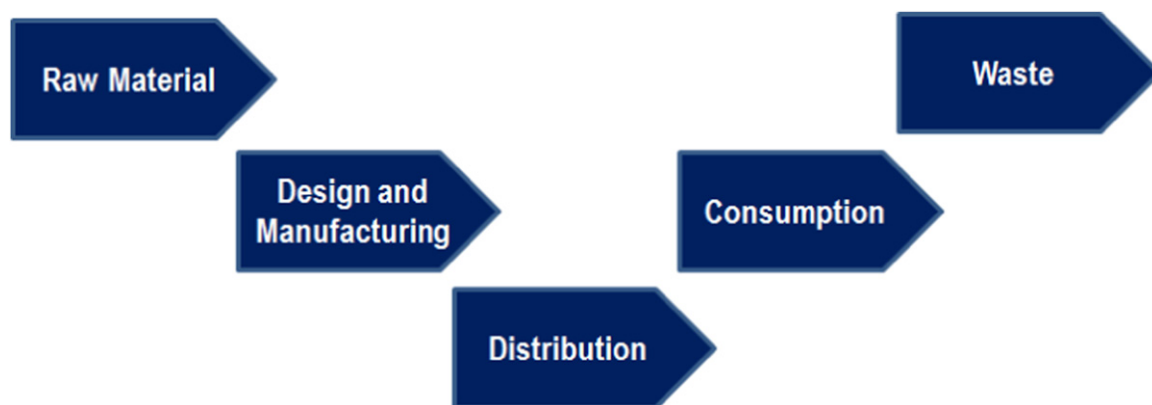


Fig. 1 Linear economy. Source: Created by Author.

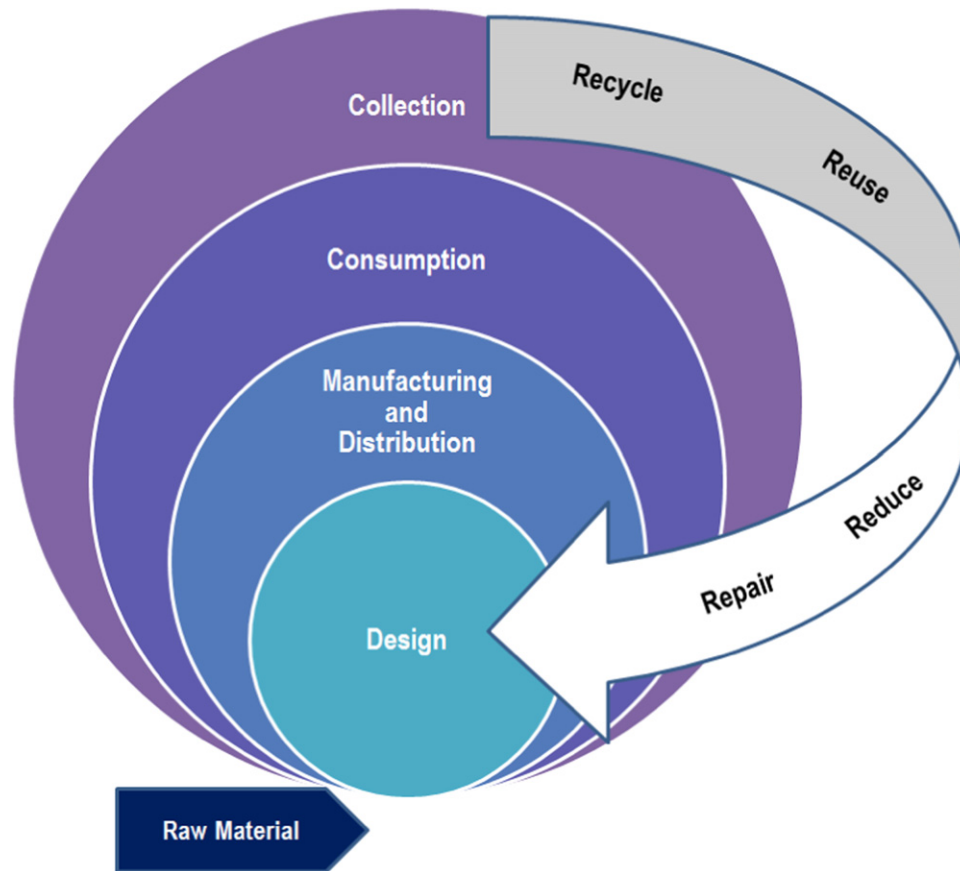


Fig. 2 Circular economy. *Source:* Created by Author.

hyper-competition. In this scenario, new entrants like Uber, Airbnb and Ola disrupted the industry dynamics by launching innovative shared economy business models. *Fifth*, countries are tightening the regulatory laws and policies to penalize the companies responsible for carbon emissions and waste generation.

Underlying Challenges in Adoption of Circular Economy

Adoption of CE is still in a stage of infancy due to multiple challenges like consumption oriented business models, antiquated public policies, lack of push by the governments in promoting circular strategies, and need for educating the businesses and individuals about the merits of CE.

Technology companies pose a major challenge by promoting “Consumption-led” business models. Take the example of mobile industry. Around 50 million tons of e-waste was generated in 2018 (Shenoy, 2018). More than 50% of e-waste was due to the rapid growth of personal devices like mobiles, laptops, computers, TVs and iPads. Only 20% of the e-waste gets recycled and remaining 80% goes into landfills every year. The total value of raw materials in e-waste was estimated to be more than USD 60 billion in 2018 (Bandela, 2018). This was higher than GDP of large number of countries globally.

An average person tends to change his/her mobile every one year and discards the existing mobile thereby contributing to an increasing stockpile of e-waste on this planet. The majority of the mobile manufacturing companies tend to focus on increasing volumes with new models and designs. There has been little focus on promoting the drive for recycling or refurbishing the obsolete mobile handsets. Both the consumers and producers need to change the mind-set from over-consumption led economy to sustainable consumption oriented economy.

The majority of countries lag in terms of designing waste conservation policies, building the right infrastructure for recycling industry, creating a sense of urgency for the companies and individuals as well as making provisions for giving incentives to the individuals and companies going circular. The volume of solid and e-waste has been increasing rapidly resulting in landfills and dumping sites around. For example, India produced around 62 million tons of municipal solid waste in 2017. This included more than 26,000 tons of plastic waste getting generated on daily basis. As per the current production, consumption and disposal trends, solid waste is expected to reach beyond 165 million tons by 2030 and 450 million tons by 2045 in India (Samaddar and Bandyopadhyay, 2018).

Multiple reasons are responsible for this growing challenge in developing economies like India. *First*, municipal infrastructure is obsolete with insufficient waste processing infrastructure in developing economies. This has led to increasing number of landfill sites across the cities. *Second*, there is a lack of clear government intent and policies to make the people and companies accountable for waste generation and segregation. This allows the companies to leverage political patronage for bypassing the waste, pollution and recycling norms and standards. *Third*, waste collection and segregation is still considered to be a menial job in countries like India thereby denying the socio-economic parity and respect for the people and the companies doing the same. Due to this, most of the companies and individuals lack interest and motivation in becoming a part of waste processing industry.

Understanding Circular Economy Models and Paradigms

CE involves action across three dimensions (Tse *et al.*, 2015). The *first* dimension involves undertaking actions and processes to reduce waste during the production and consumption processes. The *second* dimension involves propagating the “Servitization” approach where the focus shifts from product or asset based business models to service oriented ones. The *third* dimension involves extending the usable life-cycle of a product by recycling, reuse or repair. Going “Circular” is not just a case of incremental innovations but implies embracing real innovation and change in mind-set and business models (Edie Newsroom, 2016). Products should be designed for long-term use, ease of dis-assembly and ease of repair. Companies need to implement effective take-away and collection mechanism for obsolete products.

Fundamentally, there are five main CE business model typologies, which are being implemented by the companies globally (Riel, 2018; MEFD, 2016).

Circular Supply Chain Model

This involves making use of fully biodegradable, renewable and recyclable inputs across the supply chain. This makes the supply chain efficient and cost effective for the company, suppliers and customers. This model also included removing inefficiencies in the supply chain. This model is useful for companies having major carbon footprints or dealing with scarce commodities.

Resource Recovery Model

This includes recycling the product at end of life into diverse upscale product offerings thereby eliminates waste, creating alternate revenue streams and yielding environmental benefits. This model is useful for companies generating large volumes of by-product or companies yielding waste material which can be reprocessed cost effectively.

Product Life-Cycle Extension Model

This model relates to extending the life-cycle of products and assets by repairing, reconditioning, re-treading, re-marketing or re-manufacturing the used products and selling them in price conscious markets. This model is relevant for capital-intensive B2B (business-to-business) companies like industrial enterprises or B2C companies (business-to-consumer) having price-sensitive product offerings.

Sharing Platform Model

This model relates to launching a shared platform for sharing of assets, happy hours usage during low peak demand thereby increasing productivity and utilization. This model encourages collaboration among product users thereby ensuring demand-supply mapping and optimization of returns on under-utilized or segregates assets. This is applicable for all types of products and service offerings having under-utilization due to product ownership based usage. Companies like Uber and Airbnb spotted this opportunity and introduced innovative business models for car and home sharing respectively. During 2008–2015, Airbnb expanded its presence to more than 34,000 cities in 137 countries.

Product as a Service Model (PAS)

This model involves offering products on lease or pay-for-use. The companies adopting this model need to ensure product durability, reusability, and service excellence. From user perspective, PAS model eliminates the need for ownership to make use of any product. From supplier perspective, PAS model ensure optimal utilization of assets thereby replacing obsolescence and waste with long lasting efficiency and better revenue streams. This creates alternate revenue streams, better accessibility and availability for larger set of customers without the need for ownership. For Example, General Electric and Pratt & Whitney offer jet engines on rental basis. This model is applicable for companies offering expensive products to the market. This model works better for those products where better upgrade and maintenance is required.

Circular Economy in Practice

Country and Cities Level Examples

Countries and cities have started initiating a dialog with the industries to set up common goals towards sustainability and ecological balance. Cities globally are launching awareness drives and incentivizing the companies and individuals as per the behavior change orientation towards CE initiatives. Cities are redesigning their procurement policies and public institutions in accordance with circularity principles (Plastrick and Cleveland, 2018).

In 2013, Oslo city introduced public transportation buses powered by banana peels. This was a novel city level initiative, wherein residents in Oslo were asked to put the food waste in special green bags (Plastrick and Cleveland, 2018). This waste was recycled into biogas and used as a clean fuel for running the buses. This initiative was aimed at reducing the GHG (greenhouse gases) emissions from decaying waste. In 2002, San Francisco set up a target of “zero waste by 2020”. The actions involved converting city food waste into compost to be used by the farmers. The similar CE approach of converting food waste into fuel or compost has been adopted by many other European cities over the years.

In 2018, city of Ontario in Canada passed North America’s first Circular Economy law (Riel, 2018). This made it mandatory for producers and importers of electrical and electronic components to ensure recycling of e-waste rather than diverting the same to landfills. The companies in Canada started designing electronic components with ease of disassembly and recycling in accordance with the Ontario Law 2018.

Countries like USA and China transformed the waste collection, segregation and processing into a technology driven ecosystem providing respectable job opportunities to the people as well. According to Institute of Scrap Recycling Industries (ISRI), scrap industry in USA generated over 150,000 direct jobs and 323,000 indirect jobs in 2015 (Samaddar and Bandyopadhyay, 2018). In China, recycling industry generated 1.5 million direct jobs and 10 million indirect jobs (Samaddar and Bandyopadhyay, 2018). In India, metal recycling industry employed around 1.75 million people and contributed around 2% to the GDP.

Several developed economies especially the European nations initiated policy level actions to drive the adoption of CE approach (Bhutani and Arya, 2017). Sweden offered tax breaks for repair activities (50% cut on value-added tax) and passed the law that mandated electronic goods retailers to accept the same quantity of goods as sold by them for reuse or recycling. Similarly Japan and Netherlands announced strong CE legislations. China passed the Circular Economy Promotion Law (CEPL) in 2009 to promote the adoption of sustainable CE practices. According to Waste and Resources Action Programme (WRAP), UK CE ecosystem led to recycling of more than 75% of the solid waste by 2018.

Industry and Company Level Examples

Due to gradual push by the governments globally, companies have started providing correct labeling of products regarding the end of life. Also, companies have started setting up collection centers and providing reimbursements or monetary incentives to customers to encourage the collection of products reaching end of life (Bordoloi, 2016).

Dell introduced *2020 Legacy of Good Plan* in 2013. This plan called for an increased focus on enhancing the use of recycled material and minimizing e-waste by adopting the closed-loop supply chain and enhancing the useful life of plastics (Tse et al., 2015, 2016). The company recycled old computers and plastic bottles, which were being collected via “take-back” scheme and used those in the manufacturing of monitors and desktops. This resulted in significant cost savings and reduction in carbon emissions. CE orientation has given a tremendous boost to the brand image of Dell (Himmelfab and O’Dea, 2015).

Unilever launched Zero-Waste drive as a part of CE orientation in early 2000. The objective of this drive was to send across zero non-hazardous waste to landfill from the network of 240 factories in 67 countries (Himmelfab and O’Dea, 2015). The measures involved smart sourcing of raw materials, reusing and recycling manufacturing excess by composting or cross using those in other industrial chains. Zero waste orientation led to considerable cost savings besides create a positive brand image among the consumers as an environment friendly company.

PepsiCo initiated buy-sell drive and collaborated with different players for buying and selling used products. It undertook cross-farm collaboration to source slurry from Dutch and Belgium dairy and pig farms and used the same as natural fertilizer on their potato farms. The use of slurry reduced the need for chemical-based soil enhancers and associated carbon emissions (Himmelfab and O’Dea, 2015).

Similarly, P&G’s launched GARP (Global Asset Recovery Purchases) initiative where it started selling unusable fibers from Mexico based toilet-paper plant to the local companies for manufacturing low-cost roof tiles.

Coca Cola adopted circular packaging by cleaning and reusing glass bottles as well as recycling PET bottles and aluminum cans into upscale products. The company collaborated with partners like Ekocycle while introducing plant-bottle technology (Himmelfab and O’Dea, 2015). This technology was used by Coca Cola for creating recyclable PET bottles from agricultural by-products like sugarcane waste.

In Turkey, Frito Lay focused on composting while going for a circular business model. The company generated biogas and organic digestate by processing waste from potatoes, corns and broken chips. The company used the biogas for meeting up to 35% of the power consumption need of the manufacturing plant in Turkey. It converted digestate into compost and gave it to the local orchards for enriching soil of their farms.

Starbucks collaborated with Japanese contact lens manufacturer, Menicon for recycling coffee grounds into livestock feed (Himmelfab and O'Dea, 2015). Menicon used lactic acid fermentation technique to supplement the coffee grounds with nutrients and offered the same as cattle feed.

Telefonica introduced circular oriented culture in the company by taking up series of actions (Telefonica Website, 2018). First, it created purchase agreements with the suppliers showing clear preference for the suppliers making use of renewable resources and offerings products having least environmental impact. Second, it implemented a paperless invoice setup for its 53 million customers thereby saving thousands of trees per annum. Third, it created an ecosystem for recycling and reuse of e-waste generated by the company in the form of cables, batteries, tubes, papers, routers, customer telephones etc. It set up a digital waste management system across all its offices. Fourth, it started branding itself as an environmental conscious and ecological friendly company. The company incentivised the customers by facilitating the reuse or recycling of their old mobiles phones while going for a new one.

Conclusion

There is a well-placed belief today that circular thinking can transform the lives of everybody on earth and will make the planet liveable for future generations. It is important to bring a behavior change orientation among the stakeholders by promoting system thinking, putting price on the negative externalities and change perceptions regarding the true value of natural resources (Bordoloi, 2016). As per calculations, every ton of discarded textile getting reused can save up to 20 tons of CO₂ and every 1000 tons of used textile collection and processing can create at least 7 direct and 15 indirect jobs (Bordoloi, 2016). Similarly, circular approach in the food industry can help reduce hunger, social inequality and generate millions of jobs in up cycling initiatives. In electronics industry, push towards the end of life for electronic goods by recycling, repair or reuse can generate millions of jobs in e-waste industry besides reducing the huge dumping of e-waste. Plastic is one of the major contributors to solid waste and ecological imbalance. Minimizing the use of plastic via government legislation and processing the discarded plastic bags into construction of tar roads can create a tremendous ecological impact. As per calculations, every kilometer of road being laid out using CE approach utilizes equivalent of million plastic bags, saving around a ton of asphalt and cost savings by 8%.

One does not need to be a rocket scientist for circular orientation. The companies can start identifying and implementing circular thinking in their day-to-day operations across the value chain. How can we encourage use of renewable resources? How do we encourage water and electricity conservation? How can we enhance the usability of what we consume and what we produce? How do we create a recycle value chain? How do we encourage the circular thinking and behavior among the employees? These are some of the questions which individuals and companies need to evaluate every day and take appropriate actions. The whole idea of CE is to look at products from regenerative or restorative perspective. "Use and Throw" and "End of Life" mind-set need to be replaced by recycling, reuse and repair of product offerings thereby eliminating the waste through circular value chain as well as innovative business models (MacArthur, 2013). Finally, no drive can be successful without the active role and contribution of the government. It is mandatory for the governments globally to design and implement strong policies and regulations that will ensure the right focus and attention towards circular orientation by all the stakeholders (companies, individuals, institutions etc.).

See also: Circular Economy in the Built Environment: Designing, Deconstructing, and Leasing Reusable Products. The Circular Economy: Additive Manufacturing and Impacts for Materials Processing

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Subtractive Versus Hybrid Manufacturing

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Subtractive Manufacturing

During last decades, significant progresses are developed in the industrial sector in the field of conventional subtractive operations. Here, conventional machining operations occupied and dominated the entire manufacturing sector. New advancements in manufacturing of the machines and tools used for cutting are mostly led by the conventional machining operation. Along with it, it also showed a new pathway for manufacturing of product through an ultimate process planning systems including certain small variation during selection of cutting tool, coolant, lubricant and using the optimum parametric setting. The new technology involved in the subtractive processes controls the machining time, adaptively, and helps in reducing the repetition and error generation on the surface quality. Machining process is one the oldest and versatile method used in the subtractive manufacturing of the today's generation products and services. It has numerous categories depicting the ways to achieve the desired geometry by full filling all dimensional, mechanical, and metallurgical requirements. The broad classification of the conventional machining operation in term of subtractive machining is shown in the Fig. 1.

The critical improvement is seen in conventional machining techniques during manufacturing of complex and integrated shape and size of components in industry. The adoption of conventional machining operation critically depends on the machine performance and machinability aspects. These involves cutting forces, temperature generation at tool-workpiece interface, tool life and surface integrity (Arrazola *et al.*, 2013). The fundamental needs of machining and outcomes of the machining process are shown in Fig. 2. Its involves input parameters, machining techniques, process planning, machine and machine tools to get the desired product or outputs in terms of minimal waste of billet, with high tool life in an efficient and convenient way.

Grinding

Grinding is an abrasive machining process that uses a grinding wheel as the cutting tool. The chips formed during operation are mostly microscopic or in powdery formed. The removal of the materials occurred by means of ploughing and shearing action (Malkin and Guo, 2008). Through grinding operation very close tolerances with high precision and good quality of the surface can be achieved during manufacturing of the components. Grinding operation needs a higher amount of specific energy, resulting high heat generation that increases the machining zone temperature and affects product characteristics (Pederson, 2004).

Therefore, the selection of the grinding wheel materials is very important, most of the case SiC abrasive are the major choice in the industry (Jackson and Hitchiner, 2011). Mostly the heat generates and the friction occurred during grinding operation is reduced through minimum quantity cooling and lubrication method (Mao *et al.*, 2013). Choi and Eastman used a nano particles

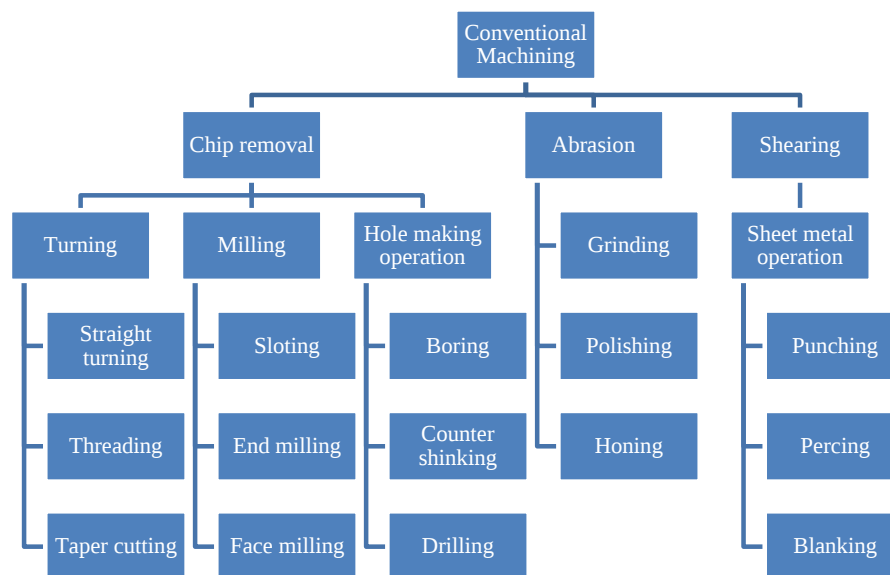


Fig. 1 Classification of conventional machining operation.

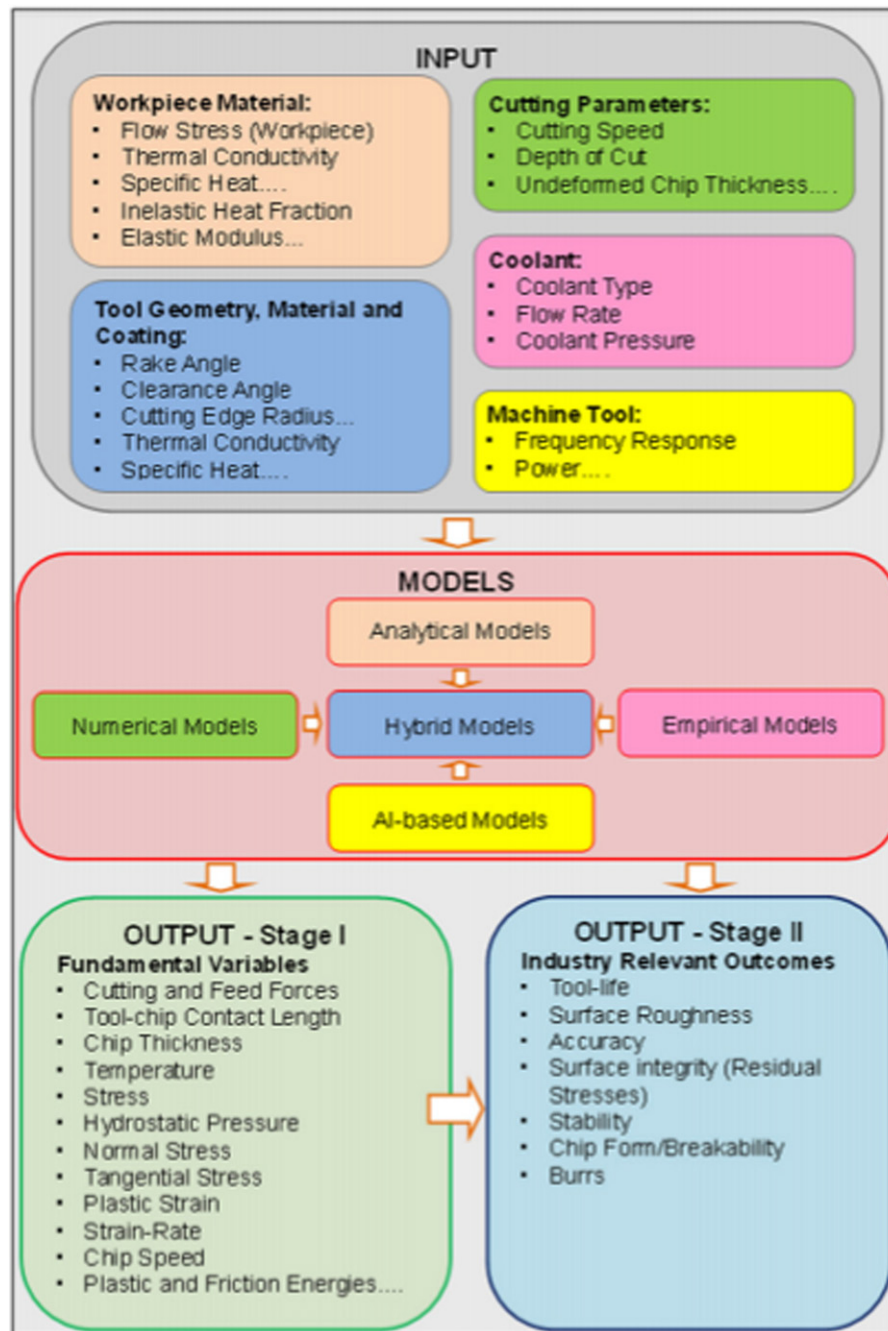


Fig. 2 Approach executed during machining process. Reproduced from Arrazola, P., Özel, T., Umbrello, D., Davies, M., Jawahir, I., 2013. Recent advances in modeling of metal machining processes. *CIRP Annals* 62 (2), 695–718.

fluid medium to enhanced thermal properties. Kalita *et al.* (2010) reduced the forces and friction generation at the wheel wear through using the MoS₂ with paraffin and soybean oil. Mao *et al.* (2013) used deionized water during grinding operation along with Al₂O₃ nanoparticle. This reduced the grinding force and temperature by improving the surface finish of the surface. Setti *et al.* (2015) studied the behavior of the wheel at different environment condition of grinding operation during grinding Ti-6Al-4V. The changes in the formation of the chips are also being studied. From Fig. 3, it is found that the high temperature formation leads to the creation of the wear flats on the surface of the wheel. The application of nanofluid reduces the temperature and dislodging of the gathered chip particle from the pores preserves the wheel conditions and thus reduces the wear flats.

The formation of the chips reveals that during dry and wet machining larger size of chip are produced but some time spherical shape of the chips is also formed during wet grinding. The cluster and fractured chips types of chip produced because of the chemical reaction between Al₂O₃ and titanium alloy as shown in Fig. 4.

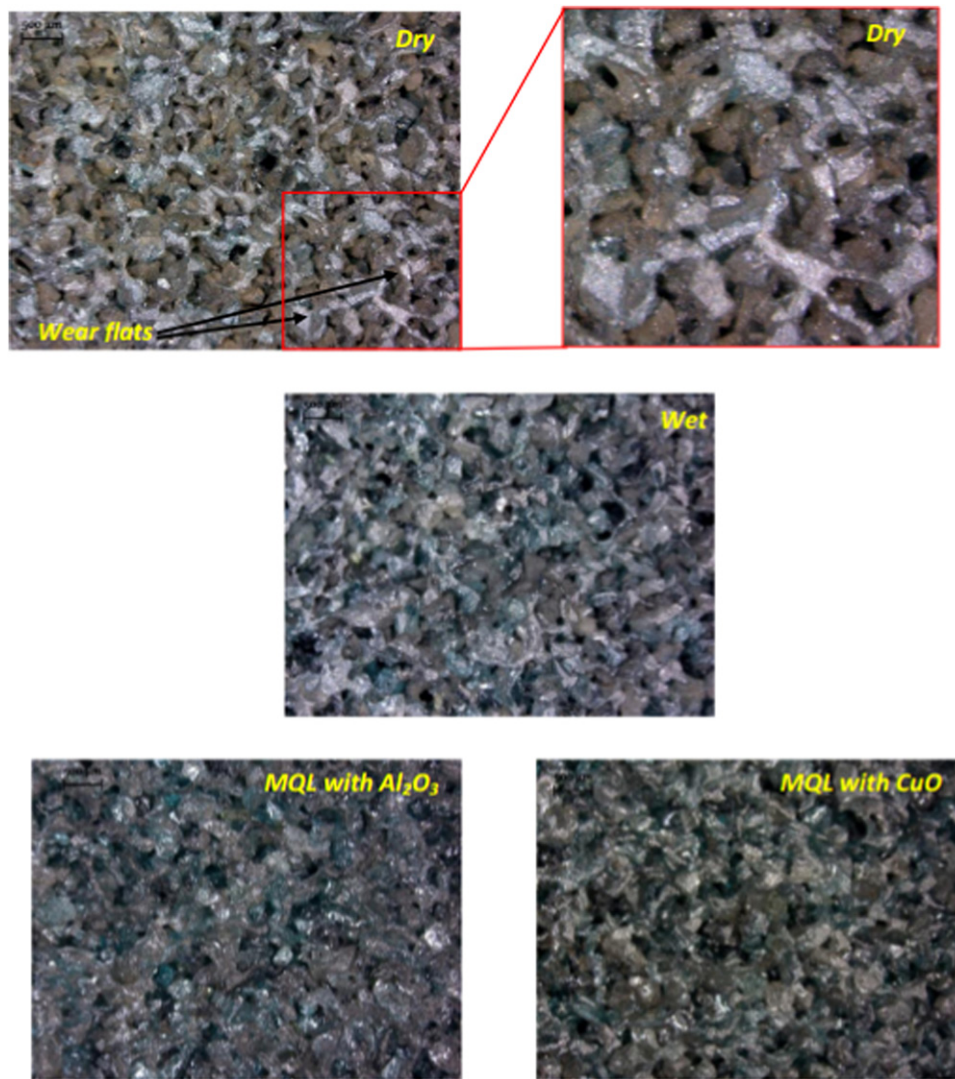


Fig. 3 Morphology of the grinding wheel at different cutting condition. Reproduced from Setti, D., Sinha, M.K., Ghosh, S., Rao, P.V., 2015. Performance evaluation of Ti-6Al-4V grinding using chip formation and coefficient of friction under the influence of nanofluids. *International Journal of Machine Tools and Manufacture* 88, 237–248.

Rabiei *et al.* (2015) studied the friction coefficient, forces, surface morphology and surface roughness of CK45 and S305 steel during grinding operation with aluminum oxide wheel. The cooling condition considered during machining were dry, fluid and MQL cooling. It revealed that MQL machining techniques shows better results by decreasing the grinding forces and friction coefficient of the steels. Fritsche and Bleicher (2016) studied the dynamic behavior of the grinding wheel. In this sensor are integrated in the grinding wheel to know the deformation and stiffness. Tyagi *et al.* (2017) studied the dressing and truing techniques to achieve higher productivity. Dressing is required to maintain the sharpness and protrusion. While truing regains the shape of the grinding wheel which diverted because of the deformation. The concentricity of the wheel with principal bore can be made aligned with truing.

Turning

Turning is a machining process in which a cutting tool, typically a non-rotary tool bit, describes a helix tool path by moving more or less linearly while the workpiece rotates. Turning can be done manually, in a traditional form of lathe, which frequently requires continuous supervision by the operator, or by using an automated lathe. In turning material is removed in the form of chips. Most of the research had been made to find out the optimum process parameter to achieve a better machinability of the material. Asiltürk *et al.* (2016) Optimized the process parameter to accomplished a better surface quality of the Co28Cr6Mo medial material. The optimum setting founded was 318 RPM, 0.1 mm/rev feed, 0.7 mm depth of cut and 0.8 mm of tool nose radius. Chew *et al.* (Nee *et al.*, 2018) also studied surface roughness of the Co28Cr6Mo medial material through the differential evolution

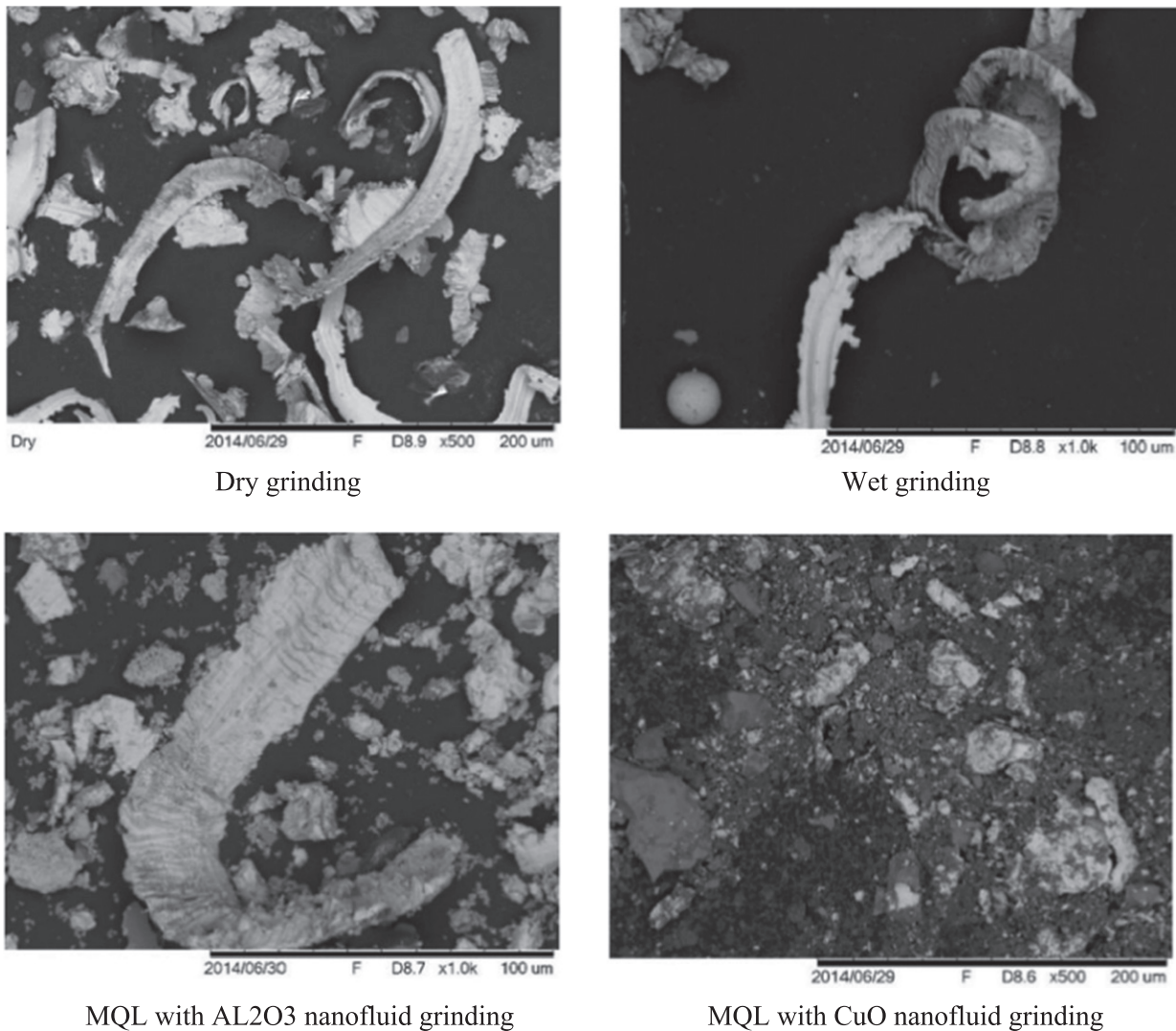


Fig. 4 Chip formation at different grinding conditions. Reproduced from Setti, D., Sinha, M.K., Ghosh, S., Rao, P.V., 2015. Performance evaluation of Ti-6Al-4V grinding using chip formation and coefficient of friction under the influence of nanofluids. *International Journal of Machine Tools and Manufacture* 88, 237–248.

technique (DE). It governs an algorithm that is simple fast and population based developed by [Storn and Price \(1997\)](#). The convergence profile of the surface roughness in terms of generation is shown in the [Fig. 5](#). The quality of the surface formed after machining increase the value and demands of production of the product ([Celik et al., 2017](#); [Yan, 2009](#)). The surface roughness studied portrays the fatigue strength, creep, wear and corrosion resistance of the machined surface. Therefore, it is necessary to control the factors affecting the surface roughness. A controlled surface roughness is achieved at a lower cutting speed and feed. Since increase in the tool wear with the cutting speed and feed aggravated surface roughness ([Celik et al., 2017](#)).

The Chatter produced in the tool during turning operation lead toward the inaccuracy of the machining and detritions in the cutting inserts. So the study had been made to reduce the chatter formation by changing the process parameter or through some new techniques. Some of the measuring instrument of signal processing technique used to detect the chatter such as dynamometers ([Kumar and Singh, 2018](#); [Toh, 2004](#)), multi-sensors ([Kuljanic et al., 2008](#)) and ammeters ([Soliman and Ismail, 1997](#)). Some other methods used by the researcher to suppress the tool chatter are piezoelectric actuation ([Albizuri et al., 2007](#)) active structural control ([Dohner et al., 2004](#)), magnetic bearing ([Chen and Knospe, 2007](#)), ultrasonic elliptical vibration ([Ma et al., 2011](#)) and spindle speed variation technique ([Wu and Chen, 2010](#); [Hajikolaie et al., 2010](#)). The wear of the cutting tool also depends upon the cutting parameters. The tool wear differs for CVD and PVD coating of tungsten carbide cutting tools. The tool wear increases with increase in the cutting speed for both CVD and PVD coated cutting tool. Tool wear increases because high cutting speed aggravate the cutting temperature during machining, since the materials possess low thermal conductivity. Also the area of the tool cutting edge and chips surface reduced increases the cutting temperature that accelerate the tool wear ([Astakhov, 2007](#); [Gorczyca, 1987](#)). The tool wear is more in CVD coated cutting tool as compared to the PVD cutting tool. This due to the

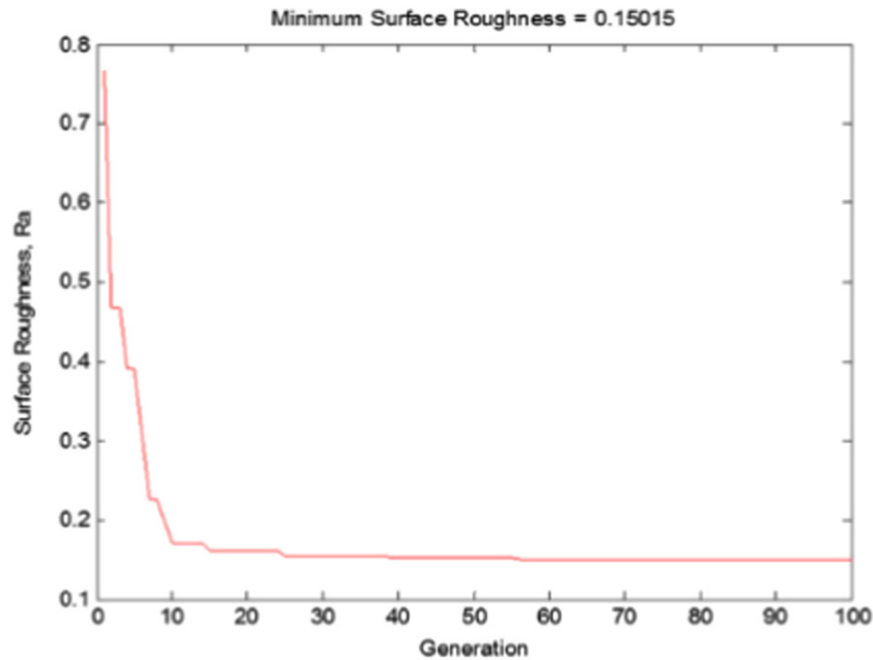


Fig. 5 Surface roughness DE convergence profile. Reproduced from Celik, Y.H, Kilickap, E., Guney, M., 2017. Investigation of cutting parameters affecting on tool wear and surface roughness in dry turning of Ti-6Al-4V using CVD and PVD coated tools. *Journal of the Brazilian Society of Mechanical Sciences and Engineering* 39 (6), 2085–2093.

chemical composition, the carbon percentage is high in CVD coated i.e., 32.13 wt% and also the presences of some other element such as oxygen and chlorine fascinates the reduction in the tool wear. The SEM images [Fig. 6](#) also justify a higher wear rate of CVD coated carbide cutting tool as compared to the PVD coated cutting tool. The higher cutting parameter effects the cutting temperature, pressure and increases the chances of chemical reactivity between the cutting tool and the workpiece, lead the development of tool wear in-terms of adhesion, dissolution and diffusions ([Sun et al., 2015](#); [Coppini et al., 2018](#)).

Milling

Milling is the process of machining using rotary cutters to remove material by advancing a cutter into a workpiece. This may be done varying direction on one or several axes, cutter head speed, and pressure. Milling covers a wide variety of different operations and machines, on scales from small individual parts to large, heavy-duty gang milling operations. It is one of the most commonly used processes for machining custom parts to precise tolerances. In milling operation, the material is removed from the workpiece by providing minimum feed rate with high speed rotation of the milling cutter. The cutting parameters are the most influencing factors that affect the responses. The cutting parameter can be spindle speed, depth of cut, feed rate, materials of the workpiece and tool, uncontrolled parameter such as uneven disturbances and machine errors ([Mahesh et al., 2015](#); [Jang et al., 1996](#)). The output responses such as tool wear, surface roughness, cutting force etc., have to be considering in achieving a better machinability of the materials. Surface responses are mostly affected by the feed rate ([Wang and Chang, 2004](#)). Surface roughness and waviness are the irregularities appeared on the machined surface due to the vibration, deflection, human and machined errors ([Arias, 1983](#)). Researcher suggest that it can be control through various theoretical approach ([Quintana et al., 2010](#)), analytical approach ([Mansour and Abdalla, 2002](#); [Alauddin et al., 1997](#)), experimental investigation through orthogonal array and response surface approach ([Chang et al., 2007](#); [Coker and Shin, 1996](#); [Gologlu and Sakarya, 2008](#); [Dhokia et al., 2008](#)). In some case the optimum cutting parameter had been achieved through various neural network, genetic algorithm, fuzzy logic and neural fuzzy method ([Tsai et al., 1999](#); [Benardos and Vosniakos, 2002](#); [Brecher et al., 2011](#); [Ali and Zhang, 1999](#)).

Tool wear accelerate by the size and thickness of the chips, the mechanics of material removal rate depend upon the ploughing region where the materials deform plastically, due to this high friction and stress generated between the cutting tool and the workpiece ([Teng et al., 2018](#)). This weakens the cutting edge by acquiring the highest load in the tip portion of the cutting edges. Some of the tool wear occurred due to the catastrophic failure of the cutting tool during milling operation ([Li et al., 2011](#); [Tansel et al., 1998](#)). [Tansel et al. \(2000\)](#) concluded that fatigue and stress generation and chip clogging breakage of the cutting edge are the most important factors considered for reducing the life of the cutting tool. Higher cutting force generation also reduces the sharpness of the cutting edge and decreases the life of the cutting tool. [Rahman et al. \(2001\)](#) observed that tool wear occurred in the major and minor cutting edge of the tool was due to the non-uniform chip and the adhesion of chip on to the surface of cutting edged because of the high cutting temperature and pressure generated at higher cutting force. [Filiz et al. \(2007\)](#) found that

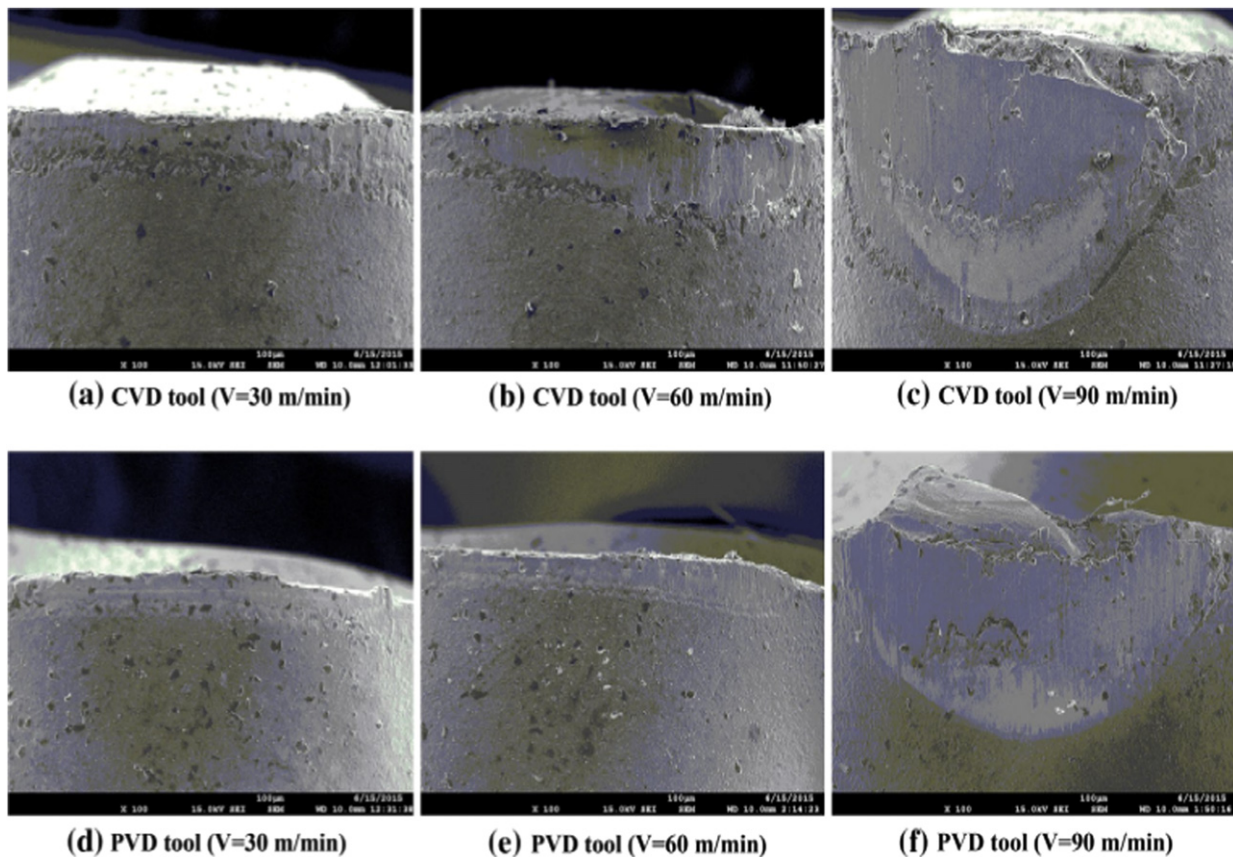


Fig. 6 Flank wear at different cutting speed with feed 0.104 mm/rev and depth of cut 1.5 mm. Reproduced from Celik, Y.H, Kilickap, E., Guney, M., 2017. Investigation of cutting parameters affecting on tool wear and surface roughness in dry turning of Ti-6Al-4V using CVD and PVD coated tools. *Journal of the Brazilian Society of Mechanical Sciences and Engineering* 39 (6), 2085–2093.

during micro-milling of copper the tool failure of the tungsten carbide was observed due to the abrasion wear. The micro chipping action during machining blunt the edges by diffusion mechanism, where the workpiece materials diffuse into the WC-Co binder with respect to the adhesion effects (Imran *et al.*, 2014). Kiswanto *et al.* (2014) studied the surface roughness and burr formation during miniaturized micro machining operation by varying spindle speed and feed rates. It is observed that surface roughness is affected by feed rate and machining time. Wang *et al.* (2005) justified that tool diameter and spindle speed increases surface roughness. The improvement of surface quality can be made by increasing the structure and stiffness of the cutting tool, since it's reduces the vibration and chatter. Vazquez *et al.* studied the surface roughness behavior by varying the spindle speed, depth, feed per tooth, depth of cut per pass and the coolant. It is observed that surface roughness of the aluminum and copper is affected by feed per tooth and coolant application (Vázquez *et al.*, 2010). Whereas, Jin *et al.* (2009) observed that burr size and surface roughness increase due to the variation in lower feed per tooth and cutting edge radius. Hashimura *et al.* (1999) divides the formation of burr by its milling location, mechanism and shapes i.e., entrance burr, exit burr, side burr and top burr. Litwinski added the bottom burr formation concept for micro end milling operation (Litwinski *et al.*, 2006), as shown in Fig. 7.

The feed is linearly proportional to the height of the burr results in decreasing of the tool wear (Lee and Dornfeld, 2005). The radius of the milling cutter and the axial depth of cut affect the top burr formation (Chen *et al.*, 2012). Chu and Dornfeld (2005) found that burr height is influence by the uncut chip thickness and radius of the cutting edge. Biermann and Steiner (2012) found that top burr formation is also affected by the lubrication method and feed per tooth. Top types burr was formed on the top surface of the workpiece. The quality of the machined surface became poor due to the formation of top burr. Kiswanto *et al.* (2014) revealed for the experimental study that, the top burr can be minimized, refer Fig. 8, if optimizing the spindle speed and feed rate.

During the burr formation study, the size of the burr i.e., the width and length of the burr was measured as shown in Fig. 9. It is observed that an uneven burr formation is formed in the micro channel also it's facilitated along the cutting process. But some detachment or the dissipated burr formation is formed due to the formation of built up edge. The burr size varies according to the tool wear which occurs due to the chipping action at the tool edge as shown in Fig. 10.

Now-a-days, the sheet metal manufacturing has become a challenges due to the use of advanced high strength steel (AHSS) as blanks. Most of the automotive industry used this AHSS for the convenience safety requirements and manufacturing of light weight vehicle (Mackensen *et al.*, 2010; Kleiner *et al.*, 2003; Rahmaan *et al.*, 2017; Scales *et al.*, 2016; Bai and Wierzbicki, 2010, 2008; Papisidero *et al.*, 2015; Ubhayaratne *et al.*, 2017; Shang and Daehn, 2011; Seth *et al.*, 2005; Choomlucksana *et al.*, 2015). (Fig. 11).

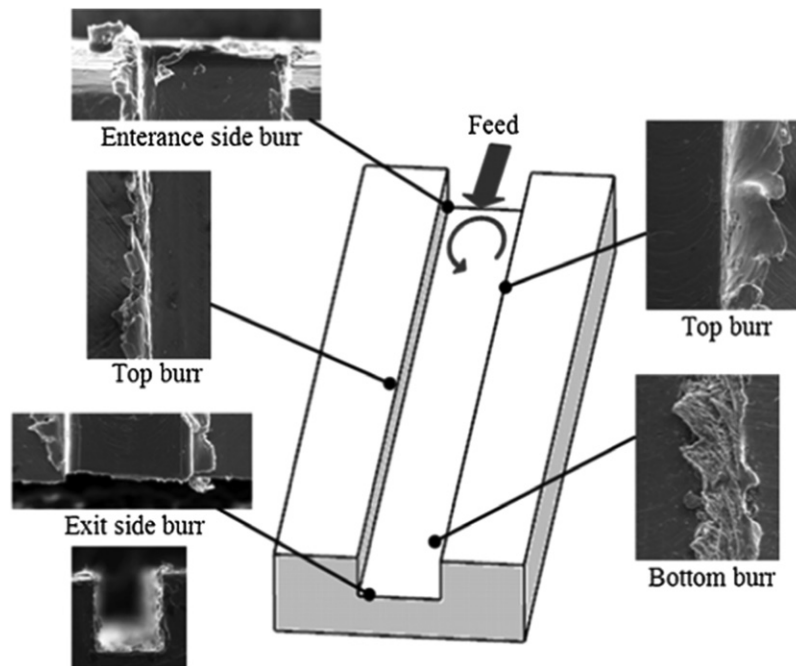


Fig. 7 Classification of burr formation during milling operation. Reproduced from Kiswanto, G., Zariatin, D., Ko, T., 2014. The effect of spindle speed, feed-rate and machining time to the surface roughness and burr formation of aluminum alloy 1100 in micro-milling operation. *Journal of Manufacturing Processes* 16 (4), 435–450.

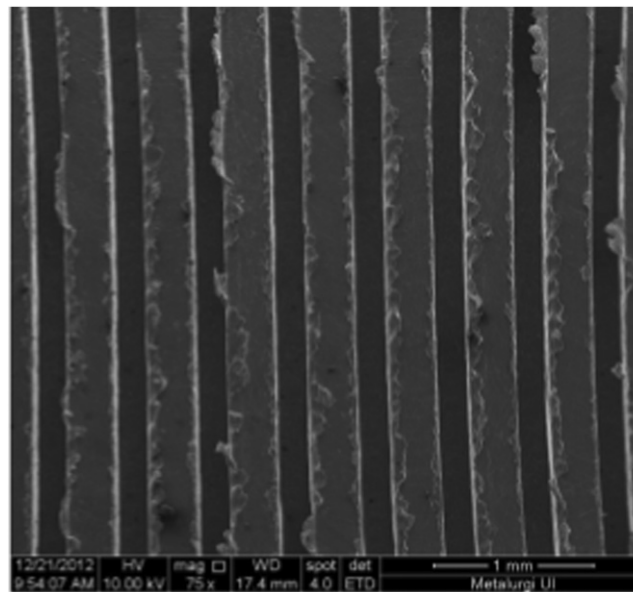


Fig. 8 Formation of top burr in the micro channel. Reproduced from Kiswanto, G., Zariatin, D., Ko, T., 2014. The effect of spindle speed, feed-rate and machining time to the surface roughness and burr formation of aluminum alloy 1100 in micro-milling operation. *Journal of Manufacturing Processes* 16 (4), 435–450.

Advancements in Subtractive Manufacturing

Subtractive manufacturing defines the formation of physical shapes by removing the material in the form of chips, burs, slices, etc. Generally, during the production of huge number of product, formation of co-ordination between various involved process parameters is a hurdle for rapid production in the industrial sector. Therefore, the recent studies in the field of subtractive machining are advance in the field of analytical modeling and finite element simulation. Yue *et al.* (Liu *et al.*, 2018) studied the

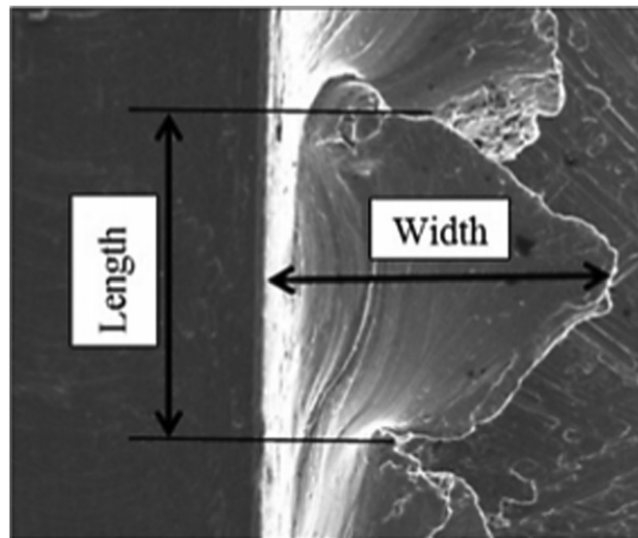


Fig. 9 The width and length of the burr. Reproduced from Kiswanto, G., Zariatin, D., Ko, T., 2014. The effect of spindle speed, feed-rate and machining time to the surface roughness and burr formation of aluminum alloy 1100 in micro-milling operation. *Journal of Manufacturing Processes* 16 (4), 435–450.

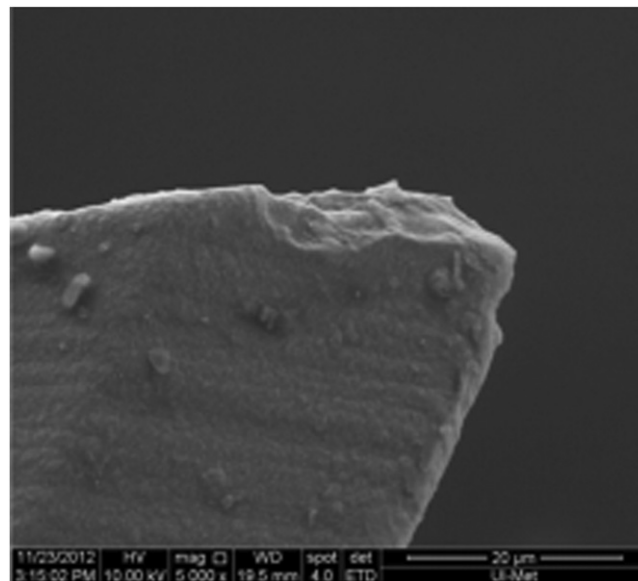


Fig. 10 Flank wear during machining operation. Reproduced from Kiswanto, G., Zariatin, D., Ko, T., 2014. The effect of spindle speed, feed-rate and machining time to the surface roughness and burr formation of aluminum alloy 1100 in micro-milling operation. *Journal of Manufacturing Processes* 16 (4), 435–450.

grinding pattern during correction made by grinding operation of rail profile. The new designed profile reduced the rail's maintenance time by increasing the service life. In this study the analytical model is developed using some of the wheel characteristics such as feeding feed, rotational speed and pressure applied to the rail. An algorithm developed to recognize and generate the grinding pattern. It is validated through the grinding quality and error in the rail profile as shown in [Fig. 12](#). [Azarhoushang et al. \(2018\)](#) observed that by grinding Si₃N₄ using laser assisted grinding process the material removal rates increased. This reduction is achieved due to the development of induced lateral cracks on the surfaces of silicon nitrides ceramics as shown in [Fig. 13](#).

[Agrawal and Patil \(2018\)](#) developed a new cutting approach by using green cutting fluid. The effect of surface roughness and tool wear during turning of M2 steel with minimum quantity lubrication using aloe Vera oil as cutting fluid are studied. The comparison is made with conventional cutting fluid. Results revealed that, surface roughness improved by 6.7% and the tool wear is lowered by 0.14%. [Pathak et al. \(2018\)](#) optimized the cutting parameters through taguchi fuzzy logic during turning of AISI A2

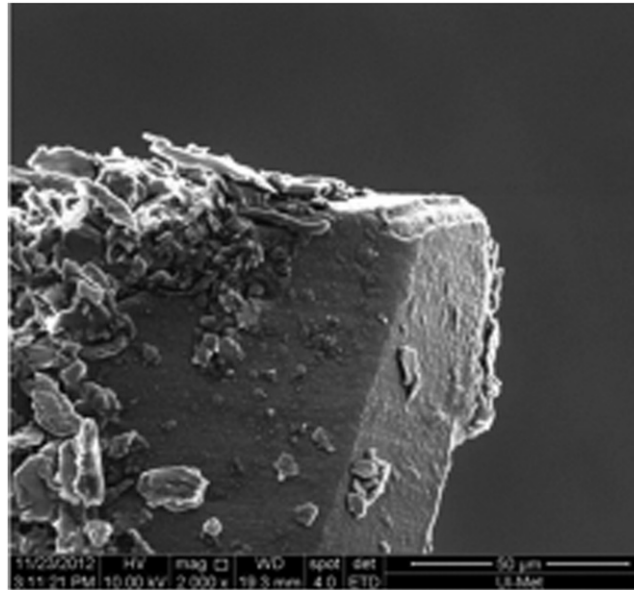


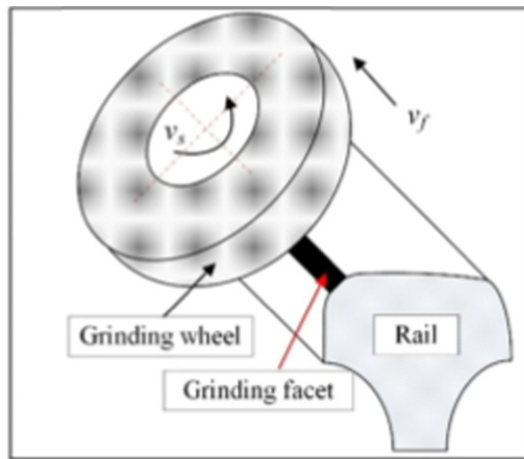
Fig. 11 Edge chipping during machining operation. Reproduced from Kiswanto, G., Zariatin, D., Ko, T., 2014. The effect of spindle speed, feed-rate and machining time to the surface roughness and burr formation of aluminum alloy 1100 in micro-milling operation. *Journal of Manufacturing Processes* 16 (4), 435–450.

steel with carbide cutting tool. Since A2 steel is mostly used in making of forged dies, punch and machine tool parts. Detection of optimum setting for cutting such types of metal is important. During any subtractive machining operation, the reduction and controlling of residual stress is a difficult task. [Il et al. \(2018\)](#) experimentally obtained the internal temperature generates during milling of Al2024-T3 workpiece. Afterwards, it has been found that the residual stress using X-ray techniques and developed the relationship between the cutting parameter and workpiece internal temperature. Chatter is another important factor need to be control during subtractive machining. Deniz and Yusuf used CNC ([Aslan and Altintas, 2018](#)) system real time data for detection of on-line chatter using Fourier spectrum of drive motor current command. They used the frequency response function and eliminate the forced vibration components to detect the presence of chatter during milling operation. [Helo and Hao \(2017\)](#) used the cloud manufacturing system for sheet metal operation. [Li et al. \(2017\)](#) used a magneto-rheological fluid during bidirectional pressure forming on sheet metal. [Luksaz et al. \(Bohdal et al., 2018\)](#) performed 3D finite element modeling of sheet metal blanking operation to analyzed the contact friction, constitutive damage, dynamic effects and mechanical coupling during deforming 1018 steel. [Table 1](#) briefly summarizes the various activities done to hybridize the conventional manufacturing systems.

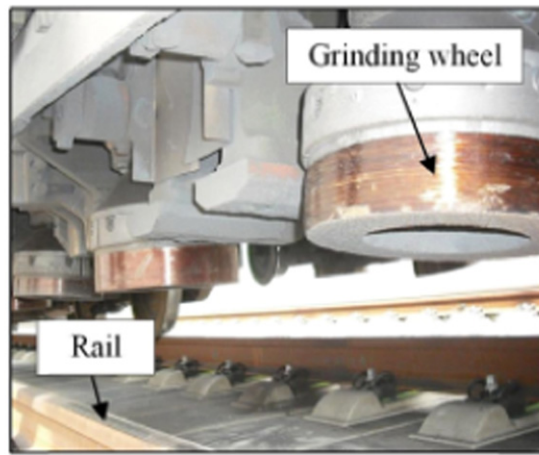
Computer Controlled Conventional Manufacturing

The computer numeric control (CNC) systems are the results of an increased demand of the military equipment, automobiles, smartphones and various other consumer products which exerted a huge pressure on manufacturing sector to maximize its resources. Therefore, the development of CNC machines is one of the means for manufacturing sector to deliver on increased demands. CNC technology brings together accuracy, precision and efficiency together, while delivering higher production rates. The highly sophisticated CNC machine tools found in various forms and diverse range in the field of manufacturing processing had very humble beginnings. Some of the earliest research and development work in this field was completed in the USA after the Second World War ([Bollinger and Duffie, 1988](#)). CNC machines are designed to be operated with minimum supervision and are more precise and consistent as compared to traditional machine tools ([Mattson, 2009](#)). This method of manufacturing is an appropriate choice for large volume production runs. The workflow of the hybrid additive subtractive manufacturing process, as shown in [Fig. 14](#), is similar to additive manufacturing workflow, but the significant difference is facility a subtractive manufacturing facility can be provided to manufacturing services to external customers which is less common in case of case of additive manufacturing.

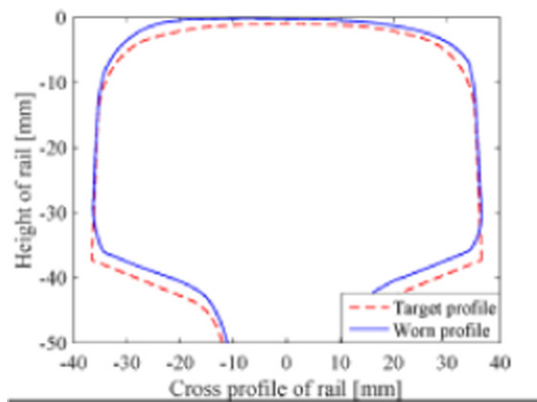
This technique presents the significant opportunities for improvement and utilization of materials, For producing complexity and quality products. Advanced numerical control (NC), and computer-aided design (CAD), manufacture (CAM) and inspection (CAI) are playing a vital role to govern the process ([Flynn et al., 2016](#)). [Yampolskiy et al. \(2017\)](#) compared the additive and subtractive manufacturing from security perspective and outlines were given for analyzing attacks on or using additive manufacturing systems and subtractive systems. It was revealed that there is significant overlap concerning security, fundamental differences in the two manufacturing paradigms require a separate investigation of additive manufacturing security. [Flynn et al. \(2016\)](#) discussed the working of a system by combination of and subtractive processes within a single workstation and revealed that these type of techniques can play significant role in future for the improvement of These techniques present significant



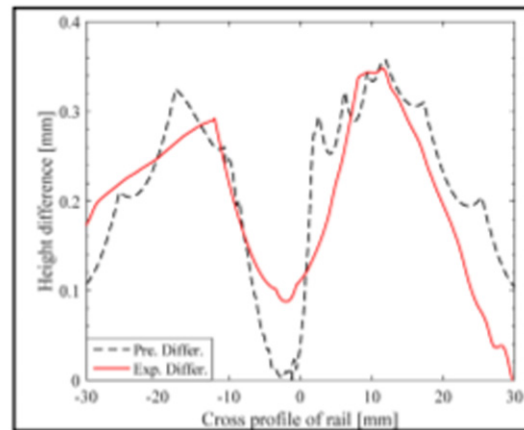
(a) Grinding wheel with rail



(b) Rail grinding car with grinding wheel



(c) Error in the rail profile



(d) Height difference error of cross rail profile

Fig. 12 Profile correction in grinding operation of rail profile. Reproduced from Liu, Y.M., Yang, T.Y., He, Z., Li, J.Y., 2018. Analytical modeling of grinding process in rail profile correction considering grinding pattern. *Archives of Civil and Mechanical Engineering* 18 (2), 669–678.

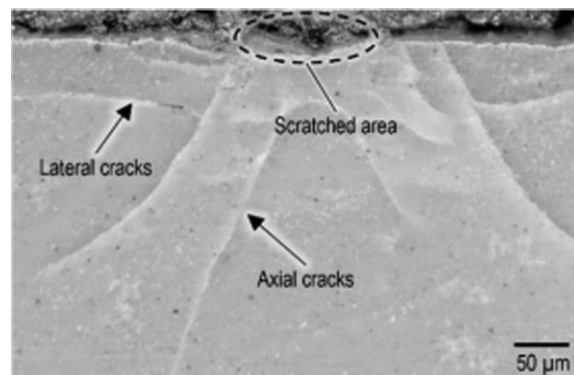


Fig. 13 Generation of lateral cracks. Reproduced from Azarhoushang, B., Soltani, B., Daneshi, A., 2018. Study of the effects of laser micro structuring on grinding of silicon nitride ceramics. *CIRP Annals* 67, 329–332.

opportunities to improve material utilization, part complexity, and quality management in functional parts as these methods facilitate the manufacture of internal, overhanging and high aspect ratio features with desirable geometric accuracy and surface characteristics. Fig. 15 shows the machine tool configurations that are emerging as preferred methods of integration for CNC machining.

Table 1 List of activities performed on hybrid conventional manufacturing

References	Workpiece and tooling	Techniques	Output measures	Findings
(Sofuoglu <i>et al.</i> , 2018a)	Hastelloy-X, Titanium alloy	Hot ultrasonic assisted turning (HUAT) FEM analysis	Average cutting forces, Effective stress, Cutting temperatures	In this hybrid machining approach of HUAT the cutting forces decreased by 50% as compared to conventional turning operation. The effective stress is reduced from 1600 MPa to 1250 MPa. The cutting temperature increases due to application of the external heat source
(Sofuoglu <i>et al.</i> , 2018b)	Hastelloy-X	Ultrasonic-assisted turning, Hot machining	Surface roughness, Chatter stability, Cutting tool temperature, Chip morphology	This paper combined the Ultrasonic assisted turning with hot machining. This method improves the surface roughness with a stable cutting depth. Whereas the tool life was reduced because of the higher cutting temperature. The variation in the chip thickness also reduced
(Sanchez <i>et al.</i> , 2010)	AISI D2 tool steel	Hybrid Minimum Quantity of Lubricant (MQL)-low temperature CO ₂ system, Biocut 3000 oil is used	Grinding wheel life, surface quality	The creation of durable tribofilm around the grits improves the sliding and lubrication action during grinding at extreme pressure conditions. The surface finish and force ratio is increase by 28%
(Sharma <i>et al.</i> , 2018)	AISI 304 stainless steel	Hybrid cutting fluid, blending Multi-walled carbon nanotubes (MWCNTs) with alumina-based nanoparticles into cutting fluid	Cutting temperature, Flank wear	This hybrid approach machining method reduced the flank wear by 11% and cutting temperature by 27.36%
(Jeng and Lin, 2001)		Metal rapid prototypes and molds fabricated using hybrid processes of selective laser cladding (SLC) and milling		By hybrid process of SLC and milling the accumulation of the powder and clad height is controlled accurately. The top surface was also found smooth through milling operation. By this process the layer thickness was reduced by significantly increasing the building time
(Nag <i>et al.</i> , 2018)	A359 aluminum alloy as base matrix and 2% B4C and 2% Al ₂ O ₃ as reinforcing particles	Tangential abrasive water jet (AWJ) turning of hybrid aluminum matrix composite fabricated by electromagnetic stir casting technology	Abrasive mass flow rate, surface quality, Reduction in sample diameter	This process reduced the tool wear. Nearly 30% in diameter reduction is observed. The olivine abrasive generated more internal cracks as compared to garnet

Hao *et al.* (2018) proposed the novel process planning algorithm for additive and subtractive manufacturing (ASM) system to remanufacture the disused part, the skeleton of the model was generated using the matching algorithm was developed for recognizing the different features between the initial model and the final model based on skeleton tree. Kerbrat *et al.* (2010) purposed the method for estimating the complexity of for subtractive and additive manufacturing to over the constraints at initial stage, i.e., designing of machine tools using CAD models. Li *et al.* (2018) proposed the 6-DOF hybrid additive-subtractive manufacturing (HASM) process model to overcome the limitations of additive manufacturing by integrating it with subtractive manufacturing. Newman *et al.* (2015) introduced the framework for process planning using the subtractive and additive technologies.

Hybrid Manufacturing

The hybridizations under this class of manufacturing basically involved the combinations of additive and subtractive manufacturing under a unified machine system. For instance, additive manufacturing in the form of laser cladding could be used to build up a metal form that, when cooled, is machined using traditional methods. Moreover, when laser cladding is used to build a metal form it needs to be machined with traditional machining. Fig. 16 shows the process build an overhang structure on a 2.5D and multi-axis deposition system. Coupled between the additive and the subtractive processes into a single workstation, the integrated process, or hybrid process, can produce a metal part with machining accuracy and surface finish (Liou *et al.*, 2007).

Zhang and Liou (2013) presented a parametric curve for automatic path planning hybrid manufacturing during material deposition and removal without the support structure. The parametric representation of STL-based layer geometry is presented to overcome the issue of complexity in multiaxis machining. Boivie *et al.* (2012) discussed the advantages of hybrid manufacturing for the production of high performance parts. Yamazaki (2016) discussed the possibility of developing the Hybrid Multi-tasking



Fig. 14 Software and control flow for the HASM process. Reproduced from Li, L., Haghighi, A., Yang, Y., 2018. A novel 6-axis hybrid additive-subtractive manufacturing process: Design and case studies. *Journal of Manufacturing Processes* 33, 150–160.

machine tool using Laser Metal Deposition functionality in addition to existing integrated turning and milling capabilities. It was concluded that Hybrid Multi-tasking machine tool with application examples and demonstrates possibilities and tasks for the next generation manufacturing, refer Fig. 17.

Karunakaran *et al.* (2010) discussed the features of both CNC machining (subtractive method) and Rapid Prototyping (additive method) and by combining these process for hybrid manufacturing. Müller and Wings (2016) discussed the advantages of hybrid manufacturing in context to the manufacturing of complex parts accuracy, less production time, and lower costs, etc. Skeebea *et al.* (2016) discussed various cases studies related to hybrid manufacturing and described the outlines some aspects of the future development of an integrated hybrid manufacturing system. Strong *et al.* (2018) discussed the advantages of hybrid manufacturing is required to achieve Geometric Dimensioning and Tolerancing (GD&T), surface finish and desired mechanical properties and also discussed the various challenges of traditional manufacturers to participate in the rapidly evolving supply chain of direct digital manufacturing (DDM).

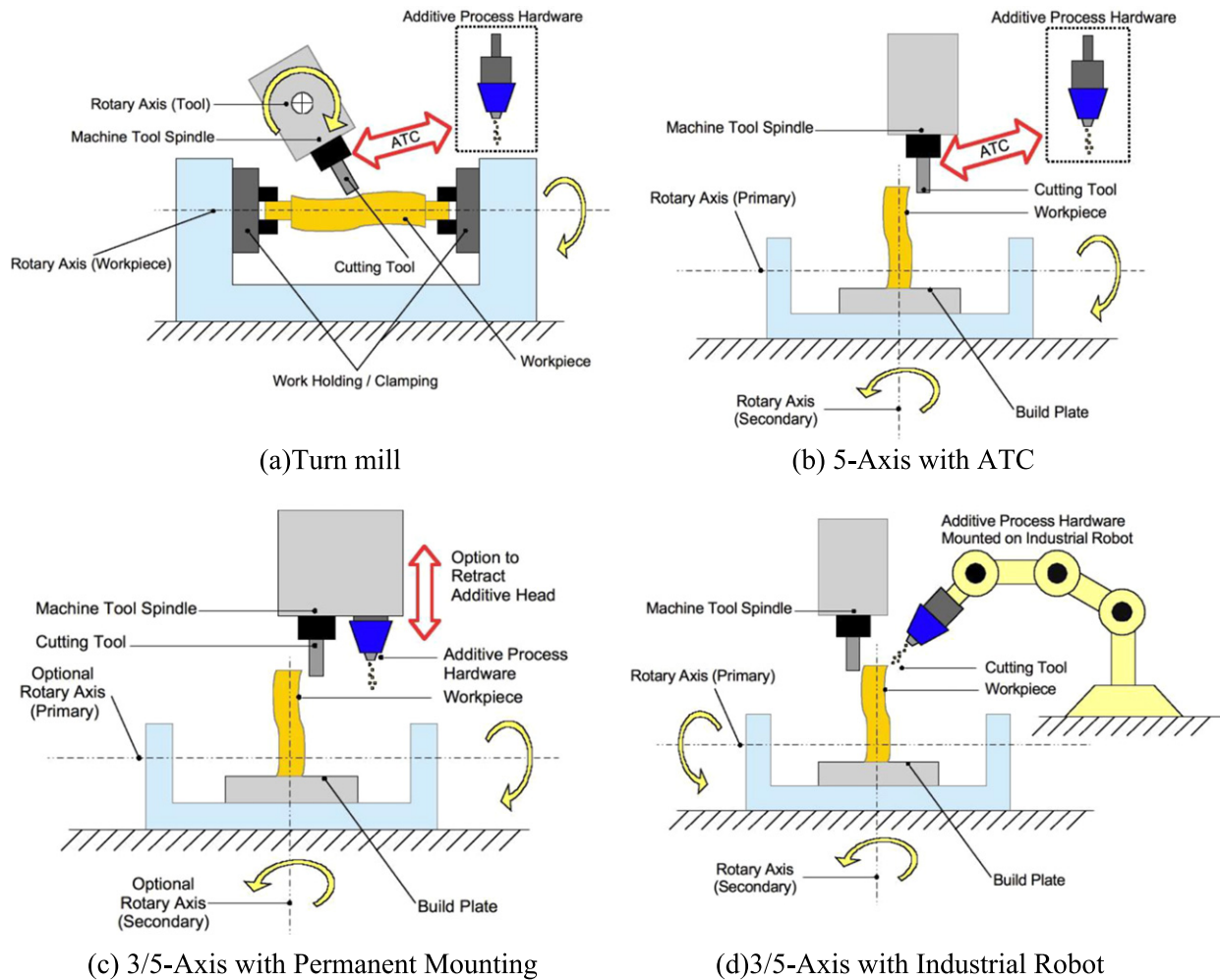


Fig. 15 Machine tool configurations that are emerging as preferred methods of integration for CNC machining. Reproduced from Flynn, J.M., Shokrani, A., Newman, S.T., Dhokia, V., 2016. Hybrid additive and subtractive machine tools – Research and industrial developments. *International Journal of Machine Tools and Manufacture* 101, 79–101.

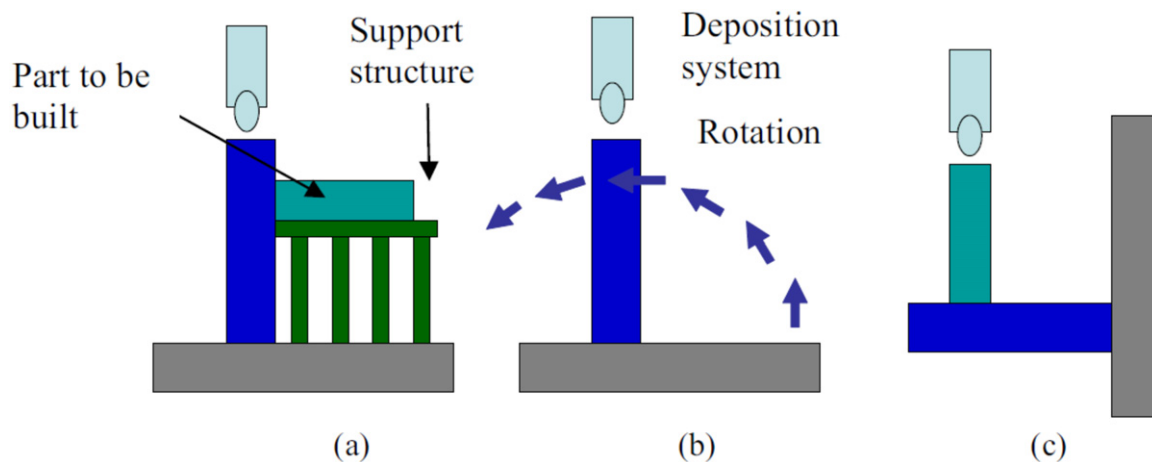


Fig. 16 (a) Build part with support structure; (b) with multi-axis capability, after building the column, the table can be rotated; (c) after rotation, continue to build the component from another direction. Reproduced from Liou, F., Slattery, K., Kinsella, M., *et al.*, 2007. Applications of a hybrid manufacturing process for fabrication of metallic structures. *Rapid Prototyping Journal* 13 (4), 236–244.

- CNC Milling

Milling-son *et al.* (Son *et al.*, 2009) 5-Axis CNC milling machines are essential in many industries ranging from aerospace to consumer-die-mold machining because they can deliver high machining accuracy with a spindle tilting capacity. They showed that the degree of over-constraint depends on machine size. We have designed a small hybrid 5-axis motion platform, the MIT-SS-1, refer Fig. 18, which can tolerate this over-constraint through a unique layout of axes. García Nieto *et al.* (2016) highlighted that

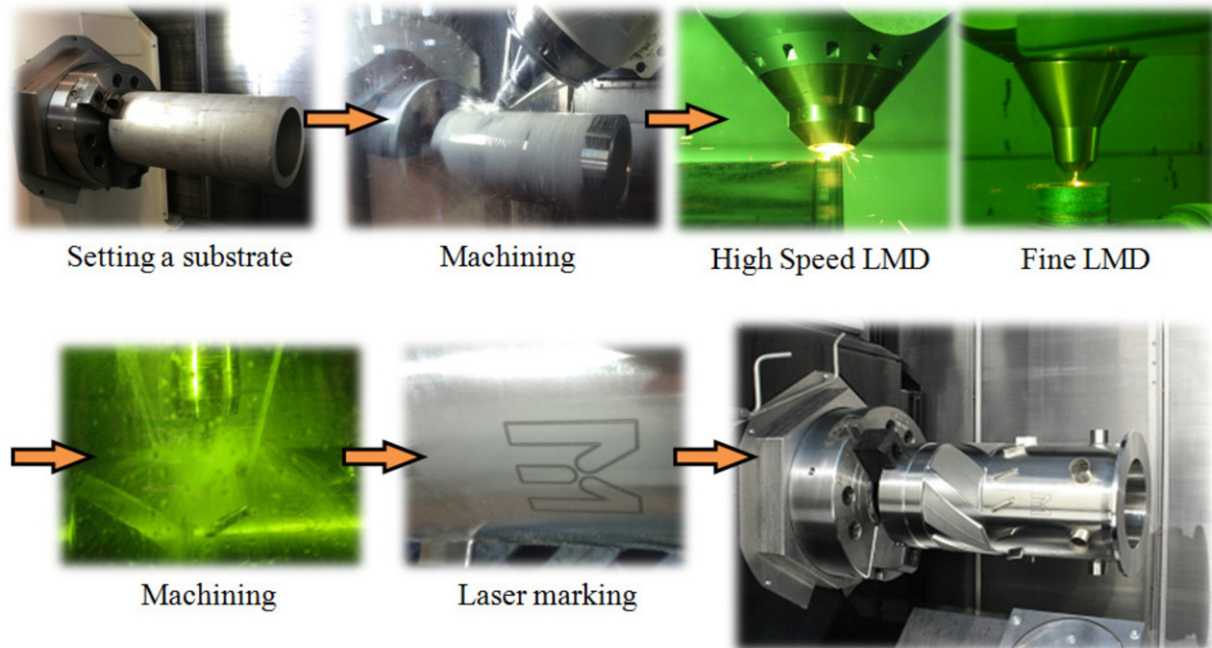


Fig. 17 Application example of a hybrid process by INTEGREX i-400 AM. Reproduced from Yamazaki, T., 2016. Development of a hybrid multi-tasking machine tool: Integration of additive manufacturing technology with CNC machining. *Procedia CIRP* 42, 81–86.

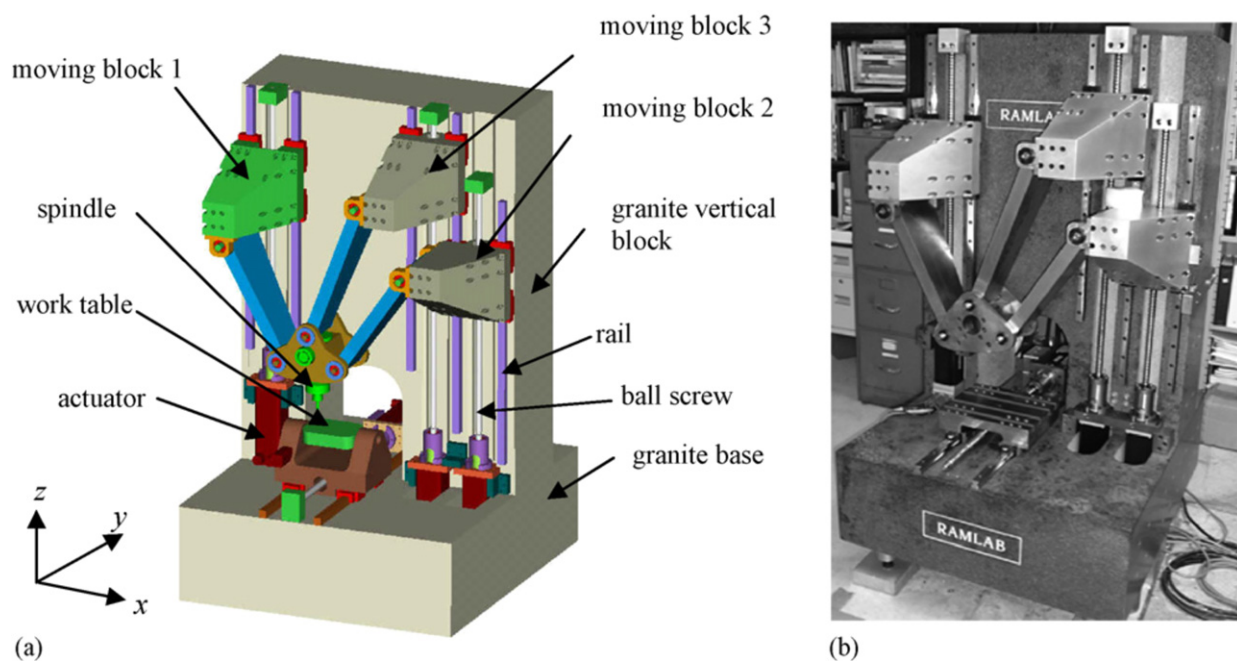


Fig. 18 The MIT-SS-1, PRR type hybrid CNC milling machine. (a) Solid model of the MIT-SS-1. (b) Prototype. Reproduced from Son, S., Kim, T., Sarma, S.E., Slocum, A., 2009. A hybrid 5-axis CNC milling machine. *Precision Engineering* 33 (4), 430–446.

milling cutters are essential cutting tools used in milling machines to perform milling operations, which are prone to wear and subsequent failure.

Dave *et al.* (2014) reviewed a paper that showed various papers related to Portable Milling Machine. They included different types of portable milling machine, their parts, and modifications. As well as construction, structural design, working setup, functioning and machining tests are observed in this survey of Portable Milling Machine. Xie *et al.* (2014) developed a hybrid milling machine with actuation redundancy capable of five-face milling in one setup.

- CNC Grinding

Abrasive machining is one of the most critical finishing processes used in industries. Therefore continuous effort is going on these days to enhance the efficiency of this process by decreasing abrasive forces, increasing machining efficiency decreasing the temperature, improving shape accuracy and machined surface, etc., one such effort is the development of hybrid machining system for this process especially for grinding of special materials, alloys, composites, and ceramics. Ruszaj *et al.* (2017) presented the review various applications of hybrid grinding and electrochemical machining for sintered carbides, titanium alloys, nickel alloys and metal matrix based composites. It was worth to underline that recent developments in abrasive hybrid manufacturing processes also meet high industrial demands and challenges regarding geometrical precision and surface.

Sudiarso and Atkinson (2010) proposed the electrical dressing method for the dressing of grinding wheel to restore its cutting ability by developing a hybrid electrical dressing method for metal-bonded diamond grinding wheels which was a combination of electrochemical and electro-discharge dressing. Holtermann *et al.* (2014) presented the modeling and simulation of Internal traverse Grinding. Which is high performance grinding process incorporating a high rate of material removal combined with a high surface quality because of its unique grinding wheel geometry. Zhu *et al.* (2011) presented a hybrid process of grinding and

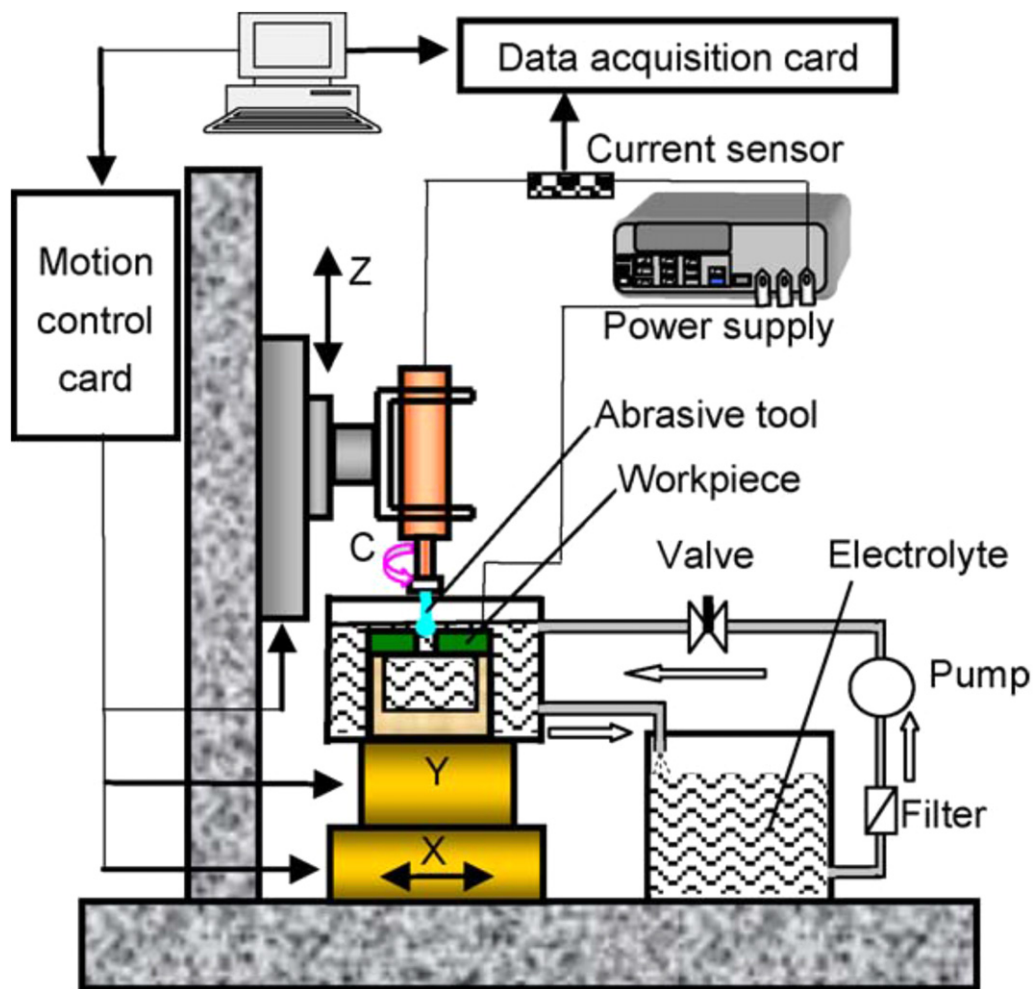


Fig. 19 Shows schematic sketch of experimental system. Reproduced from Zhu, D., Zeng, Y.B., Xu, Z.Y., Zhang, X.Y., 2011. Precision machining of small holes by the hybrid process of electrochemical removal and grinding. *CIRP Annals-Manufacturing Technology* 60 (1), 247–250.

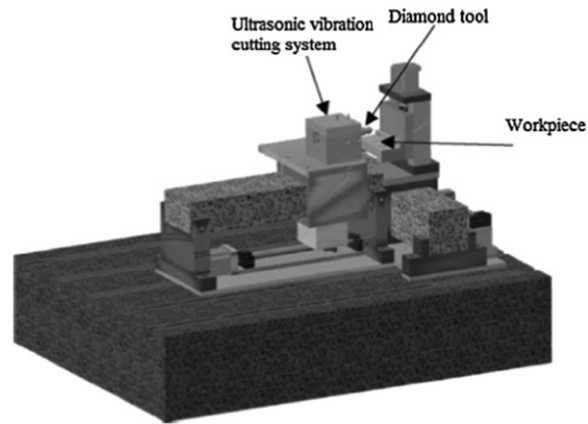


Fig. 20 Schematic of ultrasonic vibration assisted micro grooving. Reproduced from Lee, J.S, Lee, D.W, Jung, Y.H, Chung, W.S., 2002. A study on micro-grooving characteristics of planar lightwave circuit and glass using ultrasonic vibration cutting. *Journal of Materials Processing Technology* 130–131, 396–400.

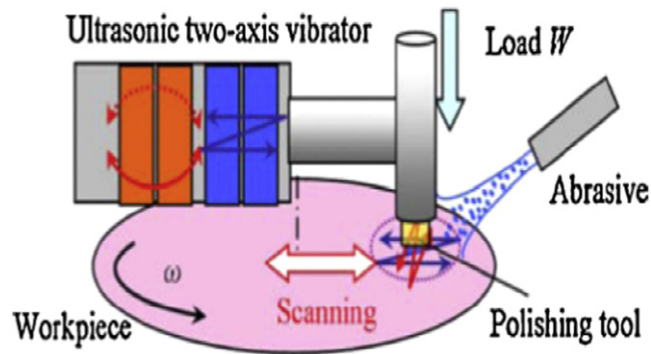


Fig. 21 Schematic of ultrasonic vibration assisted polishing. Reproduced from Suzuki, H., Hamada, S., Okino, T., *et al.*, 2010. Ultraprecision finishing of micro-aspheric surface by ultrasonic two-axis vibration assisted polishing. *CIRP Annals – Manufacturing Technology* 59, 347–50.

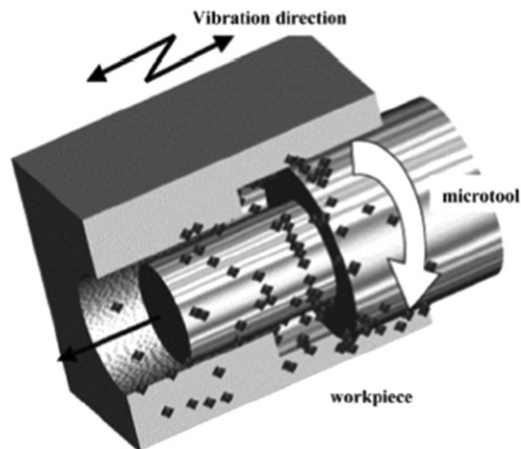
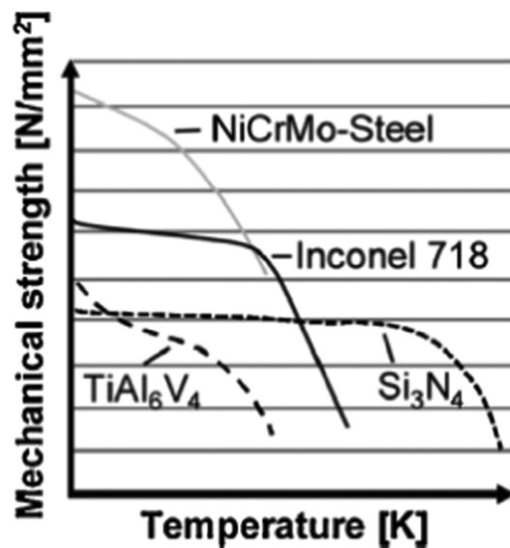


Fig. 22 Schematic of vibration assisted lapping process. Reproduced from Wang, A.C, Yan, B.H., Li, X.T., Huang, F.Y., 2002. Use of micro ultrasonic vibration lapping to enhance the precision of microholes drilled by micro electro discharge machining. *International Journal of Machine Tools and Manufacture* 42, 915–923.

electrochemical refer [Fig. 19](#) for set up, removal for machining of small precision holes with hard-to-machine materials. The results revealed that precision holes with sharp edges and without burrs could be obtained while the material removals on grinding and electrochemical machining, were well balanced by rationally determining machining voltage, tool rotation speed and feed rate which is a practical, effective way to remove the recast layer ([Curtis *et al.*, 2009](#)).

Table 2 Vibration assisted hybrid manufacturing processes for different workpieces

Assisted hybrid manufacturing processes	Workpiece material	Outcomes
Vibration assisted		
Milling	H13 (Li and Wang, 2014), Al 6061 (Lian <i>et al.</i> , 2013; Ko <i>et al.</i> , 2011), Al6061-T6 (Chern and Chang, 2006)	Surface roughness heights reduced (Ko <i>et al.</i> , 2011), Reduction in tool life reported (Chern and Chang, 2006)
Grooving	Glass (Lee <i>et al.</i> , 2002), Al2024 (Koshimizu and Aoki, 2013; Ammouri and Hamade, 2012), Brass 28 (Kim and Loh, 2013), Pure nickel (Kim and Loh, 2011), Nickel alloy (Kim and Loh, 2011), Copper (Brocato, 2005; Brehl and Dow, 2007)	Micro-groove shapes are better (Gorczyca, 1987; Lee <i>et al.</i> , 2002) Chips average size get reduced (Koshimizu and Aoki, 2013)
Engraving	Al alloy (Koshimizu and Aoki, 2013), stainless steel (Koshimizu and Aoki, 2013)	Reduction in cutting forces observed (Koshimizu and Aoki, 2013)
Grinding	Ultra-fine grain cemented carbide (Onikura <i>et al.</i> , 2000)	Micro tools with smaller diameter and higher aspect ratio fabricated (Onikura <i>et al.</i> , 2000)
Drilling	Glass (Egashira <i>et al.</i> , 2002), AA2017 (Aziz <i>et al.</i> , 2012), SS41 (Chern and Lee, 2006)	Reduction in cutting forces upto 60%–70% reported (Egashira <i>et al.</i> , 2002)
Polishing	Binderless tungsten carbide (Suzuki <i>et al.</i> , 2006; Suzuki <i>et al.</i> , 2010; Chee <i>et al.</i> , 2011)	Achieved surface roughness in nm (Suzuki <i>et al.</i> , 2006; Suzuki <i>et al.</i> , 2010; Chee <i>et al.</i> , 2011)
Lapping	Silicon (Zhang <i>et al.</i> , 2006), Ti-6Al-4V (Wang <i>et al.</i> , 2002)	10 nm surface roughness achieved (Zhang <i>et al.</i> , 2006)
EDM	Stainless steel (Wang <i>et al.</i> , 2002; Yu <i>et al.</i> , 2009), copper (Gao and Liu, 2003), WC (Jahan <i>et al.</i> , 2010a; Jahan <i>et al.</i> , 2011; Jahan <i>et al.</i> , 2010b; Jahan <i>et al.</i> , 2012; Hung <i>et al.</i> , 2006), steel (Tong <i>et al.</i> , 2008), polycrystalline diamond (Mahardika <i>et al.</i> , 2012), brass (Endo <i>et al.</i> , 2008), nitinol (Huang <i>et al.</i> , 2003)	2/3 times increase of material removal rate (Mahardika <i>et al.</i> , 2012), increase machining efficiency by 60 times (Huang <i>et al.</i> , 2003)
WEDM	Ti-6Al-4V (Hsue <i>et al.</i> , 2012), tungsten carbide (Bhattacharyya <i>et al.</i> , 2007)	Machining efficiency increase 2.5 times (Hsue <i>et al.</i> , 2012)
ECM	Copper (Ruszaj <i>et al.</i> , 2003), tool steel (Ruszaj <i>et al.</i> , 2003), SUS304 (Ghoshal and Bhattacharyya, 2013)	Average surface roughness reduced upto 2.1 nm (Ghoshal and Bhattacharyya, 2013)

**Fig. 23** Mechanical strength vs. temperature. Reproduced from Sun, S., Brandt, M., Dargusch, M.S., 2010. Thermally enhanced machining of hard-to-machine materials – A review. *International Journal of Machine Tools and Manufacture* 50, 663–80.

Advanced Subtractive Technology

In case of advanced subtractive technology, manufacturing process energy supply is entirely different from conventional; however, the ultimate aim is to improve the material removal rate, surface finish, precision as well as effectiveness of the machining processes. In this case, the hybrid manufacturing processes existed can be classified as follows:

- Assisted Hybrid Processes
- Combined/Mixed Hybrid Processes

Table 3 Laser assisted hybrid manufacturing processes for different workpieces

Assisted hybrid manufacturing processes		Workpiece material	Outcomes
Laser assisted	Milling	H13 (Singh and Melkote, 2007; Singh <i>et al.</i> , 2008), Ti-6Al-4V (Ding <i>et al.</i> , 2012; Mohid <i>et al.</i> , 2014), A2 tool steel (Melkote <i>et al.</i> , 2009; Kumar and Melkote, 2012; Kumar <i>et al.</i> , 2012), Inconel 718 (Ding <i>et al.</i> , 2012), AISI D2 (Mohid <i>et al.</i> , 2014)	Mean thrust force reduction (Singh and Melkote, 2007; Singh <i>et al.</i> , 2008), increase material removal rate and reduction in resultant force (Ding <i>et al.</i> , 2012; Mohid <i>et al.</i> , 2014)
	Grinding	Al ₂ O ₃ (Chang <i>et al.</i> , 2012), Si ₃ N ₄ (Chang <i>et al.</i> , 2012)	Lower surface roughness is achieved (Chang <i>et al.</i> , 2012)
	Turning	Particulate reinforced MMC (Dandekar and Shin, 2013), Ti-6Al-4V (Dandekar <i>et al.</i> , 2010), steel parts (Ding and Shin, 2010), silicon (Mohammadi <i>et al.</i> , 2015)	Machining cost decreased by 30% (Dandekar <i>et al.</i> , 2010), improve in the machinability and good surface finish (Ding and Shin, 2010), surface roughness improved by 80% as compared conventional machining (Mohammadi <i>et al.</i> , 2015)
	Electrochemical machining	Stainless steel (Long <i>et al.</i> , 2015)	Improved machining rate and precision (Long <i>et al.</i> , 2015)
	Jet electrochemical machining	Al alloy, Ti alloy, Hastelloy and Stainless steel (De Silva <i>et al.</i> , 2004; Pajak <i>et al.</i> , 2006; De Silva <i>et al.</i> , 2011; Pajak <i>et al.</i> , 2004), Inconel 718 (Malik and Manna, 2017a; Malik and Manna, 2018a,b), EN-31 tool steel (Malik and Manna, 2019)	Increase in material removal rate, reduction in hole taper (De Silva <i>et al.</i> , 2004; Pajak <i>et al.</i> , 2006; De Silva <i>et al.</i> , 2011; Pajak <i>et al.</i> , 2004), reduction in taper, overcut, average spark affected zone (Malik and Manna, 2017a), reduction in surface height (Malik and Manna, 2018a), increase in material removal rate (Malik and Manna, 2018b)
	Electro discharge machining	2% Ni - 2% Cr case hardened steel (Li <i>et al.</i> , 2006), Ni-Ti based shape memory alloy (Al-Ahmari <i>et al.</i> , 2015)	70% reduction in drilling time with 42% cost reduction, improve production capacity by 90% (Li <i>et al.</i> , 2006), machining time reduced by 56%–65% without compromise hole quality (Al-Ahmari <i>et al.</i> , 2015)
	Water jet machining	Stainless steel sheets (Hock <i>et al.</i> , 2012), Brass sheets (Hock <i>et al.</i> , 2012), Polycrystalline CBN (Melaibari <i>et al.</i> , 2012),	Dross free cuts with small kerf width and reduced heat affected zone in water jet laser cutting (Hock <i>et al.</i> , 2012), increase cutting efficiency with improvement in surface quality (Melaibari <i>et al.</i> , 2012)

In case of *assisted hybrid manufacturing processes*, material is removed with the help of main/primarily machining process and the addition of secondary process is just to assist the primary machining process and improve the effectiveness of the machining. Secondary machining process may not directly engage in material removal. The assisted machining process increases the machinability of the material and enhances the performance of the main machining process.

Manufacturing process technology can be improved by combining two or more different machining action at the same time during workpiece machining. The combination of two or more manufacturing processes at the same time is known as *Combined hybrid manufacturing*. *Hybrid technology* is defined as the combining of at least two different sources of energy for production of different components (Mahdy, 2001).

Hybrid manufacturing is a promising technique, which is recently used in today's manufacturing industries for improving quality of machined parts for different superalloys and difficult to machine materials (Kozak *et al.*, 2004; Wang *et al.*, 2003; Kozak and Rajurkar, 2000; Yadava *et al.*, 2002; Rajurkar *et al.*, 1999; Nau *et al.*, 2011; Lauwers *et al.*, 2010, 2014). Rajurkar *et al.* (1999) described "*Combination of two or more machining processes for material removal*".

Assisted Hybrid Micro-Manufacturing Processes

In assisted hybrid micro-manufacturing there are basically two or more types of energy (such as thermal, mechanical, chemical or electrochemical etc.) is used to enhance the materials machining performance (Heisel *et al.*, 2011).

● Vibration Assisted Micro Manufacturing (VAMM)

In VAMM process vibrations of small amplitude applied to the tool, workpiece or work fluid during machining. Due to vibrations during cutting tool and chips loses contact on specified amplitude. This vibration assistance approach is applied to various conventional as well as non-conventional machining processes. In vibration-assisted micro cutting (VAMC) at a specified amplitude contact between the cutting tool and chips breaks resulting decrease in the machining forces and improves surface finish as well as tool life (Brehl and Dow, 2008). In VAMC surface cracks results due to tool hammering action (Lauwersa, 2011), in vibration-assisted EDM (Gao and Liu, 2003; Yu *et al.*, 2009; Sundaram *et al.*, 2008; Gama *et al.*, 2011; Jahan *et al.*, 2010a,b, 2011, 2012; Hung *et al.*, 2006; Tong *et al.*, 2008; Kim *et al.*, 2006b; Ichikawa and Natsu, 2012, 2013), in vibrations applied between the workpiece and the tool, which improves the flushing efficiency with increasing material removal rate and surface finish. Vibration also helps in removing of the debris

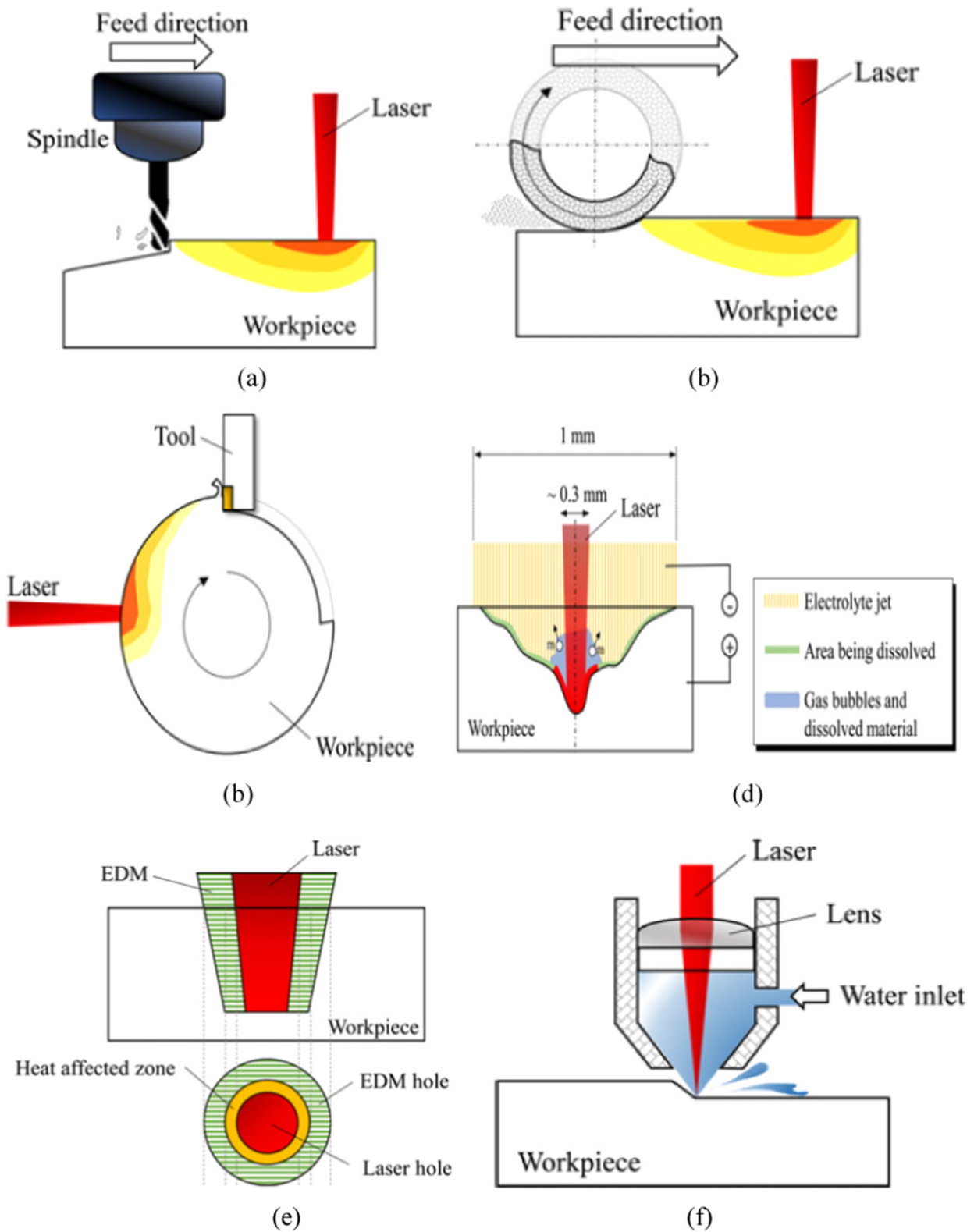
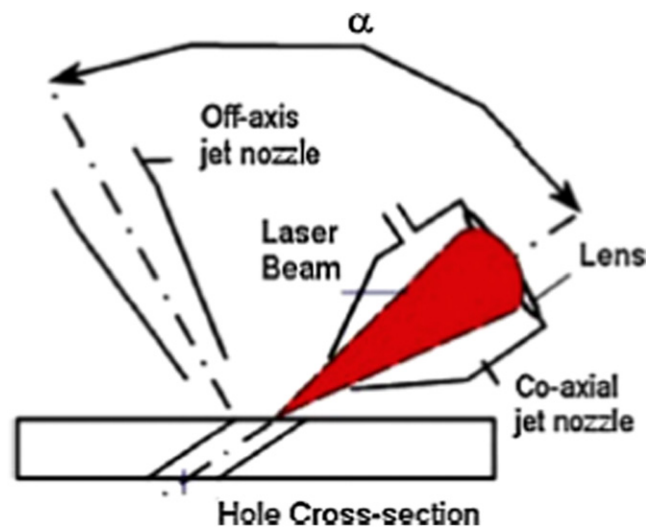


Fig. 24 Schematic of laser assisted milling (a), laser assisted grinding (b), laser assisted turning (c), laser assisted jet electrochemical machining (d), laser assisted electro discharge machining (e), and laser assisted water jet machining (f). Reproduced from Lee, C.M., Woo, W.S., Kim, D.H., Oh, W.J., Oh, N.S., 2016. Laser-assisted hybrid processes: A review. *International Journal of Precision Engineering and Manufacturing* 17 (2), 257–267.

Table 4 Fluid assisted hybrid manufacturing processes for different workpieces

Fluid assisted micro manufacturing processes	Workpiece material	Outcomes
Water assisted laser machining	Silicon (Kaakkunen <i>et al.</i> , 2011), alumina (Jang and Kim, 2006), PMMA (Jang and Kim, 2006), LCD glass (Tsai and Li, 2009), PET (Jang and Kim, 2006)	Material removal rate increases upto 200% (Kaakkunen <i>et al.</i> , 2011), heat affected zone size reduced with lesser micro cracking (Tsai and Li, 2009), surface quality improves (Jang and Kim, 2006)
Gas assisted laser drilling	Thermal barrier coated nickel alloy (Sezer <i>et al.</i> , 2009)	Drilled holes without delamination (Sezer <i>et al.</i> , 2009)
Chemical assisted ultrasonic machining	Glass (Choi <i>et al.</i> , 2007)	Improved material removal rate and surface finish upto 40% (Choi <i>et al.</i> , 2007)
Electrochemical assisted machining	Stainless steel 304 (Sebastian <i>et al.</i> , 2014)	Reduction in the cutting forces (Sebastian <i>et al.</i> , 2014)
Electrorheological fluid assisted ultrasonic machining	Quartz (Tateishi <i>et al.</i> , 2009a,b,c)	Efficiency and accuracy during machining improved (Tateishi <i>et al.</i> , 2009a,b,c)

**Fig. 25** Schematic of gas assisted laser drilling. Reproduced from Sezer, H.K., Li, L., Leigh, S., 2009. Twin gas jet-assisted laser drilling through thermal barrier-coated nickel alloy substrates. *International Journal of Machine Tools and Manufacture* 49, 1126–1135.**Table 5** Combined hybrid micro manufacturing processes for different workpieces

Combined hybrid micro manufacturing processes	Workpiece material	Outcomes
Electrochemical Spark/discharge machining (ECSM/ECDM)	Glass (Wuthrich <i>et al.</i> , 2005; Wuthrich and Hof, 2006; Wuthrich <i>et al.</i> , 2006; Maillard <i>et al.</i> , 2007; West and Jadhav, 2007; Jalali <i>et al.</i> , 2009; Abou Ziki <i>et al.</i> , 2012; Abou Ziki and Wüthrich, 2013), steel (Coteață <i>et al.</i> , 2011), quartz (Yang <i>et al.</i> , 2010; Yang <i>et al.</i> , 2011; Kulkarni <i>et al.</i> , 2011), silicon nitride (Sundaram <i>et al.</i> , 2008), copper (Kulkarni <i>et al.</i> , 2011), pyrex glass (Kim <i>et al.</i> , 2006a; Zheng <i>et al.</i> , 2008; Cheng <i>et al.</i> , 2010), soda lime glass (Kulkarni <i>et al.</i> , 2011; Furutani and Maeda, 2008; Paul and Hiremath, 2014), borosilicate glass (Abou Ziki and Wüthrich, 2012), tantalum (Kulkarni <i>et al.</i> , 2011), alumina (Al_2O_3) (Abou Ziki and Wüthrich, 2012), stainless steel (Huang <i>et al.</i> , 2014), E-glass fibre epoxy composite (Manna and Narang, 2012)	Effectively used for the machining of nonconductive materials (Wuthrich <i>et al.</i> , 2005; Wuthrich and Hof, 2006; Wuthrich <i>et al.</i> , 2006; Maillard <i>et al.</i> , 2007; West and Jadhav, 2007; Jalali <i>et al.</i> , 2009; Abou Ziki <i>et al.</i> , 2012; Abou Ziki and Wüthrich, 2013, 2012; Yang <i>et al.</i> , 2010; Yang <i>et al.</i> , 2011; Kulkarni <i>et al.</i> , 2011; Kim <i>et al.</i> , 2006a; Zheng <i>et al.</i> , 2008; Cheng <i>et al.</i> , 2010; Furutani and Maeda, 2008; Paul and Hiremath, 2014; Manna and Narang, 2012)
Travelling wire electrochemical spark machining (WECSM)	E-glass fibre epoxy composite (Malik and Manna, 2016, 2017b; Manna and Malik, 2014), quartz (Kuo <i>et al.</i> , 2015; Rattan and Mulik, 2017), borosilicate glass (Bhuyan and Yadava, 2013, 2014), glass (Liu <i>et al.</i> , 2017)	Effectively machining of E-glass fibre epoxy composite in micron (Malik and Manna, 2016, 2017b; Manna and Malik, 2014), magnetic field introduction increased MRR with spark current reduction (Rattan and Mulik, 2017)

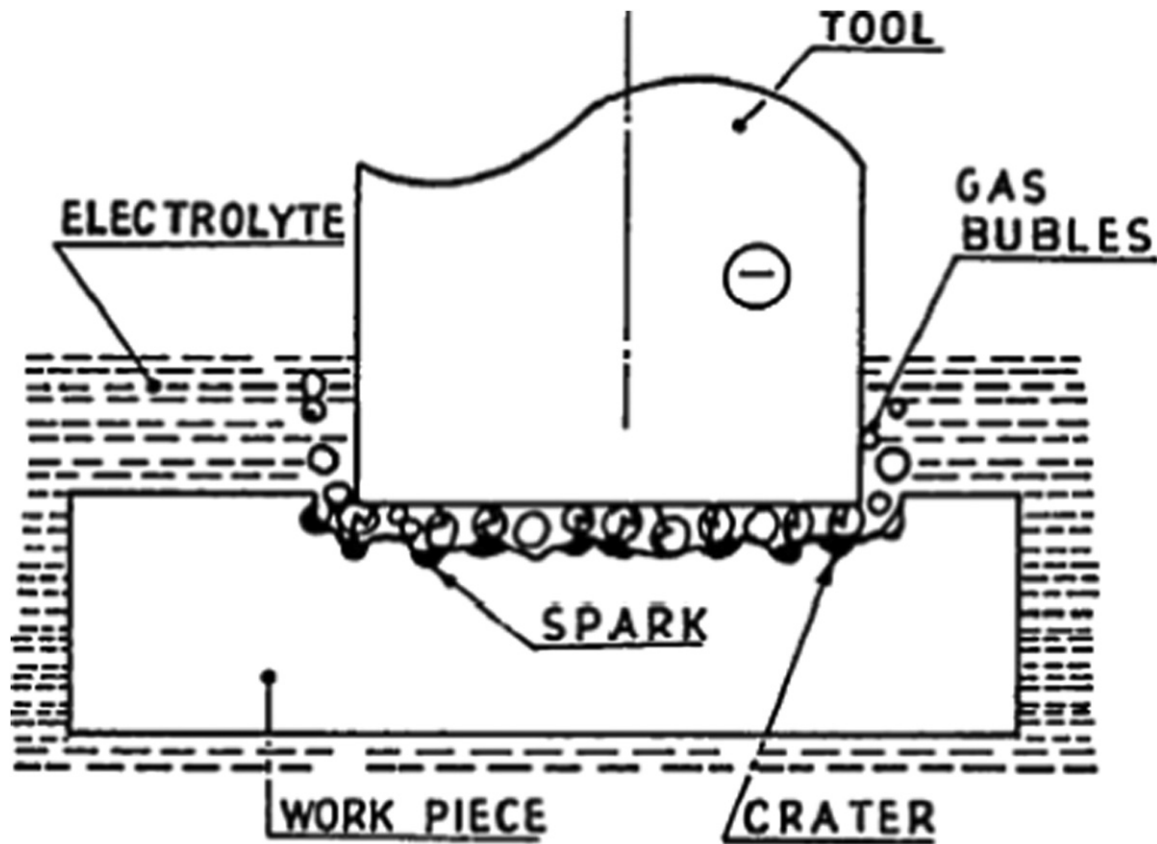


Fig. 26 Electrochemical Spark/discharge machining operation. Reproduced from Bhattacharyya, B., Doloi, BN., Sorkhel, SK., 1999. Experimental investigations into electrochemical discharge machining (ECDM) of non-conductive ceramic materials. *Journal of Materials Processing Technology* 95 (1–3), 145–154.

which results in lower thermal stresses, smaller heat affected zone and lesser surface cracks. **Figs. 20–22** shows schematic of some vibration assisted machining processes. **Table 2** shows the various vibration assisted machining processes.

- Laser Assisted Micro Manufacturing (LAMM)

High strength and heat resistant materials are often difficult to machine due to their physical and mechanical properties such as high strength and low thermal conductivity, which make the cutting forces and cutting temperature very high and lead to a short tool life. Because the flow stress and strain hardening rate of materials normally decrease with the increase of temperature due to thermal softening, thermal-assisted machining becomes a possibility when machining the hard-to-machine materials (refer **Fig. 23**) (Sun *et al.*, 2010). **Table 3** gives an overview of the performed studies on the laser-assisted micro-machining processes. The major work on laser-assisted micro-machining is to study some parameters such as surface roughness and micro-machining forces by manufacturing simple micro-grooves and then to compare with those obtained by conventional micro-machining. **Fig. 24(a–f)** shows schematic of some laser assisted micro-machining processes.

- Fluid Assisted Micro Manufacturing (FAMM)

This hybrid assisted micro-machining process includes applying water, gas, chemicals or special fluids on the workpiece with the aim of increasing the process performance. **Table 4** gives an overview of the micro-machining processes carried out with the assistance of various fluids. **Fig. 25** shows the schematic of the gas assisted laser micro drilling manufacturing process.

- Combined Hybrid Micro Manufacturing

In combined hybrid micro-machining, all the constituent micromachining processes simultaneously contribute to the material removal and affect the machining zone. Combined hybrid micromachining processes have giant potential to produce more complex parts with enhanced material removal rate, surface integrity and dimensional accuracy in a relatively short production time. Primary research in combined hybrid micro-machining field is on the application of electrical and electrochemical phenomena. Although combined hybrid micro-machining processes such as ECDM have been mostly used to fabricate 3D micro-shapes on nonconductive materials like glass and quartz, there is still a lack of such processes for manufacturing complicated 3D micro-structures. **Table 5** shows some work reported in the area of combined hybrid micro manufacturing.

Micro ECDM process involves a complex combination of the electrochemical (EC) reaction and electro discharge (ED) action. The electrochemical action helps the generation of the positively charged ionic gas bubbles, e.g., hydrogen (H₂). The electrical dis-

Table 6 Comparison between subtractive and hybrid machining processes

Type of machining	Machining process	Advantages and disadvantages	Applications/Type of cutting tool/Cost
Subtractive machining	Grinding	Advantages ● Investment is less ● Working principle and operation is simple ● It does not require additional skills ● Surface finishing will be approximate 10 times better as compared to milling and turning process of machining. ● Dimensional accuracy will be quite good ● Grinding process could be performed on hardened and unhardened workpiece Disadvantages ● Required tool is high cost ● Process is also a costly one ● It cannot remove the high amount of material; it only removes a little amount ● For removing the required amount from work it consumes more time	Applications ● Slitting & parting, ● Surface finishing, ● Deburring & descaling, ● Abrasive milling, ● Finishing cylindrical and flat surface, ● Grinding of various tools and cutters Type of cutting tool Multi-Point cutting tool Cost Installation cost is less but running cost is high
	Turning	Advantages ● All types of materials can be turned ● A most versatile machine capable of producing external and internal circular profile and flat surfaces ● Low tooling cost ● Large components can be turned Disadvantages ● Turning operation requires skilled operator ● Low production rate in turning machining operation ● Close tolerances and surface finish cannot be achieved	Applications ● Parting off ● Turbine parts ● Cylindrical shafts ● Gear wheel ● Bone and dental screw Type of cutting tool Single-Point cutting tool Cost Installation cost is high but running cost is lesser
	Milling	Advantages ● Variety of shapes including flats, slots and contours can be obtained through milling operation ● Versatile operation with a wide variety of tooling's and attachments ● Suitable for low and medium production rate ● Better dimensional control and surface finish Disadvantages ● Milling operation requires skilled operator ● Tooling relatively more expansion	Applications ● Surface contouring ● Slitting ● Gear cutting ● Straddle milling ● Key slots ● Grooves cutting ● Face and edge finishing Type of cutting tool Multi-Point cutting tool Cost Installation cost and running cost both are higher than grinding and turning
Hybrid machining	Laser assisted machining (LAM)	Advantages ● Increased machining rate ● Improved machining precision ● Machined any material irrespective of its hardness (i.e., conductive, non-conductive materials and polymers) ● Improve process productivity Disadvantages ● Microstructure of machined surface ● Presence of heat affected zone ● Thermal stresses developed ● Highly skilled operator is required	Applications ● Turbine blades parts ● Micro machining ● Die sinking ● MEMS fabrication ● Micro holes ● Surface texturing Cost Installation cost is more due to costlier laser assembly

(Continued)

Table 6 Continued

Type of machining	Machining process	Advantages and disadvantages	Applications/Type of cutting tool/Cost
	Vibration assisted machining (VAM)	Advantages ● Increased machining rate ● Improved machine precision ● Machined any material irrespective of its hardness ● Increased tool life, micro hole aspect ratio and micro cutting forces ● Increased flushing efficiency in fluid related machining ● Conductive, non-conductive materials and polymers Disadvantages ● Highly skilled operator is required	Applications ● Turbine blades ● Micro machining ● MEMS fabrication ● Micro and macro holes ● Surface texturing Cost Installation cost is less as compared to the LAM
	Fluid assisted machining (FAM)	Advantages ● Increased machining rate ● Improved machine precision ● Metals, polymers and ceramics ● Helps in flushing of reaction byproducts Disadvantages ● Less material removal rate as compared to conventional subtractive machining ● Handling of used fluid is also difficult ● Highly skilled operator is required	Applications ● Micro channels ● Micro machining ● MEMS fabrication ● Surface texturing and profiling Cost Installation cost is less as compared to the LAM and VAM
	Combined hybrid machining	Advantages ● Increased machining rate ● Improved machine precision ● Machined any material irrespective of its hardness ● Conductive, non-conductive materials, composites and polymers can be machined depends upon machine used ● Improved surface integrity Disadvantages ● Less material removal rate as compared to conventional subtractive machining ● Highly skilled operator is required ● Harmful gases generated during machining (i.e., ECDM, TWECSM)	Applications ● Micro holes/channels ● Micro machining ● Micro slits ● MEMS fabrication ● Surface contouring Cost Cost is lesser as compared to the LAM, VAM and FAM.

charge action takes place between the tool and the workpiece due to the breakdown of the insulating layer of the gas bubbles as the DC power voltage is applied between the tool (or cathode) and the anode, resulting in material removal due to melting, vaporization of the workpiece material and mechanical erosion. Gas bubble formation and sparking phenomena as in the ECDM process are exhibited as shown in Fig. 26.

Comparison Between Subtractive and Hybrid Machining

Table 6 shows comparison between subtractive and hybrid machining processes with their advantages, disadvantages, application and cost involved.

Summary

In the present book article various classes of widely used subtractive manufacturing technologies and their hybridizations have been reviewed. On the basis of the observations studies, following conclusions may be drawn:

- It has been found that the subtractive manufacturing class has undergone through various types of innovations that resulted into formation of better principle, procedures and also the machine tools.

- In comparison of manual systems, the CNC based subtractive technologies have produced great benefits not just in-terms of rapid production cycles but also to achieve better accuracies that led to the standardizations. Moreover, CNC based systems enabled the manufacturers with greater flexibilities to inculcate multiple operations all together and formed the concept of 'Hybrid Manufacturing'.
- In the recent decade, most of the research efforts have been made on the collaborations of the additive and subtractive manufacturing technologies which can deal with sophisticated engineering and other applications. Unfortunately, despite of the attempts made so far, no such technology has been commercialized as of today. The main reason behind may be the short outcomes of the research efforts or limited explorations of such innovations.
- Hybridizations of the non-conventional manufacturing technologies also played a great role in today's manufacturing sector, however, the output of such technologies usually lie on micro scale and are likely to be un-practical for mass production applications. Rather, the main role of such systems is economical and useful for small scale or job production runs.
- The future research efforts should be focused on the development of empirical and analytical relationships amongst the various process variables which can provide the practitioners a better control of the achievable characteristics.

See also: Environmental Impact Subtracting Versus Additive Manufacturing. Recent Advancement and Challenges of Additive Manufacturing Geospatial Images Solution Integration. Renewability Assessment of a Production System

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Sustainability Indicators in Supply Chains

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Introduction

The World Summit on Sustainable Development (WSSD), or the ONG Earth Summit 2002, in Johannesburg, S. Africa, held under the aegis of United Nations, discussed the core issue of sustainable development faced by the world. WSSD proposed a key triplet term *people – planet – prosperity* to reflect the emerging view that sustainability requires a holistic balancing of economic, social, and environmental issues (White and Lee, 2009). Indeed, rising consciousness have brought in a much needed focus towards environment protection.

In general, the economic and environmental concerns have been perceived to be at odds with each other. However, lately, the issue of environmental consciousness, or “green management”, is being seen as intimately intertwined with the economic concerns. Indeed, Porter and van der Linde (1995) exhorted the businesses early on to end the stalemate between being green and competitive. Extant examples from practice, such as, Commonwealth Edison, Pepsi-Cola, Texas Instruments and Dow Corning, vouch for the economic benefits of the green practices (Wilkerson, 2005).

LMI Report (2003) mentions that organizations have witnessed an enhanced examination of not only the products flowing through various processes of a supply chain, but also the effects of these processes on environment and communities. The effort to reduce the impact of these activities on the environment has been labeled as green (or sustainable) supply chain management. As per this report, sustainable supply chain management approaches taken by various organizations can broadly be classified in two categories- external and internal. The external approach increasingly looks at the greening initiatives and their integration with the suppliers of the organization. The second approach involves an internal examination of how a firm designs, produces, and ships its products.

Green or sustainable supply chains, which are usually agile, adaptable, and aligned with both suppliers (on the upstream side) and customers (on the downstream side) provide companies with sustainable competitive advantages (Lee, 2004). Thus, it is imperative for organizations to measure the sustainability performance of their supply chains. The aspect of measurement is important since a common adage suggests that what gets measured gets improved. Measurement will thus help in improving and communicating the sustainability related performance of a supply chain. This is important in organizational goals and strategic priority setting. The measurement imperative has also become important in wake of recent environmental factors such as competition, globalization, uncertainty, regulation, public awareness, consumer rights and limited resources (Saeed and Kersten, 2017).

While the importance of the measurement indicators of sustainability practices in supply chain management cannot be emphasized enough, it appears that, due mainly to varied demand on the organizations to adhere to environmental standards, there is no common set of metrics for measuring sustainability performance of an organization, or its supply chains. Even when some metrics are reported in the literature, often there are inconsistencies or incompatibilities between various measures (Lehtinen and Ahola, 2010; Hassini *et al.*, 2012). Thus, the prime objective of this paper is to posit, based on the extant literature, a general set of sustainability indicators in supply chains. As discussed above, such a set of indicators would be helpful for future researchers as a reference framework to develop further studies in an area of important concern to supply chain managers and researchers.

The rest of this paper is organized as follows. The next section provides some basics of the supply chain of an organization, and the issues faced in its management. Section “Sustainable (or Green) Supply Chain Management” then specifically focuses on the sustainability (or greening) aspects of a supply chain. In Section “Sustainability Indicators in Supply Chains”, we develop the sustainability indicators of a supply chain. The next section provides a select group of case studies in the textile sector; a sector chosen to highlight the sustainability aspects of supply chain management. We conclude in the last section with implications for researchers, managers, and practitioners.

Supply Chain and its Management

As discussed extensively by Chopra and Meindl (2007), in its most general form, a supply chain can be defined as comprising of all of the entities involved in fulfilling a customer order. Specifically, we can visualize a supply chain as a system of organizations, people, activities, information, or resources involved in moving a product or service from supplier to customer. Thus, supply chain management involves activities that convert raw materials to finish goods to be delivered to a customer. In sustainable supply chain systems, several of these used products may re-enter the supply chain for recycling and reuse.

The above systemic view point of supply chain management is depicted in Fig. 1. As shown in the figure, the supply chain view emerges at the ‘input’ stage. The role of suppliers, availability of raw materials, natural resources, components, and managerial competencies is important at this stage. The second stage, that of ‘process’, involves the transformation of the input to saleable product or service. This stage involves the emphasis on manufacturing, production or services within the organization, often

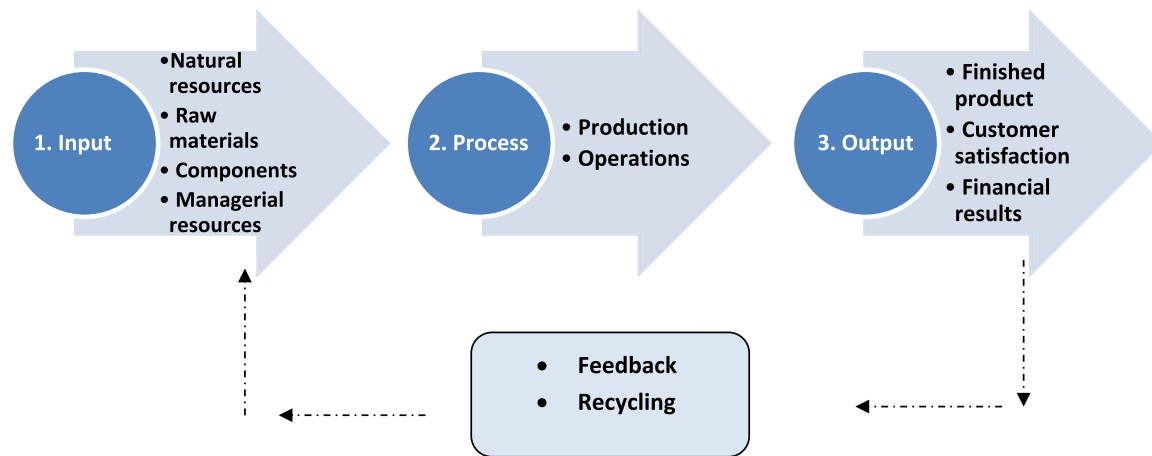


Fig. 1 A systemic view of supply chain management.

involving the work-in-process. The third stage of 'output' focuses on the finished product as a result of the conversion process in Stage 2. This stage also lays emphasis on the customer related aspects like satisfaction, and consequently, linking it with the ultimate financial results of the company in terms of market share, revenues and profitability. From the above explanation of the first three stages, the following salient points emerge:

- (1) It is pertinent to note here that inherent in the factors at Stage 3 are the aspects of market demand, and distribution of the products (We will elaborate on the distribution aspects slightly later in this section).
- (2) This systems view of input-process-output has also appeared in the other management disciplines or discourses, and in particular, marketing. However, one indirect stage, which has specifically been included here, is that of feedback or recycling. This indirect stage has been shown by the dotted arrows in [Fig. 1](#).
- (3) The *feedback* aspect is important from the informational standpoint. Any information at the output stage (such as, about demand, customer satisfaction, or financial results) must be fed back to the input stage in order to take any corrective actions. This aspect takes care of the *control* aspect in the systemic view.
- (4) The *recycling* aspect in the indirect stage is more closely related to the sustainability of the supply chain of the organization. Thus, as depicted in [Fig. 1](#), after the product has been distributed and consumed, a responsible and sustainable organization needs to take care of the post-consumption treatment (or recycling) of the product, its packaging, and other related material. It is clear that the recycling aspect of the systemic view is closely related to the distribution view of a supply chain. This distribution view is presented below.

We now discuss the distributional aspect of a supply chain. This view is motivated from the marketing distribution channel (or value chain) of an organization and is presented in [Fig. 2](#). As shown in the figure, a typical supply chain comprises of several entities starting from the suppliers to the manufacturer, to wholesaler, to retailer, and eventually, for the end consumption by the consumer. Several pertinent points emerge from this conceptualisation:

- (1) While a single entity (such as supplier, or manufacturer) has been shown at each level, typically, there would be several entities at each horizontal level of a supply chain. Thus, the resultant supply chain structure that finally emerges is quite a complex one.
- (2) In a more complex structure, there may be a greater number of levels between the suppliers and end consumers. Thus, the role of information availability, or feedback, becomes quite crucial in longer supply chains. Due to stochasticity of demand, and information asymmetries, this problem may reveal itself in the form of bullwhip effect, which has been studied extensively in the extant literature ([Lee et al., 1997](#)). The downstream players, such as retailers, are closer to the end consumer and have faster and more accurate picture of demand.
- (3) In the distributional definition of a supply chain also, the importance of recycling is quite apparent. As can be seen from the figure, the post-consumption collection of the used product from the end consumer, and its recycling, have important ramification from the sustainability (or greening) standpoint of a supply chain. The recycling can be done at the level of both suppliers and manufacturers.
- (4) From [Fig. 2](#), it is clear that any greening initiative by a supply chain needs an integrated effort from the entire supply chain. Thus, the issue of channel power becomes quite important in this regard. Thus, if the manufacturer is a more powerful player in a supply chain, say, Procter and Gamble, then a number of greening initiatives may be initiated by the manufacturer from the upstream level. Alternatively, if the retailer is relatively more powerful player, say, Walmart, then the greening initiatives may be championed from the downstream level. It is clear from this explanation that suitable incentives (or contracts) should be in place for all the members of a supply chain to put in an integrated greening effort ([Swami and Shah, 2013](#)).

The conceptualisation of sustainable (or green) supply chain management is provided in the next section.

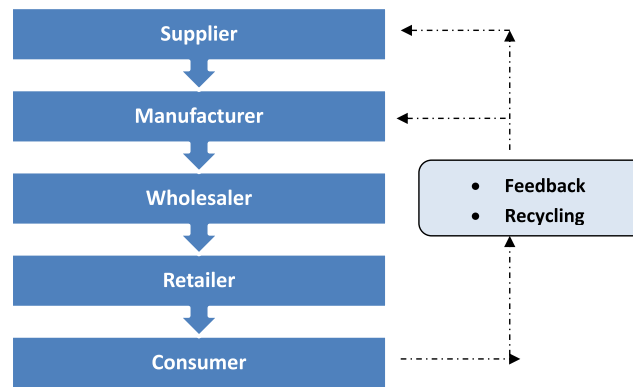


Fig. 2 A distributional view of supply chain management.

Sustainable (or Green) Supply Chain Management

In 2015, the United Nations adopted 17 sustainable development goals, with an aim to strive towards a sustainable world by the year 2030 (see “Relevant Websites section”). Some of these goals pertain to clean water and sanitation, affordable and clean energy and responsible production and consumption. Several countries adopted the UN agenda and agreed to strive to achieve these goals. While several of these goals are specific to responsibilities of governments and policy making bodies to design necessary regulatory frameworks and create ecosystems to help businesses and societies achieve sustainable development, much of the onus also lies with firms.

Several of these sustainable development goals provide directions for businesses to consider their impact on societies and environment besides just economic priorities. This three pronged approach means that firms can no longer continue to simply focus on economic objectives or profitability only, but also include environmental and social objectives in their strategic plans. Such an approach is also termed as the Triple Bottom Line Approach (see “Relevant Websites section”).

By its definition, the Triple Bottom Line approach tasks managers with a challenging yet achievable task of broadening firm’s objectives beyond profit making motive and includes aspects of environmental and social benefits. This is especially important in the context of supply chains, since growth of outsourcing over the last few decades has increased flow of raw materials, semi-finished and finished goods spread across geographical boundaries. A smartphone sold in a store in New York for example, may have been designed in Chicago, manufactured and assembled at Shenzhen and shipped via a third party logistics service provider in Hong Kong. Such product flows have led to increase in harmful impact of sourcing, production, transportation and packaging activities on environment and societies. Hence, the focus on environmental and social impact of firm operations and supply chains have assumed critical importance.

We now discuss the core concept of sustainability. The United Nations defines sustainable development as “*development that meets the needs of the present without compromising the ability of future generations to meet their own needs*.” (see “Relevant Websites section”) This means that firms may work towards economic goals, but should not exploit natural resources or societies to the extent of driving them extinct. Sustainability has thus, environmental and social dimensions. However, in this paper, we primarily discuss sustainability from an environmental (or greening) standpoint.

Environmentally friendly (or greening) initiatives of firms have received considerable attention from practitioners and researchers. Negative externalities related to firms’ operations and supply chains have led to increased focus on environmental impact of supply chains (For example, Bangladesh Factory fires (see “Relevant Websites section”) and Mattel toy recalls (see “Relevant Websites section”), to name a few). This has driven calls for closer integration of supply chains and environmental considerations. Such an integrated approach is referred to as Green Supply Chain Management (GrSCM). GrSCM is defined as “*integrating environmental thinking into supply chain management, including product design, material sourcing and selection, manufacturing processes, delivery of the final product to the consumers as well as end-of-life management of the product after its useful life*” (Srivastava, 2007).

Antecedents and Consequents of GrSCM

Analyzing this definition of GrSCM provides us with the following components of GrSCM activities, namely, green sourcing, green design, green manufacturing, green remanufacturing, reverse logistics and waste management. These components essentially form the antecedents of GrSCM construct.

On the consequences of GrSCM, several studies have shown that GrSCM activities lead to benefits for firms in the form of *price premium effect*, *cost reduction effect* or *demand expansion effect*. The consequences of the GrSCM construct can be further understood by revisiting the simple profit equation of a firm, which states that,

$$\text{Profit} = (\text{price} - \text{unit cost}) * \text{quantity sold} \quad (1)$$

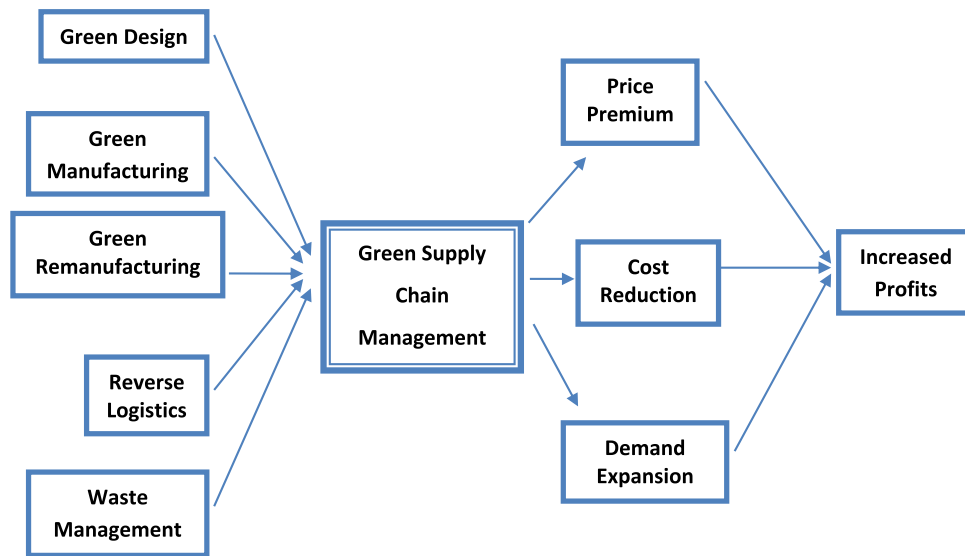


Fig. 3 Green supply chain management framework.

The profit function is influenced by three parameters, namely, *price*, *unit cost* and *quantity sold*. It can be observed that *ceteris paribus*, an increase in price (or price premium) increases firm's profitability, decrease in unit cost (or cost reduction) increases firm's profitability and lastly, increase in quantity sold (or demand expansion) also increases firm's profitability. Thus, the relationship between economic performance of a firm and price, unit cost and quantity, give rise to consequences of GrSCM practices.

The price premium potential is realized when a consumer pays higher prices for the environmentally friendly product. Such an effect can arise out of higher willingness to pay for the green product or a positive image that a firm builds out of its environmentally friendly initiatives. The cost reduction effect is facilitated by reduction in wastage or efficient use of materials during conversion processes and is supported by remanufacturing and recycling efforts. The demand expansion effect is realized when market demand of the product increases as a result of greening activities of the firm (Ramani and Swami, 2017). In other words, with two manufacturers selling competing products, the consumer would be willing to purchase more of the product which is environmentally friendly. The above conceptualisation is summarized in Fig. 3 (For a detailed exposition, also refer Swami and Shah, 2009).

It can be thus, argued that economic consequences of greening initiatives of firms often lead managers to undertaken sustainability initiatives.

Environmental Taxation

A critical driver of GrSCM initiatives which may not be driven by economic consequences, but has the potential to significantly change the competitive landscape for firms is environmental taxation. While greening initiatives of firms can lead to economic consequences as illustrated through the previously discussed framework, governments and policy makers also play an important role in driving firms to adopt GrSCM initiatives. By using taxation as a tool, policy makers drive adoption of environmental initiatives in firms. For example, the Waste Electrical and Electronic Equipment Directives (WEEE) and Restriction on Hazardous Substances (RoHS) that came into effect in the European Union forced manufacturers to modify their products and supply chains (see "Relevant Websites section"). This also meant increased challenges in product design, setting up product collection centers, installing testing facilities, investing in testing equipment and personnel while also developing better products for longer lifecycles.

Environmental taxation can also lead to change in competitive strategy of firms (Ghosh *et al.*, 2018). For example, pollution norms or waste disposal norms enforced within an industry can create significant competitive advantage for firms which have already invested in zero emissions, zero waste disposal and recycling technologies. In contrast, laggards in the industry can stand to face penalty for inability to adhere to stricter pollution norms. Pollution intensive industries such as plastic manufacturing, textile and apparel manufacturing, paints and chemical manufacturing, among others, remain under constant scrutiny of governments globally. Similarly, stringent pollution norms in automotive industry have often forced manufacturers to invest in fuel efficient vehicles, hybrid technologies, fuel cells, electric vehicles and environmentally friendly vehicles. Firms like Toyota and Volvo for example, have increasingly improved their vehicle designs to make them more environmentally friendly (both internal manufacturing processes and external usage impact) (KPMG, 2016). Thus, it can be argued that in areas where voluntary initiatives or economic incentives of firms may not drive sustainability initiatives, policy makers often play an important role in driving green changes.

Given the various factors that drive sustainability initiatives in firms across different types of industries, a pertinent question that arises is what are the sustainability indicators that firms can adopt to measure sustainability performance? We discuss this in the following section.

Sustainability Indicators in Supply Chains

Given the requirements of measurement and dissemination of information on sustainability actions of firms, one of the key initiatives of firms have been the adoption of Global Reporting Initiatives (GRI) Guidelines. GRI is an international independent standards organization that has developed guidelines on sustainability reporting and helps companies report sustainability impact (see “Relevant Websites section”). The GRI standards developed by the organization cover any type of firm across sector, location and size. The standards continuously evolve and cover economic, environmental and social aspects. Some of the key factors that are considered under environmental and social aspects are provided in **Table 1**.

A closer look at **Table 1** provides an intuitive view of some of the key categories appear in each dimension. NASA, for example, provides evidence of the deteriorating air quality in parts of the world particularly in countries, such as, South Africa, Middle East, India and China (see “Relevant Websites section”). While much of this is attributed to the economic growth in these regions, policy makers in US, Europe and China have undertaken significant steps in designing provisions for air quality control. From India’s perspective, areas such as water and air quality continue to remain of primary concern for the economy. In this context, [Shah \(2017\)](#) analyzes the state of groundwater governance in India and suggests that greater coordination among various stakeholders is needed to improve groundwater sustainability in India. [Rehman and Hussain \(2017\)](#) discuss India’s solar energy requirements and propose a model of clean energy financial support to bridge the gap between solar energy requirements and development costs. These issues are also critical for businesses as their focus on energy and water requirements continue to grow.

The next key question is – what are the key sustainability indicators in which businesses focus on? [Aswani and Swami \(2017\)](#) have studied, in Indian context, the frequency of environmental phrases that occur in the sustainability reports of companies across Automotive, Conglomerate, Food and Beverage and Personal and Household sectors and report that firms have emphasized on issues related to emissions, pollution and climate change. The frequently recurring themes under each environmental category are highlighted in **Table 2**.

It can be observed that much of the sustainability reporting broadly covers key issues faced by firms. Sustainability reporting along the dimensions identified in **Table 2** have seen an increasing trend and more companies are adopting sustainability disclosures along with financial statements. While for many organizations sustainability reporting is still voluntary, in several countries, sustainability reporting has been made mandatory. For example, in India, Securities and Exchange Board of India (SEBI) has mandated top 100 listed entities to submit Business Responsibility Reports (see “Relevant Websites section”). In addition, the Companies Bill, 2011, in India has mandated firms to include Corporate Social Responsibility (CSR) policy in their reports (see “Relevant Websites section”).

Thus, the pertinent question arises on whether there are significant differences in sustainability indicators across sectors? [Kumar et al. \(2015\)](#) analyze the dimensions of sustainability reporting in the context of emerging economy such as India and conclude that there are no significant differences in sustainability reporting between different sectors as the majority of sustainability issues remain common to firms. However, [Aswani and Swami \(2017\)](#) find that the extent of disclosure may vary between firms. Interestingly, conglomerates with diversified businesses cover significant aspects of sustainability indicators compared to firms in a specific sector.

Table 1 Sustainability dimensions and key categories in each dimension (For a detailed exposition on the GRI standards, refer: <https://www.globalreporting.org/standards/gri-standards-download-center/>)

Sustainability dimensions	Category
Environmental	Materials, Water, Energy, Waste, Emissions, Biodiversity and Environmental Management Systems (EMS), Environmental Compliance
Social	Employment, Occupation Health and Safety, Labor/Management Relations, Training and Education, Diversity and Opportunity, Non-discrimination, Community Involvement, Customer Health and Safety

Table 2 Frequency of environmental phrases used

Category	Phrases
Water	Water, Groundwater, River, Marine, Lake, Abstraction
Energy	Renewable, Energy Efficiency, Energy Usage, Green Energy
Waste	Hazardous, Emissions, Recycle, Pollution, Toxic, Landfill, Incineration, Waste Discharge
Emissions	Climate Change, Greenhouse Gas, Carbon Dioxide
Biodiversity	Forest, Ecosystem, Ecology, Habitat, Greenfield, Land use, Wildlife, Brownfield
EMS	ISO 14001, Management systems, Environmental Audit

Note: Aswani, K., Swami, S., 2017. Analysis of sustainability reporting of Indian companies. In: Dhir, S., Sushil (Eds.), Proceedings of International Conference on Strategies in Volatile and Uncertain Environment for Emerging Markets, July 14–15, 2017, pp. 537–549. New Delhi: Indian Institute of Technology Delhi.

This leads to the next pertinent question on what sustainability actions have firms undertaken on measurement, and dissemination along key indicators? We discuss cases of few firms which have undertaken various initiatives in this area, in the following section.

Case Studies in Sustainability Initiatives

To understand the sustainability measurement initiatives better, we take a look at few global firms which are also often subject to the scrutiny of stakeholders for the environmental impact of their supply chains. Specifically we discuss the textile and fashion industry.

The consumption of textile in various forms is estimated at more than 30 million tons a year, which causes serious social and environmental impacts within a supply chain (Chen and Burns, 2006). The issues related to sustainability are critical in the textile industry, and its associated industries like the fashion industry. In order to reduce production costs, textile or apparel firms have been accused of traditionally taking benefit of low environmental awareness and lax regulatory systems in emerging economies. However, lately, some fashion companies, recognizing the importance of environmental imperatives, have tried to incorporate greening operations in their supply chains. Such firms include H&M, Zara, Patagonia, Levis, Uniqlo, The North Face, and so on. It is interesting to note that greater sensitization towards environmental perspectives has not only come through firms, but has also been demanded by their consumers. Indeed, the consumers' environmental attitudes have been found to directly influence their consumption pattern in the case of fashion products (Chan and Wong, 2012). There are also some evidences from prior literature that fashion consumers prefer green products and are even willing to pay higher prices for them (Shen *et al.*, 2014). The production process in this industry is highly intensive in its use of chemicals and water. Thus, the sustainability requirements are immensely important and are required to be followed under standards such as ISO 14000 (Li *et al.*, 2014).

We present some representative case studies of apparel fashion brands that have introduced the operational aspects of sustainability in their supply chains. The requirements of coordination and resultant conflict of being both green and profitable are apparent at each stage of supply chain, which includes production, distribution, marketing and retailing.

Zara

Zara is a chain of fashion stores owned by Inditex, one of the largest apparel manufacturer and retailer of Spain. It employs more than 170,000 persons. In 2017, the sales of Inditex were reported at 25.3 billion euros, having 7475 retail outlets, 450 million items a year, in more than 96 countries (Inditex Annual Report, 2017). With a fickle demand scenario that Zara faces, it has shown a rapid growth. Its business strategy is hinged on responsiveness and a relatively affordable price range. As compared to the average apparel industry design-to-sales cycle times exceeding six months, Zara has achieved it in five to six weeks.

Unlike the competitors which mostly manufacture in Asia, Zara uses a hybrid strategy of sourcing with flexibility and speed through European sources and low cost alternatives in Asia. About 60% of the manufacturing volume is outsourced by Inditex. The uncertain demand is met through European, and more predictable orders are serviced out of Asia. The responsiveness in meeting demand has been possible due to its initiatives like Green-to-Pack programme, which fills distribution trucks as densely and efficiently as possible, and using these trucks also in the reverse logistics to bring back returned items. The logistics centers of Zara have an EMS (environmental management system), which is ISO 14001 certified. Each Zara outlet sends a fixed number of orders per week (usually, two) on pre-specified days. Timings of trucks' arrival and leaving a store are fixed at specific times. The labeling and pricing of the garments are completed before arrival at a store, making them ready for sale. Because of the specificity of this well-designed system, every supply chain member, ranging from manufacturing, transportation to even customers, are aware of its timeline and the impact of various activities.

Some of the sustainable initiatives by Zara include the use of eco-friendly and sustainably sourced materials, such as, organic cotton. It also utilizes recycled materials, engages in upcycling, and creation of new fibers. Its procurement team also focuses on the waste reduction and reuse of the fabric material, under its Closing the Loop program. Zara uses special boxes and free collections services to collect clothing donations by the customers at both its stores and from homes. Still, a high-speed supply chain of Zara's requires constant attention if its members, managers and partners. The supply chain team of Zara continually observes the demand and keeps making adequate adjustments to the production plans.

H&M (Hennes and Mauritz)

Hennes and Mauritz (H&M), a leading fashion brand, was founded by Erling Persson in 1947 in Sweden. In 2017, it had more than 4500 stores in about 100 markets with more than 150,000 employees (H&M Group Sustainability Report, 2017). The analysis of its supply chain reflects a product design success story with several designers and pattern makers having a penchant for spotting latest fashion trends. The company's integrated logistics function supports cost-efficient supply. The bulk of its production is out of Asia, while a smaller proportion is in Europe. Distribution is the key aspect of its supply chain system with adequate supply controls and demand rationalizations. Through outsourcing and off-shoring, H&M maintains the agility and flexibility during the shifting trends.

Under sustainable operations practices, H&M has undertaken the objective, that, by 2020, it will use 100% sustainably sourced cotton; and, by 2030, it will use fully recycled or sustainable materials. It also aims at zero waste target to the landfills. H&M recycles cotton, polyester, polyamide, plastic, and wool material. It is certified by independent third party certification for categories, such as, organic fabric is certified by Global Organic Textile Standard (GOTS) and recycled ones are certified by Global Recycling Standard (GRS). From 2017, its Global Change Award annual innovation initiative would fulfill the objective of shifting to a circular fashion economy. Under this initiative, some of the awarded ideas include making vegan leather using grape waste from wine production, cow manure into textile fibers, and invention of digital threading.

Under its old garment collection program, it categorizes the collected garments as re-wears, re-usables, and recyclables into other fabrics. Recognizing that a large proportion of its carbon footprints is due to the transportation activity, H&M's has switched to more efficient and cleaner modes of transport, such as ferry and trains. It also makes sure that even the transportation boxes are reused. H&M follows the local environmental standards of the countries to which it ships the products.

The company also has an up-cycling program, which reprocesses the used textiles and fabrics to create upcycled and appreciated products. Customers are given additional discounts on the purchase of the upcycled products. Transparency is maintained in providing all information to the consumers through the website. Additional revenues accrued from such programmes are used for further funding of coupons, donations, and reinvestments in sustainability programmes. All of this results in an overall winning strategy from the perspectives of consumer, H&M, and environment.

Patagonia

Patagonia, is an American outdoor clothing company based in California that is in manufacturing and distribution of a wide variety of apparel and accessories for the outdoor lifestyles consumers. It has created quality products, which are sustainable and responsive to the environment. The company was formed in 1973 by an entrepreneur, Yvon Chouinard, who was himself quite enthusiastic about outdoor lifestyle. The mission statement of the company is to "build the best product, cause no unnecessary harm, use business to inspire and implement solutions to the environmental crisis" (O'Rourke and Strand, 2017).

Patagonia makes its business decisions on the basis of the assessment of environmental impacts every level of its production process. In 1996, it commenced its Common Threads Recycling Program, to switch to organic fibers despite having to incur some initial losses. Patagonia has a keen focus on technology and innovation. It invested a substantial amount of its reserves in R&D, including a new material testing laboratory. Some popular and patented sustainable fabrics developed by Patagonia include: Synchilla (recycled polyester fleece), Capilene (moisture-wicking polyester fabric), and a wetsuit lined with chlorine-free wool for increased insulation (see "Relevant Websites section").

Patagonia undertook significant strides in sustainability initiatives and launched a program called 'The Footprint Chronicles' to trace and track the flow of materials from sourcing to final goods stage. The objective of the program was to track the material flow for products of Patagonia. Out of several outcomes of this exercise, an important finding by the firm was the presence of harmful chemicals such as per fluoro-octanoic acid (PFOA) used in rain shell jackets which accumulated in the bloodstream of consumers with repetitive use. The finding was also covered by business press and non-governmental organizations (NGOs). The increased pressure from consumers, NGOs and media, coupled with the proactive sustainability initiatives of the firm, led it to work with its suppliers to find alternative sources of chemicals which would be environmentally and health friendly, while maintaining the quality of the final products of Patagonia. This was easier said than done. The change in design and sourcing material required costly investments by the company to stop the use of PFOA and design and develop alternative chemical sources for its rain shell jacket. Over a period of time Patagonia worked with its suppliers, to find alternative chemical substitutes, changed its solvent recovery system and developed a more eco-friendly version of the rain shell jacket (Ghosh and Shah, 2012).

Patagonia believes that better alternative sources of chemicals can be developed as substitutes and constantly innovates in the design and sourcing of material in collaborations with its suppliers. Patagonia has also decided to incorporate transparency in its supply chain and displays all its supplier activities, manufacturing processes and product flows to consumers. Patagonia has also come up with an interactive newsletter, Footprint Chronicles, to build customers' and stakeholders' awareness about its company's global operations. Since some customers might want to make decisions based on environmental or social issues, they are provided benchmark data on such parameters as a complete transparency effort. This initiative is further corroborated by the company's Reference Library, which provides extensive information on sustainable alternatives, say ranging from inventing bamboo fabric to having wool free of chlorine treatment. The decision to bring in a new partner into Patagonia's supply chain, known as "4-Fold," involves the assessment of its balance on four parameters: sourcing, quality, social and environmental (O'Rourke and Strand, 2017). Thus, Patagonia works consistently to make their supply chain more sustainable and socially responsible (see "Relevant Websites section").

Conclusion

Rising environmental consciousness has shifted much of the focus of business practice towards sustainability. In this paper, we underscore the strategic importance of supply chains and highlight factors that drive sustainability initiatives in them. With a particular focus on the Sustainable Development Goals of the United Nations, we discuss the evolution of Triple Bottom Line and Green Supply Chain management. We delve into the antecedents and consequences of green supply chain management and argue

that economic benefits can drive sustainability initiatives of firms. In this context, using the simple profit equation of a firm, we argue that green initiatives can lead to higher profitability, either through cost reduction, price premium or demand expansion effect. It is to be noted that these economic benefits are not mutually exclusive and can overlap each other. In other words, a firm can generate twin benefits of cost reduction and price premium effect through changes in its process and product design.

In several cases, where voluntary initiatives of firms may not suffice to bring in much needed change, policy makers and governments play an important role in implementing environmental taxation to drive green initiatives. Such policy changes can significantly alter the competitive landscape for firms and those who have proactively engaged in adopting environmental initiatives may stand to benefit vis-à-vis their competitors.

We also discuss various sustainability indicators that firms can adopt in reporting their initiatives. In this regard, with a particular focus on environmental reporting, we look at some key dimensions along which measurement and further information dissemination can be done. Finally, we look at various initiatives undertaken by firms globally to incorporate environmental changes in their products and processes.

The lessons drawn in this paper have wide applicability across industry sectors. While we have attempted to closely integrate supply chains and environmental consciousness in our discussion, much needs to be in done in practice to stem the harmful effects emanating out of supply chain activities. There is an urgent need to align supply chain activities in line with Sustainable Development Goals for environmental protection.

Much of the issues discussed here have implications for researchers. While anecdotal evidence supports the conceptual green supply chain framework presented in this paper, scope for empirically validating the framework remains. Further, researchers can also look to analytically validate the model by incorporating cost reduction and price premium effects, or cost reduction and demand expansion effects. Analytical models incorporating uncertainty of green demand could also be built.

While the paper highlights various sustainability indicators adapted by firms, the metrics evolve on a periodic basis. Both practice and research have much to contribute here, since the development of sustainability metrics could be done with close tie up between academia and industry. The applications of improved sustainability metrics would further assist effective sustainability reporting.

See also: Corporate Social Responsibility in Supply Chains. Evaluation of Sustainability Indicators of Buildings. Expediting Faster Housing Supply in India Using Straw Bale as Prefab Building Material. Sustainable Supply Chain Management in Developed vs. Emerging Economies: Evidence From the UK and China's Manufacturing Industry

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- <https://indiacorplaw.in/2011/12/companies-bill-2011-csr.html>
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Waste electronic equipment – Environment – European Commission.

Sustainability Manufacturing Systems Design

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Introduction

Environmental concerns have grown exponentially owing to the increasing consumption of natural resources and pollution. Therefore, to address the aforementioned concerns it becomes important to successfully implement the sustainable manufacturing systems. A number of definitions have been proposed to define the word sustainability. For instance sustainability has been defined by former Prime Minister of Norway Gro Harlem Brundtland as the framework wherein the needs of the present generation are met without compromising the ability of future generations in meeting their requirements (Jawahir, 2008). In accordance with Jawahir and Wanigarathne, sustainability meets the requirements of the customer base with simultaneous management of available resources (Jaafar *et al.*, 2007; Rosen and Nazzal, 2013). They opined on the three pillars that define the term *sustainability*: Social directions, economic factors, and environmental concerns.

Specific objectives are associated with each of these sustainability aspects. These specific objectives are to be met to ensure the development and implementation of sustainable environment. Ethics, quality of life, safety, and improvement in health are the major objectives related to the social aspect of sustainability. New business opportunities, new job roles and employment, and process and product development are the major objectives associated with the economic aspects of sustainability. The environmental aspect of sustainability is met with implementation of regulations on clean water, air, and soil (Epstein, 2018).

The three main levels that aid in identification and analyzing the conceptual framework of sustainability are system, process, and product levels. Required sustainability goals can be achieved through effective interactions amongst the aforementioned levels. The perception of product level focuses on recycling, remanufacturing, recovering, reusing, reducing, and redesign. The process level focuses on reduction of toxic waste, hazards, and energy consumption. This is achieved through the employability of optimized processes, which in turn is reflected in an effective methodology related to process planning. An efficient supply chain reflects the system level perception of sustainable manufacturing. The supply chain will be sustainable if it considers all the stages related to the life-cycle of a product, that is, premanufacturing phase followed with manufacturing stage and ultimately the usage phase and postusage stage (Badurdeen *et al.*, 2009). In totality, the following are the major objectives of a sustainable manufacturing framework: Reduction in consumption of energy, waste reduction, improvement in durability of the product, elimination of toxic waste, removal of health hazards, enhanced remanufacturing, reuse, and recycling.

Owing to the importance of sustainability, the present article is a genuine effort to review the approach of sustainable manufacturing through analysis of assessment methods, techniques, and tools for implementation and the related concepts. As such the article begins with a discussion on elements of sustainable manufacturing, which is followed with the associated needs and concepts. Design for sustainable manufacturing systems is elaborated in the subsequent section. The article then goes on to discuss the effective implementation of sustainable manufacturing framework followed by elaboration on assessment of approaches for sustainable manufacturing. Future trends in the domain of sustainable manufacturing have been highlighted towards the end of the article, which terminates with the concluding remarks.

Key Elements Related to Sustainable Manufacturing

Evolution of sustainable manufacturing has taken place through several paradigm shifts of manufacturing, that is, traditional, lean, green, and sustainable (Hartini and Ciptomulyono, 2015). The existing 3R approach has been modified to 6R by the addition of three more dimensions related to sustainability: Remanufacture, redesign, and recover. Postuse activities are carried out to collect the end-of-life products and therefore serve the objective for the recover phase. Simplification of postuse processes serves to achieve the challenges associated with environmental concerns and hence the redesign element of the 6R approach. The remanufacture element aids in enhancing the product performance by concentrating on savings of cost, energy, resources, and produced waste. Information on implementation of sustainable manufacturing framework is one of the critical aspects in development and enhancement of sustainable business models. The successful implementation of a sustainable business framework involves three major phases (Hamalainen *et al.*, 2018): Research, development, and commercialization. In the research phase, the specific requirements related to sustainability are examined, evaluated, and developed. This may include the impacts of climate change, various causes of pollution, and utilization of easily available and abundant renewable resources. The main goal of this phase of implementation is to ensure that sustainability is established and maintained at the precompetitive level and therefore has a very high potential in successful implementation of a sustainable manufacturing environment. The research phase concentrates on the major environmental issues related to manufacturing. In the second phase of implementation, that is, the development phase, various tools and methods (Mota *et al.*, 2015; Nazzal *et al.*, 2013) are employed to enhance environmental performance. Design for environment, life cycle analysis, and assessment of environmental footprint are some key indicators for environmental

performance. The last phase of implementation is the commercialization phase, which aids in refining the previous phases. Effective cooperation is established between the suppliers, vendors, and the customers.

Needs Related to Sustainable Manufacturing

Another important aspect that plays a critical role in achieving a sustainable manufacturing system is the comprehension of needs in defining the path to adoption of sustainable manufacturing (Cherrafi *et al.*, 2016). According to the literature, there are three important elements that define and describe completely the requirements of sustainable manufacturing: Information, management and culture, and procedures. Effective assessment can be made by providing the required qualitative and quantitative information. Specialized departments oriented to sustainability have to be built inside an organization to promote the development of sustainability culture. Procedures must be in place to ensure the application of the strategies and the objectives for a sustainable organization.

However, to enhance the performance pertaining to sustainable manufacturing, a number of needs are desired including concepts, data, government policies, integration, research, manufacturing practices and methods, and tools. The comprehensive examination of environmental, social, and economic aspects as well as other considerations is one of the additional needs for the improvement of sustainability performance. These concepts of sustainability are supported through development and continual enhancement of the developed method and tools. Requirement of comprehensive and robust data aids in analysis of environmental impact as well as related sustainability assessments. Data is however required across the various phases of the product life cycle. Sustainability indicators are required to monitor the effectiveness of practices in place to ultimately result in increasing awareness of sustainability amongst the customers and suppliers. Government policies on sustainability programs are required to ensure cooperation between the companies and the government itself. The policies are created considering the environmental impact. For continuous improvement in sustainable systems, industrial and academic research is indeed required that focuses on design and manufacturing in the backdrop of environmental considerations. Integration of the aforementioned needs representing the sustainability requirements on societal, economic, and environmental aspects is a very important requirement of enhancing the performance of sustainable manufacturing.

Sustainable Manufacturing and Design Approaches

To achieve the desired target for design for sustainability systems, several objectives are to be met. These objectives are designing for effectiveness of cost, optimal usage of material, efficiency of energy, disassembly of products, recycling, repair and reuse of products, remanufacturing, and continuous improvements (Jovane *et al.*, 2008).

The concept of “design for sustainability” is often considered as unique loop encompassing integration between substance and information loops (Jovane *et al.*, 2008). Design for remanufacturing, recyclability, manufacturability, social impact, resource utilization, environmental impact, and economy forms the major pillars for sustainable manufacturing environment when looked at from the perspective of process and product levels. The main objectives in accomplishing design related to environmental impact are efficiency, cobalance, and effects of environmental factors (Bhamra and Lofthouse, 2016). On the other hand, renewable sources of energy, operational costs, utilization of material resources, consumption of power, and energy efficiency results into achieving design for utilization of resources and economy (El-Halwagi, 2017). Design related to manufacturability considers development of newer techniques for storage, enhancing methods of manufacturing, establishment of newer methods for transportation, and assembly of products and packaging (Anderson, 2014). Different aspects such as product reliability, effectiveness of product function, ergonomics, ease of product use, and durability are the key elements for achieving design for functionality (Badurdeen *et al.*, 2013; Arnette *et al.*, 2014). Design pertaining to social impact considers ethical responsibility, health-wellness effect, and operational safety (Bennett *et al.*, 2017; Sutherland *et al.*, 2016). Smart techniques and hence development of advanced methods for recycling and remanufacturing are accounted in design for remanufacturability and recyclability (Veelaert *et al.*, 2017; Prendeville and Bocken, 2017). This aids in enhancing the efficiency of energy and material usage.

Implementation of Effective Sustainable Manufacturing Systems

Effective implementation of sustainable manufacturing systems can be ensured once the needs, elements, and the models associated with sustainable manufacturing have been defined. On achieving the aforementioned objectives, implementation of a sustainable manufacturing environment can take place with suitable understanding of the different implementation methodologies. The present section of the article discusses different practices and recommendations for effective implementation of sustainable manufacturing systems. The major requirement relating to the practical aspects of system, product, and process levels needs to be fulfilled to achieve sustainable manufacturing systems. A few of the related aspects are (Chen *et al.*, 2014) applications of principles related to utilized materials that are recyclable and nonhazardous and hence the related inputs; employability of efficient systems for logistics and transportation; development and planning of manufacturing processes that consumes less power,

water, and materials; development and application of design concepts that promote the usage of fewer resources; and development of product design concepts resulting in recyclability, remanufacturability, and reusability.

There are number of implementation stages that require their major objectives to be fulfilled so that the overall objective of the sustainable manufacturing approach is achieved. The various steps in implementation are development of work practices and maintenance strategies, optimization of process, substitution of raw materials, new technologies, and lastly the design of new product (Fargani *et al.*, 2017; Rodrigues *et al.*, 2016; Engert and Baumgartner, 2016). A brief discussion on each implementation steps follows next.

Development of work practices and strategies of maintenance: This implementation step of sustainable manufacturing system is often referred to as the housekeeping step. Production operations are made effective through the monitoring mechanisms, management, and scheduling of inventory. Effectiveness can be measured in terms of sustainable training programs, maintenance of equipment, and reduction of losses from leaks.

New product design: This step of implementation of sustainable manufacturing systems is often considered as the most difficult step. This step involves the transfer of the entire system of an organization from a zero sustainable environment to a full and well-established sustainable one.

Substitution for raw material: One of the major steps in achieving a sustainable manufacturing environment is to replace the hazardous chemicals and materials with the sustainable materials that have less adverse effect on the environment and health. Therefore, the major objective of this step is the reduction of concerns related to health and the environment. Furthermore, the goal of reduction in regulatory costs pertaining to storage and disposal of materials is also met through this step.

Optimization of different processes: This step involves the development of manufacturing processes such that waste materials can be reused, raw materials can be conserved, and waste is minimized. This can be achieved for instance by determination of optimal settings for each operation, changing of certain steps in specific manufacturing processes, and relocation of the machines so that the total movement of the machines can be minimized. Energy-efficient technologies that offer a supporting framework for sustainable manufacturing environment are another step to successful implementation of sustainable manufacturing systems. Energy efficiency can be achieved through the use of minimum lubrication, promoting dry cutting (Kaynak *et al.*, 2013), artificial intelligence methods (Renzi *et al.*, 2014), waste management principles (Kerry, 1988), and cryogenic approach (Wang and Rajurkar, 2000).

Newer methodologies and technologies: The step depends on the employability of energy systems with relatively higher efficiency. Energy efficient systems will ultimately aid in enhancing the environmental impact and the associated performance levels. The energy efficient methods have the potential ability to save heat and energy. However, a huge capital investment is required for effectively keeping such systems in place to achieve the desired sustainability effect.

Previous studies have revealed many successful attempts for implementation of sustainable manufacturing systems. Furthermore, attempts have also been made to link between manufacturing needs and the aspects related to sustainability such as management of waste, consumption of energy, and health and environmental concerns (Pereira *et al.*, 2017a,b; Polvorosa *et al.*, 2017; Hegab *et al.*, 2018a,c,d; Hegab and Kishawy, 2018; Eltaggaz *et al.*, 2018a,b).

Assessment For Sustainable Manufacturing Models

Once the sustainable manufacturing models have been implemented, it is also required to put in place an effective assessment model to evaluate the performance of sustainability systems. Personal health and safety, consumption of energy by various processes, management of the generated waste, environmental impact, and manufacturing costs are the five major elements that aid in assessing the sustainable manufacturing environment (Álvarez *et al.*, 2016; Chang *et al.*, 2017; Hegab *et al.*, 2018e). Subclusters and individual metrics related to each of the elements have (Kishawy *et al.*, 2018) been depicted in Figs. 1–5 respectively. Numerical and analytical models can be established for modeling of waste management, manufacturing cost, and

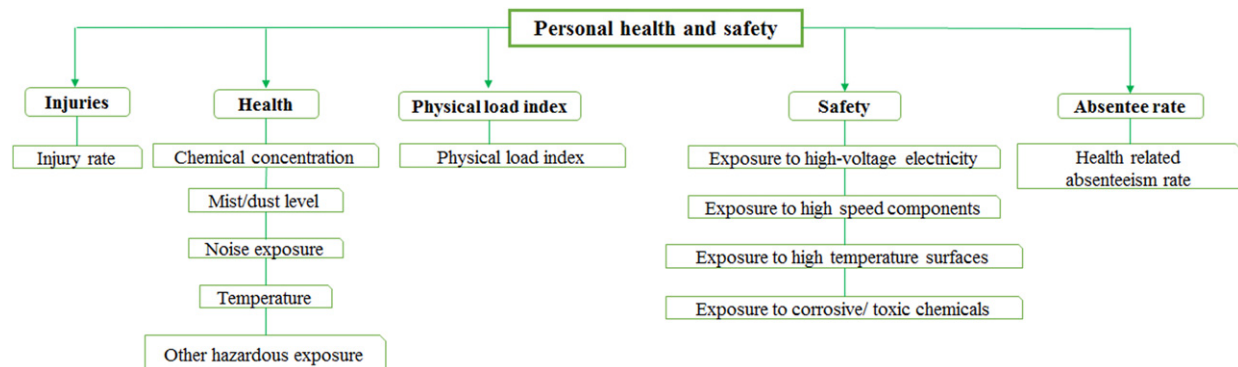


Fig. 1 Subclusters and individual indicators metrics for personal health and safety.

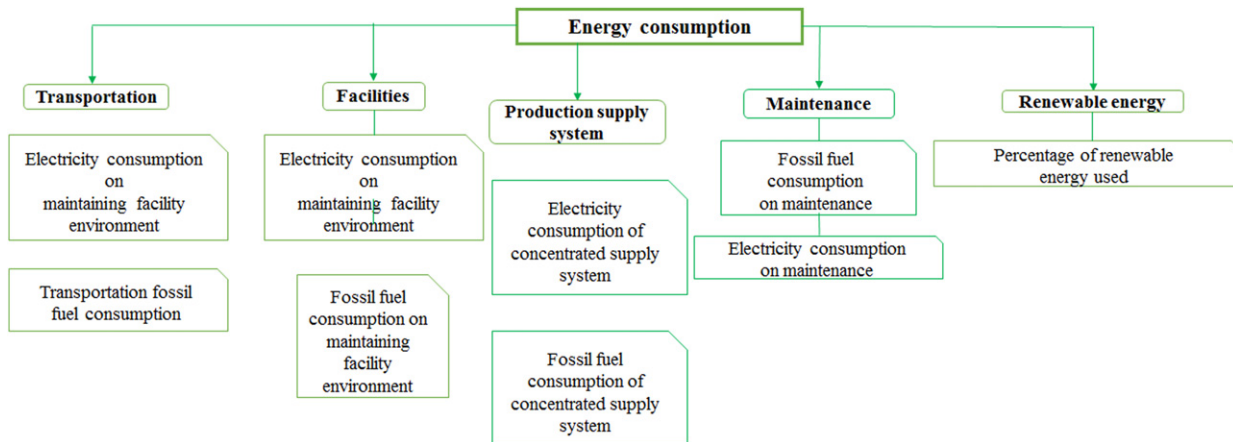


Fig. 2 Subclusters and individual indicators metrics for energy consumption.

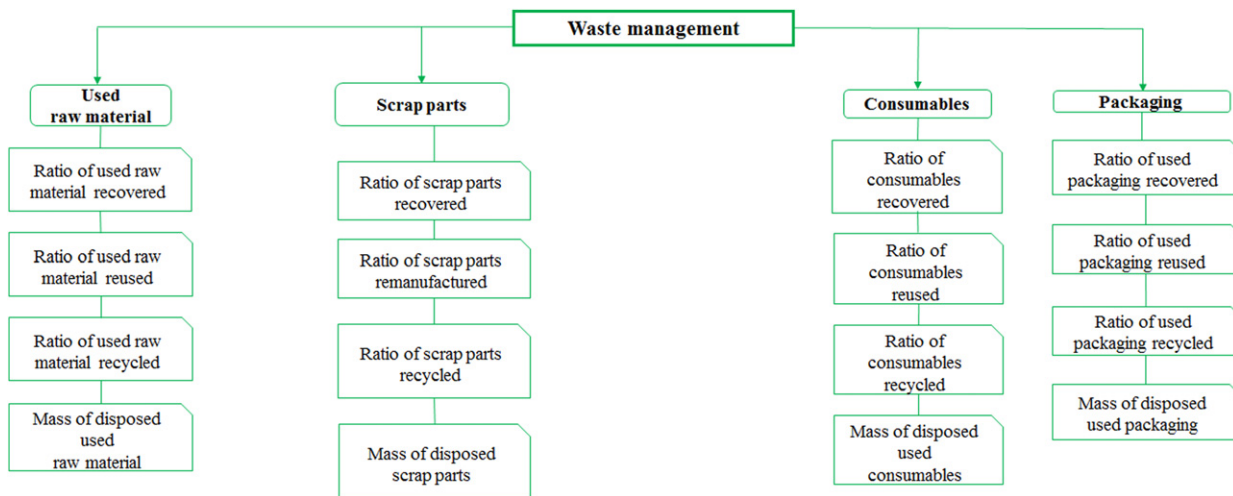


Fig. 3 Subclusters and individual indicators metrics for waste consumption.

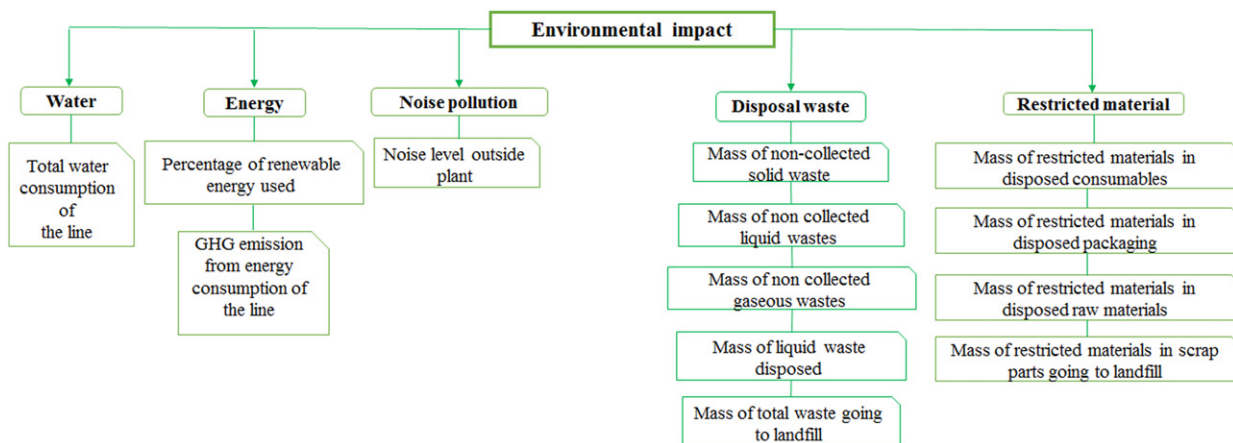


Fig. 4 Subclusters and individual indicators metrics for environmental impact.

energy consumption (Bertoni, 2017; Nee, 2015). However, the experience of the designer and their judgment can be used to express other key elements, that is, impact of environment and personal health and safety (Liu *et al.*, 2008). The assessment model must be able to effectively integrate and analyze the effects of all five major elements simultaneously.

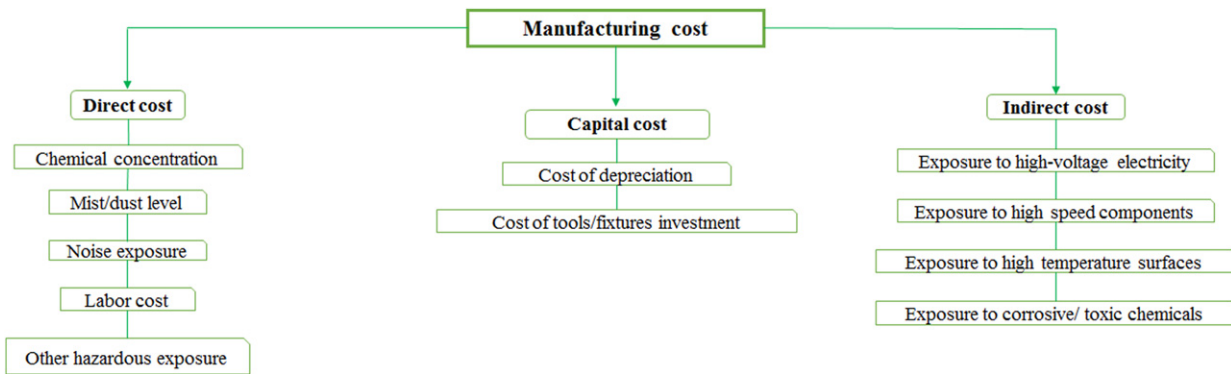


Fig. 5 Subclusters and individual indicators metrics for manufacturing cost.

Another perspective from the product point of view can be expressed in terms of three main elements, that is, social, environmental, and economic aspects (Zhang and Haapala, 2015). The social impact aspect includes the following subclusters: Regulations related to social impact, human rights implementation, characteristics and benefits to employees, and health and safety impacts. Waste and emissions, end of life product, efficiency of material utilization, and energy usage are the subclusters related to the environmental aspect. As far as the economic aspect is concerned, the major subclusters are financial losses, economic growth benefits, indirect costs, direct costs, and initial investments.

A number of advantages are associated with the application of sustainable manufacturing models. As for instance, reduction in energy consumption, reduced waste, enhanced durability of product, enhanced performance of the systems, and better conditions for health and safety.

Conclusion

The present article has presented a discussion on sustainable manufacturing approach. This has been presented in the context of design, concepts, and techniques of implementation, and methods of assessments. The required target of sustainability has been achieved through the interaction amongst various levels, that is, system, product, and process. The following key subobjectives were identified in achieving the overall objective of sustainable manufacturing environment: Motivation towards usage of renewable energy resources, enhanced quality of life, enhanced quality of product, reduction in environmental impact, elimination of the health hazards, and improvement in durability of product, reduction in wastage of material, and reduction in consumption of energy. Several needs were identified to achieve the aforementioned subobjectives. These are integration, research, data, methods, and approach. Several aspects related to design that play an instrumental role in implementation of sustainable manufacturing environment are design for social impact, design for functionality, design for manufacturability, design for utilization of resources and economy, and design for environmental impact. Different stages key to the implementation of implementation of sustainability systems as identified from the literature surveyed were development of improved work practices, optimization of manufacturing and the associated processes, substitution of hazardous raw materials, employment of newer technologies, and development of newer designs of product. Solid assessment models and their need after the implementation phase have also been highlighted. It can be concluded that an effective sustainable manufacturing environment and its periodic analysis through different assessment models can aid in providing optimal performance levels.

Although there is a greater focus on the sustainable environment in the scenario where there is a greater concern towards the environment, the concepts and the related definitions are still inconsistent with the scientific community. There are wide variety of performance measures and instruments for judging sustainability. However, this presents another complexity to define completely the effective implementation of a sustainable environment. Thus definitions and proper understanding of the concepts of sustainability are one of the key barriers for its acceptance amongst the industries.

Manufacturing units need to evolve through the associated complexities and implement the various elements of sustainable manufacturing effectively so as to counter the growing concern towards the environment and hence human health.

Future Scope of Research

The present article has outlined the crucial understanding on the needs, techniques of implementation, and methods of assessments in accomplishing a sustainable manufacturing environment. Furthermore, the three major phases to achieve and hence successfully implement the expectations of manufacturing systems with sustainability characteristic features, that is, research, development, and commercialization, have also been highlighted in the present context. The major research gap lies in the

identification of effective implementation techniques and the desired needs. Therefore, a lacuna still exists for a detailed guidelines that can ultimately aid in defining the related conceptual framework and sustainable manufacturing practice techniques. Furthermore, artificial intelligence based models need to be promoted to achieve the goals of sustainable manufacturing. Also it is required to develop and enhance the current technologies relating to sustainability so that more benefits can be achieved through the employability of a sustainable environment.

See also: Environmental Impact Subtracting Versus Additive Manufacturing. Green Manufacturing: Progress and Future Prospect. Impact of Environmental Initiatives on Environmental Performances: Evidence From the UK Manufacturing Sector. Quality of Environment and Clean Manufacturing. Subtractive Versus Hybrid Manufacturing. Sustainability Indicators in Supply Chains. The Potential Role of Re-Distributed Manufacturing in Improving Industrial Sustainability

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Sustainable Production and Consumption – Business Perspective

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Introduction

The contemporary business environment witnesses a heightened concern toward sustainable development. Sustainable development seeks to surpass the standalone pursuit of economic progress, and advocates a further consideration to the environmental and social goals in business decisions. Sustainable development now stands as an agenda of international prominence, and the paradigm of sustainable production and consumption (SPaC) forms a key goal of the 'United Nations Development Programme' to transform modern-day nations, society, and businesses in the frame of sustainability. SPaC thus represents an ambitious response to the targets of sustainable development through its integrated consideration toward production-consumption systems in the modern economy. This response specifically aims to achieve the production and consumption of products, services, and resources through innovative ways that are environmentally benign, economically viable, and socially beneficial. The realization of SPaC depends on the active contribution of various stakeholders such as government, business, communities, households, and other non-business actors.

The Rationale of Sustainable Production and Consumption

Response to sustainable development concerns prevailing in the business environment has traditionally been either production- or consumption-orientation. While the production-oriented response lays an overarching focus on regulating the production systems to yield sustainable products and services, the consumption-oriented response is a standalone focus to generate awareness among the consumers to consume responsibly. It is however the 'rebound effect' that underscores the fundamental shortcoming inherent in these standalone approaches by accounting the logical offsetting of sustainability leads generated within one front (either production or consumption) by uncontrolled advancements over the other. For example, energy-efficient products may lead to a rise in household consumption due to cheaper operating costs. Overcoming this limitation is highly dependent on an integrated consideration to production-consumption systems. SPaC is therefore a more proactive response to the sustainable development agenda, which advocates the amalgamation of production and consumption perspectives to reveal a clearer picture of challenges and solutions by focusing on the complex inter-relationships between the two fronts (Roy and Singh, 2017). Fig. 1 presents the conceptual representation of SPaC.

SPaC is thus an advanced perspective to govern the effectiveness of public policies and business models for a sustainable business environment. This can be better achieved through diverse interpretations which the view of amalgamation (Fig. 1) inherent in SPaC facilitates.

The first key interpretation of SPaC lies in a production-dominant logic that addresses the question 'how production systems can foster sustainable consumption?'. This logic of SPaC outlines explicit enabling mechanisms that can facilitate the development of sustainable products and services to promote responsible consumption patterns. The typical guiding philosophies comprise of (a) produce through responsible consumption of resources, (b) produce through responsible disposal/treatment of wastes and pollution prevention, (c) design for sustainability, (d) consumer involvement in product design, (e) product service/repair,

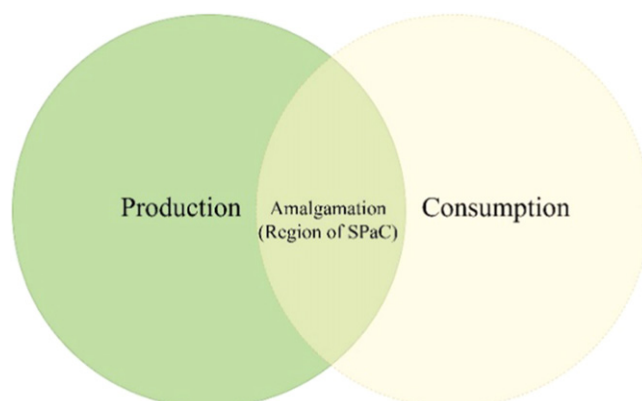


Fig. 1 The region of sustainable production and consumption (SPaC). Adapted from Roy, V., Singh, S., 2017. Mapping the business focus in sustainable production and consumption literature: Review and research framework. *Journal of Cleaner Production* 150, 224–236. doi:10.1016/j.jclepro.2017.03.040.

(f) certification and product labeling to inform consumers about sustainable product/service offering, (g) fair trade – assurance of minimum price and benefits to producers at the bottom of pyramid, (h) ethical marketing – marketing approaches that do not promote overconsumption, (i) production-based responsible consumption – producer's role in educating consumers on sustainable consumption patterns and sustainable products, (j) using less – producer's role in facilitating reduction in the rate of consumption, (k) increase wisely – facilitating coordinated increase in the consumption of under-consumers, and (l) responsible procurement (Lebel and Lorek, 2008).

The second key interpretation of SPaC propagates a consumption-dominant logic which outlines the key role of consumers in affecting the production decisions of firms. For example, consumers may prefer to not consume a product or service that was produced unsustainably. This logic explains the critical role of consumers in pressurizing firms to facilitate (a) choices with sustainable product portfolios, (b) responsible and fairly priced consumption options, (c) replacing products with services, (d) greater accessibility to sustainable and resource-efficient products, (e) products that are easy to repair, (f) products that are innovative and multi-functional, (g) sharing of products, and (h) recycling and take-back policies based on extended producer responsibility (Haake and Jolivet, 2001).

These logics are complementary to each other in strengthening the position of SPaC in the contemporary business environment. They characterize the extension of responsibility for both producers and consumers to systematically involve each other in decision making. The interaction of these logics is however required to be interpreted through the contextual lens of economic development based on the developed and developing economies. First, it is critical for developing economies to facilitate SPaC in a manner that does not curtail economic welfare. Realizing this aspect forms the key challenge in the progress of SPaC. The current state of knowledge suggests that the radical goal of SPaC needs to be attained through the appropriation of achievable targets. For example, it can be feasible for a developing economy to embark on the transition toward SPaC – by jointly working on boosting the environmental and social quality of local production, and on fostering the preliminary awareness regarding sustainable consumption patterns. Second, given the advent of globalization, it is also important to focus on the responsibility of developed economies in leading the SPaC initiative on a global scale. For example, how can a firm situated in the developed economy can support its outsourcing business partners in the less developed nations to achieve SPaC.

The innate distinction in these economic contexts suggests that SPaC can primarily initiate from a policy focus to develop tailor-made pathways to sustainable development. The policy focus outlines the intervening role of government in supporting the multiple layers of the economy such as global trade, national market, and everyday life in regards to SPaC. The typical policy responses can be based on the principles of efficiency, sufficiency, and deliberation. The approach of efficiency focuses on boosting the technological competence of infrastructures to generate sustainable products and services with lesser resources and pollution. The sufficiency framework relies on regulating overconsumption by prompting the consumers to carefully evaluate their purchase decisions in the frame of sustainable integrity. The approach of deliberation develops information sharing and awareness generating mechanisms to achieve an overall consensus among the producers and consumers to achieve SPaC. These approaches are however constrained by the key responsibility of the government to mitigate the chances of market failures that may result from the interaction between sustainability principles and traditional profit-maximizing protocols prevailing in the business environment.

Apart from the government's role in defining policies, SPaC can also initiate from the secondary position of voluntary commitment by corporates to shift to innovative business models based on SPaC principles. Corporates may alternatively respond to the stakeholder pressures from governments (national and international), local communities, activist groups (such as NGOs), business partners, shareholders, and employees. Stakeholder pressures typically account a firm responsible for the social and environmental externalities generated from its economic activities. Ignoring such pressures may attract lawsuits, penalties, legal actions, public relations expenses, litigation fees, reputational damage, and the loss of consumer/employee confidence. Apart from the view of pressures, firms can recognize the potential competitive advantage and incentives inherent in SPaC based business. As such, SPaC compliance facilitates the firm with access to newer business opportunities in the globalized economy that specify sustainability as the precondition to supply.

The tertiary position regarding the initiation of SPaC in the business environment may involve an advanced state of collaborative action between governments, corporates, and other stakeholders to assign concrete roles and responsibilities. Such a state can profoundly govern the formalization of sustainable development agenda in the business environment toward the creation of a circular economy. It is however important to note that this progressive state of SPaC implementation is highly dependent on the achievement of significant advances along the primary and secondary fronts of SPaC initiation.

Based on these fronts, important characteristics can be derived to inform the contexts of developed and developing economies. The developed economies are more advanced in propagating SPaC through policy frameworks and voluntary involvement of corporates. Countries for example Finland, Germany, and United Kingdom have even moved to the advanced stages of SPaC by developing integrated systems that link production and consumption (Berg and Hukkinen, 2011; Lehtoranta *et al.*, 2011). The developing economies however witness preliminary efforts of the corporates to embrace SPaC, and government policies in these countries largely remain oriented toward economic development. The developing countries in the advanced stages of economic growth such as emerging economies (India, China, Brazil, Russia, South Africa, etc.) have started to face stakeholder pressures demanding stringent regulations on SPaC through dedicated policy frameworks. Such nations have resultantly started to consider the trade-off between economic development and sustainability, and have embarked on pilots to model policy frameworks targeting SPaC. For example, emerging economies such as China, India, and Turkey have developed government replacement and

subsidy policies in various industries to promote remanufacturing and generation of demand for remanufactured products (Wang *et al.*, 2019).

SPaC thus represents the facilitation of radical shift in the business environment to move away from the usual business outset of profit maximization. Implementation of SPaC is heavily dependent on the development of concrete agendas that guide the noted fronts. This requires accessing the strategic and operational issues embedded in the pathway of SPaC implementation to gauge the real picture of challenges and potential solutions.

The Strategic and Operational Issues in the Implementation of SPaC

The Strategic Issues

The achievement of transformation toward SPaC in businesses can be characterized as a complex journey which involves a multitude of stakeholders including the government, corporates, and consumers. The complexity emerges from the outset of the journey toward sustainable development which intends to propagate itself in the premise of established protocols of economic development. The journey therefore witnesses a natural resistance from the stakeholders involved in terms of their willingness to embrace radical shifts. Thus, the fundamental aspect concerns with facilitating a buy-in among stakeholders toward sustainable development at the systems level. The key strategic issues in this regard are segregated in the following.

Mainstreaming

Mainstreaming is the initial strategic response in this regard, where the key focuses lie in raising the awareness of stakeholders regarding sustainable development, and advocating the need to embrace SPaC in traditional production-consumption systems by locating the entry points. This can be achieved by systematically integrating the SPaC concern into existing programs and policies through gradual phases of developments (Cohen, 2010).

The first phase of mainstreaming involves the mapping of government, political, and socio-economic conditions to locate the contextual forces that would influence the course of transformation toward SPaC. The typical aspects to focus on targeted consultations with stakeholders may include (a) mapping the perspectives of diverse agents such as industry bodies (industry associations, chamber of commerce), business (owners, proprietors), NGO, governments (provincial and federal), civil society, media, academics and research institutions, consumer lobby groups, and retailers – in shaping the production and consumption trends, (b) locating key individuals/authorities among these agents that influence decision making and may influence the transformation process, (c) understanding how budgets and strategies can be defined to shape resource use and rights allocation toward SPaC-based trade and industrial development in the key areas of water, natural resources, energy, and environment, (d) understanding how relevant sectoral policies can be formulated that indicate the priorities (technical, institutional, and political) regarding sustainable development and economic development, (e) understanding the extent to which the existing policies and processes have relevance to SPaC, and (f) understanding the time-boundedness of SPaC outcomes.

The second phase of mainstreaming focuses on identifying country-specific priority areas and opportunities regarding SPaC. A consideration to social, environmental, and economic developmental priorities is helpful in weaving national-level SPaC programs. The specific issues to be explored involve understanding (a) the priority areas regarding SPaC in other similar countries, (b) in which areas SPaC would be most difficult or easiest to implement, (c) the extent to which discontinued/completed policies address the targeted SPaC priorities, (d) which processes in the existing production-consumption system are under ongoing transformation, and can provide a space for SPaC oriented change, (e) the status quo in the country regarding resource production and consumption, trade flows, and research and development, and (f) the forecast regarding future production and consumption trends in regards to the growing population in the country.

The third phase of mainstreaming requires assessing the institutional and capacity needs within specific industrial sectors in the backdrop of governmental and political contexts. It is specifically important to understand the strengths and weaknesses of existing institutions and capacities in constraining or promoting SPaC. This can reveal a picture regarding the scope of futuristic capability developments, and the available support of businesses, industries, and consumers.

The fourth phase of mainstreaming focuses on identifying and engaging champions to raise awareness and building partnerships in regards to SPaC. This can be achieved through workshops, one-on-one meetings, field visits, media campaigns, etc. Champions can be primarily comprised of representations from the broader stakeholders such as government, NGO, media, civil society, and consumer bodies. They may also involve influential decision-making authorities at the local, regional, national, and sectoral levels for example government officials, key members of business associations, prominent industry figures, academic scholars, and international agencies. Champions are needed to be engaged across the industrial sectors to propagate SPaC as a legitimate business agenda. It is however important to ensure the thorough mentoring and training of champions in regards to SPaC.

The fifth phase of mainstreaming revolves around the setting of formal mechanisms to facilitate sustained mainstreaming. Establishment of a 'leading institution' is a vital step in this regard to demonstrate a strong strategic buy-in toward SPaC. This role can be fulfilled by institutional bodies such as the Ministries of Finance, Planning, and Environment or the Office of Presidency. Another step may involve the establishment of 'steering committee' to ensure multi-body representation to guide the mainstreaming efforts. The sectoral level initiatives can consider establishing 'task teams' possessing specialized domain knowledge to

enhance the reach of mainstreaming. These mechanisms need to target developing common management frameworks regarding technical assistance, work plans for mainstreaming, and timely monitoring/reporting of progress in mainstreaming efforts. It is important for the reporting to be based on qualitative and quantitative data for example industrial production-consumption records, material flow accounts, input-output balances, eco-efficiency/resource efficiency data, and trade data.

The strength of mainstreaming efforts governs the emergence of explicit policies and strategies to guide the SPaC transformation among firms and consumers. The policies can be understood as the formal inclusion of SPaC agenda in the budget of government to facilitate explicit provisions regarding SPaC efforts. The critical aspects involve (a) availability of financing sources for firms to support SPaC, (b) firm's access to knowledge regarding SPaC implementation in terms of technical advisory support, twinning cooperation between firms and national/international organizations, formal training etc., (c) formal inclusion of SPaC agenda in the education system, and (d) institutional cooperation mechanisms between the public and private sector through the definition of new positions and roles based on SPaC.

Furthering from the linkage between mainstreaming efforts and the emergence of policy frameworks, the strategic scope of SPaC also focuses on further explicit mechanisms to ensure SPaC transformation at the systems level.

Incorporating SPaC in design thinking

The strategy of 'Design for Sustainability' focuses on incorporating systematic changes in design thinking to foster sustainable patterns in production and consumption. This can be achieved by focusing on enhancing the functionality, innovation, life span, and resource efficiency of products and services by considering environmental, social, and economic aspects (Niinimäki and Hassi, 2011).

The design of sustainable products incorporates guiding principles that ensure a long product life cycle, product attachment, emotional satisfaction, customization, halfway products, modular structure, co-creation, and open source design.

The lifecycle of a product can be lengthened by radically restructuring the product inputs based on sustainable and high-quality materials. Accommodating such restructuring however demands a relook into production processes through innovative approaches (recycle, re-use, source reduction, etc.) and high ethical values (waste management, sustainability accounting, ethical labor practices, etc.). Design considerations that seek to augment the characteristics of product attachment and emotional satisfaction among users are helpful in facilitating extended consumption of products. Selection of product attributes that remain meaningful to consumers over an extended period of time is important in this regard. A way to achieve an emotional connection between the product and its user involves the strategies of customization and mass customization. These strategies are helpful in empowering the user in a limited frame of choices for example color and style to create a personalized product.

The extent of user involvement in product design and production can be further increased through the concept of the half-way product. This concept relies on the principle of design for easy disassembly. Products can thus be offered as kits to demand the participation of users in translating their personalized creativity and significant assembly efforts. Doing so improves the user knowledge regarding the product, and the ability to repair the product when needed. The modular structure is another variation in this line of design thinking. It focuses on the production of products based on disintegrated modules that can be easily assembled, disassembled, and repaired. Co-creation and open source design emphasize the mass-level participation of end consumers in the product design process. While the co-creation involves seeking design inputs from a limited scope of target consumers, the open source design seeks design inputs from the users worldwide.

Sustainability in services can be achieved through systematic design considerations that facilitate intensive and longer utilization of a product-service system. The first important aspect is to explore competitive ways that would prompt consumers to purchase functions rather than products. This involves considerations such as questioning the relevance of product ownership, high-quality service experience, user-friendliness, shared usage, a non-profit network for sharing/lending/exchange among consumers, renting/leasing, and innovative options that replace goods with services. The service thinking inherent in these considerations demands thorough involvement of the service provider in understanding the vital attributes of consumer satisfaction. This understanding is helpful in improving sustainability performance and product utilization flexibility. Second, apart from the orientation of maximizing consumer value, service design must offer good product performance without increasing waste streams.

However, the achievement of sustainability in design thinking is critically dependent on the collaborative efforts between producers and consumers to generate new knowledge on SPaC transition. Education thus forms the vital aspect of knowledge building in this regard.

Educating for SPaC

Strategic educational interventions focusing on enhancing the knowledge of stakeholders on SPaC are helpful in strengthening the linkage between producers and consumers toward a multi-stakeholder alliance (Petry et al., 2011).

Educating organizational actors about SPaC is an elemental intervention focusing on engaging corporations as learners and educators. This can be achieved through training programs, workshops, and knowledge symposiums to facilitate enabling inputs on SPaC. A further emphasis involves facilitating sector-specific know-how on the incorporation of SPaC practices. For example, the apparel and textile industry can focus on understanding various SPaC practices that can facilitate long-lasting apparels and improve sustainability performance. These focuses can be facilitated by systematically aligning the educational programs around new skill building and creating change agents. New skill building emerges from knowledge on systems and life cycle thinking, social and technical innovations, material reduction, sustainable grades of materials, recyclability and reusability, extended product lives, waste treatment and reduction, collaborative inter-firm action, and energy efficiency. Change agents rely on approaches

such as communication for leading the SPaC agenda, engaging stories, changing perceptions on business outcomes, setting new aspirations, and societal responsibility.

Another educational intervention regarding SPaC focuses on creating innovation-oriented social learning networks. The awareness and adoption of sustainable technologies can be achieved through social arrangements which integrate multiple stakeholders in a common platform. For example, in the Netherlands, several challenges are organized based on the teamwork of stakeholders such as companies, universities, schools, and local communities. One such challenge is the 'Frisian Challenge' which intends to build capacity for solar business development in the region. This challenge engages social teams into the construction and race of solar-powered boats. The inherent social learning framework is helpful in enhancing the sustainability awareness of masses. It also facilitates the exchange of knowledge and technical expertise, the formation of newer alliances, new experience, and new outcomes such as business ideas to promote solar energy.

Further educational intervention approaches focus on the aspects of the development of standards or certification systems to facilitate 'cradle-to-cradle' business systems, development of sustainable communities, and formal incorporation of sustainability agenda through SPaC in b-school curriculums. Standards or certifications facilitate explicit guidelines and documentation requirements to coordinate various intra- and inter-firm processes in the frame of sustainability. Industrial standards for example environmental management systems, food safety standards, social sustainability standard of fair trade can be considered as preliminary steps in this regard. Future developments into certifications must focus on sustainability in an integrative manner to consider the production and consumption along the social, environmental, and economic fronts. Development of sustainable communities can be achieved through promoting resource sharing and trade of used products. Innovative means for example web-based applications, portals are helpful in this regard. Incorporation of the sustainability agenda based on SPaC in b-school curriculums more profoundly contributes to the development of responsible managers and future leaders.

The radical scope of shifts in the transitional pathway of SPaC relies on newer ways of organizing businesses. It is therefore important to focus on how business models can be better aligned with the SPaC paradigm.

SPaC-oriented business models

The paradigm of SPaC is elemental in facilitating sustainable products and services in the contemporary business environment. Conceptualizing business models that enable SPaC to create distinct value for the product/service offerings is the necessary prerequisite.

The newer business models can propagate from the two classic strategic orientations that govern the operations of a firm in the business environment (Wong *et al.*, 2016). While the 'low-cost' strategic orientation focuses on creating products and services that are available to customers at competitive prices, the strategic orientation of 'differentiation' emphasizes on distinguishing the firm's offerings from that of competitors in terms of innovation, speed, flexibility, and quality. Low-cost products and services can benefit from SPaC by modeling business practices around aspects of resource efficiency, shared consumption, buy-back, remanufacturing, and so on. Differentiated offerings, on the other hand, can better respond to the market competition by creating innovative products and services – that are produced through advanced SPaC principles and provide a unique value to consumers by establishing a market niche. Furthermore, the strategies can be hybridized in a product-service system by setting low cost based SPaC as the production agenda, and differentiated service based on SPaC as the consumption agenda.

Scenario building plays a vital role in the selection of an appropriate strategy by the firm to carve SPaC based products and services. This involves system analysis where it is important for the firm to locate key factors that may influence the efficacy of its operations for example market competition, bargaining power of suppliers/customers, firm's internal competence, access to newer business opportunities, complexities, and stakeholder resistance to change. These inputs can better guide the development of future options by systematically considering the aspects such as the importance of self-sufficiency in the society, extent of consumerism, economic growth, and social exclusion (Lorenz and Veenhoff, 2013). Scenario building can be conducted at the local, regional, and global levels to understand the attributes that would govern the demand and supply of sustainable products and services. These considerations also form the inputs regarding the selection of 'SPaC enabling mechanisms' (as noted) for governing the strategic orientation of the business model (Haake and Jolivet, 2001; Lebel and Lorek, 2008).

Another key issue concerns to effectively distinguish the sustainable products and services in the market and convey its unique value to the consumers. This can be achieved by institutionalizing sustainability meta labeling that certify the nature/extent of SPaC sophistication the offering has undergone (Dendler, 2014). An effective sustainability meta labeling scheme is easy to institutionalize, conveys the positive sustainability outcome, distinguishes itself from other labeling schemes in terms of its key emphasis to social and environmental issues, stringency and sophistication of production processes, specific and easily revisable to be adapted to local conditions, and easily aggregates a large amount of information. The acceptance of a labeling scheme among the consumers can be enhanced by focusing on (a) procedural legitimacy which delineates the legitimacy of production process, (b) knowledge legitimacy which highlights the extent to which the labeling extends scientific facts based on research and development, (c) charismatic legitimacy which outlines the extent to which the labeling is supported by trusted organizations in the society, and (d) regulatory legitimacy which characterizes the extent of engagement of government actors in the conceptualization of labeling.

The ultimate focus of a SPaC-based business model is to evolve as a governance mechanism for guiding the creation of sustainable supply chains by integrating the chain of buyers, suppliers, and customers along the principles of SPaC. SPaC is

instrumental in setting the guiding agenda for sustainable supply chain management by defining the scope of sustainable product (and service) portfolio, selection of appropriate business partners (suppliers and customers) to form a supply chain, selection of appropriate SPaC enabling mechanisms to define explicit practices to be implemented throughout the supply chain (Niesten and Lozano, 2015; Roy and Singh, 2017). SPaC is therefore a strategic notion to define the length and breadth (or sophistication) of sustainable business practices to be primarily incorporated by a firm and secondarily incorporated by its supply chain partners. However, the notion of sustainable supply chain management operates as dedicated literature in the domain, and deals with in-depth operational issues, surrounding the coordination of sustainability performance of the supply chain through sustainable business practices (refer. Roy *et al.*, 2018b). Apart from these aspects, the strategic intent of SPaC further extends to operational issues to guide the pathway of SPaC implementation.

The Operational Issues

The operational front of SPaC implementation primarily concerns developing practical approaches to realize the SPaC-oriented shift in firms. Apart from the development of sustainable practices, this front also focuses on addressing operational challenges to facilitate the implementation of sustainability practices in business or organizational routines. The following describes these aspects in greater detail.

SPaC practices

The SPaC practices are explicit protocols that specify a SPaC-oriented shift in the traditional production-consumption practices of firms. They can be simply understood as the operational definition of SPaC enabling mechanisms (Section “The Rationale of Sustainable Production and Consumption”) for reflecting the conceptual space of amalgamation of production and consumption perspective in business practices. SPaC practices are categorized under four heads to reflect diverse firm-level practices (Barber, 2007). Production-oriented practices focus on incorporating changes in production processes to realize sustainable products and reduce resource consumption. For example, industrial ecology practices, cleaner production practices, lifecycle analysis, extended producer responsibility, integrated product policy, safety and health standards in production workspace, modifying product design, source reduction, waste management, sustainability management standards, sustainable supply chain management practices etc. Consumption-oriented practices focus on raising awareness and changing consumption behavior of consumers through approaches such as consumption behavior and trend analysis, consumer information, educating consumers, right-to-know, consumer awareness campaigns, product boycotts, need analysis, etc.

Distribution-oriented practices aim to coordinate the flow of products and services through approaches for example ethical advertising, ethical sales, ethical packaging, ethical pricing, responsible trade, labeling, etc. Investment-oriented practices aim to influence private or public decisions to coordinate investments for achieving SPaC through approaches such as government procurement, sustainability taxes, subsidy reform, investment guidelines, socially responsible investment, and financial institutions reforms and so on. These approaches are evolving and further developments are desired in the area of how more innovative practices can be defined to operationally translate the SPaC enabling mechanisms.

Operational challenges

The key operational challenge concerns bridging the knowledge gap for linking SPaC practices to traditional business protocols. As such, incorporation of SPaC practices in the firm’s routines creates newer and unprecedented conditions to demand significant efforts of firm-level stakeholders toward adaptation (Preuss and Walker, 2011). For example, production processes to facilitate the reuse of input materials demand an upgraded expertise of operators in terms of innovative response for remodeling the explicit and tacit production protocols regarding reuse. Adaptation toward SPaC is therefore dependent on knowledge generating efforts of firm’s stakeholders to innovatively redefine the explicit and tacit knowledge bases of businesses – for successfully accommodating the targeted SPaC practices in the firm’s routines. Innovative responses to SPaC must however fulfill the key elements of products and services, and must be easy to reproduce and replicate. This demands an understanding of consumers in their own context by employing multi-stakeholder processes based on the involvement of local and non-business actors (e.g., NGOs).

The more operational challenges in the production phase includes upgrading the performance management systems to measure SPaC benefits, monitoring costs, customer’s urge on low cost and quick delivery, technical feasibility of innovative responses to SPaC, price competition prevailing in the market, unsuitability of traditional technology, initial investment toward technology upgrade, lack of internal firm resources and capabilities, lack of financial resources, trade-off between mass production and innovation, lack of supply chain infrastructure, complex coordination with inter-firm partners on SPaC, lack of top management commitment, lack of corporate strategy toward SPaC, conflicting sustainability targets and design requirements, and lack of guidance frameworks to guide employees operational decisions. The consumption phase involves the challenges regarding unclear stakeholder responsibility toward SPaC, lack of viable end-of-life recycling framework to integrate consumers, difficulties in reusing/recycling mixture of materials, lack of expertise in remanufacturing, and lack of consumer support in coordinating rising consumption (Tseng *et al.*, 2013; Pallaro *et al.*, 2015; Dubey *et al.*, 2016).

Discussion

Realizing SPaC in business systems is a multifarious agenda involving intricate processes at the strategic and operational levels. These processes are intended to produce radical shifts by reorienting the existing business practices toward sustainability. Given the wider scope of actions involved, it is important to ensure the interconnectedness and complementarity between the strategic and operational aspects of SPaC implementation. Thus, the critical agenda is to mitigate the discrepancy between the intended and actual outcomes in the pathway of SPaC implementation processes (Berg and Hukkinen, 2011). This can be better achieved by thorough monitoring of SPaC progress based on the multi-stakeholder framework. The government's role in monitoring the nationwide progress toward SPaC forms an important focus in this regard (Gandenberger *et al.*, 2011; Kielin-Maziarz, 2013). Future developments need to explicate how policy frameworks can be created around monitoring of SPaC progress through stimulating partnerships among businesses, state of inter-firm relationships, influencing and gauging the state of consumer choice in regards to sustainability, and stimulating and sustaining the behavioral change of firms and masses toward SPaC.

From the firm's perspective, it is important to understand how strategic and operational difficulties in the pathway of SPaC can be mitigated. From a strategic viewpoint, it is important to understand how innovative business models can be developed around SPaC. It is also important to understand how SPaC philosophy can serve as a guiding mechanism to shape more sustainable supply chains. Presently, these literatures lack connect to develop more holistic perspectives regarding the interaction of sustainable development agenda and roles of businesses and consumers. Conceptually, sustainable supply chain management (SSCM) focuses on the strategic development of inter-firm sustainability coordination among businesses to maximize the social, environmental, and economic value of the supply chain. SPaC, on the other hand, is a much broader concept to outline the roles and accountability of wider stakeholders such as governments, businesses, and consumers for ensuring a sustainable future. In the backdrop of the linkage between SPaC and SSCM, the firm-level purview of SPaC is responsible to experiment with business practices and innovative sustainable approaches for enabling SPaC at the intra-firm level. SSCM draws on sustainable business practices and further extends on how such practices can be employed to meet the performance frontiers in the contemporary business landscape. The SPaC knowledge can thus facilitate vital inputs to the SSCM view in terms of different sustainable business practices a supply chain can seek to implement at the chain level (Roy and Singh, 2017; Roy, 2018; Roy *et al.*, 2018a,b).

The operational aspect of SPaC therefore needs to focus on how innovative business practices can be developed to translate the notion of SPaC in firm-level practice. It is important to understand how operational challenges can be mitigated through structured approaches by prioritizing the areas of gradual action in terms of domains such as production/consumption of products and services, design, usage, and disposal. Further approaches can focus on financing innovative implementation, capacity building activities, market-based instruments to attract the attention of producers and consumers, and life cycle thinking.

Overall, the business perspective of SPaC concerns with how the standalone fronts of production and consumption can be amalgamated to generate more profound actions for guiding the sustainable development agenda in the business environment. The key aspects inherent in the notion of SPaC concern the conceptual interpretation surrounding the integration of production and consumption fronts, strategic issues, and operational issues to enable the paradigm.

See also: Barriers and Benefits Towards Sustainability Driven Business Models. Green Energy Fuel From Biomass and Sea Water. Low Carbon Economy for Sustainable Development. Renewability Assessment of a Production System. Sustainable Biodiesel Production. Toyota Production System – Monitoring Construction Work Progress With Lean Principles

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Sustainable Production of High Performance Concrete

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Introduction

The history of the application of cementitious materials dates back to the period of the Romans. However, with the progress of time, there have been substantial changes in the manufacture, development, and production of concrete. The compressive strength of concrete is generally used as an indicator of quality, which is relatively easy to measure. Knowledge based on extensive studies about how to manipulate the composition of concrete to achieve the desired compressive strength is readily available. However, knowledge relating to other attributes of the composition of concrete is still inadequate and therefore engineers/scientists are actively working on this. Another challenging issue which remains, is to address continuous concrete deterioration due to aging, corrosion, exposure due to aggressive environments. Hence, with the further progress of time, research shifted towards improving the durability of concrete structures. To address these issues higher strength concrete (HSC) applications became popular, which are also a preferable choice in constructing heavily loaded compression members of tall buildings. However, the necessity of a workable mix further inhibited the productivity of HSC. This led to the development of superplasticizer, which enabled engineers to achieve high strength at good workability. Achieving high strength requires high cement content with a tremendous increase in the cost. Apart from this, it has also been realized that just achieving high strength will not be sufficient to achieve the required durability. This necessity proposed utilization of industrial by-products having pozzolanic properties to achieve high strength and durability. Today, with the combined application of mineral and chemical admixtures (superplasticizers), it is possible to obtain high performance in concrete in terms of strength and durability, which is known as high-performance concrete (HPC).

HPC is an engineered concrete whose mix is tailored by adopting low water to binder ratio, and optimal aggregate-to-binder proportion with the incorporation of mineral admixtures and superplasticizers to achieve more workability, high strength, and high durability. HPC possesses one or more of the following characteristics, which can be: (i) low- heat of hydration, porosity, water-binder ratio, bleeding, plastic shrinkage ratio, permeability; or (ii) high - early age strength, workability, and resistance to chemical attack. The following section describes the methodology in selecting materials and design mixes for sustainable production of HPC (Swamy, 1996; Aitcin, 1998; Mehta, 2004; Al-Hadithi and Alani, 2018).

Materials Selection for Conventional HPC

It is necessary to get the maximum performance out of all materials involved in producing concrete. When attempting to produce HPC, any material incompatibility may be detrimental to the finished product. High-performance concrete will contain not only Portland cement, aggregates, and water, but also superplasticizers and supplementary cementing materials. The desirable details of the material properties for production of HPC is given here.

Cement

The basic principle for designing HPC mixes is replacement or substitution of cement by supplementary cementitious material (SCM) with minimal or absence of tri-calcium aluminate, tri-calcium silicate, and di-calcium silicate. The particle size distribution and shape of alternate SCM should be selected similarly to that of the cement to control the rheology of the mixes. The selected cement should develop strength with age and facilitate rheological properties during fresh state. The chemical composition of cement should have a little amount of Tri-Calcium Aluminate (C3A) preferably in cubic form, this helps in enhancing the reactivity of cement and improves the quality and rate of production of ettringite. To impart strength in the cement Tri-Calcium Silicate (C3S) should be fairly present and cement should be finely grounded. It should be noted the presence of soluble sulfate in cement is very important for the selection of cement for HPC. The finer particles hydrate rapidly than coarse particles and hence enhance the early age strength of concrete. But this may also cause loss in workability due to the higher dispensation of heat of hydration. A suitable particle size distribution is to be established so that both the workability retention over a longer period for fresh concrete and higher early age strength is simultaneously achieved.

Fine Aggregate and Coarse Aggregate

The proper selection of fine aggregate becomes very important as rise in target compression strength, makes aggregates weakest location to inhibit failure. Coarser sand corresponding to a fineness modulus range of 2.7–3.0 is preferred over finer sand, as finer sand will require more water and hence lead to workability and segregation issues. The sand packing density should be designed to achieve minimum void ratio; as higher void content will require more water. Another important ingredient for achieving HPC is

coarse aggregate. The incorporation of coarse aggregate leads to the reduction in drying shrinkage and improves permeability of concrete against any ingress of moisture. Coarse aggregates of larger size have less specific surface and hence preferred over smaller size coarse aggregate to attain high workability. Similarly, equidimensional aggregates or cubic aggregates also produce stronger and better mix compared to HPC mixes with flat and elongated aggregates.

Water

The quantity of water required for HPC should be designed and limited to the amount required for binding activity of the hydrated cement gel, as any excess water would lead towards the formation of undesirable voids and capillaries causing the reduction in strength and durability of hardened concrete. In general, the water qualified for drinking purpose is as good for the production of concrete. However, tests should be conducted to check whether the initial hydration rate of cement is affected by the presence of salt in water.

Materials Selection for Sustainable HPC

One of the alternative ways for sustainable production of HPC is the application of industrial by-product as cement replacement or incorporation of superplasticizers for enhancing workability and durability (Shi *et al.*, 2011). The details of the materials are listed hereafter:

Fly Ash

It is a pozzolanic material and produced as an industrial by-product during combustion of coal. Physical properties of fly ash differ from the quality of coal utilized for combustion and appear as spherical, hollow and angular-shaped. Chemically fly ash is classified as Class F (low calcium) and Class C (high calcium). Class F fly ash is produced by combustion of anthracite or sub-bituminous coal while Class C fly ash is produced by burning lignite or bituminous coal. This is also grouped as silicoaluminous (Class F), silicocalcic (Class C) and sulfocalcic group based on the high presence of sulphur and an equal amount of calcium and sulphur, respectively (Wang *et al.*, 2017).

Ground Granulated Blast-Furnace Slag (GGBS)

The reaction between iron oxide, fluxing stone and coal in the blast furnace during the manufacture of pig iron produces slag as the by-product. When the slag is cooled slowly, crystalline shaped aggregates are formed which is utilized as aggregate for concrete, road or embankments. But if the slag is quenched in water immediately after its production, it solidifies into vitreous form and after proper grinding, it attains cementitious properties. It is to be noted that the temperature at which slag is quenched is very important because at higher temperature only vitreous nature is observed and it becomes more reactive. The quality of GGBS can be evaluated easily by subjecting the samples to X-ray diffractogram, where a definite peak of melilite is observed. The slag as binder component is blended with cement after grinding or intergrounded in the clinker. The incorporation of slag reduces heat of hydration, improves pore structure, increases permeability against chemical attack and resistance against sulfate, chlorides, and water. It should be also noted that as the w/b ratio is decreased, the incremental intrusion plot shifts towards the lower range of pore size, macrocapillaries reduces while microcapillaries and gel pores increases. The threshold diameter is also reduced due to the addition of fly ash/slag (Biskri *et al.*, 2017).

Silica Fume

It is a by-product obtained from the manufacture of silicon metal and silicon alloys. The amount of silicon dioxide in the silica fume is greater than 90% and 85% when fabricated from silicon metal and ferrosilicon alloys, respectively. The silica fume is a very fine particle of spherical shape, size ranging less than 1 μm in diameter. The specific gravity of the material is 2.2 and possesses a specific surface area of 15000–25000 m^2/kg compared to the specific surface area of cement being approximately 1500 m^2/kg . The extreme fineness of silica fume causes filler effect and makes it a natural location for germination of crystals of calcium hydroxide, while amorphous nature and high amount of silicon dioxide make it a very reactive pozzolanic material.

Super plasticizer: The selection of proper superplasticizer is very important for dispersing the cement particles adequately to achieve high performance. They are classified into melamine, naphthalene, lignosulfonate and polyacrylates based superplasticizers. In general naphthalene based superplasticizers are preferred due to higher solids content, better control on the rheology and are cost effective. However, to evaluate the performance of compatibility between the cement and superplasticizer it is advised to conduct mini-slump and the Marsh cone tests. Mini-slump method requires less material compare to Marsh cone test but the predicted results are indicative of a static behaviour compared to the more dynamic condition in marsh cone test. The superplasticizer is also responsible to improve the filler effect between cement and other particles such as silica fume.

Mix Design of High Performance Concrete

The main parameters influencing the proportioning of normal concrete mixes are water/cement ratio, cement content, aggregate/cement ratio, size and shape of aggregate etc. However, the conventional methods of obtaining mix proportions for normal concrete cannot be extended due to HPC due to the application of cement replacement materials (CRM) or supplementary cementitious material (SCM). It should be noted that mineral admixtures having pozzolanic properties are known as CRM when utilized as replacement of cement while SCM when incorporated to mix as an addition to the cement. For the design of sustainable HPC, the existing ACI method is modified and the inclusion of the efficiency factor for mineral admixtures is adopted. The efficiency factor (k) is an equivalent factor which on multiplication with the mass of fly ash (f) or selected CRM is equivalent to the mass of cement. Hence the water (w)/cement (c) ratio is replaced with water (w)/binder(b) ratio and designated as $w/(c + kf)$. The steps are as follows (Bharatkumar *et al.*, 2001, 2005):

Methodology I

Step I - Selection of reference mix: For this step well established ACI method is adopted to obtain mix (without superplasticizer) having a slump in the range of 25–50 mm with a w/b ratio of 0.50. If the mix is not having proper workability, the quantity of fine and coarse aggregate is altered, by maintaining the same w/b ratio and aggregate/binder ratio.

Step II - Selection of water content: The obtained ratios in step I is used to cast mixes (three to four number) having reduced water content levels. The workability of the mixes is improved by the addition of superplasticizer. Further charts can be developed to obtain the relationship between the price of superplasticizer plus cement with respect to decrease in water content. The desired optimal water content is selected from the comparison charts.

Step III - Selection of efficiency factor: The efficiency factor is calculated from linear regression method using the strength values obtained without CRM and with CRM. The equations are further modified with respect to replacement level percentage and given by efficiency of mineral admixture ($k(t,p)$). With the help of evaluated efficiency factor compressive strength relation with effective w/b ratio is obtained using the selected materials.

Step IV - Final mix design: After finalization of w/b ratio for the target compressive strength mix proportion of all the ingredients (cement, aggregate, mineral admixtures, the dosage of superplasticizer) can be calculated.

Three sets of mix design results with varying mineral admixture contents are presented. The mix design adopts the concept of efficiency factor for designing. The properties of the binder and coarse aggregate is given in Tables 1 and 2, respectively. The fine aggregate passed 4.75 mm sieve size and have specific gravity and fineness modulus as 2.62 and 2.48, respectively. A sulphonated naphthalene formaldehyde type SP is chosen for the current study.

Set 1

The cement replacement levels in set1 mixes consisted of (i) fly ash – 15%, 25% and (ii) slag 15%, 30%, and 50%. The experimental results of the adopted reference mix are given in Table 3. In the next step Abram's law arbitrary constants $A1$ and $A2$ as per Eq. (1) is obtained. In the next step, linear regression is conducted between $A2$ and the age in days (t) to obtain Eq. (2) using experimental values given in Table 4. After substituting Eq. (2) in Eq. (1), Eq. (3) is obtained which gives the relation between the compressive strength versus c/w relationship for mix with mineral admixtures. Where, $S(t,p)$ and $k(t,p)$ are the strength of HPC and efficiency of mineral admixture, respectively, at the end of t days and for a replacement level p percentage by weight of binder (i.e., $f/(c + f)$), c , w , and f are the cement, water and CRM content in unit volume. $k(t,p)$ can be obtained after further simplification and given by Eq. (4).

$$S = A1(c/w) + A2 \quad (1)$$

$$A2(t) = B1(t/28)^{B2} \quad (2)$$

Table 1 Properties of binder materials

Properties (%)	Cement			Fly ash	Slag
Silica	19.11			58.8–59.1	33.67
Alumina	6.43			39.9–40.3	20.56
Iron oxide	5.22				1.01
Magnesium oxide	0.71			0.22–0.34	9.63
Lime	63.78			0.86–1.02	32.45
Sulfate	1.29			–	0.10
Specific gravity, g/cc	3.14			2.15	2.95
Compressive strength (MPa) at	Set-1	Set-2	Set-3	–	–
3 days	27.40	35.8	26.49		
7 days	36.22	46.4	33.21		
28 days	55.32	66.1	53.42		

Table 2 Physical properties of coarse aggregate

Properties	12.5 mm	20 mm
Specific gravity	2.71	2.68
Dry rodded unit weight (kg/m ³)	1550	1700
Water absorption (%)	0.5	0.4

Table 3 Details of mix proportions and concrete properties for two extreme values of w/c (with OPC only, Set-1)

Mix designation	Unit	AO	BO
Water/cement ratio		0.50	0.35
Cement	(kg/m ³)	340	486
Fine aggregate		819	684
Coarse aggregate		1054	
Water		170	
Wet density		2340	2417
SP (% by weight of binder)		0.50	
Slump (mm)	mm	20	25
Compressive strength (MPa) at age of			
3		23.86	57.10
7		29.20	63.67
28		40.93	75.07
56 and		44.52	79.51
90 days		45.52	79.64

Mix designations:

First letter A or B denotes $w/b = 0.50$ or 0.35 respectively.

Second letter O denotes OPC mix.

$$S(t, p) = A1(c + k(t, p)f)/w + B1(t/28)^{B2} \quad (3)$$

$$k(t, p) = (1/f) \left\{ -c + w(S(t, p) - B1(t/28)^{B2})/A1 \right\} \quad (4)$$

For evaluation of efficiency factor $k(t, p)$ of mineral admixtures (fly ash 15% and 25%, and Slag 15%, 30%, and 50%), in mixes for w/b ratios of 0.5 and 0.35, coarse aggregate content and water content is kept constant. The fine aggregate content is revised to achieve similar volume of concrete per unit mass by. No volume adjustment is applied for application of slag, as the specific gravity of slag is similar to cement. The concrete mix proportions and the compressive strength at various ages are given in **Table 3**.

From these strength results, the values of $k(t, p)$ are obtained using the relationship given in **Eq. (4)**. The average values of the efficiency factor obtained for the material investigated and the replacement level used are given in **Table 5**. The main advantage of this method is the use of operating water content based on the effectiveness of the superplasticiser, cost of superplasticiser and cost of cement, whereas existing methods arbitrarily reduce the water content by 5%–10% when SP is added. The proposed method uses the efficiency factor evaluated for the given set of materials to obtain the compressive strength vs effective w/b ratio relationship, which will be used to calculate the effective w/b ratio required for any desired compressive strength, whereas the existing methods use the relationships given in the codes of practice and if the compressive strengths are not close to the desired value, then mix is reportioned for different w/b ratios. The existing methods require a large number of trial mixes to arrive at a mix having minimum cement content, while in the proposed method based on the effective binder values, various combinations of cement and mineral admixtures can be obtained to have mix with minimum cement content.

Set- 2

Set 2 consists of concrete mixes with 20% and 40% cement replacement levels by fly ash while 50% and 70% of cement replacement by slag. The reference concrete mix proportion is given in **Table 6** while mixes with CRM is given in **Table 7**. The obtained formulation for efficiency factor and values is given in **Eq. (4)** and **Table 8**, respectively.

Set- 3

Set-3 consists of concrete mixes with 50% cement replacement by slag. The reference concrete mix proportion is given in **Table 9** while mixes with CRM is given in **Table 10**. The efficiency factor $k(t, p)$ is found to be 0.58, 0.85, and 0.91 at 7, 28 and 56 days for $p = 0.5$.

Table 4 Details of mix proportions and concrete properties for two extreme values of w/b (with CRM, Set-1)

Mix designation	AF15	AF25	AS15	AS30	AS50
	$w/b = 0.50$				
Cement, kg/m ³	289	255	289	238	170
Fly ash, kg/m ³	51	85	—	—	—
Slag, kg/m ³	—	—	51	102	170
Fine aggregate, kg/m ³	800	787	819	819	819
Coarse aggregate, kg/m ³	1054				
Water, kg/m ³	170				
SP, % by weight of binder	0.60	0.70	0.60	0.65	0.65
Slump, mm	35	40	15	25	20
Wet density, kg/m ³	2338	2342	2338	2330	2333
Experimental compressive strength (MPa) of concrete at					
3 days	17.33	16.11	23.24	17.31	14.41
7 days	26.34	24.71	30.05	27.41	23.30
28 days	35.28	33.53	35.61	38.28	40.03
56 days	43.52	44.18	44.35	46.17	46.44
90 days	45.97	45.46	46.09	47.57	48.85
Mix designation	BF15	BF25	BS15	BS30	BS50
	$w/b = 0.35$				
Cement, kg/m ³	413	365	413	340	243
Fly ash, kg/m ³	73	121	—	—	—
Slag, kg/m ³	—	—	73	146	243
Fine aggregate, kg/m ³	652	631	684	684	684
Coarse aggregate, kg/m ³	1054	1054	1054	1054	1054
Water, kg/m ³	170				
SP, % by weight of binder	0.60	0.75	0.70	0.75	0.85
Slump, mm	15	25	20	15	40
Wet density, kg/m ³	2393	2397	2411	2402	2415
Compressive strength (MPa)					
3 days	48.87	45.24	45.57	43.58	39.60
7 days	59.95	51.56	60.54	59.60	53.95
28 days	72.06	65.58	70.08	72.93	75.46
56 days	76.96	73.00	74.78	77.72	79.36
90 days	79.01	76.57	80.71	79.91	81.28

Mix designations:

First letter A or B denotes $w/b = 0.50$ or 0.35 respectively.

Second letter F or S denotes fly ash or slag respectively as CRM.

Numerical value 15, 25, 30 or 50 represents the % replacement of cement with CRM.

Table 5 Efficiency factor $k(t,p)$ for CRM

Age	Efficiency factor $k(t,p)$ for CRM				
	Fly ash		Slag		
	15%	25%	15%	30%	50%
7 days	0.90	0.76	0.98	0.97	0.88
28 days	0.86	0.78	0.81	1.00	1.04
56 days	0.98	0.94	0.97	1.05	1.06
90 days	0.98	0.95	1.05	1.04	1.05

Methodology II

One of the other popular methods for production of HPC using ACI 363 Committee on high-strength concrete is described hereafter. The first step is to select required strength and slump. The target to be achieved is 25–50 mm without superplasticizer. The second step is to select the maximum size of the coarse aggregate (MSA) depending upon the target strength. For concrete grades having strength less than 65 MPa, 19 or 25 mm size aggregates are recommended. Similarly, for achieving strength greater than 85 MPa aggregate sizes of 10–13 mm and for concrete strength lying in the range of 65–85 MPa, 25 mm aggregates of good quality are

Table 6 Details of mix proportions and concrete properties for two extreme values of w/c (with OPC only, Set-2)

Mix designation	AO	BO
	w/c = 0.52	w/c = 0.33
Cement, kg/m ³	331	521
Fine aggregate, kg/m ³	887	715
Coarse aggregate, kg/m ³	1018	1018
Water, kg/m ³	172	172
SP, % by weight of binder	0.60	0.60
Slump, mm	35	45
Compressive strength (MPa) of concrete at		
7	44.75	70.93
28 and	53.73	80.00
56 days	54.80	82.10

Mix designations:

First letter AO or BO denotes w/b = 0.52 or 0.33 respectively.

Second letter O denotes OPC mix.

Table 7 Details of mix proportions and concrete properties for two extreme values of w/b (with CRM, Set-2)

Mix designation	AF20	AF40	AS50	AS70
	w/b = 0.52			
Binder cement, kg/m ³	265	198	165	99
Fly ash, kg/m ³	66	132	—	—
Slag, kg/m ³	—	—	165	232
Fine aggregate, kg/m ³	851	825	868	864
Coarse aggregate, kg/m ³	1018	1018	1018	1018
Water, kg/m ³	172	172	172	172
SP, % by weight of binder	0.70	0.75	0.65	0.65
Slump, mm	40	30	40	30
Compressive strength (MPa)				
7	37.74	27.34	25.82	23.90
28 and	49.26	40.23	47.19	43.02
56 days	58.35	49.00	57.59	55.16
Mix designation	BF20	BF40	BS50	BS70
	w/b = 0.33			
Binder cement, kg/m ³	417	313	261	156
Fly ash, kg/m ³	104	208	—	—
Slag, kg/m ³	—	—	261	365
Fine aggregate, kg/m ³	674	633	700	695
Coarse aggregate, kg/m ³	1018	1018	1018	1018
Water, kg/m ³	172	172	172	172
SP (Ceraplast 300), % by weight of binder	0.70	0.85	0.65	0.70
Slump, mm	30	35	30	30
Experimental compressive strength (MPa) of concrete at				
7 days	60.74	41.58	46.28	37.07
28 days	78.33	60.85	64.46	56.50
56 days	89.54	71.83	78.52	70.14

Mix designations:

First letter A or B denotes w/b = 0.52 or 0.33 respectively.

Second letter F or S denotes fly ash or slag respectively as CRM.

Numerical value 20, 40, 50 or 70 represents the % replacement of cement with CRM.

suggested. In the third step the dry weight of coarse aggregate content is evaluated by multiplying the dry-rodded unit weight (%) and dry-rodded unit weight. The formula is applicable for sand having fineness modulus between 3.2 and 2.5. In the fourth step the amount of water is calculated by assuming the entrapped air content between the voids of aggregates. The next steps are to select the water/ binder ratio based on the required strength at 28 and 56 days and cast trial mixes with full or partial replacement of cement using absolute volume method. Finally based on the results of trial mixes amount of fine and coarse aggregate, water, cement,

Table 8 Efficiency factor $k(t,p)$ for CRM (Set-2)

Age	Efficiency factor $k(t,p)$ for CRM			
	Fly ash		Slag	
	20%	40%	50%	70%
7 days	0.26	0.01	0.24	0.34
28 days	0.74	0.33	0.66	0.62
56 days	1.32	0.68	0.97	0.89

Table 9 Details of mix proportions and concrete properties for two extreme values of w/c (with OPC only, Set-3)

Mix designation	AO	BO
	$w/c = 0.50$	$w/c = 0.35$
Binder cement, kg/m^3	320	458
Fine aggregate, kg/m^3	779	662
Coarse aggregate, kg/m^3	1151	1151
Water, kg/m^3	160	160
SP (Ceraplast 300), % by weight of binder	0.8	0.8
Slump, mm	45	55
Experimental compressive strength (MPa) of concrete at		
7 days	32.26	53.26
28 days	43.50	64.03
56 days	48.90	68.95

Mix designations:

First letter A or B denotes $w/b = 0.50$ or 0.35 respectively.

Table 10 Details of mix proportions and concrete properties for two extreme values of w/b (with CRM, Set-3)

Mix designation	AS50	BS50
	$w/b = 0.50$	$w/b = 0.35$
Binder cement, kg/m^3	160	229
Slag, kg m^3	160	229
Fine aggregate, kg/m^3	779	662
Coarse aggregate, kg/m^3	1151	1151
Water, kg/m^3	160	160
SP (Ceraplast 300), % by weight of binder	0.9	0.9
Slump, mm	60	75
Experimental compressive strength (MPa) of concrete at		
7 days	20.69	40.87
28 days	33.79	64.68
56 days	38.99	68.35

Mix designations:

First letter A or B denotes $w/b = 0.50$ or 0.35 respectively.

S denote slag as CRM (50%).

cementitious material (fly ash, silica fume, GGBS), superplasticizer dosage is redesigned to achieve required physical and mechanical properties. The results of the HPC mixes obtained as per the ACI method are given for ready reference of the readers in **Tables 11–16**, and described here after (Peter *et al.*, 1999; Rajamane *et al.*, 2003; Gopalakrishnan *et al.*, 2005).

Recent Trends for Sustainable Production of HPC

There are two methods for sustainable production of HPC. One method is application of mineral admixtures as binder and other method is application of alternative aggregates. Calcium sulfoaluminate (CSA) cements is found to be one of the promising

Table 11 Fly ash based concretes (50 MPa at 28 days) with different cement replacement levels (CRL)

Ingredients (kg/m ³)	Mix Id.					
	CC	FAC1	FAC2	FAC3	FAC4	FAC5
Fly ash class		F	F	F	C	C
CRL(%)	–	30	50	70	30	50
Cement	340	290	230	160	290	230
Fly ash	0	120	230	370	120	230
Binder	340	410	460	530	410	460
Water	177	172	161	148	172	161
w/b	0.52	0.42	0.34	0.27	0.32	0.42
Sand	765	740	712	685	740	763
Coarse aggregate < 10 mm	805	803	773	740	803	773
Coarse aggregate 10–20 mm	345	344	331	317	344	331
Superplasticizer (%)	0.1	1.025	1.38	3.18	1.64	3.68
Retarder (%)	0	0	0	0	0.1	0.3
Slump (mm)	165	120	100	80	75	60
Wet density (kg/m ³)	2493	2470	2398	2324	2472	2402

Table 12 Details of HPC mixes (High Str.) with fly ash

Mixture designation	C1	C2	C3	C4	C5
Fly ash (%)	0	15	20	25	30
W/B	0.30				
W/C	0.30	0.35	0.37	0.40	0.43
Cement content (kg/m ³)	534	454	428	401	374
Fly ash content (kg/m ³)	0	80	106	135	160
Total aggregate content (kg/m ³)	1848	1848	1848	1848	1848
Water (l/m ³)	160	160	160	160	160
SP (l/m ³)	13.3	13.2	13.3	13.4	13.2
Retarder (l/m ³)	0.4	0.4	0.4	0.4	0.4
28 day Compr Str MPa	84	90	87	85	75
90 day Compr Str MPa	94	94	95	94	86

Table 13 Details of HPC mixes with GGBS

Mix	HPC-0S	HPC-20S	HPC-30S	HPC-50S	HPC-70S	CC1	CC2
%GGBS	0	20	30	50	70	–	–
W/B	0.30	0.30	0.30	0.30	0.30	0.5	0.7
W/C	0.30	0.375	0.43	0.60	1.0	0.5	0.7
Cement (kg/m ³)	534	428	374	267	160	315	300
GGBS (kg/m ³)	0	107	160	267	374	–	–
Total aggr. kg/m ³	1765	1765	1765	1765	1765	1840	1800
Water (l/m ³)	160	160	160	160	160	160	210
SP (l/m ³)	13.3	13.2	13.3	13.4	13.2	–	–
Retarder (l/m ³)	0.4	0.4	0.4	0.4	0.4	–	–
28d Compr. str MPa	84	82	78	74	91	43	26
90d Compr. str MPa	94	94	95	91	88	47	30

candidate as an alternative binder. CSA generally require smaller amount of limestone compared to production of cement and hence reduces carbon dioxide emission. Due to its higher porosity it also improves grinding. High volume slag is another methodology to propel the substitute for cement. It enhances workability, toughness, chemical and corrosion resistance while at the same time also decreases water absorption, pH value, and chloride ion penetration. Apart from mineral admixtures rice husk ash having pozzolanic properties produced HPC with higher compressive strength, at low water/binder ratio with marginal loss in elastic modulus and Poisson's ratio. However, it is also found that rice husk ash mixes have more cracking at lower stress levels and hence may cause brittle failure. In other studies, it found that ceramic waste power can be used up to 20%–30% replacement of

Table 14 Silica fume based HPC (Ingredients of control concrete mixtures)

Mixture designation	w/c	Cement content (C) (kg/m ³)	Sand (kg/m ³)	Coarse Aggregate (CA) (kg/m ³)		Water (w) (l/m ³)
				10 mm	20 mm	
C1	0.33	480	672	360	745	158
C2	0.40	480	672	360	745	192
C3	0.45	480	672	360	745	216
C4	0.50	480	672	360	745	240

Table 15 Ingredients of concrete mixtures with SF and FA

Mix Id.	w/b	C	SF	FA	Sand	CA	W
		(kg/m ³)					(l/m ³)
C1D1	0.33	441.6	38.4	–	672	1105	158
C2D1	0.40	441.6	38.4	–	672	1105	192
C4D1	0.50	441.6	38.4	–	672	1105	240
C1D2	0.33	422.4	57.6	–	672	1105	158
C2D2	0.40	422.4	57.6	–	672	1105	192
C4D2	0.50	422.4	57.6	–	672	1105	240
C2U1	0.40	441.6	38.4	–	672	1105	192
C2U2	0.40	441.6	38.4	–	672	1105	192
C2F1	0.40	360	–	120	672	1105	192
C2F2	0.40	360	–	240	672	1105	192
C2T1	0.40	321.6	38.4	120	672	1105	192
C2T2	0.40	201.6	38.4	240	672	1105	192
C2T3	0.40	302.4	57.6	120	672	1105	192
C2T4	0.40	180.4	57.6	240	672	1105	192

Table 16 Strength and transport properties of concrete mixes with SF & FA

Mix Id.	w/b	C (kg/m ³)	SF	FA	Sand (kg/m ³)	CA (kg/m ³)	W (l/m ³)
C1D1	0.33	441.6	38.4	–	672	1105	158
C2D1	0.40	441.6	38.4	–	672	1105	192
C4D1	0.50	441.6	–38.4	–	672	1105	240
C1D2	0.33	422.4	57.6	–	672	1105	158
C2D2	0.40	422.4	57.6	–	672	1105	192
C4D2	0.50	422.4	57.6	–	672	1105	240
C2U1	0.40	441.6	38.4	–	672	1105	192
C2U2	0.40	441.6	38.4	–	672	1105	192
C2F1	0.40	360	–	120	672	1105	192
C2F2	0.40	360	–	240	672	1105	192
C2T1	0.40	321.6	38.4	120	672	1105	192
C2T2	0.40	201.6	38.4	240	672	1105	192
C2T3	0.40	302.4	57.6	120	672	1105	192
C2T4	0.40	180.4	57.6	240	672	1105	192

cement. The obtained HPC have lower early age strength but similar strength at the age of 28 days when compared with conventional HPC with ceramic waste. However, from microstructural studies it is found that the ceramic waste does not participate in the hydration reaction and acts as filler (Prem *et al.*, 2018a).

As aggregate replacement in HPC artificial aggregates such as steel slag or crystallized slag is found to increase the strength and durability. However, it should be noted that the mix should be judiciously designed to account for higher specific gravity of this aggregates compared to limestone aggregates. Steel slag aggregates increases strength due to their high strength and better adhesion between cement and paste. The durability parameters are however found to lower in case of water porosity and gas permeability. Few studies also highlight incorporation of polyethylene terephthalate or PET waste in HPC as sand replacement. PET aggregate changes failure mode from brittle to ductile with a reduction in compressive strength. The tensile, flexure strength are found comparable to HPC without PET while durability performance against freeze and thaw resistance is enhanced significantly. In

other studies, fine and coarse recycled concrete aggregate are utilized as alternate aggregate for HPC. It is observed that heat treated recycle aggregates significantly improves physical properties of HPC. The ductility of HPC is also improved by addition of steels fibers, basalt fibers, polypropylene fibers and hybrid fibers

The Way Forward

With more demand of high performance concrete, stringent durability requirements and necessity to obtain low maintenance concrete, currently research have progressed towards development of Ultra high performance concrete (UHPC). UHPC is one of the emerging concrete materials having compressive strength greater than 150 MPa, very high durability and ductility. The concept of HPC have now changed towards UHPC. Recently several industries have commercialized UHPC and its application can be found in form of bridge decks, buildings, precast applications and several niche applications ([Prem *et al.*, 2015, 2018b](#)).

Acknowledgements

Authors acknowledge the retired scientists Gopalakrishnan, S., Lakshmanan, N., Rajamane, N.P., Krishnamoorthy, T.S., Neelamegam, M., Chellappan, A., Annie Peter, J., and Dattatreya, J.K. of CSIR-SERC for their seminal work in the area of HPC.

See also: A Review on Utilization of Electronic Waste Plastics for Use Within Asphaltic Concrete Materials: Development, Opportunities and Challenges for Successful Implementation. Life-Cycle Impact of Concrete With Recycled Materials. Recycled Ceramics in Concrete. Recycled Concrete

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Sustainable Supply Chain Management in Developed vs. Emerging Economies: Evidence From the UK and China's Manufacturing Industry

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Introduction

Over the past few decades, rapid industrial modernization has led to increasing negative environmental impacts, including various types of pollution, emissions, waste and chemical spills (Carter and Easton, 2011). In response to the growing global environmental concerns, sustainable supply chain management (SSCM) has emerged as a concept that combines elements of corporate environmental management and supply chain management and aims to promote sustainability-related issues along the intra- and inter-firm management of the upstream and downstream supply chain (Tseng *et al.*, 2015).

Today, organizations are consistently attempting to integrate environmental practices into their strategic thinking and minimize the environmental impact of their operations, as a consequence of pressure from regulatory bodies, heightened customer expectations and competitors (Zhu *et al.*, 2013). With increasing concern about environmental sustainability issues on a global scale, firms' reputation along with their stakeholders' value will be at risk if they are unable to demonstrate a rational position on sustainability (Sarkis *et al.*, 2010). The current sustainability agenda is pushing manufacturing industries to extend their focus beyond traditional economic goals to more broadly address and embrace the environmental and social aspects of the supply chain (Seuring and Müller, 2008a; Gimenez *et al.*, 2012). In light of this, many organizations have begun to adopt sustainability-related supply chain initiatives to manage the environmental and social responsibility of their business operations beyond their immediate organizational boundaries (Carter and Easton, 2011). As a result, SSCM has become a pivotal research theme in the management literature, which has explored the incorporation and management of sustainability-related issues encompassing the environmental, social and economic domains throughout the supply chain (Varsei *et al.*, 2014).

This has generated significant attention within industry, academia, and policy-makers and has become a widely topical particularly with respect to the manufacturing context (Lai *et al.*, 2013). The manufacturing sector is deemed to be the main polluter and resource consumer, as it has been traditionally associated with higher-than-average resource consumption, waste generation and lower implementation of environmental management practices (Zhu *et al.*, 2013). With respect to developed economies, the on-going environmental sustainability agenda, predominantly driven by institutional pressures (Govindan *et al.*, 2014), more pressingly urges manufacturing firms operating within the developed market to take environmental concerns into consideration and accept the necessity of environmental management (Jayarama and Avittathur, 2015). This has led a growing number of manufacturing firms within the developed market to undertake proactive environmental initiatives across their supply chains (Hollos *et al.*, 2012). However, the increasing emphasis on sustainability is not just a phenomenon of the developed world. In emerging economies, manufacturing firms have also started to pay attention to various environmental programmes within their supply chain, as they have faced tighter environmental restrictions from their governments and intense scrutiny from an increasingly educated society and also more environmentally friendly emerging competitors (Esfahbodi *et al.*, 2016).

In view of this, manufacturers in emerging markets have started to adopt various proactive and boundary-spanning SSCM practices – sustainable procurement, sustainable production, eco-design, sustainable distribution, and so forth – in order to minimize the impact of their operations on the natural environment, alleviating scarcity of resources and environmental degradation in these countries (Tseng *et al.*, 2015; Jia *et al.*, 2018). This not only enables manufacturing firms in emerging markets to meet their domestic expectations, but also permits them to compete in the global market, because they conform to international legislation (Esfahbodi *et al.*, 2016).

Economic performance has traditionally been, and continues to be, the key priority for almost all organizations, irrespective of their market orientation, in developed and emerging economies (Zhu and Sarkis, 2007; Green *et al.*, 2012a). Arguably, this is largely associated with the fact that the recognition of financial benefits gained from environmental initiatives in firms' bottom line is crucial for the adoption of such environmental initiatives (Gimenez *et al.*, 2012). It is therefore critical for firms to consider the impact of SSCM adoption on both their environmental performance and their business performance. However, the adoption of SSCM practices is traditionally associated with the hope of mitigating environmental damage while achieving financial performance gains (Rao and Holt, 2005).

While prior research has explored the relationships between the adoption of SSCM practices and firm performance, reporting positive impacts on both environmental and economic performance (Zhu and Sarkis, 2007; Vachon and Klassen, 2008; Lee *et al.*, 2012), recent emergent studies have started to throw doubt onto this issue, offering mixed views (Green *et al.*, 2012a; Esfahbodi *et al.*, 2017). Recent studies conducted in developed economies (Hollos *et al.*, 2012; Green *et al.*, 2012b) have found that the adoption of SSCM does not necessarily lead to better financial performance, arguing that the implementation of SSCM practices is not always both environmentally beneficial and commercially viable. Thus, there is a degree of ambiguity within the existing literature on the developed economies concerning the merits of undertaking SSCM practices as to whether they can deliver both environmental improvements and economic benefits (Hollos *et al.*, 2012; Seuring and Müller, 2008a). Similarly, there is concern within the current literature on the emerging economies as to whether the adoption of SSCM practices will ultimately translate into improved financial performance

(Rao and Holt, 2005; Zhu *et al.*, 2013). Therefore, this study is deemed an important complement to the prior research on SSCM implementation and its commensurate performance gains conducted in developed economies and emerging markets as well.

Although research on sustainable supply chains in developed economies has made many valuable contributions (Green *et al.*, 2012a; Hollos *et al.*, 2012), there is a paucity of empirical evidence and theoretical reflection on characteristics of SSCM in developing and emerging economies (Govindan *et al.*, 2014; Jayarama and Avittathur, 2015). Concerning the impact of SSCM adoption on firm performance, much research has been conducted in developed economies. The SSCM literature concerning emerging economies is in the early stages of development, with related articles dealing primarily with theoretical discussions and anecdotal evidence (Hsu *et al.*, 2013), calling for further empirical investigation. Accordingly, the goal of this study is to enhance the understanding of how sustainability-related issues of supply chain can impact firm performance in both emerging and developed economies. It therefore endeavors to bridge the existing gap surrounding the lack of empirical evidence concerning SSCM adoption in the context of emerging economies together with the lack of consensus on this topic.

Furthermore, despite recent developments in the literature, more empirical research is needed to establish the impact of SSCM practices on firms' performance outcomes, particularly from a holistic and integrated perspective (Green *et al.*, 2012b). It is necessary to view the phenomenon from the whole supply chain perspective, covering both upstream and downstream aspects, which allows a thorough and rigorous picture of SSCM implementation to be captured (Carter and Easton, 2011). Thus, this study also aims to extend the contemporary literature with a better and more comprehensive understating of SSCM and its main components and their impacts on firms' environmental and economic performance.

In order to bridge the aforementioned gaps in the literature and advance the contemporary understanding of sustainable supply chains, this research seeks to investigate integrated SSCM Practices → Performance Outcomes relationships. Adopting the UK as a developed economy and China as an emerging economy enables this study to draw comparative conclusions on these two different markets. The value of a cross-economy empirical comparison of SSCM adoption within two different markets is that it will help to distinguish potential similarities and contradicting directions within developed and emerging economies. This study therefore provides a general comparative analysis of SSCM adoption along with its performance gains, with a focus on similarities and differences between these two economies, in order to consolidate our understanding.

The remainder of this paper is organized as follows: Section "Literature Review and Hypothesis Development" presents a literature review and develops the hypothesis, Section "Research Method" presents the research method along with a summary of the samples and data, Section "Results" presents the results, Section "Discussion" outlines theoretical implications of the study and Section "Conclusions" concludes the paper.

Literature Review and Hypothesis Development

Sustainable Supply Chain Management (SSCM)

SSCM has become an increasingly important topic in the current literature, owing to various factors supporting its acceptance and favouring its adoption such as tighter governmental regulations, social pressures, competitive pressures, heightened customer expectations, the scarcity of natural resources and corporate image (Govindan *et al.*, 2014). Environmental sustainability and pollution are global concerns that affect manufacturing industries in both developed and developing countries (Esfahbodi *et al.*, 2016). According to Beamon (1999), "waste generation and natural resource use, primarily attributed to manufacturing, contribute to environmental degradation". These increasing global issues indicate an imperative need for manufacturing firms to realign their strategies and operations to address sustainability-related issues along the upstream and downstream supply chain.

The SSCM approach aims to 'close the loop' by including the implications of reuse, remanufacturing, and recycling of products and materials in a common forward supply chain (Zhu *et al.*, 2008c) with the purpose of minimizing negative environmental impacts and wasted resources, from the acquisition of raw materials up to the final use and disposal of products (Hsu *et al.*, 2013). This study defines SSCM as the management of raw materials, components and processes from manufacturers to suppliers to final customers along with the product being taken back through the lifecycle stages with the purpose of having the lowest possible negative environmental impact (Hu and Hsu, 2010; Esfahbodi *et al.*, 2016).

According to contemporary literature, pressure from a variety of stakeholders and institutional pressures are the main driving forces that have pushed manufacturing firms to pursue and undertake SSCM practices in the developed economies, and recently in emerging economies as well (Jayarama and Avittathur, 2015). Consequently, manufacturing firms have begun to implement a set of SSCM practices to minimize the negative environmental impacts associated with the entire lifecycle of their products or services, starting from design through the acquisition of raw materials to consumption and product disposal (Lai *et al.*, 2013). Today, the SSCM approach has evolved to include boundary-spanning activities such as sustainable procurement (Carter and Carter, 1998), eco-design (Zhu *et al.*, 2008a), sustainable distribution (Vachon and Klassen, 2006), and investment recovery (Zhu and Sarkis, 2007). Given the multi-dimensional expansion of the SSCM literature, this study focuses on four major SSCM practices: sustainable procurement, eco-design, sustainable distribution and investment recovery. These four areas represent the full implementation of SSCM practices, as they encompass the main upstream and downstream activities and sustainability-related operations within the supply chain (Zhu *et al.*, 2013).

SSCM Practices and Performance Implications

Previous research has explored the links between the implementation of SSCM practices and performance outcomes, including operational, environmental, and economic performance (Green *et al.*, 2012a; Zhu *et al.*, 2013; Esfahbodi *et al.*, 2017). Existing literature has offered significant insights into the potential for sustainable supply chain initiatives to achieve strong environmental improvements (Rao and Holt, 2005; Zhu and Sarkis, 2007; Green *et al.*, 2012a), supporting positive impacts on environmental performance. However, opinions on whether SSCM practices cause or relate to positive or negative economic performance are still mixed (Tseng *et al.*, 2015). While Rao and Holt (2005) indicated that greening the supply chain delivers economic benefits leading to improved financial performance, Green *et al.* (2012a) suggested that benefits from SSCM practices are not being reaped in terms of short-term profitability and financial performance. Therefore, there is a degree of inconclusiveness on the relationships between SSCM practices and performance outcomes within the existing knowledge in this area that necessitates further empirical investigation. This study primarily focuses on the environmental and economic dimensions of SSCM performance, mainly due to the dearth of recorded relevant and validated social performance measures within the SSCM context (Varsei *et al.*, 2014).

This study seeks to examine whether UK and Chinese manufacturing firms perceive improvements in both their economic and environmental performance due to the adoption of SSCM practices. In essence, Chinese manufacturer are at a relatively early stage of adopting sustainability-related supply chain initiatives, which may leave more room for further development and improvement (Lai *et al.*, 2013). In the UK, however, manufacturing firms have been practising SSCM initiatives for a longer period, approaching SSCM piecemeal and therefore better performance implications have more precedent (Esfahbodi *et al.*, 2017). For example, the European Union has enacted various Environmental Directives such as Restriction of Hazardous Substances (RoHS), Energy-using Products (EuP), Waste Electrical and Electronic Equipment (WEEE), End of Life Vehicle (ELV), and so forth, which have led manufacturers to minimize negative environmental impact (Grote *et al.*, 2007). Such international regulatory policies not only push UK manufacturers to undertake environmental initiatives across their supply chains, but also force manufacturers in developing countries which intend to export and sell to Europe to embark upon the adoption of SSCM practices (Sarkis *et al.*, 2010; Esfahbodi *et al.*, 2017).

Among the various SSCM initiatives that have been implemented by UK manufacturing firms and also adopted by Chinese manufactures, specific importance has been placed on four fundamental practices: sustainable procurement, eco-design, sustainable distribution and reverse logistics (Esfahbodi *et al.*, 2017). In the context of UK and Chinese manufacturers, each initiative represents the extent to which each firm in these two countries engages in sustainable supply chain practices. While the four major SSCM initiatives are not unique to the UK and China, and are prevalent in other emerging and developed economies including Germany, France, Australia, India and Brazil, they represent a strong commitment that these countries' governments had made through their strategic environmental plans to focus on such initiatives to foster SSCM approaches (Jia *et al.*, 2018).

SSCM Practices-Performance Model

This study developed a structural model linking the main SSCM practices to firm performance. The relationships between SSCM practices and environmental and economic performance are posited in order to assess the impact of SSCM implementation on the firm's performance. The structural model is a path analytical framework with six latent variables (shown in Fig. 1): sustainable procurement, sustainable distribution, eco-design, investment recovery, environmental performance and economic performance. The four SSCM practices represent the main sustainability-related operations within the upstream and downstream supply chain, while environmental and economic performance cover performance outcomes (Zhu *et al.*, 2008a; Esfahbodi *et al.*, 2016). Each of the hypotheses depicted in Fig. 1 is theorised as being direct and positive. Definitions of the variables incorporated in the model are presented in Table 1. Generally, SSCM practices are the focal constructs in the structural model, with environmental and economic performance as consequences.

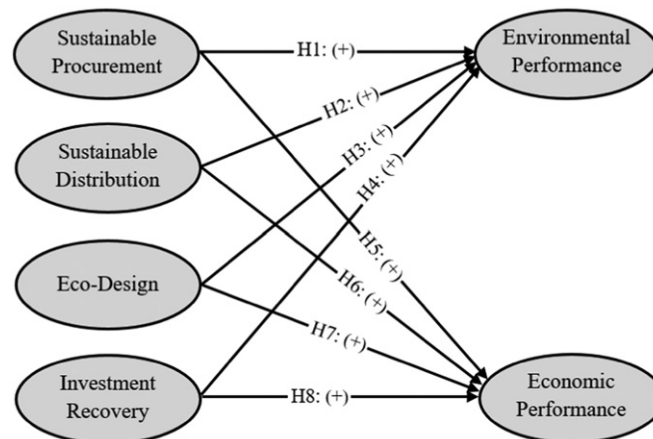


Fig. 1 SSCM practices-performance model.

Table 1 Construct definitions

Construct	Definition
Sustainable procurement (SP)	Sustainable procurement focuses on cooperating with suppliers for the purpose of developing products that are environmentally sustainable (Zhu <i>et al.</i> , 2008a).
Sustainable distribution (SDIST)	Sustainable distribution refers to the environmentally conscious transportation of products or services from suppliers to manufacturers to final customers with the purpose of having the least possible negative environmental impact (Esty and Winston, 2009; Green <i>et al.</i> , 2012b).
Eco-design (ED)	Eco-design requires that manufacturers design products that minimize the consumption of materials and energy, facilitate the reuse, recycling and recovery of component materials and parts, and avoid or reduce the use of hazardous products within the manufacturing process (Grote <i>et al.</i> , 2007; Zhu <i>et al.</i> , 2008a).
Investment recovery (IR)	Investment recovery refers to the process of recovering and recapturing the value of end-of-life products and unproductive assets through effective reuse and surplus sales. It requires the sale of excess inventories, scrap and used materials and excess equipment (Zhu <i>et al.</i> , 2008a).
Environmental performance (ENV)	Environmental performance relates to a manufacturing plant's ability to reduce energy usage, materials consumption, air emissions, effluent waste and solid waste and to decrease consumption of hazardous substances and toxic materials (Zhu <i>et al.</i> , 2008a).
Economic performance (ECN)	Economic performance relates to the manufacturing plant's ability to reduce costs associated with energy consumption, purchased materials, waste treatment, waste disposal, waste discharge, and fines or penalties for environmental accidents (Zhu <i>et al.</i> , 2008a).

Sustainable supply chain management practices and environmental performance

The majority of recent articles have argued that SSCM practices can improve environmental performance in most cases (Rao and Holt, 2005; Vachon and Klassen, 2006; Zhu and Sarkis, 2007). In particular, recent studies have tended to agree on a positive relationship between sustainability-related supply chain initiatives and environmental performance (Hollos *et al.*, 2012; Green *et al.*, 2012b). The main SSCM practices of sustainable procurement, sustainable distribution, eco-design, and investment recovery are environmentally friendly initiatives by nature, which are designed to minimize a product's environmental impact without creating a negative trade-off with other performance dimensions, such as costs and functionality (Green *et al.*, 2012a). This is also in line with Porter and Van der Linde's (1995) argument for a balance between a society's desire for environmental protection and the economic burden on industry. The implementation of each individual SSCM practice is deemed to have direct environmental results, as measured by reductions in air emissions, effluent waste, solid waste and the consumption of toxic materials (Zhu and Sarkis, 2007; Seuring and Müller, 2008b). Therefore, the implementation of sustainable procurement, sustainable design, sustainable distribution, and investment recovery is expected to result in improved environmental performance due to their capability to reduce material consumption, waste, emissions, energy usage, and excessive inventory (Zhu and Sarkis, 2007; Seuring and Müller, 2008a).

According to Carter and Carter (1998) and Zhu *et al.* (2008a), sustainable procurement requires working closely with suppliers to develop products or services that are environmentally friendly. Suppliers' involvement is crucial in improving firms' environmental performance, as it is the suppliers who are capable of ensuring the purchased materials are environmentally friendly and have been made using environmentally conscious processes (Hsu *et al.*, 2013). In supporting this, Vachon and Klassen (2008) argued that, in the manufacturing context, strong relationships and collaboration with suppliers aid the adoption and development of innovative environmental technologies. Hollos *et al.* (2012) also asserted that cooperating with suppliers, partnership agreements and joint research and development lead to improvements in environmental performance. Considering the main aim of sustainable procurement, cooperating with suppliers that possess green resources, capabilities, and expertise required for the acquisition of environmentally friendly inputs in order to develop environmentally friendly products or services (Esfahbodi *et al.*, 2017), a positive relationship between sustainable procurement and environmental performance is proposed.

Sustainable distribution deals with environmental issues related to sustainable transportation, packaging, warehousing, storage maintenance, inventory control, and facility location allocation decisions that aim to have the least possible negative environmental impact (Sarkis, 2006). Sustainable distribution is developed specifically to improve environmental performance as it focuses on the elimination of emissions associated with the transportation of products throughout the supply chain (Green *et al.*, 2012b). Green packaging characteristics such as materials, shape, and size, play an important role in sustainable distribution, because of their impact on transportation, e.g., carbon footprint implications (Zhu *et al.*, 2008c). Firms can benefit from better packaging along with rearranged loading patterns as this can increase space utilization in the warehouse and reduce materials usage and the amount of handling required, leading to improved environmental performance (Esty and Winston, 2009). Lakshmideera and Palanisamy (2013) also asserted the environmental benefits of the sustainable distribution practice, particularly with respect to the design of the logistics network, highlighting options such as central warehouses or distributed networks, direct shipping or hub-and-spoke, third-party services or private fleet, and intermodal or single mode.

Eco-design, the most significant sub-attribute of sustainable manufacturing (Green *et al.*, 2012a), aims to design and develop a product or a service with environmental considerations, minimizing negative environmental impact (Grote *et al.*, 2007). Eco-design practice facilitates the reduction of the negative environmental impacts of products with the design characteristics of lower material usage and energy consumption in the product development (Seuring and Müller, 2008a). According to Green *et al.* (2012a), eco-design can potentially improve environmental performance, as the impetus of the designers will be towards reducing

the environmental impact of the design. Eco-design practice largely focuses on the elimination of wastes associated with environmental sustainability across the supply chain (Zhu *et al.*, 2008a). Arguably, such waste minimization should deliver environmental improvements leading to better environmental performance.

Investment recovery, the last construct of the SSCM practices, generally involves the task of recapturing the value of unused products or unproductive assets through effective reuse or surplus sales and divestment (Zhu *et al.*, 2008a). The practice of investment recovery, a sub-attribute of reverse logistics (Lai *et al.*, 2013), has the potential to deliver environmental benefits with its focus on recovering and recapturing the value of unused or end-of-life assets (Green *et al.*, 2012a). In a manufacturing setting, investment recovery draws in reuse and surplus sales of used materials, which should eventually lead to a decrease in the emissions and waste generated by by-products (Zhu *et al.*, 2008a). Thus, with this set of arguments, this study postulates the following hypotheses.

- H1. Sustainable procurement directly and positively impacts environmental performance.
- H2. Sustainable distribution directly and positively impacts environmental performance.
- H3. Eco-design directly and positively impacts environmental performance.
- H4. Investment recovery directly and positively impacts environmental performance.

Sustainable supply chain management practices and economic performance

The main focus of SSCM practices is on the elimination of wastes associated with material acquisitions, product design, delivery and disposal (Green *et al.*, 2012a; Esfahbodi *et al.*, 2017). Arguably, such waste minimization should yield cost reductions, leading to better economic performance. Prior studies have shown that environmental management programmes such as sustainability-related supply chain initiatives have a positive relationship with firm financial performance (Rao and Holt, 2005). According to Tan *et al.* (2014), SSCM practices can enhance corporate reputation, brand image, and customer satisfaction, which can in turn bring improved economic performance. The majority of existing studies conducted in the sustainable supply chain context have argued that SSCM practices are positively related to economic performance, given their cost-saving nature (Rao and Holt, 2005; Sarkis, 2006; Zhu *et al.*, 2012). Furthermore, Sarkis *et al.* (2010) argued that success in addressing environmental issues may provide new opportunities for competition and new ways to add value to core business programmes. Therefore, the implementation of SSCM practices is expected to result in better economic performance due to their potential for cost reduction.

Undertaking sustainable procurement facilitates the acquisition of environmentally friendly inputs, which in turn eliminates associated wastes and emissions (Carter, 2005). Arguably, cost reductions associated with such waste minimization should lead to improved economic performance. Moreover, firms can benefit from a range of tangible and intangible green purchasing cost savings features, for example, in minimizing risk occurrences that can potentially damage its product image (Shi *et al.*, 2012). It has been further argued by Shi *et al.* (2012) that green purchasing can help manufacturing firms to achieve long-term savings by protecting them from potential damage to their brand value. Rao and Holt (2005) also maintained this and demonstrated a positive linkage between adopting green purchasing and economic performance through empirical investigation. The same can be argued about sustainable distribution which aids the minimization of energy and emissions associated with transportation throughout the supply chain, which in turn can result in effective cost savings. Hollos *et al.* (2012) found a significant direct linkage between sustainable distribution and financial performance. Their results suggested that the benefits of green packaging and green logistics characteristics can be reaped in long-term profitability.

Eco-design can positively influence economic performance due to its significant cost-saving features that stem from the capability of reducing material usage and energy consumption at the design stage. Eco-design requires manufacturers to minimize the consumption of materials and energy required for the whole cycle of product development, which can potentially lead to reduced costs associated with material and energy consumption, delivering economic benefits (Esty and Winston, 2009). Moreover, the waste minimization focus of eco-design practice is expected to lead to reduced costs associated with waste treatment or waste discharge, affecting economic performance (Green *et al.*, 2012a). Rao and Holt (2005) supported this proposition and demonstrated a significant direct linkage between eco-design and financial performance, reporting that the SSCM practice of eco-design has the capacity to enhance economic performance and lead to competitiveness. Investment recovery can also have an impact on a firm's economic performance, as it involves surplus sales of scrap and used materials, and capital excess equipment (Green *et al.*, 2012b). Zhu and Sarkis (2007) found a linkage between investment recovery and financial performance and reported that investment recovery has the capacity to affect economic performance through effective surplus sales and divestment. Therefore, this study hypothesizes the following:

- H5. Sustainable procurement directly and positively impacts economic performance.
- H6. Sustainable distribution directly and positively impacts economic performance.
- H7. Eco-design directly and positively impacts economic performance.
- H8. Investment recovery directly and positively impacts economic performance.

Research Method

Survey Development

Zhu *et al.* (2008a) developed and empirically verified a measurement model for SSCM practices and their commensurate performance constructs. They found four underlying variables which reflect the key dimensions of SSCM practices along with performance measures of environmental and economic performance. The present study directly adopted these measurement items

of Zhu *et al.* (2008a) for the Sustainable Procurement and Investment Recovery constructs. For the Sustainable Distribution and Eco-Design measures of Zhu *et al.* (2008a), this study utilized additional items found in other studies (Esty and Winston, 2009; Green *et al.*, 2012b). These measurement items were operationalised in a survey questionnaire to assess the environmental and economic performance consequences of the implementation of SSCM. Respondents were asked to evaluate the implementation of individual SSCM practices, using a five-point Likert scale ranging from 1 = no implementation to 5 = implemented fully. In addition, a five-point scale for evaluating the significance level of performance improvement due to the adoption of SSCM practices was provided, ranging from 1 = not at all to 5 = significant.

Samples

The constructs incorporated into the proposed model were defined and described with a focus on the manufacturing context. Considering this manufacturing focus, data was collected from a sample of manufacturing managers working for UK and Chinese manufacturing firms. Anticipating the difficulties associated with recruiting knowledgeable and experienced respondents, the convenience sampling technique was employed to target managers with knowledge of their firm's SSCM practices and environmental and economic performance (Malhotra and Grover, 1998). The questionnaire was administered using convenience sampling to a sub-set of the population of manufacturing managers, e.g., plant managers, industrial waste managers, logistics managers, purchasing managers, engineering managers, supply chain managers, operations managers, and sales managers.

Data Collection

The surveys were conducted via a Web-based survey service (Bristol Online Surveys) from March 2014 to April 2014 and data was collected from 218 managers of various manufacturing firms, 146 in the UK and 72 in China. The data collection process was managed by Bristol Online Surveys and was structured so as to ensure unique responses from validated employees of UK and Chinese manufacturers. A total of 600 managers were contacted via email for the UK survey, 36 were screened out as non-managers and 194 managers completed the survey. Of the 194 respondents, 48 selected the 'other manager' category. Because of concerns related to a lack of sufficient understanding of SSCM practices and environmental and economic performance, data from these 48 was not included in the dataset analyzed. Finally, data from 146 manufacturing managers who have the necessary knowledge to fully complete the survey was included in the UK dataset that is subsequently analyzed. With respect to the China survey, of the 600 individuals sent email requests to participate, 42 were screened out as non-managers and 110 managers completed the survey. Of the 110 respondents, 38 selected the 'other manager' category, which were excluded in the Chinese dataset due to concerns

Table 2 Sample's demographics summary

<i>Title</i>	<i>UK number</i>	<i>China number</i>
Plant Manager	16	8
Logistics Manager	19	10
Operations Manager	28	14
Purchasing Manager	13	9
Supply Chain Manager	36	16
Sales Manager	11	7
Engineering Manager	17	5
Industrial Waste Manager	6	3
<i>Total</i>	<i>146</i>	<i>72</i>
<i>Industry classification (UK SIC – Standard Industrial Classification)</i>		
Manufacture of Food Products	14	6
Manufacture of Beverages	6	9
Manufacture of Textile	1	5
Manufacture of Rubber and Plastics Products	2	10
Manufacture of Wood and of Products of Wood and Cork	5	4
Manufacture of Paper and Paper Products	8	7
Manufacture of Chemicals and Chemical Products	17	5
Manufacture of Basic Metals	12	3
Manufacture of Electrical Equipment	23	7
Manufacture of Machinery and Equipment	14	4
Manufacture of Motor Vehicles, Trailers and Semi-Trailers	42	7
Manufacture of Basic Pharmaceutical Products and Pharmaceutical Preparations	2	6
<i>Total</i>	<i>146</i>	<i>72</i>
Mean years in current position	6.85	8.26
Mean number of employees	594.62	638.62

related to a lack of knowledge of SSCM practices and performance. Subsequently, data from 72 manufacturing managers who have the necessary knowledge to complete the survey was included in the Chinese dataset. [Table 2](#) displays the sample's demographics.

All of the respondents hold management positions in manufacturing firms. The majority of respondents are operations and supply chain managers, 43% for the UK sample and 40% for the Chinese sample. The respondents selected 12 different industry classifications representing a diverse array of manufacturing firms. They work for firms with an average of 594.62 employees for the UK sample and 638.62 employees for the Chinese sample. According to [Gimenez et al. \(2012\)](#), firms are classified as large if they have 250 employees or more and small/medium if they have fewer than 250 employees. This research sought to target large manufacturing firms because they are likely to have undertaken some sustainable supply chain initiatives.

Results

Common Method and Non-Response Bias

To ensure avoidance of the common method bias (CMB), procedural control was conducted together with Harman's one-factor statistical test. To avoid 'common rater' effects as one of the key causes of common method bias ([Podsakoff et al., 2003](#)) due to respondents' perceived need to provide consistent or socially desirable answers, options were provided such that respondents could choose to remain anonymous on both the respondent and the company. A confidentiality statement was also included at the beginning of the survey stating that no information of respondents and their companies would be revealed in the study reports. Harman's one-factor test was also used to examine the possibility of the CMB problem. In this test, a principal component factor analysis was performed using the Varimax rotation method with all variables in the proposed model. The results of the factor analysis revealed that three factors explain 70.68% of the variance of the variables with 22.15% explained by the first extracted factor. Based on the recommendation by [Podsakoff and Organ \(1986\)](#), substantial common method bias is signaled by the emergence of either a single factor or one 'general' factor that explains a majority of the total variance. Hence, there was neither evidence that a single factor emerged nor any factor explaining most of the variance. Thus, the common methods bias is not a serious problem with the survey data.

To test for non-response bias, the responses of the early and late waves of the returned surveys were compared, based on the assumption that the opinions of late respondents are representative of the opinions of theoretical non-respondents ([Rogelberg and Stanton, 2007](#)). Respondents were categorised as responding to either the initial or follow-up requests that were sent approximately two weeks later. A comparison of the means of the demographic variables and the summary variables for the two groups of the two samples was conducted using one-way ANOVA. The comparisons resulted in statistically non-significant differences at the 0.01 level. Since non-respondents have been found to descriptively resemble late respondents ([Lambert and Harrington, 1990](#)), this finding of general equality between early and late respondents indicates that the non-response bias has not impacted the data set, suggesting that the non-response bias was not a problem ([Green et al., 2012a](#)).

Scale Assessment

The measurement scales were assessed for reliability and validity. Since all scales were taken directly from prior research ([Zhu et al., 2008a](#); [Esty and Winston, 2009](#); [Green et al., 2012a](#)), content validity was assumed. Following [Gerbing and Anderson \(1988\)](#), each pair of scales under consideration was tested for discriminant validity using a chi-square difference test. Chi-square difference tests for pairings of each scale with other scales returned significant differences at the 0.01 level, indicating sufficient discriminant validity for all scales ([Garver and Mentzer, 1999](#)).

The construct validity of the theoretical constructs was also assessed using exploratory factor analysis (EFA) to "determine whether the majority of the variance can be accounted for by one general factor" ([Podsakoff et al., 2003](#)). As a result of the exploratory factor analysis, the 'Sustainable Procurement' (SP4), 'Sustainable Distribution' (SDIST5), and 'Environmental Performance' (ENV6 and ENV7) measurement items were excluded. Consequently, all of the constructs yield an average factor loading of 0.84, exceeding the recommended 0.70 level, providing evidence of self-reporting scales ([Kline, 1998](#)). This confirmed that all of the remaining measurement items in each construct represent one factor, indicating sufficient construct validity ([Hair et al., 2010](#)).

Furthermore, all standardised coefficients for scale items presented in [Table 3](#) exceed the recommended 0.70 minimum and are significant at the 0.01 level, indicating sufficient convergent validity ([Garver and Mentzer, 1999](#)). All of the reliability coefficients (Cronbach alpha values) for all of the measurement scales exceed the recommended 0.70 level, indicating sufficient reliability ([Garver and Mentzer, 1999](#)). The standardised coefficients for measuring items and their associated t-values along with the Cronbach alpha values for all of the scales are displayed in [Table 3](#).

Measurement Model Assessment

The measurement items were also assessed within the context of the full measurement model using confirmatory factor analysis (CFA), as recommended by [Koufteros \(1999\)](#). For the UK sample, the measurement model fits the data well, with a relative chi-square value of 1.368, a root mean square error of approximation (RMSEA) value of 0.052, a comparative fit index (CFI) value of 0.981, an incremental fit index (IFI) value of 0.988, and a non-normed fit index (NNFI) value of 0.964. Likewise, for the China

Table 3 Measurement model results

Constructs	Alpha (α) (UK)	Alpha (α) (China)	Standardised coefficient (β) (UK)	Standardised coefficient (β) (China)	t-values (UK)	t-values (China)
Sustainable procurement	0.816	0.668				
SP1			0.83	0.58	12.46	7.18
SP2			0.85	0.49	13.24	5.85
SP3			0.80	0.57	11.69	7.58
SP5			0.88	0.68	14.11	9.33
SP6			0.89	0.57	14.25	7.47
Sustainable distribution	0.738	0.796				
SDIST1			0.82	0.66	12.41	9.36
SDIST2			0.86	0.62	13.66	9.08
SDIST3			0.86	0.64	13.58	9.24
SDIST4			0.78	0.66	11.28	9.08
SDIST6			0.79	0.59	11.39	7.28
Eco-design	0.853	0.759				
ED1			0.90	0.58	14.69	6.94
ED2			0.89	0.75	14.22	10.38
ED3			0.86	0.58	13.77	7.62
ED4			0.92	0.73	15.52	9.98
ED5			0.88	0.54	14.13	6.16
ED6			0.88	0.58	14.05	6.46
Investment recovery	0.705	0.688				
IR1			0.77	0.77	10.84	12.36
IR2			0.78	0.64	11.08	9.26
IR3			0.78	0.52	11.20	5.63
Environmental performance	0.795	0.766				
ENV1			0.84	0.69	12.71	8.35
ENV2			0.85	0.55	13.15	6.08
ENV3			0.82	0.74	12.32	10.96
ENV4			0.81	0.63	12.08	8.02
ENV5			0.90	0.51	14.48	5.56
Economic performance	0.788	0.715				
ECN1			0.87	0.50	13.93	5.24
ECN2			0.82	0.58	12.33	6.44
ECN3			0.91	0.68	15.06	9.38
ECN4			0.88	0.76	14.19	10.86
ECN5			0.81	0.55	11.89	6.18

Notes: UK: Chi-Square Ratio = 1.368; RMSEA = 0.052; NFI = 0.95; NNFI = 0.96; CFI = 0.98; IFI = 0.98. China: Chi-Square Ratio = 1.742; RMSEA = 0.068; NFI = 0.81; NNFI = 0.91; CFI = 0.92; IFI = 0.92.

sample, the measurement model fits the data fairly well, with a relative chi-square value of 1.742, RMSEA value of 0.068, CFI value of 0.920, IFI value of 0.920, and NNFI value of 0.910.

For both sample groups, the relative chi-square value is less than the 3.00 maximum recommended by Kline (1998) and the RMSEA value is below the maximum of 0.08 (Schumacker and Lomax, 2004). According to Byrne (1998), the Comparative Fit Index (CFI) and Incremental Fit Index (IFI) are more appropriate fit indicators when the sample size is small. The IFI and CFI values for both samples are greater than the recommended 0.90 level (Byrne, 1998). The results concerning the fit of the model generally support a claim of good fit. Table 3 displays the measurement model results along with the model fit indices. All of the t-values of the measurement items exceed the recommended value of 2.575 for both samples and are significant at the 0.01 level, indicating sufficient convergent validity (Byrne, 1998). Furthermore, none of the standardised residuals exceeds the 4.00 maximum recommended by Hair et al. (2010), suggesting that there is no concern regarding a potential unacceptable degree of error.

Structural Equation Modeling (SEM) Results

Multicollinearity was tested by calculating the variance inflation factors (VIF) for each regression coefficient before reporting SEM results. A threshold of a VIF value that is less than or equal to 10.0 is a commonly used criterion to determine the presence of multicollinearity (Hair et al., 2010). The VIF values range from 1.136 to 2.074, significantly below the recommended threshold of 10.0 recommended by Hair et al. (2010), suggesting that multicollinearity does not pose a problem to the proposed model. Furthermore, the correlation coefficients are positive and significant at the 0.01 level for all variable pairings for both samples, except for investment recovery (IR) in the China sample, which is significant at the 0.05 level. The results indicate that there is a

Table 4 Correlation matrix for the UK and China samples

	<i>SP</i>	<i>SDIST</i>	<i>ED</i>	<i>IR</i>	<i>ENV</i>	<i>ECN</i>
UK (Sample)						
SP	1					
SDIST	0.536 ^a	1				
ED	0.544 ^a	0.610 ^a	1			
IR	0.364 ^a	0.377 ^a	0.442 ^a	1		
ENV	0.578 ^a	0.616 ^a	0.638 ^a	0.486 ^a	1	
ECN	0.604 ^a	0.593 ^a	0.615 ^a	0.407 ^a	0.619 ^a	1
China (Sample)						
SP	1					
SDIST	0.884 ^a	1				
ED	0.736 ^a	0.684 ^a	1			
IR	0.136 ^b	0.126 ^b	0.171 ^a	1		
ENV	0.788 ^a	0.748 ^a	0.724 ^a	0.396 ^a	1	
ECN	0.518 ^a	0.709 ^a	0.392 ^a	0.133 ^b	0.575 ^a	1

^aIndicates significance at the level 0.01.^bIndicates significance at the 0.05 level.

Notes: SP = Sustainable Procurement; SDIST = Sustainable Distribution; ED = Eco-Design; IR = Investment Recovery; ENV = Environmental Performance; ECN = Economic Performance.

certain degree of association between the variables, permitting further regression analysis. The correlation coefficients are displayed in [Table 4](#).

The proposed structural model was analyzed using partial least squares structural equation modeling (PLS-SEM) provided by the SmartPLS 3.2.6 software. SmartPLS was employed to test the research hypotheses as it is appropriate when the sample size is small ([Chin and Newsted, 1999](#)). According to [Chin and Newsted \(1999\)](#), SmartPLS can provide valid results in the case of a small sample and the minimum threshold of sample size is 10 times the largest number of structural paths directed at a particular construct in the structural model. [Fig. 2](#) illustrates the model with the SEM results specified in the SmartPLS output. The SEM results related to individual hypothesis tests are also displayed in [Table 5](#).

All hypotheses are positive and significant with the exception of H6 (SDIST → ECN), H7 (ED → ECN) for both sample groups and H8 (IR → ECN) for the China sample. For both samples, H1, H2, H3, and H4, which predict a positive association between SSCM practices and environmental performance, are positive and significant as expected, indicating that SSCM implementation in the context of UK and Chinese manufacturers leads to higher levels of environmental performance. However, H5 through H8, which predict positive associations between SSCM practices and economic performance, offer another side to the story: While the link between sustainable procurement and economic performance is significant and positive, eco-design practice negatively impacts on economic performance and sustainable distribution does not impact on economic performance for both samples. Moreover, although the link between investment recovery and economic performance is significant and positive in the UK sample, it does not significantly impact on cost performance with respect to Chinese manufacturers.

The results demonstrate a significant linkage between the implementation of SSCM practices and the environmental performance of manufacturing firms operating in UK and China. However, the results related to the linkage between the adoption of SSCM practices and economic performance is less clear-cut. While there are significant linkages between the implementation of SSCM practices and economic performance through sustainable procurement and sustainable design, there is no significant linkage between economic performance and sustainable distribution for either UK or Chinese manufacturers. In essence, the results suggest that the adoption of SSCM practices leads to higher levels of environmental performance, resulting in environmental improvements, but does not necessarily lead to improved economic performance, as only sustainable procurement is positively and significantly linked to economic performance in both samples.

Discussion

The results show that the impact of the implementation of SSCM practices on performance gains is roughly similar irrespective of the sample group, particularly in relation to environmental performance. Hence, it may well be argued that there are more similarities than differences between SSCM practices and their associated effect on performance in these two different economies. As the model depicts (see [Fig. 2](#)), all of the SSCM practices result in improved environmental performance. This indicates that the adoption of SSCM practices leads to higher levels of environmental performance and greater environmental improvements in both developed and emerging economies on different trajectories, the UK and China, although with different degrees of impact. However, the results surrounding the impact of SSCM implementation on economic performance are less clear-cut. Specifically, the results associated with sustainable design for both samples are contentious, as is that for the investment recovery practice for the China sample, which is different from the UK samples.

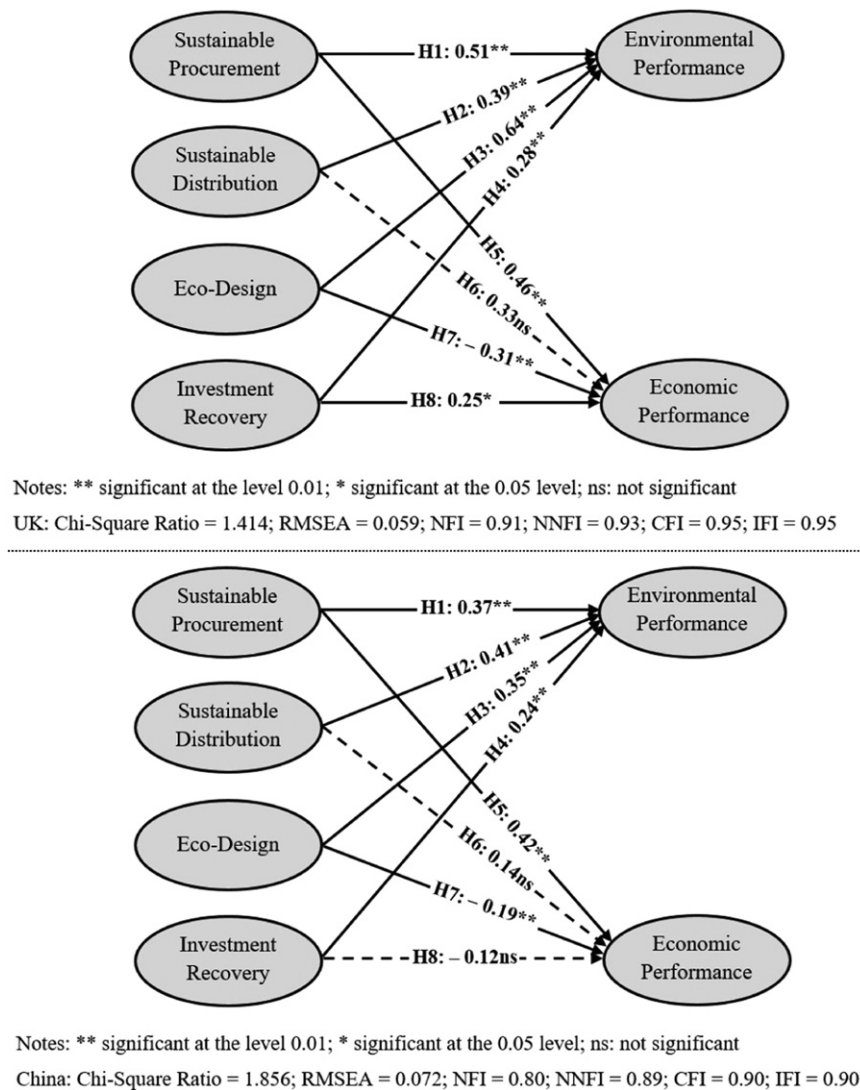


Fig. 2 SSCM practices-performance model with results.

In terms of UK manufacturing firms, sustainable procurement positively and significantly impacts on both environmental and economic performance. This can be explained by the fact that the practice of sustainable procurement is focused on decreasing the levels of environmental pollutants. From an economic standpoint, responsibility for sustainable procurement may lie with the supplier rather than the manufacturer, and thus it is potentially less costly for manufacturers to implement than other SSCM practices (Zhu *et al.*, 2008a). The result associated with sustainable procurement for the China sample is roughly similar to that for UK manufactures but with a lower degree of association. This denotes that sustainable procurement is being implemented by Chinese manufacturers and also delivering economic benefits, but to a lesser extent. This can be explained by the fact that the sustainable supply chain approach has only recently begun to emerge in China, and therefore there are few suppliers with green resources and expertise capable of providing environmentally friendly materials or services to manufacturers in China, compared to the UK. Sustainable procurement is considered to be a little more costly in the context of emerging Chinese manufacturers due to the lack of sufficient green suppliers, hindering the achievement of a higher degree of economic performance.

On the other hand, the SSCM practice of eco-design positively impacts environmental performance, and negatively and significantly impacts economic performance within both samples. Such a positive and significant relationship can be explained by the fact that most of the environmental impacts of a product and its processes are 'locked' into the design stage when materials are selected and product performance is largely determined (Grote *et al.*, 2007). The result associated with sustainable procurement for the UK sample is roughly similar to that for Chinese manufacturers, but with a greater degree of association (UK: $\beta = 0.64$, sig. at 0.01 level; China: $\beta = 0.35$, sig. at 0.01 level). This indicates that eco-design is being very well adopted by UK manufacturing firms, delivering improved economic performance to a greater extent compared to Chinese manufacturers. This can be explained by the fact that the SSCM approach, particularly green design-related issues, was introduced to UK manufacturers earlier than to emerging economies and has been put into practice for a longer period compared to China, which has only recently begun to undertake such

Table 5 Summary of hypothesis testing

Model link	UK sample		China sample	
	Std coefficient	Support	Std coefficient	Support
Hypotheses tests				
SP →				
ENV	0.51 ^a	H1: supported	0.37 ^a	H1: supported
ECN	0.46 ^a	H5: supported	0.42 ^a	H5: supported
SDIST →				
ENV	0.39 ^a	H2: supported	0.41 ^a	H2: supported
ECN	0.33 ns	H6: not supported	0.14 ns	H6: not supported
ED →				
ENV	0.64 ^a	H3: supported	0.35 ^a	H3: supported
ECN	− 0.31 ^a	H7: not supported	− 0.19 ^a	H7: not supported
IR →				
ENV	0.28 ^a	H4: supported	0.24 ^a	H4: supported
ECN	0.25 ^b	H8: supported	− 0.12 ns	H8: not supported

^aSignificant at the 0.01 level.^bSignificant at the 0.05 level.

Notes: UK: Chi-Square Ratio = 1.414; RMSEA = 0.059; NFI = 0.91; NNFI = 0.93; CFI = 0.95; IFI = 0.95. China: Chi-Square Ratio = 1.856; RMSEA = 0.072; NFI = 0.80; NNFI = 0.89; CFI = 0.90; IFI = 0.90; SP = Sustainable Procurement; SDIST = Sustainable Distribution; ED = Eco-Design; IR = Investment Recovery; ENV = Environmental Performance; ECN = Economic Performance; ns: not significant.

environmental initiatives. (Grote *et al.*, 2007) argued that the aim of eco-design is to “reduce a product’s environmental impacts without creating a negative trade-off with other design criteria, such as functionality and costs”. It appears, then, that eco-design has not fully accomplished the intended aim in terms of cost performance. This may be because eco-design initiatives require further development and improvement and necessitate more capital investment. In addition, the capacity of eco-design to reduce environmental pollutants is counterbalanced by increases in the associated costs, perhaps related to materials purchases (Green *et al.*, 2012a).

Sustainable distribution directly impacts environmental performance but does not significantly impact economic performance in either sample. This can be explained by the fact that the practice of sustainable distribution is focused on decreasing the levels of environmental pollutants, which has the capacity to enhance the environmental performance. From an economic standpoint, the lack of appropriate infrastructure hinders the benefits of such SSCM practice from being reaped in terms of profitability and financial improvement. This necessitates further infrastructure investment in order to tackle the potential lack of green logistics, resources, and capabilities. Furthermore, green distribution’s capability to reduce environmental pollutants is restrained by increases in associated costs related to the implementation of sustainable distribution initiatives.

While investment recovery positively impacts environmental performance for both samples, it does not significantly impact economic performance for the China sample. Conversely, investment recovery is significantly associated with improved economic performance within UK manufacturing firms. This may be explained by the fact that the practice of investment recovery has received much less attention in China than in developed countries such as the UK (Zhu *et al.*, 2008a). Zhu and Sarkis (2007) found different findings on investment recovery practices and reported that while investment recovery is positively associated with economic performance, it is not significantly associated with environmental performance. The difference in the results may be attributed to differences in the samples employed in terms of size and segments. However, our results are consistent with the findings of more recent work by Green *et al.* (2012a), which solidifies the position of the findings of this research.

Conclusions

The findings of this study suggest that the implementation of SSCM practices results in a higher level of environmental performance in both developed and emerging economies, but may not ultimately lead to improved economic performance, particularly in emerging economies. The results suggest a number of interesting insights concerning the SSCM literature. First, this study developed an integrated SSCM practice-performance model to investigate the relationships between greening the supply chain and performance gains and found a trade-off between environmental and economic performance. Second, the contribution of this research is significant in that it is one of a few empirical studies that have attempted to use diverse samples from both developed and emerging economies on different trajectories, extending the literature on sustainable supply chains in the manufacturing context.

While not all of the individual hypotheses are supported, the theoretical model holds together reasonably well. Furthermore, based on the relative good fit of the theorised model, the model is deemed to be a good representation of the relationships among the research constructs. Using structural equation modeling, the results show that there are more similarities than differences concerning the impact of SSCM implementation on the performance of manufacturers operating in the UK and China. It can be

concluded that the adoption of sustainable practice across the supply chain leads to higher levels of environmental performance for manufacturing firms in both developed and emerging economies, resulting in environmental improvements. However, the study provides evidence that the adoption of SSCM practices in the context of emerging economies does not necessarily lead to improved economic performance, as only sustainable procurement is positively and significantly linked to economic performance.

The results of this research clarify the proposition that SSCM practice is indeed environmentally necessary, but that the benefits might not be being reaped in terms of short-term profitability, particularly within emerging economies. Firms operating in developing countries must undertake environmental initiatives with a broader consideration of the firm's overall economic objectives. In other words, firms need to undertake SSCM practices in a bearable and equitable sense that does not harm their financial bottom line. This promises to allow firms in developing countries to balance existing in a growing economy with environmental protection. Furthermore, this ensures a win-win situation for supply chain partners with green capabilities and minimizes trade-offs between environmental and economic performance. Therefore, this research asserts that a sustainable supply chain can be successfully adopted in emerging economies if it is commercially viable to be able to take a long-term view on the profits gained.

Implications

In terms of practical implications, practitioners are provided with a validated framework for assessing the synergistic impact of SSCM practices on environmental and economic performance. Moreover, the SSCM practices validated in this work can help manufacturing firms operating in developed and emerging economies to identify those areas that require improvement and prioritization in terms of their green efforts. This work can be useful for manufacturing industries that need to convert their traditional supply chain into a more sustainable one. In the resource-constrained environment of the UK and China, the research framework points to the key environmental initiatives in the supply chain that need to be implemented, i.e., sustainable procurement, eco-design, sustainable distribution, and investment recovery. Collectively, the key SSCM practices can serve as an audit tool and later on as a benchmarking tool for managers to evaluate the perceptions of SSCM in their organizations. Developing countries should invest more in appropriate infrastructures that enhance green resources, expertise, and capabilities. This will enable the benefits of sustainability to be reaped in terms of long-term profitability and financial performance in the emerging economy context.

Limitations and Future Direction

Future studies may include the role of SSCM driving forces in the research framework and investigate their impact on SSCM implementation and its commensurate performance gains. Studies on SSCM are still at the early stage in developing appropriate measurements of social performance, particularly in the manufacturing context, and future research may develop and verify social dimension of SSCM performance. To increase the generalizability of this research, repeating this study in different developed and emerging countries will be another research direction. A robust theorization process to outline the boundary conditions around the SSCM practice-performance relationship is recommended for the continuing growth of this body of knowledge. Moreover, future studies may examine other emerging markets to eliminate the potential effect of country-level variance such as market size, economic development, and legal systems. Furthermore, the research sample is limited to large manufacturing firms and therefore, small and medium-sized enterprises (SMEs) are poorly represented. Further research could examine the study's findings using SME samples, conducting comparative research. Lastly, this research has been developed primarily with a focus on manufacturing firms, and little consideration has been given to the service sector. Therefore, future studies may examine the applicability of findings from this investigation for the service sector.

See also: Corporate Social Responsibility in Supply Chains. Evaluation of Sustainability Indicators of Buildings. Expediting Faster Housing Supply in India Using Straw Bale as Prefab Building Material. Sustainability Indicators in Supply Chains

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Further Reading

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Sustainable Technologies in Agriculture Sector: Ensuring Green Food Production for Resource Conservation

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Introduction

The role of agriculture technologies played a vital role to increase food grains and transformed conventional farming to modernize farming, however, its put a burden on natural environment in the form of different anthropogenic activities, including methane emissions, nitrous oxide emissions, carbon emissions, fossil fuel energy consumption and its resulting impact on excessive greenhouse gas (GHG) emissions (Nagothu, 2018). The need of sustainable technologies largely rises that limit global temperature less than 2°C without compromising food security (Frank *et al.*, 2017). The era of globalization largely provoked the need of information and communication technologies (ICTs) that could be used in every walk of economic activities, including technology oriented green revolution, technology driven green supply chain management, technology based green financing, etc. This study considered different ICTs factors for increasing agriculture yield, including broadband subscriptions, telephone subscriptions, computer communications, mobile and internet penetration. The previous studies largely used these ICTs factors in improving agriculture production (see, McDonough, 2012; Jespersen *et al.*, 2014; Irungu *et al.*, 2015; Tzounis *et al.*, 2017; Treinen *et al.*, 2018, etc).

The developed economies largely spend enormous expenditures on research and development (R&D) for increasing sectoral value added. European countries designated high R&D expenditures on regulating economic affairs while these economies largely used sustainable technologies in agriculture sector for massive food production (Olesen and Bindi, 2002; Long *et al.*, 2016, etc). The latest report of European Union (Europa, 2018) emphasized the need of smart solution for sustainable agriculture by smart technologies to reduce pesticides and water consumption for agriculture production. Europa (2016) report confined that new technologies are required more state-of-the-art of R&D in agriculture farming for improving agriculture yield. European seed association (ESA, 2016) discussed the viability of technical solution for sustainable agriculture in the European Union and drafted the report for policy intervention in agriculture farming through innovation and confined that technical solution will provide more sustainable agriculture inputs that improve livelihood of the farmers. The Global Forum for Innovations in Agriculture (GFIA, 2018) conferred the smart food application techniques through technological innovations and its solution in Europe that considered one of the milestones in EU sustainable agriculture farming.

Tilman *et al.* (2002) argued that high pace of population growth possesses serious challenges for sustainable farming and ecosystem that need new policies and incentives for agriculturist to meet the demand of farm yields for environmental integrity. Smith *et al.* (2007) concluded that innovative technologies could improve efficient use of land resources that helpful to eradicate poverty, hunger, and malnutrition, which further translated in to adaptation of global warming policies to mitigate GHG emissions from agriculture sector. Rao (2007) devoted an integrated ICTs framework in agriculture development and confined its importance in increasing agriculture yield. Van Ittersum *et al.* (2008) discussed three viable strategies through which sustainable agriculture system could developed across Europe, i.e., the use of agriculture mechanization to transform primitive agriculture, environmental conservation strategies, and rural support programmes, all these combined to improve agriculture sector contribution at large scale. Koutsouris (2010) critically reviewed the importance of ICTs in rural development and comes to the point that it creates 'digital divide' that linked with urban-rural divide, which create large inequalities in rural sector. Thus, if the problem area is not address with caution, the problem of intra-rural digital divide tends to show in low human development and unsustainable rural development. Horlings and Marsden (2011) found that agriculture and ecological approaches support the gigantic increase in human population to feed, thus it required real green revolution that transformed primitive and old farming techniques in to modernize farming, which required R&D expenditures to convert isolated agriculture food practices in to technology embedded farming. Tschamtkke *et al.* (2012) discussed the global food security challenges that is merely due to feed massive population, while on the same time conservation of biodiversity is compromised due to large agriculture intensification on land, thus the efficient use of land resources devoted for food production should be segregated and/or integrated with wildlife friendly farming, however, the ongoing debate on land segregation and land integration has failed to achieved the stated objectives so far. Andreopoulou (2012) discussed green informatics in environment and sustainability agenda that is connected with number of smart technologies, however, the share of these smart technologies in GHG emissions largely increases to form 'carbon footprint', which need sustainable ICTs instruments for conserving natural ecosystem. Nakasone *et al.* (2014) confined the role of mobile phones penetration in agriculture sector development at macro level, while its impact at micro level still need more policy interventions in order to get desirable results. Adenle *et al.* (2015) discussed the number of constraints that developing countries limitize investment in R&D in appropriate technologies, including, weak land resource reforms, inadequate agriculture research, limited disbursement of credit, and imperfect agriculture technology transfer, these constraints lead to low adaption of climate change. Dodo and Reith (2015) discussed the viability of sustainable computing in agriculture and rural sector development across developing countries and found that solar powered computers is the optimized solution to get access with latest ICTs embedded technology to rural sector which save carbon intensity per year up to 22 kg of CO₂ emissions. Syiem and Raj (2015)

concluded that ICTs are largely penetrated in agriculture base farming where farmers are largely used mobile phones for social communication, health emergencies, inputs availability, information about input quality, management of crops by preventing it from disease, and contacting middle men and experts for marketing and advisory support. Thus, the viability of mobile phones penetration in agriculture farming is assumed to give better payoff in terms of increasing agriculture yield. Luthra *et al.* (2018) considered the importance of internet of things (IoT) based technologies in agriculture supply chain management (ASCM) and confirmed that the application of IoT based technologies are imperative for the promotion of ASCM in a developing countries. Kabbiri *et al.* (2018) extended the technology acceptance model by adding two more constructs, i.e., 'perceived advantage' that users bring mobile phones for farming communications and 'socio-economic characteristics' by which farmer's age, experience, and household head responsibility tend to put in force to use mobile phones for increasing agriculture production. The technology embedded agriculture growth largely decrease digital divide and farmers get received an enormous income by large agriculture production. Petridis *et al.* (2018) found that diffusion of innovation in rural income, export promotion activities, farmer's education, and female employment significantly enlarge that improve agri-food business across countries.

The need of sustainable technologies is the key of economic development and without achieving agriculture transformation from conventional farming to modernize farming; this objective would be a dream for attaining sustainable development. The research questions are based upon the stated theme, which is important for the policy makers to device sustainable policies in order to modernize agriculture without rising global GHG emissions. The first research question is related with agriculture mechanization and agriculture base emissions, i.e., *does agriculture mechanization would improve quality and quantity of food grains without increasing agriculture methane emissions and nitrous oxide emissions?* This question need more attention in order to access the food exported quality and food imported items while its possible impact on natural environment in the form of agriculture emissions. The second question is about the role of ICTs in food production, i.e., *to what extent ICTs may improve the quality and quantity of food production?* This question indicates the efficient use of ICTs in agro-based farming that could improve agriculture production many times from conventional based farming. The final question is all about ICTs impact on natural environment, i.e., *does ICTs may helpful to reduce carbon-fossil emissions by improving agriculture sector through modernizing farm level inputs?* This question would draw policy inferences for the adaptation of modern technology at farm level activities to increase cereal yield with zero emissions. The study has a following key objectives, i.e.,

- (1) To examine the impact of agriculture technology, agriculture CH₄ emissions, agricultural N₂O emissions, high-technology exports, R&D expenditures and insurance and financial services on food exports and imports.
- (2) To examine the role of telephone, mobile, and internet penetration in food production, and
- (3) To analyze the role of ICTs exports in carbon-fossil emissions.

These objectives need fair assessment in order to device sustainable policies for increasing agriculture value added in a panel of selected countries.

This study has a novel contribution in food-environment modeling where ICTs factors mediate in the process to explore its positive impact on food production and environmental conservation policy actions to achieve sustainable development agenda. The previous studies limited to find either the role of ICTs in agriculture production (see, May *et al.*, 2007; Odongo *et al.*, 2013, etc.) or the role of ICTs in environmental sustainability (see, Hilty *et al.*, 2006; Fuchs, 2008; Melville, 2010; Wu *et al.*, 2018, etc.), while the literature is limited to include sustainable technologies in food industry (see, Ruiz-Garcia *et al.*, 2009). The study has a further noteworthy contribution by including, telephone, computer, mobile, and internet penetration in food-environment modeling, which clearly distinguished with the previous literature that add few technology indicators in a given scenario. Besides that, the study used 12 agriculture and resource factors, 4 environmental factors and 7 growth-specific factors, while in total the study explored 29 important factors that determine the impact of sustainable technologies on food industry. The study used sophisticated econometric technique to handle country-specific and time-invariant shocks during the study time period for robust inferences.

Data Source and Methodological Framework

The study used number of promising factors that is associated with three stated models, i.e., Model 1 comprises the nexus between agriculture insurance, R&D expenditures and food production, where food imports (denoted by *fimp*) and food exports (denoted by *fexp*) served as a response variables while agriculture machinery (denoted by *agrmac*), agriculture methane emissions (denoted by *agrch4*), agriculture nitrous oxide emissions (denoted by *agrm2o*), agriculture exports (denoted by *agrex*), agriculture value added (denoted by *agrval*), insurance and financial services (denoted by *ifs*), livestock production index (denoted by *lpi*), and R&D expenditures (denoted by *r&d*) served as explanatory factors. Model 1 comprises two equations, which is represented below, i.e.,

Model 1: Agriculture, insurance, R&D expenditures, and food production

$$fimp_{it} = \beta_0 + \beta_1(agrmac)_{it} + \beta_2(agrch4) + \beta_3(agrm2o)_{it} + \beta_4(ifs)_{it} + \beta_5(r \& d)_{it} + \nu_i + \gamma_t + \varepsilon_{it} \quad (1)$$

$$fexp_{it} = \beta_0 + \beta_1(agrmac)_{it} + \beta_2(agrch4) + \beta_3(agrm2o)_{it} + \beta_4(agrex)_{it} + \beta_5(agrval)_{it} + \beta_6(agrcereal)_{it} + \beta_7(ifs)_{it} + \beta_8(lpi) + \beta_9(r \& d)_{it} + \nu_i + \gamma_t + \varepsilon_{it} \quad (2)$$

where, β_1 to β_9 shows coefficient values of the respective variables, β_0 shows constant value, ν shows country specific shocks, γ shows time specific shocks, i shows 26 countries, t shows time period from 2000 to 2017, and ε shows noise disturbance term.

It is expected that agriculture machinery increases food production that escalate agricultural commodity exports, while its import food technology to improve agricultural value added. The agricultural emissions, i.e., agricultural methane emissions and nitrous oxide emissions would be negative impact on net food exports. It is expected that higher agriculture exports tend to increase food exports, which is further supported by country's insurance and financial services, livestock production, and R&D expenditures. Food imports are expected to increase by higher R&D expenditures and insurance and financial services across European countries. Model 2 is related with information and communication technologies and its impact on food production, which is shown by two given equations, i.e.,

Model 2: Technology and food production

$$fbt_{it} = \beta_0 + \beta_1(fbs)_{it} + \beta_2(fis) + \beta_3(ht\ exp)_{it} + \beta_4(mcs)_{it} + \beta_5(int\ ernet)_{it} + \beta_6(gdppc)_{it} + \beta_7(indvad) + \beta_8(top)_{it} + \beta_9(fdi)_{it} + \nu_i + \gamma_t + \varepsilon_{it} \quad (3)$$

$$fpi_{it} = \beta_0 + \beta_1(fbs)_{it} + \beta_2(fis) + \beta_3(ht\ exp)_{it} + \beta_4(mcs)_{it} + \beta_5(int\ ernet)_{it} + \beta_6(gdppc)_{it} + \beta_7(indvad) + \beta_8(top)_{it} + \beta_9(fdi)_{it} + \nu_i + \gamma_t + \varepsilon_{it} \quad (4)$$

In Eqs. (3) and (4), food, beverages, and tobacco consumption (denoted by fbt) and food production index (denoted by fpi) both served as a response variables, while fixed broadband subscriptions (denoted by fbs), fixed telephone subscriptions (denoted by fis), high-technology exports (denoted by $htexp$), mobile cellular subscription (denoted by mcs), internet penetration (denoted by $internet$), GDP per capita (denoted by $gdppc$), industry value added (denoted by $indvad$), trade openness (denoted by top), and FDI inflows (denoted by fdi) served as explanatory factors. It is expected that information and communication technologies would be a positive impact on food, beverages, and tobacco consumption and food production, which is further mediated by GDP per capita, industry value added, trade openness, and FDI inflows. Model 3 shows the nexus between environmental factors, food production, and ICT in a panel of selected European countries. The model comprises two equations, which are as follows, i.e.,

Model 3: Environment, food production, and ICT exports

$$CO2_{it} = \beta_0 + \beta_1(f\ exp)_{it} + \beta_2(fpi)_{it} + \beta_3(ht\ exp)_{it} + \beta_4(agr\ mac)_{it} + \beta_5(ict)_{it} + \beta_6(chm)_{it} + \beta_7(waste)_{it} + \beta_8(comp)_{it} + \beta_9(gdppc) + \beta_{10}(gdppc)^2_{it} + \beta_{11}(lucp)_{it} + \beta_{12}(lpi)_{it} + \nu_i + \gamma_t + \varepsilon_{it} \quad (5)$$

$$FFUEL_{it} = \beta_0 + \beta_1(f\ exp)_{it} + \beta_2(fpi)_{it} + \beta_3(htexp)_{it} + \beta_4(agr\ mac)_{it} + \beta_5(ict)_{it} + \beta_6(chm)_{it} + \beta_7(waste)_{it} + \beta_8(comp)_{it} + \beta_9(gdppc) + \beta_{10}(gdppc)^2_{it} + \beta_{11}(lucp)_{it} + \beta_{12}(lpi)_{it} + \nu_i + \gamma_t + \varepsilon_{it} \quad (6)$$

In Eqs. (5) and (6), carbon dioxide emissions (denoted by CO_2) and fossil fuel energy consumption (denoted by $FFUEL$) served as a response variables, while food exports, food production index, high-technology exports, agriculture machinery, ICT exports (denoted by ICT), chemical (denoted by chm), combustible renewables and waste (denoted by $waste$), computer communications (denoted by $comp$), GDP per capita, land used for cereal production (denoted by $lucp$), and livestock production index (denoted by lpi) are served as explanatory factors. It is assumed that food exports, food production index, high-technology exports, agriculture machinery, ICT, chemicals, waste, land devoted for cereal production, and livestock production index, all factors would increase high mass carbon emissions and fossil fuel emissions, while computer communication exports and ICT goods exports would decrease high mass emissions in order to support technology free emissions. It is assumed that there would be an inverted U-shaped relationship between per capita income and carbon-fossil emissions, which supported United Nation sustainable agenda across European countries. Table 1 shows the list of variables and its measurement.

The basis of this study is inspired by the latest work of Zaman et al. (2016), which shows some overwhelming fact about European countries for food poverty and food inequality trapped and concluded with the fact that European countries required sustainable policy instruments in order to increase agriculture production. However, this study extends this relationship and includes sustainable technologies in order to increase food grains by agricultural mechanization process. The study collected a data from World Bank (2018) for 26 European countries on the basis of availability of the data. The missing values are in between the sample period of 2000–2017 of the given variables series are filled by preceding and succeeding values of the respective variables for improving degree of freedom. Table 2 shows the sample of countries for ready reference.

The study started with the mechanism of 'Technology Acceptance Model (TAM)' as suggested by Davis et al. (1989), which shows some interactive linkages between the end users and technology adaptation. The users that ultimately intend to adopt the new technology, the number of influential factors act on a same time that either support to use new technology or it negatively averted not to use that technology. The perceived usefulness and perceived ease of use are subject to the most influential factor that may influence the behavior and attitude of the users to actual use the technology.

Table 1 List of variables and its measurement

<i>Factors</i>	<i>Variables</i>	<i>Measurement</i>
Agriculture and food resources	Food, beverages and tobacco consumption	% of value added in manufacturing
	Food production	Index (2004–2006 = 100)
	Food exports	% of merchandise exports
	Food Imports	% of merchandise imports
	Land under cereal production	hectares
	Livestock production	Index (2004–2006 = 100)
	Agricultural machinery	Number of tractors used in agriculture
	Agricultural methane emissions	thousand metric tons of CO ₂ equivalent
	Agricultural nitrous oxide emissions	thousand metric tons of CO ₂ equivalent
	Agricultural raw materials exports	% of merchandise exports
	Agriculture, forestry, and fishing, value added	constant 2010 US\$
Information and communication technologies	Cereal yield	kg per hectare
	Fixed broadband subscriptions	Subscriptions in numbers
	Fixed telephone subscriptions	Subscriptions in numbers
	Mobile cellular subscriptions	Subscriptions in numbers
	Individuals using the Internet	% of population used
	Communications, computer, etc.	% of service exports
Environmental factors	ICT goods exports	% of total goods exports
	CO ₂ intensity	kg per kg of oil equivalent energy use
	Fossil fuel energy consumption	% of total energy consumed
	Combustible renewables and waste	% of total energy waste
Growth-specific factors	Chemicals	% of value added in manufacturing
	GDP per capita	constant 2010 US\$
	High-technology exports	% of manufactured exports
	Industry (including construction), value added	constant 2010 US\$
	Trade Openness	% of GDP
	Foreign direct investment, net inflows	US\$
	Insurance and financial services	% of commercial service exports
	Research and development expenditure	% of GDP

Source: World Bank, 2018. World Development Indicators. Washington D.C.: World Bank.

Table 2 List of European countries

Albania	Estonia	Italy	Portugal	Switzerland
Austria	Finland	Latvia	Romania	Ukraine
Belarus	France	Lithuania	Russian Federation	26 countries
Belgium	Greece	Luxembourg	Slovak Republic	
Bulgaria	Hungary	Macedonia, FYR	Slovenia	
Czech Republic	Ireland	Poland	Spain	

Source: World Bank, 2018. World Development Indicators. Washington D.C.: World Bank.

The study extended the technology acceptance model in an interactive environmental modeling where external factors are represented with ICTs, high-technology exports, FDI inflows, and trade openness, which positively influenced agriculture mechanization process. Agriculture mechanization process is subject to the perceived usefulness and ease of use, which upgrade the technology, however, on the cost of electronic waste in the food production. Thus it suffers the sustainable food production agenda, which is contrary to the mission and vision of United Nation sustainability agenda across countries. Fig. 1 shows the research framework of the study.

The study employed panel regression technique, which is discriminated by Hausman test for model specification. Panel least square regression has serious limitations in terms of handling country-specific and time invariant shocks, which is approached by panel fixed effect and/or panel random effect models. The fixed effect model is given by the following equation, i.e.,

$$y_{it} = \alpha + \beta x_{it} + \mu_i + v_t \quad (7)$$

Y is the dependent variable and x is the set of regressors. μ_i is the white noise error term that affect dependent variable for each cross-sectional unit, while the time specific shocks is shown by v . The least squares dummy variable approach is used to capture the fixed effect model that extend Eq. (7) in a given form, i.e.,

$$y_{it} = \alpha + \beta x_{it} + \mu_1 D1_i + \mu_2 D2_i + \mu_3 D3_i + \dots + \mu_N DN_i + v_{it} \quad (8)$$

where, $D1_i$ to DN_i shows dummy variables that correspond the value of one against its cross-section while zero otherwise.

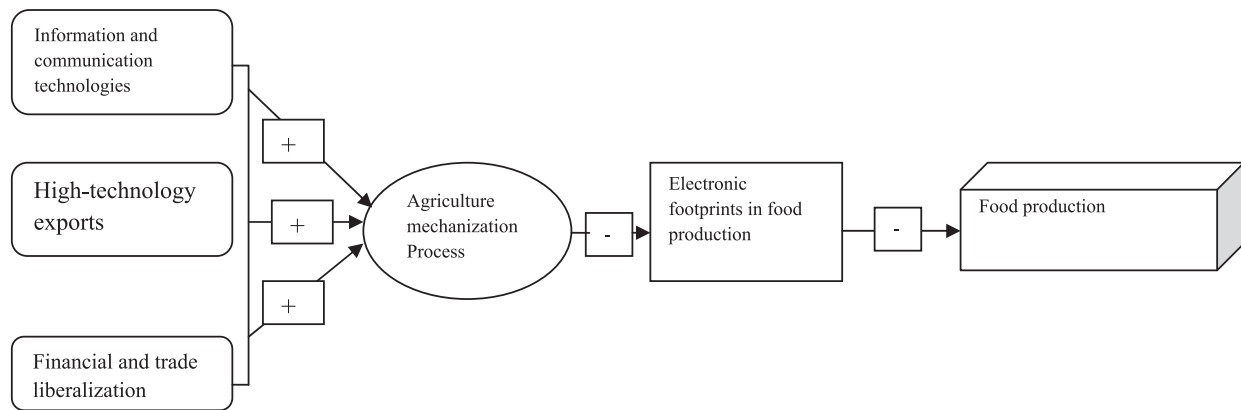


Fig. 1 Research framework of the study. *Source:* Self extract.

The error component model is an alternative method that proposed different constant terms, i.e., α for each cross-section that are assumed to constant over time. In addition, a stochastic term, i.e., ε_i varies cross-sectionally and it constant over time. The random effects model is as follows, i.e.,

$$y_{it} = \alpha + \beta x_{it} + \omega_{it}, \quad \omega_{it} = \varepsilon_i + v_{it}$$

Where, ε_i has zero mean, v_{it} has constant variance.

The Hausman test is designed to discriminate in between fixed effect model and random effect model. The significant chi-square test confirmed the viability of fixed effect model while insignificant chi-square statistics confirmed the model specification in favor of panel random effect model.

Results and Discussion

Table 3 shows the descriptive statistics of the studied variables. The mean value of agriculture methane emissions and agriculture nitrous emissions are 8382.151 thousand metric tons of CO₂ equivalent and 6737.056 thousand metric tons of CO₂ equivalent respectively. The maximum value of food exports, food imports, agriculture exports, and high-technology exports are 9.471% of merchandise exports, 9.386% of merchandise exports, 2.5009% of merchandise imports, and 10.684% of merchandise exports respectively.

The average value of fixed broadband subscriptions, fixed telephone subscriptions, and mobile cellular subscriptions are 2,870,113, 7,231,192, and 21,116,185 respectively. The maximum value of food, beverages, and tobacco consumption, and chemicals used in manufacturing is about 15.7384% of value added in manufacturing and 10.03285% of value added in manufacturing respectively. The mean value of food production index and livestock production index is about 104.1359 and 101.165, respectively, with a standard deviation of 169.07 and 153.75, respectively. The mean value of land used under cereal production and total cereal yield is about 4,003,523 hectares and 4457.366 kg per hectare respectively with a positively skewed distribution and high kurtosis value. The maximum value of trade openness and R&D expenditures is about 111.1018% of GDP and 1.249% of GDP respectively. The average value of GDP per capita, industrial value added, agriculture value added, and FDI inflows are about US\$26186.3, US\$1.05E + 11, US\$1.01E + 10, and US\$1.52E + 10 respectively with high kurtosis value. The minimum value of tractors used in agriculture is about 5917, maximum value is 1,755,501 and average value is about 324,498.5. The average value of individuals using the internet is 51.697% of population, computer communication is 38.307% of service exports, ICT goods exports is about 5.613% of total goods exports, CO₂ intensity is about 2.295 kg per kg of oil equivalent energy use, fossil fuel energy consumption is about 73.148% of total energy consumed, and combustible renewables and waste is about 8.169% of total energy waste. The positive skewed distribution and high kurtosis value exhibit the data variability on the right hand side of the distribution with considerable peak of the distribution. **Table 4** shows the model specification test by Hausman chi-square statistics.

The results show that Eqs. (1), (2), and (4) has a significant chi-square statistics at 1% level of significance, thus its confirmed that the given equations would used fixed effect regression model, while the remaining equations, i.e., Eqs. (3), (5), and (6) does not fall in the critical region at 5% level of significance, thus these equations would used panel random effect regression model. The results clarify that the given models influenced with country-specific and time-invariant shocks, thus its need sophisticated panel regression apparatus to minimize these shocks for obtaining robust inferences. After specify the panel regression models, the study estimated Eqs. (1)–(6) for parameter estimates (see, **Table 5**).

The results show that agriculture machinery largely increases food production both in terms of food exports and food imports, while its impact is invisible on carbon emissions and fossil fuel emissions during the study time period. The results imply that tractor that are used in agriculture production for harvesting and threshing the crops increases food production, which ultimately

Table 3 Descriptive statistics

Variables	Mean	Maximum	Minimum	Std. Dev.	Skewness	Kurtosis
AGRCH4	8382.151	58,083	603.9996	11,241.39	2.271547	8.023261
AGREXP	2.500932	29.47066	0.187518	3.274271	4.389211	28.01848
AGRMAC	324,498.5	1,754,401	5917	469,968.2	1.952344	5.505781
AGRN2O	6737.056	37,534.85	257.8987	8808.597	1.975742	6.098137
AGRVAD	1.01E + 10	6.57E + 10	1.02E + 08	1.46E + 10	1.99573	5.8574
CEREAL	4457.366	9842.2	1561.4	1738.784	0.769402	3.019328
CHM	10.03285	48.69719	0.902462	8.596966	2.502956	10.28366
CO ₂	2.295161	4.6566	1.249891	0.565558	0.651727	3.873477
COMP	38.30791	75.74495	8.59727	15.08971	0.331711	2.441776
FBS	2,870,113	30,872,788	20	5,250,796	3.067465	12.74903
FBT	15.7384	32.83875	5.368572	6.555802	0.722557	2.943501
FDI	1.52E + 10	2.35E + 11	-2.99E + 10	2.61E + 10	3.472057	21.0551
FEXP	9.471499	41.87713	1.247004	5.764255	1.481584	7.528328
FFUEL	73.14857	96.24776	12.29389	16.60156	-1.12663	4.425769
FIMP	9.386244	21.83443	2.909511	3.429086	0.824613	3.69015
FPI	104.1359	169.07	74.99	15.15732	1.540679	5.980956
FTS	7,231,192	45,539,288	152,687	10,586,791	2.115501	6.533988
GDPPC	26,186.3	111,968.3	1817.997	23,662.02	1.578709	5.45265
HTEXP	10.68487	47.83989	0.120348	7.776425	1.426703	5.325011
ICT	5.613284	36.81885	0.066223	6.325337	1.964657	6.979681
IFS	7.541914	71.59303	-0.4334	13.74928	3.176766	12.94452
INDVAD	1.05E + 11	5.34E + 11	9.80E + 08	1.49E + 11	1.77247	4.691938
INTERNET	51.69743	98.1367	0.114097	25.51499	-0.37876	2.039003
LPI	101.165	153.75	75.55	11.11972	1.235269	6.986785
LUCP	4,003,523	44,576,100	27,782	8,180,487	3.672757	16.82899
MCS	21,116,185	2.38E + 08	29,791	37,625,645	3.68486	18.60268
R&D	1.249586	3.74943	0.08735	0.807221	0.95898	3.287991
TOP	111.1018	423.9863	45.60912	58.62478	2.211351	10.12199
WASTE	8.169891	34.4444	0.180816	6.629945	1.675249	5.926587

Source: World Bank, 2018. World Development Indicators. Washington D.C.: World Bank.

Table 4 Hausman test for model specification for Model 1 to Model 3

Models	Equations	Ch-square statistics	Chi-square degree of freedom	Probability values	FE/RE
Model 1	Eq. (1)	56.208	5	0.000	FE
	Eq. (2)	44.114	9	0.000	FE
Model 2	Eq. (3)	14.825	9	0.095	RE
	Eq. (4)	38.934	9	0.000	FE
Model 3	Eq. (5)	7.348	12	0.833	RE
	Eq. (6)	17.046	12	0.147	RE

Source: Authors estimation.

Note: FE shows fixed effect and RE shows random effect.

reap economic profit by its exports and imports. Delgado *et al.* (1994) argued that agricultural technology is helpful to interlinked sectoral growth, which is one of the desirable policy options for getting economic incentives via production more food grains to feed massive population growth. Sekhon (2014) concluded that technology has a wider role in order to produce more food grains that could be applied on pesticide and fertilizers for more crop production. The negative impact of agricultural methane emissions on food exported items is visible, which impede agriculture value added. The policies to minimize food export losses by agricultural methane emissions are imperative for sustainable farming. Mosier *et al.* (1998) discussed the mitigation strategies of CH₄ emissions by improving animal productivity and agricultural crops, which is deemed desirable for conservation of natural environment. Saunois *et al.* (2016) found that global CH₄ emissions is rapidly increasing due to biogenic process, which becomes one of the major source of GHG intensive scenarios that need to be limitize by sustainable agriculture policy instruments. Wollenberg *et al.* (2016) emphasized the need to reduce global temperature up to 2°C by adopting sustainable mitigation options related with agriculture based methane emissions and soil carbon. Agriculture nitrous oxide emissions are largely evident during food exports, which need more sustainable agriculture instruments in order to reduce emissions and improve food exports across European countries. Dobbie *et al.* (1999) found that agricultural N₂O emissions chiefly attributed by intensive agricultural fields with increasing soil water- filled pore space, rising temperature, and an increase in fertilizer application on soil mineral nitrous

Table 5 Estimates of panel fixed effect model/panel random effect model

Variables	<i>Eq. (1)</i>	<i>Eq. (2)</i>	<i>Eq. (3)</i>	<i>Eq. (4)</i>	<i>Eq. (5)</i>	<i>Eq. (6)</i>
	DV: FIMP	DV: FEXP	DV: FBT	DV: FPI	DV: CO ₂	DV: FFUEL
Constant	4.127405 ^a	-0.428035	20.71605 ^a	85.67032 ^a	2.599761 ^a	82.70448 ^a
AGRMAC	1.48E - 05 ^a	2.98E - 05 ^a	—	—	-7.29E - 08	-8.83E - 07
AGRCH4	-9.74E - 06	-0.001186 ^a	—	—	—	—
AGRN20	-0.000132	0.000835 ^c	—	—	—	—
IFS	-0.083663 ^a	—	—	—	—	—
R&D	1.650984 ^a	-0.627682	—	—	—	—
AGREXP	—	-0.219095 ^a	—	—	—	—
AGRVAD	—	1.86E - 10	—	—	—	—
CEREAL	—	0.001121 ^a	—	—	—	—
IFS	—	-0.156710 ^a	—	—	—	—
LPI	—	0.001940	—	—	0.000642	0.025861
FBS	—	—	3.28E - 07 ^a	-1.46E - 06 ^a	—	—
FTS	—	—	2.11E - 07 ^b	-7.66E - 07 ^b	—	—
HTEXP	—	—	-0.192361 ^a	0.973638 ^a	-0.001334	0.278719 ^a
MCS	—	—	-3.61E - 08 ^a	2.89E - 07 ^a	—	—
INTERNET	—	—	-0.012510	0.418833 ^a	—	—
GDPPC	—	—	-5.55E - 05	0.000370	-2.42E - 06	0.000117
GDPPC ²	—	—	—	—	3.28E - 11	-1.15E - 09
INDVAD	—	—	-1.48E - 11 ^b	-4.90E - 11	—	—
TOP	—	—	-0.008947	-0.128008 ^a	—	—
FDI	—	—	1.09E - 12	-1.89E - 11	—	—
FEXP	—	—	—	—	0.001721	0.030678
FPI	—	—	—	—	-7.61E - 05	-0.037274 ^b
ICT	—	—	—	—	0.005331	-0.143555 ^c
CHM	—	—	—	—	-0.012571 ^a	-0.050021
WASTE	—	—	—	—	-0.037113 ^a	-1.137869 ^a
COMP	—	—	—	—	0.001909	-0.084534 ^a
LUCP	—	—	—	—	2.66E - 09	2.13E - 07
Statistical tests						
R ²	0.852	0.841	0.121	0.571	0.214	0.439
Adjusted R ²	0.842	0.828	0.104	0.537	0.193	0.424
F-statistics	84.005 ^a	67.393 ^a	7.050 ^a	16.959 ^a	10.364 ^a	29.696 ^a

^aIndicates 1% level of significance.^bIndicate 5% level of significance.^cIndicate 10% level of significance.

Source: Authors estimation.

oxide contents. Tian *et al.* (2015) argued that CH₄ emissions and N₂O emissions both are largely influenced global GHG emissions after CO₂ emissions, however, the intensity to influence on climate change is still unexplored that have a serious impact on ecosystem health. Snyder *et al.* (2014) opined that it is imperative to develop broad based sustainable policies to mitigate N₂O emissions by efficiently used *N* per unit of animal products, land area and per unit crop. The improvement in insurance and financial services should be stronger enough to influence positively on food imports. Xiong (2017) argued that food safety is desirable for imported food items to mitigate food security risks. Was and Kobus (2018) concluded that crop insurance played a vital role in order to received compensation in the past yields that is affected, while its further supported to large food grains, intensification of crop production and improving soil quantity. There is a positive relationship found between R&D expenditures and food imports, as higher the R&D spending on food production, largely it will increase food imports of sustainable agriculture items (see, Hurley *et al.*, 2014). Agriculture sector provides food grains to the economy; therefore, high agriculture exports reduce total food exports due to feed high mass population growth across countries. The positive impact of cereal production on food exports tend to show the valuable contribution of cereal production per hectare in total food exports, which is good sign to earn more economic profits through food items trade (see, Cassman, 1999; Hussain, 2010, etc).

The importance of information and communication technologies in agricultural production is quite visible in terms of agriculture mechanization process that gives an increase in food grains and cereal yields to the economy (see, Rao, 2007; Aker, 2011; Janssen *et al.*, 2017, etc). The two important factors of ICTs are fixed broadband subscriptions and telephone subscriptions that are used here to analyze the impact of telephone and broadband subscribers on the consumption of food, beverages, and tobacco and found positive relationship between them, interestingly, the impact of both the ICTs factors on total food production index is negative, which required more intensive ICTs factors in agriculture production across countries (see, Abu *et al.*, 2017; Aldosari *et al.*, 2017, etc). The impact of high-technology exports on food, beverages, and tobacco consumption is

negative, however, it supports total food production index on the cost of high fossil fuel emissions in a panel of selected countries. The result implies that high-technology exports associated with high fossil fuel emissions simultaneously with high food production that need to make vigilant sustainable policies to reduce fossil footprints from food production (see, [Bauer et al., 2016](#)). The next two ICT factors, i.e., mobile cellular subscriptions and internet penetration are used in food production models and found that mobile cellular subscriptions negatively impact on food, beverages, and tobacco consumption, however, its importance in food production index is largely evident that emphasize the need of mobile cellular penetration in food modeling (see, [Shah et al., 2014](#); [Aker and Ksoll, 2016](#), etc). The results of the study further confirmed the internet penetration in food production index, where internet technology substantially increases food production index across countries (see, [De Silva et al., 2017](#); [Duncombe, 2016](#), etc).

The study result does not verify the inverted U-shaped relations between emissions, per capita income, and food production and tend to show a flat relationship between the variables in different regression apparatus. There is a negative relationship between industry value added and food, beverages, and tobacco consumption, which confined that industrial value added largely comprises durable commodities in order to reap more economic incentives instead of agriculture intensive production. The impact of trade openness on food production index is negative that tend to show capital intensive trade instead of agriculture intensive food trade across countries. The United Nation agenda for environmental sustainability is achieved by sustainable food production, chemicals used in manufacturing value added, computer communications, combustible and renewable waste, and green ICT consumption, as these are less sensitive to carbon-fossil emissions in a panel of selected countries (see, [Jägermeyr et al., 2017](#); [Raghavan and Pargman, 2017](#), etc).

Conclusions

The era of globalization is largely provoked the need of efficient and sustainable technologies that could be used for mitigating global GHG emissions through mechanized farming, sustainable production and consumption, renewable energy mix, clean water and sanitation, climate action, and long-term global cooperation between the developed and developing countries for conservation of natural resources. These are related with United Nation sustainable development goals, which is imperative for long-term sustained growth across countries. This study focused on sustainable technologies that used in agriculture sector for improving the quality and quantity of food grains without increasing agriculture methane emissions, nitrous oxide emissions, carbon emissions, and fossil fuel energy consumption. The study considered a panel of 26 European countries for a period of 2000–2017 for policy formulation. The study used panel fixed effect model/panel random effect model in three developed models to adjust country-specific and time-invariant shocks during the study time period. The results conclude that information and communication technologies largely improve food production without deteriorating natural environment by reducing carbon-fossil emissions, while agriculture methane emissions and nitrous oxide emissions have a negative impact on food exports. Agriculture technology improves net food exports while high-technology exports increases food production on the cost of fossil fuel emissions. Thus, the policies to reduce environmental footprints in food production modeling required sustainable technologies in order to lessen the environmental cost on agriculture value added. It is evident that due to global warming and increase rice cultivation area mainly lead to increase methane emissions, while nitrous oxide emissions mainly occurred due to high use of nitrogen fertilizer use, thus, it is imperative to device sustainable agro-base policy instruments in order to mitigate climate change. would be more important to the farmers to efficiently used nitrogen as farm inputs that could reduce the risks of nitrogen oxides up to 1/3rd of the total emissions. The policies for green growth could be possible only when we achieve green revolution in agriculture sector and it is aforementioned that cleaner technologies and ICTs may play a vital role in order to improve agriculture yields. Thus, the usage of sustainable technologies in food industry is pivotal for green revolution.

See also: Conversion of Renewable and Food Wastes into Useful Products With Environmental Perspectives. Eco-Innovation Options in Food Processing. Food Residue, Loss and Waste as Animal Feed. Food Waste for Sustainable Packaging Materials. Local Food and Healthy Eating for Wholesome Life: Some Policy Considerations. Upcycling Fresh Food Items in Retail Operations

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Toyota Production System – Monitoring Construction Work Progress With Lean Principles

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Introduction

Since the 1950s the Toyota Motor Corporation has honed an advanced method of production design, control, and management referred to as the Toyota Production System (TPS). TPS is also referred to as a total, lean manufacturing, or just-in-time (JIT) production system. It adds value to the (final) customer through the utilization of cost-effective resources, elimination of waste, and continuous improvement (Brown, 2005). TPS has resulted in a quicker assembly of automobiles with high reliability and high quality-to-cost, which were attained even with the high wages of Japanese workers before the internationalization of Toyota's production (Liker, 2004). Currently, Toyota stands as the largest automotive manufacturer and the sixth largest company by revenue in the world (Fortune Global 500, 2018). The next section introduces the history behind TPS.

History

In the early 1900s, Sakichi Toyoda was an entrepreneur who designed and produced looms that were less expensive than and superior in quality to those commercially available. Later on, Sakichi leveraged steam power to streamline the weaving process through an automated loom. The weaving loom stopped when a string tore with the objective to reduce defects (Ohno, 1988; Liker, 2004). The concept of a smooth production process through autonomation (*Jidoka* in Japanese) was the essence of Sakichi's innovation and was later adopted within TPS.

In 1926, Sakichi established the Toyoda Automatic Loom Works, Ltd. In 1929, commercialization rights of the patented loom design were sold to Platt Brothers in London for £100,000 (pound value at the time). In 1930, Kiichiro Toyoda founded Toyota Motor Corporation with the profits from this transaction (Ohno, 1988; Liker, 2004). Initially, the company focused on the production of trucks (Liker, 2004).

Later, in the 1950s, Toyota's Chief Officer Eiji Toyoda – cousin of Kiichiro Toyoda – and other corporate managers traveled to the United States with the objective to learn from the direct observation of the assembly (production) lines at Ford Motor Company and General Motors Company. Despite their business success, Toyota's cohort of managers realized many inherent flaws in the assembly processes. Examples of shortcomings included uneven workflow, large inventories, wait times, disorganized workplaces, or quality issues. Upon return, Eiji Toyoda commissioned Taiichi Ohno with the design of a robust approach that could boost Toyota's production (Ohno, 1988; Liker, 2004).

Waste

Indeed, Taiichi Ohno, Toyota's chief production engineer, centered his analysis on differentiating value-added tasks and nonvalue-added tasks from a customer's perspective. Such perspective unambiguously enabled to ascertain the design aspects that added value and tracked such value through design, supply, production, and management. Ohno, while conceiving TPS, determined seven categories of waste or lack of value (*Muda*) (Ohno, 1988; Liker, 2004), which are detailed below.

- (1) *Overproduction*. Production of goods or products before they are required by downstream production (intermediate products) or customer demand (finished products).
- (2) *Waiting*. Idle time of workers, for example, waiting due to machine time, lack of parts, or tool or machine issues.
- (3) *Unnecessary handling*. Unnecessary handling of materials, parts, or goods/products. This is sometimes referred to as double- or multiple-handling. In addition to the inherent waste associated with unnecessary handling, it is also at the source of damage or quality issues and increased safety incidents.
- (4) *Overprocessing and inappropriate processing*. Overprocessing refers to processing in excess of design specifications, quality requirements, or customer expectations. Inappropriate processing reflects an inadequate use of methods, techniques, or tools and equipment. Inappropriate processing can also result from a product design with poor manufacturability and/or omissions and errors. Design omissions and errors eventually result in quality issues.
- (5) *Excessive buffers*. Excessive inventories of materials, parts, and intermediate or finished products increase production and storage costs, safety incidents, and can result in the damage of stored items.
- (6) *Unnecessary motion*. The unnecessary motion of workers or equipment/machinery. It includes unnecessary traveling, bending, reaching, or lifting. When routinely performed, unnecessary motion continuously builds waste and costs. Unnecessary motion negatively impacts workers' health and safety.

- (7) *Quality issues.* Defects or quality issues in parts or products, or the work time and equivalent costs wasted reworking defects or replacing parts or products.

Indeed, Taiichi Ohno summarized the foundation of TPS by stating that “all we are doing is taking a gander at the timeline from the minute the client gives us a request to moment that we gather money. What is more, we are decreasing the timeline by expelling nonvalue-added waste” (Ohno, 1988).

Theoretical Underpinning of Toyota Production System

In reality, in Ohno’s broadest vision, everything between a client’s command (e.g., car dealer) and the delivery of the finished product (e.g., cars) could be regarded as waste, whether it added value or not. In practice, though, nonvalue-added or actual waste was the enemy and had to be continuously eradicated. The theoretical underpinning of TPS is embedded in such a vision and rests on five main pillars. The organizational behaviors of elimination of waste (*Muda*) and continuous learning (*Kaizen*) support and feed the technical components of autonomation (*Jidoka*), JIT, and standardization (Liker, 2004). The rest of this section details the last four pillars that, when combined with waste elimination, result in the theoretical foundation of TPS. See Fig. 1.

Kaizen

Kaizen represents the organizational behavior aspect of continuous learning or improvement and sustains the work culture. Kaizen techniques aim at promoting and reinforcing continuous learning, and ultimately enhance TPS, for example contributing to waste elimination or increased efficiency. “5 Whys?” and “5S” are examples of continuous learning. “5 Whys?” is a simple technique that triggers a search for the ultimate cause of problems. Instead of asking “why?” once, it seeks a response to six questions: Who?, What?, Where?, When?, Why?, and How? (five Ws and one H) (TMMK, 2006). In addition, “5S” aims at organizing the workspace in a clean, efficient, and safe manner, with the overall goal of a productive work environment. It includes five phases (Veres et al., 2018). Sort (*Seiri*) removes what is not needed and clears the workspace. Set-in-order (*Seiton*) prepares the sequence of necessary items/tools/parts so that they can be efficiently reached and returned. Shine (*Seiso*) aims at regularly clearing equipment and workplace and including routine inspections during the clearing process. Standardize (*Seikutsu*) documents and standardizes processes and procedures in support of 5S. Finally, sustain (*Shitsuke*) aims at continuously maintaining processes and procedures, inclusive of work audits, so that these become habits within the work culture.

Just-in-Time

JIT aims at providing what is needed (i.e., materials, parts, products) in the required amount at the right location and at the right time. JIT enhances efficiency and enables quick responses to changes (TMMK, 2006). JIT reduces inventory and rework and improves quality by identifying and enabling the resolution of quality issues in real-time (Billesbach, 1987). JIT techniques include *Heijunka*, *Kanban*, or value stream mapping (VSM). *Heijunka* seeks to level production both by volume and by product type

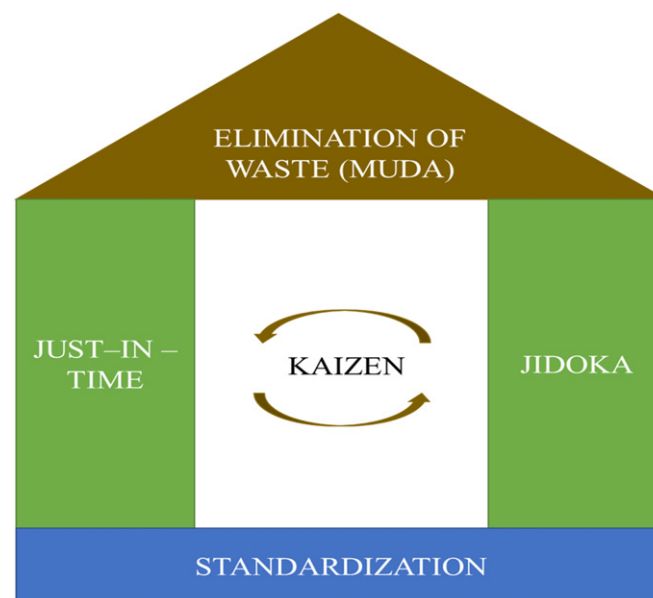


Fig. 1 Theoretical underpinning.

(e.g., car model) against variable customer demand (TMMK, 2006). Toyota's managers envisioned that stable and lean production required an average production by volume and product type based on long-term demand forecasts as opposed to production responses to variations in short-term demand. In *Heijunka*, inventories of finished products represent buffers against sudden peaks of demand so that customer orders can be met without altering production. In addition, *Kanban* is a scheduling approach that matches inventories (e.g., parts) with actual consumption. *Kanban* is supported with signboards (such is its Japanese meaning) that inform parts that need to be made available within the production unit/facility or by outside suppliers. Such visual signs are also leveraged to control overproduction and uneven production rates (TMMK, 2006). Finally, VSM is a value improvement technique that aims at optimizing human, material, and information resources to complete business and production processes efficiently. Also, it results in the coordination of the major actors, for example, suppliers and distributors (Sundar et al., 2014).

Jidoka

Jidoka aims at the design of equipment that automatically detects production issues and stops when such issues occur. Examples of issues are equipment malfunctions, quality problems, or worker late responses (TMMK, 2006). A visual system alerts workers who assist the machine. In TPS, such type of interaction is called *autonomation*. *Autonomation* refers to “automation with a human touch” (Ohno, 1988) or intervention. Thus, workers are empowered by sensing-equipped machines to intervene and eventually stop production (e.g., with line-stop buttons), and thus prevent the flow of quality defects and production issues into downstream tasks. *Poke Yoke* and *Andon* are instances of Jidoka. *Poke Yoke* avoids mistakes by workers. Thus, a worker cannot make a specific movement or start a task on a machine if the predecessor movement or task has not been completed. Also, *Andon* refers to the notification of quality or production issues to workers and management. A visual display board with the current state of production, work instructions, issues, or progress information is an instantiation of *Andon*. *Andon* also enables a mechanism of control that triggers quick corrective actions when issues arise (TMMK, 2006).

Standardization

Standard processes and procedures enable stable, predictable, and efficient production. The organizational behavior aspect of TPS requires standardization of processes and procedures across work, supply, business, and management functions. For instance, setting the sequence of human-machine motion is an example of standardization. TPS's standardization also includes *takt time*, work sequence, and standard work-in-process inventories (TMMK, 2006). *Takt time* is the average production pace between task or workstations that matches customer demand. *Takt time* is calculated with the presumption of 100% machine production capacity (TMMK, 2006). Second, work sequence defines the detailed step-by-step order of tasks in the production line that maximizes production and minimizes waste. Finally, standard work-in-process represents the minimum inventory to maintain work. Maintaining such a minimum inventory enables workers to perform routine work continuously (TMMK, 2006).

In addition, standardization is inclusive of processes and procedures within business partners, for example, suppliers. Overall, lack of standardization precludes continuous learning.

Toyota Production System

TPS encompasses an advanced method of production design, control, and management. TPS has been observed to become “a superior way to provide better products in wider variety at lower cost, equally providing more challenging and fulfilling work for employees at every level” (Womack et al., 1990). TPS implementation and success relies on continuous learning, and knowledge consolidation and transfer within the organization and across partner organizations. There are 14 TPS principles. Each of these principles is detailed below based on the discussion by Liker (2004).

- *Principle 1. Make decisions on a long-term vision.* Maintain and communicate a vision that sets a continuous direction and prevents ever-changing responses to transient events. The long-term vision should be maintained even at the expense of lower short-term profits.
- *Principle 2. Maintain continuous flow.* Create a continuous flow of materials, parts, products, and information that brings problems to the surface.
- *Principle 3. Use “pull” production.* A task or activity signals its predecessor(s) when a feed (parts, product, and materials) is needed. Pull production results in the right quantity of products to satisfy customer orders. Pull eliminates or minimizes overproduction.
- *Principle 4. Level out workload and reduce unevenness.* Eliminate unevenness across production tasks (e.g., workstations) and schedule. Leveling out eliminates the overburdening of workers and equipment. *Takt time* is the average production pace between task or workstations that matches customer demand.
- *Principle 5. Stop to fix problems.* Design equipment that detects problems and stops when problems occur. Complementary, a visual system alerts workers that assist the machine (i.e., *autonomation*). The worker has the authority and is accountable for stopping the production/assembly line when an issue is identified.

- *Principle 6. Standardize.* Adopt stable and repeatable processes and procedures that maintain timing, predictability, and outputs. The organizational behavior aspect of continuous learning is also standardized through best practices.
- *Principle 7. Control problems visually.* Control problems with visual indicators that immediately communicate information. Visual controls prioritize the identification and/or communication of information and thus do not need to be sophisticated, even though they can be. Examples of visual controls include charts, mark tapes (e.g., on floors), arrows, colors, shapes, signboards, or displays.
- *Principle 8. Use reliable and tested technologies.* Technology is to assist employees. Avoid a technology that can conflict with the organizational culture, or that could disrupt stability, reliability, and predictability. Consider thoroughly tested technologies (i.e., proven through trials) that can serve employees and improve processes and procedures.
- *Principle 9. Grow leaders internally.* Leaders must be grown internally. Provide continuous support for exceptional employees so that they become a role model. Leaders should be embedded in the organizational behavior and understand the daily work details.
- *Principle 10. Develop exceptional people and teams.* Train individuals and teams who believe in the organizational behavior to work together and achieve outstanding results. Use cross-functional teams to enhance quality, productivity, and flow by solving difficult technical challenges. Ultimately, success relies on the team.
- *Principle 11. Respect your partners and suppliers.* Respects partners and suppliers, but at the same time challenge them to do better and help them to improve. For example, provide cross-functional teams to help and train suppliers to recognize and address problems so that they can become exceptional partners.
- *Principle 12. Go and experience by yourself.* Managers and employees alike must go to the source of a problem to observe and collect evidence as a first step to effectively solve the problem. This is sometimes referred to as *Gemba Walks*, in which employees literally walk where the problem occurs and thus enhance observation, personal interaction, and verification of issues and data. Hands-on experience is essential to resolve practical issues.
- *Principle 13. Make decisions by consensus and rapidly implement them.* Evaluate all possible solutions/alternatives before making a decision, but when a solution is devised implement it quickly and cautiously. Although looking for possible alternatives is often time-consuming, it enhances knowledge through discussions and often results in an optimum resolution.
- *Principle 14. Set a continuous learning and innovation culture.* Use relentless reflection and continuous improvement to become a learning organization. Becoming a learning organization is the final goal of TPS and feeds and supports the previous principles. A learning organization is characterized by an attitude of continuous improvement and innovation. At the same time, such continuous improvement requires reflection and analysis of previous efforts and the communication of insights, for instance through lessons learned or similar knowledge base. Continuous learning must become an intrinsic behavior within the organization.

Impact on Industry Sectors

Many companies across distinct industries have supported and improved their production capabilities with TPS principles. Instances of influence on manufacturing, medical, and construction sectors follow.

The adoption of TPS principles on distinct manufacturing industries indicates a unanimous positive impact. For example, a sensor manufacturing company integrated TPS techniques and reduced lead time by 46%, work-in-process inventory by 83%, finished inventory by 91%, overtime by 50%, and achieved 81% improvement in aggregate productivity (Liker, 2004). The implementation of TPS principles in aerospace manufacturing resulted in 20% production capacity growth (Crute *et al.*, 2003). The implementation of lean principles in tile manufacturing increased profits by 63.4 % and productivity by 47.4 %, and reduced labor cost in 11.3% and lead time by 50% (Lander and Liker, 2007).

In the health sector, the adoption of TPS principles has resulted in improved patient experience and enhanced medical performance. The design of operating rooms with TPS principles reduced patient time and thus enabled an 11% increment in surgical procedures (Castaldi *et al.*, 2016). The use of lean principles in the design of a health care facility resulted in the reduction of patient travel by 25%, staff travel by 27%, and the number of steps required to complete care procedures by 35% (Hicks *et al.*, 2015). A cardiac surgery program decreased mortality rate by 61% and major complications rate by 57% when compared against similar programs in the geographical region (Culig *et al.*, 2011). Savings of \$3,497 per each coronary artery bypass procedure were documented.

Impact on the Construction Sector: Lean Construction

Lean construction concepts and techniques were developed after TPS principles and in consideration of the unique challenges in construction, such as on-site production, outdoor conditions, industry defragmentation, or workers moving through a static product (such as a building or facility) to produce work. Construction is characterized by endemic low productivity rates when compared with the rest of nonfarming industries (Bureau of Labor Statistics, 2018). Until the recent adoption of TPS concepts, the traditional focus of management had targeted the completed product or project outcome (Grau *et al.*, 2014; Grau and Back, 2015; Grau *et al.*, 2016, 2017). Thus, management techniques had been historically developed to target the conversion of outputs from

inputs while neglecting the production process required to achieve those outputs (Howell and Ballard, 1996; Koskela, 2000). The so-called lean construction concepts and techniques emerged in the 1990s as an attempt to revamp endemic planning and production shortcomings. For example, the Last Planner System (LPS) (Ballard, 2000) has become a mainstream planning technique aiming at the improvement of workflow and minimization of variability and waste. Conceived in the early 2000s, LPS measures the number of construction tasks completed against the total number of tasks initially planned within a specified period, for example, typically a week. LPS focuses on removing constraints that can negatively affect work before supervisors commit to the work plan. With LPS, the percentage of weekly completed activities consistently exceeds 80%.

In addition, new technologies have been tested to provide visibility and inform work status in an immediate manner (Abbaszadegan and Grau, 2015). Thus, advanced sensing, computing, and information technologies have been leveraged to provide fine-grained information on construction work (e.g., steel or concrete crews) in real- or near real-time, so that such information can trigger immediate corrective actions from managers and workers when deviations occur.

Thus, the monitoring of a drywall installation activity for a new hospital facility indicated that the immediate communication and analysis of workflow triggered proactive actions that resulted in the stabilization of flow when deviations occurred (Cruz-Rios *et al.*, 2015). When meaningful differences existed between actual and planned flows, the intervention of managers resulted in reverting the actual workflow back to the planned flow rate or close to it. Deviations eventually reemerged and required additional corrective actions. In addition, pilot participants indicated the need to leverage automation during field data collection and also support information extraction and analysis with automated reasoning and alert mechanisms.

Overall, lean construction advocates envision that efficient and effective production must satisfy the three lean construction axioms of transformation-flow-value (Koskela, 2000). The transformation of outputs based on inputs reflects the traditional management focus on the finished product (Seppänen, 2009). The value aspect of production aims at optimizing the amount of value delivered to the customer. Finally, the flow aspect of production aims at the minimization of nonvalue-added steps or the simplification of production with the objective to eradicate waste. Even though far from trivial, the adoption of TPS principles within construction promises to ultimately yield production, safety, and quality records close to those in other nonfarming industries.

Conclusions

This article detailed TPS, which stands for an advanced method of production design, control, and management. TPS origin and history were explained through the entrepreneurial and innovation mindset of Kiichiro Toyoda, who founded Toyota Motor Corporation with financial resources generated through his father's loom business. Improved quality, value-added to customer, waste elimination, JIT, and continuous improvement are the main traits of TPS, which is sustained on 14 fundamental principles. Such principles can be categorized between techniques, such as pull production and work leveling, and organizational behaviors, such as continuous learning or making decisions through the lens of a sustained vision. Behavior principles result in a strong organizational culture that not only sustains the implementation of TPS but also enables its continuous refinement through data collection, analysis, and communication of lessons learned. The success of TPS is mirrored in its widespread implementation and adoption across multiple and diverse industry sectors. The unique challenges in the construction sector make lean construction – the TPS equivalent in the sector – a continuous focus for researchers and practitioners alike.

See also: Advanced Vehicle Systems and Technologies: Economic and Environmental Implications. Recycling and Downstream Processing of Aluminium Alloys for Automotive Applications. Renewability Assessment of a Production System

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Upcycling Fresh Food Items in Retail Operations

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Introduction

A key challenge in retail operations is managing inventory. The retailer is constantly faced with the problem of matching demand with supply. This is particularly difficult for perishable items such as fresh produce that have limited shelf life. The value of the fresh food decreases over time, and beyond a certain point, the item can no longer be sold. To mitigate the problem of wasted food, some retailers have incorporated into their business model a practice that is common in households worldwide: Using “leftovers” or unused parts of food items to create new dishes. For example, apples close to the end of their shelf life exhibit diminished appearance, and thus could not be sold, or would need to be discounted. However, the apples could be used as an ingredient in apple pie. In fact, the use of the apples in pie may command a higher margin than selling them as fresh fruit. In this sense, the secondary use of fresh apples in pie can be considered a form of upcycling.

Reducing the Amount of Wasted Food

A critical benefit of upcycling fresh food is the reduction of wasted food. A report by the United States Department of Agriculture (USDA) estimates that 12% (4.4 billion pounds) of fresh fruit and 10% (5.2 billion pounds) of fresh vegetables were wasted at the retail level in 2010 (Buzby *et al.*, 2014). Reasons for these losses included overstocking and culling of blemished, misshapen, or wrong-sized items to accommodate esthetic criteria. At the retail level, the overall food loss (including fruits and vegetables, grain products, meat products, dairy products, etc.) was estimated to be 43 billion pounds, or 10% of the total amount.

Wasted food not only has negative economic impact, but also environmental and social impacts. The production and supply chain activities that delivered food to the retail store consumed natural and capital resources. Moreover, these activities produced by-products such as farm run-off, emissions, and road congestion, the costs of which are borne by communities. These efforts and costs borne are wasted when the food is lost. Wasted food also has detrimental social implications. The USDA estimates that 14% of US households are food insecure (USDA, 2017). That egregious amounts of food are wasted while a significant proportion of the population are vulnerable to food insecurity is particularly improvident.

The Environmental Protection Agency has endorsed a food recovery hierarchy (EPA, 2018): (1) source reduction, (2) feed hungry people, (3) feed animals, (4) industrial uses, (5) composting, (6) incineration or landfill. The process of upcycling fresh produce in retail operations is an innovative form of source reduction – the most preferred method of food recovery.

Types of Upcycling

There are two types of fresh food upcycling.

Serial Upcycling

In the “leftover” process, food is wasted when the food item is not used/consumed in a timely manner, and it degrades to the point it cannot be used in the original intended manner. For example, the selling process in a retail grocer’s fresh produce department creates leftover fresh fruits and vegetables when the produce reaches its sell-by date. However, the produce can be culled from the fresh produce department before the sell-by date and used as an ingredient to make prepared food – apples can go into apple pie, avocados into guacamole, vegetables into soup, cabbage into coleslaw, etc. (Whole Food’s Market, 2012). This is an example of *serial upcycling* – first there is an attempt to use the food item in a primary process, and if that attempt is not successful, then it is deployed in a secondary process.

Coproduct Upcycling

Another form of upcycling is when different parts of a food item are used in different products. This practice is prevalent in households and restaurants worldwide. For example, the meat of a chicken can be used for a main course dish and the bones used for chicken soup. The main course and soup use the chicken in noncompetitive ways. In fact, the more chickens that are used for the main course, the more chicken bones that are available to make soup. This form of upcycling is what we call *coproduct upcycling*. Two or more products can be produced by sharing a raw material resource. An industrial example of coproduct upcycling is the joint production of sugar and paper using sugarcane (Zhu *et al.*, 2007). Sugarcane is crushed to extract the juice, which is used to make sugar in a primary process. The dried cane residue (bagasse) is a fibrous material that is not used for sugar production but can be used in a secondary process to make

paper products. Making paper from bagasse makes productive use of a high volume by-product that would be economically and environmentally costly to dispose of, and avoids the use of virgin raw material to make paper.

Operationalizing Upcycling

Upcycling creates operational synergies and challenges. The ability to use raw material resources more productively can clearly be cost effective – both in terms of reducing raw material cost and waste disposal cost. However, upcycling can increase the complexity of an operation. There is a stream of literature that studies joint production in industrial settings [see [Lee \(2016\)](#) for a review]. We focus here on a retail grocer setting and the productive use of food waste streams in a joint production operation (upcycling).

Operationalizing Serial Upcycling

The operationalization of serial upcycling in a retail grocer setting is studied in [Lee and Tongarlak \(2017\)](#). Grocery stores face two major business risks because of the perishability of the food and the uncertainty of the demand at the time of ordering. If the grocery store carries “too little” inventory, it faces the risk of running out of stock, which results in lost sales and customer dissatisfaction. Consumers have been trained to expect constant availability of staple products. As a result, to ensure customer satisfaction, grocery stores typically carry more food than the demand forecast. This increases the risk of excess inventory (“leftover” items beyond their sell-by date), which is costly to dispose and wasteful from a natural resource perspective.

If a grocery store implements serial upcycling, then unsold fresh fruits and vegetables can be removed from the shelves before the sell-by date and used as ingredients in the prepared food department. The link between the two departments creates the synergy in serial upcycling. The waste stream from the primary process “feeds” the secondary process. From the opposite perspective, the secondary process “consumes” the waste stream of the primary process (see [Fig. 1](#)). This synergy (sometimes referred to as “by-product synergy”) has obvious cost saving benefits. The prepared food department (secondary process) utilizes the excess produce from the fresh produce department (primary process), thus avoiding both the virgin raw material cost and the waste disposal cost. By-product synergy (BPS) also provides environmental benefits in the form of waste reduction.

Some alternative ways to reduce food waste in the retail setting are stocking less, sending excess food to reclamation centers, and using pricing (discounting) to drive sales. However, stocking less leads to lower service levels and also potentially lower profit. Sending excess food to a reclamation center may not be practical for fresh produce because handling and logistics are difficult and costly. Discounting lower quality food may result in significant margin loss as the value of the item decreases considerably over time.

[Lee and Tongarlak \(2017\)](#) studied how a retail grocer can effectively implement serial upcycling, focusing on the retailer's ordering policy. The paper derives the optimal order decisions of the retailer in the “Fresh Only” and BPS settings. In the Fresh Only setting, the retailer only operates the fresh produce department (no serial upcycling). In the BPS setting, the retailer operates a prepared food department in addition to a fresh produce department and implements serial upcycling. The paper compares these two settings to determine the economic, environmental, and social implications of implementing BPS (serial upcycling).

In the Fresh Only setting, the retailer's ordering problem involves choosing the optimal quantity of the fresh produce when demand is uncertain. Suppose that the per unit cost of the fresh food item is c_1 and per unit price is r_1 . The excess fresh produce, if any, is removed from the fresh produce department and can be salvaged at a per unit value of $v_1 < c_1$. Note that the salvage value could be negative, implying disposal cost. If retailer orders “too much,” she loses her procurement cost for each unsold unit minus any salvage value ($c_1 - v_1$) – this is often referred to as the cost of overage. On the other hand, all unsatisfied demand is lost if the retailer orders “too little,” and she loses the margin ($r_1 - c_1$) for each missed opportunity to sell a unit (underage cost). The trade-off between overage cost and underage cost can be resolved optimally by a straightforward application of the Newsvendor model (see [Porteus, 2002](#)).

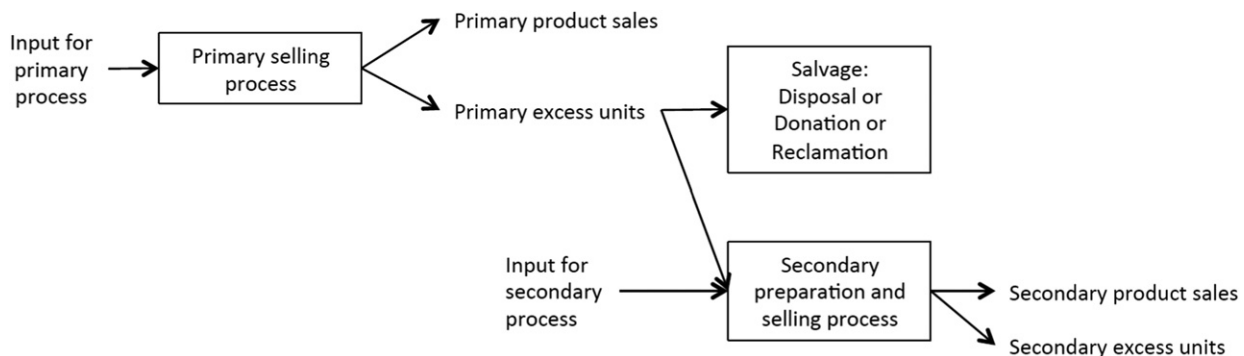


Fig. 1 Process flow diagram for the serial upcycling operation.

In the BPS setting, the retailer faces demand uncertainty for both the primary (fresh produce) and secondary (prepared food) products. She can jointly optimize the orders in the fresh produce and prepared food departments. Suppose that the per unit cost of other inputs in the prepared food plus the conversion cost is c_2 , the per unit price of prepared food is r_2 , and the per unit value of excess prepared food is v_2 . In the prepared food department, the optimal order quantity for new fresh produce input ingredient depends on the quantity of excess fresh produce transferred from the fresh produce department as well as the costs c_1 , v_1 , c_2 , v_2 , and the price r_2 . Lee and Tongarlak (2017) represent the optimal order-up-to level of fresh produce input ingredient for the secondary process as a function of the amount ordered in the fresh produce department, forming an extension of the Newsvendor problem. Then, the retailer's ordering problem reduces to finding the optimal orders in the fresh produce department, which is implicitly derived in the paper.

A key insight is that the optimal order quantity in the BPS setting is greater than the optimal order quantity in the Fresh Only setting. The synergy from serial upcycling drives up the amount of fresh produce ordered in the fresh produce department because the produce has the potential to be used in the prepared food department. This creates an indirect benefit from serial upcycling – the increase in the fresh produce order quantity increases the service level in fresh produce department. That is, the probability that a customer finds the fresh produce in stock (service level) is higher in the BPS setting.

The benefits of serial upcycling can only be realized if there is coordination between the two departments. In practice, coordinating separate departments to make globally optimal decisions can be organizationally more challenging for the retailer than allowing each department to optimize their own operations (resulting in lower overall profit). In particular, in the BPS setting, the primary department must overorder, thereby reducing the profit of its own operations, whereas the secondary department gains from the overordering. Therefore, even though the combined profits of the two departments increases, the primary department's performance looks worse compared with under Fresh Only.

A slight modification to BPS, called hybrid-BPS, is proposed by Lee and Tongarlak (2017) to address this organizational hurdle. In the hybrid-BPS setting, the autonomy of the departments and much of the benefit of serial upcycling synergy are preserved. The fresh produce department orders the optimal quantity presented in the Fresh Only setting. The prepared food department receives the excess inventory of the fresh produce department as in the BPS setting, and therefore chooses the order-up-to level of fresh produce input ingredient according to the optimal Fresh Only order. Compared with BPS, the expected profit is lower because the autonomous ordering of the departments results in suboptimal ordering for the retail store overall. Essentially, the fresh produce department does not “overorder” to feed the prepared food department – it simply orders what is optimal for the fresh produce department. Lower orders in the primary process also results in lower service level. However, despite the lower expected profit and service level of hybrid-BPS, the retailer may find it more desirable than optimal BPS because it is more straightforward to implement.

In addition to economic benefits to the retailer, serial upcycling can create positive environmental impact through waste reduction. Lee and Tongarlak (2017) compare the environmental impact (food waste reduction) of serial upcycling and two regulatory mechanisms used to reduce food waste: Disposal fee and donation tax credits. Disposal fees are typically charged on a per unit weight basis (e.g., landfill tip fees). A higher disposal fee reduces the salvage value of the excess inventory and thus discourages the retailer from ordering excessively in the fresh produce department. This, in turn, reduces waste, but the service level in the fresh produce department will also decrease. In contrast, serial upcycling can create more overall value because the service level in the fresh produce department increases (or at least stays the same), and food waste is reduced by diverting excess fresh produce to the prepared food department.

Giving tax credit for donation is another regulatory mechanism that diverts excess food from disposal to help those in need. The mechanism creates environmental and social value by reducing food waste and helping food insecure individuals. If the retailer donates excess fresh produce inventory, she can receive a tax credit. Lee and Tongarlak (2017) show that the waste disposal fee and tax credit are substitute mechanisms for inducing donation. The higher the disposal fee, the lower the tax credit required to induce the retailer to donate rather than to dispose. Tax credit for donation pays partially or fully for the fixed (e.g., administrative) and variable (e.g., handling and labor) costs incurred to set up an inventory donation program. Therefore, the tax credit needs to be high enough to incentivize the retailer to donate instead of disposing of excess food. If the retailer implements serial upcycling, the threshold tax credit required for donation is higher than under Fresh Only. Serial upcycling productively uses leftover fresh produce in the secondary process thereby reducing the quantity available for donation. The small amount of excess produce may not achieve the scale needed to incentivize donation. Thus, serial upcycling may have a negative impact on donation.

In summary, serial upcycling can be economically beneficial to the retailer. The optimal implementation requires coordination between the fresh produce and prepared food departments, with the fresh produce department being willing to “overorder” to supply the prepared food department. An alternate, simpler implementation allows for the two departments to operate autonomously but is not as profitable as ordering optimally. Serial upcycling helps to decrease food waste (an environmental benefit), while simultaneously increasing the service level of the fresh produce department. However, because the operation is so effective at productively using “leftover” fresh produce, there is very little excess food available for donation.

Operationalizing Coproduct Upcycling

In coproduct upcycling, the primary product uses only part of the input raw material, leaving the rest as a by-product. For example, the production of guacamole (primary product) uses the flesh of the avocado fruit, creating a by-product stream of avocado skins and pits. These by-products can then be used to produce tea (secondary product) (Beurteaux, 2018). By sharing the raw material in

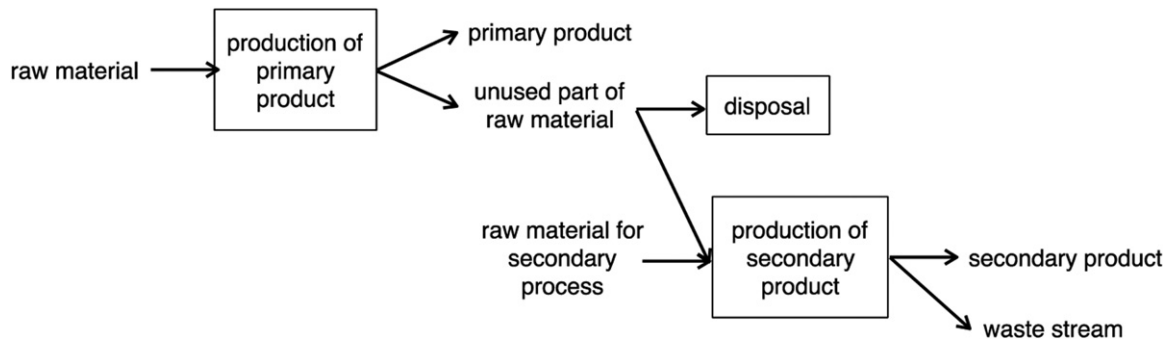


Fig. 2 Process flow diagram for the coproduct upcycling operation.

a noncompetitive way, value is created by avoiding disposal cost in the primary product production, avoiding raw material cost in the secondary product production, and also potentially reducing the processing cost of the secondary product (e.g., the avocado pit has already been separated from the flesh).

Clearly, there is a quantity relationship between the amount of guacamole and the amount of avocado tea that can be produced from a given quantity of avocado. The quantity relationship is determined by the intrinsic characteristics of the avocado. However, that quantity relationship is unlikely to coincide with the relative market sizes of these products. **Fig. 2** shows the process flow diagram for the coproduct upcycling operation.

Lee (2012) studied coproduct upcycling in an industrial setting. Although the study does not focus particularly on food, the insights derived from the quantity relationship imposed by the shared material resource can shed light on joint production of food products. Suppose that for every unit of primary product that is produced, γ units of the secondary product can be produced from the unused part of the raw material. For example, suppose a pint of guacamole uses 10 avocados, and one avocado pit makes 250 ml of tea. In this case, γ is equal to 2.5 l of tea (secondary product) per pint of guacamole (primary product). However, because the primary and secondary product markets are not linked, the ratio of the optimal production quantities of the two products may not be exactly γ . Therefore, one of three policies may be optimal for a coproduct operation:

- (1) *Partial conversion*: Use only part of the unused raw material to produce the secondary product. Thus, the primary production process still disposes of some waste.
- (2) *Exactly-full conversion*: All of the unused raw material from the primary production process is used to produce the secondary product, and the secondary production process only uses the by-product stream to meet its production quantities.
- (3) *Full-plus conversion*: All of the by-product from the primary production process is used to produce the secondary product, and additionally, the secondary production process sources virgin raw material to increase production quantities beyond what is achievable with the by-product stream from the primary production process.

By joining the production of the primary and secondary processes, the cost structures of the two processes change, thereby changing the optimal production quantities. In particular, the cost of disposal is avoided in the primary process, and the cost of raw material is avoided in the secondary process.

Lee (2012) shows how the optimal operating policy depends on the relative attractiveness of the primary and secondary markets, the per unit amount of by-product generated γ , and the disposal and raw materials costs. If the primary market is relatively more attractive than the secondary market and/or the per unit amount of by-product generated γ is high, then the optimal policy is either partial conversion or exactly-full conversion. The disposal cost determines which of the two policies is optimal. For low disposal cost, partial conversion is optimal. This is intuitive because the primary market is large compared with the secondary market and disposal cost is low, so it would be optimal to only convert some of the by-product stream into the secondary product. As the disposal cost increases, it will be optimal to convert more of the by-product stream into secondary product, until a threshold level disposal cost is reached where it would be optimal to convert all of the by-product stream into secondary product.

In comparison, if the secondary market is relatively more attractive than the primary market and/or the per unit amount of by-product generated γ is low, then the optimal policy is either exactly-full or full-plus conversion. The raw material cost determines which policy is optimal. For low raw material cost, full-plus conversion is optimal – because the secondary market is robust and raw material cost is low, it's optimal to supplement the by-product stream from the primary process with virgin raw material to increase the quantity of secondary product produced. However, as raw material cost increases past a threshold amount, exactly-full conversion becomes optimal. Even though the secondary market is an attractive market, if the virgin raw material cost becomes too high, it is optimal to only make secondary product using the less expensive by-product stream from the primary process.

Another effect that coproduct upcycling has is that on average, more primary and secondary products are produced. In fact, to feed the secondary process, it may be optimal to “overproduce” the primary product (similar to the serial upcycling process). That is, the profit of the primary product could suffer from overproduction, but that is more than compensated by the increase in profit from the secondary product. Clearly, jointly producing coproducts requires making tradeoffs between the two products, but capturing the synergies can create economic, environmental, and social value. In particular, the productive use and increase in diet of fresh food can improve human health.

Future Research

The studies in this article have focused primarily on vertically integrated upcycling operations. However, as awareness of the detrimental impacts of food waste becomes more prevalent, entrepreneurs are finding innovative ways to productively use the waste streams of other organizations. A vertically disintegrated serial upcycling example is Daily Table, a nonprofit retail store that takes donations of surplus food items from a network of farmers, supermarkets, and manufacturers and either sells those items at cost or uses them to prepare “grab-n-go” meals for its customers in urban food deserts (Kowitt, 2017).

Coproduct upcycling can also be implemented in a vertically disintegrated supply chain. In fact, it is often two firms in different industries that can make use of different parts of the same raw material input. For example, the coffee cherry fruit consists of the coffee bean, surrounded by an outer husk. The coffee bean is used to make coffee, and typically, the husk has been discarded. However, Lazy Bear Tea (2018) started marketing tea drinks brewed with coffee fruit husks. Coffee farmers can now sell the bean to coffee makers and the husk to Lazy Bear Tea, thereby increasing the productive use of the coffee fruit and reducing wasted food.

When the upcycling supply chain becomes vertically disintegrated, coordination challenges surface because there is not a central planner that can facilitate the global optimization of two operations. The two processes are owned by different organizations and therefore the tradeoff between the primary and secondary processes cannot be internalized by one organization. The pricing, quantity, delivery schedule, and quality of the by-product stream must be negotiated between the two exchange parties. Given the importance of addressing the problem of wasted food, and the potential benefits to human health of increased consumption of fresh food (particularly fruits and vegetables), these supply chain challenges are important avenues for future research.

See also: Conversion of Renewable and Food Wastes into Useful Products With Environmental Perspectives. Food Residue, Loss and Waste as Animal Feed. Food Waste for Sustainable Packaging Materials

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Subject Index

Note

This index is in letter-by-letter order, whereby hyphens and spaces within index headings are ignored in the alphabetization, and it is arranged in set-out style, with a maximum of three levels of heading.

Cross-reference terms in *italics> are general cross-references, or refer to subentry terms within the main entry (the main entry is not repeated to save space).*

Location references refer to the volume number, in bold, followed by the page number.

Page numbers followed by “*f*” and “*t*” refer to figures and tables, respectively.

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